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ORIGINAL PAPER

Development novel eco-friendly proton exchange membranes doped with nano sulfated zirconia for direct methanol fuel cells

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Abstract

The proton exchange membrane is the main component of direct methanol fuel cells (DMFCs). It has binary function of separating oxidant and fuels, besides transporting protons. In this study, a binary polymer blend is formulated from inexpensive and ecofriendly polymers, such as iota carrageenan (IC) and poly vinyl alcohol (PVA). Super acidic sulfated zirconia (SO_4ZrO_2) was synthesized from an one pot, solvent free and simple calcination method and later embedded as a doping agent into the polymeric matrix with a percentage of 1–7.5 wt. %. The membranes formed were characterized by FTIR, TGA, DSC and XRD. The results revealed that, the oxidative stability and mechanical properties were enhanced with increasing doping addition due to an increase in numbers of hydrogen bonds formed between the polymers functional groups and oxygen functional groups of SO_4 ZrO_2. In addition to, the membrane with doping ratio of 7.5 wt. % of SO_4 ZrO_2 achieved methanol permeability of 1.95×10^{-7} cm^2 s^{-1} which much less than Nafion 117 (14.1×10^{-7} cm^2 s^{-1}) and ionic conductivity of 22.3 mS cm^{-1} which is close to Nafion 117 (34 mS cm^{-1}).

Keywords Proton exchange membrane · Poly vinyl alcohol · Iota carrageenan · Sulfated zirconia · Fuel cell

Introduction

Fuel cell converts chemical energy into an electrical energy directly and can efficiently perform energy conversion and storage. It had different types of fuel such as methanol, hydrogen, ethanol, etc. with zero emissions or low pollution [1]. The direct methanol fuel cell (DMFC) as kind of proton exchange membrane fuel cells (PEMFC) is broadly used in home appliances, automobiles, aerospace and other aspects [2].

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A membrane is used as a separator in the fuel cell between the fuel and oxidant compartments and allows good ion transport to maintain charge balance in the fuel cell. The Nafion family is the most perfluorinated PEMs used in the DMFCs because it provides good mechanical and chemical stability and ionic conductivity [1, 3]. However, Nafion membranes fabrication is expensive and requires a complex process which limits their commercialization [4, 5]. For that, their replacement by green and cost effective polymeric membranes is essential and necessary [6–8].

Membrane fuel cell development includes polymer sulfonation or polymer blending, and/or doping agent incorporation in the polymeric matrix, such as functionalized carbon materials and porous and functionalized inorganic materials to replace Nafion membranes [5, 9]. Nonperfluorinated polymers, such as poly(ether ether ketone) (PEEK), poly(styrene) (PS), poly(arylene ether sulfone) (PSU) and poly(benzimidazole) (PBI), are the most common polymers used to synthesize novel alternative polymeric membranes [5, 9, 10]. The synthesis of these nondegradable polymers requires toxic organic solvents, time and temperature, thus making the membrane synthesis costly, complex and not ecofriendly. From an economical and technological point of view, using biodegradable, inexpensive and green polymers, such as iota carrageenan (IC) and polyvinyl alcohol (PVA) is a more attractive approach than developing novel complex polymers or modifying current commercial membranes [5, 11–13]. Furthermore, the catalysts and the membrane are the essential parts of a DMFC. Therefore, producing a costly effective membrane makes the DMFC systems closer to wide applications.

PVA is a nontoxic, biodegradable and inexpensive polymer that is known for its excellent chemical stability, hydrophilicity, adhesive and film-forming properties [5, 14, 15]. Therefore, polyvinyl alcohol is widely used in medical, commercial and industrial applications. However, the rigid and semicrystalline structure of polyvinyl alcohol reduces its proton conductivity and subsequently its usage as a proton exchange membrane in fuel cells. Therefore inserting doping agents or blending with another polymer electrolyte to fix this defect is important [5, 12, 14]. For instance, Gouda et al. blended PVA with IC via hydrogen bonds interactions between -OH groups of IC and PVA for DMFC application and the result was enhancement in physicochemical properties of membranes formed [16, 17]. However, IC is biopolymer frequently used in the synthesis of polymer electrolyte membranes [18] due to its chemical stability, flexibility, and nontoxicity.

To enhance the membrane properties (mechanical, thermal, dimensional, methanol crossover hindering, oxidative stability and ionic conductivity) many researchers have followed a common strategy such as inserting doping agents into polymer structures to produce nanocomposite membranes [8, 9, 19, 20]. Sulfated zirconia (SO_4ZrO_2) incorporation into polymer matrices has been attractive in fuel cell applications as a result of its large surface area, mechanical strength, chemical stability and fuel crossover barrier [21–27]. SO_4ZrO_2 contains hydrophilic functional groups containing oxygen, such as sulfate groups, which improve water adsorption and thereby create channels for proton conduction [4, 9, 10]. Upon insertion of SO_4ZrO_2 into polymer blends hydrogen bonds will form between the -OH groups of polymer chains and oxygenated groups in SO_4ZrO_2, and these hydrogen bonds will compact the membrane matrix and reinforce it, preventing excess swelling and water uptake [14, 28, 29]. Further increasing the ionic conductivity of nanocomposite membranes, including SO_4ZrO_2 is possible, as a result of the presence of sulfate groups in their structure, which in turn increase the number of proton conducting sites.

