

# Nanosized TiO<sub>2</sub>-Filled Sulfonated Polyethersulfone Proton Conducting Membranes for Direct Methanol Fuel Cells

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**ABSTRACT:** This paper presents an evaluation of the effect of titanium dioxide nanoparticles in sulfonated polyethersulfone with sulfonation degree of 70%. A series of inorganic-organic hybrid membranes was prepared with a systematic variation of titanium dioxide nanoparticles content. Their water uptake, methanol permeability, and proton conductivity as a function of temperature were investigated. The results show that the inorganic oxide network decreases the proton conductivity and water swelling. Increase in in-

organic oxide content leads to decrease of methanol permeability. In terms of morphology, membranes are homogeneous and exhibit good adhesion between inorganic domains and the polymer matrix. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 98: 1875-1878, 2005

**Key words:** nanocomposites; membranes; polyethersulfone; morphology

## INTRODUCTION

In the past decade, direct methanol fuel cells (DMFC) have attracted considerable attraction, since they offer numerous potential benefits, such as high efficiency, high power density, low or zero emission, and reliability.<sup>1-3</sup> 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 overpotential of the cathode, thus resulting in lower cell performance.<sup>4</sup> Although perfluorinated membranes such as Nafion or Flemion are very 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.<sup>5,6</sup> Several methods for Nafion modifications were reported such as substituting a part of H<sup>+</sup> in Nafion 117 with Cs<sup>+</sup> ions<sup>7</sup> or treating an ionomer with plasma etch or palladium sputter.<sup>8</sup> Another direction is the development of polymer/inorganic oxide composite membranes.<sup>9,10</sup> In recent work it has been shown that sulfonated polyethersulfone is very promising for fuel cell applications;<sup>11-14</sup> the single-phase pure polymer can be modified by the incorporation of

finely dispersed solid oxide component. The present work aims at the characterization of novel organic-inorganic nanocomposite membranes with an extended range of titanium oxide contents (2-10 wt %).

## EXPERIMENTAL

### Chemicals and materials

Polyethersulfone (Ultrason 6010) was purchased from BASF; titanium isopropoxide, i.e., Ti(OiPr)<sub>4</sub>, sulfuric acid (95-98 wt %), *N*-methyl pyrrolidone, and ethanol were supplied by Aldrich Chemical.

### Preparation of polymer nanocomposite membranes

#### Preparation of nanosized titanium oxide

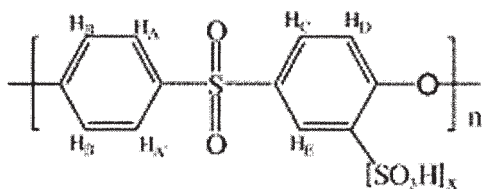
Nanosized titanium oxide was synthesized by the sol-gel method according to a procedure reported elsewhere.<sup>15</sup> Titanium isopropoxide, Ti(OiPr)<sub>4</sub> (8 mL 27 mmol) dissolved in absolute ethanol (82 mL) under nitrogen, added drop by drop to 250 mL of a solution of ethanol/water 1 : 1 under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

#### Preparation of sulfonated poly(phenylene oxide)

Recent reports by Li and Wang<sup>14</sup> indicate that sulfonated polyethersulfone (SPES) polymer with degree of sulfonation (DS) 70% is very good for DMFC application. Therefore, polyethersulfone was sulfonated up to sulfon-

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**Figure 1** Chemical structure and atom numbering of SPES,  $x = \text{DS}$ .

ation degree of 70% according to the procedure reported elsewhere.<sup>14</sup> The sulfonated polyethersulfone samples were prepared according to the following procedure. Twenty grams of PES was added to 100 mL concentrated sulfuric acid (98%) in a three-neck reaction flask and dissolved by stirring for about 2 h at room temperature to form a homogeneous solution. Chlorosulfonic acid was transferred into a dropper and then gradually and slowly added to the PES solution while the solution was stirred at 800 rpm at 10 °C. The resulting reaction mixture was stirred for one more hour. After a determined reaction time, the mixture was gradually precipitated into ice-cold deionized water under agitation, and the resulting precipitate was recovered by filtration and washed with deionized water until the pH was 6–7.

