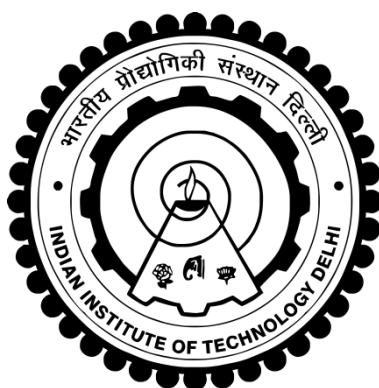


**STUDIES ON IONIC LIQUID BASED COMPOSITE  
PROTON EXCHANGE MEMBRANES FOR HIGH  
TEMPERATURE FUEL CELLS**

**RAJENDER SINGH MALIK**



**CENTRE FOR POLYMER SCIENCE AND ENGINEERING  
INDIAN INSTITUTE OF TECHNOLOGY DELHI  
DECEMBER 2015**

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by

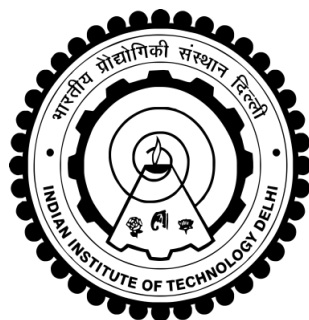
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Submitted

in fulfillment of the requirements of the degree of  
**Doctor of Philosophy**

to the



**Indian Institute of Technology Delhi**

**December, 2015**

*Dedicated to  
My Parents*

# CERTIFICATE

This is to certify that the thesis entitled, “**STUDIES ON IONIC LIQUID BASED COMPOSITE PROTON EXCHANGE MEMBRANES FOR HIGH TEMPERATURE FUEL CELLS**” being submitted by **Mr. RAJENDER SINGH MALIK** to the Indian Institute of Technology Delhi, for the award of the degree of **Doctor of Philosophy** is a record of bonafide research work carried out by him. **Mr. RAJENDER SINGH MALIK** has worked under my guidance and supervision. He has fulfilled the requirements for the submission of this thesis, which to my knowledge has reached the requisite standard.

The results contained in this thesis are original and have not been submitted, in part or full, to any other University or Institute for the award of any other degree or diploma.

Date

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**Rajender Singh Malik**

# ABSTRACT

The development of green, efficient and economic energy generation technology is gaining importance to reduce the dependence on non-renewable energy sources and decrease pollution. Polymer electrolyte membrane fuel cells (PEMFCs) received much attention due to several advantages such as relatively high efficiency, high current density, quick startup and light weight. Solid polymeric electrolyte is the heart of PEMFCs which separate anode and cathode. The perfluorosulfonic acid membranes, in particular, Nafion<sup>®</sup> has been a material of choice and technology standard. Owing to the drawbacks associated with Nafion<sup>®</sup>, engineering thermoplastics such as poly(ether ether ketone) [PEEK], polyimides [PI] and poly(benzimidazole) (PBI) emerged as a promising alternative to the state of art perfluoroionomer membranes. To overcome the technical challenges such as tolerance of CO impurity in fuel and complex water and heat management, efforts have been focused to develop high temperature (HT)-PEMFCs.

The present thesis is mainly focused on to develop cost effective and high performance proton exchange membranes which can work at high operating temperature under dry conditions. The thesis comprised of seven chapters.

**Chapter I** of the thesis is devoted towards the extensive literature survey on past and present research work on PEMs with special emphasis on describing various approaches adopted for HT-PEMFCs by replacing water with some protic solvents.

**Chapter II** consists of the materials and methods used. The detailed procedures adopted for the preparation of composite membranes by using various amounts of ionic liquids ([bmim][OTf] and [bmim][NTf<sub>2</sub>]) with SPEK/SPEEK as polymer matrix, cross-

linked membranes based on PVA, functionalized quantum dots (FQD) and sulfonated poly(ether ether ketone), composite membranes based on various amount of ionic liquid with SPEEK (cross-linked by different cross-linker such as ethylene glycol (EG) and PVA/FQDs) and composite membranes based on ABPBI and ionic liquid. The details of characterization techniques such as FTIR, differential scanning calorimeter, thermogravimetric analysis, dynamic mechanical analysis, scanning electron microscopy, X-ray diffraction, water uptake, leaching of ionic liquids, Proton conductivity are also included in this chapter.

In **Chapter III**, effect of varying amounts of hydrophilic and hydrophobic ionic liquids on the properties of SPEK (DS 43%) /SPEEK (DS 72%) was investigated. The interactions occurring among components were investigated by vibration spectroscopy (FT-IR ATR). All the composite membranes exhibited good thermal stability as compared to neat SPEK/SPEEK membranes due to electrostatic interactions between cation of ionic liquids and sulfonic acid groups of polymer matrix. Proton conductivity of all the composite membranes increased with increasing temperature and amount of ILs and proton conductivities of composite membranes under anhydrous conditions were found to be up to two orders of the magnitude (~100 times) higher than neat polymeric material. Hydrophilic IL was more compatible with SPEK and gave membranes with higher mechanical stability as compared to membranes based on hydrophobic IL. Ionic liquid based membranes are more flexible than neat membrane due to the plasticization effect by the ionic liquids. SPEEK based composite membranes showed better proton conductivity than SPEK due to the high degree of sulfonation.

