Electrochemical Properties of Trirutile-type Li$_2$TiF$_6$ as Cathode Active Material in Li-ion Batteries

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The electrochemical properties of lithium hexafluorometalates as positive electrode materials were studied. Trirutile-type Li$_2$TiF$_6$ was synthesized through a complex-formation reaction under mild temperature conditions. In addition, a spray-drying technique was used to obtain electrodes with a large surface area. The electrochemical performance of the resultant Li$_2$TiF$_6$ powders was investigated vs. Li metal as negative electrode. Li$_2$TiF$_6$ exhibited an initial discharge capacity of 100 mAh g$^{-1}$ at 2.7 V.

Key Words : Metal Fluoride Cathodes, Trirutile Compounds, Spray Drying, Li$_2$TiF$_6$

1 Introduction

Nowadays, the chemistry of fluoride-based and fluorine-containing compounds has become intriguing in the field of lithium batteries research. The high theoretical capacity and attractive output voltages of fluorides have provoked exploration into their electrochemical activity. Several kinds of 3d-transition metal fluorophosphates containing lithium, such as Li$_2$CoPO$_4$F,$^3$ Li$_2$M(PO$_4$)$_2$F$_z$ (M = V, Cr),$^2$ and LiMPO$_4$F (M = V, Fe),$^2$ NaVPO$_4$F,$^4$ Na$_2$FePO$_4$F,$^5$ and Na$_2$V$_2$(PO$_4$)$_3$F$_z$ have been reported as cathode active materials. In fact, the redox couples used in fluorine-containing compounds showed an increase in operating potential compared to their phosphate analogues. It is reasonable to expect a higher operating voltage by use of fluorine anions in the cathode material composition, because the energy of the antibonding M-d orbitals of the transition metal ion is stabilized by ionic M-F bonds.$^7$ On the other hand, the presence of large polyanions such as PO$_4$ groups restricts the theoretical capacity. Based on the above considerations, we suppose that the use of pure fluorides as an active material in the cathode composition could contribute to increasing both the working potentials and the reversible capacities. Compared to the broad and extensive research on oxides as electrode materials, the knowledge of fluoride compounds is limited. In their pioneering study, Arai et al. examined a group of 3d metal trifluorides MF$_3$ (M = Mn, Fe, Co, V, Ti and Ni) for their properties as cathode active materials.$^8$ In this first study, the transition metal fluorides showed insufficient reversible capacity due to their low electroconductivity owing to the highly ionic character of the metal-halogen bond, which induces a large energy band gap. This problem was successfully overcome by use of FeF$_3$/C nanocomposite. In their study, Badway et al. proved that high energy ball milling with carbon brings huge reversible capacity more than 600 mAh g$^{-1}$ at 70 °C for FeF$_3$/C nanocomposites as conversion cathode material.$^9,10$

In fact, few lithium-based metal fluorides have been synthesized. Several studies have demonstrated the existence of a series of LiAMP$_x$ compounds (A = Mg, Ca, Sr and Ba, M = Ti, V, Cr, Mn, Fe, Co and Ni). A majority of combinations between thermodynamically compatible divalent and trivalent first-row transition-metal fluorides formed a trirutile lattice with the composition LiM$^+$M$^{2+}$F$_6$.$^11,12$ Koyama et al. reported operating potential of 5.80 V for LiCaCoF$_6$ based on predictive calculations.$^{14}$ However, there are no experimental data on such fluorides as electrode materials reported. In this work, we investigated the electrochemical properties of Li$_2$TiF$_6$ to study the effect of fluorine on the working potential upon the insertion and extraction of lithium.

2 Experimental

2.1 Preparation

As a precursor, H$_2$TiF$_6$ was first formed by dissolution of dried anatase-type TiO$_2$ (99% WAKO) dissolved in 46% hydrofluoric acid (HF) in a PTFE crucible. By adding an equivalent amount of Li$_2$CO$_3$ (99% WAKO), a precipitate was obtained. White crystalline phase was obtained after evaporation to dryness at T < 110 °C of filtrated precipitate solution. To ensure the total removal of absorbed water and HF, additional vacuum drying at T > 300 °C was performed because at higher temperature Li$_2$TiF$_6$ undergoes a primary decomposition to LiF and TiF$_4$. When heated in air, Li$_2$TiF$_6$ decomposes by hydrolysis, resulting in the formation of TiO$_2$, LiF and HF.$^{13}$ As an alternative method of preparation, the spray-dry technique was used to fabricate submicron-scale materials. The solution was atomized via a nozzle at an air pressure of 0.2 MPa, and was dried with hot air in a spray-dryer (Buchi Mini Spray Dryer B-290). The inlet air temperature was 120 °C, and the exit air temperature was 80 °C.
2.2 Characterization

