



Short communication

Homopolymer-like sulfonated phenyl- and diphenyl-poly(arylene ether ketone)s for fuel cell applications[☆]Baijun Liu^{a,c}, Yu Seung Kim^b, Wei Hu^c, Gilles P. Robertson^a, Bryan S. Pivovar^b, Michael D. Guiver^{a,*}^a Institute for Chemical Process and Environmental Technology, National Research Council, Ottawa, Ontario K1A 0R6, Canada^b Los Alamos National Laboratory, Electronic and Electrochemical Materials and Devices, Los Alamos, NM 87545, USA^c Alan G. MacDiarmid Institute, Jilin University, Changchun 130023, PR China

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ABSTRACT

Two series of homopolymer-like sulfonated aromatic poly(ether ketone)s (SPEKs) were readily prepared and post-sulfonated using mild conditions. The homopolymer-like SPEKs exhibited advantages in synthesis and physical properties over typical post-sulfonated random copolymers, such as rapid and mild sulfonation conditions, high molecular weights, site specificity and control over IEC, as well as an excellent combination of dimensional swelling stability, low methanol permeability and high proton conductivity. These beneficial membrane properties are reflected in the attractive direct methanol fuel cell (DMFC) and polymer electrolyte membrane fuel cell (PEMFC) performance of these homopolymer-like SPEKs as compared with typical random copolymer SPEKs.

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1. Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) and direct methanol fuel cells (DMFCs) are currently under intense study as efficient and clean electrochemical power devices. One of the challenges is to develop new high-performance proton conductive membranes as alternatives to the perfluorinated sulfonic acid polymer electrolyte membranes (PEMs) such as Nafion[®] [1–3]. Sulfonated aromatic hydrocarbon polymers have been widely investigated as promising PEM materials because of their low cost, simplicity of preparation and their good thermal and chemical stability. Most sulfonated poly(ether ketone)s (PEKs) are prepared either by post-sulfonation of polymers or by direct copolymerization of sulfonated monomers [4,5]. The post-sulfonation approach is attractive because of the relatively simple reaction procedure in comparison with the synthesis and purification of sulfonated monomers, enabling the process to be scaled up. However, post-sulfonation may lead to difficulties in achieving precise control of the site of sulfonation and the target degree of sulfonation (DS), resulting in a random or less defined distribution of sulfonic acid groups along the polymer chains. In addition, vigorous reaction conditions are often required, such as high temperature and strongly acidic sulfonating agents, which in some cases may lead to

side-reactions and degradation of the polymer backbone [6]. Therefore, it is of practical interest to prepare PEM materials by a facile and mild post-sulfonation method whereby improved control of the site of sulfonation and DS could be achieved.

Site-controlled post-sulfonated polymers have been reported, wherein it was suggested that polymers with sulfonated pendant phenyl groups are more stable to thermal degradation, hydrolysis and oxidation [5]. Almost all reported sulfonated polymers with an ion exchange capacity (IEC) or DS in the range suitable for PEM applications are derived from a copolymer-type framework, whereby the resulting random distribution of hydrophilic moieties varies with reaction conditions and may lead to a greater degree of undesirable water swelling in comparison with homopolymers of well-defined and uniform structure [4]. Most investigations of these copolymers are concerned with the synthesis and characterization of the basic properties relative to the proton conductivity. There is less systematic study showing relationships between structure and single cell performance [4,7]. The aim of this communication is to report the DMFC and PEMFC performance of new homopolymer-like sulfonated phenylated PEKs and diphenylated PEKs that were made by a rapid, mild and controllable post-sulfonation (Scheme 1).

