

Surface modification and performance evaluation of lithium-ion Surface Modification of Cathode Active Materials for Batteries and Performance Evaluation

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ABSTRACT

Lithium-ion batteries are rechargeable batteries that have high energy density and can be repeatedly charged and discharged. As electric vehicles become more popular in the future, there is a need for even higher performance. Electrochemical reactions involving insertion/desorption in lithium-ion batteries occur on the surface of particles, so surface modification is one of the effective methods to improve electrode properties. In previous research, fluorination using highly reactive fluorine gases such as F_2 and NF_3 to modify the surface of cathode active material improved charge-discharge capacity, but it was difficult to control the fluorine content of the cathode active material surface layer, and excessive amounts of fluorine resulted in the formation of a fluoride layer that caused resistance and reduced electrode properties. However, it was difficult to control the fluorine content in the surface layer of the cathode active material. In a previous study, it was found that there are two types of CeF_4 (stable CeF_4 and metastable CeF_4) obtained from the reaction of CeF_3 and F_2 , and metastable $CeF_4 (=CeF_{3+x})$ can be applied as a fluorinating agent that can release fluorine at room temperature if certain conditions are met. In this study, we aim to optimize the surface fluorination conditions of cathode materials using metastable $CeF_4 (=CeF_{3+x})$ to improve the electrochemical properties of cathode active materials for lithium-ion batteries.

1. INTRODUCTION

Lithium-ion batteries are rechargeable batteries that have high energy density and can be repeatedly charged and discharged. As electric vehicles become more popular in the future, there is a need for even higher performance. Since electrochemical reactions involving insertion/desorption in lithium-ion batteries occur on the surface of particles,

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surface modification is one of the effective methods to improve electrode properties. Previous studies have shown improvement in charge/discharge capacity by surface modification of cathode active material with F_2 or NF_3 , but the fluorination method using highly reactive fluorinated gases makes it difficult to control the fluorine content in the surface layer, and the formation of fluoride layer with excessive fluorine results in resistance and reduced electrode properties. Previous studies have shown that there are two types of CeF_4 (stable CeF_4 and metastable CeF_4) obtained from the reaction of CeF_3 and F_2 , and that metastable $CeF_4 (=CeF_{3+x})$ can be applied as a fluorinating agent that can release fluorine at room temperature if certain conditions are met. In this study, we aim to optimize the surface fluorination conditions using metastable $CeF_4 (=CeF_{3+x})$ to improve the electrochemical properties of cathode active materials for lithium-ion batteries.

2. EXPERIMENTAL DETAILS

2.1 Fluorination of CeF_3

To synthesize fluorinating agent (CeF_{3+x}), it was necessary to react CeF_3 (KCE-OF-014, Shin-Etsu Chemical Co.Ltd.Net 100grs.) with fluorine. CeF_3 was placed in a reaction tube, and after the apparatus and reaction tube were evacuated to less than 1.0 Pa, fluorination was performed under different fluorination conditions (①280°C, 50.7 kPa, 1h ②280°C, 67.5 kPa, 1h ③300°C, 101.3 kPa, 1h) to prepare CeF_{3+x} .

2.2 Fluorination of cathode active material with prepared CeF_{3+x}

The prepared CeF_{3+x} was then placed in a reaction tube with ternary (Ni, Mn, Co) cathode active material($LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$:LMXO-13104, TANAKA CHEMICAL CORPORATION, NET Wt 1kg) and the cathode active material was fluorinated at room temperature for 1 hour.

2.3 Characterizations of samples

The structural and electronic properties of samples were investigated using XRD (X-ray diffraction; D8 ADVANCE, Bruker AXS) and XPS (X-ray photoelectron spectroscopy; JPS-9010MC, JEOL, Ltd.). The particle surface was observed using FE-SEM (Field Emission-scanning electron microscopy; ULTRA plus, ZEISS).

2.4 Battery production

For electrochemical measurements, each cathode active material sample, conductive material (acetylene black), and binding agent (polyvinylidene fluoride:W#7200 KUREHA CORPORATION, Mw: 6.3×10^5) were mixed at a weight ratio of 8:1:1, and a quantity of NMP (N-methyl-2-pyrrolidinone:000-50485 KISHIDA CHEMICAL CO.,LTD;99.5 purity,500mL) was added as coating solution. After standing in a dryer at 120°C for at least 1 hour, the electrode plates were cut into circles, pressed at 2 MPa for 10 minutes, and vacuum-dried for at least 24 hours.

