



Lowering the operational temperature of all-solid-state lithium polymer cell with highly conductive and interfacially robust solid polymer electrolytes



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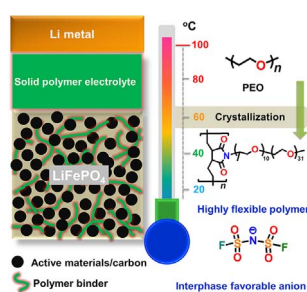
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HIGHLIGHTS

- Super soft solid polymer electrolyte (SPE) with Li[N(SO₂F)₂] is prepared.
- The prepared SPE is highly conductive at ambient temperature.
- The prepared SPE has good electrochemical compatibility with Li metal electrode.
- Li | LiFePO₄ cell using the prepared SPE can be cycled at ambient temperature.

GRAPHICAL ABSTRACT



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ABSTRACT

Novel solid polymer electrolytes (SPEs), comprising of comb polymer matrix grafted with soft and disordered polyether moieties (Jeffamine[®]) and lithium bis(fluorosulfonyl)imide (LiFSI) are investigated in all-solid-state lithium metal (Li⁺) polymer cells. The LiFSI/Jeffamine-based SPEs are fully amorphous at room temperature with glass transitions as low as ca. –55 °C. They show higher ionic conductivities than conventional poly(ethylene oxide) (PEO)-based SPEs at ambient temperature region, and good electrochemical compatibility with Li⁺ electrode. These exceptional properties enable the operational temperature of Li⁺ | LiFePO₄ cells to be decreased from an elevated temperature (70 °C) to room temperature. Those results suggest that LiFSI/Jeffamine-based SPEs can be promising electrolyte candidates for developing safe and high performance all-solid-state Li⁺ batteries.

1. Introduction

The deployment of new technologies like portable electronics, electric vehicles (EVs) and now power plants of renewable energy sources has led to an extensive worldwide demand from the battery community [1,2]. Safety issues and insufficient energy density of the state-of-art lithium-ion batteries (LIBs) justify the search for all-solid-state lithium metal (Li⁺) batteries (ASSLMBs), which could offer better

safety and higher energy density [3,4]. Solid polymer electrolytes (SPEs) have good processability and in principle are easier to be scaled up for large-format batteries (i.e. lamination process) compared to inorganic electrolytes. It has been already demonstrated by the launch and expansion of Bluecar[®] from Blue Solutions, where SPEs are applied exclusively as electrolyte components for EV batteries, in several cities (e.g., Paris, Bordeaux, Lyon, Indianapolis, etc.) [5].

Poly(ethylene oxide) (PEO) is one of the most widely used polymer

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matrices, since the electron-donating nature of ethylene oxide (EO) units can effectively facilitate the dissolution and dissociation of various lithium salts [6]. However, low ionic conductivity due to the presence of crystalline phase at temperatures below the melting point of PEO (ca. 65 °C) impedes the operation of PEO-based ASSLMBs at ambient temperature [7]. As a result, a thermal control system is necessary for maintaining the satisfying cycling performance for those PEO-based ASSLMBs. Clearly, the incorporation of an extra thermal accessory/system causes a reduced energy efficiency and density for the battery pack [8]. To this end, reducing the operational temperature of SPEs-based ASSLMBs to ambient temperature region is highly desired, not only for preserving their advantageous energy densities at battery pack level, but also for underlining their claimed merits, such as good Li metal compatibility, low price, safety, etc.

The main barriers for developing SPEs-based ASSLMBs operational at ambient temperature are the low ionic conductivity of SPEs and poor interfacial compatibility with electrode materials, especially vs. Li⁺ anode. In this regards, tremendous efforts have been devoted to the design and synthesis of polymer matrices, aiming at preparing non-crystallized and low glass transition polymers [7,9,10], due to the fact that ionic transportation of SPEs is generally coupled with segmental motion of polymer segments in the amorphous phases, i.e., the lower crystallinity and glass transition temperature (T_g), the higher ionic conductivity [11]. Those molecular level modifications of polymer matrices include architecture alteration by branching polymer segment [12], random [13] and/or comb copolymerization [14,15]. Besides, the choice of lithium salt has been proven to be extremely important for improving transport properties of SPEs [6]. Among the numerous salts studied, sulfonimide (–SO₂–N–SO₂–) based salts are capable of enhancing the ionic conductivity by effectively decreasing the crystallinity of SPEs and promoting the dissociation of Li⁺ cation due to the flexible S–N bond and highly delocalized negative charge of sulfonimide anions [16]. To date, ionic conductivities up to 10^{−4} S cm^{−1} at room temperature can be achieved in fully amorphous systems [17].

