A new iron oxyfluoride cathode active material for Li-ion battery, Fe_2OF_4

Irina D. Gocheva [a], Ichiro Tanaka [b], Takayuki Doi [b], Shigeto Okada [b,*], Jun-ichi Yamaki [b]

[a] Interdisciplinary Graduate School of Engineering and Material Sciences, 6-1, Kasuga Koen, Kasuga-shi 816-8580, Japan
[b] Institute of Materials Chemistry and Engineering, Kyushu University, 6-1, Kasuga Koen, Kasuga-shi 816-8580, Japan

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ABSTRACT

The electrochemical properties of iron oxyfluoride of the Fe_2OF_4 type were investigated. The material exhibits a working potential at 3.0 V with a capacity of 200 mAh/g and cyclic reversibility in the range of 1.5–4.5 V. X-ray photoelectron spectroscopy (XPS) investigation of discharged material showed that iron was reduced to the divalent state. In this study, we report that Fe_2OF_4 material incorporates 1.4 Li per formula unit.

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1. Introduction

Iron-based positive electrode materials such as olivine-type $LiFePO_4$ have been the subject of intense investigation. Iron-based compounds are suitable for large-scale lithium-ion batteries, because of their natural abundance and non-toxicity. However, new advances are needed in the search for positive electrodes with higher capacities. As a special class of promising active materials, fluoride-based compounds have become intriguing. Recently, we showed that perovskite-type 3d-transition metal trifluorides, MF_3 (M = Fe, V), are attractive as large-capacity cathode materials suitable for Li and Na intercalation at RT [1]. Some previous research has also shown a beneficial specific reversible capacity for FeF_3 of more than 600 mAh/g at 70 °C, indicating that the all redox potentials of the metal could be utilized by means of a conversion reaction [2].

The ionic character of fluorine-based compounds provides some advantages over other common materials such as sulfides, phosphates, oxides, and nitrides, leading to increased operating voltage in lithium cells. However, fluorides have practically been discarded as electrode materials because of their insulating characteristics. The poor conductivity can be improved by adding carbon into the electrode paste or by introducing more covalent bonds into the structures. Since the ionic radii of oxygen and fluorine are very similar, the substitution of one for the other could results in small structural distortions. Therefore, we have shifted our research interest to iron oxyfluorides. Furthermore, some literature reports have indicated that this partial substitution is beneficial for better utilization of the theoretical capacity of the material and for improved electrochemical activity through the presence of oxygen in the fluoride matrix [3].

$M^{3+}OF$ (M = Fe, Ti, V, etc.) is a typical family of transition metal oxyfluoride compounds. The first synthesized compound of the group was rutile-type FeOF because of its useful physical properties as ferroelectricity, pyroelectricity, and piezoelectricity. The existence of a solid solution with the composition FeO_xF_{2-z} (0 < x < 0.18, 0.92 < z < 1) was also determined [4]. Similarly, TiOF, VOF, and the solid solutions $Ti_2O_{4-x}F_x$ and $V_2O_{4-x}F_x$ were synthesized in a tetrahedral anvil at pressures of 60–65 kbar [5,6]. Thus far there have no reports regarding their possible electrochemical activity. The oxyfluorides are promising candidates for positive electrode materials due to the advantages of their higher theoretical capacity even they are not suitable for use in today's lithium-ion batteries, because they deliver no extractable lithium-ions during the first charge. Lithiation of metal oxyfluorides with the cubic ReO_3 structure (NbO_2F, TaO_2F and $TiOF_2$) by treatment with n-BuLi, which leads to $Li_{0.43}TiOF_2$ and $Li_{1.50}TiOF_2$ at 50 °C, has been reported [7]. The electrochemical behavior of these compounds under deep discharge–charge conditions with Li-metal has also been described [8].

