



Crystal chemistry of the *Pmnb* polymorph of $\text{Li}_2\text{MnSiO}_4$

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ABSTRACT

The crystal structure of the *Pmnb* polymorph of $\text{Li}_2\text{MnSiO}_4$ (prepared by solid-state synthesis in argon at 900 °C) is characterized by Rietveld refinement of structural models using high resolution synchrotron X-ray and neutron powder diffraction data. The crystal structure is confirmed to be isostructural with $\text{Li}_2\text{CdSiO}_4$ with lattice parameters $a=6.30694(3)$, $b=10.75355(4)$, and $c=5.00863(2)$ Å, which are in good agreement with previously published data. No evidence was found for mixed lithium/manganese sites. Testing of the material as a cathode in a lithium cell shows that 1.3 lithium ions per formula unit can be extracted on the first charge cycle but very little lithium can be re-inserted. These results are compared with those of other phase-pure $\text{Li}_2\text{MnSiO}_4$ polymorphs.

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1. Introduction

Over the last ten years, the emphasis in lithium-ion battery development has shifted from small-scale portable applications to large-scale systems. These large-scale systems are required both for electric vehicles and as storage to compensate for the variable output of renewable-energy systems. Current lithium-ion battery chemistries cannot fully meet the demands of these applications in terms of cost as well as cycle- and calendar-life. Research to find new systems and to optimize existing systems is on-going [1–3].

Expensive raw materials are a major contributor to the cost of large-scale lithium ion batteries, with the cathode as the most expensive single component. To meet the market targets for the price of these batteries it is essential to develop low-cost cathode materials [4]. The lithium transition metal orthosilicates ($\text{Li}_2\text{M-SiO}_4$ where M=Fe, Co, or Mn), represent a new class of lithium-ion battery cathode and offer potential cost advantages because of the natural abundance of silica, iron, and manganese [5–9]. $\text{Li}_2\text{FeSiO}_4$ has shown promise as a cathode material [9,10], but $\text{Li}_2\text{MnSiO}_4$ is even more attractive. For $\text{Li}_2\text{MnSiO}_4$, the possibility exists for the extraction of two lithium ions per formula unit at moderate voltages, resulting in a high theoretical capacity ($> 300 \text{ mA h g}^{-1}$ for the complete removal and re-insertion of two lithium ions per formula unit). $\text{Li}_2\text{MnSiO}_4$ has, however, so far

failed to be developed as a cathode because of several limiting factors outlined below [10–14].

The practical application of $\text{Li}_2\text{MnSiO}_4$ as a cathode is limited by its low electronic conductivity of $5 \times 10^{-16} \text{ S cm}^{-1}$ at room temperature, increasing to $3 \times 10^{-14} \text{ S cm}^{-1}$ at 60 °C, which is 5–6 orders of magnitude smaller than that of the poorly conducting LiFePO_4 at room temperature [5,15]. Nanostructuring of particles and application of a conductive carbon coating on particles are both strategies employed to overcome the problem of low conductivity in LiFePO_4 [16]. Carbon addition is also common practice in the synthesis of $\text{Li}_2\text{MnSiO}_4$, resulting in composite materials with both enhanced electronic properties and improved electrochemical performance compared to carbon-free samples [10–14,17–19]. Despite efforts aimed at improving the electronic properties of $\text{Li}_2\text{MnSiO}_4$ by carbon addition, all reported cycling data for $\text{Li}_2\text{MnSiO}_4$ have shown a steady decrease in capacity with cycling. This is in contrast to cycling data for $\text{Li}_2\text{FeSiO}_4$, which maintains a stable discharge capacity for multiple cycles [10,20]. The failure of $\text{Li}_2\text{MnSiO}_4$ to cycle reversibly has been attributed to structural collapse and amorphization upon lithium extraction [5,21]. Detailed studies of the partially delithiated *Pmnb* polymorph of $\text{Li}_2\text{MnSiO}_4$ using in-situ XRD, TEM, and NMR have clearly indicated that partial amorphization of the $\text{Li}_2\text{MnSiO}_4$ structure occurs upon lithium extraction [22]. This raises the question as to whether this amorphization is common to all polymorphs of $\text{Li}_2\text{MnSiO}_4$, or whether other polymorphs perform differently when lithium is extracted.

