Süleyman Demirel Üniversitesi
Fen Bilimleri Enstitüsü Dergisi
Cilt 23, Sayı 3, 709-716, 2019

Süleyman Demirel University
Journal of Natural and Applied Sciences
Volume 23, Issue 3, 709-716, 2019

DOI: 10.19113/sdufenbed.529398

The Effect of Cross-linking Technique on Membrane Performance for Direct Methanol Alkaline Fuel Cell Application

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(Alınış / Received: 19.02.2019, Kabul / Accepted: 03.10.2019, Online Yayınlanma / Published Online: 30.12.2019)

Keywords
Fuel cell,
Poly(vinyl alcohol),
Cross-linking

Abstract: In this study, anion exchange membranes (AEM) based on poly(vinyl alcohol) (PVA) were prepared by two different cross-linking techniques and the effects of application sequence of thermal and chemical cross-linking technique on properties of AEM were investigated. Poly(ethylene glycol) diglycidly ether (PEGDGE) was used as a chemical cross-linking agent instead of the commonly used glutaraldehyde (GA). Evaluation of the fuel cell-related properties of the prepared membranes showed that the technique of cross-linking and the application sequence of techniques affected the properties of membranes. Promisingly, it was found that the membranes prepared by firstly chemical cross-linking and then thermal cross-linking at 150˚C (PPP150) exhibited high ionic conductivity (47 mS/cm), membrane selectivity values (89 x10^4 S.s/cm^3) and sufficient mechanical strength. These encouraging results indicate that AEMs-based on PVA cross-linked by chemical technique with PEGDGE and then thermal technique may be considered as a promising membrane for Direct Methanol Alkaline Fuel Cell (DMFC) applications.

Doğrudan Metanol Alkali Yakıt Hücresi Uygulamaları İçin Çapraz Bağlama Yönteminin Membran Performansı Üzerine Etkisi

Anahtar Kelimeler
Yakıt hücresi,
Polivinil alkol,
Çapraz bağlama

Özet: Bu çalışmada poli (vinil alkol) (PVA) esaslı anyon değişim membranlar (AEM) iki farklı çapraz bağlama tekniği ile hazırlanmış ve ısıl ve kimyasal çapraz bağlama tekniklerinin uygulanma sırasının AEM'ın özellikleri üzerine etkisi incelenmiştir. Kimyasal çapraz bağlayıcı olarak en çok kullanılmakta olan glutaraldehit (GA) yerine poli(etilen glikol) diglisidil eter (PEGDGE) kullanılmıştır. Hazırlanan membranların yakıt hücresi ile ilgili özellikleri değerlendirildiğinde, çapraz bağlama tekniğinin ve farklı tekniklerin uygulama sırasının membranın özelliklerini etkilediği görülmüştür. Önce kimyasal sonra 150˚C'de ısıl çapraz bağlama uygulanarak hazırlanan membranın (PPP150) yüksek iyonik iletkenlik (47 mS/cm), membran seçimlilik (89 x10^4 S.s/cm^3) ve yeterli mekanik dayanıma sahip olduğu görülmüştür. Elde edilen sonuçlar, önce PEGDGE ile kimyasal, sonra ısıl olarak çapraz bağlanan PVA esaslı anyon değişim membranların Doğrudan Metanol Alkali Yakıt Hücresi (DMFC) uygulamaları için ümit veren membranlar olarak düşünülebileceğini göstermiştir.

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1. Introduction

In the last decade, development in the solid alkaline fuel cell (SAFC) technology have directed the scientists to design of Direct Methanol Alkaline Fuel Cell (DMAFC). Using methanol as fuel in fuel cells provides advantage for the portable power sources due to, low emission, their high power density and easy storage/supply/transport of fuel. SAFCs enable to use the noble metal free catalyst (e.g. Ni, Ag) due to the faster kinetic of oxidation/reduction reaction of alcohol/oxygen in alkaline medium [1]. Also, the methanol crossover is low because of the opposite direction of ion transport with respect to electroosmotic resistance through the membrane. These properties allow a cost reduction of fuel cell device.

