



Thermal stability of FeF₃ cathode for Li-ion batteries

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ARTICLE INFO

Article history:

Received 3 February 2010

Received in revised form 24 February 2010

Accepted 24 February 2010

Available online 3 March 2010

Keywords:

Lithium-ion battery

Cathode

Iron fluoride

Safety

Thermal stability

ABSTRACT

The thermal stability of a FeF₃ cathode was quantitatively studied by differential scanning calorimetry (DSC). The cycled electrode without electrolyte was examined and found to become more thermally stable after Li-ion insertion. On the other hand, mixtures of cycled electrodes and electrolyte were investigated by changing the ratio of cycled electrode to electrolyte. The thermal decomposition of the electrolyte was mainly responsible for the exothermic heat for the discharged electrode and electrolyte combination. Although a reaction between the active materials of the electrode and electrolyte was observed for the mixture of the charged electrode and electrolyte, the exothermic heats were small. In contrast to lithium transition-metal oxide cathodes for lithium-ion batteries, the exothermic heat was suppressed by the FeF₃ electrode. Therefore, FeF₃ as a cathode for Li-ion batteries shows more thermal stability at elevated temperatures.

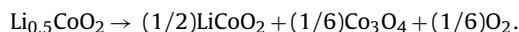
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1. Introduction

Nowadays Li-ion batteries have been extensively studied due to their high performance and potential. They have been widely used in the portable electronics market and are being pursued as possible power sources for hybrid electric vehicles and electric vehicle applications [1,2]. However, there are also potential safety problems in their use due to thermal runaway. The safety of lithium-ion batteries is mainly related to the thermal stability of their constituent materials [1–5]. Exothermic reactions in terms of both the reactions between the electrolyte and the electrodes, and the decomposition of the electrolyte in the battery can cause thermal runaway at elevated temperatures. Hence, it is important to study the thermal stability of cathodes for Li-ion batteries.

In generally, the layered intercalation compound LiCoO₂ is utilized as a cathode in most commercial lithium-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 acceptable, have been introduced. Unfortunately, when Li_xCoO₂, Li_xNiO₂, and Li_xMn₂O₄ ($x < 1$) are used as cathodes, they are known to release oxygen gas at elevated temperatures, which could react with organic solvent exothermally [6–14]. As an example, Li_xCoO₂ is known to release oxygen gas from the material according to the following reaction

[11–14]:



In addition, the exothermic heat caused by the reaction between the charged cathode Li_{0.49}CoO₂ cathode and the electrolyte was found to be ca. 1000 J g⁻¹ [13]. Therefore, researchers are now attempting to find a cheaper and safer alternative.

Recently, metal fluorides have been studied as optional candidates for cathode materials with large theoretical capacity and high discharge voltages due to their highly ionic metal–ligand bonds and small atomic weight [15–17]. The electrochemical properties of metal fluorides with the perovskite structure such as FeF₃, VF₃, and TiF₃ were investigated by Arai et al. [15]. A discharge capacity of 80 mAh g⁻¹ was reported, which was about 34% of the theoretical capacity corresponding to the Fe³⁺/Fe²⁺ redox reaction. The poor electronic conductivity with wide energy gap combined with the questionable ionic character of the metal/halogen bond for metal fluorides, results in a disparity between the specific capacity and the theoretical capacity. However, the electrochemical activity of metal fluorides has been improved through mechanical milling with carbon, and a good reversible behavior of approximately 200 mAh g⁻¹ has been achieved for FeF₃ cathodes [16,17]. In addition, the reversible conversion reaction of FeF₃ was enabled, and high capacities (>600 mAh g⁻¹) are accessible at elevated temperatures. The ability to reversibly reduce to the metal, i.e., the reformation of the metal fluoride, provides an avenue to a high-specific-capacity cathode based on the reversible conversion reaction in applications of Li-ion batteries [18]. However, the thermal stability of metal fluoride cathodes has not yet been examined.

