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Hydrothermal Synthesis of Li$_2$MnSiO$_4$: Investigation of the Effects of Different Reaction Conditions

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Hydrothermal Synthesis of Li$_2$MnSiO$_4$: Investigation of the Effects of Different Reaction Conditions

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**Major Qualified Project**
April 30$^{th}$, 2014
Abstract

Lithium ion batteries have been studied as major power resource for decades due to their high energy density, cycling ability and low self-discharge rate. For the next generation of such batteries, intensive research has been done to develop improved electrode materials. The objective of this project was to produce a new kind of cathode material, which would be applied to different industrial areas. The synthesis of Li$_2$MnSiO$_4$ through hydrothermal reaction was examined in terms of optimal reaction conditions. The results indicated that heating the raw materials at 180°C for 42h, and then annealing it at 700°C for 10h would produce better products. Hydrothermal reaction is a promising method to produce the Li-rich cathode due to high yields, low reaction temperature, and short reaction time.
Acknowledgement

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Executive Summary

Lithium ion batteries are widely used in today’s world because of their unique advantages: high voltage, low self-discharge rate, and low toxicity (Meng Zhang, 2012). However, the existing lithium-ion batteries still need to be improved due to several disadvantages, such as comparatively low capacity or cycling ability. Scientists spend their effort trying to find out ways that can improve electrical performance of lithium ion batteries, and a lot of researches have been done on some potential cathode materials. Lithium silicate (Li$_2$MSiO$_4$, M=Co, Ni, Mn and Fe) is one of the potential candidates since it possesses higher theoretical capacity and can be synthesized in an easier pathway. For example, Li$_2$FeSiO$_4$ is such a new kind of cathode material, which is low-cost, environmentally friendly, safe, and electrochemical stable (Meng Zhang, 2012).

The goal of this project was to figure out the optimal reaction conditions when synthesizing Li$_2$MnSiO$_4$ using hydrothermal method. Compared with the popular synthesis method-sol gel method, the hydrothermal method is promising because the target product can be produced at a low temperature, which is around 170-180°C, and heated for a short time period. The mechanism of hydrothermal reaction is similar to that of sol gel synthesis. Firstly, one of the raw materials tetraethyl orthosilicate (Si(OC$_2$H$_5$)$_4$) is hydrolyzed to form HO-Si(OC$_2$H$_5$)$_3$ and C$_2$H$_5$OH, then pieces of HO-Si(OC$_2$H$_5$)$_3$ can polymerize together to form network structure of -Si-O-Si-, the last step is calcination, Li$^+$ and M$^{2+}$ add to the -Si-O-Si- network structure to produce Li$_2$MSiO$_4$ (M=Co, Ni, Mn and Fe) complex.
In the synthesis process, the ratio of was set as Li:Mn:Si=2:1:1 accord with the molecular formula of Li$_2$MnSiO$_4$. In order to find the optimal temperature and reaction time, a series of experiments were done. Firstly, one group of raw materials was heated at 200°C for 42h, but the result was not as good as the one referred in literature (Jintae Hwang, 2013). Then, six groups of raw materials were heated at 180°C for 14h, 28h, 42h, 56h and 70h respectively. The best products were synthesized when heated for 42h at 180°C.

Figure 13 is the Scanning Electron Microscope (SEM) image of this sample. The particles are in nano-scale, with size of approximately 100nm, and they are identical and uniform. Figure 17 is the X-ray Powder Diffraction image, and the marked peaks came from the database of PANalytical, which are the characteristic peaks of Li$_2$MnSiO$_4$.

Based on the research results, we concluded that uniform target nanoparticles were successfully synthesized when heating the raw materials for 42h at 180°C. Hydrothermal synthesis method was proved to be promising due to the easier reaction conditions compared with the sol gel method. However, the electrochemical performance of the cathode material synthesized by hydrothermal reaction has not been investigated, so further work should be done to test its electrochemical properties. Only at that point, the hydrothermal method can be proved to be a better alternative method to produce better lithium silicate cathode materials.
Chapter 1: Introduction

After two decades of extensive research, lithium ion battery has appeared to be approaching optimal power and energy density with cost and safety remaining as major concerns (Ilias Belharouak, 2009). Most mature lithium ion batteries revolutionized the portable electronics market, and now they are being intensively pursued for electric vehicle applications (T. Muraliganth, 2010). The success of lithium ion technology for the future applications will depend mostly on the cost, safety, cycle life, energy, and power, which are in turn controlled by the component materials used (Manthiram, 2011). Active materials with higher lithium ion content per formula unit can demonstrate higher capacity (Jintae Hwang, 2013). The silicate Li$_2$MSiO$_4$ (M=Mn and/or Fe) is one kind of Li-rich cathode combined with active material. This material emerged in 2005 as promising high-energy cathodes materials because of the theoretical possibility of exchanging two lithium ions per molecule (D. Santamaría-Pérez, 2012). In theory, the capacity of Li-ion batteries should be double (Masaki Yoshio, 2009). Compared with other transition metal complexes, such as LiNiO$_4$ and LiCoO$_4$, which have the ability to exchange only one electron per molecule, the Li-rich complex is promising.

