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LETTERS TO THE EDITOR

Synthesis and Structural Characterization of a Novel Layered Lithium Manganese Oxide, $Li_{0.36}Mn_{0.91}O_2$, and Its Lithiated Derivative, $Li_{1.09}Mn_{0.91}O_2$

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A novel layered lithium manganese oxide, $Li_{0.36}Mn_{0.91}O_2$, has been prepared from Li_2MnO_3 by acid digestion. The structure of the product consists of alternate layers of trigonal prisms, partially occupied by Li^+ ions, and edge-shared octahedra, occupied almost completely by Mn^{4+} ions. Lithiation of this product with LiI at 80°C forms a rock-salt phase, $Li_{1.09}Mn_{0.91}O_2$, in which the cubic close-packed oxygen array of the parent Li_2MnO_3 structure is regenerated.

Introduction

Layered compounds such as $LiCoO_2$ (*1*) and $LiNiO_2$ (*2*) are of interest as insertion electrodes for rechargeable lithium cells because lithium can be extracted from and reintroduced into their structures with a concomitant change in the oxidation state of the transition-metal cation. Although an isostructural $LiMnO_2$ compound is not known, a recent report has indicated that it might be possible to synthesize related layered $Li_y(Mn_zLi_{1-z})O_2$ structures ($0 \leq y < 1$, $0.67 < z \leq 1$) by leaching Li_2O from the rock-salt phase Li_2MnO_3 (*3*). In this communication the synthesis and structural features of a novel $Li_{0.36}Mn_{0.91}O_2$ (or alternatively, $Li_{0.27}(Mn_{0.91}Li_{0.09})O_2$, $y = 0.27$, $z = 0.91$) compound and its lithiated derivative $Li_{1.09}Mn_{0.91}O_2$ ($Li(Mn_{0.91}Li_{0.09})O_2$, $y = 1$, $z = 0.91$) are reported.

Experimental

Li_2MnO_3, or alternatively, $Li(Mn_{0.67}Li_{0.33})O_2$ ($y = 1$, $z = 0.67$), was prepared at 400°C in air by reacting electrolytic manganese dioxide (EMD) with a stoichiometric quantity of Li_2CO_3 for 2 weeks. A long reaction time was required to obtain a single-phase product at this temperature. Single-phase $Li_{0.36}Mn_{0.91}O_2$ was prepared by digesting Li_2MnO_3 in 2.25 *M* H_2SO_4 at 25°C for 64 hr. The sample was heated at 100°C for 24 hr to remove surface water. A H^+-ion analysis of the heated sample showed that $Li_{0.36}Mn_{0.91}O_2$ contained a small amount of residual occluded water associated with grain boundaries and possibly some ion-exchanged protons within the structure ($[H^+] = 0.5\%$ by mass). It has not been possible as yet to obtain anhydrous materials because of their thermal instability at higher temperatures. Nevertheless, the presence of the occluded water did not prevent the structure analysis of the lithium-manganese-oxide component.

Samples were analyzed for lithium and manganese by atomic absorption spectroscopy to determine the Li : Mn ratio in the compounds. $Li_{1.09}Mn_{0.91}O_2$ was synthesized

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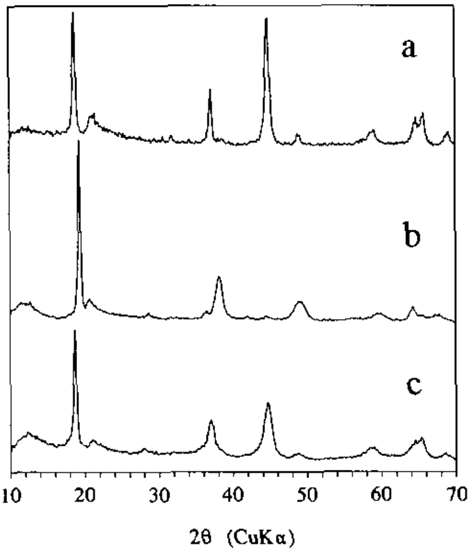

FIG. 1. The powder X-ray diffraction patterns of (a) Li_2MnO_3 (400°C), (b) $Li_{0.36}Mn_{0.91}O_2$, and (c) $Li_{1.09}Mn_{0.91}O_2$.

by reacting a slight excess of LiI with $Li_{0.36}Mn_{0.91}O_2$ in acetonitrile at 80°C according to the reaction

$$Li_{0.36}Mn_{0.91}O_2 + 1.10LiI \rightarrow Li_{1.09}Mn_{0.91}O_2 + 0.37LiI_3,$$

in which the occluded water has been omitted for simplicity. $Li_{0.36+x}Mn_{0.91}O_2$ compounds with intermediate values of x could be obtained by using lesser amounts of LiI.

