



High ion and lower molecular transportation of the poly vinylidene fluoride–hexa fluoro propylene hybrid membranes for the high temperature and lower humidity direct methanol fuel cell applications[☆]

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ABSTRACT

Poly vinylidene fluoride–hexa fluoro propylene hybrid membranes are prepared by directly blending the copolymer with different sizes of acidified stannous oxide particles. Steric repulsion between the hydrophobic host polymer and hydrophilic acidified particles generates cavities in the hybrid membranes. The infrared and energy dispersive spectroscopic studies confirmed the structural characterization of the hybrid membranes. The high acid moieties of stannous oxide particles conscript higher ion channels whereas the hygroscopic property favors high water molecules retention and provokes the self-humidification of the hybrid membranes. Though high ionic conductivities are achieved for the hybrid membranes, inferior methanol permeabilities are also maintained due to the hydrophobic units and methanol resistive behavior of host polymer and stannous oxide particles, respectively. By the combined efforts of high ion and lower molecular transportation, direct methanol fuel cells performance is facilitated for the fabricated hybrid membranes and influences its potential application in fuel cells field.

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1. Introduction

Booming power demand of the present decade triggers various research activities in the development of polymer ion conductive membranes which effectively replaces the liquid electrolyte systems and promotes the efficiency of emission free energy sources such as fuel cells and lithium battery [1,2]. Especially the role of a polymer electrolyte membrane in direct methanol fuel cells (DMFC) is predominant and can solely determine the fuel cells efficiency [3]. Though the commercially available membranes such as Nafion, Dow, and Asahi govern the fuel cells global market, their higher fuel permeability, higher temperature and lower humidity operation difficulties, tedious preparation methods, and environmental hazards not only impede their large scale application and also hinder the commercialization of fuel cells [4,5]. In order to tackle the aforementioned difficulties of polymer electrolyte membranes,

various researches and industrial level activities have been stimulated with the various types such as hydro carbon, acid–base, and fluorinated polymer electrolyte membranes [6]. Among the aforementioned types of polymers utilized, fluorinated polymer especially PVdF–HFP effectively tackles the aforementioned hindrances due to its semi-crystalline nature, high dielectric constant, elevated thermal, chemical, and physical behaviors etc., [7,8]. Besides, the C–F bond inferred in the copolymer decreases the methanol permeation and plays a vital role in the determination of DMFC efficiency [9]. In general, the acidification of polymer membranes conscripts the ionic conductivity. Though an increment of acidification yields high ionic conductivity, it also leads to a decrement of physical behavior and higher fuel permeability. So a balance should be maintained between the ions and molecular transportation for the effectual DMFC performances.

So far various acidification processes have been developed for the fuel cell polymer electrolyte membranes such as liquid electrolyte activation [10], irradiation [11], plasma [12], and direct acid blend [13,14]. Though the electrolyte activation method ensures the ionic conductivity and other electrochemical properties via a single route, high electrolyte leakage of the polymer membrane leads to a durability crisis. Even if the effective results could be obtained through the irradiation and plasma techniques, their

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Table 1
Nomenclature of the fabricated membranes.

PVdF–HFP (wt.%)	SnO ₂ (wt.%)	Nomenclature
10		PV
10	5 (2–4 nm size)	PVS4-5
10	10 (2–4 nm size)	PVS4-10
10	15 (2–4 nm size)	PVS4-15
10	20 (2–4 nm size)	PVS4-20
10	5 (90–100 nm size)	PVS100-5
10	10 (90–100 nm size)	PVS100-10
10	15 (90–100 nm size)	PVS100-15
10	20 (90–100 nm size)	PVS100-20

tedious preparation methods and the need of highly sophisticated equipments increase the cost of polymer membranes which significantly lowers the thirst of fuel cells applications. Among the methods described above, direct acid blend method is well known for its easier preparation, lesser time consumption, and high durability etc.,

The direct acidification processes have been extensively applied in other polymers. But the direct acidification process of PVdF–HFP is limited due to its high inert nature. Though few efforts have been addressed on the direct acid blend of PVdF–HFP polymer with poly-styrene sulfonic acid [15], chloro sulfuric acid [16], and sulfo succinic acid [17], they were not effectual due to their non-homogeneous nature. The non-homogenous membrane impedes the membrane electrode assembly process and no fuel cells performances were reported on these types of membranes. Hence an effort has been carried out on the direct acidification process of PVdF–HFP polymer with the stannous sulfuric acid for the high DMFC power efficiency. Moreover this study inclines the time consumption of separate acidification and ceramic fillers inclusion via a single material stannous sulfuric acid. The impact of different sizes of the included stannous oxide particles on the thermal and electrochemical properties leads to a new dimension of nano-technology application in the fuel cells polymer membrane field.

