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Colour-Coded Batteries – Electro-Photonic Materials Circuitry for Enhanced Electrochemical Energy Storage and Optically Encoded Diagnostics

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Abstract

For consumer electronic devices, long-life, stable, and reasonably fast charging Li-ion batteries with good stable capacities, are a necessity. For exciting and important advances in the materials that drive innovations in electrochemical energy storage (EES), modular thin film solar cells, and wearable, flexible technology of the future, real-time analysis and indication of battery performance and health is crucial. Here, developments in colour-coded assessment of battery material performance and diagnostics are described, and a vision for using electro-photonic material architectures and all-optical probes to assess, characterise and monitor the processes in new materials non-destructively in real time, are outlined. By structuring any cathode or anode material in the form of a photonic crystal, or as an 3D macroporous inverse opal, colour-coded 'chameleon' battery strip electrodes may provide an amenable way to distinguish the type of process, the voltage, material and chemical phase changes, remaining capacity, cycle health and state of charge or discharge, or existing of new materials in Li-ion or emerging alternative battery types, simply by looking at its colour (change).

Keywords: energy storage, materials science, optics, batteries, photonic crystals

Engineering improved function and performance in new Li-ion battery materials

An ongoing theme in battery materials research has been to alter composition, structure and size to maximize the energy densities and power densities of batteries,^[1] in order to feed our growing need for portable power and the move to EVs. Lithium-ion battery technology has been part of the solution in this regard because it combines greater specific energy density and specific power density than other types of batteries or electrochemical supercapacitors.

Currently, as many consumers appreciate, Li-ion batteries are in some cases heavy when it comes to portable electronics, and could benefit from better capacities or energy density.^[2] The need to charge a battery every day for these devices through average use is now commonplace and expected, and with ever increasing functionality expectations from consumers, the need for extra power is outweighing improvement in battery capacity. Capacities can of course be increased, but so too does the bulk design, size and weight of the battery – this can become a problem for thin, svelte modern designs of smartphones for example, and also for uni-body, single block phones where the battery is often not readily replaceable.

Today's batteries can suffer from capacity fading^[3] and reduction in battery life that often results from electrolyte reactions, increases in overall cell resistance, and many other factors.^[4] Disintegration of battery material after many charge-discharge cycles is also an issue for batteries designed to store a lot of charge, or provide full depths of discharge for hundreds of cycles – the material itself can affect the stability, reversibility, and the voltage, and so the energy and power of the cell.^[5] The insertion/extraction of charge and mass into/from an active material in a rechargeable battery is accompanied, typically, by a volume change in that material^[6, 7]. In some materials, this is linked to the irreversible capacity loss during the very first charge-discharge cycle with subsequent knock-on effects in terms of cell efficiency during cycling, depending on the rate of charge or discharge.

Lithium-ion electrodes store electrochemical charge by intercalating lithium ions into the lattices of crystalline solids and into disordered vacancies within amorphous hosts ^[8]. Some materials alloy reversibly with lithium. For anodes, low voltage reactions also involve electrolyte decomposition that forms a stabilizing layer on the anode surface in many cases, which is beneficial for preventing lithium dendrite short circuiting when operating at high rate (large power demands),^{[9] [10]} in addition to other uses. The cathode materials (the higher voltage side of the battery) also reversibly accommodate a lot of Li, and the crystal structure of these materials needs to have suitably sized voids or regions within the crystal lattice to accommodate volume swelling and contraction each time the battery is discharged and charge, without disintegrating.^[11] New materials have been developed in recent years, each with some improvement under some operation conditions, and so considerable progress is being made in tackling capacity fading, reversibility limitation, voltage stability, reduction in overall cost and of course, safety.^[12]

To tackle the charging rate issue in a manner that allows the active material to maintain structural integrity, a good electrochemical conductivity and capacity, battery researchers have considered using porous materials that wet a greater volume of electrolyte, so that the diffusion distance of Li-ions is reduced both in the electrolyte, and in the material if it too is reduced to nanoscale dimensions.^[13] Other methods involve overlayers that shuttle Li ions to the preferable crystalline facets on some materials.^[9] Essentially, these limits on ionic mobility are at least partially overcome by fabricating battery components that have solid-state ion diffusion path lengths on a nanometer-length scale ^[14]; it is their arrangement that in principle allows the electrolyte to reach all the active surface. In larger, bulk-like materials, the rate limiting step (at a given voltage) is the much slower movement of Li ion into the crystalline structure. Even under a chemical potential that promotes ionic insertion, some crystal facets prefer to uptake Li-ions at a faster rate than others.^[15] Thus, alleviating

