



# Synthesis of sulfonated poly(bis(phenoxy)phosphazene) based blend membranes and its effect as electrolyte in fuel cells

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## ABSTRACT

In the present study, acid–base blend membranes are synthesized to imply as electrolytes in polymer electrolyte membrane fuel cells (PEMFCs). Poly(bis(phenoxy)phosphazene) (POP) is sulfonated with sulfuric acid to impart the ionic conductivity and then blended with sulfonated poly(ether ether ketone) (sPEEK). The blend membranes are fabricated by varying the sulfonated poly(bis(phenoxy) phosphazene) (sPOP) content from 2 to 4 wt.% in relation to sPEEK. The strong hydrophobic backbone of POP improves the mechanical strength of the membrane which is critical for the long term operation of PEMFCs. SAXS analysis suggests the change and enhanced dimension of ionic clusters in sPOP-sPEEK blend membrane in comparison with pristine sPEEK. Hydrophobic and hydrophilic phase distinction in the blend is determined by AFM analysis. Blend membranes exhibit higher ionic conductivity than pristine sPEEK membrane due to the acid–base interactions between sPEEK and sPOP. When subjected to cell polarization, blend membranes of sPOP-sPEEK attain peak power density of  $935 \text{ mW cm}^{-2}$  in PEMFCs which is on par with the peak power density observed for commercial Nafion-212 membrane. Apart from its higher performance, the sPOP (3 wt.%)–sPEEK blend also shows low fuel crossover and comparable stability to Nafion-212 membrane under cell operation.

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## 1. Introduction

Fuel cells are considered to be one of the best alternative energy conversion systems due to their low environmental pollution, high efficiency and quick start up [1]. Among all the other types of fuel cells, polymer electrolyte membrane fuel cells (PEMFCs) are extensively studied in recent times due to their wide range of transport and stationary applications. Till date, the major hindrance in commercialization of PEMFCs lies in the cost and their long term durability of the components which include Pt based catalyst, proton exchange membrane (PEM) and bipolar plates [2–4]. Among these components, PEM plays a major role in determining the performance of PEMFCs; and Nafion® is the widely used membrane for the same due to its superior proton conductivity in humid environment in conjunction with its high mechanical strength and electrochemical stability [5,6]. However, the practical applications of these membranes are determined by several factors. Primarily, the cost of Nafion® membrane is still too high for commercial applications and its dehydration at elevated temperature significantly reduces proton conductivity [7,8]. To address these issues, immense efforts are in progress to modify Nafion® membranes for improved conductivity and stability. Other approach is to develop cost effective

alternative hydrocarbon membranes with better ionic conductivity and stability in relation to Nafion® membranes [9–13].

Among the wide range of alternative membranes studied for PEMFCs, hydrocarbon polymer based membranes like sulfonated poly(ether ether ketone) (sPEEK) is considered to be a suitable candidate due to its ease of processing and unique physico-chemical properties [13,14]. However, the proton conductivity of the sPEEK membrane is less as it possesses many dead-end ion conducting channels which limits the proton transport across the membrane in comparison with Nafion®, wherein the ionic domains are well inter-connected [15]. Hence it is necessary to modify the sPEEK membranes in order to open up these dead end channels and also for enlarging the channel interconnectivity intended for enhanced conductivity. In polymers like sPEEK, the required proton conductivity can be achieved with increased degree of sulfonation, but its mechanical properties tend to deteriorate when the sulfonation content is higher than an optimal level. Moreover, higher sulfonation increases the water uptake due to which the membrane dimensional stability is gradually lost on long term operation and this phenomenon will still be serious when the fuel cell operates at higher temperatures and humidity levels [16]. To clearly understand and tackle these issues, one of the best approaches would be to disperse the inorganic/inorganic nanocomposite systems with superior thermomechanical properties [17–19].