The DS (the fraction of repeat units bearing a  $-\text{SO}_3\text{H}$  groups as shown in Fig. 1) of SPES was determined by titration: 1–2 g of SPES was kept in 0.5M aqueous NaOH for 1 day and then was back titrated with 1M HCl using phenolphthalein as an indicator.

#### Membrane preparation

Dried SPES powder was mixed with *N*-methylpyrrolidone to make 10 wt % solution in an ultrasonic bath to which the desired weight percentage of  $\text{TiO}_2$  powder was added. 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 % was 150, 125, 133, 146, 117, and 128  $\mu\text{m}$ , respectively.

#### Characterization methods

##### Water uptake

Water uptake measurements were performed 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  $20 \times 20$  mm were immersed in deionized 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 percent-

age 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.

##### Conductivity measurement

The proton conductivity of the samples was measured by AC impedance spectroscopy over a frequency range  $10\text{--}10^7$  Hz with 50–500 mV oscillating voltage, using a Solatron analyzer. Films having 13 mm diameter, sandwiched between two stainless-steel electrodes with a contacting area of 25 mm<sup>2</sup>, were connected from the FRA, horizontally pressed the membrane to be tested. The measured temperature was controlled from room temperature to 80 °C.

The conductivity ( $\sigma$ ) 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 semicircle on a complex impedance plane with the  $\text{Re}(z)$  axis.

##### Water and methanol pervaporation measurements

Water and methanol permeability coefficients were evaluated from pervaporation measurements using a differential refractometer at room temperature with a 1M methanol solution. The permeability  $P$  was calculated from the slope of the straight-line plot of methanol concentration versus 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.

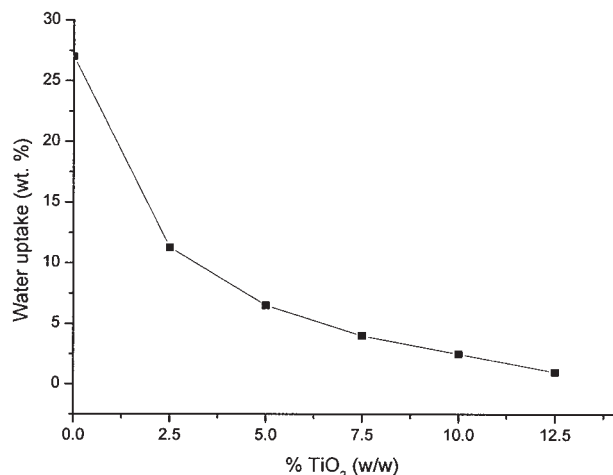
##### Membrane morphology

The membrane morphology was investigated by field emission scanning electron microscopy using Jeol 6400F equipment. The samples were coated with carbon for observation in the microscope.

## RESULTS AND DISCUSSION

### Water uptake

The water content of the SPES/ $\text{TiO}_2$  composite membranes decreases with increase in filler content (Fig. 2), presumably due to the higher sulfonic acid content with its strong affinity to water. The water content of the composite membranes decreased with increasing titanium dioxide nanoparticles incorporation, because inorganic nanoparticles reduce the membrane free volume and swelling ability. These results indicate

