



Aminated Perfluorosulfonic Acid Ionomers to Improve the Triple Phase Boundary Region in Anion-Exchange Membrane Fuel Cells

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We propose an approach to improve the triple phase boundary (TPB) of catalyst layers in anion-exchange membrane fuel cells by using aminated Nafion ionomers with amine molecules of ethylenediamine (EDA) and diethylenetriamine (DETA) as anion conductor. Aminated Nafion ionomers were characterized and clarified by Fourier transform IR spectroscopy, Raman spectroscopy, and transference number measurements. The transference number of the aminated Nafion ionomers with DETA (DETA-modified Nafion, $t_- = 0.89$) was larger than that of the EDA-modified Nafion ($t_- = 0.81$). Pt/C catalyst layers with EDA- and DETA-modified Nafion ionomers were constructed, and their oxygen reduction currents were evaluated under the same conditions as in anion-exchange membrane fuel cells. Electrochemical measurements of oxygen reduction currents showed that the order of electrode performance was DETA-modified > EDA-modified > K-form Nafion (neutralized Nafion with KOH). We effectively improved the TPB region in catalyst layers by introducing aminated Nafion ionomers and revealed the relationship between the conductivity of OH⁻ ion in the aminated Nafion ionomers and the number of amine functional groups in an amine molecule. © 2010 The Electrochemical Society. [DOI: 10.1149/1.3483105] All rights reserved.

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There is increasing interest in the application of anion-exchange membrane fuel cells (AEMFCs) as a next-generation electric power source. In contrast with conventional proton exchange membrane fuel cells (PEMFCs), AEMFCs have some advantages for an electrochemical system in working principles. First, cell reactions in AEMFCs proceed under basic conditions, which lead to faster kinetics of electrode reactions. Second, nonprecious metal catalysts can be accepted to efficiently enhance cell reactions. Nowadays, there has been considerable research about AEMFCs because of the above advantages and the development of various anion-exchange membranes (AEMs).

Both AEMFCs and PEMFCs are in the same type of fuel cells: polymer electrolyte fuel cells (PEFCs). PEFCs usually include ion-conducting membranes such as AEMs and proton exchange membranes, and hydrogen-oxidation and oxygen-reduction reactions occur to generate electric power. In these PEFCs, cell reactions mainly occur at the encounter points of catalysts, ion conductors, and gaseous reactants. These reactive points are called as the triple phase boundary (TPB) regions. Even if a point lacks one phase, the point becomes inactive for cell reactions. Therefore, the amount and conditions of the TPB play a dominant role on the performance of PEFCs.^{1,2}

In particular, proton-conducting ionomer solutions such as Nafion solution are used to fabricate an appropriate TPB region in catalyst layers in PEMFCs. The method of casting Nafion solution into a porous catalyst layer was invented,^{1,3,4} and recently, a catalyst layer was made from a slurry of catalyst powder containing Nafion solution.⁵ These proton-conducting ionomer solutions drastically increase the performance of PEMFCs. In the same manner as Nafion acts as a proton-conducting ionomer in PEMFCs, ion conductors in AEMFCs should be OH⁻ ion conductors. Varcoe and co-workers prepared a cross-linked alkaline polymer as an anion-conducting agent.⁶ However, because the study on AEMFCs is in an early phase, it would be desirable to explore more efficient methods for introducing anion-conducting paths in catalyst layers to improve TPB regions in AEMFCs.

In this study, we focused on the amination of perfluorosulfonic

acid ionomer (PFSI) (e.g., Nafion) to obtain anion-conducting ionomers for AEMFCs. This amination involves the reaction of amine molecules with the sulfonic acid groups of PFSI and attaches amine molecules with strong coulombic attraction to PFSI frameworks. This reaction differs from the formation of sulfonamide –SO₂NHR, which contains a covalent bond between sulfur and nitrogen atoms.⁷ PFSI has been widely investigated from the viewpoints of the mechanism of ion conductivities, polymer structures, long-term stability, etc.⁸⁻¹³ Therefore, this fundamental information may be useful to understand the nature of the amination of Nafion ionomers. Furthermore, we can leverage the knowledge about Nafion ionomers in such a way that aminated Nafion is effectively introduced in the process of preparing fuel cells.

