Study of the Influence of Synthesis Parameters on the Morphology of γ- and α/γ-MnO_2 Compounds Prepared using the Electrochemical-Hydrothermal Technique

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Manganese dioxides are promising materials for 3V rechargeable lithium batteries. Among the advantages, manganese oxides are less costly and less toxic than other transition metal oxides. Several polymorphs of manganese dioxides exist, among which α and γ-MnO_2 are of particular interest.

The structure of α-manganese dioxide can be described as double chains of edge-sharing MnO_6 octahedra connected by corners in such a way as to form 2x2 and 1x1 channels through the structure. The structure of γ-MnO_2 is more complicated, consisting of an intergrowth of ramsdellite (2x1 channels) and pyrolusite (β-MnO_2, 1x1 channels), as first described by de Wolff.[1] Another characteristic of γ-MnO_2 compounds is the presence of microtwinning defects, proposed by Chabre and Pannetier, who developed a method of quantifying both the pyrolusite intergrowth (P_r, in percent) and microtwinning (Tw, in percent) from the X-ray diffraction patterns of γ-MnO_2 samples.[2] Our group has developed a slightly different method for the determination of the amount of defects in γ-MnO_2, with Mt corresponding to the amount of microtwinning.

We have employed the electrochemical-hydrothermal synthesis method with the aim of preparing new or modified MnO_2 compounds.

Using the electrochemical-hydrothermal technique, MnO_2 compounds with the α, β and γ structures were synthesized, as well as materials containing both α- and γ- phases (α/γ-MnO_2) or both γ- and β-phases.[3] A TEM study of the α/γ-MnO_2 materials has revealed that some of these compounds are characterized by an intergrowth/interconnectivity (with a precise orientation relationship) of the two phases.[4] These compounds are denoted as α·γ-MnO_2.

An investigation of the morphologies of the γ-MnO_2 containing compounds by scanning electron microscopy revealed many different morphologies and particle sizes. Examples of some of the observed morphologies are shown in Figure 1. Additionally, both α/γ-MnO_2 and α·γ-MnO_2 compounds displayed morphologies different from the pure α- and γ-phases. It was found that the morphology of the materials was dependent on the synthesis parameters (temperature, acidity of the solution, presence (or not) of Li_2SO_4 during the synthesis, and applied current density), and not on the structure or structural parameters (P_r,Mt) (in the case of γ-MnO_2). A discussion of the different morphologies in relation to the synthesis parameters will be presented.

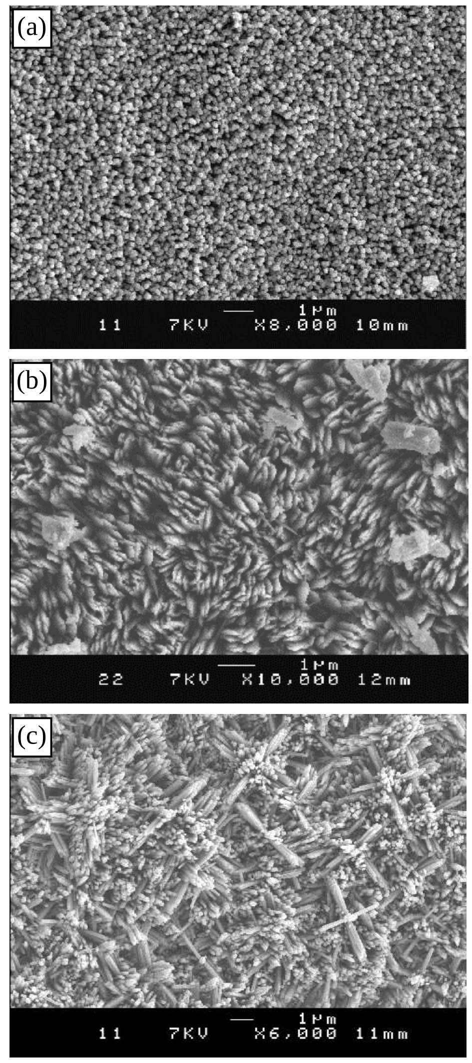

Figure 1. SEM micrographs showing the morphology of (a) γ-MnO_2 (49,17), (b) γ-MnO_2 (63,15) and (c) α/γ-MnO_2.

References

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4. L. I. Hill, R. Portal, A. Verbaere and D. Guyomard, *Electrochem. Solid-State Lett.*, **4**, A180 (2001).