The Root Cause of the Rate Performance Improvement After Metal Doping: A Case Study of LiFePO₄

ChangKyo Park,^{†,‡} Sung Bin Park,[†] Ji Hun Park,^{†,‡} Ho Chul Shin,[§] Won Il Cho,[‡] and Ho Jang^{†,*}

[†]Department of Materials Science and Engineering, Korea University, Seoul 136-713, Korea. *E-mail: hojang@korea.ac.kr

[‡]Advanced Battery Center, Korea Institute of Science and Technology, Seoul 136-791, Korea

[§]Energy Materials Lab, R&D center, GS Caltex Corporation 104-4, Daejeon 305-380, Korea

Received October 25, 2010, Accepted January 11, 2011

This study investigates a root cause of the improved rate performance of LiFePO₄ after metal doping to Fe-sites. This is because the metal doped LiFePO₄/C maintains its initial capacity at higher C-rates than undoped one. Using LiFePO₄/C and doped LiFe_{0.97}M_{0.03}PO₄/C (M=Al³⁺, Cr³⁺, Zr⁴⁺), which are synthesized by a mechanochemical process followed by one-step heat treatment, the Li content before and after chemical delithiation in the LiFePO₄/C and the binding energy are compared using atomic absorption spectroscopy (AAS) and X-ray photoelectron spectroscopy (XPS). The results from AAS and XPS indicate that the low Li content of the metal doped LiFePO₄/C after chemical delithiation is attributed to the low binding energy induced by weak Li-O interactions. The improved capacity retention of the doped LiFePO₄/C at high discharge rates is, therefore, achieved by relatively low binding energy between Li and O ions, which leads to fast Li diffusivity.

Key Words : LiFePO₄, Doping, Rate performance, XPS, Binding energy

Introduction

Olivine-type lithium iron phosphate (LiFePO₄) has been considered as a promising candidate for a cathode material in the lithium-ion batteries after first introduced by Goodenough's group in 1997.¹ This is because LiFePO₄ has the advantages of high theoretical capacity (170 mAh g⁻¹), excellent thermal stability, and non-toxicity^{2,3} compared to conventional LiCoO₂. However, its low electronic conductivity (10⁻⁹~10⁻¹⁰ S cm⁻¹) and low lithium ion diffusivity lead to slow electron movement and poor Li ion transfer under rapid rates, impeding the rate capability.⁴⁻⁷ To overcome the drawbacks of LiFePO₄, recent efforts have been given to the improvement of rate performance by coating carbonaceous conductors⁸⁻¹¹ and substituting Li with metals such as Nb, Mg, Zr, or Cr.^{12,13} Concerning the position of the added metals in the lattice, Fe sites have been also considered as a suitable position to enhance the rate performance of LiFePO₄. Baker *et al.*¹⁴ incorporated Mg ion to Fe ion sites and delivered initial capacity 156 mAh g⁻¹. Wang *et al.*, on the other hand, improved initial capacity and reversibility by producing P-type semiconductor regions in a LiFePO₄ particle by doping Ti ions.¹⁵ They ascribed the beneficial doping effects to the improvement of electronic conductivity after doping.

In this study, the binding energy and chemical compositions of LiFePO₄/C and LiFe_{0.97}M_{0.03}PO₄/C (M=Al³⁺, Cr³⁺, Zr⁴⁺) are measured by X-ray photoelectron spectroscopy (XPS), and Atomic absorption spectroscopy (AAS) is used to examine the amount of Li content. The mechanism of improved rate performance is examined by comparing the binding energy, chemical composition, and Li content of the

LiFePO₄ before and after doping.

Experimental

A mixture of Li₂CO₃ (Aldrich, ≥ 99%), FeC₂O₄·2H₂O (Junsei, ≥ 99%), (NH₄)H₂PO₄ (Junsei, ≥ 99%), and 3 wt % of carbon black powder were placed in a zirconia bowl and the mechanochemical reaction was carried out for 3 hrs in a planetary mill (FRITSCH Pulverisette 5). The rotation speed was 250 rpm and the ball-to-powder weight ratio was 20:1. The resulting powder mixture was heat treated at 750 °C for 10 hours under Ar+5% H₂ atmosphere to produce carbon coated LiFePO₄. The metal doped LiFe_{0.97}M_{0.03}PO₄/C (M=Al³⁺, Cr³⁺, Zr⁴⁺) powder was also prepared by the same procedure. The precursors such as Al(C₂H₅O)₃ (Aldrich, ≥ 97%), (CH₃CO₂)₃Cr(OH)₂ (Aldrich, ≥ 97%), and Zr(OC₂H₅)₄ (Aldrich, ≥ 97%) were used to dope Al, Cr, and Zr ions, respectively. The crystal structure of LiFePO₄ was analyzed by X-ray diffraction (XRD; D/MAX-II A) using Cu K_α radiation varying between 15°-45° (2θ). The morphology of the LiFePO₄ was examined by a field emission scanning electron microscope (FE-SEM, Hitachi, S-4200, Japan).

