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Novel cross-linked copolymer gel electrolyte supported by hydrophilic polytetrafluoroethylene for rechargeable lithium batteries



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ABSTRACT

A novel hydrophilic polytetrafluoroethylene (PTFE)-supported gel polymer electrolyte (GPE) membrane based on the cross-linked poly(ethylene glycol) and poly(glycidyl methacrylate) block copolymer (PEG-*b*-PGMA) is successfully prepared by cationic ring-opening polymerization and followed by in situ cross-linking process. The poly(ethylene glycol) side chains of PEG-*b*-PGMA interact with the liquid electrolyte and hold it inside the membrane, while the hydrophilic and highly-porous PTFE membrane offers mechanical support for the cross-linked GPE. The ionic conductivity of the optimized GPE-3 reaches $1.30 \times 10^{-3} \text{ S cm}^{-1}$ at 25 °C and is high enough to be applied in lithium secondary batteries. The GPE is electrochemically stable up to 4.5 V versus Li/Li⁺. Moreover, the optimized GPE membrane demonstrates non-flammability and good dimensional stability at elevated temperature, which can improve the safety of the cell. The Li/LiFePO₄ cell using the GPE-3 exhibits stable cycling behavior and superior rate performance comparable to the cell based on conventional liquid electrolyte. Therefore, the reported GPE is very promising for the use in rechargeable lithium batteries.

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1. Introduction

Rechargeable lithium (or Li-ion) polymer batteries have been regarded as important next-generation power sources for electric vehicles and stationary energy storage systems [1,2]. Traditional liquid electrolytes with organic solvents possess high ion conductivity. However, they are unsafe because of their several shortcomings, such as high volatility, easy leakage and flammability. Conventional poly(ethylene oxide) (PEO)-based all-solid-state polymer electrolytes have been extensively studied, and exhibit the conductivities ranging from $10^{-7} \text{ S cm}^{-1}$ to $10^{-5} \text{ S cm}^{-1}$ at room temperature, which is not sufficient for practical application [3]. Gel polymer electrolytes (GPEs) are just good alternatives between all-solid-state polymer electrolytes and conventional liquid electrolytes. Various polymers including PEO [4], poly(propylene oxide) (PPO) [5], poly(methylmethacrylate) (PMMA) [6], poly(acrylonitrile) (PAN) [7] and poly(vinylidene fluoride) (PVdF) [8] have been investigated as GPE matrices and high ionic conductivity with other desirable properties have been achieved by incorporation of ceramic fillers and polar plasticizer [9,10]. For example, Oh and Amine [11] prepared a poly(ethylene oxide)-*co*-poly(propylene oxide) random copolymer (abbr. as P(EO-PO)) based GPE having ionic conductivity higher than $10^{-3} \text{ S cm}^{-1}$ and good battery performance. However, these GPE membranes mostly present poor mechanical properties because they have been softened by uptake of liquid electrolytes. This drawback

might cause problems of winding tension and internal short-circuits during the cell assembly and operation, and it is one of the most important reasons for preventing them from being used in practical rechargeable lithium batteries.

On the other hand, chemical cross-linking leads to the formation of an irreversible gel. Thus, chemically cross-linked GPEs show good thermal and dimensional stability. The cross-linked polyether system is regarded as one of the most potential gel bases for GPEs because of the ideal interaction between lithium ion and ethylene oxide (EO) unit. However, the mechanical properties of chemically cross-linked GPEs are also unsatisfactory. In order to enhance mechanical strength of cross-linked GPEs, the microporous polyolefin separators have been employed as a dimensional support to reinforce the cross-linked GPEs [12–14]. Such membrane-supported cross-linked GPEs show sufficient mechanical strength for the fabrication of lithium batteries. Nevertheless, the porosity of the commercial microporous polyolefin separators is generally not high, which limits ionic conductivity of the composite films.

