



Polymeric ionic liquid-plastic crystal composite electrolytes for lithium ion batteries



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HIGHLIGHTS

- Polymeric ionic liquid-plastic crystal composite electrolytes are obtained.
- The composite electrolytes show high ionic conductivity.
- The composite electrolytes present favorable mechanical properties.
- The composite electrolytes reveal impressive battery performance.

ARTICLE INFO

Article history:

Received 28 August 2015

Received in revised form

18 December 2015

Accepted 9 January 2016

Available online xxx

Keywords:

Polymeric ionic liquid

Plastic crystal

Succinonitrile

Composite polymer electrolyte

Lithium ion battery

ABSTRACT

In this work, composite polymer electrolytes (CPEs), that is, 80%[(1-x)PIL-(x)SN]-20%LiTFSI, are successfully prepared by using a pyrrolidinium-based polymeric ionic liquid (P(DADMA)TFSI) as a polymer host, succinonitrile (SN) as a plastic crystal, and lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) as a lithium salt. XRD and DSC measurements confirm that the as-obtained CPEs have amorphous structures. The 80%[50%PIL-50%SN]-20%LiTFSI (50% SN) electrolyte reveals a high room temperature ionic conductivity of $5.74 \times 10^{-4} \text{ S cm}^{-1}$, a wide electrochemical window of 5.5 V, as well as good mechanical strength with a Young's modulus of 4.9 MPa. Li/LiFePO₄ cells assembled with the 50% SN electrolyte at 0.1C rate can deliver a discharge capacity of about 150 mAh g⁻¹ at 25 °C, with excellent capacity retention. Furthermore, such cells are able to achieve stable discharge capacities of 131.8 and 121.2 mAh g⁻¹ at 0.5C and 1.0C rate, respectively. The impressive findings demonstrate that the electrolyte system prepared in this work has great potential for application in lithium ion batteries.

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1. Introduction

Lithium ion batteries employing polymer electrolytes have attracted great interest because of shape variability, electrolyte leakage-proof, no separator needed and high safety [1–3]. However, most of polymer electrolytes suffer from low room temperature ionic conductivity ($10^{-5} \sim 10^{-6} \text{ S cm}^{-1}$), which limits their practical application [3,4]. Up to now, several approaches have been adopted to enhance the ionic conductivity, such as heterogeneous

doping with fillers [5,6], blending with other polymers [7,8], forming copolymer [9,10], and cross-linking synthesis [11,12], while the ionic conductivity is still not promising. As a result, immobilizing liquid electrolytes into polymer hosts to form gel polymer electrolytes has been developed, and as-obtained electrolytes could achieve higher ionic conductivity; nevertheless, the mechanical properties will be concomitantly deteriorated [13,14].

Plastic crystals that show one or more solid–solid phase transition below room temperature generally reveal local rotatory motions [15]. Such rotatory motions result in structural disorder, thereby enhancing the molecular mobility [16]. Succinonitrile (NC–CH₂–CH₂–CN, SN) is a representative non-ionic plastic crystal and has a phase transition at about –40 °C, above which SN shows a plastic phase until it melts at around 60 °C [15,17]. The presence of plasticity in SN and its high polarity are responsible for its good ability of dissolving various lithium salts [18]. It has been reported

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that SN/lithium salt systems can provide high ionic conductivity due to *trans-gauche* isomerism involving the molecules rotation [16,18]. For example, room temperature ionic conductivity of higher than 10^{-3} S cm^{-1} can be realized in the case of the SN/lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) system [18]. Recently, SN has been introduced into polymer-based electrolytes, such as poly(ethylene oxide) (PEO) [19–22], polyethylene glycol dimethyl ether (PEG) [21], poly(vinylidene fluoride-co-hexafluoropropylene) (P(VDF–HFP)) [14,20,23,24], poly(acrylonitrile) (PAN) [21] and chitosan [25]. With the addition of SN, ionic conductivities of polymer-SN electrolytes are significantly increased, as well as the beneficial mechanical strength can be achieved. Moreover, above-mentioned electrolytes have been applied in lithium ion batteries [14,20,23,25,26]. The battery tests revealed that polymer-SN electrolytes allowed successful battery operation at room temperature (25 °C) under the low current rate (e.g. 0.1C rate). Relative to them, researches involving battery performance at higher rate are quite rare [14]. Therefore, developing new polymer-SN electrolytes, which can exhibit favorable properties, especially good battery performance at higher rate, is still an attractive and urgent topic.

As already reported, polymeric ionic liquids (PILs), which are different from the conventional polymers [27], exhibit interesting performance such as film forming ability and good electrochemical properties [28]. Ohno et al. have firstly synthesized variety of PILs, and demonstrated the influence of the PIL structure on the thermal and electrochemical properties [29–31]. Other research groups have also investigated synthesis and properties of PILs [28,32–35]. Furthermore, PILs show excellent performance as polymer hosts for gel polymer electrolytes together with ionic liquids and lithium salts [36–39]. Inspired by above analysis, in this work, we have prepared a new class of pyrrolidinium-based PIL (P(DADMA)TFSI)-SN electrolyte systems with different weight ratio of P(DADMA)TFSI/SN. The structures, thermal and electrochemical properties for as-obtained electrolytes were studied, and their potential applications in lithium ion batteries were evaluated.

