Thermal characteristics of a FeF_3 cathode via conversion reaction in comparison with $LiFePO_4$

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ABSTRACT

The thermal stability of a FeF_3 cathode via a conversion reaction was quantitatively studied using differential scanning calorimetry (DSC). Mixtures of charged and discharged FeF_3 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 FeF_3 electrodes in the electrolyte demonstrated better thermal stability than $LiFePO_4$ electrodes at elevated temperatures.

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 $LiCoO_2$ 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 $LiNiO_2$ and $LiMn_2O_4$, which are more environmentally friendly, have been introduced. The thermal behavior of $LiCoO_2$, $LiNiO_2$ and $LiMn_2O_4$ 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_xCoO_2, Li_xNiO_2 and $Li_xMn_2O_4$ ($x < 1$) 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], $LiFePO_4$ has been considered to be a high-potential cathode material for electronic vehicle applications. However, $LiFePO_4$ has relatively low energy density and specific capacity. Hence, researchers are currently attempting to discover a safer and better alternative to $LiFePO_4$.

Recently, metal fluorides, such as FeF_3, VF_3 and TiF_3, 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, FeF_3 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 FeF_3 between 2.0 and 4.5 V involving the Fe^{3+}/Fe^{2+} 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 FeF_3 theoretical capacity (235 mAh g^{-1} vs. 237 mAh g^{-1}) in the 2.0–4.5 V region has been achieved [19–26].
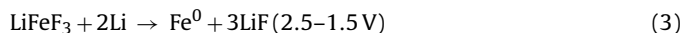
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Unlike layered compounds, the reversible conversion process enables the full redox utilization of transition-metal compounds through the following reaction [23–25]:

$$n\text{Li}^+ + ne^- + \text{Me}^{n+}\text{X} \rightleftarrows n\text{LiX} + \text{Me} \quad (1)$$

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:

$$\text{FeF}_3 + \text{Li} \rightarrow \text{LiFeF}_3 \,(4.5\text{–}2.5\,\text{V}) \quad (2)$$

$$\text{LiFeF}_3 + 2\text{Li} \rightarrow \text{Fe}^0 + 3\text{LiF} \,(2.5\text{–}1.5\,\text{V}) \quad (3)$$

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 LiPF_6/EC + 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 LiPF_6/EC + 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 μm and 3 μm, 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 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 mA cm^{-2} with an ending capacity of 474 or 711 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 mA cm^{-2} (Charge capacity is 151 mAh g^{-1}, and discharge capacity is 152 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.
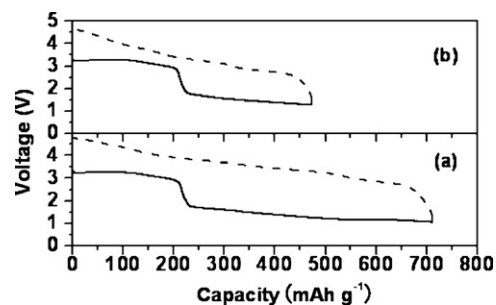

Fig. 1. Charge and discharge curves of a FeF_3 electrode in a 1 M LiPF_6/EC + DMC electrolyte.

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 coulostatic method. For the 2Li conversion reaction, both the discharge and charge capacities were set as 474 mAh g^{-1}, which is twice the theoretical capacity of FeF_3 (237 mAh g^{-1}). For the 3Li conversion reaction, the discharge and charge capacities were set as 711 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 LiPF_6/EC + 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 μl, an exothermic peak was observed at temperatures between 210 and 320 °C, and increased significantly with
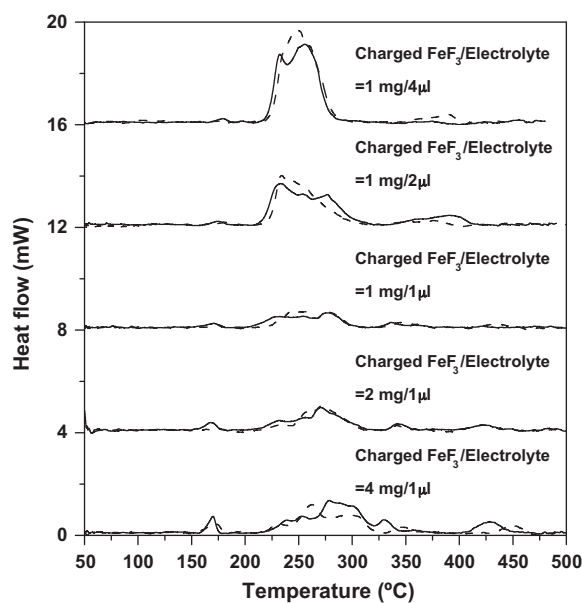