2. Experimental

2.1. Preparation of stannous sulfuric acid

The stannous oxide particles with two different sizes (2–4 and 90–100 nm) were synthesized according to the procedure described elsewhere [18]. The 500 mL suction flask was charged with the as synthesized stannous oxide particles and appropriate amount of chloro sulfuric acid was added drop wise over a period of 30 min at room temperature. Hydrogen chloride (HCl) gas was immediately evolved from the reaction vessel. After the completion of reaction, the mixture was shaken for 30 min and subjected for the further experiments.

2.2. Membrane preparation

Poly vinylidene fluoride–hexa fluoro propylene (PVdF–HFP) (Kynarflex 2801, Japan) was dissolved in acetone and magnetically stirred for 1 h at 60 °C. To this appropriate amount (Table 1) of stannous sulfuric acid was added, stirred for 90 min at 60 °C and the resultant viscous homogenous solution was cast as a membrane. The fabricated membranes were kept at 70 °C for 12 h and subjected for further experiments. The nomenclatures of the fabricated membranes are given in Table 1.

2.3. Morphological and structural characterizations

Morphological properties of the membranes were characterized by JSM-5410LV scanning electron microscopy (SEM) equipped

with energy dispersive spectroscopy (EDS). FT-IR spectra of the fabricated membranes were recorded between 4000 and 400 cm⁻¹ in the transmittance mode using a Jasco FT-IR-300 spectrophotometer. Thermal properties of the membranes were examined by PerkinElmer instrument in the range from 30 to 800 °C under a nitrogen atmosphere with a heating rate of 20 °C min⁻¹.

2.4. Liquid uptake

The dried membranes were weighed (W_d) and soaked in deionized water for 20 h. Subsequently, the membranes were taken out, wiped carefully, and weighed (W_f) [9]. Water uptake of the fabricated membranes was calculated according to the equation:

$$\text{Water uptake (\%)} = \left[\frac{W_f - W_d}{W_d} \right] \times 100 \quad (1)$$

This experiment was also carried out with 2 M methanol solution and designated as methanol uptake.

2.5. Ionic conductivity and methanol permeability characterizations

Ionic conductivities of the fabricated membranes were measured by using BektTech conductivity test cell in conjunction with a PGZ 301 Dynamic EIS Voltammeter [9,19]. Methanol permeation rates were measured using a house permeation cell at 30 °C as reported elsewhere [4].

2.6. Fuel cell performance

Direct methanol fuel cell performance was examined in a Scribner 850C Compact fuel cell test station. Membrane electrode assembly (MEA) was fabricated by using the E-Tek commercial electrodes with 0.5 (Pt) and 1.5 mg cm⁻² (Pt–Ru) catalysts loading. A mixture of deionized water, Nafion ionomer, and isopropanol was sprayed onto the commercially available electrodes by spray method. The impregnated electrodes were dried at 60 °C for 30 min. Then the prepared hybrid membrane was sandwiched between the electrodes and hot pressed at 70 °C with a pressure of 90 kg cm⁻² for 3 min. The DMFC performances of the fabricated MEAs were evaluated with a single-cell fixture having an active area of 5 cm² (Electrochem Inc.). 2 M methanol solution was fed into the anode at a flow rate of 4 mL min⁻¹ by a peristaltic pump and unhumidified air was fed into the cathode at a flow rate of 200 mL min⁻¹ with a back pressure of 20 psi. The *I*–*V* curve data was collected at 80 °C by measuring cell voltages which were stabilized for about at least 10 min after applying currents in the potentiostatic mode.

