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Manganese dioxides as cathodes for lithium rechargeable cells: the stability challenge

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Abstract

A wide range of manganese oxides is under study for possible use as the cathode of high energy density batteries. The spinel, LiMn_2O_4 , although the most studied has a relatively low energy density and appears unstable under charge. This review emphasizes non-spinel oxides, in particular those with layered or tunnel structures that offer enhanced behavior in lithium ion and lithium polymer cells. A major focus is on stabilizing these manganese oxide structures against conversion to the spinel phase. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Manganese oxide; Spinel; Cubic close packing; Metastable phase; Pillars

1. Introduction

The use of intercalation compounds as electrodes in lithium batteries began about 20 years ago. The prototypical intercalation compound is titanium disulfide, which has been extensively studied [1,2] as the cathode in high energy density lithium batteries. However, even though TiS_2 is one of the few solid cathode materials that can sustain current densities of the order of $5\text{--}10\text{ ma/cm}^2$, as required for many applications, its voltage is insufficiently high when combined with a lithium alloy or carbon anode even for the new generation of 2 volt electronic devices. LiCoO_2 [3], as used in the commercial SONY Li-ION cell, can provide the desired voltage, but is too expensive for large scale applications and only

cycles 0.5 Li. Thus, new cathode materials, which combine the reversibility and current drain capabilities of TiS_2 with the electrode potential of oxides such as LiCoO_2 are desired.

In the last 10 years much effort has been focussed on manganese because of its low cost, low toxicity and familiarity to the battery field. This has centered on the spinel phase, LiMn_2O_4 and on several layered manganese oxides. The spinel phase cycles well only for 0.5 Li/Mn, and has stability problems at elevated temperatures; work in this area has been the subject of reviews by Thackeray [4] and Tarascon [5]. The layered manganates, with the same structure as LiCoO_2 have been studied by Piffard [6,7], Whittingham [8–12], Bruce [13], Delmas [14,15] and Bach et al. [16–18]. The lithium content of the synthesized material can vary from $x=0$ to 1 in Li_xMnO_2 , depending on the synthesis approach used; x is around 0.5 in aqueous based preparations and can approach unity in non-aqueous based ion-exchange

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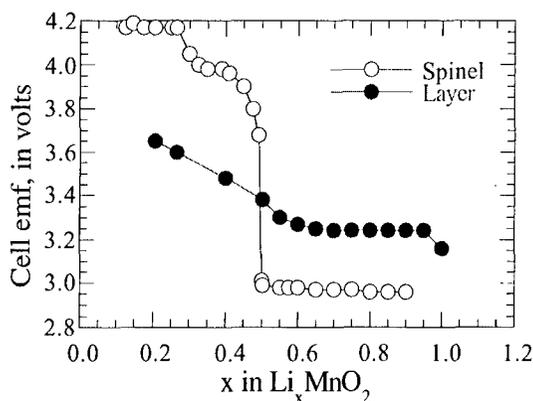


Fig. 1. Cell voltages of the layered and spinel phases of manganese oxide, data from Bruce and Whittingham labs, from [19].

reactions from Na_xMnO_2 . These researchers all showed that these layered phases can be cycled, but that the capacity fades with time. This appears to be due to diffusion of manganese leading to the spinel, or spinel-like phases [10]. Fig. 1 shows the variation of potential with lithium content, which indicates the higher stability of the spinel phase at low lithium contents [19]. Critically it indicates that in the layered material more than 0.8 Li can be cycled over less than a 0.5 volt range. Recent studies [10] suggest that layered manganates can be stabilized by pillaring with cations that are larger than both lithium and manganese; these pillars appear to impede the diffusion of manganese ions into the interlayer region because of the energetically unfavorable sites present.

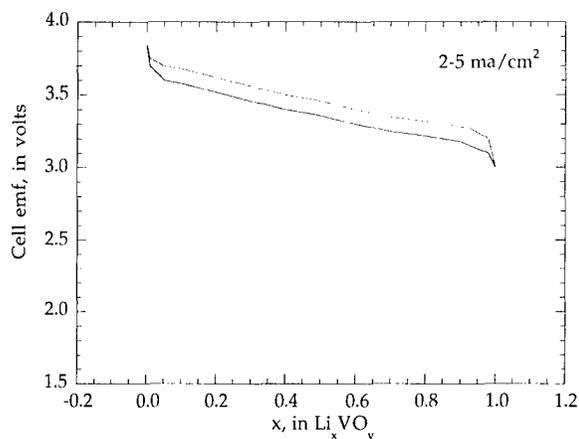


Fig. 2. Ideal behavior for a lithium battery cathode, from [19].

