

Polyvinyl Alcohol (PVA) Supported Tin Phosphate (SnP/PVA) Ion Exchange Membrane

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Abstract—A polyvinyl alcohol (PVA) impregnated with tin phosphate (SnP/PVA) composite ion exchange membrane was prepared to be used as electrolyte polymeric membrane in direct methanol fuel cell (DMFC). Homogenous Poly vinyl alcohol (PVA) gel was prepared in distilled water. Tin phosphate sol was prepared by mixing sol of trisodium orthophosphate and stannic chloride. The membrane have been prepared by blending tin phosphate sol into polyvinyl alcohol gel and then by cross linking the PVA chains with glutaraldehyde (GA). The resulting mixture was casted on acrylic sheet with controlled thickness. The doping of ion exchanger in polymer matrix was confirmed with Fourier transform infrared spectroscopy (FT-IR) and Scanning electron microscopy (SEM). The Prepared membrane was characterized in terms of its electrochemical property i.e. ion exchange capacity (IEC). An IEC count (1.06 meqg^{-1}) of prepared membrane was higher to that of Nafion.

1. INTRODUCTION

Ion exchange membranes (IEMs), as electrolyte, have been used in energy devices like fuels cells. The research in fuel cells gained momentum due to increased demand of energy and environmental concerns. Nowadays, DMFC employs Nafion which is widely accepted for commercial applications because of its high proton conductivity, good mechanical, thermal and chemical stability [1]. Major problems with Nafion are its high cost, high methanol permeability and decrease in proton conductivity at high temperature [2, 3]. Conductivity at 80 °C is reduced by more than 10 fold relative to that at 60 °C. The approach of making composite membrane is beneficial in improving the properties of polymer electrolyte membrane as the desired properties can be had in one membrane instead of two. Inorganic material provides high thermal stability, ion exchange capacity (IEC) and organic support gives better chemical and mechanical stability. Poly vinyl alcohol (PVA) has potential to be used as polymeric support due to its good mechanical properties, chemical stability, low cost, film forming ability, high hydrophilic behavior [4, 5]. But, PVA membrane needs modification as it does not have any negative charged ions. Ion exchange membranes are synthesized by impregnating trivalent metal acid (TMA) salts in polymer like phosphotungstic acid (PWA) and polyvinylidene fluoride (PVDF) [6]. In this work, Tin phosphate belonging to TMA was chosen as ion exchanger

and PVA as organic support. We have prepared composite ion exchange membrane by blending tin phosphate into cross linked PVA. Prepared membrane was characterized using physical techniques (FT-IR and SEM) and electrochemical properties (IEC).

2. EXPERIMENTAL

2.1 Materials

Stannic chloride (SnCl_4), trisodium orthophosphate (Na_3PO_4) and hydrogen chloride were purchased from Fisher scientific, India. Poly vinyl alcohol (PVA) was purchased from HiMedia laboratories Pvt. Ltd. Other chemicals like sodium chloride, sodium hydroxide, sulphuric acid and potassium hydroxide were purchased from Rankem Pvt. Ltd., India. Double Distilled water was used for all the experiments.

2.2 Synthesis (preparation of SnP/PVA)

Poly vinyl alcohol (PVA) 5 wt. % was first dissolved in water to make transparent homogenous PVA gel. Tin phosphate sol was prepared by adding 0.2 M trisodium orthophosphate to sol of 0.2 M of stannic chloride. Glutaraldehyde (GA) of 2 ml and HCl were added to PVA solution for cross linking and solution was stirred for 1 h at a temperature of 40 °C. Blending was achieved by adding sol of tin phosphate to PVA gel. The resulting mixture was stirred for 3 h and was casted on acrylic sheet with controlled thickness. The resulting membrane was dried for 10 h in oven at 70 °C to remove solvent. The prepared membrane was peeled off and kept in distilled water before using it in the experiments.

2.3 Characterization Methods

Fourier transform infrared spectroscopy (FT-IR) was used to identify the formation and presence of tin phosphate in polymer PVA. FT-IR spectra was obtained using Agilent-6700 over a wave number range of $500\text{--}4500 \text{ cm}^{-1}$. The morphology and surface defects of the membrane was investigated using scanning electron microscopy SEM (Hitachi, model; S-3600N) with a potential of 10 kV under magnifications ranging from 200x to 5000x. The Ion exchange capacity (IEC) of prepared membrane was determined using titration method.

About 0.2 g of membrane was immersed into 1 M HCl and boiled for 6 h to convert it into H^+ form which was further soaked and stirred in 0.5 M aqueous NaCl for 18 h. NaOH was employed to back titrate the NaCl solution which has been neutralized by the SnP/PVA membrane. Phenolphthalein was used as an indicator.

3. RESULTS AND DISCUSSIONS

FT-IR spectrum of the SnP powder is shown in Fig. 1(a). SnP has three characteristic peaks at 1064.75 cm^{-1} , 944 cm^{-1} , 657 cm^{-1} . Strong peak at 1067 cm^{-1} was due to P-O bonds in PO_4 groups. Phosphate ion has frequency in between $1000\text{--}1100\text{ cm}^{-1}$ [7]. Peak obtained at wavenumber 657 cm^{-1} is due to Sn-O bonds. Peak visible at 944 cm^{-1} was due to P-O-P Bridge [8]. This confirms the formation of tin phosphate. The FT-IR spectrum of the SnP/PVA is shown in Fig. 1 (b). Peaks at 3332 cm^{-1} and 1664 cm^{-1} were attributed to asymmetric and symmetric hydroxo-OH and aqueous-OH. Band at 2920 cm^{-1} and 2851 cm^{-1} was attributed to C-H stretching related to aldehydes and band at 1735 cm^{-1} was due to presence of C=O. Peak at 1093 cm^{-1} due to the ether (C-O) and the acetal ring (C-O-C) bands formed by the cross linking reaction of PVA with GA [9-11]. This infers the formation of cross linked PVA. The other prominent peaks at 1071 cm^{-1} , 948 cm^{-1} and 675 cm^{-1} are due to presence of SnP ion exchanger. Thus FT-IR results confirmed the PVA cross-linking as well as impregnation of tin phosphate tungstate over the PVA film.

