

Basicity-based screening of aniline derivative for composite proton exchange membranes

Vinay K. Sachan,¹ A. Michael Rajesh,² Niharika Panday,¹ Rajaram K. Nagarale,²
 Prashant K. Bhattacharya¹

¹Department of Chemical Engineering, Indian Institute of Technology, Kanpur Uttar Pradesh 208016, India

²Electro Membrane Processes Division, Central Salt and Marine Chemicals Research Institute, Council of Scientific & Industrial Research (CSIR), G.B. Marg, Bhavnagar Gujarat 364 002, India

Correspondence to: R. K. Nagarale (E-mail: rknagarale@csmcri.org) or P. K. Bhattacharya (E-mail: pkbhatta@iitk.ac.in)

ABSTRACT: The aim of this study was to find a suitable aniline derivative to develop composite sulfonated poly(ether ether ketone) (SPEEK) membranes and detail evaluation of their physico- and electrochemical properties. The hypothesis was high basicity of the aniline derivatives could form good composite membranes with better physicochemical and electrochemical properties. To assess the basicity we measured the zeta potentials of the polymers and correlated them with ion-exchange capacities, water uptakes, transport numbers, water-diffusion coefficients, conductivities, and methanol permeabilities. The obtained values of zeta potentials at pH 7 were 6.52, -14.66, -25.17, and -28 for SPEEK/polynaphthalene (PNAPH), SPEEK/polyanisidine (PANIS), SPEEK/polyaniline (PANI), and SPEEK/polyxylylene (PXYL), respectively supports the hypothesis and strongly suggests polyaniline derivative's basicity-dependent properties. Of the four derivatives (PNAPH, PANIS, PANI, and PXYL), the SPEEK/PXYL composite membrane had the lowest methanol permeability of 1×10^{-4} cm²/s and highest proton conductivity of 161 mS/cm. These values are far better than the neat SPEEK and SPEEK/PANI composite. The suitability of SPEEK/PXYL can be explained by the high basicity of the PXYL composite membrane, which leads to the formation of effective Debye spheres, meaning that the ionic complex can interact with surrounding hydronium ions and form hydrophilic channels resulting in high proton conductivity and low methanol permeability. These results suggest that SPEEK/PXYL is a highly suitable membrane for methanol fuel cells or other electrochemical applications. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43978.

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INTRODUCTION

Fuel cells are considered one of the more promising clean energy technologies that basically consumes hydrogen and methanol as fuel. Direct methanol fuel cells (DMFCs), where methanol as a fuel, have the potential to power future micro-electronic and portable electronic devices.^{1,2} The proton exchange membrane (PEM) is a key element of DMFCs used for the transfer of H⁺ from the anode to the cathode.³⁻¹⁰ For good performance, PEMs should have high H⁺ conductivity and low methanol permeability.^{8,9} The perfluorinated ionomer Nafion has been used in DMFCs because of its excellent chemical and electrochemical stability, together with its high proton conductivity when hydrated.¹⁰ However, this membrane has some drawbacks, such as high cost, loss of conductivity at high temperatures (>80 °C), dimensional instability under humid conditions, and high methanol permeability, all of which limit its DMFC applications.¹¹

To overcome these problems, other alternating proton-conducting membranes have been used, such as poly(arylene ether sulfones),¹²⁻¹⁶ polybenzimidazoles, and polyimides.¹⁷⁻²² Although these membranes have high chemical, electrochemical, and dimensional stabilities, they currently require further optimization. Sulfonated poly(ether ether ketone) (SPEEK) is a strong PEM candidate, cheap, easily to handle, low methanol crossover, moderate proton conductivity, good mechanical and high thermal stabilities which has a potential to be used in DMFCs.^{23,24} However, at high degree of sulfonation the SPEEK membrane loses its mechanical stability and increases its permeability to methanol. These problems can be resolved by modifying SPEEK membranes by blending the material with other polymers, i.e., by making hybrid or composite membranes, or by pore filling of the membrane using electrolyte fillers.²⁵⁻²⁹

Crosslinking SPEEK membranes increase their stability and limits uptake of water, which leads to low methanol permeability.

Sulfonated poly(arylene ether ketone) was studied by forming thin layers of polyaniline (PANI) and phosphotungstic acid (PWA) multilayers which showed that methanol permeability was less than that of Nafion 117.^{30,31} Miyatake et al concluded that hydrophilic regions present around clusters of aryl ether/fluoroalkane copolymer chains lead to absorption of water, leading to easier proton transfer.³²

In this study, we have prepared a series of composite membranes based on SPEEK using aniline and several of its derivatives (1-naphthylamine, *o*-anisidine, and 2,6-xylydine). The morphologies and crosslinking structures of the composite membranes were investigated using Fourier transform infrared spectroscopy (FTIR). Properties of the composite membranes that were studied included membrane coating densities, basicities and zeta potentials of the derivatives, thermal stabilities, water diffusion coefficients, proton conductivities, transport numbers, and selectivity for methanol permeability. The superior properties of the SPEEK/PXYL composite membrane for DMFC applications are also discussed in detail.

EXPERIMENTAL

Materials

PEEK flakes were purchased from Solvay Ltd. (India). Ethanol was purchased from Changshu Yangyuan Chemicals (China). Dimethyl acetamide (DMAc), H₂SO₄, HCl, NaOH, FeCl₃, NaCl, 1-naphthylamine, 2,6-xylydine and *o*-anisidine were obtained from Loba Chemie (India). All the chemicals purchased were analytical grade and used as received.

