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Partially sulfonated polyaniline induced high ion-exchange capacity and selectivity of Nafion membrane for application in direct methanol fuel cells

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ABSTRACT

Traditionally used Nafion membranes in direct methanol fuel cells (DMFCs) suffer from high methanol permeabilities, as well as, high material costs; therefore, alternative and more efficient polymer electrolyte membrane (PEM) materials need to be synthesized in order to realize better cell performances. We recently synthesized and reported the use of low cost partially sulfonated polyaniline (SPANi) as a co-constituent along with partially sulfonated poly(vinylidene fluoride-co-hexafluoro propylene) as an effective PEM material. This PEM material exhibited extremely low methanol permeability and very high membrane selectivity. Based on these positive attributes, we demonstrate in this work that blend of Nafion and SPANi can serve as an alternative PEM material; since PEM fabricated using 30 wt% of SPANi and 70 wt% of Nafion produced selectivity ratios of 7.91×10^4 Ss cm⁻³ (at 20 °C) and 1.97×10^5 Ss cm⁻³ (at 60 °C), an ion-exchange capacity of 1.2 meq g⁻¹ (at 20 °C), methanol permeabilities of 9.12×10^{-8} cm² s⁻¹ (at 20 °C) and 1.2×10^{-7} cm² s⁻¹ (at 60 °C), and a current density of 128.7 mA cm⁻² at +0.2 V and 60 °C and a corresponding maximum power density of 25.76 mW cm⁻² using 6 M methanol feed concentration. The cell performance, thus observed, is far better than that produced by pristine Nafion membrane under the same operating conditions.

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1. Introduction

The state-of-the-art perfluorosulfonic acid ionomer membranes, i.e. Nafion[®] membranes (a commercial product of DuPont Co.), possess good chemical and electro-chemical stabilities and high proton conductivity [1,2]. However, these membranes suffer from drastically high methanol permeability, high cost and generation of high cross-potential when used as polymer electrolyte membranes (PEMs) in direct methanol fuel cells (DMFCs) [3–7]. While the high methanol crossover effect gives rise to low selectivity (i.e. the ratio of proton conductivity to methanol permeability) of Nafion[®] membranes; generation of high cross-potential leads to low current and power outputs of DMFCs [8–11]. As a result, the commercial viability of DMFC as an alternative energy harnessing device is in jeopardy [12,13]. Therefore, the major thrust of the research involved in the development of PEMs for DMFCs has been the modification and substitution of “Nafion” as a PEM material [14–20].

A PEM for DMFC should possess a high membrane selectivity, which can be achieved by reducing its methanol permeability and/

or enhancing its proton conducting ability. Increased proton conductivity and water affinity have been observed for polymers possessing pendant sulfonic acid (–SO₃H) groups within their chemical structures [21–26], as well as, for hydrophilic π -conjugated aromatic conducting polymers [27–30]. On the other hand, hydrophobic polymers, such as poly(vinylidene fluoride) (PVdF) and poly(vinylidene fluoride-co-hexafluoro propylene) (PVdF-co-HFP), have exhibited reduced methanol affinity and methanol permeability [31–33]. Decreased methanol permeability has also been achieved for blend and composite membranes in which “methanol flow channel” or “pore” blocking phenomenon occurs [4,34–37].

The structural uniqueness of the π -conjugated aromatic conducting polymer polyaniline (PAni) has imparted within it a combination of outstanding properties [38–41], which, in turn, has enabled its utilization in a number of applications, including device fabrications [30,42]. Dutta et al. recently reported that blend and coated membranes constituted of sulfonated PAni (SPANi) and sulfonated PVdF-co-HFP (SPVdF-co-HFP) have exhibited superior results over that of pristine SPVdF-co-HFP in terms of membrane selectivity, methanol permeability, ion-exchange capacity (IEC), proton conductivity, as well as, the DMFC performance (Table S1) [43–45]. These improvements in all aspects of membrane properties have been undoubtedly the result of contribution

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of SPAni. However, the proton conductivity, IEC, and cell performance of these SPVdF-co-HFP/SPAni blend and coated membranes were found to be inferior to that of commercial Nafion-117 membrane (Table S1) [43,44]. Therefore, in order to overcome these drawbacks and to find a suitable alternative to Nafion as a PEM material, blend membranes composed of SPAni and Nafion were fabricated, primarily due to two prospective potentialities: (a) SPAni particles can block the pores present in Nafion and can reduce the methanol permeability and the resulting generation of cross potential; and (b) the presence of lone pair of electrons on N-atoms present in SPAni, along with the incorporated $-SO_3H$ groups, can result in producing substantial levels of IEC and proton conductivity. In this work, we demonstrate (i) the best blend composition in terms of both properties and performance by varying the wt% of Nafion and SPAni; (ii) the resulting enhancements of water uptake (WU) capacity, membrane selectivity ratio and IEC, as well as, reduction in methanol permeability of this blend membrane compared to pristine Nafion; and (iii) the generation of higher current and power density outputs exhibited by this blend membrane at higher methanol feed concentration, compared to pristine Nafion. However, it should be noted, that following our objective of realizing a low cost DMFC operation, we maintained the following conditions: (a) graphite bipolar plates were not subjected to any additional treatments before DMFC testing; (b) locally obtained catalysts were used, since they are much cheaper than commercial E-TEK catalysts; and (c) low reactant flow rates were employed at both the electrodes.

