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Structural and Thermal properties of functionalized biopolymer based polymer electrolyte membranes for fuel cell applications

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Abstract — *Polymer electrolyte membranes based on organic – inorganic nanocomposites consisting of sulfonated chitosan and sulfonated titania are developed using simple solution casting technique. Compared to pure chitosan membranes, sulfonated titania incorporated membranes exhibit higher thermal, oxidative stabilities and better structural property due to the strong electrostatic interaction and hydrogen bonding between the polymer and nanoparticles. The miscibility studies have been performed by using X-ray diffraction spectrometer. Nanocomposite membrane filled with 8 wt% s-TiO_2 has the highest proton conductivity of 3.41 × 10^{-2} S/cm at room temperature. The membranes were also characterized using techniques such as SEM and AFM. All the prepared s-CS/PEO/s-TiO_2 nanocomposite membranes exhibit better thermal stability. Sulfonated chitosan/PEO/s-TiO_2 membrane exhibits the best overall performance as a membrane, which is mainly due to the strong interactions between chitosan matrix and nanoparticles. The present study provides a promising strategy for the design and fabrication of high performance polymer electrolyte membranes for fuel cell applications, which is cost effective and eco friendly.*

Keywords- *Thermal stability, Functionalization, Biopolymer, SEM*

I. INTRODUCTION

The growth of industry worldwide has tremendously increased the generation and accumulation of waste byproducts. In general, the production of useful products has been focused on and the generation of waste byproducts has been largely ignored. This has caused severe environmental problems that have become a major concern. Researchers all over the world have been working on various approaches to address this issue. Titanium dioxide (TiO2) is one of the most attractive transition-metal oxides because of its superior physical and chemical properties, which has been widely applied in environmental clean-up, energy conversion, energy storage, security (sensors), panel display (transparent conducting films), biomedical devices, and so forth [1–3]. The performance of TiO_2 in these applications highly depends on its structural, electronic, optical, and morphological as well as the surface properties (exposed facets). Great effort has been devoted to adjust these properties and apparent progress has been made on the nanostructured TiO_2 materials. TiO_2 belongs to the family of transition metal oxides. There are four commonly known polymorphs of TiO_2 found in nature: anatase (tetragonal), brookite (orthorhombic), rutile (tetragonal), and TiO_2 (B) (monoclinic) [4]. Besides these polymorphs, two additional high-pressure forms have been synthesized from the rutile phase. These are TiO_2 (II) [29] with a PbO_2 structure and TiO_2 (H) [5] with a hollandite structure. In this review, only the crystal structures [6-7] and properties of the rutile, anatase and brookite polymorphs are considered. A polymer nanocomposite containing inorganic nanofillers can alleviate the performance constraints of sulfonated chitosan/PEO by enhancing the membrane's water molecule adsorption and restraining polymeric chain alignment. Metal oxides have been extensively investigated as inorganic additives in proton conducting membranes used as ionic separators in polymer electrolyte membrane fuel cells (PEMFCs). Always the hydrated membrane form gives better performance, because the water molecules create a path for transport of protons. But in case of high temperature the water molecules get evaporated from the membrane [6]. To retain the hydrated form of the membrane at high temperature the metal oxides have been used. Sulfonated groups of TiO_2 not only create a path for proton transport but also act as vehicle due to its negative charge. Whereas both metal oxide (-OH group metal oxide) and water molecule can only create a path for proton transport but cannot act as vehicle due to their neutral charge.

II. Experimental Procedure

A. Materials

Biopolymer Chitosan (Mw~6x10^5 g mol^{-1}), Poly (ethylene oxide) (PEO) of an average molecular weight~8,000 and TiO_2 nanoparticles (25 nm) were purchased from SRL, India. 1,3 Propane Sultone and Acetic Acid were procured from Spectrochem, India.

