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High performance nitrile copolymers for polymer electrolyte membrane fuel cells[☆]

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ABSTRACT

This paper reports the fuel cells (DMFC and PEMFC) performance using sulfonated poly(arylene ether ether nitrile) (SPAEEEN) copolymers containing sulfonic acid group arranged in structurally different ways. The membrane electrode assembly (MEA) fabricated from SPAEEEN containing 60 mol% of angled naphthalenesulfonic acid group (*m*-SPAEEEN-60) had superior performance over those derived from pendent naphthalenesulfonic acid group (*p*-SPAEEEN) or sulfonated hydroquinone (HQ-SPAEEEN) in H₂/air and/or DMFC conditions. For example, the current density of the MEA using *m*-SPAEEEN-60 at 0.5 V and 2.0 M methanol was 250 mA/cm², whereas the current densities of the MEAs using *p*-SPAEEEN-50 and HQ-SPAEEEN-56 were 185 and 190 mA/cm², respectively. In addition, compared with the sulfonated polysulfone (BPSH-35) and Nafion membranes, the copolymer containing nitrile group showed the improved cell performance. For example, the power density of the MEA using *m*-SPAEEEN-60 at 250 mA/cm² and 2.0 M methanol was 125 mW/cm², whereas the power densities of the MEAs using sulfonated polysulfone (BPSH-35) and Nafion were 115 and 113 mW/cm², respectively. *m*-SPAEEEN-60 showed stable cell performance during extended operation (>100 h).

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1. Introduction

Fuel cells, especially proton exchange membrane fuel cells (PEMFCs), are believed to be promising for transportation applications because of their fast start up and immediate response to change in the demand for power and their tolerance to shock and vibration due to plastic materials and immobilized electrolyte. Current demands to improve PEMFC efficiencies and to reduce cost and complexity of the systems require operating temperatures above 100 °C. The membranes must be designed to maintain high proton conductivity at these temperatures, preferably approaching 100 mS/cm, in combination with a high chemical and mechanical stability to endure fuel cell operation in excess of 5000 h [1].

Current PEMFCs typically run at ≤80 °C because of the working temperature limitation of the materials (usually Nafion). New polymer electrolyte membranes (PEMs) that have high proton conductivity, low reactant permeability and reduced water uptake

(WU) at high temperature are required for fuel cell applications [2,3]. The requirements for DMFC membranes are somewhat related to those of PEMFC, but with an additional factor that since the fuel supplied to the anode is in liquid rather than gaseous form, swelling and crossover by methanol fuel must be controlled. The high permeability of methanol fuel from the anode to the cathode (crossover) through the currently used perfluorinated sulfonic acid membrane (Nafion) and the sluggish oxidation kinetics of methanol at the cathode pose serious problems for the commercialization of DMFC technology [4]. As a result, considerable efforts have been directed to creating PEM materials with reduced methanol permeability while maintaining high proton conductivity. Most of this research has been limited to the polymer synthesis and characterization of stand-alone membranes, while much fewer membrane electrode assembly (MEA) studies of hydrocarbon-based sulfonated copolymers have been conducted for fuel cell application because of issues with dimensional swelling, high methanol permeability and oxidative and hydrolytic stability under fuel cell operating conditions [5–9]. Some polymer systems with optimized structures and ion exchange capacity (IEC) show performance comparable to that of Nafion. It was reported that the DMFC performance of sulfonated poly(ether ether ketone) (SPEEK) with a degree of sulfonation (DS) of ~50% is comparable to or better than that of Nafion 115 [6]. However, the operating temperature was limited to 65 °C, because the post-sulfonated copolymers

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exhibited excessive swelling at higher temperatures as well as problems with mechanical integrity [6]. Fenton reported that a series of multilayer structure membranes, with a thin and lower DS (41%) SPEEK barrier layer covered by two higher DS (60%) SPEEK outer layers, showed significantly suppressed methanol crossover and acceptable cell resistance [10]. Harrison et al. reported that wholly aromatic sulfonated poly(arylene ether sulfone)s prepared by direct copolymerization with a degree of disulfonation of 35% (BPSH-35) outperformed Nafion 117 at 80 °C under DMFC conditions [8]. Although the membranes outperformed Nafion, issues of interfacial incompatibility between the membrane and Nafion-based electrodes remained that limited long-term performance. Reported interfacial losses and long-term stability were improved by tuning water uptake of the PEMs to better match the characteristics of the electrodes [8,9].

