

Titanium dioxide nanoparticle incorporated PVDF-HFP based composite membrane for direct methanol fuel cell application

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Abstract

Two composite polymeric membranes were synthesized using poly vinylidene fluoride-hexafluoropropylene (PVDF-HFP) host in polyvinyl alcohol and with or without TiO₂ nanoparticles as a porous substrate. The structure of the membranes was PDVF-HFP/PVA and PVDF-HFP/PVA/TiO₂. The composition of the synthesized membranes was analyzed by FTIR spectrum. The porosity of the polymer membranes were measured by immersing the membranes into n-butanol. The conductivity of the composite membranes was determined by impedance spectroscopy and the methanol permeability of the membranes was obtained from diffusion experiments. The surface morphology images were investigated by scanning electron microscope (SEM). The SEM image of the composite membrane incorporated with TiO₂ has many pores which increased the conductivity of the membrane as compared to non TiO₂ incorporated one. The composite membrane with TiO₂ showed a good balance between proton conductivity and methanol permeability. The cell with PVDF-HFP/PVA/TiO₂ composite membrane showed higher power density.

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Introduction

Realizing the depleting natural energy sources with increasing energy consumption, there is a compulsion to find non-conventional energy sources for today's science and technology which will cater to the increasing energy demand in future. Recently, scientists are looking for fuel cells as one of the possible options because they are relatively efficient and clean energy producers. Among the fuel cells, direct methanol fuel cell (DMFC) is a promising candidate. Some of the attractive characteristics of the DMFC are portability, emission-free clean energy, low cost, low temperature operation, high efficiency and fuel safety (Dillon *et al.*, 2004; Patil *et al.*, 2004; Kumar *et al.*, 2008a). Commercially available membranes in DMFC are still Nafion membranes, due to their excellent proton conductivity, high thermal resistance and chemical stability; however, high methanol

permeability and cost are the main disadvantages for using this kind of membrane (Kumar and Nahm *et al.*, 2008b). An increase in the methanol permeability leads to poisoning of cathode catalysts, increased reaction overpotential due to the mixed potential, loss of fuel, and emissions of low-concentration toxic materials (Shen *et al.*, 2006; Yamauchi *et al.*, 2007). Therefore, several attempts have been made to develop new electrolyte polymeric membranes that can be used as an alternative membrane for DMFCs (Rhim *et al.*, 2004; Cai *et al.*, 2017; Miyake *et al.*, 2017; Fujiyama *et al.*, 2008; Tian *et al.*, 2007; Noshay *et al.*, 1976; Chen *et al.*, 2012; Bahlakeh *et al.*, 2013; Chae *et al.*, 2014; Qing *et al.*, 2005; Yue *et al.*, 2015; Xu *et al.*, 2007; Liu *et al.*, 2015; Iizuka *et al.*, 2013; Cleemann *et al.*, 2013; Wang *et al.*, 2012; Hwang *et al.*, 2014; Jia *et al.*, 2015; Staiti *et al.*, 2001).

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For example, Polybenzimidazole composite, Fluorine-free sulfonated aromatic polymers (Miyake *et al.*, 2017), Sulfonated Poly (aryl ether ketone) Random Copolymers (Fujiyama *et al.*, 2008), perfluorosulfonic acid (PFSA) membranes (Tian *et al.*, 2007), sulfonated polysulfone (SPSF) (Noshay *et al.*, 1976), sulfonated polyether sulfone (SPES) (Chen *et al.*, 2012), sulfonated poly (ether ether ketone) (SPEEK) (Bahlakeh *et al.*, 2013; Chae *et al.*, 2014), polybenzimidazole (PBI) (Qing *et al.*, 2005; Yue *et al.*, 2015; Xu *et al.*, 2007), and polyvinylidene fluoride (PVDF) (Liu *et al.*, 2015), phosphoric acid (PA) doped polybenzimidazole (PBI) composite membranes (Iizuka *et al.*, 2013; Cleemann *et al.*, 2013; Wang *et al.*, 2012; Hwang *et al.*, 2014), nanoparticle enhanced polymers (Jia *et al.* 2015; Staiti *et al.*, 2001), sulfonated poly (vinyl alcohol) (Prakash *et al.*, 2002), polystyrene sulfonic acid crosslinked within a poly (vinylidene fluoride) matrix (Xing *et al.*, 2004), and sulfonated poly (etherether ketone) (Li *et al.*, 2003) have been developed for use in DMFCs.

