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University College Cork, Ireland Coláiste na hOllscoile Corcaigh

The Role of Structure in the Electrochemical Performance of Nanostructured Metal Oxides for Lithium Ion Battery Anodes

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Presented for the degree of Doctor of Philosophy to the National University of Ireland

> Supervisor: Doctor Colm O'Dwyer Head of Department: Professor Martyn E. Pemble

> > February 2015

Declaration

I, Michal Jaroslaw Osiak, certify that this Thesis is my own work and I have not obtained a degree in this University, or elsewhere, on the basis of this thesis.

Michal Jaroslaw Osiak

Abstract

The Li-ion battery has for a number of years been a key factor that has enabled an ever increasing number of modern consumer devices, while in recent years has also been sought to power a range of emerging electric and hybrid electric vehicles. Due to their importance and popularity, a number of characteristics of Li-ion batteries have been subjected to intense work aimed at radical improvement. Although electrode material selection intrinsically defines characteristics such as maximum capacity or cell voltage, careful engineering of the electrode structure may yield significant improvements to the lifetime performance of the battery, which would not be available if the material was used in its bulk form.

The body of work presented in this thesis describes the relationship between the structure of electrochemically active materials and the course of the electrochemical processes occurring within the electrode. The focus of this work was placed on the metal oxide nanostructures, with particular emphasis on indium and tin oxides. Chapter one describes the motivation behind the research presented herein. Chapter two serves to highlight a number of key advancements which have been made and detailed in the literature over recent years, pertaining to the use of nanostructured materials in Li-ion technology. Chapter three details methods and techniques applied in developing the body of work presented in this thesis. Chapter four details structural, molecular and electrochemical characteristics of tin oxide nanoparticle based electrodes, with particular emphasis on the relationship between the size distribution and the electrode performance. Chapter five presents findings of structural, electrochemical and optical study of indium oxide nanoparticles are investigated for the conduct of the electrochemical performance of the electrodes under varying rate of change of potential. Chapter 7 presents the overall conclusions drawn from the results presented in this thesis, coupled with an indication of potential future work which may be explored further.

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You are holding the fruit of a number of couple of years of work and research, and although there is only one author written below the title, a number of people deserve credit for the completion of this body of work.

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List of Publications

Osiak, M., Geaney, H., Armstrong, E., & O'Dwyer, C. Structuring materials for Lithium-ion batteries: Advancements in nanomaterial structure, composition, and defined assembly on cell performance. J. Mater. Chem. A 2, 9433-9460 (2014).

Osiak, M., Armstrong, E., Kennedy, T., Torres, C. M. S., Ryan, K. M., O'Dwyer, C. Core-shell tin oxide, indium oxide, and indium tin oxide nanoparticles on silicon with tunable dispersion: Electrochemical and structural characteristics as a hybrid Li-ion battery anode. ACS Appl. Mater. Interfaces 5, 8195-8202 (2013).

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Armstrong, E., Khunsin, W., Sotomayor Torres, C. M., Osiak, M. & O'Dwyer, C. Synthetic routes for the preparation of ordered vanadium oxide inverted opal electrodes for Li-ion batteries. ECS Trans. 58 (25), 7-14 (2014).

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Armstrong, E., Khunsin, W., Osiak, M., Blömker, M., Sotomayor Torres, C. M. & O'Dwyer, C. Ordered 2D colloidal photonic crystals on gold substrates by surfactant-assisted fast-rate dip coating. Small 10, 1895-1901 (2014). See the Frontispiece.

Glynn, C., Osiak, M., McSweeney, W., Lotty, O., Jones, K., Quiroga-González, E., Holmes, J. D. and O'Dwyer, C. Semiconductor Nanostructures for Antireflection Coatings, Transparent Contacts, Junctionless Thermoelectrics and Li-ion Batteries. ECS Trans. 53, 25-44 (2013).

Kennedy, T., Mullane, E., Geaney, H., Osiak, M., O'Dwyer, C. Ryan, K. M. High-Performance Germanium Nanowire-Based Lithium-Ion Battery Anodes Extending over 1000 Cycles Through in Situ Formation of a Continuous Porous Network. Nano Lett., 2014, 14 (2), pp 716–723

CHAPTER I

INTRODUCTION

1.1 Introduction

1.1.1 Background

The development of the human race can be closely related to the development of new and better sources of energy generation and storage. Initially, a crude fire made out of wood served as a source of heat, light and safety. Progressive evolution of human species, conjoined with an increase in our cognitive abilities required more advanced and dense energy sources. The first industrial revolution began with the invention of the rotary steam engine developed by James Watt in the late XVII century [1]. Steam engines, fueled by coal and wood allowed for industrialization of the western world and expansion of European culture throughout the continents. The industrial age was also an age of extremely fast scientific developments, yielding inventions of electricity and oil refining, laying the foundations of our modern society.

Energy generation innovation from the early XIX century was followed closely by improvements in energy storage technology. Since the industrial age, the most important form of energy storage was related to electrochemical reactions. The underlying principle governing all electrochemical transformations requires that a supply of energy from an external source can be stored through a chemical reaction between two species (lithium and carbon, lead and sulphur as just two examples). The resulting product of the chemical reaction can release the stored energy when required in an external circuit. Initial electrochemical cells could only undergo the aforementioned transition only once, becoming obsolete after just a single energy storage cycle. Developments in understanding of the underlying principles of the electrochemical energy storage, by pioneers like Volta [2], Faraday, [3] and many others allowed for creation of reversible electrochemical energy storage.

Currently, we are experiencing a persistent increase of the research into the material properties and structure engineering that could enable batteries with exceptionally high charge storage capacities, larger power and energy densities, and lower environmental burden. The research interest is in principle driven by tremendous market growth (see Figure 1.1), itself fuelled by the need for developing power solutions to power the next mobile revolution.



Total Lithium-ion Battery Market: Revenue Forecast, Global, 2012-2020

Figure 1.1 Growth forecast for lithium ion battery market.[4]

The advent of wearable technology (such as smart watches and mobile phones) combined with increasing interest in electric vehicles (EVs) reinforces research efforts centred around material science and structure engineering of the next-generation electrode compounds.

Among various technologies both established and emerging, lithium ion batteries (LIBs) appear to be the closest to achieving the requirements of the next-generation energy storage systems. The low atomic weight of lithium (6.94 g mol⁻¹), resulting in low density (0.53 g cm³) results in exceptionally high specific capacity (the total amount of charge that can be stored per unit mass) of 3860 Ah kg⁻¹. High operation voltages, low

self-discharge (loss of stored electrochemical energy) and low maintenance requirements offer significant advantages over alternatives such as lead-acid batteries [5]. The first commercial battery based on Li-ion chemistry was released by SONY in 1990 [6]. Since then, the market for LIBs has grown tremendously, reaching 105.5 billion in 2010. Increasing demand will drive further revenue growth, resulting in potential market size of over \$132 billion in 2016. Ubiquitous sensing, wearable and portable medical devices will be the main market growth drives. Other established and emergent applications, such as electric vehicles and grid power systems will strongly depend on LIBs to deliver improved performance and sustain commercial revenue growth. To demonstrate the superiority of LIBs over other battery technologies, one can quote the comparison between the Tesla Roadster, a modern electric sports car powered by LIBs and the Mahindra Reva, powered by lead-acid batteries. The Tesla has a single charge time of around 3.5 hours and a maximum driving rage of over 245 miles. The Reva's charging time is almost twice that of the Tesla at 6 hours, with the maximum driving range over 4 times shorter, at 50 miles [7].



Figure 1.2 Components and principle of operation of a lithium ion battery [4].

1.2 The Lithium-ion Battery

1.2.1 General Overview

The main components of LIBs are: the anode – negative electrode, cathode – positive electrode separated by a membrane soaked in electrolyte (see Figure 1.2). Current state-of-the-art devices utilise $LiMn_2O_4$ or $LiCoO_2$ as their cathode (with $LiFePO_4$ also being commercialized) [8]. The anode is usually made of lithiated graphitic carbon (LiC_6). In principle, lithium ion battery operation is based on the electrochemically driven transport of Li^+ ions from an anode to cathode during discharge, resulting in current and power flowing to the device. During the charge process, energy is supplied to drive the Li^+ ion back to the anode. The electrolyte provides facile ionic transport while preventing electron flow from cathode to the anode within the battery.

Most current LIB electrolytes use a solvent blend of ethylene carbonate (EC) and a various other carbonates, such as dimethyl carbonate (DMC), diethyl carbonate (DEC) and ethlymethyl carbonate (EMC) [9]. To provide ionic conduction through the distance separating the anode and cathode, a lithium salt, most commonly lithium hexafluorophosphate (LiPF₆), is added to the carbonate solvent mixtures. Such solution provides high ionic conductivity (>10¹³ S cm⁻¹) as well as high Li⁺ transference number (0.35) [10]. The transference number describes the fraction of the total current that is carried by the ion during electrolysis. Additionally, LiFP₆ is safe within the LIB operating voltage range.

The performance of the LIB is influenced by a number of factors. The choice of the cathode and anode materials will impact the potential energy and power density, the operating voltage, electrode stability and possible battery lifetime. The choice of the electrolyte has a huge impact on the battery safety (as demonstrated by numerous events where LIBs spontaneously caught fire in operation) [11]. Binders, which are

commonly used to improve the active material adhesion to the current collector do not contribute to the charge storage capacity, while impacting the performance. Importantly, the structure of the electrode itself is one of the key factors affecting the device performance. Material synthesis developments improved the ability to prepare structures with length scales below 100 nm in one significant dimension, resulting in improvement of key electrode characteristics [12]. Excellent control over the structure of the batteries also impacted the performance of the device, allowing us to engineerout some of the most persistent problems occurring in next generation electrode materials.

LIBs used currently are based on the well-known LiCoO₃ – graphitic carbon chemistry. The layered structure of graphitic carbon used in the negative electrode allows for unperturbed diffusion of Li⁺ ion into the host material. Carbon however is intrinsically limited, due to its low specific capacity (372 Ah kg⁻¹) combined with low stability at high charge rates and excessive solid electrolyte interphase (SEI) formation, leading to irreversible capacity loss and poorer performance [13]. Alternative materials, researched with great interest as potential replacements for both anode and cathode include silicon [14], tin [15], vanadium oxide [16], and many others [17]. Importantly, negative electrode materials alloying with lithium, such as Sn and Si offer capacities that are many times higher than capacities provided by carbon. High capacity values are however accompanied by limitations, often caused by the materials response to a large volume fraction of lithium. Extremely high uptake of lithium by host material results in large volumetric expansion, leading to irreversible mechanical damage, loss of electrical contact with current collector and subsequent significant and rapid capacity loss.

1.2.2 Li-ion battery materials.

To fully realize the potential capabilities of alloying materials as lithium ion battery anodes, significant efforts has been dedicated towards improving the charge transfer characteristics as well as mechanical integrity of the electrodes based on these materials. The most successful approach to date involves engineering the electrode structure to decrease one of the dimensions of the electrode material to below 100 nm [18]. Numerous studies have reported that nanostructuring of the electrode improves the electronic transport while offering sufficient space and mechanical strength to withstand volumetric expansion intrinsic to alloying materials. Approaches taken involve bottom up and top down synthesis of nanowires, nanorods and nanoparticles of Si and Sn, as well as top down structural engineering. Recent important examples of LIB structural engineering include Metal Assisted Chemical (MAC) etching, where Si etching is catalysed by silver metal ions [19] as well as templating approaches where hard materials act as templates for further structural engineering[20, 21].

Developing an improved understanding of the physical and electrochemical properties of nanostructured based batteries is a key factor in producing reliable low cost batteries. Importantly, improving the understanding of the properties of nanomaterials can provide opportunities for developing novel applications for the electrodes. For example, developing batteries with high optical transparency may lead to power source with functional devices where transparency is the key property, or provide optical methods of battery testing. Thus it is important to investigate material properties beyond simple electrochemical performance, particularly for the novel nanostructured electrodes.

In this thesis, a detailed examination and characterization of several types of nanostructures prepared by both top down and bottom up approaches are presented. The chapters outline the electrochemical processes present in composite nanostructured

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battery electrodes with high optical transparency, electrochemical and structural changes in tin and tin oxide composite electrode composites, as well as electrochemical processes occurring in monolithic hierarchically structured and porous inverted opal structures of tin oxide.

1.3 Overview of thesis

Chapter 2 gives a review of nanostructured electrodes for lithium ion batteries with emphasis on the electrochemical performance dependence on the structural characteristics of the electrode, focusing on the inverted opal alloying materials. Recent developments in the analytical methods, electrochemical response, and the structure, composition, size, shape and defined assembly of active materials for a wide range of Li-ion cathodes and anodes are also compared and assessed with respect to cell performance.

Chapter 3 gives an outline of the experimental techniques used throughout this thesis, with full details on sample preparation, deposition, cell assembly, analysis, and structural and electrochemical characterization methods.

Chapter 4 presents an investigation into the chemical composition and structure of indium oxide nanoparticles prepared by molecular beam epitaxy on silicon substrates. The refractive index grading caused by introducing a degree of porosity in the indium film due to nanoparticle structure improves the transmittance of infrared radiation, while improving reflectivity in visible band. Additionally, the excellent adhesion of the nanoparticles to the substrate caused by low lattice mismatch and the degree of the growth control provided by molecular beam epitaxy (MBE) growth leads to good structural stability during electrochemical cycling as a lithium-ion battery anode.

Chapter 5 is a study on the morphology, composition and electrochemical performance of the tin oxide nanoparticles prepared by MBE on silicon. The degree of oxidation of the nanoparticle shell influences the electrochemical performance of the nanoparticle based electrodes. Moreover, a correlation between the size distribution of the nanoparticles and the electrochemical processes present during lithium insertion and removal is described in detail.

Chapter 6 describes detailed route towards the preparation of SnO₂ inverse opal (IO) structures based on chlorine-free tin oxide precursors from PS templates prepared by electrophoretic deposition. The correlation between the infiltration protocol, and the morphology of the inner IO wall. Cyclic voltammetry was used to describe the electrochemical processes present at the electrode when assembled as a Li-ion battery anode and the influence of the rate of the potential change on the charge storage mechanism.

Chapter 7 presents the conclusions of the thesis and recommendations for future work.

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CHAPTER II

LITERATURE REVIEW

2.1 Introduction

The earliest research that can be connected to lithium-ion batteries originates in a graduate thesis written by Harris [1, 2], demonstrating the possibility of electrodepositing Li metal under controlled non-aqueous conditions. This converged with earlier studies in sodium ion transport in beta alumina [3] where ions intercalate, or insert into a crystalline lattice, or through porous one dimensional channels in some crystalline structures, or indeed between two dimensional layers in crystalline solids. In 1976, Whittingham at Exxon, reported intercalation electrodes arranged into a functioning rechargeable lithium battery [2]. Following that, in 1980s Armand introduced the rocking chair concept [4], where the conduction of Li ions can move repeatedly from one side of the battery to other, i.e. diffuse from the anode to cathode during charge and from cathode to anode during discharge. Development of materials that could undergo this process numerous times resulted first in commercialization of primary (single use) and subsequent widespread utilization of secondary Li-ion batteries (rechargeable LIBs).

2.1.1 Lithium Ion battery Structure

Rechargeable Li-ion batteries are one of the most extensively researched power sources for applications in modern portable electronics, hybrid electrical vehicles and sensor networks, as highlighted by a number of recent review articles [5-8]. Newer consumer electronics that are developed require power sources with higher energy density (amount of energy stored per unit mass), higher power density (time rate of energy transfer), longer lifetime (the number of cycles of battery charge/discharge) and improved safety of operation. Early secondary Li-ion batteries suffered greatly from thermal instabilities caused by dendritic depositions of Li from the metallic Li anode

through to the cathodes [9], leading to the formation of short circuit connections between the electrodes and in some cases ignition of the battery package when certain electrolytes were used. This problem was overcome by replacing metallic Li anode with various non-metal compounds [10], capable of storing and reversibly exchanging a large number of Li ions. The reduction of Li plating effects (and associated safety improvement) gave way to widespread introduction of Li-ion batteries into consumer markets[11]. The elements of LIB listed below are also presented in Figure 1.2

2.1.1.1 Cathode

The cathode is the positive electrode of the battery, which means it is the source of positive ions (Li⁺) and accepts negative ions (e⁻). In currently used batteries, cathodes are most commonly made of (but not limited to) layered, or spinel lithiated metal oxides.

In layered cathodes, the composition is denoted by LiM_xO_{2x} here M corresponds to Co [12, 13], Ni [14], or Mn [15]. LiCoO₂ is currently the most popular option, despite the high cost of cobalt, as it is relatively easy to prepare a high quality electrode with a layered structure of extremely high quality. This material and associated battery construct has also benefited from decades of research, development and real-world applications. Nickel manganese [16] and vanadium [17] are being extensively investigated in order to improve their structural stability, reversibility and cost-effectiveness for some applications. Spinel cathodes (e.g. LiMn₂O₄) offer the advantage of a robust cubic oxygen array with 3-dimensional Li ion diffusion, allowing fast insertion/removal of Li ions during discharge/charge processes[18].

2.1.1.2 Electrolyte

At high operating potentials (up to 4.5-5 V vs Li/Li⁺ for some advanced cathode materials) associated with operation of Li-ion batteries, aqueous solutions would

electrolyze easily if used as an electrolyte for a Li cell, leading to a possible combustive event. Thus, aprotic, non-aqueous solvents are used [19]. Commonly used electrolytes LIBs include propylene carbonate, dimethyl-carbonate, ethylene carbonate, vinylene carbonate and mixtures of these solvents[20]. As liquid electrolytes do not fully prevent formation of dendrites on the surface of the anode, often solid state polymer electrolytes are used. The electrolyte needs to satisfy certain conditions:

- High Li ion conductivity, very low electronic conductivity
- Wide temperature range of operation
- The energy gap between the electrolyte's lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) needs to be higher than the difference between energy levels of cathode and anode; it needs to be thermodynamically stable at the operating voltages.
- It should ideally be environmentally friendly.

In the electrolyte Li salts such as $LiClO_4$, $LiBF_4$, and $LiPF_6$ are dissolved to act as a source of Li^+ ions. The use of vinylene carbonate additives in some carbonate electrolytes, among others, promotes Solid Electrolyte Interphase (SEI) formation at the anode through radical polymerization, which is beneficial for stabilizing the interface during repetitive insertion (or alloying) and removal of lithium ions [21].

2.1.1.3 Separator

The separator provides a barrier which prevents short circuiting of the cathode and anode. It should be sufficiently porous to allow the electrolyte to freely connect the two electrodes. Most commonly, separators are made of polytetrafluoroethylene (PTFE) and other inert polymer membranes with defined porosity and ionic conductivity.

2.1.1.4 Anode

The anode is the negative electrode of the Li ion battery. In currently used commercial packages, the anode consists of layered graphitic carbon. The storage mechanism is based on the intercalation of Li⁺ ions into van der Walls spacings found between the graphitic monolayers. The theoretical specific capacity of graphitic carbon is 372 mAhg⁻¹, based on following reaction:

$$LiC_6 - e^- \leftrightarrow 6C + Li^+$$
 (2.1)

Graphitic carbon electrodes allow for good cycle lifetime, but suffer from low rate capability, and irreversible capacity losses caused by electrolyte decomposition at low potentials, and formation of a solid electrolyte interphase (SEI). SEI is a common name given to a passivating layer formed on the surface of the electrode due to reductive decomposition of the electrolyte [22]. It forms at low potentials (typically, 0.7 V vs Li/Li⁺). In the initial cycle, the formation of a SEI layer contributes to the loss of reversible capacity. However, in subsequent cycles, the SEI layer prevents additional decomposition of the electrolyte, improving reversible capacity and ensuring better cycling of the battery. To optimize electrode performance, the SEI layer should be insoluble in the electrolyte, be a good electronic insulator and ionic conductor. Importantly, the SEI layer should be able to remove a thin solvation layer around the Li⁺ ion, to prevent the exfoliation or delamination of layered active material that could result from by co-intercalation of the solvent [23-26].

Battery research is driven by the economical need to satisfy consumer demand for higher power and higher energy batteries. Every smartphone user would like to see their phone operate for a prolonged period of time under high demand usage. Global climate change makes the prospect of all-electrical cars a welcome alternative to petrol, gas or diesel-fuelled transport. The "always on, always connected society" with strong

demands on wireless sensor networks will require more advanced power solutions than those currently available, in smaller volumes with long term stability for operation in remote locations. So far, many possible replacement materials have been identified for both anode and cathode, and these require even more development for any non-lithium based electrochemical power sources. Moreover, the advent of nanotechnology has facilitated battery architectures which are no longer entirely reliant on traditional bulk/thin film approaches, but with structurally engineered porous, 1, 2 or 3 dimensional designs offering improvements in performance [6, 27, 28]. This review will describe some of the most recent findings in both the structural design and the materials chemistry of next generation battery electrodes.

2.2 Choosing materials for Li-ion batteries

As mentioned above, novel materials for Li-ion batteries have been extensively investigated over a number of years. Several materials have been identified as potential replacements of cathode and anode in next generation battery anodes (summarised in Figure 2.1) and have been in some cases commercialized, demonstrating great potential for currently researched materials. However, before wide-scale adaptation of new materials, a deeper and better understanding of all the factors affecting battery performance (its chemistry, upscaling, packaging and maintenance) needs to be developed. Many excellent reviews provide details of material performance, and their performance and fundamental response as lithium-battery electrode materials and the reader is referred to other reviews for selected ranges of materials [5, 7, 8, 29, 30].



Figure 2.1. Diagram illustrating the Li ion capacity and electrochemical reduction potentials with respect to Li metal for a range of cathode and anode materials [11].

A pioneering method for materials choice and for future development is being developed by Ceder et al. at MIT, using what they term the *Materials Genome Project* [31]. The Materials Genome Project has a goal of applying knowledge gained from largescale property computation on all known inorganic compounds for materials research and discovery. While applicable to many functional applications involving materials whose properties information would be useful, it has immediate valuable application to Li-ion and emerging alternative battery chemistries. Many tens of thousands of materials have been screened in terms of Li⁺ intercalation voltage or chemical potential, theoretical charge capacity, electrode voltage and other parameters. Figure 2.2 shows the voltage calculated using density functional theory as a function of the theoretical capacity for thousands of oxides, phosphates, borates, silicates, and sulfates. The continuing work is also focused on the safety of high voltage materials is various electrolytes and structural effects that are related to cycling behaviour and

performance.[32] It forms a new and extremely useful approach to Li-ion battery materials design, within the limitations of DFT.



Figure 2.2. Calculated lithium insertion voltage versus theoretical capacity for several thousand compounds. Reproduced from [33] with permission form American Vacuum Society.

In general, next-generation Li-ion battery materials can be divided into subcategories based on their Li⁺ ion storage mechanism: intercalation electrodes, conversion electrodes and alloying electrodes.

2.3 Intercalation Electrodes

Intercalation electrodes involve materials with crystalline structure enabling the diffusion of Li ions into the interstitial sites of the crystalline lattice. The most common crystalline structures include layered [34], olivine [35, 36] and spinel [37] (Figure 2.3). Their main appeal lies in their excellent structural stability and long cycle lifetime. Currently used cathodes consist of layered LiCoO₂, LiCo_{1-v}Ni_vO₂ and LiMn₂O₄. These cathode materials have some practical limitations however. LiCoO₂ can only intercalate in the $LiCoO_2 - Li_{0.5}CoO_2$ range, limiting available capacity to about 130 mAhg⁻¹. Cheaper and more environmentally friendly LiCo_{1-v}Ni_vO₂ suffers from strong Li-Ni cation mixing, which affects the structure formation and subsequent ionic transport. LiMn₂O₄ in turn has a limited stability and may undergo a phase transition at room temperature [38]. Further computational investigations showed however, that the addition of some nickel, to form Li(Mn_{0.5}Ni_{0.5})O₂, yields an almost ideal cathode material in theory, due to the stability of the closed-packed framework of Mn⁴⁺ coordinated to oxygen [39]. However, the rate capability for this material was very poor and the mobility of Li ions within the framework was found to be strongly linked to the distance between the oxygen layers.

For battery safety, particularly at high deintercalation rates or under typical discharge/charge at elevated temperatures, self-catalysed exothermic reactions of the active material with the electrolyte may occur [40], leading to thermal instabilities, thermal runaway and ultimately a failure (and sometimes explosion) of the battery. Recent reports of fires caused by exploding LIBs are an example of a result of instabilities arising from the interaction of the highly charged cathode with the electrolyte, often aided and sometimes facilitated by electrical shorting from Li dendrite formation [41]. Cathode materials with inherently active or unstable oxidation states can potentially be reduced by liberating oxygen, which overcomes its kinetic limitations

at elevated temperatures caused by heat from surrounding environment or possibly by self-discharge and cell heating. The oxygen can vigorously react and burn the electrolyte. However, there are many materials (cathode materials) that have a large negative chemical potential (difficult to reduce in their charged state) and thus are inherently safe in this regard, LiFePO₄ being cited as possibly the ideal example. Interestingly, and widely known, is that the most prevalent battery chemistry employing LiCoO₂ is inherently one of the least safe in its charged state, but does offer good cycling capability. Advances in the engineering of battery packs has largely removed these issues, but several high profile accidents have reignited the issue of battery safety and raise the question of safer chemistries by choosing safer electrolytes or electrode materials [42].

Layered and spinel materials however suffer from low Li ion diffusivity, and therefore can only satisfy limited power demands. In recent years, research has been mainly focused on improving the electrode kinetics [43-45]. Nanostructuring the active material offers significant benefits, such as: shortened diffusion lengths, improving electrical and ionic performance/rate by placing conductive additives as a surface coating on active materials, as opposed to a random mixture of powder additives [46, 47]. Some of the various nanostructures formed include, but are not limited to, nanosheets [48], nanoparticles [49], nanowires [50] and nanotubes [51].


Figure 2.3. (a) A range of different oxide, sulfide and phosphate crystal structures capable of Li intercalation to various regions of their crystal structure Reproduced from [52] with permission from Intech Open. (b) Common intercalation compounds as a function of decreasing calculated chemical potential of oxygen in their charged state. A lower oxygen chemical potential is deemed safer. Reproduced from [33] with permission from American Vacuum Society.

2.4 Conversion materials

A different type of Li storage mechanism is a reversible electrochemical reaction of Li with transition metal oxides [53, 54]. The mechanism of the energy storage is conventionally referred to as conversion reaction, described as follows:

$$M_a X_b + (b \cdot n) Li \leftrightarrow aM + bLi_n X$$
 (2.2)

where M = transition metal, X = anion and n is the formal oxidation state of X. Conversion reactions have been reported for some oxides, sulfides and fluorides, with different degrees of reversibility. The main focus of researchers working with conversion based electrodes is the improvement of electrode kinetics and reversibility, in particular, formation of nanoparticles of reduced metals that would be very active

towards the Li_nX matrix in which they are interspersed. At the moment, however, conversion type electrodes are still in development, and much investigation is required into fundamental characteristics of conversion materials and electrode design.

2.5 Alloying materials

Reversible electrochemical alloying of metals and semi-metals with Li has been known since 1970s [55]. Metals reversibly alloying with Li offer tremendous improvement in specific Li storage capacity. Silicon has a highest known theoretical Li storage capacity, higher even than that of Li (3700 mAhg⁻¹) equal to 4400 mAhg⁻¹ [6]. Other examples of alloying materials include tin and tin oxides [56], antimony [57], germanium [58], and others like phosphorus, magnesium and silver [7], each offering excellent theoretical Li storage capacity. However, these materials suffer greatly from large volumetric expansion and contraction caused by insertion and removal of a large amount of Li⁺ ions, as well as fast charging/discharging rates. Severe mechanical stresses and strains resulting from repeated cycles of volume changes lead to irreversible structural changes, formation of cracks in active material causing loss of structural and electrical integrity of the electrode, pulverization and irreversible capacity fading. The most common strategies directed at the improvement of electrode performance are focused on the accommodation of volumetric expansion through providing free space around the active material [5] and creating various composites [59-62] aimed at protection of the active material against structural degradation or ensuring consistent and stable electrical contact between the active material and external current collector.

The scope of this section is to summarise recent advances in the field of alloying materials research, with improved characteristics for next generation Li-ion battery anodes.

2.5.1 Silicon

Silicon has for a long time been investigated as a possible replacement for graphitic carbon in next generation anode materials. In terms of specific capacity, the Li-Si alloy phase can store >4000 mAhg⁻¹, compared to 372 mAhg⁻¹ for graphitic carbon. Silicon is also the second most abundant material in the earth's crust, making it economically viable for mass production of LIBs [63]. The abundance of the element, combined with the benefits of well-developed industrial infrastructure and exceptionally high theoretical specific capacity, has made Si one of the most promising materials for next generation battery anodes. However, the large number of Li ions that can be inserted into Si cause extremely large volumetric changes, where the final volume is three times the initial volume. Mechanical failure often follows, leading to irreversible capacity loss and decrease in cycle lifetime, effectively preventing successful application of Si in next generation battery anodes.



Figure 2.4. (a-c) Schematics of SEI layer formation and stable cycling of double-walled $SiO_2@Si$ nanotubes. Reproduced from [64] with permission from Nature Publishing Group. Schematic changes occurring in (d) Si thin film. (e) Si nanoparticles. (f) Si nanowires. Adapted from [65] with permission from Nature Publishing Group.

Si nanostructures such as nanowires and nanoparticles have been designed and fabricated through numerous routes [6, 66]. Additionally, some nanostructures have been specifically engineered in order to accommodate the volume changes occurring in Si, such as core shell nanotubes [64] and yolk-shell type nanoparticles [67]. Figure 2.4

demonstrates improvements in structural stability of nanostructured Si electrode materials.

Widespread research into formation of Si NWs and their application in electrochemical energy storage, allowed better insight in the processes occurring during lithiation, and in particular the structural changes caused by formation of reversible alloying of Li with Si. In-situ TEM observations indicated preferential anisotropic swelling of <112> Si nanowires in the <110> direction [68]. The Li⁺ diffusion study revealed deformation followed by a build-up of tensile stress in the nanowires, resulting in fracture [69]. Numerical modelling indicated that Li⁺ ions prefer to diffuse along <110> direction, where surface energy of the planes is preferable for Li⁺ interactions. The electrochemical lithiation of crystalline silicon leads to formation of a core-shell structure, with Li-rich amorphous Li_sSi alloy forming the shell, and crystalline silicon forming the core. The formation of the interface between the amorphous and crystalline phases is related to the stress-induced Li⁺ diffusion retardation, and may lead to the local loss of mechanical integrity due to large stress build-up at the interface [70, 71].

One-dimensional (1D) nanostructures were first described for use in Li-ion anodes in a seminal paper published in 2008 by Chan et al. [65], and similar studies published around the same time period [72, 73] where Si NWs were applied as anodes. Chan et al. prepared Si NWs directly on a stainless steel current collector, by goldseeded chemical vapour deposition (CVD). The nature of the synthesis resulted in excellent adhesion of the active material to the substrate and in significant porosity of the electrode. Constraining the volumetric expansion through the design of the electrode morphology (Figure 2.4) resulted in significant improvements in electrochemical performance of the Si based electrodes. The Si nanowire arrays

displayed a capacity of > 2100 mAhg^{-1} at a C/20 rate, without large decrease in reversible capacity and change in the morphology of the nanowires.

Despite the promise of these CVD grown Si NWs for LIB applications, typically used gold catalysts have recently been shown to be detrimental to the electrochemical performance (in terms of initial capacity, capacity retention and rate capability) of NW based electrodes. Furthermore, Au is costly, shows poor lithium activity and is much denser than Si which strongly impacts the gravimetric capacity for a given total anode [74]. To circumvent these issues presented by the Au catalyst, recent approaches have been developed to prepare NWs through different routes, such as high boiling point solvent syntheses using electrochemically active catalyst materials such as Sn [75, 76] or shifting the grown method entirely to a metal assisted chemical etching regime.[77]

Composite Si nanostructures have also been proposed in order to improve the electrochemical performance. By incorporating the nanoscale Si inside an elastically deformable conductive host the stress changes the cause mechanical breakdown associated with electrochemical lithiation can be better accommodated, while also providing robust electronic conduction pathways.

A different approach to improving the electrochemical performance of the Si based LIBs is preparing Si-C composites. Two strategies for preparing Si-C composites have been widely employed. Carbon structures such as nanotubes, nanosheets of graphene or carbon fibres have been used as supports for nanoscale active material [78-81]. By providing continuous electrical pathway from the active material to the current collector, the influence of the electrochemically induced agglomeration of the nanoparticles on the electrochemical performance is greatly reduced. Moreover, using carbon support offers excellent porosity allowing for better penetration of electrolyte

throughout the electrode, shortening diffusion lengths, allowing for higher rates of charge/discharge as summarised in Figure 2.5.



Figure 2.5. Constant current line-sweeps and cyclic performance for a) carbon coated. Reproduced from [82] with permission from American Chemical Society. b) carbon supported Si nanostructures. Reproduced from [83] with permission from American Chemical Society

In contrast to the supported electrodes, carbon coatings are a different strategy for preparing carbon composites with Si [84-87]. By applying a thin (few to few tens to at most few tens of nanometres) coatings of carbon on the surface material, a mechanically stable layer that can provide support to the nanostructures, and thus preserve their mechanical integrity during repeated charge-discharge cycles, can be formed. Additionally, the continuous layer present on the surface of the active alloying material acts as a stable conductor from the electrode to the current collector. An extension of this strategy is the preparation of composites in which nanostructures of alloying materials are embedded in a carbonaceous matrix. Carbon forms a stable SEI layer with the species present in the electrolyte, and has been shown to provide a degree of mechanical support against rapid expansion and contraction during electrochemical cycling in randomly mixed slurries, but also in 3D ordered porous materials with

electrochemically active materials embedded within the carbon matrix [88]. The problems arising from this approach are mostly related to low ionic conductivity of carbonaceous matrix and resulting low rate capability of such prepared nanostructures.

Within a vast multitude of structures prepared for Si based anodes, nanotubes seem to offer the best electrochemical performance, due to the mechanisms of Si lithiation, and free space provided for volumetric expansion of the nanostructures. To alleviate the repeated re-formation of SEI layer, an electrochemically-inactive SiO₂ layer was used in order to ensure SEI layer stability. The mechanical robustness of SiO₂ provides buffering against stress induced cracking within the nanotubes, while ensuring formation of a stable SEI layer. To date, SiO₂@Si nanotubes show one the best electrochemical performance for Si based anodes [64] (see Figure 2.4). The need to commercialize Si based batteries will undoubtedly result in further improvements in the Si based LIB performance.

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for LIB anodes.

Composition	Morphology	Initial Capacity	Final Capacity (#	Reference
		(C-rate)	cycles)	
Si	NWs	4277 (C/20)	3500 (20)	[65]
Si@SiO _x /C	NPs	1600	1100 (60)	[89]
Si@C	Mesoporous CS NWs	3163C/5	2751 (80)	[82]
Si	3D Porous	2820 (C/5)	2780 (100)	[90]
C-Si	Core-shell NWs	700 (C/15)	1600 (47)	[91]
Si-C	Carbon coated	3344	1326(40)	[92]
	NWs			
Si	Nanotubes	3648 (C/5)	2800 (200)	[93]
Si-Graphene	Composite	2158 (C)	1168 (30)	[94]
Si-CNT	Composite	2300 (C/10)	1400 (50)	[83]
Si	NWs	4000 (C/10)	1600 (50)	[95]
Si/C	Nanocomposite	2000(C/20)	1700 (100)	[96]
Si	Nanotubes	3200 (C/20)	2800 (50)	[97]
Cu-Si	Nanocables	1500 (C/3)	1400 (100)	[98]
B-doped Si	NWs	3354 (C/10)	1500 (250)	[99]
SiO ₂ @Si	Nanotubes	1780(C/5)	1600 (2000)	[64]

Table 2.1. Summary of the relative performance of different Si based electrodes.

2.5.2 Germanium

Germanium can also store Li through similar alloying reactions to those associated with Si. Fully lithiated Li_{4.4}Ge has a high theoretical capacity of 1600 mAhg⁻¹ [58]. Similarly, large amounts of Li atoms stored in Ge, cause it to expand and contract upon cycling, with volume changes reaching 370% [58]. One very exciting property of Ge based anodes is the fact that Li diffusivity in Ge is 400 times greater than in Si, indicating that Ge may be an attractive material for high-power rate anodes [100, 101]. Additionally, the electrical conductivity of Ge is about 4 orders of magnitude higher than Si. Initial investigation into thin films of Ge showed that crystalline Ge suffers from large irreversible capacity loss during initial cycles. In contrast, amorphous and nanocrystalline films of Ge show greater capacity retention, with capacities as high as

1700 mAhg⁻¹ reported after over 60 cycles (see Figure 2.6a). Shortened diffusion lengths also allowed for much improved kinetics of the Li insertion and removal, permitting charge/discharge rates as high as 1000 C with little capacity loss[100] (Figure 2.6).



Figure 2.6. (a) Cycle life of Ge nanocrystals. (b) Cycle life of thin film Ge at 1000 C charge and 1 C discharge. Reproduced from [100] with permission from Electrochemical Society.

A variety of nanostructures have been prepared in order to further improve the performance of Ge based electrodes [58, 102-105]. For instance, Au-seeded Ge nanowires prepared by CVD showed high capacities of over 850 mAhg⁻¹ at C/20 rates, and were able to deliver more than 600 mAhg⁻¹ at 2C rates. Effects arising from incorporation of Au into the nanowire (given the aforementioned issues stated in the last section) during growth however remain a problem [74].

In another example, Park et al [105], used the Kirkendal effect to prepare Ge nanotubes from core-shell Ge-Sb nanowires. Coating with antimony (Sb) acetate and polyvinyl pyrrolidone was followed by high temperature annealing. As outward diffusion of Ge atoms is much faster than inward diffusion of antimony, void formation begins in places where Ge atoms us to reside. Prolonged thermal treatment allows for

the formation of amorphous nanotubular structures of Ge, with very low concentration of Sb. The unique structure of the nanotubes permitted facile accommodation of mechanical stresses and improved cycle performance, with capacities as high as 900 mAhg⁻¹ after 50 cycles at C/5, and 600 mAhg¹ after 25 cycles at 20C.

In composite electrode materials, the use of carbon with Ge results in more stable electrodes, which has been evidenced by an improvement in electrochemical properties. The Ge-C composite can also reduce the degree of mechanical failure arising from multiple cycling. One effective strategy is the dispersion of nanosized material into a carbon matrix, where carbon acts as both structural buffer and electroactive material during Li incorporation/extraction. Cui et al. [102] prepared Ge nanoparticles encapsulated with carbon, through solid state pyrolysis of PTA-Ge, thermally polymerized from tetraallylgermane (TA-Ge). Initial discharge and charge capacities of 1190 and 923 mAhg⁻¹, and low capacity fading confirmed the effectiveness of the carbon matrix in improving the electrochemical performance of the Ge nanostructures. Carbon coating is another effective strategy to improve performance. For example, Yoon et al. prepared carbon coated Ge composites by high energy ballmilling of commercial Ge powders and poly(vinyl alcohol) (PVA)[106], producing carbon coated composites with good high initial capacities of up to 1600 mAhg⁻¹ and good capacity retention for up to 50 cycles. A variety of other reports was also produced detailing preparation and characteristics of Ge-C composites, including formation of core shell Ge@C nanoparticles [107], self-assembled Ge/C nanostructures [108], graphene-supported Ge [109], or carbon coated Ge nanowires [110].

Multiple element composites are also being researched for alternative anode materials based on Ge. Ge/Cu₃Ge/C composites [111] were prepared by pyrolysis and high energy mechanical milling, showing improved performance compared to Ge on its

own, or Ge/C composite. The improvement in electrochemical performance was attributed to the presence of inactive Cu as well as the carbon matrix. Cu was used also in core-shell nanowire arrays [112]. Hierarchical structures of these types of anodes have great advantages for electrochemical performance of the battery, allowing for up to 80% Coulombic efficiencies in the initial discharge as well as over 1400 mAg⁻¹ after 40 cycles. The excellent properties of such anodes are attributed to unperturbed electrical contact of the current collector with the electrochemically active material, as well as large porosity of the Ge/Cu anodes.

Significant efforts dedicated to improvement of Ge based anodes show that Ge is a promising candidate for next generation LIBs. Further work is however required to fully utilize its potential, in particular to improve mechanical stability of the electrode. Moreover, ensuring formation of stable SEI layer should contribute to the overall cycling performance of Ge-based anodes in appropriate electrolytes.

2.5.3 Tin and tin oxide

Tin and its oxides have also attracted significant research attention due to their ability to alloy with Li. Their low cost combined with high theoretical capacities, equal to 980 mAhg⁻¹ for tin, 864 mAhg⁻¹ for tin (II) oxide, and 780 mAhg⁻¹ for tin (IV) oxide, make these materials a very attractive prospects for future generation Li ion batteries. However, their implementation has been hindered by the comparable volumetric expansion and contraction experienced by Sn and other alloying materials. As was the case for Si and Ge, many efforts have been undertaken in order to improve the electrochemical performance of Sn and tin oxide based batteries.

Research on tin and tin oxides for application in battery anodes dates back to two papers published in 1997 by Dahn et al. [113] and Idota et al. [114] detailing structural changes and electrochemical properties of tin oxide based anodes. Since then,

most of the research has focused on determining fundamental properties of the lithiation of tin oxide, with some interesting results, and improvement of cycle life and rate capacity. Investigations into the origin of large irreversible capacity in tin oxide anodes, causes of agglomeration of tin nanostructures upon repeated cycling as well as formation and stability of SEI layer allowed better insight into the fundamental processes in Sn-based anodes. Relatively few studies focus on the performance of metallic Sn, rather looking at SnO₂. The half-cell insertion reaction, corresponding to lithiation of SnO₂ depends on electrochemical reduction of SnO₂ to metallic Sn. The overall reaction can be written as follows:

 $SnO_2 + 4Li^+ + 4e^- \rightarrow Sn + 2Li_2O$ (2.3) $Sn + xLi^+ + xe^- \leftrightarrow Li_xSn (0 < x < 4.4)$ (2.4)

The reduction of SnO₂ to metallic tin is generally considered to be irreversible, and leads to large capacity loss in the first cycle, when the associated charge for that process is factored into the coulometric response of an alloying system [113]. Moreover, the electrode undergoes an electrochemically driven solid state amorphization process. Examination of individual nanowire-type structures, reproduced in Figure 2.7, has shown that during lithiation, SnO₂ nanowires elongate by about 60% axially and widen by 35% radially to accommodate the volume changes [115]. These changes are associated with a wire with a certain crystal orientation, and are likely linked to the rate of insertion/alloying at different facets, or possibly from preferential and confined axial electronic transport in tandem with preferential ionic transport to the NW walls [116].





Figure 2.7. In situ TEM observation of the lithiation process of SnO₂ NW Reproduced from [115] with permission from Royal Society of Chemistry.

These types of informative single-structure measurements serve to demonstrate that low- or confined-dimensional structures undergo anisotropic volume increases, but it has yet to be determined whether these effects are from the isotropy in the measurement and from the innate anisotropy of the structure and its crystallography with respect to Li diffusion and associated alloying processes.

Li insertion into crystalline SnO₂ leads to dense dislocation zones forming at the interface, separating crystalline oxide and amorphous Li-Sn phases. The nanowire morphology allows for accommodation of large degrees of strain and stress, but repeated cycling of the nanostructures may lead to pulverization and loss of mechanical integrity.

In order to improve the electrochemical performance of Sn anodes, similar strategies to those applied in Si and Ge were employed. Both nanostructuring and

preparing material composites yielded some interesting results [56, 117]. Tin oxide nanostructures such as nanoparticles[118], nanowires, nanotubes all have benefits contributing to better performance of the battery electrode. In one study [119], heterostructures of indium oxide and tin oxide were prepared by thermal evaporation. Tin oxide nanowires grew with indium oxide adsorbed onto the surface of the nanowire, forming a surrounding shell. This unique concept allowed for better conductivity of SnO₂ NWs and high specific capacity, compared to SnO₂ and In₂O₃ NWs on their own. Even though nanostructuring of the electrodes has its benefits, the problem of reduced capacity due to cracking, pulverization and agglomeration of nanostructures remains. In order to further reduce the influence of physical changes on the overall performance of the battery, nanostructured composites are extensively investigated with some very exciting results. For example, core shell tin oxide-multi wall carbon nanotubes (MWCNTs) composites were prepared by hydrolysis of SnCl₂ in presence of HCl [120]. The resulting excellent electrochemical performance was attributed to nanostructuring resulting in shortening diffusion lengths for Li ions, as well as the presence of MWCNT, which greatly improved the conductivity of the electrode, capacity retention and Coulombic efficiency, through increased mechanical stability and persistent conduction pathways.

Tin oxide composites with other materials are also of great interest.[121-134] The benefit of using materials that are not electrochemically active, or do not undergo drastic changes has been shown in numerous studies. Materials such as copper [128, 131] nickel [135], sulphur [129], cobalt oxide [136], or titania were confirmed to benefit the performance of the battery. Copper and nickel are mainly used as support for electrochemically active tin oxide. Generally, the benefits of the electrochemically inactive electrode support allows for large improvements in capacity retention, due to conserved electrical continuity between the active material and the current collector.

However, addition of this "dead weight" material (which does not add to capacity but adds weight to the anode) may reduce the gravimetric capacity of the electrode below the capacities achieved in pristine films, so care needs to be taken to ensure that the gravimetric energy density is not lower than the electrodes composed of solely active materials. The overall capacity of composite batteries will be however limited by the combined performance of both positive (cathodes) and negative (anode) electrodes.

At the moment, cathode chemistry can limit the maximum capacity obtainable by a battery and thus, using negative electrode materials with capacities lower than the theoretical limits may be beneficial, in particular in situations where rate capability and cycle life are important. Active/inactive composites may benefit in those situations, as the active coating thickness is usually quite low, similar to the diffusion length of Li ions and so insertion and removal of ions may be extremely fast. Material such as CoO [136] form polymer like structures preventing agglomeration of tin oxide nanoparticles and improving diffusion kinetics of Li ions, improving capacity retention and rate performance (Figure 2.8).



Figure 2.8. (a-d) SEM images of CoO-Sn; (e) Cycle performance of CO-Sn composite. (f) Rate performance of CoO composite. Reproduced from [131] with permission from International Society of Chemistry.