2.5 Charging and Discharging Tests

Charge-discharge tests were conducted using the prepared electrode plates at a charge rate of 0.1C and a discharge rate of 0.1C for 5 cycles at a termination potential of 4.5V and a starting potential of 3.0V. The cycle test was then conducted at a charge rate of 0.5C and discharge rate of 0.5C for 50 cycles at a termination potential of 4.5V and a starting potential of 3.0V.

Table 1. Sample names and reaction conditions of CeF₃ treated with F₂

Sample name	F ₂ pressure /kPa	Time /min	Temperature /°C
CeF _{3.1} (①)	56.0	60	280
CeF _{3.4} (②)	67.5	60	300
CeF _{3.9} (③)	101.3	60	300

3. RESULTS and DISCUSSION

3.1 Structural analysis of CeF_{3+x} samples

Fig. 1(A) shows the XRD analysis results of CeF_{3+x} samples synthesized under various fluorination conditions. In the synthesized samples, it was confirmed that the crystal structure changed from CeF₃ to CeF₄ as the fluorination temperature and fluorine pressure increased. Fig. 1(B) shows the XRD analysis results of the CeF_{3+x} sample after fluorination treatment of the cathode active material surface. x value decreased due to fluorine release compared to Fig. 1.

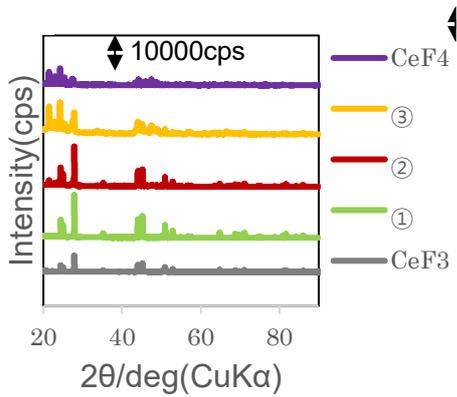


Fig. 1(A) XRD patterns of untreated (CeF_3 , CeF_4) and the produced CeF_{3+x} (①, ②, ③)

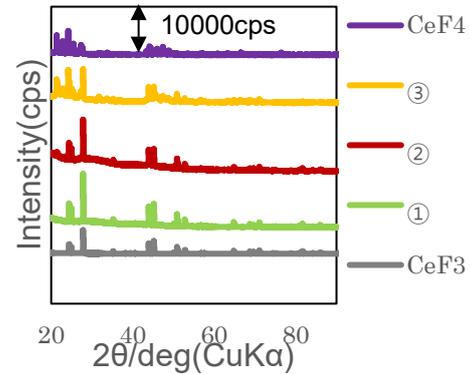


Fig. 1(B) XRD patterns of untreated (CeF_3 , CeF_4) and CeF_{3+x} after fluorination of active material (①, ②, ③)

3.2 Surface composition of CeF_{3+x} sample

Fig.2 (A) shows the F1s spectrum of the prepared CeF_{3+x} sample (B) shows the F1s spectrum of the CeF_{3+x} sample after fluorination of the active material. (Comparing (A) and (B), the F1s peak of the CeF_{3+x} sample shifts slightly to the lower binding energy side (= CeF_4 side) when F is released in vacuum at room temperature. The CeF_{3+x} sample in the Ce3d5/2 spectrum (C) is also in the middle of the Ce3d5/2 spectra of CeF_3 and CeF_4 . Comparing (C) and (D), the Ce3d5/2 peak of the CeF_{3+x} sample shifts slightly to the low binding energy side (= CeF_4 side) as does the F1s peak when F is released in vacuum and at room temperature. (= CeF_4 side) is due to the retention of F_2 on the surface of CeF_{3+x} particles by F_2 released from the CeF_{3+x} sample, which is thought to move to the low binding energy side.

