Supplementary Information

Understanding the mechanism behind improved cycling stability of FeF₃ cathode in lithium bis(fluorosulfonyl)amide-concentrated electrolytes

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Experimental

Materials

Battery-grade LiFSA, EC, PC, and dimethyl carbonate (DMC) were purchased from Kishida Chemical. All reagents were used as received. 1.2 M LiFSA/EC:PC (LiFSA:EC:PC=1:5:5 by mole), 3.2 M LiFSA/EC:PC (LiFSA:EC:PC=1:1.5:1.5 by mole), and 5.3 M LiFSA/EC:PC (LiFSA:EC:PC=1:0.65:0.65 by mole) electrolytes were prepared by dissolving a given amount of LiFSA in mixed solvents of EC and PC in an Ar-filled glovebox (Miwa Manufacturing, H_2O and $O_2 < 1$ ppm).

Anhydrous FeF₃ powder (Strem Chemicals) and acetylene black (Li-250, Denka) were ball-milled in a weight ratio of 80:5 at 200 rpm for 24 h in an Ar atmosphere using a planetary ball mill (Pulverisette 7, Fritsch). The obtained mixture, acetylene black (Li-250, Denka), and poly(vinylidene fluoride) (PVdF, L#9305, Kureha) were mixed in a weight ratio of 85:10:5 in *N*-methyl-2-pyrrolidone (Kishida Chemical). The obtained slurry was coated on carbon-coated Al foil (20 µm thickness, SDX-PM, Showa Denko) using a doctor blade and dried at 90 °C for 90 min in an air oven. The obtained sheet was pressed, dried at 140 °C under vacuum for 12 h, and then punched to form disk electrodes (15 mm diameter). All the above-described procedures were performed in a dry room (dew point < -50 °C). The mass loading of the active material and the cathode areal capacity were approximately 3.1 mg cm⁻² and 2.0 mAh cm⁻², respectively.

Li foil (400 µm thickness) was purchased from Honjo Metal. 2032-type coin cell parts (Al-coated stainless steel cathode case, stainless steel anode case, stainless steel spring, stainless steel spacer, and polypropylene gasket) were purchased from Hohsen.

Electrochemical Measurements

Li/FeF₃ cells were assembled as 2032-type coin cells in the dry room. An Al-coated stainless steel cathode case was used, and an Al foil (19 mm in diameter) was placed on the cathode case to avoid the corrosion of the stainless steel. A glass fiber filter (GF/F, Whatman) was used as a separator. The volume of the electrolytes was 160 μ L to fully wet the separator and the electrodes. Galvanostatic discharge/charge tests of the Li/FeF₃ cells were performed using a charge/discharge test system (TOSCAT-3100, Toyo System) at 25 °C. The cycling tests were conducted at 0.1C rate in a voltage range of 1.0–4.5 V. The 1C rate was 712 mA g⁻¹ based on the FeF₃ weight.

Characterization

The density and viscosity of the electrolytes at 20–60 °C were determined using a density meter (DMA 4500 M, Anton Paar) and an electromagnetically spinning viscometer (EMS-1000S, Kyoto Electronics Manufacturing), respectively. The molarity (mol dm⁻³ or M) was calculated from the molar ratio and density.

The ionic conductivity of the electrolytes was measured by electrochemical impedance spectroscopy (EIS, HZ-7000, Hokuto Denko) using a four-electrode cell with two inner platinum wire electrodes and two outer platinum disk electrodes (SB1400, EC Frontier) with an applied AC voltage amplitude of ± 10 mV in a 1–200 kHz frequency range at 25–60 °C.

The coordination environments of the electrolytes were studied using Raman spectroscopy with a 785 nm laser (inVia, Renishaw) at approximately 25 °C. The electrolytes and solvents were enclosed in a quartz cell in the glovebox to avoid exposure to ambient air.

To investigate the cycled FeF₃ electrodes, the Li/FeF₃ cells were disassembled after 5 and 20 discharge/charge cycles in the glovebox. Then, the cycled FeF₃ electrodes were washed with DMC to remove the residual electrolyte components and dried under vacuum. The sticking behaviors of a ferrite magnet to the FeF₃ electrodes were investigated to confirm the formation of residual Fe particles in the cycled electrodes. The crystal structures of the pristine and cycled FeF₃ electrodes were identified by X-ray diffraction (XRD, D2 PHASER, Bruker) with Cu K α radiation ($\lambda = 1.5418$ Å).

