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Synthesis and Characterization of Novel Green Hybrid Nanocomposites for Application as Proton Exchange Membranes in Direct Borohydride Fuel Cells

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Abstract: Organic-inorganic nanocomposite membranes for potential application in direct borohydride fuel cells (DBFCs) are formulated from sulfonated poly(vinyl alcohol) (SPVA) with the incorporation of (PO₄-TiO₂) and (SO₄-TiO₂) nanotubes as doping agents. The functionalization of PVA to SPVA was done by using a 4-sulfophthalic acid as an ionic crosslinker and sulfonating agent. Morphological and structural characterization by transmission electron microscopy (TEM), scanning electron microscopy (SEM), Fourier-transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), energy-dispersive X-ray spectroscopy (EDX) and X-ray diffraction (XRD) confirmed the successful synthesis of the doping agents and their incorporation into the polymer. The influence of PO_4 -Ti O_2 and SO_4 -Ti O_2 doping and their content on the physicochemical properties of the nanocomposite membranes was evaluated. Swelling degree and water uptake gradually reduced to 7% and 13%, respectively, with increasing doping agent concentration. Ion exchange capacity and ionic conductivity of the membrane with 3 wt.% doping agents were raised 5 and 7 times, respectively, compared to the undoped one. The thermal and oxidative stability and tensile strength also increased with the doping content. Furthermore, lower borohydride permeability $(0.32 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1})$ was measured for the membranes with higher amount of inorganic doping agents when compared to the undoped membrane $(0.71 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1})$ and Nafion[®]117 $(0.40 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1})$. These results pave the way for a green, simple and low-cost approach for the development of composite membranes for practical DBFCs.

Keywords: poly (vinyl alcohol); sulfated titanium oxide nanotubes; phosphated titanium oxide; polymer electrolyte membrane; direct borohydride fuel cell

1. Introduction

Fuel cells are technologies for energy conversion aiming at the elimination of conventional pollution derived from fossil fuels [1]. A fuel cell provides electricity with an efficiency above 50% and can give high power density for a long time at low operating temperatures [2]. Direct borohydride fuel cells (DBFCs) are polymer electrolyte fuel cells having some advantageous features, such as low operating temperatures and higher cell voltage when compared to hydrogen or alcohol fuel cells. The use of these reactants in a liquid, at ambient pressure and temperature, simplifies the internal processing of the fuel cell system and their applications [3,4]. It is a green approach to use hydrogen peroxide or oxygen (oxidants) and sodium borohydride (fuel) as they are carbon-free



reactants. DBFCs can theoretically produce eight electrons from direct oxidation of borohydride anion (BH_4^-) , with sodium (Na^+) cations crossing via a membrane [5]. Besides the membrane role as a separator between the cathodic and the anodic compartments, the membrane must have the ability to transfer the sodium ions (Na^+) effectively while hindering the BH_4^- (fuel) crossover [2,6]. Two basic types of membranes are assigned according to the charge of the transported ions, as anion exchange membranes (AEM) for anion transport and cation exchange membranes (CEM) for cation transport [2,7]. Nafion membranes are well-known CEM that have been always employed in several low-temperature fuel cells. However, these membranes have disadvantages, such as complex processing and high cost, which demands further research for the development of green and cost-effective membranes [8].