In an alternative approach, active-active composites improve the performance of the batteries, without the gravimetric density reduction penalty associated with activeinactive composite. Previously mentioned carbon-tin/tin oxide composites are included in this class of battery architectures. Other materials used in conjunction with tin are titanium oxide and cobalt. Dahn et al [137] prepared a library of Sn-Co-C composites, indicating that only a narrow composition range favours amorphous phase formation, beneficial for extended electrochemical cycling. Kim et al. [138] developed a method to prepare a nanocomposite of Sn and Ge, with improved capacity retention compared to pristine Sn and Ge. The improvements in capacity retention were attributed to the separation of Ge nanoparticles during lithiation/delithiation cycles and resulting formation of conduction pathways. The nature of the nanocomposite results however in a substantial degree of surface reactions, such as electrolyte decomposition and Li carbonate formation, resulting in unwanted contributions to irreversible capacity and internal resistance, among other effects. In cases where large surface area nanostructures are used, it is particularly important to understand the reactions taking place at the SEI. It has also been suggested that tin, formed by the reduction of tin oxide during electrochemical reactions, may contribute to large capacity fading, not due to agglomeration of nanoparticles, but due to Sn-catalyzed electrolyte decomposition [139]. In particular, this phenomenon is favoured at high current densities, where enough thermal energy is provided to accelerate diffusion of Sn, driven by desire to reduce interfacial energy. Figure 2.9shows a schematic diagram of the self-catalyzed agglomeration of Sn nanoparticles.

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Figure 2.9. Schematic diagram detailing formation and aggregation of Sn nanoparticles. Reproduced from [58] with permission from American Chemical Society.

Recently, Sony has commercialised its Nexelion [140] range of Li-ion cells containing anodes consisting of Sn-Co-C. Such alloys have shown excellent cycling abilities attributed to active-inactive relationship between Sn and Co [122, 124]. Other alloys including active-inactive system are Sn-Ni-C and Sn-Cu. The Nexelion device demonstrates improved capacity and cycling performance compared to traditional carbon based batteries. In a study carried out by the Army Research Laboratory [141], Nexelion batteries showed good performance at elevated temperatures, and stability at high discharge rates. Although, as the study notes, cycle-to-cycle capacity retention of the Nexelion is slightly worse than standard 14430 cell, its increased initial capacity allows it to retain higher reversible capacity after 220 cycles. The commercial utilisation of Sn has demonstrated its purposeful character as battery anode material in cost effective and efficient manner.

Composition	Morphology	Initial Capacity	Final Capacity	Ref
SnO ₂ -In ₂ O ₃	NWs	2000 (C/5)	780 (10)	[119]
SnO2- SWCNT	Composite	1399	1000 (100)	[142]
SnO ₂ -MWCNT	Composite	1500 (C/10)	404 (20)	[143]
Sn-Co-C	Composite	451 (C/8)	486 (40)	[124]
Sn-C	Composite	600 (C/8)	311 (200)	[144]
Sn-Co	Composite	1200 (C/2)	845 (50)	[136]
SnO ₂ –C	GNS-NP	1800 (C/15)	570 (30)	[145]
Sn-C	Composite Composite	806 (C/10)	737 (200)	[146]
Sn-Au	Composite	1200 (C/10)	600 (150)	[147]
$SnO_2 - C$	CNT .	1466(C/5)	402 (100)	[120]
SnO_2	composite Nanocrystal	2156 (C/10)	550 (20)	[148]
Sn-SnO ₂	NWs	2400 (C/8)	845 (100[149])	[149]
SnO ₂ –C	NPs	1200 (C/2)	492 (100)	[150]
SnO_2	Mesoporous	960 (C/6)	600 (100)	[151]
Sn-C	Nano Sn-Hard	580	300 (30)	[152]
SnO_2	Carbo Mesoporous -	1400 (C/5)	675 (50)	[153]
SnO_2	NW Nanosheets	1860 (C/10)	593 (20)	[154]
Sn-C	3D porous	1425 (C/20)	638 (315)	[155]
Sn-C	RGO-Sn	1572 (C/8)	710 (50)	[156]
SnO ₂ -C	Graphene Composite	1100 (C/8)	872 (200)	[60]

Chapter II

Table 2.2. Summary of the performances of different Sn and SnO_2 based electodes. The C rate and the cycle numbers are indicated in brackets.

Table 2.2 details the electrochemical performance of a variety of recently prepared SnO₂ nanostructures which further highlights the promise of Sn and Sn composite based materials as low cost, high performance anode materials.

2.6 Role of electrode structure on electrochemical performance

The previous section of this review dealt mainly with material chemistry considerations for next generation battery electrodes, their response to lithiation and relation to performance. One additional factor that needs to be considered while designing new electrodes is the architecture or arrangement of the active material. The majority of currently available commercial Li ion battery electrodes are formed as thin films on the order of hundreds of microns thick. These films often consist of an active-material powder, polymer-based binders and additives aimed at increasing electric conductivity of the electrode. These additives have a negative effect on the gravimetric energy density, and as such are undesirable, although necessary in current cells. The geometric considerations of the electrode design are important in the light of inherent limitations of the charge transport characteristics of the electrode, and both concentration and activation polarizations. For instance, in LiFePO₄ and graphite, the Li ion conductivities are of an order of 10^{-10} cm²s⁻¹, compared to 10^{-6} cm²s⁻¹ in commonly used electrolytes [19, 157]. Li ions, from the surface of the active material diffuse inwards, filling the vacancies in active materials microstructure, and creating bottlenecks that impede additional ion transport. The structure of the electrodes, their thickness and the length of diffusion pathways, obstruct ionic mobility and limit the batteries to slower rates than could otherwise be possible.

For these reasons, 3-dimensional, porous electrode architectures have attracted a lot of attention, particularly because battery size and mass are expected to be reduced in next generation power systems, without a reduction in energy density in principle.

One primary driver for power source improvement and also miniaturization is Moore's Law, which empirically links the increase in the density of transistor elements on a microchip (or the reduction in the feature size for these transistors) with computational power or operations per second, which has increased since its inception. The performance of portable electronics, batteries, unfortunately has an annual improvement 'curve' characterized by just a 10% increase in energy density.

One analogy between electronic computation speed and improved energy storage and supply materials in battery power sources is the mobility of the charge carriers: electrons and holes for electronics; electrons and ion for batteries. The classical diffusion relation $L^2 \propto D\tau$ shows that a reduction in length scale (L) is beneficial when considering diffusion lengths of Li (or other cations) and the associated diffusion constant (D) into (at least) the pristine active material during discharge (rate dependent). However, battery chemistries during discharge are complex, even for very well understood bulk analog of useful or promising materials; performance improvements can be significant, however, when many factors are taken into account. Inherent transport kinetics unique to certain crystal structures are often predefined and affected by the crystal structure, orientation and chemical potential; size reduction does not automatically improve performance or rate capability. Shorter transport distances (faster times to cation insertion) and higher surface-to-volume ratios that improve redox accessibility and time for ion and electron transport can be achieved when the discharge chemistry and phase formation are well understood. By providing pathways for lithium insertion, phase formation, shorter diffusion lengths in 3D can alleviate rate limitations or improve cyclability for 'gentler' depths of discharge in many systems. Once at the interface of an active particle, Li ions enter from the outside inward, filling the atomicscale vacancies in the active material's exterior microstructure and therefore creating

diffusion bottlenecks that impede additional ion transport. Acting in concert, the dense nature of electrode composites, electrode thicknesses of ~100s mm, and micrometerscale diffusion path lengths in active electrode particles obstruct ion mobility and limit lithium-ion batteries to slower discharging and recharging rates than are otherwise possible. These elements also add significant 'dead weight' to all current commercial batteries and would make it extremely difficult to assemble as an ordered smooth layered battery. This design, as will be discussed further on, also allows faster charging and discharging rates, and the possibility of strongly asymmetric charge/discharge cycles optimizing power delivery and shortening charging times. Such changes may first take place in the use of small devices, where the total amount of energy stored is small. Only 360 W is required to charge a 1Wh cell phone battery in 10 s (at a 360 C charging rate, where the C-rate is the inverse of time in hours required to fully charge or discharge an electrode or battery). Even at the highest charge rate tested thus far for these materials (50 C), corresponding to a time of 72 s (as opposed to 3.5 hrs based on the mass of active material in bulk form) to fully discharge the capacity, the material achieves about 80% of its theoretical capacity.

Porous electrodes offer numerous important benefits that are listed below [158]:

- Pores provide good access for the low surface-tension electrolyte to the electrode surface ordinarily taken up with polymer binders and carbon additives that are no longer required.
- Large surface area of the porous electrode facilitates charge transfer across the electrode/electrolyte interface, reducing the impact of the activation polarization.

- Ionic diffusion path-lengths are reduced due to lower wall thickness less than the limiting solid state diffusion length of lithium for discharging and lower overpotential charging.
- The active material is used more efficiently due to better electrolyte penetration and reduced wall thickness.
- Continuous electron pathways are provided from the active material to the external load.
- The volumetric energy density is comparable with packed particle electrodes
- In some cases no binders or conductive additives are required, reducing dead weight (better gravimetric energy density).
- Void spaces separating particles can accommodate volumetric changes of active material.
- Porous composites can incorporate a secondary conductive phase to improve high rate performance of active phases with low intrinsic conductivity.

Depending on the electrode preparation method, porous electrodes can be divided into those that are hard-templated or soft-templated. The size of the pores allows categorization of the porous electrodes as follows: microporous (pore size <2 nm), mesoporous (pore size 2-50 nm) and macroporous (pore size >50 nm).

Soft templating usually involves surfactants as structure directing agents. The pore architecture can be controlled by the choice of surfactants, solvents and synthesis conditions. Evaporation induced self-assembly (EISA) is particularly useful for formation of thin films with precisely controlled porosity [159]. It can be however difficult to obtain high crystallinity of the walls of the solid, if the temperature of the crystallization of the inorganic phase is higher than the temperature at which the surfactant block copolymer is removed. In this situation, hard templating approaches

are much more successful. Templates such as aluminium anodic oxide (AAO) membranes, preformed porous solids, and assemblies of colloidal particles are used.

2.6.1 AAO templated nanomaterials

Figure 2.10 presents a schematic of formation of porous material using AAO template, with isolated pores. In this case, solid products form inside the template, replicating the shape of the void space. Usually, structures such as 1D nanotubes and nanowires are formed. AAO templates are commonly used, due to ease of the preparation of the template, as well as uniform pore size [160]. AAO membranes can also be used in conjunction with soft templating materials to prepare solid structures with hierarchical porosity [161]. A variety of inorganic electrode materials can be prepared using this method, including metals, metal oxides and various composites.



Figure 2.10 AAO templating mechanism. Reproduced from [162] American Chemical Society. .

2.6.2 Nanocasting of nanoscale battery materials

Nanocasting is a name given to the transformation of a porous solid into hollow replicas. In the nanocasting process, porous solids are infiltrated with the precursor of target electrode material (see Figure 2.11). After thermal treatment, the template is removed. The product is an inverted replica structure of the original hard template.

The molds with bicontinuous pore structures produce mesoporous replicas, whereas templates with cylindrical mesopores in hexagonal arrangement produce nanowire arrays, which are interconnected only if the template contains secondary pores between the main cylindrical pores.



Figure 2.11. Nanocasting of mesoporous electrode materials. (a) Nanocasting process in mesoporous silica. (b) TEM image of mesoporous TiO_{2.} Reproduced from [163] with permission from German Chemical Society. (c) Nanocasting process in mesoporous silica SBA-15 Reproduced from [82] with permission from American Chemical Society. (d) TEM image of mesoporous Si-C nanowire formed from SBA-15 template

The most commonly used hard templates are mesoporous silica materials. To remove these template materials, simple wet etches can be carried out, either through extraction with HF, hot NaOH or KOH solutions. Mesoporous electrodes with numerous compositions have been synthesized by hard templating, including MnO_2 [164, 165], Cr_2O_3 ,[166] Co_3O_4 [167], SnO_2 [168] NiO [169]. In particular, SnO_2 , nanocasting allows the formation of mesoporous solids with a higher degree of crystallinity, and more order compared to soft templating, due to protection from excessive grain growth by sintering present in soft-templated materials [158].

2.6.3 Colloidal crystal templating

Colloidal crystal templating allows for the formation of porous electrodes with an excellent degree of control over the pore size and the template solid structure. Facile templating methods are compatible with a variety of precursors and allow the formation of inverted opals (IO) of many materials. The general procedure for IO preparation is demonstrated in Figure 2.12, where a hard template is infiltrated by an appropriate precursor, and then removed either chemically or thermally.



Figure 2.12. Schematic diagram detailing preparation of inverted opal electrode. Reproduced from [170] with permission from Royal Society of Chemistry. Through various mechanisms, the arrangement of spheres dictates the periodic porosity of the resulting inverted opal structure.

The template preparation mechanism generally involves self-assembly of template spheres (usually a hard polymer like polystyrene or poly(methyl methacrylate), [171] or silica on the surface of the substrate. This makes it possible to form inverted opal structures of a variety of metals and metal oxides [158, 170, 172, 173] and metal fluorides [174]. Typically, inverted opals have wall thicknesses in the range of 10s to 100s of nanometres, and have been prepared and characterized in multiple compositions, for Li ion anodes, cathodes and solid state electrolyte materials.

IOs generally exhibit higher power densities than bulk materials, due to excellent electrolyte penetration. Although they may not the best choice for electrodes composed of materials which undergo large volumetric expansion upon lithiation (e.g. alloying materials), using a bicontinuous approach allows for formation of IO electrodes from alloying materials as well. Excellent control over the morphology of the IOs and an extensive range of compositions make IO structures very exciting in other areas of research, ranging from catalysis[175], gas sensing, to optics and filtration.

The following section will detail the various implementations of IO structures as active materials for LIB anode and cathodes.

2.7 Inverted Opal structures for Lithium ion battery applications

2.7.1 Inverted opal cathode

Vanadium oxide was the first material to be electrochemically characterized as a cathode material in an inverted opal arrangement [176]. In this study, colloidal crystals consisting of polystyrene spheres was deposited on an ITO glass current collector and infiltrated with a diluted vanadyl alkoxide precursor. Subsequently, the precursor was transformed into solid V_2O_5 gel network. (see Figure 2.13).



Figure 2.13. (a-d) Schematic diagram detailing formation of V_2O_5 IO cathodes. (e) Rate performance of the V_2O_5 IO cathodes. Reproduced from [176] with permission from Royal Society of Chemistry.

Chemical removal of PS sphere template results in the formation of inverted opal structures of V_2O_5 amibgel. At low discharge rates, the ambigel electrodes exhibit reversible behaviour without significant loss of capacity. This study also demonstrated excellent rate performance of IO based electrodes, indicating that the hierarchical structure might reduce polarization via improved mass transport. Electrochromic properties of an IO prepared from V_2O_5 have been also shown [177] demonstrating improvements such as faster switching speed and better coloration contrast, when compared to bulk films.

In a different study, LiCoO₂ was formed in an IO structure through a nanocasting route. Mixed precursors of Li and Co salts precipitate as oxalates within colloidal crystal template voids [178]. At precursor ration of 1:1, it is possible to form LiCoO₂, however, it is difficult to preserve the IO structure due to the high temperatures required for the formation of the LiCoO₂ phase. None of the LiCoO₂ powders formed, even with addition of PEG as chelating agent, preserve the IO structure. However, the high interconnectivity and large porosity of the sample allows sustaining high rate cycling. At 700 mAg⁻¹, the mesoporous structure of LiCoO₂ is able to sustain a capacity of 40 mAg⁻¹, while the corresponding bulk film fails to charge due to high polarization.

Another binary oxide formed as an IO structure (LiNiO₂) was prepared through a salt precipitate procedure [179]. Stoichiometric LiNiO₂ has a layered structure in which Li⁺ ions occupy octahedral sites in alternate layers of cubic close packed (ccp) oxide ions. At high temperatures, LiNiO₂ readily decomposes to Li_{1-x}Ni_{1+x}O₂ due to vapour pressure differences between Li salts and formation of Ni²⁺. Adding excess Li salt and introducing higher oxygen gas partial pressure to suppress reduction of Ni atoms, allows formation of IO structures.

LiMn₂O₄ spinels were fabricated using precursors that solidify before destruction of colloidal crystal template during annealing [180]. Gradually increasing the temperature, however, during template removal, allowed for transformation of amorphous Li-rich sites within the electrode to spinel phase with Li ions in tetrahedral and octahedral sites. LiMn₂O₄ showed remarkable capacity retention, with no more than 7% capacity loss after 10000 full cycles at 9 C (full discharge in ~7 minutes) (see Figure 2.14) , compared to more than 80% reduction in the charge capacity for bulk LiMn₂O₄.



Figure 2.14. Cycling behaviour of solid and porous LiMn₂O₄ electrodes. Reproduced from [180] with permission from Royal Society Chemistry..

The excellent electrochemical performance of IO electrodes can be ascribed to high crystallinity, ensuring stability during cycling; high degree of porosity, shortening diffusion lengths and a reduction of polarization.

Lithium iron (II) phosphate is an alternative cathode material that has been extensively researched since the original paper on the material application in battery electrodes in 1997 [181]. Iron represented a cheaper alternative to expensive cobalt and nickel materials. However it suffers from low ionic and electronic conductivity, making

high power applications difficult to realize. The IO structure should improve the ionic conductivity by providing nanoscopic walls with shortened diffusion lengths and opened pore networks that facilitate electrolyte penetration. Lu et al. [182] prepared LiFePO₄ IOs by mixing Li, P and Fe precursors in stoichiometric ratio. Subsequent calcination under nitrogen resulted in the formation of IOs with residual carbon interspersed in the LiFePO₄. The carbon content contributed to the conductivity of the IO and allowed for high charge rates, resulting in an initial capacity of 100 mAhg⁻¹ at 5.9 C.

Recently, Doherty et al. described the preparation of LiFePO₄ IOs based on PMMA colloidal templates, with sphere sizes varying from 100-270 nm [183]. The templates were not filled completely, which improved the electrolyte penetration and ionic and electronic charge transfer. Sintering at 800 °C improved charge transfer resistance in the electrodes and allowed for charge rates of 10 C with capacity retention close to 100 mAhg⁻¹ after 50 cycles. Template sphere size was also shown to have an influence on the electrochemical performance of the IO electrodes, as larger spheres created a continuous macropore network, ensuring facile flow of the electrolyte to all of the parts of the electrode. Residual amorphous carbon present after calcination in N₂ also enhanced electronic conductivity of the olivine material, although a balance is necessary, as high weight percentage of C may create a Li diffusion barrier and hinder high rate performance.

2.7.2 Inverted opal anodes

2.7.2.1 Carbonaceous inverted opal anodes

Graphitic carbon is currently used in commercial LIB as an anode electrode. It offers excellent stability, and relatively long cycle life (1000s of cycles). However, its

performance at high discharge rates is hindered by low Li ionic conductivity in carbon. IO structure offers a possibility to improve the performance of carbon based electrodes, through facilitating easier electrolyte penetration and shortening Li ion diffusion lengths in active material matrix. The first C-based IOs were prepared in 1998 by Zakhidow et al [184], via a vapour deposition technique, forming diamond, glassy carbon and graphite inverted opals were published. Solution based processes for carbon IO formation were then reported, using sucrose [184] and phenyllic resin [185] as carbon precursors. In 2005, there were published two separate articles investigating the electrochemical performance of carbon based inverted opal electrodes. In one approach [186] PMMA templates were infiltrated with resorcinol-formaldehyde (RF) sol gel precursor. This allowed the formation of IO monoliths with mesoporous walls and a surface area of 326 m²g⁻¹. Large surface area is associated with randomly distributed micropores between the graphene nanosheets in hard carbon solid walls.



Figure 2.15. SEM image of carbon inverted opals. Carbon inverted opals experience much less polarization than bulk carbon of same composition. Adapted from [186] with permission from Wiley-VCH.

The monoliths were found to be electronically and ionically conductive. Good conductivity, excellent electrolyte penetration related to the porosity of the IO and shortened diffusion path lengths allowed carbon IOs to experience much less polarization at current rates as high as C/2. (Figure 2.15).

In another study, carbon IOs were prepared by CVD of benzene using silica IOs as templates [187]. The resultant 10-20 nm coating of graphite on silica was electronically and ionically conductive and was suited as an anode active material. This material exhibited specific capacities as high as 260 mAhg⁻¹ at current rates of 1000 mAg⁻¹ (\sim 2.7C), with good cycling stability (90 % capacity retention over 60 cycles).

More recently, particulate inverse opal structures with mesoporous walls were prepare via solution casting of PS spheres with phloroglucinol and formaldehyde mixture containing F127 block copolymer [188]. Incorporating soft templating methods into the IO formation procedure resulted in increased surface area (from 109 m²g⁻¹ to 466 m²g⁻¹). A large irreversible capacity was attributed to formation of SEI layer on the electrode, and inherent properties of hard carbon. The mesoporous carbon was however capable of sustaining charge rates as high as 300 mAg⁻¹ with reversible capacity of over 300 mAhg⁻¹.

An interesting means of increases the capacity of carbon based IOs is to introduce a secondary active material, usually in a form of nanoparticles embedded in the conductive matrix of carbon IO. Materials such as SnO_2 [88, 187], Si [189] or TiO₂ [190] have been incorporated in the carbon based inverted opals, with significant influence on the electrochemical performance[191]. One of the most recent studies demonstrated an IO electrode concept with SnO_2 NPs entrapped in macroporous carbon IO prepared by infiltration of PMMA colloids by tannic acid Sn^{4+} complexes [88]. Optimization of infiltration and calcination parameters resulted in nanometre scale walls and improvement in the rate performance of the electrodes. They were able to sustain current rates in the range of 1-10 Ag^{-1} (~3-30 C) without any significant capacity loss. High porosity (including hierarchical length scale of multiple porosities) in the electrode resulted in low volumetric energy density of prepared electrodes, confirming

the need for further improvements in the electrode design. With respect to inverse opals, three-dimensionally interconnected macropores facilitate the rapid flux of liquid electrolyte solutions, such that $100 \text{ m}^2 \text{ g}^{-1}$ of electrode interfaces are simultaneously accessible to Lithium or other mobile cationic charges. This degree of macropore interconnectivity is intentionally tailored into PhCs from self-assembled close-packed templates. For example, the ionic conductivity of a 1 M LiPF₆ liquid electrolyte solution is only impeded by a factor of two when ion transport occurs through the interconnected macropores of monolithic carbon inverse opals (electrode thicknesses: $300 \,\mu\text{m}$ – $3 \,\text{mm}$).

2.7.2.2 Three-Dimensionally structured alloying anodes

The first reports of alloying electrodes in IO form appeared in 2004 [192]. PMMA colloidal crystal templates were infiltrated with $SnCl_2$ dissolved in DI water and 30 wt% H_2O_2 . IOs of SnO_2 were formed after thermal removal of PMMA template. The morphology of the walls of IOs was influenced by the calcination temperature, becoming more granular and interrupted by grain boundaries with the increase in the calcination temperature[173]. Galvanostatic cycling of the IOs resulted in significant morphological changes in the electrodes. The wall thickness increased significantly on the alloying of SnO_2 with Li, with nodules appearing on the previously smooth structure (see Figure 2.16).



Figure 2.16. SEM images showing morphologies of SnO₂ IOs at different stages of charging. Reproduced from [192] with permission from Royal Society of Chemistry.

Repeated cycling caused increase of the wall thickness, and finally loss of the IO morphology. The authors concluded that the large volumetric expansion of the IO SnO₂ electrodes made them impractical for applications in LIBs. Additionally, the granular structure of the SnO₂ walls caused very high polarization, caused by high resistance of the granular walls of the IO. Different approaches were used to alleviate the drawbacks caused by the properties of SnO₂. Using a carbon-SnO₂ composite was one of the strategies employed [187, 193]. Stable capacity of 300 mAhg⁻¹ could be delivered by carbon SnO₂ composite at 100 mAg⁻¹. The improved cyclability was attributed to the confinement effect provided by the mesoporous carbon framework, which served as a structural buffer for volume variation of Sn nanoparticles during repeated cycling. Stability of the SEI layer also contributed to the good cyclability of the IOs.

In another approach, Ni support was used to improve the stability of the SnO₂ IO based electrode [194]. In this study, a colloidal crystal template was infiltrated using

electroplating. A mixture of SnCl₂ and NiCl₂ was deposited from an aqueous solution through electroplating, and tested electrochemically. Repeated cycling caused delamination of the IO electrode from the current collector, possibly due to epitaxial mismatch of the Ni-Sn alloy and the Cu current collector. During cycling, the electrode underwent rapid morphological changes and as a result, capacity retention was poor. After 100 cycles, the reversible capacity sustained by the electrode was only about 95 mAhg⁻¹.



Figure 2.17. (a) CV for hollow FTO. (b) CV for porous FTO. (c) Initial charge and discharge curves for porous FTO. (d) Cyclic performance for porous FTO. Reproduced from [195] with permission from Royal Society of Chemistry.

Recently, [195], fluorinated tin oxide (FTO) and antimonated tin oxide (ATO) IOs showed significant improvements in electrochemical performance compared to pure SnO_2 IOs, in both capacity and cycling stability (see Figure 2.17). The improved performance of the FTO and ATO electrodes was attributed to improved integrity of the nanoporous structure, allowing for better tolerance of large volume changes caused

by repeated cycling of the electrode. Good electrochemical performance of highly conductive transparent oxides may enable their applications in solar cells, electrochromic devices or sensor applications.

Si is another material that has been investigated electrochemically and structurally in IO architecture. Esmanski et al. [196] prepared a variety of Si based IO films: amorphous hydrogenated Si IOs (prepared through CVD), nanocrystalline Si-IOs, carbon coated nanocrystalline Si-IOs and carbon IOs with amorphous Si coating. Amorphous hydrogenated Si IOs demonstrated good initial discharge capacity (2500 mAhg⁻¹). The cycling stability of the IO electrodes was also satisfactory, with over 70% of discharge capacity retained after 145 cycles. Sphere size was also shown to have an influence on the performance of the IOs, as the electrodes prepared from templates with lower diameter spheres performed poorly, due to blockage of the pore openings by swelling electrode material. The rate performance of the IO was limited by the amorphous structure of the IO walls. In order to increase conductivity, amorphous IOs were annealed at 800 °C in an inert atmosphere resulting in the formation of nanocrystalline Si-IO. The crystalline structure of the IO walls resulted in improved Li mobility in the electrode material, and better rate performance. Capacity retention however was extremely poor, reaching negligible values by the 15th cycle at best. Similar electrochemical behaviour was observed for carbon coated nanocrystalline Si IOs.

In the same study, a different approach was also presented. Carbon IOs were coated with thin layer of amorphous Si via CVD. The initial capacity of the IOs was around 2000 mAhg⁻¹, with the first cycle coulombic efficiency reaching around 80%, increasing to 98-99% after 5th cycle. The rate performance of the IO was poor, compared to amorphous Si samples, with the capacities reaching negligible levels at 10C rates. The carbon support allowed for better mechanical and structural stability of the
IOs, resulting in good capacity retentions of over 80% after 145 cycles. Esmanski's findings agreed well with results published by Kim et al. [90], who prepared 3D porous Si particles through deposition of sol-gel mixtures of Si and silica particles and subsequent HF etching. The 3D particles demonstrated excellent capacity retention and rate capability, delivering 2668 mAhg⁻¹ after 100 cycles at 1C rate.

In a more recent study, nanoscale Ni metal scaffold supported bicontinuous 3D IO based batteries were prepared by Paul Braun's group [197]. The formation mechanism for these electrodes is shown in Figure 2.18.



Figure 2.18. (a) Loss of electrical contact during cycling. (b) Good electrical contact between Si film and Ni substrate. (c) Bicontinuous bulk anode consisting of silicon thin film on 3D porous Ni scaffold. (d) Fabrication procedure for the bicontinuous electrode Reproduced from [198] with permission from Nature Publishing Group.

Initially, nickel was electrodeposited in a PS template. Following thermal template removal, the Ni IO was electropolished and a thin film of Si was deposited on the surface of Ni support through CVD. The self-supported Si anodes showed excellent electrochemical performance, delivering stable capacity of 2660 mAhg⁻¹ while conserving over 48% of its slow rate capacity when charged at 9.5 C.

The same bicontinuous approach was also successfully employed in an operational battery [198], where MnO₂ cathodes were prepared by electrodeposition of MnSO₄ on electropolished Ni metal current collector. Superior rate performance of the bicontinuous films was attributed mainly to excellent electrolyte penetration, reduced polarization by providing a low resistivity current collector throughout the electrode and shortened diffusion lengths. Such prepared electrodes were able to deliver capacities of over 75 mAhg⁻¹ at an exceptionally high rate of 1114 C, which corresponds to full discharge in less than 4 seconds (see Figure 2.19).



Figure 2.19. Ultrafast discharge of the lithiated MnO₂ cathode. Reproduced from [198] with permission from Nature Publishing Group.

The most recent report [199] concerning 3D battery architectures, describes a high power microbattery capable of delivering power densities as high as 7.4 mW cm⁻² μ m⁻¹ (see Figure 2.20). In this study, polystyrene spheres were deposited over gold electrodes etched on glass substrate. Subsequently, a nickel metal support was electrodeposited over the gold electrodes to form a stable current collector. A Ni-Sn alloy and MnOOH were then electrodeposited on the current collector, before

submersion of the microbattery in LiNO₃ and LiOH, to form a lithiated cathode. Such microbattery design allowed the authors to achieve over 2000× the power and twice the energy density observed in the best microbattery designs presented thus far. The energy densities demonstrated of up to 15 μ Wh cm⁻² μ m⁻¹, and the power densities of up to 7.4 mW cm⁻² μ m⁻¹ are comparable with the best supercapacitors. The improvements in power and energy density were attributed to shortened ionic diffusion lengths, and reduced resistivity of the electrode. Successful demonstration of a high power microbattery allows compact integration of a full battery package for microelectronics applications. The versatility of this approach also permits development of different types of electrode chemistry for specific applications.



Figure 2.20. (a) Schematic diagram of microbattery fabrication procedure. (b) Microbattery design. (c) SEM cross-section of the microbattery. (d) Top-down SEM image of the microbattery interdigitated electrodes. (e) Constant current line sweeps at different rates. (f) Rate performance of the microbatteries. Adapted from [199] with permission from Nature Publishing Group.

Table 2.4 summarizes some of the developments in IO Li-ion battery electrode research.

Composition	Morphology	Initial capacity (C- rate)	Final capacity (# of	Ref
VO	IO		cycles)	[200]
V_2O_5	IO IO	-	-	[200]
$LiNiO_2$		-	-	[4.0.0]
SnO_2	IO IO		-	[192]
	10	299 (15.2 mAg ⁻¹)	-	[186]
Sn/C	Sn(a)C IO	$348 (15.2 \text{ mAg}^{-1})$	-	F 4 0 F 7
C	Graphitic C	326 (C/10)	320 (60)	[187]
Sn/C	IO Sn@C	415 (C/10)	375 (60)	
T_iO_2/C	TiO	$158 (50 \mu \text{A cm}^{-2})$	40 (15)	[201]
	102000	$150 (50 \mu \text{A cm}^{-2})$	10(13) 145(70)	[201]
	10	173 (C/10)	173(70)	[202]
$E_{14} = 15 O_{12}$	IO	173(C/10) 137(C/10)	120(100)	[203]
1×10^{4}		137(C/10)	110 (50)	[204]
L1W112O4/L11.5A10.5111.5(PO4)3	composite	04 (-)	-	[205]
LiMn ₂ O ₄	IO	-	-	[206]
Sn/C	Sn@C	$1500 (100 \text{ mAg}^{-1})$	96 (100)	[193]
Si/C	Si@C	3180 (-)	-	[189]
LiFePO	IO	115 (5C)	120 (50)	[183]
Si	a-Si th IO	2500 (C/10)	1750	[100]
	nc-Si IO	3000 (C/10)	(145)	
Si-C	nc-Si-C IO	2400 (C/10)	(115)	
	a-Si-C IO	2406 (C/10)	0(12)	[196]
	a-01-0 10	2400 (C/10)	2133	
			(145)	
NL/So	NE Se	$315 (50 \text{ m } \Lambda \text{ m}^{-1})$	(1+3)	[104]
111/511	Composito	515 (50 m/g)	(100)	[194]
L'Ma O	Composite		(100)	[1.0.0]
$L_{11}Mn_2O_4$		-	-	[100]
$MnO_2 (\underline{a}) N_1$	1 hin	/4 (1114 C)	-	[198]
	film/IO			
	Bicontinuous		100 (20)	F4 77 47
FeF ₃	IO Di i	$540 (50 \text{ mAg}^{-1})$	190 (30)	[174]
$S_1 (a) N_1$	Bicontinuous	3568 (C/20)	2660	[197]
	IO	4.	(100)	
SnO_2/C	$SnO_2(a)C$	$1659 (0.5 \text{ Ag}^{-1})$	715 (500)	[88]
TiO ₂	IO	442 (25 mAg ⁻¹)	117 (200)	[207]
С	IO	359 (-)	315 (20)	[188]

Table 2.3. Summary of the performance of various types of IO based electrodes.

2.8 Pseudocapacitors offering good power and energy densities

Capacitive charge storage has some particular advantages compared to non-faradaic intercalation batteries. Supercapacitors can be charged within seconds, cycled hundreds

of thousands of times, are stable and ideal for delivering high power, which for some uses is preferably to a higher energy density.[208] Several options exists for charge storage at the electrode-electrolyte interface, which are sensitively dependent on structure and composition, chemical potential redox potential and many other factors. In secondary or rechargeable batteries, cations intercalate into interlayer gaps (van der Waals gaps) of layered or tunnel materials [209] or form alloys with phases of other materials. The specific type of materials that permit intercalation however, can offer in some conditions, faradaic and non-faradaic processes, thereby adding energy and power density benefits of both systems.

Cations that can electrochemically adsorb onto the surface of a material through charge-transfer processes facilitating non-intercalation based charge storage, similar to electrochemical double layer capacitors to some extent. This can in some cases remove the limitation of long diffusion times for ions through the van der Waals gaps, and is energetically easier. Such pseudocapacitance when this form of insertion is capacitive, i.e. the electrochemical intercalation processes stem from cations that are faradaically stored and changes in materials structure do not occur.[210] While there are many textbooks that deal with the fundamentals of capacitive and intercalation charge storage mechanisms, there are some salient features that are important for materials that ordinarily store charge through intercalation, but exhibit surface charge storage when polarised at higher rates.

Increasing the rate of a cyclic voltammagram for structured or porous energy storage materials has a large influence on the course of the electrochemical reaction many cations. One characteristic is that the current peaks associated with many processes such as SEI formation, reduction, oxidation, alloying or intercalation, are often convoluted within the total cumulative charge and the curve resembles that of an

asymmetric supercapacitor to some degree. The current response is however much larger than for the slow rate scan, suggesting that there is additional charge storage mechanism operating at large potentials. The total stored charge, for any electrochemical energy storage process can be separated into three components: The faradaic contribution from the Li⁺ ion insertion processes, the faradaic contribution from the charge transfer process with the surface atoms, referred to as pseudocapacitance and the non-faradaic contribution from the double layer effect [211]. When the porosity of the electrode increases, both types of capacitive contributions (pseudocapacitance and double layer charging) can be significant. The capacitive effects can be characterized by analysing data from cyclic voltammetry experiments carried out at different scan rates, according to [212]:

$$i = av^b \qquad (2.6)$$

where the measured current *i* obeys a power law relationship with the sweep rate v. Both *a* and *b* are adjustable parameters, with *b* value, determined from the slope of log(i) vs. log(v). There are two well-defined conditions, b = 0.5 and b = 1. For b = 0.5 the current is proportional to the square root of the scan rate, according to the equation:

$$i = nFAC^* D^{\frac{1}{2}} v^{\frac{1}{2}} \left(\frac{\alpha nF}{RT}\right)^{\frac{1}{2}} \pi^{\frac{1}{2}} \chi(bt) \qquad (2.7)$$

where C^* is the surface concentration of the electrode material, α is the transport coefficient, D is the chemical diffusion coefficient, n is the number of electrons involved in the electrode reaction, A is the surface area, R is the molar gas constant, F is the Faraday constant, T is the temperature, and $\chi(bt)$ represents the normalized current for a completely irreversible system, as indicated by cyclic voltammetry.

The other defined condition is when b = 1, which is representative of capacitive response, as the capacitive current is proportional to the scan rate, according to:

$$i = v C_d A \qquad (2.8)$$

To obtain the *b*-value for a given material system, current values from cyclic voltammagrams carried out at different scan rates are recorded at specified potential values. Then, the slope of the plot of the log(i) vs log(v) is the *b*-value at that potential.

As a pertinent example of many in the literature, Brezesinski et al. [213] recently showed that controlling the morphology of mesoscale porous materials such as films of iso-oriented α -MoO₃ can facilitate a change from non-faradic process to a mixture that helps increase the overall energy density of capacitor-based storage devices, using pseudocapacitive effects controlled by reaction kinetics. These properties were unique to their mesoporous crystalline materials and were superior to those of either mesoporous amorphous material or non-porous crystalline MoO₃ (See Figure 2.21). The iso-oriented layered crystalline domains enabled Li-ions to be inserted into the van der Waals gaps of the α -MoO₃ and importantly, occurs on the same timescale as redox pseudocapacitance.



Figure 2.21 (a) Morphology of mesoporous α -MoO₃ with highly oriented crystalline walls. Low-magnification bright-field TEM micrograph. Inset: A higher magnification micrograph. (b) AFM image of the top surface. Inset: A tilted AFM image with height variations in the 1–5 nm range. (c) Cyclic voltammograms for mesoporous amorphous and crystalline films of MoO₃ systems at a sweep rate of 1 mV s⁻¹. (c) Kinetic behaviour of the various mesoporous films. The total amount of charge storage (gravimetrically normalized) as a function of charging time for each film. Adapted from [213] with permission from Nature Publishing Group

As electrochemically active materials approach nanoscale dimensions, pseudocapacitive effects become increasingly important.[214] In a recent report, Dunn et al. established the dependence of pseudocapacitance on the particle size of anatase TiO₂ nanocrystals.[211] The results showed that for particles smaller than 10 nm in diameter, more than half of the total stored charge is capacitive. As anatase TiO₂ has no van der Waals gap, all of its capacitance is believed to be redox pseudocapacitance. Layered crystal structure materials have also been shown to exhibit such phenomena. TiO₂(B), TiS₂ and H₂Ti₃O₇ are able take up LiC through pseudocapacitive processes [215, 216]. In cases where redox pseudocapacitance contributes to the overall energy

density, its contribution can be established by cyclic voltammetry. By varying voltage sweep rates, a transition from faradaic to non-faradaic processes can be assessed in many forms of high surface area materials.

The performance of most advanced IO based LIBs can be compared to a different type of device that is able to simultaneously deliver high power and high energy densities are pseudocapacitors, which store energy electrochemically between two electrode plates. As the energy storage employs fast and reversible redox reactions between electrodes and the electroactive species, most pseudocapacitors use metal oxides with high number of valence states. They are however difficult to mass produce, and suffer from energy density loss at high scan rates. A recent study by Li et al. [217] demonstrated Ni(OH)₂ nanospheres with excellent electrochemical performance (see Figure 2.22), related to high purity of the surface of the nanospheres, large surface area and the amorphous phase of the nanospheres.



Figure 2.22 (a) CV curves of the amorphous Ni(OH)₂ nanospheres at various scan rates in 1 M KOH. (b) Specific capacitance of the amorphous Ni(OH)₂ nanospheres as a function of the scan rates based on the CV curves. (c) CV curves of the blank electrode at various scan rates. Reproduced from [217] with permission from Nature Publishing Group

In a different study, graphene based supercapacitors were prepared by microfabricating electrodes and subsequent deposition of reduced graphene oxide, on both flexible and robust substrates [217]. The energy density of such structures is

comparable with the energy density of LIBs, while their power densities are higher than power densities of capacitors based on metal oxides. Altering carbon-based electrodes and structuring them with ordered 3D porosity was also demonstrated recently by Huang et al. [88]. By creating SnO_2 nanoparticles inside an inverted opal carbon matrix (Figure 2.23), they demonstrated improved anode kinetics in a Li-ion battery cell. The electrodes exhibit simultaneously enhanced ion and electron transport kinetics as well as geometrically constrained active nanoparticles delivering up to 94.17% of theoretical capacity over 1000 discharge/charge cycles at a current density of 2.0 A g⁻¹, and exhibits good rate capability in the high current density range of 1.0–10.0 A g⁻¹. Creating hybrid materials with two or more active materials offers some potential advantages depending whether energy density and/or cycle life are important.

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Figure 2.23 (a) Schematic illustration showing the preparation of SnO2@C inverted opal electrode. (b) Li-ion battery performances of SnO2@C inverse opal electrodes [90]

Development of such novel manufacturing techniques, optimization of the device configurations and improvement of the used materials will further enhance the performance of the supercapacitors, and we recommend recent reviews on this subject for more detailed information. Developments in the area of ordered porous selfsupported batteries with power densities comparable to supercapacitors offer power improvement options for materials that are fundamentally limited to low intercalative or non-faradaic charge capacities. Designing bi- or multi-phasic materials with different Li insertion voltage ranges could potentially allow for a predetermined capacity without fully discharging each active materials. Constraining one active materials within another with high deformation plasticity, could also potentially give a structurally stable matrix that better accommodated volumetric changes that are not buffered in a polymermaterials slurry in standard cell electrode designs. Recent findings in dual charge storage mechanisms using SnO2 nanoparticles on Si as a hybrid anode [118] and their exploitation will help optimize tailored design of many other sophisticated electrode materials in electrochemistry and energy storage materials influenced by the end application.

Choosing pseudocapacitance and supercapacitance is also possible using twodimensional (2D) nanosheets such as graphene or transition metal dichalcogenides (TMDCs) [218]. Charge storage mechanisms here involve the insertion/extraction of protons or ions in the first few nanometers on the surface of electrode materials for pseudocapacitors and the adsorption/desorption of ions at the electrode-electrolyte interface for electrochemical double-layer capacitors [219, 220]. Enhancing performance is again a function of reduced lithium ion diffusion distance within the materials if the former case and within the electrolyte for the latter case. With the boost of wearable and flexible consumer electronics that have an aesthetic appeal and unique functionality, flexibility and shape versatility or adaptability is a useful property in charge storage

materials and their electrochemical cells [221-223]. The state-of-the-art flexible supercapacitors generally use carbon networks. Without the carbon networks pseudocapacitive materials can barely be used to fabricate the flexible electrodes, so as to assemble the flexible supercapacitors (Figure 2.24). Shi et al. [224], as one example, showed that flexible asymmetric supercapacitors with excellent electrochemical performance and in the form of quasi-transparent energy storage cells could be fabricated by using two kinds of ultrathin 2D nanosheet materials (MnO₂ and graphene). The 2 nm-thick MnO₂ nanosheets with a thickness of ~2 nm exhibited a high capacitance of 774 F g⁻¹ and good rate performance. Flexible asymmetric supercapacitors using the ultrathin 2D MnO₂ and graphene in aqueous Ca(NO₃)₂-SiO₂ gel electrolyte realized excellent electrochemical performance with an energy density up to 97.2 Wh kg⁻¹ much higher than traditional MnO₂ based supercapacitor and no more than 3% capacitance loss even after 10,000 cycles.

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Figure 2.24 (a) Photographs of the screen-printed asymmetric nanosheets-based supercapacitor electrodes of various designs (b) Ragone plots of MS/GA and MS/MS supercapacitor compared with other MnO2 based asymmetric supercapacitors in literature (based on the total mass of active materials)

2.9 Summary and outlook for energy storage material design and performance

In this review, a description of some of the recent advances in nanomaterials design, chemistry, size, shape, structure and assembly on the performance of Li-ion batteries was given. Particular focus was given to the influence of material parameters on cell performance and on emerging functional material architectures with engineered porosity as active Li-ion battery and pseudocapacitor materials. It is becoming clearer from the progress to date, that the improvements associated with changes of the electrode's chemical composition, combined with developments in electrode

architecture offer excellent opportunities for commercialization of next generation Liion batteries and emerging alternative chemistries[225]. Various mechanisms for lithium storage combined with simple routes towards particular morphologies of active material create a multitude of opportunities for electrode design.

However, it is important to note that to date, only a handful of modern materials and electrode architectures have been commercialized. The advances in anode material science and design have not been followed to the same extent by improvements in the cathode chemistry and performance. A pressing challenge is the dearth of true, cell-level investigations of known and promising new materials in true Li-ion cells. Most cathode investigations form lithium batteries with a lithium electrodes; anode studies are half cells. While the fundamental advancements are motivating, many new materials and systems need to be thoroughly investigated using pair-matched anodes and cathodes in suitable electrodes as full Li-ion cells and classified for their optimum performance and loading conditions dictated by the end application.

Inverted opal architectures have been demonstrated to improve the performance of battery electrodes based on a variety of materials. The shortened diffusion lengths and excellent electrolyte infiltration allow for largely increased charge/discharge rates, while the void space allows for facile relaxation of strain and stress caused by repeated cycling of the electrode. Moreover, using a composite approach, where the inverted opal current collector acts as a support for active materials. This design approach can help minimize unwanted polarization and resistances, and achievement of outstanding charge/discharge rates. Such electrodes may achieve power densities more often seen in supercapacitors, while delivering energy densities characteristic for traditional LIBs. The use of engineered or programmed porosity is potentially very useful for materials that have inherently lower Li ion

diffusivity within the crystal structure of the active material. Care should be taken to ensure that the structure of the porous network does not introduce significant increases in electrical resistance through material contacts or grain boundaries for example, or variable SEI film structure at anodes. Ideal scenarios would likely involve engineered porosity of a well crystallized material that itself does not have a high kinetic barrier to Li diffusion within its structure, made porous in a manner that maximizes ambipolar (ionic and electronic) conductivity (tuned for power or energy density requirements at a prescribed rate), forms stable SEI layers at low potentials (anodes), and offers useful volumetric or gravimetric energy densities, among other attributes. Recent efforts for some materials have shown that defining the porosity or dispersion of active materials can also give extra degrees of freedom for volume expansion common for many high capacity materials.

Ultimately, the successful application of materials chemistry and electrode design will be decided by the industry. Undoubtedly, the drive for better LIBs, motivated by automotive and consumer electronics market will have a dominating influence on the types of batteries used. Templated materials with good ionic conductivities can allow for variants of thin film batteries, where the charge storage cell is designed around the shape of the electronic device, rather than the other way round. Although Li-ion battery packs are compact and volumetrically efficient, the 'swiss-roll' design strategy limits the batteries to rectangular or cylindrical shapes, which constrains the form factors of devices. While many factors need to be considered, not least a high quality, repeatable way of producing such thin film batteries and battery skins, scope exists to lay down energy storage cells in parallel with energy conversion or energy harvesting thin film technologies such as solar cells and thermoelectrics, on a single platform. Recent work on unconventional battery designs [226] focused on their accommodation into devices without constraining their form factors. Battery designs

such as flexible batteries [227] stretchable paper-type batteries, and even printed transparent [228] batteries, show that such atypical batteries are possible. The use of IO materials is one way forward, allowing for possibilities of interpenetrating networks with Li-containing polymer electrolytes and sequentially layering of anode and protective encapsulating layers. Painting has proven its usefulness in applying functional materials onto almost any type of substrate for electronic devices and it may be applied to energy storage such as batteries. Printing (or generally, painting)[229] is already considered a viable technique for large-area fabrication of electronic devices (circuits, photovoltaics, displays, etc.) on virtually any type of substrate. Recent work has shown the intriguing possibility of literally painting the layers of materials required for a Li-ion battery [230].