The cathode was composed of active materials, acetylene black, and polyvinylidene fluoride (PVDF) at a weight ratio of 85:10:5 and was coated onto an Al foil. The cathode was held in a vacuum oven at 80 °C for 12 hrs. After drying it, the cathode was 60 μm thick, containing approximately 5-7 mg cm⁻² of the active materials. 1 M LiPF₆ in an ethylene carbonate/dimethyl carbonate/ethylmethyl carbonate (EC/DMC/EMC) solution and lithium foil were used as electrolyte and the counter electrode, respectively. A standard coin cell (2032 type) was used to examine the charging and

discharging activities of the cathode. The Maccor 4000 battery cycler with cut-off voltages in the range of 2.5–4.3 V was used to analyze the rate performance at various C rates. The samples were discharged five cycles at 0.2, 0.5, 1, 2, 5, 10, 15, 20, 25, and 30 C, respectively, and charged at 0.2 C for an accurate comparison of the electrochemical properties. Cyclic voltammetry (CV) was carried out at scan voltage range from 2.8 to 4.2 V at 0.01 mV s^{-1} . Chemical delithiation of LiFePO_4 was carried out by mixing LiFePO_4 with $\text{K}_2\text{S}_2\text{O}_8$ at the ratio of 4:1.¹⁶ The mixture of LiFePO_4 and $\text{K}_2\text{S}_2\text{O}_8$ was dissolved in water and stirred at room temperature for 24 h. After filtered and dried at 800°C , the composition of the powder was obtained by inductively

coupled plasma (ICP, POLYSCAN-61E) except Li and Fe, which were analyzed by Atomic absorption spectroscopy (AAS, SOLAAR M) to compare Li content before and after chemical delithiation. To examine the binding energy and chemical composition of the LiFePO_4 , X-ray photoelectron spectroscopy (XPS, PHI 5000 VersaProbe, Ulvac-PHI) was used.

Results and Discussion

The particle morphology of the sample was examined first since the particle size determines the diffusion distance through the particle and effective surface area for the electrochemical reaction. Figure 1 shows the SEM images of the undoped and metal doped $\text{LiFe}_{0.97}\text{M}_{0.03}\text{PO}_4/\text{C}$ ($\text{M}=\text{Al}^{3+}$, Cr^{3+} , Zr^{4+}). They showed similar fine particles in the size range of 100–200 nm. The small adherents on the surface of LiFePO_4 particles appeared to be carbon black. This carbon layer restrains particle growth during heat-treatment and improved electrochemical properties by decreasing the Li ion diffusion path.¹⁷

The structure of the LiFePO_4/C and $\text{LiFe}_{0.97}\text{M}_{0.03}\text{PO}_4/\text{C}$ ($\text{M}=\text{Al}$, Cr , Zr) was investigated by XRD (Fig. 2). XRD profiles showed pure phases with an ordered olivine structure and the secondary phases such as Fe_2P and Li_3PO_4 were not detected. The lattice parameter obtained from the samples showed slightly changed (Table 1), which indicated that Fe ion might be substituted by M ion ($\text{M}=\text{Al}$, Cr , Zr). Figure 3 shows three different XRD peaks from (101), (111)/(201), and (211)/(202) planes of LiFePO_4/C , $\text{LiFe}_{0.97}\text{Al}_{0.03}\text{PO}_4/\text{C}$, $\text{LiFe}_{0.97}\text{Cr}_{0.03}\text{PO}_4/\text{C}$, and $\text{LiFe}_{0.97}\text{Zr}_{0.03}\text{PO}_4/\text{C}$. The figures clearly illustrate the peak shift from 0.04° to 0.14° after metal doping, which lead to change the lattice parameter. This result substantiates the doped ion such as Al, Cr and Zr ion replace Fe ion.

The CV profiles of LiFePO_4/C and $\text{LiFe}_{0.97}\text{M}_{0.03}\text{PO}_4/\text{C}$ ($\text{M}=\text{Al}^{3+}$, Cr^{3+} , Zr^{4+}) were obtained at a scan rate of 0.01 mVs^{-1} during the redox reaction and shown in Figure 4.

