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Redox Characterization of an All-Solid-State Fluoride-Ion Battery using Hard X-Ray Photoelectron Spectroscopy

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Fluoride-ion batteries (FIBs) have been attracting academic attention in recent years as next-generation rechargeable batteries. Among transition metal fluorides, CuF_2 is a promising positive electrode material for FIBs because of its high theoretical capacity and moderately high redox potential [1,2]. In this study, a dual cation fluoride, $AgCuF_3$, is proposed as a novel positive electrode material for FIBs, which shows high redox potential and moderately high theoretical capacity. The electrochemical performances of $AgCuF_3$ in a bulk-type all-solid-state FIB were evaluated at 200 °C, and its reaction mechanism was investigated using hard X-ray photoemission spectroscopy (HAXPES).

$AgCuF_3$ was synthesized by ball-milling AgF and CuF_2 [3]. The composite cathode was prepared by ball-milling $AgCuF_3$, $Ca_{0.5}Ba_{0.5}F_2$ (solid electrolyte), and acetylene black (AB, conductive agent). $La_{0.95}Sr_{0.05}F_{2.95}$ (LSF) was used as a separator for the positive and negative electrodes. Pb foil was used for the negative electrode. The composite cells of Pb|LSF|$AgCuF_3$ were fabricated by uniaxially pressing. Discharge-charge tests were performed at 200 °C with a current density of 0.05 mA cm^{-2}. After the tests, the cells were disassembled in a glove box and used for HAXPES measurements. The HAXPES measurements were performed using a PHI Quantes (ULVAC-PHI) with monochromatic Cr K_α radiation (5414.9 keV). The pass energy was set to 69 eV. Dual-beam charge neutralization was applied to suppress sample charging. Binding energies were calibrated for the C 1*s* signal from AB at 284.6 eV.

The $AgCuF_3$ electrode showed good reversible capacities up to 10 cycles at 200 °C. The Cu $2p_{3/2}$ core-level spectra of the $AgCuF_3$ electrode are shown in Fig. 1. The as-synthesized $AgCuF_3$ powder and the pristine electrode shows a peak at 936.4 eV and a satellite band at ~943 eV, characteristic of Cu^{2+}. The pristine electrode included an additional peak at 932.6 eV from Cu^0 because of the partial reduction during electrode preparation. It is shown that $AgCuF_3$ was transformed to Cu^0 by discharging (1d, 10d in Fig. 1) and then back to Cu^{2+} by the subsequent charging (1c, 10c). The chemical shifts were negligible in the Ag $3d_{5/2}$ spectra, but the Auger LMM2 spectra showed some changes with the discharge-charge cycle (not shown). These results suggest that $AgCuF_3$ changes metallic Cu and Ag by discharging (defluorination) and returns to $AgCuF_3$ (and partly CuF_2 + AgF) by charging (fluorination).

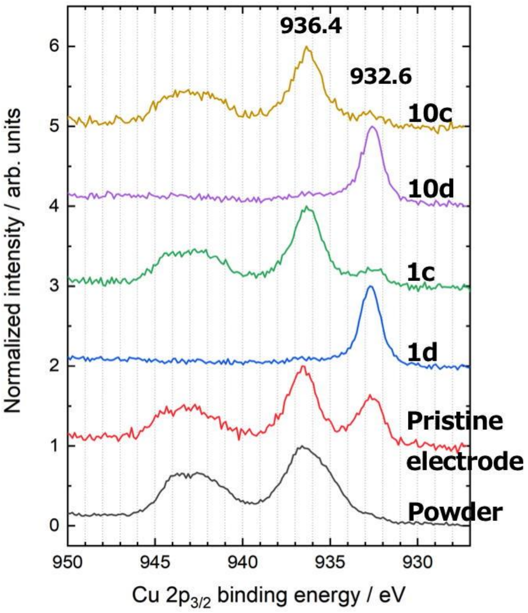

Fig. 1 Cu $2p_{3/2}$ core-level spectra of the $AgCuF_3$ electrode during discharge-charge cycle.

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References

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