Hydrothermal Fabrication of Three-Dimensional Secondary Battery Anodes

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High energy and power density rechargeable (secondary) battery designs, as well as lower cost battery manufacturing protocols are currently under active exploration.\[1\]-\[3\] One route to increase power and energy is electrode mesostructuring, which is fabricating the electrode with characteristic dimensions and pores that optimize ion and electron transport, as well as accommodating the large volume changes of high energy density active materials such as silicon. Our general design strategy for mesostructured battery electrode has been to coat an electrically conductive and structurally robust three-dimensional (3D) scaffold with a layer of electrochemically active material.\[4\]-\[6\] Other groups have formed 3D-structured electrodes from porous conductive polymer hydrogels,\[7\] macroporous carbon,\[8\] stainless-steel meshes,\[9\] Ni networks,\[10\] and Ni foams.\[11\] A recent set of interesting examples of 3D structured electrodes has been reported by Alshareef, in which a series of carbon fiber and sponge current collectors\[12\]-\[14\] were reported.

While many approaches have now been developed to deposit electrochemically active materials onto 3D templates\[13\] to form battery electrodes, including electrodeposition,\[16\] chemical vapor deposition (CVD),\[17\] and atomic layer deposition (ALD),\[18\] these methods have significant limitations. Deep infilling of active materials into porous 3D templates can be difficult. Often the material of interest simply coats the surface or near-surface region of the 3D scaffold. CVD and ALD are generally slow and expensive, and provide only a limited selection of active materials. There is a limited subset of materials which can be electrodeposited, and electrodeposition normally involves several steps to convert the deposited material into the electrochemically active phase. A new large-area, low-cost method that can coat 3D scaffolds with active nanomaterials would be of great benefit. Here we present a generalized hydrothermal strategy for fabricating 3D mesostructured battery electrodes. While hydrothermal synthesis is a low-cost process that can produce high-quality materials with well-controlled morphologies,\[19\] hydrothermal growth of mesostructured electrodes has not been previously demonstrated. We show via hydrothermal processing the facile uniform deposition of electrochemically active materials throughout the entire internal structure of a 3D mesostructured electrode which may overcome many of the limitations of electrodeposition, CVD, and ALD.

A series of electrochemically active anode materials (SnO\(_2\), Co\(_3\)O\(_4\), and Fe\(_3\)O\(_4\)) with the potential to exceed the energy density of commonly used graphite-based anodes (theoretical capacity of 372 mA h g\(^{-1}\))\[3\] were hydrothermally deposited onto both Ni and SiO\(_2\) inverse opal 3D scaffolds. The electrodes are found to have well-controlled morphologies and good uniformity through the electrode thickness. In addition, multilayered structures can also be formed via the hydrothermal strategy (we find that for some systems a multilayered design offers improved performance). Three specific electrode designs were fabricated, SnO\(_2\) nanoparticles (NPs) hydrothermally grown on a Ni inverse opal followed by hydrothermal coating with flake-like SiO\(_2\), Co\(_3\)O\(_4\) nanoplatelets hydrothermally deposited onto a Ni inverse opal, and Fe\(_3\)O\(_4\) hydrothermally grown on a sol–gel-derived SiO\(_2\) inverse opal. All of these three systems can potentially be improved by mesostructuring. SnO\(_2\) for example, possesses a theoretical capacity of 782 mA h g\(^{-1}\); however, its poor conductivity, electrochemical instability, large volume expansion upon lithiation, and unstable solid electrolyte interface (SEI) have limited its use.\[20\] Related issues are present for Co\(_3\)O\(_4\) and Fe\(_3\)O\(_4\)-based electrodes.\[21,22\] We and others have shown that through mesostructuring, and by reducing size of the primary particles to the nanoscale, it may be possible to overcome some of these issues.\[23,24\]

Using a combined electrodeposition and hydrothermal deposition strategy, the multi-layered inverse opal Ni@SnO\(_2\) NPs@SiO\(_2\) anode described in Figure 1 was formed. Briefly, an electrodeposited Ni inverse opal current collector, is used as foundation for the SnO\(_2\) NP growth. A dense layer of SnO\(_2\) NPs with a diameter of ca. 5 to 8 nm was hydrothermally grown onto the Ni inverse opal, followed by annealing. The SnO\(_2\) was then coated with a flake-like SiO\(_2\) layer to protect the SnO\(_2\) against degradation. The Ni inverse opal provides good electrical conductivity and a high structural stability, the active SnO\(_2\) NP layer possesses a short solid-state diffusion length for Li ions, and the Li-ion permeable SiO\(_2\) coating improves the cycle life, perhaps by preventing the SnO\(_2\) NPs from detaching from the
current collector during cycling as they expand and contract, and by stabilizing the SEI layer.

