**Showcasing the research of a new fluoride ion battery working at room-temperature, presented by Fabienne Gschwind and Maximilian Fichtner from the Helmholtz Institute Ulm and the Karlsruhe Institute of Technology.**

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

This work reports a novel liquid electrolyte based on a fluoride-doped polymer matrix, which was developed for anion transportation. The battery cells were tested at room-temperature and showed a first discharge capacity of around 189 mA h g^{-1}.
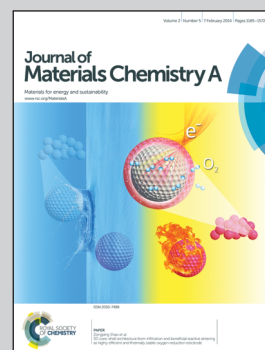
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A fluoride-doped PEG matrix as an electrolyte for anion transportation in a room-temperature fluoride ion battery†

Fabienne Gschwind,*[ab] Zhirong Zao-Karger[a] and Maximilian Fichtner[ab]

Using liquid electrolytes could increase the efficiencies of fluoride ion batteries. Such an electrolyte should demonstrate good fluoride transfer, be soluble in common solvents, and exhibit stability against decomposition. We have developed a new electrolyte system, which is based on an ammonium bifluoride-doped polyethylene glycol matrix. This compound shows good stability to thermal decomposition up to about 340 °C. The good ionic conductivity at low concentration (0.02 M) could make this compound an appropriate electrolyte. We tested our fluoride-doped PEG matrix in test cells and the first discharge capacity was found to range around 189 mA h g^{-1} (with respect to the active mass of the cathode) under nonoptimized conditions. Furthermore, we also examined the impact of lithium ions that may dissolve from the anode into the electrolyte.

Introduction

There exist many different battery systems based on ions such as Li$^+$, Na$^+$, Mg^{2+}, H$^+$, and OH$^-$ that are currently being investigated or are commercially available. The use of fluoride would be another interesting approach for secondary batteries owing to the high electronegativity of fluorine that yields a good reaction potential. The formation of metal fluorides results in a large change in free energy, which corresponds to high theoretical potentials in electrochemical cells.[1,2] If bivalent or trivalent metals are used as an electrode material, more than one electron can be stored per metal atom, and a higher theoretical energy density may be obtained. If an appropriate metal/metal fluoride pair is combined with a suitable fluoride-conducting electrolyte, a high-voltage electrochemical cell can be constructed. A proof-of-concept of such a secondary fluoride ion battery was recently demonstrated.[1] The following cathodic and anodic reactions were demonstrated to occur during discharge at the electrodes:

Cathode
$$xe^- + MF_x \rightarrow M + xF^-$$

Anode
$$M' + xF^- \rightarrow M'F_x + xe^-$$
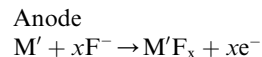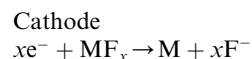
These processes can be reversed during charging.[1] In the solid-state fluoride battery system designed by Reddy *et al.*, LaF$_3$-doped BaF$_2$ salt acts as an ionic conductor and was used as a solid-state electrolyte. Metal fluorides (such as BiF$_3$ and CuF$_2$) and metallic cerium were used as the cathodes and anodes, respectively. The working temperature of this system was 150 °C. Only 60% of the theoretical maximal capacity was reached during the first cycle, and the capacity decreased on further cycling.

The system should ideally operate at room temperature to be practical. Therefore, the incorporation of a liquid electrolyte is a primary requirement, which should then be followed by the optimization of anode and cathode materials.

Such a liquid electrolyte should ensure mass and charge transfer between both electrodes and not lead to passivation on the electrode surfaces. In principle, various possible approaches exist for the synthesis of electrolytes for fluoride transport. One strategy involves metal complexes with fluoride salts, whereas another could be based on ionic liquids (ILs). ILs based on sulfonium, phosphonium, piperidium, and pyridinium, could be used as building blocks for organic fluoride salts.[3] The best IL that was proposed for fluoride transport had an initial discharge capacity of up to 103 mA h g^{-1} and worked for over 2 cycles. The electrolyte was a mixture of tetramethylammonium fluoride and 1-methyl-1-propylpiperidinium bis(trifluoromethanesulfonyl)imide.[2,3]

