Research Article
Araştırma Makalesi

Bartın University International Journal of Natural and Applied Sciences
JONAS, 4(2): 169-175 e-ISSN: 2667-5048
31 Aralık/December, 2021

SYNTHESIS AND POTENTIAL ENERGY APPLICATION OF MIL-140A AS A FILLER IN PVA MEMBRANE

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Abstract

Ion exchange membranes are used in many areas from fuel cells to redox batteries, from electrolysis to catalytic membrane applications. The high ion variation capacity of these membranes, their stability in aqueous environments, and the most importantly their low prices, increase their usability. The most important component of energy applications, especially batteries, is electrolyte membranes. In this study, MIL-140A type metal organic framework was synthesized and added to the PVA (an inexpensive engineering polymer) membrane at a ratio of 1-4%. This membrane was synthesized for the first time in the literature. The usability of the membrane in batteries or fuel cells was determined by means of swelling test, water uptake capacity, ion exchange capacity and proton conductivity tests. As the MIL-140A ratio increased in the PVA matrix the stability of the membrane and the proton conductivity increased significantly. When the MIL-140A ratio increased from 0% to 3%, the dimensional swelling decreased from 145 % to 24 %, and the proton conductivity increased from 0.0011 S/cm to 0.00286 S/cm.

Key Words: Composite membrane, ion exchange membrane, MIL-140A, PVA

1. Introduction

Polymer electrolyte membranes, or proton conductive membranes, are smart materials that used in battery and fuel cell, electrolysis, and catalytic applications. Due to the proton conductive groups, they have become the most important components that provide electricity production and storage in both fuel cells and other batteries. Nafion membranes are the most well-known and commercially used proton conductive membranes. However, the price of Nafion membranes is high that prevents their usage in commercial scale. Besides Nafion, many membrane materials have been developed as alternatives. The disadvantages of these membranes are manufacturing difficulties, high fuel, or electrolyte permeability in batteries and chemically instability. However, appropriate modifications improve the properties of the membranes. Basically, there are some important features in a potential PEM membrane such as low cost, high ion (proton) conductivity, low fuel permeability, high mechanical strength, and high oxidative stability (Wang et al., 2011; Kim et al., 2015). Many different membranes are used in the literature. Mainly used membranes are polymeric or composite membranes. Fluorocarbon-based ion exchange membranes, polyether sulfones, polyether ketones, poly (arylene ethers), polyesters and polyimides are used in fuel cells, batteries, and energy storage application (Kim et al., 2015).

In order to improve the conductivity and durability of polymeric membranes during the long-time operation, inorganic fillers or functional materials such as metal oxide, heteropoly acid are incorporated (Smitha et al., 2005). In the literature, graphene-based materials, functionalized zeolites or clays, metal organic frameworks are used as filler in fuel cells and other batteries. Metal organic frameworks (MOFs) are organic-inorganic materials that include positively charged metal ions. The metal ions are surrounded with linker material. These materials are highly porous, and the cage size of the material is changed according to the metal ions and linkers. They have very large internal surface. Therefore, they can be used as absorber, catalyst, and separation material. Recently, MOFs membranes or MOFs incorporated membranes have been used for energy application (Morozan et al., 2012; Li et al., 2016). The cage structure of MOFs metal ions acts as a proton carrier in fuel cell and battery application. Moreover, the small pore size of materials contributes to prevent fuel passage through the membrane.

MIL-140A is a kind of MOF materials. Compared to other MOFs, MIL-140A consists of triangular lattices and short bonds (Voorde et al., 2015). MIL 140 and other derivatives (140 B,C,D, ect..) are zirconium metal-based MOFs like UiO-66. They have porous structure, high resistance to corrosion, superior chemical, and water. Owing

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Geliş (Received) : 19.11.2021
Kabul (Accepted) : 03.12.2021
Basım (Published) : 31.12.2021

to the one-dimensional triangular channels and shorter binder, the water stability is higher than that of UIO-66. Since the binder length of MIL 140s are shorter, they have smaller pore sizes compared to UIO-66 (MIL-140A, MIL-140B=0.32 nm) (Sui et al., 2019; Yahaya et al., 2020).

