Development of a Rare-Metal-Free Cathode for Next-Generation Lithium Ion Batteries

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ABSTRACT

Conversion-type active materials show promise for use in large-scale lithium-ion batteries by virtue of their low cost and large specific capacities. However, there are some challenges in the application of these materials to practical Li-ion batteries. To adapt the conversion-type active materials to the next-generation Li-ion batteries, it is necessary that we understand the conversion reaction in detail. In this review, the electrochemical properties of the iron-based conversion cathode are introduced, and their reaction mechanisms are described based mainly on our own experiments. Finally, we introduce a composite of LiF as an Li source and FeO as an anion accepter as a novel cathode system for the next-generation Li-ion batteries.

Keywords: Conversion-type cathode, Composite cathode, Next-generation Li-ion batteries, X-ray analysis

1. Introduction

To realize a society that does not rely on either fossil fuels or nuclear power sources, it is necessary to identify and exploit effective sources of renewable energy. At the same time, in order to realize an energy supply system centered on renewable energy, it is important to develop a large-scale energy storage system with low cost and large energy. The Li-ion battery has attracted attention as such a storage system because it has the largest energy density among the commercially available secondary batteries. However, its energy density is currently restricted, since insertion-type cathodes such as LiCoO₂, LiMn₂O₄, and LiFePO₄ are used in the commercially available Li-ion batteries. Therefore, the performance of Li-ion batteries is mainly determined by the energy density of the cathode materials.

As a breakthrough in the large-scale Li-ion batteries, iron-based conversion-type cathodes, which can utilize all valence changes between the ionic and metallic state of cations in the cathode, have attracted attention for their low environmental impact and large theoretical capacity. In fact, an FeF₃ cathode with an energy density of 1200 Wh kg⁻¹, more than twice that of LiCoO₂, has been developed. Therefore, many researchers have focused on the iron-based conversion-type cathode to support the development of large-scale lithium storage with higher energy density. However, the conversion-type cathodes show large overpotential during their discharge-charge cycles, such that their rechargeable capacity is almost zero after a few cycles. To overcome this drawback, we previously elucidated the detailed mechanism underlying the deterioration of the rechargeable capacity of the FeF₃ cathode. To understand the cause of the large overpotential, we measured the quasi-open circuit voltage (QOCV) profiles (Fig. 1). We applied an intermittent current density of 0.2 mA cm⁻² for 1 h, followed by equivalent 1, 12, and 24 h relaxation times. For the 24 h relaxation time, the voltage difference (V_{diff}) at the same state of lithiation between the discharge and charge states became smaller than that for the 1 h or 12 h relaxation time. In particular, the relaxation voltage for the 24 h relaxation time was large below 2.0 V, and it was also large during the charge process. However, V_{diff} did not become zero after the 24 h relaxation time. Moreover, Liu et al. reported that the V_{diff} of FeF₃ for a relaxation time of 72 h was 280 mV, and Li et al. also clarified that it did not become zero after a relaxation time of 24 h. These results suggested that the slow chemical kinetics of the conversion reaction contributed to voltage overpotential during the discharge-charge cycle. This slow chemical kinetics of the conversion reaction may require an elevated temperature. The discharge rate capability of FeF₃ between 1.0 V and 4.5 V (Fig. 2(a)) was evaluated using various currents ranging from 35 mA g⁻¹ (0.05 C) to 712 mA g⁻¹ (1 C). The initial discharge capacity remained 250 mAh g⁻¹, and the capacity maintenance
followed by an equivalent 1, 12, and 24 h relaxation time.

The quasi-open circuit voltage (QOCV) curves of FeF$_3$ cathode at an intermittent current density of 0.2 mA cm$^{-2}$ for 1 h, followed by an equivalent 1, 12, and 24 h relaxation time.