The aim of this work is to produce nanocomposite membranes prepared by simple processing of low cost polymers by using water as a solvent to walk a step toward DMFC commercialization. Poly vinyl alcohol was chosen as the essential polymer in the membranes due to its excellent ability to form films with IC polymer. SO_4ZrO_2 was synthesized and embedded as a doping agent into the polymers matrix in different concentrations to create novel composite membranes, named SPVA/IC/SO_4ZrO_2. The oxygen groups from SO_4ZrO_2, including sulfate groups, bonded to the -OH groups of IC and PVA via hydrogen bonds creation, are expected to enhance the membranes' oxidative stability, hydrogen ions conductivity, mechanical resistance and obstacle the methanol crossover, while decreasing the extreme water uptake, hence enhancing the DMFC performance using such membrane.

Materials and methods

Iota carrageenan (type V) and PVA (99% hydrolysis and medium MW, USA). Glutaraldehyde (GA) (Alfa Aesar, 50 wt. % in H_2O) and 4-sulfophthalic acid (SPA) (Sigma-Aldrich, 99.9 wt.% in H_2O) were used as covalent and ionic cross-linkers, respectively [16, 17].

Synthesis

Synthesis of nano sulfated zirconia (SO_4 ZrO_2)

Nano SO_4ZrO_2 was prepared by a simple calcination method by using ammonium sulfate $(NH_4)_2SO_4$ and zirconium oxychloride octahydrate $ZrOCl_28H_2O$ in absence of any solvent [30]. The molar ratio of $(NH_4)_2SO_4$ and $ZrOCl_28H_2O$ by 6:1 respectively were ground in a mortar and placement for 18 h at room temperature. The powder was calcined for 5 h at 600 °C, finally the powder was ground in a ball mill for 10 min to obtain nanosized particles.

Preparation of SPVA / IC / SO_4ZrO_2 membranes

First, 10 g of PVA was dissolved in 100 mL deionized H_2O at 90 °C for 2 h and 2 g of IC was dissolved in 100 mL deionized H_2O at 80 °C for 1 h then blending PVA: IC (95:5) wt%. After that, crosslinking the polymers blend by GA (5 g, 50 wt%) as covalent crosslinker and SPA (5 g, 99.9 wt%) as ionic crosslinker and sulfonating agent for PVA, to convert to sulfonated polyvinyl alcohol (SPVA) [31, 32]. Then the inorganic—organic nanocomposite was prepared by incorporating different concentrations of SO_4ZrO_2 (1, 2.5, 5, 7.5 wt %) in polymeric blend and were named SPVA/ IC/ SO_4ZrO_2 -1, SPVA/ IC/ SO_4ZrO_2-2.5, SPVA/ IC/ SO_4ZrO_2-5, SPVA/ IC/ SO_4ZrO_2-7.5 respectively.

Figure 1 explains the possible structure of the SPVA/ IC/ SO_4ZrO_2 membrane where IC and PVA were ionically crosslinked by esterification reactions between carboxylic groups of SPA and hydroxyl groups of polymers. In addition, the two polymers were covalently crosslinked by acetal reactions between aldhyde groups of GA and hydroxyl groups