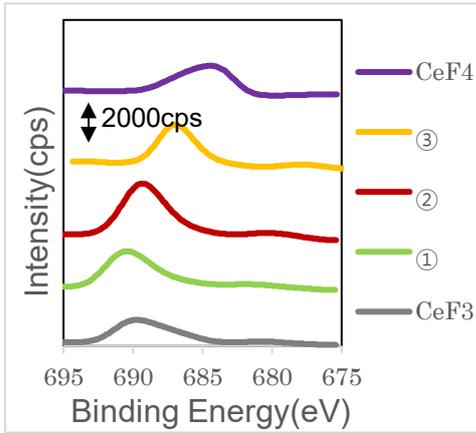


Fig. 2(A) XPS spectra of F1s untreated (CeF₃, CeF₄) and the produced CeF_{3+x}(①,②,③)

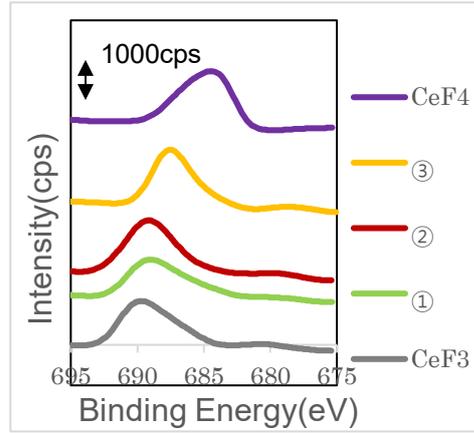


Fig. 2(B) XPS spectra of F1s untreated (CeF₃, CeF₄) and CeF_{3+x} after fluorination of active material (①,②,③)

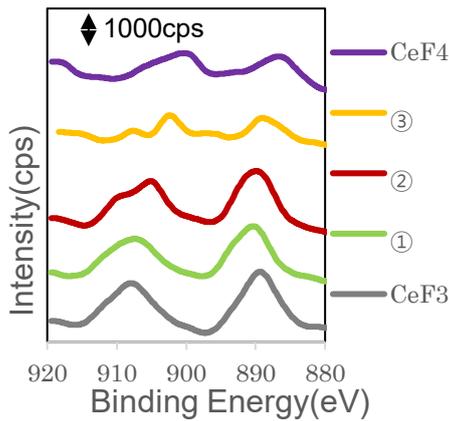


Fig. 2(C) XPS spectra of Ce3d_{5/2} untreated (CeF₃, CeF₄) and the produced CeF_{3+x}(①,②,③)

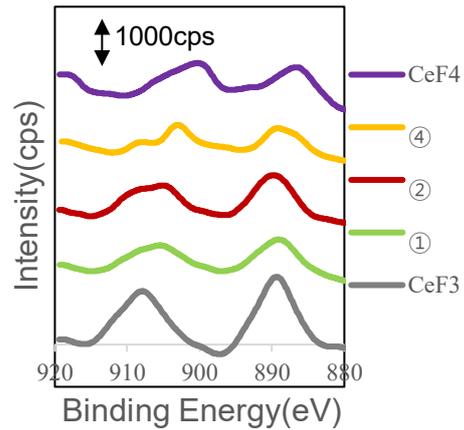


Fig. 2(D) XPS spectra of Ce3d_{5/2} untreated (CeF₃, CeF₄) and CeF_{3+x} after fluorination of active material (①,②,③)

3.3 Surface observation of particles

FE-SEM images of CeF_3 , CeF_4 and CeF_{3+x} ($280^\circ C$, $300^\circ C$) are shown in Fig. 3. As can be seen from Fig. 3, the effect of fluorination on the surface state of the CeF_{3+x} particles cannot be seen in the FE-SEM images because the particles are melted by the high temperature. (1) and (2) are considered to exist in the intermediate between CeF_3 and CeF_4 , while (3) is considered to be closer to CeF_4 .

