Preparation and Electrochemical Performance of Li$_x$MnO$_2$ Materials by a Reduction and Lithiation Method

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The preparation of Li$_x$MnO$_2$ materials via a novel reduction and lithiation method is reported. The effect of lithium concentration, lithiation temperature and lithiation time on the composition, structure and electrochemical performance of the resulting materials was investigated. Altering the lithiation conditions resulted in distinct materials with different lithium contents of x = 0.07, 0.12 and 0.16. XRD suggested that these materials were stabilized γ-MnO$_2$, a swollen lithiated manganese dioxide phase, and a Li$_2$MnO$_2$/γ-MnO$_2$ mixture, respectively. The materials showed superior electrochemical performance over ten cycles, in a non-aqueous coin cell containing a Li metal anode, compared to Li$_2$MnO$_3$ materials with equivalent x, prepared by co-precipitation. In particular, the Li$_{0.12}$MnO$_2$ and Li$_{0.16}$MnO$_2$ materials showed unexpectedly high reversible capacities of 160 mAh/g at high discharge rate of 30 mAh/g.

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Experimental

Sample preparation.—The γ-MnO$_2$ sample used for study was prepared by Delta EMD Australia. In short, a hot (90–98°C) solution of acidified (0.3 M H$_2$SO$_4$) MnSO$_4$ (1.0 M) was anodically electrolyzed (65 A/m$^2$) to deposit the manganese dioxide onto a titanium substrate. After sufficient deposit had been collected on the substrate (~3 days) the entire electrode was removed from the electrolyte and the solid manganese dioxide mechanically stripped from the titanium. The resultant chunks of manganese dioxide were then milled to a ~105 μm powder using a zirconia orbital mill, and then suspended in Milli-Q ultra-pure water (resistivity > 18.2 MΩ cm) which was subsequently neutralized over the course of 24 hours by the addition of 0.1 M NaOH. Once the pH of the suspension had stabilized it was filtered and the collected solid was then further washed with copious amounts of DI water. The powder was then dried at 60°C in air, before being stored in an airtight container. Since this material was produced electrolytically, it was named electrolytic manganese dioxide (EMD).

The first step in chemical reduction of the γ-MnO$_2$ was to dry the EMD at 110°C for 24 hours under vacuum to totally remove all surface water that would otherwise affect the chemical reduction process. 20 g of this dried EMD was then immersed in 400 mL of 2-propanol (Sigma Aldrich; HPLC grade) in a sealed glass container and left to react at ambient temperature (22 ± 1°C) with constant stirring. After 72 hours the suspension was filtered, and the EMD thoroughly washed with acetone to remove any residual 2-propanol. This chemically reduced EMD was then dried under vacuum at ambient temperature. Lithiation was carried out by immersion of the dry, reduced EMD in an aqueous LiOH solution for a selected period of time, after which the EMD was filtered and washed with thoroughly with Milli-Q water until the filtrate returned (from basic) to neutral (pH ≈ 7). The washing step was undertaken to minimize LiOH adsorption to the EMD surface. Following this, heat-treatment was carried out by heating the sample in air from ambient to 350°C over the course of 1 hour, after which the sample was held at this temperature for a further 2 hours before being allowed to cool back to room temperature.

For the purposes of comparison, lithiation of samples was also carried out by co-precipitation followed by heating. Here the same EMD sample was suspended in Milli-Q water containing a known quantity of LiOH (99.9%, FMC Lithium). Suspensions containing various lithium to manganese ratios were prepared. After mixing these...
were placed in a synthetic air (80:20 N₂/O₂), to avoid Li₂CO₃ formation from CO₂ in the air, purged oven at 60 °C for several days to allow the water to evaporate and the lithium to precipitate on the EMD surface. Subsequently, the dry LiOH/EMD mixture was heated in a similar synthetic air atmosphere. Beginning at ambient temperature, the sample was heated up to 350 °C over the course of a 1 hour period. After heating at 350 °C for 2 hours, the sample was allowed to cool naturally back to ambient conditions. Heat treated EMD (HEMD) was prepared using the same heat-treatment regime without the prior co-precipitation step.

**Structural and chemical characterization.** — X-ray diffraction (XRD) patterns were obtained using a Philips 1710 diffractometer with Cu Kα radiation at 40 kV and 30 mA. The setup used fixed slits and the divergence and scatter slits were set at 1° and the receiving slit at 0.2°. Scans were carried out between 10–90 2θ using a step size of 0.1° and a count time of 2.5 seconds. The lithium content of each sample was determined through the use of inductively coupled plasma – optical emission spectrometry (ICP-OES) using a Varian Liberty Series II ICP-OES as reported previously. The Mn(III) content of each sample, formed either as a result of chemical reduction or sample lithiation, was determined by potentiometric titration, as outlined in Vogel.

