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SnO_2 nanoparticles loaded Cashew Nut Shell resin modified polyvinyl alcohol nanocomposite membranes for PEMFCs

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Abstract:

In this work, SnO_2 nanoparticle dispersed Cashew nut shell liquid blended polyvinyl alcohol membrane was developed through dialdehyde crosslinking of PVA and CNSR, in addition to the preamble of mercapto succinic acid into the double bonds of CNSR. The CNSR was blended in polyvinyl alcohol at 10 wt% using DMSO as solvent. The blend membranes were analysed using SEM and FTIR analysis, further, 1%, 2% and 3% SnO_2 NPs loaded PVA with CNSR (10wt%) nanocomposite membranes were prepared and characterized for their ion exchange capacity, swelling ratio, water uptake, oxidative stability and proton conductivity. The hydrophilic nature of the PVA was retained even after blending with CNSR with slight reduction in water uptake ratio. The incorporation of carboxylic acid groups through the rection between CNSR and mercaptsuccinic acid was found to enhance the ion exchange capacity. The PVA/CNSR found to have superior ion exchange capacity, water uptake and oxidative stability than that of neat polvinylalcohol membrane. The examination on proton exchange capacity reveals that the obtained PVA/CNSR has higher proton conductivity with a highest value of 0.011S cm^{-1}.

Keywords: Proton exchange membrane fuel cell, Polyvinyl alcohol, Cashew Nut Shell Resin, SnO_2 NPs, Thermal stability, Polymer nanocomposites.

1. INTRODUCTION

Significant exploration of energy production devices are aimed at investigating new route to minimize the price, increase effectiveness, and lower the footprint of power generation systems on the environment. Fuel cell encompass promising advantages that warrant the expansion of a sustainable power generation system for future energy demand. Amongst the various types of fuel cell, the Proton Exchange Membrane Energy Cell has entered quick development in present decade owing to their high effectiveness, low environmental impact and low-temperature operation [1-3]. Among the synthetic polymers used in PEMFCs, Nafion membranes and polyfluorosulfonate ionomer membranes are the familiar marketable films engaged in the PEMFC owing to their higher proton conductivity [4]. Nonetheless, usuage of these polymers are restricted by high price tag and specific operation temperatures [5]. A broad choice of accoutrements as a cover for Nafion has been reported [6-8]. A foremost progress in this view is witnessed for sulfonated polymers such as sulfonated poly (phenylene oxide) (SPPO) [9], sulfonated poly ether ether ketone (SPEEK) [10], sulfonated polyimide [11] and sulfonated poly ether sulfone (SPES) [12].

A huge string of commercial polymers can be employed as matrix in the manufacture of PEM, among them polyvinyl alcohols (PVA) are recognized for their superior characteristics such as: and high impact and tensile strength, stability during exposure of solvents oils and alkalis, being compatible to

bioenvironment, bio-inertia, hydrophilicity and ionic conductivity made them suitable for industrial applications [13-18]. However, in order to use it in PEMFCs the enhancement of its properties is essential. Blending of different polymers is well thought-out as an valuable method to alter and ameliorate the performance of commercial polymers [19]. It is also demonstrated that the PEM made by blending two different sulfonated polymers redounded in miscible structure exhibiting excellent performance and high proton conductivity [20]. The synergistic properties of individual polymers will produce the membranes with desirable performance [21-22].

So as to ameliorate the characteristics of PEMs, the amalgamation of PVA and CNSR was planned, in this work. An oily material uprooted from cashew nut shells (CNSR) is admixture of phenols [23-25], with the most significant ingredients such as cardanol, cardol and anacardic acid [26-28]. The phenolic OH group of CNSR is anticipated to crosslink with PVA through dialdehyde acetal formation. In addition, the double bond present in the CNSR is reacted with mercaptosuccinic acid to incorporate carboxylic acid functionality, as required for proton conduction. To the best of our knowledge the CNSR has not been blended with PVA through dialdehyde crosslinking so far. In addition, we have prepared 1%, 2%, 3%, of SnO_2 NPs incorporated PVA/CNSR nanocomposite membranes and the PEMFC performance was studied at 100 °C.