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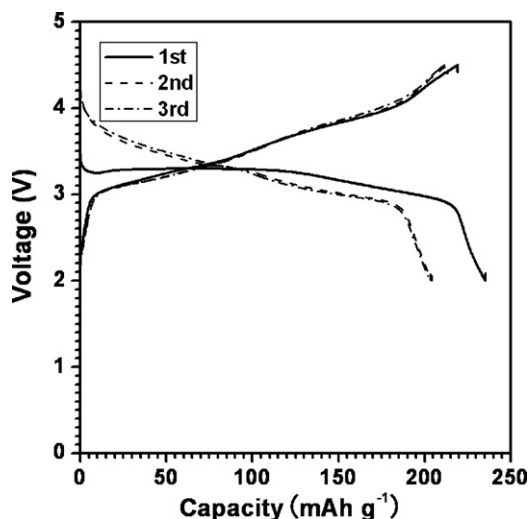


Fig. 1. Charge and discharge curves of FeF_3 electrode in EC + DMC-based electrolyte.

In this study, FeF_3 was applied as the active cathodic material in Li-ion batteries. By changing the ratio of cycled electrode to electrolyte, the thermal stability of the FeF_3 electrode in the EC + DMC-based electrolyte was studied by differential scanning calorimetry (DSC) to clarify the mechanism of the exothermic reaction at elevated temperatures.

2. Experimental

Commercially available FeF_3 (Soekawa Chemical Co.) was used in this research. It was analytical grade. 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 in an Ar atmosphere. FeF_3 -C composites were mixed with 5 wt% polytetrafluoroethylene (Daikin Industries, Ltd.), and then pellets were fabricated in the form of disks (ca. 30 mg in weight and 10 mm in diameter) in an Ar-filled glove box and dried at 110 °C under a vacuum for 12 h.

The electrochemical properties of metal fluorides 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 LiPF₆ dissolved in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1 in volume, Tomiyama Pure Chemical Industries, Ltd.). The cell was cycled between 2.0 and 4.5 V at a constant current density of 0.2 mA cm⁻². After the third charging or discharging, the coin cell was disassembled in a glove box to take out the cathode. The electrode was rinsed and soaked in DMC for 4 h, and then dried under vacuum at room temperature for 12 h to remove low-molecular-weight compounds. 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. No leakage was verified by the absence of weight loss in TG curves during heating.

3. Results and discussion

The charge/discharge profile of the FeF_3 electrode is shown in Fig. 1. The initial discharge (lithium-ion insertion into the FeF_3 electrode) and charge (lithium-ion extraction from the FeF_3 electrode) capacities were 235 and 219 mAh g⁻¹, respectively. Hence, the irreversible capacity in the first cycle for FeF_3 was 16 mAh g⁻¹.

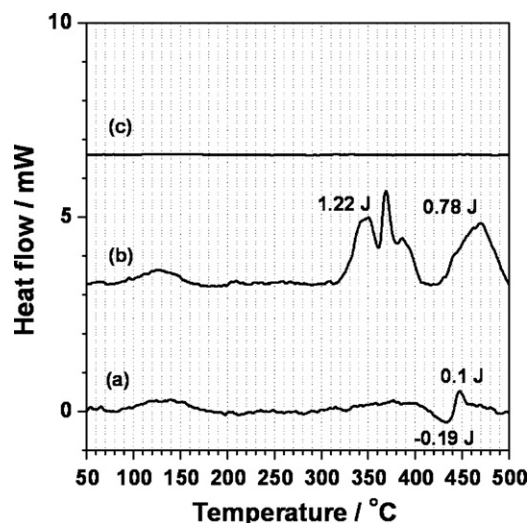


Fig. 2. DSC curves of 8 mg: (a) discharged FeF_3 electrode powder after 2.5 cycles, (b) charged FeF_3 electrode powder after 3.0 cycles, and (c) pristine FeF_3 powder.

The theoretical capacity of FeF_3 is 237 mAh g⁻¹; therefore, 0.99 Li ions were inserted into FeF_3 during the first discharge process. After the second cycle, the charge and discharge reaction proceeded reversibly and the irreversible capacity was negligibly small, as is consistent with the results reported in the literature [16,17].