Figure 1. SEM micrographs of (a) LiFePO_4/C , (b) $\text{LiFe}_{0.97}\text{Al}_{0.03}\text{PO}_4/\text{C}$, (c) $\text{LiFe}_{0.97}\text{Cr}_{0.03}\text{PO}_4/\text{C}$, and (d) $\text{LiFe}_{0.97}\text{Zr}_{0.03}\text{PO}_4/\text{C}$.

Figure 2. XRD profiles of LiFePO_4/C , $\text{LiFe}_{0.97}\text{Al}_{0.03}\text{PO}_4/\text{C}$, $\text{LiFe}_{0.97}\text{Cr}_{0.03}\text{PO}_4/\text{C}$ and $\text{LiFe}_{0.97}\text{Zr}_{0.03}\text{PO}_4/\text{C}$ were heat-treated at 750°C for 10 h.

Table 1. The lattice parameters of LiFePO_4/C and doped LiFePO_4/C

	a (Å)	b (Å)	c (Å)	V (Å ³)
LiFePO_4/C	10.2867	6.0021	4.6825	289.1057
$\text{LiFe}_{0.97}\text{Al}_{0.03}\text{PO}_4/\text{C}$	10.2547	5.9846	4.6684	286.4985
$\text{LiFe}_{0.97}\text{Cr}_{0.03}\text{PO}_4/\text{C}$	10.2488	5.9676	4.6747	285.9074
$\text{LiFe}_{0.97}\text{Zr}_{0.03}\text{PO}_4/\text{C}$	10.2729	5.9989	4.6782	288.2948

Figure 3. XRD peak profiles of LiFePO_4/C and doped $\text{LiFe}_{0.97}\text{M}_{0.03}\text{PO}_4/\text{C}$ in plane (a) (101), (b) (111)/(201), and (c) (211)/(020).

Distinct anodic (charge) and cathodic (discharge) peaks were found from the samples indicating a redox reaction in a

Figure 4. CV profiles of LiFePO_4/C and doped LiFePO_4/C at a scan rate of 0.01 mV s^{-1} . **Figure 5.** (a) Rate performance at various C rates and (b) cycleability at 2 C rate of LiFePO_4/C , $\text{LiFe}_{0.97}\text{Al}_{0.03}\text{PO}_4/\text{C}$, $\text{LiFe}_{0.97}\text{Cr}_{0.03}\text{PO}_4/\text{C}$ and $\text{LiFe}_{0.97}\text{Zr}_{0.03}\text{PO}_4/\text{C}$.

two phase system. However, the shape and intensity of the current peaks were changed considerably after doping. The doped LiFePO_4/C cathodes exhibited narrower peaks than undoped LiFePO_4/C , which suggested that the metal ion incorporation facilitated Li ion diffusion during the redox reaction. In addition, $\text{LiFe}_{0.97}\text{M}_{0.03}\text{PO}_4/\text{C}$ ($\text{M}=\text{Al}^{3+}$, Cr^{3+} , Zr^{4+})

showed the reduced peak separation between the cathodic and anodic peaks which indicated that metal doping weakens the polarization. Shin *et al.*¹⁸ reported a similar result with the narrow current peaks after Cr doping, which was attributed to the decreased polarization resistance of the cathode.

The rate performance of LiFePO_4/C and doped LiFePO_4/C were compared at discharge rates from 0.2 C to 30 C and shown in Figure 5 (a). The initial capacity of the LiFePO_4/C was 147.9 mAh g^{-1} at 0.2 C. On the other hand, the doped LiFePO_4/C showed slightly lower initial capacity of 143.3 mAh g^{-1} , 144.4 mAh g^{-1} , and 143.7 mAh g^{-1} , from $\text{LiFe}_{0.97}\text{Al}_{0.03}\text{PO}_4/\text{C}$, $\text{LiFe}_{0.97}\text{Cr}_{0.03}\text{PO}_4/\text{C}$, and $\text{LiFe}_{0.97}\text{Zr}_{0.03}\text{PO}_4/\text{C}$, respectively. However, as the discharge current density increased, LiFePO_4/C showed severe capacity reduction down to 26.2 mAh g^{-1} at 30 C. On the other hand, $\text{LiFe}_{0.97}\text{M}_{0.03}\text{PO}_4/\text{C}$ ($\text{M}=\text{Al}^{3+}$, Cr^{3+} , Zr^{4+}) exhibited excellent capacity retention at high C-rates. Even at 30 C, the capacities of $\text{LiFe}_{0.97}\text{Al}_{0.03}\text{PO}_4/\text{C}$, $\text{LiFe}_{0.97}\text{Cr}_{0.03}\text{PO}_4/\text{C}$, and $\text{LiFe}_{0.97}\text{Zr}_{0.03}\text{PO}_4/\text{C}$ were maintained at 71.3 mAh g^{-1} , 110.8 mAh g^{-1} , and 94.5 mAh g^{-1} , respectively. The doped LiFePO_4/C , in general, exhibited excellent rate capability and $\text{LiFe}_{0.97}\text{Cr}_{0.03}\text{PO}_4/\text{C}$ was found to have the best performance. Figure 5 (b) showed the cycleability of LiFePO_4/C and doped LiFePO_4/C at 2 C charge-discharge rate. The doped LiFePO_4/C maintained their initial capacity, while LiFePO_4/C showed capacity reduction after 60 cycles. These results demonstrate the positive role of metal doping for the fade resistance of LiFePO_4 , which leads to the improvement of the electrochemical performance at high C rates. The improvement of the rate performance by metal doping has been observed by others and they explained the performance improvement by enhanced electronic conductivity.¹²⁻¹⁵

