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Functionalized titania nanotube composite membranes for high temperature proton exchange membrane fuel cells

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ABSTRACT

In this study, functionalized titania nanotubes (F-TiO₂-NT) were synthesized by using 3-mercaptopropyl-tri-methoxysilane (MPTMS) as a sulfonic acid functionalization agent. These F-TiO₂-NT were investigated for potential application in high temperature hydrogen polymer electrolyte membrane fuel cells (PEMFCs), specifically as an additive to the proton exchange membrane. Fourier transform infrared spectroscopy (FT-IR) and X-ray photoelectron spectroscopy (XPS) results confirmed that the sulfonic acid groups were successfully grafted onto the titania nanotubes (TiO₂-NT). F-TiO₂-NT showed a much higher conductivity than non-functionalized titania nanotubes. At 80 °C, the conductivity of F-TiO₂-NT was 0.08 S/cm, superior to that of 0.0011 S/cm for the non-functionalized TiO₂-NT. The F-TiO₂-NT/Nafion composite membrane shows good proton conductivity at high temperature and low humidity, where at 120 °C and 30% relative humidity, the proton conductivity of the composite membrane is 0.067 S/cm, a great improvement over 0.012 S/cm for a recast Nafion membrane. Based on the results of this study, F-TiO₂-NT has great potential for membrane applications in high temperature PEMFCs.

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1. Introduction

Hydrogen as a storage and carrying medium of renewable energy resources can be converted to electricity by using electrochemical energy converters like proton exchange membrane fuel cells (PEMFCs) [1]. Proton exchange membrane fuel cells (PEMFCs), also known as polymer electrolyte fuel cells, have emerged as promising power supply systems for stationary, vehicular, and portable applications [2,3]. These devices are traditionally based on perfluoro-sulfonic acid membrane electrolytes, given the commercial name Nafion. However, Nafion membranes are restricted to operating

temperatures below 100 °C. At temperatures approaching the boiling point of water, Nafion exhibits a drastic ionic conductivity loss which hinders the PEMFC operation at temperatures higher than 80 °C and/or reduced relative humidity (RH <100%). In addition, the mechanical and dimensional stability of the polymer chains can be diminished at high temperatures as a result of the relatively low glass transition temperature of Nafion [4,5]. To achieve a timely, sustainable commercialization of PEMFC, the development of proton exchange membranes for high temperature operation is a necessity and has been receiving a great deal of attention. The ability to perform at high operation temperatures in the

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range of 100–130 °C is desirable in order to significantly boost PEMFC performance. This results from the enhancement of several important parameters including (i) electrode reaction kinetics (mainly the oxygen reduction reaction (ORR)), (ii) carbon monoxide (CO) tolerance, and (iii) simplified water and thermal management of the fuel cell system [4,6–8].

To overcome the temperature limitations of the current electrolyte materials, several organic/inorganic hybrid membranes have become the focus of intense research recently [9,10]. So far, many kinds of inorganic fillers, such as TiO₂, SiO₂, ZrO₂, zeolite nanoparticles as well as mesoporous silica (MCM41) have been employed for use in these organic/inorganic hybrid membranes for PEMFC applications at high temperatures [11–25]. Such composite electrolytes have been proposed as potential replacements for Nafion in PEMFCs operating at a temperature range of 100–150 °C and/or low relative humidity. Because they have good water retention and enhance the membrane stability [8,9,26–28]. The proton conductivity of these hybrid membranes is still inferior when compared to recast Nafion membranes, which is believed to derive mainly from the increased barrier properties of the membranes, due to the incorporation of inorganic fillers (an increase in inorganic particle agglomeration at higher concentrations of inorganic additives) [29,30]. In order to increase the proton conductivity of these hybrid membranes, functionalized nanoparticles have been employed. After functionalization, the nanoparticles can display improved proton conductivity, the ability to hold more water and a more homogeneous dispersion among the hydrophilic sites of the Nafion, compared with non-functionalized nanoparticles [31–34]. Moreover, dimensionality plays a critical role in governing the properties of materials due to the different ways that electrons interact with nanostructures of varying dimensions (3-D, 2-D, 1-D and 0-D). Compared with 0-D nanostructures (i.e. nanoparticles) and 2-D nanostructures (i.e. thin films), 1-D nanostructures (including nanotubes, nanowires and nanorods) are ideal for various potential applications such as composite materials, due to their unique electronic and structural properties [20,35,36]. Among them, nanotubes have attracted interest for potential application in high temperature PEMFCs, due to their distinct morphology, high specific surface area, thermal stability and corrosion resistance [37–41]. Their 1-D nanostructure leads to higher water retention and it is proposed that they can produce a continuous channel to improve the proton conductivity [37,38,42–44]. Also, among all the previously mentioned nanostructured metal oxides, TiO₂-based nanotubes (TiO₂-NT) with a high specific surface area and ion-changeable capabilities have been considered for use in a variety of applications [38,45–48]. Matos et al. [45] employed TiO₂-NT in high temperature PEMFC Nafion composite membranes. Their results indicated that the addition of TiO₂-NT resulted in a decrease in the overall proton conductivity, attributed to the low conductivity of the nanotube additives within the Nafion matrix. An enhanced fuel cell performance, however, was observed at temperatures greater than 120 °C, which can be attributed to the larger water retention capacity of TiO₂-NT which originates from their high specific surface area [45].

In this study, TiO₂-NT were functionalized by using 3-mercaptopropyltri-methoxysilane (MPTMS 98 wt.%) as

a precursor for the formation of sulfonate groups. These nanotubes have a high specific surface area and when combined result in highly ordered nanotube arrays which provide excellent pathways for protons. Moreover, functionalization can provide sulfonate groups which will serve to increase the proton conductivity of these materials. Therefore, by combining these two distinct advantages, functionalized TiO₂-NT (F-TiO₂-NT) has potential for application in high temperature PEMFCs. The structure and proton conductivity of F-TiO₂-NT and F-TiO₂-NT/Nafion composite membranes were studied at high operating temperatures and low relative humidity in order to evaluate their advantages at high temperature PEMFCs. F-TiO₂-NT/Nafion composite membranes are presented as potential replacements for commercial Nafion membranes in high temperature PEMFCs.