Fig. 2 shows DSC curves of pristine powder and charged/discharged electrode powder without electrolyte. When 8 mg of cycled electrode powder was sealed in a stainless-steel pan, exothermic peaks were observed from DSC curves. A small broad peak at around 100–160 °C was observed for both charged and discharged FeF_3 electrodes, while no exothermic peak was seen for pristine powder as shown in Fig. 2c. The formation of a surface film on the cathode has been reported [19–21] and has been shown to cause an exothermic reaction at low temperatures [21]. Therefore, the exothermic peak at around 100–160 °C in the present study could be attributed to the decomposition of the surface film which formed on the electrodes during the cycling. The difference between the charged and discharged electrode was distinct. The charged electrode gave exothermic peaks at temperatures in the range of 315–405 °C and above 420 °C. On the other hand, small endothermic and exothermic peaks were observed at temperatures ranging from 400 to 455 °C for the discharged electrode. Hence, heat generation from the discharged electrode was milder than that of the charged electrode. The mechanism of the exothermic reaction has not been clarified yet, perhaps due to the decomposition of the electrodes at elevated temperatures. Therefore, these results suggest that the FeF_3 electrode tends to be thermally stable after lithiation.

Fig. 3 shows the variations in DSC curves for mixtures of 1.0 mg discharged FeF_3 electrode powder and given amounts of electrolyte. When the amount of electrolyte increased from 0.5 to 4 μ l, dominant exothermic peaks appeared at around 270 °C and the heat values increased with the amounts of electrolyte. In addition, small exothermic peaks were observed at around 330 and 410 °C when the amount of a coexisting electrolyte was 4 μ l. The discharged electrode powder was thermally stable at temperatures below 400 °C, and the heat value was very small even above 400 °C, as shown in Fig. 2a, and hence the exothermic heat observed in Fig. 3 cannot be attributed to the decomposition of the discharged electrode. Comparing Fig. 3 with the DSC curve of the EC + DMC-based electrolyte shown in Fig. 4, it is evident that the exothermic behaviors of the mixture of discharged electrode and electrolyte were quite similar to that of the electrolyte only. Therefore, the

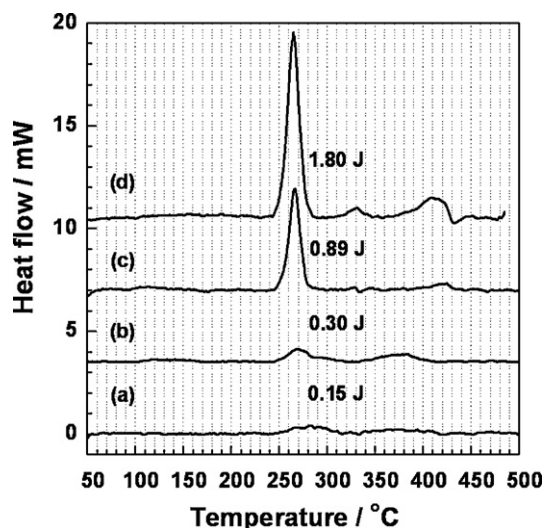


Fig. 3. DSC curves of mixtures of (a) 0.5 μl , (b) 1 μl , (c) 2 μl , and (d) 4 μl electrolyte and 1 mg discharged FeF_3 electrode powder after 2.5 cycles.

exothermic reaction at about 270 $^{\circ}\text{C}$ should be closely related to the electrolyte decomposition. On the other hand, the exothermic temperatures for dominant peaks seen in Fig. 3 are lower than that for the electrolyte decomposition. These results indicate that the electrolyte decomposition reaction might be accelerated on the discharged FeF_3 electrode. This assumption can be examined by a detailed analysis of the heat values. Fig. 5 shows the correlation between the heat values and the amount of electrolyte for the electrolyte only and for mixtures of 1 mg discharged electrode and given amounts of electrolyte. The heat values increased in proportion to the amount of electrolyte in both cases. Linear fitting was carried out by the least-squares method, and the slope of lines was almost the same. These results support the above assumption. In addition, the heat values of the mixtures were smaller than that of electrolyte itself. This phenomenon indicated that some of the electrolyte was consumed before thermal decomposition. This consumption of electrolyte should be associated with the reac-

