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Comparing Cycling and Rate Response of SnO₂ Macroporous Anodes in Lithium-Ion and Sodium-Ion Batteries

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Tin oxide (SnO₂) is a useful anode material due to its high capacity (1493 mAh g⁻¹ and 1378 mAh g⁻¹ vs Li/Li⁺ and vs Na/Na⁺, respectively) and natural abundance (tin is one of the thirty most abundant elements on Earth). Unfortunately, only moderate electrical conductivity and significant volume expansion of up to 300% for Li-ion, and as much as 520% for Na-ion can occur. Here, we use an ordered macroporous interconnected inverse opal (IO) architectures to enhance rate capability, structural integrity, and gravimetric capacity, without conductive additives and binders. Excellent capacity retention is shown during cycling vs Na/Na⁺ relative to Li/Li⁺. Cyclic voltammetry (CV) analysis, galvanostatic cycling, and differential capacity analysis extracted from rate performance testing evidence the irreversibility of the oxidation of metallic Sn to SnO₂ during charge. This behavior allows for a very stable electrode during cycling at various rates. A stable voltage profile and rate performance is demonstrated for both systems. In a Na-ion half cell, the SnO₂ retained >76% capacity after 100 cycles, and a similar retention after rate testing. © 2023 The Author(s). Published on behalf of The Electrochemical Society by IOP Publishing Limited. This is an open access article distributed under the terms of the Creative Commons Attribution 4.0 License (CC BY, <http://creativecommons.org/licenses/by/4.0/>), which permits unrestricted reuse of the work in any medium, provided the original work is properly cited. [DOI: 10.1149/1945-7111/ad0ff5]



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Lithium-ion (Li-ion) battery chemistries dominate the commercial range of energy storage systems available due to superior energy density, lifetime, and stability compared to other chemistries. The ethical issues surrounding cobalt, one of the key components of Li-ion battery cathodes, have been well documented.¹ Lithium reserves are finite, and the current high demand is growing rapidly during the transition to a green energy future. Issues related to ethics and safety also surround the mining of lithium.^{2,3} Alternative systems must be considered including lithium sulfur,^{4,5} redox-flow,^{6,7} potassium-ion,^{8,9} and aluminium-ion.¹⁰ Possibly the most promising substitute is sodium-ion (Na-ion). Sodium lies in the top ten most abundant elements on Earth and can be easily extracted by isolating seawater (sodium chloride) and performing electrolysis when in its cooled, molten form. Given that graphite has maintained its status as the gold standard anode material for Li-ion systems, battery research has been dominated by efforts to maximize the performance of cathode materials, the limiting factor for energy density.

However, there is a dramatic drop in the capacity provided by graphite anodes in Na-ion systems. Many reports show an experimental discharge capacity of 35 mAh g⁻¹ in Na-ion systems compared to the 335 mAh g⁻¹ which can be achieved in Li-ion systems. Intercalation efficiency of alkali-ions in graphite can be evaluated by the formation energy of the corresponding intercalation compound. The two contributions to this formation energy are: (1) structural deformation energy and (2) binding energy.^{11,12} Structural deformation energy corresponds to the energy required to expand the spacing between graphitic layers to accommodate ions. As a result, structural deformation energy minimum for lithium relative to the other alkali ions and this energy contribution increases along the alkali metal group. However, the binding energy contribution does not follow the same trend. Sodium requires a much higher binding energy than lithium, yet the binding energy of potassium is the minimum of the three. The binding energy is a direct consequence of the interaction between the *p*-orbitals of the carbon atoms of

graphite and the interacting ions.¹³ A review of the binding energies of the three alkali ions with carbon shows that sodium requires the maximum energy, due to the least overlap with carbon in its sp² hybridized state. By obtaining the sum of the two energy contributions, the overall formation energy is minimum for lithium, and a maximum for sodium.^{12,14}

Fortunately, there are alternatives to intercalation materials, such as those which follow conversion¹⁵ and alloying mechanisms.¹⁶ The intercalation mode mechanism of charge transfer employed by graphite involves the shuttling of ions in and out of openings within the host structure. When conversion materials undergo electrochemical cycling, the active ions are inserted into nanosized binary compounds denoted by MX (M for transition metals such as Fe, Cu, Co, etc and X for O, S, F, etc.) which results in the reduction of M cations to M⁰ and the formation of LiX or NaX for Li-ion and Na-ion batteries, respectively. The microstructures suffer great changes and are usually associated with the recrystallization of active materials.¹⁷ The alloy mechanism proceeds by direct bonding between the inserted active ion and the host element A (A for Si, Sn, Ge, etc) leading to the formation of Li-A and Na-A alloys for Li-ion and Na-ion batteries, respectively.¹⁸ The motivation for alloy materials for Li-ion batteries is based on the high theoretical capacity of Li metal (3860 mAh g⁻¹), but many of these materials are associated with serious safety issues. For Na-ion batteries, Na metal also demonstrates high capacity (1166 mAh g⁻¹), but is highly reactive, yielding yet greater safety concerns. Li and Na alloys can be used which take advantage of the high capacities of each metal while maximising safety. In general, charge storage is directly so differently between the three mechanisms that there are distinct contrasts between the resultant capacity and morphology of the electrode.

Dual storage mechanism materials exist, known as conversion/alloy materials. These deliver high capacities but can suffer from significant issues such as large volume expansion,¹⁹ mechanical brittleness, and unwanted side reactions with sodium-based electrolytes.²⁰ The associated issues mean that experimentally, a wide range of novel adaptations and manipulations of the materials are introduced to improve performance.

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One conversion-alloy material with potential for high performance in Na-ion systems is tin oxide (SnO_2), which provides a theoretical capacity of 1378 mAh g^{-1} and is highly sustainable, appearing in nature as the mineral cassiterite which can be mined from alluvium and placer deposits at seabeds²¹ and processed without the high CO_2 emissions of graphite.^{22,23} SnO_2 is notorious for its volume expansion, up to 300% in a Li-ion system.^{24–26} Unsurprisingly, volume expansion is further enhanced in Na-ion systems, up to 520%.^{27–29} In the literature, efforts to improve performance of SnO_2 -based materials for Na-ion, and in fact Li-ion systems, appear in two primary forms: nanostructure design to buffer volume expansion, and carbon-based nanocomposites to improve electronic conductivity. Typically, pure SnO_2 nanostructures for Li-ion and Na-ion batteries are designed with specific morphologies such as nanorods and nanotubes by involved methods like hydrothermal synthesis and electrospinning. Carbonaceous nanocomposites are often of complex designs such as hollow^{29–31} or yolk-shell structures,^{32–35} along with the embedding of SnO_2 nanoparticles into carbon or the encapsulation of SnO_2 nanostructures by carbon in forms such as graphene,^{36–38} reduced graphene oxide (RGO),^{39–42} and carbon nanotubes (CNTs),^{43–46} among others. These complexities prompt an alternative approach.

Inverse opals (IOs) can be formed simply by colloidal self-assembly of a parent opal template, followed by infiltration by a metal alkoxide precursor and calcination of the template to form the IO. Detailed information on self-assembly of the opal template^{47,48} and subsequent IO preparation is provided elsewhere.^{49–51} IOs consist of a macroporous, interconnected network with periodicity in three dimensions, usually a metallic or metal oxide material.^{52–56} A type of photonic crystal, they possess the ability to reflect wavelengths determined by the refractive index contrast and periodicity of the material.^{57,58} There are multiple benefits to their use as battery electrodes, and some trade-offs.^{59,60} Porosity provides high surface area to volume ratio. The interconnectivity removes the need for conductive additives/binders, which mitigates to a limited degree, the reduced volumetric mass loading of the porous material. For conversion-alloy materials such as SnO_2 , significant volume expansion is a characteristic issue faced during electrochemical cycling. The macroporosity of IOs provides excellent tolerance for such volume expansion. While mesoporous materials provide a similar tolerance for volume expansion and a higher surface area to volume ratio, the smaller pore size can adversely affect rate capability, inhibiting Li-ion (or Na-ion) flux into the electrode. The IOs studied in this work are formed as islands of interconnected material, each contacted to the underlying current collector. While the growth of crack-free IOs using evaporation coassembly methods has been performed elsewhere,^{61–64} the cracks between islands in the IOs studied here provide an good environment for electrolyte soakage. For materials like SnO_2 which suffer from such dramatic volume expansion, electrode degradation and possible delamination which may occur can be localized the area covered by the specific island of material. The primary motivation for the use of IOs here, lies in their charging and discharging rate capability. Thin pore walls consisting of an agglomeration of the active nanoparticles result in short ion diffusion distances, the limiting factor for rate performance.⁶⁵

Here, structural analysis and electrochemical characterization provide a comparative study of the behaviour of macroporous SnO_2 anode materials in Li-ion and Na-ion systems. We show these electrodes provide good capacity retention for the Na-ion system and we use analyses from cyclic voltammetry (CV), galvanostatic cycling and differential capacity to define and compare the nature of the reactions of macroporous SnO_2 with Li and Na during charging and discharging. Finally, the rate performance of the macroporous SnO_2 show excellent cyclability and capacity recovery, particularly for the Na-ion case. Comparing the SnO_2 anodes in Li-ion and Na-ion systems simultaneously reveals the underlying causes underpinning the contrast in the response between the two systems.

Experimental Methods

Preparation of SnO_2 IOs.—Colloidal solutions of polystyrene (PS) spheres in 2.5% (w/v) aqueous suspension with a nominal diameter of 510 nm were purchased from Polysciences Inc. The sphere suspension possessed a net negative charge due to functionalization using a sulfate ester during formation to aid in self-assembly. The substrates used 316 L stainless steel with a 15.5 mm diameter and 0.2 mm thickness. All substrates were cleaned using the same process: Successive sonication in acetone (reagent grade 99.5%; Sigma Aldrich), isopropyl alcohol (reagent grade 99.5%; Sigma Aldrich) and de-ionized water, each for 5 minutes. All cleaned samples were dried at room temperature in an inert atmosphere. The samples were treated in a Novascan PSD Pro Series digital UV-ozone system for 1 h to maximize hydrophilicity of the surface of the substrates immediately prior to opal template formation.

Opal templates were formed using evaporation-induced self-assembly where first the substrates were immersed in a diluted PS sphere solution with volume fractions in the range of 0.1% to 0.2% which were placed inside a Binder convection oven at temperatures between 55–60 °C for ~24 h. Once the sphere solution was evaporated fully, the substrates were removed and left to dry in inert atmosphere at room temperature.

SnO_2 inverse opals were formed via infiltration of the opal template with a SnCl_2 precursor by drop casting followed by calcination at 450 °C in air for 1 h to oxidize and crystallize the material. The SnCl_2 complex used was a 0.1 M solution of titanium (IV) chloride tetrahydrofuran complex ($\text{TiCl}_4 \cdot 2\text{THF}$, 97%; Sigma-Aldrich).

