A Highly Selective Novel Green Cation Exchange Membrane Doped with Ceramic Nanotubes Material for Direct Methanol Fuel Cells

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Abstract: Herein, a pair of inexpensive and eco-friendly polymers were blended and formulated based on poly (ethylene oxide) (PEO) and poly (vinyl alcohol) (PVA). FTIR, XRD, EDX and TEM techniques were used to describe a Phosphated titanium oxide ($\text{PO}_4\text{TiO}_2$) nanotube synthesised using a straightforward impregnation-calcination procedure. For the first time, the produced nanoparticles were inserted as a doping agent into this polymeric matrix at a concentration of (1–3) wt.%. FTIR, TGA, DSC and XRD were used to identify the formed composite membranes. Furthermore, because there are more hydrogen bonds generated between the polymer’s functional groups and oxygen functional groups $\text{PO}_4\text{TiO}_2$, oxidative stability and tensile strength are improved with increasing doping addition and obtain better results than Nafion117. The permeability of methanol reduced as the weight % of $\text{PO}_4\text{TiO}_2$ increased. In addition, the ionic conductivity of the membrane with 3 wt.% $\text{PO}_4\text{TiO}_2$ is raised to (28 mS cm$^{-1}$). The optimised membrane (PVA/PEO/PO$_4$TiO$_2$-3) had a higher selectivity ($6.66 \times 10^5$ S cm$^{-3}$ s) than Nafion117 (0.24 $\times 10^5$ S cm$^{-3}$ s) and can be used as a proton exchange membrane in the development of green and low-cost DMFCs.

Keywords: proton exchange membrane; poly (vinyl alcohol); poly (ethylene oxide); titanium oxide; direct methanol fuel cell; fuel cell

1. Introduction

Chemical energy is instantly converted into electrical energy by the fuel cell. It is a sort of power-producing equipment that can efficiently convert and store energy. Hydrocarbons such as methanol or ethanol can be used as fuel in those cells. It produces zero emissions or minimum pollution [1]. As a type of proton exchange membrane fuel cell (PEMFC), the direct methanol fuel cell (DMFC) is widely utilised in home appliances, vehicles, aerospace and other fields. [2].

A membrane separates the fuel and oxidant compartments in a fuel cell, allowing for efficient ion transport and charge balance. Due to its chemical stability, mechanical properties and ionic conductivity, the Nafion membranes are the most perfluorinated PEMs utilised in DMFCs [1,3]. However, nafion membrane manufacture is expensive and time-consuming, which limits its commercialisation [4,5]. As a result, replacing them with ecologically benign and cost-efficient polymeric films is crucial and essential [6–8].

To replace Nafion membranes, sulfonation or blending of polymers [9] and/or doping agents, such as porous and functionalised inorganic materials and functionalised carbon materials, are inserted into the polymeric matrix [10–15]. The most prevalent non-perfluorinated polymers utilised to build novel alternative polymeric membranes are poly(styrene) (PS), poly (ether ether ketone) (PEEK), poly(benzimidazole) (PBI) and poly (arylene ether sulfone) (PSU). However, the use of toxic chemical time, solvents and temperature in the preparing of these non-degradable polymers makes membrane synthesis
expensive, complicated and environmentally unfriendly. Therefore, using biodegradable, cheap and green polymers such as polyethene oxide (PEO) and polyvinyl alcohol (PVA) is a more appealing strategy from an economic and technological standpoint than inventing innovative complicated polymers or adapting existing commercial membranes [10,16–18]. In addition, the catalysts and film are critical components of a DMFC. As a result, building a cost-effective membrane brings DMFC systems closer to widespread use.

