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SYNTHESIS AND CHARACTERIZATION OF POLYVINYL ALCOHOL BASED AND TITANIUMDIOXIDE DOPED NANOCOMPOSITE MEMBRANE

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Abstract: Today, perfluoro sulfonic acid membranes are the most widely used membranes. However proton conductivity of these membranes is very small at high temperatures and they are very expensive. Therefore studies have been focused on the investigation of alternative membranes. In this study, it is aimed to synthesize an organic-inorganic composite membrane that has better properties than the Nafion® membrane. In this study nano sized titanium-dioxide (TiO_2) doped phosphonated polyvinyl alcohol (PVA) based membranes were synthesized. Also these membranes were subjected to the characterization experiments such as, determination of water uptake capacity and ion exchange capacity, swelling properties, Fourier Transform Infrared Spectroscopy (FT-IR), fenton tests, mechanical tests and electrochemical impedance analysis (EIS). As a result of all these studies it was determined that the 15% TiO_2 doped membrane has the better properties such as highest proton conductivity (0.03 $S.cm^{-1}$), ion exchange capacity (1.04 $meq.g^{-1}$) and water uptake (45%). Regarding the values reported in the literature and depending on the knowledge gained during the fuel cell studies it was concluded that any membrane which has the above properties is suitable for the fuel cell applications.

Anahtar Kelimler: Fuel cell, Synthesis of membrane, Characterizations of membrane, Polyvinyl alcohol.

TiO_2 KATKILI POLİVİNİL ALKOL BAZLI NANOKOMPOZİT MEMBRAN SENTEZİ VE KARAKTERİZASYONU

Özet: Günümüzde elektrolit olarak kullanımı en yaygın olan membranlar perfluoro sülfonik asit membranlardır. Ancak bu membranların yüksek sıcaklıkta proton iletkenliği düşüktür ve çok pahalıdır. Bu nedenle çalışmalar alternatif membranlar arayışı üzerine yoğunlaşmıştır. Bu çalışmada Nafion® içerikli membrana göre daha iyi fiziksel ve kimyasal özelliklere sahip, hem organik hem de inorganik yapıyı bir arada bulunduran kompozit membran sentezi amaçlanmıştır. Yapılan çalışmada nano boyutta TiO_2 katkılı fosfolanmış PVA bazlı membranlar sentezlenmiştir. Sentezlenen membranlar su tutma kapasitesi, şişme özelliği, Fourier Dönüşüm Kızıl Ötesi Spektroskopisi (FT-IR), iyon değiştirme kapasitesi (IEC), elektrokimyasal empedans ölçümleri, mekanik dayanım testleri ve fenton testi gibi karakterizasyon deneylerine tabi tutulmuştur. Çalışmaların sonucunda %15 TiO_2 katkılı membranın diğer membranlara göre daha yüksek proton iletkenliği (0,03 S/cm), iyon değiştirme kapasitesi (1,04 meq/g) ve su tutma kapasitesine (%45) sahip olduğu belirlenmiştir. Literatürede rapor edilen değerler ve çalışma kapsamında edinilen bilgilere dayanılarak bu özelliklere sahip bir membran yakıt hücrelerinde elektrolit olarak kullanıma uygundur olduğu düşünülmektedir.

Keywords: Yakıt hücresi, membran sentezi, membran karakterizasyonu, Polivinil Alkol.

NOMENCLATURE

m_{wet}	wet weight, [g]
m_{dry}	dry weight, [g]
$m_{membrane}$	weight of membrane, [g]
N_{NaOH}	normality of sodium hydroxide, [$mol.L^{-1}$]
N_{HCl}	normality of hydrochloric acid, [$mol.L^{-1}$]
V_{NaOH}	volume of sodium hydroxide, [mL]
V_{HCl}	volume of hydrochloric acid, [mL]
$t_{membrane}$	membrane thickness, [μm]
R	resistance, [Ω]
A	electrode surface area, [cm^2]
T	temperature, [K]
E_a	activation energy, [$kJ.mol^{-1}$]

Greek Symbols

σ	proton conductivity, [$S.cm^{-1}$]

Acronyms

EIS	Electrochemical impedance analysis
FT-IR	Fourier transform infrared spectroscopy

IEC	Ion exchange capacity
PBI	Polybenzimidazole
PEM	Proton exchange membrane
PEMFC	Proton exchange membrane fuel cell
PFSI	Partially fluorinated acid ionomer
PVA	Polyvinyl alcohol
SPPO	Sulfonated poly(2,6-dimethyl-1,4-phenylene oxide)

INTRODUCTION

Membrane is the one of the most important parts of the fuel cells not only due to efficiency of the Proton exchange fuel cells (PEMFC) depends in great extent on its performance but also due to fact that it is the one of the cost determining item of the fuel cell. The most widely used membranes are perfluoro sulfonic acid membranes (Mauritz and Moore, 2009; Savadogo, 1998; Hickner et al. 2004) which have some important disadvantages such as high cost, low conductivity at low humidity and/or high temperature, and high methanol crossover (Kreuer, 1996; Heinzel and Barragan, 1999).