3. Results and discussion

3.1. Morphological properties

Among the various ceramic fillers utilized in the polymer electrolyte membranes field, stannous oxide particles are well known for its high thermal stability, high electro-negativity, and high concentration of dissociated protons etc., [20,21]. When the stannous oxide particles contact with the atmosphere, it absorbs many hydroxyl groups on its surface. The surface hydroxyl groups reacts with the added chloro sulfuric acid and the sulfonic acid groups are covalently attached with the stannous oxide particles with the evolution of hydro chloric acid as given in Eq. (1).



Fig. 1 exhibits the morphological images of the fabricated membranes. The pure PVdF–HFP membrane exhibited a flat surface whereas the hybrid membrane PVS4-20 revealed a porous nature

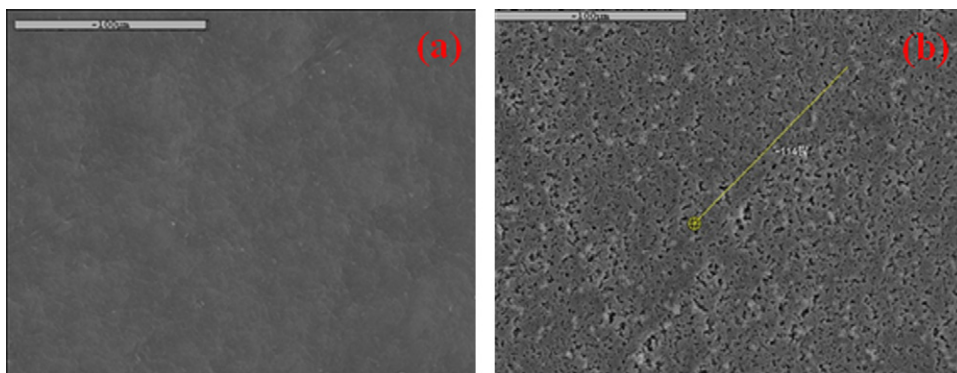


Fig. 1. Morphological images of (a) pure PVdF-HFP and (b) PVS4-20 membranes.

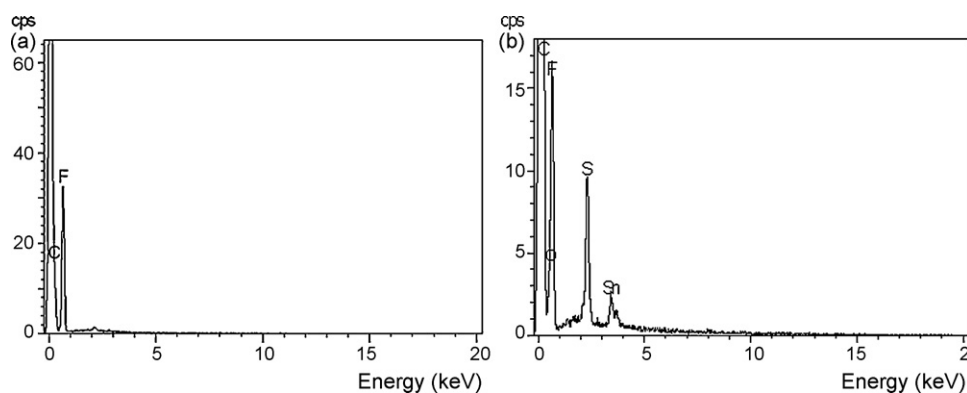


Fig. 2. EDS spectra of the (a) pure PVdF-HFP and (b) PVS4-20 membranes.

as shown in Fig. 1. The PVdF-HFP copolymer is hydrophobic in nature and the synthesized stannous sulfuric acid is hydrophilic in nature. The hydrophobic property of the copolymer strongly repels the hydrophilic sulfonic acid units and generates the porous nature [17,22]. The generated cavities are strongly interconnected and influences the higher number of ions migration.

Fig. 2 exhibits the EDS spectra of pure PVdF-HFP and PVS4-20 membranes. The pure PVdF-HFP membrane exhibits carbon and fluorine elements (Fig. 2a) which are the constituents of the host polymer. The hybrid membrane exhibits carbon, fluorine, sulfur, oxygen, and stannous elements (Fig. 2b). The presence of carbon and fluorine elements represents the host polymer whereas the sulfur, oxygen, and stannous elements symbolize the incorporated stannous sulfuric acid. Thus the EDS spectrum clearly reveals the complete incorporation of stannous sulfuric acid molecules with the PVdF-HFP polymer.

