Enhanced Electrochemical Performance of Stable SPES/SPANI Composite Polymer Electrolyte Membranes by Enriched Ionic Nanochannels

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Supporting Information

ABSTRACT: Herein, we present the results of sulfonated polyaniline (SPANI) and sulfonated poly(ether sulfone) (SPES) composite polymer electrolyte membranes. The membranes are established for high-temperature proton conductivity and methanol permeability to render their applicability. Composite membranes have been prepared by modifying the SPES matrix with different concentrations of SPANI (e.g., 1, 2, 5, 10, and 20 wt %). Structural and thermomechanical characterizations have been performed using the transmission electron microscopy, differential scanning calorimetry, thermogravimetric analysis, and dynamic mechanical analyzer techniques. Physicochemical and electrochemical properties have been evaluated by water uptake, ion-exchange capacity, dimensional stability, and proton conductivity. Methanol permeability experiment was carried out to analyze the compatibility of prepared membranes toward direct methanol fuel cell application and found the lowest methanol permeability for PAS-5. Also, the membranes reveal excellent thermal, mechanical, and physicochemical properties for their application toward high-temperature electromembrane processes.

INTRODUCTION

Energy is the basic requirement for human life. Most of the electrochemical energy systems require polymer electrolyte membranes (PEMs) and thus studied widely.1,2 The emphasis of present scenario is on the generation of nonconventional energy because the conventional sources of energy are continuously diminishing. Fuel cells are a promising alternative for energy production that produces electrical energy. PEM is an important component of polymer electrolyte membrane fuel cell (PEMFC), as they allow only appropriate ions to pass between anode and cathode. The membrane required for PEMFC should not only act as a barrier for methanol but also be a good conductor of protons. Perfluorinated membrane, Nafion, is used as a polymer electrolyte because it possesses high proton conductivity along with excellent chemical stability at room temperature (RT).3 The main drawback of Nafion is its high cost and the loss of conductivity at temperature above 90 °C, realizing its use in high-temperature fuel cells.4 So, an inexpensive PEM having better performance with comparative characteristics is the area of interest to the researchers. Aromatic conjugated polymer, polyaniline (PANI), is a material of considerable interest due to attractive electronic, electrochemical, and optical properties that enable its application in the field of biosensors, rechargeable batteries, fuel cell, supercapacitor, separation science, and so on.5–12 PANI is intrinsically a conducting polymer with high ionic and electronic conductivities and can be easily synthesized.13–15 Different types of cation and anion exchange membranes have been synthesized to fulfill such requirements.16,17 Inan et al. have prepared sulfonated poly ether ether ketone (SPEEK) and fluorinated polymer-based PEMs for their applications in fuel cell.18 Aili et al. have synthesized a high-temperature PEMFC based on polybenzimidazole and sulfonated polyhedral oligosilsequioxane.19 Blend PEM based on sulfonated poly(1,4-phenylene ether-ether-sulfone) and poly(vinylidene fluoride) have been synthesized for same application.20 Highly conducting PEM for fuel cell has also been synthesized by Gahlot et al.21 Significant amount of work has been performed on PANI-based membranes.22,23 Furthermore, composites based on functionalized PANI possess better electrochemical properties.24,25 Sulfonated polyaniline (SPANI) has more ion-conducting groups, providing the path for conduction of protons in PEM and enhancing its solubility and mechanical properties.26 Lin et al. studied the externally doped sulfonated polyaniline multiwalled carbon nanotube composites.26 Dutta et al. have reported a highly stable PEM by the blending of
partially sulfonated PANI and PVdF-co-HFP for direct methanol fuel cell (DMFC) application. Sulfonated poly(ether sulfone) (SPES), containing sulfonic acid groups in its backbone, is a thermomechanically stable polymer with good film-forming properties and widely used for PEMs and other applications.31,32

The present article describes the synthesis of SPANI, SPES, and its composite membranes for fuel cell application. SPANI possesses excellent stability and is easily synthesized. Incorporation of SPANI may improve the performance of composite membranes. Various SPES concentrations have been incorporated within the SPES matrix, for example, 1, 2, 5, 10, and 20 wt %. The prepared membranes are analyzed for structural and thermomechanical properties. Further, ionic conductivity at high temperature and other physicochemical properties are analyzed.

