Nanoscale Materials for Lithium-Ion Batteries

Charles R. Sides, Naichao Li, Charles J. Patrissi, Bruno Scrosati, and Charles R. Martin

Abstract

Template synthesis is a versatile nanomaterial fabrication method used to make monodisperse nanoparticles of a variety of materials including metals, semiconductors, carbons, and polymers. We have used the template method to prepare nanostructured lithium-ion battery electrodes in which nanofibers or nanotubes of the electrode material protrude from an underlying current-collector surface like the bristles of a brush. Nanostructured electrodes of this type composed of carbon, $LiMn_2O_4$, V_2O_5, tin, TiO_2, and TiS_2 have been prepared. In all cases, the nanostructured electrode showed dramatically improved rate capabilities relative to thin-film control electrodes composed of the same material. The rate capabilities are improved because the distance that Li^+ must diffuse in the solid state (the current- and power-limiting step in Li-ion battery electrodes) is significantly smaller in the nanostructured electrode. For example, in a nanofiber-based electrode, the distance that Li^+ must diffuse is restricted to the radius of the fiber, which may be as small as 50 nm. Recent developments in template-prepared nanostructured electrodes are reviewed.

Keywords: *energy storage, nanofibers, rechargeable lithium batteries, template synthesis.*

Introduction

Since their introduction by Sony in 1991, lithium-ion batteries have rapidly taken over the high-performance rechargeable-battery market.[1–4] These batteries can store two to three times more energy per unit weight and volume than lead-acid or Ni-Cd batteries, have long cycle lives (>1000 cycles), low self-discharge, and long shelf life. In spite of this success in the commercial marketplace, there is currently an enormous international research effort aimed at improving Li-ion battery technology. This effort focuses on all aspects of the battery, including research aimed at developing improved anodes,[5–8] cathodes,[9–13] and electrolytes.[14–19] An area where improvement is critically needed concerns the rate capability of the battery, that is, its ability to deliver large capacity when discharged at high C rates (a rate of C/1 corresponds to the current required to completely discharge an electrode in 1 h). An improvement in the rate capabilities of Li-ion batteries is required for the use of these batteries for communications and remote sensing devices, where transmission of digitized and compressed voice data requires high-power pulses.[4] During such high-discharge-rate periods, the capacity that the battery can deliver decreases to a fraction of its low-rate value.

It is now well established that these limitations in the rate capabilities of Li-ion batteries are caused by slow solid-state diffusion of Li^+ within the electrode materials.[2,20–34] As a result, there is tremendous current research interest in the development of nanostructured Li-ion battery electrodes. Of particular note are studies on nanostructured Sn-based anodes, where it has been shown that the nanoparticle-based system improves cycle life.[29–31,35,36] There are also a number of interesting recent reports on Li^+ intercalation in fullerene nanotubes for anode applications,[37,38] while vanadium oxide nanotubes have been considered as cathode materials.[39,40] Finally, aerogels, highly porous structures created by removing water under supercritical conditions, have emerged as a promising class of nanostructured battery cathode materials.[41–45]

Nanoparticle electrodes mitigate the problem of slow diffusion because the distance that Li^+ must diffuse in the solid state is limited to the radius of the nanoparticle. We have investigated electrodes of this type prepared by the template method.[22–34] This method entails synthesis of the desired material within the cylindrical and monodisperse pores of a microporous membrane or other solid (Figure 1). We have used microporous polycarbonate filters, prepared by means of the track-etch method[46] (Figure 1a), and microporous aluminas, prepared electrochemically from Al foil[47] (Figure 1b), as our template materials. Cylindrical nanostructures with monodisperse diameters and lengths are obtained, and depending on the membrane and synthetic method used, these may be solid nanofibers or hollow nanotubes.