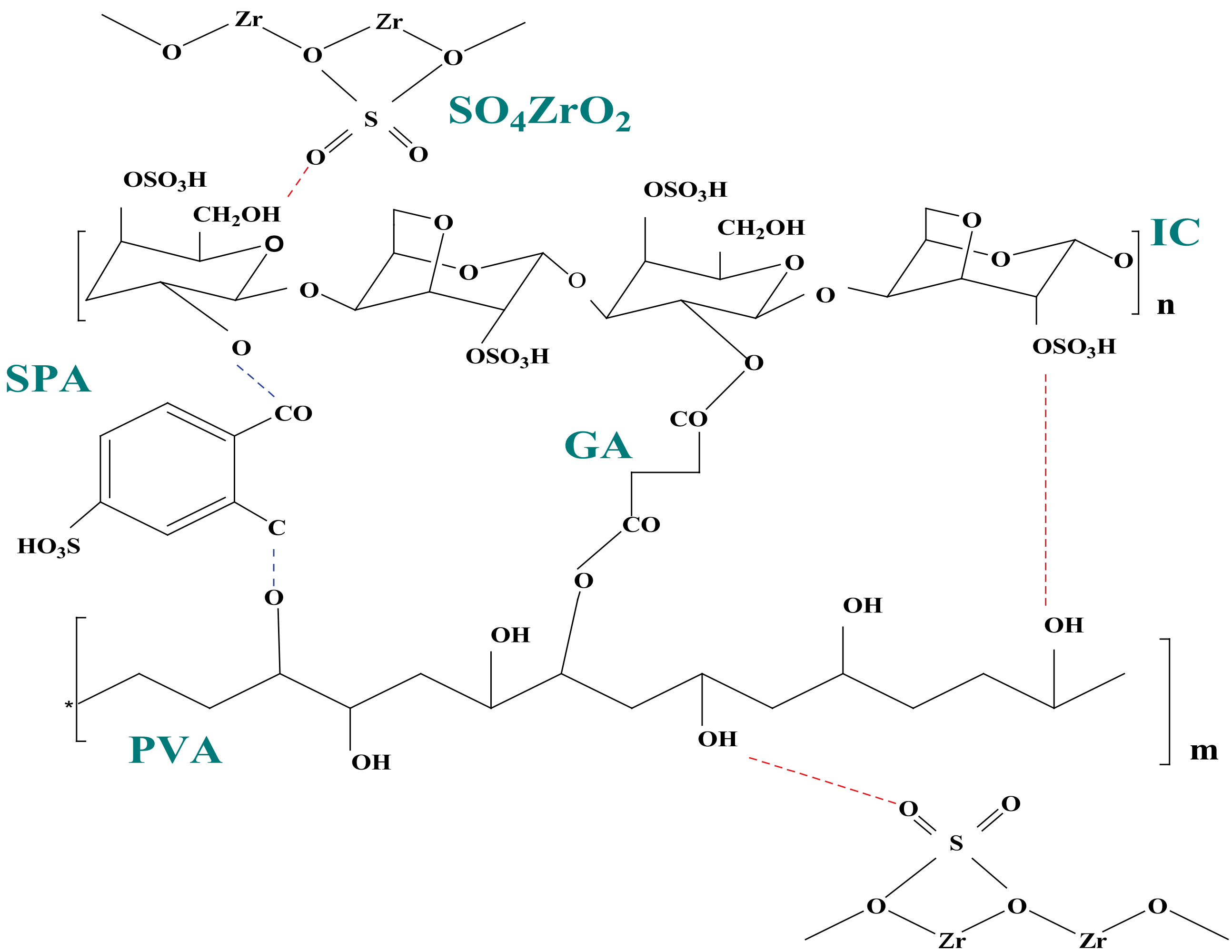

Fig. 1 Possible structure of the SPVA/IC/ SO_4ZrO_2 membrane

of the polymers. Furthermore, the interactions of hydrogen bonds formed between the oxygenated groups of the doping agent and the -OH groups of the polymers [16].

Characterization

The characteristic functional groups of SO_4ZrO_2 powder and the nanocomposite membranes were monitored by Fourier transform infrared spectrophotometer (Shimadzu FTIR-8400 S- Japan), while the structures were evaluated by X-ray diffractometer (Schimadzu7000-Japan). Thermal changes of SPVA/ IC/ SO_4ZrO_2 membranes were traced by using thermogravimetric analyzer (Shimadzu TGA-50, Japan). The temperature range was 25–800 °C, under a nitrogen atmosphere, and the heating rate was 10 °C min^{-1}. Additionally, differential scanning calorimetry (DSC) (Shimadzu DSC-60, Japan) in the range of 25–300 °C was used to evaluate the membranes. The morphological structure of the SPVA/ IC/ SO_4ZrO_2 -7.5 membrane was shown by scanning electron microscopy (SEM) combined with energy-dispersive X-ray analysis (EDX) (Joel Jsm 6360LA-Japan). SO_4ZrO_2 was visualized by using transmission electron microscopy (TEM, JEM 2100 electron microscope).

Contact angles between membrane surfaces and water drops were measured to evaluate the hydrophilicity of the membranes by using contact-angle analyzer (Rame-Hart Instrument Co. model 500-FI). To measure the swelling ratio (SR) and water uptake (WU), the dry membrane was cut, and its dimensions were measured and weighed. Then, the samples were placed in deionized H_2O for one day, then dried with tissue paper and weighed again. The SR and WU of the composite membranes were calculated according to Eqs. (1) and (2), respectively,

$$SR(\%) = \frac{L_{wet} - L_{dry}}{L_{dry}} \times 100 \tag{1}$$

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

where L_{dry} and L_{wet} are the lengths of dry and wet composite membranes, respectively, while W_{dry} and W_{wet} are the weights of dry and wet composite membranes, respectively.

The ion exchange capacity (IEC) of prepared nanocomposite membranes was determined by using acid–base titration [33]. The weighed samples were placed in 50 cm^3 of a 2 M NaCl solution for two days, and then the solutions were titrated with a 0.01 N NaOH solution. IEC calculated as follows:

$$IEC(m_{eq}/g) = \frac{V_{NaOH} \times C_{NaOH}}{W_d} \times 100 \quad (3)$$

where: V_{NaOH}, C_{NaOH}, and W_d are the volume of sodium hydroxide consumed in titration, the concentration of sodium hydroxide solution, and the weight of the dry sample, respectively.

To evaluate the ionic conductivity of nanocomposite membranes, resistance measurements were evaluated by electrochemical impedance spectroscopy (EIS) using a PAR 273A potentiostat (Princeton Applied Research, Inc.) coupled to SI 1255 HF frequency response analyzer (FRA, Schlumberger Solartron). First, samples were placed in 1 M H_2SO_4 solution at room temperature for 24 h then completely washed [1]. The membranes were placed between two stainless steel electrodes at an open circuit potential of 5 mV with signal amplitude in the 100 Hz—100 kHz frequency range. The high frequency intercept on the Nyquist plot real axis shows the bulk membrane resistance, whereas the membranes ionic conductivity was measured from estimated resistance according to Eq. (4),

$$\sigma = \frac{d}{RA} \quad (4)$$

where σ (S cm^{-1}) is the ionic conductivity of membrane, R (Ω) is the membrane resistance, A (cm^2) is the membrane area, d (cm) is membrane thickness.

