

Structural and Electrochemical Characterization of LiFePO₄ Synthesized by Hydrothermal Method

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Phospho-olivine LiFePO₄ cathode materials were prepared by hydrothermal reaction. Carbon black was added to enhance the electrical conductivity of LiFePO₄. The structural and morphological performance of LiFePO₄ and LiFePO₄-C powders were characterized by X-ray diffraction (XRD), scanning electron microscope (SEM) and transmission electron microscope (TEM). LiFePO₄/Li and LiFePO₄-C/Li cells were characterized electrochemically by cyclic voltammogram (CV), charge/discharge experiments and ac impedance spectroscopy. The results showed that the discharge capacity of LiFePO₄/Li cell was 147 mAh/g at the first cycle and 118 mAh/g after 30 cycles, respectively. The discharge capacity of LiFePO₄-C/Li cell with 5 wt% carbon black was the largest among LiFePO₄-C/Li cells, 133 mAh/g at the first cycle and 128 mAh/g after 30 cycles, respectively. It was demonstrated that cycling performance of LiFePO₄-C/Li cell with 5 wt% carbon black was better than that of LiFePO₄/Li cell.

Keywords : LiFePO₄, Carbon black, Cathode material, Hydrothermal method

1. INTRODUCTION

Since the commercialization of rechargeable lithium-ion batteries by Sony Energy Tech.[1] 15 years ago, they have been widely utilized as the power sources in a wide range of applications, such as mobile phones, laptop computers, cameras, electrical vehicles (EV), and hybrid electrical vehicles (HEV). In the rechargeable lithium ion batteries, cathode material is the key component, and mainly devoted to the performance of the batteries. Among the known cathode materials, the layered LiCoO₂, LiMnO₂ and LiNiO₂, spinel LiMn₂O₄, and elemental sulfur have been studied extensively[2-10]. LiCoO₂ has been nowadays utilized for commercial lithium-ion batteries. However, novel cathode material must be developed not only in relation to battery performance, but also in relation to safety and cost.

Recently, lithium transition metal phosphates with an ordered olivine-type structure, LiMPO₄ (M = Fe, Mn, Ni, and Co), have attracted extensive attention due to a high theoretical specific capacity(170 mAh/g)[11]. The potential of the M³⁺/M²⁺ redox couple versus Li/Li⁺ of LiMPO₄ is as follows; 3.5 V for LiFePO₄, 4.1 V for LiMnPO₄, 5.2-5.4 V for LiNiPO₄, and 4.8 V discharge plateau for LiCoPO₄. Among these phosphates, LiFePO₄ is the most attractive because of its high stability, low

cost, high compatibility with environment[12,13]. However, it is difficult to attain its full capacity because its electronic conductivity is very low, and diffusion of Li⁺ ion in the olivine structure is slow. It is found that small amount of Fe²⁺ is oxidized to Fe³⁺ during hydrothermal process or annealing process[14,15]. There are two methods to improve the electronic conductivity. One method is to introduce conductive additives including carbon coating[16-20] and supervalent cation doping[21,22]. Another method is to control the particle size by optimizing the synthesis conditions[23].

In this study, phospho-olivine LiFePO₄ was prepared by hydrothermal reaction. In order to enhance the electrical conductivity of LiFePO₄, carbon black was added. LiFePO₄/Li and LiFePO₄-C/Li cells were fabricated in an argon-filled glove box and their electrochemical properties were analyzed by means of CV, ac impedance and charge-discharge experiments.

