

**UNIVERSITY GRANTS COMMISSION  
BAHADUR SHAH ZAFAR MARG  
NEW DELHI – 110 002**

**Final Report of the work done on the Major Research Project**

- 1. Title of the Research Project** : Development of polymer blends as proton-exchange membranes for Direct Methanol Fuel Cells (DMFCs) using charged surface modifying macromolecules (cSMM)
- 2. Name and address of the Principal Investigator** : **Dr. A. Nagendran**, Assistant Professor  
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Karaikudi – 630 003  
Sivaganga District, Tamilnadu
- 4. UGC approval letter No and Date** : F.No. 41-219/2012(SR), Dated 17.07.2012
- 5. Date of Implementation** : 01.07.2012
- 6. Tenure of the project** : 01.07.2012 to 31.12.2015  
(Extended by UGC from 30.06.2015 to 31.12.2015)
- 7. Total grant approved** :Rs. 12,93,300/-  
**Total grant allocated** :Rs. 12,66,461 (UGC letter dt. 23.06.2015)  
(FD Diary No. 266, dt. 30.04.2015)
- 8. Total grant received** : Rs. 11,85,845/-

**10. Title of the Research Project** : Development of polymer blends as proton-exchange membranes for Direct Methanol Fuel Cells (DMFCs) using charged surface modifying macromolecules (cSMM)

**11. Objectives of the project**

- Synthesis of charged surface modifying macromolecules (cSMM)
- Characterization of cSMM by FT-IR and NMR, DSC, CHNS analyzer
- Synthesis and characterization of sulfonated graphene oxide
- Synthesis and characterization of N-phthaloyl chitosan (NPHCs)
- Sulfonation of polymers like poly(1,4-phenylene ether ethersulfone) (PEES), poly(ether sulfone) (PES), poly(vinylidene fluoride-co-hexafluoropropylene) (PVdF-co-HFP) by concentrated sulfuric acid and chlorosulfonic acid
- Characterization of sulfonated polymers such as SPEES, SPES and sPVdF-co-HFP by FT-IR and NMR.
- Preparation of blend membranes of SPEES/cSMM, SPES/cSMM, sPVdF-co-HFP/cSMM, SPES/NPHCs
- Preparation of composite membrane based on SPEES/PEI, SPEES/PEI-SGO, SPEES/tungtosphoric acid-polypyrrole
- Characterization of blends and composite membranes in terms of water uptake, ion exchange capacity, thermal stability (TGA), state of water (DSC) and morphology (SEM & AFM).
- Characterization of hydrophilicity of the SPEES, SPEES/cSMM, sPVdF-co-HFP and sPVdF-co-HFP/cSMM blend membranes by contact angle measurements.
- Performance of blends and composite membranes in terms of proton conductivity (AC impedance), methanol permeability (Refractometer and cyclic volatmetry) and selectivity.

## 12. Whether objectives of the were achieved : YES

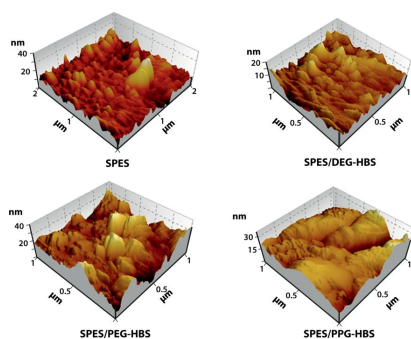
- cSMM based on different polyol and different end-capping agent was synthesized successfully using two-step solution polymerization method and characterized by FT-IR, NMR, DSC and CHNS analyzer.
- SGO and NPHCs were synthesized effectively and characterized
- Sulfonated PEES, PES and sPVdF-co-HFP were synthesized successfully using concentrated sulfuric acid and chlorosulfonic acid
- Sulfonated polymers were characterized by FT-IR and NMR
- Proton exchange membrane based on pure and blends of SPEES (15 wt%), SPES (20 wt%), sPVdF-co-HFP (10 wt%), SPEES/cSMM, SPES/cSMM, sPVdF-co-HFP/cSMM, SPEES/PEI, SPES/NPHCs, SPEES/PEI-SGO were prepared successfully.
- Characterization of blends and composite membranes were studied in terms of water uptake, ion exchange capacity, thermal stability (TGA), state of water (DSC) and morphology (SEM & AFM).
- Characterization of hydrophilicity of the SPEES, SPEES/cSMM, sPVdF-co-HFP and sPVdF-co-HFP/cSMM blend membranes were achieved by contact angle measurements.
- Performance of blends and composite membranes were studied in terms of proton conductivity (AC impedance), methanol permeability (Refractometer and cyclic voltammetry) and selectivity.

## 13. Achievements from the project

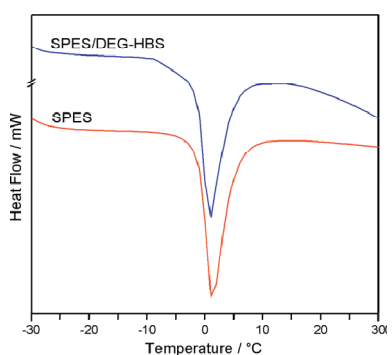
Proton exchange membranes from the blends of (i) SPES/cSMM, (ii) sPVdF-co-HFP/cSMM, (iii) SPEES/cSMM, (iv) SPEES/PEI, (v) SPES/ NPHCs, (vi) SPEES/TPA-Ppy and (vii) SPEES/PEI-SGO, were prepared and characterized successfully for fuel cell applications.

(i) **SPES/cSMM blend membranes**

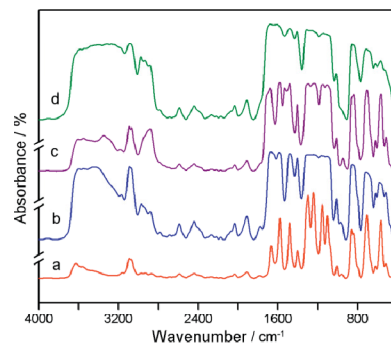
The pristine SPES and modified SPES membranes were prepared by blending with different charged surface modifying macromolecules (cSMMs) namely, SPES/DEG-HBS, SPES/PEG-HBS and SPES/PPG-HBS. The blend membranes showed an increase in hydrophilicity, water uptake, and proton conductivity compared to the pristine SPES membranes. The highest values of water uptake and proton conductivity were obtained for the SPES/PPG-HBS blend membrane. Morphological studies revealed that the nodule size and surface roughness also influenced the water uptake, apart from the additional  $-\text{SO}_3\text{H}$  group. Among the modified membranes, the SPES/DEG-HBS blend membrane exhibited a lower methanol permeability value of  $8.895 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$  than the corresponding SPES membrane. The other two cSMM blend membranes showed higher methanol permeability values than SPES but still a smaller value than Nafion 117. The highest relative selectivity was obtained with the SPES/DEG-HBS blend membrane. These results showed that the SPES/cSMM blend membranes have promise for possible use as a proton exchange membrane in DMFC applications.



AFM images of SPES/cSMM



DSC melting curves of SPES/cSMM



FT-IR spectra of SPES/cSMM

### Characterization of SPES/cSMM blend membranes

Membrane	IEC, (meq g <sup>-1</sup> )	Water uptake, %	Proton conductivity, S/cm	Methanol permeability, cm <sup>2</sup> s <sup>-1</sup>	Relative selectivity, ×10 <sup>4</sup> S s cm <sup>-3</sup>	Tensile strength (MPa)
SPES	1.31	28	3.15 × 10 <sup>-3</sup>	11.19 × 10 <sup>-8</sup>	2.80	39.8
SPES/DEG-HBS	1.39	35	5.60 × 10 <sup>-3</sup>	8.89 × 10 <sup>-8</sup>	6.20	35.4
SPES/PEG-HBS	1.45	41	7.86 × 10 <sup>-3</sup>	22.50 × 10 <sup>-8</sup>	3.40	34.5
SPES/PPG-HBS	1.40	46	9.60 × 10 <sup>-3</sup>	2.78 × 10 <sup>-7</sup>	3.45	30.3

### Membrane roughness parameter

Membrane	Roughness parameters		
	R <sub>m</sub> (nm)	R <sub>q</sub> (nm)	R <sub>z</sub> (nm)
SPES	0.83	1.13	6.27
SPES/DEG-HBS	1.32	1.72	7.03
SPES/PEG-HBS	1.51	1.95	9.33
SPES/PPG-HBS	3.9	5.86	28.7

R<sub>m</sub>- the mean roughness, R<sub>q</sub>- the root mean square of Z data, and R<sub>z</sub>- mean height of roughness profile.