METHODS

Sulfonation of PEEK

Membrane Preparation

SPEEK membranes were prepared using the solvent evaporation method. Dry SPEEK powder was dissolved in DMAc to get a 15% (w/v) solution. This was filtered and cast onto glass plates using a thin film applicator, then dried for 24 h at 70–80 °C in a drying chamber. The dried membranes were then removed from the glass plates. The thickness of the resulting membranes was between 100–120 μm.

Preparations of Composite Membranes

The aniline-derivatized composite membranes were prepared in multiple steps. The first step was the activation of the SPEEK membranes by dipping them in a 1M FeCl₃ solution for 8 h followed by washing them with distilled water. This process exchanges H⁺ ions initially present in SPEEK membrane for Fe³⁺ ions. The second step involved the polymerization of aniline derivatives (aniline, 1-naphthylamine, *o*-anisidine, and 2,6-xylydine) onto separate SPEEK membranes. This was carried out by soaking SPEEK membranes in 10% (v/v) solutions of the respective aniline derivatives in 1 M HCl for 24 h. This step was followed by washing with distilled water. Before being used in electrochemical characterizations, all the membranes were activated by treating them three times with 0.1 M HCl and NaOH alternately, washing them with distilled water, and equilibrating with 1 M of HCl solution for further experiments. The resulting membranes were referred to as SPEEK/polyaniline (SPEEK/PANI), SPEEK/polynaphthylamine (SPEEK/PNAPH),

SPEEK/polyanisidine (SPEEK/PANIS) and SPEEK/polyxylydine (SPEEK/PXYL) respectively.

Membrane Characterization

The thickness of the membranes was measured by using a digital micrometer (Mitutoyo Corporation, Japan) at several different locations and averaging the results to give the values used for the calculations. The thickness of all the membranes was 100 μm (±10 μm). Sulfonation was confirmed using Fourier transform infrared spectroscopy (FTIR) using a Bruker Vertex-70 FTIR spectrometer. The Perkin Elmer diamond DTA/TGA (USA) instrument was used for thermo gravimetric analysis (TGA).

Estimation of Water Content. The water uptake of the membranes was measured using an automatic moisture balance (Citizen MBC 50) fitted with an IR/halogen lamp that heated the samples to 120 °C. Before the measurements, the membrane samples were immersed in water for 12 h at room temperature. The surface water was wiped off the membranes with tissue paper, immediately after which samples were transferred to the sample pan and heated. Measurements of the reduction in weight due to the evaporation of water in the temperature range of 60 °C–120 °C were made in the dynamic mode, and the final results were recorded when no more moisture could be removed at 120 °C. The percentage water uptake by the membrane was calculated using:

$$W = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{wet}}} \quad (1)$$

where W_{wet} and W_{dry} are the wet and dry weight of the membranes, respectively.

Estimation of Ion Exchange Capacity (IEC). The IECs of all the membranes were estimated by acid–base titration. Know weight of membrane samples were immersed in 0.1N HCl for 6 h, washed completely with water to remove excess HCl, then immersed in 0.1M NaOH for 6 h, followed by a final wash with distilled water. This process was repeated three times, after which the membranes were soaked in 2M NaCl solution for a minimum of 12 h at room temperature. The membranes were removed from the solution, and the amount of HCl formed in the NaCl (via ion exchange) was measured by titration against 0.01N NaOH, using phenolphthalein as an indicator. The IEC (milli-equivalents of Na⁺ per unit of dry weight of polymer membrane) was calculated using:

$$\text{IEC} = \frac{N \cdot V}{W_{\text{dry}}} \quad (2)$$

where N is the normality of NaOH used for titration and V is the volume of NaOH solution used.

Estimation of Membrane Conductivity. Proton conductivity of the membranes was calculated by measuring membrane resistance with a four-probe ac impedance technique and a BT-112 conductivity cell (Scribner Associates, Inc.). The impedance was measured using an impedance analyzer (C.H. Instruments, India). The impedance analyzer was operated in potentiostatic mode with amplitude of 50 mV over a frequency range of 1 Hz to 0.1 MHz. The membrane specimens (2 cm × 2 cm) were

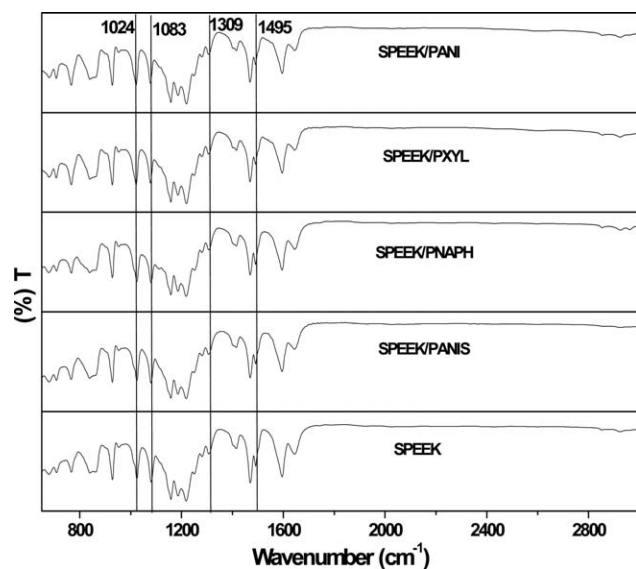


Figure 1. FTIR spectra of the composite membranes.

immersed in electrolyte solution (20 mM H₂SO₄) for 12 h. After equilibration, membranes were placed in the conductivity cell's membrane holder. Data was recorded at room temperature and proton conductivity (σ) was obtained using following equation:

$$\sigma = \frac{l}{R \cdot W \cdot T} \quad (3)$$

where σ is proton conductivity (S/cm), l is the distance between the electrodes used to measure the potential (cm), R (Ω) is the measured impedance of the membrane, T is the thickness of the membrane (cm), and W is the width of the membrane (cm).

