UNIVERSITY OF CALIFORNIA

Los Angeles

Lithium Manganese Silicate Positive Electrode Material

A thesis submitted in partial satisfaction of the requirements for the degree Master of Science in Chemical Engineering

by

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ABSTRACT OF THE THESIS

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Master of Science in Chemical Engineering
University of California, Los Angeles, 2015
Professor Yunfeng Lu, Chair

As the fast development of the electronic portable devices and drastic fading of fossil energy sources. The need for portable secondary energy sources is increasingly urgent. As a result, lithium ion batteries are being investigated intensely to meet the performance requirements. Among various electrode materials, the most expensive and capacity limiting component is the positive materials. Based on this, researches have been mostly focused on the development of novel cathode materials with high capacity and energy density and the lithium transition metal orthosilicates have been identified as possible high performance cathodes. Here in, we report the synthesis of a kind of lithium transition metal orthosilicates electrode lithium manganese silicate. Lithium manganese silicate has the advantage of high theoretical capacity, low cost raw material and safety. In this thesis, lithium manganese silicate are prepared using different silicon sources. The structure of silicon sources preferred are examined. Nonionic block copolymers surfactant, P123, is tried as carbon source and morphology directing agent. Lithium manganese silicate's performances are improved by adding P123.
The thesis of Qiong Yang is approved.

Selim Senkan

Robert Hicks

Yunfeng Lu, Committee Chair

University of California, Los Angeles
2015
DEDICATION

To Dr. Lu, a longtime mentor, for sparking my interest in nanotechnology and in China and providing me outlets to explore and grow both of those interests. With gratitude for the support and opportunities you’ve provided me, the friends you’ve introduced me to, and for inspiration along the way: Thanks for everything.
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INTRODUCTION

A. Lithium Ion Batteries Background

As the fast development of the electronic portable devices and drastic fading of fossil energy sources. The need for portable secondary energy sources is increasingly urgent.

In 1895, the first rechargeable battery, lead-acid battery, was invented by Gaston Planté. In 1899, Waldemar Jungner, a Swedish scientist named created the nickel-cadmium battery in which a potassium hydroxide solution serves as electrolyte. This is the first battery to use an alkaline electrolyte. Nickel–metal hydride battery, abbreviated NiMH or Ni–MH was the modified version of Ni-Cd battery. A NiMH battery can have two to three times the capacity of an equivalent size NiCd, and their energy density were improved. As shown in fig. 1.1 the performances of rechargeable batteries were significantly improved after the invention of Lithium ion batteries[1].
The lithium-ion battery was developed in response to these need. The first lithium-ion battery was created in Japan by Asahi Kasei Co.1 and first commercialized by Sony Co.2 in 1991, followed by A&T Battery Co. (a joint company of Toshiba Battery and Asahi Kasei Co.) in 1992[2]. Lithium ion batteries soon become promising energy storage materials because of its high-energy density, good efficiency, and no memory effect. The advantages and disadvantages of lithium ion battery are listed in Table 1.1

Table 1.1 Advantages and disadvantages of lithium ion batteries

<table>
<thead>
<tr>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemistry with the highest energy (Wh/g)</td>
<td>Relatively expensive</td>
</tr>
<tr>
<td>and lightest weight (Wh/kg)</td>
<td></td>
</tr>
<tr>
<td>No memory effect</td>
<td>Lightest weight</td>
</tr>
<tr>
<td>Good cycle life</td>
<td>Requires protection circuitry for safety and to</td>
</tr>
<tr>
<td></td>
<td>prevent overcharge and overdischarge</td>
</tr>
<tr>
<td>High energy efficiency</td>
<td>Nominal 3-h charge</td>
</tr>
<tr>
<td>Good high-rate capability</td>
<td>Not tolerant of overcharge and overdischarge</td>
</tr>
<tr>
<td>Added advantages and disadvantages of Li-Ion</td>
<td>Thermal runaway concerns</td>
</tr>
<tr>
<td>polymer/laminate cells</td>
<td></td>
</tr>
<tr>
<td>Flexible footprint</td>
<td></td>
</tr>
<tr>
<td>Plasticized electrolyte</td>
<td></td>
</tr>
<tr>
<td>Internal bonding of anode</td>
<td></td>
</tr>
<tr>
<td>Cathode and separator</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Limited high rate capability</td>
</tr>
<tr>
<td></td>
<td>More expensive</td>
</tr>
<tr>
<td></td>
<td>Poor low-temperature performance</td>
</tr>
</tbody>
</table>

B. Positive electrode materials

Lithium ion batteries generally use an intercalated lithium compound as one electrode material and metallic lithium as another electrodes. Lithium ions travels
in the electrolyte between two electrodes during which materials are oxidized or reduced in positive and negative electrodes. One of the advantages of this kind of structures is that the operating voltage and discharge capacities of the batteries can be adjusted by the lithium compound electrode[2]. The mechanism of lithium ion batteries are shown in fig. 1.2. For years scientists have been looking for positive-electrode materials which can perform higher operating velocity or larger capacity.

Fig.1.2 a schematic illustration on a lithium-ion battery consisting of two lithium insertion electrode

A typical positive electrode material is LiCoO$_2$ which was announced by Sony in 1991[3]. LiCoO$_2$ shows a flat voltage of 3.9V. Some other positive electrodes in the form of LiMxOy were developed after that. LiMn$_2$O$_4$ with spinel-framework structure has a flat operating voltage of 3.95–4.1V with theoretical capacity of 148 mAh g$^{-1}$[4]. LiNiO$_2$ was followed with a operating voltage up to 3.9mAh/g [5]. In 1997, A. K. Padhi reported lithium ions' intercalation to LiFePO$_4$ in a voltage window of up to
3.5V. This opens a new class of positive electrode materials in the form of LiMPO4 (M=Fe, Co, Ni, Mn) [6]. It was not until 2005 that PO₄³⁻ was substituted by SiO₄³⁻ and first LiFeSiO₄ was introduced by Anton Nye [7].

Since energy density is the product of voltage and capacity, high voltage and large capacity are both necessary. Energy density is proportion to second order of voltage. Positive materials with higher Oxide-reduction Potential are particularly of interest these years. The voltage windows of the positive electrode materials are summarized as follows.

