# Preparation and characterization of proton exchange membranes from polystyrene grafted poly(vinylidene fluoride) powder

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**Abstract** Proton exchange membranes (PEMs) were prepared in three steps: grafting of polystyrene onto PVDF powder using pre-irradiation graft polymerization technique, processing the grafted PVDF powder into membranes of around 50-µm thickness, and sulfonating them with cholorosulfonic acid to form poly(vinylidene fluoride)-g-poly(styrene sulfonic acid) membranes. Kinetics of the graft polymerization was studied. The existing of polystyrene side-chains in the grafted PVDF powders, and PSSA groups in PEMs, were proved by FT-IR. Properties of the PEMs, i.e. the ion exchange capacity, water uptake, proton conductivity, thermal property and oxidative stability, were characterized. Dependence of properties on the degree of grafting was investigated, too.

Key words Proton exchange membrane, Pre-irradiation graft polymerization, Polystyrene, PVDF powder

# 1 Introduction

In recent years, the world has been confronted with an energy crisis due to the exhausting fossil fuel resources and the increased attention to environmental issues. Hydrogen has a strategic importance in the pursuit of a low-emission, environment-benign, cleaner and more sustainable energy system<sup>[1-4]</sup>. Thus, the hydrogen-based energy system, such as polymer electrolyte fuel cells (PEFCs), has attracted more and more attention of engineers and environmental scientists<sup>[5]</sup>. Proton exchange membrane (PEM), a vital component part in PEFCs, acts as an electrolyte to transport protons and a fuel gases separator<sup>[6,7]</sup>. Owing</sup> to the high cost of current popular perfluoride PEMs<sup>[8]</sup>, such as Nafion<sup>®</sup> membranes, radiation-induced grafting of styrenic monomer into polymer films followed by sulfonation has been reported as an alternative route to make proton exchange membranes<sup>[9-13]</sup>. Generally, using pre-irradiation grafting method, the graft polymerization of styrene or co-monomers is initiated after the fluoropolymer films or membranes are irradiated by  $\gamma$ -rays or electronbeams. Sulfonating the grafted films or membranes yields the PEMs.

Introducing the graft chains, however, causes the weight and volume increase of the films or membranes, hence their decreased mechanical properties<sup>[11]</sup>. out-of-flatness Also. surface in micrometer order is commonly found with the resulting membranes<sup>[14]</sup>. In order to overcome these problems, poly(vinylidene fluoride) (PVDF) powder instead of membranes is used as the starting material at our lab, and the polystyrene-grafted PVDF powders are processed into membranes. Another potential merit for this new approach is that it is possible to blend the grafted powders with nano-scale inorganic additives such as SiO<sub>2</sub> and TiO<sub>2</sub> or heteropoly acid.

In this work, PEMs were made by pre-irradiation grafting technique, which involves three key steps: grafting of polystyrene onto PVDF powder, processing the grafted powders (denoted as PVDF-g-PS) into membranes and sulfonating the membranes to obtain PEM (denoted as PVDF-g-PSSA). The kinetics of graft polymerization

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of PVDF-g-PS was studied and its structure is determined by FT-IR spectrometry. Water uptake (*WU*), ion exchange capacity (*IEC*), proton conductivity, thermal property and oxidative stability of the PVDF-g-PSSA membranes were measured.

# 2 Experimental

# 2.1 Materials

PVDF ( $M_w$ =420 000) powder of 0.1-mm diameter was provided by Solvay Solexis Inc. Styrene, toluene, chlorosulfonic acid, dichloroethane and <u>isopropanol</u> (denoted as iPrOH) were supplied by Sinopharm Chemical Reagent Co. Ltd., Shanghai. All of the materials were used without further purification. For comparison, Nafion<sup>®</sup> NRE-212 membranes (products of Du Pont) were pretreated with 3 vol.% H<sub>2</sub>O<sub>2</sub> and 5 wt.% H<sub>2</sub>SO<sub>4</sub> (aq.) at 80°C for 30 min, respectively, rinsed with distilled water several times, and stored in deionized water before use.

