

Direct synthesis of Cryolite type Li_3FeF_6 and its characterization as positive electrode in Li cell

Irina D. GOCHEVA^{*1,†}, Yuichi KAMIMURA^{*1}, Takayuki DOI^{*2}

Shigeto OKADA^{*2}, Jun-ichi YAMAKI^{*2} and Tetsuaki NISHIDA^{*3}

[†]E-mail of corresponding author: *gocheva4@asem.kyushu-u.ac.jp*

(Received April 30, 2009)

We have synthesized a Cryolite type iron hexafluoroferrates by mild chemistry complex formation reaction. For the first time their electrochemical properties as positive electrode materials in rechargeable batteries were studied. The α - Li_3FeF_6 delivered a 116 mAh/g reversible capacity at an average discharge voltage of 3.0 V maintaining good capacity retention of about 30 cycles at a 0.2 mA/cm² rate. The preliminary results are reported.

Key words: *metal fluoride cathodes, Cryolite, lithium cell*

1. Introduction

Lithium ion batteries have been intensively used in various kinds of portable electronics. They are also considered as important energy storage devices for future hybrid electric vehicles. Numerous materials as transitions metal oxides, sulphides, nitrides were found capable of reversible lithium ions insertion and have been investigated during the past years. Shifting the study from oxides and nitrides to

highly ionic fluorides will provide potentials high enough for use as positive electrode (Fig.1).

Therefore, in search for new materials with large capacities and higher intercalation voltages, the fluoride compounds become challenging. This class of materials, utilizing FeF_3 as an example, was shown to exhibit good reversible behavior of approximately 200 mAh/g in the 3 V region^{1, 2)}. Reversible conversion processes have been previously reported with metal oxides^{3, 4)} and metal nitrides⁵⁾.

Nevertheless, the relatively low conversion potentials were only suitable for use as negative electrode materials. The increased operating potentials of the fluoride based compounds simultaneously with ability to utilize all of the metal redox potentials make them suitable for positive electrode materials in rechargeable batteries⁶⁾. Therefore as pure ionic compounds fluorides have numerous advantages but because of their insulators character so far they were neglected as perspective electrode materials.

On the other hand, many obstacles are associated with synthesis of pure fluorides. The fluorine substances in particular attacks the surface of the vessels in which they are contained, they are insoluble in the usual solvents or tend easy to decompose by moisture when exposed in ambient atmosphere⁷⁾. The compounds reported as positive electrode materials are fluorophosphates as $\text{Li}_2\text{CoPO}_4\text{F}$

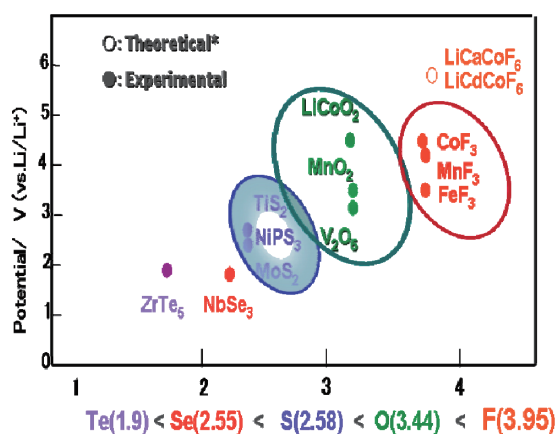


Fig.1. Order of electronegativity of the anion.

*1 Department of Applied Science for Energy and Materials.

*2 Institute for Materials Chemistry and Engineering.

*3 School of Humanitary -Oriented Science and Engineering, Kinki University.

⁸⁾, LiFePO_4F ⁹⁾, LiVPO_4F ⁹⁾, $\text{Li}_5\text{V}(\text{PO}_4)_2\text{F}_2$ ¹⁰⁾ and NaVPO_4F ¹¹⁾, $\text{Na}_2\text{FePO}_4\text{F}$ ¹²⁾ and $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$ ¹³⁾. Indeed, replacement of $[\text{PO}_4]^{3-}$ with $[\text{PO}_4\text{F}]^{4-}$ allows a new family of host lattice structures because it alters the charge balance of the corresponding phosphate. But the large polyanionic groups restrict theoretical capacity.