2. Experimental

2.1. Synthesis of the titania nanotubes

TiO₂-NTs were prepared by the alkaline hydrothermal method [38,42]. A brief description is outlined here. First, 0.9 g of titania nanoparticle (TiO₂-NP; <25 nm) was mixed with 120 mL of 10 M NaOH solution. The resulting mixture was stirred and ultrasonicated for several minutes before pouring the solution into a stainless steel/Teflon autoclave which was heated for 48 h at 140 °C. Finally, the solution was filtered with deionized water, washed with 40 mL of 0.1 M HCl and dried overnight.

2.2. Functionalization of TiO₂-NT

The functionalization of titania nanotubes was performed by using MPTMS as the sulfonic acid functional group precursor [43]. The reaction was carried out in toluene at a temperature of 110 °C under reflux conditions for 24 h, with 1:2:20 molar ratios of TiO₂-NT, MPTMS and toluene, respectively. The mercapto groups grafted onto the TiO₂-NT were then oxidized to sulfonic acid groups by using 30 wt.% H₂O₂ solution at 25 °C for 24 h. The prepared samples were filtered and washed with ethanol and water to remove the precursor residue. Samples were dried overnight prior to characterization. For comparison, titania nanoparticles were also functionalized under the same procedure as mentioned above.

2.3. Membrane fabrication

In order to cast the pure Nafion membrane, 15 wt.% Nafion solution was mixed with an appropriate amount of ethanol. The mixture was then sonicated in an ultrasonic bath for 30 min followed by heating at 60 °C until the liquid evaporated. Finally, it was heated for 2 h at 100 °C and for 1 h at 140 °C.

F-TiO₂-NT/Nafion composite membrane was casted by mixing 5 wt.% F-TiO₂-NT with an appropriate amount of 15 wt.% Nafion solution and ethanol mixture. After, as same as the pure Nafion casting procedure, it was ultrasonicated for 30 min and heated at 60 °C until the liquid evaporated. Finally, it was heated at 100 °C for 2 h and then 140 °C for 1 h [10].

Both pure Nafion and F-TiO₂-NT/Nafion composite membranes were pretreated by boiling in a 3% H₂O₂ aqueous solution for 1 h, rinsed in boiling deionized water for 1 h, boiled in 0.5 M H₂SO₄ for 1 h, and finally rinsed again in deionized water before being tested [15].

2.4. Physical characterization

The morphology of unmodified TiO₂-NT was examined by using transmission electron microscopy (TEM, JEM-100CX II). The specific surface areas of TiO₂-NT and F-TiO₂-NT were determined by the Brunauer–Emmett–Teller (BET) method. After functionalization, the F-TiO₂-NT was analyzed using Fourier transform infrared spectroscopy (FT-IR, Perkin Elmer-283B FT-IR Spectrometer) and X-ray diffraction (XRD, RigakuD/max 2500 v/pa, Cu K α , 40 kV, 200 mA, 8° min⁻¹). X-ray photoelectron spectroscopy (XPS, Thermal Scientific K-Alpha XPS spectrometer) was used to investigate the elemental composition and atomic configuration of TiO₂-NT. To probe the dehydration properties, thermogravimetric analysis (TGA) of the unmodified and modified TiO₂-NT was performed on a TGA Q500V20.10 Build 36 system in a temperature range from 50 to 700 °C at a heating rate of 10 °C/min in a N₂ atmosphere.

2.5. Water uptake

In order to measure the water retention capability of the membranes, the Water Uptake (WU) was calculated. For this, they were first immersed and saturated in deionized water at room temperature for 24 h. Then the wet membranes were taken out and weighed immediately after the water droplets were removed from the surface. Then, they were vacuum dried at 80 °C for 24 h, put into a plastic sealing bag immediately and weighed. This experiment was replicated 4 times for each membrane and the water uptake was determined from the following equation [49,50]:

$$WU(\%) = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100 \quad (1)$$

where WU (%), W_{wet} and W_{dry} are the water uptake by weight percentage, the weight of wet membrane and the weight of dry membrane, respectively.

2.6. Proton conductivity

The proton conductivity of TiO₂-NT, F-TiO₂-NT and titania nanoparticles were measured using a two-electrode setup under controlled temperature and degree of water saturation [51]. First, each of the powdered samples was individually loaded into a tube cell with a diameter of 1.6 mm in which the two electrodes are inserted from the top and bottom. Then, they were pressed for several hours. To attain water-saturated conditions (100% humidity), the fixture was disassembled from the top and 20 μ L of double deionized water was injected with a syringe onto the sample in each cell. The water was allowed to soak into the samples for 30 min. Then the top electrodes were replaced, the fixture was reassembled, and the sample cells were retorqued.

The proton conductivity of pure Nafion membrane and F-TiO₂-NT/Nafion composite membrane was measured using a four-electrode AC impedance method [52,53] under various conditions of relative humidity and temperature. During measurements, the humidity was controlled by mixing water-saturated nitrogen gas with dry nitrogen gas, while the temperature was fixed at 80, 100 and 120 °C. On average, the needed equilibration time to reach the steady state for each relative humidity was 45 min.

The conductivity of all powdered samples and different membranes was then measured in the longitudinal direction, and was calculated using the following equation [46,52–54]:

$$\sigma = \frac{L}{AR} \quad (2)$$

where σ , L , R , and A denote the ionic conductivity, sample length (or distance between the reference electrodes in the membrane), the resistance of the sample (or the membrane), and the cross-sectional area of the sample (or the membrane), respectively.

3. Results and discussion

The TEM of TiO₂-NT is shown in Fig. 1. Several TiO₂-NT are observed, displaying uniform outer diameters of approximately 5 nm. The BET surface area of titania nanoparticles (TiO₂-NP) was 186.5 m²/g, while that of titania nanotubes (TiO₂-NT) increased to 381.2 m²/g which would be advantageous for the application of the nanotubes in the structure of Nafion nanocomposite to boost the proton conductivity of the electrolyte membrane.