**RESULTS AND DISCUSSION**

**Structural Characterization of Prepared Materials and Membranes.** Fourier transform infrared (FTIR) spectra of PANI, SPANI, and composite membranes are presented in Figure 1. The frequency at 1564 and 1436 cm\(^{-1}\) for PANI corresponds to the quinoid and benzenoid rings, respectively.31,32 Peaks at 1297 and 1115 cm\(^{-1}\) are assigned to C=N and C=N stretching, respectively, for PANI. Stretching vibration at 801 cm\(^{-1}\) is ascribed to the C=N bond in the PANI spectra. According to the FTIR spectra of SPANI, a shift was observed in the peak positions as compared with PANI. This shift is due to the protonation of PANI, resulting in the formation of self-doped stable structure.31 Vibration at 1042 and 1063 cm\(^{-1}\) are allocated to the asymmetric and symmetric O=S=O stretching, respectively, and those at 801 and 695 cm\(^{-1}\) are allied with the S=O and C=S vibration, indicating the existence of sulfonic acid species in SPANI. The interaction between SPANI and SPES polymers is also determined by the FTIR spectroscopy (Figure 1ce). Composite membranes yield several new peaks, as presented in the spectra. The peaks at 3360 and 3234 cm\(^{-1}\) designate O=H vibration and stretching at 2942 and 2886 cm\(^{-1}\) specify the occurrence of O=H (acidic group) in the SPES and PAS-5, respectively. Peaks close to 1170 and 1016 cm\(^{-1}\) in PAS-5 and 1025 cm\(^{-1}\) in PAS-10 are accredited to the asymmetric and symmetric vibrations, indicating the presence of −SO\(_3\)H group in the composite membranes. A shift in the vibration frequencies in PAS-10 membranes was observed as compared to PAS-5 due to the enhanced interaction between polymer and SPANI. The uniform distribution of functional group inside the membrane plays an important role, which was confirmed by the IR imaging of the SPES and composite membranes as shown in Figures 2 and S-1. The images show the uniform distribution of −SO\(_3\)H group inside the SPES and composite membranes between 1120 and 1190 cm\(^{-1}\). \(^{13}\)C solid-state NMR spectroscopy of PANI and SPANI was also performed to analyze their chemical structure, as presented in Figure S-2. The \(^{13}\)C spectra show characteristic peaks at a lower field similar to PANI of emeraldine base and matched well with the literature.34,35 The recorded Raman spectra of PANI and SPANI in Figure S-3 confirms the emeraldine structure.36 Functional groups of PANI were found at ∼1645 cm\(^{-1}\) due to the C−C of the benzenoid ring and at ∼1570 cm\(^{-1}\) due to the C=C vibration of the quinoid ring. The peaks at ∼1496 cm\(^{-1}\) and ∼1449 cm\(^{-1}\) are attributed due to the quinoid ring for C≡N and C−C stretching, respectively. However, vibration at ∼1341 cm\(^{-1}\) (C=N stretching of the quinoid ring) and ∼1288 cm\(^{-1}\) confirms the presence of functional groups in PANI.37 In the case of SPANI, the peak at 1546 cm\(^{-1}\) arises from the C=C stretching of the benzenoid ring and that at 1341 cm\(^{-1}\) arises from the C≡N stretching.38 The \(I_{D}/I_{G}\) factor increased on the functionalization of PANI. The X-ray diffraction (XRD) spectra of the synthesized PANI, SPANI, and composite membranes are shown in Figure 3. The peaks are observed at 12.1, 19.8, and 25° for PANI and at 11.9 and 18.16° for SPANI. The intensity of peaks in SPANI is less than that of the peaks in PANI. This decrease in 2θ indicates the transition of the crystalline regions of PANI to the amorphous structure of SPANI because of the incorporation of −SO\(_3\)H.39 Composite membranes reveal no sharp peak due to the amorphous nature of SPES.

Transmission electron microscopy (TEM) and scanning electron microscopy (SEM) images of SPANI at different resolutions are shown in Figure S-4A,B (TEM) and Figure S-4C,D (SEM). All of the images are well matched with the literature reported previously.40,41 Figure 4 demonstrates the atomic force microscopy (AFM) and SEM images of composite membranes. Surface morphology can be observed in the AFM images in Figure 4A,C, which shows the SPES, PAS-2, and PAS-10 membranes. The image of SPES presents a smooth structure with the average roughness of 4.483 nm, whereas a significant increase in the surface roughness is observed in the composite membranes from 10.44 to 11.62 nm for PAS-2 and PAS-10, respectively. It is clear from the pictures that the average roughness tends to increase as the content of SPANI within the membranes increases. The surface and cross-sectional SEM images of PAS-5 and PAS-10 are shown in Figure 4D,F. The figure suggests a uniformly dispersed granular kind of structure of SPANI over the SPES surface.

