



Nafion-assisted cross-linking of sulfonated poly(arylene ether ketone) bearing carboxylic acid groups and their composite membranes for fuel cells

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ABSTRACT

In this study, a new type of cross-linked composite membrane is prepared and considered for its potential applications in direct methanol fuel cell. Nafion and sulfonated poly(arylene ether ketone) bearing carboxylic acid groups (SPAEC-C) are blended and subsequently cross-linked by a Friedel–Craft reaction using the carboxylic acid groups in the SPAEC-C to achieve lower methanol permeability. The perfluoroalkyl sulfonic acid groups of Nafion act as a benign solid catalyst, which assist the cross-linking of SPAEC-C. The physical and chemical characterizations of the cross-linked composite membranes are performed by varying the contents of SPAEC-C. The c-Nafion-15% membrane exhibits appropriate water uptake (10.49–25.22%), low methanol permeability ($2.57 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$), and high proton conductivity (0.179 S cm^{-1} at 80°C). DSC and FTIR analyze suggest the cross-linking reaction. These results show that the self-cross-linking of SPAEC-C in the Nafion membrane can effectively reduce methanol permeability while maintaining high proton conductivity.

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1. Introduction

There has been great interest in perfluorosulfonate ionomers and their applications as proton exchange membranes (PEMs). The function of a PEM in a fuel cell is to conduct protons and to be a separator of fuels between the anode and the cathode. Nafion, a commercially representative perfluorosulfonate ionomer, has been widely used in polymer electrolyte and direct methanol fuel cells (PEFCs and DMFCs) owing to its high oxidative stability and superior proton conductivity at moderate temperatures ($\leq 80^\circ\text{C}$) and 100% relative humidity (RH) [1,2]. However, methanol readily migrates through Nafion membrane between the electrodes, resulting in the reduction of DMFCs voltage and poisoning the catalysts at the cathode.

One strategy to mitigate the problem of methanol crossover in DMFC is to develop alternate membrane materials that are less permeable to methanol. In this regard, several fluorine-free ionomer membranes such as sulfonated polysulfones [3,4], sulfonated polyimide [5,6], and sulfonated poly(arylene ether ketone)s (SPAECs) [2,7–9,10–13] have been extensively investigated. These materials possess good thermal stability and mechanical properties, and the proton conductivity of them can be controlled by the degree of sulfonation [14–17]. It was found that the SPAEC membranes with an optimum degree of sulfonation

indeed exhibited lower methanol crossover than Nafion in DMFC [12].

Cross-linking of polymer membrane is another powerful and simple method to alleviate and to overcome the methanol crossover problem. This method is also used to control water swelling and prevent dissolution of highly sulfonated polymers. So far, much work has been done to use the cross-linking method in the area of proton exchange membranes for DMFC to reduce methanol crossover successfully [18–20]. However, in most of these cases, the proton conductivity decreased significantly due to the addition of non-conductive materials or diminishing free proton of conductive materials.

Recently, Lee and coauthors reported the preparation of covalently cross-linked sulfonated poly(phenylene sulfide sulfone nitrile) membranes using 4, 4'-oxybis (benzoic acid) (OBBA) as a cross-linker to achieve lower water swelling and lower methanol permeability [21]. The carboxylic acid groups in OBBA can undergo Friedel–Craft acylation with the nucleophilic phenyl rings in the main chain of polymer rather than the sulfonic acid groups in the same polymer [22–24]. This cross-linking route can efficiently avoid the elimination of sulfonic acid groups. However, the extra addition of the chemical additives and impurities for the cross-link reaction may dilute the concentration of sulfonic acid groups in the membrane.

In this study, a high sulfonated degree, self-cross-linkable sulfonated poly(arylene ether ketone)s bearing pendant carboxylic acid groups (SPAEC-C) were synthesized and then blended with pure Nafion solution. After blending, the cast membranes were

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heated at 160 °C to induce cross-link between carboxylic acid groups and the nucleophilic phenyl rings in the SPAEK-C. The sulfonic acid groups in Nafion or SPAEK-C can, therefore, serve as not only proton transport facilitators but also acid sources for the Friedel–Craft reaction with the aid of vacuum for dehydration. The composite membranes based on Nafion and cross-linked SPAEK-C can form semi-interpenetrating polymer networks with the membranes. Therefore, the methanol permeability of pure Nafion membrane could be greatly reduced. Furthermore, the composite membranes were also expected to possess high proton conductivity due to the introduction of highly conductive SPAEK-C. The ion-exchange capacity (IEC), water uptake, and thermal properties of the cross-linked membranes were also investigated.