The FT-IR spectra of the TiO₂-NT and F-TiO₂-NT are shown in Fig. 2. The peaks at 669 cm⁻¹ and 1634 cm⁻¹ are attributed to the Ti–O–Ti and hydroxyl groups, respectively. By comparing the unmodified TiO₂-NT with F-TiO₂-NT, it can be observed that the sulfonic acid group shows a peak which is located at 1044 cm⁻¹. This analysis confirms the successful presence of the sulfonic acid group that has been grafted onto the TiO₂-NT.

The XRD pattern of unmodified and functionalized TiO₂-NT is shown in Fig. 3. The intensive diffraction peaks in this pattern can be attributed to the anatase phase of TiO₂ (JCPDS 89-4921), corresponding to the (101), (004), (200), and (204) planes. It should be noted that there is a slight deviation between the unmodified and functionalized titania nanotubes at the (101) plane of TiO₂ anatase phase. This difference may be attributed to the functionalization which causes a shift in the crystalline structure.

The chemical composition of both unmodified and functionalized titania nanotube (TiO₂-NT and F-TiO₂-NT) was characterized by XPS measurements. Typical XPS patterns are presented in Fig. 4. It can be seen that the TiO₂-NT and F-TiO₂-NT particles contain the Ti 2p and O 1s peaks of the titanium dioxide (Fig. 4a and b). The spectrum of the F-TiO₂-NT particles also contains C 1s and S 2p peaks in addition to the Ti 2p and O 1s peaks, confirming the presence of the MPTMS surface modifier.

Fig. 5 shows the TGA for F-TiO₂-NT and TiO₂-NT samples. For both membranes, the mass loss below 160 °C is due to the

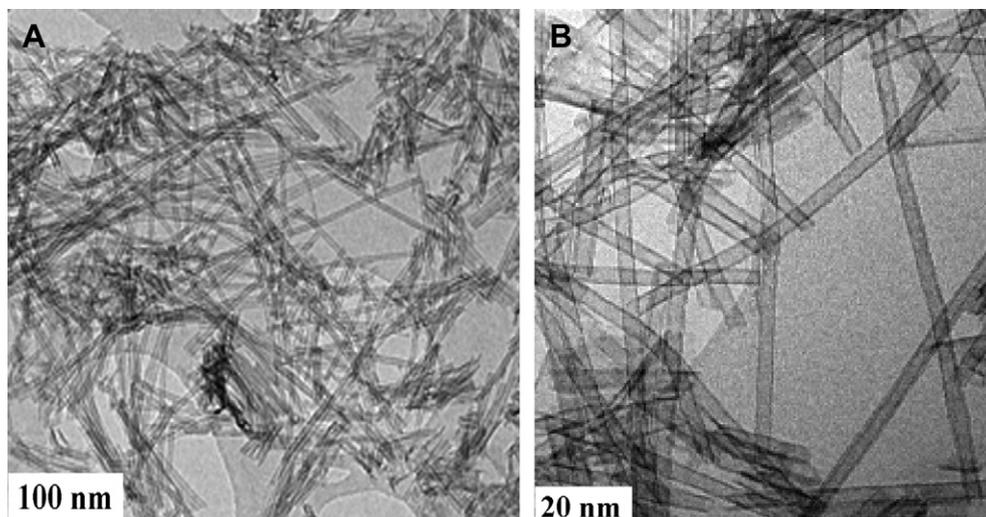


Fig. 1 – TEM image of $\text{TiO}_2\text{-NT}$ at (A) low and (B) high resolutions.

removal of water which is 14.3% F- $\text{TiO}_2\text{-NT}$ and 17.2% for $\text{TiO}_2\text{-NT}$. This water may be present in the form of membrane hydration, or in the structure of acidic solid for F- $\text{TiO}_2\text{-NT}$. For the pristine $\text{TiO}_2\text{-NT}$ no other weight loss is observed. However, the TGA graph for F- $\text{TiO}_2\text{-NT}$ shows significant decomposition at 220 °C which can be attributed to the loss of functional groups in the sample [55,56].

In Table 1, the water uptake of 5 wt.% F- $\text{TiO}_2\text{-NT}$ and 5 wt.% functionalized titania nanoparticle (F- $\text{TiO}_2\text{-NP}$) Nafion composite membranes are compared to recast and commercial Nafion 112. It is seen that the water uptake of F- $\text{TiO}_2\text{-NT}$ /Nafion composite is about 7, 4 and 2% higher than Nafion 112, recast Nafion and F- $\text{TiO}_2\text{-NP}$ /Nafion, respectively. These results suggest that the one-dimensional structure of nanotubes with high specific surface areas leads to higher water retention of Nafion composite membranes than any other tested structure. This can be explained by the reduction of crystallinity and stronger interactions between the absorbed

water and the network of the F- $\text{TiO}_2\text{-NT}$ /Nafion membrane which results in enhancement of its proton conductivity. Specifically, when the membrane absorbs higher amount of water, the number of exchange sites available per cluster increases, resulting in an increment in the proton conductivity [57].

Impedance spectroscopy is performed to investigate the conductivity of F- $\text{TiO}_2\text{-NT}$ at different temperatures. Typical impedance spectra are shown in Fig. 6 in which the data exhibit high frequency, depressed semicircle, and the often observed low-frequency tail, indicative of ionic conductivity. The DC resistance of each sample is read from the low-frequency intercept of the semicircular arc with the real axis or by curve-fitting a semicircular arc to the data. From Fig. 6, the F- $\text{TiO}_2\text{-NT}$ at 20 °C exhibits a larger resistance than that at 80 °C.

Fig. 7 shows the proton conductivity of the unmodified and functionalized $\text{TiO}_2\text{-NT}$ at 100% relative humidity and

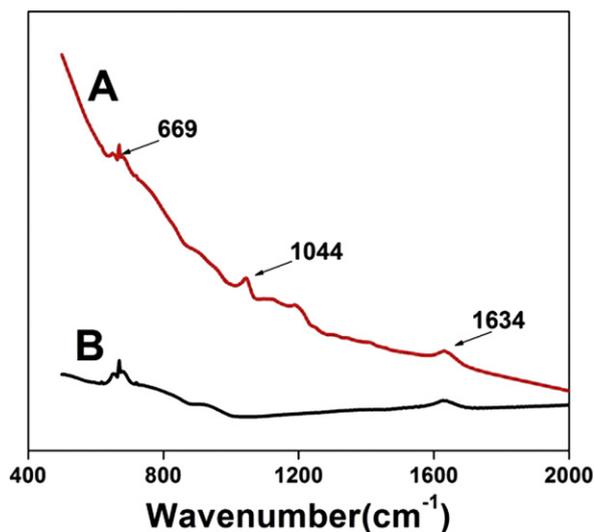


Fig. 2 – FT-IR spectra of (A) F- $\text{TiO}_2\text{-NT}$ and (B) $\text{TiO}_2\text{-NT}$.

