

Electrochemical Characteristics of Carbon-coated LiFePO₄ as a Cathode Material for Lithium Ion Secondary Batteries

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Abstract: The electrochemical properties of LiFePO₄ as a cathode for Li-ion batteries were improved by incorporating conductive carbon into the LiFePO₄. X-ray diffraction analysis and SEM observations revealed that the carbon-coated LiFePO₄ consisted of fine single crystalline particles, which were smaller than the bare LiFePO₄. The electrochemical performance of the carbon-coated LiFePO₄ was tested under various conditions. The carbon-coated LiFePO₄ showed much better performance in terms of the discharge capacity and cycling stability than the bare LiFePO₄. The improved electrochemical performances were found to be attributed to the reduced particle size and enhanced electrical conductivity of the LiFePO₄ by the carbon.

Keywords: Lithium iron phosphate, Carbon coating, Lithium ion batteries, Mechanochemical activation, X-ray diffraction.

1. Introduction

Lithium iron phosphate (LiFePO₄), since first proposed by Goodenough's group in 1997,¹⁾ has been investigated as a viable alternative for a cathode material for lithium-ion batteries due to its relatively large theoretical capacity (170 mAhg⁻¹), high safety, and low cost.^{2,3)} The LiFePO₄, however, has not been used as a cathode material due to its low electrical conductivity (10⁻⁹⁻⁻¹⁰ Scm⁻¹).^{4,7)} This is because the LiFePO₄ has an ordered olivine structure, in which Li, Fe, and P atoms occupy octahedral 4a, octahedral 4c and tetrahedral 4c sites, respectively, and FeO₆ octahedra are separated by PO₄ polyanions.

Recently, several research groups made efforts to overcome this problem and showed possibility to overcome the limitation by coating LiFePO₄ with carbon,⁸⁻¹¹⁾ doping transition metal ions,¹²⁻¹⁴⁾ and reducing the particle size.^{15,16)} Ravet *et al.*⁸⁾ reported that LiFePO₄ showed a capacity close to 160 mAh/g at 80°C when coated with about 1 wt.% carbon. Yamada *et al.*¹⁵⁾ showed that good electrochemical performance (>95%, 165 mAhg⁻¹) was possible even at room temperature by decreasing the particle size at moderate sintering temperatures (500-600°C). Huang *et al.*¹⁰⁾ fabricated carbon-coated LiFePO₄ composites containing small (100-200 nm) carbon particles by mixing precursors with a carbon gel before sintering. This composite showed good rate capability and excellent cycle stability at room temperature. However, these synthesis routes were complicated and needed a sintering process at high temperatures for a long time. Franger *et*

*al.*¹⁷⁾ and Kwon *et al.*¹⁸⁾ found that the mechanical alloying produced fine carbon-coated LiFePO₄ particles and reduced the heat-treatment time.

In this study, the mechanochemical process was employed to synthesize the carbon-coated LiFePO₄ using the precursor Li₂CO₃ as Li source and acetylene black as a carbon source. The emphasis of the current investigation was to find the underlying cause of the improvement of the electrochemical properties of the carbon-coated LiFePO₄. In order to examine the role of carbon on the electrochemical properties of LiFePO₄ particles, analysis using XRD, SEM, and electrochemical tests were performed.

2. Experimental

Li₂CO₃ (Aldrich, ≥99%), FeC₂O₄·2H₂O (Aldrich, ≥99%), and (NH₄)₂H·PO₄ (Aldrich, ≥99%) were used as starting materials. This mixture containing the precursors based on the stoichiometry of the compound was placed in a zirconia bowl and the mechanochemical activation was carried out using zirconia balls for 3 hours using a planetary mill (FRITSCH Pulverisette 5) in the air. The rotating speed was 250 rpm and the ball-to-powder weight ratio was 20:1. The activated powders after the mechanochemical processing were heat treated at 700°C in an Ar + 5% H₂ atmosphere in a tube furnace for 10 h. For carbon-coated LiFePO₄, 5 wt.% acetylene black powders were added to the mixture of the starting materials. After the same mechanochemical treatment, the carbon-coated LiFePO₄ powders were synthesized with the same heat-treatment conditions for the bare LiFePO₄.

After the heat-treatment, the gray (bare LiFePO₄) and the

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black (carbon-coated LiFePO_4) powders were air-cooled to room temperature. The crystal structure of the bare and carbon-coated LiFePO_4 powders were examined by XRD analysis (RINT/DMAX-2500, RIGAKU/JAPAN). Surface morphology and particle size of the powder was analyzed by scanning electron microscopy (Hitachi S-4200).

