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Novel anhydrous composite membranes based on sulfonated poly (ether ketone) and aprotic ionic liquids for high temperature polymer electrolyte membranes for fuel cell applications

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ABSTRACT

Novel composite membranes were prepared using imidazolium type aprotic ionic liquids and sulfonated poly (ether ketone) (SPEK) as polymer matrix by solution casting process. All the prepared membranes were characterized for their thermal stability, mechanical properties, ion exchange capacity, proton conductivity and leaching out of ionic liquids in presence of water. Ionic liquid based membranes were more flexible than neat SPEK membrane due to the plasticization effect of ionic liquids. The interactions and compatibility occurring among components were investigated by vibration spectroscopy (FTIR ATR) and scanning electron microscopy respectively. The thermal stability of composite membranes was higher than unmodified membranes. The ion conductivity of composite membranes under anhydrous conditions was found to be dependent on temperature, type and concentration of ionic liquid in SPEK matrix. Ion conductivities of composite membranes under anhydrous condition were found to be up to two orders (~100 times) higher than neat SPEK membrane and it was found to be ~5 mS/cm at 140 °C for SPEK/OTf-70. These composite membranes can be successfully operated at temperatures ranging from 40 °C to 140 °C under anhydrous conditions.

Introduction

Fossil fuels are non-renewable, environment polluting and major cause of global warming, therefore, the need of hour is to produce energy using environmentally benign approaches. Today, research is focused on the use of hydrogen in a clean and zero emission technology such as fuel cells [1–3]. Among the various types of fuel cells, polymer electrolyte membrane fuel cells (PEMFCs) have received significant attention due to many advantages. Polymer electrolyte membrane (PEM) is the key component of PEMFC which transfers protons from anode

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to cathode. The most commonly used polymer membranes are perfluorosulfonated membranes [PFSA], such as Nafion which exhibit excellent thermal, chemical and mechanical strength [4,5]. However, shortcoming of current PEMs such as high cost, high methanol permeability [6], complicated water management and low conductivity at high temperature [7,8] limited their further extensive applications. Some non-fluorinated and inexpensive engineering thermoplastics such as sulfonated poly (aryl ether ketone) (SPAEK) [9,10], sulfonated poly (aryl ether sulfone) (SPAES) [11,12], sulfonated polyphenylene [13], sulfonated polyimides (SPI) [14,15] etc. have been studied and emerged as promising alternative to perfluoroionomer membranes.

The operation of polymer electrolyte membrane fuel cells at high temperatures (>100 °C) is attractive for mobile and stationary power sources due to enhanced reaction kinetics at electrodes, high energy efficiency, simplified water and heat management as well as enhanced tolerance to CO impurity of fuel gas [16–19]. Many alternative approaches have been adopted for developing elevated-temperature polymer electrolyte membranes. These are generally classified broadly into three categories.

First approach is the modification of PFSA membrane to improve water retention at operating temperatures by adding inorganic additives (to prepare organic-inorganic composite/blend membranes) such as SiO_2 (Silica) [20–23], TiO_2 (titanium dioxide) [24,25], and proton conductor filler like metal phosphate (zirconium phosphate, boron phosphate) [26–29], heteropolyacids [30,31] and heterocyclic compounds including imidazole, benzimidazoles etc [32–34]. However, these membranes at temperature higher than 100 °C require a high-pressure humidification system to maintain high humidity in order to achieve acceptable proton conductivities. Second approach is fabrication of membranes with new materials containing proton conducting groups [35,36].

