Modification of Hydrophilic Channels in Nafion Membranes by DMBA: Mechanism and Effects on Proton Conductivity

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Received 18 March 2014; revised 26 May 2014; accepted 16 June 2014; published online 28 June 2014
DOI: 10.1002/polb.23540

ABSTRACT: Modification of proton conductive channels (PCCs) in Nafion has been achieved with the assistance of 3, 4-dimethylbenzaldehyde (DMBA). During annealing, ionic clusters develop from small isolated spheres (1.72 nm) to wide continuous channels (5.15 nm), and the crystallinity of Nafion/DMBA membranes is also improved from 17% to 32% as shown by X-ray diffraction. Molecular dynamic simulation reveals that hydrogen bonding and hydrophobic interaction between DMBA and Nafion work synergistically to achieve better phase separation. The morphology–property relationship shows that, versus various PCCs width, the corresponding proton conductivities vary greatly from 0.079 to 0.139 S/cm at 80 °C. By carefully tuning the width of PCCs, the proton conductivity shows an improvement of 22–34% as compared with pristine Nafion. A significant enhancement on the maximum power density is achieved for the membrane electrode assembly on Nafion/DMBA-8h (as high as 1018 mW/cm²²), yielding an enhancement of 39% on pristine Nafion-8h (730 mW/cm²²).


KEYWORDS: molecular dynamics; phase separation; polyelectrolytes; proton conductive channels; self-organization

INTRODUCTION Proton-exchange membrane (PEM) fuel cells are widely considered as alternative energy conversion devices because of their high efficiency and minimal pollution properties.1–3 The PEM used in such fuel cells is the central and performance-limiting component.4,5 Perfluorosulfonated ionomers, especially Nafion, are the most commonly used PEM materials for their good chemical and mechanical stability.6,7 However, the proton conductivity of Nafion, although usually higher than its nonfluorosulfonated alternatives, is still not satisfactory. Ohmic losses at high current density and proton conductance deterioration at high temperature or low humidity were always observed.8

Two main strategies have been developed to improve the proton conductivity of Nafion membranes. One is to explore composite polymer materials for PEM.9–11 A wide range of nanofillers such as silica,12–14 active carbon,15 titanium dioxide (TiO₂),11,16 and phosphotungstic acid17 have been used in Nafion-based composite PEM. Although the nanosized hydroscopic inorganic fillers can increase the water uptake of the membranes and even provide extra proton-exchange sites, the intrinsic poor compatibility of inorganic fillers with polymer matrix usually decreases the mechanical stability of PEM and limits their applications.15 The other is to tune the proton conductive channels (PCCs) in Nafion membrane. Proton conductivity strongly depends on the morphology of PCCs within PEM. Connected, wide, and less branched hydrophilic channels greatly favor the proton conduction.18–23 Accordingly, several processing methods, such as thermal annealing,24 application of electric fields,26,27 uniaxial pre-stretching,28–30 have been adopted to tune the PCCs morphology without introducing extra components.31 It has been reported that thermal annealing at elevated temperatures could alter the configuration of the ionic domains from cluster-like to chain-like structure.24 Lin et al. applied an electric field on Nafion membranes at 120 °C for 30 min. Alignment of the ionic domains along the membrane thickness direction was achieved, leading to a higher proton conductivity by 30% at 75 °C, 95% RH.26 However, the effects of these methods are limited and it is difficult to obtain connectivity and alignment of PCCs across macroscopic length scales in the membranes.32

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tetrachloroethylene\(^8,^{33}\) into Nafion casting solution as self-organization inducers. A higher degree of phase separation of Nafion observed by transmission electron microscopy (TEM) and the corresponding proton conductivities were enhanced significantly. \(^3, 4\)-dimethylbenzaldehyde (DMBA) is also reported as a self-organization assistant that can increase the crystallinity and proton conductivity of Nafion membrane, and enhance its mechanical and polarization properties.\(^{34}\) However, the facilitated mechanism of self-organization inducers to the self-organization of Nafion has not been investigated yet.