The present paper describes, for the first time, an effective approach for the use of aminated Nafion ionomers with ethylenediamine (EDA) and diethylenetriamine (DETA) to improve TPB regions for oxygen reduction by introducing OH⁻-conducting paths in catalyst layers.

Experimental

Amination of Nafion membranes and ionomers.—Aminated Nafion membranes were prepared by soaking Nafion membranes in amine solutions. Before the amination, Nafion membranes were pre-treated using a common procedure.¹⁴ Nafion 112 membranes (DuPont, thickness: 51 μm) were immersed in the solution of EDA (99.8%, Nacalai Tesque, Guaranteed Reagent) for 2 h. Then, these membranes were repeatedly soaked in ultrapure water enough to remove excess EDA molecules from the Nafion membranes. Hereafter, this Nafion membrane aminated by EDA is denoted as the “EDA-modified Nafion” membrane. The “DETA-modified Nafion” membranes were also prepared by immersing a Nafion 112 membrane in the solution of DETA (99.8%, Nacalai Tesque, Guaranteed Reagent) for 2 days, followed by washing with ultrapure water (>18 MΩ cm) in the same way as the EDA-modified Nafion.

The amination of the Nafion ionomer in catalyst layers was also conducted by immersing catalyst layers containing a Nafion ionomer in amine solutions. First, to prepare catalyst layers, a certain amount of Nafion solution (Aldrich, 5 wt % Nafion ionomer) was coated on carbon papers (Toray, TGPH-120) with carbon-supported Pt catalyst (Pt/C) (E-TEK, 20 wt % Pt/C, 1 mg_{Pt} cm⁻²). Second, these catalyst layers were immersed in EDA solutions to allow the Nafion ionomer to be modified with EDA, followed by washing in ultrapure water to

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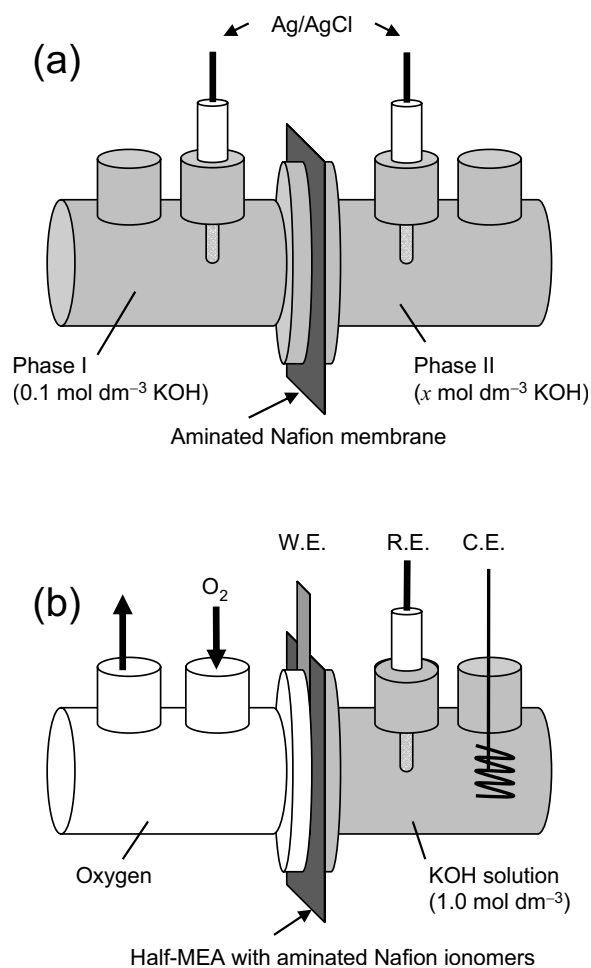


