



Batwing-like polymer membrane consisting of PMMA-grafted electrospun PVdF–SiO₂ nanocomposite fibers for lithium-ion batteries



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ABSTRACT

To retain the electrolyte within the fibrous poly(vinylidene fluoride) (PVdF) membranes in a lithium-ion battery, poly(methylmethacrylate) (PMMA) was grafted onto electrospun SiO₂–PVdF nanocomposite fibers via radical polymerization, producing a batwing-like polymer membrane. The obtained polymer membrane was activated with the electrolyte (1.0 M LiPF₆ in a mixture of ethylene carbonate and diethylene carbonate) to form a fibrous gelled-polymer electrolyte (FGPE). The effects of grafting of PMMA on the morphology, mechanical properties, and electrochemical properties of the fibrous membranes were investigated. The SiO₂–PVdF fibrous membrane that was grafted with 20 wt% of PMMA possessed an ionic conductivity of $2.31 \times 10^{-3} \text{ S cm}^{-1}$ at room temperature and a tensile strength of 8.2 MPa. The Li–LiFePO₄ cells assembled by this FGPE delivered specific capacities of 156 and 130 mAh g⁻¹ at the rates of 0.1 and 2 C, respectively, and they retained 97% of the initial capacity at 0.1 C-rate after 90 cycles. The results indicate that FGPE is suitable for high-performance lithium-ion batteries.

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1. Introduction

Owing to their high specific energy density, safe operation, and flexibility in packaging, polymer lithium-ion batteries (PLiBs) have been popular power sources for portable electronics such as laptop computers, mobile phones, digital cameras, toys, and small tools. A polymer electrolyte membrane acts not only as the ionic conductor but also as the separator in the batteries. Its electrochemical properties strongly affect the battery performance in terms of rate capability and cyclability [1–3]. Fortunately, porous gelled-polymer electrolytes (PGPEs) based on a poly(vinylidene fluoride) (PVdF) matrix have been extensively studied because PVdF has excellent chemical stability, high dielectric constant, and

strong hydrophobicity [4–17]. In fact, the PVdF matrix could provide the resultant PGPE with strong mechanical support and high adsorption of a non-aqueous electrolyte. In addition, filling the polymer matrix with nanoscale inorganic oxides such as silicon dioxide (SiO₂), titanium dioxide (TiO₂), and aluminum oxide (Al₂O₃) could improve the ionic conductivity at room temperature and the mechanical strength of the PGPE [18]. Owing to their industrialized production and low cost, SiO₂ nanoparticles were chosen as the oxide to fill the electrospun PVdF fibers in this study.

Many researchers have taken different approaches, including those employing thermo-induced phase inversion [19], non-solvent-induced phase inversion [20–21], foaming [22], hard template [23], and electrospinning [24–41], to prepare PGPEs based on PVdF or its copolymer, poly(vinylidene fluoride-hexafluoropropylene) (PVdF-HFP). Among the approaches, electrospinning has been widely utilized to fabricate fibrous gelled-polymer electrolytes (FGPEs) because the polymer membranes possess high porosity and good interconnectivity of pores. The polymer membranes with higher porosity are able to absorb much liquid electrolyte while those with better interconnectivity possess more continuous channels for the migration of ions. As a result, an electrospun FGPE has a high ionic conductivity up to $10^{-3} \text{ S cm}^{-1}$ at room temperature. However, owing to the existence of the interconnected micrometer-scale pores in the FGPE, the absorbed electrolyte might leak from the PVdF matrix during cycling, resulting in deterioration of the battery capacity. Thus, it is essential

