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Synthesis And Characterizationof Sulfonatedchitosan/PEO Based Polymer Electrolyte Membranes For Fuel Cell Applications

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Abstract — *An organic species bearing an organic sulfonic acid (HSO3-) was grafted onto the surface of Titanium oxide (TiO2) by sulfuric acid and the composite membranes were cast together with sulfonated chitosan and PEO. The performance of the s-chitosan/PEO/s-TiO_2 composite membranes for microbial fuel cells (MFCs) was evaluated in terms of proton conductivity, oxidative stability and Ion Exchange Capacity (IEC).The IEC, proton conductivity of the composite membrane increased dramatically with increasing contentof s-TiO_2 in the composite membrane. The combination of these effects led to a significantimprovement in the performance of MFCs made with s-chitosan/PEO/s-TiO_2 composite membranes. All the prepared s-chitosan/PEO/s-TiO_2 nanocomposite membranes exhibit better stability against oxidativedegradation, water uptake and retention ability proton conductivity. The membranes were investigated by FTIR, XRD. Thus, through chemical modifications the physico-chemical properties of naturalabundant biopolymer chitosan can be enhanced for its use as an environmentally sustainable PEM in MFC technology.*

Keywords- *IEC, Oxidative stability, Microbial fuel cell, nanocomposites.*

I.INTRODUCTION

The demand for alternative, non-fossil-fuel-based technologies as well as their research is being rapidly promoted, together with the implementation of environmentally oriented management leading to decentralized options and renewable sources especially regarding waste-to-energy [1]. As a result, more and more attention has been paid to microbial fuel cells as a promising alternative energy resource, from which wastewater treatment and reuse along with bioenergy generation can be accomplished with many operational and functional advantages including cleaner, safer and quieter performance, low emissions, high efficiency, moderate operating temperatures and direct electricity recovery. Almost all kinds of waste water, can be used as a source of energy in a microbial fuel cell application [2]. Chitosan (CS), a cost effective and eco-friendly polymer electrolyte-based membrane from the exoskeleton of crustaceans such as crabs and shrimps and from the cell walls of fungi, is expected to a promising substitute utilized in fuel cells. It is a natural polymer with repeating structural units of 2-amino-2-deoxy-(1,4)-β-D-glucopyranose [3-4]. It is also among the best candidates to replace Nafion for fuel cell application due to its excellent biocompatibility, biodegradability, non-toxicity and chemical and thermal stability. Nevertheless, the proton conductivity and mechanical strength of CS films are comparatively lower than those of Nafion. This drawback presents decisive problems and limits the use of this material in a variety of fields. Fortunately, the backbone of CS has certain functional groups—free amine (-NH2) and hydroxyl (-OH) groups—that can provide CS with high hydrophilicity. Moreover, these functional groups allow chemical modification to improve the properties of chitosan membrane. Various chemical modifications of CS have been performed to improve its properties [5-7]. A common modification is cross-linking to stimulate its mechanical and chemical stability. In this process, three dimensional networks are formed through interconnection between CS chains by sulfonation. Sulfonation, an organic reaction in which a hydrogen atom on functional groups of CS is replaced by a sulfonic acid functional group, has also been investigated by many researchers.

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 previously reported [6]. 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 100 μm 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 complex formation between the polymer and the nano clay has been confirmed by Fourier Transform Infrared Spectroscopy (FTIR) spectra using SPECTRA RXI PerkinElmer spectrophotometer over a wave number range of 400–4000 cm^{-1} in transmission mode. 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 10 mV which has been designed for through the membrane, to obtain bulk resistance of the membrane.

