Synthesis of Na$_2$FePO$_4$F using polytetrafluoroethylene

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Polytetrafluoroethylene (PTFE), composed of fluorine and carbon atoms, has a potential to produce carbon-coated fluorides in the calcination of inorganic compounds. We synthesized high voltage cathode material for Na ion secondary battery, Na$_2$FePO$_4$F, using PTFE as the carbon-coating and fluorine source. The Na$_2$FePO$_4$F carbon-coated by a thermal decomposition of PTFE showed high discharge capacity (64.4 mAh g$^{-1}$) at the first cycle of galvanostatic cycling by the improvement of conductivity.

Key-words : Fluoride electrode materials, Polytetrafluoroethylene, Na-ion battery, Na$_2$FePO$_4$F

1. Introduction

Na ion batteries (NIBs), using earth abundant and inexpensive sodium, are expected to be next-generation batteries for large-scale electric power storage devices and electric vehicles.$^{1-11}$ Phosphate cathode materials such as Na$_3$V$_2$(PO$_4$)$_3$, have been paid much attention because of high stability, safety, and suitable operating voltages. High operating voltage of phosphate cathode is due the inductive effect of the poly-anion, which enhances the ionicity of bonds between oxygen and transition metal atoms by strong covalent bonds of phosphorus and oxygen atoms.$^{12,13,14}$ For the next generation of the secondary battery, the high operating voltage is crucial to generating high energy density as well as high discharge capacity. Fluorinated phosphate Na$_2$FePO$_4$F, the theoretical capacity is 124 mAh g$^{-1}$, and the redox potential is 2.9 and 3.1 V.$^{6,9,10}$ The inductive effect of the PO$_4^{3–}$ groups and the high electronegativity of the F$^–$ anion, fluorophosphates are considered to be promising high potential cathode materials for the NIBs.$^{6–11,17–21}$ However, poor electronic conductivities of poly-anion type materials are a problem to be solved.$^{7,8}$ Surface carbon-coating is a promising way to solve this problem. For example, the synthesis of carbon-coated cathode material through calcination with pyrolyzed polystyrene, was reported as a low cost process.$^5$ The surface conductive carbon layers improve the conductivity$^{12}$ and suppress the growth of phosphates or fluorophosphates p articles. The reduction in the particle size causes improvement of the electrochemical property attributed to the shortening of Na or Li-ion diffusion-pass.$^{1–3,12}$ Besides, commonly used hydrofluoric acid (HF) for the synthesis of fluorides presents high acidity and corrosivity.$^{21,22}$ The HF is hard to handle at the ordinary condition, because the HF exists as liquids or gases. Therefore, to ensure safety, a new approach to the synthesis of fluorides is required.

In our previous study, we successfully synthesized high charge–discharge capacity perovskite-type cathode FeF$_3$ using polytetrafluoroethylene (PTFE) as a carbon and fluorine source.$^{23}$ In the past, the PTFE has been used as the fluorine source in the partial fluorination of the cuprate high-temperature superconductor.$^{23}$ The PTFE consists of carbon and fluorine atoms is chemically stable$^{22–24}$ and decomposed between 400 and 600°C.$^{22}$ This pyrolysis gas realizes dense the carbon-coating and fluoridation of FeF$_3$ simultaneously through calcination. In this study, the fluorophosphates Na$_2$FePO$_4$F was synthesized by similar vapor method using the decomposition of PTFE. For comparison of the effect on carbon-coating of Na$_2$FePO$_4$F, we synthesized Na$_3$FePO$_4$F without carbon-coating using NaF as a fluoridation source.

2. Experimental

2.1 Synthesis of the Na$_2$FePO$_4$F using PTFE as a fluorine source

The carbon-coated Na$_2$FePO$_4$F (NFPF/C) was prepared by a hybrid method of solid-state reaction and vapor phase reaction with a PTFE as a fluorine source. The
stoichiometric amount of NaHCO₃ (Wako Pure Chemical Industries, Ltd. 99.5%), FeC₂O₄·2H₂O (Kanto Chemical Industries, Ltd. 98.5%) and NH₄H₂PO₄ (Kanto Chemical Industries, Ltd. 99.0%) were used as the starting materials. These materials were mechanically mixed with toluene as a solvent using a ball-milling apparatus for 2 h. The homogeneous mixture was pre-heated in a tubular furnace at 300°C for 2 h in a flow of nitrogen gas (100 ml/min). Then, equal amount of the pre-heated powder and PTFE powder (Sigma-Aldrich, particle size 1 μm) were set in an alumina boat. The boat was placed in the center of a tubular furnace to be set PTFE powder in upstream of nitrogen gas (100 ml/min). Pre-heated in a tubular furnace at 650°C for 10 h in a flow of nitrogen gas (100 ml/min).

