

## Supplementary Information

### Manganese Electrode for All-Solid-State Fluoride Batteries

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#### Experimental

MnF<sub>2</sub> (99.9%) was purchased from Rare Metallic. BaF<sub>2</sub> (99.9%) and Mn (98.0%) were purchased from Fujifilm Wako Pure Chemical. LaF<sub>3</sub> (99.95%) was purchased from Kishida Chemical. MnF<sub>3</sub> (99.9%), Pb (99.95%), PbF<sub>2</sub> (99%), and SnF<sub>2</sub> (99%) were purchased from Sigma-Aldrich. Acetylene black (AB) was purchased from Denka.

The BLF solid electrolyte was synthesized by a mechanical milling method from a stoichiometric mixture of BaF<sub>2</sub> and LaF<sub>3</sub>; mechanical ball-milling was conducted at 600 rpm for 12 h under Ar. The ball-to-powder mass ratio was kept constant at 20:1 during this synthesis process, and ZrO<sub>2</sub> jars (80 mL volume) and 36 g balls (3 mm diameter) were used as milling media with a planetary-type mill (Pulverisette 7, Fritsch). The MnF<sub>3</sub> electrode (Starting from defluorination) was prepared by mixing MnF<sub>3</sub>, BLF, and AB (MnF<sub>3</sub>-BLF-AB) in a 6:10:1 weight ratio. BLF and AB were first mixed at 600 rpm for 12 h under Ar. MnF<sub>3</sub> was then added and mixed at 150 rpm for 12 h under Ar. The MnF<sub>3</sub> powder was first ball-milled at 600 rpm for 12 h under Ar before use. A Mn electrode (Starting from fluorination) was prepared by mixing Mn, BLF, and AB (Mn-BLF-AB) in a 2.97:10:1 weight ratio. BLF and AB were mixed at 600 rpm for 12 h under Ar. Metallic Mn was then added and mixed at 600 rpm for 12 h and 800 rpm for 1 h under Ar. The Mn powder was first ball-milled at 600 rpm for 12 h under Ar before use. A two-layer counter electrode was used as reported previously, including a Pb layer and a PbF<sub>2</sub>-SnF<sub>2</sub>-AB composite layer.<sup>27</sup> The potential of this two-layer counter electrode is 0.02 V against PbF<sub>2</sub>/Pb at 433 K. The Pb layer was prepared by pressing Pb powder. The PbF<sub>2</sub>-SnF<sub>2</sub>-AB composite layer was prepared by pressing a composite powder containing PbF<sub>2</sub>, SnF<sub>2</sub>, and AB; this powder was prepared by mechanically ball-milling a mixture of PbF<sub>2</sub>, SnF<sub>2</sub>, and AB combined in a 3:1.4:0.286 weight ratio. PbF<sub>2</sub> and SnF<sub>2</sub> and 10 ZrO<sub>2</sub> balls (10 mm diameter) were first mixed at 600 rpm for 24 h under Ar. AB was then added to the PbF<sub>2</sub> and SnF<sub>2</sub> powder mixture, and the resultant mixture was mixed at 600 rpm for 10 h under Ar and then calcined at 637 K for 1 h.

Each all-solid-state fluoride cell was assembled using an insulating cell die (polyether ether ketone (PEEK)) sandwiched between two stainless steel rods. The cell was assembled under Ar by pressing the cathode, electrolyte, and counter electrode materials together under an applied force of 510 MPa to obtain a 10 mm diameter disk. The obtained four-layer cell (Pb layer, 380 μm / PbF<sub>2</sub>-SnF<sub>2</sub>-AB layer, 370 μm / Ba<sub>0.6</sub>La<sub>0.4</sub>F<sub>2.4</sub> layer, 700 μm / MnF<sub>3</sub>-BLF-AB layer, 88 μm) was employed for electrochemical measurements. Electrochemical discharge-charge measurements were performed in galvanostatic mode using a discharge-charge cycling apparatus (HJ1020mSD8, Meiden Hokuto). Each cell was cycled at 433 K at 0.08 mA cm<sup>-2</sup> in an Ar-filled glove box in the voltage range between -2 and 2 V or -2 and 4 V.