<table>
<thead>
<tr>
<th>Positive Electrode</th>
<th>Voltage Window</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiCoO₂</td>
<td>3.5-4.7</td>
<td>[3]</td>
</tr>
<tr>
<td>LiMnO₂</td>
<td>1.5-4.5</td>
<td>[4]</td>
</tr>
<tr>
<td>LiNiO₂</td>
<td>2.8-4.3</td>
<td>[5]</td>
</tr>
<tr>
<td>LiFePO₄</td>
<td>2.0-4.3</td>
<td>[6]</td>
</tr>
<tr>
<td>LiMnPO₄</td>
<td>2.5-4.4</td>
<td>[8]</td>
</tr>
<tr>
<td>Li₃V₂(PO₄)₃</td>
<td>3-4.5</td>
<td>[9]</td>
</tr>
<tr>
<td>LiNiPO₄</td>
<td>3.5-5.2</td>
<td>[10]</td>
</tr>
<tr>
<td>LiCoPO₄</td>
<td>3.0-5.2</td>
<td>[11]</td>
</tr>
<tr>
<td>Li₂FeSiO₄</td>
<td>2.2-4.4</td>
<td>[12]</td>
</tr>
</tbody>
</table>
C. Lithium Manganese Silicate

After the successful preparation of Li$_2$FeSiO$_4$ by A. Nyten in 2005. A new class of polyanions cathode materials, Li$_2$MSiO$_4$ has been attracting interests. In 2006, R. Dominko and his group reported the preparation of another material from this class: Li$_2$MnSiO$_4$[13].

Li$_2$MnSiO$_4$ shows similar structure as Li$_2$FeSiO$_4$. Generally, the lithium and transition metal cations are situated in tetrahedral sites in a distorted hexagonal-close-packed oxygen array[14]. The same as other transition metal orthosilicates, Li$_2$MnSiO$_4$ has four ambient polymorphs which are differ in the arrangement of the tetrahedra in the distorted hexagonally close-packed oxygen array. Among these four polymorphs, two of them are orthorhombic forms (Pmn21 and Pmnb) and another two are monoclinic forms (P2$_1$/n and Pn). The orthorhombic polymorphs have two-dimensional structure while in the monoclinic forms Li ion positions are three-dimensionally interconnected.

The crystal structure of the four forms of Li$_2$MnSiO$_4$ are shown as below.
Fig. 1.3 crystal structures of the four known ambient pressure polymorphs of Li$_2$MnSiO$_4$ (a) Pmn21[15], (b) Pmnb[16], (c) P21/n[17] and (d) Pn[18]. Li tetrahedra are shown in green, Mn tetrahedra in purple and Si tetrahedra in blue, red spheres represent oxygen atoms. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Most of the electrochemical data reported up till today is Pmn21 polymorph. In 2007, Politaev et al reported the existence of the P21/n space group by solid state reaction at 750-1150°C[19]. In 2011, ion-exchange from Na$_2$MnSiO$_4$ was tried by Hugues Duncan and Li$_2$MnSiO$_4$ adopting the Pn space group was obtained[20]. However, this kind of polymorph is not stable and will convert to Pmn21 polymorph above 370. Both of these two polymorphs display similar charge-discharge curves.

Li$_2$MnSiO$_4$ is advantageous for its unique composition which results in a theoretical capacity of 333mAhg$^{-1}$. The low cost of the synthesising material also makes it a promising cathode material. From 2005 to now, various ways have been used to synthesise Li$_2$MnSiO$_4$. Most of the Li$_2$MnSiO$_4$ reported are synthesised through sol-gel method[21]. The starting precursors were lithium acetate dihydrate, manganese acetate tetrahydrate and SiO$_2$ particles or tetraethyl orthosilicate. All precursors were dissolved in water-ethanol system and dried until gel formed. When gel formed, lithium and manganese salts where uniformly distributed in the void space.
of gel. The obtained xerogel were sintered at 600-800°C under Nitrogen or Argon atmosphere for 1-12hrs to form Li$_2$MnSiO$_4$ crystals.

Another commonly used way to prepare Li$_2$MnSiO$_4$ were solid state synthesis method. Precursors were mixed and ball milled for several hours before sintering at 700-900°C for 6-12 hrs. [22]

Except for the commonly used method, some novel method were successfully used in obtaining Li$_2$MnSiO$_4$. In 2010, T. Muraliganth and his group synthesized Li$_2$MnSiO$_4$ by a facile microwave solvothermal method[23]. Tetraethyl orthosilicate, lithium hydroxide, manganese acetate were dissolved in tetraethyleneglycol(TEG) and irradiated in microwave machinge to 300°C for 20min with an operating frequency of 2.45Hz and 600W. The Li$_2$MnSiO$_4$ crystals were precipitated and dried. Carbon coating was achieved by mixing the powder with sucrose and further calcinated at 650°C. Nanoparticles of Li$_2$MnSiO$_4$ in the size of 20nms were obtained. However, no significant improvement in electrochemical performace were observed.

Hydrothermal method were also used to prepare Li$_2$MnSiO$_4$ cathode materials[24]. The starting precursors were LiOH, Mn(Ac)$_2$, Si(OC$_2$H$_5$)$_4$. The optimized temperature is 200°C and reaction time is 72h. The dried precipitates were further annealed at 700. Hydrothermally synthesized Li$_2$MnSiO$_4$ shows superior stability and improved cycling performance. The improvement in performance can be attributed to the unique flower-like morphology which has a
larger surface area than the commonly obtained bulk aggregated particles.

Bin Shao and his group synthesised Li$_2$MnSiO$_4$ via a combination of spray pyrolysis and wet ball milling followed by annealing method[25]. The Schematic diagram of the experimental apparatus for SP is shown in fig 1.4. Spray pyrolysis method obtain particles directly by drying super small droplets of aqueous precursor solution and has the advantage of narrowing particle size distribution and getting uniform chemical composition. However, no significant improvement in performance was observe.

Fig. 1.4. schematic diagram of the experimental apparatus for SP.