# 2.2 Pre-irradiation induced grafting

The PVDF powder was irradiated to 15 kGy in air at room temperature in a  ${}^{60}$ Co  $\gamma$ -ray source. The irradiated PVDF powder (20 g) was added into an erlenmeyer flask with monomer suspension containing 20 mL styrene, 40 mL iPrOH, and 40 mL deionized water. Ferrous ammonium sulfate hexahydrate of  $4 \times 10^{-4}$  mol was added as inhibitor, whereas the control was the same solution without the inhibitor. The flask was purged with nitrogen gas for 15 min to remove oxygen, and sealed. The graft polymerization was performed at 60°C under stirring for a definite time period. After filtered and washed, the PVDF-g-PS powder was Soxhlet extracted with toluene for 72 h to remove residual styrene monomer and homopolymer. Finally, it was vacuum dried at 80°C to constant weight. The degree of grafting (DG) was calculated by fluorine contents of the samples before  $(F_p)$  and after  $(F_g)$  grafting copolymerization, as shown in Eq.(1).

$$DG = [(F_p - F_g)/F_g] \times 100\%$$
 (1)

#### 2.3 PEM preparation

The PVDF-g-PS powder samples of different DGs were processed into membranes in thickness of around 50  $\mu$ m by hot-pressing at 240°C on a plate

vulcanization machine. The PVDF-g-PS membranes were sulfonated by soaking in a mixture of 10% (v/v) chlorosulfonic acid in dichloroethane at room temperature for 24 h and washed with deionized water<sup>[15,16]</sup>. The PEM is named as PVDF-g-PSSA, i.e. poly(vinylidene fluoride)-g-poly(styrene sulfonic acid).

### 2.4 Characterization

FT-IR spectra were taken on a Nicolet Avatar 370 spectrometer. The spectra were measured 32 times in a wave number range of  $4000-400 \text{ cm}^{-1}$  with a resolution of 4 cm<sup>-1</sup>.

To evaluate *IEC* values of the PVDF-g-PSSA membranes, dried samples were soaked in 0.5 M KCl solution for 24 h to liberate the sulfonic acid protons by exchange with  $K^+$  ions. After taken out the sample, the residual solution was titrated with 0.05 M NaOH solution to pH 7. *IEC* value of the sample was calculated according to Eq.(2):

$$IEC(meq/g) = V_{NaOH} M_{NaOH}/W$$
 (2)

where  $V_{\text{NaOH}}$  and  $M_{\text{NaOH}}$  are the volume (mL) and molar concentration of NaOH solution used in the titration, respectively; and W is the sample weight.

For evaluating WU of the PVDF-g-PSSA membranes, the samples were immersed in distilled water at room temperature for 24 h. They were taken out, wiped with tissue paper, and weighed immediately on an electronic balance. The water uptake was calculated by Eq.(3),

$$WU = [(W_w - W_d)/W_d] \times 100\%$$
 (3)

where  $W_w$  and  $W_d$  are the weights of the wet and dried sample, respectively.

Proton conductivity was measured by means of AC impedance spectroscopy on a HIOKI 3522-50 LCR HITESTER in a frequency range of 0.1 Hz to 100 kHz at different temperatures. After immersing the samples in deionized water for 24 h at room temperature, the PVDF-g-PSSA and Nafion<sup>®</sup> NRE-212 membranes were successively clamped between two 1 cm×1 cm Pt electrodes for impedance spectroscopy measurement. The conductivity was calculated from the membrane resistance, electrode area, and the membrane thickness measured with a micrometer.

In order to evaluate the thermal property of the resulting PEMs, the DSC and TG analysis were carried out using a METTLER TOLEDO DSC822e and a Netzsch TG 209 F3. After a 24-h vacuum drying at 60°C, the samples placed in 40  $\mu$ L aluminum crucible were measured in a temperature range of 40–220°C at heating rate of 10°C/min under N<sub>2</sub> atmosphere. TGA curves were recorded in a temperature range of 50–800°C at heating rate of 10°C/min under N<sub>2</sub>.