Among the various polymers, poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) attracts researchers for its crystalline and amorphous nature, in which the amorphous phase promotes the ionic conductivity and the crystalline nature influences the mechanical strength of the membrane (Dutta *et al.*, 2014). Poly (vinylidene fluoride-co-hexafluoro propylene) is a promising polymer for the fabrication of membranes in direct methanol fuel cells, because of its low methanol permeability, high mechanical integrity and significantly low cost compared to conventionally used Nafion membrane. However, low proton conductivity has hindered its independent use; therefore, most studies on this prospective copolymer have been done by using it in conjunction with Nafion. Nevertheless, partial sulfonation of this copolymer has resulted in increased proton conductivity while maintaining its low methanol permeability. Therefore, it seems appropriate that blending this sulfonated copolymer with a second low cost component, which can complement its low conductive nature, can result in PEMs with high selectivity (Kumar *et al.*, 2009).

In this study, in order to improve membrane affinity towards water rather than methanol, polyvinyl alcohol is being incorporated into the polymer which has –OH as a functional group. Poly vinyl alcohol (PVA) is a cheap polymer and has a 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 (Martinelli *et al.*, 2006; Aricò *et al.*, 2005). On the other hand, the interactions between TiO₂ nanoparticles surface and polymer chains are recently considered as a promising mechanism for the increase in

ionic conductivity (Kumar *et al.*, 2010). As far as my knowledge goes, only a few attempts have been made for modification of PVdF-HFP for DMFCs application (Kumar *et al.*, 2009; Li *et al.*, 2003).

Therefore, in this study, PVDF-HFP was used to make polymeric composite membranes as PVDF-HFP/PVA and PVDF-HFP/PVA/TiO₂ and characterized their performances for DMFCs application.

Materials and methods

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) were utilized in the study.

Membrane preparation

Two membranes were prepared such as: 1) The PVDF-HFP copolymer (7 wt %) was dissolved in dimethyl formamide (DMF) and mixed well by stirring. After that of PVA (4.6 wt %) was added and stirred until it mixed (Dutta *et al.*, 2014). The mixture was magnetically stirred for 24 h at 60°C. The concentrated solution was cast as a film onto a glass substrate. 2) The PVDF-HFP copolymer (7 wt %) was dissolved in dimethyl formamide and mixed well by stirring. After that of PVA (4.6 wt %) was added and stirred until it mixed (Dutta *et al.*, 2014) Finally, TiO₂ nanoparticles (2 wt %) was added and stirred for 24 h at 60°C. The concentrated solution was cast as a film onto a glass substrate. Then these two films were kept at 80°C for 12 h in vacuum in order to evaporate the solvent. Then, the films were soaked in double distilled water at 60°C for 20h to remove the PVA content from the film and dried at 100°C in vacuum for 10h to remove the traces of water. The dried membranes were soaked in 6M sulfuric acid at 60°C for 24 h for functionalization (Kumar *et al.*, 2009). The resulting membranes were dried and subjected to characterization. Schematic diagram of preparation procedures for PVDF-HFP/PVA/TiO₂ and PVDF-HFP/PVA membranes was presented in Fig. 1 and a schematic diagram of working principles of DMFCs was shown in Fig. 2 respectively.