2. Experimental

2.1. Materials

SPAEK-C was synthesized *via* aromatic nucleophilic polycondensation of sodium 5,5'-carbonyl-bis(2-fluobenzene-sulfonate) (SDFBP), 4,4'-difluorobenzophenone (DFBP) and phenolphthalein (PPL) according to a procedure described in our previous work [25]. 5% (w/v) of Nafion solution was purchased from DuPont Co. All other reactants and solvents were obtained from Tianjin Tiantai Chemical Company and used as received without further purification.

2.2. Membrane preparation and cross-linking treatment

Nafion solution was evaporated to dryness, and boiled in 5 wt.% peroxide solution at 80 °C, 1 M aqueous sulfuric acid solution at 80 °C, and deionized water, in that order. Then Nafion and SPAEK-C were separately dissolved in DMF to obtain a 15 wt.% solution. The SPAEK-C solution was added to Nafion solution at room temperature under vigorous stirring. The weight ratios of SPAEK-C in the blends varied from 5% to 15%. The mixtures were cast onto glass dishes and dried under vacuum at 80 °C. Finally, the cast membranes were dried at 160 °C for 10 h to complete cross-linking reaction. The thickness of the cross-linked Nafion membranes was measured to be $60 \pm 10 \mu\text{m}$. The final cross-linked Nafion/SPAEK-C composite membranes were noted as c-Nafion-*x*% (*x*% refers to weight percent of SPAEK-C in the cross-linked Nafion membranes). Moreover, the recast Nafion via DMF was prepared by Nafion solution with a thickness of $\sim 50 \pm 10 \mu\text{m}$ which was used to compare the properties. The c-Nafion-*x*% and recast Nafion membranes were stored in deionized water before use.

2.3. Characterization

Inherent viscosities of SPAEK-C were measured in DMF at 25 °C with a polymer concentration of 5.0 g l^{-1} . ^1H NMR spectra (in d_6 -DMSO) were recorded on a 500 MHz Bruker Avance 510 spectrometer. The chemical shift of tetramethylsilane was used as the internal reference standard. FT-IR spectra of powder samples were obtained between 4000 and 400 cm^{-1} with a Bruker Vector 22 FT-IR spectrometer. Differential scanning calorimetry (DSC) measurements were performed on a Mettler Toledo DSC 821e instrument at a heating rate of $20 \text{ }^\circ\text{C min}^{-1}$ under nitrogen. Thermo-gravimetric analysis (TGA) was recorded on a Pyris-1 (PerkinElmer) series thermal analysis system at a heating rate of $10 \text{ }^\circ\text{C min}^{-1}$ under N_2 atmosphere. Before testing, all the membranes were preheated to 120 °C and kept at this temperature for 20 min to remove any residual moisture and solvent.

2.4. Water uptake, methanol permeability and proton conductivity of membranes

The water uptake (WU) was determined by measuring the change in the weight between the dry and swollen membranes. A detailed procedure was reported previously [26]. And the methanol permeability was determined according to a detailed procedure reported previously [25].

The IEC values of membranes were determined by classical titration. The membrane sample was immersed in 1 M NaCl solution for at least 24 h to exchange the H^+ ions from Na^+ . The exchanged protons within the solutions were titrated with 0.05N NaOH solutions using phenolphthalein as an indicator. Each sample must be measured at least three times until it had reached to a constant value. The IEC values were recorded in unit of millimole NaOH per gram of the membrane samples (mequiv. g^{-1}) as an average value for each sample.

The proton conductivity was measured by a four-electrode ac impedance method from 0.1 Hz to 100 kHz, 10 mV ac perturbation and 0.0 V dc rest voltage using a Princeton Applied Research Model 2273 potentiostat/galvanostat/FRA. The membranes were cut into 1 cm wide, 4 cm long and were fixed in a measuring cell made of two outer gold wires to feed current to the sample and two inner gold wires to measure the voltage drops. All the membranes were mounted between two polytetrafluoroethylene (PTFE) plates. A detailed procedure was reported previously [25]. The cell was immersed into water during measurement. Before measurement, the films were full hydrated in water for 24 h.

