

Pre-irradiation grafting of styrene and maleic anhydride onto PVDF membrane and subsequent sulfonation for application in vanadium redox batteries

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Abstract

A poly(vinylidene difluoride) (PVDF) membrane was grafted with styrene (St) and maleic anhydride (MAN) using an electron-beam-induced pre-irradiation grafting technique. The grafted membrane (PVDF-*g*-PS-*co*-PMAN) was then sulfonated and hydrolyzed to give an ion exchange membrane (denoted as PVDF-*g*-PSSA-*co*-PMAc) for vanadium redox flow batteries (VRB) use. Micro-FTIR analysis indicated that PVDF was successfully grafted and sulfonated at the above condition, and the membrane with a high grafting yield (GY) can be easily prepared in a St/MAN binary system at low dose due to a synergistic effect. The water uptake and ion exchange capacity (IEC) of the PVDF-*g*-PSSA-*co*-PMAc membrane increased with GY, so too did the conductivity. At a GY of 33.6%, the resulting PVDF-*g*-PSSA-*co*-PMAc membrane showed a much higher IEC and conductivity than a conventional Nafion117 membrane, and a much lower permeability of vanadium ions: ca. 1/11 to 1/16 of that through Nafion117. Open circuit voltage measurements showed that the VRB assembled with the PVDF-*g*-PSSA-*co*-PMAc membrane maintained values above 1.3 V after a period of 33 h, which was much longer than that with the Nafion117 membrane. It is expected that this work provides a new approach for the fabrication of ion exchange membranes for VRB.

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1. Introduction

Vanadium redox flow batteries (VRB) employ V(II)/V(III) and V(IV)/V(V) redox couples in the negative and positive half-cells separated by the ion exchange membrane [1]. The function of the membrane is to prevent the mixing of the negative and positive electrolytes, whilst allowing transport of ions to com-

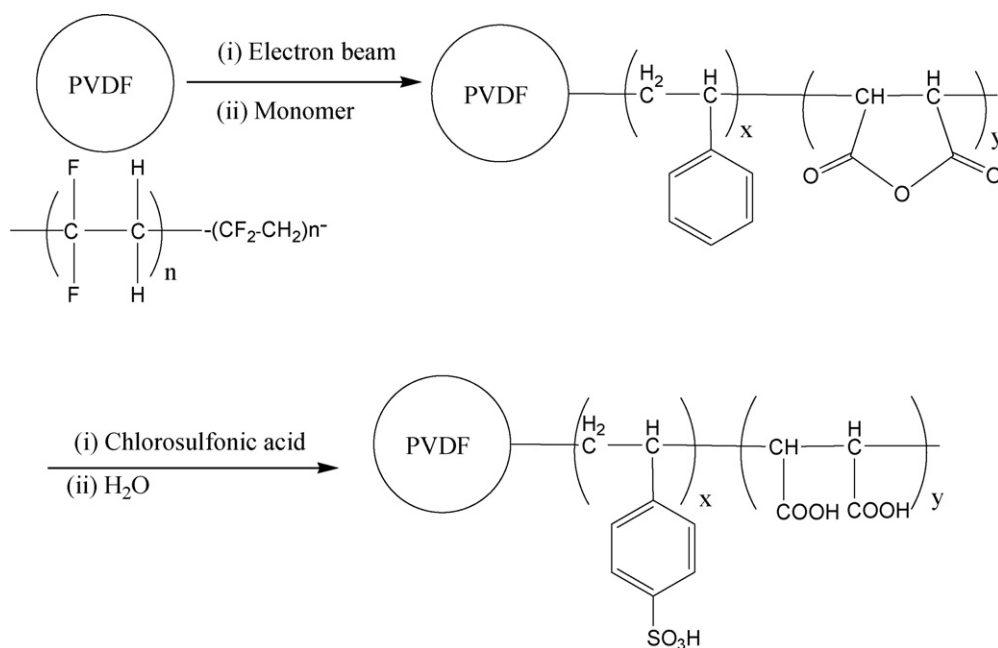
plete the circuit. The ideal membrane should have the following properties: low permeation rates of vanadium ions to minimize self-discharging; high conductivity; good chemical stability; low manufacturing cost to reduce the overall cost of the battery. However, the commercial membranes are too expensive to use and their performances in VRB are unsatisfactory. For example, the Selemon CMV membrane (Asahi Glass Co., Japan) exhibits a very poor chemical stability [2], while the Nafion membrane (Du Pont, USA) suffers from a high permeability of vanadium ions [3].

