Performance of solid alkaline fuel cells employing anion-exchange membranes

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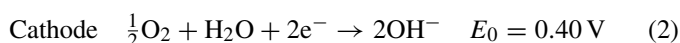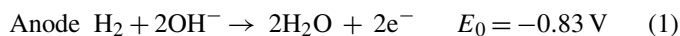
Abstract

For the performances of solid alkaline fuel cells (SAFCs) using anion-exchange membranes (AEMs), anion-exchange membranes were prepared via chloromethylation and amination of polysulfone and membrane-electrode assemblies (MEAs) were fabricated using the AEMs as an electrolyte, the ionomer binder prepared by the AEMs and Pt/C and Ag/C electrocatalysts as an anode and a cathode, respectively. Anion-exchange membranes were aminated by a mixing amine agent of trimethylamine (TMA) as a monoamine and various diamines such as N,N,N',N'-tetramethylmethanediamine (TMMDA), N,N,N',N'-tetramethylethylenediamine (TMEDA), N,N,N',N'-tetramethyl-1,3-propandiamine (TMPDA), N,N,N',N'-tetramethyl-1,4-butanediamine (TMBDA) and N,N,N',N'-tetramethyl-1,6-hexanediamine (TMHDA). Amination using various diamines enabled to investigate the effect of the length of alkyl chain of the diamines on membrane properties such as ion conductivity and thermal characteristics. The AEMs aminated by the amination agent of mixing TMA and TMHDA (with longer alkyl chain) showed better hydroxyl ion conductivity and thermal stability than those aminated by a diamine. The H_2/air SAFC performance of the MEA with 0.5 mg cm^{-2} Pt/C at the anode and the cathode, respectively, was comparable to one with 0.5 mg cm^{-2} Pt/C at the anode and 2.0 mg cm^{-2} Ag/C at the cathode, *i.e.*, approximately 28–30 mW cm^{-2} of the peak power density range.

1. Introduction

Limitation of the use of acidic polymeric electrolytes (*e.g.*, in polymer electrolyte membrane fuel cells and direct methanol fuel cells) – (i) slow electrode-kinetics, (ii) CO poisoning of Pt and Pt-based electrocatalysts at low temperatures and (iii) high costs of the membrane, catalyst – can be overcome by using alkaline polymeric electrolytes (*i.e.*, anion-exchange membranes, AEMs). It is well known that electro-kinetics of oxygen reduction in an alkaline medium is much enhanced in comparison with an acid medium as shown in the following equations:

$$\text{Anode} \quad H_2 + 2OH^- \rightarrow 2H_2O + 2e^- \quad E_0 = -0.83\,V \quad (1)$$

$$\text{Cathode} \quad \tfrac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2OH^- \quad E_0 = 0.40\,V \quad (2)$$

$$\text{Overall} \quad H_2 + \tfrac{1}{2}O_2 \rightarrow H_2O \quad E_0 = 1.23\,V \quad (3)$$

It leads to use non-precious catalysts (*e.g.*, Ni, Ag, perovskite-type oxides, etc.) [1–4].

Fuel cells using AEMs have the electrochemical and structural analogy with alkaline fuel cells (AFCs) except the use of solid-state electrolytes instead of liquid alkaline solutions, *e.g.*, KOH(l). That is why it can be called as solid alkaline fuel cells (SAFCs) as shown in Fig. 1. The use of AEMs prevents undesirable formation of carbonate/bicarbonate in the liquid alkaline solutions due to CO_2 reactions from the oxidant gas stream at cathodes of AFCs.

For good SAFC operations good membrane-electrode assemblies (MEAs) are required. An MEA consists of a membrane, two electrodes, and two pieces of gas diffusion layer (*e.g.*, carbon paper, felt or cloth). One of main components in MEAs is a membrane, *i.e.*, anion-exchange membrane. AEMs with good properties such as high OH$^-$ conductivity and good thermal and

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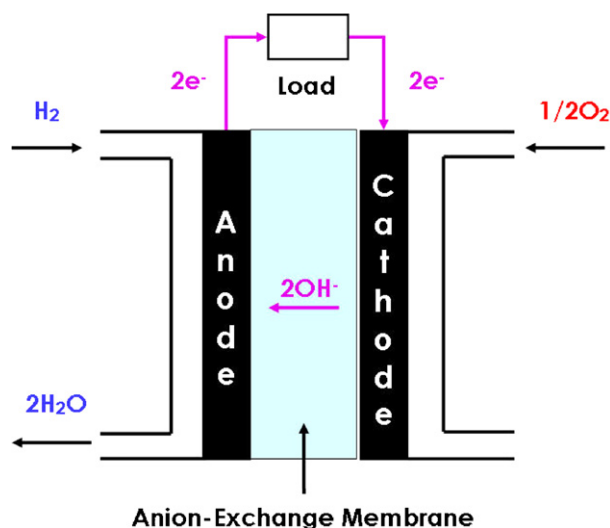*E-mail address:* park@kier.re.kr (J.-S. Park).