Proton Transport Number. The transport numbers of the membranes were calculated by measuring membrane potentials. A custom-made two compartment experimental cell separated by a membrane was used to measure membrane potentials. To avoid the effect of boundary layers on the generated potential, the solutions in both compartments of the cell were continuously stirred using magnetic stirrers. The potential difference across the membranes was recorded with a digital multimeter (Systronics, India) using saturated calomel electrodes and salt bridges, with a reproducibility of up to 0.10 mV. The membrane potentials (E^m) were obtained for the different membranes in HCl, NaOH, KCl, NaCl, Na₂SO₄, CaCl₂, MgCl₂, and NiCl₂ solutions (mean concentration, C_s , was 0.055 M). The ratio of electrolyte concentrations (C_1/C_2) in the two sides of the cell was maintained at 10.0 while $\Delta C/C_s = 1.63$, where C_1 and C_2 are the electrolyte concentrations, $\Delta C = C_1 - C_2$ and $C_s = (C_1 + C_2)/2$.

Methanol Permeability. Methanol permeabilities of the composite membranes were estimated in a custom-made airtight two compartment cell. The effective membrane area was 20 cm². The volume of each compartment was 100 cm³, with provisions for constant stirring. Before experiments began, the membranes were equilibrated in water–methanol mixtures for 12 h in the experimental cell, with one compartment containing 30% (v/v) methanol–water mixture, while the other contained

double distilled water. Methanol flux across the membrane was recorded by determining the increase in methanol concentration over time while constantly stirring at 200 rpm. Methanol concentrations were determined by measuring the refractive index of the solution using a digital refractometer (Mettler Toledo RE40D refractometer). The methanol permeability (P) was calculated using a previously reported method.³¹

RESULTS AND DISCUSSION

FTIR Spectra and Coating Density of Composite Membranes

The formation of the composite membranes was studied by ATR-FTIR spectra (Figure 1). The vibrational bands at 1024 cm⁻¹ and 1083 cm⁻¹ confirm the presence of sulfonic acid in the membranes. The vibrations can be assigned to symmetric and asymmetric stretching of the sulfone group in sulfonic acid.^{34–36} The peaks at 1495 cm⁻¹ and 1592 cm⁻¹ were assigned to benzoidal and quinoidal stretching of the aromatic rings of in the aniline derivatives.²⁸ The peaks around 1309 cm⁻¹ indicate the C–N stretching of the secondary aromatic amine in all the composite membranes. The peak at 1034 cm⁻¹ shows the in-plane bending vibration of aromatic rings, and peaks at 927 cm⁻¹ and 857 cm⁻¹ can be assigned to the out-of-plane bending vibrations of the aromatic ring in the composite membranes. These peaks confirm that SPEEK membranes formed composites with the aniline derivatives.

The coating densities of the composite membranes are shown in Figure 2. The effect of polymerization time on the coating densities of aniline, xylydine, naphthylamine, and anisidine was studied by measuring the weight difference seen in membranes before and after polymerization. As polymerization time increased, coating densities of the derivatives on the base SPEEK membrane increased. For different monomers, the coating densities followed the order PNAPH > PANIS > PANI > PXYL. The highest coating density observed was for SPEEK/PNAPH (0.068 g/cm³ after 1.5 h). The poor solubility of the PNAPH in

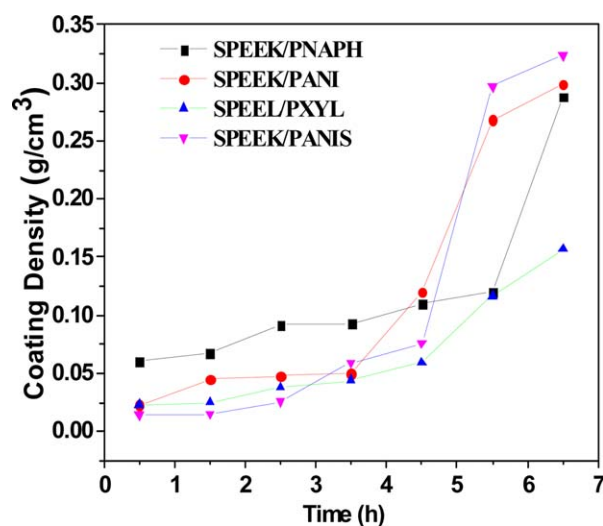


Figure 2. Time dependent coating density of the PANI derivatives on SPEEK membrane catalyzed by ferric chloride solution at room temperature. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