Figure 1. Schematic illustrations of (a) a symmetric cell for potential difference measurements and (b) an asymmetric cell for oxygen-reduction activity measurements.

remove excess EDA molecules. Additionally, catalyst layers with the DETA-modified Nafion were also prepared by using DETA in the same way as the EDA-modified Nafion. Finally, these catalyst layers with aminated Nafion ionomers were pressed onto AEMs (Tokuyama Corp., A-006) to fabricate a half membrane electrode assembly (MEA) for electrochemical oxygen-reduction measurements. Furthermore, to compare with aminated Nafion, K-form Nafion, a neutralized Nafion, was prepared with KOH solution.

Characterization of aminated Nafion.—The aminated Nafion membranes were characterized with Fourier transform infrared (FTIR) spectroscopy, Raman spectroscopy, and transference number measurements. FTIR spectra were measured for the aminated Nafion membranes in the range of 1000–4000 cm^{-1} . Raman spectra of the modified Nafion membranes were recorded using a triple monochromator (Jobin-Yvon, T-64000). Excitation was carried out with a 514.5 nm line (50 mW) from an Ar-ion laser (NEC, GLG2265). Transference number measurements were conducted using a symmetric electrochemical cell with two compartments, as shown in Fig. 1a. The aminated Nafion membranes were sandwiched between two compartments and measured a potential difference between two compartments using Ag/AgCl electrodes by varying the concentration of KOH in one compartment while the concentration of the other was fixed.

Evaluation of the TPB regions.—To evaluate the influence of the aminated Nafion ionomers on the TPB regions, oxygen reduction activities of half-MEAs containing aminated Nafion ionomers were

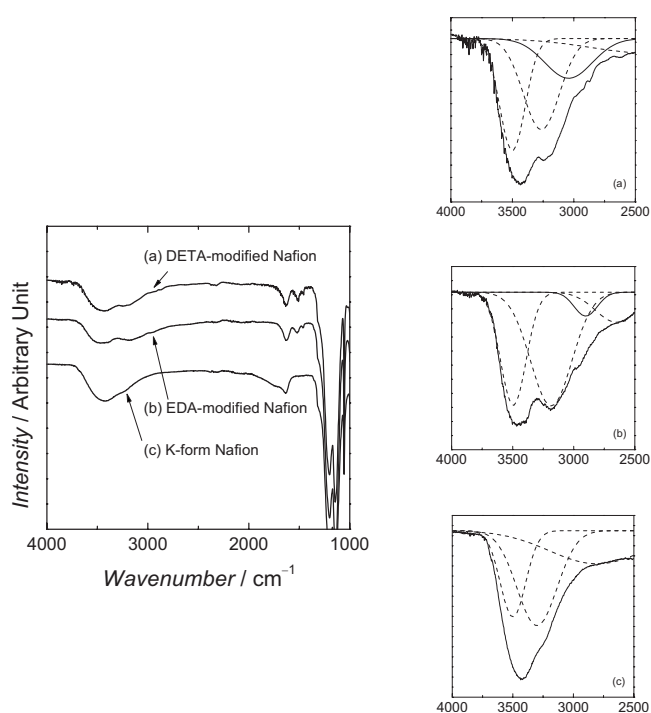


Figure 2. (Left) FTIR spectra of (a) DETA-modified, (b) EDA-modified, and (c) K-form Nafion. (Right) Magnified and deconvoluted spectra in the range of 4000–2500 cm^{-1} .

measured. Half-MEAs were settled in an asymmetrical electrochemical cell, as shown in Fig. 1b, in which one compartment was filled with 1.0 mol dm^{-3} KOH solution and the other compartment was supplied with humidified oxygen gas at 50 mL min^{-1} . In 1.0 mol dm^{-3} KOH solution, a Pt wire and Ag/AgCl (3 mol dm^{-3} KCl) were used as the counter and reference electrodes, respectively. The working electrodes were Pt/C catalyst layers in half-MEAs containing aminated Nafion ionomers. By using these half-MEAs and an asymmetric electrochemical cell, steady-state polarization measurements were conducted for oxygen-reduction reaction at given electrode potentials.

