

# sSEBS/40SiO<sub>2</sub>-40P<sub>2</sub>O<sub>5</sub>-20ZrO<sub>2</sub> Sol-Gel Infiltrated Membranes for DMFCs

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## 1. Introduction

Nafion membranes are known for their excellent proton conductivity, good mechanical properties and high thermal, chemical and electrochemical stability; unfortunately, they also present several known disadvantages: decreasing of proton conductivity above 80 °C and low humidified conditions, high methanol crossover in the particular case of direct methanol fuel cells (DMFCs) and high cost. For several years, sulfonated polystyrene-containing block copolymers, such as sulfonated styrene-ethylene-butylene-styrene triblock copolymer (sSEBS) are being investigated as alternative to perfluorinated Nafion type membranes. This very economical starting material combines the processability of thermoplastics with the functional behavior of elastomers allowing the synthesis of ionomers by partial sulfonation of polystyrene blocks and thereby the obtaining of high proton conductivity electrolyte membranes. Additionally, partially sulfonated sSEBS presents microphase separated morphology whereby the polymer chains (ionic and non-ionic) are self-organized into hydrophilic and hydrophobic domains which decrease the methanol crossover. However, sSEBS based membranes with high loadings of acid groups loss their mechanical properties and performances due to an excessive water swelling [1]. The infiltration of sSEBS with a phosphosilicate by sol-gel process arises as a potential method to decrease this water swelling and enhance the mechanical stability of the membranes [2].

The aim of this work is to study the behaviour of hybrid membranes with different level of infiltration, which is a function of infiltration time, against sSEBS for their use in DMFCs. Thus, the different properties of hybrid membranes have been compared with pristine sSEBS and characterized in terms of water uptake, dimensional changes, IEC, morphology (AFM), thermal stability (TGA), microstructure (DMA), proton conductivity (EIS) and performance in direct methanol single cells.

## 2. Experimental

### 2.1 Sol-Gel synthesis

Sols were prepared by mixing two solutions. The first one was prepared at room temperature by mixing TMP, TEOS, half the volume of propanol (solvent) (molar ratio of propanol/TEOS+TMP+TPZr = 2) and water as HCl 0.1N (molar ratio of water/TMP = 0.75 and water/TEOS=1), stirring for 2 h. The second solution was prepared by mixing TPZr, the other half of propanol and acetylacetone (molar ratio of acetylacetone/TPZr = 1) stirring at room temperature for 2 h. Both solutions were subsequently mixed together for 1 hour. No final step of acidification of the sol is needed because the used of sulfonation process provides an acid medium that helps in forming silica/siloxane polymer within the sSEBS membrane. The inorganic filler materials have high affinity to water and assist proton transport across the electrolyte membrane of the polymer electrolyte fuel cell.

### 2.2 Hybrid membrane preparation

Polymer membranes of SEBS were prepared by casting from chloroform solutions using Dr Blade technique (BYK Instruments). The heterogeneous sulfonation reaction of SEBS was performed by immersing the polymer membranes in a 0.3 M solution of trimethylsilyl chlorosulfonate in DCE for 2 hours. For the infiltration process, sSEBS membranes were previously swelled in H<sub>2</sub>SO<sub>4</sub> 1M at 80 °C for 2 hours and then immersed in the SiO<sub>2</sub>-P<sub>2</sub>O<sub>5</sub>-ZrO<sub>2</sub> sol solution at 80 °C for different times (5, 10 and 20 minutes). At the end of the treatment, the membranes were cleaned with ethanol to avoid the formation of surface-attached phosphosilicate layers, and dried at 50 °C for 1 hour and 120 °C for 2 hours to ensure gels formation. Finally, hybrid membranes were cleaned with ethanol at 80 °C for 2 hours and dried at 80 °C for 1 hour. The obtained membranes had thicknesses about 45-55 μm.

### 2.3 Hybrid membrane characterization

Dynamic mechanical properties of the samples were measured using a TA Instrument 983 dynamic mechanical analyzer in tension mode. Samples were heated from -100 to 260 °C, at three frequencies (3, 5 and 10 Hz), with a programmed heating rate of 2 °Cmin<sup>-1</sup>.

Thermal stability of the membranes was studied by thermogravimetric analysis (TGA) on a TA Instruments TA-Q500 thermogravimetric analyzer. The samples were heated to 900 °C at a rate of 10 °Cmin<sup>-1</sup> in air atmosphere.

AFM measurements were carried out with a Cervantes AFM System (Nanotec Electronica S.L., SPAIN) operating in non-contact dynamic mode with amplitude modulation and non-coated silicon nitride cantilevers.