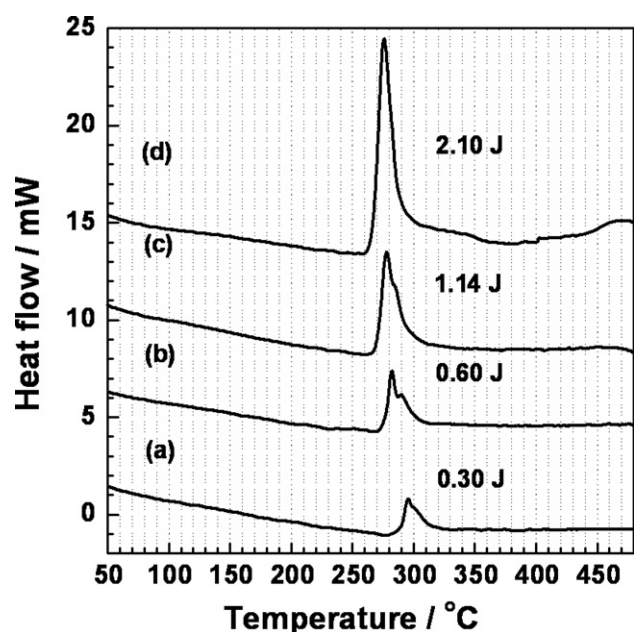


Fig. 4. DSC curves of (a) 0.5 μl , (b) 1 μl , (c) 2 μl , and (d) 4 μl of EC+DMC-based electrolyte.

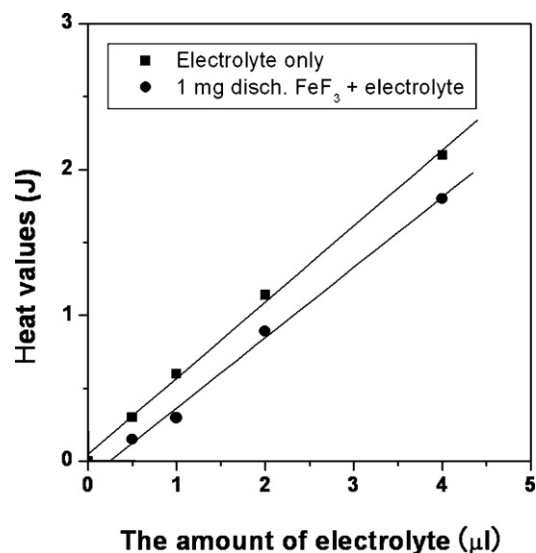


Fig. 5. Correlation between the heat values obtained in discharged state and the amount of electrolyte sealed in a pan. The heat values were evaluated by integrating DSC curves at temperatures ranging from 240 to 320 $^{\circ}\text{C}$.

tion between the electrolyte and the Li ions in the discharged electrode.

As described above, the heat generation from a system consisting of the discharged electrode and electrolyte was suggested to be mainly due to the electrolyte. However, the amount of electrode material also plays an important role; thus, the effect of the discharged FeF_3 electrode on the heat generation was studied. Fig. 6 shows DSC curves of 1 μl of electrolyte with given amounts of discharged electrode (ranging from 0.5 to 4 mg). When the amount of the coexisting discharged electrode was 0.5 mg (Fig. 6a), an exothermic peak was observed at around 270 $^{\circ}\text{C}$. With the amount of discharged electrode increasing, the exothermic heat at around 270 $^{\circ}\text{C}$ caused by thermal decomposition of the electrolyte gradually faded, and shifted to higher temperatures. This phenomenon was found even in the electrolyte-only DSC curve when the amount of sealed electrolyte decreased (Fig. 4). These results support the above assumption that the electrolyte was consumed by the discharged electrode before thermal decomposition,