2. EXPERIMENTAL SECTION

2.1 Materials

1, 4 Dibromo butane, $SnCl_2.2H_2O$, p-Hydroxy benzaldehyde, $CHCl_3$, and Dimethyl sulfoxide were procured from Avra chemicals. KI, NaOH Ammonium acetate (AA), Urea, were purchased from Himedia. Concentrated Sulfuric acid, Ferrous ammonium sulfate (FAS), Glacial CH_3COOH, 30% H_2O_2, and Phenolphthalein indicator were acquired from SD fine chemicals. CNSR is obtained from Sathiya cashews Pvt. Ltd., Chennai, India

2.2 Preparation of SnO_2 nanoparticles and 4, 4'-(butane-1,4-diylbis(oxy))dibenzaldehyde (DiAl)

The preparation of SnO_2 nanoparticles and DiAl was carried out as per the procedure reported in our earlier studies [29].

2.3 Preparation of PVA/CNSR blended membrane

Polyvinyl alcohol and CNSR blend films was prepared by solution casting method followed by solvent evaporation. Dope solution was prepared by taking 18 % of PVA/CNSR polymer and 82% of DMSO. A compositions of 5, 10 and 15% of CNSR-SA (see Scheme-1) and PVA were added with DMSO and stirred for 12 hours and then DiAl were added. The contents are kept at ultrasonication for 1 h at 27 °C to obtain a homogenous solutionand casted on a glass plate through doctor blade method. The membrnae was dried for 48 h and thicknesses was measured and cut into required dimension with a clean scissor.

2.4. Preparation of SnO_2 NPs doped crosslinked PVA/CNSR membranes

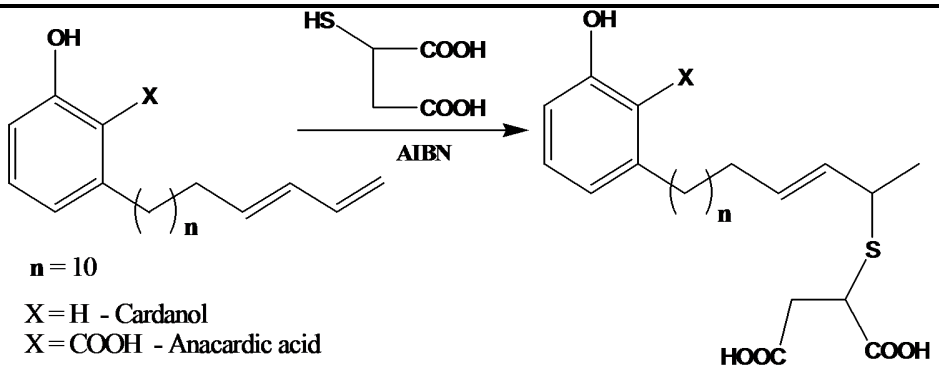
SnO_2 nanoparticle was added into the above solution of PVA/CNSR (10wt%) to maintain 1%, 2%, and 3wt % with respect to polymer weight, and a PVA/CNSR without SnO_2 nanoparticle was also casted. The contents are kept at ultrasonication for 1 h at 27 °C to obtain a homogenous solution and casted on a glass plate through doctor blade method. The membrnae was dried for 48 h and thicknesses was measured and cut into required dimension with a clean scissor.

2.5. Characterization

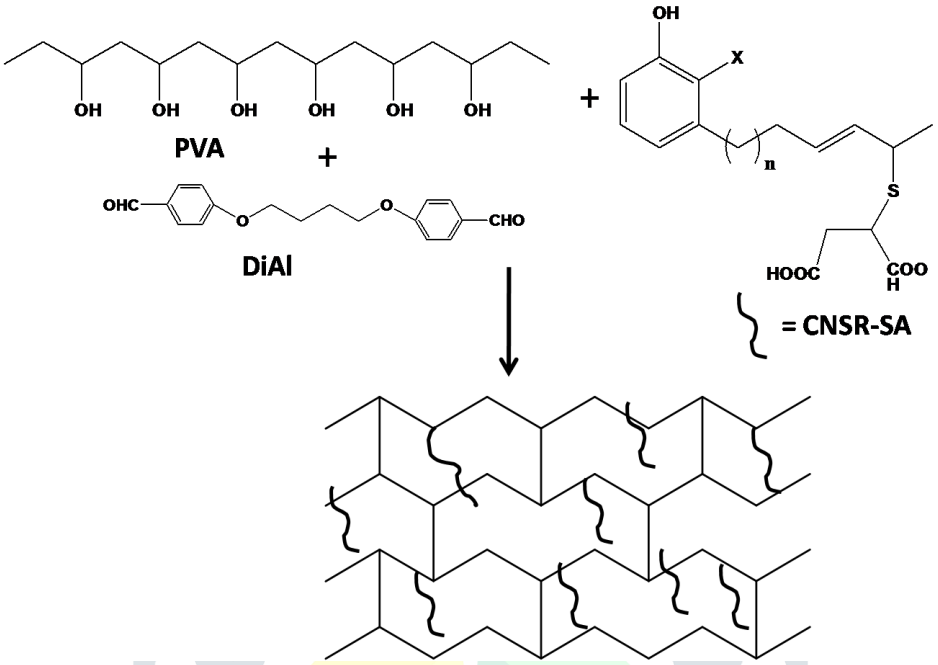
A Bruker Spectrometer was used to record infrared spectra of solid PVA/CNSR polymer samples within wave number region of 4000–400 cm^{-1}, at RT. The morphology of PVA/CNSR and SnO_2/ PVA/CNSR composites were analysed with the help of scanning electron microscopy (SEM), Hitachi, S-3400N 15 kV. The details of the characterization methods for the determination of swelling ratio (SR), water Uptake (WU), oxidative Stability, proton conductivity (PC) and ion exchange capacity (IEC) are described in our earlier publications [29-32].

