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by

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ABSTRACT

The structural stability of LiMn_2O_4 , which is of interest as an insertion electrode for rechargeable lithium batteries, is discussed with respect to processing techniques, composition, the Li-Mn-O phase diagram, and electrochemical behavior. Particular attention is paid to processing conditions that result in the formation of lithium-manganese-oxide spinel products in which Mn^{2+} ions partially occupy the tetrahedral sites of the spinel structure. The electrochemical behavior of electron-beam and rf-magnetron sputtered thin-film electrodes suggests the existence of partially inverse $\text{Li}_{1-x}\text{Mn}_2\text{O}_4$ spinel structures during an initial charge to 5.3 V.

INTRODUCTION

Lithium-ion cells that operate between 3 and 4 V are gaining increasing popularity for powering electronic equipment such as cellular phones, camcorders, and laptop computers^[1]. Commercial cells currently contain a carbon anode, a liquid electrolyte consisting of a lithium salt dissolved in an organic solvent, and a LiCoO_2 cathode. Because of the relatively high cost of cobalt, considerable effort is being made to develop other suitable cathode materials. The spinel $\text{Li}[\text{Mn}_2]\text{O}_4$ provides an attractive alternative because it is a low-cost, environmentally acceptable material^[2-5]. Unfortunately, a wide range of solid solution exists in the Li-Mn-O spinel system, which makes it difficult to fabricate an electrode with an exact, predetermined composition^[6-8]. When the electrode has the ideal, *normal*

spinel distribution of cations, $\text{Li}[\text{Mn}_2]\text{O}_4$, the lithium ions occupy the tetrahedral sites (8a) of the spinel structure (space group $\text{Fd}\bar{3}\text{m}$), and the manganese ions, the octahedral sites (16d). A Li/liquid electrolyte/ $\text{Li}_x[\text{Mn}_2]\text{O}_4$ cell operates at approximately 4 V over the range $0 < x \leq 1$, and at approximately 3 V over the range $1 \leq x \leq 2$. Over the 4 V range, lithium ions occupy the 8a tetrahedral sites, and over the 3 V range, predominantly the 16c octahedral sites. The 1 V drop reflects the difference in energy between the spinel-related phase, $\text{Li}_{1-x}\text{Mn}_2\text{O}_4$, and the rock-salt-related phase, $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$.

It has recently been reported that all-solid-state lithium/lithium-phosphorus-oxynitride (Lipon)/ LiMn_2O_4 cells, in which the LiMn_2O_4 electrode is fabricated in thin-film form by electron-beam (e-beam) evaporation or rf-magnetron sputtering, can deliver an appreciable amount of capacity above 4 V^[9,10]. On charge, these cells show a voltage plateau at 5 V, in addition to the expected voltage plateau at 4 V. In some instances, a voltage plateau at 4.6 V is observed during the initial charge to 5.3 V. The upper stability limit of the Lipon solid electrolyte is ≥ 5.5 V.

Because a wide range of solid solution exists within the Li-Mn-O family of spinel compounds, and because the composition of the spinel electrode plays a pivotal role in controlling the rechargeability of the electrode, careful process control is essential when synthesizing these electrodes at elevated temperatures. In this paper, the structural stability of LiMn_2O_4 is discussed in relation to processing techniques, reaction temperature, and electrochemical performance. An attempt has been made to interpret the electrochemical behavior of thin-film LiMn_2O_4 electrodes in terms of the cation distribution in electrode structures prepared by e-beam evaporation and rf-magnetron sputtering.

EXPERIMENTAL

LiMn_2O_4 was synthesized by reaction of thoroughly blended powders of LiOH and chemically prepared manganese dioxide (CMD) at 750°C . X-ray data were collected on a Siemens D-5000 diffractometer with graphite monochromated $\text{CuK}\alpha$ radiation. High-temperature X-ray diffraction patterns of samples were collected on a Pt/Rh heating strip, in air, with a Buhler HDK S1 high-temperature attachment. Samples were heated at 20°C intervals and held at each temperature for 15 minutes prior to data collection. X-ray diffraction patterns were recorded at a scan rate of $1.44^\circ\text{C}/\text{min}$ between 15 and $80^\circ 2\theta$. Lattice constants were determined by least-squares refinement of the peak positions in the powder X-ray diffraction patterns.