Materials analysis.—All scanning electron microscope (SEM) imaging was performed using a Zeiss Supra 40 high-resolution SEM at an accelerating voltage of 2 kV. SEM images and feature dimensions were analysed using ImageJ software. Transmission electron microscopy (TEM) combined with electron diffraction analysis was conducted using a JEOL JEM-2100F TEM operating at 200 kV to investigate structural parameters at the nanoscale. X-ray photoelectron spectroscopy (XPS) was performed using a Kratos AXIS ULTRA spectrometer with a detection limit of <0.1 at %, ~1 mm² detection area, analysis depth of ~10 nm to determine the binding energies between the core electrons occurring in the materials. Raman spectroscopy was performed with a Renishaw InVia Raman Spectrometer using a 30 mW Ar-ion laser under 532 nm excitation. The beam was focused onto the samples using a 50× objective lens and spectra were collected using a RenCam CCD camera. X-ray diffraction (XRD) measurements were performed using a Phillips Xpert PW3050 diffractometer with a Cu anode, $K\alpha$ radiation with wavelength $\lambda = 0.15406 \text{ nm}$, operating voltage 40 kV, current 20 mA.

Cell assembly.—Two cell configurations were used for Li-ion and Na-ion testing. (1) El-Cell PAT cells (ECC1-01-0012-A/L, 18 mm diameter, 0.65 mm thickness) operated as half-cells. (2) CR2032 coin cells (SS304, 20 mm diameter, 3.2 mm thickness prior to crimping).

Li-ion cells.—The working electrode was an SnO_2 IO on stainless steel substrate, Li metal counter electrode, and 1 M solution of lithium hexafluorophosphate (LiPF_6) in a 1:1 (v/v) mixture of ethylene carbonate: dimethyl carbonate (SigmaAldrich, battery grade), and no additives or binders were used.

Na-ion cells.—The same configuration was used apart from a Na metal counter electrode and electrolyte which consisted of 1 M sodium perchlorate (NaClO_4 , AlfaAesar, ≥99%) in propylene carbonate (PC, $\text{C}_4\text{H}_6\text{O}_3$, SigmaAldrich, 99.7%). 5% fluoroethylene carbonate ($\text{C}_3\text{H}_3\text{FO}_3$, AlfaAesar, ≥99%) additive was used.

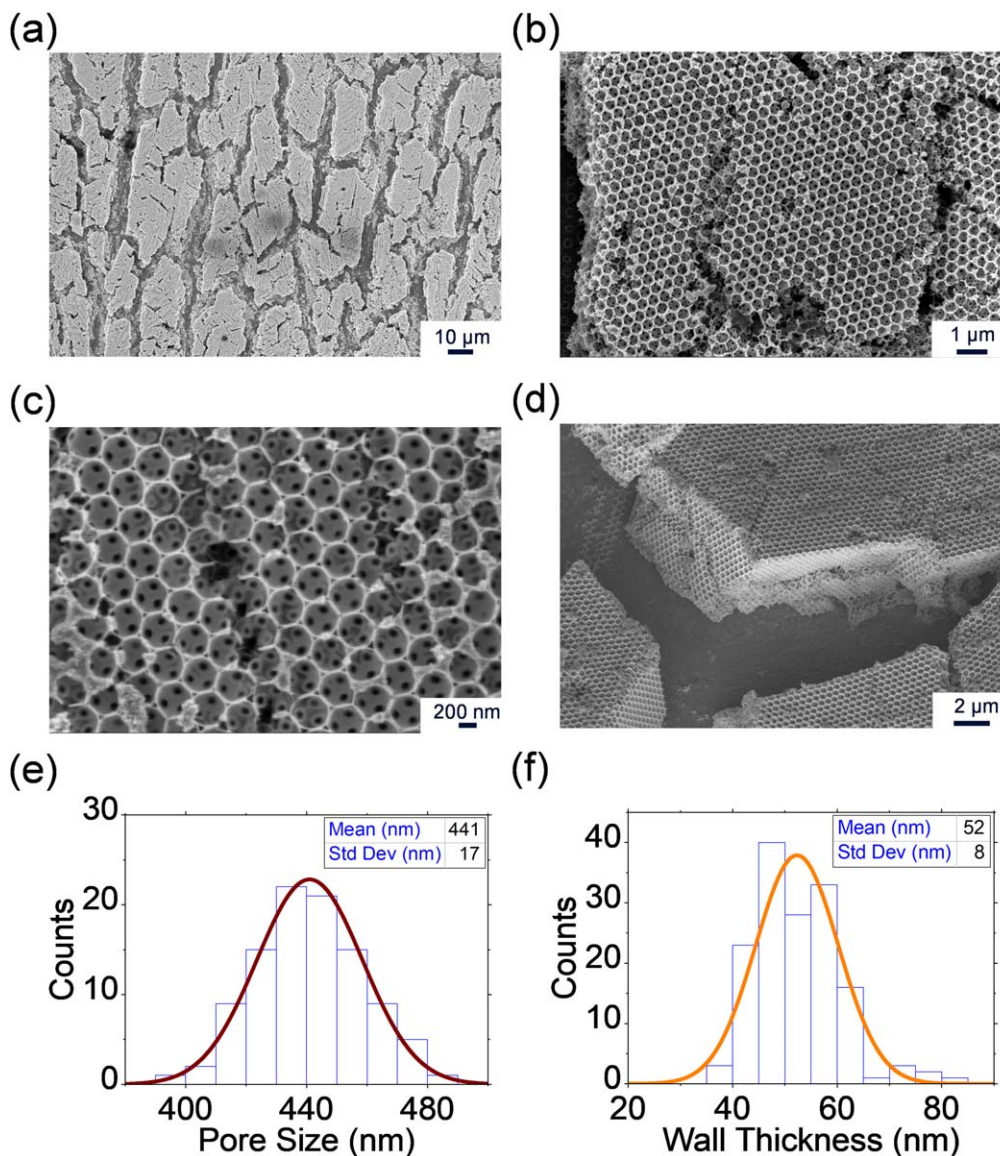


Figure 1. (a)–(c) Planview SEM images of SnO_2 IO at various levels of magnification. (d) Cross-sectional SEM image at a tilt angle of 30° . (e) Pore size distribution of SnO_2 IO obtained from SEM images. (f) IO wall thickness distribution obtained from SEM images.

Electrochemical characterization.—All electrochemical tests were conducted on a multichannel BioLogic VSP Potentiostat/Galvanostat. Electrodes were examined using cyclic voltammetry (CV) and constant current (galvanostatic) potentiometry. The details of potentials, applied currents, scan rates or voltage ranges are provided in the captions to each relevant figure.

Differential capacity analysis was performed on the galvanostatic rate testing data, where current density was ramped in four steps from $50\text{--}450\text{ mAh g}^{-1}$, followed by a final step at 50 mAh g^{-1} for 20 cycles at each rate. From the capacity-voltage data, discharge and charge data was segregated at all rates. Numerical differentiation was performed on the discharge and charge data for both the Li-ion and Na-ion cells to obtain dV/dQ data, with the reciprocal taken to generate differential capacity data. Differential capacity plots (DCPs) were constructed as a plot of voltage versus cycle number vs differential capacity. A total of four DCPs corresponding to the discharge and charge profiles for the Li-ion and Na-ion systems were formed with an appropriate colour scale applied based on the differential capacity range observed.

Results and Discussion

Structure of macroporous SnO_2 electrode material.—The details of the three-dimensional interconnected macroporous architecture of the SnO_2 inverse opals (IOs) are demonstrated by scanning electron microscope (SEM) images in Fig. 1. IOs grown from calcination of opal templates infilled with a sol-gel precursor, results in multi-layered islands of IO material as shown in Fig. 1a. Throughout these IO samples, the islands consist of highly ordered, “honeycomb” layers of interconnected SnO_2 , dominated by face-centered cubic (FCC) symmetry, evident in the higher magnification SEM images in Figs. 1b and 1c. Growth of the opal template occurs perpendicular to the (111) plane of the FCC lattice.^{66,67} The symmetry of the IO is a direct consequence of the parent opal template. However, while these IOs have been considered as the direct inverse of their parent opal templates in the literature, recent work from our group has revealed that a slight deviation occurs from the symmetry of the template.⁶⁸ The cross-sectional SEM image in Fig. 1b, obtained at an angle of 30° , shows that the honeycomb structure is continuous in three dimensions, rather than just the surface.

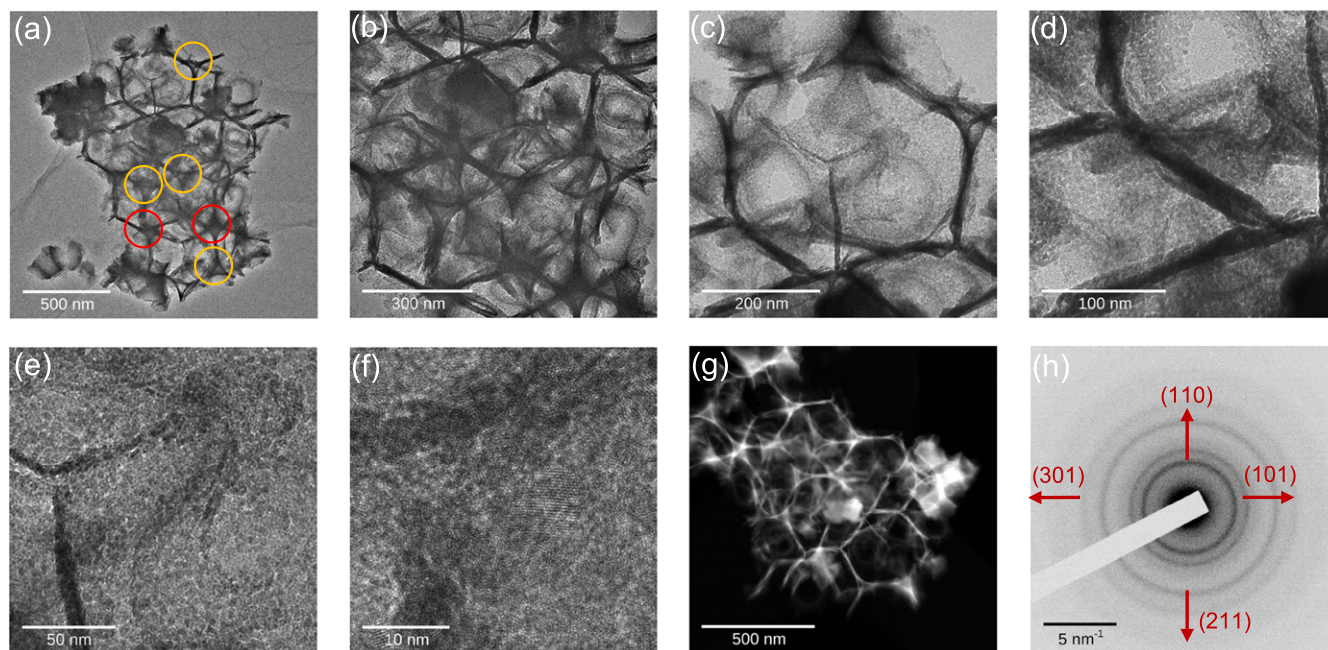


Figure 2. (a)-(d) TEM images of SnO_2 IO at various levels of magnification. Red circles: Octahedral sites. Orange circles: Tetrahedral sites. (e)-(f) HRTEM images showing configuration of nanoparticles within the pore walls and the fringes of the SnO_2 lattice. (f)-(g) STEM image of SnO_2 IO. (h) Electron diffraction pattern of SnO_2 IO with indexed lattice planes.

