



Carbonate-linked poly(ethylene oxide) polymer electrolytes towards high performance solid state lithium batteries



Weisheng He^{a,b}, Zili Cui^b, Xiaochen Liu^{a,b}, Yanyan Cui^b, Jingchao Chai^b, Xinhong Zhou^{a,*}, Zhihong Liu^{b,*}, Guanglei Cui^{b,*}

^a College of Chemistry and Molecular Engineering, Qingdao University of Science & Technology, Qingdao 266042, PR China

^b Qingdao Industrial Energy Storage Research Institute, Qingdao Institute of Bioenergy and Bioprocess Technology, Chinese Academy of Sciences, Qingdao 266101, PR China

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ABSTRACT

The classic poly(ethylene oxide) (PEO) based solid polymer electrolyte suffers from poor ionic conductivity of ambient temperature, low lithium ion transference number and relatively narrow electrochemical window (<4.0 V vs. Li^+/Li). Herein, the carbonate-linked PEO solid polymer such as poly(diethylene glycol carbonate) (PDEC) and poly(triethylene glycol carbonate) (PTEC) were explored to find out the feasibility of resolving above issues. It was proven that the optimized ionic conductivity of PTEC based electrolyte reached up to $1.12 \times 10^{-5} \text{ S cm}^{-1}$ at 25°C with a decent lithium ion transference number of 0.39 and a wide electrochemical window about 4.5 V vs. Li^+/Li . In addition, the PTEC based $\text{Li}/\text{LiFePO}_4$ cell could be reversibly charged and discharged at 0.05 C-rates at ambient temperature. Moreover, the higher voltage $\text{Li}/\text{LiFe}_{0.2}\text{Mn}_{0.8}\text{PO}_4$ cell (cutoff voltage 4.35 V) possessed considerable rate capability and excellent cycling performance even at ambient temperature. Therefore, these carbonate-linked PEO electrolytes were demonstrated to be fascinating candidates for the next generation solid state lithium batteries simultaneously with high energy and high safety.

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1. Introduction

The state-of-the-art electrolyte solvents of lithium ion batteries almost exclusively consist of cyclic and linear carbonates such as ethylene carbonate (EC), dimethyl carbonate (DMC), diethyl carbonate (DEC) and ethylmethyl carbonate (EMC), possessing both high dielectric permittivity (to dissolve the salt) and low viscosity (to facilitate ion transport). These solvents can simultaneously provide interfacial compatibility on both anode and cathode [1,2]. However, these carbonate solvents are highly volatile and flammable, probably leading to fire or explosion hazards under some battery abuses [3]. So, it is urgent to pursue highly safe solid polymer electrolytes to substitute the conventional liquid electrolytes [4,5].

The classic solid polymer electrolyte, i.e. poly(ethylene oxide) PEO/salt system, pioneered by Wright and Armand in 1979 possessed considerable ionic conductivity about $10^{-7} \text{ S cm}^{-1}$ at room temperature [6,7]. These advantages of PEO-based solid

polymer electrolytes are widely acknowledged [8] and attracted extensive interests in academic field as well as industrial community. However, there are two severe drawbacks limiting their extensive application in solid state battery fields. One is that the PEO main chains readily crystallize at room temperature, hampering the ion migration and resulting in decreased ionic conductivity by two orders of magnitude [9]. The other is that its electrochemical stability window is lower than 4.0 V vs. Li^+/Li , which could not be qualified for the high voltage cathode materials towards high energy batteries [10].