X-ray diffraction (XRD; Miniflex, Rigaku) patterns for the powder samples and battery pellets were recorded with Cu Kα radiation. The surface and cross-sectional morphology of the pellets and also Energy dispersed Spectroscopy measurement were investigated using field-emission scanning electron microscopy (FE-SEM; JSM-IT700HR/LA, JEOL). The cross-sectional

processing of the battery was carried out using Ar ion milling (E-3500, Hitachi). X-ray absorption spectroscopy (XAS) data using soft X-rays were acquired at the BL-12 beamline station of the SAGA Light Source. All experiments were performed without exposure to air, except during SEM observations and Ion milling.

Figures

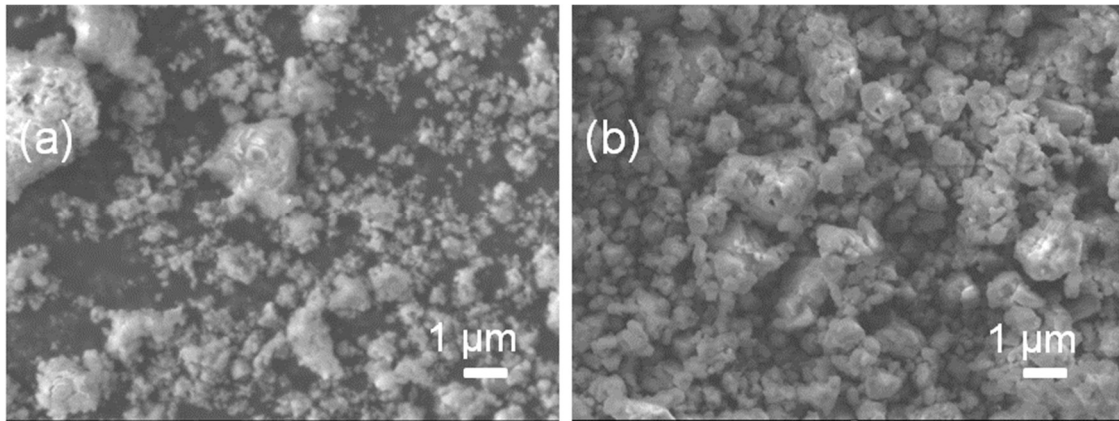


Figure S1. SEM images of MnF<sub>3</sub> powder before and after ball-milling.

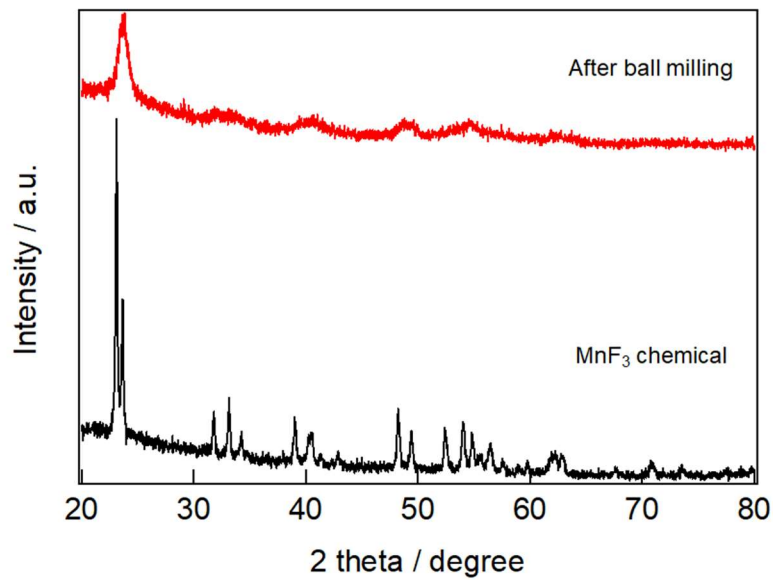


Figure S2. XRD patterns for MnF<sub>3</sub> powder before and after ball-milling.

