Sulfonated polyimides containing triphenylphosphine oxide for proton exchange membranes

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HIGHLIGHTS

- Triphenylphosphine oxide containing sulfonated polyimides (SPIs) was synthesized.
- The SPIs showed good oxidative and hydrolytic stability and high proton conductivity.
- TEM analysis revealed well separated morphology of the SPIs.

GRAPHICAL ABSTRACT
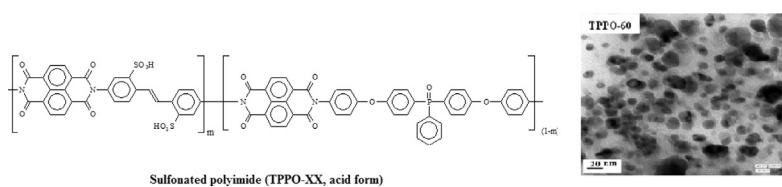
Sulfonated polyimide (TPPO-XX, acid form)

ABSTRACT

A series of sulfonated co-polyimides (co-SPI) were prepared by one pot polycondensation reaction of a combination of diamines namely; 4,4′-diaminostilbene-2,2′-disulfonic acid (DSDSA) and prepared non-sulfonated diamine (DATPPO) containing triphenylphosphine oxide with 1,4,5,8-naphthalenetetracarboxylic dianhydride (NTDA). All these soluble co-SPI gave flexible membranes with high thermal stability and showed good mechanical property. Transmission electron microscopy (TEM) analysis revealed the microphase separated morphology with well-dispersed hydrophilic (cluster size in the range of 5–55 nm) domains. The co-SPI membranes showed high oxidative and hydrolytic stability with higher proton conductivity. All these co-SPI membranes exhibited low water uptake and swelling ratio. The co-SPI membrane TPPO-60 (60% degree of sulfonation) with $IEC_W = 1.84$ mequiv g^{-1} showed high proton conductivity (99 mS cm^{-1} at 80 °C and 107 mS cm^{-1} at 90 °C) in water with high oxidative (20 h) and hydrolytic stability (only 5% degradation in 24 h).

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1. Introduction

Polymer electrolyte membrane (PEM) fuel cells have been widely considered as an automotive, portable and stationary power sources to alleviate most of the problems associated with the production and consumption of energy [1–5]. Environment-benign technologies of fuel cells provides pollution free operation, high energy conversion efficiency and low maintenance costs [6]. The electric power generated in these systems from two electrochemical reactions: the oxidation of hydrogen (or precursor) at the anode and the reduction of oxygen at the cathode. PEM acts as an essential component in the fuel cell system which not only transfers protons from anode to cathode, completing the electric circuit, but also acts as a barrier to fuel crossover, oxidant and electrons between the electrodes. In the present scenario perfluorosulfonic acid (PFSA) ionomer membranes, Nafion®, Aciplex®, Flemion® are considered as state-of-the-art membrane for fuel cell applications due to excellent chemical and physical stability along with high proton conductivity. However, difficult synthetic procedure, low glass transition temperature, restricted operation temperature (<80 °C), high fuel crossover limited their applicability. Henceforth, a number of sulfonated aromatic polymer membranes, such as sulfonated poly(arylene ether)s (SPAEs) [7], sulfonated polyimides (SPIs) [8–10], poly(arylene ether sulfone)s (PAESs) [11,12] and

polytriazoles (PTAs) [13] have extensively investigated to overcome the drawback of the PFSA membranes. Furthermore, the environmental incongruity of fluorine has directed to develop for an alternative non-fluorinated hydrocarbon membrane [14,15].

Among PEM materials, sulfonated polyimide membranes are one of the potential candidates known for their high thermal and chemical stability, mechanical durability, excellent film forming ability, strong resistance to fuel crossover and high proton conductivity [16–18]. Most of the co-SPIs are generally synthesized through the direct copolymerization of the sulfonated monomers to avoid the possible consequence of imide hydrolysis in the post-polymerization acidification process. Moreover, the chemical and physical properties can be easily varied by simply changing the composition of the non sulfonated co-monomer in direct copolymerization method. The first generation sulfonated polyimides resulting from five-membered anhydride are generally unstable towards acid due to the ease of hydrolysis of the imido linkages. A well known second generation sulfonated polyimide derived from six member ring containing naphthalene tetracarboxylic dianhydride (NTDA) showed improved performance as proton exchange membranes than the polymer derived from five membered dianhydrides [19]. Due to the lower ring strain, six membered polyimides have superior chemical and thermal stability compared to the more common five membered polyimides [20]. However, they also have some disadvantages such as poor solubility and low process ability. Research efforts are going on to overcome these challenges associated with the NTDA based sulfonated polyimides. Many research groups introduce flexible ether linkages in the polymer backbone for the improvement of solubility along with chemical and dimensional stability [17,20]. Oxidative stability is another essential factor in the practical application of fuel cell. In recent years, Watanabe et al. reported that introduction of phenylphosphine oxide moiety in the polymer backbone gives outstanding oxidative stability and high proton conductivity [14]. In addition, it is reported that phenylphosphine oxide moiety provides excellent adhesive properties with the catalyst layer [21], with the added benefits of excellent thermal stability and miscibility because of strong hydrogen bonding [22,23]. The water uptake and swelling ratio of the membranes are also crucial factors which affect PEM Fuel cell performances since a high water uptake and swelling ratio increases fuel crossover and deteriorate the mechanical properties. Although the structure of sulfonated diamine made a greater impact on the chemical stability as well as other properties of the co-SPIs, the structure of non sulfonated diamine also plays an important role. Therefore, the optimization of the polymer structure is required to achieve high proton conductivity, low fuel permeability, low water uptake and low swelling ratio for high end applications.