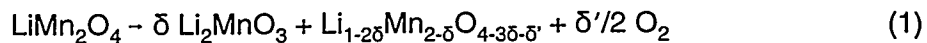
The electrochemical data were obtained from thin-film LiMn_2O_4 samples prepared by e-beam evaporation and rf-magnetron sputtering. These data were provided by Dr. John Bates of Oak Ridge National Laboratory. Detailed descriptions of electrode preparation, cell fabrication, and cell testing have been given elsewhere ^[9,10].

RESULTS AND DISCUSSION

Thermal stability of LiMn_2O_4

The X-ray diffraction (XRD) patterns of a heated LiMn_2O_4 sample show that several phase changes occur between room temperature and 1200°C (Fig. 1). These results are consistent with previously reported thermogravimetric analysis (TGA) data and differential thermal analysis (DTA) data, which show the onset of distinct processes at approximately 780 , 915 , and 1060°C ^[5,11]. These combined data provide evidence of the following reaction sequence:

(1) 780-915°C (surface reaction)



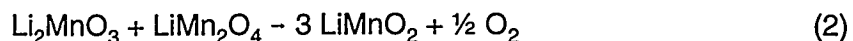
During this reaction, oxygen is lost from LiMn_2O_4 and lithium diffuses to the particle surface, resulting in a disproportionation of LiMn_2O_4 into a tetragonal spinel phase, $\text{Li}_{1-2\delta}\text{Mn}_{2-\delta}\text{O}_{4-3\delta-\delta'}$ and a stable rock-salt phase, Li_2MnO_3 . The tetragonal phase, in which the manganese oxidation state is less than 3.5, manifests itself in the XRD pattern at 840°C by the splitting of the [311] peak of the cubic LiMn_2O_4 phase into the [311] and [113] peaks of the tetragonal phase (Fig. 1). The extent of the tetragonal (Jahn-Teller) distortion depends on the amount of oxygen lost from the sample and on the concentration of Mn^{3+} (d^4) cations on the octahedral sites of the spinel structure [6]; at 840°C, the c/a ratio of the tetragonal phase is 1.02, indicative of only a small deviation from ideal cubic symmetry ($c/a=1.00$).

Note that in reaction (1), no Li_2O is lost from the sample because it is contained by the Li_2MnO_3 phase on the particle surface. Note also that the tetragonal phase need not be an oxygen-deficient spinel phase, $\text{LiMn}_2\text{O}_{4-\delta}$, as reported by Tarascon [4] and Yamada [5]; it could, in principle, be a stoichiometric spinel phase that lies on the tie-line between LiMn_2O_4 and Mn_3O_4 in the Li-Mn-O phase diagram, designated $\text{Li}_{1-\delta}\text{Mn}_{2-\delta}\text{O}_{4-4/3\delta}$ in Fig. 2.

(2) ≥915°C

Previously reported TGA and DTA data have shown the onset of a reversible phase transition at 915°C [11], which is accompanied by a rapid loss of oxygen. The XRD data in Fig. 1 indicate that this phase transition can be attributed to the formation of an LiMnO_2 phase; it is formed at the expense of the Li_2MnO_3 rock-salt phase, which reacts with

some of the tetragonal spinel phase. In an ideal simplified case, the reaction between the rock-salt phase and the spinel phase can be represented by

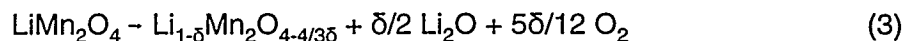


The LiMnO_2 phase exists to approximately 1120°C , after which it recombines with the residual spinel phase to yield a single- phase (spinel) product.

(3) 1060°C

The transition that was observed at 1060°C for previously reported DTA and TGA data has been attributed to a reversible transition of a tetragonal spinel phase to cubic symmetry^[11]. This transition was confirmed by the powder XRD pattern of the sample after rapid cooling to room temperature. At 1200°C , the pattern could be indexed to a cubic unit cell with $a = 8.61(1)\text{\AA}$ (Fig. 1), whereas after cooling the compound had tetragonal symmetry, with $c/a = 1.12$ (Fig. 3). This behavior is similar to that observed with Mn_3O_4 , which transforms from tetragonal ($c/a = 1.16$ at room temperature) to cubic symmetry ($c/a = 1.00$) at 1160°C ^[12]. The c/a ratios of various spinel-related phases, such as $\text{Li}_2\text{Mn}_2\text{O}_4$ ($c/a = 1.16$)^[13], Mn_3O_4 ($c/a = 1.16$)^[13], $\text{Li}_5\text{Mn}_4\text{O}_9$ ($c/a = 1.14$)^[6], and $\text{Li}_7\text{Mn}_5\text{O}_{12}$ ($c/a = 1.11$)^[6], were compared with the concentration of Mn^{3+} ions on the octahedral sites. This comparison indicated that a c/a ratio of 1.12 corresponds to the composition $(\text{Li}_{0.6}\text{Mn}_{0.4})_{\text{tet}}[\text{Mn}_2]_{\text{oct}}\text{O}_4$. Because Mn^{2+} ions have a stronger preference than Mn^{3+} and Mn^{4+} for tetrahedral sites, it is believed that the valence distribution of the cations in $\text{Li}_{0.6}\text{Mn}_{2.4}\text{O}_4$ is $(\text{Li}_{0.6}^{1+}\text{Mn}_{0.4}^{2+})_{\text{tet}}[\text{Mn}_2^{4+/3+}]_{\text{oct}}\text{O}_4$, with the manganese ions on the $[\text{Mn}_2]\text{O}_4$ subarray having an average oxidation state of 3.3.

