



Heat-resistant and rigid-flexible coupling glass-fiber nonwoven supported polymer electrolyte for high-performance lithium ion batteries



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ABSTRACT

A heat-resistant and rigid-flexible coupling glass-microfiber nonwoven supported cyanoethyl- β -polyvinyl alcohol composite polymer electrolyte membrane (GFMPE) has been successfully fabricated explored for high-performance lithium batteries. It was demonstrated that the GFMPE possessed enhanced mechanical property, superior dimensional thermostability ($>200^\circ\text{C}$). In addition, Ethylene carbonate (EC)/Dimethyl carbonate (DMC) solvent soaked GFMPE exhibited a superior Li ion transport number of 0.86, wide electrochemical window up to 4.8 V vs Li^+/Li and high ionic conductivity of 0.89 mS/cm at 25°C . Moreover, $\text{LiCoO}_2/\text{graphite}$ cells using such polymer electrolyte with EC:DMC (1:1, v/v) showed excellent cycling stability and superior rate capability at room temperature. It is important to note that the $\text{LiFePO}_4/\text{Li}$ cell using GFMPE/propylene carbonate (PC) can also operate very well at an elevated temperature of 120°C . These fascinating results would endow GFMPE a very promising polymer electrolyte in high-performance lithium batteries with improved safety and reliability.

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1. Introduction

With the development of hybrid electric vehicles, electronic devices and power grids, rechargeable lithium batteries are urgently to meet the demand of modern society to address the challenge of the safety in the case of high energy storage [1–4]. Polymer electrolytes are very promising approaches to replace the combustible and water-sensitive organic liquid electrolytes to enhance safety issues for large capacity batteries [5]. In this regards, solid polymer electrolytes (SPEs) often suffered from low conductivity (10^{-8} – 10^{-5} S cm^{-1}) [6] at room temperature, most of research efforts have been devoted to gel polymer electrolytes (GPEs) with high ionic conductivity [7–9]. GPEs, formed by trapping a liquid electrolytes in a polymer matrix, present an electrochemical stability exceeding that of the counterpart. However, GPEs suffer from their inferior thermally dimensional stability, poor mechanical properties [10]. To mitigate these shortcomings, many endeavours have been carried out to boost the performance over the past two decades, such as composite

polymer electrolytes [11–16], crosslinked polymer matrix [17], and interpenetrating network polymer electrolytes [18]. Recently, using a porous nonwoven to enhance GPE was explored as an effective strategy to address the challenges mentioned above [17,19,20].

In this study, cyanoethyl- β -polyvinyl alcohol (PVA- β -CN) was selected as polymer electrolyte host due to the presence of ether and cyan coordination sites that enable the dissociation of salts, together with a flexible macromolecular structure that assists ionic transport. Noejung Park et. al [21] have reported a gel electrolyte consisted of PVA-CN and EC:EMC/ LiPF_6 , and revealed its good electrochemical performance, but the poor mechanical strength and thermally dimensional stability were still critical issues for application in LIBs. Hence, it is significant to explore rigid-flexible coupling PVA- β -CN composite polymer electrolytes for LIBs. Besides, it is important to note that glass-microfiber membrane (GFM, prepared by papermaking process) as the framework owing to the properties of low cost, thermal stability and simple manufacture process [16]. To the best of our knowledge, rare relevant studies have reported this composite electrolyte system.

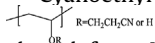
In the present study, we have combined the advantages of PVA- β -CN, GFM and $\text{Li}(\text{SO}_2\text{CF}_3)_2$ (heat-resistant Li-salt) to design and fabricate a rigid-flexible coupling composite polymer electrolyte

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membrane (hereafter abbreviated as “GFMPE”) by impregnating homogenous PVA- β -CN/LiN(SO₂CF₃)₂ (LiTFSI) electrolyte into glass-microfiber mat (GFM). Herein, GFM is incorporated as a compliant skeleton to improve mechanical properties and dimensional stability of PVA- β -CN gel electrolytes. It is demonstrated that such polymer electrolyte membrane can be an excellent separator toward lithium ion battery. It exhibits higher ionic conductivity after dipping a certain amount of Ethylene carbonate (EC)/Dimethyl carbonate (DMC) solvent (GFMPE-LS) than that of conventional liquid electrolyte. Moreover, it is further proved that the corresponding lithium battery with PC-GFMPE can also operate well even at an elevated temperature of 120 °C, thus proving the enhanced safety issues of lithium ion battery.

2. Experimental section

2.1. Materials

Cyanoethyl- β -polyvinyl alcohol PVA- β -CN, chemical formula:  weight-average molecular weight: 120000, purchased from Wuxisanyou chemical Co., Ltd, China. Bistrifluoromethanesulfonimide lithium salt (LiTFSI), purchased from Sigma-Aldrich Co. LLC. Glass microfiber (1–3.5 μ m), purchased by JohnsManville (USA). PP separator (Celgard 2500), purchased from Celgard Company (USA).

