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Short communication

Liquid electrolyte based on lithium bis-fluorosulfonyl imide salt: Aluminum corrosion studies and lithium ion battery investigations

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ABSTRACT

The performance of a liquid electrolyte composed of lithium bis-fluorosulfonyl imide (LiFSI) in a 1:1 volume of ethylene carbonate and dimethyl carbonate is evaluated for use in lithium ion batteries. Imide salts offer the benefits of higher thermal stability and could provide a safer alternative to LiPF_6 which is prone to the formation of HF. However, the most studied lithium imide salt, lithium bis(trifluoromethanesulfonyl) imide, is well known to have a problem with corrosion of aluminum which is commonly used as the cathode current collector. Consequently, the corrosion properties of liquid electrolytes based on lithium bis-fluorosulfonyl imide are also investigated.

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1. Introduction

Lithium ion batteries have rapidly dominated the market for power sources for portable electronic devices and, more recently, for power tools. The characteristics of combining high energy density with excellent charge retention have led to this success. Lithium ion batteries are currently the leading contender for being the electrical storage system of choice for plug-in hybrid electric vehicles (PHEVs). As good as the currently available lithium ion batteries are, there is still much scope for further improvements. In particular, questions about the safety of commonly used liquid electrolytes have been raised [1]. The electrolyte salt used in almost all commercial lithium ion batteries currently, LiPF_6 , has poor thermal stability and is very prone to decomposition reactions that lead to the formation of HF. Lithium imide salts are potentially a good alternative to LiPF_6 that could both improve the thermal and chemical stability of the electrolytes used in lithium ion batteries. However, the most studied of the lithium imide salts, lithium bis(trifluoromethanesulfonyl) imide, $\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$ (abbreviated as LiTFSI), is well known to be quite corrosive to the aluminum current collectors used for the

cathode in lithium ion batteries. Since LiTFSI corrodes aluminum at potentials as low as 3.7 V versus Li^0/Li^+ [2], it is not even feasible to use it in combination with low voltage cathodes such as LiFePO_4 . This problem has greatly hindered its market penetration in lithium ion technology since it is only useful as an additive to other salts [3]. To overcome this difficulty, other imide salts that might be less corrosive to aluminum should be examined.

Salts containing F–S or F–P bonds have been proposed to improve the corrosion properties of the anions relative to the aluminum current collector [4]. In particular, lithium bis-fluorosulfonyl imide, $\text{Li}(\text{SO}_2\text{F})_2\text{N}$ (abbreviated as LiFSI), has been shown to a useful salt for PEO-based gel electrolytes for lithium ion batteries with LiFePO_4 cathodes [5,6]. However, we are not aware of any reports on cycling performance of LiFSI in liquid electrolytes for lithium ion batteries or of any investigations of its corrosion properties on aluminum. Consequently, we have investigated the cycling performance of LiFSI in liquid electrolytes with LiFePO_4 and LiCoO_2 cathodes and measured its electrochemical stability relative to aluminum corrosion. We also report here on the conductivity of LiFSI dissolved in 1:1 by volume ethylene carbonate (EC) and dimethyl carbonate (DMC) as a function of temperature and on the study of its electrochemical stability by cyclic voltammetry.

2. Experimental

The lithium bis-fluorosulfonyl imide (LiFSI) salt was prepared by an ion exchange reaction of LiBF_4 with $\text{KN}(\text{SO}_2\text{F})_2$ in acetonitrile.

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The potassium salt was first obtained by the reaction of $\text{NH}(\text{SO}_2\text{Cl})$ with anhydrous KF. The thermal data of the salt were obtained on a differential scanning calorimeter [TA Instruments 2920] at a heating rate of $10^\circ\text{C min}^{-1}$ in a nitrogen atmosphere. Electrolyte solutions were made by dissolving the pre-weighed amount of $\text{Li}(\text{SO}_2\text{F})_2\text{N}$ in a 1:1 by volume mixture of ethylene carbonate (Aldrich) and dimethyl carbonate (Aldrich) in an Argon filled glove box. A concentration of 0.85 M LiFSI was used for all studies.

