Solid-state reaction synthesis and characterization of Mn-doped LiFePO₄ cathode material

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Abstract. Olivine type LiFePO₄ has great advantages for Li-ion batteries due to its non-toxicity, high safety, and good cycle life performance. However, its low-rate capability and low energy density make some challenges for this LiFePO₄. Several methods like doping with transition metals were used, and Mn ion was used in this work to improve the overall electrochemical properties. LiMnₓFe₁₋ₓPO₄ is promising cathode material owing to high voltage, structural and chemical stability. However, the electrochemical performance of these materials depends on phases and structures obtained from synthesis. In this work, the effect of solid-state reaction conditions, including calcination temperature and duration, on morphology, structure, and electrochemical properties of LiMnₓFe₁₋ₓPO₄ cathode materials with the composition of x = 0.5 was investigated. The morphology, crystallography and local structure of the synthesized materials were examined by field emission scanning electron microscope (FE-SEM), X-ray diffractometer (XRD) and Fourier-transform infrared spectrometer (FTIR), respectively. The surface area was also determined by the Brunauer-Emmett-Teller (BET) model. The effect of calcination temperature and reaction time upon the morphology, structures of the synthesized cathode materials were studied and discussed. The results could be essential for further development and employment of LiMnₓFe₁₋ₓPO₄ in Li-ion batteries.

1. Introduction

Olivine-type lithium-transition metal phosphates (LiMPO₄) (M = Fe, Mn, Co, Ni, etc…) are taken into account for potential cathode materials due to high theoretical specific capacity, superior safety capacity, environmental friendliness and low cost [1]. Among these LiMPO₄, LiFePO₄ (theoretical capacity of 170 mAhg⁻¹ and operation potential of 3.4 V vs. Li/Li⁺) is well known for the aforementioned advantages as well as has been investigated intensively and successfully commercialized [2]. However, this material possesses drawbacks of low electronic conductivity (<10⁻⁹ Scm⁻¹) and poor Li⁺ ion diffusion. In addition, its low working potential (3.4 V vs. Li/Li⁺) restricts to use in high power applications, such as electric vehicles.
Several methods can be used to tackle the drawbacks such as tailoring morphology, coating conductive carbon on primary particles and doping with some transition metal ions (e.g., Mn⁺, Co⁺, Ni⁺, Mg²⁺, Cr³⁺, Ti⁴⁺, etc.) [6, 7].

Owning the same structure as LiFePO₄, lithium manganese phosphate (LiMnPO₄) is also a promising alternative cathode material [8]. Containing Mn element gives benefits in terms of material cost and environmental friendliness. Compared with LiFePO₄, it exhibits a higher potential of 4.1 V vs. Li/Li⁺, which leads to being more suitable for high power applications [9, 10] Nevertheless, structural change during intercalation and deintercalation of Li ions, Jahn-Teller distortion of unstable Mn³⁺ ion and poor electronic conductivity make this cathode material imperfect. Similar improvement methods can be implemented to enhance the properties of LiMnPO₄ [11, 12]. For example, Jo et al. reported that the composition of LiMn₀.₇₁Fe₀.₂₉PO₄ cathode material prepared by polyol method showed the high volumetric capacity of 243 and 128 mAh cm⁻³ at 0.1C and 7C, respectively, and excellent cycling performance [13]. Moreover, LiMn₀.₅Fe₀.₅PO₄ prepared by a solvothermal route exhibited long term cycling stability and good high rate performance up to 1000 cycles [9].

Various synthesis methods, such as sol-gel and solid-state reaction, can be used to prepare LiMnₓFe₁₋ₓPO₄ and the synthesis condition can strongly influence electrochemical performance [6, 12, 14]. By adjusting synthesis parameters, the morphology of the materials can be tailored to nanostructure. Among all techniques, a solid-state reaction is often applied due to simplicity and low cost. Many research works have applied this method to synthesize the cathode materials, but most of the works used long two-step calcination at high temperatures, which is quite energy and time consuming [8, 14]. Only a few works demonstrate a synthesis condition using short calcination time. Therefore, in this work, LiMnₓFe₀.₅PO₄ with x = 0.5 was synthesized by a solid-state reaction method and, then thermally treated at 450°C and 550°C for a given time (i.e., 2, 6 and 12 h). The particle morphology, structure, local structure, and specific surface area obtained from different calcination times was investigated and discussed. This relationship could emphasize the importance of synthesis condition optimization for performance improvement.

2. Experimental

2.1. Synthesis of LiMn₀.₅Fe₀.₅PO₄ Materials

LiMn₀.₅Fe₀.₅PO₄ cathode materials were synthesized by a solid-state reaction method. Manganese (II) carbonate (Aldrich, 99.9%), iron (II) oxalate dihydrate (Aldrich, 99%) and lithium phosphate monobasic (Aldrich, 99%) were used as starting materials and ethanol was used as a dispersant. The stoichiometric ratio of Li: Mn: Fe (1: 0.5: 0.5) and an appropriate amount of ethanol were mixed by jar rolling with yttrium-stabilized zirconia balls as grinding media for 18 h. Then, the mixture was dried overnight at 80°C to evaporate the ethanol. After that, the dried powder was ground. Finally, the materials were calcined at 450°C and 550°C for 2, 6 and 12 h in argon (Ar) atmosphere to obtain the final powder of LiMn₀.₅Fe₀.₅PO₄.

