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## Journal of Membrane Science

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# An efficient proton conducting electrolyte membrane for high temperature fuel cell in aqueous-free medium



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## ARTICLE INFO

## Article history:

Received 1 May 2013

Received in revised form

20 August 2013

Accepted 18 September 2013

Available online 25 September 2013

## Keywords:

SPEEK

Ionic liquids

Anhydrous conductivity

HT-PEMFC

## ABSTRACT

A novel composite membrane, derived from a simple combination of a phosphate based alkylimidazolium ionic liquid used as an anhydrous proton conductor in sulfonated poly (ether ether ketone) polymer matrix, was first proposed and characterized. Observed thermal, mechanical and chemical stabilities of ionic liquid doped composite membranes were finest to use in fuel cell applications. The effective anhydrous proton conductivity with respect to various ionic liquid compositions was studied as a function of different temperatures. Under anhydrous environment the composite membranes were found to have a comparatively good conductivity in the range of  $1.25\text{--}3.16\text{ mS cm}^{-1}$  at  $145\text{ }^\circ\text{C}$  as measured by impedance analyzer. Fuel cell performance with SPEEK/50% IL doped composite membrane gave a maximum power density of  $203\text{ mW/cm}^2$  at  $145\text{ }^\circ\text{C}$ . This study foresees that the new composite membranes could be a promising water-free anhydrous proton transport membrane for fuel cells.

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## 1. Introduction

The environmental impact of energy use from traditional sources presents serious challenges to environmental protection and the sustainability of natural resources. In recent years fuel cells have become an increasingly popular research topic and it will play an important role in the energy system of tomorrow due to their promise for clean and efficient energy conversion [1]. Efficiency of membranes have been demonstrated to significantly improve the overall performance of fuel cells. An ideal membrane should be chemically and mechanically stable at higher temperatures, inhibit the transfer of substrate and oxygen, and allow respective ions to pass through it efficiently with preferable low-costs. One of the major hurdles for advancing the PEMFC technology is currently the demand for new durable low-cost polymeric membranes that will allow fuel cell operation at high temperatures without extensive humidification. Nowadays, proton exchange membrane (PEM) fuel cells, or PEMFCs, are becoming increasingly important as alternative power sources for stationary, automobile and portable applications because of their high power density, low operating temperature (to ensure quick start-up), and high efficiency than any other type of fuel cells [2–5]. The most common PEM material, Nafion still possesses several limitations for its application and commercialization. When Nafion reaches the operating temperature of about  $80\text{ }^\circ\text{C}$ , it results in dehydration and loss of proton conductivity. The need of

increasing the operating temperature of proton exchange membrane (PEM) fuel cells is desirable for many reasons, including increased tolerance to CO poisoning of the catalyst and improved waste heat rejection [3–5].

So far a number of research efforts have been pursued to obtain PEMs with high thermal stability and high conductivity at elevated temperatures under anhydrous condition. These methods mainly include synthesis of acid–base composites [6,7], chemical cross-linking [8], incorporation of hydrophilic inorganic fillers [9,10], functionalization of polymer side chains [11–13], fabrication of ionomer nanofibers to reinforce the ionomer membrane [14,15] and replacement of water with non-aqueous proton carriers, such as phosphoric acid [16]. The above mentioned composite membranes need low humidity condition to maintain appropriate hydration level for achieving high proton conductivity. For achieving high-temperature anhydrous conductivity of PEM, water need to be replaced with an alternative proton solvent. One of the effective high-temperature proton carriers, ionic liquids (ILs), has recently received much attention because of their negligible volatility, high proton conductivity, excellent thermal stability and larger electrochemical window than water [17–20]. These unique properties of ionic liquids are believed to improve the performance of the membrane. However among these properties, the thermal stability of the ILs is the most important factor for the fuel cell operation. Various IL based composite membranes were reported earlier with improved proton conductivity [21,22]. However, the hydrolytic instability, of halogen or halides fluorophosphate and fluoroborate based ionic liquids are limited to only anhydrous condition [23]. Therefore it is important to find the

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alternative intrinsically halogen- and halide-free ionic liquids with significant hydrolytic stability. Recently, dialkylphosphate ions based ILs have received special interest when compared to the other ILs with sulfate or borate ions because phosphate ions have high hydrolytic stability as well as anhydrous proton conductivity [24]. All the above characteristics make ionic liquids a potential basis for anhydrous proton conductors that allow PEMFCs to operate at higher temperatures [25,26]. It is well known that the sulfonated poly ether ether ketone (SPEEK) polymer has exhibited excellent thermal stability, with relatively good proton conductivity [27,28].

In this report, for the first time we report an anhydrous proton conducting membrane based on the halogen free ionic liquids containing imidazole cations of 1-ethyl-3-methylimidazolium (EMIM), anions of diethyl phosphate (DEP) and sulfonated poly (ether ether ketone) (SPEEK) made using the simple solution casting method. The formed composite membranes were operated at elevated temperature (100–145 °C) in anhydrous conditions. Additionally, the thermal stability, chemical stability and the possible proton conducting mechanism of the composite membrane were investigated.

## 2. Experimental techniques

### 2.1. Materials

Poly (ether ether ketone) (PEEK) powder (medium melt viscosity Grade 150, XF) was obtained from Victrex PLC, UK. 1-Ethyl-3-methylimidazoliumdiethyl phosphate (EMIM DEP) was received from Sigma–Aldrich and used as received without any further purification. All other reagents and chemicals (AR grade) were procured from Merck Chemicals, and used directly for preparation.