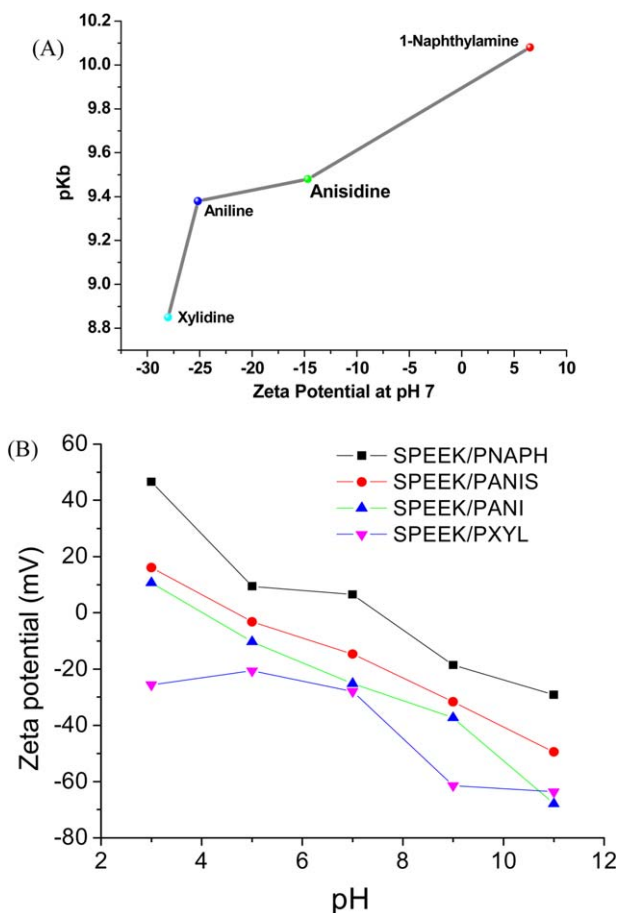


Figure 3. A: pKb values with respect to zeta potential at pH 7. B: Zeta potential of the powdered SPEEK, PANIS, PNAPH, PANI, and PXYL pH solutions. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the reaction mixture led to rapid precipitation on the SPEEK surface, and hence high coating densities in a short period. In the case of SPEEK/PANIS and SPEEK/PANI, coating densities of 0.059 and 0.050 g/cm³ were achieved over 3.5 h. Both monomers exhibited good solubility in the reaction mixture, meaning it took some time to grow the polymer, which attached to the SPEEK surface via ionic bonding once it was over a certain molecular weight. This result could also be explained by looking at the basicity of the monomers [Figure 3(A)]. PNAPH has the lowest basicity and yielded the highest coating density, while PANIS and PANI have similar basicities and similar coating densities. The lowest coating density obtained was for PXYL, which also has the highest basicity. According to the trend, the coating density of PXYL should be the highest, but experimentally it showed the lowest of 0.050 g/cm³ with an increase in 4.5 h. This could be explained by looking at the mechanism of polymerization. Giuseppe *et al.*³⁷ studied the effect of alkyl group substitution on the kinetics of the polymerization of aniline derivatives and showed that it resulted in slower polymerization. The poor kinetics is due to the low reactivity of the intermediate anilinium ions, which explains our experimental observation of low coating densities for PXYL.

Zeta Potentials and Basicities of Composite Membranes

In order to assess the ability of the different PANI derivatives to form strong polysalts with SPEEK, zeta potential measurements of powdered samples were carried out [Figure 3(B)]. The addition of aniline derivatives to the SPEEK membrane changed its surface charge. The zeta potential values at pH 7 were 6.52, -14.66, -25.17, and -28 for SPEEK/PNAPH, SPEEK/PANIS, SPEEK/PANI, and SPEEK/PXYL, respectively. While SPEEK/PNAPH has a positive zeta potential, SPEEK/PANIS, SPEEK/PANI, and SPEEK/PXYL all have negative zeta potentials at pH 7. Figure 3A is a plot of basicity vs zeta potential at pH 7. From the figure, it is clear that lower the basicity of the polymer, the higher the zeta potential. This order can be explained by the adsorption of counter ions on the surface of the polymers.³⁷ High basicity materials have more negative zeta potentials because they adsorb higher numbers of counter ions, as observed in case of SPEEK/PXYL.³⁸

Thermal Stabilities

The thermal stabilities of all the composite membranes were studied using TGA. The results of the TGA for all the composite membranes are presented in Figure 4. These curves show different degradation stages arising from the loss of water and incomplete polymerization, thermal desulfonation, and thermal oxidation of the polymer matrix. The first weight loss occurred below 100 °C and was assigned to loss of absorbed water molecules from the membrane matrix. The second weight loss region (120 °C–350 °C) corresponds to the loss of -SO₃H. In the third weight loss region (>350 °C), the polymer remains were degraded. From the Figure 4, the maximum weight loss of ~17% for SPEEK/PNAPH corresponds to incomplete polymerization of naphthylamine monomer. The monomer is highly hydrophobic and during polymerization oligomers may be precipitated on the polymer film which get further polymerized with heating and hence more weight loss. SPEEK/PANI and