To find the root cause of the improvement of rate performance after metal doping, chemical delithiation of the LiFePO_4 was conducted by atomic absorption spectroscopy (AAS) and inductively coupled plasma (ICP). Table 2 shows the initial compositions of the four different samples before chemical delithiation. The Li content of LiFePO_4/C was 1 mol, while the doped LiFePO_4/C contained Li content from 0.98 to 0.99 mol. The deficiency of the Li ion in the doped

LiFePO_4/C is attributed to the charge compensation after doping Al^{3+} , Cr^{3+} , and Zr^{4+} ions instead of Fe^{2+} ion,¹⁹ causing the slight drop of initial capacity at 0.2 C, as shown in Figure 5. Table 3 represents the composition of the samples after chemical delithiation. It shows that $\text{LiFe}_{0.97}\text{Al}_{0.03}\text{PO}_4/\text{C}$, $\text{LiFe}_{0.97}\text{Cr}_{0.03}\text{PO}_4/\text{C}$, and $\text{LiFe}_{0.97}\text{Zr}_{0.03}\text{PO}_4/\text{C}$ contain 0.57, 0.55, and 0.56 mol of Li, respectively, so that 0.42, 0.43, and 0.43 mol of Li ion escape from the particle. On the other hand, 0.66 mol of Li remains in the undoped LiFePO_4/C , indicating that more Li ions are extracted from the doped LiFePO_4/C than LiFePO_4/C during chemical delithiation. This result suggests that the doped LiFePO_4/C has a weaker binding force between Li and other surrounding elements than that of LiFePO_4/C . It facilitates the Li ion diffusion so that the Li ion can escape the particle easily. The result of elemental composition is well coincided with the rate performance. In other words, the metal doped LiFePO_4/C , which contained a smaller amount of Li content after chemical delithiation demonstrated excellent capacity retention, while undoped LiFePO_4/C showed sharp capacity fading.

In order to understand the experimental result from chemical delithiation, the chemical binding energy of the

Figure 6. Peaks of chemical binding energy from XPS analysis of bare LiFePO_4/C and $\text{LiFe}_{0.97}\text{M}_{0.03}\text{PO}_4/\text{C}$ ($\text{M}=\text{Al}^{3+}$, Cr^{3+} , Zr^{4+}).

Table 2. Elemental composition of the samples before chemical delithiation

	Li (wt %)	Fe (wt %)	M (wt %)	P (wt %)	C (wt %)	Li:Fe:M:P (P=1)
LiFePO_4/C	3.93	32.0	—	17.5	2.97	1.00:1.01:1
$\text{LiFe}_{0.97}\text{Al}_{0.03}\text{PO}_4/\text{C}$	3.78	30.5	0.47	17.1	2.89	0.99:0.99:0.03:1
$\text{LiFe}_{0.97}\text{Cr}_{0.03}\text{PO}_4/\text{C}$	3.72	30.1	0.85	16.9	2.95	0.98:0.99:0.03:1
$\text{LiFe}_{0.97}\text{Zr}_{0.03}\text{PO}_4/\text{C}$	3.61	29.3	1.43	16.2	3.01	0.99:1.00:0.03:1

Table 3. Elemental composition of the samples after chemical delithiation

	Li (wt %)	Fe (wt %)	M (wt %)	P (wt %)	C (wt %)	Li:Fe:M:P (P=1)
LiFePO_4/C	2.91	35.7	—	19.7	2.95	0.66:1.01:1
$\text{LiFe}_{0.97}\text{Al}_{0.03}\text{PO}_4/\text{C}$	2.40	34.3	0.50	18.9	2.91	0.57:1.01:0.03:1
$\text{LiFe}_{0.97}\text{Cr}_{0.03}\text{PO}_4/\text{C}$	2.36	34.8	0.99	19.2	2.97	0.55:1.01:0.03:1
$\text{LiFe}_{0.97}\text{Zr}_{0.03}\text{PO}_4/\text{C}$	2.35	33.9	1.50	18.6	2.98	0.56:1.01:0.03:1