Recently, it was found that the introduction of nitrile groups into sulfonated poly(aryl ether sulfone) and sulfonated poly(aryl ether ketone)s reduced their water uptake and dimensional swelling when compared with the polymers that did not contain nitrile, at similar ion exchange capacities [11–14]. In addition, the introduction of nitrile groups into polymer chains is thought to be beneficial for composite membranes as promoting adhesion of the polymeric matrix to inorganic fillers [15,16]. The DMFC performance of MEAs using nitrile copolymers has been reported as superior to either Nafion or BPSH MEAs [4]. The copolymers were derived from sulfonated dihalodiphenylsulfone monomer and contained both sulfone and nitrile. However, the increase in proton conductivity and decrease in water uptake of this copolymer could not be wholly attributed to incorporation of benzonitrile groups because this copolymer was also partially fluorinated. We synthesized sulfonated poly(aryl ether ether nitrile)s (SPAEEENs) [15,17] derived from sulfonated dihydroxyaryl monomers, and also reported that the PEM properties of copoly(aryl ether ether nitrile)s containing sulfonic acid bonded to naphthalene in structurally different ways [16], which are structurally new polymers with fully nitrile-based main-chain at higher nitrile concentrations to those reported before.

Herein, we report the comparative PEMFC and DMFC performance of poly(arylene ether ether nitrile) copolymers containing sulfonic acid group bonded in structurally different ways (*m*-SPAEEENs, *p*-SPAEEENs, and HQ-SPAEEENs), which are non-fluorinated and have nitrile groups in both the hydrophilic and hydrophobic repeat units. The DMFC performance of the MEAs is compared at 0.5 and 2 M methanol feed concentration. Our goal is to investigate the effect of sulfonic acid position on the fuel cell performance of similarly structured aromatic poly(arylene ether ether nitrile) copolymers and provide important insight on the benefits of highly conductive, low methanol permeability and low water swelling nitrile copolymers over current state of the art membranes.

2. Experimental

2.1. Preparation of materials

Aromatic poly(arylene ether ether nitrile)s containing naphthalene structure with sulfonic acid groups *meta* to ether linkage (*m*-SPAEEEN), pendent on a phenyl ring (*p*-SPAEEEN) and sulfonated hydroquinone (HQ-SPAEEEN) were prepared via direct aromatic nucleophilic substitution polycondensation of 2,6-difluorobenzonitrile (2,6-DFBN), 4,4'-biphenol (4,4'-BP), and one of the sulfonated monomers 2,8-dihydroxy-naphthalene-6-sulfonate sodium salt (2,8-DHNS-6), 2,3-DHNS-6 or sulfonated hydroquinone (SHQ) [16–18]. The mol ratio of sulfonated 2,8-DHNS-6, 2,3-DHNS-6 or SHQ monomers to unsulfonated 4,4'-biphenol monomer for this study was 50:50 (*m*-SPAEEEN-50, *p*-SPAEEEN-50), 56:44 (HQ-SPAEEEN-56) and 60:40 (*m*-SPAEEEN-60, *p*-SPAEEEN-60). It is important to note here that the polynitrile copolymers HQ-SPAEEEN-56, *m*-SPAEEEN-60, and *p*-SPAEEEN-60 were selected for this study so as to have the same IEC_w values (1.9 mequiv./g). The polynitrile copolymer membranes cast from in the sodium sulfonate form were converted to the corresponding acid form by a reported procedure [18,19]. Chemical structures of each copolymer are shown in Fig. 1. The polynitrile copolymer membranes were compared against two types of membranes. The widely utilized perfluori-

Fig. 1. Chemical structures of sulfonated (aryl ether ether nitrile)s and sulfonated poly(arylene ether sulfone)s (BPSHs).

nated sulfonic acid Nafion membranes with various thicknesses (DuPont, EW = 1100) were used as a universal standard comparison. In addition, the non-fluorinated hydrocarbon copolymer sulfonated biphenylpolysulfone (BPSH) was also used.

2.2. Characterization methods

2.2.1. Water uptake and ion-exchange capacity

The membrane density was measured from a known membrane dimension and weight after drying at 75 °C for 2 h. Water uptake was measured after drying the membrane in acid form at 100 °C under vacuum overnight. The dried membrane was immersed in water at 30 °C and periodically weighed on an analytical balance until a constant water uptake weight was obtained. Then, the volume-based water uptake (WU) was obtained. A volume-based IEC (IEC_V) was obtained by multiplying the membrane density by the IEC_W values, which were estimated from the sulfonic acid content (SC) in the copolymer structure. This calculation resulted in IEC_V (dry) based on the dry membrane density. An IEC_V (wet) was then calculated based on membrane water uptake.

2.2.2. Proton conductivity

The proton conductivities of the membranes were estimated from AC impedance spectroscopy data using a Solartron 1260 gain phase analyzer. Each specimen was placed into water with a temperature controlled cell open to the air by a pinhole. The conductivity (σ) of the samples in the longitudinal direction was calculated, using the relationship $\sigma = L/(R \times d \times W)$ where L is the distance between the electrodes, d and W are the thickness and width of the sample stripe, respectively. R was derived from the low intersect of the high frequency semi-circle on a complex impedance plane with the $Re(Z)$ -axis.

