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Surface redox polymerized SPEEK–MO_2–PANI (M = Si, Zr and Ti) composite polyelectrolyte membranes impervious to methanol

Bijay P. Tripathi, Vinod K. Shahi*

Electro-Membrane Processes Division, Central Salt and Marine Chemicals Research Institute, Council of Scientific & Industrial Research (CSIR), G.B. Marg, Bhavnagar 364002, Gujarat, India

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ABSTRACT

We reported sulfonated poly(ether ether ketone) (SPEEK, 61% degree of sulfonation)–metal oxides (MO_2:SiO_2, TiO_2 and ZrO_2)–polyaniline composite membranes. Metal oxides were incorporated into the swelled SPEEK membrane by sol–gel method and cured by thermal treatment. SPEEK–metal oxide membranes surfaces were modified with polyaniline (PANI) by a redox polymerization process. It was observed that water retention capacity of membrane was increased and methanol permeability was reduced due to synergetic effect of metal oxides and surface modification with polyaniline. These composite membranes showed extremely low methanol permeability ($1.9–1.3 \times 10^{-7}$ cm^2 s^{-1}), which was lower than till reported values either for SPEEK–metal oxide or SPEEK/PANI membranes. Relatively high selectivity parameter (SP) values at 343 K of these membranes, especially S–SiO_2–PANI and S–TiO_2–PANI, indicated their great advantages over Nafion117 (N117) membrane for targeting on moderate temperature applications due to the synergetic effect of MO_2 and PANI in SPEEK matrix. S–TiO_2–PANI and N117 showed comparable cell performance in direct methanol fuel cell (DMFC).

1. Introduction

Polymer electrolyte membranes (PEMs) with high proton conductivity, stabilities and extremely low mass/fuel crossover are desired in order to reduce Ohmic losses and enhance their efficiencies during applications in direct methanol fuel cell (DMFC) [1–4]. Nafion117 (N117), a perfluorinated PEM, has been used in the fuel cell technologies due to their high proton conductivity and substantial stabilities [1,2,5–8]. Although, N117 membrane showed very high proton conductivity (about 0.01 S cm^{-1}), their three major drawbacks: very high cost; loss of proton conductivity at high temperature; and high methanol permeability ($\sim 10^{-6}$ cm^2 s^{-1}), drastically reduces their DMFC performance [8–13]. Several efforts were made to improve Nafion performance by reducing methanol crossover by its modification using inorganic fillers such as SiO_2 [14], mordenite [15], inorganic acids [16], metal oxides [17], polyvinyl alcohol [18], polypyrrole [19], or preparing Nafion/polyaniline/silica composite membranes [20]. Previous efforts to enhance the water retention of N117 and related membranes by incorporating metal oxide particles produced promising results [17,21]. Among the nonfluorinated aromatic ionomers, SPEEK is very promising since it is cheap, possesses good mechanical properties, high thermal stability, and its proton conductivity is directly related to degree of sulfonation. Highly sulfonated membranes showed excessive swelling under the humidified conditions of fuel cell environment and loss their dimensional stability with high methanol crossover [22]. Further, membrane dehydration also causes the membrane to shrink, which reduces the contact between the electrodes and membrane, leading to the crossover of fuel [23]. To avoid these problems, several authors reported modification of SPEEK membrane surface by polyaniline (PANI) for reducing methanol crossover, swelling due to formation of acid–base composite and enhancing the hydrophobic nature of the surface. But, SPEEK–PANI composite membranes showed about $5–6 \times 10^{-7}$ cm^2 s^{-1} methanol permeability [24,25], which was quite high for DMFC applications. Blends of metal oxides and SPEEK are also reported for reducing membrane swelling, dehydration and methanol crossover [22,26–28]. Although, these types of blended membranes showed remarkable reduction in methanol and water permeability [26], blending of two polymers/materials with quite distinct properties led to the membranes with poor mechanical properties [29]. Mauritz et al. [21,30] proposed sol–gel approach for incorporating SiO_2 to N117 providing superior performance, because it dispersed at molecular level homogenously in the polymer matrix and reduced methanol transport without any deterioration in mechanical stability.

Herein, we are reporting SPEEK–MO_2–PANI composite PEMs, in which MO_2 was incorporated by a sol–gel reaction within

* Corresponding author. Tel.: +91 278 2569445; fax: +91 278 2567562x2566970.
E-mail addresses: vkshahi@csmcri.org, vinodshahi1@yahoo.com (V.K. Shahi).

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pores/cavities of the swollen membrane without any deterioration in membrane mechanical stability, while surface modification with PANI was achieved by a redox reaction. Due to synergetic effect of metal oxides and PANI, SPEEK–MO_2–PANI membranes showed extremely low methanol permeability ($1.9–1.3 \times 10^{-7}$ cm^2 s^{-1}), which is lower than till reported values either for SPEEK–MO_2 or SPEEK–PANI membranes [24,25]. Further, in SPEEK–PANI system, dehydration was faster than SPEEK membrane [25], but we observed that for SPEEK–MO_2–PANI composite membrane, dehydration was comparatively slower in spite of their opposing properties.

2. Materials and methods

2.1. Materials

Poly(ether ether ketone) (PEEK) (medium melt viscosity grade 450 PF) was obtained from Victrex PLC England. Tetraethylorthosilicate (TEOS) 98%, titanium(IV) butoxide 97%, zirconium(IV) propoxide (70%, w/w solution in 1-propanol), and N117 (perfluorinated) membrane obtained from Sigma–Aldrich Chemicals were used as received. H_2SO_4, HCl, H_2O_2, NaOH, NaCl, $FeCl_3$, dimethylacetamide (DMAC), methanol and ethanol (AR, S.D. Fine Chemicals, India) were used as received. Aniline (AR grade, S.D. Fine Chemicals, India) was distilled prior to use. For all the purpose double distilled water was used.

