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Hierarchical battery electrodes based on inverted opal structures

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The synthesis of a novel battery electrode architecture based on an ordered arrangement of interconnected macropores is reported; the mesoporous vanadium oxide electrode is designed to have a hierarchical architecture, which is beneficial for mass transport and should reduce polarization accordingly.

The use of monodisperse colloidal spheres to fabricate three-dimensionally ordered macroporous materials has become a very active area of research.[1–3] By using opal-like arrays of colloidal spheres, highly ordered, three-dimensional porous structures with precisely controlled pore sizes in the 10 nm to 10 μm range have been prepared. The synthetic approach is generic and applicable to a wide variety of materials. After the monodisperse colloidal spheres of the desired size have formed an opal-like array, the space between them is infiltrated with a fluid precursor that undergoes condensation reactions (*e.g.* as in sol–gel synthesis), or with a dilute suspension of nanoparticles.[4,5] The precursor is selected so that it solidifies after filling the void space between the spheres. Removal of the colloidal spheres leaves a 3-D interconnected porous architecture, often referred to as an inverted opal. Included among the materials prepared as inverted opals are several different metals,[2,4] carbon,[6] metal oxides,[1–3] chalcogenides,[5,7] and a variety of organic polymers.[1,8] Subsequent processing can facilitate crystallization, oxidation, or reduction of the solid phase, depending upon the nature of the precursor and the desired product.

One of the principal areas of research for inverted opals is that of photonic crystals.[1–3] Accordingly, a number of studies have been reported on inverted opals prepared from wide band-gap semiconductors, including diamond, II–VI compounds, and high refractive index oxides such as TiO_2 and SnO_2.[1–3,5,6] Interesting optical properties have also been described for porous metals,[4] and the prospects for using inverted opal materials in catalysis have been discussed.[3] The communication is directed at electrochemical properties and represents the first demonstration of these properties in electrodes with the inverted opal morphology; in this case, as a novel reversible electrode for the incorporation of lithium. In this study, we report the synthesis of a hierarchical electrode architecture that combines the templating of polystyrene spheres with sol–gel chemistry. The templating leads to ordered pore volumes which minimize tortuosity and enhance mass transport throughout the electrode.

The performance of lithium-ion battery electrodes can be limited by mass transport of anions and cations through the pores of the electrodes.[9–11] Under normal operating conditions, ions are transported through the porous electrode network either to or from the bulk electrolyte. Ideally, ion transport should be one-dimensional, *i.e.* a direct path between anode and cathode. This ensures that ion incorporation into the bulk electrolyte is facile, thus avoiding ion depletion regions or concentration gradients that can degrade cell performance, especially at high reaction rates. However, the nature of conventional electrode structures does not provide "line-of-sight" channels. Instead, the ions are required to travel tortuous paths which impede mass transport and lead to polarization. The polarization (ΔE_{iR}) is calculated using an empirically determined parameter known as tortuosity, T, given by eqn. 1.[11]

$$T = \left(\frac{P\rho_{\mathrm{m}}}{\rho_{\mathrm{b}}}\right)^{1/2} \tag{1}$$

where P is the volume fraction occupied by electrolyte in the porous membrane, and ρ_{m} and ρ_{b} are the resistivities of the electrolyte through a porous membrane and in the bulk, respectively. Typically, ρ_{m}, ρ_{b}, and porosity are measured to determine tortuosity. Combining the relationships ($R_{\mathrm{m}} = \rho_{\mathrm{m}} l A^{-1}$) and ($\Delta E_{iR} = iR_{\mathrm{m}}$) with eqn. 1 gives eqn. 2.

$$\Delta E_{iR} = \frac{il\rho_{\mathrm{b}}T^2}{PA} \tag{2}$$

where R_{m} is the ohmic resistance associated with mass transport through the porous membrane, l = membrane thickness, A = membrane area, i = current, and ΔE_{iR} is the polarization associated with mass transport through the porous membrane (refer to ref. 11 for derivation details). In lithium batteries, the electrode area is, typically, a fixed parameter and ΔE_{iR} varies linearly with thickness and porosity. Hence, to minimize ΔE_{iR} under high current, adjusting the tortuosity parameter is preferred, since it has a quadratic dependence rather than a linear dependence. A typical value for tortuosity in electrodes is 3. Therefore, if tortuosity can be decreased by a factor of 3, ΔE_{iR} decreases by nearly an order of magnitude.