The initial discharge capacity of the obtained FeOF was 900 mAh g$^{-1}$ down to 0.7 V, which almost corresponds to the theoretical capacity based on the 3Li$^+$ conversion reaction (885 mAh g$^{-1}$). However, the initial charge capacity was 680 mAh g$^{-1}$, and there was also a large overpotential between the initial discharge-charge voltage profile. For cyclability of FeOF (Fig. 3) down to 2.0 V, the initial discharge capacity was 192 mAh g$^{-1}$ and it remained at 180 mAh g$^{-1}$ even after 30 cycles. In the case of the deeper cycle between 1.3 and 4.0 V, the initial discharge capacity was more than doubled, which corresponds to 60% of the theoretical capacity based on the 3 Li$^+$ conversion reaction. The cycling efficiency of FeOF between 1.3 and 4.0 V was 70.9%. For comparison, a FeF$_3$ between 1.3 and 4.5 V$^3$, and a FeF$_2$ between 1.5 and 4.5 V$^5$ exhibited a 29.2% and a 40–50% cycling efficiency, respectively. However, the cyclability after the complete conversion reaction (down to 0.7 V) was also deteriorated within a few cycles. Although it may be difficult to utilize the complete conversion reaction of FeF$_3$ or FeOF, many researchers have investigated the detailed reaction mechanism to improve the electrochemical properties for the conversion reaction.

Recently, our group has also been investigating the conversion reaction of TiF$_3$, which has the same structure as FeF$_3$. The electrochemical properties of TiF$_3$ have already been reported by our group.$^6$ However, the reported rechargeable capacity was only 60 mAh g$^{-1}$, corresponding to 0.2 Li$^+$ mol$^{-1}$, at a rate of 0.2 mA cm$^{-2}$ between 2.0 V and 4.5 V. The case of FeF$_3$, the
conversion reaction was also observed below 2 V in the discharge process. Since it is considered that the conversion reaction of TiF₃ also proceeds below 2 V, we optimized the discharge-charge voltage range (Fig. 4(a)). In the voltage range between 1.5 and 3.5 V, the initial discharge capacity of TiF₃ was 186 mAh g⁻¹ with an average voltage of 2.5 V and the initial charge capacity was 170 mAh g⁻¹ with a quite small overpotential. When the potential window was extended between 0.5 and 4.0 V, the initial discharge capacity was 730 mAh g⁻¹, which almost corresponds to 2.9 Li⁺ mol⁻¹. This suggests that the discharge capacity of 730 mAh g⁻¹ included a conversion reaction to titanium metal. In particular, the discharge-charge overpotential of TiF₃ including the conversion reaction was still smaller than that of FeF₃. Moreover, the cyclability of TiF₃ was better than that of FeF₃, not only in the insertion reaction region but also in the conversion reaction region (Fig. 4(b)), although the 0.9 V average voltage of TiF₃ in the conversion reaction region is lower than that of FeF₃. Comparing the electric conductivities of FeF₃ and TiF₃ in order to confirm the cause, the obtained electric conductivity of TiF₃ (1 × 10⁻¹⁰ S cm⁻¹) was higher than that of FeF₃ (1 × 10⁻¹¹ S cm⁻¹). That is, it was suggested that the smaller overpotential and the better cyclability of TiF₃ was a reflection of the better conductivity of TiF₃ than FeF₃. To improvement of the electrochemical properties for the conversion-type cathode, the development of novel cathode materials with higher electric conductivity is considered indispensable.

3. The Reaction Mechanism between the FeF₃ and Li Metal

To examine the reaction mechanism between Li and FeF₃ during the initial discharge-charge cycle, we performed XRD measurements of the FeF₃ electrode at various discharge and charge states. In addition, we performed XANES measurements to examine the oxidation states of iron after the initial discharge-charge cycle. For XANES measurement, the Fe K-edge position evidently shifted to lower energy from the initial state following the discharge reaction down to 2.0 V from the initial state. At the discharge region below 2.0 V, the pre-edge feature approaches that of metallic iron. These results suggested that the oxidation state of Fe changed from Fe³⁺ to a metallic state down to 1.0 V. On the other hand, the Fe K-edge position returned to almost the original position after the charged state. Therefore, the oxidation state of Fe returned to Fe³⁺ from the metallic state in the charge reactions up to 4.5 V. Figure 5(a) shows the XRD profiles of the FeF₃ pellet in the different discharge-charge states. All the XRD peaks in the pellet discharged to 2.0 V shifted to lower angles, and this diffraction peak intensity decreased during the initial discharge to 2.0 V. On the other hand, the diffraction peak intensities of (1 1 3) and (1 1 6) increased with the discharge to