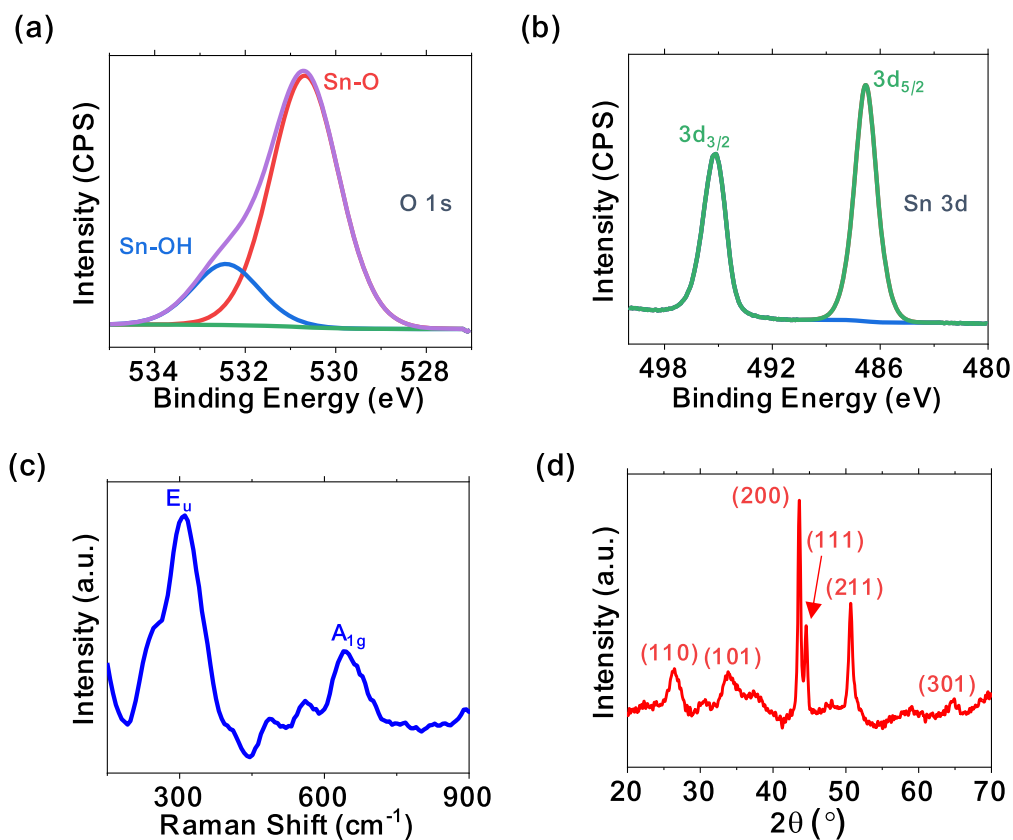


Figure 3. XPS core-level photoemission spectra of the (a) O 1s region and (b) Sn 3d region for a SnO_2 IO. (c) Raman scattering spectrum of SnO_2 IO. (d) XRD spectrum of SnO_2 IO showing reflections associated with tetragonal SnO_2 .

The SnO_2 IO pore size is also a direct consequence of the sphere diameter of the parent opal. Shrinkage occurs upon calcination of infiltrated opals. Here, the IO pore size distribution is shown in Fig. 1e, with a mean diameter D of ~ 441 nm based on a parent opal

template with a nominal sphere diameter of 510 nm. This macroporosity results in a high surface area to volume ratio, while adequate space is provided for optimal electrolyte infiltration. The specific surface area can be approximated based on the calculated

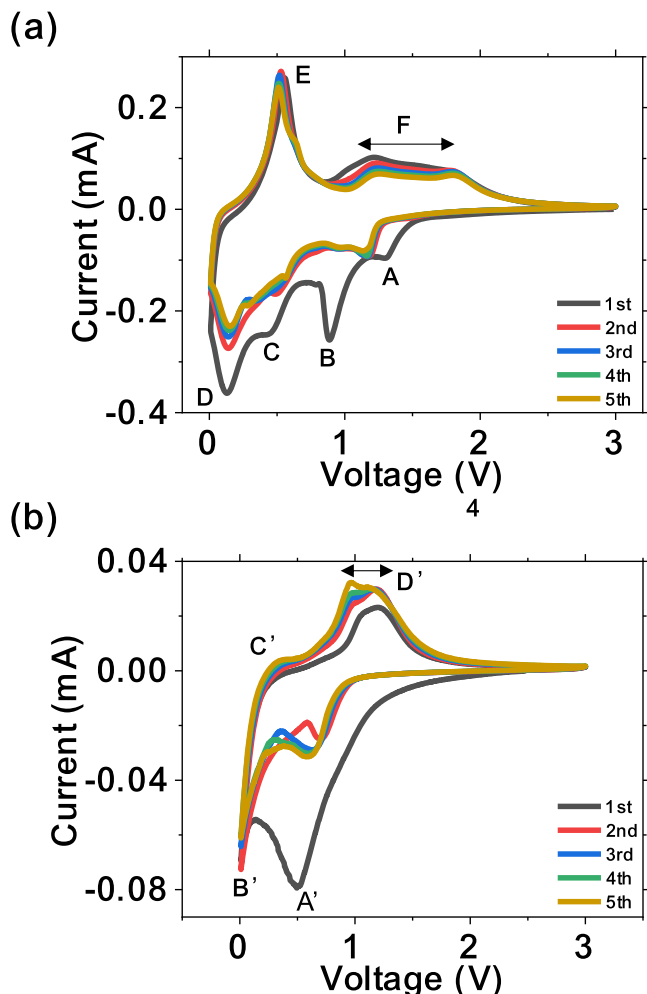


Figure 4. Cyclic voltammetry curves obtained over 5 cycles for SnO₂ IO in (a) Li-ion system and (b) a Na-ion system in a potential window of 0.01 V to 3.0 V at a scan rate of 0.1 mV s⁻¹. The electrode was initially swept from 3.0 V to 0.01 V in each case.

average macropore diameter assuming the IO has perfect FCC symmetry and neglecting the micropores and mesopores within the IO walls. Each FCC unit cell contains 4 macropores and the volume of each unit cell can be approximated as a^3 , where the lattice parameter $a = D\sqrt{2}$. The surface area per unit volume can then be found by multiplying the surface area per unit cell by the number of unit cells per unit volume, resulting in a specific surface area per unit volume of 10.05 m² cm⁻³. The specific surface area per unit mass can be calculated based on the density of SnO₂ (6.95 g cm⁻³)⁶⁹ and the volume fraction of SnO₂ material of a perfectly ordered FCC IO (0.26%) as 5.56 m² g⁻¹. Both calculated values are in good agreement with reports for IO structured metal oxide materials in the literature.^{70,71}

Figure 1f shows the size distribution of the IO walls. One of the principal motivations for IO use as battery electrode materials, is the ability of interconnected macroporous materials to show excellent rate capability compared to dense or compact materials. The rate performance is a consequence of the thin IO pore walls in an electrolyte-soaked electrode, with a mean value of ~52 nm. Additional SEM images are provided in Fig. S1 in the Supplementary Material.

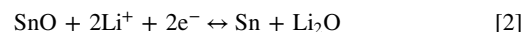
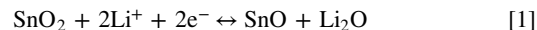
Bright-field transmission electron microscopy (TEM) images in Figs. 2a–2c show the morphology of the IO pores. For a structure dominated by FCC symmetry, contact points between layers occur as octahedral and tetrahedral interstitial sites, indicated in Fig. 2a. These sites arise from the ABC stacking arrangement of each layer.

Each FCC unit cell of the porous SnO₂ material consists of eight tetrahedral and four octahedral sites all connected with walls of SnO₂.⁶⁸ Figures 2d and 2e show high resolution transmission electron microscope (HRTEM) images of the crystalline SnO₂ nanoparticles that comprise the IO walls. Scanning transmission electron microscope (STEM) images of the SnO₂ IO are shown in Figs. 2f and 2g, focusing on the surface of the IO structure. Further TEM images are provided in Fig. S2 of the Supplementary Material.

While the HRTEM images are not of a sufficient resolution to accurately measure the d-spacings between lattice fringes, the electron diffraction pattern in Fig. 2h provides the same information. The concentric rings demonstrate the highly ordered, polycrystalline structure of the SnO₂ IO. The low index lattice planes are identified by red arrows. Based on the radii of the indexed rings, the measured d-spacing of the atomic planes of the SnO₂ IO is 0.33 nm, in good agreement with the theoretical value for the (110) lattice plane of tetragonal SnO₂.^{72–74} The remaining measured d-spacings are 0.26 nm, 0.17 nm, and 0.14 nm, associated with the, (101), (211) and (301) lattice planes, respectively.

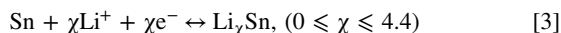
Figure 3a shows obtained X-ray photoelectron spectroscopy (XPS) measurements for SnO₂ IO samples corresponding to the O 1s core-levels in SnO₂. The strong photoemission observed at 530.7 eV is in good agreement with values in the literature corresponding to the O 1s core level electrons of SnO₂.⁷⁵ A weaker peak is observed at 532.4 eV which, based on reports, is caused by the multiplicity adsorbed hydroxyl species at the material surface.⁷⁶ Figure 3b shows the XPS spectrum corresponding to the Sn 3d region. For the 3d core-level region, peaks occur at 495.24 eV and 486.77, corresponding to the binding energies of Sn 3d_{3/2} and Sn 3d_{5/2},⁷⁷ respectively. The doublet photoemission confirms the formation of Sn⁴⁺ and thus the presence of SnO₂. The associated Raman scattering spectrum is shown in Fig. 3c. Two primary peaks are observed at ~643 cm⁻¹ and ~312 cm⁻¹. The prior is the characteristic A_{1g} band of SnO₂, which appears due to expansion and contraction of the Sn-O bond.^{78,79} The latter is ascribed to the E_u band, which is indicative of amorphous or nanocrystalline character, arising due to the nanoparticulate nature of the SnO₂ IO.⁸⁰ The X-ray diffraction spectrum in Fig. 3d suggests that the nanocrystallites within the IO pore walls exist in the characteristic tetragonal SnO₂ phase with space group *P42/mnm* with two SnO₂ molecules per unit cell.⁸¹ The calculated d-spacing for the SnO₂ IO based on the observed (110) reflection is 0.34 nm, in good agreement with the value of 0.33 nm calculated previously from the electron diffraction pattern. The d-spacings from all observed reflections were calculated and used to determine the lattice parameters of tetragonal SnO₂ as a ~0.47 nm and c ~0.32 nm which agree with values reported in the literature for nanoparticulate SnO₂.^{82–84}