Figure 2a,b and Figure S1 in the Supporting Information show the sample morphology during the fabrication process. After annealing at 95 °C for 3 h, the PS spheres slightly sinter, increasing the size of their contact points (Figure S1a,b, Supporting Information). Following Ni electrodeposition and PS sphere removal, the 3D inverse opal is formed (Figure S1c,d, Supporting Information). The SnO$_2$ NPs were then hydrothermally deposited and the structure was heated to 450 °C, resulting in the Ni scaffold being coated with a dense layer of SnO$_2$ NPs (Figure 2a). Cross-sectional images and elemental mappings (Figure S1e and S3, Supporting Information) confirm SnO$_2$ is deposited throughout the entire 3D Ni inverse opal. A SiO$_2$ film ca. 20 nm thick was then coated on the surface of the SnO$_2$ NPs via a sol–gel process (Figure S1f,g, and S2a,b, Supporting Information), and transformed into a flake-like form by a hydrothermal treatment (Figure S1i,j, and S2c,d in the Supporting Information), probably due to a dissolution and redeposition processes. During the hydrothermal treatment, sodium tetrahydridoborate slowly reacts with water, producing hydrogen and sodium metaborate, increasing the pH, which increases the solubility of the amorphous silica. Meanwhile, the increasing concentration of sodium metaborate leads to the precipitation and redeposition of silicate.$^{25}$ Importantly, from the cross-sectional SEM image (Figure S1j,k, Supporting Information), it appears that the Ni@SnO$_2$ NPs@SiO$_2$ structure is uniform throughout the inverse opal electrode (elemental distributions in Figure S4, Supporting Information). The nanocrystalline nature of the SnO$_2$ has been confirmed by XRD and TEM (Figure S5 and S6, Supporting Information). Calculated using the Sherrer equation,$^{26}$ the average SnO$_2$ NP size is about 7.6 nm. The SnO$_2$ NPs are in close contact, perhaps important for facile charge transfer, and they are highly crystalline.

The electrochemical properties of the Ni@SnO$_2$ NPs@SiO$_2$ structure are shown in Figure 2c–f. The electrodes were cycled galvanostatically at 0.16C with low and high voltage cut-offs of 0.005 and 2.0 V vs Li, respectively. The first cycle discharge and charge capacities of the Ni@SnO$_2$ NPs@SiO$_2$ electrode (Figure 2c,d) are ca. 1880 and 1040 mA h g$^{-1}$, respectively, significantly higher than the theoretical value for SnO$_2$ (782 mA h g$^{-1}$). The capacity reduces to roughly the theoretical capacity of SnO$_2$ after about 10 cycles, and after 45 cycles, the capacity is about 615 mA h g$^{-1}$. On a full electrode basis (including SnO$_2$, SiO$_2$, and Ni), the electrode exhibits an energy density of ca. 204 mA h g$^{-1}$ after 45 cycles. This structure is 40.1% w/w Ni, which we have already demonstrated can be reduced to 13.4% by electropolishing,$^{28}$ in which case the energy density would be 295 mA h g$^{-1}$ without any additional optimization. The high apparent early cycle capacity is likely from SEI formation and because of the first-discharge irreversible reaction of SnO$_2$ + 4Li$^+$ + 4e$^-$ → Sn + 2Li$_2$O.$^{27,28}$ although it is also possible hydrothermally deposited SnO$_2$ has a different capacity than conventionally grown SnO$_2$. Following SnO$_2$ reduction, the relevant electrochemical reaction is Sn + xLi$^+$ + xe$^-$ ↔ Li$_x$Sn (0 ≤ x ≤ 4.4). Although we did not attempt to reduce the SnO$_2$ to Sn metal prior to cycling, doing so would presumably increase the energy density of the electrode.$^{29,30}$ Figure 2e provides voltage vs capacity showing the energy loss during cycling which becomes smaller with cycling. The energy loss can be further quantified by integrating the charge–discharge curves (Figure S7, Supporting Information). Figure S8 in the Supporting Information presents CV during cycling.