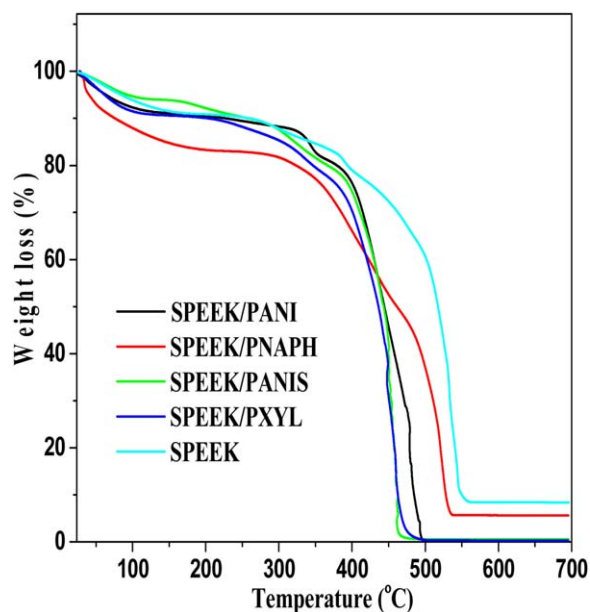


Figure 4. TGA analysis of the composites membranes. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

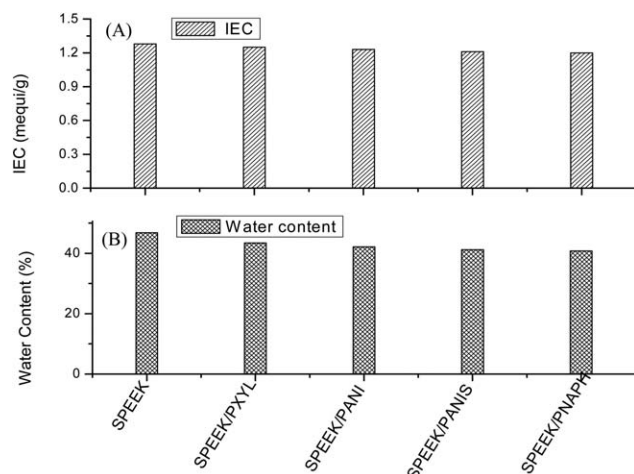


Figure 5. A: Ion exchange capacity and (B) water content of the 0.060 g/cm³ coated composite membranes.

SPEEK/PXYL shows the similar weight loss of ~9%, whereas SPEEK/PANIS and neat SPEEK has ~5% weight loss. The second weight loss which is mainly coming from the degradation of the functional group is highest ~8% for the SPEEK/PANIS, followed by SPEEK/PXYL, neat SPEEK, SPEEK/PNAPH, and SPEEK/PANI. The values corresponds to ~6%; 5%, 4%, and 2% respectively. Suggesting depending on the functionality of aniline derivative the stability also varies. But it did not follow the trend of basicity. The third weight loss is because of the polymer degradation.

IECs and Water Uptake Properties

The IEC, represented as milli-equivalents of Na⁺ per g of the dry membranes, is a quantitative measure of the presence of ionic groups in the membrane. It also accounts for the density of ionizable hydrophilic groups in the membrane matrix, which are responsible for the ionic conductivity of the membranes. The IEC and water uptake values for all the prepared composite membranes are presented in Figure 5(A,B). Pristine SPEEK membrane had the highest IEC of 1.25 milli equiv. of Na⁺/g and water uptake values of 45%, while decreases in IEC and water uptake values were similar for all the composite membranes. The obtained trend is as follows: SPEEK > SPEEK/PXYL > SPEEK/PANI > SPEEK/PANIS > SPEEK/PNAPH. This decrease in IEC and water uptake values is associated with the partial neutralization of the sulfonic acid groups of the PEM by the secondary amines of the PANI derivatives. The increase in the IEC and water content of the SPEEK/PXYL membrane is due to the high affinity of hydronium ions for the negatively charged nitrogen. Gebel has reported that protons are transported through hydrated ionic domains of proton exchange membranes, and that proton conductivity is highly dependent on the connectivity of the hydrated ionic domains to yield a network of hydrophilic channels.³⁹ This shows that adding PXYL to SPEEK does not lead to a deterioration of the IEC and water content of the membrane.

Desorption Behavior of Composite Membranes

The water diffusion coefficient is the proportionality constant between water vapor and water-saturated polyelectrolyte membranes, as per Higuchi's model.^{40,41} This was calculated from the water retention ability of the membrane, as is shown in Fig-

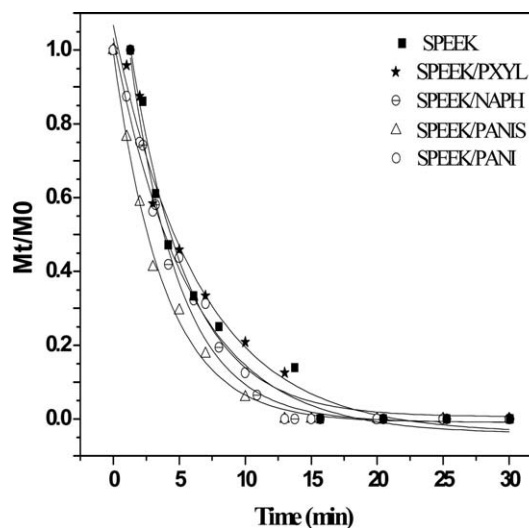


Figure 6. Plot of water desorption versus time for 0.060 g/cm³ coated composite membranes.

ure 6. A plot was made of (M_t/M_∞) versus time (t); where M_∞ and M_t are the amounts of water at the start of the experiment ($t=0$) and at any time t , respectively. Then applying the Higuchi model,⁴² the proportionality constant k was determined from the slope of the plot of (M_t/M_∞) versus $t^{1/2}$. The straight lines obtained for all the composite membranes suggest a good fit of the results to Higuchi's model (Figure 8). Higher loadings of the aniline derivatives in the SPEEK membrane leads to an increase in the rate of water desorption. The diffusion coefficients for all the membranes were calculated using eq. (4):

$$\frac{M_t}{M_\infty} = 4 \left(\frac{Dt}{\pi \delta^2} \right)^{1/2} = k' \sqrt{t} \quad (4)$$

where δ is the thickness of the membrane, and D is the diffusion coefficient.

