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A Microblock Ionomer in Proton Exchange Membrane Electrolysis for the Production of High Purity Hydrogen

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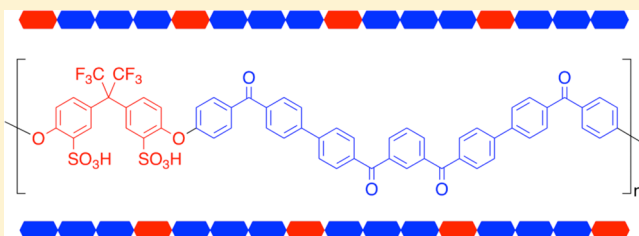
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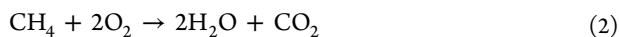
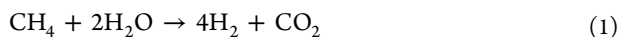
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ABSTRACT: Proton exchange membranes (PEM's) are currently under investigation for membrane water electrolysis (PEMWE) to deliver efficient production of the high purity hydrogen needed to supply emerging clean-energy technologies such as hydrogen fuel cells. The microblock aromatic ionomer described in this work achieves high mechanical strength in an aqueous environment as a result of its designed, biphasic morphology and displays many of the qualities required in a PEM. The new ionomer membrane thus shows good proton conductivity (63 mS cm^{-1} at 80°C and 100% RH), while retaining mechanical integrity under high temperature, hydrated conditions. Testing in electrolysis has shown good energy efficiency (1.67 V at 1 A cm^{-2} and 80°C , corresponding to 4 kWh/Nm^3 of H_2), making this ionomer a potential candidate for commercial application in PEMWE.



INTRODUCTION

The depletion of fossil fuel resources, combined with the widely accepted link between carbon dioxide emissions and adverse environmental effects such as global warming, has driven much recent research into low-carbon energy technologies.¹ A wide range of renewable energy resources (wind, solar, hydroelectric, and tidal, for example) are now potentially available for commercial implementation, but a major limitation to the global use of renewable energy is that of efficient energy storage.² Hydrogen has been evaluated positively, in economic terms, as a potential technology for moving the energy industry away from carbon-based fossil fuels,³ but current hydrogen production is based primarily on steam-reforming of methane (eq 1),⁴ which generates as much CO_2 as would be produced by simply burning the methane (eq 2).



An alternative, zero-carbon approach to hydrogen production involves proton exchange membrane water electrolysis (PEMWE) powered by renewable energy resources.⁵ Electrolysis of water via PEMWE^{6–9} offers a potential route to energy-efficient production of the sustainable hydrogen required to supply clean power-generation technologies such as the hydrogen fuel cell.¹⁰ Membrane electrolysis has considerable benefits over current hydrogen production via alkaline electrolysis, in that it has improved response times to

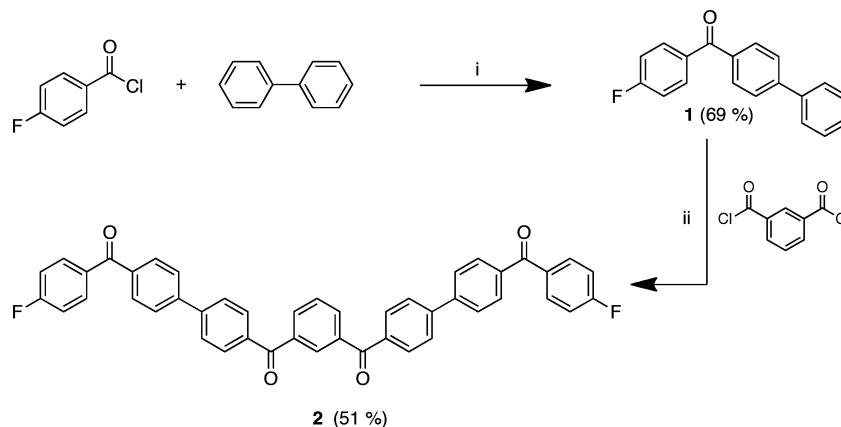
the power fluctuations characteristic of renewable resources⁵ as well as lower power consumption and generation of much higher purity hydrogen.¹¹

The potential of sulfonated aromatic poly(ether–ketone)s as proton exchange membranes (PEMs) has received considerable attention over the past few decades, as this type of material provides a possible alternative to perfluorinated sulfonic acid (PFSA) membranes in proton exchange membrane fuel cell (PEMFC) applications.^{12–15} Sulfonated polyaromatic systems have been shown to provide higher mechanical stability under fuel-cell operating conditions, good proton conductivities, and, perhaps crucially, lower production costs than PFSA-based materials.^{16–18}

A recent development has been the design and realization of microblock aromatic ionomers in which fully specified sulfonated and nonsulfonated sequences alternate along the polymer chain.¹⁹ These ionomers show a much higher degree of microphase separation between ionic and nonionic regions than analogous random copolymers and have demonstrated low degrees of swelling and excellent mechanical stability at high hydration levels in hydrogen fuel cell applications.^{19,20} It was anticipated in the present work that an aromatic ionomer of this type, with its highly specified structure and membrane morphology,¹⁹ could also perform well in proton exchange

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Scheme 1. Synthesis of the 7-Ring Monomer **2** via Intermediate **1** Using Sequential Friedel–Crafts Acylations^a

^aReaction conditions: (i) AlCl₃, 1,2-dichlorobenzene (DCB), 100 °C; (ii) AlCl₃, DCB, 140 °C.