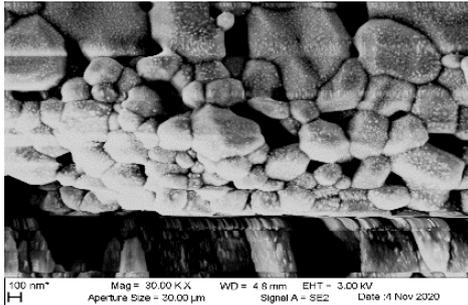


Fig. 3(A) FE-SEM images of untreated CeF_3

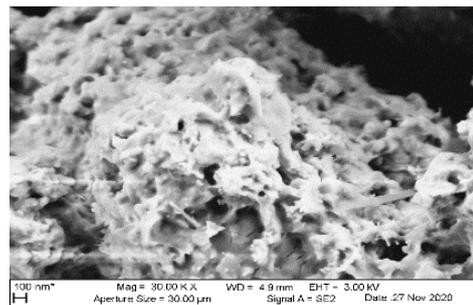


Fig. 3(B) FE-SEM images of untreated CeF_4

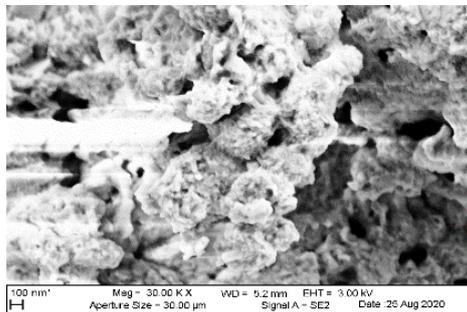


Fig. 3(C) FE-SEM images of the produced CeF_{3+x} (①、②)

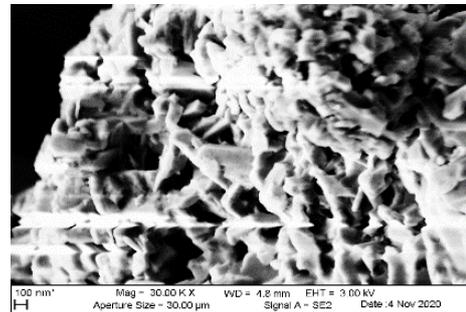


Fig. 3(D) FE-SEM images of the produced CeF_{3+x} (③)

3.4 Surface composition of Cathode active material

The F1s spectrum of the active material after fluorine treatment in the CeF_{3+x} sample is shown in Fig. 5.

The appearance of the peak indicates that surface fluorination treatment was performed on the active material. The peak appearing around 684eV is due to Li-F bonding, and the peak appearing around 686eV is derived from M-F (M: transition metal Ni, Co, Mn).

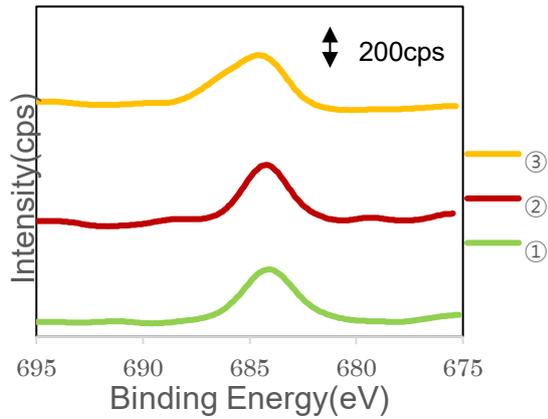


Table 2 Amount of fluorine adhered to cathode active material surface

	①	②	③
Atomic%(F)	2.0%	2.4%	3.6%

Fig. 4 XPS spectra (F1s) of active material after fluorination

3.5 Charging and Discharging Tests

Fig. 6 shows the results of charge-discharge tests of batteries assembled using active materials fluorinated with CeF_{3+x} . The rate is 0.1C 3rd cycle Cut off :3V~4.5V. By fluorinating the surface of active material with CeF_{3+x} , both charge and discharge capacities increased compared to the untreated sample. Especially in condition (2), an increase in discharge capacity of about 8% or more was confirmed.

