Titanium Dioxide Nanoparticles filled Sulfonated Poly(ether ether ketone) Proton Conducting Nanocomposites Membranes for Fuel Cell

Prashantha Kalappa, Chang-Eui Hong, Sung-Kwan Kim, and Joong-Hee Lee*
*Correspondent: Department of Polymer·Nano Science and Engineering, Chonbuk National University, Duckjin-dong, 1Ga 664-14, Jeonju, Jeonbuk 561-756, Korea.
e-mail: jhl@chonbuk.ac.kr

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ABSTRACT:
This paper presents an evaluation of the effect of titanium dioxide nanoparticles in sulfonated poly(ether ether ketone) (SPEEK) with sulfonation degree of 57%. A series of inorganic-organic hybrid membranes were 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 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 morphology, membranes are homogeneous and exhibit a good adhesion between inorganic domains and the polymer matrix. The properties of the composite membranes are compared with standard nafion membrane.

1 INTRODUCTION

In the last decade, direct methanol fuel cell (DMFC) have attracted a considerable attraction, 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, this resulting in lower cell performance(4). Although perflu orinated 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 and high methanol and water permeability(5-6). Several methods for nafian® modifications were reported such as substituting a part of H^+ in nafian 117 with Cs^+ ions (7), or treating a 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 possess a good thermal stability, mechanical strength and adequate conductivity (11-14). The present work aims at the characterization of novel organic-inorganic nanocomposite membranes with an extended range of titanium oxide contents (2 –10 wt.%) and the obtained results were compared with standard nafion 115® performance.

2 EXPERIMENTAL

2.1 Chemicals and Material

PEEK 450PF was purchased from Victrex®. $Ti(OiPr)_4$, sulfuric acid (95-98 wt.%) N-methyl pyrrolidone and ethanol were supplied by Aldrich Chemical Corporation

2.2Preparaation of Polymer Nanocomposite Membranes

2.2.1 Preparation of Nanosized Titanium Oxide

Nanosized titanium oxide was synthesized by sol-gel method (15). Titanium isopropoxide, (8 mL 27 m mol) 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 filter to obtain a white precipitate, which was dried in air (100-100 °C) for 15 hours.

2.2.3 Preparation of sulfonated PEEK

Poly(ether ether ketone) (SPEEK) was

sulfonated up to sulfonation degree of 57% according to the procedure reported elsewhere (13). The PEEK to be sulfonated is the PEEK 450PF supplied by Victrex in powder form. It was 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 PEEK powder is dissolved carefully by adding small portions to one liter of the stirred acid. Then immersing the reaction vessel in ice bath stops the reaction. The polymer is precipitated in demineralised 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.

2.2.4 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 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 an vacuum oven for 24 h at 90°C.

2.3 Characterization Methods

2.3.1 Water Uptake

Water uptake measurements were performed in batch process at room temperature. Weighed films with an area of 20mm X 20 mm were immersed in demonized water at room temperature for 24 h. The membranes were saturated with water until no further weight gain was observed. The change in weight of films was recorded. The percentage weight gain with respect to the original membrane weight was taken as water uptake.

2.3.2 Conductivity Measurement

The proton conductivity of the samples were measured by AC impedance spectroscopy over a frequency range 10-10^7 Hz with 50-500mV oscillating voltage, using a Solatron analyzer.

2.3.3 Water and Methanol Perevaporation Measurements.

Water and methanol permeability coefficients were evaluated from pervaparation measurements using a differential refractometer at room temperature

2.3.4 Membrane Morphology

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

3. RESULTS AND DISCUSSIONS

3.1 Water Uptake

The composite membranes showed higher water content than the Nafion membrane, presumably due to the higher sulfonic acid content with its strong affinity to water. These results indicate that the water content, which greatly influences the methanol crossover. Comparing the water uptake studies and the corresponding proton conductivity, higher water uptake leads 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

Figure 1 shows the effects of the titanium oxide incorporation in the SPEEK polymer. It is worth noting that for the membrane with the highest content of inorganic incorporation (12.5 wt.% TiO_2). It was reported that the proton conductivity is related to the ion cluster formation and water uptake content (17). Therefore low conductivity in SPEEK/12.5 wt.% TiO_2 composite membrane can be related to the insufficient water content. However, lower water uptake content in composite membranes can also decrease methanol crossover.

