



Short communication

Highly fluorinated comb-shaped copolymer as proton exchange membranes (PEMs): Fuel cell performance[☆]Dae Sik Kim^a, Yu Seung Kim^b, Michael D. Guiver^{a,*}, Jianfu Ding^a, Bryan S. Pivovar^b^a Institute for Chemical Process and Environmental Technology, National Research Council, 1200 Montreal Road, Ottawa, Ontario K1A 0R6, Canada^b Materials Physics and Applications, Sensors and Electrochemical Devices Group, Los Alamos National Laboratory, Los Alamos, NM 87545, USA

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ABSTRACT

The fuel cell performance (DMFC and H₂/air) of highly fluorinated comb-shaped copolymer is reported. The initial performance of membrane electrode assemblies (MEAs) fabricated from comb-shaped copolymer containing a side-chain weight fraction of 22% are compared with those derived from Nafion and sulfonated polysulfone (BPSH-35) under DMFC conditions. The low water uptake of comb copolymer enabled an increase in proton exchange site concentrations in the hydrated polymer, which is a desirable membrane property for DMFC application. The comb-shaped copolymer architecture induces phase separated morphology between the hydrophobic fluoroaromatic backbone and the polysulfonic acid side chains. The initial performance of the MEAs using BPSH-35 and Comb 22 copolymer were comparable and higher than that of the Nafion MEA at all methanol concentrations. For example, the power density of the MEA using Comb 22 copolymer at 350 mA cm⁻² and 0.5 M methanol was 145 mW cm⁻², whereas the power densities of MEAs using BPSH-35 were 136 mW cm⁻². The power density of the MEA using Comb 22 copolymer at 350 mA cm⁻² and 2.0 M methanol was 144.5 mW cm⁻², whereas the power densities of MEAs using BPSH-35 were 143 mW cm⁻².

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1. Introduction

New polymer electrolyte membranes (PEMs) that have high proton conductivity, low reactant permeability and reduced water uptake are desired for fuel cell applications [1]. 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 anode pose serious problems for the commercialization of DMFC technology. As a result, a substantial amount of current research is aimed at designing and developing higher-temperature and lower-cost alternative polymer materials based on non-fluorinated or partially fluorinated polymeric systems with reduced methanol permeability while maintaining high proton conductivity [2]. The majority of this work is based on non-fluorinated, polyaromatic-based condensation polymers that contain ionic functionality in the form of sulfonic acid groups located along the polymer backbone. Generally, these polymers can achieve suitable conductivities only at high ion-exchange capacities (IECs), resulting in high water uptake and large membrane dimensional changes that are unsuit-

able for practical PEM applications. It has been suggested that these sulfonated polymers are unable to form defined hydrophilic domains, as the rigid polyaromatic backbone prevents continuous ionic clustering from occurring [3].

Nafion is a statistical copolymer comprising a perfluorinated hydrophobic backbone that contains a number of short, flexible pendant side chains with single hydrophilic sulfonic acid groups. This delicate balance of hydrophobic–hydrophilic properties within the material, coupled with the increased mobility of the flexible ionic side-chain, which, in the hydrated form, leads to networks of ionic channels through the material [4].

One promising way to enhance the mechanical integrity of the membrane is to distinctly separate the hydrophilic sulfonic acid group and the hydrophobic polymer main chain by locating the sulfonic acid groups on side chains grafted onto the polymer main chain [3,5]. Holdcroft et al. reported that graft copolymers yield membranes which tolerate much higher ionic contents without excessive swelling and dissolution, and which leads to membranes that possess highly concentrated, isotropically connected ionic domains. In contrast, the diblock copolymers provide a higher degree of long-range, ionic order. This can lead to membranes that swell excessively at low IEC, diluting the proton concentration, and limiting the IEC attainable [3].

