Sulfonated Poly(ether ketone ketone) Ionomers as Proton Exchange Membranes

Sulfonated poly(ether ketone ketone) ionomers (SPEKK) with ion-exchange capacities (IEC) between 0.2 and 3.4 meq/g were prepared by sulfonating PEKK with a mixture of concentrated and fuming sulfuric acids. Sulfonation occurs only on the phenyl rings attached to ether and ketone groups. The glass transition temperature of the dry SPEKK ionomers increased linearly with increasing IEC, and the ionomers were thermally stable to ~250°C, above which desulfonation occurred. Water-swollen ionomers exhibited microphase separated morphologies, and the average correlation length determined by small angle X-ray scattering increased with increasing IEC. The proton conductivity of hydrated SPEKK membranes measured by impedance spectroscopy ranged from $10^{-3}$ to $10^{-1}$ S/cm as the IEC increased from ~1.0 to 2.4 meq/g. Single cell performance curves on membrane-electrode assemblies (MEA) indicated that the SPEKK membranes approached the performance of Nafion™ for an IEC of 2 meq/g.

INTRODUCTION

Fuel cells represent an attractive alternative to conventional methods for generating remote power, such as the combustion of fossil fuels or batteries. They have no moving parts, relatively low fuel costs, and do not emit common air-pollutants such as SO₂, NOₓ, and unsaturated hydrocarbons. Proton exchange membrane (PEM) fuel cells provide an efficient source of power that is ideal for the replacement of conventional metal-ion batteries in portable power applications such as cell phones, laptop computers, and power tools [1, 2]. The byproducts of a direct methanol fuel cell (DMFC) are carbon dioxide and water, and fuel cells do not have the disposal and recycle problems associated with metal-ion batteries.

The polymer electrolyte membrane is a crucial component of a PEM fuel cell. It serves both as the electrolyte and as a separator to prevent direct physical mixing of the hydrogen from the anode and oxygen supplied to the cathode. The polymer electrolyte contains ionizable groups, usually sulfonic acid groups, in which the mobile cations (i.e., protons) are electrostatically associated with the fixed anionic charges on the polymer. The protons migrate through the membrane by “hopping” sequentially from one fixed charge to another, and are stabilized during this transfer by several water molecules.

The commercial development of cost-effective fuel cells has been hampered, in part, by the need for better polymer electrolyte membranes, specifically with regard to the balance of mechanical properties, conductivity, and, especially for the DMFC, methanol crossover resistance. The essential property requirements of a PEM are chemical and electrochemical stability, adequate mechanical stability and strength to ensure dimensional stability when swollen and under tension, surface properties compatible with bonding catalytic electrodes to the membrane, low permeability for reactants and products (e.g., in a DMFC, methanol transport needs to be minimized or eliminated), and high ionic conductivity for large current densities and low internal resistances [3]. In addition, low-cost membranes are needed, especially if fuel cells are to be utilized in portable electronics.

The current state-of-the-art fuel cell technology primarily involves the use of perfluorosulfonate ionomer membranes; the most common commercial product is Nafion™, which is produced by DuPont de Nemours Corp. These materials are relatively expensive, ~$800/m², and although their chemical and oxidative resistance is excellent, their durability and reactant permeability become problematic when thinner membranes are used to reduce the membrane resistance [1]. As a result, a contemporary thrust in PEM fuel cell research concerns the development of new membrane materials.

Polymer electrolyte membranes based on aromatic hydrocarbon polymers are attractive for a variety of reasons, including potentially lower cost, easier processing, and higher use-temperatures. In recent years, a variety of new
Ionomers have been prepared and characterized as membrane candidates for PEM fuel cells. These include sulfonated polyimides [4–8], sulfonated poly(arylene ether sulfones) [9–16], sulfonated poly(arylene ether phosphine oxides) [17, 18], and sulfonated polyketones [19–23]. These materials show some promise with respect to conductivity, stability, methanol crossover, and water transport, though none has as yet been commercialized as a viable replacement for Nafion™.

