Stabilization of LiMnO₂ in the α-NaFeO₂ Structure Type by LiAlO₂ Addition

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LiMnO₂ compounds have come to be of interest as intercalation electrodes for rechargeable lithium batteries because of their high theoretical capacity (285 mAh/g), about twice that of LiMn₂O₄, and low cost relative to LiCoO₂. Orthorhombic LiMnO₂ (hereafter referred to as α-LiMnO₂) has been known since 1956 and has an ordered rock salt structure of space group Pmnm. It is now well known that α-LiMnO₂ transforms irreversibly to a material with spinel-like ordering upon electrochemical cycling. Another phase of interest in this system is the monoclinic polymorph of LiMnO₂ (hereafter referred to as m-LiMnO₂), which has the cation ordering of the α-NaFeO₂ structure, in which Li⁺ ions are located in octahedral sites between MnO₂ layers. Unlike LiCoO₂, which is rhombohedral (R3m), LiMnO₂ is monoclinic (C2/m) because the coordination polyhedron around the Mn²⁺ ions is distorted from a regular octahedron due to the Jahn-Teller effect. Recently, m-LiMnO₂ has been obtained by an ion-exchange reaction of LiCl and LiBr with α-NaMnO₂. As with α-LiMnO₂, this material appears to convert from its original layered α-NaFeO₂ structure to a spinel-like structure during cycling, based on X-ray diffraction after electrochemical cycling and the appearance of both 4 and 3 V plateaus in the charge/discharge curves.

LiMnO₂ shows significant capacity fade when cycled over both the 4 and 3 V plateaus. The onset of the Jahn-Teller distortion and the consequent structural instability when LiMnO₂ is discharged to an average manganese valence < 3.5 (i.e., at x = 2) is generally believed to contribute to the rapid capacity loss. Even when LiMnO₂ is cycled over only the 4 V plateau, a slow capacity fade is usually observed. Some efforts have been made, as reviewed in Ref. 19, to extend the capacity to include the 3 V plateau without significantly deteriorating the cycling behavior.

Both m- and LiMnO₂ have shown better cycleability than LiMnO₂ when both the 4 and 3 V plateaus are utilized. The reversible capacity reported to date for long-term cycling seems much less than the theoretical capacity. For example, 45-200 mAh/g has been obtained from α-LiMnO₂ between 2.5 and 4.3 V depending on the synthesis condition and charge/discharge rate. The materials of higher capacity also appear to fade more rapidly upon cycling. A greater fraction of the theoretical capacity may be achievable with appropriate modifications of these phases.

Although doped LiMnO₂ spinels have been studied, to our knowledge the stabilization of α- or m-LiMnO₂ by doping has not been reported. We chose to study LiAlₓMn₁₋ₓO₂ solid solutions for several reasons. Ab initio calculations by Aydinol et al. have shown that LiAlO₂ has a theoretical intercalation voltage of 5.4 V (against lithium metal anode). While pure LiAlO₂ is electrochemically inactive, the solid solution of LiAlO₂ with various lithium transition-metal oxides can potentially increase the intercalation voltage and cathode energy density.

This effect has recently been confirmed for LiAlCoO₂, α-LiMnO₂, solid solutions. LiAl₁₋ₓMnₓO₂ solid solutions are of interest as another test of these voltage mixing rules. Second, the fact that LiAlO₂ is stable in the α-NaFeO₂ structure at temperatures below ~600°C suggests that it could have a stabilizing effect on LiMnO₂. Finally, its low cost and low density make LiAlO₂ attractive as a constituent of intercalation electrodes.