Jannasch and coworkers reported a sulfophenoxybenzoyl polysulfone and sulfonaphthoxybenzoyl polysulfone that was

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prepared by attaching pendant sulfonated aromatic side chains to polysulfone, showing proton conductivities of 11–32 mS cm⁻¹ at 120 °C [6]. Einsla and McGrath reported that poly(arylene ether sulfone) copolymers containing pendant sulfonic acid groups were prepared using barium pentafluorobenzenesulfonate and 4-nitrobenzenesulfonyl chloride, showing lower proton conductivity (1–8 mS cm⁻¹) [7].

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 [8–11]. Some polymer systems with optimized structures and ion-exchange capacity (IEC) show performance comparable to that of Nafion.

We already reported the comb-shaped copolymer wherein the main chain of the polymer is composed of a highly fluorinated poly(arylene) ether, while the side-chain segments comprise flexible, monodisperse poly(α -methyl styrene) containing multiple sulfonic acid groups (Fig. 1(b)) [12]. In the present paper we report the fuel cell performance of comb-shaped copolymer. The water-absorption properties of comb-shaped copolymer, sulfonated poly(arylene ether sulfone)s (BPSHs) (Fig. 1(c)) and Nafion based on volume percent were analyzed. The properties of MEAs are discussed in terms of high-frequency resistance (HFR) and methanol crossover limiting current. Then, the H₂/air and DMFC (0.5, 1.0, and 2.0 M MeOH) performance of the MEAs using the comb-shaped copolymer, BPSHs, and Nafion membranes are compared.

2. Experimental

2.1. Preparation of membrane

Preparation of the polymer side chains, in the form of macromonomers, was achieved using anionic polymerization techniques as shown in Fig. 1(a). Copolymers containing side-chain weight fraction of 22% were prepared by direct aromatic nucleophilic substitution polycondensation of decafluorobiphenyl, 4,4'-hexafluoroisopropylidene diphenol (6F-BPA), and macromonomer in dimethylacetamide (DMAc). This copolymer was sulfonated by acetyl sulfate in dichloroethane (Fig. 1(b)). A weight fraction of 22% was originally selected as the comb-shaped copolymer predicted to have conductivity similar to that of Nafion, since the 25% copolymer was above that of Nafion; however, the conductivity value was lower than expected. Detailed synthesis procedures and characterization of these copolymers were reported previously [12]. Membranes were prepared from copolymer solutions in DMAc and drying the cast films at 50 °C under a constant purge of argon for 2–4 days. The membrane thickness used for MEA fabrication was 33 μ m.

2.2. Membrane characterization

The density of membrane 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.

The proton conductivities of the membranes were estimated from AC impedance spectroscopy data using a Solartron 1260 gain phase analyzer according to the method in the literature [13].

Membrane electrode assemblies (MEAs) were prepared from standard catalyst inks using a known procedure [1]. Unsupported

platinum (6 mg cm⁻²) and platinum–ruthenium (10 mg cm⁻²) catalysts (Johnson Matthey) were used for cathode and anode, respectively. 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, respectively. All the MEAs tested were prepared by the same procedure.

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 [14,15].

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 hydrogen/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⁻¹; 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 \sim 2 kHz where capacitive contributions to cell impedance were minimized.

