Effect of Solvent on Ball Milling PVdF-HFP-based composite membrane for DMFCs

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Abstract: ***In this study poly (vinylidene fluoride-hexafluoroprropylene) (PVdF-HFP) porous copolymer based membrane were prepared with polyvinyl alcohol as well as with and without titanium oxide as ceramic filler using two types of solvent (DMF and acetone). The effects of two type solvent were also compared on the properties of the membranes. The membranes were characterized by FT-IR, porosity, conductivity, methanol permeability and cell performances. From the investigation of ionic conductivity and methanol permeability impels that the ball milling PVdF-HFP/PVA/TiO_2 (DMF) have a higher and balance ionic conductivity and methanol permeability than others. Among the membranes the cell performances were examined for PVdF-HFP/PVA/TiO_2 (DMF) and PVdF-HFP/PVA/TiO_2 (Acetone). The cells performance indicated that the PVdF-HFP/PVA/TiO_2 (DMF) has a better membrane than that of PVdF-HFP/PVA/TiO_2 (Acetone).***

Keywords: ball milling PVdF-HFP, solvent, titanium oxide, membrane, DMFC.

1. Introduction

The energy demand all over the world is increasing day by day. Scientist are trying find out alternative energy source rather than conventional energy. Among the many sources the fuel cells as one of the possible options because they are relatively efficient and clean energy producers. And DMFCs are promising candidates to replace existing batteries as power generators in portable devices. Easy refueling and high energy storage capacity are their main advantages. DMFC produces power by direct conversion of methanol. The DMFC components are anode, cathode, membrane and catalysts [1]. Hydrogen is not fed to the fuel cell. Hydrogen ions are on the anode side of the system. Methanol reacts with water to produce carbon dioxide, electrons and protons at the anode. The electrons and protons are transferred with external circuit and electrolyte membrane, and they react with oxygen to produce water at the cathode. Some of the attractive characteristics of the DMFC are portability, emission-free clean energy, low cost, low temperature operation, high efficiency and fuel safety [2-4]. There are some disadvantages as well such as low power density due to poor kinetics of the anode reaction, significant fuel crossover, safety concerns, etc. Commercially available membranes in DMFC are still perfluorinated membranes, such as Nafion membranes, due to their excellent proton conductivity, high thermal resistance and chemical stability; however, high methanol permeability and cost are main disadvantages for using this kind of membrane in DMFC [5]. An increase in the methanol permeability leads to poisoning of cathode catalysts, increased reaction over potential due to the mixed potential, loss of fuel, and emissions of low-concentration toxic materials [6-7] Therefore, several efforts have been made to develop new electrolyte polymeric membranes that can be used as an alternative membrane for DMFCs. For an example sulfonated poly(vinyl alcohol) [8], polystyrene sulfonic acid crosslinked within a poly(vinylidene fluoride) matrix[9], and sulfonated poly(etherether ketone) [10] have been developed for use in DMFCs.

Among the various polymers, poly(vinylidene fluoride-co-hexafluoropropylene) (PVdF-HFP) attracts the researchers for its crystalline and amorphous nature, in which the amorphous phase promotes the ionic conductivity and crystalline nature influences the mechanical strength of the membrane[11]. In order to improve membrane affinity towards water than methanol, it is being incorporated with the polymer which has –OH as a functional group. Poly vinyl alcohol (PVA) is a cheap polymer and has high selectivity of water to alcohol to reduce the methanol permeability. Moreover, the functional –OH groups of PVA have the potential for cross-linking which satisfy the stability parameter of the membranes [12-13]. On the other hand, the interactions between TiO_2 nanoparticles surface and polymer chains are recently considered as a promising mechanism for the increase in ionic conductivity [14].

Therefore, the polymeric composite membrane was made by PVdF-HFP/PVA/TiO_2 with modification of PVdF-HFP for DMFCs application [15]. The membrane was composed by ball milling PVdF-HFP) with polyvinyl alcohol as well as with and without titanium oxide as ceramic filler using two types of solvent (DMF and acetone). To best of my knowledge, there are no articles that compare solvent effect with modification of PVdF-HFP for DMFCs application.

