

Performance of membrane electrode assemblies based on proton exchange membranes prepared by pre-irradiation induced grafting

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Abstract

Proton exchange membranes (PEMs) were prepared by pre-irradiation induced grafting of styrene (S) or styrene/divinylbenzene (S/DVB) into the radiation-crosslinked polytetrafluoroethylene (RX-PTFE) films and then sulfonated. The thicknesses of the obtained PEMs were lower than 20 μm and the ion exchange capacity (IEC) values were around 2 meq g^{-1} . The surfaces of the PEMs and carbon electrodes were coated with Nafion[®] dispersion, and then membrane electrode assemblies (MEAs) were prepared by hot-pressing them together. A MEA based on a Nafion[®] 112 membrane was also prepared under same procedure for comparison. The performances of the MEAs in a single cell were tested under different cell temperatures and humidifications. Electrochemical impedance spectra (EIS) were measured with ac frequencies which ranged from 100 kHz to 1 Hz at a dc density of 0.5 A cm^{-2} . The obtained impedance curves in Nyquist representation were semicircular.

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Keywords: Fuel cell; Proton exchange membrane; Membrane electrode assemble; Pre-irradiation induced grafting; Styrene/divinylbenzene

1. Introduction

For applications in polymer electrolyte fuel cell (PEFC), radiation induced grafting of S and co-monomers in fluorinated polymer films, such as PTFE, FEP, PFA, ETFE, PVDF, etc., followed by sulfonation is designed as an alternative route to the preparation of relatively low cost PEMs. There are many reviews summarizing the results of this method [1–3]. Among previous work, Scherer's research group reported some fuel cell performance and durability of the PEMs prepared from S/DVB grafted and sulfonated FEP films [4–6]. Recently, they reported [6] a durability experiment using synthesized PEM at 80–85 °C for over 7900 h, and the result was quite encouraging. This suggested that the radiation induced grafting method is a competitive way to synthesize low cost long lifetime PEMs.

RX-PTFE is a newly developed fluorinated polymer which has a network structure, prepared by γ -ray or electron beam

irradiation above its melting temperature under an oxygen-free atmosphere [7–10]. RX-PTFE has shown remarkable improvements in several mechanical properties, radiation resistance and so on, compared with non-crosslinked PTFE [11–13].

Our research group is developing new PEMs based on RX-PTFE films with different crosslinking density by pre-irradiation induced graft polymerization of S and co-monomers and successive sulfonation [14–21]. In previous research we found that using the crosslinker co-monomer, DVB, in the grafting system, resulted in some difference in the properties of the PEMs: (i) the formation of the network structure in the poly(styrene–sulfonic acid) (PS–SA) graft chains effectively suppressed the water uptake of the PEMs due to the restrained PS–SA chains mobility [20], (ii) as observed by XPS analysis, the surfaces of the PEMs grafted by S were C-atom rich, while the surfaces of the PEMs grafted by S together with DVB were F-atom rich [17], (iii) the chemical resistance of the PEMs grafted by S/DVB to the oxidative radicals are much higher than those grafted by S. Also, the increasing in the crosslinking density of the RX-PTFE films has a positive effect on improving the chemical resistance of the PEMs [18,20]. Therefore, it could be concluded that the synthesized PEMs benefit from introducing DVB in the grafting system as revealed by *ex situ* characterizations.

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However, the effect of the network structure formation in the PS–SA graft chains on the fuel cell *in situ* performance of the PEMs is not well known. Therefore, we prepared MEAs based on synthesized PEMs of a different network structure, that is, different crosslinking densities in both RX-PTFE main chains and PS–SA graft chains. Here we report the single cell performance and the EIS of the MEAs under different temperature and humidification conditions. The MEA based on a Nafion® 112 membrane was prepared and tested under the same conditions for comparison.

2. Experiments

2.1. Preparation of the PEMs

The RX-PTFE films used in this work were crosslinked by electron beam irradiation to doses of 150 and 450 kGy, abbreviated as RX150 and RX450 films.