Sol-gel process to synthesize Li$_2$MSiO$_4$ has been widely studied. This technique with additives was used to overcome the disadvantages of Li$_2$MSiO$_4$, such as poor electrical conductivity and severe capacity fading, by reducing the particle size and coating the particles with carbon. However, the reported capacities were still much lower than the theoretical capacity (R. Dominko, 2007). Hydrothermal synthesis is known as more energy effective than sol-gel synthesis, and Jintae Hwang etc. conducted hydrothermal
reaction to synthesize Li$_2$MnSiO$_4$ successfully (Jintae Hwang, 2013). Hydrothermal synthesis allows the accurate control of reaction conditions in a closed system such as pH, pressure, temperature, and surfactant addition (Wojciech L. Suchanek, 2006). Despite of these advantages mentioned above, the literature resources about the hydrothermal reaction to synthesis Li$_2$MSiO$_4$ (M=Mn and/or Fe) is rare. Thus, further studies about the optimal conditions need to be conducted. Different temperatures and reaction times were set up to perform different reactions. SEM and XRD techniques were utilized to characterize the synthesized products. In order to investigate whether this method could improve the electrochemical performance of Li$_2$MSiO$_4$, the electrochemical tests needs to be conducted in the future.
Chapter 2: Background

The relevant background information about lithium ion batteries is provided as follows. Firstly, the history of Li-ion batteries is discussed to give detailed information about the development of Li-ion batteries in early years. Due to the advanced technologies, the techniques to produce lithium batteries were improved in a great degree. Thus it is necessary to know the trends of development of Li-ion batteries. Besides the history and development, the mechanism of Li-ion batteries will also be discussed to give general theoretical background. In order to know more about lithium silicate materials, the information about the materials themselves and characterization methods will be displayed in this section.

2.1 Development of Li-ion Batteries

Brodd etc. in their book says that Sony Co. firstly introduced lithium-ion batteries to the commercial market in 1991 (Masaki Yoshio, 2009). After being popular all over the world, lithium-ion batteries were immediately being used to power digital products such as cell phones, digital cameras, laptops, and other portable electronics due to their high energy density, high cycling ability, long retention of charge memory and small self-discharge rate. Expansion of lithium ion battery technology into automobiles, aerospace, and power-grid applications demand the development of lightweight, high-longevity batteries (Dinesh Rangappa, 2012). Lithium is the lightest metal, has the greatest electrochemical potential, and provides the largest energy content. This allows the lithium-ion battery to provide the same amount of energy in a smaller, more lightweight
package than the competing technologies (Kevin Keane, 2013). From 1991 to 2006, the demands and supplies of lithium-ion batteries experienced a great growth. Researches on li-ion batteries continued to improve their electrochemical properties. The huge demands from the commercial market and the advanced technologies push researchers to create higher-quality, safer and multifunctional lithium ion batteries.

The future of lithium ion batteries is promising. After prevalently being used on portable products, the researches has already turned their research topic on those products have big shapes, such as vehicles, for recent years. The United States government has created a department called the Advanced Technology Department (ATD), which is intended to assist the development of lithium ion batteries for use in electric cars (Boucher, 2012). The electric car will be a breakthrough not only in the cars industry, but also in the electronic industry. In terms of the current studies, the problem of the development of fully electric cars is that the comparatively low capacity of lithium ion batteries. The lithium ion battery typically reduced their capacity after being used for one year, though some of them could be improved to extend the lifetime to 2 or 3 years, which is still far away from the needs for an electric car. Due to the deficiency of the capacity, a fully electric car cannot travel far because it needs to be recharged after traveling only several hours. Recharging is not a task as easy as refilling gas oil. It usually takes many hours to recharge an electric car.

Changing the electrode or electrolyte materials is a way to create higher-quality lithium ion batteries. In this project, we synthesized new kind of cathode material to investigate
the optimal reaction conditions. The results could be used for further researches on electrochemical property testing.

2.2 Mechanism of Li-ion Batteries

Lithium ion battery is one of the most promising secondary batteries, according to “Searching for Better Batteries” done by Riezenman in 1995 (Riezenman, 1995). Figure 1 shows the electrochemical properties of several batteries still used in today’s market (Riezenman, 1995).