2. Experimental

2.1 Materials

Poly(vinylidene fluoride-co-hexafluoropropylene) (PVdF-

HFP)(Kynar Flex 2801, Arkema, Japan), Poly vinyl alcohol(PVA) (Aldrich, Molecular weight: 98,000),Titanium(IV)oxide (Aldrich, nanopowder, ~21nm particle size), N,N-Dimethyl Formamide (Sigma), Acetone (Sigma-Aldrich) were purchased and utilized.

2.2 Membrane Preparation

Two types of solvent (Acetone and Dimethyl Formamide) was used for preparation of membrane.

a) The PVdF-HFP was ball-milled for 20 h at 400 rpm using a Fritsch Pulverisette 6 planetary mono mill ball-milling machine. The 7 wt% of ball milled PVdF-HFP copolymer was dissolved in acetone and mixing well with stirring. After that 4.6 wt % of PVA [11] added and stirring until it mixed. And finally 2 wt % of TiO_2 was added and stirred for 1 h at 60^0C. The concentrated solution was cast on a glass substrate. The film was made with and without TiO_2. The prepared films were kept at 60^0C for 8 h in vacuum in order to evaporate the solvent. Then, the films were soaked in double distilled water at 60^0C for 20h to remove the PVA content from the film and were dried at at 100^0C in vacuum for 10h to remove the traces of water. The dried membranes were soaked in 6M sulfuric acid at 60^0C for 24 h for the functionalization. The resulting membranes were dried and subjected for characterization.

b) The 7 wt% of ball milled PVdF-HFP copolymer was dissolved in Dimethyl formamide and mixing well with stirring. After that 4.6 wt % of PVA added and stirring until it mixed. And finally 2 wt % of TiO_2 was added and stirred for 24 h at 60^0C. The concentrated solution was cast on a glass substrate. The film was made with and without TiO_2. The prepared films were kept at 80^0C for 12 h in vacuum in order to evaporate the solvent. Then, the films were soaked in double distilled water at 60^0C for 20h to remove the PVA content from the film and were dried at at 100^0C in vacuum for 10h to remove the traces of water. The dried membranes were soaked in 6M sulfuric acid at 60^0C for 24 h for the functionalization. The resulting membranes were dried and subjected for characterization.

3. Characterizations

3.1 FT-IR. Porosity and Acid uptake

FT-IR was recorded at room temperature in the region 400-4000 cm-1 by Perkin Elmer spectrum 1000 with a resolution of 4.0 cm^{-1} to confirm the structure of the blending polymeric membranes. The porosity of the polymer membranes was measured by immersing the membrane into n-butanol for 1 h and weighing the membrane before and after absorption of the n-butanol. The porosity was calculated using the following equation [16-17]:

$$P(\%)=\frac{\dfrac{M_b}{\rho_b}}{\dfrac{M_p}{\rho_p}}\times\frac{M_b}{\rho_b}\text{ ……………………………………(1)}$$

Where p % is porosity of the membrane, Mp is mass of the membrane, Mb is the mass of absorbed n-butanol, ρp is the density of the membrane and ρb is the density of n-butanol.

The membranes were soaked in 6M sulfuric acid solution at 60^0C for 24 h for the activation of the electrolyte membrane. After the excrescence of the solution at the surface of the polymer electrolyte, the membrane was dried and weighed:

$$Aciduptake(\%)=\frac{W_{wet}-W_{dry}}{W_{DRY}}\times 100\text{.....................(2)}$$

Where,Wwet and Wdry denote the mass of wet sample and dry samples respectively.

3.2 Proton conductivity

The proton conductivity of the samples in the transverse direction was measured by the AC impedance spectroscopy technique over a frequency range of 1-106Hz with oscillating voltage 10mV, using a frequency response analyzer (FRA) (Autolab PGSTAT20). The membranes were clamped between two block stainless steel electrodes with diameter 5mm. Before the test, the membranes were dipped in water until sufficiently wet and compressed tightly between the blocking electrodes. The conductivity (σ) of the samples was calculated from the impedance data, using the relation:

$$\sigma=\frac{d}{RS}\text{ ....(3)}$$

Where d and S are the thickness of the samples and the face area of the electrodes, and R is derived from the intersect of the beeline at high frequency with the Re (z) axis on a complex impedance.