III. Result and Discussions

A. XRD analysis

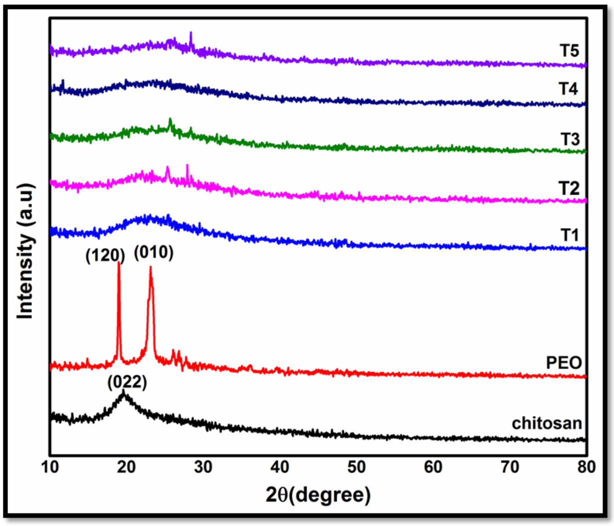

Figure 1. XRD spectrums of prepared electrolyte membranes (T1) s-chitosan/PEO/s-TiO_2 (2 wt%), (T2) s-chitosan/PEO/s-TiO_2 (4 wt%), (T3) s-chitosan/PEO/s-TiO_2 (6 wt%) (T4) s-chitosan/PEO/s-TiO_2 (8 wt %), (T5) s-chitosan/PEO/s-TiO_2 (10 wt%).

X-ray diffraction measurements were 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 2θ = 19.8°. Pure PEO spectrum of XRD shows maximum intensity peak at 2θ =19.36° and 23.72° which are assigned to (120) and (010) planes. The Sharpe 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 [5]. 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 nanoparticles .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 seggregation of the nano particles within the polymer matrixes.

B. FTIR analysis of pure and prepared electrolytes

The bonding of the sulfonated species was revealed by the FTIR spectra (Figure 2 and 3). The bands at 3400 cm^{-1} and 1644 cm^{-1} can be attributed to the stretching and bending vibrations of the O–H group on the surface of the nano composites. In the spectrum of pure TiO_2, there is a stretching vibration around 653 cm^{-1} corresponding to Ti-O-Ti bonds. In comparison with TiO_2, new absorption bands between 1237 and 985 cm^{-1} are observed in sulfonated Tio_2. The band at 1040 cm^{-1} is assigned to the asymmetric stretching vibration of S–O groups, whereas the bands at 1139 and 1237 cm^{-1} are attributed to the splitting of the S=O group into symmetric and asymmetric stretching vibrations, respectively. This implies the existence of SO_3H species as bidentate complexes coordinated to TiO_2. The peaks at 2930 and 2890 cm^{-1} of s-chitosan spectra represents the CH stretching vibrations and 1153 and 1063cm^{-1} peaks represents to saccharide structure (C-O-C vibrations of glucose rings and glycosidic linkage of chitosan [6, 7]. Sulfonated chitosan membrane showed two absorption bands at 1634 and 1567cm^{-1} which is corresponds to characteristic bending vibrations of NH^{3+} group of chitosan membrane. The NH^{3+} group obtained in the membrane results the protonation of NH_2 group by CH_3COOH during dissolution of chitosan [8]. From the FTIR spectra the presence of peaks at 1650 cm^{-1} for amide I and 1560 cm^{-1} for amide II confirms the presence of amino groups in chitosan molecule [9]. These peaks are slightly shifted to higher wavenumber in prepared complex. In pure PEO spectrum, a large broad band appears centered at 3446 cm^{-1}. This is due to the hydration of PEO, thus show that the PEO is highly hydrophilic. Pure PEO shows a large broad band of CH_2 stretching between 2957 and 2840 cm^{-1} [10]. However, in prepared polymer electrolyte the bands are shift to 2918 and 2884 cm^{-1} corresponding to asymmetric CH_2 stretching ($\gamma(CH_2)_a$) and symmetric CH_2 stretching ($\gamma(CH_2)_s$) vibrations respectively. Two clear vibrational modes appear in PEO at 1464 cm^{-1} and 1373 cm^{-1} which corresponds to asymmetric CH_2 bending ($\delta(CH_2)_a$) and symmetric CH_2 wagging and some C-C stretching ($\omega(CH_2)_a$)+ (γ(CC)) vibrations respectively.