Fig. 3 exhibits the line mapping of sulfur and stannous elements. The aforementioned elements enroll the electrochemical properties of the fabricated fuel cells membranes. Line mapping indicates the uniform distribution of the respective elements (Fig. 3) and enrolls the high homogeneity of the fabricated membranes.

3.2. Structural characterization

FT-IR spectroscopy is an effective tool which determines the molecular vibrations of the synthesized materials. The molecular vibrations observed for the fabricated pure PVdF-HFP membrane via the FT-IR analysis (Fig. 4a) is described as follows: the band observed at 1403 cm^{-1} represents the deformed vibration of CH_2 group with the weakening interaction between H atoms of CH_2 groups and F atoms of CF_2 groups. The asymmetric and symmetrical stretching vibrations of CF_2 are found at 1085 and 1190 cm^{-1} , respectively. The α , β , and γ phases of PVdF-HFP are found at

976 , 489 , and 842 cm^{-1} , respectively [9,23]. The peak observed at 3440 cm^{-1} represents the C-H aromatic stretching of the host polymer.

The IR spectrum (Fig. 4b) observed for the PVS4-20 hybrid membrane is attributed as follows: a high intensity of the band observed at 3450 cm^{-1} represents the higher amount of absorbed water molecules. The larger amount of absorbed water molecules is strongly attributed to the hygroscopic nature of the incorporated stannous oxide particles. Besides, the band observed at $1640\text{--}1650\text{ cm}^{-1}$ represents the bending of molecular water [24]. The S=O and γSO_2 stretching vibrations of the fabricated hybrid membrane are confirmed by the peaks found at 1041 and 1126 cm^{-1} , respectively and confirmed the presence of sulfonic acid moieties [9,25]. The peak found at $610\text{--}620\text{ cm}^{-1}$ represents the Sn-O stretching modes. From the obtained FT-IR spectrum it

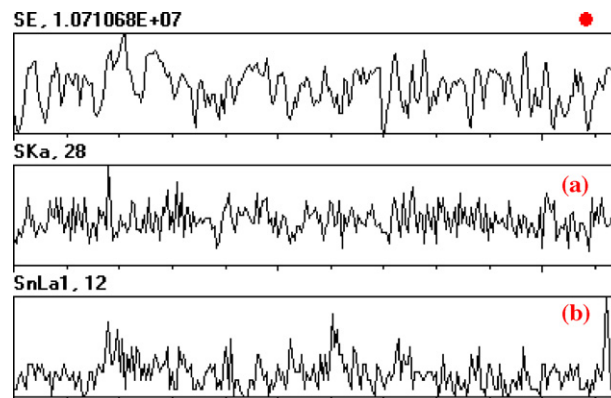


Fig. 3. Line mapping of (a) sulfur and (b) stannous elements of PVS4-20 membrane.

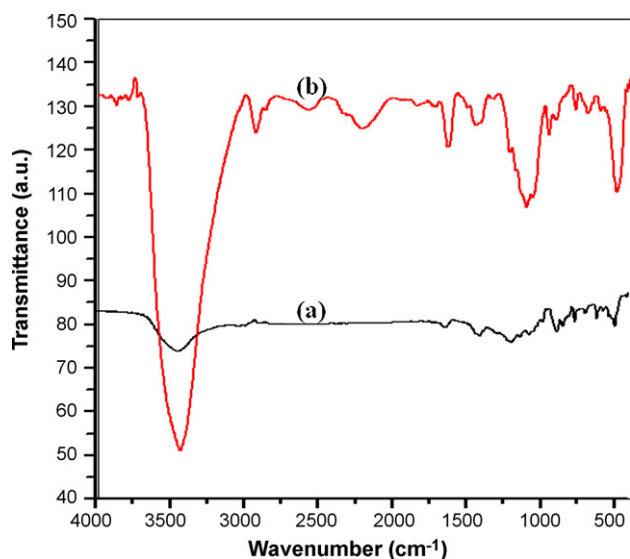


Fig. 4. FT-IR spectra of (a) pure PVdF-HFP and (b) PVS4-20 membranes.

is clear that stannous sulfuric acid is completely blended with the PVdF-HFP polymer. There were no significant morphological and structural changes observed between the different sizes of sulfonated stannous oxide incorporated hybrid membranes.

