

Effects of the surface fluorination with various fluorine gases on the electrochemical properties of LiFePO₄ cathode material for LIB

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ABSTRACT

LiFePO₄ cathode material were improved good for the electrochemical properties by the surface fluorination with NF₃ gas at a pressure 0.67kPa at 25°C. In this condition for LiFePO₄ precursor, the fluorine had been 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. Even though the NF₃ gas has less reactive than F₂ gas, it is to enable the surface fluorination of LiFePO₄. By controlling of introducing accurately fluorine on the surface of the cathode material, LiFePO₄ is promising as a cathode material in high power and long term usable lithium-ion cells for HEVs.

1. INTRODUCTION

Lithium secondary battery has a high energy density and light weight of its own, since it is possible to repeatedly charged, it is expected as using in the role of a mobile power source for electric vehicles and plug-in hybrid ones and stationary power source for industrial and household in the world, therefore, the research has been actively conducted. Lithium-containing transition metal oxide such as LiCoO₂, LiNiO₂, LiMn₂O₄ and LiFePO₄, especially LiFePO₄, has a many advantages over the others, for example, less resource limitations for using iron of raw materials, high repeat charge / discharge characteristics and thermochemical characteristics for strong crystal structure. Because of these advantages, LiFePO₄ has been attracting great attention as a hopeful new cathode material for lithium-ion batteries. On the other hand, LiFePO₄ has not yet been industrially used as a mainstream of the lithium-ion battery. As the factors, LiFePO₄ has poor electron conductivity and the low diffusivity of Li⁺. Great approaches have been performed to improve the electrochemical performance more than decades. They can be categorized with the following sections: particle size and shape optimization [1–6] and metal doping [7], and mixing with the electronically conductive materials like carbon, metal and metal oxide [8–10]. In these methods used for amelioration electrochemical properties of LiFePO₄, carbon coating is one of the majority techniques to enhance the specific capacity, rate characteristic, and cycling life [11, 12]. However, it should be further discussed on the optimum conditions with the thickness and formation of carbon

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layer. The modification of the surface of the cathode material must have strongly effects on the battery performance because the electrochemical reaction takes place at the interface among the active material, carbon 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 with various fluorine gases 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 Ar 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, XRD-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 t). 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 0.1 C (discharge rate) and 0.1 C (charge rate) (Hokuto Denko Co., HJ101SM6). The temperature of cathode was controlled at 25 $^{\circ}\text{C}$. Cut off potentials were 3.0 V (discharge) and 4.0 V (charge). Cyclic test was carried out at the currents of 1 C (discharge rate) and 1 C (charge rate). The other conditions were the same as in the case of 0.1C.

2.4 Thermochemical measurements

The prepared electrode was made into cell, the cell was carried out test of charge/discharge at the current of 0.1C, furthermore, the cell was only charged at the current of 0.1C. Cut off potentials were 3.0 V (discharge) and 4.0 V (charge). In an Ar atmosphere, the cathode finished charge was took out from the cell, and the cathode was washed with dimethyl carbonate(Wako Pure Chemical Industries). This cleaning process was repeated 3 times. The cathode was cut into a disk with 2.8mm ϕ and put into the SUS container 4mm ϕ . The SUS container included the electrolyte 1 μL . Thermal stability test was performed by differential scanning calorimetry(DSC, DSC6220, SII). The sample was heated at a rate of 10 $^{\circ}\text{C}/\text{min}$ from 20 $^{\circ}\text{C}$ to 450 $^{\circ}\text{C}$.

3. RESULTS and DISCUSSION

3.1 Characterization of sintered LiFePO_4

Fig. 1 shows XRD profiles of samples after sintering of untreated (a), fluorinated with F_2 at 0.67 kPa (b), fluorinated with F_2 at 1.33 kPa (c) and fluorinated with NF_3 at 0.67 kPa (d) precursors. All XRD profiles agreed with that of phosphor-olivine LiFePO_4 [23]. There were no extra peaks in the profiles. Also, there were no changes in the intensity and FWHM of the peak for LiFePO_4 . samples prepared with an untreated and fluorinated precursors.