The IR spectrum was collected on a Bruker FT-IR spectrometer (model Tensor 27). Conductivity measurements were performed by the impedance spectroscopy technique between 0.1 Hz and 5 MHz using a Solatron SI 1260 and a platinum conductivity cell ($K=1\text{ Scm}^{-1}$). For the determination of the window of electrochemical stability, cyclic voltammetry was performed at room temperature in the voltage range of -0.5 to 6 V at a scan rate of 10 mVs^{-1} on a Princeton Applied Research potentiostat/galvanostat (Parstat 2263) with Ag as the reference electrode and Pt electrodes as both the working and counter electrodes. For the studies of corrosion on Al, cyclic voltammetry was performed on a freshly cut wire of aluminum suspended in a solution of 0.85 M LiFSI in 1:1 EC-DMC. Lithium metal was used for both the counter and reference electrodes. The anodic potential range was limited to 2.0 – 5.2 V versus Li^+/Li^0 to avoid reduction of the EC in the electrolyte.

Electrochemical evaluations were carried out in coin cells (size 2325) assembled with either lithium metal (Foote Mineral) or graphite (MCMB, Osaka Gas) anodes and either LiCoO_2 (Seimi) or LiFePO_4 (Phostech) cathodes. The graphitic anodes were prepared by making slurries of MCMB (80 wt%), super S carbon black (10 wt%) and a binder (10 wt%) from a solution of polyvinylidene difluoride (Kynarflex 2800) dissolved in *N*-methyl-2-pyrrolidinone (Aldrich). The slurries were then tape cast onto copper foil current collectors by the doctor blade method and dried under vacuum at 110°C overnight. Electrode discs of 14.5 mm diameter were cut from the cast and weighed. A very similar method was used for the preparation of cathode discs, in which a slurry was formed by mixing the active material, LiCoO_2 or LiFePO_4 (84 wt%), Super S carbon black (4 wt%), graphite (4 wt%), and binder (8 wt%) from a solution of polyvinylidene fluoride (Kynarflex 2800) dissolved in *N*-methyl-2-pyrrolidinone. The slurry was coated onto an aluminum current collector. The cathodes were dried under vacuum at 110°C overnight and then discs of 14.2 mm diameter were punched and weighed. The cells were assembled in an Argon filled glove box. A

sheet of microporous polypropylene (Celgard 3501) was used for the separator. A volume of $70\text{ }\mu\text{L}$ of electrolyte solution was used in each cell. Cell tests were conducted at room temperature by galvanostatic cycling at C/12 rate between 2.5 and 3.9 V for LiFePO_4 cells and between 2.5 and 4.1 V for LiCoO_2 on an Arbin battery cyclers.

3. Results

The LiFSI was synthesized by a procedure similar to that of Beran and Prihoda [7], with the exception that LiBF_4 was used in place of LiClO_4 for the ion exchange with $\text{K}(\text{SO}_2\text{F})_2\text{N}$. The potassium salt was first obtained by the reaction of $\text{NH}(\text{SO}_2\text{Cl})$ with anhydrous KF. The purity of the potassium salt, characterized by its IR spectrum in Fig. 1, is a good match to the prior work of Beran and Prihoda [8]. The LiFSI was prepared by the reaction of LiBF_4 with $\text{KN}(\text{SO}_2\text{F})_2$ in acetonitrile. The DSC scan of LiFSI salt, in Fig. 2, shows a single peak at 132°C attributed to its melting point [7].

The conductivity of a 0.85 M solution of LiFSI in 1:1 (by vol.) EC/DMC as a function of temperature is shown in Fig. 3. At 25°C , a conductivity of 12 mS cm^{-1} was found. This is higher than 9 mS cm^{-1} observed for 1M LiTFSI in 1:1 (by vol.) EC/DMC [9].