In order to overcome these problems scientists have focused their studies on the development of alternative membranes and one of the results of these studies is the development of aromatic hydrocarbon membrane materials (Jannasch, 1999; Chen et al. 2004; Rikukawa and Sanui, 2000; Hickner and Pivovar, 2005). Also there have been great progresses in the preparation of hydrocarbon membrane materials as alternative PEMs (Won and Park, 2003; Won and Choi, 2003; Joseph, 2007).

Although there are huge number of studies exist in order to find out an alternative membrane synthesis, structural modification and blending of existing proton exchange membranes (PEM), organic/inorganic composite membranes as well as hybride membranes preparation are among the most successful approaches for enhancement of PEMFC performance (Mahdi et al. 2011; Adjeman et al. 2002; Ahmad et al 2010; Deluca et al 2006; Fu et al 2007; Hasani et al. 2010; Şahin et al 2009; Şahin et al 2010).

Synthesized membranes divided into five different groups according to their main chain composition and functional groups, namely PFSI membranes, partially fluorinated acid ionomer membranes, nonfluorinated acid ionomer membranes, polybenzimidazole (PBI)/H_3PO_4 membranes, and alkaline ionomer membranes, by Zhang and Shen, 2012.

Purposes of structural modification and blending of existing membranes are to enhance their ionic conductivity especially at high temperatures and under dry conditions, to improve their mechanical and chemical stability (Bose et al. 2011). For example Muriithi and Loy, 2012, modified the Nafion to prepare a composite membrane by using 20 and 400 nm in diameter silica particles via using a modified Stober procedure. They showed the small silica particles improve the proton conductivity of the membrane in greater extent than the larger particles.

Organic –inorganic composite membranes combine the advantages of the organic and inorganic materials (Tripathi and Shahi, 2011) such as rigidity, thermal stability and flexibility, dielectric, ductility and processability respectively (Zou et al. 2008). In order to improve the membrane properties such as, thermal stability, ionic conductivity, water retention, etc. numerous studies on organic-inorganic hybride membranes take place in literature. For example TiO_2 was used as to improve the proton conductivity (Lobato et al. 2011), zirconium dioxide was used to both increase the proton conductivity and thermal stability (Park et al. 2008) where as silicates were used to improve water retention property of the membranes. A.K.Mishra et al. 2012 states that, “among these particles, silicate-based nanoparticles were extensively studied because of their lower cost, inferior electrical conductivity and better water retention properties compared to those of other nanoparticles”.

Hybride membranes are one of the most promising solution for the major drawback of water-swollen membranes such as perfluorosulfonic acid copolymers, that significant decrease in their proton conductivities at the severe operating conditions that arises mainly due to their dehydration (So et al. 2010; Li et al 2003).

In literature there are huge numbers of studies in which different types of polymer, such as PVA, chitosan, polybenzimidazole (PBI) and sulfonated poly(2,6-dimethyl-1,4-phenylene oxide) (SPPO) are used as organic phase for preparing cation exchange hybrid membranes. Among these membranes PVA is the one of the most widely used polymer (Hao et al 2013; Merle et al 2012; Praptowidodo, 2005; Molla et al. 2011; Qiao et al 2010; Kima et al. 2004; Yang et al. 2010) due to its low-cost, water-soluble, good flexibility and film forming properties (Muriithi and Loy, 2012). Further that, it has C–OH groups in its polymer chain available for the reaction with –Si(OR)3 groups via sol–gel route that make the PVA as a good starting material for synthesis of organic–inorganic hybrid membranes.

In this study it was tried to synthesize a membrane for PEMFCs with high mechanical and chemical stability, having a high proton conductivity, and suitable to study at high temperatures. It was planned to use PVA as skeloton for the membrane matrix. Since PVA based membranes are not mechanically stable in water due to the presence of the hydroxil (OH-) bonds within their structure, formaldehyde was added to solution in order to enhance the crosslinking and hence improve the mechanical stability of the membranes. Beside, hypophosporous acid was added to the membrane solution in order to increase the active groups attached to the polymer chain and hence to enhance the proton conductivity of the membrane. After the synthesis of the membranes, their characterization experiments were performed by using the appropriate techniques.

