Electronic Supplementary Material (ESI) for ChemComm.
This journal is © The Royal Society of Chemistry 2019

Engineering Frenkel defects of anti-perovskite solid-state electrolytes and their applications in all solid-state lithium–ion batteries

Li-Hong Yin [a, b], Huimin Yuan [c], Long Kong [a,]*, Zhouguang Lu [c], Yusheng Zhao [a, b,] *

[a] Academy for Advanced Interdisciplinary Studies, Southern University of Science and Technology, Shenzhen 518055, China

[b] Department of Physics, Southern University of Science and Technology, Shenzhen, 518055, P. R. China

[c] Department of Materials Science and Engineering, Guangdong Provincial Key Laboratory of Energy Materials for Electric Power, Southern University of Science and Technology, Shenzhen Guangdong, 518055, China

Email: zhaoys@sustech.edu.cn; kongl3@sustech.edu.cn

I. Supporting Text

1. Experimental

1.1 Materials preparation and characterization

The $Li_2OHBr_{1-x}F_x$ electrolyte was prepared by hand mixing of LiBr, LiOH, and LiF in a mortar with specific mole ratios. The thoroughly mixed powders were subjected to a heat treatment at 500°C for 5 hour, followed by cooling down to room temperature. All synthesis operations were performed under an argon-filled glove box.

The structure of samples was studied by X-ray diffraction (XRD, SmartLab 9kW) in the 2θ range from 10 to 80° with a step size of 0.01°. The morphologies of the samples were observed by a Tescam Mira 3 scanning electron microscope (SEM). Energy-dispersive X-ray spectrometer (EDS) analysis and corresponding elemental mapping were performed using the Oxford Instruments X-Max^N. X-ray photoelectron spectroscopy (XPS) was recorded on a PHI 5000 VersaProbe spectrometer using monochromatic Al K(alpha) X ray source.

1.2 Electrochemical measurements

Ionic conductivity of prepared solid electrolytes was measured by electrochemical impedance spectroscopy (EIS) analysis with a Solarton Impedance Analyzer (Model 1470E) in the applied frequency from 10^6 to 0.1 Hz. The home-made cell was assembled by sandwiching the solid state electrolyte between two stainless steel blocking electrodes (d=10.0 mm). The fabricated cell was kept at targeted temperature at least for one hour before measurement to eliminate thermal gradient among samples.

The ionic conductivity of LiRAP electrolytes was calculated based on the following equation:

$$\sigma = (L/A)/R_b$$

where σ is the ionic conductivity (S cm^{-1}), R_b is the bulk resistance, and L and A are the thickness and area of the test sample, respectively. The R_b is obtained by the high frequency intercept of the Nyquist plot by analysing the impedance profile. The activation energy of $Li_2OHBr_{0.98}F_{0.02}$ (LiOHBrF) was derived from the ionic conductivity measured from 273.15 K to 393.15 K. The resulting values are fitted with Arrhenius equation:

$$ln(\sigma T) = ln\sigma_0 - \frac{E_a}{RT}$$

where σ is the ionic conductivity, E_a is equivalent to the activation energy, R is the gas constant, T is the experimental temperature.

The all solid-state cell was fabricated in our home-made cell models. The cathode was prepared by slurry-coating method. Typically, 0.70 g $LiFePO_4$, 0.10 g carbon black, 0.10 g LiTFSI and 0.10 g PVDF were thoroughly mixed in NMP solvent to form a homogeneous slurry. The obtained slurry was directly coated on aluminum current collector by a doctor blade, which was further dried at 80°C for 4 h. The composite electrode was then available after punching into disks with a diameter of 10.0 mm. The areal $LiFePO_4$ loading was ~0.4 mg cm^{-2} for cell measurements. The disk was placed on the bottom of the cell. The solid electrolyte powders with a weight of 150.0 mg LiOHBrF was uniformly spread on the disk and then pressed at 200 MPa. Finally the lithium metal anode with the thickness of 400 μm was pressed at 100 MPa onto the other side. The diameters of solid-state electrolyte and lithium metal anode foil are both 10.0 mm.