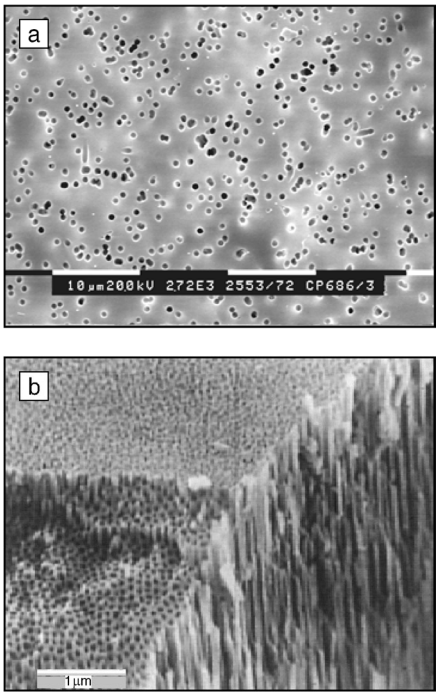

Figure 1. Scanning electron micrographs of template membranes. (a) As-received 50-nm pore diameter polycarbonate template membrane. (b) High-porosity alumina template membrane. Note the order of magnitude reduction of (b) as compared with (a) in the scale bar.

When applied to Li-ion battery electrode materials, template synthesis yields electrodes in which nanofibers or nanotubes of Li^+ insertion materials protrude from an underlying current-collector surface like the bristles of a brush (Figure 2). We have used the template method to prepare such nanostructured electrodes based on carbon,[22–24] $LiMn_2O_4$,[25,26] V_2O_5,[27,28] tin,[29–31] TiO_2,[32,33] and TiS_2.[34] In all cases, the rate capabilities were dramatically improved, relative to thin-film control electrodes composed of the same material. Recent developments in template-prepared nanostructured electrodes are reviewed here.

Rate Capabilities and Cycle Life of Nanofiber Sn-Based Anodes

Sn-based anodes derived from oxides of tin (e.g., SnO_2) have been of considerable recent interest because they can, in principle, store over twice as much Li^+ as the carbon anodes currently used in Li-ion batteries.[5,6,35,36] The Li^+ electrochemistry of such SnO_2-based electrodes is interesting because it entails first the irreversible conversion of tin oxide to metallic tin,

$$4Li^+ + 4e^- + SnO_2 \Rightarrow 2\,Li_2O + Sn, \qquad (1)$$

and then the reversible alloying/dealloying of the Sn with Li,[8]

$$xLi^+ + xe^- + Sn \Leftrightarrow Li_xSn,\ 0 \le x \le 4.4. \qquad (2)$$

It is this alloying/dealloying process that gives this material its charge-storage capacity. In theory, as many as 4.4 Li atoms can be stored per atom of Sn, which would give this anode a maximum theoretical charge-storage capacity of 781 mAh g^{-1} versus 372 mAh g^{-1} for graphite. However, large volume changes occur during the alloying/dealloying process, and with conventional electrode designs, this causes internal damage to the electrode, resulting in loss of capacity and reduced cycle life.

Our nanostructured Sn-based anodes were prepared by sol-gel template synthesis of SnO_2 within the pores of the polycarbonate template membranes.[29–31] This yields an array of 100-nm-diameter SnO_2 nanofibers that protrude, brush-like, from a Pt current collector. That such nanostructured electrodes have improved rate capabilities is demonstrated in Figure 3a, which shows the ratio of the discharge capacity of the nanostructured Sn electrode to that of a thin-film control electrode (prepared under identical conditions, but without the template membrane) as a function of discharge (C) rate. Metallic lithium served as the counter electrode. The electrolyte was 1 M $LiClO_4$ in a solution of ethylene carbonate and diethyl carbonate, 30:70 by volume. At the highest C rate, the nanostructured electrode delivers a capacity that is more than two orders of magnitude higher than the control electrode. Our record in this regard was obtained for a nanostructured V_2O_5 cathode (discussed later), which yielded 60% of its theoretical capacity at the remarkable discharge rate of 4000C.