Experimental

LiOH·H₂O (Alfa Aesar, 98%), Mn(NO₃)₂·6H₂O (Aldrich, 98%), and Al(NO₃)₃·9H₂O (Alfa Aesar, 98%) were used to prepare the precursors. Precursors with and without aluminum doping were prepared by the same method. Precursors (A) were aluminum-doped at the levels y = 0.05 and y = 0.25, and had a Li:Mn+Al atomic ratio of 1:0.5:1. The slight excess of Li was included to compensate for loss during firing. Precursor (B) was undoped with a Li:Mn atomic ratio of 1:0.5:1. For precursors (A), a mixed manganese-aluminum hydroxide was co-precipitated from mixed aqueous solutions of Mn(NO₃)₂·6H₂O and Al(NO₃)₃·9H₂O. The precipitate was purified of nitrate ion species, which otherwise re-form low-melting metal nitrates upon firing, by a rinsing procedure described in Ref. 29. The precipitate was then dispersed in an aqueous solution of LiOH·H₂O yielding the total compositions given above. This suspension was atomized into liquid nitrogen, and the frozen droplets were freeze-dried (VirTis Consol 12LL, Gardiner, NY). Precursor (B) was obtained by the same method but using Mn(NO₃)₂·6H₂O alone. A more detailed description of this synthesis method can be found in Ref. 29.

The precursor powders were fired for 2 h at 945°C in various partial pressures of oxygen and furnace-cooled to room temperature. LiMnO₂ and LiAlO₂ were the phases usually obtained when oxides with LiMn~1 are fired in air. A reducing atmosphere was used in order to obtain a high Mn³⁺ fraction. The effect of oxygen partial pressure on the phase stability was studied by firing in the range pO₂ = 10⁻² to 10⁻⁷ atm, controlled by flowing premixed argon/oxygen or CO/CO₂ mixtures. The calcined powders were characterized by X-ray diffraction (XRD) using a Rigaku diffractometer (RTP500RC) with Cu Kα radiation.

For electrochemical evaluation, cathodes were prepared by mixing together the oxide powders, carbon black (Cabot), graphite (TIMCAL America), and poly(vinylidene fluoride) (PVDF, Aldrich) in the weight ratio of 7:8:6:10. PVDF was predissolved in γ-butyrolactone (Aldrich) before mixing with the other components. After the γ-butyrolactone was evaporated at 150°C in air, the components were compacted at about 4 t/cm² pressure to form pellets 10-25 mg in weight and 0.5 cm² in cross-sectional area. The pellets were then dried at 140°C under primary vacuum for 24 h and transferred into an argon-filled glove box.
The electrochemical test cell consisted of two stainless steel electrodes with a Teflon holder. Lithium ribbon of 0.75 mm thickness (Aldrich) was used as the negative electrode (anode). The separator was a film of Celgard 2400™ (Hoechst-Celanese, Charlotte, NC), and the electrolyte consisted of a 1 M solution of LiPF₆ in ethylene carbonate (EC) and diethyl carbonate (DEC). The ratio of EC to DEC was 1:1 by volume. All cell handling was performed in an argon-filled glove box. Charge-discharge studies were performed with a MACCOR automated test equipment (series 4000). Data were taken at a constant current density of 0.40 or 0.133 mA/cm², corresponding to a rate of C/5 or C/15, between 2.0 and 4.4 V at room temperature.

Results and Discussion

XRD patterns of the oxide powders obtained by firing the aluminum-doped precursors at 945°C in various oxygen partial pressures are shown in Fig. 1. At the higher oxygen partial pressures of 10⁻² and 10⁻³ atm, the resulting phases are LiMn₂O₄, Li₂MnO₃, and γ-LiAlO₂ (tetragonal phase). As the oxygen partial pressure is reduced further, however, new phases begin to form. At 10⁻⁴ atm, these new phases are sufficiently distinct to be identifiable as being isostructural with m-LiMnO₂ and o-LiMnO₂.