Fig. 1. A schematic diagram of solid alkaline fuel cells (SAFCs) using anion-exchange membranes.

chemical stability are essential. Many researchers have reported anion-exchange membranes for fuel cell applications [1,3–5] because most commercial available AEMs are too much thick (200–300 μm) for fuel cell applications and have problems on (i) the chemical stability, *i.e.*, nucleophillic displacement by the hydroxyl ions for the quaternary ammonium functional groups and (ii) the thermal stability of styrene-type backbone.

In our previous study [1], the anion-exchange membranes were prepared by aminating the chloromethylated polymer using various amine agents: (i) trimethylamine (TMA), (ii) N,N,N',N'-tetramethyl-1,6-hexanediamine (TMHDA) and (iii) the mixture of TMA and TMHDA with a molar ratio of 3:1. As a result, it was noted that OH$^-$ conductivity and thermal stability of the AEMs followed the order: AEM aminated by TMA/TMHDA mixture > TMA > TMHDA. The lowest OH$^-$ conductivity and thermal stability of the AEMs aminated by the diamine was due to extremely short amination time which resulted from quick cross-linking of halomethylated polymers, finally resulting in gelation. However, the mixture of the amine agents allowed having enough amination time which was as same as the monoamine did. Komkova et al. [6] reported the properties and stability of the AEMs in the alkaline solution. They used various diamines with different length of aliphatic chain to aminate the halomethylated polymers and concluded that the membrane properties such as resistance and water uptake and the degradation of the AEMs in an alkaline solution depended on the length of the alkyl chain in the diamine units.

Another essential component of MEAs for SAFC operations is two electrodes, *i.e.*, anode and cathode. MEAs. As mentioned earlier, SAFCs can use non-precious catalysts such as nickel or silver due to the favorable cathodic reaction. In this regard, Varcoe et al. showed the H$_2$/O$_2$-SAFC performance results of MEAs with Pt/C, Ag/C and Au/C cathode.

In this study we aim at investigating the length effect of alkyl chain of diamines on membrane properties such as OH$^-$ conductivity and thermal stability when halomethylated polymers are aminated by a diamine or a mixture of monoamine and diamine. Furthermore, the performances of the MEAs employing the AEMs and commercially available non-precious Ag/C catalyst with different loading at cathode are investigated and the loading amount of Ag/C is found in the performance comparable to MEAs with Pt/C cathode.
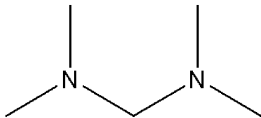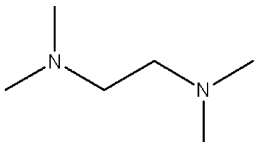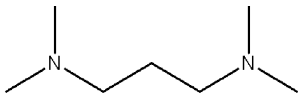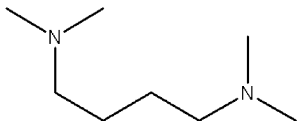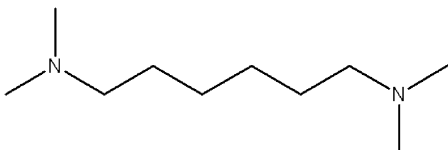
2. Experimental

