Final Technical Report

Nanomaterials in Secondary Battery Research and Development

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I. Introduction.

Under this contract, we have explored the rate capabilities of nanostructured Li-ion battery electrodes. These nanostructured electrodes were prepared via the template method, a general procedure for preparing nanomaterials pioneered in the P.I.'s laboratory. The template method entails synthesizing the desired material within the pores of a microporous template membrane. The membranes employed contain cylindrical pores with monodisperse pore diameters. Corresponding cylindrical nanostructures of the desired material are obtained; these may be solid nanofibers or hollow nanotubules.

For the battery application the nanofibers or nanotubules are composed of a Li-ion battery material. Specifically, we have prepared and investigated nanotubular and fibrillar forms of the cathode materials V_2O_5 and $LiMn_2O_4$ and of the anode materials carbon and tin. These electrodes were prepared in a novel brush-like configuration where the nanotubules or nanofibrils of the electrode material protrude from a current collector surface like the bristles of a brush.

II. Materials Synthesis.

Two types of template membranes were used for these studies – microporous aluminas and microporous polycarbonates. Both types of membranes were obtained from commercial sources. The V_2O_5, and Sn-based nanostructured electrodes were prepared by doing sol-gel chemistry within the pores of the microporous polycarbonate membranes. Sol-gel chemistry is a very versatile route for materials synthesis. The $LiMn_2O_4$ nanostructured electrodes were prepared via a hydrothermal synthesis within the pores of the polycarbonate membrane. C-based anodes were prepared by doing chemical vapor deposition of carbon within the pores of the microporous alumina templates. In all cases, the template membrane was removed after materials synthesis to yield nanotubules or nanofibrils of the electrode material protruding from a current collector surface like the bristles of a brush.
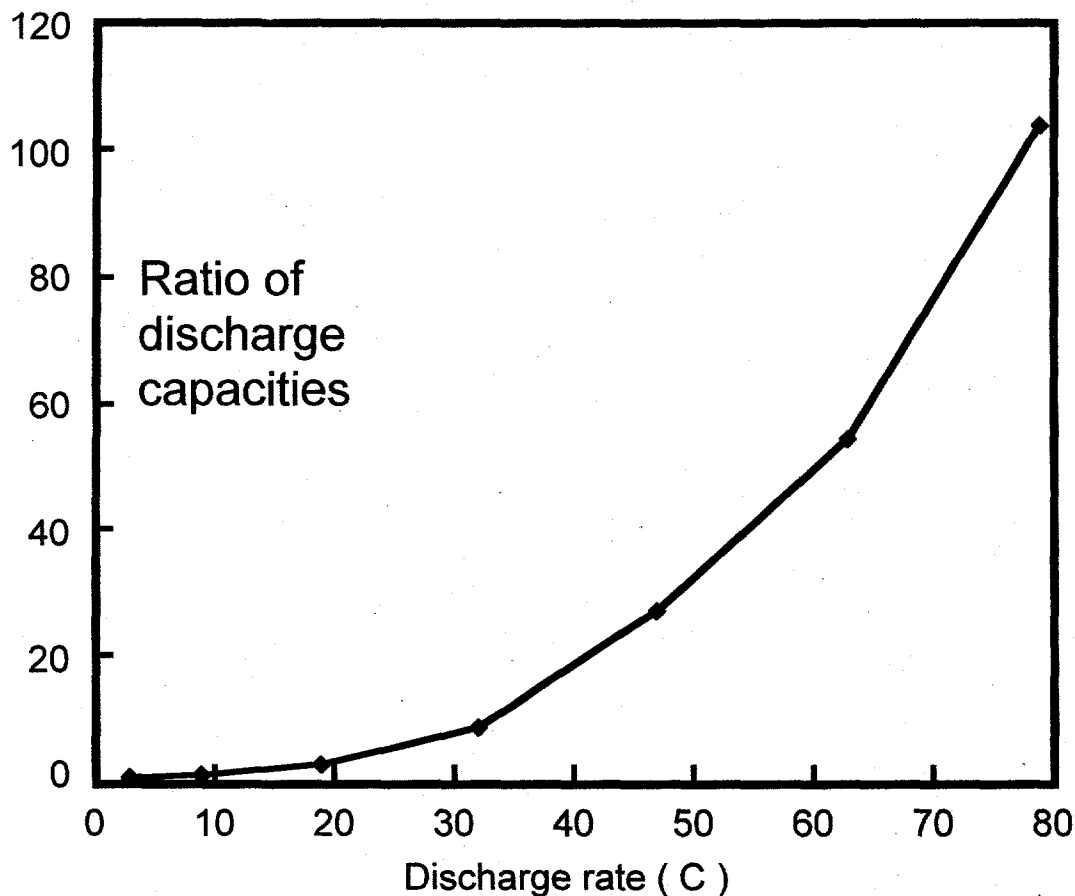
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III. Electrochemical Experiments.