In this regard, the current trend of novel polymeric membranes for fuel cells goes in the direction of polymer functionalization generally with the incorporation of doping agents in the polymer matrix [8,9]. Indeed, metal oxides such as ZrO_2 , SiO_2 and TiO_2 , due to their versatility to tailoring and easy accessibility, have been widely used as doping agents to design nanocomposite membranes with enhanced properties, such as good chemical and mechanical stability, lower fuel permeability and high ionic conductivity, resulting in a better fuel cell performance [10]. TiO₂ is an inorganic substance with versatile features, as it generally induces in the polymeric composites higher mechanical strength, thermal stability, non-flammability and corrosion resistance [11]. Besides, it is an economical material. In the energy field, fuel cell and battery performance have been improved due to the high surface of modified TiO₂ nanoparticles used either as a doping agent in polymer electrolytes or as an electrocatalyst support or co-catalysts [11,12]. With regard to the polymer electrolytes for fuel cells, TiO₂ functionalization has become a more common approach and has the aim of adding more charge groups into the membrane in order to increase the compatibility between the polymer matrix and TiO_2 particles in addition to providing interconnecting ionic channels for ions transfer [10]. The use of proton-conducting fillers, such as titania nanotubes, can improve the mechanical stability and lower the fuel permeability without drastically reducing the conductivity of the composite. Developed titania nanotubes have high hydrophilicity, high specific surface area, and good proton conductivity $(\sim 10^2 - 10^3 \text{ mS cm}^{-1})$ at high relative humidity, making them good candidates to be used as fillers in polymer electrolyte membranes [13]. Modification of TiO_2 with phosphate and sulfate anions by acid treatments allows the introduction of acidic groups into TiO_2 , which is expected to enhance the ionic conductivity, the water adsorption, and the ion exchange capacity while reducing the fuel permeation of the membranes [14,15]. Incorporation of nanosized TiO₂ powders into different polymer matrices has been the subject of many studies. A composite membrane of polybenzimidazole with dispersed TiO₂ exhibited superior ionic conductivity as well as hydrophilicity when compared to the undoped polybenzimidazole [10]. A polyether-based polymer doped with TiO₂ particles revealed a higher proton conductivity than one doped with Al_2O_3 or SiO_2 [16]. Particles of TiO_2 added into a sulfonated polysulfone membrane had a positive impact on the fuel cell performance [17]. Fuel crossover resistance and ion conduction were increased in a composite membrane containing amino-acid-functionalized TiO_2 and sulfonated poly(ether ether ketone) polymer [18]. TiO_2 nanotubes added in a polymer mixture of poly(styrene sulfonic acid) and poly(vinyl alcohol) (PVA) resulted in an electrochemical performance better than Nafion[®]117 and a lower fuel permeability [19]. The importance of using available, simple and environmentally friendly basic polymers, such as PVA, in membrane preparation must be considered, taking into account the advantages of their widespread commercialization and easy industrial processing, rather than designing new complex polymers that imply further industrial efforts [20]. Moreover, the acid–base composite method, using a basic polymer and acidic inorganic particles, is a simple approach providing flexible design, synergetic effect, cost reduction, and easy processing of novel composite membranes [21]. However, as far as we know there is nearly no information in the literature regarding sulfonated PVA polymer doped with binary functionalized TiO₂ particles as an alternative polymer electrolyte for fuel cell application. PVA is a cheap widespread basic polymer with good chemical stability and hydrophilicity that allows easy film formation but has a lower ionic conductivity [8]. To overcome this drawback, one approach is to functionalize PVA to

sulfonated poly (vinyl alcohol) (SPVA) by using a 4-sulfophthalic acid as a sulfonating agent and ionic crosslinker simultaneously. Moreover, adding doping agents is necessary to form a miscible blend as a result of hydrogen bonds existing between (–OH) side groups of PVA and acid groups of inorganic doping agents.

Therefore, the polymer composite blending creates a hydrogen bond network that facilitates ion transport via the membrane. TiO_2 nanoparticles, either functionalized or not, have been added into the functionalized polymer to improve the physicochemical properties of the membranes.

Herein, a low-cost polymer blend made of PVA and a functionalized TiO₂ doping agent consisted of acid treatment of TiO₂ to add phosphate or sulfate groups to TiO₂ through an impregnation-calcination method. Then, phosphated-TiO₂ and sulfated-TiO₂ were mixed together to form a doping agent (sulfated and phosphated titanium dioxide, SPTiO) that was incorporated equally in different concentrations into the polymer in order to formulate novel nanocomposite membranes, which are assigned as SPVA-SPTiO. Considering the compatible interaction between the inorganic-polymer blend through hydrogen bonds, and/or the acid–base interaction between the basic polymer with the acidic groups in the SPTiO doping agents, the concentration of doping agents is expected to affect the physicochemical properties of the developed membranes. This should provide the membrane with higher ion exchange capacity, higher ionic conductivity, higher oxidative stability, higher mechanical resistance and lower BH_4^- crossover, introducing this nanocomposite membrane as a competitor to Nafion for application in direct borohydride fuel cells.

2. Experimental

2.1. Materials

PVA (MW 77,000 g mol⁻¹, Sigma Aldrich, 99% of hydrolysis) was used as the base polymer. Glutaraldehyde (GA, Alfa Aesar, 50 wt.% in water) and 4-sulfophthalic acid (SPA, Sigma-Aldrich, 50 wt.% in water) were used as cross-linkers. Titanium (IV) oxide rutile powder (TiO₂, <5 μm, ≥99.9 wt.%, Sigma-Aldrich), H₃PO₄ (85 wt.%, Fisher Chemical) and H₂SO₄ (98 wt.%, Spectrum Chemical MFG Corp) were used to prepare phosphated titanium dioxide (PO₄-TiO₂) and sulfated titanium dioxide (SO₄-TiO₂), respectively.

2.2. Synthesis of PO₄-TiO₂ and SO₄-TiO₂ Nanotubes Doping Agents

The functionalization of TiO₂ either with the PO_4^{3-} anion or SO_4^{2-} anion was done by an impregnation-calcination method according to the literature [22–24] and is explained briefly herein. The PO₄-TiO₂ powder was obtained as follows: TiO₂ powder was mixed with 0.1 M H₃PO₄ in a 1:1 molar ratio and the solution was shaken in a water bath (80 °C). The suspension was filtered and dried in an air oven at 110 °C for a day. Then, calcination was performed at 450 °C in a muffle furnace. SO_4 -TiO₂ nanotube and TiO₂ powder was mixed with 200 mL of 10 M NaOH in a closed container and stirred at 110 °C for a day. The paste was filtered, neutralized with 0.1 M HCl and then washed with deionized water several times. The TiO₂ nanotubes (1.0 g) were mixed with H₂SO₄ (5 mL) and the solution was kept at 110 °C for 24 h for the evaporation of the liquid. Subsequently, the obtained SO₄-TiO₂ NTs were calcinated at 450 °C in a muffle furnace.