2.1. Preparation of anion-exchange membranes

Polysulfone (Udel$^®$ P-1700, Solvay Advanced Polymers, L.L.C., USA)-based AEMs were prepared by chloromethylation using chloromethylmethylether (CMME) and amination using mono- (trimethylamine, TMA, Sigma–Aldrich) and/or diamines. They were used without further purification. Chloromethylation of Psf was carried out in a four-neck round-bottom flask fitted with a mechanical stirrer. 12.8 g of the Psf was dissolved in 87.2 g of 1,1,2,2-tetrachloroethane (TCE) to make a 12.8 wt.% solution. Then, 9.5 g of chloromethyl-methylether (CMME) (Psf:CMME = 1:4 in mol) was added in the presence of ZnCl$_2$ as catalyst. The solution was transferred to the reaction flask and heated over an oil bath to 40 °C under an N$_2$ atmosphere for 3.5 h. The chloromethylated polysulfone (CMPsfs) were precipitated in methanol, washed for 24 h and then dried in a vacuum oven for 24 h at 80 °C. For amination, dried CMPsfs were dissolved to be 12.5 wt.% solutions in DMAc. Two different types of the amination agents were used such as (i) diamines such as N,N,N',N'-tetramethylmethanediamine (TMMDA, Acros-Organics), N,N,N',N'-tetramethylethylenediamine (TMEDA, Fluka), N,N,N',N'-tetramethyl-1,3-propandiamine (TMPDA, Acros-Organics), N,N,N',N'-tetramethyl-1,4-butanediamine (TMBDA, Acros-Organics) and N,N,N',N'-tetramethyl-1,6-hexanediamine (TMHDA, Acros-Organics) and (ii) mixtures of mono-/diamine (TMA:diamine = 3:1 in a molar ratio and CMPsf:amine agent = 1:4 in a molar ratio). The diamines used in this study are summarized in Table 1. Each amination agent was added in the solutions. The solutions were transferred to the reaction flask and heated in an oil bath to 40 °C for 3 min (the reason will be discussed later) and 48 h (optimized in the previous study [1]), respectively, under vigorous stirring. The resulting solutions were precipitated in methanol, washed in deionized water for 24 h at 80 °C. Dry aminated CMPsfs were dissolved in DMAc to be 11 wt.% solutions. The solutions were degassed under vacuum and were cast onto flat-bottom Petri dishes for membrane formation. The membranes were dried in an oven at 80 °C for 12 h and then under vacuum at 100 °C for 1 day. Dry membranes were peeled off from the substrate with deionized water. All the prepared AEMs were mechanically stable and transparent. Thickness range of all the membranes was in 85–100 μm. Membrane thickness for MEA fabrication was in 90 ± 2 μm. The membranes were soaked in a 0.5 M KOH solution for over 1 day prior to their use.

When the AEMs were aminated by the diamine, the gelation of the polymer solution took place. The gelation time with the type of diamine is summarized in Table 1. As the alkyl chain increases the gelation time substantially decreases. In other

Table 1
Type of diamines used in this study for amination and gelation time when AEMs were aminated by a 1:4 molar ratio of halomethylated polymer to diamine

Diamine compound	Chain structure	Gelation time (min)
N,N,N′,N′-Tetramethylmetanediamine (TMMDA)		71
N,N,N′,N′-Tetramethylethylenediamine (TMEDA)		41
N,N,N′,N′-Tetramethyl-1,3-propandiamine (TMPDA)		13.5
N,N,N′,N′-Tetramethyl-1,4-butanediamine (TMBDA)		12
N,N,N′,N′-Tetramethyl-1,6-hexanediamine (TMHDA)		7.2

words, the amination by the diamine with longer alkyl chain greatly influenced the cross-linking of CMPsfs. In order to the net effect of the length of alkyl chain of diamines on membrane properties, the same amination time, 3 min, was used. As a result, the AEMs aminated by the diamine were mono- and/or bi-quaterized as shown in Fig. 2a and the amination with the mixture of the mono- and diamine proceeds as a quaternization by the monoamine and a mono- and bi-quaternization by the diamine, simultaneously as shown in Fig. 2b.

2.2. Characterization of the anion-exchange membranes

The OH⁻ conductivity of the membranes was measured by an AC impedance spectroscopy using a Solarton 1260 frequency response analyzer interfaced to an EG&G 270 multistat. The measurement was carried out in the potentiostatic mode over the frequency range from 1 Hz to 1 MHz with an oscillating voltage of 5 mV. The laboratory-made four-probe conductivity cell configuration is found elsewhere [1]. The conductivity of the samples was calculated by the following equation:

$$\sigma = \frac{L}{RWd} \qquad (4)$$

where σ is the hydroxyl ion conductivity, L the length between two potential sensing platinum wires, R the membrane resistance derived from the impedance value at zero phase angle, W the width of the potential sensing platinum wire and d is the membrane thickness. The membranes for each measurement

were prepared by the following procedures: (i) the samples were equilibrated in 0.5 M KOH for 1 day and KOH solution on the surface of the samples was removed; (ii) the samples were placed in the vessel at the same conditions (*i.e.*, temperature, 25 °C and relative humidity, 100%) at which the samples were measured.