SAFCs are similar to Proton Exchange Membrane Fuel Cell (PEMFC) except using of anion-conducting polymer electrolyte membrane. In SAFCs, the solid

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** Corresponding author: gulsen@istanbul.edu.tr* electrolyte is Anion Exchange Membrane (AEM) and hydroxide anions are transported through AEMs from cathode to anode. AEMs are generally classified as homogeneous, interpenetrating and heterogeneous membranes. A heterogeneous membrane consists of a water soluble polymer and hydroxide salt. In these membranes, the alkaline salt provides the conductive properties of AEMs while the polymer provides the mechanical properties [2]. In case of the homogeneous membranes, cationic functional groups that is responsible for the conduction of hydroxide anions are covalently bound to a polymer backbone [3].

In the past several years, new AEMs based on different polymer matrix such as polysiloxane [4], polysulfone [5], copolymer of poly(epichlorohydrine) and poly(ethylene oxide) [6], polybenzimidazole [7] and poly (vinyl alcohol) (PVA) [2,8] were reported. Among them, PVA is the most attractive polymer matrix to AEM preparation because of its high density of reactive hydroxyl group, high hydrophilicity and film forming-capacity [8]. Up to now, a lot of studies about both heterogeneous, homogenous and interpenetrating membrane-based on PVA have been reported [10-15].

In our recent study, we investigated the effects of crosslinker type on the properties of AEMs based on Poly(vinyl alcohol)-Poly(diallyldimethylammonium chloride) (PVA/PDDA) [9]. The ionic conductivity results showed that PVA membranes with cross-linked by Poly(ethylene glycol diglycidyl ether) (PEGDGE) exhibited higher conductivity than the membranes cross-linked with glutaldehyde (GA). But, the water uptake value also excessively increased with the addition of PEGDGE as a crosslinker and this resulted in weakening of mechanical properties. Therefore, we have still examined the PVA-based AEMs. On the other hand, the influences of cross-linking processes consisting of a combined thermal cross-linking and chemical cross-linking with glutaraldehyde (crosslinker) technique on the properties of PVA/PDDA-based AEMs was discussed by Zhang et al. in detail [10]. They reported that both water uptake and ionic conductivity of membranes were improved by pre-heat treatment in addition to chemical cross-linking. This result encouraged us and we decided to continue our study about PVA membranes with cross-linked with PEGDGE. Because, the effects of thermal cross-linking on PVA/PDDA membrane which is chemically cross-linked with PEGDGE have not been reported so far.

In this study, it was aimed to prepare PVA-PDDA based AEMs with enhanced ionic conductivity and mechanical properties. For this purpose, two different cross-linking methods were applied; thermal and chemical cross-linking. The effects of thermal cross-linking temperature and the different application sequence of two cross-linking techniques on the properties of prepared AEMs were investigated. PEGDGE was used as a cross-linking agent instead of the commonly used GA.

2. Material and Method

2.1. Materials

PVA (99% hydrolyzed, M_w=89,000-124,000) was purchased from Aldrich. Poly(ethylene glycol diglycidyl ether) (PEGDGE) as cross-liker and Poly(diallyldimethylammonium chloride) (PDDA) (M_w=240,000) as cationic polyelectrolyte were obtained from Aldrich.

2.2. Membrane preparation

The aim of our study was to compare the effect of different cross-linking methods on the mechanical and conductivity properties PVA-based AEMs. Firstly, PVA-PDDA mixture was prepared, then, the cross-linking procedure was applied. 5 wt% PVA solution was prepared in hot water at 90°C. After a transparent solution was obtained, 10 wt% PDDA solution was added in solution at room temperature, in which the PVA/PDDA was 1:0.5 by mass. Obtained solution was mixed for 2 h and were treated by thermal and/or chemical cross-linking process. To determine the most acceptable procedure of cross-linking, four ways were followed;

(i) Chemical cross-linking of PVA was carried out by PEGDGE. The cross-linking proceeded between the hydroxyl groups of PVA and epoxy groups of PEGDGE [2]. This membrane was abbreviated as PPP. An appropriate of the PEGDGE (PVA:PEGDGE = 1:1 in weight ratio) was added to PVA-PDDA solution under stirring. After the mixture became a homogeneous solution, mixture solution was cast onto petri dish and dried at 50°C for 24 h.