the slow kinetics of solid-state ion diffusion into bulk electrode materials and improve capacity retention needs to consider crystal growth and design, some form of beneficial porosity to infill electrolyte and provide space for the swelling materials during discharge without breakup (physical and electrical disintegration).^[16] We recently surveyed many promising materials and nanoscale sizes for emerging battery constructs, and engineering material structure from the atomic scale to the electrode scale is crucial for future advances in energy storage ^[12, 13]. The ordered porous 3D material architecture ^[17] provides definable short electron and ion transport lengths in the active material and electrolyte (yielding high-power density) while maintaining a high volume of active material (maintaining high-energy density). ^[18-20] Charge rates from several hundred C up to 1000 C (~ 4 s at the charge rate used) for lithium-ion chemistries could potentially be achieved, enabling fabrication of a Li-ion material that can be fully charged in a matter of minutes or seconds.^[21]

Knowledge of ordered architectures for improving charging rates, while delivering high energy densities over sensible usage times and/or device demands, will help support the development of bespoke, device oriented, moulded battery materials for Li-ion or indeed alternative energy storage technologies^[22] – the materials, their structural and electrochemical behaviour, and structuring to maximize response to lithiation, are key to advanced EES systems,^[23] particularly for the advent of wearable or stretchable textiles that need power sources.

Recent efforts on unconventional battery designs ^[18] have worked towards developing battery technologies that are not defined by their form factors of the devices they power. Some examples are thin and flexible batteries ^[24, 25], stretchable textile energy storage ^[26, 27]^[27], paper batteries, microbatteries and transparent batteries. ^[28] The development of smart devices/objects has further generated interest in self-powered electronics with integrated storage. Such energy conversion-storage hybrids may require forms of charge storage that

can be integrated directly into the object or surface of choice – new materials and methods will be required to transition to non-planar, flexible or curved batteries,^[25] and opportunities exist to encode state of charge, health check, power check capabilities and performance diagnostics into the battery itself. Several excellent reviews ^[13, 29-31] and reports highlight the shortfall in knowledge on non-planar battery designs ^[11]. 3D porous materials ^[32, 33] have received recent attention ^[34], but aside from promising performance, there are many properties of these ordered materials that can provide very important information on their response to charging and discharging.

So, here I describe the development of cross-cutting methods that address materials science challenges in Li-ion and emerging alternative battery research, while providing a vision for the involvement of optics and photonics in performance assessment of new electrochemical energy storage (EES) materials that are fabricated as photonic crystals. Potentially new and useful scientific and technological tangents are conceptually feasible using 3D structuring and integration of electrode materials in an electro-phonic architecture. These materials permit optical readout of encoded electrochemical state by probing the variation in structural periodicity, development of disorder, index contrast, electrical and optical conductivity, and diffraction of visible to near-IR light. This provides an accurate and very sensitive assessment of the battery material, and a performance assessment and materials health or diagnostic toolset that uses the imposed photonic crystal arrangement to gauge the electrochemical response under essentially any working condition. For new compositions or materials, primary challenges in their behaviour may be monitored in real-time. With the coupling of optical physics and materials electrochemistry, electro-phonic battery materials circuitry can fundamentally describe the very mechanism of energy storage or conversion. By comparing with the state of the art in the field and our recent work in electrochemical and

optical materials development, opportunities for skin-type energy storage solutions or chameleon battery indicators are described.

Colour-coding materials science for electrochemical energy storage

For materials that in nature, define the colours of many insects, marine life and bird feathers,^[35-38] and that have been adopted in the optics communities as photonic crystals, there is as yet no overlap for exploiting the optical functionality of photonic crystal-like materials with compositions engineered to have excellent Li-ion performance. Inverse opal PhC's^[23] reflect certain wavelengths at particular angles depending on the refractive index contrast and periodicity of the material.^[39] Li insertion and removal at different rates, alters the crystal structure causing a variation in the index contrast and ordered periodicity from compositional (and thus dielectric) changes and structural distortions (periodicity and order variation) of the material, (see Fig. 1).^[40, 41] This has not been measured *in-situ* for any material. Specifically, materials whose capacity retention is inherently linked to a contribution from material disorder, and those for which the mechanism is a hetero- or homogenous (de)lithiation, will undergo a refractive index contrast caused by a change in dielectric constant with various degrees of lithium uptake, if they are prepared in a macroporous ordered arrangement – the reversible processes can be interrogated and mapped.