2.3. Preparation of SPVA-SPTiO Blend Membranes

First, PVA (10 g) was dissolved in 100 mL deionized water at 90 °C under brisk stirring. The polymer blend was divided into four portions. Aqueous suspensions of an equal amount of SO_4 -TiO₂ and PO_4 -TiO₂ doping agents were added to three of them in amounts of 1, 2 and 3 wt.% with respect to PVA. The mixtures were stirred for one hour to achieve uniform dispersion of the coupled doping agents. Crosslinking agents, GA (4 g) and SPA (4 g) were added to the mixtures and stirring was kept at room temperature for an additional 30 min. Finally, the mixtures were poured into clean Petri dishes and left to dry at room temperature for 2 days to allow for solvent evaporation (casting method).

Depending on the doping agent wt.%, the prepared membranes are ascribed as SPVA-SPTiO-1 (1 wt.%), SPVA-SPTiO-2 (2 wt.%) and SPVA-SPTiO-3 (3 wt.%); the undoped membrane is referred to as SPVA.

A possible structure of the PVA membrane crosslinked with GA and SPA is shown in Figure 1. The membrane is composed of the PVA (–OH) groups crosslinked with functional groups of doping agents via hydrogen bonds. PVA was covalently crosslinked by GA, with acetal and hemiacetal reactions occurring between –CHO and –OH groups, and was ionically crosslinked by SPA via esterification reactions between the –COOH and –OH groups. SPA was used also as a sulfonating agent for PVA to convert to SPVA and so the obtained membrane is considered a proton exchange membrane [25,26]. The two crosslinkers were used to simultaneously enhance the membrane mechanical stability (by using GA) and improve the ionic conductivity (by using SPA).



Figure 1. Possible interaction structure of the SPVA-SPTiO membrane cross-linked with SPA and GA.

2.4. Characterization of Doping Agents and SPTiO-Polymer Composite Membranes

2.4.1. Structural Analysis and Morphology

Fourier-transform infrared spectroscopy (FTIR, Shimadzu FTIR-8400 S) was used to characterize the prepared PO₄-TiO₂ and SO₄-TiO₂ powders, as well as the polymer membranes without and with SPTiO doping agent. X-ray diffraction (XRD, Shimadzu-7000, using CuK α radiation operating at 30 kV and 30 mA and scanning rate of 2° min⁻¹) was used to compare titanium dioxide crystallinity before and after acid treatments, and the impact of inorganic doping agents on the membrane's structure. The doping agent morphology and particle size were examined by a transmission electron microscope (TEM, JEM-2100 plus). The morphology of nanocomposite membranes was revealed by scanning electron microscopy (SEM, JEOL SM 6360 LA). An inductively coupled plasma-atomic emission spectrophotometer (ICP-AES, Prodigy, Teledyne Leeman Labs) was used to measure the concentration of S and P elements in the doping agents.

2.4.2. Thermal and Mechanical Analysis

Thermogravimetric analysis (TGA) of the nanocomposite membranes was done using a thermogravimetric analyzer (Shimadzu TGA-50). The temperature range was set at 25–800 °C and the heating rate at 20 °C min⁻¹, under nitrogen atmosphere. A tensile strength test, i.e., the mechanical stress until membrane breaking, was evaluated in the dry state at room temperature using Lloyd Instruments LR10k. An average value was determined after three measurements of each membrane.

2.4.3. Swelling Ratio, Water Uptake and Contact Angle

Determination of swelling ratio (SR) and water uptake (WU) of the nanocomposite membrane was conducted as follows: Dry membranes were cut, weighed and their dimensions were measured. Then, the membranes were put in deionized water for one day, softly dried and their length and weight measured again. The calculations of SR and WU were made using Equations (1) and (2), respectively,

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

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

where L_{dry} and L_{wet} are the length of dry and wet membranes, respectively, and W_{dry} and W_{wet} are the weight of dry and wet membranes, respectively. The hydrophilicity of the surface of the membrane was evaluated through the contact angle measurement between the membrane surface and a water drop, using a contact-angle analyzer (Rame-Hart Instrument Co. model 500-FI).

2.4.4. Oxidative Stability

Fenton's reagent, a solution of 3 wt.% H_2O_2 containing 2 ppm FeSO₄, was used to test the oxidative stability of the prepared membranes. The membranes were weighed to evaluate the mass loss after immersion in the Fenton's reagent at 68 °C for 24 h [9]. The chemical stability of the prepared membranes was also evaluated in simulating solutions of a DBFC for 48 h. The catholyte consisted of 5 M H_2O_2 in 1.5 M HCl and the anolyte consisted of a solution of 1 M NaBH₄ in 4 M NaOH [25].

