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E-Futures

Mini-project report:

**Synthesis and characterisation of
 $\text{Li}_2\text{MnSiO}_4$ for use as a Li-Battery Cathode
Material.**

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ASSIGNMENT COVER SHEET 2011/2012

A completed copy of this sheet MUST be attached to coursework contributing towards theme 2 assessment.

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Degree Course:	E-Futures DTC
Supervisor:	Prof Tony West
Signature:	

I declare that this work is my own and that I have made appropriate reference to any sources used. I am aware of the handbook section on 'Plagiarism' and declare that this work is consistent with those guidelines.

Mini-Project Mark Sheet

Student:

Grade: fail/satisfactory/good/very-good/excellent

Supervisor:

Feedback:

	Excellent	Good	Average	Poor	Very Poor	Not Done	Not applicable
Introduction to the problem / subject							
Statement of aims							
Experimental description							
Presentation of results / findings							
Quality and depth of discussion / interpretation							
Relevance of conclusions							
Quality of English							
Use of reference material							
Evidence of external reading							
Quality of presentation							
Use of figures							

Comments:

Abstract:

A novel solid state synthesis was developed for a potential lithium battery cathode material $\text{Li}_{2+2x}\text{Mn}_{1-x}\text{SiO}_4$ ($-0.1 \leq x \leq 0.2$) using Li_4SiO_4 and Mn_2SiO_4 as precursors. Samples were characterised using powder x-ray diffraction and studied using electrochemical impedance measurements which suggested a 4 order of magnitude increase in conductivity from the stoichiometric product to the $x=0.1$ composition. Initial battery testing was also carried out on the materials using coin cells.

Introduction:

Consumer electronics, electric vehicles and small scale medical devices have triggered a high demand for both compact and lightweight portable energy sources¹. These requirements have subsequently led to the development and commercialisation of modern rechargeable Li-ion batteries¹. The first examples used the Sony cell incorporating LiCoO_2 and either graphite or lithium metal as the electrodes. See fig 1 for details.

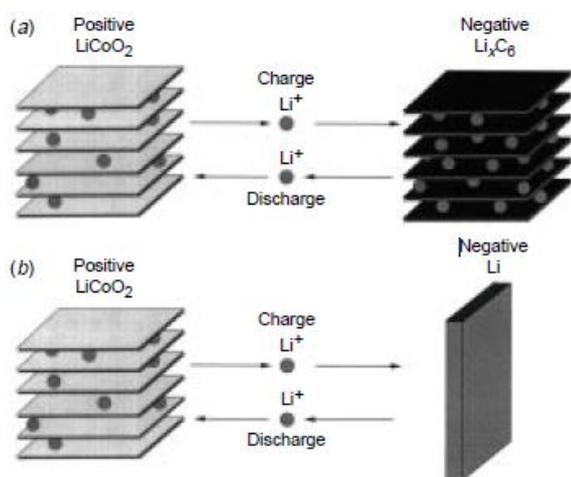


Figure 1 - Sony Cell setup – Image taken from¹

The electrical energy in these devices is stored and released during the movement and intercalation of Li^+ ions from one electrode to another, the charge being maintained by electrons flowing around an external circuit. Both electrodes are required to be good intercalation hosts and also to reversibly release Lithium over many charge-discharge cycles. While LiCoO_2 fits these requirements, much research is involved in finding alternate cathode materials that are less

toxic, cheaper and more stable². One of these potential new cathode materials is $\text{Li}_2\text{MnSiO}_4$.

The synthesis, crystal structure and battery testing of $\text{Li}_2\text{MnSiO}_4$ were first reported by Dominko et al in 2006². The compound was synthesised using a Sol-Gel approach, giving an orthorhombic crystal system which unfortunately showed poor conductivity. Further studies by various groups using both sol-gel and solid state synthesis methods have since showed similar results^{3,4,5}. Several approaches such as carbon coating, nanoparticles and mixes with other structures such as $\text{Li}_2\text{FeSiO}_4$ have also been tried, along with the conduction of various modelling studies^{6,7,8,9,10,11}.

In 2007, Politaev et al. reported on the cation-deficient and cation-excess solid solutions $\text{Li}_{2+2x}\text{Mn}_{1-x}\text{SiO}_4$ ($-0.2 \leq x \leq 0.2$), but their work was for a higher temperature solid state synthesis which seemed to result in a monoclinic crystal system¹². The majority of the studies thus far have focused only on cycling data in electrochemical cells and do not report on the electrical properties of the raw material using techniques such as impedance spectroscopy, which could be useful in understanding more about the electrochemical performance of tested material.