Characterization of membrane

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 blending

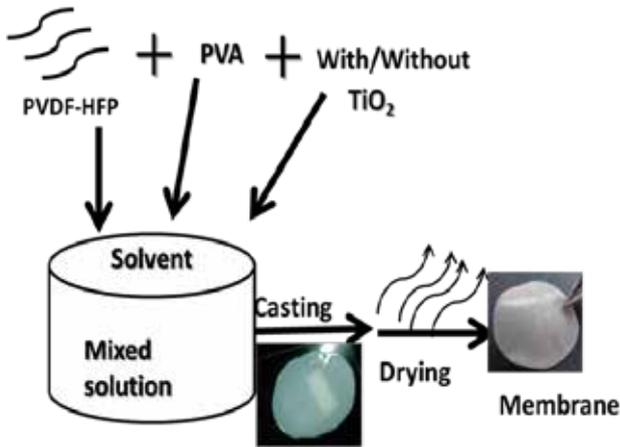


Fig. 1. Schematic diagram of preparation procedures for PVDF-HFP/PVA and PVDF-HFP/PVA/TiO₂ embranes

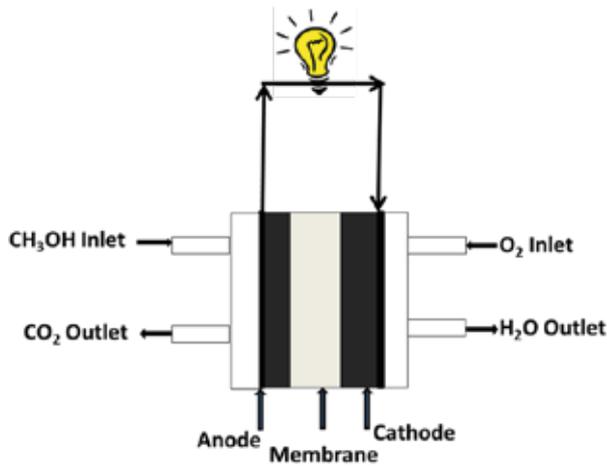


Fig. 2. A schematic diagram of working principles of DMFCs

polymeric membranes. A sample was made by dissolving small amount of membrane in chloroform solvent and a drop was place in sample dice, which was later placed in sample holder to measure the FTIR analysis. 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 (Zhng *et al.*, 2009; Kumar *et al.*, 2008).

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

where p % is porosity of the membrane, M_p is mass of the membrane, M_b is the mass of absorbed n-butanol, ρ_p is the density of the membrane and ρ_b is the density of n-butanol.

The membranes were soaked in 6M sulfuric acid solution at 60°C for 24 h for the activation of the electrolyte membrane(Kumar *et al.*, 2009). After the excrescence of the solution at the surface of the polymer electrolyte, the membrane was dried and weighed.

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

where W_{wet} and W_{dry} denote the mass of wet and dry samples, respectively.

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 blocks of stainless steel electrodes with diameter 5mm. Before the test, the membranes were dipped in water until they were sufficiently wet and compressed tightly between the blocking electrodes. The conductivity (σ) of the samples was calculated from the impedance data, using the relation.

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

where d and S represent the thickness of the samples and the face area of the electrode respectively, and R is derived from the intersection of the beeline at high frequency with the Re(z) axis on a complex impedance.

The methanol permeability was determined using a diaphragm diffusion cell (Yamauchi *et al.*, 2007; Martinelli *et al.*, 2006). 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

deionized 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.

The membranes were soaked in deionized water for 24h before the preparation of membrane electrode assemblies (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/cm² and 2mg/cm² for anode and cathode, respectively. The effective electrode area of the single cell was 4.0cm². As a fuel 2M CH₃OH was used and delivered at 5 ml/min by a micropump as well as the oxygen pressure was maintained 0.2 MPa at 50 ml/min. The data was collected at a temperature of 80°C.