For charge storage technology capable of high performance, faster charging, and stable, safe capacity retention during operation can be moulded to the device shape – this will significantly help advance portable device power technology options such as consumer devices and wireless sensor nodes for example. Consequently, there is huge interest in developing a fully paintable energy storage technology, and a seamless integration of these energy storage systems into electronic devices is still a significant hurdle. Probing how an ordered architecture is that can be assembled layer-by-layer on shaped surfaces, and new non-destructive spectroscopic methods to investigate how a new areal battery shape can be probed during its operation will be very advantageous for future thin film, moldable battery designs and material architectures.

Advances in Li-air and Li-S designs and other 'beyond lithium' systems such as emerging Mg and Na-ion batteries [231, 232] might challenge the supremacy of the Liion system in the future, offering higher energy densities at reduced cost. Some investigations consider multivalent cations offering more than one electron per redox event. As summarised earlier, hybrid systems involving the power density benefits of

supercapacitors and the energy density performance of batteries in the form of ratedependent pseudocapacitors may also have niche application. However, for now, LIBs are very likely to remain the main solution for power systems, and thus drive further improvements in both electrode chemistry and architecture [233].

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CHAPTER III

EXPERIMENTAL

3 Chapter 3. Experimental

3.1 Molecular Beam Epitaxy

Molecular beam epitaxy (MBE) is a method for the preparation of thin films, where the substrate acts as the seed crystal and the deposited atoms follow the structure of the substrate. Two distinct types of epitaxy are used. In homoepitaxy, the deposited film is of the same composition as the substrate, but with much higher crystalline purity. In heteroepitaxy, the deposited film is of different composition than the substrate. Different methods of achieving epitaxial film growth have been developed over the years. Vapour phase epitaxy uses chemical reaction rather than physical deposition to deposit thin films [1]. The most common application of liquid phase epitaxy is the growth of large size semiconductor crystals in Czochralski method [2]. MBE applies evaporated beam of particles in very high vacuum to condense thin films on the substrate [3]. Ultra-pure elements are heated in separate quasi-Knudsen effusion cells, until they begin to slowly sublimate. The gas phase then condenses on the substrate. The term "beam epitaxy" reflects the fact that the evaporated atoms do not interact with each other or with other vacuum chamber gases until they reach the substrate [4].

MBE of Sn and In was carried out on a silicon substrate in a custom built system designed in cooperation with MBE Komponenten GMBH. Prior to the deposition, the surface of silicon was cleaned using standard RCA silicon cleaning procedures. After rinsing, a second treatment in a H₂O₂:HCl:H₂O (1:1:5) solution was used to remove metallic and organic contamination. For deposition of Sn and In, a custom-built MBE high-vacuum chamber with two high temperature effusion cells for metallic Sn or In targets, combined with an electron beam evaporator was designed in cooperation with MBE Komponenten GmbH. Prior to the tin oxide growth the silicon and glass substrates were cleaned using the standard process. In this respect, the sample

was first emerged in a H₂O₂:NH₄OH:H₂O (1:1:1) solution at 80°C for about 30 min. After rinsing the sample in deionised H₂O, a second treatment was performed in a H₂O₂:HCl:H₂O (1:1:5) solution with an adjacent rinsing in deionised H₂O. Through this process metallic and organic contamination is removed. In the latter step the surface is oxidised, so that a thin and clean SiO₂ layer forms at the surface (~2-3 nm). Dipping the sample in HF shortly before introducing it into the evaporator removes the oxide layer and passivates the surface with hydrogen (H). Due to H-passivation the Si surface becomes hydrophobic. Thus, a further oxidation of the surface, e.g. due to O₂ in the air, can be avoided. After rinsing, a second treatment in H₂O₂:HCl:H₂O (1:1:5) solution was used to remove metallic and organic contamination. For deposition high purity metallic Sn and In targets were deposited using an electron beam evaporator

3.2 Electrophoretic Deposition

In electrophoretic deposition (EPD), charged colloidal particles dispersed or suspended in a liquid medium are attracted and deposited onto a conductive substrate of opposite polarity due to application of DC electric field [5]. It has been widely applied for the rapid preparation of wear resistant and antioxidant ceramic coatings, fabrication of functional films for advanced microelectronic devices and solid oxide fuel cells, as well as the preparation of advanced composites or coatings for medical devices. The main driving force for EPD is the charge on the particle and the electrophoretic mobility of the particles in the solvent under the influence of an applied electric field.

Two groups of constraints control the characteristics of EPD process – those related to the suspension and those related to the forces, such as the nature of the electrodes, electrical conditions, deposition time, particle concentration etc.

For the EPD of particles, part of the current should be carried not only by the charged particles but also by free ions co-existing in the suspension. Thus, the amount

of deposited particles is not simply related to the current, unless the amount of free ions is negligible. The first attempt to correlate the amount of particles deposited during EPD with different parameters was proposed (separately) by Hamaker [6] and Avgustnik [7]. Hamaker's law relates the weight of deposited particles (w) to the strength of the electric field applied (E), the electrophoretic mobility (μ), the surface area of the electrode (A) and the particle mass concentration in the suspension (C) through the following equation:

$$w = \int_{t_1}^{t_2} \mu EAC \ dt$$
 (3.1)

Avgustnik's law is based upon cylindrical, coaxial electrodes. In his description, the electrophoretic mobility was expanded and is represented in terms of permittivity(ε), the zeta potential (ζ) and the viscosity of suspension (η).

$$w = \frac{l \mathcal{E} \varepsilon \zeta C t}{3 \ln(a/b)\eta}$$
(3.2)

(3.2)where l and a are the length and radius of the deposition electrode, b is the radius of the coaxial counter electrode.

These classical equations were expanded and developed into more complex modes of deposition process by Biesheuval and Verweij [8]. In their description, they considered the presence of three distinct phases: a solid phase, suspension phase and a phase containing little or no solid particles. The deposit phase and the particle-free liquid phase both grow at the expense of the suspension phase. By considering the movement of the boundary between the deposit and the suspension phases with time, along with the continuity equation and expression for velocity of particles in the suspension, they derived the following equation (based on the initial equation derived by Avgustnik et al):

$$w = \frac{2\pi\mu lEC_d}{\ln a/b} \left(\frac{\phi_s}{\phi_d - \phi_s}\right) t \quad (3.3)$$

where ϕ_s and ϕ_d are the columetric concentration of particles in suspension and deposit respectively, C_d is the mass concentration of particles in the deposit, μ is the electrophoretic mobility ($\mu = \epsilon \zeta / 6\pi \eta$)

Ishikare *et al.* [9] and Chen and Liu [10] used the following equation for the weight (w) of charged particles deposited per unit area of electrode in the initial period, ignoring the charge carried by the free ions

$$w = \frac{2}{3} C \varepsilon_0 \varepsilon_r \zeta \left(\frac{1}{\eta}\right) \left(\frac{E}{L}\right) t \quad (3.4)$$

where C is the concentration of the particle, ε_0 is the permittivity of the vacuum, ε_r is the relative permittivity of the solvent, ζ is the zeta potential of the particles, η is the viscosity of the solvent, E is the applied potential and L is the distance between the electrodes. The above equations, termed often as Hamaker equations, suggest that the deposition weight of the charged particles under ideal electrophoretic deposition depends on the above parameters. However, in the solvent, the particles and the electrodes are fixed so the factors ζ , ε_r , η , L in the above equation are constant. Thus, the mass of the deposited particles, and in particular the thickness of the deposited film, can be easily controlled by the concentration of the suspension, applied potential and the deposition time.

The solution of PS spheres for the EPD process was prepared by dispersing a small quantity of PS spheres in ethanol, followed by the drop wise addition of ammonium hydroxide until the pH of the solution was close to 10. Subsequently, after

dispersing PS spheres by sonication, flat and aligned stainless steel electrodes were placed in the solution (see Figure 3.1).



Figure 3.1. Schematic diagram of electrophoretic deposition setup

The fundamental mechanism of EPD has been described in the literature in the framework of the Derjaguin-Landau-Vervey-Overbeek (DLVO) theory and in relation to the distortion of the double layer formed around the particle, as described by Sarkar and Nicholson [11].

A constant electric field of up to 500 V/m was applied between the electrodes between 20 minutes and 2 hours to form stable films of PS spheres on stainless steel. Before removal of the electrodes from the solution, a short pulse of 30 kV/m was applied between the electrodes to improve the stability of the prepared films. Subsequently, the samples were removed and used for inverted opal preparation without further modification.
3.3 Infiltration of opal templates

Typically, for an inverted opal, a hard template is infiltrated by a suitable precursor of the required compound. Subsequent thermal or chemical treatments of infiltrated templates result in the formation of a solid network in the template. To improve the template infiltration, vacuum assisted methods are typically used to enhance the capillary flow of the precursor in the template network. The degree of the infiltration can be controlled by the number of infiltrations carried out and the concentration of the precursor in the applied sol.

Two distinct precursors were used to prepare tin oxide inverted opals. Tin ethylhexanoate-diisopropoxide was mixed with 2-methoxy ethanol for a 10% v/v solution, while excess tin (II) acetate was dissolved in ethanol. The supernatant was collected and used for infiltrations without further treatment



Figure 3.2 Chemical structures of a) tin ethylhexanoate-diisopropoxide. b) tin (II) acetate.

A single infiltration cycle involved applying a small volume (~100 μ l) of the precursor to the surface of the template, subjecting it to a subsequent drying process at 40 °C for 2 hours to ensure full solvent evaporation. The infiltration cycles were repeated required number of times to ensure full infiltration of the template with the precursor solution.

3.4 Characterization methods

3.4.1 X-Ray Diffraction

X-Ray Diffraction (XRD) is one of the principle experimental techniques dedicated to determination and refinement of crystal structures and identification of unknown crystal compounds [12]. The mathematical description of X-Ray diffraction was introduced by W. L Bragg in 1913, who described the reflection of a coherent beam of Roentgen rays (X-Rays) from the sets of planes in a regular crystal. If the wavelength of the X-ray radiation is of the order of the magnitude of separation between the neighbouring planes, a reflection of the incident ray satisfies Braggs Law [13]:

$$n\lambda = 2dsin\theta$$
 (3.5)

where λ is the wavelength of radiation, *d* is the interplanar spacing and θ is the diffraction angle.

Typical X-ray diffractometers use a copper anode for the generation of the incident radiation with peak intensity at certain wavelengths (called "lines"). For Cu, these lines are called K_{α} , corresponding to transition from 2p to 1s orbital, and $K_{\rm B}$, corresponding to the transition between 3p and 1s orbital. The corresponding wavelengths of radiation are 1.541 Å and 1. 394 Å, respectively. Typically, the $K_{\rm B}$ line is selectively filtered to increase monochromaticity of the incident beam on the sample. By scanning over the range of angles (θ) and recording the reflected beam intensity, it is possible to determine angles that satisfy Bragg's condition. Since crystals reflect incident X-Rays at angles that are characteristic for their crystalline structure, XRD may be used to determine unknown crystalline substances by comparison to a database of known

crystal structures, maintained by the Joint Committee for Powder Diffraction Standards (JCPDS) [14].



Figure 3.3 Illustration of the interaction of incident X-rays with a set of atoms from a cubic type crystal lattice

Wide angle XRD patterns of SnO_2 IOs were collected on a Phillips X'Pert MPD pro diffractometer operating at 40 kV and 35 mA. Typically, scans were collected over the range $20^{\circ} < 20 < 70^{\circ}$ using a step size of 0.015° and a time-per-step of 2s.

3.4.2 Electron Microscopy Techniques/Characterization

Conventional microscopy techniques involve the interaction of visible light with matter. The resolution of the image, obtained by conventional microscopy, can achieve a maximum diffraction limited resolution of up to ~ 200 nm. The maximum resolution of optical microscopy is related to wavelength by following equation [15]:

$$\delta = \frac{0.6 \, \mathrm{i}}{\mu \sin \beta} \quad (3.6)$$

where, λ is the wavelength of light and $\mu \sin \beta$ corresponds to the numerical aperture of the objective lens.

The resolution limit of the optical microscopy excludes its widespread application in the characterization of nanomaterials. To overcome these limitations, a beam of high energy electrons, whose energy may be approximated by de Broglie equation:

$$\lambda \approx \frac{1.22}{E^{\frac{1}{2}}} \qquad (3.7)$$

A high energy beam of electrons will result in a small de Broglie's wavelength and will decrease the theoretical resolution limit for electron microscopy. When an accelerating voltage of 100 kV is applied, this results in a wavelength of approximately 0.0039 nm, which is 137,500 times shorter than that of green light (550 nm) [15].

3.4.2.1 Scanning Electron Microscopy

Scanning Electron Microscopy (SEM) is a microscopy technique that operates by scanning (rastering) a beam of relatively high energy electrons (2-40 kV) across the surface of a specimen. SEM imaging typically proceeds by collecting elastically scattered electrons (electrons whose interaction with the atomic orbitals of the specimen surface results in no loss of kinetic energy) which are secondary, or backscattered in nature (see Figure 3.4).

SEM images of all SnO₂ IOs were collected using an FEI Quanta 650 FESEM microscope operating at 10 kV under high vacuum mode (> 1.0×10^{-6} Torr). Samples were prepared by placing the samples on carbon tabs mounted on Al specimen stubs Surface morphologies and the chemical composition of the nanostructured dispersions

were also investigated by scanning electron microscopy (SEM) using a Hitachi SU-70 with an Oxford-50 mm² X-Max detector for energy dispersive X-ray analysis (EDX). The acceleration voltage used for imaging was equal to 10 kV, unless stated otherwise. Size data and shape descriptors were calculated using ImageJ software package. The analytical approach involves the following steps: The SEM image was opened in ImageJ software package. The contrast and brightness as well as the image sharpness were adjusted in order to obtain best image for future analysis. Subsequently, histogram thresholding was employed in order to isolate areas of interest for measurements



Figure 3.4 Possible interactions of a thin, solid specimen, with a beam of high energy electrons; the arrows indicate a general relationship to signal strength

3.4.2.2 Transmission electron microscopy

Transmission electron microscopy (TEM) is used for the high-resolution imaging of samples due to the extremely small de Broglie's wavelengths of the electrons used. Typically, electron beams are in the range of 100-300 kV which provide resolution in

the order of 3.9-1.3 pm. Such wavelengths are considerably smaller than the diameter of single atom. Since the incident energy of the electrons is also much higher than those used in SEM, the electrons are able to penetrate through suitably thin specimen samples. The interaction between the electrons and the atoms provides detailed information about the structure of the investigated sample. Owing to its high-resolution capability, TEM can be used to identify detailed structural information related to crystallographic orientation (stacking, faults, twinning, etc).

TEM analysis was performed using a JEOL 2100 TEM operating at 200 kV. Energy Dispersive X-ray Spectroscopy was conducted on an Oxford Instruments large area Si diffused EDX system fitted to the electron microscope. Additional imaginG was carried out with a JEOL JEM-2100F field emission microscope operating at 200 kV, equipped with a Gatan Ultrascan CCD camera and EDAX Genesis EDS detector for atomic resolution crystal structure and composition examination

Cross-sectioning of the SnO₂ nanoparticles formed by MBE was carried out with an FEI Helios Nanolab Dual Beam FIB System. A protective layer of platinum was deposited over the surface of the sample to minimize surface damage. Crosssectional TEM sample preparation was performed on the slice using a standard FIB lift out technique described elsewhere [16].

3.4.3 X-Ray Photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) is a non-destructive technique used for surface chemistry investigation. It is based on photoelectric effect, where x-ray photons remove electrons from inner shell orbits of an atom. Each of these electrons has a binding energy (E_B) that is characteristic for an atom. Electrons that are removed from the atom structure possess kinetic energy (E_K) which can be related to the incident Xray photon through: [17]

$$E_K = h\nu - E_B \tag{3.8}$$

The quantum nature of energy levels leads to formation of a kinetic energy distribution in the form of bands, which is associated with the electronic structure of the atom. This ultimately allows for the identification of elements present on the surface.

There are two main points of information that can be inferred from an XPS spectrum. The binding energy can reveal the elemental composition of the surface that is investigated, due to close relationship between the electronic structure and the number of protons in an atom. Secondly, the oxidation state of the investigated compound is readily identifiable, as the binding energy is directly proportional to the oxidation state. Higher oxidation states will cause "shifts" of core level spectra to lower E_{κ} . Measurement of the binding energy shifts can produce important information about the bonding state of particular species. In the practical application of XPS, the ability to resolve between atoms with slightly different chemical shifts is limited by a number of factors, in particular the lifetime and the width of initial energy level as well as the linewidth and lifetime of incident photon.

It is important to note that C1s core levels are used as reference peaks, so that offsets between data from different spectrometers can be adjusted and directly compared

X-ray photoelectron spectroscopy (XPS) was acquired using a Kratos Axis 165 monochromatized X-ray photoelectron spectrometer equipped with a dual anode (Mg/Al) source. Survey spectra were captured at as pass energy of 100 eV, step size of 1 eV, and dwell time of 50 ms. The core level spectra were an average of 10 scans captured at a PE of 25 eV, step size of 0.05 eV, and dwell time of 100 ms. The spectra were corrected for charge shift to the C 1s line at a binding energy of 284.9 eV. A

Shirley background correction was employed, and the peaks were fitted to Voigt profiles.

3.4.4 Spectroscopic ellipsometry

Ellipsometry is an optical technique for determining properties of surfaces and thin films. It uses linearly polarized light with a known polarization orientation reflected from the analysed surface. The reflection introduces elliptical polarization to the incident wave. The shape and orientation of the polarized wave depends on the angle of incidence, the direction of the polarization of the incident light and the reflection properties of the surface. From these orientations and the direction of polarization of the incident light, we can calculate the relative phase change (Δ) and the relative amplitude change (Ψ) introduced by reflection from the surface. A schematic is illustrated in Figure 3.5.



Figure 3.5 Representation of incident and elliptically polarised light due to reflection from a sample surface..

An ellipsometer measures these changes in the polarization state of light when it is reflected from a sample, given by the following equation:

$$\rho = \tan(\psi)\exp^{i\Delta} = \tan\left(\frac{R_p}{R_s}\right)\exp^{i(\delta_p - \delta_s)} = \frac{E^r_{\ p}/E^i_{\ p}}{E^r_{\ s}/E^i_{\ s}} = \frac{R_p}{R_s}$$
(3.9)

An important application of ellipsometry to the study of optical properties of thin films. A thin film is a layer of material with thickness of several hundred nanometres. Ellipsometry is a very sensitive technique, permitting determination of the optical properties of films with thicknesses of only a few nanometres.

Spectroscopic ellipsometry in this thesis was carried out using a J. A. Woollam & Co. M2000D Fast Spectroscopic Ellipsometer with a spectral range of 193 – 1000 nm. The data was typically acquired in the spectral range of 350 – 950 nm. All ellipsometric data was acquired *ex-situ*, in ambient air at room temperature. Optical constants such as refractive index and extinction coefficients are extracted from thickness-based models such as a Cauchy layer model. To account for porosity and variable dielectric constant in non-uniform or porous material coverage, the Effective Medium Approximation (EMA) was employed.

3.5 Electrochemical Methods

3.5.1 Chronopotentiometry

Any change in the electrochemical potential at the working electrode caused by application of constant current to the electrochemical cell can be measured [18]. The current will cause the cell to deviate from an open circuit voltage (which is approximately equal to the equilibrium cell potential) to that of closed circuit voltage condition. Although chronopotentiometry is specifically related to changes in the potential, per unit time (s), it can be also applied to determine the change in electrical

charge with time $\langle \frac{dQ}{dt} \rangle$, from an initial Q_0 to final Q_f , between two potential limits, where total charge is $Q_f - Q_0$. The total charge (Q) is a measure of the charge transferred via the working electrode, and is one of the prime indicators of the performance of the LIB cell [19]. Current rate dependant characteristics of the electrochemical process can be also determined through this approach. It is a common approach in LIB research to replace Ampere-seconds, which are inconvenient when working with small electrochemical cell, with Ampere-hours (Ah where 1 Ah =3600 C). The storage capacity of the LIB is usually represented in terms of its gravimetric capacity, i.e. the capacity delivered per unit mass: mAhg⁻¹. This expression is of particular importance to the LIB industry as it indicates the mass of the electrode material required to form a battery of a certain capacity. Active materials with higher gravimetric capacity allow building of smaller batteries with better performance.

Chronopotemtiometry may be used to acquire a plot of electrochemical potential measured relative to the reference electrode (typically Li/Li⁺) against gravimetric capacity. Such plots are usually termed charge-discharge, or voltage curves, for a given electrode material. Charge-discharge plots give a tremendous insight into the fundamental properties of LIBs. Information that can be acquired from voltage curves consist of: a) capacity at a given potential, b) formation of redox species, which can be inferred from plateau regions in the curve, c) the average cell potential d) specific energy and e) polarisation, which can be determined from the potential difference between the charge and discharge plateaus (see Figure 3.6). These combined five factors give an adequate description of the general working performance of a LIB.

Chapter III



Figure 3.6 Representative plot of electrochemical potential versus gravimetric capacity for a reversible, single charge/discharge process..

Chronopotentiometry can be carried out at various current densities (current per unit mass of active material) over successive cycles between two set potential limits vs. Li/Li⁺. The application of current densities are also relevant to the theoretical charge/discharge rates of a given electrode. A current density of 100 mAg⁻¹ applied to an electrode of theoretical capacity of 100 mAhg⁻¹ equates to the 1 C rate, where 1 C is equal to one total discharge in one hour. The current densities applied in this body of work were varied between 20 and 200 mAg⁻¹, and between potential limits of 0-2.5 V vs Li/Li⁺.

3.5.2 Cyclic Voltammetry

Cyclic voltammetry is a versatile technique used to establish the fundamental properties (potential, reversibility, charge current etc) of a redox system of the form $0 + xe^- \leftrightarrow R$. The technique is based on sweeping a ramping voltage to the working electrode from an initial open circuit potential between two potential limits [20]. The current is sensed

between reference and counter electrodes which in the testing of Li-ion electrodes usually refers to metallic Li acting as both.

A reversible redox process of the form $0 + xe^- \leftrightarrow R$ may show a typical CV beahaviour, with a dual set of redox features (peaks) of about the same area and height. Symmetry within the voltammogram is a good indication of the degree of reversibility of the system. The reversibility of the system is a prime concern in the design of secondary batteries. To obtain quantitative information, the Nernst equation (See equation 1, where R is gas constant, T absolute temperature, n the number of transferred electrons and F is Faraday's constant) needs to be applied to obtain standard equilibrium potential, by combining both cell potential and Gibbs energy ($\Delta G = -nRF$).

$$\Delta E = \frac{2.3RT}{nF} \qquad (3.10)$$

The Nernst equation can be used to determine the potential difference between oxidation and reduction features. For an ideal system, ΔE (See Figure 3.7) tends to zero. For a quasi-reversible system, ΔE increases and the redox features broaden. A truly irreversible process leads to complete asymmetry in the voltammagram and lack of oxidation or reduction features.



Figure 3.7 Cyclic voltammagram of a) fully reversible redox system displaying a small potential difference between redox features, b) quasi-reversible system with broadened features and a light asymmetry and c) irreversible system with significant asymmetry and absence of redox features.

In the investigation of secondary cells, cyclic voltammetry is employed to measure the potential at which oxidation and reduction occurs in the working electrodes. The difference between these potentials determines the active operating potential of the electrodes and may be further used in chronopotentiometry techniques. Additionally, cyclic processes involving the formation of intermediate or additional

redox species may feature multiple redox features which may be used to determine cyclic mechanisms during the charge/discharge processes.

3.5.3 Potentio/Galvanostats

The most common and widely employed tools for electrochemical characterization of samples are Potentio/Galvanostats, collectively known as potentiostats. These analytical tools are capable of performing a range of electrochemical techniques such as chronopotentiometry, chronocoulometry, cyclic voltammetry and impedance spectroscopy. The typical setup of an electrochemical experiment involves feeding information to the potentiostat from three inputs, or electrodes. The electrodes are usually referred to based on their function in the experiment: working electrode, counter electrode and reference electrode. The working electrode is generally connected to the electrochemically active material. In LIB research, the working electrode consists of either a slurry of active electrode material or pristine active material deposited on a suitable electronically conductive substrate. Slurries are usually formed by mixing of active material with a suitable conductive binder (binders are used to circumvent the drawbacks caused by poor conductivity of active materials). The counter electrode (auxiliary electrode) forms a full electronic circuit with the active electrode.

In LIB research, lithium metal is used as the counter electrode as it provides Li⁺ ions for the electrochemical process. In a two electrode setup, only the working and counter electrodes are used to provide information about the electrochemical processes taking place. A third electrode can be employed in the event where mass and ion transfer occur at the counter electrode, which may affect its potential vs any electrode not taking part in electrochemical reaction), and this electrode serves to ensure the accuracy of the measurements of electrochemical potential changes. The third electrode

is commonly referred as reference electrode. It does not take active part in electrochemical reaction but only provides a stable benchmark potential against which the potential of working electrode is measured.

Potentiostats can carry out electrochemical measurements in two distinct modes, depending on the controlled parameter of the circuit. In the potentiostatic mode, the potential of the counter electrode is accurately controlled against that of the working electrode so that the potential difference between the working and reference electrode is well defined and corresponds to the value specified by the user. In the galvanostatic mode, the current flowing between the working and auxiliary electrodes, as well as the potential between the working electrode and reference electrode, is closely monitored and adjusted by negative feedback loops (see Figure 3.8).



Figure 3.8 Circuit diagram of a Potentio/Galvanostat that can be easily switched between potentiostatic and galvanostatic mode of operation [21]

The information required in LIB battery research encourages the application of potentio- and galvanostatic techniques. Chronopotentiometry allows insight into the charge-discharge properties of electrochemical cells, particularly when information about multiple charge-discharge cycle performance is required. Voltammetric

techniques (particularly cyclic voltammetry) give insight into redox processes present in the active material.

All electrochemical measurements were carried out on Bio-Logic VSP Multi-Channel, Autolab PGSTAT10 and Multi Autolab 101 potentiostats, operating at room temperature using Li as both counter and reference electrodes. All potentials, unless otherwise stated, are relative to Li⁺/Li. Samples were prepared for electrochemical measurements by adopting the protocol outlined below. Firstly, the as-prepared substrates were cut into pieces of the same area, equal to ~0.5 cm². The cut samples were then placed in a vacuum oven for over 10 h at 115°C to remove moisture adsorbed on the surface. Subsequently, dried samples were placed in an argon filled glovebox for assembly. Custom build Swagelok-type cells were used with counter and active material electrode separated by a polypropylene separator soaked in 1 mol dm⁻³ solution of LiPF₆ in ethylene carbonate:dimethyl carbonate (EC:DMC) in a 50:50 v/v ratio. The electrodes were potentiodynamically cycled using a scan rate of 0.1 mV s⁻¹, unless stated otherwise. Afterwards, the electrodes were carefully washed in acetonitrile and a 10⁴ mol dm⁻³ solution of acetic acid to remove the electrolyte residue.

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CHAPTER IV

CORE-SHELL TIN OXIDE, INDIUM OXIDE, AND INDIUM TIN OXIDE NANOPARTICLES ON SI WITH TUNABLE DISPERSION: ELECTROCHEMICAL AND STRUCTURAL CHARACTERISTICS AS A HYBRID LI-ION BATTERY ANODE

4.1 Abstract

Tin oxide (SnO_2) is considered a very promising material as a high capacity Li-ion battery anode. Its adaption depends on a solid understanding of factors that affect electrochemical behavior and performance such as size and composition. We demonstrate here, that defined dispersions and structures can improve our understanding of Li-ion battery anode material architecture on alloying and cointercalation processes of Lithium with Sn from SnO₂ on Si. Two different types of well-defined hierarchical Sn@SnO₂ core-shell nanoparticle dispersions were prepared by molecular beam epitaxy (MBE) on silicon, composed of either amorphous or polycrystalline SnO2 shells. In2O3 and Sn doped In2O3 (ITO) NP dispersions are also demonstrated from MBE nanoparticle growth. Lithium alloying with the reduced form of the NPs and co-insertion into the silicon substrate showed reversible charge storage. Through correlation of electrochemical and structural characteristics of the anodes, we detail the link between the composition, areal and volumetric densities and the effect of electrochemical alloying of Lithium with $Sn@SnO_2$ and related nanoparticles on their structure and, importantly, their dispersion on the electrode. The dispersion also dictates the degree of co-insertion into the Si current collector, which can act as a buffer. The compositional and structural engineering of SnO₂ and related materials using highly defined MBE growth as model system allows a detailed examination of the influence of material dispersion or nanoarchitecture on the electrochemical performance of active electrodes and materials.

4.2 Introduction

Lithium-ion batteries are widely used today in portable electronics, telecommunication and medical devices. Li-ion technologies are rechargeable and offer advantages such as high energy density, lack of unwanted memory effects and relatively long cycle lifetimes [1-4]. Rapidly developing new technologies require lithium ion batteries with even higher capacities, better rate performance and increased safety for advanced applications and to satisfy consumer demand for portable electronic devices needing greater power over longer time periods [5, 6]. However, current battery anodes made from layered graphitic carbon are limited by a theoretical capacity of 372 mAh g⁻¹ [7], which limits the overall cell capacity when paired with a high capacity cathode material. Additionally, higher rates tend to lower the overall cell capacity and voltage even for well-established Li-ion chemistries with defined discharge protocols, and so the ongoing search for high capacity, high-rate-capable, safe and stable materials and chemistries, continues.

Considerable research is therefore being directed to the study of emerging alternative anode materials with higher capacities such as Sn (990 mAh g⁻¹) [8], SnO (876 mAh g⁻¹), SnO₂ (780 mAh g⁻¹) [7, 9-14], Sb (660 mAh g⁻¹) [15], Si (4200 mAh g⁻¹) [16] and Ge (1600 mAh g⁻¹) [17]. Among these materials, SnO₂ is receiving renewed interest due to its simpler synthesis and reports of improving performance [7, 13, 18-20]. However, SnO₂ (like all the materials listed above) undergoes drastic volume changes (~200%) when electrochemically alloying with lithium after being reduced to metallic Sn during repeated charge/discharge cycles[21]. These changes may cause capacity loss and poor cycle life, which can come from loss of electrical contact between the active material and current collector as well from agglomeration of active material, preventing electrolyte access to the surface of the active material [22]. Preparing

nanostructures with shorter diffusion lengths may greatly improve the rate capability of SnO₂ based anodes by allowing one dimension of the crystal structure to be smaller than the characteristic diffusion length of Li⁺ [23]. Additionally, the lower dimensionality would not negatively influence electronic conduction in most intercalation or alloying materials as the resistance of a 2D version of a 3D material would not greatly increase. Moreover, investigation of the density of active materials or their architecture in an electrode could lead to better understanding of their influence on all important aspects of a battery anode operation, including protective SEI layer formation.

Effective strategies have been proposed to resolve issues arising in SnO₂ based Li-ion battery anodes. Among them, synthesis of nanoscale SnO₂ with porous, layered, or multiphasic structures, such as nanosheets [24, 25], nanotubes [25, 26] and core-shell nanostructures [27, 28] have been investigated. These reports demonstrated the sensitivity of performance to the nanoscale structure. These types of structures allow for a high density of materials with small diffusion lengths which improves Li⁺ insertion rates[29]. High porosity is effective in allowing the stress caused by expansion and contraction to be accommodated so long as the electrochemical properties and electrical conductivity are not adversely affected. However, most of these structures are metastable and do not markedly improve long term cycle stability [30]. As an alternative, various composites have been proven to be more effective in enhancing the stability of SnO₂ based electrodes[31, 32]. Solvothermal and hydrothermal and microwave processes [33, 34], plasma jet reactor synthesis [35], AAO assisted etching [36] and various other templating methods [37-40] were extensively used to prepare nanorods, nanoplates, nanowires, and core-shell particles of SnO2. A number of composite structures (such as CNT-SnO₂ or Fe_3O_4/SnO_2) [41, 42] were also developed

that demonstrated a large influence of their composite morphology and chemistry on the performance as an anode[43-46]. More investigation is needed to understand the changes occurring at the interface between the active materials and their interference with current collector, especially in the situation where the current collector can also react with lithium. Current collectors that can provide reversible charge storage capabilities are not always beneficial and can adversely affect the interface to the active material. In cases where co-insertion (reversible) can be accommodated in such hybrid electrodes, there is potential for the provision of a degree of protection from volume change stress[47]; buffering Li⁺ insertion can be very useful in cases where the expansion rates of the material are associated with excessive stress and strain, causing loss of electrical contact and mechanical integrity in porous or discontinuous active materials penetrated by electrolyte, and requires further investigation.

Compared to commonly used techniques, molecular beam epitaxy (MBE) offers excellent control over the crystalline quality, phase and morphologies of deposited structures, and their chemical composition. These benefits make MBE an ideal method for detailed investigations of electroactive materials with very well defined compositions, shapes and crystallinity[48].

In this chapter, the growth of several novel types of Sn@SnO₂ core-shell nanoparticle dispersions prepared by MBE[49] on silicon is demonstrated, and through electron microscopy and spectroscopies, their respective behaviour in response to lithium alloying as Li-ion battery anodes is outlined. Oxidative crystallization in air after deposition of the respective metal (Sn, In, or both for ITO) results in a characteristic size dispersion of epitaxial SnO₂ nanoparticles with core-shell structure, and also In₂O₃ and Sn-doped In₂O₃ (ITO) nanoparticles. Detailed structural characterization and electrochemical cycling was carried out to elucidate how the reversible alloying process

with Li is inherently dependent on size dispersion, core-shell structure and composition. The volumetric expansion of Si (that acts as the current collector) during lithium insertion is observed to provide a degree of mechanical buffering against loss of electrical contact between SnO₂ NPs. This work defines the influence of controlled crystal structure, architecture and volumetric/spatial density on the electrochemical processes occurring in a Sn@SnO₂-Si hybrid nanomaterial anode, and also the structural changes associated with Li alloying and dealloying process introduced by cycling in a series of core-shell SnO₂ In₂O₃ and ITO NPs on silicon.

4.3 Epitaxial growth of indium and tin oxide nanostructures

Prior to the deposition, the surface of silicon was cleaned using standard RCA silicon cleaning procedures. After rinsing, a second treatment in a H₂O₂:HCl:H₂O (1:1:5) solution was used to remove metallic and organic contamination. For deposition of Sn and In, a custom-built MBE high-vacuum chamber with two high temperature effusion cells for metallic Sn or In targets, combined with an electron beam evaporator was designed in cooperation with MBE Komponenten GmbH. Prior to the tin oxide growth the silicon and glass substrates were cleaned using the standard process. In this respect, the sample was first emerged in a H₂O₂:NH₄OH:H₂O (1:1:1) solution at 80°C for about 30 min. After rinsing the sample in deionised H_2O , a second treatment was performed in a H_2O_2 :HCl:H₂O (1:1:5) solution with an adjacent rinsing in deionised H₂O. Through this process metallic and organic contamination is removed. In the latter step the surface is oxidised, so that a thin and clean SiO_2 layer forms at the surface (~2-3 nm). Dipping the sample in HF shortly before introducing it into the evaporator removes the oxide layer and passivates the surface with hydrogen (H). Due to Hpassivation the Si surface becomes hydrophobic. Thus, a further oxidation of the surface, e.g. due to O_2 in the air, can be avoided.

The SnO₂ films were deposited on silicon (001) and glass substrates simultaneously, using a thermal evaporation chamber from MBE Komponenten GmbH. The chamber is equipped with effusion cells for precise control of reactant effusion. The substrate is heated by radiation through backside heating and the temperature is measured 5 mm above the sample and is controlled to within ± 0.2 °C. The mass flow of metal is controlled to within ± 6 % for Tin by setting the temperature of the effusion cells according to the calibration data (see Figure 4.1 Tin growth rate vs. temperature variation as measured using a quartz crystal monitor used to calibrate the deposition rate of tin metal.)shows measured tooling factor for Sn where an exponential thickness increase is found at constant pressure, substrate temperature and oxygen partial pressure during deposition.



Figure 4.1 Tin growth rate vs. temperature variation as measured using a quartz crystal monitor used to calibrate the deposition rate of tin metal.

A uniform layer of Sn metal was deposited at pre-defined rates on a Si(100) substrate at a predefined temperature, with precise control over the nominal thickness. Similar procedures were followed for the deposition of In to form In_2O_3 nanoparticles, as detailed in theh next chapter. For formation of ITO, Sn and In were used at 10:90 weight ratio.

To analyse the size dispersion of grown NP layers, ImageJ software package developed by National Academy of Sciences was used. Typically, brightness, contrast and intensity window and level were adjusted until an image suitable for thresholding. Following that, built-in particle analysis algorithms were applied to obtain particle parameters such as area, diameter, circularity and other shape descriptors. Figure 4.2 presents results of image processing for a typical SEM image.



Figure 4.2 a) SEM image of the ATO nanoparticle layer. b) SEM image with brightness/contrast and window/level adjusted. c) Thresholded binary image of the NP

layer. Dark areas correspond to grey NPs in (a). d) Outlines displayed after particle analysis procedure completion.

4.4 Core-shell Sn@SnO2 nanoparticle dispersions

MBE growth of Sn at elevated temperatures (400° C- 600° C) and subsequent oxidation in air results in the formation of two different types of SnO₂ core-shell nanoparticles (NPs) as shown in Figure 4.3a. The first type of NPs consists of highly crystalline Sn metal core NPs with a thin amorphous coating of SnO₂ (ATO), and the second type comprises a crystalline Sn metal core with a polycrystalline SnO₂ shell (PCTO), forming Sn@SnO₂ NPs. Both are formed by simple two step deposition and oxidation mechanism. The SEM image in Figure 4.3b shows a dispersion of ATO NPs on the Si substrate ATO NPs typically have a high size dispersion, ranging from a few nm to over 500 nm in diameter, with an average interparticle distance of ~60 nm, covering about 65% of the sample surface The NPs are generally close to hemispherical shape, with some deviations probably related to their crystallization process. Small NPs are interspersed between the larger ones indicating that the growth undergoes simultaneous and progressive Sn deposition, surface diffusion of nucleated crystals and coalescence of neighboring particles.



Figure 4.3 (a) Schematic diagram highlighting steps in formation of core-shell SnO₂ NPs. (b) SEM image showing the ATO NP dispersion. Inset shows the diameter distribution for ATO NPs. (c) High resolution SEM image showing a single ATO NP with small crystallites growing on the surface. (d) SEM image of PCTO NP layer. Inset: diameter distribution histogram for PCTO NP layer. (e) Low voltage (2 kV) SEM image of PCTO layer showing the core-shell structure of the NPs. (f) High resolution SEM image of PCTO NP layer showing texturing of the NP surface.

The high resolution SEM image in Figure 4.3c shows that some of the larger ATO NPs also have smaller NPs growing on their surface. The smaller hierarchical NPs that form on the surface or larger NPs, is believed to occur when the coalescence mechanism that forms larger NPs is interrupted by oxidative crystallization of the liquid-phase Sn droplets on the larger NP surface. Defect-related or roughness-induced nucleation sites characteristic of some MBE growth likely contributes to the roughness development on the NPs. In₂O₃ NPs layers grown by MBE also showed similar

hierarchical structure, with additional nanowire growth sometimes found from these crystallite seeds [47]. The exact origin of the nanocrystallites on the surface of the ATO NPs is however unclear. Crystalline core-polycrystalline shell NPs of SnO_2 (PCTO) are shown in Figure 4.3d-f, where their core-shell structure is visible in the low voltage secondary electron image in Figure 4.3e. Analysis shows a much smaller size dispersion and lower average interparticle distance (~ 25 nm), which is related to lower deposition temperature, allowing particles to form without as much surface diffusion in their liquid state as found for ATO NPs. Compared to the ATO NPs, the PCTO NPs show much lower size dispersion, with the majority of the NPs ~ 100 nm in diameter (Figure 4.3d inset); the total surface coverage is higher than for ATO NPs, amounting to ~80% coverage of the sample surface. High magnification SEM imaging of the NP shows a texture on the surface (Fig. 3f) which is associated with surface roughness (shown also in Figure 4.4) specifically from the structure of the polycrystalline shell. During MBE, the small interfacial strain between the deposited film and the substrate greatly influences the structure growth. For low lattice mismatch, the growth will follow the Stranski-Krastanov (SK) mode [50], corresponding to complete wetting of the substrate surface by the deposited adatoms followed by formation of islands. Here, these islands are initially liquid, as the deposition is carried out above the melting temperature of Sn. Surface diffusion of liquid droplets occurs in parallel with the deposition, leading to coalescence of nearest-neighbour particles and formation of SnO₂ NPs upon subsequent oxidative crystallization in ambient air. The smaller NPs interspersed between larger crystals cover a large portion of the substrate ($\sim 30\%$), indicating that progressive deposition of Sn resulted in formation of large number of small nanodroplets which then coalesced through surface diffusion to form large crystals.

The coalescence occurs at slower rate (lower substrate temperature) in case of PCTO NPs resulting in better monodispersity in the surface coverage.

The amorphous layer formed around the crystalline core in ATO NPs is shown in Figure 4.4a and b. Both amorphous and polycrystalline shells (shown in Figure 4.4c and d), are formed during oxidative crystallization of the outer layer of the Sn droplet after the deposition. TEM analysis confirms that some of the small crystallites growing on the surface of large ATO particles also exhibit core-shell structure.



Figure 4.4(a) Dark-Field TEM image showing a cross-section through a layer of PCTO NPs. (b) TEM image showing a cross-section of a single PCTO NP. (c) FIB cross-section through a single ATO NP, highlighting formation of amorphous shell beneath the contact point of NP with the substrate. (d) TEM image of NPs grown hierarchically on the surface of ATO NP.

This hierarchical consistency in core-shell construction indicates that formation of the surface crystallites and NP shells were simultaneous; the thickness of the ATO shell is similar for all particles, despite the 1-2 orders of magnitude difference in core diameter. Moreover, the structure of the crystallites on the surface of ATO is similar to the structure of the PCTO, with a polycrystalline shell around a crystalline core forming a hierarchy of core-shell NPs. The thickness of the amorphous layer is ~10 nm for all NPs on the surface of the substrate or those on other NPs, and the shell also extends below the contact point with the substrate (Figure 4.4c) as well as at the interface between hierarchical core-shell NPs. This suggests that the formation of the amorphous shell progresses through diffusion of the oxygen through the top layer of the crystalline Sn. The thickness of polycrystalline shell in case of PCTO NPs is of similar order to the ATO NP shell (7-13 nm). This indicates a similar shell formation rate for both NPs.

To analyze chemical composition of the ATO and PCTO NPs XPS and EDX spectral measurements were carried out. The Sn 3d core level spectra for both ATO and PCTO samples are presented in Figure 4.5a. The 3d core-level spectra from Sn in both PCTO and ATO NP structures contain a doublet with binding energies of 487 eV (3d_{5/2}) and 495.3 eV (3d_{3/2}) referenced to the C1s core level of 284.8 eV, which suggests the (IV) oxidation state of Sn, *i.e.* SnO₂. A slight shift of 0.1 eV between PCTO and ATO core levels is equal to the measured shift in their respective adventitious C1s core levels.

It is important to note that the differentiation between SnO and SnO₂ in photoemission studies is complicated due to only a very small shift in the Sn 3d core level binding energy. Consequently, stoichiometric ratios of elements were calculated from the XPS spectra according to [51]: $S_{ij} = \frac{C_i}{C_j} = \frac{I_i/ASF_i}{I_j/ASF_j}$ where C_i and C_j are the

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concentrations, I_i , I_j are the background corrected photoelectron emission line intensities, and ASF_i, ASF_j are the atomic sensitivity factors for photoionization of the *i*th and *j*th elements. Following this procedure we determined the concentration of oxygen (O) to be ~2 times the concentration of Sn, which corresponds to the SnO₂ stoichiometry of the oxide formed on the surface of the sample.



Figure 4.5 (a) Sn 3d and O1s core level spectra for ATO and PCTO NPs. (b) EDX linescan of the PCTO NP cross-section shown in (d). (c) EDX linescan of the surface of the ATO NPs. (d) Dark-field TEM image of PCTO NP layer. Line indicates the measurement site for the linescan presented in (b).

Furthermore, intensities for the deconvoluted O1s signals are not equal for both core-shell structures. This can be attributed to different silicon surface coverage of the sample with the NPs. In the case of ATO, the intensity of the deconvoluted O1s peak located at 532.1 eV, related to oxygen in SiO_x is higher than for PCTO. As the surface

coverage of the sample is larger for PCTO than ATO, it is expected that SiO_x signal would be higher for ATO NPs with lower surface coverage. The EDX line spectra taken from the FIB cross section of PCTO and the surface of ATO sample, also corroborate these results. Particularly, in Figure 4.5b, an increase in measured intensity of the O K α line indicates larger concentration of oxygen atoms close to the edges of the NP indicating the core shell of PCTO NPs. SEM EDX line-scan taken from the surface of the ATO NP layer also confirms oxygen presence within the penetration depth of the EDX beam, corroborating XPS results.

4.5 Reversible lithiation in core-shell SnO₂ NPs

As SnO₂ based materials are being considered for use as anodes for Li-ion secondary batteries[31, 52], its electrochemistry with lithium was investigated here for a variety of structures including core-shell SnO₂ NPs, but also comparative In_2O_3 and ITO NP dispersions and. There are limited reports on Si-Sn composites as Li-ion battery anodes [53], and so both ATO and PCTO NP alloying reactions with lithium, and the structural changes of the NPs and their dispersions on Si during lithiation processes were investigated with cyclic voltammetry and high resolution ex-situ electron microscopy. The Li alloying reaction with the Sn NP core is possible if the outer oxide coating can be reduced to Sn⁰ from the respective SnO₂ on PCTO and ATO NPs.

Cyclic voltammetry was used to investigate this process. The specific measurement details are described in the Experimental chapter 3. In a CV, each alloying, growth, removal, oxidation and reduction process can be examined in each cycle, at the respective potential for each process. This is especially useful in the present case, where numerous processes and several materials are present. The cathodic processes involve the alloying of Li with the reduced form of SnO₂ to form a Li-Sn alloy (charging) and the anodic process follows Li extraction or dealloying (discharging).