3.3 Methanol permeability

The methanol permeability was determined using a diaphragm diffusion cell [6,12]. The cell consisted of two identical compartments (25ml) separated by the test membranes. One compartment was filled with a solution of methanol (1M) and the other was filled with deionized water. Prior to testing, the membranes were hydrated in deionized water for at least 24h. Both compartments were magnetically stirred during the permeation experiment. The concentration of methanol in the initially pure water compartment versus time was measured using gas chromatography (Tianmei T9700). The methanol permeability was calculated from the slope of the straight-line plot of methanol concentration versus permeation time. The data was collected from room temperature to 80°C.

3.3 Single Cell Performance

The membranes were immersed in deionized water for 24h before the preparation of MEAs. Catalyst slurries were prepared by mixing 2-propanol solution, and 20% Pt/C for cathode ink and 60% PtRu/C for anode ink supplied by E-TEK. For fabrication of MEA, the catalyst slurry was coated on carbon paper (TORAY, Japan) for the electrode substrate. The Pt loadings were approximately $1mg/cm^2$ and $2mg/cm^2$ for anode and cathode, respectively. The effective electrode area of the single cell was $4.0cm^2$. The fuel was 2M CH_3OH

delivered at 5 mL/min by a micropump and oxygen pressure was 0.2MPa at 50 mL/min. The data was collected at a temperature of 80℃.

4. Results and discussion

Porosity of the composite membrane was examined by n-butanol absorption [11]. The maximum porosity of the composite membrane was obtained 55% in this study which favors the high acid absorption as shown in Table 1.

FT-IR spectroscopy was investigated to confirm the structural configuration of composite membrane as shown in Fig.1. The absorption peak found at 3500-2850 cm^{-1} appearing most strongly should not be of water itself but of such a chemical species derived from water such as H_3O^+. It may decompose with the release of water to combine with coexisting RSO_3^- to produce RSO_3H with the progress of dehydration in the membrane. The peaks found at 1161, 833 cm^{-1} indicate the presence of [SO_4^{2-}]. The peaks found at 1399, 1034 cm^{-1} are readily assigned to HSO_4^-. The sulfate ion is expected to give characteristic feature at 1154 cm^{-1} [11]. From this IR spectrum, it is clear that sulfuric acid content has been completely entrapped in the porous PVdF-HFP polymer composite matrix and confirms the structural configuration of the composite membrane.

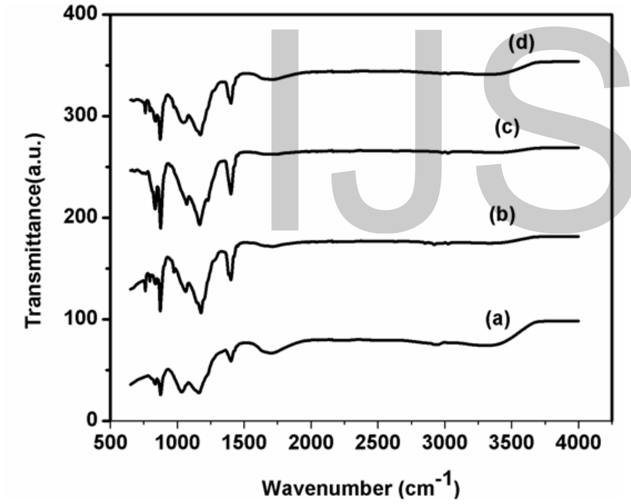

Figure 1. FT-IR spectrum of ball milling PVdF-HFP-basaed membranes.

