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Stable cycling of lithium metal electrode in nanocomposite solid polymer electrolytes with lithium *bis*(fluorosulfonyl)imide

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ABSTRACT

Nanocomposite solid polymer electrolytes (NSPEs) comprising lithium salt based on two representative sulfonylimide anions (i.e., *bis*(fluorosulfonyl)imide ($[N(SO_2F)_2]^-$, FSI^-) and *bis*(trifluoromethanesulfonyl)imide ($[N(SO_2CF_3)_2]^-$, $TFSI^-$)) have been prepared by simply dissolving the corresponding lithium salt in poly(ethylene oxide) matrix in the presence of inert nano-sized Al_2O_3 fillers. The physicochemical and electrochemical properties of the FSI- and TFSI-based NSPEs are investigated, in terms of phase transition, ion transport behavior, chemical and electrochemical compatibility with Li metal. With the addition of nano-sized Al_2O_3 fillers, a significant improvement in chemical and electrochemical compatibility with Li metal has been observed in both the FSI- and TFSI-based NSPEs. Particularly, the symmetric cell using the FSI-based NSPE can be continuously cycled for > 1000 h at 70 °C. The Li|$LiFePO_4$ cell with the FSI-based NSPEs shows good cycling stability and capacity retention. These promising results make them attractive electrolytes for safe and stable rechargeable Li metal batteries.

1. Introduction

The replacement of flammable electrolytes and enhancement of the energy density of Li-ion batteries (LIBs) have been the forefront of research in both academia and industry. Li metal has an extremely high theoretical capacity (3860 mAh g^{-1}) and the lowest negative electrode potential (− 3.040 V vs. standard hydrogen electrode), and is being intensively investigated as anode for rechargeable Li metal batteries (LMBs), such as Li-sulfur, Li-air batteries, and solid-state Li metal-polymer batteries [1–7]. However, the progresses in non-aqueous electrolyte for rechargeable LMBs are hindered by several seemingly insurmountable barriers, including dendritic Li growth and rapid capacity fade (i.e., limited Coulombic efficiencies (CEs)) during repeated Li deposition/dissolution processes in non-aqueous electrolytes [8–10].

Solid polymer electrolytes (SPEs) offer many advantages over liquid electrolytes, such as no risk of electrolyte spillage, excellent flexibility, and low cost in design [7,11–14]. SPEs have been intensively investigated as safe electrolytes for application in solid-state rechargeable LMBs over the past four decades. The success of SPEs is well demonstrated by their preliminary application as electrolytes of solid-state rechargeable LMBs for an electric car, Autolib®, in France and USA [15].

As Li metal anode is thermodynamically unstable with any kind of polar organic solvents and polymer matrices, it reacts with the electrolyte components, thus forming a solid-electrolyte-interphase (SEI) film on the Li metal side which strongly impacts the cycling performance of LMBs [8–10]. The properties of such SEI films are intrinsically affected by the anion type of the lithium salt. Among all the lithium salts being investigated for SPEs, lithium *bis*(trifluoromethanesulfonyl) imide ($Li[N(SO_2CF_3)_2]$, LiTFSI) has been the most extensively studied as conducting salt, due to its good plasticizing effect, excellent thermal, chemical and electrochemical stability [11,13,16]. However, LiTFSI-based SPEs suffer from a relatively poor compatibility with Li metal electrode [17,18] and from the depassivation at high voltage of the Al current collector on the positive side, leading to corrosion [19].

Here we describe a new type of nanocomposite solid polymer electrolyte (NSPE), obtained by simply dissolving the lighter homologue of LiTFSI, lithium *bis*(fluorosulfonyl)imide ($Li[N(SO_2F)_2]$, LiFSI) in a poly(ethylene oxide) (PEO) matrix in the presence of nano-sized Al_2O_3 fillers, improving markedly the cycling performance of solid-state rechargeable LMBs. Such NSPE was conceived on the base of three considerations. Firstly, LiFSI has shown excellent compatibility with Li metal and other electrodes in both liquid and polymer electrolytes [18,20–26]. Secondly, the addition of ceramic nanofillers into polymer