Electrochemical measurements were carried out in a conventional three-electrode electrochemical cell consisting of the nanostructured working electrode, and a Li metal counter and reference electrode. The electrolyte was 1 M $LiClO_4$ in a 30:70 (v/v %) mixture of ethylene carbonate and diethyl carbonate (). Both constant current discharge experiments and cyclic voltammetry was done for all electrode materials studied.
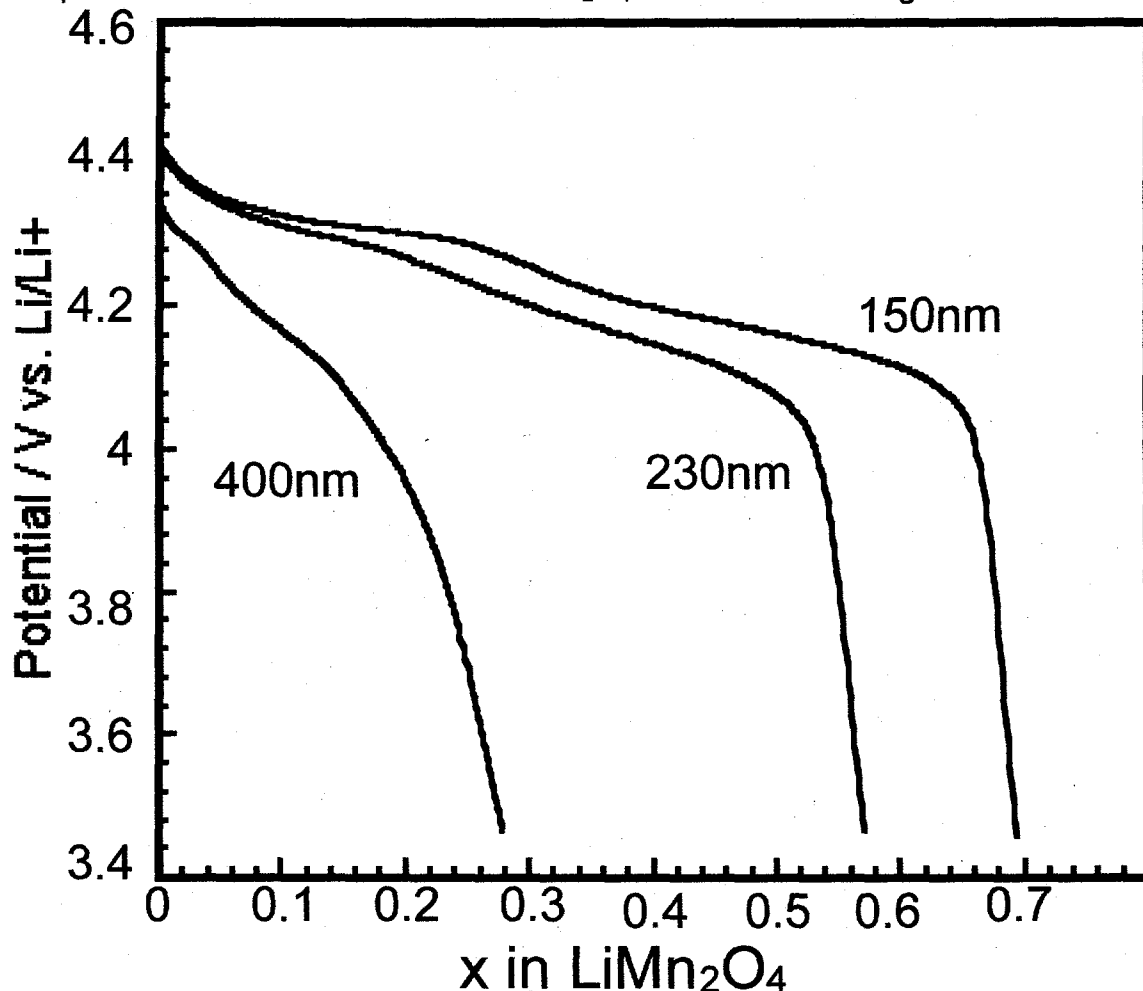
IV. Key Results.

The key findings of these studies are as follows: In all cases the nanostructured electrode showed better rate capabilities than a corresponding control electrode, which was a thin-film electrode composed of large (micron-sized) particles of the same electrode materials. Specifically, the nanostructured electrode delivered higher capacity (i.e., a greater percentage of the theoretical capacity) at high current densities than the control electrode. This is shown in the following figure for the Sn-based electrodes.

Ratio of the discharge capacity of the nanostructured Sn electrode to the discharge capacity of the thin film control Sn electrode as a function of discharge rate.

Two very remarkable things should be noted. First, the ratio of the discharge capacities becomes enormous at high discharge rates. It can be seen from this figure that the nanostructured electrode material **delivers two orders of magnitude higher capacity** than the control material at the highest discharge rate. Second, the discharge rates achievable by the nanostructured material are nothing short of amazing. To my knowledge, there is no other example in the literature of discharging an electrode material at a rate of 80 C. To calibrate the reader, the Li-ion batteries in a typical laptop computer discharge at rates well below 1 C.

The second general feature observed with the nanostructured materials is that the improvement in the rate capabilities scales inversely with the distance the Li^+ must diffuse within the nanoparticle. The shorter the distance of diffusion in the material (slow solid-state diffusion) the greater the enhancement in rate capabilities. This is shown for the $LiMn_2O_4$ electrodes in the figure below.

Discharge Curves for Nanostructured $LiMn_2O_4$ Electrodes for Three Different Nanostructure Diameters.

The further the discharge curve proceeds horizontally along the y-axis (the capacity axis) before the curve turns sharply downward, the greater the capacity of the material. We see that the smallest diameter nanostructured electrode delivers the highest capacity.

V. The Future.

We are continuing our investigations of these interesting nanostructured electrodes. We would like to know what the maximum achievable enhancements in rate capabilities are and what determines this maximum. Clearly the role of electronic conductivity of the material must ultimately be considered because the electronic resistance of a nanofiber increases with decreasing diameter of the nanofiber. We will also explore the issue of self-discharge of these nanostructured materials. Finally, our experiments to date have been half-cell experiments. We would like to make full-cells consisting of both nanostructured anode and cathode materials.

VI. Papers Published Citing DOE Support.

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