Preparation and Characterization of Nano Titania modified PVA-Pectin polymer electrolyte membranes for DMFC

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***Abstract*——— In this study, poly vinyl alcohol and pectin are *in situ* cross-linked using dual cross-linker comprising a mixture of sulfosuccinic acid and glutaraldehyde followed by solvent casting.Titanium dioxide nanoparticles are incorporated into polymer solutions that controls alignment and disentanglement of polymer chains at molecular level. It is shown that rational design of membrane microstructure with proper arrangement of hydrophobic and hydrophilic domains has been formulated by blending PVA with PC. Water sorption through nanocomposite membrane enhanced when optimum quantity of titanium dioxide particles are present. In addition, titanium dioxide nanoparticles help to provide more inter-connected proton conducting pathways and acts as reinforcing units. Through the hydrogen bonds formed between surface functional groups of titanium oxide nanoparticles and polymer chains, protons are transferred through the membrane both by hopping and vehicular mechanisms. Titanium dioxide nanoparticles also act as fillers and effectively prevent the methanol permeation. Polymer voids are occupied by the presence of Titanium dioxide nanoparticles that selectively allow protons to pass through form anode to cathode side. Both improved proton conductance and lower methanol permeability, electrochemical selectivity of nano Titanium dioxide modified PVA-Pectin polymer electrolyte membrane is enhanced. With further enriched proton conductivity by the presence of titanium dioxide nanoparticles, fabricated pectin polyvinyl alcohol hybrid nanocomposite membrane exhibit higher electrochemical selective factor.**

***Index Terms*—Green electrolytes; Methanol permeability; Nanocomposite; Pectin; Selective transport**

I. INTRODUCTION

Direct methanol fuel cells (DMFCs) are considered to be one of the most promising candidates for portable and stationary applications in the view of their advantages such as high energy density of methanol, high efficiency as well as they operate with liquid fuel which could be used without requiring any fuel-processing units [1]. Due to growing demand for clean and sustainable energy, fuel cells have been touted as an eco-friendly, efficient alternate for conventional fossil fuel power sources. Direct methanol fuel cells (DMFCs) are considered to be one of the most promising candidates for portable and stationary applications in the view of their advantages such as high energy density, easy manipulation, high efficiency as well as they operate with liquid fuel which could be used without requiring any fuel-processing units Polymer Electrolyte Membrane (PEM) stand for an integral component of DMFC. Widely used perfluorosulfonic acid ionomer (Nafion®) membrane is advantageous for its high proton condcutvity but high methanol permeation rate severely prohibit its extensive application as well stimulated continuing interest in the direction of developing alternate low-cost, bio-degardable, methanol impermeable polymer electrolytes. [2,3]. Accordingly, PEMs based on sulfonated aromatic polymers, irradiation graft polymers, cross-linked polymers, and blend polymers were developed [4]. On the other hand, there exist a demand for environmentally-benign raw materials in the view of depletion of raw materials and fossil fuels, particularly the areas in which an increasing industrial requirement is expected. This emphasizes the significance of developing cost-effective, eco-friendly materials derived from natural sources such as polysaccharides, proteins, lipids etc.,Pectin (PC) is a least explored class of polysaccharide with respect to DMFC application and investigations on PC based is hardly available in literature except preliminary evaluation on the utility of amidated PC as a DMFC electrolyte proposed by Mishra *etal*., [5]. Blending polymers is one of the most promising approaches owing to the fact that resulting blend restrains attractive features of individual component at the same time diminishes their defective qualities. It is quite interesting to combine natural polymer with a synthetic polymer, accordingly PC is blended with PVA. In the present study, PC has been blended with PVA in order to fabricate polymeric membranes with adequate mechanical stability, ionic conductivity and methanol selectivity. In order to further promote ionic conductivity, nano-titanium dioxide particles (n-TiO2) are incorporated into the blends to formulate nanocomposite membranes. It is illustrious that n-TiO2 acts as a filler and leads to an increase in net acid content by incrementing number ion-conducting groups per unit volume. These membranes are rationally designed to possess higher selectivity for conducting protons rather than methanol. PC inserts an incredible impact on hydrophilic/hydrophobic microstructure of polymeric network consequently helps to improves ionic conductivity and mitigate methanol permeation simultaneously. Cross-sectional

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area of hydrophilic domains through which proton and methanol transport occurs has been condensed due to the presence of pectin and the resulting polymeric blends preferentially transport protons (or hydronium ions) and greatly reduce methanol transport.TiO_2 nanoparticles introduced in the flexible polymer blend further ameliorates this selective sorption feature, which is seminal for desirable DMFC performance.