2.2. Preparation of GFM

The membrane of microfiber was fabricated through a paper making process of suction filtration. The details can be found in literature [22,23]. Compared to the commercial glass microfiber membrane (more than 1 mm), the obtained glass microfiber film was as thin as about 40 μ m.

2.3. Preparation of GFMPE

PVA- β -CN/LiTFSI polymer electrolyte solution was prepared firstly by dissolving predetermined amounts of LiTFSI and PVA- β -CN into acetone solvent. After the mixture became homogeneous under gentle stirring for 3 hrs, it was transferred into porous glass-fiber mat and the solvent was removed by oven at 60 °C for several hours. The obtained film was finally dried at 80 °C in vacuum dry box for 6 hrs. The molar ratio of CN segment (repeating unit of PVA- β -CN) to Li ion was 1:2 (Fig. S1).

2.4. Characterization

The tensile properties of samples were tested by tensile-machine (AI-7000M, GOTECH). Tensile speed was 100 mm/min.

The X-ray diffraction (XRD) pattern of composite polymer electrolyte were measured by a diffractometer (rigaku D/max2500/PC) using a Cu-K α radiation ($\lambda = 1.5406 \text{ \AA}$).

SEM images of the films were taken by FE-SEM HITACH S4800 with operating voltage of 3.0 kV.

Differential scanning calorimeter (Diamond-DSC, PerkinElmer) was used to evaluate the thermal properties of the samples. Samples were scanned from 50 °C to 300 °C at a heating rate of 10 °C/min under a nitrogen atmosphere.

Raman spectra were recorded at room temperature using a Thermo Scientific DXRXI system with excitation from an Ar laser at 532 nm.

Electrochemical stability of composite membranes was evaluated by linear sweep voltammetry (LSV). The membrane was sandwiched between a stainless steel working electrode and a

lithium metal electrode as both the counter and reference electrode. The Autolab PGSTAT 302N system was used to record the electrochemical stability and the voltage was swept at a scan rate of 1 mV/s in the range of 2.0 V ~ 6.0 V at 25 °C and 100 °C, the sweep rate was 10 mV/s.

Ionic conductivity of membranes was determined by electrochemical impedance spectroscopy (EIS) using an Autolab PGSTAT 302N system. The composite electrolyte membranes were sandwiched between two stainless-steel plate electrodes and the spectra were recorded in a frequency range of 0.01 Hz–1 MHz with an AC amplitude of 20 mV at various temperatures. The bulk resistance of membranes was determined from the impedance spectrum. The ionic conductivity was calculated from Eq. (1):

$$\sigma = L/R_b S \quad (1)$$

where R_b is the bulk resistance, L and S are the thickness and area of the composite membrane, respectively.

The Li ion transference numbers (t^+) of composite electrolytes can be calculated from Eq. (2). The composite electrolyte membrane was sandwiched between two lithium metal disks. The frequency range of 0.1 Hz–1 MHz, the applied voltage for DC polarization test was 0.01 V.

$$t^+ = \frac{I_s(\Delta V - I_0 R_0^{el})}{I_0(\Delta V - I_s R_s^{el})} \quad (2)$$

where I_0 and I_s are the initial and steady-state currents, respectively. ΔV is the applied voltage, R_0^{el} and R_s^{el} are the initial resistance and steady state resistance, respectively.

The CR2032 coin cell was assembled by sandwiching the polymer electrolyte membrane between cathode and anode, and then plasticized by PC. All cells were assembled in an argon-filled glove box. The charge-discharge capacity of cell was evaluated with a battery testing system (CT2001A, Wuhan Land Electronics Co., China).

3. Results and discussion

3.1. Morphological characterization and Mechanical property

The morphology of glass-fiber mat was observed in Fig. S3, the fibers are crossed and super imposed each other with loosen micro-structure. The average diameter of fibers is about 2 μ m, and there is irregularly large-sized pores between glass fibers, which is not ideal to be used as separator, but well suitable to be framework for polymer electrolyte.

The as-prepared composite electrolyte SEM images shown in Fig. 1(a–c), is corresponding to the weight proportion of GFM/Polymer-electrolyte of 1/1, 1/5, 1/9, respectively. It is clear that, with the increasing proportion of polymer electrolytes, the morphology of glass-fiber become more and more indistinct, indicating the polymer electrolyte is transferred into framework successfully. When the proportion is up to 1/9, it is difficult to observe the glass fibers, indicating the polymer electrolytes almost filled glass fiber mat fully. Similarly, from the cross-section image (Fig. 1d) at the ratio of 1/9, the smooth surface (only few glass fibers can be seen) indicated a well polymer electrolyte filled morphology.

Strength and thickness of polymer electrolytes are two vital parameters for battery assembly and operation. Fig. 2 depicts the variation of mechanical performance with the different proportion of GFM/Polymer-electrolyte. It is clear that, in the range among 1/0 and 1/9 of the weight ratio GFM/Polymer-electrolyte, the tensile strength increases linearly with the rising of polymer electrolyte concentrations, from 0.5 MPa to 12 MPa. When the polymer electrolyte proportion continue to increase, the tensile

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