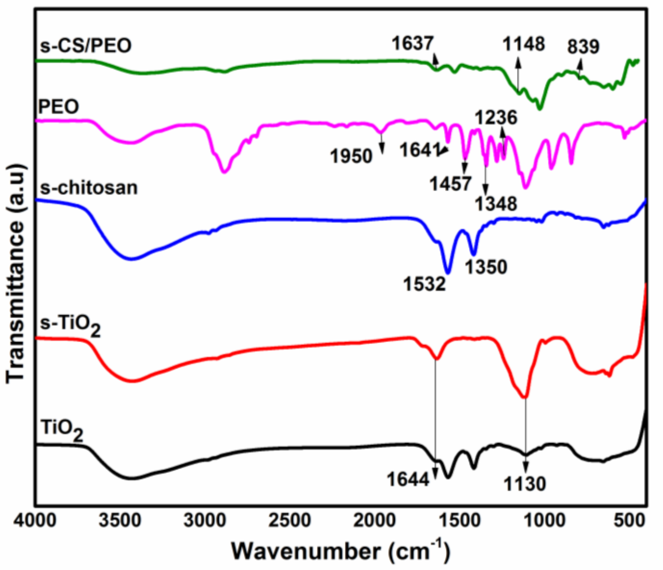

Figure 2. FTIR spectrum of pure and blend membranes

From figure the peaks at 1352, 1278, 1236 and 961 cm^{-1} represent the CH bending, CH_2 asymmetric twisting, CH_2 symmetric twisting and C-O-C symmetric and asymmetric stretching in pure PEO [11]. Intense peak at 1567 cm^{-1} is assigned to an ether oxygen group of PEO, which is shifted to the higher wave numbers 1569, 1573, 1575 and 1577 cm^{-1} in all the prepared complexes respectively. The peak found at 3552 cm^{-1} in s-chitosan is present in the blend membrane, which may be due to the interaction between the ether oxygen and the free O-H groups of chitosan via hydrogen bonding. The C-H stretching band appearing at 2957 cm^{-1} is slightly shifted to the higher frequencies and this clearly indicates that there is a strong interaction between s-chitosan and PEO. In s-CS/PEO spectra the intensity of the hydroxyl group, amide I, amide II bands in the composite membrane increases compared to pure chitosan. The peaks at 1640, 3400-3500 cm^{-1} bands ensure the high water molecules absorption of the composite membrane. It has been observed that the characteristic signal of –OH at 3400 cm^{-1} widened after the addition of sulfonated TiO_2. The appearance of $NH^{3+}$and T=O band and the disappearance of crystalline band indicate the successful protonation of the amino group, while the hydrogen bond and crystalline structure in the chitosan are damaged to some extent. In all the materials, the typical Ti-O-Ti bands around 1644, 1130, and 510 cm^{-1} associated with the formation of a condensed titania network are present, and weak peaks associated with non-condensed Ti-OH groups around 960 cm^{-1} are also present. FTIR spectrum shows the stretching vibration of OH group in sulfonic acid at 2890 cm^{-1} and stretching vibration of sulfoxide in sulfonic acid at 1152 cm^{-1}, revealing the presence of sulfonic groups in the sulfonated chitosan. This indicates that the sulfonation reaction involved with amino groups in chitosan and amino groups of secondary amide groups. In prepared electrolyte spectrum the –OH and –NH_2 broad peaks were sharpened because the strength of the hydrogen interaction and overlapping between –OH and the NH_2.

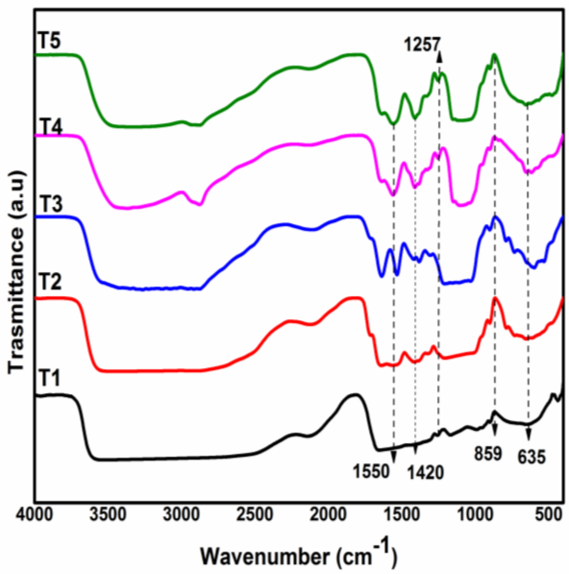

Figure 3. FTIR spectrums of prepared electrolyte membranes (T1) s-chitosan/PEO/s-TiO_2 (2 wt%), (T2) s-chitosan/PEO/s-TiO_2 (4 wt%), (T3) s-chitosan/PEO/s-TiO_2 (6 wt%) (T4) s-chitosan/PEO/s-TiO_2 (8 wt%), (T5) s-chitosan/PEO/s-TiO_2 (10 wt%).

