

Preparation and Characterization of TiO₂ Filled Sulfonated Poly(ether ether ketone) Nanocomposite Membranes for Direct Methanol Fuel Cells

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Abstract - A series of inorganic-organic hybrid membranes were prepared with a systematic variation of titanium dioxide nanoparticle content. Their water uptake, methanol permeability and proton conductivity as a function of temperature were investigated. The results obtained show that the inorganic oxide network decreases the proton conductivity and water swelling. It is also found that increase in inorganic oxide content leads to decrease of methanol permeability. In terms of the morphology, membranes are homogeneous and exhibit good adhesion between inorganic domains and the polymer matrix. The properties of the composite membranes are compared with the standard nafion membrane.

Keywords: Sulfonated Poly Ether Ether Ketone, Membrane, Direct Methanol Fuel Cell, TiO₂

1. Introduction

In the last decade, direct methanol fuel cells (DMFC) have attracted considerable attention, since they offer numerous potential benefits, such as high efficiency, high power density, low or zero emission and reliability[1-3]. However, the crossover of methanol through the electrolyte membrane in DMFC still restricts their performance and applications. The methanol crossover to the cathode not only reduces the fuel efficiency, but also increases the over potential of the cathode, resulting in inferior cell performance[4]. Although perfluorinated membranes such as Nafion® or Flemion® are highly suitable for hydrogen fuel cells, they are not suitable for DMFC applications due to their very high cost, loss of conductivity at high temperature(>80°C), and high methanol and water permeability[5-6]. Several methods for nafion® modifications were reported such as substituting a part of H⁺ in nafion 117 with Cs⁺ ions[7], or treating an ionomer with plasma etch or palladium sputter[8]. Another direction is the development of polymer/inorganic oxide composite membranes[9-10]. In recent work it has been shown that

SPEEK is very promising for fuel cell applications as it possesses good thermal stability, mechanical strength and adequate conductivity[11-14]. The single phase pure polymer can be modified by the incorporation of finely dispersed solid oxide components. The present work aims at the characterization of novel organic-inorganic nanocomposite membranes with an extended range of titanium oxide contents (2.5 –12.5 wt.%) and the obtained results were compared with the standard nafion 115® performance.

2. Experimental

2.1 Chemicals and Materials

PEEK 450PF was purchased from Victrex®. Ti(OiPr)₄, sulfuric acid (95-98% pure), N-methyl pyrrolidone and ethanol were supplied by Aldrich Chemical Corporation.

2.1.1 Preparation of Polymer Nanocomposite Membranes

a. Preparation of Nanosized Titanium Oxide

Nanosized titanium oxide was synthesized by sol-gel method according to a procedure reported elsewhere[15]. Titanium isopropoxide, Ti(OiPr)₄ (8 mL 27 mmol) dissolved in absolute ethanol (82 mL) under nitrogen was added drop by drop to 250 mL of a solution of ethanol/water 1:1 under rapid stirring for 10 minutes, then filtered to obtain a white precipitate, which was air dried (100-100°C) for 15 hours.

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b. Preparation of sulfonated PEEK

Earlier reports by Lei *et al.* [13] indicate that SPEEK polymer can be used if the degree of sulfonation above 60% is not suitable for DMFC application. Therefore, Poly(ether ether ketone) (SPEEK) was sulfonated up to a sulfonation degree of 57% according to the procedure reported elsewhere [13]. The SPEEK to be sulfonated is the SPEEK 450PF supplied by Victrex in powder form, dried in a vacuum oven at 100°C overnight. Concentrated sulfuric acid (98% extra pure, as received) is heated to 55°C. An amount of 60 g SPEEK powder is dissolved carefully by adding small portions to one liter of the stirred acid. The reaction mixture is stirred for up to 7 hours at controlled temperature to achieve the desired conversion. Immersing the reaction vessel in an ice bath stops the reaction. The polymer is precipitated in demineralized water of maximum 5°C and washed until the pH is nearly 7. Then the polymer is dried subsequently on the lab table and in an oven at 100°C. The degree of sulfonation (the fraction of repeat units bearing a --SO₃H groups) of SPEEK was determined by titration: 1-2 grams of SPEEK was kept in 0.5M aqueous NaOH for 1 day and then was back titrated with 1M HCl using phenolphthalein as an indicator.

c. Membrane Preparation

Dried SPEEK powder was mixed with N-methyl pyrrolidone to make 10 wt.% solution in an ultrasonic bath to which desired weight percentage of TiO₂ powder was added, and the slurry was cast over a glass substrate heated to 70°C for solvent evaporation. Then, the membranes were stored in a vacuum oven for 24 h at 90°C. The thickness of the prepared membranes with 0.0, 2.5, 5.0, 7.5, 10.0 and 12.5 wt.% were 75, 86, 93, 96 and 88µm respectively.