In the literature, there are some studies on the use of MOFs in energy application (Patel et al., 2016; Morozan et al., 2012; Li et al., 2016). There are also studies on the use of UIO-66, a similar zirconium-based MOF, in energy application (Lin et al., 2020). However, there is no study on the use of MIL140-based MOFs. On the other hand, it has been reported that the MIL-140A contributes to enhance the hydrogen transition mechanism due to its lattice size (Prakash et al., 2015). Therefore, in this study, MIL-140A was synthesized and its effects on proton conductivity were investigated. In addition, it is aimed to increase the usability of polyvinyl alcohol (PVA) polymer, which is non-conductive and has low water resistance, as a fuel cell or battery membrane by enhancing its stability in the aqueous media. According to the author's knowledge, MIL-140A loaded PVA membranes was prepared for the first time to be used as an ion conductive membrane. The effect of MIL-140A content on the water uptake, membrane swelling, ion exchange capacity and proton conductivity were investigated.

2. Materials and Methods

Polyvinyl alcohol (Mowiol), zirconium chloride (≥99.5% purity) and terephthalic acid (98% purity) were purchased from Sigma Aldrich. Acetic acid ((≥ 99%, analytical grade), N,N-dimethylformamide (DMF) (99.8% purity), and methanol (anhydrous, 99.8%) were purchased from Merck Chemicals.

2.1. MIL-140A preparation

MIL-140A was synthesized by using solvothermal method (Soares et al., 2016). 0.06 mol terephthalic acid, 0.03 mol zirconium chloride, 35 ml DMF and 0.32 ml acetic acid was mixed and heated to 220 °C. The mixture was stirred at least for 5 hours. The solvent was allowed to cool at room temperature and washed with methanol, stirred overnight and filtrated. The X-ray diffraction analysis was done to determine the crystalline structure of MIL-140A. Powders were dried at 120 °C prior to XRD (PANalytical EMPYREAN) analysis. The test was conducted in the 2θ range 4−60° with the scan rate of 2°.

2.2. Membrane preparation

For the preparation of the pristine and MIL-140A loaded PVA membrane; an aqueous solution of 10 wt. % of PVA was prepared and mixed for 5 hours at 80 °C. MIL-140A was dissolved in acetic acid for 15 minutes using a sonicate mixer. Then, the polymer solution was added to the MIL-140A-acetic acid solution and was stirred for 2 hours at a stirring speed of 500 rpm. After obtaining a homogeneous mixture, the solution was poured onto a Teflon plate and kept at room temperature. The concentration of MIL-140A in the PVA matrix was arranged according to the weight of the polymer (from 1wt.% to 4wt.%). The membrane's morphology was investigated using scanning electron microscopy.

2.3. Water uptake test

The water uptake tests were done by immersing the membranes in distilled water at 60 ℃ for 24 hours. The water uptake capacity (WU) is calculated with the following equation (Eq.1) according to the difference between the dry (Wd) and the swollen (Ws) weight of the membrane. The dimensional swelling ratio of the membrane is calculated according to Equation 2 depending on the change in dimension (length) of the swollen (Ls) and dry (Ld) membrane

$$WU(\%) = \frac{Ws-Wd}{Wd} x100 \qquad (1)$$

$$SD(\%) = \frac{Ls-Ld}{Ld} x100 \qquad (2)$$

2.4. Proton Conductivity

Proton conductivities were determined by means of electrochemical impedance spectroscopy (EIS, VersaSTAT 3 Potentiostat Galvanostat). For this test, the membranes were washed with distilled water. Then, they were kept in

1M H_2SO_4 solution for two days and washed again. The conductivity was calculated by measuring the resistance of the membranes in a temperature-controlled conductivity test system. The conductivity (σ) is calculated with the following Equation (Eq.3). I and S represent the membrane thickness (cm) and the surface area (cm^2), respectively. R (Ω) is the electrical resistance of the membrane.

$$\sigma = \frac{l}{RS} \tag{3}$$

2.5. Ion Exchange Capacity

Ion Exchange Capacity (IEC) of the membrane is important factor to determine ion conductivity capacity of the membrane. For this test, dry membranes were kept in 50 ml of 0.1N NaOH solution for 24 hours at 40°C. This solution was titrated with 0.1 N of HCl solution. IEC is calculated using the Equation 4 (Trindade et al., 2019).

$$IEC = \frac{(N_{NaOH} x V_{NaOH}) - (N_{HCl} x V_{HCl})}{Wd} x100 \tag{4}$$

where, N represents the normality of the solvent, V represents the volume of the solvent (spent volume of HCl)

3. Results and Discussion

3.1. Material preparation and characterization

The crystal structure of the prepared MIL-140A material was analyzed by means of X-ray diffraction test. The diffractions are seen in Figure 1. The positions and intensities of diffraction peaks revealed at the figure are in perfect agreement with the reported literature data (Liang et al. 2016). The pattern is an evidence that the MIL-140A was successfully prepared.

