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An electron energy loss spectroscopy and electron diffraction study of the \( Pmn\) polymorph of Li\(_2\)MnSiO\(_4\)

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Abstract

The Mn valency and the crystallinity of Li$_2$MnSiO$_4$ cathodes (Pmnb form) were examined with electron energy-loss spectroscopy (EELS) and selected area electron diffraction (SAED) both before and after electrochemical lithium extraction. A decrease in the crystallinity of the delithiated charged cathode particles compared to the as-prepared material was observed. The decrease in crystallinity varied from particle to particle. EELS analysis showed that the non-uniform decrease in crystallinity was due to a non-uniform extraction of lithium from the particles. The observed decrease in discharge capacity of the Pmnb polymorph of Li$_2$MnSiO$_4$ with cycling was attributed to the progressive loss of crystallinity and the structural collapse of Li diffusion pathways.

Keywords: electron energy loss spectroscopy; transition metal alloys and compounds; energy storage materials; crystal structure; amorphisation

1. Introduction

Research into the application of Li$_2$MnSiO$_4$ as a high-capacity lithium-ion battery cathode material is on-going despite difficulties with low electronic conductivity, polymorphism and instability of the Li$_2$MnSiO$_4$ structure on charge [1-13]. Recent results obtained from nano-structured materials produced with low temperature synthesis routes have shown vastly improved reversibility compared to bulk materials and electrochemical capacities approaching the theoretical prediction of 333 mAh$^{-1}$ for the $P2_1/n$, $Pmn2_1$ and $Pn$ polymorphs of Li$_2$MnSiO$_4$ [14-16]. Recently the Pmnb polymorph of Li$_2$MnSiO$_4$, earlier reported by other investigators [17, 18], has been synthesized by a facile route in...
phase-pure form [19]. The difficulty in preparing this polymorph without impurities in the past has meant that it has been relatively unexplored compared to the other structural forms of Li$_2$MnSiO$_4$.

The disappointing preliminary electrochemical performance of this polymorph as a cathode in Li/Li$_2$MnSiO$_4$ cells [19] was tentatively ascribed to both the poor electronic properties of the material and the likely structural collapse analogous to that of the well-described *Pmn*$_2$$_1$ polymorph [20, 21].

The electron energy loss spectroscopy (EELS) spectra of lithium-transition metal compounds can be used to determine the valence state of the transition metal cations in the cathode. Since EELS spectrometers are integrated into transmission electron microscopes (TEM’s), a spectrum of a nanosized area can be obtained and can be coupled with structural data from electron diffraction spectra and composition data obtained by Energy Dispersive X-ray analysis (EDS). This combined analysis can be applied to ex-situ cathodes to give important insight into the chemical and structural changes that occur in lithium-ion battery cathode materials during electrochemical cycling [22]. EELS analysis has been applied to lithium battery cathodes including LiMn$_2$O$_4$ [23], LiNi$_{0.5}$Mn$_{1.5}$O$_4$ [24], LiFePO$_4$ [25-27] and the FeOF/C [28] electrode system. In this study we present both electron diffraction and EELS analysis to examine the structure and Mn valence state of ex-situ *Pmn*$_b$ Li$_x$MnSiO$_4$ (0 ≤ x ≤ 2) cathodes before and after electrochemical Li extraction in Li/Li$_2$MnSiO$_4$ cells.

2. Experimental

2.1 Synthesis and Electrochemical Delithiation of Li$_2$MnSiO$_4$

Li$_2$MnSiO$_4$ (*Pmn*$_b$ form) was synthesized by a solid-state route as detailed in [19]. Electrodes were prepared in a ratio of active material:carbon:PVDF of 60:20:20. The active material and the carbon were milled in a vibratory mill under Ar atmosphere for 2 hours using ZrO$_2$ grinding media. The
mixture was then mixed with PVDF dissolved in NMP and coated onto Al foil current collectors. Cathodes were dried in a vacuum drying oven at 120°C for 10 h. Swagelok test-cells were assembled in an Ar glovebox with 1M LiPF₆ in a 1:1 mixture by volume of ethylene carbonate and dimethyl carbonate (Merck Selectipure LP30) electrolyte. The anode was lithium foil with two discs of microporous polypropylene (Celgard 2500) as separators.

