Electronic States in the Discharge Process of AgCuF₃ as a Positive Active Material for a Solution-based Fluoride-ion Battery

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The silver copper fluoride (AgCuF₃) perovskite active material was synthesized *via* mechanochemical reaction from the corresponding fluoride precursors. The defluorination/fluorination reaction of the AgCuF₃/C composite electrode was demonstrated in the electrolyte solution of the fluoride-ion battery at 298 K, and the capacity of 80 mAh g⁻¹ was obtained in the first discharge process. The XPS spectra of the Cu 2*p* region clearly showed that metallic Cu⁰ species were formed on the surface of the composite electrode after the discharge. In addition, the F 1*s* spectrum indicated that the metal-bound fluorine species were formed after discharge, although the Cu²⁺ species still remained inside the composite electrode. That is, the defluorination reaction of AgCuF₃ clearly took place at the interface between the electrode and the electrolyte solution.

1. Introduction

Rechargeable batteries with high energy density that can store energy from renewable sources have been required for recent applications such as battery electric vehicles and large-scale energy storage. Fluoride-ion batteries (FIBs) have attracted much attention as a candidate for innovative batteries to outperform current lithium-ion batteries, because by selecting appropriate active materials for the positive and negative electrodes, high energy density batteries can be prepared [1]. In the FIBs, conversion between a metal fluoride (MF_x) and metal (i.e., the defluorination/fluorination of MF_x) occurs at the electrodes during the discharge process as follows:

 $MF_x + xe^- \rightarrow M + xF^-$ (at the positive electrode) $M' + xF^- \rightarrow M'F_x + xe^-$ (at the negative electrode)

Most research on the FIBs has been conducted in all-solid-state cells at high temperatures [2]. In contrast, liquid electrolytes can operate at room temperature and could be expected to maintain good contact at the electrode-electrolyte interface during the charge and discharge processes [3]. In this study, AgCuF₃ with a theoretical capacity of 352 mAh g⁻¹ for 3 e⁻ reduction was considered as a candidate for the positive active material. Then, we investigated the defluorination/fluorination reaction of the AgCuF₃/C composite electrode in a liquid electrolyte of the FIB at room temperature. Previously, AgCuF₃ was investigated as an active material for the conversion type lithium-ion battery [4]. Therefore, this is the first attempt to fabricate the solution-based FIBs using the AgCuF₃ perovskite active material. The defluorination reaction of AgCuF₃ during the

discharge process has been characterized based on the electronic state of the Cu species.

2. Experimental

AgCuF₃ was synthesized via mechanochemical reaction between AgF (Sigma-Aldrich, 99%) and CuF₂ (Sigma-Aldrich, 98%) precursors using a planetary ball milling [4,5]. Due to the extreme sensitivity of the reagents and product to air, all manipulations were carried out in an argon-filled glovebox. Thus-prepared AgCuF₃ powder was confirmed by X-ray diffraction analysis (XRD, not shown), and its pattern agreed well with the reference pattern #174407 in the ICSD database. Electrochemical measurements, such as cyclic voltammetry (CV) and galvanostatic chargedischarge (GCD) test, were performed using an AgCuF₃/carbon composite electrode prepared as follows. The AgCuF3 and acetylene black (AB; FUJIFILM-Wako) were well mixed via ball milling in a wet process with an organic solvent. The composite powder was then mixed with the PVdF/Nmethyl-2-pyrrolidone (NMP) solution (KF polymer L#9130, Kureha) to prepare the composite slurry. The slurry was then coated on Al sheet as a current collector with a thickness of 200 µm. Consequently, composition the electrode the of was AgCuF₃:AB:PVdF=6:3:1 in weight ratio after sufficient evaporation of NMP. The liquid electrolyte was prepared by dissolving tetramethylammonium fluoride (TMAF; Sigma-Aldrich) in N,N,Ntrimethyl-N-propylammonium bis(trifluoromethanesulfonyl)amide (TMPA-TFSA; Kanto Chemical)



Fig. 1 CV of the AgCuF₃/C composite electrode in TMAF/TMPA-TFSA at a scan rate of 1 mV s⁻¹ at 298 K.

with various concentrations such as 0.075 mol dm⁻³ (the molar ratio of TMAF:TMPA-TFSA=1:50). TMAF was sufficiently dehydrated by azeotropic distillation prior to use. The Pt wire and Pb plate were used as the counter electrode for CV and GCD test, respectively, and the potential was controlled based on the Pb wire on which PbF2 was electrochemically deposited as the reference electrode (denoted as Pb|PbF₂). After the GCD test, the cell was disassembled and the composite electrode was washed several times with acetonitrile. The electrode was analyzed as follows. The X-ray photoemission spectrum (XPS) was measured using a scanning X-ray photoemission apparatus (PHI Quantes, ULVAC-PHI) with Al Ka (1486.7 eV) source at SA-1 in Ritsumeikan SR Center. Cu L-edge X-ray absorption spectrum (XAS) measurement was performed at beamline BL-2 in Ritsumeikan SR Center. The spectra were taken with the partial fluorescence yield (PFY) modes under vacuum.