Results and discussion

The FTIR spectra are an important tool to characterize and analyze the structural changes in polymer, to identify

–CH=CF- skeletal breathing of PVDF-HFP polymer. For the sulfuric acid entrapped membranes, the observed peaks are attributed as follows: The hydronium ion (H₃O⁺) formation in the membrane is found at 3409 cm⁻¹ and 3418 cm⁻¹ respectively. This peak should not be of water itself, but is attributed to hydronium ion, which can combine with coexisting RSO₃ - to produce RSO₃H and release water with the progress of dehydration in the membrane (Kumar *et al.*, 2009). From this IR spectrum, it is clear that sulfuric acid electrolyte has been completely entrapped in the porous PVDF-HFP polymer matrix and confirms the structural configuration of the composite membrane. Thus, a strong interaction occurred between the host polymeric units, PVA and the sulfuric acid that guaranteed the durability of the fabricated porous membranes.

Porosity of the composite membrane was examined by *n*-butanol absorption (Dutta *et al.*, 2014; Wu *et al.*, 2005). The maximum porosity of the composite membrane was obtained 55% in this study which favors the high acid absorption as shown in Table I.

The ionic conductivity of the composite membrane is shown in Fig. 4. Ion transport of these membranes depends on the

Table I. Composition of membranes (wt %), acid absorption (wt %), conductivity properties and structure of composite polymer membranes

PVdF - HFP (wt%)	PVA (wt%)	TiO ₂ (wt%)	Acid absorption (wt%)	Conductivity (s/cm)	Structure of composite membrane
7	4.6	-	58	0.010	PVDF -HFP/PVA
7	4.6	2	62	0.025	PVDF -HEP/PVA/TiO ₂

functional groups, interactions and complexation of polymer composite. The vibrational bands of PVDF-HFP polymer at 704 cm⁻¹ (-CH₂ rocking vibration), 742 cm⁻¹ (-CF₂ stretching vibration) belong to crystalline nature of VDF units of the polymer. The transmittance peaks at 1024 cm⁻¹, 1063 cm⁻¹, 1101 cm⁻¹ indicate CF₂ symmetric stretching and 1232 cm⁻¹ asymmetric stretching of PVDF-HFP polymer peaks which are found to be disappeared on addition of TiO₂. The reason is because of weak interaction between H atoms of CH₂ groups and F atoms of CF₂ groups. The vibration band peaks formed at the wave number 1397 cm⁻¹, 1402 cm⁻¹ correspond to CH₂ wagging of the polymer PVDF-HFP. Further the absorption peaks at 1690 cm⁻¹, 1702 cm⁻¹ correspond to

doped acids (sulfuric acid). The 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 releases H⁺, which leads to the protonation of the membranes. Besides, sulfuric acid can be dissociated into HSO₄⁻ and SO₄²⁻. It is well known that cations as well as anions enhance the conductivity of the membranes (Dutta *et al.*, 2014). The conductivity of the membranes was measured at temperature ranging from 21°C to 115°C. It is obvious that the proton conductivity of PVDF-HFP/PVA/TiO₂ composite membranes is higher than the PVDF-HFP/PVA membrane. Furthermore, the proton conductivity of