(ii) For thermal cross-linking, PVA-PDDA mixture was cast onto petri dish and dried at 50°C for 24 h, then the obtained membranes were annealed at various annealing temperature ranging from 110°C to 150°C for an hour. These membranes were abbreviated as PP110/ PP130/ PP150.

(iii) For combined cross-linking technique, firstly, the membranes obtained by the above process (i) and then were annealed at 110, 130 and 150°C for an hour. These membranes were denoted as PPP110/PPP130/PPP150.

(iv) Unlike the previous technique (iii), thermal cross-linking was firstly applied to membrane as mentioned in (ii) , then, the membranes were dipped into chemical cross-linking solution containing 20 wt % PEGDGE at room temperature for an hour. These membranes were denoted as PP110P/PP130P/PP150P.

Table 1: Designation of AEMs

	PPP	PP110	PP130	PP150	PP110P^a	PP130P^a	PP150P^a	PPP110^b	PPP130^b	PPP150^b
Thermal cross-linking	-	110°C	130°C	150°C	110°C	130°C	150°C	110°C	130°C	150°C
Chemical cross-linking	+	-	-	-	+	+	+	+	+	+

a: Firstly thermal cross-linking and then chemical cross-linking

b;Firstly chemical cross-linking and then thermal cross-linking

The designation of all sample is illustrated in Table 1. All AEMs in Cl^- form due to PDDA were immersed into 1 M KOH for 24 h to converted to OH^- form.

2.3. Membrane characterization

A Perkin Elmer Spectrum One Fourier Transform Infrared Spectroscopy with attenuated total reflectance unit (FTIR-ATR) was used to determine the structure of membranes with a wavenumber resolution of 4 cm^{-1} in the range of 600-4000cm^{-1}.

The thermogravimetric analysis (TGA) of membranes was carried out with Seiko Exstar 6000-TGA/DTA 6300 model instrument by heating from 30 to 550°C at a heating rate of 10°C/min under nitrogen atmosphere.

The water uptake and swelling ratio of AEMs were determined as following procedure; the dried membranes were weighed and measured the dimensions, then immersed into deionized water at ambient temperature for 48 h. The wet membranes were weighed and their dimensions were measured after removing the free water on the membrane surface. The water uptake (WU) and swelling ratio (SR) value were calculated as follows:

$$WU = \frac{(W_w - W_d)}{W_d} \tag{1}$$

$$SR\ (\%) = \frac{(L_w - L_d)}{L_d} \times 100 \tag{2}$$

where W_w and W_d respectively are the mass of wet and dry membrane in g, L_w and L_d respectively are the length of wet and dried membrane in cm.

The ionic conductivity (σ) of the AEMs was measured at 25°C in water by two-probe technique using a Solartron AC impedance spectrometer (1260 impedance analyser) in the frequency ranging from 1 Hz to 20MHz with 10 mV amplitude. The conductivity of AEMs was calculated with the following equation:

$$\sigma = \frac{L}{R \times w \times d} \tag{3}$$

where L is the distance between platinum electrodes (1 cm), w and d are the length and thickness of the membrane in cm,respectively, R is the membrane resistance in ohms and σ is the conductivity of the membrane in S/cm. The alkaline stability of AEMs was evaluated by monitoring the changes in ionic conductivity. The time dependent ionic conductivity measurement of the membranes kept in 1 M KOH at room temperature was carried out during 19 days.

The methanol permeability through an AEM was determined bu using a U-shape home-made apparatus. The test system was described in our previous paper [11].

Dynamic mechanical analysis (DMA) of the prepared AEMs were performed by using Seiko SII 6100 DMA at heating rate of 2°C/min in tension mode in the temperature range of 20-180°C.

