Polymer Blend for Fuel Cells Based on SPEKK: Effect of Cocontinuous Morphology on Water Sorption and Proton Conductivity

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ABSTRACT: Proton-exchange membranes (PEM), suitable for micro and small sized fuel cells, were obtained by blending sulfonated poly(ether ketone ketone) (SPEKK) polymers with different ionic exchange capacity (IEC). This approach was used to limit the amount of swelling caused by water sorption without significantly decreasing the proton conductivity of the membrane. In particular a membrane with a cocontinuous biphasic morphology was obtained by blending two SPEKKs, with respectively, an IEC equal to 1.2 and 2.08 in the weight ratio 60/40, casted from 5% (w/v) solutions in dimethylacetamide. The effect of a cocontinuous morphology on water sorption and proton conductivity in comparison to neat SPEKK was investigated. In the range of temperatures between 40 and 70 °C, which is typical for small and micro fuel cells conditions, it was found that the ratio of proton conductivity to water sorption could be maximized. This has been attributed to the presence of percolative pathways for proton transport provided by the cocontinuous morphology along with the constraint effect of the less sulfonated component on the overall capacity of swelling of the membrane.

Keywords: blends; fuel cells; ionomer; proton conductivity; swelling; water sorption

INTRODUCTION

The design of proton-exchange membrane (PEM) materials for fuel cells is a challenging task. A PEM has the combined function of acting as a solid electrolyte with high proton conductivity and as a separator between the anode (hydrogen or methanol) and cathode (oxygen/air). A certain amount of water is required to achieve high proton mobility between the two electrodes of the fuel cell.1,2 High temperature operations (80–120 °C), which are typical of high power applications, enhance the performance of the fuel cells and reduce the level of contamination of the catalysts. Thus, PEM materials for such applications need to be stable at high temperature and at high humidity and in
oxidative environments. Recently, polymeric PEMs for hydrogen and direct methanol micro fuel cells working in the range of 25–70 °C have gained importance as batteries in microelectronic devices and for microelectromechanical systems (MEMS). Because high proton conductivity for these systems is achieved under conditions of very high humidity, the membrane swelling becomes a critical parameter despite the low operation temperatures. In fact, membrane swelling can destroy the adhesion between the electrode and the membrane, which compromises the mechanical integrity of the fuel cell.

Perfluorinated polymer electrolyte membranes such as Nafton\textsuperscript{TM} have historically been the main choice for PEMs. The hydrophobic, fluorocarbon backbone provides both mechanical and chemical integrity, while the sulfonated perfluoroether side-chains give rise to high proton conductivity in humid environments. These materials, however, have relatively poor resistance to methanol transport, which is important in a direct methanol fuel cell, and they have poor mechanical properties when highly swollen by water. Furthermore, they are expensive and unsuitable for low cost applications such as microfuel cells and MEMS.

Blending polymers is a widely used approach to produce less expensive materials with special tailored properties, since each component of the blend can be chosen to fulfill a different requirement. One of the benefits of using a polymer blend for PEMs is the possibility to control the membrane morphology to optimize separately the proton conductivity and the membrane integrity. Such optimization is not possible in homopolymer ionomer membranes due to the distribution of ionic domains throughout the bulk of the material. This prevents the creation of continuous pathways for transport of protons unless the ionic group concentration is sufficiently high to cause at the same time an high level of swelling in typical application conditions.

A cocontinuous, interconnected morphology obtained by blending polymers with different ionic content represents a potentially viable approach for controlling the ionic pathway in a PEM. Percolation of the component with high proton conductivity can be developed and, as well, a constraint on the overall swelling of the blend may be provided by the less conductive, and therefore less hydrophilic, component. This paper discusses the proton conductivity and water mass transport of a cocontinuous morphology blend obtained by mixing two sulfonated poly(ether ketone ketone)s (SPEKK), one with an ion exchange capacity, IEC, = 2.08 meq/g and another with IEC = 1.2 in a mass ratio of 40/60. It is hypothesized that, although the proton conductivity of the PEM ionomer was rather low, it could, nevertheless, contribute to the overall conductivity of the system. Polarization data obtained by Swier et al.\textsuperscript{6} on this type of cocontinuous SPEKK/SPEKK blend at 80 °C and high relative humidities, showed substantial improvements in performance and structural stability over a pure SPEKK membrane. To understand the more peculiar features of this type of blend, water sorption and proton conductivity data were compared to those of an SPEKK homopolymer membrane with an IEC equal to the average IEC of the blend and to the two neat SPEKKs components of the blend.