Figures 6 and 7 show the increase in the obtained water diffusion coefficients with loading of aniline derivatives. This

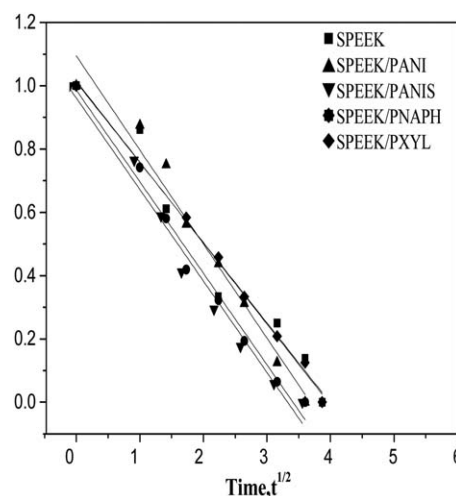


Figure 7. Desorption behavior through fitting of Higuchi model for 0.060 g/cm³ coated composite membranes.

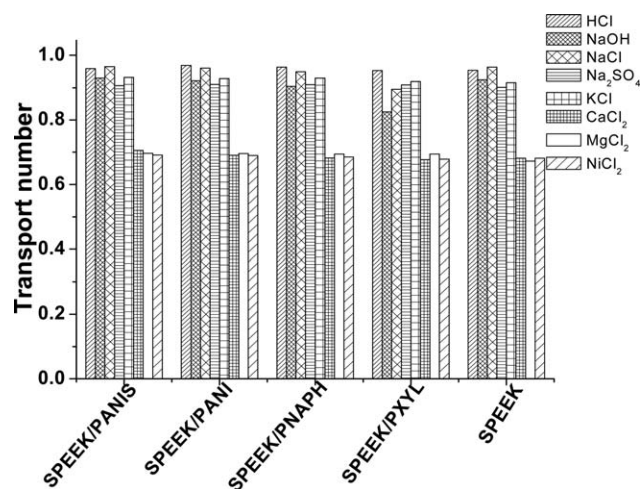


Figure 8. Transport number of composite membranes in different mono-valent and bivalent salt solutions.

suggests that the water retention of the composite membranes is because of inter- and intra-molecular interactions of hydronium ions with the lone pair electrons of the nitrogen atoms. The increase in the water diffusion coefficient is because of the increase in the number of functional groups in the membrane matrix compared to pristine SPEEK membranes. Furthermore, the free water in the ionic membrane matrix is less mobile, because it is bound in the hydrophilic domains of the composite membranes.⁴³

Proton Transport Numbers across the Membranes

When electrolyte solutions of unequal concentrations are separated by a membrane, an electrical potential difference develops across the membrane due to differences in the mobilities of oppositely charged ions caused by dissimilar membrane permselectivities for counterions.⁴⁴ The magnitude of the membrane potential depends on the electrical characteristics of the membrane in addition to the natures and concentrations of the counterions.⁴⁵ Membrane potentials (E^m) were obtained for the composite membranes in HCl, NaOH, KCl, NaCl, Na₂SO₄, CaCl₂, MgCl₂, and NiCl₂ solutions (mean concentration, C_s , was 0.055M); $C_1/C_2 = 10$ and $\Delta C/C_s = 1.63$) and were used for the estimation of H⁺ transport numbers in the membrane phase. The TMS approach was used to measure (t_+^m), as was the following equation:

$$E^m = (2t_+^m - 1) \frac{RT}{F} \ln \frac{a_1}{a_2} \quad (5)$$

where a_1 and a_2 are the activities of the electrolyte solutions. Figure 8 shows the transport numbers of composite membranes in different mono-valent and bivalent salt solutions. The transport numbers of PXYL and PANIS membranes were close to those of pristine SPEEK membranes in similar electrolytic environments, while the t_+^m values for polynaphthylamine and polyaniline membranes were slightly lower. This observation was also supported by the IEC values. Figure 8 also suggests that all composite membranes are selective for bivalent ions over mono-valent ions.

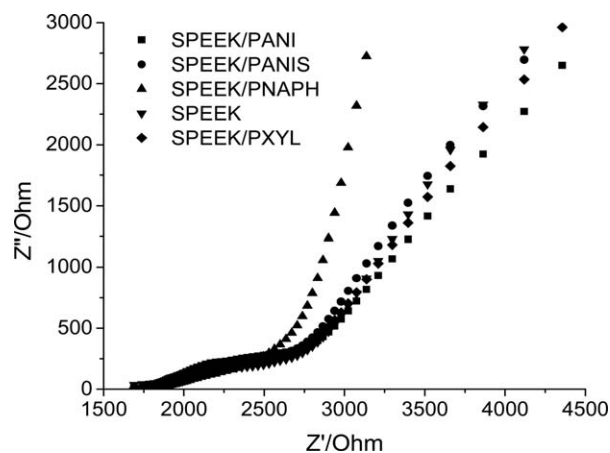


Figure 9. Impedance spectra of the composite membranes recorded in the frequency range 1–10⁻¹ Hz in 20 mM H₂SO₄ solution.