The transition of LiMn_2O_4 from cubic to tetragonal symmetry requires the loss of both lithium and oxygen. If the final product is assumed to be a spinel that falls on the LiMn_2O_4 - Mn_3O_4 tie line (Fig. 2), the overall reaction at 1200°C is given by



At elevated temperatures, manganese ions replace Li^+ ions on the tetrahedral sites of the spinel structure; if all the lithium were replaced, the product would be Mn_3O_4 at $\delta = 1$. These high temperature data, therefore, provide evidence of lithium-manganese-oxide spinels with Mn^{2+} , Mn^{3+} , and Mn^{4+} cations within a single close-packed oxygen array.

LiMn_2O_4 electrodes deposited by e-beam evaporation or rf-magnetron sputtering

The LiMn_2O_4 electrodes that were deposited by e-beam evaporation or rf-magnetron sputtering had electrochemical charge/discharge profiles that were significantly different from profiles that are normally observed with powder LiMn_2O_4 samples in liquid electrolyte cells (Fig. 4(a-d)) [9,10]. A typical voltage profile for a Li/liquid electrolyte/ LiMn_2O_4 cell is given in Fig. 4a; it shows a two-step reaction at approximately 4 V, which is associated with the insertion of lithium into tetrahedral sites of the spinel structure, and a voltage plateau at approximately 3 V, which is associated with the insertion of lithium into octahedral sites. By contrast, the voltage profiles obtained from three separate Li/lipon/ LiMn_2O_4 cells (Fig. 4(b-d)) show processes that occur between 2.2 V and 5 V [10].

Figures 4(b-d) show that Li/lipon/ LiMn_2O_4 cells deliver approximately one-half of their capacity below 3 V. These data are consistent with a spinel-electrode composition LiMn_2O_4 . Moreover, the XRD patterns of e-beam and rf-sputtered LiMn_2O_4 electrodes are, in general,

characteristic of a cubic, single phase spinel product with a lattice parameter $8.16 \text{ \AA} \leq a \leq 8.20 \text{ \AA}^{[10]}$, which is slightly smaller than that of the stoichiometric “normal” spinel $\text{Li}[\text{Mn}_2]\text{O}_4$ (8.24 \AA)^[13]. The voltage drop between 2.8 V and 2.1 V that is observed in Figs. 4(b-d) can be attributed to a polarization effect; it is associated with the diffusion of lithium across the interface that separates the tetragonal $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$ spinel phase on the surface of the film from the unreacted, cubic LiMn_2O_4 phase below the surface. The voltage of the cell on open circuit relaxes to the expected 3 V for the two-phase electrode, as shown in Fig. 4b.

Of particular interest to this study are the voltage profiles of the charge and discharge processes that occur above 3 V. These profiles can vary significantly from one electrode to another; they indicate that the cations in thin-film LiMn_2O_4 electrodes are distributed in arrangements that differ from the “normal” distribution of cations in $\text{Li}[\text{Mn}_2]\text{O}_4$. If some manganese ions are permitted to occupy either the tetrahedral 8a or interstitial 16c sites of the spinel, then, in principle, it would be possible for stoichiometric LiMn_2O_4 to adopt the following configurations:



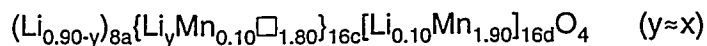
This configuration has a partial inversion of the spinel structure, in which Mn^{2+} ions occupy the tetrahedral sites. Note that the end member (at $x = 0.5$) has the formulation $(\text{Li}_{0.5}\text{Mn}_{0.5}^{2+})_{8a}[\text{Li}_{0.5}\text{Mn}_{1.5}^{4+}]_{16d}\text{O}_4$, in which the manganese ions on the octahedral sites are all tetravalent.