Unfortunately, the aforementioned concepts do not account for the poor solubility of fluoride compounds in nonaqueous

*a*Karlsruhe Institute of Technology (KIT), Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany. E-mail: fabienne.gschwind@kit.edu; Tel: +49 72160828972

*b*Helmholtz-Institute Ulm (HIU), Albert-Einstein-Allee 11, 89081 Ulm, Germany. Tel: +49 72160828972

solvents. Furthermore, side reactions involving nucleophilic displacement with the nucleophile "F⁻" can degrade the electrolyte, and create problems.[3,4] Moreover, the desired charge-carrier will not be the only molecule moving along the potential gradient, but other charged molecules will move, as well.[5]

In order to circumvent these issues we developed and tested an approach where small organic fluoride salts were encapsulated and partly coordinated in a polymer. In principle, such a matrix could (i) fix the cationic part without covalent bonding (*e.g.*, by hydrogen bonding); (ii) avoid migration of the uninvolved charged molecules due to coordination at the polymer matrix; (iii) protect the cationic part from side reactions; (iv) make compounds soluble in nonaqueous solvents that would otherwise be insoluble.

Here we report a F⁻-conducting electrolyte based on a polyethylene glycol polymer and an ammonium bifluoride salt.

These new compounds can be seen as an ion conductive polymer. Other polymers with ionic conductivity for Li⁺ have also been developed as an electrolyte for a lithium ion battery.[5,6] The "coordination" of small organic salts within the polymer to make them ionically conductive was also achieved by Lightfoot *et al.*[7]

In our work, ammonium bifluoride and polyethylene glycol were chosen as the components of the electrolyte system; we aimed at obtaining a hydrogen-bonded PEG ammonium bifluoride matrix. The idea was to form N–H⋯O bonds to "coordinate" the ammonium cation to the polyethylene glycol and N–H⋯FHF bonds to coordinate the bifluoride anion to other hydrogen atoms on ammonium (Fig. 1), which would lead to a completely hydrogen-bonded PEG matrix.

Bifluorides, also known as hydrogen(difluorides) (F_2H^-), are often confused with fluoric acid (HF) due the similarity in the chemical formula. The bifluoride anion forms a triatomic linear and centrosymmetric molecule, which contains the strongest H–F bond known in the literature.[8] The bond length and structure of F_2H^- are mostly unaffected by the accompanying cation. It is theoretically possible to investigate the three nuclei using NMR spectroscopy (mainly the investigation of the J_{HF} coupling constant). In our case, fast proton and fluoride transfer between different species prevented us from using NMR spectroscopy to investigate the coupling constant of the three nuclei.[9] The fluoride anion can easily act as a hydrogen acceptor and form different FHF clusters that are also very stable, such as $H_2F_3^-$, $H_3F_4^-$, or even $F_4H_5^-$.[10,11] It should be possible to use complexes with F_2H^- metal salts to investigate the coupling constant in NMR.[12]

Synthesis

All reactions were carried out under standard laboratory conditions in air. 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 solvents. ^{1}H-NMR and ^{19}F-NMR were registered on a Bruker 500 MHz Ultrashield spectrometer with $CDCl_3$ or D_2O as a solvent. FT-IR pellets were prepared with dried KBr and their spectra were recorded on a Perkin-Elmer Spectrum GX. TGA-DSC curves were measured on a Setaram SenSysPro. X-ray powder diffractograms were recorded on Bruker D8 Advance and Philips X'Pert diffractometers. Higlyme – a blend of small liquid PEG oligomers with an average weight of about 450 g mol^{-1} – was purchased from BASF.

For the synthesis of the fluoride-doped PEG matrix (1), PEG6000 was methylated at the –OH group by performing a standard alkylation reaction with iodomethane and KOH.[13]

The methylated PEG6000 (1 g, 0.16 mmol) and a large excess of ammonium bifluoride (0.095 g, 1.6 mmol) were 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 was heated to reflux for 2 h and filtrated to discard unreacted ammonium bifluoride. The solvent was evaporated and the remaining pale yellow solid was dried *in vacuo*. Yield: 0.86 g (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. ^{1}H NMR (CDCl$_3$, ppm): 3.631 (glycol units, approx. 589 H), 3.356 (CH$_3$, 6H).