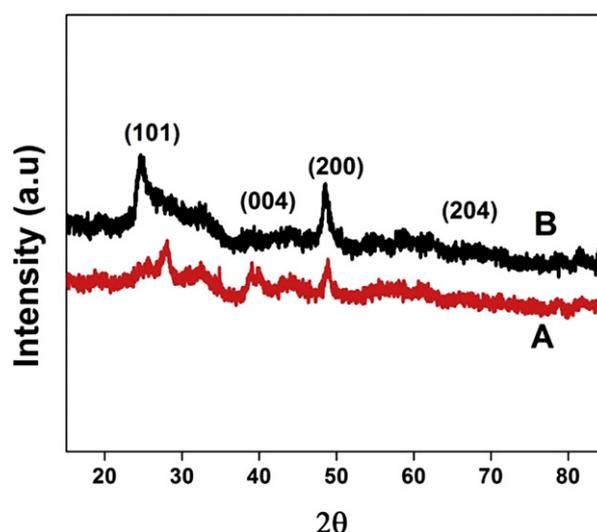


Fig. 3 – XRD of (A) F- $\text{TiO}_2\text{-NT}$ and (B) $\text{TiO}_2\text{-NT}$.

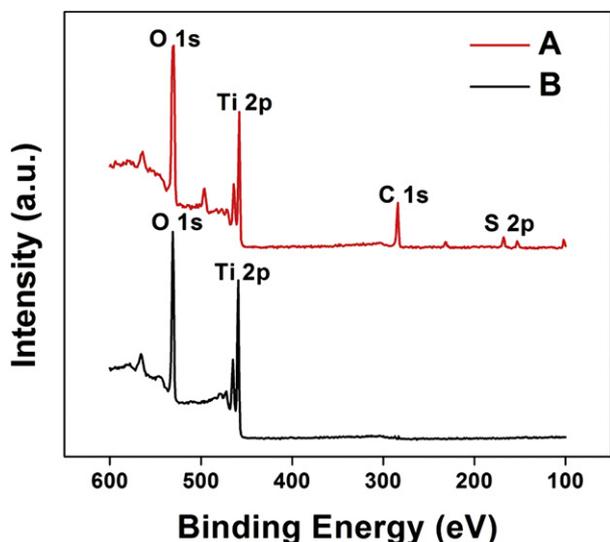


Fig. 4 – XPS survey spectra of (A) F-TiO₂-NT and (B) TiO₂-NT.

different temperatures. It can be seen that by raising the temperature from 20 °C to 80 °C the proton conductivity of TiO₂-NT has not considerably changed (~0.0011 S/cm). However, the conductivity of the F-TiO₂-NT has increased from 0.013 to 0.08 S/cm as a result of this temperature increase. It is believed that the sulfonic acid groups have strongly affected this change. Thereby, this beneficial improvement can pave the way for significant enhancements in PEMFC efficiencies at higher temperatures.

Fig. 8 indicates that after functionalization the conductivity of TiO₂-NT (0.08 S/cm) is much higher than titania nanoparticles (0.03 S/cm) at 80 °C and 100% humidity. This is due to the significantly higher specific surface area of the TiO₂-NT, that when functionalized, can anchor a higher number of sulfuric acid groups compared to titania nanoparticles. Therefore, the F-TiO₂-NT shows a higher overall proton conductivity.

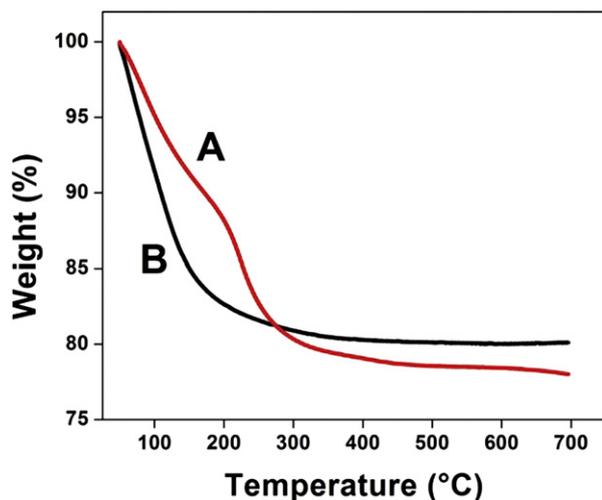


Fig. 5 – TGA of (A) F-TiO₂-NT and (B) TiO₂-NT.

Table 1 – Membrane water uptake values at 25 °C.

Type of membrane	Water uptake (%)	Standard deviation
5 wt.% F-TiO ₂ -NT/Nafion	27.18	±0.2075
5 wt.% F-TiO ₂ -NP/Nafion	23.72	±0.3202
Recast nafion	25.53	±0.2347
Nafion 112	20.19	±0.3294

Fig. 9 is the Arrhenius plot of the unmodified and functionalized TiO₂-NT, illustrating the temperature dependence of proton conductivity. It is seen that at 100% relative humidity level, ion conductivities increased with increasing temperature, however, that for F-TiO₂-NT was much higher compared to TiO₂-NT. Moreover, the conductivity of F-TiO₂-NT showed an Arrhenius behavior (Eq. (3)), while that of TiO₂-NT displayed some deviation from the trend. This shows that after functionalization, TiO₂-NT has high and relatively stable proton conductivity; i.e. the natural logarithm of conductivity for F-TiO₂-NT increases more linearly with temperature rise than that for non-functionalized TiO₂-NT. The natural logarithmic form of the Arrhenius equation is as follows:

$$\ln(\sigma) = \ln(A) - \frac{E_a}{RT} \quad (3)$$

where σ , A , E_a , R and T represent ion conductivity, exponential prefactor, activation energy, gas constant and temperature, respectively. The activation energy (E_a), the minimum energy required for proton transport across the membrane, can be calculated from Eq. (3):

$$E_a = -S \times P_A \quad (4)$$

where P_A and S are the Arrhenius parameter and the slope of the line in Fig. 9, respectively. According to Eq. (4), the activation energies of proton conduction in TiO₂-NT and F-TiO₂-NT were calculated to be 51.34 and 26.95 kJ/mol, respectively. As it is seen, there is a significant decrease in the