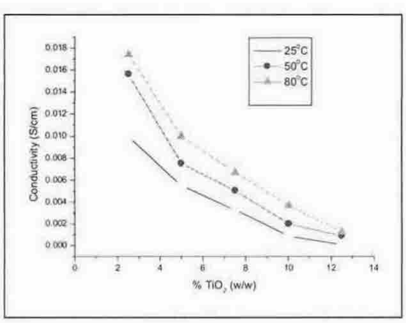

Figure. 1 Proton Conductivity of the membranes as a function of the TiO_2 weight percentage

Further it was 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 Pervaparation Measurements

Pervaparation measurements at room temperature showed that the membranes permeability towards methanol decreases with the amount of titanium oxide (Fig.2), 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 TiO_2 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 TiO_2 content, which can be assumed as an advantage for DMFC.

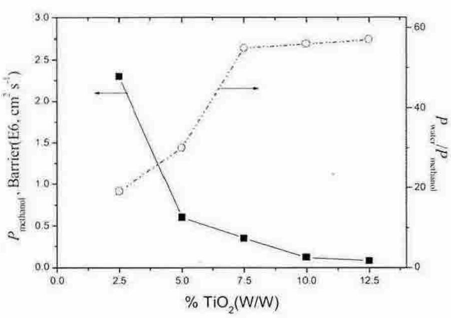

Figure.2 Water and methanol pervaparation measurement as a function of the TiO_2 weight percentage

The measured methanol permeability of Nafion® 115 membrane is 2.32×10^{-6} cm^2/s at room temperature, It is important to note that the methanol permeability of composite membranes is in between 0.5X 10^{-6} to 2X 10^{-6} cm^2/s (Fig.3), which is considerably smaller than that of Nafion® 115 membrane

3.4 Microscopy

The morphological changes in the membranes were presented in Fig.4, where in Fig. 4 (a) shows membranes without TiO_2 nano particles and Fig. 4 (b) show the composite membrane with 2.5 wt.% TiO_2, from the SEM micrographs it can be considered as lower percentages of TiO_2 filled polymer is homogeneous and dense and higher percentages of filler leads to agglamoration of particles. It can be observed that no cavities are present and that TiO_2 particles have dimension smaller than ~100nm.

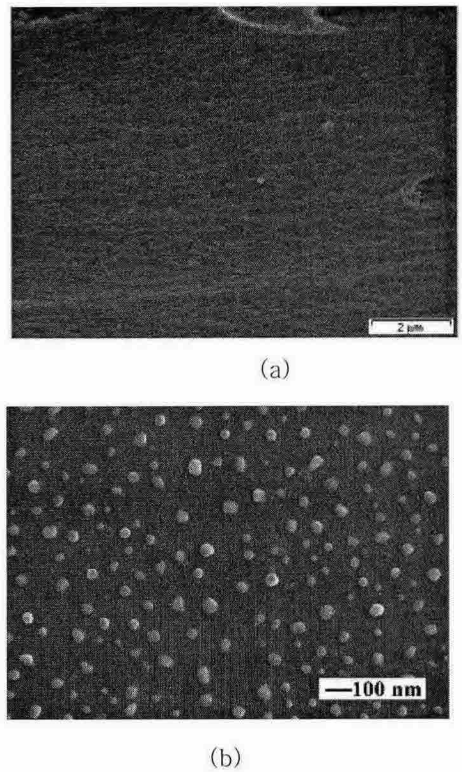

Figure.4 Scanning electron micrograph of (a) cross section of SPEEK membrane (b) SPEEK with 2.5% of TiO_2

4.Conclusions

The results showed that increasing the titanium oxide content in the SPEEK 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 with the increasing amount of inorganic filler in the membranes, which increases the membranes barrier properties in terms of mass transport. These features are advantages for the direct methanol fuel cell performance because they prevent reactants loss and increase 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 showed a good adhesion between inorganic particles domains and the polymer matrix (no cavities) and that the particles have dimensions smaller than ~ 100 nm. A critical evaluation of the relationship between the proton electrolyte membrane properties and the DMFC performance

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