**MATERIALS**

PEKK with a terephthaloyl (T)/isophthaloyl (I) ratio (T/I ratio) of 6/4 (OXPEKK SPb, T<sub>g</sub> = 154 °C, T<sub>m</sub> = 300 °C) was obtained from Oxford Performance Materials, Enfield, CT. The PEKK was sulfonated with a 5% (w/v) solution mixture of 53/47 (v/v) concentrated sulfuric acid to fuming sulfuric acid. The extent of sulfonation was varied by changing the time during which the polymer was kept in the sulfuric acid solution. The sulfonated polymer was precipitated by drop-wise addition of the SPEKK solution into six volumes of rapidly stirred de-ionized ice water. The precipitated SPEKK was filtered, washed repeatedly with de-ionized water to remove excess acid and dried at 60 °C overnight and then kept 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 treated with a saturated aqueous sodium chloride solution overnight. The HCl product so obtained was then titrated with a normalized sodium hydroxide solution using phenolphthalein as an acid-base indicator.

Membranes of SPEKK and SPEKK/SPEKK blends were prepared by casting 5% (w/v) solutions in dimethylacetamide (DMAc, bp = 165 °C) onto glass plates. The solvent was allowed to evaporate for about 1 day at 60 °C, after which the films were washed with de-ionized water to extract residual solvent.

The samples were further treated with 0.5 M H<sub>2</sub>SO<sub>4</sub> solutions at 40 °C for 1 h to ensure that...
the membranes were in H$^+$ form. After that, the membranes were rinsed in water until the removal of free acid was complete.

**EXPERIMENTAL**

**Morphology Examination**

An Asylum Research MFP-3 days-IO atomic force microscope (AFM) was used for morphological characterization. The sample preparation consisted of embedding membranes in an Epon™ Araldite® followed by ultra-microtomy with a diamond knife to obtain thin sections. These sections were placed on precleaned glass cover slips. Drying of the sections on glass resulted in shrinkage of the swollen ionomer phase (microtomed sections were initially floated onto water), and the higher IEC SPEKK phase, which shrank the most, corresponded to areas that were lower in topography.

**Water Vapor Sorption Measurements**

Water vapor sorption isotherms were obtained using an apparatus consisting of a quartz spring placed in a water jacket glass cell connected to a solvent reservoir and to a pressure transducer. Before each test, a high volume container, connected via a valve to the sorption cell, was pressurized with water vapor at a fixed pressure connecting it to the vapor phase in equilibrium with a degassed liquid water reservoir. The equilibrium sorption values, as well as the differential sorption kinetics were determined using step activity increments. This procedure enables the evaluation of the dependence of the diffusivity coefficient of the penetrant on its concentration due to the limited concentration interval of each sorption test. The quartz spring used for these experiments (provided by Ruska Instrument Corp. Houston Texas) had a sensitivity of 5 mg/cm. Spring elongation was monitored using a traveling microscope capable of measuring displacements as small as 0.005 mm. Water vapor activity was evaluated as $p/p_0$ ratio (assuming ideal behavior of the vapor phase), where $p$ is the pressure of water vapor and $p_0$ is the water vapor pressure at the test temperature. The vapor water sorption measurements of the samples were carried out at 40, 60, and 70 °C in the range of activity 0–0.8, corresponding to the different extents of hydration of hydrogen fuel cells in the transient startup phase. The isotherms obtained in this range of water activity were extrapolated to a water vapor activity of ~0.9, which is in the range of the typical steady state conditions of hydration for small and micro fuel cells. This value is above the maximum activity attainable in the sorption apparatus without the risk of condensation in cold spots.

