Preparation and Characterization of Sulfonated Poly (ether ether ketone)/Phosphated Zirconia Nanoparticles Composite Proton-conducting Membranes

Hongze Luo, Shan Ji, Guntars Vaivars*, Ben Bladergroen and Vladimir Linkov

Department of Chemistry, University of the Western Cape, Private Bag X17, Bellville, Cape Town, 7535 South Africa.

ABSTRACT

Proton-conducting membranes of organic–inorganic (sulfonated poly (ether ether ketone)/phosphated zirconia nanoparticles) composite were prepared by incorporating various ratios of phosphated zirconia nanoparticles (ZP) in sulfonated poly (ether ether ketone) (SPEEK). SPEEK/ZP showed an improvement of properties compared with those of the parent SPEEK membrane. Key amongst these is increased proton conductivity to 0.02 S cm^{-1}, reduced water uptake to 22 % and reduced methanol permeability to 1.13×10^{-7} cm^2 s^{-1}. The methanol permeability was decreased by 28 % compared with SPEEK membrane. It was decreased by one order of magnitude compared with commercial Nafion® 117 (1.39×10^{-6} cm^2 s^{-1}).

1. Introduction

Fuel cell technology is expected to become one of the key technologies of the 21st century both for stationary and for portable applications. The proton-conducting membrane (PEM) is one of the key components of the direct methanol fuel cell (DMFC), which has the double functions of conducting protons and separating the fuel from the oxidant. Currently perfluorinated polymers, such as Nafion®, are used in DMFC.[1] However, the high cost of those polymers limits the large-scale commercialization of the proton-conducting membrane fuel cells.[2] A shortcoming of the perfluorinated membranes especially related to their application in DMFC is their high methanol permeability, which drastically reduces DMFC performance.[3] Therefore, developing alternatives has become an active area of research.

In the last few decades, numerous types of arylene main chain polymers have been developed. Many of these polymers have also been sulfonated in order to obtain the proton-conducting membranes. Among these polymers SPEEK[4–8] possesses many of the required properties (such as good thermal stability, chemical inertness, good mechanical properties, low cost and adequate proton conductivity) as a proton-conducting membrane for fuel cell applications, which makes it a promising alternative material for fuel cell applications. However, the mechanical properties of PEEK tend to deteriorate progressively with degree of sulfonation (DS).[9] The swelling of the membrane leads to the loss of its mechanical stability. It might be prevented by incorporating inorganic particles (SiO$_2$, P$_2$O$_5$, ZrO$_2$, etc.). Recently, nano-zirconia powder was blended with sulfonated poly (ether sulfone). *In situ* generation of zirconium hydrogen phosphate was carried out by treating with H$_3$PO$_4$.[10] In such a methodology, it is difficult to control the size and hence the agglomeration of the inorganic materials inside the polymer matrix.

In this paper, we report the preparation of SPEEK/ZP composite membranes using an alternative procedure and their characterization by scanning electron microscopy, methanol permeability, water uptake and proton conductivity measurements. The investigated composite membranes were found to be suitable candidates for fuel cells. They exhibited high proton conductivity within the temperature range of fuel cell application and methanol cross-over lower than that of Nafion®.

The novel material phosphated zirconia nanoparticles (ZP)[11] was incorporated into SPEEK because of the following properties: (1) high proton conductivity when humidified (approaching 10^{-2} S cm^{-1}) and high surface area, as reported by Vaivars *et al.*;[11] (2) the decrease of the polymer methanol permeability was reported;[12] (3) simple synthesis procedure and (4) low cost.

2. Experimental

2.1. Materials

N,N-Dimethylacetamide (DMAc) 99.8 % and poly (ether ether ketone) (PEEK) were supplied by Aldrich; zirconia nanoparticles were purchased from Degussa; and acetic acid (99.8 %), sulphuric acid (98 %), phosphoric acid (85 %) and methanol (99.5 %) were supplied by KIMIX.