In addition to improved rate capabilities, the nanostructured Sn anode does not suffer from the poor cyclability observed for conventional Sn-based electrodes. This is because the absolute volume changes in the nanofibers are small, and because of the brush-like configuration, there is room to accommodate the volume expansion around each nanofiber.[7,48] This improved cycle life is illustrated by the data in Figure 3b, which shows that the nanostructured electrode can be driven through 1400 charge/discharge cycles without loss of capacity.

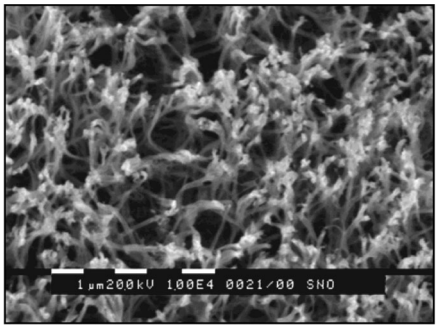

Figure 2. Scanning electron micrograph of a template-synthesized V_2O_5 electrode prepared from 50-nm pore diameter polycarbonate template membranes.

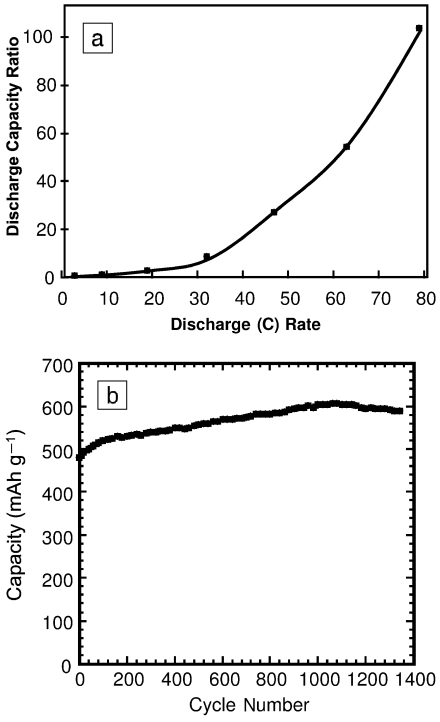

Figure 3. Rate capabilities and cycle life of Sn-based nanostructured electrodes. (a) Discharge capacity ratio versus discharge rate (C rate) for the Sn-based nanostructured electrode as compared with the thin-film control electrodes. A rate of C/1 corresponds to the current required to completely discharge the electrode in 1 h. (b) Discharge capacity versus cycle number for the Sn-based nanostructured electrode.

Improving the Energy Densities of Nanostructured V_2O_5 Cathodes

These improvements in rate capabilities for the Sn anodes have been observed for all of the template-prepared Li-ion battery electrode materials we have investigated to date.[22–34] However, if the polycarbonate template is used, improved rate capabilities come at a cost—loss of volumetric energy density for the electrode. This is because, as shown in Figure 1a, the porosity of the polycarbonate membranes is very low. For example, commercially available membranes with 50-nm-diameter pores have a porosity of only 1.2% (i.e., 1.2% of the membrane surface is made up of pores). This low porosity means that the number density of nanofibers of the electrode material protruding from the current-collector surface is correspondingly low (Figure 2).

One approach for improving volumetric energy density is to use the much-higher-porosity alumina membranes (Figure 1b) as templates. However, the final step in all of these template syntheses is to remove the template membrane to expose the nanofibers of the electrode material. With the alumina templates, this is accomplished by dissolution of the membrane in aqueous acid or base. Unfortunately, most of the electrode materials that we have investigated are also soluble in such solutions. For these materials, the nanofibers would be dissolved away with the template membrane (literally throwing the baby out with the bath water). The one exception is carbon, which of course is not soluble in an aqueous solution, and thus the alumina templates have been used to prepare high-nanotube-density carbon anodes.[22–24]