There is a substantial difference between CVs for ATO (Figure 4.6a) and PCTO (Figure 4.6). The large irreversible peak (indicated in the CVs by \mathbf{I}) is typically regarded as being due to the formation of a stable SEI layer and to electrochemical reduction of SnO₂ to a system of three phases consisting of LiO₂, O₂ and SnO. Mohamedi et al. detailed these reaction products and their formation when examining amorphous SnO₂ films prepared by electrostatic spray deposition at elevated temperature [54]. This reaction is complete at ~1.5 volts and is present in both CVs. Subsequently, SnO is reduced to metallic Sn, indicated by large peak present at ~ 1 V for both systems (I for PCTO, II-III for ATO). A shift in voltage for this peak occurs in subsequent cycles for PCTO, indicating improved kinetics of the reaction as well as decreased lithium concentration in the phase formed at that peak potential. Two reversible peaks appear in the cathodic scan (V-VI for ATO, V-VII for PCTO) which can be attributed to the formation of particular Li alloys with Sn: Li2.33Sn formed at 0.55 V and Li4.4Sn is formed at 0.15 V. Oxidation peaks appearing at 0.57 V, 0.81 V, 0.87 V, 0.91 V and 1.21 V correspond to the dealloying of Li_xSn and partially reversible oxidation of Sn to SnO₂. The full electrochemical process occurring during reversible alloying of lithium with Sn can be described[55] by the following set of equations:

$$Li^+ + e^- + electrolyte \rightarrow SEI$$
 (4.1)

$$SnO_2 + 4Li^+ + 4e^- \rightarrow Sn + 2Li_2O$$
 (4.2)

$$Sn + xLi^{+} + xe^{-} \leftrightarrow Li_{x}Sn \ (0 < x < 4.4) \tag{4.3}$$

The reaction in Eqn. 2 is normally regarded as irreversible and a cause of capacity loss in Sn-based anodes regardless of consistency in electrical connectivity of the active material, phase conversion, and resistance changes, while in this case the reduction peak at 1.25 V (I for ATO and PCTO NPs) and corresponding oxidation

peak at 1.23 V (VI for ATO NPs, VII for PCTO NPs) remain stable over the 5 cycles indicating partial reversibility of this reaction compared to bulk SnO₂. Moreover, a small amount of lithium is introduced into the silicon current collector. The insertion and removal potentials for silicon are typically 0.2 V and 0.5 V, respectively. The relatively higher rate of reaction as shown by the larger current in this potential range indicates insertion of lithium into Si coexists with alloying of lithium with Sn.



Figure 4.6 (a) Cyclic voltammograms for ATO and (b) PCTO NPs on silicon. (c) Schematic diagram describing formation of porous NP layers upon lithiation cycling. (d) Dark-field STEM image showing highly porous layer comprising pulverized NPs formed by electrochemical cycling of the PCTO NP layer. The brighter regions are Sn and SnO₂.

For ATO NPs, the large irreversible area in the 1.6-0.8 V range (**I**), corresponds to reduction of SnO₂ to metallic Sn, and the succeeding peak at 0.39 V (**II-III**) corresponds to formation of a Li_xSn phase, where x ranges from 0 < x < 4.4. This is also found for the PCTO NPs, implying that the crystal structure of the thin shell coatings are less critical than their stoichiometric phases, which are identical. In the lower voltage range corresponding to insertion of lithium into Si, a large peak at ~0.1 V (**IV**) is present. In the anodic part of the CV, two reversible peaks at ~0.65 V (**V**) and ~1 V (**IV**) are found. The first peak can be attributed to the removal of lithium from silicon while the second corresponds to removal of lithium from Sn[23], and it occurs at a similar voltage in both ATO and PCTO core-shell NPs.

The Si insertion and removal rates as indicated by the current in corresponding CV peaks increase with cycling, indicating an activation effect characteristic for Si-based anodes[2, 16, 56-58]. Specifically, volumetric expansion of lithiated material causes cracks and exposure of unreacted Si to the electrolyte, which in turn allows more lithium to be incorporated into material at the same potential. Usually it is considered a negative effect, causing an increasing degree of cracking and loss of electrical contact between the active material and the current collector. As it is not the active material, expansion occurs only where the SnO₂ NPs are not present. Comparing the differences between the ATO and PCTO NPs and their spatial density and size dispersion on the Si, ~25% higher rate of lithium insertion into ATO sample is observed, which correlates well with the surface coverage difference between ATO and PCTO. Moreover, formation of an SEI layer (from the voltammetric response) is more pronounced for PCTO samples, which can be attributed to a higher areal mass loading of polycrystalline SnO₂ shell.

To further analyze changes induced in the structure of the anode during lithiation, FIB cross-sections of both types of NPs were investigated by TEM (Figure 4.7). Figure 4.7a shows an SEM image of the ATO NP layer after cycling. A change in ATO NP shape is found (see Figure 4.3b and Figure 4.7b inset for comparison), but significantly, the size of the ATO NP has not increased laterally. PCTO NPs on the other hand, shows extensive modification after cycling (shown in Fig. 7b). The NP underwent pulverization likely due to expansion and contraction during cycling that results in a higher density of smaller NPs on the surface. The initial interparticle distances between ATO NPs are significantly larger than between PCTO NPs and are devoid of NP-NP contacting within the layer. PCTO NPs are, prior to lithiation, formed with much smaller interparticle distances, and thus the expansion during lithium insertion will lead to larger degree of NP agglomeration and coalescence.


Figure 4.7 (a) SEM images showing a layer of ATO NPs before (inset) and after cycling. (b) SEM image showing PCTO NP layer after cycling. (c) Dark-field TEM image showing a porous layer formed due to electrochemical cycling of PCTO NPs. White line indicates the site for the line-scan presented in (e). (d) TEM image showing the interface between the silicon current collector and the PCTO NP layer after cycling, with α -Si layer highlighted. (e) EDX line-scan through PCTO NP layer after cycling. Site of measurement is indicated by the white line in (c).

Figure 4.7c shows a dark-field TEM cross-section of the PCTO NP layer. The structural changes confirm the observation from Figure 4.7b, (see Figure 4.4 for 129

comparison) where the NP layer is transformed into a porous layer of Sn nanocrystals after cycling that are much smaller (by a factor of \sim 4) than their as-formed size. Bright areas (larger atomic weight electron scatterers) seen in Figure 4.7c correspond to Sn present in the resulting layer. The existence of a porous layer with thickness corresponding to the diameter of the largest PCTO indicates that the expansion of NPs allows for agglomeration and coalescence of nearest neighboring NPs during chargedischarge cycles. Multiple NP expansions can cause the formation of a largely porous, but also highly interconnected layer. A small number of the NPs are still present in their metallic non-distorted form (see Figure 4.7d and the white particle in Figure 4.7c) probably due to lack of contact with the electrolyte after initial phase of the reaction.

The stability of the contact is in this case is mainly caused by co-insertion of the lithium into silicon current collector, which offers some degree of buffering by intercalating lithium ions at the Si-electrolyte interface that exceed the alloying limit of the volumetric density of NPs on the surface. As discussed further on, the lower areal density of SnO₂ NPs is correlated with a higher Si interface, and the Si interface allows some degree of buffering by intercalating excess Li⁺ at lower potential to the alloying reaction with Sn. Such buffering effects have been observed in SnO₂/C composites, where the composite alleviates large scale material breakdown[59]. NPs were deposited on single crystalline Si, and the formation of α -Si layer underneath the porous PCTO (Fig. 7d) layer after cycling indicates that the reversible Li_sSi Zintl phases[60, 61] of silicide are formed in parallel with expansion/contraction due to oxide reduction to metallic Sn and subsequent lithiation of the original PCTO NP. EDX analysis (Figure 4.7e) also shows uniform distribution of Sn within the composite material matrix, confirming formation of a porous Sn layer. ATO NPs after 5 insertion-removal cycles seen in Figure 4.7a also show significant structural changes, mainly seen for the

largest NPs. The elemental distribution post cycling is shown in Figure 4.7e, confirming that the porous film consists of from Sn with Si interspersed in the layer close to the surface of the current collector.

The electrochemical response of NP dispersions was also examined for a range of NPs prepared by MBE: in addition to core-shell SnO_2 , we investigated In_2O_3 and ITO NP dispersions whose CVs and corresponding size dispersions are presented in Fig. 8.



Figure 4.8 Single cycle voltammograms, SEM image of the surface of the NP layer, and corresponding size dispersion histogram for (a) PCTO NPs, (b) ATO NPs, (c) In₂O₃ NPs, and (d) Sn-doped In₂O₃ (ITO) NPs. De-intercalation potential windows are shaded for Li_xSi (green), Li_xSn (pink) and Li_xIn (yellow).

The cyclic voltammetric response of the various SnO₂ and In₂O₃ NPs dispersions in Figure 4.8, show that the lithium insertion and removal characteristics are strongly dependent on the shape and size dispersion of the NPs and their volumetric density; all sample exhibit at least bimodal sizes, with one mode dominating in the case of highly coalesced ATO and In₂O₃ NP dispersions. As all are deposited from In, Sn or In + Sn using MBE, the distributions are characteristics of a similar formation mechanism, outlined earlier for SnO₂. In terms of electrochemical reduction, alloying, intercalation and the reverse processes, there is similarity between responses for PCTO and ITO NPs (Figs 8a and d), and between ATO NPs and In₂O₃ NP layers (Figure 4.8b and c).

Analysis of the data in Figure 4.8 shows that both areal density and volumetric density need to be considered, especially when using hybrid systems such as the present case where the current collector (silicon) is capable of intercalating lithium. Lithium insertion and removal peaks for Li_sSi are more pronounced (as measured from the magnitude of the current and integrated charge) for ATO and In₂O₃ NP dispersions, while alloying reactions with active material (In, Sn) dominates for PCTO and ITO NP layers. This trend is due to the areal coverage, whereas the relative contribution of the alloying to intercalation response in these electrodes is linked to the volumetric density of active material. The shape of the voltammetric response in each case thus includes different relative contributions from the CV response of Li-Si formation. For the PCTO and ITO NP dispersions (Figs 8a and d), the Li_sSi phases (*cf.* Figure 4.7) are observed, but dominated by the In- and Sn-containing material. As the volumetric density is lower for these electrodes (in spite of higher areal coverage), the corresponding currents are lower. The opposite trend is found for ATO and In₂O₃ NP

dispersion with lower areal coverage, regardless of the volumetric density of active material.

In such cases, charging and discharging in specific potential windows can select alloying and/or intercalation process dissimilar materials the where are electrochemically active, but this work shows that the relative contributions are linked to the dispersion of the material in addition to its structure and composition. For much smaller PCTO and ITO NPs < 200 nm in diameter, all of the Li-Sn alloving occurs prior to co-insertion with silicon. During cycling however, material break is observed for SnO_2 when large (>250 nm) NPs are used. Generally, the dispersion of nanoscale active materials should also consider the diameter or thickness of the active material in addition to the effective porosity, especially in composite systems where insertion or alloying occurs at different potentials via different mechanisms. By varying the dispersion and thus the effective porosity of the active material, hybrid electrodes involving electrochemically active current collectors can also offer some degree of stress-change buffering during deep charging and discharging.

4.6 Conclusions

Using molecular beam epitaxy, we detailed the growth of two distinct and well defined types of Sn/SnO₂ core-shell nanoparticles with crystalline metallic Sn cores and either amorphous or polycrystalline SnO₂ shells. In₂O₃ and Sn doped In₂O₃ (ITO) NP dispersions are also demonstrated using this approach. Electron microscopy and spectroscopy analyses confirmed a hierarchical core-shell structure of the SnO₂ NPs with different diameters to give a range of volumetric and areal densities of material. Lithium alloying with the reduced form of the NPs and co-insertion into the substrate (which also serves as current collector) showed reversible charge storage via alloying

with Sn or In. The effect of lithium insertion and removal on different NP dispersions monitored by electron microscopy and cyclic voltammetry, showed that the electrochemical behavior depends on the relative size via the volumetric density of the NPs and their areal dispersion on the surface, in addition to their composition. The knowledge can be extended to a range of other active (nano)materials and systems so that active material arrangements and densities can influence performance, in addition to the structure, size and composition. In cases where the material spacing is larger the volumetric expansion can be accommodated radially while maintaining mechanical and electrical contact. In this regard, co-insertion into the Si facilitates this process and is dictated by the active material dispersion. The compositional and structural engineering on SnO₂ and related materials using highly defined MBE growth as model system has allowed a detailed examination of the influence of material dispersion or nanoarchitecture on the electrochemical performance.

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CHAPTER V

EPITAXIAL GROWTH OF VISIBLE TO INFRA-RED TRANSPARENT CONDUCTING In₂O₃ NANODOT DISPERSIONS AND REVERSIBLE CHARGE STORAGE AS A LI-ION BATTERY ANODE

5.1 Introduction

The marked increase in portable electronic device sales together with huge demand for flat screen high-definition televisions (HDTVs) are the main driving forces behind the need for batteries and continued research into various materials and forms for transparent conducting oxides (TCOs) and similar coatings. Among TCOs, materials such as indium oxide (IO), tin oxide (TO) or tin-doped indium oxide (ITO) [1-6] and emerging alternatives such as graphene and Cu or Ag NWs for example [7, 8], have been a consistent focus of research interest where transparency is a useful visible range or indeed other wavelength regions of interest [9], is matched by sheet resistances below 10 Ω/\Box [10]. ITO is the TCO used most often and its applications vary from thin film transistors [2, 6, 11-13] optical circuits [14] displays [15, 16], touch screens [17], and also as a transparent contact in solar cells [5, 18-20]. Low sheet resistances are typically required for thin-film solar cells and the solar photon flux-weighted optical transparency of ITO on glass is about 80%. The battery however, a key component in the majority of portable electronics, has only very recently been demonstrated as a transparent device [21], and scope exists for the development of true see-through charge storage materials [16, 22-26], where touch screens, solar cells and charge storage batteries can co-exist with transparent, or optically addressable form.

Their metallic properties cause most TCO's to be reflective in the infrared and for most TCO's a trade-off exists between transparency and conductivity, and sheet resistance for thin films [27]. In line with this, transparency in battery electrodes gives the opportunity for *in-situ* and non-destructive diagnostic analysis of material changes during operation and the development of conductive current collectors and electrode materials that reversibly intercalate lithium with sufficiently high volumetric energy densities. This research could also allow the possibility of investigating kinetics of insertion mechanisms and the influence of certain lithiated phases of TCO materials on

transparency and conductivity. This is critical for the analysis and development of both new battery materials and chemistries, but also for the examination of TCO materials for charge storage applications [28-32].

Transparency can be provided by using miniscule quantities of materials, or very thin films of uniform deposits [33], but to have functioning volumetric energy densities, strategies to improve transparency while maximizing active material coverage of an electrode would be advantageous. The only formally transparent element in a typical battery is its electrolyte, which is soaked into a porous polymeric membrane and sealed with opaque materials between two sheets of metal. One method to allow transparency in a battery is to reduce active material dimensions below their optical absorption length; there are no currently used battery materials with absorption lengths that are sufficiently long in the full potential window in which the battery operates. Architectures of materials that influence optical properties have shown promise in this regard. Varying surface coverage using dispersions that promote UV, visible and NIR transparency is also possible. The recent demonstration of a fully transparent battery prototype [20] also involved testing of a continuous In₂O₃ thin film electrode. During cycling however, it was found that metal nanodots and lithium oxides and peroxides formed to such an extent that transparency was significantly reduced.

In this chapter, In_2O_3 {111}-oriented crystalline nanodot dispersions have been successfully grown from an MBE deposition of an In layer and subsequent oxidation at elevated temperature. The method results in unique areal and size dispersions of nanodots varying in size from hemispherical 2 nm dots to larger, faceted ~500 nm crystals, on the Si current collectors. Angle-resolved transmittance measurements confirm that the deposits maximize transparency in the infra-red, while maintaining characteristic transparency in the visible with a beneficial reduction in resistivity and sheet resistance; this overcomes the transparency limitations for In_2O_3 nanomaterials by

index matching with air through a unique size dispersion. The nanodots form as $In@In_2O_3$ core-shell crystals, and form a stable SEI layer and reversibly alloy with lithium allowing them to function as visible-to-IR transparent, visibly antireflective Liion battery electrodes. These properties could potentially lead to further development of similarly controlled dispersions of a range of other active materials. The approach shown here is straightforward and scalable and may be applied to the fabrication of high quality optoelectronic, electronic and sensor devices and as a beginning of visible-to-IR transparent conducting TCOs that reversibly store (electro)chemical charge, and also for the development of non-destructively, optically addressable materials and interfaces for *in-situ* monitoring of electrochemical processes.

5.2 Epitaxial growth of indium oxide nanostructures

Before growth on silicon and glass substrates, the respective surfaces were cleaned using a standard RCA process. After rinsing, a second treatment in a H₂O₂:HCl:H₂O (1:1:5) solution was used to remove metallic and organic contamination. For evaporation of the In sources, a home-built MBE high-vacuum chamber with a distinct effusion cell for In together with an electron-beam evaporator, was designed in cooperation with MBE-Komponenten GmbH, with calibrated growth rates. As detailed Figure 5.1, a uniform layer of In metal was deposited at a rate of 0.1 Å s⁻¹ at a substrate temperature of 400°C, with precise control over the nominal thickness, (see chapter III for detailed description of deposition procedure).



Figure 5.1 . Indium growth rate vs. temperature variation as measured using a quartz crystal monitor used to calibrate the deposition rate of indium metal.

Specifically for optical characterization in this chapter, variable angle spectroscopic ellipsometry (VASE) was performed using a J. A. Woollam Co., Inc. M-2000U variable angle spectroscopic ellipsometer over a wavelength range of 300 to 900 nm. Reflectance measurements were carried out in a Bruker FT-IR spectrometer IFS66/V on nanodot samples and ITO on glass. Different configurations of beam splitters, detectors and sources were used to cover the infrared (5 µm) to visible ranges. For angular resolved measurements, a NIR512 Ocean Optics spectrometer was used as a detector in a home-built reflectance/transmittance setup using a collimated Xenon arc lamp as a light source.

5.3 Results and discussion

Figure 5.2a shows a SEM image of the nanostructures grown by MBE of indium in an oxygen atmosphere. The MBE deposition was conducted at a rate of 0.1 Å s⁻¹; such a slow deposition rate is typically used to ensure initial seeding of the substrate with a metallic seed layer [34]. Subsequent oxidation in ambient air allows the formation of a specific size dispersion of oxide crystals after In growth, as shown in Figure 5.2b. The dispersion consists of larger crystals interspersed with a high density of very small (~2-5 nm) nanodots (Figure 5.2c). Some of the larger crystals have clearly developed facets (Figure 5.2d), generally growing in a deviated hexagonal shape (Figure 5.2e). High resolution SEM images of the nanodots show that a number of small crystallites are found on the top surfaces of the crystals in a hierarchical fashion (Figure 5.2d).



Figure 5.2 (a) Schematic of the MBE growth steps for In_2O_3 nandot dispersions (b) SEM image showing the final epitaxial In_2O_3 nanodot dispersion on Si. (c) SEM image showing small, hemispherical nanodots interspersed between larger crystals. (d) Tilted SEM image of the larger, faceted crystals. Arrow indicates small crystallites growing hierarchically on the top surfaces of large crystals. (e) SEM image of frustrated-faceted

nanodots (which are also single crystal). Arrow indicates long nanowires growing from the edges of the nanodots.

The initial formation of a dewetted liquid In 'layer' comprising a high density of metallic nanodots (maintained in a liquid state on a substrate heated to 400 °C), and the progressive nature of their deposition allows hierarchical nanodot seeds to form on the high energy facet edges of the larger crystals. In some cases we observe subsequent growth of long, straight In₂O₃ nanowires (see Figure 5.1e) with lengths reaching hundreds of nanometres and diameters not exceeding the diameter of hierarchical dots. The nanodot dispersions (and also the progressively nucleated dots-on-dots) form by thermally driven (substrate heating) ripening, coalescence, oxidation crystallization, and continued progressive In deposition.

It was previously shown by Hao *et al.* that the surface energy of the main faces during growth of In_2O_3 crystals (and many crystals in general) follow a gradient in surface free energy and subsequent growth rates, *i.e.* $\gamma[111] < \gamma[100] < \gamma[110]$ [35]. In low saturation MBE deposition, these relationships greatly influence the final shape of the nanodots. We used electron backscattered diffraction from the terminating surfaces of both faceted and non-faceted nanodots to quantify their epitaxial relationship to their substrate and also their relative orientational distribution. The measurements were taken at 70° tilt (Figure 5.3) and a pole plot of the nanodot texture orientation distribution (Figure 5.3b) was formed by monitoring the Kikuchi diffraction patterns from the top surface lattice planes of the nanodots shown in Figure 5.2c and d; the growth orientations from 3D crystal symmetry are visible as diffraction 'paths' in orientationspace. The measurements confirm a dominant {111} surface termination for the nanodots. Interestingly, for both faceted and non-faceted crystals, their terminating planes are near-identical, as are their overall heights of ~50 nm, see Figure 5.2. Any

'flow' of material pre-oxidation occurs almost entirely parallel to the substrate and thus a perfect faceted crystal is not required to give an iso-terminated nanodot dispersion.



Figure 5.3 (a) SEM image of the In₂O₃ nanodots. Arrows indicate the location of the points at which the EBSD pattern was recorded. (b) Pole figure showing the relative orientation distribution of {111} termination of the nanodots. (c-d) Kikuchi band overlays recorded from the regions indicated in (a). The cross on each image indicates the orientation of the planes at their measurement point.(e) Two nanodots during coalescence. (f) Fully coalesced nanodot with no discernible boundary between coalesced nanodots.

Being extremely sensitive to tilt or variations in the top surface of the crystals, the corresponding pole plots shown in Figure. 5.3b were acquired to map the distribution of textures around major growth directions. The texture pole plot is centered around the {111} directions. It is clear from the texture distributions in the in Figure 5.3b, that the particles grow with horizontal hexagonal {111} planes, parallel to the (100) substrate of the silicon wafer. The three areas of high frequency distribution

located around 70.5 degrees is related to similarity between [111] plane equivalent directions: {111}, {-111}, {1-11} as well as {11-1} growth directions. The In_2O_3 nanodots were epitaxially deposited as metal nanodot seeds and subsequently oxidized in air and EBSD analysis confirms that their oxidation to In_2O_3 nanodots results in a final single crystal structure with the slowest {111} growth planes parallel to the substrate. Pole plots of the dispersion of the texture of the nanodots around remaining two pole directions are shown in Figure 5.4, indicating angular relationships between growth planes and polar directions.



Figure 5.4 Pole figures showing the relative distributions of nanodots terminations

A three-fold symmetry with three distinct peaks of similar intensity was observed in pole figure of {111} reflections and consists of the central [111] zone axis (centre pole) and [-111], [1-11] and [11-1] at 70.5° from the centre pole. Different rotations of the growth plane can be seen in the equivalent cell representations in Figure 5.4 acquired from individual diffraction measurements from the surface of a number of separate nanodots. The growth rate perpendicular to {111} planes is comparatively slower than {110} and {100} planes. As a result, growth in lateral direction progresses faster than in vertical, which we find regardless of the degree of crystal faceting. Such arrangement results in formation of truncated octahedral structures that coalesce with their nearest neighbours during growth (Figure 5.3e). In such cases, the reason for the formation of non-faceted particles can results from reflow of metallic In with next

nearest neighbours (necking and ripening), which was captured after solidifying oxidative crystallisation in Figure 5.3e.

One of the important factors in MBE growth of oxide films and particularly when these materials undergo volume expansion during uptake of Li ions during charging, is the quality of physical contact to the substrate, indicated by the lattice mismatch $f = (a_f - 2a_{sub})/2a_{sub}$, where a_f and a_{sub} are the lattice constants in the growth plane of $In_2O_3(111)$ and Si(100), respectively. The mismatch parameter should be as low as possible to minimize the additional strain placed on the deposit due to electrochemical reduction from In₂O₃ to metallic In and subsequently during volumetric expansion accompanying electrochemical Li-insertion. For In₂O₃, the (111) lattice parameter is 1.074 nm, leaving a mismatch of 1.13% between a_f and $2a_{sub}$ (for a Si(100) lattice spacing of 1.086 nm). The resulting strain between the nanodot-substrate interface is low; the surface free energy of $In_2O_3(111)$ is much lower than that of Si(100) [36]. This orientation offers the least possible interfacial strain between In_2O_3 and Si(100). The deposition of the first few atomic layers of In results in complete wetting of an area of the surface according to the Frank van-der Merwe (FM) growth mechanism. Subsequent deposition of adatoms causes accumulation of strains and leads to change of growth mechanism from FM to Stranski-Krastanow (SK) resulting in 3dimensional islands on 2D wetting layer, since the liquid In dewets to form droplets on the surface as the adatom concentration shifts the metastable deposition to an unstable condition [37]. This qualitatively also explains why we consistently observe nanodots beginning to form via a hierarchical mode with smaller length scales on top of crystallizing dots. Although the lattice constant is formally the same for In_2O_3 on In_2O_3 , this only holds when the orientation of the crystal deposit matches that of the underlying dot; when this is not the case, strain-relieved dots-on-dots are possible.

The composition of the MBE nanodots were determined using XPS and EDX. Figures 5.5a, b show the In 3d and O 1s core-level photoelectron emission spectra of the nanodots. Core-level emission corresponding to In 3d_{5/2} and In 3d_{3/2} were observed at 444.34 eV and 452.03 eV indicative of In₂O₃. The peak at 444.34 eV shows hyperfine levels, one at 443.9 eV from In(0) and at 445.1 eV related to In 3d_{5/2} from In₂O₃. Corelevel emission from O 1s was composed of two spectral bands at 531.2 eV and 529.6 eV, which can be deconvoluted into three components consistent with In₂O₃. The signal at 531.2 eV is attributed to lattice oxygen, while that at 529.6 eV stems from some In(OH)₃, which is known to form from exposure of In₂O₃ to water vapour. Corresponding EDX maps of In and O (shown in Figure 5.5b-e) corroborate oxide composition of the nanodots.



Figure 5.5 X-ray core-level photoelectron spectra of (a) O 1s and In 3d of the In_2O_3 nanodot dispersion. (b-e) EDX maps of In_2O_3 nanodot showing distributions of oxygen, indium and silicon respectively..

5.4 In₂O₃ nanodot dispersions and electrode coverage

To determine the coverage of the nanodot dispersions, their size distribution were analysed by factoring the anisotropy in non-hemispherical shape, summarised in Figure 5.6. Due to the large variance in sizes and asymmetrical shapes, the Feret diameter is used to describe a shape-nulled size distribution. Complete Feret data provides a rich source of information of particle shape that allow determination of particle shape descriptors and the details of this analysis is outlined in the previous chapter.

Size data and shape descriptors were calculated using ImageJ software package (see Experimental chapter). Histogram thresholding was employed in order to isolate areas of interest for measurements. A typical output of the thresholding is presented in Figure 5.6. Resulting binary particle representation can be subjected to particle analysis. The usual procedure for Feret diameter determination involves measurement of the distance between two points at the boundary of binary particle representation at various angles and determination of maximum and minimum distance. The maximum distance measured at arbitrary angle is the Feret diameter. The average circularity defined as $C = 4\pi \frac{A}{D^2}$ is equal to 0.84 for analysed particles.



Figure 5.6 (a) Original SEM image for size analysis. (b) Original SEM image after brightness/contrast adjustment. (c) Binary representation of thresholded SEM image showing only areas of interest. (c) Particle representation after measurements. Ellipses represent measured particles

Figure 5.7 shows the distribution of In_2O_3 nanodots interspersed between the larger surface crystals (Figure 5.7b). At the end of growth, these particles coarsen during dewetting of the liquid In during progressively forming nanodots. In this case, the deposition has a dynamically changing free surface area. Figure 5.7d represents the final size distribution from oxidative crystallization. The size distributions at the respective length scale as see by SEM are shown in Figure 5.7c and d. The overall bimodal distribution, confirmed by the existence of two peaks in the histogram in Figure 5.7d, results in a high degree of surface coverage, with the nanodots at ripening-coalescence

stage of growth comprising ~60% of the sample surface and ~10% of the sample surface covered with nanodots in the nucleation-ripening stage of growth. The overall mass distribution is estimated to be ~70 μ g cm⁻².



Figure 5.7 Feret diameter distribution histograms for In_2O_3 nanodots. (a) Nucleation and ripening mode, (b) ripening and coalescence mode. The inset shows indicates how the Feret Diameter of a nanodot is defined for this work. (c) SEM image showing particles with growth distribution described in (a), and (d) SEM image showing nanodots with the growth distribution described in (b).

The existence of two primary peaks in the size distributions suggests a two-stage overall growth mechanism [38]. Firstly, nucleation and ripening of adatom species from MBE results in the formation of small nanocrystals on the surface of the silicon, with a

maximum eventual average size determined to be \sim 30 nm. Continuous ripening growth of the nanodots results in their growth and transition from nucleation and ripening, to ripening, coalescence and further growth (including a second phase of nucleation on the surface of nanodots already on the surface, as shown in Figure 5.2d). The dispersion with two primary length scales allow a particular in-plane porosity of \sim 20% with maximal associated areal coverage of the substrate.

A bimodal model of growth is outlined below, that approximates particle size distribution variation in time using two discrete modes: Mode 1 for nucleation and ripening and Mode 2 for ripening and coalescence. The representative size of Mode 1 is fixed at the smallest particle size $v_1 = v_m$, and the average size of Mode 2, v_2 is allowed to vary with time during the growth of the particle. The average ratio of the particle sizes be assumed be v_1 and v_2 can to r;i.e. $v_2 = rv_1$. The rate of change of the particle number concentration in Mode 1, N_t , due to surface growth and coalescence can be written as:

$$\frac{dN_1}{dt} = \frac{1}{2}\beta_{11}N_1^2 \frac{r}{r-1} - \beta_{12}N_1N_2 - \frac{G(v_1,a_1)}{v_1}N_1 \frac{1}{r-1} + R$$
(5.1)

The first term on RHS accounts for the effect of the intramode coagulation of particles within Mode 1 (with collision frequency β_{11}), the second term corresponds to a reduction rate of the growth by intermode coagulation (with frequency β_{12}). The third term accounts for surface growth in Mode 1 with $G(v_1, a_1)$ denoting surface growth rate. The last term represents the rate of particle formation by nucleation. Similarly, the evolution of the particle number concentration of Mode 2 can be expressed by the following:

$$\frac{dN_2}{dt} = \frac{1}{2}\beta_{11}N_1^2 \frac{1}{r-1} - \beta_{22}N_2^2 - \frac{G(v_1, a_1)}{v_1}N_1 \frac{1}{r-1}$$
(5.2)

The particle number concentration in Mode 2, N_2 grows by intramode coalescence in Mode 1 (first RHS term) and by surface growth in Mode 1. N_2 also decreases by intramode coalescence in Mode 2. Intramode coalescence between Mode 1 and Mode 2 cannot affect N_2 . This corresponds well with a previously proposed observation for growth of In₂O₃ nanoparticles, where small islands ripen to form large nanoparticles, which in turn coalesce when their size is sufficiently large. Such a mechanisms is distinctly different to Ostwald ripening, due to the dynamic nucleation and growth of new particles during coalescence of particles linked to their dispersion and size.

5.5 Enhanced IR transparency of the In₂O₃ nanodot dispersions

In₂O₃, as a wide bandgap semiconductor ($E_g^{d} \sim 3.6 \text{ eV}$; $E_g^{i} \sim 2.6 \text{ eV}$), has a transparency that it fundamentally interlinked with it conductivity; the transition occurs on or around its plasma frequency related to the electron density according to the Drude model by $\omega_p^2 = nq/m^*\epsilon_0$, where m^* and q are the effective mass and charge of an electron, and ϵ_0 the high-frequency dielectric constant. For the single-sided In₂O₃ nanodot dispersion, the transmission is limited by Fresnel reflection due to the step discontinuity in refractive index at the rear flat surface [33, 39], depicted for an ITO film on glass and the nanodots on silicon in Figure 5.8. The refractive index of asreceived Si(100) substrate is 3.42 and that of In₂O₃ is 1.46 at the interface, which reduces to 1.24 at the nanodots-air interface measured by spectroscopic ellipsometry (Figure 5.8).



Figure 5.8 Cauchy dispersion of refractive index and extinction coefficient of the In_2O_3 nanodot dispersion, shown schematically in the inset, on Si(100), measured by spectroscopic ellipsometry. The inset shows the variation of refractive index for the nanodot dispersion as a function of wavelength.

The nanodots-air interface is reasonably uniform and analysed as a porous Cauchy layer [40, 41]. In our case, the NP nanodots dispersion 'layer' acts as a porous thin film (considering the NP dispersion and their size dispersion), whose refractive index and extinction coefficients, shown in Figure 5.8, are different with respect to a bulk film (n = 2.4), forming a several-step reducing index on the material-containing side of the electrode. The reduced nanodot effective refractive index reduces Fresnel reflection within the nanodot dispersion compared to a flat ITO film by reducing the step change in index, enhancing transmission and antireflection.

Angle resolved transmission measurements of the nanodot dispersions and an ITO thin film were determined and summarised in Figure 5.9. The position of the plasma frequency indicated by ω_p , red shifts and the reflectance of the In₂O₃ nandots

dispersion and the ITO thin film decreases with angle near their respective plasma frequencies, shown in Figure 5.9a, while the reflectance decreases substantially after the plasma frequency relative to that before the onset of the plasma frequency. The red-shifting of the entire angle-resolved spectrum for the nanodots dispersions is also seen in Figure 5.9a, where at visible wavelengths the transmission varies from 55% at near incidence and at 40°, and importantly, remains 87% transparent at wavelengths up to 4 μ m (Figure 5.9b-c).



Figure 5.9 (a) Transmittance of the In_2O_3 nanodot dispersions and that of an ITO thin film of similar nominal thickness. (*Inset*) Polar plot of the angle-resolved transmission of the nanodots at visible wavelengths. (b, c) Optical images of the In_2O_3 nanodots showing antireflection characteristics in the visible. (d) Angle-resolved reflectance of an ITO film.

Corresponding angle-resolved reflectance of an ITO film in Figure 5.9d, confirms a blue-shift of the plasma frequency with increasing angle, but even at normal incidence the comparison comparative ITO film is similarly conductive but much less transparent at IR wavelengths. The nanodot dispersions allow a shifting the maximum in transmission (and minimum in normal reflectance) to longer wavelengths while maintaining identical transmission in the same energy window as commercial ITO on glass (Figure 5.9a), and with the added benefit of a lower effective sheet resistance into the IR. These layers offer excellent visible-infrared transmission, and also antireflection properties, as seen in the optical images in Figure 5.9 b and c.

5.6 Reversible electrochemical Li-insertion

The ability of the In_2O_3 nanodot dispersions to reversibly intercalate or alloy Li, and its insertion and removal potentials, was examined using cyclic voltammetry. Figure 5.10a shows the cyclic voltammetric response of the Li|Li⁺-electrolyte|In₂O₃(111)|Si(100) system. For this cell the cathodic process involved the insertion of Li into In₂O₃ to form a Li-In alloy (charging) and the anodic process follows Li extraction or dealloying (discharging). A related process is known to occur for Li alloying with Sn [42], but there are limited investigations of Li insertion in to In-containing materials [43]. The general alloying process can be described using the following equation:

$$6\text{Li}^+ + 6e^- + \ln_2 0_3 \longrightarrow 3\text{Li}_2 0 + 2\text{In}$$
 (5.3)

which accounts for the two cathodic peaks found in the cyclic voltammogram the correspond to In_2O_3 reduction to In^0 . The cathodic current peak visible at 0.8 V

corresponds to reaction in which 8.66 Li⁺ is inserted to indium, summarised by the general reaction for discharging

$$zLi^+ + ze^- + In \rightarrow Li_zIn \quad (0 < z \le 4.33)$$
 (5.4)

As a result, the total reaction from processes 1 and 2:

$$14.66\text{Li}^+ + 14.66\text{e}^- + \ln_2 0_3 \rightarrow 3\text{Li}_2 0 + 2\text{Li}_{4.33}$$
 (5.5)

There are three main peaks in the charging (cathodic) part of the voltammetric response (see main text). They are located at 0.31, 0.48 and 0.72 V. The peak at 0.71 V can be attributed to removal of lithium from indium. It was previously reported that the removal of lithium form indium occurs through the following steps:

$$\text{Li}_{4.33}\text{In} \rightarrow \text{Li}_{3.5}\text{In}(\text{Li}_{4}\text{In} + \text{Li}_{3}\text{In}) + 0.83\text{Li}^{+} + 0.83\text{e}^{-}$$
 (5.6)

$$\text{Li}_{3.5}\text{In} \rightarrow \text{Li}_{1.7} \text{Jn}(\text{Li}_{2}\text{In} + \text{Li}\text{In}) + 1.75\text{Li}^{+} + 1.75\text{e}^{-}$$
 (5.7)

$$\text{Li}_{1.7} \ \text{Jn} \to 1.75 \ \text{Li}^+ + 1.75 \ \text{e}^-$$
 (5.8)

Here, the rate of the first reaction is controlled by thermodynamical processes and the rate of the final reaction being controlled by diffusion. During the first negative scan, two weak irreversible peaks appear at 1.2 V and 0.8 V from the reduction of In_2O_3 to In^0 . Once reduced from In_2O_3 to In^0 , the indium is never oxidized again in the potential range examined. Zhou *et al.* [32] have shown reoxidation, but cycled the anode to over 3.5 V, a voltage window typical of cathode materials. We cycled the anode in 0 -2.5V, a potential window below oxidation potential of In^0 (2.7 V vs. Li^+/Li) [44].

A large reversible peak appears at 0.4 V from the insertion process of Li insertion into In^0 . The rate of this reaction, indicated by measured current is found to reduce with increasing cycle number. The reversible Li insertion-removal process occurs in a voltage window of 0.4 – 0.7 V are the reversible processes described by zLi^+ +

 $ze^- + In \leftrightarrow Li_z In \ (0 < z \le 4.33)$. For the Li|Li⁺-electrolyte|In₂O₃(111)|Si(100), buffering of polarization effects is provided by the Si current collector, which can accommodate the highest Li storage capacity of all anode materials [45, 46].



Figure 5.10 (a) Cyclic voltammetry of In_2O_3 nanodot electrodes between 0.0 - 2.5 V. Inset shows the corresponding integrated charge vs. voltage curve for 5 cycles. SEM images show the nanodots before (b) and after cycling (d). (c) Cyclic voltammograms for first and second cycle highlighting the SEI layer formation. Arrows indicate phases formed during insertion and removal processes.

The free surface area ($\sim 20\%$) between neighbouring particles allows Li to be coinserted into the silicon current collector, which is indicated by the existence of two additional peaks in the anodic part of the insertion reaction, at 0.32 V and 0.5 V. Those peaks relate to the removal of lithium from silicon [47]. Figure 5.10c shows the first 2 cycles of this system, and we note that the reduction of In₂O₃ and related insertion processes dominate over Li_xSi phase formation and insertion of lithium into silicon in the first cycle. This co-insertion into the active material and current collector equilibrates after the second cycle. The increasing rate of Li-Si formation can be attributed to an activation effect [46] linked to lithiation-induced volumetric expansion that causes cracking and the exposure of unreacted material to the electrolyte. Successive cycling then allows more lithium to intercalate into silicon, providing a degree of stress buffering for the In alloving process without requiring carbon, conductive additives or polymeric binders. The rate of insertion and removal are consistently balanced in each cycle (Figure 5.10, inset), and apart from charge associated with SEI formation and reduction to In⁰, negligible charge fading is found for all processes in all subsequent cycles.

During co-insertion into the active material and current collector, both of which are reversible, the variation in volumetric changes and accompanying effects is considered. The SEM images in Figure 5.10c and d show the condition of the electrode surface before and after cycling. Using the size distribution analysis (*cf.* Figure 5.7), the reduction in average nanodot size is 30-50%. The brightness of the secondary electron emission stems from a reduced conductivity of the Li_xIn phase. As the nanodots are epitaxial, their adhesion to the substrate is excellent, and lithium insertion is not likely to occur directly under each nanodot, unless they are extremely small. In this case, we that some of the smallest nanodots are removed from the substrate, but this occurs when their diameter is less than the change in volume of the near surface of the silicon. The

molar volume of In^0 is a factor of 2.45 less than the In_2O_3 and by comparison to the size reduction observed, it is clear that no significant volume change effects occur in stable In^0 nanodots; faceting related to the structure of In_2O_3 is also lost during electrochemical reduction to the pure metal.

Previous reports show that the electrochemical performance of In_2O_3 is strongly influenced by its microstructure and composition [32]. Here, the dispersion of the nanodots, while permitting transparency and conductivity into the IR region, also allows lithium insertion into the current collector, and remains structurally stable due to strong epitaxial adhesion and lithium co-insertion buffering by the silicon current collector. The partial porosity of the variable size nanodot distribution prevents stress build up in the In^0 (when reduced from In_2O_3) and promotes optical transparency. The removal of the smallest nanodots by volume expansion of the underlying silicon does not largely affect the gravimetric energy density, and it serves to buffer polarization of the Li_sIn by reversibly intercalating Li^+ . Detailed size distribution analysis before and after cycling shows that some volume expansion occurs in the alloyed Li-In phase, but it does not affect the structural integrity of the electrical contact to the current collector.

5.7 Conclusions

The unique size dispersion of In₂O₃ nanodots prepared by MBE deposition of indium and subsequent oxidation in air at elevated temperature, has allowed the development of a Li-ion battery electrode with enhanced IR transparency with sacrificing electrical conductivity, and lithium co-insertion processes with high Coulombic efficiency that results in stable cycling and charge storage. The In₂O₃ nanodots show bimodal size distribution confirming a two-step epitaxial growth mechanism, and good surface coverage with unique shape and (111) crystalline orientation. The nanodot dispersions

were successfully shown to reversibly alloy with lithium after reduction to metallic indium; the specific size distributions allow reversible lithium co-insertion with a silicon current collector as well as the active material on the surface. Moreover, the specific size offers excellent antireflective properties and enhanced transparency reaching $\sim 87\%$ at 4 µm, potentially allowing for further development of transparent battery electrodes or the possibility for in-situ non-destructive spectroscopic monitoring of structural and electrochemical processes.

5.8 References

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CHAPTER VI

TIN OXIDE INVERTED OPAL BATTERY ELECTRODES

6.1 Abstract

The formation of ordered porous structures has been a topic extensively researched over a number of years. In particular, Inverted Opals (IO) formed by infiltration of an ordered particle template and its subsequent thermal or chemical removal, have attracted much attention due to excellent control over the pore size and arrangement. Amongst materials that have been used to prepare IO structures, tin oxide (TO) offers potential for a variety of applications, such as photonics and charge storage sensing capacity. To our knowledge, within the vast quantity of reports on 3-dimensionally porous structures, either crystalline, amorphous, ordered or disordered, neither IO synthesis by Tin(IV) isopropoxide solutions (though being reported for the synthesis of for instance thin films) nor the formation of SnO₂ inverted opal 3-DOM photonic crystals with mesoporous walls has been reported to date. Here we present a detailed route to the formation of tin oxide inverted opals formed from an opal photonic crystalline polystyrene template. Hierarchically structured and porous inverted opals are prepared from tin isoproposide and tin acetate, with IOs from different precursors exhibiting characteristic morphological differences. The SnO₂ IO structures were characterized as an anode for lithium ion batteries. Detailed cyclic voltammetric measurements indicate that at higher voltage scan rates, the electrochemical energy storage mechanism transitions from a true hybrid storage mechanism involving reversible alloying to a pseudocapacitive charge compensation.

6.2 Introduction

The synthesis and preparation of periodic porous materials such as inverse opals (IOs) has attracted significant attention due to their potential application in a variety of fields [1-4]. Particularly, IOs of inorganic oxide materials that can be used in catalysis [5] photonic crystal devices due to their photonic bandgap (PBG) [6] or electrochromics [7]. The IOs are formed from infiltration of the polymeric colloidal crystal template with inorganic precursors and consist of solid walls that surround interconnected closepacked spherical voids. The size of the voids depends on the size of the template sphere, typically 200 nm $- 2 \mu m$. The periodicity of the IOs with unit cell dimensions on the order of visible to IR wavelengths, generated significant interest in IOs as photonic crystals [6, 8], where a complete PBG is possible, in addition to wavelength selective diffraction based on periodicity and refractive index contrast. Other applications, such as those involving the reactivity of the porous matrix (catalysis, biomaterials) [5, 9] can also benefit from the IO structure. The non-photonic applications of IOs comprise of diverse fields such as chemical and biological sensing [10, 11], simultaneous chromatographic separation and optical sensing [12, 13], biomedical research [14, 15], catalysis [5, 16, 17] and power storage and generation [18-21].

The properties and functionality of the IOs can be modified and enhanced by coating the pore surfaces not only with small organic groups but also with active films and nanoparticles [22]. The nanoscale structure of the IO skeleton provides a large surface area, short diffusion lengths, facile access and faster transport kinetics for reagents inside the porous structures.

In the energy storage field, lithium ion batteries offer the best specific energy densities compared with the majority of other electrochemical energy sources, storing

energy through a variety of mechanisms [7, 23]. The energy storage mechanism can employ lithium intercalation [24], lithium alloying [25] or conversion [26] materials as both positive and negative electrodes. The main advantage of alloying materials used as battery anode, in comparison with currently used graphitic carbon, is their significantly higher charge storage capacities. Silicon-based negative electrodes show the highest capacities as negative electrodes, exceeding even that of metallic lithium (4400 mAh g^{-1} vs 3900 mAh g⁻¹). Other types of alloving materials, such as Sn (990 mAh g⁻¹) [27], SnO (876 mAh g⁻¹), SnO₂ (780 mAh g⁻¹) [28-34], Sb (660 mAh g⁻¹) [35], Si (4200 mAh g⁻¹) [36] and Ge (1600 mAh g⁻¹) [37] also offer significant improvements in charge storage capacity when compared to the current technologies. One challenge present when using alloying anodes is the substantial volumetric expansion associated with storage of large amount of lithium [1, 7, 29] when limited to alloying processes as the primary charge storage mechanism. Repeated cycling of electrodes based on alloying materials leads to accumulation of stress and strain, causing pulverization that reduces charge capacity with cycle life in some materials, and leads to repeated formation of the solid electrolyte interphase layer (SEI), arising from the decomposition of electrolyte on the surface of active material, which also adds to irreversible storage capacity loss.

Capturing charge in storage mechanisms other than alloying in Sn-based and related anode materials is possible using periodic porous inverted opal structures with the materials structured on nm-and µm length scales. Such IO structures offer some key advantages for LIB electrodes based on alloying materials. The diffusion lengths for Li ions are shortened, as the thickness of the IO wall can be structured with assemblies of nanocrystals, nominally improving the rate capability of alloying or intercalation reactions [38]. Moreover, the large surface area can result in a current density decrease per unit volume, leading to further increases in rate capability, and also offer the possibility of double layer charge storage and other non-faradaic processes such as

redox pseudocapacitance [39]. Additionally, the size of macropores improves electrolyte infiltration into the structure of active material, resulting in reduction of the concentration polarization. The continuity of the interface between the active material and the underlying current collector offers binder-free options for active materials, improving the limitation on gravimetric density caused by the functional porosity. Lastly, and most importantly for the alloying electrodes, the free space provided by macropores in IO structure should permit efficient volumetric expansion and prevents agglomeration of active material upon repeated charge/discharge cycles.