**Electrochemical characterization.** — Cathodes were prepared by pressing (at 7.5 MPa for 1 min) ~250 mg of a 1:8:1 by weight mixture of the Li,MnO₂, graphite (Timcal, 3.5 μm) and polyvinylene fluoride (PVdF; binder, Fluka), respectively. This led to a cathode pellet 13 mm in diameter and ~300 μm thick. The cathodes were then dried under vacuum at ~110 °C for 12 hours and subsequently transferred to a dry and oxygen free argon filled glove box. CR2O3 coin cells (Hosiden Inc.) were assembled in the glove box as described previously. A lithium metal anode (FMC Lithium; >99.9%), Li₂, MnO₂ cathode, and an electrolyte of 1 M LiPF₆ in 1:1 (v/v) mixture of ethylene carbonate and dimethyl carbonate was used. Electrochemical cell testing was carried out using a Perkin Elmer VMP 16-channel potentiostat/galvanostat, using a constant current charging and discharging protocol. Initially, discharge at a particular current density for cell testing was carried out using a Perkin Elmer VMP 16-channel potentiostat/galvanostat, using a constant current charging and discharging protocol. Initially, discharge at a particular current density was undertaken from the open circuit potential (V ~3.2 V) to 2.0 V. The cell was subsequently charged using the same magnitude current, until a potential of 3.5 V was reached. The cell was held at this potential for a further 150 minutes, with decaying current, to ensure a complete recharge. This protocol was repeated for at least 10 cycles for each cell.

**Results and Discussion.** — Potentiometric titration of the reduced EMD prepared by immersion in 2-propanol indicated that 46.4% of the manganese was in the Mn(III) form, a substantial increase from the 3.3% present in the unreduced sample. This is consistent with previous work, and indicates significant reduction of Mn(IV) to Mn(III). Lithiation of the reduced (and an unreduced control sample) was achieved by immersion in aqueous LiOH solutions under various conditions (see Table 1). After filtering and washing with Milli-Q water, the EMD + LiOH samples were heat treated at 350 °C, and the lithium content of the resultant materials determined as described in the Experimental section. Table 1 summarizes the effect of various experimental lithiation conditions on the lithium content (determined by ICP-OES) of the materials (x in LiₓMnO₂).

Lithiation of the EMD reduced for 6 days at 22 ± 1 °C in 1.0 M LiOH resulted in an incorporation of 0.06 mole of Li per mole of Mn, giving a Li₅MnO₂ material. This corresponds to only 15% of the protons associated with Mn(III) species in the reduced γ-MnO₂ structure being exchanged with lithium ions. Increasing the reaction time to 11 days only slightly increased the lithium content, resulting in a Li₆MnO₂ material (15% of protons displaced) indicating that the majority of ion exchange occurred within the first 6 days. Lithiation of unreduced EMD under the same conditions gave Li₆MnO₂, confirming that reduction prior to immersion in LiOH enhances lithium uptake of the material, as expected. Heating during immersion in LiOH solution was seen to promote ion exchange, with an increase in the lithium content from x = 0.07 to 0.12 observed upon increasing the temperature from 22 °C to 50 °C. Raising the LiOH concentration from 1.0 to 5.0 M brings about an even more significant increase in lithium incorporation, with a lithium content of x = 0.16 being obtained. It should be noted that this lithium content corresponds to the displacement of only 35% of the available Coleman protons present after reduction with Li⁺ ions. However, the subsequent heat-treatment at 350 °C is expected to oxidize the majority of remaining Mn(III) to Mn(IV), and remove the associated protons by thermal diffusion.

Figure 1 shows XRD patterns obtained for EMD, heat treated EMD (HEMD), and LiₓMnO₂ materials prepared by our reduction and lithiation process. Comparison of the EMD and HEMD patterns shows disappearance of the 110 peak at ~21 20 and the emergence of peaks characteristic of a spinel LiₓMn₅O₁₂ phase.

| Table 1. Lithium content of LiₓMnO₂ materials prepared by lithiation, followed by heat-treatment at 350 °C. |
|-----------------|-----------------|-----------------|-----------------|
| Treatment | Time (days) | [LiOH] (mol/L) | Temperature (°C) | x in LiₓMnO₂ |
| ----------------- |-----------------|-----------------|-----------------|
| RL | 6 | 1.0 | 22 ± 2 | 0.062 |
| | 11 | 1.0 | 22 ± 2 | 0.071 |
| RL | 11 | 5.0 | 22 ± 2 | 0.119 |
| L | 11 | 1.0 | 50 ± 5 | 0.164 |
| L | 11 | 1.0 | 22 ± 2 | 0.444 |

RL = Reduction (to 46.4% Mn(III)) followed by lithiation.
L = Lithiation without prior reduction. Mn(III) content prior to lithiation is 3.3% of total manganese.

