RAMSDELLITE-MnO₂ FOR LITHIUM BATTERIES: THE RAMSDELLITE TO SPINEL TRANSFORMATION

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Abstract—A pure and highly crystalline form of ramsdellite-MnO₂ has been synthesized by acid treatment of the spinels LiMn₂O₄ and Li₂Mn₃O₈ at 95°C. Although the ramsdellite-MnO₂ framework remains intact on lithiation at 70°C, the hexagonally-close-packed oxygen array buckles towards a cubic-close-packed structure to accommodate the inserted lithium ions. The reaction is reversible but the instability of the structure on cycling limits the utility of ramsdellite-MnO₂ as a rechargeable electrode in lithium cells. The ramsdellite structure can be stabilized by reaction with LiOH or LiNO₃ at 300–400°C; this reaction, which displaces manganese ions from the MnO₂ framework into interstitial octahedral sites, generates spinel-related domains that coexist with the lithiated ramsdellite phase. At 300°C, under vacuum, the lithiated ramsdellite phase Li₁ₓMnO₂ transforms to the spinel LiMn₂O₄; at 300–400°C, in air, it oxidizes slowly and transforms to a defect spinel LiMn₂O₄₋ₓ (0 < x < 0.5) via an intermediate compound. A mechanism for the ramsdellite-spinel transition is proposed.

Key words: ramsdellite, spinel, manganese dioxide, structure, lithium batteries.

INTRODUCTION

The advent of lithium battery technology has led to the investigation of many of the polymorphs of manganese dioxide as possible cathode materials for rechargeable cells. The materials include:
1. α-MnO₂ ( hollandite-type structure)[1-3];
2. γ-MnO₂ ( intergrowth of rutile- and ramsdellite-type structures)[4, 5];
3. δ-MnO₂ ( layered structures)[6, 7];
4. λ-MnO₂ ( spinel-type structure)[8-10].

The structural and electrochemical properties of these materials have been reported widely over several years; they have been made either in pure form or stabilized with lithium. Examples of the lithium-doped materials are the defect spinel Li₂Mn₄O₈ (Li₂O·4MnO₃)[11] and “CDMO” products that are synthesized typically by the reaction of LiOH (or LiNO₃) with γ-MnO₂ using a Li:Mn ratio of 3:7 at 370°C[12, 13].

The best known MnO₂ polymorph used by the battery industry is γ-MnO₂; it is synthesized either chemically (CMD) or electrolytically (EMD). In Zn/MnO₂ cells it has been demonstrated by neutron-diffraction that protons are inserted into the ramsdellite domains during discharge to form α-MnOOH (grotite)[14, 15]. On the other hand, proton insertion into the rutile-MnO₂ domains causes a transformation to a Mn(OH)₂ (pyrochroite) product which has a layered structure. It is believed that the structural incompatibility between grotite and pyrochroite limits the rechargeability of γ-MnO₂ electrodes in aqueous cells.

In Li/γ-MnO₂ cells it is generally acknowledged that discharge occurs predominantly by lithium insertion into the (2 x 1) channels of the ramsdellite domains. The β-MnO₂ domains can only accommodate 0.2 Li⁺ ions in the (1 x 1) channels[16]; at higher lithium loadings β-MnO₂ transforms to the [Mn₂O₄ spinel framework[17]. Therefore, because the β-MnO₂ domains in γ-MnO₂ structures appear to have a negative impact on the operation of both zinc and lithium cells, it seemed advantageous to prepare a pure ramsdellite phase to enhance the performance of these cells.

In this paper the synthesis and structural characterization of ramsdellite-MnO₂ (hereafter referred to as R-MnO₂, for convenience) and several lithiated derivatives are described. The electrochemical properties of R-MnO₂ have been evaluated in lithium cells. The results of these studies shed further light on the mechanisms by which Li/γ-MnO₂ cells operate.

