



# A novel polyvinylidene fluoride/microfiber composite gel polymer electrolyte with an interpenetrating network structure for lithium ion battery



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## ARTICLE INFO

### Article history:

Received 26 September 2013  
Received in revised form 24 January 2014  
Accepted 27 January 2014  
Available online 8 February 2014

### Keywords:

Lithium ion battery  
Phase inversion  
Poly (vinylidene fluoride)  
Interpenetrating network  
Composite.

## ABSTRACT

In this present study, macroporous PVDF/microfiber composite gel polymer electrolyte with an interpenetrating network structure was prepared by phase inversion method. The structure and electrochemical performance of the composite membrane were characterized by scanning electron microscopy, stress-strain testing, charge/discharge testing etc. These results exhibit that its electrochemical and mechanical properties were improved by introducing the microfiber network into the macroporous PVDF matrix to form an interpenetrating network structure. The results from electrochemical measurements show that the composite gel electrolyte is stable, and the cells with the PVDF/microfiber network composite membrane have higher discharge capacities and better cycling stability than that assembled with pure macroporous PVDF membrane.

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## 1. Introduction

A separator placed between a cathode and an anode provides the efficient ionic conduction and electrical insulation, which is an inactive and critical component in a lithium ion battery [1–3]. Polyethylene separator has been one of the most dominant commercial separators for lithium ion batteries. However, its safety performance is jeopardized due to the use of liquid organic solvents in the electrolyte. Much attention has been currently focused on employing gel polymer electrolytes (GPEs) to replace traditional liquid electrolyte solution and polyethylene separator. The GPEs exhibit several advantages including high energy density, low volatility, and good safety performance [4–6]. At present, many polymers such as polyacrylonitrile (PAN) [7,8], polyvinylidene fluoride (PVDF) [9,10], polyvinyl chloride (PVC) [11] polymethylmethacrylate (PMMA) [12] are used as GPEs matrices [13–15]. Among these materials, PVDF has been considered as the next generation separator candidate for high performance lithium ion batteries because of its appealing properties such as good chemical resistance, large dielectric constant ( $\epsilon=8.4$ ) and high thermal stability [16–24]. Macroporous PVDF matrix membranes have been

prepared by various methods, including solution casting, phase inversion, plasticizer extraction and electrospinning [22,23,25–28]. Compared with other methods, those prepared by phase inversion method exhibit a more uniform porous structure with controllable porous sizes and porosities, which are important to improving stability of entrapped liquid electrolyte, ensuring uniform current density distribution, reducing the risk of battery internal shorting and increasing the ion conductivity [29,30]. Although ionic conduction of macroporous PVDF GPEs ( $> 0.5 \text{ mS cm}^{-1}$ ) is adequate for battery application, practical application of macroporous PVDF membrane has not been realized due to the poor mechanical stability, especially after forming the GPEs in a liquid electrolyte [31,32]. Up to now, the mechanical strength of the macroporous PVDF membrane can be improved by adding nanosized metal oxides such as  $\text{SiO}_2$ ,  $\text{TiO}_2$ ,  $\text{Al}_2\text{O}_3$  to obtain composite polymer membrane [33–36]. The metal oxide surface groups are physical cross-linking centers for the polymer segments, which will enhance the mechanical strength of gel polymer electrolyte by interacting with the polymer segments. However, performance of GPEs is still unsatisfactory though extensive research has been carried out to improve the mechanical strength of macroporous PVDF GPEs [37–42].

In this paper, we present a novel frame structure composite with the microfiber three dimensional(3D) network and the macroporous PVDF polymer membrane, see Fig. 1 for schematic illustration. First of all, the frame of the microfiber three dimensional networks is highly flexible and acts as a support for macroporous PVDF

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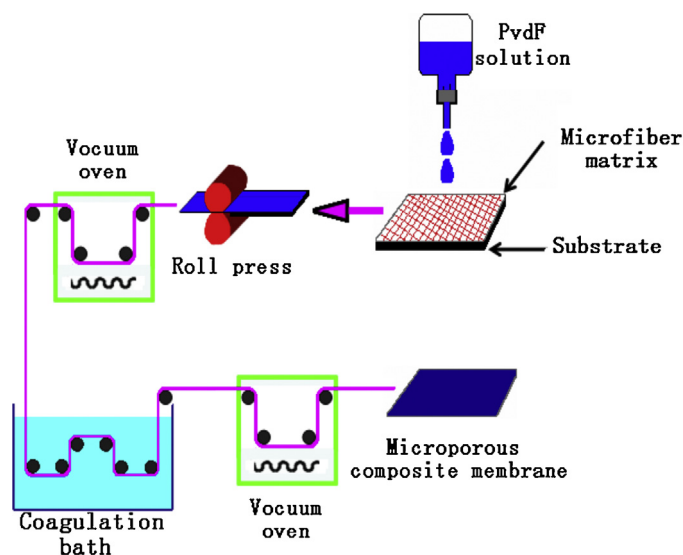


Fig. 1. Schematic drawings of the fabrication processes of the macroporous composite membrane with an interpenetrating network structure.