Figure 1. XRD patterns of EMD (peaks indexed to a ramsdellite unit cell), HEMD, and LiₓMnO₂ materials, prepared as described in Table 1. (+) indicates peaks characteristic of an expanded ramsdellite structure, while (*) indicates peaks characteristic of the spinel LiₓMn₅O₁₂ phase.
of a broad peak at ~28-20, which is indicative of the formation of y-MnO₂ phase upon heating of γ-MnO₂, consistent with the previous reports. The XRD pattern of the Li₀.₁₂MnO₂ material is similar to that of HEMD, differing only in a shift to lower angles in the XRD patterns in the material prepared by reduction and then lithiation. (Figure 2). This is consistent with the formation of Mn₂O₄ impurities within the material. The XRD peaks have previously been observed when LiₓMnO₂ materials are prepared by a classical solid state reaction (chemical mixing of the precursors followed by heating) but only at high levels of lithiation such as x = 0.5 (although the results have not been interpreted in this manner). Hence we propose that the higher LiOH concentration used during pretreatment in the case of the LiₓMnO₂ material increases the lithium concentration on and near the surface of the MnO₂ particles, and that this relatively strongly bound lithium is not removed during the washing step (see Experimental). The consequence of this is the formation of the spinel phase in these regions, while the relatively low lithium content within the bulk of particles leads to the formation of a LiₓMnO₂-like material. This can be contrasted to the case of the Li₀.₁₂MnO₂ material, lithiated with low LiOH concentration solutions at elevated temperature, which shows increased penetration of lithium into the structure, and hence a more uniform phase change throughout the structure.

Table II. Comparison of lithium and Mn(III) content of LiₓMnO₂ materials.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>n(III)/n(Mn total)</th>
<th>x in LiₓMnO₂</th>
<th>(n(III)/n(Mn total)) - x</th>
</tr>
</thead>
<tbody>
<tr>
<td>RL</td>
<td>0.11</td>
<td>0.07</td>
<td>0.04</td>
</tr>
<tr>
<td>L</td>
<td>0.09</td>
<td>0.12</td>
<td>-0.03</td>
</tr>
<tr>
<td>L</td>
<td>0.14</td>
<td>0.16</td>
<td>-0.03</td>
</tr>
<tr>
<td>L</td>
<td>0.05</td>
<td>0.04</td>
<td>0.01</td>
</tr>
</tbody>
</table>

RL = Reduction (to 46.4% Mn(III)) followed by lithiation. L = Lithiation without prior reduction. Mn(III) content prior to lithiation is 3.3% of total manganese.

Furthermore, the 221/240 peaks at 56°28 remain and no peak at 53°28 is seen to emerge, indicating the formation of the monoclinic tunnel-structured LiₓMnO₂ has not taken place. However, differences between the LiₓMnO₂ and LiₓMnO₂ materials are observed, with the latter exhibiting weak signals at 18°, 44° and 58°26, which are not present in the former. These peaks are consistent with the formation of spinel LiMn₂O₄ impurities within the material. Spinel peaks have previously been observed when LiₓMnO₂ materials are prepared by a classical solid state reaction (physical mixing of the precursors followed by heating) but only at high levels of lithiation such as x = 0.5 (although the results have not been interpreted in this manner). Hence we propose that the higher LiOH concentration used during pretreatment in the case of the LiₓMnO₂ material increases the lithium concentration on and near the surface of the MnO₂ particles, and that this relatively strongly bound lithium is not removed during the washing step (see Experimental). The consequence of this is the formation of the spinel phase in these regions, while the relatively low lithium content within the bulk of particles leads to the formation of a LiₓMnO₂-like material. This can be contrasted to the case of the Li₀.₁₂MnO₂ material, lithiated with low LiOH concentration solutions at elevated temperature, which shows increased penetration of lithium into the structure, and hence a more uniform phase change throughout the structure.

