



Advanced semi-interpenetrating polymer network gel electrolyte for rechargeable lithium batteries



Qingwen Lu^{a,b}, Jun Yang^{a,*}, Wei Lu^c, Jiulin Wang^a, Yanna Nuli^a

^a School of Chemistry and Chemical Engineering, Shanghai Jiao Tong University, Shanghai 200240, PR China

^b National Key Laboratory of Power Sources, Tianjin Institute of Power Sources, Tianjin 300381, PR China

^c Department of Chemical Engineering, University of Michigan, Ann Arbor, MI 48109, USA

ARTICLE INFO

Article history:

Received 21 September 2014

Received in revised form 26 November 2014

Accepted 26 November 2014

Available online 28 November 2014

Keywords:

UV-cured

Semi-interpenetrating polymer network

Mechanical properties

Gel polymer electrolyte

Rechargeable lithium battery

ABSTRACT

A new type of semi-interpenetrating polymer network (Semi-IPN) gel polymer electrolyte (GPE) membrane based on the cross-linked poly(ethylene glycol) diacrylate-co-poly(vinylene carbonate) P(EGDA-co-VC) and PVDF-HFP linear polymer is successfully synthesized by UV-cured technology. The cross-linked P(EGDA-co-VC) can accommodate a large amount of liquid electrolyte inside the non-porous membrane via its strong interaction with Li⁺ and solvents, which avoids the liquid electrolyte leakage. The ionic conductivity of the Semi-IPN GPE reaches $1.49 \times 10^{-3} \text{ S cm}^{-1}$ at 25 °C and the electrochemical stability window up to 4.2 V (versus Li/Li⁺). It demonstrates excellent interface stability to lithium metal electrode, superior thermal stability and good mechanical properties. A symmetric Li/Li cell with the above electrolyte displays a lower voltage polarization and longer valid cycle life than that based on conventional liquid electrolyte. Moreover, the Li/LiFePO₄ cells using the Semi-IPN GPE show superior cycling stability and rate performance comparable to the cell based on conventional liquid electrolyte. This Semi-IPN GPE is promising for rechargeable lithium batteries with high safety and energy density.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

Rechargeable lithium (or Li-ion) batteries have been regarded as important next-generation power sources for electric vehicles and energy storage systems [1,2]. Moreover, safety issue becomes crucial for the application of high power rechargeable lithium batteries. Traditional lithium ion batteries adopt porous membrane separators, which impregnate liquid electrolytes. Such a battery system is unsafe because the used organic solvents are often highly volatile, flammable, and easily leaky. In order to improve the battery safety, poly(ethylene oxide) (PEO)-based all-solid-state polymer electrolytes, also functioned as a separator, have been extensively studied. They exhibit the ionic conductivities ranging from 10^{-7} to $10^{-5} \text{ S cm}^{-1}$ at room temperature, which are not sufficient for practical application [3]. Gel polymer electrolytes (GPEs) have the acceptable conductivity and can suppress the solvent volatilization and avoid the leakage. Thus, they are just good alternatives to all-solid-state polymer electrolytes and conventional liquid electrolytes. Various polymers including PEO [4], poly(propyleneoxide)

(PPO) [5], poly(methylmethacrylate) (PMMA) [6,7], poly(acrylonitrile) (PAN) [8] and poly(vinylidene fluoride) (PVdF) [9,10] have been investigated as GPE matrix to absorb electrolyte solutions. However, these GPE membranes mostly present poor mechanical property because they have been softened after uptake of liquid electrolytes. This drawback might cause the problems of winding tension and internal short-circuits during the cell assembly and operation, and it is the main obstacle for the practical application.

