



Short communication

Quaternized-chitosan membranes for possible applications in alkaline fuel cells

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ABSTRACT

Novel crosslinked quaternized-chitosan membranes were fabricated and further investigated for possible applications in alkaline polyelectrolyte fuel cells. Impedance analysis indicated that some hydrated membranes could exhibit a conductivity close to $10^{-2} \text{ S cm}^{-1}$. Several membranes were selected and integrated into unit fuel cells for the evaluations on their cell performance, using hydrogen as fuel, air as oxidant and platinum as the electrode catalyst, and a current density of 65 mA cm^{-2} was already achieved with a flow rate of hydrogen at 50 mL min^{-1} and air at 250 mL min^{-1} at a relatively low running temperature of 50°C .

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1. Introduction

Fuel cells have been considered a highly promising alternative for future energy needs, especially for portable power applications. Among the several types of fuel cells, the proton-exchange membrane fuel cells (PEMFCs) and the direct methanol fuel cells (DMFCs) both utilize proton conducting polymer membranes as carriers of cations [1]. A key issue for both the DMFC and the PEMFC is the polyelectrolyte membranes. Numerous efforts have been dedicated to developing highly proton-conducting membranes for decades [2], and up to now, the perfluorinated ionomer membrane, commercially named as Nafion, has been relatively successful. Nonetheless, Nafion membranes are strongly restricted in the range of temperature within which they can be reliably used and their high cost is another factor which must be considered [3]. Additionally, when Nafion membranes are applied to the DMFCs, the relatively low activity of the membranes and the parasitic methanol crossover become main problems [4–6].

In recent years, an intensive research effort has been devoted to developing alkaline polyelectrolyte membranes for PEMFCs and DMFCs [7–11]. It has been suggested that if alkaline polyelectrolyte membranes are employed for DMFCs, then several potential benefits can be obtained: (1) facile kinetics at the cathode as well as at the anode [7]; (2) more effective oxidation of methanol in alkaline media [12,13]; (3) reduced level of methanol crossover from

anode to cathode; (4) cheaper non-noble metal catalysts [14] (such as nickel and silver) and (5) cheaper, more easily machined metal bipolar plates, and minimizing electrode weeping and component corrosion [15,16].

Chitosan, principally derived from chitin by deacetylation with alkali, is a low-cost biopolymer and a weak alkaline polyelectrolyte [17]. The presence of hydroxyl and amino groups on the backbone of chitosan affords chitosan membranes with a high degree of hydrophilicity, which is important for the fuel cell operation [18]. In its natural state (dry state), a crosslinked unmodified chitosan membrane is almost non-conductive. However, when fully hydrated, it can show ionic-conductive properties with a conductivity of around $10^{-4} \text{ S cm}^{-1}$ or a slightly higher value [19]. Nevertheless, our previous results revealed that although an open circuit voltage of around 0.9 V was reached by directly applying this type of membrane to an alkaline fuel cell, we could only obtain a lower current density [20], suggesting that conductivity value of the membrane might not be high enough for practical fuel cell operation and the ionic migration rate through the membrane also needs increasing.

Several chitosan blend membranes have been investigated for proton-conducting polyelectrolytes [21–24]. However, to the authors' knowledge, very little research is being conducted for effective hydroxide-ion-conducting chitosan membranes. Chitosan derivatives with quaternary ammonium salt side chains could function as positive-charge-rich gels and have been used antimicrobial and antibacterial reagents [25,26]. Provided that these derivatives could be fabricated into well-constructed membranes, they might serve as novel polyelectrolytes for alkaline fuel cells.

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In this communication, we presented our recently obtained results about crosslinked quaternized-chitosan membranes and their applications in fuel cells. *N*-[(2-hydroxy-3-trimethylammonium)propyl] chitosan chloride (referred to HTCC), was first synthesized, followed by fabrication of crosslinked HTCC membranes. After being post-processed into the hydroxide-ion-conducting style, these membranes were examined in the unit alkaline fuel cells. Preliminary results involving the preparation and ionic conductivity of the membranes as well as the evaluations on the performance of the unit cell were mainly reported.