3. Results and discussion

Figure 1 shows a CV of the AgCuF₃/C electrode



Fig. 2 GCD profiles of the Pb|TMAF/TMPA-TFSA| (AgCuF₃/C) cell at the 1/200C rate at 298 K. The potential was controlled by the Pb $|PbF_2$ electrode.

at a scan rate of 1 mV s⁻¹. During the first sweep to negative potential, the anode current gradually increased from 0.65 V vs. Pb|PbF2 and peaked at 0.1 V. In subsequent cycles, the anodic peak remained stable and was observed at about 0.4 V. Meanwhile, Figure 2 shows the GCD profiles of the cell composed of Pb|TMAF/TMPA-TFSA|(AgCuF₃/C) at the 1/200C rate. The initial discharge capacity was about 80 mAh g^{-1} , and the first step discharge reaction occurred between 0.85 V and 0.4 V. The following first charge capacity was further reduced to 38 mAh g⁻¹, which was 48% of the first discharge capacity. The second and third profiles were similar, i.e., the discharge plateau was in the range of 0.6-0.5 V. Here, the defluorination reaction of AgCuF₃ is considered to proceed in two steps as follows.

$$AgCuF_3 + e^- \rightarrow Ag + CuF_2 + F^-$$
(1)

 $\begin{array}{ll} CuF_2+2e^- \rightarrow Cu+2F^- \qquad (2)\\ \mbox{Previously, we confirmed the formation of metallic} \end{array}$

Ag (Equation 1) by XRD and electron microscopy observation after the initial discharge reaction (not shown). However, the formation of metallic Cu (Equation 2) could not be confirmed by XRD.



Fig. 3 (a) Cu $2p_{3/2}$, (b) Ag 3*d* and (c) F 1*s* photoemission spectra of the AgCuF₃/C composite electrodes in the initial state (black line) and after discharge (blue line).

Therefore, we attempted to investigate the electronic states of copper species in the composite electrode by XPS and XAS after the discharge process.

Figure 3 shows XPS spectra in the region of Cu $2p_{3/2}$, Ag 3d and F 1s before and after the first discharge. In the Cu $2p_{3/2}$ region, the peak corresponding to the metallic Cu⁰ species was obviously observed at 933 eV, in contrast to the significant decrease in the intensity of the Cu2+ species at 936 eV, shown as an arrow after the discharge. Similarly, in the F 1s region, the peak intensity of the metal-bound fluorine species at 684.5 eV was relatively low compared to the peak derived from PVdF. These results indicate that the electronic state of the copper in the AgCuF₃/C composite electrode was changed from Cu²⁺ to Cu⁰ during the discharge. However, considering that the discharge capacity in Fig. 2 is only 23% of the theoretical capacity, much of the Cu should be present as fluoride. This issue will be discussed later, along with the results of the XAS analysis. In addition, the shift of the peak in the Ag 3d region has not been considered at this time. It is necessary to analyze in detail both before and after discharge.

Figure 4 shows X-ray absorption near edge structures (XANES) at Cu L3-edge of AgCuF3 before and after the first discharge. The absorption peaks were observed at 931.0 eV and 951.1 eV for the composite electrode before discharge, whereas the peaks were observed at 931.7, 934.3, and the broad absorption was around 954 eV after discharge. The absorption peak at 931.7 eV after discharge indicated that Cu²⁺ species remained on the composite electrode, reflecting the low discharge capacity in Fig.2. XPS analyzes the shallow surface of the electrode sheet, while XANES, obtained in the PFY modes, is derived from the deeper electronic state of the electrode sheet. Here, the presence of Cu⁺ (monovalent) was a concern because the Cu⁰ and Cu⁺ peaks are observed at very close energies (Fig. 4) and similarly, are also close in the Cu 2p region of the XPS (Fig. 3a). In general, the monovalent fluoride of copper is considered to be unstable. As for the oxide (Cu₂O), no metal-bound O peak was detected in the O 1s region of XPS (not shown). For these reasons, we concluded that Cu⁺ species were not formed after the discharge. Measurement of the Auger region of Cu using a different X-ray source (e.g., Mg Ka) would be clear about it. These results suggest that metallic Cu⁰ species are formed near the surface of the electrode sheet as a result of the defluorination reaction, while fluoride is still present in the interior of the composite electrode sheet. These results indicate that the AgCuF₃/C composite electrode was partially defluorinated in the electrolyte solution at room temperature. It is suggested that this reaction occurred near the surface of the composite sheet, i.e.,



Fig. 4 Cu L_3 -edge XANES of the AgCuF₃/C composite electrode before (black line) and after discharge (blue line) obtained in the PFY modes.

at the interface between the electrode and the electrolyte solution. Additionally, the reaction potential of Ag species and its mechanism are still unclear and require further investigation.

4. Conclusions

The AgCuF₃/C composite electrode was able to discharge and charge in the TMAF/TMPA-TFSA electrolyte solution of the FIB at 298 K, and the capacity of 80 mAh g⁻¹ was obtained as the first discharge process. The XPS spectrum of Cu 2p region clearly showed that metallic Cu⁰ species were formed on the surface of the composite electrode after the discharge. In addition, the F 1s spectrum indicated that the metal-bound fluorine species were reduced after the discharge. Cu L3-edge XANES analysis showed that the metallic Cu⁰ species were formed after the discharge process, although the Cu²⁺ species still remained in the composite electrode. That is, the defluorination reaction of AgCuF₃ clearly took place in the electrolyte solution-based FIB.

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