



Short communication

Synthesis of FeOF using roll-quenching method and the cathode properties for lithium-ion battery

Ayuko Kitajou^a, Hideyuki Komatsu^b, Rintarou Nagano^c, Shigeto Okada^{d,*}^aResearch and Education Center of Carbon Resources, Kyushu University, 6-1 Kasuga-koen, Kasuga 816-8580, Japan^bGraduate School of Integrated Frontier Sciences, Kyushu University, 6-1 Kasuga-koen, Kasuga 816-8580, Japan^cInterdisciplinary Graduate School of Engineering Sciences, Kyushu University, 6-1 Kasuga-koen, Kasuga 816-8580, Japan^dInstitute for Materials Chemistry and Engineering, Kyushu University, 6-1 Kasuga-koen, Kasuga 816-8580, Japan

HIGHLIGHTS

- Rutile-type FeOF can be quickly synthesized in 1 min by the roll-quenching method.
- The obtained FeOF has exceedingly high energy density about 500 mAh g⁻¹.
- Although it is the conversion-type cathode, the cyclability was relatively good.

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ABSTRACT

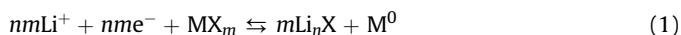
Rutile-type FeOF is a promising cathode for lithium-ion batteries, because it has a relatively large theoretical capacity of 885 mAh g⁻¹ in eco-friendly iron-based cathodes. Although it is difficult to synthesize by conventional solid-state synthesis methods, it can be quickly synthesized by the roll-quenching method. The quick synthesis method is suitable to reduce the produce cost, but also to avoid the fluorine gas release during synthesis procedure. The obtained FeOF by roll-quenching method has kept some crystallinities, and provides a large discharge capacity (900 mAh g⁻¹) between 0.7 and 4.0 V. The charge and discharge reaction mechanism was investigated by structural analyses.

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1. Introduction

The demands for Li-ion batteries have been increasing in recent years due to their wide application to electric power storage for electric vehicles and small electric devices. Li-ion batteries constitute the current state of the art in high-energy-density rechargeable energy storage cells. Further advances in energy density have been limited by the energy density of their cathodes. The insertion-type cathodes of commercially available Li-ion batteries generally consist of lithium 3d-transition metal oxides such as LiCoO₂, LiMn₂O₄, and LiFePO₄. In many cases, the voltage is relatively high, but the specific capacities are not so large, because they are limited to a 1Li insertion/extraction based on 1 steep redox reaction such as

Co³⁺/Co⁴⁺. On the other hand, the conversion-type electrodes can utilize all of the valence change between ionic and metallic state of cation of the electrode active material with breakdown of the initial crystal structure as follows;



where M = Fe, Co, Ni, Cu etc., and X = S²⁻, O²⁻, F⁻, etc.

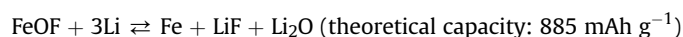
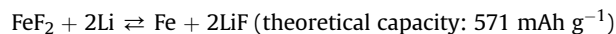
Reversible conversion reaction, which is denoted above have been demonstrated with metal sulfides [1,2], oxides [3], and finally fluorides [4–7]. Here, the idea to exploit metal fluorides as the conversion-type cathode arises from the ability to generate high voltage and large capacity. Both of these attributes come as a direct result of the large electro-negativity and small electrochemical equivalent of fluorine. In particular, FeF₃ cathode showed a larger discharge capacity for the insertion reaction of about 200 mAh g⁻¹ at approximately 3.3 V vs. Li metal with a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) dissolving with

* Corresponding author. Tel./fax: +81 92 583 7841.

E-mail addresses: s-okada@cm.kyushu-u.ac.jp, s-okada@mx3.canvas.ne.jp (S. Okada).

1 mol dm⁻³ LiPF₆, which corresponds to 99% of the theoretical specific capacity (238 mAh g⁻¹) based on the FeF₃ content [4]. Furthermore, the theoretical capacity of FeF₃ based on a complete 3 Li conversion reaction can be estimated with 712 mAh g⁻¹. Actually, FeF₃-based nanocomposites showed that a reversible specific capacity over 600 mAh g⁻¹ was realized at an average voltage of 2.2 V at 70 °C [5]. However, FeF₃-based nanocomposites using conversion reactions showed poor cyclability.

Moving from iron fluorides into iron oxyfluoride, one can expect improvement of the cyclability and conductivity by covalent M–O bonds introduced into the highly ionic fluoride structure. In addition, iron oxyfluoride, FeOF, has also been proposed as a new candidate with larger theoretical capacity than that of FeF₂ or FeF₃ as follows:



In order to investigate the impact of introducing oxygen into the fluoride structure on electrochemical performance, we tried to synthesize iron oxyfluoride compounds. F. J. Brink et al. has previously reported the solid-state synthesis at elevated temperatures (950 °C, 24 h) of FeO_xF_{2-x} solid solutions utilizing FeF₃ and Fe₂O₃ precursors [8]. Moreover, N. Pereira and co-authors [9] reported carbon-iron oxyfluoride nanocomposites (FeOF/C) synthesized using a solution process. The discharge capacity of FeOF/C was 430 mAh g⁻¹, which corresponded to 48.6% of the theoretical capacity based on the 3 Li reaction per FeOF (885 mAh g⁻¹). However, it is difficult to synthesize the uniform single phase by conventional solid-state or solution-process synthesis. In particular, in order to decrease the volatilization amount of fluorine in FeOF, it is necessary to shorten the synthesis duration at elevated temperature.

