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Preparation and characterization of nanocomposite ionic liquid-based gel polymer electrolyte for safe applications in solid-state lithium battery

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ABSTRACT

Gel electrolyte is one of the most direct and appropriate ways to solve the safety problem of battery before the most challenging technological hurdles to all solid-state batteries have not yet been overcame. A major challenge towards gel polymer electrolyte (GPE) is making an electrolyte that is effectively combine with electrochemical performance, thermal safety and the stability to lithium. Here, PVDF-HFP-LiTFSI/SiO_2/EMITFSI polymer electrolyte composite membrane (ILGPE) is prepared via solution casting method, in which nano-silica and ionic liquid positively effect on the performance of polymer electrolytes, such as ionic conductivity, electrochemical stability and thermal safety stability. It remarkably enhances the interface compatibility between ILGPEs and lithium metal. Significantly, we characteristically elucidate the possible transmission mechanism and interaction within the materials of ILGPE. Furthermore, Li/$LiFePO_4$ battery based on such ILGPEs can exhibit fascinating interfacial stability and cycling performance. Herein, cells based on ILGPEs can overcome the drawbacks of solid electrolytes and volatile organic liquid electrolytes, which suggest a promising method for highly secure lithium batteries with appreciably enhanced performance.

1. Introduction

Polymer electrolytes (PEs) with excellent properties such as light weight, safety, easy processing and other advantages have been proposed for implementation in popular power sources [1–6]. However, solid polymer electrolytes (SPEs) can hardly apply in large-scale commercial electronic equipment effectively due to the low ion conductivity and other defects [7]. Fortunately, the polymer-gel electrolytes (PGEs) are formed by introducing significant amount of organic solvents in SPEs, which can offer advantages in terms of high ionic conductivity and good interfacial compatibility with electrodes [8]. Compared with recent organic solvents, ionic liquids (ILs) is constituted by ions with unique properties such as high ionic conductivity, non-volatility, high thermal stability and wide electrochemical windows [9,10]. Therefore, the replacement of volatile organic solutions with ILs entrapped in a polymer host forming ionic liquid based gel polymer electrolytes (ILGPEs), which combine with the advantages of IL and polymer electrolytes are regarded as promising electrolytes [9,11].

Poly(acrylonitrile) (PAN), poly(methyl methacrylate) (PMMA), poly (ethylene oxide) (PEO), poly(vinylidenedifluoride) (PVDF) and its *co*-polymer poly(vinylidene fluoride-*co*-hexafluoropropylene) (PVDF-HFP) are the most common polymer host used in the electrolyte matrix [12–16]. Among them, the PVDF-HFP matrix has excellent electrochemically stable owing to the strong electron-withdrawing group-CF [17–26]. Meanwhile, the higher dielectric constant ($\varepsilon = 8.4$) of this polymer will help to dissociate the lithium salt and increase the carrier concentration [27,28]. Thus, PVDF-HFP is widely regarded as a preferred matrix for gel polymer electrolytes.

In this paper, a family of ILGPEs based on LiTFSI and SiO_2 nanoparticles dispersed in PVDF-HFP is proposed. Meanwhile, the polymer molecules are swelled by IL, the ions can therefore transport in the space provided by the free volume around the polymer host, which means ILGPE possesses the advantages of both IL and solid polymer electrolytes, including high ionic conductivity, stable electrochemical window, especially, good thermal stability and non-volatile. Hereafter, the interplay between properties and structures is investigated, and the feasibility of solid-state lithium battery using this type electrolyte is characterized as well. All of these results suggest that the ILGPE has great promise for safe applications in solid-state lithium battery.