Chemical cross-linking can significantly enhance thermal and dimensional stability of GPEs. The cross-linked polyether system is regarded as one of the most potential gel bases for GPEs because of the ideal interaction between electrolyte components (lithium ion and solvent) and ethylene oxide (EO) unit. Nevertheless, the chemically cross-linked GPEs are mostly brittle, being short of the necessary flexibility for battery assembling and application. On the other hand, although thermal curing is a feasible method for preparation of a cross-linked GPE and has been used for the practical lithium ion battery with gel polymer electrolyte [11], the processing at the elevated temperature (around 60–100 °C) might produce impurities during chemical crosslink and the unwanted side reactions including gas evolution owing to the use of the thermal initiators, and thereby might degrade the battery performance [12].

* Corresponding author. Tel.: +86 21 5474 7667; fax: +86 21 5474 7667.

E-mail address: yangj723@sjtu.edu.cn (J. Yang).

In order to improve the mechanical properties of chemically cross-linked GPE, here we report the synthesis and characterization of a new semi-interpenetrating polymer network (Semi-IPN) gel polymer electrolyte membrane by irradiation with UV-light. The advantage of UV-curing is its high energy efficiency, short polymerization time and easy processing control. A notable feature of the semi-IPN is the finely tuned architecture integration of a cross-linked polymer network and a flexible linear polymer, which leads to synergistic effects, particularly regarding the dimensional stability and mechanical properties [13]. D. He et al. [14] has prepared a semi-IPN solid polymer electrolyte which shows good ionic conductivity more than $5.0 \times 10^{-4} \text{ S cm}^{-1}$ at 30 °C. However, its mechanical strength is not sufficiently high for practical application due to the high concentration of solid-state plasticizer. The semi-IPN matrix proposed in this study is based on incorporation of highly cross-linked PEGDA-co-PVC network with a linear PVDF-HFP polymer. The former tends to endow GPE with a strong rigidity and thermal stability, while PVDF-HFP with flexible backbone chains may bring about mechanical softness. The mechanical and electrochemical properties of this semi-IPN gel polymer electrolyte system are systematically investigated.

2. Experimental

2.1. Materials

Poly(ethylene glycol) diacrylate (PEGDA) with the number-averaged molecular weight of 575 Da, poly(vinylidene fluoride-co-hexafluoropropylene (PVDF-HFP) and 2-hydroxy-2-methyl-1-phenyl-1-propanone (HMPP) were purchased from Aladdin. Vinylene carbonate (VC) was purchased from Fujian Chuangxin Technology Co., Ltd. Other materials, such as methanol and acetone were used as received. 1.0M liquid electrolyte was made by dissolving a certain quality of LiPF_6 in ethylene carbonate (EC)/dimethyl carbonate (DMC) (1:1 in volume, Shenzhen Capchem Technology Co., Ltd.). Commercial polyethylene (PE) separators (ENTEK ET 20-26, thickness: 20 μm ; porosity: 37%) were purchased from ENTEK International Ltd. Commercial carbon-coated LiFePO_4 was from Phostech Lithium Company (average particle size: 0.2 μm ; carbon content: 2 wt.%).

2.2. Synthesis of semi-interpenetrating polymer network

The proper PVDF-HFP was dissolved in acetone and stirred continuously for 2 h to form a homogeneous solution. Then, PEGDA, VC and photo-initiator HMPP were added into the solution (the concentration of HMPP was 0.5 wt% based on curable monomer). The curable mixed solution was coated on glass surface and after 10 min of drying, it was irradiated with UV light for 90 s. Finally, the Semi-IPN membranes consisting of PVDF-HFP and cross-linked P(EGDA-co-VC) were obtained. After polymerization, the Semi-IPN membranes were washed with methanol for three times to remove the unreacted PEGDA and VC, and dried under vacuum for 12 h at 60 °C. The thickness of Semi-IPN membranes is around 100 μm . The obtained membrane shows good mechanical properties when the optimized weight ratio of PEGDA: VC: PVDF-HFP was 1:4:1.

The PVDF-HFP membrane (porosity: 35%) used as the control sample with an average thickness of ca. 97 μm was prepared by the phase inversion process [9].