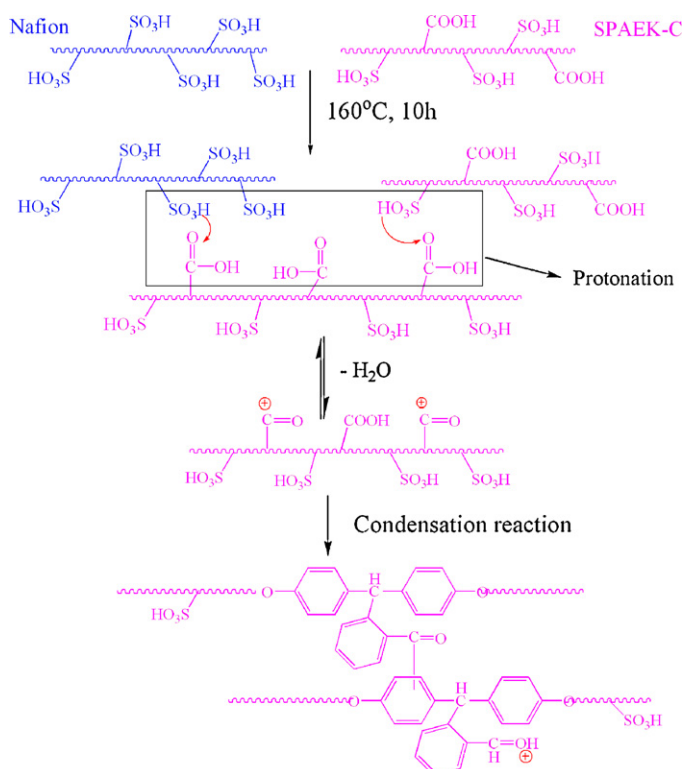
3. Results and discussion

3.1. Preparation of cross-linked membranes

SPAEK-C copolymers containing pendant carboxylic acid groups were synthesized by a nucleophilic aromatic substitution ($\text{S}_{\text{N}}\text{Ar}$) polycondensation of activated aromatic halides with phenolphthalein under standard conditions. The inherent viscosity of the SPAEK-C is 0.81 dl g^{-1} in DMF at 25 °C, indicating that high molecular weights were obtained. To achieve high proton conductivity of SPAEK-C, the degree of sulfonation (the number of SO_3H groups per repeating unit) obtained from ^1H NMR spectrum is controlled to be 1.36. The detailed characterization was reported previously [25]. We expected here that the synthesized SPAEK-C containing simultaneously sulfonic and carboxylic acid groups can be readily cross-linked by just thermal treatment without introducing additional cross-linkers.

The preparation of cross-linked Nafion membranes was performed by two steps. Nafion solutions in DMF blending with different weight ratios of SPAEK-C were cast into films and subsequently thermally treated at high temperature (160 °C) in vacuum for 10 h. The cross-linking reaction of SPAEK-C was obtained by a Friedel–Craft reaction at 160 °C between carboxylic acid groups and the nucleophilic phenyl rings in the SPAEK-C. The cross-linking mechanism is shown in Scheme 1 and the schematic presentation of proton conductor polymeric matrix is shown in Scheme 2. Under acidic conditions, a carboxylic acid group on a phenyl ring is very reactive towards an aromatic ring. An electrophilic aromatic substitution reaction could occur between them in SPAEK-C, resulting in a cross-linked structure. The sulfonic acid groups in Nafion and SPAEK-C not only serve as proton transport facilitators, but also as a benign solid catalyst for the Friedel–Craft reaction at higher temperature [21].

