

Nanomaterial-based Li-ion battery electrodes

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Abstract

We have been exploring the use of the template method to prepare nanostructured Li-ion battery electrodes. These nanostructured electrodes show improved rate capabilities relative to thin-film control electrodes prepared from the same material. In this paper we discuss nanostructured Sn-based anodes. Li-ion battery anodes derived from oxides of tin have been of considerable recent interest because they can, in principle, store over twice as much Li⁺ as graphite. However, large volume changes occur when Li⁺ is inserted and removed from these Sn-based materials, and this causes internal damage to the electrode resulting in loss of capacity and rechargability. We describe here a new nanostructured SnO₂-based electrode that has extraordinary rate capabilities, can deliver very high capacities (e.g. >700 mAh g⁻¹ at 8°C), and still retain the ability to be discharged and recharged through as many as 800 cycles. These electrodes, prepared via the template method, consist of monodisperse 110 nm-diameter SnO₂ nanofibers protruding from a current-collector surface like the bristles of a brush. The dramatically-improved rate and cycling performance is related to the small size of the nanofibers that make up the electrode and the small domain size of the Sn grains within the nanofibers. © 2001 Elsevier Science B.V. All rights reserved.

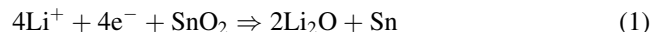
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Lithium-ion batteries are becoming the power sources of choice for modern consumer electronic devices [1–6]. Although, commercially available, these batteries are still the subject of intense research activity aimed at the development of new high-performance electrode and electrolyte materials. Research on alternative anodes focuses on materials that have higher Li⁺ storage capacities than the carbonaceous materials (e.g. graphite) currently employed. Anodes derived from oxides of tin (e.g. SnO₂) have been of considerable recent interest because they can, in principle, store over twice as much Li⁺ as graphite [7,8]. However, large volume changes occur when Li⁺ is inserted and removed from these Sn-based materials, and this causes internal damage to the electrode resulting in loss of capacity and rechargability [9–11].

Prior work has shown that both the size of the particles making up the electrode, and the size of the grains within these particles, play critical roles in this unwanted decomposition process, specifically, electrodes composed of smaller particles and grains show better cyclability [9,12]. This suggests that combining basic research efforts in nanomaterials and Sn-based electrodes might yield better anode

materials for Li-ion batteries. We describe here a new nanostructured SnO₂-based electrode that can deliver very high capacity (>700 mAh g⁻¹) at very high discharge currents, and still retain the ability to be discharged and recharged through many cycles.

The Li⁺ electrochemistry of the SnO₂-based electrodes is interesting because it entails first the irreversible conversion of the tin oxide to metallic tin



and then the reversible alloying/dealloying of the Sn with Li [11]



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. In addition, this charge is stored at high energies, within one volt of the reduction potential for Li⁺ to Li metal. However, as noted above, Sn undergoes dramatic volume changes (up to 300%) upon formation of the Li–Sn alloy, which results in internal damage and loss of capacity with cycling [9–11].

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We have previously shown that the template method [13,14] can be used to prepare electrodes that consist of nanofibers or nanotubules of Li^+ insertion materials that protrude from an underlying current collector surface like the bristles of a brush [15–20]. These nanostructured electrodes show vastly superior rate capabilities relative to control electrodes prepared from the same materials. The template method is a general approach for preparing

nanomaterials that entails synthesizing the desired material within the pores of a microporous membrane or other solid [13–20]. The membranes employed contain cylindrical pores with monodisperse diameters, and corresponding cylindrical nanostructures are obtained. In this case, a microporous polycarbonate filter (Poretics) was used as the template; this membrane had a nominal pore diameter (supplied by the manufacturer) of 50 nm and a pore density

