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Zirconium Oxide Modified Sulfonated Poly(ether ether ketone) Membranes for Direct Methanol Fuel Cell Applications

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Abstract. In order to perform a critical analysis of the zirconium oxide effects in sulfonated poly(ether ether ketone) (SPEEK) membranes with two sulfonation degrees (SD), 71 and 87%, the characterization of composite membranes prepared with a systematic variation of the inorganic content is proposed. The method involves preparation of inorganic composite membranes with a wide range of properties which concern water swelling, chemical and thermal stability, methanol and water permeations and, finally, proton conductivity. A good balance between high proton conductivity, good chemical stability and low methanol permeability is reached for the SPEEK polymer with a 7.5% (w/w) ZrO_2 content and SD=87%. Compared to NAFION® 112, this membrane is 3-times more selective towards water/methanol permeation and has a similar proton conductivity (81 compared to 88 mS/cm).

Introduction

There is nowadays a growing interest in new materials for direct methanol fuel cell (DMFC) polyelectrolyte membranes that have good barrier properties for methanol, high proton conductivity and good thermal and chemical stability. DMFC require membranes that allow protons to move from the anode to the cathode and prevent the methanol crossover. Today, perfluorinated ion-exchange polymers, such as Nafion® from Dupont and Flemion® from Asahi Chemical, are the most commonly used for DMFC. However, it has been reported that methanol is readily transported across perfluorosulfonic acid membranes [1-4]. Methanol crossover from the anode to the cathode is detrimental to DMFC performance as it reduces the Coulombic efficiency and cell voltage. It has been shown that the methanol crossover during fuel cell operation leads to an efficiency reduction down to 35% [5]. On the other hand, the water permeability should be minimized because it may cause cathode flooding and, thus, lower cathode performance [4].

In order to improve the performance of the DMFC, it is necessary to eliminate or, at least, to reduce the methanol crossover without decreasing the proton conductivity. Non-fluorinated membranes based on sulfonated poly(ether ether ketone) (SPEEK) have been presented in some studies [6-7] as being promising for fuel cells applications. However, for high sulfonation degrees the methanol permeability is in many cases still relatively high. Nevertheless, SPEEK has also been used as a matrix for the inclusion of inorganic oxides and proton conductors [8-10], which may lead to a reduction in methanol permeability. However, the analysis of the incorporation of zirconium oxide via sol-gel chemistry in high sulfonation degree SPEEK was not yet reported.

The present work focuses on the characterization of organic-inorganic composite membranes based on sulfonated poly(ether ether ketone) modified by the incorporation of zirconium oxide via sol-gel chemistry. The *in situ* generation of inorganic alkoxides via sol-gel chemistry enables wide possibilities of material processing [11-12]. The systematic variation of the inorganic content can be used to obtain a wide range of modifications on polymer electrolyte membranes' properties. For instance, by changing the zirconium oxide content in the composite membrane, water swelling,

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chemical and thermal stability, methanol and water permeations and, finally, proton conductivity can be affected. The aim of this study is to perform a critical analysis of the zirconium oxide effects in SPEEK membranes with two high sulfonation degrees, 71 and 87%, and to achieve a good balance between high proton conductivity, good chemical stability and low methanol permeability. NAFION® 112 was used as a reference material.

Experimental

Materials and methods. Sulfonated poly(ether ether ketone) (SPEEK) polymer with sulfonation degrees of 71 and 87% (Ion exchange capacity = 1.97 and 2.31 meq/g, respectively) was prepared following the procedure reported in the literature [4]. Poly(ether ether ketone) was supplied as pellets by Victrex. Zirconium tetrapropylate (70% solution in iso-propanol) and acetyl acetone (ACAC) were purchased from Gelest. Commercially available NAFION® 112 was purchased from Aldrich.