Experimental Details

PVA, (99.7% hydrolyzed, M.W. 115,000), PC (M. Wt 3.0 × 10^4–1.0 × 10^5) was obtained from LobaChemie, India. Hydrophilic fumed TiO_2 with an average particle size of 21 nm was procured from Aeroxide. Sulfosuccinic acid (SSA) and methanol were obtained from SRL chemicals. Glutaraldehyde (25% aqueous) and sulfuric acid (98%) were obtained from S.D. Fine Chemicals, India. All the chemicals were used as received. De-ionized (DI) water (Resistivity 18.4 MΩ cm) from Millipore was used during the experiments.

Preparation of Pectin-PVA/n-TiO2 Hybrid Nanocomposites

PC-PVA/n-TiO_2 hybrid nanocomposite membranes were prepared by solution-casting technique. Briefly, 30 mL of 4 wt. % PVA solution was prepared by dissolving the required amount of PVA in water at 60° C followed by stirring until a clear solution was obtained. Similarly, 20 ml of 25 wt. % Pectin in relation to PVA was dissolved in de-ionised water followed by stirring until a homogeneous solution was obtained. Both the solutions were mixed together and stirred for 4 h to form a compatible blend. Required quantity of n-TiO_2 was dispersed in de-ionised water under ultra-sonication for 2 h. The resultant solution was added drop-wise to the above Pectin-PVA blend solution under continuous stirring for 24 h. Sequential binary cross-linking with a mixture consisting of 10 wt. % sulfosuccinic acid (SSA) and 5 wt. % glutraldehyde (GA) (with respect to PVA polymer). The resulting solution was cast on a flat Plexiglass plate and dried at room temperature and the membranes were peeled off from the glass plate and washed thoroughly before subjecting to further studies. PC-PVA blend membranes were prepared in the similar manner without addition of n-TiO_2. The composition of n-TiO_2 was varied from 1wt. % to 10 wt. % in relation to PVA. PC-PVA/n-TiO_2 hybrid nanocomposite membranes comprising 1wt. %, 5wt. % and 10 wt. % of n-TiO_2 are designated as PC-PVA/n-TiO_2-I, PC-PVA/n-TiO_2-II and PC-PVA/n-TiO_2-III respectively. It is to be noted that when level of s-TiO_2 is beyond 10 wt. %, membrane develops fragility and brittleness. The thickness of all the membranes was maintained at ~ 160 µm.

II. Physico-Chemical Analysis

Sorption measurements were conducted by immersing circularly-cut membrane samples into de-ionized water for 24 h to attain equilibrium and weighed (diameter = 2.5 cm) before dipping into sorption chamber. The membranes were surface blotted and their sorbed weights were measured.

Proton conductivity measurements were carried out with PC-PVA blend, PC-PVA/n-TiO2 hybrid nanocomposite in a two-probe conductivity cell by AC impedance technique. The conductivity cell comprised two electrodes, each of 20 mm diameters. The membrane was placed between these two electrodes to have a through plane contact and then mounted in a Teflon block and kept in a closed glass-container filled with water to maintain 100 % humidity which also has the provision to heat. The membranes were equilibrated for 24 h in this condition before measuring ionic conductivity. Conductivity measurements were done with the increased temperature from 30oC to 100oC. AC impedance spectra for the membranes were recorded in the frequency range between 1 MHz and 10 Hz with 10 mV amplitude using an Autolab PGSTAT 30. Methanol permeability is determined using Gas chromatographys

III. Results and Discussion

Sorption phenomenon of a PEM reflects extent of absorption of solvent molecules and ability to retain solvent molecules without significant deformation in its structure. Water sorption is determined by both the availability of the free-voids in polymeric matrix and intrinsic hydrophilicity of the material. Consequently, swelling properties have a huge influence on proton transport, stability and methanol permeability characteristics.Sorption data associated with PC-PVA blend and PC-PVA/n-TiO_2 hybrid nanocomposites measured at 70° C with water and aqueous methanol is shown in Fig.1.

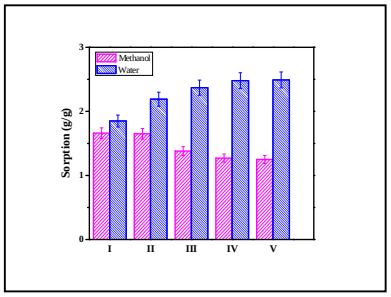


Fig.1. Sorption properties of membranes measured with water and methanol

Percentage of water sorption rapidly increases on increasing n-TiO_2 from 1 wt. % to 5 wt. % but tend to saturate when increased from 5 wt. % to 10 wt. %. Hence, it can be inferred that PC-PVA based polymeric membranes are suitable for DMFCs.