3. RESULT AND DISCUSSION

The functionalization of CNSR with mercaptosuccinic acid has been done as given in the scheme-1, the product was purified and blended with PVA to prepare PVA/CNSR blend matrices. The PVA was made into water insoluble by crosslinking procedure using the reaction of dialdehyde and hydroxyl of PVA through the formation of acetal and blending of PVA and CNSR has been illustrated in scheme-2.



Scheme-1. Functionalization of CNSR with mercaptosuccinic acid.



Scheme-2. Crosslinked polyvinyl alcohol and CNSR network matrices

3.1 FTIR analysis

The FTIR spectrum of PVA/CNSR and PVA membrane is depicted in Figure 1. The stretching vibration corresponding to hydroxyl group is observed at 3000 to 3400cm^{-1} in FTIR of both PVA and PVA/CNSR samples. Aromatic C-H stretching vibration is observed at 3009cm^{-1} in Fig 1b, confirms the presence of aromatic ring of Cardanol and Anacardic acid. The absorption band 1596cm^{-1} coresponding to C=C stretching frequency which confirms the presence of alkene double bond present in Cardanol and Anacardic acid.

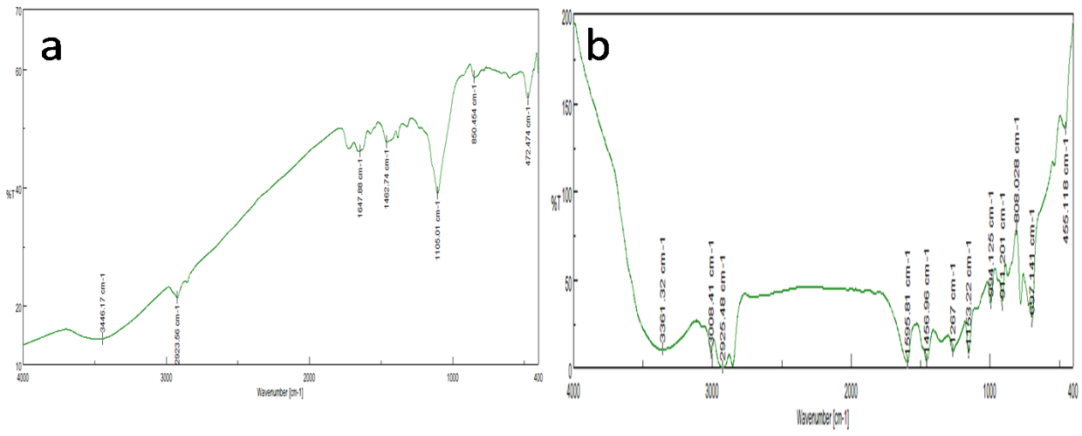


Fig. 1 FTIR spectra of (a) PVA and (b) PVA/CNSR

3.2 Scanning electron microscope (SEM)

The microstructures of PVA, PVA/CNSR and SnO_2/PVA/CNSR nanocomposites were studied by SEM and are publicized in figure 2 (a-c). The Fig.2a indicates a smooth and fractured surface morphology of PVA film. The Fig.2b reveals globular microstructure of PVA/CNSR fractured surface. The SEM image of

SnO_2 PVA/CNSR polymer blends is shown in figure 2 (c), display the smooth morphology and inflated sheet-like microstructure all along with the SnO_2 NPs loaded PVA/CNSR polymer membranes, in addition to a comparable smooth morphology. These images evidently prove that PVA/CNSR adopt a neat and homogenous morphology.