**Stability of Material and Membranes.** Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) analysis are used to evaluate the thermal stability of PANI, SPANI, and composite membranes. PANI and SPANI show one-step decomposition (Figure 5). Evaporation of the absorbed water and unreacted aniline can be observed below 150 °C. The weight loss around 250 °C may be due to the decomposition of sulfonic acid present in SPANI.42 The decomposition temperature for SPANI is found to be higher than that of PANI because of the higher thermal stability of sulfonic acid groups. The TGA of the composite membranes is
demonstrated in Figure 6; it is clear from the micrograph that all of the membranes are subjected to weight loss, which is noticed between 50 and 150, 300 and 400, and 500 and 600 °C probably due to bound water, sulfonic acid groups, and decomposition of polymer backbone, respectively. PAS-20 shows the highest thermal stability among the prepared membranes. The transition temperatures are investigated by the DSC analysis. The DSC thermograph of PANI, SPANI, and composite membranes is shown in Figures S-5 and S-6. The DSC of PANI displays two endothermic peaks at 97.8 and 268.8 °C; the first peak at 97.8 °C shows the disappearance of moisture and the second peak at 268.8 °C shows the degradation of PANI. In the case of SPANI, an incremental shift is noted in both the peaks. In the DSC curve (Figure S-6) of composite membranes, endothermic peaks are observed from 97 to 135 °C where composite membranes show the endothermic peaks at higher temperature comparative to SPES membrane. Mechanical properties of composite membranes measured by universal testing machine (UTM) analysis are shown in Table 1 and Figure 7. The elastic modulus of the composite membranes increases by SPANI content and reaches to 10.72 MPa for PAS-10 membrane. On the other hand, the elongation at break decrease by the incorporation of PANI into SPES. The stress on the membrane also increases by increasing the PANI content and reaches to 39.96 for PAS-10 membrane. It is clear from the data that the membranes have sufficient mechanical strength and PAS-5 shows adequate mechanical stability for its applications to the fuel cell.

**Ion-Exchange Capacity (IEC) and Water-Uptake Behavior.** Physicochemical properties of composite membranes are demonstrated in Table 2. Water uptake has an intense
impact on proton conductivity, proton mobility, and mechanical stability of the membranes. Water uptake increases with the increasing amount of SPANI. Maximum water uptake is observed for PAS-20 membranes, that is, 19.87%. Water retention capability $\lambda$ for SPES is found to be 4.8, but it increases for PAS-1, that is, 5.45, which is maximum among all of the membranes. Afterward, the value of $\lambda$ reduces to 5.36 for PAS-20 membrane. Dimensional change is observed to be decreasing. Due to the hydrophilic nature of SPANI composite membrane, more water molecules enfold the sulfonic groups. Further, it is observed that membranes with high water uptake exhibited lower dimensional change, that is, PAS-20. The reason behind this phenomenon is the formation of dense and compact structure, which hinders the accommodation of water. The IEC tends to increase from SPES to PAS-5, but decreases.

Table 1. Membrane Mechanical Properties

| membrane type | modulus (MPa) | elongation at break (%) | stress (MPa) |
|---------------|--------------|------------------------|--------------|
| SPES          | 2.69         | 9.99                   | 19.74        |
| PAS-2         | 5.43         | 10.56                  | 37.44        |
| PAS-5         | 4.77         | 6.04                   | 44.31        |
| PAS-10        | 10.72        | 7.12                   | 39.96        |

Figure 4. AFM images of (A) SPES, (B) PAS-2, and (C) PAS-10; SEM image of (D) PAS-5; and (E) cross-sectional images of PAS-5 and (F) PAS-10.

Figure 5. TGA of PANI and SPANI (inset differential thermogravimetry).

Figure 6. TGA of composite membranes.