 Poly(aryl ether ketone)s (PAEK), have good abrasion resistance, high fatigue endurance, excellent hydrolysis resistance, radiation resistance, thermal stability, and mechanical properties. The family of PAEKs consists of polymers with different ratios of arylene ether and arylene ketone groups (see Table 1). The most common variant is poly(ether ether ketone), PEEK, though other PAEKs, most notably poly(ether ketone) (PEK) and poly(ether ketone ketone) (PEKK), are also commercial high temperature thermoplastics. PEKK is a relatively new engineering plastic that has high temperature stability, excellent chemical and solvent resistance, and excellent mechanical properties. PEKK is actually a family of copolymers with different ratios of terephthaloyl (T) and isophthaloyl (I) moieties [24] (Fig. 1). This paper is concerned with the sulfonation of PEKK with T/I ratios of 6/4 and 8/2 and the properties of PEMs produced from sulfonated PEKK (SPEKK).

Sulfonation is an electrophilic substitution reaction [25]. Oxygen withdraws electron density from the sulfur atom making it electrophilic and reactive towards the delocalized electrons of an aromatic ring. The reaction is favored when the aromatic ring is attached to electron-donating groups, such as the two ether linkages in PEEK. Sulfonation of PEKK is a bit more problematic, because the ketone groups withdraw electron density from the aromatic ring making it less reactive towards sulfonation. In general, as the K/E ratio increases, sulfonation becomes more difficult and more reactive sulfonation reagents are required. Ulrich and Rafler [26] reported sulfonating PEKK using mixtures of sulfuric acid and oleum (liquid sulfur trioxide). Bauer et al. [27] also described the sulfonation of PEKEKK, which has a slightly lower K/E ratio than PEKK, with sulfuric acid and oleum, as well as the sulfonation of PEEKK and PEEK, and their use as ion-exchange membranes. Soczka-Guth et al. [28] reported the use of sulfonated PEK membranes in fuel cells.

No kinetic information is available for the sulfonation of PEKK, but the sulfonation of PEEK and the reaction kinetics have been described by several research groups [29–36]. For the sulfonation of PEEK with a large excess of concentrated sulfuric acid, Shibuya and Porter [32, 33] reported that the kinetics of the reaction is first order in the concentration of the PEEK chain repeat unit and inversely proportional to the concentration of the sulfonated PEEK units. The latter effect was attributed to a competing desulfonation reaction that occurs for arylsulfonic acids in an acidic medium [25]. Huang et al. [34], however, reported that the

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**TABLE 1. Common poly(aryl ether ketone)s.**

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Repeat unit</th>
<th>K/E</th>
<th>$T_g$ (°C)</th>
<th>$T_m$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly(ether ether ketone)</td>
<td><img src="structure1.png" alt="Structure" /></td>
<td>0.5</td>
<td>142&lt;sup&gt;b&lt;/sup&gt;</td>
<td>340&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>Poly(ether ketone)</td>
<td><img src="structure2.png" alt="Structure" /></td>
<td>1.0</td>
<td>156&lt;sup&gt;b&lt;/sup&gt;</td>
<td>370&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>Poly(ether ketone ketone)</td>
<td><img src="structure3.png" alt="Structure" /></td>
<td>2.0</td>
<td>155</td>
<td>358</td>
</tr>
</tbody>
</table>

<sup>a</sup>Ketone/ether ratio.<br><sup>b</sup>Ref. 24.
sulfonation of PEEK followed first-order kinetics, dependent only on the concentration of the PEEK repeat unit.

An advantage of using PEEK in a PEM fuel cell is its excellent oxidative stability. The oxidative stability of PAEKs increases with increasing K/E ratio of the repeating unit. Linkous [37] reported that PEK, PEKEKK, and PEKK were stable in a water-saturated hydrogen environment to 400°C and in water-saturated oxygen to 300°C. Among those materials, PEKK showed the least weight loss in an oxygen/steam environment at 400°C.

In this study, PEKK was sulfonated with a mixture of concentrated sulfuric acid and fuming sulfuric acid. The sulfonated PEKKs (SPEKKs) were characterized by differential scanning calorimetry (DSC), thermal gravimetric analysis (TGA), Fourier transform infrared spectroscopy (FTIR), and small angle X-ray scattering (SAXS). The proton conductivity of the hydrated SPEKK membranes was measured by impedance spectroscopy and single cell performance curves of membrane electrode assemblies were determined.

