Influence of Structural Parameters and Physico-chemical Properties on the Li-Insertion Behavior of γ- and α/γ-MnO_2 Compounds Prepared by Electrochemical-Hydrothermal Synthesis

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Among the many candidates for positive electrodes in 3V rechargeable lithium batteries, manganese dioxides (notably γ- and α-MnO_2) appear promising. They are particularly attractive due to their low cost, toxicity, and high average voltage in comparison with vanadium oxides.

The structure of γ-MnO_2 is an intergrowth of two structures: ramsdellite with double chains of edge-sharing MnO_6 octahedra sharing corners to form 2x1 channels, and pyrolusite with single chains of octahedra sharing corners to form 1x1 channels.[1] Also present are microtwinning defects.[2] Both the amount of pyrolusite intergrowth in the ramsdellite structure (P_r, in percent) and the amount of microtwinning (Mt, in percent) can be determined from information contained in the X-ray powder patterns.[2, 3] Thus the designation γ-MnO_2 actually describes a family of compounds, with P_r and Mt ranging from 0 to 100. The structure of α-MnO_2 is much more straightforward, with double chains of octahedra sharing corners to form 2x2 and 1x1 channels running through the structure.

Considering the relative sizes of the pyrolusite and ramsdellite-like tunnels, it is expected that materials with lower values of P_r will exhibit better lithium insertion properties. Since microtwinning involves a change in the direction of the tunnels, likewise it is expected that materials with lower Mt values will have superior insertion behavior.

Working with the goal of synthesizing new or modified MnO_2 compounds approaching the ramsdellite limit, we have employed the electrochemical-hydrothermal synthesis method. Using this method, a variety of MnO_2 materials with the α, γ and β structures, as well as intimate mixtures of the α and γ or the γ and β structures were prepared.[4, 5] TEM studies of the α- and γ-MnO_2 mixtures show that some of the samples consist of a macroscopic mixture of the two phases, which we denote α/γ-MnO_2, while others are made up of crystals characterized by an intergrowth (with a precise orientation relationship) of the two structures, which we denote α·γ-MnO_2.[6]

The γ-MnO_2 compounds can be prepared over a wide range of P_r values by changing the synthesis conditions (temperature, pH, presence or not of Li_2SO_4, and current density), with relatively low Mt values (near 20) for all samples. In addition to the different (P_r,Mt) values, these samples also exhibit a number of different morphologies.

The present study aims to understand and relate the differences in the lithium insertion behavior to the structural parameters (P_r, Mt), morphology, and other physico-chemical properties. An example of the possible differences is shown in Figure 1. Also to be discussed is the presence of variations in the lithium insertion behavior of α/γ-MnO_2 and α·γ-MnO_2 related to their structural differences.

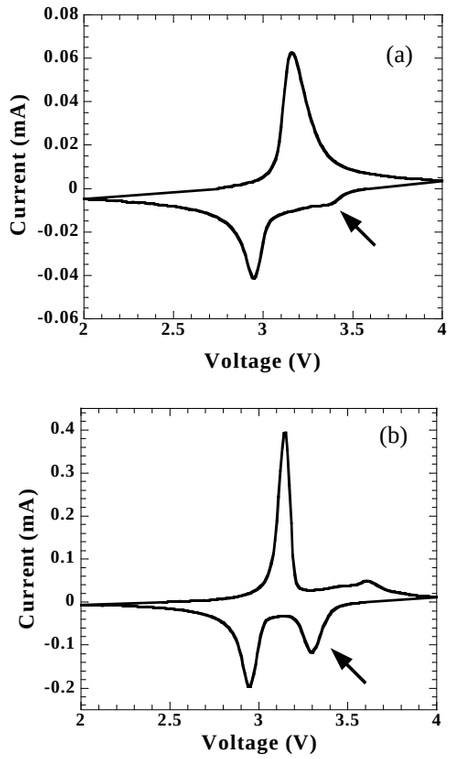

Figure 1. Current vs. voltage curves for two γ-MnO_2 compounds ((a) P_r=60; Mt=17and (b) P_r=45; Mt=14) cycled in potentiodynamic mode at 20 mV/h showing different lithium insertion behavior. Note the difference in the peak at 3.4 V (indicated by arrows).

References

1. P. M. De Wolff, *Acta Crystallogr.*, **12**, 341 (1959).
2. Y. Chabre and J. Pannetier, *Prog. Solid State Chem.*, **23**, 1 (1995).
3. S. Sarciaux, Ph.D. Thesis, Université de Nantes, Nantes, France (1998).
4. L. I. Hill, R. Portal, A. Le Gal La Salle, A. Verbaere and D. Guyomard, *Electrochem. Solid-State Lett.*, **4**, D1 (2001).
5. L. I. Hill, A. Verbaere and D. Guyomard, *J. Electrochem. Soc.*, submitted for publication (2002).
6. L. I. Hill, R. Portal, A. Verbaere and D. Guyomard, *Electrochem. Solid-State Lett.*, **4**, A180 (2001).