

Supporting Information

A fluoride-doped PEG matrix as an electrolyte for anion transportation in a room-temperature fluoride ion battery

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Synthesis, Analysis and Methods

All reactions were carried out under standard labor conditions. The solvents for electrolyte synthesis were dried and stored over molecular sieves. Karl Fischer Titration (Mettler Toledo C30) was performed to determine the water content of the different solvent. For making electrolyte: compound **1** was dried over one day in high vacuum with slight heating prior dissolving it in the solvents. ^1H -NMR and ^{19}F -NMR were registered on a Bruker 500MHz Ultrashield spectrometer with CDCl_3 or D_2O as solvent. FT-IR pellets were prepared with dried KBr and recorded on a Perkin-Elmer Spectrum GX. TGA-DSC was measured on a Setaram SenSysPro. Powder diffractograms were recorded on a Bruker D8 Advance and a Phillips X'Pert. Higlyme -a PEG blend- was purchased by BASF.

Synthesis of the starting compound bismethyl-PEG6000,

Reaction after a modified synthesis of the standard alkylation reaction.

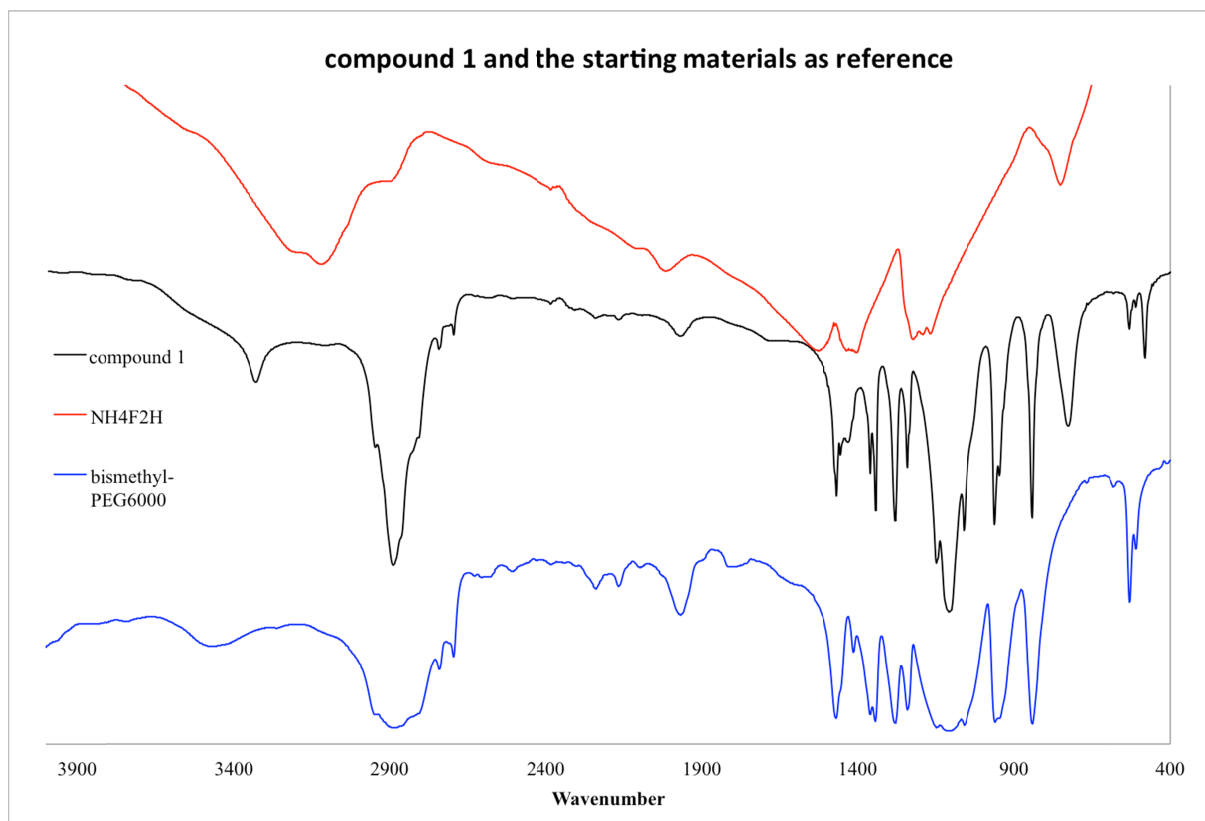
PEG (4.6 g, 0.76 mmol) and KOH (0.4 g, 7 mmol) are dissolved in acetonitrile (20 ml). To help the dissolution of KOH a few drops of water can be added. After the dissolution is complete iodomethane (0.4 ml) is added. The mixture is stirred over 2 days. 80 ml dichloromethane is added and the mixture is extracted 3 times with 120ml of water. The organic phase is evaporated to dryness. Yield: 3.32g (68 %). IR (KBr-Pellets, cm^{-1}): 3500 br, 2906 br, 2256 w, 2174 w, 1982 m, 1826 m, 1474 s, 1418 w, 1364 s, 1288 s, 1246 s, 1134 br, 966 s, 846 s, 530 m. ^1H NMR (D_2O , ppm): 3.742 (glycol units, approx. 592 H), 3.42 (CH_3 , 6H)