Cathodes were manufactured by mixing 85 wt.% of the prepared LiFePO_4 , 10 wt.% acetylene black as a conductor, and 5 wt.% polyvinylidene difluoride as a binder. The mixture slurry was coated on an Al foil and dried at 80°C 24 h. The charge and discharge characteristics of the cathodes were examined using a coin cell (2032 type). The cell consisted of a cathode, electrolyte, a lithium metal anode, and a Celgard 2500 separator. The electrolyte was a 1M LiPF_6 -ethylene carbonate/dimethyl carbonate/ethylmethyl carbonate (EC/DMC/EMC) solution. The galvanostatic charge-discharge experiment was performed between 2.8 and 4.2 V using a Maccor 4000 battery cycler.

3. Results and Discussion

3.1 Structure and morphology of the carbon coated LiFePO_4

Fig. 1 shows XRD patterns of the bare (Fig. 1(a)) and the carbon-coated (Fig. 1(b)) olivine LiFePO_4 . The XRD pattern of the bare LiFePO_4 could be indexed by the orthorhombic system (space group Pnmb). Noticeable structural changes were not observed in the XRD pattern of the carbon-coated

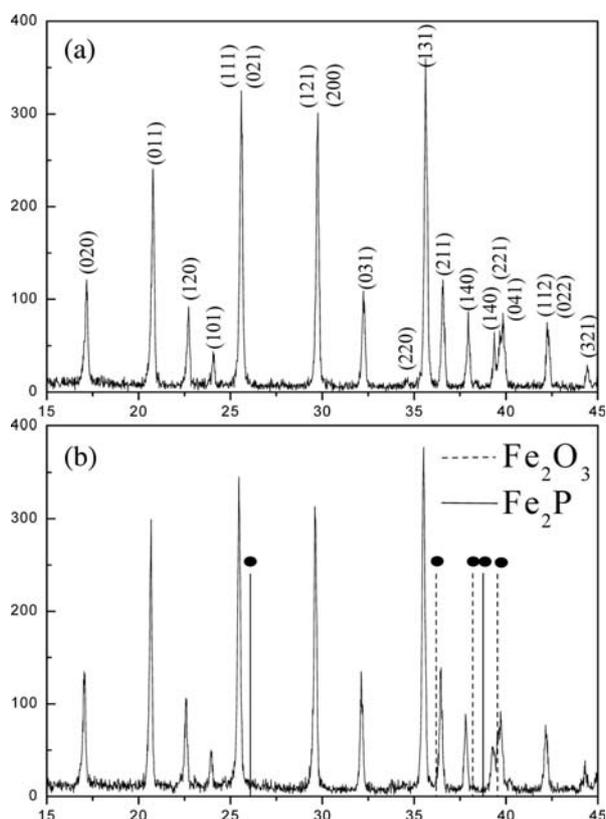


Fig. 1. XRD patterns of (a) the bare LiFePO_4 and (b) the carbon-coated LiFePO_4 after heat-treating at 700°C for 10 h.

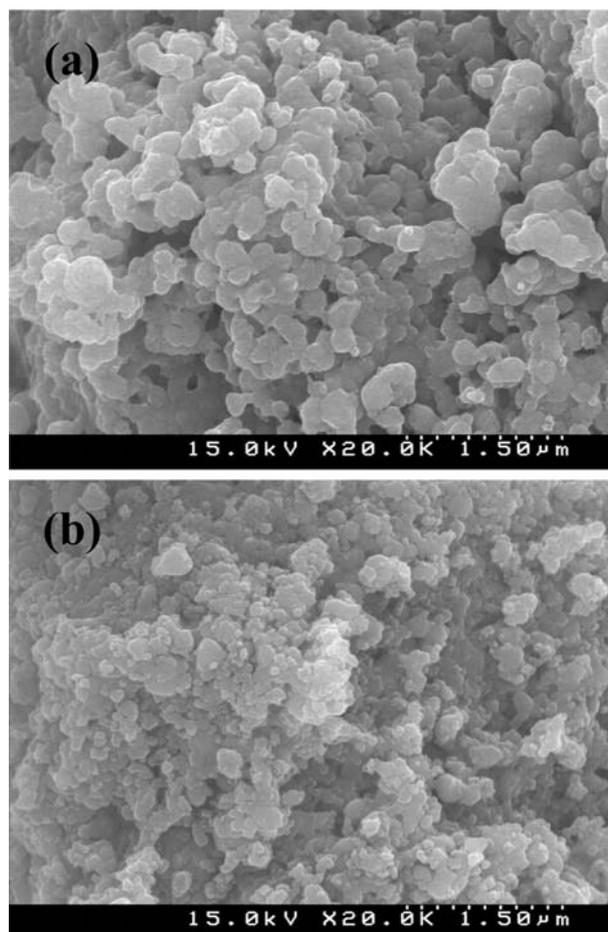


Fig. 2. SEM micrographs of (a) the bare and (b) the carbon-coated LiFePO_4 particles.