EXPERIMENTAL

R-MnO₂ was prepared by reaction of the spinels LiMn₂O₄ and Li₂Mn₃O₈ in 2.5 M H₂SO₄ at 95°C for 24 h. The spinel precursors were synthesized by solid state reaction of Li₂CO₃ and MnCO₃ in air at 750 and 400°C. The resulting R-MnO₂ products were washed in water and dehydrated at 200°C prior to chemical and electrochemical lithiation.
Chemical lithiation of R-MnO$_2$ was achieved by two methods:

1. Li$_{0.3}$MnO$_2$, Li$_{0.4}$MnO$_2$ and Li$_{0.9}$MnO$_2$ were prepared by reacting R-MnO$_2$ with a solution of LiI in acetonitrile at 70°C for 5 h. A stoichiometric quantity of LiI dissolved in 25 ml of acetonitrile was used for the preparation of Li$_{0.3}$MnO$_2$ and Li$_{0.4}$MnO$_2$, whereas a three-times excess of LiI was used for Li$_{0.9}$MnO$_2$.

2. Two lithiated R-MnO$_2$ products were prepared by reaction of R-MnO$_2$ with LiNO$_3$ in a 7:3 molar ratio at 300 and 380°C. The reactions were carried out in air for 20 h.

The lithium and manganese contents in the individual samples were determined by atomic absorption analyses. X-ray diffraction data were collected on a Rigaku powder diffractometer with CuKα radiation, monochromated by a graphite crystal. Time-of-flight neutron diffraction data were collected on the Polaris diffractometer at the Rutherford Appleton Laboratory (U.K.). Structures of R-MnO$_2$ and lithiated products were refined either with X-ray data using the Wiles, Young and Saktivel profile refinement program DBW 3.2s as adapted by Schneider[18], or with neutron data using the programs of the Cambridge Crystallographic Subroutine Library (CCSL)[19] and software developed by David and Iberson[20]. Electrochemical data were collected from flooded electrolyte, prismatic cells. Lithium foil compacted onto nickel gauze was used for both the anode and reference electrodes. The cathode contained typically 25 mg of R-MnO$_2$ intimately mixed with 20% teflon acetylene black (TAB) compacted onto a nickel gauze disc, 1 cm in diameter. In the TAB mixture the ratio of teflon:acetylene black was 1:2. The electrolyte was a 1 M solution of LiClO$_4$ in propylene carbonate or propylene carbonate:dimethoxyethane (1: 1 volumetric ratio). Cells were discharged at 0.4 mA and charged at 0.2 mA. Open-circuit voltage readings were recorded at regular intervals allowing a 72 h equilibration time at each point. Cyclic voltammetry data were recorded from similar cells; a scan speed of 0.2 mV s$^{-1}$ was employed in these experiments.

RESULTS AND DISCUSSION

Structural characterization of Li$_x$MnO$_2$ (0 ≤ x ≤ 0.9)
The powder X-ray diffraction patterns of R-MnO$_2$ and three lithiated derivatives Li$_{0.3}$MnO$_2$, Li$_{0.4}$MnO$_2$ and Li$_{0.9}$MnO$_2$ obtained by reaction with LiI at 70°C are given in Fig. 1a-d. Lithiation results in single-phase Li$_x$MnO$_2$ products, the X-ray patterns of which could be indexed to an orthorhombic unit cell with the same symmetry as the parent R-MnO$_2$ (Pnam). The unit cell expands significantly on lithiation from 11.1% in Li$_{0.3}$MnO$_2$ to a massive 21.5% in Li$_{0.9}$MnO$_2$. The increase in cell volume is a result of large increases in the a and b lattice parameters; the c parameter is effectively unchanged by lithiation (Table 1). Atomic parameters of the various products are listed in Table 2.

The structure of R-MnO$_2$ was determined by profile refinement of neutron data (Fig. 2) and X-ray data (Fig. 3). The lattice parameters derived from these refinements (a = 9.372 Å, b = 4.471 Å, c = 2.851 Å) are in agreement with those reported for natural ramsdellite-MnO$_2$[21]. A [001] Fourier projection of the neutron data, clearly shows the positions of the Mn and O atoms (Fig. 4a). A difference Fourier projection (Fig. 4b) indicates some residual scattering at the Mn and O positions; there is no evidence of scattering from the interstitial octahedral sites in the (2 x 1) channels of the structure. It was therefore concluded that in this particular sample there was an insignificant concentration of β-MnO$_2$ (rutile) domains in the R-MnO$_2$ structure.