![Table of electrochemical properties of batteries](image)

<table>
<thead>
<tr>
<th>Cell type</th>
<th>Nominal voltage, V</th>
<th>Specific energy, Wh/kg</th>
<th>Energy density, Wh/L</th>
<th>Specific power, W/kg</th>
<th>Power density, W/L</th>
<th>Self-discharge, %/month</th>
<th>Cycle life*</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkaline†</td>
<td>1.5</td>
<td>150</td>
<td>375</td>
<td>14</td>
<td>35</td>
<td>0.3</td>
<td>1</td>
<td>Not rechargeable</td>
</tr>
<tr>
<td>Lead-acid</td>
<td>2.0</td>
<td>35</td>
<td>70</td>
<td>-200</td>
<td>-400</td>
<td>4-8</td>
<td>250-500</td>
<td>Least-cost technology</td>
</tr>
<tr>
<td>Lithium-ion</td>
<td>3.6+</td>
<td>115</td>
<td>260</td>
<td>200-250</td>
<td>400-500</td>
<td>5-10</td>
<td>500-1000</td>
<td>Intrinsically safe; contains no metallic lithium</td>
</tr>
<tr>
<td>Lithium-polymer‡</td>
<td>3.0</td>
<td>100-200</td>
<td>150-350</td>
<td>&gt;230+</td>
<td>&gt;350+</td>
<td>-1</td>
<td>200-1000</td>
<td>Not yet available commercially; contains metallic lithium</td>
</tr>
<tr>
<td>Nickel-cadmium</td>
<td>1.2</td>
<td>40-60</td>
<td>60-100</td>
<td>140-220</td>
<td>220-360</td>
<td>19-20</td>
<td>300-700</td>
<td>Exhibits memory effect</td>
</tr>
<tr>
<td>Nickel-metal hydride†</td>
<td>1.2</td>
<td>60</td>
<td>220</td>
<td>130</td>
<td>475</td>
<td>30</td>
<td>300-600</td>
<td>May exhibit slight memory effect—experts disagree</td>
</tr>
<tr>
<td>Zinc-air+</td>
<td>1.2</td>
<td>146</td>
<td>204</td>
<td>130</td>
<td>190</td>
<td>-5</td>
<td>-200</td>
<td>Requires air manager to limit self-discharge</td>
</tr>
</tbody>
</table>

* Very broad ranges are shown because cycle life is strongly dependent on how the battery is treated.
† Data on the popular Duracell alkaline D cell is included just to put rechargeable batteries in perspective.
‡ Li-ion cells with petroleum coke anodes drop from about 4.0 to about 3.0 V, in fairly linear fashion as they go from fully charged to fully discharged.
§ Since commercial units are at least a year away, these figures are only predictive.
+ These power figures apply at full charge; they will drop considerably as the cell discharges.
¹ Ni-MH data applies to 2.9 Ah 4/5 A cell, of the kind made by Duracell and Toshiba.
‡ Zinc-air data is for the cell that Zinc-Air Power is about to use in a prototype battery for electric vehicles.

Figure 1: The electrochemical performance of promising batteries in commercial market.
Lithium ion batteries are light, compact and work with a voltage of the order of 4V with specific energy ranging between 100 Wh Kg$^{-1}$ and 150 Wh Kg$^{-1}$. A common structure of lithium ion battery is shown in Figure 2 (Bruno Scrosati, 2010).

![Figure 2: Scheme of a common lithium ion battery](image)

In general, a lithium ion battery contains a cathode made up of lithium complex material, an electrolyte material can be liquid or solid with lithium salt, and a anode consisted of graphite. In most common cases these batteries are based on the C/LiPF$_6$ in EC-DMC/LiMO$_2$ sequence and operate on a process:

$$yC + LiMO_2 \leftrightarrow LixCy + Li(1-x)MO_2, x \sim 0.5, y = 6, \text{voltage} \sim 3.7 \text{ V}$$

involving the reversible extraction and insertion of lithium ions between two electrodes with concomitant removal and addition of electrons (Bruno Scrosati, 2010). That’s to say, the
battery emit stored energy by exchange electrons and ions. And it must be a completed circuit, when recharging happens, the lithium ion travel from cathode to anode, and electrons travel from cathode to anode through the external circuit; while discharging takes place, the lithium ions on the anode pass through the separator in the electrolyte and insert in cathode material, and the electrons on the anodes travel to cathode through the external circuit. Current is generated through electrons movement in the external circuit. As all of the lithium ions are extracted from cathode and reached to anode, the recharge process is completed. While, reversing the reaction by forcing electrons release from the battery to drive the ions in electrolyte move from the cathode to the anode to complete the discharge process.