LiFePO_4 indicating that the olivine structure was well maintained after carbon coating. Impurities phases such as Fe_2O_3 or Fe_2P , which were reported by others,^{12,18} were not observed in the carbon-coated LiFePO_4 .

Fig. 2 shows SEM images of the bare (Fig. 2(a)) and the carbon-coated (Fig. 2(b)) LiFePO_4 . It showed that the carbon-coated LiFePO_4 was consisted of non-uniform fine particles with the size ranged between 100-300 nm. The size of the carbon-coated LiFePO_4 particle was much smaller than that for the bare LiFePO_4 . This indicated that the addition of carbon inhibited the particle growth of the LiFePO_4 particles during sintering. A similar result was reported by Huang *et al.*¹⁰ suggesting that the addition of fine carbon to the precursors reduced the particle size of the LiFePO_4 . Prosini *et al.*⁹ and Chen *et al.*¹¹ also showed that the particle size decreased as the amount of carbon increases. The coating layer, however, was not uniform over the whole surface. SEM images revealed the carbon layer on the carbon-coated LiFePO_4 , suggesting that the carbon played an important role in reducing the LiFePO_4 particle size during synthesis process.

3.2 Electrochemical properties of the carbon-coated LiFePO_4

Electrochemical performance of the carbon-coated LiFePO_4

was examined by charge-discharge tests and cycle voltammetry. The cell was cycled between 2.8 and 4.2 V and charged at 0.1 C. Excellent cathode properties were obtained by using the carbon-coated LiFePO_4 prepared in this study (Fig. 3). The charge-discharge curves showed flat voltage plateaus at 3.4-3.5 V range, indicating the two-phase nature of the lithium extraction and insertion reactions between LiFePO_4 and FePO_4 .¹⁾ Fig. 3 also showed voltage profiles at different discharge rates. The specific capacity was 150 mAhg^{-1} at 0.05 C and the plateau voltage and the specific discharge capacity decreased as the discharge current density increased. The discharge voltage plateaus were maintained at constant values regardless of discharge current density. When carbon-coated LiFePO_4 was used, the cell delivered a capacity of 135 mAhg^{-1} with a plateau at 3.3 V vs. Li/Li^+ at the high discharge rate of 1 C. At low discharge rate, on the other hand, the small voltage difference between the charge and discharge plateaus was obtained. Mi *et al.*¹⁹⁾ reported that this small voltage difference indicated its enhanced kinetics of the carbon-coated LiFePO_4 during electrochemical process comprising diffusion of lithium ions and electron transfer.

The carbon coating effect on the electrochemical properties of the LiFePO_4 was also supported by cyclic voltammetry shown in Fig. 4. The voltage differences of the bare LiFePO_4 and the carbon-coated LiFePO_4 exhibited almost same intervals. However, anodic and cathodic peak intensities of the carbon-coated LiFePO_4 were much larger than that of the bare LiFePO_4 . This indicated that Li ions and electrons were participating actively in redox reactions due to the carbon coating of the LiFePO_4 allowing reversible electrochemical reactions during extraction and insertion of Li ions.

The cycling performance of the bare and the carbon-coated LiFePO_4 were described in Fig. 5. It clearly showed that the capacity of the bare LiFePO_4 decreased faster during the early cycles, indicating that the two-phase redox reactions usually caused significant capacity reduction during the early charge-discharge cycling. The capacity reduction of the bare LiFePO_4 was also attributed to the slow diffusion of Li-ion