2.4.5. IEC, Ionic Conductivity and Borohydride Permeability

The acid–base titration method was used for evaluating the ion exchange capacity (IEC) of the prepared membranes. The samples were put in 2 M NaCl solution (50 mL) for two days in order to replace the protons by sodium ions. The resulting solution was titrated by 0.01 M sodium hydroxide solution using phenolphthalein indicator [25]. IEC was calculated from Equation (3),

$$IEC(m_{eq} g^{-1}) = \frac{V_{NaOH} \times C_{NaOH}}{W_{dry}}$$
(3)

where C_{NaOH} , W_{dry} and V_{NaOH} are the NaOH titrant solution concentration, the dry membrane weight, and the volume of consumed NaOH, respectively.

The ionic conductivity of the membrane was estimated from the resistance measurements using the electrochemical impedance spectroscopy (EIS) technique. A potentiostat PAR 273A (Princeton Applied Research, Inc.) coupled with an SI 1255 HF frequency response analyzer (FRA, Schlumberger Solartron) was used. Membrane samples were soaked in 4 M NaOH solution for 30 min at room temperature

before conducting the EIS measurements. The membrane samples were mounted between two stainless steel plate electrodes. The spectra were acquired at open circuit potential with a signal amplitude of 5 mV in the frequency range of 100 Hz–100 kHz. The membrane resistance was determined from the intercept of the impedance spectra at the high-frequency region with the real axis in the complex impedance plot. The ionic conductivity of all investigated membranes was determined according to Equation (4), based on the values of the measured resistance (R, Ω),

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

where σ is the membrane ionic conductivity (mS cm⁻¹), d is the membrane thickness (cm) and A is the membrane area (cm²).

To measure the membrane permeability with regard to borohydride anion (BH_4^-), the composite membranes were put vertically in a homemade glass diffusion cell between two symmetrical reservoirs of 100 mL each. The first reservoir (A, donor reservoir) was filled with 1 M NaBH₄ in 4 M NaOH solution (to simulate the anolyte solution in a DBFC), and the second reservoir (B, receptor reservoir) was filled with deionized water. BH_4^- anion diffuses from A to B via the membrane due to the difference in concentration between the two reservoirs. An inductively coupled plasma-atomic emission spectrophotometer (ICP-AES, model Prodigy, Teledyne Leeman Labs) was used to monitor the boron element concentration from the BH_4^- present in the water reservoir (B) [25]. The permeability of BH_4^- from A to B as a function of time was calculated by Equation (5),

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

where A is the membrane diffusion area (cm²), V_B is the receptor reservoir volume (cm³), L is the thickness of the membrane (cm), C_A and C_B are the concentrations of BH_4^- (mol cm⁻³) in the reservoirs A and B, respectively, (t-t₀) interval is the time needed for the BH_4^- crossover and P is the membrane's BH_4^- permeability (cm² s⁻¹).

3. Results and Discussion

3.1. Characterization of PO₄-TiO₂ and SO₄-TiO₂ Doping Agents

The FTIR spectra of TiO₂-based doping agents and TiO₂ are compared in Figure 2. TiO₂ bands located at 715 and 1026 cm⁻¹ are attributed to Ti-O bonds, and the bands at 3387, 1622 and 1396 cm⁻¹ correspond to O-H bonds due to the moisture sorption on the powder surface [23]. In the case of SO₄-TiO₂, a strong band at 1153 cm⁻¹ is attributed to sulfate ion coordinated to the Ti⁴⁺ metal cation. The bands at 3390 and 1651 cm⁻¹ are due to O-H bonds from moisture sorption on the TiO₂ surface and became wider as SO₄-TiO₂ is more hydrophilic than pure TiO₂ [27]. For PO₄-TiO₂, the band located at 690 cm⁻¹ corresponds to the Ti-O bond. The bands at 1085, 889 and 1269 cm⁻¹ are attributed to the P-O bonds of the PO₄ anion incorporated into the TiO₂ structure. The band at 1427 cm⁻¹ is related to the P = O bond. The O-H bonds from H₂O molecules sorption are depicted by the bands at 3117 and 1628 cm⁻¹. The band appearing at 2374 cm⁻¹ is related to the presence of atmospheric CO₂ [28,29].