3. Results

3.1. Influences of chemical cross-linking

PVA-derived membranes must be cross-linked to enhance mechanical and chemical stability of membranes. PVA is commonly cross-linked with dialdehyde such as glutaraldehyde(GA) via a reaction between hydroxyl groups in PVA and aldehyde groups in GA. PEGDGE as a cross-linking agent has been used for amine-, hydroxyl- and carboxyl-functional polymers and the hydroxyl groups in PVA react with ethylene oxide groups in PEGDGE in order to form the cross-linked PVA structure [2]. In our recent work, the membranes cross-linked with PEGDGE showed higher conductivity than the membranes cross-linked with GA [9]. Therefore, in this study, PVA-PDDA blend was chemically cross-linked by PEGDGE and the physical properties of the obtained membrane (PPP) is summarized in Table 2. Water uptake and swelling ratio of PPP were found to be 4.1 $g_{water}/g_{membrane}$ and 83%, respectively. The ionic conductivity of AEMs must be high to enhance the fuel cell performance. In our study, the ionic conductivity of PPP membrane was found to be 12 mS/cm. At the end of 19th day, loss percent in conductivity was determined as 31 %. The methanol permeation rate of PPP membrane was calculated as $1x10^{-7}$ cm^2/s.

3.2. Influences of thermal cross-linking

The thermal cross-linking of polymer helps increase the thermal stability and also density of membrane [12]. In our study, thermal treatment was applied for an hour at three different annealing temperature in order to observe particularly the effect of annealing temperature on the dimensional stability of the PVA-PDDA membranes. It was seen from Figure 1 that the structure and the thermal stability of the membranes weren't affected from the annealing temperature.

Table 2. Comparison of cross-linking techniques for physical properties

	PPP	PP110	PP130	PP150
WU (g/g)	4.1	3.2	2.3	1.6
SR (%)	83	90	78	78
Ionic conductivity (mS/cm)	12	19	13	20
Loss percent in conductivity (%)	31	39	53	70
Methanol permeation rate (x10^{-7} cm^2/s)	1.0	1.8	0.9	0.5

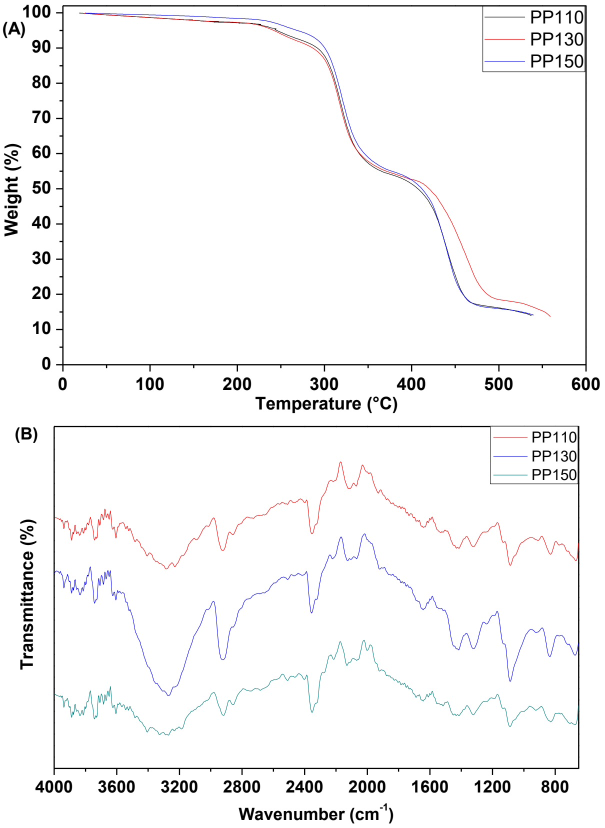

Figure 1. TGA (A) curves and FTIR (B) spectrum of PP110, PP130 and PP150 membranes

The dimensional stability and the water uptake of membranes can be achieved by adequate cross-linking. Our results showed that thermally cross-linked membranes exhibited lower water uptake and swelling ratio values than chemically cross-linked membrane (PPP). It has been thought that this decrease arose from higher cross-linking degree of thermal cross-linked membranes than one of chemically cross-linked membranes. When the obtained results were evaluated in terms of annealing temperature, it was seen that both water uptake and swelling ratio decreased with increased annealing temperature (Figure 2). In the literature, it is explained that the thermal cross-linking makes microstructure of membranes more disordered and compact at higher temperature in consequence of structure shrinkage of membrane [13]. Also, the forming of three dimensional network structure is seen during thermal cross-linking through thermal rearrangement and cross-linking of polymer chain. Those effects cause the diffusion of water in molecular structure to be obstructed. Hence, PP150 showed the lowest WU value among the only thermally cross-linked membranes.