Other novel synthesis method like supercritical fluid process[26] or electrospinning method[27], molten salt method[28] are also tried to make Li$_2$MnSiO$_4$ crystals.
Despite the high theoretical efficiency, the as synthesised pristine \( \text{Li}_2\text{MnSiO}_4 \) can only display 10mAh/g capacity. Several reasons are responsible for the poor electrochemical performances. The first drawback is the extremely low electronic conductivity. Secondly its intrinsic structural instability in charge/discharge process. Another disadvantage is the structure collapse of \( \text{Li}_2\text{MnSiO}_4 \) crystal. There is a number of reports showing that \( \text{Li}_2\text{MnSiO}_4 \) cathode material undergoes amorphization in the first few charging/discharging cycles [29]. One explanation is Jahn – Teller distortion associated with lattice parameters changes during \( \text{Mn}^3+ \rightarrow \text{Mn}^4+ \) transition. The degradation of crystalline structure can also be explained by the occurrence of secondary reactions between electrolyte and delithated forms of lithium manganese silicate (\( \text{LiMnSiO}_4 \) and \( \text{MnSiO}_4 \)). The third reason is the unavoidable impurity phases formed during the synthesis such as \( \text{MnO}, \text{MnSiO}_4, \text{Li}_2\text{SiO}_4 \). Those impurities are electrochemically inactive material. However, up till today there is no effective way to totally eliminate the impurities.

Various ways have been used to resolve the problems. Carbon coating, morphology modification and doping with impurity elements all show effective in achieving better properties.

It is known that carbon coating can introduce a layer of conductive material on the particles which will reduce the electric impedance and provide good electrochemical. Carbon coating also has the effect of inhibiting the particle from growing large.
Smaller particles generally have larger surface area which will also result in better contact between electrolyte and electrode material and shorter ion and electron pathways during the charge and discharge process.

The first carbon coating was made using citric acid by R. Dominko. in sol-gel method. In 2013, Jing Liu used citric acid as carbon source in solid state synthesis of Li$_2$MnSiO$_4$ which achieves a superior electronic properties[30]. The highly crystalline Li$_2$MnSiO$_4$ nanoparticles in the size of 20-50 nm are coated by a uniform carbon layer in a thickness of 2-5 nm. At a rate of 0.05 C, the Li$_2$MnSiO$_4$/C nanocomposite exhibits a discharge specific capacity as high as 268 mAh g$^{-1}$ for the first cycle and a reversible capacity of about 136 mAhg$^{-1}$ after 140 cycles at room temperature. Except for citric acid, other carbon sources also conducted effective carbon coating on lithium manganese silicate. Akkisetty Bhaskar made a uniform coating of amorphous carbon on Li$_2$MnSiO$_4$ on using starch as carbon source.115mAh/g capacity of the as synthesised material was retained after 30 cycles[31]. V. Aravindan tried 0.1M Adipic Acid as carbon sources in solid state synthesis and successfully prepared carbon coated Li$_2$MnSiO$_4$ which exhibits a stable discharge behavior $\sim$140mAh/g[32]. Another carboxylic acid, tartaric acid is also used as effective carbon source[33]. The tartaric acid-assisted sol-gel synthesised LMS electrode exhibited a reversible capacity of 113mAh$^{-1}$ in the first discharge and the discharge capacity was stabilized at $\sim$110 and $\sim$105mAh 1 after 15 and 30 cycles, respectively. Despite the larger surface area and more efficient electron transport path facilitated by the
conductive carbon coating. The tartaric acid coated Li$_2$MnSiO$_4$ has higher purity than common prepared Li$_2$MnSiO$_4$ which was verified by the very weak peak at approximately $2\theta =31$ in XRD patterns correspondng to MnSiO$_3$ crystal. The purer phase was attributed to the extra hydroxyl on tartaric acid which made the gel more homogeneous and stoichiometric.

Carbon not only acts as conductive coating on the active material but also has the effect of modifying the morphology of the electrode material. Li$_2$MnSiO$_4$ material of a porous structure was made by using carbon as hard template. First of all, the interconnected network of pores allows electrolyte penetrating into the bulk of the electrode enabling fast kinetics of lithium diffusion. Secondly, mesoporous structure also provide short lithium diffusion distance from the pore space into the thin pore walls which 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[34]. Takashi Kawase loaded and dispersed the Li$_2$MnSiO$_4$ materials on CMK3 and CMK8 carbon frameworks[35]. After loading with different amount of Li$_2$MnSiO$_4$, the material has a BET surface area from 245m$^2$/g to 1431m$^2$/g and a carbon weight from 17% to 41%. After subtracting the contribution of carbon, the net discharge capacity of the best LMS+CMK3 battery was 300 mAh/g in the first cycle and stabilized at 180mA/g after 10th cycle. The structure is shown in fig.1.5
Hyunjung Park and his group prepare Li$_2$MnSiO$_4$ via a sol-gel and electrospinning method with poly(ethylene oxide)(PEO) as an electrospinning agent[27]. The process was conducted by electrospining a solution of stoichiometric mixture of lithium and manganese acetates with tetraethyl orthosilicate and poly(ethylene oxide)(PEO) as an electrospinning agent. The as-prepared nanocrystallites are connected through continuous electrically conducting one-dimensional (1D) fibers, ensuring efficient pathways for electron transport. The structure of the as prepared porous structure lithium manganese silicate is shown in fig.1.6
Fig. 1.6 scheme illustration of lithium manganese silicate nanoparticles in porous structure carbon nanofibers.

Guang He prepared $\text{Li}_2\text{MnSiO}_4$/C nanocomposite with hierarchical macroporosity using poly(methyl methacrylate) (PMMA) colloidal crystals as a sacrificial hard-template and water-soluble phenol-formaldehyde (PF) resin as the carbon source as shown in figure.1.7 [36].