Oxidative stability of the obtained PVDF-g-PSSA membranes was evaluated in Fenton's reagent  $(3\% \text{ H}_2\text{O}_2 \text{ containing 2 ppm Fe}^{2+})$  at 60°C for a constant time interval. The stability was assessed by the weight loss. The weight loss fraction (*W*o) was calculated using Eq.(4),

$$W_0 = [(W_b - W_a)/W_b] \times 100\%$$
 (4)

where  $W_b$  and  $W_a$  are the weights of PEM before and after oxidative stability test, respectively.

## **3** Results and discussion

In a radiation-induced graft polymerization system, an inhibitor is usually added to depress the homopolymerization. Therefore, grafting of polystyrene onto PVDF powder with or without inhibitor is performed and compared, and the kinetic curves are shown in Fig.1. The DGs increase quickly at first, and level off after 3 hours. Compared to the system with inhibitor, it is noteworthy that graft copolymerization reaction without inhibitor proceeds quicker and the DG gets higher. After reacted for 4 h, DG is almost 35% in the system without inhibitor, while it is about 25% for those with 4 mmol/L  $Fe^{2+}$  ions. The reason is that the ferrous ammonium sulfate hexahydrate not only stops homopolymerization but also terminates those macromolecular radicals which should initiate the graft polymerization. Therefore, both homopolymerization and graft polymerization are depressed, in a compromise of decreased DG, though [17].

FT-IR spectra of pristine PVDF, PVDF-g-PS and PVDF-g-PSSA membranes are shown in Fig.2. In the spectra of the PVDF-g-PS membrane, polystyrene grafts is confirmed by the presence of the 699 cm<sup>-1</sup> peak attributing to the C-H bond of phenyl rings<sup>[18]</sup>, together with skeletal C=C plate-stretching vibrations of phenyl rings situated at 1450, 1490 and 1600 cm<sup>-1[19]</sup>. After sulfonation, additional peaks at 1035 cm<sup>-1</sup>, due to symmetric stretching of SO<sub>3</sub><sup>-</sup>, and 1008 cm<sup>-1</sup>, which are assigned to absorption of para-substituted of phenyl rings<sup>[18]</sup> are observed. Moreover, The broad peak at 3410 cm<sup>-1</sup> is assigned to water molecules involved in hydrogen bonding with the SO<sub>3</sub><sup>-</sup> groups<sup>[20]</sup>. These characteristic peaks indicate the successful introduction of sulfonic acid group.



**Fig.1** Kinetic curves of polystyrene graft polymerization with and without inhibitor.



**Fig.2** FT-IR spectra of pristine PVDF, PVDF-g-PS and PVDF-g-PSSA membranes.

The *IEC* value and *WU* of the PVDF-g-PSSA membranes of different DGs are measured. In Table 1 the results are given, together with those of Nafion<sup>®</sup> NRE-212 membrane. The *WU* and *IEC* values of PVDF-g-PSSA membranes increase with the DG, with *IEC*=1.47 meq/g and *WU* =39.4% at *DG*= 36.0% of the PVDF-g-PSSA, while the Nafion<sup>®</sup> NRE-212 membrane displays an inferior ion exchange capacity of 0.91 meq/g, and a weak water uptake.