II. Supporting Figures

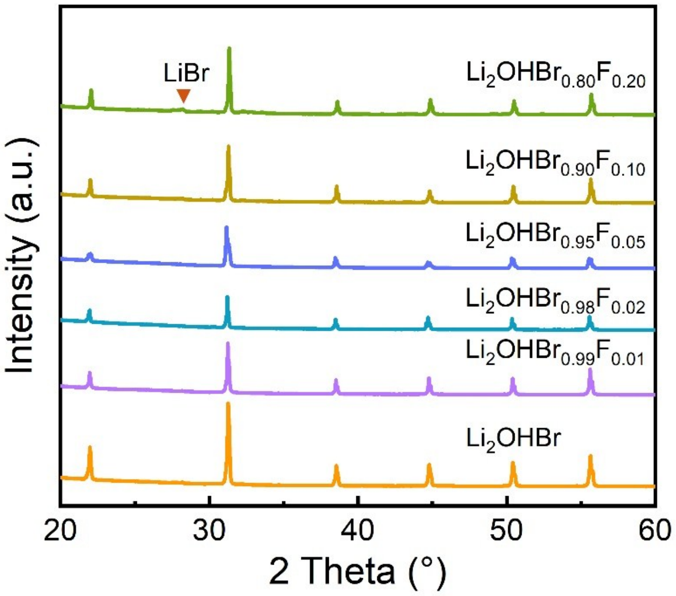

Fig. S1. XRD patterns of fluorine-doped LiOHBr with different fluorine contents.

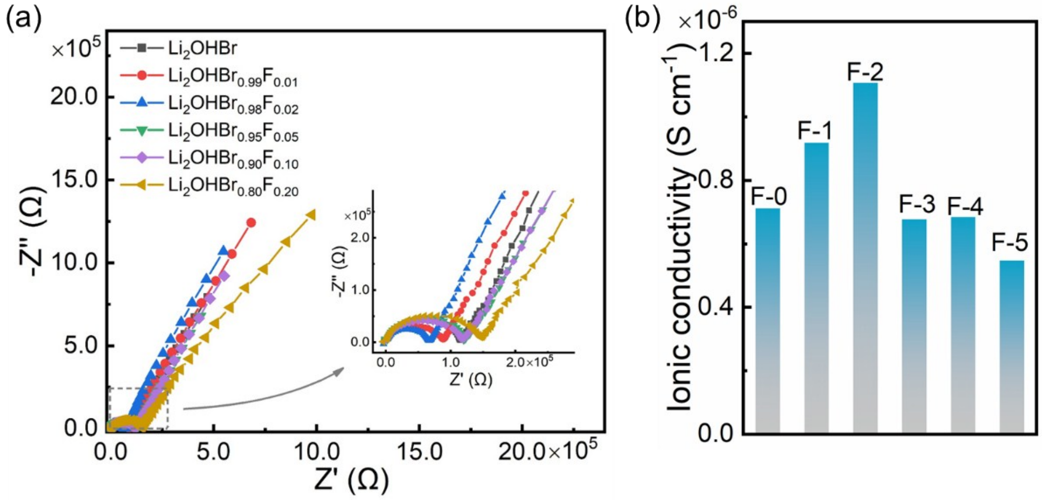

Fig. S2. (a) EIS profiles and (b) ionic conductivities of the fluorine-doped LiOHBr with different fluorine contents. F–0, F–1, F–2, F–3, F–4, F–5 represents Li_2OHBr, $Li_2OHBr_{0.99}F_{0.01}$, $Li_2OHBr_{0.98}F_{0.02}$, $Li_2OHBr_{0.95}F_{0.05}$, $Li_2OHBr_{0.90}F_{0.10}$, $Li_2OHBr_{0.80}F_{0.20}$, respectively. $Li_2OHBr_{0.98}F_{0.02}$ is denoted as LiOHBrF for simplicity in the discussion. The EIS measurement was performed at 25°C.