The RX150 and RX450 films were grafted by S without or with 10% DVB (55% *m*-, *p*-divinylbenzene in ethylvinylbenzene) at 70 °C in the liquid phase under the pre-irradiation induced grafting method.

The degrees of grafting (DOGs) were determined as the weight increase of the samples according to the following equation:

$$\text{degree of grafting (DOG) (\%)} = \frac{W_g - W_o}{W_o} \times 100\% \quad (1)$$

where W_g and W_o are the weights of the samples after and before grafting, respectively.

The grafted films were sulfonated by chlorosulfonic acid in carbon tetrachloride (1:9, v/v) at room temperature for 24 h and the PEMs were obtained. The IEC values of the PEMs were determined by titration.

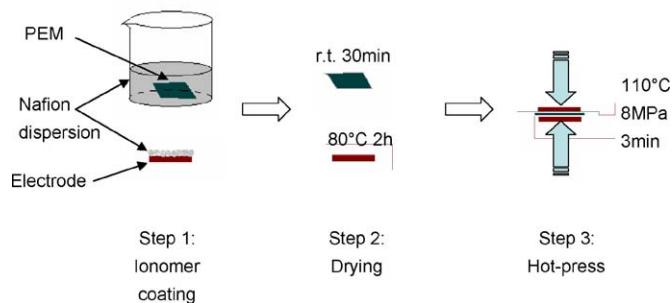
The degree of swelling was tested at room temperature and calculated according to the following equation:

$$\text{degree of swelling (DOS) (\%)} = \frac{W_w - W_d}{W_d} \times 100\% \quad (2)$$

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

Details of the preparation and characterization of the PEMs were reported in our previous papers [18,20].

The Nafion® 112 membrane was purchased from DuPont de Nemours Ltd. (USA) and was used as a reference. The labels and properties of the PEMs used in this work are listed in Table 1.



Scheme 1. Stand procedure for the preparation of the MEAs.

2.2. MEA preparation and fuel cell running

Carbon electrodes with 1 mg cm^{-2} Pt (20 wt.% Pt/VXC72) loaded were purchased from ElectroChem Inc. (USA). Nafion® (5%) dispersion type of DE-521 was purchased from DuPont Fluoroproducts (USA). The electrodes were cut into the desired size and coated with the ionomer dispersion and then dried at 80 °C for 2 h. The typical amount of ionomer dispersion coating was about 0.8 mg cm^{-2} . PEMs were also coated with the ionomer dispersion and dried at room temperature for 30 min. The MEAs were then prepared by hot pressing at 110 °C under 8 MPa for 3 min. The standard procedure for MEA preparation is shown in Scheme 1.

Fuel cell tests were performed on a JARI standard fuel cell from Takahashi Semitsu Kougyo Co. Ltd. (Japan). The hydrogen and oxygen gases were supplied at 0.2 MPa and the flux were fixed at 50 cc min^{-1} . The hydrogen gas was humidified by passing it through a water tank with set temperature while the oxygen gas was dry. The effective areas of the MEAs were 1 cm^2 .

The fuel cell was controlled by a HZ-3000 Electrochemical analysis system, Hokuto Denko Co. (Japan), which consists of a 50 V/10 A power unit, an automatic polarization system together with a NF5080 Frequency Response Analyzer, from NF Electronic Instruments Co. (Japan). Under different fuel cell test conditions, the MEAs were firstly activated by running under different current density continuously until the cell voltages were constant. Thus, the polarization curves were collected. The OCV values of the MEAs under different test conditions were taken at the beginning of the polarization curve measurement. The EIS was measured using the four-electrode frequency response analyzer method, and was taken at a dc current density of 0.5 A cm^{-2} with an ac frequency ranging from 100 kHz to 1 Hz.