**EXPERIMENTAL**

PEKKs with T/I ratios of 8/2 (OXPEKK-C) and 6/4 (OXPEKK SPb) were obtained from Oxford Performance Materials, Enfield, CT. Concentrated sulfuric acid (96.3%) and fuming sulfuric acid (30% free SO3) were obtained from Fisher Scientific. Sulfonation of PEKK was achieved by dissolving the polymer (5% w/v) in a mixture of 53/47 (v/v) concentrated sulfuric acid and fuming sulfuric acid at room temperature. The extent of sulfonation was varied by how long the polymer was kept in the sulfuric acid solution. The resulting sulfonated polymer, SPEKK, was precipitated by drop-wise addition of the solution into six volumes of rapidly stirred de-ionized ice water. The SPEKK was filtered, washed repeatedly with de-ionized water to remove excess acid, and dried at 60°C overnight and then under vacuum at 120°C for 3 days. The sulfonation level was determined from the carbon/sulfur ratio obtained from elemental analysis and/or by titration of the sulfonic acid groups. For the latter method, SPEKK was ion-exchanged with excess saturated aqueous sodium chloride solution overnight. The HCl product was then titrated with a normalized sodium hydroxide solution using phenolphthalein as an acid-base indicator. Note that the Na neutralized SPEKK ionomer, obtained as a by-product of this titration procedure, was filtered out, washed with de-ionized water, and dried for further analysis.

SPEKK membranes were prepared by solution casting 5% (w/v) polymer solutions in N-methyl-2-pyrrolidone (NMP) onto glass plates at 60°C. The solvent was allowed to evaporate for about 1 day, after which the films were dried at 120°C under vacuum for 3 days.

The thermal properties of the polymers were measured using a TA Instruments Q100 DSC equipped with an RCS cooling unit. Samples of ~10 mg were heated in a nitrogen atmosphere using a heating rate of 20°C/min. The thermal stability of the polymers was measured in a nitrogen atmosphere with a TA Instruments Q500 TGA and a heating rate of 20°C/min. In order to remove any residual water absorbed by the relatively hydrophilic sulfonated polymers during transfer, the samples were first dried for 15 min at 170°C in the TGA furnace prior to the thermal stability scan.

FTIR spectra were obtained in transmission on cast films (thickness ~2 μm) with a Nicolet 560 FTIR using 64 scans with a resolution of 2 cm⁻¹. ¹³C-NMR spectra were measured with a Bruker 400 FT-NMR spectrometer using solutions in deuterated dimethyl sulfoxide. SAXS measurements were made on films at room temperature using a Rigaku rotating anode (40 kV accelerating voltage; 100 mA current) and a Bruker SAXS instrument that included a two-dimensional Hi-Star detector. Data were obtained over a scattering vector range of q = 0.5–3.5 nm⁻¹ (q = 4πsinθ/λ, where 2θ is the scattering angle and λ is the X-ray wavelength) using CuKα radiation (λ = 0.1542 nm), a Ni-filter, and pinhole collimation. Wide angle X-ray diffraction (WAXD) was performed with a Bruker D8 Advance wide-angle X-ray diffractometer.

Proton conductivity measurements of hydrated membranes were made at room temperature over a frequency range of 10 mHz to 10⁶ Hz and an AC voltage amplitude of 50 mV using a frequency response analyzer (Solartron SI 1260, impedance/gain-phase analyzer) combined with a potentiostat (Solartron SI 1287, electrochemical interface). The potentiostat was also used to measure the resistance of the membranes using a four-point DC probe that consisted of two current-carrying electrodes made with Pt foil and two inner potential-sensing electrodes fabricated from thin platinum wire. Measurements were made on 15- to 30-μm-thick membranes that were hydrated in various relative humidity (RH) environments at room temperature.