Water content of the membranes was determined from the difference in weight before and after hydration. Membrane samples were dried at 110 °C under vacuum until constant weight is recorded as W_{dry}. The samples were then immersed in deionized water for 1 day at the given temperature (*i.e.*, 25 °C), removed from water, surface attached water was wiped out with filter paper and immediately weighed (W_{wet}). Water content was reported as absorbed water weight percent with respect to dry membranes:

$$\text{water content}\,(\%) = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100 \qquad (5)$$

Thermogravimetric analysis (TGA) was carried out on TGA 2050 instrument from TA instruments, USA. Initially the samples were heated under nitrogen atmosphere up to 150 °C, cooled down to 80 °C to remove moisture of the samples and reheated until 400 °C at the rate of 10 °C min⁻¹ under nitrogen atmosphere.

2.3. Fabrication of membrane-electrode assemblies (MEAs)

For fabrication of membrane-electrode assemblies (MEAs) the aminated CMPsf membranes prepared in this study were
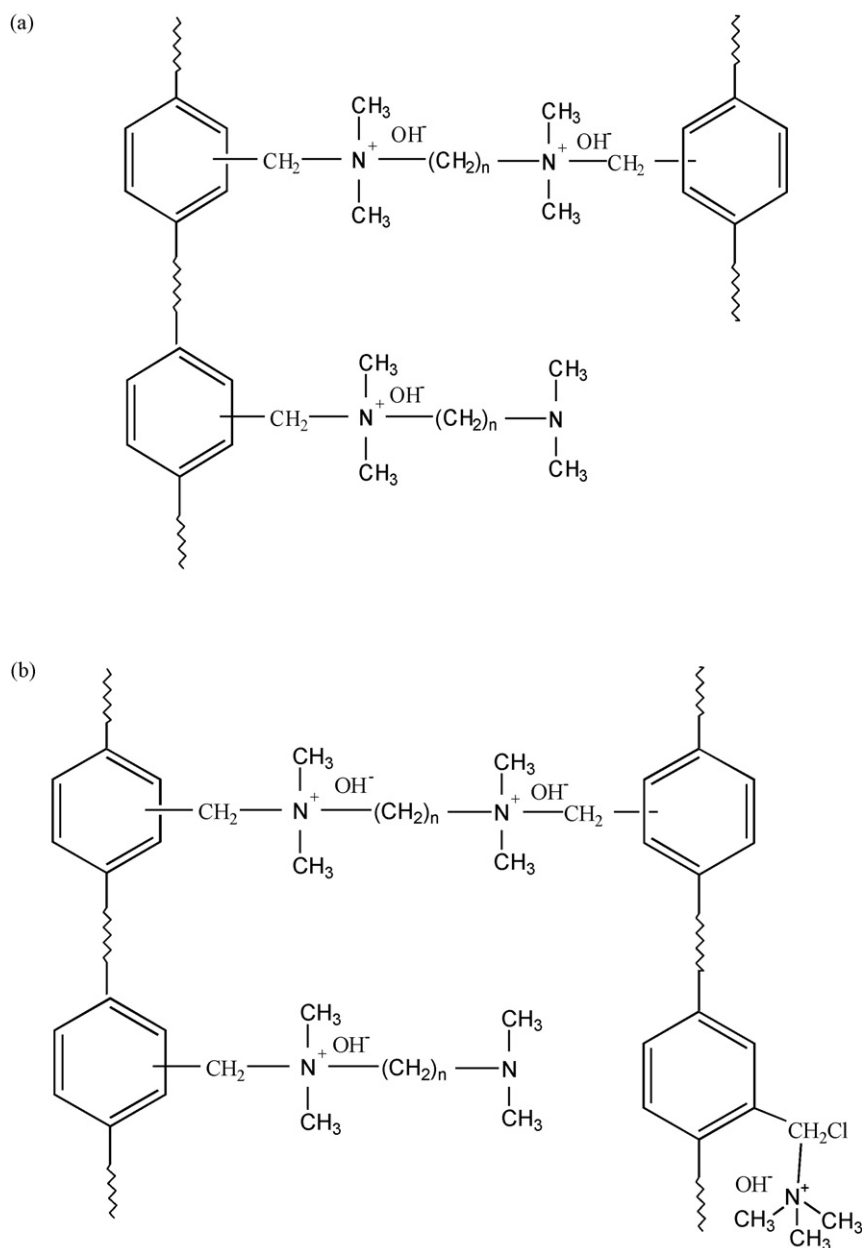
Fig. 2. (a) Mono- and bi-quaternization of CMPSfs by (a) the diamine with various length of the alkyl chain and (b) quaternization and mono/bi-quaternization of CMPSfs by the mixture of the mono- and diamine with various length of the alkyl chain (n is the number of the alkyl chain in diamines).

