

Effects of the surface fluorination on the electrochemical properties of LiFePO₄ cathode material for lithium-ion batteries

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ABSTRACT

The electrochemical properties of LiFePO₄ cathode were improved by the surface fluorination with F₂ gas at a pressure less than 0.67 kPa at 25°C. In case of fluorinated LiFePO₄ precursor, the fluorine was still existed on the surface even after 700°C of sintering process. The fluorine on LiFePO₄ did play a role to improve the electrochemical properties of LiFePO₄. However, excess fluorination on the surface of LiFePO₄ was caused to the loss of performance of LiFePO₄. Therefore, the controlling of surface fluorination is very important to improve the electrochemical properties of LiFePO₄ as a promising cathode in high power lithium-ion cells for HEVs.

1. INTRODUCTION

Lithium secondary battery has been widely studied because of a large terminal voltage and a large energy density. Lithium containing transition metal oxides, LiCoO₂, LiNiO₂, LiMn₂O₄, LiFePO₄ and their derivatives have been investigated to obtain the high performance cathode active materials of lithium secondary battery. Among these cathode materials, LiFePO₄ has flat voltage profile, good electrochemical/thermal stability, relatively low cost for synthesis, and environmental compatibility with less toxicity than other cathode materials. Due to these advantages, LiFePO₄ has been attracting much attention as a promising new cathode electrode material for lithium-ion batteries. However, the low intrinsic electronic conductivity of LiFePO₄ and the low diffusion coefficient of Li⁺ are the main shortcoming that limits its application in industry. Extensive efforts have been performed to improve its electrochemical performance over decades, which can be classified into the following categories: particle size/shape optimizing [1–6] and metal doping [7], and mixing with the electronically conductive materials like carbon, metal and metal oxide [8–10]. Among these methods used for improving electrochemical properties of LiFePO₄, carbon coating is one of the most frequent techniques to enhance the specific capacity, rate performance, and cycling life [11, 12]. However, it should be further discussed on the optimum conditions with the thickness and formation of carbon layer. The modification of the surface of the cathode active material must have strongly effects on the battery performance because the electrochemical reaction takes place at the interface among the active material, carbon

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as the electroconductive material and the electrolyte. In our previous study, the surface modification of LiMn_2O_4 with fluorine/carbon nanocomposite by using NF_3 has been reported [13, 14]. Charge/discharge capacity and cycle ability of LiMn_2O_4 as a cathode material were enhanced by optimizing the arrangement of nano-thickness carbon film and surface fluorination, which was superior to the only carbon coated LiMn_2O_4 . In this study, the effects of surface fluorination on the electrochemical properties and thermal stability of LiFePO_4 were investigated.

2. EXPERIMENTAL DETAILS

2.1 Materials

The hydrothermal synthesis is a useful method for preparing fine particles. It also has other advantage such as simple synthesis process and energy efficient. LiFePO_4 can be prepared by hydrothermal reaction [15-20]. We have prepared LiFePO_4 from weak basic precursor solutions consisting of $\text{LiOH}\cdot\text{H}_2\text{O}$ (Kanto Chemical Corporation), $\text{FeSO}_4\cdot 7\text{H}_2\text{O}$ (Wako Pure Chemical Industries), H_3PO_4 (Wako Pure Chemical Industries) by hydrothermal method. The molar ratio of Li:Fe:P in the precursor solution was 3:1:1. In order to prohibit the conversion of Fe^{2+} to Fe^{3+} , the water was degassed by N_2 gas bubbling for 30 min prior to preparing the solution, and the mixing process was carried out under nitrogen atmosphere. The concentration of Fe^{2+} in the solution was in the range of 0.2-1.0 mol/dm³. Forty milliliters of the precursor solution was put into a Teflon vessel (inner volume: 120mL) sealed in a stainless steel autoclave, and the reactor was heated at 190°C in an oven for 3 h. During this hydrothermal process, precipitation took place inside the reactor. After the hydrothermal reaction, the reactor was cooled down to room temperature. The precipitated powder was washed with deionized water and acetone. Then, the obtained powder was dried at 150°C for 1h. And then, the obtained powder was fluorinated at 25°C and 0.67–1.33 kPa for 1h with F_2 gas. Details of the fluorination apparatus have been given in our previous paper [21, 22]. Finally, the untreated and fluorinated samples were sintered at 700°C for in Ar.

2.2 Material characterization

The structural and electronic properties of the samples were investigated using powder X-ray diffraction (XRD, XD-6100) and X-ray photoelectron spectroscopy (XPS, XPS-9010). The surface morphology of various samples was observed using a scanning electron microscope (SEM, s-2400; Hitachi Ltd.).