To evaluate the methanol permeability of the nanocomposite membrane, two small tanks of 100 mL each were placed vertically in a glass diffusion cell. The first tank, donor tank (A), was filled with 2 M methanol and the second tank, receptor tank (B), was filled with water [16]. Methanol diffuses from A to B via the composite membrane as a result of the concentration difference between the two tanks, and the methanol concentration which transferred to tank (B) was detected by HPLC. The crossover of methanol from A to B as a function of time was determined by Eq. (5),

$$C_B(t) = \frac{A}{V_B}\frac{P}{L}C_A(t - t_0) \quad (5)$$

where A (cm^2) is the diffusion area, V_B (cm^3)is the receptor tank volume, L (cm)is the membrane thickness, C_B and C_A (mol L^{-1}) are the methanol concentrations in the tanks B and A, respectively, the interval (t—t_0) is the time of the methanol crossover and P is the methanol permeability of the membrane (cm^2 s^{-1}). The membrane selectivity (the ratio of the ionic conductivity to the methanol permeability) was calculated, because it can provide an important indication of fuel cell performance.

The oxidative stability of fabricated membranes was measured by calculating the weight loss of the nanocomposite membrane (1.5 × 1.5 cm^2) in Fenton's reagent (3 wt.% H_2O_2 containing 2 ppm $FeSO_4$) at 68 ºC for 24 h [34].

A tensile strength test, until membrane breaking, was measured for the dry nanocomposite membranes at room temperature by using Lloyd Instruments LR10k. [34].

The I-V characteristic was evaluated for the prepared membranes by using Potentiostat/Galvanostatic (VoltaLab 40 PGZ301) with software Voltamaster4. The experiment was performed on a single cell membrane electrode assembly (MEA) with active surface area of 25 cm^2, at room temperature, 60% relative humidity, ambient pressure and gas flow rate of hydrogen and oxygen were 50 cc min^{-1} and 100 cc min^{-1}, respectively. Nafion117 (Ion Power Company-USA) was used as a commercial reference membrane for comparison purposes.

Results and discussion

Characterization of SO_4ZrO_2 and nanocomposite membranes

Figure 2a shows a wide peak at around 3400 cm^{-1} and peaks at approximately 1630 cm−1, which may be referred to the adsorbed H_2O molecules, and a peak at approximately 500 cm^{-1} due to Zr-O band. While, IR band of SO_4^{2-}group is in the region of 1200–900 cm^{-1} [35], with peaks at 1217, 1128 and 1016 cm^{-1} are characteristic of S–O. For the prepared membranes as shown in Fig. 2b, the bands at approximately 3250 are characteristic of –OH groups of PVA and IC and the band at1600 $cm^{-1}$is attributed to the O–H bonds from water molecules that are more adsorbed as the concentration of sulfated zirconia increases due to its hydrophilic features. The characteristic peak for iota carrageenan sulfate groups at 830 cm^{-1}. While, the bands at 2840 and 2300 cm^{-1} can be assigned to the C-H bonds in the polymer structure [34]. The weak bands at 1700 and 1750 cm^{-1} refer to C = O bonds and bending of C-H in the aromatic structure of sulfophithalic acid (SPA) respectively, which proves that the crosslinking process is achieved. In addition, the bands at 950 and 1100 cm^{-1} are attributed to sulfate groups of the doping agent.

In Fig. 3 it was observed the amorphous structure for the fabricated membranes increased with increasing the doping

