Synthesis of FeF₃ fluoride electrode material using polytetrafluoroethylene

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A fluoride electrode material for lithium-ion batteries, FeF₃, was synthesized by a novel solid-state reaction method using polytetrafluoroethylene (PTFE) as a fluoride source instead of HF. FeF₃ was obtained as the main phase according to the XRD patterns of the samples prepared in the present study. Furthermore, the synthesized FeF₃ particles were nanosize. The initial discharge and charge capacities of the FeF₃ sample were 387 and 293 mAh g⁻¹, respectively, in the 4.5–1.0 V region.

Key-words : Lithium-ion battery, Fluoride electrode materials, Polytetrafluoroethylene

1. Introduction

Recently, perovskite-type transition metal fluorides, MF₃ (M = Ti, V, Mn, Fe), have attracted attention due to their potential application as next generation high-voltage and large-capacity electrode materials in lithium-ion batteries, because they have high electronegativity in comparison with sulfide and oxide cathodes.¹⁻⁹ In particular, the theoretical specific capacity of FeF₃ (237 mAh/g) is higher than that of conventional olivine-type phosphate LiFePO₄ (170 mAh/g), which is considered as the most promising rare-metal free cathode in Li-ion batteries for electric vehicles.¹⁰,¹¹ In this study, in contrast, we successfully synthesized the perovskite-type transition metal fluoride electrode material FeF₃ using PTFE as the fluoride source and the properties of the synthesized material were investigated.

2. Experimental

\[ \gamma-Fe_2O_3 \] (C. I. Kasei, particle size 20–30 nm) and polytetrafluoroethylene (PTFE; Aldrich) were mixed using a mortar. When PTFE is heated in a flow of air, its monomer, C₂F₄, is oxidized to carbon and oxygen gas. The homogenous mixture of the sample powder was characterized by a powder X-ray diffractometer (XRD) using a Cu Kα radiation. The microstructure of the sample powder was examined by a transmission electron microscope (TEM).

The cathodes used for electrochemical characterization were fabricated by blending the prepared active material powders with acetylene black and PTFE binder in a weight ratio of 70:25:5. Two-electrode electrochemical cells consisting of lithium metal foil as the negative electrode, a polypropylene separator, and an electrolyte of 1 M LiClO₄ in propylene carbonate/dimethyl carbonate (1:1 by volume) were assembled in an argon-filled glove box. The electrochemical tests of the cells were performed using an automatic galvanostatic charge and discharge unit (Hokutodenko, HJ-101M6) in the 4.5–2.0 and 4.5–1.0 V regions using PTFE as the fluoride source. A fluoride synthesis technique using PTFE or polyvinylidene fluoride (PVDF) as a fluoride source has already been reported in the superconductor research field; however, no one has yet succeed in synthesizing complete fluorides.¹²⁻¹⁵ In this study, therefore, we developed a novel synthesis technique using PTFE or polyvinylidene fluoride (PVDF) as a fluoride source.

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3. Results and discussion

Figure 1 shows the XRD patterns of the FeF$_3$ as a weight ratio of [γ-Fe$_2$O$_3$]:[PTFE] = 22:78 synthesized for 1 min under 400, 500, and 600°C. The standard XRD pattern of FeF$_3$ from the inorganic crystal structure database (ICSD) is also shown in Fig. 1 as a reference. The sample synthesized at 400°C was observed the mixed phase of γ-Fe$_2$O$_3$ and PTFE, which are raw materials, while no diffraction peaks evident of FeF$_3$ phase are present in the XRD patterns. On the other hand, the diffraction peaks corresponding to FeF$_3$ observed as a main phase in the sample synthesized at 500 and 600°C, although a weak impurities corresponding to FeF$_2$ and α-Fe$_2$O$_3$. However, the peak intensity of FeF$_3$ was decreased with the increase in the calcination temperature. This can be attributed to the decomposition temperature of PTFE. Figure 2 shows the thermal analysis result for PTFE, in which a drastic weight loss leading to the decomposition of PTFE was confirmed over 400°C and PTFE is completely decomposed at 600°C.