Phase-pure samples of $\text{Li}_2\text{MnSiO}_4$ are difficult to prepare as the lithium transition metal orthosilicates exhibit several different

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polymorphs when synthesized under moderate conditions [8,21,23]. Arroyo-deDompablo et al. [21] have reported that there are, at least, three polymorphs of $\text{Li}_2\text{MnSiO}_4$ that form at ambient pressure – two orthorhombic forms (adopting $Pmn2_1$ and $Pmnb$ space group symmetries) and a monoclinic form (adopting $P2_1/n$ space group symmetry). Both the low-temperature orthorhombic forms are more stable than the monoclinic form, which can only be prepared above 900 °C [24,25]. The crystal structures of $\text{Li}_2\text{MnSiO}_4$ belong to the group of tetrahedral oxides with all cations tetrahedrally coordinated between distorted close-packed layers of oxygen atoms. The polymorphs can be related to the different polymorphic forms of Li_3PO_4 and differ in the orientation and connectivity of the cation tetrahedra. Structural refinements of the $Pmn2_1$ and the $P2_1/n$ forms have been reported [6,25]. In contrast, while X-ray diffraction data has been collected [21,24], no in-depth structural analysis of the $Pmnb$ form has been reported to date. All synthesized samples of this polymorph have included significant impurities, such as Li_2SiO_3 , Mn_2SiO_4 , MnO , and the $P2_1/n$ polymorph [21,24], preventing accurate structural determination of the $Pmnb$ form of $\text{Li}_2\text{MnSiO}_4$.

In this study we report the facile synthesis by solid-state techniques of essentially single-phase samples of the $Pmnb$ polymorph of $\text{Li}_2\text{MnSiO}_4$ and its crystal-structure determined using synchrotron X-ray powder diffraction (SXRPD) and neutron powder diffraction (NPD) data. Morphological and FTIR spectroscopy data, as well as galvanostatic cell-cycling performance in lithium cells, are also reported.

2. Experimental

Samples of $\text{Li}_2\text{MnSiO}_4$ were synthesized by a solid-state route. Stoichiometric quantities of LiOH (Sigma–Aldrich, > 98%), MnCO_3 (Sigma–Aldrich, > 99.9%), SiO_2 (fumed, Sigma–Aldrich, 0.007 μm), together with 20 mol% adipic acid, were milled with dry hexane in a vibratory ball mill for 1 h. The mixed powders were heated at 1 °C per min to 450 °C for 10 h under dynamic vacuum to decompose the precursors. The resulting fine, dark brown powder was ground in a mortar and pestle and then heated to 700 °C for 10 h in argon in a tube furnace to prevent oxidation of the Mn^{2+} . To complete the reaction, the sample was heated to 900 °C for a further 10 h in argon and allowed to cool to room temperature in the furnace. Sample powders were stored in an argon glovebox.

The synthesized powders were initially characterized by conventional X-ray powder diffraction (XRPD) using a Siemens D5000 and a Panalytical X'pert Pro X-ray diffractometer with Cu-K_α radiation. Additional high-resolution SXRPD data were collected on the Powder Diffraction beamline (10-BM-1) [26] at the Australian Synchrotron using a wavelength (λ) of 0.82599(2) Å, determined using the NIST 660a LaB_6 standard reference material. Powder samples were packed and sealed in 0.5 mm glass capillaries in an argon glovebox and data were collected for 6 min at ambient temperature using Debye–Scherrer geometry. Neutron powder diffraction (NPD) data were collected using the high-resolution powder diffractometer, ECHIDNA, at the Open Pool Australian Light-water (OPAL) reactor facility at the Australian Nuclear Science and Technology Organisation (ANSTO) [27]. Data were collected at $\lambda=1.62285(2)$ Å for 9 h in the 2θ range $14 \leq 2\theta \leq 154^\circ$, with the wavelength determined using the NIST Al_2O_3 SRM 676. Samples were sealed in 6 mm diameter vanadium cans with indium gaskets in an argon glovebox and data were collected at ambient temperature. Rietveld refinements were carried out using the GSAS [28] software suite with the EXPGUI [29] software interface. The SXRPD and NPD datasets were initially refined separately. Finally, a combined refinement of both the