For materials which are ideally Fickian (Fick’s constitutive law for mass diffusive flux and constant mutual diffusivity $D$) an analytical solution for the sorption-desorption kinetics for a film with thickness $l$ was given by Crank$^9$:

$$M(t)/M_{eq} = 2(Dt/l^2)^{1/2} \times \left[ \pi^{-1/2} + 2 \sum_{n=0}^{\infty} (-1)^n ierfc \frac{nl}{\sqrt{(Dt)}} \right]$$

(1)

where $ierfc$ is the integrated complementary error function,$^9$ $M(t)$ is the penetrant sorbed at time $t$ and $M_{eq}$ is the mass sorbed at equilibrium. For $M(t)/M_{eq} < 0.5–0.6$, the terms of the summation are negligible and eq 1 can be approximated by:

$$M(t)/M_{eq} = 2(Dt/l^2)^{1/2} \pi^{-1/2}$$

(2)

For non ideal Fickian behavior, that is, $D$ dependent on concentration, it is still possible to use eq 2 in the same range of $M(t)/M_{eq}$ but $D$ now represents an estimate of the integral mean of the diffusivity in the range of concentration used for such experiments. In particular in the case of differential sorption experiments, $D$ is an estimate of the average diffusivity in the concentration range given by initial and final concentrations used in the test. The mutual diffusion coefficient, $D$, at each activity step was determined by a linear fit of $M(t)/M_{eq}$ as a function of the square root of the time in the early stage of the differential sorption curves.

**Proton Conductivity Measurements**

The proton conductivity of the membranes was measured by a 4-probe method using an ac impedance analyzer. The membrane was placed in the Membrane Conductivity Test Cell (Bekktech Company LLC, Loveland, Colorado) made of two outer foils and two inner platinum wires. The control of humidity and temperature was achieved by placing the Membrane Conductivity Test Cell inside a water jacketed glass cell connected to a solvent reservoir formed by a water jacketed cell containing deionized liquid water in equilibrium with its vapor. The system was connected to a pump to remove the residual air. [Fig. 1(a)]. The water
activity was fixed by setting the temperatures of both the reservoir and the test cell and it is given by the ratio of vapor water tension at the reservoir cell temperature to vapor water tension at the temperature of the test cell. The Membrane Conductivity Test Cell allowed the determination of the lateral conductivity of the membrane, by using a 4-probe system that minimizes the interfacial electrode-membrane resistances [Fig. 1(b)]. The measurement cell was connected to an electrochemical workstation formed by a potentiostat and a frequency response analyzer (Solartron SI 1280B). The Spectroscopy impedance method was used to evaluate the proton resistivity $R$ of the membrane between the two inner electrodes, by applying current ($I$) through the two outer Pt-probes and measuring voltage drops ($V$) across the two inner Pt-probes. The proton conductivity $\sigma$ of the membrane is given by\(^{10}\):

$$\sigma = \frac{l}{R \cdot S}$$  (3)

where $S$ represents the cross-sectional area of the membrane and $l$ represents the distance between the two inner Pt-probes. It is worth not-

**Figure 1.** Schematic description of the system used for the proton conductivities measurements at fixed water activity and temperature (1a). Geometry of the four probe system used for the measurement of the lateral membrane proton conductivity (1b). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
ing that eq 3 is only valid if the density of the current is constant on the surface $S$ and this was achieved by the optimized geometry of the four probe system for the range of membrane thickness tested. The impedance measurements were carried out in the frequency region from 1 to $10^5$ Hz and in the ac current amplitude of 1 mA using a Solatron SI 1280B electrochemical impedance analyzer with ZPLOT software.

The measurements were carried out at 20, 40, and 60 °C and at a vapor water activity of 0.98.

**RESULTS AND DISCUSSIONS**

**Morphological Characterization**

The AFM micrograph shown in Figure 2 provides a fairly clear indication that the 40/60 (w/w) SPEKK IEC 2.08-SPEKK IEC 1.2 (the IEC is reported as meq/g) blend has a cocontinuous morphology. On the basis of a previous analysis this type of blend morphology is expected to give the highest proton conductivity to water sorption ratio. In fact, starting from a “droplet-wise morphology” where the matrix is the high IEC component and the low IEC component constituted the dispersed phase, an increase of the low IEC component content resulted in a large reduction in water sorption and only a slight decrease in the proton conductivity, provided that the amount of the high IEC component was still above the percolative threshold concentration as shown by Swier et al.

In this way, the cocontinuous morphology of the blend likely provided a continuous path of the more conductive SPEKK component (i.e., the one with IEC 2.08), and the continuous SPEKK IEC 1.2 phase constrained the overall swelling of the blend. It is worth noting that when the concentration of the component with IEC 1.2 was higher than 60% (w/w), the low IEC component became the only continuous phase and the conductivity decreased accordingly.