Membrane preparation. SPEEK polymer was dissolved in dimethylsulfoxide or dimethylacetamide (8%, w/w). The zirconium oxide modification was performed by hydrolysis of $Zr(OPr)_4$ [11]. Acetyl acetone (ACAC) was used as chelating agent to avoid the precipitation of the inorganic compound. The proportion of ACAC compared to alkoxide used was varying from 2:1 and 3:1. The polymer/ACAC solution was left to stir for three hours before adding the zirconium tetrapropylate in order to have a good mixture. To accomplish hydrolysis, 0.1g of water per g polymer was added to the solution and stirred for about 16 h at room temperature. After filtration, the final solutions were cast in a hydrophobised glass plate heated to 70°C. After casting, the membranes were stored in a vacuum oven for 24 hours at 90 °C. Thickness of the prepared membranes varied from 110 to 190 μm.

Methanol and water permeability measurements. The water and methanol permeabilities were evaluated through pervaporation measurements at 55°C with a 20 % (w/w) methanol solution. In the pervaporation setup, a Millipore cell with a 47 mm membrane diameter was used. The permeate was collected in a glass trap immersed in liquid nitrogen, at time intervals ranging from 1 to 2 hr. Then, the permeate was weighted and the composition determined by refractive index measurements. The selectivity of the membranes towards water/methanol was evaluated dividing the ratios between the water and methanol molar fraction in the permeate by the ratio in the feed. Prior to all measurements, samples were immersed in deionized water at room temperature for 3 days.

Proton conductivity measurements. Conductivity measurements were carried out at 25°C using ac impedance spectroscopy, determining the impedance at null phase shift. A membrane sample was placed in a 0.33M H_2SO_4 solution between two platinum electrodes, which have a diameter of 2.8 cm and a distance between them of about 2 mm. As pretreatment, samples were immersed in water at room temperature during 3 days to ensure total leaching. One hour before the measurement, the samples were immersed for 1 hour in 0.33M H_2SO_4. The spectrometer used was a HP 4284A working in the frequency range between 100 and 10^5 Hz.

Water swelling and chemical stability studies. Swelling studies were performed on dry samples of the prepared membranes. The pretreatment procedure was started by drying the samples in a vacuum oven at 90 °C for 5 hours. After drying, four samples of each membrane were weighted, immersed in deionized water and equilibrated for 3 days at room temperature. The swollen membranes weights were measured after carefully removing the water from both surfaces. Water uptake (%) was evaluated calculating the ratio between the difference of the wet and dry weight and the dry weight. The average error obtained with the four samples analysis procedure was 4.7% (*t* distribution, 95% confidence interval). The chemical stability of the membranes was evaluated qualitatively immersing the membrane samples in a 20 % (w/w) methanol solution (6M) at 60°C.

Results and Discussion

Water uptake and chemical stability of the composite membranes. The water uptake is a measure of water solubility in the membrane. It is usually correlated by several groups to the water permeability across the membrane. Solubility is one of the main factors, which contributes to the permeability but it is not the only one. Pervaporation may provide a more direct estimation of methanol and water crossover. But water uptake can additionally give a good indication on how the membrane dimension may change in the cell when humidified. This is an important factor when preparing membrane-electrode-assemblies. High water uptake is usually a sign for low stability in DMFC operation. The proton conductivity in many cases [13] can be well correlated to the water uptake. In the case of sulfonated polymers, higher sulfonation degree not only means higher water solubility (water uptake), but also more acid sites for proton transport.

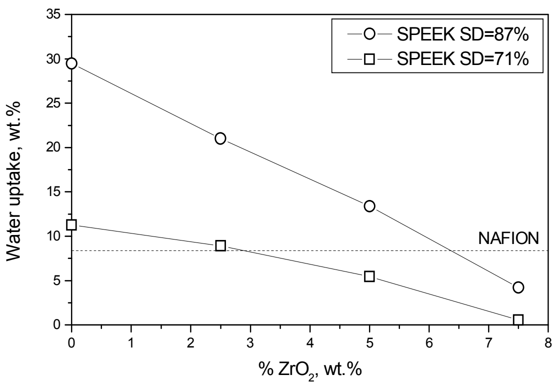

Fig. 1. Water uptake of SPEEK membranes as a function of ZrO_2 content (data at room temperature). NAFION® 112 given as reference.