The contact area of the electrodes with the electrolyte controls the energy of the external current in the circuit. Larger contact area leads higher ability for the ions to react, which means more places to carry out reaction. Another aspect related to the transference of energy is the ions themselves. Lithium ion is readily being accepted due to the structure of the lithium complex shown in Figure 3 (Explaining Lithium-ion Chemistries, 2014):
The ideal chemical structure of LiMn$_2$O$_4$ is a layered crystal. When the cathode material is produced, the matrix with lithium ions filled into the holes of the matrix is formed (Explaining Lithium-ion Chemistries, 2014).

2.3 Lithium Silicate Materials

Researchers are trying their best to find alternative lithium materials for decades. The alternatives should be cheaper, safer, more stable and less toxic. Iron based active material is a well-known ideal candidate. Before Li$_2$FeSiO$_4$ being investigated, the LiFePO$_4$ material attracts researchers’ attention due to its strong stability because of the strong covalent P-O bond. However, the shortage of this complex is that it has low electron conductivity. Since the first report of Li$_2$FeSiO$_4$ in 2005, the new Li$_2$MSiO$_4$
silicate class of cathode materials \((M = \text{Fe, Mn, and Co})\) has drawn increasingly more attention (Guang He, 2013). Then the Lithium iron silicate material is proved to be quite good material that holds better reversible capacity (84% of the theoretical value) (N. Kuganathan, 2009). In 2006, Dominko etc. did research on the structure and electrochemical performance of \(\text{Li}_2\text{MnSiO}_4\) and \(\text{Li}_2\text{FeSiO}_4\) proved that the lithium silicates show a better stability even in a harsh condition and high ionic conductivity. That’s the starting point of researches on lithium silicates (R. Dominko, 2007).

The definition of polymorphism is the capability of crystalline materials existing in more than one crystal structure within material chemistry. The polymorphism can be found in many crystalline materials, such as polymers, minerals, and transitional metals. Silica is able to form many kinds of polymorphs. Those polymorphs have different stabilities and may spontaneously convert from an unstable form to a stable form at a particular temperature. They also exhibit different melting points and solubilities, x-ray crystals and diffraction patterns (Kevin Keane, 2013). Kalpakjian gave out various conditions that will influence the polymorphs of crystalline. These conditions are as follows:

1) Effects of solvent (packing types of crystals may be different in polar and nonpolar solvents);

2) Certain impurities that inhibit the growth pattern and favor the growth of a metastable polymorph;

3) Level of super-saturation from which a material is crystallized (the higher the concentration above the solubility is, the more likely of metastable formation is);

4) Temperature at which crystallization occurs;
5) Geometry of covalent bonds (different covalent bonds lead to different conformation polymorphism);

6) Modification in stirring conditions (Kalpakjian, 1995).

2.3.1 \(\text{Li}_2\text{MnSiO}_4\)

\(\text{Li}_2\text{MnSiO}_4\) has been identified recently as one of the first cathode battery materials that, at least in theory, could exchange 2 lithium ions per redox-active transition metal ion (Anton Kokalj, 2007). The structure of \(\text{Li}_2\text{MnSiO}_4\) cathode materials for lithium batteries was studied by Santamaría-Pérez et al. in 2012 (D. Santamaría-Pérez, 2012). Figure 4 shows the structures of the \(\text{Li}_2\text{MSiO}_4\) (\(M=\text{Fe, Mn, Co}\)) polymorphs crystallizing in the \(Pbn2_1\) and \(Pmn2_1\) groups, which is the densest polymorph (D. Santamaría-Pérez, 2012).
Figure 4: (a) Crystal structure of the Li$_2$CoSiO$_4$ polymorph crystallizing with space group $Pbn\overline{2}_1$. (b) 3D framework of the [CoSiO$_4$]$^{2-}$ anion consisting of four- and eight-membered rings similar to those of compounds Rb[AlSiO$_4$] and Li(H$_2$O)[AlSiO$_4$]. (c) Crystal structure of the Li$_2$FeSiO$_4$ polymorph crystallizing with space group $Pmn\overline{2}_1$. (d) Layers formed by the [FeSiO$_4$]$^{2-}$ anion. Color code: Li, yellow; Co, cyan; Fe, orange; Si, gray; O, red.