One approach to minimizing tortuosity is through the design and synthesis of novel electrode architectures. The hierarchically ordered, inverted opal structure is one such architecture; it can provide well-defined, ordered channels that enhance mass transport throughout the electrode. These channels should minimize tortuosity and provide one-dimensional paths, as described above. One proposed structure consists of an ordered array of interconnected, cubic close-packed, spherical pores. In this configuration, the solid matrix, *i.e.* the electrochemically active network, resides in the interstices of the ordered pore network. The electrochemically active phase also contains pores, but these pores are orders of magnitude smaller than those produced by the template. The purpose of incorporating the additional mesoscale pores is to improve access of the electrolyte to the electrochemically active phase.

This communication reports the fabrication of a hierarchically ordered electrode with the inverted opal structure and demonstration of its electrochemical activity. The electrode material selected for this study is vanadium pentoxide, which can be synthesized using sol–gel methods[12,13] and is, therefore, compatible with the templating process. The specific type of sol–gel V_2O_5 synthesized is the "ambigel" form, which has an

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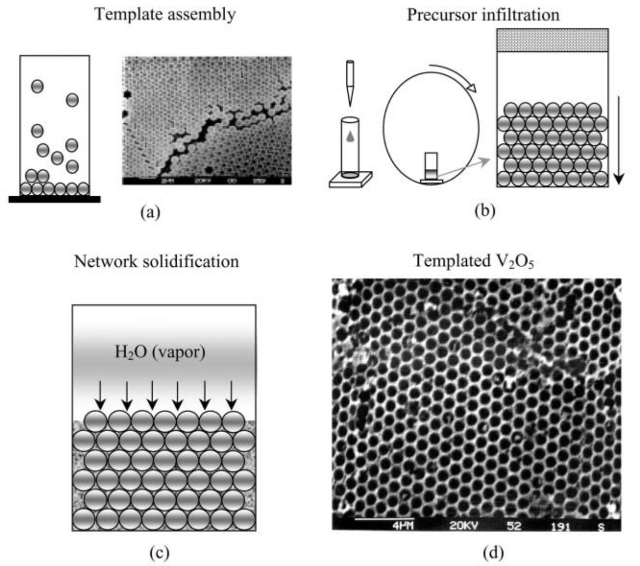

Fig. 1 Process for fabricating the hierarchical V_2O_5 electrode: (a) polystyrene spheres are assembled into a close-packed configuration; (b) vanadium alkoxide precursor is infiltrated into the template; (c) the precursor is exposed to water vapor for hydrolysis and condensation; (d) the template is removed and ambient temperature drying yields the inverted opal electrode of V_2O_5 ambigel.

aerogel-like morphology, including a high surface area (200 m^2 g^{-1}) and high porosity ($>80\%$).[14–16] The pore size distribution is relatively narrow, with most of the pores between 10 and 30 nm. The mesoporosity of the ambigels permits electrolyte penetration and access to the solid phase.[16] In addition, it has been shown that V_2O_5 ambigels exhibit promising behavior as a cathode material for lithium batteries, delivering greater than 400 mA h g^{-1} between 4.0 and 1.5 V.[16,17] The electrochemical results presented herein indicate that the hierarchical electrode provides a comparable level of performance.

