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Polycarbonate-based polyurethane as a polymer electrolyte matrix for all-solid-state lithium batteries

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HIGHLIGHTS

- Solid polymer electrolyte is fabricated by polycarbonate-based polyurethane.
- This SPE can simultaneously control ionic conductivity and mechanical integrity.
- The SPEs exhibit excellent interfacial stability against lithium electrode.
- The special polyurethane improves the cycling performance of the batteries.

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ABSTRACT

Four kinds of polycarbonate-based polyurethane with 8–14 wt% hard segments content are synthesized via reactions of polycarbonatediol, hexamethylene diisocyanate and diethylene glycol. The mechanical strength of the polyurethanes increase with the increase of hard segments content. Solid polymer electrolytes composed of the polycarbonate-based polyurethanes and LiTFSI exhibits fascinating characteristics for all-solid-state lithium batteries with a high ionic conductivity of 1.12×10^{-4} S cm^{-1} at 80 °C, an electrochemical stability window up to 4.5 V (vs. Li^+/Li), excellent mechanical strength and superior interfacial stability against lithium metal. The all-solid-state batteries using $LiFePO_4$ cathode can deliver high discharge capacities (161, 158, 134 and 93 mAh g^{-1} at varied rates of 0.2, 0.5, 1 and 2 C) at 80 °C and excellent cycling performance (with 91% capacity retention after 600 cycles at 1 C). All the results indicate that such a polyurethane-based solid polymer electrolyte can be a promising candidate for all-solid-state lithium batteries.

1. Introduction

The development of solid electrolytes for advanced lithium batteries is currently highly desirable as there exist some safety issues with the conventional liquid electrolytes [1,2]. Solid polymer electrolytes (SPEs) composed of polymeric matrices and lithium salts have received increasing attention due to their advantages such as flexibility, dimensional stability, low flammability and readiness to fabricate [3]. Among the polymeric matrices, poly(ethylene oxide) (PEO) has been the most extensively studied in the past two decades [4]. The PEO owns excellent solubility of lithium salts and high ionic conductivities (10^{-4}-10^{-3} S cm^{-1}) can be obtained when the operating temperature is above the melting temperature (around 60 °C) of PEO [5]. However, the pristine PEO-based SPE still suffers from a low lithium ion transference number (< 0.3), a narrow electrochemical stability window (< 4.0 V vs. Li^+/Li), inferior compatibility with lithium anode and poor mechanical strength (< 2 MPa) [6–8], which have restricted the further improvement of all-solid-state lithium batteries.

Recently, polycarbonate (PC) has been reported as an alternative polymer matrix for SPEs [9,10]. PC has a good salt solubility because the typical carbonate group (−O-(C═O)−O−) is highly polar and possesses Li^+-coordinating oxygen [11]. By designing the molecular structure of polycarbonate, the all-solid-state lithium batteries using PC-based SPEs can operate from ambient to elevated temperatures. Various PC-based SPEs such as poly(trimethylene carbonate) (PTMC) [12,13], poly(trimethylene carbonate) and poly(ε-caprolactone)

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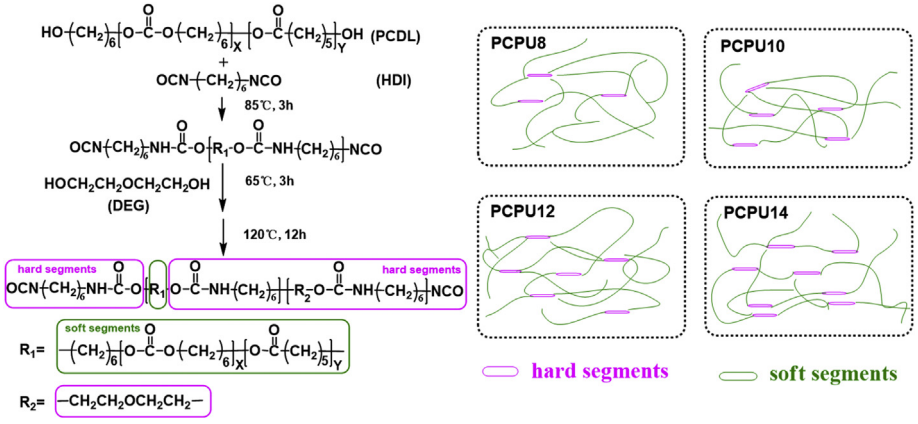

Scheme 1. Schematic representation of synthesis of PCPU and the soft and hard domains of PCPU with different hard segments content.

