

An Investigation of LiFePO₄/Poly(3,4-ethylenedioxythiophene) Composite Cathode Materials for Lithium-Ion Batteries

Jin Yi Shi,^{†,‡} Cheol-Woo Yi,^{§,*} and Keon Kim^{†,*}

[†]Department of Chemistry, Korea University, Seoul 136-701, Korea. *E-mail: kkim@korea.ac.kr

[‡]Jilin Institute of Chemical Technology, Jilin 132022, China

[§]Department of Chemistry and Institute of Basic Science, Sungshin Women's University, Seoul 136-742, Korea

*E-mail: cheolwoo@sungshin.ac.kr

Received May 8, 2010, Accepted July 19, 2010

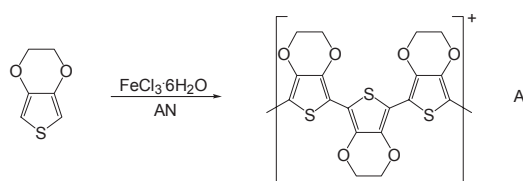
Key Words: Coating, Lithium-ion battery, Poly(3,4-ethylenedioxythiophene), Lithium iron phosphate, Conductive polymer

Lithium iron phosphate (LiFePO₄) is one of the most promising cathode materials for lithium-ion batteries, and it has advantages such as its environmental benignity, low-cost, stable structure, etc.¹⁻² However, due to its poor electrical conductivity, LiFePO₄ causes an increase in the impedance and a decrease in the rate capability.^{1,3-4} In order to overcome these obstacles, LiFePO₄ which is coated by highly conductive materials has been extensively studied. For instance, various materials,⁴⁻⁷ such as metal and/or metal oxide nano-particles, carbon, and conductive polymers, have been used to improve the overall conductivity of composite electrodes. Recently, poly(3,4-ethylenedioxythiophene) (PEDOT)⁸⁻⁹ has been used as a coating material to improve the electrical conductivity of certain cathode materials such as LiCoO₂ and LiMn₂O₄.¹⁰⁻¹² In addition, it has been reported that PEDOT is utilized as cathode active material¹³ because it has high electrical conductivity, good thermal and chemical stability, high specific capacity, and the promotion of the reduction reaction of the cathode. Hence, it is expected that the use of the highly conductive PEDOT may serve as an outer layer to assist the transportation of Li ions.

The pristine LiFePO₄ powders were prepared by a wet-milling, solid-state method. Against a traditional solid-state method, this wet-milling method offers an effective way to obtain a homogeneous mixture of raw materials and provides the product having relatively small particle size since it reduces

the reaction period and the reaction temperature.⁴ The X-ray diffraction (XRD) pattern of pristine LiFePO₄ is presented in Figure 1. XRD shows that the prepared LiFePO₄ has a standard olivine structure (orthorhombic *Pnmb* space group). This result is in good agreement with previous publications.^{1,14-15} Even though any XRD feature of impurity phases, such as Li₃Fe₂(PO₄)₃, Fe₂P, Li₃PO₄, Li₄P₂O₇, etc.,¹⁴⁻¹⁵ is not observed, it was reported that amorphous FeP or Fe₂P created under reduction conditions cannot be excluded.¹⁴

In order to overcome the poor rate capability of LiFePO₄ attributed to its low electrical conductivity,^{1,3-4} PEDOT was coated on the surface of LiFePO₄. The electrical conductivity of PEDOT is ~1.2 S/cm¹² which is significantly higher than that of LiFePO₄ (~10⁻¹¹ S/cm).⁷ In this study, PEDOT powder was synthesized by an oxidative chemical polymerization of EDOT (Scheme 1).¹⁶ Fourier transform-infrared (FT-IR) spectroscopy was performed to identify the structure of prepared PEDOT



Scheme 1

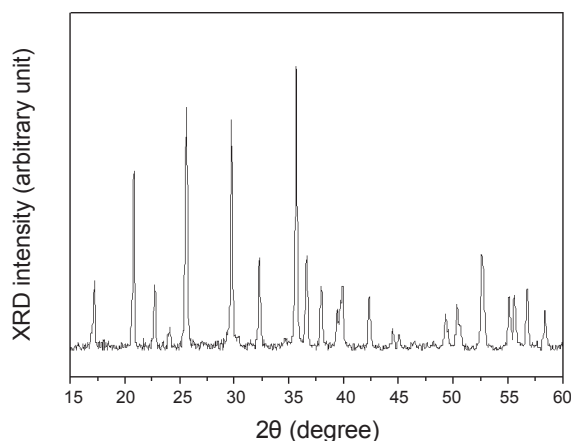


Figure 1. XRD pattern of pristine LiFePO₄ prepared by wet-milling, solid-state method.