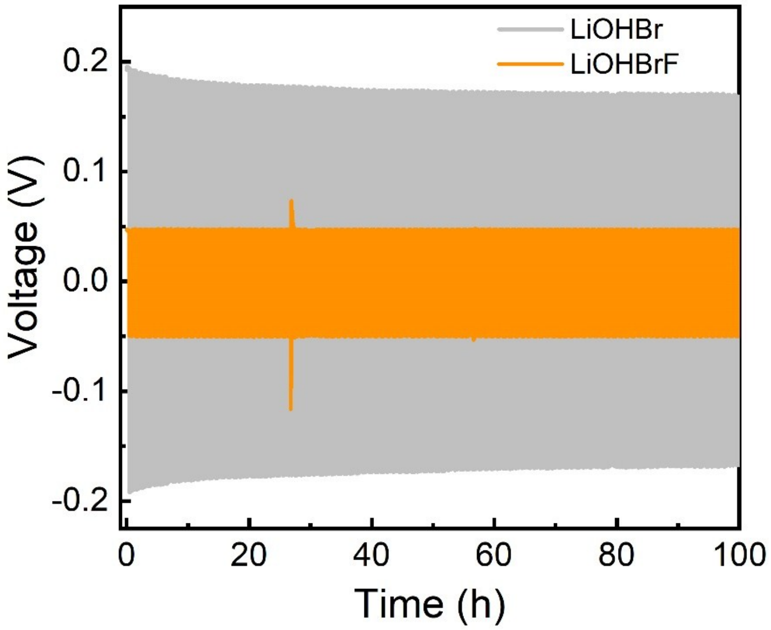

Fig. S3. Voltage profiles for the Li | SE | Li symmetric cell with a current density of 0.02 mAcm^{-2} for 0.5 h.

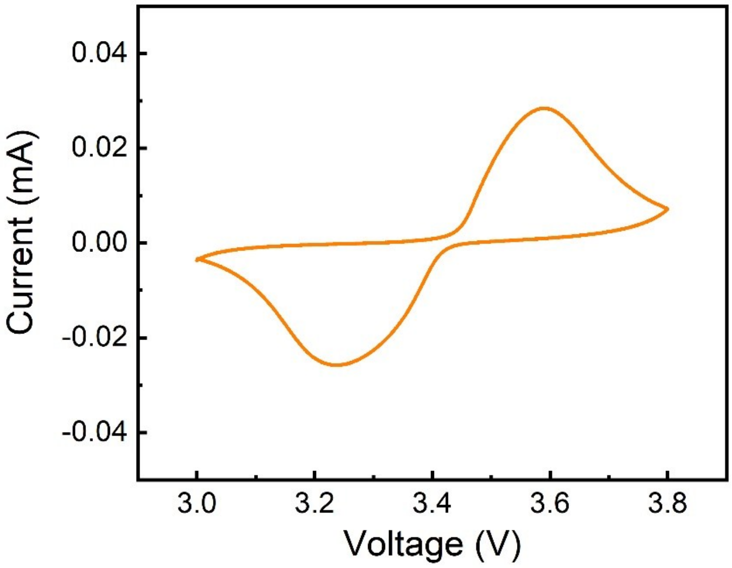

Fig. S4. Cyclic voltammogram for the $LiFePO_4$ | LiOHBrF | Li cell configuration with a scan rate of 0.05 mV s^{-1}.