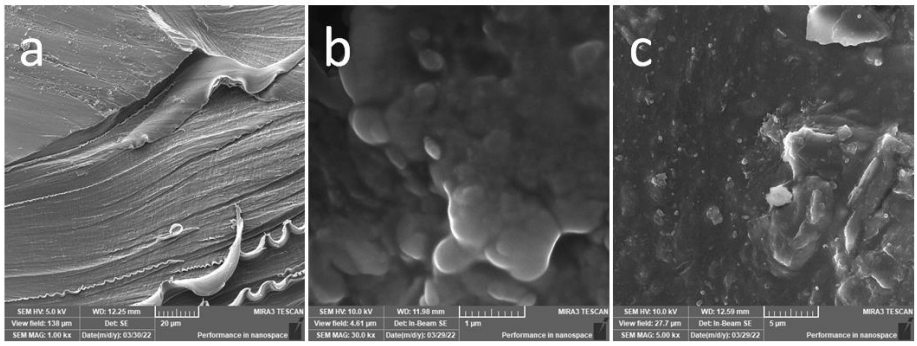


Fig. 2 SEM images of (a) PVA (b) PVA/CNSR and (c) SnO_2/ PVA/CNSR

3.3. Water uptake, swelling property Ion exchange capacity,

IEC is a significant factor that assesses the performance of polymer films towards PEMFCs, which is calculated in meq/g or mmol/g. The IEC gives data of the density of available active spots that could grasp and relieve cations on the polymer film [33]. The ion exchange capacity of unmodified PVA and the PVA/CNSR blends was calculated by volumetric acid-base titration, by following the reported procedure [32], the outcome are displayed in **Table 1.** It is observed from Table 1 that there is a noteworthy persuasion of CNSR-SA on the ion exchange capacity of polyvinylalcohol. The polymer blend of 10% CNSR in polyvinyl alcohol exhibited the upper value of IEC (1.2 mmol/g) than neat polyvinylalcohol film (0.9 mmol/g). The mercaptosuccinic acid provided proton exchangeable carboxylic acid groups to CNSR, adding up to a carboxylic acid group at anacardic acid, which are accountable for the higher IEC of PVA/CNSR.

The percentage water absorption of fuel cell membranes is a chief factor that determines the mechanical stability and proton conductivity. The presence of more water molecule within the polymeric membrane will aid the transport of proton, thus, provides higher ionic conductivity. However, higher water content will eventually decrease mechanical stability of the membrane. Therefore, optimum concentration of water (wetness) of fuel cell membrane is receommended for better performance. As a result, water uptake of PVA/CNSR has been determined and publicized in Table 1. From the **Table 1**, it is exposed that the combination of CNSR-SA 10% with polyvinylalcohol minimizes the water uptake character owing to the presence of nonpolar aliphatic chain portions of CNSR. However, the loading of SnO_2 nanoparticle increased the water uptake of PVA/CNSR.

The amount of water absorption is also induce swelling of polymeric membrane which leads to the change in shape and volume of the membrane. Thus relative amount of the swollen membrane and swollen free membrane is a noteworthy parameter of PEM. The higher swelling of membrane will increase the size of the membrnae layer which in-turn separate the layers of membrane electrode assembly. The results of swelling ratio obtained for PVA/CNSR is shown in Table.1, it is understood that that the incorporation of CNSR slightly reduces swelling ratio due to the alipathic chain segments of CNSR, however the loading of SnO_2 nanoparticle increased the swelling ration of PVA/CNSR.

Sample code	Swelling ratio (%)	Water uptake (%)	Oxidative Stability (% degradation)	Ion exchange capacity (mmol/g)
PVA	26.54	130.62	4.17	0.9
PVA/CNSR	20.45	121.16	4.28	1.2
PVA/CNSR//SnO_2(1%)	19.09	102.15	4.37	1.3
PVA/CNSR//SnO_2(2%)	19.47	122.06	4.56	1.6
PVA/CNSR//SnO_2(3%)	18.09	129.21	4.79	1.8

Table 1. Water uptake, Ion exchange capacity, Swelling ratio and oxidative stability of membranes