2.2 Synthesis of the Na₂FePO₄F using NaF as a fluorine source

Na₂FePO₄F without a carbon source (NFPF), using NaF as a fluorine source, was prepared by a solid-state reaction method as a reference sample.⁷,⁸ The stoichiometric amount of NaHCO₃ (Wako Pure Chemical Industries, Ltd. 99.5%), NaF (Kanto Chemical Co., Inc. 99.0%), FeC₂O₄·2H₂O (Kanto Chemical Industries, Ltd. 98.5%) and NH₄H₂PO₄ (Kanto Chemical Industries, Ltd. 99.0%) were used for the starting materials. These materials were mechanically mixed with toluene as a solvent using a ball-milling apparatus for 2 h. The homogeneous mixture was pre-heated in a tubular furnace at 300°C for 2 h in a flow of nitrogen gas (100 ml/min). Then, the pre-heated powder was calcined in a tubular furnace at 650°C for 10 h in a flow of nitrogen gas (100 ml/min).

2.3 Cell preparation

85 wt% NFPF/C or NFPF, 8 wt% acetylene black (Denka) and 7 wt% polyvinylidene fluoride (Kureha Co.) were mixed using a planetary centrifugal mixer, adding N-methyl-2-pyrrolidone (Kanto Chemical Co., Inc.) for viscosity modification. The obtained slurry was coated on an aluminum foil and then dried at 75°C for 40 min in vacuum. The solvent-eliminated electrodes were pressed and dried under at 130°C for 5.5 h in vacuum. Two electrode cells were assembled in an argon-filled glove box using a sodium metal (Kanto Chemical Co., Inc.) as an anode, a polypropylene separator and 1M NaPF₆ in propylene carbonate (Kishida Chemical Co., Ltd.) as an electrolyte.

2.4 Characterization

The crystal structure of the samples was identified by X-ray powder diffraction (XRD) using a Cu Kα radiation with a Ma-X-Labo (Mac Science Ltd.). The microstructure of the sample was observed by a field-emission transmission electron microscope (FE-TEM) with a JEM 2100F (JEOL). The Raman spectrum in the range of 300–1800 cm⁻¹ was measured using a 532 nm laser as an excitation source with a JOBIN YVON Lab RAM HR (Horiba Ltd.). Galvanostatic cycling was performed using a PFX2011S charge-discharge unit (Kikusui Electronics Co.) at 30°C in the voltage of 1.0–4.0 V and at a current density of 0.1 C. The elemental analysis of NFPF/C were performed using Electron Probe Micro Analyzer (EPMA) EPMA-1610 (Shimadzu) without a carbon coating. The particle size of the samples was observed by a scanning electron microscopy (SEM) with a JSM-5310MVB (JEOL). The powder were coated by an Au sputtering as a preprocessing to prevent a static charge of sample. To determine the carbon content, NFPF/C was dissolved in a dilute 4M HCl (Kanto Chemical Co., Inc.), following the suction filtration of the solution. Although the Na, Fe, P, O and F components were dissolved in HCl, the carbon component was not dissolved in HCl. The obtained residue was dried in vacuum at room temperature and weighed.⁷,⁸

3. Results and discussion

The XRD patterns of (a) NFPF/C and (b) NFPF and the reference pattern of Na₂FePO₄F from ICSD are shown in Fig. 2. Trace amount of impurity phases corresponding to NaFePO₄ and NaF in the NFPF/C, and unknown phase in NFPF were observed from their XRD profiles. However, main products of synthesized both NFPF/C and NFPF were Na₂FePO₄F. Interesting behavior of the novel PTFE synthesis method for the NFPF/C is carbon-coating and fluoridation of Na₂FePO₄F via generated pyrolysis gas of PTFE during calcination, as shown in the schematic diagram of Fig. 1. The XRD profile of NFPF/C clearly shows that the vapor phase PTFE can act as a fluorine
source of Na$_2$FePO$_4$F in a hybrid method of solid-state reaction and vapor phase reaction. To compare the novel hybrid reaction and the conventional solid-state reaction using the PTFE for the Na$_2$FePO$_4$F, all raw materials, NaHCO$_3$, FeC$_2$O$_4$·2H$_2$O, NH$_4$H$_2$PO$_4$ and PTFE were mixed and then calcined at 650°C for 10 h in a flow of nitrogen gas (100 ml/min). Fluoride, NaFeF$_3$ was obtained as a main phase by the conventional solid state reaction, because the ability of fluorination by the PTFE was too strong for the oxide raw material. This maybe due to strong reduction ability for the oxide by the carbon component produced in the initial stage. Since the reactivity of PTFE derived gas phase can be controlled by the flow rate or concentration, the hybrid method using pyrolysis gas of PTFE is suitable for the synthesis of oxyfluoride Na$_2$FePO$_4$F.

