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Synthesis and characterization of novel sulfonated polyimide with varying chemical structure for fuel cell applications

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ABSTRACT

Sodium 2-(2, 3-bis (4-aminophenyl) propyl) benzenesulphonate (APBS), a novel sulfonated diamine (NSDA) was synthesized and characterized by ^{13}C NMR. NSDA along with 4,4′-oxydianiline (ODA) and 4,4′-oxydiphthalic anhydride (OPDA) were used for the synthesis of novel sulfonated polyimide (NSPI) thin film through the random copolymerization process via two-step classical method: (1) synthesis of sulfonated poly(amic acid) (SPAA), the precursor; (2) thermal imidization of SPAA film. Novel sulfonated polyimide (NSPI) with a pendant sulfonic acid group was fabricated by the use of this novel NSDA. The imidization of novel NSPI membrane was confirmed by FTIR spectroscopy. Thermal stability, water uptake, ion exchange capacity, hydrolytic and oxidative stabilities were also studied. Relatively high proton conductivity even at 110 °C, makes this SPI membrane suitable to be used as a polymer electrolyte membrane for fuel cell.

1. Introduction

Fuel cell (FC) technology is a viable solution to the global problems of energy crisis and environmental pollution [1,2]. Among different types of fuel cells proton exchange membrane fuel cells (PEMFCs) are the most promising clean energy source for portable devices, fuel cell vehicles and residential power stations. Proton exchange membranes (PEMs) being the integral part of proton exchange membrane fuel cells PEMFCs must have the potential to split the chemical reactions at the anode from cathode both chemically and electronically. Beside this, facilitation of the free movement of the proton is the main feature of a fuel cell membrane [3–5]. This prerequisite has forced lot of researchers to work on ion exchange membranes, which provides the motivation needed for technological enhancement.

Nafion® membrane is the most common and commercially available proton exchange membrane (PEM), which possess excellent properties such as good chemical, mechanical, and thermal stability along with high proton conductivity [6,7]. Despite their favorable features, these membranes (Nafion®) have several disadvantages, i.e., fuel permeability, high cost and low performance accompanying with the dehydration at temperatures above 80 °C. Fuel cell operation at low temperatures is associated with some drawbacks such as energy inefficiency, carbon monoxide poisoning, rough heat and water management and insecure electrode kinetics. Development of the low cost and stable membrane, capable of operating at high temperature is thus a priority. Low production costs obviously involve the use of conventional hydrocarbon polymers or eventually light fluorinated ones. Since aliphatic polymer chains are not stable in the highly oxidative environment encountered in the fuel cells, most of the alternative membranes are therefore aromatic polymers [8–11]. Aromatic polymers intrinsically are not proton conductors, to make them conductive they should be either doped or functionalized [12,13]. Although strong acid doping can be possible in case of some polymer e.g. polybenzimidazoles but possibility of elution in the presence of water might result in low ionic conductivity. Functionalization by grafting of sulfonic acid is therefore now generally preferred. Among numerous families of polymers which have been proposed as a possible alternative membranes to Nafion, sulfonated polyimides (SPIs) are thought to be a potential candidate for use as proton exchange membrane (PEM). SPIs have mechanical, thermal and chemical strength of polyimide which is due

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to their backbone's similarity with polyimide [14,15] whereas presence of sulfonic acid group in SPIs makes them hydrophilic due to which they starts conducting protons as well. All these characteristics make the SPIs true replacement of Nafion®. One of the main disadvantage of sulfonated polyimide (SPI) based membranes is their tendency of hydrolysis under the fuel cell operating conditions, causing four times decrease in the average length of the macromolecules after 200 h of testing at 130 °C [16–18]. This in turn deteriorates the mechanical properties of the membrane. Initially water molecules join the carbonyl carbon resulting in the destruction of the imide cycle and the main polymer chain. Electrophilicity of the carbonyl carbon of the imide ring can be reduced by several different ways among which introduction of the sulfonic acid group in the side chain of the polymer rather than the main chain is one of the important factor which will reduce the electron accepting effect of the sulfonic acid group [19]. In literature few attempts were made to prepare proton exchange membranes (PEMs) having sulfonic acid group on the side chain e.g. T. Yasuda et al. [20] investigated the effect of alkyl side chain on the properties of polyimide as PEM. They found that sulfonated alkyl side chain has better hydrolytic stability than main chain sulfonated polyimides. Y. Yin et al. [21] synthesized a series of sulfonated copoyimide bearing pendant sulfonic acid groups from 1,4,5,8-naphthalenetetracarboxylic dianhydride, bis (3-sulfopropoxy)benzidines and nonsulfonated diamine. The co-SPI membranes displayed a water uptake value of 39–94 wt% and proton conductivity of 0.05–0.16 S/cm at 50 °C with IEC values of 1.95–2.32 meq/g. These membrane showed hydrolytic stability of 300 h at 100 °C. S. Chen et al., [22] synthesized a novel side chain aromatic diamine. This novel side chain diamine along with 1,4,5,8 naphthelene tetracarboxylic dianhydride and non-sulfonated diamine were used to synthesize sulfonated copolyimides. These sulfonated copoyimide displayed good solubility in common aprotic solvent with high desulfonation temperature. K·Chen et al. [23] synthesized a series of SPIs from a novel sulfonated diamine bearing sulfophenyl pendant groups. These SPIs membrane displayed proton conductivity of 1.04–1.3 mS/cm with an IEC value of 1.80 meq/g and 50% relative humidity at 60 °C. These membrane showed a hydrolytic stability of 500 h at 130 °C.