2.1.2 Characterization Methods

a. Water Uptake

Water uptake measurements were taken in batch process at room temperature. Before measurements, the membranes were dried in a vacuum oven at 120°C for 24 h. Weighed films with an area of 20mm X 20mm were immersed in demineralized water at room temperature for 24 h. The membranes were saturated with water until no further weight gain was observed. The liquid water on the surface of wetted membranes was removed using tissue paper before weighing. The change in weight of films was recorded. The percentage weight gain with respect to the original membrane weight was taken as water uptake. Each sample was tested with three specimens, and the average of three test results was tabulated.

b. Conductivity Measurement

The proton conductivity of the samples was measured by AC impedance spectroscopy over a frequency range 10-10⁷ Hz with 50-500mV oscillating voltage, using a Solatron analyzer. Films 13mm in diameter, sandwiched between two stainless steel electrodes with a contacting area of 25 mm², connected from the FRA, horizontally pressed the membrane to be tested. The measured temperature was controlled from room temperature to 80°C.

The conductivity was calculated from the impedance data, using the relation

$$\sigma = l/RS$$

where *l* and *s* are the thickness and area of the membrane, respectively, and *R* was derived from the low intersect of the high frequency semi circle on a complex impedance plane with the Re(*z*) axis.

c. Water and Methanol Permeation Measurements.

Water and methanol permeability coefficients were evaluated from pervaporation measurements using a differential refractometer at room temperature with a 1 M methanol solution. The permeability *P* was calculated from the slope of the straight-line plot of methanol concentration vs. permeation time. The water/methanol selectivity of the composite membranes was obtained as the ratio between water and methanol permeability coefficients. Prior to all measurements, samples were immersed in deionized water at room temperature for 3 days.

d. Membrane Morphology

The membrane morphology was investigated by field emission scanning electron microscopy in a JEOL 6400F apparatus. The samples were coated with carbon for observation by microscope.

3. Results and Discussion

3.1 Water uptake

The water content of the SPEEK/TiO₂ composite membranes and the Nafion membranes are shown in Fig. 1. The water content of the Nafion membrane in our experiments was 21.6 wt.%, which is similar to values given in Ref. 13. The sulfonated composite membranes indicated higher water content than the Nafion membrane, presumably due to the higher sulfonic acid content with its strong affinity to water. The water content of the composite membranes decreased with the increasing incorporation of titanium dioxide nano particles, because inorganic nano particles reduce the membrane free volume and the swelling ability.

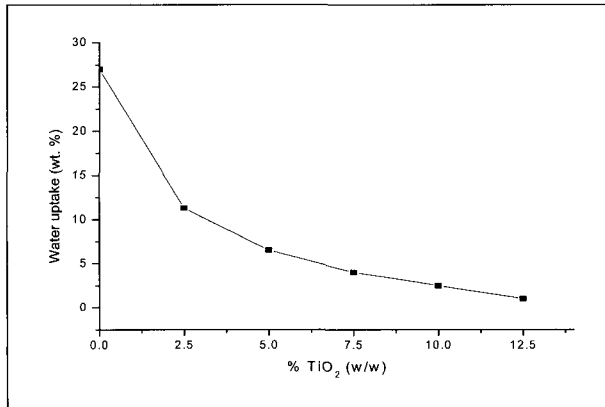


Fig. 1 Water uptake of SPEEK composite membranes as a function of the TiO₂ weight percentage

These results indicate that the water content, which greatly influences the methanol crossover, can be controlled by the addition of nano TiO₂ particles. Comparing the water uptake studies and the corresponding proton conductivity (Fig. 2), higher water uptake leads to higher proton conductivity, showing the importance of sorbed water in the proton conductivity of sulfonated membranes, in agreement with previous studies (16).