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Another unique approach to improve the properties of sPEEK is to form blend membranes with basic polymers. Basic polymers fine tune the ionic domains of sulfonated polymers in the form of blend/composite [20]. Among the basic polymers, we have selected poly(phosphazenes) which contain  $\text{—P=N—}$  inorganic moiety as backbone and are known for their better chemical and mechanical stabilities. These polymers can also be modified precisely by attaching the ion conducting sulfonic acid groups through substitution reaction on the aromatic ring [21–24]. Polymer electrolytes with additives having basic character lead to improved physicochemical and electrochemical properties [25]. Previously, composite membranes of sPEEK and poly(bis(phenoxy)phosphazene) (POP) were studied as PEM for direct methanol fuel cells (DMFCs). POP being the inert/hydrophobic (no charge) component of the blend membrane, greatly reduced the methanol permeation in DMFCs with appreciable compromise in the proton conductivity [26]. The present study establishes the sulfonation of POP to form a compatible blend with sPEEK and is applied as PEM in  $\text{H}_2\text{—O}_2$  fuel cells. The blend membranes exhibit improved proton conductivity, lower reactant crossover ( $\text{H}_2$  and  $\text{O}_2$ ) in comparison with pristine sPEEK membranes. The membrane electrode assemblies (MEAs) comprising these blend membranes exhibit higher peak power density in PEMFCs in relation to pristine sPEEK and Nafion-212 membranes.

## 2. Experimental

### 2.1. Materials

Sulfonated poly(ether ether ketone) (sPEEK,  $M_w = 50,000 \text{ g mol}^{-1}$ ,  $M_n = 14,000$ , with IEC of  $1.54 \text{ meq g}^{-1}$  and degree of sulfonation (DS) 54%) was procured from FuMA-Tech GmbH, Germany. Poly(bis(phenoxy)phosphazene) was purchased from Sigma Aldrich, India. Dimethyl acetamide was obtained from Acros organics India. Commercial GDL (SGL-DC-35) was supplied by Nikunj Exim Pvt. Ltd., India. Pt/C (40 wt.% Pt on Vulcan XC-72R carbon) was obtained from Alfa Aesar (Johnson Matthey, India) chemicals.

### 2.2. Sulfonation of POP and synthesis of blend membranes

Poly(bis(phenoxy)phosphazene) was sulfonated through electrophilic substitution reaction as reported in the literature [24]. The typical sulfonation process is as follows: 0.2 g of POP was dissolved in mixture of conc.  $\text{H}_2\text{SO}_4$  and DMAc (1:2 vol. ratio) at  $80^\circ\text{C}$  with continuous stirring for 2 h. The clear transparent solution was then neutralized with ice-cold water to quench the reaction to form the product precipitate. The precipitate is then filtered and washed with distilled water to remove the residual acid and the white precipitate obtained was dried in hot air oven at  $60^\circ\text{C}$  to get sPOP particles.

The blend membranes of sPOP-sPEEK were synthesized by varying the amount of sPOP (2–4 wt.%) in sPEEK. Initially the required amount of sPOP was dissolved in DMAc at  $80^\circ\text{C}$ . Then the transparent solution obtained is mixed with 2 wt.% sPEEK that was already dissolved in DMAc. The mixture was stirred for 3 h for blending and the blend solution was cast uniformly on to a Plexi glass plate and dried in vacuum at  $80^\circ\text{C}$  for 12 h. Finally the membranes were peeled out from the glass plate and dipped in 0.5 M  $\text{H}_2\text{SO}_4$  for the activation of ion conducting groups. The membranes were then repeatedly washed with de-ionized water to remove any residual acid till neutral pH and then stored in the same for further studies. Thickness of all the membranes was in the range of 50–60  $\mu\text{m}$ . For ease of comparison, Nafion-212 of similar thickness was used.