Basic information on cathode or anode performance through correlation of structural changes^[42] to cycle life can be gleaned non-destructively using the optical phenomena associated with arranging any material in a ordered, porous arrangement. Mitigating against strain and stress in new Li-ion or EES materials is of prime importance to safe and stable capacities if applied to long term cycling Li-ion batteries – the degree to which ordered porosity alleviates these problems can be determined or re-examine such that the true role of porosity vs crystal structure for longevity can be uncovered.^[19] Stress mapping and other

mechanical properties can be assessed optically by arranging the material and the interface with (transparent) current collectors in inverse-opal form.

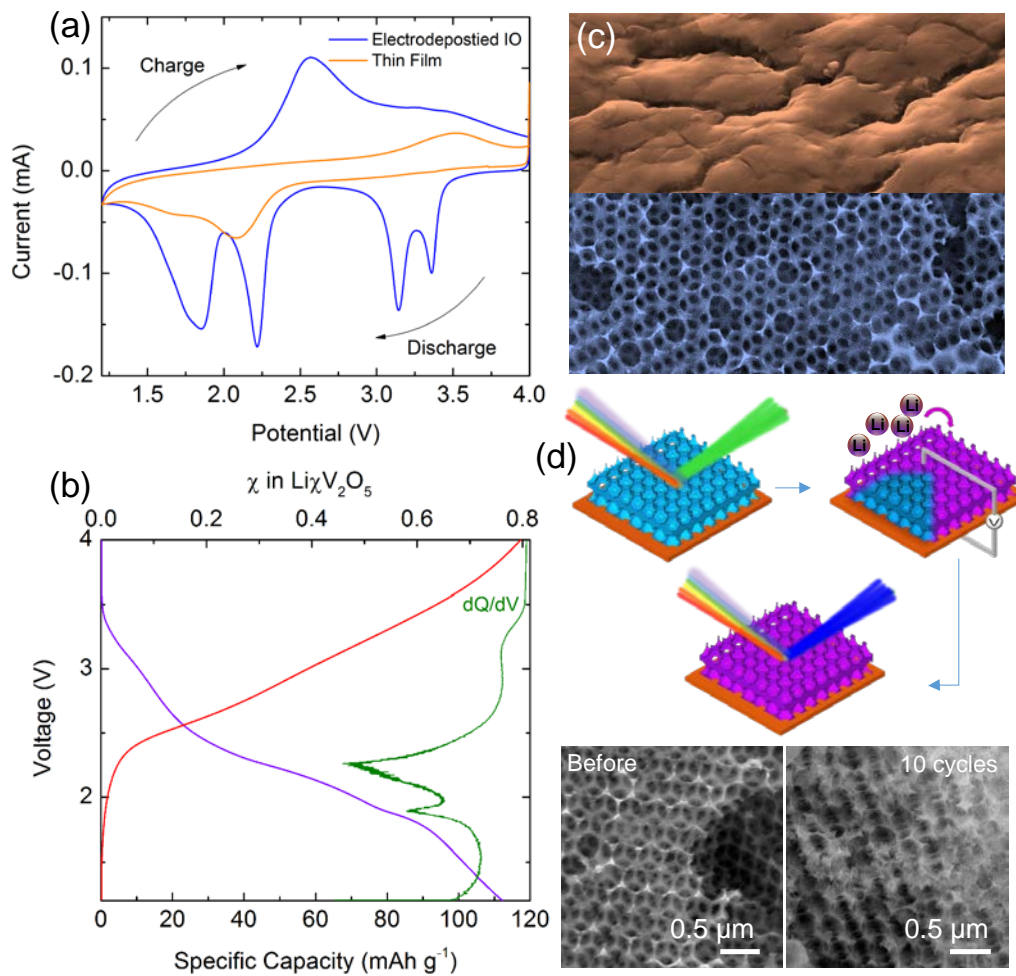


Figure 1. (a) Cyclic voltammograms of electrodeposited inverse opal V_2O_5 and thin film (non-templated) material. In the potential range 4.0 – 1.2 V (vs, Li^+/Li), the IO facilitates efficient intercalation and phase changes in the nanoscale crystals of the IO. (b) Typical charge-discharge curves from IO V_2O_5 showing negligible capacity fading with cycling. (c) SEM images of a planar and IO V_2O_5 Li-ion cathode material. (d) Schematic representation of Li-induced variation in IO periodicity, dielectric and index contrast influence on 2D Bragg diffraction or 3D photonic band gap changes during charge and discharge.