2.2.3. H_2 and O_2 gas permeability

The membrane was immersed in water at 30 °C. The water on the surface was removed. The gas permeabilities of the membranes were measured by the constant volume method. The membrane area was 10 cm². The feed pressure and temperature were kept at close to 1 atm and 35 °C, respectively.

2.2.4. Membrane electrolytes assemblies

MEAs were prepared from standard catalyst inks using a known procedure [4]. Unsupported platinum (6 mg/cm²) and platinum–ruthenium (10 mg/cm²) catalysts (Johnson Matthey) were used for the DMFC cathode and anode, respectively. Carbon-supported platinum catalyst (0.2 mg/cm² Pt/C) was used for the

PEMFC anode and cathode (Johnson Matthey–Platinum 20% on Vulcan XC-72R carbon). The geometric active cell area was 5 cm². Single- and double-sided hydrophobic carbon cloths (E-TEK, Inc.) were used as anode and cathode gas diffusion layers for DMFC, respectively, while double-sided hydrophobic carbon cloths (E-TEK, Inc.) were used as anode and cathode gas diffusion layers for PEMFC. All the MEAs tested were prepared by the same procedure.

2.2.5. Limiting methanol crossover current

Limiting methanol crossover currents through the membrane in a cell were measured to estimate the methanol crossover. For the data reported here, 0.5 M methanol solution was fed to one side of the cell, while humidified nitrogen at 500 sccm and ambient pressure was supplied to the other side. The methanol permeation flux was determined from the limiting current density resulting from transport-controlled methanol electro-oxidation at the other side of the cell using a potential step experiment described in greater detail elsewhere [20,21].

2.2.6. Cell performances

Cell resistance and polarization curves for single cells were performed using a fuel cell test station (Fuel Cell Technology, Inc.) after 12 h break-in under H_2 /air conditions at a cell voltage of 0.7 V. For DMFC testing, the cell was held at 80 °C; 0.5 and 2 M aqueous methanol solution was fed to the anode with a flow rate of 1.8 mL/min; 90 °C humidified air was fed at 500 sccm to the cathode without back pressure (high humidification and stoichiometry were used to minimize cathode effects). High-frequency resistance (HFR) was measured by applying a sinusoidal wave perturbation of ~2 kHz where capacitive contributions to cell impedance were minimized.

3. Results and discussion

3.1. Membrane properties

Copolymers from three investigated sulfonated bisphenols (2,8-DHNS-6, 2,3-DHNS-6, and SHQ) are denoted as *m*-SPAEEEN, *p*-SPAEEEN, and HQ-SPAEEEN individually. All membranes were used to test the MEA at 80 °C except the *p*-SPAEEEN-60 because it was fragile when completely dehydrated [16].

The properties of PEM materials, such as mechanical strength, thermal stability, water swelling, proton conductivity, and adhesion to the electrodes, are crucial for the FC performance. The thermal stability of SPAEEEN and sulfonated biphenylpolysulfone (BPSH) copolymers has been described in previous studies [16–18].

Table 1

Properties of the membranes (water uptake and conductivity measured at 20 °C)

Copolymer	Density ^a (g/cm ³)	Nitrile content (mol%)	IEC_W^b (mequiv./g)	IEC_V^c (mequiv./cm ³)		Water uptake		Proton conductivity (mS/cm)	Conductivity/water uptake (vol%)
				Dry	Wet	wt% ^d	vol% ^e		
<i>m</i> -SPAEEEN-60	1.18	50	1.91	2.25	1.70	28	33	78	2.36
HQ-SPAEEEN-56	1.17	50	1.90	2.22	1.59	34	40	60	1.51
<i>p</i> -SPAEEEN-60	1.34	50	1.90	2.55	1.59	45	60	84	1.39
BPCN-35 ^f	1.33	32.5	1.87	2.49	1.62	40	53	78	1.47
BPSH-45 ^f	1.41	0	1.92	2.71	1.14	98	138	140	1.01
Nafion	1.98	0	0.90	1.78	1.29	19	38	76	2.02

Water uptake and proton conductivity measured at 20 °C.

^a Based on dry state.

^b Based on weigh of dry membrane.

^c Based on volume of dry and/or wet membranes (IEC_V (wet) = IEC_V (dry)/(1 + 0.01 WU)).

^d WU (mass%) = $(W_{wet} - W_{dry})/W_{dry} \times 100$.

^e WU (vol%) = $((W_{wet} - W_{dry})/\delta_w)/((W_{dry}/\delta_m) \times 100)$ (W_{wet} and W_{dry} are the weights of the wet and dry membranes, respectively; δ_w is the density of water (1 g/cm³), and δ_m is the membrane density in the dry state).

^f Data taken from Ref. [22].