employed as polymeric electrolyte. The MEAs contained precious and non-precious electrocatalysts such, respectively, as Pt/C (40 wt.%, Johnson & Matthey) and Ag/C (40 wt.%, E-Tek). Pt/C was used as anode and Ag/C and Pt/C as cathode. Ionomer binder was prepared using the aminated CMPSf to be a 5 wt.% solution in DMAc. The catalyst slurries were prepared by mixing the catalyst powder, deionized water and the 5 wt.% ionomer binder and were sprayed on PTFE-impregnated Toray 250 carbon paper (waterproof by 8% PTFE). Finally, the electrodes on the carbon paper sandwiched the membrane under 100 kgf cm^{-2}. A few pieces of fabricated MEAs were evaluated at H$_2$/air, 100% RH, 60 °C and ambient pressure for solid alkaline fuel cells (SAFCs). Detail experimental conditions for SAFC operations are summarized in Table 2.

3. Results and discussion

Sata et al. reported the electrochemical properties of anion-exchange membranes with various anion-exchange groups [7]. The electrical resistance of the membrane increased with increasing chain length of the alkyl chain of monoamines because larger amines are difficult to react with the chloromethyl groups of the membranes due to steric hindrance. This steric hindrance arises from the alkyl groups attached to positively charged amine nitrogen. In other words, as alkyl chain length increased the steric complexity is severed, resulting in hindering hydrated-ion exchanging. Komkova et al. reported that even a significant excess of the diamine with shorter alkyl chain did not produce good AEM because the shorter chain diamine might be

Table 2
Experimental conditions for MEA fabrication and SAFC operation

SAFC	Anode	Cathode
Catalyst	Pt/C[a]	Pt/C or Ag/C[b]
Ionomber binder[c]	TMA/TMHDA-aminated CMPSf	TMA/TMHDA-aminated CMPSf
Catalyst loading amount (mg cm^{-2})	0.5	0.5 (Pt/C); 0.5/1.0/2.0 (Ag/C)
Active area (cm^2)	10	10
Fuel/oxidant[d]	H_2	Air
Utilization (%)	70	40
Cell temperature (°C)	60	60

[a] 40 wt.% from Johnson & Matthey.
[b] 40 wt.% from E-Tek.
[c] 5 wt.% solution in DMAc.
[d] Humidified at 55 °C.

difficult to make cross-linking between halomethylated polymers and diamine groups due to their short aliphatic chain. This fact needed different excess amount of diamines with alkyl chain length to produce AEMs. In this study, the mixtures of a monoamine and diamines with different alkyl chain length were used to aminate halomethylated polymer. It is expected that there is no aforementioned steric hindrance by monoamine because the same type of monoamine was used. In this view, it can be expected that longer alkyl chain in diamine mitigates the steric hindrance. In addition, the net effect of alkyl chain in diamine on the membrane properties will be discussed because the same amount of diamine in mole with respect to halomethylated polymer was added.

