



Article 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 (PO_4TiO_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 PO_4TiO_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 PO_4TiO_2 increased. In addition, the ionic conductivity of the membrane with 3 wt.% PO_4 -TiO₂ is raised to (28 mS cm⁻¹). The optimised membrane ($PVA/PEO/PO_4TiO_2$ -3) had a higher selectivity (6.66 × 10⁵ S cm⁻³ s) than Nafion117 (0.24 × 10⁵ 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



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Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). 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 filmforming 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 practise 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-sulfophithalic 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 cross-linkers, respectively [30]. Titanium (IV) oxide rutile (TiO₂, <5 μ m, ≥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)

 TiO_2 nanotubes were synthesised as mentioned in the previous work [19]. TiO_2 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 H_2O 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 deionizedH₂O: 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/ PO₄TiO₂membrane.

2.2. Characterisation

A Fourier transform infrared spectrophotometer (Shimadzu FTIR-8400 S- Japan) was used to monitor the functional groups of PO_4TiO_2 nanotubes and composite membranes, while an X-ray diffractometer was used to analyze the structures (Schi-madzu7000-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).

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

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

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

The nanocomposite membranes' ion exchange capacity (IEC) was estimated by acidbase titration [32]. The weighted membranes were submerged in a 50 cm³ 2M NaCl solution for two days before titrating with a 0.01 N NaOH solution. The IEC was calculated using Equation (3) below:

$$IEC\left(\frac{meq}{g}\right) = \frac{V_{NaOH} \times C_{NaOH}}{W_d}$$
(3)

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

$$\sigma = \frac{d}{RA} \tag{4}$$

where σ (S cm⁻¹) is the membrane's ionic conductivity, R (Ω) is its resistance, A (cm²) 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),

$$C_{B}(t) = \frac{A}{V_{B}} \frac{P}{L} C_{A}(t - t_{0})$$
(5)

where A (cm²) is the active membrane area, VB (cm³) is the capacity of the receptor vessel, L (cm) is the crosssection film thickness, CB and CA (mol L⁻¹) are the concentrations of methanol in vessels B and A, respectively, and the period (t–t₀) is the time of the methanol crossover (cm² 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_2O_2 containing 2 ppm FeSO₄)] 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 TiO_2 and PO_4 - TiO_2 were presented separately in Figure 2. For TiO_2 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 bonds due to moisture adsorption on the material's surface [20,33]. For the chart of PO₄- TiO_2 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).

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).



10kV X5,000 54m











(b)



Figure 4. SEM images for (a) undoped membrane, (b,c) doped membrane ($PVA/PEO/PO_4TiO_2-1$) surface and crosssection (d) EDX analysis for PO_4TiO_2 , (e) TEM image for PO_4TiO_2 nanotubes and (f) the frequency distribution plot of PO_4TiO_2 nanotubes size from TEM image.

3.2. Mechanical and Thermal Properties

The addition of TiO₂ or functionalisation of TiO₂ develops the mechanical tensile characteristics of the polymeric form significantly [19–21]. For example, as displayed in Table 1, increasing the amount of PO_4TiO_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_4TiO_2 nanoparticles, via ionic, covalent and hydrogen interactions interfacial adhesion, as compared to the neat membrane.

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/PO4TiO2-1	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

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

* 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_4TiO_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_4TiO_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_4TiO_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].



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 PO_4TiO_2 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 PO_4TiO_2 as a dopant improves polymeric composite protection against OOH and OH radical. The PVA/PEO/PO_4TiO_2-3 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/ PO₄TiO₂-3 (6.66×10^5 S cm⁻³ s) showed higher selectivity, indicating that the nanocomposite membranes 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)	Methaanol 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/PO4TiO2-2	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_4TiO_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_4TiO_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_4TiO_2-3) could be used as a cation exchange composite membrane to construct environmentally friendly and low-cost DMFCs.