This work aims to report on further research into the solid state synthesis of $\text{Li}_2\text{MnSiO}_4$, focusing on filling some of the gaps in the literature by both developing a synthesis for the $\text{Li}_{2+2x}\text{Mn}_{1-x}\text{SiO}_4$ analogues in the orthorhombic crystal system and reporting on the corresponding impedance spectroscopy of these compounds.

Experimental Work:

Consistent with similar research in the field, initial synthesis methods were based on a three component system. Li_2CO_3 and $\text{Mn}(\text{OAc})_2$ were chosen as the lithium and manganese sources respectively and were ground well with SiO_2 before the reaction took place. Synthesis was then carried out in a tube furnace under a nitrogen atmosphere using a programmed heating cycle. The heating cycle involved a slow decomposition of the acetates, regrinding and analysis using x-ray diffraction, then reheating and reaction at 800°C .

A second and much more successful synthetic method was also explored: synthesis from the two corresponding silicates (Li_4SiO_4 and Mn_2SiO_4). Similar to the method above the reactants were ground together and then heated under a N_2 atmosphere to 800°C . The reaction had distinct advantages over the previous method due to the lack of slow heating required to remove the acetates, easier variation of stoichiometry and less components to form various side products. The precursors however need to be synthesised separately. Phase purity of all methods were analysed via x-ray powder diffraction and samples were reheated where necessary.

Impedance data was recorded using 10mm diameter pellets sintered at 800°C for 4 hours. Gold electrodes were added using Au paste and dried at 800°C for 2 hours. The heating and impedance measurements were recorded under a N_2 atmosphere.

Results and discussions:

Synthesis using the three component system produced a multiphase solid solution which after re-reacting had increased amounts of the desired $\text{Li}_2\text{MnSiO}_4$ product, however ultimately failed to reach phase purity. This can be seen in fig 2.

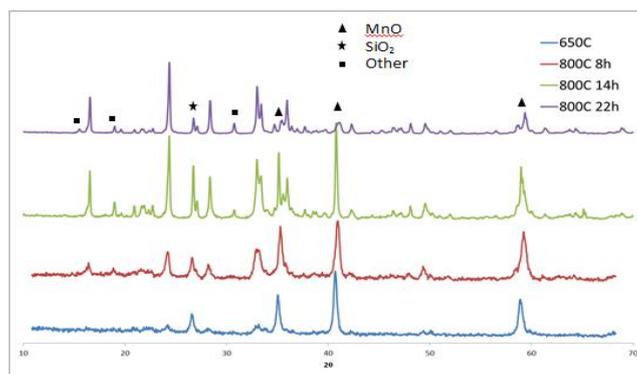


Figure 2 - Progress of three component reaction (non-marked peaks correspond to the desired $\text{Li}_2\text{MnSiO}_4$ phase)

Overall it was deemed that this synthetic route was too inefficient to be explored further. The reaction required extensive reaction time and involved significant mass loss due to decomposition of the acetates and carbonate.

The synthesis from the two silicates, however, was significantly more effective; the precursors were easily synthesised using modified literature methods and when combined produced almost phase pure $\text{Li}_2\text{MnSiO}_4$ from only one heating cycle of 12 hours. The stoichiometry could also be easily varied to give $\text{Li}_{2+2x}\text{Mn}_{1-x}\text{SiO}_4$ of $x = -0.1, 0, 0.1, 0.2$. The XRD Patterns can be seen in fig 3.

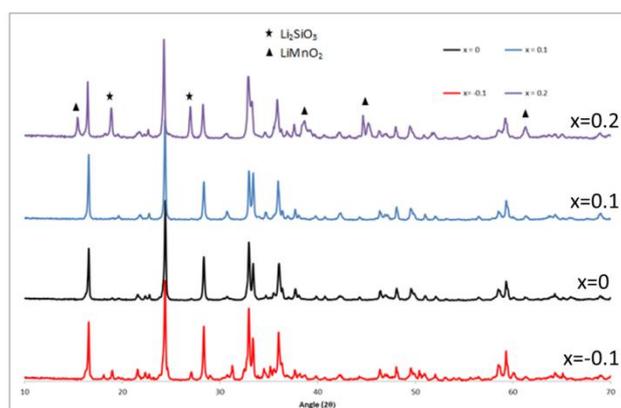


Figure 3 - XRD Patterns for $\text{Li}_{2+2x}\text{Mn}_{1-x}\text{SiO}_4$ (unmarked peaks are for desired phase in the orthorhombic crystal system)