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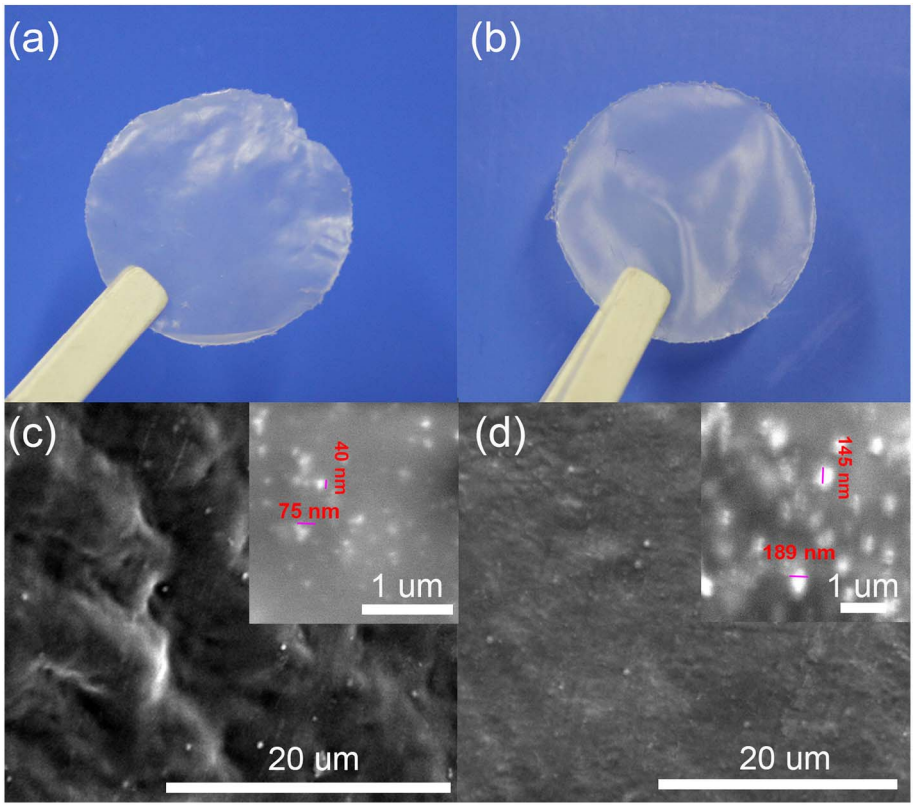

Fig. 1. Physical appearance of the as-prepared membrane of the (a) FSI- and (d) TFSI-based NSPEs, Typical SEM micrographs the (c) FSI- and (d) TFSI-based NSPEs.

matrices has been proven to be a simple and efficient method for enhancing the physicochemical and electrochemical properties of SPEs. The addition of ceramics nano powders improves the mechanical properties of PEO-based SPEs as well as their interfacial behavior in contact with Li metal electrode [27–31]. Al_2O_3 was chosen as a filler for its resistance to reduction by lithium, which is not the case for nano-SiO_2 [27]. The 10 wt% Al_2O_3 was added in the FSI- and TFSI-based polymer electrolytes, since previous work revealed that this composition of Al_2O_3 afforded relatively high ionic conductivities and good interfacial properties with Li metal [32,33]. Thirdly, it is potentially easier to scale up this simple particle adding method for preparing large surfaces SPE films than resort to arduous the modifications of polymer matrices (e.g., block copolymers) [34]. In this work, the physicochemical, electrochemical properties of FSI- and TFSI-based NSPEs, as well as their compatibility with Li metal are presented.

2. Experimental

2.1. Preparation and characterization of SPEs

Polymer electrolytes with an average thickness of 50 μm were prepared by conventional solvent casting method followed by hot-pressing (High Temperature Film Maker Controller, Specac) [35]. The polymer was dissolved into acetonitrile and then the salt either lithium *bis* (fluorosulfonyl)imide (LiFSI, battery grade, Suzhou Fluolyte, China)), or lithium *bis*(trifluoromethanesulfonyl)imide (LiTFSI, battery grade, Solvionic, France), and filler (γ-Al_2O_3 nanoparticles; 99.99%, hydrophilic; 5 nm, US Research Nanomaterials) were added. In all cases the salt concentration was 20:1 (the molar ratio of $–CH_2CH_2O–$ ([EO])/[Li^+]), and the amount of filler added was 10 wt% of the total LiX/PEO weight. Surface morphology of the as prepared membrane was examined by a field emission Quanta 200 FEG (FEI), operated at 5 kV.

2.2. Phase behavior

The phase transition behavior of the electrolyte was measured on a differential scanning calorimeter (Q2000, TA Instruments). The prepared electrolyte sample with average weight of ca. 5–10 mg was hermetically sealed in an aluminum crucible in an argon-filled glove box. The sample was measured for two successive scans at a cooling and heating rate of 10 °C min^{-1} in the temperature range of − 80 to 100 °C. At the two temperature extremes at the low (− 80 °C) and high (100 °C) ends in each scan, the sample was allowed to stand for five minutes. The glass transition temperature (T_g) was taken at the onset of the heat capacity change, while the melting (T_m) and crystallizing (T_c) points were taken at the peak of the heat capacity change.

2.3. Cathode preparation

The slurry of $LiFePO_4$ based polymer cathode was prepared by mixing carbon-coated $LiFePO_4$ (LFP, Aleees, Taiwan) active material (63 wt%), carbon Super P C65 (7 wt%) and binder (30 wt%, LiFSI/PEO and LiTFSI/PEO electrolytes), followed by casting on Al current collector. After pre-drying in air over 10 h, the cathode was dried at 45 °C for 12 h under dynamic vacuum, and then transferred in an argon-filled glove box.

2.4. Electrochemical test

The measurements of ionic conductivity were carried out on a VMP3 potentiostat (Biologic) by the complex impedance method. The Li-ion transference number ($T_{Li}{}^+$) of the polymer electrolyte at 70 °C was measured by a combination measurement of ac impedance and dc polarization using a symmetric Li|SPEs|Li cell, as described by Bruce and Abraham [36,37]. The details of both experiments can be found in our previous work [35,38].

CR2032 cells (Li|Li and Li|$LiFePO_4$) were assembled in an argon-filled glove box. For Li symmetric cells storage at 70 °C, the ac