In essence, innovative and important scientific advances in EES using photonic band gap materials offers the possibility to interrogate many effects that are possible for any material system in EES, such as:

- (1) Uncovering the degree of material volume change depending on the degree of lithium uptake, and its spatial homogeneity, and the effect of the rate of lithiation (charging and discharging) in ultrafast charging battery materials
- (2) Monitoring the change in visible diffraction and photonic band gap modification due to changes in:
 - (i) Material periodicity in the ordered porous cathodes or anodes – exploiting physics of photonic crystals to interrogate electrochemical processes
 - (ii) Contrast in refractive index due to dielectric constant modification
 - (iii) Optical conductivity variation – linking optics to electrochemistry and cell resistance, identifying capacitance charge versus intercalation-mode charge storage, and deconvoluting electrochromism and photoconductive effects
- (3) Defining the depth of discharge, and state of charge and capacity health visually from changes in light-matter interactions and the bandwidth of forbidden frequencies of light caused by the PBG in the structure EES material. These parameters can be assessed without required additional power from the battery to cause, separately, a chemical and a structural colour change indicative of the current state of charge, depth of discharge, capacity (when calibrated to a known change in index contrast, morphology variation and/or photonic band gap (PBG) shift/spectral width) and real-time voltage stability.

In principle, *operando* spectroscopic methods that probe electro-photonic materials circuitry in the form of a new anode or cathode materials might be able to address and characterise many questions in battery materials research in general, and be applied to range of material-based EES technologies. ^[43]

Optical techniques applied to functioning battery materials *in-situ* are rare in the literature. We have used expertise from optics and physics ^[44] to chemical spectroscopy and

crystal structure photonics and phononics to investigate the properties of many nanomaterials and hybrid composites/assemblies,^[43-45] and recently demonstrated IR transparent battery materials based on hierarchically sized nanocrystal coated electrodes,^[28] and the link between optical transmission and the lithiation of the electrode (see Fig. 2). Only recently, photonic crystals have been used to enhance the photo-absorption characteristics of perovskite halide solar cells using structural colour to tune the absorption across the entire visible spectrum^[46], and proven methods for photonic crystal transfer to DSSC's^[47] and coupling to TiO₂ based solar cells systems^[48] have shown their advantages – adapting the knowledge of photonics and geometrical optics is an approach that can tackle critical questions in materials science for EES.