Fig.1.7 structure of lithium manganese silicate in porous PMMA
Li2MnSiO4 with mesoporous structure was also made directly by using mesoporous silica. Sue Jin Kim synthesized mesoporous Li2MnSiO4 using mesoporous silica as template and silicon source and citric acid as carbon source[37]. The as synthesised material has a BET surface of 584.5m2/g. Rosalind J. Gummow optimized this method by using emulsion synthesis and surfactant as carbon source. The product has a initial discharge capacity of 150mAh/g and stablized at 100mAh/g after 20 cycles[38]. Yi Zhao and his group loaded a porous SiO2 layer and raw material on the surface of graphene oxide using cetyltrimethylammonium bromide (CTAB) and converted to RGO by heating at 800 °C under Ar[39]. The Li2MnSiO4 material with this unique structure retains a high capacity of 290mAh/g after 40 cycles at 0.05C.

![Schematic diagram showing the formation of mesoporous lithium manganese silicate from SBA-15 using emulsion synthesis](image)
Reducing Impurities

Impurity phases have been an unavoidable problem in lithium manganese silicate synthesis process. However, the impurity phases have been minimized by alternating the precursors and stoichiometry. Long Qu reported that replacing the commonly used manganese source from manganese acetate to Mn₃O₄ has reduced the content of impurities while not enlarging the particle size [40]. Haiyan Wang and his co-workers made Lithium deficient Li₂₋ₓMnSiO₄ compounds by adding extra manganese and silicon source to the in the raw material. This method also shows effective in decreasing impurity phases.
Introduction Reference


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Chapter 1

Lithium Manganese Silicate Synthesized using Different Organo Silane as Silicon Sources

1 Introduction

Li$_2$MnSiO$_4$ has been extensively studied as potential cathode material for lithium ion batteries due to its low cost, environmental friendliness, high thermal stability from strong Si–O bonding and synthesis simplicity. Meanwhile, due to the Mn$^{2+}$/Mn$^{3+}$ and Mn$^{3+}$/Mn$^{4+}$ redox couples, it is possible to extract two lithium ions per formula unit, providing a high theoretical capacity of 332 mAh g$^{-1}$ which is higher than the traditional cathode materials of LiMn$_2$O$_4$ and LiFePO$_4$ with relatively low capacities of 130 and 170 mA h g$^{-1}$, respectively. Despite these advantages, lithium manganese silicate didn't show satisfactory electrochemical performances based on the experimental data reported so far. Pure lithium manganese silicate exhibits reversible capacities less than 10 mAh g$^{-1}$ up to 5 cycles.

Several reasons have been demonstrated to account for the low capacity and poor cycle stability. The main challenge for lithium manganese silicate is the extremely low electrical and ionic conductivity. The electrical conductivity of lithium manganese silicate is in the range of $10^{-14}$~$10^{-16}$ S cm$^{-1}$ which is three to five fold lower than the LiFePO$_4$ in magnitude. In order to circumvent the low conductivity, researchers have been tried to coating the particles with a layer of conductive carbon.
For example Jing Liu used citric acid as carbon source in solid state synthesis of Li$_2$MnSiO$_4$ which achieves a superior electronic properties[30]. The tartaric acid-assisted sol-gel synthesised LMS electrode exhibited a reversible capacity of 113 mAh$^{-1}$ in the first discharge and the discharge capacity was stabilized at $\sim$110 and $\sim$105 mAh$^{-1}$ after 15 and 30 cycles, respectively.

Carbon sources are introduced to the system generally by mixing with the precursors by ball-milling in solid state synthesis and dissolving in the solution of precursors in sol-gel route. In both of the two methods, carbon sources are mixed mechanically with lithium manganese silicate precursors which means that how carbon sources are distributed among the precursors depends on the operating condition. It is possible that carbon can not coated uniformly on all the particles so the electrochemical performances are affected.

One way to address this concern is to use carbon in the molecule of the precursor as carbon source for coating. Forming of lithium manganese silicate structure and carbonization happen at the same molecule which ensures carbon to be very adjacent to lithium manganese silicate particle and better coating property is likely to be achieved through this way. Since the existing of numbers of various organo silane, replacing the commonly used silicon source, silicon oxide or tetraethyl orthosilicate, by organo silanes containing carbons is a way to realized the as stated method.
Another drawback of lithium manganese silicate is the unavoidable impurity phases such as MnO and \( \text{Li}_2\text{SiO}_3 \). Dompablo et al. have succeeded in preparing the \( \text{Li}_2\text{MnSiO}_4 \) material in the absence of MnO under various pressure conditions. However, the formation of \( \text{Mn}_2\text{SiO}_3 \) could be unavoidable under such abnormal pressure conditions. The impurity phases constitute the inactive part of the products, which hindered the electron and ion transfer and decomposes to undesirable products under the high operating voltage. The mechanism of the forming of impurities is still not clear up to now. However, it is certainly that better mixing property of the starting materials can minimize the formation of impurity phases. Therefore, we hypothesize that starting materials could be distributed uniformly by chemical force instead of mechanical stirring or milling. In order to realize this hypothesis, an organo silane with function groups as complexing agent need to be found.

In the context, we prepare lithium manganese silicate using four different organo silane as silicon source. The purposes of this work is to introduce carbon into the synthesizing system by using silicon sources with carbon in the molecule and achieve better mixing of silicon sources and lithium and manganese salts by using functional group in organo silanes as complexing agents to attach manganese and lithium salts to silicon source. The structure, carbon content and electrochemical performance are investigated.

2 Experimental
<table>
<thead>
<tr>
<th>Organo Silane</th>
<th>Structure</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diphenylsilanediol</td>
<td><img src="image1" alt="Structure" /></td>
<td>Li$_2$MnSiO$_4$</td>
</tr>
<tr>
<td>Dimethoxydiphenylsilane</td>
<td><img src="image2" alt="Structure" /></td>
<td>Li$_2$MnSiO$_4$</td>
</tr>
<tr>
<td>+TEOS(1:1)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Trimethoxyphenylsilane</td>
<td><img src="image3" alt="Structure" /></td>
<td>Li$_2$MnSiO$_4$</td>
</tr>
<tr>
<td>N-(2-aminoethyl)-3-aminopropytrimethoxysilane</td>
<td><img src="image4" alt="Structure" /></td>
<td>Li$_2$MnSiO$_4$</td>
</tr>
</tbody>
</table>

The synthesis of Li$_2$MnSiO$_4$ was carried out using a modified Pechini sol–gel process. The starting precursors were lithium acetate dihydrate (Sigma-Aldrich), manganese (II) acetate tetrahydrate (Sigma-Aldrich) and selected organo silane. Different silicon sources used in synthesizing Li$_2$MnSiO$_4$ and the corresponding structure are summarized in Table 2.1. Solutions were prepared by dissolving 0.004 mol LiAc, 0.002 mol MnAc$_2$ and 0.002 mol organo silane in 40 ml ethanol. In the case of trimethoxyphenylsilane, dimethoxydiphenylsilane + TEOS and diphenylsilanediol the pH of the solution was adjusted to pH= 2 by HCl to assist the polymerization of the silanes for monatomic silanes will evaporate at low temperature. In the case of N-(2-aminoethyl)-3-aminopropytrimethoxysilane, the original solution is alkline.
which assist the polymerization. The solution was stirred and dried at 70°C. The obtained products was further sintered at 700°C for 10hrs under nitrogen.

