



Ambient temperature solid-state Li-battery based on high-salt-concentrated solid polymeric electrolyte

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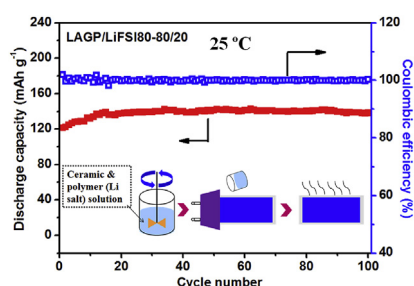
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HIGHLIGHTS

- High-salt-concentrated PPC-based SPE with conductivity of 0.6 mS cm^{-1} at 30°C .
- Li transference number of 0.75 for high-salt-concentrated PPC-based SPE at 25°C .
- Ceramic/polymer composite electrolyte fabricated via doctor-blade coating method.
- SSBs based on ceramic/polymer composite electrolyte perform well at 25°C .
- A reversible discharge capacity of 138.3 mAh g^{-1} was achieved at 0.1 C at 25°C .

GRAPHICAL ABSTRACT



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ABSTRACT

The ambient temperature application of solid-state batteries (SSBs) based on ceramic/PEO composite solid electrolyte has been restrained by the poor ionic conductivity of PEO-based polymer. Herein, we have studied high-salt-concentrated polymeric electrolyte comprising poly(propylene carbonate) (PPC) and lithium bis-(fluorosulfonyl) imide (LiFSI), as well as its application in ceramic/polymer composite solid electrolytes based SSBs. The PPC-LiFSI 80 wt.% electrolyte showed a significantly improved ionic conductivity on the order of $10^{-4} \text{ S cm}^{-1}$ at ambient temperature, Li transference number of 0.75, and anodic stability up to 4.5 V versus Li/Li^+ . The $\text{LiFePO}_4/\text{Li}$ cell with $\text{Li}_{1.5}\text{Al}_{0.5}\text{Ge}_{1.5}(\text{PO}_4)_3$ (LAGP)/PPC-LiFSI 80 wt.% composite electrolyte showed stable charge/discharge profiles and excellent cycling performance, which delivered a specific discharge capacity of 138.3 mAh g^{-1} at 0.1 C and a high capacity retention of 97.1% after 100 cycles. According to EIS results, we found that the reduced cell deterioration and polarization is attributed to the improved interface between the electrode and the solid electrolyte, which is realized by introducing the flexible and conductive high-salt-concentrated polymeric electrolyte PPC-LiFSI 80 wt.%. The results indicate that ceramic/high-salt-concentrated PPC-based polymer composite electrolyte is promising for ambient temperature solid-state lithium batteries.

1. Introduction

Currently, the bottleneck of safety issue in lithium ion batteries (LIBs) based on non-aqueous liquid electrolyte has stimulated research

interests for durable solid-state batteries (SSBs) with nonflammable solid electrolytes (SEs). As the most crucial component in SSBs, different types of SEs have been employed [1]. Among them, solid polymeric electrolytes (SPEs) take the advantage of high flexibility, easy

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processability, and good interfacial compatibility [2,3]. However, the low lithium-ion conductivity of SPEs, such as poly(ethylene oxide) (PEO) based SPE, generally require a high operation temperature above 70 °C and prevents rate capability of the batteries [4]. Compared with SPEs, although inorganic ceramic electrolytes possess a relatively higher conductivity at ambient temperature, they are suffering from the high interfacial resistance and mechanical failure through cracking due to the brittle nature [5]. In addition, dendrites may enter into polycrystalline solids and penetrate the membranes along grain boundaries of these inorganic ceramic, leading to short-circuit [6]. All these drawbacks restrict the mass application of either inorganic ceramic or polymeric electrolytes in commercial batteries.

A combination of inorganic ceramic and polymeric electrolytes may integrate the benefits from both of them and address the problems of each. Zhou et al. [7] designed a polymer/ceramic membrane/polymer sandwich electrolyte (PCPSE) using cross-linked Li⁺ polymer conductor poly(ethylene glycol) methyl ether acrylate (CPMEA), which improved the efficiency and dendrite suppression capability in solid-state battery. Chen et al. [8] proposed a synergistic all-composite approach based on Al-doped LLZTO/PEO-based SPE composite electrolyte achieving flexible all-solid-state LIBs with high surface capacity and energy density. Recently, Huo et al. [9] reported batteries based on composite electrolytes consisting of PEO (Li-salt-free) and Li_{6.4}La₃Zr_{1.4}Ta_{0.6}O₁₂ particles which showed superior cycle stability at ambient temperature, but interfacially wetted by using ionic liquid [BMIM]TF₂N was indispensable. In our previous work, we combined the use of LAGP/PEO-based SPE composite solid electrolyte and the modification of Li anode with PEO-based SPE to effectively prevent the Li anode from dendrite growth, and the as-obtained Li/LiMn_{0.8}Fe_{0.2}PO₄ (LiMFP) solid-state battery provided a satisfactory cycling performance at 50 °C [10]. Even though the PEO-based SPE content in LAGP/PEO-based SPE composite was controlled to as low as 1% (wt.), the room temperature (RT) conductivity of LAGP/PEO-based SPE composite solid electrolyte decreased by one to two orders of magnitude compared with LAGP ceramic, which resulted in undesirable battery performances at ambient temperature. Obviously, the slow kinetics of ceramic/polymer composite solid electrolyte is ascribed to the polymeric part with low ionic conductive property.