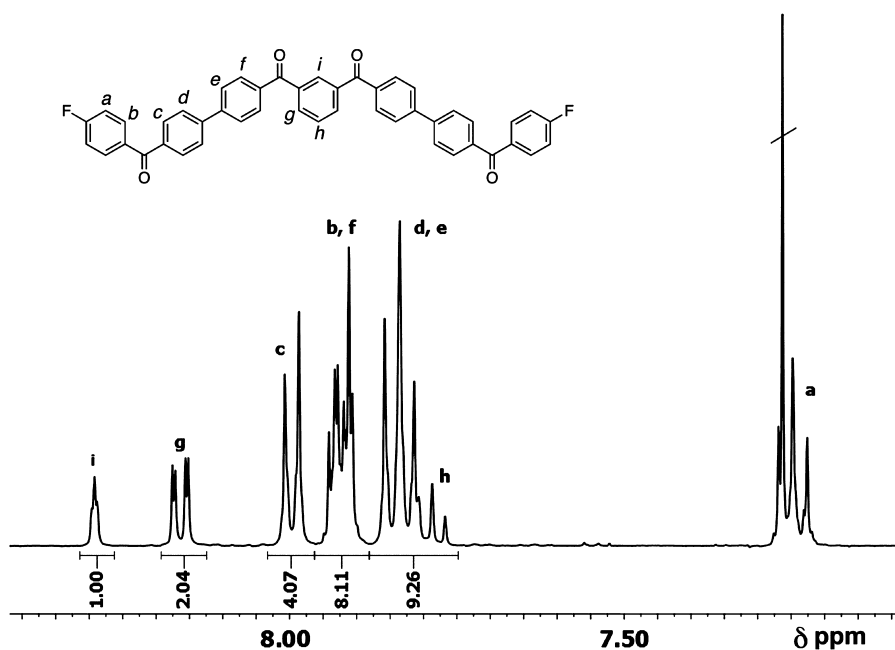


Figure 1. ¹H NMR spectrum (CDCl₃/TFA, 6:1, v/v) of monomer **2**, with assignments.

membrane water electrolysis as a result of the comparable chemical and physical properties required. The primary difference between PEMFC and PEMWE is that water electrolysis systems do not suffer the problem of membrane dehydration and consequent loss of conductivity in fuel cells at high temperatures¹⁰ because the PEMWE membrane remains hydrated at all times.

Here we describe the synthesis, characterization, membrane fabrication, and preliminary performance assessment in PEMWE of a novel microblock ionomer membrane that exhibits higher efficiency than the current technology standard, the perfluorinated sulfonic acid membrane Nafion. The new ionomer, as a result of its microblock molecular architecture and consequent microphase-separated morphology, maintains sufficient mechanical strength to function effectively in PEMWE at high temperatures, even when fully hydrated.

RESULTS AND DISCUSSION

The fluoroaryl ketone **1** reacts with isophthaloyl chloride under Friedel–Crafts conditions (Scheme 1) to afford an extended,

seven-ring difluoroketone monomer, **2**,²¹ which was isolated using the precipitation method described for related long-chain monomers by Kricheldorf et al.²² The nonsulfonatable monomer **2** was designed to generate a new variant of the “microblock” type of ionomer reported previously.¹⁹ Specifically, this monomer contains only aromatic rings bound to one or more electron-withdrawing carbonyl groups that render the associated rings resistant to electrophilic substitution—specifically to electrophilic sulfonation in concentrated sulfuric acid. Under such conditions the carbonyl groups are protonated, so rendering them even more effective in deactivating their associated aromatic rings toward electrophilic attack.

Analysis by ¹H NMR spectroscopy (Figure 1) confirmed the successful isolation of monomer **2** in high purity (>99% by DSC and ¹H NMR spectroscopy). The characteristic low-field resonance of the single, unique proton H_i in the central aromatic ring, ortho to both carbonyl groups (Figure 1), can be a useful reference in ¹H NMR analysis of the polymers derived from this monomer, as integration of this resonance against

Scheme 2. Polycondensation of Monomer **2** with Hexafluorobisphenol-A, via Nucleophilic Aromatic Substitution, to Yield Polymer **3**; Ionomer **4** is Produced by Regioselective Sulfonation of **3** (Disubstitution at the Bisphenol Residue) in Concentrated Sulfuric Acid