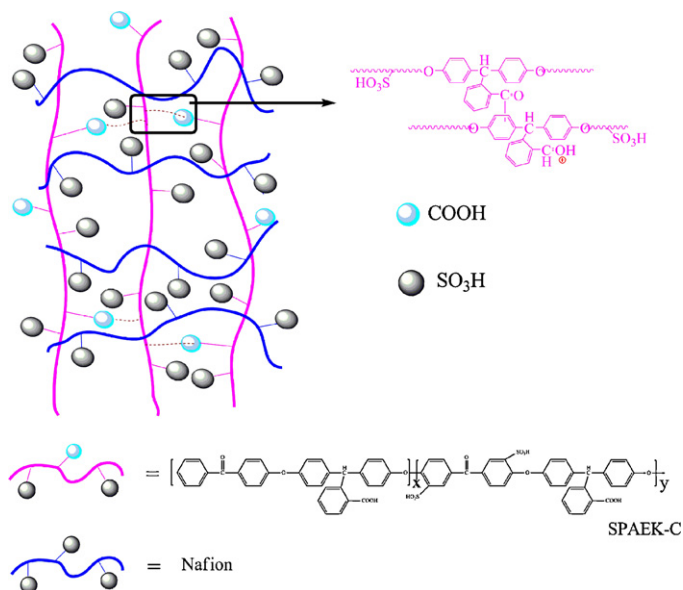
DSC analysis was performed to confirm that a cross-linking reaction indeed occurred in the Nafion/SPAEK-C composite membrane. As shown in Fig. 1, the exothermic peak associated with the cross-linking reaction of SPAEK-C copolymer appeared at about 160 °C.



Scheme 1. Schematic representation of the cross-linking mechanism in the composite membranes.

Thus, the thermal curing of the composite membrane at 160 °C for a sufficient time can form a cross-linked SPAEK-C network structure within Nafion membrane.

Fig. 2 shows the FT-IR spectra of pristine SPAEK-C, recast Nafion membrane, and a cross-linked Nafion/SPAEK-C membrane. SPAEK-C exhibited two characteristic bands at 1082 and 1027 cm^{-1} for asymmetric and symmetric O=S=O stretching vibrations of sulfonic acid groups. These characteristic bands for sulfonic acid groups were also observed in the spectrum of a cross-linked Nafion/SPAEK-C membrane. For the recast Nafion membrane, the



Scheme 2. Schematic representation of the fabrication of c-Nafion-x%.

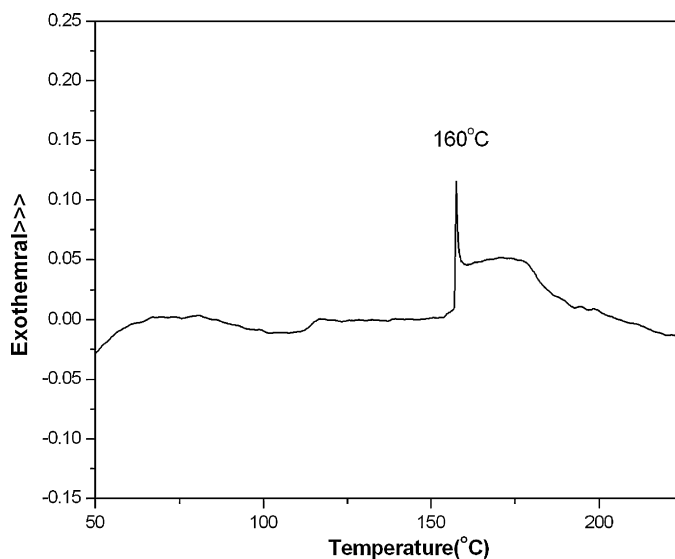


Fig. 1. DSC analysis of the c-Nafion-10%.

peak at 1048 cm^{-1} was attributed to S–O stretching vibration of pendant perfluoroalkyl sulfonic acid groups. However, this location shifted to 1057 cm^{-1} in the cross-linked composite membrane. This shift was induced by the protonation between the sulfonic acid groups in Nafion and carboxyl groups in SPAEK-C, as shown in Scheme 1. In the present case, perfluoroalkyl sulfonic acid groups might have formed weak hydrogen bonds with carboxyl groups and promote the self-cross-linking reaction of SPAEK-C. Finally, the strong absorption at 1708 cm^{-1} due to the C=O asymmetric stretching of the carboxylic acid groups (COOH) in SPAEK-C almost disappeared in the cross-linked composite membrane. A new absorption band at 1736 cm^{-1} corresponding to the C=O stretching of cross-linkage was observed instead. All of these results suggested that the self-cross-linking of SPAEK-C was achieved successfully with the assistance of Nafion.