| Table 1. Lattice parameters of ramsdellite-related Li$_x$MnO$_2$ compounds (Space Group Pnam) |
|-------------------------------------|-------------------------------------|-------------------------------------|-------------------------------------|
| R-MnO$_2$                          | R-MnO$_2$                          | Li$_{0.3}$MnO$_2$                   | Li$_{0.4}$MnO$_2$                   |
| (neutron data)                     | (X-ray data)                       |                                    |                                    |
| a (Å)                              | 9.351 (1)                          | 9.372 (2)                          | 9.446 (5)                          |
| b (Å)                              | 4.449 (1)                          | 4.471 (1)                          | 4.932 (4)                          |
| c (Å)                              | 2.845 (1)                          | 2.851 (1)                          | 2.850 (1)                          |
| Unit cell volume (Å$^3$)            | 118.4 (1)                          | 119.5 (1)                          | 132.9 (2)                          |
| Volume expansion                   |                                    |                                    |                                    |
|                                    |                                    | 11.1%                               | 13.7%                              |
|                                    |                                    |                                    | 21.5%                              |
The structure of R-MnO₂ is shown in Fig. 5a. The structures of the lithiated products Li₀.₃MnO₂, Li₀.₉MnO₂ and Li₀.₉MnO₂ as determined by profile refinements of X-ray data are shown in Fig. 5b–d. These refinements demonstrate that at 70°C the R-MnO₂ framework remains intact over the whole compositional range of LiₓMnO₂ (0 ≤ x ≤ 0.9). Although it was not possible to determine accurately the positions of the Li⁺ ions in the structures from the X-ray data, a small amount of scattering was detected from the interstitial octahedral sites of the R-MnO₂ framework (Fig. 5b–d). Lithium insertion into the hexagonally-close-packed oxygen array of R-MnO₂ causes a shear of the (2 × 1) ramsdellite blocks and a buckling of the structure in response to an increase in electrostatic interactions between lithium and manganese ions in face-shared octahedra. The shear transforms the R-MnO₂ structure, in which the close-packed oxygen layers are initially parallel to the ac plane, to a lithiated structure in which the close-packing of the oxygens develops parallel to the bc plane. In Li₀.₉MnO₂ the layering adopts a sequence ABACABAC which is a combination of hexagonal-close-packing (ABA) and cubic-close-packing (BAC) (Fig. 5d).

The reaction of R-MnO₂ with LiNO₃ at 300 and 380°C

It is now well known that lithiated γ-MnO₂ products formed by the reaction of LiOH or LiNO₃ with CMD or EMD at 350–420°C offer superior cycling properties in rechargeable lithium cells compared to conventionally heat-treated CMD and EMD electrodes. The lithium-stabilized materials are
Fig. 3. The observed and calculated X-ray diffraction patterns of R-MnO₂.

now generally known as CDMO materials after Sanyo[12]. An optimum performance is obtained when CMD or EMD (sometimes pretreated with HNO₃ or H₂O₂) is reacted with LiNO₃ or LiOH in a 7:3 molar ratio at 370°C[22-25]. The nature of this product has been interpreted in several ways:

1. as a single-phase γ-related LiₓMnO₂ product in which x varies between 0.2 and 0.3[22];
2. as a composite electrode containing domains of a lithiated γ-MnO₂ phase and LiₓMnO₂[12, 13]; or
3. as an intergrown structure containing domains of a lithiated γ-MnO₂ phase and a spinel-related phase[26].

The nature of the X-ray patterns of these CDMO materials is critically dependent on properties of the precursor materials, for example, decomposition temperature, particle size and surface area, and on processing techniques and conditions such as mixing (eg hand mixing or ball-milling), oxygen partial pressure, reaction temperature and time of reaction. In an attempt to clarify the structural issues around the different interpretations, a study of the reaction of R-MnO₂ with LiNO₃ (Mn:Li = 7:3) at 300 and 380°C was undertaken. The preliminary results of this study have been reported elsewhere[26]. The X-ray diffraction patterns of the products are shown in Fig. 6a and b, together with a typical pattern of a product obtained from the reaction of CMD and LiNO₃ for comparison (Fig. 6c).