Fig. 2 shows the proton conductivities of PC-PVA based membranes measured at different temperatures from 30° C to 100° C. Combining PC with PVA generates a flexible polymer framework, resulting PC-PVA blend with stretchable polymeric chains offer more space for water molecules to reside and these water molecules facilitate ionic mobility.

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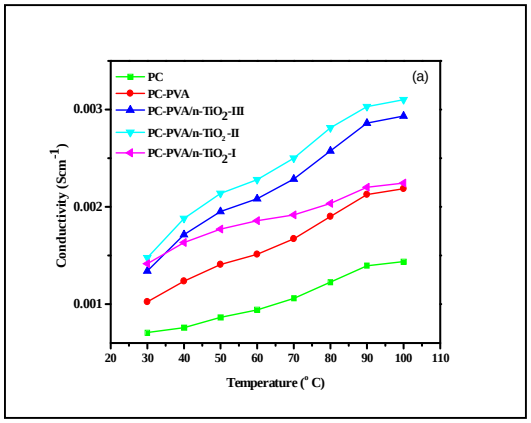


Fig. 2 shows the proton conductivities of PC-PVA based membranes measured at different temperatures

Proton conductivities of PC-PVA-n-TiO_2 nanocomposite membranes are obviously higher compared to their blend membrane. n-TiO2 nanoparticle promotes proton conduction both through hopping and vehicular mechanism. Degree of hydration of a PEM produces a profound effect on proton conductivity, being hydrophilic in nature. PC attracts more number of water molecules, because of these water molecules which are confined within hydrophilic domains, enhanced proton mobility in the polymer framework takes place. Combining PC with PVA or CS generates a flexible polymer framework, resulting PC-PVA or PC-CS blend with stretchable polymeric chains offer more space for water molecules to reside and these water molecules facilitate ionic mobility. In other words, appropriate balance between hydrophobic and hydrophilic domains is established in PC-PVA or PC-CS polymer matrix, which allows a fast exchange between the mobile ions and the fixed charged sites through hydrated hydrophilic network.

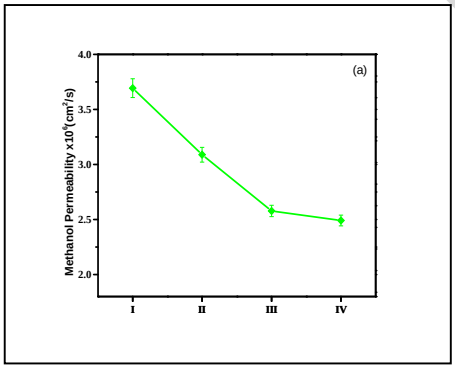


Fig. 3 shows Methanol permeability values of PC-PVA based membranes

Methanol permeability values through different PC-PVA/s-TiO_2 nanocomposite membranes have rapidly decreased by nearly 40% due to presence of n-TiO2. Dispersed n-TiO2 nanoparticles create closely packed network with lower volume of free-void space, which effectively block passage of methanol molecules. Electrochemical selectivity of membranes for protons over methanol can be defined as the proton conductivity (σ) divided by methanol permeability (P), which is often used to evaluate the membrane-electrolyte performance in DMFC.

Pectin based cost-effective natural polymeric blends tailored with n-TiO2 nanoparticles to realize a composite membrane for application in DMFC has been explored. Combining pectin with PVA generates flexible blend polymeric network, which is appropriate for incorporation of inorganic fillers. Effect of blending pectin with polymers has been systematically followed by rheological measurements.

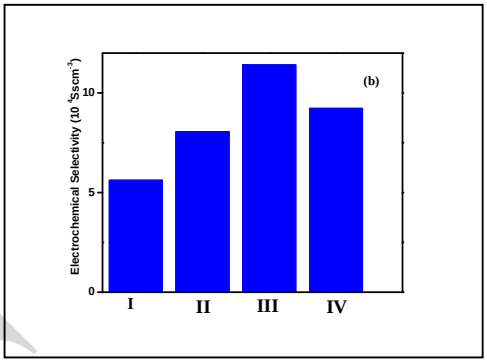


Fig. 4 Electrochemical selectivity values of membranes under study

Pectin transforms morphological properties of PVA, results in construction of a slackly-packed network with higher affinity for water which greatly reduces methanol permeation. Fine dispersion of n-TiO2 increases the compactness of ion-conducting groups resulting in nanocomposites ultimately appropriate for DMFC application. Together with improved thermo-mechanical stabilities, low-cost eco-friendly components, ready availability and convenient method of preparation are essential highlights of these membranes that may be regarded as bio-based materials for DMFC applications.

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