Pre-treatment effect on the transport properties of sulfonated poly(ether ether ketone) membranes for DMFC applications

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1. Introduction

Liquid feed direct methanol fuel cells (DMFCs) employing proton-exchange membranes (PEMs) are promising candidates for portable power applications [1]. However, the use of perfluorinated membranes as polymer electrolyte leads to a significant decrease in the fuel cell Faraday efficiency due to methanol crossover [1]. Non-fluorinated membranes based on sulfonated poly(ether ether ketone) (sPEEK) have been presented as promising materials due to their high proton conductivity [2]. Also, in order to improve the membrane properties for DMFC applications, the single-phase sPEEK polymer was modified by the incorporation of zirconium oxide (ZrO₂), which decreases the methanol permeation [3]. Furthermore, the membrane properties are also influenced by proper sample pre-treatment. The present study aims to characterize sPEEK membranes and to perform a critical study regarding the pre-treatment effects on the membrane properties. Nafion® 1135 (from Aldrich) was used as reference material.

2. Experimental

A sPEEK polymer with a sulfonation degree (SD) of 42% was used in the present study together with a sPEEK composite membrane with 1 wt.% of ZrO₂ prepared by in situ zirconia formation [3]. Conductivity measurements were carried out at 25°C in a cell described in [2], using ac impedance spectroscopy and an acid electrolyte (0.33 M sulfuric acid). The methanol permeability coefficients were obtained through pervaporation measurements as described elsewhere [3]. The pervaporation experiments were performed at 40°C, 55°C and 70°C (6.0 M aqueous methanol feed). As pre-treatment, the membranes were immersed in boiling water for 1 h, 1 day before characterization.

3. Results and discussion

From Table 1, it can be seen that the untreated sPEEK membranes, with and without

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inorganic modification, have considerably lower proton conductivity than Nafion® 1135. Along with, it can be observed that the incorporation of ZrO$_2$ in the sPEEK polymer matrix leads to a conductivity decrease; lower hydrophilicity and increased barrier properties [3]. On the other hand, in terms of the pre-treatment effect on the proton transport properties, both sPEEK showed to be very sensitive and the proton conductivity increased by a factor of ca. 6 (Table 1). We believe that this is due to improved water-assisted proton conductivity (broader water channels) [2]. A less favorable effect is observed for Nafion® which proton conductivity increases by ca. 1.3. From Fig. 1 it can be observed that the pervaporation feed temperature increases the methanol permeability coefficients for the studied pre-treated and untreated membranes (broader water channels) [2]. It can be also seen that the methanol permeability coefficients for Nafion® are always higher than those of the sPEEK membranes, with or without ZrO$_2$. Besides, it can be seen that the pre-treatment increases the methanol permeability coefficients for all the studied membranes. It is worth noting, however, that this trend is much more noticeable for the pre-treated Nafion® (higher increase). In terms of both plain and composite sPEEK membranes, the incorporation of zirconium oxide leads, within the experimental uncertainty, to lower permeability coefficients, in agreement with previous data [3]. Although increasing the methanol permeability coefficients, the pre-treatment applied enabled to obtain a sPEEK SD = 42% plain membrane with a higher proton conductivity than that of Nafion® 1135 (Table 1) and with improved barrier properties in terms of methanol permeation (Fig. 1).

4. Conclusions

From the experimental characterization results it can be seen that the pre-treated sPEEK SD = 42% enables the preparation of PEMs with improved properties compared to Nafion® due to its higher proton conductivity and lower permeability towards methanol. Therefore, we believe that such a material is very promising for DMFC applications, and its deeper study will be the aim of future work. Along with, the morphological stability and low methanol permeation of this membrane are also improved by the incorporation of 1 wt.% of ZrO$_2$, although decreasing about 20% the proton conductivity.
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References