The reaction products were identified by X-ray powder diffraction (Rigaku RINT2100HLR/PC) using Cu Kα radiation at a 2°/min scan rate. Scanning electron microscopy (FE-SEM) using a JEOL JSM-340F was performed to observe the morphology of obtained samples. The X-ray photoelectron spectroscopy (XPS) measurements were performed with a JPS-9000 (JEOL) with Mg Kα radiation (1253.6 eV). The test cathode pellets were placed on the holder under an argon atmosphere and transferred into the XPS sample chamber without being exposed to air. The synthesized materials were subjected to electrochemical evaluation in a coin-type cell 2032 vs. Li metal as a negative electrode. Celgard 3501 was used as a microporous separator. The pellet-type electrodes were composed of 70 wt% active material, 25 wt% acetylene black, and 5 wt% PTFE as a binder. The electrolyte used here was 1 M LiPF₆ in 1:1 ethylene carbonate/diethyl carbonate, and was aged for 12 h before the electrochemical measurements to ensure full absorption of the electrolyte into the electrode. The galvanostatic tests at an ambient temperature of 25°C between 2.0 V and 4.5 V were conducted using an automatic cycler unit (Nagano BTS-2004). A 60 min rest period was performed between the charge and discharge steps.

3 Results and Discussion

The XRD pattern of the obtained lithium hexafluorotitanate is shown in Fig. 1. The Li₃TiF₆ pattern corresponded to ICDD No. 24-662 indexed as trirutile type (space group P42/mnm). Further, the diffraction peaks of Li₃TiF₆ are quite narrow (Fig. 1a), indicating high crystallinity of the sample obtained by complex-formation. On contrary, the sample subjected to additional spray-drying demonstrated broader peaks in the XRD pattern due to decreased particle dimensions (Fig. 1b). Previous report revealed that lithium ions in trirutile structure of Li₃TiF₆ were located in the comparatively wide spaces around the TiF₆-octahedron. We regarded it as a precondition for better Li ionic conductivity in the crystal structure. However, the reported conductivity of sintered fluorocomplexes was 2 × 10⁻⁸ S cm⁻¹ at 300°C for Li₃TiF₆. Extrapolating this data to room temperature, one gets a very low conductivity. Practical conductivity of the hexafluorotitanate could be obtained by ensuring good conductive carbon coatings around the active particles. On the other hand, preparing an electrode material with small particle dimensions should improve its performance, as well. Therefore we choose a spray-drying method as a low-cost and low-temperature synthesis route to obtain material with fine particles in order to increase the number of active sites available for surface reactions.

Figure 2 shows FE-SEM images of Li₃TiF₆ powders prepared by a complex-formation reaction (Fig. 2a) and those obtained via the spray-drying method. The particle size of the sample with higher crystallinity (Fig. 2a) was in the range of micrometers (with a particle size distribution up to 8.5 μm). The spray-drying procedure gave spherical agglomerates (Fig. 2b) consisting of oval-like nanostructures (100 - 150 nm wide). In addition, the powders with lower crystallinity were rounded without sharp edges, having a common morphology for materials spray-dried in air.

The electrochemical characteristics of Li₃TiF₆ have not yet been demonstrated or discussed in detail. The theoretical capacity for receiving the end member Li₃TiF₆ of the material by a single electron reaction of a Ti⁴⁺/Ti³⁺ redox couple is 152 mAh g⁻¹. Figure 3a shows the cycling profile of a representative cell of Li₃TiF₆ active material obtained by complex-formation reaction. The Li₃TiF₆/Li cell delivers an initial discharge capacity of 98 mAh g⁻¹ at room temperature. The plateau of the discharge curve was observed at 2.7 V, where the reduction of Ti⁴⁺ takes place.