The introduction of highly polar nitrile has been suggested to improve mechanical strength of the polymers and promote their adhesion to various substrates. Table 1 summarizes the density, ion exchange capacity (IEC), water uptake of the sulfonated poly(arylene ether ether nitrile)s (*m*-, or *p*-SPAEEENs, HQ-SPAEEEN-56), polysulfones (BPSH-45 and BPCN-35), and Nafion. The changes in length scale (reflected in volume measurements) are expected to directly impact observed properties, because electrochemical properties such as proton conductivity and permeability occur over length scales under operating conditions independent of mass [22].

The water uptake directly affects the sulfonic acid concentrations within the polymer matrix under hydrated conditions which can be gauged by comparing wet volume-based IEC ($IEC_V(\text{wet})$) values with IEC_W values. Although the *m*-SPAEEEN-60 has same IEC_W of *p*-SPAEEEN-60, the $IEC_V(\text{wet})$ of *m*-SPAEEEN-60 is higher than that of *p*-SPAEEEN-60 as listed in Table 1. The sulfonic acid concentration of the dry *m*-SPAEEEN polymer was retained when in the hydrated state, while *p*-SPAEEEN exhibited an excessive swelling property and the sulfonic acid concentration of *p*-SPAEEEN was thereby diluted in the hydrated state. Compared with *p*-SPAEEEN-60, HQ-SPAEEEN-56, and BPSH-45 with similar IEC_W , the *m*-SPAEEEN-60 showed the highest $IEC_V(\text{wet})$. This means that the *m*-SPAEEEN-60 has the lowest water uptake because the amounts of sulfonic acid group in the three membranes based on IEC_W are same. The water uptake (vol%) of *m*-SPAEEEN-60 is lower than that of *p*-SPAEEEN-60 and HQ-SPAEEEN-56. The effectiveness of proton conduction (proton conductivity/water volume uptake) increases from BPSH-45 to BPCN-35 to nitrile copolymers, showing the same order of nitrile

content of copolymers, as listed in Table 1. To some extent, this suggests that increasing nitrile content leads to increased effectiveness of proton conduction. However, *p*-SPAEEEN-60 was less effective than BPCN-35 due to its excessive swelling property.

The sulfonated poly(arylene ether ether nitriles) have lower water uptake than BPSH copolymer when compared at similar IEC_W . For example, the water uptake at 20 °C of *m*-SPAEEEN-60 (IEC_W 1.91 mequiv./g, $IEC_V(\text{wet})$ 1.70 mequiv./cm³) was 33 vol%, which is less than the water uptake of BPSH-45 (IEC_W 1.92 mequiv./g, $IEC_V(\text{wet})$ 1.14 mequiv./cm³). In addition, the *p*-SPAEEEN-60 and HQ-SPAEEEN-56, both having 1.90 mequiv./g of IEC_W , showed water uptakes of 60 vol% and 40 vol%, respectively, which are less than that of BPSH-45.

A plausible factor for the low water uptake of copolymers containing nitrile groups is the presence of strong nitrile dipole interchain interactions that combine to limit swelling in water [23].

Since nitrile groups appear to play an important part in the improved performance properties of the PEM materials, it is relevant to discuss some of their characteristics. It is one of the most polar functional groups, having a high dipole moment of ~3.9 Debyes. In polymers containing functional groups, the energy of intermolecular dispersion interaction (E in kJ/mol) follows the order $-\text{COOH}$ (45.1) > $-\text{OH}$ (30.5) > $-\text{C}\equiv\text{N}$ (26.3) > $\text{C}=\text{O}$ (15.1) > $-\text{NH}_2$ (15.1), $-\text{F}$ (7.3) [24].

Polyacrylonitrile (PAN) is a familiar commercial aliphatic poly(nitrile). The $-\text{C}\equiv\text{N}$ has a high dipole moment that can result both in attraction or repulsion interactions, depending upon spatial orientation with respect to each other. Along the PAN backbone, the

Fig. 2. Molecular modeling of chain conformation of the sulfonated segments of *D*-SPAEEEN, *m*-SPAEEEN, and *p*-SPAEEEN nitrile copolymers.

nitrile groups have intra-molecular repulsion interaction with each other, since the orientation is 'C to C' and 'N to N'. This results in a kinked conformation of the polymer backbone, with the nitrile groups facing outwards [25,26]. Contrary to this, strong inter-molecular interactions from 'C to N' and 'N to C' nitrile orientation lead to the appearance of a physical network, which is somewhat weakened when hydrated due to nitrile–water hydrogen bonding [27].

In the sulfonated poly(arylene ether ether nitrile)s, there are two strongly polar functional groups to consider, $\text{C}\equiv\text{N}$ and SO_3H , both of which have hydrogen bonding interaction with water. A comparison of three similarly structured SPAEEN copolymers, all containing sulfonic acid bonded to naphthalene, reveals the significance of spatial orientation of these two functional groups and their effect on physical properties. *m*-SPAEEEN-60, *p*-SPAEEEN-60, and *D*-SPAEEEN-30 (a copolymer derived from a disulfonated naphthalene monomer) all have very similar IEC values, but quite different physical properties such as proton conductivities, water uptake, and dimensional swelling [16].