3. Results and discussion

3.1. Membrane properties

Preparation of the polymer side chains, in the form of macromonomers, was achieved using anionic polymerization techniques. The comb-shaped copolymers containing side-chain weight fractions of 22% (denoted as Comb 22) were produced by condensation copolymerization of a mixture of hexafluorobisphenol A (bisphenol AF), decafluorobiphenyl, and macromonomers in DMAc at 80 °C. Comb 22 (IEC = 1.2 mequiv. g⁻¹, density = 1.35 g cm⁻³) was obtained after sulfonation using acetyl sulfate. The density, ion-exchange capacity (IEC) and water uptake of the comb-shaped copolymer (Comb 22), polysulfones (BPSH-35), and Nafion[®] are compared in Table 1. The volume-based IEC_v and weight-based IEC_w are reported, because electrochemical properties such as proton conductivity and permeability occur over length scales under operating conditions (hydrated membranes) independent of mass [16]. The water uptake directly affects the proton exchange concentrations within the polymer matrix under hydrated conditions, which can be gauged by comparing wet volume-based IEC [IEC_v(wet)] values with IEC_w values. The IEC_v(dry) of Comb 22 and Nafion are 1.62 mequiv. cm⁻³ and 1.78 mequiv. cm⁻³, respectively. However, the IEC_v(wet) of Comb 22 and Nafion are 1.38 mequiv. cm⁻³ and 1.29 mequiv. cm⁻³, respectively. In the case of Comb 22, even when a high concentration of sulfonic acid groups was present in the dry state (IEC_{v-dry}: 1.62 mequiv. cm⁻³), it was not greatly reduced when the membrane was equilibrated in water (IEC_{v-wet}: 1.38 mequiv. cm⁻³), because the dimensional swelling was restrained. In the case of Nafion (IEC_{v-dry}: 1.78 mequiv. cm⁻³), and BPSH-35 (IEC_{v-dry}: 2.06 mequiv. cm⁻³), it was greatly reduced when the membrane was equilibrated in water compared to the dry state (Nafion: 1.29 IEC_{v-wet} mequiv. cm⁻³, BPSH-35: 1.40 IEC_{v-wet} mequiv. cm⁻³). Even though the IEC_w of Comb 22 is higher than that of Nafion, the water uptake of Comb 22 is lower than that of Nafion. Table 1 also shows the proton conductivity and conductivity per water uptake (vol.%) ratio. The ratio