The electrodes were prepared by casting and pressing a mixture of 70 wt% of this material, 10wt% of a PVDF(Sigma-Aldrich) and 20 wt% of carbon black (Sigma-Aldrich) on aluminum foil and drying in vacuum at 70°C for 24 h. The electrolyte used was a 1 M solution of LiPF₆ in EC:DMC (1:1 ratio by volume).

X-ray diffraction measurements were conducted on a Bruker D8 Advance diffractometer at 40.0 kV and 120 mA using Cu-Kα radiation (λ=1.54 Å).

Thermogravimetric analysis was conducted on a Perkins-Elmer Pyris 6 TG Analyzer. In this technique the change in sample weight (mass) is measured while the sample is heated at a constant rate (or at constant temperature) using a thermobalance (micro balance) within a controlled atmosphere under air (oxidative) or nitrogen (inert) (Sibilia, 1988). The system allows for the sample to be simultaneously weighed and programmed to be heated or cooled, and the mass, time, and temperature data to be recorded and processed. Thermogravimetric analysis has been used to determine the carbon content of materials by heating from 25-800°C under nitrogen at 10°C/min and measure weight changes of the product.

3 Results and Discussion
Fig. 2.1 a) Li$_2$MnSiO$_4$ prepared using N-(2-aminoethyl)-3-aminopropyl trimethoxysilane b) Li$_2$MnSiO$_4$ prepared using trimethoxyphenylsilane c) Li$_2$MnSiO$_4$ prepared using dimethoxydiphenylsilane and TEOS in a molar ratio of 1:1 d) Li$_2$MnSiO$_4$ prepared using diphenylsilanediol.

The XRD pattern of the as-synthesized Li$_2$MnSiO$_4$/C powder are shown in Fig. 2.1. Majority of reflectance peaks can be assigned to Li$_2$MnSiO$_4$ phase, which have an orthorhombic unit cell in space group $Pmn2_1$. The lattice constants are $a = 6.3109(9)\,\text{Å}$, $b = 5.3800(9)\,\text{Å}$ and $c = 4.9662(8)\,\text{Å}$. Five intense diffraction peaks are corresponding to the (0 1 0), (0 1 1), (1 1 1), (2 1 0) and (0 0 2) planes, respectively. However, a small amount of impurities at least MnO and MnSiO$_3$ are detected in all the cases. The obvious large peak widths indicate that the crystallite size is small. According to following Scherrer’s equation:
\[ \delta = 0.9 \frac{\lambda}{B \cos \theta} \]

where \( \delta \) is the crystallite size, \( \lambda \) is the X-ray wavelength (\( \lambda = 1.5406 \text{Å} \)) and \( B \) is the full width at half maximum (FWHM) of the XRD peak in radians. Fig. 2.1 shows the XRD patterns of Lithium Manganese Silicate prepared using four different organo silane as silicon sources. It is shown that lithium manganese silicate was successfully synthesized with all of the four organo silanes. However, impurities are found in all of the four products. \( \text{Li}_2\text{MnSiO}_4 \) prepared using diphenylsilanediol shows the most significant impurity phase according to the XRD peaks while \( \text{Li}_2\text{MnSiO}_4 \) prepared using \( N-(2\text{-aminoethyl})-3\text{-aminopropyl trimethoxysilane} \) as silicon source shows the least impurity peaks. This can be explained by the following reasons. 1) Lithium manganese silicate prepared using diphenylsilanediol has the most impurities because of the phase separation of polymerized diphenylsilanediol and lithium and manganese salts. During the heating treatment, chain-structure polydiphenylsilanediol became oily and separated from the salts. This destroyed the well mixing of precursors thus resulted in large amount of MnO and MnSiO\(_3\) as shown in the XRD Patterns. \( \text{SiO}_2 \) in the amorphous state is also possibly exists which can not be shown in XRD peaks. 2) Lithium manganese silicate prepared using trimethoxysilane, dimethoxydiphenylsilane + TEOS and \( N-(2\text{-aminoethyl})-3\text{-aminopropyl trimethoxysilane} \) as silicon source is better than the one prepared using diphenylsilanediol as silicon source because of the crosslinking structure formed during polymerization of the first three silicon sources. The cross-linking structure
prevent the silicon precursors from turning into liquid state and separating from the salts. 3) Lithium manganese silicate prepared using N-(2-aminoethyl)-3-aminopropyl trimethoxysilane has the best purity not only because of the cross-linking structure but also because of the function of amino group in attaching manganese and lithium ion to the silicon source. Lithium manganese silicate prepared using N-(2-aminoethyl)-3-aminopropyltrimethoxysilane achieves the best mixing of lithium, manganese and silicon source.

![Thermogravimetric(TG) analysis curve of Li₂MnSiO₄ synthesised with difference silicon sources.](image)

Fig.2.2 Thermogravimetric(TG) analysis curve of Li₂MnSiO₄ synthesised with difference silicon sources.