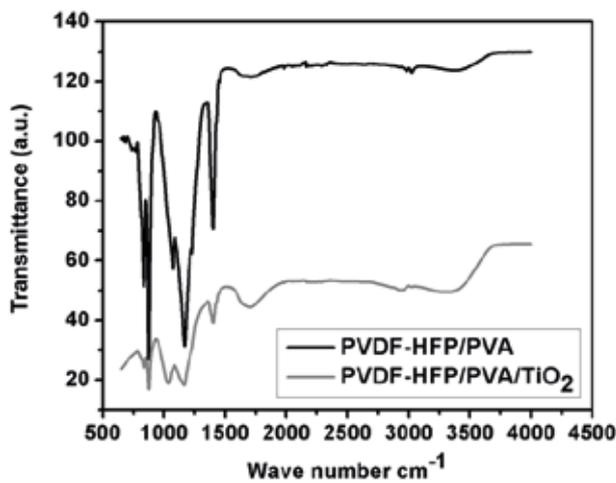


Fig. 3. FT-IR spectrum of PVDF-HFP-based composite membranes

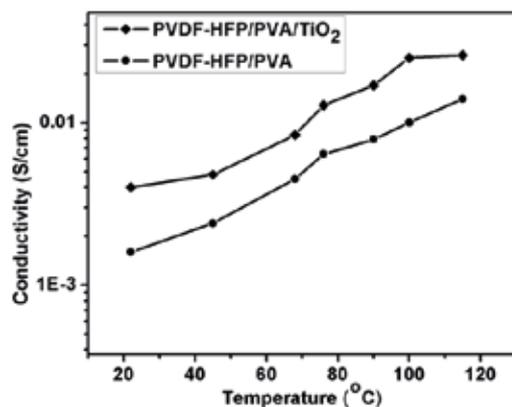


Fig. 4. Conductivity of PVDF-HFP-based membranes

PVDF-HFP/PVA/TiO₂ membrane has reached 0.025 S/cm at 100°C. As the TiO₂ particle size is sufficiently small, the existing waters of hydration of sulfuric acid may form a bridge between the 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 (Kumar *et al.*, 2010). The porosity also has a vital role in increasing conductivity. Conductivity of the membrane increased with increasing porosity of the membrane. The increase in temperature influences proton transfer and structural reorganization which results in an increased proton conductivity.

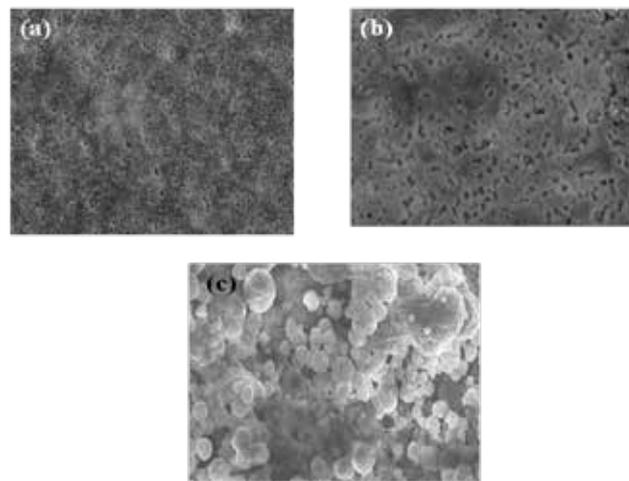


Fig. 5. SEM image of membranes: a. pure PVDF-HFP membrane, b. PVDF-HFP/PVA composite membrane, and c. PVDF-HFP/PVA/TiO₂ composite membrane

Surface morphology of pure PVDF-HFP, PVDF-HFP/PVA, and PVDF-HFP/PVA/TiO₂ membranes were shown in Fig. 5. The pure PVDF-HFP membrane surface was presented by Fig. 5 (a) and no porous was found. The Poly (vinylidene fluoride-hexafluoropropylene) (PVDF-HFP) copolymer was used as a main back bone polymer for preparing the composites membranes. The uniform pore size distribution throughout the membrane consist of PVDF-HFP/PVA was shown in Fig. 5(b). Since polyvinyl alcohol (PVA) has porogenic properties and in these composite membranes PVA act as a porogenic agent. The PVA was removed by immersion period of 20 h in water; completely eliminated the porogen agent PVA from the prepared composite membranes. The PVDF-HFP/PVA/TiO₂ membrane surface morphology was presented in figure 5(c). In the membrane surface, some coagulated structures of TiO₂ nanoparticles were found at certain position of the membrane and it favors the acid absorption as shown in Table I. The acid absorption facilitated by large porosity consequently enhances the proton conductivity (Croce *et al.*, 2006).