2. Experimental

2.1. Materials

Chitosan was received in the powder form. To obtain highly deacetylated chitosan, the purchased chitosan samples were treated for 2 h in 50 wt.% NaOH solution at 100 °C, and the alkali treatment was repeated again [27]. The viscosity average molecular weight of chitosan was examined using 0.25 M CH₃COOH/0.25 M CH₃COONa as a solvent system [19] and the degree of deacetylation (DDA) of chitosan was determined using the results from the first derivative UV spectrum with a CARY 5E UV-vis-NIR spectrometer [28]. The DDA value and viscosity average molecular weight of chitosan were measured as 96.4 (±2.1) % and 3.18 (±0.14) × 10⁵, respectively.

All other chemicals were obtained from Aldrich and used as received: acetic acid, sodium acetate, glutaraldehyde (GA, 25% by weight in water), potassium hydroxide pellets, sodium borohydride, glycidyltrimethylammonium chloride (GTMAC), ethanol and acetone.

Gas-diffusion electrodes (1.0 mg cm⁻² Pt on 20 wt.% Vulcan XC-72, GDL: Toray O60 (8 mil)) were purchased from ElectroChem Inc. (USA). The bipolar plates and cell fixtures were provided by Dupont Canada.

2.2. Synthesis of HTCC and preparation of crosslinked quaternized-chitosan membranes

The HTCC was synthesized using a method similar to that described elsewhere [29]. The preparation of crosslinked quaternized-chitosan membranes was performed in follows: typically, 1.6 g of HTCC was dissolved in 80 mL of ca. 0.2% (v/v) aqueous acetic acid (HAc) solutions at 40 °C, followed by the addition of a given amount of GA, depending on the degree of quaternization of HTCC. After stirring for 1.5 h, a 10 wt.% NaBH₄ solution (1.5-fold excess to added GA) was introduced, and the solution was stirred for an additional hour. The mixture was then cast into a membrane and the resulting membrane was then allowed to dry in an oven at 40 °C for 24 h. In order to change the attached chloride ions at the end of quaternary ammonium side chains into hydroxide ions, the dried membrane was immersed in a large excess of potassium hydroxide (0.5 M, aq.) for 48 h and then in water for additional 48 h with frequent water changes to remove any trapped potassium hydroxide [30]. Finally, the obtained membrane was thoroughly dried in air.

2.3. Characterization

The IR spectra of HTCC were recorded on a Nicolet 510P FTIR spectrometer in transmission mode with 64 scans and a resolution of 2 cm⁻¹. All samples were prepared as KBr pellets and were scanned against a blank KBr pellet background.

Degree of quaternization (DQ) was determined via two different methods. HTCC was dissolved in 0.1 M HAc solution and DQ was determined by titrating the amount of Cl⁻ ions on the HTCC with

aqueous AgNO₃ solution according to a reported method [31]. The content of C, H, and N in HTCC was also measured using a Vario EL III elemental analysis instrument and DQ was calculated using the results of elemental analysis.

The crosslinking density (ρ) of the membranes, which is inversely related to the average molecular weight per crosslinking unit and is also indirectly linked to the physical strength of the membranes, was estimated from the network theory of rubber elasticity according to the following relationship [32]:

$$\rho = \frac{E'}{3d\phi RT} \quad (1)$$

where the storage modulus, E' , was determined using a dynamic mechanical analyzer (DMA 2980, TA Instruments) at a frequency of 1 Hz and a temperature of 40 °C; d is membrane density which was determined using mixed solvents composed of carbon tetrachloride (density: 1.586 g cm⁻³) and ethanol (density: 0.816 g cm⁻³) via a floating method; ϕ is the front factor (where $\phi = 1$); R , the gas constant; and T , the absolute temperature.

The ionic conductivity was calculated through impedance analysis [33] in which a Hewlett-Packard model 4194A impedance/gain-phase analyzer was employed. Complex impedance measurements were carried out in the AC mode, in the frequency range of 0.1 to 10⁴ kHz, with a 1.0 V amplitude of the applied AC signal. In the case of dry membranes, they were sandwiched between two brass blocking electrodes in the measurement cell for data collections. For impedance measurements in the hydrated state, the membranes were immersed in deionized water at room temperature for 1 h prior to measurements, the surface water was carefully removed, and the swollen membrane was quickly placed between electrodes in the measurement cell. The water content of the membrane was assumed to remain constant during the short period of time required for the measurements.