METHOD

In this study a new modified sol-gel method was used as a membrane synthesis method instead of classical sol gel method which is the most frequently encountered method in the literature (Ren et al. 2013). Method based on the dissolution of base PVA (Sigma Aldrich 99% M_w:124000) directly within the solution that containing active groups, instead of addition of active groups in dropwise manner into the base polymer solution. Aim of this modification is attachment of active groups to the structure in a more homogeneous manner. In this way, a uniform structure of the active participation of groups considered. TiO_2 (Sigma Aldrich 99.98%) was subjected to the size reduction process before it was doped to the membrane. Mixture was first put into an aqueous solution form and then it was mixed by using mechanical mixer. Then it was taken into ultrasonic homogenizer (BANDELİN Sonoplus HD3100) in order to reduce the size of TiO_2 particles by using sonic waves. TiO_2 was doped in different proportion (5%, 10, 15 ,20 25, 30 and 40%) to the membranes. After base polymer dissolved in the appropriate amount of acid so that its phosphonation degree adjusted to 25%, formaldehyde (Sigma Aldrich 34.5%) was added to the solution in a ratio of 2:1 by volume. After that additive was added to the polymer solution and it was rigorously mixed at room temperature to obtain a homogeneous solution. Critical point in this procedure is the casting of membrane before the formation of the salt as a result of the reaction between the formaldehyde and phosphorous acid. Therefore the mixing time and temperature after the phosphonation are the very important parameters. Any retardation in casting leads to formation of phosphinate salts that results the impurities in membrane structure and consequently a significant decrease in its mechanical strength. Codes and contents of prepared membranes are given in Table 1.

Table 1. Codes and composition of synthesized composite membranes.

Code	Composition
5T	5 % TiO_2 added membrane
10T	10 % TiO_2 added membrane
15T	15 % TiO_2 added membrane
20T	20 % TiO_2 added membrane
25T	25 % TiO_2 added membrane
30T	30 % TiO_2 added membrane
40T	40 % TiO_2 added membrane

After the preperation of the membranes given in above table, characterization experiments were carried out.

RESULTS AND DISCUSSION

Water Uptake Capacities

In order to membranes have high proton conductivity and low resistance, it is desired they have a high water uptake capacity. Water uptake capacity tests were carried out at room temperature, 60ºC, 70ºC and 80ºC. Synthesized membranes were dried at 100 ºC and they were weighted after their weight reach to a constant value. After that they were immersed in hot water at the temperatures described above for 24 hours. At the end of 24 hours, membranes were taken out from hot bath and excess water on their surface was wiped out. Water hold-up capacities of membranes were calculated from obtained data by using Equation 1.

$$\%\ \text{Water uptake} = \frac{m_{wet} - m_{dry}}{m_{dry}} \times 100 \qquad (1)$$

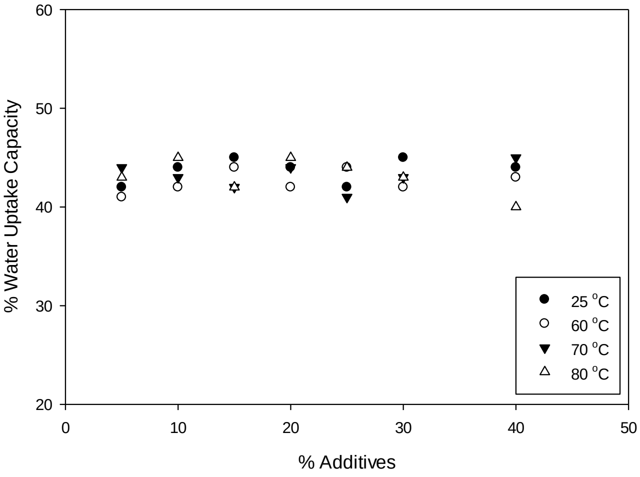

Figure 1. Variation of water uptake of membranes with TiO_2 additive with temperature

Variation of water uptake capacities of membranes with amount of TiO_2 additive and with temperature was given in Figure 1. There is no any regular relationship between the water uptake capacity and temperature. Water uptake capacities of membranes were not change significantly with increasing temperature and they reached to a constant value with increasing amount of additive. TiO_2 has the hydrophobic character, therefore it is expected that the water hold-up capacities of membranes are not change with temperature.