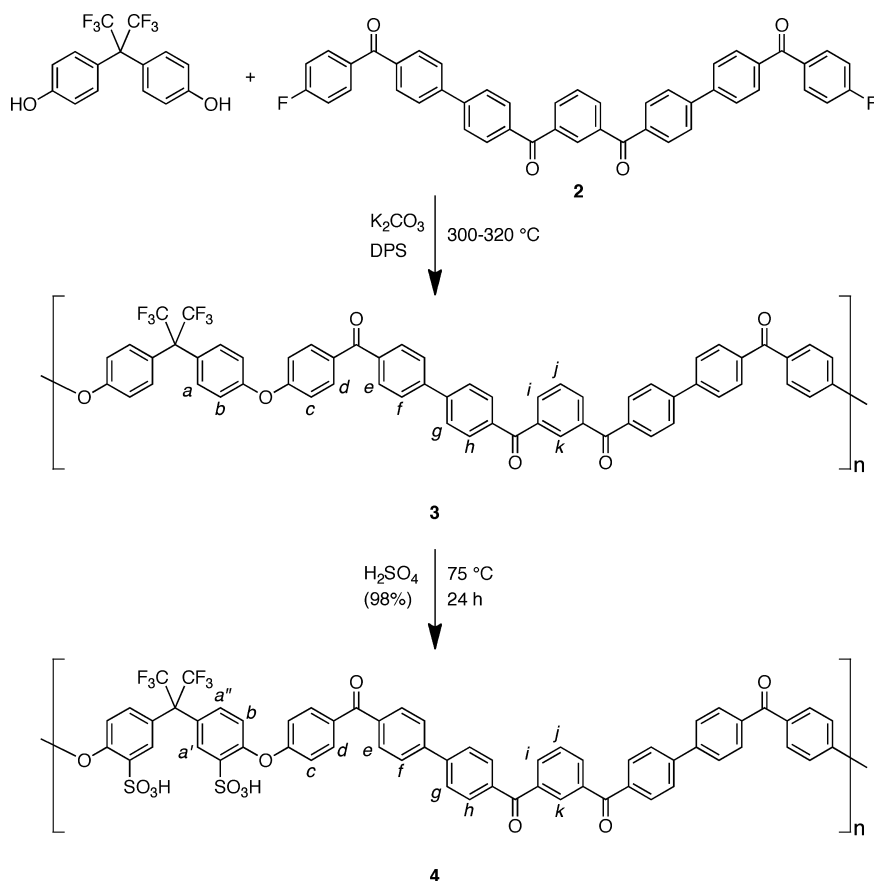


Table 1. Characterization Data for Polymer **3** and Ionomer **4**

polymer batch no.	η_{inh}^a (dL g ⁻¹)	ionomer batch no.	η_{inh}^b (dL g ⁻¹)	M_n^c (kDa)	M_w^c (kDa)	reaction time (h)	final reaction temp (°C)	Δ^d (rpm)
3.1	1.4	4.1	5.3	150	230	3.1	320	28
3.2	1.3	4.2	3.0	120	190	3.0	305	37
3.3	1.3	4.3	3.0	110	180	1.2	290	34

^aIn 98% H₂SO₄ as solvent. ^bIn NMP as solvent. ^cGPC in DMF/LiBr (0.1) as eluent, with polystyrene calibration standards. ^dDrop in stirrer speed during polycondensation reaction.

other resonances in the ionomer spectrum enables the degree of sulfonation, and hence the ion exchange capacity of the ionomer, to be determined (see below).

Monomer **2** undergoes facile polycondensation with hexafluorobisphenol-A (HFBis-A) to yield poly(ether-ketone) **3** containing a repeat unit of nine aromatic rings (Scheme 2). Each repeat unit contains two aromatic rings (those derived from the bisphenol) that are activated to postpolymerization sulfonation, as a result of the mesomeric π -donor effect of the newly formed ether linkages. The choice of hexafluorobisphenol-A was dictated by its tendency to inhibit polymer crystallization during synthesis, so avoiding premature termination of polycondensation, and also by the stability of its residue under the strongly acidic conditions encountered during postpolymerization sulfonation. Bisphenol-A residues cleave readily under acidic conditions via a carbonium ion mechanism, but in residues derived from hexafluorobisphenol-A this mechanism is strongly inhibited by the electron-withdrawing effect of the trifluoromethyl groups. Polycondensation was carried out in the presence of potassium carbonate

as base, using diphenylsulfone as solvent. The reaction temperature was raised progressively from 190 to 300–320 °C over 6–8 h, and this procedure enabled very high molecular weights ($M_n > 100$ kDa; see Table 1) to be achieved—a critical parameter in the production of PEMs with high mechanical strength and stability.²³

The molecular weights of different batches of polymer **3** were assessed in terms of inherent viscosity (η_{inh}) in concentrated sulfuric acid. Polymers having η_{inh} values below 1.0 dL g⁻¹ were not taken forward to generate ionomer **4** or its subsequently formed membranes. High molecular weights could, however, be achieved reproducibly (Table 1, 3.1–3.3), and a clear correlation was established between the inherent viscosity values for the base polymers and GPC analyses of the final ionomers **4** (4.1–4.3).

Samples of base polymer **3** were converted to ionomer **4** by postpolymerization sulfonation in 98% sulfuric acid at 75 °C for 16 h. Reactions at lower temperatures led to incomplete sulfonation as demonstrated by ¹H NMR spectroscopy (Figure 2). The spectrum of the unsulfonated polymer **3.1** (Scheme 2)

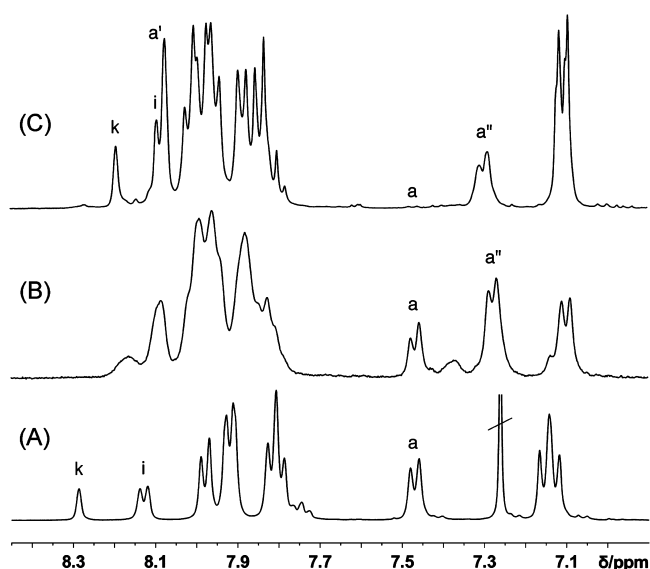


Figure 2. ^1H NMR (400 MHz) spectra of (A) polymer 3.1 (in CDCl_3/TFA), (B) ionomer 4.1 (in $\text{DMSO}-d_6$) after sulfonation for 16 h at 50 $^\circ\text{C}$, and (C) ionomer 4.1 (in $\text{DMSO}-d_6$) after sulfonation for 16 h at 75 $^\circ\text{C}$. Peak assignments are shown in Scheme 2.