As is well known, Nafion membrane suffers from high methanol crossover, diminishing the development in DMFC applications. From Table 1, the pure Nafion membrane can be easily dissolved

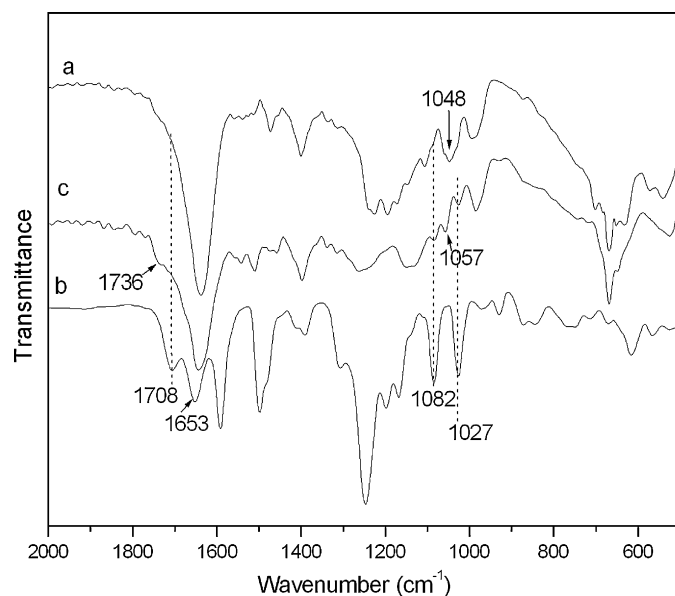
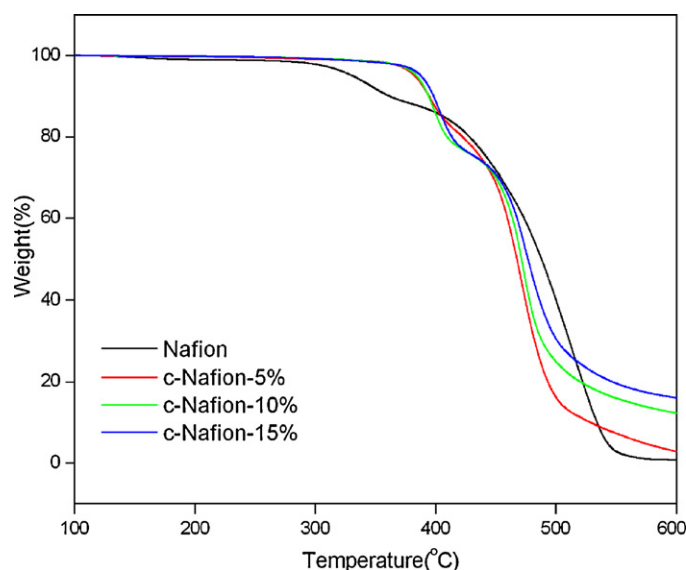


Fig. 2. FT-IR spectra of (a) recast Nafion membrane, (b) pristine SPAEK-C, and (c) a cross-linked Nafion/SPAEK-C membrane.

Table 1
Solubility of the pure Nafion and c-Nafion-x%.

Membranes	Methanol		DMF		NMP	
	25 °C	80 °C	25 °C	80 °C	20 °C	80 °C
c-Nafion-5%	–	+–	–	+–	–	+–
c-Nafion-10%	–	–	–	+–	–	+–
c-Nafion-15%	–	–	–	++–	–	++–
Pure Nafion	+	+	+	+	+	+

+: soluble; –: insoluble; +–: slightly swollen; ++–: seriously swollen.

**Fig. 3.** TGA curves of the pure Nafion and c-Nafion-x%.

in methanol at room temperature, while the cross-linked composite membranes, c-Nafion series, are insoluble even at 80 °C. The Nafion membranes can be easily dissolved in common organic polar solvents, such as DMAc, NMP, and DMSO, while c-Nafion membranes become insoluble in these solvents after fully thermal-treated at 160 °C. This result also suggested the formation of a cross-linked network among SPAEK-C polymer chains in the Nafion membranes.

3.2. Thermal stability

The thermal stability of membranes, which is critical for the durability during fuel cell operation at high temperature, was evaluated using TGA experiments and the results are presented in Fig. 3. It was shown that the thermal degradation profiles were very similar to one another. They all decomposed in three stages. The first stage (250–400 °C) was associated with a desulfonation process, while the second stage (400–500 °C) was related to side-chain decomposition and the third stage (500–600 °C) to PTFE backbone decomposition [27]. However, the temperature corresponding to the onset of thermal degradation (T_d) was different