Single-cell performance curves of the SPEKK membranes were determined using a membrane electrode assembly (MEA). The hydrated membrane was fixed to a Teflon frame, allowed to dry, and then covered by a mask. Multiple layers of a catalyst ink were applied to the membrane with a N₂-gas brush; a catalyst loading of ~0.5 mg/cm² was obtained. The anode ink was made from ETEK-40% PtRu/C (E-TEK Corp.), and cathode ink was made from ALFA-40% Pt/C (Alfa Aesar). An isopropanol dispersion of a perfluorosulfonate ionomer, Nafton™ (ew = 1100 g/mol, Solution Technologies), was added to achieve a polymer content of 25% in the dry mixture for both electrodes. Carbon-graphite paper was used as a gas diffusion layer.

In one method, the methanol permeability was determined from the flux through the membrane separating two well-mixed cells. The bulk concentration of methanol on one side of the membrane was about 50 wt% in water and on the other side it was 0 wt% (pure water). The volume of each of the two compartments of the permeation cell was 50 mL. The bulk concentration of methanol in each compart-
ment was measured as a function of time using gas chromatography.

Methanol crossover in the MEA set-up was determined by the limiting current method using linear sweep voltammetry, with a Solartron SI 1287 electrochemical interface. The flow rate of methanol solution (1M) at the anode side was 3 mL/min while the nitrogen flow rate at the cathode side was 50 mL/min. The current that was generated by methanol oxidation at the fuel cell cathode was recorded as the voltage was swept from 0.05 to 0.9V at a 4 mV/s scan rate. The methanol oxidation current increased until a current was reached where the oxidation reaction was “limited” by the transport of methanol through the membrane to the cathode side. The measured limiting current provided the methanol crossover flux of the membrane studied.

**RESULTS AND DISCUSSION**

**Sulfonation of PEKK**

The sulfonation level may be expressed in three different ways that are commonly used in the ionomer literature: 1) a degree of sulfonation, $X_s$, defined as the average number of sulfonate groups per repeat unit; 2) equivalent weight (ew in g/mol), which is the mass of polymer per sulfonate group: $ew = (300 + 81X_s)/X_s$; or 3) as a concentration of sulfonate groups, $c_s$, which is expressed as ion-exchange capacity (IEC; equivalents per mass, IEC = 1/ew). For the sulfonation of PEKK with fuming sulfuric acid, sulfonation can occur on either of the aromatic rings that have one ether and one ketone substituent (see rings 1 and 3 in Fig. 1); the aromatic ring attached to two ketone groups (ring 2 in Fig. 1) is not susceptible to an electrophilic substitution reaction [26]. Sulfonation of an aromatic ring also deactivates that ring to further sulfonation, so the maximum degree of sulfonation of PEKK is two sulfonate groups per (EKK)-repeat unit. That also corresponds to a maximum sulfonate concentration of $c_{s,max} = 4.3$ meq/g and a minimum equivalent weight of $ew_{min} = 231$ g/mole. For the remainder of this paper, IEC will be used. That measure provides a clearer means to compare different ionomers, e.g., the IEC of Nafion™ 117, a commonly used PEM, is 0.9 meq/g.

The sulfonation level of the SPEKKs was measured by elemental analysis and by titration of the sulfonic acid groups. The agreement between the two methods using two different parent PEKKs (with T/I ratios of 8/2 and 6/4) was very good, as shown in Fig. 2. The sulfonation reaction was also verified by FTIR spectroscopy, see Fig. 3. Sulfonation decreased the intensity of the aromatic C-C vibration at 1495 cm$^{-1}$ and produced a new C-C vibration at 1476 cm$^{-1}$ that increased with increasing IEC. Bands specific for the S-O vibrations of aromatic sulfonic acid groups were also observed at 1080 cm$^{-1}$, 1021 cm$^{-1}$, and 950 cm$^{-1}$.

Substitution of the sulfonate group on the oxy-1,4-phenylene-carbonyl ring was confirmed with $^{13}$C NMR (Fig. 4). The resonances at 121.4 and 156.5 are due to substituted carbons in the oxy-1,4-phenylene-carbonyl ring [26]. The $^{13}$C NMR data show no evidence of substitution of the phenyl rings attached to two ketone groups.