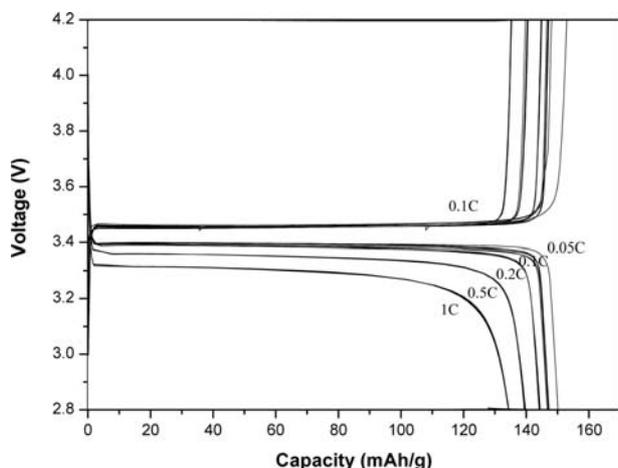


Fig. 3. Charge-discharge curves of the carbon-coated LiFePO_4 at different discharge rates. Specific charge current was $15 \text{ mA} \text{g}^{-1}$ at 0.1 C.

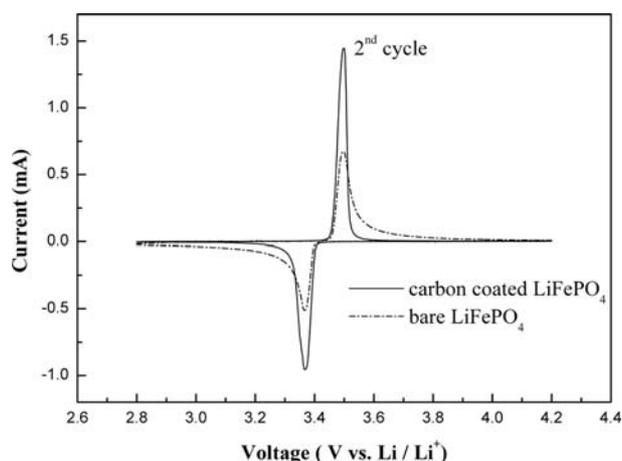


Fig. 4. Cyclic voltammograms of the LiFePO_4 and the carbon-coated LiFePO_4 at a scan rate of 0.01 mVsec^{-1} .

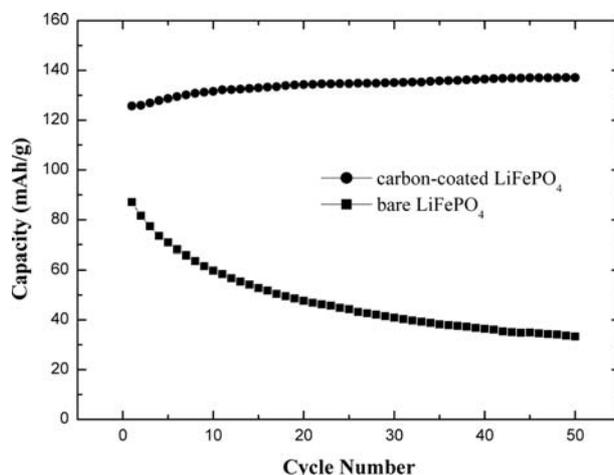


Fig. 5. Cycling performance of the bare LiFePO_4 and the carbon-coated LiFePO_4 at 0.5 C.

in the LiFePO_4 and the poor electrical contact between the LiFePO_4 particles and conductors. On the contrary, the carbon-coated LiFePO_4 exhibited excellent capacity retention without significant capacity fading. The reversible capacity was approximately 140 mAhg^{-1} at 0.5 C.

The improved electrochemical properties of the carbon-coated LiFePO_4 appeared due to two factors. One was the reduced size of carbon-coated LiFePO_4 particles, which shortened the distance of the diffusion path for Li ions. The other was the improved electrical conductivity of the cathode since the carbon in the LiFePO_4 provided good electrical contacts between the LiFePO_4 particles and the conductor in the cathode composite.

4. Conclusions

Electrochemical properties of the carbon-coated LiFePO_4 , which was synthesized by mechanochemical activation method, were investigated. The carbon-coated LiFePO_4 particles showed the olivine structure and the size of the particles

were significantly reduced by the addition of carbon. The electrochemical performance of the carbon-coated LiFePO_4 showed higher specific capacity and better capacity retention compared to the bare LiFePO_4 . At room temperature, the carbon-coated cathode showed stable capacity of 150 mAhg^{-1} at 0.05 C and 135 mAhg^{-1} at 1 C, respectively. The improved electrochemical properties were attributed to the reduced LiFePO_4 particle size and enhanced electrical contacts by carbon. The results suggested that the carbon-coated LiFePO_4 is a good candidate for the cathode materials that can meet high rate performance and cyclic stability.