The morphology of the PVA film and SnP/PVA composite membrane was investigated by scanning electron micrographs, which is represented in Fig. 2. It gives the information of surface topology and defect in the structure. Pure PVA exhibited good and smooth surface as seen in Fig. 2 (a).

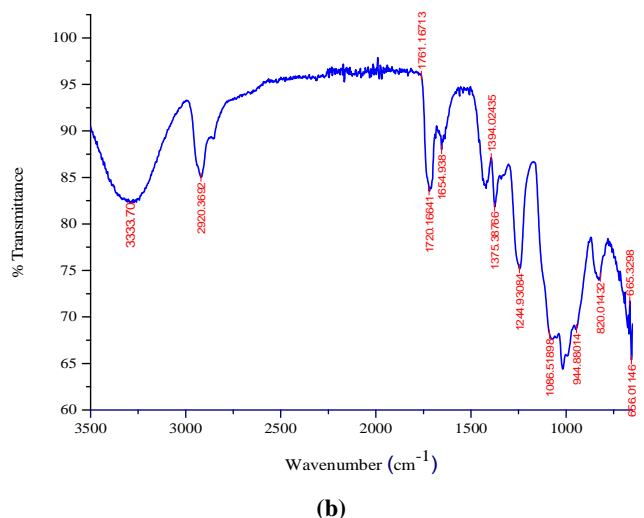
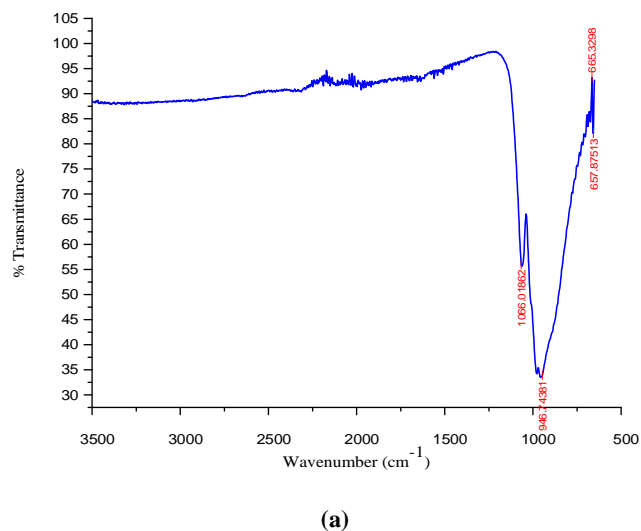


Figure 1: FT-IR spectra (a) for the SnP powder and (b) synthesized SnP/PVA composite membrane.

Micrographs of the composite membrane are different from that of polymeric support PVA. Before filling ion exchanger into PVA matrix it showed particle free surface and after doping ion exchanger over PVA matrix can be observed in micrographs. Thus indicating dispersed presence of SnP particles into cross-linked PVA matrix. All micrographs even up to 5000x did not show any evidence of cracks in membrane.

Ion-exchange capacity (IEC), measures the ability of a membrane to undergo replacement of ions which are loosely embedded in the structure with oppositely charged ions present in the surrounding environment. It is an important parameter which links directly with the ionizable functional groups present in the membrane. IEC of tin phosphate is 3 meqg^{-1} . The IEC of synthesized SnP/PVA membrane was 1.06 meqg^{-1} higher than the Nafion-117 (0.9 meqg^{-1}). Higher IEC indicates higher conductivity as more ion exchangeable sites can be used to transport ions.

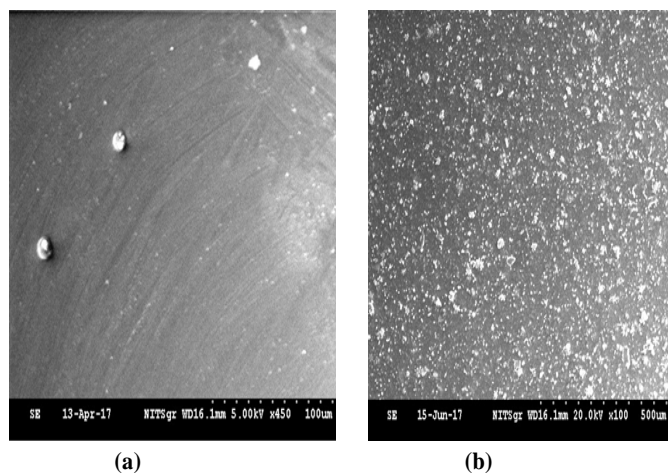


Figure 2. SEM images of (a) Pure PVA film at 450X, (b) synthesized SnP/PVA membrane at 100X.

4. CONCLUSION

Cation exchange membrane SnP/PVA prepared have potential in DMFC application. Cross linking in PVA matrix and formation of SnP was confirmed by FT-IR which indicated the presence of Tin phosphate into PVA matrix. Further micrographs validated the presence of ion exchangers in the membrane. The result showed that the prepared membrane exhibited better electrochemical properties.

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