2.2. Membrane preparation

Sulfonation of PEEK was carried out by direct aromatic electrophilic substitution as reported earlier [24,31]. By ^1H NMR studies degree of sulfonation of SPEEK was obtained about 61% [31], while ion-exchange capacity (IEC) was found to be about 1.697 meq. g^{-1}. SPEEK membrane was formed by solution casting method with a 10% (w/v) solution in DMAC on clean glass plate. Membrane was dried at room temperature for 24 h and further at 60 °C under vacuum for 12 h. Thus obtained membranes were treated by H_2O_2 (3%, v/v) at 40 °C for 1 h, and then with H_2SO_4 (0.5 M) to convert it into H^+ form. The SPEEK–MO_2 (where M = Si, Zr and Ti) membranes were obtained by in situ condensation of either TEOS, zirconium(IV) propoxide or titanium(IV) butoxide (5%, w/w) separately as described elsewhere [23,32]. Membranes were swelled in methanol/water (50%, v/v) solution, and metal alkoxide solution in alcohol was then infiltered to the swelled membrane. In this method, metal alkoxide molecules suppose to migrate into the ionic clusters of SPEEK membrane. After the sol–gel reactions, the in situ inorganic phase was cured by placing the membrane in a vacuum oven at 100 °C. Under these condition sol–gel transformations was achieved by in situ hydrolysis, while heating temperature was sufficient for crosslinking. In this technique the nano-hybridization of organic polymer and inorganic oxides were made by in situ sol–gel hydrolysis in hydrophilic clusters of SPEEK membrane. Thus obtained SPEEK–MO_2 composite membranes were further modified with polyaniline by a redox polymerization process [24]. Composite membranes were first catalytically activated with iron chloride (0.1 M) by replacing the hydrogen ion with Fe^{3+} ions. Polymerization of aniline was induced by dipping the membrane in mixture of aniline (10%, v/v) and HCl (1.0 M). All steps were repeated several times in order to obtain a multilayer coating of polyaniline with desired amount (2.5%, w/w). Polyaniline modification was evident because of the dark green coloration of the emeraldine salt due to the protonation of polyaniline by the sulfonic acid groups of SPEEK membrane [33]. These composite membranes were identified as S–MO_2–PANI membrane, where M represents Si, Zr or Ti. To remove the residual Fe^{3+} ions from membranes, it was stored in 0.1 M HCl or HNO_3 for 24 h. Before subjected to characterization, membranes were conditioned in 0.1 M NaOH and HCl and boiled in double deionized water.

2.3. Membrane characterization

2.3.1. Instrumental characterization

Fourier transform infrared (FTIR) spectra were recorded using spectrum GX series 49387 by attenuated total reflection (ATR) technique. For scanning electron microscopy (SEM), gold sputter coatings were carried out on the desired membrane samples at pressure ranging in between 0.1 and 1 Pa. SEM images were recorded using Leo microscope after gold sputter coatings. Thermogravimetric analyses (TGAs) were performed using Mettler Toledo TGA/SDTA851^e with star^e software, under nitrogen atmosphere with a heating rate of 10 °C/min from 50 to 600 °C. Differential scanning calorimetry (DSC) measurements were carried out using a Mettler Toledo DSC822^e thermal analyzer with star^e software. The dynamic mechanical stability of the composite membranes were evaluated by using Mettler Toledo dynamic mechanical analyzer (DMA) 861^c instrument with star^c software under nitrogen environment with a heating rate of 10 °C/min from 30 to 300 °C under 10 Hz frequency. Contact angle measurements were obtained by capillary flow porometer of model number CFP1500AEX.

2.3.2. Membrane water uptake, ion-exchange capacity, dimensional and oxidative stabilities

For each membrane, water uptake and density were determined by the gravimetric method. The size and weight of the membrane samples were measured in the fully hydrated state, equilibrated either in water or in water–methanol mixture (30%, v/v). Then the membranes were dried in vacuum oven for 24 h at 70 °C and weighed again. The water uptake was determined as the volume fraction in the membranes using the following equation:

$$\varphi_w = \frac{W_h - W_d}{W_d} \quad (1)$$

where W_h and W_d are the weight of hydrated and dry membrane, respectively.

Ion-exchange capacity (IEC) was determined by equilibrating the different membranes in 1.0 M HCl solutions to convert the membrane into H^+ form. The membranes were then washed to free of excess HCl with distilled water and equilibrated over night to remove last trace acidity. Membrane in H^+ form was then immersed in a definite volume of 0.1 M NaCl solution for 24 h and the IEC was determined from the increase in acidity by acid–base titration.

Number of water molecules associated per ionic sites (λ_w) was calculated according to the following relationship:

$$\lambda_w = \frac{(W_h - W_d)/MW_{H_2O}}{IEC \times W_d} = \frac{\varphi_w}{IEC \times MW_{H_2O}} \quad (2)$$

where MW_{H_2O} is the molecular weight of water.

Dimensional changes of the membranes were investigated by immersion of square pieces of the samples into water at 70 °C temperature for 12 h. Which were then taken out and placed in an ambient condition for another 12 h. Change in volume fraction (Φ) of S–MO_2–PANI composite membranes was estimated by the following equation [10]:

$$\Phi = \frac{L_x L_y L_z - L_{xo} L_{yo} L_{zo}}{L_x L_y L_z} \quad (3)$$

where L_x, L_y and L_z is length/width/thickness, respectively, of the swollen membrane and subscript o denote the dimensions in ambient conditions.

Oxidative strength of the synthesized membranes was evaluated in Fenton's reagent. Small piece of membrane samples of