In this study, we aim to investigate the facilitated mechanism of DMBA to the self-organization of Nafion and the relationship of PCCs morphology to proton conduction. First, by molecular dynamic (MD) simulation, hydrogen bonding, and hydrophobic interaction between DMBA and Nafion were revealed to work synergistically to achieve better phase separation for the first time. This provides helpful guidance for exploring new inducer/polymer system for PEM with high performance. Second, to the best of our knowledge, the relationship of PCCs width to proton conduction has not been studied systematically until now. Interestingly, by altering the annealing time, PCCs with different width were obtained in Nafion/DMBA. The relationship between PCCs width and proton conductivity was established. This presents profound significance for designing next-generation PEM materials.\(^{30}\)

Here, pristine Nafion and Nafion/DMBA membranes were prepared by solution-casting method. TEM, small angle X-ray scattering (SAXS), and X-ray diffraction (XRD) were used to characterize the microstructures of the membranes. MD simulation was used to study the self-organization process of Nafion, by which the facilitation mechanism of the DMBA is explored. The morphology–property relationship was established, which shows tuning the morphology of the hydrophilic channels can increase the conductivity of Nafion membranes at 80 °C by 24% in water and 34% at 40% humidity. Finally, fuel cell performances were studied to understand the overall effect of DMBA on PCCs.

### EXPERIMENTAL

#### Materials

The 20 wt % Nafion solution (equivalent weight of \(1100\)) was purchased from Aldrich. Nafion 211 membrane was supplied by DuPont de Nemours. DMBA (98%) was provided by Aldrich. \(N, N\)-dimethylformamide (99.5%, DMF) and \(N, N\)-dimethylacetamide (99%, DMAc) were used as cosolvents to prepare the Nafion membrane.

#### Preparation of Nafion and Nafion/DMBA Membranes

Pristine Nafion membranes and Nafion/DMBA membranes were prepared by solution-casting method and high temperature annealing: First, dilute the commercial 20 wt % Nafion solution to 5 wt % by the cosolvent of isopropanol and water (50/50 wt %). Second, the solution composing of 5 wt % Nafion, DMF, and DMAc at a volume ratio of 4:1:1 was prepared and then mixed with 0.5 wt % (10 wt % toward Nafion polymer) DMBA by sonication bath. Third, the prepared solution was cast onto a glass Petri dish and dried at 80 °C in a nonconvection oven for 2 h. Further drying and high temperature annealing at 160 °C, which was above \(T_g\) (\(T_g\) of Nafion is between 110 and 130 °C),\(^{35,36}\) were applied on both pristine Nafion and Nafion/DMBA membranes in vacuum for 0, 1, 2, 4, and 8 h. Subsequently, acid treatment was applied on the membranes by soaking in a 5 vol % H\(_2\)O\(_2\) solution at 80 °C for 1 h and then in a 0.5 M H\(_2\)SO\(_4\) solution at 80 °C for 1 h, followed by washing with deionized (DI) water until neutral. Finally, the membranes were deposited in DI water for further use. The preparation details and designation of membranes are listed in Table 1.

Before and after acid treatment, the concentrations of DMBA in Nafion/DMBA membranes were measured by gas chromatography–mass spectrometry (GCMS) and Fourier transform infrared spectroscopy (FTIR), respectively. Before acid treatment, the concentration of DMBA in Nafion/DMBA membranes is plotted in Figure 1. It gradually decreases from the initial value of 2.74 wt % (annealing time = 0 h) to a negligible level (less than 6.3E-3 wt %) when the annealing is used for more than 4 h. In addition, after acid treatment, the presence of DMBA was measured by FTIR and the results are shown in Figure 2. There is no DMBA detected for all the

![FIGURE 1 DMBA concentration in Nafion/DMBA membranes with different annealing time by GCMS (before acid treatment).](image)

<table>
<thead>
<tr>
<th>Samples</th>
<th>Treatment at 80 °C (h)</th>
<th>Annealing at 160 °C (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine Nafion-0h</td>
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</tr>
<tr>
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<td>4</td>
</tr>
<tr>
<td>Nafion/DMBA-8h</td>
<td>2</td>
<td>8</td>
</tr>
</tbody>
</table>

### TABLE 1 Preparation Details and Designation of Membranes

*Abbreviations used*: **DI** = deionized water; **SAXS** = small angle X-ray scattering; **XRD** = X-ray diffraction; **MD** = molecular dynamic; **GCMS** = gas chromatography–mass spectrometry; **FTIR** = Fourier transform infrared spectroscopy.
Nafion/DMBA membranes with any annealing time. It proves DMBA has been removed from all the membranes after acid treatment, resulting in pure Nafion polymer. The only difference among these Nafion/DMBA and pristine Nafion membranes is the phase-separation morphology.