m-LiMnO₂, marked by its strongest peak at 2θ = 18.3°, becomes the major phase at oxygen partial pressures below 10⁻⁴ atm. Under these conditions, a solid solution between the LiAlO₂ and LiMnO₂ end members is achieved. It should be noted that the XRD pattern of m-LiMnO₂ is very similar to that of tetragonal Li₂Mn₂O₄ spinel, which has been obtained by lithiation of LiMn₂O₄ spinel. Capitaine et al. have argued that these two phases can be distinguished from each other by the diffraction lines in the 64-68° 2θ range. For a more detailed examination, we simulated the XRD patterns of m-LiMnO₂, Li₂Mn₂O₄, and a hypothetical solid solution m-LiAl₀.₂₅Mn₀.₇₅O₂, using the commercial software Cerius² (v.3.5, Molecular Simulations Inc., San Diego, CA). The structure of m-LiMnO₂ was simulated using crystallographic data from Armstrong and Bruce, that for Li₂Mn₂O₄ using data from Mosbah et al., and that for m-LiAl₀.₂₅Mn₀.₇₅O₂ using the lattice parameters determined in this study (see below) and the Armstrong and Bruce oxygen parameters, assuming completely ordered α-NaFeO₂ structure except for the substitution of 25% of the Mn by Al.

The simulated results are shown in Fig. 2 in comparison with the experimental XRD pattern for LiAl₀.₂₅Mn₀.₇₅O₂. Clear differences between the three simulated patterns can be seen in the positions and relative intensities of peaks in the 60-68° range, expanded in the inset for each pattern. The monoclinic phases, m-LiMnO₂ and m-LiAl₀.₂₅Mn₀.₇₅O₂, exhibit exclusively the m-LiMnO₂ phase when fired in reducing atmosphere (PₐO₂=10⁻⁷ atm, Fig. 1). The XRD results indicate that the predominant manganese valence state is 3+ at oxygen partial pressures below 10⁻⁴ atm. Under these conditions, a solid solution between the LiAlO₂ and LiMnO₂ end members is achieved.

Figure 1. Powder XRD patterns of LiAl₀₉₅Mn₀.₅O₂ after firing for 2 h at 945°C in various oxygen partial pressures. (●: m-LiMnO₂; with hkl indicated; ▲: o-LiMnO₂; +: Li₂MnO₃; △: Li₂MnO₃; and ◊: γ-LiAlO₂). The top pattern for LiAl₀.₀₅Mn₀.₉₅O₂ corresponds to PₐO₂=10⁻⁷ atm firing conditions.

Figure 2. Simulated XRD patterns for (a) m-LiMnO₂, (b) m-LiAl₀.₂₅Mn₀.₇₅O₂, and (c) Li₂Mn₂O₄, compared with (d) the experimental pattern for LiAl₀.₂₅Mn₀.₇₅O₂.
LiAl$_{0.25}$Mn$_{0.75}$O$_2$, exhibit (202) and (020) peaks at 65.1 and 66.6°, respectively, with the latter being of higher intensity. Li$_3$Mn$_2$O$_4$ has (400) and (323) peaks at 66.1 and 67.°, respectively, with the former being of higher intensity. The experimental pattern in Fig. 2(d) exhibits peak positions (65.1 and 66.6°) as well as relative intensities that correspond to the monoclinic phase. According to our results, the statement by Capitaine et al. that $\alpha$-LiMn$_2$O$_4$ has two peaks in the 64-68° range while Li$_3$Mn$_2$O$_4$ has only one is not quite correct.

Another distinguishable feature between the different phases is observed in the range 61-62°. $m$-LiMnO$_2$ has two peaks (311) and (113), which become more closely spaced in $m$-LiAl$_{0.25}$Mn$_{0.75}$O$_2$. Li$_3$Mn$_2$O$_4$ has only one peak (224) in this 20 range. The experimental pattern (Fig. 2d) matches the simulation for $m$-LiAl$_{0.25}$Mn$_{0.75}$O$_2$ better than that for $m$-LiMnO$_2$. Taken together, the XRD results strongly support the identification of the present phase as being of the monoclinic structure, and having Al substituted for Mn. Direct observation and energy-dispersive X-ray mapping of the oxide powder particles with scanning transmission electron microscopy has also confirmed that the Al and Mn are uniformly distributed throughout the particles.

