

## Structural Fatigue in Spinel Electrodes in High Voltage (4 V) Li/Li<sub>x</sub>Mn<sub>2</sub>O<sub>4</sub> Cells

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Evidence of structural fatigue has been detected at the surface of discharged Li<sub>x</sub>[Mn<sub>2</sub>]O<sub>4</sub> spinel electrodes in (4 V) Li/Li<sub>x</sub>[Mn<sub>2</sub>]O<sub>4</sub> cells. Under nonequilibrium conditions, domains of tetragonal Li<sub>2</sub>[Mn<sub>2</sub>]O<sub>4</sub> coexist with cubic Li[Mn<sub>2</sub>]O<sub>4</sub>, even at 500 mV above the thermodynamic voltage expected for the onset of the tetragonal phase. The presence of Li<sub>2</sub>[Mn<sub>2</sub>]O<sub>4</sub> on the particle surface may contribute to some of the capacity fade observed during cycling of Li/Li<sub>x</sub>[Mn<sub>2</sub>]O<sub>4</sub> cells.

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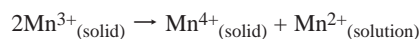
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The exponential growth in the electronics industry has led to an increasing demand for lightweight power sources with high energy density and power capability.<sup>1,2</sup> This demand has been satisfied largely by the advent of rechargeable lithium-ion batteries. The best-known system is Li<sub>x</sub>C/LiCoO<sub>2</sub>. Because of the relatively high cost of cobalt, a major international effort is underway to develop alternative positive electrodes, for example, those derived from the spinel Li[Mn<sub>2</sub>]O<sub>4</sub>.<sup>3-5</sup> A disadvantage of Li[Mn<sub>2</sub>]O<sub>4</sub> spinel electrodes is that they lose capacity during cycling, which limits the life of the cell.<sup>5-11</sup> The capacity loss is particularly noticeable at 50°C, a typical temperature that can be reached in devices such as laptop computers. Recent reports have attributed the capacity fade to an unstable electrode surface and to solubility effects at the top of charge.<sup>6-11</sup>

It is well known that the cycle life of lithium-ion cells depends critically on the structural integrity of the host electrode structures during charge and discharge.<sup>12</sup> In the Li<sub>x</sub>[Mn<sub>2</sub>]O<sub>4</sub> spinel system (0 < x < 2), the [Mn<sub>2</sub>]O<sub>4</sub> spinel framework provides a three-dimensional interstitial space for lithium-ion transport. Lithium extraction from Li<sub>x</sub>[Mn<sub>2</sub>]O<sub>4</sub> (i.e., for 0 < x < 1) occurs at 4 V vs. metallic lithium. The electrode cycles well over this range because the cubic structure (space group *Fd3m*) expands and contracts isotropically during lithium insertion and extraction.<sup>3-5,12</sup> For 1 < x < 2, lithium is inserted electrochemically into the spinel structure in a two-phase reaction process at a constant voltage; the open-circuit voltage for this reaction is 2.96 V.<sup>13</sup> This two-phase reaction is associated with the onset of an anisotropic (Jahn-Teller) distortion. As a result, the cubic symmetry of Li[Mn<sub>2</sub>]O<sub>4</sub>, in which the lithium ions occupy tetrahedral sites, is reduced to tetragonal Li<sub>2</sub>[Mn<sub>2</sub>]O<sub>4</sub> (space group *F4<sub>1</sub>/ddm*), in which the lithium ions occupy octahedral sites in an ordered rock-salt structure.<sup>13-15</sup> This crystallographic distortion, which results in a 16% increase in the *c/a* ratio of the unit cell parameters, is too severe for the electrode to maintain its structural integrity during cycling. Consequently, a Li<sub>x</sub>[Mn<sub>2</sub>]O<sub>4</sub> spinel electrode cycles poorly over the range 1 < x < 2, and the cell suffers a capacity loss. It is, therefore, understandable from a structural viewpoint that for good cycle life, the composition of the Li<sub>x</sub>[Mn<sub>2</sub>]O<sub>4</sub> spinel electrode must be kept within the limits of the cubic structure (i.e., 0 < x < 1). Nevertheless, despite strict voltage controls to keep the lower discharge limit above 2.96 V to prevent the onset of the Jahn-Teller distortion in the spinel electrode, Li/Li<sub>x</sub>[Mn<sub>2</sub>]O<sub>4</sub> cells still lose capacity slowly at 20°C,<sup>5</sup> and more rapidly at 55°C,<sup>11</sup> if charged and discharged between 4.5 and 3.0 V.