In addition to its chemical stability, hydrophilicity, adhesive properties and film-forming abilities, PVA is also environmentally friendly and low cost [19–21]. Polyvinyl alcohol is therefore commonly employed in medicinal, commercial and industrial settings. Polyvinyl alcohol’s proton conductivity and, as a result, its stiff and semi-crystalline structure hampers its use as a proton exchange membrane in fuel cells. As a result, adding doping agents or mixing with another polymer electrolyte to correct this flaw is a viable option [19,22,23]. Since hydrogen connections develop between the -OH groups of PVA and the ether linkage of polyethene oxide, blending PVA with PEO is preferred [20,24]. On the other hand, PEO is an environmentally acceptable polymer that is utilised to synthesise polymer electrolyte systems in various energy devices due to its improved ionic conductivity, low toxicity and flexibility [25,26].

To increase membrane properties, many researchers adopted the conventional practice of incorporating doping compounds into polymer matrix to create nanocomposite barrier membranes [27–31]. Due to its huge surface area, mechanical toughness, chemical resistance, barrier to fuel crossing, cheap price and low level of toxicity, phosphated titania (PO₄TiO₂) in a polymer matrix has been studied for use in fuel cell applications [19,20]. PO₄TiO₂ also includes oxygen-containing hydrophilic functional groups, which enhance water sorption and produce proton conduction channels [20]. When PO₄TiO₂ nanotubes are embedded into polymers, the hydrogen bonds will be generated between hydroxyl groups along the polymer backbone and oxygen groups of PO₄TiO₂. These hydrogen bonds will reflect on the membranes’ mechanical properties, strengthening them and limiting extreme swelling and water sorption [20,26], enhancing the ionic conductivity of formulated membranes containing PO₄TiO₂ nanotubes.

This project aims to develop innovative nanocomposite membranes constructed from mild processing of environmentally safe and economic polymers compatible with water as the principal solvent to further DMFC commercialisation. Due to its exceptional capacity to build films with PEO polymer, polyvinyl alcohol was selected as the key polymer for the membrane. The polymers were crosslinked completely and concurrently converted to sulfonated PVA using crosslinkers such as 4-sulfophthalic acid (SPA) and glutaraldehyde (GA). SPVA/PEO/PO₄TiO₂ nanotubes were synthesised and injected as a doping agent in the PVA matrix at various ratio to create new nanocomposite membranes. The parameters such as oxidative chemical stability, proton conductivity, mechanical resistance and restriction of the methanol permeability will be controlled due to the formation of hydrogen bond of formulated matrix and oxygen groups of PO₄-TiO₂, which could be improved DMFC performance employing such membranes.

2. Materials and Methods

PEO (MW: 900,000 g mol⁻¹, Acros Organics) and PVA (99% hydrolysis and medium MW, USA). Glutaraldehyde (GA) (Alfa Aesar, 25 wt.% in H₂O) and 4-sulphophthalic acid (SPA) (Sigma-Aldrich, 99.9 wt.% in H₂O) were used as covalent and ionic crosslinkers, respectively [30]. Titanium (IV) oxide rutile (TiO₂, <5 µm, ≥99.9%, Sigma-Aldrich, Darmstadt, Germany) and H₃PO₄ (Fisher Chemical, 85 wt.%)

2.1. Synthesis

2.1.1. Synthesis of Phosphated Titanium Oxide Nanotube (PO₄-TiO₂)

TiO₂ nanotubes were synthesised as mentioned in the previous work [19]. TiO₂ nanotubes were mixed to 0.1 mol/L⁻¹ phosphoric acid in a molar ratio 1:1 and the suspension
was shaken in hot water (80 °C). The mixture was rinsed with H₂O and dried overnight at 110 °C. The powder was then burned in a muffle furnace at 450 degrees Celsius.