Characterization Methods

TEM analysis was used to investigate the microstructure of the membranes on a JEOL 2010 microscope. Super thin TEM samples (about 90 nm) were prepared using microtome based on membranes in dry state. The poststaining treatment by RuO$_4$ vapor was used to identify the cluster and crystallite morphology of dry Nafion membranes.

SAXS spectrums on a D/Max-2400 powder X-ray diffractometer (Cu K$_x$ radiation, $\lambda = 0.1541$ nm) were collected to explore the ionic cluster structure. All membranes were immersed in DI water for 24 h before measurement.

To investigate the crystallinity of membranes, XRD measurements were performed on a Philips PW 1825 diffractometer using Cu K$_x$ source ($\lambda = 0.1541$ nm, 40 kV, 50 mA).

A four point AC impedance method by a potentiostat (IviumStat) was used to measure the in-plane proton conductivity. The relative humidity was controlled by a constant temperature and humidity chamber (HS-50) to measure the humidity-dependent conductivity. Parallel-sided strips membrane samples were prepared with dimensions of $30 \times 5$ mm$^2$. The conductivity was calculated using eq 1,

$$\sigma = \frac{L}{R (\Omega)} \left( \frac{S}{cm} \right)$$

where $L$ (cm) and $R$ ($\Omega$) are the distance and resistance between the two potential electrodes, respectively, $w$ (cm) and $\delta$ (cm) are the width and thickness of the membranes strips.

Polarization curves of membrane electrode assemblies (MEAs) were tested by an Arbin instrument using a single cell test fixture (5 cm$^2$) without humidifier. The flow rates of dry H$_2$ and O$_2$ were 200 sccm with a back pressure of 0.1 MPa. The temperature of the fuel cell was controlled at 80 $^\circ$C.

**Model Constructions and Simulation Details**

MD simulation was performed for Nafion membranes with 0 and 3 wt% DMBA at different humidity conditions (0, 5, 10, and 20 wt% H$_2$O content) by utilizing materials studio (Accelrys, San Diego, CA). Nafion polymers of 20 units were adopted. COMPASS force field was applied. The initial periodic cell was constructed by Amorphous Cell module based on the compositions mentioned above, followed by a minimization of the potential energy of the whole cell by Discover module. Subsequently, the resulting atomic structures were treated by an annealing procedure. Temperature of 450 K was selected according to high temperature annealing (160 $^\circ$C) of experimental operation. Constant number, pressure, and temperature (NPT) ensembles of 50 ps were conducted from 300 to 450 K followed by a constant number, volume, and temperature (NVT) ensemble at 450 K. Then, NPT ensembles of 50 ps were conducted from 450 to 300 K followed by NVT ensemble at 300 K. The temperature interval was 50 K.

**RESULTS AND DISCUSSION**

**DMBA Effect on Phase Separation Morphology of Nafion Membranes**

The phase separation morphology of Nafion has been experimentally confirmed, where hydrophobic crystallites provide stability and hydrophilic ionic channels dominate proton conductivity. In this study, the morphology evolution of Nafion membranes induced by DMBA was observed by TEM and shown in Figure 3.