Molecular modeling of three of the naphthalene sulfonic acid copolymers *m*-SPAEEEN, *p*-SPAEEEN, and *D*-SPAEEEN provides some insight and a possible explanation for this behavior. Repeat units of each of the copolymers were constructed using HyperChem 7, one ring at a time and energy minimized at each stage. Each ring and flexible linkage was set to several initial conformations, thereby reducing the occurrence of local energy minima. Typically, a total of three to four complete repeat units were constructed for each copolymer, though only short sulfonated segments are illustrated in Fig. 2 to guide the discussion below.

The *D*-SPAEEEN copolymer contains a symmetrical naphthalene unit whereby the ether linkages are at the 2,7-sites, and the sulfonic acid units are ortho- to the ether linkages at the 3,6-sites [16]. Both ether linkages are connected to an aromatic ring containing a nitrile group at the ortho-site. Neglecting the influence of water present in the system, which likely has a significant effect, both nitrile groups assume a conformation placing them in proximity to the sulfonic acid groups to allow hydrogen bonding intrachain interactions. This may account for the lower water uptake, and low λ value ($n \text{ H}_2\text{O}/\text{SO}_3\text{H}$), and relatively low proton conductivity, since the sulfonic acid competes for water while having the nitrile interaction, reducing the overall content in the copolymer.

The *m*-SPAEEEN assumes an entirely different conformation. The repeat units are asymmetric and angularly contorted. Counter-intuitively, the nitrile is not able to assume a conformation that allows any intrachain interaction with the sulfonic acid group. Of the three copolymers, this copolymer has the least planar conformation, and the benzonitrile rings are skewed out-of-plane. The relatively longer and more contorted segment length of this polymer may be favorable for retention of water while the out-of-plane benzonitriles could provide suitable conformations for strong interchain polar nitrile–nitrile interactions, leading to an ideal combination of high proton conductivity and low water swelling.

By visual inspection of its molecular structure, it might be expected that the *p*-SPAEEEN copolymer would exhibit similar behavior to *m*-SPAEEEN, since both contain naphthalene sulfonic acid. Although the chemical structure of *p*-SPAEEEN suggests that it might be contorted, molecular modeling reveals that its conformation is in contrast with *m*-SPAEEEN in being relatively planar, with the benzonitrile rings more or less in plane with respect to the naphthalene ring. The longer spatial distance from the nitriles to sulfonic acid groups rule out any intrachain H-bonding interactions, leaving them to associate with water. In addition, the more in-plane benzonitrile rings may provide less opportunity for inter-chain polar interactions. A combination of these properties could

explain the reason for the relatively higher proton conductivity and the relatively higher swelling.

Preliminary modeling of the HQ-SPAEEEN copolymer, which is asymmetric, shows that it is contorted with the benzonitrile rings out of plane, a characteristic shared with the *m*-SPAEEEN. Although the performance of HQ-SPAEEEN-56 copolymer does not match that of *m*-SPAEEEN-60, nevertheless, it has the second best performance of the copolymer series. This suggests that polymer chain and nitrile conformation may be an important factor in achieving a good combination of proton conductivity and water uptake. In this polymer, nitrile does not appear to have a direct interaction with the sulfonic acid group.

It appears that spatial conformation is an important contributing factor in the copolymer properties. The molecular modeling provides an insight and a possible explanation, albeit from a much simplified model in a much complex system. A more detailed analysis and discussion on this topic will be the subject of a future publication.

Table 1 also shows the proton conductivities of the sulfonated poly(arylene ether ether nitrile), BPSHs, and Nafion that were measured on free-standing membranes. Conductivity below 50 mS/cm can lead to significant ohmic losses under fuel cell operation, while minimum membrane thickness is often practically limited due to membrane fabrication and integrity or mechanical properties [28]. In free-standing membranes, the *m*-SPAEEEN-60, *p*-SPAEEEN-60, and HQ-SPAEEEN-56 exhibited good conductivity (60–84 mS/cm), comparable to Nafion (76 mS/cm). BPCN-35 and BPSH-45 showed good conductivity (78–140 mS/cm).

The relative water uptake and proton conductivity of the membranes to Nafion 1135 are shown in Fig. 3. A comparison of the hydrocarbon PEMs with similar proton conductivity (shown in Fig. 2) reveals that the water uptake of sulfonated poly(arylene ether ether nitrile) is significantly lower than that of BPSH, showing the practical advantages of PEMs containing nitrile group on restraining and maintaining low water uptake and swelling while improving conductivity. For example, the proton conductivity and water uptake (WU) at 80 °C of *m*-SPAEEEN-60 (IEC_v (wet) 1.90 mequiv./g) were 115 mS/cm² and 45 vol%, respectively, while those of BPSH-35 (IEC_w 1.40 mequiv./g) were 126 mS/cm² and 67 vol%, respectively. Membranes with a high relative water uptake can result in increased difficulties in MEA fabrication,

Fig. 3. Relative water uptake and conductivity values of the membranes to those of Nafion at 80 °C (the data of BPSH-35 and Nafion were taken from Ref. [19]).