#### (ii) sPVdF-co-HFP/cSMM blend membranes

Surface modified blend membranes based on sPVdF-co-HFP with four different cSMMs for DMFC application was prepared. In this investigation four different polyols (diethylene glycol, polyethylene glycol 200, polyethylene glycol 400, polypropylene glycol 425) were used to prepare cSMMs. Properties of the blend membranes were depend on the polyols used for the cSMM preparation. Water uptake, IEC, proton conductivity and membrane selectivity of the surface modified membranes were higher than the pristine sPVdF-co-HFP membrane. The surface contact angle measurement was employed to assess the surface migration of cSMM. The AFM images showed that the surface of cSMM modified and unmodified membranes are not smooth and possess a nodule like structure and nodule aggregates. The roughness parameter and

the nodule size were increased in the same order to water uptake. The ionic conductivities of the prepared membranes are in the order of  $10^{-3} \text{ Scm}^{-1}$ . The proton conductivity was found to be dependent upon the water uptake of the membranes. Among the cSMM modified membranes, the sPVdF-co-HFP/DEG-HBS blend membrane shows lower methanol permeability ( $2.04 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ ) whereas the sPVdF-co-HFP/PPG-HBS blend membrane displayed the highest proton conductivity ( $4.99 \times 10^{-3} \text{ S cm}^{-1}$ ). DSC measurement confirmed the highest bound water content in sPVdF-co-HFP/DEG-HBS membrane, which resulted lower methanol permeability. Addition of four different cSMMs into the sPVdF-co-HFP matrix reduced the rigidity of polymer backbone, which lowers the tensile strength of the blend membrane. Furthermore, the sPVdF-co-HFP/PEG200-HBS membrane has the highest membrane selectivity value of  $21.8 \times 10^3 \text{ Scm}^{-3}\text{s}$ , which is an order of magnitude higher than Nafion 117.

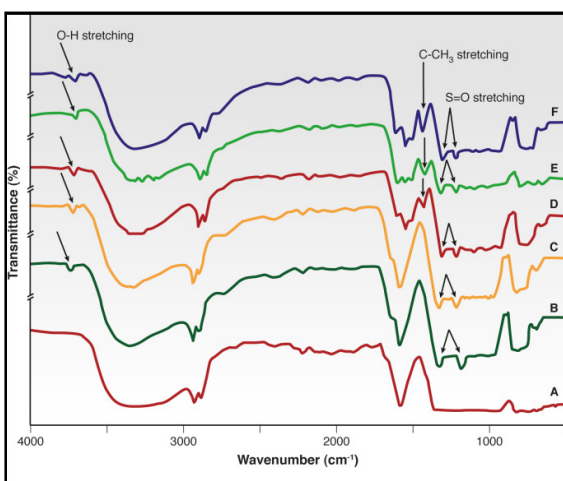
#### Properties of sPVdF-co-HFP/cSMM blend membranes

Membrane	IEC, Meq/g	Water uptake, %	Ratio, %		$\Delta H_f$ , J/g	Tensile strength, MPa	Contact angle, °	
			Free water/ Total water	Bound water/ Total water			Top surface	Bottom surface
sPVdF-co-HFP	0.35	15.2	55.3	44.7	28.16	19.58	66.5	66.9
sPVdF-co-HFP/cSMM-1	0.38	16.3	48.5	51.5	26.31	17.21	61.2	65.4
sPVdF-co-HFP/cSMM-2	0.44	18.4	59.8	40.2	36.76	16.65	62.6	64.9
sPVdF-co-HFP/cSMM-3	0.41	18.9	62.4	37.6	39.38	16.41	63.2	64.4
sPVdF-co-HFP/cSMM-4	0.37	20.4	64.2	35.8	43.6	15.63	64.2	64.9

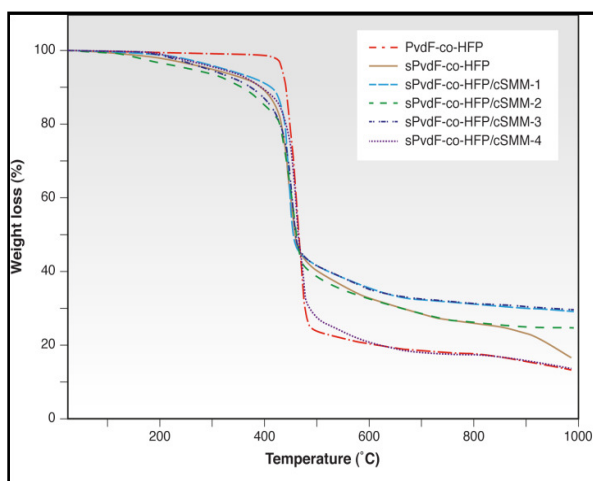
## Proton conductivity, methanol permeability, relative selectivity and roughness parameters of blend membranes

Samples	Proton conductivity $\times 10^{-3} \text{ S cm}^{-1}$	Methanol permeability $\times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$	Relative selectivity $\times 10^3 \text{ S cm}^{-3} \text{ s}$	Roughness parameter		
				$R_m(\text{nm})$	$R_q(\text{nm})$	$R_z(\text{nm})$
sPVdF-co-HFP	2.36	2.21	10.67	1.16	1.04	5.25
sPVdF-co-HFP/cSMM-1	3.49	2.04	17.1	1.73	2.24	10.3
sPVdF-co-HFP/cSMM-2	4.89	2.24	21.83	2.05	2.75	13.3
sPVdF-co-HFP/cSMM-3	4.94	2.65	18.64	2.19	2.80	13.6
sPVdF-co-HFP/cSMM-4	4.99	3.19	15.64	3.6	5.09	26.6

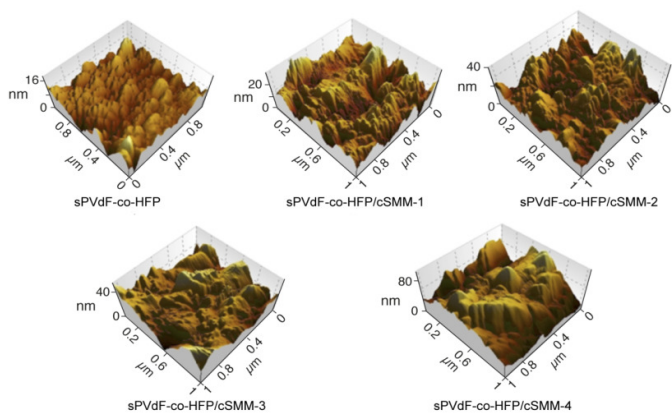
$R_m$ - the mean roughness,  $R_q$ - the root mean square of Z data, and  $R_z$ - mean height of roughness profile.