Figure 3(a,c) shows the morphology of pristine Nafion-0h and Nafion/DMBA-0h, which were only dried at 80 $^\circ$C, not high temperature annealed. The amorphous morphology [Fig. 3(a)] shows a poor microphase separation in pristine Nafion membrane before high temperature annealing. In contrast, a clear phase separation is shown in Figure 3(c), indicating that DMBA induced the phase separation of Nafion at 80 $^\circ$C. After high temperature annealing is applied, the concentration of DMBA decreased gradually (Fig. 1). However, the self-organization of Nafion further developed, based on the preformed phase separation at 80 $^\circ$C. It shows that for Nafion/DMBA-1h, the sulfonic acid groups aggregated and formed isolated sphere clusters [Fig. 3(d)]. For Nafion/DMBA-2h, these clusters expanded further with an increasing diameter, and some of them even agglomerated to form rod-like morphology. When the annealing went on, continuous PCCs with larger width were obtained eventually for Nafion/DMBA-4h and Nafion/DMBA-8h. The widths of PCCs were measured by image analysis software (Leica Qwin) and listed in Table 2. During high temperature annealing, the width of PCCs increases from 1.70 to 3.93 nm (increased by 130%) for pristine Nafion, and from 1.72 to 5.15 nm (increased by
200%) for Nafion/DMBA membranes. Coincident with ref. 33,34 the introduction of DMBA increases the width of PCCs more significantly. Besides that, PCCs of Nafion/DMBA-8h also exhibit better connectivity than that of pristine Nafion-8h, which also greatly favors the proton conduction.

Furthermore, SAXS was used to study the PCCs morphology of hydrated membranes. Figure 4 shows the corresponding SAXS patterns of these hydrated membranes. The scattering factor $q$ is defined as $4\pi\sin\theta/\lambda$, the Bragg spacing $d$ as: $d = 2\pi/q$. And the ionomer peaks are ascribed to the interparticle scattering from ionic domains according to literature.38–41

In Figure 4(a), the pristine Nafion-8h shows a weak scattering reflection with an average interparticle dimension of 5.11 nm (at $q = 1.23$ nm$^{-1}$). In comparison, Nafion/DMBA-8h exhibits a peak with a bigger average interparticle dimension of 7.85 nm (at $q = 0.80$ nm$^{-1}$), indicating a bigger interspacing dimension of ionic clusters. This is consistent with TEM images (Fig. 3). Besides, the ionomer peak of Nafion/DMBA-8h is much sharper than that of pristine Nafion-8h,
which means that the introduction of DMBA in membrane casting process enhanced the ordering of cluster channels. Combined with TEM observations, we could conclude that well-ordered and continuous PCCs within Nafion are induced by DMBA. In addition, the water uptake of pristine Nafion-8h and Nafion/DMBA-8h membranes are 25% and 30% (at 20 °C), respectively, indicating the formation of larger and more effective hydrophilic clusters in hydrated Nafion/DMBA membrane, which contributes to high proton conduction.

Figure 4(b) displays the SAXS profiles of Nafion/DMBA membranes with various annealing time. There is a broad peak for Nafion/DMBA-0h, while no obvious peak is detected for Nafion-0h, indicating that DMBA could induce the phase separation of Nafion primarily at 80 °C. Along annealing, the peak position shifts to lower scattering factors gradually with enhanced reflection intensities. The corresponding average interparticle dimension is increased from 5.71 nm (at $q = 1.10 \text{ nm}^{-1}$) to 7.85 nm (at $q = 0.80 \text{ nm}^{-1}$). This is ascribed to the broadening of PCCs and hydrophobic domains during high temperature annealing. The increasing reflection intensities are attributed to the better ordered ionic clusters developing during annealing.

To investigate the degree of organizational order of hydrophobic domain (CF$_2$ backbone), XRD analysis was conducted.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Width of PCCs (nm)</th>
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</tr>
<tr>
<td>Pristine Nafion-8h</td>
<td>3.93</td>
</tr>
<tr>
<td>Nafion/DMBA-0h</td>
<td>1.72</td>
</tr>
<tr>
<td>Nafion/DMBA-1h</td>
<td>1.95</td>
</tr>
<tr>
<td>Nafion/DMBA-2h</td>
<td>3.13</td>
</tr>
<tr>
<td>Nafion/DMBA-4h</td>
<td>5.13</td>
</tr>
<tr>
<td>Nafion/DMBA-8h</td>
<td>5.15</td>
</tr>
</tbody>
</table>