The ionic conductivity of the composite membrane is shown in Figure 2. Ion transport of these membranes depends on the doped acids (sulfuric acid). High degree of sulfonation can occur with sulfuric acid which is favorable for the ionic conduction. The protons are highly mobile in sulfuric acid. Sulfuric acid in the acid doped membranes release H^+, which leads to the protonation of the membranes. Besides, sulfuric acid can be dissociated into HSO_4^- and SO42- . It is well-known that cations as well as anions enhance the conductivity of the membranes [11]. The conductivity of the membranes was measured at temperature ranging from 21^{0}C to 115^{0}C. It is obvious that the proton conductivity of ball milling PVdF-HFP/PVA/TiO_2 composite membranes is higher than that of the ball milling PVdF-HFP/PVA membrane. Furthermore, the proton conductivity of PVdF-HFP/PVA/TiO_2 membrane has has reached 0.025 S/cm at 100^{0}C. As theTiO_2 particle size is sufficiently small, the existing waters of hydration of sulfuric acid may form a bridge between shrunken clusters, thereby providing a pathway for proton hopping from one cluster to another. In this manner the activation energy for hopping may be reduced [14]. The porosity also has a vital role to increase conductivity. Conductivity of the membrane was increased with increasing the porosity of the membrane. The increasing in temperature influences proton transfer and structural reorganization which results in increased proton conductivity.

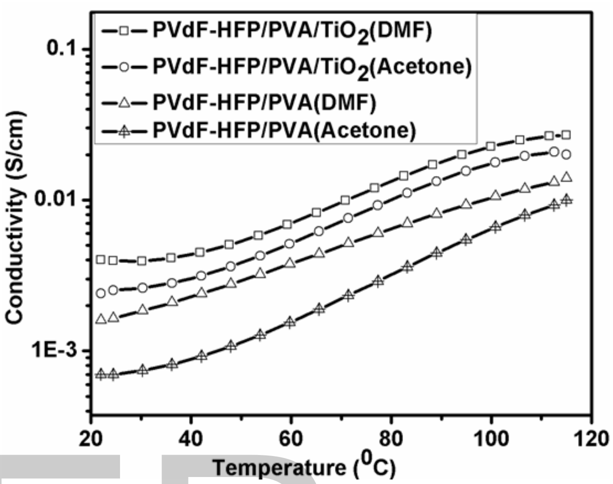

Figure 2. Conductivity of ball milling PVdF-HFP-basaed membranes.

The methanol permeability as a function of temperature for composite membranes is shown in Figure 3. A proton conducting membrane with lower methanol permeability is required in DMFC. Methanol permeability is the product of diffusion coefficient and sorption coefficient in which the diffusion coefficient reflects the effect of a surrounding environment on the molecular motion of the permeant and the sorption coefficient correlate with the concentration of a component in the fluid phase [18]. The methanol permeability of the polymer membranes with ball milling PVdF-HFP/PVA (Acetone) decreased compared to other membrane which is possibly due to the difference in microstructure. It is might be due to ceramic as well as solvent.

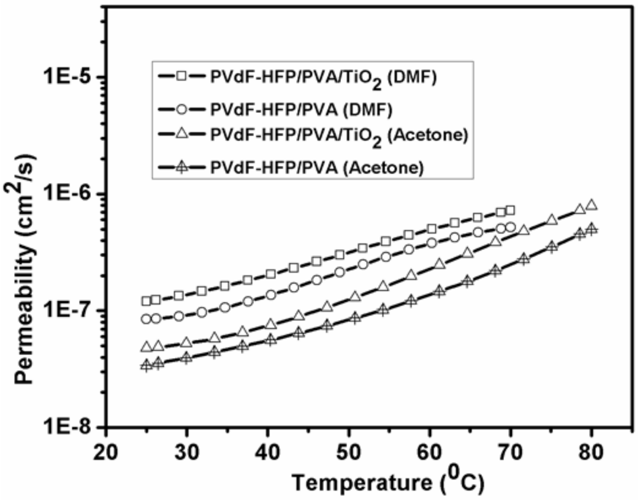

Figure 3. Methanol permeability of ball milling PVdF-HFP-basaed membranes.