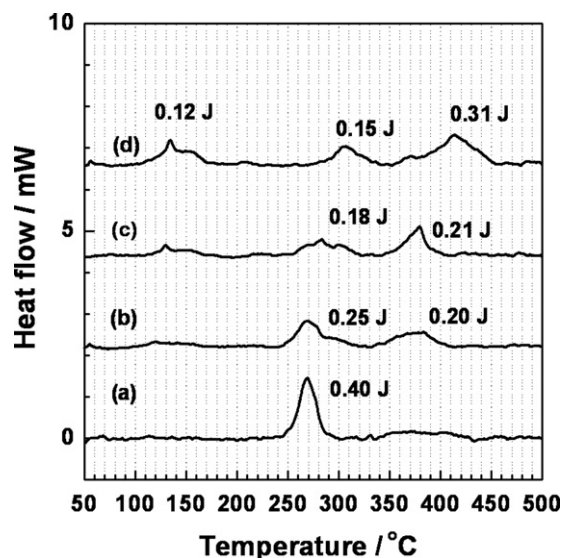


Fig. 6. DSC curves of mixtures of 1 μl electrolyte and (a) 0.5 mg, (b) 1 mg, (c) 2 mg, and (d) 4 mg discharged FeF_3 electrode powder after 2.5 cycles.

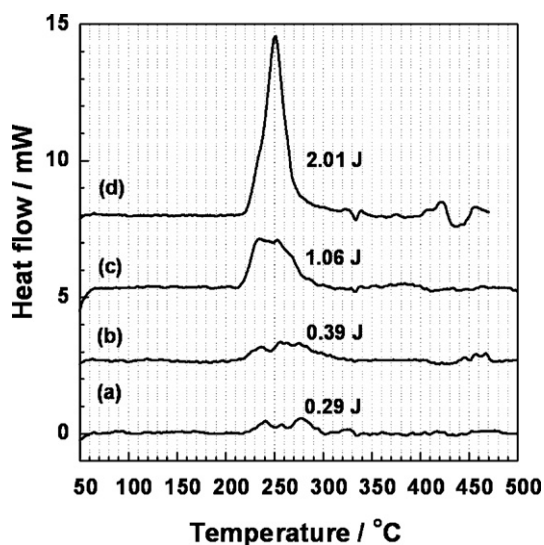


Fig. 7. DSC curves of mixtures of 1 mg charged FeF_3 electrode powder after 3.0 cycles and (a) 0.5 μl , (b) 1 μl , (c) 2 μl , and (d) 4 μl of electrolyte.

thereby decelerating the decomposition reaction of the electrolyte. By contrast, the exothermic peak at around 100–160 °C increased significantly, together with a new exothermic peak at higher temperature above 340 °C. The exothermic peak at about 100–160 °C should be attributed to the thermal decomposition of the surface film and the reaction between Li ions and the electrolyte, which is discussed below. Thus, the exothermic heat at higher temperatures above 340 °C is likely caused by further thermal decomposition of the products of the reaction between the Li ions and the electrolyte.

Although small exothermic heat was observed, it was clear that heat generation from a hermetic system consisting of the discharged electrode and electrolyte could mainly be attributed to thermal decomposition of the electrolyte. Therefore, the electrolyte in the mixture of discharged FeF_3 electrode and electrolyte is mainly responsible for the thermal risk.

The thermal behaviors of the charged electrode were found to be quite different from those of the discharged electrode. Fig. 7 shows DSC curves of 1 mg charged FeF_3 electrode powder with given amounts of electrolyte ranging from 0.5 to 4 μl . Exothermic peaks were observed at temperatures ranging from 210 to 310 °C, and their exothermic heat increased with the amount of electrolyte. Comparing Fig. 7 to the results obtained for the electrolyte in Fig. 4, the exothermic onset temperatures were 40 °C lower and the exothermic reactions occurred in a wider temperature range. These behaviors suggest that the electrolyte may have been activated by the charged electrode and decomposed at lower temperature. On the other hand, pristine FeF_3 powder was investigated by DSC measurements as shown in Fig. 8. Exothermic reactions occurring at temperatures ranging from 210 to 310 °C were also seen for the mixture of pristine FeF_3 powder and electrolyte, which were not found in the pristine FeF_3 powder only (Fig. 2c). Further, the exothermic behaviors were quite similar to those of the charged electrode coexisting with the electrolyte, but the observed difference in DSC curves (Figs. 7 and 8) may have been due to the electrode containing additives such as binder and carbon, and the amount of trapped Li ions in the electrode. In addition, the charged electrode itself was decomposed exothermally at above 315 °C as shown in Fig. 2b, which was not seen in Fig. 7. Therefore, exothermic peaks in Fig. 7 can be attributed to decomposition of the electrolyte and the reaction between the charged electrode and electrolyte.