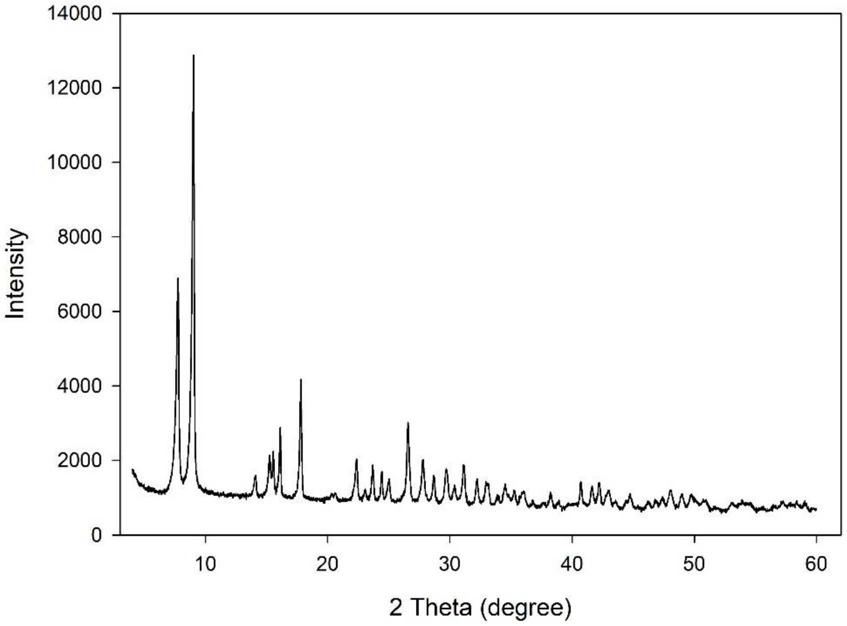

Fig. 1. XRD patterns of MIL-140A

The morphology of the synthesized MIL-140A and the composite membrane (2 wt.% MIL-140A loaded) was determined by means of SEM. Figure 2a shows that the structure of the prepared MIL-140A and it is good agreement with the reported micrographs in the literature (Liang et al., 2016). In the Figure 2b, the dark phase and small particles represent the PVA matrix and MIL-140A, respectively. In the cross-sectional view of the membrane, it is important to observe homogeneous and non-porous structure. In particular, the selective structure of the membrane is important for selective proton transfer and for preventing the cross-passage of other fuels. Figure 2b indicates that the membrane is dense, non-porous and has a defect-free structure. The small particles seen in the micrographs show that the distribution of the MIL-140A material within the matrix is uniform.

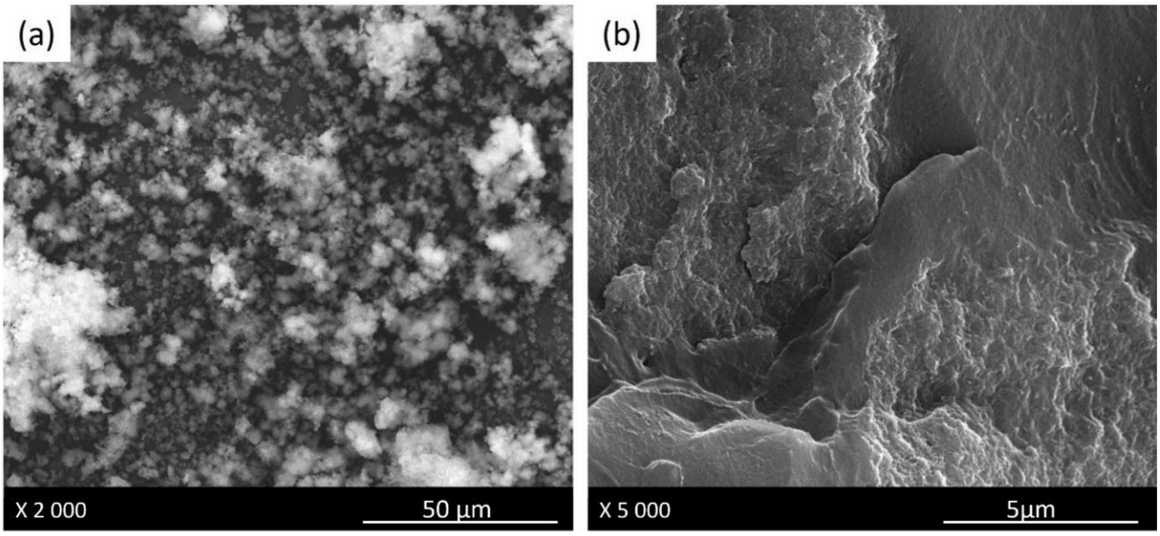

Fig. 2. Synthesized MIL 141A (a) and the cross-Sectional SEM micrograph of 2wt.% MIL-140A loaded PVA membrane (b)

