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# Simultaneous tuning of methanol crossover and ionic conductivity of sPEEK membrane electrolyte by incorporation of PSSA functionalized MWCNTs: A comparative study in DMFCs

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## HIGHLIGHTS

- Surface modification of CNTs by incorporation of PSSA through covalent grafting.
- Dispersion of PSSA–CNTs in to sPEEK to form a composite membrane electrolyte.
- Methanol crossover and direct methanol fuel cell performance studies using sPEEK–PSSA–CNT composite membrane electrolyte.

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## ABSTRACT

A novel composite membrane for direct methanol fuel cells (DMFCs) have been prepared by incorporation of polystyrene sulfonic acid (PSSA) functionalized multi-walled carbon nanotubes (PSSA–MWCNTs) into sulfonated polyether ether ketone (sPEEK) matrix. The composite membranes were prepared with different weight percent of PSSA–MWCNTs by adopting solution casting procedure. Interaction of PSSA–CNTs with sPEEK was confirmed by different characterization techniques. Uniform dispersion of PSSA–CNTs in sPEEK improves the mechanical and thermal properties along with ionic conductivity in turn decreasing the methanol crossover through the membrane in comparison with pristine sPEEK membrane. Composite membranes of sPEEK–PSSA–CNTs showed higher DMFC performance in relation to pristine sPEEK and Nafion membranes.



## 1. Introduction

Polymer electrolyte fuel cells (PEFCs) are one of the promising environmental friendly chemical engineering technologies available in recent times owing to their capability of quick start up and low-temperature operation [1,2]. In comparison with different types of polymer electrolyte fuel cells, direct methanol fuel cells (DMFCs) are the green and alternative technology for the energy conversion, and are more advantageous than $H_2$ based fuel cells due to the storage and safety issues associated with hydrogen. Although small amount of $CO_2$ is emitted in DMFCs, there is no emission of hazardous gases like sulfur and nitrogen oxides. Further the fuel used in DMFCs is methanol which is water soluble and environmental friendly [3]. Due to these advantages, DMFCs have potential applications in many fields like portable, domestic and mobile appliances. However for the commercialization of DMFCs, one of the major impediments is the methanol crossover from anode to cathode which arises due to the diffusion behavior of the methanol through polymer electrolyte.

Polymer electrolyte membrane (PEM) plays a key role in DMFC by transferring protons from anode to cathode. Perflurosulfonic acid membranes like Nafion are the commercially available membranes widely used as PEM in DMFCs. Even though Nafion has good chemical stability and high ionic conductivity but its utilization for DMFC as PEM is hampered by elevated methanol crossover and high cost [4]. Several attempts have been made to improve DMFC performance by using other alternate arylene group of polymers like sulfonated polyether ether ketone (sPEEK) that can act as a viable option of PEM for DMFCs because of its good mechanical, thermal and chemical stabilities [5]. Further sPEEK is relatively cost-effective and its ionic conductivity could be easily controlled by the degree of sulfonation. Narrow and more branched pores of sPEEK showed less methanol permeability in DMFCs in comparison with Nafion [6]. However excessive swelling of sPEEK due to high degree of sulfonation may hamper its long term use in DMFCs [7].

Many attempts have also been made to prepare the polyblends of sPEEK. Notably, Han-Lang Wu et al. prepared sPEEK-poly

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(vinylpyrrolidine) blend membrane that could decrease the methanol crossover in DMFCs without affecting the ionic conductivity [8]. Incorporation of inorganic oxides ($SiO_2$, $ZrO_2$, and $TiO_2$, etc.), phosphates and heteropolyacids to sPEEK were the other methods to reduce the methanol crossover and increase the ionic conductivity in DMFCs [9–11]. Our earlier reports focused on the modification of sPEEK with methane sulfonic acid and zeolite 4A (sPEEK-MSA-zeolite 4A) to show the excellent improvement in ionic conductivity and decrease in methanol crossover in DMFCs through this polymer electrolyte. The elevation in ionic conductivity was due to the formation of MSA blend with sPEEK and the lower methanol crossover was due to the distinct molecular sieving effect of zeolite 4A [12]. Further to this, impact on sPEEK ionic channels through the addition of inert (no charge/hydrophobic) polyphosphazene were also studied to understand the methanol crossover behavior in DMFCs [13].

Carbon nanotubes (CNTs) have excellent thermal and mechanical properties with low density which is used as fillers in PEMs to improve the membrane properties [14]. However it is difficult to disperse pristine CNTs in a polymer matrix due to the Van der Waals interactions of the bare tubes. This situation can be overcome by modifying the surface of CNTs by carboxylation and sulfonation before dispersing in polymer matrix, hitherto used for variety of applications [15–19]. These factors can also be tackled by grafting of polystyrene sulfonic acid (PSSA) on to the surface of CNTs for improving the dispersion of CNTs and to induce ionic conductivity due to the unique presence of sulfonic acid groups in it [20–26].