Thus, a search is on to find manganese oxides that are stable over the full range from MnO_2 to LiMnO_2 , and that exhibit the ideal cycling characteristics shown in Fig. 2 [19].

2. Manganese dioxides

Manganese oxides, with the approximate Mn:O ratio of 1:2, form a wide range of crystalline structures as shown in Fig. 3. Many of these structures are stabilized by other ions, such as lithium in the spinel LiMn_2O_4 , barium in the hollandite $\text{BaMn}_8\text{O}_{16}$, or potassium in cryptomelane $\text{KMn}_8\text{O}_{16}$ — both of which have the 2×2 tunnel structure. Many of these structures are also stabilized by the presence of protonic species. This large variety of structures almost certainly means that in the compound Li_xMnO_2 , a variety of structures will become the thermodynamically stable phase as the lithium content is changed over the range of $0 \leq x \leq 1$. Moreover, the stable phase will also change with temperature, so that the phase formed under elevated temperature conditions may not be stable at room temperature. In addition, the oxygen content will in some cases also be a function of temperature as pointed out by Delmas [20]. In the following sections, recent electrochemical data is discussed for a cross-section of these structures.

3. Layered structure manganese dioxides

Fig. 4 shows the cycling behavior of layer structure K_xMnO_2 in lithium cells, and Fig. 5 compares the capacity on cycling of Li_xMnO_2 , Na_xMnO_2 and K_xMnO_2 [10]. We found that the magnesium and rubidium analogs have inferior behavior. In similar cells the spinel LiMn_2O_4 , loses capacity even faster when cycled in the 3 volt regime than layered LiMnO_2 . Whereas lithium ions are in octahedral coordination between the MnO_2 sheets in Li_xMnO_2 , potassium ions are not, thus the oxygen ion arrangement is no longer cubic close packed as in the spinel phase. Thus, it will be necessary for the oxygen ions as well as the manganese ions to diffuse in order for the structure to convert to the spinel structure on cycling in lithium cells. This may explain in part the