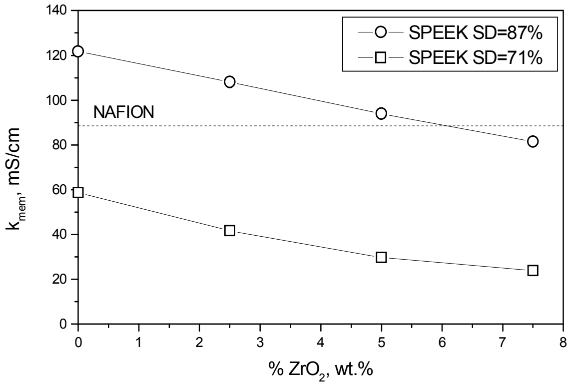

Fig. 2. Proton conductivity of SPEEK membranes as a function of ZrO_2 content (25°C in 0.33M H_2SO_4). NAFION® 112 given as reference.

Fig. 1 shows the water uptake of the membranes at room temperature. It can be seen that SPEEK membranes with SD = 87% always exhibit a higher water uptake than those with SD=71%. As reported in [7], sulfonation of the PEEK polymer makes it more hydrophilic by increasing the protonated sites (-SO_3H). It can be also observed that the amount of ZrO_2 in the SPEEK composite membrane has a large impact on the swelling properties of the composites. For the 87% sulfonated SPEEK membrane, introduction of 7.5% (w/w) ZrO_2 leads to a water uptake decrease of nearly 85%. On the other hand, for the SPEEK membrane with SD=71%, the incorporation of 7.5% of inorganic compound results in a composite membrane that practically doesn't sorbs water.

In terms of chemical stability, it was observed that for ZrO_2 contents over 5% (w/w) for SD=87% and over 2.5% (w/w) for SD=71%, the membranes become stable in 6M methanol aqueous solution at 60°C. It is worth noting that the standard methanol concentration in a DMFC is 1.5 M, although for the qualitative test, a more active solution was chosen.

Proton conductivity measurements. One of the more important characterization methods that can be applied to select the right material for fuel cells application is the proton conductivity technique. It is known that the main function of a polymer electrolyte membrane in the DMFC is to conduct protons while preventing reactants crossover from the anode to the cathode. The well-known and characterized NAFION® can be used as a standard material in terms of conductivity and stability [14]. The effect of the zirconium oxide content in the proton conductivity of SPEEK membranes is shown in Fig. 2. The plots indicate an almost linear decrease of the membrane's conductivity with increasing zirconium oxide content. As mentioned previously, decreasing the hydrophilicity of the membranes leads to an increase in proton transfer resistance and, consequently, the conductivity decreases. In comparison with NAFION 112®, the incorporation of 5% (w/w) ZrO_2 in the SPEEK membrane with SD=87% leads to a higher proton conductivity - 94 compared to 88 mS/cm (Fig. 2).

For the SPEEK membrane with SD=71%, the proton conductivity observed was always lower than that obtained for NAFION® 112.

Permeability measurements. Transport of water and methanol in inorganic-organic membranes depends on the complex interactions between the permeates and the organic-inorganic materials [14]. The present main task is to reduce the water and methanol permeation without decreasing the conductivity of the membrane.

Figs. 3 and 4 show the measured water and methanol fluxes in the membranes. For the two polymers analyzed, the introduction of ZrO_2 in the range of2.5% to 5% (w/w) led to a much higher reduction in water and methanol permeations than in the proton conductivity (Figs. 2-4). It can be also seen that water and methanol fluxes remained practically unchanged with the introduction of 5% or 7.5 % (w/w) ZrO_2. Comparatively with the fluxes obtained for NAFION 112®, the incorporation of 5% or 7.5 % (w/w) ZrO_2 in the two polymeric matrixes led to a 3-times reduction of water and methanol fluxes. In terms of selectivity to water/methanol permeation (Fig. 5), it can be noticed that the higher levels of zirconium oxide used proved to yield SPEEK membranes

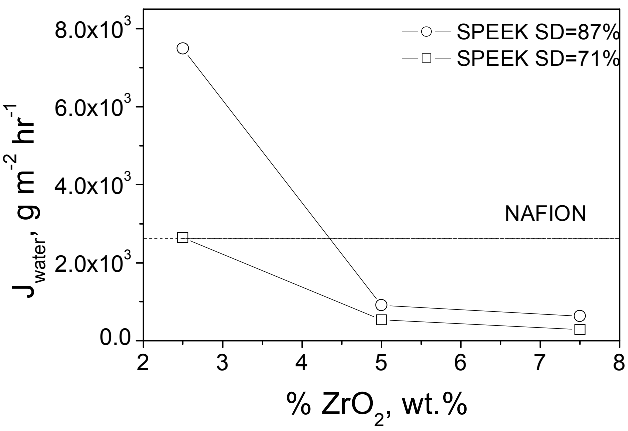

Fig. 3. Water flux through SPEEK membranes as a function of ZrO_2 content (pervaporation experiments at 55 °C). NAFION® 112 given as reference.