in CDCl_3/TFA contains a doublet at 7.47 ppm which corresponds to the four protons (a) on the HFBis-A residue meta to the ether linkage. On sulfonation, this resonance progressively diminishes and is replaced by a doublet at higher field (δ 7.30 in $\text{DMSO}-d_6$) ultimately integrating as only two protons and assignable to the protons (a'') para to the site of sulfonation in ionomer 4 (Scheme 2). Quantitative sulfonation (i.e., two sulfonic acid groups per HFBis-A residue) is marked by the complete disappearance of the original doublet (a , Figure 2). At the same time, a new, singlet resonance (also two protons) appears at δ 8.12, corresponding to the protons (a') ortho to the site of sulfonation. The relative integrals of resonances a and a'' in the final spectrum can be used to determine the degree of sulfonation (DS) (eq 3), though at very high conversions eq 3 suffers from the disadvantage of requiring an accurate integral for a vanishingly weak resonance (a). This can be avoided by instead comparing the relative integrals of resonances corresponding to protons k and $[a' + i]$

(eq 4), or else integrals k and a'' can be used (eq 5). For example, integration of the topmost spectrum of Figure 2, using these three different methods, led to DS values of 96%, 110%, and 106%, respectively. Given the problems of integrating broad resonances and non-baseline peak resolution, these values together indicate essentially quantitative sulfonation according to Scheme 2, and thus an ion-exchange capacity for ionomer 4 (in the hypothetical dry state) of 1.75 ($\pm 5\%$) mequiv g^{-1} .

$$\text{DS} (\%) = 100(1 - a/2a'') \quad (3)$$

$$\text{DS} (\%) = 100[(a' + i) - 2k]/2k \quad (4)$$

$$\text{DS} (\%) = 100a''/2k \quad (5)$$

Analysis by ^1H NMR spectroscopy thus provides a useful approach to monitoring the sulfonation reaction. The theoretical ion exchange capacity of ionomer 4 at 100% sulfonation is achieved after some 16 h at 75 $^\circ\text{C}$ in 98% sulfuric acid, following which no further reaction is observed.

Ionomer 4.2 displayed good thermochemical stability, with only dehydration (6.5 wt %) being evident up to 150 $^\circ\text{C}$. There was no further weight loss up to 300 $^\circ\text{C}$, when desulfonation occurred between this temperature and 400 $^\circ\text{C}$ (12.2% weight loss), with a final onset of polymer degradation above 500 $^\circ\text{C}$.

Tough, flexible membranes were obtained reproducibly by dissolving the ionomer (in its acid form) in either *N*-methylpyrrolidinone (NMP) or *N,N*-dimethylacetamide (DMAc) at 15% (w/v) concentration. Once homogeneous, the ionomer solution was filtered through cotton fiber, poured onto a degreased glass plate, and drawn down with a Gardner knife to a defined thickness, typically in the range 200–400 μm . Evaporation of the solvent under vacuum at progressively increasing temperature (60–110 $^\circ\text{C}$) resulted in membranes of uniform and reproducible thickness ($\pm 5 \mu\text{m}$) which spontaneously debonded from the glass plate on equilibrating with atmospheric moisture for 24 h.

Thermal transitions—notably T_g —play a critical rôle in determining the thermomechanical stability of ionomer membranes. The ionomer glass transition should therefore, ideally, be above the desired working temperature range of the membrane (60–120 $^\circ\text{C}$ for PEMWE). Analysis of ionomer 4 by DSC showed a glass transition well above that of the cell

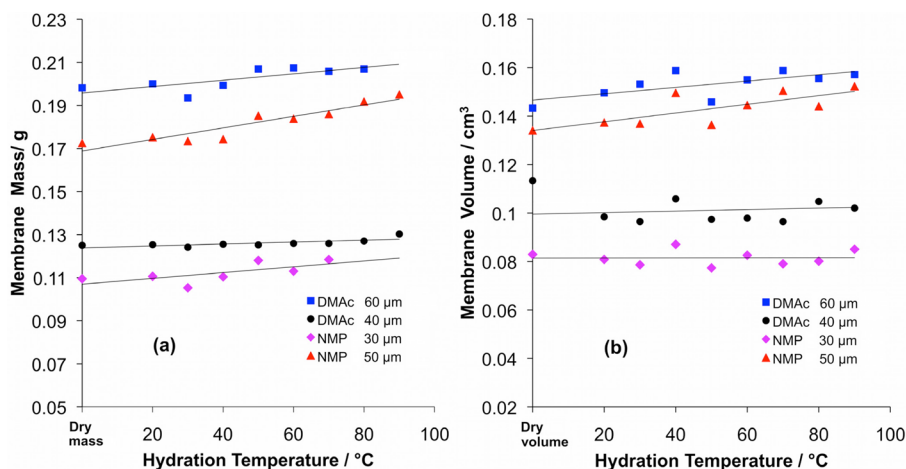


Figure 3. (a) Mass variation with increasing hydration temperature for membranes cast from DMAc or NMP. (b) Volume change for these membranes under the same conditions.

operating temperatures, but specific T_g values are known to be dependent upon the casting solvent used (due to the presence of strongly bound residual solvent in the cast membrane).²⁴ In the present work, T_g values of 156 and 179 °C were measured for ionomer membranes in the acid form, cast from NMP and DMAc, respectively. These values are certainly promising for high-temperature (>100 °C) electrolyzer and fuel-cell operation, although hydration of an ionomer can sometimes markedly lower the T_g .