Voltammetric comparison in Li-ion and Na-ion cells.—Cyclic voltammetry (CV) experiments were conducted at a scan rate of 0.1 mV s⁻¹ in a voltage window of 0.01 V to 3.0 V vs Li⁺/Li and vs Na⁺/Na for Li/SnO₂ and Na/SnO₂ half cells, respectively. The results for the first five cycles are shown in Figs. 4a and 4b. Based on previous reports, the reversible redox conversion process between SnO₂ and metallic Sn in a Li-ion system proceeds as follows:⁸⁵



In the first cathodic scan of the Li-ion system shown in Fig. 4a, peak A is observed at 1.31 V, indicative of the onset of the reduction process of SnO₂ to metallic Sn.³² This grows to form a distinct peak in the second scan at 1.18 V which is incrementally shifted with subsequent scans ending at 1.13 V for the fifth. Peak B at 0.89 V is attributed to the formation of the SEI layer.⁸⁶ The onset of the alloying mechanism is indicated by peak C at 0.41 V and the strongest, broad peak of the first cathodic scan occurs at 0.13 V (peak D), corresponding to the maximum current response of the

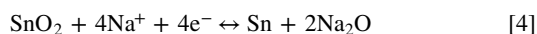
alloying mechanism of metallic Sn with Li to form nanoparticulate Li_χSn as below:⁸⁷



For the alloying peak, the current response decreases significantly for the second scan while only a minor decrease occurs in those that follow. There is slight change in the potential, with the peak centre shifted only from 0.14 V and 0.15 V from the second to the fifth scan. Minor current responses and additional smaller peaks are observed in the vicinity of the broad alloying peak after the first scan, indicating a more progressive alloying regime as cycling continues.⁸⁸

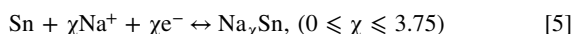
In the anodic portion of the CV scans for the Li-ion system, the strong, relatively narrow peak E occurs for all five cycles due to the dealloying process of Li_χSn back to metallic Sn. In the first anodic scan, the peak is centred at 0.56 V and gradually shifts towards lower potentials for each cycle. The peak current increases for the second scan before decreasing incrementally for subsequent scans as expected. Peak F corresponds to the oxidation of metallic Sn to SnO_2 which occurs at 1.22 V in the first anodic scan and shifts to slightly higher potentials for the following scans. The large width of the peak indicates that like the alloying process, oxidation from metallic Sn to SnO_2 is progressive, even for the first cycle in this case. The peak width increases with each scan.

In Fig. 4b, the electrochemical response of SnO_2 in the Na-ion system is illustrated. While the reaction steps are similar to the Li-ion case, the reversibility of the reaction is significantly limited in a Na-ion system.⁸⁹ Such irreversibility reduces capacity, given that the total capacity delivered is the sum of the capacities delivered by the Sn redox and Sn-Na alloying processes. Based on the literature, the conversion process proceeds as follows:⁹⁰



In the first cathodic scan, a steep current gradient begins at ~ 1.23 V and forms the largest peak A' at 0.51 V, which represents the reduction of SnO_2 to metallic Sn. An absence in any discernible peak representative of SEI formation is noted, which is expected to appear at ~ 0.4 V based on previous reports.⁹¹ The initial conversion process to form metallic Sn causes significant structural changes in the presence of sodium. The electrolyte species are susceptible to decomposition, catalysed by the reduced Sn nanoparticles.⁹² While electrolyte decomposition is problematic in both Li-ion and Na-ion systems, sodium-based electrolytes are relatively unstable.⁹³ Wang and coworkers reported peaks between 0.6 V and 0.1 V associated with irreversible decomposition of the electrolyte during the first cathodic scan for their $\text{SnO}_2/\text{MWCNT}$ nanocomposite Na-ion batteries.⁴⁶ The reported difficulties in controlling SEI species for these Na-ion batteries prompted the use in this work of FEC as a stabilization additive. The current gradient between ~ 1.23 V and 0.51 V, caused by localized phase changes, possible effects due to volume expansion, electrolyte decomposition and unstable SEI species masks any peak related to SEI formation and reaches a maximum where the rate of conversion to metallic Sn is highest at 0.51 V. For the second cathodic scan, the current is significantly lower and shifted to a higher voltage of 0.7 V. For subsequent scans, the current response increases, and the peaks are shifted to incrementally lower voltages. The trend indicates that conversion of the SnO_2 nanoparticles to metallic Sn occurs gradually throughout the structure during the first few cycles.

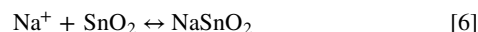
Peak B' occurs sharply at 0.01 V in the first cathodic scan and can be attributed to the alloying of metallic Sn with Na to form amorphous Na_χSn nanoparticles dispersed in an Na_2O matrix as below:⁹⁴



When χ is 3.75, Na_χSn crystallizes into the final discharge product, $\text{Na}_{15}\text{Sn}_4$. Unlike the peak associated with reduction of SnO_2

to metallic Sn, the magnitude of the alloying peak current sees little change through the five cycles examined and there is a negligible voltage shift. There is a stark contrast in the relative peak currents between the reduction and alloying processes in the first cycle compared to all subsequent cycles. The reduction peak current is greater by a multiple of three than the alloying peak during the first cathodic scan. For the following scans, the situation is reversed, and the alloying peak current is greater by a multiple of two than the reduction peak current. The results show that while the alloying regime provides the dominant capacity contribution throughout the lifetime of the cell, the conversion of SnO_2 to metallic Sn dominates the first cycle. Volume expansion is maximal during the first cathodic scan. This step, which includes both a significant structural change to the entirety of electrode material that undergoes an uptake of sodium ions, and a distinct chemical reaction, which forms a new compound from which the energy of the system is extracted, heavily influences the performance of the system throughout subsequent cycles.

An additional insertion reaction has been found during the beginning of the first discharge process by Wang and co-workers which proceeds as follows:⁹⁵



However, there is no current response in the first cathodic scan to indicate such insertion has taken place here. Occurrence of the insertion reaction significantly enhances capacity above that provided by the conversion and alloying reactions, but the galvanostatic cycling results in the following section show no evidence of such additional capacity.

During the first anodic scan, there is an absence of any discernible peak corresponding to the dealloying mechanism of Na_χSn . However, a positive current gradient begins at ~ 0.31 V (point C'), which indicates the beginning of the dealloying process. The positive current gradient continues from this point up to the distinct peak D' at 1.21 V, indicative of the oxidation process of metallic Sn to SnO_2 , so it is difficult to determine the point at which dealloying ceases and oxidation begins. Like the Li-ion case, peak D' is broad and indicates a gradual oxidation process. The low current response, combined with reports from the literature strongly suggests that neither process nears completion.^{96,97} The difficulties related to detection of the dealloying mechanism can be understood based on work by Ghu et al. in 2013.⁹⁸ The failure mechanism of nanowire SnO_2 in Na-ion batteries was probed using in situ TEM. It was found that during the alloying mechanism where Na_χSn is formed, massive structural change causing volume expansion of over 100% (its contribution to a possible volume expansion of 520% throughout cycling) occurs. Simultaneously, a Na_2O matrix is formed, surrounding the Na_χSn particles. The matrix then acts as an impediment to the dealloying process. When dealloying does occur, vacancies arise which lead to a disconnected network within the electrode. In the subsequent scans, the sharp peak at 1.21 V broadens to form a doublet peak, with maxima at 1.1 V and 0.96 V for the fifth cycle. The broad, doublet peak indicates a two-step oxidation process after the first cycle, like the equivalent oxidation process in the Li-ion system.

These CV results demonstrate distinct differences in the electrochemical processes that govern the current response from an SnO_2 anode in Li-ion and Na-ion systems, which can be summarized by three main points. (1) Overall current response: For the Na-ion system, the magnitude of the current during each CV scan is much lower, where all peak currents associated with both conversion and alloying processes are greater by multiples for the Li-ion system. Low charge flow is often a result of low conductivity, indicating that a large proportion of active material remains unused, and the associated reactions are incomplete.⁹⁷ (2) Lithiation versus sodiation: Broad, well-defined peaks are observed for all processes over the 5 cycles investigated for the Li-ion system. For the Na-ion system, not all the peaks are clearly defined, with some of the

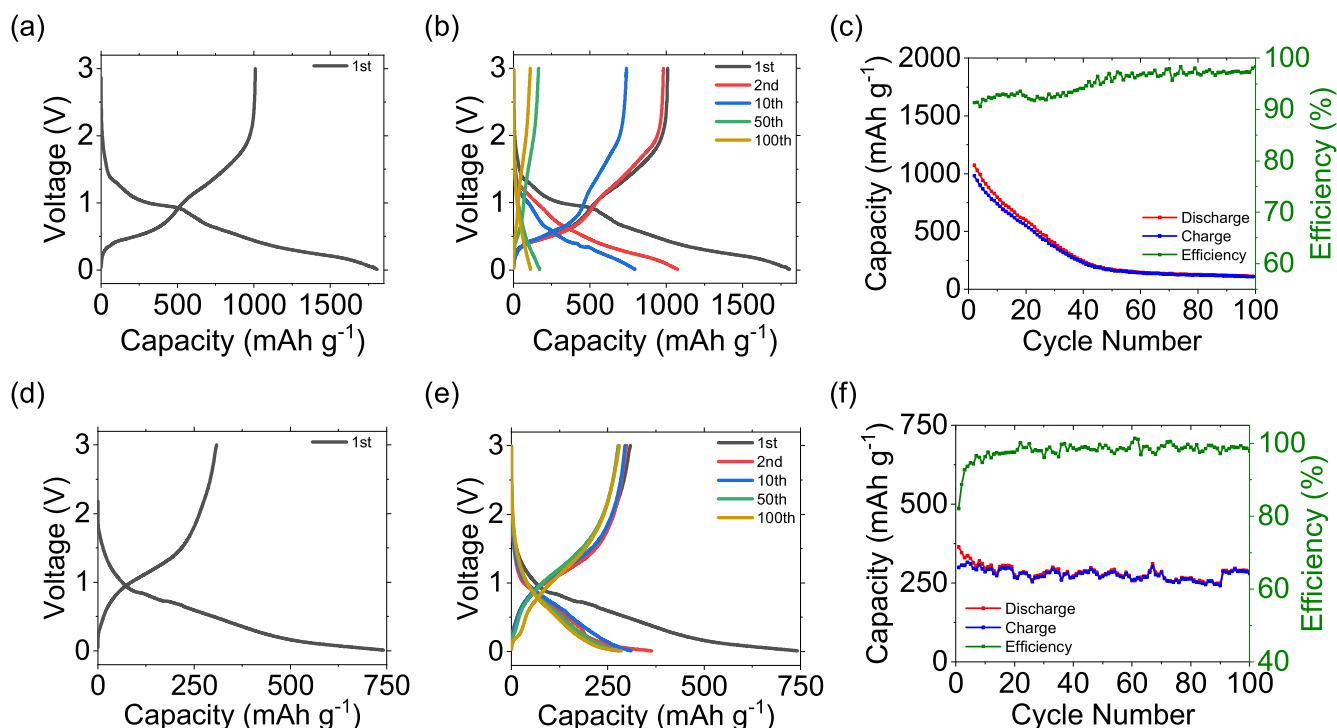


Figure 5. Galvanostatic cycling for a SnO_2 IO in a Li-ion half-cell at a specific current of 50 mA g^{-1} showing (a) charge and discharge voltage profiles for first cycle, (b) a range of select charge discharge profiles up to the 100th cycle and (c) specific capacity and coulombic efficiency (CE) as a function of cycle number. Galvanostatic cycling results for a SnO_2 IO in a Na-ion half-cell at a specific current of 50 mA g^{-1} showing (d) charge and discharge voltage profiles for first cycle, (e) a range of select charge discharge profiles like the Li-ion half-cell and (f) specific capacity and coulombic efficiency as a function of cycle number.

