Preparation and Electrochemical Performance of Li_xMnO_2 Materials by a Reduction and Lithiation Method

Joshua Lehr,^{a,c} Wesley M. Dose,^a Marina Yakovleva,^{b,*} and Scott W. Donne^{a,*}

^aDiscipline of Chemistry, University of Newcastle, Callaghan NSW 2308, Australia

^bFMC Lithium, Bessemer City, North Carolina 28016, USA

The preparation of Li_xMnO_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 $\gamma\text{-MnO}_2$, a swollen lithiated manganese dioxide phase, and a $\text{LiMn}_2\text{O}_4/\gamma\text{-MnO}_2$ 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_xMnO_2 materials with equivalent x , prepared by co-precipitation. In particular, the $\text{Li}_{0.12}\text{MnO}_2$ and $\text{Li}_{0.16}\text{MnO}_2$ materials showed unexpectedly high reversible capacities of 160 mAh/g at high discharge rate of 30 mA/g.

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The emergence of portable hand held consumer electronic devices has created a demand for high capacity rechargeable batteries. While lithium ion batteries have, to a large extent, satisfied this demand, the desire to produce ever more power hungry devices drives the development of superior cathode materials, so as to provide higher capacities and improved cycle counts.¹ Lithium cobalt oxide (LiCoO_2) has been extensively used as a cathode active material in lithium ion cells despite its toxicity, high cost and safety concerns. Lithium iron phosphate (LiFePO_4) has been investigated subsequently as an alternative to LiCoO_2 . However, due to its poor conductivity, LiFePO_4 requires extensive processing, making commercialization expensive.^{1,2}

Manganese dioxide offers a low cost, high capacity (theoretically 308 mAh/g) alternative to LiCoO_2 and LiFePO_4 .³ While manganese dioxide has been extensively used in primary cells (both aqueous and non-aqueous), its incorporation into secondary non-aqueous lithium ion batteries has encountered difficulties. Evolution of structural water present in manganese dioxide during cycling results in gassing and loss of cell capacity, while heat-treatment to remove structural water leads to the transition from $\gamma\text{-MnO}_2$ to a mixed $\gamma/\beta\text{-MnO}_2$ phase^{4,5} causing significant capacity loss upon cycling.⁶

A number of workers have shown that heat-treatment of $\gamma\text{-MnO}_2$ in the presence of a lithium source (e.g., LiOH) leads to the formation of Li_xMnO_2 phases (where $x \leq 0.33$) which exhibit improved capacity retention upon cycling in non-aqueous cells.⁶⁻⁹ The mechanochemical synthesis of lithiated manganese dioxide has also been described.¹⁰ We have recently shown¹¹ that the phase formed, and hence the performance of the material, depends on the extent of lithiation (i.e., x in Li_xMnO_2). At low lithium concentrations of $x \approx 0.08$ a lithiated $\gamma/\beta\text{-MnO}_2$ -like phase is formed which exhibits excellent performance at higher discharge rates (30 mA/g). At $x \approx 0.15$ a lithiated $\gamma\text{-MnO}_2$ -like phase is formed, indicating lithium stabilizes the $\gamma\text{-MnO}_2$ structure and prevents transition to $\gamma/\beta\text{-MnO}_2$ upon heat-treatment. This lithiated manganese dioxide (LiMD) phase was first prepared by Bowden by ion exchange followed by heating,^{12,13} but has since been obtained by co-precipitation and heating.¹¹ When $x \approx 0.3$ a monoclinic tunnel structured Li_xMnO_2 material¹⁴ is obtained. Such $\text{Li}_{0.3}\text{MnO}_2$ cathodes have been shown to exhibit excellent capacity retention (up to 190 mAh/g) upon repeated cycling, proving superior to the other Li_xMnO_2 materials at low (5 mA/g) discharge rates.¹¹

In the present work we describe a novel reduction and lithiation process for obtaining Li_xMnO_2 materials. Initial chemical reduction of the $\gamma\text{-MnO}_2$ phase is expected to open up the structure via proton insertion. Upon immersion of the reduced $\gamma\text{-MnO}_2$ in LiOH

solution, exchange of the inserted protons with Li^+ ions is expected to occur. The structural and electrochemical properties of the resulting materials are compared to those previously produced by classical mixing and heat-treatment methods,¹¹ and the effect of lithiation conditions on the structure obtained is investigated.