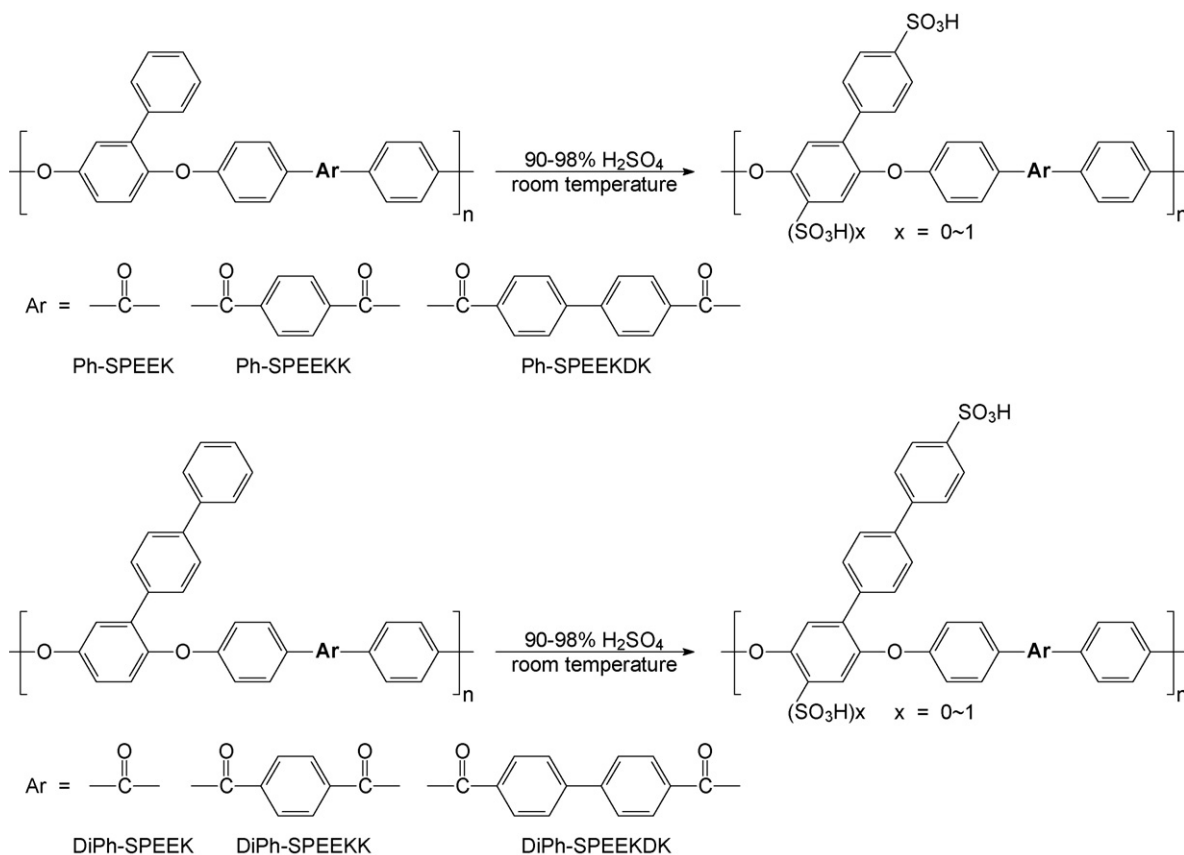
2. Experimental

The novel sulfonated diphenylated PEKs were prepared according to the reported synthetic procedure of the sulfonated phenylated PEKs [6], and improved conditions and longer sulfonation time for both above polymers were adopted in this study. MEAs

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Scheme 1. Sulfonation reactions of phenylated and diphenylated PEKs.

were prepared from standard catalyst inks using unsupported platinum and platinum–ruthenium catalysts. To prepare the catalyst ink mixtures, a 5% Nafion dispersion (1100 equivalent weight, Solution Technology, Inc.) was added to the water-wetted catalysts. For DMFC MEAs, the anode ink composition was 86 wt% 1:1 platinum–ruthenium (Johnson Matthey) and 14 wt% Nafion, and the cathode ink composition was 90 wt% platinum black (Johnson Matthey) and 10 wt% Nafion. Catalyst inks were mixed by sonication for about 90 s and then transferred to a pre-dried membrane in acid form by direct painting at 75 °C. The painted MEAs were dried at 75 °C for 20 min on a vacuum plate. The anode and cathode catalyst loading was approximately 10 and 6 mg cm⁻², respectively. High catalyst loadings were used to minimize catalyst effects in order to provide a better performance comparison of the membrane component against Nafion. Single- and double-sided hydrophobic carbon cloths (E-TEK, Inc.) were used as anode and cathode gas diffusion layers, respectively. For PEMFC MEAs, the catalyst ink composition was 71 wt% platinum/carbon (20% platinum on carbon) and 29 wt% Nafion. Catalyst inks were mixed with glycerol and tetrabutyl ammonium solution by vigorous stirring for 12 h and transferred to decal. After drying at 140 °C for at least 6 h, catalyst layers were transferred to proton exchange membranes in their salt form by pressing at 280 °C for 3 min. The MEAs then were converted to acid form by immersing them in boiling 0.5 M H₂SO₄ for 90 min, then washing in boiling deionized water for a further 90 min. The anode and cathode catalyst loading was 0.2 mg cm⁻². Double-sided hydrophobic carbon cloths (E-TEK, Inc.) were used as anode and cathode gas diffusion layers. The geometric active cell area was 5 cm².