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References

- 1. Yuan, C.; Wang, Y. Synthesis and characterization of a crosslinked membrane based on sulfonated poly(aryl ether sulfone) and sulfonated polyvinyl alcohol applied in direct methanol fuel cells. *J. Polym. Res.* **2020**, *27*, 329. [CrossRef]
- Beydaghi, H.; Javanbakht, M.; Salarizadeh, P.; Bagheri, A.; Amoozadeh, A. Novel proton exchange membrane nanocompo-sites based on sulfonated tungsten trioxide for application in direct methanol fuel cells. *Polymers* 2017, 119, 253–262. [CrossRef]
- Zhiwei, W.; Hao, Z.; Qiang, C.; Sumei, Z.; Feng, Y.; Jian, K.; Jinyao, C.; Ya, C.; Ming, X. Preparation and characterization of PVA proton exchange membranes containing phosphonic acid groups for direct methanol fuel cell applications. *J. Polym. Res.* 2019, 26, 200. [CrossRef]
- 4. Pandey, R.P.; Shukla, G.; Manohar, M.; Shahi, V.K. Graphene oxide based nanohybrid proton exchange membranes for fuel cell applications: An overview. *Adv. Colloid Interface Sci.* 2017, 240, 15–30. [CrossRef] [PubMed]
- 5. Ye, Y.-S.; Rick, J.; Hwang, B.-J. Water Soluble Polymers as Proton Exchange Membranes for Fuel Cells. *Polymers* **2012**, *4*, 913–963. [CrossRef]
- Ma, J.; Choudhury, N.A.; Sahai, Y. A comprehensive review of direct borohydride fuel cells. *Renew. Sustain. Energy Rev.* 2010, 14, 183–199. [CrossRef]