Only free SO$_3$ produces sulfonation of the active sites of

![Graph 1](image1.png)

**FIG. 2.** Comparison of the IEC of SPEKKs measured by titration and by elemental analysis; SPEKK with T/I ratio of 8/2 (○) and 6/4 (●). The solid line is the $x = y$ line.

![Graph 2](image2.png)

**FIG. 3.** FTIR spectra of SPEKKs (T/I ratio 8/2). a: IEC = 0.8 meq/g; b: IEC = 1.2 meq/g; c: IEC = 1.5 meq/g; d: IEC = 2.0 meq/g; e: IEC = 2.9 meq/g; f: IEC = 3.5 meq/g.
PEKK. Thus, for PEKK the polymer can be dissolved in concentrated sulfuric acid without initiating the sulfonation reaction. The subsequent addition of fuming sulfuric acid begins the reaction, from which one can unambiguously define time zero for the reaction, unlike the case of the sulfonation of PEEK where the reaction occurs during the dissolution of the polymer in concentrated sulfuric acid. Sulfonation should be first order in the concentration of SO$_3$ and first order in the concentration of active sites on the polymer chain. However, since an excess of SO$_3$ was used, pseudo first-order kinetics was expected to describe the reaction:

$$IEC = IEC_0 + (IEC_\infty - IEC_0)[1 - \exp(-kt)] \tag{1}$$

where, $IEC_0$ and $IEC_\infty$ are the sulfonation concentrations, expressed as the IEC, at time equal to zero and at the completion of the reaction, respectively, and k is the reaction rate constant.

The experimental sulfonation vs. time curves for PEKK are shown for a range of temperatures from 40°C to 72°C in Fig. 5. The kinetics of sulfonation followed the pseudo first order dependency represented by Eq. 1, which is demonstrated by the least squares fits shown in Fig. 5. An activation energy $E_a = 72$ kJ/mol can be obtained from the Arrhenius plot of this data in agreement with values found for PEEK sulfonated with concentrated sulfuric acid [32–34]. A detailed study of the sulfonation kinetics of PEKK shows that a retardation effect occurs for $IEC > 2$ meq/g, originating from the deactivation of the sulfonate groups neighboring the remaining active sites [35].

Sulfonation of PEKK decreased its crystallinity, as shown by the loss of the crystalline reflections in the WAXD in Fig. 6 as the sulfonation level increased. A similar effect was reported for sulfonation of PEEK [29]. SPEKK was insoluble in water, toluene, chloroform, and 2-propanol. For $IEC = 2.6$ meq/g, the SPEKK was highly swollen by water. For T/I = 8/2, SPEKK was soluble in N-methyl pyrrolidone (NMP) when $IEC > 1.6$ meq/g. and in dimethylacetamide (DMAc) when $IEC > 1.9$ meq/g. SPEKK with T/I = 6/4 was more soluble, presumably because the isophthaloyl groups produce a more flexible backbone; in that case, the SPEKK dissolved in NMP and DMAc when the $IEC > 0.8$ meq/g.

**Thermal Behavior**

Sulfonation increased the glass transition temperature, $T_g$, of PEKK, see Fig. 7. The increase was linear with sulfonation level for both the acid and sodium salt derivatives, but the increase was much greater for the salt than for the acid. In the case of the sulfonic acid derivative of SPEKK, the $T_g$ increased about 14°C/(meq/g), which is undoubtedly mostly a consequence of the hydrogen bonding between sulfonic acid groups that suppresses the segmental motion of the chains. For the Na-salt, the increase of $T_g$ was 90°C/(meq/g). In that case, the stronger intermolecular ionic interactions between the metal sulfonate ion-pairs are thought to produce the increase of $T_g$. Similar results have
been observed in other ionomers, e.g., sulfonated PEEK [29].