Fig. 6. shows the methanol permeability as a function of temperature for composite membranes. 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 correlates with the concentration of a component in the fluid phase ((Kumar *et al.*, 2009). The methanol permeability of the polymer membranes with PVDF-HFP matrix decreases obviously compared to Nafion117

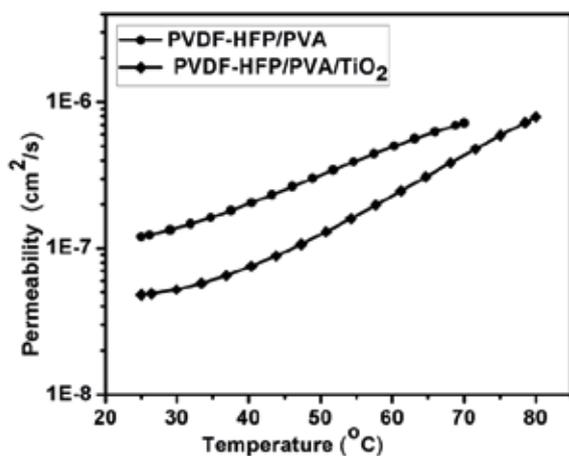


Fig. 6. Methanol permeability of PVDF-HFP-based membranes

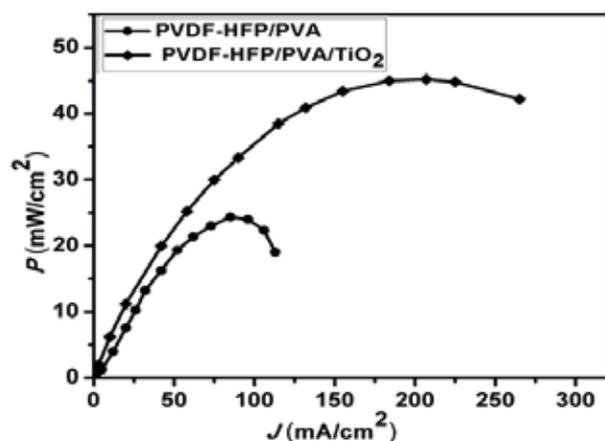


Fig. 7. Power density curves of PVDF-HFP/PVA/TiO₂ and PVDF-HFP/PVA for DMFCs application

membrane which is possibly due to the difference in microstructure between PVDF-HFP and Nafion117 membrane. The hydrophobic nature of the host polymer PVDF-HFP hinders the methanol transport. As a result, low methanol permeability was obtained for all the membranes. On the other hand, the smaller hydrophilic-hydrophobic separation and the lesser flexibility of the polymer backbone of PVDF-HFP produce narrow proton channels and a highly branched structure which baffle the transfer of methanol. In Fig.6, it can also be found that the incorporation of TiO₂ causes less methanol permeability because the nanosized dispersion of TiO₂ prevents methanol from migrating through the membrane and the covalent cross-linking structure

between -SO₃H of PVDF-HFP and TiO₂ 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 low water and methanol permeability.

Power density curves for MEAs equipped with PVDF-HFP/PVA/TiO₂ and PVDF-HFP/PVA composite membranes at 80°C are shown in Fig.7. It is clearly shown that the performance of the single cell with composite membrane is better. The cell with PVDF-HFP/PVA/TiO₂ composite membrane having higher peak power density of composite membrane reaches 45mW/cm² while the circuit density is 180mA/cm². The higher peak power density indicates a better performance of composite membrane because of its moderate proton conductivity and lower methanol permeability.

Conclusion

PVDF-HFP/PVA and PVDF-HFP/PVA/TiO₂ composite membranes have been prepared by phase inversion technique to examine usability to DMFC. The dispersion of nano-TiO₂ in the membrane increases proton conductivity and has lower methanol permeability than other membranes. But the composite membranes show a good balance in higher proton conductivity and lower methanol permeation. The cell performance shows the cell with PVDF-HFP/PVA/TiO₂ membrane has a high power density than any commercially available membrane, though TiO₂ has some influence on the stability of the polymer. Therefore, this membrane is a promising candidate for application in direct methanol fuel cells in future.

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