Table II compares the lithium content (determined by ICP-OES) with the Mn(III) content (determined by potentiometric titration) of selected LiₓMnO₂ samples. At low levels of lithiation (x = 0.07) the Mn(III) content is slightly higher than the lithium content, indicating the presence of Mn(II) in the structure that is not charge balanced by the presence of lithium. We attribute this to the formation of a Mn(III) containing oxide such as Mn₂O₃ upon heating, since both LiMn₂O₄ and spinel LiMn₂O₄ carry one lithium and one Mn(III) ion each.

**Electrochemical characterization.**— Figure 3 shows the electrochemical performance (selected discharge curves and total capacity per cycle) of the LiₓMnO₂ material prepared in this work by reduction and lithiation at discharge rates of 5 and 30 mA/g. For the sake of comparison, its performance is compared to a LiₓMnO₂ material prepared by co-precipitation and heating. Both discharge rates LiₓMnO₂ material prepared by the reduction and lithiation procedure proved superior to the similar composition material prepared by co-precipitation and heating, in terms of both initial capacity and capacity retention upon cycling. The difference in performance (which is especially pronounced at the 5 mA/g discharge rate) is surprising considering the similarities in the XRD patterns between the LixMnO₂ prepared by reduction and lithiation.
Figure 3. (a) Selected discharge curves for Li_{0.07}MnO_2 prepared by reduction and lithiation at discharge rates of 5 and 30 mA g\(^{-1}\); and (b) capacity of Li_{0.07}MnO_2 (●) made by reduction and lithiation and Li_{0.09}MnO_2 (○) prepared by co-precipitation (data reproduced from Reference 11) as a function of cycle count, at discharge rates of 5 and 30 mA g\(^{-1}\).

(Figure 1) and that of Li_{0.08}MnO_2 prepared by co-precipitation and heating. Furthermore, it is unlikely that the 1% difference in lithium content between the two materials can be used to account for the capacity differences. One possible explanation is deeper penetration of lithium into the structure for reduced material, leading to a more uniform composition throughout the particle, giving superior stabilization of the structure.

Cycling of Li_{0.12}MnO_2 (■) and Li_{0.16}MnO_2 (□) materials prepared by the reduction and lithiation process were investigated and compared to Li_{0.15}MnO_2 (Δ) prepared by co-precipitation and heating. Figure 4 shows selected discharge curves (a) and (b) and capacity versus cycle number (c) for these materials using discharge rates of 5 and 30 mA g\(^{-1}\), respectively. At the low discharge rate of 5 mA g\(^{-1}\) the Li_{0.16}MnO_2 and LiMn_{0.12}O_2 materials show approximately the same capacity as the Li_{0.15}MnO_2 material prepared by mere co-precipitation and heating. However, at the higher discharge rate of 30 mA g\(^{-1}\), both the Li_{0.15}MnO_2 and Li_{0.16}MnO_2 materials show significantly higher discharge capacities than the Li_{0.15}MnO_2 prepared by co-precipitation. In the case of Li_{0.15}MnO_2, this can be explained by enhanced penetration of lithium into the MnO_2 structure upon reduction and heating, leading to a more
open structure, and hence enhanced Li$^+$ diffusion. The explanation for the higher capacity in the case of the Li$_{0.12}$MnO$_2$ material is less clear.

Conclusions

The effect of the lithiation conditions on the composition, structure and electrochemical performance of Li$_x$MnO$_2$ materials, prepared by a novel reduction and lithiation method, were investigated. The lithium content (x in Li$_x$MnO$_2$) was seen to increase with reaction time, lithium concentration and lithiation temperature. At ambient temperature, and relatively low lithium concentrations, a stabilized y-MnO$_2$, Li$_{1.85}$MnO$_2$ phase is formed, structurally similar to Li$_0.35$MnO$_2$ previously formed via lithiation by co-precipitation, but exhibiting superior performance. At elevated temperature, or lithium concentration.
Li$_{1/2}$Mn$_2$O$_4$ and Li$_{16}$Mn$_2$O$_7$ materials were formed, respectively. The former was determined to be a swollen LiMn$_2$O$_4$ (previously described by Bowden$^{12,13}$) whereas the latter exhibited XRD pattern that may be interpreted in terms of a material consisting of a stabilized y-MnO$_2$ structure incorporating spinel LiMn$_2$O$_4$ impurities. Both of these materials proved superior to the Li$_{16}$Mn$_2$O$_7$ materials previously reported at a high discharge rate of 30 mA/g. The electrochemical results presented in this paper point to a clear advantage, in terms of reversible capacity, of the use of the reduction and lithiation process over the preparation by mere co-precipitation.

Acknowledgments

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References