Several reasons have been proposed for the capacity loss of 4 V Li/Li<sub>x</sub>[Mn<sub>2</sub>]O<sub>4</sub> cells<sup>5-11</sup>

(i) Solubility of the spinel electrode in the electrolyte. The solubility has been attributed to acid attack and a disproportionation reaction at the particle surface



(ii) An instability of the delithiated spinel structure (for example, by oxygen loss) in organic electrolyte solvents at the top of charge.

(iii) The onset of a Jahn-Teller effect at the end of discharge (particularly at high current density). Under dynamic, non-equilibrium conditions above 3 V, it has been proposed that some crystallites can be more lithiated than others, thereby driving the composition of the electrode surface into a Mn<sup>3+</sup>-rich Li<sub>1+x</sub>[Mn<sub>2</sub>]O<sub>4</sub> region.<sup>5,12</sup>

Most of the evidence reported thus far points to solubility at the top of charge as the major reason for the capacity fade in Li/Li<sub>x</sub>[Mn<sub>2</sub>]O<sub>4</sub> cells. No direct evidence has been obtained to support the hypothesis of structural fatigue, described in point (iii) above, as a contributing factor to capacity loss. Therefore, in order to investigate the possibility that structural effects may also contribute to the capacity fade of Li/Li<sub>x</sub>[Mn<sub>2</sub>]O<sub>4</sub> cells, we have undertaken a systematic study of Li<sub>x</sub>[Mn<sub>2</sub>]O<sub>4</sub> electrodes using high-resolution electron diffraction and imaging. (Conventional powder X-ray and neutron diffraction techniques are not sufficiently sensitive for detecting such structural effects at the particle surface.) In this article, we provide the first evidence, obtained by high-resolution electron diffraction and imaging, that some of the capacity fade observed when high voltage (4 V) Li/Li<sub>x</sub>[Mn<sub>2</sub>]O<sub>4</sub> cells are deeply discharged may be attributed to structural fatigue at the electrode surface. These findings have implications for the development of stabilized Li<sub>1+x</sub>Mn<sub>2-x</sub>O<sub>4</sub> spinel electrodes (0 < x < 0.1).

### Experimental

Li[Mn<sub>2</sub>]O<sub>4</sub> was prepared at 750°C as reported previously.<sup>5</sup> For electrochemical experiments, coin cells (size 1225, typical capacity: 1.5 mAh) with the configuration Li/1 M LiPF<sub>6</sub>, ethylene carbonate/dimethyl carbonate (50:50)/Li<sub>1+x</sub>Mn<sub>2-x</sub>O<sub>4</sub> were constructed. The cell assembly is described elsewhere.<sup>16</sup> Cells were charged and discharged with the following routine: eight or nine cycles at 0.2 mA (charge and discharge) followed by five or six cycles at 0.3 mA (charge and discharge). The voltage limits were kept constant in

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each experiment. Cells were cycled over the ranges: 4.2-3.5, 4.2-3.3, and 4.2-3.0 V. In addition, one cell was cycled five times at 0.2 mA over the lower voltage region between 3.3 and 2.2 V. All tests were terminated at the end of discharge.

Powder X-ray diffraction patterns were collected on a Siemens D5000 diffractometer with Cu  $K_{\alpha}$  radiation. Electron diffraction patterns and images were obtained on a JEOL-JEM 4000FEX-1 transmission electron microscope (TEM) under an accelerating voltage of 200 keV. The spinel samples were stable in the electron-beam.

### Results and Discussion

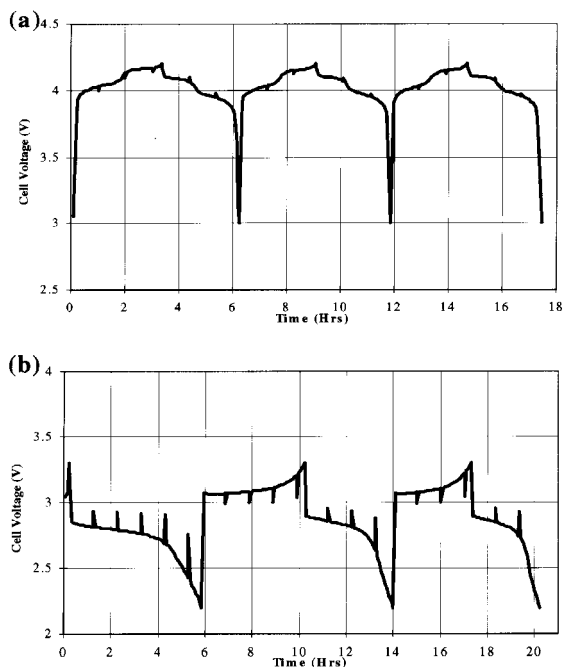
The unit cell parameter  $a$  of  $\text{Li}[\text{Mn}_2]\text{O}_4$  was determined by profile refinement of the powder X-ray diffraction pattern to be 8.241(2) Å, in good agreement with the JCPDS powder X-ray diffraction data.<sup>17</sup>