As further support, undoped Li$_3$Mn$_2$O$_4$ is known to be unstable under the temperature and atmosphere conditions of this study, transforming to $\alpha$-LiMnO$_2$. Figure 3 shows the XRD pattern of the undoped LiMnO$_2$ sample obtained by firing precursor (B) at 945°C in 10^-6 atm oxygen partial pressure, $\alpha$-LiMnO$_2$ is indeed seen to be the predominant phase, consistent with the reported stability of this phase under these conditions.

It is therefore clear that the stabilization of $m$-LiAl$_{1-x}$Mn$_x$O$_2$ phase is due to the addition of aluminum and not to the firing conditions alone. We also note that the $\alpha$-NaFeO$_2$ polymorph of LiAlO$_2$ ($\alpha$-LiAlO$_2$) is not the stable phase under these conditions; it is known to irreversibly transform to $\gamma$-LiAlO$_2$ above 600°C. The present LiAl$_{1-x}$Mn$_x$O$_2$ solid solution is therefore seen to crystallize in the $\alpha$-NaFeO$_2$ cation ordering under conditions where neither end member, LiAlO$_2$ nor LiMnO$_2$, is stable in this structure.

The lattice parameters of the $m$-LiAl$_{0.25}$Mn$_{0.75}$O$_2$ have been calculated from the XRD data using Cohen’s least-squares method, and are compared with those for pure $m$-LiMnO$_2$ obtained by the ion-exchange method in Table I. Within the precision of the data, no significant differences are found in the values of $b$ and $\beta$, while $a$ and $c$ are slightly decreased.

Figure 4 shows the first charge-discharge curve (C/5 rate) of a cell prepared using the $m$-LiAl$_{0.25}$Mn$_{0.75}$O$_2$ (fired at 945°C, $P_{O_2}$ = 10^-6 atm) as the cathode and lithium metal as the anode. It can be seen that the cell exhibits a single charging voltage plateau at ~4 V, and has about 203 mAh/kg of first-charge capacity. A similar result has been reported for the first charging cycle of pure $m$-LiMnO$_2$ by Vitins and West. There does not appear to be a significant difference in average voltage between pure $m$-LiMnO$_2$ and $m$-LiAl$_{0.25}$Mn$_{0.75}$O$_2$, although the comparison may not be exact since the materials are prepared and tested under different conditions. In addition, this sample is not purely single phase (Fig. 1), and the aluminum concentration in the monoclinic phase may be somewhat less than the nominal composition. Furthermore, evidence for a change in cation order during cycling (see below) indicates that the observed potential may include the energetics of other simultaneous processes. In Li(Al,Co)O$_2$, an increase of the average voltage by ~0.15 V has been observed at this aluminum doping level. More-detailed studies are necessary to understand if the voltage mixing rules are indeed different in these two systems.

The first-discharge curve shows a capacity of about 119 mAh/g and the emergence of two voltage steps. After further cycling, the voltage steps become more distinct. Figure 4 also shows the charge-discharge curve at the 20th cycle, where two plateaus at ~4 and ~3 V are clearly seen, indicating intercalation at two distinct lithium sites. This behavior is characteristic of the spinel phase Li$_x$Mn$_2$O$_4$ in which lithium is inserted into the tetrahedral sites over the 4 V plateau corresponding to 0≤x≤1, while lithium is inserted into the octahedral sites over the 3 V plateau corresponding to 1≤x≤2. It can be concluded that the present $m$-LiAl$_{0.25}$Mn$_{0.75}$O$_2$, which initially has only octahedral cation occupancy, has transformed upon cycling to a material with at least a local spinel-like cation ordering. Taking these results and previous observations together, it is clear that both the monoclinic and orthorhombic polymorphs of LiMnO$_2$ have a strong tendency to transform to a spinel-like cation ordering during electrochemical cycling.

