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Short communication

Highly fluorinated comb-shaped copolymer as proton exchange membranes (PEMs): Fuel cell performance☆

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ABSTRACT

The fuel cell performance (DMFC and H_2/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}.

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 unsuitable 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 sulfonaphthyloxybenzoyl 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(

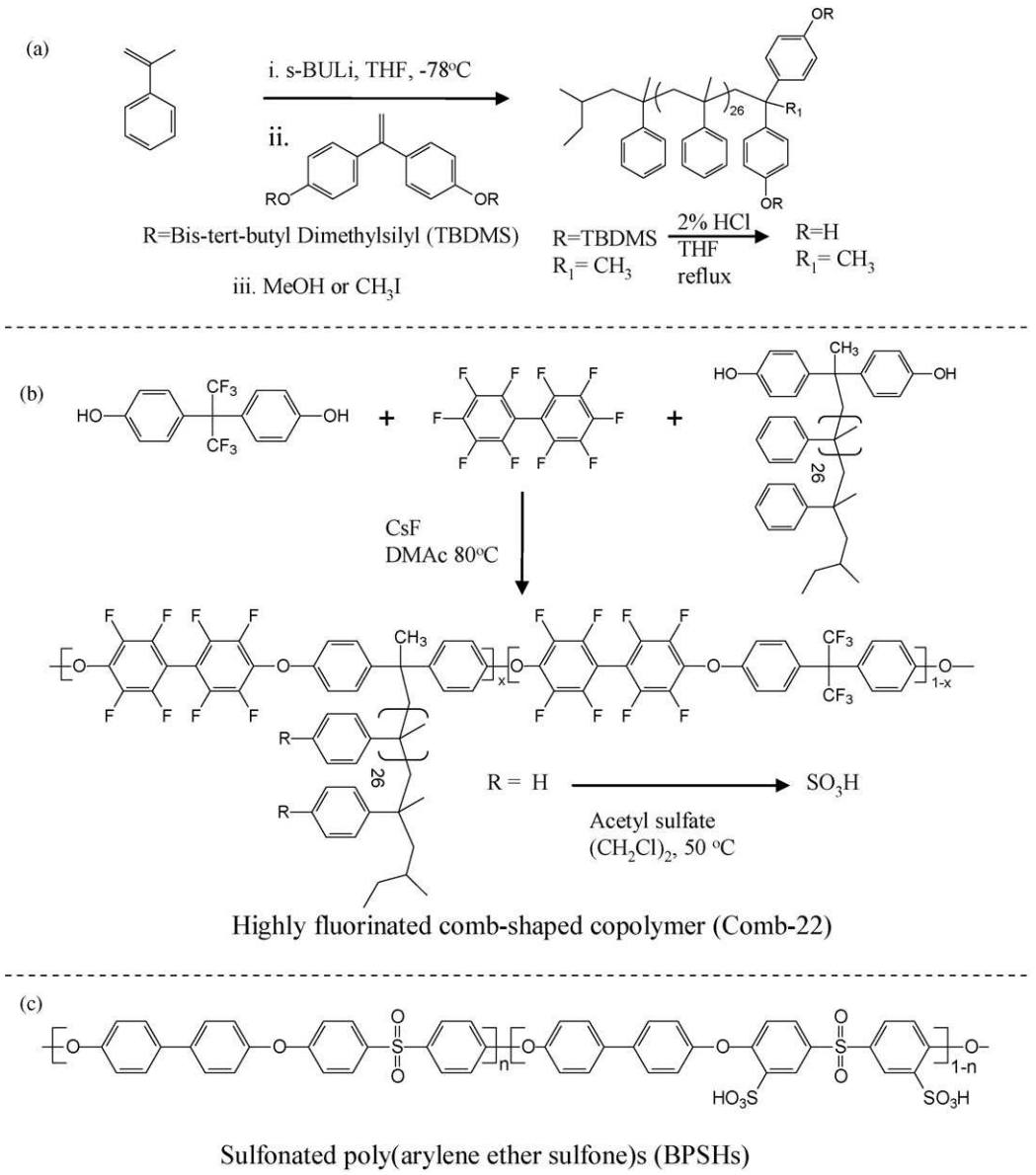

Fig. 1. Synthesis of (a) macromonomers, (b) sulfonated comb-shaped copolymer and (c) chemical structure of sulfonated poly(arylene ether sulfone)s (BPSHs).

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%) = $(W_{wet} - W_{dry})/W_{dry} \times 100$.
[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 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].