The ions migration ability in PEO-based SPE is generally restricted by cross-linking (coupling) structures between lithium ions (Li⁺) and dipoles of the polyether chains [11–15]. In contrast, polycarbonates with large dipole moment carbonate group (–O–(C=O)–O–) can dissociate more salts and interact with Li⁺ [16–19]. Additionally, tight coordination or solvation in the PEO–salt complexes could be ignored in this “decoupling” system [20,21]. Lithium bis-(fluorosulfonyl) imide (LiFSI) is not only compatible with graphitized carbon electrode but also with Li metal electrode. LiFSI shows better conductive characterization, which is essentially attributed to its higher dissociation and a medium-range size for FSI[−] [22–24]. Therefore, we have designed a high-salt-concentrated polymeric electrolyte based on poly(propylene carbonate) (PPC) and LiFSI as a promising alternative of PEO-based SPE in ceramic/polymer composite electrolyte to enhance the ionic conduction in this work. The electrochemical properties of a series of PPC-based SPEs with high salt concentrations were comprehensively studied. Furthermore, high-salt-concentrated PPC-based SPEs were employed in the ceramic/polymer composite solid electrolyte system using for SSBs. It is worth to note that devices based on ceramic/high-salt-concentrated PPC-based SPE composite solid electrolytes prepared by doctor-blade coating method exhibited stable charge/discharge profiles, excellent cycling performance and satisfactory rate capability, indicating this kind of composite solid electrolytes is a promising candidate for mass-scale ambient temperature SSBs.

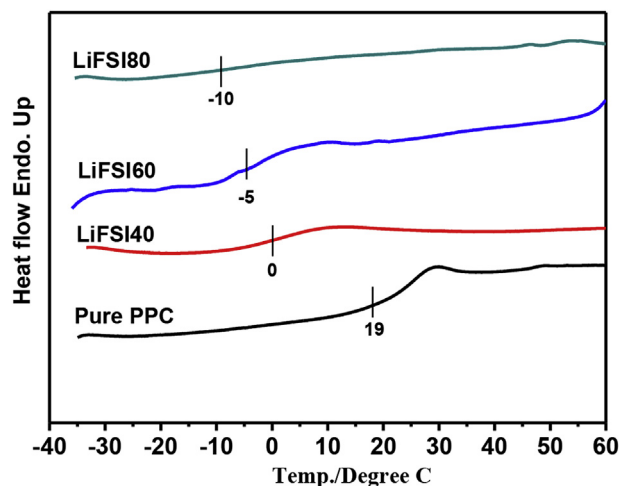


Fig. 1. DSC traces of neat PPC and PPC-LiFSI electrolytes with various salt concentrations (40, 60 and 80 wt%).

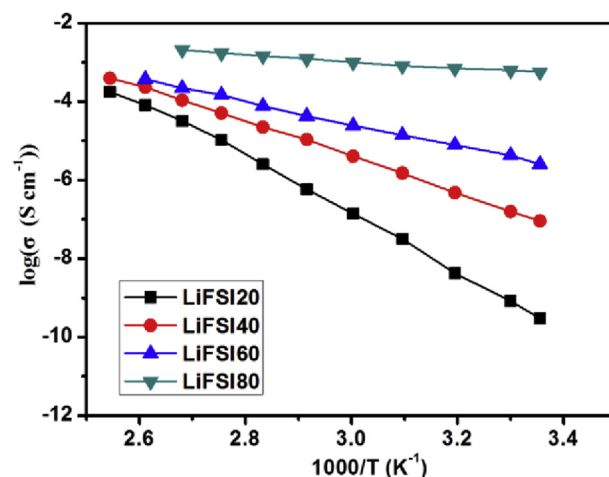


Fig. 2. Arrhenius plots of ionic conductivity for the PPC-LiFSI electrolytes with various salt concentrations (20, 40, 60 and 80 wt%).

2. Experimental

2.1. Materials and electrolyte preparations

PPC ($M_w = 50,000$, Sigma-Aldrich) or PEO-based ($M_w = 100,000$, Alfa Aesar) solid polymeric electrolytes (SPEs) were fabricated by solution-casting method. PPC and LiFSI (Suzhou Fotai New Materials Co. Ltd.) with various weight ratios (80:20, 60:40, 40:60, 20:80) were added into dimethylacetamide (DMAc, > 99%, Sigma-Aldrich) and stirred to form homogeneous solutions, respectively. On the basis of the LiFSI content, the samples were designated as LiFSI20, LiFSI40, LiFSI60 and LiFSI80, respectively. The molar concentrations for LiFSI80, LiFSI60, LiFSI40, and LiFSI20 are 4.28, 3.21, 2.14 and 1.07 mol kg^{−1}, respectively. As contrast experiment, PEO/lithium bis (trifluoromethanesulfonyl) imide (LiTFSI, Suzhou Fotai New Materials Co. Ltd.) solution was prepared based on EO: Li = 8: 1 (mol%), designated as PEO-SPE, which is the best ratio reported in the literature [25]. PPC-based or PEO-based homogeneous solutions were poured into Φ 16 disc cellulose nonwoven membranes, followed by the evaporation of the solvent in vacuum at 70 °C for 48 h. Pristine PPC-based or PEO-based SPE samples without cellulose nonwoven matrix were prepared by the similar method.

To prepare composite solid electrolyte, LAGP (dealt with 300-mesh sieves) were dissolved into PPC-based (or PEO-based) SPE solution and

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