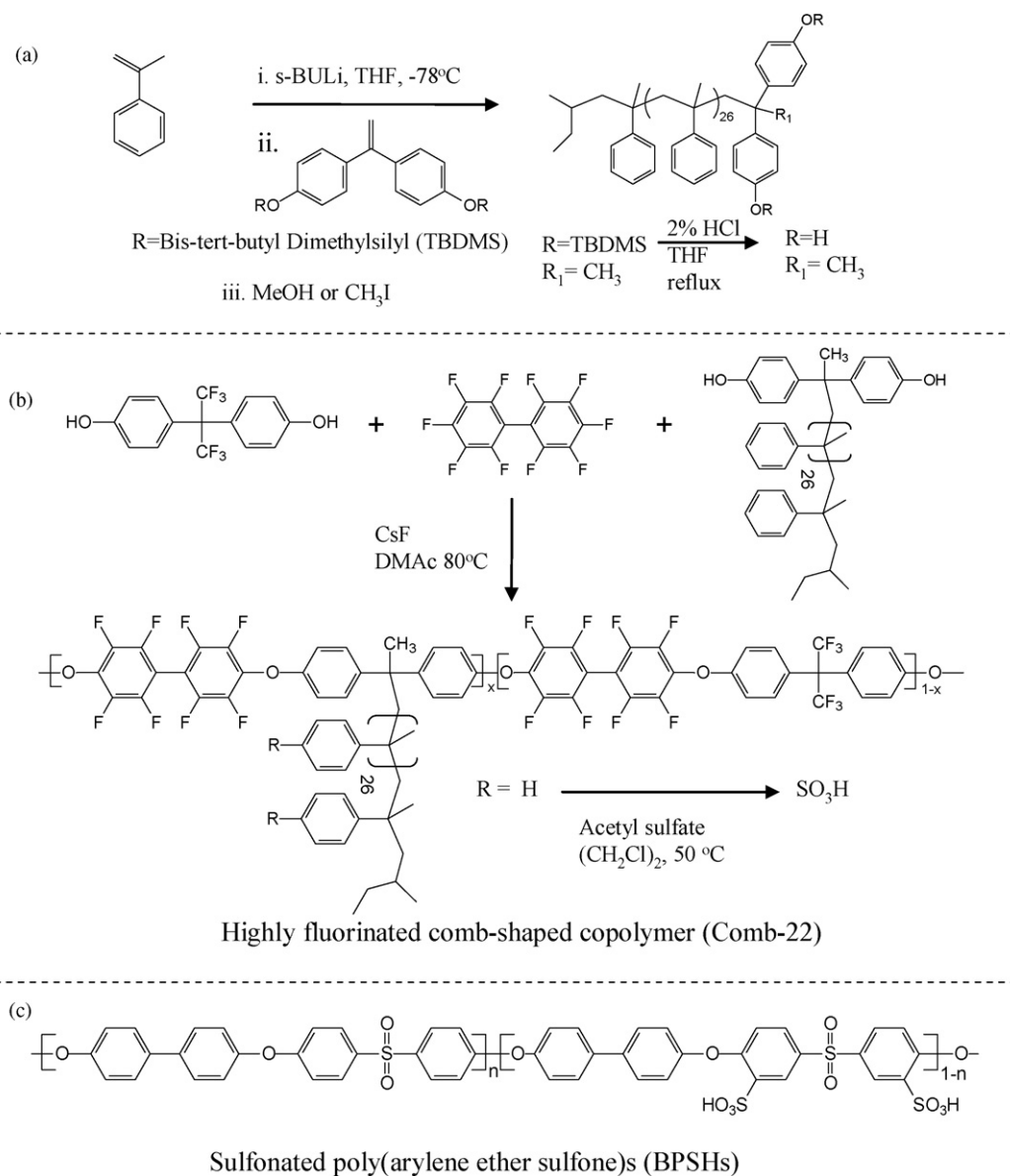


Fig. 1. Synthesis of (a) macromonomers, (b) sulfonated comb-shaped copolymer and (c) chemical structure of sulfonated poly(arylene ether sulfone)s (BPSHs).

of conductivity per water uptake (vol.%) of Comb 22 is higher than that of BPSH-35 and Nafion, although the proton conductivity of Comb 22 is lower than other membranes. The water molecules in the Comb 22 are more activated to proton transfer than those in

the other membranes. Although the relative proton conductivity of Comb 22 is lower than that of BPSH-35 (Fig. 2), the relative water uptake of Comb 22 is enough to maintain high conductivity per water uptake.

Table 1

Properties of the membranes (water uptake and conductivity measured at 25 °C)

Copolymer	Density ^a (g cm ⁻³)	IEC _w ^b (mequiv. g ⁻¹)	IEC _v ^c (mequiv. cm ⁻³)		Water uptake		Proton conductivity (mS cm ⁻¹)	Ratio of conductivity/water uptake (vol.%)
			Dry	Wet	wt% ^d	vol.% ^e		
Comb 22	1.35	1.20	1.62	1.38	13	18	43	2.53
BPSH-35 ^f	1.34	1.54	2.06	1.40	35	47	72	1.53
Nafion 1135	1.98	0.90	1.78	1.29	19	38	76	2.01

^a Based on dry state.

^b Based on weight of dry membrane.

^c Based on volume of dry and/or wet membranes (IEC_v(dry) = density × IEC_w, IEC_v(wet) = IEC_v(dry)/(1 + 0.01 WU)).

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

^e WU (vol.%) = ((W_{wet} - W_{dry})/δ_w)/((W_{dry}/δ_m) × 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 cm⁻³), and δ_m is the membrane density in the dry state).

^f More detail information of BPSH-35 is shown in Ref. [16].

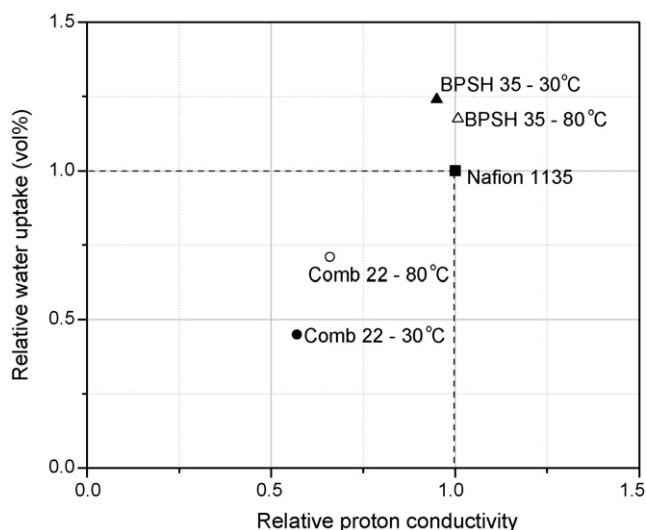


Fig. 2. Relative proton conductivity and relative water uptake of the membranes to those of Nafion at 30 °C and 80 °C.

