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An Impedance Study on the sPEEK/ZrO_2 Membranes for Direct Methanol Fuel Cell Applications

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Abstract. Electrochemical impedance experiments were carried out in order to study the influence of the ZrO_2 inorganic incorporation on the proton conductivity of sulfonated poly(ether ether ketone) (sPEEK) membranes. The impedance data was fitted to an extension of Randles' circuit, within the inorganic content and temperature ranges considered. The model fits quite well for ZrO_2 loads up to 10 wt.%. Such a model allows for characterizing the diffusion phenomena (Warburg) of the membrane electrode assembly (MEA), membrane and electrodes resistances, capacitive and inductive behavior. Proton conductivity was obtained from the impedance spectra and it was observed that it increases with temperature and decreases with the inorganic content. As a general trend, the Warburg parameter decreases slightly with the temperature, except for the 5 wt. % ZrO_2 membrane that suffers a more pronounced influence. The Warburg parameter also decreases with the ZrO_2 content.

Introduction

The major challenge of developing polymer electrolyte membranes (PEM) for direct methanol fuel cell (DMFC) applications is to improve the proton conductivity and long-term structural integrity while decreasing the permeability towards methanol of the presently available membranes [1]. Perfluorinated membranes (e.g. Nafion) present some of the desired properties, however they have high permeability towards methanol and water and are very expensive.

Regarding these shortcomings, non-fluorinated membranes gained prominence, leading to the appearance of new polymer membranes, such as PEEK (poly(ether ether ketone)). It has been shown that the sulfonated PEEK (sPEEK) is very promising for the DMFC applications as it combines good mechanical, chemical and thermal properties with adequate proton conductivity [2].

Higher proton conductivities could be achieved increasing the sulfonation degree, but an excessive swelling can occur, leading to a lower mechanical stability. In order to obtain enhanced PEM properties, the sPEEK membrane can be modified using an inorganic additive. In the last years, several inorganic additives have been investigated, namely zirconium phosphate [3], titanium oxide [4] and zirconium oxide [5]. It was observed that ZrO_2 incorporation on the sPEEK matrix improves the structural integrity and reduces methanol crossover, water swelling and proton conductivity [5].

Proton conductivity is determined by electrochemical impedance spectroscopy (EIS). EIS is a non-invasive technique that provides a mean of characterizing the electrical properties of electrochemical systems. This technique allows the determination of the electrical contributions of both the membrane and the electrolyte solution separately. On the other hand, EIS allows obtaining the parameters of an idealized model circuit of discrete electrical components [6].

Impedance spectra of sPEEK membranes with ZrO_2 contents ranging from 5.0 to 12.5 wt.% and covering the whole frequency from 10 mHz to 100 kHz were obtained. These spectra allowed modelling the electrical behaviour of the composite PEMs.

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Experimental

Material and Methods. Sulfonated poly(ether ether ketone) (sPEEK) polymers with a sulfonation degree of 87% were prepared to obtain composite membranes with a ZrO_2 content of 5.0, 7.5, 10.0 and 12.5 wt. %. PEEK was supplied as pellets by Victrex. The sulfonation degree was determined by elemental analysis and by H-NMR.

Membranes preparation. The sPEEK composite membranes were prepared using *in situ* formation of zirconia with zirconium tetrapropylate as alkoxide and acetyl acetone as chelating agent. First, the sPEEK polymer was dissolved in dimethylsulfoxide (6 wt.% solution) and the incorporation of ZrO_2 was performed as described in detail elsewhere [7]. The water/alkoxide ratio was always maintained higher than 1 to ensure the formation of a finely dispersed inorganic phase in the polymer solution. The mixtures were cast in a hydrophobised glass plate heated to 70°C for solvent evaporation. After that the membranes were stored in a vacuum oven for 24 hours at 90 °C. Thicknesses of the prepared membranes with 5.0, 7.5, 10.0 and 12.5 wt.% of ZrO_2 were 432, 535, 459 and 369 µm, respectively. A micrometer (Digital Micromaster, Brown & Shap) was used to evaluate the membrane thickness.

Proton conductivity. Conductivity measurements were carried out on membranes, 10 mm in diameter, sandwiched between two ETEK® electrodes which were pressed on the membrane surfaces through porous stainless steel cylinders. The experiments were performed using water vapor as described in [8]. The operation conditions considered were 100% relative humidity and temperatures ranging from 50 to 110ºC. The impedance studies were carried out using a Zahner IM6e electrochemical workstation.

Results and discussion

It is known that PEEK is a semicrystalline thermoplastic polymer based in a rigid para-connected aromatic backbone structure. The sulfonic acid groups attach to the aromatic rings of the sPEEK, showing a pendant configuration. When the inorganic phase is introduced in the sPEEK matrix, a deep change in membrane's properties is obtained.