3.2 Conductivity Measurements

Fig. 2 shows the effects of the titanium oxide incorporation in the SPEEK polymer. The conductivity of the composite membranes decreases continuously with the increase in inorganic content. It can be observed that proton transport resistance increases with the amount of inorganic filler. It is worth noting that for the membrane with the highest content of inorganic incorporation (12.5 wt.% TiO₂), the resistance becomes very high. It would thus be useful to explore experimentally how much each membrane can absorb water and how the proton conductivity in the composite membranes is affected by the amount of water uptake. It was reported that the proton conductivity is related to the ion cluster formation and water uptake content [17]. Therefore low conductivity in the SPEEK/12.5 wt.% TiO₂ composite membrane can be related to the insufficient water content. However, lower water uptake content in composite membranes can also decrease methanol crossover.

As expected, proton conductivity of the composite membranes increases with temperature, relating to high thermal stability in the structure and sulfonic group. This can lead us to the tentative conclusion that incorporation of high thermal stable TiO₂ particles increased thermal stability in the main backbone, suppressing transformation from the unassociated sulfonic groups and obstructing dehydration of water even at high temperature in the composite membranes. However, the decrease of the proton

conductivity with increase in filler content is believed to derive mainly from the increased barrier properties of the membranes due to the incorporation of inorganic fillers [18].

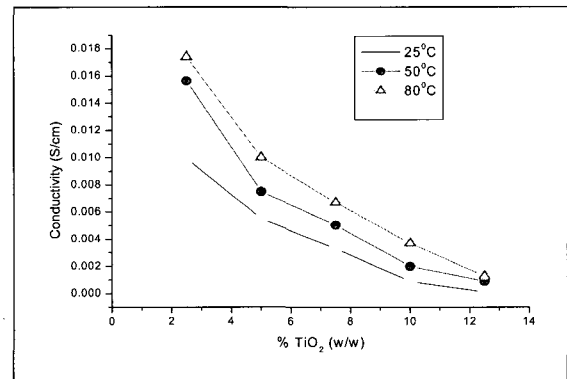


Fig. 2 Proton Conductivity of the membranes as a function of the TiO₂ weight Percentage

It was additionally found that the proton conductivity of composite membranes exceeded 10^{-2} S/cm at 80°C, which is close to the Nafion® 115 membrane under the same condition.

3.3 Water and Methanol Pervaporation Measurements

Pervaporation measurements at room temperature revealed that the membrane's permeability towards methanol decreases with the amount of titanium oxide (Fig. 3). As observed previously for the water uptake and proton conductivity properties, at lower TiO₂ contents, the effects in the permeability coefficients of water and methanol are much more pronounced. Moreover, from Fig. 4, it can be observed that the titanium oxide content leads to an increase in the water/methanol selectivity. The reduced permeability towards DMFC species of the TiO₂ filled composite membranes is believed to derive from the weaker hydrophilicity of the polymer, higher concentration of rigid back scattering sites and increased tortuous pathways that molecules encounter during permeation due to the presence of inorganic particles [18]. Consequently, the barrier properties increases with the TiO₂ content, which can be assumed as an advantage for DMFC applications because it reduces the reactant loss and increases the overall fuel cell efficiency. Nevertheless, the verified proton conductivity decrease with the increase in inorganic content should also be taken into account.

The measured methanol permeability of the Nafion® 115 membrane is 2.32×10^{-6} cm²/s at room temperature. It is important to note that the methanol permeability of composite membranes is in between 0.5×10^{-6} to 2×10^{-6} cm²/s (Fig. 4), which is considerably smaller than that of the Nafion® 115 membrane.

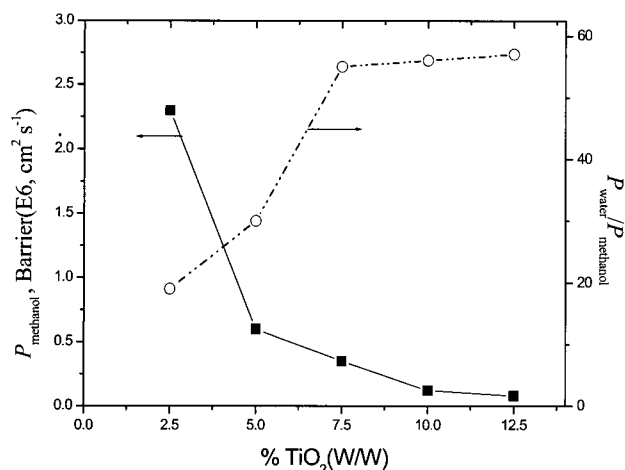


Fig. 3 Water and methanol pervaporation measurement as a function of the TiO₂ weight percentage