expected current responses such as SEI formation undetected. The contrast indicates a more efficient, progressive lithiation relative to sodiation, despite that sodiation speed has been found to be $\sim 20\times$ lower than that of lithiation.⁹¹ More efficient charge flow in the Li-ion system results in greater utilization of the active material, and a more uniform lithiation process. While the sodiation speed is slower, its utilization of less active material means that sharp current responses, as seen for the alloying process, occur due to more instantaneous sodiation in localized areas rather than a gradual mechanism throughout the entire electrode. (3) Impact of first CV scan: For the Li-ion system, each CV scan demonstrates the same set of peaks, except for those related to SEI formation in the first scan. Peak currents decrease incrementally, with slight voltage shifts as expected. For the Na-ion system, there is a stark contrast between the first scan and all subsequent scans. Considerable volume expansion and unstable electrolyte evolution is assumed to occur during the first scan, and the associated peak currents are not representative of the subsequent behaviour of the system. Following this first scan, the curves follow a much more stable pattern, with incrementally lower peak currents and slight voltage shifts as in the Li-ion case.

Galvanostatic cycling comparison in Li and Na half cells.—The response of SnO_2 IOs in Li-ion and Na-ion half cells is demonstrated here using the galvanostatic cycling results presented in Fig. 5 at a current density of 50 mA g^{-1} in both cases.⁹⁹ The calculation for SnO_2 is based on the sum of the capacities of conversion and alloying charge storage mechanisms.

For the alloying reaction in a Li-ion system based on the maximum molar ratio of 4.4 during conversion as per Eq. 3 the theoretical capacity is 782 mAh g^{-1} . The equivalent calculation for the Na-ion system, based on a molar ratio of 3.75 during conversion, results in a theoretical capacity of 667 mAh g^{-1} . In both systems, the conversion reactions result in a capacity of 711 mAh g^{-1} . The total theoretical capacity for the Li-ion and Na-ion systems are 1493 mAh g^{-1} and 1378 mAh g^{-1} , respectively.

Figure 5a shows the capacity-voltage profile for the first cycle in the Li-ion system. The current density of 50 mA g^{-1} corresponds to a C-rate of 0.033 C, based on a theoretical maximum for $1 \text{ C} = 1493 \text{ mA g}^{-1}$, corresponding to the sum of the theoretical capacities delivered by the reduction to metallic Sn, and the formation of the $\text{Li}_{4.4}\text{Sn}$ alloy. The first discharge capacity is 1806 mAh g^{-1} . Above the theoretical value, this additional capacity can be attributed to the formation of the SEI layer on the IO surface, along with the formation of quasi-reversible Li_2O from SnO_2 nanoparticles.¹⁰⁰ The voltage plateau of the first discharge begins just above 1 V as expected based on the CV results, where the onset of the reduction mechanism begins. The plateau is further enhanced below 0.5 V, where alloying begins. Figure 5b shows the evolution of the capacity-voltage profiles for select cycles up to the 100th cycle. A significant drop in capacity for the 2nd cycle is observed as expected, with a value of 1075 mAh g^{-1} , which is below the theoretical capacity. While in the first cycle capacity above the theoretical is provided by the energy related to SEI formation, the drop below the theoretical for the second cycle is a result of irreversible capacity loss from the initial reduction and alloying processes, along with volume expansion of the electrode material and unwanted side reactions with SEI species.

In Fig. 5c, the maximum specific capacities for the discharge and charge of each cycle, along with the Coulombic efficiency (CE) for the Li-ion system are shown. The most notable aspect of these results is the relatively poor capacity retention. Most of the capacity is lost in the first 40 cycles, and the capacity stabilizes considerably after 60 cycles. The discharge capacity at the 100th cycle is 112 mAh g^{-1} . The continued stability at this capacity level up to 250 cycles is demonstrated in Fig. S3 of the Supplementary Material. Low initial CE is a symptom of the large initial irreversible capacity due to large volume expansion of SnO_2 upon lithium uptake.¹⁰¹ While an initial low CE is typical of SnO_2 anodes,¹⁰² the value remains low for the first 40 cycles, where the most dramatic loss in capacity occurs, an atypical trend as the CE usually stabilizes in early stage cycling, indicating that during the first 40 cycles, the rate of lithium insertion is

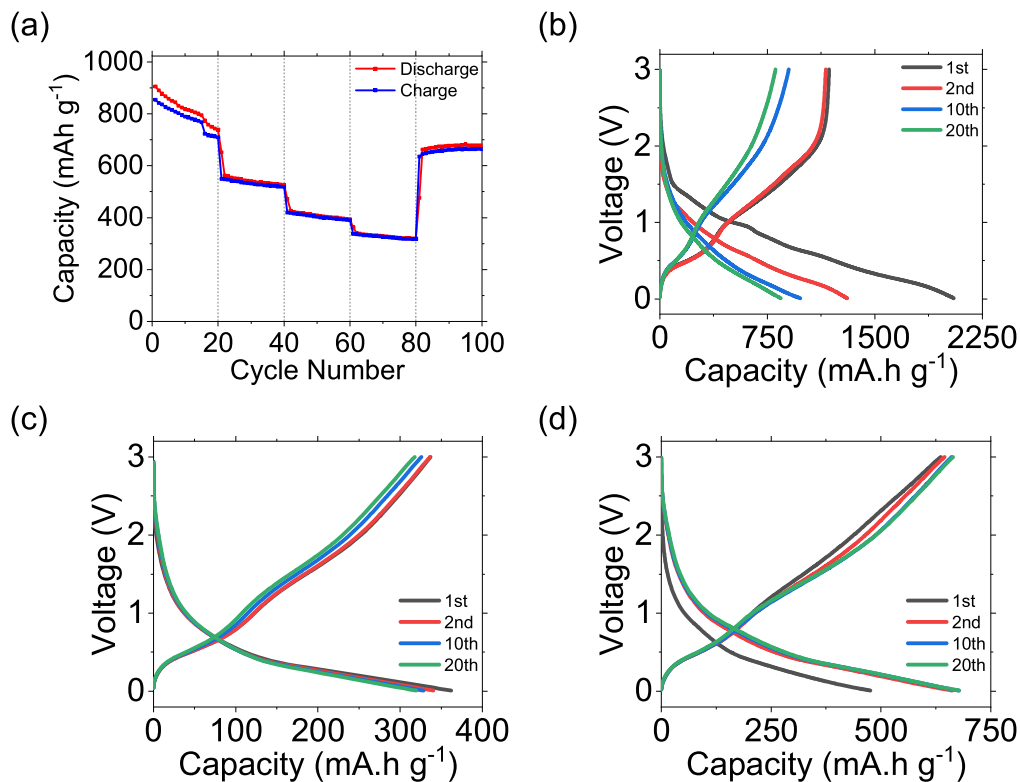


Figure 6. (a) Rate capability testing of SnO_2 IO in Li-ion system. Galvanostatic cycling curves (b) for initial specific settling current of 50 mA g^{-1} prior to the rate test, (c) maximum specific current applied during rate test of 450 mA g^{-1} , and (d) charging and discharging at a final current of 50 mA g^{-1} .

affected at a far greater rate than its removal. The value then increases and stabilizes to a value of 98% at 60 cycles.

The first discharge for the Na-ion system, shown in Fig. 5d, is 741 mAh g^{-1} . The value is considerably lower than the theoretical capacity of 1378 mAh g^{-1} predicted by Faraday's law, which is the sum of the capacities delivered by the reduction to metallic Sn and the formation of the $\text{Na}_{3.75}\text{Sn}$ alloy. However, it is representative of the first discharge capacities reported in the literature for SnO_2 anodes in Na-ion systems.¹⁰³ Given that the difference between the theoretical and practical capacity of SnO_2 in Na-ion systems is well established, more accurate C-rate calculations can be performed here if based on the nominal capacity of 667 mAh g^{-1} . The current density of 50 mA g^{-1} corresponds to 0.075 C based on $1 \text{ C} = 667 \text{ mA g}^{-1}$. In Fig. 5e, the second discharge capacity is 364 mAh g^{-1} . The large irreversible capacity loss here is again attributed to SEI formation, along with the irreversibility that has been documented in both the initial conversion and alloying reactions for SnO_2 vs Na/Na^+ . The voltage plateaus occur at a slightly lower voltage than the Li-ion case, starting at about 1 V with the reduction of SnO_2 to metallic Sn. A second increase in the plateau is observed below 0.1 V , attributed to the alloying reaction of metallic Sn to form the Na_xSn phase. Figure 5f shows the maximum specific capacities for the discharge and charge for each cycle, along with the CE for the Na-ion system. Like the Li-ion system, the initial value is indicative of SEI formation which tends to prevent Na^+ insertion at a greater rate than its removal. However, the value stabilizes at 20 cycles and does not drop below 96% past this point. While the capacity of the second cycle is approximately half that of the Li-ion system, the capacity retention is significantly better. The capacity of the 100th cycle is $\sim 280 \text{ mAh g}^{-1}$, representing a total loss from the 2nd to the 100th cycle of only 85 mAh g^{-1} , a capacity retention of 76.6%. The impressive capacity retention of the SnO_2 IO in the Na-ion system is one of the key results of this work.

Comparing rate capability in Li- and Na-ion cells.—Figure 6a shows the results from macroporous SnO_2 IO rate performance

testing for a Li-ion system. Figure 6b shows the capacity-voltage profiles for select cycles performed prior to rate testing to demonstrate the initial capacities reached. The profiles in Fig. 6c correspond to cycles during maximum rate testing at 450 mA g^{-1} . Figure 6d shows profiles from the last stage of rate testing where the current density was reduced back to the initial testing value of 50 mA g^{-1} to evaluate the ability of the electrode to recover some of the capacity not accessed at higher rates. Comparison of the capacity achieved at low current density in the initial and final stages of rate testing is indicative of the extent to which the electrode has been degraded.