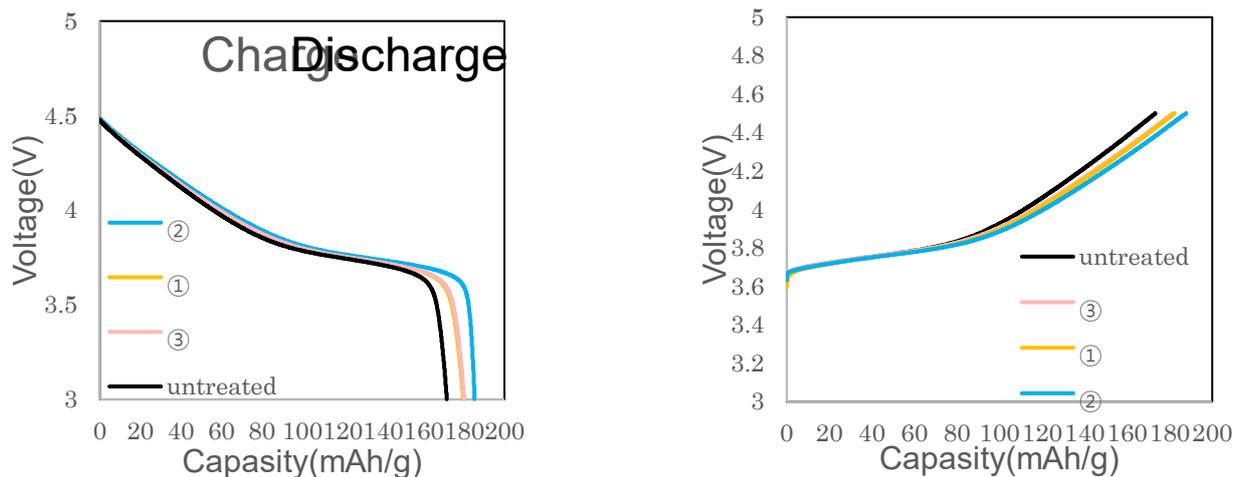


Fig. 5 Charge and Discharge capacity of untreated and fluorinated samples
 (Charge 0.1C Discharge 0.1C)

3.6 Cycle test

Fig. 7 shows the results of the cycle test. The rate is 0.5C Cut off 3 to 4.5V. In the evaluation of battery capacity retention, the capacity retention of the fluorine-treated sample batteries was greatly improved over the untreated batteries. If surface modification by fluorine treatment with low activity level like this can be achieved, the insertion and desorption of lithium ions will not be inhibited for cathode active materials, indicating that they can be activated efficiently.

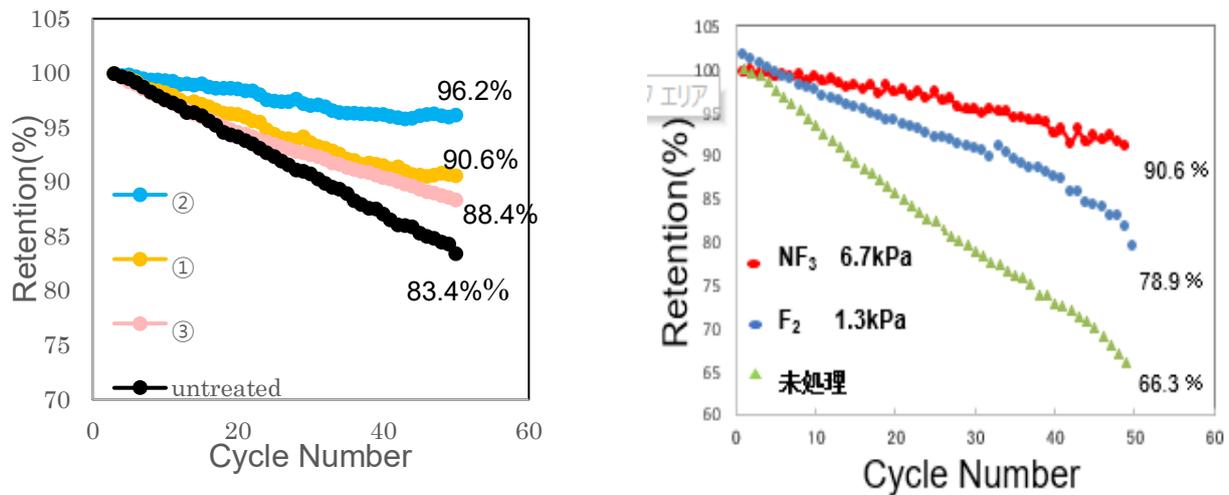


Fig. 6 Discharge capacity as a function of cycle number Fluorinated Sample
 (Charge 0.5C Discharge 0.5C)

4. CONCLUSIONS

It was confirmed that metastable CeF_4 ($=CeF_{3+x}$) can be prepared by fluorination of CeF_3 , which releases a very small amount of F_2 at room temperature ($25^\circ C$) and in a vacuum, but at about $110-140^\circ C$, H_2O and F_2 react and release a small amount of HF . Therefore, it is necessary to react with the active material in a vacuum and at room temperature ($25^\circ C$). The amount of fluorine adhered to the active material surface varies depending on the prepared CeF_{3+x} ($x=0\sim 1$) because the thickness of the layer reacting with fluorine is different and the amount of F emitted from the inside of the surface layer is different. It was confirmed that fluorination of active materials can be performed using the prepared CeF_{3+x} . The capacity of the battery with fluorinated active material using the prepared CeF_{3+x} was confirmed to be higher than that of the battery with NF_3 gas (165mAh/g) in the previous study.

In addition, it was confirmed that the battery was less degraded than the untreated battery in the cycle test.

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