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Solid electrolyte based on waterborne polyurethane and poly(ethylene oxide) blend polymer for all-solid-state lithium ion batteries

Junjie Bao[a,b], Xinbo Qu[b], Guoqin Qi[b], Qikai Huang[b], Shufan Wu[b], Can Tao[b], Minghao Gao[b], Chunhua Chen[a,*]

[a] CAS Key Laboratory of Materials for Energy Conversions, Department of Materials Science and Engineering, Collaborative Innovation Center of Suzhou Nano Science and Technology, University of Science and Technology of China, Anhui, Hefei 230026, China
[b] School of Chemistry and Chemical Engineering, Anhui University, Anhui, Hefei 230601, China

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ABSTRACT

A series of solid polymer electrolytes (SPEs) based on waterborne polyurethane (WPU), poly(ethylene oxide) (PEO) and lithium bis(trifluoromethane sulfonimide) (LiTFSI) are fabricated via a solvent free process. Field emission-scanning electron microscopy, X-ray diffraction, Fourier transform infrared spectroscopy and differential scanning calorimetry techniques are used to characterize the morphological features of the SPEs. The self-supported blend SPEs have sufficient mechanical strength and electrochemical stability compared to the pristine PEO electrolyte. The SPE2 (30 wt% LiTFSI in PEO:WPU = 3:1) electrolyte presents the superior comprehensive performance with a stress of 1.3 MPa and electrochemical window exceeding 4.8 V. All-solid-state $LiFePO_4$/SPE2/Li cell using this blend solid polymer electrolyte exhibits both superior discharge capability and cycle performance (high initial discharge capacity of 160 mAh g^{-1} at 0.2 C, 122 mAh g^{-1} discharge capacity and 96% capacity retention after 100 cycles at 1 C) at 80 °C. All of these results demonstrate that this new WPU/PEO blend solid polymer electrolyte is a promising candidate for all-solid-state lithium ion batteries.

1. Introduction

Lithium ion batteries (LIBs) have been widely used in portable and consumable electronic devices, hybrid and all-electric vehicles nowadays [1,2]. However, the conventional LIBs based on organic liquid electrolytes encounter some safety risks such as flammability, leakage of electrolyte, poor thermal stability and internal short circuiting especially for electric vehicles [3,4]. As an alternative, all-solid-state LIBs based on solid electrolyte have been regarded as a promising solution to those safety issues [5,6]. Solid polymer electrolytes (SPEs), which possess several advantages like absence of leakage of organic solvents, flexibility and light weight, have attracted much attention recently [7–9].

Among various of polymer materials, poly(ethylene oxide) (PEO) have been widely investigated as SPEs due to its good capability of dissolving lithium salts and high ionic conductivity when the operating temperature is above its melting temperature [10]. However, the batteries using pristine PEO based SPEs often encounter severe drawbacks such as poor mechanical strength, bad dimensional thermostability, inferior electrochemical window and low ionic conductivity at room temperature [11,12]. Therefore, many strategies have been carried out to improve the performance of pristine PEO like copolymerization [12,13], cross-linking [14], semi-interpenetrating [15], polymer blending [16,17] and adding inorganic or organic composites [18,19]. Compared to other techniques, the polymer blending method possesses some advantages such as simple, economic, high efficiency and easy control of properties by compositional changes [8]. PEO blending with PMMA [20], PVDF [21] and cellulose [22] have been reported in earlier literature. Very recently, Jinisha et al. [23] prepared blend polymer electrolytes composed of PEO, poly (vinyl pyrrolidone) (PVP) and $LiNO_3$ that showed remarkable room temperature ionic conductivity and good thermal stability. Pradeepa et al. [24] reported a SPE with high thermal stability by blending PEO, PVDF-HFP and $LiClO_4$. Although great advances have been achieved by the blending method, inventing new polymer matrix to improve the comprehensive performance of SPEs is still a creative research. Furthermore, the preparation of SPEs always requires the usage of volatile and toxic solvents such as acetonitrile (ACN) to dissolve the polymer, which is not benign to the environment.

Aqueous polymers are promising environmentally friendly candidates as new polymer matrix for SPEs. As an environmentally friendly material, waterborne polyurethane (WPU) has been used as binder,

* Corresponding author.
E-mail address: cchchen@ustc.edu.cn (C. Chen).

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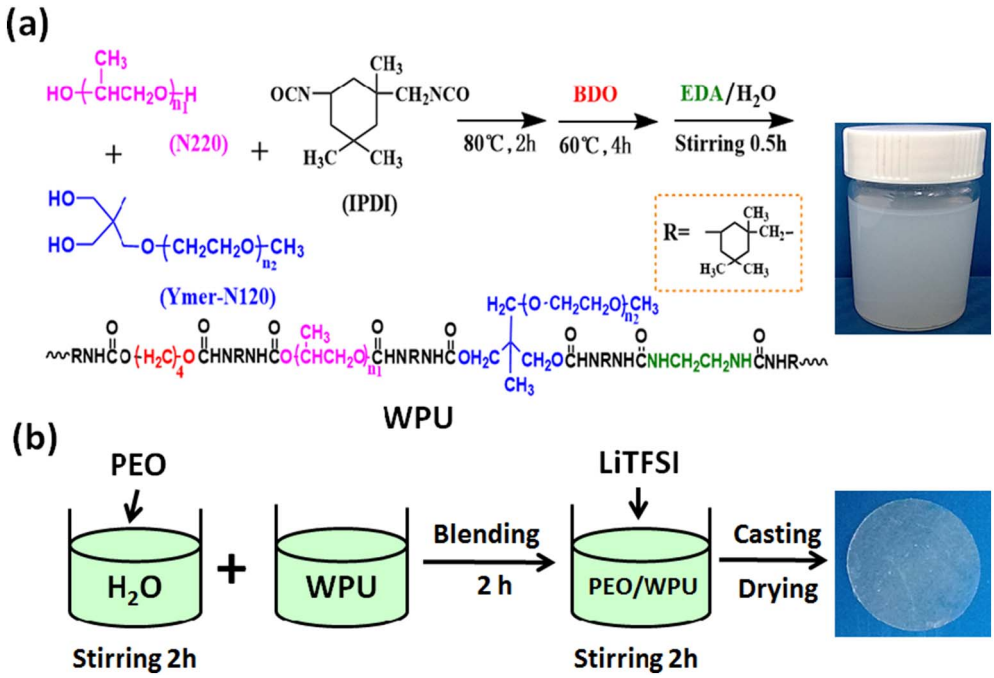