Figure 7. XPS depth profile of O1s peaks: (a) LiFePO_4/C , (b) $\text{LiFe}_{0.97}\text{Al}_{0.03}\text{PO}_4/\text{C}$, (c) $\text{LiFe}_{0.97}\text{Cr}_{0.03}\text{PO}_4/\text{C}$, and (d) $\text{LiFe}_{0.97}\text{Zr}_{0.03}\text{PO}_4/\text{C}$.²³

samples were measured by X-ray photoelectron spectroscopy (XPS). Figure 6 shows the O1s peaks obtained from four different samples which describes the chemical environment between Li and O. The figure illustrates that the XPS peaks from doped LiFePO_4/C are decreased slightly compared to undoped LiFePO_4/C . The binding energy of LiFePO_4/C was 531.38 eV, while that of $\text{LiFe}_{0.97}\text{Al}_{0.03}\text{PO}_4/\text{C}$, $\text{LiFe}_{0.97}\text{Cr}_{0.03}\text{PO}_4/\text{C}$, and $\text{LiFe}_{0.97}\text{Zr}_{0.03}\text{PO}_4/\text{C}$ were 531.25 eV, 531.13 eV, and 531.13 eV, respectively. The result was well consistent with the binding energy of O1s peak obtained from Liu *et al.*²⁰ and Lu *et al.*,²¹ which demonstrated the binding energy of O1s peak at 531.5 eV and 531.6 eV, respectively. Wang *et al.*²² also reported a similar result showing the reduction of the O1 binding energy after doping metal ions to LiFePO_4/C .

Figure 7 shows the O1s peak profiles from four different samples. The O1s peak from LiFePO_4/C consisted of three distinct peaks corresponding to P_2O_5 , Li_2O , and Fe_2O_3 and the Li_2O peak coincided well to the O1s peak, which indicated that Li_2O was dominant in oxygen bonding. On the other hand, when the metals such as Al, Cr, and Zr were incorporated instead of Fe, the O1s peaks were consisted of four different peaks. This is because new compositions were established after metal doping and the new peaks were corresponded to Al_2O_3 , Cr_2O_3 , and ZrO_2 . As a result, the

shape and intensity of the three original peaks were altered due to newly created peaks. In the case of undoped LiFePO_4/C , a Li_2O peak was the most dominant peak and it almost coincided with the O1s peak, indicating that Li-O bonding maintained sufficiently strong interaction in the undoped LiFePO_4/C . Whereas, the Li_2O peaks from the doped LiFePO_4/C was decreased by metal doping and as a result, newly produced peaks corresponding to Al_2O_3 , Cr_2O_3 , and ZrO_2 or already existing P_2O_5 and Fe_2O_3 peaks were increased. This suggested that Li-O interaction was weakened by metal doping, which improved the rate performance of the doped LiFePO_4/C due to high Li diffusion.

Conclusions

The chemical binding energy of LiFePO_4/C and $\text{LiFe}_{0.97}\text{M}_{0.03}\text{PO}_4/\text{C}$ ($\text{M}=\text{Al}^{3+}$, Cr^{3+} , Zr^{4+}) was measured using XPS techniques to find the cause of the improvement in rate performance after metal doping. The position of the O1s peaks from doped LiFePO_4/C was decreased in the range of 0.13 to 0.25 eV compared to undoped LiFePO_4/C , and the analysis of the peak profiles of XPS demonstrated that the intensity of Li_2O peak was significantly decreased after doping. The results of the elemental composition before and after chemical delithiation illustrated that approximately

0.43 mol of the Li content escaped from the doped LiFePO_4/C , while only 0.34 mol of Li content is extracted from the undoped LiFePO_4 . Both the results confirmed that the Li-O interaction was weakened by metal doping and it facilitated Li diffusion, which is the root cause of the improved rate performance of the doped $\text{LiFe}_{0.97}\text{M}_{0.03}\text{PO}_4/\text{C}$ ($\text{M}=\text{Al}^{3+}$, Cr^{3+} , Zr^{4+}).

Acknowledgments. This work was supported by Energy Resource R&D Programs (2009201010003B-11-3-020 and 2008EEL11P0800002009) under the Ministry of Knowledge Economy, Republic of Korea.

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