Electronic Supplementary Material (ESI) for ChemComm.


Supporting Information

# Copper Metal Electrode Reversibly Hosts Fluoride in a 16 *m* KF Aqueous Electrolyte

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### *Electrochemical Characterization*

Free-standing film electrodes were used in this study. They were composed of 60 wt.% copper powder, 30 wt.% multiwalled carbon nanotubes (Aldrich, 98% carbon basis), and 10 wt.% polytetrafluoroethylene (PTFE) binder. Studies with KF solid added in the electrode were conducted using free standing films created by adding KF directly into the mixture of active mass and carbon additive before electrode fabrication. The mass of salt added corresponds to the total number of ions needed to provide a capacity of 300 mAh/g (based on the mass of Cu) for the conversion of Cu to $CuF_2$. To prevent oxidation of Cu electrodes, they were fabricated in an argon filled glovebox and dried under vacuum at 50°C. Cells were assembled in a Swagelok three-electrode configuration. An Ag/AgCl reference electrode (CH Instruments CHI11P) filled with 3 M KCl was used. The counter electrode was fabricated with 80 wt.% activated carbon, 10 wt.% KB, and 10 wt.% PTFE binder, with an active mass loading of 200 mg/cm$^2$. Galvanostatic charge-discharge (GCD) profiles and cycle life were evaluated on a Landt CT3002A battery test system. Cyclic voltammetry (CV) tests were conducted on WMP-3 multichannel workstation.

### *Physical Characterization*

*Ex situ* X-ray diffraction (XRD) patterns were collected on a Rigaku Ultima IV diffractometer with Cu Kα radiation (λ = 1.5406 Å).

X-ray photoelectron spectroscopy (XPS) results were acquired on a Physical Electronics VersaProbe III using a monochromatic Al Ka X-ray source. The data were collected from an 800um X 200 um area using low energy ion and electron neutralization. The data were subsequently charge corrected with respect to the carbon *1s* at 284.8 eV. The spectrometer's energy scale is calibrated with Au *4f* at 84.0 eV and Cu $2p_{3/2}$ at 932.7 eV.

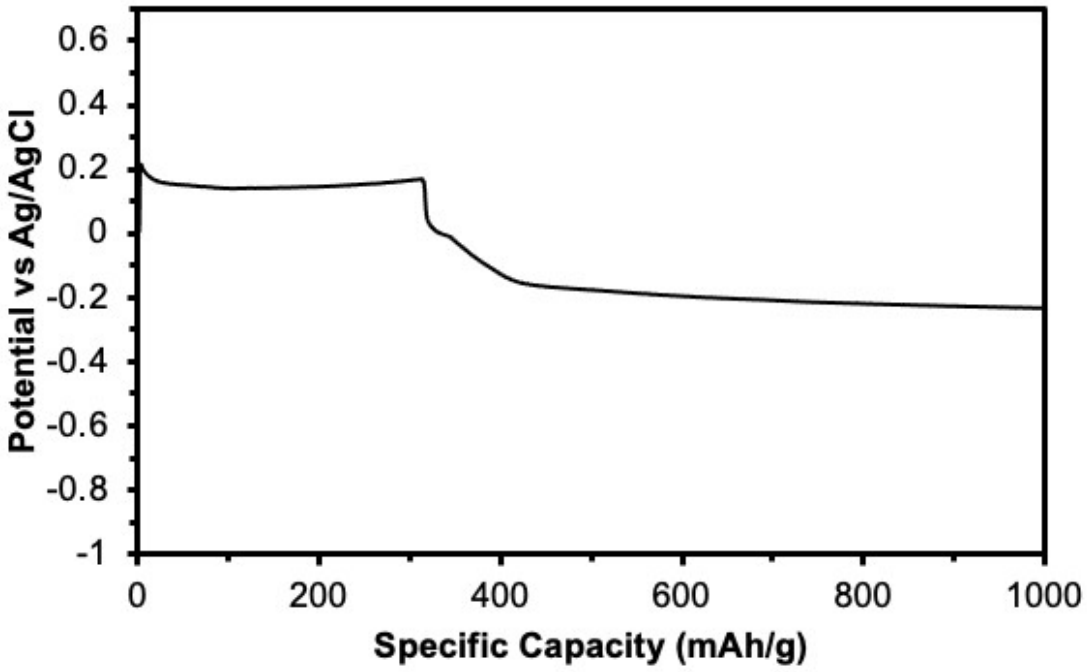


**Figure S1**. GCD potential profile for the 1st charge in 1 *m* KF at 500 mA/g. The cell failed before the discharge process starts.