The $Pbn\overline{2}_1$ polymorph shown by Figure 4a is the most stable form of Li$_2$MSiO$_4$ (except for Mn) and this structure consists of parallel chains of alternating [LiO$_4$] and [M(Si)O$_4$]
tetrahedral along the a axis. As far as known, the structures of all Li$_2$MSiO$_4$ polymorphs are built up from [SiO$_4$], [LiO$_4$], and [MO$_4$] tetrahedral units. But this tetrahedral structure is identified as a drawback for optimal electrochemical performance (Shaohua Luo, 2012). Half of the Si ions replaced by M ions, so the complex Li$_2$MSiO$_4$ is regarded as a tectosilicate. The denser polymorph Pmn2$_1$, usually found in the synthesis of Li$_2$MnSiO$_4$ is shown by Figure 4c and 4d. Pmn2$_1$ is built up from infinite layers of composition [SiMO$_4$]$_\infty$ lying on the ac plane and linked along the b axis by [LiO$_4$] tetrahedral. Within these layers, each [SiO$_4$] tetrahedron shares its four corners with four neighboring [MO$_4$] tetrahedral, and vice versa (D. Santamaría-Pérez, 2012). The results of this experiment demonstrated that the difficulty in preparing novel high-pressure polymorphs of Li$_2$MnSiO$_4$ is not attributable to the low compressibility of the Li$_2$MnSiO$_4$ structures but rather to the strong cationic repulsion that would exists in the denser forms. In order to improve the electrochemical performance of Li$_2$MnSiO$_4$ compounds, chemical modifications should be applied.

2.3.2 Li$_2$FeSiO$_4$

The structures of Li$_2$FeSiO$_4$ polymorphs were reported in 2012 (P. Zhang, 2012). In that report, the equilibrium voltage and structural stability has also been reported. Researches focused on the Pmn2$_1$, P2$_1$/n and Pmnb three crystalline space groups, studying their structural characteristics, thermodynamic stability and the electrochemical performances. The results illustrate that the strong Si-O bonds remain unchanged during the lithiation-delithiation process for all the polymorphs (See Figure 5), which contribute mostly to the structural stability.
The differences in local environments around FeO₄ tetrahedra-structure can be translated into varying degrees of distortion of FeO₄ that influenced the structural stability and the equilibrium voltage in all Li₂FeSiO₄ polymorphs. In addition, a high degree of distortion of FeO₄ tetrahedron results in low structural stability. A polymorph with more stable Li₂FeSiO₄ structure has been shown to output a higher voltage. It is in agreement with that Li₂FeSiO₄ has the possibility to extract more than one lithium-ion per molecule in terms of P2₁/n polymorph (P. Zhang, 2012).

### 2.4 Characterization Methodologies

In this project, Scanning Electron Microscopy (SEM) and X-ray Powder Diffraction (XRD) were used to characterize the unknown complex. These two methods are popular imaging and analysis tools generally used in many research areas, such as the chemistry
of materials and life science, to displace the features or characteristics of a certain material, which helps researchers to determine the structure and properties of that material.

2.4.1 Scanning Electron Microscopy (SEM)

The first commercial used scanning electron microscope (SEM) was invented in 1965 as an advanced researcher tool for cell biology. As technology develops, different kinds of SEMs were produced to satisfy different needs from different scientific research areas. The SEM permits the observation and characterization of heterogeneous organic and inorganic materials on scales from nanometer (nm) to micrometer (µm) scale. The popularity of the SEM stems from its capability of obtaining three-dimension images of the surfaces within a very wide range of materials (Joseph Goldstein, 2003).

SEM is provided for producing a scan image at high spatial resolution and in a low acceleration voltage area (United States Patent No. 5,872,358, 1999). After being scanned by SEM, a 3D structure image of a specific material will be displayed. Through this image, researchers can observe the morphology and composition of that material. Generally, the sample is scanned when a beam of electrons with high energy emitted by the machine and react with the material atoms. There are various signals generated, which can be detected. The image signals of greatest interest are the secondary and backscattered electrons because these vary as results of differences in surface topography (Joseph Goldstein, 2003). By analyzing these signals, the detailed information including
morphology, crystalline structure and composition etc. of the sample can be reflected by the image.

The operating principles were talked by Lerner etc., in their report published in 2008, they said that the conventional microscopes use light and several lenses to magnify images, whereas SEM uses electron beams to sweep the surface of specimens, producing magnified images in black and white. In most SEMs, samples are placed in a vacuum chamber after being prepared to be electric conductive. When the sample is placed in the chamber, the air is extracted and an electron gun at the top of the chamber emits a beam of electrons, which passes through a series of magnetic lenses that condense the beam into an extremely fine focus, capable of sweeping nanoparticles on the sample surface. A scanning device near the bottom of the vacuum chamber controls the movement of the electron beam across the sample. As the electron beam sweeps the surface of sample, it simulates electrons existing in the atomic structure of molecules, which causes some of them to escape from the surface. These escaping electrons have specific energies that can be measured. When they are released from each part of the sample, they are collected and counted by a detector that sends their amplified signals. The various electronic energies are analyzed by computer software, and the resulting image is displayed on a computer monitor (Lerner, 2008). Figure 6 shows the general structure of the scanning electron microscopes (Reimer, 1998).
2.4.2 X-ray Powder Diffraction (XRD)

X-ray powder diffraction is an important technique in the field of materials characterization to get information on an atomic scale from both crystalline and noncrystalline materials (C. Suryanarayana, 1998). The X-rays are made to contact the sample at a range of different angles and the diffraction intensities are measured for each, and the intensities can be reflected by the height of peaks. Every crystalline structure for
every chemical compound has a unique diffraction pattern. The International Center Diffraction Data (ICDD) maintains a database of all known diffraction patterns. These known patterns can be compared to an unknown sample to identify the species (Boucher, 2012).