To develop dry solid polymer electrolytes with high ionic conductivity and interfacial stability, many strategies, such as synthesizing PEO copolymers [11–16], tailoring blend polymers [17], preparing branched PEO polymers [18–20] or cross-linked PEO polymers [21–23] and compositing ceramic fillers [8,24–32] have been extensively studied [33]. A self-doped solid block copolymer electrolyte was synthesized combining a single-ion poly(lithium methacrylate-co-oligoethylene glycol methacrylate) (P(MALi-co-OEGMA)) and a structuring polystyrene block (PS). These PS/PEO copolymer design attained attractive ionic conductivity of up to $2.0 \times 10^{-5} \text{ S cm}^{-1}$ at room temperature [34]. In 2013, Armand et al. proposed a kind of triblock copolymer

* Corresponding authors. Tel.: + 86 532 80662746; fax: +86 532 80662744

E-mail addresses: zxhhx2008@163.com (X. Zhou), liuzh@qibebt.ac.cn (Z. Liu), cuiql@qibebt.ac.cn (G. Cui).

P(STFSiLi)-b-PEO-b-P(STFSiLi) as an outstanding electrolyte for lithium batteries [16]. A novel blended polymer electrolyte was then reported by Armand and Zhou et al. composed of lithium salt of a polyanion, poly[(4-styrenesulfonyl)(trifluoromethyl(S-trifluoromethylsulfonylimino)sulfonyl)imide] (PS₂TFSI⁻), and poly(ethylene oxide), which became a promising solid polymer electrolyte for lithium batteries [35]. The UV cross-linked ternary PEO electrolyte, in presence of the plasticizing LiTFSI and an ionic liquid of N-alkyl-N-methylpyrrolidinium TFSI, delivered high ionic conductivity of nearly $10^{-3} \text{ S cm}^{-1}$ at room temperature as a result of the reduced crystallinity of the ternary electrolytes [36,37]. Other all solid state PEO polymer electrolytes were also prepared by a UV cross-linked process and a hot-pressing method manifesting improved performance [38,39]. Very recently, Cui et al. reported that monodispersed SiO₂ nanospheres were incorporated into PEO polymer electrolyte via an in situ synthesis to significantly suppress the crystallization and thus facilitate chain segments mobility [33]. Moreover, there were other recent trends in this direction, such as biopolymers [40], composites [41] and semi-interpenetrating networks (ITN) electrolytes [42,43].

Inspired by the advantages of the conventional liquid carbonate electrolytes readily decomposed into polycarbonate species and resulting in stable SEI on both electrodes [2], polycarbonate-based electrolytes have recently attracted great interests in lithium battery field. Since poly(vinylene carbonate) and poly(trimethylene carbonate) based solid electrolyte were firstly reported by Shriver and Smith, respectively, fifteen years ago [44,45], Some more polycarbonate-based solid polymer electrolytes, such as poly(ethylene carbonate) [46,47], p(CL-co-TMC) [48–50] and poly(propylene carbonate) [51] have achieved great success in high performance of solid polymer lithium batteries. Moreover, poly(ethylene carbonate) and poly(vinylene carbonate) electrolytes possessing short ethylene oxide (EO) side chains were also reported and both revealed that longer side chains favored better ionic conductivity [52,53]. Poly(diethylene glycol carbonate) was also developed and their sodium ion conducting properties was briefly studied [54,55]. To the best of our knowledge, the polycarbonate owning longer EO units into the main chains have not been discussed yet. Herein, poly(triethylene glycol carbonate) solid polymer electrolytes were presented and found that they possessed an enhanced ionic conductivity of $1.12 \times 10^{-5} \text{ S cm}^{-1}$ which was favorable for ambient temperature solid state lithium batteries.

2. Experimental

2.1. Materials

Diethylene glycol, triethylene glycol, diethyl carbonate, potassium carbonate and dichloromethane were purchased from Sinopharm Chemical Reagent Limited Company. Anhydrous acetonitrile (99.9%, Alfa Aesar), tetrahydrofuran (THF, 99.8%, super

dry, J&K) and lithium bis(trifluoromethane sulfonimide) (LiTFSI, GR, Aladdin) were commercially obtained and stored in an argon-filled glove-box. All these chemicals were used as received without further purification.