The hexafluorometalates has never been studied as possible candidates for positive electrode materials. In fact with exception of Koyama's predictive calculation of about 5.80 V discharge voltage for trirutile type LiCaCoF_6 ¹⁴⁾ there are no experimental neither theoretical studies on pure fluoride based compounds as electrode material reported. We have already described electrochemical properties of some purely fluoride-based compounds of perovskite type and their possible use for positive electrodes in Na rechargeable batteries ¹⁵⁾ and for the first time we discussed the electrochemical properties of Trirutile type Li_2TiF_6 ¹⁶⁾. In attempt to find new fluoride based materials suitable for reversible insertion and deinsertion of Li, we focused our research on hexafluorometalate complexes with Cryolite structure.

2. Experimental

2.1 Preparation

A novel route was adopted to synthesize functional hexafluorometalate complexes. For the first time Li_3FeF_6 was obtained directly by reaction of lithium carbonate (99,0%, WACO) with iron (III) chloride (99,0%, WACO) in aqueous hydrofluoric acid by means of complex-formation reaction process at low temperatures. The moist iron (III) chloride and LiF were placed in a PTFE beaker to which 46% hydrofluoric acid was added drop wise with stirring to obtain a clear solution. Light yellowish precipitate of Li_3FeF_6 was obtained by addition of ethanol. The compound was filtered washed with ethanol, and finally dried in at 80°C.

2.2 Characterization

The reaction products were estimated by XRD powder diffraction (Rigaku RINT2100HLR/PC) using $\text{Cu K}\alpha$ radiation from $2\theta = 10^\circ - 80^\circ$ at 2.0°/s scan rate. Morphology of the samples was observed by FE-SEM (JEOL JSM-340F). Thermal stability of obtained materials were investigated by

TG-DSC (Rigaku Thermo Plus TG8210), with heating rate of 5 °C min^{-1} up to 700 °C in an Ar atmosphere. Mössbauer spectroscopy was applied to consider iron oxidation state. A constant acceleration method was performed using the Mössbauer spectrometer (Laboratory Equipment Corp.). As the Mössbauer source and the reference for the isomer shift we used 370 MBq of ^{57}Co (Pd) and $\alpha\text{-Fe}$ foil enriched with ^{57}Fe . Chemical analysis has been accomplished by Atomic Absorption Spectrometer (Hitachi Z-2300), for evaluating element composition of the obtained Cryolite type hexafluoroferrates.

Electrochemical evaluation of the synthesized materials was examined in a coin-type cell 2032 with Li metal as the negative electrode in $\text{LiClO}_4/\text{EC}:\text{DMC}$ as electrolyte composition with polypropylene separator Celgard 3501. The positive electrodes with loadings approximately 30mg were composed of 70wt% active material, 25wt% acetylene black and 5wt% PTFE as binder. Electrode diameter of 10 mm was used throughout. Cycling tests were performed using an automatic galvanostatic charge-discharge unit (Nagano BTS-2004) at various current 2.0-4.5V for lithium cells at ambient temperature of 25 °C.

3. Results and discussion

Numerous compounds with the general chemical formula $\text{A}_3\text{M}^{3+}\text{F}_6$ ($\text{M}=\text{V}, \text{Ti}, \text{Fe}, \text{Mn}, \text{Co}, \text{Ni}$) and with tolerance factor $0.8 < t < 1$ are

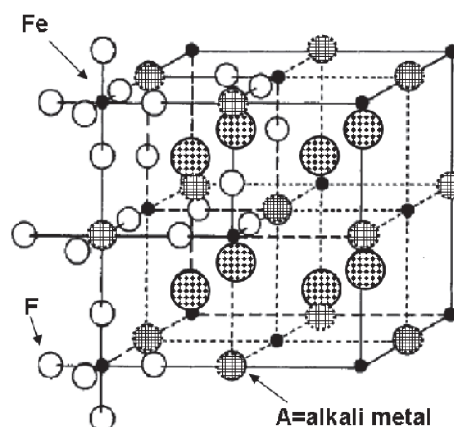


Fig.2. Arrangement of the octahedral $(\text{FeF}_6)^{3-}$ in structure of A_3FeF_6 .

known to crystallize in the cubic structure $Fm\bar{3}m$ called Elpasolite-Cryolite (ordered Perovskite). The atomic arrangement in

Cryolite structure is characterized by an open framework of MF_6 octahedra which lie at the corners and face centers of a nearly cubic lattice (Fig.2).