Table 1
The PEMs used in the fuel cell performance test

Label	Basic film	Monomer composition	DOG (%)	IEC (meq g ⁻¹)	Degree of swelling (%)	Wet thickness (μm)
Nafion	Nafion® 112	–	–	1.0	21	60 ± 1
RX150-S	RX-PTFE, 150 kGy	S	26	1.7	35	17 ± 1
RX450-S	RX-PTFE, 450 kGy	S	37	2.2	48	18 ± 1
RX150-D	RX-PTFE, 150 kGy	90% S, 10% DVB	38	2.2	30	18 ± 1
RX450-D	RX-PTFE, 450 kGy	90% S, 10% DVB	36	2.1	24	17 ± 1

Table 2
Experimental conditions for the fuel cell test

Parameters	Condition 1 (25) ^a	Condition 2 (60) ^a	Condition 3 (80) ^a	Condition 4 (80) ^a
Anode				
H ₂ gas flux (cc min ⁻¹)	50			
Humidification temperature (°C)	25			60
Cathode				
O ₂ gas flux (cc min ⁻¹)	50			
Humidification temperature (°C)	Supplied as dry gas			

^a Cell temperature (°C).

3. Results and discussion

3.1. Cell temperature and humidification conditions

In the present work, the IEC values of the synthesized PEMs were around 2 meq g⁻¹, and the thicknesses of the membranes were lower than 20 μm, which means the synthesized PEMs were highly hydrophilic. The high IEC values and low thicknesses were believed to benefit the using of PEMs under relative low humidification conditions. Working at a relative high temperature and low humidification can help to simplify the humidification system for fuel cell stacks and reduce the energy used to humidify the reaction gases. Thus, in this work, we tested the *in situ* performance of our synthesized PEMs under relatively low humidity conditions.

The detailed experimental conditions of cell temperature and humidification in the fuel cell test are listed in Table 2. From conditions 1 to 3, the cell temperature was increased from 25 to 80 °C but the humidification temperature of the hydrogen gas was fixed at 25 °C. From conditions 3 to 4, the cell temperature was fixed at 80 °C but the humidification temperature of the hydrogen gas was raised to 60 °C.

3.2. Performance of the MEAs

Fig. 1 shows the polarization curves of the MEAs under condition 1, where the cell temperature was 25 °C. The performance of the MEAs based on the synthesized membranes is lower than

Table 3

The dependence of the performance at 0.5 A cm⁻² on the experiment conditions

Label	Voltage @ 0.5 A cm ⁻² (V)			
	Condition 1	Condition 2	Condition 3	Condition 4
Nafion	0.60	0.64	0.58	0.66
RX150-S	0.52	0.57	0.56	0.60
RX450-S	0.53	0.55	0.57	0.62
RX150-D	0.53	0.58	0.58	0.64
RX450-D	0.55	0.60	0.58	0.65

that of the MEA based on the Nafion membrane, although the synthesized PEMs have much higher IEC values. But when the current density exceeded 1.25 A cm⁻², the MEAs based on the PEMs grafted by S/DVB showed a better performance than that of the MEA based on the Nafion membrane which was confused by mass transport limitations [22].

Since practically the MEAs are supposed to be operated in the voltage range from 0.7 to 0.5 V, the performance in the corresponding current density area is important to the MEAs, and usually ranging from 0.1 to 0.5 A cm⁻². Therefore, the performance of the MEAs can be characterized by voltage at the current density of 0.5 A cm⁻², which is listed in Table 3.

From the table, it can be found that when working under condition 1, the voltage of the MEAs based on the synthesized membranes ranged from 0.52 to 0.55 V, which are inferior to that of the MEA based on the Nafion membrane.