C. Ionic Conductivity

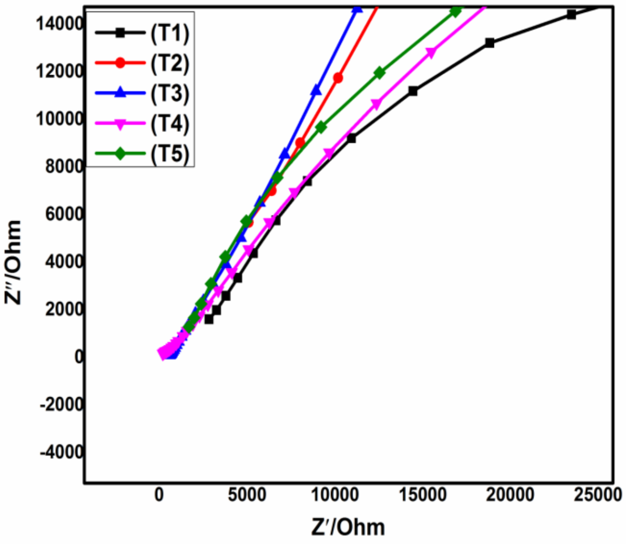

Figure 4. Conductivity spectrums of prepared electrolyte membranes (T1) s-chitosan/PEO/s-TiO_2 (2 wt%), (T2) s-chitosan/PEO/s-TiO_2 (4 wt%), (T3) s-chitosan/PEO/s-TiO_2 (6 wt%) (T4) s-chitosan/PEO/s-TiO_2 (8 wt %), (T5) s-chitosan/PEO/s-TiO_2 (10 wt%).

Typical impedance plots of s- chitosan /PEO with different wt% (2, 4, 6, 8 and 10) of s-TiO_2 at room temperature depicted in figure. 4. In the frequency range of 1 HZ to 1 MHZ .The highest ionic conductivity of the s-chitosan /PEO/ s-TiO_2 (8 wt%) membrane was 4.35×10^{-2} S/cm. The conductivity of the composite membrane increased from 0.910 to 4.35×10^{-2} S/cm. when increasing the amount of s-TiO_2 from 2 to 8 wt % s-TiO_2 and then decreased above 8 wt % membrane use the hygroscopic property of metal oxide to retain the water retenation capacity of the membrane. The reason for proton conductivity of sulfonated composite membranes is water uptake of the composite membrane increased with the s-TiO_2 addition as shown in table.1. An additional proton conduction path way was created due to molecular water absorption by s-TiO_2 , part of the proton can be conducted by hopping mechanism between TiO_2-SO_3 –OH and water molecules [12]. The protonic conductor of s-TiO_2 enhances the ionic conductivity of the s-chitosan/PEO membrane further, owing to the higher hydrophilic channels *via* the sulfonic acid moieties of chitosan and TiO_2. However, higher s-TiO_2 loading (10 wt%) did not contributed to any addition increase in proton conductivity. The increased H^+ diffusion of the s-TiO_2 based s- chitosan / PEO membranes. An increase in the s-chitosan/PEO/s-TiO_2 content up to 8 wt% results in a linear increase in the ionic conductivity values, while a further increment in the s-TiO_2 content yields a decrease in ionic conductivity due to the blockage of s-chitosan/PEO conduction channels by the agglomerated s-TiO_2 fillers.