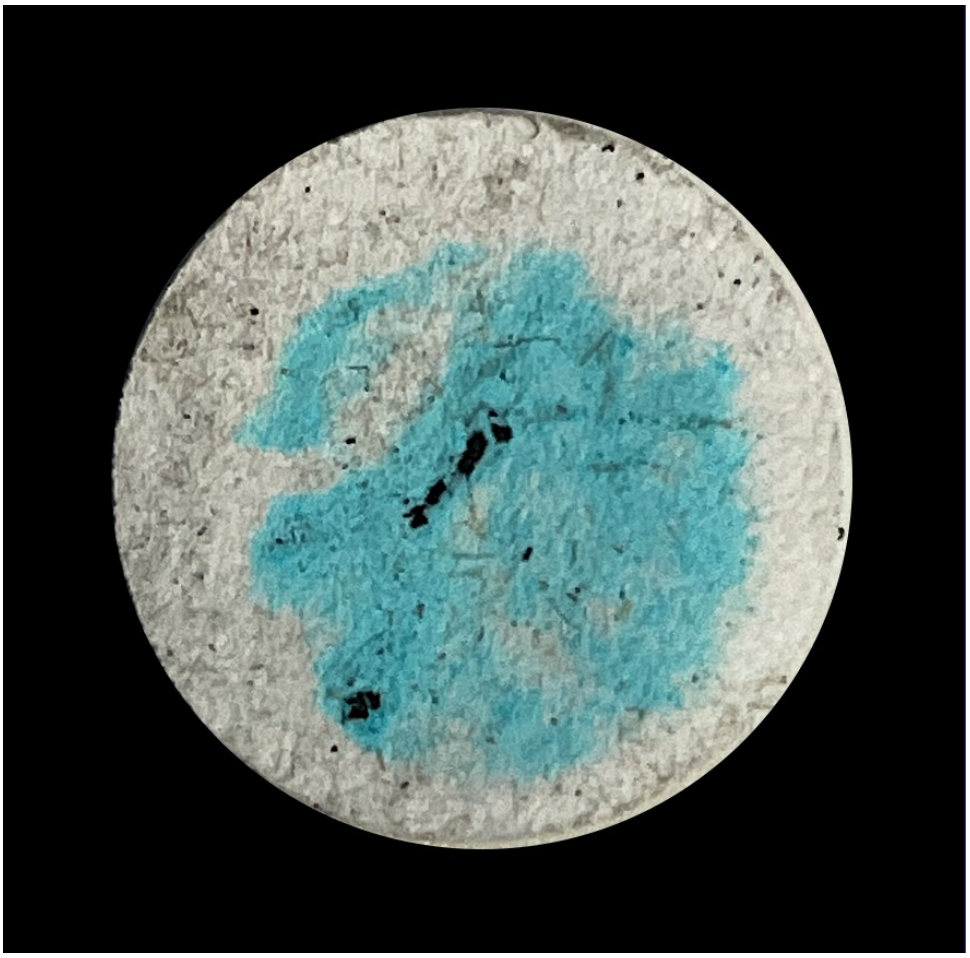

**Figure S2**. Image of the separator from a cycled cell after 300 cycles in 16 *m* KF. The separator was collected and dried/stored under vacuum.