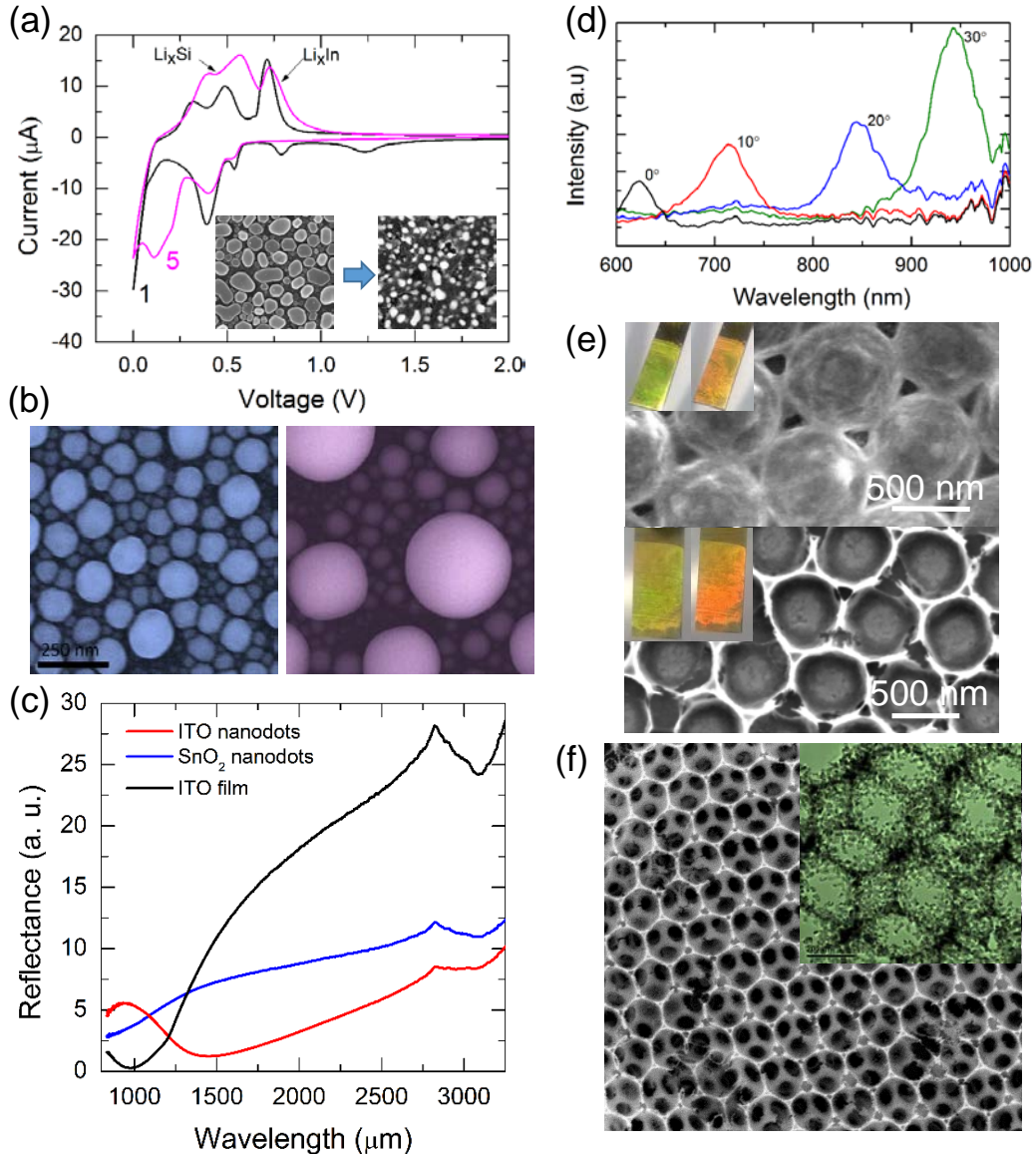


Figure 2. Cyclic voltammograms of lithium alloying in In_2O_3 nanocrystal Li-ion electrodes with hierarchical size distributions, shown in the SEM images in (b) with a corresponding SnO_2 nanoparticle electrode. (c) Optical reflectance of antireflection indium tin oxide and SnO_2 nanocrystal distributions. Transparent Li-ion electrode facilitate in-situ optical spectroscopy of phase and morphology change by monitoring changes in reflectance, development of absorbance beyond the plasma frequency as the material becomes more conductive, and scattering effects from morphology changes. (d) Angle-resolved reflectance measurements of the artificial opal template exhibiting tilt-variable structural colour. (e) 2D hollow sphere arrays and 2D monolayer inverse opal V_2O_5 materials and (inset) associated diffraction of visible light whose colour depends on the tilt angle, and amenable to colour change variation as a function of the state of charge/phase change. (f) SEM and TEM (inset) images of a SnO_2 inverse opal electrode material.

The type of EES mechanism can also be identified for new materials under a range of electrochemical parameters. It constitutes a powerful method for examining the response of

the material to operation via coupled electrical and visible-to-near infrared spectroscopies. Colour-coded ‘chameleon’ battery materials in the form of indicator thin films strips can also facilitate real-time diagnostics by comparison to planar deposits of the same electroactive material, by quantifying the voltage associated with electrochemical processes of the battery under test, and phase changes and specific capacity by looking at its ‘structural’ colour – a useful tool-set for *in-situ* and *operando* profiling of the electrode processes during any type of charge-discharge tests on an IO or photonic crystal electrode.

