

Structural fatigue in spinel electrodes in $\text{Li}/\text{Li}_x[\text{Mn}_2]\text{O}_4$ cells

Y. Shao-Horn^b, S.A. Hackney^b, A.J. Kahaian^a, K.D. Kepler, E. Skinner^{a,c},
J.T. Vaughey^a, M.M. Thackeray^{a,*}

^a *Electrochemical Technology Program, Chemical Technology Division, Argonne, IL 60439, USA*

^b *Department of Metallurgical and Materials Engineering, Michigan Technological University, Houghton, MI 49931, USA*

^c *Department of Chemical Engineering, School of Chemical Sciences, University of Illinois, Urbana-Champaign, IL 61801, USA*

Abstract

Evidence of structural fatigue has been detected at the surface of discharged $\text{Li}_x[\text{Mn}_2]\text{O}_4$ spinel electrodes in $\text{Li}/\text{Li}_x[\text{Mn}_2]\text{O}_4$ cells. Transmission electron microscopy has revealed a degradation of the structural integrity of $\text{Li}[\text{Mn}_2]\text{O}_4$ crystals in electrodes that were cycled between 3.3 and 2.2 V, where the transformation from cubic $\text{Li}[\text{Mn}_2]\text{O}_4$ to tetragonal $\text{Li}_2[\text{Mn}_2]\text{O}_4$ is expected. It has also been observed in cells cycled at voltages above the 3 V plateau that domains of tetragonal $\text{Li}_2[\text{Mn}_2]\text{O}_4$ coexist with cubic $\text{Li}[\text{Mn}_2]\text{O}_4$, even at 500 mV above the thermodynamic voltage expected for the onset of the tetragonal phase. It is proposed that the presence of $\text{Li}_2[\text{Mn}_2]\text{O}_4$ on the particle surface may contribute to some of the capacity fade observed during cycling of $\text{Li}/\text{Li}_x[\text{Mn}_2]\text{O}_4$ cells. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: $\text{Li}/\text{Li}_x[\text{Mn}_2]\text{O}_4$; Spinel electrode; Structural fatigue

1. Introduction

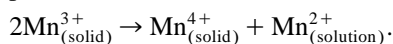
The exponential growth in the electronics industry has led to an increasing demand for light weight power sources with high energy density and power capability [1,2]. This demand has been satisfied largely by the advent of rechargeable lithium-ion batteries. The best known system is $\text{Li}_x\text{C}/\text{LiCoO}_2$. 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 $\text{Li}[\text{Mn}_2]\text{O}_4$ [3–5]. A disadvantage of $\text{Li}[\text{Mn}_2]\text{O}_4$ spinel electrodes is that they lose capacity on cycling, which limits the life of the cell [5–11]. 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 [12]. In the $\text{Li}_x[\text{Mn}_2]\text{O}_4$ spinel system ($0 < x < 2$), the $[\text{Mn}_2]\text{O}_4$ spinel framework provides a three-dimensional interstitial space for lithium-ion transport. Lithium extraction from $\text{Li}[\text{Mn}_2]\text{O}_4$ (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 extrac-

tion [3–5,12]. 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 [13]. This two-phase reaction is associated with the onset of an anisotropic (Jahn–Teller) distortion. As a result, the cubic symmetry of $\text{Li}[\text{Mn}_2]\text{O}_4$, in which the lithium ions occupy tetrahedral sites, is reduced to tetragonal $\text{Li}_2[\text{Mn}_2]\text{O}_4$ (space group = $F4_1/ddm$), in which the lithium ions occupy octahedral sites in an ordered rock-salt structure [13–15]. 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 on cycling. Consequently, a $\text{Li}_x[\text{Mn}_2]\text{O}_4$ 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 $\text{Li}_x[\text{Mn}_2]\text{O}_4$ 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, $\text{Li}/\text{Li}_x[\text{Mn}_2]\text{O}_4$ cells still lose capacity slowly at 20°C [5], and more rapidly at 55°C [11], if charged and discharged between 4.5 and 3.0 V.

Most of the evidence reported thus far points to solubility of the spinel electrode in the electrolyte as the major

* Corresponding author

reason for capacity fade. The solubility has been attributed to acid attack and a disproportionation reaction at the particle surface:



No direct evidence has been obtained to support the hypothesis of structural fatigue as a contributing factor to capacity loss [5,12]. Therefore, in order to investigate the possibility that structural effects may also contribute towards the capacity fade of Li/Li_x[Mn₂]O₄ cells, we have undertaken a systematic study of Li_x[Mn₂]O₄ 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). We have previously reported data, obtained by high resolution electron diffraction and imaging, showing that some of the capacity fade observed when high voltage (4 V) Li/Li_x[Mn₂]O₄ cells are deeply discharged may be attributed to the formation of the tetragonal structure above 3 V [16]. In this report, we examine direct observations of microstructural features which are consistent with structural fatigue of oxide crystallites in deeply discharged Li/Li_x[Mn₂]O₄ cells.