Thermogravimetric (TG) Analysis was conducted to ascertain the exact carbon content in lithium manganese silicate. The sample was isothermed at 120°C before raising to 800°C under air. As indicated in the TGA curve, the sample suffers weight loss between 300-400°C which was reported to be the carbon loss temperature range.
for lithium manganese silicate products. Thus the carbon content of the four samples was measured. Unexpectedly, all of the four samples have carbon contents less than 7% as shown in fig.2.2. According to previous literatures, lithium manganese silicate reported to have satisfactory performances generally contains carbon of 15%~30% in weight due to the extremely low intrinsic electronic and ion conductivity of Li$_2$MnSiO$_4$. Therefore, the 7%wt carbon is hardly enough to provide effective conductive layer for the active materials. The low carbon content indicates that the char yield of the silanes are low although they contain relatively high amount of carbon in molecule. The char yield is influenced by the intrinsic property of the material as well as the pyrolysis condition such as the temperature raising rate and the ultimate temperature. More efforts have to be made in finding appropriate silicon source which have enough carbon for coating.

Fig. 2.3 cycling performance of lithium manganese silicate prepared using different silicon source.
Fig. 2.3 gives the cycling performance of three Li$_2$MnSiO$_4$ composites between 1.5 and 4.8V with a rate of 1/16 C (10mA g$^{-1}$). It can be shown that all of the four samples have capacitances below 60mAh/g which is much inferior than the performances reported in papers. The reasons can be attributed to the high impurity contents and uneffective carbon coating as stated before.

4 Conclusions.

In conclusion, lithium manganese silicate was successfully prepared using organo silanes as silicon sourced for the first time. The XRD analysis indicates the high amount of impurity phases in lithium manganese silicate product synthesised using trimethoxyphenylsilane, dimethoxydiphenylsilane and TEOS in a molar ratio of 1:1. and diphenylsilanediol whereas the relatively low impurity phases in lithium manganese silicate synthesised using N-(2-aminoethyl)-3-aminopropyl trimethoxysilane. The high amount of impurities can be attributed to the separation of silane and salts resulted from the chain-structure of silanes. Crosslinking - structure polymerized organo silane can remain mixed with manganese and lithium salts so results in less impurities. Silanes with effective function groups which could complex Mn$^{2+}$ achieves the best mixing property of the precursors which is proved by the least impurity peaks in XRD patterns. Thermogravimetric Analysis detected carbon loss of less than 7%wt for all of the four different silanes which indicates that the carbon in the silane molecules can not provide enough coating on the lithium manganese silicate
particles. The poor cycling performances of the four different samples in the charge and discharge test can be caused by the impurities and lack of effective carbon coating.
Chapter 2
Preparing Lithium Manganese Silicate using P123 as Carbon Source and Morphology Directing Agent

1 Introduction

Lithium manganese silicate is a promising cathode electrode material for high energy density. However, the potential benefits of Li$_2$MnSiO$_4$ were not developed because of some drawbacks that occur in lithium manganese silicate system. One of the major drawbacks is the extremely low intrinsic conductivity. As stated before, carbon decorating is an effective way to improve electrochemical performance because it can not only enhance the electronic and ion conductivity but also prevent the agglomeration of nanoparticles.

Another shortcoming of lithium manganese silicate is the structure collapse during the charge and discharge process because of the Jahn-Teller effect of manganese ion and volumetric changes during cycling. Therefore, mosoperous structured lithium manganese silicate was made in order to accommodate volumetric changes during lithium ion insertion or extraction, which was thought to reduce the collapse of structure. Besides, lithium manganese silicate with a porous structure also constructs the interconnected network of pores which allows electrolyte penetration into the bulk of the electrode and enables fast kinetics of lithium diffusion. Mesoporous structure also provides short lithium diffusion distance from the pore space into the
thin pore walls which allows rapid kinetics and full utilization of the bulk of the material. Based on this, porous structure manganese silicate are quite of interest these years.

Both carbon and Mesoporous silica have been used as template to prepare mesoporous Li$_2$MnSiO$_4$. Takashi Kawase loaded and dispersed the Li$_2$MnSiO$_4$ materials on CMK3 and CMK8 carbon frameworks. Sue Jin Kim and his group synthesized mesoporous Li$_2$MnSiO$_4$ using mesoporous silica as template and silicon source. However, these synthesis methods fall in the shortage of complex procedures. Mesoporous template has to be prepared before loading the active material. Therefore, single-step preparation of lithium manganese silicate of a mesoporous structure deserved to be tried.

In this chapter, porous structure lithium manganese silicate was prepared by adding surfactant to the starting materials. Surfactant has been used in preparing mesoporous silica. They periodicly arranged in the silicon oxide structure and highly ordered pores formed after sintering at 400-600°C. By adding surfactant in the precursors of Li$_2$MnSiO$_4$, we are trying to combine the preparation of template and Lithium manganese silicate to one step. Nonionic block copolymers are an interesting class of structure-directing agents. In this context, porous structure Li$_2$MnSiO$_4$/C composites are synthesized with poly(ethylene oxide)-b-poly(propylene oxide) - b-poly(ethylene oxide) triblock copolymer P123 (EO20PO70EO20). P123 also acts as carbon source.
in this case.

2 Synthesis Method

In a typical synthesis procedure, 0.5 g, 1g, 1.5g triblock copolymer Pluronic P123 (EO20PO70EO20) was dissolved in 20 ml dionized water under vigorous magnetic stir. Then 2 mmol of N-(2-aminoethyl)-3-aminopropyltrimethoxysilane was added to the solution, resulting in a homogeneous mixture with a certain viscosity. After stoichiometric amounts of lithium acetate and manganese acetate were added into above solution in sequence. The solution was stirred at 50°C until dry. The as-obtained products were then scraped from the dishes and calcinated at 650°C for 10 hours in a N₂ flow. Black Li₂MnSiO₄/C composite powder was then obtained after cooling to the room temperature.

The electrodes were prepared by casting and pressing a mixture of 70 wt% of this material, 10wt% of a PVDF(Sigma-Aldrich) and 20 wt% of carbon black (Sigma-Aldrich) on aluminum foil and drying in vacuum at 70°C for 24 h. The electrolyte used was a 1 M solution of LiPF₆ in EC:DMC (1:1 ratio by volume).

