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Synthesis and characterization of composite membranes based on α-zirconium phosphate and silicotungstic acid

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Abstract

The functional properties of the composite membrane generated from polyvinyl alcohol, zirconium phosphate and silicotungstic acid are described. The fabricated membranes were characterized by using FT-IR, XRD, TGA, DSC and SEM techniques. These fabricated membranes showed reduced methanol cross over (for possible application in DMFC) relative to that of Nafion® 115. A maximum proton conductivity of 10^{-2} S cm^{-1} at 60% RH was attained with 30 wt% STA incorporated composite membrane. This is however lower than that observed for Nafion® 115 at 100% RH.

Keywords: Composite membrane; Methanol crossover; Zirconium phosphate; Silicotungstic acid

1. Introduction

Fuel cells are emerging as an alternate energy source for mobile and stationary applications. The successful performance of a fuel cell depends critically on the role of the membranes. Though Nafion® (a perfluorosulfonated polymer marketed by Ms. Du Pont) has been identified as the preferred membrane for PEM fuel cells, various attempts have been made to develop alternate, adaptable and acceptable class of membranes. Nafion® membranes currently employed in hydrogen oxygen fuel cells are not appropriate for use in DMFC since Nafion® exhibits reduced conductivity at low humidity condition and/or at elevated temperatures. In addition considerable fuel crossover takes place. Nafion® based membranes are unstable at temperatures higher than 353 K. These limitations have prompted search for alternate membranes. Various approaches have been made like: (i) modifying perfluorosulfonic acid (PFSA) membranes to improve their water retention properties at temperatures above 373 K by crosslinking [1–5], or by forming composites with hygroscopic oxides, MO_2 (M = Zr, Si, Ti) [6,7] or with inorganic proton conductors [8–13], (ii) by selecting other non fluorinated polymer electrolytes such as sulfonated polyetherketones [14], and sulfonated polyetheretherketones [15,16], sulfonated poly arylene ethersulfone (PES) [17], basic polymers such as, poly(4-vinylpyridine) [18], polybenzimidazole [18]. However, sulfonation of these polymers are not simple, and will demand exacting experimental conditions [19] and (iii) designing inorganic organic composite membranes [20–28]. This has attracted attention, because such composites may show controllable physical properties, such as thermal, electrical and mechanical behavior, by combining the properties of both organic polymers and inorganic compounds (solid inorganic proton conductors). Solid inorganic proton conductors like zirconium phosphates, heteropolyacids (HPAs), metal hydrogen sulfates have dual role of being both hydrophilic and proton conducting. However, HPAs are generally water-soluble. Consequently, a major research objective is to fix the HPAs in stable structure by forming composites [25,29–31] which can maintain their high proton conductivity. Composite matrix reduces the leaching of HPA. The scope of the present study is to investigate a composite membrane made of polyvinyl alcohol (PVA) and zirconium phosphate (α-ZrP) with silicotungstic acid (SWA) as an active moiety. Water insoluble zirconium phosphate was added to suppress crack formation due to the shrinkage caused during drying. It also contributes to protonic conduction through the proton of phosphate moiety and crystalline water thereby

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reducing the humidity dependence on conductivity. The driving force for this attempt is to design newer class of membranes, which may not demand the exacting experimental conditions and critical management of chemical environments that are necessary for the synthesis of membranes like Nafion® and other sulfonated polymers.

2. Experimental

2.1. Materials and membranes preparation

Polyvinyl alcohol (PVA; MW: 125,000), silicotungstic acid (SWA) were obtained from SRL chemicals, orthophosphoric acid (H_3PO_4) was obtained from the E-Merck and zirconium oxychloride ($ZrOCl_2 \cdot 8H_2O$) was obtained from Loba Chemie and were used as received.

2.1.1. Preparation of zirconium phosphate

Zirconium phosphate is prepared by taking 1 M aqueous solution of $ZrOCl_2 \cdot 8\,H_2O$ and it is slowly added to a 10 times excess of 1 M H_3PO_4. The precipitate was washed several times with deionized water, dried 2 h at 368 K and stored at 100% RH and room temperature.