Fig. 3 shows the OH$^-$ conductivity and water uptake with the length of alkyl chain in diamine. The amination with TMA, i.e., N(CH$_3$)$_3$, has the highest degree of conversion of –CH$_2$Cl groups (the methylated part of the CMPsf) to the positively charged groups [8]. In Fig. 3a, this fact is proved in that the OH$^-$ conductivity for the TMA amination (at $n = 0$) is higher than all the diamines' amination except the TMHDA amination. In addition, the AEMs aminated by the mixture (TMA:diamine = 3:1 in mole) have higher conductivity than those by the diamines. In case of TMHDA, the conductivity result is consistent with the previous result [1]. In this study, for monoamine amination, TMA was added excessively to the chloromethylated polymers (CMPsf:TMA = 1:4 in mol). Similarly, for the mixture amination, TMA was excessive to give a quaternization (i.e., attachment of quaternary ammonium groups to CMPsf) to the polymers because it is general that OH$^-$ conductivity decreases, resulting from a loss of ion-exchange capacity due to cross-linking, but there is no loss in conductivity for the mixtures except the TMA/TMMDA mixture. In Fig. 3a, the conductivity trend for diamine amination shows that the conductivity increases with increasing the alkyl chain length. It can be inferred that the cross-linking by a diamine with shorter alkyl chain length causes steric hindrance on hydrated-ion exchanging due to the short interval between two polymers (see Fig. 2a) similar to the steric hindrance by the amination of monoamine with longer alkyl chain. Furthermore, it supports the fact that the conductivity for the TMA/TMMDA mixture is the lowest. An increase in conductivity for diamines' amination with increas-

ing the alkyl chain length infers that excess of diamine was added due to the consistence with the previous result [6] which is that, at excess amount of diamine, the amount of the quaternary ammonium groups increases more rapidly than the amount of the tertiary ammonium groups, indicating that the cross-linking is favored in comparison to the mono-quaternization reaction (see Fig. 2a). It can be expected that the conductivity might decrease if mono-quaternization was favored due to the steric hindrance by long side chain attached to the positively charged amine nitrogen (see Fig. 2a). Fig. 3b shows a similar trend to the conductivity result. This similar trend well supports the steric hindrance on hydrated-ion exchanging.

From the conductivity and water uptake results, it can be fully expected that the cross-linking property of diamines influences thermal stability of AEMs. In fact, Fig. 4a shows better thermal stability for diamines' amination (only in case of $n \leq 3$) than
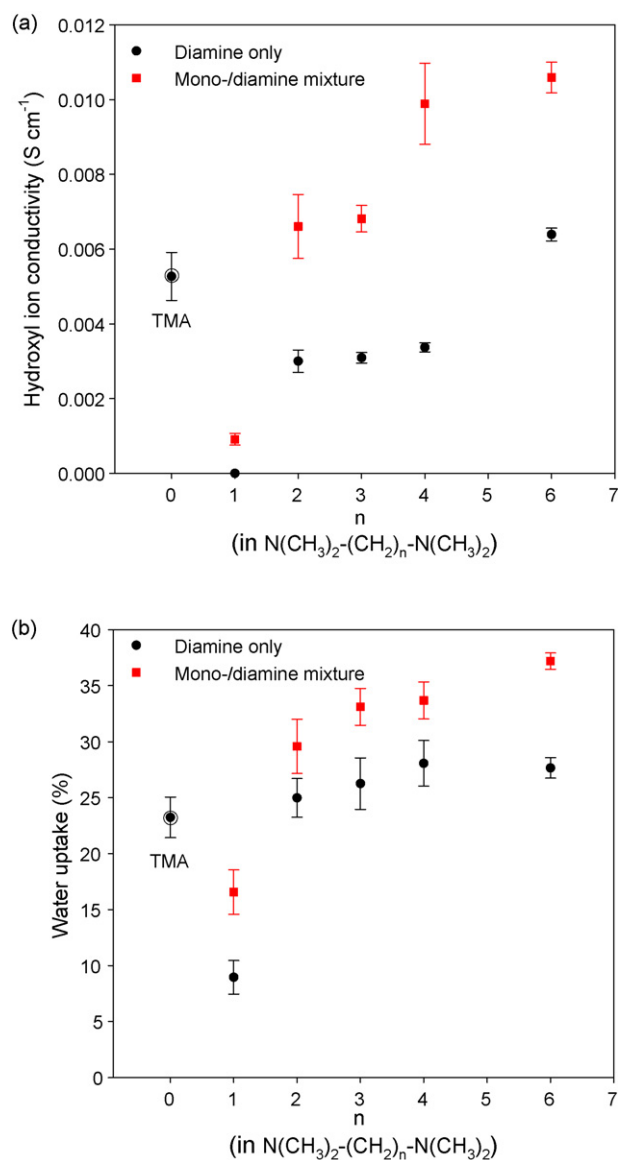