In addition, the production of FeF$_3$ is also strongly dependent on the calcination time in this method using PTFE (Fig. 3). The diffraction peak intensity evident of α-Fe$_2$O$_3$ was increased with the increases in the calcination time and a single phase of the α-Fe$_2$O$_3$ was observed in the sample calcined at 500°C for 3 h, which is considered to be due to the oxidation from FeF$_3$ to α-Fe$_2$O$_3$.

Figure 4 shows the XRD patterns of the sample synthesized at 500°C for 1 min as a function of different weight ratio of [Fe$_2$O$_3$]:[PTFE]. It is obvious that the optimum weight ratio of [Fe$_2$O$_3$]:[PTFE] for synthesis of FeF$_3$ as a single phase is 22:78. When the amount of PTFE is insufficient, the α-Fe$_2$O$_3$ phase was observed as an impurity phase due to the phase transition from unreacted γ-Fe$_2$O$_3$. In contrast, PTFE was observed in the sample with an excess amount of PTFE. These results indicate that the optimum conditions of synthesis of a single phase FeF$_3$ using PTFE as a fluorine source are flowing that; i) weight ratio of [Fe$_2$O$_3$]:[PTFE] is 22:78, ii) calcination temperature and time is 500°C and 1 min. However, the calcination time is very short to evaporate the carbon of PTFE in the sample, as a resulted, the FeF$_2$ phase was observed in the sample synthesized at 500°C for 1 min as an impurity phase.

Figure 5 shows a TEM image of the synthesized FeF$_3$. It is at a current density of 0.1 C rate.
obvious that the obtained FeF$_3$ sample has granular particle morphology and a particle size of 20–100 nm, characteristics that are similar to those of the Fe$_2$O$_3$ starting raw material. This result suggests that the particle growth of FeF$_3$ was effectively suppressed by using PTFE as the fluorine source due to the low decomposition temperature and high activation rate, which led to the short reaction time and low reaction temperature for synthesis of the FeF$_3$ sample. Figure 6 shows the charge and discharge curves of the intercalation reaction in the 4.5–2.0 V region of the synthesized FeF$_3$. The initial discharge and charge capacity of the obtained FeF$_3$ was 32 and 138 mAh/g, respectively. The reversible capacity of the charge and discharge also decreased with increasing cycle number, and at the 5th cycle, the reversible capacity was approximately 320 mAh/g. In addition, the plateau of the conversion reaction was confirmed in the 2.0–1.0 V region in the discharge curves. It is well known that the charge and discharge capacity of normal perovskite-type transition metal fluoride (MF$_3$) electrode materials is extremely deteriorated by the conversion reaction. However, in the FeF$_3$ obtained in this study, this extreme deterioration was not confirmed. This could be explained by the suppression of the particle growth by using PTFE as the fluorine source. As a result, the synthesized FeF$_3$ had nanosized particles, which are well known as a suitable particle size for conversion reactions with high capacity. These results indicate that the FeF$_3$ obtained in this study could be used as a suitable particle size for conversion reactions with high capacity. In addition, improvement of the capacity is expected by optimization of the preparation process in order to synthesize single phase FeF$_3$. This optimization could be accomplished using techniques such as flux treatment or after annealing treatment; the obtained samples mixed with a small amount of PTFE and heat again at 500°C for 1 min to remove the carbon in the obtained FeF$_3$ sample and to oxidize from Fe$^{2+}$ (FeF$_3$) to Fe$^{3+}$ (FeF$_3$).

4. Conclusion

A perovskite-type transition metal fluoride electrode material, FeF$_3$, was synthesized by new synthesis technique using polytetrafluoroethylene (PTFE) as a fluorine source. The fluoride electrode material obtained in the present study was successfully synthesized for the first time as a complete metal fluoride without hydrofluoric acid or hydrogen fluoride gas. Using PTFE as a fluorine source was significantly effective for suppressing the particle growth and for obtaining high capacity in the intercalation and conversion reactions.

References

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