2.3 Electrochemical measurements

The cathode mixture was consisted of the treated LiFePO_4 sample, Acetylene Black (AB) and polyvinylidene difluoride (PVDF) in weight ratios of 8:1:1. The mixture was rolled spread to 0.1mm thickness film and the film was cut into a disk with 13mm^φ. And then, it was pressed onto a titanium mesh welded on the bottom of SUS304 container (20mm^φ x 3mm[†]). The cathode was fully dried by vacuuming ($\sim 10^{-1}$ Pa) for 12 hrs at

room temperature prior to use. The solution of propylene carbonate (PC) and dimethoxyethane (DME) mixed in the volume ratio of 1:1 containing 1.0 mol dm^{-3} LiPF_6 was used as an electrolyte solution. Li metal foil (0.2 mm^t Kyokuto Kinzouku Co. Ltd.) was used as the reference and counter electrodes. Charge/discharge test was carried out at the currents of 0.2 C (discharge rate) and 0.2 C (charge rate) (Hokuto Denko Co., HJ101SM6). The temperature of cathode was controlled at 25°C. Cut off potentials were 3.0 V (discharge) and 4.0 V (charge).

3. RESULTS and DISCUSSION

3.1 Characterization of sintered LiFePO_4

Fig. 1 shows XRD profiles of samples after sintering of untreated (a), fluorinated at 0.67 kPa (b) and at 1.33 kPa (c) precursors. All XRD profiles agreed with that of phosphor-olivine LiFePO_4 [23]. There was no extra peak in the profiles. Also, there was no change in the intensity and FWHM of the peak for LiFePO_4 samples prepared with an untreated and fluorinated precursors.

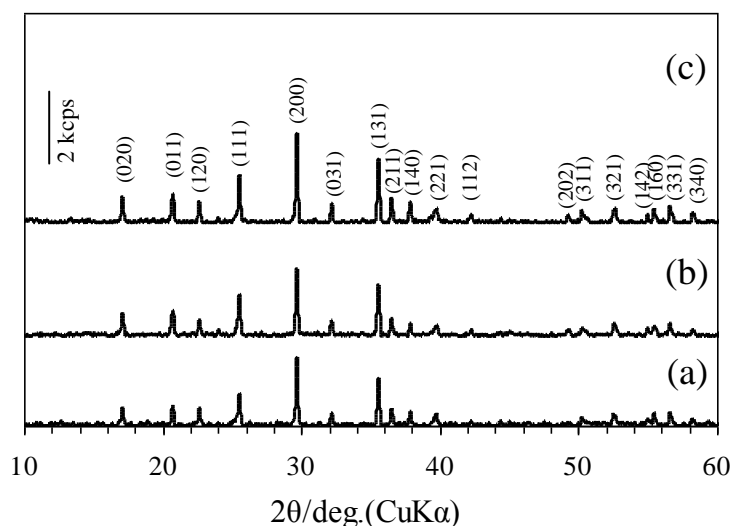


Fig.1 XRD profiles of LiFePO_4 samples prepared with untreated (a), fluorinated at 0.67 kPa (b) and at 1.33 kPa (c)

SEM images of LiFePO_4 samples after sintering of untreated (a), fluorinated (b, c) precursors are presented in Fig. 2. No change was observed in the shape and morphology of the surface of LiFePO_4 particles. The powders have an average size between 1 and 5 μm . The fluorination effect on the surface morphology of LiFePO_4 particles could not be detected in the SEM images. However, the existence of fluorinated surface layer of LiFePO_4 particles was confirmed in the XPS data.

Fig. 3 indicates XPS spectra of F1s electron for untreated and fluorinated LiFePO_4 samples after Ar^+ ion etching. All binding energies were calibrated to the C 1s peak at 284.8 eV of carbon. An F 1s peak located at the binding energy (BE) of 684.5 eV was