In 1912, Max von Laue discovered that the characteristics of x-rays make them particularly well suited for studying the atomic spacing and crystal structure of a substance (Dutrow, 2011). Its immediate application to structure determination happened in 1913, Bragg paved the way for successful utilization of this technique to determine crystal structures of metals and alloys, minerals, inorganic compounds, polymers, and organic materials. Subsequently, the technique of X-ray diffraction was also applied to derive information on the structure of materials-crystallite size, lattice strain, chemical composition and state of ordering, etc. (C. Suryanarayana, 1998).

Figure 7 shows the three basic components of an X-ray diffractometer, which are X-ray source, sample and X-ray detector (Dutrow, 2011).
The angle between the plane of the sample and the X-ray source is called Bragg angle $\theta$. The angle between the projection of the X-ray source and the detector is $2\theta$. For this reason the X-ray diffraction patterns are produced with this geometry are often known as $\theta$-$2\theta$ scans. In the $\theta$-$2\theta$ geometry the X-ray source is fixed, and the detector moves through a range of angles. The radius of the focusing circle is not constant but increases as the angle $2\theta$ decreases (Dutrow, 2011).

X-rays are generated by directing an electron beam in high voltage to a metal target anode inside an evacuated X-ray tube. In a typical x-ray diffraction experiment, a thin layer of crystalline powder is spread evenly onto a planar slide, which is often a nondiffracting material such as a glass microscope slide, and exposed to the X-ray beam.
When an X-ray beam, which is a kind of high-energy electromagnetic radiation, contacts with the atom’s electrons. The interaction will alter the path of the X-rays. In almost all directions the diffracted X-rays from each atom will combine and effectively cancel each other out. However, when all the atoms are arranged in a periodic fashion (definition of a crystal), in certain directions, the interferences will combine to produce a diffracted x-ray beam (Chapter 7: Basics of X-ray Diffraction, 1999).
Chapter 3: Experiments

The reaction mechanism is shown in Figure 8. Firstly, one of the raw materials tetraethyl orthosilicate (Si(OC\textsubscript{2}H\textsubscript{5})\textsubscript{4}) hydrolyzed to form HO-Si(OC\textsubscript{2}H\textsubscript{5})\textsubscript{3} and C\textsubscript{2}H\textsubscript{5}OH, then pieces of HO-Si(OC\textsubscript{2}H\textsubscript{5})\textsubscript{3} can polymerized together to form network structure of -Si-O-Si-, the last step is calcination, LiR+M\textsuperscript{2+}R\textsubscript{2}+-Si-O-Si- to produce Li\textsubscript{2}MSiO\textsubscript{4} (M=Co, Ni, Mn and Fe).

- **Hydrolysis**
  \[ \text{Si(OC}_2\text{H}_5)_4 + \text{H}_2\text{O} \rightarrow \text{HO-Si(OC}_2\text{H}_5)_3 + \text{C}_2\text{H}_5\text{OH} \]

- **Polymerization**
  \[ -\text{Si-OH+HO-Si} \rightarrow -\text{Si-O-Si} + \text{H}_2\text{O} \]
  \[ -\text{Si-OC}_2\text{H}_5 + \text{HO-Si} \rightarrow -\text{Si-O-Si} + \text{C}_2\text{H}_6\text{O} \]

- **Calcination**
  \[ \text{LiR+M}^{2+}\text{R}_2 + \text{SiO}_2 \rightarrow \text{Li}_2\text{MSiO}_4 \] \(\text{R=organic acids, M=Fe}^{2+},\text{Mn}^{2+}\)