3.3. Thermal behavior

Thermal stability is an influential characteristic of the polymer electrolyte membranes which effectively determine the fuel cell reaction kinetics. In general, a high C-F bond strength involved in the PVdF-HFP copolymer induces a high thermal stability of the corresponding membrane [9]. For the pure PVdF-HFP membrane, a single weight loss was observed at around 487 °C due to the degradation of polymeric backbone PVdF-HFP units (Fig. 5) [26]. The incorporated acidic stannous oxide particles decreased the thermal behavior of the fabricated hybrid membranes due to their high hydrophilic nature. There were four significant weight losses observed for the prepared hybrid membranes (Fig. 5). The first weight loss observed at 100 °C is attributed to the evaporation of physisorbed water molecules. A second weight loss was observed at 200 °C and attributed to the desorption of chemisorbed water molecules. A degradation of sulfonic acid units of the fabri-

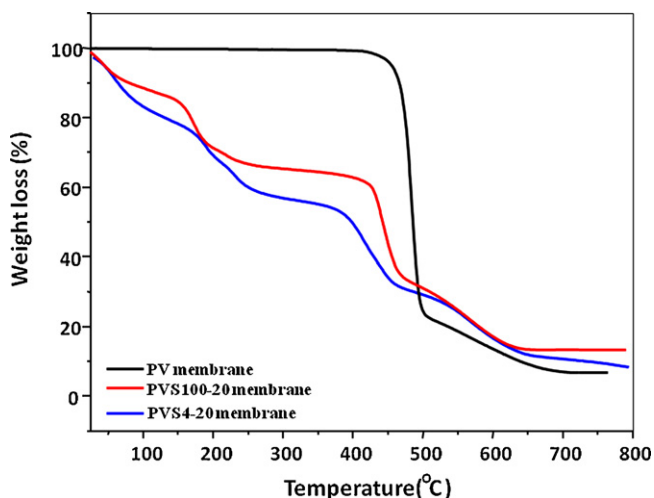


Fig. 5. Thermo gravimetric analysis of the fabricated membranes.

cated hybrid membranes was observed at 300 °C and the polymeric units thermal degradation was observed at 400 °C [27]. The thermal properties were varied for the different sizes of stannous oxide particles incorporated hybrid membranes. A decrease in the filler size effectively increases the relative surface area of the membrane which in turn increases the heat transfer area of the corresponding hybrid membrane. It results in the higher thermal degradation of smaller sized fillers incorporated hybrid membrane (PVS4-20) at lower temperatures but till the membranes can be applicable for high temperature fuel cells applications. From the obtained thermal spectra it is clear that the fabricated hybrid membranes consist of higher amount of water molecules and sulfonic acid units which collectively have a remarkable effect on the electrochemical properties and be discussed later.

3.4. Liquid uptake

The water and fuel transportation of the polymer membranes can be determined by liquid uptake which directly governs the fuel cells performances [4]. An increase in the sulfonated stannous oxide particles increases the liquid uptake as shown in Fig. 6a and b. In general, hydrophilic and hygroscopic characters determine the over all liquid uptake of the membranes. The hygroscopic and hydrophilic characters given to the PVdF-HFP copolymer via stannous and sulfuric acid molecules effectively influence the water uptake of the corresponding membranes. A decrease in the stannous oxide particles lead to a high acidification which correspondingly increases the hydrophilic character. The hygroscopic property of the prepared stannous oxide particles effectively absorbed the water molecules in its pores and tightly packed in its voids. Besides, the hybrid membranes interconnected cavities also eventually determined the high water uptake and water migration via its channels. The lower methanol uptake (Fig. 6b) obtained for the prepared membranes is conferred to the C-F bonds of hydrophobic polymer and methanol resistive behavior of stannous oxide particles.