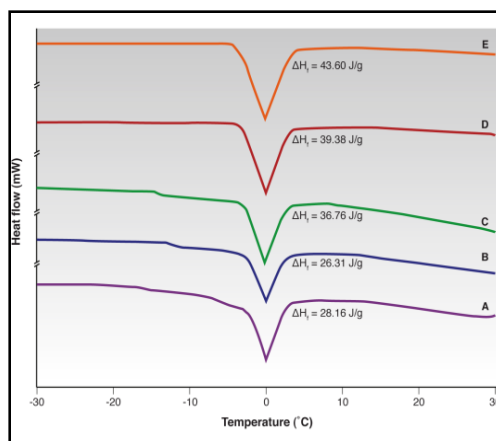
FT-IR spectra of blend membranes



TGA curves of blend membranes



AFM images of blend membranes



DSC melting curves of blend membranes

**(iii) SPEES/cSMM blend membranes**

Blend membranes comprising sulfonated poly (phenylene ether ethersulfone) (SPEES) - charged surface modifying macromolecules (cSMMs) were fabricated as an alternative proton exchange membrane (PEM) for H<sub>2</sub>/O<sub>2</sub> fuel cell applications. Prepared membranes were characterized by determining the ion exchange capacity, water uptake, proton conductivity, oxidative stability and dimensional stability. The water uptake of SPEES/cSMM blended membrane was found to be higher than that of the pristine SPEES and the Nafion 117 membranes. Proton conductivity of the blend membranes is in the range of 10<sup>-3</sup> to 10<sup>-2</sup> Scm<sup>-1</sup>. The conductivity of the prepared membranes increases with temperature, in particular, poly (propylene glycol) – hydroxy benzene sulfonate (PPG-HBS) blended SPEES membrane shows rise in conductivities from 1.61 × 10<sup>-2</sup> Scm<sup>-1</sup> (25 °C) to 5.22 × 10<sup>-2</sup> Scm<sup>-1</sup> (80 °C). Surface morphology of the membranes was investigated by tapping mode atomic force microscopy (AFM), which indicates that the nodule size and surface roughness are increased by the incorporation of cSMM into the SPEES matrix. Surface modified blend membranes exhibited excellent thermal stability and acceptable dimension stability in 80 °C, which implies that the SPEES/cSMM blended membranes are promising materials for PEMFC application.

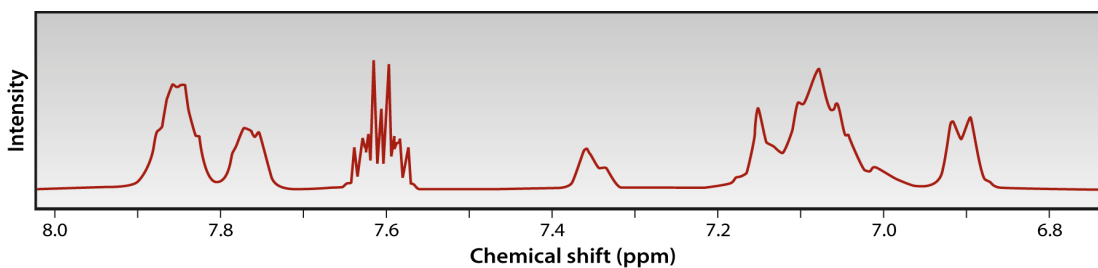
**Sulfur content, thermal and molecular weight characterizations data of cSMM**

cSMM	S, wt%	T <sub>g</sub> (°C) at onset	T <sub>g</sub> (°C) at midpoint	M <sub>w</sub> (Daltons)	PDI
PPG-HBS	0.954	-18.3	-11.6	5.34 × 10 <sup>4</sup>	2.18
PPG-HPS	0.892	20.5	28.9	4.82 × 10 <sup>4</sup>	1.97

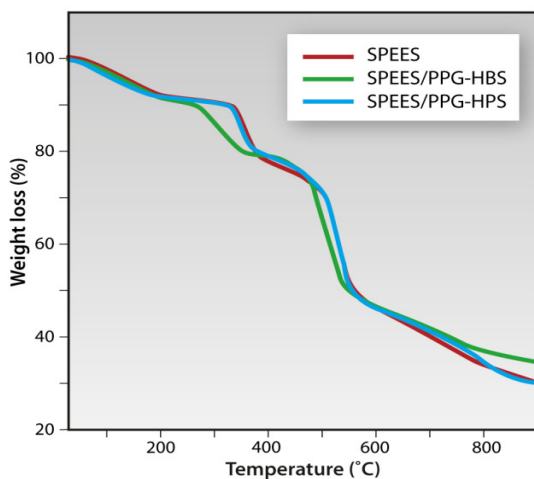


## Properties of SPEES/cSMM blend membranes

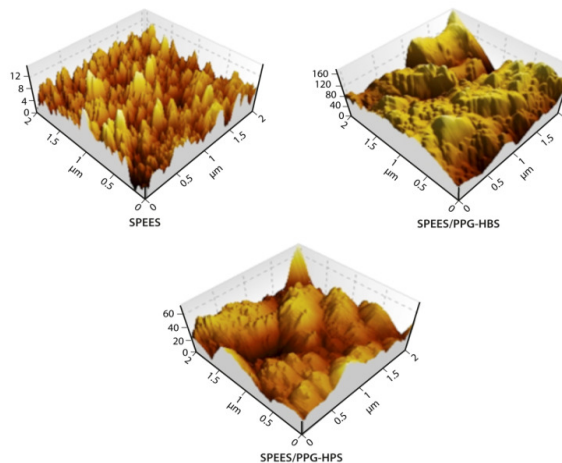
Membrane	WU, %	IEC, meq/g	$\lambda$ Value	Contact angle, °	Oxidative stability, min	Proton conductivity, S/cm	
						25 °C	80 °C
SPEES	42.65	1.32	17.9	78.8±1.9	280	$6.70 \times 10^{-3}$	$1.43 \times 10^{-2}$
SPEES/PPG-HBS	66.11	1.39	26.4	75.2±2.3	264	$1.61 \times 10^{-2}$	$5.22 \times 10^{-2}$
SPEES/PPG-HPS	61.47	1.36	25.1	73.1±2.1	269	$9.59 \times 10^{-3}$	$4.37 \times 10^{-2}$



<sup>1</sup>H NMR spectra of SPEES



TGA curves of blend membranes



TGA and AFM images of blend membranes

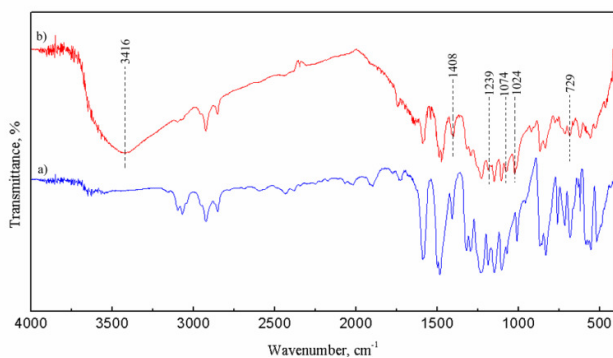
## Membrane roughness parameter

Membrane	Roughness parameter		
	R <sub>m</sub> (nm)	R <sub>q</sub> (nm)	R <sub>z</sub> (nm)
SPEES	1.73	2.28	11.0
SPEES/PPG-HBS	6.39	7.95	30.8
SPEES/PPG-HPS	3.61	4.15	15.4

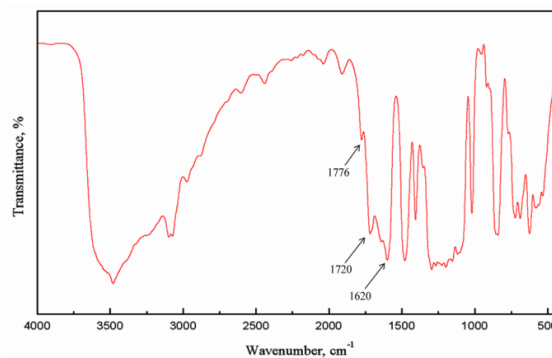
R<sub>m</sub>- the mean roughness, R<sub>q</sub>- the root mean square of Z data, and R<sub>z</sub>- mean height of roughness profile.