Water uptake capacities of TiO_2 that have hydrophobic character, containing membranes were not changed with the increasing temperature. In this way characteristic properties of membranes are dominate and membranes showed a stable structure. This stuation indicates the high thermal stability. Wu et al. (2008) added 3%-15% TiO_2-SO_4^{-2} to the membrane matrix and they found that the water uptake capacities of membranes decreased from 36% to 32% with the increasing amount of additive. Due to the enhancing effect of the hydrophosphorous acid on proton conduction mechanism, water uptake capacity of synthesized membranes does not change with the amount of additive and it remains nearly constant.

Swelling Properties

Membranes were encountered with water at cathode side. If membranes were swelling due to the absorption of water, distance that protons have to travel becomes longer and it will cause higher diffusional resistivity and hence proton conductivity of membranes will decrease. Therefore membranes must have higher water uptake capacity without swelling.

Swelling properties of the membranes were measured. at 60 º C, 70 º C and 80 ° C as well as water-uptake capacity measurements. Swelling properties were determined in terms of increasing thickness and aspect ratio. Membrane samples for swelling measurements were prepared by cutting membranes in 2cm x 2cm dimensions and thickness of the membranes were measured with Sheen Brand Minitest 3100 model thickness gauge. Size was measured again after the membranes were stored in water. A close investigation of change of thickness and surface area of membranes shows that, changes in these properties of the membranes are decrease with the increasing the temperature.

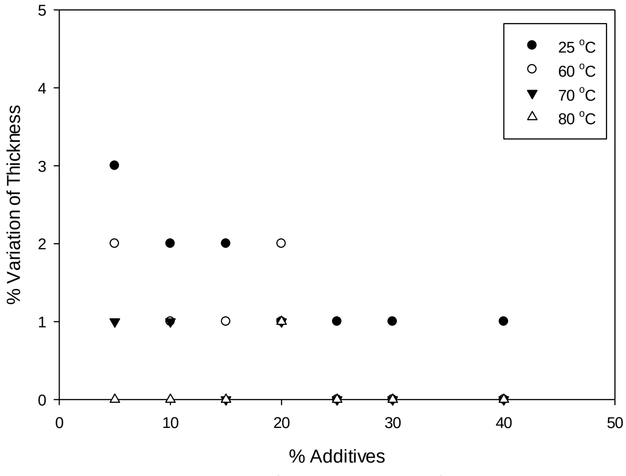

Figure 2. Variation of thickness of TiO_2 doped membranes with temperature.

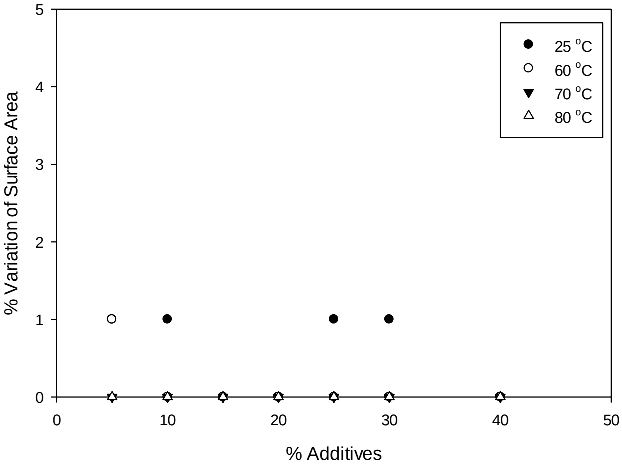

Figure 3. Variation of surface area of TiO_2 doped membranes with temperature.

Variation of the thickness and surface area of TiO_2 doped membranes with amount of additives and temperature were shown in Figure 2 and Figure 3 respectively. Change in the thickness and surface area of the synthesized membranes was decreased with the increasing temperature. Since the variation of thickness and surface area of the membranes at temperatures higher than 60 °C were very small, it can be concluded that the membranes are not swelling beyond that temperature. This result confirms with the results reported in the literature very well. For example, Wu et al. (2008) found that the membranes containing TiO_2 as additive, were not show swelling property.

