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A new strategy for preparing oligomeric ionic liquid gel polymer electrolytes for high-performance and nonflammable lithium ion batteries

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ABSTRACT

In the present work, a new strategy is used to economically synthesize an oligomeric ionic liquid from conventional phenolic epoxy resin. This oligomeric ionic liquid is further blended with PVdF-co-HFP and organic liquid electrolyte to prepare a high performance, nonflammable gel polymer membrane. Although the liquid electrolyte uptake is low ($<$ 50%) for this novel gel polymer electrolyte, it possesses high ionic conductivities of 2.0 mS cm^{-1} at 30 °C and 6.6 mS cm^{-1} at 80 °C, respectively. The AC impedance results show that the interfacial compatibility between this gel polymer electrolyte and the electrodes is good. These two factors result in high cell capacity under different charge/discharge rates. Further, excellent cell-cycle stability after being charged and discharged 100 cycles is also demonstrated with the columbic efficiency to be up to 99. Due to the existence of the oligomeric ionic liquid, this novel gel polymer electrolyte exhibits superior dimensional stability; that is, at high temperature (150 °C) the dimensional change is less than 1%. Notably, the electrolyte's limiting oxygen index can be as high as 29, meaning that it achieves the flame-retardant requirement under a normal atmosphere, which is essential to the safety of lithium ion batteries. These features allow this novel gel polymer electrolyte to function as a high performance and high safety lithium ionic conductor as well as a separator for lithium-ion batteries.

1. Introduction

Over the past decades, lithium ion batteries have been considered as an attractive power source for a variety of wide applications such as consumer electronics, electric vehicles and energy storage systems [1,2]. Although organic liquid electrolytes are the most common employed electrolytes in such batteries due to their high conductivities, they have a high risk of leakage during packaging and use. Particularly for large capacity batteries, the existence of highly flammable organic liquid electrolytes raises serious safety concerns [3]. For this reason, gel polymer electrolytes are being explored as replacements for liquid electrolytes since they can maintain high ionic conductivity, good mechanical strength without the risk of leakage [4–6].

Pyrrolidinium- and imidazolium-based ionic liquid hosts are an important class of electrolytes due to their sufficient ionic transport abilities, good electrochemical stability, and non-flammable/non-volatile property [7–12]. Typical ionic liquid similar to molecular solvents have poor mechanical strength when applied as polymer-membrane host. And currently, ionic liquid-based gel polymer electrolytes have low conductivity ($\sim 10^{-4}$ S cm^{-1}) due to the high viscosity of the ionic liquid [10,13–16]. Further, polyionic liquid electrolytes show even worse conductivity as a result of the low movability of ionic moiety [15,17,18].

Polyvinylidene fluoride-co-hexafluoropropylene (PVDF-co-HFP) based electrospinning and non-woven separators feature flexibility, non-flammability and electrochemical stability, and so are widely used as host polymer membranes for lithium batteries [19–22]. Although the high porosity retains large amount of liquid electrolytes and results in high conductivity, the liquid electrolyte-leakage problem remains [23,24]. To overcome the leakage safety issue, PVDF-co-HFP with ionic liquid has been studied as a replacement of traditional gel polymer electrolytes. However, the ionic conductivity and capacity are still insufficient [13,25]. Accordingly, to ensure PVDF-co-HFP is a viable gel polyelectrolyte, solving these disadvantages becomes critical.

In the present work, a series of oligomeric ionic liquids are blended with PVDF-co-HFP and an electrolyte solution to form an oligomeric ionic liquid-type gel-polymer electrolytes to solve the

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above-mentioned problems. Herein, we use a novel strategy to economically synthesize the oligomeric ionic liquid from epoxy resin of suitable molecular weight. The oligomerization enhances the mechanical properties of the ionic liquid and also offer high conductivity. Most importantly, these gel polymer electrolytes feature non-flammability and stable heat resistance. Moreover, they also shows high conductivity, low interfacial resistance and high long-term durability. Therefore, they hold promise to be used as high safety and high performance gel polymer electrolytes.

2. Experimental

2.1. Ring-opening bromination reaction of phenolic epoxy resin

Phenolic epoxy resin (PNE 177, Chang Chun Plastics, average molecular weight 1600 g mol^{-1}, EEW 172-182 g eq^{-1}) was washed by chloroform and precipitated in hexane before using. Subsequently, the purified phenolic epoxy resin was dissolved in chloroform (Tedia, 99.9%), the solution of which was cooled in an ice bath. Then, hydrobromic acid (Acros Organics, 48.0%) was slowly added into the solution and stirred for 6 h to obtain a reaction mixture. Thereafter, the reaction mixture was washed with water to remove unreacted hydrobromic acid, and the solvents removed using a rotary evaporator. A brominated intermediate polymer was thus obtained.

2.2. Synthesis of phenolic epoxy resin-based oligomeric ionic liquid with bromide ion

The brominated intermediate polymer was dissolved in dimethyl sulfoxide (DMSO), mixed with 1-methylimidazole (Alfa Aesar, 99.0%) at 80 °C, and then stirred for 36 h. Subsequently, the oligomeric ionic liquid with bromide counter-ion (OIL-Br anion) was precipitated in ethyl acetate. The product was then dried under vacuum at 80 °C for 24 h.