An effective method to decrease the overall cost of the ion exchange membrane is to introduce ion exchange groups into low-cost membrane. Moreover, by changing the functional monomer, the corresponding ion exchange membrane can be employed in different applications. Consequently, studies on the preparation of ion exchange membranes using grafting tech-

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Scheme 1. Synthesis route for the preparation of PVDF-*g*-PSSA-*co*-PMAc ion exchange membranes.

niques have attracted considerable attention in the past few years. For example, the Daramic membrane [4,5], low-density polyethylene (LDPE) [6], etc., have been used as matrix membranes to prepare the ion exchange membranes for VRB. The obtained membranes showed better performances after grafting. However, these membranes still could not satisfy all the requirements of the battery due to the lack of stability [5] or the serious crossover of vanadium ions [4] through the membrane. Accordingly, the new type ion exchange membranes with better performances in VRB should be further investigated.

Poly(vinylidene difluoride) (PVDF) is a kind of membrane with suitable mechanical properties, i.e. a lower tensile modulus than both polyester (PET) and poly(tetrafluoroethylene) (PTFE). The radiation-induced grafting of styrene (St) onto PVDF and subsequent sulfonation has been widely used to prepare ion exchange membranes [7–10]. In order to obtain an appropriate grafting yield (GY) for further preparing the ion exchange membranes, a high concentration of St and high dose were usually used. However, although the radiation stability of PVDF is better than that of PTFE, it has also been reported that the mechanical properties of PVDF membranes would be weakened under irradiation: the energy to break the membrane was regularly decreased to a low value due to the chain scissions under irradiation [11]. Hence, the radiation damage should also be considered in the radiation grafting of PVDF membranes. Maleic anhydride (MAN) is difficult to form homopolymers under irradiation. However, a synergistic effect in the copolymerization or grafting copolymerization of St and MAN has been proved by both experimental work and a detailed analysis of the copolymerization mechanism [12,13]. Moreover, in our previous work [14], a kind of ion exchange membrane has been prepared by the simultaneous radiation grafting of St and MAN onto PTFE membranes, and it was found that a much higher GY could be obtained at the same dose after MAN was incorporated.

In this work, St and MAN were grafted onto PVDF membranes under electron-beam irradiation, and then the grafted membranes were sulfonated with chlorosulfonic acid. It was found that the addition of MAN could effectively reduce the required dose; moreover, the properties of the prepared ion exchange membrane (PVDF-*g*-PSSA-*co*-PMAc) were investigated and compared with that of Nafion117 in order to develop an appropriate method to prepare ion exchange membranes for VRB.

2. Experimental details

2.1. Materials

A PVDF membrane with thickness of 50 μm was purchased from Kureha Company (JP) and used as the grafting matrix. St (Acros) with purity of more than 99% was used without further purification. MAN and acetone (analytical reagent) was supplied by Beijing Chemical Regents Company. Chlorosulfonic acid was purchased from Beijing Yili Fine Chemical Co. Ltd. VOSO_4 (analytical reagent) was supplied by Shanghai LvYuan Fine Chemical Plant. The Nafion117 membrane (Du Pont) was immersed into deionized water for 24 h prior to use.

2.2. Pre-irradiation grafting of St and MAN onto PVDF membrane

The preparation route of the PVDF-*g*-PSSA-*co*-PMAc membrane is shown in Scheme 1. The PVDF membrane was pre-irradiated under electron-beam irradiation (1 MeV) at a dose rate of 5 kGy pass^{-1} . Irradiation was carried out under a N_2 atmosphere at -20°C using dry ice for cooling. The irradiated membrane was then immersed immediately into a 1.5 mol L^{-1} St/0.5 mol L^{-1} MAN solution and heated at 50°C for 18 h to

prepare the PVDF-*g*-PS-*co*-PMAm membrane, while the PVDF-*g*-PS membrane was also prepared in a 2 mol L⁻¹ St solution at the same condition for comparison. Acetone was used as the solvent for the above grafting system. The grafted membrane was taken out after the reaction and washed with acetone to remove the residual monomers and non-grafted polymers. GY was calculated according to the following equation:

$$\text{GY} (\%) = 100 \times \frac{W_g - W_0}{W_0} \quad (1)$$

where W_g and W_0 are the weights of the membrane after and before grafting, respectively.

The St moiety grafted onto the PVDF membrane was sulfonated with chlorosulfonic acid in chloroform solution (5%, v/v) for about 16 h to afford styrene sulfonic acid (SSA) according to the work of Chen et al. [15]. The sulfonated membrane was washed several times with deionized water to remove the residue; in the meantime, the MAn grafted on the PVDF membrane was hydrolyzed into maleic acid (MAc). The final PVDF-*g*-PSSA-*co*-PMAc ion exchange membrane was obtained by further drying in vacuum.