The initial discharge capacity during rate testing at 50 mA g^{-1} is $\sim 900 \text{ mAh g}^{-1}$. The initial discharge capacity during the last stage of rate testing when returned to 50 mA g^{-1} is $\sim 660 \text{ mAh g}^{-1}$, representing a capacity retention of $\sim 73\%$. For comparison, one study reported SnO_2 nanotubes which demonstrated a capacity retention of $\sim 52\%$ after rate performance testing for 50 cycles.¹⁰⁴ Our rate performance results are similar to those reported previously in our group for an SnO_2 anode tested in a Li-ion system.¹⁰⁵

While there is a significant reduction in the capacity during the 10 cycles at the first rate of 50 mA g^{-1} , it stabilizes from the second rate. The capacity reduces with each increase in current density as expected. The capacity recovery after maximum rate cycling is at the higher end of values reported in the literature.^{106,107} From the capacity-voltage profiles, those in Fig. 6b demonstrate the expected shape based on the conversion and alloying reactions of SnO_2 in a Li-ion system. In Figs. 6c and 6d, the curves are attenuated relative to those corresponding to the initial rate, indicating that the reactions are inhibited from reaching completion particularly at voltages above 1 V .

Figure 7a shows rate performance testing results for a SnO_2 IO in a Na-ion system. The current densities used for rate testing are identical to those used for the Li-ion system. A total of 20 cycles at 25 mA g^{-1} were performed prior to rate testing and the associated charge-discharge curves are shown in Fig. 7b. Low initial current densities are used for most reports in the literature for pure SnO_2

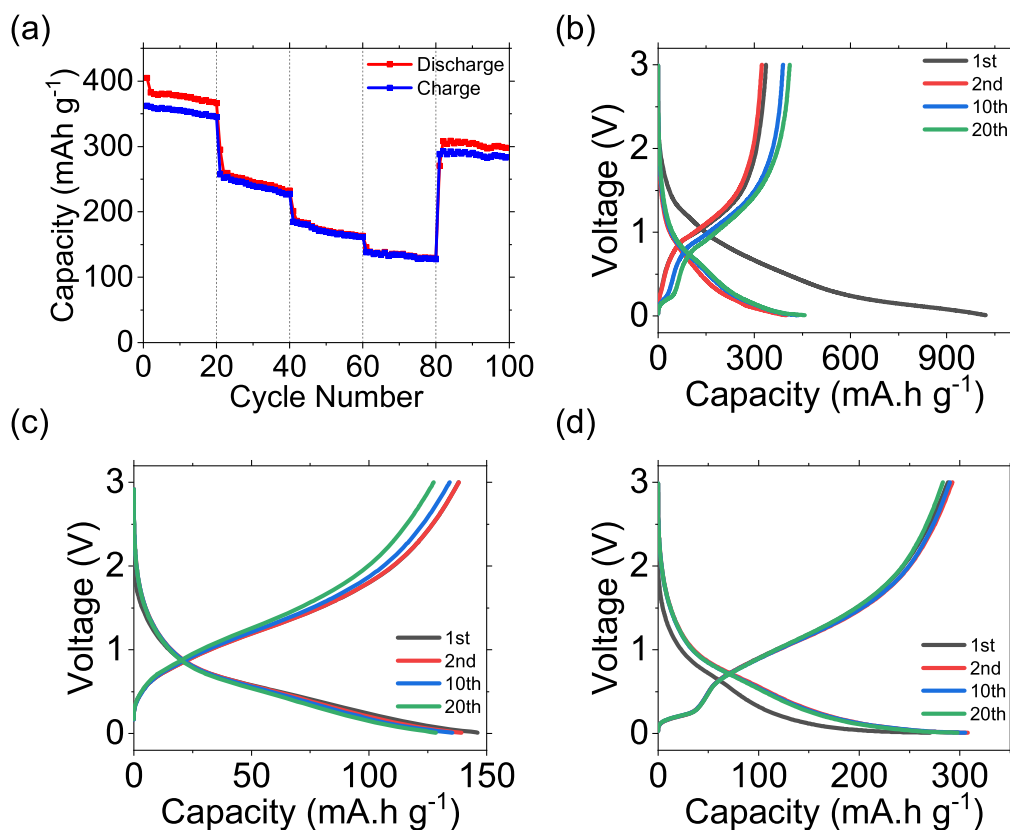


Figure 7. (a) Rate capability testing of SnO₂ IO in Na-ion system. Galvanostatic cycling curves (b) for initial specific settling current of 25 mA g⁻¹ prior to rate test, (c) maximum specific current applied during rate test of 450 mA g⁻¹, and (d) final current of 50 mA g⁻¹.

anodes in Na-ion systems.^{30,108} The low current densities are due to the significant volume expansion typical of the conversion and alloying reactions between SnO₂ and Na/Na⁺. For alkali-ion batteries, the beginning of any cycling regime corresponds to the most vulnerable stage and the system typically only stabilizes after the first few cycles.^{109,110} The initial discharge capacity for the rate test is ~400 mAh g⁻¹. From the rate performance data, there are two key findings. Firstly, efficient cyclability is evident. Stable capacities are observed for each rate with a gradual increase in capacity as current density increases, reaching a minimum of 150 mAh g⁻¹ at the highest rate of 450 mA g⁻¹. The associated charge-discharge curves are shown in Fig. 7c which further emphasise the stability in that their shape is retained with a strong plateau during discharge still observed just below 1 V. Second, for the final rate where current density is lowered back to 50 mA g⁻¹, the system demonstrates excellent capacity recovery to 298 mAh g⁻¹. The associated charge-discharge curves are shown in Fig. 7d. The capacity retention of the system after the rate performance test over the 100 total cycles is ~74%.

The rate capability of SnO₂ IO anodes has been demonstrated here for both Li-ion and Na-ion systems. For Na-ion systems, the capacity values and stability at higher specific currents match or exceed many previous reports on purely nanostructured SnO₂ anodes,^{66,72} and even with reports of more conductive carbonaceous SnO₂ nanocomposites.^{111–113} Table S1 of the Supplementary Material provides a breakdown of the retained capacities for a range of pure SnO₂ nanostructures and carbonaceous SnO₂ nanocomposites after rate performance testing compared to the SnO₂ IOs investigated in this work.

Reversibility of conversion between SnO₂ and metallic Sn.—

The conversion and alloying mechanisms dominate charge delivery for SnO₂ in both Li-ion and Na-ion systems. The peaks associated with these mechanisms are evident in the CVs, as shown earlier for a

fixed scan rate of 0.1 mV s⁻¹. For a perfectly reversible system, the potentials at which these peaks occur remain unchanged, irrespective of the scan rate applied. One of the ways to distinguish between reversible, quasi-reversible and irreversible processes is by examining the change to the CVs with scan rate. Li⁺ and Na⁺ intercalation reactions tend to follow quasi-reversible processes, where peak potential shift to higher values with an increase of scan rate due to overpotential.¹¹⁴ The conversion reactions between SnO₂ and both Li⁺ and Na⁺ follows a similar trend. However, the conversion mechanism of SnO₂ in Na-ion batteries has been documented as less reversible. Figures 8a and 8b show CVs for a range of scan rates from 0.05 mV s⁻¹ to 5 mV s⁻¹ for the Li-ion and Na-ion systems, respectively. These results were obtained after five cycles at a fixed scan rate of 0.1 mV s⁻¹. CV scans obtained within the same range of scan rates without any prior fixed rate scanning are provided in Fig. S4 of the Supplementary Material. The overall current response increases as a function of scan rate as expected. The irreversibility of the oxidation and reduction mechanisms can be quantified by the peak separation (ΔV_{conv}) between the oxidation peak potential ($V_{\text{p,a}}$) during the anodic scan, and the reduction peak potential ($V_{\text{p,c}}$) during the cathodic scan. Figure 8c shows ΔV_{conv} as a function of scan rate for the Li-ion and Na-ion systems. At scan rates below 0.25 mV s⁻¹, peak separation is minimal. Above this, the peak separation for the Na-ion system is more than double that of the Li-ion system, indicating irreversibility for the Na-ion system.

The reactions which govern the peak currents in a battery system are a sum of the contributions of Faradaic (capacitive) and non-Faradaic (diffusive) processes.¹¹⁵ The relationship between the magnitude of observed peak currents and the scan rate (ν) can be described by the Randles-Sevcik equation and used to quantify the diffusive and capacitive contributions to peak current at a specific potential.¹¹⁴ For a capacitive-driven process, the associated current response is proportional to ν . For a diffusion-driven process, the current response is proportional to $\nu^{1/2}$. The current associated with

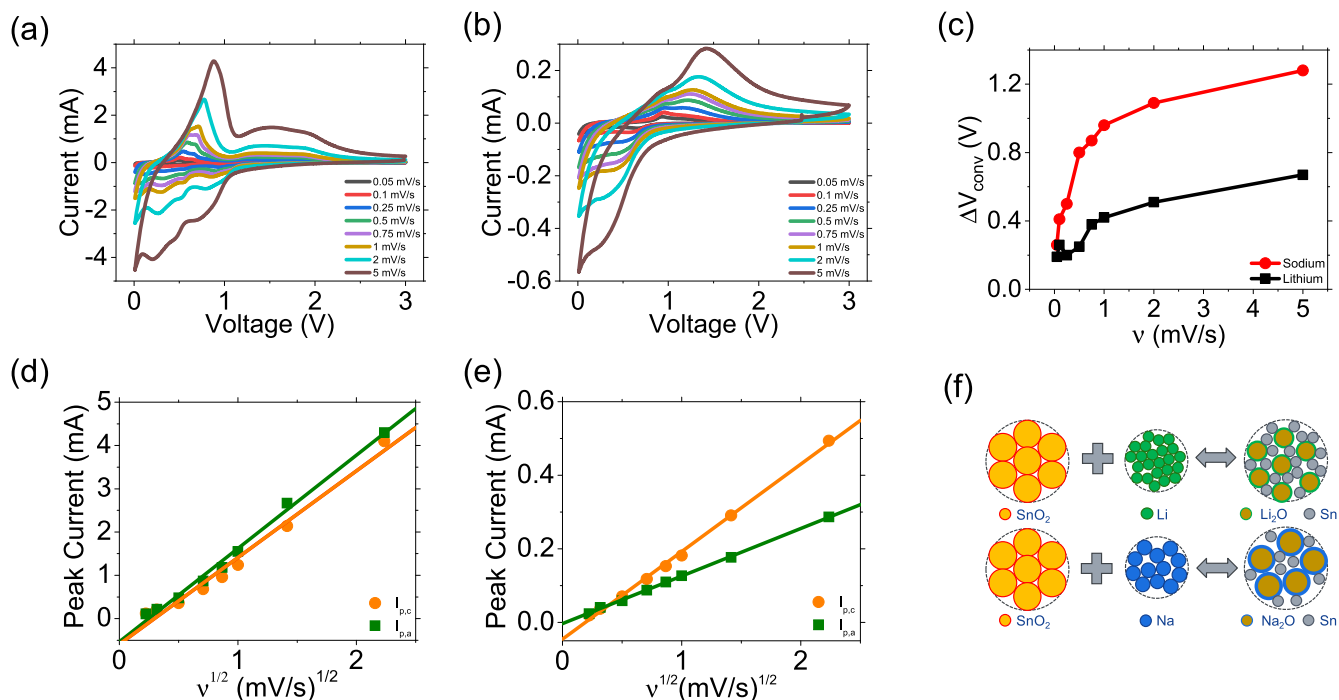


Figure 8. Cyclic voltammetry for a range of scan rates from 0.05 mVs^{-1} to 5 mVs^{-1} for a SnO_2 IO (a) vs Li/Li^+ and (b) vs Na/Na^+ . (c) Potential separation between oxidation and reduction peaks as a function of scan rate for the Li-ion and Na-ion systems. (d) Peak current response as a function of the square root of scan rate for the anodic oxidation ($I_{p,a}$) and cathodic reduction ($I_{p,c}$) reactions in the (d) Li-ion system and (e) Na-ion system. The lines are linear fits to each data set. (f) Visual representation of the conversion reactions between SnO_2 and metallic Sn in both the Li-ion and Na-ion systems.

the oxidation ($I_{p,a}$) and reduction ($I_{p,c}$) peaks are shown as a function of ($\nu^{1/2}$) for the Li-ion system in Fig. 8d. Figure 8e shows the same two relationships for the Na-ion system. For any battery system, diffusive currents should exceed capacitive currents. Ion transport can be described by a mechanistic three-step process, where diffusion acts as the rate-limiting step.¹¹⁶ One of the primary benefits of the IO morphology is the provision of excellent opportunities for efficient ion diffusion through the thin pore walls.