3.5. Ionic conductivity

Ionic conductivity of the prepared hybrid membranes with respective of different temperatures is shown in Fig. 7. Pure PVdF-HFP membrane does not exhibit the appreciable protonic conductivity due to its high hydrophobic nature. The addition of stannous sulfuric acid generates hydrophilic channels in the PVdF-HFP polymer via the acid moieties and governs the ionic conductivity. An increase in the stannous sulfuric acid content promotes the number of acid molecules which in turn enhances the ionic conductivity (Fig. 7). Though the membranes could be prepared beyond 20 wt.% of stannous sulfuric acid, they were not physically stable and hindered the membrane electrode assembly fabrication processes. So far Nafion is considered as the standard benchmark of all kind of fuel cell membranes due to its high chemical and thermal stability. But an increase in the operation temperature beyond 80 °C results in the ionic conductivity decrement due to the evaporation of water molecules. Whereas the fabricated hybrid membranes exhibited an increment in the ionic conductivity at higher temperatures due to the tight packing of the sorbed water molecules in the polymer membrane via the hygroscopic effort of sulfonated stannous oxide particles.

Among the hybrid membranes studied, 2–4 nm sized acidified stannous oxide particles incorporated hybrid membranes exhibited higher ionic conductivity than that of 90–100 nm sized stannous oxide particles incorporated hybrid membranes. 2–4 nm sized stannous oxide particles have a larger outer surface than that of 90–100 nm sized stannous oxide particles which facilitate the

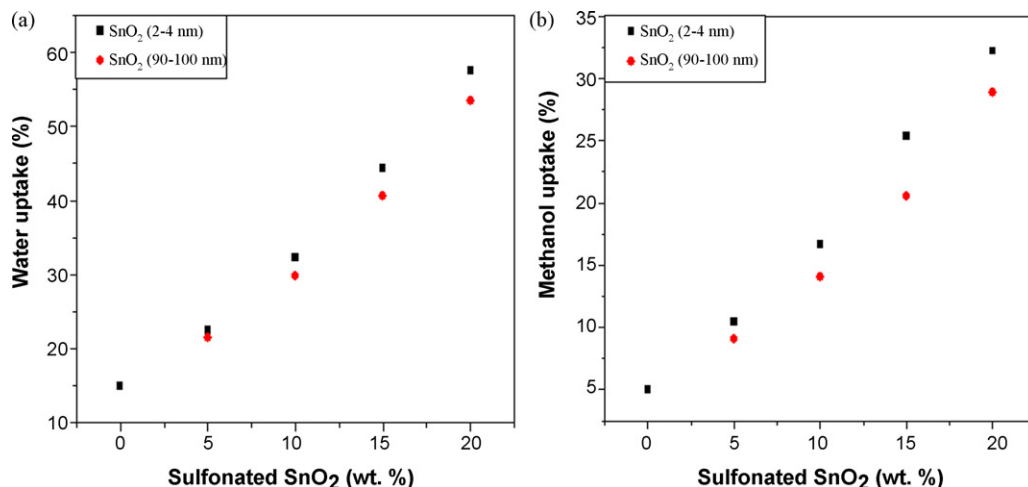


Fig. 6. (a) Water uptake and (b) methanol uptake of the fabricated membranes.

water migration and high acid functionalization. A decrement of particle size leads to a high acidification which in turn induces excess protons on its surface and promotes the hybrid membrane's ionic conductivity further. A decrement of particle size also leads to a high surface area which promotes the surface area of the corresponding membrane and responsible for the structural changes of polymer–filler interface. The increment of surface area of the smaller sized filler incorporated membranes got ensured by the higher heat transfer area via the thermal studies [22,28].

Fig. 8 shows the ionic conductivity of the prepared hybrid membranes as a function of relative humidities. Nafion membrane highly depends on the relative humidity and exhibited a dramatic drop in the ionic conductivity under lower humidity conditions [29]. Stannous oxide particles exhibit the structural, bonded, and adsorbed water molecules from the condensed hydroxyl groups, hydrogen bonded water, and physisorbed water molecules, respectively. The aforementioned water molecules humidify the polymeric chains of PVdF–HFP and the corresponding hybrid membranes exhibited a prompt ionic conductivity even at lower humidity conditions. The size of the added hygroscopic oxide has also an impact of the ionic conductivity with respective of different relative humidities. A smaller size of the stannous oxide particles exhibited higher ionic

conductivity due to the higher amount of sorbed water molecules as evidenced from the thermal studies.