3.2. MEA properties

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 [1,13–15]. 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. We already reported that the high-frequency resistance (HFR) increases and methanol crossover limiting current decreases as a function of increasing of membrane thickness within a copolymer family [13]. This comparison of membranes allows the effects of methanol crossover and ohmic losses to be considered together when evaluating performance potential of a DMFC. The HFR and methanol crossover limiting current are affected by thickness and optimum operating conditions may be very different for different systems. Therefore, it is difficult to make a meaningful comparison of the performance of different types of membrane using polarization curves. In order to lessen the uncertainty caused by methanol crossover, we selected membranes having an appropriate thickness for which methanol crossover limiting currents were similar (40–50 mA cm⁻²) across different polymer systems; the limiting current are listed in Table 2.

Table 2 lists HFR and methanol crossover limiting current of single cells using the Comb 22, BPSH-35 and Nafion at 80 °C under DMFC operating conditions (0.5 M MeOH). A membrane with ideal properties should have very low HFR (ohmic losses) and low methanol crossover (low crossover losses). The Comb 22 copolymer membrane showed the lowest HFR and MeOH limiting current compared with other membranes. Methanol crossover and cell resistance are directly related to the methanol permeability and the proton conductivity of the membranes. Comb 22 copolymers have a much higher selectivity compared with the selectivity of Nafion and BPSH-35.

3.3. Fuel cell performance

The voltage–current characteristics (H₂/air polarization curves) of MEAs using the Comb 22 copolymer, BPSH-35, and Nafion are compared and shown in Fig. 3. Catalysts and loadings are

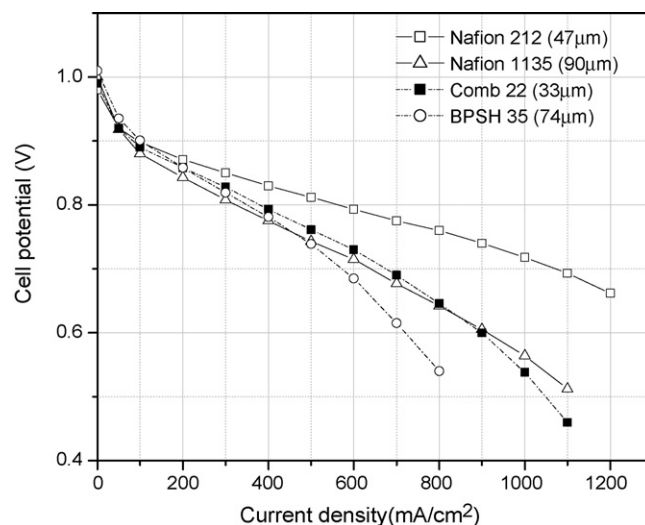


Fig. 3. H₂/air performance of Comb 22 copolymer, BPSH-35, and Nafion.

those typically used for DMFC. MEAs using Comb 22 copolymer showed inferior performance to Nafion 212 (47 µm) control MEA but improved initial performance compared with MEA using polysulfone BPSH-35. However, the initial performance of Comb 22 copolymer was comparable to that of Nafion 1135 (90 µm). For example, the order of the current density at 0.8 V is Nafion 212 (47 µm, 570 mA cm⁻²) > Comb 22 copolymer (33 µm, 390 mA cm⁻²) > BPSH-35 (74 µm, 350 mA cm⁻²) > Nafion 1135 (90 µm, 315 mA cm⁻²). Compared with Nafion 212 (47 µm), the performance of Nafion 1135 (90 µm) decreased because the HFR increases as a function of increasing of membrane thickness (see Table 2). Although the Comb 22 copolymer showed the lowest relative proton conductivity, the initial performance of Comb 22 copolymer was comparable to that of Nafion 1135 (90 µm) due to low HFR derived from the thin membrane. A qualitatively good correlation between cell resistance and polarization characteristics indicates that interfacial incompatibility between membrane and electrode and resulting performance loss is minor, due to relatively low water uptake of the tested membranes [17].