2.1.2. Preparation of SPVA/PEO/PO₄TiO₂ Membranes

Here, 100 mL of PVA solution (10%) was prepared, and PEO (2 g) was dissolved in 100 mL deionized H₂O: ethanol (80:20) vol percent at 50 °C for 1 h, before blending PVA: PEO (85:15) wt. percent and covalent crosslinking the polymers blend with glutaraldehyde (0.5 g, 50 wt. percent). The inorganic-organic nanocomposite (structure illustrated in Figure 1) was then made by incorporating varying concentrations of PO₄-TiO₂ nanotubes (1, 2, 3 wt. percent relative to PVA) in the polymeric mix, and they were given the names PVA/PEO, PVA/PEO/PO₄TiO₂-1, PVA/PEO/PO₄TiO₂-2 and PVA/PEO/PO₄TiO₂-3 accordingly.

![Figure 1. Probable structure of the SPVA/PEO/PO₄TiO₂ membrane.](image_url)

2.2. Characterisation

A Fourier transform infrared spectrophotometer (Shimadzu FTIR-8400 S- Japan) was used to monitor the functional groups of PO₄TiO₂ nanotubes and composite membranes, while an X-ray diffractometer was used to analyze the structures (Shimadzu7000-Japan). A thermo-gravimetric analyser (Shimadzu TGA-50, Tokyo, Japan) was used to track SPVA/PEO/PO₄TiO₂ membranes; the temperature range was 25–800 °C, with the heating rate was 10 °C/min under nitrogen environment. The membranes were also evaluated using differential scanning calorimetry (DSC) (Shimadzu DSC-60, Japan) at temperatures ranging from 25 to 300 °C. The SPVA/PEO/PO₄-TiO₂-1 membrane’s morphological structure was revealed using a scanning electron microscope (SEM). Transmission electron microscopy (TEM, JEM 2100 electron microscope) and energy-dispersive X-ray (EDX) were used to visualise the PO₄-TiO₂ nanotube (Joel Jsm 6360LA-Japan).
The hydrophilicity of membranes was determined by measuring the contact angles between membrane surfaces and water drops. A Rame-Hart Instrument Co. model 500-FI contact-angle analyser was used to analyse the measurements. To determine swelling ratio (SR) and water uptake, a certain weight of membrane with actual dimensions was soaked in deionised water for 24 h then gently dried on tissue paper to remove surface water before analysis again. Finally, the composite membranes’ SR and WU were calculated using Equations (1) and (2).

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

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

where $L_{\text{dry}}$ and $L_{\text{wet}}$ denote the length of dry and wet of tested membranes, respectively, and $W_{\text{dry}}$ and $W_{\text{wet}}$ denote the weight of dry and wet tested sample.

The nanocomposite membranes’ ion exchange capacity (IEC) was estimated by acid-base titration [32]. The weighted membranes were submerged in a 50 cm$^3$ 2M NaCl solution for two days before titrating with a 0.01 N NaOH solution. The IEC was calculated using Equation (3) below:

$$\text{IEC (meq g$^{-1}$)} = \frac{V_{\text{NaOH}} \times C_{\text{NaOH}}}{W_{\text{d}}}$$

The volume of sodium hydroxide consumed in titration, the concentration of sodium hydroxide solution, and the dry sample weight, respectively, are represented by $V_{\text{NaOH}}$, $C_{\text{NaOH}}$ and $W_{\text{d}}$.

To investigate the proton conductivity of formulated films, the electrochemical impedance spectroscopy (EIS) will be utilised using PAR 273A potentiostat (Princeton Applied Research, Inc., Oak Ridge, TN, USA) and a SI 1255 HF frequency response analyser (FRA, Schlumberger Solartron). according to the published method in the literature with modification [1]. the ionic conductivity of the membranes was estimated using Equation (4),

$$\sigma = \frac{d}{RA}$$

where $\sigma$ (S cm$^{-1}$) is the membrane’s ionic conductivity, $R$ (Ω) is its resistance, $A$ (cm$^2$) is its area and $d$ (cm) is its thickness.