2. Materials and methods

2.1. Chemicals and instruments used

Nafion-117 membrane and the catalysts, Pt-Ru and Pt, were purchased from M/S Anabond Synergy Fuel Cell India. The monomer aniline and the oxidant ammonium persulfate (APS) were bought from Sigma Aldrich. HCl (reagent grade) was obtained from Loba Chemie. Chlorosulfonic acid (CSA), methanol, acetone, and NMP (1-methyl-2-pyrrolidone) were purchased from Merck Millipore India. All chemicals were used as received. De-ionized (DI) water was used for all the experiments. FT-IR characterizations of the blend membranes were done with a Bruker Alpha FT-IR spectrophotometer (Model: Alpha E) at 20 °C, using a wave number window of 500 cm^{-1} to 4000 cm^{-1} . The X-ray diffraction (XRD) analyses were conducted using a Goniometer. The applied angle was 2θ , within the range of 0–50°, and the scan rate was fixed at 1° min^{-1} . Differential scanning calorimetric (DSC) analysis was conducted on a Mettler Star SW 9.01 differential scanning calorimeter, using an empty aluminum pan as a reference and indium and zinc as standards, at a constant heating rate of 10 °C min^{-1} within a temperature range of 30–280 °C and under a nitrogen atmosphere. The initial weight of the blend sample used for DSC analysis was 5 mg. A Gamry potentiostat-600 instrument was used to determine the proton conductivities of the membranes. Morphologies of the membranes were determined using a Jeol 7600F Scanning Electron Microscope. Methanol permeabilities were analyzed by measuring the difference in the absorption peak intensities of the methanol fuel solution, using an Optizen UV-vis spectrophotometer. The tensile strengths of the membrane samples were determined by using universal tensile testing machine (Nexygen plus, Lloyd Instruments Ltd.), according to the procedure ASTM D 882-02. A 5 T tensiometer, at a crosshead speed of 5 mm min^{-1} and at a temperature of 25 °C, was used for this purpose. DMFC performance test was carried on a single cell stack, connected with a fully automated DMFC test station (K-PAS Electronic India Ltd.), and was measured using a DC programmable

load bank (K-PAS Electronic India Ltd.) attached to the DMFC Test Station.

2.2. Polymerization of aniline and partial sulfonation of PAni

PAni was synthesized from monomer aniline by following the standard procedure [46]. Briefly, the monomer (0.1 M) was first dissolved thoroughly in DI water (acidified with 1 M HCl), followed by addition of 0.1 M of the oxidant APS. Then the polymerization was allowed to continue for 24 h. The obtained polymer was filtered, washed repeatedly with DI water and vacuum-dried.

CSA was used as a sulfonating agent for the sulfonation of the vacuum-dried PAni granules (emeraldine base form). The sulfonation was carried out in a round-bottom flask at 80 °C for 5 h under constant stirring, using 1.5 g of PAni and 20 mL of CSA. The sulfonation reaction was marked by a characteristic change of color from dark purple to dark blue. After 5 h, the reaction mixture was drop-wise added to 200 mL of methanol kept in a beaker placed on an ice-bath. This was followed by addition of 100 mL of acetone, resulting in a precipitation of green powder. This precipitate was then filtered using a Buckner funnel, washed repeatedly with 40 mL portion of methanol until the pH of the filtrate became neutral, and vacuum-dried for 24 h [43].

2.3. Preparation of blends of Nafion and SPAni

Blends of Nafion and SPAni were prepared using five wt% compositions, i.e. Nafion:SPAni=90:10, 85:15, 80:20, 75:25, and 70:30. Following the typical procedure, the abovementioned ratios of the polymers were separately dissolved in NMP solvent under stirring conditions at 60 °C. The resulting blend solutions were then casted on flat glass plates, and kept in an oven for 24 h under a constant temperature of 70 °C. It should be noted that increase in SPAni content of the blend beyond 30 wt% was not possible due to phase separation and resulting loss of mechanical integrity of the corresponding blend, preventing fabrication of membranes.

2.4. Pre-treatment of PEMs

The prepared membranes were first immersed into a 5 M H_2O_2 solution, followed by treatment with a mixture of water and H_2SO_4 (7:3) for 2 h under continuous stirring. The membranes were then washed with DI water until a neutral pH was obtained. They were finally kept in an oven under a constant temperature of 80 °C [10].

2.5. WU, swelling ratio (SR), methanol uptake (MU), IEC, methanol permeability, and proton conductivity

All of these analyses and the resulting calculations were conducted following the exact procedures reported in our earlier works [22,43–45]. Therefore, we are not mentioning the details in this paper. The temperature was maintained at 20 °C and 60 °C for WU, SR, methanol permeability and proton conductivity experiments, and at 20 °C for MU and IEC analyses. Methanol permeability tests were conducted in a conventional two-compartment glass diffusion cell, where compartment “a” was filled with 2 M methanol and compartment “b” was filled with pure water [22,43–45,47]. The chromogenic reagent used for this purpose was SNP, which is a mixture of sodium nitroprusside, potassium ferrocyanide, NaOH and water in a certain proportion [22,45]. The permeability values were calculated by employing the following equation [48]:

$$-\ln(1 - 2C_b/C_a) = 2ADK(t - t_0)/lV_b \quad (1)$$

where C_b and C_a are concentrations of methanol in compartments b and a, respectively; DK is the permeability of the membrane (where

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