The less explored oxyfluoride compound is Fe_2OF_4, discovered and reported by Ostrovskaya in 1969 [9]. The existence of Fe_2OF_4 was confirmed as result of dehydration of $FeF_2 \cdot 4H_2O$ in air. As a consequence the material has been synthesized and indexed after heating of FeF_2 in oxygen flow. By improving the synthesis path, we succeeded in obtaining Fe_2OF_4 and studying its electrochemical performance as an intercalation host for Li.

* Corresponding author. Tel./fax: +81 92 583 7841.
E-mail address: s-okada@cm.kyushu-u.ac.jp (S. Okada).

2. Experimental

In this study, we used commercially available FeF$_2$·4H$_2$O (Aldrich) and FeF$_2$ (Soekawa Chem. Ind.) as starting materials. The syntheses were carried out under oxygen flow of 400 ml/min, were all the precursors being heated for different periods of time. The obtained materials were indexed by XRD powder diffraction (Rigaku RINT2100HLR/PC) using Cu Kα radiation from $2\theta = 10°–80°$ at a 2.0°/s scan rate. FE-SEM (JEOL JSM-340F) was used for observing the morphology of the obtained samples. XPS measurements were performed with a JPS-9000(JEOL Ltd.) with Mg Kα radiation (1253.6 eV). To improve the S/N ratio, the XPS spectra were recorded for 15 sweeps. The binding energy was calibrated according to the C 1s level (284.3 eV).

The iron oxyfluoride/carbon nanocomposites were fabricated by mechanical milling with the Premium line-7 planetary ball mill (Fritsch GmbH., Germany) under Ar. The iron oxyfluoride Fe$_2$OF$_4$ was mixed with 25 wt% acetylene black (Denki Kagaku Co.) for 3–5 h at a slow milling speed of 350 rpm to prevent possible reduction of iron during the ball milling.

Electrochemical evaluation of the synthesized materials was carried out in a coin-type cell 2032, assembled in an Ar-filled glove box using 1 mol dm^{-3} LiPF$_6$/EC + DMC, 1:1 in vol. (Tomiyama Pure Chemicals Industries, Ltd.) as electrolyte composition against Li-metal (Honjo metal), as negative electrode and microporous polypropylene separator (Celgard Inc.). The pellet-type electrodes are composed of 95 wt% Fe$_2$OF$_4$/C nanocomposite and 5 wt% PTFE as binder. Galvanostatic tests at RT were conducted using an automatic cycler (Nagano BTS-2004).

3. Results and discussion

Dehydration of FeF$_2$·4H$_2$O yields a mixture of oxide, fluoride, and/or oxyfluoride in the solid residue when it is carried out under a flow of pure Ar or in air, as has been reported elsewhere [9]. When it is heated in an oxygen atmosphere, the following reaction is expected: $2FeF_2·4H_2O + 0.5O_2 = Fe_2OF_4 + 8H_2O$. Our experiments show that depending on the period of heating, a small amount of crystal water always remains captured in the fluoride structure which leads to different end products. Because FeF$_2$·4H$_2$O is moisture sensitive, we suggest using anhydrous, vacuum dried FeF$_2$ as a starting material.

Fig. 1 shows an XRD pattern of the resultant powder prepared at 430 °C for 6 h under O$_2$ flow. Very similar XRD patterns were obtained for the powder prepared at temperatures ranging from 380 °C to 430 °C. The synthesis reactions should proceed at these temperatures as follows: $2FeF_2 + 0.5O_2 = Fe_2OF_4$. The starting material of FeF$_2$ belongs to a rutile system while the crystal group of Fe$_2$OF$_4$ was not identified, as we observed a slight difference from the Fe$_2$OF$_4$ reported previously [9]. This variation is probably due to minor compositional deviations attributed to some traces coming from the starting materials. The morphology of the microcrystalline compound is shown in inset. In the field of vision, the oblong rod-like structures 200–500 nm in width and 0.7–3.0 μm in length were observed with SEM. Additional grinding of material with acetylene black under Ar produced the nanostructured composition of carbon–iron oxyfluoride.