The templating process used to develop the ordered pore network for the hierarchical electrode is described in Fig. 1. Polystyrene spheres [Fig. 1(a)] are initially suspended in an aqueous medium (Duke Scientific; 1 µm diameter spheres). 200 µL of suspension is transferred into a glass tube and centrifuged at 1800 rpm for 2 h. One end of the glass tube was attached with epoxy resin to an indium tin oxide (ITO)-coated glass slide, while the other end was left open. During centrifuging, both centrifugal force and capillary force (the latter comes from solvent evaporation) act together to assemble the spheres in a cubic close-packed configuration. Next, 5 µl of diluted vanadyl alkoxide precursor (1 part by volume vanadyl triisopropoxide oxide and 8 parts by volume isopropanol) is pipetted into the template assembly, capped with a rubber stopper and centrifuged for 5 min [Fig. 1(b)]. Capping the assembly prevents evaporation of the precursors during centrifuging and hydrolysis from ambient air. The centrifugal forces help the precursor to penetrate the void region between the polystyrene spheres. Once the precursor has permeated the template assembly, the cap is removed to expose the precursor to water vapor [Fig. 1(c). Rapid hydrolysis and condensation transform the liquid precursor into a solid V_2O_5 gel network within approximately 1 min of exposure. The templated V_2O_5 gel is aged for 24 h and then immersed in toluene for 24 h to selectively dissolve the polystyrene template [Fig. 1(d). The templated gel is then transferred to a cyclohexane bath for 24 h, for solvent exchange purposes. The cyclohexane is allowed to evaporate under ambient conditions with a final step of drying at 125 °C at 10^{-3} Torr for 30 min. The use of cyclohexane as a solvent minimizes capillary forces during solvent evaporation and leads to an aerogel-like material.[15]

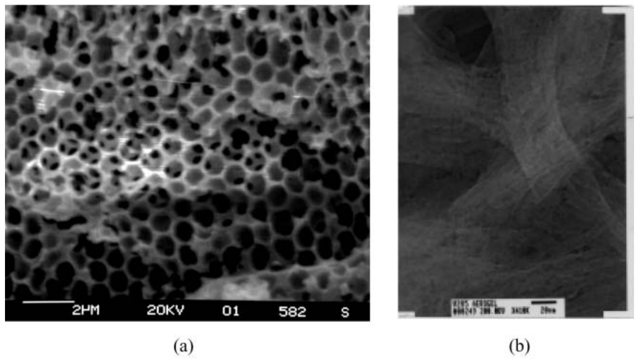

Fig. 2 Microstructure of the hierarchical V_2O_5 electrode: (a) SEM image of the fracture surface, showing the interconnected porosity; (b) TEM image of V_2O_5 wall region between the macropores. The bar represents 20 nm.

The vanadium oxide electrode templated with 1 µm diameter spheres has a high degree of ordering [Fig. 1(d) and 2(a)]. After template removal and ambient temperature drying, the ordered pore diameter was measured and found to be in the range of 800 nm, with a wall thickness of approximately 150 nm. The fracture surface [Fig. 2(a) indicates that the network is three-dimensional with interconnected porosity. TEM images of the walls between pores [Fig. 2(b)] reveal the morphology of the V_2O_5 ambigel; it consists of ribbons that are tens of nanometers wide, several nanometers thick and hundreds of nanometers long. Unlike the ordered pores from the 1 µm polystyrene templates, the pores within the V_2O_5 ambigel matrix are of the order of tens of nanometers in diameter. Thus, the electrode structure is hierarchical in nature, consisting of an ordered network of relatively large pores produced by templating, while the walls between the pores contain an interconnected network of mesopores from the ambient drying process. In this structure, the macro and mesoscale porosity are linked so that electrolyte from the large pores will effectively fill the smaller ones.

Electrochemical cells were prepared by filling the glass tube that contained the hierarchical electrode with an electrolyte of 1 M $LiClO_4$ (Aldrich) in anhydrous propylene carbonate. The $LiClO_4$ was dried by heating under vacuum at 145 °C for 4 h. A three-electrode cell configuration was employed, with the hierarchical V_2O_5 electrode and scraped lithium foil (Alfa) as the counter and reference electrodes, respectively. All cell preparation and testing was conducted in an argon-filled glove box ($O_2 < 0.5$ ppm; $H_2O < 1$ ppm). Galvanostatic and cyclic voltammetry experiments were carried out using a computer-controlled EG&G PAR 273A potentiostat/galvanostat.