**Water Sorption**

The sorption isotherms for the neat SPEKKs with IEC 1.2, 1.54, and 2.08 (corresponding to the IEC of the less sulfonated component, the average IEC and the IEC of the more sulfonated component of the cocontinuous blend respectively) are shown in Figure 3. The sorption isotherms do not depend on temperature and all the curves display a sigmoidal shape, which is a typical feature of ionomers. In general, sorbed water molecules in ionomers consist of two populations: those tightly bound to specific groups (e.g., sulfonic groups) and those dissolved in the bulk according to physical equilibrium. The former contribution is akin to chemisorption and can be taken into account by using models specifically developed for ionomers or using finite-layer BET theory. The latter contribution is accounted by using ionomer-water molecules mixing theories which could include also the possible elastic response of the polymer.

![Figure 2. AFM micrograph (height signal) of a 40/60 (w/w) SPEKK2.08/SPEKK1.2 blend (SPEKK 2.08 dark gray domains, SPEKK 1.2 light gray domains).](image)

![Figure 3. Water sorption isotherms of neat SPEKK with IEC 1.2, 1.54, and 2.08. The lines represent Brunauer–Emmett–Teller (BET) fittings at 40 °C for IEC 2.08 (dash-dot line), IEC 1.54 (dashed line), and IEC 1.2 (solid line).](image)
network which resists to swelling because of the physical crosslinking effect contributed by the presence of clusters of fixed ionic groups.\textsuperscript{11,13} Since the materials investigated here were all glassy in the dry state at the test temperature,\textsuperscript{6} it is worth discussing briefly some aspects related to this ‘physical’ sorption mechanism. At low activities, polymer-water mixing also includes the contribution of adsorption of water molecules within the frozen-in excess free volume microvoids present in the glassy matrix (out-of-equilibrium structure). As the water activity increases, the absorbed water promotes matrix plasticization which induces a depression of the glass transition temperature ($T_g$)\textsuperscript{14} and a concurrent disappearance of excess free volume and of the associated adsorption capacity. As a consequence, at high enough activities and/or test temperatures, the adsorption contribution vanishes and the physical sorption mechanism can be accounted for by using the classical Flory–Rehner theory,\textsuperscript{15} which includes both mixing and entropic elastic response of the macromolecule.

Actually, the water sorption isotherms of the neat SPEKK samples did not depend on temperature, which suggests that the test temperatures investigated were not high enough to match the $T_g$ of the water–polymer system, even at high activities.\textsuperscript{6} Hence, the SPEKK neat samples were likely in a glassy state at all the temperatures and water activities investigated.

In conclusion for the system under investigation, the downward concavity observed in the sorption isotherms at low activities was likely due to the binding of the strongly interacting first layer of water molecules to sulfonic groups and to the possible adsorption on the excess free volume microvoids. The upward concavity evident at high activities is mainly due to the formation of further solvation layers characterized by a lower degree of interaction and to water-matrix mixing which can be interpreted using simply the lattice Flory theory.

It is worth noting that the increase of concentration of ‘free’ water molecules occurring at high activities is a prerequisite for high proton conductivity of the hydrated membrane.\textsuperscript{16} As a matter of fact, matrix plasticization induced by the free volume increase due to penetrant addition actually promotes a depression of the elastic modulus, thus further favoring the swelling of hydrated ionic clusters formed by the sulfonic groups. That results in an increase of water sorption and, hence of the concentration of free water molecules.\textsuperscript{13,17}

Despite the complexity of the water sorption modeling in such systems, the behavior of our samples was reasonably well described by a multilayer Brunauer–Emmett–Teller (BET) sorption model.\textsuperscript{12} For the interpolation of our data, the BET model is a good fitting model with a reasonably small number of parameters for all sorption isotherms over a wide range of activity (up to 0.9). Although the limited number of data points available are insufficient to draw definitive conclusions, the results suggest that the prevailing sorption contribution likely derives from the several shells of water molecules associated with specific ionic moieties whose formation was enabled by the plasticization of the polymeric matrix.

