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Effects of Li/Mn mole ratio on the synthesis of 
Li$_{1+x}$Mn$_{2-x}$O$_4$ by low temperature solid-state reaction 
for cathode materials

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Abstract

This study aims to determine the effects of the mole ratio of precursor on the synthesis of Li$_{1+x}$Mn$_{2-x}$O$_4$ ($x$=0; 0.02; 0.04; 0.06; 0.08; 0.1) by low temperature solid-state reaction. The variable examined in this study was the mole ratio of Li/Mn in Li$_{1+x}$Mn$_{2-x}$O$_4$. The compound was characterized by XRD, SEM-EDS, TEM and FTIR while the microstructural analysis of LiMn$_2$O$_4$ was performed by Direct Method using several programs including winPLOT, DICVOL, Checkcell and Diamond using XRD data. It is found that the mole ratio of the precursor affects the size, crystallinity and structure of Li$_{1+x}$Mn$_{2-x}$O$_4$. The results shows that Li$_{1+x}$Mn$_{2-x}$O$_4$ has a cubic crystal structure with Fd$\bar{3}$m phase and the increase in the mole precursor causes a change in the material structure of Li$_{1+x}$Mn$_{2-x}$O$_4$ into orthorhombic Fddd.

Keywords: Li$_{1+x}$Mn$_{2-x}$O$_4$; Li/Mn mole ratio; low temperature; solid state reaction.

1. Introduction

Lithium battery has received great attention in research. In addition to having high power, lithium battery is light and can be used multiple times (rechargeable). With the rapid
development of technology, the needs for more capable lithium battery to produce higher energy becomes indispensable (Thackeray, 2004; Armand & Tarascon, 2008; Song, 2011).

The performance, the price and safety of Li-ion batteries mainly depend on the properties of cathode materials. Attention has been paid to the development of high capacity, cheap and safe cathode materials (Ritchie & Howard, 2006). LiMn₂O₄ is very promising candidate because its low cost and safety characteristics are superior compared to layered cobalt or nickel oxides (Aifantis et al., 2010; Manjunatha et al., 2010; Xu et al., 2012). LiMn₂O₄ is quite distinct from such layered oxides in that it is a three-dimensional host. The spinel structure space group Fd3m consists of cubic closed-packed oxide ions Mn ions in one half of the octahedral sites and Li⁺ in one eighth of the tetrahedral sites within the cubic close-packed oxide array. The Mn₂O₄ framework of the spinel structure is highly stable, and defines a series of tunnels formed by the face-sharing of tetrahedral lithium (8a) and empty octahedral (16c) sites. These tunnels intersect in three dimensions and support rapid lithium diffusion but, unlike the layered compounds, the spinels are selective for lithium ions over solvent molecules or other larger cations because of their greater structural rigidity (Bruce, 1997; Patil et al., 2008; Julien & Massot, 2003).

There are various approaches to the synthesis of LiMn₂O₄ spinel including conventional solid reaction (Kim et al., 2008; Lee et al., 2010), sol-gel reaction (Lakshmi et al., 1997; Kumar et al., 2003), and Pechini process. Compared to sol-gel and Pechini approaches, in which additional starting materials and synthetic materials and synthetic procedures are generally needed for preparation and separation of the targeted Li-Mn precursors, solid reaction is simpler and easier to handle. Therefore, in this work we used solid reaction to synthesize LiₓMn₂₋ₓO₄ (x=0; 0.02; 0.04; 0.06; 0.08; 0.10).

A series of LiMn₂O₄ compounds were prepared using a low temperature solid-state reaction, i.e., reflux technique at various Li/Mn mole ratios. The advantage of this technique is that it can be done for a longer time without the need for adding more solvent or fear of the reaction vessel boiling dry, as the vapour is immediately condensed. In addition, as a given solvent will always boil at a certain temperature, one can be sure that the reaction will proceed at a constant temperature. The effects of the synthetic Li/Mn mole ratio on the structure of the products are to be investigated in details.