B. Sulfonation Process of Chitosan

The sulfonation process of chitosan according to the method reported by our previous work [7]. 5 g of Chitosan (1% w/v) solution was prepared by adding Chitosan powder to 2% (v/v) acetic acid solution, stirring for completely dissolution of Chitosan in aqueous acetic acid and then adding 1,3 Propane Sultone to the solution. The mixture was allowed to react at 60 °C for 10 h. The resulting solution was poured into cold acetone to precipitate. The crude solid was

washed sufficiently with methanol to remove the excess 1,3 Propane Sultone and dried in a vacuum oven at 50 °C over night followed by 120 °C for 6 h, the s-CS was obtained as a white powder.

C. Sulfonation Process of Titania Nanoparticles

Sulfonation alters the chemical structure of a polymeric substrate by introducing sulfonic groups on its surface. In the sulfonation process, one gram of TiO_2 nanoparticless was sulfonated in the presence of methanol and H_2SO_4. The titania nanoparticles (TiO_2) (1g) was added with 10 ml of above mixture solution under continuous stirring at room temperature for 12 h. After that, it was dried at 70 °C. At the end of the sulfonation reaction white powder was obtained.

D. Preparation of polymer nano composite membrane

In order to obtain a variety of sulfonated Chitosan/PEO/s-TiO_2 electrolyte system, preliminary investigations related to room temperature impedance spectroscopic measurements were performed on all the freshly prepared s-Chitosan/PEO polymer blends. It was found that the optimized composition namely 60:40 wt% ratio of Chitosan and PEO would possess an appreciably high ionic conductivity at room temperature. Eventually, five different concentrations involving 2, 4, 6, 8 and 10 weight percentage of sulfonated TiO_2 were dissolved in respective aqueous acetic acid solutions containing (s-Chitosan : PEO) polymer blend and the same procedure of solution casting technique as mentioned above was repeated for obtaining a new series of the blended polymer electrolyte system Chitosan-PEO-s-TiO_2. These free-standing electrolyte samples of approximately 100µm thickness were subjected to various characterization techniques during the course of the present investigation.

E. Instrumentation and Characterization

The persuasive evidence for the intercalation of s-SiO_2 could be obtained from XRD patterns of the nano composites. Radical scan was recorded in the reflection scanning mode with 2θ being changed from 10° - 80°. The amorphous nature of the polymer electrolytes has been investigated by X-ray diffraction (XRD) analysis with the help of X'pert PRO PANanalytical X-ray diffractometer. The morphology of gold sputter coated composite membranes was examined by scanning electron microscopy (SEM) (FEI Quanta 250 Microscope, Netherlands). The proton conductivity of hydrated membranes was measured by impedance spectroscopic technique at different temperatures using a computer controlled µ-autolab type III Potentiostat/Galvanostat in the frequency range 10 Hz to 1 MHz at room temperature and the signal amplitude of 10mV which has been designed for through the membrane, to obtain bulk resistance of the membrane. The tapping mode AFM images of the membranes were acquired in APE Research-model no: A100SGS. Surface roughness of the membranes was compared using various roughness parameters, such as the mean roughness (Rm), the root mean square of z data (Rq) and the mean difference in the hight (Rz). The membrane samples were in try condition and the tests were run at the room temperature. A thermogravimetric analyzer PYRIS Diamond (DSC/TGA SDT Q600) was employed to assess the thermal stability of the nano composite membranes. The membranes were heated from 20 °C to 900 °C both at heating rate of 10 °C/min, under a nitrogen atmosphere.

III. Result and Discussions

A. SEM with EDAX

The element on the surface of the s-TiO2 nanocomposite is shown in figure 1. The EDX results are from the SEM image (Figure 1a) it is shown that the S element is present on the surface of s-TiO_2 nano composite, which means that the organic sulfonic acid group (-SO_3H) has condensed with the hydroxyl groups of s-TiO_2.