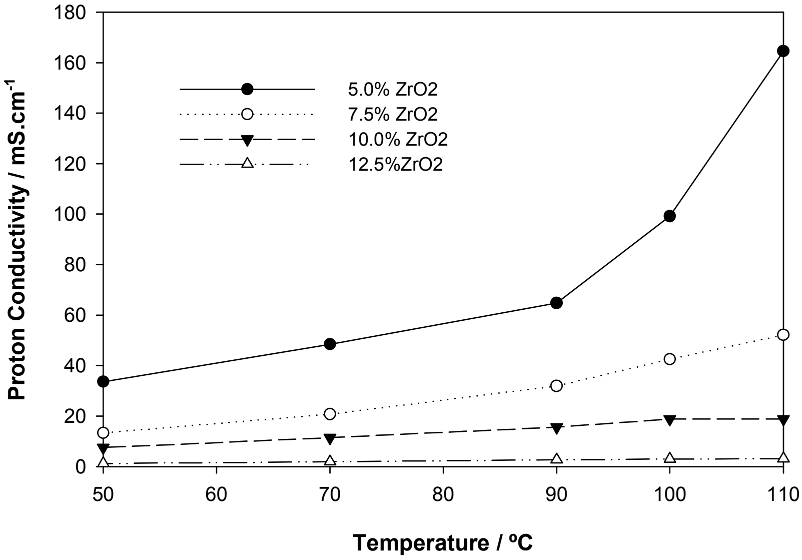

Fig. 1 – Proton conductivity as a function of the temperature at different levels of ZrO_2 incorporation.

In Fig.1 is plotted the proton conductivity as a function of temperature for different levels of ZrO_2 incorporation. It can be seen that the inorganic modification has an appreciable influence on the proton conductivity, which decreases significantly with the incorporation of ZrO_2. Such pattern suggests that ZrO_2 particles act as barriers concerning the proton mobility [9]. Furthermore, some authors suggest that the incorporation of the inorganic particles implies the partial deactivation of the proton conduction sites due to the formation of the Zr-O-SO_2R bonds [10]. On the other hand, it was also observed that the proton conductivity increases with the temperature, in the range between 50 and 110ºC, but the effect is more pronounced at lower inorganic content levels.

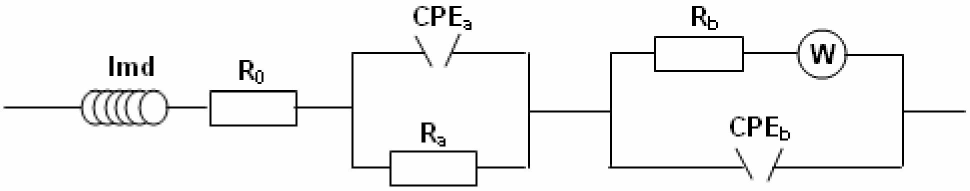

Fig. 2 – Electric analogue of the composite membranes.

The impedance results were fitted to an extension of the Randles' model. The corresponding electric analogue is given in Fig. 2. In this figure, the first component, $\mathbf{I_{md}}$, represents the inductance associated with signals caused by the wiring and metal magnetic fields. $\mathbf{R_0}$ includes all the resistances inherent to the contact between the electrode and the membrane between the electrode and the conductivity cell. The constant phase element, **CPE,** is a pseudo-capacitance and is intimately related with the double electrochemical layer phenomena at the electrode-membrane interfaces. The electrodes are described by the combination of a resistance with an element of constant phase in parallel. The membrane is finally described in a similar way to the electrodes but with an additional parameter, the Warburg element, **W**, to represent the proton diffusivity.

The obtained impedance spectra at different temperatures and different ZrO_2 contents were fitted to the previous model, Fig. 3, minimizing the sum of the square residues. The model fits quite well the experimental results except for the membrane containing 12.5 wt.% ZrO_2, which experimental values were not possible to fit. Model parameters resulting from the fitting are given in Table 1.

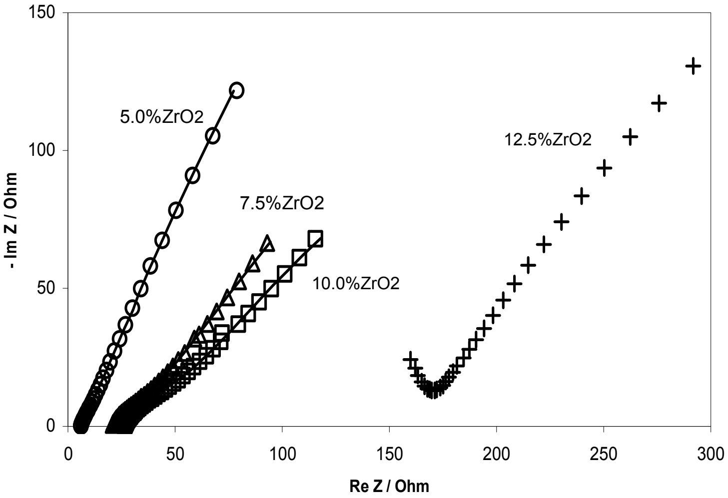

Fig. 3 – Imaginary impedance as a function of the real impedance at 50ºC (symbols for experimental values and lines for model results).