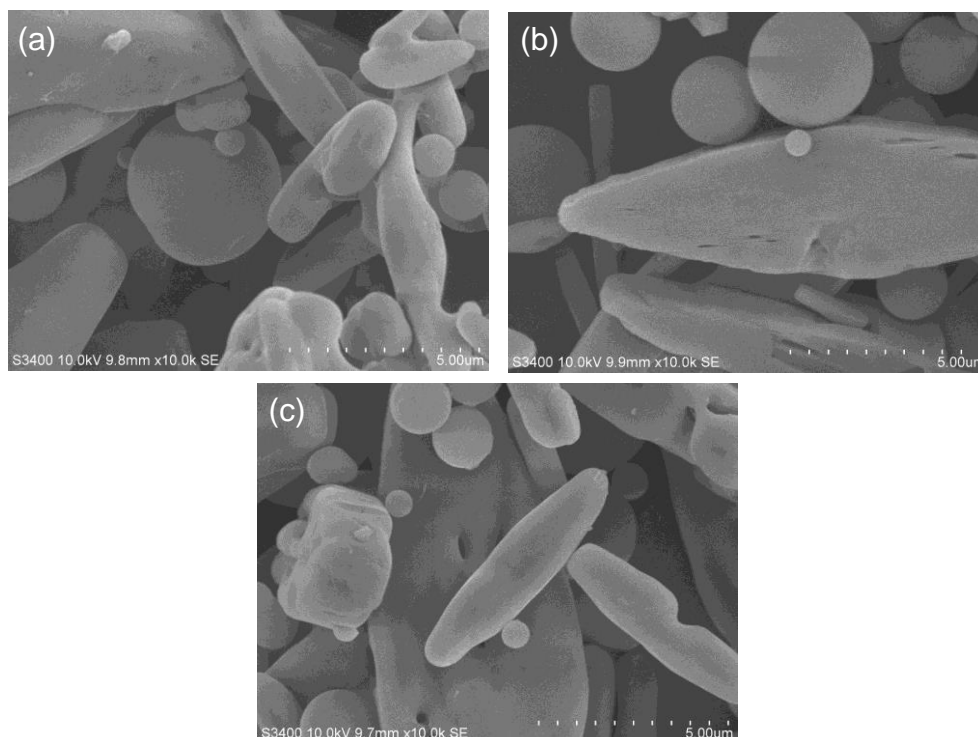


Fig.2 SEM images of LiFePO_4 samples prepared with untreated (a), fluorinated at 0.67 kPa (b), and fluorinated at 1.33 kPa (c)

detected in only sample (b). However, the fluorine peak at 685 eV almost disappeared after Ar^+ ion etching. Because the Li–F bond at 685 eV is not strong covalent bond, they can be easily eliminated by low-energy argon etching (300V, 5s) [24]. In case of sample (c), almost fluorine may be reacted with carbon existed on LiFePO_4 during sintering process. As reported in previous paper [25], the fluorine seems to make a bond with Li in LiFePO_4 at first, and then it may react with carbon on LiFePO_4 with increasing the fluorine contents.

3.2 Electrochemical properties of fluorinated LiFePO_4

Fig. 4 shows the discharge curves of LiFePO_4 samples after sintering of untreated (a) and fluorinated (b,c) precursors. The shape of discharge curves is similar to each other. However, the discharge capacity was changed by the surface fluorination. Comparing with untreated sample (a), the discharge capacity of sample (b) was almost same value (123 mAh/g). However, in case of sample (c), the discharge capacity was obviously decreased. It may be reasoned for the decreasing of electro-conductivity due to the reaction between fluorine the carbon on the surface.

Fig. 5 shows results of capacity retention of LiFePO_4 prepared with untreated (a), fluorinated at 0.67 kPa (b), and fluorinated at 1.33 kPa (c) during 50 cycles. Comparing with untreated thing (a), the capacity retention of fluorinated sample (b) was drastically