Ion Exchange Capacity

Ion Exchange capacity is a measure of proton conductivity. Firstly synthesized membranes were put in a 30 mL 0.1 N NaOH solution at a certain temperature and time. During this time, the Na^+ ions replaced by H^+ ions. Then membranes were removed from NaOH solution and titreted with 0.1 N HCl solution. Shotte TA500 plus brand and model, 0.01 mL, precision, computer controlled titration device was used for titrations. Ion exchange capacities were calculated by means of Equation 2.

$$\mathrm{IEC} = \frac{(N_{NaOH} \times V_{NaOH}) - (N_{HCl} \times V_{HCl})}{m_{membrane}} \qquad (2)$$

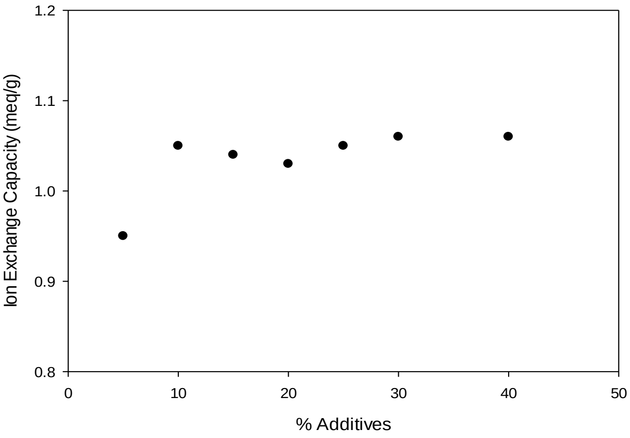

Figure 4. Change of ion exchange capacity with amount of additive

Ion Exchange capacities of TiO_2 doped membranes were not change significantly. Obtained ion exchange capacity values are comparable with the ion exchange capacity of Nafion membrane (0.99 meq/g).

Electrochemical impedance spectroscopy (EIS)

Proton conductivity is the most important property of the membranes. Proton conductivities of membranes were measured by using the Solartron 1260, 1287 and test cell which is made new. Impedance spectroscopies were performed with two probe technique, between 1MHz and 100 Hz, at room temperature and at 100% humidity. After this characterization method, resistivities of the membranes were found.

Proton conductivities of the membranes were found with the using the resistivities of the membranes and Equation 3.

$$\sigma = \frac{t_{membrane}}{R \cdot A} \qquad (3)$$

All of the proton conductivities data obtained at different temperatures were fit with Arrhenius equation.

Activation energies of the membranes were found by using Equation 5, that is obtained by the lineerization of Equation 4.

$$\sigma = \sigma_0 e^{-Ea/RT} \qquad (4)$$

$$\ln\sigma = \ln\sigma_o - Ea/RT \qquad (5)$$

Change proton conductivities of the TiO_2 doped membranes with increasing temperature were shown in Figure 5. Proton conductivities of the membranes were increased with the increasing temperature. Unchanged water uptake capacity have played an important role in the transport mechanism and increase the mobility of protons in TiO_2 doped membranes with proton conductivity values showed a regular increase.