It is known that at elevated temperatures, such a structure undergoes a phase change to from usual monoclinic to cubic. The compositions corresponding to the formula A_3MF_6 are especially rich in polymorphism

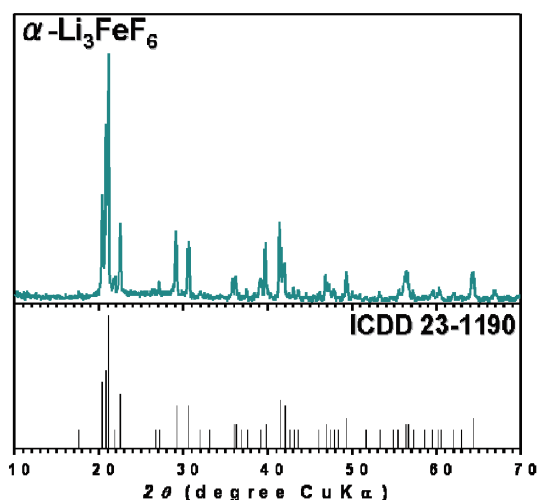


Fig.3. XRD pattern of $\alpha\text{-Li}_3\text{FeF}_6$ obtained by mild complex-formation.

when $\text{A} = \text{Li}^+$. However, the structures of most of the Li_3MF_6 polymorphs have not yet been clarified. We succeed in obtaining the $\alpha\text{-Li}_3\text{FeF}_6$ from two known polymorph forms for lithium hexafluoroferrate but because of absence of the isotypic phase for the $\alpha\text{-Li}_3\text{FeF}_6$ the space group cannot be identified. The XRD pattern of the powdered sample is shown in Fig.3.

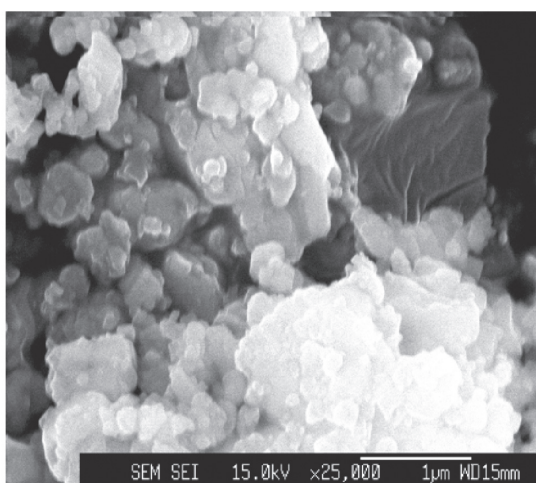


Fig.4. Fe-SEM image of Li_3FeF_6 obtained after precipitation with 20 cm^3 ethyl alcohol.

The Fe-SEM images show the morphology of Li_3FeF_6 powder obtained by the complex-formation reaction (Fig.4). The sample was gained after precipitation with different amount of ethyl alcohol from 20 cm^3 to 100 cm^3 . Actually the solvent influences crystal growth through its effect on diffusivity, viscosity and molecular density. Therefore, the morphology of the resulting crystalline particles can be significantly affected by the chemistry of the ethanol used. Also, the size of A_3FeF_6 particles could be controlled by modifying the nucleation/growth parameters through fine tuning of the precipitation conditions varying the volume ratio of water to ethyl alcohol and reaction temperatures for our future experiments.

Assuming that the samples are a single phases with a homogeneous Li distribution, the atomic absorption analysis gives a Li content corresponding to the formula Li_xFeF_6 ($2.6 < x < 3.2$) based on Li/Fe ratio. We found that by new method of synthesis tuning of lithium content to $[\text{FeF}_6]^{3-}$ ligand to with dependence of its coordination number is possible.

To check the importance of such defect chemistry on the electrochemical performance,