The product formed at 300°C consists predominantly of a lithiated R-MnO₂ phase (Fig. 6a). It is evident from the smaller shifts of certain peaks to lower 2θ values, for example, the [211], [221] and [420] reflections, that the extent of shear in this product is less than it is in single-phase LiₓMnO₂.
Fig. 5. The structures of: (a) R-MnO$_2$; (b) Li$_{0.5}$MnO$_2$; (c) Li$_{0.9}$MnO$_2$; and (d) Li$_{0.9}$MnO$_2$ as determined from powder X-ray diffraction data.

products (Fig. 1b–d). Although the [110] peak in Fig. 6a is still clearly resolved at 21°/20, there is substantial broadening of this peak. The broadening can be attributed to the reordering of the oxygen ions and the development of a close-packed oxygen array parallel to the bc planes; it marks the onset of the spinel [111] reflection at 19.2°/20 and manganese migration from octahedral sites in the parent R-MnO$_2$ structure to interstitial octahedral sites.

It is important to note that in R-MnO$_2$, as in all the chemically-lithiated products Li$_x$MnO$_2$ synthesized at 70°C (Fig. 5a–d), the manganese ions are distributed equally in adjacent layers between the oxygen planes that lie parallel to the bc plane. At 300–400°C lithiation induces a shear of the (2 x 1) ramsdellite blocks and a migration of the manganese ions that changes the manganese distribution from the 2:2 ratio in the adjacent layers towards the 3:1 ratio as required by the [MnO$_2$] framework of the Li[Mn$_x$]O$_2$ spinel structure. The 3:1 ratio is favored over the 4:0 ratio required by the layered rocksalt Li$_x$MnO$_2$ structure, because of the Li:Mn ratio (1:2.33) used in the starting mixture.

The X-ray pattern of the product formed at 380°C (Fig. 6b) is characteristic of intergrown domains consisting of:

(i) a small concentration of R-MnO$_2$ (probably containing a minor amount of lithium) as evident from the residual [110] peak at 22°/20;
(ii) a lithiated R-MnO$_2$ phase as evident from the [110] peak at 20.5°/20; and
(iii) a spinel phase within the system Li$_x$Mn$_{2-x}$O$_4$ (0 ≤ x ≤ 4/3, 0 ≤ z ≤ 1/3) as evident from the [111] peak at 19°/20.

At 380°C the cubic-close packing of the oxygen ions and the manganese layering in the spinel

Fig. 6. The powder X-ray diffraction patterns of: (a) the reaction product of R-MnO$_2$ and LiNO$_3$ (Mn:Li = 7:3) at 300°C; (b) at 380°C; and (c) the reaction product of CMD and LiOH at 370°C. Reflections from the orthorhombic ramsdellite phase are denoted R, those from a cubic spinel phase are denoted S.
domains is better established than it is at 300°C as indicated by the more dominant [111] and [400] peaks at 19°/2θ and 44.5°/2θ, respectively. The spinel phase could be indexed to a cubic unit cell with a lattice parameter of 8.15 Å, which is consistent with the values for other spinel phases within the Li₅Mn₅O₁₂ solid solution system[8]. The X-ray pattern of a product obtained from the reaction of CMD and LiOH at 370°C is shown in Fig. 6c for comparison; it clearly shows the presence of a lithiated γ-MnO₂ phase and a spinel phase. The absence of a strong [110] peak at 20.5°/2θ is significant; it demonstrates the absence of a lithiated-ramsdellite component in the structure. These data therefore suggest that lithiated γ-MnO₂ materials, for example, those derived from typical CMD and EMD products that contain a significant β-MnO₂ component, have a greater tendency to transform directly to the spinel phase.

The migration of manganese from the octahedral sites to interstitial octahedral sites is believed to be the key factor that stabilizes R-MnO₂ and γ-MnO₂ electrodes for rechargeable lithium cells; it is responsible for the creation of stable cubic-close-packed spinel-related domains that are intergrown with the lithiated-ramsdellite phase. These domains suppress the shearing process and the concomitant volume expansion/contraction of the unit cell that accompany lithium insertion/extraction reactions with unstabilized R-MnO₂ and γ-MnO₂ structures.

