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Amorphous xLiF-$FeSO_4$ ($1 \leq x \leq 2$) composites as a cathode material for lithium ion batteries

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ABSTRACT

Although the synthesis is not so easy, $LiFeSO_4F$, a high-voltage iron-based cathode, is attractive by virtue of its low cost and small environmental impact. We prepared amorphous xLiF-$FeSO_4$ ($1 \leq x \leq 2$) using the dry ball-milling method. Moreover, we succeeded to synthesize tavorite-type $LiFeSO_4F$ by sintering amorphous LiF-$FeSO_4$ at 280 °C. Amorphous 1.3LiF-$FeSO_4$ exhibited the highest reversible capacity, of about 130 mAh g^{-1}, among all the xLiF-$FeSO_4$ series ($1 \leq x \leq 2$), with an average voltage of 3.5 V. In addition, we found that the obtained amorphous xLiF-$FeSO_4$ cathodes have excellent cyclability and rate capability, also.

1. Introduction

Beyond Li-ion batteries are being developed to power electric vehicles and to efficiently utilize renewable energies, such as solar and wind power. In particular, researchers worldwide are intensely pursuing novel electrode materials for further advances in energy density. As potential cathodes for beyond Li-ion batteries, iron-based cathode materials have attracted attention by virtue of their low cost and the abundance of iron resources. Among these materials, $LiFePO_4$ has a high operating voltage of 3.3 V corresponding to Fe^{2+}/Fe^{3+} redox by the inductive effect of PO_4^{3-} polyanions [1]. Lithium iron sulfate $Li_2Fe(SO_4)_2$ [2], which substitutes sulfate SO_4^{2-} with phosphate PO_4^{3-} anions, shows the highest operating voltage of 3.75 V (vs. Li^+/Li) among iron-based cathode materials, although its theoretical capacity is restricted by the high molecular weight of SO_4. On the other hand, the theoretical capacity can be increased to 150 mAh g^{-1} from 102 mAh g^{-1} by changing from $Li_2Fe(SO_4)_2$ to $LiFeSO_4F$. This $LiFeSO_4F$ has been reported to have two types of crystal structures, tavorite-type and triplite-type $LiFeSO_4F$, which showed operating voltages of 3.6 V and 3.75 V, respectively [3,4]. However, the reported $LiMSO_4F$ (M = Fe, Co, Ni) is not stable at the high temperatures (over 500 °C) used in the normal solid-state method. In addition, the other reported $LiFeSO_4F$ also required a special synthesis route such as ionic liquid, vacuum condition, or $FeSO_4$ hydrate [5–7]. Because these synthesis routes are very costly, it is necessary to develop a simple process for synthesis of $LiFeSO_4F$. Triplite-type $LiFeSO_4F$ has already been obtained from nonhydrate $FeSO_4$ and LiF by the dry ball-milling method [8]. However, its rechargeable capacity was 100 mAh g^{-1}, corresponding to < 0.7 electron reaction per mole, and the calculated energy density was only 350 Wh kg^{-1}. In this work, in order to develop a simple and low-cost synthesis method of $LiFeSO_4F$ and to improve the cathode properties, we used the dry ball-milling method to prepare amorphous LiF-$FeSO_4$ having the same chemical composition as $LiFeSO_4F$. Moreover, it is already known that the electric conductivity for solid electrolyte can improve by increasing Li concentration in amorphous compound. Therefore, we are interested in determining whether this theory is effective for amorphous cathode materials. So, we also prepared amorphous xLiF-$FeSO_4$ ($1 \leq x \leq 2$) with the dry ball-milling method and evaluated its cathode properties against Li metal anodes in Li-salt electrolytes.

2. Experiment

Amorphous xLiF-$FeSO_4$ composites (x = 1.0, 1.2, 1.3, 1.5, 1.7 and 2.0) were prepared by dry ball-milling. Mixtures of LiF (Wako Pure Chemical Industries) and $FeSO_4$ with a molar ratio of xLiF:$FeSO_4$ were put in an Ar-filled atmosphere control container with ϕ3-ZrO_2 balls (ca. 40 g). The mixtures were ball-milled using a planetary mill (Fritsch, Pulverisette7) at 600 rpm under ambient Ar for 6 h. Here, to obtain $FeSO_4$ as a starting material, $FeSO_4{\cdot}7H_2O$ (Wako Pure Chemical Industries) was sintered at 300 °C for 12 h under Ar. To obtain a uniform xLiF-$FeSO_4$ ($1 \leq x \leq 2$) and carbon composite, the obtained

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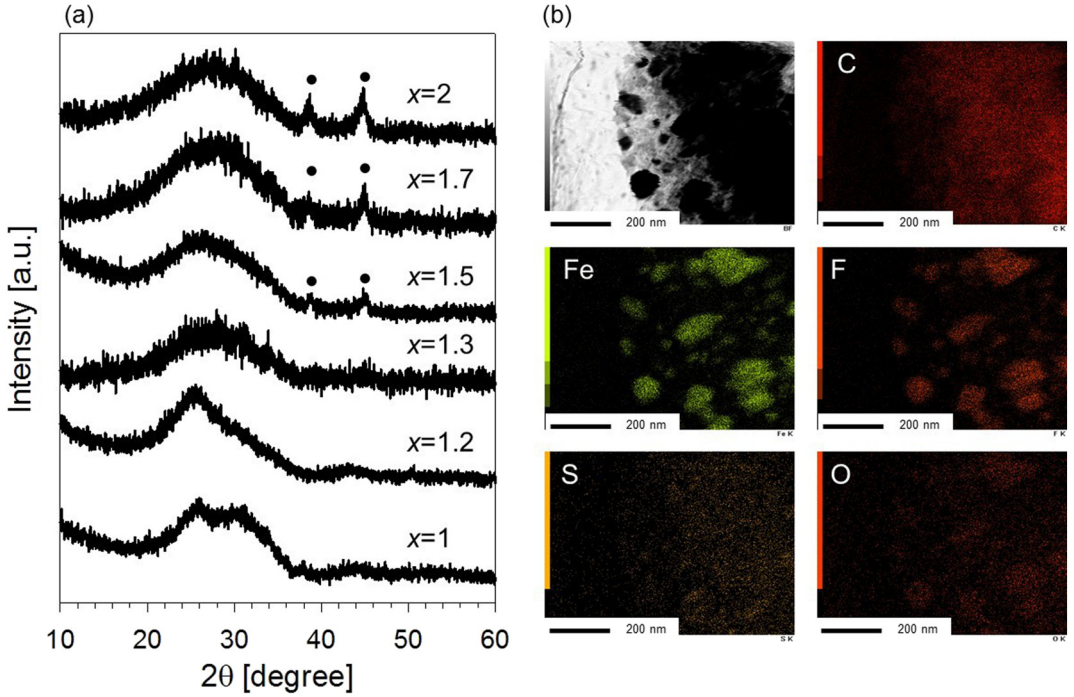