For fuel cell applications, the conductivity is essentially depend on the chemical structure of the membrane. PDDA bearing quaternary ammonium groups is a cationic polymer, thus it is capable of transporting the hydroxyl ions. In this study, all membranes were prepared with the same amount of PDAA, nevertheles, they exhibited different ionic conductivity and loss percent in conductivity.

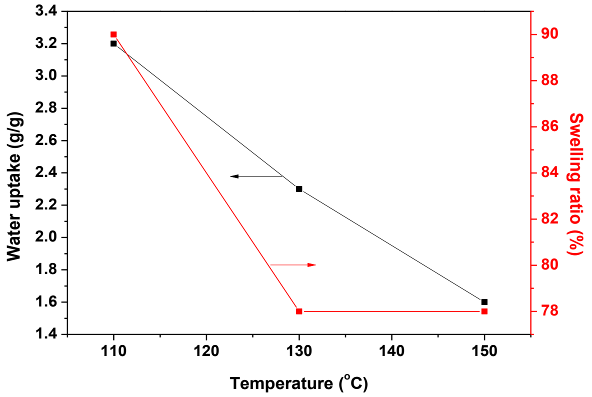

Figure 2. The effect of annealing temperature on the water uptake and swelling properties

This result showed that the conductivity of the cross-linked membrane was affected by the cross-linking technique and the annealing temperature. From Table 2, it can be seen that the thermally cross-linked membranes demonstrated higher ionic conductivity than chemically cross-linked membrane. It can be stated that PEGDGE as a molecularly long crosslinker causes the decrease in level of hydroxide diffusivity through membrane. Also, high water uptake of PPP would lead to a dilution of the concentration of the charge carriers. When the effects of annealing temperature on the ionic conductivity were evaluated, it was seen that the ionic conductivity changed with variation of annealing temperature and reached to 20 mS/cm at the annealing temperature of 150°C.

In order to investigate the alkaline stability of the obtained membranes, membranes were kept in 1 M KOH solution for 19 day and the loss in conductivity were recorded over the time. At the end of 19 days for thermally cross-linked membranes, a sharp decrease in the loss percent in conductivity was determined. It may be arisen from much more degradation of quaternary ammonium groups in PDDA structure under alkaline condition at elevated temperature (150°C).

The methanol crossover through membranes is important problem for Direct Methanol Fuel Cell applications. High methanol permeation leads to loss of fuel and cell performance. Therefore, membranes are desired to exhibit low methanol crossover. As one can see from Table 2, the methanol permeation rate decreased with increase in annealing temperature for thermally cross-linked membranes. This decrease can be directly attributed to the incerase in cross-linking density with increasing annealing temperature. This result agreed well with the water uptake result. Compared to literature, thermally cross-linked PVA membranes obtained by our study exhibited excellent barrier properties against methanol [14].

3.3. Influences of combined chemical and thermal cross-linking

In this study, we tried to prove the effects of different cross-linking techniques on the properties of PVA-based AEMs. The membranes were prepared using different application sequence of thermal and chemical cross-linking technique. Figure 3 showed that the order of cross-linking techniques affected the thermal behavior of obtained membranes. The existence of chemical cross-linking agent in the structure was effective over the thermal stability of AEM, especially for the cross-linked membrane by firstly chemical then thermal cross-linking technique. In Figure 3, it can be seen that the membranes showed nearly the same absorbance peak in the FTIR spectra apart from the fact that the appreciable increment at 1100cm^{-1} resulted from the presence of ether group in PEGDGE. For all annealing temperature, similar results were obtained, therefore, the results of membranes annealed at only 130˚C were shown in Figure 3.