**Figure 8: The reaction mechanism of hydrothermal synthesis method**

Lithium acetate (CH\textsubscript{3}COOLi\cdot2H\textsubscript{2}O), Manganese (II) acetate tetrahydrate (Mn(Ac)\textsubscript{2}·4H\textsubscript{2}O), and Tetraethyl orthosilicate (Si(OC\textsubscript{2}H\textsubscript{5})\textsubscript{4}) were used as the starting materials for the hydrothermal synthesis of Li\textsubscript{2}MnSiO\textsubscript{4}. The molar ratio of Li: Mn: Si was set as 2:1:1. A mixture consisted of 1.0g of Mn(Ac)\textsubscript{2}·4H\textsubscript{2}O, 0.91g of CH\textsubscript{3}COOLi·2H\textsubscript{2}O, 0.92mL of Si(OC\textsubscript{2}H\textsubscript{5})\textsubscript{4} and 3.08ml distilled water was prepared, and the total volume of the solution to be 4ml. The mixture was stirred at room temperature for 10 minutes and then transferred to a 5ml Teflon-lined vessel sealed in a stainless steel autoclave. In the first assay, the mixture in the autoclave was heated at 200 °C for 42 hours. The following six groups of mixtures were heated at 180 °C for 14h, 28h, 42h, 56h and 70h respectively.
After cooling down to room temperature, the products were collected by suction filtration. The precipitates were dried in vacuum furnace (Figure 9(c)) and then annealed at 700 °C for 10 hours with the protection of nitrogen (Figure 9(d)). Figure 8 shows the process of the whole experiment. Figure 9(a) shows the raw materials, the 5ml Teflon-lined vessel and a steel autoclave used in this project. Figure 9(b) is the furnace used to heat the raw materials for different time periods at different temperatures. After being synthesized, the product samples were put into SEM and XRD (Figure 9(e)) to be characterized.

<table>
<thead>
<tr>
<th></th>
<th>14h</th>
<th>28h</th>
<th>42h</th>
<th>56h</th>
<th>70h</th>
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<td><strong>180°C</strong></td>
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<td><strong>200°C</strong></td>
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Table 1: Different temperatures and heating time periods used in experiments
Figure 9: Flow Chart of Experiment

CH$_3$COOLi•2H$_2$O: 0.91g
Mn(CH$_3$COO)$_2$•4H$_2$O: 1.0g
Si(OC$_2$H$_5$)$_4$: 0.92ml
DI H$_2$O: 3.08ml
Li:Mn:Si=2:1:1

Reaction:
Condition 1: 180°C, 1.2883bar: 14h, 28h, 42h, 56h, 70h
Condition 2: 200°C, 1.3451bar: 42h

Drying: 80°C 12h vacuum

Annealing $^7$: at 700°C for 10 h Under N$_2$ flux
Chapter 4: Results and Discussions

The synthesized products were characterized by using scanning electron microscope and X-ray powder diffraction. SEM testing provided morphology information of Li$_2$MnSiO$_4$. From the SEM images, the complex particle size and distribution can be figured out. XRD analyzing gives the components information about the final products. The following section provides detailed results and analysis of the synthesized products, and more images can be found in appendices.

4.1 Physical Features of Synthesized Products

Before doing SEM and XRD analysis, the physical features of the synthesized products under different reaction conditions were recorded. Three products produced under 180°C are displayed in Figure 10. They were heated for 28h, 42h and 70h separately (from left to right). The color of the left one is grey-white, and there are several tiny particles among the sample powder. The middle one is in grey color and no tiny particles exist. The right sample powder is in grey-brown, it seems that not only one compound exists, but also some impurities. Figure 11 below shows product samples which were obtained after heating for 42h at 180°C and 200°C separately. The starting materials that heated at 200°C give a brown powder with metal-like stuff mixed.
Figure 10: Product samples which were got after heating at 180°C for different time periods

Figure 11: Product samples which were got after heating for 42h at 180°C and 200°C separately
4.2 SEM results

Due to different reaction conditions, the synthesized products show different morphologies. Figure 12 and Figure 13 are SEM images of lithium manganese silicate that was produced though 42 hours heating at 180°C. Figure 12 is the one that magnified 3000 times, and Figure 13 is the image magnified by 5000 times. These images show that the particles of this complex are in nano-scale, and the size of these particles is around 100 nanometers. Almost all of the nanoparticles are in identical sizes, and mostly they are in small round shape. In Figure 13, there are few large particles, the size of which are around 1μm. In terms of the overall particles, the distribution of them is uniform.
Figure 12: SEM image of Li2MnSiO4 under the reaction condition: heating 42h at 180°C (3000)

Figure 13: SEM image of Li2MnSiO4 under the reaction condition: heating 42h at 180°C (5000)
4.3 XRD results

Each compound has its own characteristic peaks, when compare the peaks generated by XRD analysis with those recorded in certain database, the identification of certain products can be identified. Peaks in Figure 14 and 16 are the characteristic peaks quartz. In figure 15 and 17, the marked peaks are identical with the characteristic peaks of Li$_2$MnSiO$_4$ recorded in the PANalytical database. Those unmarked peaks are own to the impurities. All of the peaks are not very high, even the highest one of quartz is only about 800, and the highest one of products only about 500. The height represents the intensity. That is to say, all of the intensities are not strong.
Figure 14: The RXD image of the products synthesized at 180°C and heated for 28h

Figure 15: The RXD image of the products synthesized at 180°C and heated for 28h
Figure 16: The RXD image of the products synthesized at 180°C and heated for 42h

Figure 17: The RXD image of the products synthesized at 180°C and heated for 42h
4.4 Discussion

We can predict which product sample is the target product by viewing its physical properties. Firstly, in terms of the color, only the one heated for 42h at 180°C shows a grey color. The other products, such as the one heat for 14h shows a pink-grey color, which means that the starting materials were not completely consumed during the reaction; the ones show brown color indicated that the raw materials were overheated during the synthesis process. Thus, the grey color is one index for researchers to predict whether the product sample is the target one or not.