It has been reported that the typical stoichiometry of lithiated manganese oxide products obtained by reacting CMD (or EMD) with LiNO₃ (in a 7:3 molar ratio) at 370°C is Li₅Mn₅O₁₂ (Li₃ΣMnO₅)[24, 25]. The reaction demonstrates that, under specific processing conditions, the MnO₂ precursor is reduced to accommodate the inserted lithium. It is of particular interest to note that Li₅Mn₅O₁₂ products are not single-phase like Li₅Mn₅O₁₂ prepared at 70°C from R-MnO₂ and LiI (Fig. 1b) despite having the same composition; they have X-ray patterns similar to those of the lithiated MnO₂ products shown in Fig. 6a-c.

The ramsdellite-spinel transformation

When lithiated R-MnO₂ of composition Li₅Mn₅O₁₂ (Fig. 7a) is heated under vacuum at 300°C for 48 h a transition to a single-phase LiMn₂O₄ product (a = 8.250 Å) is observed (Fig. 7b). It is therefore evident that at 70°C there is insufficient energy to displace the manganese ions from the octahedral sites of the R-MnO₂ framework to interstitial sites, whereas the use of higher temperatures assists the diffusion of the manganese cations and the rearrangement of the oxygen ions to ideal cubic-close-packing.

A proposed mechanism for the R-MnO₂-spinel transformation is given in Fig. 8a-c. The driving force behind the transformation is the increase in electrostatic interactions between the inserted Li⁺ ions and the manganese ions that reside in neighbouring face-shared octahedra of the hexagonally-close-packed oxygen array. The transformation is described in two stages: The R-MnO₂ structure initially responds to the lithium–manganese interactions by the shear of (2 x 1) R-MnO₂ blocks in the directions shown in Fig. 8a to yield the R-MnO₂ framework in Li₅Mn₅O₁₂ (Fig. 8b); this is followed by a cooperative displacement of the manganese ions and a second shear to generate the spinel framework (Fig. 8c). In the transformation to spinel it is necessary to displace only one quarter of the manganese ions to achieve the ideal 3:1 layering of the manganese ions in the [Mn₃]O₄ spinel framework.

When Li₅Mn₅O₁₂ is heated in air it oxidizes slowly to form a Li₅Mn₅O₁₂, (0 < y ≤ 0.25) product with domains of varying composition and structure; the product ultimately transforms to a defect spinel of composition LiMn₂O₄,⁺⁺ (0 < δ ≤ 0.5). The transformation to a defect spinel in air is more sluggish than the transformation under vacuum to the stoichiometric spinel LiMn₂O₄. This is to be expected because oxygen must be incorporated into the LiMn₂O₄ structure during the transformation.

Figure 7c-e shows the X-ray diffraction patterns of the products formed by heating Li₅Mn₅O₁₂ in (i) at 300°C for 16 h (Fig. 7c); (ii) at 370°C for 6 h (Fig. 7d); and (iii) at 400°C for 60 h (Fig. 7e). Figure 7f shows the X-ray pattern of a typical LiMn₂O₄, product synthesised from the reaction of MnCO₃ and Li₂CO₃ at 400°C[11]. These X-ray patterns show that the transformation of Li₅Mn₅O₁₂ to the defect spinel LiMn₂O₄, occurs via an intermediate phase indicated, for example, in Fig. 7d by the
Fig. 8. The R-MnO$_2$ to spinel transformation. The manganese ions are located in shaded octahedra. (a) R-MnO$_2$, showing the directions of the initial shear on lithium insertion. (b) The R-MnO$_2$ framework at a composition Li$_{x}$MnO$_2$. Solid arrows indicate the direction of manganese ion displacement. Broken arrows indicate the direction of shear to generate the cubic close-packed oxygen array. (c) The [MnO$_4$]$_2$ framework of Li[Mn$_{1-x}$]O$_2$. Li$^+$ ions (〇) are located in tetrahedral sites in the interstitial space of the framework.