Table .1 Conductivity values of prepared electrolytes at different ratio of s-TiO_2

Sample code	Ratio (CS:PEO)/s-TiO_2	Conductivity × (10^{-2} S/cm)				
		303K	*313K*	*323K*	*333K*	*343K*
T1	*98:2*	*0.910*	*1.137*	*1.207*	*2.579*	*3.721*
T2	*96:4*	*1.85*	*2.933*	*3.29*	*3.49*	*4.57*
T3	*94:6*	*3.109*	*3.383*	*4.16*	*4.414*	*4.56*
T4	***92:8***	***4.35***	***4.937***	***5.026***	***5.49***	***5.87***
T5	*90:10*	*3.83*	*4.143*	*4.48*	*5.16*	*5.795*

D. Temperature dependence conductivity

It is seen from the figure that as the temperature increases, the frequency at which the dispersion becomes prominent shifts to higher frequency region. In other words, the bulk relaxation shifts to higher frequencies with the increase of temperature. As the result the conductivity increases. From the conductivity values of polymer electrolyte membrane of different wt% of s-TiO_2 at various temperature .The linear variation of log σ Vs. 1000/T figure 5 suggest as Arrhenius – type thermally activated process represented by the relation

$$\sigma = \sigma_0 \exp(-E_a/KT)$$

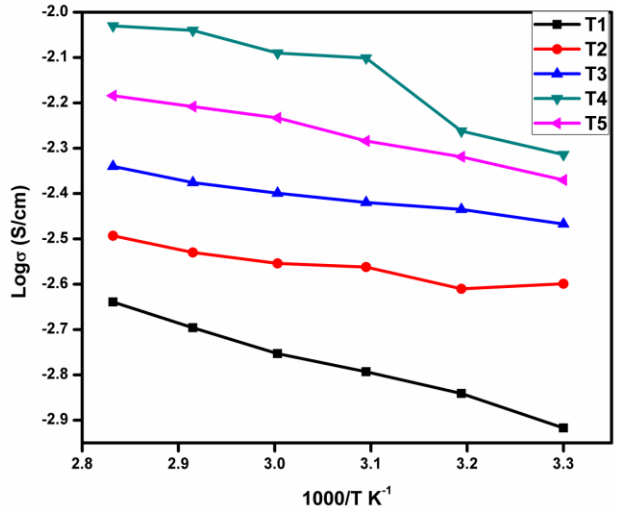

Figure 5. Temperature dependence spectrums of prepared electrolyte membranes (T1) s-chitosan/PEO/s-TiO_2 (2 wt%), (T2) s-chitosan/PEO/s-TiO_2 (4 wt%), (T3) s-chitosan/PEO/s-TiO_2 (6 wt%) (T4) s-chitosan/PEO/s-TiO_2 (8 wt%), (T5) s-chitosan/PEO/s-TiO_2 (10 wt%).

Arrhenius plots indicate that the ionic conductivity increases with increasing temperature in all composition of the polymer electrolytes system. There changes in the conductivity with temperature in solid polymer electrolyte to segmental (polymer chain) motion, which results in an increase in the free volume of the system when the temperature increases. The segmental movement of the polymer chain causes the mobility of the ions to increases and the segmental motion of polymer chain causes the conductivity increases [13]. However, at higher temperatures where the amorphous region progressively increases, the polymer chains acquire faster internal modes in which bond rotations produce segmental motion. The activation energy is a combination of energy of charge carrier creation and the energy of ion migration that can be evaluated by linear fitting to the log σ Vs. 1000/T plots. The equation energy is found to decrease gradually with increases of s- TiO_2, confirmly the increases in amorphous nature of polymer electrolyte with the addition of nano fillers.