(iv) **SPEES/PEI blend membranes**

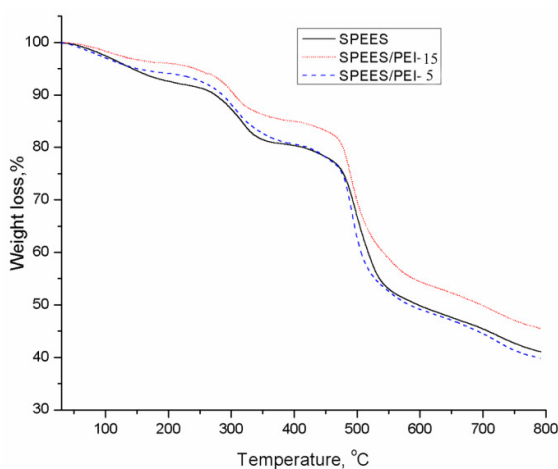
Polymer blend membranes based on SPEES membrane with varying concentrations of poly(ether imide) (PEI) were prepared. The sulfonation of PEES was carried out with concentrated sulfuric acid at 10 °C, and the sulfonation degree was maintained as 70 %. The hydrogen bond formation between the imide group of PEI and sulfonic acid group of SPEES was confirmed by the FT-IR. Increasing the PEI content on SPEES matrix effectively suppressed the water uptake, IEC and swelling ratio of the blend membranes. The blend membranes are thermally stable than virgin SPEES membrane, and stable in nitrogen up to 250 °C, which is sufficiently high for common fuel cell application. The oxidative stability, mechanical strength and methanol resistance power of the blend membranes were increased with increasing the PEI content. SEM study revealed that the PEI was well mixed with SPEES matrix and exhibited flat and smoother surface without obvious agglomeration. Although the blend membranes exhibited low proton conductivity in comparison to pristine SPEES, the presence of PEI led to an improvement in chemical stability of the membranes. The methanol permeability of the composite membranes gradually decreases from  $4.23 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$  to  $8.84 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ , which is lower than that of the Nafion117 membrane. The relative selectivity of the 15 % of PEI-incorporated SPEES membranes ( $1.63 \times 10^4 \text{ S cm}^{-3} \text{ s}$ ) was higher than that of the Nafion membranes ( $0.997 \times 10^4 \text{ S cm}^{-3} \text{ s}$ ). From the observed results, the prepared SPEES/PEI-15 blend membrane can be considered as apposite polymer electrolyte membranes for the application of direct methanol fuel cells (DMFCs).



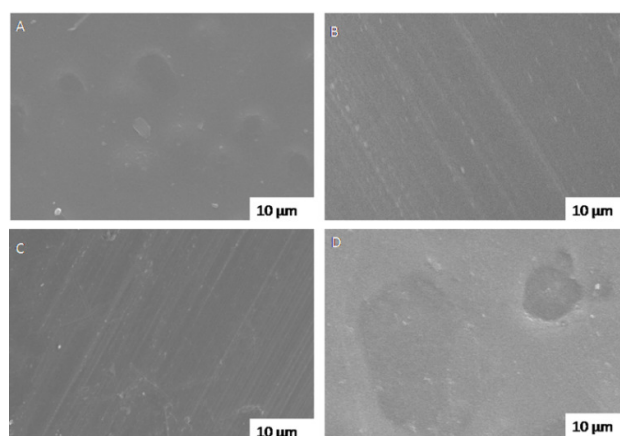
FT-IR spectra (a) PEES, (b) SPEES polymers



FT-IR spectra of SPEES/PEI-15 blend membrane



TGA curves of SPEES/PEI blend membranes



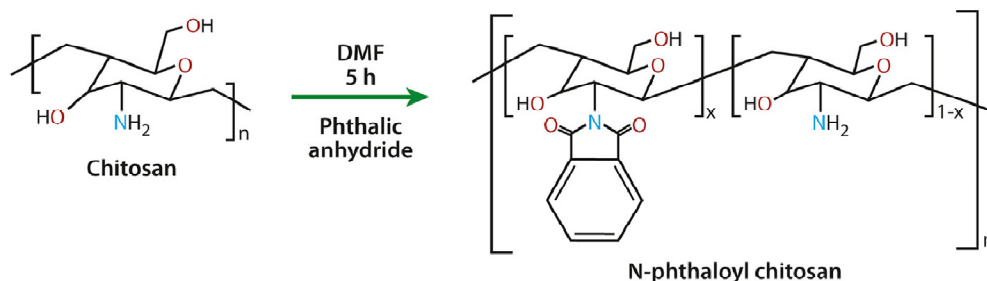
SEM images of SPEES/PEI composite membranes, (A) SPEES, (B) SPEES/PEI-5, (C) SPEES/PEI-15 and (D) SPEES/PEI-25

### Properties of SPEES/PEI blend membranes

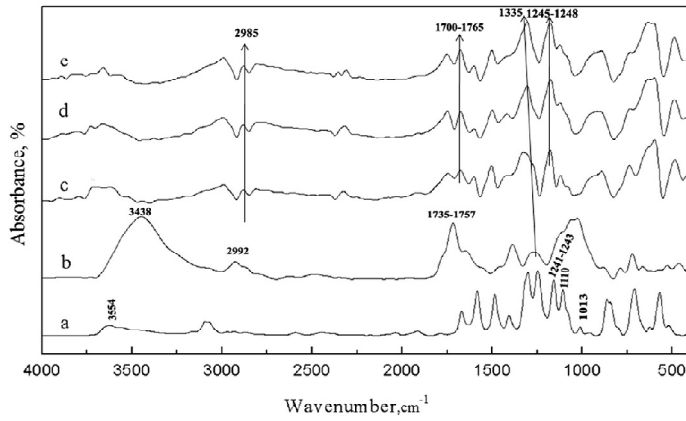
Membrane	IEC, meq.g <sup>-1</sup>	Water uptake, %	Oxidative stability		$\lambda$ Value	Proton conductivity, S cm <sup>-1</sup>	Methanol permeability, cm <sup>2</sup> s <sup>-1</sup>
			Rupture time in min	Retained weight (%)			
SPEES	1.46	46.04	254	91.8	17.5	$1.07 \times 10^{-2}$	$4.23 \times 10^{-7}$
SPEES/PEI-5	1.39	41.31	266	93.6	16.5	$9.78 \times 10^{-3}$	$3.87 \times 10^{-7}$
SPEES/PEI-10	1.33	37.87	289	95.9	15.8	$7.37 \times 10^{-3}$	$3.55 \times 10^{-7}$
SPEES/PEI-15	1.28	33.04	304	98.6	14.3	$5.32 \times 10^{-3}$	$3.26 \times 10^{-7}$
SPEES/PEI-20	1.20	27.24	324	100	12.6	$2.56 \times 10^{-3}$	$2.67 \times 10^{-7}$
SPEES/PEI-25	1.09	23.19	349	100	11.8	$1.85 \times 10^{-3}$	$1.51 \times 10^{-7}$
SPEES/PEI-30	0.92	19.38	375	100	11.7	$8.76 \times 10^{-4}$	$8.84 \times 10^{-8}$
Nafion 117	0.91	18.16	-	-	11.1	$3.40 \times 10^{-2}$	$3.41 \times 10^{-6}$

(v) **SPES/NPHCs blend membranes**

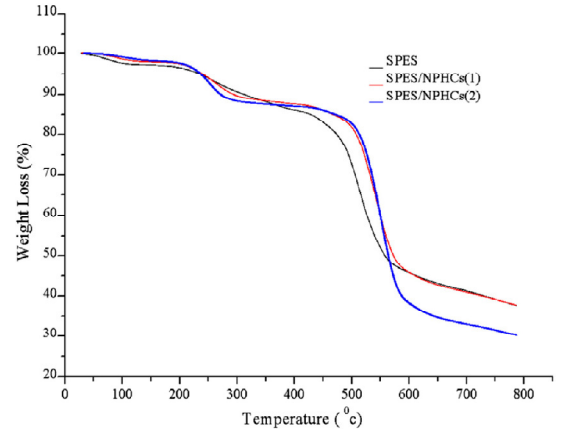
Chitosan is modified by phthaloylation using an excess of phthalic anhydride at 130 °C and blended with the sulfonated polyethersulfone (SPES) to produce blend membranes. In particular the introduction of the phthaloyl group into the chitosan matrix increases its solubility in organic solvent, film formability, flexibility, low methanol permeability and with suitable ion conductivity. The proton conductivity of blend membranes improved with increasing NPHCs content in SPES matrix due to high hydrophilicity provided by NPHCs which facilitates proton mobility. Maximum proton conductivity ( $9.2 \times 10^{-3} \text{ Scm}^{-1}$ ) with blend membranes is attained at an intermediate loading of NPHCs content, where NPHCs improves water retention characteristic of the membrane without affecting the continuity of the proton conduction path in SPES matrix. The thermograms display the good thermal stabilities of blend membranes than Nafion-117. The methanol crossover of blend membranes could be effectively reduced by excess of NPHCs content at the expense of their ion exchange capacity and proton conductivity. All the membranes fabricated in our study, exhibit better relative selectivity than Nafion-117 membrane and hence it could be identified as a suitable candidate for polymer electrolyte membrane in a fuel cell as well as DMFC environments.