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 0.5 V. For DMFC testing, the cell was held at 80 °C; 0.5 M methanol was fed to the anode with a flow rate of 1.8 mL min⁻¹; 90 °C humidified air was fed at 500 sccm without back pressure. High humidification and stoichiometry were used to minimize cathode effects. For PEMFC testing, the cell was held at 80 °C; 105 °C humidified hydrogen was fed at 200 sccm with 20 psig back pressure; 90 °C humidified air was fed at 500 sccm with 20 psig back pressure. High-frequency resistance (HFR) was measured by applying a sinusoidal wave perturbation at 2 kHz and 30 mV. Proton conductivity and methanol permeability were measured from HFR and methanol crossover limiting current, respectively.

3. Results and discussion

Concentrated sulfuric acid acts as both a good solvent and a mild sulfonation reagent for PEK-type polymers. Phenylated PEK polymers (Ph-PEK)s achieve a high DS (DS ~ 1) in 95–98% sulfuric acid at room temperature within several hours, which is extremely rapid in comparison with the sulfonation of commercial Victrex poly(ether ether ketone) (PEEK) [8]. In order to demonstrate the effect of polymer structure on the outcome of the sulfonation reaction, commercial PEEK (Victrex, fine powder), phenylated PEEK (Ph-PEEK, fine powder) and diphenylated PEEK (DiPh-PEEK, fine powder), were sulfonated using the same polymer concentration (0.2 g/10 ml 95–98% H₂SO₄) at room temperature and the same stirring speed for a long reaction period. The resulting DS values were calculated from ¹H NMR spectra. The *para* position of the pendant benzene rings of both Ph-PEEK and DiPh-PEEK could be fully mono-sulfonated within 2–3 h. For extended reaction times, no sulfonation on the Ph-PEEK mainchain was detected within 20 h, but

after 15 days, the ratio of mainchain to pendant-phenyl substitution was $<0.4:1$. In the case of DiPh-PEEK, the mono-sulfonated biphenyl pendant substituent led to the mainchain having greater activation towards sulfonation than Ph-PEEK, resulting in a ratio 1:1 within 3 days. Reaction on the pendant biphenyl substituent was limited to mono-sulfonation. In comparing PEEK, Ph-PEEK, and DiPh-PEEK, sulfonation of pendant phenyl or diphenyl PEKs from the latter two starting polymers could easily be achieved within a short reaction time, even at a 50 g scale, resulting in homopolymer-like PEM materials. All the PEKs including PEEKK and PEEKDK backbones containing the same pendant groups being used for the present MEA studies showed similar sulfonation characteristics. The structures of all the polymers were fully characterized by ^1H , ^{13}C and a variety of 2D NMR experiments [6,9]. It is apparent that this approach could be used generally, to produce readily sulfonated PEKs of the required IEC (or equivalent weight) simply by selecting a comonomer of appropriate molecular weight. A further advantage is that high molecular weight copolymers may be prepared, since the non-sulfonated monomers are readily soluble during the polymerization process.