2. Experimental

2.1. Materials

Poly(diallyldimethylammonium) chloride solution (average M_w 400,000–500,000, 20 wt.% in H_2O) was purchased from Aldrich. Succinonitrile (99.9%) was purchased from Fujian Chuangxin Science and Develops Co., Ltd. Lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) was kindly provided by Zhangjiagang Guotai Huarong Chemical New Material Co., Ltd. All the reagents were used as received.

2.2. Synthesis of pyrrolidinium-based polymeric ionic liquid P(DADMA)TFSI

Pyrrolidinium-based polymeric ionic liquid, Poly-(diallyldimethylammonium) bis(trifluoromethanesulfonyl)imide (P(DADMA)TFSI), was synthesized by an anion exchange reaction according to the literature [28]: 20 g (24.74 mmol of monomeric units) of poly(diallyldimethylammonium) chloride solution (20 wt.% in H_2O) was diluted with 100 mL of deionized water, and then mixed with a solution of 8.52 g (29.68 mmol) of LiTFSI in 20 mL of deionized water. After stirring for 2 h at room temperature, a large amount of white solid precipitated from the solution. The white solid was collected after filtration, and washed with deionized water five times. The solid was dried at 105 °C in vacuum for 48 h to obtain the resulting white P(DADMA)TFSI, of which chemical structure is depicted in Fig. 1 (a). Fig. 1 (b) presents the ^1H NMR spectrum of P(DADMA)TFSI. The spectrum is in agreement

with the expected structure, and is similar to that reported previously [28]. Furthermore, AgNO_3 titration test, that is, the addition of AgNO_3 to the P(DADMA)TFSI/acetone solution, was carried out in order to examine if Cl^- anions remain in the P(DADMA)TFSI [28,40]. The test confirms the absence of Cl^- anions because no AgCl precipitation occurs.

2.3. Preparation of P(DADMA)TFSI–SN composite polymer electrolytes (CPEs)

The composite polymer electrolytes with different P(DADMA)TFSI–SN weight ratio (Table 1) were prepared by dissolving the P(DADMA)TFSI, succinonitrile and LiTFSI in acetone. The mixtures were cast onto PTFE slides followed by evaporating the solvent under the argon atmosphere for 24 h. Then the electrolyte membranes were dried at 30 °C in vacuum for 48 h and moved into an argon-filled glove box ($\text{O}_2 < 0.1$ ppm, $\text{H}_2\text{O} < 0.1$ ppm) for 24 h to remove the final trace of the solvent. The thickness of as-obtained membranes is about 250–300 μm . A picture of an electrolyte membrane sample (50% SN), which is self-standing and transparent, is depicted in Fig. 1(c). It should be pointed out that as x is further increased above 60%, i.e. 70–100%, the electrolytes could not be casted into self-standing membranes.

2.4. Measurements

The chemical structure of P(DADMA)TFSI was confirmed by the ^1H NMR (Avance III400) experiment.

X-ray diffraction measurements were performed by using Rigaku D/max-2200 with $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418$ Å). The samples were scanned from 5° to 80° with a rate of 6° min^{-1} .

The calorimetric measurements were conducted using a differential scanning calorimeter (DSC, TA Q2000) from –80 °C to 200 °C. The samples were sealed in aluminum pans, then heated and cooled at a rate of 10 °C min^{-1} under a nitrogen atmosphere. The thermal data were collected during the second heating scan.

The ionic conductivity of the electrolyte membranes was tested by impedance spectroscopy measurements with a CHI660D electrochemical workstation in the frequency range from 0.1 Hz to 100 kHz with amplitude 5 mV at temperatures from 25 °C to 80 °C. The ionic conductivity (σ) of the electrolyte membranes was determined using the following equation:

$$\sigma = \frac{L}{R_b S} \quad (1)$$

Here, R_b is the bulk ohmic resistance of the electrolytes, and L and S are the thickness and area of the electrolytes, respectively.

The lithium ion transference number (t_{Li^+}) was tested by the chronoamperometry combined with electrochemical impedance spectroscopy at 25 °C according to the method of Bruce and co-workers [41]. In the chronoamperometry measurement, a voltage pulse (ΔV) of 20 mV was applied to a symmetrical Li/electrolyte/Li cell to measure the initial current I_0 and the steady-state current I_s . Electrochemical impedance spectroscopy was conducted before and after the chronoamperometry measurement to detect the initial and the final interfacial resistances, R_0 and R_s . The lithium ion transference number, t_{Li^+} , can be calculated by:

$$t_{\text{Li}^+} = \frac{I_s \Delta V - I_0 R_0}{I_0 \Delta V - I_s R_s} \quad (2)$$

Linear sweep voltammetry (LSV) was recorded at 25 °C with a CHI660D electrochemical workstation (scan rate: 1 mV s^{-1}). The cells used for this measurement were assembled by sandwiching the film between the stainless steel and a lithium foil, in which the

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