Abbreviations: AIBN, 2,2'-azobis(isobutyronitrile); DEC, diethylene carbonate; DMF, *N,N'*-dimethylformamide; DSC, differential scanning calorimetry; EC, ethylene carbonate; EGDMA, ethylene glycol dimethacrylate; FGPE, fibrous gelled-polymer electrolyte; FTIR, Fourier-transform infrared; MMA, methyl methacrylate; PMMA, poly(methylmethacrylate); PVdF, poly(vinylidene fluoride); R, electrolyte retainment; R_b, bulk resistance of FGPE; SEM, scanning electron microscope; SiO₂–PVdF-g-xPMMA, SiO₂–PVdF fibrous membrane with x mass percent of grafted PMMA; SS, stainless steel; T_m, melting temperature of the crystalline phase of a fibrous membrane; U, electrolyte uptake; W, mass of fibrous membrane; X_c, crystallinity; XRD, X-ray diffraction; ΔH_f, melting enthalpy; ΔH₁₀₀, melting enthalpy of perfectly crystalline PVdF; σ, ionic conductivity

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for the FGPE to retain the electrolyte effectively within the polymer matrix.

Researchers have made many efforts to resolve this problem, including preparing polymeric fibers by electrospinning a mixed solution of PVdF and other polymers that are compatible with the electrolyte based on organic carbonates [26,29,31,32,35,38]. The blended polymers, nevertheless, could dissolve into the organic carbonates so easily that the electrospun polymer fibers might be fractured, leading to possible failure of the lithium-ion batteries. Other researchers have attempted to use PVdF membranes to sandwich the polymers that are compatible with the electrolyte [27,33,36]. However, the electrolyte that has been physically absorbed by the membranes still has the potential for leakage from the fibrous polymer matrix during the cycling process.

Herein, we present an alternative route to retain the electrolyte within the fibrous PVdF membranes as well as to improve their mechanical performance by surface grafting poly(methylmethacrylate) (PMMA) to the electrospun SiO₂-PVdF nanocomposite fibers [42]. The electrospun fibers are surrounded by PMMA and merge into a single organic entity. In particular, the PMMA is chemically grafted to the PVdF fibers and is thus unable to leave the polymer matrix of the FGPE. As a result, the absorbed electrolyte is well retained within the FGPE. The effects of the amount of grafting of PMMA on the mechanical and electrochemical properties of the FGPE were investigated in detail. The results suggest that the FGPE has great promise for application in high-performance lithium-ion batteries.

2. Experimental

2.1. Materials

PVdF was purchased from Kynar LBG, Arkema, France. Silicon dioxide (SiO₂, 30 nm) particles were used as received from Zhejiang Mingri Co., Ltd., China. *N,N*-dimethylformamide (DMF), potassium hydroxide (KOH), acetone, and ethyl alcohol were purchased from Xilong Chemical Co. Ltd., China, and used as received. Ethylene glycol dimethacrylate (EGDMA), 2,2'-azobis(isobutyronitrile) (AIBN), and methyl methacrylate (MMA) (> 99%) monomers were purchased from Shanghai Chemical Reagents Co., China.

2.2. Preparation of the grafted fibrous membrane

First, PVdF was dried at 80 °C for 12 h before use. 4 g of PVdF powder was then dispersed in a 5 M KOH solution in 100 mL of a water-ethyl-alcohol mixture (1:1, v/v) by stirring at 60 °C for 8 h, forming a dark-brown suspension. The suspension was then filtered, washed with double-distilled water until the pH reached 7, and dried in a vacuum oven at 60 °C for 24 h to obtain the modified PVdF powder.

Next, 3 g of the modified PVdF powder was dissolved in 20 mL of DMF-acetone (7:3, v/v). Then, 0.15 g of SiO₂ nanoparticles was added and ultrasonically agitated for 0.5 h to form the spinning solution. The spinning solution was electrospun under a high voltage of 28 kV, collected on an Al plate with a tip-to-collector distance of 20 cm, and dried under vacuum at 80 °C for 12 h to form a self-supporting membrane. The obtained membrane was peeled off the Al plate and hereafter denoted as the SiO₂-PVdF fibrous membrane. A pristine SiO₂-PVdF fibrous membrane was also prepared by this method, except that the PVdF powder was not treated with the KOH solution.