**FIGURE 4** SAXS patterns of Nafion membranes. (a) Pristine Nafion-8h and Nafion/DMBA-8h membranes. (b) Pristine Nafion-0h and Nafion/DMBA membranes with various annealing time. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

**FIGURE 5** XRD spectra for Nafion membranes. (a) Nafion 211, pristine Nafion, and Nafion/DMBA membranes with annealing time of 8 h. (b) Nafion/DMBA membranes with various annealing time. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
The crystallite of hydrophobic domain provides the thermal and mechanical stability. Therefore, high crystallinity is desired. XRD spectra of Nafion 211, Nafion, and Nafion/DMBA membranes with various annealing time were collected and shown in Figure 5, respectively.

All the membranes exhibit a broad diffraction peak at $2\theta = 10$ to $22^\circ$, which is composed of a broad amorphous peak ($2\theta = 16^\circ$) and a crystalline peak ($2\theta = 17.5^\circ$). To better identify the crystallinity, deconvolution is applied according to eq 2 using Gaussian function,

$$W_{cr} = \frac{\int_{10}^{22} I_{cr}(2\theta)d(2\theta)}{\int_{10}^{22} I_{cr}(2\theta)d(2\theta) + \int_{10}^{22} I_{am}(2\theta)d(2\theta)}$$

(2)

where $I_{cr}$ and $I_{am}$ are the relative intensities of the crystalline and amorphous peaks, respectively.

The results of crystallinity and crystallite size were listed in Table 3. Due to the introduction of DMBA, the crystallinity of Nafion membrane was enhanced from 24% (pristine Nafion-8h) to 32% (Nafion/DMBA-8h), consistent with the reported values in literature. An increase of crystallite size from 4.93 to 5.18 nm is also observed. Furthermore, the Nafion/DMBA membranes with various annealing time were systematically studied. Pristine Nafion-0h was also plotted in Figure 5(b) for comparison. Without high temperature annealing, Nafion/DMBA-0h shows a much higher crystallinity (17%) than Nafion-0h (6%). This proves that, DMBA, acting as a nucleate agent, induced the phase separation of Nafion at $80^\circ C$ initially. When high temperature annealing (at $160^\circ C$) was applied subsequently, the crystallinity was increased from 17% to 32%. This reveals that the self-organization of Nafion further developed during annealing, based on the preformed phase separation at $80^\circ C$, although DMBA was removed from the system gradually. Moreover, full width at half maximum of Nafion/DMBA membranes decreases during annealing, indicating that the perfection of the crystallites in the membranes become high gradually. The phenomena are in good agreement with TEM and SAXS results in previous sections. DMBA appeared to nucleate the crystallization in the hydrophobic CF$_2$ domains, leading to more intensive phase separation morphology and higher crystallinity.

Facilitation Mechanism of DMBA to the Self-Organization of Nafion

Nafion morphology induced by DMBA was carefully investigated in terms of TEM, SAXS, and XRD. All of these results confirmed that during high temperature annealing, a wide and continuous PCCs morphology was developed induced by DMBA. To explore the facilitation mechanism of DMBA to the self-organization of Nafion, MD simulation was performed by Materials Studio (Accelrys).

Temperature of 450 K was selected according to high temperature annealing of experimental operation. A snapshot after a NVT ensemble at 450 K is shown in Figure 6(a), where aldehyde groups are found to point to sulfonic acid...
groups, and a hydrogen bonding (around 1.795 Å) was detected between aldehyde oxygen of DMBA and hydrogen of sulfonic acid group. This is consistent with the result of radial distribution function analysis [Fig. 6(b)]. Both of these findings suggest the presence of hydrogen bonding in this complex system. Aldehyde oxygen, with high electron density, can form hydrogen bonds with hydrogen of sulfonic acid group. Moreover, in Figure 6(a,b), CF2 backbone surrounds closely around the benzene ring of DMBA, but shares a longer distance [above 3 Å, Fig. 6(b)] to aldehyde oxygen of DMBA. It demonstrates the presence of hydrophobic interaction between CF2 backbone and the benzene ring of DMBA. Therefore, hydrogen bonding and hydrophobic interaction between DMBA and Nafion were revealed by MD simulation.