#### 2.4 Electrochemical characterization of the MEA's

Through-plane proton conductivity of the membranes has been determined on the MEA's at 60 °C by means of electrochemical impedance spectroscopy (EIS) using a Potentiostat/Galvanostat Model 273A and SI 1255 FRA. During measurements, the single cell was continuously supplied with 1M methanol solution (3 mL·min<sup>-1</sup>) to the anode and pure nitrogen (250 mL·min<sup>-1</sup>) to the cathode. The spectra were recorded under DC bias potential of 0.3 V with an amplitude of the sinusoidal signal of 10 mV and a frequency range from 10 kHz to 1 Hz. The through-plane proton conductivity  $\sigma_{TP}$  (S·cm<sup>-1</sup>) was obtained using the following equation:

$$\sigma_{TP} = L / (R \times S) \quad (1)$$

In order to validate the potential use of these membranes in DMFC, they have been tested in a single cell of 3.8 cm<sup>2</sup> of active area at 60 °C and 70 °C [3]. Pt-Ru/C electrodes with 3 mg PtRu·cm<sup>-2</sup> and Pt/C electrodes with 1 mg Pt·cm<sup>-2</sup> have been used as anode and cathode, respectively. During polarization tests the single cell was continuously supplied with 1M methanol solution (3 mL·min<sup>-1</sup>) to the anode and pure oxygen (250 mL·min<sup>-1</sup>) to the cathode.

### 3. Results and Discussion

By incorporating the inorganic gel into the polymer structure, the water uptake decreased in all cases compared to the pure polymer.

The IEC of the hybrids is lower than that of pure sSEBS and decreases over infiltration time, which is in agreement with the trend observed for water uptake results.

TGA results show higher water retention in hybrids since the weight losses associated with the first stage of dehydration are much lower than in sSEBS.

Two distinct glass transition temperatures are observed in DMA analysis; one corresponds to the ethylene-butylene blocks at low temperature ( $T_g^{EB}$ ) and the other is associated to the sulfonated polystyrene blocks and observed at higher temperature ( $T_g^{PS}$ ). As it is shown, the incorporation of the inorganic component has influence only on  $T_g^{PS}$ , which is strongly affected by the inorganic presence; not only in a slight shift towards higher temperature but especially in the values of  $\tan \delta$ , indicating that infiltration method has been effective and phosphosilicate gel resides exclusively into the ionic domains.

AFM shows that the morphology of sSEBS changed from long worm-like to flat microstructures with increasing immersion time.

The 10 min infiltrated membrane shows the same proton conductivity as pure sulfonated polymer, around 0.021 S·cm<sup>-1</sup>.

The polarization curves, Fig. 1, show that pure sSEBS achieves higher power densities than hybrid (10minSOL). The hybrid membrane has a higher slope in the ohmic region than sSEBS which is consistent with IEC and proton conductivity tests.

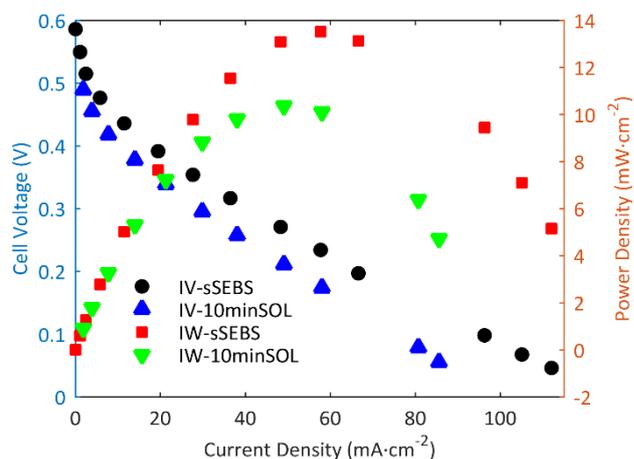


Fig. 1. Polarization and power density curves of sSEBS and hybrid (10minSOL) MEAs.

### 4. Conclusions

All hybrid membranes presented lower water uptake and higher dimensional stability than pure sulfonated polymer (sSEBS). IEC values decreased as a function of infiltration time.

Proton conductivity was similar for infiltrated and pure sSEBS membranes.

The infiltration of phosphosilicate gel into ionic domains was confirmed by AFM and DMA analysis and it leads to the formation of stronger hydrogen bond interactions between Si-OH, P-OH and -SO<sub>3</sub>H groups. Thermal stability was greater than sSEBS.

In single DMFC tests, sSEBS still shows better performances than hybrid membrane (10minSOL).

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### 6. References

- [1] C. del Río, O. García, E. Morales, P.G. Escibano, *Electrochimica Acta* 176 (2015) 378-387.
- [2] M. Aparicio, L.C. Klein, *J. Electrochemical Society*, 152 (3) (2005) A493-A496.
- [3] T.J. Leo, M.A. Raso, E. Navarro, E. Sánchez de la Blanca, M. Villanueva, B. Moreno, *Int. J. Hydrogen Energy* 35 (2010) 11642-8.