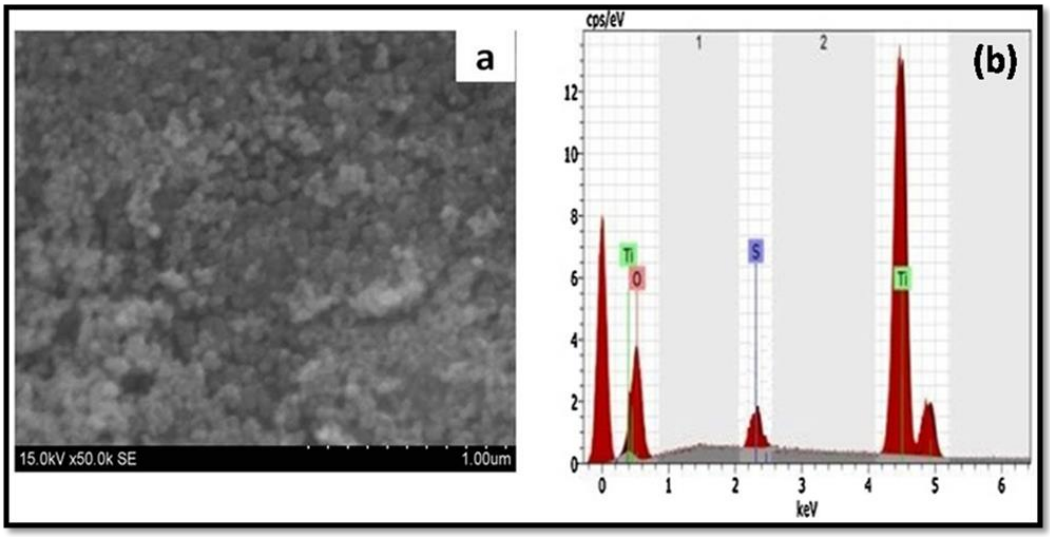

Figure .1 SEM and EDAX spectrum of s-TiO_2

B. SEM of prepared electrolytes

Scanning electron microscopy is often used to access the capability between various phases through the detection of phase's separations and interfaces. As shown in figure .2a, the pure chitosan film posses a very smooth surface and compact structure. Distinct spherulites separated by dark boundaries can be dissolved in the polymer blend membrane [Figure.2b] chitosan/PEO. The spherulites texture is essentially associated with the lamellar structure of the crystalline phase, while the dark regions correspond to partial amorphicity [8]. As can be deduced from figure. 2d, although the addition of s-TiO_2 nanoparticles to the sulfonated chitosan/PEO membrane sample led to the formation of a homogeneous structure owing to the strong interaction between chitosan chains and s-TiO_2, a few s-TiO_2 agglomerations were formed in the membrane matrices [2]. s-Chitosan/PEO/s-TiO_2 rough surface occur due to the embedded and well dispersed of s-TiO_2 into the s-chitosan/PEO matrix. Also it seems that the s-Chitosan/PEO/s-Tio_2 sample has the roughest surface which might be due to the rough interlinked network structure of its matrix. SEM micrographs of pure and complexed polymer blend electrolyte were different surface morphologies. X-ray diffraction and FTIR studies of the blend sample support these observations. The addition of s-TiO_2 nanoparticle resulted in a significantly increased for s-Chitosan/s-TiO_2 film when compared with the pure sulfonated chitosan/PEO film. The increasing resulted from the increased internal friction in the chitosan film matrix when s-TiO_2 nanoparticles were added to create a crystal structure.