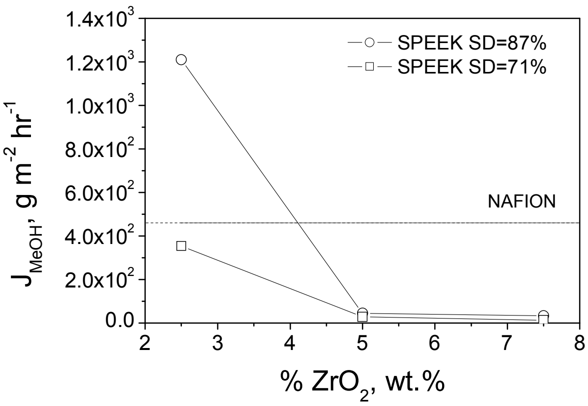

Fig. 4. Methanol flux trough SPEEK membranes as a function of ZrO_2 content (pervaporation experiments at 55 °C). NAFION® 112 given as reference.

with water permeation selectivities in the range between 5 and 6. In comparison with NAFION® 112, for example, the 5% (w/w) ZrO_2 SPEEK membrane with a sulfonation degree of 87% led to a 3-times more selective membrane. Even membranes with low ZrO_2 contents present a higher selectivity than NAFION® 112.

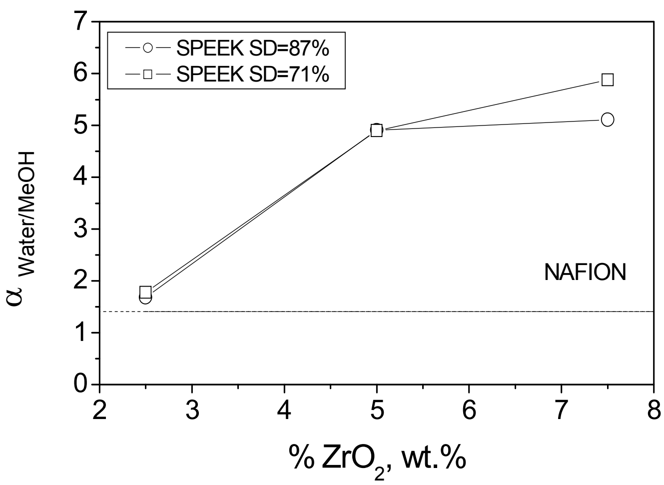

Fig. 5. Selectivity towards water/methanol of SPEEK membranes as a function of ZrO_2 content (pervaporation experiments at 55 °C). NAFION® 112 given as reference.

Conclusions

Several composite membranes with sulfonated poly(ether ether ketone) as polymeric matrix (with sulfonation degrees of 71 and 87%) and containing different amounts of ZrO_2 were prepared and characterized. In order to select the proper level of ZrO_2 in the SPEEK polymer for DMFC applications, the present study investigates the transport properties of the composite membranes as a function of the amount of zirconium oxide. The characterization methods used involved determination of: water swelling and chemical stability, methanol and water permeability, selectivity towards water/methanol permeation and proton conductivity.

It is observed that water swelling, proton conductivity and water/methanol permeation decrease with the amount of ZrO_2 in the composite membrane. However, the decrease observed in the permeability of water/methanol is much higher compared with the other analyzed parameters. In contrast, the chemical stability and the selectivity to water permeation of the composite membranes increase with the inorganic compound content. Based on the criterion of low methanol/water permeability, high proton conductivity, good chemical stability and low swelling, the incorporation of 7.5% (w/w) ZrO_2 in the SPEEK membrane with SD=87% was found to be the most favorable and might be useful for DMFC applications.

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