2. Experimental

Li[Mn₂]O₄ was prepared at 750°C as reported previously [5]. For the electrochemical experiments, coin cells (size 1225) with the configuration Li/1 M LiPF₆, ethylene carbonate/dimethyl carbonate (50:50)/Li_{1+x}Mn_{2-x}O₄ were constructed. The cell assembly is described elsewhere [17]. Cells were charged and discharged with the following routine: 8 or 9 cycles at 0.2 mA (charge and discharge) followed by 5 or 6 cycles at 0.3 mA (charge and discharge). The voltage limits were kept constant in each experiment. Cells were cycled over the ranges: 4.2 to 3.5 V, 4.2 to 3.3 V, and 4.2 to 3.0 V. In addition, one cell was cycled 5 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 CuK_α radiation. Electron diffraction patterns and images were obtained on a JEOL-JEM 4000 FEX-1 transmission electron microscope (TEM) under an accelerating voltage of 200 keV. The spinel samples were stable in the electron beam.

3. Results and discussion

The unit cell parameter (*a*) of Li[Mn₂]O₄ 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 [18].

Typical voltage profiles of Li/Li_x[Mn₂]O₄ cells in which the upper and lower voltage limits were 4.2–3.0 V,

and 3.3–2.2 V, respectively, are shown in Fig. 1a and b; for clarity, only the first 3 cycles are shown. The data are consistent with earlier electrochemical studies of these materials [3–5] and clearly demonstrate that greater cycling stability is achieved in the upper voltage range.

The electron diffraction patterns of the Li_x[Mn₂]O₄ 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 Li[Mn₂]O₄ and tetragonal Li₂[Mn₂]O₄, consistent with earlier X-ray diffraction studies [13,14] (Fig. 2a). Direct imaging of the sample revealed that a small fraction of the particles (< 10%) showed small nanoscale crystallites which appeared to have separated from the larger crystallites during cycling (Fig. 2b). This type of microstructure was not observed in the parent sample. Of particular significance was the electron imaging and diffraction data of electrodes cycled above 3 V. Convergent beam electron diffraction was used to analyze the crystal symmetry of a number of crystallites extracted from the electrodes. This point counting technique is effective in determining the relative fraction of crystallites that contain some tetragonal phase, but it is difficult to extract information about volume fraction using this approach. The convergent beam electron diffraction technique did provide convincing evidence for the presence of the tetragonal phase in the cells, discharged to 3.5, 3.3 and 3.0 V, respectively (Fig. 3a). Note that the relative fraction of

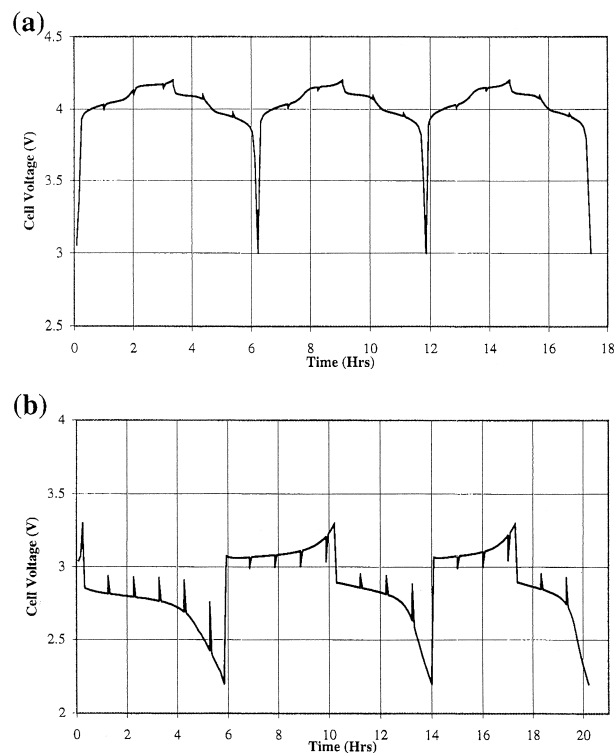


Fig. 1. (a) Voltage profiles for the first 3 cycles of a Li/Li_x[Mn₂]O₄ cell charged and discharged between 4.2 and 3.0 V; (b) voltage profiles for a similar cell charged and discharged between 3.3 and 2.2 V. The spikes in the profiles indicate current interruptions.