To estimate the methanol permeability, The tested membrane was seated within two vessels in a glass diffusion chamber to assess its methanol permeability. The receptor vessel (B) was charged with water, while the other vessel (A) was filled with 2 M methanol [29]. the crossing of methanol through membrane as a function of time was calculated according to Equation (5),

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

where $A$ (cm$^2$) is the active membrane area, $V_B$ (cm$^3$) is the capacity of the receptor vessel, $L$ (cm) is the crosssection film thickness, $C_B$ and $C_A$ (mol L$^{-1}$) are the concentrations of methanol in vessels B and A, respectively, and the period ($t-t_0$) is the time of the methanol crossover (cm$^2$ s$^{-1}$). The selectivity of the membranes (the ratio of ionic conductivity to methanol permeability) was determined since it can provide vital information about the fuel cell’s performance.

The oxidative stability of tested membranes was measured gravimetrically as a function of membrane weight soaked in oxidative solution [Fenton’s reagent (3 wt.% H$_2$O$_2$ containing 2 ppm FeSO$_4$)] at 68 °C for 24 h [19].

The dry nano-composite membranes were put through a tensile strength test at room temperature until they broke, using Lloyd Instruments LR10k [32].
3. Results

3.1. Characterisation of PO₄-TiO₂ Nanotube and Nanocomposite Membranes

The FT-IR spectra of prepared nanoparticle TiO₂ and PO₄-TiO₂ were presented separately in Figure 2. For TiO₂ nanoparticles, Ti-O bonds are responsible for the bands at 715 cm⁻¹ and 1025 cm⁻¹. The bands at 1622 cm⁻¹ refer to the bending vibration of the Ti-OH band. The band at 3387 cm⁻¹ are assigned to O-H stretching vibration bands due to moisture adsorption on the material’s surface [20,33]. For the chart of PO₄-TiO₂ particles, the band at 690 cm⁻¹ corresponds to the stretching of the Ti-O bond. The bands at 890, 1085 and 1270 cm⁻¹ are referred to as P-O bonds vibration. The band located at 1425 cm⁻¹ is attributed to the stretching vibration band of the P=O bond. The O-H bonds from H₂O molecules adsorption are proofed by the bands at 1630 and 3117 cm⁻¹. The band located at 2374 cm⁻¹ is related to the presence of CO₂ [34,35].

![Figure 2. FTIR spectra of PO₄TiO₂ (left chart), PVA/PEO/PO₄TiO₂ membranes (right chart).](image)

For the membranes, the Figure 2 shows that the bands around 3250 cm⁻¹ refer to the characteristic stretching vibration band of hydroxyl groups on PVA and PEO. The bands at 1650 cm⁻¹ are attributed to the bending vibration O-H bonds. The band at 1112 cm⁻¹ is the characteristic band of PEO [36]. Bands at 2840 cm⁻¹ can be assigned to the vibration of methylene C-H bonds in the polymer’s structure. The characteristic peak for sulfate groups of sulfophithalic acid (SPA) was cited at 900 cm⁻¹, while the small bands at 1700 cm⁻¹ indicate C=O bonds of the sulfophithalic acid (SPA), which confirms the crosslinking process. The band at 1100 cm⁻¹ is assigned to P-O bonds of phosphate titanium oxide.

In Figure 3, show the XRD pattern of TiO₂ and PO₄TiO₂ (on the left side) and composite membranes on the right side. The constructed membranes’ amorphous shape shows good ion conduction [37], while the titanium dioxide rutile characteristic peaks intensity at two angles of 28, 36, 41 and 54 [38]. This is because the phosphate entering the titanium oxide lattice changed its original crystalline phase due to the different synthesis processes for PO₄TiO₂. Therefore, the intensity of the sharp peak of the original titanium oxide at 28° is disappeared in the diffractogram of phosphate titanium oxide. In comparison, the ridge at 54° of the TiO₂ is absent in the diffractograms of PO₄TiO₂.