2.3. Characterization of PVDF-*g*-PSSA-*co*-PMAc membrane

2.3.1. FTIR analyses of the membrane

Micro-FTIR analysis was performed on a Nicolet (Magna-IR 750) spectrometer. The spectra were measured in absorbance mode in the wave number range of 4000–600 cm⁻¹.

2.3.2. Basic properties of PVDF-*g*-PSSA-*co*-PMAc membrane

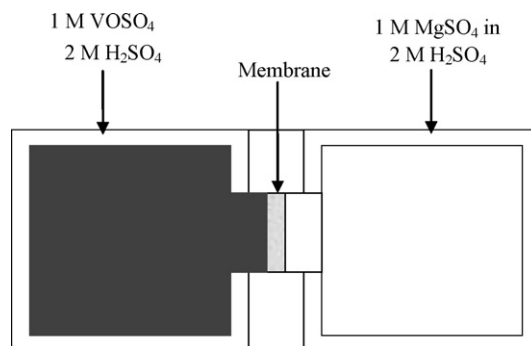
Ion exchange capacity (IEC) was determined by titration. Dried PVDF-*g*-PSSA-*co*-PMAc membranes with certain weight were immersed into 0.05 mol L⁻¹ NaOH solution overnight and stirred occasionally. The solution was then back-titrated with 0.05 mol L⁻¹ HCl solution to afford a neutral solution. IEC (mmol g⁻¹) was calculated according to the following equation:

$$\text{IEC} = \frac{M_{0,\text{NaOH}} - M_{\text{E},\text{NaOH}}}{W} \quad (2)$$

where $M_{0,\text{NaOH}}$ and $M_{\text{E},\text{NaOH}}$ are the moles of NaOH before and after the equilibration, respectively; W is the weight of the dry membrane.

To determine the content of SSA and MAc in PVDF-*g*-PSSA-*co*-PMAc, the membrane of certain weight was immersed into 1 M KCl solution and equilibrated for 24 h. Then the solution was titrated with 0.05 M NaOH solution. As the ionization of MAc will be suppressed, this part of the IEC (IEC_{SSA}) can be attributed to SSA. IEC_{SSA} was calculated according to the amount of NaOH and the weight of the membrane. Furthermore, the amount of St and MAn in the PVDF-*g*-PS-*co*-PMAm membrane can also be calculated according to the content of SSA and MAc in the PVDF-*g*-PSSA-*co*-PMAc membrane [16].

To evaluate the water uptake of PVDF-*g*-PSSA-*co*-PMAc membrane, the membrane with certain weight was immersed into deionized water. After equilibrating for 24 h, the mem-



Scheme 2. Illustration of the equipment for vanadium permeability evaluation.

brane was taken out and the water adhering to the surface was quickly wiped using absorbent paper, and the membrane was weighed again. The water uptake was determined according to the following equation:

$$\text{water uptake} (\%) = 100 \times \frac{W_w - W_d}{W_d} \quad (3)$$

where W_w and W_d are the weights of the PVDF-*g*-PSSA-*co*-PMAc membrane in the wet and dry state, respectively.

Moreover, to evaluate the water uptake of the PVDF-*g*-PSSA-*co*-PMAc membrane in the electrolyte solution, the membrane was immersed into a 1 mol L⁻¹ VOSO₄/2 mol L⁻¹ H₂SO₄ solution. The water uptake in the vanadium solution was also calculated according to Eq. (3).

The proton conductivity of the PVDF-*g*-PSSA-*co*-PMAc membrane was obtained by impedance spectroscopy measurement using an electrochemical work station (EG & G instrument) with a AC perturbation of 10 mV. The membranes were hydrated for 24 h before determination and clamped between two Pt electrodes for recording of the impedance spectroscopy. The proton conductivity (σ) was calculated as

$$\sigma = \frac{L}{RS} \quad (4)$$

where R is the real impedance taken at zero imaginary impedance in the impedance spectroscopy, L and S are the thickness and area of the membrane between the electrodes, respectively.

2.3.3. Permeability of vanadium ions through PVDF-*g*-PSSA-*co*-PMAc membrane

According to the method described in the work of Luo et al. [17], the permeability of vanadium ions through the PVDF-*g*-PSSA-*co*-PMAc membrane was investigated using the equipment as shown in Scheme 2. A 1 mol L⁻¹ V(IV) solution was prepared by dissolving VOSO₄ in 2 mol L⁻¹ H₂SO₄ solution, while V(V) and V(III) solutions were obtained by electrochemical oxidation and reduction of the V(IV) solution. The V(II) solution was not taken for analysis, because the V(II) was unstable. As shown in Scheme 2, the left reservoir was filled with vanadium solution and the right one was filled with a 1 mol L⁻¹ MgSO₄ in 2 mol L⁻¹ H₂SO₄ solution. MgSO₄ was used to balance the ionic strength and reduce the osmotic pressure. The area of the membrane exposed to the solution was 1.77 cm² and the volume of solutions in both sides was 25 mL. The MgSO₄ solu-