The discharge/charge curves in the working region 1.5 V–4.5 V for a cell with Fe$_2$OF$_4$/C as a positive electrode vs. Li/Li$^+$ at RT are given in Fig. 2. The cell shows a plateau at around 2.0 V during the first lithiation with a homogeneous one-phase reaction and a capacity of 200 mAh g^{-1}. On the second discharge, this value increased slightly to 2.9 V. Even though the first discharge profile differs from the subsequent ones, acceptable performance over 20 cycles was retained (see inset). The increasing in cell potential is
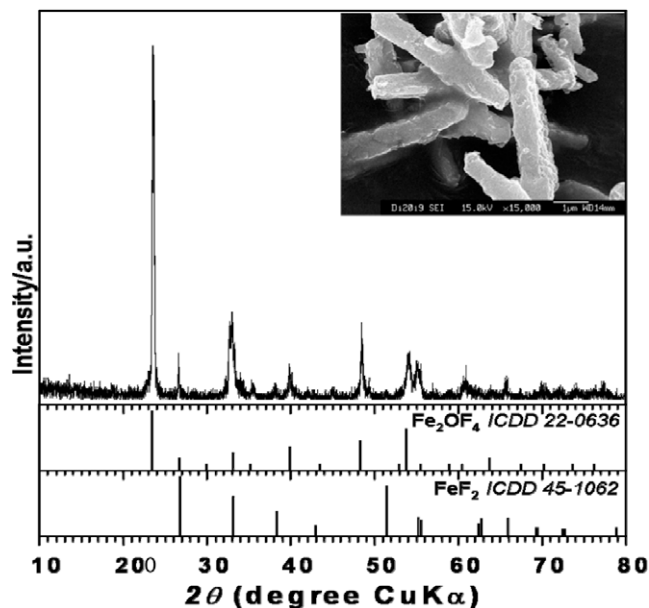

Fig. 1. XRD pattern of Fe$_2$OF$_4$ obtained by heat treatment under oxygen flow at 430 °C. FE-SEM image (in inset).
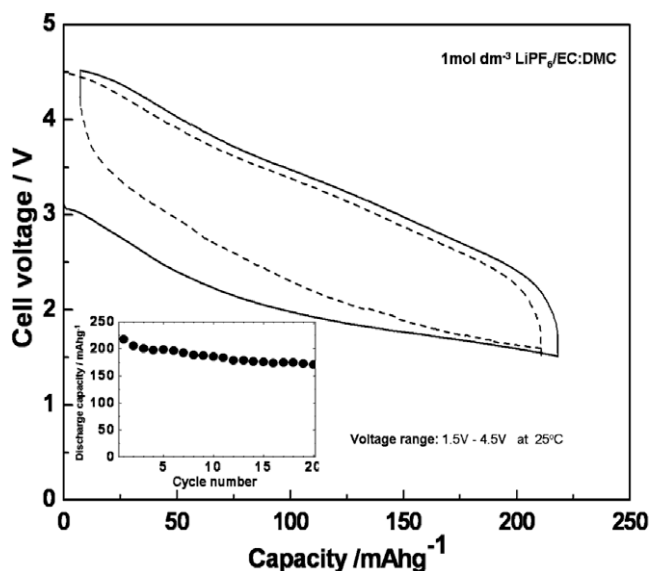

Fig. 2. First and second discharge–charge curves of Fe$_2$OF$_4$/C vs. Li/Li$^+$ in LiPF$_6$/EC:DMC (1:1 in volume) with a current density of 0.2 mA cm^{-2} for the potential range 1.5–4.5 V and cycleability (in inset).