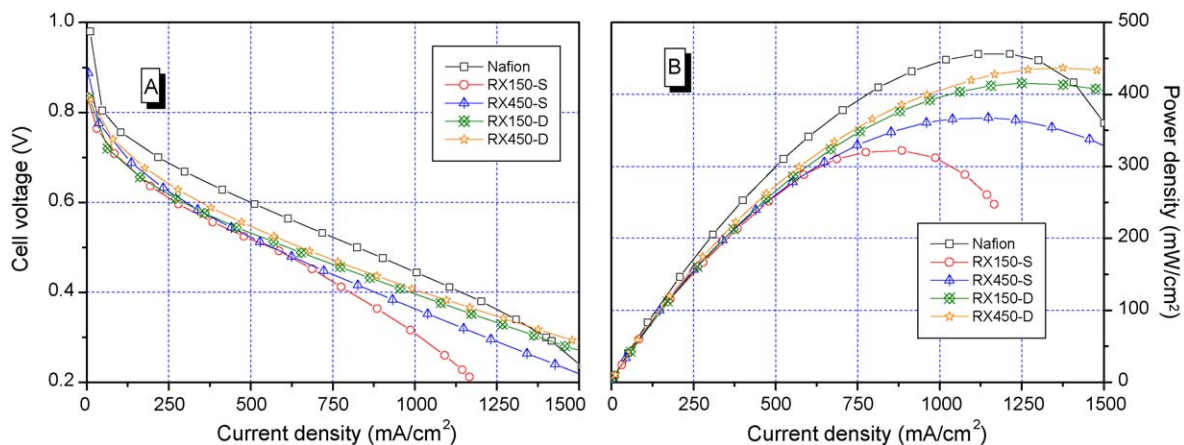


Fig. 1. The polarization curves of the MEAs at condition 1: the cell temperature was 25 °C and H₂ gas was humidified at 25 °C. (A) The cell voltage vs. the current density. (B) The power density vs. the current density.

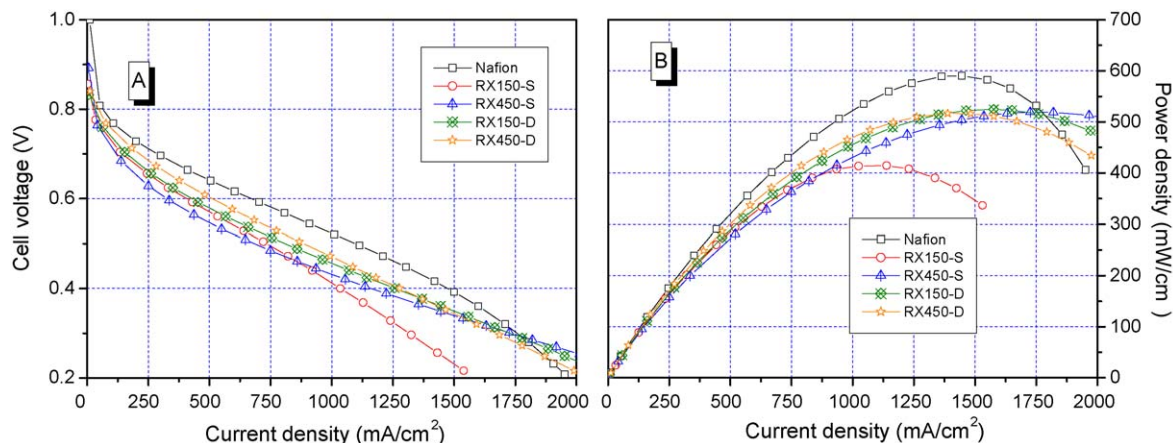


Fig. 2. The polarization curves of the MEAs at condition 2: the cell temperature was 60 °C. H₂ gas was humidified at 25 °C. (A) The cell voltage vs. the current density. (B) The power density vs. the current density.

Fig. 2 shows the polarization curves of the MEAs under condition 2, when the cell temperature was 60 °C. As compared to those curves at 25 °C, the performance of the MEAs increased with the humidification temperature unchanged. Similar to those results under condition 1, the MEA base of the Nafion membrane had the best performance until the high current density range. The voltage at the current density of 0.5 A cm⁻² increased about 0.03–0.05 V for all the MEAs as compared with the corresponding values under condition 1.

The polarization curves of the MEAs under condition 3, where the cell temperature was 80 °C and the hydrogen gas was humidified at 25 °C, are presented in Fig. 3.

Due to the enhanced water evaporation at 80 °C, the performance of the MEA based on the Nafion membrane was worse compared with condition 2 and the voltage at a current density of 0.5 A cm⁻² decreased about 10%.

The performance of the MEAs based on the synthesized PEMs under condition 3 was similar compared to condition 2, where the voltages at the current density of 0.5 A cm⁻². The higher IEC values of the membranes, which mean a higher hydrophilicity, helped to delay the drying of the PEMs.