Water-uptake and swelling analyses revealed good dimensional stability for proton-exchange membranes derived from ionomer 4. The membranes thus exhibited only low levels of swelling on hydration at high temperature, regardless of which casting solvent (NMP or DMAc) was used (Figure 3). Volume change with increasing hydration temperature was lower for the thinner membranes (30–40 μm , Figure 4). Both casting

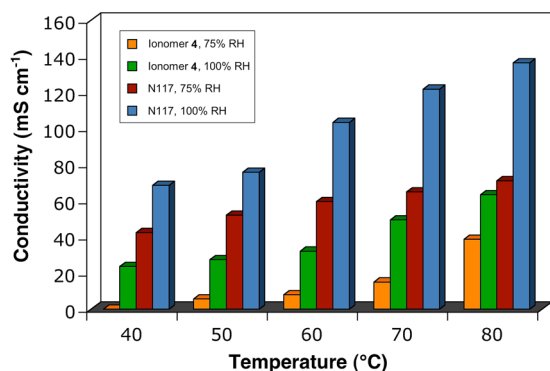


Figure 4. Variation of proton conductivity of ionomer 4 (gold and green) with temperature at different humidity levels, reaching 63 mS cm^{-1} at 80 °C, and of Nafion 117 under the same conditions (brick red and blue), reaching 136 mS cm^{-1} at 80 °C.

solvents (DMAc, NMP) afforded durable membranes, although literature reports indicate that DMAc may result in lower conductivities as a result of decomposition giving dimethylamine, which then neutralizes and binds to the sulfonic acid moieties.²⁵ Consequently, in the present work, NMP was the preferred casting solvent for membrane fabrication.

Membranes cast from ionomer 4.3 in NMP were compared to Nafion 115CS (Table 2) in terms of their swelling

Table 2. Swelling Behavior of Membranes from Ionomer 4.3 and Nafion 115CS in Water at 25 °C

ionomer	dry thickness (μm) at 23 °C, 50% RH	hydrated thickness (μm)	increase in thickness (%)
4.3	40	42	5
Nafion 115CS	127	142	12

characteristics in water at room temperature, with the new ionomer showing only about 40% of the dimensional change (thickness) found for the fluorocarbon material. This indicates good potential for mechanical stability of ionomer 4 in an operational MEA and PEMWE stack.

The in-plane proton conductivity of ionomer 4, measured under single-cell conditions, increased significantly with temperature and humidity, from 23 mS cm^{-1} at 40 °C and 100% RH to 63 mS cm^{-1} at 80 °C and 100% RH. In Figure 4, these values are compared with the proton conductivity of a Nafion 117 membrane, measured under the same conditions.

Increasing relative humidity clearly has an increasing impact on the conductivity of ionomer 4 as the temperature rises, suggesting better electrolyzer performance with fully hydrated membranes in the PEMWE environment.

Determining the efficiency of ionomer 4 in an actual, operating PEMWE environment is important to gauge the overall performance of the material. The efficiency for electrolysis can be quantified by comparing the thermodynamic maximum voltage to that measured under standard conditions for the electrolysis of water, where the values of reversible voltage E_{rev}° and thermoneutral voltage E_{tn}° are 1.229 and 1.481 V, respectively.⁵ The latter voltage does not result in electrolysis unless additional thermal energy is provided. Any voltage above E_{tn}° across an electrolysis cell is attributed to cell losses, either ohmic or resulting from activation overvoltage (electrode kinetics) or concentration overvoltage (mass transport processes). A membrane from ionomer 4.3 was analyzed in a single cell test, with an MEA constructed using an iridium dioxide-based catalyst ink at the anodic side (oxygen evolution reaction) and platinum–carbon electrodes at the cathodic side (hydrogen evolution reaction). The ionomer gave impressive results in electrolysis, with efficiency increasing considerably with temperature (Figure 5). The efficiency for

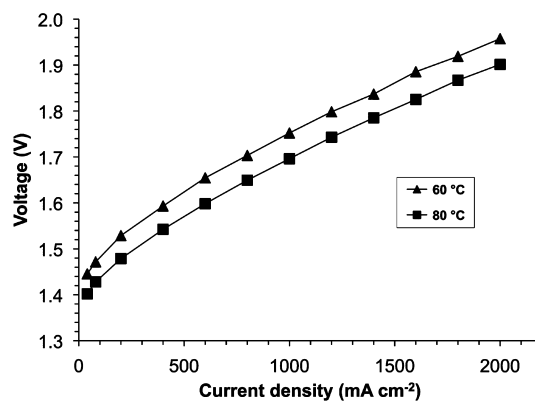


Figure 5. Single-cell electrolysis using a membrane from ionomer 4.3 at 60 and 80 °C, giving cell voltages at 1 A cm^{-2} of 1.733 and 1.684 V, respectively. These figures correspond to energy consumption values of 4.14 and 4.02 $\text{kWh/Nm}^3 \text{H}_2$.

PEMWE can be obtained by comparing the specific energy consumption for hydrogen (C_e) to the higher heating value (HHV, 3.54 kWh/Nm^3). In the present work, the MEA based on ionomer 4.3 yielded an efficiency of 86% (4.14 kWh/Nm^3) at 60 °C, increasing to 88% (4.02 kWh/Nm^3) at 80 °C. Despite the lower proton conductivity of ionomer 4.3 relative to Nafion, the aromatic microblock ionomer membrane clearly provides higher efficiencies in electrolysis, with values of 75% and 79% being measured for Nafion at 60 and 80 °C, respectively.⁵

The very high purity of hydrogen produced via PEMWE is one of the main advantages of this technology,⁵ as it enables the hydrogen to be used directly in technologies such as PEM fuel cells which require high purity hydrogen as fuel.¹⁰ Oxygen purity is also of importance as, above 4% hydrogen, the O_2/H_2 gas mixture poses an explosion hazard.¹¹ The proportion of hydrogen in the produced oxygen was measured during the single cell test, showing a decrease in hydrogen crossover during the test (Figure 6), ultimately falling to around 0.6% H_2 in O_2 at 1 A cm^{-2} and 60 °C. The single cell test also showed