3.6. Methanol permeability

The fuel permeability of the fabricated membranes is shown in Fig. 9. An increment of acid molecules increases the methanol permeability due to the high swelling of the corresponding membranes [30,31]. High methanol permeability of Nafion membrane is the major drawback for its DMFC applications. Nafion membrane highly swells in methanol solution which in turn increases the methanol permeability values. High fuel permeation decreases the over all DMFC efficiency. But the prepared hybrid membranes exhibited lower methanol permeability values due to the strong resistive methanol behavior of stannous oxide particles. Besides, hydrophobic nature of the host polymer also played a decisive role in the resistance of excessive swelling. The effect of different sizes of stannous oxide particles played a major role in the determination of molecular permeation. Decrease in the particle size increases the hydrophilic character of the corresponding membrane via the higher number of acid molecules which in turn promotes the methanol permeation than that of larger size fillers as shown in

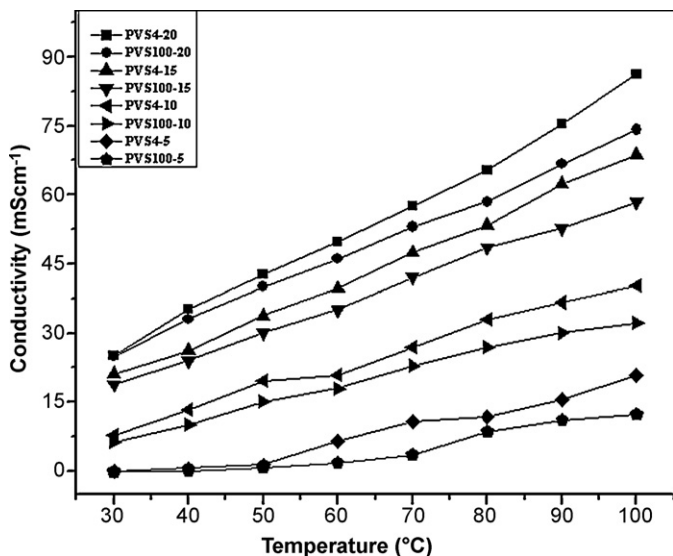


Fig. 7. Ionic conductivity of the fabricated hybrid membranes as a function of temperatures under 100% RH.

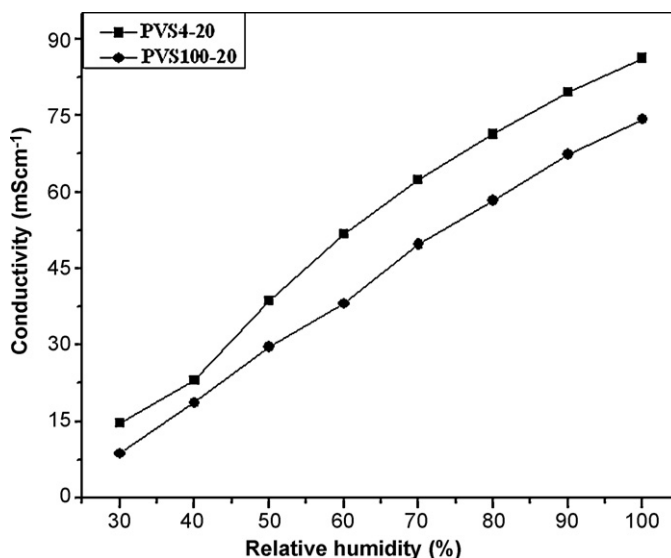


Fig. 8. Ionic conductivity of the fabricated membranes as a function of relative humidities measured at 100 °C.

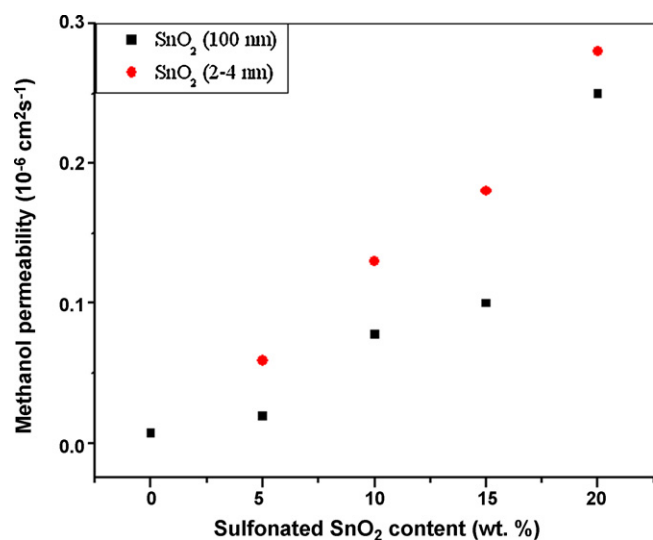


Fig. 9. Methanol permeation of the hybrid membranes measured at 30 °C.