### 2.2. Preparation of SPEEK

Sulfonated poly (ether ether ketone) (SPEEK) was synthesized according to the literatures [29,30]. Briefly, 5 g of PEEK powder was dried in a vacuum oven at 100 °C for overnight and dissolved in 75 ml of concentrated H<sub>2</sub>SO<sub>4</sub> solution (98%) at room temperature under vigorous stirring for 6 h. The mixture was then decanted into a large excess of ice–water under continuous agitation. The precipitated polymer was filtered and washed several times with de-ionized water until neutral pH and dried at room temperature for 24 h. Further, dried at 60 °C in a vacuum oven for another 24 h. The degree of sulfonation (DS) of SPEEK was 64% determined from ATR-FTIR (Fig. 1) spectra as reported earlier [31].

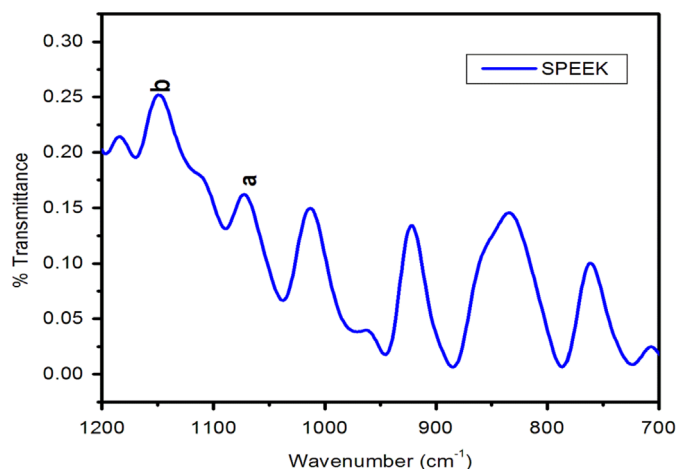


Fig. 1. Determination of Degree of Sulfonation (DS).

### 2.3. Composite membrane preparation

The composite membrane SPEEK/(EMIM DEP) was prepared by the solution casting method. Initially SPEEK solution was prepared with N-methyl pyrrolidone (NMP) and ionic liquid (EMIM DEP) was mixed separately with the various concentrations such as 10, 30, and 50 wt% with respect to the SPEEK weight percentage. The above mixture was vigorously stirred for 24 h and continuously goes with the ultra-sonication for 30 min under ambient conditions. Finally, the solution were cast on well cleaned glass plates and dried for 24 h at 80 °C in a vacuum oven results in free-standing slight yellowish membrane and stored in a moisture-free environment. And the membranes are named as SP-10, SP-30 and SP-50. For comparison the pristine SPEEK membrane was also prepared with the same procedure. The unique chemical structures of SPEEK and their possible interaction with EMIM DEP are shown in (Fig. 2).

### 2.4. Characterization

The Fourier-transform infrared (FTIR) spectra of composite membranes were obtained using Alpha Bruker spectrometer in ATR mode. Thermal stability of the composite membranes was investigated using a thermo gravimetric analyzer (TGA model SDT Q600 V8. 0 build 95 systems) under nitrogen atmosphere at a heating rate 10 °C/min from room temperature to 800 °C. Surface observation of the prepared membranes was examined using Hitachi S-3400 model Scanning Electron Microscope.

The membrane conductivity under anhydrous conditions was measured over the frequency range of 100 Hz–5 MHz using HIOKI 3035 Impedance Analyzer by four probe method from ambient temperature to 150 °C. The mechanical stability of the membranes was measured using a Dynamic Mechanical Analyzer (TA Instruments, DMA Q800 model) equipped with a heating ramp of 5 °C/min from 30 to 200 °C in air atmosphere. The measurements on conductivity and mechanical strength were performed under nonhumidification conditions.

### 2.5. Membrane electrode assembly and fuel cell test

To assemble the membrane electrode the following procedures were followed as similar to our earlier reports; first the gas diffusion layers (Carbon cloth) were made using the mixture of 70 wt% Vulcan XC-72, 30 wt% polytetrafluoroethylene (PTFE) binder and few drops (ml) of DI water and isopropyl alcohol to make slurry inks. The slurry was coated onto carbon cloth and it was dried in a vacuum oven at 100 °C for 2 h followed by heat treatment for 6 h at 350 °C in muffle furnace. Similarly, the catalyst layer was formed over the diffusion layers as same as that of the slurry coating which was prepared by mixing the 20 wt% Pt on

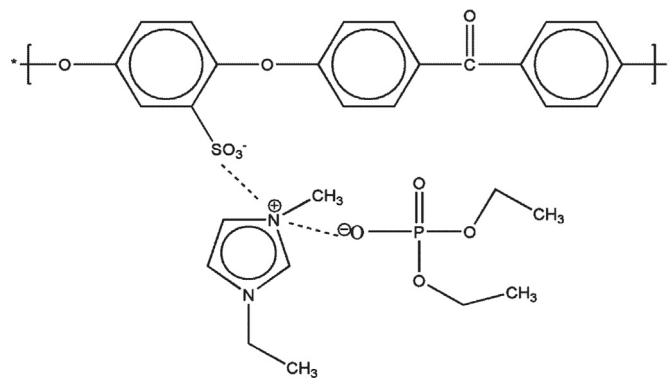


Fig. 2. Chemical structure and interaction of ionic liquid with SPEEK.

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