Manthiram and Yang reported the DMFC performance of sulfonated PEEK (Victrex) [10]. Although SPEEK membranes with $\text{DS} \sim 0.5$ ($\text{IEC} \sim 1.7$ mequiv. g^{-1}) exhibited comparable DMFC performance to Nafion due to the lower relative methanol crossover counteracting the lower proton conductivity, the operating temperature had to be limited to $<65^\circ\text{C}$ due to the problem of the hydrocarbon PEM undergoing swelling at elevated temperature. For example, SPEEK with IEC 1.74 had more than 500% water uptake at 80°C , so that no cell performance could be measured. SPEEK with IEC 1.62 also had unacceptably high water uptake ($\sim 140\%$) for fuel cell operation. We reported that homopolymer-like side-group-acid Ph-SPEEKK and Ph-SPEEKDK have some advantageous physical properties compared with SPEEK and other sulfonated copolymers, such as good thermal, oxidative and dimensional swelling stability, excellent tensile strength, high proton conductivity and low methanol permeability [6]. For example, homopolymer-like Ph-SPEEKK with $\text{IEC} = 1.82$ mequiv. g^{-1} had a much lower dimensional swelling of 15% compared with a similarly structured random copolymer ($\text{IEC} \sim 1.75$ mequiv. g^{-1}), also containing pendant phenyl sulfonic acid groups, which had dimensional swelling of 32% [6]. The superior DMFC and PEMFC performance of Ph-SPEEKK ($\text{DS} = 1.0$, $\chi = 0$, $\text{IEC} = 1.82$ mequiv. g^{-1}), Ph-SPEEKDK ($\text{DS} = 1.0$, $\chi = 0$, $\text{IEC} = 1.60$ mequiv. g^{-1}) and DiPh-SPEEKDK ($\text{DS} = 2.0$, $\chi = 1$, $\text{IEC} = 2.32$ mequiv. g^{-1}) with well-defined homopolymer-like structures is reported for the first time, which may provide some insight for design strategies for fuel cell membrane materials.

The utilization of thinner membranes in DMFCs is possible when membranes have good mechanical integrity and methanol crossover is low and this provides benefits such as improved fuel utilization and efficiency, size and weight reductions and lower cost [11,12]. Relatively thick Nafion membranes (Nafion 117, 180 μm) are used in DMFC, in spite of the resultant ohmic resistance increase, to avoid excessive methanol crossover. MEAs of Ph-SPEEKK ($\text{DS} = 1.0$), Ph-SPEEKDK ($\text{DS} = 1.0$), and DiPh-SPEEKDK ($\text{DS} = 2.0$) were prepared and compared with Nafion in both DMFC and H_2/air PEMFC. The performance of Ph-SPEEKK (60- μm thick film) outperformed Nafion at 80°C in tests for all methanol feed concentrations (0.5, 1.0 and 2.0 M). For example, the current density of Ph-SPEEKK at 0.5 V at 80°C in 1.0 M methanol reached 255 mA cm^{-2} , which is much higher than Nafion 117 (194 mA cm^{-2}) and Nafion 1135 (143 mA cm^{-2}), as shown in Fig. 1. The improved performance of Ph-SPEEKK could be explained by a combination of proton conductivity comparable with Nafion and a lower relative methanol crossover, as supported by the lower methanol crossover limit-