Typical voltage profiles of  $\text{Li}/\text{Li}_x[\text{Mn}_2]\text{O}_4$  cells in which the upper and lower voltage limits were 4.2-3.0 and 3.3-2.2 V, respectively, are shown in Fig. 1a and b; for clarity, only the first three cycles are shown. The data is consistent with earlier electrochemical studies of these materials<sup>3-5</sup> and clearly demonstrate that greater cycling stability is achieved in the upper voltage range.

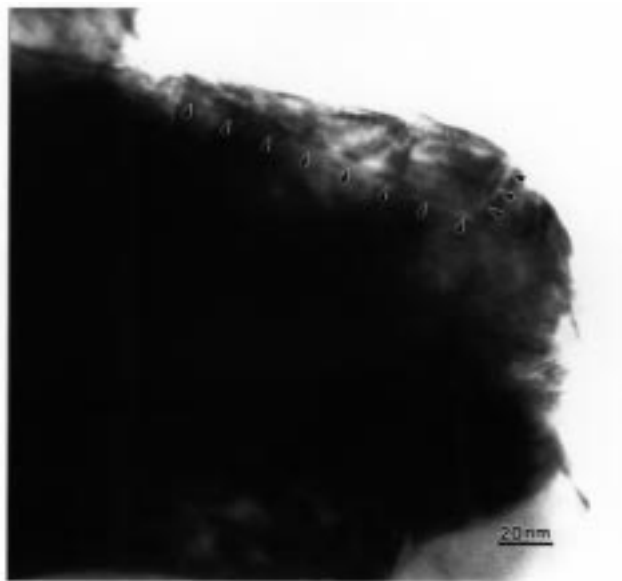
The electron diffraction patterns of the  $\text{Li}_x[\text{Mn}_2]\text{O}_4$  electrodes cycled between 3.3 and 2.2 V (i.e., over the range  $1 < x < 2$ ) showed a two-phase electrode consisting of cubic  $\text{Li}[\text{Mn}_2]\text{O}_4$  and tetragonal  $\text{Li}_2[\text{Mn}_2]\text{O}_4$ , consistent with earlier X-ray diffraction studies.<sup>13,14</sup> Of particular significance, however, was the electron diffraction data for electrodes cycled in the high voltage regions. Clear evidence of the tetragonal phase was found in the cells discharged to 3.5, 3.3, and 3.0 V, respectively. Since these voltages are above that expected for the onset of the Jahn-Teller distortion (2.96 V), this finding supports the hypothesis that this damaging crystallographic effect can occur above 3 V under dynamic, nonequilibrium conditions;<sup>5,12</sup> it can occur at as much as 500 mV above the thermodynamic value. A semiquantitative analysis of the electrodes by transmission electron microscopy showed, as expected, that the amount of the tetragonal phase increased upon lowering the end voltage from 3.5 to 3.0 V. Fifty-five single-crystal electron diffraction patterns were obtained from  $\text{Li}_x[\text{Mn}_2]\text{O}_4$  electrodes that had been cycled between 4.2 and 3.3 V. Nine of these patterns (16%) could be indexed to the tetragonal  $\text{Li}_2[\text{Mn}_2]\text{O}_4$  phase; high-resolution images showed that the tetragonal phase resided on the crystallite surface.