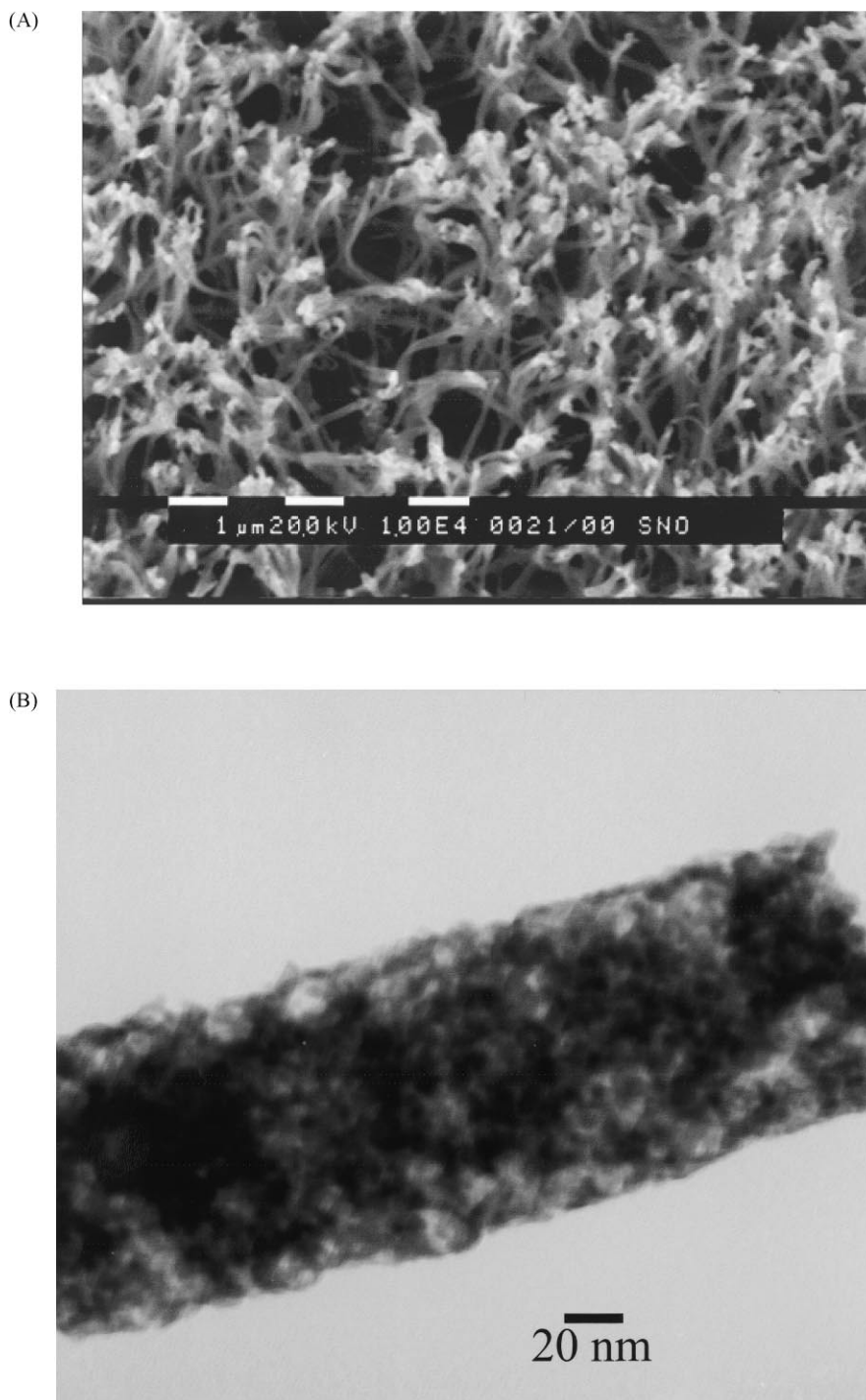


Fig. 1. (A) Scanning electron micrograph of the nanostructured SnO_2 electrode. The nanofibers are protruding from an underlying Pt current-collector surface; (B) Transmission electron micrograph of a single SnO_2 nanofiber before electrochemical cycling.

of 6×10^8 pores per cm^2 of membrane surface area. A solution-based method was used to deposit the cylindrical SnO_2 nanofibers within the pores of this membrane.

The membrane was immersed for 24 h into a solution consisting of 0.338 g $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, 0.03 ml 37% HCl, and 0.47 ml ethyl alcohol and then applied to the surface of a Pt foil current collector. The solvent was removed at 80°C in air, and the template membrane was burnt away using an oxygen plasma. This left nanofibers of a tin oxide precursor material which was heated at 440°C in air to convert them into crystalline SnO_2 (cassiterite, as proven by X-ray diffraction) nanofibers. Electron microscopic analyses (Fig. 1) showed that these nanofibers were 110 nm in diameter, $6.0 \mu\text{m}$ in length (thickness of template), and that there were 5×10^8 nanofibers per cm^2 of current collector surface. As discussed previously, [19] it is typically the case that the nanofibers obtained have larger diameters than the nominal pore diameter of the template membrane. From the diameter, density, and length of the nanofibers it is easy to show that these electrodes have 10 cm^2 of SnO_2 area per cm^2 of substrate electrode area. A thin-film control electrode was prepared by doing the same synthesis on a Pt current collector without using the polycarbonate template membrane. This electrode contained the same quantity of SnO_2 (0.081 mg) as the nanostructured electrode. Electron microscopic analysis showed that this film was 550 nm in thickness.