The poor linear fits in Fig. 8d show that diffusive current contribution is much lower than expected for the Li-ion system. The excellent agreement of the linear fits in Fig. 8e show that the total current for the Na-ion system is dominated by the diffusive contribution. Clearly, a greater buildup of capacitive current occurs in the Li-ion system, a potential cause of the rapid capacity degradation and instability in the first 40 cycles observed earlier for galvanostatic cycling in the Li-ion system. On the same basis, the excellent approximation of the $\nu^{1/2}$ for the peak current in the Na-ion system stipulates that the conversion reactions between SnO_2 and Sn are diffusion driven.¹¹⁷

Furthermore, valuable insight into the rate performance of the Na-ion system can be gleaned from direct comparison of the rate of change of the anodic and cathodic peak currents. Examination of Fig. 8e shows that the rate of change of $I_{p,c}$ as a function of scan rate is far greater than $I_{p,a}$ for scan rates above 1 mVs^{-1} . The contrast suggests that the degree of cathodic reduction of SnO_2 to metallic Sn takes place at a greater rate than the reverse process, anodic oxidation of SnO_2 to Sn. A study by Ding et al. in 2014 reported the presence of unreacted $\beta\text{-Sn}$, surrounded by amorphous Na_xSn , alluding to a potential explanation for the irreversibility of the oxidation process. As cycling continues, the amount of unreacted Sn increases. The impediment caused by the surrounding amorphous Na_xSn alloy prevents its partaking in the oxidation process back to SnO_2 .¹¹⁸ While irreversibility proves advantageous here, those interested in its regulation can consult previous work on improving electrochemical performance of nanoparticulate SnO_2 anodes by tailoring oxygen vacancy.¹¹⁹

A visual representation of the conversion between SnO_2 and metallic Sn in both Li-ion and Na-ion systems is shown by the

schematic in Fig. 8f. The conversion reaction involves the reversible formation and decomposition of an associated metal oxide, which acts as a “buffer matrix” for relieving volume change and improves cycling stability in which the metallic Sn particles are embedded.¹²⁰ This model describes the situation in the $\sim 50 \text{ nm}$ thick walls that comprise the electrolyte-soaked IO structure. Nevertheless, the matrix induces large voltage hysteresis due to sluggish reaction kinetics. The size of the metal oxide molecules also impacts the insertion and removal of Sn particles to and from the matrix as conversion proceeds. The smaller Li_2O molecules permit easier movement of Sn particles in and out of the matrix for the Li-ion system while the opposite is true for the larger Na_2O molecules. Consequently, an aggregation of elemental (Sn) particles can occur which leads to a less reversible Na-ion conversion reaction.¹²¹ Additionally, intrinsic kinetic limitation of the sodiation reaction as a result of poor Na-ion diffusion and low electronic conductivity of the intermediate reaction products in SnO_2 has been proposed.¹²²

In Figs. 9a–9e, differential capacity plots (DCPs) are shown corresponding to the discharges from the previously presented rate performance testing of the SnO_2 IO anode in a Li-ion system. Figures 9f–9j shows the equivalent DCPs for the corresponding charge profiles. The DCPs are presented in the order of current densities used for rate testing. An evident trend in both the discharges and charges is in the similarities between the initial and final rates, both at a current density of 50 mA g^{-1} . Likewise, there is a similarity between the three DCPs at higher currents, 150 mA g^{-1} , 300 mA g^{-1} , and 450 mA g^{-1} .

For the discharges, the DCPs are shown for a reduced voltage range, as little change was observed above 2 V . As voltage is swept downwards from 2 V , there is a positive gradient in differential capacity to 0.5 V as conversion of SnO_2 to metallic Sn takes place. A mosaic pattern is observed below 0.5 V as alloying begins, a result of the progressive alloying regime to form Li_xSn . The same regime was described earlier in the CV analysis section, where it presented as a major alloying peak at 0.01 V with other lower intensity peaks in its vicinity. The mosaic pattern indicates that the capacity delivered by the alloying reaction varies in magnitude between

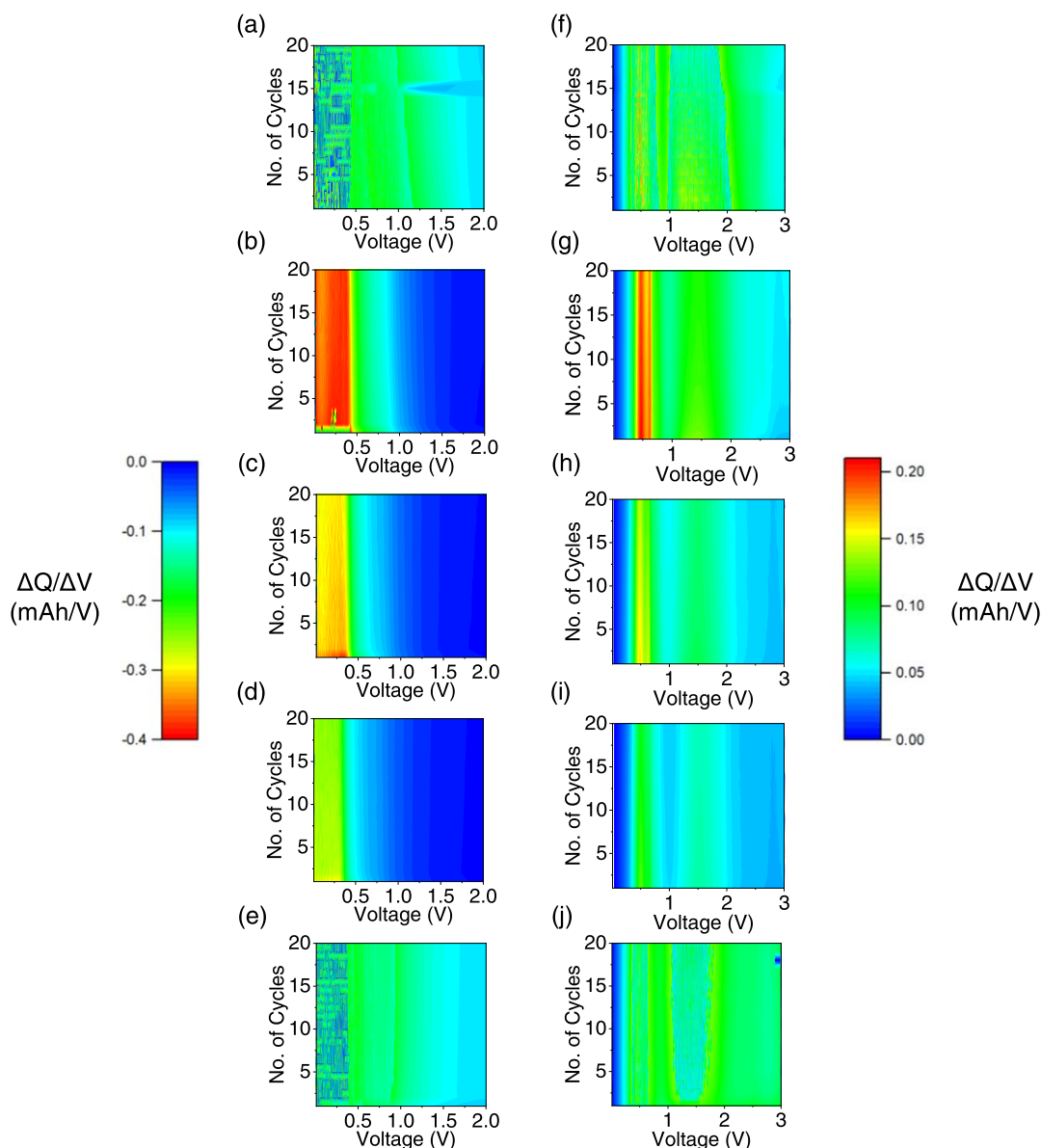


Figure 9. Differential capacity colour maps obtained from rate capability testing of the SnO_2 IO in the Li-ion system at current densities presented in the following order from top to bottom: 50 mA g^{-1} , 150 mA g^{-1} , 300 mA g^{-1} , 450 mA g^{-1} , 50 mA g^{-1} , generated from discharges (a)–(e) and charges (f)–(j). Colour bars associated with discharges and charges positioned left and right, respectively.

cycles here. There is little to no gradient between the conversion and alloying reactions, their contributions are on the same order of magnitude at this stage. Interestingly, the DCP corresponding to the final rate at the same current density of 50 mA g^{-1} in Fig. 9e follows an almost identical pattern.

For discharges at the higher current densities in Figs. 9b–9d, each of the three DCPs follows a similar pattern, with three distinct stages. (1) $2 \text{ V} \rightarrow 1 \text{ V}$: A blue region at the three rates, minimal capacity change, no major electrochemical reactions take place here. (2) $1 \text{ V} \rightarrow 0.5 \text{ V}$: Increased differential capacity designated by green at 150 mA g^{-1} , narrows and diminishes towards blue for the two highest rates. (3) $0.5 \text{ V} \rightarrow 0.01 \text{ V}$: Maximum differential capacity illustrated by a vibrant red region at 150 mA g^{-1} , with some fluctuations observed for the first three cycles at this rate. From the diminishing of the two lower voltage regions in the DCPs, a reduction in capacity from the reduction and alloying processes occurs for each increase in rate, in line with the literature.¹²³ The narrowing shows that each increase in rate results in much sharper reduction and alloying processes.

