Synthesis, Characterization, and Lithium Insertion Properties of α-, β-, and γ-MnO_2 Materials Prepared by the Electrochemical-Hydrothermal Method

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Manganese dioxides are the subject of much research as positive electrodes in 3V rechargeable lithium batteries due to their relatively low cost and toxicity compared to other transition metal oxides.

β-MnO_2 (Pyrolusite), has the rutile structure, with single chains of MnO_6 octahedra being connected by corners to form 1x1 (1 MnO_6 octahedron by 1 MnO_6 octahedron) tunnels through the structure. The structure of α-MnO_2 consists of double chains of octahedra sharing corners to form larger 2x2 tunnels, as well as 1x1 tunnels. In the mineral Ramsdellite-MnO_2, the double chains of octahedra are connected to form 2x1 tunnels. de Wolff[1] first described the γ-MnO_2 structure as an intergrowth of the pyrolusite and ramsdelllite structures. Chabre and Pannetier[2] expanded upon this model by introducing another defect, microtwinning, and also developed a method to determine the relative amounts of pyrolusite intergrowth (P_r, in percent) and microtwinning (Tw, in percent) from the X-ray powder patterns. Our group has further expanded on this method[3, 4] (with different distribution statistics for the microtwinning defects), using the parameter Mt (in percent, ≈½Tw) to represent the relative amount of microtwinning in the samples.

α-MnO_2 is usually prepared by chemical synthesis.[5-7] γ-MnO_2 is industrially prepared by oxidation of acidic $MnSO_4$ solutions. These materials typically contain a relatively large amount of defects, with P_r~50 and Mt≥50.[2] Since the 2x1 tunnels in ramsdellite are better adapted to accommodate Li^+ ions than the 1x1 tunnels of pyrolusite, and microtwinning may impede the diffusion of Li^+ through the structure, it is anticipated that materials with lower P_r and Mt values will show improved performance in lithium batteries.

The electrochemical-hydrothermal method has recently been shown to be useful for the synthesis of various known compounds such as mixed titanium oxides[8] and $LiMO_2$ (M=Ni, Co),[9] as well as new structures of transition metal phosphates[10] and vanadates.[11] With the goal of synthesizing new or modified MnO_2 compounds approaching the ramsdellite limit, we have applied the electrochemical-hydrothermal technique for the preparation of manganese dioxides.[12, 13]

MnO_2 materials with the α, β, γ, or mixtures α/γ, γ/β were obtained by oxidation under hydrothermal conditions of acidic $MnSO_4$ or A_2SO_4/$MnSO_4$ (A=Li, Na, K, NH_4) solutions. The structure of the material obtained is dependent on the synthesis conditions (temperature, pH, applied current density, presence or not of A^+). An example of the effects of temperature and pH for an $MnSO_4$ solution is shown in Figure 1. The γ-MnO_2 containing materials can be obtained over a wide range of P_r values, with relatively low levels of microtwinning defects, as shown in Figure 2.

The materials were analyzed using X-ray powder diffraction, TGA/DTA, ICP/AAS, BET surface area determination, redox titration for Mn oxidation state determination, and scanning electron microscopy to study the morphology.

The relationship between structural parameters, physico-chemical properties and Li-insertion behavior will be discussed.

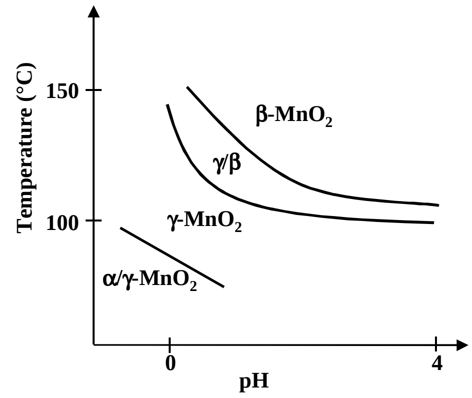

Figure 1. Phase diagram as a function of temperature and pH for materials obtained from acidic $MnSO_4$ solutions.

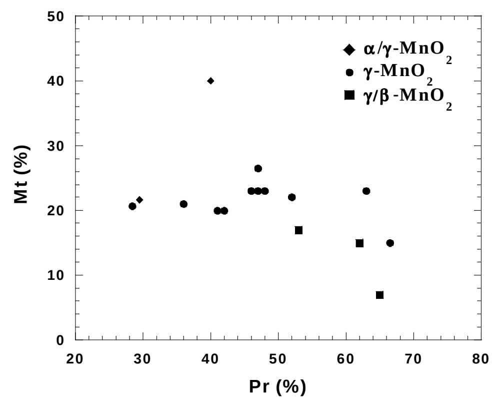

Figure 2. Placement in the (P_r,Mt) plane of some of the samples synthesized by the hydrothermal-electrochemical method.

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