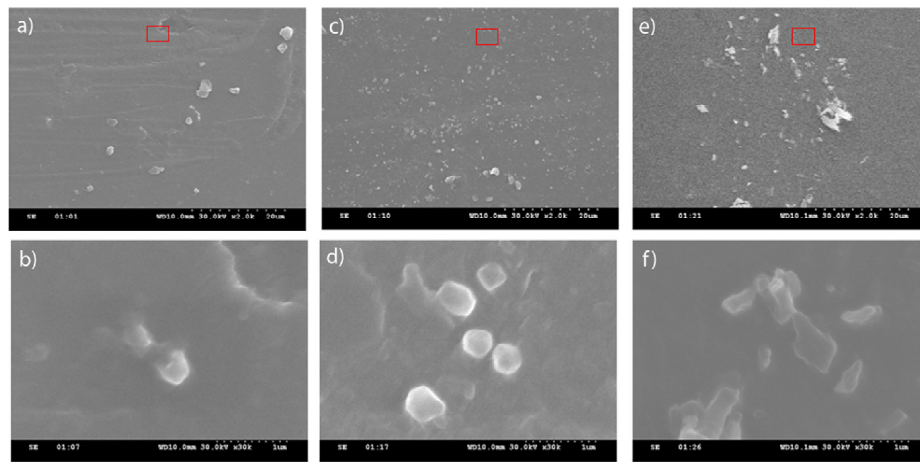
Synthetic route for the preparation of NPHCs



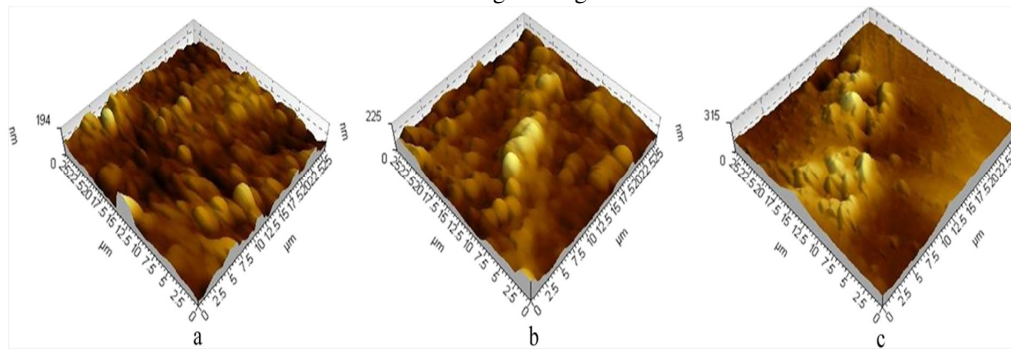
FTIR spectra for: a) SPES, b) NPHCs, c) SPES/NPHCs (0.5), d) SPES/NPHCs (1) and e) SPES/NPHCs (2) membranes



TGA curves of SPES/NPHCs blend membranes



SEM images for a) SPES/NPHCs (0.5), c) SPES/NPHCs (1), e) SPES/NPHCs (2) and b, d, f) SEM images of blend membranes at higher magnification



AFM images for a) SPES/NPHCs (0.5), b) SPES/NPHCs (1), and c) SPES/NPHCs (2) blend membranes

### Properties of SPES/NPHCs blend membranes

Membrane	IEC (meq/g)	Water uptake, %	Proton conductivity, $\times 10^{-3} \text{ S cm}^{-1}$		Methanol Permeability, ( $\times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ )	Relative selectivity, ( $\times 10^4 \text{ S cm}^{-3} \text{ s}$ )
			25 °C	80 °C		
SPES	1.31	28	3.15	5.8	11.18	2.8
SPES/NPHCs (0.5)	1.3	35	6.8	8.3	14.69	4.6
SPES/NPHCs (1)	1.29	38	9.2	12.1	17.1	5.3
SPES/NPHCs (2)	1.26	42	4.8	7.7	6.21	7.7

### Membrane roughness parameter

Membrane	Roughness parameter		
	$R_m$ (nm)	$R_q$ (nm)	$R_z$ (nm)
SPES/NPHCs (0.5)	8.2	10.1	46.3
SPES/NPHCs (1)	11.7	16.0	65.2
SPES/NPHCs (2)	15.6	18.0	77.7

$R_m$ - the mean roughness,  $R_q$ - the root mean square of Z data, and  $R_z$ - mean height of roughness profile.

#### (vi) SPEES/TPA-Ppy hybrid membranes

Hybrid membranes were fabricated using SPEES with 30 wt% of tungstophosphoric acid (TPA) followed by surface modification with polypyrrole (Ppy) layer. The formation of Ppy layer on SPEES/TPA membrane surface was confirmed by the elemental analysis. Ppy was used to preserve the TPA inside the SPEES matrix. Incorporation of TPA significantly increased the proton conductivity of the SPEES membrane. Ppy coating on the membrane surface suppress the decomposition of polymer chain, which enhanced the thermal stability of the hybrid membranes. As the number of Ppy layer increases in the membrane surface, it becomes harder for free radicals to attack the polymer chain. Surface modification of SPEES/TPA membrane with Ppy

reduced the methanol permeability and increased the mechanical strength. The methanol permeability of SPEES/TPA-Ppy4 hybrid membrane was found to be  $2.1 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ , which is 2.35 times lower than pristine SPEES membrane. The SPEES/TPA-Ppy4 membrane exhibits highest relative selectivity ( $2.86 \times 10^4 \text{ S cm}^{-3} \text{ s}$ ) than the other membrane with low TPA leaching. Surface morphological study revealed that the Ppy coated membrane had smooth surfaces with reduced surface roughness parameters. The interaction between Ppy with SPEES and TPA makes the membrane surface more compact. The water stability test of the hybrid membranes revealed that the weight loss of TPA was reduced gradually with the increasing the Ppy layer. The SPEES/TPA-Ppy5 membrane loses only 1% of its weight indicates TPA particles immobilized in SPEES matrix. Even though, SPEES/TPA-Ppy4 hybrid membrane showed slightly lower proton conductivity than pristine SPEES, displayed higher membrane selectivity than pristine SPEES and Nafion 117 membrane.

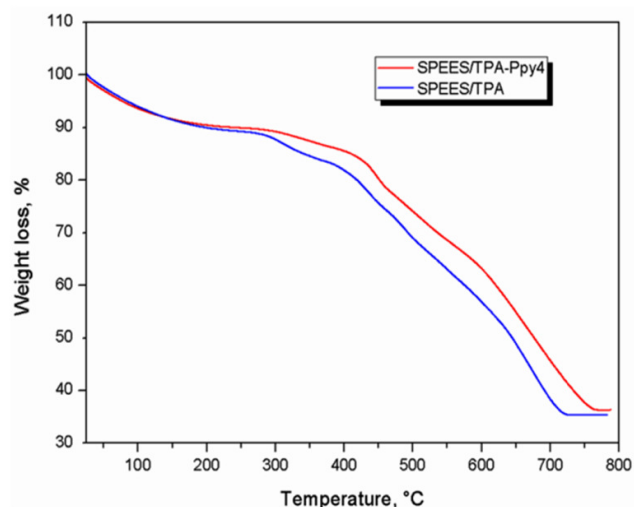
#### C, H and N content of SPEES/TPA-Ppy(n) hybrid membranes