3.4. Oxidative stability of membranes

Resistance towards exposure to oxidative chemical environment was studied using Fenton test which necessitate the degradation of the polymer membrane upon contact to Hydrogen peroxide and ferrous ammonium sulphate, under heating. 150 mL of 3 v/v% Hydrogen peroxide and 4ppm of ferrous ammonium sulphate was mixed and pre-weighed PVA/CNSR membranes were immersed into the reagent. The whole content was heated at 68 °C for 8 h. The membrane was drawn from Fenton solution and dried at 60 °C. The membranes are reweighed and the mass loss was determined, and the outcomes are summed up in **Table 1**, it is observed that the PVA/CNSR10% exhibited increased chemical stability. In addition, the introduction of SnO_2 found to enhance the chemical stability of membranes.

3.5 Proton conductivity (PC)

Electrochemical impedance analyzer was engaged to study the propton conductivity of phosphoric acid dopped PVA/CNSR membranes. The proton conductivity is mainly depend on thickness, water uptake percentage and IEC. The proton conductivities of PVA, PVA/CNSR and (1, 2, 3%) SnO_2 loaded membranes are measured and displayed in figure 3. From figure 3, it is observed that that the PC of the PVA/CNAR films is superior to that of unmodified polyvinyl alcohol membrane, owing to the incorporation of added carboxylic acid functional groups through the crosslinking of mercaptosuccinic acid. The proton conductivities of SnO_2 nanoparticle embedded PVA/CNSR nanocomposite films are determined to be higher than the conductivity of PVA/CNSR. Among them 3% SnO_2 was observed to show high proton conductivity than other PVA blend membranes with a value of 0.011Scm^{-1}.

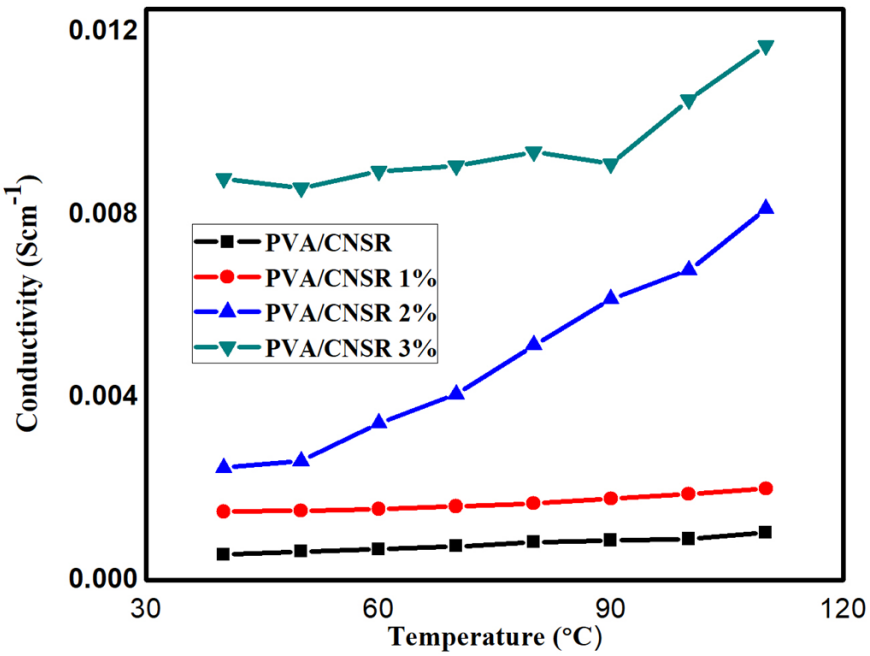


Fig. 3 Proton conductivities of PVA, PVA/CNSR and (1,2,3%) SnO_2 loaded membranes

4. CONCLUSION

The PVA/CNSR polymer blend and SnO_2 NPs loaded PVA/CNSR membranes was successfully casted doctor blade method. The synthesized polymer films were analysed by SEM and FTIR analyses, further 1%, 2% and 3% SnO_2 NPs loaded PVA/CNSR nanocomposite membranes were prepared and characterized for their water uptake, ion exchange capacity, swelling ratio, oxidative stability and proton conductivity. The SEM images evidently prove that PVA/CNSR adopt a neat and homogenous morphology. The nanocomposite membranes found to possess enhanced chemical stability, IEC and proton conductivity. 3% SnO_2 NPs dispersed PVA/CNSR membrane exhibited higher proton conductivity value of 0.011 S/cm^{-1} at 110 °C.

Conflicts of Interest

There are no conflicts to declare

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