 Table 1
 Water uptake and Ion exchange capacity of Nafion

 NRE-212 and PVDF-g-PSSA membranes

Samples	WU(%)	IEC
Nafion NRE-212	30.7	0.91
PVDF-g-PSSA, <i>DG</i> =26.3%	37.2	1.37
PVDF-g-PSSA, <i>DG</i> =36.0%	39.4	1.47

The proton conductivity as a function of temperature for the PVDF-g-PSSA and Nafion<sup>®</sup> NRE-212 membranes are shown in Fig.3.The proton conductivity of both PVDF-g-PSSA and Nafion NRE-212 membranes increase with temperature. However, temperature dependence of proton conductivity of the PVDF-g-PSSA membranes is stronger than that of Nafion<sup>®</sup> NRE-212 membrane, which means the activation energy for proton conduction of PVDF-g-PSSA membranes is higher than that of Nafion<sup>®</sup> NRE-212 membrane. Also, proton conductivity of the PVDF-g-PSSA membranes increases with the DG. And proton conductivity of the PVDF-g-PSSA membranes is higher than that of Nafion<sup>®</sup> NRE-212 membrane under similar test conditions.



**Fig.3** Proton conductivity versus temperature for PVDF-g-PSSA and Nafion NRE-212 membranes.

Figure 4 shows the DSC curves of PVDF-g-PSSA membranes. The PEMs have the endothermic peaks at about 170°C, which should be attributed to the occurrence of PVDF melting. The melting enthalpy of the PVDF-g-PSSA membrane of DG= 26.3% is 19.1 J/g, while it is 18.2 J/g for the PVDF-g-PSSA membrane of DG=36.0%. Thus, using the melting enthalpy of 100% crystalline PVDF, 104.7 J/g<sup>[21]</sup>, the apparent crystallinity of PVDF-g-PSSA

membranes can be estimated. It decreases with increasing DGs. Another endothermic peak at about 120°C in Fig.4 is due to the evaporation of absorbed water in the PSSA side chain.



Fig.4 DSC curves of the PVDF-g-PSSA membranes.

Figure 5 shows TGA curves of the PVDF-g-PSSA membranes. For the PEMs, the weight loss is of a typical multi-step degradation pattern. The degradation below 300°C should be caused by elimination of water and the sulfonic acid groups. The weight loss of the PEMs below 300°C increases with DG, which indicates that PVDF-g-PSSA membrane of higher DG holds larger amount of sulfonic acid groups and absorbed water, which is consistent with the proton conductivity data of the PEMs. The mass loss occurs at 300–400°C and above 400°C should be attributed to the degradation of PS graft-chains and the PVDF matrix, respectively<sup>[22,23]</sup>.



Fig.5 TGA curves of the PVDF-g-PSSA membranes.

The oxidative stability of PVDF-g-PSSA membranes was tested in feton reagent at 60°C (Fig.6). All curves show a one-step decomposition pattern. The

remaining weight fraction of PEMs after full decomposition decreases with increasing DGs. At DG=36.0%, the weight loss is ca. 50%, while it is ca. 38% at DG=26.3%. The weight loss is the fraction of PSSA graft-chains with water absorbed, and the remaining weight fraction is attributed to the PVDF main-chains.



Fig.6 Oxidative stability of the PVDF-g-PSSA membranes.

# 4. Conclusion

Proton exchange membranes were successfully achieved by pre-irradiation grafting of polystyrene onto PVDF powders, which were hot-pressed into membrane, and sulfonated for PEMs. The kinetic curves of graft polymerization with or without the inhibitor show that the reaction proceeds quicker and the DG gets higher without the  $Fe^{2+}$  ion inhibitor.

The *IEC*, *WU* and proton conductivity of the PEMs increases with the *DG*. The ion exchange capacity of that PEM obtained at *DG*=36.0% is 1.47 mmol/g, corresponding to a proton conductivity of ca. 23 mS/cm at 80°C and *WU* of 39.4%. The proton conductivity of the PEM is higher than that of Nafion<sup>®</sup> NRE-212 membrane under similar test conditions.

Thermal property of the PVDF-g-PSSA membranes is measured by using DSC and TGA. The apparent crystallinity of the resulting PEMs decreases with increasing *DG*. And the TGA curve has a multi-step degradation pattern.

Oxidative stability analysis shows a one-step decomposition pattern of the PEMs.

All the results proved that grafting PVDF powders is an effective alternative to make proton exchange membranes.

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