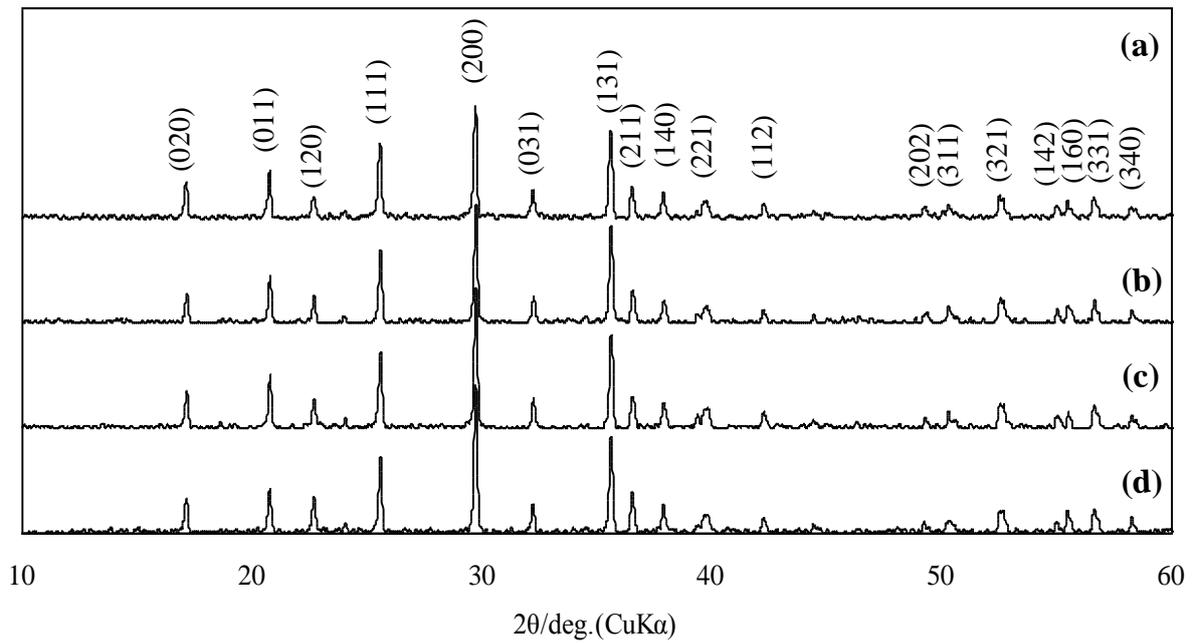


Fig.1 XRD profiles of LiFePO_4 samples prepared with untreated (a), fluorinated with F_2 at 0.67 kPa (b), and fluorinated with F_2 at 1.33 kPa (c), fluorinated with NF_3 at 0.67 kPa (d)