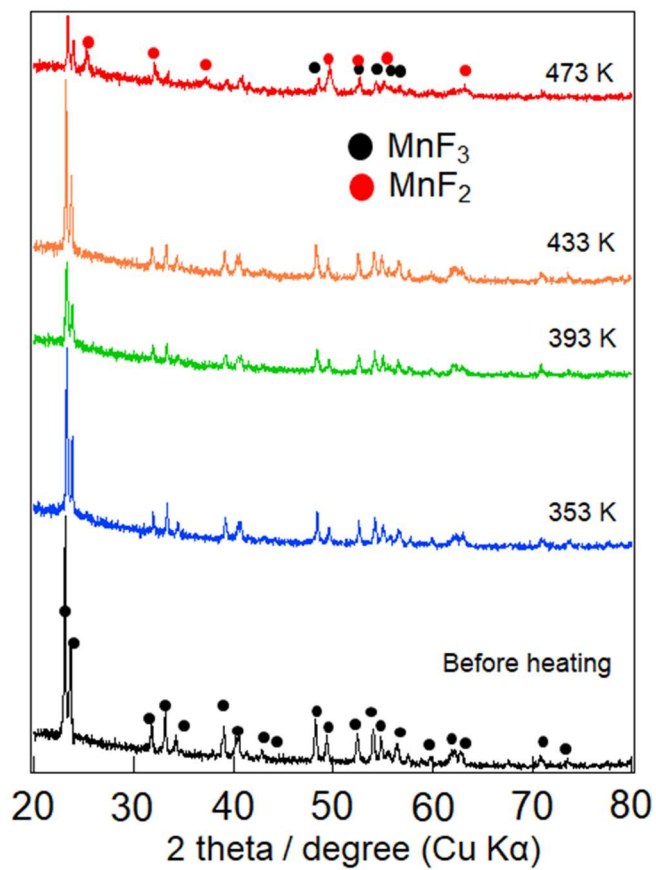


Figure S3. XRD patterns for  $\text{MnF}_3$  powder before and after heating at various temperatures.

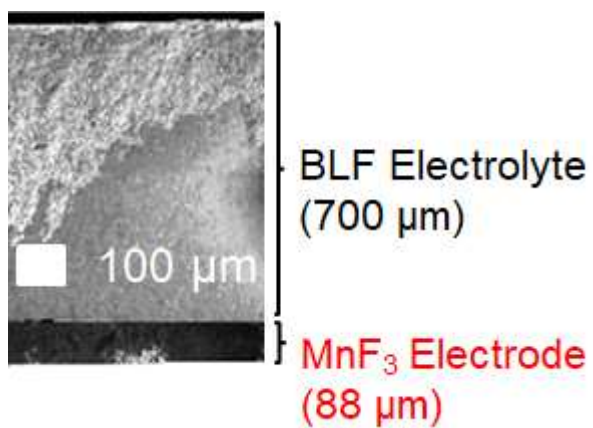


Figure S4. Cross-sectional SEM image of  $\text{MnF}_3$  electrode/BLF electrolyte interface after heating at 433 K (100 $\times$  magnification).

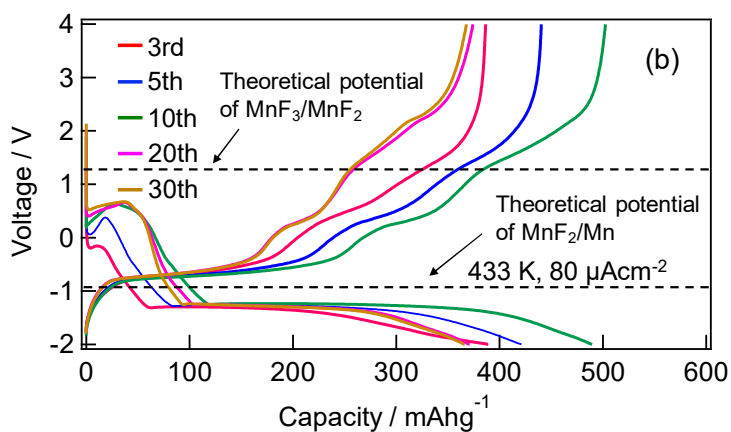
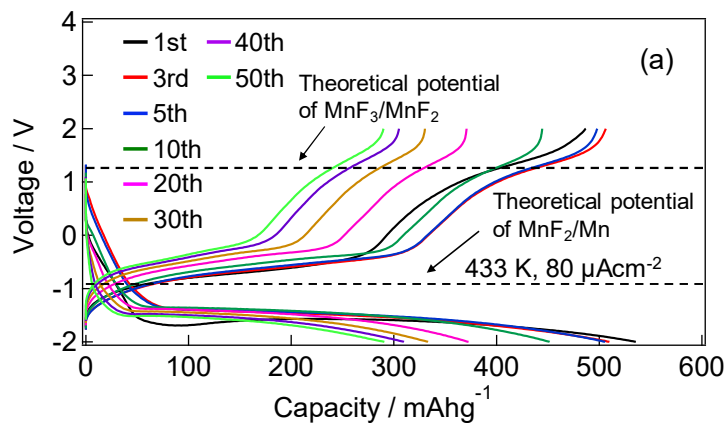


