Thermal Lithiation of Manganese Dioxide: Effect of Low Lithium Concentration ($x \leq 0.3$ in Li$_x$MnO$_2$) on Structure and Electrochemical Performance

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The effect of lithium concentration on Li$_x$MnO$_2$ ($x \leq 0.3$) materials prepared by co-precipitation/heating is investigated. Lithium concentration determines the phase formed, with three different phases identified in the concentration range. Low levels of lithiation ($x = 0.08$) leads to the formation of $\gamma$- and $\beta$-type MnO$_2$ material. As the lithium concentration is increased to $x = 0.15$, a lithiated $\gamma$-MnO$_2$ phase is formed. Finally, at $x = 0.28$, a tunnel-structured monoclinic MnO$_2$ is obtained. Increasing the concentration of lithium inhibits the formation of the undesired inactive Mn$_3$O$_4$ phase, which is formed upon heat-treatment of MnO$_2$. At 5 mA/g charge/discharge rate the monoclinic Li$_{0.28}$MnO$_2$ material gave the best performance, while at 30 mA/g the Li$_{0.08}$MnO$_2$ material proved superior.

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The development of a range of portable consumer electronic devices over the past two decades has created significant demand for small, high energy, rechargeable batteries. Lithium-ion batteries have, to some extent, met this demand, offering high energy densities and cycle counts. Nevertheless, the development of ever more powerful, portable electronic devices, coupled with the desire for development of rechargeable batteries for electric cars to stem carbon dioxide emissions continues to drive research and development of superior lithium ion batteries. Much of this work has focused on the development of stable high capacity cathode materials. Research into the use of lithium cobalt oxide (LiCoO$_2$) and lithium iron phosphate (LiFePO$_4$) as active positive electrode materials for lithium ion batteries has led to the development of commercial cells integrating these materials. These cells exhibit excellent cycling, combined with decent capacities of approximately 150 mAh/g, they also have a number of disadvantages. The high toxicity and lack of abundance of cobalt complexes makes LiCoO$_2$ less ideal as a cathode active material. Due to poor conductivity, the alternative LiFePO$_4$ cathode materials require extensive processing making their incorporation into commercial cells costly.

Manganese dioxide (MnO$_2$) is an attractive cathode material due to its abundance, low cost, low toxicity, relatively high conductivity, and high theoretical capacity of 308 mAh/g. Furthermore, cells incorporating MnO$_2$ cathode materials can be produced in the fully charged state. While MnO$_2$ has been widely used in primary aqueous ($\gamma$-MnO$_2$) and non-aqueous ($\beta$-MnO$_2$) cells, its integration in secondary lithium ion cells has proven more problematic. Initial investigations were hampered by the evolution of structural water present in $\gamma$-MnO$_2$ which severely limits cell rechargability. Heat treatment of the material was found to remove the structural water, but this was also accompanied by the undesirable transition of the $\gamma$-MnO$_2$ structure to a $\alpha$-MnO$_2$ form, and the resulting material was again seen to be unstable to extended cycling.

A number of workers have reported that thermal lithiation of MnO$_2$, achieved by heating MnO$_2$ to temperatures of 300–450°C in the presence of a lithium source, leads to improved capacity retention in non-aqueous cells. Some early work on these lithium manganese dioxide compounds (Li$_x$MnO$_2$) found a lithium to manganese ratio of 1:3 (i.e., $x = 0.33$) to be optimum in terms of the performance of the material. In another report, an optimum composition of Li$_{0.38}$MnO$_2$ was identified, although materials with this composition consisted of Li$_{0.38}$MnO$_2$ as a component phase. The structure of Li$_{0.38}$MnO$_2$ has been interpreted in a number of ways. Purukawa and coworkers originally proposed a composite structure of Li$_{0.37}$MnO$_2$ and $\gamma$-$\beta$-MnO$_2$, whereas Thackeray and coworkers suggested the material consists of a composite of $\gamma$-$\beta$-MnO$_2$ and a spinline Li$_3$Mn$_5$O$_8$-like phase. However, neither of these proposals can account for the electrochemical performance or X-ray diffraction patterns of Li$_{0.33}$MnO$_2$. These considerations prompted Li et al. to propose the formation of a single Li$_{0.33}$MnO$_2$ phase. This proposal is supported by the work of Aurbach and coworkers who found good agreement between experimental data and a simulated XRD pattern for a single phase, tunnelled, monoclinic Li$_{0.33}$MnO$_2$ material using the Rietveld method. This result has been supported by subsequent reports.