Figure 3 shows that higher IEC of the neat SPEKK results in higher amounts of water sorbed. This is related to the higher concentration of specific interactive sites which is directly responsible for a higher amount of water sorbed via interactions with sulfonic acid groups and is indirectly responsible for the enhanced overall sorption as a result of the higher extent of plasticization effect. As a consequence the differences of the water isotherms at the various IECs are more evident at high water activities, where the water uptake increases more than linearly with the IEC.

The effect of temperature dependence of the sorption isotherms is rather complex. Sorption at specific interaction sites, adsorption on excess free volume and water clustering are all exothermic phenomena. Polymer-water physical mixing, which is likely endothermic, should promote an increase of sorption as the temperature increases. The trade-off of these effects produces the athermal behavior observed in the 40–70 °C range for SPEKKs.

Figure 4(a–c) compare the BET fitting isotherms for the experimental sorption of (i) the cocontinuous blend, (ii) the SPEKK with equivalent average IEC of the blend (i.e., 1.54 meq/g), (iii) the SPEKK with IEC 2.08, (iv) the SPEKK with IEC 1.2 and (v) the theoretical isotherms for additive behavior of the two components of the blend. The BET fitting is shown instead of the experimental data for the sake of clarity.

The water sorption isotherms for the cocontinuous blend exhibited a sigmoidal shape, similar to the case of neat SPEKK samples but in contrast to them, the water up-take was temperature-dependent. As a consequence, the behavior of the cocontinuous blend was clearly nonadditive over the range of temperature investigated. In particular, it is worth noting that at 40 °C the water sorption of the cocontinuous blend was very close to being
additive, but at 60 °C the water sorption isotherm of the cocontinuous blend was similar to that for the SPEKK with IEC 1.54. At 70 °C, the behavior approached that of the SPEKK with IEC 2.08. This temperature-dependent behavior, which contrasts with the athermal behavior of neat SPEKK, is likely related to the cocontinuous morphology of the blend and results from a trade-off between the mechanical constraint of the low IEC component that limits the swelling of the high IEC component, and the tensile stress that the higher swelling of the high IEC component exerts on the low IEC one. At 40 °C the temperature of the system was probably already high enough to overcome the constraint effect of the low IEC component on the overall swelling of the blend, but the chain mobility was not yet high enough for an additional swelling contributed by the SPEKK with IEC 1.2. Hence the macroscopic water sorption of the two components appeared additive. However, when the temperature was increased, the swelling of the higher sulfonated component

Figure 4. Water sorption isotherms of the SPEKKs with IEC 1.2, 1.54, and 2.08 and of the cocontinuous blend 40/60 (w/w) SPEKK IEC 2.08-SPEKK IEC 1.2 at 40 °C (4.a), 60 °C (4.b) and 70 °C (4.c). Theoretical sorption isotherm representing an ideal additive sorption behavior of the blend is also reported. Lines represent Brunauer–Emmett–Teller (BET) fittings.
produced an increase swelling of the low IEC component, because of the enhanced chain mobility. As a consequence, the water sorption of the membranes at 60 and 70 °C was not additive and approached that of the neat SPEKK 2.08 at 70 °C.

In applications such as membranes for fuel cells, an important factor is the water diffusivity since it controls the hydration rate of the membrane. Mutual water diffusivities were determined at three temperatures using sorption experiments with a step change of the water vapor activity.

The blend water diffusivity values are shown in Table 1. They result lower than those reported for Nafion™, which are within the range 10⁻⁷ to 10⁻⁶ cm²/s for the same conditions.¹⁸ This is a plausible consequence of the different structure of Nafion™, which consists of more nanophase-separated ionic domains homogeneously dispersed in a single hydrophobic matrix.⁶,¹⁷ The water mutual diffusivities found for the SPEKK homopolymers tested were very similar to those of the blend and are not reported here. Diffusion is a typically activated process, so the diffusivity coefficient increases with temperature at a fixed concentration of penetrant inside the polymeric membrane. However, the sorption can decrease with temperature at a fixed penetrant activity causing a reduction of the additive free-volume contributed by the penetrant. Hence, it is possible that diffusivity increases less or does not increase with the temperature at a fixed activity. For the cocontinuous blend analyzed in this paper, at low activities the sorption was approximately constant with temperature for a fixed penetrant activity, while at high activities it increased with temperature; so the diffusivity always increased with temperature at a fixed penetrant activity.

