

## Electrochemical Synthesis under Hydrothermal Conditions of $\alpha$ -MnO<sub>2</sub> Compounds: Characterization and Li-Insertion Behavior

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Manganese dioxides are of technological interest as positive electrodes in rechargeable 3V lithium batteries. The advantages of manganese dioxides are their lower cost and toxicity, as well as their higher average voltage compared to vanadium oxides. There exist many different structures of MnO<sub>2</sub>, of which  $\alpha$  and  $\gamma$  are of particular interest for practical applications.

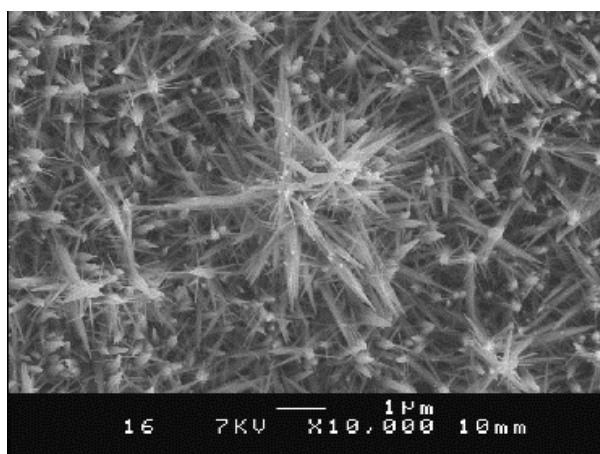
The structure of  $\alpha$ -MnO<sub>2</sub> is made up of double chains of edge sharing MnO<sub>6</sub> octahedra, which share corners to form 2x2 as well as 1x1 tunnels, the former being of sufficient size to easily accommodate the diffusion of Li<sup>+</sup> ions.  $\alpha$ -MnO<sub>2</sub> containing Li<sup>+</sup> or H<sup>+</sup> in the large 2x2 channels of the structure is usually synthesized by ion-exchange of large cations such as K<sup>+</sup> or NH<sub>4</sub><sup>+</sup>,<sup>1,2</sup> or directly by chemical methods.<sup>3,4</sup>

Electrochemical-hydrothermal synthesis has recently been used to prepare titanium oxides,<sup>5</sup> LiMO<sub>2</sub> (M=Co, Ni)<sup>6</sup> and transition metal phosphates<sup>7</sup> and vanadates.<sup>8</sup>

We have used the electrochemical-hydrothermal synthesis route to synthesize  $\alpha$ -MnO<sub>2</sub> materials.<sup>9</sup> By varying the synthesis conditions, such as temperature, acidity of the MnSO<sub>4</sub> solution, presence of Li<sup>+</sup>, or applied current density, the structure and physical characteristics of the material obtained can be controlled. The  $\alpha$ -MnO<sub>2</sub> materials can thus be synthesized to contain a small amount of lithium ( $\leq 0.05$  Li/Mn) or to contain only H<sup>+</sup> and H<sub>2</sub>O in the channels.

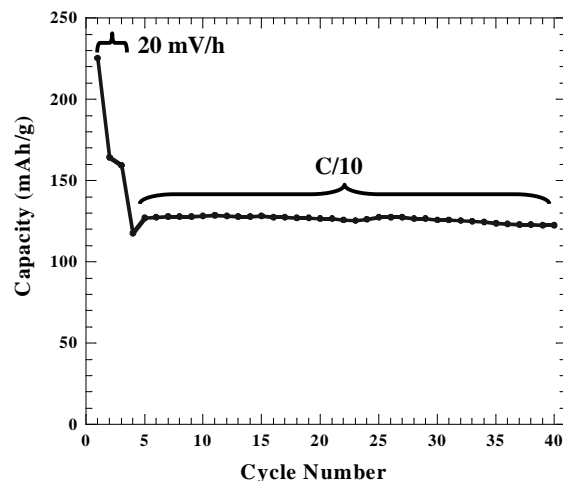
An SEM study of the deposited materials has shown that by changing the synthesis conditions, one can control the particle size and morphology of the obtained phases. An example of one of the  $\alpha$ -MnO<sub>2</sub> morphologies is shown in Figure 1.

Depending on the characteristics of the material, the  $\alpha$ -MnO<sub>2</sub> compounds prepared by the electrochemical-hydrothermal method show very stable cycling behavior. An example is shown in Figure 2.



**Figure 1.** SEM micrograph of  $\alpha$ -MnO<sub>2</sub> prepared by the electrochemical-hydrothermal synthesis technique.

The purpose of the current study is to explore the relationship between the structural properties, morphology and lithium insertion behavior of  $\alpha$ -MnO<sub>2</sub> compounds prepared by the electrochemical-hydrothermal synthesis technique.



**Figure 2.** Cycled capacity of  $\alpha$ -MnO<sub>2</sub> prepared by the electrochemical-hydrothermal technique, the first three cycles in potentiodynamic mode followed by cycling in galvanostatic mode

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