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Fabrication and electro chemical properties of poly vinyl alcohol/para toluene sulfonic acid membranes for the applications of DMFC

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ABSTRACT

The novel acid–base membranes composed of para toluene sulfonic acid (pTSA) as an acidic compound, and poly vinyl alcohol (PVA) as a basic compound were fabricated. The morphological and structural properties of the prepared membranes were analyzed by scanning electron microscopy and Infra red spectroscopy. Inclusion of Glutaraldehyde (GLA) and para toluene sulfonic acid (pTSA) promotes the amorphous character of a polymer which causes the free volume for the movement of ions. Thermal and mechanical stability of the acid–base membranes were influenced by the crosslinking agent glutaraldehyde. By the suitable charge carriers of pTSA, hydrophilic channels were promoted for the composite membranes which ensure the ionic conductivity. A high ionic conductivity-methanol permeability selectivity ratio obtained for the prepared PVA/pTSA membrane influences its viable application in direct methanol fuel cells.

1. Introduction

Direct methanol fuel cells are fascinating the world by its favorable characteristics such as portability, low temperature operation, high efficiency and innocuous waste emission etc. [1–2]. Commercially available membrane Nafion is widely used in fuel cell applications due to its high ionic conductivity, elevated thermal and chemical stability. But a decrease in the ionic conductivity beyond 80 °C and high methanol permeability of Nafion eventually decrease the fuel cell efficiency [3]. More over high cost of the Nafion membrane impedes the market penetration of DMFC. The research and developmental activities are focusing its keen interest on the development of alternative polymer electrolyte membranes to wide open the doors for commercialization.

Acid–base composite membrane is an emerging research field, which has opened the possibility of tailoring new materials for the high electro chemical properties. Most of the polymer electrolyte membranes possess sulfonic acid as a functional group for the immurement of ionic conductivity and other electro chemical properties. The high ionic conductivity of the sulfonic acid group is achieved by their strong attractive forces with hydrogen ions. In these membranes, proton transfer is expected to be associated with the water molecules. In order to improve its affinity towards water than methanol, it is being incorporated with the polymer which has –OH– as a functional group. Poly vinyl alcohol is a cheap polymer and been extensively used in textile sizing, adhesives, desalination, food wrappings and oxygen resistant films [4]. The high selectivity of water to alcohol of PVA reduces the methanol permeability. Besides, the functional –OH groups of PVA have the potential for cross-linking which satisfy the stability parameter of the membranes [5]. Many studies were explored on PVA such as poly(vinyl alcohol)/poly(styrene sulfonic acid) blend [6], poly(vinyl alcohol)/poly(styrene sulfonic acid–co-maleic acid)blend [7], poly(vinyl alcohol)/sulfo succinic acid/silica [8], poly(vinylalcohol)/poly(2-acrylamido-2-methyl-1-propanesulfonicacid) [9]. So far, to the best of our knowledge no attempt has been made on the development of composite polymer electrolyte membranes based on polyvinyl alcohol and para toluene sulfonic acid. In the following account fabrication, structural characterization and electro chemical properties of the prepared PVA/pTSA acid–base composite membranes have discussed. It focuses low cost, elevated chemical and thermal stability, high proton conductivity and lower methanol permeability to satisfy the needs of DMFC.

2. Experimental

2.1. Materials

Poly vinyl alcohol (Aldrich, Molecular weight: 90,000), para toluene sulfonic acid (Aldrich, Molecular weight:190.22), Glutaraldehyde (Junsei chemical company) were purchased and utilized.

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Table 1
Experimental conditions and mechanical behavior

Sample name	PVA (wt.%)	pTSA (wt.%)	Elongation (%)	Tensile strength (MPa)
PV	10	–	68	30.65
PVT1	10	2.5	60	27.29
PVT2	10	5	52	25.31
PTV3	10	7.5	48	21.90
PVT4	10	10	39	20.54

2.2. Preparation of the membrane

Polyvinyl alcohol was dissolved in water and magnetically stirred for 2 h at 90 °C. To this mixture, a desired amount of para toluene sulfonic acid was added and magnetically stirred for 6 h (Precise experimental conditions and nomenclatures are given in Table 1). Then the mixture was cast as a membrane and kept in an oven at 90 °C for 16 h to remove the solvent. The dried membranes were then crosslinked in a glutaraldehyde bath (the mixture contains 5 vol.% of glutaraldehyde, 90/10 vol.% of IPA/water and 1 vol.% of hydrochloric acid as a catalyst) for a period of 15 min. After crosslinking for 15 min, the membranes were stored in distilled water for 20 h to remove traces of un reacted glutaraldehyde remaining in the membrane, if any, and to prevent further crosslinking. Then the membranes were dried and subjected for the following characterizations.