To circumvent these issues present work aims to increase the oxidative stability, hydrolytic stability of the PEMs accompanying their proton conductivity. A series of nonfluorinated copolyimides with a controlled degree of sulfonation were synthesized using a combination of diamines; a sulfonated diamine (DSDSA) and triphenylphosphine oxide containing diamine (DATPPO) with an aromatic dianhydride (NTDA). In this work the polymers were also designed to investigate the effects of triphenylphosphine oxide units in the co-SPI backbone on membrane properties. Detailed structural characterization, physical properties, morphology and proton conductivities of the membranes are reported.

2. Experimental

2.1. Starting materials

1,4,5,8-Naphthalenetetracarboxylic dianhydride (NTDA, 98.0%)

was purchased from TCI (U.S.A.), and 4,4′-diaminostilbene-2,2′-disulfonicacid (DSDSA, 95.0%) was purchased from Alfa Aesar and dried under vacuum at 120 °C for 12 h prior to use. Triethylamine (TEA, 99.0%), m-cresol (99.0%), benzoic acid (>99.5%) and concentrated sulfuric acid (95%) were purchased from E. Merck (India) and were used as received. Nafion® membrane was purchased from Alfa Aesar (USA). The membrane was treated with hot 5 wt% H_2O_2 aqueous solution for 1 h followed by boiling 1 M H_2SO_4 aqueous solution for 1 h and washed several times with deionized water before use. The compound bis-(4-fluoro phenyl) phenylphosphine oxide (1) was prepared according to our previous reported literature [24]. DATPPO (2) was prepared from (1) and shown in Scheme 1 [25]. N, N-dimethylacetamide (DMAc), dimethyl sulfoxide (DMSO), N-methyl pyrrolidone (NMP), dichloromethane (DCM), acetone and isopropanol were purchased from Spectrochem (India) and used as received.

2.2. Measurements

^{1}H NMR spectra of the copolymers were recorded on a 600 MHz instrument (Switzerland), using $CDCl_3$ and DMSO-d_6 as a solvent and TMS as a reference. Attenuated Total Reflectance-Fourier Transform Infrared (ATR-FTIR) spectra of the copolymers were recorded from a NEXUS 870 FTIR (Thermo Nicolet) spectrophotometer at room temperature under humid free atmosphere. The viscosity of the polymers was measured by Ubbelohde viscometer dissolving the polymer in NMP (concentration 0.5 g dL^{-1}) at 30 °C. Thermal stability of the polymers was evaluated from thermogravimetric analysis (TGA) using TA Instruments TGA Q50 thermal analyzer under synthetic air (N_2:O_2 = 80:20) at a heating rate of 10 K min^{-1} upto 800 °C. The densities of the membranes were measured using a Wallace High Precision Densimeter-X22B (UK) (isooctane displacement) at 30 °C. The mechanical properties of the membranes (10 mm × 25 mm) in their acid form were measured at 30 °C using a tensile testing machine from TINIUS OLSEN H5KS at a speed of 5 mm min^{-1}. The acidified membranes were dried under vacuum at 100 °C for 10 h and cooled to room temperature (30 °C) before performing the mechanical tests and reported as mechanical properties in dry condition. The dry membranes were immersed in deionized water for 24 h and wiped out any adhere water using tissue paper and the mechanical properties reported as in wet condition. Transmission electron microscopy (TEM) of the membranes was performed using a TEM instrument, FEI -TECNAI G2 20S TWIN. Before the analysis, the samples in acid (H^+) form were stained with silver ion (Ag^+) by immersing them overnight in 0.5 M $AgNO_3$ aqueous solution followed by rinsing with water and dried at room temperature for 12 h. The stained membranes were embedded with epoxy resin and sectioned to yield 100 nm thick, using a Leica Ultracut UCT EM FCS, Austria and placed on copper grids. The in-plane proton conductivities of the polymer membranes were determined using 4-probe conductivity cell attached with AC impedance spectroscopy. Resistance values (R) were determined from the impedance plot (Nyquist type plot) obtained in the frequency range of 100 Hz–1 MHz. The proton conductivity (σ) was calculated from the equation, $\sigma = L/(A \times R)$ where A and L are the conducting area and the membrane length, respectively. A sample of the rehydrated membrane of dimension 2 cm × 1 cm was clamped between two platinum electrodes in the conductivity cell. The membrane between the two electrodes was exposed to allow its equilibrium with deionized water during the experiment. The concentration of the ion conducting units is usually represented as the molar equivalents of ion conductor per mass of dry membrane and is expressed as weight based ion exchange capacity (IEC$_w$), or mill equivalents of ion per gram (equiv. g^{-1} or mmol g^{-1}) of polymer (EW = 1000/IEC$_w$). The ion exchange capacity for di-sulfonated