The diffusivity coefficient exhibited a maximum with activity at each temperature, which is typical behavior of ionomers. In particular, this behavior was reported for Nafion™ by Legras et al.¹⁸ who suggested that the diffusion at high activities was based on the movement of clusters of water molecules. Therefore the minimum critical free-volume for a diffusive jump increased and the diffusivity decreased. This simplistic explanation, however, is physically sound only in the case of water sorption in moderately hydrophobic polymers.⁸ In fact, for these types of polymers, at high activities water molecules tend to minimize their contact with the matrix by forming clusters (Zimm model of water clustering¹⁹). This is not likely the case for ionomeric polymer with percolative hydrophilic pathways.

The presence of a maximum in the diffusivity versus activity curves for polymer-penetrant systems can, alternatively, be explained by considering that the diffusivity coefficient obtained by sorption and/or desorption data is the mutual diffusion coefficient. For a low mass fraction of penetrant (values lower than 0.2) this coefficient can be evaluated by multiplying the self-diffusion coefficient by a thermodynamic coefficient that represents the sensitivity of penetrant chemical potential on the penetrant concentration,²⁰ see eq 4,

\[
D = \frac{D_1(1 - x_1)}{RT} \left( \frac{\partial \mu_1}{\partial \ln x_1} \right)_{T,P}
\]

where \(D_1\) represents the self-diffusion coefficient of the penetrant, \(D\) is the mutual diffusivity coefficient, \(x_1\) is the mole fraction, \(\mu_1\) the chemical potential, \(T\) the temperature in Kelvin, and \(R\) the universal gas constant.

The self-diffusivity is linked to the intrinsic mobility of water molecules inside the membrane and steadily increases with penetrant concentration due to the related increase of free volume of the polymer-penetrant mixture. In contrast, the thermodynamic coefficient generally decreases with

<table>
<thead>
<tr>
<th>Vapor Water Activity</th>
<th>Mutual Diffusivity (D)</th>
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<tr>
<td></td>
<td>(T = 40 \degree C) (cm²/s)</td>
</tr>
<tr>
<td>0–0.1</td>
<td>1.2e⁻⁸ ± 2e⁻⁹</td>
</tr>
<tr>
<td>0.1–0.3</td>
<td>3.7e⁻⁸ ± 2e⁻⁹</td>
</tr>
<tr>
<td>0.3–0.5</td>
<td>4.4e⁻⁸ ± 2e⁻⁹</td>
</tr>
<tr>
<td>0.5–0.7</td>
<td>6.0e⁻⁸ ± 2e⁻⁹</td>
</tr>
<tr>
<td>0.7–0.9</td>
<td>2.3e⁻⁸ ± 2e⁻⁹</td>
</tr>
</tbody>
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the penetrant concentration. These two opposing effects can produce a maximum of penetrant mutual diffusivity as function of penetrant concentration.\textsuperscript{20–22}

Still another interpretation can apply to the case of glassy polymers, as is the case of the SPEKK and the SPEKK blend analyzed in this paper. The reduction of diffusivity as the penetrant concentration increases (known as the antiplasticization effect\textsuperscript{23}) could be related to a decrease of the excess free volume of the glassy polymer caused by its relaxation caused by the presence of the penetrant. The depression of free volume can outweigh the increase of free volume associated with penetrant sorption, causing a maximum of the self-diffusion coefficient as a function of penetrant activity and, consequently, also the mutual diffusion coefficient will change in a similar manner.\textsuperscript{23} This explanation is consistent with the observation that the maximum is located at a higher activity at 40°C as compared to the case for 60 and 70°C. In fact, the drop in the excess free volume is more significant at lower activities as temperature increases, since the membrane is closer to the $T_g$ of the water–polymer system\textsuperscript{14,21}

### Proton Conductivity

The proton conductivity of the cocontinuous blend and of the SPEKK neat samples, for membrane thicknesses of 50–100 μm (typical of fuel cell membranes), measured at intermediate water activities (0.5–0.75) were extremely low and below the sensitivity threshold of our equipment. But, an increase of the water activity produced a sharp increase of the proton conductivity. Table 2 reports the proton conductivities of the SPEKK systems at a water activity of 0.98. That is a typical condition for obtaining high proton conductivity in small and micro hydrogen fuel cells applications at low working temperatures (20–70°C). This sharp drop of proton conductivity for water activities below the 0.90–0.98 range, is a limitation of SPEKK in comparison to Nafion\textsuperscript{TM}. This behavior occurs despite the fact that SPEKK membranes typically considered in such applications have a higher IEC than Nafion. As already mentioned, this is likely due to poorer phase separation between the ionic and hydrophobic regions in SPEKK\textsuperscript{6} and to the lower acidity of the sulfonic acid in a hydrocarbon media as opposed to a fluorocarbon matrix.\textsuperscript{16}