The X-ray diffraction patterns of original TiO₂ and of the prepared PO₄-TiO₂ and SO₄-TiO₂ doping agents can be seen in Figure 3. The typical peaks of rutile TiO₂ at 20 values of 28°, 36°, 41° and 54° can be observed [30]. Inclusion of either sulfate or phosphate in the titanium dioxide lattice changed the rutile crystalline phase. The diffractograms reveal that the PO₄-TiO₂ and SO₄-TiO₂ have different structures when compared to the original TiO₂ rutile phase, although they were submitted to the same temperature of calcination; this may be related to the different synthesis methods. The intensity of the peak of rutile TiO₂ at 28° is reduced in the SO₄-TiO₂ diffractogram and it disappears in the PO₄-TiO₂ diffractogram. The other peak at 54° of the pure rutile TiO₂ is absent in the diffractograms of PO₄-TiO₂ and SO₄-TiO₂. The PO₄-TiO₂ diffractogram shows characteristic peaks at 25°, 26°, 38°, 48° , 54° and 55° [22], whereas the characteristic peak of SO₄-TiO₂ clearly appears at 23° [31]. It can be observed from Table 1 that the mass content values of S in SO₄-TiO₂ and P in PO₄-TiO₂ measured by energy-dispersive X-ray spectroscopy (EDX) and inductively coupled plasma-atomic emission spectrophotometry (ICP-AES) are close. That confirms the successful functionalization of TiO₂ with acid groups.



Figure 2. FTIR spectra of TiO₂, PO₄-TiO₂, and SO₄-TiO₂.



Figure 3. XRD patterns of TiO₂, PO₄-TiO₂, and SO₄-TiO₂.

Table 1. ICP and EDX data of phosphated/sulfated titanium oxide.

Sample	Ti _{EDX}	O _{EDX}	S _{EDX} /S _{ICP}	P EDX/P ICP
	wt.%	wt.%	wt.%	wt.%
SO ₄ -TiO ₂ PO ₄ -TiO ₂	41.7 40.3	52.8 54.0	5.5/4.9	- 5.7/5.3

TEM images also show the morphological differences of the PO_4 -Ti O_2 and SO_4 -Ti O_2 . Figure 4 shows the nanotubes structure of SO_4 -Ti O_2 with a length ranging between 150 nm and 400 nm and a diameter of ca. 12 nm. On the other hand, PO_4 -Ti O_2 is characterized by an irregular particle shape with particle size ranging from 50–400 nm.



Figure 4. TEM images of (**a**) SO₄-TiO₂ nanotubes and of (**b**) PO₄-TiO₂.

3.2. Characterization of Membranes

3.2.1. Structural Analysis and Morphology

Figure 5 shows the FTIR spectra for both doped and undoped membranes. A band appearing at ca. 1650 cm⁻¹ represents bands that result from hydrogen bonding [32] between –OH of PVA and oxygen functional groups of the doping agent. A band appearing at ca. 2200 cm⁻¹ is attributed to the C-H bonds of the polymer in the membranes [33]. A board band around 3000 cm⁻¹ can be assigned to the O-H bonds from H₂O molecules which are more adsorbed as the content of doping agents increases due to their hydrophilic features. In addition, the strong band appearing around 3500–3600 cm⁻¹ is characteristic of the hydroxyl group of the PVA polymer [34]. The weak band at 1850 cm⁻¹ refers to C-H bending in the aromatic structure of the SPA, which ensures the crosslinking.



Figure 5. FTIR spectra of the SPVA-SPTiO membranes in the presence (different contents) and in the absence of PO₄-TiO₂ and SO₄-TiO₂.

Morphology of the polymer blend membranes with and without doping agents is displayed in Figure 6. The undoped membrane (Figure 6a) has a smooth surface. In the SPVA-SPTiO-3 composite membrane, PO_4 -TiO₂ and SO₄-TiO₂ doping agents are clearly observed under the surface of the SPVA-SPTiO-3 membrane, with no visible sign of voids or pores and good distribution (Figure 6b). A cross section of the SPVA-SPTiO-3 membrane shows a compact structure provided by the doping agent based TiO₂ included in the polymer matrix (Figure 6c).



Figure 6. SEM images of (**a**) the surface of the undoped membrane and of (**b**) the surface and (**c**) the cross section of the nanocomposite membrane with 3 wt.% of PO₄-TiO₂ and SO₄-TiO₂.

3.2.2. Thermal and Mechanical Analysis

TGA curves of the membranes with and without PO_4 -Ti O_2 and SO_4 -Ti O_2 doping agents are represented in Figure 7. The first weight loss (~7%) at 140 °C refers to the evaporation of moisture adsorbed onto the surface of the membrane [19]. The second weight loss corresponds to the degradation of the functional groups on the composite membranes (starts at 140–250 °C), which is caused by the decomposition of functional groups containing oxygen. Above 250 °C starts the final degradation state of the polymer chains and of the polymer backbone of the membrane. Furthermore, it can be observed that the composite membrane with 1.0 wt.% of PO_4 -Ti O_2 and SO_4 -Ti O_2 and the undoped membrane have approximately the same thermal stability behavior. As the content of doping agents increases to 2 wt.% and to 3 wt.%, the membrane thermal stability gets higher due to the nature of doping agents with remarkable thermal stability [35].



Figure 7. TGA curves of the fabricated membranes.