Delithiated cathodes were prepared by electrochemical extraction of lithium in Li/Li₂MnSiO₄ cells. A typical cell was cycled at a current rate of 5 mAg⁻¹ between voltage limits of 4.8 and 1.8 V in constant current mode for 2 cycles. To maintain the discharge capacity the cell was then charged in CC-CV mode to 4.8 V (charged at 5 mAg⁻¹ to 4.8V and then held at 4.8V until the current decayed to 1/10th of the initial charge current). The cell was then discharged at 5 mAg⁻¹ to a lower voltage cut-off of 1.8V. This CC-CV cycling regime was used for cycles 3 and 4. Finally the cell was charge to 4.8 V in CC-CV mode as before. Cells were disassembled in an Argon glovebox and the cathodes were rinsed with DME, vacuum dried and stored in Ar for analysis.

2.2 Transmission Electron Microscopy (TEM) sample preparation and analysis

The TEM samples of the as-synthesized material were dispersed in ethanol. Drops of the dispersion were placed onto a holey carbon-coated copper grid and cleaned in Ar plasma. Charged cathodes were scraped from the current collector, dispersed in acetone and then prepared as for the as-synthesized material.

EELS spectra were collected with a Gatan GIF-2001 spectrometer attached to a JEOL 2010F field emission microscope operating at 200 keV. For EELS acquisition the spectrometer entrance aperture was set to 2 mm and the TEM operated in diffraction mode. The convergence semi-angle was 11 mrad and the collection semi-angle 28 mrad. In this configuration the energy resolution was
approximately 1.8 eV. Spectra were acquired at 0.5 eV per channel and exposure time was 0.2 sec. Spectra were recorded from areas of the specimen with thickness less than 0.5 mean free path length for inelastic scattering, therefore ZLP deconvolution was not applied.

Different techniques to quantify the \( L_3/L_2 \) intensity ratios have been used by other investigators [29-31]. In this study the background was first removed by subtracting the extrapolated pre-edge curve from the post-edge region then the continuum contribution was removed by inserting a step function as illustrated in Fig 1. After subtraction of the continuum, the white line intensities of the \( L_3 \) and \( L_2 \) lines were obtained by integration of the areas under the peaks. In agreement with the findings of Wang et al. [30] the \( L_3/L_2 \) intensity ratio was found to be a more sensitive measure of the Mn oxidation state than the absolute values of the energy positions of the edges, which are strongly affected by electromagnetic noise.

3. Results and discussion

3.1 As-prepared \( \text{Li}_2\text{MnSiO}_4 \) material

3.1.1 Selected Area Electron Diffraction (SAED) and Energy Dispersive Spectroscopy (EDS) analysis

The material used in this study is a single-phase \( Pmn b \) polymorph of \( \text{Li}_2\text{MnSiO}_4 \) with lattice constants \( a = 6.30693(2) \text{ Å}, b = 10.75355(4) \text{ Å} \) and \( c = 5.00863(2) \text{ Å} \) [19]. An experimental electron diffraction (SAED) pattern and a simulated pattern down the [0, 1, -1] zone axis are shown in Fig.2a and b respectively. The experimental pattern shows a well-defined spot-pattern consistent with the \( Pmn b \) model. This finding was repeated with several different crystallites. Weak spots not present in
the simulated pattern and labelled dd are attributed to multiple scattering events. EDS results for the sample, collected with the TEM, gave a Si: Mn ratio of 1:0.98(3) confirming the nominal stoichiometry.

3.1.2  Electron Energy-Loss Spectroscopy (EELS)

The EELS spectra of the as-prepared Li$_2$MnSiO$_4$ (*Pmnb*) and a MnTiO$_3$ (Mn$^{2+}$) standard (Fig. 2 c) show well-defined peaks associated with the O-K edge (525-560 eV) and the Mn L$_3$ and L$_2$ edges (630-660 eV). The intensity axis shows nominal values with the spectra displaced vertically for clarity. The energy loss and L$_3$/L$_2$ intensity ratios of the as-prepared sample agree well with the data for the Mn$^{2+}$ standard and with results reported for Mn$^{2+}$ oxides (Fig. 2 (c) and Table 1) [22, 32,33], confirming the Mn$^{2+}$ oxidation state.