Proton Conductivities

Data obtained from electrochemical impedance spectroscopy was analyzed by non-linear regression. The equivalent circuits and Nyquist plots for the composite membranes are included in Figure 9. Proton conductivity is an important way to assess the contributions of various functional groups in the composite membranes.³¹ Membrane conductance data (K^m), for the composite membranes, are presented in Figure 10. The obtained values were 161, 138, 68, 68, and 37 mS/cm, for neat SPEEK, SPEEK/PXYL, SPEEK/PANIS, SPEEK/PANI, and SPEEK/PNAPH, respectively. The order from lowest to highest is SPEEK/PNAPH < SPEEK/PANIS < SPEEK/PANI < SPEEK/PXYL. This trend is in accordance with the basicities and zeta potentials of the polymers. The low conductivity of SPEEK/PNAPH is also associated with its hydrophobicity, while the high conductivity of SPEEK/PXYL is related to the formation of extended hydrogen bonding with protonated water molecules or formation of Debye spheres due to the high basicity and/or zeta potential. The observed conductivity of SPEEK/PXYL is also similar to neat SPEEK, suggesting that the use of the PXYL derivative has no effect on conductivity but does affect fuel crossover, as discussed below.

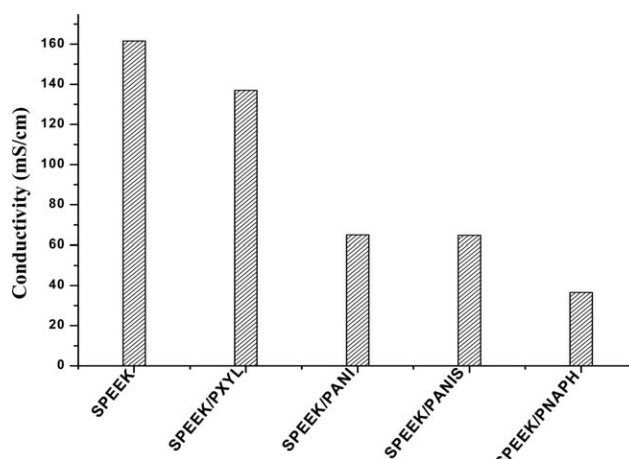


Figure 10. Conductivity of composite membranes measured in 20 mM H₂SO₄ solution at room temperature.

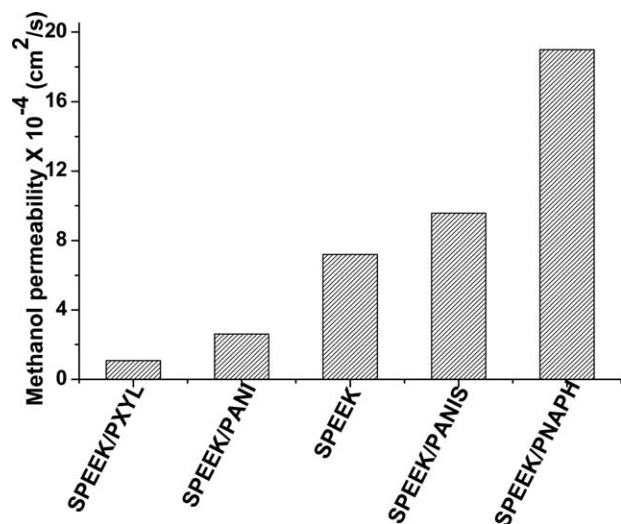


Figure 11. Methanol permeability of the composite membranes measured with 30% methanol/water mixture in indigenously developed two compartment cell.

Methanol Permeability

The fuel crossover was studied by measuring the methanol permeabilities of all the composite membranes, the results of which can be seen in Figure 11. Obtained methanol permeability values were 1×10^{-4} , 3×10^{-4} , 7×10^{-4} , 10×10^{-4} , and 19×10^{-4} for SPEEK/PXYL, SPEEK/PANI, SPEEK, SPEEK/PANIS, and SPEEK/PNAPH, respectively. It follows the trend of SPEEK/PNAPH > SPEEK/PANIS > SPEEK > SPEEK/PANI > SPEEK/PXYL, which is the order of basicities and zeta potentials of the membranes. The lowest basicity composite had the highest methanol permeability, while the derivative with the highest basicity had the lowest methanol permeability. The high basicity polymer formed strong ionic bonds with SPEEK, effectively blocking the pores

through which methanol could permeate. In the case of the low basicity derivative, the ionic bonds between SPEEK and the PANI derivative could not effectively block these diffusion pores. In addition, PNAPH is slightly soluble in methanol, which may contribute towards its high methanol permeability. The SPEEK/PANIS and SPEEK/PANI have similar basicities and zeta potentials, and hence similar methanol permeabilities.⁴⁶