2. EXPERIMENTAL

LiFePO₄ was prepared with starting materials of LiOH·H₂O (Aldrich Co. 99.95 %), FeSO₄·7H₂O (Aldrich Co. 99+%), H₃PO₄ (Aldrich Co. 99.999+%) and

$C_6H_8O_6$ (Aldrich Co. 99+%). After $LiOH \cdot H_2O$ was dissolved in distilled water to obtain 1M solution, H_3PO_4 and $FeSO_4 \cdot 7H_2O$ powders were added to $LiOH$ solution in a molar ratio for $Li:Fe:P = 3:1:1$. Addition of ascorbic acid as a reducing agent to the precursor was useful in prohibiting the conversion of Fe^{2+} to Fe^{3+} during the hydrothermal reaction and generation of $\alpha-Fe_2O_3$ during the annealing process. The mixed solution was heated at $150\text{ }^\circ\text{C}$. After being cooled to room temperature, the solution was filtered to separate the precipitate powder, the powder was washed with ultrapure water. The obtained powder was dried at $100\text{ }^\circ\text{C}$ for 1 h under vacuum. The dried powders were further dried at $400\text{ }^\circ\text{C}$ for 1 h in nitrogen atmosphere. In order to improve low electron conduction of $LiFePO_4$, carbon black with different content (5 wt%, 10 wt% and 15 wt%) was added.

The crystalline phases were identified with X-ray diffraction (XRD, Dmax/1200, Rigaku). The X-ray diffraction pattern was collected by a step-scanning mode in the range of $10^\circ \sim 80^\circ$ with a step time of $5^\circ/\text{min}$. Powder morphologies were observed by SEM (JEOL JSM-5400) and TEM (JEOL JEM-2000 FXII). A composite electrode was prepared by mixing $LiFePO_4$ or $LiFePO_4-C$ with carbon black and polyvinylidene fluoride (PVDF) in a weight ratio of 70:25:5. This mixture was coated onto an Al-foil, cut into $2 \times 2\text{ cm}$ sections and heated at $110\text{ }^\circ\text{C}$ for 24 h under vacuum. A lithium foil was used as an anode. Electrolyte was 1M $LiPF_6$ dissolved in ethylene carbonate/dimethyl carbonate (EC:DMC=1:1). The beaker-type cells were fabricated for the electrochemical tests. Charge/discharge testing was performed using automatic charge/discharge equipment (WBCS3000, WonaTech Co.) in a potential range of 2.5-4.3 V at a constant current density of 0.1 mA/cm^2 . Electrochemical impedance measurements were performed using an IM6 impedance system (Zahner Elektrik Co.). The spectrum was potentiostatically measured by applying an ac voltage of 10 mV over the frequency range from 2 MHz to 10 mHz. The WBCS3000 (Wonatech) Battery Tester System was also used for measurements of cyclic voltammetry at a scan rate of 0.1 mV s^{-1} .

3. RESULTS AND DISCUSSION

3.1 Crystal structure

XRD patterns of $LiFePO_4-C$ powders are shown in Fig. 1. All the patterns can be indexed to a single-phase material having an orthorhombic olivine-type structure (space group $Pmnb$), which are the same as the theoretical value. No impurity is found in all the $LiFePO_4-C$ powders.

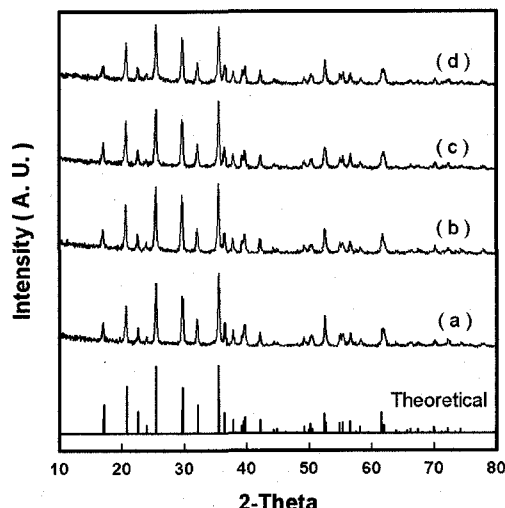


Fig. 1. XRD patterns of $LiFePO_4$ (a), $LiFePO_4-5\text{ wt}\%$ (b), $LiFePO_4-10\text{ wt}\%$ (c) and $LiFePO_4-15\text{ wt}\%$ carbon black (d).