Membrane	C. wt%	H. wt%	N. wt%
SPEES	53.08	4.164	-
SPEES/TPA-Ppy1	40.62	3.191	0.699
SPEES/TPA- Ppy3	37.24	3.008	0.977
SPEES/TPA- Ppy5	34.78	2.870	1.139

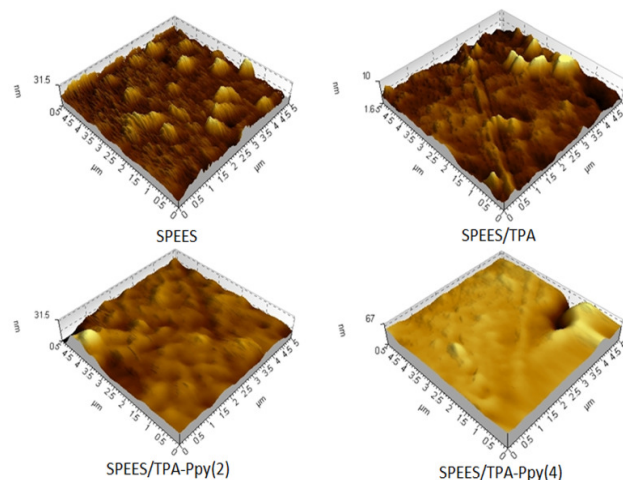
#### Roughness parameters and tensile strength of the SPEES/TPA-Ppy(n) membranes

Membrane	R <sub>m</sub> (nm)	R <sub>q</sub> (nm)	R <sub>z</sub> (nm)	Tensile strength, MPa
SPEES	4.93	5.46	19.2	30.2
SPEES/TPA	3.99	5.7	31.1	26.7
SPEES/TPA-Ppy2	1.87	2.24	8.03	28.9
SPEES/TPA-Ppy4	1.39	1.6	5.57	32.4

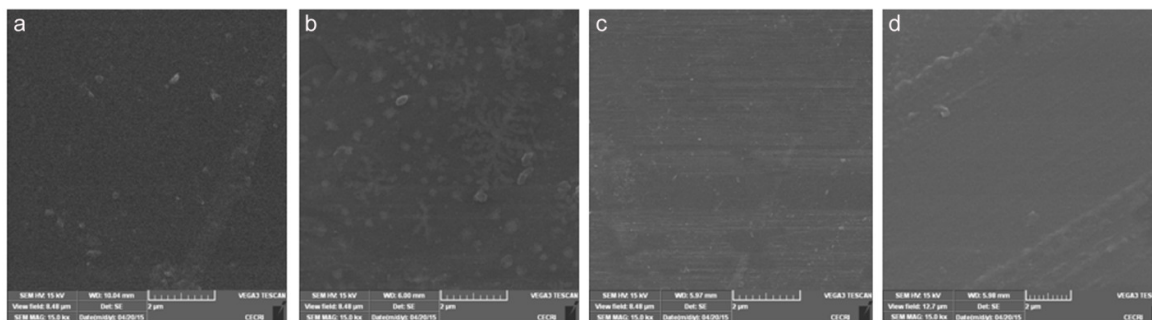
R<sub>m</sub>- the mean roughness, R<sub>q</sub>- the root mean square of Z data, and R<sub>z</sub>- mean height of roughness profile.



TGA curves of SPEES/TPA-Ppy hybrid membranes



AFM images of SPEES/TPA-Ppy hybrid membranes



SEM images of SPEES/TPA-Ppy hybrid membranes, (A) SPEES, (B) SPEES/TPA, (C) SPEES/TPA-Ppy2 and (D) SPEES/TPA-Ppy4

### Properties of the SPEES/TPA-Ppy(n) hybrid membranes

Membrane	IEC, meq/g	Lambda value	Proton conductivity S/cm	Methanol permeability, $\text{Cm}^2 \text{s}^{-1}$	Relative selectivity, $\text{S cm}^{-3} \text{s}$	Weight loss of TPA, %
SPEES	1.32	17.9	$6.7 \times 10^{-3}$	$4.0 \times 10^{-7}$	$1.66 \times 10^4$	-
SPEES/TPA	1.36	20.5	$1.1 \times 10^{-2}$	$4.2 \times 10^{-7}$	$2.51 \times 10^4$	95.2
SPEES/TPA-Ppy1	1.31	19.8	$8.1 \times 10^{-3}$	$3.8 \times 10^{-7}$	$2.13 \times 10^4$	82.4
SPEES/TPA-Ppy2	1.26	19.1	$7.4 \times 10^{-3}$	$3.1 \times 10^{-7}$	$2.39 \times 10^4$	61.6
SPEES/TPA-Ppy3	1.18	18.8	$6.7 \times 10^{-3}$	$2.6 \times 10^{-7}$	$2.58 \times 10^4$	33.9
SPEES/TPA-Ppy4	1.14	18	$6.0 \times 10^{-3}$	$2.1 \times 10^{-7}$	$2.86 \times 10^4$	7.3
SPEES/TPA-Ppy5	1.08	17.9	$4.7 \times 10^{-3}$	$1.7 \times 10^{-7}$	$2.76 \times 10^4$	1.1

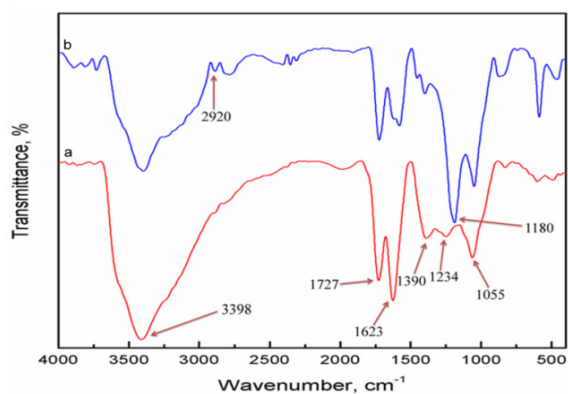


(vii) **SPEES/PEI-SGO composite membrane**

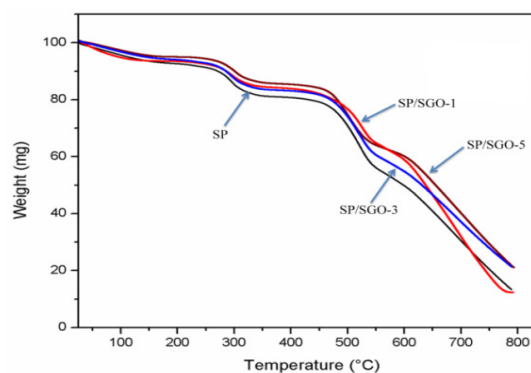
SPEES/PEI-SGO-X composite membranes were prepared by solution casting method. The water uptake and IEC of the composite membranes were increases with increasing SGO content. AFM study showed that the addition of SGO in to the SP (SPEES/PEI) matrix increases the surface roughness of the membranes. The introduction of SGO (contains hydroxyl and epoxy groups) into the membrane matrix helps to form hydrogen bond and thus increase the proton conductivity. Tensile strength and proton conductivity of the composite membranes increased with increasing SGO content. The maximum conductivity of  $8.87 \times 10^{-3} \text{ S cm}^{-1}$  was achieved at 25 °C upon addition of 0.8 wt% of SGO. All the SP/SGO membranes exhibited methanol permeability lower than  $3.26 \times 10^{-7} \text{ cm/s}$ , which was much lower than that of Nafion 117 ( $3.41 \times 10^{-6} \text{ cm}^2 \text{ S}^{-1}$ ). Furthermore, the composite membranes exhibited much higher relative selectivity compared with SP and Nafion 117 membranes. It was found that the SP/SGO-0.8 composite membrane appears to be a good candidate for using in DMFC application.