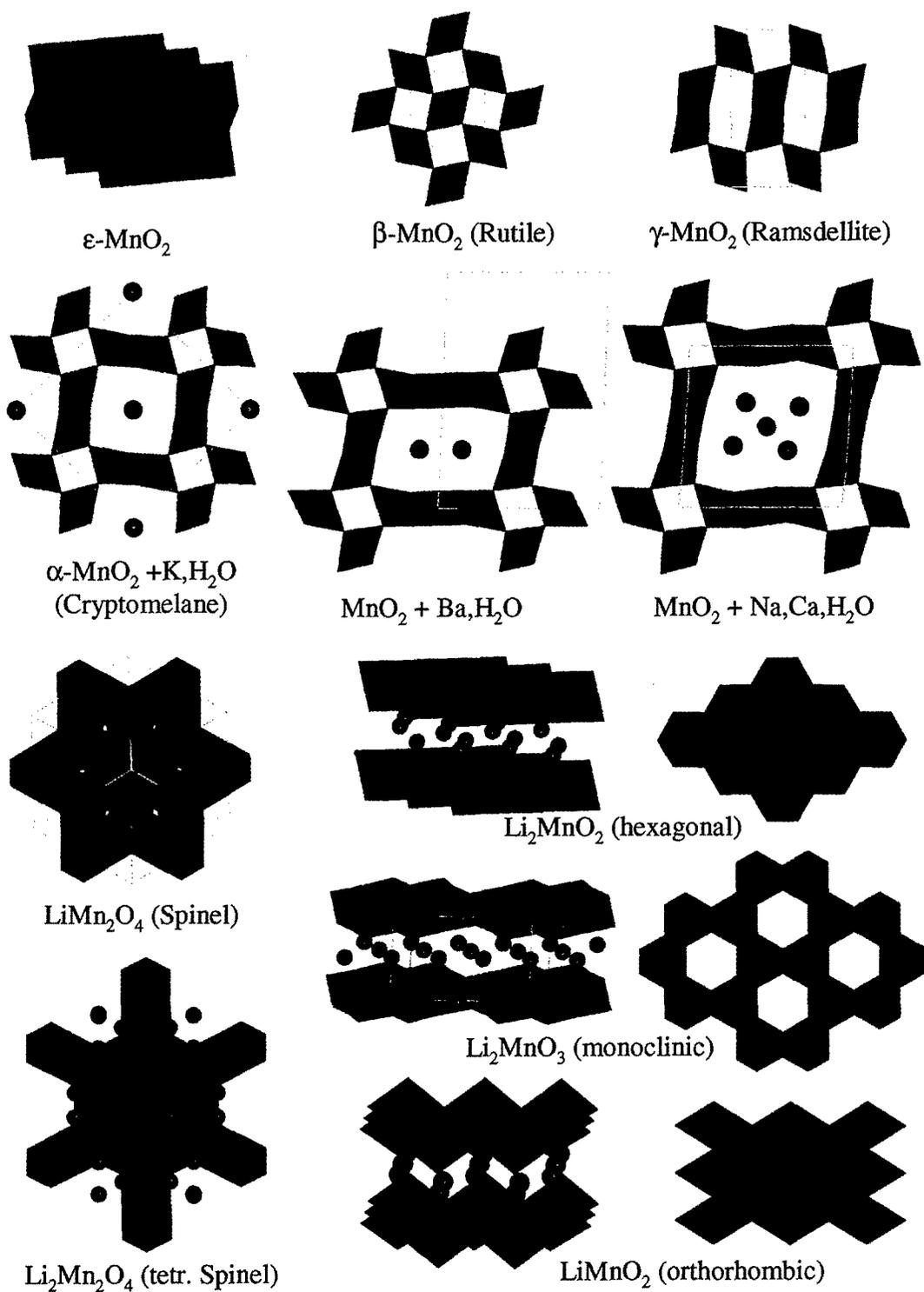


Fig. 3. Structures of some MnO_2 phases.

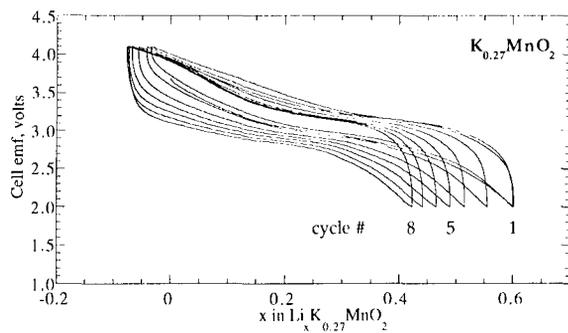


Fig. 4. Cycling behavior of layered potassium manganate, from [10].

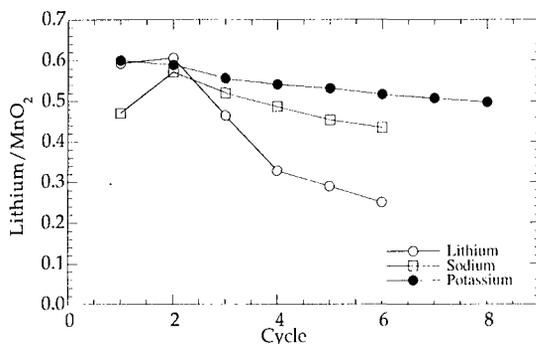


Fig. 5. Capacity as a function of cycle for Li_xMnO_2 , Na_xMnO_2 , and K_xMnO_2 , from [10].

added stability of the K_xMnO_2 structure relative to spinel. As noted earlier, an array of hexagonal close packed oxygen layers in Li_xMnO_2 would certainly inhibit conversion to the cubic close-packed oxygen layers.

