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Enhanced performance of a novel gel polymer electrolyte by dual plasticizers

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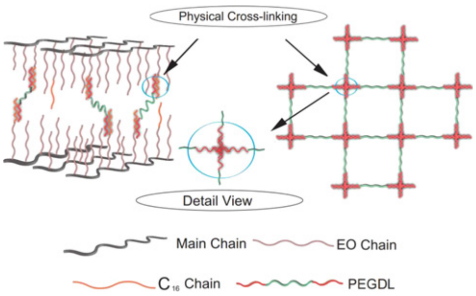
HIGHLIGHTS

- Polyethylene glycol dilaurate is adopted as the physical cross-linking agent in GPE.
- The GPE exhibits good mechanical property and a relatively high ionic conductivity.
- A cell Li/GPE/$LiFePO_4$ shows discharge capacity 152 mAh/g at 0.1 C at 30 °C.

GRAPHICAL ABSTRACT



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ABSTRACT

In this contribution, polyethylene glycol dilaurate (PEGDL) is synthesized and adopted as the physical cross-linking agent to enhance the performance, especially the mechanical property of the gel polymer electrolytes (GPEs). With polyethylene glycol dimethyl ether (PEGDME) as the main plasticizer and PEGDL as the secondary plasticizer, several gel polymer electrolytes based on a copolymer of methoxy-poly(ethylene glycol) methacrylate (MPEGM) and hexadecal-poly(ethylene glycol) methacrylate (HPEGM) are prepared by UV radiation curing. The relationship between the composition of the GPE and the physical properties, e.g., thermal property, mechanical property and ionic conductivity, is investigated. The lithium ion transference number, lithium/GPE interfacial property and charge–discharge performance of the lithium polymer cell based on the physically cross-linked GPE are studied. The gel polymer electrolyte prepared with the optimum composition exhibits excellent mechanical properties and a relatively high ionic conductivity (8.2×10^{-4} S cm^{-1} at 30 °C). A coin cell Li/GPE/$LiFePO_4$, shows a discharge capacity 152 mAh g^{-1} and 163 mAh g^{-1} when cycled at 30 °C and 50 °C, respectively, under a current density of 0.1 C.

1. Introduction

Polymer electrolytes in lithium ion batteries have attracted much attention recently due to the fabrication flexibility in shape and size for roll-up displays and wearable electronic devices, etc. [1,2], as well as the improvement of reliability and safety to replace the liquid electrolytes. The area of solid polymer electrolytes has gone through various developmental stages. First proposed by Wright [3], polyethylene oxide (PEO) and its derivatives as polymer matrixes could dissolve salts and allow ion transport in amorphous phase [4–6]. However, the linear PEO of high molecular weight tends to crystallize below 65 °C [7], and therefore exhibits fairly low ionic conductivity (10^{-8}–10^{-7} S cm^{-1}). In order to suppress the crystallization, Oligo-(ethylene oxide) is grafted to different polymer backbones, such as polyphospazene [8], polysiloxane [9,10], and polymethacrylate [11,12]. Even though the solid polymer electrolytes (SPEs) show good mechanical property and chemical

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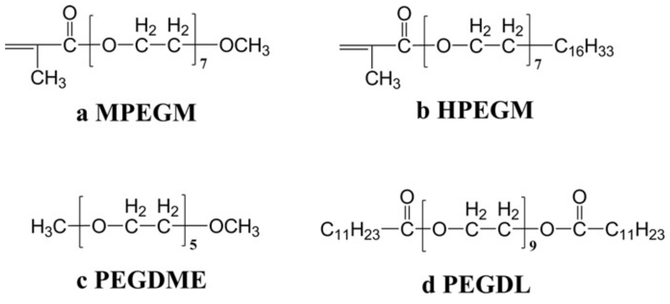
a MPEGM **b HPEGM** **c PEGDME** **d PEGDL**

Fig. 1. Chemical structures of MPEGM, HPEGM, PEGDME and PEGDL.

stability, they still suffer from poor ion conductivity about 10^{-5}–10^{-4} S cm^{-1}, which is far from the practical application level. By incorporating organic solvents (plasticizer) into SPEs, gel polymer electrolytes are developed to increase the ion conductivity [13]. Recently, oligomeric poly(ethylene glycol) dimethyl ether (PEGDME) is used as the plasticizer to enhance the ionic conductivity and the safety of polymer electrolyte because of its high donor number and high flash point [14]. The addition of PEGDME into the polymer electrolyte decreases the glass transition temperature (T_g) of the EO chains, enhances segmental motion, and improves ionic conductivity, but promotes deterioration of the electrolyte's mechanical property. Chemical cross-linking has been widely adopted to improve the mechanical stability of the GPEs while ensuring the good conductivity at room temperature. At present the conductivity of the chemical cross-linked gel electrolytes is about 2.1×10^{-4}–7.8×10^{-4} S cm^{-1} [15–20].