2. Experimental

2.1. Preparation of ILGPE

The ILGPE membranes were prepared using solution-casting technique. PVDF-HFP was completely dissolved in butanone (which was

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stirred at 50 °C for 30 min) to obtain 6.7 wt% of polymer clear solution. The lithium bis(trifluoromethane)sulfonamide (LiTFSI, 99.9%, Aldrich), silicon dioxide (SiO_2) and 1-ethyl-3-methylimidazolium triluoromethanesufonate (EMITFSI) with different weight ratio (the values of $m_{PVDF\text{-}HFP}$:m_{LiTFSI}:$m_{EMITFSI}$:m_{SiO2} changed from 5:5:7:0.5 to 5:5:7:1.75) were added into the clear solution under argon atmosphere. The resulting mixture was magnetic stirring for 3 h and ultrasonically agitated for 20 min to from a homogeneous casting solution in a sealed container. Then, the solution was casted onto a Teflon plate to from the wet membrane and dried for 12 h at 60 °C in vacuum condition. Finally, the free standing ILGPE membrane was cut into circles with diameters of 19 mm.

2.2. Characterization of the ILGPE membrane

The surface microstructures of the ILGPEs were observed by HITACHI S-4800 scan electron microscopy (SEM). The crystal structure of the membranes was obtained using X-ray diffraction (XRD) with Cu Kα radiation in the range of 10–60°. The Fourier transform infrared (FTIR) spectra were acquired on a Bruke V70 spectrometer. Raman spectra was recorded on a Bruker V70-FRA106 Raman module. The thermal properties of the electrolytes evaluated by Differential Scanning Calorimetric (DSC) and Thermogravimetric analysis (TGA) were carried out at a scan rate of 10 °C min^{-1} under N_2 atmosphere. The ionic conductivity of the ILGPEs was measured by the AC impedance method using symmetrical stainless steel electrodes at different temperature range from 0 to 100 °C. The electrochemical stability of the ILGPEs was measured by linear sweep voltammetry (LSV) and cyclic voltammograms (CV) using the cell structure of Li/ILGPE/SS at the scanning rate of 0.1 mV s^{-1}. They were measured from 2.5 V to 6 V (LSV, vs. Li^+/Li) and between −0.5 V to 2.5 V (CV, vs. Li^+/Li) respectively.

The $LiFePO_4$ electrode was prepared by the mixed slurries coated on Al foils, the slurries contain $LiFePO_4$ powders, carbon black and PVDF-HFP which was contained in ingredient of ILGPE-20%SiO_2 at 8:1:1 weight ratio in *N*-methylpyrrolidone (NMP) solvent. The loading density of $LiFePO_4$ cathode was controlled to be 1.5 mg cm^{-2}. The composite cathode was dried in a vacuum oven for 12 h. The battery performance of the ILGPE based on lithium anode and $LiFePO_4$ cathode was evaluated by galvanostatic charging-discharging tests. Cells were assembled in an argon-filled glove box and cyclic voltammetry (CV) of the cell was measured at a scanning rate of 0.1 mV s^{-1} between 2.5 and 4.5 V. The testing experiments were conducted in the voltage range of 2.7–3.85 V at room temperature according to the LAND CT2001A.

3. Results and discussion

3.1. Morphology of the ILGPE membrane

The schematic diagram of preparation process about ILGPE and the solid-state battery is shown in the Fig. 1a. Because of the swelling of IL, the dissociation of the lithium salt and the movement of the polymer molecular chains are improved, relating properties of the electrolyte are also changed. The prepared membrane looks semi-transparent and flexible self-retaining (Fig. 1b). And the surface is homogeneous and crack-free, as shown in SEM images (Fig. 1b). On the one hand, the SiO_2 particles are disperse in the PVDF-HFP polymer matrix uniformly, on the other hand, the IL entrapped around polymer matrix making the hybrid electrolyte shows no obvious porous structure from the interior to the surface.