Also, the lower thickness facilitated the feedback of the water produced at the cathode side to the anode side. The above two reasons describe the superior performance of the MEAs based on the synthesized membranes at low humidification.

Fig. 4 shows the polarization curves of the MEAs under condition 4, where the cell temperature was 80 °C and the hydrogen gas was humidified at 60 °C. Because the humidification was raised, the performance of all the MEAs obviously improved that the voltages at a current density of 0.5 A cm⁻² under condition 4 increased by about 10% compared with those values under condition 3.

The performances of the MEAs based on the membranes grafted with S were inferior to that of the MEA of Nafion, while the performance of the MEAs based on the membranes grafted with S/DVB were close to that of the MEA based on Nafion. Especially the MEA based on the RX450-D membrane, which showed the superior performance than that of the MEA based on the Nafion membrane when the current density exceeded 0.75 A cm⁻², and the maximum power density of 0.79 W cm⁻² was obtained.

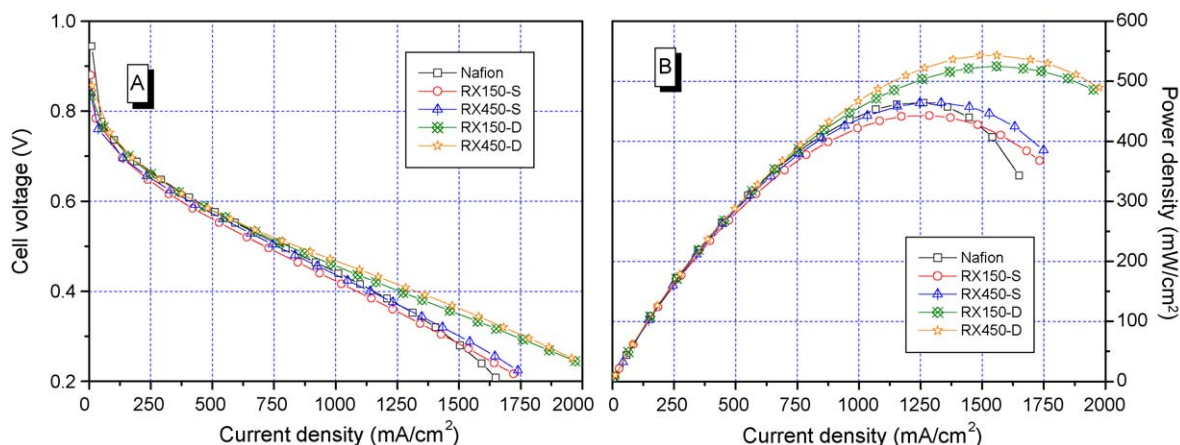


Fig. 3. The polarization curves of the MEAs at condition 3: the cell temperature was 80 °C and H₂ gas was humidified at 25 °C. (A) The cell voltage vs. the current density. (B) The power density vs. the current density.