Results and Discussion

Characterization of aminated Nafion ionomers.—FTIR spectra of two aminated Nafion and K-form Nafion are shown in Fig. 2. Additionally, magnified spectra in the range of 2500–4000 cm^{-1} with deconvoluted peaks centered at ~ 2750 , 2900, 3200, and 3500 cm^{-1} are also shown in Fig. 2. In the deconvoluted spectra, each film had the peaks at ~ 2750 , 3200, and 3500 cm^{-1} derived from Nafion membranes.¹⁵ A new peak (shown in a solid line) appeared at ~ 2900 cm^{-1} in Fig. 2a and b. This peak corresponded to $-\text{NH}_3^+$ stretching vibration of amine molecules.¹⁶ The $-\text{NH}_3^+$ stretching peak confirmed the presence of amine molecules (EDA and DETA) in the aminated Nafion membranes. Furthermore, the intensity of the peak at ~ 2900 cm^{-1} in the DETA-modified Nafion was stronger than that in the EDA-modified Nafion. This would be due to the difference of amine functional group contents in one molecule; DETA has three amine functional groups in one molecule even though EDA has two groups. The larger content of amine groups in the aminated Nafion should be preferable from the viewpoint of ion conductivity, because a large carrier density leads to the high ion conductivity. Therefore, the DETA-modified Nafion ionomers may work better than the EDA-modified Nafion ionomers as an anion-conducting agent.

The Raman spectra of the DETA-modified Nafion, pristine Nafion, and DETA solution are shown in Fig. 3. Nafion shows many Raman active vibration modes,^{17,18} and DETA has two characteristic

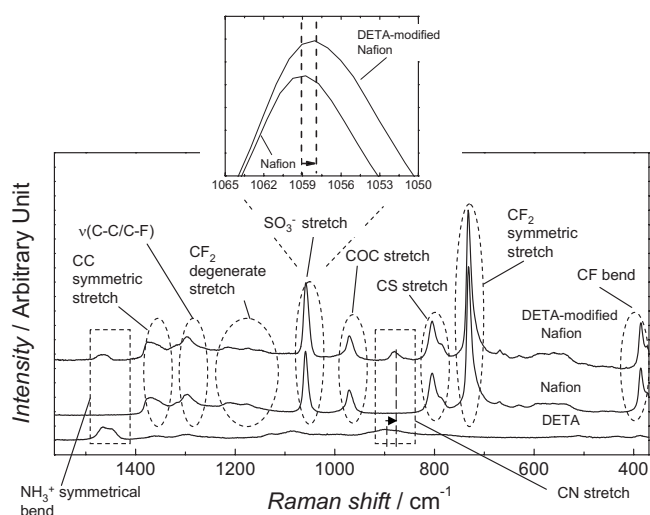


Figure 3. Raman spectra of Nafion membrane, DETA-modified Nafion membrane, and DETA solution.

vibration modes: C–N stretching mode at 880 cm^{-1} and NH_3^+ symmetrical bend mode at 1450 cm^{-1} .^{19,20} In these Raman spectra, there was a clear difference in the C–N stretching vibration between the DETA-modified Nafion and DETA solution: the peak of C–N stretching vibration in the DETA-modified Nafion was negatively shifted compared to that in the DETA solution. This is due to the softening phenomenon of the C–N bond vibration in DETA caused by the interaction between the DETA molecule and the sulfonic acid cation of the Nafion structure through the ion–ion interaction. This strong interaction is supported by the previous paper that amine molecules are strictly fixed with Nafion due to the strong binding energy between $-\text{NH}_2$ and $-\text{SO}_3\text{H}$.²¹