Experimental

Sample preparation.— The $\gamma\text{-MnO}_2$ sample used for study was prepared by Delta EMD Australia. In short, a hot ($90\text{--}98^\circ\text{C}$) solution of acidified (0.3 M H_2SO_4) MnSO_4 (1.0 M) was anodically electrolyzed (65 A/m²) 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 $\sim 105\text{ }\mu\text{m}$ powder using a zirconia orbital mill, and then suspended in Milli-Q ultra-pure water (resistivity $\rho > 18.2\text{ M}\Omega\cdot\text{cm}$) 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 $\gamma\text{-MnO}_2$ 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 ($22 \pm 1^\circ\text{C}$) 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 ($\text{pH} \approx 7$). 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

*Electrochemical Society Active Member.

^cPresent address: Physical and Theoretical Chemistry Laboratory, University of Oxford, Oxford OX1 3QZ, United Kingdom.

^eE-mail: scott.donne@newcastle.edu.au

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 K_α 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.¹¹ 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.¹⁵

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_xMnO₂, graphite (Timcal, 3.5 μm) and polyvinylidene 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. CR2032 coin cells (Hohsen Inc.) were assembled in the glove box as described previously.¹⁶ A lithium metal anode (FMC Lithium; >99.9%), Li_xMnO₂ 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 was undertaken from the open circuit potential (~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

Sample composition.— Potentiometric titration of the reduced EMD produced 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,¹⁷ 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 I). 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 I summarizes the effect of various experimental lithiation conditions on the lithium content (determined by ICP-OES) of the materials (x in Li_xMnO₂).

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 Li_{0.06}MnO₂ material. This corresponds to only 13% 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 Li_{0.07}MnO₂ 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 Li_{0.04}MnO₂, con-

Table I. Lithium content of Li_xMnO₂ materials prepared by lithiation, followed by heat-treatment at 350°C.

Treatment	Time (days)	[LiOH] (mol/L)	Temperature (°C)	x in Li _x MnO ₂
RL	6	1.0	22 ± 2	0.062
	11	1.0	22 ± 2	0.071
	11	1.0	50 ± 5	0.119
	11	5.0	22 ± 2	0.164
L	11	1.0	22 ± 2	0.044

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.

firming 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.¹⁸

Figure 1 shows XRD patterns obtained for EMD, heat treated EMD (HEMD), and Li_xMnO₂ materials prepared by our reduction and lithiation process. Comparison of the EMD and HEMD patterns shows disappearance of the 110 peak at ~21° 2θ and the emergence

Figure 1. XRD patterns of EMD (peaks indexed to a ramdellite unit cell), HEMD, and Li_xMnO₂ materials, prepared as described in Table I. (+) indicates peaks characteristic of an expanded ramdellite structure, while (*) indicates peaks characteristic of the spinel LiMn₂O₄ phase.

Figure 2. XRD patterns of $\text{Li}_{0.12}\text{MnO}_2$ prepared by reduction and lithiation (black line, produced from Figure 1) and $\text{Li}_{0.15}\text{MnO}_2$ prepared by co-precipitation and heating (gray line, reproduced from Reference 11).