- Merino-Jiménez, I.; León, C.P.; Shah, A.A.; Walsh, F.C. Developments in direct borohydride fuel cells and remaining chal-lenges. J. Power Sources 2012, 219, 339–357. [CrossRef]
- Gouda, M.H.; Elnouby, M.; Aziz, A.N.; Youssef, M.E.; Santos, D.M.F.; Elessawy, N.A. Green and Low-Cost Membrane Electrode Assembly for Proton Exchange Membrane Fuel Cells: Effect of Double-Layer Electrodes and Gas Diffusion Layer. *Front. Mater.* 2020, *6*, 337. [CrossRef]
- Mohy Eldin, M.S.; Hashem, A.E.; Tamer, T.M.; Omer, A.M.; Yossuf, M.E.; Sabet, M.M. Development of cross-linked chitosan/alginate polyelectrolyte proton exchanger membranes for fuel cell applications. *Int. J. Electrochem. Sci.* 2017, 12, 53840–53858.
- 10. Tamer, T.M.; Omer, A.M.; Sabet, M.M.; Youssef, M.E.; Hashem, A.I.; Mohy Eldin, M.S. Development of polyelectrolyte sulfonated chitosan-alginate as an alternative methanol fuel cell membrane. *Desalin. Water Treat.* **2021**, 227, 132–148. [CrossRef]
- 11. Pourzare, K.; Mansourpanah, Y.; Farhadi, S. Advanced nanocomposite membranes for fuel cell applications: A comprehen-sive review. *Biofuel Res. J.* 2016, 12, 496–513. [CrossRef]
- 12. Mohy Eldin, M.S.; Abd Elmageed, M.H.; Omer, A.M.; Tamer, T.M.; Yossuf, M.E.; Khalifa, R.E. Novel proton exchange mem-branes based on sulfonated cellulose acetate for fuel cell applications: Preparation and characterization. *Int. J. Electrochem. Sci.* **2016**, *11*, 10150–10171. [CrossRef]
- Mohy Eldin, M.S.; Omer, A.M.; Tamer, T.M.; Abd Elmageed, M.H.; Youssef, M.E.; Khalifa, R.E. Novel aminated cellulose acetate membranes for direct methanol fuel cells (DMFCs). *Int. J. Electrochem. Sci.* 2017, 12, 4301–4318. [CrossRef]
- 14. Mohy Eldin, M.S.; Abd Elmageed, M.H.; Omer, A.M.; Tamer, T.M.; Yossuf, M.E.; Khalifa, R.E. Development of novel phosphorylated cellulose acetate polyelectrolyte membranes for direct methanol fuel cell application. *Int. J. Electrochem. Sci.* **2016**, *11*, 3467–3491. [CrossRef]
- 15. Bakangura, E.; Wu, L.; Ge, L.; Yang, Z.; Xu, T. Mixed matrix proton exchange membranes for fuel cells: State of the art and perspectives. *Prog. Polym. Sci.* 2016, *57*, 103–152. [CrossRef]
- 16. Wei, Q.; Zhang, Y.; Wang, Y.; Chai, W.; Yang, M. Measurement and modeling of the effect of composition ratios on the properties of poly(vinyl alcohol)/poly(vinyl pyrrolidone) membranes. *Mater. Des.* **2016**, *103*, 249–258. [CrossRef]
- Maarouf, S.; Tazi, B.; Guenoun, F. Preparation and characterization of new composite membranes containing polyvinylpyrrolidone, polyvinyl alcohol, sulfosuccinic acid, silicotungstic acid and silica for direct methanol fuel cell applications. *J. Mater. Environ. Sci.* 2017, *8*, 2870–2876.
- Pintauro, P. Perspectives on Membranes and Separators for Electrochemical Energy Conversion and Storage Devices. *Polym. Rev.* 2015, 55, 201–217. [CrossRef]