2.2. Preparation of SPEEK

PEEK pellets were dried in a vacuum oven at 100 °C overnight. 10 g of PEEK pellets were added slowly to 200 mL concentrated sulphuric acid (98 %) with vigorous magnetic stirring. After 63 h the sulfonated polymer was precipitated in a large excess of ice-water. The polymer precipitate was filtered and washed several times with deionized water until the pH reached 7. The filtered polymer was dried under vacuum at 60 °C for one week. SPEEK with DS = 0.79 was determined by TGA according to Zaidi *et al.*[8] The method is based on the assumption that the first degradation step between 318 and 400 °C is entirely caused by SO$_3$ release. The 5 mass % solution of SPEEK in N,N-dimethylacetamide (DMAc) was used for membrane preparation.

2.3. Preparation of Phosphated Zirconia Nanoparticles (ZP)

ZP was prepared by phosphorization of ZrO$_2$ nanoparticles

* To whom correspondence should be addressed. E-mail: gvaivars@uwc.ac.za

with phosphoric acid solution according to the method described earlier.[11,12] A ZrO_2 nanoparticle suspension was prepared by mixing 3 g of ZrO_2 nanoparticle powder with 97 g of 2 M acetic acid solution. The mixture was stirred with a magnetic stirrer until a milky solution was obtained and mixed with 8 % phosphoric acid solution (in mass relation 1 ZrO_2: 2 phosphoric acid). The mixture was slowly heated up to 80 °C, then dried in a vacuum oven at 80 °C.

2.4. Membrane Preparation

The SPEEK solution was mixed with different amounts of ZP using a magnetic stirrer and heated up to 60 °C for 2 h then placed in an ultrasonic bath for 1 h for better dispersion. After further magnetic stirring for 1 h the mixture was cast on a flat plate. The plate was kept in a vacuum oven at 60 °C for 48 h and at 120 °C for 24 h for solvent removal. After cooling down to room temperature, the resultant membranes were peeled off from the glass after immersion in deionized water for 30 min.

A series of composite membranes with different ratios of SPEEK/ZP was prepared. The membranes were immersed in a 1 M sulphuric acid solution at 80 °C for 24 h. The composite membranes were kept in deionized water before use. The thickness of the dried composite membranes was in the 0.09–0.2 mm range (measured using a micrometer).

2.5. Characterization of SPEEK/ZP Composite Membranes

2.5.1. *Fourier Transform Infrared (FTIR) Study*

FTIR spectra were recorded on a Perkin Elmer Paragon 1000 Fourier transform spectrometer. ZP and ZrO_2 samples were ground into fine powders with mortar and pestle and dried at 110 °C overnight. FTIR spectra were recorded in the scanning range 4000–600 cm^{-1}.

2.5.2. *Thermal Gravimetric Analysis (TGA)*

Samples (*ca.* 10 mg) were analysed in a N_2 atmosphere by using a Thermal Analyzer STA 1500 (CCI-3, Rheometric Scientific) in the temperature range from 20 °C to 800 °C at a heating rate of 10 °C min^{-1}.

2.5.3. *Water Uptake*

The membrane water uptake was determined by measuring the mass difference between the fully hydrated membrane and the dried membrane. Before the measurement, the membrane (1 cm × 5 cm) was kept in deionized water at room temperature for one day. The membrane was saturated with water until no further mass gain was observed. The water uptake was measured at 80 °C. The membranes were immersed in water at 80 °C for one hour before the mass determination. The liquid water from the surface of the wet membrane was quickly removed using tissue paper, and the membrane immediately weighed. Subsequently, the membranes were dried in an oven at 100 °C for 6 h and reweighed. The percentage mass gain with respect to the mass of a dried membrane was taken as a water uptake. The following formula was used:

$$\text{Water uptake } s = \frac{G_w - G_d}{G_d} \times 100 \text{ %},$$

where G_w is the mass of the wet membrane, and G_d is the mass of the dry membrane.