Figure 5 shows the evolution of the charge and discharge capacities during cycling between 2.0 and 4.4 V at C/5 rate. While an initial drop in capacity to about 100 mAh/g is seen over the first 5 cycles, with further cycling the discharge capacity increases progressively, and saturates after about 15 cycles at ~148 mAh/g. The initial decrease in capacity is likely related to existence of an intermediate stage of cation ordering. The fact that cycling can be conducted over both the 4 and 3 V plateaus without capacity fade is a remarkably different behavior from that of LiMn$_2$O$_4$ spinel, in which the capacity decreases rapidly.

**Table I.** Monoclinic unit cell parameters of the present $m$-LiAl$_{1-x}$Mn$_x$O$_2$ in comparison with those of pure $m$-LiMnO$_2$ obtained by ion-exchange reaction.

<table>
<thead>
<tr>
<th>Compound</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>β (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$m$-LiAl$<em>{0.25}$Mn$</em>{0.75}$O$_2$</td>
<td>5.426 ± 0.003 Å</td>
<td>5.438(7) Å</td>
<td>5.433(6) Å</td>
<td>115.96 ± 0.03°</td>
</tr>
<tr>
<td>$m$-LiMnO$_2$</td>
<td>5.439(3) Å</td>
<td>5.439(3) Å</td>
<td>5.390 Å</td>
<td>115.96(3)°</td>
</tr>
<tr>
<td>$m$-LiAl$<em>{0.25}$Mn$</em>{0.75}$O$_2$</td>
<td>5.384 ± 0.003 Å</td>
<td>5.381(8) Å</td>
<td>5.395(4) Å</td>
<td>115.97(5)°</td>
</tr>
</tbody>
</table>

Figure 5. Specific capacity vs. cycle number for m-LiAl$_{0.25}$Mn$_{0.75}$O$_2$ tested against a lithium metal anode at 0.4 mA/cm$^2$ current density (C/5 rate) between 2.0 and 4.4 V.

Figure 6. Discharge curves for m-LiAl$_{0.25}$Mn$_{0.75}$O$_2$ at C/5 and C/15 rates. The C/5 curve is the 20th discharge after cycling between 2.0 and 4.4 V. The C/15 curve represents an accelerated cycling experiment in which the sample was first cycled 12 times at C/5 rate between 2.0 and 4.4 V, and the 13th cycle (shown) was conducted at C/15 rate. The corresponding energy densities are shown.

upon cycling into the 3 V region. A similar resistance to capacity fade has been seen in o-LiMn$_2$O$_4$ prepared under certain conditions. However, the resulting material shows excellent cyclability and high reversible capacity when cycled over both voltage plateaus, unlike the LiMn$_2$O$_4$ spinels. A composition LiAl$_{0.25}$Mn$_{0.75}$O$_2$ exhibited 148 mAh/g reversible capacity at C/5 rate (545 Wh/kg energy density) and 182 mAh/g at C/15 rate (545 Wh/kg). m-LiAl$_{0.25}$Mn$_{0.75}$O$_2$ solid solutions may therefore be attractive cathode materials for low-cost, high-energy-density lithium rechargeable batteries.

Conclusions

A LiAl$_{0.25}$Mn$_{0.75}$O$_2$ solid solution can be crystallized in the monoclinic derivative of the α-NaFeO$_2$ structure upon firing in a reducing environment to control the Mn$^{3+}$ content. During electrochemical cycling, this compound develops two voltage plateaus (4 and 3 V, vs. a lithium anode), suggesting spinel-like cation ordering, as previously observed for o-LiMn$_2$O$_4$ and m-LiMn$_2$O$_4$ prepared by other methods. However, the resulting material shows excellent cyclability and high reversible capacity when cycled over both voltage plateaus, unlike the LiMn$_2$O$_4$ spinels. A composition LiAl$_{0.25}$Mn$_{0.75}$O$_2$ exhibited 148 mAh/g reversible capacity at C/5 rate (450 Wh/kg energy density) and 182 mAh/g at C/15 rate (545 Wh/kg). m-LiAl$_{0.25}$Mn$_{0.75}$O$_2$ solid solutions may therefore be attractive cathode materials for low-cost, high-energy-density lithium rechargeable batteries.

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