Morphological analysis of membranes was studied using SEM and presented in Figure 4. Figure 4a, b demonstrates SEM images of membranes that show a smooth surface with no defects for the undoped crosslinked membrane. At the same time, particles of phosphate titanium oxide tubes appeared in the doped membrane, which was further confirmed by EDX spectra as shown in Figure 4e. However, the SEM image in Figure 4c illustrate the porous structure of the cross-sectional of the doped membrane. Consequently, these voids lead to an improvement in the ionic conductivity of the films [39]. While TEM image of phosphate titanium oxides shown in Figure 4e proofed the forming of nanotubes shape with nanoscale size as illustrated in Figure 4f.
Figure 3. XRD patterns of PO₄TiO₂ (left chart) and PVA/PEO/PO₄TiO₂ membranes (right chart).

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Figure 4. Cont.
3.2. Mechanical and Thermal Properties

The addition of TiO$_2$ or functionalisation of TiO$_2$ develops the mechanical tensile characteristics of the polymeric form significantly [19–21]. For example, as displayed in Table 1, increasing the amount of PO$_4$TiO$_2$ in the polymeric film enhanced the tensile strength of the composite films by improving their compatibility. This behaviour can be explained by improving the interaction between functional groups along two polymer backbones, such as ether linkages, hydroxyl groups and the various phosphate groups of PO$_4$TiO$_2$ nanoparticles, via ionic, covalent and hydrogen interactions interfacial adhesion, as compared to the neat membrane.

Table 1. Physicochemical parameters of the formulated composite membranes compare to Nafion 117 [1,24].

| Membrane               | Thickness (µm) | WU (%) | SR (%) | Contact Angle (°) | Tensile Strength (MPa) | Oxidative Stability (RW, %) * |
|------------------------|----------------|--------|--------|-------------------|-------------------------|-----------------------------|
| SPVA/PEO              | 130            | 95     | 90     | 65.36             | 15.5                    | 90                          |
| SPVA/PEO/PO$_4$TiO$_2$-1 | 150          | 40     | 42     | 67.23             | 24.9                    | 94                          |
| SPVA/PEO/PO$_4$TiO$_2$-2 | 175          | 22     | 13     | 70.36             | 32.5                    | 98                          |
| SPVA/PEO/PO$_4$TiO$_2$-3 | 184          | 16     | 10     | 72.30             | 40.3                    | 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.

The TGA of formulated composite films in the presence or absence of PO$_4$TiO$_2$ nanoparticles is shown in Figure 5. Moisture evaporation in all membranes can be defined as the initial weight loss of all manufactured membranes at 150 °C (10%) [40]. The following weight loss of composite membranes was demonstrated between (150–300) °C range, possibly due to the breakdown of functional groups [41,42]. Finally, from 300 to 580 °C, all samples show a significant decomposition, which could be connected to polymeric chain decomposition [43], which began at 250 °C for the undoped membrane and began at 310 °C with a lower weight % for the doped membranes, with 3 wt percent doping. According to these findings, the addition of PO$_4$TiO$_2$ to composite membranes increases their thermal stability by increasing hydrogen bonding in the composite. Furthermore, the presence of only one endothermic peak in DSC, as shown in Figure 5, demonstrates flawless membrane miscibility, and the removal of this peak at PO$_4$TiO$_2$ (3 wt.%) may be
attributed to constructing new physical bonds (i.e., hydrogen bonds) between the nanoparticles and the polymeric matrix [29]. When a result, as the concentration of the doping agent increased, the melting temperature of the membranes fell. This behaviour may be described by hydrogen bond interactions that partially degrade membrane crystallinity, lowering the melting point and increasing ionic conductivity [29].

![TGA of PVA/PEO/PO4TiO2 membranes (left chart) and DSC of PVA/PEO/PO4TiO2 membranes (right chart)](image)

Figure 5. TGA of PVA/PEO/PO4TiO2 membranes (left chart) and DSC of PVA/PEO/PO4TiO2 membranes (right chart) curves of nanocomposite membranes.