Unlike Li$_{0.33}$MnO$_2$, thermally prepared Li$_x$MnO$_2$ materials with $x < 0.33$ have received little attention with no detailed studies of the effect of $x$ in Li$_x$MnO$_2$ on structure and electrochemical performance reported to date. In the present work we investigate the structure and electrochemical performance of thermally lithiated electrolytic manganese dioxide (EMD). The extent of lithiation ($x$ in Li$_x$MnO$_2$, where $x < 0.33$) is varied, and the effect on structure, and electrochemical performance of the material is investigated.

Experimental

Sample preparation.— Lithiation was achieved by suspension of electrolytic manganese dioxide (EMD; Delta EMD, <32 µm particle size) in Milli Q water containing a known quantity of LiOH (99.9%, FMC Lithium). Suspensions containing various (see Table I) lithium to manganese ratios were prepared. After mixing these were placed in a synthetic air (80:20 N$_2$ : O$_2$) 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 (HTEM) was prepared using the same heat-treatment regime without the prior co-precipitation step.

Chemical characterization.— Inductively coupled plasma optical emission spectrometry (ICP-OES) was carried out using a Varian Liberty Series II ICP-OES to determine the lithium content. Samples for analysis were prepared by dissolving a known quantity of sample in a solution containing 5% H$_2$O$_2$ in 0.1 M HNO$_3$. Standards with the same matrix as the samples were used. All calibrations had a correlation coefficient R$^2 > 0.990$ with at least five standards used. The Mn(III) content of various EMD materials was determined using a potentiometric titration technique as outlined in Vogel.

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Table I. Comparison between expected and actual lithium content upon thermal lithiation of EMD.

<table>
<thead>
<tr>
<th>Expected x in Li₄MnO₂ from co-preparation</th>
<th>x in Li₄MnO₂ from ICP-OES</th>
<th>% Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.019</td>
<td>0.020</td>
<td>2.7</td>
</tr>
<tr>
<td>0.037</td>
<td>0.038</td>
<td>2.6</td>
</tr>
<tr>
<td>0.074</td>
<td>0.081</td>
<td>8.8</td>
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<tr>
<td>0.220</td>
<td>0.222</td>
<td>1.1</td>
</tr>
<tr>
<td>0.300</td>
<td>0.280</td>
<td>7.2</td>
</tr>
</tbody>
</table>

Structural and morphological characterization.— X-ray diffraction (XRD) analysis of the resultant materials was carried out using a Philips 1710 diffractometer with Cu Kα radiation operating at 40 kV and 30 mA. A scan range of 10 to 90° 20, a step size of 0.05°, and a count time of 2.5 s was used. Divergence and receiving slit widths of 0.1° were also used.

Sample morphology was determined using scanning electron microscopy (SEM) and gas adsorption measurements. SEM was conducted by mounting the sample for study on an appropriate Al stub using double-sided conductive carbon tape. The mounted sample was then carbon coated using an SPI Instruments Carbon Coater, before being examined at a range of different magnifications using a Philips XL30 SEM. Gas adsorption measurements (N₂ as the adsorbate at 77 K) were conducted using a Micromeritics ASAP 2020 unit, on samples that had been previously degassed under vacuum at 120°C for 2 hours. The specific surface area of each sample was then determined using the linearized BET isotherm in the partial pressure range 0.05–0.30.

Electrochemical characterization.— Cathodes were prepared by pressing approximately 250 mg of a 1:8:1 mixture of Li₄MnO₂:graphite:binder (polyvinylidene difluoride) in a KBr die press under 7.5 MPa (1 kN on 13 mm diameter) for 1 min. After pressing, cathodes were dried at 110°C under vacuum for at least 12 hours prior to being transferred to a Ar filled glove box. Coin cells were assembled (in the glove box) as described previously using a lithium metal anode (FMC Lithium) and the MnO₂ derived cathodes. A 1 M solution of LiPF₆ in 1:1 (v/v) of ethylene carbonate (EC) and dimethyl carbonate (DMC) was used as the electrolyte. All electrochemistry was carried out using a Princeton Applied Research VMP 16 channel potentiostat/galvanostat. Cycling of the cells was conducted using a constant current charge/discharge protocol. The cells were initially discharged from open circuit potential (~3.2 V) to 2.0 V after which they were recharged, at the same rate, until a potential of 3.5 V was reached. The cell was then held at this potential for a further 150 minutes prior to subsequent discharge. This protocol was repeated at least 20 times for each cell.