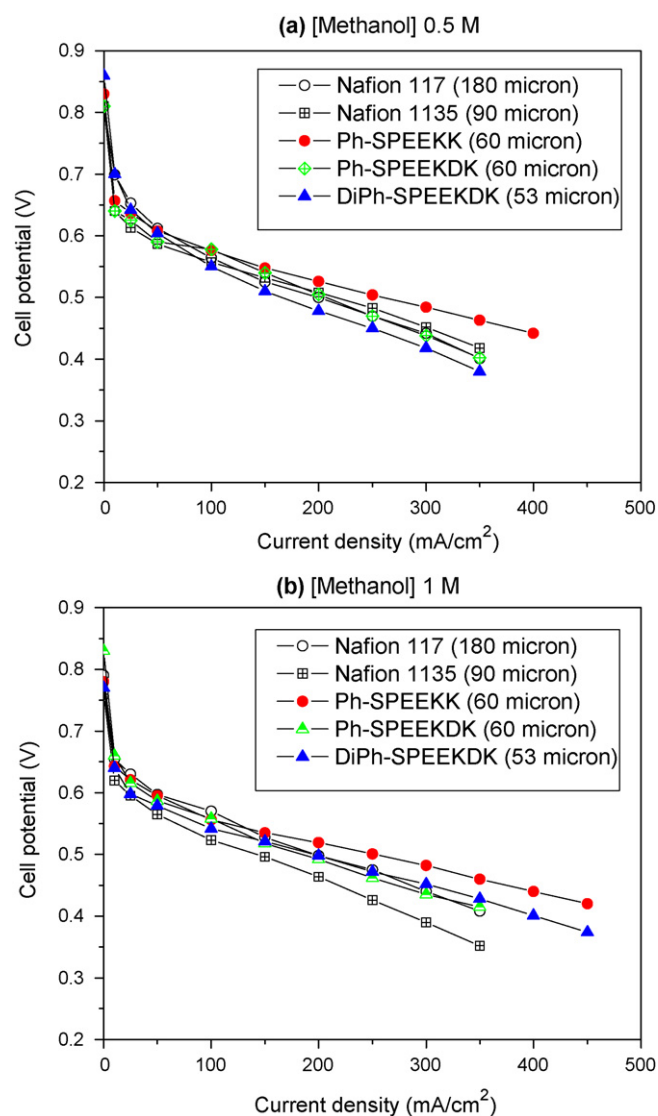


Fig. 1. DMFC performance of the polymers: (a) methanol feed concentration 0.5 M and (b) methanol feed concentration 1 M. Cell temperature, 80°C ; cathode temperature, 90°C ; methanol feed rate, 1.8 mL s^{-1} ; air flow rate, 500 sccm ; cell hardware, 5 cm^2 ; anode, Pt-Ru 8 mg cm^{-2} ; cathode, Pt 6 mg cm^{-2} .

ing current density [13,14]. Proton conductivities derived from HFR measurements and methanol permeabilities derived from methanol crossover limiting current [11] were used to evaluate the materials. As shown in Table 1, Ph-SPEEKK had proton conductivity of 85 mS cm^{-1} (room temperature, 21°C) and methanol permeability of $21 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ compared with the values of 99 mS cm^{-1} and $38 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$, respectively, for Nafion 1135, giving a relative selectivity (defined in Ref. [12]) of 1.6. Ph-SPEEKDK and DiPh-SPEEKK had conductivities of 28 and 60 mS cm^{-1} , methanol permeabilities of 6.0 and $16.5 \text{ cm}^2 \text{ s}^{-1}$, and relative selectivities of 2.5 and 1.6, respectively. In addition, as an obvious improvement of cell performance over main-chain sulfonated PEEK-type membranes, Ph-SPEEKK with IEC 1.82 could run at an operating temperature of 95°C , without evidence of instability in hot water.

Ph-SPEEKDK had a similar DMFC polarization curve to Nafion 117, while DiPh-SPEEKDK membranes showed lower performance at 0.5 M methanol feed concentration. Although Ph-SPEEKDK had a good relative selectivity of 2.5, it had a much lower proton conductivity than Ph-SPEEKK. DiPh-SPEEKDK had the same relative

Table 1
Property comparison of SPEK polymers measured at initial cell operating conditions using 0.5 M methanol feed at 80 °C

Property	Polymer			
	Nafion 1135	Ph-SPEEKK	Ph-SPEEKDK	DiPh-SPEEKDK
Membrane thickness (μm) ^a	90	60	60	53
Ion exchange capacity (mequiv. g^{-1}) ^a	0.91	1.82	1.60	2.32
Proton conductivity (mS cm^{-1}) ^b	99	85	28	60
MeOH permeability ($\times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$) ^b	38	21	6.0	16.5
High-frequency resistance (HFR) ($\text{m}\Omega \text{ cm}^2$)	91	71	215	88
Methanol crossover limiting current (mA cm^{-2})	137	110	23	90

^a Measured at room temperature.

^b Proton conductivity and methanol permeability was measured from HFR and methanol crossover limiting current, respectively.

selectivity as Ph-SPEEKK, but a lower conductivity. However, the membranes outperformed Nafion at a higher feed concentration of 2.0 M. For example, the current density of Ph-SPEEKDK at 0.5 V reached 160 mA cm^{-2} , which is three times higher than Nafion 1135 (50 mA cm^{-2}). This behavior is easily rationalized by the methanol permeability of Ph-SPEEKDK, which is 6.3 times lower than that of Nafion.

Very limited PEMFC data using PAE-type polymers are available in the scientific literature, probably due to the insufficient mechanical stability of the highly sulfonated membranes and also the delamination problem of MEAs [11]. Lakshmanan et al. reported the H_2 /air fuel cell performance of sulfonated PEEK-based membranes having acid–base interaction at 75 °C. The current density of the MEA using the membrane (IEC 1.7 mequiv. g^{-1} , $100 \mu\text{m}$) was 19% lower than the MEA using Nafion 117 [14]. Kerres reported fuel cell performance of PAE membranes having ionic or covalent cross-linking [15]. The current density of the MEA using an ionically cross-linked membrane (IEC 1.3 mequiv. g^{-1}) was more than 0.4 A cm^{-2} at 0.6 V in the temperature range of 65–75 °C. Both PEMFC performance of above mentioned membranes were claimed to be close to Nafion at 100 °C. We provide here a comparison of PEMFC performance for Nafion 212, Ph-SPEEKK and DiPh-SPEEKDK as references, as shown in Fig. 2. The cell polarization curve shows that Ph-SPEEKK (40 μm) had comparable initial PEMFC performance to Nafion 212 (40 μm). For example, the current density of Ph-SPEEKK membrane was 0.61 A cm^{-2} at 0.6 V, which is similar to Nafion 212 (0.62 A cm^{-2}). Ph-SPEEKK membrane had a higher open circuit voltage (OCV) than Nafion 212.