Electrochemical experiments were conducted in a three-electrode cell using either the nanostructured or thin-film SnO_2 as the working electrode and Li foils as the counter and reference electrodes. The electrolyte was 1 M LiClO_4 in a 30:70 (vol.%) mixture of ethylene carbonate and diethyl carbonate. The reversible capacity was measured by conducting constant current charge/discharge experiments between potential limits of 0.2 and 0.9 V versus Li^+/Li . Prior to charge/discharge experiments, the electrodes were charged from the open circuit potential (~ 2.5 V) to the lower potential limit of 0.2 V, then discharged back to the upper limit of 0.9 V. The results of these experiments are summarized in Fig. 2. At very low discharge rates both the nanostructured and thin-film control electrodes show experimental capacities that are essentially identical. As is always observed, [10,15–20] capacity falls off with increasing discharge rate, however, the extent of capacity loss is dramatically reduced for the nanostructured electrode.

Fig. 3 compares the discharge capacity versus the number of charge/discharge cycles for the nanostructured and control electrodes. There is absolutely no loss of capacity with cycling for the nanostructured electrode, indeed there is a slight increase in capacity with increasing cycle number. We have now cycled nanostructured electrodes through 800 cycles; the capacity ultimately stabilizes and no further increase is observed. We are currently investigating this interesting result of increasing capacity with increased cycle number. In contrast, the thin-film control electrode shows a decay in capacity with cycling (Fig. 3). The charging and

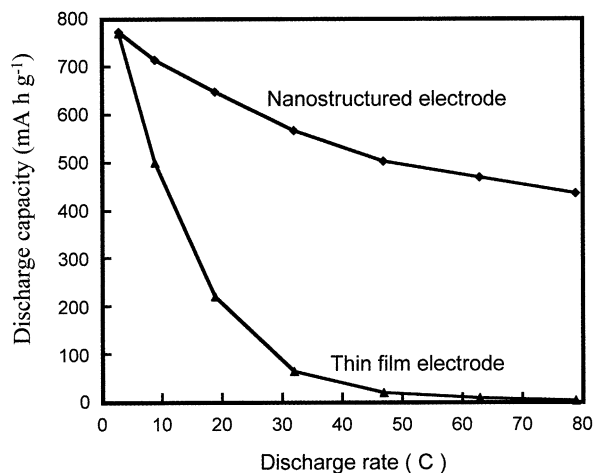


Fig. 2. Discharge capacity vs. charge/discharge rate for the nanostructured and thin-film control electrodes. From reference 20; used with permission.

discharging were done at a very high rate, 8°C , which corresponds to a current density of 0.32 mA cm^{-2} . In spite of this high rate, the capacity of the nanostructured electrode is still large, $>700 \text{ mAh g}^{-1}$. This, again, emphasizes the extraordinary rate capabilities of this electrode. The coulombic efficiency was 97%.

This paper has shown that combining basic research efforts in nanomaterials and Sn-based anodes could lead the way to the development of a new class of nanostructured anodes for Li-ion batteries. It is clear, however, that much additional research will be required before practical nanostructured anodes will be developed. It is of interest to note that another report on nanostructured Sn electrodes (prepared via a different route) has recently appeared, however, these electrodes showed poor cyclability and rate capabilities [21]. Other approaches for preparing microstructured electrode materials have been described [22–24]. The extended cycle life of our template-prepared electrodes is undoubtedly related to the small size [9,12] of the nanofibers

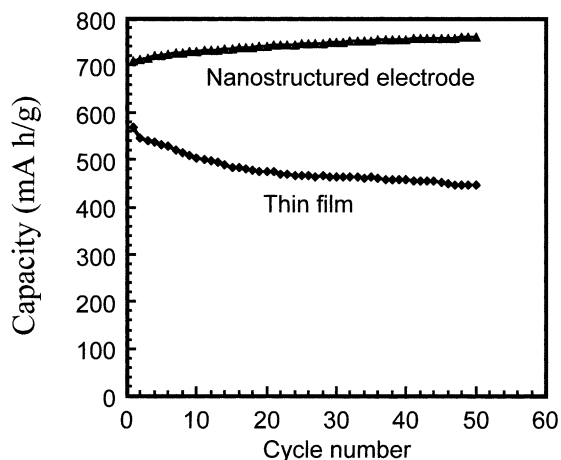


Fig. 3. Capacity vs. cycle number for the nanostructured and thin-film control electrodes at a charge/discharge rate of 8°C over the potential window of 0.2–0.9 V. From reference 20; used with permission.

that make up the electrode. In addition, Fig. 1B shows that the nanofibers are composed of very small grains of electrode material, which has also been shown to be beneficial to the cycle life of these materials. A detailed study of the properties and characteristics of the nanostructured SnO₂ electrodes is currently underway.

Acknowledgements

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