3.2  Electrochemically delithiated Li$_2$MnSiO$_4$

3.2.1  Electrochemical cycling and delithiation of Li$_2$MnSiO$_4$

The Li/Li$_2$MnSiO$_4$ cell used for the preparation of the delithiated cathodes (Fig. 3) gives a capacity of 254 mAhg$^{-1}$ on the first charge cycle and 113 mAhg$^{-1}$ on the first discharge to 1.8 V. The initial charge capacity agrees well with that reported earlier for the *Pmnb* material [19] but the first discharge capacity is much larger. The increase in the discharge capacity may be due firstly to the increased carbon content of 20% as opposed to 13% in the earlier experiments, secondly an increase in milling time from 1 h to 2h and lastly to the lower current rate of 5mAg$^{-1}$ compared to the 20 mAg$^{-1}$ rate reported earlier [19]. The large irreversible capacity on the first cycle may be explained by the fact that some of the initial charge capacity is likely due to side reactions of the electrode material with the electrolyte or electrolyte decomposition at the high voltages reached on charge. On the second discharge the capacity is 78 mAhg$^{-1}$. The CC-CV cycling regime, used after the first two
cycles, improves the discharge capacity on the 3rd cycle to 85 mAhg\(^{-1}\) but the capacity continues to decline on the 4th cycle (75 mAhg\(^{-1}\)). The discontinuities in the 2nd charge and 1st discharge curves (Fig. 3) are due to unavoidable short current interruptions during the cell cycling procedure.

Detailed investigations of the \(Pmn2_1\) polymorph of \(\text{Li}_2\text{MnSiO}_4\) as a cathode in Li/\(\text{Li}_2\text{MnSiO}_4\) cells have shown that the material loses crystallinity with cycling resulting in a collapse of the crystal structure and eventual amorphization [3, 4, 20, 21]. The observed capacity fade of the \(Pmn2_1\) polymorph cathodes when cycled in Li/\(\text{Li}_2\text{MnSiO}_4\) cells has been attributed to this mechanism. Earlier reports of SAED of partially delithiated \(\text{Li}_2\text{MnSiO}_4\) cathodes with the \(Pmn2_1\) structural form showed evidence for non-uniform amorphization. From these results it was suggested that lithium extraction from this polymorph was non-uniform and a phase separation model for lithium extraction was proposed [20]. However, no direct evidence was given for non-uniform delithiation. In this study SAED and EELS analysis of the charged \(Pmnb\) \(\text{Li}_2\text{MnSiO}_4\) cathode material was undertaken to investigate whether amorphization occurs in the \(Pmnb\) form and whether there is any direct evidence for non-uniform lithium extraction in this case.

### 3.2.2 SAED and EDS

Fig. 4 (a) and (c) show the experimental SAED patterns of two adjacent particles in the charged \(Pmnb\) electrode TEM sample shown in the bright field image in Fig. 5. Note that, although the particles were adjacent in the TEM image, the original position of the particles in the electrode itself cannot be determined as the sample was removed from the current collector and dispersed in solvent during the TEM sample preparation procedure. The first pattern is typical of an essentially crystalline material, although the crystallinity is markedly reduced compared to the as-prepared sample (Fig 2(a)). The zone axis of the particle in Fig. 4(a) is close to \([0, 2, 1]\). A simulated SAED pattern of the
The Pmnb form of Li$_2$MnSiO$_4$ with the [0, 2, 1] zone axis is shown in Fig. 4(b) for comparison. The second experimental SAED pattern (Fig 4 (c)) is typical of material that has been mostly amorphized – showing only two remaining well-defined spots from the residual crystalline phase and diffuse diffraction rings due to the amorphous component. These results show that, in agreement with the findings for the Pmn2$_1$ polymorph [20], there is a non-uniform loss of crystallinity when Li is extracted from the Pmnb form of Li$_2$MnSiO$_4$.

Li is not detectable by EDS, however the measured Mn:Si ratio of the crystalline and amorphous particles was 0.996 and 1.007, respectively. This is in close agreement with the nominal 1:1 stoichiometry for both particles.