3.4 Microscopy

The morphological changes in the membranes are presented in Fig. 4. Fig. 4 (a) shows membranes without TiO₂ nano particles and Fig. 4 (b), 4 (c) and 4 (d) present the composite membrane with 2.5, 7.5 and 12.5 wt.% TiO₂. From the SEM micrographs it can be considered as homogeneous and dense. Higher magnification electron microscopy indicates good adhesion between inorganic fillers and the polymer matrix in lower levels of filler, and agglomeration of nanoparticles in higher levels of filler content in the polymers. It can be observed that no cavities are present and that TiO₂ particles have dimensions smaller than ~100nm.

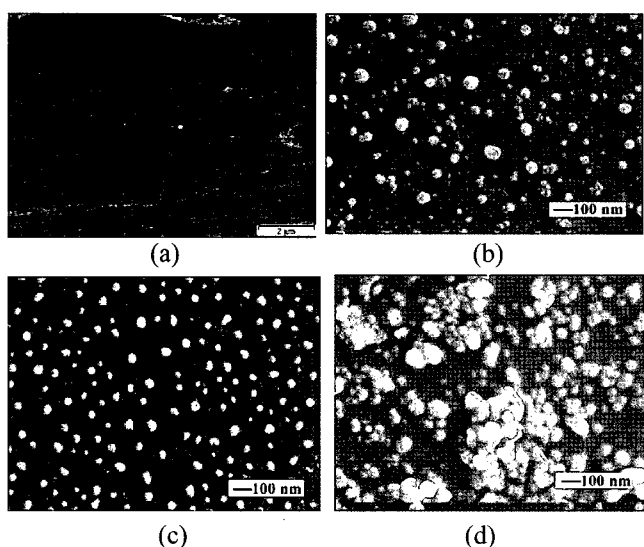


Fig. 4 Scanning electron micrograph of (a) cross section of SPEEK membrane (b) SPEEK with 2.5% of TiO₂ (c) SPEEK with 7.5% of TiO₂ (d) SPEEK with 12.5% of TiO₂

4. Conclusion

The results showed that increasing the titanium oxide content in the SPEEK composite membranes leads to a decrease of the reactant's permeability coefficients and an increase of the water/methanol selectivity. The reason for these results is related with the increasing amount of inorganic filler in the membranes, which raises the membranes barrier properties in terms of mass transport. These features are advantages for the direct methanol fuel cell performance because they prevent reactant loss and boost the PEM long-term stability. However, results showed that the titanium oxide incorporation has the detrimental effect of decreasing the proton conductivity. The micrographs obtained by scanning electron microscopy indicated a good adhesion between inorganic particle domains and the polymer matrix (no cavities) and that the particles have dimensions smaller than ~100 nm. Furthermore, the different contents of titanium oxide in the SPEEK polymer organic matrix enabled the preparation of composite membranes with a wide range of properties concerning proton conductivity, water uptake and methanol and water permeation. The proton conductivity of composite membranes exceeded 10⁻² S/cm at 80 °C, which was close to that of the Nafion® 115 membrane under the same condition and the methanol permeability of SPEEK membranes was considerably lower than that of the Nafion® 115 membrane. Therefore, these membranes can be used in the future to make a critical evaluation of the relationship between the proton electrolyte membrane properties and the DMFC performance.

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References

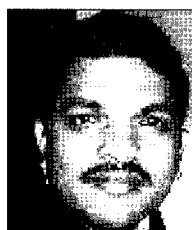
- [1] M.P. Hogarth and G.A. Hards, "Direct methanol fuel cells, technological advances and further requirements", *Platinum Met. Rev.* vol. 40, no. 4, pp. 150-162, 1996.
- [2] S. Surampudi, S.R. Narayanan, E. Vamos, H. Frank, G. Halpert, A. LaConti, J. Kosek, G.K. Surya Prakash and G.A. Olah, "Advances in direct oxidation methanol fuel cells", *J. Power Sources* vol. 47, pp. 377-385, 1994.