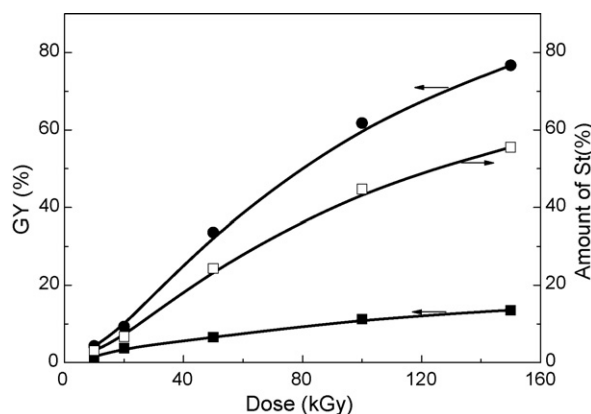


Fig. 1. Effect of the absorbed dose on the GY of PVDF-g-PS (■), PVDF-g-PS-co-PMAN (●) and the amount of St in the PVDF-g-PS-co-PMAN (□) membranes, respectively.

tion was taken for inductively coupled plasma atomic emission spectrometry (ICP-AES) (Leeman, Profile) analysis at a regular time and the concentration of vanadium ions in the solution was determined. Before use, all the membranes were activated by immersing into deionized water for about 24 h. The permeability of vanadium ions through the Nafion 117 membrane was also tested using the same method for comparison.

2.3.4. Open circuit voltage of VRB assembled with PVDF-g-PSSA-co-PMAC membrane

The VRB used was fabricated by sandwiching the membrane between two pieces of graphite carbon electrodes and using 1.5 mol L^{-1} V(II)/V(III) and V(IV)/V(V) in 3 mol L^{-1} H_2SO_4 solution as the electrolytes in the positive and negative half-cells, respectively. The membrane area was 30 cm^2 and the volume of the electrolytes solution in each half-cell was 40 mL. The battery was first charged to 1.7 V at a current of 600 mA, and then the open circuit voltage was measured at room temperature.

3. Results and discussions

3.1. Preparation of PVDF-g-PSSA-co-PMAC membrane

St and MAn were grafted onto PVDF membranes using an electron-beam-induced pre-irradiation grafting technique. The relationship between the GY and absorbed dose is shown in Fig. 1. It can be seen that for both PVDF-g-PS and PVDF-g-PS-co-PMAN membranes, the GY increases with the dose, while the GY of PVDF-g-PS-co-PMAN membrane is much higher than that of PVDF-g-PS membrane at the same dose. Świtłała-Żeliazkowska [18] investigated the radical copolymerization of St and MAn, and calculated the reactivity ratio using the Fineman–Ross method to give $r_1 = 0.032$, $r_2 = 0.60$, which indicated that the St and MAn tended to form alternative copolymers. Li et al. [13] grafted St and MAn onto polypropylene (PP) and found that St could improve the grafting reactivity of MAn, because St was reacted with MAn to form the St–MAn copolymer before grafting onto PP. The grafting of the St–MAn copolymer onto PP greatly enhanced the GY of

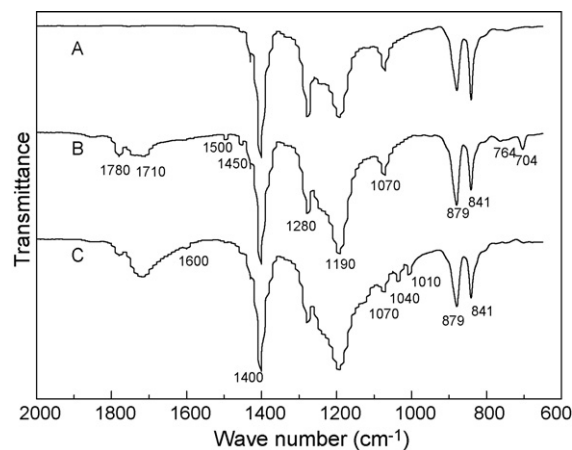


Fig. 2. FTIR spectra of the membranes: (A) original PVDF membrane; (B) PVDF-g-PS-co-PMAN membrane; (C) PVDF-g-PSSA-co-PMAC membrane. The GY of the membrane is 33.6%.

MAn. In our previous work [12], St and MAn were grafted onto a PTFE membrane under γ -ray irradiation. It was also found that there is a synergistic effect and the highest GY could be obtained at a mole ratio of St/MAn = 3:1. Accordingly, it can be seen from Fig. 1 that the membrane with high GY can be easily prepared in the St/MAN binary system at low dose.