The effect of the reduction of particle size on the electrochemical performance is shown in Fig. 3b. Unfortunately, in this pilot study, we can report only a 10% improvement of discharge capacity for the samples obtained by the spray-drying method. After a few cycles, the capacity faded, but about 70% of the maximum capacity is still maintained as shown in Fig. 4.

The reason for the rapid decrease in capacity is still
Fig. 3 First and second discharge-charge curves of as prepared (a) and spray-dried (b) Li$_2$TiF$_6$ in LiPF$_6$/EC: DMC (1 : 1 wt %) with a current density of 0.2 mA cm$^{-2}$.

Fig. 4 Variation of discharge capacity with cycle number for as-synthesized Li$_2$TiF$_6$ (○) and obtained by the spray-drying method (■).

Fig. 5 An XRD pattern of Li$_2$TiF$_6$ for cathode pellets taken on Al holder. Cells were opened after the first discharge (b) and after 1 cycle (a).

Fig. 6 XPS spectra of F 1s, Ti 2p and Li 1s at room temperature of Li$_2$TiF$_6$ in different electrochemical stages (△: initial fresh pellet; O: discharged down to 20 V; -X- after 1 cycle).

unclear although partial dissolution of the active material was suggested due to the more significant solubility of ionic compounds as fluorides in a polar solvent such as propylene carbonate or ethylene carbonate than that of covalent compounds. An XRD measurement of the pellet electrodes after first discharge and subsequent charge states showed no significant difference from structures of the initial composition and the sample after electrochemical Li insertion (Fig. 5). A small peak is seen in the discharged state, but it cannot be indexed and attributed to structure changes. Therefore, the reason for the rapid decrease in capacity is still unclear. The mechanism of the capacity fading upon cycling is complicated, and much more work, such as MS or FTIR studies, should be done to elucidate its origin.

The electronic structure and the variation of binding energies in charge/discharge states for pellet cathodes at room temperature were studied by XPS measure-
ments (Fig. 6). All data were corrected by the C 1s binding energy of carbon, which corresponded to 284.3 eV. The spectrum taken from the surface of the fresh pellet, before being subjected to electrochemical measurement, shows a binding energy of 462.6 eV for Ti 2p$^{3/2}$. This value is in agreement with the reported one for the analogous sodium compound Na$_2$TiF$_6$. In the discharged state, the binding energy shifted downward by 0.7 eV for the Ti 2p envelope along with a change in the valence state from Ti$^{4+}$ to Ti$^{3+}$ upon lithium insertion, and returned to a higher energy in the charged state.

In order to view the spectra associated with each of the elements of interest, XPS narrow scans of F 1s and Li 1s were also carried out. There was no distinguishable difference between the binding energies of F 1s electrons with different states of charge and discharge. Two components could be clearly seen in the F 1s spectra, consisting of sharp peaks at 685.7 eV and 689.2 eV, respectively. The latter peak is attributed to $(-\text{CF}_2)_{n}$ from the PTFE binder used in electrode composition. We also observed that when the pellet was etched with an Ar ion beam for 5 s, PTFE decomposed and this second peak was completely eliminated from the spectra.

4 Conclusions

The electrochemical properties of trirutile Li$_2$TiF$_6$ as an active material for Li-ion batteries were investigated. From our preliminary data, it was found that the Li$_2$TiF$_6$ framework allowed reversible insertion of up to 0.7 Li per formula weight and delivered an initial discharge capacity of 100 mAhg$^{-1}$ at 2.7 V. The reversible capacity decreased over repeated charge and discharge cycles even though the crystal structure of Li$_2$TiF$_6$ was maintained. Hence, some amount of the Li-ions could be consumed by the decomposition of electrolyte or by partial dissolution of the active material. To the best of our knowledge the value of operating potential of 2.7 V for Li$_2$TiF$_6$ is highest reported for Ti$^{4+}$/Ti$^{3+}$ redox couple. The results indicate that the use of a more electronegative species in the active materials composition should result in an increase in the potential at where lithium insertion takes place. To further improve the electrochemical performance of Li$_2$TiF$_6$ as a cathode active material, we must study the effects of conductive additives and thereby optimize the amount of the carbon coating around the active particles.

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References