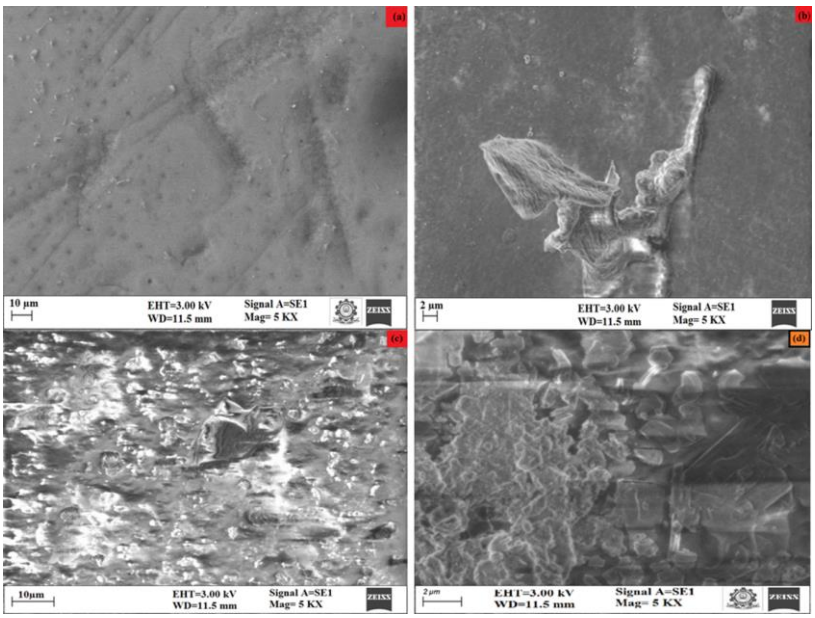

Figure .2 SEM images of prepared electrolytes (a) chitosan, (b) chitosan/PEO, (c) s-chitosan/PEO and (d) s-chitosan/PEO/s-TiO_2 (8 wt%)

C. XRD analysis

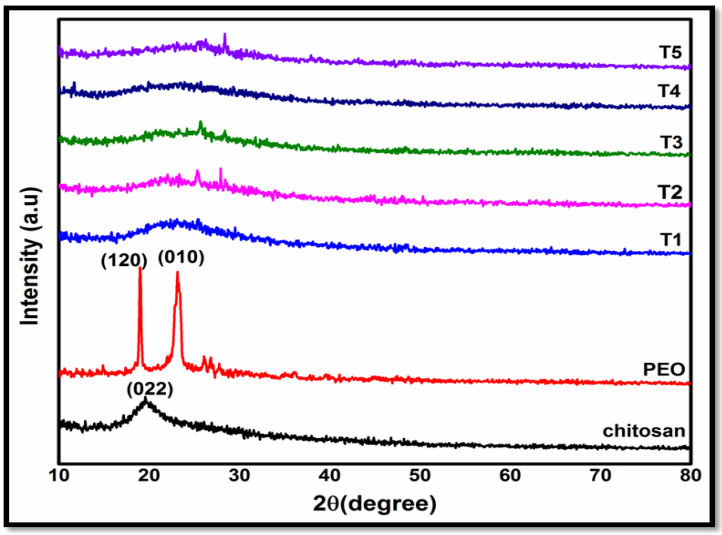

Figure .3shows XRD spectrums of preparedelectrolytemembranes (T1) s-chitosan/PEO/s-TiO_2 (2 wt %), (T2) s-chitosan/PEO/s-TiO_2 (4 wt %), (T3) s-chitosan/PEO/s-TiO_2 (6 wt %) (T4) s-chitosan/PEO/s-TiO_2 (8 wt %), (T5) s-chitosan/PEO/s-TiO_2 (10 wt %) respectively.

X-ray diffraction measurement was performed to examine the crystallinity of the s- chitosan /PEO/ s-TiO_2 nano composite membranes. Figure shows the XRD pattern of prepared nano composite membrane based on sulfonated chitosan /PEO/s-TiO_2. It is well known that the pure chitosan exhibited the peak at an angle $2\theta = 19.8°$. Pure PEO spectrum of XRD shows maximum intensity peak at $2\theta = 19.36°$ and 23.72° which are assigned to (120) and (010) planes [9-11]. The shape peaks are attributed to the crystalline phase of PEO, which originates from the ordering of polyether side chains due to the strong intermolecular interaction between PEO chains through the hydrogen bonding. The crystalline structure of PEO is a monoclinic unit cell. It was found that the peak intensity of the prepared nano composite electrolyte was greatly reduced compared with chitosan and PEO due to the addition of s- TiO_2 nano particles. This implies that the amorphous domain in the nanocomposite membrane were augmented (the degree of crystallinity decreased). Beyond 8 wt% of s-TiO_2 the intensity of the peak increases. The XRD pattern of the electrolyte show good homogenized mixing between the polymer matrix and filler nanoparticles. At a higher concentration of about 10 wt% of s-TiO_2 the peak intensity increases due to the high loading/ which leads to segregation of the nano particles within the polymer matrixes.