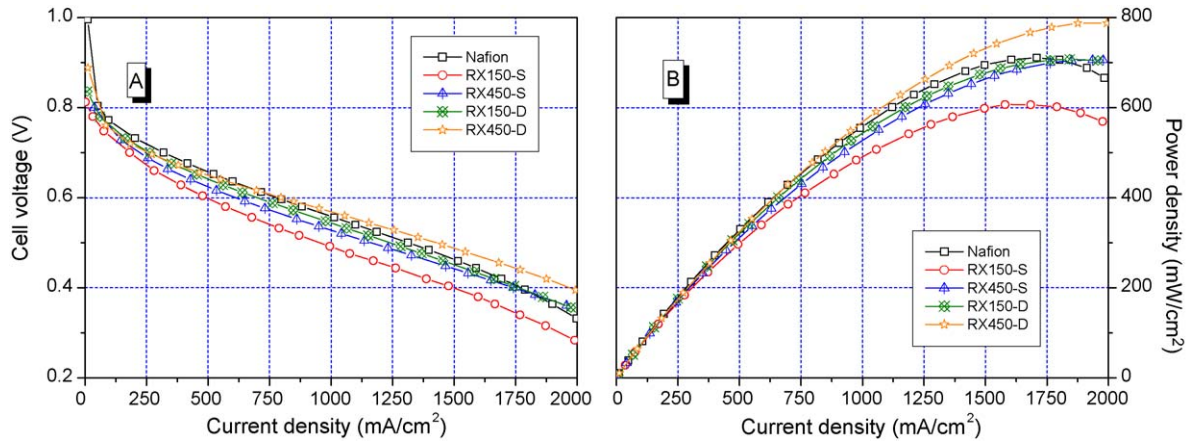


Fig. 4. The polarization curves of the MEAs at condition 4: the cell temperature was 80 °C and H₂ gas was humidified at 60 °C. (A) The cell voltage vs. the current density. (B) The power density vs. the current density.

3.3. Open circuit voltage

The dependence of the OCV values on the cell operation conditions are listed in Table 4. From the table, it is obvious that the MEAs based on the synthesized membranes suffered from low OCV, which is about 0.10–0.15 V lower than that of the MEA based on Nafion, under conditions 1–4. The main reason for the lower OCV is the thicknesses of the membranes were less than 20 μm. This thickness is one third of that of Nafion 112. The thinness results in higher gas crossover. But, increasing the crosslinking density in both the PTFE matrix and PS–SA grafts improved the OCV values.

For certain MEAs, the OCV slightly decreased with the increasing in cell temperature, as shown in conditions 1–3 of Table 4. Also, the increase in humidification slightly suppressed the OCV values, as shown in conditions 3–4 of Table 4.

3.4. Electrochemical impedance spectra measurements

All the EIS were measured at a dc current density of 0.5 A cm⁻². The range of the ac frequency was from 100 kHz to 1 Hz. A standard EIS test takes 2 min, and the disturbance of the cell voltage during the test was normally within ±1%.

The typical EIS curves of the MEAs in Nyquist presentation under condition 1 when the cell temperature was 25 °C is shown in Fig. 5.

All the curves are semicircular. Therefore, the equivalent circuit would be the one shown in Scheme 2 [23,24], which is a very rough model, and the inductance is omitted. As reported

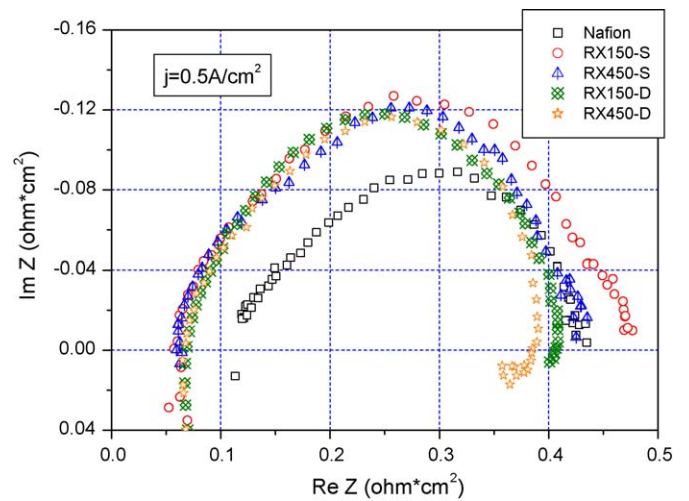


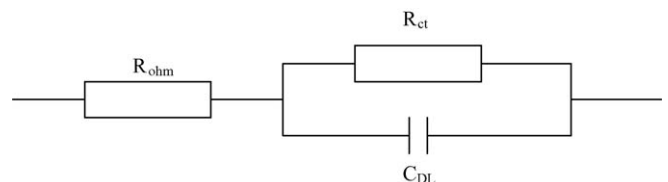
Fig. 5. The EIS of the MEAs in Nyquist presentation. Condition 1: the cell temperature was 25 °C and H₂ gas was humidified at 25 °C.

in Ref. [6], if the PEMs degraded during fuel cell operation, there will be a low frequency arc appearing due to mass transport limitations as the result of degradation products blocking the transport of reactants and products to the electrodes. In these cases, the present equivalent circuit would not be applicable.