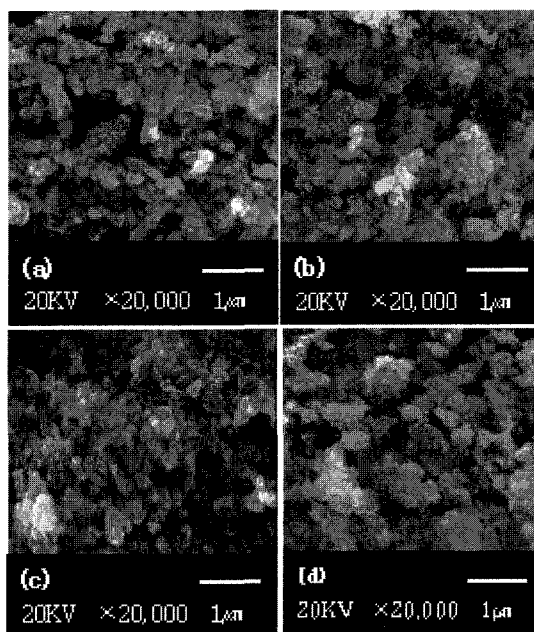


Fig. 2. SEM images of $LiFePO_4$ (a), $LiFePO_4-5\text{ wt}\%$ (b), $LiFePO_4-10\text{ wt}\%$ (c) and $LiFePO_4-15\text{ wt}\%$ carbon black (d).

3.2 SEM and TEM

SEM and TEM images of $LiFePO_4-C$ powders are shown in Fig. 2 and Fig. 3, respectively. As can be seen from Fig. 2(a), the average particle size of $LiFePO_4$ is around 350 nm. It is shown from Fig. 2(b), Fig. 2(c) and Fig. 2(d) that the average particle size of $LiFePO_4-C$ powders with 5 wt%, 10 wt% and 15 wt% is around 250,

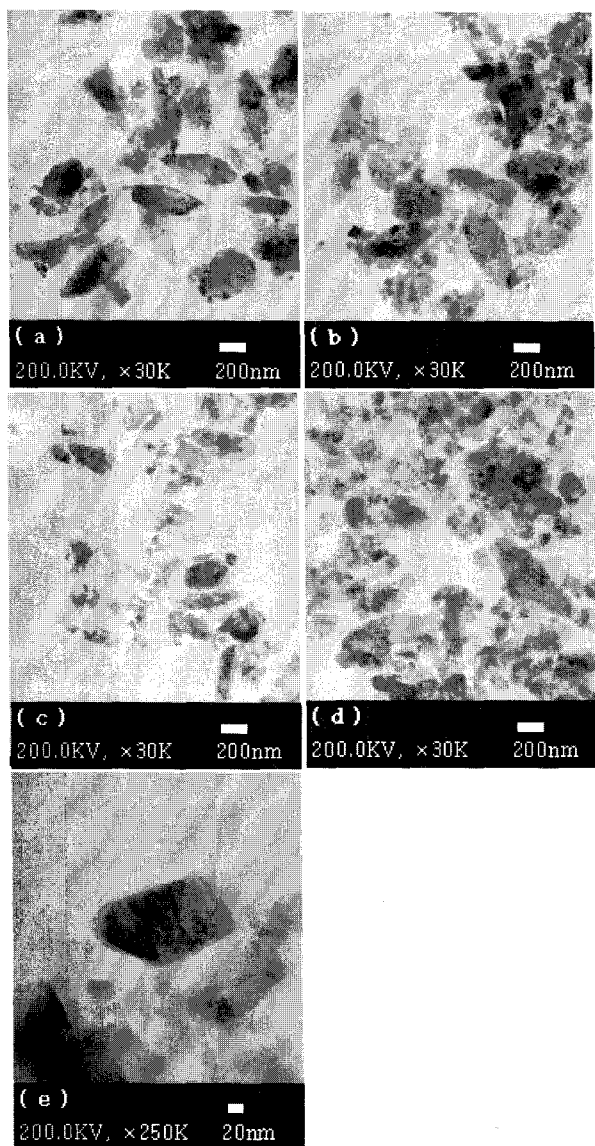


Fig. 3. TEM images of LiFePO₄ (a), LiFePO₄-5 wt% (b), LiFePO₄-10 wt% (c), LiFePO₄-15 wt% (d) and magnified LiFePO₄-5 wt% carbon black (e).

