

PREPARATION AND CHARACTERIZATION OF ION EXCHANGE MEMBRANES BASED ON POLYVINYLIDENE FLUORIDE

Bo Tian, Chuan-wei Yan* and Fu-hui Wang

State Key Laboratory for Corrosion and Protection, Institute of Metal Research,
Chinese Academy of Sciences, Shenyang 110016, China

Abstract A new ion exchange membrane based on polyvinylidene fluoride (PVDF) and sulfonated poly(styrene-divinylbenzene) was prepared by *in-situ* polymerization. The incorporation of sulfonic groups into the polyvinylidene fluoride composite membrane was confirmed by infrared spectroscopy (IR), ion exchange capacity (IEC) and energy dispersive X-ray analysis (EDAX). Area resistance, IEC and water uptake of the treated membrane were evaluated. When 20% of the crosslinked membrane was sulfonated at 80°C for 22 h, the PVDF ion exchange membrane can attain $0.8 \Omega \cdot \text{cm}^2$ area resistance in NaCl aqueous solution at 25°C, IEC is as high as 2.43 millimoles per gram of the wet membrane. The hydrophilicity of PVDF membrane is also significantly improved after treatment. When 60% of crosslinked membrane was sulfonated at 80°C for 6 h, water uptake of the treated membrane can attain 64.7%.

Keywords Polyvinylidene fluoride, Composite membrane, Sulfonation, Ion exchange membrane

INTRODUCTION

Ion exchange membranes have been widely used in various industrial fields, such as electrodialysis for desalination of brackish water, production of table salt, recovery of valuable metals from the effluents of the metal-plating industry^[1] and separators for redox flow batteries^[2]. For these applications, some processes are conducted under severe conditions of high temperature and strongly oxidizing conditions, for example, in the field of vanadium redox flow batteries. Evaluation of a number of commercial ion exchange membranes has shown that except for a few, which are generally perfluorinated membranes, most of the membranes are unsuitable due to their poor stability under those conditions^[3]. However, these perfluorinated ion exchange membranes are rather expensive.

An ion exchange membrane can be prepared by incorporation of ion transporting material into an inexpensive, nonconductive membrane with high chemical and physical stability. PVDF is famous for its outstanding chemical and thermal stability, as well as mechanical strength^[4], and it can be used as base material for preparing excellent ion exchange membranes. In previous publications, many studies were carried out to introduce functionality such as the sulfonic group into PVDF^[5–9]. The methods were usually monomer grafting and polymer blending. For monomer grafting, styrene was grafted onto PVDF by gamma ray or X-ray irradiation. Sulfonation then followed to prepare sulfonated polyvinylidene fluoride. For polymer blending, polystyrene sulfonic acid was directly used to mix with PVDF solution, then PVDF composite membrane containing sulfonic group was prepared. These resulting membranes prepared by the above two methods all exhibit good physical and chemical properties. However grafting method is somewhat expensive and complicated for the preparation process, and polymer blending can be only applied to a limited number of ion exchange membranes due to the problem of immiscibility^[10, 11].

* Corresponding author: Chuan-wei Yan (严川伟); E-mail: cwyan@imr.ac.cn
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To overcome these problems, a sorption method for preparing ion exchange membrane based on PVDF was proposed. PVDF membrane was first soaked in a mixed solution containing styrene and divinylbenzene monomers. Then styrene and divinylbenzene were copolymerized in the pores of base material by *in-situ* polymerization. Cationic exchange capability was introduced into the composite membrane by using sulfonation. The physical and electrochemical characteristics of the resulting ion exchange membrane were characterized.

EXPERIMENTAL

Materials and Reagents

PVDF microporous membrane (Shanghai Nuclear Grade Resins Co. Ltd) of thickness 59 μm was used as the base polymer. Divinylbenzene (DVB) was reagent grade and used without further purification. All other chemicals used were analytically pure grade.

Preparation of Ion Exchange Membrane

PVDF membrane was soaked for 24 h in a solution consisting of styrene, DVB and ethanol together with an initiator, benzoyl peroxide (BPO) at ambient temperature. The soaked PVDF membrane was then sealed between two glass plates, and heated in a constant-temperature oven to obtain PVDF composite membrane. Following this, the composite membrane was soaked in distilled water and released from the glass plates.

Sulfonation of the PVDF composite membrane was carried out using concentrated sulfuric acid at different temperatures. Silver sulfate was used as the catalyst (1 wt%) for the sulfonation reaction.