2.3. Characterizations

2.3.1. Morphological and structural characterizations

The surface morphology of the membranes was analyzed by JSM-5410LV scanning electron microscopy (SEM) under vacuum combined with energy dispersive X-ray spectroscopy (EDX). The distribution of sulfur over the surface of the membrane was determined by X-ray mapping. XRD measurements were performed using a conventional diffractometer (Rigaku D/max 2500 VPC) that employs copper K_a radiation and the scanning angle ranged from 10° to 70°. FT-IR spectra of the samples were recorded at room temperature using Jasco FT-IR-300 E in the region 400 to 4000 cm^{-1}.

2.3.2. Thermal gravimetric analysis

Thermal gravimetric analysis was carried out using Perkin Elmer instrument. The TGA measurements were carried out under a nitrogen atmosphere with a heating rate of 20 °C/min from 30 to 800 °C.

2.3.3. IEC measurement

The prepared hybrid membranes were placed in 1 M NaCl solutions for overnight to exchange all the H^+ with Na^+. The proton content in the salt solution was determined by titration with 0.01 N NaOH solution using phenol red as the endpoint indicator.

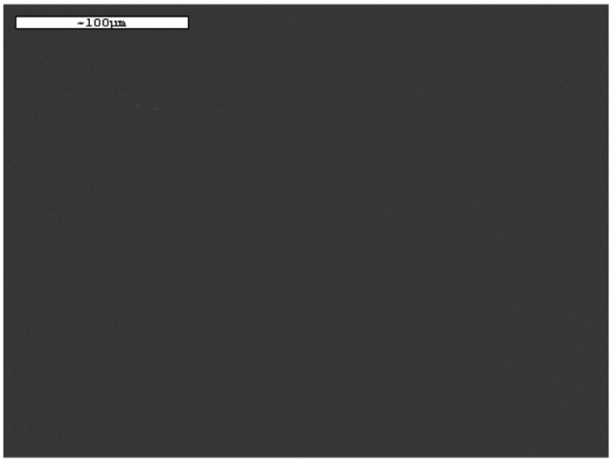

Fig. 1. SEM image of PVT4 membrane.

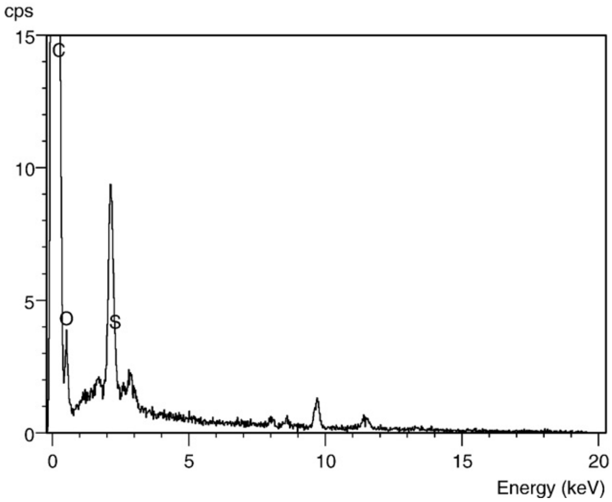

Fig. 2. EDX picture of PVT4 membrane.

2.3.4. Liquid uptake

The membranes were soaked in DI water/2 M methanol for 8 h for the determination of liquid uptake. After removing the excrescent solution from the surface of the polymer electrolyte, the membrane was dried for 1 h and weighed.

$$\text{Water uptake}(\%) = \left[\left(W_{\text{wet}} - W_{\text{dry}}\right)/W_{\text{dry}}\right] \times 100$$

where W_{dry} and W_{wet} denote the mass of dried sample and wet samples respectively.

2.3.5. Mechanical behavior

The mechanical behavior of the prepared membranes was measured at room temperature by means of a universal tensile machine (Instron model 5565, Lloyd).

2.3.6. Ionic conductivity

Four-probe conductivity measurements were taken for all the membranes using the BekkTech conductivity test cell in conjunction with a PGZ 301 Dynamic EIS Voltammeter. The BekkTech cell functioned as the hydrogen pump with sense wires set up along the transverse direction. Temperature and humidification were controlled using the Globe Tech Computer Cell GT fuel cell test stand. A dew point system consisting of temperature regulation and a DI water inlet controls the humidity within the testing chamber. Four-point conductivity measurements involved the use of four electrodes which were placed around the cell to obtain resistance values. Two electrodes were attached to the current collectors of the test cell and the other two electrodes were attached directly to platinum sense wires to measure the potential drop across the membrane. Strips of membrane material approximately 5 cm length and 2 cm width were cut and placed into the BekkTech conductivity test cell in order to test the ionic conductivity. Length, width and thickness of samples were recorded in order to calculate conductivity. Here, an alternating current (AC) was passed through two outer electrodes and the resistive drop of the sample was obtained from an ac potential difference between the two inner electrodes. A pre-installed Lab view controls the entire system and obtains data by using the following equation and that is reported in mS/cm.

$$\sigma = L/(R \times W \times T)$$

where σ is the conductivity, L is the length (cm) parallel to the ion flow, R is the resistive drop (ohm) between center two electrodes, W is width (cm) and T is the thickness (cm).