The addition of doping agents into the polymeric matrix is expected to enhance the mechanical properties of the composite membranes. The tensile strength analysis of the fabricated membranes is presented in Figure 8 and in Table 2. In general, PO_4 -TiO₂ and SO_4 -TiO₂ doping agents provided stronger interfacial adhesion to the polymer matrix of nanocomposite membranes by forming hydrogen bonds between hydroxyl groups of PVA and acid groups of doping agents, besides the formed covalent bonds (by GA) and ionic bonds (by SPA) in the PVA matrix, which improve their breaking resistance when compared to the Nafion[®]117 membrane. The composite membrane with 3 wt.% of PO₄-TiO₂ and SO_4 -TiO₂ showed a tensile strength seven times higher than the undoped membrane, and even higher than that of Nafion[®]117.



Figure 8. The stress vs. strain curves of the prepared membranes.

Table 2. Thickness, tensile strength, water uptake, swelling ratio and contact angle of the prepared membranes and Nafion[®]117 [36].

Membrane	Thickness/µm	Water uptake/%	Swelling ratio/%	Contact angle/°	Tensile strength/MPa
SPVA	110	110	90	75	4.5
SPVA-SPTiO-1	140	60	28	77	11.5
SPVA-SPTiO-2	145	30	17	78	20.3
SPVA-SPTiO-3	150	13	7	80	28.2
Nafion [®] 117	183	15	8	102	25

3.2.3. Swelling Ratio, Water Uptake and Contact Angle

The membranes' physicochemical properties, such as the swelling ratio, water uptake and contact angle were measured and compared in Table 2. The incorporation of PO_4 -TiO₂ and SO_4 -TiO₂ particles sharply reduced the swelling degree and water uptake because these doping agents give a barrier effect [30]. In other words, the increase of doping agent content turned the membranes thicker and more compact resulting in a much lower dimensional change and water sorption, as observed for the SPVA-SPTiO-3 membrane (WU of 13% and SR of 7%) in comparison with the undoped membrane (WU > 110% and SR of 90%). The contact angle was also evaluated and the values were less than 90°

for all the membranes demonstrating their hydrophilic character. Increasing the contact angle values (from 75–80°) with increasing concentration of doping agents (0–3 wt.%) was noted.

3.2.4. Oxidative Stability

Membranes which are applied in DBFC should be stable to oxidation by using a strongly oxidizing H_2O_2 solution in acidic media as catholyte. Figure 9 and Table 3 give the oxidative stability behavior of the membranes. SPVA-SPTiO-1 shows good improvement compared to the undoped membrane. SPVA-SPTiO-2 membrane remained nearly intact (RW of 99.5%) which is a sign of oxidative stability enhancement with inclusion of 2 wt.% of PO_4 -TiO₂ and SO_4 -TiO₂. However, increasing the doping agent concentration to 3 wt.% resulted in a membrane with slightly lower oxidative stability (RW of 98%), probably due to some defects inside the membrane matrix caused by the doping agent agglomeration. This is a common phenomenon ascertained when titanium dioxide concentration is higher than 2 wt.% [35]. Still, the addition of doping agents with 2 and 3 wt.% increases the oxidative stability in acidic H_2O_2 solution (catholyte). On the other hand, all the composite membranes were stable in the alkaline sodium borohydride (NaBH₄) solution (anolyte).



Figure 9. Oxidative stability plots for the prepared membranes.

Table 3. Ion exchange capacity (IEC), oxidative stability, borohydride permeability and ionic conductivity of the fabricated membranes and Nafion[®]117 [37,38].

Membrane	Oxidative stability/RW, % [*]	IEC/meq g ⁻¹	Borohydride permeability/cm ² s ⁻¹	Ionic Conductivity /mS cm ⁻¹
SPVA	80	0.10	0.71×10^{-5}	1.25
SPVA-SPTiO-1	90	0.25	0.49×10^{-6}	3.12
SPVA-SPTiO-2	99.5	0.40	0.39×10^{-6}	5.57
SPVA-SPTiO-3	98	0.50	0.32×10^{-6}	7.13
Nafion [®] 117	92	0.89	0.40×10^{-6}	45.0

The values are based on membrane retained weight (RW) after one-day immersion in Fenton's reagent.

3.2.5. IEC and Borohydride Permeability

Membrane features, such as borohydride permeability and IEC (Table 3), are essential to understand the effect of doping agent concentration on membrane behavior. The IEC values of composite membranes increased from 0.10–0.50 meq g⁻¹ with increase of the doping agent concentrations (0–3 wt.%). This indicates that the charge density increased in the nanocomposite matrix. There was a clear improvement in the ionic conductivity of nanocomposite membranes when compared to the undoped membrane. Table 3 shows a significant increase in the ionic conductivity from 1.2–7.1 mS cm⁻¹ when increasing the doping agents content from 0–3 wt.%, probably due to a significant decrease in the membrane resistivity (Figure 10) and crystallinity.



Figure 10. Impedance measurements of the doped membranes and of the undoped membrane.

Figure 11 displays the XRD patterns of the composite membranes. For the undoped membrane, a sharp peak at 20 values of 19° appeared due to the semi-crystalline structure of the PVA. The patterns of the nanocomposite membranes reveal that the structure of membranes turned more amorphous with increasing content of PO_4 -Ti O_2 and SO_4 -Ti O_2 .