Nitrogen adsorption isotherms were measured using a Micromeritics ASAP 2020 (Micromeritics Instrument Corporation, Norcross, GA). Analysis was conducted at 77 K. Specific surface areas were calculated using the BET method with the adsorption branch relative pressure between 0.04 and 0.25. TEM images were obtained on a
Philips CM120 operated at 120 kV (Philips/FEI Inc., Eindhoven, The Netherlands).

Thermogravimetric analysis was conducted on a Perkins-Elmer Pyris 6 TG Analyzer. In this technique the change in sample weight (mass) is measured while the sample is heated at a constant rate (or at constant temperature) using a thermobalance (microbalance) within a controlled atmosphere under air (oxidative) or nitrogen (inert) (Sibilia, 1988). The system allows for the sample to be simultaneously weighed and programmed to be heated or cooled, and the mass, time, and temperature data to be recorded and processed. Thermogravimetric analysis has been used to determine the carbon content of materials by heating from 25-800°C under nitrogen at 10°C/min and measure weight changes of the product.

3 Results and Discussion

![Graph](image)

Fig.3.1 cycling performance of lithium manganese silicate synthesized using different amount of P123.
Fig. 3.1 gives a comparison of the cycling performance of three Li$_2$MnSiO$_4$/C composites between 1.5 and 4.8V with a rate of 1/16 C (10mA g$^{-1}$). It can be shown that lithium manganese silicate prepared using P123 as structure directing agent and carbon source is much better than the one prepared without P123. This is probably because the surfactant created pores which offer a short length for Li$^+$ ion diffusion from the core to the surface of the particles and provide a large surface area for electrode–electrolyte contact during electrochemical reactions. It can also be due to the larger amount of carbon form P123 which effectively enhance the kinetics and stabilize the crystal structure to improve the electrochemical performance of the cathode materials.

As far as we know, Li$_2$MnSiO$_4$ usually suffers from a rapid capacity fading in the initial cycles, due to its poor electron conductivity, structure instability and manganese dissolution during cycles. The capacity fade is not exceptional in this case. The discharge capacity of the Li$_2$MnSiO$_4$/C composite prepared using 2mmol lithium manganese silicate precursors and 0.5g P123 has the highest initial discharge capacity of 155mAh g$^{-1}$ and decreases to 60 mAh g$^{-1}$ up to 20 cycles. For the Li$_2$MnSiO$_4$/C composites prepared using 2mmol lithium manganese silicate precursors with 1g and 1.5g P123, the initial capacity is 139mAhg$^{-1}$, which is a little lower than the one prepared using 0.5g P123. Although the cycling stability of the last two Li$_2$MnSiO$_4$/C is better with a capacity drop to 75mAh/g for Li$_2$MnSiO$_4$ prepared
using 1g P123 and 80mAh/g for Li2MnSiO4 prepared using 1.5 g P123, the fading of capacity is still drastic.

![Galvanostatic charge-discharge curves](image)

Fig.3.2 Galvanostatic charge-discharge curves of the Li2MnSiO4/C prepared using 1g P123 with 2mmol Li2MnSiO4 precursors

Typical galvanostatic charge-discharge curves of the Li2MnSiO4/C composites are presented in fig 3.2. Lithium manganese silicate prepared using 1g P123 with 2mmol Li2MnSiO4 precursors is charged and discharged between 1.5 and 4.8V with a rate of 1/16 C (10mA g−1). It is interesting to find that the first charge curve is different from the subsequent ones, while the first and the following discharge curves are similar. A characteristic shift of the plateau on the first charging to a lower and stable potential on later cycles is observed. This phenomenon is related to the structural rearrangements of Li2MnSiO4 in the first charge process. As seen in Fig 3.2, the 2nd and 20th charge-discharge curves present two sloping plateaus at two different broad
potential ranges at around 3.0 and 4.2 V, corresponding to the Mn$^{2+}$/Mn$^{3+}$ and Mn$^{3+}$/Mn$^{4+}$ redox couples. The electrode polarization, given as the difference between the plateau on charging and a “quasi” plateau on discharging, is much increased after 20 cycles, resulting in a considerably decreased reversible capacity (50% of the initial capacity)

Table 3.1 BET Surface Area and Pore Size of Li$_2$MnSiO$_4$ Prepared with Different Amount of P123

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET Surface Area ($m^2/g$)</th>
<th>BJH Desorption Average Pore Size(nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine Li$_2$MnSiO$_4$</td>
<td>9.74</td>
<td>51.88</td>
</tr>
<tr>
<td>Li$_2$MnSiO$_4$+0.5gP123</td>
<td>93.67</td>
<td>6.60</td>
</tr>
<tr>
<td>Li$_2$MnSiO$_4$+1gP123</td>
<td>56.27</td>
<td>10.53</td>
</tr>
<tr>
<td>Li$_2$MnSiO$_4$+1.5gP123</td>
<td>53.16</td>
<td>11.49</td>
</tr>
</tbody>
</table>

Nitrogen adsorption isotherms were measured to obtain the surface areas and pore structure of the as prepared samples. Table 3.1 shows the BET specific surface area of the samples calculated from the N$_2$ adsorption–desorption isotherm curves of lithium
manganese silicate prepared using 0.5g, 1g, 1.5g P123. It can be shown that adding P123 to the system significantly increased the surface area of lithium manganese silicate product. Lithium manganese silicate prepared using 0.5g P123 has the largest BET surface area of is 93.67 m² g⁻¹ and the BET surface area decreased with increasing amount of P123 while pore size increases in a different direction. However, the surface area is still much less than the ordered porous structure silica prepared with P123 which has a N₂ BET surface area up to 1160 m²/g.

As shown in Fig.3.3, the nitrogen adsorption curve of lithium manganese silicate prepare with P123 all show type III isotherm with H₃-type hysteresis loop, which indicate disordered lamellar pore structure with slit and wedge shape and a broad pore-size distribution. The nitrogen adsorption curve suggested that although the surface area has been enlarged to some extent, no orderly arranged structure has formed.

Fig. 3.3 Adsorption–desorption isotherm curves of lithium manganese silicate synthesized using 0.5gP123
Fig. 3.4 Adsorption–desorption isotherm curves of lithium manganese silicate synthesized using 1gP123

Fig. 3.5 Adsorption–desorption isotherm curves of lithium manganese silicate synthesized using 1.5gP123
Fig.3.6 Thermogravimetric (TG) analysis cure of Li$_2$MnSiO$_4$ synthesised with difference silicon sources.