Fig. 2. DSC curves for mixtures with various ratios of charged FeF_3 electrode to 1 M LiPF_6/EC + DMC electrolyte. The samples obtained via 2Li and 3Li conversion reactions were marked with dashed and solid lines, respectively.
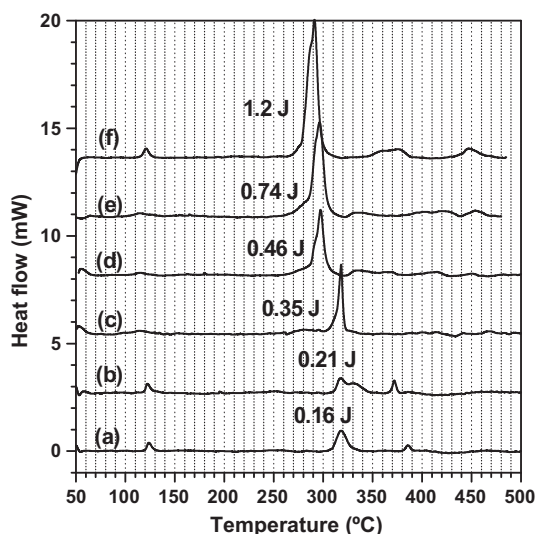
Fig. 3. DSC curves for mixtures of 1 mg discharged FeF₃ electrode via a 2Li conversion reaction and (a) 0.5, (b) 1, (c) 2, (d) 2.5, (e) 3 and (f) 4 μl of electrolyte.

Fig. 4. DSC curves for (a) 5 mg of discharged FeF₃ electrode powder and for mixtures of 1 μl electrolyte and (b) 0.5, (c) 1, (d) 2 and (e) 3 mg of discharged FeF₃ electrode via a 2Li conversion reaction.

the amount of electrolyte. When the amount of coexisting electrode increased from 1 to 4 mg, a small and broad exothermic peak was observed at temperatures ranging from 210 to 380 °C, and the heat generation slightly increased. These results indicated that the thermal risk of mixtures was closely related to the electrolyte. Compared to the results obtained for the mixtures of charged FeF₃ electrode via an insertion reaction and the electrolyte [21], the DSC curves were found to be extremely similar. The following observations were made: the variational tendency of exothermic peak was quite similar when the electrode/electrolyte ratio was altered; the exothermic onset temperatures were the same; the exothermic reactions occurred in the same temperature range; and the exothermic peaks showed similar peak position and shape. Accordingly, the exothermic reactions occurred between 210 and 320 °C were mainly caused by the electrolyte decomposition, which has been previously reported by our group [21]. Additionally, the cycling depth had almost no effect on the thermal stability of the charged electrode in the electrolyte. As a cathode material for rechargeable Li-ion batteries, the structure of the FeF₃ electrode should be reversible, which has been reported by Yamakawa et al. [23]. The thermal stability of material should be closely related to its structure. Thus, the thermal stability of electrode in charged state was supposed to be independent of the cycling depth, which supported the above suggestion.