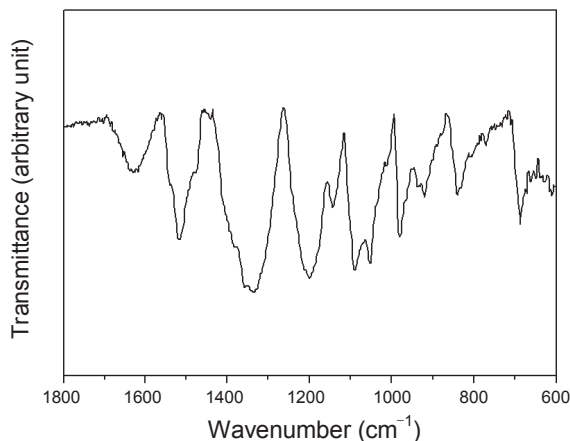


Figure 2. FT-IR spectrum of PEDOT prepared by oxidative chemical polymerization.

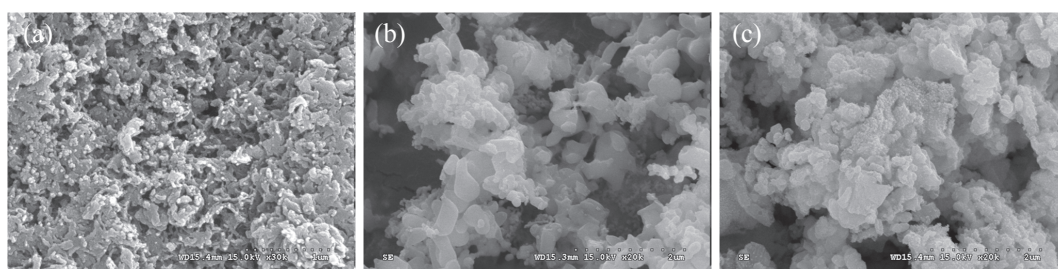


Figure 3. SEM images of (a) PEDOT, (b) pristine LiFePO₄, and (c) LiFePO₄/5 wt % PEDOT.

powder. Figure 2 shows the FT-IR spectrum of PEDOT powder, and the major absorption bands are in the range of 1600 - 600 cm^{-1} . The high frequency bands are assigned to the stretching modes of thiophene ring. Specifically, the vibrations at 1518 and 1475 cm^{-1} are attributed to the ring stretching modes of the thiophene ring, and the absorption feature at 1342 cm^{-1} is assigned to the C-C stretching mode.¹⁷⁻¹⁸ The stretching modes of C-S in the thiophene ring appear at 982 and 840 cm^{-1} , and an weak vibrational feature at 688 cm^{-1} is assigned to the bending mode of C-S-C bond (in-plane deformation).¹⁸⁻¹⁹ The other bands observed at 1194, 1140 and 1090 - 1055 cm^{-1} are assigned to the stretching of C-O-C bond.^{13,18-19} The IR spectrum of PEDOT shown in Figure 2 is corresponding spectrum to the literatures.¹⁷⁻²⁰ However, it is noteworthy that the electrical conductivity is related to the intensity of vibrational features at 1550 - 1500 cm^{-1} assigned to the stretching modes of double bond in the EDOT ring (symmetric and asymmetric vibrations), and the absence of this absorption feature indicates a poor electrical conductivity of PEDOT¹⁸ because it indicates the destruction of conjugated chain related to its electrical conductivity.