The surfaces of the pristine and cycled FeF_3 electrodes were studied by X-ray photoelectron spectroscopy (XPS, Kratos Ultra 2, Kratos Analytical) with a monochromatic Al K α X-ray source (1486.7 eV). The cross-section of the FeF₃ electrodes was observed by a focused ion beam-scanning electron microscope (FIB-SEM, NB5000, Hitachi High-Tech). The samples were transferred to the XPS and FIB-SEM chambers using transfer vessels without exposure to ambient air. The binding energy of the obtained spectra was calibrated against the C 1s peak of amorphous carbon at 284.6 eV.

The pristine and cycled FeF_3 particles were observed and analyzed by a scanning transmission electron microscope (STEM, Titan3 G2 60-300, FEI) equipped with energy dispersive X-ray spectroscopy (EDS) and electron energy-loss spectroscopy (EELS, GIF Quantum, Gatan). The samples were obtained from the FeF₃ electrodes and directly dispersed on a holey carbon film supported on a Cu mesh for STEM analysis in an Ar atmosphere. The samples were transferred to the STEM without exposure to the ambient atmosphere using the transfer holder.

The amount of Fe deposited on the cycled Li foil was measured by inductively coupled optical atomic emission spectroscopy (ICP-OES, iCAP PRO, Thermo Fisher Scientific). To avoid Fe contamination from the stainless steel coin cell parts and to improve the quantitative accuracy of the ICP-OES measurements, Li/FeF₃ cells were assembled as pouch cells using aluminum laminated films and large area FeF₃ electrodes (4 cm^{-2}) in the dry room. A glass fiber filter (GF/F, Whatman) was used as a separator. The volume of the electrolyte was 300 µL. The Li/FeF₃ cells after five discharge/charge cycles were disassembled in the dry room, and the collected Li foil was used for the measurements.



Figure S1. Temperature dependence of (a) density, (b) viscosity, (c) ionic conductivity for 1.2 M, 3.2 M, and 5.3 M LiFSA/EC:PC electrolytes. (d) Walden plots at 25 °C for the electrolytes.



Figure S2. Raman spectra of 1.2 M, 3.2 M, and 5.3 M LiFSA/EC:PC electrolytes within the regions of the (a) ring breathing mode of EC and (b) S–N stretching mode of FSA⁻ and ring bending modes of PC and EC. Bands were assigned according to previous literature. ^{1, 2}



Figure S3. (a) Initial discharge/charge curves of the Li/FeF₃ cells using 1.2 M, 3.2 M, and 5.3 M LiFSA/EC:PC electrolytes at 0.1C rate in a voltage range of 1.0–4.5 V. (b) Discharge/charge curves of the cell using 3.2 M LiFSA/EC:PC electrolyte. (c) Discharge capacity and (d) Coulombic efficiency vs cycle number of the cell using 3.2 M LiFSA/EC:PC electrolyte. Coulombic efficiency was calculated by dividing the charge capacity by the discharge capacity.



Figure S4. XRD patterns (Cu K α radiation) of the FeF₃ electrodes before and after 20 discharge/charge cycles in 1.2 M, 3.2 M, and 5.3 M LiFSA/EC:PC electrolytes. The phase identification was performed according to previous literature. ^{3, 4}



Figure S5. C 1s, N 1s, O 1s, Li 1s/Fe 3p, and Fe 2p XPS spectra of the FeF₃ electrodes before and after five discharge/charge cycles in 1.2 M and 5.3 M LiFSA/EC:PC electrolytes. Peak assignments were performed according to previous literature. ⁴⁻⁷



Figure S6. (a) ADF-STEM image, (b) O, (c) F, and (d) Fe elemental maps of a pristine FeF₃ particle.



Figure S7. (a) ADF-STEM image, (b) C, (c) N, (d) O, (e) F, (f) S, and (g) Fe elemental maps of the FeF₃ particle after five discharge/charge cycles in 1.2 M LiFSA/EC:PC electrolyte.



Figure S8. (a) ADF-STEM image, (b) C, (c) N, (d) O, (e) F, (f) S, and (g) Fe elemental maps of the FeF₃ particle after five discharge/charge cycles in 5.3 M LiFSA/EC:PC electrolyte.

Concentration of Li ⁺ (M)	Molar ratio of LiFSA:EC:PC	Density (g cm ⁻³)	Viscosity (mPa s)	Ionic conductivity (mS cm ⁻¹)
1.2	1:5:5	1.35	8.6	7.3
3.2	1:1.5:1.5	1.50	110	1.8
5.3	1:0.65:0.65	1.65	790	0.48

Table S1. Physicochemical properties of LiFSA/EC:PC electrolytes at 25 °C.

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