2.4. Membrane electrode assembly (MEA) and preliminary evaluation on fuel cell performance

Several selected membranes, HTCC(1), HTCC(2) or HTCC(3), were used for this evaluation. The membranes were boiled in a 1 M KOH solution for 15 min just prior to its use in the MEA. Two electrodes were attached on the two opposite surfaces of the membrane and, then the MEA was made by pressing the membrane and the electrodes together under 4 × 10³ kg for 10 min at 25 °C. The resulting MEA was incorporated into a single test fixture followed by installation of the whole unit fuel cell into the Fuel Cell Automated Test Station (Hydrogenics Inc.). The active surface area of the electrode was automatically recorded as around 25.0 cm² by the test station.

3. Results and discussion

3.1. Synthesis and parameters of HTCC

Fig. 1 shows IR spectra of chitosan and HTCC. In Fig. 1(A), a typical band at 1590 cm⁻¹ for chitosan is assigned to its amide II: amino groups [27]; and a shoulder at around 1654 cm⁻¹ for the N–H is usually shown for the chitosan with a high DDA [29]. Compared to the spectrum of chitosan, in Fig. 1(B), a strong peak of HTCC that corresponds to the C–H bending of trimethylammonium group is registered at 1480 cm⁻¹ [29,31], confirming the existence of the quaternary ammonium salt. It should also be noted that the peak corresponding to the primary amine (1590 cm⁻¹) of chitosan disappears and a new peak at around 1646 cm⁻¹ for HTCC is recorded, revealing the change of the primary amine to the secondary amine structure due to the reactions at NH₂ sites on the

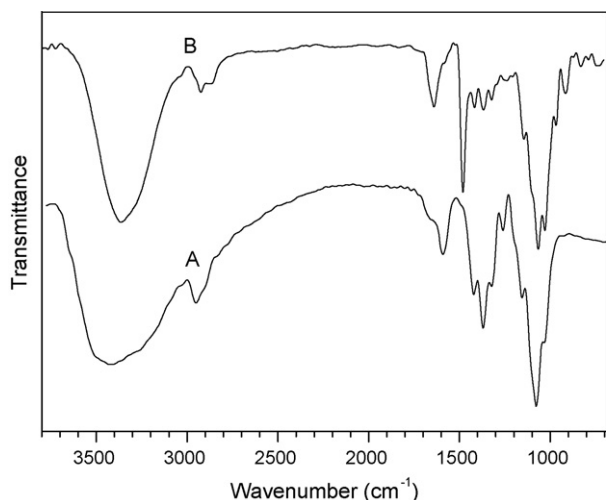


Fig. 1. FTIR spectra of (A) chitosan and (B) HTCC9 (GTMAC/chitosan = 5).

chitosan chains. In addition, it is observed that the characteristic peaks of primary alcohol and secondary alcohol between 1155 and 1075 cm^{-1} remain unchanged in HTCC compared to chitosan. These results demonstrate that quaternary amino groups were effectively incorporated onto chitosan backbone. Some parameters for HTCC are summarized in Table 1. It is observed that under present reaction conditions, DQ proportionally increased with GTMAC/chitosan feed ratio until the ratio reached a value of around 3.5, and after that, it only showed a slight change; the resultant HTCC showed various solubilities depending on its DQ. The data in Table 1 further confirm that quaternary ammonium side chains have been successfully grafted on chitosan chains.

3.2. Preparation and parameters of crosslinked HTCC membranes

It is generally accepted that GA is an effective crosslinker for preparing crosslinked chitosan membranes, and a typical mechanism suggested the Schiff base formation between the amino groups of chitosan and the aldehyde groups of GA [34]. As indicated in Table 1, HTCC with a high DQ (for example, >70%) is soluble in water. We noted that it would be very difficult to process water-soluble HTCC into well-crosslinked membranes by using GA, and such crosslinked HTCC membranes usually show a high swelling ratio, leading to very poor mechanical performance and dimensional stability. It is known that the Schiff base structure is not very stable under both acidic and basic conditions, and in the present case, linkages built up by the Schiff base could be broken during the post-processing through which the resultant membranes