As-prepared PEDOT, pristine LiFePO₄, and LiFePO₄/5 wt % PEDOT powders were investigated by scanning electron microscopy (SEM), and the results are shown in Figure 3. PEDOT powders are agglomerated together, and pristine LiFePO₄ synthesized by a wet-milling, solid-state method has smooth surface with a particle size of 500 nm to 1 μm , as shown in Figures 3(a) and (b), respectively. LiFePO₄/5 wt % PEDOT composite shows the morphology that LiFePO₄ particles are conglomerated together by PEDOT and form secondary particles with an average size of 2 - 3 μm . The fact that the polymer with high electrical conductivity covers the whole surface of LiFePO₄ particle suggests that the electrical conductivity of the composite material increases. Moreover, PEDOT provides a conductive bridge between the individual particles. The electrochemical impedance spectroscopy (EIS) was performed to investigate the electrical conductivity. The typical EIS spectra of the pristine LiFePO₄ and LiFePO₄/5 wt % PEDOT electrodes are shown in Figure 4. Each EIS curve consists of two semicircles representing the resistance of the surface electrolyte interface (SEI) film in the high frequency and the charge-transfer resistance in the medium frequency.²¹⁻²² The value of each resistance is determined using the equivalent circuit shown in the inset of Figure 4. The LiFePO₄/5 wt % PEDOT electrode exhibits significantly lower charge-transfer and SEI film resistances (20.73 and 5.296 Ω) than pristine LiFePO₄ (35.02 and 6.397 Ω). This much lower charge-transfer resistance of LiFePO₄/5 wt % PEDOT electrode is attributed to the coating of highly conductive polymer,

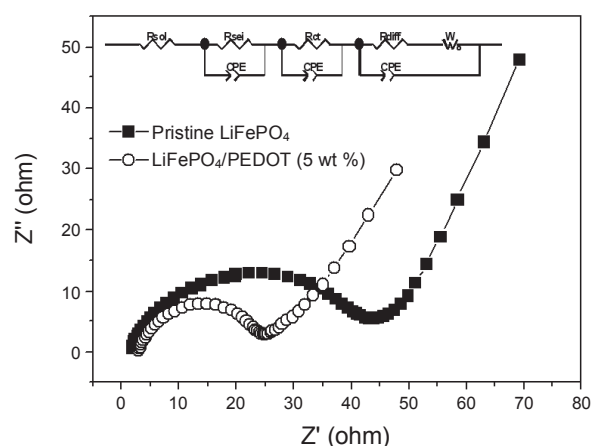


Figure 4. EIS spectra of pristine LiFePO₄ and LiFePO₄/5 wt % PEDOT electrode after 3 cycles.

and it facilitates the transportation of Li ions.

The charge-discharge cycling performance of pristine LiFePO₄ and LiFePO₄/PEDOT composite cathodes was measured at a current density of 200 mA/g, and the results are shown in Figure 5(a). The electrode demonstrates the enhanced cyclability as the amount of PEDOT increases. After 50 cycles, LiFePO₄/5 wt % PEDOT shows a good capacity retention ratio, 86.72%, which is higher than that of the pristine LiFePO₄ (74.48%). Figure 5(b) displays the normalized discharge capacity of pristine LiFePO₄ and LiFePO₄/PEDOT composite electrodes with various C-rates. LiFePO₄/PEDOT electrode has better rate capability than the pristine LiFePO₄ at higher current density. The addition of highly conductive PEDOT to LiFePO₄ increases the conductivity of the composite resulting in the enhancement of the practical capacity and rate capability, and it improves capacity retention with increasing the number of charge-discharge cycles.

In summary, LiFePO₄/PEDOT composites were prepared by oxidative chemical polymerization and wet-milling solid-state method. XRD shows the well-ordered LiFePO₄ phase, and the results obtained by SEM and IR spectroscopy presented the successful synthesis of PEDOT and the LiFePO₄/PEDOT composites without destruction of conjugated polymer chain. The electrochemical measurements demonstrate that LiFePO₄/PEDOT cathodes exhibit better cyclability and rate capability in comparison with the pristine LiFePO₄ cathode. The impedance measurements reveal that the PEDOT coating significantly reduces charge-transfer and SEI film. Therefore, PEDOT-coated LiFePO₄ electrode demonstrates the improved electrochemical performance and cycling stability of the electrodes.

