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Polyethylene glycol-based waterborne polyurethane as solid polymer electrolyte for all-solid-state lithium ion batteries

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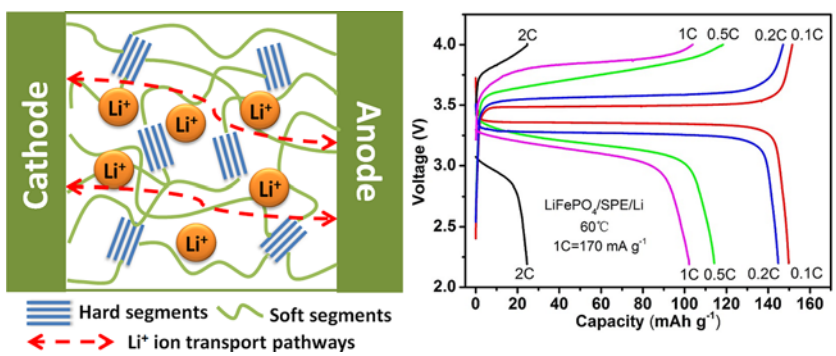
HIGHLIGHTS

- A waterborne polyurethane (WPU) dispersion was synthesized from polyethylene glycol and hexamethylene diisocyanate.
- Solid polymer electrolytes were prepared by blending waterborne polyurethane and LiTFSI.
- All solid state battery based on WPU showed attractive electrochemical properties and discharge capacity.

GRAPHICAL ABSTRACT



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ABSTRACT

An environmental friendly waterborne polyurethane (WPU) dispersion was synthesized from polyethylene glycol (PEG), hexamethylene diisocyanate (HDI), diethylene glycol (DEG) and dimethylol propionic acid (DMPA). Solid polymer electrolytes based on WPU and LiTFSI were fabricated via an organic solvent free process. The LiTFSI salts were found to be dissolved in WPU by the coordination of Li^+ ion with carbonyl and ether group in WPU. The as-prepared WPU showed a semi-crystalline structure and became amorphous after adding lithium salts. The ionic conductivities increased with the increase of salt concentration and followed the Arrhenius behavior. The 20 wt% LiTFSI in WPU electrolyte showed a superior comprehensive performance with an ionic conductivity of 7.3×10^{-4} and 2.2×10^{-3} S cm^{-1} at 60 °C and 80 °C. All-solid-state $LiFePO_4$/SPE/Li cell using this electrolyte exhibited an initial discharge capacity of 151 mAh g^{-1} at 0.1C under 60 °C. All of these results demonstrate that this new WPU-based solid polymer electrolyte is a promising environmentally friendly candidate for all-solid-state lithium ion batteries.

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1. Introduction

Lithium ion batteries (LIBs) have been successfully used as the efficient energy storage equipment for the consumable electronic devices and electric vehicles in the past decades [1,2]. However, the conventional LIBs which use the organic flammable liquid electrolytes can cause some safety and environmental problems [3,4]. All-solid-state lithium ion

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batteries which use non-flammable solid electrolytes have received increasing attention recently for their performances are superior than the conventional LIBs especially in the safety issues [5–7]. As the key component of all-solid-state LIBs, solid electrolytes should possess high ionic conductivity and ion transference number, good mechanical strength, chemical compatibility with the electrodes and wide electrochemical window [5,8]. Therefore, the main issue right now is to design solid electrolytes with better comprehensive performance.

Currently, various of solid electrolytes include solid oxide-based electrolytes (i.e. LLZO [9] and LAGP [10]), solid sulfide-based electrolytes (i.e. LGPS [11]) and solid polymer electrolytes (SPEs) have been extensively developed and successfully applied to the all-solid-state LIBs. However, the oxide-based electrolytes exhibit great stability in air but show a large interfacial resistance between the electrode and solid electrolyte [12]. Solid sulfide-based electrolytes possess high ionic conductivity at room temperature but they are very unstable in air and polar solvents [13]. Compared to inorganic solid electrolytes, SPEs possess several advantages like flexibility, light weight, well interface contact between electrode and electrolyte and easy to fabricate on a large scale [5,14]. These features make SPEs the most promising candidate electrolytes for all-solid-state LIBs. SPEs are usually comprised of polymer matrix and lithium salt. Various polymer materials such as poly (ethylene oxide) (PEO)[15,16], polycarbonate [17], polyphosphazenes [18], polymethacrylate [19], polysiloxane [20], single-ion polyelectrolyte [21] and polyurethane [22] have been investigated as polymer matrix. However, looking for new polymer matrix to improve comprehensive performance of SPEs is still an important issue for all-solid-state LIBs. Furthermore, the fabrication of SPEs is usually use solution casting method, which requires the usage of toxic and volatile organic solvent such as dimethyl formamide (DMF) and acetonitrile (ACN) to dissolve the polymer [23]. This process will lead to a considerable release of volatile organic compounds (VOCs) which is harmful to the environment.