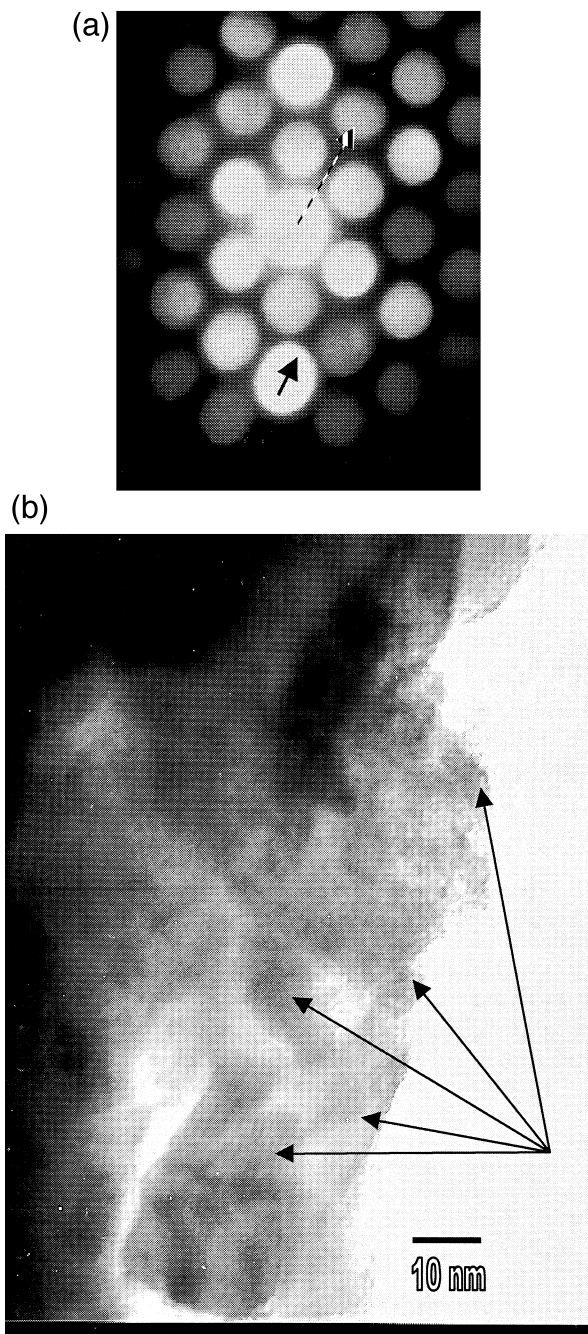


Fig. 2. (a) A TEM electron diffraction image of the $[1-10]$ zone axis of a $\text{Li}_x[\text{Mn}_2]\text{O}_4$ crystallite in an electrode discharged from 3.3 to 2.2 V. The solid black arrow indicates the displacement of intensity of the 004 reflection along a $\langle 112 \rangle$ direction (patterned arrow) due to the tetragonal distortion within a cubic crystal. (b) Spinel crystallites less than 100 Å in diameter are indicated by the black arrows. These crystallites may have formed by fracture from a parent crystallite during the electrochemical cycling on the low voltage plateau.

tetragonal phase increases as the discharge voltage is decreased, as expected.

It was also found that crystal defect structures in the spinel are associated with the presence of the tetragonal phase (Fig. 3b). When viewed along the $[110]$ zone axis, as

in Fig. 3b, there is an evident disruption in the crystal periodicity corresponding to lines of relatively high transmitted intensity (bright lines) parallel to the (-111) plane. That is, the trace of these bright lines is along a $[1-12]$ direction. The structural interpretation of this contrast has not been quantitatively confirmed, but one possibility is the association with a local crystallographic shearing of the unit cell along $[1-12]$ to accommodate the Jahn–Teller distortion and the reduction of symmetry to tetragonal. The single crystal electron diffraction patterns are certainly consistent with this interpretation. More significant, however, is that such a defect will result in significant elastic/plastic strain and would be expected to predispose the crystallite to the type of structural disruption observed here for crystallites undergoing deep discharge.