The open-circuit-voltage profile of a Li/R-MnO$_2$ cell is shown in Fig. 9. On closed circuit the R-MnO$_2$ electrode delivers a capacity of 220 mAh g$^{-1}$ to a 2 V limit, which is 71% of the theoretical capacity (308 mAh g$^{-1}$). The open-circuit voltage profile shows that discharge occurs in three distinct stages to a composition LiMnO$_2$ with interruptions in the profile at $x \approx 0.3$ and $x \approx 0.9$. In view of the structural information given above, the first two stages can be attributed to the following processes:

1. $0 \leq x \leq 0.3$: Insertion of lithium into an essentially hexagonally-close-packed R-MnO$_2$ structure. This finding is consistent with X-ray data reported by Ohzuku et al. for heat-treated EMD samples that show the onset of structural changes in Li$_x$MnO$_2$ samples at $x \approx 0.3$ [4, 5].

The spinel-ramsdellite transition is reversible but higher temperatures and long reaction times are required to allow the reaction to go to completion in the reverse direction. The reversibility of this system is consistent with reports that spinel structures in the Li$_x$Mn$_{1-z}$O$_2$ system ($0 \leq x \leq 4/3$, $0 \leq z \leq 1/3$) are favoured over other structure types when synthesized in the temperature range 300-400°C, particularly when the Li:Mn ratio falls within the range 1:1.2 to 1:2.0 [26].
2.0.3 \leq x \leq 0.9$: Insertion of lithium into an R-MnO₂ framework structure in which the packing of the oxygens is essentially ABACABAC.

The process at the end of discharge (0.9 \leq x \leq 1.0) is not yet clearly understood; it can possibly be attributed to lithium insertion into an R-MnO₂ framework structure in which the packing is ABCABC. In this event the end product is a rocksalt phase LiMnO₂ in which the close-packed oxygen array is distorted from ideal cubic-close-packing by the Jahn–Teller Mn³⁺ (d⁴) ions.

Preliminary investigations of the rechargeability of room temperature Li/R-MnO₂ cells indicate that the R-MnO₂ electrode does not cycle well on deep discharge (Fig. 10). The capacity drops from an initial 230 mAh g⁻¹ to 160 mAh g⁻¹ on the second discharge; thereafter the capacity declines steadily to reach a value of 115 mAh g⁻¹ after 10 cycles. The capacity loss can be attributed to the large expansion and contraction of the unit cell on deep discharge and recharge, and to concomitant structural modifications that occur on cycling lithium between an essentially hexagonally-close-packed structure and one which has cubic-close-packed character. If the cycling regime is controlled to allow the electrode to operate only on the second plateau (0.3 \leq x \leq 0.9) an improved capacity retention can be expected; such an electrode has a theoretical capacity of 181 mAh g⁻¹. This observation is in good agreement with the performance of EMD electrodes heated at 250°C which, after an initial discharge capacity of 220 mAh g⁻¹, deliver steady capacities of 150 mAh g⁻¹ when cells are cycled between 3.8 and 2.0 V at low current rates (0.17 mA cm⁻²) [5].

The significant decrease in the reduction peak on the second cycle of a cyclic voltammogram confirms the capacity loss observed in the Li/R-MnO₂ cell (Fig. 11). On the anodic scan, the voltammogram shows a two-stage process for lithium extraction that corresponds to the first two reduction processes observed on the OCV vs. composition plot in Fig. 9. The first anodic peak at 3.6 V is therefore attributed to the removal of lithium from the intergrown hexagonal/cubic-close-packed anion array (ABACABAC); the second anodic peak at 4.1 V is attributed to the further removal of Li⁺ ions from the structure and a concomitant shear to regenerate the original hexagonally-close-packed structure.

CONCLUSIONS

Lithiation of R-MnO₂ has been demonstrated by chemical and electrochemical methods. The stability of R-MnO₂ electrodes and rechargeability of Li/R-MnO₂ cells (and by inference Li/γ-MnO₂ cells) are dependent on a Li₂MnO₃ structure with domains that are characterized by an oxygen array with cubic-close packed character. When R-MnO₂ is stabilized by reaction with a lithium salt (Mn:Li = 7:3) at 300–400°C, the displacement of manganese ions from the octahedral sites of the R-MnO₂ framework into interstitial octahedral sites provides cubic-close packed domains with spinel character that coexist with domains of a lithiated ramsdellite phase; the concentration of the spinel domains in the intergrown structure increases as the reaction temperature is raised.

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Ramsdellite-MuO$_4$ for lithium batteries