PEKK is thermally stable to about 550°C (Fig. 8). The TGA curves in Fig. 8 for the acid form of SPEKK show a two-step decrease in mass. The derivative weight loss curve, illustrated in Fig. 9, was used to determine the temperature range of the first mass loss step (A), namely 250°C to 440°C. This is similar to what was observed for SPEEK and can be attributed to desulfonation [38]. The mass loss by desulfonation provided a quick estimate of the sulfonation level of the polymer. All samples were dried in the TGA at 170°C for 30 min prior to the heating experiment. The dry polymer therefore corresponds to 100% and the amount of desulfonation can be quantified by calculating the mass loss between 250°C and 440°C. The desulfonation values obtained in this way correlated well with the IEC measured by titration of the SPEKK, see Fig. 10. Included in the data in Fig. 10 are data taken from the literature [37–39] for SPEEK.

**Water Vapor Sorption**

Water is crucial for proton transfer in PEM fuel cells, since it facilitates the proton transport through the membrane [41]. Equilibrium water sorption for (8/2) SPEKK hydrated at 25°C immersed in liquid water and exposed to...
a 98% RH environment is plotted against IEC in Fig. 11. The lower water activity, i.e., the lower RH, produced lower water sorption for the same IEC. The increase of water sorption with increasing sulfonation is a consequence of the increase in hydrogen bonding sites for water. The hydration number, \( n(H_2O)/n(SO_3H) \), for the immersed SPEKK membranes with an IEC of \( 2.5 \) meq/g was about 10.

**Microstructure**

Although the exact details of the spatial and geometric arrangement of the ions in the ionic aggregates of ionomers has remained exclusive despite nearly 30 years of investigation, it is generally agreed that ion-rich nanometer-size aggregates occur in the dry ionomers as a result of microphase separation [42]. Microphase separation arises from the incompatibility of the ionic and non-charged repeat groups of the ionomer, as well as electrostatic interactions between the ionic species. The fact that the ionic groups are bonded to the polymer chain limits phase separation to the dimensions of the chain or less. The primary evidence for microphase separation is the presence of a broad peak in the structure factor obtained from SAXS experiments. The origin of the “ionic peak” is generally believed to be due to a correlation length associated with an average inter-aggregate interference [42]. The “ionic peak” is usually difficult to resolve by SAXS for the sulfonic acid ionomer derivatives, but it has been observed for polystyrene-sulfonic acid ionomers [43, 44]. The SAXS for dry and hydrated films of SPEKK (IEC = 2.4 meq/g) are shown in Fig. 12. No scattering peak was observed for the dry samples, which may simply be a result of insufficient electron density contrast between the acidic domains and the PEKK matrix. The hydrated sample, however, does show the typical “ionic peak” that is usually seen in ionomers. In that case, the preferential swelling of the ionic microdomains by water provided contrast between the two microphases. The peak in the SAXS covered a range of scattering vectors, \( q = 0.6–2.5 \) nm\(^{-1} \), which corresponds to correlation lengths in real space of \( d = 2.5–10.4 \) nm, where \( d = 2\pi/q \). The maximum in the scattering peak occurred at ca \( q_{max} = 1.1 \) nm\(^{-1} \), which corresponds to an average characteristic length of 5.7 nm, which is comparable to the size observed by SAXS for hydrated perfluorosulfonate membranes [45, 46]. The characteristic distance for the hydrated ionomer may either be a correlation between water-swollen ionic domains or between domains of the water-poor polymer regions, depending on the extent of hydration and whether a microphase inversion occurred, i.e., discrete ionic domains dispersed in a water-poor matrix vs. hydrocarbon microdomains dis-
persed within a water-swollen ion-rich continuous region [47].

In general, $q_{\text{max}}$ increased for increasing IEC, or increasing hydration, which corresponds to a larger characteristic size. The larger correlation distance may be due either to swelling of the ionic microdomains, which increases their distance of closest approach, or to dilution of the non-polar microdomains with increasing water if the morphology has undergone a phase inversion. Unfortunately, the SAXS result can only show that the materials microphase separated; it cannot distinguish which is the dispersed microphase [48]. What is apparent from consideration of the conductivity data discussed later in this paper is that the swelling of the ionic domains was sufficient to develop a percolation pathway of the ion-rich phase through the membrane. This implies that the microstructure was distinguished by either overlapping acidic domains (the usual schematic of this prevalent in the literature is of spherical ionic domains connected by small cylinders [45]) or a continuous water-swollen ion-rich microphase. The high water concentration within the domain structure facilitates proton diffusion by effectively solvating the proton from the sulfonate anion bound to the polymer chain. The scattering curves in Fig. 12 for both samples also showed an intensity upturn in scattering intensity at low $q$, which is a feature also commonly seen in ionomers and believed to be due to large scale density fluctuations arising from an inhomogeneous distribution of the discontinuous microphase [42].