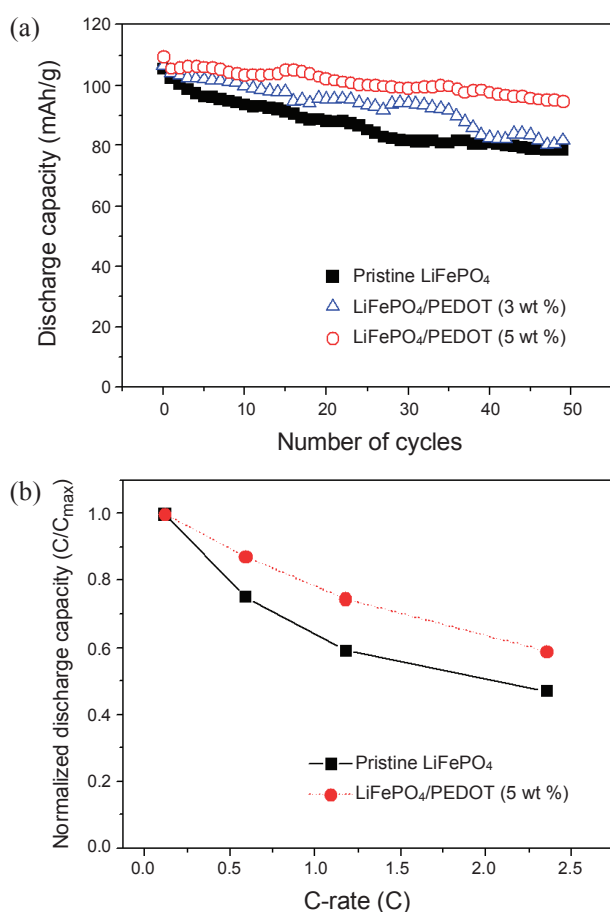


Figure 5. (a) The discharge capacity as a function of cycle numbers for pristine LiFePO₄ and LiFePO₄/PEDOTs; (b) the change of normalized discharge capacity with various C-rates.

Experimental Section

Synthesis of LiFePO₄/PEDOT composites. LiFePO₄ was synthesized by a solid-state reaction using Li₂CO₃ (Junsei), FeC₂O₄·2H₂O (Aldrich) and NH₄H₂PO₄ (Aldrich). The mixture of these raw materials was dispersed in an acetone medium and ball-milled for 24 hours. After the evaporation of acetone, the obtained precursor was calcined at 600 °C for 9 hours in Ar atmosphere. PEDOT was prepared via an oxidative chemical polymerization of EDOT.¹⁶ The polymerization was performed in aprotic solvent, acetonitrile (AN), because EDOT has a limited solubility in an aqueous medium.²³⁻²⁴ FeCl₃·6H₂O plays a role as an oxidizing agent. The mole ratio of EDOT : FeCl₃·6H₂O was set to 1 : 17. The polymerization was carried out at room temperature for 24 hours. Thus-formed product was filtered and then washed with acetonitrile. Subsequently, it was dried at 80 °C in a vacuum oven for 12 hours. LiFePO₄/PEDOT composites were prepared by dispersing LiFePO₄ powders in FeCl₃/AN solution, and then a desired amount of EDOT monomer (3 and 5 wt %) was added to LiFePO₄-FeCl₃/AN solution. To obtain the electrodes, 10 mg of pristine LiFePO₄ or LiFePO₄/PEDOT and 6 mg of teflonized acetylene black were mixed, and the mixture was pressed into 1 cm² pellets. It was dried in vacuum at 120 °C for 12 hours. Lithium metal and polypropylene were used as the anode and the separator, respectively. The electro-

lyte was 1.0 M LiPF₆ dissolved in an 1:1 mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) solution (TECHNO Semichem Co.). The coin-type cell (CR2032) was assembled in an argon-filled glove box.

Physical characterizations and electrochemical measurements. The structure of LiFePO₄ powders was characterized by XRD (Rigaku DMAX-III diffractometer) equipped with a Cu target, and the morphology of PEDOT and LiFePO₄/PEDOT powders was examined by field emission-SEM (Hitachi S-4300, Japan). The prepared PEDOT powder was characterized using a Nicolet 380 FT-IR spectrophotometer. To elucidate the electrochemical behaviors, we performed charge-discharge tests and electrochemical impedance spectroscopy. The charge-discharge tests were carried out using a WBCS 3000 instrument (WonA Tech, Korea). The EIS tests were run on an IM6 electrochemical instrument (ZAHNER elektrik, Germany).