Hydrolytic Stabilities of the Composite Membranes

Figure 12 shows photographs of SPEEK and the composite membranes after hydrolytic stability studies. Hydrolytic stability tests were carried out at 110 °C and 100% relative humidity over a period of 24 hours. All of the composite membranes retained their stability, flexibility, and toughness, while the SPEEK membrane did not. It was observed that all composite membranes were stable under hydrolytic conditions and did not show wrinkles or weight loss, instead remaining in membrane form. On the other hand, the neat SPEEK membrane showed wrinkles and became a gel-like material. The good stability of the composite membranes was due to the lack of free sulfonic acid groups, which prevents the water molecules interacting with PANI derivatives.⁴⁷

Based on the above explanation for membrane conductivities, methanol permeabilities, and hydrolytic stabilities of the composite membranes, a depiction of the interactions between the PANI derivatives and SPEEK membranes is presented in Figure 13. The ionic interactions are represented by broken lines, with colored lines. The SPEEK/PNAPH composite membrane has weak interactions between the acidic groups in SPEEK and the basic amine/imine groups of PNAPH due to the low basicity of PNAPH. The slightly shorter broken lines in SPEEK/PANIS and SPEEK/PANI represent the higher basicities of ANIS and PANI compared to PNAPH. The SPEEK/PXYL composite membrane has low methanol permeability and high hydrothermal stability



Figure 12. Hydrolytic stability of the membranes at elevated temperature. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

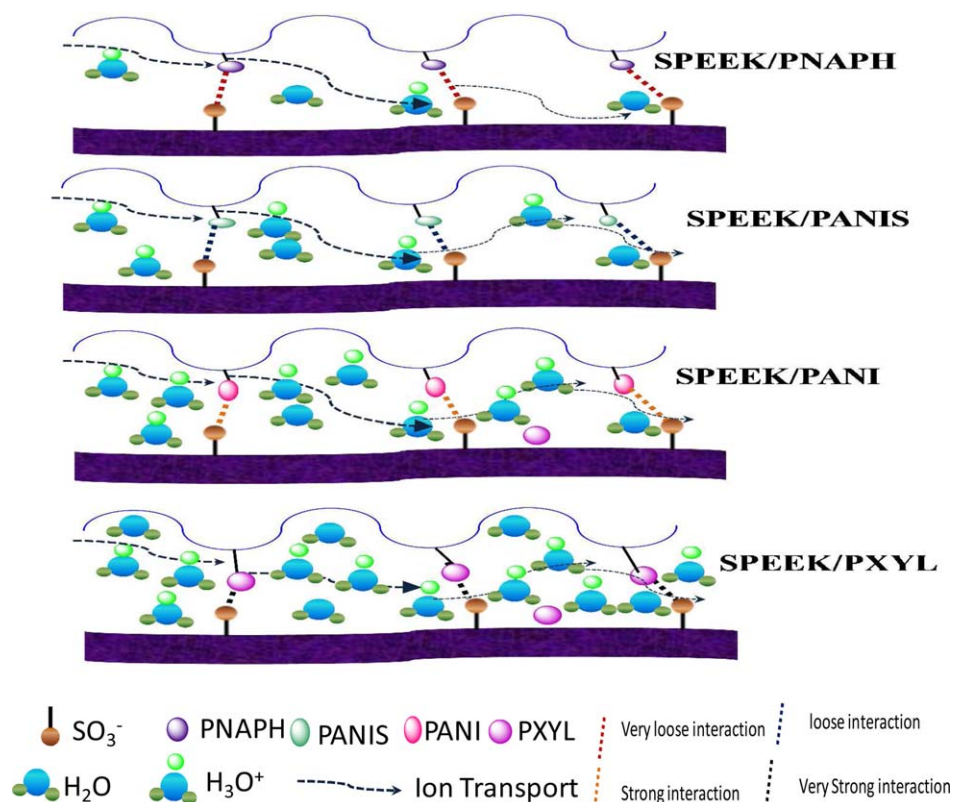


Figure 13. Schematic diagram showing the proton transfer in polyaniline derivative membranes. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

and suggesting strong interactions. Depending on the basicity, we have also denoted the Debye spheres, with fewer hydronium ions showing low basicity and weak interactions, while more hydronium ions indicate high basicity and strong interactions.

CONCLUSIONS

A series of composite membranes were prepared by *in situ* polymerization of different derivatives of aniline onto the surface of SPEEK membranes. The physico- and electrochemical properties of the resulting polyaniline derivative membranes were studied. The basicities and zeta potentials of the polyaniline derivatives were correlated with their ion-exchange capacities, water uptakes, transport numbers, water diffusion coefficients, conductivities, and methanol permeabilities. Composite membrane properties were highly dependent on the basicities of the aniline derivatives. Of the prepared polyaniline derivatives, the SPEEK/PXYL composite membrane had the lowest methanol permeability and highest proton conductivity. The results concluded that PXYL derivative has a high basicity that allows the formation of effective Debye spheres (i.e., formation of ionic complexes with surrounding hydronium ions) which enables hydrophilic channels to form resulting in high proton conductivity and low methanol permeability.

1. Sulfonation was carried out by gradually adding 10% (w/v) PEEK to vigorously stirred concentrated sulfuric acid at room temperature to obtain a homogenous mixture. This mixture was then transferred to a water bath at 50 °C for 2 h. The white SPEEK was then precipitated by pouring the mix-

ture into excess ice-cold water, after which the SPEEK was washed with deionized water for 24 h to remove any traces of acid. Finally, the polymer was rinsed with ethanol and dried in a vacuum oven at 60 °C for 24 h.

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