Inverted opal based batteries have been studied by several research groups in recent decade, (see Table 2.3) . The improvements in the performance, particularly at high charge-discharge rates was attributed to the macroporous structure of the electrode [40-48]. Most recently, an improved approach to IO based batteries was demonstrated by Pikus et al. [19, 20, 49] where a bicontinuous IO-structured metallic scaffold coated with a thin film of active materials showed remarkable improvements in the electrochemical performance of the batteries, allowing charge rates of over 1000C, without major capacity fade.

Tin, like other alloying materials, suffers from large volumetric expansion, and relies on the electrochemical stability of SnO_2 based electrodes [33]. Deeper understanding however is needed of SnO_2 structures where the surface area is maximised. A transition to pseudocapacitance behaviour that limits Li-Sn phase formation and volume changes may improve the power density without severe capacity fade. SnO_2 IO anodes investigated by Lyttle et al.[50] were limited by contraction of the active material, electrochemical amorphization of SnO_2 and electrochemically induced agglomeration of the nanostructures. However, recent studies showed that potential window may have a large effect on the performance of SnO_2 [51] based anodes. A

summary of the comparative performance of Sn-based anodes in cells is provided in Table 2.2.

Recent reports of pseudocapacitive effects in materials that can also store energy through Li intercalation or alloying mechanisms, and this hybrid storage mechanism can be controlled by both the increased double-layer capacitance of high surface area semiconductors, and by the rate change of the applied voltage [52, 53]. Designing oxides as high performance anodes could benefit from alloying and pseudocapacitive charge storage.

Here, a hybrid energy storage is presented using hierarchically structured SnO_2 IOs formed from electrophoretically deposited templates using Cl-free precursors that charge compensate from reversible Li alloying, double layer charging at SnO_2 surfaces and redox pseudocapactive behaviour from Sn(IV)/Sn(II) centers that is controlled by nanostructuring of the SnO_2 IO, and by the rate of applied potential. The structure of IOs is largely dependent on the type of the precursor used, and ranges from assembly of nanocrystals to hierarchical nanocrystalline walls that are either continuous but mesoporous, or an assembly of nanocrystals. The following details the formation of the inverted opal, its structural and chemical characteristics as well as the electrochemical performance.

6.3 Experimental Section

All chemicals were used as received without further purification. Tin 2ethylhexanoatediisopropoxide, styrene, dimethyl carbonate, ethylene carbonate and tin acetate were purchased from Sigma Aldrich.

6.3.1 PS sphere synthesis

Monodisperse polystyrene (PS) spheres were prepared by aqueous alcohol emulsion polymerization described elsewhere [54]. Briefly, 4.5 ml of styrene was mixed with 10⁻¹

mol dm⁻³ sodium hydroxide to remove emulsion polymerization. It was then added to 70 ml of aqueous alcohol solution at 2:5 H₂O:EtOH ratio in three-neck round bottom flask. The aqueous alcohol was aerated with nitrogen for 30 minutes to de-oxygenate the solution. Prior to addition of styrene, a 0.11g of sodium dodecyl sulphate surfactant was dissolved in the aqueous ethyl alcohol solution according to the procedure described in [54]. After the addition of styrene to the flask, the reaction vessel was sealed under nitrogen atmosphere, and equilibrated at 70 °C. To initiate the polymerization, a 0.121g of the potassium persulfate, initiator dissolved in aqueous alcohol was injected into the reaction vessel under rapid stirring. Subsequently, the reaction was carried out in isothermal conditions for 8 hours. Monodisperse polystyrene spheres were collected and washed with DI water multiple times to ensure complete removal of unreacted monomer. The PS spheres were then dispersed in DI water at 2.5 wt% concentration.

6.3.2 Electrophoretic deposition

Electrophoretic deposition was carried out in order to prepare IO PS templates with large size and good degree of ordering. Briefly, 1 ml of the PS spheres solution was placed in 5 ml glass vial. 3 ml of ethanol were then added to the vial. Subsequently, 60 μ l of NH₄OH was added to the solution, until a pH ~10. Two stainless steel electrodes of 2.5 cm² polished to a mirror finish were placed in custom made holder 5 mm apart. In the vial containing the PS sphere solution, a constant electric field of 400-600 V m⁻¹ was then applied for electrophoretic depositions for 1-2 h. Subsequently, upon removal of the electrodes from the solution, an electric field impulse of 30 kV m⁻¹ was applied between the electrodes for 5 s to fuse the spheres. All templates were dried and used for infiltration without further treatment.



6.3.3 Template infiltration

Figure 6.1 Schematic diagram detailing preparation of IO structures. 1. Electrophoretic deposition of latex spheres 2. Template infiltration. 3. Heat assisted template removal4. Formed IO structures.

To infiltrate the template two types of tin oxide precursors were used. Tin acetate was dissolved in ethanol at 80 °C and mixed for at least an hour. Tin ethoxyethanol-diisopropoxide (98%) was mixed with 2-methoxyethanol in a glass vial to for a 10% solution and used without any further treatment. To infiltrate the templates, precursor solution was placed in a syringe, and a small quantity of the precursor was deposited on the surface of the template. Capillary forces allowed for infiltration of the inter-sphere voids by the precursor solution. Subsequently, the infiltrate template was placed in a vacuum desiccator, and vacuum was applied for at least 30 minutes to ensure complete infiltration of the template by precursor solution. Subsequently, the template was dried in an oven for 30 minutes at 40 °C to ensure complete evaporation of the precursor solvent. The infiltration procedure was repeated 1-3 times to ensure complete infiltration of the template by the precursor solution. Subsequently, the infiltration of the template by the precursor solution.

remove template spheres through oxidation of polystyrene. The heating ramp rate was set to 1 °C min⁻¹. The template preparation is summarised in Figure 6.1

6.3.4 Structural characterization

Surface morphologies and the chemical composition of the nanostructured dispersions were investigated by scanning electron microscopy (SEM) using a Hitachi SU-70 with an Oxford-50mm² X-Max detector for energy dispersive X-ray analysis (EDX). The acceleration voltage used for imaging at 10 kV, unless stated otherwise. Transmission electron microscopy (TEM) analysis was conducted with a JEOL JEM-2100F field emission microscope operating at 200 kV, equipped with a Gatan Ultrascan CCD camera and EDAX Genesis EDS detector for atomic resolution crystal structure and composition examination. Before imaging, samples were ground using agate mortar and pestle, and dispersed in isopropyl alcohol (IPA) before depositing on holey-carbon TEM grid.

X-ray photoelectron spectroscopy (XPS) was acquired using a Kratos Axis 165 monochromatized X-ray photoelectron spectrometer equipped with a dual anode (Mg/Al) source. Survey spectra were captured at as pass energy of 100 eV, step size of 1 eV, and dwell time of 50 ms. The core level spectra were an average of 10 scans captured at a PE of 25 eV, step size of 0.05 eV, and dwell time of 100 ms. The spectra were corrected for charge shift to the C 1s line at a binding energy of 284.9 eV. A Shirley background correction was employed, and the peaks were fitted to Voigt profiles.

To investigate the electrochemical insertion (alloying) and removal of Li, cyclic voltammetry measurements were carried out in a 3-electrode setup using a Multi BioLogic VSP potentiostat, using Li as both counter and reference electrodes, to which all potentials, are referenced. As prepared IOs were cut so their nominal electrode area

~0.5 cm². Electrodes were then dried overnight in a vacuum oven to ensure sufficient dryness of the substrate. IOs electrodes were separated from Li counter and reference electrodes by glass fibre separator soaked in 1 mol dm⁻³ solution of LiPF₆ in ethylene carbonate:dimethyl carbonate (EC:DMC) in a 50:50 v/v ratio. The electrodes were potentiodynamically cycled at various scan rates. Afterwards, the electrodes were carefully washed in acetonitrile and a 10^{-4} mol dm⁻³ solution of acetic acid to remove the electrolyte residue. Additionally, constant current measurements were carried out using similar experimental setup.

6.4 Results and discussion

6.4.1 Inverted Opal Preparation

During emulsion polymerisation, synthesized PS spheres retain sulphate ions on their surface due to the presence of sodium dodecyl sulphate (SDS) surfactant. Sodium ions create a layer of surface charge around the polystyrene spheres, and facilitate EPD of an ordered opal template as shown in Figure 6.1. The colloidal crystal (CC) ordering is possible with a relatively low electric field (400-600 V m⁻¹). Large sphere sizes (~750 nm) form well-ordered opal templates with good adherence to the substrate. To improve the structural integrity of the opal templates, both thermal treatment and high voltage pulses at the end of the deposition cycle were applied. Heating briefly close to the glass transition temperature ($T_g = 95$ °C) improved the adhesion of neighbouring spheres due to limited "necking effect" where the neighbouring spheres form connected solids. A high voltage pulse (150 V for 5 s) allows for electrostatic fusion of nearest spheres and also results in improved adhesion of the template to the substrate. Templates with thicknesses reaching over 50-60 layers can be formed within 1 h,

usefully faster that layer-by-layer assembly, dip-coating, or evaporation induced selfassembly (EISA) methods.



Figure 6.2 a) Schematic diagram detailing formation of PS templates. b) Large-scale view of the surface of the deposited PS template. Common IO template defects are indicated c) high magnification SEM image of the deposited template. d) Domains of PS sphere assemblies formed under certain deposition conditions.

PS spheres preferentially form CCs in a cubic close-packed arrangement, with [111] faces parallel to the surface of the substrate. An SEM image of the surface of the template after EPD is shown in Figures 6.2b and c. Point defects (1) and edge dislocations (2) are the most common defects in EPD growth of the PS templates. We also observed that deposition of PS spheres at high electric field strengths or concentrations above 10 wt%, will result in formation of largely disordered colloidal

template (Figure 6.1) Formation of colloidal crystal templates is also possible if spheres of larger sizes are used. Gravity may become a dominant force however and the colloidal interactions will be unable to prevent sedimentation of the PS spheres. In order to prepare colloidal templates using spheres with sizes above 1 μ m, either shorter deposition times or additional agitation [55] are required, to ensure uniform sphere concentration across the colloidal solution during EPD.

6.4.2 Inverted Opal Structure

CCs were used to prepare inverted opals (IOs) of tin oxide. Two types of tin oxide precursors were used – tin ethylhexanoate-diisopropoxide (TI) and tin acetate (II, TA). Figure 6.3 shows typical inverted opal structures formed by infiltration of CC templates. IOs formed from TI are shown in Figure 6.3a. The characteristic honeycomb structure is related to the direction of ordering of CC template. Figure 6.3b shows IOs formed from TA. The [111]-oriented and [110]-oriented surface regions of the CC template transferred into the IO crystal.





Figure 6.3 a) SEM image of an IO formed from TI inset: SEM image of a single IO cell. b) SEM image of IO formed from TA. c) Tilted SEM image showing the thickness of the IO structure, d) SEM image of inverted photonic glass structure. e) Tilted SEM image of the IO monolayer. f) Tilted SEM image showing honeycomb – like structure of the IO monolayer.

Multiple infiltrations are required to form an IO structure with a continuous wall morphology. In the case of TI, 3 infiltrations were found to be sufficient in order to achieve excellent IO sidewall continuity, see Figure 6.3 a and b. For TA, as the IOs were infiltrated with supersaturated solution of tin acetate in ethanol. The concentration of TI should be kept below 10 wt% as it affects the infiltration process. Formation of

gradient in surface tension between the dry side of thin film (high surface tension) and dewetted side of the thin film causes lift-off of the top layer of the spheres from the template. Lowering the precursor concentration leads to easier and more reproducible formation of infiltrated IO template and hollow spheres, due to the improved template infiltration.

Infiltration of the monolayer template only results in formation of a complete IO structure if the concentration of precursor in the solvent is reduced to about than 2.5 wt% for tin alkoxide. Saturated TA solution forms ordered IO structures after a single infiltration. Infiltration of photonic glass (disordered CC) templates can yield the morphologies shown in Fig. 6.3d. The opening in the nanostructure walls corresponds to contact points between the neighbouring spheres, while the sidewalls correspond to voids between the spheres in the photonic glass template. The monolayer IO is shown in Figure 6.3f. Depending on the amount of sol used, it is possible to prepare honeycomb-like thin films, or slightly thicker layers of IOs, corresponding to almost complete coverage of template spheres with the precursor solution, as shown in Figure 6.3 e and f.





Figure 6.4 XPS spectrum of SnO₂ IOs for a) Sn 3d b) O1 core levels.

To confirm the oxidation states of TO IOs, high resolution XPS spectra were acquired and are shown in Figure 6.4 a. C 1s peaks used for calibration of the binding energy (B. E.) levels of Sn and O are located at 284.8 and 284.7 eV consistent with spinorbit coupled hyperfine splitting from a single oxidation state for each IO sample prepared from TA and TI precursors respectively. The small shift in B. E. levels observed for C1s peak (~0.1 eV) does not correspond to shifts in energy levels for Sn 3d peaks (+0.4 eV), located at 486.3 and 486.7 eV for TA and TI respectively. It is difficult to determine the precise relative concentration of Sn⁴⁺/Sn²⁺, as the difference in B. E. between both oxidation states is very low. The small shift in the B. E. between IOs formed from TI and TA indicates that the oxidation states of the Sn atoms in both IOs are different; the tin oxidation state in TA is Sn²⁺ and is Sn⁴⁺ in TI.

Deconvolution of the O1s peaks presented in Figure 6.4 clearly demonstrates that the concentration of the Sn atoms at different oxidation levels is not identical

between the IOs prepared from TA and TI. The deconvoluted peaks of the O1s bond can be attributed to oxygen atoms chemisorbed at the surfaces (531.9 eV), as suggested by Mulla et al. and to the $O-Sn^{2+}$ and $O-Sn^{4+}$, at 530.6 and 529.3 eV respectively, separated by ~1.3 eV. The difference in relative concentrations of Sn^{4+} and Sn^{2+} in two different inverted opals is associated to the corresponding oxidative states of the precursors from which IOs are prepared. The intermediate oxidation state of the two IO samples is equal to 3.02 for IOs prepared from Sn Acetate and 3.16 for the samples prepared from Sn isopropoxide. The small difference in the relative oxidative states corresponds to the relative intensities of the deconvoluted XPS spectra and is also related to the initial precursor used.

To probe the crystalline structure of the IOs and their relation to the mechanism of growth, HRTEM analysis is presented in Fig. 6.5 for the nanostructure of the TA-based IO.



Figure 6.5 a) Low magnification TEM image of the IO sample prepared from TI. b) TEM image showing IO sample prepared from TA inset – high resolution TEM showing a single crystallite. c-d) High resolution image showing IOs prepared from TA. Inset presents ED pattern taken from the imaged area. e) XRD patterns for IOs from TIPO, TA, and a reference pattern for the blank steel substrate.

The XRD characterization of crystal phase and purity of the IOs from Sn(II) and for comparison, and IO formed from Sn(IV) acetate precursors, shown in Figure 6.6. X-ray diffraction patterns showing peaks that are indexed to (110), (101), (200) and (211) reflections of tetragonal cassiterite phase SnO₂ (space group P42/*mnm*). Furthermore, the XRD pattern exhibits no additional peaks, indicating the absence of crystalline or heterophase impurities such as *e.g.* SnO.



Figure 6.6 XRD patterns of SnO₂ IOS from a) Sn (IV) Acetate b) Sn(II) Acetate.

Figure 6.5 shows typical low magnification images of the SnO₂ IOs structures. High resolution TEM images demonstrate good crystalline quality of the prepared IOs as a macro-structure, but with no long range ordering of the nanocrystals that comprise the IO walls. Prior to TEM imaging samples were ground up using an agate mortar and pestle, and it is believed that the long range order visible in the SEM image was lost due to the grinding process. The high resolution TEM images reveal the presence of the

small size pores (2-3 nm) within the walls of the IO. The walls of the IOs only take mesoporous structure if the precursor used is TI. In case of the TA the walls form as an assembly of tin oxide nanoparticles, without lower order porosity, but with significant surface roughness. The crystalline structure of each IO was confirmed using X-Ray diffraction and is shown in Figure 6.6. Reflections from (111), (101) and (211) peaks characteristic for tin oxide tetragonal rutile structure. Significant broadening of those peaks is small size of the nanocrystals comprising the IO walls, as confirmed by HRTEM. The average crystallite size estimated from the Debye-Scherrer relation of broadened line-widths is \sim 4 nm. The small nanocrystal size of is related to the rapid nature of the hydrolysis of the TI precursor, resulting in random orientation of nanocrystals as an interconnected assembly that form the walls of the IO. In the case of TA, the small nanocrystal size is likely due to the make-up of the colloidal solution of TA nanoparticles in the infiltrated sol. This sol blend self-assembles in the voids of CC template during solvent evaporation, and forms its characteristic structure during calcination to form the IO walls.

6.4.3 Electrochemical characterization of SnO₂ IOs

Cyclic voltammetry, carried out at various potential scan rates, was employed to better understand the electrochemical processes occurring in the TO IOs. Samples were used for the assemblies of the electrodes, with equal electrode surface area, in three electrode setup with lithium used as counter and reference electrode. Specific experimental details can be found in chapter 3. To understand the influence of the rate of electrode voltage change (potential scan rate) on the electrochemical energy storage mechanism, the scan rate of the voltammetric polarization was increased in regular intervals from 0.1 - 20mV s⁻¹.

To characterize and describe processes present during potentiodynamic cycling of the SnO_2 IOs, a number of CV measurements were carried out. A typical resulting voltammogram is shown in Figure 6.7.



Figure 6.7. Cyclic voltammogram for SnO₂ inverse opal electrodes carried out at 0.1 mV/s vs Li/Li*

Figure 6.7 presents a voltammogram demonstrating changes occurring at the SnO_2 IO electrode., The changes are identified by cathodic (charge) and anodic (discharge) current peaks corresponding to the course of lithium alloying, SEI formation, and dealloying and Sn^0 reoxidation in slow scan rate quasi-static thermodynamic conditions. In the CV in Figure 6.7, the anodic part of the scan is associated with lithium insertion into SnO_2 IOs (charge), while the cathodic part of the voltammogram is associated with removal of Li from SnO_2 IOs (discharge). The slow rate of change of the applied potential allowed for better resolution recording of the processes occurring within the electrode and thus detailed description of the course of

electrochemical alloying/dealloying. In the first cycle, a small cathodic peak is present at 1.33 V, and can be associated with reduction of tin oxide and dioxide to metallic tin. This process is believed to be irreversible and is required to enable alloying of tin with lithium [25, 56, 57]. In subsequent cycles this peak shifts to a lower voltage, indicating improved reaction kinetics and a higher chemical potential for lithiation of complete or partially dealloyed and reduced Sn. The secondary electrolyte interphase (SEI) that is formed an anode materials at voltages approaching the redox potential of the Li⁺/Li couple, is formed in the first cycle, at ~0.7 V, through reductive or reactive decomposition of the electrolyte often catalysed by the surface of the active material. The decomposition of the electrolyte results in formation a variety of carbonaceous and fluoride compounds of lithium, and forms an ionically conductive and electronically insulating (but thin) interface separating active material and the electrolyte. As the SEI layer is a good ionic conductor of Li, its formation on the active electrode is seen as beneficial for the performance of the battery, provided that repeated cycling does not result in its deterioration and additive formation of SEI layer on freshly exposed active material in each cycle. CV analysis for high surface area SnO_2 IOs (Fig. 6.7) shows that the SEI layer forms in the first cycle, as indicated by lack of presence of well-defined cathodic peak at ~0.7 V in second and subsequent cycles. Alloying of Sn^0 with Li occurs at potentials below 0.5 V. The formation of different Li_xSn phases due to alloying is clearly seen as a number of cathodic peaks are present in the 0.0-0.5 V potential range. The composition of the phases of Li_xSn alloy associated with each peak are shown in Table 6.1.

Peak	Peak potential vs Li/Li ⁺	Phase formed
1	0.84 V (cathodic/charge)	SEI layer, SnO₂→Sn ⁰
2	0.55 V (")	Li ₂ Sn ₅

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3	0.41 V (")	LiSn
4	0.31 V (")	Li ₇ Sn ₃
5	0.16 V (anodic/discharge)	Li ₂₂ Sn ₅
6	0.53 V (")	Li ₂₂ Sn₅→Sn
7	1.1 V	Sn→SnO

Table 6.1. Peak potentials and associated phases of Li-Sn alloy formed.

In the cathodic or charging part of the voltammogram of SnO₂ IOs at potentials below 0.25 V, a number of phases are formed simultaneously, as the Li content per Sn atom increases to maximum 4.4 Li per Sn [25]. The structure Li₅Sn₂, Li₁₃Sn₅, Li₇Sn₂ and Li₂₂Sn₅ is similar, and the phases only differ by arrangement of Li and Sn atoms in the alloy lattice [25]. In the anodic part of the scan, the main feature is the peak associated with removal of Li from Li_xSn alloy, present at~0.53 V. A smaller peak is also present at ~1.05 V. This peak is generally accepted as being associated with partially reversible reoxidation of Sn to form SnO. This observation is consistent with the repeated observation of the small peak located at ~1.1 V in the cathodic part of the voltammogram, appearing only after the second cycle, which is attributed to repeated reduction of SnO.

Under anodic polarization, the peak associated with the removal of Li from the Li_xSn decreases in intensity with the cycle number. Additionally, a second peak appears in the cathodic part of the cycle at about 0.66 V, and does not increase in intensity in subsequent cycles. The presence of this peak may be attributed to the changes of reaction kinetics caused by increased degree of electrochemical amorphization of SnO_2 IOs. The lithiation of SnO_2 occurs through transfer of reaction front through SnO_2 crystalline structure [58]. The movement of the dislocation front through the crystalline solid increases the free energy of the IOs sufficiently to result in formation of

amorphous phase with small crystallites of SnO_2 dispersed in it. The lithiation or alloying of Sn^0 from reduced SnO_2 causes large volumetric expansion, often leading to formation of cracks and voids in the active material on repeated cycling. The cracking may also expose some fresh unreacted material to the electrolyte, resulting in formation of SEI layer. The existence of the second peak at ~0.88V in the cathodic part of the CV can be explained by repeated cycling of amorphous unlithiated phase.

It is also important to note that the peak present at around 1.1 V is believed to correspond to reaction of partial reoxidation of metallic Sn to SnO. This reduction of SnO_2 to Sn is generally considered irreversible. However, the repeated presence of this peak in the first and subsequent cycles indicates that the redox reaction of SnO/SnO_2 as assembled nanocrystals in the hierarchical length scale structure of the inverse opal, is partially reversible.

6.4.4 Transition to Pseudocapacitive Charge Storage in IOs

Figure 6.8 shows the cyclic voltammogram cycles of SnO₂ IO samples carried out with increasing applied potential scan rate. It is important to note that for smaller potential scan rates (low enough to approximate a thermodynamically controlled reaction), the electrochemical processes occurring on the electrode can be associated with the alloying regime that is principally found in constant current charge-discharge tests. Standard battery electrode charge-discharge measurements are incapable of probing the mechanism of charge storage that is influence by the rate of potential variation, since the current is constant and thus a set reaction rate is enforced.

The measurements shows that the definition of current peaks related to specific oxide reduction, SEI formation (1st cycle predominantly), and Li-Si alloying and dealloying reactions become less defined at higher scan rates. After several cycles at slow scan rates, the alloying reactions affect the structure of the IO electrodes varying

with cycling, such that the dealloying form high mole fraction $Li_{22}Sn_5$ dominates at potential less than ~1 V. In other words, the cyclic alloying reactions form a minimum lithiated Li-Sn phase such that the current peak (reaction rate) associated with its dealloying reduces and shifts to high potential.

In principle, three processes contribute to the measured currents in potentiodynamic experiments: (1) double layer charging of the SnO_2 nanocrystal surfaces, (2) pseudocapacitive Faradaic current associated with redox reaction of $Sn^{2+/4+}$ centres, and (3) non-Faradaic reactions of either Sn^{2+} or Sn^{4+} (for SnO and SnO₂) requiring Li⁺ alloying for charge compensation. For increasing potential scan rates, the influence of pseudocapacitive energy storage associated with Faradaic processes occurring on the electrode/electrolyte interface becomes dominant over the alloying of Li with the active material (Sn⁰).





Figure 6.8 a) Cyclic Voltammograms for Sn IOs carried out at scan rates in the range 0.2 - 20 mV/s in a potential window of 0 - 2.5 V vs Li⁺/Li. b) 150 CV cycles acquired from SnO₂ IO material at a scan rate of 20 mV s⁻¹.

Figure 6.8 also shows a series cyclic voltammetric cycles for SnO₂ IO carried out at 20 mV/s. The shape of the curve (absence of defined peaks) indicates that the pseudocapacitive processes dominate over the lithium alloying for the SnO₂ IO electrode material. Here, a transition from true hybrid energy storage to predominantly pseudocapacitance is found, with current peaks indicative of charge compensation mechanisms of charge storage within the double layer that do not affect the potential associated with a phase change. Here, successive cycling results in a greater overall cumulative integrated charge capacity. This is common at faster scan rates, where we assume more of the surface area becomes accessible to electrolyte in time, leading to a fixed cyclical charge capacity. A series of voltammograms acquired at 20 mV s⁻¹ for 150 scans (Figure 6.8b) confirms a dominant and consistent pseudocapacitance response, and we surmise that significant length of time at low voltages in a lithium salt containing electrolyte facilitate some structural or chemical modification to the IO.



Figure 6.9 a) Cyclic voltammograms for IO samples cycled at 0.1 mV/s and 20 mV/s. Inset – cyclic voltammogram for IO sample cycled at 20 mV/s. b) Capacity per unit area calculated for IO samples at various scan rates. c) SEM image of a pristine IO sample. d,e) Surface of the IO sample cycled at 20 mV/s. f) SEM of the surface of the IO sample cycled at 0.1 mV/s. Fibres present in the imaged area are from the glass separator.

Figure 6.9 shows the comparison between the cyclic voltammograms taken from scans carried out at 0.1 mV/s and 20 mV/s. It is evident that at high rates of potential change, the main mode of electrochemical energy storage changes from alloying to pseudocapacitive redox reaction. Figure 6.9b shows the charge capacity calculated from the voltammograms using the following formula:

$$C = \frac{1}{mv(V_c - V_a)} \int_{V_a}^{V_c} I(V) dV$$
(6.1)

The capacity is given per unit area as due to the nature of IO samples accurate determination of sample mass is difficult, but the net mass remains invariant in each set of CVs during cycling since no lithiation induced mass changes occur.

Structural changes of the SnO₂ IOs that underwent electrochemical reactions with different rate of change of the potential applied to the working electrode are shown in Figure 6.9c-f. Multiple-level porosity discernible in are reduced to single-level porosity associated with template spheres during cycling with high rate of change of the electrode potential. Evidently, the high right of change of the potential does not affect the integrity of the IO, even while it changes the surface roughness and porosity. This can be attributed to limited alloying of Li with the Sn-containing surface of the nanocrystalline walls of the IO structure, and subsequent electrochemical amorphization, which due to fast rate of change of the electrode, is limited and does not cause extensive damage of the active electrode material.

To contrast the electrochemically induced changes from high potential rate of change electrode we present the surface morphology of IOs samples that had undergone the quasistatic electrochemical reaction. In Figure 6.9f no ordered IO structure can be discerned, as the electrode had undergone significant electrochemical amorphization, resulting in virtually a complete loss of hierarchical, ordered porosity. This is in contrast with IOs cycled at fast rate of change of applied voltage, where the porosity can be discerned even after multiple cycles. The non-Faradaic contribution from the Li⁺ ion insertion processes, the faradaic contribution from the charge transfer processes with the surface atoms, referred to as pseudocapacitance and contributions from the double layer effect [59]. When the porosity of the electrode increases, both types of capacitive contributions (pseudocapacitance and double layer charging) can be

significant. The capacitive effects can be characterized by analysing data from cyclic voltammetry experiments carried out at different scan rates, according to [60]:

$$i = av^b \tag{6.2}$$

where the measured current i obeys a power law relationship with the sweep rate v. Both a and b are adjustable parameters, with b value, determined from the slope of log(i) vs. log(v). There are two well-defined conditions, b = 0.5 and b = 1. For b = 0.5 the current is proportional to the square root of the scan rate and thus a diffusion limited process linked to reversible (de)alloying like a classic Li-ion battery anode, according to the equation:

$$i = nFAC^* D^{\frac{1}{2}} v^{\frac{1}{2}} \left(\frac{\alpha nF}{RT}\right)^{\frac{1}{2}} \pi^{\frac{1}{2}} \chi(bt)$$
(6.3)

where C^* is the surface concentration of the electrode material, α is the transport coefficient, D is the chemical diffusion coefficient, n is the number of electrons involved in the electrode reaction, A is the surface area, R is the molar gas constant, F is the Faraday constant, T is the temperature, and $\chi(bt)$ represents the normalized current for totally irreversible system, as indicated by cyclic voltammetry. This relationship describe planar diffusion, which is deemed to be correct (as opposed to cylindrical diffusion) for a porous material soaked with electrolyte and no passivating regions separating the nanocrystals.

The other defined condition, is when b = 1, which is representative of capacitive response, as the capacitive current is proportional to the scan rate, according to:

$$i = \nu C_d A \tag{6.4}$$

To obtain the *b*-value, current values from cyclic voltammograms carried out at different scan rates are recorded at specified potential values. Then, the slope of the plot of the log(i) vs log(rate) is the *b*-value at that potential (see Figure 6.10).



Figure 6.10 a) Plot of log of the current peaks from 0 - 3 V from cyclic voltammograms of SnO₂ IO electrodes acquired at scan rates in the range 0.1 - 20 mV s⁻¹. b) *b*-value plot of SnO₂ IOs determined using equations 1 and 2.

In Figure 6.10, a plot of log of the current vs. log of the scan rate is shown for each voltammetric peak in a series of voltammograms acquired at scan rates in the range 0.1 - 20 mV s⁻¹. The slope of curves fitted to the current rates recorded give the *b* value – (see Figure 6.10b), at a potential corresponding to the potential at which the current was measured. In Figure 6.10b, we show a plot of *b*-value vs potential (vs Li/Li⁺). The *b*-value is close to around 0.55, at potentials associated with the insertion of Li into Sn, while it increases at higher insertion potentials. As the *b*-value corresponds to the charge storage mechanism, we can infer from the plot of the *b*-value, that the main charge storage mechanism at high scan rates is pseudocapacitive, in particular at higher voltages.

A closer examination of the voltammetric dependence on the sweep rate allows better insight into the capacitive contribution to the current response during charging and discharging. Concepts explained above allow the expression of the current as a combination of two separate mechanisms, surface capacitive effects and diffusion controlled alloying processes, as follows:

$$i(V) = k_1 v + k_2 v^{\frac{1}{2}} \tag{6.5}$$

Equation 4 can be rearranged for analytical purposes:

$$\frac{i(V)}{v^{\frac{1}{2}}} = k_1 v^{\frac{1}{2}} + k_2 \tag{6.6}$$

In equation 5, $k_1 v$ and $k_2 v^{\frac{1}{2}}$ correspond to the surface capacitive effects and the diffusion controlled alloying processes, respectively. By determining k_1 and k_2 the determination of the relative contributions from the pseudocapacitive and diffusion driven effects are possible, while identifying current limits and voltage windows where $i(V) \propto v$ and where $i(V) \propto v^{1/2}$, i.e. reversible alloying and pseudocapacitance, are dominant.



Figure 6.11. Plot of *k*-value calculated for voltage values between 0.3 - 0.8 V in the cathodic (charging) sweep of a CV of SnO₂ IO carried out at scan rates in the range 0.1 - 20 mV s⁻¹.

In Figure 6.11 the current measured at voltages above and below potentials corresponding to known reduction and alloying processes of Li with Sn⁰ and SnO₂ is plotted as a function of scan rates that span the transition from dominant reversible alloying to hybrid alloying/pseudocapacitance response, based on the analytical relation in Equation (5). The alloying reactions that can occur at these potentials are summarised in Table 6.1. The linear behaviour shown in Figure 6.11 allows us to determine k_1 (pseudocapacitance) and k_2 (diffusion-limited alloying) from the slope and the y-axis intercept point of a straight line, respectively at each fixed potential. From this procedure the quantitative determination between the currents arising from lithium ion

(de)alloying and those occurring from capacitive processes can be assessed from a single CV, and then compared to separate experiments a different scan rate for direct assessment of the charge storage mechanism. From Figure 6.11, the ratio of the slope to the intercept, i.e. k_1/k_2 confirms hybrid mechanisms where alloying reactions dominate at slow scan rates ($k_1/k_2 = 0.256$ at 0.1 mV s⁻¹ in the range 0.3 – 0.8 V)), for all potentials and associated processes. Importantly, figure 6.11 confirms invariant changes in this ratio for all charging (cathodic) processes at slow scan rates. As the scan rate increases to 20 mV s⁻¹, the k_1/k_2 ratio increases (over the full scan rate range) to 2.04, confirming dominant pseudocapacitive contributions to cumulative charge storage. Separate CV curves were also obtained for fixed potentials between 0.1 and 0.6 V in the cathodic sweep, so that the relative capacitive contribution to slow and fast scan rates form pseudocapacitance can be visualized. The calculated contributions are presented in Figure 6.12.



Figure 6.12. Voltammetric data for TO IOs obtained experimentally. The relative voltammetric contributions from the pseudocapacitive and lithium insertion processes. Shading indicates calculated pseudocapacitive contributions calculated for anodic part of the cycle in the 0-0.1 V range.

6.5 Conclusions

This work demonstrated structural and electrochemical characteristics of tin oxide inverted opals prepared from electrophoretically deposited polystyrene templates infiltrated by either organic (tin isopropoxide) or inorganic (tin acetate II). The inverted opals prepared through fast, scalable and facile method show good, large scale ordering with hierarchical porosity. Hierarchical porosity of the inverted opal structures has a large influence on the electrochemical performance of the IO based negative LIB electrodes, but can potentially be used in applications where large surface to area ratio combined with high chemical activity are required. In electrochemical energy storage, the large surface area combined with unique, hierarchically porous morphology of the IOs influences the main mechanism of electrochemical energy storage at different potential change rates. At slow rates, electrochemical lithiation of SnO_2 , indicated by clear and defined cyclic voltammogram peaks causes expansion of the crystalline structure resulting in significant structural changes, and leading to electrochemical performance deterioration. Faster rate of change of the electrode potential influences the main mechanism of charge storage, changing it from the dominant lithium alloying with the bulk crystalline SnO, towards surface based, Faradaic pseudocapacitive reactions largely related to the surface morphology of the electrode material. Pseuocapacitive charge storage, demonstrated by fast rate of change cyclic voltammetry may also result in structural changes of the electrode material, however, the changes occur at much slower rate. The pseudocapacitive effect observed on SnO based electrode materials indicates that the need for detailed electrochemical studies of active charge storage materials has not decreased. Various families of metal oxides with different surface morphologies require detailed investigations to determine the mechanisms of electrochemical energy storage and their dependence on the rate of

change of the potential at the electrode. This knowledge could be valuable in improving electrical performance of next generation batteries and energy storage systems.

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CHAPTER VII

SUMMARY, CONCLUSIONS AND FUTURE WORK

The relationship between the structure and the performance of the lithium ion battery materials has been intensely researched recently. Advancements in material structure engineering and associated battery performance encourage further studies into the relationship between the "form and function" for a variety materials and applications. As metal oxides offer excellent performance characteristics such as large specific charge capacity and rate capability, the focus on finding the balance between structure of the electrode material and the optimal performance of the battery has steadily increased. In some careful investigations, seemingly atypical electrochemical responses are now being assessed as alternative mechanisms of storing charge (involving space charge storage that does not affect the structure of the material), and it was the material type and structure that facilitated these mechanisms when tested in suitable electrolytes. As the progress of research into the LIB moves forward, the need for further investigations into the connection between material morphologies tailored for specific application and performance characteristics required in these applications is only going to become more apparent. The purpose of this thesis was to investigate these properties in detail and to uncover the electrochemical response and performance of a variety of metal oxide nanostructures as LIB anodes. In particular, structured materials were shown to specifically influence the fundamental mechanism of electrochemical operation and help to understand the response of these materials to defined electrochemical testing.

Chapter 2 presented a detailed review of recent progress in the advances of nanostructured LIB electrodes, focusing on the relationship between the morphology and the performance. The chapter outlined the developments in the structure, composition, size, and shape control of many important and emerging Li-ion battery materials on many length scales, and detailed very recent investigations on how the assembly and programmable order in energy storage materials have not only influenced

and dramatically improved the performance of some Li-ion batteries, but offered new routes toward improved power densities. The chapter also described and discussed material aspects of hybrid and multiphasic materials including silicon, germanium, a wide range of metal oxides, alloys and crystal structures, carbons and other important materials. Methods including engineered porosity that offer the energy density of Li-ion batteries and the power density of pseudocapacitors were also highlighted. Recent developments in the analytical methods, electrochemical response, and the structure, composition, size, shape and defined assembly of active materials for a wide range of Li-ion cathodes and anodes were compared and assessed with respect to cell performance. Perspectives on the future development of energy storage materials based on structure as well as chemistry, some of which were addressed in this thesis, were also outlined.

In Chapter 4, tin oxide nanoparticle battery anodes prepared by molecular beam epitaxy of Sn on silicon were assessed and their influence and response to reversible electrochemical alloying was identified in detail. In situ oxidation of the deposited nanoparticles during growth resulted in formation of core-shell morphologies, with size distribution dependant on the temperature of the deposition. Detailed structural analysis suggested a hierarchical formation of secondary nanoparticles on the surface of the primary nanoparticles deposited on silicon. The shell formed on the nanoparticles is the key feature separating two distinct types of the crystals grown. Nanoparticles grown at lower temperature form with an amorphous tin oxide-shell while nanoparticles deposited at higher temperature grow polycrystalline shell around metallic core. Size distribution analysis of the nanoparticles on the surface of the silicon has also a significant influence on the course of the electrochemical reaction between specifically different metal oxide active materials with Li ions. Nanoparticles with amorphous shell

show bimodal distribution of the diameters, which in turn leads to increased Si lithiation when compared with nanoparticles with polycrystalline shell with single-mode diameter distribution. In cases where the material spacing is larger the volumetric expansion can be accommodated radially while maintaining mechanical and electrical contact. In this regard, co-insertion into the Si facilitates this process and is dictated by the active material dispersion. The compositional and structural engineering on SnO₂ and related materials using highly defined MBE growth as model system allowed a detailed examination of the influence of material dispersion on the electrochemical performance.

Chapter 5 presented a detailed structural and electrochemical study of indium oxide nanoparticles prepared by molecular beam epitaxy of indium in oxygen atmosphere. The nanoparticles grown on silicon are formed with well-defined distorted hexagonal shape, with lowest energy <111> crystalline faces of indium oxide cubic crystalline cell parallel to the surface of the substrate. The growth of nanoparticles progresses from nucleation and growth through Stranski-Krastanov growth mode with coalescence of neighbouring nanoparticles. The electrochemical lithiation of indium oxide nanoparticles is also influenced by the size distribution. As In_2O_3 nanoparticles grow with bimodal size distribution, there is a significant contribution to the charge storage from the silicon substrate. Interestingly however, due to excellent substrate adhesion caused by minimal lattice mismatch between In_2O_3 and Si, the structural damage to the interface between the nanoparticles and the substrate is minimal, and the nanoparticle interfacial integrity is preserved. The porosity introduced in the In_2O_3 film leads to significant improvements in the optical transmission of IR radiation through nanoparticle film and improved reflectivity in visible.

In chapter 6, a detailed route to the formation of ordered tin oxide inverted opals prepared from polystyrene templates electrophoretically deposited on the surface of stainless steel was outlined. PS templates were infiltrated with tin ethylhexanoate diisopropoxide precursor solution, or with tin acetate solution in ethanol. Templates were then removed through high temperature calcination, leading to formation of well-ordered, thick layers of inverted opal films with hierarchical multiple length scale porosity. The precursors used influence the morphology of the sample formed. Electrochemical testing of the IO samples indicates that the charge storage mode is largely dependent on the rate of change of the potential applied to the electrode, with non-faradaic processes similar to pseudocapacitive behaviour dominating when voltage-change rates are in excess of 10 mV⁻¹, even in Li-ion containing electrolytes.

In this thesis, the importance of the relationship between the electrode structure and the performance in LIB battery was examined in detail. Structural engineering of the electrode material may lead to improvement in the electrode transparency, indicated by findings of chapter 5. Simple modification of only one of the growth parameters results in significant changes in the electrochemical performance of tin oxide electrodes, as indicated in chapter 4. Additionally, the morphology of the electrode may result in changing of the way the sample stores charge (transition from reversible alloying with phase changes to pseuocapacitive double layer charging without lithium alloying) at different ramping voltages. The importance of understanding of the performancestructure relationship is evident from this investigation.

Future work based on these findings should focus on developing deeper understanding of this relationship, while extending it to a variety of nanomaterials and nanomorphologies, and their composites. One study could investigate the electrochemical performance of the IO composite where one of the infiltration

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materials used is not electrochemically active. Moreover, the characterization of such IO nanostructures should extend beyond electrochemical energy storage, as IO structures offer significant benefits for a variety of fields, ranging from catalysis to tissue regeneration and growth. Improving the understanding between the form and function of nanomaterials is a very important field, which undoubtedly will experience significant growth in coming years.

Appendices



STRUCTURING MATERIALS FOR LITHIUMION BATTERIES: ADVANCEMENTS IN NANOMATERIAL STRUCTURE, COMPOSITION, AND DEFINED ASSEMBLY ON CELL PERFORMANCE

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1. Introduction

The earliest research that can be connected to lithium-ion batteries originated in a graduate thesis written by Harris,^{1,2} demonstrating the possibility of electrodepositing Li metal

^aDepartment of Chemistry, Tyndall National Institute, University College Cork, Cork, Ireland. E-mail: c.odwyer@ucc.ie; Fax: +353 (0)21 4274097; Tel: +353 (0)21 4902732 ^bMicro and Nanoelectronics Centre, Tyndall National Institute, Dyke Parade, Cork, Ireland under controlled non-aqueous conditions. This converged with earlier studies on sodium ion transport in beta alumina³ where ions intercalate, or insert into a crystalline lattice, through porous one dimensional channels in some crystalline structures, or indeed between two dimensional layers in crystalline solids. In 1976, Whittingham at Exxon reported intercalation electrodes arranged into a functioning rechargeable lithium battery.² Following that, in the 1980s Armand introduced the rocking chair concept,⁴ where Li ions can move repeatedly from one side of the battery to the other, *i.e.* diffuse from the anode to



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performance

ence of ordered porosity and structure on reversible Li intercalation and pseudocapacitive behaviour.



Structuring materials for lithium-ion batteries:

advancements in nanomaterial structure,

composition, and defined assembly on cell

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This review outlines the developments in the structure, composition, size, and shape control of many important and emerging Li-ion battery materials on many length scales, and details very recent investigations on how the assembly and programmable order in energy storage materials have not only influenced and dramatically improved the performance of some Li-ion batteries, but offered new routes toward improved power densities. This review also describes and discusses material aspects of hybrid and multiphasic materials including silicon, germanium, a wide range of metal oxides, alloys and crystal structures, carbons and other important materials. Methods including engineered porosity that offer the energy density of Li-ion batteries and the power density of pseudocapacitors are also highlighted.

Recent developments in the analytical methods, electrochemical response, and the structure,

composition, size, shape and defined assembly of active materials for a wide range of Li-ion cathodes

and anodes are compared and assessed with respect to cell performance. Perspectives on the future

development of energy storage materials based on structure as well as chemistry are also outlined.

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development of novel catalyst materials for Li-air battery cathodes.

the cathode during charge and from the cathode to the anode during discharge. Development of materials that could undergo this process numerous times resulted first in commercialization of primary (single use) and subsequent widespread utilization of secondary Li-ion batteries (rechargeable LIBs).

Rechargeable Li-ion batteries are one of the most extensively researched power sources for applications in modern portable electronics, hybrid electrical vehicles and sensor networks, as highlighted by a number of recent review articles.5-8 Newer consumer electronics that are developed require power sources with higher energy density (amount of energy stored per unit mass), higher power density (time rate of energy transfer), longer lifetime (the number of cycles of battery chargedischarge) and improved safety of operation. Early secondary Li-ion batteries suffered greatly from thermal instabilities caused by dendritic depositions of Li from the metallic Li anode through to the cathodes,9 leading to the formation of short circuit connections between the electrodes and in some cases ignition of the battery package when certain electrolytes were used. This problem was overcome by replacing the metallic Li anode with various non-metal compounds,10 capable of storing and reversibly exchanging a large number of Li ions. The reduction of Li plating effects (and associated safety improvement) gave way to widespread introduction of Li-ion batteries into consumer markets.11 Fig. 1 presents a schematic diagram of a secondary Li-ion battery. It consists of the following elements, from left to right in the image (Fig. 1).

1.1 Cathode

The cathode is the positive electrode of the battery, which means it is the source of positive ions (Li^+) and accepts negative ions (e^-) . In currently used batteries, cathodes are most commonly made of (but not limited to) layered or spinel lithiated metal oxides.

In layered cathodes, the composition is denoted by $LiMO_2$, where M corresponds to Co,^{12,13} Ni,¹⁴ Mn¹⁵ or V.^{16,17} $LiCoO_2$ is

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developing three-dimensionally ordered macro-porous cathodes for use in lithium-ion batteries as well as optical spectroscopy techniques for structural monitoring through photonic band-gap changes in 3D porous battery materials.



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Fig. 1 Structure and principle of operation of a Li ion battery.

currently the most popular option, despite the high cost of cobalt, as it is relatively easy to prepare an electrode with a layered structure of extremely high quality. This material and its associated battery construct have also benefited from decades of research, development and real-world applications. Nickel manganese¹⁸ and vanadium¹⁹ are being extensively investigated in order to improve their structural stability, reversibility and cost-effectiveness for some applications. Spinel cathodes (*e.g.* LiMn₂O₄) offer the advantage of a robust cubic oxygen array with 3-dimensional Li ion diffusion, allowing fast insertion/ removal of Li ions during discharge–charge processes.²⁰

1.2 Electrolyte

At high operating potentials (up to 4.5-5 V vs. Li/Li⁺ for some advanced cathode materials) associated with operation of Li-



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Fig. 2 Diagram illustrating the Li ion capacity and electrochemical reduction potentials with respect to Li metal for a range of cathode and anode materials.¹¹

ion batteries, aqueous solutions would electrolyze easily if used as an electrolyte for a Li cell. Thus, aprotic, non-aqueous solvents are used.²¹ Commonly used electrolytes for LIBs include propylene carbonate, dimethyl-carbonate, ethylene carbonate, vinylene carbonate and mixtures of these solvents.²² As liquid electrolytes do not fully prevent formation of dendrites on the surface of the anode, often solid state polymer electrolytes are used. The electrolyte needs to satisfy certain conditions:

- High Li ion conductivity, very low electronic conductivity.
- Wide temperature range of operation.

• The energy gap between the electrolyte's lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) needs to be higher than the difference between energy levels of the cathode and anode; it needs to be thermodynamically stable at the operating voltages.