A study of the electrochemical stability of LiFSI solutions was made by cyclic voltammetry with an Ag electrode for reference. As

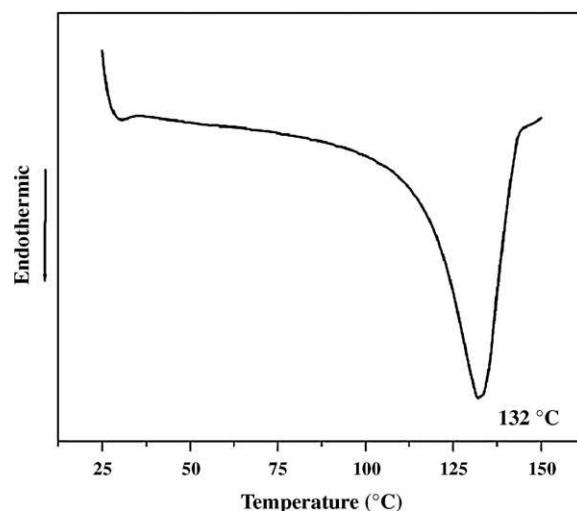


Fig. 2. DSC scan of lithium bis-fluorosulfonyl imide (LiFSI) salt.

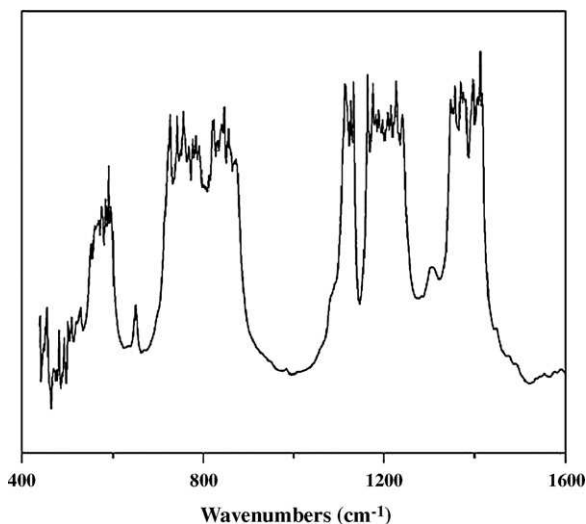


Fig. 1. IR spectrum of $\text{KN}(\text{SO}_2\text{F})_2$.

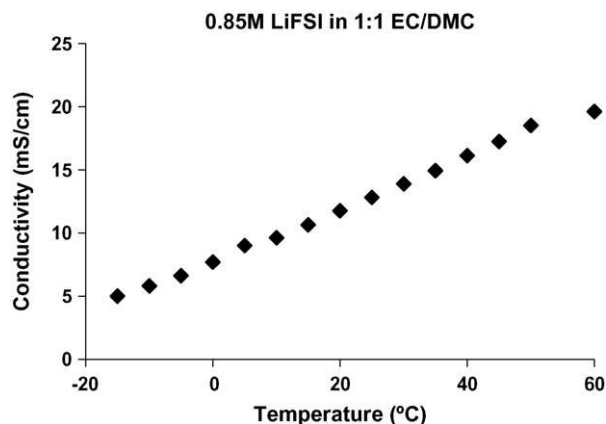


Fig. 3. Plot of variation of ionic conductivity of 0.85 M LiFSI in 1:1 EC/DMC as a function of temperature.

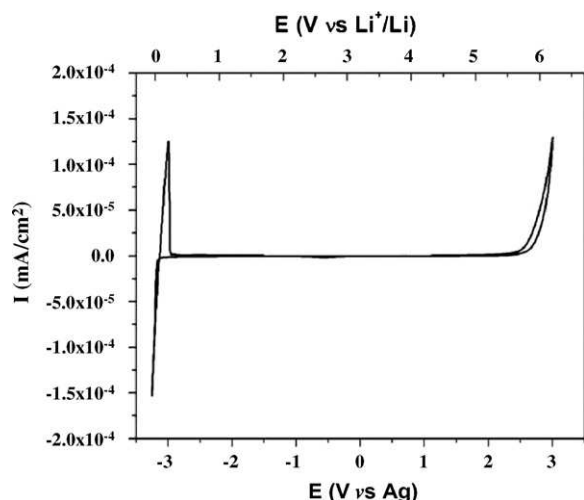


Fig. 4. Cyclic voltammograms of 0.85 M LiFSI in 1:1 EC/DMC using Ag as the reference and Pt for both the working and counter electrodes.

shown in Fig. 4, for 0.85 M LiFSI in EC/DMC, the cyclic voltammetry shows very good anodic stability to about 5.6 V versus Li^+/Li^0 .