200 and 150 nm, respectively. It is obvious that the average particle size of LiFePO₄-C powders is much smaller than that of LiFePO₄ powders. This demonstrates that carbon black in the mixture retards the particle growth during calcination. When carbon content is 10 wt% and 15 wt%, the particles agglomerate and form the secondary particles. The smaller particles, which shorten the lithium ions diffusion distances between the surfaces and center during lithium intercalation and de-intercalation, are expected to contribute the enhanced electrochemical performance of the carbon-coated LiFePO₄.

As can be seen from Fig. 3(a), an amorphous layer is clearly observed for the hydrothermally synthesized LiFePO₄, but this amorphous layer is crystallized by heat-treatment at 400 °C, as shown in Fig. 3(b), Fig. 3(c)

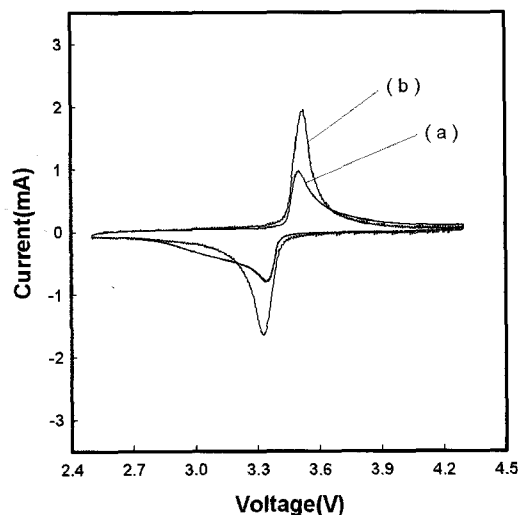


Fig. 4. Cyclic voltammetry of LiFePO₄/Li (a) and LiFePO₄-C(5 wt%)/Li cell (b).

and Fig. 3(d). To confirm how carbon black is dispersed in LiFePO₄-C powders, a part of LiFePO₄ powders which contain 5 wt% carbon (Fig. 3(b)) is magnified, as shown in Fig. 3(e). It is obvious from the image that the surfaces of LiFePO₄ powders are coated by carbon coating layer.

3.3 Cyclic voltammetry

Cyclic voltammetry of LiFePO₄/Li and LiFePO₄-C/Li cell with 5 wt% carbon black is shown in Fig. 4. As can be seen from Fig. 4(a), reduction and oxidation peak positions for LiFePO₄/Li cell appear at 3.375 and 3.54 V vs Li/Li⁺, respectively. It is shown from Fig. 4(b) that reduction and oxidation peak positions for LiFePO₄-C/Li cell with 5 wt% carbon black appear at 3.32 and 3.54 V vs Li/Li⁺, respectively. It is obvious that the reduction and oxidation peak currents of LiFePO₄-C/Li cell are greater than that of LiFePO₄/Li. It is demonstrated that the reversibility of LiFePO₄-C/Li cell with 5 wt% carbon black is better than that of LiFePO₄/Li.

3.4 Charge/discharge properties

Cycling performance of LiFePO₄/Li and LiFePO₄-C cells is shown in Fig. 5. As can be seen from Fig. 5, the discharge capacity of LiFePO₄/Li cell is 147 mAh/g at the first cycle and 118 mAh/g after 30 cycles, respectively. The initial discharge capacity of LiFePO₄ with 5 wt%, 10 wt% and 15 wt% carbon black is 133, 115 and 105 mAh/g, respectively. After 30 cycles, the discharge capacity of LiFePO₄ with 5 wt%, 10 wt% and 15 wt% carbon black is 128, 112 and 106 mAh/g, respectively. It is demonstrated that cycling performance of LiFePO₄-C/Li cell is better than that of LiFePO₄/Li cell and the discharge capacity is the largest when carbon content is 5 wt%. It is consistent with the CV results in Fig. 4.