The ability to monitor battery materials during operation, non-destructively, would be very advantageous and is in principle applicable to any material that can be infilled into an artificial opal or photonic crystal template formed by assembly of polymer or silica spheres, or through periodically patterned substrates or current collectors,^[49] and we have recently reviewed the many uses of photonic crystal and templated materials for a whole range of applications.^[50, 51]

In addition to tracking changes in periodicity, order, index contrast, rate of lithium insertion (thin versus thick films, variation in gravimetric or volumetric loading etc.) and other parameters that are inherent in the definition of an inverse opal or photonic crystals, EES mechanisms may also imbue specific spectroscopic signatures due to the nature of the energy storage mechanism. For example, changes in composition, Li or cation doping, potential-dependent electrochromism, cation insertion rate-dependent dielectric constant modification, and photonic signatures of spatially inhomogeneous lithium insertion into an ordered 3D array structure of active material, may also be monitored by making battery materials in an inverse opal or 3D macroporous structure. A brief comparison of current measurements techniques and photonic spectroscopy analogues that could be used when materials are fashioned into ordered, porous arrangements, are provided elsewhere.^[40]

Controlling the flow of light at subwavelength scales can be severely limited by diffraction effects^[52] as there are so many variables of the material and arrangement that can change during an electrochemical measurement. However, 3D structured EES materials do not require pristine, defect-free large scale arrays^[53] of electroactive deposits as would be required in photonics^[54] that use semiconducting inverse opals for optics, telecommunications, optical interconnects, and silicon photonics, as pertinent examples.^[55] Deep physical understanding of light-matter interactions in photonic crystals,^[56] including knowledge from random lasing systems,^[57] should allow researchers to develop probes for photon transport and collimation enhanced by transverse Anderson localization in the electrochemically anisotropic 3D structured cathode or anode material. Often, in scalable and high mass-loaded electrochemical electrodes, even ordered macroporous materials contain some degree of disorder, which is often a function of the appropriate length scale. For instance, order as defined in the macroscopic periodicity of an inverse-opal is comprised of inherently disordered assemblies of quantum-dot size nanocrystal assemblies that make up the wall structure of the IO material (see Fig. 3). Whereas the index contrast and periodicity (among other parameters) are interrogated at visible to NIR wavelengths, the absorption of materials in the UV-vis range due to their band-structure will be altered by crystal structure modification at that length scale, even if the changes in PBG are comparatively negligible.

Additionally, where large scale changes to order do occur, diffraction effects can be almost erased by cascaded resonant tunnelling through guided mode resonances; changing the material order allows the link between phase and disorder via analysis of disorder-induced transverse localization effects can probe heterogeneous reversible phase change, while dedicated spectroscopy in higher energy ranges can assess variations in the electronic nature of the constituent nanocrystalline material.