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References

1. A. K. Padhi, K. S. Nanjundaswamy, and J. B. Goodenough, "Phospho-olivines as Positive-Electrode Materials for Rechargeable Lithium Batteries", *J. Electrochem. Soc.*, **144**, 1188 (1997).
2. D. D. MacNeil, Z. Lu, Z. Chen, and J. R. Dahn, "A comparison of the electrode/electrolyte reaction at elevated temperatures for various Li-ion battery cathodes", *J. Power Sources*, **108**, 8 (2002).
3. M. Takahashi, S. I. Tobishima, K. Takei, and Y. Sakurai, "Reaction behavior of LiFePO_4 as a cathode material for rechargeable lithium batteries", *Solid State Ionics*, **148**, 283 (2002).
4. A. K. Padhi, K. S. Nanjundaswamy, C. Masquelier, S. Okada, and J. B. Goodenough, "Effect of Structure on the $\text{Fe}^{3+}/\text{Fe}^{2+}$ Redox Couple in Iron Phosphates", *J. Electrochem. Soc.*, **144**, 1609 (1997).
5. M. Takahashi, S. Tobishima, K. Takei, and Y. Sakurai, "Characterization of LiFePO_4 as the cathode material for rechargeable lithium batteries", *J. Power Sources*, **97-98**, 508 (2001).
6. J. Barker, M. Y. Saidi, and J. L. Swoyer, "Lithium Iron(II) Phospho-olivines Prepared by a Novel Carbothermal Reduction Method", *Electrochem. Solid-State Lett.*, **6**, A53 (2003).
7. A. S. Andersson, B. Kalska, L. Haggstrom, and J. O. Thomas, "Lithium extraction/insertion in LiFePO_4 : an X-ray diffraction and Mössbauer spectroscopy study", *Solid State Ionics*, **130**, 41 (2000).
8. N. Ravet, Y. Chouinard, J. F. Magnan, S. Besner, M. Gauthier, and M. Armand, "Electroactivity of natural and synthetic triphylite", *J. Power Sources*, **97-98**, 503 (2001).
9. P. P. Prosini, D. Zane, and M. Pasquali, "Improved electrochemical performance of a LiFePO_4 -based composite cathode", *Electrochim. Acta*, **46**, 3517 (2001).
10. H. Huang, S. C. Yin, and L. F. Nazar, "Approaching Theoretical Capacity of LiFePO_4 at Room Temperature at High Rates", *Electrochem. Solid State Lett.*, **4**, A170 (2001).
11. Z. Chen and J. R. Dahn, "Reducing Carbon in LiFePO_4/C Composite Electrodes to Maximize Specific Energy, Volumetric Energy, and Tap Density", *J. Electrochem. Soc.*, **149**, A1184 (2002).
12. S. Y. Chung, J. T. Bloking, and Y. M. Chiang, "Electronically conductive phospho-olivines as lithium storage electrodes", *Nat. Mater.*, **1**, 123 (2002).
13. S. Shi, L. Liu, C. Ouyang, D. S. Wang, Z. Wang, L. Chen, and X. Huang, "Enhancement of electronic conductivity of LiFePO_4 by Cr doping and its identification by first-principles calculations", *Phys. Rev. B*, **68**, 195108(2003).
14. D. Wang, H. li, S. Shi, X. Huang, and L. Chen, "Improving the rate performance of LiFePO_4 by Fe-site doping", *Electrochem. Acta*, **50**, 2955(2005).
15. A. Yamada, S. C. Chung, and K. Hinokuma, "Optimized LiFePO_4 for Lithium Battery Cathodes", *J. Electrochem. Soc.*, **148**, A224 (2001).
16. H. S. Kim, B. W. Cho, and W. I. Cho, "Cycling performance of LiFePO_4 cathode material for lithium secondary batteries", *J. Power Sources*, **132**, 235 (2004).
17. S. Franger, F. L. Cras, C. Bourbon, and H. Rouault, "Comparison between different LiFePO_4 synthesis routes and their influence on its physico-chemical properties", *J. Power Sources*, **119-121**, 252 (2003).
18. S. J. Kwon, C. W. Kim, W. T. Jeong, and K. S. Lee, "Synthesis and electrochemical properties of olivine LiFePO_4 as a cathode material prepared by mechanical alloying", *J. Power Sources*, **137**, 93(2004).
19. C. H. Mi, X. B. Zhao, G. S. Cao, and J. P. Tu, "In Situ Synthesis and Properties of Carbon-Coated LiFePO_4 as Li-Ion Battery Cathodes", *J. Electrochem. Soc.*, **152**, 483 (2005).