were immersed into KOH solution for exchanging chloride ions into hydroxide ions. Therefore, HTCC having a DQ not higher than 40% was provisionally selected for further producing crosslinked membranes before a more effective crosslinker could be available for the HTCCs with a high DQ. In addition, NaBH_4 was employed to reduce the Schiff base structure ($-\text{N}=\text{CH}-$) into the secondary amine structure ($-\text{NH}-\text{C}-$) [26] in order to improve the mechanical strength and dimensional stability of the resultant membranes. Table 2 provides the relevant parameters for crosslinked membranes made of HTCC with varied DQs. It is noted that by fixing the feed ratio of GA to HTCC constant and changing DQ of HTCC from around 23 to 37%, the crosslinking density of the resultant membranes showed measurable changes, and the increasing DQ in HTCC resulted in a decreasing ρ . These data probably reflect that the HTCC with a higher DQ could establish a relatively bulky environment and hinder $-\text{NH}_2$ groups of chitosan backbone from reacting with crosslinker, enabling the resultant membranes a lower ρ . The results recorded in Table 2 might also imply that the DQ in HTCC could exert a significant impact on the ρ of the membranes and the necessary higher amount of crosslinker would be needed if a higher ρ is required.

To examine the effect of GA amount on ρ , by maintaining the DQ of HTCC constant and varying the feed ratio of crosslinker, some crosslinked membranes were produced and relevant data were collected in Table 3. Since it was found that the membranes usually showed a brittle characteristic once the GA content was higher than a crucial value, the feed ratio of crosslinker was therefore set lower than 0.13275. Table 3 indicates that ρ only exhibits a slight increase with the increasing feed ratio of crosslinker, suggesting that under present reaction conditions ρ could not be significantly modulated by the GA amount. In considering the effect of both DQ and GA on the ρ of the membranes, it could be concluded that the physical strength and dimension stability would be mainly modulated by DQ under the present processing conditions.

The crosslinked HTCC membrane contained chloride ions and they cannot directly serve for an alkaline fuel cell because these attached chloride ions will generate acidic products and as a result, the assembled fuel cell would not function. By post-processing the crosslinked membranes in KOH solution, the attached chloride ions at the end of quaternary ammonium side chains would be replaced by hydroxide ions. Hence, the corresponding hydrated membranes would contain freely movable hydroxide ions as the functional ionic source and could serve as ion carriers in alkaline polyelectrolyte fuel cells.

Two typical complex-plane plots of imaginary impedance ($-Z''$) versus real impedance (Z') for the membranes after hydration for 1 h at room temperature are illustrated in Fig. 2. These spectra consist of two well-defined regions in the complex plane: a typical partial semicircle arc in the high frequency zone that is

Table 1
Basic parameters of HTCC

| Samples | Feed ratio of GTMAC to chitosan (wt./wt.) | DQ (%) ^a | | Solubility ^b | |
|---------|---|---------------------|--------------------|---------------------------|-------|
| | | Titration | Elemental analysis | 0.2% Acetic acid solution | Water |
| HTCC1 | 1.0:1 | 21.4 (± 1.5) | 22.7 (± 1.2) | – | – |
| HTCC2 | 1.5:1 | 25.2 (± 1.7) | 26.9 (± 1.4) | – | – |
| HTCC3 | 2.0:1 | 36.8 (± 2.1) | 35.1 (± 1.6) | + | – |
| HTCC4 | 2.5:1 | 45.1 (± 2.9) | 46.3 (± 1.3) | + | – |
| HTCC5 | 3.0:1 | 64.5 (± 2.3) | 62.4 (± 1.7) | + | – |
| HTCC6 | 3.5:1 | 72.3 (± 1.6) | 74.8 (± 1.8) | + | + |
| HTCC7 | 4.0:1 | 78.7 (± 2.4) | 77.2 (± 1.5) | + | + |
| HTCC8 | 4.5:1 | 79.3 (± 2.7) | 78.6 (± 1.9) | + | + |
| HTCC9 | 5.0:1 | 80.1 (± 2.5) | 79.7 (± 1.6) | + | + |

^a DQ is calculated as an average from four specimens for each sample.

^b "+" means that HTCC is soluble and "–" indicates that HTCC is insoluble or only partially soluble.