Figure 3 shows that the reaction was successful for the $x=0$ and 0.1 compositions, both indexing to an orthorhombic crystal system that is close to reports in literature². The lattice parameters of $x=0$ and $x=0.1$ varied slightly in the a and c dimensions, $a=6.3117$, $b=5.3740$, $c=4.9940$ and

$a=6.3084$, $b=5.3738$, 4.9997 respectively. Further investigation using other compositions is required to identify any trends. Slight impurities existed in the $x=-0.1$ composition and larger impurities are present in $x=0.2$. These two compositions were synthesised in pelletized form rather than in powders and therefore it is unknown if the reaction is still incomplete and requires additional heating, or if it is because the compositions cannot be formed by this method.

Impedance spectroscopy was carried out on both the $x=0$ and $x=0.1$ compositions. The $x=0$ showed very high resistance even at high temperatures (10^8 Ohms at 500°C), whereas $x=0.1$ showed significant conductivity improvements from the parent composition. Figure 4 shows the Nyquist plots from varying temperatures under N_2 atmosphere.

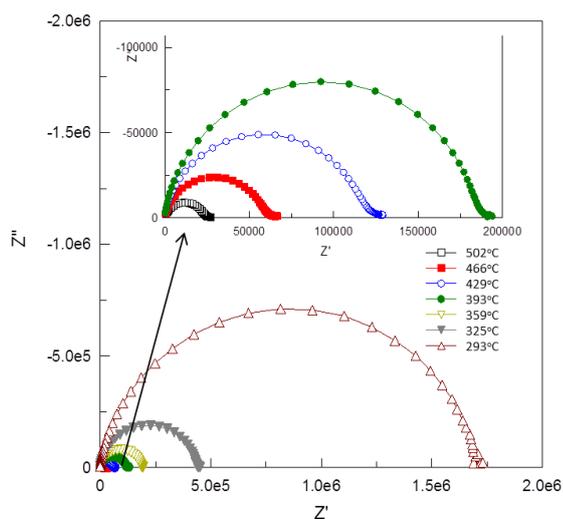


Figure 4 - Nyquist plot for $x=0.1$

This impedance data could suggest either ionic or electronic conductivity; the semicircle is not completely symmetrical, but there is no obvious spike suggesting an ionic conductor. Figure 5 shows the Arrhenius plot for both compositions, the values for $x=0$ are estimated from incomplete semi-circles due to its high resistance and therefore are only suggestive of the order of magnitude of the points. The data indicates a 4 order of magnitude increase in conductivity for the increased lithium composition. The linearity of

the data points also suggests that the material can be modelled by the Arrhenius equation, and therefore an activation energy of 0.93eV can be calculated. This value is reasonable for the type of material, but a good ionic conducting cathode material would be expected to have a value of $0.4\text{--}0.5\text{eV}$.

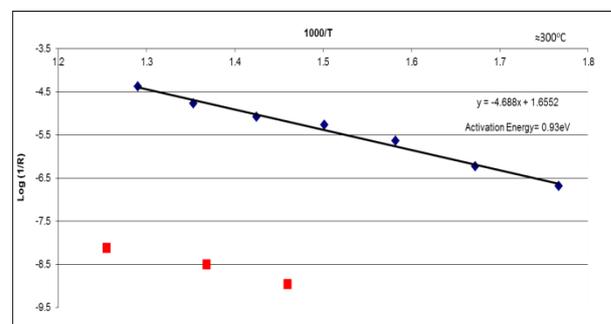


Figure 5 - Arrhenius Plot for $x=0$ and $x=0.1$ compositions. Red markers represents $x=0$, blue markers represent $x=0.1$

Initial battery testing showed poor results for both compositions tested. Cell preparation involved pellet formation using the active material, carbon and PDVF in a ratio of 80:10:10 respectively. This composition resulted in weak pellets which may not have survived under the pressing process in coin cell assembly.

Conclusions:

Phase pure synthesis for the $x=0$ and $x=0.1$ compositions of $\text{Li}_{2+2x}\text{Mn}_{1-x}\text{SiO}_4$ in an orthorhombic crystal system was successfully achieved using Li_4SiO_4 and Mn_2SiO_4 precursors. Impedance data collected on these compositions has shown roughly a 4 order of magnitude increase in conductivity for the increased lithium content composition ($x=0.1$), compared to the stoichiometric material. This result is promising for the development of the material as a cathode, however further research on the synthesis of other compositions and their electrochemical characterisation is required. Further work on battery testing is also required, particularly in the preparation technique.

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