Figure S5. Charge–discharge profiles for all-solid-state fluoride battery with  $\text{MnF}_3$  electrode in voltage range between  $-2$  V and  $4$  V along with theoretical redox potential for manganese fluoride. Cell structure is  $\text{Pb/PbF}_2\text{-SnF}_2\text{-AB/BLF/MnF}_3\text{-BLF-AB}$ . The capacity was calculated based on the weight of  $\text{MnF}_3$ .

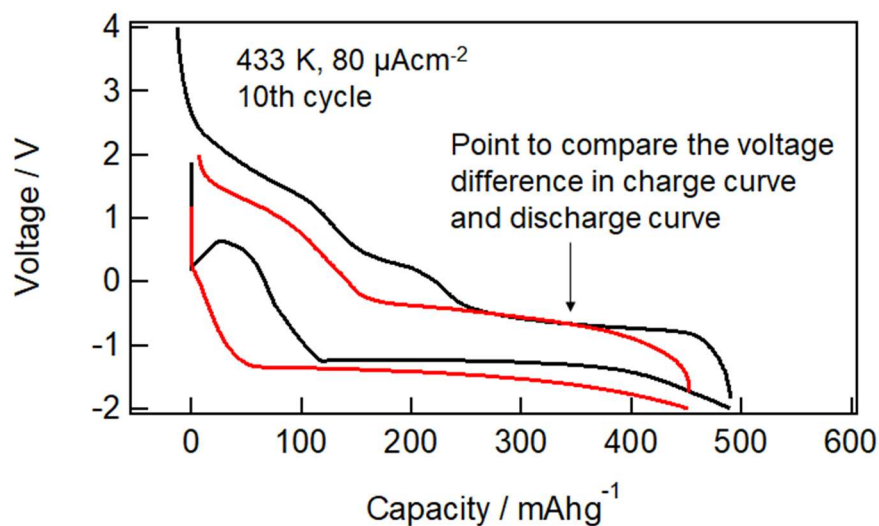


Figure S6. Comparison point for voltage difference for 10th discharge-charge cycle with capacity at  $350$   $\text{mAh g}^{-1}$ . Cell structure is  $\text{Pb/PbF}_2\text{-SnF}_2\text{-AB/BLF/MnF}_3\text{-BLF-AB}$ . The capacity was calculated based on the weight of  $\text{MnF}_3$ .