Results and Discussion

Sample composition.— Table I compares the expected lithium content, based on LiOH and MnO₂ added during co-preparation, to the empirical lithium content of the materials (after heat-treatment at 350°C for two hours) determined by ICP-OES.

Essentially all lithium co-precipitated with manganese is retained upon heat-treatment, indicating that accurate degrees of lithiation can be achieved by co-preparation using LiOH, an assumption that is often made, but not verified, in the literature. For convenience the samples will be referred to using the Li₄MnO₂ nomenclature, where x is the moles of lithium per mole of manganese determined by ICP-OES.

Structural analysis.— Figure 1 shows the XRD patterns of the Li₄MnO₂ materials, the parent EMD, and the corresponding non-lithiated HEMD. Comparison of the EMD and HEMD XRD patterns shows the merging of the peaks at ~21° 2θ (110 peak for orthorhombic γ-MnO₂) and ~34° 2θ (031 peak for γ-MnO₂) to form a single peak at ~28° 2θ (as indicated by the arrows in Figure 1). This change is associated with the conversion of γ-MnO₂ (EMD) to γ-β-MnO₂ during heating. The pattern for Li₀.08MnO₂ is similar to that of HEMD, differing only in that it exhibits a slightly stronger peak at 21° 2θ. Lithium is known to stabilize the γ-MnO₂ structure during heat-treatment. In the case of Li₀.08MnO₂ only a weak stabilizing effect is observed, due to the low concentration of lithium, and hence the material has undergone considerable transformation to γ-β-MnO₂ upon heat-treatment, as seen by comparison with the EMD pattern which exhibits a more distinct 21° 2θ peak.

Increasing the lithium content from x = 0.08 to 0.15 results in strengthening of the γ-MnO₂ peak at ~21° 2θ, indicating increased stabilization of the γ-MnO₂ structure with increasing lithium content. Similar results have been reported by Bowden and coworkers who suspended MnO₂ particles (in some cases pre-treated with H₂SO₄) in LiOH solution. After a specific period of time the solution was filtered and the precipitate heated to 350°C in air. Magic angle spinning (MAS) NMR indicated that immersion of the EMD in LiOH brings about exchange of surface and Rucetschi (associated with cation vacancies) protons with lithium ions, while Coleman protons (associated with Mn(III)) are not affected. Subsequent heat-treatment results in migration of lithium ions from the cation vacancy sites to the (1 × 2) ramsdellite tunnels, leading to the formation of a lithium ordered intergrowth phase named ‘lithiated manganese dioxide’ (LiMD). XRD patterns of the LiMD indicated preservation of the γ-MnO₂ structure after heat-treatment. It was found that the lower limit, in terms of lithium concentration, for the formation of LiMD was x = 0.125 in Li₄MnO₂. This is consistent with the XRD patterns presented in Figure 1 which indicate a lower limit for the formation of the γ-MnO₂-like LiMD at a lithium concentration between x = 0.08 and 0.15. Hence, the results obtained in the present work indicate the...
LiMnO material reported by Bowden and coworkers can be obtained by a simple co-precipitation/heating procedure, provided the required quantity of LiOH is used.

As the lithium content is increased above x = 0.22, the XRD patterns show the disappearance of the (merged) 221/240 peaks situated at 56°-28°, and the emergence of the new 411 peak at 53°-28°. Simultaneously, a further peak is seen to emerge at ~18°-28°, particularly for the x = 0.28 sample. Note that the peak at ~18°-20° is not present for the x = 0.22 sample, indicating that there may be a preferred growth axis for this phase. These changes in the XRD patterns have been previously observed upon thermal lithiation with x ≈ 0.3. As mentioned in the Introduction, this material has been assigned to a single phase monoclinic (c2/m) structure incorporating an ordered alternation of (1 × 1) and (1 × 2) tunnels. In the present work, Figure 1 indicates this structure is formed using lithium concentrations between x = 0.22 and 0.28.