Model II: $(\text{Li}_{1-x-y})_{8a}\{\text{Mn}_x\text{Li}_y\Box_{2-x}\}_{16c}[\text{Li}_x\text{Mn}_{2-x}]_{16d}\text{O}_4$ ($0 < x \leq 0.5$, $0 \leq y \leq x$)

In this configuration, a fraction of the manganese ions partially occupy the interstitial octahedral 16c sites of the spinel structure (\Box refers to a vacancy). All the manganese ions reside in edge-shared MnO_6 octahedra, as they do in $\text{Li}[\text{Mn}_2]\text{O}_4$; they are of mixed $\text{Mn}^{4+/3+}$ valence. The presence of Mn in the 16c sites destabilizes the tetrahedral 8a sites. Although the simultaneous occupation of the 8a tetrahedra and 16c octahedra (which share faces with one another) by lithium and manganese may seem unlikely and energetically unfavorable, neutron diffraction data indicate that in the lithiated spinel $\text{Li}_2[\text{Mn}_2]\text{O}_4$, the lithium ions are distributed over both sets of sites [14]. It is, therefore, postulated that metastable Model II-type compounds occur with some Mn on the 16c sites, particularly when the compounds are fabricated under uncontrolled sputtering conditions. With such an arrangement of cations, a small fraction of lithium ions on the tetrahedral sites is expected to be displaced into neighboring octahedral sites to minimize Li-Mn electrostatic interactions.

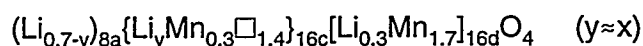
No satisfactory explanation for the electrochemical behavior of LiMn_2O_4 electrodes in Figs. 4(b-d) could be found solely in terms of Model I-type structures. On the other hand, Model II- type structures do offer a possible explanation. In the interpretation of the voltage profiles in Figs. 4(b-d) that follows, the relative amounts of lithium that were inserted into, or extracted from, the LiMn_2O_4 structures were determined from the capacities delivered over selected compositional ranges.

For example, the voltage profile in Fig. 4c can be interpreted in terms of a cation distribution in which $x = 0.1$:



During the initial charge to 5.3 V, 0.8 Li⁺ ions are removed from the tetrahedral sites over the voltage range 3.9 to 4.2 V. The Mn³⁺ ions on the 16c-16d subarray of the spinel structure are oxidized to Mn⁴⁺ and are not displaced during the extraction of lithium. The small inflection on the electrochemical curve when one-half of the lithium has been extracted from the tetrahedral sites is consistent with an ordering process on the 8a tetrahedra, also observed in Li_{1-x}[Mn₂]O₄ at x ≈ 0.5 [2]. The remaining 0.2 Li⁺ ions are extracted at 5 V from octahedral sites; this is consistent with the voltage that was necessary to extract lithium from the octahedral sites of the spinel V[LiNi]O₄ [15]. With this interpretation, the final MnO₂ product in Fig. 4a would have the cation distribution {Mn_{0.1}□_{1.9}}_{16c}[Mn_{1.9}□_{0.1}]_{16d}O₄.

Figure 4b can be interpreted in terms of a Model II configuration with x = 0.3, i.e., with the cation distribution:



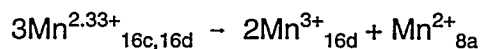
The single phase reaction process that occurs on charge between 3.9 and 4.3 V can be attributed to the extraction of 0.4 Li⁺ ions from the tetrahedral 8a sites. The remaining lithium ions are extracted from the 16c and 16d octahedral sites at 5 V. The relatively flat voltage profile at 5V indicates that extraction of lithium from the crystallographically independent 16c and 16d sites cannot be readily distinguished during the first charge, consistent with Fig. 4c. If the Mn₂O₄ subarray remains intact during lithium extraction, then the resulting MnO₂ defect rock-salt phase would have the cation distribution {Mn_{0.3}□_{1.7}}_{16c}[Mn_{1.7}□_{0.3}]_{16d}O₄ at the top of charge. The subsequent discharge from 5.3 to 3.9 V indicates a two-stage reaction

during which lithium is believed, first, to occupy octahedral sites (predominantly the 16d sites) and thereafter to partially fill the 8a tetrahedral sites.