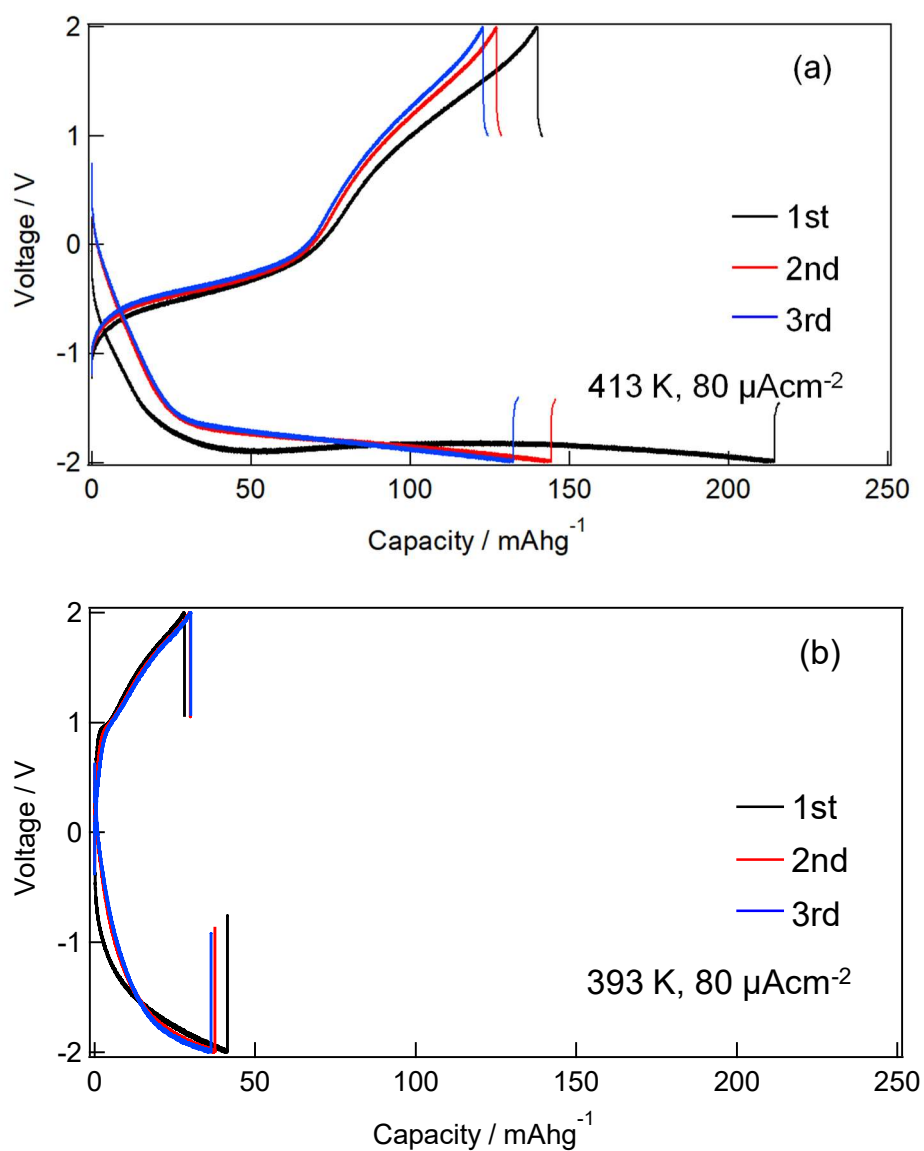


Figure S7. Charge–discharge profiles for all-solid-state fluoride battery with  $\text{MnF}_3$  electrode in voltage range between  $-2$  V and  $2$  V along at (a)  $413$  K and (b)  $393$  K. Cell structure is  $\text{Pb/PbF}_2\text{-SnF}_2\text{-AB/BLF/MnF}_3\text{-BLF-AB}$ . The capacity was calculated based on the weight of  $\text{MnF}_3$ .

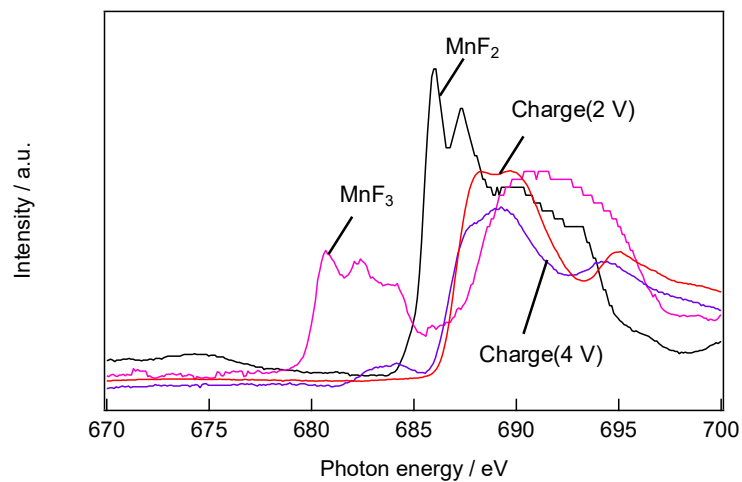


Figure S8. F K-edge XAS spectra of  $\text{MnF}_3$  electrodes charged to different voltages.  $\text{MnF}_3$  and  $\text{MnF}_2$  chemical are also shown.