The electrochemical behavior of a freshly cut Al wire electrode in 0.85 M LiFSI in EC/DMC (1:1 in vol.) was investigated by cyclic voltammetry. The anodic potential range was limited to 2.0–5.2 V versus Li^+/Li^0 to avoid reduction of EC. Unfortunately, as can be seen in Fig. 5, the 0.85 M LiFSI in EC/DMC electrolyte solution was observed to corrode Al at a potential of only 3.3 V versus Li^+/Li^0 . This is a significantly lower potential than the 3.7 V observed for the onset of Al corrosion for LiTFSI in EC/DMC [2]. However, it should be noted that the potential for onset of Al corrosion at 3.3 V is near that which might be expected if some residual chloride ions had been carried through from the $\text{NH}(\text{SO}_2\text{Cl})$ used in the synthesis. This possibility will need to be investigated further.

The performance of liquid electrolyte based on LiFSI was evaluated in lab scale coin cells. A half cell assembled with a Li metal anode, a LiFePO_4 cathode and 0.85 M LiFSI in 1:1 EC/DMC as the electrolyte showed exceptionally good capacity retention (Fig. 6). The cell maintained very stable discharge capacities for more than 100 cycles with capacities greater than 137 mAh g^{-1} and with excellent coulombic efficiency. A complete lithium ion

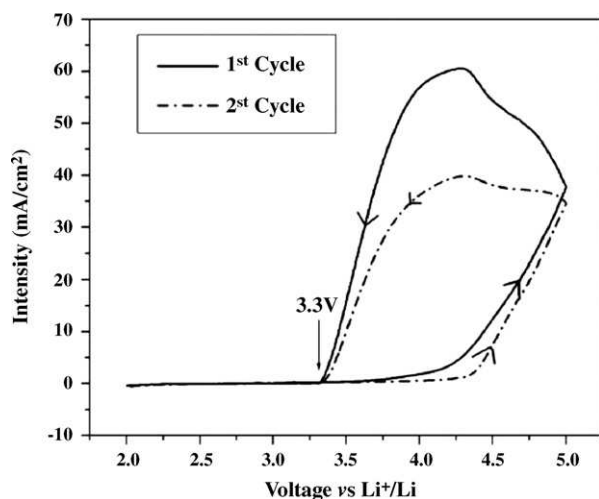


Fig. 5. Cyclic voltammogram of 0.85 M LiFSI in 1:1 EC/DMC using Al as the working electrode and Li metal for both the counter and reference electrodes.

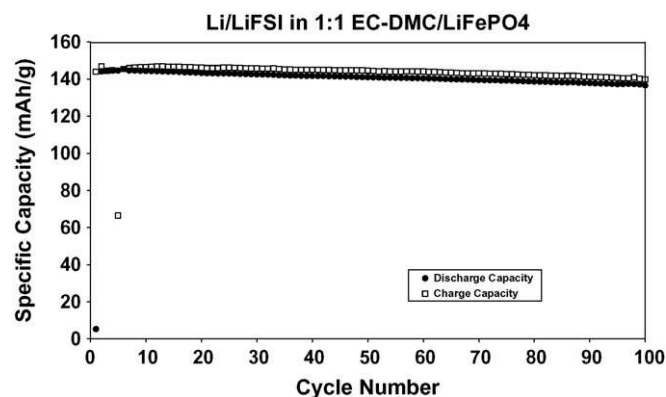


Fig. 6. Plot of specific charge–discharge capacities versus cycle number for Li/0.85 M LiFSI in 1:1 EC/DMC/LiFePO₄ cell at C/12 rate.

cell, shown in Fig. 7, with a graphite (MCMB, Osaka Gas) anode, a LiFePO_4 cathode and 0.85 M LiFSI in 1:1 EC/DMC electrolyte had somewhat reduced capacity and slightly poorer capacity retention. These effects are most probably due to imbalance between the anode and cathode capacities. A half cell assembled with a LiCoO_2 cathode, a Li metal anode and 0.85 M LiFSI in 1:1 EC/DMC electrolyte, shown in Fig. 8, was also found to have quite good capacity, coulombic efficiency and showed only moderate capacity fade on cycling.