3.2. Water Uptake and Swelling Degree

Figure 3 shows the water uptake and swelling degree results of the pristine PVA and MIL-140A loaded composite PVA membrane. Although the water uptake is a factor that increases the conductivity of the membrane, these values should be controlled since the mechanical and chemical stability of the membrane may decrease due to the excessive swelling and dimensional changes. Depending on the hydrophilic/hydrophobic properties of the membrane, the water uptake capacity facilitates the proton transport across the membrane. However, crossing of other ions along with proton (hydrogen) can occur through an excessive swollen membrane unselectively. In addition, due to the weaken intermolecular hydrogen bond, the mechanical strength of the membrane may undergo. Therefore, it is desired that the fuel cell and battery membranes to adsorb water until a certain point and to maintain its dimensional stability.

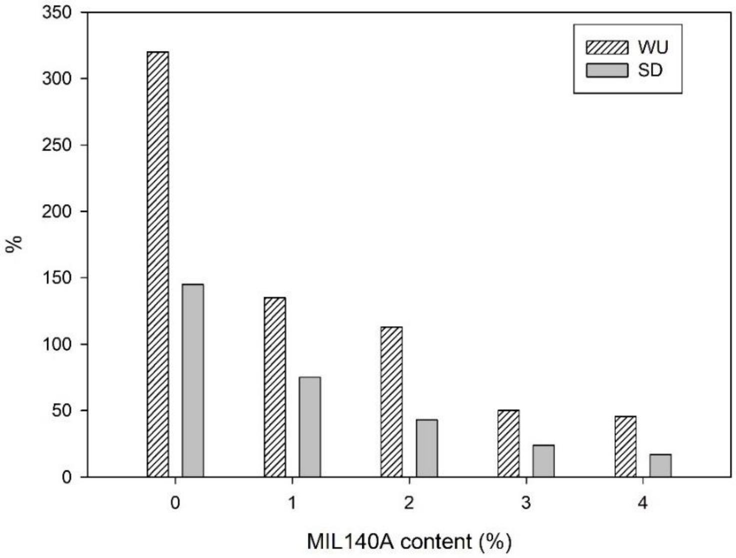

Fig. 3. Water uptake (WU) and Swelling Degree (SD) results of the membranes

As can be seen in Figure 3, the swelling degrees and the water uptake capacity of the membranes decreased significantly by MIL-140A incorporation. Since the PVA is a weak membrane against the water it was cross-linked prior to use in the present study. Although this procedure prevented the dissolving of the PVA membrane in water, excessive swelling was not prevented. On the other hand, MIL-140A is a stable material in aqueous media. Therefore, the MIL-140A incorporation significantly reduced the water uptake capacity of the PVA membrane. It also increased its dimensional stability (DS results). The only negative side of this situation is the possibility of the decrease in the conductivity.

3.3. Ion Exchange Capacity

Figure 4 shows the effect of MIL-140A loading on the ion exchange capacity (IEC). The amount of ion exchange groups in a membrane is evaluated according to the IEC values. This value is also giving an idea about the proton conductivity behavior of the membrane. The proton conductivity of membranes enhances by increasing exchangeable ion numbers inside the membrane. As seen in the figure, IEC values are increasing with the addition of MIL-140A. A slight decrease is observed when the MIL ratio was 4wt.%. This should be related to the pore blocking effect of the excessive fillers. These results should be evaluated with the result of the proton conductivity.