Table 2
Gas permeability of the membranes

Copolymer	$P(\text{H}_2)^a$	$P(\text{O}_2)$
<i>m</i> -SPAEEEN-60	2.46	0.15
<i>p</i> -SPAEEEN-50	3.44	0.54
HQ-SPAEEEN-56	2.78	0.16
Nafion	7.85	1.18

^a Barrer (1 Barrer = 1×10^{-10} cm³ (STP) cm/(cm² s cm Hg)).

membrane–electrode interfacial resistance, and membrane creep and deformation. Therefore, the target membranes are shown in dotted circle in Fig. 3.

3.2. Gas permeability

The O₂ gas can be transported from the cathode through the membrane and react at the anode. Therefore, it is desirable to use membranes having low O₂ gas permeability. O₂ will be transported more easily through the wet plasticized membrane, which occurs under DMFC conditions. The O₂ gas permeability thus depends on the hydrated state of the membrane matrix. H₂ and O₂ permeabilities of the selected membranes are listed in Table 2. The H₂ and O₂ permeability of all the aromatic polymer membranes was lower than that of Nafion due to the high glass transition temperature resulting from the more rigid aromatic main backbone. Both the O₂ gas permeability (Table 2) and water uptake (Table 1) of *m*-SPAEEEN-60 are similar to those of HQ-SPAEEEN-56, which are both much lower than the *p*-SPAEEEN-50. A possible explanation for this is that the sulfonic acid groups in these two polymers are in a configuration that permits strong interchain interactions through H-bonding, which decreases the O₂ permeability with increasing SO₃H concentration. Further, it is possible that the nitrile groups are in a configuration supporting closer interchain polar interactions in the case of *m*-SPAEEEN compared with *p*-SPAEEEN. Secondly, the O₂ molecules absorbed into the water may interact and bind with sulfonic acid group in the polymer matrix. Due to this bound molecular water, O₂ molecules limit their transport through the membrane matrix. In general, the ratio of the bound water is higher in aromatic polymer than in Nafion [29,30]. The aromatic polymer membrane having higher levels of bound water molecules should result in a lower O₂ permeability.

3.3. MEA properties

The sulfonated poly(arylene ether ether nitrile) copolymers, BPSH-35, and Nafion membranes were used for MEA study, excluding *p*-SPAEEEN-60 and BPSH-45 due to its mechanical fragility under dehydrated conditions. Membranes with excessive water swelling tend to be (i) less effective in proton conduction and (ii) mechanically fragile and subject to dimensional changes under dehydration/hydration cycling [23]. However, the nitrile copolymers showed lower HFR than BPSH-35, which is an apparent benefit from these low swelling, high IEC copolymers.

Methanol crossover and cell resistance play a major role in determining DMFC performance. Methanol crossover in the MEA was estimated by measuring the limiting methanol crossover current [4,20,21]. Cell resistance is composed of the membrane resistance, electronic resistances of the fuel cell components (flow field, current collectors, and gas diffusion layers), the resistance of the electrodes and interfacial resistances associated with the interfaces between electronic components and between the electrode and the membranes. Therefore, cell resistance from these cumulative factors is always higher than the associated free-standing membrane resistance. Table 3 lists the high frequency resistance (HFR)

Table 3
Electrochemical properties of hydrocarbon membranes and Nafions at 80 °C (0.5 M MeOH)

Copolymer	Thickness (μm)	HFR (mΩ cm ²)	MeOH limiting current (mA/cm ²)	Selectivity (α)
<i>m</i> -SPAEEEN-60	53	97	52	198
<i>p</i> -SPAEEEN-50	80	140	38	188
HQ-SPAEEEN-56	60	101	54	183
BPSH-35	56	150	72	93
	74	199	55	91
Nafion	90	100	125	80
	250	250	51	78

Membrane thickness was adjusted to provide methanol crossover limiting currents that were similar (50–55 mA/cm²).

and methanol crossover limiting current of single cells using the hydrocarbon copolymers and Nafion at 80 °C under DMFC operating conditions (0.5 M MeOH). The HFR of sulfonated poly(arylene ether ether nitrile) had a lower value than that of BPSH-35 at a similar membrane thickness. The *m*-SPAEEEN-60 (53 μm) showed the highest selectivity compared with other membranes, indicating that it had the best relative performance. A polymer with ideal properties should have very low HFR (ohmic losses) and low methanol crossover (low crossover losses). Of the selected polymers shown, Nafion shows the poorest DMFC performance, having the lowest selectivity resulting from a combination of the higher membrane thickness (resulting in higher HFR) required to compensate for high methanol crossover.