copolymers (PTMC-PCL) [14,15], poly(ethylene carbonate) (PEC) [16,17], poly (vinylene carbonate) [18], poly(propylene carbonate) (PPC) [19], carbonate-linked poly(ethylene oxide) [20], poly(propylene carbonate allylglycidyl ether) (PPCAGE) [21], poly(heptamethylene carbonate) [22] and interpenetrating network poly(diethylene glycol carbonate) (IPN-PDEC) [23] have been reported for the next generation of all-solid-state lithium batteries (The properties of the above SPEs are listed in Table S1, Supporting Information). Compared to the PEO-based SPEs, PC-based SPEs possess higher lithium ion transference numbers and ionic conductivities, wider electrochemical window and better compatibility with the lithium metal anode. However, the pure polycarbonate-based SPEs usually suffer from poor mechanical properties. Zhang et al. [24] has reported that the mechanical strength of pure PPC-based SPEs is only 3.8 MPa. In order to improve the mechanical properties, they use a cellulose-based nonwoven to form rigid-flexible coupling cellulose supporting PPC-based SPE which possesses a stress of 25 MPa.

On the other hand, polyurethane (PU) is one of the most important engineering polymers in industries and it is used as a foam, elastomer, coating, ink, sealant or binder [25]. PU possesses a unique structure which consists of soft and hard segments and shows phase separation morphology for the thermodynamic incompatibility between the soft and hard segments [26]. The soft segments consist of long-chain diols, which show a rubbery state at room temperature and endow PU with stretchable and flexible capabilities. The hard segments are formed by diisocyanates and short-chain diamines and/or diols which exhibit a glass state and provide mechanical strength to PU [27]. Polyurethanes can be varied from soft thermoplastic to brittle thermoset elastomers, which are dependent on the type, functionality and content of the materials used in their synthesis [28]. Due to this unique structure, various of polyurethanes based on different soft segments such as Jatropha-oil [29], poly(ethylene glycol) (PEG) [30] and poly(tetramethylene oxide glycol) (PTMG) [31] have been used as polymer matrices for solid polymer electrolytes. The soft segments can dissolve the lithium salts and favor the transportation of the lithium ions. The hard segment can ensure the dimensional stability of the electrolytes. However, few papers have reported using polycarbonate as the soft segments for PU-based electrolytes.

In this work, a series of high molecular weight polycarbonate-based polyurethanes (PCPU) were synthesized by an addition polymerization reaction with different contents of polycarbonatediol (PCDL), 1,6-hexamethylene diisocyanate (HDI) and diethylene glycol (DEG). The effects of the soft and hard segments composition on the properties of PCPU were investigated. The PCPU-based SPEs were fabricated by blending the polymer with LiTFSI. The thermal stability, mechanical and electrochemical properties of PCPU-based electrolytes were studied. The performances of $LiFePO_4$/SPE/Li all-solid-state lithium batteries using PCPU-based electrolyte were characterized as well. The results indicated that all-solid-state lithium battery using this kind of SPEs can deliver a high specific capacity of 134 mAh g^{-1} at 1 C with excellent cycling stability (91% capacity retention over 600 cycles) at 80 °C, which are comparable to other PC-based SPEs reported by previous literature (See Table S1. Supporting Information). The PCPU is a promising candidate for the applications of all-solid-state lithium batteries.

2. Experimental sections

2.1. Chemical and materials

Polycarbonatediol (PCDL, Mn = 2000, UBE Industries, Ltd.), 1,6-hexamethylene diisocyanate (HDI, Bayer AG), diethylene glycol (DEG, Aldrich), dibutyltin dilautrate (DBTDL, Bayer AG), lithium bis(trifluoromethane)sulfonilimide (LiTFSI, Aldrich) and N,N-dimethylformamide (DMF, Aldrich) were used as obtained.

2.2. Synthesis of polycarbonate-based polyurethane

Polycarbonate-based polyurethanes (PCPU) with different composition of soft and hard segments were prepared by polymerization reaction as shown in Scheme 1. The stoichiometric ratio of the adding materials and the compositions of the soft and hard segments are listed in Table 1. The HDI and PCDL were added in a four-necked flask equipped with a thermometer, mechanical stirrer, nitrogen inlet and spiral condenser. The reaction was carried out at 85 °C for 3 h, and then DEG and DMF as solvent were added to the mixture and reacted for 3 h at 65 °C. In addition, 0.5 wt% DBTDL was mixed as a catalyst. Subsequently, the prepolymer was heated at 120 °C for 12 h then cooled to room temperature and stored in sealed glass bottles. The hard and

Table 1
The composition and weight molecular of as-prepared PCPU.

Samples	$n_{HDI}/n_{PCDL}/n_{DEG}$ mol/mol	Hard segments content (wt%)	Soft segments content (wt%)	Mn (g/mol)	Mw (g/mol)	PDI
PCPU8	1.02/1.00/0	8	92	145,799	392,068	2.7
PCPU10	1.20/1.00/0.17	10	90	132,408	450,186	3.4
PCPU12	1.40/1.00/0.37	12	88	101,614	363,011	3.6
PCPU14	1.60/1.00/0.57	14	86	92,218	411,645	4.4