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**Lithium-Oxide -Stabilized Alpha Manganese Dioxide
for Rechargeable Lithium Batteries**

by

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Lithium-Oxide-Stabilized Alpha Manganese Dioxide for Rechargeable Lithium Batteries

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Alpha manganese dioxide is an attractive cathode material for 3 V rechargeable lithium batteries, demonstrating modest capacities of 160 mAh/g and good cycle life (1-3). The material contains (2x2) channels which extend down the c-direction of the tetragonal unit cell. Stabilizing cations such as K^+ , Rb^+ , Ba^{2+} , and NH_4^+ are commonly found within these channels. However, these cations may block lithium diffusion in the channel and lead to low rate capability. Recently, synthesis routes have been optimized to produce a crystalline material (hydrated $\alpha\text{-MnO}_2 \cdot n\text{H}_2\text{O}$, $n \approx 0.2\text{-}0.36$) that contains molecular water (H_2O) instead of cations within the channels (4). The heat-treated version of this material, however, showed poor electrochemical cycling performance.

The objective of this study was to increase the reversible cycling capacity of the anhydrous $\alpha\text{-MnO}_2$ by stabilizing its structure. In this work, we have synthesized various $\alpha\text{-MnO}_2$ materials and modified their structural properties via lithium-oxide addition (lithia doping) in a focused effort to determine what properties are important for controlling cycling performance. A set of new stabilized $\alpha\text{-}[x\text{Li}_2\text{O}]\cdot\text{MnO}_2$ ($x < 0.2$) cathode materials was synthesized, structurally characterized and electrochemically evaluated.

Starting materials consisted of hydrated $\alpha\text{-MnO}_2$ powders synthesized from Mn_2O_3 (4). The $\alpha\text{-MnO}_2$ structure was modified by reaction with LiOH at 275°C (2-3). The unit cell parameters of several samples with varying Li:Mn mole ratios were calculated from powder X-ray diffraction data. The unit cell expands, almost linearly, with increasing lithium content to a Li:Mn ratio of 0.3:1 without the appearance of a second phase; at this ratio the unit cell parameters are $a = 9.932 \text{ \AA}$, and $c = 2.852 \text{ \AA}$. Chemical analysis of lithia-doped products quantitatively verified the reactant Li:Mn mole ratio.

Rietveld profile refinement on neutron diffraction data collected on the $\alpha\text{-}[0.15\text{Li}_2\text{O}]\cdot\text{MnO}_2$ phase indicates that O^{2-} anions from the Li_2O molecule occupy crystallographic positions within the (2 x 2) channels, normally occupied by stabilizing cations; the lithium cations are coordinated to the oxygen atoms of the framework structure and those located within the (2 x 2) channels (Fig. 1).

Fig. 2 shows the evolution of the discharge capacity versus cycle number for two button cells (size 1225; metallic lithium anode; 1M LiPF_6 in 50/50 EC/DMC electrolyte), one containing an anhydrous $\alpha\text{-MnO}_2$ cathode

and one containing a lithia-doped $\alpha\text{-MnO}_2$ cathode. When subjected to constant current cycling, the lithia-doped cathodes have a higher retained capacity than the anhydrous undoped cathodes (146 vs. 116 mAh/g) after 10 cycles. The cycle life of cells with lithia-doped cathodes extends past 80 cycles (130 mAh/g; 0.4 mA rate) without a change of the lithium anode. Parallel electrochemical studies with an all-solid-state polyethylene-oxide-based polymer electrolyte, resulted in similar cycling behavior for the two types of electrodes. The capacity difference between the two materials is accounted for almost entirely on the first charge. For lithia-doped $\alpha\text{-MnO}_2$, the cycling efficiency on the first charge is $>95\%$, whereas for the anhydrous undoped $\alpha\text{-MnO}_2$ electrode, it is only 60-70%. Both types of electrodes show two S-shaped curves on the first discharge, indicative of two single-phase reaction processes. After repeated cycling, however, the discharge profiles adopt a single slope, characteristic of one single-phase lithium insertion reaction.

ACKNOWLEDGMENTS

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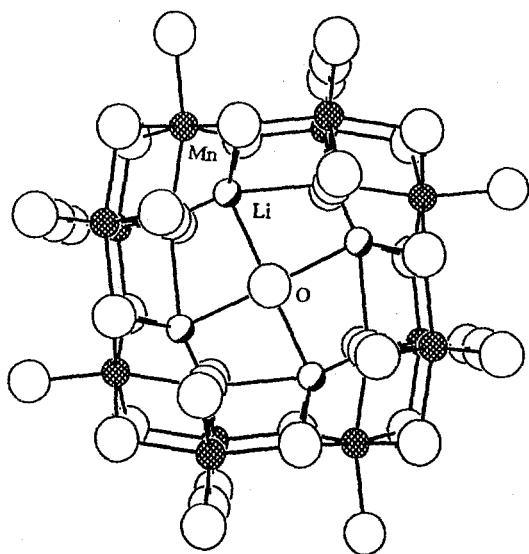


Fig. 1. Structure of α -[0.15Li₂O]•MnO₂ as viewed down the c-direction of the unit cell.

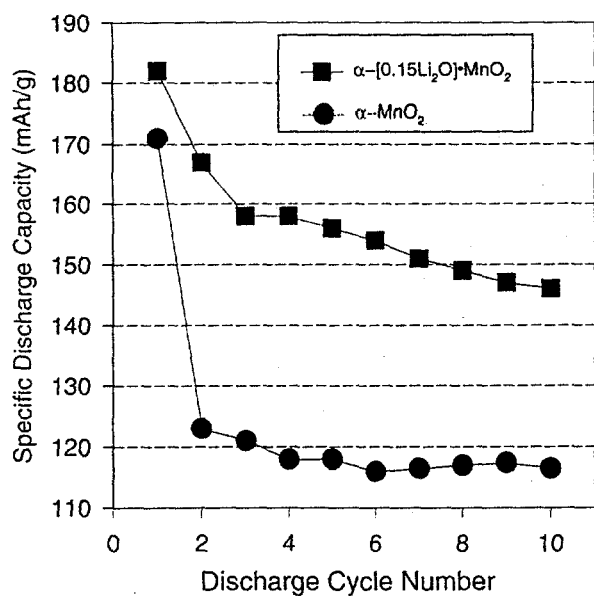


Fig. 2. Discharge capacity vs. cycle number at a 0.1 mA rate. Voltage limits were 3.5 to 2.0 V.