As well known, microporous polytetrafluoroethylene (PTFE) membrane has been widely used in the proton exchange membrane fuel cells [15], lithium-air batteries [16], membrane distillation [17,18] and water purification systems [19] because of its outstanding mechanical and thermal stability, good toughness and chemical inertness. In addition, the high porosity up to 80% is obtainable for this kind of membrane. These excellent performances indicate that it could be a stable support to reinforce the GPEs. In this work, the hydrophilic microporous PTFE membrane was first used as a dimensional support to enhance the mechanical strength of the cross-linked PEG-*b*-PGMA gel electrolyte. The block copolymer PEG-*b*-PGMA was prepared via

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the cationic ring-opening polymerization from glycidyl methacrylate (GMA) and methoxypolyethylene glycols (PEG) oligomer. The PEG-*b*-PGMA consists of two chemically dissimilar segments: the ethylene oxide (EO) chains act as ionophilic units and the glycidyl methacrylate with double bonds serve as cross-linking groups. Methoxypolyethylene glycol was chosen because the ethylene glycol side chains have high affinity to the liquid electrolyte, thus keeping it inside the membrane to avoid cell leakage. The mechanical, heat-resistant and electrochemical properties of this gel polymer electrolyte system were systematically investigated. Furthermore, a Li/LiFePO₄ cell using the optimized GPE-3 was assembled and tested.

2. Experiment

2.1. Materials

Glycidyl methacrylate (GMA), ethylene glycol dimethacrylate (EGDA) and methoxypolyethylene glycols (PEG) oligomer with the number-averaged molecular weight of 1000 Da were purchased from Aladdin. Lithium bis-trifluoromethanesulphonimide (LiTFSI, purity: 99%, Shenzhen Capchem Technology Co., Ltd.) was heated at 100 °C under vacuum prior to electrolyte preparation. Dichloromethane (CH₂Cl₂) was refluxed by CaH₂ before use. Boron trifluoride diethyl etherate (BF₃(OEt)₂, purity: 98%, Aladdin) was dried with activated molecular sieve. Other materials, such as benzoyl peroxide (BPO), methanol and diethyl ether were used as received. 1.0 M liquid electrolyte was made by dissolving a certain quality of LiTFSI in ethylene carbonate (EC)/dimethyl carbonate (DMC) (1:1 in volume, Shenzhen Capchem Technology Co., Ltd.). Hydrophilic microporous PTFE membranes (thickness: 25 μm; porosity: 80%; pore size: 1 μm) were purchased from Shanghai Minglie Chemical Industry Science and Technology Co., Ltd. Commercial polyethylene (PE) separators (thickness: 20 μm; porosity: 37%) were purchased from ENTEK International Ltd. Commercial carbon-coated LiFePO₄ was from Phostech Lithium Company (average particle size: 0.2 μm; carbon content: 2 wt%).

2.2. Synthesis of PEG-*b*-PGMA curable block copolymer

PEG-*b*-PGMA was synthesized according to a one-pot method in previous study [20]. The schematic PEG-*b*-PGMA synthesis procedure is illustrated in Fig. 1a. The cationic ring-opening polymerization of GMA with PEG and BF₃(OEt)₂ was carried out in a dried three-neck flask equipped with a magnetic stirrer flask under argon gas. In a typical reaction, PEG (15 g, 0.015 mol; Mn = 1000 Da) and GMA (14.20 g, 0.1 mol) were dissolved in 80 ml of dried CH₂Cl₂. When the mixture was cooled to -12 °C in an ice-salt bath, BF₃(OEt)₂ (1.6 ml, 0.012 mol) was quickly dropped into it by syringe. After 50 min, a little methanol was added to the

mixture to end the cationic polymerization. The resulting block copolymer was concentrated with a rotator evaporator and isolated by pouring the polymerization mixture into a large excess of ether. The resulting block copolymer was dissolved into methanol and reprecipitated in ether at least three times. A transparent, jellylike, viscous liquid was obtained. Then, this copolymer was kept in a refrigerator. The samples were freeze-dried before the measurement of ¹H NMR.