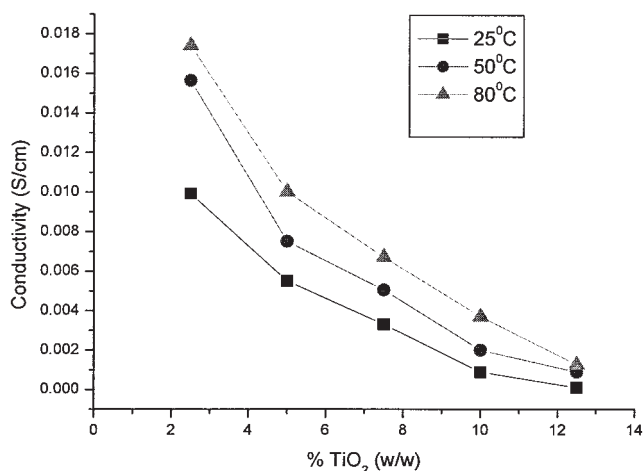


**Figure 2** Water uptake of SPPO composite membranes as a function of the TiO<sub>2</sub> weight percentage.

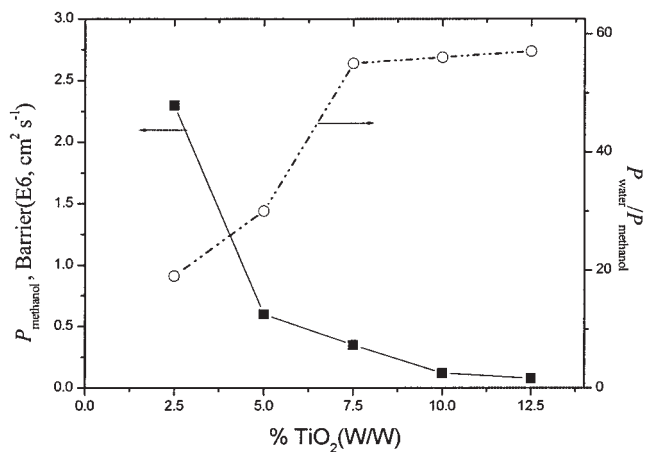
that the water content, which greatly influences the methanol crossover, can be controlled by the addition of nano TiO<sub>2</sub> particles. Comparing the water uptake studies and the corresponding proton conductivity (Fig. 2), higher water uptake leads to higher proton conductivity, showing the importance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

### Conductivity measurements

Figure 3 shows the effects of the titanium oxide incorporation in the SPES polymer. The conductivity of the composite membranes decreases continuously with 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



**Figure 3** Proton conductivity of the membranes as a function of the TiO<sub>2</sub> weight percentage.



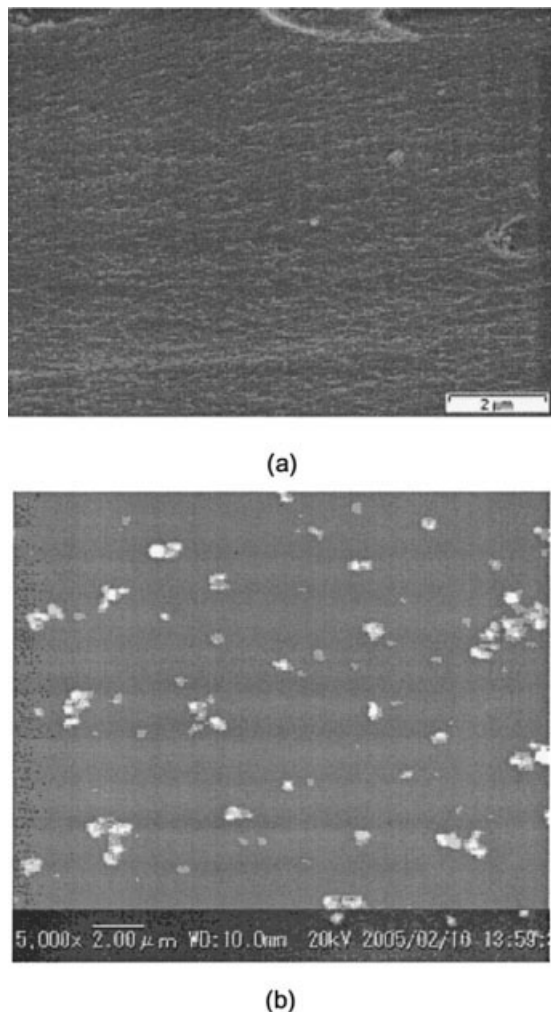
**Figure 4** Water and methanol pervaporation measurement as a function of the TiO<sub>2</sub> weight percentage.

wt % TiO<sub>2</sub>), 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.<sup>17</sup> Therefore, low conductivity in SPES/12.5 wt % TiO<sub>2</sub> composite membrane can be related to 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 TiO<sub>2</sub> particles increased thermal stability in the main backbone, suppressing transformation from the unassociated sulfonic groups and obstructing dehydration of water even at high temperatures 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.<sup>18</sup>

### Water and methanol pervaporation measurements

Pervaporation measurements at room temperature showed that the membrane's permeability toward methanol decreases with the amount of titanium oxide (Fig. 4). As observed previously for the water uptake and proton conductivity properties, at lower TiO<sub>2</sub> contents the effects in the permeability coefficients of water and methanol are much more pronounced. Moreover, from Figure 4 it can be observed that the titanium oxide content leads to an increase in water/methanol selectivity. The reduced permeability toward DMFC species of the TiO<sub>2</sub> filled composite membranes is believed to derive



**Figure 5** Scanning electron micrograph of (a) cross section of SPES membrane and (b) SPES with 2.5% TiO<sub>2</sub>.

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.<sup>18</sup> Consequently, the barrier properties increase with the TiO<sub>2</sub> content, which can be assumed to be an advantage for DMFC applications because it reduces the reactant loss and increases the overall fuel cell efficiency. Nevertheless, it should also be taken into account that the verified proton conductivity decreases with increase in inorganic content.