Results and discussion

Powder X-ray diffraction (PXRD) analysis of the solid did not indicate any unreacted ammonium bifluoride, indicating that the reaction had proceeded to completion (ESI†).

^{1}HNMR analysis showed the presence of the PEG compound, and ^{19}FNMR showed two peaks at −150.6 and −152.3 ppm (in CDCl$_3$). The ^{19}F signal of the F_2H^- anion can typically be found in the region from −150 to −160 ppm,[8,14,15] but its standard resonance is at −150 ppm.[16] The second peak at −152.3 ppm might be due to F(HF)$_n$ clusters such as $F_2H_3^-$.[15]
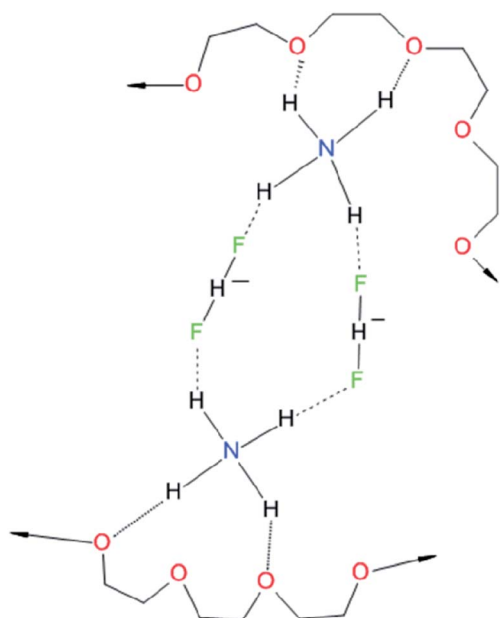

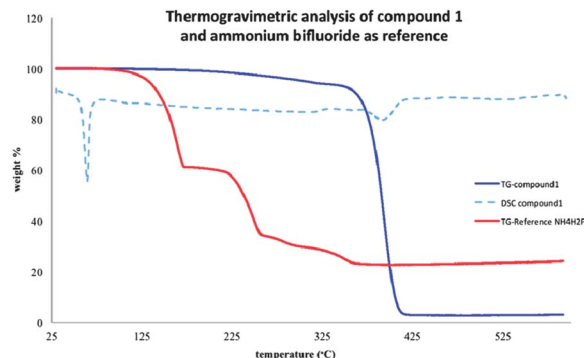**Fig. 1** A schematic drawing of possible hydrogen bonds, which could occur in a hydrogenbifluoride-doped PEG matrix.

Fig. 2 The TGA and DSC curves of compound **1** (blue) and the decomposition of the starting material NH_4F_2H (red) as a reference.

The thermal stability of compound **1** was determined using thermogravimetric analysis/differential scanning calorimetry (TGA-DSC) (Fig. 2). Intriguingly, TGA-DSC showed a phase change at 65 °C (melting of **1**) followed by only one major decomposition step starting at about 340 °C. The high thermal stability is surprising since NH_4F_2H starts to decompose at about 130 °C. This supports the assumption that the ammonium cations and the fluoride clusters are completely embedded within the PEG matrix, which makes the compound resistant to thermal decomposition.

Infrared spectroscopy (ESI†) indicates the disappearance of the free N–H bonds (the large peak at around 3200 cm^{-1} in the starting material), which can be explained by coordination of the NH_4^+ cation to the PEG matrix. This coordination *via* H-bonding of the NH_4^+ cation to the glycol-type functional group was also demonstrated using single crystal X-ray diffraction.[17,18]

The liquid electrolyte, compound **1**, was dried under high vacuum and dissolved in dry MeCN. The conductivity tests were performed in pure acetonitrile with concentrations ranging from 0.1 M to 0.0001 M. A concentration of 0.02 M exhibited a conductivity of about 2.1 mS cm^{-1} (Fig. 3), whereas pure PEG6000 in acetonitrile has a conductivity of 0.007 mS cm^{-1}.