3.2. Thermal stability of the discharged FeF₃ cathode via a 2Li conversion reaction

Fig. 3 shows the DSC curves for mixtures of 1 mg discharged FeF₃ electrode and given amounts of the electrolyte ranging from 0.5 to 4 μl. When the amount of coexisting electrolyte was above 2 μl, a sharp exothermic peak at around 290 °C was observed, and the heat values, which were evaluated by integrating DSC curves in the range of 250–350 °C, increased with the amount of coexisting electrolyte. The exothermic behavior was quite similar to that of the electrolyte alone, including the peak position and shape [3,21]. Thus, the exothermic peak at around 290 °C might be associated with the electrolyte decomposition. When the amount of coexisting electrolyte was equal or less than 2 μl, a small exothermic peak at around 320 °C was observed in the DSC curves. The exothermic heat decreased with a decrease of the coexisting electrolyte; the heat values were evaluated to be 0.35, 0.19 and 0.16 J when the amount of coexisting electrolyte were 2, 1 and 0.5 μl, respectively.
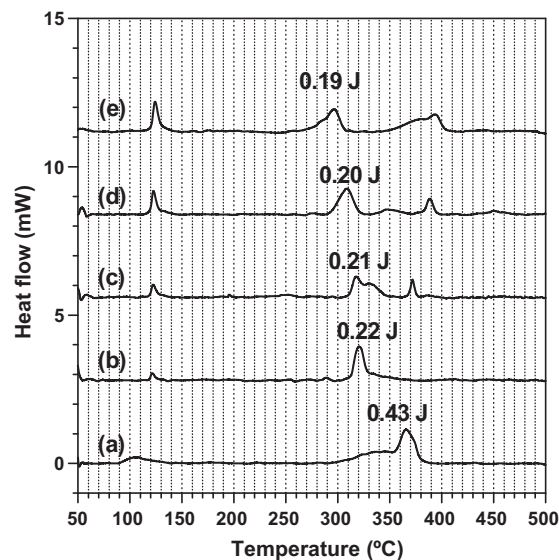
Compared with the obtained results for the electrolyte [3,21], the exothermic peak was 45 °C higher and the heat values were much less. Hence, the exothermic peaks at around 320 °C could have been involved in the reaction between the discharged electrode and electrolyte, rather than the thermal decomposition of electrolyte.

Fig. 4 shows the DSC curves for mixtures of 1 μl electrolyte and given amounts of discharged FeF₃ electrode (from 0.5 to 3 mg). The DSC curve representing a reference with 5 mg of discharged FeF₃ electrode powder is also represented in Fig. 4. A small exothermic peak was observed at around 120 °C, also seen in Fig. 3, and increased significantly with the amount of coexisting electrode. A similar phenomenon was observed for the mixture of discharged FeF₃ electrode via an insertion reaction and the electrolyte and we concluded from our various DSC data that "the exothermic peak at around 100–160 °C is mainly due to the electrolyte and the Li ions in LiFeF₃" [21]. A similar reaction occurred even for the FeF₃ after 2Li and 3Li discharge. The exothermic peak at about 120 °C in Figs. 3 and 4 was only obtained with the discharged FeF₃ electrode, but not with the charged FeF₃ electrode (Fig. 2). As a result, the electrolyte decomposed at about 120 °C during the DSC analyses, accompanied by consumption of Li-ions in the electrode.