The interfacial property between electrode and electrolyte is further examined by EIS measurement. Fig.3.7 shows the Nyqvist plots of Li$_2$MnSiO$_4$/C with different amount of P123. All Nyquist plots contain a semicircle in the high-to-medium frequency region and a slope line in the low frequency region. The semicircle can be attributed to the charge transfer impedance between the electrolyte and electrode material, and the slope line is related to the Li$^+$ diffusion in the electrode material. In the inset of Fig.3.5, an equivalent circuit is proposed to model the Nyquist plot. The symbols Re, Rct, CPE, and Zw represent the ohmic resistance of the cell, charge transfer resistance, double layer capacitance, and Warburg diffusion impedance, respectively. It is seen that the Li$_2$MnSiO$_4$/C electrode without P123 exhibits a relatively huge charge transfer resistance of 650. However the charge transfer resistance decrease with the increasing amount of P123. This trend is in correspondence with the result in the the
TGA curves which means the better conductivity is majorly the contribution of higher amount of carbon in the sample. Higher carbon coating on the products allows better ion and electronic conductivity of the products. It shows that the recyclability is enhanced with increase in carbon and lower of transfer resistance while the initial capacity correlate to the BET surface area of the material. This can be explain as high surface area provide more area for ion and electron exchange in the first cycle while thicker carbon coating better prevent the structure collapse. Another reason for better stability is may be attributed to the larger pore size which is more facile for lithium ion insertion and extraction without affect the MnSiO$_4$ framework. However, the reason still need to be further proved.

Fig.3.5 Electrochemical impedance spectrum of Li$_2$MnSiO$_4$. 
4 Conclusion

In conclusion, lithium manganese silicate was for the first time prepared by using P123 as carbon source and morphology directing agent. Applying P123 to lithium manganese silicate system has successfully enlarged the surface area and decreased pore size of the product. Lithium manganese silicate prepared using 0.5g P123 has the largest BET surface area of \( 93.67 \, \text{m}^2 \, \text{g}^{-1} \) and the BET surface area decreased with increasing amount of P123. However, as indicated by the adsorption–desorption isotherm curves, no ordered pores were formed. Thermogravimetric Analysis was performed and the carbon amount of the as prepared samples were detected to increase with the increasing amount of P123 added to the system, which was corresponding to the decrease in charge transfer impedance as shown in electrochemical impedance spectrum curve. The discharge capacity of the \( \text{Li}_2\text{MnSiO}_4/\text{C} \) composite prepared using 2mmol lithium manganese silicate precursors and 0.5g P123 has the highest initial discharge capacity of 155mAhg\(^{-1}\). However, the cycling stability of the composite with 1g and 1.5g P123 is better. It shows that the cyclability is enhanced with increase in carbon and lower of transfer resistance while the initial capacity is correlated to the BET surface area of the material. This can be explain as high surface area provide more area for ion and electron exchange in the first cycle while thicker carbon coating better prevent the structure collapse. Another reason for better stability may be attributed to the larger pore size which is more facile for lithium ion insertion and extraction without affecting the \( \text{MnSiO}_4 \) framework. However, the reason still need to be further proved.
As evidenced by the large volume of projects underway in battery and capacitor materials synthesis, energy materials engineering as a field that doesn’t lack recommendations. Suggestions are limited here to a few ideas that immediately relate to the lithium manganese silicate project:

A Optimization the Synthesis Condition
As shown before, the nitrogen adsorption curve suggested that although the surface area has been enlarged to some extent, no orderly arranged structure has formed. However, highly ordered mesoporous silica with different morphologies have been successfully made using P123 as pore-creating agent.

Fiberlike mesoporous SBA-15 was synthesized by using P123 as the structure-directing agent. The synthesis was conducted in 4M HCl water solution and heated at 100 °C for 24 h[1]. Doughnutlike mesoporous SBA-15 powder was prepared by using N,N-dimethylformamide (DMF) as a cosolvent. A typical reaction composition was 2.0 g of P123: 30 g of H₂O:15 g of DMF:30 g of (4 M) HCl:4.4 g of TEOS. The calcination was carried out in an oven at 500 °C for 6 h in air to remove the block copolymer species.
The above synthesis method shows that the condition of synthesizing lithium manganese silicate such as pH of the solution, synthesizing temperature, and cosolvent have a significant influence on the structure of the mesopores. The synthesis was generally conducted in acid atmosphere. However, the original solution of starting materials is alkaline because of the amino group. Changing pH may change the function of amino group in attaching lithium and manganese salts. Further research need to be made to find an appropriate synthesis condition or better surfactant as pore creating agent.

B Aerosol Preparation of Lithium Manganese Silicate

In addition to sol-gel chemistry, spray processing is also an effective way in preparing nano particles. In aerosol technology, homogeneous solution is sprayed by an aerosol atomizer and the droplets created by the atomizer are blew to a heating tube by continuous inert gas flow and dried to super small particles. The diagram of aerosol reactor is shown in Fig 4.1. The atomizer produces aerosol droplets with a size distribution characterized by a geometric standard deviation of 2 which ensures the uniformity of the final particles.
In combination with template techniques, porous particles have been prepared by adding surfactant to the solution. Voids formed after the burn-off of the template and pore system is created in this way.

In 1999, spherical mesostructured particles was made through an aerosol technology using TEOS plus surfactant in a concentration much less than the critical micelle concentration in water-ethanol system by Yunfeng[2]. In 2014, Lintao Zeng and his group prepared spherical porous silica particles with well-defined mesoscopic pore structures by spray drying of nano colloidal SiO2, using polyvinylpyrrolidone (PVP) as pore template[3].

Therefore, we can assume that nano-scale lithium manganese silicate can also be made through such process simply by adding lithium and manganese salts to the silica-template solution in a stoichiometric ratio. However, the solubility of lithium and manganese salts in silica-template solution has to be considered. Besides, the pH of the solution, drying temperature are also important for the property of final products. Further researches need to be conducted in finding the best synthesis condition.
Reference