Fig. 3. (a) OH$^-$ conductivity and (b) water uptake of the AEMs aminated by the diamines and the mixtures of the mono- and diamine as a function of the number of the alkanoic chain in diamines.
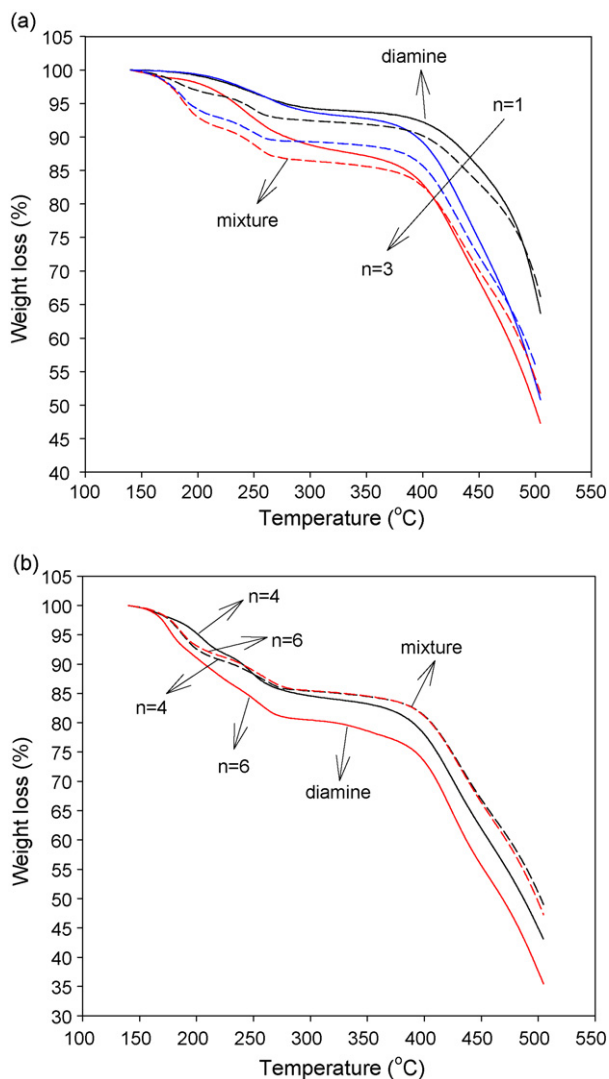
Fig. 4. Thermogravimetric analysis curves of the AEMs aminated by diamines and the mixtures of the mono- and diamine ((a) $n \leq 3$ and (b) $n \geq 4$ where, n is the number of the alkyl chain in diamines).

for mixtures' amination due to the favored bi-quaternization by diamines. However, this trend is changed for $n \geq 4$. The thermal property for TMBDA amination and the mixture of TMA/TMBDA is similar and the better thermal property of the AEM aminated by the mixture of TMA/TMHDA than by TMHDA is shown. It is consistent with the result in the previous study [1] as aforementioned in the Introduction section. It might
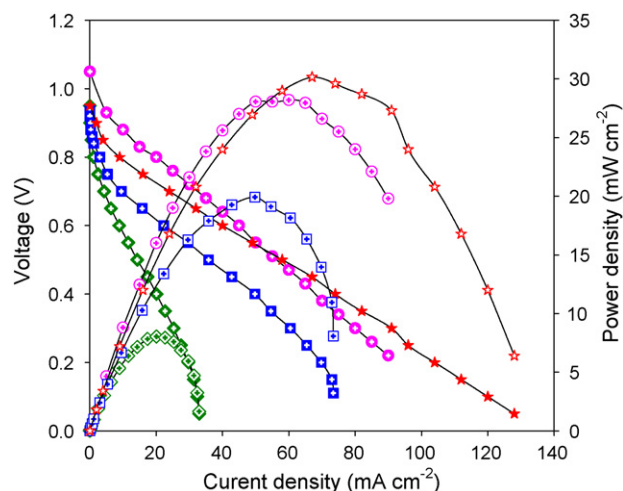

Fig. 5. I–V polarization curves of the MEAs employing the AEMs aminated by the mixture of TMA and TMHDA with a ratio of 3:1 in mole as membrane and the Pt/C (40 wt.%, 0.5 mg cm^{-2}) anodes and various cathodes (Diamond: Ag/C, 40 wt.%, 0.5 mg cm^{-2}; Square: Ag/C, 40 wt.%, 1.0 mg cm^{-2}; Star: Ag/C, 40 wt.%, 2.0 mg cm^{-2}; Circle: Pt/C, 40 wt.%, 0.5 mg cm^{-2}) as electrode.

