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Hybrid blend membrane using PVA–g–PMA for direct methanol fuel cell applications

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In the present study, a novel PVA–g–PMA hybrid membrane was developed for application in direct methanol fuel cell (DMFC). Maleic anhydride (MA) was grafted on polyvinyl alcohol (PVA) both ionically and chemically using potassium persulfate (KPS), for the first time. The PVA–g–PMA thus synthesized was then blended with 3–Amino–4–[3–(triethylammonium sulfonato)phenyl amino]phenylene hydrochloride. The prepared membranes were characterized by FT–IR, TGA. 0.0104 S/cm of proton conductivity was found for the membrane. The ion exchange capacity was found to be 2.175 meq/g and the water uptake capacity as 14.9%. The single-chamber fuel cell power density was higher (34.72 mW/cm^2) and current density (62.11 mA/cm^2) when compared to Nafion 117 membrane.

Keywords: polyvinyl alcohol, maleic anhydride, direct methanol fuel cell, ion exchange capacity, proton-conducting membrane

1. INTRODUCTION

In the DMFC, perfluorinated membranes like Nafion®offer high proton conductivity but cause problems like high methanol cross-over and thus result in poor performances (Gouda et al., 2020; Kim et al., 2006; Yang et al., 2006). Therefore recent advances are being made to develop substitute materials that are as conductive as Nafion, but more resistant to methanol. PVA is a polymer with a low methanol permeability of two orders of magnitude lower than Nafion. The literature shows that bis-conjugated amine groups of the monomers need to be synthesized before the PBI polymer can be prepared using the chemical reaction of the conjugated amine with an acid group (Jouanneau et al., 2007). After synthesizing the grafted polymers i.e. PVA-grafted maleic acid (PVA–g–PMA), they were further blended to modify with compound ATSPP, which gave imidazolium group after reacting with an acid functional group on heating (Duangkaew and Wootthikanokkhan, 2008; Kang et al., 2002; Kulkarni et al., 2008).

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2. EXPERIMENTAL SECTION

Dimethyl sulfoxide (DMSO) and analytical grade acrylic acids have been procured from S.D. Fine Chemicals (Mumbai, India) and Poly vinyl alcohol (PVA) from Loba Chemie.

The 3–Amino–4–[3–(triethylammonium sulfonato)phenyl amino]phenylene hydrochloride (ATSPP·2HCl) was synthesized using 1–Chloro 2–nitro benzene. In the first step, 1–Chloro 2–nitro benzene (15.42 ml, 132 mmol), metanilic acid (28.7 g, 165 mmol), triethylamine (45 ml, 230 mmol), and DMSO (120 ml) were added in a 500 ml conical flask at 120 °C for 6 hours. The yellow powder obtained was filtered from the solution and recrystallized in ethanol. 50% hydrazine hydrate solution (200 ml) was added and allowed to stand for 2–3 hours (step II). The literature reveals that bis-conjugated amine groups of the monomers with different structures need to be synthesized before the PBI polymer can be prepared using the chemical reaction of the conjugated amine with an acid group. Then a 100 ml of 50% hydrochloric acid solution was added to get the precipitate. The off-white precipitate was filtered to get nearly 70 gm of 3–Amino–4–[3–(triethylammonium sulfonato)phenyl amino]phenylene hydrochloride. Figure 1 shows the FT–IR spectrum of the compound synthesized. The IR peaks (cm^{-1}) of C–H are represented by 2625, the N–H bond is shown to occur at 3403, the NH in NH_2 by 2058, SO_3^- group by 1029. A large number of peaks in the region 730–793 represents the ortho and the meta disubstituted benzene rings (Duangkaew and Wootthikanokkhan, 2008; Jouanneau et al., 2007; Kang et al., 2002; Kulkarni et al., 2008). In the synthesis, 5 gm of PVA was dissolved in 85 ml of distilled water at 70 °C using a stirrer. After some time, KPS (0.5 g, 0.001 mol) was added as an initiator to which MA (5 g, 0.04 mol) was added and the reaction proceeded for 5 hours at 70 °C. To the above solution, 1.5 g of ATSPP dissolved in 10ml of water was added and this polymer solution was spread on a glass plate for membrane casting and dried at room temperature and then at 180 °C for a period of two hours for cross-linking at the carboxylic groups of the grafted chains.