2. Experimental section

2.1 Synthesis of MnO₂ and LiMn₂O₄ nanorods

Analytical grade of Mn(CH₃COO)₂ and Na₂S₂O₈ (Aldrich) were used to prepare MnO₂ nanorods by reflux technique. All chemicals were used without further purification. In a typical synthesis, Mn(CH₃COO)₂ and Na₂S₂O₈ were dissolved at room temperature with a molar ratio of 1:1 in 80 mL deionized distilled water by magnetic stirring to form a homogeneous clear solution. The mixed solution was transferred into boiling flask and heated at 120 °C for 12 hours. The obtained powder was subsequently dried at 100 °C for 12 h in air (Purwaningsih et al., 2015).

A typical synthesis of LiMn₂O₄ is as follows: 0.00143 moles of LiOH and 0.0028 moles of as-synthesized MnO₂ were dispersed into 2 mL high purity ethanol to form a thick slurry, ground to form a fine mixture for several hours and dried at room temperature. The above process was repeated two or three times to produce a well-mixed powder. The powder was
then calcined at 750 °C for 5 hours. The same procedure was conducted for Li$_{1.02}$Mn$_{1.98}$O$_4$; Li$_{1.03}$Mn$_{1.97}$O$_4$; Li$_{1.06}$Mn$_{1.94}$O$_4$; Li$_{1.08}$Mn$_{1.92}$O$_4$ and Li$_{1.10}$Mn$_{1.90}$O$_4$.

2.2 Characterization of Li$_{1+x}$Mn$_{2-x}$O$_4$ microstructure

The synthesized MnO$_2$ and Li$_{1+x}$Mn$_{2-x}$O$_4$ (x = 0, 0.02, 0.04, 0.06, 0.08, and 0.10) nanostructures were characterized using an X-ray diffractometer (XRD Rigaku, Miniflex) with Cu Kα radiation (λ = 0.15406 nm at 40 kV and 40 mA). Using XRD data, the structural analysis of the products was performed by the Direct Method using several programs that are winPLOTR, DICVOL, Checkcell and Diamond. The size and shape of the nanoparticles were observed by Transmission Electron Microscopy (TEM).

3. Results and discussions

3.1 Structure and morphology of LiMn$_2$O$_4$

![Fig. 1. (a) SEM images (b) TEM images (c) SAED pattern of LiMn$_{2}$O$_{4}$.](image)

Single phase spinels with a Li:Mn ratio of 1:2 of composition LiMn$_2$O$_4$ are formed around in 750 °C in air. Irrespectively, of the choice of the Li and Mn starting material, nearly black material with a cubic cell and a lattice constant 8.2452 Å are obtained. According to the Scanning Electron Microscopy (SEM) observations, the material is well formed and exhibits clearly developed crystal faces (Fig. 1). The TEM images and selected area of the electron diffraction (SAED) pattern further revealed that LiMn$_2$O$_4$ has the high quality cubic (space group Fd3m) crystalline nanorods with diameter 50-100 nm.

![Fig. 2. (a) XRD pattern (b) Microstructure of LiMn$_2$O$_4$.](image)
From the structural calculation using Direct Method, it is showed that LiMn$_2$O$_4$ in the space group $Fd\bar{3}m$. This is in agreement with the complete occupation of the site 8a by Li, the site 16d by Mn, and the site 32e by oxygen.

3.2 Structure and morphology of Li$_{1.02}$Mn$_{1.98}$O$_4$ and Li$_{1.04}$Mn$_{1.96}$O$_4$

The TEM images and SAED pattern further revealed that Li$_{1.02}$Mn$_{1.98}$O$_4$ and Li$_{1.04}$Mn$_{1.96}$O$_4$ have the high quality cubic (space group $Fd\bar{3}m$) crystalline nanorods. The nanorods were well-dispersed and one-dimensional with an average diameter between 50-100 nm. The corresponding SAED pattern supports the formation of structure of cubic crystalline nanorods.