We have carried out a series of electrochemical measurements on the V_2O_5 hierarchical electrode. Electrochemical activity was demonstrated in voltammetry experiments which show similar lithium intercalation behavior to that reported previously for V_2O_5 ambigel materials.[14,16,17] The more interesting results are from the galvanostatic rate experiments, which begin to address the question of whether the hierarchical electrodes exhibit improved mass transport characteristics and reduced polarization. In the experiments shown in Fig. 3, the current was referenced to the peak current measured in the voltammetric response, which, based on previous work, corresponds to a specific current of $\sim$160 mA g^{-1}.[18]

The data in Fig. 3 show two important characteristics. At low discharge rates (48 mA g^{-1}), the hierarchical electrodes exhibit reversible behavior, as several discharge–charge cycles are shown with no significant loss in capacity [Fig. 3(a)]. The voltage characteristics are similar to those observed for V_2O_5 ambigels with conventional electrode structures.[17] Discharge curves for a range of rates are shown in Fig. 3(b). In these experiments, the highest discharge rate (4800 mA g^{-1}) was used

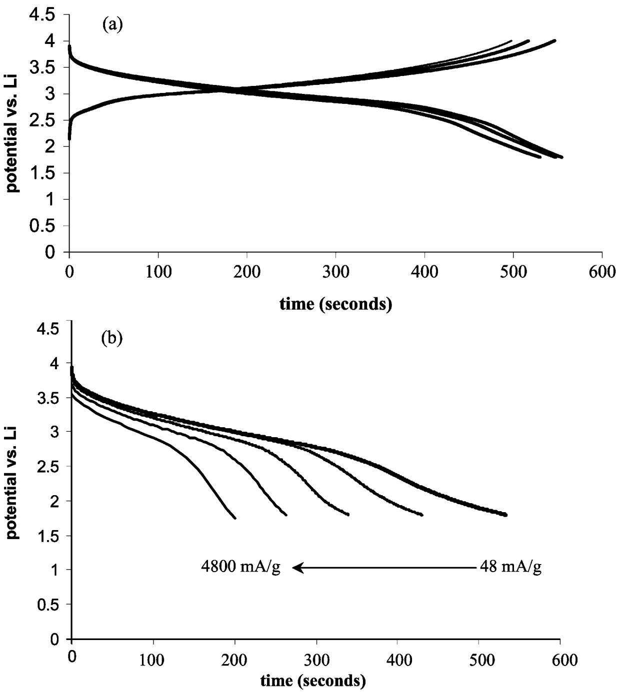

Fig. 3 Galvanostatic characteristics for the hierarchical V_2O_5 electrode: (a) discharge–charge behavior at 48 mA g^{-1} for three cycles; (b) discharge curves for a series of rates varying from 48 to 4800 mA g^{-1}.

in the first discharge and the lowest discharge rate (48 mA g^{-1}) was used in the last discharge. The behavior shown in Fig. 3(b) was reproduced with two other nominally identical electrodes, which varied only in terms of discharge time because of slight differences in electrode mass. As the discharge rate increases, the electrode capacity falls in accordance with usual behavior. The decrease in capacity observed for the hierarchical electrode is about a factor of 2.5 (*i.e.* ~60%) when the discharge rate increases by a factor of 100 (48 to 4800 mA g^{-1}). This behavior is decidedly better than conventional electrodes prepared with V_2O_5 ambigel. In electrodes containing the minimum amount of carbon black (*i.e.* those most comparable to the hierarchical electrode, which contains no carbon black) the capacity decreases by a factor of between 4 and 5, despite the fact that the discharge rate is varied over a much smaller range—from 112 to 2800 mA g^{-1} (a factor of 25).[17] Thus, the hierarchical electrode exhibits less polarization at the higher discharge rates. Although this comparison is qualitative, these results underscore the potential benefit of the hierarchical structure, that of reducing polarization *via* improved mass transport.

In summary, we have demonstrated the electrochemical activity of a hierarchically ordered electrode with the inverted opal structure. The architecture of the electrode is designed to reduce tortuosity and the resulting polarization associated with mass transport. The initial galvanostatic results, although qualitative, are nonetheless quite promising. They suggest that improved mass transport through the templated electrode can effectively deliver higher capacity at higher discharge rates. More definitive experiments with this electrode are in progress.

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