In charge balanced, pure, single phase LiMnO material containing no structural protons, one would expect the amount of lithium and Mn(III) present in the structure to be identical. Hence, comparison of the lithium content (determined by ICP and presented in Table I) and the Mn(III) content (determined by potentiometric titration) can give additional information regarding the phase and purity of the materials, especially since no peaks corresponding to various lithium salts were observed in the diffraction data in Figure 1. Table II compares the lithium (nLi) and Mn(III) /Mn(II) content of selected LiMnO materials, EMD, and HEMD. A higher Mn(III) content is observed for HEMD than for EMD, despite the expected removal of Coleman protons (associated with Mn(III) in the structure) during heating at 350°C. This can be explained by the incorporation of a small amount of amorphous MnO2, which is known to form during heating of MnO2 and would not necessarily be expected to be observed in the XRD patterns at such low levels. The Li0.08MnO2 material shows only 0.044 mole of Mn(III) per mole of Mn, after Mn(III) ions associated with lithium have been subtracted from the total Mn(III) content. This indicates Li0.08MnO2 has approximately half the MnO2 content of HEMD, and suggests lithiation inhibits MnO2 formation. The effect is more pronounced for the Li0.11MnO2 and Li0.28MnO2 materials, which have near identical Mn(III) and lithium contents, indicating significant amounts of MnO2 are not present. The absence of MnO2 in the structure would be expected to improve performance of the material as a cathode active material in lithium ion cells.

Morphological analysis.— Typical images from the SEM analysis on samples prepared in this work are shown in Figures 2a–2d. The starting EMD material (Figure 2a) consists of a range of very jagged irregular particles, covering a wide range of sizes. This very irregular particle shape is as a result of the synthesis process used to make EMD, which includes a high energy milling stage to break the thin anodic EMD deposit (1–2 cm thick) down into a suitable particle size.5,22 Heat treatment of this starting material apparently has very little effect on morphology, as can be seen in Figure 2b. Similarly, surface lithiation followed by heat-treatment also has little effect on morphology, as seen in Figure 2c and 2d, which were taken from the Li0.11MnO2 and Li0.28MnO2 samples, respectively.

The BET surface area of the starting EMD sample measured from gas adsorption was 32.2 m²/g, which is typical of a commercial EMD sample.27 Heat treatment of this material at 350°C for 2 hours (HEMD) led to a significant decrease in surface area down to 24.3 m²/g. This result was expected based on previous work conducted in our laboratory.28 Lithiation and heat-treatment of the EMD

| Table II. Comparison of lithium and manganese (III) content of selected materials. |
|----------------|----------------|----------------|
| Material       | nLi / Mn(III) | x in Li₄MnO₂   |
| Li₀.₂₈MnO₂      | 0.1250        | 0.0810        |
| Li₀.₁₁MnO₂      | 0.1463        | 0.1480        |
| Li₀.₄₄MnO₂      | 0.2724        | 0.2800        |
| HEMD            | 0.0882        | 0.00          |
| EMD             | 0.0833        | 0.00          |

Figure 2. SEM images of (a) starting EMD, (b) HEMD, (c) Li₁.₁₅MnO₂ and (d) Li₂₈MnO₂.
led to samples with BET surface areas within ±3% of the straight heat treated material, with no trend apparent in the results. This allows us to conclude that it is the heat-treatment alone that affects material surface area, rather than lithiation and heat-treatment.

**Electrochemical characterization.**—The cycling performance of HEMD, \( \text{Li}_{0.08}\text{MnO}_2 \), \( \text{Li}_{0.15}\text{MnO}_2 \), and \( \text{Li}_{0.23}\text{MnO}_2 \) was evaluated at discharge rates of 5 and 30 mA g\(^{-1}\), the results from which are shown in Figure 3 (discharge performance versus cycle number) and Figure 4a–4d (discharge curves from various cycles). At both discharge rates the HEMD control sample (Δ) shows high initial capacity, but exhibits significantly more capacity fade upon repeat cycling than the \( \text{Li}_x\text{MnO}_2 \) phases (cf. Figures 3 and 4a). The high initial capacity of HEMD can be attributed to the large number of intercalation sites in the un lithiated MnO\(_2\) structure, while more rapid capacity fade for un lithiated material compared to \( \text{Li}_x\text{MnO}_2 \) phases, has been previously reported.\(^7,8\)