The C-rate performance of the Ni@SnO$_2$ NPs@SiO$_2$ inverse opal electrode was investigated (Figure 2f). As expected, the capacity decreases as the C-rate increases. At 0.8C (626 mA g$^{-1}$), the early discharge capacity is 514 mA h g$^{-1}$ and the Coulombic efficiency is higher than 95%. 75 cycles later, when the C-rate returns to 0.8C, the electrode capacity is 470 mA h g$^{-1}$ (8.5%
capacity fade). The Supporting Information contains additional discussion on the effect of the C-rate, as well as a detailed discussion of the significance of the SiO₂ coating, which, in brief, greatly reduces capacity fade. We note that compared with other reports on SnO₂-based electrodes, [31,32] the hydrothermally grown Ni@SnO₂ NPs@SiO₂ electrode shows both good stability and rate performance, perhaps because the SiO₂ coating prevents fragmentation of the active layer, and helps maintain a stable SEI.

Through hydrothermal processing, a 3D Co₃O₄-based anode was also fabricated (Figure 3). As can be seen in cross-sectional SEM (Figure 3a,b), the Co₃O₄ nanoplatelets grow throughout the Ni inverse opal, the composition and structure were confirmed by XRD and HRTEM (Figure S13 and S14, Supporting Information). Figure 3c presents the electrode C-rate performance. The plateaus during charging can be ascribed to the reversible oxidation of Co to a series of cobalt oxides, while those during discharging can be ascribed to the conversion of Co₃O₄ to CoO and finally metallic Co.[33] On a Co₃O₄ basis, the discharge capacity is about 906 mA h g⁻¹ at 0.4C and about 475 mA h g⁻¹ at 2.2C. When the C-rate returns to 0.4C, the discharge and charge capacities recover to about 875 and 853 mA h g⁻¹, respectively. While the Co₃O₄ loading of this electrode is only 20.8% w/w, further improvements should be possible by at least polishing the Ni scaffold, and perhaps by increasing the native Co₃O₄ loading. The Co₃O₄ system will be fully described in a future publication.

The generalization of hydrothermal electrode fabrication strategy was demonstrated by growing Fe₃O₄ on a sol–gel-derived SiO₂ inverse opal (Figure S15 and Figure S16, Supporting Information). The Fe₃O₄ grows uniformly and densely on the template throughout the SiO₂ inverse opal (Figure 4a and Figure S16d–g in the Supporting Information). After Fe₃O₄ deposition, pores with a diameter of ca. 80 nm still remain.
Figure 3. a) Cross-sectional SEM image of the Ni@Co3O4 inverse opal. b) High-magnification SEM image at the substrate side of the Ni@Co3O4 inverse opal. c) Charge–discharge curves of the 3D Ni@Co3O4 electrode at a series of increasing C-rates followed by a 0.4C cycle. At each C-rate, the electrode was cycled 10 times.

(Figure 4b), which enables both ion diffusion through the structure and supports any volume expansion during the charge–discharge process. XRD indicates the deposit is Fe3O4 (Figure S16h, Supporting Information).

Figure 4c,d show the electrochemical performance of the Fe3O4 3D electrode. In Figure 4c, a long plateau at about 0.8 V in the first discharge process is observed, which has been ascribed to the reduction of Fe2O4 to Fe0 accompanied with the formation of Li2O[34,35] which may involve an intermediate phase of Li3Fe2O4[36]. During charging, the broad oxidation plateau at around 1.7 V can be attributed to the oxidation of Fe0 to Fe3+ and Fe2+. Starting around the fifth cycle, the charge–discharge capacity remains stable at ca. 900 mA h g⁻¹ (Fe3O4 basis), and the Coulombic efficiency exceeds 98% (Figure 4d). On a full electrode basis, without any scaffold optimization, the energy density is 380.7 mA h g⁻¹ (still higher than the theoretical value of graphite) with a typical Fe3O4 loading of 42.3% w/w. Interestingly, the SiO2-scaffolded electrodes, despite the poor electrical conductivity of SiO2, exhibit good C-rate performance. The fact that the conductivity of Fe3O4 (10⁻² S cm⁻¹) is significantly higher than some other oxide active materials, e.g., TiO2 (10⁻¹⁰ S cm⁻¹) and SnO2 (10⁻³ S cm⁻¹),[37] and that there is carbon possibly present in the structure may be why this is the case. Ferrocene was employed as the iron source for the hydrothermal reaction and during hydrothermal growth of Fe3O4 (190 °C for 36 h) carbonaceous materials may have been formed.[38] We note, more complicated structures can also be formed. For example, a SiO2@Fe3O4@SnO2 electrode can be hydrothermally fabricated (Figure S17, Supporting Information).