The sulfonation and hydrolysis of St and MAn grafted on PVDF resulted in the formation of sulfonic acid groups and carboxylic groups in the PVDF membranes, respectively. Indeed, the sulfonation and hydrolysis reactions resulted in the formation of a PVDF-g-PSSA-co-PMAC ion exchange membrane. By comparing the experimental and theoretical values of the mass change of PVDF-g-PS-co-PMAN membranes after sulfonation, it can be found that the degree of sulfonation of all membranes achieved values close to ca. 100%. Therefore, the ratio of sulfonic acid groups to phenyl groups of PS on a PVDF membrane can be considered to equal unity. Consequently, all the membrane properties are discussed only in relation to the GY in the following sections.

The grafting of St and MAn onto a PVDF membrane was confirmed by FTIR spectra (Fig. 2). It can be seen that after grafted with St and MAn, additional absorption bands at 1780 cm^{-1} , 1710 cm^{-1} , 1500 cm^{-1} , 1450 cm^{-1} , 764 cm^{-1} and 704 cm^{-1} can be observed. According to the work of Gregorio et al. [19–21], the absorption bands at 1780 cm^{-1} and 1710 cm^{-1} are assigned to the vibration of the carboxyl groups of MAn; the absorption bands at 1500 cm^{-1} and 1450 cm^{-1} are due to the C=C in-plane stretch vibration of the benzene ring, while the absorption bands at 764 cm^{-1} and 704 cm^{-1} are due to the aromatic C–H deformation of the substituted benzene ring. For the PVDF-g-PSSA-co-PMAC membrane, the sulfonation of the grafted St can be confirmed by the presence of the sharp absorption bands at 1040 cm^{-1} and 1010 cm^{-1} , which can be assigned to the absorption of the $-\text{SO}_3^-$ group in the PVDF-g-PSSA-co-PMAC membrane. Moreover, it can be seen that the absorption bands at 764 cm^{-1} and 704 cm^{-1} disappear, which also indicates that the benzene ring in St has been completely sulfonated.

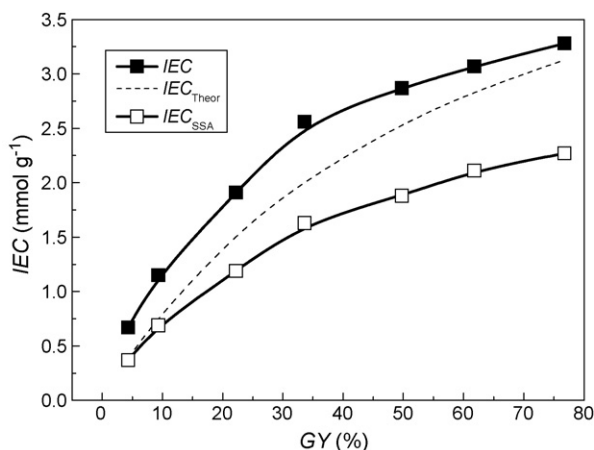


Fig. 3. Relationship between the IEC and the GY.

3.2. Properties of PVDF-*g*-PSSA-*co*-PMAc membrane

3.2.1. IEC and water uptake

IEC is an important property relating to the membrane conductivity. The effect of the GY on the IEC of the PVDF-*g*-PSSA-*co*-PMAc membrane is shown in Fig. 3. It can be seen that the IEC of the PVDF-*g*-PSSA-*co*-PMAc membrane increases with increasing GY. In order to elucidate the respective contributions of SSA and MAc to the IEC, the IEC_{SSA} has also been determined and shown in Fig. 3. It can be found that IEC_{SSA} is lower than the IEC, which indicates that the carboxylic groups in the PVDF-*g*-PSSA-*co*-PMAc membrane also contribute to the total IEC. However, the percentage of SSA in the PVDF-*g*-PSSA-*co*-PMAc membrane is higher than that of MAc. For example, at a GY of 33.6%, the mole ratio of SSA to MAc is about 3.5:1, while the IEC and IEC_{SSA} are 2.56 mmol g⁻¹ and 1.63 mmol g⁻¹, respectively. So, the SSA moieties in the PVDF-*g*-PSSA-*co*-PMAc membrane play a major role in the ion exchange ability of the membrane.

The amount of St in the PVDF-*g*-PS-*co*-PMAc membrane was calculated according to the content of SSA in the PVDF-*g*-PSSA-*co*-PMAc membrane, which is also shown in Fig. 1 for comparison. It can be found that the amount of St in the PVDF-*g*-PS-*co*-PMAc membrane is much higher than that obtained in the PVDF-*g*-PS membrane. This is because the initial concentration of St is higher than that of MAN, such that a number of the St moieties will react preferentially with the PVDF macroradicals to form stable styryl radicals, while others will copolymerize with MAN to form the St–MAN copolymer [13].