Methanol crossover and cell resistance are directly related to the methanol permeability and the proton conductivity of the membranes. MEA selectivity can be calculated as follows [4]:

$$\alpha(\text{HFR}^{-1} \text{ MeOH current}^{-1}) = \frac{1}{\text{HFR} \times \zeta_{\text{lim}}} \quad (1)$$

where ζ_{lim} limiting methanol crossover current of membrane. The values for the polymer electrolyte membranes of various thicknesses are listed in Table 3. Nafion is known to be a relatively poor polymer electrolyte for DMFC application, possessing rather low selectivity [28,31]. Compared to the selectivities of Nafion and BPSH-35, the SPAEEEN copolymers have high selectivity. The *m*-SPAEEEN-60 showed the best selectivity. While BPSH-35 shows slightly improved potential for DMFC compared with Nafion,

Fig. 4. H₂/air performance of poly(arylene ether ether) nitriles, BPSH-35, and Nafion (cell temperature: 80 °C; catalyst loading: 0.2 mg/cm² Pt/C).

the poly(arylene ether ether nitrile) copolymers (*p*-, *m*-, HQ-SPAEEEN) show significantly improved potential, having much lower methanol crossover limiting current at comparable high frequency resistance. From these results, one would expect improved DMFC performance using SPAEEEN compared to Nafion and BPSH-35.

3.4. Fuel cell performance

We compare the voltage–current characteristics (i.e. H₂/air and DMFC polarization curves) of MEAs using the three nitrile copolymers, BPSH-35, and Nafion. Fig. 4 shows the H₂/air performance of the selected membranes. For comparison, we tested relatively thin membranes in order to reduce cell ohmic resistance. MEAs using nitrile copolymers showed inferior performance in comparison with the Nafion MEA but improved performance compared with MEA using sulfonated polysulfone BPSH-35. However, it should be noted that the thickness of *m*-SPAEEEN-60 membrane (53 μm) was greater than that of Nafion 212 (47 μm). The slightly lower performance of the cell using *p*-SPAEEEN compared to the cell using BPSH-35 may be due to the increased resistance of the thicker membrane. Among the cells using nitrile copolymers, the MEA using *m*-SPAEEEN-60 showed the best performance. Qualitatively good correlation between cell resistance and polarization characteristics indicates that interfacial incompatibility between membrane

and electrode and resulting performance loss is minor, which we expect from relatively low water uptake of the tested membranes.

Because reactant crossover in DMFC operation is much greater than in PEMFC operation, the choice of membrane thickness for optimal performance in DMFCs is very important. The effects of membrane thickness and methanol feed concentration at 80 °C for Nafion control cells are shown in Fig. 5. At a methanol feed concentration of 0.5 M, the modest improvement in Nafion with a film thickness of 250 μm at low current density (<175 mA/cm²) was attributed to decreased methanol crossover, while slightly lower performance at high current density (>175 mA/cm²) was attributed to the higher resistance of the Nafion MEA. The performance of Nafion with a film thickness of 90 μm having with low HFR and high methanol crossover limiting current was superior to that of the thicker Nafion membranes at high current density (>175 mA/cm²) (Table 3 and Fig. 5(a)). However, the membrane with 250 μm thickness having high HFR and low methanol crossover limiting current showed higher performance at 2.0 M methanol feed solutions, as shown in Fig. 5(b). The performance of the 250- μm Nafion membrane in methanol feed concentration of 2.0 M is slightly lower in methanol feed concentration of 0.5 M. For example, the cell potentials of the 250- μm Nafion membrane at 200 and 300 mA/cm² current density at 0.5 M methanol concentration were 0.495 and

Fig. 5. DMFC performance of Nafion with different thickness at (a) 0.5 M and (b) 2.0 M methanol feed concentration (cell temperature: 80 °C).

Fig. 6. DMFC performance of poly(arylene ether ether) nitriles, BPSH-35, and Nafion at (a) 0.5 M and (b) 2.0 M methanol feed concentration (cell temperature: 80 °C).

0.40 V, respectively. At a higher methanol concentration of 2.0 M, the cell potentials were 0.48 and 0.42 V, respectively. However, although the 90 and 180- μ m Nafion membranes have lower HFR values than the 250- μ m membrane in 0.5 M methanol concentration, the performances of both of the thinner Nafion membranes decreased with increasing methanol feed concentration, as shown in Fig. 5(a) and (b). From the results of the Nafion MEAs (Fig. 5), we suggest that the performance of MEAs is affected more by HFR than by methanol crossover limiting current at feed conditions of low MeOH concentration (0.5 M). However, at higher MeOH concentration (2.0 M), the methanol crossover limiting current is a major factor influencing the reduction of MEA performance. Although DMFC cells using hydrocarbon membranes show the same thickness effect, the optimum thickness of each specific membrane family should be different, due to differences in the conductivity and methanol permeability of the membrane. Apart from the effect of membrane thickness, there are several other factors that make accurate performance evaluation difficult using single polarization curves: (i) methanol crossover (fuel utilization) is not fully interpreted by polarization curves and (ii) optimum operating conditions may be very different for different systems [23]. In order to lessen the uncertainty caused by methanol crossover and to provide a meaningful comparison, we selected membranes for the fuel cell tests as having an appropriate thickness for which methanol crossover limiting currents were similar (50–55 mA/cm²) across different polymer systems, as listed in Table 3.