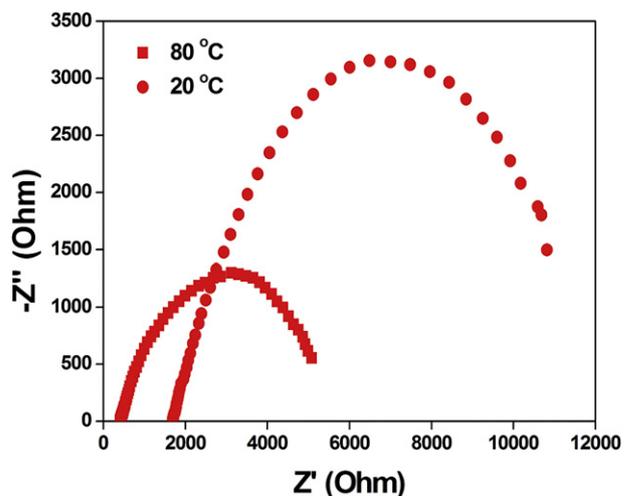


Fig. 6 – The Nyquist plot of the impedance spectrum of F-TiO₂-NT at (■) 80 °C and (●) 20 °C with 100% relative humidity.

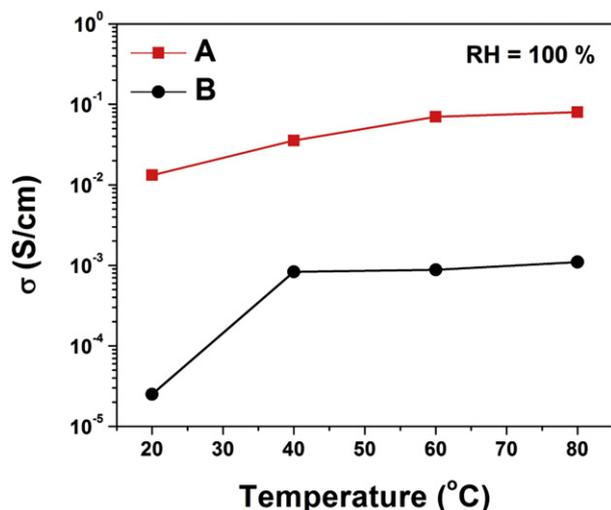


Fig. 7 – Proton conductivity of (A) F-TiO₂-NT and (B) TiO₂-NT at different temperatures and the relative humidity (RH) of 100%.

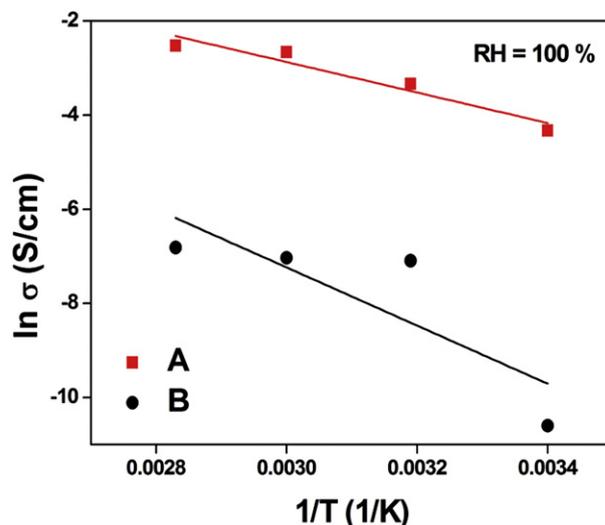


Fig. 9 – Arrhenius plot for the conductivity of (A) F-TiO₂-NT and (B) TiO₂-NT at 100% relative humidity.

activation energy of conductivity in F-TiO₂-NT, suggesting that the proton conduction is more facile with the presence of sulfonic acid groups in titania nanotubes which can enhance the transport of protons in composite membranes [58].

So far it has been shown that after functionalization, the TiO₂-NT possesses very good proton conductivity. In order to ensure that this can be demonstrated for the F-TiO₂-NT/Nafion composite membrane, the proton conductivity of both pure Nafion and F-TiO₂-NT/Nafion composite membranes was measured at different relative humidity and temperature. Figs. 10–12 show the membrane conductivity at 80 °C, 100 °C and 120 °C, respectively. The relative humidity range was from 20 to 100% at 80 and 100 °C; and from 20 to 50% at 120 °C. In Figs. 10–12, it can be seen that at

high relative humidity, both pure and composite Nafion membranes show good proton conductivity, where the conductivity of the composite membrane is always a little bit higher than the pure Nafion. However, at low relative humidity (20–40%), the F-TiO₂-NT composite membrane shows better proton conductivity compared to the pure one. This difference becomes larger at higher temperatures, at 120 °C and 30% relative humidity, the proton conductivity for F-TiO₂-NT/Nafion composite membrane is 0.067 S/cm, while pure Nafion is only 0.012 S/cm.

F-TiO₂-NT/Nafion composite membranes demonstrate a significant improvement over the unmodified one at low humidity and high temperature. The increase in conductivity can be attributed to the high specific area (greater number of protonated sites per unit mass of powder in the membrane) and good water retention of hydrophilic F-TiO₂-NT which result in higher conductivity comparing to the bare Nafion.