If we presume that only St has been grafted onto the PVDF membrane, then the theoretical IEC (IEC_{theor}) can be calculated according to the following equation [22], as shown in Fig. 3:

$$IEC_{\text{theor}} = 1000 \times \frac{GY}{100M_{\text{St}} + GYM_{\text{SSA}}} \quad (5)$$

where M_{St} is the molecular weight of St (104 g mol⁻¹) and M_{SSA} is the molecular weight of SSA (184 g mol⁻¹), respectively. It can be found that the determined IEC increases with increasing GY, and is higher than the IEC_{theor}. This is attributed to MAc in the PVDF-*g*-PS-*co*-PMAc membrane, which also indicates

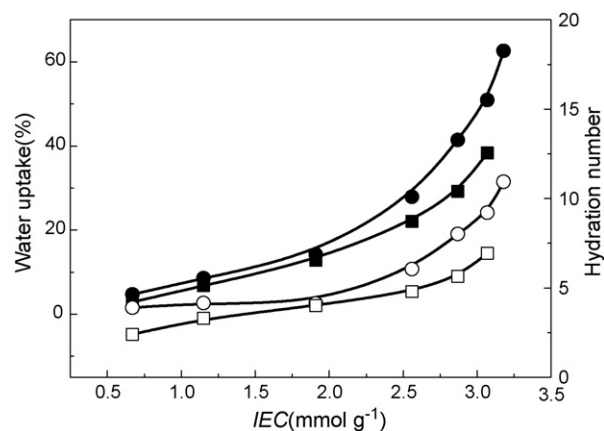


Fig. 4. Water uptake and hydration number of the PVDF-*g*-PSSA-*co*-PMAc membrane: water uptake in deionized water (●), in vanadium solution (■) and hydration number in deionized water (○), in vanadium solution (□).

that MAN has been grafted onto the PVDF membrane under irradiation.

The IEC of Nafion117 has been reported as 0.97 mmol g⁻¹. For the PVDF-*g*-PSSA-*co*-PMAc membrane, it can be seen that at a low GY of ca. 7%, the membrane shows higher IEC than Nafion117. In addition, an anion exchange membrane consisting of polysulfone and poly(phenylene sulfide sulfone) for VRB use has also been prepared by Hwang and Ohya [23]. In their work, the IEC value of the membrane is about 0.9 mmol g⁻¹, which is much lower than that of the PVDF-*g*-PSSA-*co*-PMAc membrane. Luo et al. [17] prepared a kind of PVDF-*g*-PSSA membrane for VRB use, where the IEC is about 1.2 mmol g⁻¹ at a GY of 22%. From Fig. 3, it can be seen that at a GY of ca. 10%, the PVDF-*g*-PSSA-*co*-PMAc membrane has a higher IEC than that of the PVDF-*g*-PSSA membrane.

Water uptake is another important parameter of the ion exchange membrane which is related with the conductivity and dimensional stability of the membrane. The water uptake of the PVDF-*g*-PSSA-*co*-PMAc membrane in deionized water is shown in Fig. 4. It can be seen that the water uptake of the PVDF-*g*-PSSA-*co*-PMAc membrane increases with increasing IEC. The hydration number (n) can be calculated according to the following equation and the result is also shown in Fig. 4:

$$n = \frac{\text{water uptake}}{1.8 \text{ IEC}} \quad (6)$$

As shown in Fig. 4, the hydration number of the PVDF-*g*-PSSA-*co*-PMAc membrane also increases with increasing IEC. The water uptake and hydration number of the Nafion117 membrane was reported to be about 26% and 17, respectively [24,25], which are higher than those of the PVDF-*g*-PSSA-*co*-PMAc membrane with an IEC of 0.97 mmol g⁻¹ (about 7.2% and 4, respectively).

The water uptake and hydration number of the PVDF-*g*-PSSA-*co*-PMAc membrane in vanadium solution are also shown in Fig. 4. It can be seen that both the water uptake and hydration number are lower than that obtained in deionized water. For the PVDF-*g*-PSSA-*co*-PMAc membrane with an IEC of 0.97 mmol g⁻¹, the water uptake and hydration number are 5.5%

