Mesoporous electrode materials are favourable for lithium-ion batteries as they have high surface area and provide short lithium-ion diffusion distances from the pore space into the thin pore walls. The porous morphology is also an advantage for buffering the large volume changes that can accompany lithium insertion and extraction. For this reason, this study investigates the synthesis of mesoporous lithium manganese silicate, using mesoporous silica as a template. It is shown that a mesoporous lithium manganese silicate product, retaining the mesoporous symmetry of the SBA-15 silica precursor, can be formed by emulsion synthesis followed by calcination in an inert atmosphere at 700 °C. These calcination conditions retain the decomposed surfactant as a conductive surface layer on the product phase. Undesired, electrochemically inactive MnO impurities were minimized by reducing the Li : Mn ratio to 2 : 0.7 in the starting mixture. Rietveld analysis of the X-ray diffraction patterns of the product shows that it is manganese deficient with composition \( \text{Li}_2\text{Mn}_{0.87(3)}\text{SiO}_4 \) with minor impurities of MnO and \( \text{Li}_2\text{SiO}_3 \). Excellent reversibility is observed for these cathodes in lithium cells with a voltage mode at a current rate of 20 mA g\(^{-1}\).

Rechargeable lithium-ion batteries are commonly used today to power portable, electronic devices. Lithium-ion batteries are also being applied as batteries for electric vehicles and for large-scale storage of energy generated from intermittent renewable sources like solar and wind power. Consumer demands for high capacity, long calendar life and low cost are driving the development of new electrode materials to advance this technology.\(^1,4\)

Mesoporous materials are ordered, porous materials with pores in the range 2–50 nm, typically formed using either soft templates, for example surfactants, or hard templates like mesoporous silica or mesoporous carbon.\(^5,6\) Mesoporous materials have been used as lithium-ion battery electrodes for several reasons.\(^7,8\) Firstly, the interconnected network of pores allows electrolyte penetration into the bulk of the electrode enabling fast kinetics of lithium diffusion. Secondly, the short lithium diffusion distance from the pore space into the thin pore walls allows rapid kinetics and full utilization of the bulk of the material. Thirdly, the porosity allows accommodation of volumetric changes with cycling and results in stabilization of phases that do not cycle reversibly in bulk form.\(^9,10\)

Lithium manganese silicate (\( \text{Li}_2\text{MnSiO}_4 \)) is an attractive option as a lithium ion battery cathode with a potential capacity above 300 mA h g\(^{-1}\) if both lithium ions can be extracted reversibly.\(^11\) The application of \( \text{Li}_2\text{MnSiO}_4 \) as a cathode material is, however, complex. The two main drawbacks of \( \text{Li}_2\text{MnSiO}_4 \) cathodes are, firstly, very low electronic conductivity\(^12,13\) resulting in large polarization and low capacity in bulk material,\(^14\) and, secondly, structural collapse and amorphization as a result of the large volume changes that occur when large amounts of lithium are extracted on charge.\(^12,13,15,16\) The rapid loss of capacity with electrochemical cycling of \( \text{Li}_2\text{MnSiO}_4 \) cathodes has largely been attributed to this structural collapse.\(^16,17\) Both of these problems could be overcome with a mesoporous structure with internal pores to buffer the effect of the volume changes during lithium extraction and insertion, and a conductive surface carbon coating to enhance electronic conductivity.

Herein we report the use of an emulsion synthesis route to prepare a mesoporous cathode material from a mesoporous silica precursor. Emulsion synthesis has been used to prepare a range of lithium battery cathodes.\(^20,21\) In this work a water-in-oil emulsion synthesis route is used to prepare a lithium manganese silicate. Droplets of the aqueous phase consist of Li and Mn precursors and a solid mesoporous silica template in suspension. The aqueous phase is dispersed in an organic solvent containing a surfactant. The surfactant is distributed on
the surface of the droplets of the aqueous phase (Fig. 1). During calcination in an inert atmosphere or vacuum, reaction occurs between the ordered mesoporous SiO₂ and the Li and Mn salts in the aqueous solution to form a lithium manganese silicate. The mesoporous SiO₂ acts as a template for the product and the mesoporosity and symmetry of the SiO₂ precursor is retained in the product. The mesoporous architecture ensures that the electrolyte penetrates into the bulk of the material, as well as potentially accommodating the volume changes associated with lithium insertion and extraction during cell-cycling. The surfactant molecules on the surface of the droplets decompose to form a conductive surface coating to enhance electronic conductivity.