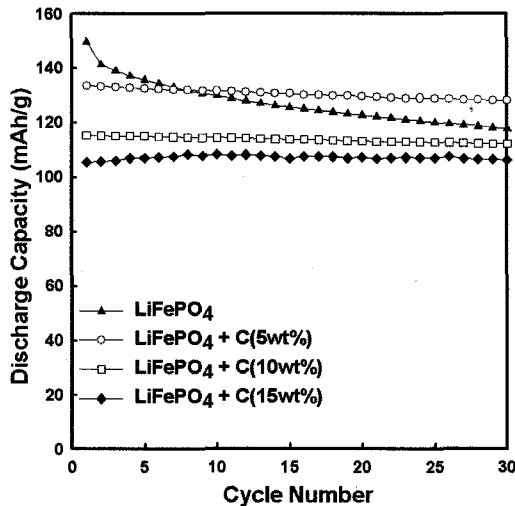


Fig. 5. Cycling performance of LiFePO₄/Li and LiFePO₄-C/Li cells.

3.5 Impedance properties

Impedance spectra of LiFePO₄/Li and LiFePO₄-C/Li cell with 5 wt% carbon black upon cycling are shown in Fig. 6. It is noted that the ac impedance response of the cell forms a broad semicircle and a line to the real axis in the lowest frequency range. The semicircle in the high frequency is mainly related to the complex reaction process at the electrolyte/cathode interface including resistance of SEI film formed on the surface LiFePO₄ particles, the particle-to-particle contact resistance, charge transfer resistance, and corresponding capacitances. The inclined line in the lower frequency is attributed to the Warburg impedance, which is associated with lithium ion diffusion in LiFePO₄ electrode. As can be seen from Fig. 6(a), the resistance is 20 Ω at the first cycle, 25 Ω after 3 cycles, 30 Ω after 5 cycles, 31 Ω after 7 cycles and 38 Ω after 9 cycles, respectively. It is obvious that LiFePO₄/Li cell resistance increases upon the cycling. As can be seen from Fig. 6(b), the resistance is 19 Ω at the first cycle, 20 Ω after 3 cycles, 21 Ω after 5 cycles, 21 Ω after 7 cycles and 22 Ω after 9 cycles, respectively. It is obvious that LiFePO₄-C/Li cell with 5 wt% carbon black resistance hardly changes upon the cycling. It is noted that the length of the inclined line in LiFePO₄/Li cell is longer than that of the inclined line in LiFePO₄-C/Li cell with 5 wt% carbon black, that is to say, lithium ion diffusion in LiFePO₄-C electrode is faster than that in LiFePO₄ electrode, therefore, as can be seen from Fig. 5, cycling performance of LiFePO₄-C/Li cell is better than that of LiFePO₄/Li cell.

4. CONCLUSION

Phospho-olivine LiFePO₄ cathode materials were prepared by hydrothermal reaction. Carbon black was