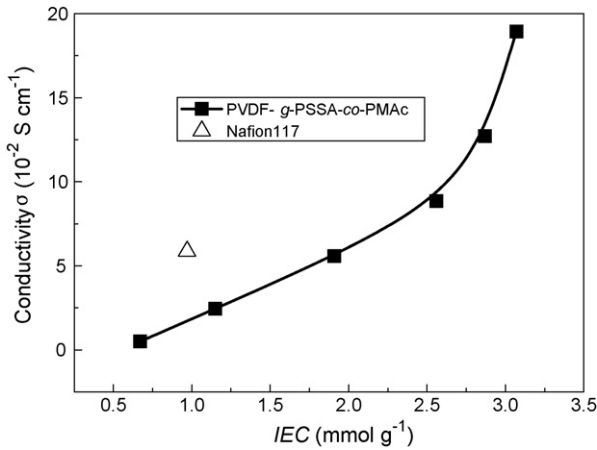


Fig. 5. Effect of the IEC on the conductivity of the PVDF-g-PSSA-co-PMAC membrane.

and 3, respectively. Because the high acidity and salinity of the vanadium solution decrease the ionization degree of the sulfonic acid groups and carboxylic groups of the PVDF-g-PSSA-co-PMAC membrane, and then inhibit the water uptake of the membrane [26,27]. The water uptake and hydration number of the Nafion117 membrane in vanadium solution have also been determined, and are found to be about 20.6% and 12.6, respectively, which are also lower than that in deionized water.

3.2.2. Conductivity of PVDF-g-PSSA-co-PMAC membrane

The effect of the IEC on the conductivity of the PVDF-g-PSSA-co-PMAC membrane is shown in Fig. 5. It can be seen that the conductivity of the membrane increases rapidly with increasing IEC. Comparing with that of Nafion117, it can be seen that the conductivity of the PVDF-g-PSSA-co-PMAC membrane is lower at the same IEC. However, when the IEC value is higher than 1.95 mmol g^{-1} , the conductivity of the PVDF-g-PSSA-co-PMAC membrane is higher than that of the Nafion117 membrane.

3.2.3. Permeability of vanadium ions through PVDF-g-PSSA-co-PMAC membrane

The crossover of vanadium ions through the ion exchange membrane is disadvantageous to VRB as it will cause serious self-discharging and result in low efficiency. Indeed, it has been found that many kinds of ion exchange membranes suffer from this problem [2,4,5,28], which has limited their applications in VRB. Consequently, establishing methods to inhibit the crossover of vanadium ions has been a problem that should be considered by researchers in membrane preparation. The permeability of vanadium ions with different valencies is shown in Fig. 6. According to the work of Luo et al., the vanadium concentration in MgSO_4 solution was given as

$$V \frac{dc_t}{dt} = \frac{SP(c_0 - c_t)}{L} \quad (7)$$

where V is the volume of the solution in both sides of the membrane; S is the area of the membrane exposed to the solution; P is the permeability parameter of vanadium ions; L is the thickness

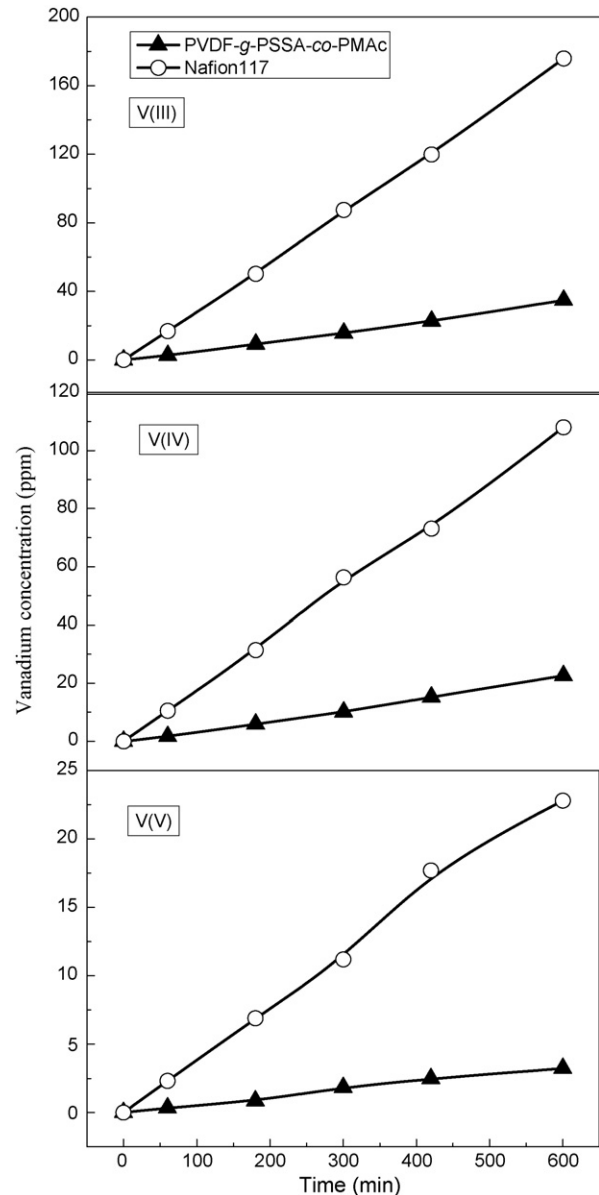


Fig. 6. Permeability of the vanadium ions through the PVDF-g-PSSA-co-PMAC membrane. The GY of the membrane is 33.6%.