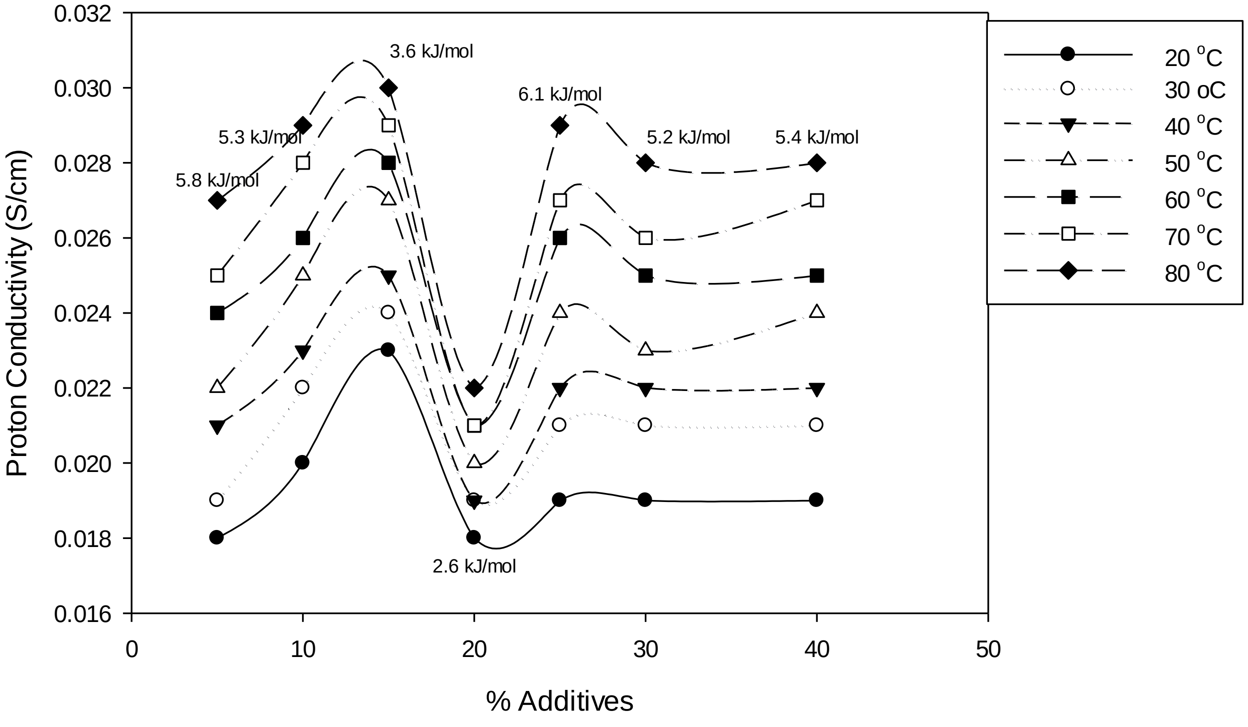

Figure 5. Variation of proton conductivities of TiO_2 doped membranes with temperature.

Wu et al.carried out a study by using different additive ratio up to 15%, and they observed a lineer relationship between the water uptake capacity and proton conductivity of the membranes (Wu et al. 2008). In this study, proton conductivity of membranes were investigated at different additive ratios by using larger additive ratio range, and it was observed that TiO$_2$ behaves like a filler and it mask the properties of the active group hypo phosphorous acid at additive ratio of 20%. In similar manner, Fenton test results showed that when additive ratio is higher than 20%, additive causes negative effects on membrane properties. Yang et al. (2010) added TiO$_2$ to PVA up to 10% and they used polystyrene sulfonic acid as active group. They observed a continuous decrease in proton conductivity of the membranes with increasing amount of additive. They obtained the highest proton conductivity value as 0.00354 S.cm^{-1} at 70 ^{o}C. This value is significantly smaller than the values obtained in this study.

Increase of the proton conductivities of TiO$_2$ membrane with the increasing temperature were fit Arrhenius equation and activation energies were found by using this relationship. 15% TiO$_2$ doped membranes have higher proton conductivity than other membranes.

FT-IR Analyses

Jasco FT/IR–480+ was used for to determine the structural properties of membranes Measurements were implemented at 4000–400 cm^{-1} wavelenght and functional groups participated in the structure were determined from peaks of the graph of absorbance against the wavelength. FT-IR spectrums of TiO$_2$ doped membranes were shown in Figure 6.

Splayed peak between 3100-3600 cm^{-1} wavelenght is the typical OH- peak. Peak which is between 2800-3100 cm^{-1} that make up the main structure of the organic structure of PVA membrane which belongs to the vibration of the C-H. Peak which is obsersegment sharply at 1700 cm^{-1} is the C=O expansion band caused by ester groups. This band is thought to stem formaldehyde. In addition, the interaction of hypophosphorous acid, TiO$_2$ in structure, the contribution from the peaks of some of the interaction is expected to be seen.

According to the literature, a peak expected to be seen at a wavelength of 474 cm^{-1} due to the particles of titanium, but this peak was observed at 500 cm^{-1} wavelength. An increase in the intensity of peaks expected increase with the increasing amount of additives. But, because of the absorbance values of these peaks is lower than peak which is from organic structure, spectrums obtained from the peaks not seen clearly. Same time, cracking was observed at peak. These phenomenon may be expressed by the presence of impurities.