The hydrophobic nature of the host polymer PVdF-HFP hinders the methanol transport. As a result, low methanol permeabilities were obtained for all the memnbranes. On the other hand, the smaller hydrophilic-hydrophobic separation and the lesser flexibility of the polymer backbone of ball milling PVdF-HFP produce narrow proton channels and a highly branched structure which baffle the transfer of methanol. In Figure 3 and Table 1, it can also be found that the incorporation of TiO_2 causes less methanol permeability because the nanosized dispersion of TiO_2 prevents methanol from migrating through the membrane and the covalent cross-linking structure between $-SO_3H$ of PVdF-HFP and TiO_2 leads to the reduction of the ion clusters. Obviously, the results of the proton conductivity and methanol permeability show a good balance of high conductivity and methanol permeability in case of milling PVdF-HFP/PVA/TiO_2 (DMF). Table 1 summarized the properties of the membranes used in this study.

Table 1. Compositions and properties of ball milling PVdF-HFP –based membranes in different solvent.

PVdF -HFP (wt%)	*PVA (wt%)*	*TiO_2 (wt%)*	*Solv-ent*	*Acid absorption (wt%)*	*Conducti-vity (S/cm)*	*Methanol Permeabil-ity (cm^2/m)*
7	4.6	-	DMF	58	0.027	7.2
7	4.6	2	DMF	62	0.021	5.2
7	4.6	-	Acetone	50	0.01	7.9
7	4.6	2	Acetone	52	0.02	5.0

Power density curves for MEAs equipped with PVdF-HFP/PVA/TiO_2(DMF) and PVdF-HFP/PVA/TiO_2(Acetone) composite membranes at 80℃ are shown in Figure 4. It is clearly shown that the performance of the single cell with composite membrane is better.

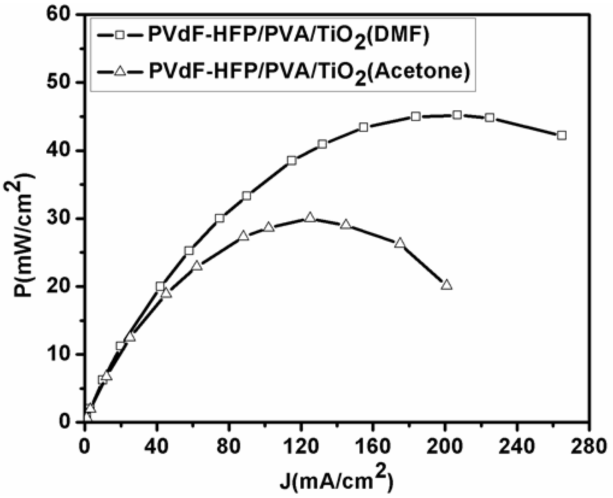

Figure 4. Power and current density of ball milling PVdF/PVA/TiO2(DMF) and PVdF/PVA/TiO_2(Acetone) membranes for DMFC

The cell with ball milling PVdF-HFP/PVA/TiO_2(DMF) composite membrane has higher power density of composite membrane reaches 45.34 mW/cm^2 while the current density is 183.65 mA/cm^2. The higher power density indicates a better performance of composite membrane because of its moderate proton conductivity and lower methanol permeability. The PVdF-HFP/PVA/TiO_2 (DMF) obtained moderate proton conductivity and lower methanol permeability due to modification of PVdF-HFP by ball milling and uniformly mixed with less volatile solvent DMF. The cell with ball milling PVdF-HFP/PVA/TiO_2 (Acetone) composite membrane has lower peak power density which was 30.49 mW/cm^2 while the current density was 125.0 mA/cm^2. The lower power and current density of ball milling PVdF-HFP/PVA/TiO_2 (Acetone) composite membrane was due to the more volatile solvent acetone.

5. Conclusion

PVdF-HFP/PVA and PVdF-HFP/PVA/TiO_2 composite membranes have been prepared using modified (ball milling) PVdF-HFP by phase inversion technique to examine usability to DMFC. The dispersion of nano-TiO_2 in the membrane increase proton conductivity and have lower methanol permeability than commercially available membrane. But the composite membranes show a good balance in higher proton conductivity and lower methanol permeation. The cell performance show the cell with PVdF-HFP/PVA/TiO_2 membrane has a high power density than commercially available membrane. Though TiO_2 has some influence on the stability of the polymer. Therefore, this membrane is promising candidate for application in direct methanol fuel cells.

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