C. AFM analysis

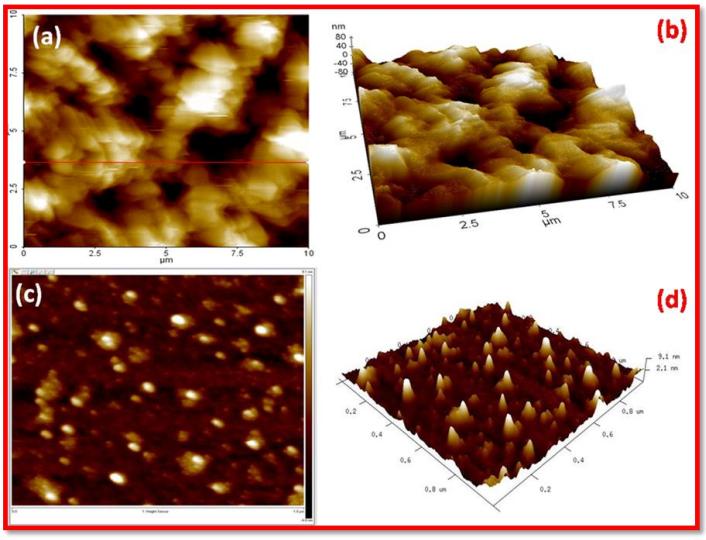

Figure 4. AFM images of (a-b) s-chitosan/PEO (c-d) s-chitosan/PEO/s-TiO_2 electrolytes

The surface topographies of the s-chitosan/PEO and s-chitosan/PEO/s-TiO_2 T4) membranes are shown in figure 4. Average roughness (R_a), root square roughness (R_q) and maximum roughness (R_{max}) are presented in table .1. The surface of s-chitosan/PEO was quite smooth (R_a = 1.06 nm). When s-TiO_2 (8 wt %) was added, the R_a increased to 1.23 nm. The addition of s-TiO_2 gave a surface with Ra of 1.23 nm. The R_{max} for pure sample showed that there was a smooth and valleys. This profile was more evidenced in sulfonated chitosan/PEO sample. The roughness increased after addition of s-TiO_2 compared to the smooth s-chitosan/PEO surface. This was an indicative that the polymer matrix fully covered the metallic surface and formed a uniform layer, as evidenced previously by XRD analyses. The polymer network formation through sulfonation groups creates a quite rough coating with free amine groups as well as sulfone ones, as already pointed out by Saidin *et al*. S-TiO_2 was dispersed over the surface, increasing the height in specific points, as evidenced by the R_{max} profile. The increases of the roughness promoted by the sulfonation of TiO_2 may be due to the conformation of chitosan chains to settle on the sufficient mobility in solution to be arranged to increase the repulsion of the amine groups present in its structure. The high roughness presented by sulfonated chitosan surface can be attributed to the chemical modification made in the chitosan and TiO_2 structure. This modification creates a charge effect more strong than that found in native chitosan, introducing a repulsion effect between sulfonate groups, while promoting an attraction effect between sulfonate and amine groups.

Table 1. Roughness parameters of the prepared electrolytes

Sample	Roughness parameters		
	R_m (nm)	**R_q (nm)**	**R_a (nm)**
s-CS/PEO	8.42	1.12	1.06
s-CS/PEO/s-TiO_2 (8 wt%)	15.1	1.78	1.23