The ionic conductivity of the electrolyte increases with temperature: an electrolyte of about 0.005 M, will almost double its ionic conductivity when measured at 4 °C and at 70 °C (ESI†).
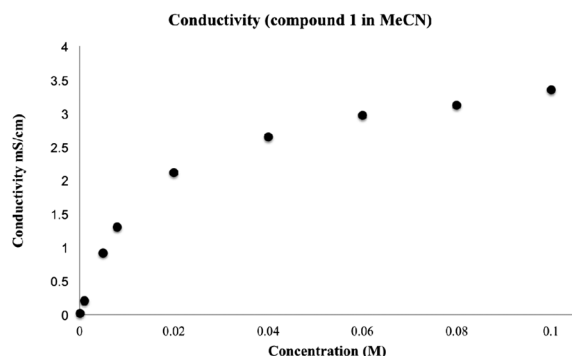
The first battery tests were conducted with a mixture of acetonitrile and dimethylcarbonate (DMC).[19–21] Cycling tests were performed with electrolyte concentrations of 0.08 M, 0.05 M, 0.02 M, and 0.008 M. The solvent mixture was 2 : 1 (v/v) MeCN–DMC. To prevent the separator from drying out, a phenomenon observed in previous tests, the glass wool separator was soaked in "higlyme".

BiF_3/C was used as the composite cathode,[1] and a piece of pure lithium foil as the anode.[2] BiF_3 systems show a theoretical capacity of 302 mA h g^{-1}. These electrodes also have the advantage that the discharge process from BiF_3 to elemental Bi can be observed using PXRD. The cells were assembled in Swagelok-type cells and discharged to a current of 1×10^{-5} A at 0.3 V and 25 °C.

Fig. 4 shows the electrochemical discharge curves. The capacities of the electrode were calculated with respect to the active mass of the cathodic material. We focused only on the first discharge capacity, since this type of battery cell has almost no cycling behavior.

A discharge capacity of 189 mA h g^{-1} was observed for the concentration of 0.05 M, whereas 0.02 M showed a discharge capacity of 136 mA h g^{-1}. Interestingly, the discharge capacity was smaller for the most concentrated solution (0.08 M). On investigating the remaining electrolyte solution, some precipitation was visible. It is possible that the concentration of 0.08 M is too close to the saturation point of the solute, and the formation of precipitate in the electrolyte could have affected the discharge process. The smallest concentration (0.008 M) exhibited almost no discharge capacity, which is possibly due to the very low fluoride content in the electrolyte (see also section influence of lithium ion contaminants in the electrolyte).

A Phillips X'Pert with a copper source was used for the PXRD measurements. The electrodes were placed directly under the beam, without further treating. The PXRD experiments were performed on a BiF_3/C cathode before and after the discharge process (Fig. 5). The strongest peaks of metallic Bi can be recognized in the PXRD pattern after the discharge and indicate a partial transformation of BiF_3 to Bi at the cathode.

At the end of the battery tests, the cells were opened. The separators were soaked in deuterated chloroform and NMR
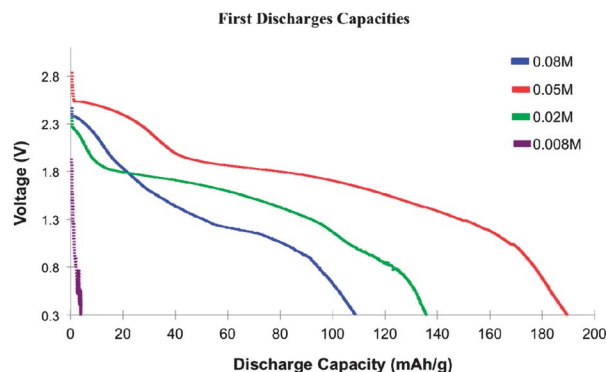

Fig. 3 Conductivity of compound **1** in acetonitrile.