Transference numbers of aminated Nafion were determined by the following Eq. 1

$$E_m = - (1 - t_-) \frac{RT}{F} \ln\left(\frac{a^{\text{II}}}{a^{\text{I}}}\right) \quad [1]$$

where E_m is the potential difference, t_- is the transference number of anion, R and F are the gas and Faraday constants, respectively, T is the absolute temperature, and a^{I} and a^{II} are the activities of OH^- ion in phase I and II, respectively. Herein, the concentration of KOH in phase I was fixed at 0.1 mol dm^{-3} and that in phase II was varied from 0.025 to 0.5 mol dm^{-3} . The values of E_m were plotted against $\ln(a^{\text{II}})$, as shown in Fig. 4.²² From the slopes of these lines [E_m vs $\ln(a^{\text{II}})$], the transference numbers of the aminated Nafion membranes were calculated to be 0.81 and 0.89 for the EDA- and DETA-modified Nafion membranes, respectively. Vassal and his colleagues reported that a copolymer of epichlorohydrin and ethylene oxide showed a similar transference number of 0.93 .²³ Therefore, the EDA- and DETA-modified Nafion membranes successfully worked as good anion conductors (OH^- -conducting agents). In general, the transference number of an electrolyte membrane refers to the selectivity of the focused ion's transportation through a membrane, and thus, a higher transference number is better for an electrolyte membrane. Among the aminated Nafion membranes by EDA and DETA, the DETA modification effectively provided higher OH^- selective transportation. This higher selectivity of the DETA-modified Nafion can be explained by the fact that the DETA modification added more amine functional groups in Nafion than the EDA modification, which was confirmed by the FTIR analysis results.

By using the EDA- and DETA-modified Nafion 115 membranes (thickness: $125\text{ }\mu\text{m}$), impedance measurements were conducted under ambient atmospheric conditions. The real part of the impedance

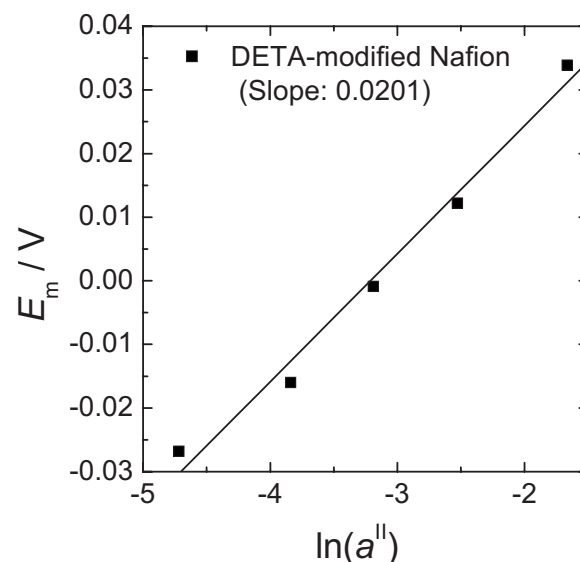
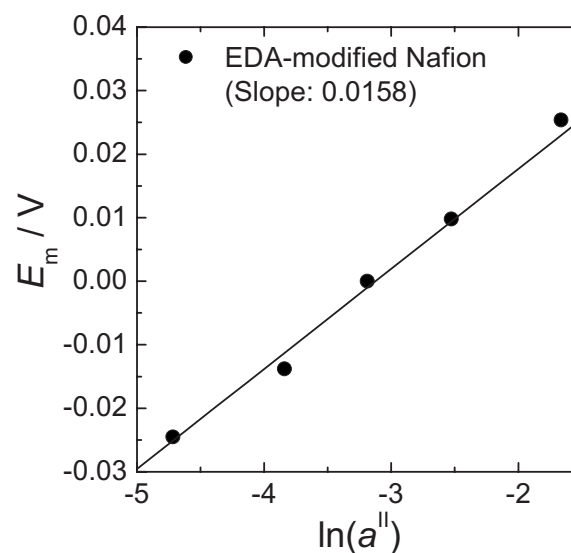


Figure 4. Plots of E_m vs $\ln(a^{\text{II}})$ of EDA- and DETA-modified Nafion membranes.