SXRPD and NPD datasets was performed. Atomic parameters for the elements in the starting model of the combined refinement were derived from the single dataset refinements, using the results from the dataset that provided the better contrast for each element relative to others. Using this approach, parameters for manganese and silicon were taken from the SXRPD data-derived model and parameters for the lithium and oxygen were taken from the NPD data-derived model.

Particle morphology was determined by analysis of scanning-electron microscope images obtained with a JEOL JSM-5410LV instrument. Lithium and manganese content was determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES) using a Varian Liberty Series II instrument. Samples were digested in hydrofluoric acid prior to analysis. Silicon is lost in the digestion process and therefore could not be analyzed.

Energy-dispersive spectroscopy (EDS) was performed on carbon-coated powder samples using an electron-probe micro analyzer (EPMA) to determine the manganese to silicon ratio of the product phases. Averages were taken of six measurements at different positions in the sample. Elements with low atomic mass cannot accurately be analyzed on this instrument so it was not possible to accurately determine lithium or oxygen contents.

FTIR spectra were collected on powder samples in transmission mode between 700 and 1400 cm^{-1} using the diamond ATR on a Perkin–Elmer FTIR spectrometer (see the [Supporting Information](#)).

To prepare electrodes for electrochemical characterization the sample powder was ball-milled with Super C-65 carbon (Timcal) in a vibratory ball-mill for 1 h. The resulting powder was mixed with polyvinylidene difluoride (PVDF, Sigma–Aldrich) dissolved in *n*-methyl pyrrolidone (NMP, anhydrous, 99.5%, Sigma–Aldrich) in a ratio of 74:13:13. Cathodes were formed by coating the resulting slurry onto aluminum foil current collectors, followed by drying in vacuum for 10 h at 120 °C and pressing with a hydraulic press to 15 MPa. Typical cathode masses were 1–2 mg with a surface area of 1.2 cm^2 . Swagelok-type electrochemical test-cells were assembled in an argon glovebox. The electrolyte used was a solution of lithium hexafluorophosphate (battery grade, > 99.9%, Aldrich) in a 1:1 mixture by volume of ethylene carbonate and dimethyl carbonate (99%, Sigma–Aldrich). The anode consisted of a 12 mm diameter disk of 0.7 mm thick lithium metal foil. The anode and cathode were separated by two disks of microporous polypropylene separator film (Celgard) saturated with the electrolyte solution. Assembled cells were cycled galvanostatically using a battery analyzer (MTI Corporation).

3. Results and discussion

3.1. Structural determination

XRPD data for the samples formed at 700 °C and 900 °C are shown in Fig. 1(b) and (c), respectively, together with a simulated XRPD pattern of the $Pmn2_1$ form of $\text{Li}_2\text{MnSiO}_4$ using the structural model of Dominko et al. [6] (Fig. 1(a)). We speculate that the presence of the carbon-containing adipic acid in the reaction mixture inhibits the formation of $\text{Li}_2\text{MnSiO}_4$ at 700 °C in argon; after 10 h peaks attributed to both Li_2SiO_3 and MnO remain (Fig. 1(b)). The disappearance of these impurity peaks on further heating to 900 °C for 10 h (Fig. 1(c)) indicates that the reaction approaches completion at this temperature. The product was a dark gray color and the relatively sharp diffraction peaks indicate that a crystalline product formed at the relatively high temperature of 900 °C. Notably, the XRPD data of the material obtained after heating to 900 °C (Fig. 1(c)) contains peaks that are not present in the $Pmn2_1$ model for $\text{Li}_2\text{MnSiO}_4$ (Fig. 1(a)), but

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