**Conductivity and MEA Performance**

A typical complex-plane plot of imaginary impedance ($-Z'$) vs. real impedance ($Z'$) for an SPEKK membrane hydrated in a 98% RH environment is shown in Fig. 13. The real ($Z'$) and the imaginary part ($Z''$) of the impedance were multiplied by the ratio of the membrane cross-sectional area and the separation of the electrodes to calculate the complex resistivity. The membrane resistivity was obtained from the intercept of the semi-circles in the impedance plot, see Fig. 13 [49], and the proton conductivity, $\sigma \ [\text{S/cm}]$, was calculated from the inverse of the resistivity using the following equation:

$$\sigma = \left( \frac{R A}{d} \right)^{-1}$$  \hspace{1cm} (2)

where $R$ is the membrane resistance (\Omega), $A$ is the cross-sectional area of the membrane (cm$^2$), and $d$ is the distance between the platinum electrodes (cm).

The conductivities of SPEKK membranes are plotted as a function of IEC in Fig. 14. These membranes were hydrated by either immersing in water or exposing to a 98% RH environment. The conductivity increased roughly exponentially with increasing IEC, and values comparable to the conductivity of Nafion™ 112 ($0.08 \text{ S/cm}$) were achieved for SPEKKs with IEC $\geq 1.9$ meq/g when hydrated with liquid water. When hydrated with 98% RH, conductivities were around 0.06 S/cm when measured in the same experimental set-up.

The single-cell performance curves plotted in Fig. 15 show that SPEKK membranes perform reasonably well in an MEA for IEC $> 1.2$ meq/g. The results were consistent with the expected increase in performance of the membrane in the MEA with increasing IEC. Table 2 compares the resistance and methanol crossover characteristics of SPEKK and Nafion™ 112 membranes. SPEKK with an IEC = 1.8 meq/g exhibited lower methanol crossover than Nafion™, though the latter had a higher proton-conductivity.
Methanol permeation in the SPEKK and Nafion™ membranes was also independently determined by measuring the flux through the membrane separating two well-mixed cells containing different concentrations of methanol in water. From Fick’s first law, the molar flux ($q$) of methanol is proportional to the methanol concentration gradient ($dC/dx$) through the diffusion layer:

$$q = \frac{V}{A} \frac{dC}{dt} = -D \frac{dC}{dx} \quad (3)$$

and the proportionality constant is the diffusivity ($D$). $V$ is the volume of each of the two cells and $A$ is the membrane cross-sectional area. Assuming the methanol concentration gradient across the membrane is linear, Eq. 3 can be written as

$$q = \frac{V}{A} \frac{dC_L}{dt} = D K \frac{C_H - C_L}{\delta} = P \frac{C_H - C_L}{\delta} \quad (4)$$

where $C_H$ and $C_L$ are the bulk concentrations of methanol in the cell with higher and lower methanol concentration, respectively. The constant $K$ is the partition coefficient or the solubility of methanol in the membrane. The product of the diffusivity ($D$) and the partition coefficient ($K$) is defined as the permeability ($P$). The rate of change in methanol concentration ($dC_L/dt$) can also be expressed in terms of the driving force by simply using the law of conservation of mass:

$$\frac{dC_L}{dt} = -\frac{dC_H}{dt}; \quad \frac{d[C_H - C_L]}{dt} = -2 \frac{dC_L}{dt} \quad (5)$$

Combining Eqs. 4 and 5 result in an equation with a single dependent variable:

$$\frac{d[C_H - C_L]}{dt} = -\frac{2PA}{V\delta} dt. \quad (6)$$

Integrating and rearranging:

$$\ln \left[ \frac{\Delta C_0}{\Delta C} \right] \frac{V\delta}{2A} = Pt \quad (7)$$

where $\Delta C$ is the instantaneous difference in the bulk concentration of methanol between the two cells, $C_i - C_j$, and $\Delta C_0$ is the initial value of the bulk concentration difference, $C_{i0} - C_{j0}$. Note that in Eq. 7, the unit of $P$ is (length)$^2$/time.