Finally, the obtained SiO₂-PVdF fibrous membrane was immersed in the mixed solution of AIBN-EGDMA-MMA (2:5:100, w/w/w), in which the amount of MMA monomers was varied,

depending on the mass of the SiO₂-PVdF fibrous membrane. The solution containing the membrane was heated at 60 °C for 24 h to produce the SiO₂-PVdF-g-xPMMA fibrous membrane, where *x* refers to the mass percent of PMMA in the grafted fibrous membrane. After the unreacted components were removed by ethyl ether, the as-prepared membrane was weighed and the grafted amount of PMMA was determined by the difference in mass of the membrane before and after polymerization of the MMA monomers. They are designated as SiO₂-PVdF-g-10PMMA, SiO₂-PVdF-g-20PMMA, and SiO₂-PVdF-g-30PMMA where *x*=10, 20, and 30 wt%, respectively.

2.3. Characterization of the grafted fibrous membrane

A scanning electron microscope (SEM; JSM-6360LV, JEOL, Japan) was used to observe the morphology.

Fourier-transform infrared (FTIR) spectra of the various membranes were recorded using an FTIR spectrometer (Spectrum One, PerkinElmer, US) with a resolution of 2 cm⁻¹ in the wavenumber range of 600–4000 cm⁻¹.

X-ray diffraction (XRD) patterns were recorded on a powder diffractometer (D8 Advanced Diffractometer System, Bruker, Germany) using a Cu K_α (λ=0.154 nm) source with a Ni filter at a scan rate of 2° min⁻¹ in the 2θ range of 5–50°. The electron accelerating voltage was 40 kV, and the anode current was 40 mA.

Differential scanning calorimetry (DSC) measurements were performed on a calorimeter (DSC Q10, PerkinElmer, USA) at 5 °C min⁻¹ under a nitrogen atmosphere. The crystallinity (*X_c*) was calculated using Eq. (1) and the melting enthalpy (Δ*H_f*) obtained from the DSC curves:

$$X_c = \frac{\Delta H_f}{\Delta H_{100}} \times 100\% \quad (1)$$

where Δ*H₁₀₀* is the crystalline melting enthalpy of perfectly crystalline PVdF (104.7 J g⁻¹) [43].

The mechanical properties of the fibrous membranes were investigated using a tensile tester (RG2000-100, Shenzhen Reger Instruments Co., Ltd., China) with rectangular specimens (length: 100 mm; width: 10 mm; thickness: ~100 μm). All tests were performed at 28 °C with a speed of 1 mm min⁻¹.

Discs with a diameter of 16 mm were punched from the fibrous membrane and then soaked in the electrolyte of 1.0 M LiPF₆-EC-DEC (1:1, v/v) in an Ar-filled glove-box. The FGPE membranes were prepared after the excess electrolyte on the disc surfaces was removed by filter paper. The electrolyte uptake (*U*) of the fibrous membrane was calculated from Eq. (2):

$$U = \frac{W - W_0}{W_0} \times 100\% \quad (2)$$

where *W*₀ and *W* are the mass of the discs of fibrous membrane before and after the electrolyte was absorbed, respectively.

The electrolyte retainment (*R*) of the fibrous membrane was evaluated by weighing the FGPE membranes. This was performed by sandwiching the membrane between two sheets of filter paper for different periods of time [39]. The value of *R* was calculated from Eq. (3):

$$R = \frac{W - W_f}{W - W_0} \times 100\% \quad (3)$$

where *W*₀ is the mass of a dry disc of fibrous membrane. *W* and *W_f* are the mass of the FGPE membrane before and after it was pressed, respectively.

Seven discs of the same fibrous membrane were immersed in seven separate bottles containing 10 mL of n-butanol for 1 h. After that, each disc was weighed to obtain the mass of the wet

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