Fluoride Intercalation of Oxyfluorosulfide as an Active Material for a Liquid-Based Fluoride Shuttle Battery

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Rechargeable batteries with high energy density have been required for recent applications such as battery electric vehicles. Fluoride shuttle batteries (FSBs) can achieve high energy density by using monovalent fluoride ions as charge carriers and multi-electron reactions of electrode active materials, and have attracted much attention as a candidate to surpass the performance of the current lithium-ion battery. Previously, an FSB using a crystal capable of fluoride intercalation (insertion-extraction) reaction as an active material has been developed[1]. Recently, an all-solid-state FSB using an oxyfluorosulfide ($Sr_2F_2Fe_2OS_2$; SFFOS) as the intercalation-type positive active material has been reported, and the battery operated with high capacity and good reversibility at 413 K[2]. In this study, we evaluated SFFOS as an active material for liquid-based FSB. Specifically, we measured the thermal effect on the intercalation reaction of SFFOS in an ionic liquid-based electrolyte solution.

The SFFOS was synthesized from four powders: SrF_2, SrO, Fe, and S, in a 1:1:2:2 molar ratio, as previously described[2,3]. The powders were ground together mechanically under argon and pressed at 6 MPa to form a pellet. Then, the pellet was vacuum-sealed in a quartz tube and sintered at 1073 K for 36 hours to obtain the SFFOS. The electrolyte solution was prepared by dissolving anhydrous tetramethylammonium fluoride (TMAF) in an ionic liquid, *N*,*N*,*N*-trimethyl-*N*-propylammonium bis(trifluoromethanesulfonyl)amide (TMPA-TFSA), at a TMAF to TMPA-TFSA molar ratio of 1:50 (0.075 mol/dm^3). The working and counter electrodes were prepared by mixing of SFFOS or PbF_2 with acetylene black and PVDF, respectively. The galvanostatic intercalation reaction of fluoride ions into SFFOS was measured using a three-electrode cell with a Pb|PbF_2 reference electrode at 298, 343, and 373 K.

The galvanostatic intercalation reaction of the SFFOS/AB/PVDF composite electrode, which corresponds to the charging process, exhibited a plateau around +0.5 V versus Pb|PbF_2. The deintercalation (discharging) reaction showed a discharge plateau around 0 V. These plateaus were similar to those previously reported for all-solid-state FSB[2]. During charging, the XRD peak assigned to (006) shifted toward smaller angles depending on the number of intercalated F^- ions.

References

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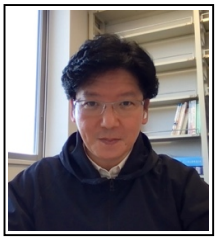

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