not surprising, as similar phenomena has often been observed with cells using Fe$_2$O$_3$ [10], FeOOH [11,12], and FeOCl [13] as positive electrode materials. Although the detail mechanism of the increasing of the discharge voltage after second cycle has not been clear, the relatively high discharge voltage supposes that the process is due only to Li intercalation, without utilizing a conversion reaction for the chosen potential region. The amount of inserted lithium was determined by AAS and is in agreement with the chronoamperometric value of approximately 1.4 mol Li insertion per formula unit calculated from the discharge duration. The discharge product of Fe$_2$OF$_4$ (Li$_x$Fe$_2$OF$_4$, $0 < x \leqslant 1.4$ for our study) appears to be stable without showing decomposition due to side reactions with electrolyte. However, additional work is required to confirm the electrochemical and thermal stability of oxyfluorides.
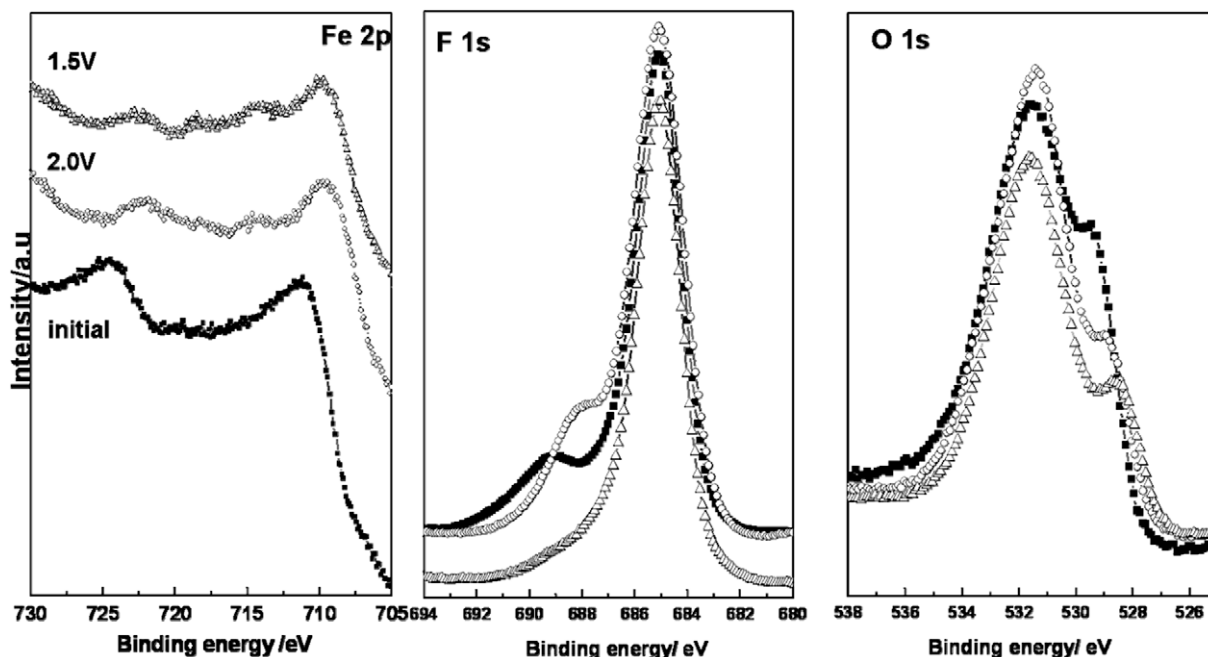
Fig. 3. XPS spectra of Fe 2p, F 1s and O 1s in Fe_2OF_4/C cathode pellets at various charge/discharge states (-■- initial fresh pellet; –○- fully discharged down to 2.0 V; –△- fully discharged down to 1.5 V).

The reduction of trivalent iron to the divalent state of discharged material has been confirmed by XPS. Fig. 3 shows the XPS emission spectra of Fe $2p_{1/2}$ and Fe $2p_{3/2}$ of Fe_2OF_4/C fresh and discharged cathode pellets in 1 M $LiPF_6$ EC/DMC (1:1) electrolyte down to different cut off voltages. The Fe $2p_{1/2}$ and Fe $2p_{3/2}$ peaks of initial Fe_2OF_4 appeared at binding energies of 724.8 eV and 711.5 eV, respectively and are consistent with the binding energies of trivalent iron with various ligands [14–16]. The electronic distribution of Fe depends on the ligand bounded therefore in case of the fluorine linkages this is the reason for the enhanced binding energy values. An increasing electronic distribution of Fe and a shift of the Fe 2p envelope peaks toward low binding energy were observed after the first discharge (709.8 eV), which provides evidence for the change in the valence state of Fe^{3+} to Fe^{2+} during the lithium insertion process.