2.5.4. *Methanol Permeability Measurements*

The membrane methanol permeability (sometimes referred to as a cross-over) was examined by using a diaphragm diffusion cell. A plastic cell containing solutions A and B in two identical compartments separated by the membrane was utilized for methanol permeability tests. Compartment A was filled with 1 M methanol solution while compartment B was filled with deionized water. The membrane was placed between the two compartments by a screw clamp and both compartments were placed in an ultrasonic bath while measuring. The concentration of the methanol in solution B was measured as a function of permeation time using a Hewlett Packard model 5890 series II gas chromatograph. The methanol permeability P was calculated from the slope of the straight line plot of methanol concentration *versus* permeation time.

Methanol permeability was calculated according to the following equation:[13,14]

$$C_B(t) = \frac{A}{V_B} \frac{P}{L} C_A(t - t_0),$$

where A is the membrane area available for diffusion; C_A is the initial methanol concentration; C_B is the final methanol concentration; L is the membrane thickness; P is the membrane permeability; $(t–t_0)$ is the permeation time; and V_B is the volume of the receiving compartment.

The methanol permeability was calculated using the following equation:

$$P = \frac{L}{A} \times \frac{V_B}{C_A} \times \frac{\Delta C}{\Delta t}.$$

2.5.5. *Scanning Electron Microscope (SEM)*

The membrane surface morphology was studied using a Hitachi X650 Scanning Electron Microscope (SEM). Specimens for the SEM were prepared by freezing the dry membrane samples in liquid nitrogen and subsequently breaking the membranes into small pieces. Thereafter, the pieces of the fractured membranes were mounted on aluminium stubs and coated with a thin layer of gold by vacuum sputtering for 3 min in order to facilitate the conductivity.

2.5.6. *Proton Conductivity Measurements*

The proton conductivities of the membranes were measured in the temperature range from ambient to 100 °C by using a Hioki 3560 AC milliohm meter (HiTester). A schematic representation of the cell for electron and proton conductivity measurements is shown in Fig. 1.

The membrane was pressed under a 2 kg pressure between two stainless steel electrodes with a contact area of 0.28 cm^2. Before the proton conductivity tests, the membrane was kept in
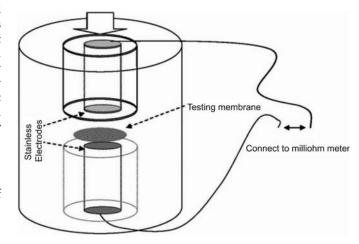

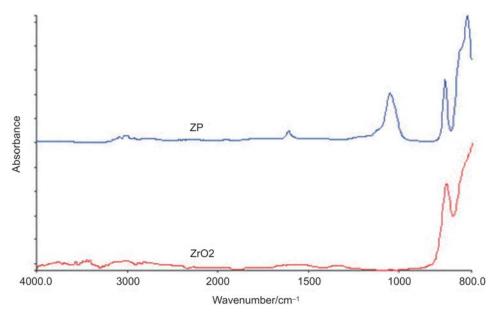**Figure 1** Schematic representation of the cell for measuring proton conductivity.

Figure 2 The FTIR spectra of ZrO_2 and phosphated zirconia nanoparticles (ZP).

a 1 M sulphuric acid solution for 6 h at room temperature. The membrane was then rinsed with deionized water several times to remove any excess H_2SO_4 and then immersed in deionized water for 6 h at 60 °C. All membranes were stored in deionized water at room temperature.

The membrane proton conductivity σ was calculated using the relationship:

$$\sigma = d/RS \,,$$

where d, R and S are the thickness, resistance and face area of the membrane, respectively.

3. Results and Discussion

3.1. Fourier Transform Infrared (FTIR) Spectroscopy

The FTIR technique proved to be a useful tool to show the presence of zirconium phosphate. The infrared spectra of ZP compared with the initial zirconia are shown in Fig. 2. After phosphorization, a new peak at *ca.* 1053 cm^{-1} was observed, which is characteristic for the P-O stretching mode of the phosphate group.[15] The weak band at 1650 cm^{-1} results from the P=O vibration.