Figure 16 shows the results of this analysis for SPEKK membranes and Nafion™; $P$ is the slope of the linear least

![Figure 15](image1.png)

**FIG. 15.** Effect of sulfonation level on single cell potential vs. current density plots for SPEKK (T/I ratio of 6/4); IEC = 2.0 meq/g (●), 1.7 meq/g (○), 1.5 meq/g (▲), and 1.2 meq/g (▼) at 80°C, 1 atm, and 75% RH and using H$_2$/O$_2$; cf. Nafion™ 112 measured in same conditions—cell potential at 200 mA/cm$^2$: 0.8 V

![Figure 16](image2.png)

**FIG. 16.** Methanol permeability plots (see Eq. 7) at 25°C for Nafion™ 117 (●), SPEKK (6/4) IEC = 1.14 meq/g (●) and SPEKK (6/4) IEC = 1.49 meq/g (○).

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Resistance ($\Omega \cdot \text{cm}^2$) ($\text{H}_2/\text{O}_2$)</th>
<th>Conductivity (S/cm)</th>
<th>Methanol crossover flux ($A/\text{cm}^2$) (1M CH$_3$OH)</th>
<th>Resistance ($\Omega \cdot \text{cm}^2$) (1M CH$_3$OH)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SPEKK* (1.8 meq/g)</td>
<td>0.07</td>
<td>0.05</td>
<td>0.22</td>
<td>0.114</td>
</tr>
<tr>
<td>Nafion™112</td>
<td>0.05</td>
<td>0.06</td>
<td>0.40</td>
<td>0.07</td>
</tr>
</tbody>
</table>

*Membrane thickness: 34 μm.
squares fit of the data. The methanol permeabilities are shown in the insert in Fig. 16. The value for the lower IEC SPEKK was about half that of Nafion™ 112, while for the higher IEC SPEKK, the permeability was comparable. The higher methanol permeability found for higher IEC is due to the corresponding increase in water sorption (Fig. 11). Note that the methanol permeability obtained from this experiment cannot be strictly compared to the methanol flux obtained from the MEA crossover experiment (Table 2) since different methanol concentrations and temperatures were used. For optimum fuel cell performance, the conductivity-to-permeability ratio should be maximized.

CONCLUSIONS

PEKK can be sulfonated using a mixture of concentrated and fuming sulfuric acids. For excess SO₃, the sulfonation kinetics exhibits a pseudo first-order dependence on the concentration of the reactive aromatic rings between ether and ketone groups. SPEKK represents a viable material for PEMs suitable for fuel cell applications. SPEKK is thermally stable up to about 250°C, which makes it a potential candidate for high temperature PEMs.

An increase in sulfonation level or water activity results in higher equilibrium water sorptions of the SPEKK membranes. SAXS indicates the water-swollen SPEKK possesses a microphase-separated morphology, consisting of either water-swollen ionic domains dispersed in a non-polar continuous phase or, at higher water contents, hydrophobic domains dispersed in a water-swollen ion-rich continuous phase. Proton conductivities at 25°C for SPEKK with IEC greater than 1.9 meq/g were comparable to that of conventional perfluorosulfonate membranes, such as Nafion™. In general, the proton conductivity increased with increasing hydration and IEC. Single-cell performance curves obtained for hydrated SPEKK membranes indicated reasonable and promising performance in MEA, e.g., a membrane with IEC = 2 meq/g had a current density of ~600 mA/cm² for a cell potential of 0.6 V. The methanol crossover in the MEA was also lower for SPEKK than Nafion™ membranes, which indicates that the SPEKK may have advantages for use in direct methanol fuel cells.

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REFERENCES