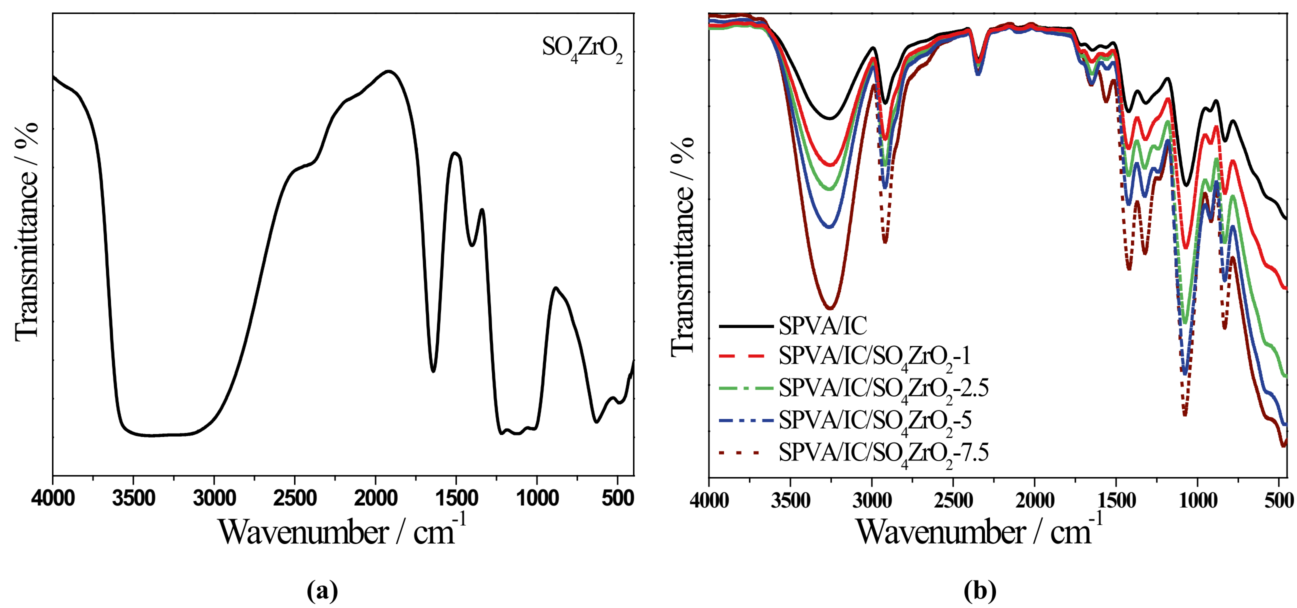

Fig. 2 FTIR spectra of (a) SO_4ZrO_2, (b) SPVA/IC/SO_4ZrO_2 membranes

agent concentration,which indicates the good ability of the prepaerd membrane to conducte ions [37],while the sulfated zirconia powder curve shows characteristic peaks intensity of SO_4ZrO_2 at a 2θ angle 28,38,54 [22, 37].

Figure 4 shows the surface without any defects for the undoped crosslinked membrane, and good dispersion without agglomeration for sulfated zirconia in the doped membrane; in addition Fig. 4c shows a compact cross sectional structure of the doped membrane. While the TEM image (Fig. 4d) of sulfated zirconia proved that the material formed fine particles with nanoscale sizes and small amounts of agglomeration which was confirmed from the frequency distribution plot (Fig. 4f) of SO_4ZrO_2 nanoparticle sizes. The sulfur groups' presence on the surface of SO_4ZrO_2 was verified by EDX spectra (Fig. 4e) which proved the synthesis of sulfated zirconia was achieved.

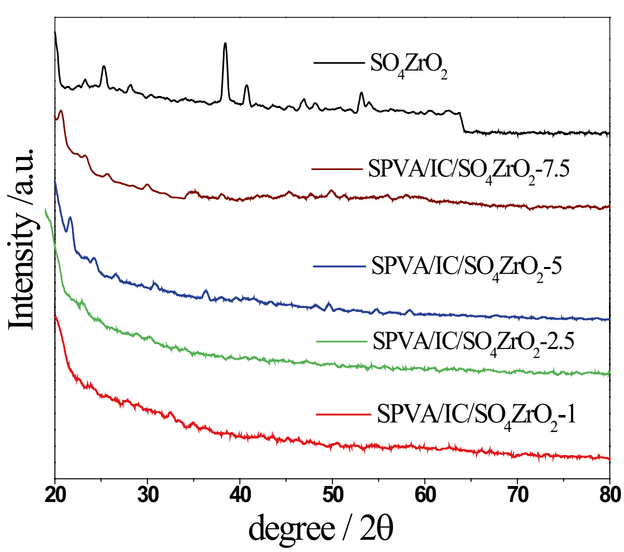

Fig. 3 XRD patterns of SO_4ZrO_2 and SPVA/IC/ SO_4ZrO_2 membranes

Mechanical and thermal and analysis

The addition of SO_4ZrO_2 improves the mechanical tensile of the polymeric matrix [36]. As shown in Table 1, by increasing SO_4ZrO_2 incorporation into the polymeric matrix, the tensile strengths of the nanocomposite membranes were increased due to increasing the compatibility of the composite membrane as a result of increasing the interaction between the two polymer functional groups, such as sulfate and hydroxyl groups, and the characteristic groups of SO_4ZrO_2 via formed hydrogen, covalent and ionic bonds which enhanced the interfacial adhesion in the nanocomposite membranes when compared to the undoped membrane.

TGA of polymeric blend membranes without and with SO_4ZrO_2 are illustrated in Fig. 5a. The initial weight loss at ~ 150 ºC (~ 8%) may be attributed to moisture evaporation in all membranes [12, 38]. The second weight loss of composite membranes occurred in the range of ~ 150—270 ºC and that may be attributed to the functional groups degradation [39, 40]. The third weight loss stage appeared by a remarkable decomposition from ~ 270—360 ºC and that may be referred to as polymeric chain decomposition [28, 38],which started at 230 ºC for the undoped membrane, while for the doped membranes it was started at 270 ºC with a lower weight loss percentage. This behavior clarifies