We have recently developed a method for improving the volumetric energy densities of nanostructured electrode materials

prepared within the pores of the polycarbonate templates.[28] This method entails chemically etching the membrane to increase its porosity prior to template synthesis. Nanostructured V_2O_5 cathodes were prepared by means of a sol-gel template method within the pores of such etched polycarbonate templates.[28] Electron micrographs of the material obtained from such an etched template (pore diameter prior to etching, 50 nm) are shown in Figure 4. Note the higher volumetric density of electrode material relative to the nanostructured electrode prepared in an unetched membrane (Figure 2). To further improve the volumetric energy density, additional sol-gel precursor material was applied to the surfaces of some of the nanostructured electrodes after template synthesis and removal of the etched membrane.[28] Hence, for these studies, we compared the rate capabilities of three different types of V_2O_5 cathodes: the thin-film control electrode (abbreviated here as TFE), the nanostructured electrode (Figure 4) prepared from the etched template (labeled here as NSE), and the nanostructured electrode to which additional sol-gel precursor was added after template synthesis (labeled here as NSE+).

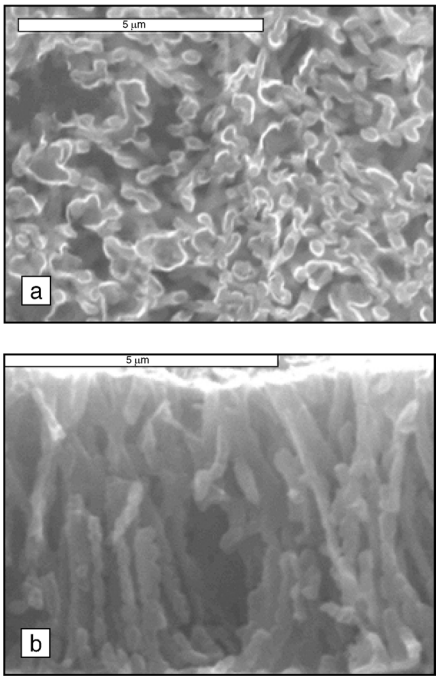

Figure 4. Scanning electron micrographs of template-synthesized V_2O_5 electrodes prepared from etched 50-nm pore diameter polycarbonate template membranes. (a) Top view of the V_2O_5 fibers. (b) Side view of these electrodes.

The charge/discharge reactions for V_2O_5 can be written as follows:

$$Li_xV_2O_5 \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftharpoons}} xLi^+ + xe^- + V_2O_5. \quad (3)$$

X-ray diffraction confirmed that V_2O_5 prepared by the sol-gel route is the crystalline orthorhombic material.[27,28] It is well known that when the voltage cutoff is 2.5 V, the maximum capacity of orthorhombic α-V_2O_5 is $x = 1$ in Equation 3; this corresponds to a specific capacity of 147 mAh g^{-1}.[49] Figure 5 shows the volumetric discharge capacities (μAh per cm^2 of membrane surface area per μm of film thickness) as a function of discharge rate for the TFE, NSE, and NSE+ electrodes.[28] Note that even at low discharge rates, the NSE+ electrode delivers higher volumetric capacity than the thin-film control. Furthermore, at higher discharge rates, the nanostructured electrode without added precursor material (NSE) shows higher volumetric capacity than the thin-film control. These data clearly show that it is possible to use the template method to prepare nanostructured electrodes that have both good rate capabilities and high volumetric energy densities. A challenge that remains is to develop methods for the mass production of such template-synthesized nanostructured electrodes.

Acknowledgments

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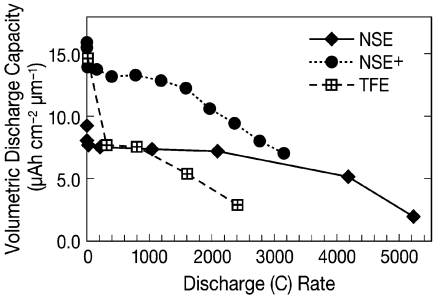

Figure 5. Comparison of volumetric capacity versus discharge rate for different V_2O_5 electrodes. NSE is the nanostructured electrode prepared from the etched 50-nm pore diameter template; NSE+ is the nanostructured electrode to which additional sol-gel precursor was added after template synthesis; and TFE is the thin-film control electrode.

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