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 capacitances. 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 the 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 (Vdiff) 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 voltage relaxation for the 24 h relaxation time was large below 2.0 V, and it was also large during the charge process. However, Vdiff did not become zero after the 24 h relaxation time. Moreover, Liu et al. reported that the Vdiff 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 was evaluated using various currents ranging from 35 mA g⁻¹ to 712 mA g⁻¹. The initial discharge capacity remained 250 mA h g⁻¹, and the capacity maintenance
followed by an equivalent 1, 12, and 24 h relaxation time.

...rate of 35 mA g⁻¹ ca. 600 mAh g⁻¹ between 1.0 V and 4.5 V with various currents from 35 mA g⁻¹. The quasi-open circuit voltage (QOCV) curves of FeF₃ show the cyclability of FeF₃ between 1.0 V and 4.5 V at a rate of 35 mA g⁻¹.

...capability was a reaction of the low conductivity. Moreover, the obtained electric conductivity of FeF₃ was 1 x 10⁻¹⁵ S cm⁻¹; namely, this lower rate capability was a reflection of the low conductivity. Moreover, Fig. 2(b) shows the cyclability of FeF₃ between 1.0 V and 4.5 V at a rate of 35 mA g⁻¹ and 712 mA g⁻¹. The rechargeable capacity, ca. 600 mAh g⁻¹ at a rate of 30 mA g⁻¹, was obtained in the initial cycle, but it was rapidly decreased to 100 mAh g⁻¹ after 10 cycles. At a rate of 712 mA g⁻¹, the rechargeable capacity was increased to ca. 400 mAh g⁻¹ after a few cycles, but it was also decreased to 100 mAh g⁻¹ after 20 cycles. These results suggested that the cyclability of FeF₃ is quite poor in the conversion reaction region.

FeOF has been proposed by N. Pereira et al. as a new candidate with larger theoretical capacity than that of FeF₃. However, it is difficult to obtain a uniform FeOF single phase from conventional solid-state or solution-process synthesis. In particular, a quick route for the synthesis of FeOF must be developed in order to decrease the volatilization amount of fluorine in FeOF. We attempted to use the roll-quenching method to quickly synthesize FeOF from a mixture of FeF₃ and Fe₃O₄. The composition of FeOF determined by an atomic adsorption spectrophotometer (AAS) and an ion chromatography (IC) was FeO₁.₁₂F₀.₉₇. The low deficiency of fluorine was caused by the stronger volatility of fluorine relative to that of oxygen. The FeOF obtained by the roll-quench method has higher crystallinity than that obtained by the ion exchanged and liquid-state. It could be indexed as a tetragonal structure with the space group P₄ᵥ̅mnm, and a small amount of the starting material, FeF₃, remained as an impurity.

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 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 FeF₃ between 1.3 and 4.5 V and a FeF₂ between 1.5 and 4.5 V 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 FeF₃ 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 TiF₃, which has the same structure as FeF₃. The electrochemical properties of TiF₃ have already been reported by our group. 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. In the case of FeF₃, 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 x 10⁻⁹ S cm⁻¹) was higher than that of FeF3 (1 x 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
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-ion 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 20$^{\text{th}}$ 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{11} Na$_2$FePO$_4$O$_3$ and Na$_2$FePO$_4$F\textsuperscript{19} 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 eorts 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}

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

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 discharge-charge 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$^{3+}$ 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{3,24} 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 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 $\rightarrow$ 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:

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

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 FeF$_3$ 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, and the study of LiFeF$_3$ should be of great importance in developing the next-generation Li-ion battery with a large capacity. However, LiFeF$_3$ cannot be obtained using conventional direct synthesis processes such as the solid-state method or hydrothermal method. As one alternative, Kim et al. proposed to utilize the LiF-FeF$_2$ nanocomposite, which has the same composition as Li$_{1-x}$FeOF, as a cathode material for Li-ion batteries. Actually, the LiF-FeF$_2$ nanocomposite showed a reversible specific capacity of ca. 190 mAh g$^{-1}$, which corresponded to 84% of the theoretical capacity based on the 1Li reaction per LiFeF$_3$ (225 mAh g$^{-1}$), with an average voltage of 3.58 V. The electrochemical reaction for this composition was proposed to be the following:

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

In this mechanism, the FeF$_2$ 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 Li$_{1-x}$FeOF.

The mixture of LiF and FeO particulate was milled by the dry ball-milling method under an Ar atmosphere for 24 h, and the obtained products were milled again with 5 wt% or 20 wt% AB. The diffraction peaks for the obtained product were observed at 36°, 43°, and 62°. These peaks were similar to those of the FeOF electrode after 1Li insertion into the FeOF structure, namely Li$_{1-x}$FeOF, which has the same structure as the discharged intermediate product of the FeOF cathode, was obtained from the ball-milling method. The obtained products were indexed as a cubic structure with the space group $Pm-3m$.

Figure 8(a) shows the initial and second charge/discharge profiles of (a) the Li$_{1-x}$FeOF vs. Li metal and (b) the Li$_{1-x}$FeOF vs. LTO anode at a rate of 0.2 mA cm$^{-2}$.

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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, Mn$_2$O$_4$ and Mn$_3$O$_4$ showed, and the electrochemical activity of the LiF-Mn$_2$O$_3$ 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, TiF$_3$ 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 materials. Moreover, our group demonstrated that the composite-/further improve the cathode properties by using another metal development of additives into active materials, it may be possible to morphologies be optimized for active materials. In particular, in the challenge for meeting current and future energy storage require-

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