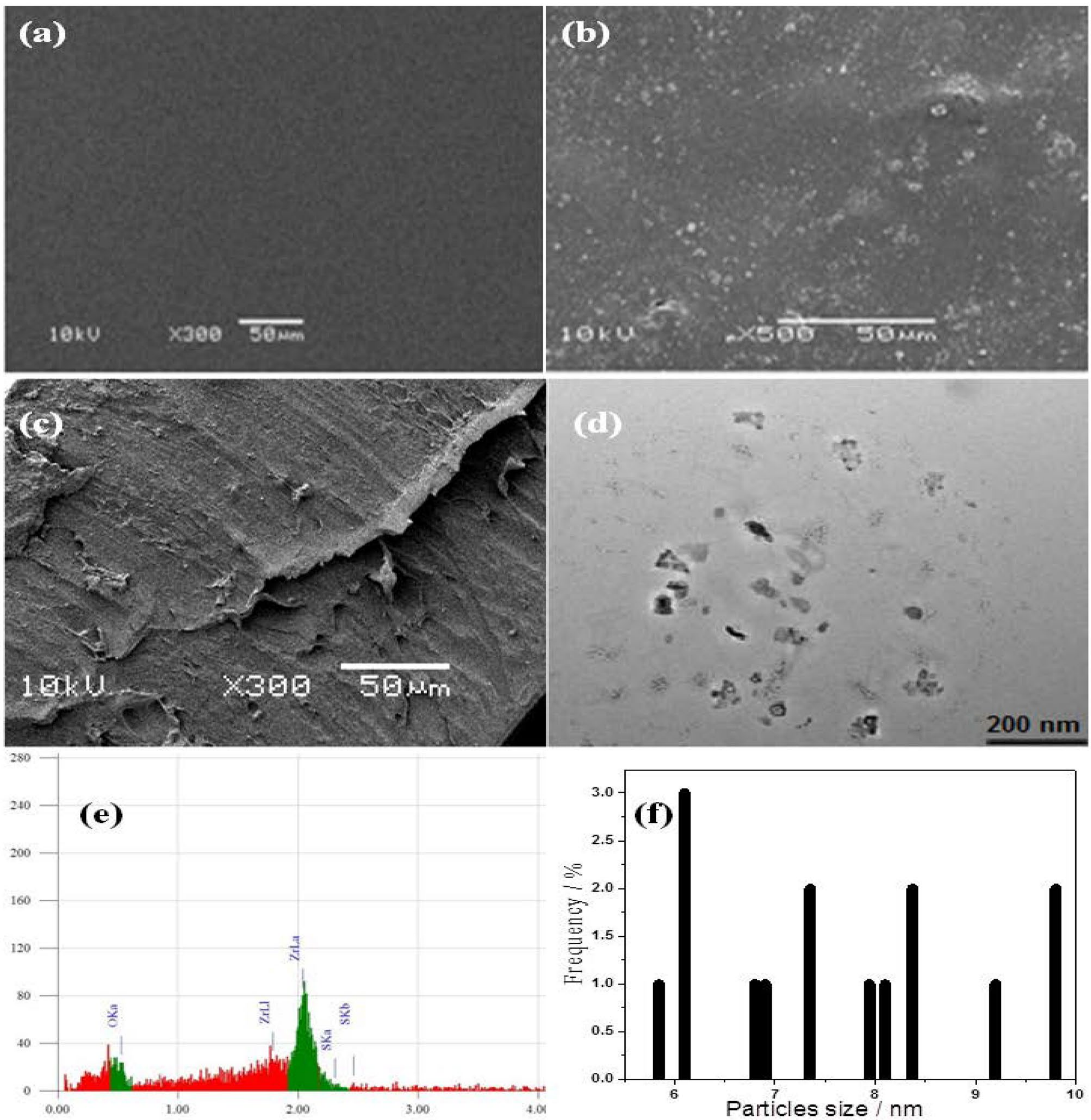

Fig. 4 SEM images for (**a**) undoped membrane, (**b**) and (**c**) PVA/IC/ SO_4ZrO_2-7.5 membrane surface and cross section, (**d**) TEM image for SO_4ZrO_2 nanoparticles, (**e**) EDX analysis for SO_4ZrO_2 and (**f**) frequency distribution plot of SO_4ZrO_2 nanoparticles size from TEM image

that doping agent incorporation enhances the thermal stability of composite membranes by increasing covalent, ionic and hydrogen bonding in the nanocomposite. For DSC, as shown in Fig. 5b, the existence of only one endothermic peak provides proof of complete miscibility in the membrane structure, and the disappearance of this peak at SO_4ZrO_2 (5, 7.5 wt%) may be attributed to the formation of many more hydrogen bonds between the doping agent and polymer structure [16, 17]. The melting temperature of the membranes decreased with the increasing doping agent concentration. This behavior could be explained by the hydrogen bonds interactions partially destroy the membranes crystallinity, which in turn reduce the melting point [16].

The behavior of the composite membranes in contact with deionized water is shown in Table 1. The membrane surfaces are considered hydrophobic when the contact angle is $\geq 90°$ and hydrophilic when the contact angle is $< 90°$. The composite membranes have a lower hydrophilic quality with

Table 1 Physicochemical properties of the fabricated membranes and Nafion 117 [1, 31]

Membrane	Thickness (µm)	WU (%)	SR (%)	Contact angle (°)	Tensile strength (MPa)	Oxidative stability (RW, %)*
SPVA/IC	110	> 100	90	45.36	12.2	81
SPVA/IC/ SO_4ZrO_2-1	154	95	40	47.53	20.9	90
SPVA/IC/ SO_4ZrO_2- 2.5	169	40	32	50.86	28.3	93
SPVA/IC/ SO_4ZrO_2- 5	173	28	20	52.21	34.3	97
SPVA/IC/ SO_4ZrO_2-7.5	179	22	16	60.60	38.5	99
Nafion 117	170	9.5	13	102	25	92

*The retained weight of membranes (RW) after immersion for a day in Fenton's reagent

higher thickness because of the increasing doping agent content [33, 41]. It was also noticed that, as the amount of SO_4ZrO_2 increased in the polymeric matrix from 1% to 7.5%, the swelling ratio and water uptake of the polymeric membranes were decreased and that are very necessary as water overload can be avoided [42]. In other words, increasing doping agent in membrane matrix leads to increasing the structure compact which in turn avoid water overload in the polymeric matrix channels when compared with undoped membrane [43–45].