Fig. 1. (a) The XRD profiles of the obtained amorphous xLiF-$FeSO_4$ ($1 \leq x \leq 2$), (b) EDS mapping for the obtained LiF-$FeSO_4$ sample.

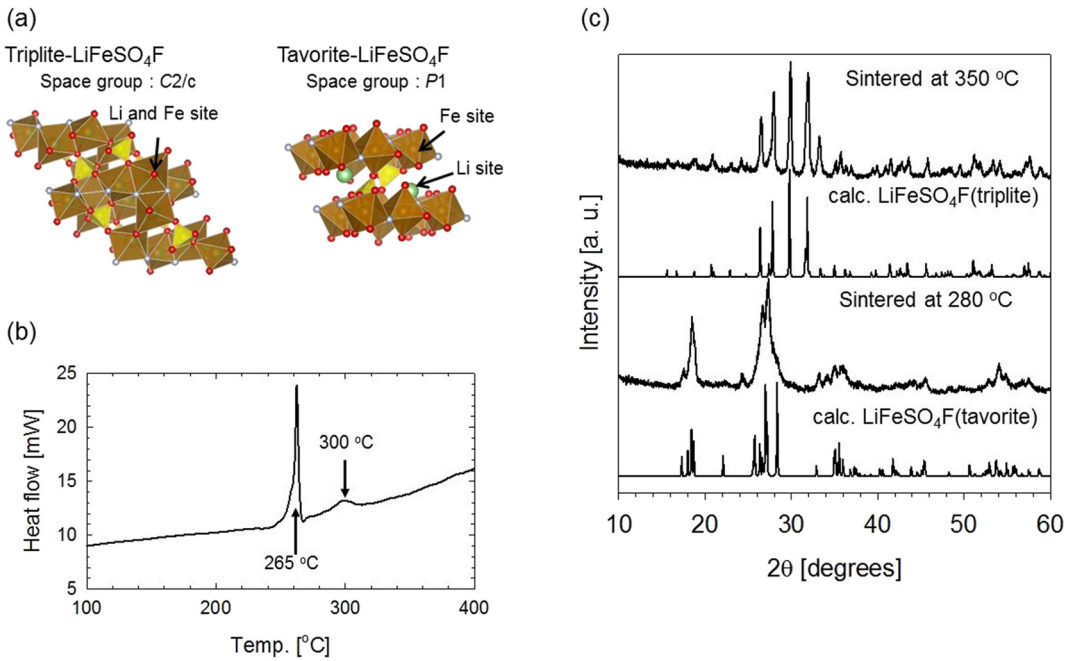

Fig. 2. (a) Structure of triplite-LiFeSO$_4$F and tavorite-LiFeSO$_4$F, (b) DSC profile for the obtained amorphous LiF-$FeSO_4$, (c) XRD profiles of the samples sintered at 280 °C and 350 °C.

products were subjected to the carbon composite process twice. The obtained amorphous xLiF-$FeSO_4$ was ball-milled with 5 wt% acetylene black (AB, Denki Kagaku) at 600 rpm for 6 h. The product was ball-milled again with 20 wt% AB in Ar. Crystalline LiFeSO$_4$F was obtained from the amorphous LiF-$FeSO_4$/C. To determine the sintering temperature, we measured the temperature profiles of amorphous LiF-$FeSO_4$/C using the Thermo Plus TG-DSC 8230L system (Rigaku). To obtain crystalline LiFeSO$_4$F, amorphous xLiF-$FeSO_4$ (x = 1.0) was sintered at 280 °C or 350 °C in a sealed SUS container. The obtained powders were characterized using powder X-ray diffraction (XRD, 50 kV and 300 mA, Cu Kα, Rigaku TTRIII). The particle size, particle morphology and EDS (Energy Dispersive X-ray Spectrometer) mapping were observed by using a transmission electron microscope (TEM; JEOL JEM 2100F). The cathode properties of the amorphous xLiF-$FeSO_4$/C and the crystalline LiFeSO$_4$F were evaluated with a 2032 coin-type cell using 1 M $LiPF_6$/EC:DMC = 1:1 in volume (Tomiyama Pure Chemical Industries) and a polypropylene separator (3501, Celgard) against lithium metal (Honjo Metal). The cathode pellets to evaluate the electrochemical properties were fabricated by mixing the xLiF-$FeSO_4$/C composite powder with a 5 wt% polytetrafluoroethylene (PTFE) Teflon binder (Polyflon PTFE F-104; Daikin Industries, Ltd.) and punched into disks (ca. 30 mg weight and 10 mm diameter).