Stoichiometric amounts of lithium acetate dihydrate (LiCH₃COO·2H₂O) and manganese acetate tetrahydrate (Mn(CH₃COO)₂·4H₂O) were dissolved in distilled water. A stoichiometric amount of either mesoporous silica SBA-15 (SiO₂), for the mesoporous sample, or fumed silica, for the bulk control sample, was added and suspended by sonication. This mixture formed the aqueous phase (Fig. 1). The oil phase consisted of cyclohexane as the primary component with 1-butanol and the surfactant Pluronic P123. The ratio of cyclohexane: 1-butanol was typically 8.3 : 1 and 2 g of surfactant was added to 112 ml of mixed organic solvents (1.8 wt%). The solution was mixed vigorously for 1/2 hour to dissolve the surfactant. The aqueous phase was then added to the oil phase to form a milky, water-in-oil emulsion which was magnetically stirred overnight at room temperature. The ratio of aqueous to non-aqueous phases was 1 : 3.7 by volume. The precipitate was then allowed to settle out, excess solvent was decanted off and the resulting product was dried on a hot-plate to give a pinky-brown gel. The gel was transferred to a crucible and heated at 500 °C for 10 h in a dynamic vacuum to remove organic phases and then at 700 °C in vacuum in a closed tube furnace. The calcination of the precursor in the product phase.

Fig. 1 A schematic diagram showing the formation of mesoporous manganese deficient lithium manganese silicate from SBA-15 using emulsion synthesis.

Fig. 2 Images of the mesoporous Mn-deficient lithium manganese silicate prepared from an SBA-15 mesoporous SiO₂ template (a) SEM image and (b) TEM image.

polymer of Li₄MnSiO₄.¹⁴ Emulsion synthesis using a stoichiometric mixture with a Mn : Si ratio of 1 : 1, gave samples containing more than 15% MnO. Since MnO and other impurity phases like Li₂SiO₃ are electrochemically inactive, their content should be minimized. The Mn content in the starting mixture was therefore reduced to give a ratio of Mn : Si of 0.7 : 1 for both the mesoporous and the bulk samples. As a result, the content of the electrochemically inactive MnO component decreased and a manganese deficient product was formed.

The morphology of the mesoporous product was characterized using scanning electron microscopy (SEM) and transmission electron microscopy (TEM) with a Zeiss Gemini Ultra Plus and a JEOL 2100, respectively. The SEM images show that the morphology of the mesoporous SBA-15 precursor (Fig. S1†) is retained in the product (Fig. 2a) and that there is residual carbon from the synthesis on the surface of the product particles. The SEM image of the bulk product is given in Fig. S2.† The TEM image of the mesoporous product (Fig. 2b) shows that the hexagonal mesoporous structure of the SBA-15 precursor, confirmed by the small angle X-ray scattering data discussed later (Fig. 3), is retained in the product after calcination, with the hexagonal order clearly visible in the upper right hand corner of the image (Fig. 2b). A carbon coating, approximately 50 nm thick, from the decomposition of the surfactant under vacuum, is also clearly seen on the surface of the particles (Fig. 2b). Small angle X-ray scattering (SAXS) data were recorded with an Anton Parr ‘SAXSess’ from q = 0.2 to 1.5 nm⁻¹ (Fig. 3),
where \( q \) is the momentum transfer vector defined as \( q = [4\pi \sin(\theta)/\lambda] \), and \( \theta \) is the scattering angle. The Bragg condition is fulfilled when \( d = 2\pi/q \). The pattern of the SBA-15 precursor can be indexed to the hexagonal \( P6_{3}mm \) space group with three well-defined peaks visible in the SAXS spectrum which can be indexed to the 110, 110 and 200 reflections with \( d(110) = 11.00 \) nm for SBA-15 to give a lattice parameter, \( a = 12.7 \) nm.\(^{22} \) The product phase also shows a well-defined 100 peak with \( d(100) = 10.8 \) nm, indicating that the product is mesoporous and retains the hexagonal symmetry of the SiO\(_{2}\) source. The higher order reflections are absent, and the intensity of the (100) peak is reduced, which indicates a reduction in the mesoporous order in the final product compared to the SiO\(_{2}\) precursor. The \( a \) lattice parameter of the mesoporous product, calculated from the planar spacing in the TEM data (Fig. 2b), is 9.8 nm, in good agreement with the value of 9.4 nm obtained from the SAXS data.