of a broad peak at $\sim 28^\circ 2\theta$, which is indicative of the formation of $\gamma/\beta\text{-MnO}_2$ phase upon heating of $\gamma\text{-MnO}_2$, consistent with the previous reports.^{4,19} The XRD pattern of the $\text{Li}_{0.07}\text{MnO}_2$ material is similar to that of HEMD, differing only in a slight splitting of the peak at $28^\circ 2\theta$ into two peaks, indicating the lithiated structures retain more $\gamma\text{-MnO}_2$ character upon heat-treatment compared to the unlithiated EMD. This stabilization of the ramsdellite domains within the $\gamma\text{-MnO}_2$ structure by lithiation has been reported previously by us,¹¹ and other workers.^{12,13,18} As the lithium concentration is increased to $\text{Li}_{0.12}\text{MnO}_2$, by heating during lithiation, a distinct peak is observed at $21^\circ 2\theta$ suggesting full retention of the $\gamma\text{-MnO}_2$ structure. This is consistent with $\text{Li}_{0.15}\text{MnO}_2$ phase formed previously by co-precipitation and then heating,¹³ and ion exchange followed by heating (without prior reduction).¹³ However, comparing the XRD pattern of the $\text{Li}_{0.12}\text{MnO}_2$ material produced by reduction and then lithiation to that of $\text{Li}_{0.15}\text{MnO}_2$ material prepared by co-precipitation and then heating shows peaks at lower angles for the material prepared by reduction and lithiation (Figure 2).

The shifting of the (merged) 221/240 peaks at $56^\circ 2\theta$ to $54^\circ 2\theta$ has been previously reported and attributed it to the formation of a single phase monoclinic tunnel-structured material.^{14,20,21} However, these materials generally had considerably higher lithium content ($x \approx 0.3$ in Li_xMnO_2), and importantly showed the emergence of a peak at $\sim 18^\circ 2\theta$ in the XRD pattern, a feature not observed for the $\text{Li}_{0.12}\text{MnO}_2$ material described here. We therefore propose that the shift to lower angles in the XRD patterns in the material prepared by reduction and then lithiation, compared to those prepared by co-precipitation and heating, is a result of a more swollen ramsdellite structure resulting from the reduction and lithiation process.

The XRD pattern for the $\text{Li}_{0.16}\text{MnO}_2$ phase prepared by lithiation in 5.0 M LiOH (rather than the 1.0 M used for the other materials) is similar to that of $\text{Li}_{0.07}\text{MnO}_2$. No significant strengthening of the 110 signal, associated with the emergence of LiMD structure, previously reported for Li_xMnO_2 materials with this lithium content,¹¹ is ob-

Table II. Comparison of lithium and Mn(III) content of Li_xMnO_2 materials.

Treatment	$n_{\text{Mn(III)}}/n_{\text{Mn(total)}}$	x in Li_xMnO_2	$(n_{\text{Mn(III)}}/n_{\text{Mn(total)}}) - x$
RL	0.11	0.07	0.04
	0.09	0.12	-0.03
	0.14	0.16	-0.03
L	0.05	0.04	0.01

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.

served. Furthermore, the 221/240 peaks at $56^\circ 2\theta$ remain and no peak at $53^\circ 2\theta$ is seen to emerge, indicating the formation of the monoclinic tunnel-structured Li_xMnO_2 has not taken place. However, differences between the $\text{Li}_{0.07}\text{MnO}_2$ and $\text{Li}_{0.16}\text{MnO}_2$ materials are observed, with the latter exhibiting weak signals at 18° , 44° and $58^\circ 2\theta$, which are not present in the former. These peaks are consistent with the formation of spinel LiMn_2O_4 impurities within the material. Spinel peaks have previously been observed when Li_xMnO_2 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 $x \geq 0.5$ (although the results have not been interpreted in this manner).⁶ Hence we propose that the higher LiOH concentration used during pretreatment in the case of the $\text{Li}_{0.16}\text{MnO}_2$ material increases the lithium concentration on and/or near the surface of the MnO_2 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 $\text{Li}_{0.07}\text{MnO}_2$ -like material. This can be contrasted to the case of the $\text{Li}_{0.12}\text{MnO}_2$ 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 Li_xMnO_2 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(III) 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 Mn_2O_3 upon heat-treatment, since Coleman protons would be expected to be completely removed from the sample after heat-treatment at 350°C for 2 hours.¹⁸ Our previous work has shown that increasing lithium content inhibits formation of Mn_2O_3 upon heating, and indeed the $\text{Li}_{0.12}\text{MnO}_2$ and $\text{Li}_{0.16}\text{MnO}_2$ materials both show slightly higher lithium content than Mn(III). The fact that lithium content after subtraction of Mn(III) content is the same for both samples is consistent with the interpretation of the XRD patterns above, since both LiMnO_2 and spinel LiMn_2O_4 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 $\text{Li}_{0.07}\text{MnO}_2$ 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 $\text{Li}_{0.08}\text{MnO}_2$ material (○) prepared by the co-precipitation and heating process described previously by us.¹¹