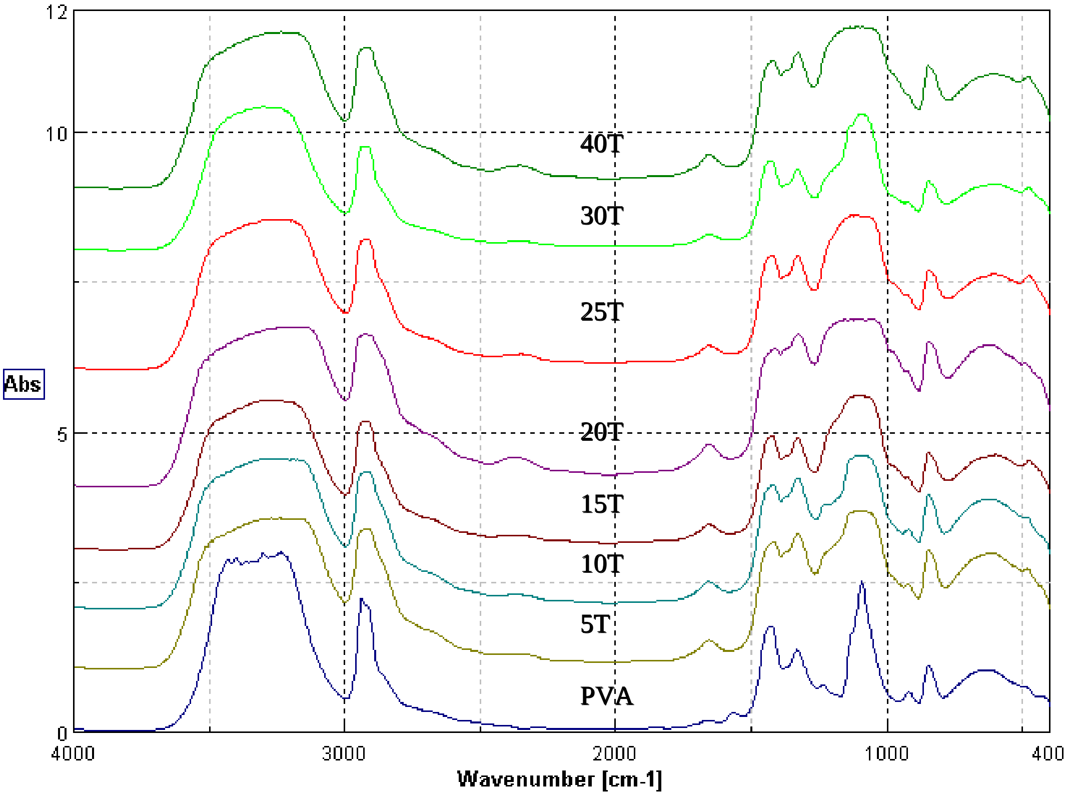

Figure 6. FT-IR spectrum of TiO$_2$ containing membrane

Mechanical Stability Tests

Mechanical stability tests of membranes were carried out by using SHIMADZU dynamic mechanical test system. Membrane samples were cutted in 15 mm x 4 mm dimensions and tightly fixed between the clips of the instrument. Mechanical stability measurements were performed at a stress rate of 2 mm min^{-1}. Measurements were repeated three times for each sample and arithmetical average of these measurements were taken as the tensile strength of the membrane. Results of these measurements were summarized in Table 2.

Table 2. Mechanical stability properties of synthesized membranes.

Code	Tensile strength (MPa)	Young's Modulus (MPa)
5T	25.21	645.86
10T	23.26	630.24
15T	23.08	617.45
20T	22.16	602.59
25T	21.84	594.62
30T	21.65	590.36
40T	21.45	580.98
Nafion	36.82	176

Mechanical stability values show that, tensile strength of the membranes decreases with the increasing amount of additive. This may be explained by the decrease of the polymer ratio in membrane matrix by the increasing amount of additive.

Na et al. (2013) found the tensile strength of Nafion membrane as 37 MPa, and its Young's modulus value as 180 MPa. In this study, these parameters of commercial Nafion membrane were measured as 36.82 MPa, and 176 MPa respectively. Li et al. (2010) synthesized the PBI based membranes and they found the highest Young's modulus value for these membranes as 550 MPa. Tang et al. (2008) showed that the Young's modulus value of the membranes decreases with the increasing their water uptake capacities. Since water uptake capacities of the membranes synthesized in this study are close to each other, their Young's modulus values are also close to each other.

Fenton Tests

Fenton tests were carried out in order to determine the oxidative stability (that may be taken also as a measure of the chemical stability of the samples) of the membranes synthesized in this study. Membrane samples prepared by cutting the small parts with surface area approximately 2 cm^2 and weight 0.5 g from membranes and immersing them in a 50 mL fenton solution containing 3% by wt H_2O_2 (Sigma Aldirch, 30% aqueous solution) and 4 ppm Fe^{2+} ($FeCl_2.6H_2O$ (Sigma Aldrich). Weight loss of the samples were determined by weight measurements in 20 hour intervals (Xiao et al. 2011; Ghassemzadeh et al. 2011). Change of oxidative stabilities of the samples with amount of additive were given in Figure 7.