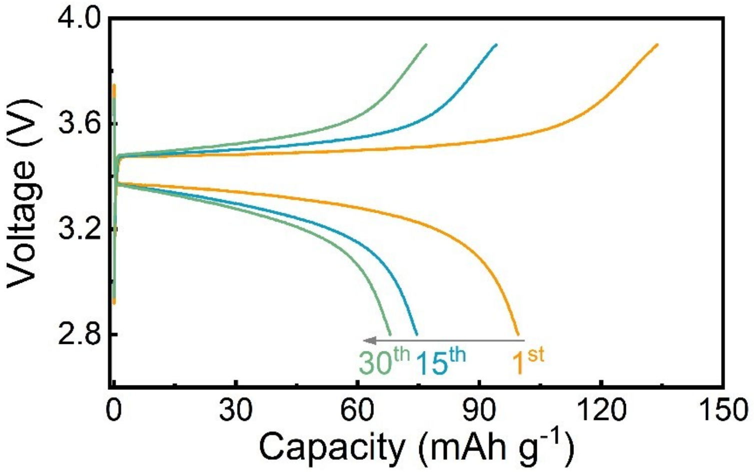

Fig. S5. Charge/discharge profiles of the all-solid-state cell based on LiOHBrF electrolytes with different cycle numbers. The cell is operated at 80°C.

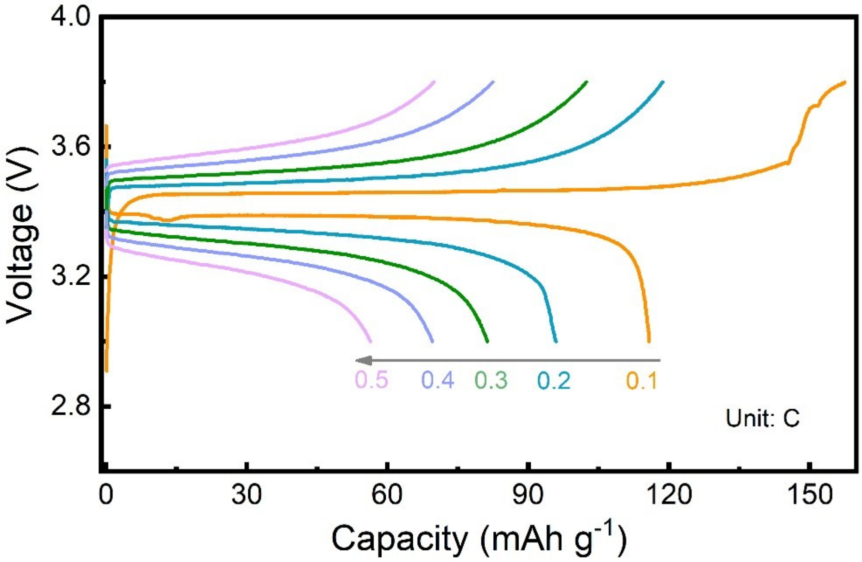

Fig. S6. Charge/discharge profiles of the all-solid-state cell based on LiOHBrF electrolytes with different current densities. The cell is operated at 80°C.

III. Supporting Tables

Table S1. Comparison of oxide-based solid electrolytes with different ionic conductivity at 25°C.

Materials composition	Ionic conductivity (S cm^{-1})	Reference
$Li_3BO_3–Li_2SO_4$	1.4×10^{-5}	1
$LLTO–SiO_2$	10^{-4} (30°C)	2
$Li_6BaLa_2Ta_2O_{12}$	4.0×10^{-5}	3
$Li_{0.33}La_{0.69}TiO_3$	10^{-4}	4
LiPON	3.0×10^{-5}	5
Li_3OCl	8.5×10^{-5}	6
$Li_2OHBr_{0.98}F_{0.02}$	1.1×10^{-6}	(This work)

References

1. M. Tatsumisago, R. Takano, K. Tadanaga and A. Hayashi, *J. Power Sources*, 2014, **270**, 603-607.
2. A. Mei, X.-L. Wang, Y.-C. Feng, S.-J. Zhao, G.-J. Li, H.-X. Geng, Y.-H. Lin and C.-W. Nan, *Solid State Ionics*, 2008, **179**, 2255-2259.
3. V. Thangadurai and W. Weppner, *J. Power Sources*, 2005, **142**, 339-344.
4. O. Bohnke, *Solid State Ionics*, 2008, **179**, 9-15.
5. B. Fleutot, B. Pecquenard, H. Martinez, M. Letellier and A. Levasseur, *Solid State Ionics*, 2011, **186**, 29-36.
6. Y. Zhao and L. L. Daemen, *J. Am. Chem. Soc.*, 2012, **134**, 15042-15047.