- Gouda, M.H.; Elessawy, N.A.; Santos, D.M.F. Synthesis and Characterization of Novel Green Hybrid Nanocomposites for Application as Proton Exchange Membranes in Direct Borohydride Fuel Cells. *Energies* 2020, 13, 1180. [CrossRef]
- Gouda, M.H.; Gouveia, W.; El Essawy, N.A.; Šljukić, B.; Nassr, A.A.; Santos, D.M.F. Simple design of PVA-based blend doped with SO₄(PO₄)-functionalised TiO₂ as an effective membrane for direct borohydride fuel cells. *Int. J. Hydrog. Energy* 2020, 45, 15226–15238. [CrossRef]
- Gouda, M.H.; Gouveia, W.; Afonso, M.L.; Šljukić, B.; Elessawy, N.A.; Santos, D.M.F. Novel ternary polymer blend membranes doped with SO4/PO4-TiO2 for low temperature fuel cells; Paper No. ICCPE 106. In Proceedings of the 5th World Congress on Mechanical, Chemical, and Material Engineering (MCM'19), Lisbon, Portugal, 15–17 August 2019. [CrossRef]
- 22. Abu-Saied, M.A.; Soliman, E.A.; Abualnaj, K.M.; El Desouky, E. Highly Conductive Polyelectrolyte Membranes Polyvinyl Alcohol)/Poly (2-Acrylamido-2-Methyl Propane Sulfonic Acid) (PVA/PAMPS) for Fuel Cell Application. *Polymers* **2021**, *13*, 2638. [CrossRef]
- 23. Eldin, M.S.M.; Abu-Saied, M.A.; Elzatahry, A.A.; El-Khatib, K.M.; Hassan, E.A.; El-Sabbah, M.M. Novel acid-base poly vinyl chloride-doped ortho-phosphoric acid membranes for fuel cell applications. *Int. J. Electrochem. Sci.* 2011, *6*, 5417–5429.
- 24. Eldin, M.S.M.; Elzatahry, A.A.; El-Khatib, K.M.; Hassan, E.A.; El-Sabbah, M.M.; Abu-Saied, M.A. Novel grafted nafion membranes for proton-exchange membrane fuel cell applications. *J. Appl. Polym. Sci.* **2011**, *119*, 120–133. [CrossRef]
- Rochliadi, A.; Bundjali, B.; Arcana, I.M. Polymer electrolyte membranes prepared by blending of poly(vinyl alcohol)-poly(ethylene oxide) for lithium battery application. In Proceedings of the Joint International Conference on Electric Vehicular Technology and Industrial, Mechanical, Electrical and Chemical Engineering (ICEVT & IMECE), Surakarta, Indonesia, 4–5 November 2015; pp. 370–373.
- Gouda, M.H.; Gouveia, W.; Afonso, M.L.; Šljukić, B.; El Essawy, N.A.; Nassr, A.A.; Santos, D.M.F. Poly(vinyl alcohol)-based crosslinked ternary polymer blend doped with sulfonated graphene oxide as a sustainable composite membrane for direct borohydride fuel cells. J. Power Sources 2019, 432, 92–101. [CrossRef]
- Khalifa, R.E.; Omer, A.M.; Abd Elmageed, M.H.; Mohy Eldin, M.S. Titanium Dioxide/Phosphorous-Functionalized Cellulose Acetate Nanocomposite Membranes for DMFC Applications: Enhancing Properties and Performance. ACS Omega 2021, 6, 17194–17202. [CrossRef] [PubMed]
- Abu-Saied, M.A.; Elzatahry, A.A.; El-Khatib, K.M.; Hassan, E.A.; El-Sabbah, M.M.; Drioli, E.; Mohy Eldin, M.S. Preparation and characterization of novel grafted cellophane-phosphoric acid-doped membranes for proton exchange membrane fuel-cell applications. J. Appl. Polym. Sci. 2012, 123, 3710–3724. [CrossRef]