Environmentally friendly waterborne polyurethane (WPU) has attracted increasing attention recently and has been widely used as binder, coating, ink and so on in the field of industrial applications [24,25]. WPU is a colloidal system in which the polyurethane particles are dispersed in water without any VOCs [26]. Polyurethane shows rubbery behavior and their properties can be designed by adjusting the interaction of soft and hard segments [27]. Benefit from these characteristics, polyurethane has been considered to be used as binder [28], separator [29] and polymer electrolyte [30] in lithium batteries. Li et al. [31] reported a WPU-based gel polymer electrolyte which showed good ionic conductivity at room temperature, however it contained organic solvent in the electrolytes. As for SPEs, Liu et al. [32] reported series of cationic PU-based SPEs and Mustapa et al. [33] reported a *Jatropha* oil-based PU used as SPEs recently. Although these polyurethane based SPEs possess excellent mechanical properties and high ionic conductivities, the organic solvent are inevitably involved in the preparation of these SPEs, which may cause serious environmental problems. In addition, the performance of all-solid-state LIBs used these PU based SPEs have not been tested.

In this work, a waterborne polyurethane (WPU) was synthesized as polymer matrix for SPEs by polymerization of polyethylene glycol (PEG), hexamethylene diisocyanate (HDI), diethylene glycol (DEG) and dimethylol propionic acid (DMPA). The SPEs were prepared by complexing the WPU with various concentration of LiTFSI and used water as the solvent during the environmentally friendly fabrication. It was demonstrated that such WPU-based SPEs achieved high ionic conductivity around 10^{-4} and 10^{-3} S cm^{-1} at 60 and 80 °C. The $LiFePO_4$/SPE/Li all-solid-state batteries were assembled and characterized with the WPU-based SPEs. It's found that the WPU-based SPEs exhibited better discharge capacity and cycle performance than the pristine PEO electrolyte and other polymer electrolyte reported recently (Table S1, Supporting Information). These WPU-based SPEs may become a promising environmentally friendly candidate for all-solid-state LIBs.

2. Experimental sections

2.1. Chemical and materials

Polyethylene glycol (PEG, Mw = 2000, Aladdin, China) was dried under reduced pressure at 80 °C for 3 h before using. Hexamethylene diisocyanate (HDI, Bayer AG, Germany), diethylene glycol (DEG, Aladdin, China), dimethylol propionic acid (DMPA, Aladdin, China), bismuth acid catalyst (BiCAT 8108, The Shepherd Chmical Company, USA), triethylamine (TEA, Aladdin, China), acetone (AC, Aladdin, China) and lithium bis (trifluoromethane) sulfonilimide (LiTFSI, Aldrich, China) were used as received.

2.2. Synthesis of waterborne polyurethane

Waterborne polyurethane was prepared by the prepolymer method as shown in Fig. 1 based on HDI (0.15 mol), PEG (0.03 mol), DMPA (0.02 mol), DEG (0.08 mol) and TEA (0.02 mol). The PEG and HDI were added into a four-necked flask equipped with a thermometer, condenser, nitrogen inlet and mechanical stirrer and reacted at 80 °C under nitrogen atmosphere. After 2 h of reaction, DMPA, EDG, BiCAT 8108 as catalysts and acetone as solvent were added into the system, the mixture was kept for about 5 h at 60 °C. Then, the mixture was cooled to 35 °C and neutralized by TEA for 5 min and dispersed in distilled water at high shearing rates to produce the WPU dispersion. Finally, the acetone was removed in a distillation equipment at 40 °C. The molecular weight and polydispersity index (PDI) of WPU are 11,827 (Mn), 20,286 (Mw) and 1.71, respectively, which were characterized by GPC (see Fig. S1, Supporting Information).

2.3. Preparation of solid polymer electrolytes

Solid polymer electrolyte samples were prepared by mixing various contents of LiTFSI range of 10–25 wt% with WPU in water and continuously stirred for 2 h. SPE films were prepared by pouring the dispersions into the Teflon mould and dry at room temperature for 5 days. Then the films were dried in a vacuum oven at 80 °C for 24 h. Finally, the dry films were obtained and placed in an Ar-filled glove-box for further testing. The water content of the SPE films was determined below 10 ppm using a Karl Fisher moisture titrator (MKC-210, Kyoto Electronics, Japan) before use. These SPEs consisted of 10, 15, 20 and 25 wt% of LiTFSI are marked as WPU-X% Li (X = 10, 15, 20 and 25), respectively.

2.4. Characterization

^{1}H NMR spectra were carried out on an Avance II 400 MHz spectrometer (Bmker, Schweizerische) using $CDCl_3$ (Aladdin, China) as solvent and tetramethylsilan (TMS, Aladdin, China) as a reference at room temperature. The polydispersity indices (PDI) and molecular

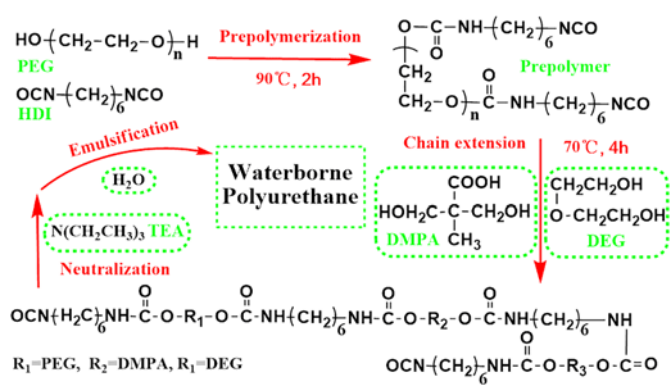

Fig. 1. Synthesis of waterborne polyurethane.

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