Differing from the hermetic system consisting of discharged FeF_3 electrode and electrolyte, the mixture of charged electrode and electrolyte gave exothermic heat attributed to the reaction

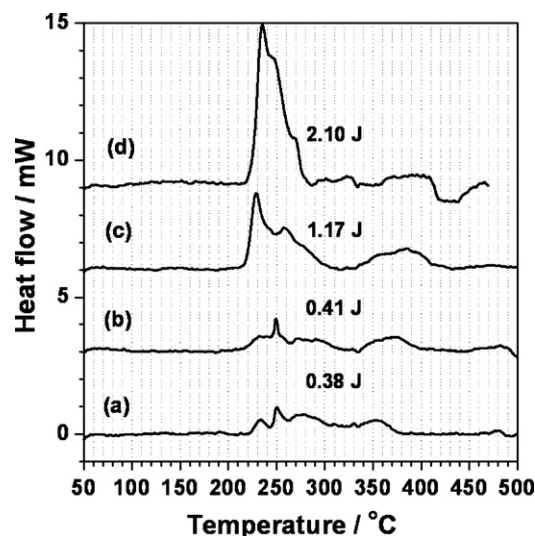


Fig. 8. DSC curves of mixtures of 1 mg pristine FeF_3 powder and (a) 0.5 μl , (b) 1 μl , (c) 2 μl , and (d) 4 μl of electrolyte.

between the active material of the FeF_3 electrode and the electrolyte. Hence, the thermal behavior was found to be much more complicated. Fig. 9 shows DSC curves of 1 μl of electrolyte with given amounts of charged FeF_3 electrode powder. Obviously, broad exothermic peaks at temperatures ranging from 210 to 310 °C were observed, and the heat values were evaluated to be 0.51, 0.39, 0.56, and 1.08 J when the coexisting charged electrode powder was 0.5, 1, 2, and 4 mg, respectively. When the amount of the charged electrode was above 1 mg, the heat value increased gradually, but not proportionally, with the increase of the charged electrode. Other than that, when the amount of the charged electrode was above 2 mg, small exothermic peaks were observed at temperatures between 320 and 380 °C, which would be due to the self-decomposition of the charged electrode, as shown in Fig. 2b. The heat values evaluated between 320 and 380 °C in Fig. 9 were much smaller than those expected from Fig. 2b, which indicates that a part of the charged electrode reacts below 320 °C. These results are consistent with the above discussion for Fig. 7. However, the exothermic peaks at around 100–160 °C, which were observed in DSC curves of discharged electrode coexisting with the elec-

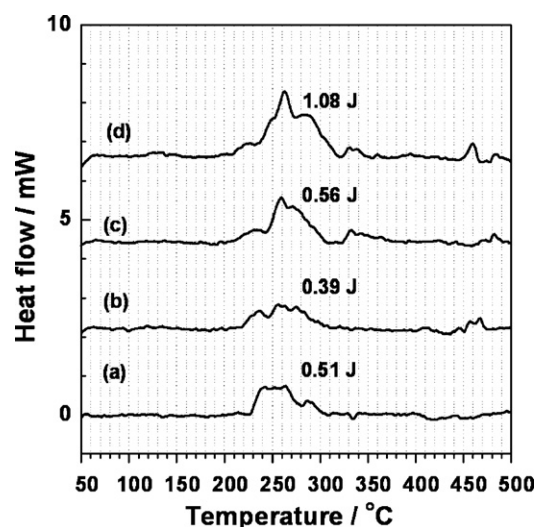


Fig. 9. DSC curves of mixtures of 1 μl electrolyte and (a) 0.5 mg, (b) 1 mg, (c) 2 mg, and (d) 4 mg of charged FeF_3 electrode powder after 3.0 cycles.