Synthesis of compound **1**, mPEG6000 doped with ammonium bifluoride

PEG6000 (1 g, 0.16 mmol) and large excess of ammonium bifluoride (0.095 g, 1.6 mmol) are dissolved in 40 ml MeCN (a few milliliters of methanol can be added to obtain a better dissolution of the ammonium bifluoride). The reaction solution is heated to reflux for 2h and filtrated to discard unreacted ammonium bifluoride. The solvent is evaporated and the remaining pale yellow solid is dried in vacuo. Yield: 0.86g (85 %).

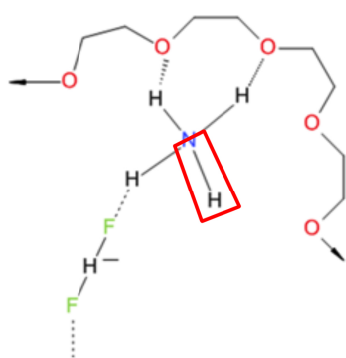
IR (KBr-Pellets, cm^{-1}): 3340 m, 2894 br, 2260 w, 2192 w, 1986 w, 1468 s, 1344 s, 1284 s, 1244 m, 1118 br, 964 s, 844 s, 734 m, 532 w, 482 m. ^1H NMR (CDCl_3 , ppm): 3.631 (glycol units, approx. 589 H), 3.356 (CH_3 , 6H)

Infrared spectroscopy, Compound 1

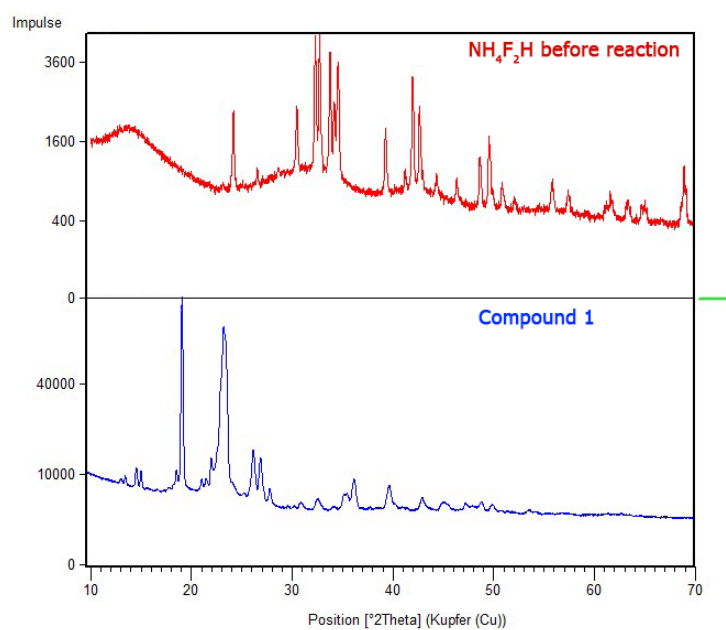


Infrared spectra of compound **1**, ammonium bifluoride and bismethyl-PEG6000

The new peak at 3400cm^{-1} , could be explain but the presence of uncoordinated “arms” of the NH_4 cation.