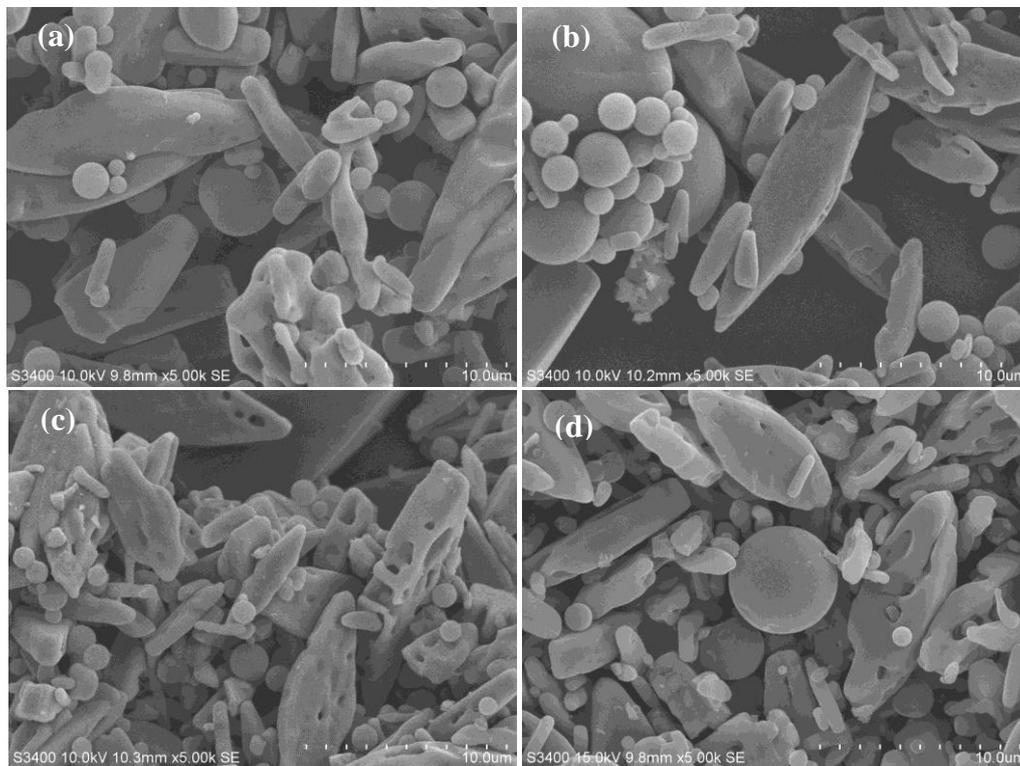


Fig.2 SEM images of LiFePO_4 samples prepared with untreated (a), fluorinated with F_2 at 0.67 kPa (b), and fluorinated with F_2 at 1.33 kPa (c), fluorinated with NF_3 at 0.67 kPa (d)

SEM images of LiFePO_4 samples after sintering of untreated (a), fluorinated (b, c, d) 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 10 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 shows XPS spectra of F1s, Li1s, Fe2p_{3/2} and O1s electron for untreated and fluorinated LiFePO_4 samples. 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 685 eV was detected in only sample (b). This bond is the Li-F bond at 685 eV. The case of sample (d), there was the existence of fluorine on the surface, nevertheless present fluorine, the binding energy was difference to sample (b). Some bond other than Li-F bond was confirmed there. In case of sample (c), almost fluorine may be reacted with carbon existed on LiFePO_4 during sintering process. As reported in previous paper [24, 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. Peak shift was not observed in those, Li1s and Fe2p_{3/2} peaks. In the O1s peak, P-O bond was observed in all samples, however, another bond was observed O-F bond on the fluorinated samples.

3.2 Electrochemical properties of fluorinated LiFePO_4

Fig. 4 shows the discharge curves of sintered LiFePO_4 samples of untreated (a) and fluorinated (b,c,d) 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) and sample (d) were approximately 5 mAh/g higher. However, in case of sample (c), the discharge capacity was obviously decreased. As indicated in Table 1, there was no fluorine on the surface in the sample (c). Therefore, it may be considered that there was the decline 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 with F_2 at 0.67 kPa (b), fluorinated with F_2 at 1.33 kPa (c) and fluorinated with NF_3 at 0.67 kPa (d) during 50 cycles. Compared with the sample (a), capacity retention of the sample (d) showed consistently the most high (50thcycle/1stcycle=73%). It may be explained that the salvation ability and polarizability may be improved by introducing a small amount of fluorine onto the surface of oxides because fluorine has the larger electronegativity than oxygen.