This K_xMnO_2 was formed hydrothermally by reaction of aqueous potassium permanganate solutions at 170°C . We have determined the structure of this $\text{K}_{0.27}\text{MnO}_2 \cdot n\text{H}_2\text{O}$ [8]. The manganese ions are in octahedral coordination, just like the titanium in KTiS_2 , and the oxygen sheets shift to give trigonal prismatic sites in the interlayer region unlike in Li_xTiS_2 or Li_xMnO_2 where the anion sheets give octahedral coordination for the lithium. The structure is trigonal, space group $R\bar{3}m$, with hexagonal axes $a = 2.849(8)$, $c = 21.536(7)$ Å; 3 Mn in $3a\ 0\ 0\ 0$ and 6 O in $6c\ 0\ 0\ 0.039(3)$. The K and H_2O mix with a fixed ratio of 1:2 on position $9d\ 1/2\ 0\ 1/2$ between the MnO_2 layers; thus, this atom is placed not in the center of a trigonal prism but on its face.

Potassium forms a range of compounds with manganese dioxide, K_xMnO_2 that depend on potassium content temperature of preparation and oxygen content [20]. These phases are shown in Fig. 6. At the highest temperatures, KMnO_2 is formed but in contrast to the Na_xMnO_2 and K_xTiS_2 systems the 1:1 composition is not a layered compound but rather is composed of MnO_2 chains held together by potassium ions [21]. Studies are underway to determine its ion-exchange and electrochemical behavior in lithium cells [22]. The $\text{K}_{0.7}\text{MnO}_2$ phase appears to be a line phase. At $x = 0.25$ the cryptomelane (hollandite) framework is formed, $\text{K}_{x/2}\text{Mn}_8\text{O}_{16}$. However, under hydrothermal conditions a layered structure is formed in this same composition range [8]. At intermediate values two layered phases are formed, a three block structure and a two-block structure. In both, the manganese ions are in octahedral sites, whereas the potassium ions are in trigonal prismatic sites. The stacking sequence is AbAcBa or AbAcBcBaCaCbA, with the former having no cations immediately above or below each other in neighboring layers.

The hydrothermally formed hydrated $\text{K}_x\text{MnO}_2 \cdot n\text{H}_2\text{O}$ is a three block structure. However, a 2-block hydrated structure has been formed by heating KMnO_4 with MnO_2 at elevated temperatures followed by a water wash to remove soluble phases [23]. Almost certainly the Delmas $\text{K}_{0.5}\text{MnO}_2$ phase [20] is formed first, and in the subsequent water wash potassium is leached out just as noted for Na_xMnO_2 [10] and Li_xTiS_2 [2].

Delmas reported [20] that there is a reduced oxygen content in K_xMnO_2 and Na_xMnO_2 phases formed above 400°C . When these high temperature formed materials are annealed in oxygen below

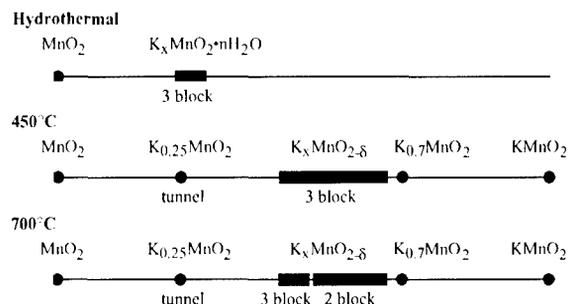


Fig. 6. Phases formed by K_xMnO_2 , after [20].

400°C, there is an oxygen uptake of 0.12 O/Mn for $K_{0.5}MnO_2$ (3 block) formed at 450°C and 0.16 for $K_{0.55}MnO_2$ (2 block) formed at 700°C

Thus, if manganese oxides are made by ion-exchange from the sodium or potassium analogs from samples synthesized at high temperatures then the oxygen composition will depend on the precursor synthesis conditions. Fig. 7 [9] shows a range of synthetic approaches to the synthesis and reactions of manganates. The central reaction schemes represent the hydrothermal approach. The initially formed one water layer structure can be swelled incorporating a second water layer for ions like sodium or magnesium. These two compounds have the mineralogical names birnessite and buserite. The two layer swelled structure can then readily exchange its cations for long chain alkylammonium ions [24], much like the vermiculites and the layered disulfides.