Figure 7. Stress–strain curves for different composite membranes.
for PAS-10 and PAS-20. The rising number of sulfonic groups increases IEC, but the effect becomes less as the amount of SPANI reaches between 10 and 20 wt %. The presence of lone pair on N atoms in PANI and SPANI is responsible for an increase in the IEC of the membranes.

**Proton Conductivity, Diffusion Coefficient, and Electronic Conductivity.** Proton conductivity of the composite membranes is measured from 30 to 90 °C, and the data are presented in Figure 8 and Table 3. Methanol permeability and proton conductivity are interrelated parameters. Reason lies in the fact that the factor responsible for low methanol permeation also impede the flow of water molecules through the membrane. However, in our case, composite membranes reveal a low methanol permeability along with a good proton conductivity. This can be explained by the fact that SPANI chains possess a conjugated bond network, which enables easy transport of protons within SPES polymer while blocking the path of methanol. It can be seen that increasing the amount of SPANI up to 5 wt % enhanced the proton conductivity, whereas a decrement is observed in PAS-10 and PAS-20 composite membranes. There is a rise in the proton conductivity values when moving toward higher temperatures from 30 to 90 °C (90 °C is the maximum value attained as the water starts boiling beyond this temperature). An increase in temperature makes the proton diffusion through the membrane easy. A high value of IEC is also an important factor because it provides supplement to the acidic groups, thus enhancing the proton conductivity. PAS-5 membrane shows the highest conductivity values and reaches up to $18.9 \times 10^{-2}$ S cm$^{-1}$ at 90 °C; the value is equivalent to the reported value of Nafton membrane at the same temperature. Conductivity of the membranes rises because of the existence of more hydrophilic proton conductive channels. However, in PAS-10 and PAS-20, the decrement in ionic conductivity is due to the impeding effect of the aggregation of SPANI.

To evaluate the performance of composite membrane as an electrode, the current−voltage characteristics have been analyzed by two-probe method and are presented in Figure 9.

### Table 2. Ion-Exchange Capacity (IEC), Water Uptake (%), Water Molecule on Functional Group ($\lambda$), Bound and Free Water (%), and Dimensional Stability of Different Membranes

| membrane type | IEC (meq/g) | water uptake (%) | $\lambda$ (SO$_3$/H$_2$O) | dimensional change (%) |
|---------------|-------------|------------------|-----------------------------|-----------------------|
| Nafton        | 1.21        | 11.93            | 5.48                        | 10.60                 |
| SPES          | 1.4         | 12.12            | 4.81                        | 19.54                 |
| PAS-1         | 1.75        | 17.18            | 5.45                        | 12.28                 |
| PAS-2         | 2.44        | 16.54            | 3.76                        | 9.25                  |
| PAS-5         | 2.47        | 17.14            | 3.85                        | 17.15                 |
| PAS-10        | 1.809       | 17.37            | 5.33                        | 14.49                 |
| PAS-20        | 2.06        | 19.87            | 5.36                        | 8.56                  |

### Table 3. Membrane Proton Conductivity ($\sigma$), Diffusion Coefficient ($D_\sigma$), Methanol Permeability ($P_m$), and Activation Energy of Proton Conduction ($E_a$) of Different PEMs

| membrane type | $\sigma$ ($\times 10^{-7}$) (S cm$^{-1}$) | $D_\sigma$ ($\times 10^{-28}$) m$^2$ s$^{-1}$ | $P_m$ ($\times 10^{-7}$) cm$^2$ s$^{-1}$ | $E_a$ (kJ mol$^{-1}$) |
|---------------|-----------------------------------------|---------------------------------|-----------------------------------|---------------------|
| Nafton        | 8.98                                    | 6.41                            | 3.27                              | 21.08               |
| SPES          | 3.45                                    | 2.13                            | 3.15                              | 18.55               |
| PAS-1         | 6.43                                    | 3.17                            | 1.32                              | 16.12               |
| PAS-2         | 7.29                                    | 3.35                            | 1.19                              | 14.32               |
| PAS-5         | 9.49                                    | 3.31                            | 1.27                              | 16.12               |
| PAS-10        | 6.33                                    | 3.02                            | 1.27                              | 16.12               |
| PAS-20        | 6.2                                     | 2.59                            | 1.27                              | 16.12               |
compared to PAS-5 membrane. The phenomena of significant increment in current for PAS-S membrane can be elucidated as follows: when a potential is applied to SPANI, the conducting channels are formed between the anode and the cathode, which establishes an Ohmic contact between the membrane and the electrode.\textsuperscript{47,48} Nonlinearity in $I$–$V$ characteristics confirms that semiconducting nature of PAS-S composite membrane and its use as a material for nanoelectrode.