Membrane Properties

IEC of the membrane was evaluated by the method described in the literature^[2]. After a membrane sample was immersed for 1 day in pure water, it was transferred to a large volume of 1 mol $\cdot$ L⁻¹ HCl aqueous solution to turn the membrane into the H-form. The membrane was then washed free of excess HCl with distilled water and equilibrated with exactly 50 mL of 0.05 mol $\cdot$ L⁻¹ NaOH aqueous solution for 24 h. The IEC was determined from the reduction in alkaline medium determined by back titration and calculated from Eq. (1).

$$\text{IEC} = (M_{0, \text{NaOH}} - M_{\text{E, NaOH}})/W \quad (1)$$

where $M_{0, \text{NaOH}}$ is the number of moles of NaOH at the start. $M_{\text{E, NaOH}}$ is the number of moles of NaOH after equilibration. W is the weight of the wet membrane (g).

The area resistance was evaluated by the methods described in the literature^[12]. The area resistance of the conductivity cell with membrane (r_1) and without membrane (r_2) was measured at 25°C. Each compartment of the cell was filled with 0.5 mol $\cdot$ L⁻¹ NaCl aqueous solution. The effective membrane area S of the cell was 1.00 cm². The area resistance of the membrane r ($\Omega \cdot \text{cm}^2$) was calculated by Eq. (2).

$$r = (r_1 - r_2) \times S \quad (2)$$

To measure the water uptake properties, the membrane was immersed in distilled water for 24 h, the surface moisture wiped off and the membrane immediately weighed. Then, this weighed wet membrane was dried at a fixed temperature (100°C) for 1 h and weighed again.

The water uptake can be calculated from Eq. (3)

$$W_C = (W_w - W)/W \quad (3)$$

W_w is the weight of the wet membrane (g). W is the weight of the dry membrane (g).

Cationic exchange groups were determined using a Nicolet Magna-IR 560 spectrometer by the reflection technique. Thermogravimetric analysis (TGA) was carried out using a Setaram Lyon-France mtb10-8 microbalance under Ar atmosphere. Morphological studies were undertaken using scanning electron microscope/energy dispersive X-ray analyzer (XL-30FEG Philips).

RESULTS AND DISCUSSION

Preparation of Ion Exchange Membrane

The IR spectrum of the resultant ion exchange membrane is shown in Fig. 1. The bands appearing in the 1100–1300 cm^{-1} region and at 1410, 887, 846 cm^{-1} are attributed to the bulk PVDF membrane. The bands in the 1100–1300 cm^{-1} region are assigned to the C–F stretching vibrations. The band at 1410 cm^{-1} is related to the scissoring vibrations of the CH_2 group, and the latter two bands at 887 and 846 cm^{-1} are assigned to C–H stretching vibrations in the PVDF backbone. The ion exchange membrane also shows characteristic bands in the 1100–1000 cm^{-1} region resulting from S=O group and the bands of the skeletal C=C stretching vibrations of the benzene rings appear at 1500 cm^{-1} and 1600 cm^{-1} . Very broad absorption bands in the 3500–3100 cm^{-1} region may be assigned to the water molecules associated with sulfonic acid and the –S–OH stretching absorption.

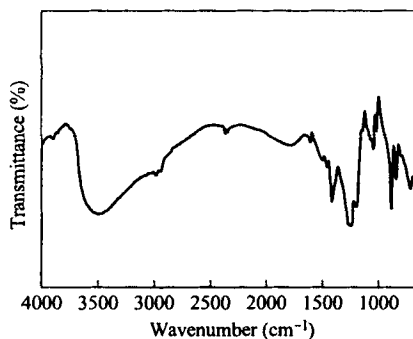


Fig. 1 IR spectrum of ion exchange membrane

Area Resistance, Ion Exchange Capacity and Water Uptake

PVDF composite membranes were initially prepared by crosslinking of polyvinylidene fluoride using different DVB/styrene ratios. Sulfonation of these composite membranes was carried out using concentrated sulfuric acid as sulfonating agent at 80°C for 6 h. IEC and water uptake of these resulting ion exchange composite membranes are summarized in Table 1. The function of ethanol is to swell the pores of PVDF, consequently more DVB and styrene can permeate into them. As a result, there should be a greater chance for the monomer to polymerize within the pores^[3]. Table 1 shows that IEC and water uptake of the ion exchange membranes increase with the ratios of DVB/styrene. When 60% (*V*) of DVB used is, IEC and water uptake attain as high as 2.70 mmol per gram of the wet membrane and 64.7% of the dry membrane, respectively. However, a high ratio of DVB/styrene caused the composite membrane to become brittle. Generally, 20% of DVB can produce an ion exchange membrane with acceptable IEC, water uptake and area resistance.