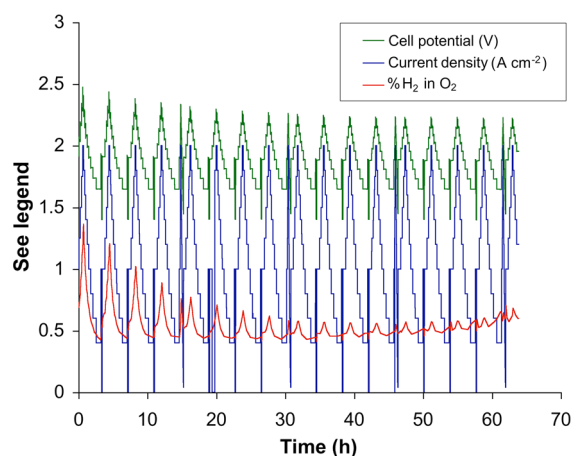


Figure 6. Time evolution of electrolysis parameters for an MEA using ionomer 4.3, operating at 60 °C.

very good electrical performance of the MEA over the entire test period (62 h), yielding stable, reproducible current and voltage through repeated cell cycling (Figure 6), indicating that the new ionomer has significant potential for application in PEMWE.

EXPERIMENTAL SECTION

Materials. Hexafluorobisphenol-A (97%), biphenyl (99.5%), 1,4-dioxane (99+%), *N,N*-dimethylacetamide (99%), *N*-methylpyrrolidone (99.5%), isophthaloyl dichloride (99%), 1,2-dichlorobenzene (99%), and 1,3,5-trichlorobenzene (99%) were all purchased from Sigma-Aldrich and used as supplied. Potassium carbonate was purchased from Sigma-Aldrich, ground in a pestle and mortar, and dried under vacuum (120 °C, 24 h) before use. Diphenyl sulfone and anhydrous aluminum chloride (99%) were purchased from Alfa Aesar and used as provided. Sulfuric acid (98%) was purchased from Fluka Analytical, and the 95% grade (used for solution viscometry) was purchased from Fisher Scientific. 4-Fluorobenzoyl chloride was purchased from Apollo Scientific.

General Procedures. Proton and ^{13}C NMR spectra were recorded at 400 and 100 MHz, respectively, on a Bruker Nanobay 400 spectrometer, referenced to residual ^1H signals from either deuterated dimethyl sulfoxide ($\text{DMSO}-d_6$) at 2.50 ppm, or deuterated chloroform (CDCl_3) at 7.26 ppm, or to TMS. FTIR spectra were obtained on a PerkinElmer Spectrum 100 instrument, using a PE Universal ATR sampling accessory. Inherent viscosity (η_{inh}) values were measured at 25 °C in 95% sulfuric acid using a semiautomated Ubbelohde viscometer (Schott Geräte 531 20 II). Gel permeation chromatography was carried out on a Polymer Laboratories GPC 220, at 60 °C, using DMF/LiBr (0.1 M) as eluent. Thermogravimetric analyses were carried out using a TA Instruments TGA Q50 attached to TGA heat exchanger, using a platinum crucible and an aluminum TA-Tzero pan. Differential scanning calorimetry (for polymer analysis and determination of small-molecule melting points) used a TA DSC Q2000 with TA Refrigerated Cooling System 90, using aluminum TA-Tzero pans and lids. Mass spectra were obtained using a ThermoFisher Orbitrap XL spectrometer in electrospray positive ionization (ESI) mode.

Monomer Synthesis. Intermediate 1. To a stirred solution of 4-fluorobenzoyl chloride (50 g, 0.315 mol) and AlCl_3 (42 g, 0.315 mol) in 1,2,4-trichlorobenzene (TCB, 130 mL), under argon, was added—dropwise over 1 h—a solution of biphenyl (51 g, 0.332 mol) in TCB (70 mL). The solution was heated at 100 °C for 4 h and then cooled and added to $\text{H}_2\text{O}/\text{HCl}$ (1 L, 3% HCl), and the suspension was stirred overnight. The precipitate was washed with methanol (1 L) and hot 3% hydrochloric acid (1 L, 60 °C), dried, and recrystallized from toluene. Yield 58 g (67%); mp 150 °C. IR (ν_{max} , cm^{-1}) 3070, 3040 (aryl C—H), 1641 (C=O), 1596 (aryl C—C), 1501, 1403, 1285, 1227, 1149, 1096, 858, 744. ^1H NMR (400 MHz, CDCl_3) δ (ppm): 7.90–

7.84 (m, 4H), 7.70 (d, J = 8.6 Hz, Ar, 2H), 7.64 (d, J = 7.1 Hz, Ar, 2H), 7.47 (t, J = 7.1 Hz, Ar, 2H), 7.40 (t, J = 7.4 Hz, Ar, 1H), 7.17 (t, J = 8.6 Hz, Ar, 2H). ^{13}C NMR (100 MHz, CDCl_3): 115.4, 115.6, 127.1, 127.3, 127.6, 128.2, 128.9, 130.6, 132.6, 132.7, 133.9, 133.9, 136.1, 139.9, 145.3, 164.1, 166.6, 194.9. MS: m/z calculated for $\text{C}_{19}\text{H}_{14}\text{FO}^+$ 277.1023; found 277.1025.