Secondly, SEM images show that 42h products gave uniform nanoparticles, and the particles are around 100 nanometers. The smaller the nanoparticle is, the better electrochemical properties it will perform. Because the smaller particle will give a relatively bigger specific surface area, which will theoretically cause a greater charge transference and initial capacity (Boucher, 2012). While the morphologies of other products are not as good as the one heated for 42h. For example, the one heated for 70h, as reaction time last long, the crystalline grew larger and larger. However, larger particles are not ideal to perform the electrochemical properties.

Thirdly, when analyzed the XRD results, we found that the 28h products, 42h products, 56h products and 70h products at 180°C gave Li₂MnSiO₄ characteristic peaks, and there were less impurities in the 42h products. The intensities of those peaks are very weak. The reasons are as follows: 1) the XRD machine is too old, the electron intensities are not so strong to cause strong X-rays; 2) there are not enough sample powders to cover the
sample holder completely; 3) the size of the nanoparticles is too small, which will reduce the X-ray intensities. The major component of 180°C 14h products and 200°C 42h products is Mn$_2$O$_3$. For the 180°C 14h product, the possible reaction is that the reaction time was too short, so the raw materials were not react completely, the color of this product also gives same result. For the one heated for 42h at 200°C, the possible reason is that the reaction temperature was too high, which may inhibit the formation of target products.
Chapter 5: Conclusions and Recommendations

Hydrothermal reaction method was used to synthesize lithium manganese silicate, which can be applied as the cathode material for a lithium ion battery. During this project, the effects of different reaction conditions were investigated to figure out the optimal reaction condition. The SEM and XRD results show that we can use hydrothermal synthesis method to generate Li$_2$MnSiO$_4$ successfully, and the optimal reaction condition is that heating the raw materials at 180°C for 42 hours will produce better products.

There is a prediction that we could shorten the reaction time by enlarge the volume of autoclave, which is the reaction container. In this project, we use a 5ml autoclave to run reactions. When heated the raw materials at 180°C, the pressure in the autoclave is about 1.2883bar caused by distilled water vapor. While heated them at 200°C, the pressure in the autoclave is about 1.3451bar. If we put the starting materials into a larger autoclave, and increase the pressure, we can accelerate the reaction rate. That’s one of the ways that can shorten the reaction time, and improve the effectiveness of hydrothermal synthesis method.

In order to figure out whether the synthesized complex Li$_2$MnSiO$_4$ is feasible to be regarded as cathode materials or not, further researches on its electrochemical performances should be done in the future. If we can figure out the electrochemical performances of Li$_2$MnSiO$_4$ synthesized by hydrothermal method is good, we can say
that the hydrothermal synthesis method is promising and can be applied to produce lithium silicate materials in the future.
Bibliography


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Appendices

Figures 18-26 show SEM images of Li$_2$MnSiO$_4$ samples that synthesized under different reaction conditions.

Figure 18: SEM image of Li$_2$MnSiO$_4$ under the reaction condition: heating 14h at 180°C (5000)
Figure 19: SEM image of Li$_2$MnSiO$_4$ under the reaction condition: heating 14h at 180$^\circ$C (9500)

Figure 20: SEM image of Li$_2$MnSiO$_4$ under the reaction condition: heating 14h at 180$^\circ$C (30000)
Figure 21: SEM image of Li2MnSiO4 under the reaction condition: heating 28h at 180°C (3000)

Figure 22: SEM image of Li2MnSiO4 under the reaction condition: heating 28h at 180°C (6000)
Figure 23: SEM image of Li$_2$MnSiO$_4$ under the reaction condition: heating 70h at 180°C (5000X).

Figure 24: SEM image of Li$_2$MnSiO$_4$ under the reaction condition: heating 70h at 180°C (30000X).
Figure 25: SEM image of Li$_2$MnSiO$_4$ under the reaction condition: heating 42h at 200°C (5000)

Figure 26: SEM image of Li$_2$MnSiO$_4$ under the reaction condition: heating 42h at 200°C (10000)
Figures 27-29 are images of XRD data of Li2SiO4 samples that synthesized under different reaction conditions.

Figure 27: The RXD image of the products synthesized at 180°C and heated for 14h
Figure 28: The RXD image of the products synthesized at 180°C and heated for 70h.

Figure 29: The RXD image of the products synthesized at 200°C and heated for 42h.