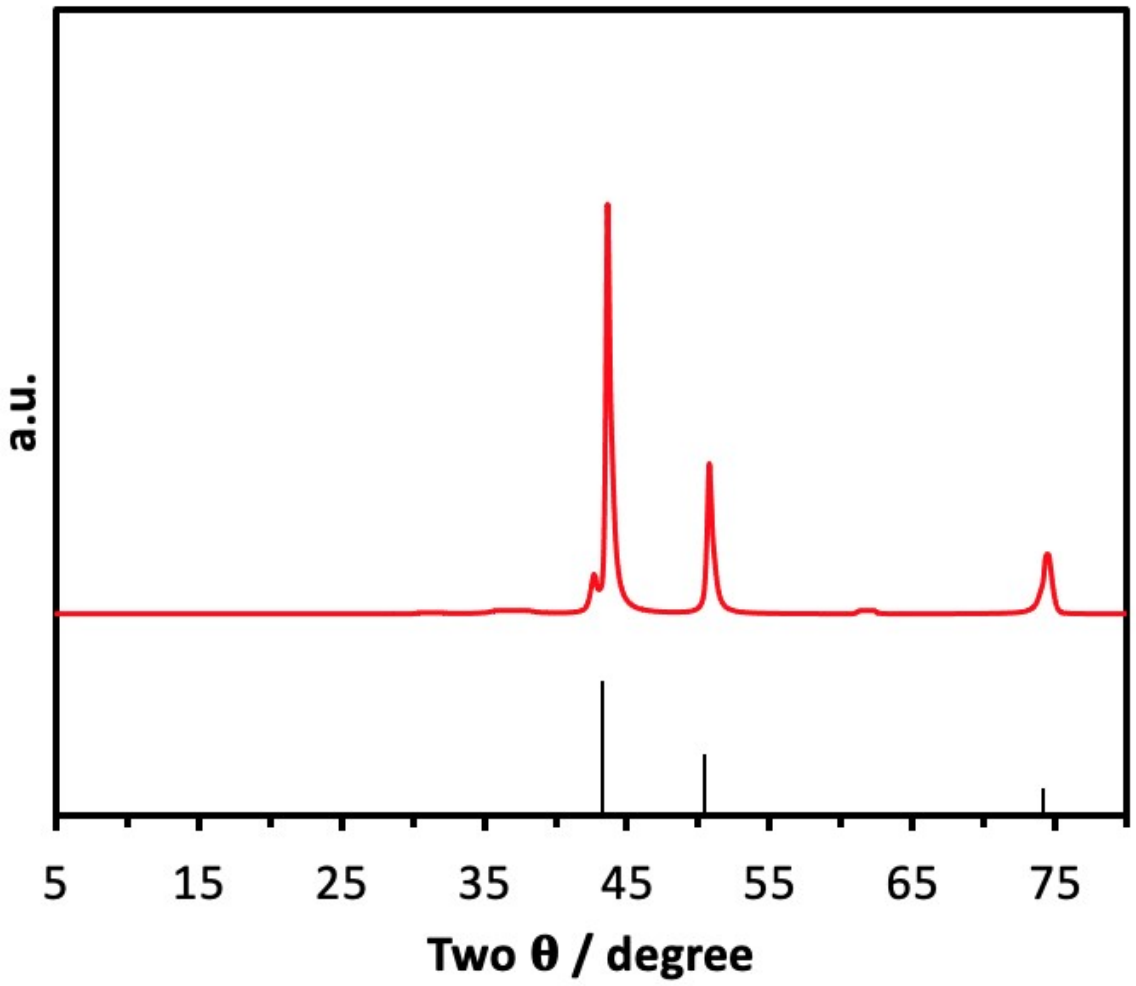


**Figure S3.** *Ex situ* XRD pattern of the fully discharged copper electrode in 16 *m* KF. The discharged electrode is confirmed to be copper (PDF#04-0836).

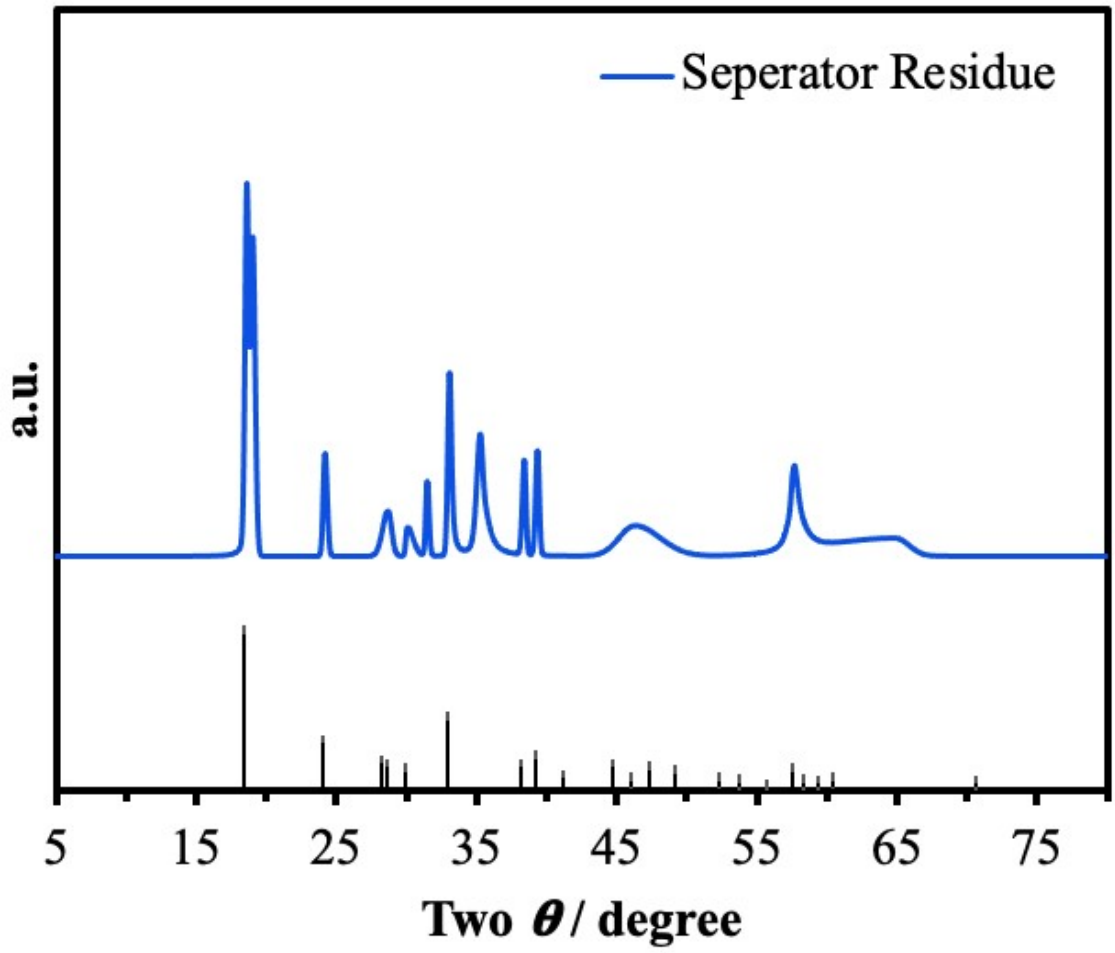


**Figure S4.** *Ex situ* XRD pattern of the separator residue. Contents on the surface of the separator were removed with a scalpel and confirmed to be monoclinic $CuF_2$ (PDF #06-143).