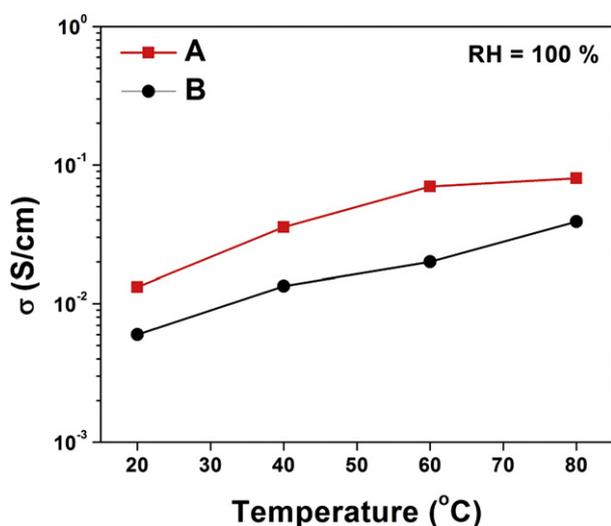


Fig. 8 – Proton conductivity of (A) F-TiO₂-NT and (B) F-TiO₂-NP at different temperatures and the relative humidity (RH) of 100%.

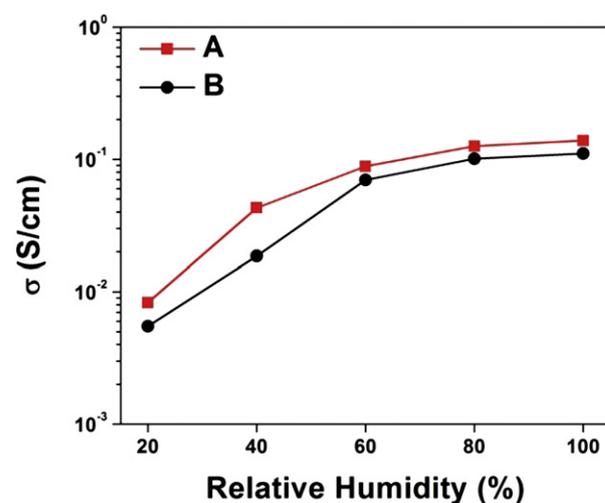


Fig. 10 – Proton conductivity of (A) F-TiO₂-NT/Nafion composite membrane and (B) recast Nafion membrane at 80 °C.

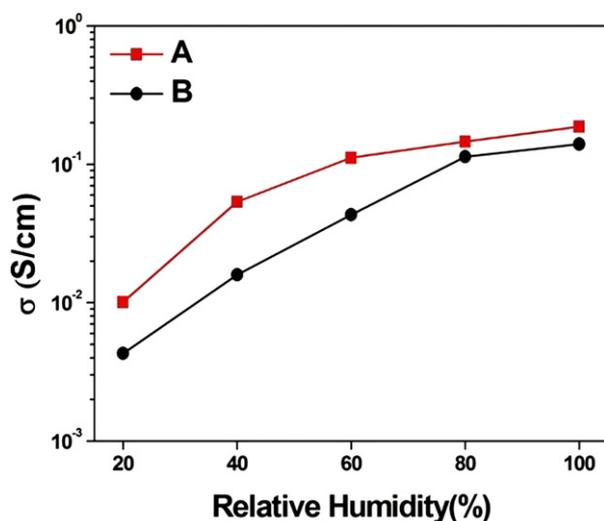


Fig. 11 – Proton conductivity of (A) F-TiO₂-NT/Nafion composite membrane and (B) recast Nafion membrane at 100 °C.

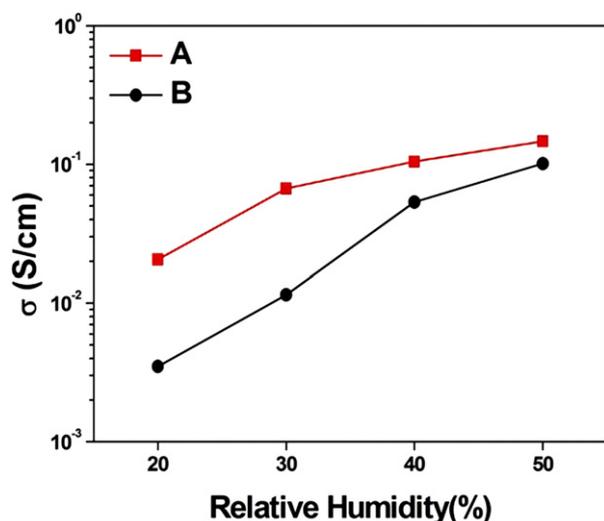


Fig. 12 – Proton conductivity of (A) F-TiO₂-NT/Nafion composite membrane and (B) recast Nafion membrane at 120 °C.

4. Conclusions

The sulfonic acid group was successfully grafted to the TiO₂-NT by using MPTMS as the sulfonic acid precursor. Proton conductivity tests indicated that the functionalized TiO₂-NT had a much higher conductivity than the unmodified one. At the temperature of 80 °C, the conductivity of F-TiO₂-NT was as high as 0.08 S/cm. By incorporating the F-TiO₂-NT into a Nafion membrane, the sulfonic acid groups of F-TiO₂-NT enhanced the conductivity of the composite membrane. The higher conductivity of F-TiO₂-NT increased

the proton conductivity of the composite membrane at higher temperatures and low relative humidity compared to pure Nafion. At 120 °C and a relative humidity of 30%, the proton conductivity for the composite membrane was 0.067 S/cm, whereas for a pure Nafion membrane a proton conductivity of only 0.012 S/cm was found. In conclusion, F-TiO₂-NT/Nafion composite membranes are presented as a potential proton exchange membrane replacement for high temperature PEMFC applications at low humidity values. Further investigations are still required in order to determine other important effects of F-TiO₂-NT/Nafion composite membranes at high temperature, including fuel cell testing.