• It should ideally be environmentally friendly.

In the electrolyte Li salts such as $LiClO_4$, $LiBF_4$, and $LiPF_6$ are dissolved to act as a source of Li^+ ions. The use of vinylene carbonate additives in some carbonate electrolytes, among others, promotes solid electrolyte interphase (SEI) formation at the anode through radical polymerization, which is beneficial for stabilizing the interface during repetitive insertion (or alloying) and removal of lithium ions.²³

1.3 Separator

The separator provides a barrier which prevents short circuiting of the cathode and anode. It should be sufficiently porous to allow the electrolyte to freely connect the two electrodes. Most commonly, separators are made of polytetrafluoroethylene (PTFE) and other inert polymer membranes with defined porosity and ionic conductivity.

1.4 Anode

The anode is the negative electrode of the Li ion battery. In currently used commercial packages, the anode consists of layered graphitic carbon. The storage mechanism is based on the intercalation of Li^+ ions into van der Waals spacings found between the graphitic monolayers. The theoretical specific capacity of graphitic carbon is 372 mA h g⁻¹, based on the following reaction:

$$LiC_6 - e^- \leftrightarrow 6C + Li^+$$

Graphitic carbon electrodes allow for good cycle lifetimes, but suffer from low rate capabilities and irreversible capacity losses caused by electrolyte decomposition at low potentials, and formation of a SEI. SEI is a common name given to a passivating layer formed on the surface of the electrode due to reductive decomposition of the electrolyte.24 It forms at low potentials (typically 0.7 V vs. Li/Li⁺). In the initial cycle, the formation of a SEI layer contributes to the loss of reversible capacity. However, in subsequent cycles, the SEI layer prevents additional decomposition of the electrolyte, improving reversible capacity and ensuring better cycling of the battery. To optimize electrode performance, the SEI layer should be insoluble in the electrolyte and be a good electronic insulator and ionic conductor. Importantly, the SEI layer should be able to remove a thin solvation layer around the Li⁺ ion, to prevent the exfoliation or delamination of the layered active material that could result from co-intercalation of the solvent.25-28

Battery research is driven by the economical need to satisfy consumer demand for higher power and higher energy batteries. Every smartphone user would like to see their phone operate for a prolonged period of time under high demand usage. Global climate change makes the prospect of all-electrical cars a welcome alternative to petrol, gas or diesel-fuelled transport. The "always on, always connected society" with strong demands on wireless sensor networks will require more advanced power solutions than those currently available, in smaller volumes with long term stability for operation in remote locations. So far, many possible replacement materials have been identified for both the anode and cathode, and require even more development for any non-lithium based electrochemical power sources. Moreover, the advent of nanotechnology has facilitated battery architectures which are no longer entirely reliant on traditional bulk/thin film approaches, but with structurally engineered porous, 1, 2 or 3 dimensional designs offering improvements in performance.6,29,30 This review will describe some of the most recent findings in both the structural design and the materials chemistry of next generation battery electrodes.

Choosing materials for Li-ion batteries

As mentioned above, novel materials for Li-ion batteries have been extensively investigated over a number of years. Several



Fig. 3 Calculated lithium insertion voltage *versus* theoretical capacity for several thousand compounds. Reproduced from ref. 35 with permission from the Materials Research Society.

materials have been identified as potential replacements of the cathode and anode in next generation battery anodes (summarised in Fig. 2), and have been in some cases commercialized, demonstrating great potential for currently researched materials. However, before wide-scale adaptation of new materials, a deeper and better understanding of all the factors affecting battery performance (its chemistry, upscaling, packaging and drivetrain) needs to be developed. Many excellent reviews provide details of material performance and fundamental response of materials as lithium-battery electrode materials and the reader is referred to other reviews for selected ranges of materials.^{5,7,8,31,32}

A pioneering method for materials choice and for future development is being developed by Ceder *et al.* at MIT, using what they term the Materials Genome Project.³³ The Materials

Genome Project has a goal of applying knowledge gained from large-scale property computation on all known inorganic compounds for materials research and discovery. While applicable to many functional applications involving materials whose properties would ideally likely be predicted, it has an immediate useful application to Li-ion and emerging alternative battery chemistries. Many tens of thousands of materials have been screened in terms of Li⁺ intercalation voltage or chemical potential, theoretical charge capacity, electrode voltage and other parameters. Fig. 3 shows the voltage calculated using density functional theory as a function of the theoretical capacity for thousands of oxides, phosphates, borates, silicates, and sulfates. The continuing work is also focused on the safety of high voltage materials, various electrolytes and structural effects that are related to cycling behaviour and performance.³⁴ It forms a new and extremely useful approach to Li-ion battery materials design.

In general, next-generation Li-ion battery materials can be divided into sub-categories based on their Li⁺ ion storage mechanism: intercalation electrodes, conversion electrodes and alloying electrodes.

3. Intercalation electrodes

Intercalation electrodes involve materials with a crystalline structure enabling diffusion of Li ions into the interstitial sites of the crystalline lattice. The most common crystalline structures include layered,³⁶ olivine^{37,38} and spinel³⁹ (Fig. 4). Their main appeal lies in their excellent structural stability and long cycle lifetime. Currently used cathodes consist of layered LiCoO₂, LiCo_{1-y}Ni_yO₂ and LiMn₂O₄. These cathode materials have some practical limitations however. LiCoO₂ can only



Fig. 4 (Left) A range of different oxide, sulfide and phosphate crystal structures capable of Li intercalation into various regions of their crystal structure. Reproduced from ref. 54 with permission from Intech Open. (Right) Common intercalation compounds as a function of decreasing calculated chemical potential of oxygen in their charged state. A lower oxygen chemical potential is deemed safer. Reproduced from ref. 35 with permission from the Materials Research Society.

intercalate in the LiCoO₂-Li_{0.5}CoO₂ range, limiting available capacity to about 130 mA h g⁻¹. Cheaper and more environmentally friendly LiCo_{1-y}Ni_yO₂ suffers from strong Li–Ni cation mixing, which affects the structure formation and subsequent ionic transport. LiMn₂O₄ in turn has a limited stability and may undergo phase transition at room temperature.⁴⁰ Further computational investigations showed however that the addition of some nickel, to form Li(Mn_{0.5}Ni_{0.5})O₂, yields an almost ideal cathode material in theory, due to the stability of the closedpacked framework of Mn₄⁺ coordinated to oxygen.⁴¹ However, the rate capability for this material was very poor and the mobility of Li ions within the framework was found to be strongly linked to the distance between the oxygen layers.

For battery safety, particularly at high deintercalation rates or under typical discharge-charge at elevated temperatures, self-catalysed exothermic reactions of the active material with the electrolyte may occur,42 leading to thermal instabilities, thermal runaway and ultimately a failure (and sometimes explosion) of the battery. Recent reports of fires caused by exploding LIBs are an example of a result of instabilities arising from the interaction of the highly charged cathode with the electrolyte, often aided and sometimes facilitated by electrical shorting from Li dendrite formation.43 Cathode materials with inherently active or unstable oxidation states can potentially be reduced by liberating oxygen, which overcomes its kinetic limitations at elevated temperatures caused by heat from surrounding environment or possibly by self-discharge and cell heating. The oxygen can vigorously react and burn the electrolyte. However, there are many materials (cathode materials) that have a large negative chemical potential (difficult to reduce in their charged state) and thus are inherently safe in this regard, LiFePO₄ being cited as possibly the ideal example. Interesting, and widely known, is that the most prevalent battery chemistry employing LiCoO₂ is inherently one of the least safe in its charged state, but does offer good cycling capability. Advancements in the engineering of battery packs have largely removed these issues, but several high profile accidents have reignited the issue of battery safety and raise the question of safer chemistries by choosing safer electrolytes or electrode materials.44

Layered and spinel materials however suffer from low Li ion diffusivity, and therefore can only satisfy limited power demands. In recent years, research has been mainly focused on improving the electrode kinetics.⁴⁵⁻⁴⁷ Nanostructuring active materials offers significant benefits, such as: shortened diffusion lengths, improving electrical and ionic performance/rate by placing conductive additives as a surface coating on active materials, as opposed to a random mixture of powder additives.^{48,49} Some of the various nanostructures formed include, but are not limited to, nanosheets,⁵⁰ nanoparticles,⁵¹ nanowires⁵² and nanotubes.⁵³

4. Conversion materials

A different type of Li storage mechanism is the reversible electrochemical reaction of Li with transition metal oxides.^{55,56} The mechanism of the energy storage is conventionally referred to as the conversion reaction, described as follows:

$$M_a X_b + (bn)Li \leftrightarrow aM + bLi_n X$$

where M = transition metal, X = anion and *n* is the formal oxidation state of X. Conversion reactions have been reported for some oxides, sulfides and fluorides, with different degrees of reversibility. The main focus of researchers working with conversion based electrodes is the improvement of electrode kinetics and reversibility, in particular, formation of nanoparticles of reduced metals that would be very active towards the Li_nX matrix in which they are interspersed. At the moment, however, conversion type electrodes are still under development, and much investigation is required into fundamental characteristics of conversion materials and electrode design.

5. Alloying materials

Reversible electrochemical alloying of metals and semi-metals with Li has been known since 1970s.57 Metals reversibly alloying with Li offer tremendous improvement in specific Li storage capacity. Silicon has a highest known theoretical Li storage capacity, higher even than that of Li (3700 mA h g^{-1}) equal to 4400 mA h $g^{-1.6}$ Other examples of alloying materials include tin and tin oxides,⁵⁸ antimony,⁵⁹ germanium,⁶⁰ and others like phosphorus, magnesium and silver,7 each offering excellent theoretical Li storage capacity. However, these materials suffer greatly from large volumetric expansion and contraction caused by insertion and removal of a large amount of Li⁺ ions, as well as fast charging-discharging rates. Severe mechanical stresses and strains resulting from repeated cycles of volume changes lead to irreversible structural changes, formation of cracks in the active material causing loss of structural and electrical integrity of the electrode, pulverization and irreversible capacity fading. The most common strategies directed at the improvement of electrode performance are focused on the accommodation of volumetric expansion through providing free space around the active material⁵ and creating various composites⁶¹⁻⁶⁴ aimed at protecting the active material against structural degradation or ensuring consistent and stable electrical contact between the active material and external current collector.

The scope of this section is to summarise recent advancements in the field of alloying materials research, with improved characteristics for next generation Li-ion battery anodes.

5.1 Silicon

Silicon has for a long time been investigated as a possible replacement for graphitic carbon in next generation anode materials. In terms of specific capacity, a Li–Si alloy phase can store >4000 mA h g⁻¹, compared to 372 mA h g⁻¹ for graphitic carbon. Silicon is also the second most abundant material in the earth's crust, making it economically viable for mass production of LIBs.⁶⁵ The abundance of the element, combined with the benefits of well-developed industrial infrastructure and exceptionally high theoretical specific capacity, has made Si one of the most promising materials for next generation battery

anodes. However, the large number of Li ions that can be inserted into Si cause extremely large volumetric changes: $\sim V_{\rm f} = 3V_{\rm i}$ where $V_{\rm f}$ and $V_{\rm i}$ denote final and initial volumes of the material. Mechanical failure often follows, leading to irreversible capacity loss and decrease in cycle lifetime, effectively preventing successful application of Si in next generation battery anodes.

Si nanostructures such as NWs and nanoparticles have been designed and fabricated through numerous routes.^{6,68} Additionally, some nanostructures have been specifically engineered in order to accommodate the volume changes occurring in Si, such as core shell nanotubes⁶⁶ and yolk-shell type nanoparticles.⁶⁹ Fig. 5 demonstrates improvements in structural stability of nanostructured Si electrode materials.

Widespread research into formation of Si NWs and their application in electrochemical energy storage allowed better insight into the processes occurring during lithiation, and in particular structural changes caused by reversible alloying of Li with Si. In situ TEM observations indicated preferential anisotropic swelling of $\langle 112 \rangle$ Si NWs in the $\langle 110 \rangle$ direction.⁷⁰ The Li⁺ diffusion study revealed deformation followed by a build-up of tensile stress in the nanowires, resulting in fracture.71 Numerical modelling indicated that Li^+ ions prefer to diffuse along the (110)direction, where surface energy of the planes is preferable for Li⁺ interactions. The electrochemical lithiation of crystalline silicon leads to formation of a core-shell structure, with Li-rich amorphous Li_xSi alloy forming the shell and crystalline Si forming the core. The formation of the interface between the amorphous and crystalline phases is related to the stress induced Li⁺ diffusion retardation, and may lead to the local loss of mechanical integrity due to large stress build-up at the interface.72,73

One-dimensional (1D) nanostructures were first described for use in Li-ion anodes in a seminal paper published in 2008 by Chan *et al.*,⁶⁷ and similar studies published around the same time period^{74,75} where Si NWs were applied as anodes. Chan *et al.* prepared Si NWs directly on a stainless steel current collector, by gold-seeded chemical vapour deposition (CVD). The nature of the synthesis resulted in excellent adhesion of the active material to the substrate and in significant porosity of the electrode. Constraining the volumetric expansion through the design of the electrode morphology (Fig. 5) resulted in significant improvements in electrochemical performance of the Si based electrodes. The Si NW arrays displayed a capacity of >2100 mA h g⁻¹ at a C/20 rate, without large decrease in reversible capacity and change in the morphology of the nanowires.

Despite the promise of these CVD grown Si NWs for LIB applications, typically used gold catalysts have recently been shown to be detrimental to the electrochemical performance (in terms of initial capacity, capacity retention and rate capability) of NW based electrodes. Furthermore, Au is costly, shows poor lithium activity and is much denser than Si which strongly impacts the gravimetric capacity for a given total anode.⁷⁶ To circumvent these issues presented by the Au catalyst, recent approaches have been developed to prepare NWs through different routes, such as high boiling point solvent syntheses using electrochemically active catalyst materials such as Sn^{77,78} or shifting the grown method entirely to a metal assisted chemical etching regime.⁷⁹

Composite Si nanostructures have also been proposed in order to improve the electrochemical performance. By incorporating nanoscale Si inside an elastically deformable conductive host the stress changes that cause mechanical breakdown associated with electrochemical lithiation can be better accommodated, while also providing robust electronic conduction pathways.

A different approach to improving the electrochemical performance of the Si based LIBs is preparation of Si–C composites. Two strategies for preparing Si–C composites have been widely employed. Carbon structures such as nanotubes, nanosheets of graphene or carbon fibres have been used as supports for the nanoscale active material.^{80–83} By providing continuous electrical pathways from the active material to the current collector, the influence of the electrochemically induced agglomeration of the nanoparticles on the electrochemical performance is greatly reduced. Moreover, using a carbon support offers excellent porosity allowing for better penetration of electrolyte throughout the electrode, shortening diffusion lengths, allowing for higher rates of charge–discharge, summarised in Fig. 6.



Fig. 5 (a-c) Schematics of SEI layer formation and stable cycling of double-walled SiO₂@Si nanotubes. Reproduced from ref. 66 with permission from Nature Publishing Group. Schematic changes occurring in (d) Si thin film. (e) Si nanoparticles. (f) Si nanowires. Adapted from ref. 67 with permission from Nature Publishing Group.



Fig. 6 Constant current line-sweeps and cyclic performance for (a) carbon coated structures. Reproduced from ref. 84 with permission from the American Chemical Society. (b) Carbon supported Si nanostructures. Reproduced from ref. 85 with permission from the American Chemical Society.

In contrast to the supported electrodes, carbon coatings are a different strategy for preparing carbon composites with Si.86-89 By applying a thin (few to few tens to at most few tens of nanometres) coating of carbon on the surface of the material, a mechanically stable layer that can provide support to the nanostructures, and thus preserve their mechanical integrity during repeated charge-discharge cycles, can be formed. Additionally, the continuous layer present on the surface of the active alloying material acts as a stable conductor from the electrode to the current collector. An extension of this strategy is the preparation of composites in which nanostructures of alloying materials are embedded in a carbonaceous matrix. Carbon forms a stable SEI layer with the species present in the electrolyte, and has been shown to provide a degree of mechanical support against rapid expansion and contraction during electrochemical cycling in randomly mixed slurries, but also in 3D ordered porous materials with electrochemically active materials embedded within the carbon matrix.90 The problems arising from this approach are mostly related to low ionic conductivity of the carbonaceous matrix and resulting low rate capability of such prepared nanostructures.

Within a vast multitude of structures prepared for Si based anodes, nanotubes seem to offer the best electrochemical performance, due to the mechanisms of Si lithiation, and free space provided for volumetric expansion of the nanostructures. To alleviate the repeated re-formation of SEI layer, an electrochemically inactive SiO_2 layer was used in order to ensure SEI layer stability. The mechanical robustness of SiO_2 provides buffering against stress induced cracking within the nanotubes, while ensuring formation of a stable SEI layer. To date, SiO_2 @Si nanotubes show one of the best electrochemical performances for Si based anodes⁶⁶ (see Fig. 5). The need to commercialize Si based batteries will undoubtedly result in further improvements in the Si based LIB performance. Table 1 presents a comparison between some of the recently prepared Si based materials for LIB anodes.

5.2 Germanium

Germanium can also store Li through similar alloying reactions to those associated with Si. Fully lithiated Li4,4Ge has a high theoretical capacity of 1600 mA h g⁻¹.60 Similarly, large amounts of Li atoms stored in Ge cause it to expand and contract upon cycling, with volume changes reaching 370%.60 One very exciting property of Ge based anodes is the fact that Li diffusivity in Ge is 400 times greater than in Si, indicating that Ge may be an attractive material for high-power rate anodes.^{102,103} Additionally, the electrical conductivity of Ge is about 4 orders of magnitude higher than Si. Initial investigation into thin films of Ge showed that crystalline Ge suffers from large irreversible capacity loss during initial cycles. In contrast, amorphous and nanocrystalline films of Ge show greater capacity retention, with capacities as high as 1700 mA h g⁻¹ reported after over 60 cycles (see Fig. 7a). Shortened diffusion lengths also allowed for much improved kinetics of the Li insertion and removal, permitting charge-discharge rates as high as 1000 C with little capacity loss¹⁰² (Fig. 7).

A variety of nanostructures have been prepared in order to further improve the performance of Ge based electrodes.^{60,104-107} For instance, Au-seeded Ge nanowires prepared by CVD showed high capacities of over 850 mA h g⁻¹ at C/20 rates, and were able to deliver more than 600 mA h g⁻¹ at 2 C rates. Effects arising from incorporation of Au into the nanowires (given the aforementioned issues stated in the last section) during growth however remain a problem.⁷⁶

In another example, Park *et al.*¹⁰⁷ used the Kirkendall effect to prepare Ge nanotubes from core–shell Ge–Sb nanowires. Coating with antimony (Sb) acetate and polyvinyl pyrrolidone was followed by high temperature annealing. As outward

Table 1	Summary of	of the	relative	performance	of	different	Si based	l electrodes
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Composition	Morphology	Initial capacity (C-rate)	Final capacity (# cycles)	Reference
Si	NWs	4277 (C/20)	3500 (20)	67
Si@SiO _x /C	NPs	1600	1100 (60)	91
Si@C	Mesoporous CS NWs	3163 C/5	2751 (80)	84
Si	3D porous	2820 (C/5)	2780 (100)	92
C-Si	Core-shell NWs	700 (C/15)	1600 (47)	93
Si-C	Carbon coated NWs	3344	1326 (40)	94
Si	Nanotubes	3648 (C/5)	2800 (200)	95
Si-graphene	Composite	2158 (C)	1168 (30)	96
Si-CNT	Composite	2300 (C/10)	1400 (50)	85
Si	NWs	4000 (C/10)	1600 (50)	97
Si/C	Nanocomposite	2000 (C/20)	1700 (100)	98
Si	Nanotubes	3200 (C/20)	2800 (50)	99
Cu–Si	Nanocables	1500 (C/3)	1400 (100)	100
B-doped Si	NWs	3354 (C/10)	1500 (250)	101
SiO ₂ @Si	Nanotubes	1780 (C/5)	1600 (2000)	66

diffusion of Ge atoms is much faster than inward diffusion of antimony, void formation begins in places where Ge atoms use to reside. Prolonged thermal treatment allows for the formation of amorphous nanotubular structures of Ge, with a very low concentration of Sb. The unique structure of the nanotubes permitted facile accommodation of mechanical stresses and improved cycle performance, with capacities as high as 900 mA h g⁻¹ after 50 cycles at C/5 and 600 mA h g⁻¹ after 25 cycles at 20 C.

In composite electrode materials, the use of carbon with Ge results in more stable electrodes, which has been evidenced by an improvement in electrochemical properties. The Ge–C composite can also reduce the degree of mechanical failure arising from multiple cycling. One effective strategy is the dispersion of nanosized materials into a carbon matrix, where carbon acts as both a structural buffer and an electro-active material during Li incorporation/extraction. Cui *et al.*¹⁰⁴ prepared Ge nanoparticles encapsulated with carbon, through solid state pyrolysis of PTA-Ge, thermally polymerized from tetraallylgermane (TA–Ge). Initial discharge and charge capacities of 1190 and 923 mA h g^{-1} , and low capacity fading confirmed the effectiveness of the carbon matrix in improving

the electrochemical performance of the Ge nanostructures. Carbon coating is another effective strategy to improve performance. For example, Yoon *et al.* prepared carbon coated Ge composites by high energy ball-milling of commercial Ge powders and poly(vinyl alcohol) (PVA),¹⁰⁸ producing carbon coated composites with good high initial capacities of up to 1600 mA h g⁻¹ and good capacity retention for up to 50 cycles. A variety of other reports was also produced detailing preparation and characteristics of Ge–C composites, including formation of core–shell Ge@C nanoparticles,¹⁰⁹ self-assembled Ge–C nanostructures,¹¹⁰ graphene-supported Ge,¹¹¹ or carbon coated Ge nanowires.¹¹²

Multiple element composites are also being researched for alternative anode materials based on Ge. Ge–Cu₃Ge–C composites¹¹³ were prepared by pyrolysis and high energy mechanical milling, showing improved performance compared to Ge on its own or the Ge–C composite. The improvement in electrochemical performance was attributed to the presence of inactive Cu as well as the carbon matrix. Cu was used also in core–shell nanowire arrays.¹¹⁴ Hierarchical structures of these types of anodes have great advantages for electrochemical performance of the battery, allowing for up to 80% Coulombic



Fig. 7 (a) Cycle life of Ge nanocrystals. (b) Cycle life of thin film Ge at 1000 C charge and 1 C discharge. Reproduced from ref. 102 with permission from The Electrochemical Society.

efficiencies in the initial discharge as well as over 1400 mA g^{-1} after 40 cycles. The excellent properties of such anodes are attributed to unperturbed electrical contact of the current collector with the electrochemically active material, as well as large porosity of the Ge–Cu anodes.

Significant efforts dedicated to improvement of Ge based anodes show that Ge is a promising candidate for next generation LIBs. Further work is however required to fully utilize its potential, in particular to improve mechanical stability of the electrode. Moreover, ensuring formation of a stable SEI layer should contribute to the overall cycling performance of Gebased anodes in appropriate electrolytes.

5.3 Tin and tin oxide

Tin and its oxides have also attracted significant research attention due to their ability to alloy with Li. Their low cost combined with high theoretical capacities, equal to 980 mA h g^{-1} for tin, 864 mA h g^{-1} for tin(π) oxide, and 780 mA h g^{-1} for tin(π) oxide, make these materials very attractive prospects for future generation Li ion batteries. However, their implementation has been hindered by the comparable volumetric expansion and contraction experienced by Sn and other alloying materials. As was the case for Si and Ge, many efforts have been undertaken in order to improve the electrochemical performance of Sn and Sn oxides based batteries.

Research on Sn and Sn oxides for application in battery anodes dates back to two papers published in 1997 by Dahn et al.115 and Idota et al.116 detailing structural changes and electrochemical properties of tin oxide based anodes. Since then, most of the research has focused on determining fundamental properties of the lithiation of tin oxide, with some interesting results, and improvement of cycle life and rate capacity. Investigations into the origin of large irreversible capacity in tin oxide anodes, causes of agglomeration of tin nanostructures upon repeated cycling as well as formation and stability of a SEI layer allowed better insight into the fundamental processes in Sn-based anodes. Relatively few studies focus on the performance of metallic Sn, rather looking at SnO₂. The half-cell insertion reaction, corresponding to lithiation of SnO₂, depends on electrochemical reduction of SnO₂ to metallic Sn. The overall reaction can be written as follows:

$$SnO_2 + 4Li' + 4e^- \rightarrow Sn + 2Li_2O$$
$$Sn + xLi^+ + xe^- \leftrightarrow Li_xSn (0 < x < 4.4)$$

The reduction of SnO₂ to metallic tin is generally considered irreversible, and leads to large capacity loss in the first cycle, when the associated charge for that process is factored into the coulometric response of an alloying system.¹¹⁵ Moreover, the electrode undergoes an electrochemically driven solid state amorphization process. Examination of individual nanowiretype structures, reproduced in Fig. 8, has shown that during lithiation, SnO₂ nanowires elongate by about 60% axially and widen by 35% radially to accommodate the volume changes.¹¹⁷ These changes are associated with a wire with a certain crystal



Fig. 8 In situ TEM observation of the lithiation process of SnO_2 NWs. Reproduced from ref. 117 with permission from the Royal Society of Chemistry.

orientation, and are likely linked to the rate of insertion/alloying at different facets, or possibly from preferential and confined axial electronic transport in tandem with preferential ionic transport to the NW walls.¹¹⁸

These types of informative single-structure measurements serve to demonstrate that low- or confined-dimensional structures undergo anisotropic volume increases, but it has yet to be determined whether these effects are from the isotropy in the measurement and from the innate anisotropy of the structure and its crystallography with respect to Li diffusion and associated alloying processes.

Li insertion into crystalline SnO₂ leads to dense dislocation zones forming at the interface, separating crystalline oxide and amorphous Li–Sn phases. The nanowire morphology allows for accommodation of large degrees of strain and stress, but repeated cycling of the nanostructures may lead to pulverization and loss of mechanical integrity.

In order to improve the electrochemical performance of Sn anodes, similar strategies to those applied in Si and Ge were employed. Both nanostructuring and preparing material composites yielded some interesting results.58,119 Tin oxide nanostructures such as nanoparticles,120 nanowires, and nanotubes all have benefits contributing to better performance of the battery electrode. In one study,¹²¹ heterostructures of indium oxide and tin oxide were prepared by thermal evaporation. Tin oxide nanowires grew with indium oxide adsorbed onto the surface of the nanowire, forming a surrounding shell. This unique concept allowed for better conductivity of SnO2 NWs and high specific capacity, compared to SnO2 and In2O3 NWs on their own. Even though nanostructuring of the electrodes has its benefits, the problem of reduced capacity due to cracking, pulverization and agglomeration of nanostructures remains. In order to further reduce the influence of physical changes on the overall performance of the battery, nanostructured composites are extensively investigated with some very exciting results. For example, core-shell tin oxide-multi walled carbon nanotube (MWCNT) composites were prepared by hydrolysis of SnCl2 in

the presence of HCl.¹²² The excellent electrochemical performance was attributed to nanostructuring resulting in shortening of diffusion lengths for Li ions, as well as the presence of MWCNTs, which greatly improved conductivity of the electrode, capacity retention and Coulombic efficiency, through increased mechanical stability and persistent conduction pathways.

Tin oxide composites with other materials are also of great interest.123-136 The benefit of using materials that are not electrochemically active or do not undergo drastic changes has been shown in numerous studies. Materials such as copper,^{130,133} nickel,¹³⁷ sulphur,¹³¹ cobalt oxide,¹³⁸ or titania were confirmed to benefit the performance of the battery. Copper and nickel are mainly used as supports for electrochemically active tin oxide. Generally, the benefits of the electrochemically inactive electrode support allow for large improvements in capacity retention, due to conserved electrical continuity between the active material and the current collector. However, addition of this "dead weight" material (which does not add to capacity but adds weight to the anode) may reduce the gravimetric capacity of the electrode below the capacities achieved in pristine films, so care needs to be taken to ensure that the gravimetric energy density is not lower than the electrodes composed of solely active materials. The overall capacity of composite batteries will be however limited by the combined performance of both positive (cathode) and negative (anode) electrodes.

At the moment, cathode chemistry can limit the maximum capacity obtainable by a battery and thus, using negative electrode materials with capacities lower than the theoretical limits may be beneficial, in particular in situations where rate capability and cycle life are important. Active–inactive composites may benefit in those situations, as the active coating thickness is usually quite low, similar to the diffusion length of Li ions and so insertion and removal of ions may be extremely fast. Materials such as CoO¹³⁸ form polymer-like structures preventing agglomeration of tin oxide nanoparticles and improving diffusion kinetics of Li ions, improving capacity retention and rate performance (Fig. 9).

In an alternative approach, active-active composites improve the performance of the batteries, without the gravimetric density reduction penalty associated with active-inactive composites. Previously mentioned carbon-tin-tin oxide composites are included in this class of battery architectures. Other materials used in conjunction with tin are titanium oxide and cobalt. Dahn et al.¹³⁹ prepared a library of Sn-Co-C composites, indicating that only a narrow composition range favours amorphous phase formation, beneficial for extended electrochemical cycling. Kim et al.140 developed a method to prepare a nanocomposite of Sn and Ge, with improved capacity retention compared to pristine Sn and Ge. The improvements in capacity retention were attributed to the separation of Ge nanoparticles during lithiation/delithiation cycles and resulting in formation of conduction pathways. The nature of the nanocomposite results however in a substantial degree of surface reactions, such as electrolyte decomposition and Li carbonate formation, resulting in unwanted contributions to irreversible capacity and internal resistance, among other effects. In cases where large surface area nanostructures are used, it is particularly important to understand the reactions taking place at the SEI. It has also been suggested that tin, formed by the reduction of tin oxide during electrochemical reactions, may contribute to large capacity fading, not due to agglomeration of nanoparticles, but due to Sn-catalyzed electrolyte decomposition.141 In particular, this phenomenon is favoured at high current densities, where enough thermal energy is provided to accelerate diffusion of Sn, driven by the desire to reduce interfacial energy. Fig. 10 shows a schematic diagram of the self-catalyzed agglomeration of Sn nanoparticles.



Fig. 9 (a-d) SEM images of CoO-Sn; (e) cycle performance of the CO-Sn composite. (f) Rate performance of the CoO composite. Reproduced from ref. 138 with permission from the Royal Society of Chemistry.



Fig. 10 Schematic diagram detailing formation and aggregation of Sn nanoparticles. Reproduced from ref. 60 with permission from the American Chemical Society.

Recently, Sony has commercialised its Nexelion¹⁵⁷ range of Li-ion cells containing anodes consisting of Sn–Co–C. Such alloys have shown excellent cycling abilities attributed to the active–inactive relationship between Sn and Co.^{124,126} Other alloys including the active–inactive system are Sn–Ni–C and Sn– Cu. The Nexelion device demonstrates improved capacity and cycling performance compared to traditional carbon based batteries. In a study carried out by the Army Research Laboratory,¹⁵⁸ Nexelion batteries showed good performance at elevated temperatures and stability at high discharge rates. Although, as the study notes, cycle-to-cycle capacity retention of the Nexelion is slightly worse than the standard 14 430 cell, its increased initial capacity allows it to retain higher reversible capacity after 220 cycles. The commercial utilisation of Sn has demonstrated its purposeful character as a battery anode material in a cost effective and efficient manner. Table 2 details the electrochemical performance of a variety of recently prepared SnO₂ nanostructures which further highlights the promise of Sn and Sn composite based materials as low cost, high performance anode materials.

6. Role of electrode structures on electrochemical performance

The previous section of this review dealt mainly with material chemistry considerations for next generation battery electrodes, their response to lithiation and relation to performance. One additional factor that needs to be considered while designing new electrodes is the architecture or arrangement of the active material. The majority of currently available commercial Li ion battery electrodes are formed as thin films on the order of hundreds of microns thick. These films often consist of an active-material powder, polymer-based binders and additives aimed at increasing electric conductivity of the electrode. These additives have a negative effect on the gravimetric energy density, and as such are undesirable, although necessary in current cells. The geometric considerations of the electrode design are important in the light of inherent limitations of the charge transport characteristics of the electrode, and both concentration and activation polarizations. For instance, in LiFePO₄ and graphite, the Li ion conductivities are of an order of 10^{-10} cm² s⁻¹, compared to 10^{-6} cm² s⁻¹ in commonly used electrolytes.^{21,159} Li ions from the surface of the active material diffuse inwards, filling the vacancies in the active material's microstructure and creating bottlenecks that impede additional ion transport. The structure of the electrodes, their thickness

		To tata 1 a constru		
Composition	Morphology	Initial capacity	Final capacity	Ref.
SnO ₂ -In ₂ O ₃	NWs	2000 (C/5)	780 (10)	121
SnO ₂ -SWCNT	Composite	1399	1000 (100)	142
SnO ₂ -MWCNT	Composite	1500 (C/10)	404 (20)	143
Sn-Co-C	Composite	451 (C/8)	486 (40)	126
Sn-C	Composite	600 (C/8)	311 (200)	144
Sn-Co	Composite	1200 (C/2)	845 (50)	138
SnO ₂ -C	GNS-NP composite	1800 (C/15)	570 (30)	145
Sn-C	Composite	806 (C/10)	737 (200)	146
Sn-Au	Composite	1200 (C/10)	600 (150)	147
SnO ₂ -C	CNT composite	1466 (C/5)	402 (100)	122
SnO ₂	Nanocrystal	2156 (C/10)	550 (20)	148
Sn-SnO ₂	NWs	2400 (C/8)	845 (100 (ref. 149))	149
SnO ₂ -C	NPs	1200 (C/2)	492 (100)	150
SnO ₂	Mesoporous	960 (C/6)	600 (100)	151
Sn-C	Nano Sn-hard	580	300 (30)	152
	carbon			
SnO ₂	Mesoporous-NW	1400 (C/5)	675 (50)	153
SnO ₂	Nanosheets	1860 (C/10)	593 (20)	154
Sn-C	3D porous	1425 (C/20)	638 (315)	155
Sn-C	RGO-Sn	1572 (C/8)	710 (50)	156
SnO ₂ –C	Graphene composite	1100 (C/8)	872 (200)	62

Table 2 Summary of the performances of different Sn and SnO₂ based electrodes. The C rate and the cycle numbers are indicated in brackets

220 cycles. The commercial utilisation of Sn has det

and the length of diffusion pathways obstruct ionic mobility and limit the batteries to slower rates than could otherwise be possible.

For these reasons, 3-dimensional, porous electrode architectures have attracted a lot of attention, particularly because battery size and mass are expected to be reduced in next generation power systems, without a reduction in energy density in principle. One primary driver for power source improvement and also miniaturization is Moore's law, which empirically links the increase in the density of transistor elements on a microchip (or the reduction in the feature size for these transistors) with computational power or operations per second, which has incessantly increased since its inception. The performance of batteries in portable electronics, unfortunately has an annual improvement 'curve' characterized by just a 10% increase in energy density.

One analogy between electronic computation speed and improved energy storage and supply materials in battery power sources is the mobility of the charge carriers: electrons and holes for electronics; electrons and ions for batteries. The classical diffusion relation $L^2 \propto D\tau$ shows that a reduction in length scale (L) is beneficial when considering diffusion lengths of Li (or other cations) and the associated diffusion constant (D) into (at least) the pristine active material during discharge (rate dependent). However, battery chemistries during discharge are complex, even for a very well understood bulk analog of useful or promising materials; performance improvements can be significant, however, when many factors are taken into account. Inherent transport kinetics unique to certain crystal structures are often predefined and affected by the crystal structure, orientation and chemical potential; size reduction does not automatically improve performance or rate capability. Shorter transport distances (faster times to cation insertion) and higher surface-to-volume ratios that improve redox accessibility and time for ion and electron transport can be achieved when the discharge chemistry and phase formation are well understood. By providing pathways for lithium insertion, phase formation, shorter diffusion lengths in 3D can alleviate rate limitations or improve cyclability for 'gentler' depths of discharge in many systems. Once at the interface of an active particle, Li ions enter from the outside inward, filling the atomic-scale vacancies in the active material's exterior microstructure and therefore creating diffusion bottlenecks that impede additional ion transport. Acting in concert, the dense nature of electrode composites, electrode thicknesses of ~100s of mm, and micrometer-scale diffusion path lengths in active electrode particles obstruct ion mobility and limit lithium-ion batteries to slower discharging and recharging rates than are otherwise possible. These elements also add significant 'dead weight' to all current commercial batteries and would make it extremely difficult to assemble as an ordered smooth layered battery. This design, as will be discussed further on, also allows faster charging and discharging rates, and the possibility of strongly asymmetric charge-discharge cycles optimizing power delivery and shortening charging times. Such changes may first take place in the use of small devices, where the total amount of energy stored is small. Only 360 W is required to charge a 1 Wh

cell phone battery in 10 s (at a 360 C charging rate, where the Crate is the inverse of time in hours required to fully charge or discharge an electrode or a battery). Even at the highest charge rate tested thus far for these materials (50 C), corresponding to a time of 72 s (as opposed to 3.5 h based on the mass of active material in its bulk form) to fully discharge the capacity, the material achieves about 80% of its theoretical capacity.

Porous electrodes offer numerous important benefits that are listed below: $^{\mathbf{160}}$

• Pores provide good access of the low surface-tension electrolyte to the electrode surface ordinarily taken up with polymer binders and carbon additives that are no longer required.

• Large surface area of the porous electrode facilitates charge transfer across the electrode/electrolyte interface, reducing the impact of the activation polarization.

• Ionic diffusion path-lengths are reduced due to lower wall thickness less than the limiting solid state diffusion length of lithium for discharging and lower overpotential charging.

• The active material is used more efficiently due to better electrolyte penetration and reduced wall thickness.

• Continuous electron pathways are provided from the active material to the external load.

• The volumetric energy density is comparable with packed particle electrodes.

• In some cases no binders or conductive additives are required, reducing dead weight (better gravimetric energy density).

• Void spaces separating particles can accommodate volumetric changes of the active material.

• Porous composites can incorporate a secondary conductive phase to improve high rate performance of active phases with low intrinsic conductivity.

Depending on the electrode preparation method, porous electrodes can be divided into those that are hard-templated or soft-templated. The size of the pores allows categorization of the porous electrodes as follows: microporous (pore size <2 nm), mesoporous (pore size 2–50 nm) and macroporous (pore size >50 nm).

Soft templating usually involves surfactants as structure directing agents. The pore architecture can be controlled by the choice of surfactants, solvents and synthesis conditions. Evaporation induced self-assembly (EISA) is particularly useful for formation of thin films with precisely controlled porosity.¹⁶¹ It can be however difficult to obtain high crystallinity of the walls of the solid, if the temperature of the crystallization of the inorganic phase is higher than the temperature at which the surfactant block copolymer is removed. In this situation, hard templating approaches are much more successful. Templates such as aluminium anodic oxide (AAO) membranes, preformed porous solids, and assemblies of colloidal particles are used.

6.1 AAO templated nanomaterials

Fig. 11 presents a schematic of formation of porous materials using a AAO template, with isolated pores. In this case, solid products form inside the template, replicating the shape of the void space. Usually, structures such as 1D nanotubes and



Fig. 11 AAO templating mechanism. Reproduced from ref. 164 with permission from the American Chemical Society.

nanowires are formed. AAO templates are commonly used, due to ease of the preparation of the template, as well as uniform pore size.¹⁶² AAO membranes can also be used in conjunction with soft templating materials to prepare solid structures with hierarchical porosity.¹⁶³ A variety of inorganic electrode materials can be prepared using this method, including metals, metal oxides and various composites.

6.2 Nanocasting of nanoscale battery materials

Nanocasting is a name given to the transformation of a porous solid into hollow replicas. In the nanocasting process, porous solids are infiltrated with the precursor of the target electrode material (see Fig. 12). After thermal treatment, the template is removed. The product is an inverted replica structure of the original hard template. The molds with bicontinuous pore structures produce mesoporous replicas, whereas templates with cylindrical mesopores in hexagonal arrangement produce nanowire arrays, which are interconnected only if the template contains secondary pores between the main cylindrical pores.

The most commonly used hard templates are mesoporous silica materials. To remove these template materials, simple wet etches can be carried out, either through extraction with HF, hot NaOH or KOH solutions. Mesoporous electrodes with numerous compositions have been synthesized by hard templating, including MnO_2 ,^{166,167} Cr₂O₃,¹⁶⁸ Co₃O₄,¹⁶⁹ SnO₂ (ref. 170)

and NiO.¹⁷¹ In particular, SnO₂ nanocasting allows the formation of mesoporous solids with a higher degree of crystallinity and more order compared to soft templating, due to protection from excessive grain growth by sintering present in soft-templated materials.¹⁶⁰

6.3 Colloidal crystal templating

Colloidal crystal templating allows for the formation of porous electrodes with an excellent degree of control over the pore size and the template solid structure. Facile templating methods are compatible with a variety of precursors and allow the formation of inverted opals (IO) of many materials. The general procedure for IO preparation is demonstrated in Fig. 13, where a hard template is infiltrated by an appropriate precursor, and then removed either chemically or thermally.



Fig. 13 Schematic diagram detailing preparation of an inverted opal electrode. Reproduced from ref. 172 with permission from the Royal Society of Chemistry. Through various mechanisms, the arrangement of spheres dictates the periodic porosity of the resulting inverted opal structure.



Fig. 12 Nanocasting of mesoporous electrode materials. (a) Nanocasting process in mesoporous silica. (b) TEM image of mesoporous TiO₂. Reproduced from ref. 165 with permission from the German Chemical Society. (c) Nanocasting process in mesoporous silica SBA-15. Reproduced from ref. 84 with permission from the American Chemical Society. (d) TEM image of mesoporous Si–C nanowire formed from the SBA-15 template.

The template preparation mechanism generally involves selfassembly of template spheres, usually a hard polymer like polystyrene or poly(methyl methacrylate),¹⁷³ or silica, on the surface of the substrate. This makes it possible to form inverted opal structures of a variety of metals and metal oxides^{160,172,174,175} and metal fluorides.¹⁷⁶ Typically, inverted opals have wall thicknesses in the range of 10s to 100s of nanometres, and have been prepared and characterized in multiple compositions, for Li ion anodes, cathodes and solid state electrolyte materials.

IOs generally exhibit higher power densities than bulk materials, due to excellent electrolyte penetration. Although they may not be the best choice for electrodes composed of materials which undergo large volumetric expansion upon lithiation (*e.g.* alloying materials), using a bicontinuous approach allows for formation of IO electrodes from alloying materials as well. Excellent control over the morphology of the IOs and an extensive range of compositions make IO structures very exciting in other areas of research, ranging from catalysis,¹⁷⁷ gas sensing, to optics and filtration.

The following section will detail the various implementations of IO structures as active materials for LIB anodes and cathodes.

7. Inverted opal structures for lithium ion battery applications

7.1 Inverted opal cathode

Vanadium oxide was the first material to be electrochemically characterized as a cathode material in an inverted opal arrangement.¹⁷⁸ In this study, colloidal crystals consisting of polystyrene spheres were deposited on an ITO glass current collector and infiltrated with a diluted vanadyl alkoxide precursor. Subsequently, the precursor was transformed into a solid V₂O₅ gel network (see Fig. 14).

Chemical removal of the PS sphere template results in the formation of inverted opal structures of the V_2O_5 ambigel. At low discharge rates, the ambigel electrodes exhibit a reversible behaviour without significant loss of capacity. This study also demonstrated excellent rate performance of IO based electrodes,

indicating that the hierarchical structure might reduce polarization *via* improved mass transport. Electrochromic properties of an IO prepared from V_2O_5 have also been demonstrated,¹⁷⁹ showing improvements such as faster switching speed and better coloration contrast, when compared to bulk films.

In a different study, $LiCOO_2$ was formed in an IO structure through a nanocasting route. Mixed precursors of Li and Co salts precipitate as oxalates within colloidal crystal template voids.¹⁸⁰ At a precursor ratio of 1 : 1, it is possible to form $LiCOO_2$, however, it is difficult to preserve the IO structure due to the high temperatures required for the formation of the $LiCOO_2$ phase. None of the $LiCOO_2$ powders formed, even with addition of PEG as a chelating agent, preserving the IO structure. However, the high interconnectivity and large porosity of the sample allow sustaining high rate cycling. At 700 mA g⁻¹, the mesoporous structure of $LiCOO_2$ is able to sustain a capacity of 40 mA g⁻¹, while the corresponding bulk film fails to charge due to high polarization.

Another binary oxide formed as an IO structure (LiNiO₂) was prepared through a salt precipitate procedure.¹⁸¹ Stoichiometric LiNiO₂ has a layered structure in which Li⁺ ions occupy octahedral sites in alternate layers of cubic close packed (ccp) oxide ions. At high temperatures, LiNiO₂ readily decomposes to $Li_{1-x}Ni_{1+x}O_2$ due to vapour pressure differences between Li salts and formation of Ni²⁺. Adding excess Li salt and introducing higher oxygen gas partial pressure to suppress reduction of Ni atoms allows formation of IO structures.

 $LiMn_2O_4$ spinels were fabricated using precursors that solidify before destruction of the colloidal crystal template during annealing.¹⁸² Gradually increasing the temperature, however, during template removal, allowed for transformation of amorphous Li-rich sites within the electrode to the spinel phase with Li ions in tetrahedral and octahedral sites. $LiMn_2O_4$ showed a remarkable capacity retention, with no more than 7% capacity loss after 10 000 full cycles at 9 C (full discharge in ~7 minutes) (see Fig. 15), compared to more than 80% reduction in the charge capacity for bulk $LiMn_2O_4$.

The excellent electrochemical performance of IO electrodes can be ascribed to high crystallinity, ensuring stability during



Fig. 14 (a-d) Schematic diagram detailing formation of V₂O₅ IO cathodes. (e) Rate performance of the V₂O₅ IO cathodes. Reproduced from ref. 178 with permission from the Royal Society of Chemistry.



Fig. 15 Cycling behaviour of solid and porous $LiMn_2O_4$ electrodes. Reproduced from ref. 182 with permission from the Royal Society of Chemistry.

cycling, high degree of porosity, shortening diffusion lengths and a reduction of polarization.

Lithium iron(II) phosphate is an alternative cathode material that has been extensively researched since the original paper on the material application in battery electrodes in 1997.¹⁸³ Iron represented a cheaper alternative to expensive cobalt and nickel materials. However it suffers from low ionic and electronic conductivity, making high power applications difficult to realize. The IO structure should improve the ionic conductivity by providing nanoscopic walls with shortened diffusion lengths and opened pore networks that facilitate electrolyte penetration. Lu *et al.*¹⁸⁴ prepared LiFePO₄ IOs by mixing Li, P and Fe precursors in stoichiometric ratios. Subsequent calcination under nitrogen resulted in the formation of IOs with residual carbon interspersed in the LiFePO₄. The carbon content contributed to the conductivity of the IO and allowed for high charge rates, resulting in an initial capacity of 100 mA h g⁻¹ at 5.9 C.