Based on these facts in present study we have synthesized the novel NSDA having a pendent sulfonic acid group. Copolymerization of this NSDA with 4,4′-oxydianiline (ODA) and 4,4′-oxydiphthalic anhydride (ODPA) resulted in novel sulfonated polyamic acid (NSPAA), further this NSPAA is converted into novel NSPI membrane. The results obtained for NSPI are quite interesting.

2. Experimental

2.1. Materials

2-formylbenzenesulfonic acid sodium salt (FBSASS,95%, Sigma Aldrich, USA), Aniline (≥99.5%, ACS), aniline hydrochloride (97%, Sigma-Aldrich, USA), triethylamine (TEA, ≥99.5) 4,4′-oxydiphthalic anhydride (ODPA, 97%, Sigma-Aldrich, USA), 4,4′-oxydianiline (ODA,97%Sigma-Aldrich, USA) dimethylacetamide (DMAc; 99.8%, Sigma-Aldrich, USA, water content < 0.005%), and ethanol (Lab-Scan, Ireland) were used for the synthesis.

2.2. Synthesis of novel sulfonated diamine (NSDA)

Scheme 1 was followed to synthesize NSDA. Reaction flask preheated at 50 °C was purged with nitrogen for 30 min to this was added mixture of 2-formylbenzenesulfonic acid sodium salt (FBSASS) (0.08 mol), aniline (0.24 mol) and aniline hydrochloride 1.07 g and refluxed for 3 h at 120 °C. After cooling 30 mL of ethanol was added to this reaction mixture, the mixture was again heated to 80 °C after that it was cooled slowly and kept. Purple colored crystals so formed were filtered and washed with ethanol followed by water to remove the salt and aniline residue. The crude product, thus formed was recrystallized from ethanol.

2.3. Synthesis of novel sulfonated polyimide

NSDA, triethylamine (TEA) and m-cresol were added in a 100 mL three necked round bottom flask equipped with magnetic stirrer and nitrogen inlet and kept at 30 °C till the complete dissolution of NSDA in m-cresol 4,4′-oxydianiline and 4,4′-oxydiphthalic anhydride were added to this solution in N_2 atmosphere and stirred for 24 h at 0 °C resulting in the formation of viscous NSPAA solution. Subsequently, the solvent elution technique was used to cast films of NSPAA. Conversion of NSPAA films into NSPI films was achieved via thermal imidization during which films were heated at 80 °C for 1 h then, the temperature was increased at a rate of 2 °C/min to 200 °C and kept at 200 °C for 24 h. Temperature was then dropped to 50 °C at a rate of 1 °C/min. NSPI film so obtained was dipped into 1 M HCl solution for 6 h to convert benzenesulfonic acid sodium salt into benzenesulfonic acid (Scheme 2). By changing the concentration, NSPI with different concentration of NSDA can be prepared by following the same procedure [17]. (See Fig. 1.)

3. Characterization

3.1. Spectroscopy

NMR-200 Oxford was used for the ^{13}C measurements using DMSO as solvent while the FTIR (6030 Galaxy, Mattson) was used to confirm the conversion of SPAA into SPI.

3.2. Water uptake

ASTM D570-98(2010) e1standard test method for water absorption of plastic was used to determine the water uptake value of membrane, according to which membranes were heated at 105 °C for 1 h and then at 50 °C for 24 h in an oven. These heated membranes were then cooled to room temperature and weighted immediately. Later on these membranes were soaked in deionized water for 24 h at room temperature. After removing from deionized water, membranes were gently wiped with tissue paper and weighted again [24,25]. Following equation was used to calculate the water uptake.

$$\mathrm{WU} = \frac{\mathrm{W_s} - \mathrm{W_d}}{\mathrm{W_d}} \times 100 \tag{1}$$

where WU stands for water uptake while W_s and W_d are the weight of wet and dry membrane respectively.

3.3. Hydrolytic stability

Loss of weight and ion exchange capacity at 140 °C under pressurized steam was used to measure the hydrolytic stability of the membrane in wet conditions [26].

3.4. Proton conductivity

Autolab impedance analyzer and proton conductivity cell were used for measuring the resistance of the SPI at different temperatures ranging from 30 to 110 °C. This resistance is then converted into conductance according to the following standard equation:

$$\delta\,(\mathrm{S/cm}) = 1/\Omega \times d/A \tag{2}$$

where Ω, d, and A are the resistance, thickness, and cross sectional area of the (novel sulfonated diamine (NSPI) film respectively [27].

3.5. Ion exchange capacity (IEC)

Water uptake and proton conductivity of the membranes were