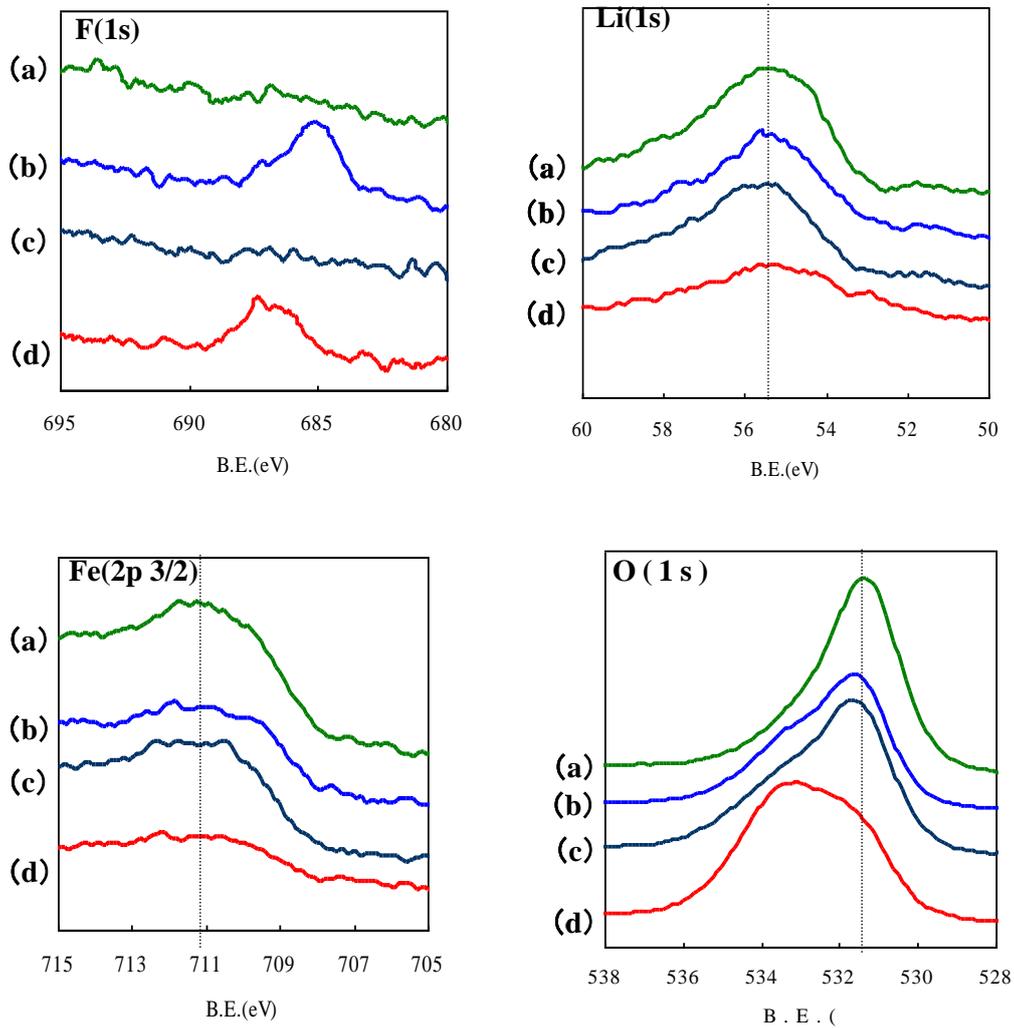


Fig.3 XPS each elements spectra of LiFePO_4 samples prepared with untreated (a), fluorinated with F_2 at 0.67 kPa (b), and fluorinated with F_2 at 1.33 kPa (c), fluorinated with NF_3 at 0.67 kPa (d)

Table.1 Element content of fluorine and oxygen of LiFePO_4 samples prepared with untreated (a), fluorinated with F_2 at 0.67 kPa (b), and fluorinated with F_2 at 1.33 kPa (c), fluorinated with NF_3 at 0.67 kPa (d)

	F(%)	O(%)
Sample (a)	0	100
Sample (b)	2.66	97.34
Sample (c)	0	100
Sample (d)	2.20	97.80

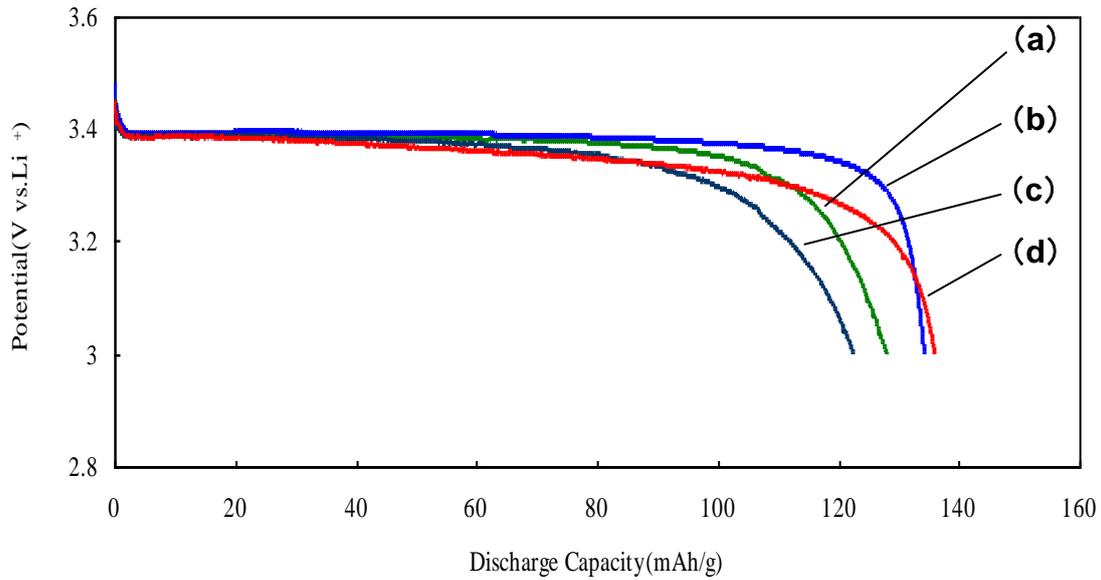


Fig.4 0.1C rate discharge curves of LiFePO₄ samples prepared with untreated (a), fluorinated with F₂ at 0.67 kPa (b), and fluorinated with F₂ at 1.33 kPa (c), fluorinated with NF₃ at 0.67 kPa (d)