3.2. Crystalline and thermal stability of the ILGPE

The XRD patterns of the ILGPE membranes with different ingredients contents are shown in Fig. 2a–b. Compared to the pure semicrystalline copolymer of PVDF-HFP, the lithium salt can weaken diffraction peaks polymer matrix to a lesser degree. It is illustrated the inferior miscibility of LiTFSI with the semi crystalline PVDF-HFP. Furthermore, a dramatic decrease on peaks intensity especially the diffraction peaks at $2\theta = 20$ and 40° can be observed with the increase of IL. These findings indicate that IL can effectively reduce the degree of crystallinity of PVDF-HFP through fully swelling the molecular chain and making molecular chains almost in the amorphous state. Thus, we can speculate that the ionic conduction of polymer electrolytes should be enhanced with the amorphous areas of polymer obviously increased.

The thermal stability of the electrolytes is studied by TGA as shown in Fig. 2c. As noticed, the decomposition of the polymer matrix PVDF-HFP (LiTFSI) starts at the lower onset temperature, and the lost weight is 80% when the temperature rises to 500 °C. The TGA curves of IL-EMITFSI show that the mass loss begins at about 352.7 °C. Therefore, this result indicates incorporation of IL could increase the thermal stability of polymer electrolytes. The degradation processes of ILGPE can be divided into two-step. A small amount of weight loss is observed in the range from 75 to 300 °C, corresponding to the decomposition of the lithium salt and the polymer PVDF-HFP. The decomposition of mass loss in the temperature range of 300–460 °C is the second step, which is more noticeable and related to the decomposition of EMITFSI. It is worth noting that the thermal stability of ILGPE is greatly improved. Meanwhile, the effect by the content of ILs on the thermal stability of ILGPEs is compared, which further proved that IL played an important role in safe electrolytes.

At the same time, we further judge whether the gel electrolyte is flammable or not from another index-the limiting oxygen index (LOI), which is an useful method to judge the relative flammability through evaluating minimum oxygen concentration [29]. Generally, the value of LOI is higher than 27 indicating that the material is flame retardant [30]. The LOI values of 1#–8# are shown in the Fig. 2d, 1# (Celgard membrane) and 2# (polymer electrolyte is not contains IL) exhibit combustible (LOI = 22) and flame retardant (LOI = 39) respectively. However, ILGPEs with different contents of IL show a higher LOI value, which can reach above 56, exhibiting absolutely flame retardant. In contrast, the calorific values of ILGPEs reflect a lower value compared to the samples of 1# and 2#, which reflect good thermal stability and non-flammability. As we know, the electrolyte membrane shrinkage problem also represents a safety hazard especially in high temperature conditions, which leads to a large area of the battery short circuit. In order to verify the above phenomenon sufficiently, the ability of suppressing thermal shrinkage experiments of membranes are carried out (Fig. 2e). The Celgard membrane is happened crimping phenomenon under the sustained heating, owing to the structure of polymer matrix changes in the high temperature. However, there is no crimping phenomenon of the ILGPEs with different content of IL under continuous heating process, indicating that ILGPE has significant advantages in terms of heat resistance.

3.3. Electrochemical properties of ILGPE and interfacial stability against electrode

The temperature dependence of ionic conductivity of ILGPEs with different contents of lithium salts, IL and filler SiO_2 are shown in Fig. 3a and b. All the ionic conductivities are gradually changed with the temperature increased. The highest ionic conductivity is observed for the mass ratio of PVDF-HFP:LiTFSI at 1:1 and PVDF-HFP:IL at 5:7, respectively, being the value of 0.67 mS cm^{-1} and 0.70 mS cm^{-1} at 25 °C·This observation shows that doping ILGPE with a larger amount of LiTFSI does not result in higher ionic conduction. This phenomenon can be explained by the formation of contact ions and salt aggregates, which decrease the actual concentration of the effective carrier of Li^+, thus, corresponding a relative decrease in the free-moving Li^+ and migration number [31]. In addition, the ionic conductivity of ILGPE ($m_{PVDF\text{-}HFP}$:m_{LiTFSI} = 1:1, PVDF-HFP:IL = 5:7) with the SiO_2 content at 20% (names as ILGPE-20%SiO_2) have a relatively maximum ionic