PXRD of compound **1**



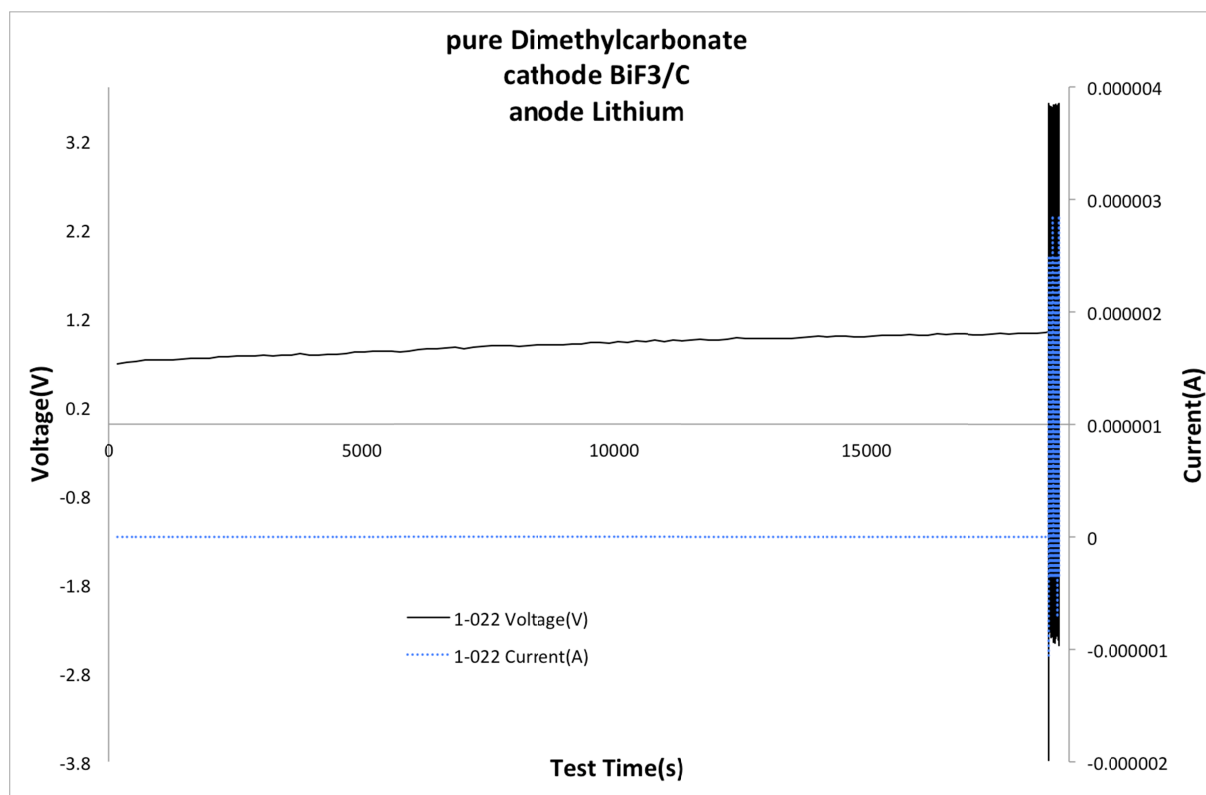
PXRD of compound **1** and NH₄F₂H as reference spectra, no unreacted ammonium bifluoride can be observed after the reaction.

Separator after cycling with lithium



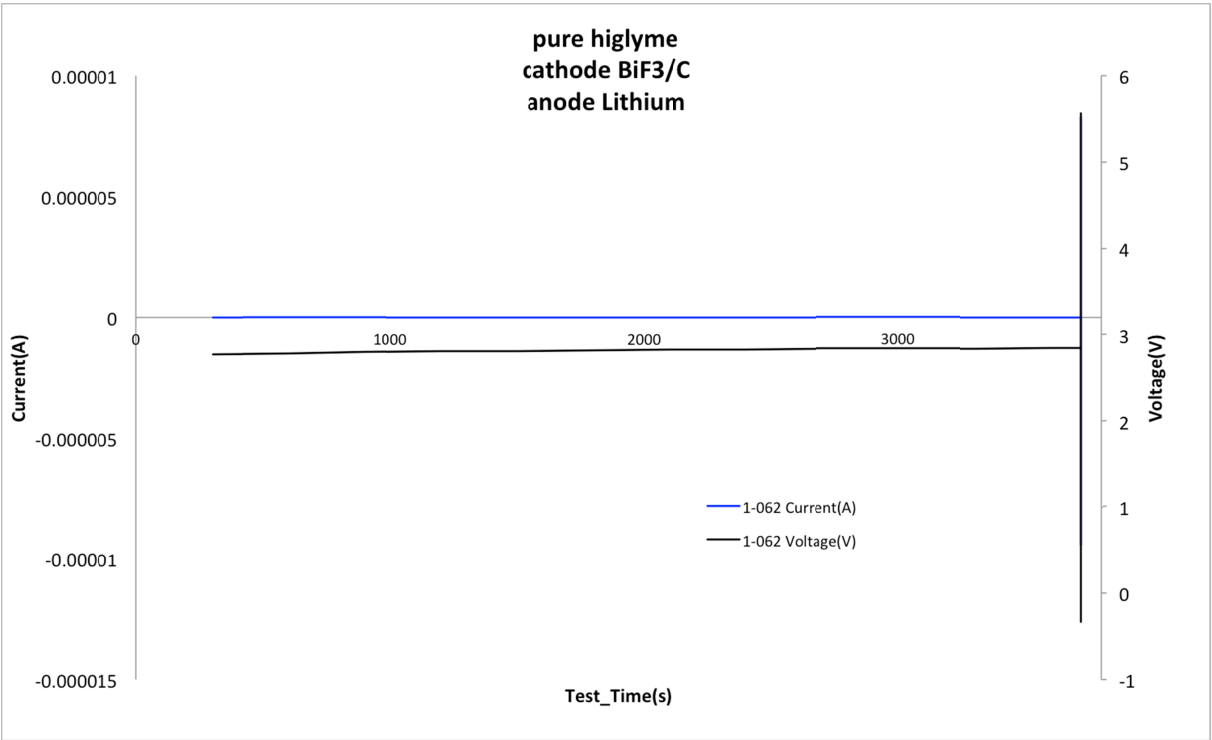
The typical yellowish color of the separator after cycling with lithium