In **Chapter IV**, PVA was modified by using varying amounts of sulfonic and carboxylic acid functionalized quantum dots followed by thermal cross-linking. The hydrolytic stability improved significantly after cross-linking as neat PVA membrane became fragile in water at room temperature and dissolved at 60 °C but cross-linked PVA retains its shape even at 100 °C. All the cross-linked membranes exhibit higher thermal stability as compared to neat PVA membrane. Proton conductivity of all the cross-linked membranes increased with increasing amounts of FQDs up to 1.2 wt % loading.

In the second part of the chapter SPEEK was cross-linked using PVA/FQDs after optimizing the PVA: FQDs ratio (98.2: 1.2). The water uptake studies were carried out at two different temperatures (25 °C and 70 °C after immersion for 24 h) and it was found that hydrolytic stability of cross-linked membranes increased with increasing amount of SPEEK in membranes. Thermal stability of PVA/FQDs/SPEEK membranes was higher than PVA/FQDs membranes because in presence of SPEEK, cross-link density increased and SPEEK itself has higher thermal stability. Proton conductivity of PVA/FQDs/SPEEK membranes was also higher than the PVA/FQDs membranes because more sulfonic acid groups were available for proton transfer in the presence of SPEEK in membranes and maximum power density of 182mW/cm<sup>2</sup> was achieved for the PEMFC using composite membrane XPVA/SP-70.

In **Chapter V**, effect of cross-linking on the performance properties of SPEEK in presence of varying amounts of IL ([bmim][OTf]) was investigated. For this purpose, cross-linking of SPEEK was done using PVA/FQD or ethylene glycol (EG). The ratio of SPEEK: PVA/FQD (70: 30) and SPEEK: EG (67: 33) was kept constant and amount

of IL was varied from 30 to 70% (w/w). A monotonous increase in conductivity was observed with increasing amount of IL and temperature (30-140 °C). This could be due to the decrease in viscosity of IL as well as polymer matrix with temperature so the ionic mobility increases which facilitate the proton transport route in the membranes. At higher loading of IL in the polymer matrix, the membrane became more flexible so ILs act as plasticizer and it helps in higher proton mobility. EG and PVA/FQD were used as cross-linkers for SPEEK to reduce the leaching out of ionic liquid and enhance the mechanical strength of membrane.

In **Chapter VI**, proton conducting membranes based on poly(2,5-benzimidazole) (ABPBI) using varying amounts of ionic liquids were studied. The ionic liquids such as [bmim][OTf], [bmim][NTf<sub>2</sub>] were incompatible with ABPBI therefore we used [bmim][H<sub>2</sub>PO<sub>4</sub>], with proton accepting anion H<sub>2</sub>PO<sub>4</sub><sup>-</sup>. Composite membranes ABPBI/IL were homogeneous, flexible with good thermal stability. A broad absorption band observed in the FTIR spectra around 2700 and 2300 cm<sup>-1</sup> is related to the protonation of nitrogen of ABPBI and assigned to  $\nu(\text{N}^+-\text{H})$  stretching mode. Composite membranes showed good proton conductivity at temperature ranging from 40 – 160 °C under dry conditions. Formation of three dimensional network structures in the composite membranes was proposed and proton conduction occurs mainly through the hydrogen bonding network by a hopping mechanism. The final summary and conclusion are given in Chapter VII of thesis. Suggestions for future work are also mentioned.

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## GLOSSARY OF SYMBOLS AND ABBREVIATIONS

%	percent
v	frequency
°C	degree centigrade
cm	centimeter
e.g.	for example
g	gram
h	hour
Hz	hertz
i.e.	that is
M	molar
mmol	millimole
mL	milliliter
nm	nanometer
TEM	transmission electron microscopy
HR	high resolution
PEMFC	polymer electrolyte membrane fuel cell
MEA	membrane electrode assembly
PEM	proton exchange membrane or polymer electrolyte membrane
DS	degree of sulfonation
PEEK	poly(ether ether ketone)
PEK	poly(ether ketone)
PVA	poly(vinyl alcohol)
ABPBI	poly(2,5-benzimidazole)
TFA	trifluoroacetic acid
SPEEK	sulfonated poly(ether ether ketone)
SPEK	sulfonated poly(ether ketone)
QDs	quantum dots
FQDs	functionalized quantum dots
DMAc	dimethyl acetamide
EG	ethylene glycol
TGA	thermogravimetric analysis
DSC	differential scanning calorimetry
DMA	dynamic mechanical analysis
IL	ionic liquid
SEM	scanning electron microscopy
XRD	X-ray diffraction
FT-IR	fourier transforms infrared spectroscopy
<sup>1</sup> H-NMR	proton nuclear magnetic resonance spectroscopy