![Figure 4](image-url)

**Figure 4.** (a) Initial and second discharge/charge profiles of TiF₃ vs. Li metal cell. (b) Cyclability of TiF₃ between 1.5–3.5 V or 0.5–4.0 V.

![Figure 5](image-url)

**Figure 5.** Ex-situ XRD profiles of FeF₃ pellets; initial pellet, followed by the pellets of 1Li lithiation, 2Li lithiation, and 3Li lithiation and the pellets charged to 4.5 V after 3Li lithiation. (b) The XRD profile of the FeF₃ pellet after the 20th cycle.
2.0 V. Recently, the discharge reaction for FeF$_3$ down to 2.0 V was reported using the DFT calculation method to progress by the following reaction:\textsuperscript{12}

$$\text{FeF}_3 + \text{Li}^+ + e^- \rightarrow \text{LiF} + \text{FeF}_2$$

However, the observed XRD profile could not be indexed as a FeF$_2$ or LiF structure. Moreover, Badway et al. demonstrated that the structure of FeF$_3$ changes from a rhombohedral to a corundum-type.\textsuperscript{3} Therefore, this reaction suggested that the discharge reaction for FeF$_3$ down to 2.0 V was the insertion reaction of Li-ions into the FeF$_3$ structure.

For the conversion reaction region below 2.0 V, Fe diffraction peaks around 45° and 65° were observed down to 1.3 V, and these peak intensities increased in the deeper cycle down to 1.0 V. However, the diffraction peak of LiF after the initial discharge process could not be clearly confirmed, suggesting that the generated LiF consisted of amorphous or nano-particles. On the other hand, the diffraction peak of LiF and Fe was observed in the charged state after the 20th cycle. And these peaks were sharper than that after the initial discharge state (Fig. 5(b)). It was thus revealed that the growth of the LiF and Fe crystal contributed to the lower cyclability of FeF$_3$. Moreover, this result suggested that it may be necessary to investigate the degraded electrode for a deeper understanding of the conversion reaction.

4. The Electrochemical Properties of the Pyrite-type FeS$_2$ Cathode for Na-ion Batteries

The Na-ion battery, which uses an abundant Na source as a novel form of energy storage, has drawn much interest as a large-scale grid system for energy storage with good cost performance. In addition, the large-scale Na-batteries are expected to become commercially viable with the use of earth-abundant transition metals such as Fe and Mn. Therefore, the minor-metal free cathode materials such as O3-type NaFeO$_2$,\textsuperscript{17} Na$_2$FeP$_2$O$_7$ and Na$_2$FePO$_4$F\textsuperscript{18} have attracted attention. However, the theoretical energy density of cathode materials for the Na-ion battery does not reach 500 Wh kg$^{-1}$, which is smaller than that of the LiMn$_2$O$_4$ cathode used for Li-ion batteries. Despite the recent research efforts in this field, the fundamental aspects of the Na host materials remain controversial. To develop Na-ion batteries with a higher energy density, another possible approach is to utilize the conversion reaction. For example, FeS$_2$ as a cathode for Na-ion batteries has a reported discharge capacity of 447 mAh g$^{-1}$ at the first cycle and 70 mAh g$^{-1}$ in 50 cycles at room temperature,\textsuperscript{20} due to the irreversibility of the electrochemical reaction between Na and FeS$_2$. T. B. Kim proposed the following reaction formula:\textsuperscript{21}