The proton conductivity is related to the proton mobility promoted by thermal activation and by the amount of water inside the membrane. As a consequence, when the equilibrium water sorption decreases with temperature, it is possible that the proton conductivity approaches a plateau or shows a minimum with changes in temperature. This second case was observed for Nafion\textsuperscript{TM}.\textsuperscript{10} As shown previously, the equilibrium water sorption is constant with temperature for the SPEKK with IEC 1.2, 1.54, and IEC 2.08 over the full range of activities, while an increase with temperature was found at high activities for the cocontinuous blend. As a consequence, the proton conductivity in all the samples examined in this investigation increased with temperature, as shown by the data in Table 2. In particular, the proton conductivity of the cocontinuous blend was lower than for the SPEKK IEC 2.08, but it was higher than for SPEKK IEC 1.54 at all the temperatures investigated. This occurred despite the fact that the water sorption (extrapolated values at vapor water activity 0.98 by using the BET model) in the blend at 20°C (data not reported) and 40°C was smaller than for SPEKK IEC 1.54. In particular, the proton conductivities of the cocontinuous blend at 60°C were clearly higher compared to that of SPEKK 1.54, despite the fact that the water sorption was similar, and approached the values of the SPEKK 2.08. That result suggests the existence in the blend of percolative pathways of the more sulfonated component.

### Table 2. Proton Conductivity at Water Vapor Activity 0.98

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>SPEKK IEC 1.2 (mS/cm)</th>
<th>SPEKK IEC 1.54 (mS/cm)</th>
<th>Co-continuous Blend (mS/cm)</th>
<th>SPEKK IEC 2.08 (mS/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>&lt;1</td>
<td>5 ± 1</td>
<td>19 ± 1</td>
<td>50 ± 1</td>
</tr>
<tr>
<td>40</td>
<td>9 ± 1</td>
<td>10 ± 1</td>
<td>29 ± 1</td>
<td>106 ± 1</td>
</tr>
<tr>
<td>60</td>
<td>20 ± 1</td>
<td>32 ± 1</td>
<td>109 ± 1</td>
<td>170 ± 1</td>
</tr>
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CONCLUSIONS

A cocontinuous blend, obtained by blending two different SPEKKs, one with low and one with high IEC was evaluated as a PEM for fuel cells in low temperature and at high vapor water activity applications. Comparison of water vapor sorption data of the blend with neat SPEKK membranes showed that the behavior of the blend was not merely additive, but it was determined by the trade-off between the temperature-dependent swelling constraint introduced by the low IEC component and the temperature-dependent tensile stress due to the high IEC component on further swelling of the low IEC component. The cocontinuous membrane water diffusivity coefficients are lower than those reported for Nafion™, since its structure exhibits a less clear separation between ionic domains and hydrophobic polymer matrix. The analysis of the proton conductivity data showed that the cocontinuous morphology also affected the mechanism of ionic transport in the blend by providing percolative pathways for the protons through the high IEC constituent. In particular, the combined analysis of sorption and conductivity data of the cocontinuous blend showed that at low temperatures the proton conductivity was higher than for neat SPEKK with IEC 1.54, even though the water equilibrium uptake was lower (at 40 °C) or similar (at 60 °C).

The results point to the efficacy of using a cocontinuous blend as a PEM for fuel cells to limit excessive swelling. However, the absolute values of proton conductivity of the blend at low temperatures (20 and 40 °C) were still not satisfactory, possibly due to the intrinsic ionomeric structure of SPEKK, which is much less effective than perfluorosulfonates for promoting proton conductivity. At the same time the water sorption of the blend was far too high for PEM applications at higher temperatures (60 and 70 °C). An improvement of the cocontinuous blend to achieve a “proton conductivity to water sorption ratio” better suited for fuel cell applications may be possible by varying the IEC of the two SPEKK components.

REFERENCES AND NOTES