3.2. The Thermal Stability Analysis

The thermal stability is crucial for fuel cell applications. The characteristic TG curves for PEEK, SPEEK and SPEEK/ZP composite membranes are presented in Fig. 3. The PEEK polymer is thermally stable up to 550 °C. Three mass loss steps are observed for SPEEK and SPEEK/ZP membranes, which are related to: (1) physically absorbed water (20–200 °C), (2) the splitting off of the sulphonic group (200–450 °C),[16] and (3) the decomposition of the main chain of PEEK (>450 °C). The thermal stability of the composite membrane is quite similar to that of pure SPEEK membrane. The results suggest that these composite membranes have adequate thermal properties for application in low temperature fuel cells. At the same time, the composite membrane contains more physically absorbed water compared with SPEEK (see conductivity measurements).

3.3. Water Uptake

The water uptake of the composite membrane was determined at room temperature (20 °C) and at 80 °C (Fig. 4). The incorporated ZP particles decrease the water uptake in both cases. It is believed that the water uptake in polymers is increased due to
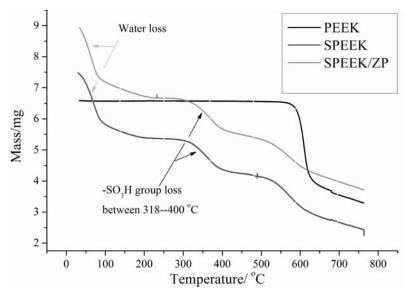

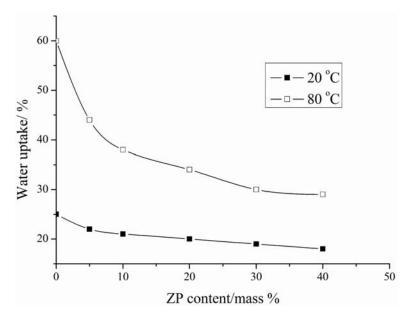**Figure 3** Thermo-gravimetric curves of PEEK, SPEEK and SPEEK/ZP.

Figure 4 Water uptake of the membranes with different ZP content.

the membrane swelling and resulting pore expansion, which is caused by interaction with a solvent. The swelling depends on the temperature and the effect is more clearly observed at higher temperatures. The incorporated ZP nanoparticles fill the pores and prevent the swelling.

3.4. Methanol Permeability

The methanol permeability of the composite membrane as a function of the ZP content is shown in Fig. 5.

The permeability of the pure SPEEK is 1.58×10^{-7} cm^2 s^{-1}, as measured in a 1 M methanol solution, and it is much lower than that of Nafion® (1.39×10^{-6} cm^2 s^{-1}) under the same conditions. At higher methanol concentrations, the SPEEK swelling increases rapidly, which limits the DMFC applications.

The composite membrane containing 5 mass % of the ZP exhibited a 28 % reduction of methanol permeability (1.13×10^{-7} cm^2 s^{-1}) compared with pure SPEEK membrane. This value (1.13×10^{-7} cm^2 s^{-1}) is 12 times lower than that of Nafion® 117 (1.39×10^{-6} cm^2 s^{-1}) as measured at room temperature, which corresponds to the published value 1.41×10^{-6} cm^2 s^{-1}.[17]

However, the methanol permeability compared with that of the SPEEK membrane increases at ZP content higher than 5 mass %. The decrease of the methanol permeability is believed to derive mainly from the enhanced barrier properties of the membranes due to the incorporation of the nano-sized ZP particles as filler. The incorporated nano-sized inorganic particles block the channels to methanol passing as was confirmed previously by water uptake measurements (Fig. 4). The minimum of the methanol cross-over is observed at ZP content equal to about 5 mass %. At higher ZP content the mechanical stability of the membrane decreases and the methanol permeability increases. This is likely to be caused by the weaker bonding between the polymer and ZP particles and an interface is formed, which could serve also as a channel for methanol transport. In order to facilitate the decrease of the methanol permeability and to keep the ZP content high better bonding between the inorganic filler and a polymer should be achieved.