2.3. Ion exchange of OIL-Br anion

The OIL-Br anion obtained in the previous step was dissolved in deionized (DI) water to obtain an OIL-Br solution. Bis(trifluoromethane)sulfonimide lithium salt (LiTFSI) (Solvay) was dissolved in the DI water to obtain a LiTFSI solution, which was added drop-wise to the OIL-Br solution and stirred for 6 h. The final product, oligomeric ionic liquid with bis(trifluoromethane)sulfonamide (OIL) was precipitated in DI water, and then *t* dried under vacuum at 80 °C for 24 h before use.

2.4. Preparation of PVdF-HFP blend OIL membranes

Both PVdF-HFP and OIL were dissolved in N-methyl-2-pyrrolidon (NMP), the solutions of which were mixed at different weight ratios (70/30, 50/50, 30/70). The polymer mixtures were then treated at 80 °C for 24 h to evaporate the solvent and form the polymer membranes, which were prepared by solution casting. Subsequently, the membranes were dried under vacuum at 100 °C for 24 h before use. The three prepared samples are identified as PVdF-HFP/*x*%OIL, where *x* represents the OIL weight ratio of the membranes.

2.5. Characterization

Fourier transform infrared spectroscopy (FTIR) was recorded with a Nicolet Magna II 550 spectrometer. Thermal gravimetric curves (TGA) were obtained by using a Perkin Elmer TGA7, with a heat increment of 20 °C min^{-1} under a nitrogen atmosphere. ^{1}H NMR spectra were recorded on a Bruker AMX600 MHz Digital NMR, for which an appropriate deuterated solvent was chosen. Further, the morphologies of the PVdF-HFP/*x*%OIL membranes were investigated by field-emission scanning electron microscopy (FESEM) (JEOL, JSM-6380LV).

The amount of liquid electrolyte uptake (η) is calculated using Eq. (1):

$$\eta = (W_t - W_0)/W_t x \ \ 100\% \tag{1}$$

where W_0 and W_{t} are membrane weights before and after absorbing the electrolyte solution, respectively. Weights were measured in a glove box.

2.5.1. Methods of electrochemical performance

To characterize of the electrochemical performance of the PVdF-HFP/*x*%OIL gel polymer electrolytes (GPEs), a 1.0 M LiPF6 in EC/DEC (1/1 v/v) liquid electrolyte was employed. The GPEs were then analyzed by ac-impedance spectroscopy on an electrochemical instrument (CHI604A, CH Instrument, Inc.) assembled between two stainless steel electrodes to characterize the ionic conductivities from 30 to 80 °C. Measurement were carried out at 0 V with an ac-impedance spectroscopy of 10 mV and a frequency variation ranging from 0.1 Hz to 1 MHz. The ionic conductivity (σ) was calculated according to the bulk electrolyte resistance (R) using Eq. (2):

$$\sigma = l/RA \tag{2}$$

where l is the GPEs thickness and A is the contact area between the GPEs and steel electrodes.

Battery performance tests of the membranes were conducted by fabricating 2032 coin-type cells with $LiFePO_4$ cathode and lithium metal anodes. The cathodes were made by pouring a NMP-based slurry onto aluminum foil, for which contained 80 wt% $LiFePO_4$ powder (Aleees, Taiwan), 10 wt% polyvinylidene fluoride (PVDF), and 10 wt% Super P. The electrodes were dried at 120 °C for 48 h under vacuum and were roll-pressed to ensure superior particulate contact and foil adhesion. The cell assembly took place in a dry, Ar-filled glove box (the moisture content is <5 ppm), and charge–discharge battery testing was conducted in the range of 2.5–4.2 V at room temperature, according to the Battery Automatic Test System (Acu Tech Systems, BAT-750B). Interfacial resistance was measured by ac-impedance spectroscopy at 10 mV before and after the battery charge/discharge, with a frequency variation ranging from 0.01 Hz to 1 MHz at the open circuit potential (OCP) of the battery.

2.5.2. Limiting oxygen index test

The limiting oxygen index (LOI) values were measured by Atlas Limiting Oxygen Index Chamber to evaluate the flammability of the samples. The percentage of O_2 in the O_2–N_2 mixture was just sufficient to enable combustion; that is the value of LOI.

3. Results and discussion

In this paper, a novel imidazolium based OIL with phenyl polymer backbone was designed using phenolic epoxy resin as reactant, and synthesis process of which is shown in Fig. 1. Fig. S1 (a) and (b) shows the ^{1}H NMR spectra of the phenolic epoxy resin and brominated phenolic epoxy resin with all assignment, respectively. The phenolic epoxy resin shows the protons of epoxy group at 2.5–2.8 and 3.1–3.3 ppm; after bromination, the protons of the brominated resin are observed at the peaks of 3.4–3.7 and 4.1 ppm. Furthermore, the obtained OIL is a light yellow, honey-like polymer, and was characterized by ^{1}H NMR, as shown in Fig. 2.