



Thermal characteristics of a FeF₃ cathode via conversion reaction in comparison with LiFePO₄

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ABSTRACT

The thermal stability of a FeF₃ cathode via a conversion reaction was quantitatively studied using differential scanning calorimetry (DSC). Mixtures of charged and discharged FeF₃ electrodes and electrolyte were measured by changing the ratio of electrode to electrolyte. A mild exothermic peak was observed at temperatures ranging from 210 to 380 °C for the mixtures of charged electrode and electrolyte even if the electrode/electrolyte ratio was changed. Moreover, the cycling depth had no effect on the thermal stability of the charged electrode in the electrolyte. For the mixtures of discharged electrode and electrolyte, exothermic reactions occurred in the range of 250–350 °C, which varied with the electrode/electrolyte ratio. Although the exothermic reactions of the mixtures varied with the electrode/electrolyte ratio, the thermal risk for both charged and discharged electrodes coexisted with the electrolyte appeared to be mainly due to electrolyte decomposition. By comparing the heat values of mixtures of the charged and discharged electrodes and electrolyte, the FeF₃ electrodes in the electrolyte demonstrated better thermal stability than LiFePO₄ electrodes at elevated temperatures.

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1. Introduction

Due to their high energy density and potential, lithium-ion batteries have been applied in a wide variety of electronic devices and are being pursued as possible power sources for hybrid electric vehicles and electric vehicle applications [1–3]. However, before Li-ion batteries can be utilized in large-scale applications, their performances must be improved with regard to battery life, rate capacity and safety. The safety of Li-ion batteries is primarily related to the thermal stability of their constituent materials [1–6]. For exothermic reactions, such as the reaction between an electrolyte and electrode, the electrolyte decomposition within the battery can cause thermal runaway if the heat output exceeds the thermal diffusion [6,7]. Therefore, it is important to study the thermal stability of cathodes to improve the safety of Li-ion batteries.

The layered intercalation compound LiCoO₂ is used as a cathode in commercial Li-ion batteries due to its high energy density and excellent cycle life. Because of the high cost of Co, other lower cost electrode materials such as LiNiO₂ and LiMn₂O₄, which are more environmentally friendly, have been introduced. The thermal behavior of LiCoO₂, LiNiO₂ and LiMn₂O₄ as cathode materials for Li-ion batteries has been investigated energetically by differential

scanning calorimetry (DSC) and accelerated rate calorimetry (ARC) [7–13]. Unfortunately, charged Li_xCoO₂, Li_xNiO₂ and Li_xMn₂O₄ ($x < 1$) are known to release oxygen gas at elevated temperatures, which can exothermally react with organic solvent. As a low-cost, environmentally friendly and highly thermally stable material [14–17], LiFePO₄ has been considered to be a high-potential cathode material for electronic vehicle applications. However, LiFePO₄ has relatively low energy density and specific capacity. Hence, researchers are currently attempting to discover a safer and better alternative to LiFePO₄.

Recently, metal fluorides, such as FeF₃, VF₃ and TiF₃, have been studied as attractive candidates for cathode materials, exhibiting large theoretical capacities and high discharge voltages due to their highly ionic metal–ligand bonds and small atomic weight [18–26]. Among these metal fluorides, FeF₃ is currently under intensive research for use as a cathode material due to its high specific capacity and good thermal stability. Aria et al. were the first to report a discharge capacity of 80 mAh g⁻¹ from FeF₃ between 2.0 and 4.5 V involving the Fe³⁺/Fe²⁺ redox reaction [18]. The poor electronic conductivity combined with the questionable ionic character for metal fluorides, results in a disparity between their specific and theoretic capacities. To overcome this problem, highly conductive carbon was used to improve the electrochemical activity of metal fluorides, and approximately 99% of the FeF₃ theoretical capacity (235 mAh g⁻¹ vs. 237 mAh g⁻¹) in the 2.0–4.5 V region has been achieved [19–26].

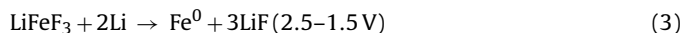
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Unlike layered compounds, the reversible conversion process enables the full redox utilization of transition-metal compounds through the following reaction [23–25]:



Of the Me^{n+}X materials, only metal fluorides can be utilized as alternative positive electrode materials for Li-ion batteries because of their high voltages. In the case of FeF_3 composites, Li et al. [26] and Badway et al. [22] have proposed the following reactions scheme:



This suggestion has clarified that the reversible conversion reaction of FeF_3 was viable, and high capacities ($>600\text{ mAh g}^{-1}$) are accessible, which provides an avenue to a high specific-capacity cathode for Li-ion battery applications.

Our group has previously reported the thermal stability of a FeF_3 cathode via an insertion reaction [21]. The FeF_3 electrode exhibited a great thermal stability in a 1 M $\text{LiPF}_6/\text{EC} + \text{DMC}$ electrolyte at elevated temperatures. In the present study, by changing the ratio of the charged or discharged electrode to electrolyte, the thermal properties of FeF_3 electrodes via a conversion reaction in a 1 M $\text{LiPF}_6/\text{EC} + \text{DMC}$ electrolyte were studied using thermogravimetry-differential scanning calorimetry (TG-DSC). For comparison, the thermal stability of a LiFePO_4 cathode was also quantitatively investigated using the same method.

