An electron energy loss spectroscopy and electron diffraction study of the *Pmnb* 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.

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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 mA h g^{-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 $Pmn2_1$ 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 (TEMs), a spectrum of a nano-sized 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 *Pmnb* Li$_x$MnSiO$_4$ ($0 < x \leqslant 2$) 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$_4$ (*Pmnb* 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 h 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 1 M LiPF$_6$ in a 1:1 mixture by volume of ethylene carbonate and dimethyl carbonate (Merck Selectipure LP30) electrolyte. The anode was lithium foil with two disks of microporous polypropylene (Celgard 2500) as separators.

Delithiated cathodes were prepared by electrochemical extraction of lithium in Li/Li$_2$MnSiO$_4$ cells. A typical cell was cycled at a current rate of 5 mA g^{-1} between voltage limits of 4.8 and 1.8 V in constant current mode for two cycles. To maintain the discharge capacity the cell was then charged in CC–CV mode to 4.8 V (charged

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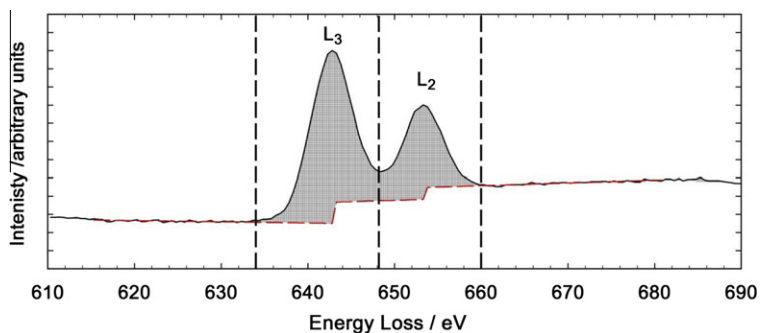*E-mail address:* Rosalind.gummow@jcu.edu.au (R.J. Gummow).

Fig. 1. A generic curve indicating the method used to extract the L_3/L_2 intensity data from the raw data. After subtraction of the background, a step function was inserted with the ratio of the step heights at 2:1 in accordance with the multiplicity of the initial states (four 2p3/2 electrons and two 2p1/2 electrons). 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.
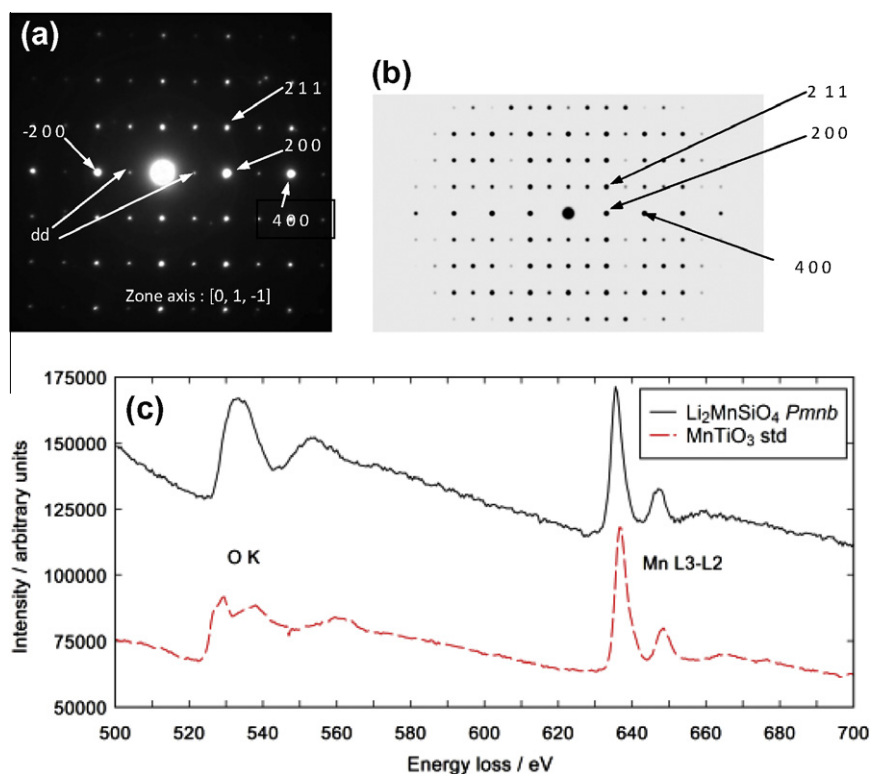

Fig. 2. (a) Electron diffraction pattern collected down the $[0, 1, -1]$ axis from the as-synthesized Li_2MnSiO_4 sample, indexed in the *Pmnb* space group. Spots due to multiple scattering are indicated dd, (b) a simulated electron diffraction for the $[0, 1, -1]$ zone axis for the *Pmnb* polymorph of Li_2MnSiO_4, (c) EELS spectra of the as-synthesized Li_2MnSiO_4 sample (*Pmnb* polymorph) and the $MnTiO_3$ (Mn^{2+}) standard. The intensity axis is nominal and spectra are offset vertically for clarity.

at 5 mA g^{-1} to 4.8 V and then held at 4.8 V until the current decayed to 1/10th of the initial charge current). The cell was then discharged at 5 mA g^{-1} to a lower voltage cut-off of 1.8 V. 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 s. 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 Li_2MnSiO_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 *Pmnb* polymorph of Li_2MnSiO_4 with lattice constants $a = 6.30693(2)$ Å,