The XPS narrow scans of F 1s and O 1s were also carried out for Fe_2OF_4/C fresh and discharged cathode pellets. On the normalized XPS spectra of F 1s the peak at the binding energy 689.5 eV in spectra of fresh pellet (initial condition) corresponds to organic oxyfluoride or carbon fluoride species, which probably coming from PTFE binder used in pellet composition. This peak decreased gradually with the depth of the discharge, as was seen for the process of lithiation down to 1.5 V. The XPS peak of F 1s at a binding energy of 685.0 eV corresponds to inorganic fluoride bonding FeF_3/FeF_2. There may also be a contribution from a $LiPF_6$ coming from the electrolyte.

The normalized O 1s spectrum has a broad feature around 531.5 eV and a shoulder at 529.5 eV, both coming from the Fe_2OF_4 oxygen. This profile agrees with the O 1s spectra of the pure powder material, which does not undergo a reaction with organic electrolyte. Nevertheless, the O 1s spectra probably contain a band that originates from both organic and inorganic compounds due to the surface film formed during the discharge process. The XPS peak shift to a lower binding energy in response to reduction of the elements could be confirmed in Fe 2p and O 1s on discharge, while there was no significant change in peak position for F 1s.

4. Conclusion

Oxyfluoride material such as Fe_2OF_4 was successfully obtained by heat treatment of anhydrous iron fluoride under oxygen flow, and its potential for lithium intercalation was investigated. The Fe_2OF_4/C nanocomposite shows reversibility over repeated cycling and excellent overall electrochemical properties upon reaction with lithium for the selected potential range, 1.5–4.5 V vs. Li/Li$^+$.

References

[1] M. Nishijima, I.D. Gocheva, T. Doi, S. Okada, J. Yamaki, T. Nishida, J. Power Sources 190 (2009) 558.
[2] F. Badway, F. Cosandey, N. Pereira, G.G. Amatucci, J. Electrochem. Soc. 150 (2003) A1318.
[3] M. Bevars, L.C. Klein, G.G. Amatucci, J. Electrochem. Soc. 153 (2006) A159.
[4] P. Hagenmuller, J. Portier, J. Cadiou, R. De Pape, Compt. Rend. 260 (1965) 4768.
[5] B.L. Chamberland, A.W. Sleight, Solid State Commun. 5 (1967) 765.
[6] B.L. Chamberland, A.W. Sleigh, W.H. Cloud, J. Solid State Chem. 2 (1970) 49.
[7] D.W. Murphy, M. Greenblatt, R.J. Cava, S.M. Zahurak, Solid State Ionics 5 (1981) 327.
[8] M.V. Reddy, S. Madhavi, G.V. Subba Rao, B.V.R. Chowdari, J. Power Sources 162 (2006) 1312.
[9] T.V. Ostrovskaya, S.A. Amirova, Russ. J. Inorg. Chem. 6 (1969) 1443.
[10] M. Hibino, J. Terashima, T. Yao, J. Electrochem. Soc. 154 (2007) A1107.
[11] K. Amine, H. Yasuda, M. Yamachi, J. Power Sources 81–82 (1999) 221.
[12] C. Benoit, C. Bourbon, P. Berthet, S. Franger, J. Phys. Chem. Solids 67 (2006) 1265.
[13] K. Kanamura, N. Imanishi, M. Fujiwara, Z. Takehara, J. Power Sources 26 (1989) 467.
[14] J.C. Carvet, G.K. Schweitzer, T.A. Carlson, J. Chem. Phys. 57 (1972) 973.
[15] M. Scrocco, Phys. Rev. B 23 (1981) 4381.
[16] S. Okada, T. Tonuma, Y. Uebo, J. Yamaki, J. Power Sources 119–121 (2003) 621.