Oxidative stability

The chemical stability of the composite membranes, as illustrated in Table 1, was measured by a Fenton's reagent test. An undoped membrane gives the lowest chemical stability, while introducing of SO_4ZrO_2 as a dopant enhances the membrane resistance to OOH and OH radicals attack. PVA/IC/SO_4ZrO_2-7.5 membrane was the most stable fabricated membrane at which its retained weight is approximately 99% and that give a proof to the addition of SO_4ZrO_2 increase the chemical stability of the polymeric membranes [26].

IEC, methanol crossover and ionic conductivity

The IEC values are presented in Table 2, and it can be noted that as the amount of SO_4ZrO_2 increases in the composite membranes, the IEC values increase because the polymeric matrix contains more acidic exchangeable groups from SO_4ZrO_2. This is directly related to the good ionic conductivity of PVA/IC/ SO_4ZrO_2-7.5 (22.3 mS cm^{-1}) when compared with the undoped membrane (10.1 mS cm^{-1}) as shown in Fig. 6a, whereas, the sulfate sites of SO_4ZrO_2 increase the charges in the polymeric matrix which in turn enhance its ionic conduction [29, 41]. Regarding the fuel permeability of composite membranes, it can be observed that the introduction of SO_4ZrO_2 into the polymeric matrix obstacles the methanol crossover. As illustrated in Table 2 the methanol permeability

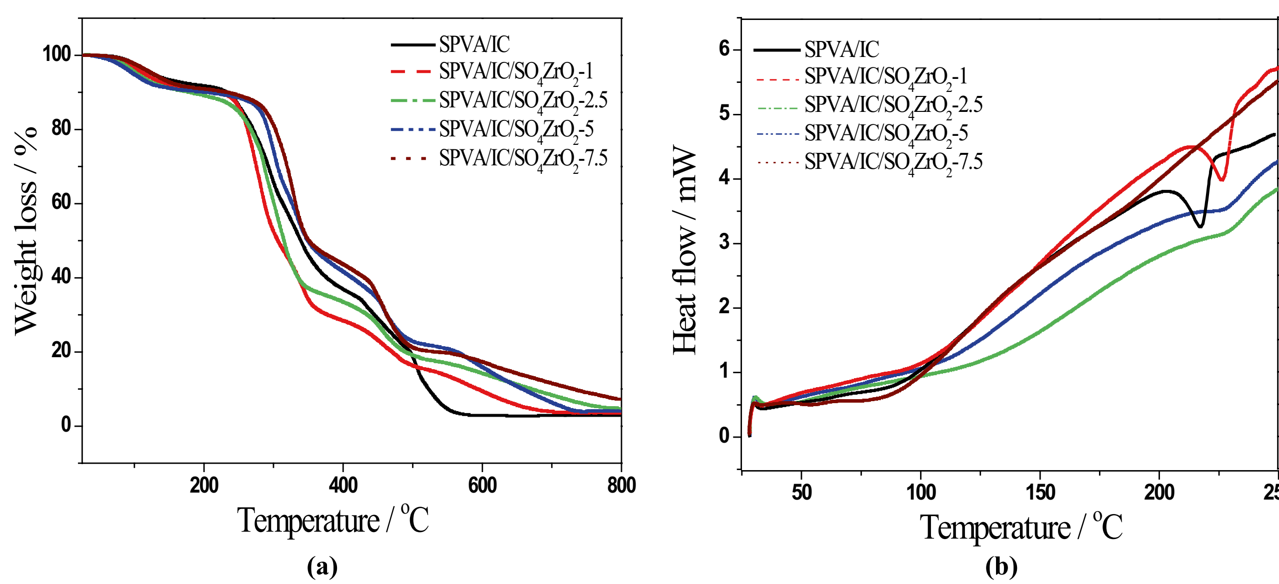

Fig. 5 TGA and DSC curves of SO_4ZrO_2 nanocomposite membranes

Table 2 Ionic conductivity, methanol permeability, IEC and selectivity of the fabricated membranes and Nafion 117 [1]

Membrane	IEC (meq g^{-1})	Ionic conductivity (mS cm^{-1})	Methanol permeability (10^{-7} cm^2 s^{-1})	Selectivity (10^5 S cm^{-3} s)
SPVA/IC	0.15	10.1	3.9	0.25
SPVA/IC/ SO_4ZrO_2-1	0.15	11.6	2.93	0.39
SPVA/IC/ SO_4ZrO_2- 2.5	0.20	13.3	2.69	0.49
SPVA/IC/ SO_4ZrO_2- 5	0.25	15.5	2.23	0.69
SPVA/IC/ SO_4ZrO_2-7.5	0.30	22.3	1.95	1.14
Nafion 117	0.89	34.0	14.1	0.24