The phase composition and crystal structure of the product phases were analyzed with X-ray diffraction data obtained using a Siemens D5000 and Cu K\( \alpha \) radiation (Fig. 4b and S3\(^{†} \)). A simulated X-ray diffraction pattern for the \( Pmn2_{1} \) polymorph of Li\(_{2}\)MnSiO\(_{4}\) is given in Fig. 4a for comparison.\(^{11} \) Rietveld refinement of crystallographic models was performed with the GSAS program\(^{23} \) suite using the EXPGUI interface\(^{24} \) and the powder X-ray diffraction data of the mesoporous Mn-deficient product. The results show that it consists of a Mn-deficient Li\(_{2}\)Mn\(_{0.87}\)SiO\(_{4}\) phase (88(5)% with impurities of MnO (4(1)%) and Li\(_{2}\)SiO\(_{3}\) (8(4)%). Peaks of the mesoporous product are in good agreement with the stoichiometric phase in terms of peak position, although the peak intensities differ significantly due to the manganese deficiency. Lattice constants of the mesoporous product are \( a = 6.307(2) \) Å, \( b = 5.389(2) \) Å and \( c = 4.979(1) \) Å, slightly different to those of the standard \( Pmn2_{1} \) polymorph of Li\(_{2}\)MnSiO\(_{4}\) reported by Dominko et al.\(^{11} \) with \( a = 6.3109(9) \) Å, \( b = 5.3800(9) \) Å and \( c = 4.9662(8) \) Å.

Research shows that it is very difficult to obtain phase-pure samples of Li\(_{2}\)MnSiO\(_{4}\) and many samples, in reported studies, contain secondary impurity phases such as MnO and Li\(_{2}\)SiO\(_{3}\),\(^{19} \) even though they are electrochemically inactive and undesirable.

FTIR spectra of the mesoporous product were acquired using a Perkin-Elmer FTIR spectrometer with a diamond ATR in transmission mode. The spectra of the SBA-15 precursor and the mesoporous product are shown in Fig. S4.\(^{†} \) The strong absorption band of the SBA-15 at \( \sim 1060 \text{ cm}^{-1} \) is replaced in the product by strong bands in the 850–950 cm\(^{-1} \) range, typical of compounds containing SiO\(_{4}^{−}\) groups.\(^{25} \) This confirms the chemical conversion of the mesoporous SiO\(_{2}\) precursor into the product phase after calcination.

The electrochemical performance of the mesoporous electrodes was evaluated in Swagelok cells. The working electrode was formed from a slurry of active material: carbon black: PVDF in a ratio of 74 : 13 : 13 in N-methylpyrrolidone (NMP). The electrode slurry was coated onto Al current collectors and dried in vacuum at 80 °C for 12 h. Cathodes were pressed at 15 MPa prior to cell assembly. Typical cathode masses were 1–2 mg. Lithium metal foil was used as the counter electrode. The electrolyte was a solution of 1 M LiPF\(_{6}\) in 1 : 1: ethylene carbonate : dimethyl carbonate (Merck Selectlyte). The electrochemical performance was determined using MTI cell cyclers at room temperature at a current rate of 20 mA g\(^{−1} \).

![Fig. 4](image)

Fig. 4 (a) A simulated X-ray diffraction pattern of Li\(_{2}\)MnSiO\(_{4}\) (b) Rietveld refinement results of structural models with the powder XRD pattern of the mesoporous Mn-deficient product phase. Black dots represent the experimental data, the model is the red line through the data and the blue line below is the difference between the model and the data.
Communication

A mesoporous lithium manganese silicate cathode was prepared in the same way. This improvement is observed in spite of amorphization of the lithium manganese silicate with cycling.

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**Conclusions**

In this study we demonstrate that a mesoporous lithium manganese silicate can be synthesised from a mesoporous SiO2 precursor using an emulsion synthesis technique. A Mn-deficient product with composition Li2Mn0.87(3)SiO4 was produced that retains the mesoporous order of the silicate precursor. The mesoporous product gives a first discharge capacity of 170 mA h g\(^{-1}\) and good capacity retention using a constant current–constant voltage charging regime at 20 mA g\(^{-1}\). The mesoporous nature of the product allows the electrolyte to penetrate into the bulk of the material to allow rapid lithium ion diffusion into the cathode. This effect results in much improved properties both in terms of capacity and capacity retention for the mesoporous material compared to bulk, non-porous material prepared in the same way. This improvement is observed in spite of amorphization of the lithium manganese silicate with cycling.

Fig. 5 Galvanostatic cycling curves of half-cells containing mesoporous cathodes (a) cycles 1–10 CC cycling (b) cycles 12–20 CC–CV cycling at room temperature and 20 mA g\(^{-1}\) (c) capacity vs. cycle number.
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