2. Experimental

Commercially available FeF_3 (Soekawa Chemical Co.) and LiFePO_4 (Hohsen Corp.) were used in this research. The particle size of FeF_3 and LiFePO_4 were $12\ \mu\text{m}$ and $3\ \mu\text{m}$, respectively (Horiba LA-950). The FeF_3 powder reagents were ground with 25 wt% acetylene black (Denki Kagaku Kogyo), using a planetary ball milling machine (Itoh Manufactory) at 200 rpm for 24 h under an Ar atmosphere. The LiFePO_4 powders were mixed together with 25 wt% acetylene black in air. After these steps, the composites were mixed with 5 wt% polytetrafluoroethylene (Daikin Industries, Ltd.). Pellets were then fabricated in the form of disks (ca. 30 mg in weight and 10 mm in diameter) and dried at 110°C under a vacuum for 12 h.

The electrochemical properties were studied by charge and discharge measurements using a two-electrode coin cell. The cell was assembled in an Ar-filled glove box. Lithium foil (Honjo Metal Co., Ltd.) and a polypropylene film (Celgard LLC) were used as the counter electrode and separator, respectively. The electrolyte used was $1\ \text{mol dm}^{-3}$ LiPF_6 dissolved in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1 in volume, Tomiyama Pure Chemical Industries, Ltd.). The FeF_3 cell was cycled at a constant current density of $0.2\ \text{mA cm}^{-2}$ with an ending capacity of 474 or $711\ \text{mAh g}^{-1}$, whereas the LiFePO_4 cell was cycled between 2.6 and 4.2 V at the same current density of $0.2\ \text{mA cm}^{-2}$ (Charge capacity is $151\ \text{mAh g}^{-1}$, and discharge capacity is $152\ \text{mAh g}^{-1}$). After charging and discharging, the coin cell was disassembled in the glove box to remove the cathode. The test electrode was rinsed and soaked in DMC for 4 h, and then dried under vacuum at room temperature for 12 h to remove the low-molecular-weight compounds. For TG-DSC analyses, a given amount of the electrode powder together with the electrolyte was packed in a crimp-sealed stainless pan. The thermal properties were investigated by TG-DSC at a heating rate of 5°C min^{-1} from room temperature to 500°C . The TG signal was monitored simultaneously during data collection to confirm that the pan was hermetic.

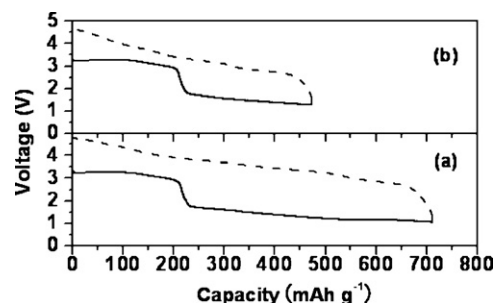


Fig. 1. Charge and discharge curves of a FeF_3 electrode in a 1 M $\text{LiPF}_6/\text{EC} + \text{DMC}$ electrolyte.

3. Results and discussion

The charge and discharge profiles of the FeF_3 electrodes via a 2Li or 3Li conversion reaction are shown in Fig. 1. The electrochemical measurements in this study were carried out using the coulometric method. For the 2Li conversion reaction, both the discharge and charge capacities were set as $474\ \text{mAh g}^{-1}$, which is twice the theoretical capacity of FeF_3 ($237\ \text{mAh g}^{-1}$). For the 3Li conversion reaction, the discharge and charge capacities were set as $711\ \text{mAh g}^{-1}$, which is triple the theoretical capacity of FeF_3 . Hence, we could assume the stoichiometry of 2Li (Fig. 1b) and 3Li (Fig. 1a) were accounted for regarding the FeF_3 electrode in its discharged state, whereas almost no Li-ion remained in the charged state of the FeF_3 electrode.

3.1. Thermal stability of the charged FeF_3 cathode via the conversion reaction

Fig. 2 shows the DSC curves for mixtures with various ratios of charged FeF_3 electrode via the 2Li or 3Li conversion reaction to 1 M $\text{LiPF}_6/\text{EC} + \text{DMC}$ electrolyte. The two DSC curve groups, represented by the solid and dashed lines, showed high similarity. For both mixture types, when the amount of coexisting electrolyte increased from 1 to $4\ \mu\text{l}$, an exothermic peak was observed at temperatures between 210 and 320°C , and increased significantly with

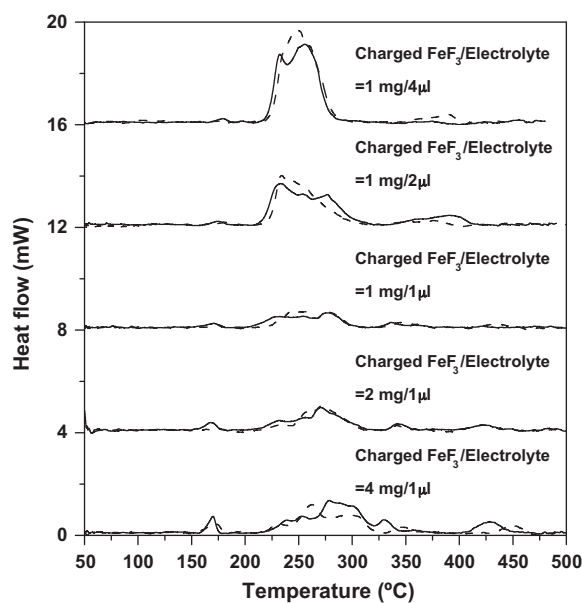


Fig. 2. DSC curves for mixtures with various ratios of charged FeF_3 electrode to 1 M $\text{LiPF}_6/\text{EC} + \text{DMC}$ electrolyte. The samples obtained via 2Li and 3Li conversion reactions were marked with dashed and solid lines, respectively.

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