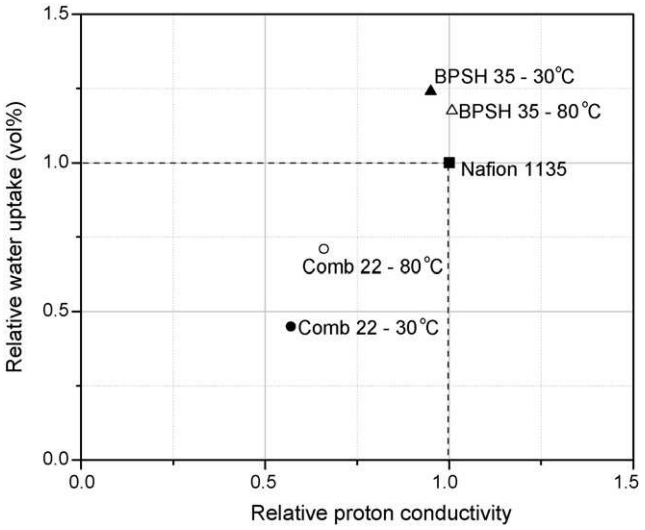

Fig. 2. Relative proton conductivity and relative water uptake of the membranes to those of Nafion at 30 °C and 80 °C.

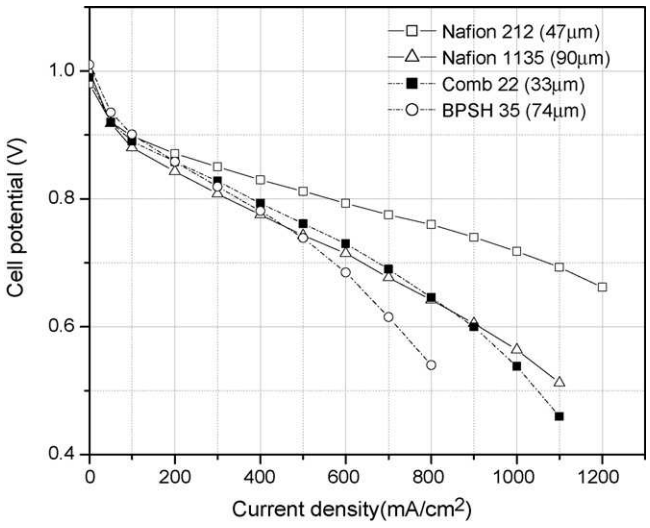

Fig. 3. H_2/air performance of Comb 22 copolymer, BPSH-35, and Nafion.

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 (H_2/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 those typically used for DMFC. MEAs using Comb 22 copolymer showed inferior performance to Nafion 212 (47

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

Copolymer	Thickness (

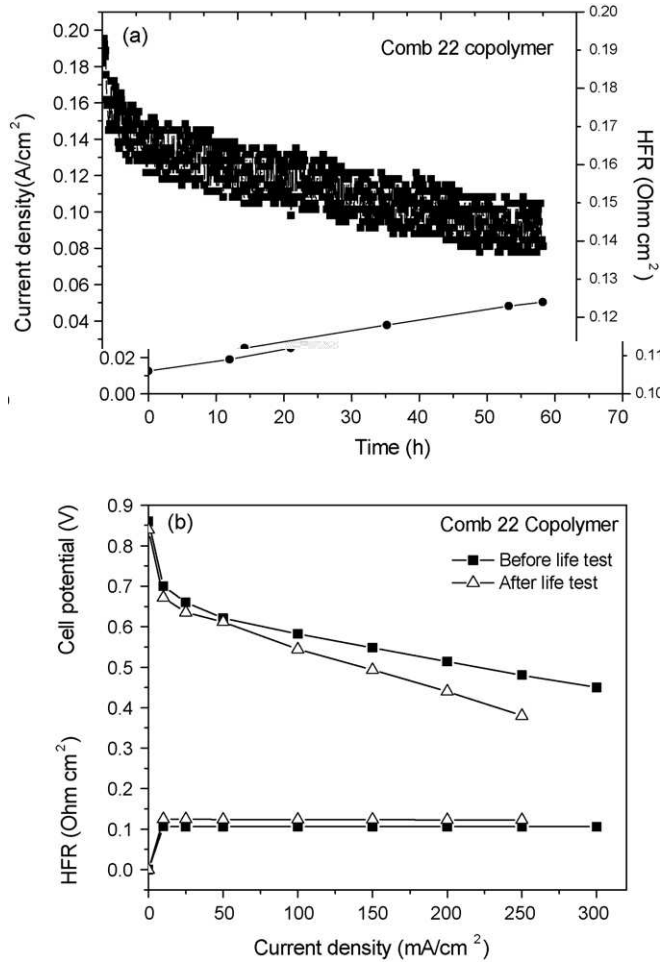

Fig. 6. (a) Current density change of the cell using Comb 22 copolymer and (b) comparison of polarization curve of Comb 22 copolymer before and after 65 h life test (operating temperature 80 °C, 0.5 M MeOH).

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 H_2/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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