polymer membrane. The relative position of the macroporous PVDF polymer membrane is fixed with the microfiber structural frame, which could relieve the force existing in the local membrane and the perpendicular direction of the membrane. This is important for improving the mechanical stability of the macroporous PVDF GPEs in large scale applications. Based on the structural and electrochemical measurements, initial results show that both electrochemical performance and mechanical properties of the as prepared composite electrolytes are improved with great promising application in lithium ion batteries

## 2. Experimental

### 2.1. Preparation of porous separator

A certain amount of PVDF ( $M_n = 500,000$ , KnyarFlex 2704 from Atofina Chem.) was dissolved in a mixture of DMF (solvent) and glycerin (non-solvent) ( $v/v = 10/1$ ) and strongly stirred to form a uniformed solution. The macroporous composite membrane was prepared by coating the PVDF solution on a microfiber three dimensional network (polypropylene, Kingstart Nonwoven Co., Ltd.), which was carried on a clean glass substrate, as shown in Fig. 1. The composite membrane thickness could be controlled in the range of 40 to 60  $\mu\text{m}$  by changing the space between two moving stages. The coated microfiber 3D network membrane was dried at 80  $^\circ\text{C}$  in vacuum. After evaporation of DMF, the membrane was then passed through a bath that was filled with distilled water to extract glycerin. Subsequently, the membrane was dried and punched into circular pieces for battery fabrication.

### 2.2. Measurement of physical properties of separator

The structure of the membranes was observed by an SEM (JEOL JSM-6360). Prior to SEM analysis, the samples were coated with gold to reduce charge effects. Tensile tests of membranes were performed with RG2000-1000 mechanical tester after saturated absorption of electrolytic solution, the speed of elongation was fixed at 10  $\text{mm min}^{-1}$ . Electrolyte uptake of the polymer membrane was measured according to the methods described in our previous work [10,43]. The porosity of the composite membrane was measured by immersing the membrane into 4-butanol for 24 h and weighing the membrane before and after absorption of the

4-butanol. The porosity was calculated using the following equation:  $P\% = \frac{M_b/\rho_b}{(M_p/\rho_p) + (M_b/\rho_b)}$ , where  $P\%$  is porosity of the membrane,  $M_p$  the mass of membrane,  $M_b$  the mass of absorbed 4-butanol,  $\rho_p$  the density of the membrane and  $\rho_b$  the density of n-butanol.

### 2.3. Electrical measurements

Electrochemical impedance spectra of the circular membrane, which was sandwiched between two symmetrical lithium piece electrodes and sealed in a coin cell, were measured using EG & G Potentiostat/Golvannostat M273 in conjunction with M5210 Lock-in amplifier electrochemical analysis system in the frequency ranging from 1 Hz to 100 kHz at an AC amplitude of 5 mV. The ionic conductivity can be calculated according to (1)

$$\sigma = \frac{d}{R_b \times S} \quad (1)$$

where  $\sigma$ ,  $R_b$ ,  $d$  and  $S$  are the ionic conductivity, bulk resistance (spectra), thickness of the polymer membrane electrolyte and area of the symmetrical electrode, respectively. Linear sweep voltammetry was used to check electrochemical stability window of the polymer membrane electrolyte. The measurement was carried out using a three-electrode electrochemical cell consisting of a stainless steel working electrode and a lithium reference and counter electrode at a scanning rate of 1  $\text{mV S}^{-1}$ . The unit cell was assembled by soaking the as prepared composite membrane in the liquid electrolyte and sandwiching it between lithium anode and  $\text{LiFePO}_4$  cathode. All assembly processes were carried out in a glove box that was filled with argon. Charge/discharge measurements were carried out between 4.2 V and 2.2 V at a constant current density at room temperature using a neware battery testing system (BTS-51, ShenZhen, China).

## 3. Results and discussion

Fig. 2 shows the morphology of the microfiber network, PVDF and PVDF/microfiber network composite membrane. SEM image in Fig. 2a demonstrates that the microfiber network is composed of interlaced 1D PP microfibers with about 30  $\mu\text{m}$  in diameter, the randomly oriented PP microfibers form interconnected pores. It can be seen that the microfibers can be melted locally into a regular, periodic configuration with four-sided frame throughout the whole membrane, which could improve the mechanical property of the nonwoven membrane. As shown in Fig. 2b, a regular, periodic configuration with four-sided frame can be still observed after wrapped by the PVDF macroporous matrix. No big broken pore is observed on the surface of the composite membrane, indicating that the homogeneous composite with an interpenetrating networks structure could be successfully prepared. As shown in Fig. 2c, there are a large number of small pores on the surface for the PVDF/microfiber network composite membrane, but there are also many closed pores in the surface. In our previous study [10], we obtained macroporous PVDF membranes based on the same solution casting and phase inversion methods. The membrane had more open pores in the surface than that using continuous prepared processing in this paper, the reason for such morphology could be the bad temperature control for our continuous prepared processing. Fig. 2d shows the cross-section morphology of the PVDF macroporous membrane, it can be found that there are many uniform pores in the internal throughout the membrane, the size of pore is distributed in the range of 3 - 5  $\mu\text{m}$ . From the cross-section morphology of the PVDF/microfiber network composite membrane (Fig. 2e), there is a similar pore structure in the pure macroporous PVDF membrane (Fig. 2d), which suggests that pore structure and morphology of PVDF matrix have not be changed after forming the

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