It was seen from Table 3 and Figure 4, the application sequence of cross-linking tecniques and cross-linking type impressed the properties of membranes. Both water uptake and swelling ratio values of membrane cross-linked chemically (PPP) were decreased with additional thermal cross-linking application (PPP110/130/150). This decrement can be attributed to the increase in cross-linking density of the membranes and the formation of a compact three dimensional network structure. Contrary to this, the water uptake and swelling ratio of the thermally cross-linked membranes (PP110/130/150) showed a little change with additional chemical cross-linking application (PP110P/PP130P/PP150P). On the other hand, the application sequence caused major variation in the properties of prepared AEMs. The membranes prepared by firstly chemical cross-linking (PPP110/130/150) exhibited lower water uptake and swelling ratio values than the membranes obtained by firstly thermal cross-linking (PP110P, PP130P, PP150P). This situation may be explained that the formation of thermally cross-linked structure may block the mobility of PEGDGE chain into membrane and, hence, limit the cross-linking density.

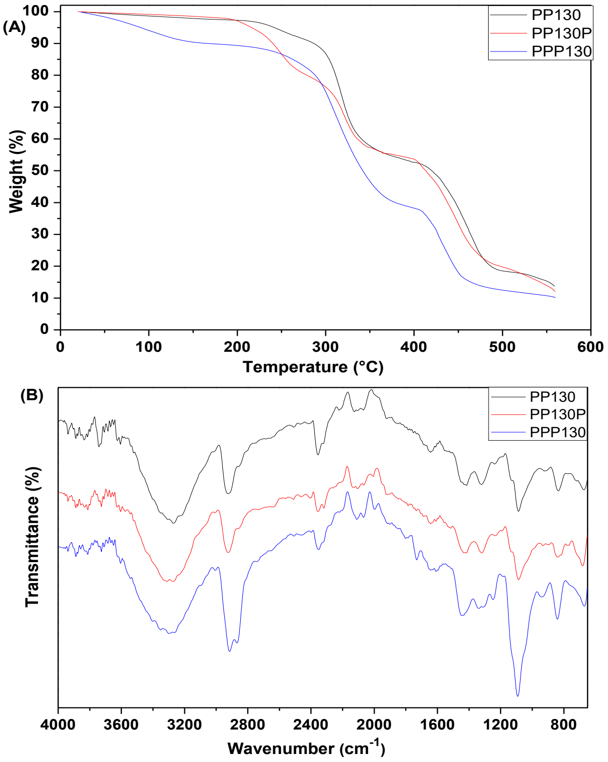

Figure 3. The effects of cross-linking way on the thermal behavior (A) and the structure of membranes (B)

The ionic conductivity of membranes were also affected by application sequence of thermal and chemical cross-linking technique. The membranes prepared by firstly chemical cross-linking (PPP110/130/150) exhibited higher conductivity than the membranes obtained by firstly thermal cross-linking (PP110P, PP130P, PP150P). The annealing temperature impressed both ionic conductivity and loss percent in conductivity as well as application sequence of cross-linking techniques. Although the loss percent in conductivity was seen higher for membranes prepared by firstly chemical cross-linking (PPP110/130/150), these membranes still exhibited higher ionic conductivity than the membranes cross-linked firstly thermally at the end of 19th day (Figure 5). After long term duration, the conductivities of PPP130 and PPP150 membranes were found to be 21.3 and 18.3 mS/cm and these values may be evaluated as acceptable and sufficient for DMFC applications.

Table 3. The effects of application sequence of cross-linking techniques on the properties of membranes

	PPP110	PPP130	PPP150	PP110P	PP130P	PP150P
WU (g/g)	2.6	1.6	1.3	3.0	2.4	1.7
SR (%)	93	50	46	114	87	78
Ionic conductivity (mS/cm)	38	52	47	19	14	27
Loss percent in conductivity (%)	62	59	61	29	38	48
Methanol permeation rate (x10^{-7} cm^2/s)	2.1	0.9	0.5	1.8	1.4	0.9
Membrane selectivity (x10^4 S.s/cm^3)	18	58	89	11	10	30