4.5. Physico-chemical studies

The adsorption of water molecules by the polymeric membranes augments the ion transport *via* proton carriers, H-networks, and large transfer paths. The inclusion of 2 to 10 wt% s-TiO_2 gradually enhances the water uptake of the sulfonated chitosan/PEO/s-TiO_2 composite membrane (Table 2), owing to the hydrophilic characteristics of s-TiO_2. However, a further increment in the s-TiO_2 content (wt%) increases the water adsorption values of the s-chitosan/PEO membrane due to the aggregation of s-TiO_2 nanostructures on the s-chitosan/PEO matrix, which block the hydrophilic channels [14]. An increment in the hygroscopic characteristics of s-TiO_2 achieved *via* sulfonation. The higher water uptake reached, s-TiO_2 fillers maximize their water uptake due to the increased hydrophilic content of the corresponding protonic conductors. The water content of the composite membranes increased with increasing sulfonated titanium dioxide nanoparticle incorporation, because inorganic nanoparticles reduce the membrane free volume and the swelling ability. These results indicate that the water content, which greatly influences the methanol crossover, can be controlled by the addition of s-TiO2 particles. The IECs of the s-chitosan/PEO/s-TiO_2 composite membranes were established to be inferior to the s-chitosan/PEO membranes (Table 2). The hydrogen bonding exerted between –SO_3H of sulfonated chitosan and the –OH groups of the ceramic fillers increases the ion-exchange functionalities in composite membranes. However, the protonic conductors of the ceramic fillers s-TiO_2 increase the IECs of the corresponding membranes over those of the s-chitosan/PEO membranes due to the high sulfonation content of the corresponding composite membranes.

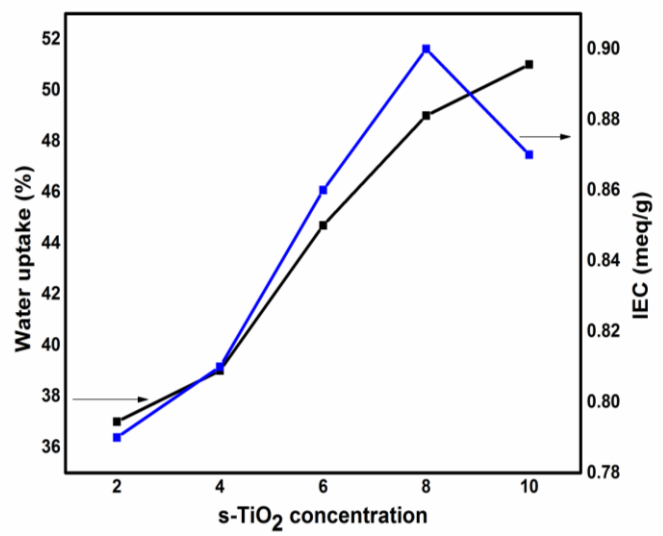

Figure 6. Water uptake and IEC spectrum of prepared electrolytes

Table 2. Values of the Activation energy and physico-chemical studies

Sample Code	Ratio of s-TiO_2 (Wt %)	Ea (eV)	Water Uptake (%)	Swelling Ratio (%)	IEC (meq/g g)
T1	*98:2*	*0.47*	*37± 0.03*	*36.2*	*0.79± 0.01*
T2	*96:4*	*0.43*	*39.01± 0.01*	*33*	*0.81± 0.05*
T3	*94:6*	*0.38*	*44.7± 0.01*	*29*	*0.86± 0.02*
T4	***92:8***	***0.34***	***49± 0.02***	***24.55***	***0.90± 0.03***
T5	*90:10*	*0.40*	*51± 0.04*	*27.9*	*0.87± 0.03*

IV. CONCLUSION

Composite membranes were prepared using aqueous acetic acid as the casting solvent and s- TiO_2 as the inorganic filler. The membranes were characterized by XRD, FTIR and conductivity. Physico -chemical properties of the membranes were studied by water uptake, swelling ratio, IEC. The introduction of the inorganic filler supplies the composite membrane with a highest IEC and improves the water uptake. The observed XRD pattern ascribe that the s-TiO_2 particles were dispersed in the membrane and its shows a particles show a more amorphous nature. FTIR analysis results proved that the sulfonated groups were indeed quantitatively introduction in to the polymers. The proton conductivity of composite membrane exceeded 4.65×10^{-2} S/cm at 30 °C, which is greater that of Nafion membrane under the same conditions in the presence of 8 wt% of s-TiO_2 in sulfonated chitosan/PEO polymer matrix. Temperature dependence conductivity possess the Arrhenius type thermally activate process. From the Arrhenius plot activation energy of the membrane decreases as increasing the sulfonated nanofillers in polymer matrix. From the obtained results, we confirm that the s-TiO_2 incorporated s-chitosan/PEO based electrolytes are suitable in the microbial fuel cell applications.

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