Table 1 – Model parameters at 50°C.

ZrO_2 content / [wt.%]	I_{md} / [nH]	R_0 / [ohm]	R_a / [ohm]	CPE_a/ [μF]	n_a	R_b / [ohm]	W / [mDW]	CPE_b / [μF]	n_b
5.0	952.0	5.9	1396.0	31.1	0.728	3.7	12.1	65.5	0.721
7.5	732.2	20.1	1247.0	23.1	0.566	15.2	1.8	11.0	0.587
10.0	588.4	25.6	571.3	22.6	0.588	28.8	1.0	7.2	0.541

From the impedance spectra (Fig.3) it was found that between 5 and 10 wt.% of ZrO_2, the high frequency semicircle overlaps with the diffusion response. For the low frequency range the system response approaches the Warburg diffusion element model of finite-length. The membrane resistance was obtained from the intersection of the impedance plot with the axis of the real component of the impedance. From Fig. 3 it can also be observed that the impedance response of the membrane with 12.5 wt.% ZrO_2 was slightly different. Prado et al. [10] concluded that up to 10 wt.% of ZrO_2 incorporation, the zirconium domains in the membrane were in the amorphous state. These authors [10] observed, however, that for 13.5 wt.% ZrO_2 incorporation the SAXS analysis indicates the possibility of scattering units with some spatial correlation. In the case of 12.5 wt.% ZrO_2 incorporation, the membrane resistance was then evaluated extrapolating the slanted line (Warburg diffusion) to the real impedance axis.

Whenever an electrochemical reaction is under partial or complete mass transport diffusion control, the impedance is called Warburg impedance. This element seems to be intimately related with the sorption concentration of water and methanol in the membrane (swelling state) and describes the proton diffusion behaviour [11]. The Warburg parameter was computed fitting the slope of the Nyquist plot Warburg element for higher frequencies, Fig.3. In the present case, the Warburg parameter relates to the proton transport in the membrane.

The Warburg parameter decreases slightly as a function of the temperature, excepted for 5 wt.% ZrO_2 content that is much more sensitive (Fig. 4). It can also be seen that the Warburg parameter decreases as the inorganic content increases up to 10 wt.% ZrO_2.

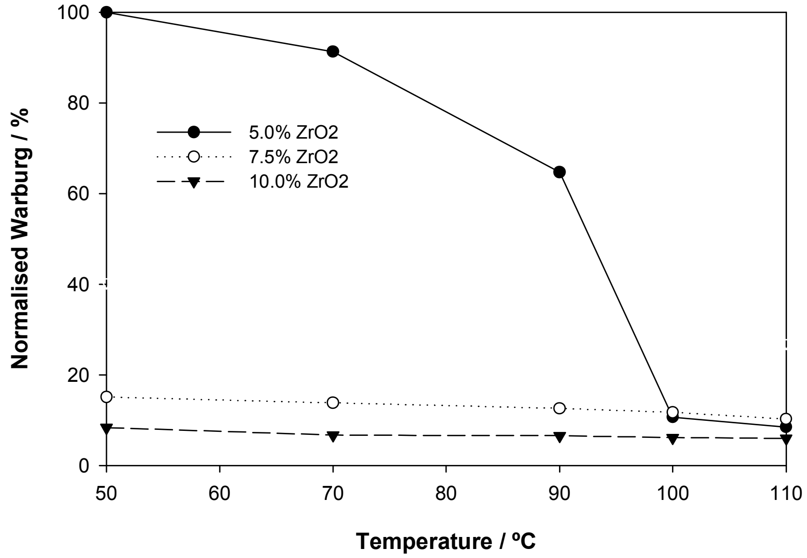

Fig. 4 - Normalised Warburg parameter as a function of the temperature.

Conclusions

The present study shows that there is an obvious interplay between the proton conductivity and the ZrO_2 content in the sPEEK matrix. Proton conductivity increases with both the solid content decrease and temperature increase. It was also found that at 12.5 wt.% ZrO_2 content the impedance spectrum was different from those at lower inorganic levels. This feature coincides with the observation that at high ZrO_2 contents zirconium domains gain some crystallinity [10]. An extension of the Randles' circuit was fitted to the determined impedance spectra. The agreement with the model is quite good for all ZrO_2 contents up to 10 wt.%. However, it was not possible to fit the model to the data of the membrane containing 12.5 wt.% ZrO_2. Finally, it was observed that the Warburg parameter decreases slightly with the temperature and more drastically for the 5 wt.% ZrO_2 membrane. The same trend was also observed as the inorganic content increases up to 10 wt.% ZrO_2.

Acknowledgements

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