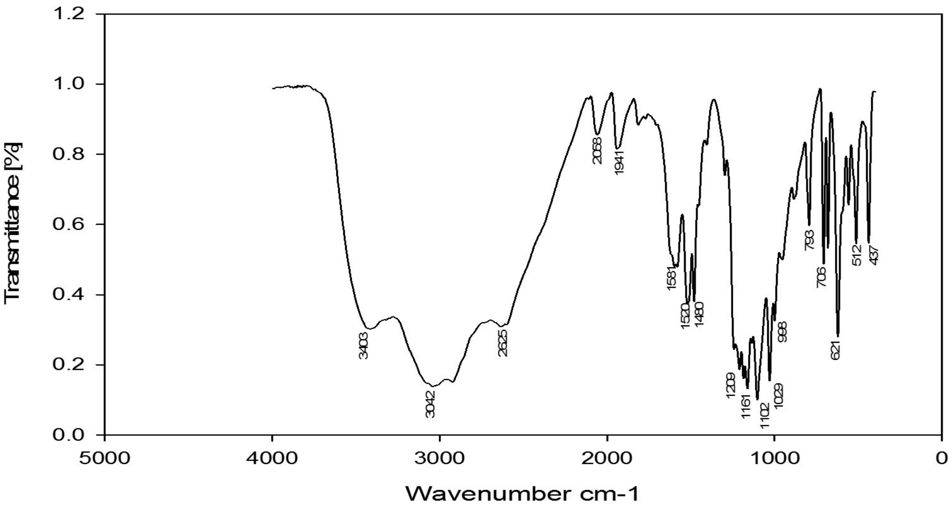

Fig. 1. FT–IR of ATSPP showing the characteristic peaks (in cm^{-1}) of N–H group (3403), C–H (2625), NH in NH_2 (2058) and SO_3^- group (1029)

The FT–IR spectrum of PVA-g-MA/C2 membrane is shown in Figure 2. The characteristic peak at 1727 cm^{-1} represents the ester group, which evidences the cross-linking reaction between hydroxyl groups of PVA and maleic anhydride. The absorbance at 1039 cm^{-1} represents the sulfonic acid group and the peaks at 1642, 1247 cm^{-1} represent the formation of C=N bond, which confirms the formation of imidazole group. The absorption band at 3427 cm^{-1} occurs because of self-associated N–H interaction of PBI chains. Thermogravimetric analysis of the membrane was carried out from 50-800 °C in the atmosphere of nitrogen, keeping heating rate of 10 °C min^{-1}. The TGA curve obtained for PVA–g–PMA-ATSPP membrane is as shown in Figure 3. The weight loss of PBI membrane occurred in the region of

50–260 °C and was due to loss of both free and bound water molecules. The TGA curve of the membrane material retained 20% of residual weight beyond 700 °C. The impedance was measured using Agilent E4980A Precision LCR meter in the frequency range of 20 Hz to 1 MHz was used. The MEA was assembled in the fuel cell and operated at 90 °C using 2M methanol and atmospheric air. The methanol flow rate was maintained at 2 ml/min using a peristaltic pump on to the anode side while on the cathode side the atmospheric air was pumped at 500 cm^3. The Voltage–Current (VI) and Power density–Current (PI) characteristics were determined after steady state was reached as shown in Figure 4.