With the addition of discharged electrode from 0.5 to 3 mg, the exothermic peaks between 250 and 350 °C gradually decreased, and shifted to lower temperature. According to the reasoning for Fig. 3, the exothermic peaks between 250 and 350 °C may have been caused by a reaction between the electrode and electrolyte. As reported by Sacken et al. [5], some of the electrolyte solvent was consumed by the reaction at around 120 °C, which results in increasing LiPF₆ concentration of the electrolyte, thereby accelerating the exothermic reactions between 250 and 350 °C. Therefore, the observed exothermic peaks between 250 and 350 °C shifted to a lower temperature with an increase of coexisting electrode. An exothermic peak at around 370 °C was observed, and gradually increased with the amount of coexisting electrode. In addition, the discharged electrode was decomposed at temperatures ranging from 300 to 380 °C, with a peak at about 370 °C, as shown in Fig. 4a. Thus, the exothermic peak at around 370 °C for the mixtures might be caused by the self-decomposition of electrode. Other than that, an exothermic peak at about 390 °C was found to increase gradually together with the increasing of the exothermic peak at about 120 °C. This phenomenon suggested that the peak at about 390 °C might be
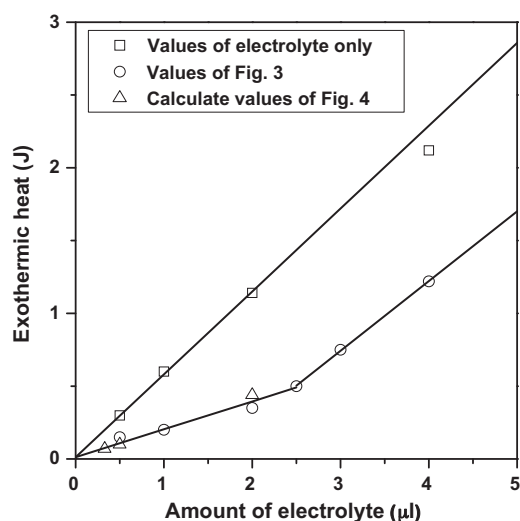
Fig. 5. Comparison of the heat generation from mixtures of 1 mg discharged electrode and given amounts of electrolyte and from the electrolyte solely. The heat values were evaluated by integrating DSC curves in the range of 250–350 °C.

Fig. 6. DSC curves for mixtures with various ratios of discharged FeF_3 electrode to 1 M $LiPF_6$/EC + DMC electrolyte. The samples obtained via 2Li and 3Li conversion reactions were marked with dashed and solid lines, respectively.

caused by a further thermal-decomposition of the products formed at 120 °C.

Fig. 5 compares the heat values obtained from the mixtures of 1 mg discharged electrode and given amounts of electrolyte and from the electrolyte solely. The heat values in Fig. 5 were evaluated by integrating the DSC curves in the range of 250–350 °C, because the dominant exothermic reactions occurred in this range. The heat values obtained from Fig. 3 are marked with the circle points, and the heat values calculated from Fig. 4, which are normalized by 1 mg of electrode, are marked with the triangle points. The square points represent the heat values of electrolyte solely. Linear fitting was carried out by the least-squares method. Obviously, the slope of the lines obtained for the mixtures changed at a break point on the electrolyte amount of 2.5 μl. This result indicated that the exothermic reactions of the mixtures were different before and after the break point. When the amount of coexisting electrolyte was more than 2.5 μl, the slope of the line for the mixtures was closely equal to that of the electrolyte. This result demonstrated that some of the electrolyte remained from the reaction with the electrode, and then thermally decomposed, which confirmed the reasoning for Fig. 3. In contrast, the electrolyte was not sufficient when the amount of coexisting electrolyte was under 2.5 μl. As a result, some of the electrode remained from the reaction with the electrolyte, and then self-decomposed, which supported the assumption for Fig. 4. In addition, the heat values of the mixtures were much smaller than that of the electrolyte itself, although the heat values increased with the amount of electrolyte. Therefore, the discharged FeF_3 electrode via the 2Li conversion reaction exhibited great thermal stability in the electrolyte.