Table 1. Effect of DVB on IEC and water uptake of ion exchange membranes

Membrane	DVB (vol%)	IEC (mmol · g ⁻¹)	Water uptake (%)
1#	0	1.00	32.5
2#	20	2.11	53.8
3#	40	2.46	60.7
4#	60	2.70	64.7

Sulfonation of PVDF composite membranes which have crosslinked previously with 20% of DVB at 60°C for 16 h was carried out at different temperatures and times. The results of IEC and the area resistance measurements of these ion exchange membranes are shown in Table 2. Aromatic hydrocarbons can easily react with sulfuric acid. This is one of the characteristics that distinguish them from parafinic hydrocarbons^[3]. From Table 2, it can be seen that the ion exchange membranes exhibit some significant IEC as high as 2.93 mmol per gram of wet membrane when they were sulfonated at 100°C for 10 h. The measured IEC can be used to evaluate

the degree of sulfonation of the ion exchange membrane. The results show that the degree of sulfonation increases with both reaction temperature and reaction time. However, higher temperature and longer time may result in deformation and severe deterioration of the membrane. Area resistance is also an important parameter for ion exchange membrane. The value of IEC is associated with area resistance, as shown in Table 2. Increasing the IEC of the membrane after sulfonation will accompany an improvement in the area resistance. The area resistance for the PVDF membrane is significantly reduced after treatment. This is probably due to the high IEC and the excellent hydrophilicity of the sulfonated membrane.

Table 2. Effect of sulfonation temperature and time on IEC and area resistance of ion exchange membranes

Membrane	Sulfonation temperature (°C)	Sulfonation time (h)	IEC (mmol · g ⁻¹)	Area resistance (Ω · cm ²)
5#	80	6	1.20	7.6
6#	80	10	1.17	7.8
7#	80	16	2.02	3.9
8#	80	22	2.43	0.8
9#	100	3	2.30	2.4
10#	100	6	2.60	1.4
11#	100	10	2.93	1.0
12#	100	18	2.39	2.2
13#	100	24	2.68	1.7

Table 3 illustrates the comparative results of some properties of the ion exchange membrane based on PVDF with some commercial membranes. The membrane with 20% DVB exhibits comparable IEC and electrical resistance to the commercial membranes.

Table 3. A comparison of some general properties between prepared (2#) and several commercial cationic exchange membranes

Membranes	2#	Nepton (CR61, DZL-183)	JCM-1	CMV
Thickness (mm)	0.06	0.58	0.13–0.14	0.12–0.15
Water content (%)	54	46	25–30	25
Ion exchange capacity (mmol/g of dry-membrane)	2.1	2.7	2.0–2.5	2.2
	(mmol/g of wet-membrane)			
Electrical resistance (Ω · cm ²) (in 0.5 mol/L NaCl solution)	2.5	11.0	1–3 (in 0.1 mol/L KCl solution)	2.0–3.5
Manufacturer		Ionics (America)	Beijing Huanyu Lida (China)	Asahi Glass (Japan)

Thermal Stability Studies

The thermal stability of prepared ion exchange membrane and the original PVDF membrane was investigated by TGA, the results of which are shown in Fig. 2. The onset of weight loss for PVDF (Fig. 2a) obviously due to the main chain decomposition, starts at about 410°C. In Fig. 2(b) two weight loss steps are observable for the ion exchange membrane. The first weight loss peak appeared at 252°C is probably due to the splitting-off of the sulfonated poly(styrene-divinylbenzene) linkages. The second weight loss at 457°C is due to decomposition of the backbone of polyvinylidene fluoride. The appearance of the onset temperature of the first decomposition suggests that the ion exchange membrane is thermally stable up to approximately 180°C.

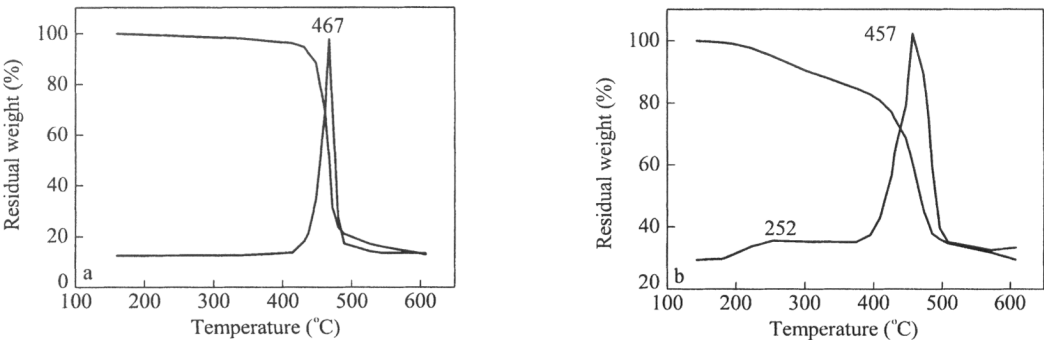


Fig. 2 TGA curves of PVDF membrane (a) and ion exchange membrane (b)