The left side of Fig. 7 shows what has become known as the sol–gel synthesis approach. An amorphous manganese oxide is first made by the reduction of permanganate by organics such as fumaric acid [18,25] and sugars [26] or by inorganics such as iodides [8]. This gel is then heated to an elevated temperature, 500–800°C forming a layered manganate. The Bordeaux group [20,27] first formed these

anhydrous manganates by a high temperature reaction between MnO_2 , Mn_2O_3 and A_2O and showed that they had a range of composition, e.g. $Na_xMn_{1-\delta}O_2$ where $0.45 = x = 0.67$. At these temperatures, the manganese oxide lattice is oxygen 'deficient', which deficiency can be diminished by an oxygen anneal around 400°C, which increases the Mn^{IV} content and converts the lattice from monoclinic to hexagonal.

We have discussed the use of pillars to stabilize the MnO_2 layer structure. Another option is to make the layered lithium manganese oxide more like $LiCoO_2$, possibly by doping with cobalt, iron or nickel to give for example $Li_xMn_{1-y}Co_yO_2$. Several workers have very recently shown enhanced behavior using this approach. Thus Armstrong [28] showed enhanced cycling behavior for $LiMn_{1-y}Co_yO_2$ with $y = 10\%$, with a capacity maintained at 200 mAh/g over 20 cycles which corresponds to 0.7Li/Mn. These cobalt substituted samples were made by ion-exchange from $NaMnO_2$ synthesized at 670°C; the Mn:O ratio in the starting material was not reported. The substitution of cobalt or iron for manganese in potassium manganese dioxides, K_xMnO_2 , caused a marked enhancement by two orders of magnitude of the conductivity of the manganese oxide [29,30], as shown in Fig. 8. The conductivity enhancement was independent of whether the sample was prepared under hydrothermal conditions at 170°C or by solid state synthesis at over 700°C. This conductivity enhancement may be the cause for the suppression of the Jahn–Teller distortion.

3.1. Tunnel structures

Manganese oxide forms several tunnel structures, as shown in Fig. 3; these have 2×2 ($BaMn_8O_{16}$ -hollandite, KMn_8O_{16} -cryptomelane, Mn_8O_{16} - α - MnO_2), 2×3 , and 3×3 (todorokite) tunnels.

One interesting tunnel structure is that commonly known as hollandite, with the unit formula $M_xMn_8O_{16} \cdot nH_2O$. This is the same 2×2 tunnel structure that is also taken up by α - MnO_2 . M is typically a large cation such as potassium or barium. These cations, however, inhibit the in-diffusion of lithium ions. Feng et al. [31] have succeeded in forming the hollandite structure with just protons and

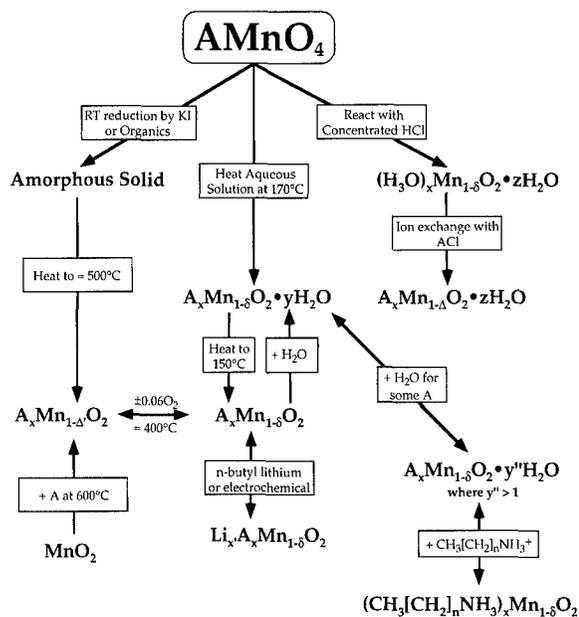


Fig. 7. Synthetic routes to A_xMnO_2 , from [9].