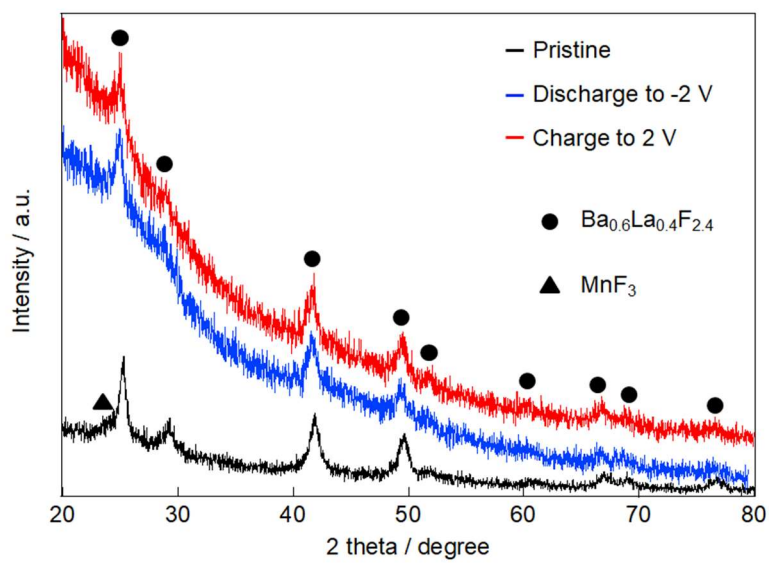


Figure S9. XRD patterns for  $\text{MnF}_3$  electrode before and after charge-discharge measurements.

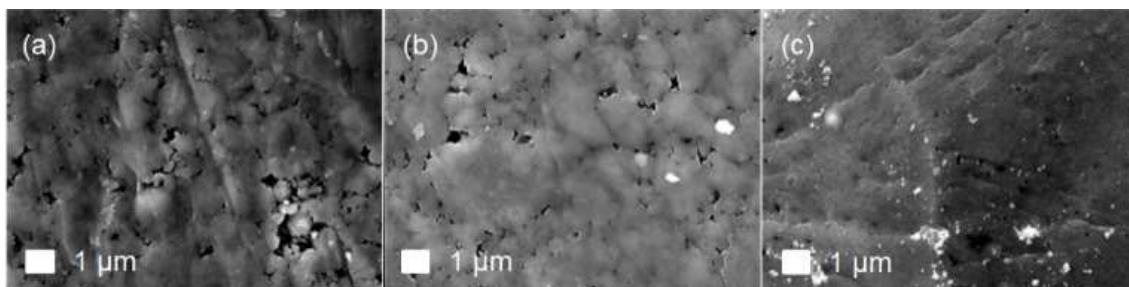


Figure S10. SEM images of MnF<sub>3</sub> electrode (a) after pelletization without heating, (b) after pelletization and with heating at 433 K, and (c) after discharge-charge cycling.