At a discharge rate of 30 mA g\(^{-1}\) the \( \text{Li}_{0.08}\text{MnO}_2 \) material (●) exhibits the best cycling of the four materials tested, giving a stable capacity of ~120 mA h g\(^{-1}\) after 20 cycles. The superior performance of \( \text{Li}_{0.08}\text{MnO}_2 \) is somewhat surprising considering structural similarities to HEMD, and indicates low levels of lithiation can effectively stabilize the structure during cycling. At both discharge rates the \( \text{Li}_{0.15}\text{MnO}_2 \) (○, LiMD) phase exhibits a drop to a low capacity after the first cycle. However, subsequent capacity gain was observed with final capacities close to that of the other materials obtained after 10–20 cycles. We attribute this behavior to a phase change occurring during cycling, perhaps somewhat similar to that observed during some of our previous work in this area.\(^9\) In this article we reported on

![Figure 3. Discharge capacity of cathode at (a) 5 mA/g and (b) 30 mA/g for cathodes containing HEMD (Δ), \( \text{Li}_{0.08}\text{MnO}_2 \) (●), \( \text{Li}_{0.15}\text{MnO}_2 \) (+), and \( \text{Li}_{0.23}\text{MnO}_2 \) (▼).](image1)

![Figure 4. Selected discharge curves for (a) HEMD, (b) \( \text{Li}_{0.08}\text{MnO}_2 \), (c) \( \text{Li}_{0.15}\text{MnO}_2 \) and (d) \( \text{Li}_{0.23}\text{MnO}_2 \) (30 mA/g discharge rate).](image2)
the phase transformations that a HEMD (β-MnO₂) sample undergoes when chemically (rather than electrochemically) reduced. In particular, the parent structure showed evidence for (i) structural expansion as a result of lithium intercalation, (ii) partial structural transformation into Li₂MnO₃, and (iii) the formation of Li₃MnO₄, presumably as the result of Li₂MnO₄ reduction. For the samples reported here, the Li₂MnO₄ (γ) material shows the best performance at a low charge/discharge rate of 5 mA g⁻¹, with a stable capacity of 160 mA g⁻¹ observed over 10 cycles. It is worth noting that the varying cycle profiles of the three lithiated materials is further evidence that three distinct phases are formed at these different lithium concentrations (Figure 3).

The overall performance of the LiₓMnO₂ materials prepared in this work is quite good in comparison to the existing positive active materials used in Li-ion systems. This is particularly true when considering that these materials can be produced at a fraction of the cost of other comparable materials. In comparison to the performance achieved compared to other similar studies, it appears that our materials demonstrated slightly inferior performance; i.e., ~150 mA h g⁻¹ compared to 170 mA h g⁻¹. To justify and explain this difference we would highlight the differences in EMD precursors used for the respective syntheses, in particular the fact that the mean particle size of EMD used in Reference 10 was ~2.5 μm compared to ~45 μm used in this work. There are abundant references in the literature where the effects of particle size and crystallite size are significant in determining the performance of a battery active material; e.g., LiFePO₄ is at present a common example.

**Conclusions**

The effect of lithium concentration on the structure and performance of LiₓMnO₂ (x < 0.3) materials, prepared by co-precipitation and heat-treatment, was investigated. Distinct phases, exhibiting different structural features and electrochemical cycling profiles were observed. As the lithium content is increased from x = 0 (HEMD) to 0.15 less conversion to the γ/β-MnO₂ phase is observed upon heating treatment. On the other hand, with the γ-MnO₂ phase almost completely retained at x = 0.15. As the lithium content is increased above x = 0.15, the monoclinic tunnel structure Li₃MnO₄ phase is formed. Increasing lithium content was also seen to inhibit formation of the undesirable Mn₂O₃ product with no formation of this phase observed when x > 0.15. All lithiated materials exhibited equivalent, or better, performance than unlithiated HEMD, at cycle rates of both 5 and 30 mA g⁻¹. At 5 mA g⁻¹ the monoclinic Li₂MnO₄ material gives a slightly higher capacity after ten cycles than the other materials. However, at a higher rate of 30 mA g⁻¹ lithiated LiₓMnO₂ material exhibited the best cycling of the materials. This is a somewhat surprising result considering structural similarity to HEMD, and indicates low levels of lithiation can effectively stabilize the MnO₂ structure to repeat cycling. Materials with this low level of lithiation have not been significantly investigated and warrant further study.

**Acknowledgments**

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**References**