$$2\text{Na} + \text{FeS}_2 \rightarrow \text{Na}_2\text{S} + \text{Fe}$$

Although the theoretical capacity of FeS$_2$ according to the above reaction formula is 447 mAh g$^{-1}$, this discharge reaction has been estimated from the Na-S binary phase diagram only. In particular, the rechargeable voltage range is a key factor in determining essential battery properties such as capacity and cycle life. The rechargeable capacities of FeS$_2$ were only reported using a potential window between 0.8 V and 2.8 V. Therefore, the electrochemical properties of FeS$_2$ were evaluated between 0.8–2.6 V and 0.5–3.0 V at 25°C, as shown in Fig. 6. For a potential window between 0.8 V and 2.8 V, the initial discharge capacity at a rate of 0.2 mA cm$^{-2}$ was 465 mAh g$^{-1}$, which corresponds to a 2.0 Na$^+$ reaction with FeS$_2$.\textsuperscript{12} On the other hand, when the potential window was extended between 0.5 and 3.0 V, the cell voltage decreased to 0.5 V through an inflection point at around 1.2 V and 0.7 V. The initial discharge capacity was 758 mAh g$^{-1}$, and the estimated cathode utilization was 85% of the 4.0 Na$^+$ reaction. This electrode behavior cannot be described by only the Fe$^{2+}$/Fe$^0$ redox reaction, and this discharge reaction of FeS$_2$ and sodium was similar to that of FeS$_2$ and lithium as determined from Fe-K edge XANES measurement and Fe Mössbauer spectroscopy.\textsuperscript{23,24} Therefore, the structure change at different sodiated/desodiated states was investigated by XRD measurement. The observed peak intensity of FeS$_2$ decreased as the deeper discharge reaction progressed. When FeS$_2$ reacted with 2Na$^+$, the pristine FeS$_2$ diffraction peaks completely disappeared and transformed into a halo peak with high background. Upon charging to 2.6 V, the XRD pattern of the electrode can be indexed as a mixture of FeS and FeS$_2$. In particular, the XRD pattern had a high background with a halo peak even after the charge, suggesting that the electrode does not recover to its pristine state. In the deeper discharge reaction below 0.8 V, the XRD profile of the FeS$_2$ electrode pellets that have reacted with 3.0 or 3.5 Na$^+$ can be indexed as Na$_2$S, and shows a halo peak with high background. These results suggested that FeS$_2$ could undergo the conversion reaction below 0.8 V, but the metallic iron could not be observed in XRD measurements. Therefore, the oxidation states of iron and sulfur during the sodiation/desodiation reaction were evaluated using Fe and S K-edge XANES. Figure 7 shows the (a) Fe and (b) S K-edge XANES spectra of the initial FeS$_2$ pellet and the 1.0 Na$^+$ through 2.0 Na$^+$ discharged states. Especially, the Fe K-edge position did not shift until the 2.0 Na$^+$ sodiation state, but the pre-edge feature near 7112 eV changed depending on the Na content per FeS$_2$. This pre-edge feature corresponds to 1s → 3d transitions that are dipole forbidden in octahedral symmetry, and their strength therefore indicates that the symmetry decreases. This indicated that there is no valence change of the iron until the 2.0 Na$^+$ sodiation states, while the local structure of iron is changing by the sodium insertion into FeS$_2$ structure. On the other hand, the S K-edge position of FeS$_2$ shifted lower with increasing Na content—namely, the charge neutrality until 2.0 Na$^+$ sodiation states was maintained by the S valence change from (S-S)$^2-$ to S$^{2-}$, instead of the Fe valence change. In addition, the existence of Na$_2$FeS$_2$ as the intermediate phase was also demonstrated using the DFT method.\textsuperscript{25} These facts suggested that the sodiation reaction until 2Na$^+$ can proceed by the following reaction:\textsuperscript{26}

$$2\text{Na}^+ + 2\text{e}^- + \text{FeS}_2 \rightarrow \text{Na}_2\text{FeS}_2$$