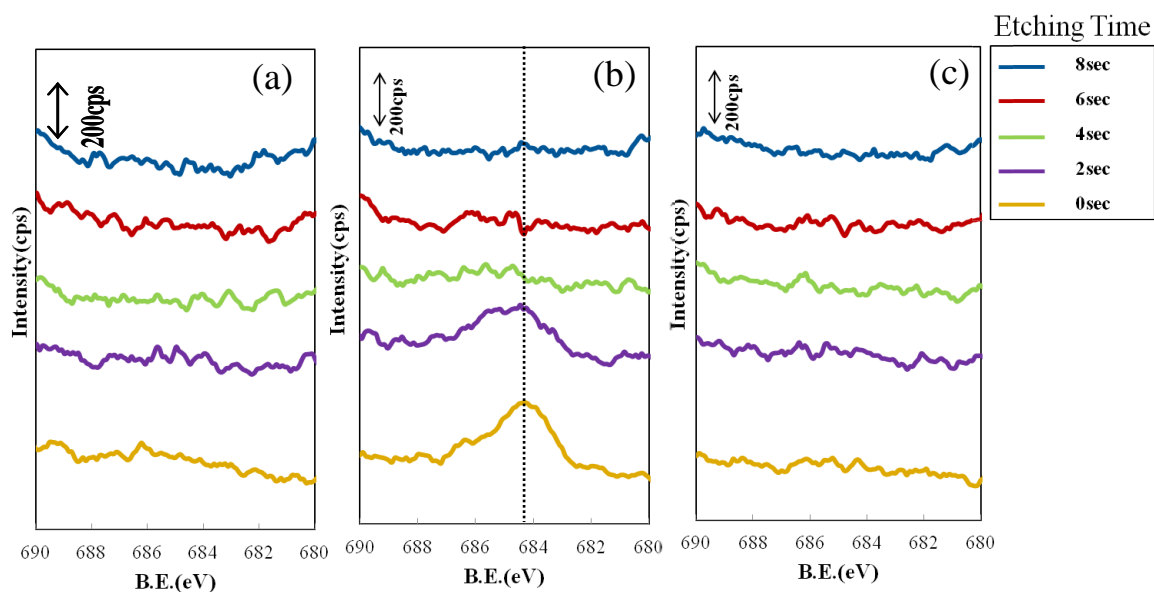


Fig.3 XPS spectra of F 1s after Ar⁺ ion etching of LiFePO₄ samples prepared with untreated (a), fluorinated at 0.67 Pa (b), and fluorinated at 1.33 kPa (c)

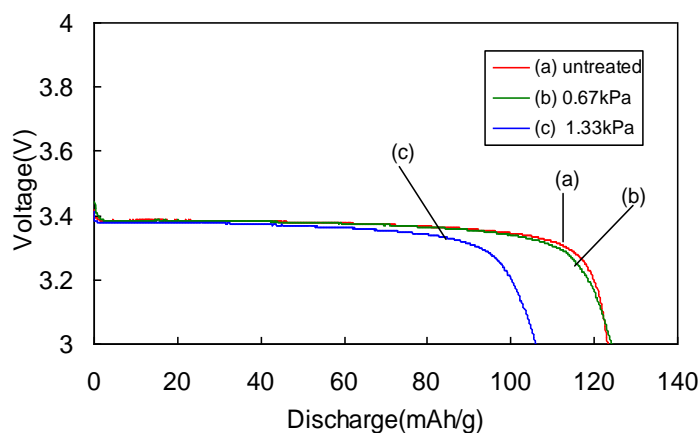


Fig.4 Discharge curves of LiFePO₄ samples prepared with untreated (a), fluorinated at 0.67 kPa (b), and fluorinated at 1.33 kPa (c)

improved above 40 cycles. It may be explained that the salvation ability and polarizability may be improved by introducing fluorine onto the surface of oxides because fluorine has the larger electronegativity than oxygen.

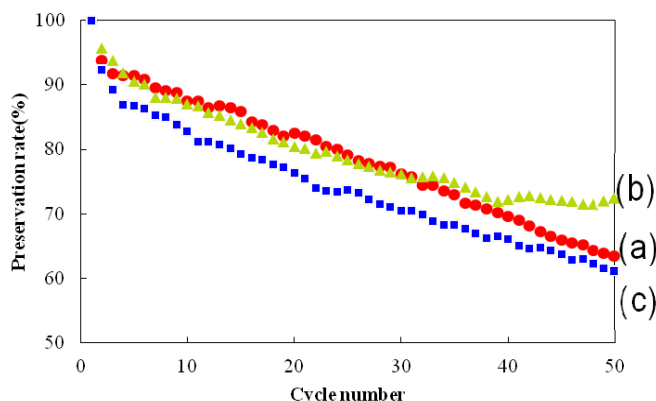


Fig.5 Results of capacity retention of LiFePO_4 prepared with untreated (a), fluorinated at 0.67 kPa (b), and fluorinated at 1.33 kPa (c) during 50 cycles.

4. CONCLUSIONS

We have reported the effects of surface fluorination on the electrochemical properties of LiFePO_4 . LiFePO_4 was prepared by using hydrothermal synthesis method. By using these prepared LiFePO_4 precursors, the fluorinated LiFePO_4 was successfully prepared by direct fluorination using F_2 gas. XRD and SEM results indicated that the surface fluorination with F_2 gas did not affect to the crystal structure and particle morphology of LiFePO_4 . However, XPS results proved the fluorinated surface layer existed on the surface of LiFePO_4 even after 700°C of sintering process. The fluorine existed after sintering process did play a role to improve the electrochemical properties of LiFePO_4 . However, excess fluorination on the surface of LiFePO_4 was caused to the loss of performance of LiFePO_4 . Therefore, the controlling of surface fluorination is very important to improve the electrochemical properties of LiFePO_4 as a promising cathode in high power lithium-ion cells for HEVs.

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