Recently, Doherty et al. described the preparation of LiFePO₄ IOs based on PMMA colloidal templates, with sphere sizes varying from 100-270 nm.185 The templates were not filled completely, which improved the electrolyte penetration and ionic and electronic charge transfer. Sintering at 800 °C improved charge transfer resistance in the electrodes and allowed for charge rates of 10 C with capacity retention close to 100 mA h g^{-1} after 50 cycles. The template sphere size was also shown to have an influence on the electrochemical performance of the IO electrodes, as larger spheres created a continuous macropore network, ensuring facile flow of the electrolyte to all of the parts of the electrode. Residual amorphous carbon present after calcination in N2 also enhanced electronic conductivity of the olivine material, although a balance is necessary, as high weight percentage of C may create a Li diffusion barrier and hinder high rate performance.

8. Inverted opal anodes

8.1 Carbonaceous inverted opal anodes

Graphitic carbon is currently used in commercial LIBs as an anode electrode. It offers excellent stability and relatively long cycle life (1000s of cycles). However, its performance at high

discharge rates is hindered by low Li ionic conductivity in carbon. The IO structure offers a possibility to improve the performance of carbon based electrodes, through facilitating easier electrolyte penetration and shortening Li ion diffusion lengths in the active material matrix. The first C-based IOs were prepared in 1998 by Zakhidov et al.,186 via a vapour deposition technique, forming diamond, glassy carbon and graphite inverted opals. Solution based processes for carbon IO formation were then reported, using sucrose¹⁸⁶ and phenylic resin¹⁸⁷ as carbon precursors. In 2005, two separate articles investigating the electrochemical performance of carbon based inverted opal electrodes were published. In one approach 188 PMMA templates were infiltrated with a resorcinol-formaldehyde (RF) sol-gel precursor. This allowed the formation of IO monoliths with mesoporous walls and a surface area of 326 m² g^{-1} . Large surface area is associated with randomly distributed micropores between the graphene nanosheets in hard carbon solid walls.

The monoliths were found to be electronically and ionically conductive. Good conductivity, excellent electrolyte penetration related to the porosity of the IO and shortened diffusion path lengths allowed carbon IOs to experience much less polarization at current rates as high as C/2 (Fig. 16).

In another study, carbon IOs were prepared by CVD of benzene using silica IOs as templates.¹⁸⁹ The resultant 10–20 nm coating of graphite on silica was electronically and ionically conductive and was suited as an anode active material. This material exhibited specific capacities as high as 260 mA h g⁻¹ at current rates of 1000 mA g⁻¹ (~2.7 C), with good cycling stability (90% capacity retention over 60 cycles).

More recently, particulate inverse opal structures with mesoporous walls were prepared *via* solution casting of PS spheres with a phloroglucinol and formaldehyde mixture containing a F127 block copolymer.¹⁹⁰ Incorporating soft templating methods into the IO formation procedure resulted in increased surface area (from 109 m² g⁻¹ to 466 m² g⁻¹). A large irreversible capacity was attributed to formation of a SEI layer on the electrode and inherent properties of hard carbon. The mesoporous carbon was however capable of sustaining charge rates as high as 300 mA g⁻¹ with a reversible capacity of over 300 mA h g⁻¹.

An interesting means of increasing the capacity of carbon based IOs is to introduce a secondary active material, usually in the form of nanoparticles embedded in the conductive matrix of carbon IOs. Materials such as SnO2 (ref. 90 and 189), Si¹⁹¹ or TiO_2 (ref. 192) have been incorporated into the carbon based inverted opals, with significant influence on the electrochemical performance.193 One of the most recent studies demonstrated an IO electrode concept with SnO2 NPs entrapped in macroporous carbon IO prepared by infiltration of PMMA colloids by tannic acid-Sn4+ complexes.90 Optimization of infiltration and calcination parameters resulted in nanometre scale walls and improvement in the rate performance of the electrodes. They were able to sustain current rates in the range of 1–10 A g^{-1} (~3–30 C) without any significant capacity loss. High porosity (including hierarchical length scale of multiple porosities) in the electrode resulted in low volumetric energy density of prepared electrodes, confirming the need for further



Fig. 16 SEM image of carbon inverted opals. Carbon inverted opals experience much less polarization than bulk carbon of the same composition. Adapted from ref. 188 with permission from Wiley-VCH.

improvements in the electrode design. With respect to inverse opals, three-dimensionally interconnected macropores facilitate the rapid flux of liquid electrolyte solutions, such that 100 $m^2 g^{-1}$ of electrode interfaces are simultaneously accessible to lithium or other mobile cationic charges. This degree of macropore interconnectivity is intentionally tailored into PhCs from self-assembled close-packed templates. For example, the ionic conductivity of a 1 M LiPF₆ liquid electrolyte solution is only impeded by a factor of two when ion transport occurs through the interconnected macropores of monolithic carbon inverse opals (electrode thicknesses: 300 µm to 3 mm).

8.2 Three-dimensionally structured alloying anodes

The first reports of alloying electrodes in the IO form appeared in 2004.¹⁹⁴ PMMA colloidal crystal templates were infiltrated with SnCl₂ dissolved in DI water and 30 wt% H₂O₂. IOs of SnO₂ were formed after thermal removal of the PMMA template. The morphology of the walls of IOs was influenced by the calcination temperature, becoming more granular and interrupted by grain boundaries with the increase in the calcination temperature.¹⁷⁵ Galvanostatic cycling of the IOs resulted in significant morphological changes in the electrodes. The wall thickness increased significantly on the alloying of SnO₂ with Li, with nodules appearing on the previously smooth structure (see Fig. 17).

Repeated cycling caused an increase of the wall thickness, and finally loss of the IO morphology. The authors concluded that the large volumetric expansion of the IO SnO₂ electrodes made them impractical for applications in LIBs. Additionally, the granular structure of the SnO2 walls caused very high polarization, caused by high resistance of the granular walls of the IO. Different approaches were used to alleviate the drawbacks caused by the properties of SnO₂. Using a carbon-SnO₂ composite was one of the strategies employed.189,195 A stable capacity of 300 mA h g⁻¹ could be delivered by the carbon–SnO₂ composite at 100 mA g⁻¹. The improved cyclability was attributed to the confinement effect provided by the mesoporous carbon framework, which served as a structural buffer for volume variation of Sn nanoparticles during repeated cycling. Stability of the SEI layer also contributed to the good cyclability of the IOs.



Fig. 17 SEM images showing morphologies of SnO_2 IOs at different stages of charging. Reproduced from ref. 194 with permission from the Royal Society of Chemistry.

In another approach, a Ni support was used to improve the stability of the SnO_2 IO based electrode.¹⁹⁶ In this study, a colloidal crystal template was infiltrated by electroplating. A mixture of $SnCl_2$ and $NiCl_2$ was deposited from an aqueous solution through electroplating and tested electrochemically. Repeated cycling caused delamination of the IO electrode from the current collector, possibly due to epitaxial mismatch of the Ni–Sn alloy and the Cu current collector. During cycling, the electrode underwent rapid morphological changes and as a result, capacity retention was poor. After 100 cycles, the reversible capacity sustained by the electrode was only about 95 mA h g⁻¹.

Recently,¹⁹⁷ fluorinated tin oxide (FTO) and antimonated tin oxide (ATO) IOs showed significant improvements in electrochemical performance compared to pure SnO₂ IOs, in both capacity and cycling stability (see Fig. 18). The improved performance of the FTO and ATO electrodes was attributed to improved integrity of the nanoporous structure, allowing for better tolerance of large volume changes caused by repeated cycling of the electrode. Good electrochemical performance of highly conductive transparent oxides may enable their applications in solar cells, electrochromic devices or sensor applications.



Fig. 18 (a) CV for hollow FTO. (b) CV for porous FTO. (c) Initial charge and discharge curves for porous FTO. (d) Cyclic performance for porous FTO. Reproduced from ref. 197 with permission from the Royal Society of Chemistry.

Silicon is another material that has been investigated electrochemically and structurally in IO architectures. Esmanski et al.¹⁹⁸ prepared a variety of Si based IO films: amorphous hydrogenated Si IOs (prepared through CVD), nanocrystalline Si-IOs, carbon coated nanocrystalline Si-IOs and carbon IOs with amorphous Si coating. Amorphous hydrogenated Si IOs demonstrated a good initial discharge capacity (2500 mA h g^{-1}). The cycling stability of the IO electrodes was also satisfactory, with over 70% of the discharge capacity retained after 145 cycles. The sphere size was also shown to have an influence on the performance of the IOs, as the electrodes prepared from templates with lower diameter spheres performed poorly, due to blockage of the pore openings by the swelling electrode material. The rate performance of the IO was limited by the amorphous structure of the IO walls. In order to increase conductivity, amorphous IOs were annealed at 800 °C in an inert atmosphere resulting in the formation of nanocrystalline Si-IO. The crystalline structure of the IO walls resulted in improved Li mobility in the electrode material and better rate performance. Capacity retention however was extremely poor, reaching negligible values by the 15th cycle at best. A similar electrochemical behaviour was observed for carbon coated nanocrystalline Si IOs.

In the same study, a different approach was also presented. Carbon IOs were coated with a thin layer of amorphous Si *via* CVD. The initial capacity of the IOs was around 2000 mA h g⁻¹, with the first cycle coulombic efficiency reaching around 80%, increasing to 98–99% after 5th cycle. The rate performance of the IO was poor, compared to amorphous Si samples, with the

capacities reaching negligible levels at 10 C rates. The carbon support allowed for better mechanical and structural stability of the IOs, resulting in good capacity retentions of over 80% after 145 cycles. Esmanski's findings agreed well with results published by Kim *et al.*,⁹² who prepared 3D porous Si particles through deposition of sol–gel mixtures of Si and silica particles and subsequent HF etching. The 3D particles demonstrated excellent capacity retention and rate capability, delivering 2668 mA h g⁻¹ after 100 cycles at 1 C rate.

In a more recent study, nanoscale Ni metal scaffold supported bicontinuous 3D IO based batteries were prepared by Paul Braun's group.¹⁹⁹ The formation mechanism for these electrodes is shown in Fig. 19.

Initially, nickel was electrodeposited in a PS template. Following thermal template removal, the Ni IO was electropolished and a thin film of Si was deposited on the surface of the Ni support through CVD. The self-supported Si anodes showed excellent electrochemical performance, delivering a stable capacity of 2660 mA h g⁻¹ while conserving over 48% of their slow rate capacity when charged at 9.5 C.

The same bicontinuous approach was also successfully employed in an operational battery,²⁰⁰ where MnO_2 cathodes were prepared by electrodeposition of $MnSO_4$ on an electropolished Ni metal current collector. Superior rate performance of the bicontinuous films was attributed mainly to excellent electrolyte penetration, reduced polarization by providing a low resistivity current collector throughout the electrode and shortened diffusion lengths. Such prepared electrodes were able to deliver capacities of over 75 mA h g⁻¹ at an exceptionally



Fig. 19 (a) Loss of electrical contact during cycling. (b) Good electrical contact between an Si film and Ni substrate. (c) Bicontinuous bulk anode consisting of a silicon thin film on a 3D porous Ni scaffold. (d) Fabrication procedure for the bicontinuous electrode. Reproduced from ref. 200 with permission from Nature Publishing Group.

high rate of 1114 C, which corresponds to full discharge in less than 4 seconds (see Fig. 20).

The most recent report²⁰¹ concerning 3D battery architectures describes a high power microbattery capable of delivering power densities as high as 7.4 mW cm⁻² μ m⁻¹ (see Fig. 21). In this study, polystyrene spheres were deposited over gold electrodes etched on glass substrates. Subsequently, a nickel metal support was electrodeposited over the gold electrodes to form a stable current collector. A Ni–Sn alloy and MnOOH were then electrodeposited on the current collector, before submersion of the microbattery in LiNO₃ and LiOH, to form a lithiated cathode. Such microbattery design allowed the authors to achieve over 2000× the power and twice the energy density observed in the best microbattery designs presented thus far.



Fig. 20 Ultrafast discharge of the lithiated MnO₂ cathode. Reproduced from ref. 200 with permission from Nature Publishing Group.

The energy densities demonstrated of up to 15 μ Wh cm⁻² μ m⁻¹ and the power densities of up to 7.4 mW cm⁻² μ m⁻¹ are comparable with the best supercapacitors. The improvements in power and energy density were attributed to shortened ionic diffusion lengths and reduced resistivity of the electrode. Successful demonstration of a high power microbattery allows compact integration of a full battery package for microelectronics applications. The versatility of this approach also permits development of different types of electrode chemistry for specific applications.

Table 3 summarizes some of the developments in IO Li-ion battery electrode research.

9. Pseudocapacitors that offer good power and energy densities

Capacitive charge storage has some particular advantages compared to non-faradaic intercalation batteries. Supercapacitors can be charged within seconds, cycled hundreds of thousands of times, are stable and ideal for delivering high power, which for some uses lead preferably to a higher energy density.²¹⁰ Several options exist for charge storage at the electrode–electrolyte interface, which are sensitively dependent on structure, composition, chemical potential, redox potential and many other factors. In secondary or rechargeable batteries, cations intercalate into interlayer gaps (van der Waals gaps) of layered or tunnel materials²¹¹ or form alloys with phases of other materials. The specific type of materials that permit intercalation, however, can offer under some conditions faradaic and non-faradaic processes, thereby adding energy and power density benefits of both systems.

Cations can electrochemically adsorb onto the surface of a material through charge-transfer processes facilitating



Fig. 21 (a) Schematic diagram of the microbattery fabrication procedure. (b) Microbattery design. (c) SEM cross-section of the microbattery. (d) Top-down SEM image of the microbattery interdigitated electrodes. (e) Constant current line sweeps at different rates. (f) Rate performance of the microbatteries. Adapted from ref. 201 with permission from Nature Publishing Group.

non-intercalation based charge storage, similar to electrochemical double layer capacitors to some extent. This can in some cases remove the limitation of long diffusion times for ions through the van der Waals gaps, and is energetically easier. Such pseudocapacitance is observed when this form of insertion is capacitive, *i.e.* the electrochemical intercalation processes stem from cations that are faradaically stored and changes in the materials' structure do not occur.²¹² While there

 Table 3
 Summary of the performance of various types of IO based electrodes

Composition	Morphology	Initial capacity (C-rate)	Final capacity (# of cycles)	Ref.
V ₂ O ₅	Ю	_	_	202
LiNiO ₂	Ю	_	_	
SnO ₂	Ю	_	_	194
С	IO	299 (15.2 mA g^{-1})	_	188
Sn-C	Sn@C IO	$348 (15.2 \text{ mA g}^{-1})$	_	
С	Graphitic C IO	326 (C/10)	320 (60)	189
Sn-C	Sn@C	415 (C/10)	375 (60)	
TiO ₂ –C	TiO ₂ @C	$158 (50 \ \mu A \ cm^{-2})$	40 (15)	203
Li ₄ Ti ₅ O ₁₂	IO	$152 (6.3 \mu A cm^{-2})$	145 (70)	204
$Li_4Ti_5O_{12}$	IO	173 (C/10)	120 (100)	205
FePO ₄	IO	137 (C/10)	110 (50)	206
LiMn ₂ O ₄ -Li _{1.5} Al _{0.5} Ti _{1.5} (PO ₄) ₃	IO composite	64 (-)	_	207
LiMn ₂ O ₄	IO	_	_	208
Sn-C	Sn@C	$1500 (100 \text{ mA g}^{-1})$	96 (100)	195
Si-C	Si@C	3180 (-)	_	191
LiFePO ₄	IO	115 (5 C)	120 (50)	185
Si	a-Si:h IO	2500 (C/10)	1750 (145)	198
	nc-Si IO	3000 (C/10)	0 (15)	
Si-C	nc-Si–C IO	2400 (C/10)	0 (12)	
	a-Si-C IO	2406 (C/10)	2133 (145)	
Ni–Sn	Ni–Sn composite	$315 (50 \text{ mA g}^{-1})$	$\sim 100(100)$	196
LiMn ₂ O ₄	Ю	_	_	182
MnO ₂ @ Ni	Thin film/IO bicontinuous	74 (1114 C)	—	200
FeF ₃	IO	540 (50 mA g^{-1})	190 (30)	176
Si @Ni	Bicontinuous IO	3568 (C/20)	2660 (100)	199
SnO ₂ –C	SnO ₂ @C	$1659 (0.5 \text{ A g}^{-1})$	715 (500)	90
TiO ₂	IO	442 (25 mA g^{-1})	117 (200)	209
C	Ю	359 (-)	315 (20)	190

are many textbooks that deal with the fundamentals of capacitive and intercalation charge storage mechanisms, there are some salient features that are important for materials that ordinarily store charge through intercalation, but exhibit surface charge storage when polarised at higher rates.

Increasing the rate of a cyclic voltammogram for structured or porous energy storage materials has a large influence on the course of the electrochemical reaction of many cations. One characteristic is that the current peaks associated with many processes such as SEI formation, reduction, oxidation, alloying or intercalation, are often convoluted within the total cumulative charge and the curve resembles that of an asymmetric supercapacitor to some degree. The current response is however much larger than for the slow rate scan, suggesting that there is an additional charge storage mechanism operating at large potentials. The total stored charge for any electrochemical energy storage process can be separated into three components: the faradaic contribution from the Li⁺ ion insertion processes, the faradaic contribution from the charge transfer process with the surface atoms, referred to as pseudocapacitance, and the non-faradaic contribution from the double layer effect.²¹³ When the porosity of the electrode increases, both types of capacitive contributions (pseudocapacitance and double layer charging) can be significant. The capacitive effects can be characterized by analysing data from cyclic voltammetry experiments carried out at different scan rates, according to:214

$$i = a\nu^b \tag{1}$$

where the measured current *i* obeys a power law relationship with the sweep rate *v*. Both *a* and *b* are adjustable parameters, with the *b* value determined from the slope of log(i) *vs.* log(v). There are two well-defined conditions, b = 0.5 and b = 1. For b =0.5 the current is proportional to the square root of the scan rate, according to the equation:

$$i = nFAC^*D^{\frac{1}{2}}\nu^{\frac{1}{2}} \left(\frac{\alpha nF}{RT}\right)^{\frac{1}{2}} \pi^{\frac{1}{2}}\chi(bt)$$
(2)

where C^* is the surface concentration of the electrode material, α is the transport coefficient, D is the chemical diffusion coefficient, n is the number of electrons involved in the electrode reaction, A is the surface area, R is the molar gas constant, F is the Faraday constant, T is the temperature, and $\chi(bt)$ represents the normalized current for a completely irreversible system, as indicated by cyclic voltammetry.

The other defined condition is when b = 1, which is representative of capacitive response, as the capacitive current is proportional to the scan rate, according to:

$$i = \nu C_{\rm d} A \tag{3}$$

To obtain the *b*-value for a given material system, current values from cyclic voltammagrams carried out at different scan rates are recorded at specified potential values. Then, the slope of the plot of the log(i) vs. log(v) is the *b*-value at that potential.

As a pertinent example of many in the literature, Brezesinski *et al.*²¹⁵ recently showed that controlling the morphology of

mesoscale porous materials such as films of iso-oriented α -MoO₃ can facilitate a change from a non-faradic process to a mixture that helps increase the overall energy density of capacitor-based storage devices, using pseudocapacitive effects controlled by reaction kinetics. These properties were unique to their mesoporous crystalline materials and were superior to those of either a mesoporous amorphous material or nonporous crystalline MoO₃ (see Fig. 22). The iso-oriented layered crystalline domains enabled Li-ions to be inserted into the van der Waals gaps of the α -MoO₃ and importantly, this occurs on the same timescale as for the redox pseudocapacitance.

As electrochemically active materials approach nanoscale dimensions, pseudocapacitive effects become increasingly important.²¹⁶ In a recent report, Dunn et al. established the dependence of pseudocapacitance on the particle size of anatase TiO₂ nanocrystals.²¹³ The results showed that for particles smaller than 10 nm in diameter, more than half of the total stored charge is capacitive. As anatase TiO₂ has no van der Waals gap, all of its capacitance is believed to be redox pseudocapacitance. Layered crystal structure materials have also been shown to exhibit such phenomena. TiO₂(B), TiS₂ and H₂Ti₃O₇ are able to take up LiC through pseudocapacitive processes.217,218 In cases where redox pseudocapacitance contributes to the overall energy density, its contribution can be established by cyclic voltammetry. By varying voltage sweep rates, a transition from faradaic to non-faradaic processes can be assessed in many forms of high surface area materials.

The performance of most advanced IO based LIBs can be compared to a different type of device that is able to simultaneously deliver high power and high energy densities as pseudocapacitors, which store energy electrochemically between two electrode plates. As the energy storage employs fast and reversible redox reactions between electrodes and the electroactive species, most pseudocapacitors use metal oxides with a high number of valence states. They are however difficult to mass produce, and suffer from energy density loss at high scan rates. A recent study by Li *et al.*²¹⁹ demonstrated Ni(OH)₂ nanospheres with excellent electrochemical performance (see Fig. 23), related to high purity of the surface of the nanospheres, large surface area and the amorphous phase of the nanospheres.

In a different study, graphene based supercapacitors were prepared by microfabricating electrodes and subsequent deposition of reduced graphene oxide, on both flexible and robust substrates.²¹⁹ The energy density of such structures is comparable with the energy density of LIBs, while their power densities are higher than power densities of capacitors based on metal oxides. Altering carbon-based electrodes and structuring them with ordered 3D porosity have also been demonstrated recently by Huang et al.90 By creating SnO2 nanoparticles inside an inverted opal carbon matrix (Fig. 24), they demonstrated improved anode kinetics in a Li-ion battery cell. The electrodes exhibit simultaneously enhanced ion and electron transport kinetics as well as geometrically constrained active nanoparticles delivering up to 94.17% of theoretical capacity over 1000 discharge-charge cycles at a current density of 2.0 A g^{-1} , and exhibit good rate capability in the high current density



Fig. 22 (a) Morphology of mesoporous α -MoO₃ with highly oriented crystalline walls. Low-magnification bright-field TEM micrograph. Inset: a higher magnification micrograph. (b) AFM image of the top surface. Inset: a tilted AFM image with height variations in the 1–5 nm range. (c) Cyclic voltammograms for mesoporous amorphous and crystalline films of MoO₃ systems at a sweep rate of 1 mV s⁻¹. (c) Kinetic behaviour of the various mesoporous films. The total amount of charge storage (gravimetrically normalized) as a function of charging time for each film. Adapted from ref. 215 with permission from Nature Publishing Group.

range of 1.0–10.0 A g^{-1} . Creating hybrid materials with two or more active materials offers some potential advantages depending on whether energy density and/or cycle life are important.

Development of such novel manufacturing techniques, optimization of the device configurations and improvement of the materials used will further enhance the performance of the supercapacitors, and we recommend recent reviews on this subject for more detailed information.²¹⁶ Developments in the area of ordered porous self-supported batteries with power

densities comparable to supercapacitors offer power improvement options for materials that are fundamentally limited to low intercalative or non-faradaic charge capacities. Designing bi- or multi-phasic materials with different Li insertion voltage ranges could potentially allow for a predetermined capacity without fully discharging each active material. Constraining one active material within another with high deformation plasticity could also potentially give a structurally stable matrix that better accommodated volumetric changes that are not buffered in a polymer-material slurry in standard cell electrode



Fig. 23 (a) CV curves of the amorphous $Ni(OH)_2$ nanospheres at various scan rates in 1 M KOH. (b) Specific capacitance of the amorphous $Ni(OH)_2$ nanospheres as a function of the scan rates based on the CV curves. (c) CV curves of the blank electrode at various scan rates in 1 M KOH. Reproduced from ref. 219 with permission from Nature Publishing Group.



Fig. 24 (a) Schematic illustration showing the preparation of an SnO₂@C inverted opal electrode. (b) Li-ion battery performances of SnO₂@C inverse opal electrodes.⁹⁰

designs. Recent findings in dual charge storage mechanisms using SnO_2 nanoparticles on Si as a hybrid anode¹²⁰ and their exploitation will help optimize tailored design of many other sophisticated electrode materials in electrochemistry and energy storage materials influenced by the end application.

Choosing pseudocapacitance and supercapacitance is also possible using two-dimensional (2D) nanosheets such as graphene or transition metal dichalcogenides (TMDCs).²²⁰ Charge storage mechanisms here involve the insertion/extraction of protons or ions in the first few nanometers on the surface of electrode materials for pseudocapacitors and the adsorption/ desorption of ions at the electrode-electrolyte interface for electrochemical double-layer capacitors.221,222 Enhancing performance is again a function of reduced lithium ion diffusion distance within the materials if the former case and within the electrolyte for the latter case. With the boost of wearable and flexible consumer electronics that have an aesthetic appeal and unique functionality, flexibility and shape versatility or adaptability is a useful property in charge storage materials and their electrochemical cells.²²³⁻²²⁵ The state-of-the-art flexible supercapacitors generally use carbon networks. Without the carbon networks pseudocapacitive materials can barely be used to fabricate the flexible electrodes, so as to assemble the flexible supercapacitors (Fig. 25). Shi et al.,226 as one example, showed that flexible asymmetric supercapacitors with excellent electrochemical performance and in the form of quasi-transparent energy storage cells could be fabricated by using two kinds of ultrathin 2D nanosheet materials (MnO₂ and graphene). The MnO_2 nanosheets with a thickness of ~ 2 nm exhibited a high capacitance of 774 F g⁻¹ and good rate performance. Flexible asymmetric supercapacitors using the ultrathin 2D MnO₂ and graphene in aqueous Ca(NO₃)₂-SiO₂ gel electrolyte realized excellent electrochemical performance with an energy density of up to 97.2 Wh $\rm kg^{-1}$ much higher than traditional $\rm MnO_2$ based supercapacitors and no more than 3% capacitance loss even after 10 000 cycles.

10. Summary and outlook for energy storage material design and performance

In this review, a description of some of the recent advancements in nanomaterials design, chemistry, size, shape, structure and assembly on the performance of Li-ion batteries was given. Particular focus was given to the influence of material parameters on cell performance and on emerging functional material architectures with engineered porosity as active Li-ion battery and pseudocapacitor materials. It is becoming clearer from the progress to date that the improvements associated with changes of the electrode's chemical composition, combined with developments in the electrode architecture, offer excellent opportunities for commercialization of next generation Li-ion batteries and emerging alternative chemistries.²²⁷ Various mechanisms for lithium storage combined with simple routes towards particular morphologies of active materials create a multitude of opportunities for electrode design.

However, it is important to note that to date, only a handful of modern materials and electrode architectures have been commercialized. The advancements in anode material science and design have not been followed to the same extent by improvements in the cathode chemistry and performance. A pressing challenge is the dearth of true, cell-level investigations of known and promising new materials in true Li-ion cells. Most cathode investigations resulted in lithium batteries with a lithium electrode; anode studies included half cells. While the fundamental advancements are motivating, many new materials and systems need to be thoroughly investigated using pair-matched anodes and cathodes in suitable electrodes as full Li-ion cells and classified for their optimum performance and loading conditions dictated by the end application.

Inverted opal architectures have been demonstrated to improve the performance of battery electrodes based on a



Fig. 25 (a) Photographs of the screen-printed asymmetric nanosheets-based supercapacitor electrodes of various designs and (b) Ragone plots of MS/GA and MS/MS supercapacitors compared with other MnO_2 based asymmetric supercapacitors in the literature (based on the total mass of active materials).

variety of materials. The shortened diffusion lengths and excellent electrolyte infiltration allow for largely increased charge-discharge rates, while the void space allows for facile relaxation of strain and stress caused by repeated cycling of the electrode. Moreover, a composite approach was used, where the inverted opal current collector acts as a support for active materials. This design approach can help minimize unwanted polarization and resistances, and achievement of outstanding charge-discharge rates. Such electrodes may achieve power densities more often seen in supercapacitors, while delivering energy densities characteristic for traditional LIBs. The use of engineered or programmed porosity is potentially very useful for materials that have inherently lower Li ion diffusivity within the crystal structure of the active material. Care should be taken to ensure that the structure of the porous network does not introduce significant increases in electrical resistance through material contacts or grain boundaries for example, or variable SEI film structures at anodes. Ideal scenarios would likely involve engineered porosity of a well crystallized material that itself does not have a high kinetic barrier to Li diffusion within its structure, made porous in a manner that maximizes ambipolar (ionic and electronic) conductivity (tuned for power or

energy density requirements at a prescribed rate), forms stable SEI layers at low potentials (anodes), and offers useful volumetric or gravimetric energy densities, among other attributes. Recent efforts for some materials have shown that defining the porosity or dispersion of active materials can also give extra degrees of freedom for volume expansion common for many high capacity materials.

Ultimately, the successful application of materials chemistry and electrode design will be decided by industry. Undoubtedly, the drive for better LIBs motivated by automotive and consumer electronics market will have a dominating influence on the types of batteries used. Templated materials with good ionic conductivities can allow for variants of thin film batteries, where the charge storage cell is designed around the shape of the electronic device, rather than the other way round. Although Li-ion battery packs are compact and volumetrically efficient, the 'swiss-roll' design strategy limits the batteries to rectangular or cylindrical shapes, which constrains the form factors of devices. While many factors need to be considered, not least a high quality, repeatable way of producing such thin film batteries and battery skins, scope exists to lay down energy storage cells in parallel with energy conversion or energy harvesting thin film technologies such as solar cells and thermoelectrics, on a single platform. Recent work on unconventional battery designs²²⁸ focused on their accommodation into devices without constraining their form factors. Battery designs such as flexible batteries,229 stretchable paper-type batteries, and even printed transparent²³⁰ batteries show that such atypical batteries are possible. The use of IO materials is one way forward, allowing for possibilities of interpenetrating networks with Li-containing polymer electrolytes and sequential layering of anode and protective encapsulating layers. Painting has proven its usefulness in applying functional materials onto almost any type of substrate for electronic devices and it may be applied to energy storage such as batteries. Printing (or generally, painting)²³¹ is already considered a viable technique for large-area fabrication of electronic devices (circuits, photovoltaics, displays, etc.) on virtually any type of substrate. Recent work has shown the intriguing possibility of literally painting the layers of materials required for a Li-ion battery.232

For charge storage technology capable of high performance, faster charging, and stable, safe capacity retention during operation can be moulded to the device shape – this will significantly help advance portable device power technology options such as consumer devices and wireless sensor nodes for example. Consequently, there is huge interest in developing a fully paintable energy storage technology, and a seamless integration of these energy storage systems into electronic devices is still a significant hurdle. Probing how an ordered architecture is that can be assembled layer-by-layer on shaped surfaces, and new non-destructive spectroscopic methods to investigate how a new areal battery shape can be probed during its operation will be very advantageous for future thin film, moldable battery designs and material architectures.

Advancements in Li–air and Li–S designs and other 'beyond lithium' systems such as emerging Mg and Na-ion batteries^{233,234} might challenge the supremacy of the Li-ion system in the future, offering higher energy densities at reduced cost. Some investigations consider multivalent cations offering more than one electron per redox event. As summarised earlier, hybrid systems involving the power density benefits of supercapacitors and the energy density performance of batteries in the form of rate-dependent pseudocapacitors may also have niche application. However, for now, LIBs are very likely to remain the main solution for power systems, and thus drive further improvements in both electrode chemistry and architecture.²³⁵

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Appendix B

EPITAXIAL GROWTH OF VISIBLE TO INFRA-RED TRANSPARENT CONDUCTING IN2O3 NANODOT DISPERSIONS AND REVERSIBLE CHARGE STORAGE AS A LIION BATTERY ANODE

ACS APPLIED MATERIALS & INTERFACES

Core–Shell Tin Oxide, Indium Oxide, and Indium Tin Oxide Nanoparticles on Silicon with Tunable Dispersion: Electrochemical and Structural Characteristics as a Hybrid Li-Ion Battery Anode

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Supporting Information

ABSTRACT: Tin oxide (SnO_2) is considered a very promising material as a high capacity Li-ion battery anode. Its adoption depends on a solid understanding of factors that affect electrochemical behavior and performance such as size and composition. We demonstrate here, that defined dispersions and structures can improve our understanding of Li-ion battery anode material architecture on alloying and co-intercalation processes of Lithium with Sn from SnO₂ on Si. Two different types of well-defined hierarchical Sn@SnO₂ core– shell nanoparticle (NP) dispersions were prepared by molecular beam epitaxy (MBE) on silicon, composed of either amorphous or polycrystalline SnO₂ shells. In₂O₃ and Sn doped In₂O₃ (ITO) NP dispersions are also demonstrated from MBE NP growth. Lithium alloying with the reduced form of the NPs and coinsertion into the silicon substrate showed reversible charge storage. Through correlation of electrochemical and structural characteristics of the anodes, we detail the link between the composition, areal and volumetric densities, and the



effect of electrochemical alloying of Lithium with $Sn@SnO_2$ and related NPs on their structure and, importantly, their dispersion on the electrode. The dispersion also dictates the degree of co-insertion into the Si current collector, which can act as a buffer. The compositional and structural engineering of SnO_2 and related materials using highly defined MBE growth as model system allows a detailed examination of the influence of material dispersion or nanoarchitecture on the electrochemical performance of active electrodes and materials.

KEYWORDS: lithium-ion batteries, tin oxide, nanoparticles, anode, electrochemistry, indium tin oxide

I. INTRODUCTION

Lithium-ion batteries are widely used today in portable electronics, telecommunication and medical devices. Li-ion technologies are rechargeable and offer advantages such as high energy density, lack of unwanted memory effects, and relatively long cycle lifetimes.¹⁻⁴ Rapidly developing new technologies require lithium ion batteries with even higher capacities, better rate performance and increased safety for advanced applications and to satisfy consumer demand for portable electronic devices needing greater power over longer time periods.^{5,6} However, current battery anodes made from layered graphitic carbon are limited by a theoretical capacity of 372 mA h g^{-1,7} which limits the overall cell capacity when paired with a high capacity cathode material. Additionally, higher rates tend to lower the overall cell capacity and voltage even for well-established Li-ion

chemistries with defined discharge protocols, and so the ongoing search for high capacity, high-rate-capable, safe and stable materials and chemistries, continues.

Considerable research is therefore being directed to the study of emerging alternative anode materials with higher capacities such as Sn (990 mA h g⁻¹),⁸ SnO (876 mA h g⁻¹), SnO₂ (780 mA h g⁻¹),^{7,9-14} Sb (660 mA h g⁻¹),¹⁵ Si (4200 mA h g⁻¹),¹⁶ and Ge (1600 mA h g⁻¹).¹⁷ Among these materials, SnO₂ is receiving renewed interest because of its simpler synthesis and reports of improving performance.^{7,13,18-20} However, SnO₂ (like all the materials listed above) undergoes drastic volume

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changes (\sim 200%) when electrochemically alloying with lithium after being reduced to metallic Sn during repeated charge/ discharge cycles.²¹ These changes may cause capacity loss and poor cycle life, which can come from loss of electrical contact between the active material and current collector as well from agglomeration of active material, preventing electrolyte access to the surface of the active material.²² Preparing nanostructures with shorter diffusion lengths may greatly improve the rate capability of SnO₂ based anodes by allowing one dimension of the crystal structure to be smaller than the characteristic diffusion length of Li^{+, 23} Additionally, the lower dimensionality would not negatively influence electronic conduction in most intercalation or alloying materials as the resistance of a twodimensional (2D) version of a three-dimensional (3D) material would not greatly increase. Moreover, investigation of the density of active materials or their architecture in an electrode could lead to better understanding of their influence on all important aspects of a battery anode operation, including protective SEI layer formation.

Effective strategies have been proposed to resolve issues arising in SnO₂ based Li-ion battery anodes. Among them, synthesis of nanoscale SnO2 with porous, layered, or multiphasic structures, such as nanoparticles (NPs),²⁴ nano-sheets,^{25,26} nanotubes,^{26,27} and core-shell nanostructures^{28,29} have been investigated. These reports demonstrated the sensitivity of performance to the nanoscale structure. These types of structures allow for a high density of materials with small diffusion lengths which improves Li⁺ insertion rates.³⁰ High porosity is effective in allowing the stress caused by expansion and contraction to be accommodated so long as the electrochemical properties and electrical conductivity are not adversely affected. However, most of these structures are metastable and do not markedly improve long-term cycle stability.³¹ As an alternative, various composites have been proven to be more effective in enhancing the stability of SnO₂ based electrodes.^{32,33} Solvothermal and hydrothermal and microwave processes, 34,35 plasma jet reactor synthesis, 36 AAO assisted etching³⁷ and various other templating methods³⁸⁻⁴¹ were extensively used to prepare nanorods, nanoplates, nanowires, and core-shell particles of SnO2. A number of composite structures (such as $CNT-SnO_2$ or Fe_3O_4/SnO_2)^{24,42,43} were also developed that demonstrated a large influence of their composite morphology and chemistry on the performance as an anode.^{44–47} More investigation is needed to understand the changes occurring at the interface between the active materials and their interference with current collector, especially in the situation where the current collector can also react with lithium. Current collectors that can provide reversible charge storage capabilities are not always beneficial and can adversely affect the interface to the active material. In cases where co-insertion (reversible) can be accommodated in such hybrid electrodes, there is potential for the provision of a degree of protection from volume change stress;⁴⁸ buffering Li⁺ insertion can be very useful in cases where the expansion rates of the material are associated with excessive stress and strain, causing loss of electrical contact and mechanical integrity in porous or discontinuous active materials penetrated by electrolyte, and requires further investigation.

Compared to commonly used techniques, molecular beam epitaxy (MBE) offers excellent control over the crystalline quality, phase, and morphologies of deposited structures, and their chemical composition. These benefits make MBE an ideal method for detailed investigations of electroactive materials with very well-defined compositions, shapes and crystallinity.⁴⁹

In this paper, we demonstrate the growth of several novel types of Sn@SnO2 core-shell NP dispersions prepared by MBE⁵⁰ on silicon, and through electron microscopy and spectroscopies, detail their respective behavior in response to lithium alloying as Li-ion battery anodes. Oxidative crystallization in air after deposition of the respective metal (Sn, In, or both for ITO) results in a characteristic size dispersion of epitaxial SnO₂ NPs with core-shell structure, and also In₂O₃ and Sn-doped In₂O₃ (ITO) NPs. Detailed structural characterization and electrochemical cycling was carried out to elucidate how the reversible alloying process with Li is inherently dependent on size dispersion, core-shell structure and composition. The volumetric expansion of Si (that acts as the current collector) during lithium insertion is observed to provide a degree of mechanical buffering against loss of electrical contact between SnO₂ NPs. This work defines the influence of controlled crystal structure, architecture, and volumetric/spatial density on the electrochemical processes occurring in a Sn@SnO2-Si hybrid nanomaterial anode, and also the structural changes associated with Li alloying and dealloying process introduced by cycling in a series of coreshell SnO₂, In₂O₃, and ITO NPs on silicon.

II. EXPERIMENTAL SECTION

Prior to the deposition, the surface of silicon was cleaned using standard RCA silicon cleaning procedures. After rinsing, a second treatment in a H_2O_2 :HCl: H_2O (1:1:5) solution was used to remove metallic and organic contamination. For deposition of Sn and In, a custom-built MBE high-vacuum chamber with two high temperature effusion cells for metallic Sn or In targets, combined with an electron beam evaporator was designed in cooperation with MBE Komponenten GmbH. A uniform layer of Sn metal was deposited at predefined rates on a Si(100) substrate at a predefined temperature, with precise control over the nominal thickness (see Supporting Information, Section S1 for the details of deposition process, thickness control, and calibration). A similar procedure was followed for the deposition of In to form In_2O_3 NPs. For formation of ITO, Sn and In were used at a 10:90 weight ratio.

Surface morphologies and the chemical composition of the nanostructured dispersions were investigated by scanning electron microscopy (SEM) using a Hitachi SU-70 with an Oxford-50 mm² X-Max detector for energy dispersive X-ray analysis (EDX). The acceleration voltage used for imaging was equal to 10 kV, unless stated otherwise. Transmission electron microscopy (TEM) analysis was conducted with a JEOL JEM-2100F field emission microscope operating at 200 kV, equipped with a Gatan Ultrascan CCD camera and EDAX Genesis EDS detector for atomic resolution crystal structure and composition examination. The size distribution of the nanodots was analyzed using Image].⁵¹

Cross-sectioning of the SnO₂ NPs formed by MBE was carried out with an FEI Helios Nanolab Dual Beam FIB System. A protective layer of platinum was deposited over the surface of the sample to minimize surface damage. Cross-sectional TEM sample preparation was performed on the slice using a standard FIB lift out technique described elsewhere.⁵²

X-ray photoelectron spectroscopy (XPS) was acquired using a Kratos Axis 165 monochromatized X-ray photoelectron spectrometer equipped with a dual anode (Mg/Al) source. Survey spectra were captured at a pass energy of 100 eV, step size of 1 eV, and dwell time of 50 ms. The core level spectra were an average of 10 scans captured at a PE of 25 eV, step size of 0.05 eV, and dwell time of 100 ms. The spectra were corrected for charge shift to the C 1s line at a binding energy of 284.9 eV. A Shirley background correction was employed, and the peaks were fitted to Voigt profiles.



Figure 1. (a) Schematic diagram highlighting steps in formation of core-shell SnO_2 NPs. (b) SEM image showing the ATO NP dispersion. Inset shows the diameter distribution for ATO NPs. (c) High resolution SEM image showing a single ATO NP with small crystallites growing on the surface. (d) SEM image of PCTO NP layer. Inset: diameter distribution histogram for PCTO NP layer. (e) Low voltage (2 kV) SEM image of PCTO layer showing the core-shell structure of the NPs. (f) High resolution SEM image of PCTO NP layer showing texturing of the NP surface.

To investigate the electrochemical insertion (alloying) and removal of Li, cyclic voltammetry measurements were carried out in a 3-electrode setup using a Multi Autolab 101 potentiostat, using Li as both counter and reference electrodes. All potentials, unless otherwise stated, are relative to Li⁺/Li. Custom built Swagelok-type cells were used with counter and active material electrodes separated by a polypropylene separator soaked in 1 mol dm⁻³ solution of LiPF₆ in ethylene carbonate:dimethyl carbonate (EC:DMC) in a 50:50 v/v ratio. The electrodes were potentiodynamically cycled using a scan rate of 0.2 mV s⁻¹. Afterward, the electrodes were carefully washed in acetonitrile and a 10^{-4} mol dm⁻³ solution of acetic acid to remove the electrolyte residue.

III. RESULTS AND DISCUSSION

A. Core-Shell Sn@SnO₂ NP Dispersions. MBE growth of Sn at elevated temperatures (400 °C-600 °C) and subsequent oxidation in air results in the formation of two different types of SnO₂ core-shell NPs as shown in Figure 1a. The first type of NPs consists of highly crystalline Sn metal core NPs with a thin amorphous coating of SnO₂ (ATO), and the second type comprises a crystalline Sn metal core with a polycrystalline SnO₂ shell (PCTO), forming Sn@SnO₂ NPs. Both are formed by simple two step deposition and oxidation mechanism. The SEM image in Figure 1b shows a dispersion of ATO NPs on the Si substrate (optical images of the NP dispersions are shown in Supporting Information, Figure S2). ATO NPs typically have a high size dispersion, ranging from a few nm to over 500 nm in diameter, with an average interparticle distance of ~60 nm, covering about 65% of the sample surface (For detailed size dispersion analysis procedure see Supporting Information, Section 2). The NPs are generally close to hemispherical shape, with some deviations probably related to their crystallization process. Small NPs are interspersed between the larger ones indicating that the growth undergoes simultaneous and progressive Sn deposition, surface diffusion of nucleated crystals, and coalescence of neighboring particles.

The high resolution SEM image in Figure 1c shows that some of the larger ATO NPs also have smaller NPs growing on their surface. The smaller hierarchical NPs that form on the surface or larger NPs are believed to occur when the coalescence mechanism that forms larger NPs is interrupted by oxidative crystallization of the liquid-phase Sn droplets on the larger NP surface. Defect-related or roughness-induced nucleation sites characteristic of some MBE growth likely contributes to the roughness development on the NPs. In₂O₃ NP layers grown by MBE also showed similar hierarchical structure, with additional nanowire growth sometimes found from these crystallite seeds.⁴⁸ The exact origin of the nanocrystallites on the surface of the ATO NPs is however unclear. Crystalline core-polycrystalline shell NPs of SnO₂ (PCTO) are shown in Figures 1d-f, where their core-shell structure is visible in the low voltage secondary electron image in Figure 1e. Analysis shows a much smaller size dispersion and lower average interparticle distance (~25 nm), which is related to lower deposition temperature, allowing particles to form without as much surface diffusion in their liquid state as found for ATO NPs. Compared to the ATO NPs, the PCTO NPs show much lower size dispersion, with the majority of the NPs ~100 nm in diameter (Figure 1d inset) ;the total surface coverage is higher than for ATO NPs, amounting to ~80% coverage of the sample surface. High magnification SEM imaging of the NP shows a texture on the surface (Figure 1f) which is associated with surface roughness (shown also in Figure 2) specifically from the structure of the polycrystalline shell. During MBE, the small interfacial strain between the deposited film and the substrate greatly influences the structure growth. For low lattice mismatch, the growth will follow the Stranski-Krastanov (SK) mode,⁵³ corresponding to complete wetting of the substrate surface by the deposited adatoms followed by formation of islands. Here, these islands are initially liquid, as the deposition is carried out above the melting temperature of Sn. Surface diffusion of liquid droplets occurs in parallel with the deposition, leading to coalescence of nearest-



Figure 2. (a) Dark-Field TEM image showing a cross-section through a layer of PCTO NPs. (b) TEM image showing a cross-section of a single PCTO NP. (c) FIB cross-section through a single ATO NP, highlighting formation of amorphous shell beneath the contact point of NP with the substrate. (d) TEM image of NPs grown hierarchically on the surface of ATO NP.

neighbor particles and formation of SnO₂ NPs upon subsequent oxidative crystallization in ambient air. The smaller NPs interspersed between larger crystals cover a large portion of the substrate (\sim 30%), indicating that progressive deposition of Sn resulted in formation of a large number of small nanodroplets which then coalesced through surface diffusion to form large crystals. The coalescence occurs at slower rate (lower substrate temperature) in case of PCTO NPs resulting in better monodispersity in the surface coverage.

The amorphous layer formed around the crystalline core in ATO NPs is shown in Figures 2a and b. Both amorphous and polycrystalline shells (shown in Figures 2c and d), are formed during oxidative crystallization of the outer layer of the Sn droplet after the deposition. TEM analysis confirms that some of the small crystallites growing on the surface of large ATO particles also exhibit core—shell structure.