Conduction of proton in PEM is directly related to the activation energy, which is the minimum energy needed for proton transport and calculated by proton conductivity at activation energy, which is the minimum energy needed for conduction is calculated by Arrhenius plot (Figure 8).\textsuperscript{49} The use as a material for nanoelectrode.

Semiconducting nature of PAS-5 composite membrane and its electrochemical performance of PAS-S membrane with higher thermomechanical and chemical stabilities make it a perfect proton-exchange membrane for high-temperature electromembrane application.

**Table 4. Diffusion Coefficient by MRI ($D_0$) and $T_1$ Relaxation (ms)**

| Membrane Type | $D_0$ ($\times 10^{-10}$ m$^2$ s$^{-1}$) | $T_1$ Relaxation (ms) |
|---------------|--------------------------------------|----------------------|
| SPES          | 1.625                                | 214.85               |
| PAS-2         | 1.463                                | 261.51               |
| PAS-5         | 1.746                                | 323.09               |
| PAS-10        | 1.129                                | 217.36               |
| PAS-20        | 1.653                                | 193.06               |

Figure 10, respectively. Table 4 shows that the self-diffusion of fully hydrated SPES membrane at 295.5 K has a value of about $1.625 \times 10^{-10}$ m$^2$ s$^{-1}$ compared with $1.746 \times 10^{-10}$ m$^2$ s$^{-1}$ for PAS-S membrane, which is in the order of values calculated by impedance spectroscopy. The spin–lattice relaxation time ($T_1$) for all of the composite membranes is presented in Table 4; their diffusion-weighted magnetic resonance images are shown in Figure S-7. The spin–lattice relaxation time ($T_1$) for SPES membrane is found to be 214.85 ms, which is increased by 50% (323.09 ms) for PAS-S membrane. It reveals an enhancement in the intramolecular interaction between $^1$H spins and $^1$H spins–lattice interaction with the addition of SPANI causing an increase in the water–proton ionic cluster size and their connectivity with the membrane channels/neighboring ionic cluster. It has been already proposed that proton transport in the proton-exchange membrane proceeds through the ionic cluster.\textsuperscript{50,51} The enhancement in ionic mobility may be due to the presence of higher water content and more interconnected ionic cluster region. The results suggest that the incorporation of SPANI increases the size and the number of interconnected ionic cluster region, which enhance the proton conductivity.

**Table 5. Methanol Permeation ($P_m$) for Composite Membranes**

| Membrane Type | $P_m$ (m$^2$ cm$^{-2}$ s$^{-1}$) |
|---------------|---------------------------------|
| PAS-20        | 1.5836                          |
| PAS-10        | 1.19                             |
| PAS-5         | 1.653                            |
| PAS-2         | 1.463                            |
| SPES          | 1.625                            |

Figure 10. Diffusion-weighted MRI images for different composite membranes.
Table 5. Comparison of Electrochemical Properties with Different Reported Membranes

| membrane                        | IEC (meq/g) | ionic conductivity (S cm⁻¹) | ref   |
|---------------------------------|-------------|----------------------------|-------|
| Naion/SPANI = 70:30             | 1.20        | 7.21 × 10⁻³                | 24    |
| PS/SERS/SPANI-CSA               | 1.24        | 1.5 × 10⁻⁷                 | 53    |
| SPVdFco-HFP/SPANI:: 60:40       | 0.71        | 6.78 × 10⁻³                | 7     |
| SPEEKK/PANI-2                   | 1.00        | 0.051                      | 54    |
| PAS-5                           | 2.47        | 9.49 × 10⁻²                | present work |

Scheme 1. Schematic Representation of SPES/SPANI Composites

estimated using acid–base titration. Proton conductivity of the membranes is calculated by the membrane resistance measurements using a potentiostat. The estimation of methanol transport is done at room temperature in a diffusion cell. The details are included in the Supporting Information.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.7b00687.

The details of the chemical, structural, and physiochemical characterization and membranes stability are included as sections S1–S5 in the Supporting Information. Figures S-1 to S-6 are also included in the Supporting Information section (PDF).

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Notes
The authors declare no competing financial interest.

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