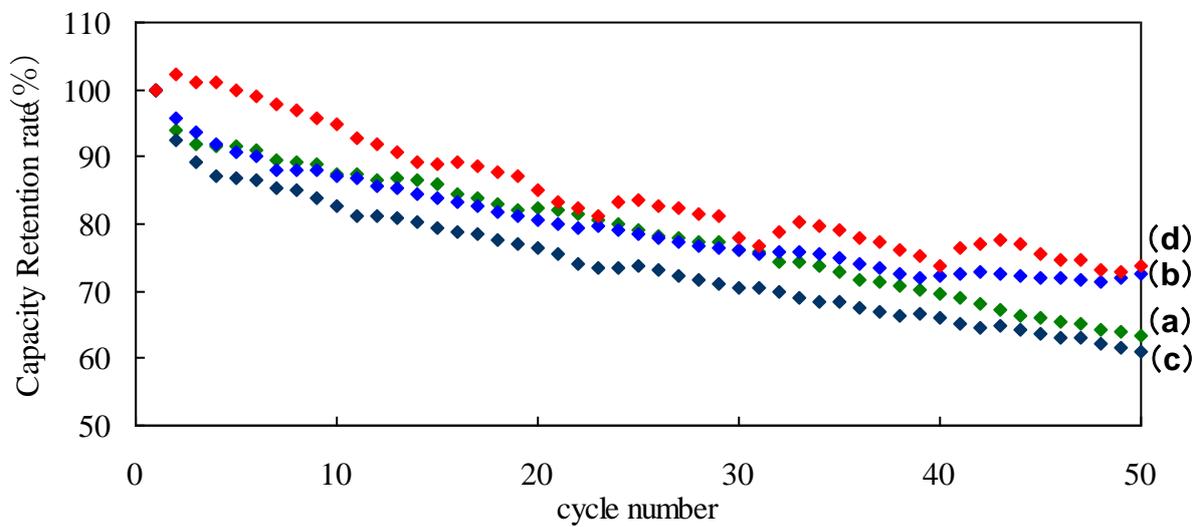


Fig.5 Results of 1C rate capacity retention of LiFePO₄ prepared with untreated (a), fluorinated with F₂ at 0.67 kPa (b), and fluorinated with F₂ at 1.33 kPa (c), fluorinated with NF₃ at 0.67 kPa (d) during 50 cycles.

3.3 Thermalchemical properties of fluorinated LiFePO_4

Fig. 6 shows three exothermic peaks state of charge of LiFePO_4 samples of untreated (a), fluorinated with F_2 at 0.67 kPa (b), fluorinated with F_2 at 1.33 kPa (c) and fluorinated with NF_3 at 0.67 kPa (d). Tab.2 exhibit 1st exothermic peak of each samples. 1st exothermic peak is considered to the oxidized deterioration by the electrolyte solution was more high in the sample (b) and sample(d) compared with sample (a). On the other hand, result of sample (c) was worse than sample (a). By Tab.1 and Tab.2, it is considered that fluorine remaining after sintering protected LiFePO_4 particle from heat.