Cycling: reference test with pure dimethylcarbonate



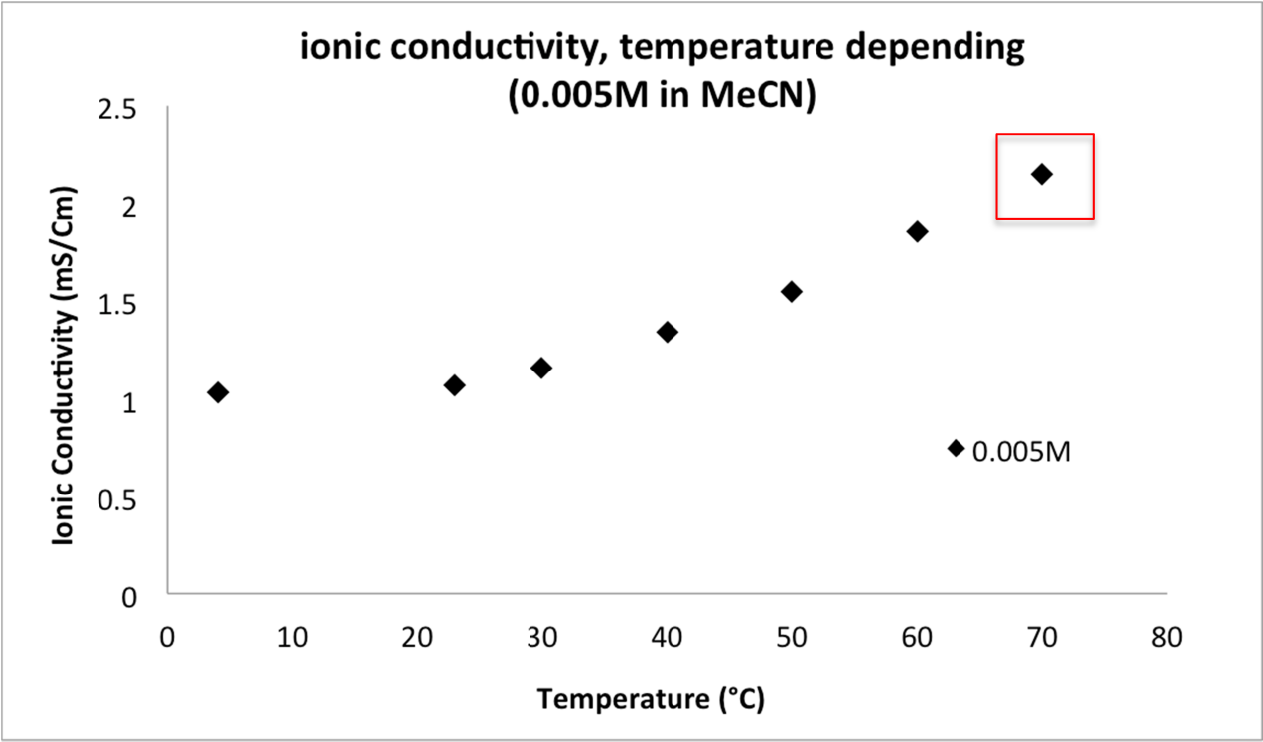
Reference cycling: separator soaked with pure dimethyl carbonate. Cathode: BiF₃/C/PVDF and anode piece of lithium foil.

Cycling: reference test with pure higlyme



Reference Cycling: separator soaked with pure higlyme. Cathode: BiF₃/C/PVDF and anode piece of lithium foil.

**Ionic conductivity temperature depending:
For Electrolyte in MeCN, 0.005M**



At about 70°C, MeCN starts slowly to evaporate.