of the membrane. c_0 is the initial concentration of the vanadium solution; c_t is the vanadium concentration in the MgSO_4 solution. An assumption is made that P is independent of concentration. According to Eq. (7), the relationship between c_t and time (t) can be given as the following equation:

$$-\ln \left(1 - \frac{c_t}{c_0} \right) = \frac{PSt}{LV} \quad (8)$$

Following Eq. (8) and Fig. 6, the permeability (P) through the PVDF-g-PSSA-co-PMAC membrane and Nafion117 membrane was calculated and listed in Table 1. For the vanadium ions with different valencies, the P decreases in the order: $V(\text{III}) > V(\text{IV}) > V(\text{V})$. Comparing with that through the Nafion117 membrane, the P of the vanadium ions through the PVDF-g-PSSA-co-PMAC membrane is about 1/11 to 1/16 of that through the Nafion117 membrane, which is favorable to

Table 1
Permeability (P) of different vanadium ions through the Nafion117 and PVDF- g -PSSA- co -PMAc membranes

Membrane	Thickness (μm)	Permeability, P ($\times 10^{-7} \text{ cm}^2 \text{ min}^{-1}$)		
		V(III)	V(IV)	V(V)
Nafion117	165	13.4	8.20	1.78
PVDF- g -PSSA- co -PMAc ^a	70	1.12	0.73	0.11

^a The GY of the membrane: 33.6%.

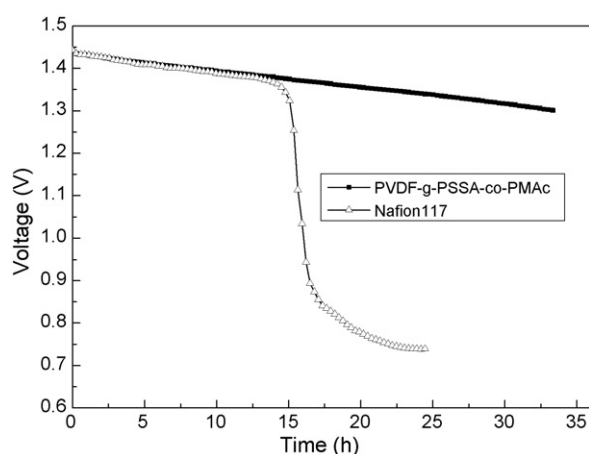


Fig. 7. Open circuit voltage of the VRB assembled with the PVDF- g -PSSA- co -PMAc membrane. The GY of the membrane is 33.6%.

reduce the crossover of the vanadium ions in VRB. Luo et al. reported that the PVDF- g -PSSA membrane also showed a low permeability. Indeed, a low permeability of the vanadium ions will bring about a low degree of self-discharging of the battery, it can be forecasted that the VRB assembling with the PVDF- g -PSSA- co -PMAc membrane will have higher columbic efficiency than that using the Nafion117 membrane.

3.2.4. Open circuit voltage of the VRB assembled with PVDF- g -PSSA- co -PMAc membrane

The relationship between open circuit voltage and time is shown in Fig. 7. It can be seen that the open circuit voltage of the VRB with the Nafion117 membrane decreased rapidly after about 14 h. In contrast, the VRB assembled with the PVDF- g -PSSA- co -PMAc membrane performs much better: the voltage is maintained above 1.3 V after a period of 33 h. This means that the self-discharging of the VRB with Nafion117 is much faster than that of the VRB with the PVDF- g -PSSA- co -PMAc membrane. The result corresponds to the permeability test: a much lower permeability of vanadium ions occurs through the PVDF- g -PSSA- co -PMAc membrane than through the Nafion117 membrane.

4. Conclusion

A PVDF- g -PSSA- co -PMAc ion exchange membrane for application in VRB has been prepared successfully by pre-irradiation grafting and subsequent sulfonation and hydrolysis, as confirmed by FTIR analysis. It was found that a much higher

GY was obtained after MAN was incorporated into the grafting system. At a GY of 33.6%, the PVDF- g -PSSA- co -PMAc membrane showed a higher IEC and conductivity, and a much lower permeability of the vanadium ions than the Nafion117 membrane. In addition, the open circuit voltage of the VRB assembled with the PVDF- g -PSSA- co -PMAc membrane was maintained above 1.3 V after a period of 33 h, which was much longer than that with the Nafion117 membrane. This new type of membrane may be a suitable candidate for use as the ion exchange membrane in VRB.

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