In contrast, the Fe K-edge position shifted to lower energy at deeper 3.0 and 3.5 Na$^+$ sodiation states as shown in Fig. 7(c). Although it was not clear whether iron metal was generated in this discharge reaction, a trace of metallic iron was confirmed in the XPS measurement. Moreover, Na$_2$S was confirmed from the XRD profile in a deeper sodiation state than 2.0 Na$^+$ per FeS$_2$. Therefore, we surmised that the sodiation reaction was advanced by the conversion reaction to amorphous Fe and Na$_2$S from FeS$_2$ at more than 2.0 Na$^+$ as follows:
5. LiF-FeO Composite as a Novel Cathode-type for Li-ion Batteries

The conversion-type active materials such as FeF₃ and FeOF cannot be used as cathodes against the pristine carbonaceous materials, which are practically used in the Li-ion battery, because of the lack of lithium for the current carrier. On the other hand, Li-containing and Li metal anodes have been widely studied, but these materials are unfavorable due to safety concerns and chemical instability. Therefore, a lithium-containing cathode is more practical.

FeOF started below 1.8 V in the discharge process— that is, the discharge reaction of the LiFeOF cathode around 1.8 V was included in the conversion reaction of FeOF. To investigate the electrochemical activity of the Li ions in the synthesized LiFeOF cathode, the fabricated cathode was applied in a full cell with LTO as the anode. The obtained products were indexed as a cubic structure with the space group Fm-3m.

Figure 8(a) shows the initial and second charge/discharge profiles of the obtained LiFeOF against Li metal at a rate of 0.2 mA cm⁻².

In this mechanism, the FeF₂ functions as an anion acceptor of fluoride ion after the electrochemical decomposition of LiF during the initial charging process. It would be interesting to observe whether this electrochemical reaction can be used for other composite cathodes. Therefore, we tried to use the LiF-FeO composite as an alternative cathode in place of LiFeOF. Upon the initial charging process, LiFeOF vs. Li metal and (b) the LiFeOF vs. LTO anode at a rate of 0.2 mA cm⁻².

\[
\text{LiF} + \text{FeF}_2 \rightarrow \text{FeF}_3 + \text{Li}^+ + \text{e}^- \quad \text{(Initial charging process)}
\]

\[
\text{Li}^+ + \text{e}^- + \text{FeF}_3 \rightleftharpoons \text{LiFeF}_3
\]

(after the 1ˢᵗ discharging process)
LTO ion-type cell progresses by insert/extract lithium for the obtained LiFeOF cathode. Both the electrochemical activity of LiF mixed with various manganese oxides such as MnO, Mn₃O₄ and Mn₂O₃ showed, and the electrochemical activity of the LiF-Mn₃O₄ composite showed a rechargeable capacity of ca. 200 mAh g⁻¹. These results suggested that their composites can be sufficiently utilized as the cathode for Li-ion batteries.

6. Conclusion

The development of improved conversion-type materials is a challenge for meeting current and future energy storage requirements. Among the members of the fluoride family, TiF₅ can provide small overpotential and good cyclability. However, before the reports have only investigated oxide and FeOF that do not be contained Li-ions. Although the previous used as an anion accepter in order to widely utilize materials such as type cathode of LiF can be used as a lithium source and FeO can be materials. Moreover, our group demonstrated that the composite-cathode of LiF can be improved the cathode properties by using another metal morphology be optimized for active materials. In particular, in the development of additives into active materials, it may be further improve the cathode properties by using another metal compound with higher electric conductivity instead of carbonaceous materials. Moreover, our group demonstrated that the composite-type cathode of LiF can be used as a lithium source and FeO can be used as an anion accepter in order to widely utilize materials such as FeOF that do not be contained Li-ions. Although the previous reports have only investigated oxide and fluoride, we believe that the development of sulfides and polyanions for use as anion acceptor will lead to a breakthrough in the exploration of active materials for next-generation Li-ion batteries.

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