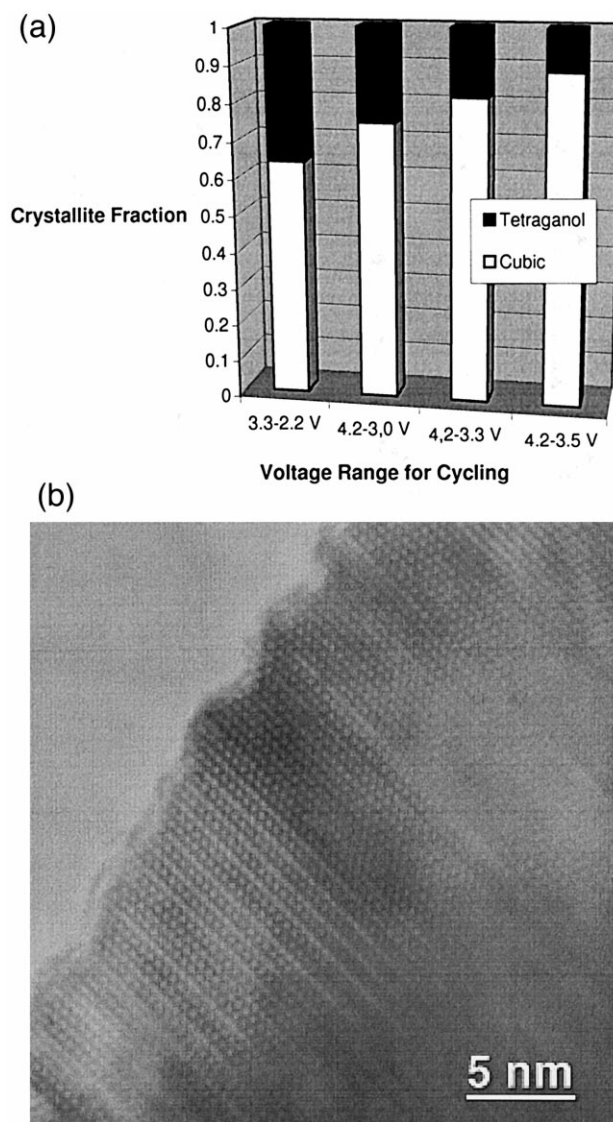


Fig. 3. (a) The fraction of crystallites containing at least a minor amount of tetragonal phase as determined by convergent beam electron diffraction. (b) Crystal defects in a crystallite from an electrode cycled between 4.2 and 3.3 V.

Acknowledgements

This work was supported by the U.S. Department of Energy Advanced Battery Program, Chemical Sciences Division, Office of Basic Energy Sciences under contract W-31-109-ENG-38.

References

- [1] B. Scrosati, *Nature* 373 (1995) 557.
- [2] S. Megahed, B. Scrosati, *J. Power Sources* 51 (1994) 79.
- [3] T. Ohzuku, M. Kitagawa, T. Hirai, *J. Electrochem. Soc.* 137 (1990) 769.
- [4] J.M. Tarascon, E. Wang, F.K. Shokoohi, W.R. McKinnon, S. Colson, *J. Electrochem. Soc.* 138 (1991) 2859.
- [5] R.J. Gummow, A. de Kock, M.M. Thackeray, *Solid State Ionics* 69 (1994) 59.
- [6] D.H. Jang, Y.J. Shin, S.M. Oh, *J. Electrochem. Soc.* 143 (1996) 2204.
- [7] G.G. Amatucci, C.N. Schmutz, A. Blyr, C. Sigala, A.S. Gozdz, D. Larcher, J.M. Tarascon, *J. Power Sources* 69 (1997) 11.
- [8] G. Pistoia, A. Antonini, R. Rosati, C. Bellitto, G.M. Ingo, *Chem. Mater.* 9 (1997) 1443.
- [9] Y. Xia, Y. Zhou, M. Yoshio, *J. Electrochem. Soc.* 144 (1997) 2593.
- [10] D.H. Jang, S.M. Oh, *J. Electrochem. Soc.* 144 (1997) 3342.
- [11] A. Blyr, C. Sigala, G.G. Amatucci, D. Guyomard, Y. Chabres, J.M. Tarascon, *J. Electrochem. Soc.* 145 (1998) 194.
- [12] M.M. Thackeray, *J. Electrochem. Soc.* 142 (1995) 2558.
- [13] M.M. Thackeray, W.I.F. David, P.G. Bruce, J.B. Goodenough, *Mater. Res. Bull.* 18 (1983) 461.
- [14] A. Mosbah, A. Verbaere, M. Tournoux, *Mater. Res. Bull.* 18 (1983) 1375.
- [15] W.I.F. David, M.M. Thackeray, L.A. de Picciotto, J.B. Goodenough, *J. Solid State Chem.* 67 (1987) 316.
- [16] M.M. Thackeray, Y. Shao-Horn, A.J. Kahaian, K.D. Kepler, J.T. Vaughey, S.A. Hackney, *Electrochem. Solid State Lett.* 1 (1998) 7.
- [17] C.S. Johnson, D.W. Dees, M.F. Mansuetto, M.M. Thackeray, D.R. Vissers, D. Argyriou, C.-K. Loong, L. Christensen, *J. Power Sources* 68 (1997) 570.
- [18] Joint Commission on Powder Diffraction Standards, International Centre for Diffraction Data, File: 35-782.