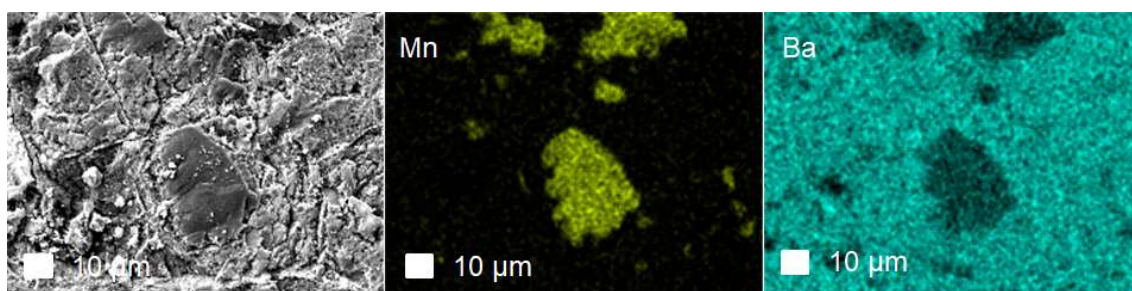


Figure S11. SEM image and EDS maps of MnF<sub>3</sub> electrode after discharge-charge cycling in voltage range between -2 V and 2 V (58 cycles).

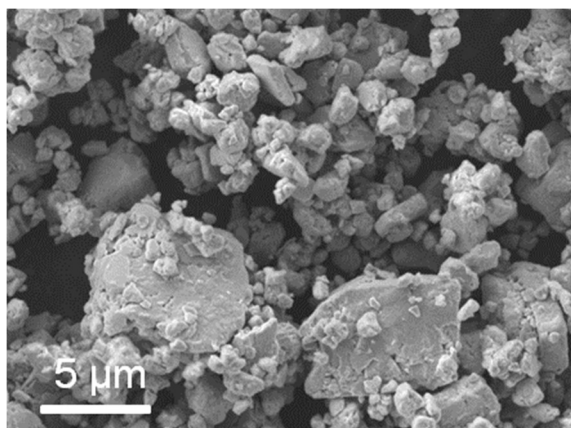


Figure S12. SEM image of metallic manganese powder after mechanical milling (600 rpm for 12 h).



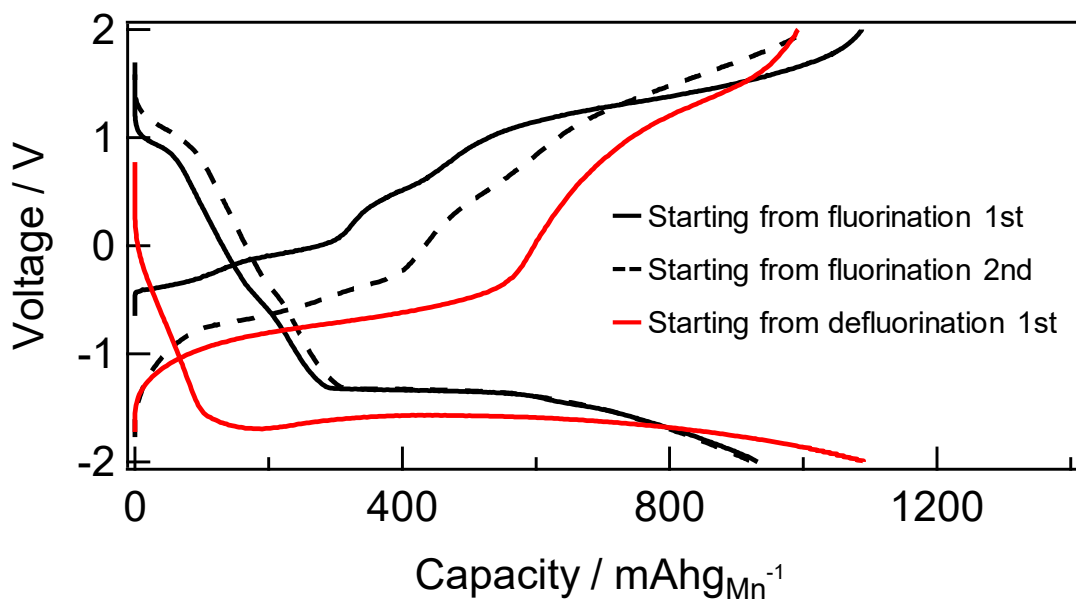


Figure S13. Charge–discharge profiles for all-solid-state fluoride battery with MnF<sub>3</sub> electrode and Mn electrode. Cell structure is Pb/PbF<sub>2</sub>–SnF<sub>2</sub>–AB/BLF/(MnF<sub>3</sub> or Mn)–BLF–AB. The capacity was calculated based on the weight of Mn.