2.3. Preparation of gel polymer electrolyte

The Semi-IPN and PVDF-HFP membranes were swelled in liquid electrolyte (1 M LiPF_6 in EC/DMC = 1/1, v/v) for 12 h. Finally, gel polymer electrolytes were formed and investigated.

2.4. Sample analysis

The surface morphology of the Semi-IPN membranes was observed by JEOL JSM-7401F field emission scanning electron microscope (FE-SEM). The UV-cured reaction of the PEGDA and VC was confirmed using a FT-IR spectrometer (Spectrum 100, Perkin Elmer, Inc. USA). The DSC and TGA measurements were performed in a temperature range from -60°C to 350°C and room temperature to 600°C at a heating rate of $10^\circ\text{C min}^{-1}$ under a nitrogen atmosphere. The mechanical properties of the optimized Semi-IPN 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 optimized Semi-IPN membrane was immersed in electrolyte solution for 12 h. Subsequently, the excess solution on the surface of the membrane was slightly absorbed using filter paper. The uptake amount was calculated from the weight difference of the samples before and after the immersion step [15].

The ionic conductivity was measured by ac impedance spectroscopy using a CHI660C electrochemical analyzer in the frequency range from 100 KHz to 1 Hz at temperatures between 25 and 80 °C. Electrochemical impedance spectroscopy (EIS) was measured using a frequency response analyzer (CHI660C) with an electrochemical interface in the frequency range from 100 KHz to 0.01 Hz. Cyclic voltammetry measurements were conducted in Swagelok cell by sandwiching the GPE or PE membrane between stainless steel (SS) as working electrode and lithium metal as reference and counter electrode at 25 °C. The voltage scan rate was 10 mV s^{-1} in the potential range from -1.0 to 5.0 V . LiFePO_4 based cathode was prepared by pasting a mixture of active material, carbon black (Super-P) and PVDF as binder at a weight ratio of 80:10:10 on Al foil. Stainless steel coin cells (CR2016-type, $\phi = 16 \text{ mm}$) were assembled in glove box containing less than 10 ppm H_2O or O_2 for electrochemical evaluation. The cycling performances of $\text{LiFePO}_4/\text{Li}$ and symmetric Li/Li cells with the Semi-IPN GPE and the liquid electrolyte (1 M LiPF_6 in EC/DMC = 1/1, v/v) soaked in polyethylene (PE) separator (ENTEK ET 20-26, thickness: 20 μm ; porosity: 37%) were measured on a Land battery test system (CT 2001, Wuhan Land Electronic Co. Ltd., China) at 25 °C.

3. Results and discussion

3.1. Physical properties of the gel polymer electrolytes

As illustrated in Fig. 1, the cross-linked P(EGDA-co-VC) copolymer was prepared from poly(ethylene glycol) diacrylate (PEGDA) and vinylene carbonate (VC), which is a well known electrolyte additive for lithium ion battery [16,17].

The UV-polymerization reaction of the PEGDA/VC mixtures is elucidated by measuring the change in the characteristic FTIR spectroscopy peaks assigned to C=C bonds ($1620\text{--}1640 \text{ cm}^{-1}$) of the PEGDA and VC. As shown in Fig. 2, the FTIR peaks of the C=C bonds in both PEGDA and VC disappeared after UV-cured. This indicates that the PEGDA and VC were successfully photopolymerized, leading to the formation of a self-standing film.

In order to discern the semi-interpenetrating polymer composite structure of the prepared membrane, the linear PVDF-HFP was dissolved out by acetone. Fig. 3 presents SEM images of the original Semi-IPN membrane and Semi-IPN membrane etched by acetone. The original Semi-IPN membrane in Fig. 3a shows unsmooth surface and compact structure. For the practical application, the surface evenness can be improved by hot-pressing. After acetone

Download English Version:

<https://daneshyari.com/en/article/6612620>

Download Persian Version:

<https://daneshyari.com/article/6612620>

[Daneshyari.com](https://daneshyari.com)