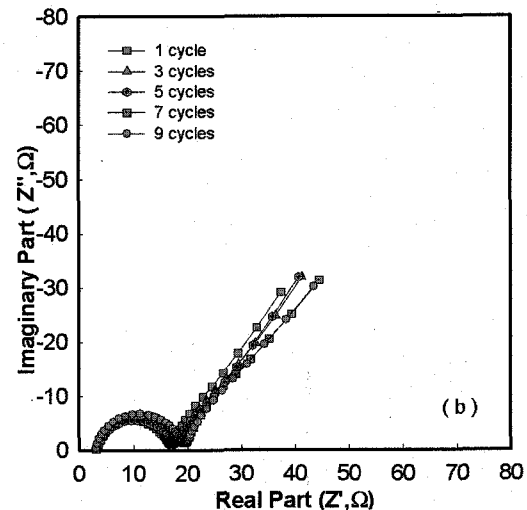
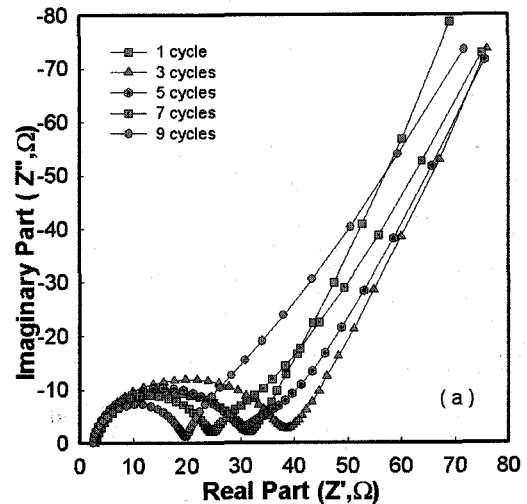


Fig. 6. Impedance spectra of LiFePO₄/Li (a) LiFePO₄-C cell with 5 wt% carbon black (b) upon cycling.

added to enhance the electrical conductivity of LiFePO₄. The average particle size of LiFePO₄-C powders is much smaller than that of LiFePO₄ powders. The discharge capacity of LiFePO₄/Li cell is 147 mAh/g at the first cycle and 118 mAh/g after 30 cycles, respectively. The discharge capacity of LiFePO₄-C/Li cell with 5 wt% carbon black is the largest among LiFePO₄-C/Li cells, 133 mAh/g at the first cycle and 128 mAh/g after 30 cycles, respectively. It is demonstrated that cycling performance of LiFePO₄-C/Li cell is better than that of LiFePO₄/Li cell.