Table 2
Properties of crosslinked membranes made of HTCC with varied DQ^a

| Membranes samples | DQ ^b (%) | ρ ($\times 10^{-2}$ mol g ⁻¹) | Conductivity (S cm ⁻¹) ^{c,d} | |
|-------------------|---------------------|---|---|-------------------------------------|
| | | | Before hydration | After hydration |
| HTCC(1) | 23.2 (± 1.7) | 2.21 (± 0.08) | 8.01 (± 0.24) $\times 10^{-9}$ | 4.8 (± 0.18) $\times 10^{-3}$ |
| HTCC(2) | 29.4 (± 1.9) | 1.91 (± 0.11) | 9.46 (± 0.17) $\times 10^{-9}$ | 5.9 (± 0.21) $\times 10^{-3}$ |
| HTCC(3) | 37.1 (± 1.6) | 1.53 (± 0.09) | 8.24 (± 0.19) $\times 10^{-9}$ | 7.5 (± 0.26) $\times 10^{-3}$ |

^a Feed ratio of GA (25 wt.% aq.) to HTCC for all samples was kept constant as 0.08296 (wt./wt.).

^b DQ was determined by elemental analysis.

^c The thickness of the membrane in the dry state (140–170 μ m) and in the swollen state (400–600 μ m) was measured before and after hydration, respectively, and the corresponding average values were used for the calculation of the conductivity.

^d Hydration time for conductivity measurements was 1 h.

Table 3
Properties of crosslinked membranes composed of HTCC with various feed ratios of GA to HTCC^{a,b}

| Membranes samples | Feed ratio of GA (25 wt.%, aq.) to HTCC (wt./wt.) | ρ ($\times 10^{-2}$ mol g ⁻¹) | Conductivity (S cm ⁻¹) | |
|-------------------|---|---|--------------------------------------|-------------------------------------|
| | | | Before hydration | After hydration |
| HTCC(A) | 0.08296 | 1.61 (± 0.08) | 8.06 (± 0.18) $\times 10^{-9}$ | 7.3 (± 0.22) $\times 10^{-3}$ |
| HTCC(B) | 0.09956 | 1.84 (± 0.09) | 7.39 (± 0.21) $\times 10^{-9}$ | 6.8 (± 0.29) $\times 10^{-3}$ |
| HTCC(C) | 0.11616 | 1.95 (± 0.11) | 9.13 (± 0.16) $\times 10^{-9}$ | 7.1 (± 0.23) $\times 10^{-3}$ |

^a All membranes were produced with a same kind of HTCC having a DQ: 36.3 (± 1.8)%, determined by the elemental analysis.

^b The measurement conditions were maintained as same as that denoted by the footnotes (c) and (d) under Table 2.

related to the conduction process in the bulk of the membrane; and a linear region in the low-frequency zone being related to the solid electrolyte–electrode interface [35]. Since the complex impedance will be dominated by the ionic conductance when the phase angle is close to zero, the bulk resistance can be directly obtained from the intercept of the complex impedance plot with the real axis (Z' axis). In the cases that complex impedance curves do not touch the real axis, the complex impedance plots are extrapolated to its intersection with the real axis, and the conductivity of the membranes is calculated with Osman's method [36]. All impedance measurements were performed before and after hydration of the membranes and relevant data are listed in Tables 2 and 3, respectively. It can be observed that the membranes in their dry state only exhibit ionic conductivities around 10^{-8} S cm⁻¹, and the conduction process occurs after the water is incorporated in the membranes. Table 2 reveals that the conductivity of hydrated membranes clearly increases with DQ of HTCC but in Table 3, there is no a clear trend or regularity recorded. It is suggested that in order to enhance the ionic conductance of the crosslinked membranes,

HTCCs with a higher DQ should be considered for further investigations. Based on the fact that some membranes have shown a conductivity close to 10^{-2} S cm⁻¹ (for example, see HTCC(3) in Table 2), which is comparable with the conductivity of Nafion N117 [37] even though there exists a difference in the functional ions, it is reasonable to expect that these quaternized-chitosan membranes could well serve as polyelectrolytes for alkaline fuel cells.