3.5. Morphology Studies by SEM

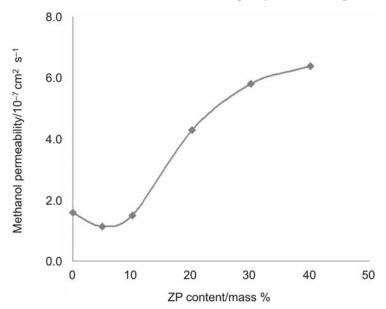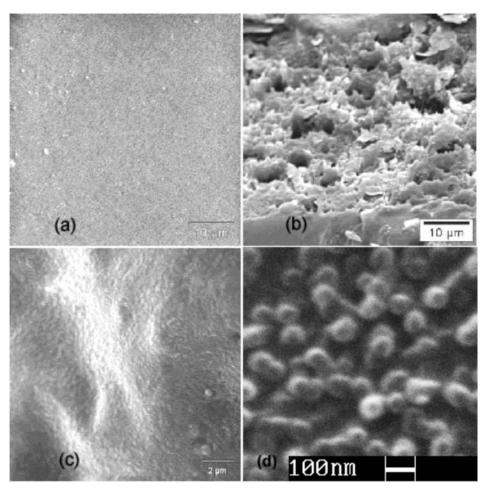The quality of the ZP dispersion in the SPEEK/ZP composite

Figure 5 Effect of the incorporated ZP content on methanol permeability.

Figure 6 SEM micrographs of SPEEK and SPEEK/ZP composite membrane: (**a**) surface of the SPEEK membrane, (**b**) cross-section of the SPEEK membrane, (**c**) surface of the composite membrane with 5 mass % of ZP, (**d**) cross-section of the composite membrane with 5 mass % of ZP.

membrane was examined by SEM. SEM micrographs of SPEEK membrane and typical examples of the composite membrane are presented in Fig. 6. The surface pictures show a dense structure without macropores (Figs 6a and 6c). However, the cross-section of the SPEEK membrane (Fig. 6b) demonstrates a developed pore structure. The cross-section of the SPEEK/5 mass % ZP composite membrane shows much denser structure (Fig. 6d) and the nano-sized pore distribution. The nano-sized ZP particles are uniformly distributed within the composite membrane without agglomeration. The presence of 3.1 % of phosphorus for incorporated ZP particles was confirmed by using Energy Dispersive Spectrometry (EDS) analysis from the SEM.

3.6. The Membrane Proton Conductivity

The proton conductivity of the composite membrane with various ZP contents was measured in the temperature range from room temperature up to 100 °C. The temperature dependence of the proton conductivity at different ZP content is presented in Fig. 7. It shows a stable increase of the proton conductivity for composite membranes, which characterizes good water retention. The addition of the ZP enhances the polymer proton conductivity. At the same time, the SPEEK membrane rapidly loses proton conductivity at temperatures approaching 100 °C due to dehydration. The proton conductivity of the SPEEK/ZP composite membrane with ZP content 40 mass % reaches 0.045 S cm^{-1} at 100 °C.

The increase of the proton conductivity for composite membrane with increasing ZP content at room temperature and at 80 °C is demonstrated in Fig. 8. As was discussed previously, the water uptake for composite membranes decreases and the proton conductivity increases with ZP incorporation. The proton conductivity is also stable at higher temperatures. It is good evidence that the proton conductivity is characteristic for composite material and it is not caused by the porosity of the material. The incorporated ZP nanoparticles enhanced the proton conductivity and decreased the material porosity on the nanoscale. While ZP increases the proton conductivity, the optimized ZP content could reduce the water uptake and the methanol permeability.