Monomer 2. A solution of intermediate 1 (40.00 g, 0.144 mol), isophthaloyl dichloride (14.34 g, 0.071 mol), and AlCl_3 (48.00 g, 0.360 mol) in 1,2-dichlorobenzene (250 mL) was heated to 85 °C, with evolution of HCl (45 min). The temperature was increased to 150 °C for 3 h, and the reaction mixture then cooled, added to ice/HCl (3% HCl, 1800 mL), and stirred overnight. The water layer was decanted, and the precipitate was filtered off and washed with methanol (1800 mL) and then with hot dilute HCl (3%, 1800 mL). The crude product was recrystallized by dissolving in *N*-methylpyrrolidone (12 mL per g of solid, 200 °C), cooling to the solution to 135 °C, adding a solution of 1,4-dioxane/ H_2O (10:1, 1 mL per mg of solid), and filtering off the precipitate. The resulting white solid was washed with acetone and dried at 150 °C under vacuum overnight. Yield 24.7 g (52%); mp 313 °C. IR (ν_{max} , cm^{-1}): 1646 (C=O), 1600 (C=C), 1000 (C—F), 853 (C—H, para disub). ^1H NMR (400 MHz, CDCl_3/TFA) δ (ppm): 8.29 (t, J = 1.8 Hz, H_{H_1}), 8.16 (dd, J = 7.8, 1.8 Hz, Ar, H_{H_2}), 7.99 (d, J = 8.2 Hz, Ar, H_{H_3}), 7.94–7.91 (m, H_{H_4}), 7.86–7.77 (m, H_{H_5}), 7.16 (t, J = 8.6 Hz, H_{H_6}). ^{13}C NMR (100 MHz, CDCl_3/TFA) δ (ppm): 109.9, 112.8, 115.6, 115.9, 116.2, 118.4, 127.6, 127.8, 129.3, 130.1, 131.4, 131.6, 131.9, 132.4, 132.4, 133.7, 133.8, 135.2, 135.3, 136.1, 137.1, 144.8, 145.6, 161.1, 161.6, 161.9, 162.4, 165.3, 167.9, 199.8, 199.9.

Polymer Synthesis. Aromatic polyethers were synthesized using a custom designed flange-type reaction vessel. The lid contained three access points: a nitrogen inlet, a vertical stirrer gland, and a port for sampling during polymerization. The vessel was heated using a sand bath (1000 W, 4 A) with a Eurotherm controller and display. A fixed overhead stirrer (Kika Labortechnik, RW20DM.n) was used with a T-shaped, stainless steel stirring rod. Polycondensations were monitored via the speed of the overhead stirrer, with a decrease of ~30 rpm, indicating that a sufficiently high molecular weight had been achieved (Table 1).

Polymer 3. The polymerization vessel was charged with monomer 2 (6.974 g, 0.010 mol), hexafluorobisphenol-A (3.434 g, 0.010 mol), anhydrous K_2CO_3 (2.965 g, 0.02145 mol, 1.05 equiv), and diphenyl sulfone (30 g) as solvent, under an argon atmosphere. The reaction mixture was heated at 190 °C until the solvent had melted whereupon stirring was initiated. After a further 30 min the temperature was raised progressively and held at 230 °C (60 min), 265 °C (45 min), 290 °C (45 min), 310 °C (70 min), and finally at 320 °C (45 min), with continuous recording of the stirrer speed as a measure of increasing viscosity. The resulting dark brown, viscous solution was poured onto an aluminum tray and allowed to cool. The resulting solid was reduced to a coarse powder using a ultracentrifuge mill, washed with acetone (3 \times 400 mL), and then extracted with acetone overnight in a Soxhlet apparatus. The polymer was then further extracted with water (3 \times 400 mL) and with acetone (5 \times 400 mL) and finally dried at 100 °C under vacuum overnight. The yield of polymer 3 was 8.81 g (88%); T_g = 195 °C, T_m = 212 °C (weak endotherm on first scan; no endotherm on second scan); η_{inh} = 1.30 dL g $^{-1}$. IR (ν_{max} , cm^{-1}): 3099 (C—H), 1663 (C=O), 1598 (C=C), 1502 (C—C), 1245 (C—O—C), 1174 (C—F), 840 (C—H, para-disub). ^1H NMR (400 MHz, CDCl_3/TFA) δ (ppm): 8.28 (s, H_{H_1}), 8.13 (d, J = 7.7 Hz, Ar, H_{H_2}), 7.98 (d, J = 7.7 Hz, H_{H_3}), 7.94–7.88 (m, Ar, H_{H_4}), 7.84–7.71 (m, H_{H_5}), 7.47 (d, J = 8.0 Hz, Ar, H_{H_6}), 7.18–7.10 (m, Ar, H_{H_7}). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 110.1, 112.9, 115.8, 118.1, 118.6, 119.0, 119.4, 117.5, 127.7, 129.1, 129.4, 131.2, 131.4, 131.6, 132.1, 133.4, 134.6, 135.7, 136.6, 137.4, 144.4, 145.1, 156.0, 159.6, 159.9, 160.4, 160.8, 161.7, 198.1, 198.6.

Ionomer Synthesis. Sulfuric acid (98%, 60 mL) was added to polymer 3 (4.0 g) under dry nitrogen. The mixture was stirred at 75 °C for 48 h, producing a dark but homogeneous solution. The solution was passed into deionized water through a PTFE colander with 1 mm holes to precipitate beads of the ionomer. The ionomer was stirred in

deionized water (4–6 washes, 30 min each) until the washings were neutral to pH paper. The ionomer beads were then dried on the filter and further dried under vacuum at 100 °C overnight. The yield of ionomer **4** was 3.3 g (84%). IR (ν_{max} , cm^{-1}): 3099 (C–H), 1663 (C=O), 1598 (C=C), 1502 (C–C), 1245 (C–O–C), 1174 (C–F), 840 (C–H, *para*-disub). ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ (ppm): 8.22 (s, 1H_k), 8.12–8.06 (m, Ar, $4\text{H}_{a'}$), 8.06–7.91 (m, Ar, 12H), 7.94–7.83 (m, Ar, 9H), 7.30 (d, $J = 7.2$ Hz, $2\text{H}_{a''}$), 7.17–7.05 (m, Ar, $6\text{H}_{b,c}$). ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$) δ (ppm): 110.1, 112.9, 115.8, 118.1, 118.6, 119.0, 119.4, 117.5, 127.7, 129.1, 129.4, 131.2, 131.4, 131.6, 132.1, 133.4, 134.6, 135.7, 136.6, 137.4, 144.4, 145.1, 156.0, 159.6, 159.9, 160.4, 160.8, 161.7, 198.1, 198.6. GPC (DMF/LiBr 0.01 M): $M_n = 120\,000$, $M_w = 190\,000$, PDI = 1.58.