Fig. 9. But a much lower methanol permeation observed for the prepared hybrid membranes ensured the lower fuel consumption and high reaction kinetics of the DMFC [32,33].

3.7. DMFC performance

Direct methanol fuel cell performances of the hybrid membranes are shown in Fig. 10. The fabricated hybrid membranes exhibited prompt DMFC performances due to the strong polymeric backbone and acid enriched hygroscopic oxides. The incorporated ceramic filler stannous oxide particles reduce the host polymer crystallinity and the ceramic-polymer grain boundary structure facilitate the rapid ions transportation via its high defect concentration [22,34]. The included acid enriched ceramic fillers provide ion channels and retain higher amount of water molecules via their acid molecules and hygroscopic properties, respectively. As evidenced from the ionic conductivity and methanol permeability values, 2–4 nm sized acidified stannous oxide particles

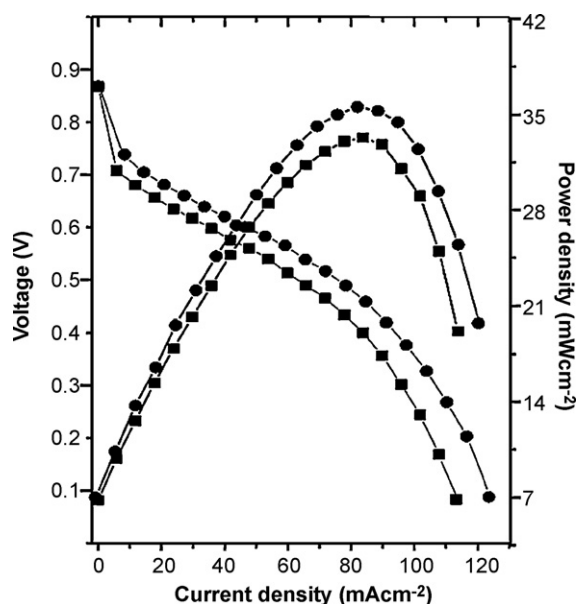


Fig. 10. DMFC performances of (●) PVS4-20 and (■) PVS100-20 membranes measured at 80 °C.

incorporated hybrid membrane PVS4-20 exhibited higher DMFC performance than that of larger size of stannous oxide particles included membrane PVS100-20 due to its larger extent of acidification, higher surface area, and more sorbed water molecules. Thus the prepared hybrid membranes selectively allow the ions and impede the molecular passage via its transportation channels which influences its high DMFC performance (Fig. 10). Cheap cost, no environmental hazards, easier preparation, higher thermal stability, high ionic conductivity under higher temperature and lower humidity conditions, lower methanol permeability, and prompt fuel cell performance values of the fabricated hybrid membranes influence its potential application in DMFC field than that of commercially available Nafion membrane.

4. Conclusions

Flourinated polymer-acidified stannous oxide hybrid membranes were fabricated for the higher DMFC performances. The EDS and IR spectra revealed the complete amalgamation of the acidified stannous oxide particles with the PVdF-HFP polymer. The ion channels were given to the PVdF-HFP polymer via the acidified hygroscopic particles and the uniform distribution of the vital elements enroll the homogeneity of the hybrid membranes. The incorporated stannous oxide particles absorb the higher amount of water molecules which in turn satisfies the high temperature and lower humidity operation of fuel cells. Though high acidification tends the membranes towards the higher methanol permeation, the methanol resistive behavior of stannous particles resisted the high fuel permeation. Thus the selected ions conduction and lower methanol permeation collectively increases the DMFC performance of the hybrid membranes and ensures its progressive role in DMFC field.

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