The ohmic resistances (R_{ohm}) values, which are the intersections on the real axis at high frequency, are presented in Table 5. The charge transfer resistance (R_{ct}) values, which can be calculated as the diameter of the semicircle on the real axis, are listed in Table 6.

Table 4
The dependence of the open circuit voltage on the experiment conditions

Label	OCV (V)			
	Condition 1	Condition 2	Condition 3	Condition 4
Nafion	1.00	0.98	0.98	0.97
RX150-S	0.85	0.84	0.83	0.82
RX450-S	0.86	0.85	0.84	0.83
RX150-D	0.89	0.88	0.87	0.86
RX450-D	0.90	0.89	0.88	0.87



Scheme 2. Equivalent circuit: R_{ohm} is the ohmic resistance, R_{ct} is the charge transfer resistance and C_{DL} is the double layer capacity.

Table 5
The dependence of the ohmic resistance on the experiment conditions

Label	R_{ohm} ($\text{m}\Omega \text{cm}^2$)			
	Condition 1	Condition 2	Condition 3	Condition 4
Nafion	113	86	115	78
RX150-S	59	48	50	38
RX450-S	60	40	41	34
RX150-D	69	43	39	35
RX450-D	68	49	43	35

Under condition 1, the R_{ohm} of the MEAs based on the synthesized PEMs was about half of the value for the MEA based on Nafion, due to the low thickness of the membranes.

The coating of the ionomer dispersion on the PEMs and electrodes was believed to improve the interfacial property of the MEA by reducing the R_{ct} [25,26]. The R_{ct} of the MEAs based on the membranes grafted by S were much higher than that of the MEA based on Nafion. However, the R_{ct} of the MEAs based on the membranes grafted by S/DVB were close to that of the MEA based on Nafion. One reason for the difference in the R_{ct} values is the different surface morphology. As reported previously [17], the surfaces of the membranes grafted by S were covered by the PS–SA chains while on the surfaces of the membranes grafted by S/DVB they were mainly F-atoms. A similar structure of the surface of the membranes grafted by S/DVB to the ionomer dispersion provided a better compatibility with the ionomer dispersion coated electrodes. Also, the higher DOS of the membranes partially accounted for the higher R_{ct} value because of the larger volume change in the hot-pressing step. The MEA based on the RX450-D membrane had a similar R_{ct} value as that of the MEA based on Nafion. This is due to the RX450-D membrane which has an F-atom rich surface and a similar water uptake to that of Nafion. This means that the improvement in the compatibility of the membrane with the ionomer dispersion and the reducing the water uptake will improve the interfacial property of the MEA by reducing the R_{ct} value.

Under condition 2, as calculated from the EIS curves in Nyquist presentation, the R_{ohm} decreased by nearly 1/3 as compared with condition 1. While, the R_{ct} decreased slightly.

When the cell temperature increased from 60 to 80 °C and the humidification temperature was kept at 25 °C, the R_{ohm} value of the MEA based on the Nafion membrane increased by 34% because of the low humidification. However, the R_{ct} value decreased about 25% (76 $\text{m}\Omega$), which should be attributed to the improved molecular mobility of the Nafion dispersion which has a relatively low glass transition temperature (T_g).

Table 6
The dependence of the charge transfer resistance on the experiment conditions

Label	R_{ct} ($\text{m}\Omega \text{cm}^2$)			
	Condition 1	Condition 2	Condition 3	Condition 4
Nafion	322	309	233	216
RX150-S	415	416	312	274
RX450-S	365	347	306	260
RX150-D	337	319	265	245
RX450-D	321	310	249	230

Table 7
The dependence of the ionic conductivity on the experiment conditions

Label	IC (mS cm)			
	Condition 1	Condition 2	Condition 3	Condition 4
Nafion	53	70	52	77
RX150-S	29	35	34	45
RX450-S	30	45	44	53
RX150-D	26	42	46	51
RX450-D	25	35	40	49

By contrast, the R_{ohm} values of the MEAs based on the synthesized PEMs showed no obvious change under condition 3 as compared to condition 2. And the R_{ct} values of all the MEAs decreased by about 50 $\text{m}\Omega \text{cm}^{-2}$ due to the higher cell temperature.