An alternative way to prepare gel polymer electrolyte is to make use of aggregating or self-assembling polymer architectures which consist of two chemically dissimilar polymer segments [21,22]. At low temperatures or in the absence of solvent, an electrostatic repulsion between the polymer segments induces their local segregation, or "micro-phase separation", into periodically spaced nanoscale domains. In this way, physically cross-linked networks are formed. With methoxy-poly(ethylene glycol) methacrylate [MPEGM, Fig. 1a] and hexadecyl-poly(ethylene glycol) methacrylate [HPEGM, Fig. 1b], a novel polymer matrix, poly(MPEGM-co-HPEGM) [PMH, Fig. 2a], was synthesized in our previous study [23]. It has been found that C_{16} chains from HPEGM may expand the space and weaken the interaction among main chains and side chains by distributing in the polymer randomly and disrupting the regular arrangement of EO chains. Therefore the ionic conductivity can be raised through the improvement in the flexibility of the main chains and the mobility of the EO chains provided that the content of HPEGM is low in the polymer. For example, PMH25 (copolymerized from 75 wt% MPEGM and 25 wt% HPEGM) exhibits a relatively high conductivity (1.3×10^{-4} S cm^{-1} at 30 °C). Hence, PMH could be a good candidate for the polymer matrix of GPEs by introducing nonvolatile polyethylene glycol dimethyl ether [PEGDME, Fig. 1c] as the ion conducting plasticizer. Our initial results show that PMH copolymerized from less than 30 wt% HPEGM can host more than 50 wt% PEGDME, thus the resulting GPE exhibits a relatively high conductivity (1.2×10^{-3} S cm^{-1} at 30 °C) but very poor mechanical stability. When the content of HPEGM is more than 30 wt% in PMH, the GPE presents good mechanical stability properly due to the formation of the physically cross-linked matrix by the aggregation of C_{16} as shown in Fig. 2b. However, the limited swelling of the polymer network can host at most 50 wt% PEGDME without leakage, resulting in relatively low conductivity of the obtained GPEs ($\sim 4 \times 10^{-4}$ S cm^{-1} at 30 °C). In order to obtain a PMH-based GPE with both sufficient mechanical stability and high conductivity, a polyethylene glycol derivative, polyethylene glycol dilaurate [PEGDL, Fig. 1d], is synthesized and incorporated into the GPE. With long hydrocarbon chains (C_{11}) on both ends, PEGDL may form physical cross-linking with either C_{16} chains [Fig. 2c] or itself [Fig. 2d], which may improve the mechanical property of the obtained GPE.

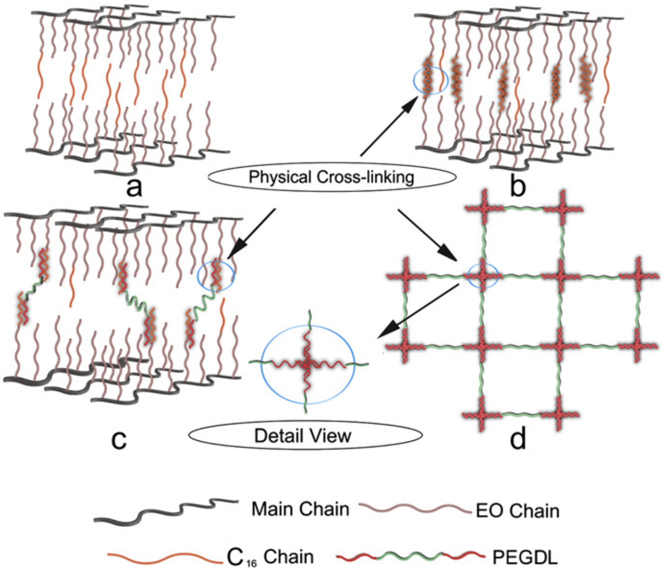

Fig. 2. Schematic illustrations for the ideal structure of: PMH with low content of HPEGM (a); PMH with high content of HPEGM (b); physically cross-linked network formed by PMH and PEGDL (c); physically cross-linked network formed by PEGDL itself (d).

In this work, PEGDME and PEGDL as the plasticizer are used to prepare the PMH-based gel electrolytes. The mechanical property of the GPEs with PEGDME is first discussed in detail. Then the GPEs with PEGDME/PEGDL at various ratios are compared to the GPEs with PEGDME only. Since the ratio of the monomers, the amounts of the plasticizers may affect the properties of GPEs, the relationship between the composition of the gel electrolyte and the physical properties, i.e., thermal property, mechanical property, and ionic conductivity, is explored to guide the preparation of the GPE with good properties. Then the lithium ion transference number, lithium/GPE interfacial property and charge–discharge performance of the lithium polymer cell based on physically cross-linked GPE are studied.

2. Experiment

2.1. Synthesis of macro-monomers

Two macro-monomers, MPEGM and HPEGM, were prepared by using methacryloyl chloride (98%, Alfa Aesar) to esterificate the terminal hydroxyl groups of methoxy-poly(ethylene glycol) (M_w = 350, Alfa Aesar) and hexadecyl-poly(ethylene glycol) (M_w = 534, TCI), respectively. A well stirred mixture of 0.10 mol methoxy-poly(ethylene glycol) [or hexadecyl-poly(ethylene glycol)] and 0.12 mol triethylamine in 250 mL dry dichloromethane (DCM) was maintained in an ice-water bath. Methacryloyl chloride (0.12 mol) was added dropwise to the above mixture. After 12-h stirring, followed by filtration, vacuum evaporation, and column chromatography purification, the macro-monomers were obtained.

2.2. Synthesis of polyethylene glycol dilaurate (PEGDL)

Polyethylene glycol dilaurate was prepared by using lauric acid (Alfa Aesar) to esterificate the terminal hydroxyl groups of poly(ethylene glycol) (M_w = 400, Aladdin). A total of 0.10 mol