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REFERENCES

- [1] K. Ozawa, "Lithium-ion rechargeable batteries with LiCoO₂ and carbon electrodes: the LiCoO₂/C system", *Solid State Ionics*, Vol. 69, p. 212, 1994.
- [2] G. Pistoia, D. Zane, and Y. Zhang, "Some aspects of LiMn₂O₄ electrochemistry in the 4 Volt range", *J. Electrochem. Soc.*, Vol. 142, p. 2551, 1995.
- [3] J. N. Resimers, J. R. Dahn, and U. von Sacken, "Effects of impurities on the electrochemical properties of LiCoO₂", *J. Electrochem. Soc.*, Vol. 140, p. 2752, 1993.
- [4] W. Li, J. N. Resimers, and J. R. Dahn, "In situ X-ray diffraction and electrochemical studies of Li_{1-x}NiO₂", *Solid State Ionics*, Vol. 67, p. 123, 1993.
- [5] J. R. Dahn, U. von Sacken, M. W. Juzkow, and H. Al-Janaby, "Rechargeable LiNiO₂/carbon cells", *J. Electrochem. Soc.*, Vol. 138, p. 2207, 1991.
- [6] I. Koetschau, M. N. Richard, J. R. Dahn, J. B. Soupart, and J. C. Rousche, "Orthorhombic", *J. Electrochem. Soc.*, Vol. 142, p. 2906, 1995.
- [7] I.-S. Jeong, J.-U. Kim, and H.-B. Gu, "Electrochemical properties of LiMg_yMn_{2-y}O₄ spinel phases for rechargeable lithium batteries", *J. Power Sources*, Vol. 102, p. 55, 2001.
- [8] B. Jin, J.-U. Kim, and H.-B. Gu, "Electrochemical properties of lithium-sulfur batteries", *J. Power Sources*, Vol. 117, p. 148, 2003.
- [9] J.-U. Kim, Y.-J. Jo, G.-C. Park, and H.-B. Gu, "Charge/discharge characteristics of LiMnO₂ composite for lithium polymer battery", *J. Power Sources*, Vol. 119-121, p. 686, 2003.
- [10] B. Jin, D.-K. Jun, and H.-B. Gu, "Electrochemical characteristics of LiMnO₂ for lithium secondary battery", *Transactions on Electrical and Electronic Materials*, Vol. 7, p. 76, 2006.
- [11] K. Phadhi, K. S. Nanjundaswamy, and J. B. Goodenough, "Phospho-olivine as positive-electrode materials for rechargeable lithium batteries", *J. Electrochem. Soc.*, Vol. 144, p. 1188, 1997.
- [12] K. Shiraiishi, K. Dokko, and K. Kanamura, "Formation of impurities on phospho-olivine LiFePO₄ during hydrothermal synthesis", *J. Power Sources*, Vol. 146, p. 555, 2005.
- [13] S. T. Myung, S. Komaba, N. Hirosaki, H. Yashiro, and N. Kumagai, "Emulsion drying synthesis of olivine LiFePO₄/C composite and its electrochemical properties as lithium intercalation material", *Electrochimica Acta*, Vol. 49, p. 4213, 2004.
- [14] S. Franger, F. L. Cras, C. Bourbon, and H. Rouault, "Comparison between different LiFePO₄ synthesis routes and their influence on its physico-chemical properties", *J. Power Sources*, Vol. 119-121, p. 252, 2003.
- [15] J. J. Chen and M. S. Whittingham, "Hydrothermal synthesis of lithium iron phosphate", *Electrochemistry Communications*, Vol. 8, p. 855, 2006.
- [16] N. J. Yun, H.-W. Ha, K. H. Jeong, H.-Y. Park, and K. Kim, "Synthesis and electrochemical properties of olivine-type LiFePO₄/C composite cathode material prepared from a poly(vinyl alcohol)-containing precursor", *J. Power Sources*, Vol. 160, p. 1361, 2006.
- [17] H. Huang, S.-C. Yin, and L. F. Nazar, "Approaching theoretical capacity of LiFePO₄ at room temperature at high rates", *Electrochemical and Solid State Letters*, Vol. 4, No. 10, p. A170, 2001.
- [18] A. A. Salah, A. Mauger, K. Zaghbi, J. B. Goodenough, N. Ravet, M. Gauthier, F. Gendron, and C. M. Julien, "Reduction Fe³⁺ of impurities in LiFePO₄ from pyrolysis of organic precursor used for carbon deposition", *J. Electrochem. Soc.*, Vol. 153, No. 9, p. A1692, 2006.
- [19] H. Liu, L. J. Fu, H. P. Zhang, J. Gao, C. Li, Y. P. Wu, and H. Q. Wu, "Effects of carbon coatings on nanocomposite electrodes for lithium-ion batteries", *Electrochemical and Solid State Letters*, Vol. 9, No. 12, p. A529, 2006.
- [20] T. Takeuchi, M. Tabuchi, A. Nakashima, T. Nakamura, Y. Miwa, H. Kageyama, and K. Tatsumi, "Preparation of dense LiFePO₄/C composite positive electrodes using spark-plasma-sintering process", *J. Power Sources*, Vol. 146, p. 575, 2005.
- [21] S. Y. Chung, J. T. Bloking, and Y. M. Chiang, "Electronically conductive phospho-olivines as lithium storage electrodes", *Nat. Mater.*, Vol. 1, p. 123, 2002.
- [22] G. X. Wang, S. Bewlay, J. Yao, J. H. Ahn, S. X. Dou, and H. K. Liu, "Characterization of LiM_xFe_{1-x}PO₄ (M= Mg, Zr, Ti) cathode materials prepared by the sol-gel method", *Electrochemical and Solid State Letters*, Vol. 7, p. A503, 2004.
- [23] A. Yamada, S. C. Chung, and K. Hinikuma, "Optimized LiFePO₄ for lithium battery cathodes", *J. Electrochem. Soc.*, Vol. 148, p. A224, 2001.