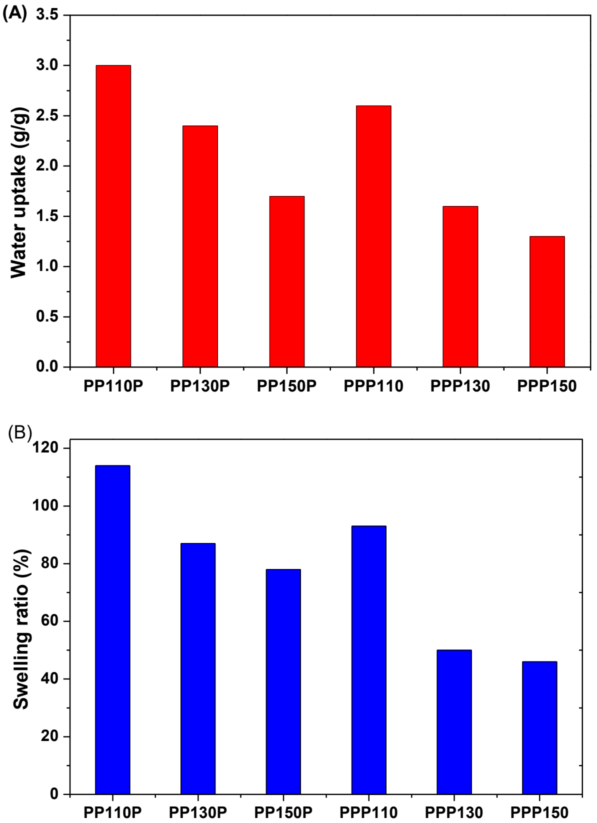

Figure 4. The effect of application sequence of cross-linking techniques on water uptake and swelling ratio

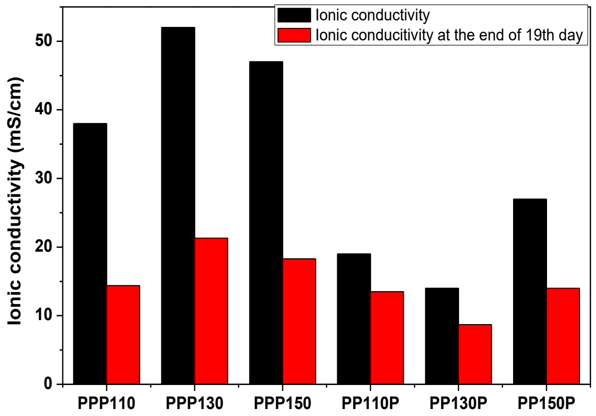

Figure 5. The effect of application sequence of cross-linking techniques on conductivity properties

In the literature, Zhang et al. reported the effects of cross-linking processes on the properties of PVA-PDDA-based AEMs in detail [10]. They used GA as a chemical crosslinker unlike our study, in which chemical cross-linking process. And their results showed, like our results, that pre-heat treatment, annealing time and temperature impressed the ionic conductivity and water uptake of AEMs. But, they obtained the highest conductivity of 7.66 mS/cm in Cl^- form and 17.5 mS/cm in OH^- form (after ion-exchange with 1 M KOH solution for 24h). However, our results showed that the application sequence of cross-linking techniques was also effective as well as cross-linking conditions and application of thermal cross-linking on the chemically cross-linked membrane contributed to improve the ionic conductivity (reached 52 mS/cm for PPP130).

As it is seen from Table 3, methanol permeation rate through membranes was affected by application sequence of cross-linking techniques and annealing temperature. Similar trend in methanol permeation rate results with the water uptake/swelling ratio results was observed apart from the membrane annealed at 110°C. PPP150 showed the minimum methanol permeation rate ($0.5x10^{-7}cm^2/s$) among the prepared membranes. This is ascribed that the increasing in cross-linking density with additional thermal cross-linking made the structure more dense and blocked the methanol diffusion through membrane. For DMFC applications, the most important aim of research is to obtain a membrane with high ionic conductivity and low methanol permeability. To evaluate the membrane performance in terms of permeability and conductivity, the membrane selectivity factor is calculated. The membrane selectivity is an indicator pointing out the suitability of a membrane and should be high for alcohol feed fuel cell such as DMFC. This factor is calculated by dividing the ionic conductivity by methanol permeation rate [11]. Figure 6 shows the selectivity of the prepared membrane. One can see from Figure 6 that the membranes prepared by firstly chemical cross-linking exhibited higher membrane selectivity than the membranes obtained by firstly thermal cross-linking. The highest membrane selectivity was achieved with PPP130 and PPP150 membranes which are almost 3/6 times higher than that of PP130P and PP150P, respectively.