For the charges, the initial and final rates are also similar. In both cases, there is no capacity change below 0.2 V as expected. Above 0.2 V , the DCP are predominantly green with intermediate capacity, a mosaic pattern observed up to 2 V , and maxima occurring mainly around 0.5 V and 1 V . At the second rate of 150 mA g^{-1} , a thin red region occurs at about 0.5 V , corresponding to the dealloying regime. From $0.65 \text{ V} \rightarrow 2 \text{ V}$, a green band appears associated with gradual oxidation of Sn to SnO_2 . Much like the initial and final rates, it is unclear here where dealloying ends and oxidation begins. As the rate increases to 300 mA g^{-1} and 450 mA g^{-1} , the separation between dealloying and oxidation bands becomes clearer. Simultaneously, the differential capacity of each band decreases. The alloying band diminishes from red to orange and the oxidation band from green towards blue.

DCPs obtained from rate testing of the Na-ion system presented previously are shown in Fig. 10 in the same order as the Li-ion case. Once again, for the discharges, DCPs obtained from the initial and final rate tests exhibit similar behaviour, while DCPs from the three higher current densities follow their own pattern. Unlike the Li-ion

system, the charges exhibit similar behaviour at all five rate testing steps. The initial and final rate DCPs are predominantly green. For the initial rate, regions of increased differential capacity occur as yellow bands. A wide band yellow band occurs between 0.4 V and 0.75 V, associated with the reduction process. At lower voltages, there are regions of varying differential capacity between cycles, with maxima close to 0.01 V where alloying occurs. Unlike the Li-ion case, the separation between reduction and alloying regimes can be detected for the initial rate. In the final rate, the separation is less clear. However, a thin yellow band occurs at 0.5 V, indicative of a more instantaneous reduction process, since there is far less active SnO_2 to be reduced in the system because of the irreversibility of the oxidation process suggested by our earlier CV analysis.

DCPs for discharges at the three higher rates show a positive differential capacity gradient consisting of three primary stages, like the Li-ion case. For the Na-ion system at the second rate of 150 mA g^{-1} , a dark blue band above 0.75 V designates the region where there is an absence of any of the primary electrochemical reactions which contribute to battery capacity. A light blue band between 0.75 V and 0.1 V designates the progressive reduction

process. As cycling continues, a split in the centre of this band appears and grows, indicating the formation of a doublet peak, which suggests a two-step reduction process. At 300 mA g^{-1} and 450 mA g^{-1} , the three bands associated with the same three stages during discharge remain, diminishing in intensity with increase in rate.

For the charges, a clearer separation between processes is observed for all rates. At the initial and final rates, a thin, red-orange band occurs at $\sim 0.2 \text{ V}$, associated with the dealloying regime. For the second rate of 150 mA g^{-1} , the dealloying band diminishes to green. For the two highest rates of 300 mA g^{-1} and 450 mA g^{-1} , the dealloying band is absent, suggesting a minimal dealloying charge contribution. Earlier CV analysis demonstrated the difficulty in detection of the dealloying process. Its detection here suggests that an initial stabilisation period, such as the 20 cycles used here prior to rate testing, creates more favourable conditions for the dealloying process to occur.

A clearly separated green band occurs from 0.8 V to 2 V, where progressive oxidation occurs. Oxidation is clearly at a maximum between 0.8 V and 0.125 V, thin red bands appear initially at each of

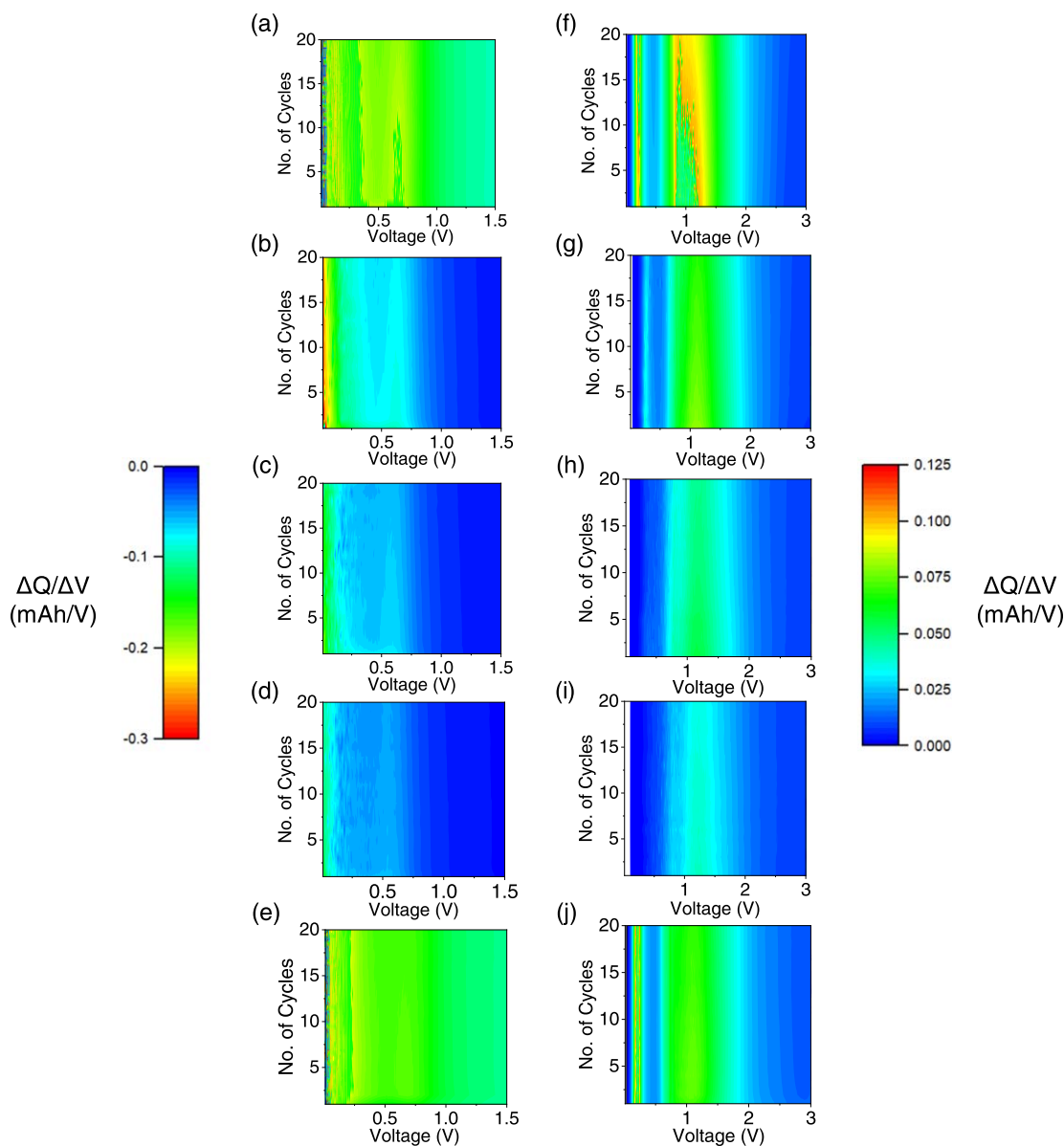


Figure 10. Differential capacity colour maps obtained from rate capability testing of the SnO_2 IO in the Na-ion system at current densities presented in the following order from top to bottom: 50 mA g^{-1} , 150 mA g^{-1} , 300 mA g^{-1} , 450 mA g^{-1} , 50 mA g^{-1} , generated from discharges (a)-(e) and charges (f)-(j). Colour bars associated with discharges and charges positioned left and right, respectively.

these potentials, before the width of each band grows gradually until they meet to form a wider band at 16 cycles. At the final rate, the system returns to similar behaviour as the initial rate. The thin dealloying peak returns. For the oxidation process, the red bands do not return, and a wide green band signifies the gradual oxidation of Sn to form SnO₂. The lower differential capacity is expected here as the irreversibility of the reaction compounds with cycle time.^{124,125} The oxidation peak remains but diminishes in intensity and width with each increase in rate.

The differential capacity analysis performed on the rate performance testing for the SnO₂ IO in both Li-ion and Na-ion systems provide a comparative overview of how the electrochemical mechanisms vary with current density (rate), revealing some key insights. (1) In both systems, there is sufficient cycling stability such that after applying current densities at a range of higher rates, each system returns to baseline, and their electrochemical mechanisms are not disrupted. (2) At higher rates (150 mA g⁻¹–450 mA g⁻¹), DCPs can be split into three distinct regions, alloying, conversion, and inactive. At these rates, the separation between alloying and conversion mechanisms is clearest, albeit that the intensity of the bands for the two capacity contributing mechanisms diminish in both width and intensity as current density is increased. (3) Despite that the DCPs at the final rate show a return to similar behaviour as the initial rate in both systems, there is a clear contrast in the band associated with the oxidation reaction for the charges in the Na-ion system, designated by the disappearance of the orange-red bands which appears at the initial rate as two separate thin bands and grow to form a single wide band. The absence of this peak at the final rate supports our earlier hypothesis concerning the irreversibility of the oxidation reaction of metallic Sn to SnO₂ during charge in the Na-ion system. The irreversibility was shown earlier to increase with scan rate and shown here to increase with current density.

Conclusions

A comprehensive comparison of the electrochemical response and rate behavior of macroporous SnO₂ IO anodes in both Li-ion and Na-ion batteries, showed how such nanostructures are beneficial particularly for Na-ion systems. Voltammetry at a fixed scan rate of 0.1 mV s⁻¹ revealed that while both systems are governed by similar electrochemical reactions, the current responses in the Na-ion system are much lower, indicating incomplete reactions and unused active material. While the initial capacity is much higher in the Li-ion system than the Na-ion system, galvanostatic cycling results demonstrate that cycling stability is greater in the Na-ion system, resulting in superior capacity retention of 76.6%, while the Li-ion system experienced dramatic capacity loss in the first 40 cycles.

The CV scan rate analysis stipulates that the conversion reaction is less reversible in the Na-ion system than the Li-ion system. Irreversibility of a reaction that provides a substantial contribution to the capacity delivered by the battery is typically considered an adverse effect, draining the capacity of the battery over time. However, conversion reactions are well documented to cause significant volume expansion, particularly in SnO₂. The results throughout this work indicate that while this irreversibility may lead to a certain capacity loss, the associated reduction in the extent of the conversion reaction mitigates volume expansion and preserves the structural integrity of the electrode. Furthermore, given the rate of reduction to metallic Sn exceeds the rate of the reverse oxidation reaction, as cycling continues, the system cycles with a progressively greater amount of metallic Sn, which improves electrical conductivity.

One of the primary motivations for the use of macroporous IOs in any binder-less, additive-free battery electrode is the short ion diffusion distances provided by the thin pore walls, which have been shown to improve rate performance. The rate performance of the SnO₂ IOs in the Na-ion system demonstrated here is commensurate with a wide variety of pure SnO₂ nanostructure slurries reported in the literature. At the highest rate of 450 mA g⁻¹, the capacity retained is

150 mAh g⁻¹. The capacity recovery to 300 mAh g⁻¹ at the last stage of rate testing indicates limited electrode degradation. Differential capacity analysis of these rate tests gave further insight into the nature of the response at different rates.

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