In this work, the roll-quenching method was tried for quick FeOF synthesis. In addition, to examine the cathode properties of the obtained FeOF, and to determine the discharge reaction mechanism between Li and FeOF, the *k* local structure and crystal structure changes during the discharge reaction were investigated by synchrotron-based X-ray absorption spectroscopy (XAS), X-ray diffraction (XRD) measurement and X-ray photoelectron spectroscopy (XPS).

2. Experimental

2.1. Synthesis and electrochemical properties of FeOF

FeOF was prepared from a stoichiometric mixture of FeF₃ (Soekawa Chemical Co., Ltd.) and Fe₂O₃ (Sigma–Aldrich) with a molar ratio of FeF₃:Fe₂O₃ = 2.33:1. The mixture was ground in an Ar-filled glove box and placed in a silica-covered Pt tube. The Pt and silica tubes have a small hole of 1 mm in diameter at the bottom for injecting the melted sample into a single copper roller. In the roll-quenching machine (Haradays Co., Ltd.), the powder sample was heated by the joule heat of the induction current in the Pt tube. After heating to over 1000 °C for 40 s, high-pressure Ar gas was injected into the melted mixture, which was quenched onto a single copper roller with rotation at 2000 rpm in an Ar atmosphere. Flake-like quenched samples were collected in the Ar chamber.

The 70 wt. % obtained FeOF powder was dry-ball-milled with 25 wt. % acetylene black (AB, Denki Kagaku Co., Ltd.) in Ar. Cathodes were prepared by mixing the FeOF/C composite powder with a 5 wt. % PVDF binder (Kureha Corp.) in *N*-methylpyrrolidinone. The slurry was coated on aluminum foil and dried at 80 °C until the solvent had evaporated completely. The electrochemical

performance of the FeOF was evaluated with a 2032 coin-type cell using a non-aqueous electrolyte (1 M LiPF₆/EC:DMC = 1:1 in volume, Kishida Chemical Co., Ltd.) and a polypropylene separator (Celgard 3501) against lithium metal (Honjo Metal Co., Ltd.). All the cells were assembled in an Ar-filled glove box. The charge–discharge measurement was performed in galvanostatic mode at a rate of 10 mA g⁻¹ (0.015 C:1 C rate corresponds to a current rate of 885 mA g⁻¹). The test temperature was 25 °C. The cathode pellets were carefully taken out from the cells in the Ar-filled glove box, washed, immersed in DMC for one night to remove the electrolyte. Then, they were dried prior to being set in Ar-filled transfer vessel for XPS. In the case of XRD and XAFS measurements, Ar-filled sample folders were used, respectively.

2.2. Physical characterization of FeOF

The characterizations of the obtained FeOF powder and pellets after the charge or discharge processes were carried out with an X-ray powder diffractometer (XRD, 50 kV and 300 mA, Cu-K α , Rigaku TTRIII). The XRD data for the pellet samples were taken under Ar atmosphere to avoid the oxidation of the bivalent iron in air. X-ray photoelectron spectroscopy (XPS) was carried out with JPS-9010 (JEOL Ltd.) using focused monochromatized Mg K α radiation (*h**v* = 1253.6 eV). X-ray absorption measurements of the iron K-edge using synchrotron radiation were carried out at room temperature at beam line BL11 of Saga Light Source using a double Si(1 1 1) monochromator. The X-ray adsorption near edge structure (XANES) and the X-ray absorption fine structure (EXAFS) were measured. The thickness of the cathodes allowed the transmission mode measurements (Fe K-edge). The composition of the obtained FeOF was determined using an atomic adsorption spectrophotometer (AAS, Hitachi Z-2300) and Ion Chromatography (IC, TOSHO IC-2001), following the powder dissolving in the mixture of 30 wt% H₂O₂ and conc. HCl.

3. Results and discussion

3.1. Characterization of obtained FeOF

The crystal structure of the obtained FeOF was characterized with XRD, as shown in Fig. 1. The obtained FeOF by roll-quench method has higher crystallinity than that by ion exchanged and liquid-state [9]. The determined composition by AAS and IC was FeO_{1.1±1}F_{0.97}. The few deficiency of fluorine was caused by the stronger volatility of the fluorine than oxygen. It was able to be indexed as a tetragonal structure with space group *P4*₂/*mnm*, and a small amount of the starting material, FeF₃, remained as an impurity. While the lattice constants of ICDD No. 018-0648 were *a* = *b* = 4.65 Å and *c* = 3.05 Å, those of the obtained FeOF were *a* = *b* = 4.67 Å and *c* = 3.10 Å. It suggests that the axis of the obtained FeOF was extended beyond that of the reported axis of FeOF by rapidly cooling from 1000 °C to room temperature.

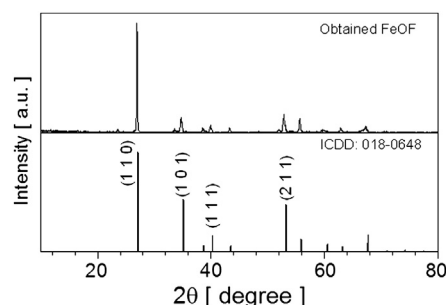


Fig. 1. X-Ray diffraction patterns for obtained FeOF.

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