E. TG analysis

Thermo gravimetric analysis of the sulfonated chitosan/PEO membrane reveals major weight losses at 110 and 455 °C (figure .5) respectively, this is due to the dehydration of water molecules, de-sulfonation and degradation of polymeric entities. Although a similar thermal profile is observed for the sulfonated chitosan/PEO/s-TiO_2 (8 wt %) composite membrane. The thermal stability of the s-chitosan/PEO membrane is enhanced with the inclusion of s-TiO_2 and is further increased with the s-TiO_2 filler, due to the robust ceramic characteristics of TiO_2. The increased hydrophilic content of the sulfonated chitosan/PEO/s-TiO_2 (8 wt %) and sulfonated chitosan/PEO/s-TiO_2 (2 wt %) membranes were achieved *via* the sulfonation of inorganic fillers (s-TiO_2), yielding a slight increases in their thermal stabilities compared to the sulfonated chitosan/PEO/s-TiO_2 (8 wt %) membranes incorporated with bare inorganic fillers (s-TiO_2). However, the obtained thermo grams clearly display the superior thermal stabilities of the sulfonated chitosan/PEO/s-TiO_2 (8 wt %) and sulfonated chitosan/PEO/s-TiO_2 (2 wt %) membranes over the bare sulfonated chitosan/PEO membrane, allowing for their use in elevated-temperature fuel cell applications.

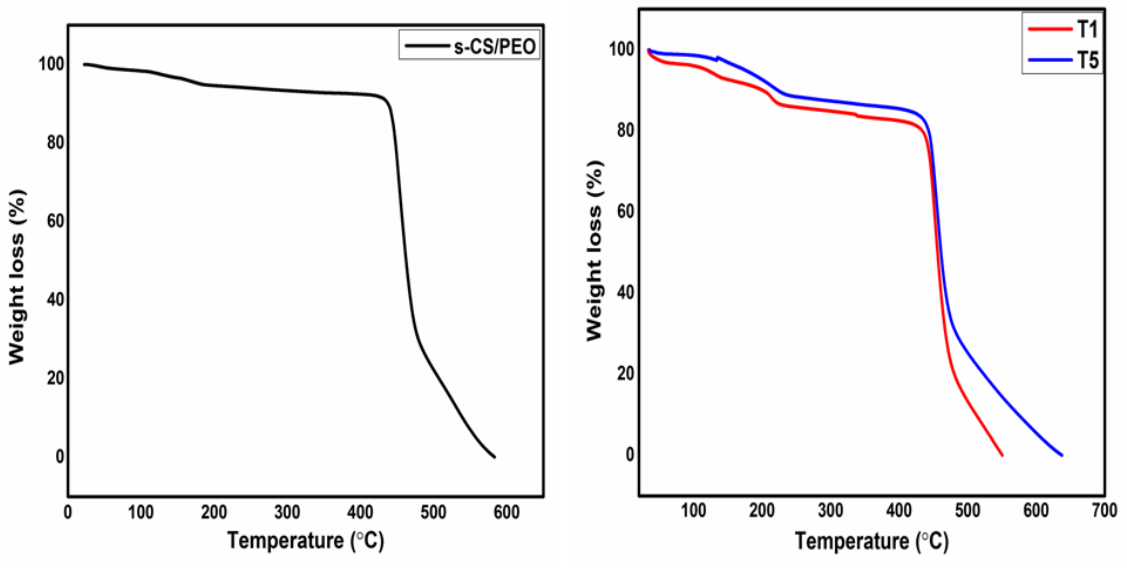

Figure 5. Tg spectrum of s-chitosan/PEO and (T1) s-chitosan/PEO/s-TiO_2 (2 wt %), (T2) s-chitosan/PEO/s-TiO_2 (8 wt %)

F. Ionic conductivity

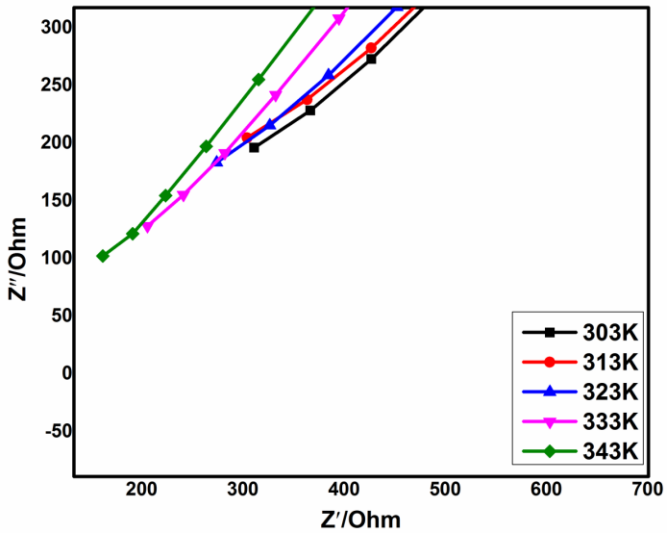

Figure 6. Conductivity spectrum of 8 wt% s-TiO_2 in s-chitosan/PEO electrolyte at different temperatures