On the other hand, highly ionic conductive, electronic insulating, and stable interfacial layers on both Li⁺ anode and cathode sides are desired for obtaining good cycling performance of ASSLMBs [14,18,19]. This requires that SPEs should afford not only high ionic conductivity but also good electrochemical compatibility with electrode materials, which is supported by the fact that most of the SPEs-based cells exhibit efficient cycling only at elevated temperatures (e.g., 70 °C) due to the lack of good chemical/electrochemical compatibility of electrolyte/electrode interphases at room temperature. In addition, the problem of internal contact for the active materials within composite cathode will be magnified when operating the SPEs-based ASSLMBs at lower temperature even at low C-rates, considering the increased cell resistance upon decreasing the temperature. The high polarization may cause the decomposition of lithium salt and/or polymer matrix, and even pulverize possibly active materials in the cathode [20]. Thus, the binders herein SPEs themselves with good ionic conductivity, stability, mechanical strength and good adhesive properties are crucial for improving the cycle life of LPBs [20,21].

In this work, we report a new type of SPE comprising of our recently presented super soft polymer matrix containing polyether side moieties

(so-called Jeffamine®) [15] (Scheme 1a) and a popular salt, lithium bis (fluorosulfonyl)imide (LiFSI, Scheme 1b), in hope of reducing the operational temperature of polymer-based ASSLMBs. Owing to the disordered oligomer part where copolymer based on ethylene oxide and propylene oxide (PPO) units are parts of the chain, together with the superior physiochemical and electrochemical properties of LiFSI [16,22–26], the SPEs comprising of LiFSI and Jeffamine-based polymer matrix exhibit unique adhesion properties, high mobility of lithium ions, and good compatibility with Li⁺ electrode. Most importantly, the Li⁺ | LiFePO₄ cells using LiFSI/Jeffamine-based SPEs can be cycled under a wide temperature range from 70 to 25 °C with decent electrochemical performances.

2. Experimental

2.1. Materials

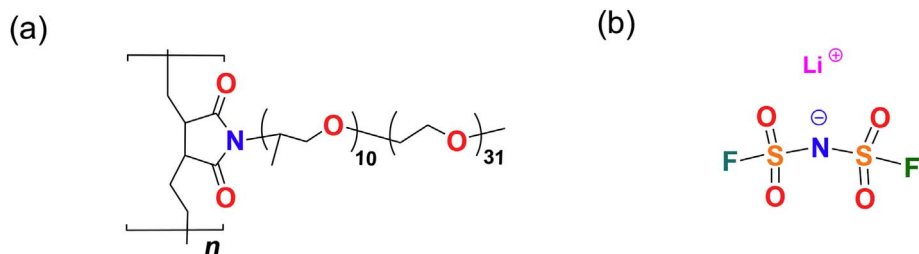
Lithium bis(trifluoromethanesulfonyl)imide (LiTFSI, battery grade, Solvionic, France), lithium bis(fluorosulfonyl)imide (LiFSI, battery grade, Suzhou Fluolyte, China), and poly(ethylene oxide) (PEO, $M_n = 5 \times 10^6$ g mol^{−1}, Sigma-Aldrich) were used as received. Jeffamine M-2070-based polymer matrix was prepared according to the procedures reported in our previous work [15].

2.2. Preparation and characterization of polymer electrolyte

The polymer electrolytes were prepared by solvent casting method. The phase transition behavior of the electrolyte was measured on a differential scanning calorimeter (Q2000, TA Instruments). Thermogravimetric analysis (TGA) was carried out on a NETZSCH simultaneous thermal analyzer (STA) 449 F3 Jupiter® under argon flow. The ionic conductivity of the prepared SPEs was measured by AC impedance spectroscopy using a VMP3 potentiostat (Biologic) in a frequency ranging from 10^{−1}–10⁶ Hz with a signal amplitude of 10 mV. A CR2032 type coin cell using two stainless steel (SS) blocking electrodes (SS | SPEs | SS) was assembled in an Ar filled glovebox and used for the measurement. The measurements of surface morphology, chemical structure, Li-ion transference number (T_{Li^+}), diffusion coefficient, and electrochemical stability of the as-prepared polymer electrolytes were presented in Supplementary Information.

2.3. Chemical and electrochemical stability of electrolyte/Li⁺ electrode interphase

Li⁺ symmetrical coin cells (Li⁺ | SPE | Li⁺) were assembled in an argon-filled glove box to investigate the electrochemical stability of electrolyte/Li⁺ electrode interphase. The AC impedance spectra and galvanostatic mode cycling of the Li⁺ symmetric cells were evaluated using the VMP3 potentiostat (Biologic) at various temperatures. For chemical stability test, the Li⁺ symmetric cells were kept at a defined temperature for 1 h, and then the corresponding AC impedance spectra were recorded in the frequency range from 10^{−1}–10⁶ Hz with a voltage amplitude of 10 mV. For the electrochemical stability test, the Li⁺ symmetric cells were cycled galvanostatically at a current density of



Scheme 1. Chemical structures of (a) the Jeffamine-based polymer matrix and (b) lithium bis(fluorosulfonyl)imide salt.

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