

The preparation of porous proton exchange membranes via *in situ* polymerization



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ABSTRACT

A novel poly(vinylidene fluoride)-graft-poly(styrene sulfonic acid) (PVDF-g-PSSA)-based proton exchange membrane (PEM) was prepared by phase inversion and a grafting method in solution. Polystyrene was successfully grafted onto the surface and into the pores of the PVDF membrane, and the membrane was subsequently treated in a KOH ethanol solution. A linear relationship was observed between the degree of grafting and the treatment time in KOH solution. Fourier transform infrared spectroscopy and scanning electron microscope were used to characterize the changes in the membrane's microstructure after grafting and sulfonation. Thermogravimetric analysis was used for evaluating the thermostability of the membrane. In addition, the proton conductivity of the solution-grafted PVDF-g-PSSA membrane was found to reach 0.13 S cm^{-1} at 80°C .

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1. Introduction

In the past decade, proton exchange membrane fuel cells (PEMFCs) have drawn much attention because they have high power density, high efficiency, and great potential as environmentally sustainable materials [1–3]. Polymer electrolyte membranes (PEMs) play a major role as a proton conductor and separator of the fuel from the oxidant in PEMFCs. Among all kinds of PEMs that have been reported, perfluorinated sulfonic acid ionomers such as Nafion membranes have been widely used because of their excellent proton conductivity and chemical resistance [4,5]. Nevertheless, the cost and high methanol permeability of these membranes has limited their usage in PEMFCs.

Extensive research attention has been devoted towards the development of new PEMs in attempts to reduce the cost of fuel cells and facilitate their mass production [6,7]. Until now, the use of radiation to graft functional groups onto polymer films and fibers has been a well-known modification strategy. Scherer et al. [8], Lehtinen et al. [9] and a group in Newcastle [10], have contributed a wealth of work in these areas. Xinpeng Qiu et al. have conducted extensive researches on the preparation of PVDF-g-PSSA membranes by a solution-grafting technique [11,12].

The morphology of PEM plays a major role in determining its final properties [13]. Normally, there is one phase separation process that occurs in the PEM, thus yielding two domains (hydrophobic and hydrophilic). The hydrophilic domain can form clusters and provide proton transport channels while the hydrophobic domain provides mechanical and chemical stability. The size and continuity of clusters ultimately

determine the membrane performance. Thus, designing membranes with well-controlled ion clusters should provide an efficient means to prepare PEMs. To realize this target, several methods have been used to prepare membranes consisting of a hydrophobic support bearing pores that are filled by a hydrophilic electrolyte, into porous hydrophobic supports. Examples of such membranes have included those incorporating porous PTFE supports bearing pores that were filled by Nafion resin solutions as well as those utilizing Daramic support with polyelectrolyte-filled pores. However, the commercial use of PTFE and Nafion resin solutions has been limited by their high cost. In the case of pore-filled Daramic materials, as the membrane is prepared via physical methods, and the hydrophilic electrolyte tends to leach during operation.

In order to reduce the cost and improve the membrane performance, a chemical method was used to design a new PEM by grafting ion exchange groups onto a porous support. Through this chemical method, the hydrophilic poly(styrene sulfonic acid) phase, was graft polymerized *in situ* within the hydrophobic phase that consisted of a porous PVDF membrane. The sizes of the proton transport channels were tuned by adjusting the grafting degree in the pores. Different PVDF pre-treatment times in a KOH/ethanol solution yielded different grafting degrees, which affected the size and continuity of the ionic clusters after sulfonation.

2. Experimental

2.1. Materials

PVDF powder and benzoyl peroxide (BPO) were purchased from Sigma-Aldrich. The solvents *N*-methyl pyrrolidinone (NMP) and

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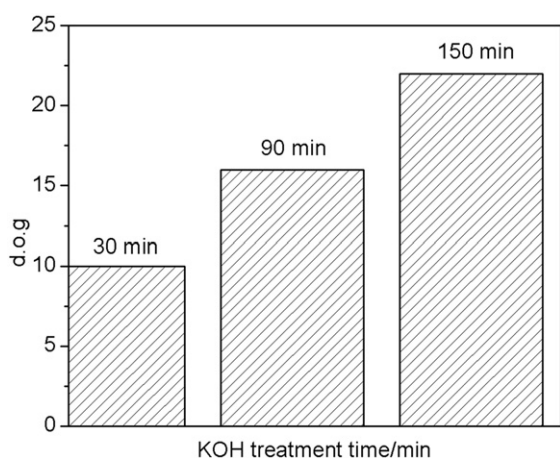


Fig. 1. The relationship between the d.o.g. of the PVDF membrane and the treatment time in an ethanol solution containing 0.007 M KOH.

tetrahydrofuran (THF) were purchased from Acros and they each had a purity of 99%. Styrene was purchased from Acros and used without any further purification. All of the other chemicals were obtained commercially and used without any further purification.