4. Conclusions

A series of sulfonated poly (ether ether ketone)/phosphated zirconia nanoparticle composite membranes was prepared and studied. The preparation procedure included incorporating varying contents of ZP into SPEEK with a DS = 0.79. The proton conductivity of the SPEEK/ZP composite membrane was increased by incorporating ZP particles. The high water uptake at higher temperatures was also reduced by incorporating ZP. It was possible to keep an excellent mechanical stability for samples with ZP content not exceeding 5 mass %. The methanol permeability of the optimized composite membrane (5 mass % of ZP) was reduced by 28 % compared with the pure SPEEK membrane. The following advantages are promising for DMFC and other applications: (1) simple preparation procedure; (2) high proton conductivity; (3) reduced water uptake, especially at higher temperatures; (4) decreased methanol permeability and (5) good thermal and mechanical stability.
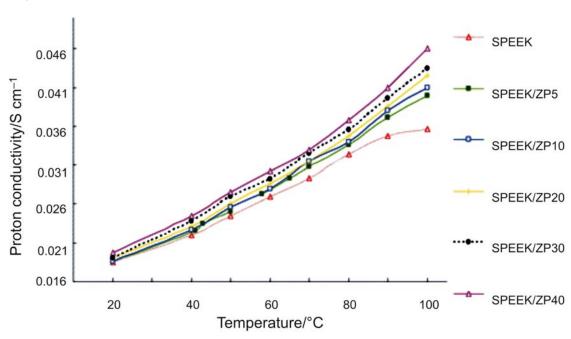
Figure 7 The proton conductivity of SPEEK/ZP membranes as a function of temperature.

Figure 8 Effect of ZP content on proton conductivity at room temperature and at 80 °C.

References

1 K.D. Kreuer, *Chem. Mater.,* 1996, **8**, 610–641.

2 A.J. Appleby, *Phil. Trans. Roy. Soc. (London),* A, 1996, **354**, 1681–1693.

3 J. Cruickshank and K. Scott, *J. Membr. Sci.,* 1998, **70**, 40–47.

4 B. Bauer, D.J. Jones, J. Roziere, L. Tchikaya, G. Alberti, M. Massinelli, A. Peraio, S. Besse and E. Ramunni, *J. New Mater. Electrochem. Syst.,* 2000, **3**, 93–98.

5 L. Li, J. Zhang and Y. Wang, *J. Membr. Sci.,* 2003, **226**, 159–167.

6 O. Savadogo, *J. Power Sources,* 2004, **127**, 135–161.

7 T. Kobayashi, M. Rikukawa, K. Sanui and N. Ogata, *Solid State Ionics,* 1998, **106**, 219–225.

8 S.M.J. Zaidi, S.D. Mikhailenko, G.P. Robertson, M.D. Guiver and S. Kaliaguine, *J. Membr. Sci.,* 2000, **173**, 17–34.

9 S.D. Mikhailenko, K. Wang, S. Kaliaguine, P. Xing, G.P. Robertson and M.D. Guiver, *J. Membr. Sci.,* 2004, **233**, 93–99.

10 G.M. Anilkumar, S. Nakazawa, T. Okubo and T. Yamaguchi, *Electrochem. Comm.,* 2006, **8**, 133–136.

11 G. Vaivars, S. Ji, G. Gericke and V. Linkov, *Appl. Organomet. Chem.,* 2005, **19**, 1096–1100.

12 G. Vaivars, T. Mokrani, N. Hendricks and V. Linkov, *J. Solid State Electrochem.,* 2004, **8**, 882–885.

13 V. Tricoli, N. Carretta and M. Bartolozzi, *J. Electrochem. Soc.,* 2000, **147**, 1286–1290.

14 B.S. Pivovar, Y. Wang and E.L. Cussler, *J. Membr. Sci.,* 1999, **154**, 155–162.

15 P. Colomban and A. Novak, *J. Mol. Structure,* 1989, **198**, 277–295.

16 S.R. Samms, S. Wasmus and R.F. Savinell, *J. Electrochem. Soc.,* 1996, **143**, 1225–1232.

17 A. Clearfield and J.A. Stynes, *J. Inorg. Nucl. Chem.,* 1964, **26**, 117–129.