2.2. Synthesis and characterization of PDEC and PTEC

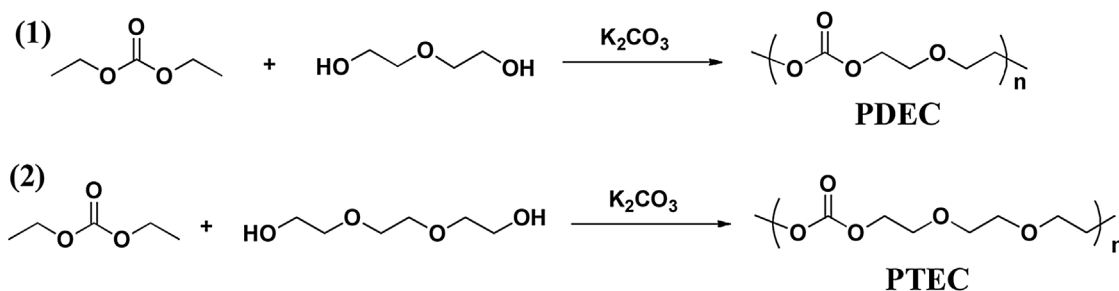
Diethylene glycol (0.25 mol), diethyl carbonate (0.325 mol) and potassium carbonate (0.15 g) were added into a 100 mL round bottom flask equipped with a condenser. The reaction mixture was preheated to 120 °C and the byproduct ethanol was evaporated and gradually removed within 10 h. The reaction temperature was raised and kept at 150 °C for 2 h and then at 190 °C for other 2 h [54,55]. After cooling to room temperature, the solid reaction mixture was dissolved in 75 mL CH₂Cl₂ and washed with 25 mL 1 M HCl once and 25 mL distilled water three times. Anhydrous MgSO₄ was used to absorb the residual water. After CH₂Cl₂ was evaporated by a rotation evaporator, 28.2 g poly(diethylene glycol carbonate) (PDEC) was obtained with 85% yield. The poly(triethylene glycol carbonate) (PTEC) was also synthesized with similar procedure by substituting diethylene glycol with triethylene glycol. Their synthetic procedure was shown in Scheme 1.

¹H NMR and ¹³C NMR spectra of these two polymers PDEC and PTEC in CDCl₃ were obtained on a nuclear magnetic resonance spectrometer (Bruker AVANCE-III). The FT-IR spectra were recorded from KBr pellets on a Thermo Scientific DXRXI system in a range of 400–4000 cm⁻¹. Gel permeation chromatography curves (GPC) were recorded by an Agilent 1200 series HPLC with a MZ-GPC column. THF was used as the elution solvent with a flow rate of 1.0 mL min⁻¹ and polystyrene was used as a standard.

The thermal behaviors of the polymers were examined by differential scanning calorimetry (DSC) using TA Instruments NETZSCH DSC-200F3 under a nitrogen atmosphere. Samples with a typical mass of 5–10 mg were encapsulated in sealed aluminum pans. They were first heated to 180 °C and then cooled to –100 °C. This was followed by a second heating scan from –100 °C to 180 °C at a heating rate of 10 °C min⁻¹. The sample of polyethylene oxide with the average weight of 8000 g mol⁻¹ (PEO8000) was also examined for comparison.

2.3. Ionic conductivity

PDEC-LiTFSI and PTEC-LiTFSI electrolyte membranes were prepared by casting their THF solutions directly on a stainless steel plate and removing THF in a vacuum oven at 60 °C for 8 h. The ionic conductivity of PDEC-LiTFSI and PTEC-LiTFSI electrolyte membranes between two stainless-steel plate blocking electrodes was measured by AC impedance spectroscopy analysis with a Zahner Zennium electrochemical working station at a frequency range from 4 MHz to 100 mHz with an amplitude of 10 mV [56]. The measurements were carried out in the temperature range between 25 °C and 80 °C.



Scheme 1. Synthetic procedure of PDEC and PTEC.

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