**Surface roughness and tensile strength of SP and SP/SGO-X composite membranes**

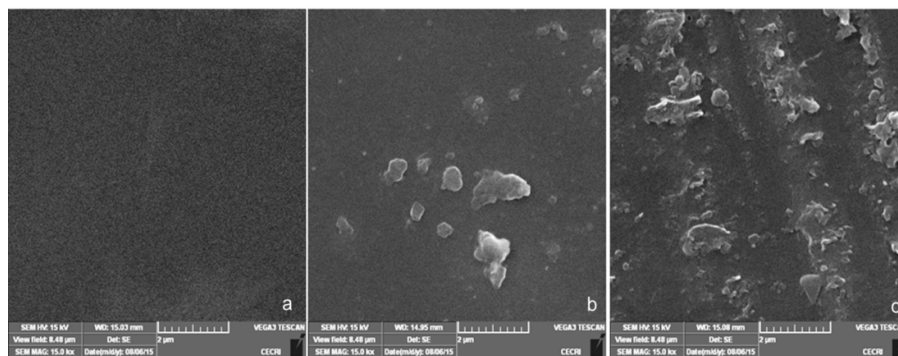
Membrane	R <sub>m</sub> (nm)	R <sub>q</sub> (nm)	R <sub>z</sub> (nm)	Tensile strength, MPa
SP	4.66	5.35	20.1	31.3
SP/SGO-0.2	1.15	1.44	7.33	32.4
SP/SGO-0.8	1.29	1.58	7.71	36.5



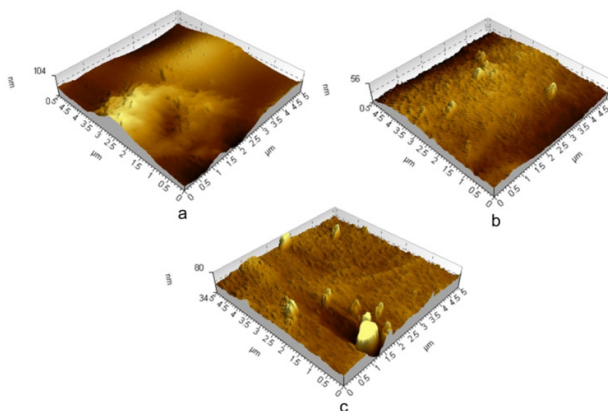
FT-IR spectra of a) GO, b) SGO



TGA curves of SP/SGO composite membranes



SEM images of SP and SP/SGO-X membranes (a) SP, (b) SP/SGO-0.2 and (c) SP/SGO-0.8



AFM images of SP and SP/SGO membranes, (a) SP, (b) SP/SGO-0.2 and (c) SP/SGO-0.8

### Properties of SP/SGO-X composite membranes

Membrane	IEC (meq/g)	Water uptake, %	Proton conductivity, $\times 10^{-3} \text{ S cm}^{-1}$	Methanol Permeability, ( $\times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ )	Relative selectivity, ( $\times 10^4 \text{ S s/cm}^3$ )
SP	1.28	33.0	$5.32 \times 10^{-3}$	$3.26 \times 10^{-7}$	$1.63 \times 10^4$
SP/SGO-0.1	1.30	34.2	$5.86 \times 10^{-3}$	$3.19 \times 10^{-7}$	$1.83 \times 10^4$
SP/SGO-0.2	1.33	36.7	$6.41 \times 10^{-3}$	$3.05 \times 10^{-7}$	$2.10 \times 10^4$
SP/SGO-0.5	1.39	40.3	$7.02 \times 10^{-3}$	$2.89 \times 10^{-7}$	$2.43 \times 10^4$
SP/SGO-0.8	1.45	44.8	$8.47 \times 10^{-3}$	$2.96 \times 10^{-7}$	$2.86 \times 10^4$

## 14. Summary of the findings

### (i) SPES/cSMM blend membranes

Proton exchange membranes based on SPES were successfully prepared in the presence and absence of different cSMMs (SPES/DEG-HBS, SPES/PEG-HBS, and SPES/PPG-HBS). FTIR spectra confirmed the presence of cSMMs in the blended membranes by the characteristic peaks of the cSMMs. Blending different cSMMs into the SPES membrane affects membrane properties such as ion-exchange capacity, water uptake, surface morphology, proton conductivity, and methanol permeability. The SPES-PPG-HBS blend membrane showed the best results in terms of membrane selectivity defined by proton conductivity/methanol permeability, which is a relevant parameter for DMFC.

### (ii) sPVdF-co-HFP/cSMM blend membranes

The sPVdF-co-HFP with degree of sulfonation 2.48% and four different types of cSMMs [MDI-DEG-HBS (cSMM-1), MDI-PEG200-HBS (cSMM-2), MDI-PEG400-HBS (cSMM-3) and MDI-PPG425-HBS (cSMM-4)] were prepared effectively. sPVdF-co-HFP/cSMM blend membranes were prepared and characterized successfully for DMFC application. The blend membranes showed good oxidative stability. The ionic conductivities of the prepared membranes are in the order of  $10^{-3} \text{ S cm}^{-1}$ . The proton conductivity was found to be dependent upon the water uptake of the membranes. Among the modified membranes, the sPVdF-co-HFP/DEG-HBS ( $2 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ ) blend membrane shows lower methanol permeability whereas the sPVdF-co-HFP/PPG425-HBS ( $5 \times 10^{-3} \text{ S cm}^{-1}$ ) blend membrane indicates the highest proton conductivity. However, the sPVdF-co-HFP/PEG200-HBS ( $21.8 \times 10^3 \text{ S cm}^{-3} \text{ s}$ ) blend membrane exhibits the highest overall membrane characteristic value. The surface modified membranes clearly demonstrate prosperous properties with respect to the ratio of proton conductivity and methanol permeability in comparison with unmodified sPVdF-co-HFP and Nafion 117 for DMFC application.

### **(iii) SPEES/cSMM blend membranes**

SPEES with DS 65% was found to be suitable to fabricate the PEM. The SPEES membrane surface was successfully modified with two different cSMMs. The hydrophilicity of the membranes increased after the incorporation of two different cSMMs. PPG-HBS incorporated SPEES membrane displayed the maximum conductivity of  $5.22 \times 10^{-2}$  S/cm at 80 °C. The oxidative stability of the blend membranes was slightly reduced than SPEES membrane. AFM study revealed that the SPEES/cSMM blend membranes had higher surface roughness and nodular size than that of pristine SPEES membrane. The increasing surface roughness and nodular size influenced the proton conductivity and water uptake of the membranes. Addition of cSMM changed the ionic channels became more interconnected with each other due to absorption of high amount of water in the polymer matrix. This study demonstrates that the blend membranes consisting of cSMM is an effective strategy to enhance the proton conductivity in PEMFC.

### **(iv) SPEES/PEI blend membranes**

SPEES with degree of sulfonation 70% was found to be effective instead of 65%, which was due to the blending with base polymer (PEI) reduces the ionic conductivity. The introduction of PEI into the hydrophilic SPEES matrix provided good chemical stability to the membrane. The hydrogen bond formation between the imide group of PEI and sulfonic acid group of SPEES was confirmed by the FT-IR. The water uptake, ion exchange capacity and proton conductivity decrease with increasing PEI content. The oxidative stability, mechanical strength and methanol resistance power of the blend membranes were increased with increasing the PEI content. SEM indicates that PEI particles are homogeneously dispersed into the composite membrane. Although the blend membranes exhibited low proton conductivity in comparison to pristine SPEES, the presence of PEI led to an improvement in chemical stability of the membranes. SPEES/PEI-15 composite membrane showed higher relative selectivity ( $1.63 \times 10^4$  S cm<sup>-3</sup> s) than Nafion 117 membrane ( $9.97 \times 10^3$  S cm<sup>-3</sup> s) with good oxidative stability.

The blend membranes with an optimized PEI content may exhibit better performance in DMFC than pristine SPEES and Nafion 117 membranes due to an enhancement in relative selectivity and a reduction in methanol permeability due to the acid base interaction.

**(v) SPES/NPHCs blend membranes**

SPEES/NPHCs blend membranes were prepared and characterized for DMFC applications. Water uptake and membrane surface roughness parameters of the blend membranes increases with increasing the NPHCs content. The proton conductivity of composite blend membranes improved with increasing NPHCs content in SPES matrix due to high hydrophilicity provided by NPHCs which facilitates proton mobility. Methanol permeability studies envisaged that NPHCs blendmembranes are impervious to methanol. The methanol permeability of the fabricated membranes was very low compared to Nafion-117. Relatively high selectivity parameter values of these membranes indicated their greater advantages over Nafion-117 membrane for targeting on fuel cell applications, especially indirect methanol fuel cell (DMFC) environments.