Under condition 4, the R_{ohm} and R_{ct} values for all the MEAs decreased with higher humidification as compared with the corresponding data under condition 3. This means that the higher humidification reduces the required internal water contents of the PEMs but also improves the interface properties between the membranes and electrodes. Thus, both the R_{ohm} and R_{ct} are decreased.

3.5. Ionic conductivity

The ionic conductivity (IC) values under every experimental condition were calculated by dividing the thickness of the PEMs by the R_{ohm} , and are listed in Table 7.

Under condition 1, the IC values of the synthesized PEMs were about 50–60% of that of the Nafion membrane. The higher IC value of the Nafion membrane can be partially attributed to the higher acidity of the perfluoride sulfonic acid than that of the aromatic sulfonic acid. Another reason is the thinning of the Nafion membrane in the hot-pressing procedure as reported [6].

Also, the IC value of the membrane grafted by S was higher than membranes grafted by S/DVB having similar IEC values. This can be attributed to the reduced mobility of the PS–SA graft chains due to the network formation in the membranes grafted by S/DVB.

Since the real thicknesses of the PEMs after MEA preparation is difficult to measure, especially in the cell test, we assumed the thicknesses of the PEMs were unchanged when calculating the IC values. Therefore, the IC values can be considered to have the same dependence on the test conditions as the R_{ohm} values.

From the polarization curves and the IC values, it can be found that the higher IC values did not definitely determine better performance. The interfacial property between the PEMs and the electrodes in the MEAs is an important factor in fuel cell applications.

4. Conclusion

Four new PEMs were synthesized by pre-irradiation induced grafting of S or S/DVB into the RX-PTFE films with different crosslinking density and then sulfonated. The IEC values of the synthesized PEMs ranged from from 1.7 to 2.3 meq g^{-1} and

the thicknesses of the PEMs were around 18 μm . The MEAs based on the synthesized PEMs were prepared by coating the electrodes and membranes with Nafion dispersion and then hot pressed. The MEA based on a Nafion 112 membrane was prepared under the same procedure for comparison.

The polarization curves, OCV values, EIS data and IC values of the MEAs were taken under low humidification conditions at cell temperature ranges from 25 to 80 $^{\circ}\text{C}$.

At the working temperature of 25 and 60 $^{\circ}\text{C}$ and with hydrogen gas humidified with 25 $^{\circ}\text{C}$ water, the performances of the MEAs based on the synthesized PEMs were inferior to those of the MEA based on the Nafion membrane. The R_{ohm} of the synthesized PEMs were only half that of the Nafion membrane, but the calculated IC values of the synthesized PEMs were lower than that of the Nafion membrane. The MEA based on the Nafion membrane has the smallest R_{ct} value. The MEAs based on the membranes grafted by S had larger R_{ct} values than those of the MEAs based on the membranes grafted by S/DVB.

When the cell temperature increased to 80 $^{\circ}\text{C}$ and hydrogen gas humidified at 25 $^{\circ}\text{C}$, the performance of the MEAs based on the synthesized membranes showed a better performance than that of the MEA based on Nafion, which suffered from increased R_{ohm} values. When the humidification condition was improved, the performance of all MEAs increased with decrease in the R_{ohm} and R_{ct} values. The experimental results showed that the MEAs based on our synthesized PEMs with a high IEC value and low thickness are more suitable for working under relatively high temperature and low humidification, while the MEA based on Nafion suffered from enhanced drying out.

The OCV values of the MEAs based on the synthesized PEMs are about 0.1 V lower than that of the MEA based on Nafion under all conditions. Also, the increasing in the cell temperature and humidification conditions reduced the OCV values slightly.

Generally speaking, the MEAs based on the PEMs grafted by S/DVB showed a better performance than the MEAs based on the PEMs grafted by S because of the lower R_{ct} value. Considering the higher chemical resistance to the oxidative radicals as revealed in *ex situ* research, the PEMs grafted by S/DVB are the better choice.

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