Fig. 3. (a) TEM images (b) SAED pattern (c) XRD pattern of Li$_{1.02}$Mn$_{1.98}$O$_4$ (d) TEM images (e) SAED pattern (f) XRD pattern of Li$_{1.04}$Mn$_{1.96}$O$_4$. 
3.3 Structure and morphology of Li$_{1.06}$Mn$_{1.94}$O$_4$, Li$_{1.08}$Mn$_{1.92}$O$_4$ and Li$_{1.10}$Mn$_{1.90}$O$_4$

Fig. 4. (a) TEM images (b) SAED pattern (c) XRD pattern of Li$_{1.06}$Mn$_{1.94}$O$_4$, (d) TEM images (e) SAED pattern (f) XRD pattern of Li$_{1.08}$Mn$_{1.92}$O$_4$, (g) TEM images (h) SAED pattern (i) XRD pattern of Li$_{1.10}$Mn$_{1.90}$O$_4$.

The TEM images and SAED pattern further revealed Li$_{1.06}$Mn$_{1.94}$O$_4$, Li$_{1.08}$Mn$_{1.92}$O$_4$ and Li$_{1.10}$Mn$_{1.90}$O$_4$ have the high quality orthorhombic (space group Fddd) crystalline. The nanorods were well-dispersed and maintained one-dimensional with an average diameter between 50-100 nm. The corresponding SAED pattern supports the formation structure of orthorhombic Fddd crystalline nanorods.

Table 1. Lattice parameter, volume and agreement factor of Li$_{1+x}$Mn$_x$O$_4$.

<table>
<thead>
<tr>
<th>Variation x</th>
<th>Space Group</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>v</th>
<th>Rp</th>
<th>Rwp</th>
<th>Re</th>
<th>Chi$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>Cubic Fd3m</td>
<td>8.245200</td>
<td>8.245200</td>
<td>8.245200</td>
<td>560.5259</td>
<td>33.4</td>
<td>18.9</td>
<td>11.8</td>
<td>2.560</td>
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<tr>
<td>0.02</td>
<td>Cubic Fd3m</td>
<td>8.242592</td>
<td>8.242592</td>
<td>8.242592</td>
<td>560.0044</td>
<td>76</td>
<td>32.6</td>
<td>35.9</td>
<td>0.914</td>
</tr>
<tr>
<td>0.04</td>
<td>Cubic Fd3m</td>
<td>8.230799</td>
<td>8.230799</td>
<td>8.230799</td>
<td>557.6041</td>
<td>60.7</td>
<td>35.9</td>
<td>28.1</td>
<td>1.639</td>
</tr>
<tr>
<td>0.06</td>
<td>Orthorhombic Fddd</td>
<td>8.234879</td>
<td>8.232482</td>
<td>8.234783</td>
<td>558.2647</td>
<td>69.4</td>
<td>32</td>
<td>32.5</td>
<td>0.967</td>
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<tr>
<td>0.08</td>
<td>Orthorhombic Fddd</td>
<td>8.229085</td>
<td>8.233565</td>
<td>8.233167</td>
<td>557.8358</td>
<td>76.3</td>
<td>38.2</td>
<td>33.2</td>
<td>1.320</td>
</tr>
<tr>
<td>0.1</td>
<td>Orthorhombic Fddd</td>
<td>8.230813</td>
<td>8.224436</td>
<td>8.225409</td>
<td>556.8091</td>
<td>59.5</td>
<td>27.3</td>
<td>27.8</td>
<td>0.964</td>
</tr>
</tbody>
</table>
From the analysis using FullProf Pattern Matching, it is seen that the stoichiometric ratio of the change in structural changes in the system Li-Mn-O of the \( Fd\bar{3}m \) cubic phase into orthorhombic \( Fddd \). These changes result from the Jahn-Teller distortion effects caused by \( Mn^{3+} \) ions. It is possible that \( Mn^{3+} \) ions replaced by \( Li^{+} \) ions.

4. Conclusions

\( Li_{1+x}Mn_{2.4}O_4 \) \( (x=0; 0.02; 0.04; 0.06; 0.08; 0.10) \) have been prepared and characterized using low temperature solid-state reaction. The results shows that \( Li_{1+x}Mn_{2.4}O_4 \) \( (x=0; 0.02 \) and \( 0.04) \) have a cubic crystal structure with space group of \( Fd\bar{3}m \) and the increase in the mole precursor causes a change in the material structure of \( Li_{1+x}Mn_{2.4}O_4 \) \( (x=0.06; 0.08; 0.10) \) into orthorhombic \( Fddd \).

References

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