The DMFC performance of Nafion membranes using different membrane thickness is shown in Fig. 4. The point of intersection (at 175 mA cm⁻²) is shown in the line of performance in 0.5 M methanol feed concentration. The performance of 250 µm Nafion membrane is higher than that of 90 µm Nafion membrane at low current density (<175 mA cm⁻²) due to low methanol crossover, and the reverse behavior is shown above this current density due to high-HFR. However, compared to that of Nafion with 90 µm thickness, the performance of Nafion with 250 µm thickness having high-HFR and low methanol crossover limiting current showed high-performance at 2 M methanol feed solution. From this behavior of Nafion MEAs, 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 [17]. From this result and in order to lessen the uncertainty caused by methanol crossover, we selected Nafion membranes having a 250 µm thickness and 51 mA cm⁻² methanol crossover limiting currents that is similar to other membranes to evaluate of DMFC performance.

Fig. 5 shows the cell performance of the MEAs using selected copolymers at methanol feed concentration of 0.5, 1.0, and 2.0 M.

Table 2
Electrochemical properties of the membranes and Nafion at 80 °C (0.5 M MeOH)

Copolymer	Thickness (μm)	HFR ($\text{m}\Omega\text{cm}^2$)	MeOH limiting current (mA cm^{-2})	Selectivity (α) ^a
Comb 22	33	110	43	210
BPSH-35	74	199	55	91
Nafion 112 ^b	50	70	152	94
Nafion 1135	90	100	125	80
Nafion 1110 ^b	250	250	51	78

^a α ($\text{HFR}^{-1} \text{MeOH current}^{-1}$) = $1/\text{HFR} \times \zeta_{\text{lim}}$ (ζ_{lim} is the limiting methanol crossover current of single cell).

^b Data from [13].

We report the HFR and methanol crossover limiting current of MEAs using Nafion and BPSH-35 as a function of membrane thickness at 80 °C, using 0.5 M methanol feed concentration [13]. The MeOH limiting currents of Nafion having 90 μm and 47 μm thickness were 125 and 152 mA cm^{-2} , respectively. The initial performance of the MEAs using BPSH-35 and Comb 22 copolymer were superior to that of the Nafion MEA at all methanol concentrations as shown in Fig. 5. The Comb 22 copolymer shows high performance compared with BPSH-35 at 0.5 and 1.0 M methanol. For example, the power density of the MEA using Comb 22 copolymer at 350 mA cm^{-2} and 0.5 M methanol was 145 mW cm^{-2} , whereas the power density of MEAs using BPSH-35 was 136 mW cm^{-2} . At 2.0 M methanol concentration, the performance of MEA using Comb 22 copolymer is similar to that of BPSH-35. The power density of the MEA using Comb 22 copolymer at 350 mA cm^{-2} and 2.0 M methanol was 144.5 mW cm^{-2} , whereas the power density of MEAs using BPSH-35 was 143 mW cm^{-2} .

Although the sulfonated hydrocarbon polymer membranes showed better initial performance than Nafion [10,11], interfacial incompatibility between membrane and Nafion-based electrodes has been shown to limit long term performance. Fig. 6(a) shows the long-term performance of Comb 22 copolymer at a constant 0.5 V, and the DMFC performance before and after life test is shown in Fig. 6(b). Although the current density of Comb 22 copolymer showed a slight loss after the life test, it is not considered to be symptomatic of a hydrocarbon membrane electrode interfacial problem. The reason is that the performance degradation is too fast and there is linear HFR increase behavior (Fig. 6(a)). The most plausible explanation is that the poly(α -methyl styrene) side-chain is susceptible to chemical degradation under fuel cell conditions, which caused a loss of the proton conducting sulfonic