Taking into consideration of all the above issues, the present study deals with the modification of CNTs with PSSA and dispersing it in the sPEEK matrix to imply as membrane electrolyte for DMFCs. In case of Nafion 117, the main drawback is the higher methanol permeability from anode to cathode through its ionic clusters. Whereas in case of sPEEK composite the pore size is relatively low which are more branched that results in lower methanol permeability in turn improving the overall DMFC performance as observed in our earlier studies [12]. Further sPEEK composite membranes are cost effective than Nafion 117. As far as fabrication of the membrane with sPEEK–CNTs is concerned, it is difficult to fabricate the membrane with pristine CNTs because of its poor dispersion. However due to the better dispersion of PSSA–CNTs in sPEEK, the fabrication becomes relatively easier. To the best of our knowledge no literature is available on sPEEK–PSSA–CNTs composite membrane electrolyte used for DMFC applications. The study proves that modification of CNTs with PSSA can have a tremendous impact on the dispersion of CNTs in sPEEK as well as to improve the overall ionic conductivity of the polymer electrolyte.

## 2. Experimental

### 2.1. Materials

Multi-walled carbon nanotubes (MWCNTs) with length 10–30 μm, outer diameter 30–50 nm were obtained from SRL chemicals India. Sulfonated polyether ether ketone (sPEEK, $M_w$ = 50,000 g $mol^{-1}$, $M_n$ = 14,000, with IEC of 1.4 meq $g^{-1}$ and Degree of sulfonation (DS) 54%) was procured from FuMA-Tech GmbH, Germany. Poly(sodium-p-styrene sulfonate) and dimethylacetamide (DMAc) were obtained from Acros organics India. Toray TGP-H-120 carbon paper was procured from Nikunj Exim Pvt. Ltd., India. Vulcan XC-72R carbon, Pt–Ru (60 wt.% in 1:1 atomic ratio) and Pt/C (40 wt.% Pt on Vulcan XC-72R carbon) were obtained from Alfa Aesar (Johnson Matthey, India) chemicals. All the chemicals were used as received.

### 2.2. Preparation of PSSA–CNTs

Surface oxidation of CNTs was carried out before attaching PSSA backbone on the surface of CNTs as reported in the literature [14]. In brief, pristine MWCNTs are sonicated with mixture of 1:1 HCl and $HNO_3$ (in volume ratio) for 30 min followed by heating at 80 °C for 2 h. CNTs were then filtered and washed with deionised water several times to remove any residual acid on the surface and dried under vacuum for 24 h. The obtained CNTs (300 mg) were mixed with poly(sodium-p-styrene sulfonate) (NaPSS) solution (3 wt.%) in a round bottom flask and stirred at 80 °C for 30 h. The reaction mixture was filtered and the product was washed repeatedly with deionised water until the pH becomes neutral and dried under vacuum for 24 h. Finally the obtained NaPSS–CNTs were treated with dilute HCl for the conversion of —$SO_3Na$ to —$SO_3H$ to form PSSA–CNTs.

### 2.3. Fabrication of sPEEK–PSSA–CNT membrane

Sulfonated polyether ether ketone (sPEEK) was dissolved in dimethyl acetamide (DMAc) to prepare 5 wt.% solution. Required weight percent (0.25, 0.5 and 1 wt.%) of PSSA–CNTs in relation to sPEEK were dispersed in DMAc and sonicated for 30 min. The PSSA–CNTs dispersion was added to sPEEK (5 wt.% in DMAc) and sonicated for 1 h followed by continues stirring for 24 h. The resultant solution was caste on a flat Plexiglas plate and dried under vacuum at 80 °C for 12 h. The dried membrane was then peeled off from the glass plate and dipped in 1 N $H_2SO_4$ for proton activation before subjecting it to further studies. The required weight percent of PSSA–CNTs is restricted to 1 wt.% due to the aggregation of particles in the sPEEK matrix at higher percentages. Similar aggregation at higher filler content is observed in the earlier reports on composite sPEEK matrices [12,27].

### 2.4. Characterization

#### 2.4.1. Characterization of PSSA–CNTs

To confirm the surface modification of CNTs by PSSA the following characterization techniques were performed. FT-IR spectra of NaPSS polymer and PSSA–CNTs were recorded using a Nicolet IR 860 Spectrometer (Thermo Nicolet Nexus-670). X-ray diffraction (XRD) measurements for pristine CNTs, NaPSS and PSSA–CNTs were performed using Bruker D8 Advanced X-ray diffractometer employing Cu Kα radiation of wavelength 1.54 Å. Energy dispersive X-Ray analysis (EDAX) studies for pristine CNTs and PSSA–CNTs were performed through JEOL JSM 35CF Scanning Electron Microscope to confirm the presence of PSSA in CNTs. Thermo-gravimetric analysis (TGA) of pristine CNTs and PSSA–CNTs were carried out by using a NETZSCH STA 449F3 TGA-DSC instrument in the temperature range between 30 °C and 900 °C at a heating rate of 5 °C $min^{-1}$ with nitrogen flushed at 60 ml $min^{-1}$. TEM images of pristine CNTs and PSSA–CNTs were recorded on a 200 kV Tecnai-20 G2 transmission electron microscope (TEM) at 50 nm and 100 nm scale to study the morphology of the samples.

#### 2.4.2. Physical characterization of the membrane

Surface and cross-sectional morphologies of pristine sPEEK and sPEEK–PSSA–CNTs composite membranes were recorded on JEOL JSM 35CF Scanning Electron Microscope (SEM). Mechanical properties of pristine sPEEK and its composites were measured on universal testing machine (UTM) (Model AGS-J, Shimadzu, Japan) with an operating head-load of 10 kN. Thermo-gravimetric analysis (TGA) of NaPSS polymer, pristine sPEEK and sPEEK–PSSA–CNTs composite membranes using the similar protocols mentioned above. Average contact angle and surface wetting energy of the membranes