Figure 11. XRD patterns of the doped and undoped membranes.

Concerning the membranes' permeability, it is known that cation exchange membranes have the ability to transport cations while preventing the fuel crossover that causes a change in the catholyte/anolyte compositions and the membrane fouling, thus leading to reduced efficiency of the fuel cell. It is known that titanium dioxide can reduce membrane permeability to different fuels [19,30]. The prepared nanocomposite membranes reduced the crossover of BH₄⁻ due to the presence of electron-rich functional groups (phosphate and sulfate) contained in the titanium dioxide structure. The SPVA-SPTiO-3 membrane has the lowest BH₄⁻ permeability (0.32×10^{-6} cm² s⁻¹) in comparison with the undoped membrane (0.71×10^{-5} cm² s⁻¹) as well as the other doped membranes and Nafion[®]117 (0.40×10^{-6} cm² s⁻¹), due to the higher concentration of doping agents.

4. Conclusions

The development of membranes based on a green and cost-effective approach to replace Nafion membranes in DBFCs is an important issue for the commercialization of this technology. In this study, organic–inorganic nanocomposite membranes based on SPVA doped with phosphated-TiO₂ and sulfated-TiO₂ nanotubes were synthesized and physicochemically characterized. These hybrid nanocomposites have shown higher tensile strength, higher oxidative stability, lower water absorption, lower swelling ratio and lower permeability to BH₄⁻ compared to the undoped membrane and Nafion[®]117. Furthermore, acid-modified inorganic doping materials enhanced the membrane's IEC and ionic conductivity 5 and 7 times, respectively, as well as its thermal stability. These good results suggest that the developed membranes have potential application in DBFCs.

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References

- 1. Merino-Jiménez, I.; León, C.P.; Shah, A.A.; Walsh, F.C. Developments in direct borohydride fuel cells and remaining challenges. *J. Power Sources* **2012**, *219*, 339–357. [CrossRef]
- 2. Ma, J.; Choudhury, N.A.; Sahai, Y. A comprehensive review of direct borohydride fuel cells. *Renew. Sustain. Energy Rev.* **2010**, *14*, 183–199. [CrossRef]
- 3. Soloveichik, G.L. Liquid fuel cells. Beilstein J. Nanotechnol. 2014, 5, 1399–1418. [CrossRef] [PubMed]
- 4. Santos, D.M.F.; Sequeira, C.A.C. Sodium borohydride as a fuel for the future. *Renew. Sustain. Energy Rev.* **2011**, *15*, 3980–4001. [CrossRef]
- 5. Stroman, R.O.; Jackson, G.S. Modeling the performance of an ideal NaBH₄-H₂O₂ direct borohydride fuel cell. *Int. J. Hydrogen Energy* **2014**, 247, 756–769.
- 6. Santos, D.M.F.; Sequeira, C.A.C. Effect of membrane separators on the performance of direct borohydride fuel cells. *J. Electrochem. Soc.* **2012**, *159*, B126–B132. [CrossRef]
- 7. Šljukić, B.; Morais, A.L.; Santos, D.M.F.; Sequeira, C.A.C. Anion- or cation exchange membranes for NaBH₄/H₂O₂ fuel cells? *Membranes* **2012**, *2*, 478–492. [CrossRef]
- 8. Ye, Y.S.; Rick, J.; Hwang, B.J. Water soluble polymers as proton exchange membranes for fuel cells. *Polymers* **2012**, *4*, 913–963. [CrossRef]
- 9. Pourzare, K.; Mansourpanah, Y.; Farhadi, S. Advanced nanocomposite membranes for fuel cell applications: A comprehensive review. *Biofuel Res. J.* **2016**, *12*, 496–513. [CrossRef]
- 10. 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]
- 11. Abdullah, N.; Kamarudin, S.K. Titanium dioxide in fuel cell technology: An overview. *J. Power Sources* **2015**, 278, 109–118. [CrossRef]