The self-organization process of Nafion during high temperature annealing involves the aggregation of hydrophobic backbones and hydrophilic side chains. To investigate the effects of hydrogen bonding and hydrophobic interaction on self-organization mobility of Nafion, mean square displacement (MSD) analysis at 450 K was performed according to eq 3.34

$$\text{MSD} = \langle (r_i(t) - r_i(0))^2 \rangle$$

(3)

where $r_i(t)$ and $r_i(0)$ represent the coordinates of atom $i$ at specific time $t$ and 0, and the bracket denotes the ensemble average.

As shown in Figure 7, with the presence of DMBA, the MSD of both CF2 backbones and sulfonic acid groups at 450 K was greatly improved by more than 100%. With enhanced self-organization mobility, a higher degree of phase separation is expected.

At 300 K, the final snapshots of configurations for pristine Nafion and Nafion/DMBA system with 5, 10, and 20 wt % water content were shown in Figure 8. A higher degree of phase separation of Nafion/DMBA, compared with that of pristine Nafion, is observed, especially at low water content. Moreover, the cluster sizes of Nafion/DMBA are bigger than that of pristine Nafion for each water content. This is caused by the higher mobility of both CF2 backbones and sulfonic acid groups. We can draw the conclusion that, the synergy effect of hydrogen bonding and hydrophobic interaction increases the mobility of both of sulfonic acid group and backbones, resulting in high degree of phase separation and well-organized continuous PCCs.

The Relationship between PCCs Width and Proton Conductivity

The synergy effect of hydrogen bonding and hydrophobic interaction between Nafion and DMBA facilitates the phase separation of Nafion and results in morphology evolution of PCCs during annealing process. The relationship between PCCs width and proton conductivity in hydrated state is further studied by AC impedance analysis. It should be mentioned that, in such isotropic membranes prepared by solution-cast, through-plane conductivity and in-plane conductivity were reported to be exactly the same.42–45 Moreover, through-plane impedance spectra were found to be distorted significantly by contact resistance and inductance.42,44 Therefore, in-plane conductivity is presented in Figure 9.

On hydration, hydrophilic domain of dry membranes will be accommodated with water and swell to water-filled network where protons transfer.22,46,47 Although the ionic clusters of dry membranes change from isolated small clusters to wider and interconnected PCCs (Fig. 3), the proton conductivity of Nafion/DMBA membranes increases significantly from 0.079 to 0.139 S/cm at 80 °C (Fig. 9), indicating that the water network of hydrated membranes are greatly influenced by the initial cluster morphology of dry membranes. The closed circle (Fig. 9) denotes the proton conductivity of pristine Nafion-8h with a PCCs width of 3.93 nm. Due to the poor connectivity of PCCs in pristine Nafion, its conductivity is well below the trend line of Nafion/DMBA membrane.
addition, form the trend line, highest proton conductivity could be anticipated with PCCs width around 5.5 nm. The temperature dependence of proton conductivities in hydrated state is shown in Figure 10. An increase in proton conductivity with temperature is found for each hydrated membrane owing to the enhancement of both structural (hopping) and vehicular diffusion of protons when the temperature is elevated. In the studied range (1.95 to 5.15 nm) of PCCs yielding from different annealing time, the proton conductivity of Nafion increases with PCCs width greatly.

Proton conductivities for Nafion 211, pristine Nafion-8h, and Nafion/DMBA-8h membranes at various relative humidity are shown in Figure 11. It shows that the conductivity increases with increasing relative humidity as expected for Nafion 211, pristine Nafion-8h, and Nafion/DMBA-8h membranes at 80 °C. Furthermore, Nafion/DMBA-8h exhibits higher proton conductivity compared with Nafion 211 and pristine Nafion-8h at each relative humidity ranging from 40% to 90% due to the high efficiency of proton conduction in wider continuous PCCs. In particular, Nafion/DMBA-8h membrane achieves 34% improvement at 40% RH and 23%
improvement at 90% RH. It means that DMBA could improve the proton conductivity more effectively at low RH, which agrees well with simulation results (Fig. 8). High proton conductivity at low RH condition is very valuable considering the avoidance of external humidifier, and the reduction of complexity of the fuel cell system.48,49