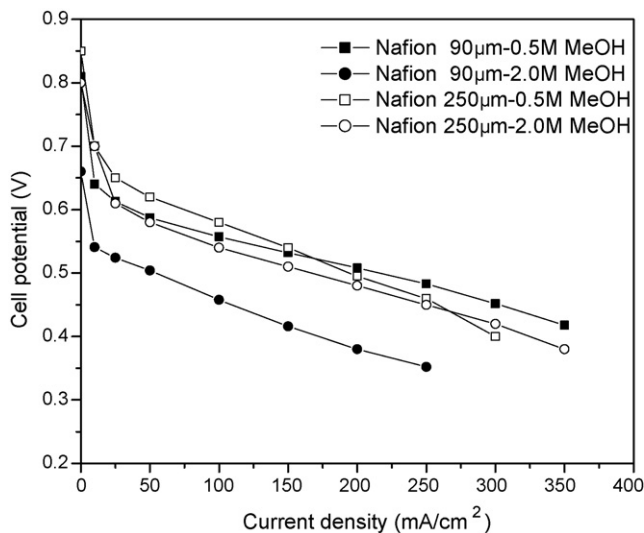


Fig. 4. DMFC performance of Nafion with different thickness and methanol feed concentration (at 80 °C).

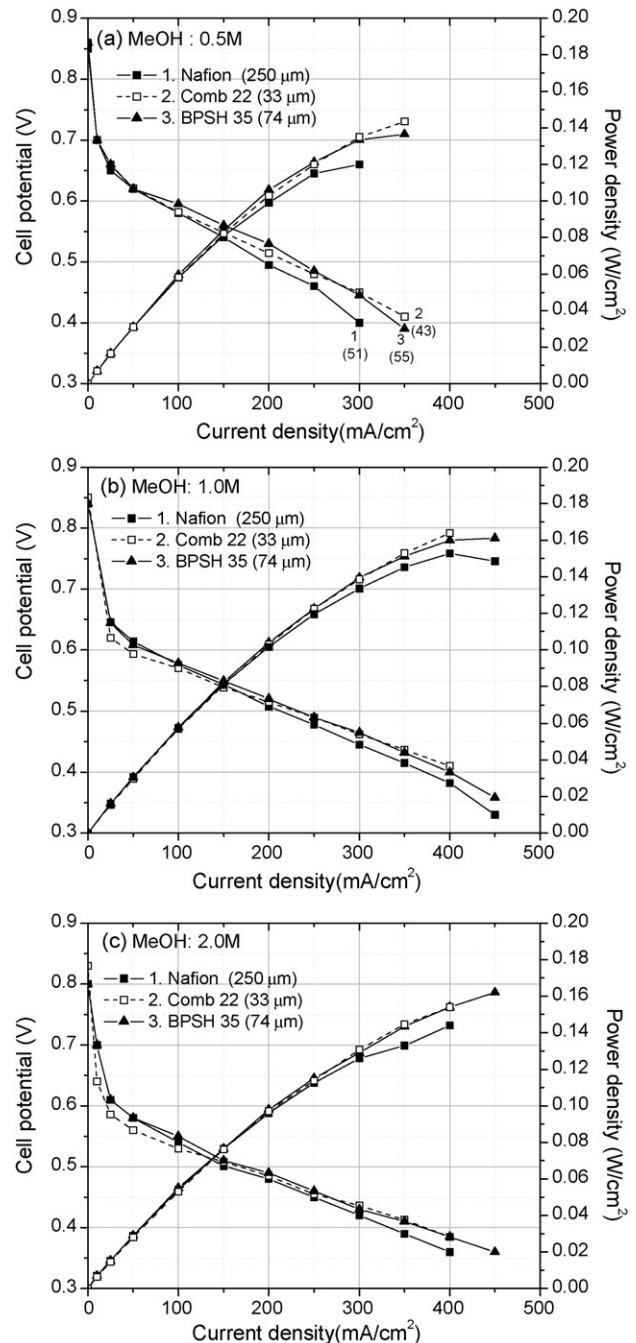


Fig. 5. DMFC performance of Comb 22 copolymer, BPSH-35, and Nafion at (a) 0.5 M, (b) 1.0 M and (c) 2.0 M methanol feed concentration, respectively (cell temperature: 80 °C; numbers in parenthesis in (a) are MeOH limiting current (mA cm^{-2})).