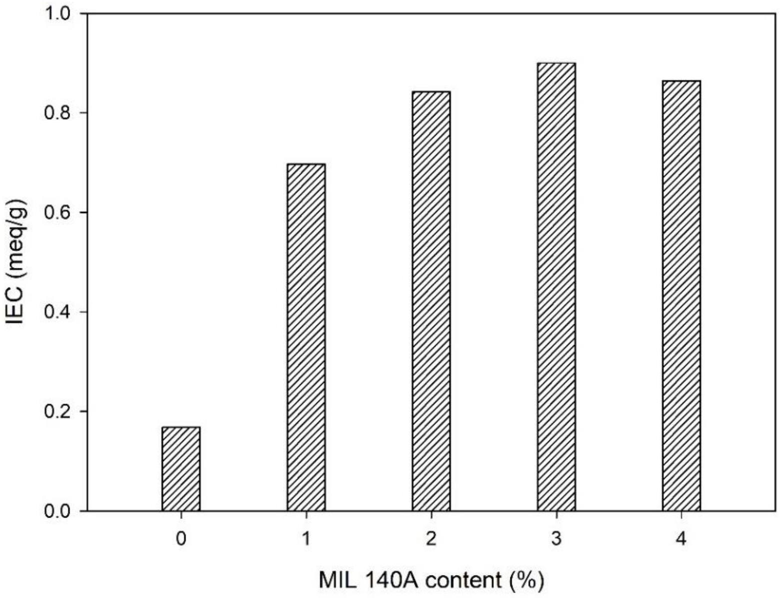

Fig. 4. IEC results of the membranes

3.4. Proton Conductivity

Figure 5 illustrates the proton conductivity results of the membranes in terms of the MIL-140A content. Proton conductivity is very important for the fuel cell or battery performance of the membrane. Especially in proton exchange membranes, this value is expected to be high. PVA is not a proton-conductive material. It has been reported in the literature that the sulfonation, adding additives such as conductivity-enhancing graphene oxide, zirconium oxide, titanium oxide, or by blending them with a conductive material improve the proton conductivity and the cell performance [Sahin, 2018; Zhiwei et al., 2019; Wong et al., 2020].

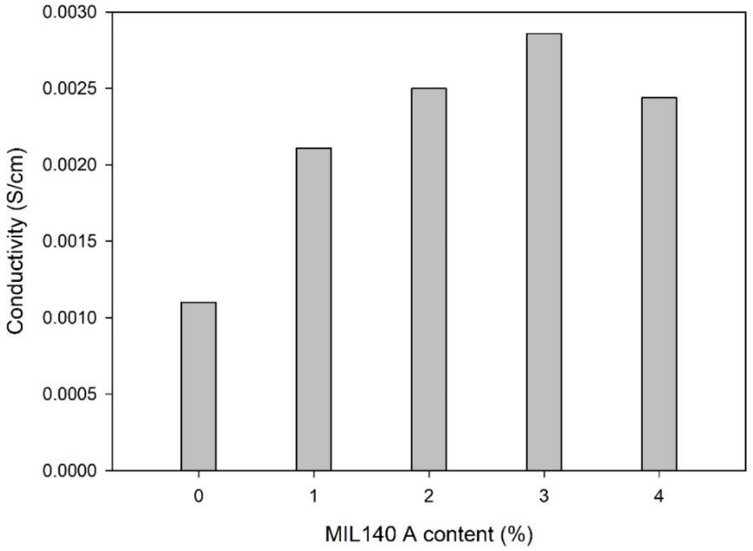

Fig. 5. Proton conductivity results of the membranes

As seen in the figure, even at the low content of MIL-140A, there is a significant improvement in the proton conductivity. The unsaturated metal sites of MIL-140A provide a hydroxyl group and it increases the number of hydrogen-bonded sites. The highest proton conductivity was obtained at 3wt.% of MIL-140A loading. When the MIL-140A content exceeded 4%, a decrease in conductivity was observed. This situation may be related to the limited water uptake. Additionally, researchers have reported that there is not a linear relationship between the conductivity or cell performance and MOFs ratio (Liu et al., 2020). The excessive incorporation of fillers may restrict the transport properties of the hydrogen. The agglomeration of MOF fillers could cause resistance to conductivity. Therefore, the ratio of the MOFs should be a reasonable value to prevent adverse effects. In the present study, that reasonable value was obtained as 3wt.% according to the polymer's weight.

4. Conclusion

In this study, nonconductive PVA polymer, was converted into a proton exchange membrane with modifications and its usability in applications such as fuel cells and batteries was investigated with characterization test. MIL-140A material prepared within the scope of the study and was added to the PVA polymer. The water uptake, swelling degrees, proton conductivities and ion exchange capacities of the pristine (without MIL-140A) and MIL-140A loaded composite membranes were investigated. According to the results, MIL-140A was successfully synthesized and properly distributed through the membrane. The incorporation of MIL-140A material into the PVA membrane prevented the excessive water retention and swelling. On the other hand, the ion exchange capacity and proton conductivity increased significantly. The highest proton conductivity value was obtained as 0.0026 S/cm with the 3% MIL-140A loaded membrane. As a result, the usability of the membrane as a proton exchange membrane in energy applications has been proven by obtaining important results within the scope of the study.

Acknowledgement

"This work was supported by the Office of Scientific Research Projects Coordination at Çanakkale Onsekiz Mart University. Grant number: FHD-2021-3583".

Conflicts of Interest

The authors declare no conflict of interest.

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