in pure Nafion and c-Nafion-x%. As the SPAEK-C content increased, TGA curve shifted to a right side. Pure Nafion membrane, c-Nafion-5%, c-Nafion-10% and c-Nafion-15% had T_d of 333.93, 382.63, 384.32 and 387.89 °C, respectively. In addition, Nafion lost about 99.2% by weight at 600 °C after thermal decomposition, while c-Nafion-5%, c-Nafion-10% and c-Nafion-15% lost about 97.15%, 87.71% and 83.93% by weight at the same temperature, respectively. TGA results provided the changes in the thermal stability as a result of the incorporation of SPAEK-C into the clusters of Nafion matrix and the formation of cross-linked network. In general, the incorporation of cross-linked poly(arylene ether ketone)s into Nafion membrane increases the thermal stability. Therefore, the TGA studies revealed good thermal properties of c-Nafion-x% as proton conducting materials.

3.3. Ion-exchange capacities and water uptake

The IEC values of c-Nafion-x% and pure Nafion membranes are shown in Table 2. The IEC value of pure Nafion and pure SPAEK-C membrane is 0.83 and 2.11 mequiv. g^{-1} , respectively [25]. Therefore, the values of the composite membranes (c-Nafion-x% series) showed an increasing trend with the content of SPAEK-C increasing.

Water uptake of a membrane is a critical parameter influencing the performance of PEM materials. Appropriate water uptake is important to provide a carrier for the proton and maintain high proton conductivity. Too much could lead to weakness or a dimensional mismatch when incorporated into a membrane electrode assembly (MEA) and too low could not maintain enough proton conductivity. Two factors may affect the water uptake of the cross-linked membranes: (i) the high sulfonated degree of SPAEK-C causes it soluble in water at 80 °C [25]; (ii) the introduction of semi-interpenetrating polymer networks with the membranes by covalent cross-linking is an effective avenue for controlling water uptake. As shown in Table 2, the water uptake of c-Nafion-x% is lower than that of pure Nafion at 25 °C because the factor (ii) dominates over the other. At 80 °C, the water uptake of c-Nafion-x% increases from 17.01% to 25.22% with the content of SPAEK-C increasing, all higher than that of pure Nafion membrane (15.01%). This is because the water uptake of additive SPAEK-C dramatically increases at high temperature of 80 °C even after cross-linked treatment. In this case, factor (i) overruns the factor (ii). Moreover, it should be noted that the water uptake decreases from 11.61% to 9.41% with the content of SPAEK-C increasing from 0% to 10% at 25 °C, but the water uptake of c-Nafion-15% is higher than those of others. This may be also because factor (i) overruns the factor (ii).

3.4. Proton conductivity and methanol permeability

As shown in Table 2, the proton conductivities of c-Nafion membranes maintained a stable value at low temperature (20 °C) and increased at high temperature (80 °C) with increasing SPAEK-C content. In order to clarify the effect of SPAEK-C content in the composite membranes, proton conductivities and water uptake

Table 2
Water uptake (WU), proton conductivity ($S\text{ cm}^{-1}$) and methanol permeability (P) of the pure Nafion and c-Nafion-x%.

Membranes	T_d (°C)	IEC (mequiv. g^{-1})	WU (%)		σ ($S\text{ cm}^{-1}$)		P ($\times 10^{-7}\text{ cm}^2\text{ s}^{-1}$)
			25 °C	80 °C	20 °C	80 °C	
c-Nafion-5%	382.8	0.90	10.50	17.01	0.075	0.159	4.56
c-Nafion-10%	384.3	0.93	9.41	20.60	0.074	0.178	3.15
c-Nafion-15%	387.9	0.953	10.49	25.22	0.07	0.179	2.57
Pure Nafion	331.1	0.83	11.61	15.01	0.096	0.153	14.2

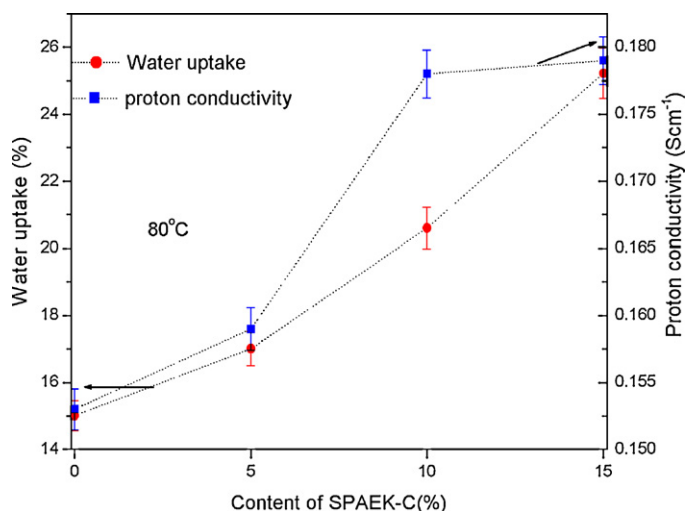


Fig. 4. Proton conductivity and water uptake of c-Nafion-x% as a function of SPAEK-C content.