Based on TEM observation and RH dependency of conductivities, a scheme of water networks from different dry state morphologies is proposed in Figure 12. Before hydration, isolated ionic clusters present in pristine Nafion-8h and well-connected PCCs present in Nafion/DMBA-8h. Under hydration, the existence of dead-ended channels originated from isolated ionic clusters would increase the tortuosity of proton transport, resulting in low proton conductivity. In comparison, neighboring water-swollen pores are bridged and interconnected when the initial well-connected PCCs were hydrated, which could offer additional hydrophilic channels and facilitate proton transfer. With the higher connectivity of hydrophilic network, both the structural and vehicular diffusion of protons could be greatly enhanced.

Fuel Cell Performance

Fuel cell performances of MEAs based on pristine Nafion-8h (27 μm) and Nafion/DMBA-8h (27 μm) were determined with dry H2 and O2 at 80 °C. The flow rates of H2 and O2 were 200 sccm with a back pressure of 0.1 MPa. (Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.)

The open circuit voltage of Nafion/DMBA-8h is 0.826 V, higher than that of pristine Nafion-8h (0.789 V). This might be attributed to the dense packing and higher crystallinity of Nafion/DMBA-8h membrane. In addition, the slope of voltage curve is lower for Nafion/DMBA-8h in the region of ohmic polarization. This is related to the higher proton conductivity of Nafion/DMBA. Finally, a significant enhancement on the maximum power density is achieved for MEA on Nafion/DMBA (as high as 1018 mW/cm2), yielding an enhancement of 39% on pristine Nafion-8h (730 mW/cm2). This phenomenon is coincident with literature.34

**CONCLUSIONS**

To modify the hydrophilic channels, Nafion/DMBA membranes were prepared by adding DMBA in casting-solution, and then removed completely in high temperature annealing processes. Induced by DMBA, enhanced self-organization of Nafion was observed at 80 °C, and the self-organization continued after DMBA was fully removed. Wider and
well-connected PCCs (5.15 nm) channels were observed by TEM in Nafion/DMBA membranes, while pristine Nafion membranes only exhibit isolated small sphere-like (3.93 nm in diameter) ionic clusters. SAXS showed the cluster–cluster distance in Nafion/DMBA membranes increased from 5.71 (at \( q = 1.10 \text{ nm}^{-1} \)) to 7.85 nm (at \( q = 0.80 \text{ nm}^{-1} \)) during annealing. XRD spectra indicated that the crystallinity was improved from 17% (in pristine Nafion membrane) to 32% (in Nafion/DMBA membrane).

The facilitation mechanism of DMBA to the self-organization of Nafion was investigated by MD simulation. At temperature of 450 K, hydrogen bonding (about 1.795 Å) and hydrophobic interaction between DMBA and Nafion were revealed in Nafion/DMBA system. Driven by these two effects, the mobility of both the backbone and side chain of Nafion was promoted by more than 100%, resulting in well-ordered continuous PCCs.

Impedance analysis revealed the relationship between PCCs width and proton conductivity: increase of PCCs widths (from 1.95 to 5.15 nm) leads to the increase of proton conductivities (from 0.079 to 0.139 S/cm at 80 °C) for hydrated membranes. By carefully tuning the width of PCCs, an improvement of 22–34% on proton conductivity was yielded for Nafion/DMBA membrane compared with that of pristine Nafion membrane over all relative humidity range.

A significant enhancement on the maximum power density is achieved for MEA on Nafion/DMBA-8h (as high as 1018 mW/cm²), yielding an enhancement of 39% on pristine Nafion-8h (730 mW/cm²). This DMBA-induced phase-separation method can also be applied to improve the hydrophilic channels and proton conductivity of nonfluorinated polymeric membranes.

ACKNOWLEDGMENTS

The authors thank the financial support of National Science Fund for Distinguished Young Scholars of China (Grant No. 21125628), National Natural Science Foundation of China (Grant No. 21176044), and Training Program of the Major Research Plan for the Central Universities (Grant No. DUT13ZD204).

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