### Microscopy

The morphological changes in the membranes are presented in Figure 5. Figure 5(a) shows membranes without TiO<sub>2</sub> nanoparticles and Figure 5(b) shows the composite membrane with 2.5 wt % TiO<sub>2</sub>. From the SEM micrographs it can be considered homogeneous and dense. A higher magnification electron microscope shows good adhesion between inorganic fillers

and polymer matrix. No cavities are present and that TiO<sub>2</sub> particles have dimension smaller than ~100 nm.

### CONCLUSIONS

The results showed that increasing the titanium oxide content in the SPES composite membranes leads to a decrease of the reactants permeability coefficients and an increase of the water/methanol selectivity. The reason for these results is related to the increasing amount of inorganic filler in the membranes, which increases the membrane barrier properties in terms of mass transport. These features are advantageous for direct methanol fuel cell performance because they prevent reactants loss and increase the PEM long-term stability. However, results showed that titanium oxide incorporation has the detrimental effect of decreasing proton conductivity. The micrographs obtained by scanning electron microscopy showed good adhesion between inorganic particle domains and the polymer matrix (no cavities) and also demonstrated that the particles have dimensions smaller than 100 nm.

Furthermore, the different contents of titanium oxide in the SPES 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. Therefore, these membranes can be used in the future to perform a critical evaluation of the relationship between proton electrolyte membrane properties and DMFC performance.

### References

- Hogarth, M. P.; Hards, G. A. *Platinum Met Rev* 1996, 40, 150.
- Surampudi, S.; Narayanan, S. R.; Vamos, E.; Frank, H.; Halpert, G.; LaConti, A.; Kosek, J.; Surya Prakash, G. K.; Olah, G. A. *J Power Sources* 1994, 47, 377.
- Wang, J.; Wasmus, S.; Savinell, R. F. *J Electrochem Soc* 1995, 142, 4218.
- Arico, A. S.; Srinivasan, S.; Antonucci, V. *Fuel Cell* 2001, 1, 133.
- Savadogo, O. *J New Mater Electr Syst* 1998, 1, 47.
- Inzelt, G.; Pineri, M.; Schultze, J. W.; Vorotyntsev, M. A. *Electrochim Acta* 2000, 45 2403.
- Tricoli, V. *J Electrochem Soc* 1998, 145, 3798.
- Jörissen, L.; Gogel, V.; Kerres, J.; Garche, J. J. *Power Sources* 2002, 105(2), 267.
- Adjemian, K. T.; Lee, S. J.; Srinivasan, S.; Benziger, J.; Bocarsly, A. B. *J Electrochem Soc* 2002, 149(3), 256.
- Silva, V. S.; Ruffmann, B.; Silva, H.; Gallego, Y. A.; Mendas, A.; Madeira, L. M.; Nunes, S. P. *J Power Sources* 2005, 140(10), 34.
- Nolte, R.; Ledjeff, K.; Bauer, M.; Mulhaupt, R. *J Membr Sci* 1993, 83, 211.
- Kerres, J.; Cui, W.; Richie, S. *J Polym Sci Part A: Polym Chem* 1996, 34, 2421.
- Manea, C.; Mulder, M. *J Membr Sci* 2002, 206, 443.
- Li, L.; Wang, Y. *J Membr Sci* 2005, 246, 167.
- Manea, C.; Mulder, M. *Desalination* 2002, 147, 179.
- Kreuer, K. A. *J Membr Sci* 2001, 185, 3.
- Li, L.; Xu, L.; Wang, Y. *Mater Lett* 2003, 57, 1406.
- Kumar, B.; Fellner, J. P. *J Power Sources* 2003, 123, 132.