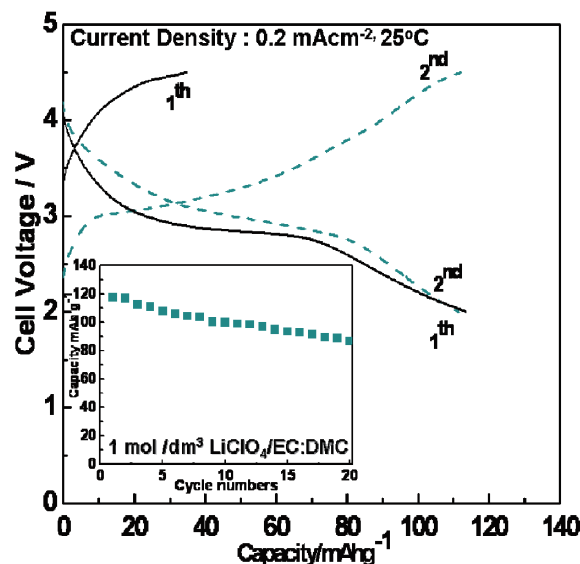


Fig.5. First and second charge-discharge curves of $\text{Li}_3\text{FeF}_6/\text{C}$ vs. Li/Li^+ in $\text{LiClO}_4/\text{EC}:\text{DMC}$ (1:1 in volume) with a current density of 0.2 mAcm^{-2} for the potential range $2.0\text{ V} - 4.5\text{ V}$ and cycleability given in inset.

Li-half cells were assembled. The charge/discharge curves for first and second cycle are shown in Fig.5. The theoretical capacity for single electron reaction of $\alpha\text{-Li}_3\text{FeF}_6$ is 140.5

mAh/g. The material delivered 116 mAh/g reversible capacity at an average discharge voltage of 2.8 V while maintaining capacity retention of about 20 cycles.

The insertion/ deinsertion process could be related to mobile lithium which introduces the Cryolite structure interstitially. In addition, the first short charge is due, as well to mixed valence of iron which consists in the structure. This is attributed to the developed method of synthesis while some impurities could be expected. Preposition for such a hypothesis comes from Mössbauer spectra of fully charged and consequently discharged material (Fig.6). In a fully charged state 100% Fe (III) with IS= 0.41 ± 0.01 mm/s and QS= 0.38 ± 0.02 mm/s was registered. On the discharged state the process is also partially complete and leads again to iron content with mixed valance of Fe^{3+} and Fe^{2+} .

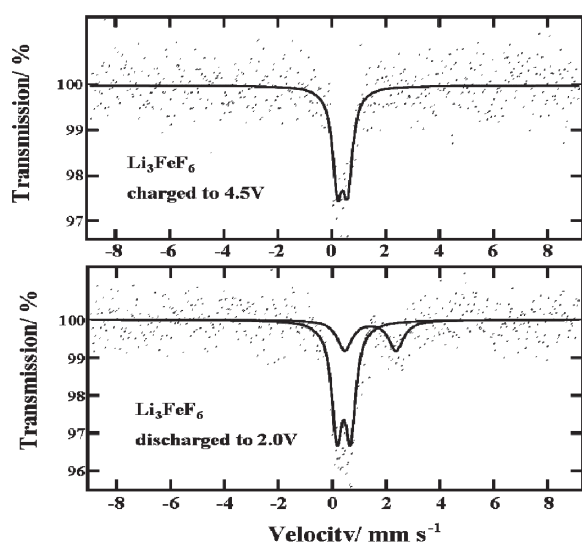


Fig.6. The ^{57}Fe Mössbauer spectra of the fully charged (a) and fully discharged Li_3FeF_6 .

As it shown on the ex situ X-ray diffractograms (Fig.7) for the pellet cathodes taken after stages of charge and discharge the basic Cryolite structure of Li_3FeF_6 sustained lithium insertion and deinsertion process for the whole voltage region of measurements without undergoing site reactions with electrolyte. Unfortunately, hitherto we cannot present the data which could suppose structure changes in Cryolite structure as it is the usual expected for such kind of compounds.

Though a structure change was not found during the electrochemical process in the coin cell, we studied the thermal stability of the

Cryolite type Li_3FeF_6 during heating in Ar atmosphere. From TG-DSC measurement no significant weight loss has been detected as well no endo- or exothermic peaks were

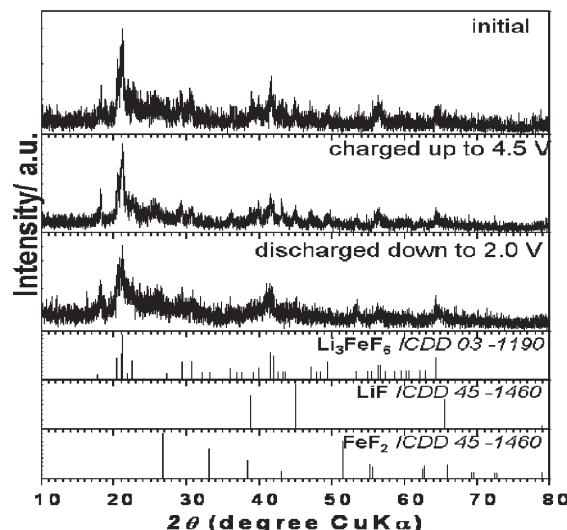


Fig.7. Ex-situ XRD patterns of Li_3FeF_6 in different stages of charge and discharge.

observed. Therefore X-ray powder diffraction was used to study changes in composition of Li_3FeF_6 with dependence of temperature. The samples were heated at elevated temperatures with dwelling for 2h after which a diffraction analysis was applied.