- 12. Bet-moushoul, E.; Mansourpanah, Y.; Farhadi, K.; Tabatabaei, M. TiO₂ nanocomposite based polymeric membranes: A review on performance improvement for various applications in chemical engineering processes. *Chem. Eng. J.* **2016**, *283*, 29–46. [CrossRef]
- Matos, B.R.; Isidoro, R.A.; Santiago, E.I.; Tavares, A.C.; Ferlauto, A.S.; Muccillo, R.; Fonseca, F.C. Nafion-titanate nanotubes composites prepared by in situ crystallization and casting for direct ethanol fuel cells. *Int. J. Hydrogen Energy* 2015, 40, 1859–1867. [CrossRef]
- 14. Lee, C.; Park, J.; Jeon, Y.; Park, J.; Einaga, H.; Truong, Y.B.; Kyratzis, I.L.; Mochida, I.; Choi, J.; Shul, Y.G. Phosphate-modified TiO₂/ZrO₂ nanofibrous web composite membrane for enhanced performance and durability of high-temperature proton exchange membrane fuel cells. *Energy Fuels* **2017**, *31*, 7645–7652. [CrossRef]
- Liu, X.; Li, Y.; Peng, S.; Lu, G.; Li, S. Modification of TiO₂ with sulfate and phosphate for enhanced eosin Y-sensitized hydrogen evolution under visible light illumination. *Photochem. Photobiol. Sci.* 2013, 12, 1903–1910. [CrossRef] [PubMed]
- 16. Tominaga, Y.; Endo, M. Ion-conductive properties of polyether-based composite electrolytes filled with mesoporous silica, alumina and titania. *Electrochim. Acta* **2013**, *113*, 361–365. [CrossRef]
- Devrim, Y.; Erkan, S.; Bac, N.; Eroglu, I. Preparation and characterization of sulfonated polysulfone/titanium dioxide composite membranes for proton exchange membrane fuel cells. *Int. J. Hydrogen Energy* 2009, 34, 3467–3475. [CrossRef]
- Salarizadeh, P.; Javanbakht, M.; Pourmahdian, S. Enhancing the performance of SPEEK polymer electrolyte membranes using functionalized TiO₂ nanoparticles with proton hopping sites. *RSC Adv.* 2017, 7, 8303–8313. [CrossRef]
- Yang, C.; Chien, W.; 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]
- 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]
- 21. Herring, A.M. Inorganic–polymer composite membranes for proton exchange membrane fuel cells. *J. Macromol. Sci. Polymer Rev.* **2006**, *46*, 245–296. [CrossRef]
- 22. Onoda, H.; Matsukura, A. Influence of concentration in phosphoric acid treatment of titanium oxide and their powder properties. *J. Asian Ceram. Soc.* **2015**, *3*, 27–31. [CrossRef]
- 23. 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]
- 24. Lin, C.; Chien, S.; Chao, J.; Sheu, C.; Cheng, Y.; Huang, Y.; Tsai, C. The synthesis of sulfated titanium oxide nanotubes. *Catal. Lett.* **2002**, *80*, 153–159. [CrossRef]
- Gouda, M.H.; Gouveia, W.; Afonso, M.L.; Šljukić, B.; El Essawy, N.A.; Nassr, A.B.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]
- Eldin, M.S.M.; 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.* 2019. [CrossRef]
- Kumar, K.S.; Rajendran, S.; Prabhu, M.R. A study of influence on sulfonated TiO₂-poly (vinylidene fluoride-co-hexafluoropropylene) nano composite membranes for PEM fuel cell application. *Appl. Surf. Sci.* 2017, *418*, 64–71. [CrossRef]
- 28. 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]
- 29. Goswami, P.; Ganguli, J. Synthesis characterization and photocatalytic reactions of phosphated mesoporous titania. *Bull. Mater. Sci.* **2012**, *35*, 889–896. [CrossRef]
- 30. 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]
- 31. Jun, Y.; Zarrin, H.; Fowler, M.; Chen, Z. Functionalized titania nanotube composite membranes for high temperature proton exchange membrane fuel cells. *Int. J. Hydrogen Energy* **2011**, *36*, 6073–6081. [CrossRef]

- 32. Huang, Y.F.; Chuang, L.C.; Kannan, A.M.; Lin, C.W. Proton-conducting membranes with high selectivity from cross-linked poly(vinyl alcohol) and poly(vinyl pyrrolidone) for direct methanol fuel cell applications. *J. Power Sources* **2009**, *186*, 22–28. [CrossRef]
- 33. Qiao, J.; Fu, J.; Lin, R.; Mac, J.; Liu, J. Alkaline solid polymer electrolyte membranes based on structurally modified PVA/PVP with improved alkali stability. *Polymer* **2010**, *51*, 4850–4859. [CrossRef]
- 34. 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.
- 35. Ozdemir, Y.; Uregen, N.; Devrim, Y. Polybenzimidazole based nanocomposite membranes with enhanced proton conductivity for high temperature PEM fuel cells. *Int. J. Hydrogen Energy* **2017**, *42*, 2648–2657. [CrossRef]
- 36. Li, T.; Zhong, G.; Fu, R.; Yang, Y. Synthesis and characterization of Nafion/cross-linked PVP semi-interpenetrating polymer network membrane for direct methanol fuel cell. *J. Membr. Sci.* **2010**, *354*, 189–197. [CrossRef]
- Parnian, M.J.; Rowshanzamir, S.; Moghaddam, J.A. Investigation of physicochemical and electrochemical properties of recast Nafion nanocomposite membranes using different loading of zirconia nanoparticles for proton exchange membrane fuel cell applications. *Mater. Sci. Energy Technol.* 2018, 1, 146–154. [CrossRef]
- An, L.; Jung, C.Y. Transport phenomena in direct borohydride fuel cells. *Appl. Energy* 2017, 205, 1270–1282. [CrossRef]



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