Fig. 6 shows the cell performance of the MEAs using selected copolymers having similar methanol crossover limiting current at

methanol feed concentrations of 0.5 and 2.0 M. The Nafion showed a better performance than sulfonated nitriles and BPSH-35 in H₂/air conditions. However, the performances of the MEAs using SPAEEN copolymers and BPSH-35 were superior to that of the Nafion MEA (0.5 M MeOH) (Fig. 6(a)). In addition, at 2.0 M methanol feed, the performances of the MEAs using SPAEEN copolymers were superior to that of the MEAs using BPSH-35. The performance of BPSH-35 was more dependant on the methanol concentration than that of SPAEEN copolymers. Although the performance of BPSH-35 was superior to the *p*- and HQ-SPAEEN at 0.5 M methanol concentration, the performance of *p*- and HQ-SPAEEN was superior to the BPSH-35 at the higher 2.0 M methanol concentration.

Among the selected membranes and Nafion, the *m*-SPAEEN-60 shows the best performance. For example, the power density of the MEA using *m*-SPAEEN-60 at 250 mA/cm² and 0.5 M methanol was 128 mW/cm², whereas the power densities of the MEAs using BPSH-35 and Nafion were 121 and 115 mW/cm² (Fig. 7). At 2.0 M methanol, open circuit potential and mass transport limitations for all MEAs decreased but the performance trend remained remarkably similar to that at 0.5 M methanol. The power density of the MEA using *m*-SPAEEN-60 at 250 mA/cm² and 2.0 M methanol was 125 mW/cm², whereas the power densities of the MEAs using BPSH-35 and Nafion were 115 and 113 mW/cm², respectively. The maximum power density of the MEA using *m*-SPAEEN-60 was shown in 1.0 M methanol. The power density at 350 mA/cm² and 1.0 M methanol was 169 mW/cm², whereas the power densities at 350 mA/cm² and 0.5 and 2.0 M were 150 and 161 mW/cm², respectively, as shown in Fig. 7(d).

Fig. 7. Power density of *m*-SPAEEN-60, BPSH-35, and Nafion at (a) 0.5 M, (b) 1.0 M, (c) 2.0 M methanol feed concentration, and (d) power density of *m*-SPAEEN-60 relative to methanol feed concentration (cell temperature: 80 °C).

Fig. 8. DMFC performance of *m*-SPAEEEN-60 before and after life test at 0.5M methanol feed concentration (cell temperature: 80 °C).

It was reported that the sulfonated hydrocarbon polymer membranes showed better performance than Nafion [8,9]. However, interfacial incompatibility between membrane and Nafion-based electrodes limited long term performance. In order to verify the interfacial stability of the MEA using *m*-SPAEEEN-60, the one showing the best performance among the selected membranes, an extended life test (>100 h) was conducted. Fig. 8 shows DMFC performance before and after life test. This result indicated that the interfacial compatibility of *m*-SPAEEEN-60 is likely good using Nafion-bonded electrodes, since there was no increase in HFR. In fact, a slight decrease in HFR was observed, which can be attributed to morphological reorganization resulting in an increase in proton conductivity of the membrane [32]. It is known that nitrile groups in polymers promote adhesion of polymer to substrates, possibly through polar interactions with other functional groups. This may be a reason for good adhesion to the catalyst-electrode layer [33].

4. Conclusions

We compare the DMFC performance of poly(arylene ether nitrile) copolymers containing sulfonic acid group bonded in structurally different ways, which are non-fluorinated and have nitrile groups in both hydrophilic and hydrophobic repeat units. The MEA using the poly(arylene ether ether nitrile) copolymers showed significantly improved performance in DMFC compared to the MEA using sulfonated polysulfone (BPSH) and Nafion membrane under optimized conditions. Especially, the poly(arylene ether ether nitrile) containing the angled naphthalenesulfonic acid group (*m*-SPAEEEN-60) showed the best performance in DMFC. The *m*-SPAEEEN-60 has relatively low water uptake, low O₂ gas permeability, and interfacial stability. It is known that nitrile groups in polymers promote adhesion of polymer to substrates, possibly through polar interactions with other functional groups. This may be a reason for good adhesion to the catalyst-electrode layer. Preliminary molecular modeling of similarly structured nitrile copolymers indicates that chain conformation and spatial positioning of the nitrile and sulfonic acid groups are important factors in the outcome of proton conductivity and water uptake.

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