Acknowledgments. This study was supported by the Research Center for Energy Conversion & Storage, Korea. CWY also acknowledges the support of this work by the Sungshin Women's University Research Grant of 2010.

References

1. Padhi, A. K.; Nanjundaswamy, K. S.; Goodenough, J. B. *J. Electrochem. Soc.* **1997**, *144*, 1188.
2. Padhi, A. K.; Nanjundaswamy, K. S.; Masquelier, C.; Okada, S.; Goodenough, J. B. *J. Electrochem. Soc.* **1997**, *144*, 1609.
3. Chung, S.-Y.; Bloking, J. T.; Chiang, Y.-M. *Nat Mater* **2002**, *1*, 123.
4. Yun, N. J.; Ha, H.-W.; Jeong, K. H.; Park, H.-Y.; Kim, K. *J. Power Sources* **2006**, *160*, 1361.
5. Panero, S.; Scrosati, B.; Wachtler, M.; Croce, F. *J. Power Sources* **2004**, *129*, 90.
6. Prossini, P. P.; Zane, D.; Pasquali, M. *Electrochim. Acta* **2001**, *46*, 3517.
7. Wang, G. X.; Yang, L.; Chen, Y.; Wang, J. Z.; Bewlay, S.; Liu, H. K. *Electrochim. Acta* **2005**, *50*, 4649.
8. Gustafsson, J. C.; Liedberg, B.; Ingan, O. *Solid State Ionics* **1994**, *69*, 145.
9. Morvant, M. C.; Reynolds, J. R. *Synthetic Met.* **1998**, *92*, 57.
10. Arbizzani, C.; Mastragostino, M.; Rossi, M. *Electrochem. Commun.* **2002**, *4*, 545.
11. Her, L.-J.; Hong, J.-L.; Chang, C.-C. *J. Power Sources* **2006**, *161*, 1247.
12. Murugan, A. V. *Electrochim. Acta* **2005**, *50*, 4627.
13. Zhan, L.; Song, Z.; Zhang, J.; Tang, J.; Zhan, H.; Zhou, Y.; Zhan, C. *Electrochim. Acta* **2008**, *53*, 8319.
14. Kang, B.; Ceder, G. *Nature* **2009**, *458*, 190.
15. Zhu, X.-J.; Cheng, L.-B.; Wang, C.-G.; Guo, Z.-P.; Zhang, P.; Du, G.-D.; Liu, H.-K. *J. Phys. Chem. C* **2009**, *113*, 14518.
16. Corradi, R.; Armes, S. P. *Synthetic Met.* **1997**, *84*, 453.
17. Sakmeche, N.; Aeiyaeh, S.; Aaron, J.-J.; Jouini, M.; Lacroix, J. C.; Lacaze, P.-C. *Langmuir* **1999**, *15*, 2566.
18. Seo, K. I.; Chung, I. *J. Polymer* **2000**, *41*, 4491.
19. Kvarnstr, C.; Neugebauer, H.; Blomquist, S.; Ahonen, H. J.; Kankare, J.; Ivaska, A. *Electrochim. Acta* **1999**, *44*, 2739.
20. Chiu, W. W.; Travas-Sejdic, J.; Cooney, R. P.; Bowmaker, G. A. *Synthetic Met.* **2005**, *155*, 80.
21. Shi, J. Y.; Yi, C. W.; Liang, L.; Kim, K. *Bull. Korean Chem. Soc.* **2010**, *31*, 309.
22. Shi, J. Y.; Yi, C. W.; Kim, K. *J. Power Sources* **2010**, *195*, 6860.
23. Lota, K.; Khomeenko, V.; Frackowiak, E. *J. Phys. Chem. Solids* **2004**, *65*, 295.
24. Pettersson, L. A. A.; Carlsson, F.; Ingan, O.; Arwin, H. *Thin Solid Films* **1998**, *313-314*, 356.