3.3. Thermal stability of the discharged FeF_3 cathode via a 3Li conversion reaction

Fig. 6 compares the DSC curves for mixtures of 1 mg discharged FeF_3 electrode via 2Li or 3Li conversion reaction and given amounts of electrolyte. An exothermic peak at around 130 °C due to the reaction between electrolyte and Li-ions was also observed for the mixture of electrode via the 3Li conversion reaction and the electrolyte. However, the peak temperature was 10 °C higher than that of the electrode via the 2Li conversion reaction, probably due to the different activity of Li-ions in the electrode. On the other hand, when the coexisting electrolyte was in excess, the thermal behavior
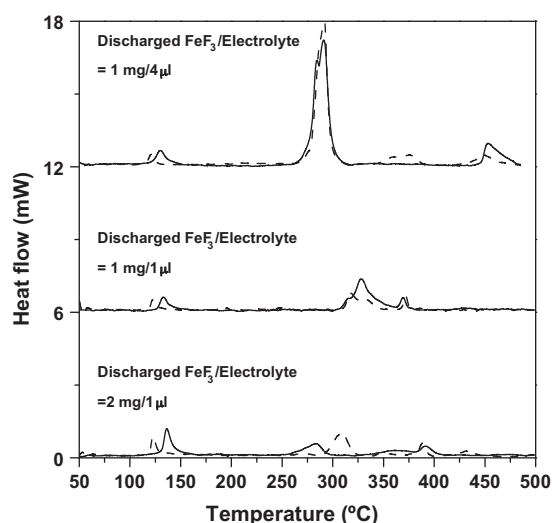
in both cases was quite similar; an exothermic peak was observed at around 290 °C, mainly due to the electrolyte decomposition. However, when the electrolyte was not sufficient, an exothermic peak was observed at a lower temperature and became weaker for the electrode via the 3Li conversion reaction. These differences could be related to the discharge depth of electrode, which will be discussed in the future.

3.4. FeF_3 in comparison with the $LiFePO_4$ cathode

To compare the thermal stability of the FeF_3 cathode to that of the $LiFePO_4$ cathode, $LiFePO_4$ electrodes were quantitatively studied using DSC with the same method as described for the FeF_3 electrodes. Both charged and discharged $LiFePO_4$ electrode powders showed good thermal stability up to 500 °C. However, when the charged and discharged $LiFePO_4$ electrodes were mixed with the electrolyte, exothermic heat was observed at elevated temperatures. The mechanism has not been clarified yet. For the mixtures of charged $LiFePO_4$ electrode and electrolyte, the dominant exothermic reactions occurred at temperatures ranging from 220 to 330 °C, and the heat values increased with the amount of coexisting electrolyte. For the mixtures of discharged $LiFePO_4$ electrode and electrolyte, an exothermic peak was observed at around 280 °C, and the heat values also increased significantly, but not proportionally, with the amount of electrolyte.

The heat generation from the mixtures of charged and discharged FeF_3 or $LiFePO_4$ electrodes and electrolyte was compared, and the heat values were evaluated by integrating the DSC curves in the range of 210–350 °C. As described above, dominant exothermic peaks in all cases were observed in this range, and their heat values increased significantly with the amount of coexisting electrolyte. The heat values of the mixtures of 1 mg charged FeF_3 or $LiFePO_4$ electrode and given amounts of electrolyte are shown in Fig. 7, while the heat values of the mixtures of 1 mg discharged FeF_3 or $LiFePO_4$ electrode and given amounts of electrolyte are shown in Fig. 8. According to the results in Fig. 7, the charged FeF_3 electrodes coexisted with the electrolyte generated slightly less heat than that of the charged $LiFePO_4$ electrode. Hence, it was reasonable to state that the charged FeF_3 electrode was more thermally stable than the charged $LiFePO_4$ electrode in the electrolyte. In contrast to the charged electrodes, the heat value differences for the mixtures between the discharged FeF_3 and $LiFePO_4$ elec-
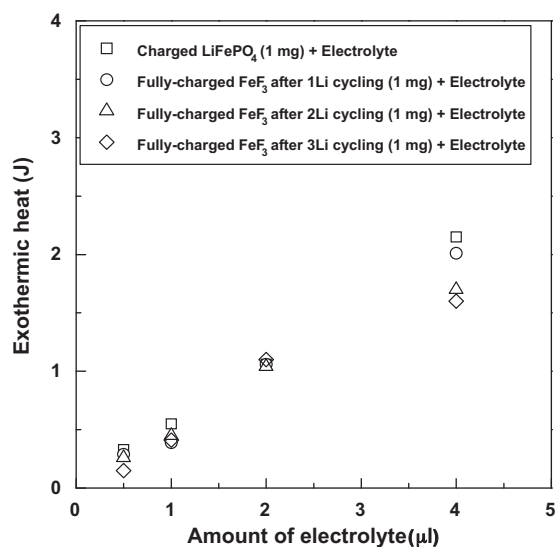
Fig. 7. Comparison of the heat generation from mixtures of 1 mg charged FeF_3 or $LiFePO_4$ electrode and given amounts of electrolyte. The heat values were evaluated by integrating DSC curves in the range of 210–350 °C.