Scheme 1. Schematic representations of (a) synthesis of WPU dispersion, (b) process of PEO and WPU blend polymer electrolyte membranes (the photograph is the membrane of SPE2).

leather and coating widely [25]. WPU is a colloidal system in which the polyurethane particles are dispersed in water [26]. Polyurethane has two-phase microstructure which consists of soft segments and hard segments. In the hard domains, the stiff isocyanate units and the hydrogen bonding between the C═O group and N—H group afford high mechanical strength to polyurethane. In the soft domains, the polyether units give polyurethane flexible capabilities [27–29]. Owing to this unique structure, polyurethane has been identified as a potential candidate polymer matrix for SPEs recently. Liu et al. [30] reported a cationic polyurethane based solid polymer electrolyte with the ionic conductivity reaching 1.1×10^{-4} S cm^{-1} when the electrolyte contains 50 wt% $LiClO_4$ at room temperature. Mustapa et al. [31] reported an oil based polyurethane as a solid polymer electrolyte used in LIBs. In order to improve the ionic conductivity of the polyurethane-based SPEs, Lv et al. [32] prepared a polyurethane acrylate (PUA) elastomer and Succinonitrile (SN)-based plastic crystal hybrid SPE exhibiting a high ionic conductivity of 0.91×10^{-4} S cm^{-1}at 30 °C, however, the tensile strength of this SPE was very poor (less than 0.2 MPa). Yu et al. [33] added $Li_7La_3Zr_2O_{12}$ powders in the thermoplastic polyurethane (TPU) to fabricate SPE, an ionic conductivity of 8.89×10^{-5} S cm^{-1} at 80 °C was achieved. Wang et al. [28] developed a blend SPE based on TPU and polysiloxane, the result indicated that the good interfacial adhesion of the two polymers are important to enhance the performance of the blend electrolytes. Porcarelli et al. [34] reported a SPE based on single-ion conducting polyurethane and ionic liquid monomer, the free-standing SPE films showed a ionic conductivity 9.2×10^{-8} S cm^{-1} at 25 °C which is still too low. In general, though the polyurethane based SPEs have shown excellent mechanical property and dimensional stability, the high hydrogen bonding in polyurethane restricts their ionic conductivity. Blending with other organic or inorganic compound may improve the performance of polyurethane-based SPEs.

In our previous work [35], we prepared a comb-like nonionic waterborne polyurethane (NWPU) based SPE. The NWPU-based SPE possessed good mechanical properties and thermal stability, however, the ionic conductivity was still low especially at room temperature. To balance among ionic conductivity, mechanical strength and dimensional thermostability for high performance LIBs, a series of blend solid polymer electrolyte membranes composed of waterborne polyurethane (WPU), PEO and lithium salt are prepared in this paper. Water is the solvent during the environmentally-friendly synthesis of SPEs. The relationships of PEO and WPU on the ionic conductivity and the thermal stability of blend SPEs are investigated. The $LiFePO_4$/SPEs/Li batteries are assembled and characterized with the as-prepared electrolytes. It is found that the blend SPEs exhibit enhanced mechanical property and electrochemical stability compared to the pristine PEO electrolyte and other polymer electrolytes reported in literature. The comparison of properties between this work and previous literature are listed in Table S1 (see the Supporting Information). Moreover, such a blend polymer electrolyte has demonstrated its application in all-solid-state lithium ion batteries.

2. Experimental sections

2.1. Chemical and materials

Poly(propylene oxide glycol) (N220, Mw = 2000, Sinopec Shanghai Gaoqiao Co.), poly(ethylene glycol monomethyl ether)-based trimethylolpropane (Ymer N120, Mw = 1000, Perstorp), Isophorone diisocyanate (IPDI, Bayer AG), 1,4-utandiol (BDO, Aladdin), ethanediamine (EDA, Aladdin), dibutyltin dilautrate (DBTDL), stannous octoate (Bayer AG), poly(ethylene oxide) (PEO, Mw = 500,000, BASF Co.), lithium bis(trifluoromethane)sulfonilimide (LiTFSI, Aldrich) were used as obtained.

2.2. Synthesis of waterborne polyurethane

The dispersion of waterborne polyurethane (WPU) was prepared like in previous study [35] by using a prepolymer method based on IPDI (0.15 mol), N220 (0.03 mol), Ymer N120 (0.02 mol), BDO (0.05 mol) and EDA (0.04 mol). A WPU dispersion with solid content of about 30 wt% was obtained after the prepolymer was dispersed in deionized water under a stirring rate of 2000 rpm for about 5 min. The structure of the synthesized WPU was listed in Scheme 1. The molecular weight and polydispersity index (PDI) of WPU are 17,764 (Mn), 26,558 (Mw) and 1.495, respectively, which were characterized by GPC.