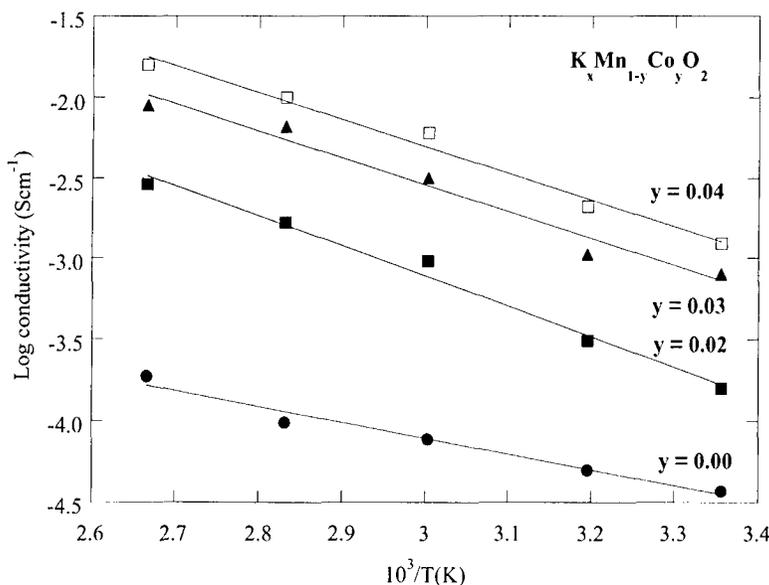


Fig. 8. Conductivity of cobalt doped layered manganese oxides, from [30].

water in the tunnel by the reaction between lithium permanganate and manganese (II) nitrate in strong, ≥ 8 M, sulfuric acid at 100°C . The structure is maintained after annealing at 300°C . In an electrochemical cell, 0.7 Li can be reversibly intercalated at 0.25 mA/cm² at an average potential of around 3 volts giving an capacity of 230 mAh/g to a cut-off of 2.0 volts; this decays to about 170 mAh/g for the 3rd to 10th cycles. This is much better stability than that observed in samples formed by sulfuric acid leaching of Li_2MnO_3 at 90°C [32]. This result on the 2×2 structure shows the inherent reversibility of manganese oxides when conversion to the spinel phase is inhibited.

The 3×3 todorokite structure of $\text{Mg}_{0.2}\text{MnO}_{1.9} \cdot 0.6\text{H}_2\text{O}$, has been shown by Nazar [33] to cycle around 0.5 Li/Mn at low current densities and cathodes containing 50% carbon. This is close to the theoretical capacity of 0.6 Li/Mn.

In addition, manganese oxide forms a complex tunnel structure with sodium, $\text{Na}_{0.44}\text{MnO}_2$, first reported by Parant et al. [27], which has the structure of $\text{Na}_4\text{Mn}_4\text{Ti}_5\text{O}_{18}$ [34]. Some recent work on this group of manganese oxides suggests that excellent cycling behavior can be obtained in manganese oxides. The tunnel compound, $\text{Na}_{0.44}\text{MnO}_2$, has been studied in sodium and lithium cells by Doeff et al.

[35,36] and shown to exhibit good reversibility. At 85°C in a polymer electrolyte cell $\text{Na}_{0.14}\text{MnO}_2$ attained 140 mAh/g. The coordination around the manganese changes somewhat as sodium is replaced by lithium [37]. In $\text{Na}_{0.44}\text{MnO}_2$ the manganese has square pyramidal coordination with the pyramidal Mn–O bond being somewhat long at 2.33 Å compared with the 1.73 and 1.86 in the basal plane, whereas in the exchanged and partially oxidized $\text{Li}_{0.27}\text{MnO}_2$ a sixth oxygen comes within bonding distance at 2.49 Å. Most recently, Armstrong et al. [38] have made the corresponding lithium compound by complete ion-exchange, $\text{Li}_{0.44}\text{MnO}_2$, and reported a capacity of 85 mAh/g without fade over 100 cycles when cycled between 3.6 and 2.8 volts. These results clearly show that manganese oxides can be stabilized against reversion to the spinel structure. However, a doubling of the capacity is needed for a viable system.

3.2. Disordered structures

Another option to avoid reversion to the spinel structure is to start with a disordered manganese oxide structure, akin to the aerogel vanadium oxides. Smyrl [39] and Manthiram [40] have begun studying such materials.

4. Conclusions

A range of pure and doped manganese oxides have been synthesized in an attempt to form the next generation cathode for high energy density lithium batteries. Some clues have been found to stabilize MnO_2 over a range of lithium content. These include pillaring of the lattice with larger cations such as potassium, doping the lattice with other transition elements such as Co or Fe, forming stable tunnel structures, and amorphous structures. Doping of the manganese lattice with elements to enhance its notoriously poor electrical conductivity appears promising but still needs studying in the tunnel and amorphous materials.

Acknowledgements

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