2.3. Preparation of gel polymer electrolyte

Fig. 1b illustrates a flow chart of the preparation procedure for in situ polymerization of the PTFE-supported cross-linked PEG-*b*-PGMA electrolyte membrane. This composite GPE membrane was prepared by a radical initiated reaction in the microporous PTFE membrane soaked with a homogeneous precursor electrolyte solution consisting of a curable PEG-*b*-PGMA, EGDA cross-linking agent, a liquid electrolyte (1 M LiTFSI in ethylene carbonate/dimethyl carbonate, 1/1, v/v) and benzoyl peroxide (BPO) as a thermal radical initiator, which was cured at 80 °C for 12 h. The exact weight ratio of PEG-*b*-PGMA:EGDA:BPO was 100:2:0.5. Hereinafter, GPE-1, GPE-2, GPE-3 and GPE-4 were respectively prepared by soaking with the PTFE membrane in the precursor solutions consisting of different PEG-*b*-PGMA concentration (5.0, 10.0, 15.0 and 20.0 wt%). All the samples were prepared in a glove box under an argon atmosphere.

2.4. Sample analysis

The surface morphology of the pristine hydrophilic microporous PTFE membrane, the GPE-1, GPE-2, GPE-3 and GPE-4 film were observed by JEOL JSM-7401F field emission scanning electron microscope (FE-SEM). Pore size, pore size distribution, and porosity of the GPE-3 composite film were tested using a model CFP1100AI Capillary Flow Porometer (CFP) manufactured by PMI. ¹H NMR spectra were recorded on a Varian Mercury Plus 400 MHz instrument with CDCl₃ as the solvent. The mechanical properties of the PE separator and the GPE-3 membrane were measured from stress-strain tests using Instron 4465 instrument with a tensile speed of 5 mm min⁻¹.

2.5. Electrochemical measurements

To determine the uptake amount of liquid electrolyte, the resulting membrane was washed with methanol for several times, and dried under vacuum for 12 h at 80 °C. Then, the PTFE-supported polymer membrane was immersed in electrolyte solution for 1 h. Subsequently, the excess solution on the surface of the membrane was slightly absorbed using filter paper. The uptake

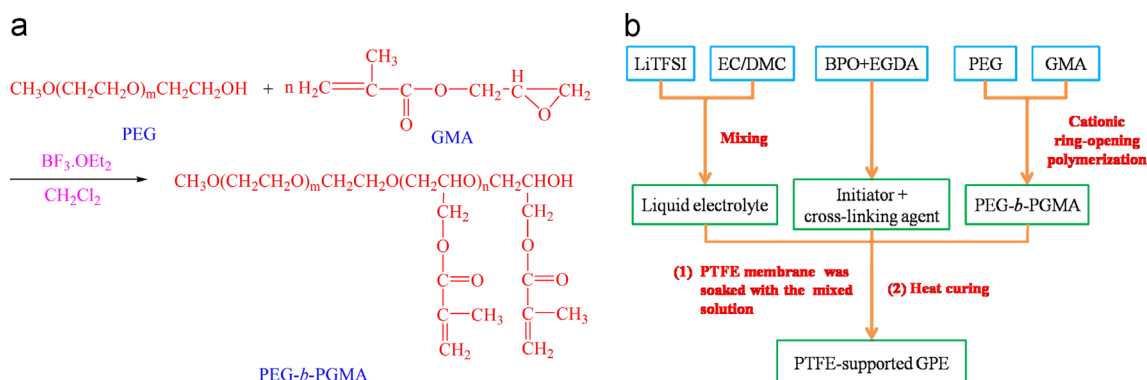


Fig. 1. (a) Schematic synthesis procedure of PEG-*b*-PGMA. (b) Flow chart of preparation procedure of the PTFE-supported cross-linked PEG-*b*-PGMA electrolyte via in situ polymerization.

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