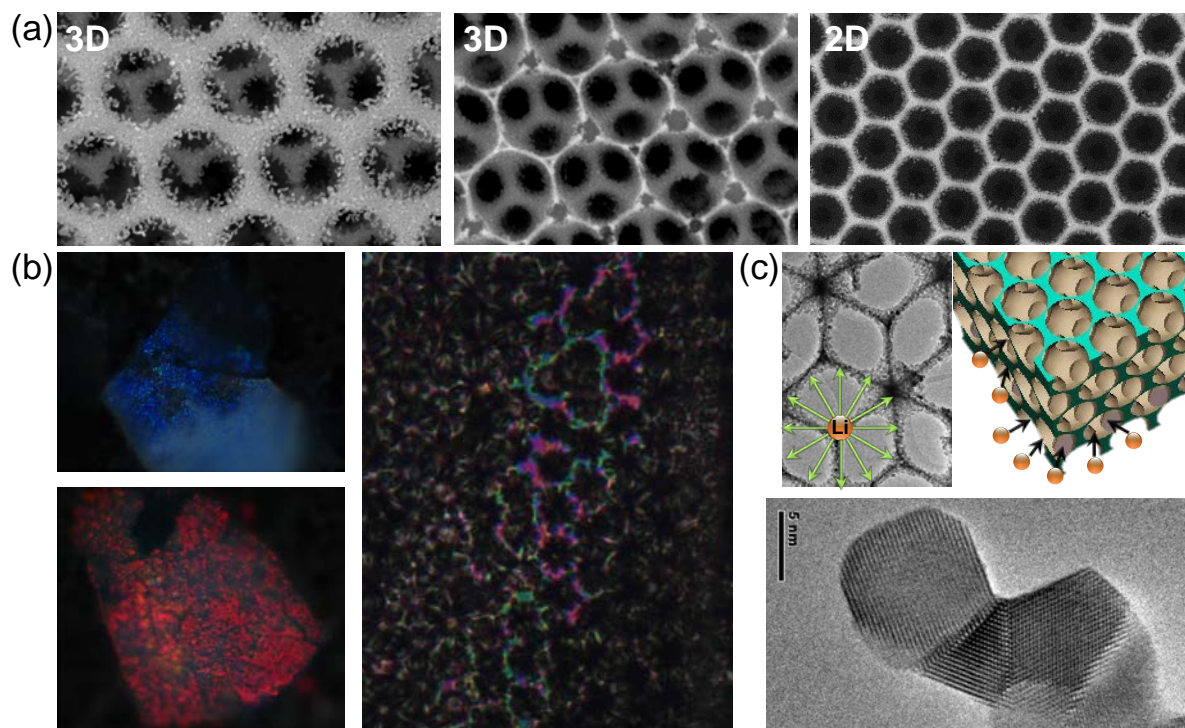


Figure 3. (a) 3D inverse opal SnO_2 comprising nanocrystalline wall with controllable fill factor and wall thickness. The 2D version provides a direct method of assessing homogeneity in material volume swelling during charge-discharge, and index and periodicity (order) change via 2D diffraction. (b) Optical microscopy of IO materials with periodicity causing consistent red and blue reflections from isotropic index contrast change. Lithiation causes a change in colour, or suppression of colour to brown when disorder is increased. Patterning of IO onto periodically patterned substrate also provide examination of three lengths scale of lithiation-induced changes: nanocrystalline phase changes, IO macrostructure changes and the heterogeneity of the patterned IO at electrode scale. (c) Schematic of shortened Li^+ diffusion distance by electrolyte soakage into the IO structure, and HRTEM data confirming the nanocrystalline structure (shorted solid state diffusion distances) of the IO walls.

Where there is no change in order or periodicity from swelling (whether homo- or heterogeneous volumetric modification), dielectric contrast changes etc., surface double layer charging effects can be spatially located and mapped. Such a possibility would be very useful in deconvoluting the effect of size, voltage and surface chemistry for metal oxide and other materials that display pseudocapacitive charge storage mechanisms in electrochemical system where they typically act as an insertion, conversion or alloying-mode battery electrode material under galvanostatic conditions.^[58-61] Thus, the deconvolution of the capacitive and intercalation/alloying contributions to porous battery materials^[61] is assessable by monitoring

the relative changes in structure from diffusion based processes compared with capacitive-based processes that does not alter crystal volume.

Moreover, as a spectroscopic diagnostic toolset, we are developing it for translation to many electrochemical energy storage and conversion materials systems beyond Li-ion batteries, such as pseudo and supercapacitors, catalytic systems involving metal NP infiltration plasmon-assisted inverse opal catalysts^[50, 62] that confine and resonantly amplify light in the catalytically active material medium, and in water splitting systems.

Advancements in 3D structured materials for Li-ion batteries

To achieve these purposes, it is critical to continue developing new materials to enhance the ion and electron transport kinetics with a view to improving material stability and capacity retention. ^[34, 63] ^[30, 64] Carbon-coated electrode active nanomaterials have shown that Li shuttling to lower chemical potential crystal facets can improve the charging rate for LiFePO₄,^[9] and various carbons, metal oxides and metalloids such as Si have been fashioned in inverse opal morphologies for ultrafast charging^[18] and other notionally better battery attributes. Increased fracture strength compared to their bulk counterparts is also possible in cathode and anode materials. ^[65, 66] Fast transport kinetics have been achieved in one dimensional (1D) carbon nanotube- and two dimensional (2D) graphene nanosheet-based hybrid electrodes. ^[67] However in 1D and 2D electrodes, the fast electron transport is restricted at least in one dimension because of the structural anisotropy of the electrodes. ^[68, 69] As a result, that dimension constrains the ambipolar (ionic and electronic) diffusion, eventually slowing down the transport kinetics in the entire battery material. Such kinetics problems become more severe at high current densities (rates). In 3D structured materials inverse opals or interconnected networked structures without carbon additives, inhomogeneities and variations in conductivity can cause localised electric field and

associated currents to vary, causing additional or alternative rate electrolyte reactions or lithiation rates. While difficult to assess until after testing in most battery setups, compositional homogenisation during lithiation or delithiation has never been spatially mapped, and where these difference caused localised changes in structure or disorder, their location and relationship to discharge/charge condition can be assessed optically. On transparent current collectors, this has been demonstrated using various transparent dispersions of tin, indium and indium tin oxide nanocrystal as battery anodes [28, 49].