2.2. Membrane preparation

The PVDF membrane was prepared by casting a solution of PVDF, THF and NMP with a mass ratio of 1:4:1 (PVDF/NMP/THF) onto a clean glass plate using a homemade casting nozzle. With a wet film thickness of 250 μm , the nascent polymer films were briefly exposed to ambient air for 60 s, and then immersed into a deionized water bath at room temperature (RT). The porous PVDF membrane was dried at 80 $^{\circ}\text{C}$ overnight. The thickness of the dry membrane was reduced to 200 μm because of the shrinkage that occurred after the phase separation process. Before the grafting reaction, the PVDF membrane was treated in a solution of 0.007 M KOH in methanol at 40 $^{\circ}\text{C}$. The membrane was washed with deionized water until a constant pH was reached prior to immersion into a mixed solution of styrene, THF and BPO. The volume ratio of styrene and THF was 4:1 and the BPO concentration was 3×10^{-3} g/mL. The BPO served as a radical initiator. The grafting reaction was performed at 80 $^{\circ}\text{C}$ for 24 h. Subsequently, the membrane was washed with chloroform to remove the unreacted monomers and any homopolymer. The grafted membranes were sulfonated with 0.2 mol/L of chlorosulfonic acid in 1,2-dichloroethane at 40 $^{\circ}\text{C}$ for 4 h and kept at ambient temperature overnight. The sulfonation occurred mainly at the *para* position of the phenyl rings [14].

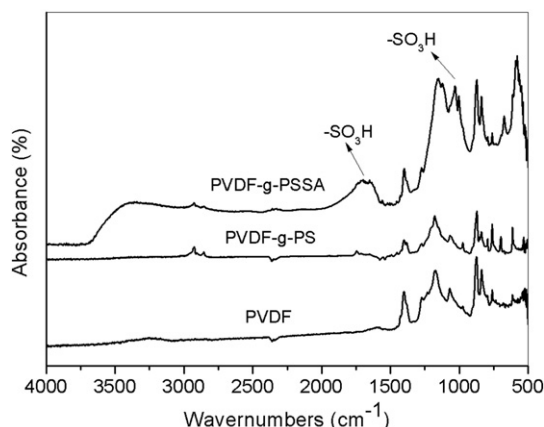


Fig. 2. The FT-IR spectra of PVDF, PVDF-g-PS and PVDF-g-PSSA.

2.3. Degree of grafting

The degree of grafting (d.o.g.) was determined gravimetrically according to Eq. (1):

$$\text{d.o.g.} = \frac{m_1 - m_0}{m_0} \times 100\% \quad (1)$$

where m_0 denotes the mass of the initial PVDF membrane and m_1 corresponds to the mass of the polystyrene-grafted membrane.

2.4. Characterization

2.4.1. Structure characterization

Fourier transform infrared (FT-IR) spectra were recorded using a Bruker infrared spectrophotometer (IFS 66v/s) over the range of 4000 to 500 cm^{-1} . The surface and cross-sectional morphology of the grafted membrane was observed via scanning electron microscopy (SEM) using a Philips XL30 FEG scanning electron microscope, this system was a semi-in-lens type microscope equipped with a cold field emission electron source. Cross-sections were obtained by cleaving the membranes under liquid nitrogen. In order to help prevent samples from accumulating charge under the electron beam, the cross-sections were coated with a thin layer of gold. This coating treatment was performed using a Cressington HR208 high-resolution sputter coater and the coating conditions involved a 2-min coating treatment at 20 mA, thus rendering the samples conductive. Contact angle measurements were performed at room temperature using a KRUSS DSA 20 contact angle meter with pure water as probe liquid.

2.4.2. Thermogravimetric analysis

The thermal properties of the PVDF-g-PSSA membranes were evaluated by thermogravimetric analysis (TGA) using a TA Instruments Q500 system. These measurements were performed under nitrogen and the temperature of the PVDF-g-PSSA sample was increased at a rate of 5 $^{\circ}\text{C}/\text{min}$ from room temperature (RT) to 600 $^{\circ}\text{C}$.

2.4.3. Conductivity measurements

The conductivities of the proton exchange membranes were measured using a Materials Mates 7260 Impedance analyzer. These measurements were performed over a frequency range of 1–10⁷ Hz at 30 $^{\circ}\text{C}$, 40 $^{\circ}\text{C}$, 50 $^{\circ}\text{C}$, 60 $^{\circ}\text{C}$, 70 $^{\circ}\text{C}$ and 80 $^{\circ}\text{C}$. The electrode and membranes were kept in a HPV200H holder that was used to keep the humidity and temperature constant during the measurements.

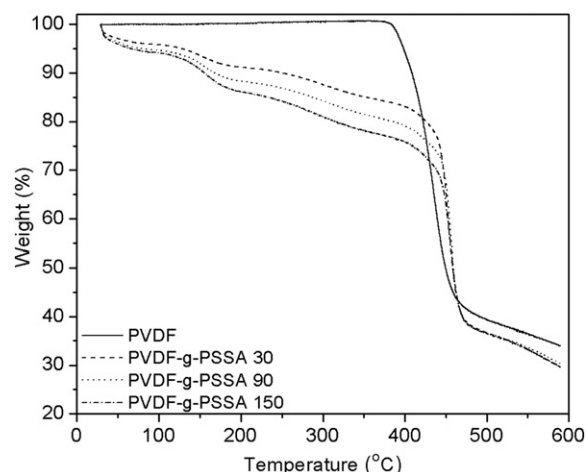


Fig. 3. The TGA curves of PVDF, PVDF-g-PSSA 30, PVDF-g-PSSA 90 and PVDF-g-PSSA 150.

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