2.1.2. Synthesis of PVA–ZrP–SWA composite membranes

The composite membranes were prepared by sol–gel process. A 10% solution of PVA in water was made by constant stirring at 343 K and to that zirconium phosphate (10 wt%) and silicotungstic acid (10, 20 and 30 wt%) was added and the resultant mixture was refluxed at 343 K for 8 h, to obtain a clear viscous solution. The resulting viscous solution was gelated for 2 days. The film was cast on a clean glass plate with the desired thickness and dried at room temperature.

2.2. Structural characterization

The FT-IR (Perkin-Elmer) spectra for the samples were recorded in the range 400–4000 cm^{-1} at room temperature. X-ray diffraction patterns were collected with a Rigaku D/max 2400 powder diffractometer using a Cu Kα radiation. The thermogravimetric analysis (TGA) was performed on a Perkin-Elmer TGA (Delta Series TGA 7) instrument at a heating rate of 20 K min^{-1} in air. The differential scanning calorimetry (DSC) measurements were performed on the dried samples, in the range of temperature between 323 and 823 K using a Perkin-Elmer DSC-7 instrument. Scanning electron microscope (FEI, Model: Quanta 200) was used to observe the microstructures of the dried membranes.

2.3. Water uptake

The water uptake of the composite membrane was determined by measuring the change in the weight after the hydration. The membrane was first immersed in deionized water for 2 h. Then the membrane was weighed quickly after removing the surface attached water to determine the weight of wetted membrane (W_{wet}). The weight of the dry membrane (W_{dry}) was determined after drying. The percentage of water uptake was calculated by using the following equation:

$$\text{water uptake}\,(\%) = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100.$$

2.4. Swelling

The surface swelling characteristics were determined by measuring the change of the membrane geometrical area upon equilibrating the membranes in water at room temperature for 2 h. The swelling ratio was calculated by the following equation:

$$\text{swelling}\,(\%) = \frac{A_{\text{wet}} - A_{\text{dry}}}{A_{\text{dry}}} \times 100$$

where, A_{dry} and A_{wet} are the area of dry and wet samples, respectively.

2.5. Ion-exchange capacity (IEC)

The ion exchange capacity of the membranes was determined through an acid–base titration. The dry composite membrane was immersed in 50 ml of 1 M sodium chloride aqueous solution for 24 h in order to extract all protons from the membrane. After taking out the membrane, electrolyte solution was titrated with 5 mM sodium hydroxide solution using phenolphthalein as an indicator. The ion exchange capacity (IEC) was calculated using the following equation:

$$\text{IEC} = \frac{V \times M}{W_{\text{dry}}}$$

where IEC is the ion exchange capacity (mequiv. g^{-1}), V the added titrant volume at the equivalent point (ml), M the molar concentration of the titrant and W_{dry} is the dry mass of the sample (g).

2.6. Proton conductivity

Proton conductivity was measured by an ac impedance technique (Autolab, PGSTAT 30) using two probe method, where the ac frequency was scanned from 1 MHz to 10 Hz at voltage amplitude of 5 mV. The proton conductivity (σ) of the samples in the longitudinal direction was calculated from the impedance data, using the relationship $\sigma = d/Rtl$, where d is the distance between the electrodes, t and l are the thickness and width of the films, respectively, and R was derived from the low intersect of the high frequency semi-circle on a complex impedance plane with the Re(Z) axis, where Re refers to 'Real' in the complex impedance plane. Prior to the proton conductivity measurements, membranes were immersed in deionised water for 24 h to attain hydration equilibrium. Fully hydrated membranes were sandwiched in a Teflon® conductivity cell equipped with Pt foil contacts and the impedance was measured by placing the cell in a temperature-controlled chamber under a temperature range of 303–373 K. Constant humidity was maintained at 60% RH by using saturated sodium nitrite and it was sensed by a