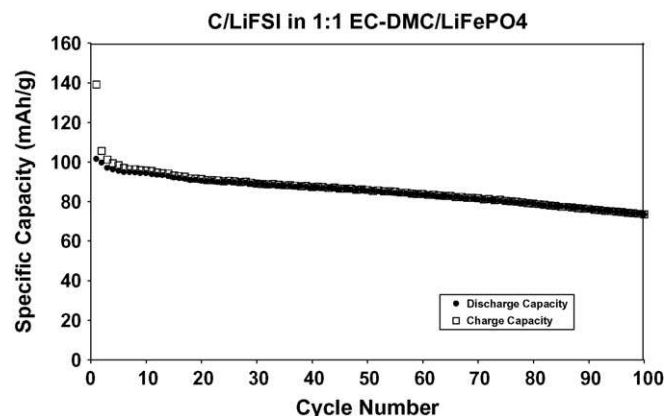


Fig. 7. Plot of specific charge–discharge capacities versus cycle number for C/0.85 M LiFSI in 1:1 EC/DMC/LiFePO₄ cell at C/12 rate.

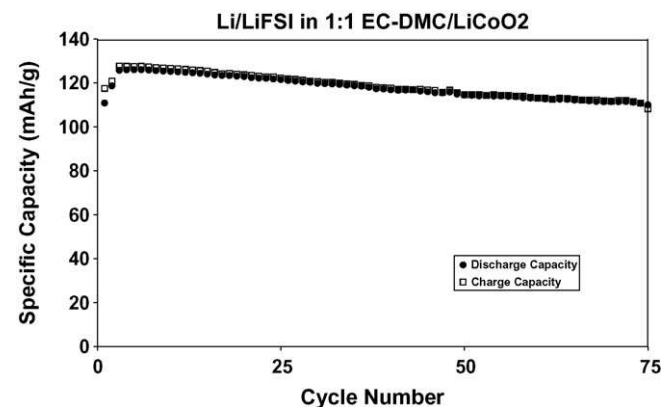


Fig. 8. Plot of specific charge–discharge capacities versus cycle number for Li/0.85 M LiFSI in 1:1 EC/DMC/LiCoO₂ cell at C/12 rate.

4. Conclusion

The performance of a liquid electrolyte composed of 0.85 M lithium bis-fluorosulfonyl imide (LiFSI) in a 1:1 volume of ethylene carbonate and dimethyl carbonate was evaluated for use in lithium ion batteries. A novel method of synthesis of LiFSI was developed that avoids the use of LiClO_4 . Solutions of LiFSI in EC/DMC were found to have quite acceptable conductivity reaching 12 mS cm^{-1} at 25°C for a 0.85 M solution. Liquid electrolytes based on LiFSI dissolved in EC/DMC were observed to have an exceptionally broad electrochemical window stretching to 5.6 V versus Li^+/Li^0 . The cycling characteristics in lithium and lithium ion cells with either LiFePO_4 or LiCoO_2 cathodes were also very encouraging, showing very good coulombic efficiencies and low to moderate capacity fade over 75–100 cycles. However, one of the key reasons for interest in LiFSI as an electrolyte salt for lithium ion batteries was the expectation that it would be less prone to corrosion of aluminum than the lithium bis(trifluoromethane sulfonyl) imide salt (LiTFSI). Unfortunately however in this study, the LiFSI electrolyte solution was found to corrode aluminum at 3.3 V versus Li^+/Li^0 which is an even lower potential than the 3.7 V observed for the onset of Al corrosion for LiTFSI dissolved in the same co-solvents. The potential for onset of Al corrosion by LiFSI is, however, very close to that expected for oxidation of Cl^- , and consequently, further investigation is needed

to confirm whether or not the observed corrosion is indeed due to the LiFSI or due to residual Cl^- from the synthesis.

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