In Fig. 8 the results of this investigation are presented. The graph showed that material under study exhibits practical thermal

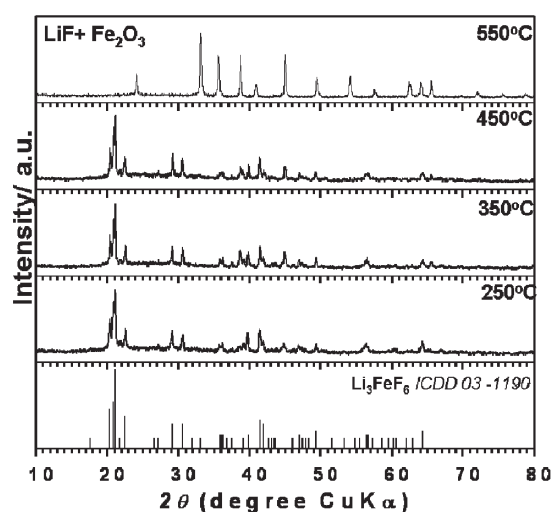


Fig.8. XRD pattern of variations in the chemical composition of Li_3FeF_6 with dependence of the temperature when heated in Ar.

stability up to 450 °C without undergoing

structure changes. At temperatures over 450 °C the chemical composition changed drastically due to decomposition of hexafluoroferrate to LiF and Fe₂O₃.

4. Summary and Conclusion

This is the first report of synthesis for lithium hexafluoroferrate by means of wet chemistry. Under mild reaction condition the homogeneous pure phase of α -Li₃FeF₆ has been achieved and has been tested as possible positive electrode in Li-cell. Obtained nonstoichiometric compositions allowed electrochemical performance for this material. In voltage range of 2.0V to 4.5V lithium hexafluoroferrate delivered about 116 mAh/g reversible capacity at an average discharge potential of 2.8 V. We showed that Cryolite structure exhibit electrochemical properties under certain conditions. Based on this preliminary result the investigation should be moved to other promising materials of the same family as orthorhombic Li₃TiF₆, Li₃MnF₆, Li₃VF₆ and Li₃CoF₆.

Acknowledgments

The present work was financially supported by the Li-EAD project of the New Energy and Industrial Technology Development Organization, Japan.

References

- 1) M. Nishijima et al., *J. Power Sources*, **190**, (2009) 558.
- 2) F. Badway, et al., *J. Electrochem. Soc.*, **150**, (2003) A1209.
- 3) Y. Idota et al., *Science*, **276**, (1997) 1395.
- 4) P. Poizot et al., *Nature*, **407**, (2000) 496.
- 5) N. Pereira et al., *J. Electrochem. Soc.*, **149**, (2002) A262.
- 6) F. Badway et al., *J. Electrochem. Soc.*, **150**, (2003) A1318.
- 7) G. Brenner et al., *Journal of Fluorine Chemistry*, **46**, (1990) 283.
- 8) S. Okada et al., *J. Power Sources*, **146**, (2005) 565.
- 9) J. Barker et al., *J. of Electrochem Soc.*, **152**, (2005) A1776.
- 10) S.-C. Yin et al., *Chem. Mater.*, **18**, (2006), 1745.
- 11) J. Barker et al., *J. of Electrochem. Soc.*, **151**, (2004) A1670.
- 12) B. L. Ellis et al., *Nature Materials*, **6**, (2007) 749.
- 13) R. K. B. Gover et al., *Solid State Ionics*, **177**, (2006), 1497.
- 14) Y. Koyama et al., *J. Electrochem. Soc.*, **147**, (10), (2000) 3633.
- 15) I. D. Gocheva et al., *J. Power Sources*, **187**, (2009) 247.
- 16) I. D. Gocheva et al., *J. Power Sources*, submitted