The initial charge to 5.3 V in Fig. 4d shows, unlike Figs. 4b and 4c, a two-phase reaction at 4.6 V. It is proposed that the presence of the 4.6 V plateau arises from a Model II-type structure, and that a critically high concentration of Mn^{3+} occurs on the 16c sites, at least in some **localized** regions (clusters) of the thin-film electrode (which could affect the crystal symmetry of localized regions*). It is proposed that the high concentration of Mn^{3+} ions on the octahedral 16c sites could nucleate the following disproportionation (internal redox) reaction at 4.6 V:

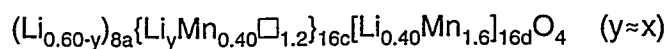


during which Mn^{2+} ions migrate into tetrahedral 8a sites to generate a partially inverse defect spinel structure. (It is possible that some tetrahedral Mn^{2+} ions may act as nucleating agents for the disproportionation reaction.) This is analogous to the situation that occurs when lithium is extracted from lithiated hausmannite $(\text{LiMn})_{16c}[\text{Mn}_2]_{16d}\text{O}_4$ [13] to generate the spinel phase, hausmannite, $\text{Mn}[\text{Mn}_2]\text{O}_4$:



With this hypothesis, the voltage profile in Fig. 4d could be interpreted in terms of a Model II-type LiMn_2O_4 electrode:

* Indeed, some e-beam and sputtered LiMn_2O_4 samples that show the 4.6 V plateau give X-ray diffraction patterns with split [111] and [311] reflections, indicating either a phase with reduced symmetry or possibly two cubic phases.



in which $x_{\text{average}} \approx 0.4$, but with x_{max} probably >0.4 in some localized regions of the structure to nucleate the disproportionation reaction.

In Fig. 4d, from 3.9 to 4.6 V, 0.2 Li^+ ions are initially removed from the tetrahedral 8a sites, with a concomitant oxidation of Mn^{3+} to Mn^{4+} on the 16c and 16d sites. At the composition $\text{Li}_{0.8}\text{Mn}_2\text{O}_4$, the average manganese oxidation state is 3.6. Further removal of lithium from the structure at 4.6 V is associated with the onset of the disproportionation reaction, which generates the partially inverse defect spinel phase $(\text{Li}_{0.40}\text{Mn}_{0.40}\square_{0.2})_{8a}[\text{Li}_{0.40}\text{Mn}_{1.60}]_{16d}\text{O}_4$. In this $\text{Li}_{0.8}\text{Mn}_2\text{O}_4$ spinel phase all the manganese ions on the tetrahedral sites are divalent, and all the manganese ions on the octahedral sites are tetravalent. Further extraction of lithium from the defect spinel phase necessitates the oxidation of the Mn^{2+} ions on the tetrahedral sites. This process causes a cooperative displacement of the tetrahedrally coordinated manganese ions back into the 16c sites of the 16c-16d subarray because of the strong octahedral-site preference of the Mn^{3+} ion. The result is a two-phase electrode consisting of the defect spinel phase and a defect rock-salt phase. It is evident from Fig. 4d that the two-phase region is associated with the removal of 0.4 Li^+ ions from the structure; in this case, the end members of the two-phase region would be $(\text{Li}_{0.40}\text{Mn}_{0.40}\square_{0.2})_{8a}[\text{Li}_{0.40}\text{Mn}_{1.60}]_{16d}\text{O}_4$ (defect spinel) and $\{\text{Mn}_{0.4}\text{Li}_{0.4}\square_{1.6}\}_{16c}[\text{Li}_{0.4}\text{Mn}_{1.6}\square_{0.4}]_{16d}\text{O}_4$ (defect rock-salt). Extraction of the remaining 0.4 Li^+ ions from the octahedral sites takes place at 5 V, consistent with the interpretation given for Figs. 4b and 4c. With this interpretation, the MnO_2 defect rock-salt phase that is formed at the top of charge would have the distribution $\{\text{Mn}_{0.4}\square_{1.6}\}_{16c}[\square_{0.40}\text{Mn}_{1.60}]_{16d}\text{O}_4$.