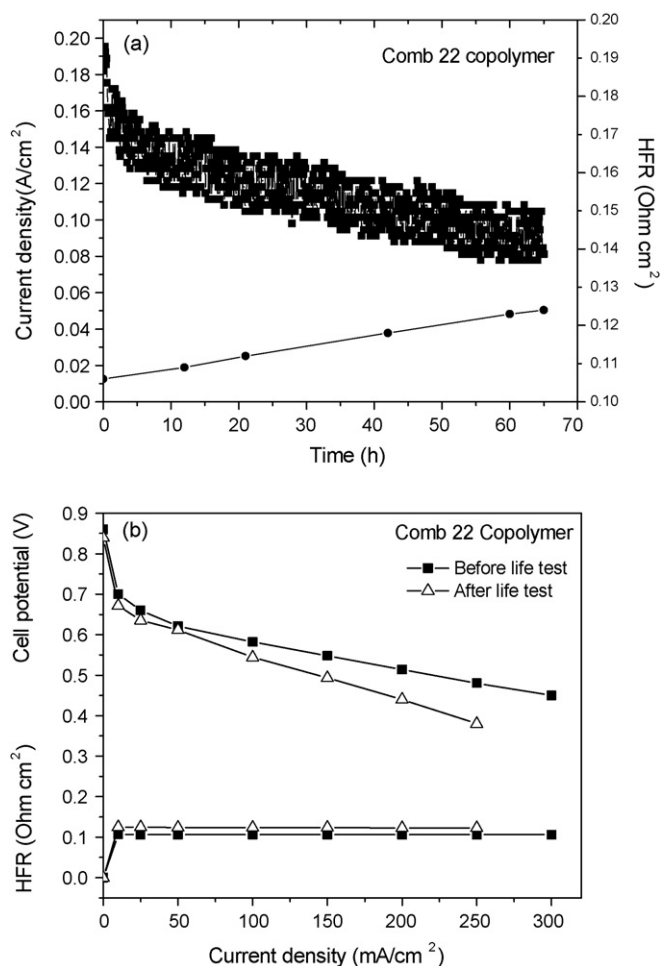


Fig. 6. (a) Current density change of the cell using Comb 22 copolymer and (b) comparison of polarization curve of Comb 22 copolymer before and after 65 h life test (operating temperature 80 °C, 0.5 M MeOH).

acid sites, thereby resulting in decreasing membrane performance. However, the structural architecture of graft and comb-shaped polymers serves to illustrate their potential to improve fuel cell performance.

4. Conclusions

The performance of comb-shaped copolymer (Comb 22 copolymer) was demonstrated in DMFC and H₂/air compared to the performance of sulfonated polysulfone (BPSH-35) and industrial standard Nafion membrane. The volume-based IEC_{v(wet)} as well as weight-based IEC_w are reported. The comb 22 copolymer has a

comparatively low water uptake allowing relatively high IEC_{v(wet)} in the hydrated polymer matrix. The increased IEC_{v(wet)} offers more effective proton conduction in the hydrated membrane. The initial performance of comb 22 copolymer is superior to that of Nafion and BPSH-35 in DMFC tests. However, the current density of Comb 22 copolymer declined after an MEA life test, which was believed to be caused by chemical instability of the polystyrene-based side-chain containing multiple sulfonic acid groups. The high initial performance of the present copolymer suggests that comb-shaped polymers with structural design that induces phase separation have the potential to greatly improve DMFC performance. With careful consideration to chemical stability in the structural design, longer-term performance is likely to be improved significantly.

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