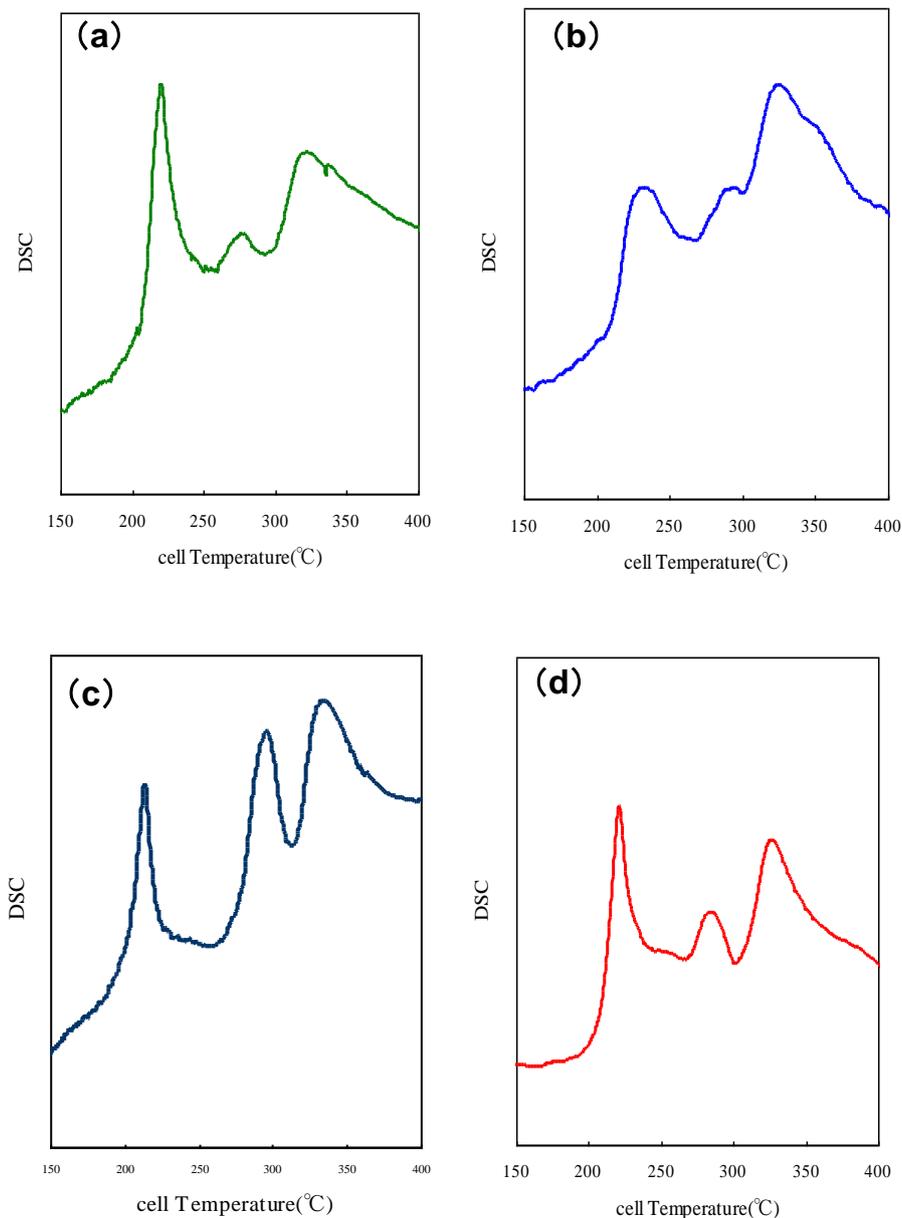


Fig.6 exothermic peaks of LiFePO_4 samples prepared with untreated (a), fluorinated with F_2 at 0.67 kPa (b), and fluorinated with F_2 at 1.33 kPa (c), fluorinated with NF_3 at 0.67 kPa (d)

Table.2 1st exothermic peak of LiFePO₄ samples prepared with untreated (a), fluorinated with F₂ at 0.67 kPa (b), and fluorinated with F₂ at 1.33 kPa (c), fluorinated with NF₃ at 0.67 kPa (d)

	sample (a)	sample (b)	sample (c)	sample (d)
1 st peak temperature(°C)	220.7	231.8	214.1	221.1

4. CONCLUSIONS

We have reported the potencies of surface fluorination on the electrochemical properties of LiFePO₄. LiFePO₄ was prepared by using hydrothermal synthesis method. By using these prepared LiFePO₄ precursors, the fluorinated LiFePO₄ was successfully prepared by direct fluorination using NF₃ or F₂ gas. XRD and SEM results indicated that the surface fluorination with NF₃ or F₂ gas did not affect to the crystal structure and particle morphology of LiFePO₄. However, XPS results proved the fluorine existed on the surface of LiFePO₄ even after 700°C of sintering process in the conditions of low pressure fluorine gases. The fluorine existed after sintering process did play a role to improve the electrochemical and thermochemical 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 confirmed that very effective to improve the electrochemical and thermochemical properties of LiFePO₄ as a hopeful cathode in high power lithium-ion cells for HEVs.

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