Membrane Fabrication. A 15 wt % solution of the ionomer (2.5 g) in NMP (99.5%) was prepared by stirring until visibly homogeneous. A glass plate (20 × 30 cm) was degreased with an abrasive cleaner and deionized water and was then given a final acetone rinse before drying. The ionomer solution was filtered through cotton fiber and poured onto the glass plate, drawing the solution down using a Gardner knife set to allow for an 80–85% reduction in thickness upon solvent evaporation. The ionomer film was dried under vacuum, initially at 60 °C for 2 h, then increasing the temperature at 10 °C h^{-1} to 110 °C, and was finally held at this temperature overnight. The membrane could be removed easily from the plate after equilibration in the presence of atmospheric moisture for 24 h.

Membrane Conductivity. The in-plane proton conductivities of ionomer **4.3** and Nafion 117 were measured by the four-probe method using a BektTech B-112 conductivity cell. The Nafion 117 membrane was pretreated by boiling in 3 wt % hydrogen peroxide solution for 15 min, deionized water for 15 min, and in 0.5 M sulfuric acid solution for 15 min. The membrane was rinsed with deionized water and soaked in deionized water at room temperature until used. Ionomer membrane **4.3** was only pretreated by soaking in deionized water before use.

The membranes were mounted in the conductivity cell, and the temperature and relative humidity of hydrogen were controlled by an in-house-designed fuel cell test station. The conductivity was measured by performing cyclic voltammetry between –0.1 and 0.1 V with a scan rate of 1 mV s^{-1} and measuring the resulting current flowing in the cell. The conductivity was measured for 75% and 100% relative humidity at temperatures from 30 to 90 °C.

MEA Fabrication. Membrane electrode assemblies (MEAs) were prepared by the “decal” method,²⁶ as follows. An IrO_2 (Surepure) catalyst ink containing 10 wt % Nafion from a dispersion in aliphatic alcohol (D-520, 5 wt %, DuPont) was sprayed onto a PTFE substrate to reach a catalyst loading of ca. 2 mg cm^{-2} . Platinum/carbon electrodes were prepared by roll coating an ink comprising Pt/C powder (TEC10 V50E, 46.1 wt %, Tanaka), 27 wt % of Nafion (D-520, 5 wt %, DuPont), and deionized water onto a PTFE substrate. Each electrode was circular, with an area of ca. 25 cm^2 . These samples were carefully weighed then hot pressed on each side of the ionomer membrane at 135 °C, under a pressure of 4 MPa. The PTFE support films were removed and weighed to determine the actual amount of catalyst deposited on the membrane. A titanium sintered disk acted as anodic current collector while a gas diffusion layer (carbon, SGL 34BC) was used on the cathodic side.

MEA Evaluation. MEAs were evaluated in a 25 cm^2 test cell. A titanium sintered disc acted as anodic current collector while a carbon gas diffusion layer (SGL 34BC) was used at the cathodic side. Two titanium plates with machined straight channels were used as monopolar plates to supply water at the anodic side and to evacuate the produced gases and excess water. The test bench was designed to carry out experiments from atmospheric pressure up to 1 MPa and from room temperature to 120 °C. The conductivity of the inlet water was recorded, and its temperature and flow, as well as the temperature and the pressure of the cell, were controlled. Excess water and produced gases are separated and water vapor were condensed at 5 °C before measuring the gas flows (mass flows) and purity (catharometer gas sensors for measuring hydrogen content in oxygen produced at the anodic side and oxygen content in the hydrogen produced at the cathodic side). The experiment was automatically stopped if the gas

mixture reached 50% of the lower explosive limit (LEL: 4% H_2 in O_2) or upper explosive limit (UEL: 5% O_2 in H_2). Tests were carried out at 60 and 80 °C and atmospheric pressure. Polarization curves were recorded from 0 to 2 A cm^{-2} in steps of 0.2 A, stabilized for 120 s.

CONCLUSIONS

A high molecular weight, microblock poly(ether–ketone) sulfonic acid ionomer was successfully synthesized by polycondensation of hexafluorobisphenol-A with a 7-ring difluoroketone monomer, followed by postpolymerization sulfonation in 98% sulfuric acid. The new ionomer displays very good mechanical strength, low swelling characteristics (ca. 5 wt % in water at room temperature), and a glass transition (when dry) well above the desired working temperature range of a PEMWE cell. The microblock structure provides a high degree of nanophase separation to facilitate effective proton transport,¹⁹ delivering proton conductivity comparable to that of the current industrial standard Nafion. In membrane electrolysis of water under single-cell test conditions, high electrolyzer efficiencies were achieved with the new membrane, and efficiency increased with temperature. Single-cell analysis also showed very good stability of current and voltage over the experimental time period (60 h). This work demonstrates that potentially low cost, microblock-type aromatic ionomers can provide the thermomechanical stability and proton conductivity needed for effective PEMWE. Further research is in progress to achieve greater control of molecular architecture, proton-exchange capacity, and membrane morphology and thereby to enhance these performance characteristics.

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Notes

The authors declare no competing financial interest.

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