Results and Discussion

The powder X-ray diffraction patterns of Li_2MnO_3, $Li_{0.36}Mn_{0.91}O_2$, and $Li_{1.09}Mn_{0.91}O_2$ are shown in Figs. 1a–1c. The pattern of $Li_{0.36}Mn_{0.91}O_2$ (Fig. 1b) differs significantly from that of the parent Li_2MnO_3 (Fig. 1a) in both peak positions and peak intensities; the pattern is also significantly different from that of well-known layered birnessite compounds which have a hexagonally close-packed oxygen array (*4*). Li_2MnO_3 has a rock-salt-type structure in which the oxygen-ion array is slightly distorted from cubic close packing and in which layers of Li^+ ions alternate with layers containing Mn^{4+} ions and Li^+ ions in a 2:1 ratio (*5*). Although the lack of high quality X-ray data and the small number of strong reflections prevented satisfactory structural refinements using the monoclinic symmetry (*C*2/*c*) of the parent Li_2MnO_3 compound, the gross structural features of $Li_{0.36}Mn_{0.91}O_2$ and $Li_{1.09}Mn_{0.91}O_2$ were obtained by profile refinement of their X-ray patterns (Figs. 1b and 1c, respectively) using the higher symmetry space group $R\bar{3}m$ that characterizes the layered $LiCoO_2$ and $LiNiO_2$ structures.

The structure refinements demonstrated that:

1. Removal of Li_2O from Li_2MnO_3 causes a shearing of the close-packed oxygen planes to yield an oxygen array in $Li_{0.36}Mn_{0.91}O_2$ comprised of alternate layers of trigonal prisms and sheets of edge-shared octahedra (Fig. 2a).

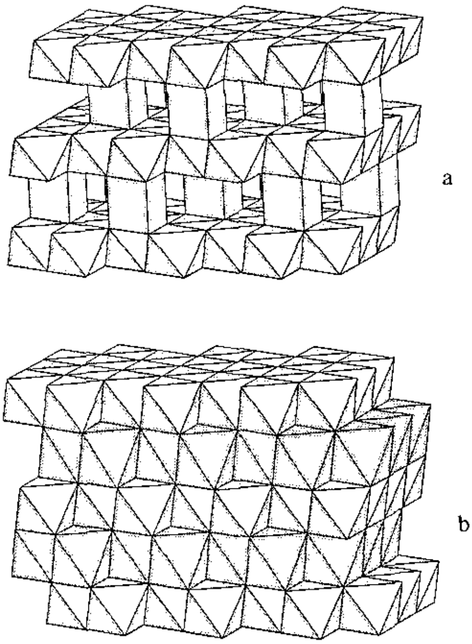

FIG. 2. The layered structures of (a) $Li_{0.36}Mn_{0.91}O_2$ ($R\bar{3}m$, a = 2.903(1) Å, c = 13.803(5) Å) and (b) $Li_{1.09}Mn_{0.91}O_2$ ($R\bar{3}m$, a = 2.851(1) Å, c = 14.259(6) Å). The partially shaded octahedra are mostly occupied by manganese ions; the fully shaded polyhedra are occupied by lithium ions.

2. The manganese ions remain in alternate layers and do not migrate to the lithium layers during the leaching process. The Li^+-ion positions could not be located because of the weak scattering power of lithium; it was presumed that they resided in the small fraction of octahedral sites that were not occupied by manganese, and partially occupied the trigonal prismatic sites. With this arrangement the structural notation would be $[Li_{0.27}]_{trpr}(Mn_{0.91}Li_{0.09})_{oct}O_2$.

3. Lithiation of $Li_{0.36}Mn_{0.91}O_2$ with LiI regenerates the close-packed oxygen array of the parent Li_2MnO_3 structure. $Li_{1.09}Mn_{0.91}O_2$ (Fig. 2b), like Li_2MnO_3, has the ideal rock-salt stoichiometry; the structure differs only in the Li : Mn ratio in the manganese-rich layer. It closely approximates the layered structures of $LiCoO_2$ and $LiNiO_2$.

Preliminary investigations have shown that layered $Li_y(Mn_zLi_{1-z})O_2$ compounds derived from Li_2MnO_3 exhibit promising electrochemical properties for use as electrodes in rechargeable lithium cells (*3*). Further work is in progress to synthesize anhydrous materials and to gather more information about the structural stability of these layered structures on cycling. A detailed description of the structural refinements of $Li_{0.36}Mn_{0.91}O_2$ and $Li_{1.09}Mn_{0.91}O_2$ will be reported elsewhere.

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