The ionic conductivities of the as-prepared membranes measured at 303 K to 343 K are provided in figure 6. The s-chitosan/PEO/s-TiO_2 composite membranes exhibit improved ionic conductivity values, owing to the hygroscopic properties of s-TiO_2. Proton transportation in s-TiO_2 is interceded with hydrogen bonding among the neighboring lattice oxygen atoms and reorientations of similar oxygen sites *via* the Grotthuss mechanism. The oxygen site in Ti-O-Ti decreases the energy barrier for ion transport and the large cations in the A-site are responsible for the lower activation energy for ion mobility. In general, the ionic conductivity of the polymeric membrane is influenced by the ion-cluster

domains and its strong interconnection and dissociation of acidic functional groups. The incorporation of s-TiO_2 increases the water adsorption characteristics of the s-chitosan/PEO membrane and the adsorbed water molecules enhance the size of ion-cluster domains and promote their interconnection. Furthermore, the adsorbed water molecules facilitate the dissociation of protons and provide possible pathways for proton transportation, thus increasing the ionic conductivity of the s-chitosan/PEO/s-TiO_2 composite membranes. Among the membranes studied, s-chitosan/PEO/s-TiO_2 membrane exhibits the maximum ionic conductivity of 5.87 $\times 10^{-2}$ S/cm at 70 °C, which is superior to that of Nafion 117 membrane. The strong hydrogen bond exerted between the s-TiO_2 and -SO_3H groups of chitosan maximizes the bound to free water ratio in the nanocomposite membranes, which contributes to the high ionic conductivity for the s-chitosan/PEO/s-TiO_2 (8 wt%) membrane. The incorporation of s-TiO_2 enhances the bond strength of water molecules in the s-chitosan/PEO membrane, owing to the enhanced hygroscopic properties of the s-TiO_2. The large surface to volume ratio of s-TiO_2 and the strong linkage exerted between the water molecules and sulfonic acid domains provide a continuous transportation channels for the smooth passage of H^+ ions. The large amount of adsorbed H_2O molecules on the s-TiO_2 facilitates the uninterrupted H^+ ions transport with the adjacent H_2O molecules *via* the hydronium (H_3O^+) ion formation. Furthermore, the hydrogen-bond interceded proton transfer among the lattice oxygen atoms in s-TiO_2 core structure maximizes the ionic conductivity of the s-chitosan/PEO/s-TiO_2 membrane.

IV. CONCLUSION

Proton exchange membranes based on sulfonated chitosan/PEO with different ratio of s-TiO_2 were prepared by solution casting technique. The SEM micrographs show good adhesion between inorganic particle domains and polymer matrix. The result showed that increasing the sulfonated TiO_2 content in s-Chitosan/PEO composite membranes leads to the crystallinity of the polymer composite and increases the conductivity. The reason for this result from the increasing amount of inorganic filler in the membrane barrier properties. These features and advantages for the fuel cell performance because they prevent reactant and increase the thermal stability. The proton conductivity of composite membrane exceeded 10^{-2} S/cm at 70 °C, which is greater than that of Nafion membrane under the same conditions. These results should be conductive to the preparation of membrane suitable for fuel cell usages. TGA results showed that the nanocomposite membranes have good thermal stabilities. From the morphological investigation, it can be concluded that the addition of s-TiO_2 altered the nature of nanocomposite membranes. From these results, we trust s-chitosan/PEO/s-TiO_2 nanoparticles membranes have good properties for use in PEM fuel cells.

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