Of particular significance is the profile of the subsequent discharge from 5.3 V to 2.8 V in Fig. 4d. The two-phase region observed at 4.6 V on charge does not occur on discharge; this finding indicates that lithium insertion does not regenerate the partially inverse spinel structure. Instead, the shape of the discharge profile is consistent with lithium insertion into a defect rock-salt MnO_2 phase; the reaction takes place in three discrete single-phase processes, associated with the lithium occupation of (i) octahedral sites (predominantly 16d) between 5.0 and 4.2 V, (ii) 8a tetrahedral sites between 4.2 and 3.9 V, and (iii) octahedral sites (predominantly 16c) between 3.9 and 2.9 V. Further insertion of lithium reduces the manganese ions below an average oxidation state of 3.5. The onset of a Jahn Teller effect results in a two-phase electrode consisting of a cubic LiMn_2O_4 phase and a tetragonal $\text{Li}_2\text{Mn}_2\text{O}_4$ phase. Assuming that the $[\text{Li}_{0.4}\text{Mn}_{1.6}]\text{O}_4$ spinel framework remains intact during lithium insertion and extraction, the tetragonal phase would have the cation distribution $\{\text{Mn}_{0.4}\text{Li}_{1.6}\}_{16\text{c}}[\text{Li}_{0.4}\text{Mn}_{1.6}]_{16\text{d}}\text{O}_4$. On the second charge to 5.3 V (curve 4 in Fig. 4d), the voltage profile does not show the onset of a two-phase reaction at 4.6 V, but rather has a shape which is closer to that of the previous discharge. Such behavior is expected if the manganese ions outside the $[\text{Li}_{0.4}\text{Mn}_{1.6}]\text{O}_4$ framework in the initial structure become randomly distributed over the 16c octahedral sites of the spinel structure during the first charge on the 4.6 V plateau, when the manganese ions move from their initial localized 16c positions to 8a sites and then back to 16c sites. On the second charge, therefore, no nucleation centers (regions of high manganese concentration) are left to aid the disproportionation reaction, so the electrode adopts a predominant defect rock-salt structure in which the manganese ions remain fixed in their octahedral sites. Note that in this model of LiMn_2O_4 , the Mn ions occupy only 20% of the available 16c sites, and that there exists an energetically favorable 16c-8a pathway for Mn diffusion during lithium extraction from the structure. By contrast, the concentration of Mn on the 16d sites is too high for these ions to

move into neighboring, energetically unfavorable, tetrahedral (8b) sites; this is a factor that contributes to the well-known stability of the $[\text{Mn}_{2-x}\text{Li}_x]_{16d}\text{O}_4$ spinel framework to lithium insertion and extraction reactions [6,13].

In conclusion, the results suggest the existence of partially inverse $\text{Li}_{1-x}\text{Mn}_2\text{O}_4$ spinel structures during an initial charge to 5.3 V of thin-film LiMn_2O_4 electrodes prepared by e-beam evaporation and rf-magnetron sputtering. It is worthwhile to point out that an electrochemical process at ~4.5 V has also been detected, to a very minor degree, in Li-Mn-O spinel electrodes prepared by conventional solid state reactions. Thus, even in powder electrodes, a deviation from the ideal *normal spinel* distribution of cations in $\text{Li}[\text{Mn}_2]\text{O}_4$ is possible [4,16]. Moreover, recent analyses of the X-ray diffraction patterns of LiMn_2O_4 powders (preparation temperature = 750°C) have shown insignificant scattering from manganese ions on the tetrahedral sites [16], consistent with a Model II-type structure. Nevertheless, further work is required to test the interpretation provided in this paper and to gain a greater understanding of the reaction processes occurring in high-voltage (>4 V) LiMn_2O_4 electrodes.

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Captions to Figures

- Fig. 1. X-ray diffraction patterns of LiMn_2O_4 recorded *in situ*, from room temperature (RT) to 1200°C . Characteristic peaks of Li_2MnO_3 (*) and LiMnO_2 (●) are indicated at 920°C and 1200°C , respectively.
- Fig. 2. A section of the Li-Mn-O phase diagram.
- Fig. 3. The X-ray diffraction pattern of tetragonal $\text{Li}_{0.6}\text{Mn}_{2.4}\text{O}_4$. The calculated pattern of Mn_3O_4 is given below for comparison.
- Fig. 4. Electrochemical charge/discharge profiles of a) a standard $\text{Li}/\text{LiMn}_2\text{O}_4$ liquid electrolyte cell ($i=0.2\text{ mA}$), and (b-d) three $\text{Li}/\text{lipon}/\text{LiMn}_2\text{O}_4$ cells ($i=0.2\text{ }\mu\text{A}$): b,c) e-beam evaporated LiMn_2O_4 and d) rf-magnetron sputtered LiMn_2O_4 . Small circles in (b) are open circuit voltage readings [10]. Numbers in (b) and (d) indicate the sequence of the charge/discharge processes.