$\sim 1\text{ kHz}$ was used for calculating the resistance of the membranes. As a result, the resistances of EDA- and DETA-modified Nafion membranes were 63 and $36\text{ }\Omega\text{ cm}^2$, respectively. The resistance of DETA-modified Nafion membranes was almost half of that of the EDA-modified membranes because the DETA modification provided more amine functional groups in the Nafion framework than the EDA modification.

TPB of half-MEAs with aminated Nafion.— Electrochemical oxygen-reduction measurements demonstrated how the amination of Nafion affected the formation of the TPB regions in catalyst layers. In the electrochemical system shown in Fig. 1b, the degree of the TPB regions of half-MEAs can be evaluated by measuring the oxygen-reduction activities of half-MEAs. Figure 5 shows the steady-state polarization curves for oxygen-reduction reaction on half-MEAs of K-form and EDA-modified Nafion. Both half-MEAs showed almost the same onset potential for oxygen reduction. These same potentials indicated that the amination did not disturb the inherent catalytic activities of Pt/C. In contrast, in the region of lower electrode potentials (-600 to -300 mV), the EDA-modified Nafion showed larger current densities than the K-form Nafion.

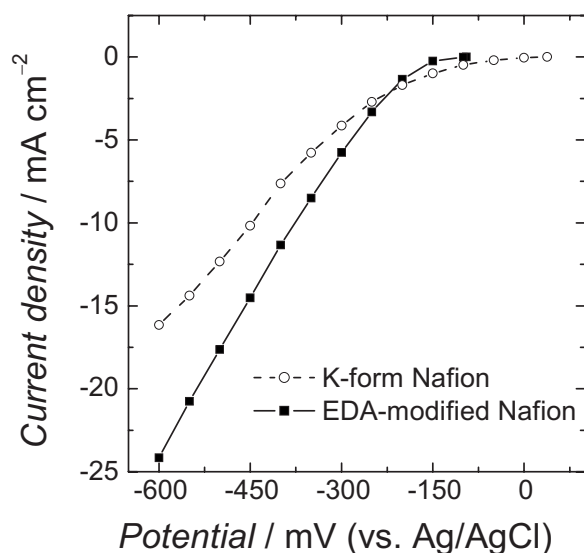


Figure 5. Steady-state polarization curves for oxygen reduction on (a) K-form Nafion coated Pt/C, (b) EDA-modified Nafion coated Pt/C. Loading amount of EDA-modified Nafion: 35 mg cm⁻²; temperature: 303 K; electrolyte: 1 mol dm⁻³ KOH; time: 600 s.

Generally, the polarization curves for oxygen reduction had two potential regions: charge-transfer control and diffusion control regions.²⁴ In the charge-transfer control region, catalytic activities are predominant to determine the current densities. In the diffusion control region, current densities are controlled by the diffusion of reactants and ions. In the lower potential region of Fig. 5, current densities were determined by the diffusion of O₂ and OH⁻. Because O₂ diffusion through the catalyst layers was not increased by the amination, higher current densities of half-MEAs of the EDA-modified Nafion ionomer were ascribed to the enhancement of OH⁻ ion diffusion.