A high-resolution transmission electron micrograph of a spinel electrode crystallite extracted from a cell that had been discharged to 3.3 V is shown in Fig. 2. The dark fringes in the image are associated with phase boundaries that separate the tetragonal phase at the surface of the crystallite from the cubic phase within the bulk. The structural differences within the crystallites were determined by convergent-beam electron diffraction. Figure 3a shows the  $\langle 100 \rangle$  electron diffraction pattern of a typical parent  $\text{Li}[\text{Mn}_2]\text{O}_4$  crystal from an uncycled cell. The  $\langle 100 \rangle$  pattern which shows the sets of  $\{220\}$ ,  $\{440\}$ , and crystallographically equivalent  $\{040\}$  and  $\{004\}$  planes, is consistent with the cubic symmetry of  $\text{Li}[\text{Mn}_2]\text{O}_4$ . The same cubic pattern was obtained from crystallites in all cycled electrodes of this investigation. [Electron diffraction patterns of cycled spinel crystallites (e.g., in the range 4.2-3.3 V, Fig. 3b) also provided unequivocal evidence of the tetragonal  $\text{Li}_2[\text{Mn}_2]\text{O}_4$  phase at the crystallite surface; the absence of diffraction spots from the set of  $\{220\}$  planes and the nonequivalence of the (040) and (004) planes are consistent with the tetragonal rock-salt phase  $\text{Li}_2[\text{Mn}_2]\text{O}_4$  (note that Fig. 3b was obtained from the same crystallite as shown in Fig. 2).] The lattice parameters ( $a = \sim 8.0$  Å,  $c = \sim 9.3$  Å) obtained from this pattern are in good agreement with previous values [e.g.,  $a = 7.994(1)$  Å,  $c = 9.329(1)$  Å] determined by more-accurate analyses of X-ray and neutron diffraction data of bulk powders of  $\text{Li}_2[\text{Mn}_2]\text{O}_4$ .<sup>13-15</sup>

The presence of  $\text{Li}_2[\text{Mn}_2]\text{O}_4$  on the particle surface in discharged  $\text{Li}_x[\text{Mn}_2]\text{O}_4$  electrodes may contribute to the capacity fade that has been observed during cycling of  $\text{Li}/\text{Li}_x[\text{Mn}_2]\text{O}_4$  cells. First,  $\text{Li}_2[\text{Mn}_2]\text{O}_4$  is a  $\text{Mn}^{3+}$ -rich spinel; it is likely, therefore, to dissolve in the electrolyte by the disproportionation reaction described earli-



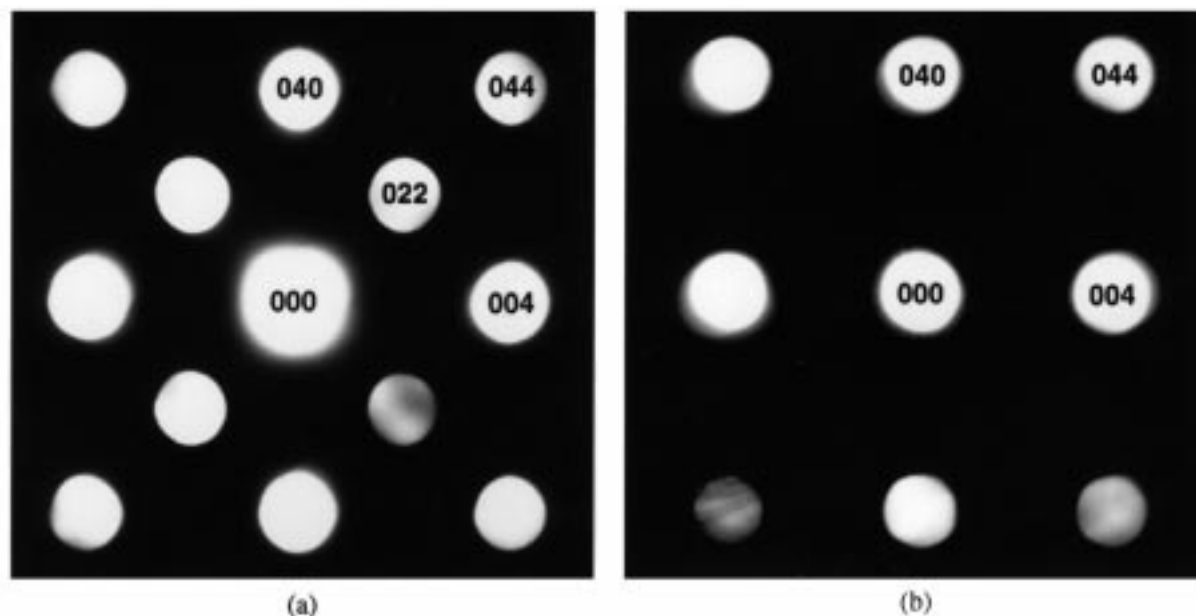
**Figure 1.** (a) Voltage profiles for the first three cycles of a  $\text{Li}/\text{Li}_x[\text{Mn}_2]\text{O}_4$  cell charged and discharged between 4.2 and 3.0 V; (b) voltage profiles for a similar cell charged and discharged between 3.3 and 2.2 V. The spikes in the profiles indicate current interruptions.