of cross-linked membranes at 80 °C were measured by changing SPAEK-C content from 0% to 15%. The results are summarized in Fig. 4. As the content of SPAEK-C increased, the water uptake increased from 15.01% to 25.22% and the proton conductivity increased from 0.153 to 0.179 S cm⁻¹. Both curves increased along the X-axis, indicating the composite membranes showed a similar trend in proton conductivity and water uptake. The higher proton conductivity could be attributed to the introduction of highly conductive SPAEK-C. Since the sulfonic acid groups were not involved in the cross-linking reaction, the composite membrane still exhibited high proton conductivity even after cross-linked treatment.

The methanol permeability of the cross-linked membranes at room temperature is shown in Table 2. They exhibited methanol permeability in the range of 4.56×10^{-7} to 2.57×10^{-7} cm² s⁻¹, gradually decreasing with the content of cross-linked SPAEK-C. They were all lower than that of pure Nafion (1.42×10^{-6} cm² s⁻¹). It is obvious that the methanol permeability can be drastically reduced by introducing cross-linked SPAEK-C network in pure Nafion.

Membranes for the practical applications in DMFCs were required to possess high proton conductivity and low methanol permeability. The selectivity, which is defined as the ratio of

proton conductivity to methanol permeability, is often used to evaluate the potential performance of DMFC membranes. In this case, the selectivity can be used just as a barometer to develop the best proton conductive polymer membranes with reducing methanol permeability. Fig. 5 shows the selectivity of the cross-linked membranes. The selectivity of c-Nafion-x% membranes was significantly improved after introducing cross-linked SPAEK-C in the pure Nafion. The result suggested that the incorporation of 15% SPAEK-C into pure Nafion membranes and the formation of cross-linking network structure had more impact on reduction of methanol permeability than proton conductivity, and the c-Nafion-x% membranes have a potential application in DMFCs.

4. Conclusion

The composite membranes were prepared from Nafion and cross-linkable SPAEK-C blended solutions. After cross-linking, it was observed that the methanol permeability was drastically reduced and the water uptake was comparable to that of pure Nafion membrane. The proton conductivity of these cross-linked membranes was slightly reduced when compared to a pure Nafion membrane at 20 °C. At 80 °C, however, the proton conductivity of the cross-linked membranes was higher than that of pure Nafion membrane. Thus, it is interesting to find that this modification can bring great improvements in reducing the methanol permeability while increasing the proton conductivity at high temperature. As a result, the selectivity of the composite membranes was significantly improved.

Acknowledgements

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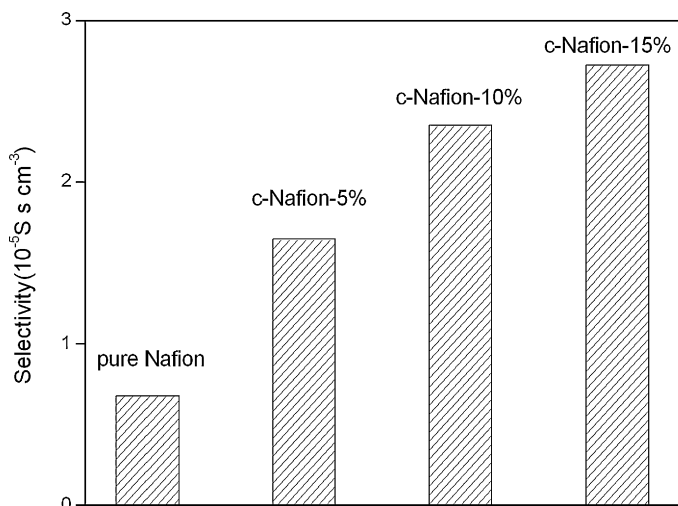


Fig. 5. Selectivity of the pure Nafion and c-Nafion-x%.

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