- 29. Gouda, M.H.; Konsowa, A.H.; Farag, H.A.; Elessawy, N.A.; Tamer, T.M.; Mohy Eldin, M.S. Novel nanocomposite membranes based on cross-linked eco-friendly polymers doped with sulfated titania nanotubes for direct methanol fuel cell application. *Nanomater. Nanotechnol.* **2020**, *10*, 1847980420964368. [CrossRef]
- Sedesheva, Y.S.; Ivanov, V.S.; Wozniak, A.I.; Yegorov, A.S. Proton-exchange membranes based on sulfonated polymers. *Orient. J. Chem.* 2016, *32*, 2283–2296. [CrossRef]
- Awang, N.; Ismail, A.F.; Jaafar, J.; Matsuura, T.; Junoh, H.; Othman, M.H.D.; Rahman, M.A. Functionalization of polymeric materials as a high-performance membrane for direct methanol fuel cell: A review. *React. Funct. Polym.* 2015, *86*, 248–258. [CrossRef]
- 32. Mohy Eldin, M.S.; Farag, H.A.; Tamer, T.M.; Konsowa, A.H.; Gouda, M.H. Development of novel iota carrageenan-g-polyvinyl alcohol polyelectrolyte membranes for direct methanol fuel cell application. *Polym. Bull.* **2020**, *779*, 4895–4916. [CrossRef]
- Benito, H.E.; Sánchez, T.; Alamilla, R.G.; Enríquez, J.M.; Robles, G.S.; Delgado, F.P. Synthesis and physicochemical characterization of titanium oxide and sulfated titanium oxide obtained by thermal hydrolysis of titanium tetrachloride. *Braz. J. Chem. Eng.* 2014, 31, 737–745. [CrossRef]
- Lu, M.; Wang, F.; Liao, Q.; Chen, K.; Qin, J.; Pan, S. FTIR spectra and thermal properties of TiO₂-doped iron phosphate glasses. J. Mol. Struct. 2015, 1081, 187–192. [CrossRef]
- 35. Goswami, P.; Ganguli, J. Synthesis characterization and photocatalytic reactions of phosphate mesoporous titania. *Bull. Mater. Sci.* **2012**, *35*, 889–896. [CrossRef]
- 36. Pucic, I.; Jurkin, T. FTIR assessment of poly(ethylene oxide) irradiated in solid state, melt and aqeuous solution. *Radiat. Phys. Chem.* **2012**, *81*, 1426–1429. [CrossRef]
- 37. Yu, X.; Qiang, L. Preparation for graphite materials and study on electrochemical degradation of phenol by graphite cathodes. *Adv. Mater. Phys. Chem.* **2012**, *2*, 63–68. [CrossRef]
- Venkatesan, P.; Dharmalingam, S. Effect of cation transport of SPEEK-Rutile TiO₂ electrolyte on microbial fuel cell performance. J. Membr. Sci. 2015, 492, 518–527. [CrossRef]
- Ngai, K.S.; Ramesh, S.; Ramesh, K.; Juan, J.C. A review of polymer electrolytes: Fundamental, approaches and applications. *Ionics* 2016, 22, 1259–1279. [CrossRef]
- 40. Kowsari, E.; Zare, A.; Ansari, V. Phosphoric acid-doped ionic liquid-functionalized graphene oxide/sulfonated polyimide composites as proton exchange membrane. *Int. J. Hydrog. Energy* **2015**, *40*, 13964–13978. [CrossRef]
- 41. Bayer, T.; Cunning, B.V.; Selyanchyn, R.; Daio, T.; Nishihara, M.; Fujikawa, S.; Sasaki, K.; Lyth, S.M. Alkaline anion exchange membranes based on KOH-treated multilayer graphene oxide. *J. Membr. Sci.* 2016, *508*, 51–61. [CrossRef]
- 42. Pandey, R.; Shahi, V. Sulphonated imidized graphene oxide (SIGO) based polymer electrolyte membrane for improved water retention, stability and proton conductivity. *J. Power Sources* **2015**, *299*, 104–113. [CrossRef]
- 43. Deshmukh, K.; Ahamed, M.B.; Sadasivuni, K.K.; Ponnamma, D.; Deshmukh, R.R.; Pasha, S.K.K.; AlMaadeed, M.A.; Chidambaram, K. Graphene oxide reinforced polyvinyl alcohol/polyethylene glycol blend composites as high-performance dielectric material. *J. Polym. Res.* **2016**, *23*, 159. [CrossRef]
- 44. Shirdast, A.; Sharif, A.; Abdollahi, M. Effect of the incorporation of sulfonated chitosan/sulfonated graphene oxide on the proton conductivity of chitosan membranes. *J. Power Sources* **2016**, *306*, 541–551. [CrossRef]
- 45. Beydaghi, H.; Javanbakht, M.; Kowsari, E. Synthesis and Characterization of Poly(vinyl alcohol)/Sulfonated Graphene Oxide Nanocomposite Membranes for Use in Proton Exchange Membrane Fuel Cells (PEMFCs). *Ind. Eng. Chem. Res.* **2014**, *53*, 16621–16632. [CrossRef]
- 46. Cheng, T.; Feng, M.; Huang, Y.; Liu, X. SGO/SPEN-based highly selective polymer electrolyte membranes for direct methanol fuel cells. *Ionics* **2017**, *23*, 2143–2152. [CrossRef]
- Luo, T.; Xu, H.; Li, Z.; Gao, S.; Fang, Z.; Zhang, Z.; Wang, F.; Ma, B.; Zhu, C. Novel proton conducting membranes based on copolymers containing hydroxylated poly(ether ether ketone) and sulfonated polystyrenes. J. Appl. Polym. Sci. 2017, 134, 45205. [CrossRef]
- Yuan, C.; Wang, Y. The preparation of novel sulfonated poly(aryl ether ketone sulfone)/TiO₂ composite membranes with low methanol permeability for direct methanol fuel cells. *High Perform. Polym.* 2021, 33, 326–337. [CrossRef]
- 49. Yang, C.C.; Chien, W.C.; Li, Y.J. Direct methanol fuel cell based on poly(vinyl alcohol)/titanium oxide nanotubes/poly(styrene sulfonic acid) (PVA/nt-TiO₂/PSSA) composite polymer membrane. *J. Power Sources* **2010**, *195*, 3407–3415. [CrossRef]
- 50. Ahmad, H.; Kamarudin, S.K.; Hasran, U.A.; Daud, W.R.W. A novel hybrid Nafion-PBI-ZP membrane for direct methanol fuel cells. *Int. J. Hydrog. Energy* **2011**, *36*, 14668–14677. [CrossRef]