This hierarchical consistency in core-shell construction indicates that formation of the surface crystallites and NP shells were simultaneous; the thickness of the ATO shell is similar for all particles, despite the 1-2 orders of magnitude difference in core diameter. Moreover, the structure of the crystallites on the surface of ATO is similar to the structure of the PCTO, with a polycrystalline shell around a crystalline core forming a hierarchy of core-shell NPs. The thickness of the amorphous layer is ~ 10 nm for all NPs on the surface of the substrate or those on other NPs, and the shell also extends below the contact point with the substrate (Figure 2c) as well as at the interface between hierarchical core-shell NPs. This suggests that the formation of the amorphous shell progresses through diffusion of the oxygen through the top layer of the crystalline Sn. The thickness of the polycrystalline shell in the case of PCTO NPs is of similar order to that of the ATO NP shell (7-13 nm). This indicates a similar shell formation rate for both NPs.

To analyze the chemical composition of the ATO and PCTO NPs XPS and EDX spectral measurements were carried out. The Sn 3d core level spectra for both ATO and PCTO samples are presented in Figure 3a. The 3d core-level spectra from Sn in both PCTO and ATO NP structures contain a doublet with binding energies of 487 eV $(3d_{5/2})$ and 495.3 eV $(3d_{3/2})$



Figure 3. (a) Sn 3d and O1s core level spectra for ATO and PCTO NPs. (b) EDX linescan of the PCTO NP cross-section shown in (d). (c) EDX linescan of the surface of the ATO NPs. (d) Darkfield TEM image of PCTO NP layer. Line indicates the measurement site for the linescan presented in (b).

referenced to the C1s core level of 284.8 eV, (see Supporting Information, Figure S4) which suggests the (IV) oxidation state of Sn, that is, SnO_2 . A slight shift of 0.1 eV between PCTO and ATO core levels is equal to the measured shift in their respective adventitious C1s core levels.

It is important to note that the differentiation between SnO and SnO₂ in photoemission studies is complicated because of only a very small shift in the Sn 3d core level binding energy. Consequently, stoichiometric ratios of elements were calculated from the XPS spectra according to:⁵⁴ $S_{ij} = (c_i/c_j) = (I_i/ASF_i)/(I_j/ASF_j)$ where c_i and c_j are the concentrations, I_i , I_j are the background corrected photoelectron emission line intensities, and ASF_i, ASF_j are the atomic sensitivity factors for photoionization of the *i*th and *j*th elements. Following this procedure we determined the concentration of oxygen (O) to be ~2 times the concentration of Sn, which corresponds to the SnO₂ stoichiometry of the oxide formed on the surface of the sample.

Furthermore, intensities for the deconvoluted O1s signals are not equal for both core-shell structures. This can be attributed to different silicon surface coverage of the sample with the NPs. In the case of ATO, the intensity of the deconvoluted O1s peak located at 532.1 eV, related to oxygen in SiO_{xy} is higher than for PCTO. As the surface coverage of the sample is larger for PCTO than ATO, it is expected that the SiO_x signal would be higher for ATO NPs with lower surface coverage. The EDX line spectra taken from the FIB cross section of PCTO and the surface of ATO sample, also corroborate these results. Particularly, in Figure 3b, an increase in measured intensity of the O K α line indicates a larger concentration of oxygen atoms close to the edges of the NP indicating the core-shell of PCTO NPs. SEM EDX line-scan taken from the surface of the ATO NP layer also confirms oxygen presence within the penetration depth of the EDX beam, corroborating XPS results.

B. Reversible Lithiation in Core–Shell SnO₂ NPs. As SnO_2 based materials are being considered for use as anodes for Li-ion secondary batteries,^{32,55} its electrochemistry with lithium was investigated here for a variety of structures including core–shell SnO_2 NPs, but also comparative In_2O_3 and ITO NP dispersions and. There are limited reports on Si–Sn composites as Li-ion battery anodes,⁵⁶ and so both ATO and PCTO NP

alloying reactions with lithium, and the structural changes of the NPs and their dispersions on Si during lithiation processes were investigated with cyclic voltammetry and high resolution ex-situ electron microscopy. The Li alloying reaction with the Sn NP core is possible if the outer oxide coating can be reduced to Sn^0 from the respective SnO_2 on PCTO and ATO NPs.

Cyclic voltammetry was used to investigate this process. In a cyclic voltammogram (CV) each alloying, growth, removal, oxidation, and reduction process can be examined in each cycle, at the respective potential for each process. This is especially useful in the present case, where numerous processes and several materials are present. The cathodic processes involve the alloying of Li with the reduced form of SnO_2 to form a Li–Sn alloy (charging), and the anodic process follows Li extraction or dealloying (discharging). There is a substantial difference between CVs for ATO (Figure 4a) and PCTO



Figure 4. (a) CVs for ATO and (b) PCTO NPs on silicon. (c) Schematic diagram describing formation of porous NP layers upon lithiation cycling. (d) Dark-field STEM image showing highly porous layer comprising pulverized NPs formed by electrochemical cycling of the PCTO NP layer. The brighter regions are Sn and SnO₂.

(Figure 4b). The large irreversible peak (indicated in the CVs by I) is typically regarded as being due to the formation of a stable SEI layer and to electrochemical reduction of SnO₂ to a system of three phases consisting of LiO2, O2, and SnO. Mohamedi et al. detailed these reaction products and their formation when examining amorphous SnO₂ films prepared by electrostatic spray deposition at elevated temperature.⁵⁷ This reaction is complete at ~ 1.5 V and is present in both CVs. Subsequently, SnO is reduced to metallic Sn, indicated by large peak present at ~ 1 V for both systems (I for PCTO, II–III for ATO). A shift in voltage for this peak occurs in subsequent cycles for PCTO, indicating improved kinetics of the reaction as well as decreased lithium concentration in the phase formed at that peak potential. Two reversible peaks appear in the cathodic scan (V-VI for ATO, V-VII for PCTO) which can be attributed to the formation of particular Li alloys with Sn: Li_{2.33}Sn formed at 0.55 V and Li_{4.4}Sn is formed at 0.15 V. Oxidation peaks appearing at 0.57 V, 0.81 V, 0.87 V, 0.91 V,

and 1.21 V correspond to the dealloying of Li_xSn and partially reversible oxidation of Sn to SnO_2 . The full electrochemical process occurring during reversible alloying of lithium with Sn can be described⁵⁸ by the following set of equations.

$$\text{Li}^+ + e^- + \text{electrolyte} \rightarrow \text{SEI}$$
 (1)

$$SnO_2 + 4Li^+ + 4e^- \rightarrow Sn + 2Li_2O$$
⁽²⁾

$$Sn + xLi^{+} + xe^{-} \leftrightarrow Li_{x}Sn \quad (0 < x < 4.4)$$
(3)

The reaction in eq 2 is normally regarded as irreversible and a cause of capacity loss in Sn-based anodes regardless of consistency in electrical connectivity of the active material, phase conversion, and resistance changes, while in this case the reduction peak at 1.25 V (I for ATO and PCTO NPs) and corresponding oxidation peak at 1.23 V (VI for ATO NPs, VII for PCTO NPs) remain stable over the 5 cycles indicating partial reversibility of this reaction compared to bulk SnO2. Moreover, a small amount of lithium is introduced into the silicon current collector. The insertion and removal potentials for silicon are typically 0.2 and 0.5 V, respectively (dedicated CVs for Si(100) electrodes without NPs are shown in Supporting Information, Figure S5). The relatively higher rate of reaction as shown by the larger current in this potential range indicates that insertion of lithium into Si coexists with alloying of lithium with Sn.

For ATO NPs, the large irreversible area in the 1.6–0.8 V range (I), corresponds to reduction of SnO₂ to metallic Sn, and the succeeding peak at 0.39 V (II–III) corresponds to formation of a Li_xSn phase, where the range of *x* is 0 < x < 4.4. This is also found for the PCTO NPs, implying that the crystal structures of the thin shell coatings are less critical than their stoichiometric phases, which are identical. In the lower voltage range corresponding to insertion of lithium into Si, a large peak at ~0.1 V (IV) is present. In the anodic part of the CV, two reversible peaks at ~0.65 V (V) and ~1 V (IV) are found. The first peak can be attributed to the removal of lithium from silicon while the second corresponds to removal of lithium from Sn,²³ and it occurs at a similar voltage in both ATO and PCTO core–shell NPs.

The Si insertion and removal rates as indicated by the current in corresponding CV peaks increase with cycling, indicating an activation effect characteristic for Si-based anodes.^{2,16,59–61} Specifically, volumetric expansion of lithiated material causes cracks and exposure of unreacted Si to the electrolyte, which in turn allows more lithium to be incorporated into material at the same potential. Usually it is considered a negative effect, causing an increasing degree of cracking and loss of electrical contact between the active material and the current collector. As it is not the active material, expansion occurs only where the SnO₂ NPs are not present. Comparing the differences between the ATO and PCTO NPs and their spatial density and size dispersion on the Si, \sim 25% higher rate of lithium insertion into ATO sample is observed, which correlates well with the surface coverage difference between ATO and PCTO. Moreover, formation of an SEI layer (from the voltammetric response) is more pronounced for PCTO samples, which can be attributed to a higher areal mass loading of polycrystalline SnO₂ shell.

To further analyze changes induced in the structure of the anode during lithiation, FIB cross sections of both types of NPs were investigated by TEM (Figure 5). Figure 5a shows an SEM image of the ATO NP layer after cycling. A change in ATO NP shape is found (see Figure 1b and Figure 5a inset for



Figure 5. (a) SEM images showing a layer of ATO NPs before (inset, scalebar 500 nm) and after cycling. (b) SEM image showing PCTO NP layer after cycling. (c) Dark-field TEM image showing a porous layer formed because of electrochemical cycling of PCTO NPs. White line indicates the site for the line-scan presented in (e). (d) TEM image showing the interface between the silicon current collector and the PCTO NP layer after cycling, with α -Si layer highlighted. (e) EDX line-scan through PCTO NP layer after cycling. Site of measurement is indicated by the white line in (c).

comparison), but significantly, the size of the ATO NP has not increased laterally. PCTO NPs on the other hand, shows extensive modification after cycling (shown in Figure 5b). The NP underwent pulverization likely because of expansion and contraction during cycling that results in a higher density of smaller NPs on the surface. The initial interparticle distances between ATO NPs are significantly larger than between PCTO NPs and are devoid of NP-NP contacting within the layer. PCTO NPs are, prior to lithiation, formed with much smaller interparticle distances, and thus the expansion during lithium insertion will lead to larger degree of NP agglomeration and coalescence.

Figure 5c shows a dark-field TEM cross-section of the PCTO NP layer. The structural changes confirm the observation from Figure 5b, (see Figure 2 for comparison) where the NP layer is transformed into a porous layer of Sn nanocrystals after cycling that are much smaller (by a factor of \sim 4) than their as-formed size. Bright areas (larger atomic weight electron scatterers) seen in Figure 5c correspond to Sn present in the resulting layer. The existence of a porous layer with thickness corresponding to the diameter of the largest PCTO indicates that the expansion of NPs allows for agglomeration and coalescence of nearest neighboring NPs during charge–discharge cycles. Multiple NP expansions can cause the formation of a largely porous, but also highly interconnected layer. A small number of the NPs are still present in their metallic nondistorted form (see Figure 5d and the white particle in Figure 5c) probably because of lack of contact with the electrolyte after the initial phase of the reaction.

The stability of the contact in this case is mainly caused by co-insertion of the lithium into the silicon current collector, which offers some degree of buffering by intercalating lithium ions at the Si-electrolyte interface that exceed the alloying limit of the volumetric density of NPs on the surface. As discussed further on, the lower areal density of SnO₂ NPs is correlated with a higher Si interface, and the Si interface allows some degree of buffering by intercalating excess Li⁺ at lower potential to the alloying reaction with Sn. Such buffering effects have been observed in SnO_2/C composites, where the composite alleviates large scale material breakdown.⁶² NPs were deposited on single crystalline Si, and the formation of α -Si layer underneath the porous PCTO (Figure 5d, and further detail in Supporting Information, Figure S5) layer after cycling indicates that the reversible Li_x Si Zintl phases^{63,64} of silicide are formed in parallel with expansion/contraction because of oxide reduction to metallic Sn and subsequent lithiation of the original PCTO NP. EDX analysis (Figure 5e) also shows uniform distribution of Sn within the composite material matrix, confirming formation of a porous Sn layer. ATO NPs after 5 insertion-removal cycles seen in Figure 5a also show significant structural changes, mainly seen for the largest NPs. The elemental distribution post cycling is shown in Figure 5e, confirming that the porous film consists of Sn with Si interspersed in the layer close to the surface of the current collector.

The electrochemical response of NP dispersions was also examined for a range of NPs prepared by MBE: in addition to core-shell SnO_2 , we investigated In_2O_3 and ITO NP dispersions whose CVs and corresponding size dispersions are presented in Figure 6.

The cyclic voltammetric response of the various SnO_2 and In_2O_3 NPs dispersions in Figure 6, show that the lithium insertion and removal characteristics are strongly dependent on the shape and size dispersion of the NPs and their volumetric density; all samples exhibit at least bimodal sizes, with one mode dominating in the case of highly coalesced ATO and In_2O_3 NP dispersions. As all are deposited from In, Sn, or In + Sn using MBE, the distributions are characteristics of a similar formation mechanism, outlined earlier for SnO₂. In terms of electrochemical reduction, alloying, intercalation, and the reverse processes, there is similarity between responses for PCTO and ITO NPs (Figures 6a and d), and between ATO NPs and In_2O_3 NP layers (Figure 6b and c).

Analysis of the data in Figure 6 shows that both areal density and volumetric density need to be considered, especially when using hybrid systems such as the present case where the current collector (silicon) is capable of intercalating lithium. Lithium insertion and removal peaks for Li_xSi are more pronounced (as measured from the magnitude of the current and integrated charge) for ATO and In_2O_3 NP dispersions, while alloying reactions with active material (In, Sn) dominates for PCTO and ITO NP layers. This trend is due to the areal coverage, whereas the relative contribution of the alloying to intercalation response in these electrodes is linked to the volumetric density of active material. The shape of the voltammetric response in each case thus includes different relative contributions from the CV response of Li–Si formation (see Supporting Information,



Figure 6. Single cycle voltammograms, SEM image of the surface of the NP layer, and corresponding size dispersion histogram for (a) PCTO NPs, (b) ATO NPs, (c) In_2O_3 NPs, and (d) Sn-doped In_2O_3 (ITO) NPs. Deintercalation potential windows are shaded for Li_xSi (green), Li_xSn (pink), and Li_xIn (yellow).

Figure S6). For the PCTO and ITO NP dispersions (Figures 6a and d), the Li_xSi phases (cf. Figure 5) are observed, but dominated by the In- and Sn-containing material. As the volumetric density is lower for these electrodes (in spite of higher areal coverage), the corresponding currents are lower. The opposite trend is found for ATO and In_2O_3 NP dispersion with lower areal coverage, regardless of the volumetric density of active material.

In such cases, charging and discharging in specific potential windows can select the alloying and/or intercalation process where dissimilar materials are electrochemically active, but this work shows that the relative contributions are linked to the dispersion of the material in addition to its structure and composition. For much smaller PCTO and ITO NPs < 200 nm in diameter, all of the Li-Sn alloying occurs prior to coinsertion with silicon. During cycling however, material break is observed for SnO₂ when large (>250 nm) NPs are used. Generally, the dispersion of nanoscale active materials should also consider the diameter or thickness of the active material in addition to the effective porosity, especially in composite systems where insertion or alloying occurs at different potentials via different mechanisms. By varying the dispersion and thus the effective porosity of the active material, hybrid electrodes involving electrochemically active current collectors can also offer some degree of stress-change buffering during deep charging and discharging.

IV. CONCLUSIONS

Using MBE, we detailed the growth of two distinct and welldefined types of Sn/SnO_2 core-shell NPs with crystalline metallic Sn cores and either amorphous or polycrystalline SnO_2 shells. In_2O_3 and Sn doped In_2O_3 (ITO) NP dispersions are also demonstrated using this approach. Electron microscopy and spectroscopy analyses confirmed a hierarchical core-shell structure of the SnO_2 NPs with different diameters to give a range of volumetric and areal densities of material. Lithium alloying with the reduced form of the NPs and co-insertion into the substrate (which also serves as current collector) showed reversible charge storage via alloying with Sn or In. The effect of lithium insertion and removal on different NP dispersions monitored by electron microscopy and cyclic voltammetry, showed that the electrochemical behavior depends on the relative size via the volumetric density of the NPs and their areal dispersion on the surface, in addition to their composition. The knowledge can be extended to a range of other active (nano)materials and systems so that active material arrangements and densities can influence performance, in addition to the structure, size, and composition. In cases where the material spacing is larger the volumetric expansion can be accommodated radially while maintaining mechanical and electrical contact. In this regard, co-insertion into the Si facilitates this process and is dictated by the active material dispersion. The compositional and structural engineering on SnO₂ and related materials using highly defined MBE growth as model system has allowed a detailed examination of the influence of material dispersion or nanoarchitecture on the electrochemical performance.

ASSOCIATED CONTENT

S Supporting Information

Details of the deposition process, optical and SEM images, and size dispersion analysis are provided. This material is available free of charge via the Internet at http://pubs.acs.org.

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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Appendix C

EPITAXIAL GROWTH OF VISIBLE TO INFRA-RED TRANSPARENT CONDUCTING In₂O₃ NANODOT DISPERSION AND REVERSIBLE CHARGE STORAGE AS LI-ION BATTERY ANODE



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Epitaxial growth of visible to infra-red transparent conducting In_2O_3 nanodot dispersions and reversible charge storage as a Li-ion battery anode

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Epitaxial growth of visible to infra-red transparent conducting In₂O₃ nanodot dispersions and reversible charge storage as a Li-ion battery anode

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Abstract

Unique bimodal distributions of single crystal epitaxially grown In₂O₃ nanodots on silicon are shown to have excellent IR transparency greater than 87% at IR wavelengths up to 4 µm without sacrificing transparency in the visible region. These broadband antireflective nanodot dispersions are grown using a two-step metal deposition and oxidation by molecular beam epitaxy, and backscattered diffraction confirms a dominant (111) surface orientation. We detail the growth of a bimodal size distribution that facilitates good surface coverage (80%) while allowing a significant reduction in In₂O₃ refractive index. This unique dispersion offers excellent surface coverage and three-dimensional volumetric expansion compared to a thin film, and a step reduction in refractive index compared to bulk active materials or randomly porous composites, to more closely match the refractive index of an electrolyte, improving transparency. The (111) surface orientation of the nanodots, when fully ripened, allows minimum lattice mismatch strain between the In₂O₃ and the Si surface. This helps to circumvent potential interfacial weakening caused by volume contraction due to electrochemical reduction to lithium, or expansion during lithiation. Cycling under potentiodynamic conditions shows that the transparent anode of nanodots reversibly alloys lithium with good Coulombic efficiency, buffered by co-insertion into the silicon substrate. These properties could potentially lead to further development of similarly controlled dispersions of a range of other active materials to give transparent battery electrodes or materials capable of non-destructive in situ spectroscopic characterization during charging and discharging.

S Online supplementary data available from stacks.iop.org/Nano/24/065401/mmedia

(Some figures may appear in colour only in the online journal)

1. Introduction

The marked increase in portable electronic device sales together with huge demand for flat screen high-definition televisions (HDTVs) are the primary driving forces behind the need for batteries and continued research into various materials and forms for transparent conducting oxides (TCOs) and similar coatings. Among TCOs, materials such as indium oxide (IO), tin oxide (TO) or tin-doped indium oxide (ITO) [1–6] and emerging alternatives such as graphene and

Cu or Ag NWs for example [7, 8] have been a consistent focus of research interest [9], where transparency in a useful visible range or indeed other wavelength regions of interest is matched by sheet resistances below 10 Ω/\Box [10]. ITO is the TCO used most often and its applications include thin film transistors [2, 6, 11–13], optical circuits [14], displays [15, 16], touch screens [17], and also transparent contacts in solar cells [5, 18-20]. Low sheet resistances are typically required for thin film solar cells and the solar photon flux-weighted optical transparency of ITO on glass is about 80%. The battery, however, a key component in the majority of portable electronics, has only very recently been demonstrated as a transparent device [21], and scope exists for the development of true see-through charge storage materials [22-28], where touch screens, solar cells and charge storage batteries can co-exist with transparent, or optically addressable form.

Their metallic properties cause most TCOs to be reflective in the infra-red, and for most TCOs a trade-off exists between transparency and conductivity, and sheet resistance for thin films [29]. In line with this, transparency in battery electrodes gives the opportunity for *in situ* and non-destructive diagnostic analysis of material changes during operation and the development of conductive current collectors and electrode materials that reversibly intercalate lithium with sufficiently high volumetric energy densities. This research could also allow the possibility of investigating kinetics of insertion mechanisms and the influence of certain lithiated phases of TCO materials on transparency and conductivity. This is critical for the analysis and development of both new battery materials and chemistries, but also for the examination of TCO materials for charge storage applications [30–34].

Transparency can be provided by using miniscule quantities of materials, or very thin films of uniform deposits [35], but, to have functioning volumetric energy densities, strategies to improve transparency while maximizing active material coverage of an electrode would be advantageous. The only formally transparent element in a typical battery is its electrolyte, which is soaked into a porous polymeric membrane and sealed with opaque materials between two sheets of metal. One method to allow transparency in a battery is to reduce active material dimensions below their optical absorption length; there are no currently used battery materials with absorption lengths that are sufficiently long in the full potential window in which the battery operates. Architectures of materials that influence optical properties have shown promise in this regard, but it does not automatically apply to small quantities of active materials or porous materials; a graded or step change in refractive index from high to low is typically required to minimize Fresnel reflections and to enhance transparency and its angular dependence to longer wavelengths. Varying surface coverage using dispersions that promote UV, visible and NIR transparency is also possible and the transparency window can be tuned by controlled variation of material dispersion, the variation in refractive index throughout the material and its inherent electronic and optical properties [2-6]. The recent demonstration of a fully transparent battery prototype [20] also involved testing of a continuous In₂O₃ thin film electrode.

During cycling, however, it was found that metal nanodots and lithium oxides and peroxides formed to such an extent that transparency was significantly reduced.

Here, In2O3 {111}-oriented crystalline nanodot dispersions have been successfully grown from an MBE deposition of an In layer and subsequent oxidation at elevated temperature. The method results in unique areal and size dispersions of nanodots varying in size from hemispherical 2 nm dots to larger, facetted \sim 500 nm crystals, on Si current collectors. Angle-resolved transmittance measurements confirm that the deposits maximize transparency in the infra-red, while maintaining characteristic transparency in the visible with a beneficial reduction in resistivity and sheet resistance; this overcomes the transparency limitations for In_2O_3 nanomaterials by index matching through a unique size dispersion and reduction in refractive index from the current collector to the electrolyte. The nanodots form as In@In2O3 core-shell crystals, and form a stable solid electrolyte interphase (SEI) layer and reversibly alloy with lithium allowing them to function as visible-to-IR transparent, visibly antireflective Li-ion battery electrodes. These properties could potentially lead to further development of similarly controlled dispersions or graded index (porosity) of a range of other active materials that facilitates enhanced transparency. The approach shown here is straightforward and scalable and may be applied to the fabrication of high quality optoelectronic, electronic and sensor devices and as a promising route towards visible-to-IR transparent conducting TCOs that reversibly store (electro)chemical charge, and also for the development of non-destructively, optically addressable materials and interfaces for in situ monitoring of electrochemical processes.

2. Experimental section

Before growth on silicon and glass substrates, the respective surfaces were cleaned using a standard RCA process. After rinsing, a second treatment in a H₂O₂:HCl:H₂O (1:1:5) solution was used to remove metallic and organic contamination. For evaporation of the In sources, a home-built MBE high-vacuum chamber, with a distinct effusion cell for In together with an electron-beam evaporator, was designed in cooperation with MBE-Komponenten, with calibrated growth rates. As detailed figure 1, a uniform layer of In metal was deposited at a rate of 0.1 Å $\rm s^{-1}$ at a substrate temperature of 400 °C, with precise control over the nominal thickness (see supporting information section S1 available at stacks.iop. org/Nano/24/065401/mmediafor the details of the deposition process). The associated activation energy for exponential film growth is $E_a = -1.435$ eV, which is consistent with the literature and calibration values for removal of indium atoms from the source.

Surface morphologies and the chemical composition of the nanostructured dispersions were investigated by electron microscopy using a Hitachi SU-70 SEM with an Oxford-50 mm² X-Max detector for energy dispersive x-ray analysis and an Oxford Instruments Nordlys EBSD detector with HKL Channel 5 acquisition software. TEM analysis was conducted with a JEOL JEM-2100F field emission microscope operating



Figure 1. (a) Schematic diagram of the MBE growth steps for In_2O_3 nanodot dispersions from In deposition, wetting layer formation and oxidative crystallization. (b) SEM image showing the final epitaxial In_2O_3 nanodot dispersion on Si. (c) SEM image showing small, hemispherical nanodots interspersed between larger crystals. (d) Tilted SEM image of larger, faceted crystals. The arrow indicates small crystallites growing hierarchically on the top surfaces of larger crystals. (e) SEM image of frustrated-facetted nanodots (which are also single crystals). The arrow indicates nanowire growth from the edges of the crystals.

at 200 kV, equipped with a Gatan Ultrascan CCD camera and EDAX Genesis EDS detector for atomic resolution crystal structure and composition examination. The size distribution of the nanodots was analysed using ImageJ [36].

X-ray photoelectron spectroscopy was carried out using a Kratos Axis 165 monochromatized x-ray photoelectron spectrometer equipped with a dual anode (Mg/Al) source. Survey spectra were captured at a pass energy of 100 eV, step size of 1 eV, and dwell time of 50 ms. The core-level spectra were an average of 10 scans captured at a PE of 25 eV, step size of 0.05 eV, and dwell time of 100 ms. The spectra were corrected for charge shift to the C 1s line at a binding energy of 284.9 eV. A Shirley background correction was employed, and the peaks were fitted to Voigt profiles.

Variable angle spectroscopic ellipsometry (VASE) was performed using a Woollam M-2000U variable angle spectroscopic ellipsometer over a wavelength range of 300–900 nm. Reflectance measurements were carried out in a Bruker FT-IR spectrometer IFS66/V on nanodot samples and ITO on glass. Different configurations of beam splitters, detectors and sources were used to cover the infra-red (5 μ m) to visible ranges. For angular resolved measurements, a NIR512 Ocean Optics spectrometer was used as a detector in a home-built reflectance/transmittance setup using a collimated xenon arc lamp as a light source.

To investigate the electrochemical insertion (alloying) and removal of Li, cyclic voltammetry measurements were carried out in a three-electrode setup using a Multi Autolab 101 potentiostat, using Li as both counter- and reference electrodes. All potentials, unless otherwise stated, are relative to Li^+/Li . Custom-built Swagelok-type cells were used with counter- and active material electrode separated by a

polypropylene separator soaked in a 1 mol dm⁻³ solution of LiPF₆ in EC:DMC at a 50:50 v/v ratio. The electrode was cycled at a scan rate of 0.5 mV s⁻¹. Afterwards, the electrode was carefully washed in acetonitrile and a 10^{-4} mol dm⁻³ solution of acetic acid to remove the electrolyte residue.

3. Results and discussion

Figure 1(b) shows an SEM image of the nanostructures grown by MBE of indium in an oxygen atmosphere. The MBE deposition was conducted at a rate of 0.1 Å s⁻¹; such a slow deposition rate is typically used to ensure initial seeding of the substrate with a metallic seed layer [37]. Subsequent oxidation in ambient air allows the formation of a specific size dispersion of oxide crystals after In growth, as shown in figure 1(b). The dispersion consists of larger crystals interspersed with a high density of very small (~2–5 nm) nanodots (figure 1(c)). Some of the larger crystals have clearly developed facets (figure 1(d)), generally growing in a deviated hexagonal shape (figure 1(e)). High resolution SEM images of the nanodots show that a number of small crystallites are found on the top surfaces of the crystals in a hierarchical fashion (figure 1(d)).

The initial formation of a dewetted liquid In 'layer' comprising a high density of metallic nanodots (maintained in a liquid state on a substrate heated to 400 °C), and the progressive nature of their deposition, allows hierarchical nanodot seeds to form on the high energy facet edges of the larger crystals. In some cases we observe subsequent growth of long, straight In₂O₃ nanowires (see figure 1(e)) with lengths reaching hundreds of nanometres and diameters not exceeding the diameter of hierarchical



Figure 2. (a) SEM image of the In_2O_3 nanodots. Arrows indicate the location of the points at which the EBSD pattern was recorded. (b) Pole figure showing the relative orientation distribution of {111} termination of the nanodots. (c), (d) Kikuchi band overlays recorded from the regions indicated in (a). The cross on each image indicates the orientation of the planes at their measurement point. (e) Two In_2O_3 crystals imaged during coalescence. (f) Fully coalesced crystal with no discernible boundary between individual merged nanodots.

dots. The nanodot dispersions (and also the progressively nucleated dots on dots) form by thermally driven (substrate heating) ripening, coalescence, oxidation crystallization, and continued progressive In deposition.

It was previously shown by Hao et al that the surface energy of the main faces during growth of In₂O₃ crystals (and many crystals in general) follows a gradient in surface free energy and subsequent growth rates, i.e. γ [111] < $\gamma[100] < \gamma[110]$ [38]. In low saturation MBE deposition, these relationships greatly influence the final shape of the nanodots. We used electron backscattered diffraction from the terminating surfaces of both facetted and non-facetted nanodots to quantify their epitaxial relationship to their substrate and also their relative orientational distribution. The measurements were taken at 70° tilt (figure 2(a)) and a pole plot of the nanodot texture orientation distribution (figure 2(b)) was formed by monitoring the Kikuchi diffraction patterns from the top surface lattice planes of the nanodots shown in figures 2(c) and (d); the growth orientations from 3D crystal symmetry are visible as diffraction 'paths' in orientation space. The measurements confirm a dominant {111} surface termination for the nanodots. Interestingly, for both facetted and non-facetted crystals, their terminating planes are near identical, as are their overall heights of ~ 50 nm; see figure 1(d). Any 'flow' of material pre-oxidation occurs almost entirely parallel to the substrate and thus a perfect facetted crystal is not required to give an iso-terminated nanodot dispersion.

Being extremely sensitive to tilt or variations in the top surface of the crystals, the corresponding pole plot shown in figure 2(b) was acquired to map the distribution of textures around major growth directions. The texture pole plot is centred around the {111} directions. It is clear from the texture distributions in figure 2(b) that the particles grow with horizontal hexagonal {111} planes, parallel to the (100) substrate of the silicon wafer. The three areas of high-frequency distribution located around 70.5° are related to the similarity between {111} plane equivalent planes: (111), (111), and (111) as well as (111) growth directions. The In_2O_3 nanodots were epitaxially deposited as metal nanodot seeds and subsequently oxidized in air, and EBSD analysis confirms that their oxidation to In₂O₃ nanodots results in a final single crystal structure with the slowest {111} growth planes parallel to the substrate. Pole plots of the dispersion of the texture of the nanodots around the remaining two pole directions are shown in supporting information figure S2 (available at stacks.iop.org/Nano/24/065401/mmedia), indicating angular relationships between growth planes and polar directions.

A threefold symmetry with three distinct peaks of similar intensity was observed in the pole figure of {111} reflections and consists of the central [111] zone axis (centre pole) and $[\bar{1}11]$, $[1\bar{1}1]$ and $[11\bar{1}]$ at 70.5° from the centre pole. Different rotations of the growth plane can be seen in the equivalent cell representations in supporting information figure S3 (available at stacks.iop.org/Nano/24/065401/mmedia), acquired from individual diffraction measurements from the surface of a number of separate nanodots. The growth rate perpendicular to {111} planes is slower than for {110} and {100} planes. As a result, growth in the lateral direction progresses faster than in the vertical, which we find regardless of the degree



Figure 3. (a) X-ray core-level photoelectron spectra of O 1s and In 3d of the In_2O_3 nanodot dispersion. (b)–(e) EDX maps of an In_2O_3 nanodot showing distributions of oxygen, indium and silicon respectively.

of crystal faceting. Such an arrangement results in formation of truncated octahedral structures, that coalesce with their nearest neighbours during growth (see figure 2(e)). In such cases, the formation of non-facetted particles can results from reflow of metallic In with next nearest neighbours (necking and ripening), which was captured after solidifying oxidative crystallization in figure 2(f).

One of the important factors in MBE growth of oxide films, and particularly when these materials undergo volume expansion during uptake of Li ions during charging, is the quality of physical contact to the substrate, indicated by the lattice mismatch $f = (a_f - 2a_{sub})/2a_{sub}$, where a_f and a_{sub} are the lattice constants in the growth plane of $In_2O_3(111)$ and Si(100), respectively. The mismatch parameter should be as low as possible to minimize the additional strain placed on the deposit due to electrochemical reduction from In₂O₃ to metallic In and subsequently during volumetric expansion accompanying electrochemical Li alloying. For In₂O₃, the (111) lattice parameter is 1.074 nm, leaving a mismatch of 1.13% between a_f and $2a_{sub}$ (for a Si(100) lattice spacing of 1.086 nm). The resulting strain between the nanodot-substrate interface is low; the surface free energy of $In_2O_3(111)$ is much lower than that of Si(100) [39]. This orientation offers the least possible interfacial strain between In_2O_3 and Si(100). The deposition of the first few atomic layers of In results in complete wetting of an area of the surface according to the Frank-van der Merwe (FM) growth mechanism. Subsequent deposition of adatoms causes accumulation of strains and leads to a change of the growth mechanism from FM to Stranski-Krastanov (SK), resulting in three-dimensional islands on a two-dimensional wetting layer, since the liquid In dewets to form droplets on the surface as the adatom concentration shifts the metastable deposition to an unstable condition [40]. This qualitatively also explains why we consistently observe nanodots beginning to form via a hierarchical mode with smaller length scales on top of crystallizing dots. Although the lattice constant is formally the

same for In_2O_3 on In_2O_3 , this only holds when the orientation of the crystal deposit matches that of the underlying dot; when this is not the case, strain-relieved dots on dots are possible.

The compositions of the MBE nanodots were determined using XPS and EDX. Figure 3(a) shows the In 3d and O 1s core-level photoelectron emission spectra of the nanodots. Core-level emission corresponding to In 3d_{5/2} and In 3d_{3/2} were observed at 444.34 and 452.03 eV (referenced to the C 1s core level of 284.9 eV, see supporting information, figure S4 available at stacks.iop.org/Nano/24/ 065401/mmedia), indicative of In₂O₃. The peak at 444.34 eV shows hyperfine levels, one at 443.9 eV from In(0) and at 445.1 eV related to In 3d_{5/2} from In₂O₃. Core-level emission from O 1s was composed of two spectral bands at 531.2 and 529.6 eV, which can be deconvoluted into three components consistent with In₂O₃. The signal at 531.2 eV is attributed to lattice oxygen, while that at 529.6 eV stems from In(OH)₃, which is known to form on exposure of In₂O₃ to water vapour. Corresponding EDX maps of In and O (shown in figures 3(b)-(e) corroborate the oxide composition of the nanodots.

3.1. In₂O₃ nanodot dispersions and electrode coverage

To determine the coverage of the nanodot dispersions, we analysed their size distribution by factoring the anisotropy in non-hemispherical shape. Due to the large variance in sizes and asymmetrical shapes, the Feret diameter (the distance between two parallel tangents at arbitrary angle, defined in figure 4) is used to describe a shape-nulled size distribution, shown in figures 4(a)–(d). Complete Feret data provide a rich source of information on particle shape that allows determination of particle shape descriptors, and the details of this analysis are outlined in the supporting information, section 2, and from image analysis of nanodot distributions shown in figure S5 (available at stacks.iop.org/Nano/24/065401/nmedia).



Figure 4. Feret diameter distribution histograms for In_2O_3 nanodots. (a) Nucleation and ripening mode, (b) ripening and coalescence mode. The inset indicates how the Feret diameter of a nanodot is defined for this work. (c) SEM image showing particles with growth distribution described in (a), and (d) SEM image showing nanodots with the growth distribution described in (b).

Figure 4(a) shows the distribution of In_2O_3 nanodots interspersed between the larger surface crystals (figure 4(b)). At the end of growth, these particles coarsen during dewetting of the liquid In during progressively deposited and crystallizing nanodots. In this case, the deposition has a dynamically changing free surface area. The overall bimodal distribution, confirmed by the existence of two peaks in the histogram in figure 4(d), results in a high degree of surface coverage, with the nanodots at the ripening-coalescence stage of growth comprising $\sim 60\%$ of the sample surface, and $\sim 10\%$ of the sample surface covered with nanodots in the nucleation-ripening stage of growth. The overall mass distribution is estimated to be $\sim 70 \ \mu g \ cm^{-2}$. Figure 4(d) represents the final size distribution from oxidative crystallization. The size distributions at the respective length scale as seen by SEM are shown in figures 4(c) and (d).

The existence of two primary peaks in the size distributions suggests a two-stage overall growth mechanism (supporting information section 3 available at stacks.iop.org/Nano/24/065401/mmedia) [41]. First, nucleation and ripening of adatom species from MBE results in the formation of small nanocrystals on the surface of the silicon, with a maximum eventual average size determined to be \sim 30 nm. Continuous ripening growth of the nanodots results in their growth and transition from nucleation and ripening, to ripening, coalescence and further growth (including a second phase of nucleation on the surface of nanodots already on the surface, as shown in figure 1(d)). The dispersion with two primary

length scales allows a particular in-plane porosity of $\sim 20\%$ with maximal associated areal coverage of the substrate.

3.2. Enhanced IR transparency of the In_2O_3 nanodot dispersions

In₂O₃, as a wide bandgap semiconductor ($E_g^d \sim 3.6 \text{ eV}$; $E_g^i \sim 2.6 \text{ eV}$), has a transparency that is fundamentally interlinked with its conductivity; the transition occurs on or around its plasma frequency related to the electron density according to the Drude model by $\omega p^2 = nq^2/m^* \in_0$, where m^* and q are the effective mass and charge of an electron, and \in_0 the high-frequency permittivity of free space. For the single-sided In₂O₃ nanodot dispersion, the transmission is limited by Fresnel reflection due to the step discontinuity in refractive index at the rear flat surface [35, 42, 43], depicted for an ITO film on glass and the nanodots on silicon in figure 5. The refractive index of as-received Si(100) substrate is 3.42 and that of In₂O₃ is 1.46 at the interface, which reduces to 1.24 at the nanodot–air interface measured by spectroscopic ellipsometry (see figure 5).

The nanodot-air interface is reasonably uniform and analysed as a porous Cauchy layer [44, 45]. In our case, the NP nanodot dispersion 'layer' acts as a porous thin film (considering the NP dispersion and their size dispersion), whose refractive index and extinction coefficients, shown in figure 5, are different with respect to a bulk film (n = 2.4), forming a several-step reducing index on the material-containing side of the electrode. The reduced



Figure 5. Cauchy dispersion of refractive index and extinction coefficient of the In_2O_3 nanodot dispersion, shown schematically in the inset, on Si(100), measured by spectroscopic ellipsometry. The inset shows the variation of refractive index for the nanodot dispersion as a function of wavelength.

nanodot effective refractive index reduces Fresnel reflection within the nanodot dispersion compared to a flat ITO film by reducing the step change in index, enhancing transmission and antireflection. This aspect is crucial for consideration of other active materials in transparent battery investigations. While many composites and nanoscale materials can be deposited with controllable porosities, to enhance transparency and reduce reflection, a graded or step reduction in the index from the current collector to the electrolyte interface is required.

Angle-resolved transmission measurements of the nanodot dispersions and an ITO thin film were determined and summarized in figure 6. The position of the plasma frequency indicated by ω_p red-shifts and the reflectance of the In₂O₃ nanodot dispersion and the ITO thin film decreases with angle near their respective plasma frequencies, shown in figure 6(a), while the reflectance decreases substantially after the plasma frequency relative to that before the onset of the plasma frequency. These layers offer excellent visible-infra-red transmission, and also antireflection properties, as seen in the optical images in figures 6(b) and (c). The red-shifting of the entire angle-resolved spectrum for the nanodot dispersions is also seen in figure 6(a), where at visible wavelengths the transmission varies from 55% at near incidence and at 40°, and importantly, remains 87% transparent at wavelengths up to 4 μ m (figure 6(a)).

The corresponding angle-resolved reflectance of an ITO film in figure 6(d) confirms a blue-shift of the plasma frequency with increasing angle, but even at normal incidence the comparison ITO film is similarly conductive but much less transparent at IR wavelengths. The nanodot dispersions allow shifting the maximum in transmission (and minimum in normal reflectance) to longer wavelengths while maintaining identical transmission in the same energy window to commercial ITO on glass (figure 6(a)), and with the added benefit of a lower effective sheet resistance into the IR.



Figure 6. (a) Transmittance of the In_2O_3 nanodot dispersions and that of an ITO thin film of similar nominal thickness. Inset, polar plot of the angle-resolved transmission of the nanodots at visible wavelengths. (b), (c) Optical images of the In_2O_3 nanodots showing antireflection characteristics in the visible range. (d) Angle-resolved reflectance of an ITO film.

3.3. Reversible electrochemical Li insertion

The ability of the In₂O₃ nanodot dispersions to reversibly intercalate or alloy Li, and its insertion and removal potentials, were examined using cyclic voltammetry. Figure 7(a) shows the cyclic voltammetric response of the Li | Li⁺ – electrolyte | $In_2O_3(111) | Si(100)$ system. For this cell the cathodic process involved the insertion of Li into In₂O₃ to form a Li-In alloy (charging) and the anodic process follows Li extraction or dealloying (discharging). A related process is known to occur for Li alloying with Sn [46], but there are limited investigations of Li insertion into In-containing materials [47]. During the first negative scan, two weak irreversible peaks appear at 1.2 and 0.8 V from the reduction of In₂O₃ to In⁰ (see supporting information, section S4 (available at stacks.iop.org/Nano/24/065401/mmedia) for electrochemical reduction and alloy processes). Once reduced from In₂O₃ to In⁰, the indium is never oxidized again in the potential range examined. Zhou et al [33] have shown reoxidation, but cycled the anode to over 3.5 V, a voltage window typical of cathode materials. We cycled the anode at 0-2.5 V, a potential window below the oxidation potential of In⁰ (2.7 V versus Li⁺/Li) [48].



Figure 7. (a) Cyclic voltammetry of In_2O_3 nanodot electrodes between 0.0 and 2.5 V. The inset shows the corresponding integrated charge versus voltage curve for five cycles. (b) Cyclic voltammograms for first and second cycles highlighting the SEI layer formation. Arrows indicate phases formed during insertion and removal processes. SEM images show the nanodots before (c) and after cycling (d).

A large reversible peak appears at 0.4 V from the alloying process of Li insertion into In⁰. The rate of this reaction, indicated by the measured current, is found to reduce with increasing cycle number. The reversible Li insertion–removal processes occurring in a voltage window of 0.4–0.7 V are described by $zLi^+ + ze^- + In \leftrightarrow Li_zIn (0 < z \le 4.33)$. For Li | Li⁺ – electrolyte | In₂O₃(111) | Si(100), buffering of polarization effects is provided by the Si current collector, which can accommodate the highest Li storage capacity of all anode materials [49, 50].

The free surface area (~20%) between neighbouring particles allows Li to be co-inserted into the silicon current collector, which is indicated by the existence of two additional peaks in the anodic part of the insertion reaction, at 0.32 and 0.5 V. These peaks relate to the removal of lithium from silicon [49]. Figure 7(b) shows the first two cycles of this system, and we note that the reduction of In₂O₃ and related alloying processes dominate over Li_xSi phase formation and insertion of lithium into silicon in the first cycle. This co-insertion into the active material and current collector equilibrates after the second cycle. The increasing rate of Li–Si formation can be attributed to an activation effect [51] linked to lithiation-induced volumetric expansion that causes cracking and the exposure of unreacted material to the electrolyte. Successive cycling then allows more lithium to intercalate into silicon, providing a degree of stress buffering for the In alloying process without requiring carbon, conductive additives or polymeric binders. The rates of alloying and dealloying, insertion and removal, are consistently balanced in each cycle (figure 7, inset), and, apart from charge associated with SEI formation and reduction to In^0 , negligible charge fading is found for all processes in all subsequent cycles.

During co-insertion into the active material and current collector, both of which are reversible, the variation in volumetric changes and accompanying effects is considered. The SEM images in figures 7(c) and (d) show the condition of the electrode surface before and after cycling. Using the size distribution analysis (cf. figure 4), the reduction in average nanodot size is 30-50%. The brightness of the secondary electron emission stems from a reduced conductivity of the Li_xIn phase. As the nanodots are epitaxial, their adhesion to the substrate is excellent, and lithium insertion is not likely to occur directly under each nanodot, unless they are extremely small. In this case, we note (supporting information, figure S6 available at stacks.iop.org/Nano/24/065401/mmedia) that some of the smallest nanodots are removed from the substrate, but this occurs when their diameter is less than the change

in volume of the near surface of the silicon. The molar volume of In^0 is a factor of 2.45 less than that of In_2O_3 , and by comparison to the size reduction observed it is clear that no significant volume change effects occur in stable In^0 nanodots⁸; faceting related to the structure of In_2O_3 is also lost during electrochemical reduction to the pure metal.

Previous reports show that the electrochemical performance of In₂O₃ is strongly influenced by its microstructure and composition [32]. Here, the dispersion of the nanodots, while permitting transparency and conductivity into the IR region, also allows lithium insertion into the current collector, and remains structurally stable due to strong epitaxial adhesion and lithium co-insertion buffering by the silicon current collector. The partial porosity of the variable size nanodot distribution prevents stress build-up in the In⁰ (when reduced from In_2O_3) and promotes optical transparency. The removal of the smallest nanodots by volume expansion of the underlying silicon does not greatly affect the gravimetric energy density, and it serves to buffer polarization of the Li_x In by reversibly inserting Li⁺. Detailed size distribution analysis before and after cycling shows that some volume expansion occurs in the alloyed Li-In phase, but it does not affect the structural integrity of the electrical contact to the current collector.

4. Conclusions

The unique size dispersion of In_2O_3 nanodots prepared by MBE deposition of indium and subsequent oxidation in air at elevated temperature has allowed the development of a Li-ion battery electrode with enhanced IR transparency without sacrificing electrical conductivity, with lithium co-insertion processes with high Coulombic efficiency, that results in stable cycling and charge storage. The In2O3 nanodots show bimodal size distribution confirming a two-step epitaxial growth mechanism, and good surface coverage with unique shape and (111) crystalline orientation. The nanodot dispersions were successfully shown to reversibly alloy with lithium after reduction to metallic indium; the specific size distributions allow reversible lithium co-insertion with a silicon current collector as well as the active material on the surface. Moreover, the specific size offers excellent antireflective properties and enhanced transparency reaching $\sim 87\%$ at 4 μ m. By controlling a reduction in refractive index form the current collector to the air or electrolyte interface, active charge storage materials can show improved transparency over wider wavelength ranges. This potentially allows for further development of transparent battery electrodes or the possibility for in situ non-destructive spectroscopic monitoring of structural and electrochemical processes.

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⁸ It has been found that translational, compressive and other forces during cell assembly and disassembly cause some of the active material to detach.

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