### 2.3. Characterization

FT-IR spectra for POP and sPOP were recorded using a Nicolet IR 860 Spectrometer (Thermo Nicolet Nexus-670). Elemental analysis for POP and sPOP was performed on Elementarvario EL 111-Germany. These

were done to confirm the sulfonation of POP. Mechanical strength of all the membranes was estimated as described in our previous literature using universal testing machine (UTM) (Model AGS-J, Shimadzu, Japan) with an operating head-load of 10 kN [27]. FT-IR spectra for sPEEK and sPOP-sPEEK membranes were recorded following similar protocols mentioned above. Thermo-gravimetric analysis (TGA) of pristine sPEEK and sPOP-sPEEK blend membranes was carried out by using a NETZSCH STA 449F3 TGA-DSC instrument in the temperature range between  $30^\circ\text{C}$  and  $1000^\circ\text{C}$  at a heating rate of  $5^\circ\text{C min}^{-1}$  with nitrogen flushed at  $60 \text{ mL min}^{-1}$ . Surface and cross-sectional morphologies of pristine sPEEK and sPOP-sPEEK blend membranes were analysed through a JEOL JSM 35CF Scanning Electron Microscope along with elemental mapping for the samples. Topological and phase images for pristine sPEEK and its blend membranes were determined by tapping mode atomic force microscopy (AFM, PicoSPM-Picoscan 2100, Molecular Imaging, USA). Small angle X-ray scattering (SAXS) analysis was done on a Bruker Nanostar machine equipped with a Cu rotating anode with a tungsten filament. The SAXS was operated at a voltage of 45 kV and current of 20 mA with  $\text{Cu K}\alpha$  radiation (wavelength =  $1.54 \text{ \AA}$ ). Detector calibration was done with silver behenate. Samples were sandwiched between Kapton films and pasted on a metallic holder. Scattering data were recorded from the multiwire gas filled Hi-star 2D area detector and were reduced to 1D using Bruker offline software. To understand the better identification of the peak shift in the membrane samples, the scattering vector ( $q$ ) scale was restricted to  $0.22 \text{ \AA}^{-1}$ .

### 2.4. IEC, water uptake and proton conductivity

Ion exchange capacity, water uptake and proton conductivity of aforesaid membranes were measured as per the procedure reported in our earlier studies [28,29]. IEC was also measured for sPOP (3 wt.%)sPEEK membrane at different time intervals till 130 h to rule out the change in IEC due to the leaching of sulfonic acid groups of sPOP. Ion exchange capacity of membranes was measured by acid–base titration method and the following equation was used to calculate the IEC values.

$$\text{IEC} = \frac{\text{Volume of NaOH} \times \text{Normality of NaOH}}{\text{Dry weight of the sample}} \text{ meq} \cdot \text{g}^{-1} \quad (1)$$

Water uptake of the membranes was determined after equilibrating the membrane sample in a sorption chamber filled with distilled water and by measuring the weight difference between the wet and dry membrane samples with the following equation.

$$\text{Water uptake} = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{wet}}} \times 100 \quad (2)$$

Proton conductivity of the membranes was measured at different temperatures ( $30^\circ\text{C}$  to  $70^\circ\text{C}$ ) under fully humidified condition using four-probe method. Subsequently activation energy for the membranes was also calculated by implementing the Arrhenius behaviour described in the literature [30,31].

### 2.5. Oxidative stability (Fenton's test)

Oxidative stability for the membranes was evaluated by Fenton's test. Fenton's solution (3 ppm) containing  $\text{Fe}^{+2}$  was prepared using 3 wt.% hydrogen peroxide and iron (II) chloride. The membrane samples were cut in equal size and dried to remove the absorbed moisture and weighed before dipping into Fenton's solution. The solution was heated to  $70^\circ\text{C}$  for 5 h and then the membrane samples were removed from the solution and washed with water and dried at  $60^\circ\text{C}$  before noting the final weight of the membrane sample. The difference between initial and final weight gives the weight loss due to the attack of hydroxyl and peroxy radicals during the Fenton's test [32].

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