In summary, we have presented a generalized hydrothermal strategy for fabricating 3D battery electrodes. Ni inverse opals coated with SnO2 NPs or Co3O4 nanoplatelets, as well as SiO2 inverse opals coated with Fe3O4 were hydrothermally fabricated. We find that hydrothermal growth can deposit electrochemically active nanomaterial uniformly throughout the complex 3D mesostructure of the scaffold. The SnO2 NPs were further hydrothermally coated with a flake-like SiO2 which serves to improve their performance. This Ni@SnO2 NPs@SiO2 electrode retains a stable capacity of 615 mA h g⁻¹ even after 45 cycles, while still possessing a good C-rate performance. The Ni@Co3O4 and SiO2@Fe3O4 electrodes also exhibit attractive properties including good C-rate performances and high Coulombic efficiencies. These results show that a hydrothermal strategy is a promising general approach for fabricating mesostructured battery electrodes.

Experimental Section

Fabrication of PS Opals and Ni Inverse Opals: The Ni inverse opal was fabricated following our previous report[9] with the following modifications. For the Ni@SnO2 NP electrodes, the Ni inverse opal was fabricated on a 1 cm × 2 cm tungsten foil (Sigma–Aldrich). Before PS opal growth, the tungsten substrates were cleaned by ultrasonication in acetone, ethanol, and Millipore water for 30 min each. 600 nm polystyrene PS spheres (Molecular Probes) were dispersed in Millipore water to prepare a 0.2 wt% suspension. After drying with blown air, the W substrates were placed vertically into vials containing the PS suspension at 55 °C, as illustrated in Figure S18 in the Supporting Information. To enlarge the pore size of the final Ni inverse opal, and to enhance the bonding between PS spheres, the PS opal was sintered at 95 °C for 3 h. Ni was subsequently electrodeposited at 2 mA cm⁻² in a commercial electroplating solution (Techni Nickel S, Technic Corp.), forming Ni inverse opals which were ca. 10 µm thick on average. The sample then soaked in toluene (Sigma–Aldrich Corp.) to remove the PS template. The Ni inverse opal was cleaned with ethanol and deionized water, and dried in an oven. For the Ni@Co3O4 and SiO2@Fe3O4 electrodes, the Ni inverse opal was fabricated on gold-coated glass substrates. The glass was cleaned with piranha (volume ratio of H2SO4 to H2O2 is 3:1) and...
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To modify the substrate surface for PS opal growth, the gold-coated substrates were put into an aqueous solution of 3-mercaptopropanesulfonic acid, sodium salt (Sigma–Aldrich Corp.) for 2 h. The steps following were the same as for the tungsten substrates.

Growth of SnO\textsubscript{2} NPs onto Ni Inverse Opal: Chemicals were purchased from Sigma–Aldrich Corp., and used directly. 0.2 mL of concentrated hydrochloric acid, 0.5 g of tin(II) chloride dehydrate, and 0.5 g of urea were added into 50 mL of 10 mM mercapto-acetic acid solution followed by ultrasonication for 15 min. The solution was transferred into a three-necked flask immersed in a water bath. A Ni inverse opal substrate fixed by an extended clamp was immersed into the solution. The magnetic stirring speed was set to 700 rpm, and the temperature was set to be 60 °C. After 4 h, the substrate was removed and alternately washed with ethanol and deionized water followed by drying in a vacuum oven at 60 °C for 3 h and annealing in a tube furnace at 450 °C for 1 h under high purity Ar. The furnace ramp rate was 10 °C min\textsuperscript{-1}.