As shown in the SEM observation (Fig. 3), the particle size of NFPF/C and NFPP were 0.2–0.5 and 1.0–3.0 μm, respectively. In the solid-state reaction, low melting temperature NaF can act as flux. The NFPF/C particles were smaller than the NFPP particles, because the synthesis using PTFE suppressed the particle growth by a dilute vapor phase reaction. The number of contact between the particles in the vapor phase reaction is smaller than that of the solid-state reaction. Additionally, the carbon layer on the particle was also suppressed the particle growth. The phosphate or fluorophosphate cathodes with low conductivity are preferable to be nano-sized particles, leading to a shorter diffusion-pass of Na ions or Li ions. The result of EPMA measurement of NFPF/C is shown in Table 1. Existence of fluorine component in the sample show that the gas phase of PTFE can worked as a fluorine source for the fluorophosphate cathode. Quantitative and qualitative analysis of carbon using this measurement is difficult because the used mounting stages are made of graphite. As shown in Fig. 4, the Raman spectra of NFPF/C revealed that two broad peaks at 1350 and 1590 cm$^{-1}$ and four peaks at 420, 567, 938 and 1017 cm$^{-1}$ were observed in the both spectra, respectively. The observed peaks at 1350 and 1590 cm$^{-1}$ were assigned to sp$^3$-hybridized and sp$^2$-hybridized carbon, respectively, and peaks at 420, 567, 938 and 1017 cm$^{-1}$ are assigned to various vibration mode from $v_1$ to $v_4$ of PO$_4^{3-}$ unit. The observed vibration peaks of PO$_4^{3-}$ unit in spectrum of NFPF/C were smaller than that of NFPP. This result shows that the particle surfaces of NFPF/C were covered with carbons derived from the PTFE.

In the TEM observation of Fig. 5(a), the particle size of NFPF/C is about 200–500 nm. This result shows the particle size of NFPF/C coincides with the value of the particle size observed SEM image [Fig. 3(a)]. Fig. 5(b), thin carbon layer, the thickness about 10 nm, was observed on the surface of an NFPF/C particle. The weight percent of the carbon amount toward NFPF/C was weighed to be 2.21 wt%.

Galvanostatic cycling of NFPF/C and NFPP were conducted five times between 1.0 and 4.0 V at 0.1 C. Figure 6(a) shows the discharge capacity of NFPF/C at first, third and the fifth cycle were 64.4, 60.2, and 58.9 mAh g$^{-1}$, respectively. The charge–discharge curves were decayed from first to the third cycle, though maintaining from third to the fifth. The charge–discharge capacity retention ratio from first to the fifth cycle was 91.5%. The redox potentials at 2.9 and 3.1 V were observed at the charge–discharge curves of NFPF/C. Figure 6(b) shows that the discharge capacity of NFPP at first, third and the fifth cycle were 3.7, 3.2, and 3.2 mAh g$^{-1}$, respectively. This extreme low discharge capacity suggests the poor electronic conductivity on the surface of NFPP particles. The poor electronic conductivity of Na$_2$FePO$_4$F leads to slow diffusion of sodium ions. Therefore, the discharge

![Fig. 3. SEM images of (a) NFPF/C and (b) NFPP.](image)

![Fig. 4. Raman spectra of (a) NFPF/C and (b) NFPP.](image)

<table>
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<tr>
<th>Theoretical composition</th>
<th>Na/mol %</th>
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<th>P</th>
<th>O</th>
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<td>11.1</td>
<td>11.1</td>
<td>44.4</td>
<td>11.1</td>
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<td>17.7</td>
<td>15.3</td>
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<td>10.8</td>
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Table 1. Quantitative compositional analysis of the NFPF/C by the EPMA.
capacity of Na$_2$FePO$_4$F was improved by carbon-coating derived from PTFE. The carbon-coating for Na$_2$FePO$_4$F is essential to the application of NIBs cathodes.

4. Conclusion

The carbon-coated fluorophosphate Na$_2$FePO$_4$F was synthesized using PTFE as a fluorine source by a hybrid method of solid-state reaction and vapor phase reaction. This safe fluoridation method using PTFE realizes carbon-coating and fluoridation simultaneously in only one process. The Na$_2$FePO$_4$F synthesized using PTFE showed high discharge capacity than Na$_2$FePO$_4$F synthesized using NaF. Well-dispersed and size-controlled carbon-coating materials were obtained using the PTFE vapor reaction, which is a new useful and powerful method for the synthesis of excellent cathode materials on the electric vehicles and large-scale electric power storage devices requiring high charge–discharge rate.

References