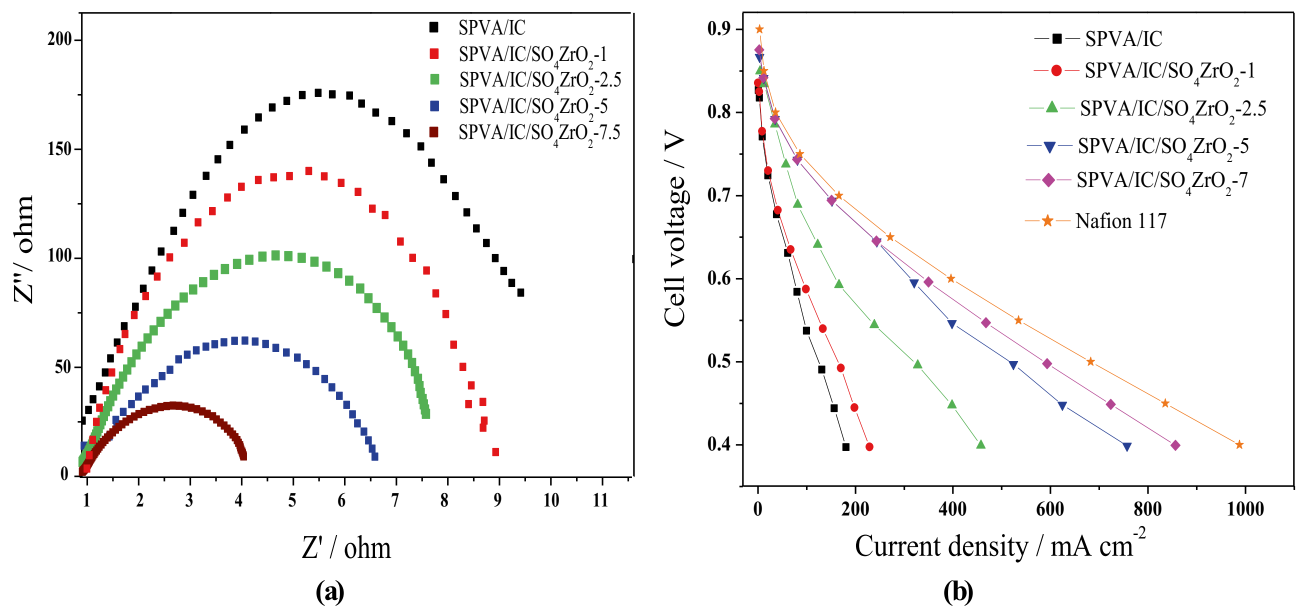

Fig. 6 (**a**) Nequest plot of SPVA/IC and SPVA/IC/SO_4ZrO_2 nanocomposite membranes, (**b**) I-V curve for MEAs of prepared membranes compared to the value of typical Nafion117

of the undoped polymeric membrane was 3.9×10^{-7} cm^2 s^{-1} and upon incorporation of SO_4ZrO_2 into the membrane matrix, the permeability decreased to a value of 1.95×10^{-7} cm^2 s^{-1} for the PVA/IC/ SO_4ZrO_2-7.5. The decrease in the methanol permeability of the membrane containing doping agent may be referred to the ability of the doping agent to narrow the polymeric matrix channels that decrease the water uptake and thus the fuel permeability will be reduced [31, 33]. The higher selectivity noted for PVA/IC/SO_4ZrO_2-7.5 was 1.14×10^5 S cm^{-3} s compared to undoped PVA/IC membrane which has selectivity approximately 0.25×10^5 S cm^{-3} s and that is an indication to the suitability of the fabricated nanocomposite membranes to be used in DMFCs [44].

The I-V characteristic was evaluated as shown in Fig. 6b using prepared membranes and Nafion 117 membrane and it was noticed that the polarization curves of the prepared nanocomposite membranes shows a slow decay of cell voltage with current density increasing compered to Nafion117, furthermore comparatively higher open circuit voltage (OCV) for SPVA/IC/SO_4ZrO_2-7.5 than other membranes may be attributed to comparatively high ion conduction through the nanochannels [46].

Conclusions

A low cost nanocomposite membrane was prepared through a simple blending and solution casting method using ecoenvironmentally and available polymers. It was appeared that the incorporation of SO_4ZrO_2 as doping agent into the polymeric blend improves the membranes properties, like ionic conductivity, mechanical stability, oxidative stability, reducing the water overload and methanol crossover limiting was enhanced, especially in the nanocomposite membrane with 7.5% of SO_4ZrO_2 which shows oxidative stability and tensile strength better than Nafion117 and fuel permeability less than Nafion 117. In conclusion, the fabricated membrane with the optimum properties (PVA/IC/SO_4ZrO_2-7.5) can be efficient as a cation exchange membrane for the development of green and low cost DMFCs.

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Author contributions The manuscript was written through the contributions of all authors. All authors have approved the final version of the manuscript.

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