Figure 6 shows the current densities for oxygen reduction as a function of the loading amount of the Nafion aminated by EDA molecules in catalyst layers. The maximum current density was obtained when the Nafion content was 5.5 mg cm⁻². Passalacqua and co-workers reported that their defined index, Nafion percentage (NFP), which is represented by the following Eq. 2

$$\text{NFP} = \frac{\text{mg Nafion cm}^{-2}}{(\text{mg Nafion cm}^{-2}) + (\text{mg cat cm}^{-2})} \times 100 \quad [2]$$

was important to determine the optimum Nafion content in catalyst layers.²⁵ In the present study, the optimum NFP was calculated to be 52% and this value was slightly larger than those reported by other groups.²⁶⁻²⁸

The comparison of reductive current densities for oxygen reduction among three half-MEAs with K-form and EDA- and DETA-modified Nafion ionomers is shown in Fig. 7. While K-form and EDA-modified Nafion showed similar behavior as shown in Fig. 6, the DETA-modified Nafion yielded much larger current densities. When the electrode potential was -500 mV (vs Ag/AgCl), the reductive current density of DETA-modified Nafion was 3.8 times larger than that of K-form Nafion and 2.9 times larger than that of EDA-modified Nafion. This superior performance of DETA-modified Nafion can be explained by the FTIR results that DETA-modified Nafion provided the larger amount of amine functional groups in the catalyst layer than EDA-modified Nafion.

As mentioned above, the amination process may proceed via the one-to-one reaction between an amine molecule and a sulfonic acid group of Nafion. Furthermore, the number of sulfonic acid groups in a catalyst layer was determined only by the Nafion content. If the Nafion contents in the catalyst layers were regulated at the same value, the number of amine molecules fixed with Nafion in the cata-

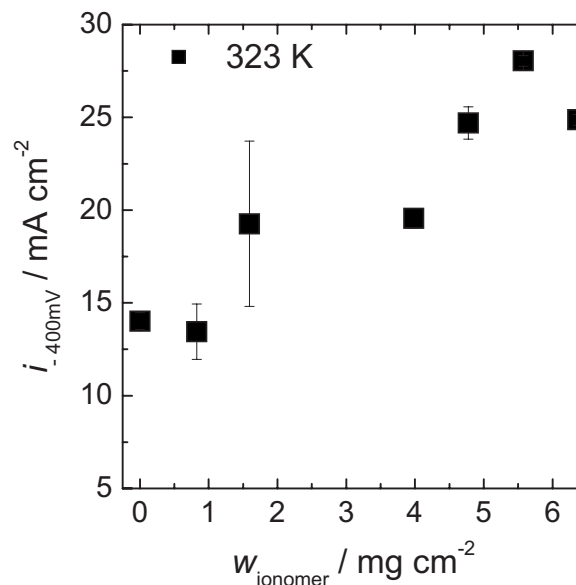
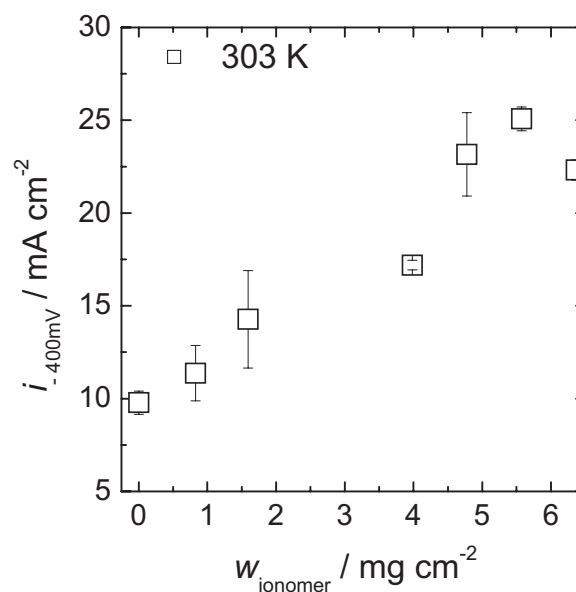


Figure 6. Current densities for oxygen reduction at the potential of -400 mV (vs Ag/AgCl) as a function of the loading amount of EDA-modified Nafion on Pt/C. Electrolyte: 1 mol dm⁻³ KOH. (Top) 303 K and (bottom) 323 K.

lyst layers must be uniform. Therefore, an important factor for better ion conductivities of an aminated Nafion is the number of amine groups one amine molecule has. Schematic illustrations to explain the amination process derived from the present paper are shown in Fig. 8. An EDA molecule has two amine functional groups in one molecule, and its one amine group is used to fix itself with Nafion, resulting in only one amine group available for OH⁻ conducting. In contrast, a DETA molecule has three amine groups in one molecule. Even if its one amine group is used, two amine groups can serve as OH⁻-conducting agent. As a result, the DETA-modified Nafion improved the TPB region in the catalyst layer more effectively than the EDA-modified Nafion.