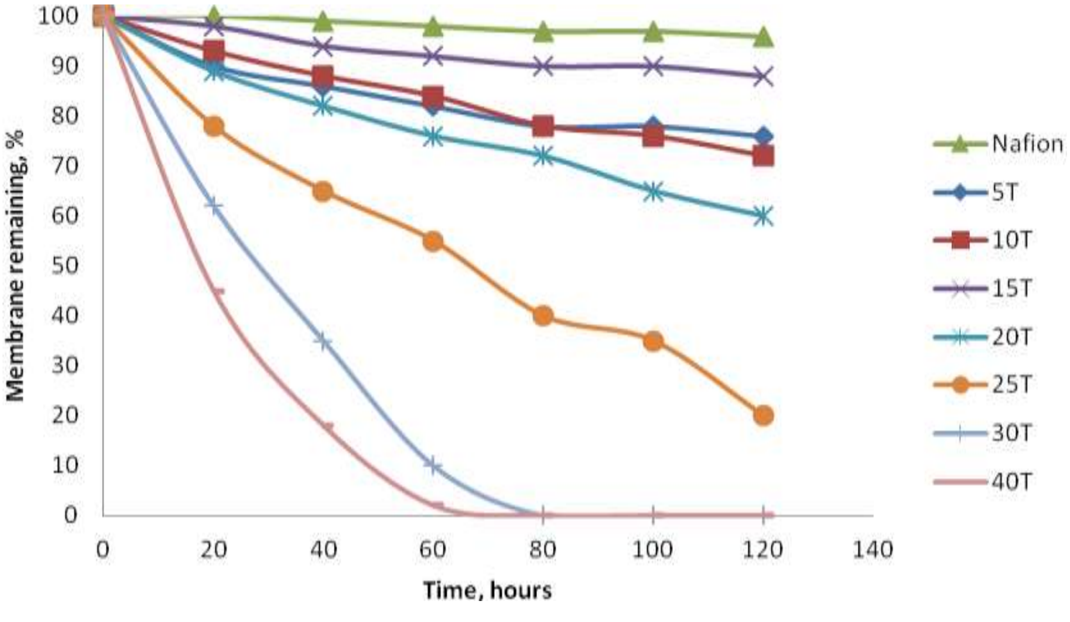

Figure 7. Oxidative stability-additive relationships of the membranes

It was observed from Figure 7 that, the oxidative stability values of membranes were increase with the increasing amount of additive up to amount of additive reach to 15%. The membrane, coded as15T, exhibited a behaviour similar to the Nafion membrane so that it hopeful in durability respect. But for the additive ratios higher than 15%, membrane undergo a rapid decomposition in oxidative medium. This behavior may be explained by the suppress of the properties of active groups in membrane matrix by the additive at high additive ratios and membrane shows only additive properties and hence its decomposition in the oxidative medium.. Ghassemzadeh at al. (2011) applied the fenton test to the Nafion 117 membrane and they reported there is no decrease in the intensity of the peaks in NMR spectrums which were taken during the two days. Nafyon 117 membranes were also tested in this study and it was found as a result of 120 hours fenton tests that there is no any significant weight loss.

CONCLUSION

In this study, PVA based membranes containing hypophosphorous acid and TiO_2 as additive in different ratios (%5,10,15,20,25,30,40) were synthesized. Depending on the water uptake capacity values, it can be said that, water uptake capacities of the membranes are not change, i.e., membranes are stable in aqueous medium. Swelling measurements were also supported this result and samples were not swelling in aqueous medium, which is a desirable property, due to their stability.

Ion exchange capacity values were not change and remain as a constant beyond a certain additive ratio. On the other hand proton conductivity values decreases at additive ratio of 20%. This can be explained by the properties of the additive becoming dominant as indicated by the fenton test results.

Results of FT-IR analysis showed that the additive can be inserted successfully into the membrane matrix and mechanical stability tests indicated that the membranes have the desired mechanical stability level.

Under the light of characterization experiments results it can be concluded that, 15% TiO_2 doped membrane has the better properties than the other membranes. This membrane has 0.023 S/cm proton conductivity at room temperature, 1.04 meg/gr ion exchange capacity and %45 water uptake capacity. Proton conductivity of this membrane was 0.030 S/cm at fuel cell conditions which is higher than the values obtained for other membranes. Comparison of properties of the membrane coded as 15T with those of Nafion membrane, leads to the conclusion that membrane coded as 15T is a promising one for the usage in fuel cells as electrolyte.

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