2.2. Materials Characterization

The crystal structure and phase of the synthesized materials were examined using an X-ray diffractometer (Philips X’Pert) with Cu Kα radiation (λ = 0.154 nm) over the range of 10° to 60° at a step size of 0.02°. The surface morphology and particle size of the particles were analyzed using a field emission scanning electron microscope (JEOL-JSM-7600F). The composition of the LiMn₀.₅Fe₀.₅PO₄ powder was analyzed by energy dispersive spectroscopy (EDS). The Fourier transform infrared (FT-IR) spectrum was obtained with KBr pellets using Bruker Alpha-E spectrometer. The specific surface areas were measured with Micromeritics 3Flex at 77 K using the Brunauer-Emmett-Teller method.
3. Results and discussion

The X-ray diffraction pattern of the cathode materials for each synthesis condition is shown in Figure 1. For all conditions, some peaks were well indexed with the orthorhombic structure with the space group of Pnmb (62) (ICDD-00-042-0580). Such peaks can be identified as LiMn0.5Fe0.5PO4. Some impurity phases, namely LiPO3, Li3PO4 and Li4P2O7 were also found. However, the impurity phases decreased when the temperature increased. This is possibly caused by an incomplete reaction at low temperatures and short calcination times. The crystallite sizes of these materials were estimated using the Scherrer’s equation and shown in Table 1. The crystallite sizes of all synthesis conditions were in the range of 25-30 nm and increased with the calcination time.

![Image](Figure 1. XRD patterns of LiMn0.5Fe0.5PO4 calcined at (a) 450℃ (b) 550℃ for 2, 6 and 12 h.)

The morphology and structure of the synthesized materials were characterized by FE-SEM and the images are shown in Figure 2(a - f). From the results, the particles of all conditions were similar. Specifically, particles were agglomerated with a primary size of 20 – 52 nm. However, the particle sizes became larger with increasing temperatures. On the other hand, increasing calcination time can slightly decrease the particles sizes. The box plot of particle size analyses of LiMn0.5Fe0.5PO4 is shown in Figure 2(g).

![Image](Figure 2. FESEM images of LiMn0.5Fe0.5PO4 (a - c) synthesized at 450℃ for 2, 6 and 12 h, respectively (d - f) synthesized at 550 ℃ for 2, 6 and 12 h, respectively and (g) box plot of particle size (yellow and blue color represents calcination at 450℃ and 550℃, respectively).)

The functional group vibration modes of LiMn0.5Fe0.5PO4 prepared at different conditions were examined by FTIR spectroscopy in the region of 4000 - 400 cm⁻¹ and are shown in Figure 3. Both spectra have similar vibrational modes. The bands at 1092 and 1052 cm⁻¹ belong to the LiMnPO4 and LiFePO4 respectively. A
single broad band found between these two bands belongs to a solid solution of LiMn$_{0.5}$Fe$_{0.5}$PO$_4$ [15]. Such a solid solution began to form at high temperatures for a long period of time. As a result, it can only be found in the condition of 550 °C for 12 h, and not found in the other conditions due to the incomplete reaction. In addition, all synthesized materials exhibited the vibrational mode of PO$_4^{3-}$: three bands between 1140 and 1043 cm$^{-1}$ corresponding to ($\nu_3$) antisymmetric stretching mode, two bands between 978 and 749 cm$^{-1}$ corresponded to ($\nu_1$) symmetric stretching mode, three bands between 636 and 552 cm$^{-1}$ corresponded to ($\nu_4$) bending mode and the band around 460 cm$^{-1}$ corresponding to ($\nu_2$) bending mode.

![Figure 3. FTIR spectra of LiMn$_{0.5}$Fe$_{0.5}$PO$_4$ calcined at (a) 450 °C and (b) 550 °C for 2, 6, and 12 h.](image)

The specific surface area of these LiMn$_{0.5}$Fe$_{0.5}$PO$_4$ materials were measured with Brunauer-Emmett-Teller (BET) model and is showed in Table 1. The materials synthesized at 550°C possessed a higher specific surface area. Increasing the reaction time can also increase the surface area which was correlated well with the primary particle size analyses. In other words, the smaller the size of particles, the greater is the specific surface area.

| Temperature (°C) | Time (h) | Crystallite size (nm) | Particle size (nm) | Specific surface area (m$^2$/g) |
|-----------------|----------|-----------------------|-------------------|-------------------------------|
| 450             | 2        | 24.3                  | 29                | 5.38                          |
|                 | 6        | 28.7                  | 24                | 5.54                          |
|                 | 12       | 29.6                  | 21                | 6.24                          |
| 550             | 2        | 23.4                  | 52                | 7.31                          |
|                 | 6        | 26.8                  | 37                | 12.06                         |
|                 | 12       | 28.3                  | 33                | 12.36                         |

4. Conclusions
Mn-doped LiFePO$_4$ cathode materials were successfully synthesized by a solid-state reaction method at different temperatures and reaction times. XRD patterns showed that materials for all conditions had identified with the reference data of LiMn$_{0.5}$Fe$_{0.5}$PO$_4$, but impurity peaks were found at low synthesis temperatures. The particle became aggregate at high temperature and the smaller particle size was achieved when increasing the reaction time. LiMn$_{0.5}$Fe$_{0.5}$PO$_4$ synthesized at 550°C possessed a higher specific surface
area than 450°C. The results can provide the optimal conditions for Mn-doped LiFePO$_4$ synthesis, which positively influences the electrochemical performance of the cathode material for Li-ion batteries.

Acknowledgements
This work was financially supported by International Collaborative Education Program for Materials Technology, Education, and Research (ICE-Matter). In addition, the authors gratefully acknowledge the facilities of the Department of Materials Engineering, Faculty of Engineering, Kasetsart University.

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