Fig. 4 First discharge capacities in the BiF_3/C to lithium battery system with varying concentrations of electrolyte solutions. The capacity was calculated with respect to active mass of the electrode.
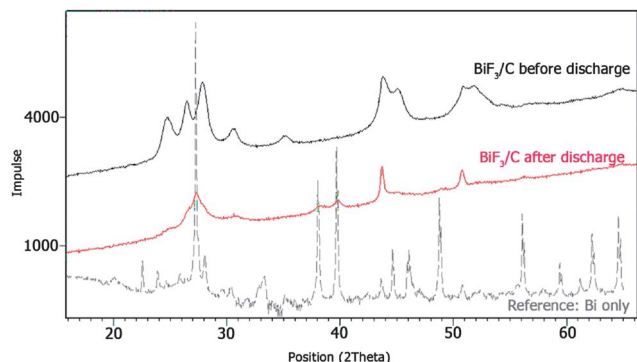
Fig. 5 Conversion of BiF_3 to Bi; X-ray patterns of the cathode composite before and after discharge.

spectra of the liquid were recorded. In some experiments, the separator underwent a color change, which ranged from very light yellow to brown. No significant changes could be observed in the structure of the PEG; however, the peaks in F-NMR shifted slightly upfield (+2 ppm) in some cases. This could be explained by the very low concentration of the electrolyte, which was transformed to deuterated fluoride clusters such as F_2D^- or $F_3D_2^-$.[22]

Influence of lithium ion contaminants in the electrolyte

Li-NMR analysis showed traces of lithium in our electrolytes after the discharge process. Lithium has a very negative reduction potential and can therefore be easily oxidized to Li^+, which makes it almost inevitable that some lithium ions will migrate into the fluoride electrolyte in case Li is used as an anode. Therefore, the impact of such lithium ion contaminants was investigated to assess potential contributions of lithium ions to the capacity of the battery.

For this study, we chose the pure solvents, MeCN, DMC, and Higlyme, and permitted the battery system of BiF_3/C to lithium to cycle in them under the conditions described two paragraphs earlier. The solvents DMC and higlyme showed neither discharge nor charge processes (ESI†), whereas dry acetonitrile

yielded a small capacity of about 2 mA h g^{-1}. The tests were repeated with different water contents in acetonitrile (30 ppm, 100 ppm, 1000 ppm, and 20% water content). The impact of the water can clearly be seen in Fig. 6. For an electrolyte that contained an unrealistically high water content (20%), the impact of the dissolved lithium ion provided a false discharge capacity of about 44 mA h g^{-1}.

These results confirm that the discharge capacity that we observed in our battery tests is mainly due to the fluoride transportation. The lithium ions which were detected after the battery tests have only a very small impact on the overall capacity (see Fig. 6) and are rather insignificant as long as the test cells are setup under dry conditions.

Conclusions

We have synthesized a PEG matrix doped with bifluoride anions. This new compound exhibited very good thermal stability, and decomposition did not occur until about 340 °C. When mixed with acetonitrile and dimethylcarbonate, the new compound can act as an electrolyte in fluoride ion batteries operating at room temperature. It had a good conductivity of 2.1 mS cm^{-1} even at low concentrations of the electrolyte (0.02 M). Battery tests with BiF_3/C as the cathode and metallic lithium as the anode showed a specific capacity of up to 190 mA h g^{-1}. For the specific electrochemical couple we found that some lithium ions dissolved in the electrolyte, and tests conducted with pure solvent showed that the impact of this dissolved lithium ion is rather insignificant (dry conditions), whereas solvents with excessive water content (20%) could provide a discharge capacity of about 44 mA h g^{-1}.

More work is under way to develop ameliorated liquid electrolytes as well as better systems for the electrodes, which could optimize the performance of the fluoride ion battery.

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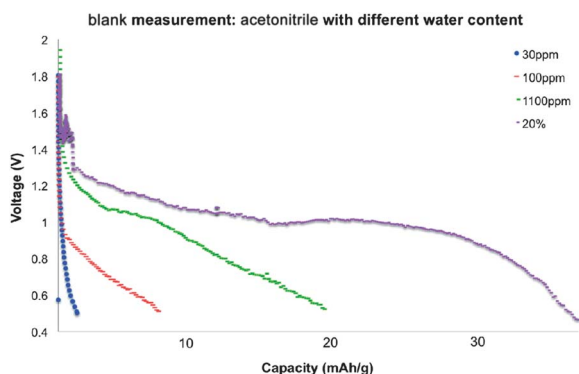11 K. M. Harmon and I. Gennick, *J. Mol. Struct.*, 1977, **38**, 97–107.

Fig. 6 Blank measurements of pure acetonitrile with varying contents of water. The acetonitrile mixture with 20% water content exhibited a discharge capacity of about 44 mA h g^{-1}.

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