**Figure 2.** A TEM electron diffraction image of a  $\text{Li}_x[\text{Mn}_2]\text{O}_4$  electrode discharged from 4.2 to 3.3 V. The black lines (arrowed) indicate the boundary between a tetragonal  $\text{Li}_2[\text{Mn}_2]\text{O}_4$  crystal and a cubic  $\text{Li}[\text{Mn}_2]\text{O}_4$  crystal.

er. Second, it is conceivable that the tetragonal phase may dissociate from the cubic phase of the bulk electrode, resulting in a loss of particle and electronic contact.

Gummow and co-workers have modified the composition of the spinel electrode by replacing a small fraction of the manganese by lithium in the structure to yield  $\text{Li}[\text{Mn}_{2-x}\text{Li}_x]\text{O}_4$  (alternatively,  $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ ), thereby significantly improving the cycling behavior of these cells.<sup>5</sup> The advantage of these modified electrodes, such as



**Figure 3.** Convergent-beam electron diffraction patterns ([100] zone axis) of (a) a cubic  $\text{Li}[\text{Mn}_2]\text{O}_4$  (parent) crystal and (b) a tetragonal  $\text{Li}_2[\text{Mn}_2]\text{O}_4$  crystal on the surface an electrochemically cycled spinel electrode (discharged from 4.2 to 3.3 V). Note that Fig. 3b was obtained from the same crystallite as shown in Fig. 2.

$\text{Li}_{1.05}\text{Mn}_{1.95}\text{O}_4$  ( $x = 0.05$ ), is that residual lithium remains in the structure to stabilize the electrode at the top of charge when the oxidation state of the manganese ions reaches 4.0 (i.e., at the composition  $\text{Li}_{0.2}\text{Mn}_{1.95}\text{O}_4$ ). Moreover, at the end of discharge, for example at 3.3 V, the electrode approaches the stoichiometric spinel composition  $\text{Li}_{1.05}\text{Mn}_{1.95}\text{O}_4$ , and the average oxidation state of the manganese ions ( $>3.56$ ) is higher than it is in  $\text{Li}[\text{Mn}_2]\text{O}_4$  (3.50). Gummow and co-workers, therefore, proposed that this condition would prevent the immediate onset of the Jahn-Teller distortion, which occurs when the average Mn oxidation state reaches 3.5,<sup>5</sup> and thereby results in higher performance electrodes.

Similar investigations of lithium-stabilized  $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$  electrodes with TEM techniques are in progress. Preliminary data of  $\text{Li}_{1.05}\text{Mn}_{1.95}\text{O}_4$  ( $x = 0.05$ ) indicate that the electron diffraction patterns of the electrodes when discharged to 2.89 V are complex. Although it has not yet been possible to fully interpret these patterns, they seem to indicate strain and structural disorder in cubic spinel crystals. These patterns show no significant indication of a tetragonal phase on the surface of the particles, even when the end voltage of the cells is lowered to 2.89 V. These findings, therefore, provide strong support for the argument that  $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$  electrodes provide a cubic "buffer" zone that prevents the onset of the Jahn-Teller effect at the particle surface when the cells reach 3 V,<sup>5,12</sup> and, therefore, that capacity fade due to structural fatigue in  $\text{Li}_x[\text{Mn}_2]\text{O}_4$  electrodes toward the end of discharge can be combated by a more stable surface in modified  $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$  electrodes.

### Conclusions

A tetragonal  $\text{Li}_2[\text{Mn}_2]\text{O}_4$  phase has been detected at the surface of discharged electrodes in 4 V  $\text{Li}/\text{Li}_x[\text{Mn}_2]\text{O}_4$  cells. Although most of the capacity fade that has been observed on cycling  $\text{Li}/\text{Li}_x[\text{Mn}_2]\text{O}_4$  cells has been reported to occur by dissolution of charged electrodes (associated with oxygen loss and a consequent disproportionation reaction  $2\text{Mn}^{3+} \rightarrow \text{Mn}^{4+} + \text{Mn}^{2+}$  at the electrode surface), it is conceivable that dissolution of the  $\text{Mn}^{3+}$ -rich

$\text{Li}_2[\text{Mn}_2]\text{O}_4$  phase at the end of discharge may also contribute to the capacity fade of the cells. Another minor contributing factor to the capacity fade may arise from the loss of particle-to-particle contact at the cubic- $\text{Li}[\text{Mn}_2]\text{O}_4$ /tetragonal- $\text{Li}_2[\text{Mn}_2]\text{O}_4$  interface in discharged  $\text{Li}_x[\text{Mn}_2]\text{O}_4$  electrodes.

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