Coating flake-like SiO\textsubscript{2} Layer on SnO\textsubscript{2} NPs: First, a SiO\textsubscript{2} film was coated onto the SnO\textsubscript{2} NP layer using a Stöber method. Typically, 8 mL of deionized water and 2 mL of ammonium hydroxide were mixed with 40 mL of ethanol. Then, a SnO\textsubscript{2} NP-coated Ni inverse opal substrate held by an extended clamp was immersed into the solution. 0.8 mL of tetraethyloxysilicate (TEOS) (Sigma–Aldrich Corp.) was added dropwise into the solution under constant stirring. After 1.5 h, the substrate was removed, thoroughly washed with ethanol and water, and dried at 60 °C. To modify the SiO\textsubscript{2} coating into the flake-like layer, a hydrothermal treatment using sodium tetrahydridoborate (NaBH\textsubscript{4}) (Sigma–Aldrich Corp.) was carried out. 0.5 g of NaBH\textsubscript{4} was dissolved into 40 mL of deionized water. The solution was transferred into a 50 mL Teflon-lined steel autoclave. The substrate was put into the autoclave facing up. The autoclave was sealed, heated at 110 °C for 6 h, and allowed to cool naturally to room temperature. The sample was removed, washed thoroughly with ethanol and Millipore water, and dried at 50 °C for 2 h. The sample was then sintered in a tube furnace at 400 °C for 1.5 h under ultrahigh purity Ar gas using a ramp rate of 5 °C min\textsuperscript{-1}.

SiO\textsubscript{2} Inverse Opal Fabrication: The SiO\textsubscript{2} sol was prepared by mixing TEO\textsubscript{5}, ethanol, and a 0.1 M HCl solution (1:10:1 volume ratio) with stirring for 6 h. The PS opal was held vertically, and the SiO\textsubscript{2} sol was slowly dripped on it. The samples were allowed to dry at room temperature for 24 h. This step was repeated for twice to more fully infiltrate the opal with the SiO\textsubscript{2} sol. The samples were then sintered at 500 °C for 4 h, removing the PS template, resulting in a ca. 8 µm-thick silica inverse opal. The ramp rate was 8 °C min\textsuperscript{-1}.

Growth of Fe\textsubscript{3}O\textsubscript{4} Nanoplatelets on Ni Inverse Opal: The Fe\textsubscript{3}O\textsubscript{4} nanoplatelets were grown on Ni inverse opal via a hydrothermal route combined with a sintering treatment. 5 mmol of Co(NO\textsubscript{3})\textsubscript{3}·4H\textsubscript{2}O, 6 mmol of NH\textsubscript{4}F, and 10 mmol of urea (CO(NH\textsubscript{2})\textsubscript{2}) were dissolved into 40 mL of Millipore water with stirring for 15 min. The solution was transferred into a 50 mL Teflon-lined steel autoclave. A 1 cm × 2 cm Ni inverse opal coated substrate was put into the solution face up. The autoclave was sealed, heated at 170 °C for 6 h, and allowed to cool naturally to room temperature. The sample was removed, washed thoroughly with ethanol and Millipore water, and dried at 50 °C for 2 h. The sample was then sintered in a tube furnace at 400 °C for 1.5 h under ultrahigh purity Ar gas using a ramp rate of 5 °C min\textsuperscript{-1}.

Characterization: The morphology, structure and composition of the samples were characterized using a Hitachi S-4700 SEM, a Hitachi S-4800 SEM equipped with an Oxford INCA energy-dispersive X-ray analyzer, a Philips X’pert MRD X-ray diffractometer with Cu K\textsubscript{α} radiation.
was used. Electrode capacities were measured by a galvanostatic mass ratio mixture of ethylene carbonate and dimethylene carbonate). The Li-ion batteries were assembled in an Ar-filled glove box. A non-aqueous electrolyte (1 M of LiClO$_4$ in a 1:1 mass ratio mixture of ethylene carbonate and dimethylene carbonate) was used. Electrode capacities were measured by a galvanostatic charge-discharge method. For the Ni@SnO$_2$ electrode, the charge-discharge capacity was measured at 0.16C over the potential range of 0.005 to 2.0 V. Cyclic voltammetry were recorded in the potential range of 0.0–2.5 V at a scan rate of 0.3 mV s$^{-1}$. Capacity measurements of the SiO$_2@$Fe$_2$O$_3$ electrode were performed at 0.45C over the range of 0.005 to 3.0 V.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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