At both discharge rates the $\text{Li}_{0.07}\text{MnO}_2$ 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 pattern between the $\text{Li}_{0.07}\text{MnO}_2$ prepared by reduction and lithiation

Figure 3. (a) Selected discharge curves for $\text{Li}_{0.07}\text{MnO}_2$ prepared by reduction and lithiation at discharge rates of 5 and 30 mA g^{-1} ; and (b) capacity of $\text{Li}_{0.07}\text{MnO}_2$ (●) made by reduction and lithiation, and $\text{Li}_{0.08}\text{MnO}_2$ (○) 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 $\text{Li}_{0.08}\text{MnO}_2$ 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 $\text{Li}_{0.12}\text{MnO}_2$ (■) and $\text{Li}_{0.16}\text{MnO}_2$ (□) materials prepared by the reduction and lithiation process were investigated and compared to $\text{Li}_{0.15}\text{MnO}_2$ (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 , respectively. At the low discharge rate of 5 mA/g the $\text{Li}_{0.16}\text{MnO}_2$ and $\text{LiMn}_{0.12}\text{O}_2$ materials show approximately the same capacity as the $\text{Li}_{0.15}\text{MnO}_2$ material prepared by mere co-precipitation and heating. However, at the higher discharge rate of 30 mA/g , both the $\text{Li}_{0.12}\text{MnO}_2$ and $\text{Li}_{0.16}\text{MnO}_2$ materials show significantly higher discharge capacities than the $\text{Li}_{0.15}\text{MnO}_2$ prepared by co-precipitation. In the case of $\text{Li}_{0.12}\text{MnO}_2$, this can be explained by enhanced penetration of lithium into the MnO_2 structure upon reduction and heating, leading to a more

Figure 4. Selected discharge curves for (a) $\text{Li}_{0.12}\text{MnO}_2$ and (b) $\text{Li}_{0.16}\text{MnO}_2$ prepared by reduction and lithiation at discharge rates of 5 and 30 mA g^{-1} , and (c) capacity of $\text{Li}_{0.12}\text{MnO}_2$ (■) and $\text{Li}_{0.16}\text{MnO}_2$ (□) materials prepared by reduction and lithiation, compared to $\text{Li}_{0.15}\text{MnO}_2$ (△) 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} .

open structure, and hence enhanced Li^+ diffusion. The explanation for the higher capacity in the case of the $\text{Li}_{0.16}\text{MnO}_2$ material is less clear.

Conclusions

The effect of the lithiation conditions on the composition, structure and electrochemical performance of Li_xMnO_2 materials, prepared

by a novel reduction and lithiation method, were investigated. The lithium content (x in Li_xMnO_2) was seen to increase with reaction time, lithium concentration and lithiation temperature. At ambient temperature, and relatively low lithium concentrations, a stabilized γ - MnO_2 $\text{Li}_{0.07}\text{MnO}_2$ phase is formed, structurally similar to $\text{Li}_{0.08}\text{MnO}_2$ previously formed via lithiation by co-precipitation, but exhibiting superior performance. At elevated temperature, or lithium concentration,

$\text{Li}_{0.12}\text{MnO}_2$ and $\text{Li}_{0.16}\text{MnO}_2$ materials were formed, respectively. The former was determined to be a swollen LiMD (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 $\gamma\text{-MnO}_2$ structure incorporating spinel LiMn_2O_4 impurities. Both of these materials proved superior to the $\text{Li}_{0.15}\text{MnO}_2$ 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.

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