**(vi) SPEES/TPA-Ppy hybrid membranes**

SPEES/TPA-Ppy hybrid PEM was successfully fabricated, in which Ppy was coated on the surface of the SPEES/TPA membrane by in-situ polymerization method. Although Ppy coating on SPEES/TPA membrane surface have some negative effects on the proton conductivity of the hybrid membranes, the methanol resistance and selectivity value are significantly increased with these membrane as compared to than pristine SPEES membrane. AFM characterization showed that the Ppy layer on the membrane surface reduces the surface roughness and nodular size of the membrane and also influenced the water uptake, proton conductivity and methanol permeability. The oxidative stability of the SPEES/TPA-Ppy membrane was obviously improved using the surface coating of Ppy. Further, Ppy coating on both sides of the SPEES/TPA surface reduces the leaching ability of TPA in the membrane. Based on the results, it could be concluded that SPEES/TPA-Ppy4 membrane appeared to have good potential as PEM in DMFC.

### **(vii) SPEES/PEI-SGO composite membranes**

A series of composite membrane based on SPEES/PEI-15 wt% with different composition of SGO were successfully prepared and characterized. GO was synthesized effectively from graphite powder by using modified Hummer's method. Then it was sulfonated by sulfanilic acid at 70 °C. Compared with SPEES/PEI composite (SP) membranes, ion exchange capacity and water uptake of the SP/SGO membranes were enhanced due to large number of hydrophilic groups in SGO. AFM images revealed that the nodule size and surface roughness are increased by increasing the concentration of SGO. Tensile strength and proton conductivity of the composite membranes were increased with increasing SGO content. The maximum conductivity of  $8.87 \times 10^{-3}$  S/cm was achieved at 25 °C upon addition of 0.8 wt% of SGO. All the SP/SGO membranes exhibited methanol permeability lower than  $3.26 \times 10^{-7}$  cm<sup>2</sup> s<sup>-1</sup>, which was much lower than that of Nafion 117 ( $3.41 \times 10^{-6}$  cm<sup>2</sup> s<sup>-1</sup>). Nevertheless, the lower cost and methanol crossover compared to those in Nafion make the SP/SGO membranes promising alternatives for DMFC.

In summary, it is inferred that different types of PEM showed good proton conductivity which is very important for electrolyte in fuel cells. They displayed good mechanical strength, thermal stability and adequate chemical stability. There is a good compatibility among the constituents in all the prepared PEMs as revealed by SEM and AFM. From the current investigation, it may be concluded that SP/SGO-0.8 wt%, SPES/PPG-HBS and SPES/NPHCs (1) membrane is suitable for DMFC application, whereas SPEES/PPG-HBS blend membrane is suitable for PEMFC application.

### **15. Contribution to the Society**

The development of alternate proton exchange membranes (for Nafion - high cost) from polymer blends of (i) SPES/cSMM, (ii) sPVdF-co-HFP/cSMM, (iii) SPEES/cSMM, (iv) SPEES/PEI, (v) SPES/ NPHCs, (vi) SPEES/TPA-Ppy and (vii) SPEES/PEI-SGO for PEMFCs and DMFCs in India's energy system will help foster clean energy and provide:

**Cleaner and More Efficient Use of Fossil Fuels:** Fuel cells can operate directly on natural gas, biofuels, methane, gasified coal or gasified biomass. They convert the energy in these fuels directly in electricity without burning or combustion which greatly improves the efficiency of these fuels and reduces their carbon impact. When the production of hydrogen is required, there is still a lifecycle greenhouse gas reduction when the hydrogen is used in a fuel cell. Furthermore, hydrogen and fuel cell technologies are very complimentary to existing power sources, in many cases representing an incremental improvement of energy use vs. a drastic paradigm shift. Fuel cells provide power without combustion, so as a result enjoy higher efficiencies than traditional power generation that relies on combustion. Adoption of hydrogen and fuel cell technology provides immediate energy efficiency gains in various applications including stationary power generation and transportation.

**Providing Clean Transportation Options** - Hydrogen and fuel cell cars and buses provide zero-emissions at the tailpipe, and significant "well to wheels" CO<sub>2</sub> reductions even when hydrogen is produced from fossil fuels. The introduction of hydrogen and fuel cell technology into India's automotive and public transportation use will immediately provide greenhouse gas savings and air quality improvements.

**Clean Power Generation in India** - India's hydrogen and fuel cell sector presents a diverse portfolio of clean power generation technologies and systems that are available now. They offer unique services to emerging and traditional energy sources that ultimately improve their efficiency and effectiveness.

Renewable energy sources such as wind, solar and run-of-river hydro may produce electricity when it is not needed. That electricity can be stored in the form of hydrogen, and using fuel cells can be turned back into usable electricity at the time it is needed. Hydrogen and fuel cells help utilities improve the reliability and quality of grid power by providing frequency regulation and

demand response services. India has unique technologies and engineering expertise that allow for the use of waste hydrogen sources in clean power generation applications.

**16. Whether any PhD enrolled/produced out of the project: Yes**

S.No.	Name of the Research Scholar	University and Reg. No.	Current Status
1	Mr. S. Neelakandan	Alagappa University Reg. No. 636/2012-13 dated 06.02.2013	Thesis submitted
2	Mrs. A. Muthumeenal	Alagappa University Reg. No. 777/2013-14 dated 23.10.2013	Research in progress

**17. No. of publication out of the project: 6 (Published- 5 and Under Revision in Journal- 1)**

S.No.	Author, Title, Journal, Volume/Year/Page	Impact Factor
1	S. Neelakandan, D. Rana, T. Matsuura, A. Muthumeenal, P. Kanagaraj, A. Nagendran. Fabrication and electrochemical properties of surface modified sulfonated poly (vinylidene fluoride-co-hexafluoropropylene) membranes for DMFC application, <b>Solid State Ionics</b> 268 (2014) 35-41 - <b>Elsevier</b>	2.561
2	A. Muthumeenal, S. Neelakandan, D. Rana, T. Matsuura, P. Kanagaraj, A. Nagendran. Sulfonated Polyethersulfone (SPES)–Charged Surface Modifying Macromolecules (cSMMs) Blends as a Cation Selective Membrane for Fuel Cells, <b>Fuel Cells</b> 14 (6) (2014) 853-861 - <b>Wiley</b>	2.080
3	S. Neelakandan, A. Muthumeenal, P. Kanagaraj, A. Nagendran, D. Rana, T. Matsuura. Enhancing proton conduction of sulfonated poly (phenylene ether ethersulfone) membrane by charged surface modifying macromolecules for H <sub>2</sub> /O <sub>2</sub> fuel cells, <b>Renewable Energy</b> 78 (2015) 306-313 - <b>Elsevier</b>	3.476
4	S. Neelakandan, P. Kanagaraj, RM. Sabarathinam, A. Nagendran. Polypyrrole layered SPEES/TPA proton exchange membrane for direct methanol fuel cells, <b>Applied Surface Science</b> 359 (2015) 272-279 - <b>Elsevier</b>	2.711
5	A. Muthumeenal, S. Neelakandan, P. Kanagaraj, A. Nagendran. Synthesis and properties of novel proton exchange membranes based on sulfonated polyethersulfone and N-phthaloyl chitosan blends for DMFC applications, <b>Renewable Energy</b> 86 (2016) 922-929 - <b>Elsevier</b>	3.476
6	S. Neelakandan, N.J. Kaleekkal, P. Kanagaraj, RM. Sabarathinam, A. Muthumeenal, A. Nagendran. Effect of sulfonated graphene oxide on the performance enhancement of acid-base composite membranes for direct methanol fuel cells. <b>RSC Advances – Manuscript under revision – Royal Society of Chemistry</b>	3.840