3.3. Evaluation on performance of single cell

The unit cell test was conducted at a hydrogen/air pressure ratio of 241/241 kPa at 50 °C with a relative humidity of 100%. Plots of cell voltage versus current density were recorded and are illustrated in Fig. 3. It can be seen that an open circuit voltage of around 1.0 V has been reached, which is a typical value for an air pressure fuel cell operating at a low temperature. Meanwhile, a current density of about 65 mA cm⁻² had been achieved (Fig. 3) using a resistor load at a hydrogen flow rate of 50 mL min⁻¹ and air-flow rate of

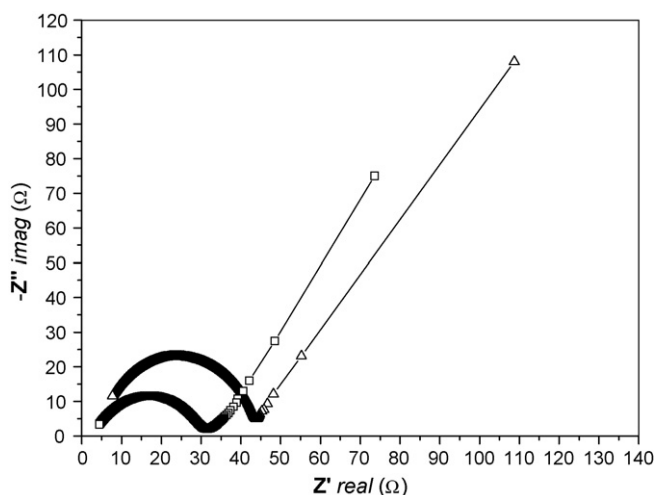


Fig. 2. Impedance spectra of crosslinked membranes after hydration for 1 h at 25 °C: (Δ) HTCC(1) and (\square) HTCC(3).

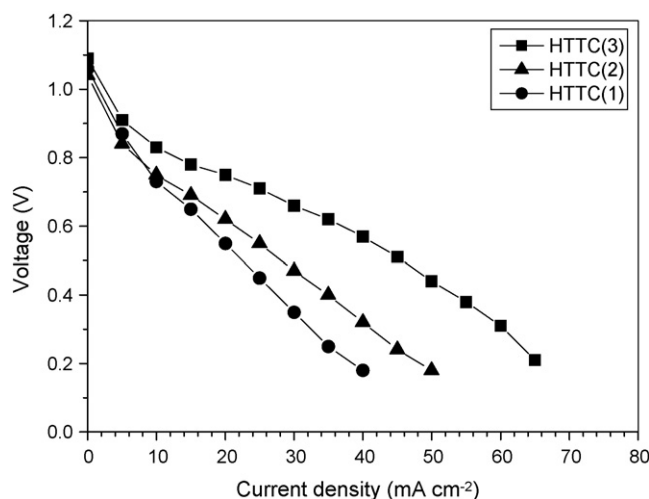


Fig. 3. Fuel cell polarization curves (the active surface area of the electrode was 20.25 cm²; running conditions: 50 °C, flow rates: H₂ 50 mL min⁻¹ and air 250 mL min⁻¹ and pressure ratio: 241/241 kPa).

250 mL min⁻¹, for the HTTC(3) membrane. As reported in Table 2, compared to the HTTC(2) or HTTC(1) membrane, the HTTC(3) membrane had a relatively high conductivity due to its higher DQ; as expected, HTTC(3) membrane showed a better fuel cell performance. The electrochemical behavior of these cells lies within the typical range of most normal polymer electrolyte fuel cells [38]. The obtained results suggest that these quaternized-chitosan membranes could be promising candidates for alkaline fuel cells.

It is known that many factors, such as DQ, crosslinker, the thickness of the membranes, MEA, inner resistance, migrating rate of ions, ion-exchange capacity, and running conditions (temperature, pressure, flow rate of fuel and oxidant, humidity), can influence the cell performance. Efforts are being devoted to improve the electrochemical properties of these membranes as well as the cell performance by examining individual parameters. The preparation and characterization of different series of membranes with further evaluations on their cell performance will be given in separate reports in greater detail.

4. Conclusions

Novel crosslinked quaternized-chitosan membranes were successfully fabricated by using glutaraldehyde as crosslinker and sodium borohydride as reducing agent. The crosslinking density of these membranes, which is closely linked to the physical strength and dimension stability of the membranes, would be mainly modulated by the degree of quaternization in chitosan chains and was not significantly influenced by the amount of the crosslinker. Some hydrated membranes could exhibit a relatively high ionic conductivity comparable with the conductivity of Nafion N117, and the evolutions on the cell performance using some selected membranes at a relatively low running temperature suggested that these membranes would be promising candidates for alkaline polyelectrolyte fuel cells.

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