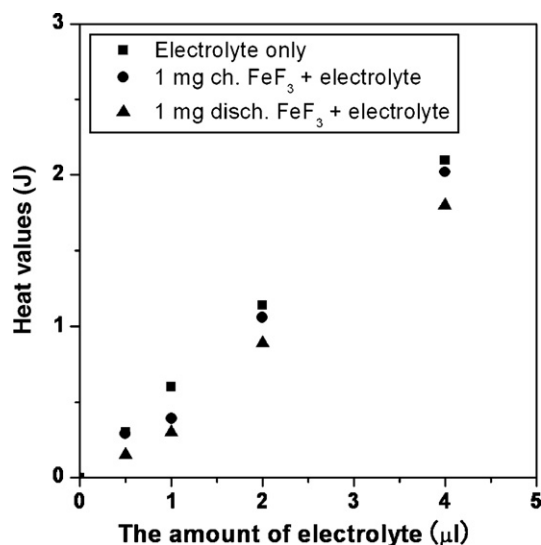


Fig. 10. Correlation between the heat values obtained in charged/discharged state and the amount of electrolyte sealed in a pan. The heat values were evaluated by integrating DSC curves at temperatures ranging from 210 to 320 °C.

trolyte (Fig. 6), were too small to be detected even when the amount of charged electrode was 4 mg. In addition, the electrolyte in mixtures of the discharged electrode and electrolyte was consumed before thermal decomposition, as described above. These results support the above suggestion that the exothermic peak at around 100–160 °C is mainly due to the electrolyte and the Li ions.

Fig. 10 shows the correlation between the heat values and the amount of electrolyte for the electrolyte only and for mixtures of 1 mg charged/discharged electrode and given amounts of electrolyte. Although the heat value increased with the amount of coexisting electrolyte, the heat values of the mixtures were smaller than that of the electrolyte by itself. These results indicate that the FeF_3 cathode did not have any negative effect on the stability of the electrolyte, which is contrary to the behavior of lithium transition-metal oxides at elevated temperatures. Therefore, FeF_3 as a cathode is more thermally stable for Li-ion batteries.

4. Conclusions

The thermal stability of a FeF_3 electrode with or without the electrolyte was studied by DSC measurements from room temperature to 500 °C. Both discharged and charged electrodes showed an exothermic peak at around 100–160 °C due to the decomposition of the surface film on the electrode. Furthermore, the electrodes tended to be thermally stable after lithiation. Thermal behaviors of the mixture of cycled electrode and electrolyte were investigated in detail by changing the ratio of cycled electrode powder to electrolyte in order to clarify the factor contributing to the thermal risk of the mixtures at elevated temperatures. For the mixture of discharged electrode powder and electrolyte, the exothermic heat appeared to be mainly attributed to the decomposition of the electrolyte at around 270 °C. With the increase of discharged

electrode powder in the mixture, the electrolyte was consumed by the electrode, resulting in a mild exothermic discharge at around 100–160 °C and a gradual discharge at high temperatures above 340 °C. The exothermic peak at about 100–160 °C was attributed to the decomposition of the surface film and the reaction between Li ions and the electrolyte, whereas the exothermic peak at temperature above 340 °C was suggested to be caused by the thermal decomposition of the products of the reaction. For the mixture of charged electrode powder and electrolyte, the thermal behavior of the mixture was much more complicated because of the reaction between active material of the electrode and the electrolyte. Hence, the mechanism has not yet been clarified, although the heat generation is not large. The thermal risk for the mixture of charged electrode and electrolyte is derived from both electrolyte decomposition and the reaction between the active material and electrolyte, which caused heat generation at temperatures ranging from 210 to 310 °C. On the other hand, based on the exothermic heat of the mixture of discharged/charged electrode and electrolyte, the FeF_3 electrode for Li-ion batteries exhibits more thermal stability than lithium transition-metal oxide electrodes at elevated temperatures.

Acknowledgment

The present work was financially supported by the Li-EAD project of New Energy and Industrial Technology Development Organization, Japan.

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