Another very interesting approach which is being used is to replace water with low volatile and thermally stable solvent as proton transporting medium in the membrane. Acid doped polymer such as phosphoric acid doped polybenzimidazole [37] and recently ionic liquids [ILs] have attracted much attention in high temperature fuel cell applications to replace water in membrane. Ionic liquids also known as room temperature ionic liquids (RTILs) are ionic salt with melting point below 100 °C and have some special properties like low-volatility, excellent chemical and thermal stability, wide electrochemical stability, high ionic conductivity, wide temperature liquid range, etc. Polymer membranes can be fabricated by impregnating ILs in membrane [38] i.e. by dissolving polymer and ILs in same solvent and cast membranes by evaporating the solvent [39–41]. Various ionic liquids have been used in different polymer matrices such as Nafion, poly (vinylidene fluoride-hexafluoropropylene), sulfonated poly (ether ether ketone) [SPEEK] and polyacrylonitrile. Doyle et al. [42] found that composite membranes based on Nafion and 1-butyl-3-methyl-imidazolium trifluoromethane sulfonate exhibited impressive proton conductivity, 0.1 S/cm at 180 °C with little weight loss of IL. Ionic conductivity of the fabricated membrane was dependent on the polymer type, conductivity of neat IL and the concentration of ionic liquid in the membrane.

Therefore, the objective of this study was to fabricate and characterize novel ion conducting membranes based on sulfonated poly (ether ketone) and aprotic ionic liquids. For this study, two types of aprotic ionic liquids i.e. 1-butyl-3-methyl-imidazolium trifluromethanesulfonate ([bmim][OTf]), and 1-butyl-3-methyl imidazolium bis (trifluoromethanesulfonyl) imide ([bmim][NTf_2]) were selected and sulfonated poly (ether ketone) [SPEK] was chosen as polymer matrix because of its high thermal and chemical stability and good proton conductivity. It was speculated that the cations of ionic liquid partially replace the protons of sulfonic group present in the matrix polymer which helps to enhance the proton transport providing IL channel by hopping mechanism. The ionic conductivity, thermal stability, mechanical strength of SPEK membrane containing hydrophilic/hydrophobic ionic liquids was investigated at eminent temperature under anhydrous conditions for fuel cell application.

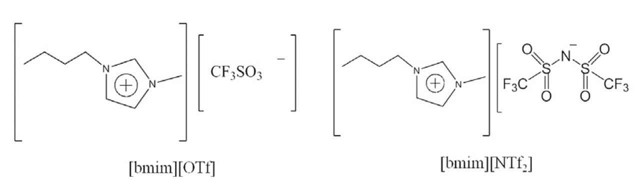
Experimental

Materials

Sulfonated poly (ether ketone) (SPEK) was obtained from Fuma-Tech, Germany, 1-butyl-3-methyl-imidazolium triflutomethanesulfonate [bmim][OTf], 1-butyl-3-methyl-imidazolium bis (trifluoromethanesulfonyl) imide [bmim][NTf_2] (Merck, Germany) [Scheme 1], dimethyl acetamide (DMAc), dimethyl sulfoxide (DMSO) and other solvents from Qualigens India, were used as received without further purification.

Preparation of composite membranes

Polymer solution was prepared by dissolving 0.2 g SPEK in 2 ml DMAc at 60 °C for 6–8 h under stirring. The calculated amounts of ionic liquid was added to the polymer solution and stirred for another 6–8 h. Then the polymer mixture was poured onto clean glass plate at 60 °C and kept for overnight followed by drying under vacuum at 120 °C for 10–12 h to remove the residual solvent. Free standing transparent membranes were obtained after solvent evaporation. All the composite membranes were stored in moisture free environment and virgin SPEK membrane was also prepared as a reference. Several samples were prepared by mixing SPEK with 50, 60 and 70% w/w of different ionic liquids. The samples prepared using 50, 60 and 70% w/w of [bmim][OTf] ionic liquid have been designated as SPEK/OTf-50, SPEK/OTf-60 and SPEK/OTf-70 respectively. Similarly, the composite membranes prepared using [bmim][NTf_2] ionic liquid were designated as SPEK/NTf_2 followed by numerical suffix representing the weight percent of ionic liquids.



Scheme 1 – Structure of ionic liquids.