Ideally, the electrode should consist of an ordered three-dimensional (3D) interconnected network, allowing faster ion and electron transport without limiting the ambipolar diffusion in any dimension (see Fig. 3). Along this line, initial strides have been made to fabricate 3D ordered macroporous electrodes by colloid templating, such as SnO₂, silicon [19] and carbon. [70] These electrodes indeed show promising potential in enhancing transport kinetics of batteries but only moderate rate performances and cycling stability are observed due to the fact that the macroporous structure in that case addressed ion transport rather than electron transport. In response to this challenge, bi-continuous porous electrodes were proposed where the electrode active materials were put on pre-prepared conductive inverse opal structured nickel. [18, 19] Although these bi-continuous electrodes give higher initial capacities and remarkable rate capabilities, they are still unable to provide a long-term cycling stability. Recently, a 3D Li_xMnO₂ cathode was demonstrated to retain 76% of its capacity when discharged rapidly at 185 C ($nC = 1/n$ hrs to full discharge). [18] A thicker (~150–200 nm) active layer caused a reduction in the capacity obtained at higher charge rates, but 60% retention at 62 C showed the promise of sacrificing gravimetric energy density, with functional porosity. However, since the performance at ultrafast charging and discharging rates is heavily influenced by the material architecture and its very composition [9], any curved or moulded electrodes with these materials should be capable of matching

planar designs.^[71] Most importantly, porous materials in the form of inverse opals have a well-established deposition methodology, with many options for infilling of electroactive materials, including atomic layer deposition (ALD), dip-coating or vacuum infiltration^[45], and we have recently advanced an electrodeposition method that provides very high quality inverse opal materials that are phase pure, single crystalline and whose mode of growth avoids air gaps or discontinuities during bottom-up formation on several forms of conductive surfaces.^[72]

Knowledge of hierarchical porosity on several lengths scales in photonic crystal oxides and hybrid nanomaterials using new precursors^[65, 73] are being assessed currently, and will be important for tuning the porosity and nanocrystal size of the new materials. Recent work in our laboratory provides many methods and materials for growing a range of oxides in defined shapes, porosities, arrangement and assemblies, and as ordered electrode materials. Nanoscale materials for Li-ion batteries,^[74] Li-O₂ batteries^[75, 76] and for a range of applications also provide a series of functional battery materials that can be rendered as inverse opals of photonic crystals. Additionally, for hybrid cathodes and anodes (carbons that contains oxides, mixtures of oxides, phosphates or semiconductors etc.) that take advantage of different degrees of volumetric expansion during intercalation or alloying are also possible through rational design of the precursor.^[77, 78] This provides a one-pot method for incorporating one material on, or within, another, which is especially important when both materials must be subsequently coated and converted to ordered macroporous electrodes.

Inverted opal oxides such as V₂O₅, Co₃O₄, MnO₂ and others have shown excellent performance as Li-ion battery electrodes in half cells, or indeed as full IO cells, maintaining specific capacities close to the theoretical maximum for each material over several hundred cycles.

Outlook and Prospects

The vision of colour-coding battery materials and developing powerful and informative multi-modal characterization and diagnostic material probes using optics and photonics is adaptable to essentially any inverse opal or photonic crystal structure imposed on an electroactive material, or indeed highly packed structures of materials with sufficient index contrast to infer either a pseudo photonic band gap, enable optical diffraction, or diffuse, scattered optical transmission/reflectance phenomena. The cross-disciplinary approach involves materials synthesis, structure-properties relations, and functional and advanced materials in electrochemical energy storage. As a power check module or diagnostic strip additional to a main battery, scalability and cost for materials are minimal.

The electrochemical, microscopy and spectroscopy knowledge and techniques applied to this research form a platform system which can be adapted for materials and electrochemical phenomena in batteries, fuel-cells, energy storage and conversion, and materials for enhanced photocatalysis^[79, 80], sensors, all-optical power-check modules, water splitting^[81] and many technologies that use porous materials or assemblies on surfaces under the influence of an applied current, voltage or chemical/compositional modification, often analysed or facilitated by illumination of visible light. *In-situ* diffractive optics and photonic probes of materials fashioned into ordered structures can hopefully assess composition, its relation to cation intercalation, alloying or conversion, and thus capacity, and also state of charge determination, and provide in-line materials analysis during research into numerous forms of energy storage materials.

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