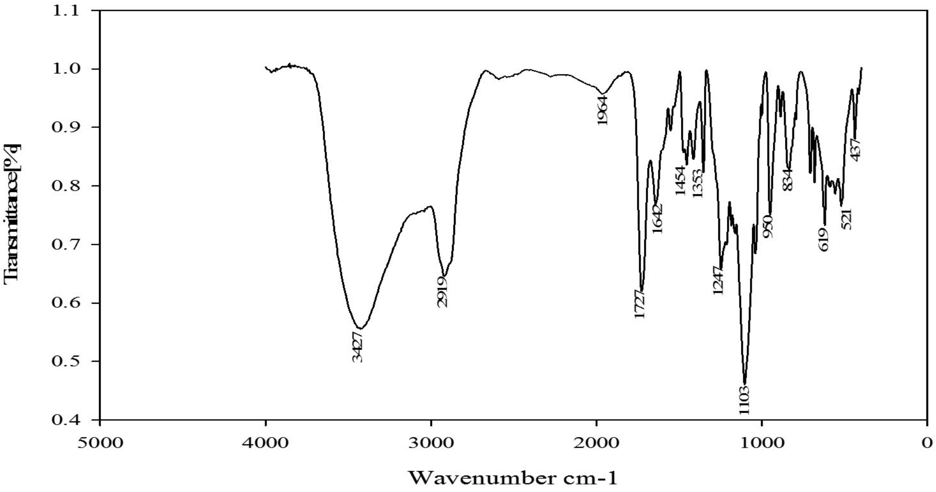

Fig. 2. FT–IR spectrum of PVA–g–PMA/ATSPP membrane showing the characteristic peaks (in cm^{-1}) of N–H group (3427), C–H (2919), SO_3^- group (1039), C=N (1642, 1247) and C–O (1727)

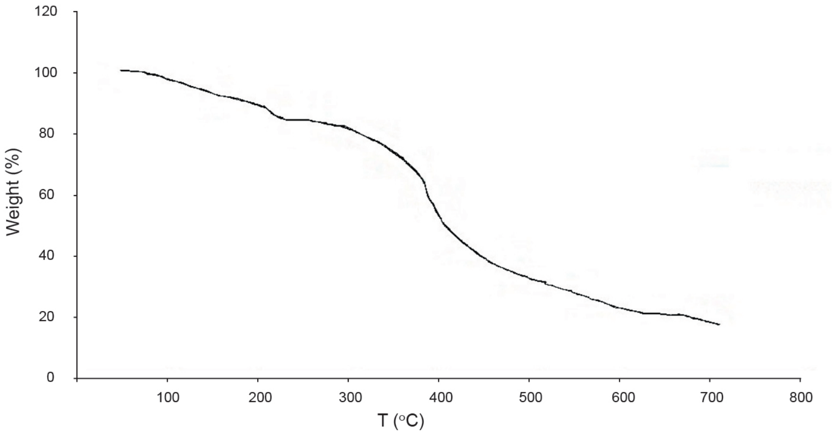

Fig. 3. TGA curve for PVA–g–PMA-ATSPP membrane

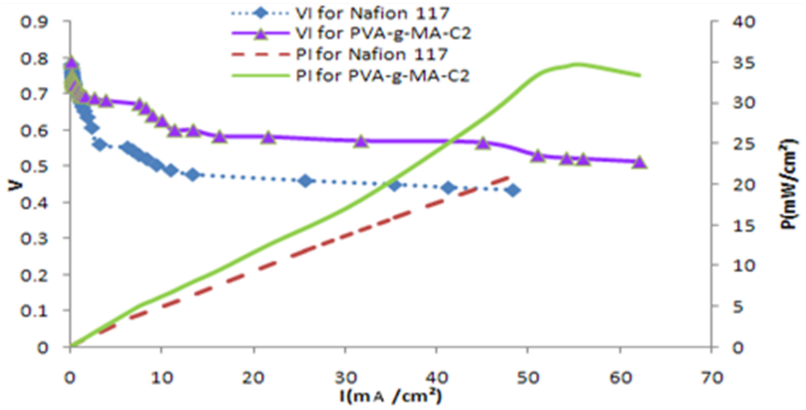

Fig. 4. VI and PI characteristics for PVA–g–PMA-ATSPP (C2) and Nafion 117

3. CONCLUSIONS

All the experiments were performed at room temperature. 0.0104 S/cm of proton conductivity was measured using the four-point probe method. The ion exchange capacity was found to be 2.175 meq/g and the water uptake capacity was 14.9%. The membrane gave more power density (34.72 mW/cm^2) and current density (62.11 mA/cm^2) as compared to Nafion 117 giving 21.025 mW/cm^2 of power density and 48.33 mA/cm^{2}of current density under the same experimental conditions. Experimentally, the membrane revealed an ion exchange capacity of 2.175 meq/g and a water uptake capacity of 14.9%. Comparison of the proposed synthesized membrane and Nafion 117 has been done using DMFC.

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