- [3] J. Wang, S. Wasmus and R.F. Savinell, "Evaluation of ethanol, 1-propanol, and 2-propanol in a direct oxidation polymer-electrolyte fuel cell, a real-time mass spectrometry study", *J. Electrochem. Soc.*, vol. 142, pp. 4218-4221, 1995.
- [4] A.S.Arico, S.Srinivasan and V.Antonucci, "DMFCs: From fundamental aspects to technology development", *Fuel Cell*, vol. 1, no. 2, pp. 133-135, 2001.
- [5] O. Savadogo, "Emerging membranes for electrochemical system. I. Solid polymer membranes for fuel cell systems", *J. New Mater. Electr. Syst.*, vol. 1, pp. 47-52, 1998.
- [6] G. Inzelt, M. Pineri, J.W. Schultze and M.A. Vorotyntsev, "Electron and proton conducting polymers: recent developments and prospects", *Electrochim. Acta.*, vol. 45 pp. 2403-2410, 2000.
- [7] V. Tricoli, "Proton and methanol transport in poly(perfluorosulfonate) membranes containing Cs⁺ and H⁺ cations", *J. Electrochem. Soc.*, vol. 145, pp. 3798-3805, 1998.
- [8] L. Jörissen, V. Gogel, J.Kerres and J. Garche, "New membranes for direct methanol fuel cells", *J. Power Sources*, vol. 105, no. 2, pp. 267-276, 2002.
- [9] K.T.adjemian, S.J.Lee, S.Srinivasan, J.Benziger and A.B. Bocarsly, "Silicon oxide nafion composite membranes for proton exchange membrane fuel cell operation at 80-140°C", *J. Electrochem. Soc.*, vol. 149, no. 3A, pp. 236-243, 2002.
- [10] V.S. Silva, B. Ruffmann, H. Silva, Y.A. Gallego, A. Mendas, L.M. Madeira and S.P. Nunes, Proton electrolyte membrane properties and direct methanol fuel cell performance: I. Characterization of hybrid sulfonated poly(ether ether ketone)/zirconium oxide membranes *J. Power Sources*, vol. 140, no. 10, pp. 34-38, 2005.
- [11] Suzhen Ren, Chennan Li, Xinsheng Zhao, Zhimo Wu, Suli Wang, Gongquan Sun, Qin Xin and Xuefeng Yang, "Surface modification of sulfonated poly(ether ether ketone) membranes using Nafion solution for direct methanol fuel cell", *J.Membr. Sci.*, vol. 247, pp. 59-65, 2005.
- [12] Peixiang Xing, Gilles P. Robertson, Michael D. Guiver, Serguei D. Mikhailenko, Keping Wang and Serge Kaliaguine. Synthesis and characterization of sulfonated poly(ether ether ketone) for proton exchange membranes *J. Membr. Sci.*, vol. 229, pp. 95-100, 2004.
- [13] Lei Li, Jun Zhang and Yuxin Wang, "Sulfonated poly(ether ether ketone) membranes for direct methanol fuel cell", *J. Membr. Sci.*, vol. 226, pp. 159-164, 2003.
- [14] S. Kaliaguine, S. D. Mikhailenko, K. P. Wang, P. Xing, G. Robertson and M. Guiver, "Properties of SPEEK based PEMs for fuel cell application", *Catalysis Today*, vol. 82, pp. 213, 2003.
- [15] V. Baglio, A.S. Aricò, A. Di Blasi, V. Antonucci, P.L. Antonucci, S. Licocchia, E. Traversa and F. Serraino Fiory. Nafion-TiO₂ composite DMFC membranes: physico-chemical properties of the filler versus electrochemical performance. *Electrochimica Acta*, vol. 50, pp. 1241-1254, 2005.
- [16] K.A. Kreuer, "On the development of proton conducting polymer membranes for hydrogen and methanol fuel cells", *J. Membr. Sci.*, vol. 185, pp. 3-8, 2001.
- [17] Lei Li, Li Xu and Yuxin Wang, "Novel proton conducting composite membranes for direct methanol fuel cell", *Mater. Lett.* Vol. 57, pp. 1406-1421, 2003.
- [18] B.Kumar, J.P.Fellner, Polymer-Ceramic composite protonic conductors. *J.Power Sources*, vol. 123, pp. 132-140, 2003.



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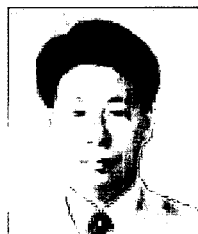
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