be due to the higher interaction between ammonium groups and hydrated-hydroxyl ions. As mentioned earlier, AEMs aminated by the mixture of TMA/diamines have higher conductivity and water uptake than those by diamines due to more ion-exchanging sites by the quaternization reaction of TMA and AEMs aminated by amine agents including diamine with longer alkyl chain have less steric hindrance. In other words, it can be inferred that the effect of the thermal stability dominated by the strong interaction of cross-linking becomes less than by the strong interaction between ammonium groups and hydrated OH$^-$ ions for $n \geq 4$. As a result, in views of electrochemical and thermal properties, it can be concluded that the TMA/TMHDA-aminated AEM is preferable to make MEAs for SAFC operations.

Fig. 5 shows the current–voltage relationships of the MEAs containing the TMA/TMHDA aminated-AEM and four different cathodes. The performance results are summarized in Table 3 (denoted as different marks such as diamond, square, star and circle). The open circuit voltage (OCV) of the MEA containing both Pt/C electrodes is 100 mV higher than the MEAs containing Pt/C-anode and Ag/C cathode, indicating that Pt/C is still a good electrocatalyst at high pH. However, the latter MEAs also have relatively good OCVs. The peak power performance of the 0.5 mg cm^{-2} Pt/C anode and 0.5 mg cm^{-2} Ag/C cathode MEA (the diamond mark) was much lower than the 0.5 mg cm^{-2}

Table 3
SAFC performance results of the MEAs employing the AEM aminated by the mixture of TMA and TMHDA with a 3:1 molar ratio and four different cathodes along with the same 0.5 mg cm^{-2} Pt/C anode

Symbol in Fig. 5	Type of electrocatalyst (loading amount in mg cm^{-2})		OCV (V)	Ohmic resistivity of the assembled cell (Ω cm^2)	Peak power density (mW cm^{-2})
	Anode	Cathode			
Diamond	Pt/C (0.5)	Ag/C (0.5)	0.95	17.8	8.1 at 0.40 V
Square	Pt/C (0.5)	Ag/C (1.0)	0.94	8.2	19.9 at 0.40 V
Star	Pt/C (0.5)	Ag/C (2.0)	0.95	1.5	30.1 at 0.42 V
Circle	Pt/C (0.5)	Pt/C (0.5)	1.05	2.3	28.2 at 0.47 V

Pt/C anode and cathode MEA (the circle mark) (28% of the latter performance). This results from the poor size distribution of the Ag/C electrocatalyst used in this study (not shown here) detected by transmission electron microscopy (TEM), compared with that of the Pt/C, which is consistent with the previous study [4]. Despite the poor size distribution, at the higher loading amount of Ag/C, the 0.5 mg cm^{-2} Pt/C anode and 2.0 mg cm^{-2} Ag/C cathode MEA (the star mark) shows the comparable performance obtained from the circle-marked MEA. This result indicates that non-precious catalysts (*i.e.*, Ag in this study) enable to have a similar oxygen reduction reaction (ORR) performance compared with Pt, which is consistent with the previous study [9]. It is, however, noted that the circle-marked MEA have a higher voltage at peak power even though the slightly higher performance at peak power for the star-marked MEA was shown. The ohmic resistivity of the two MEAs in Table 3 reflects the higher peak power of the star-marked MEA, and the higher voltage of the circle-marked MEA at peak power indicates that Pt/C still has slightly better ORR performance.

4. Conclusions

In this study, various AEMs were prepared to find out good AEMs favored for SAFC operations, which have higher OH^{-} conductivity and thermal property. Four different types of MEAs were investigated to evaluate the AEM and the possibility of using non-precious catalyst at cathode. For the favored AEM property, the mixture of mono- and diamine was used and the diamine with longer alkyl chain in the mixture enhanced OH^{-} conductivity and thermal property of AEMs. The MEA employing the AEM and Pt/C anode and cathode showed fairly good performance, indicating that the AEM prepared in this study acts as good alkaline electrolyte for SAFC operations. Furthermore, the MEA using the non-precious catalyst, *i.e.*, Ag/C, at cathode had the comparable performance compared with that using Pt/C even though Ag/C had a poor size distribution and slightly lower ORR performance. It is evident that SAFCs allow using non-precious catalysts at cathode and even at anode and the extensive work to introduce non-precious catalysts into SAFC MEAs having the performance comparable with MEAs using Pt/C is further required.

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