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REFERENCES

- [1] Yilanci A, Dincer I, Ozturk H. Performance analysis of a PEM fuel cell unit in a solar-hydrogen system. *Int J Hydrogen Energy* 2008;33:7538–52.
- [2] Vielstich W, Lamm A, Gasteiger H. *Handbook of fuel cells: fundamentals, technology, applications*, vol. 4; 2003.
- [3] Peighambaroust S, Rowshanzamir S, Amjadi M. Review of the proton exchange membranes for fuel cell applications. *Int J Hydrogen Energy* 2010;35:9349–84.
- [4] Savadogo O. Emerging membranes for electrochemical systems* 1: part II. High temperature composite membranes for polymer electrolyte fuel cell (PEFC) applications. *J Power Sources* 2004;127:135–61.
- [5] Aksoy E, Akata B, Bac N, Hasirci N. Preparation and characterization of zeolite beta-polyurethane composite membranes. *J Appl Polym Sci* 2007;104:3378–87.
- [6] Li Q, He R, Jensen J, Bjerrum N. Approaches and recent development of polymer electrolyte membranes for fuel cells operating above 100 °C. *Chem Mater* 2003;15:4896–915.
- [7] Licocchia S, Traversa E. Increasing the operation temperature of polymer electrolyte membranes for fuel cells: from nanocomposites to hybrids. *J Power Sources* 2006;159:12–20.
- [8] Arico A, Baglio V, Di Blasi A, Creti P, Antonucci PL, Antonucci V. *Solid State Ionics* 2003;161:251.
- [9] Adjemian K, Dominey R, Krishnan L, Ota H, Majsztrik P, Zhang T, et al. Function and characterization of metal oxide-nafion composite membranes for elevated-temperature H₂/O₂ PEM fuel cells. *Chem Mater* 2006;18:2238–48.
- [10] Nagarale R, Shin W, Singh P. Progress in ionic organic-inorganic composite membranes for fuel cell applications. *Polym Chem* 2009;1:388–408.
- [11] Adjemian K, Lee S, Srinivasan S, Benziger J, Bocarsly A. Silicon oxide nafion composite membranes for proton-exchange membrane fuel cell operation at 80–140 °C. *J Electrochem Soc* 2002;149:A256.
- [12] Jalani N, Dunn K, Datta R. Synthesis and characterization of Nafion-MO₂ (M = Zr, Si, Ti) nanocomposite membranes for higher temperature PEM fuel cells. *Electrochim Acta* 2005;51:553–60.