4. Conclusions

In this study, several PEKs with pendant phenyl structures were synthesized that underwent rapid sulfonation under mild conditions to provide homopolymer-like sulfonated derivatives. In terms of fuel cell materials, the homopolymer-like PEKs exhibited several advantages in the synthesis and physical properties over typical post-sulfonated random copolymers, such as rapid and mild reaction conditions, high molecular weights, site specificity and control over IEC, as well as an excellent combination of dimensional swelling stability, low methanol permeability and high proton conductivity. Pendant phenyl sulfonated PEK homopolymer-like membranes have lower water uptake and better dimensional stability compared with pendant phenyl sulfonated PEK random copolymers [6]. Ph-SPEEKK membranes have a high IEC value of 1.82 mequiv. g^{-1} but a moderately low water uptake and methanol permeability [6]. These beneficial properties are reflected in the attractive DMFC and PEMFC performance of these homopolymer-like SPEKs. MEAs of Ph-SPEEKK (DS = 1.0), Ph-SPEEKDK (DS = 1.0, IEC 1.60 mequiv. g^{-1}), and DiPh-SPEEKDK (DS = 2.0, IEC 2.32 mequiv. g^{-1}) were compared with Nafion in both DMFC and H_2 /air PEMFC. Of the present series, Ph-SPEEKK had the best balance of properties and DMFC performance, achieving higher current densities than Nafion for all methanol feed concentrations (0.5–2.0 M). The current density of Ph-SPEEKK at 0.5 V at 80 °C in 1.0 M methanol reached 255 mA cm^{-2} as compared with 194 mA cm^{-2} for Nafion 117 and 143 mA cm^{-2} for Nafion 1135. DiPh-SPEEKDK and Ph-SPEEKDK containing rigid structural units and having lower methanol permeabilities had improved DMFC performance at high methanol concentration. In the H_2 /air MEA test, Ph-SPEEKK (40 μm) had very similar initial PEMFC performance to Nafion 212 (40 μm), with current densities of 0.61 – 0.62 A cm^{-2} at 0.6 V for both materials. The facile synthesis, close control of IEC and lower cost polymer provides a potential alternative to Nafion.

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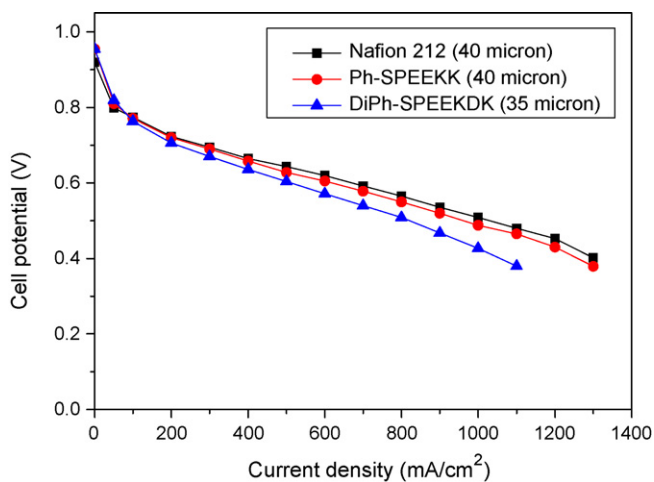


Fig. 2. H_2 /air performance of the polymers. Cell temperature, 80 °C; anode temperature, 105 °C; cathode temperature, 70 °C; hydrogen flow rate, 200 sccm; air flow rate, 500 sccm; back pressure, 20 psig; cell hardware, 5 cm^2 ; anode, Pt 0.2 mg cm^{-2} ; cathode, Pt 0.2 mg cm^{-2} .

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