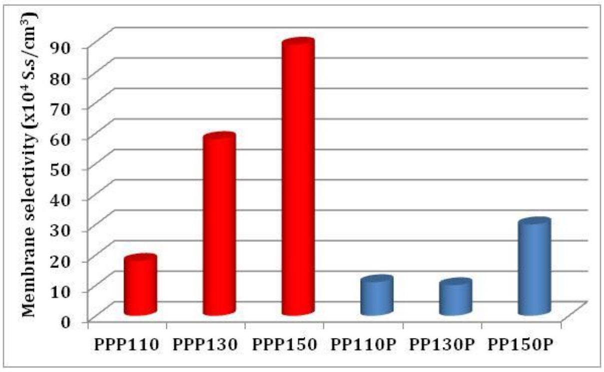

Figure 6. Comparison of membrane selectivity

The effects of combined chemical and thermal cross-linking on the mechanical property of membrane were examined by dynamic mechanic analysis. The storage and loss modules of PP130, PP130P and PPP130 are comparatively depicted in Figure 7. PP130, applied only thermal cross-linking, exhibited lower mechanical strength than membranes prepared by combined cross-linking technique. This is ascribed to the increasing in cross-linking density with a combined cross-linking technique. Also, the application sequence of cross-linking technique sligthly affected the mechanical strength. Both

PPP130 and PP130P provided acceptable strength and exhibited the storage modules of 2.8x10^8 and 8.4x10^7 Pa at 100˚C, respectively, whereas that of PP130 was 1.8x10^6 Pa at 100 ˚C. From these results, it can be interpreted that the sufficient mechanical strength is gained by performing combined cross-linking technique.

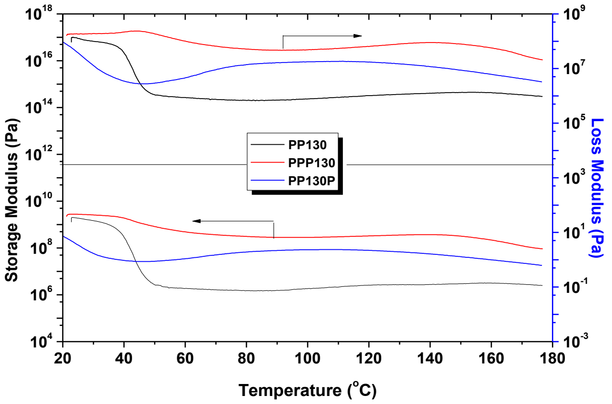

Figure 7. DMA graphs of PP130, PPP130 and PP130P membranes

4. Discussion and Conclusion

Alkaline AEM-based on PVA/PDDA composites were prepared by carrying out two different cross-linking techniques-chemical and thermal. The conclusions can be summarized in three points: (i) the only thermally cross-linked membranes exhibite different properties with changing annealing temperature, (ii) applying a combined cross-linking technique further improves the fuel cell-related properties of the prepared membranes compared to application of only thermal/chemical cross-linking, (iii) the application sequence of cross-linking technique is determined to impress the properties of membrane. Our results indicated that, except for the membrane thermally cross-linked at 110˚C, the membranes prepared by firstly chemical cross-linking and then thermal cross-linking exhibited higher conductivity, membrane selectivity and lower water uptake, swelling ratio, methanol permeation rate than the membranes obtained by firstly thermal cross-linking and then chemical cross-linking. Consequently, PPP150 membrane showed the optimum properties among the prepared membrane except for ionic conductivity results. The membrane selectivity of PPP150 was 89x10^4 S.s/cm^3 which was three times higher than PPP130, although the ionic conductivity of PPP150 was a little lower than PPP130, 47 and 52 mS/cm, respectively. In addition, DMA results revealed that applying a combined cross-linking technique improved the mechanical strength of membrane compared to application of only thermal/chemical cross-linking.

In conclusion, for PVA based AEMs, application of different cross-linking technique affects the properties of the obtained membrane and the highly cross-linked PVA network formed by application of firstly chemical cross-linking and then thermal cross-linking can be considered as a promising membrane for DMFC applications.

Acknowledgment

This work was supported by Scientific Research Projets Coordination Unit of Istanbul University under contract number of 27506.

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