3.2.3 EELS analysis

The EELS spectra of the Mn L$_{2/3}$ edges of the as-synthesized sample and the two charged particles are compared in Fig. 6 and Table 1. The energy scale has been shifted so that the L$_3$ peaks are aligned. The intensity axis is nominal and the intensities are normalized to the intensity of the L$_3$ peak maximum and displaced vertically for clarity. It is found that the Mn L$_3$/L$_2$ intensity ratio decreases in the charged particles indicating an increase in the Mn oxidation state [29, 30]. The more crystalline charged particle (particle 1) has a larger Mn L$_3$/L$_2$ intensity ratio than the amorphous particle (particle 2), consistent with a lower oxidation state of Mn in the crystalline particle. This gives the first direct evidence of the non-uniform extraction of lithium from the Pmnb form of Li$_2$MnSiO$_4$. Some particles are preferentially delithiated, becoming amorphous more rapidly, while other particles, with higher lithium content, partially retain their crystallinity. The current rate of 5mA/g used for the electrochemical cycling of the cell was low but it is possible that the use of extremely low currents may remove the observed non-uniform delithiation. Li K-edge
EELS measurements will be conducted in future studies to confirm the differences in Li content of particles with different degrees of crystallinity.

The fine structure of the O-K edges in the as-prepared, charged crystalline and charged amorphous particles (Fig. 7) shows considerable changes with Li extraction. The K\(_a\) peak at approximately 525 eV is completely absent in the as-prepared Li\(_2\)MnSiO\(_4\) material, very poorly defined in the charged crystalline material and well-defined in the charged amorphous particle. The intensity of the pre-peak increases significantly with lithium extraction - the charged crystalline particle with a lower manganese oxidation state has a low intensity pre-peak while the charged amorphous particle with a higher manganese oxidation state has a far more intense pre-peak. This peak has been attributed by some authors to the transition of the O 1s electron to O 2p orbitals hybridized with manganese 3d orbitals [32]. The number of available holes in the O 2p states depends on the degree of orbital hybridization with adjacent atoms. An increase in the pre-peak intensity implies more hybridization between oxygen and the surrounding atoms and an increase in the covalent nature of the bonds. One possible explanation is that, when Li is extracted from Li\(_{2-x}\)MnSiO\(_4\) particles, charge compensation occurs firstly by oxidation of the Mn\(^{2+}\) cations. However, in highly delithiated particles, in addition to the oxidation of the Mn, charge compensation occurs by increased hybridization of the O-Mn bonds and a resulting decrease in the charge density around the O ions. Similar effects have been observed with the delithiated oxides LiNi\(_{0.8}\)Mn\(_{0.5}\)Co\(_{0.2}\)O\(_2\) [34], LiNi\(_{1.8}\)Co\(_{0.2}\)O\(_2\) [35] and LiCoO\(_2\) [36]. However, studies by Jiang et al. [37] on silicate glasses have shown that the O K-edge pre-peak in their samples was not an intrinsic property of the material but was related to beam damage of the samples. Extended exposure to the beam resulted in an initial increase in the O K-edge pre-peak followed by a rapid decrease in its intensity. In this study several measurements were made on each particle and no systematic changes in the O K-edge pre-peak were observed during the process despite the increasing beam exposure time. Beam damage is therefore considered an unlikely
explanation for the observed changes in the O K-edge in this case but systematic studies of beam damage with increasing exposure time are required to completely exclude this possibility.

The energy separation of the L\text{3} and the O-K\text{a} peak maxima, which has been shown to be an accurate measure of the oxidation state of manganese oxides in the 3+ to 4+ range [38], yields a calculated average manganese oxidation state of 3.5 for a typical amorphous delithiated Li\textsubscript{2}MnSiO\textsubscript{4} particle. This finding was repeated with other amorphous particles. It was not possible to calculate the Mn oxidation state for the crystalline particles in this way as the O-K\text{a} edge is absent or poorly defined in Li\textsubscript{2-x}MnSiO\textsubscript{4} samples with low Mn oxidation states (Fig 7).