Surface Morphology

The morphologies of the PVDF membrane and the ion exchange membrane were studied by SEM and their micrographs are shown in Fig. 3. The morphology of the treated PVDF membrane is somewhat different from that of the untreated PVDF membrane. Pores on the surface of membrane after treatment decrease and some small pores disappeared. This may be attributed to the formation of sulfonation products in the pores which have a pore-blocking action. Microspheres that indicate the presence of semi-compatible polymer blends and copolymers are not found in the SEM image of the resulting membrane^[13], indicating that the membrane prepared in this study is a homogeneous one.

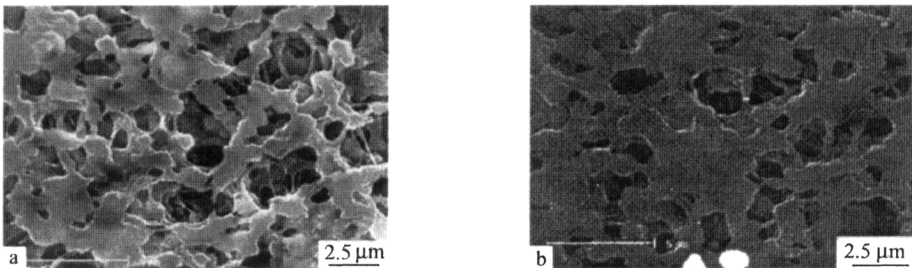


Fig. 3 SEM micrographs of PVDF membrane (a) and ion exchange membrane (b)

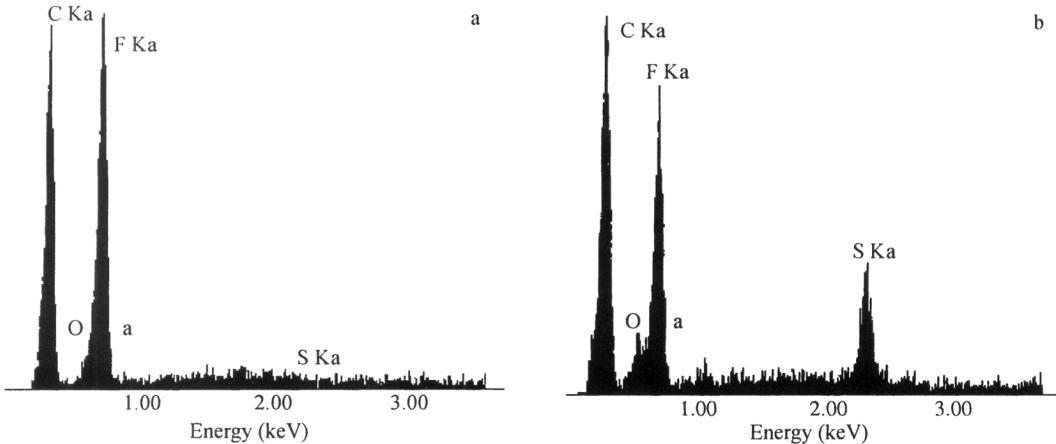


Fig. 4 EDAX spectra of PVDF membrane (a) and ion exchange membrane (b)

EDAX was carried out to identify the presence of sulfonic acid. Figure 4 shows the EDAX spectra of the untreated and treated membranes. The content of sulfur increased after sulfonating treatment as shown in Fig. 4(b). It confirms the presence of sulfonic groups in the PVDF composite membrane. A very small amount of sulfur is also observed in PVDF (Fig. 4a), it may be attributed to the contamination of PVDF before analysis.

CONCLUSIONS

The membrane treatment method which involves crosslinking with DVB/styrene and subsequent sulfonation can be used to impart cation exchange selectivity to the stable membrane, PVDF. Water uptake, IEC and area resistance of the PVDF membrane were significantly improved after treatment. The good thermal stability of the supporting backbone, PVDF, of the ion exchange membrane, is not changed. The sulfonated poly(styrene-divinylbenzene) linkages crosslinked with PVDF membrane are thermally stable up to approximately 180°C. SEM studies suggest that sulfonation products are formed in the pores of the membrane and partially block the small pores. The new ion exchange membrane is not only cheap but also it has good electrochemical properties and excellent resistance towards degradation under thermal and chemical attack.

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