trodes were significant, especially when the amount of coexisting electrolyte was above 1 μl. Obviously, the heat values of the mixtures of discharged FeF_3 electrode and electrolyte were much less than those of the discharged $LiFePO_4$ electrode. For the heat generation from the mixtures of discharged FeF_3 electrodes via an insertion or conversion reaction and electrolyte, the mixtures of discharged electrode in the conversion state and electrolyte gave much less heat, although the heat values increased with the amount of coexisting electrolyte in all cases. Therefore, the discharged FeF_3 electrode showed better thermal stability than that of the $LiFePO_4$ electrode in the electrolyte, especially for the electrode in its conversion state.

Based on the above discussions, FeF_3 as a cathode exhibited better thermal stability via both insertion and conversion reactions compared with the $LiFePO_4$ electrode. Taking account of the high specific capacity of FeF_3 via the conversion reaction, it was rea-
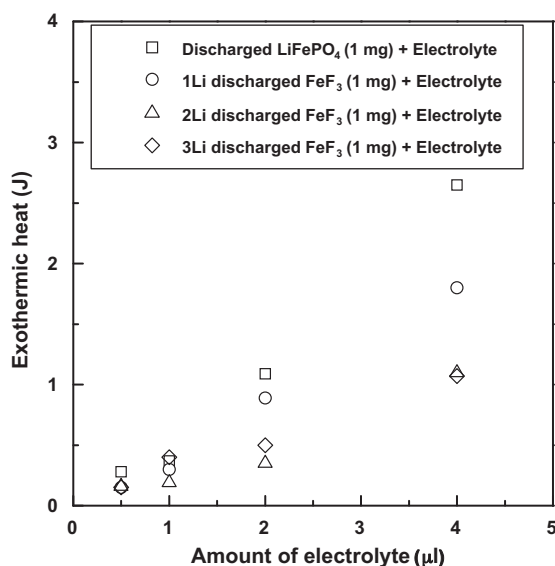
sonable to conclude that FeF_3 could serve as an attractive cathode material for vehicle power supply.

4. Conclusions

The thermal stability of the FeF_3 cathode via a conversion reaction was quantitatively studied by DSC analyses. The mixtures of charged and discharged electrodes mixed with electrolyte were investigated in detail by varying the ratio of electrode to electrolyte. For the mixtures of the charged electrode and electrolyte, a mild exothermic peak was observed in the range of 210–380 °C even if the electrode/electrolyte ratio was changed. Furthermore, the cycling depth almost had no effect on the thermal stability of the charged electrode in the electrolyte. For the mixtures of the discharged electrode and electrolyte, the exothermic reactions occurred in the range of 250–350 °C, which varied with the electrode/electrolyte ratio. When the coexisting electrolyte was in excess, a sharp exothermic peak was obtained for the mixtures at around 290 °C. In contrast, mild exothermic reactions for the mixtures occurred between 250 and 350 °C. 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 caused by the electrolyte decomposition. In addition, the exothermic heat of the mixtures of discharged electrode and electrolyte was much less than that of the electrolyte itself, which indicated that the FeF_3 cathode in its conversion state showed good thermal stability in the electrolyte. By comparing the heat values of the mixtures of charged and discharged electrodes and electrolyte, the FeF_3 electrode exhibits better thermal stability than that of the $LiFePO_4$ electrode in the electrolyte.

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Fig. 8. Comparison of the heat generation from mixtures of 1 mg discharged FeF_3 or $LiFePO_4$ electrode and given amounts of electrolyte. The heat values were evaluated by integrating DSC curves in the range of 210–350 °C.

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