4. Conclusions

In this study SAED and EELS analyses of Li\textsubscript{2}MnSiO\textsubscript{4} and charged Li\textsubscript{x}MnSiO\textsubscript{4} samples (x<1) with the Pmn\textsubscript{b} structural form were performed. It was found that electrochemical extraction of lithium from the Li\textsubscript{2}MnSiO\textsubscript{4} Pmn\textsubscript{b} polymorph leads to non-uniform amorphization as observed for the Pmn2\textsubscript{1} form [20]. Some particles are almost completely amorphized while others retain significant crystallinity even after 5 charge cycles. The EELS data confirmed that the non-uniform loss of crystallinity was due to non-uniform lithium extraction in the Pmn\textsubscript{b} form of Li\textsubscript{2}MnSiO\textsubscript{4}. The observed changes in the O K-edge of the delithiated samples also suggest the possibility that not all the charge compensation for lithium extraction occurs by oxidation of the Mn cations but that the O anions play a role in charge compensation in highly delithiated particles. Further studies are needed to completely exclude the possibility that some of the observed changes in the O-K edges are due to sample damage from extended exposure to the beam.

This study has shown that, as with the Pmn2\textsubscript{1} polymorph of Li\textsubscript{2}MnSiO\textsubscript{4}, the crystal structure collapses when the material is cycled as a cathode in Li/Li\textsubscript{2}MnSiO\textsubscript{4} cells, resulting in a destruction of
the Li ion diffusion pathways and this is the most likely explanation for the observed decrease in the discharge capacity with cycling.

Acknowledgements

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References


[34] W.S. Yoon, C.P. Grey, M. Balasubramanian, X.Q. Yang, D.A. Fischer, J. McBreen, 


Table 1

Calculated Mn L$_3$/L$_2$ intensity ratio and Mn L$_3$–O K$_{\alpha}$ peak energy difference for as-synthesized and charged Li$_2$MnSiO$_4$ cathodes and standard materials for comparison.

<table>
<thead>
<tr>
<th>Sample</th>
<th>L$_3$/L$_2$ intensity ratio</th>
<th>Energy difference Mn L$<em>3$–O K$</em>{\alpha}$ peak maxima (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnTiO$_3$ std.(Mn$^{2+}$)</td>
<td>3.8</td>
<td>-</td>
</tr>
<tr>
<td>Grain 1 Li$_2$MnSiO$_4$</td>
<td>4.3</td>
<td>-</td>
</tr>
<tr>
<td>Grain 2 Li$_2$MnSiO$_4$</td>
<td>4.2</td>
<td>-</td>
</tr>
<tr>
<td>Charged Grain 1 MnO$_2$</td>
<td>3.9</td>
<td>-</td>
</tr>
<tr>
<td>Li$_x$MnSiO$_4$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Charged Grain 2 MnO$_2$</td>
<td>1.8</td>
<td>112.6</td>
</tr>
<tr>
<td>Li$_x$MnSiO$_4$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MnO$_2$ std.(Mn$^{4+}$)</td>
<td>1.9</td>
<td>114.05</td>
</tr>
</tbody>
</table>
Fig. 1

Intensity / arbitrary units

Energy Loss / eV

L3

L2
Figure 2

(a) Zone axis: [0, 1, -1]

(b) [Diagram showing lattice points]

(c) [Graph showing intensity vs. energy loss]
Fig. 3

Voltage (mV)

Capacity (mAh/g)

- black - cycle 1
- blue - cycle 2
- red - cycle 3
- green - cycle 4
- turquoise - cycle 5

Current interruption
Fig. 5
Fig. 6

![Graph showing intensity vs. energy for three different conditions: (a) As Synthesized, (b) Charged crystalline, (c) Charged amorphous. The graph plots energy in eV against intensity in arbitrary units.](image-url)
Graphical abstract
Highlights

- First EELS spectroscopy and electron diffraction of $Pmn\bar{b}$ polymorph of Li$_2$MnSiO$_4$.
- Capacity loss explained by electron diffraction results that showed a non-uniform loss of crystallinity in the delithiated material.
- Direct evidence for lithium extraction occurring non-uniformly in the cathode from EELS data.
- O K-edge changes possibly linked to O charge compensation for lithium loss.