- [13] Sacc A, Gatto I, Carbone A, Pedicini R, Passalacqua E. ZrO₂-nafion composite membranes for polymer electrolyte fuel cells (PEFCs) at intermediate temperature. *J Power Sources* 2006;163:47–51.
- [14] Sahu A, Selvarani G, Pitchumani S, Sridhar P, Shukla A. A sol-gel modified alternative nafion-silica composite membrane for polymer electrolyte fuel cells. *J Electrochem Soc* 2007;154: B123.
- [15] Uchida H, Ueno Y, Hagihara H, Watanabe M. Self-humidifying electrolyte membranes for fuel cells. *J Electrochem Soc* 2003;150:A57.
- [16] Chen Z, Holmberg B, Li W, Wang X, Deng W, Munoz R, et al. Nafion/zeolite nanocomposite membrane by in situ crystallization for a direct methanol fuel cell. *Chem Mater* 2006;18:5669–75.
- [17] Lin Y, Yen C, Ma C, Liao S, Lee C, Hsiao Y, et al. High proton-conducting Nafion[®]-SO₃H functionalized mesoporous silica composite membranes. *J Power Sources* 2007;171:388–95.
- [18] Tominaga Y, Hong I, Asai S, Sumita M. Proton conduction in nafion composite membranes filled with mesoporous silica. *J Power Sources* 2007;171:530–4.
- [19] Wilhelm M, Jeske M, Marschall R, Cavalcanti W, Tölle P, Köhler C, et al. New proton conducting hybrid membranes for HT-PEMFC systems based on polysiloxanes and SO₃H-functionalized mesoporous Si-MCM-41 particles. *J Membr Sci* 2008;316:164–75.
- [20] Tang H, Pan M. Synthesis and characterization of a self-assembled nafion/silica nanocomposite membrane for polymer electrolyte membrane fuel cells. *J Phys Chem C* 2008;112:11556–68.
- [21] D'Epifanio A, Navarra M, Weise F, Mecheri B, Farrington J, Licocchia S, et al. Composite nafion/sulfated zirconia membranes: effect of the filler surface properties on proton transport characteristics. *Chem Mater* 2009;22:813–21.
- [22] Wang H, Holmberg B, Huang L, Wang Z, Mitra A, Norbeck J, et al. Nafion-bifunctional silica composite proton conductive membranes. *J Mater Chem* 2002;12:834–7.
- [23] Jian-hua T, Peng-fei G, Zhi-yuan Z, Wen-hui L, Zhong-qiang S. Preparation and performance evaluation of a Nafion-TiO₂ composite membrane for PEMFCs. *Int J Hydrogen Energy* 2008;33:5686–90.
- [24] Ke C, Li X, Shen Q, Qu S, Shao Z, Yi B. Investigation on sulfuric acid sulfonation of in-situ sol-gel derived nafion/SiO₂ composite membrane. *Int J Hydrogen Energy* 2011;36: 3606–13.
- [25] Pan J, Zhang H, Chen W, Pan M. Nafion-zirconia nanocomposite membranes formed via in situ sol-gel process. *Int J Hydrogen Energy* 2010;35:2796–801.
- [26] Baglio V, Di Blasi A, Aricò A, Antonucci V, Antonucci P, Trakanprapai C, et al. Composite mesoporous titania Nafion-based membranes for direct methanol fuel cell operation at high temperature. *J Electrochem Soc* 2005;152:A1373.
- [27] Li Y, Somorjai G. Nanoscale advances in catalysis and energy applications. *Nano Lett*; 2010:1.
- [28] Shao Z, Xu H, Li M, Hsing I. Hybrid nafion-inorganic oxides membrane doped with heteropolyacids for high temperature operation of proton exchange membrane fuel cell. *Solid State Ionics* 2006;177:779–85.
- [29] Chalkovaa E, Wang C, Komarneni S, Lee J, Fedkin M, Lvov S. Composite proton conductive membranes for elevated temperature and reduced relative humidity PEMFC. *ECS Trans*; 2009.
- [30] Kalappa P, Lee J. Proton conducting membranes based on sulfonated poly (ether ether ketone)/TiO₂ nanocomposites for a direct methanol fuel cell. *Polym Int* 2007;56:371–5.
- [31] Gnana Kumar G, Kim A, Suk Nahm K, Elizabeth R. Nafion membranes modified with silica sulfuric acid for the elevated temperature and lower humidity operation of PEMFC. *Int J Hydrogen Energy*; 2009.
- [32] Kannan R, Kakade B, Pillai V. Polymer electrolyte fuel cells using nafion-based composite membranes with functionalized carbon nanotubes. *Angew Chem Int Ed* 2008; 47:2653–6.
- [33] McKeen J, Yan Y, Davis M. Proton conductivity in sulfonic acid-functionalized zeolite beta: effect of hydroxyl group. *Chem Mater* 2008;20:3791–3.
- [34] McKeen J, Yan Y, Davis M. Proton conductivity of acid-functionalized zeolite beta, MCM-41, and MCM-48: effect of acid strength. *Chem Mater* 2008;20:5122–4.
- [35] Sun X, Li R, Zhou Y, Cai M, Liu H. one-dimensional metal and metal oxide nanostructures. WO Patent WO/2008/031,005; 2008.
- [36] Kelarakis A, Alonso R, Lian H, Burgaz E, Estevez L, Giannelis E. Nanohybrid nafion membranes for fuel cells. In: Wang Q, Zhu L, editors. *Functional Polymer Nanocomposites for Energy Storage and Conversion*. American Chemical Society; 2010. p. 171–85.
- [37] Matos B, Aricó E, Linardi M, Ferlauto A, Santiago E, Fonseca F. Thermal properties of Nafion-TiO₂ composite electrolytes for PEM fuel cell. *J Therm Anal Calorim* 2009;97: 591–4.
- [38] Ou H, Lo S. Review of titania nanotubes synthesized via the hydrothermal treatment: fabrication, modification, and application. *Separ Purif Technol* 2007;58:179–91.
- [39] Yuan Z, Su B. Titanium oxide nanotubes, nanofibers and nanowires. *Colloids Surf A: Physicochem Eng Aspects* 2004; 241:173–83.
- [40] Thorne A, Kruth A, Tunstall D, Irvine J, Zhou W. Formation, structure, and stability of titanate nanotubes and their proton conductivity. *J Phys Chem B* 2005;109: 5439–44.
- [41] Chen W, Wu J, Kuo P. Poly (oxyalkylene) diamine-functionalized carbon nanotube/perfluorosulfonated polymer composites: synthesis, water state, and conductivity. *Chem Mater* 2008;20:5756–67.
- [42] Kasuga T, Hiramatsu M, Hoson A, Sekino T, Niihara K. Formation of titanium oxide nanotube. *Langmuir* 1998;14: 3160–3.
- [43] Wang L, Yang M, Shi Z, Chen Y, Feng J. Two-dimensional metal-organic framework constructed from 4, 4'-bipyridine and 1, 2, 4-benzenetricarboxylate: synthesis, structure and magnetic properties. *J Solid State Chem* 2005; 178:3359.
- [44] Lucky R, Sui R, Lo J, Charpentier P. Effect of solvent on the crystal growth of one-dimensional ZrO₂-TiO₂ nanostructures. *Cryst Growth Des* 2010;10:1598–604.
- [45] Matos B, Santiago E, Fonseca F, Linardi M, Lavayen V, Lacerda R, et al. Nafion-titanate nanotube composite membranes for pemfc operating at high temperature. *J Electrochem Soc* 2007;154:B1358.
- [46] Park S, Yoo J. Peer reviewed: electrochemical impedance spectroscopy for better electrochemical measurements. *Anal Chem* 2003;75:455–61.
- [47] Pavasupree S, Ngamsinlapasathian S, Suzuki Y, Yoshikawa S. One-dimensional nanostructured TiO₂ for photocatalytic activity and dye-sensitized solar cells applications. In: *The 2nd Joint International Conference on Sustainable Energy and Environment*; 2006 Nov 21–23, Bangkok, Thailand.
- [48] Morgado Jr E, de Abreu M, Moure G, Marinkovic B, Jardim P, Araujo A. Characterization of nanostructured titanates obtained by alkali treatment of TiO₂-anatases with distinct crystal sizes. *Chem Mater* 2007;19:665–76.
- [49] Majsztzik P, Satterfield M, Bocarsly A, Benziger J. Water sorption, desorption and transport in nafion membranes. *J Membr Sci* 2007;301:93–106.

- [50] Hensley J, Way J. The relationship between proton conductivity and water permeability in composite carboxylate/sulfonate perfluorinated ionomer membranes. *J Power Sources* 2007;172:57–66.
- [51] Holmberg B, Yan Y. An apparatus for direct proton conductivity measurement of powdered materials. *J Electrochem Soc* 2006;153:A146.
- [52] Mikhailenko S, Guiver M, Kaliaguine S. Measurements of PEM conductivity by impedance spectroscopy. *Solid State Ionics* 2008;179:619–24.
- [53] Sone Y, Ekdunge P, Simonsson D. Proton conductivity of nafion 117 as measured by a four electrode AC impedance method. *J Electrochem Soc* 1996;143:1254.
- [54] Lee C, Park H, Lee Y, Lee R. Importance of proton conductivity measurement in polymer electrolyte membrane for fuel cell application. *Ind Eng Chem Res* 2005;44:7617–26.
- [55] Byrne M, McCarthy J, Bent M, Blake R, Gun'ko Y, Horvath E, et al. Chemical functionalisation of titania nanotubes and their utilisation for the fabrication of reinforced polystyrene composites. *J Mater Chem* 2007;17:2351–8.
- [56] Lin Y, Wang L, Chiu W. Preparation and characterization of titania nanotubes and hybrid materials derived from them. *J Vac Sci Technol B: Microelectron Nanometer Struct* 2005;23:2398.
- [57] Zawodzinski Jr T, Derouin C, Radzinski S, Sherman R, Smith V, Springer T, et al. Water uptake by and transport through nafion 117 membranes. *J Electrochem Soc* 1993;140:1041.
- [58] Xu K, Chanthad C, Gadinski M, Hickner M, Wang Q. Acid-functionalized polysilsesquioxane- nafion composite membranes with high proton conductivity and enhanced selectivity. *ACS Appl Mater Interfaces* 2009;1: 2573–9.