Table 1 depicts the behaviour of nanocomposite membranes in contact with deionised water. When contact angles are less than 90 degrees, membrane surfaces are deemed hydrophobic, and when they are greater than 90 degrees, they are considered hydrophilic. However, as the doping agent content increases, the composite membranes become less hydrophilic and have a lower hydrophilic quality [26,44]. When the amount of PO4TiO2 in the polymeric blend was increased from 1% to 3%, the swelling ratio and water sorption of the composite membranes were lowered, which is vital because water overload may be avoided [45]. To put it another way, increasing the doping agent in the membrane matrix makes the structure more compact, reducing water overload in the polymeric matrix channels [46,47].

3.3. Oxidative Stability

The chemical stability parameters of the formulated nanocomposite membranes were described in Table 1. The SPVA/PEO membrane has the lowest stability against the oxidation condition; however, adding PO4TiO2 as a dopant improves polymeric composite protection against OOH and OH radical. The PVA/PEO/PO4TiO2-3 membrane was the most chemically stable, with weight retention of nearly 100%, suggesting that adding a doping agent such as TiO2 or functionalising TiO2 improves the oxidation chemical stability of formulated membranes [20,48].

3.4. Ionic Conductivity, IEC and Methanol Crossover

As the composite membrane contains further acidic exchangeable groups from PO4TiO2, the IEC values increase as PO4TiO2 in the composite membranes increases. This is due to the acidic (phosphate) sites of PO4TiO2 increasing the charges in the membranes, which promotes ionic conduction [19,20]. This is due to the SPVA/PEO/PO4TiO2-3 membrane’s superior ionic conductivity (28 mS cm⁻¹) when compared to an undoped membrane (12 mS cm⁻¹). Adding PO4TiO2 to the polymeric matrix avoids methanol crossing when it comes to the fuel permeability of composite membranes. The undoped polymeric membrane exhibited a methanol permeability of 4.5 × 10⁻⁷ cm² s⁻¹, but the SPVA/PEO/PO4TiO2-3 membrane permeability of 0.42 × 10⁻⁷ cm² s⁻¹ when PO4TiO2 was added to the membrane matrix, as indicated in Table 2. The capacity of the doping
agent to restrict the polymeric matrix channels, reducing water uptake and hence fuel
permeability, may be the cause of the membrane containing the doping agent’s decreased
methanol permeability [19,20,49,50]. When compared to undoped SPVA/PEO membrane
(0.26 × 10^5 S cm^{-3} s) and Nafion 117 (0.24 × 10^5 S cm^{-3} s), SPVA/PEO/ PO_4 TiO_2-3
(6.66 × 10^5 S cm^{-3} s) showed higher selectivity, indicating that the nanocomposite mem-
branes produced are suitable for use in DMFCs [49].

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/PEO          | 0.20             | 12                            | 4.5                                         | 0.26                           |
| SPVA/PEO/PO_4 TiO_2-1 | 0.35             | 17.7                          | 2.10                                        | 0.84                           |
| SPVA/PEO/PO_4 TiO_2-2 | 0.45             | 20.5                          | 1.51                                        | 1.35                           |
| SPVA/PEO/PO_4 TiO_2-3 | 0.60             | 28                            | 0.42                                        | 6.66                           |
| Nafion 117        | 0.89             | 34.0                          | 14.1                                        | 0.24                           |

4. Conclusions

Using eco-friendly and readily available polymers, a simple blending and solution
casting approach created a more economical nanocomposite membrane. Furthermore,
incorporating PO_4 TiO_2 nanotubes into the polymeric blend improves the membrane’s
physicochemical parameters, such as ionic conductivity, mechanical properties, oxidative
stability, reducing water sorption and limiting methanol permeability, especially in the
composite membrane with 3 percent PO_4 TiO_2, that also demonstrate the most suitable
oxidative chemical stability and methanol crossover limiting. Finally, the manufactured
membrane with the best characteristics (PVA/PEO/PO_4 TiO_2-3) could be used as a cation
exchange composite membrane to construct environmentally friendly and low-cost DMFCs.

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