Conclusions

The amination of Nafion ionomers with EDA and DETA offered a novel approach for introducing a OH⁻-conducting agent in catalyst

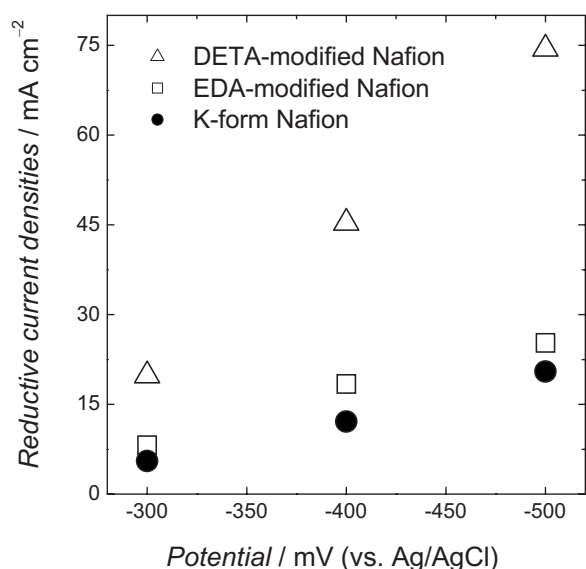


Figure 7. Reductive current densities of three different cathodes. Temperature: 323 K; oxygen flow: 50 mL min⁻¹.

layers. An amine molecule with more amine groups provided a more improved effect on the formation of a TPB region in the catalyst layers. This approach can be extended to other amines for exploring superior OH⁻-conducting materials and much more improved TPB regions.

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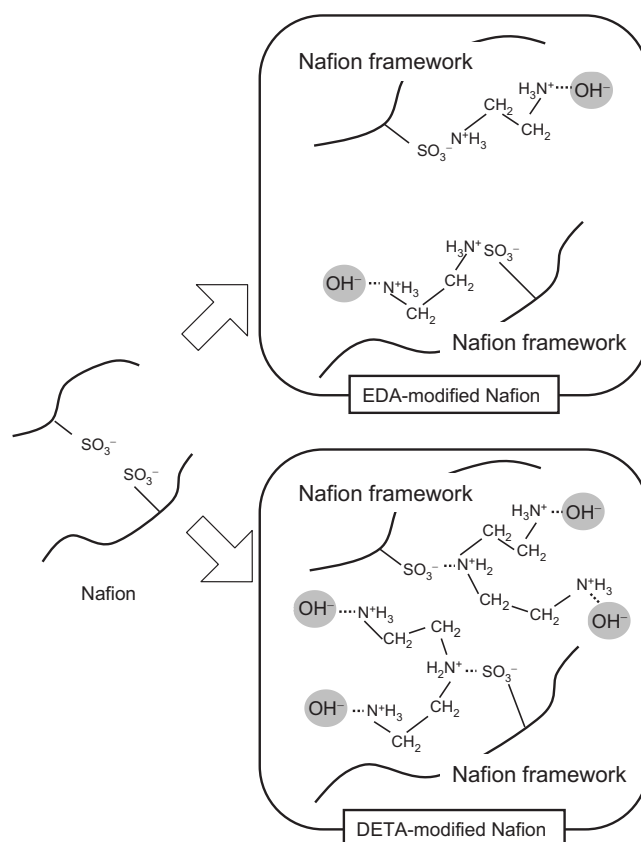


Figure 8. Schematic illustrations of the amine modification of Nafion with EDA and DETA.

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