

# Sulfonated polyether ether ketone and hydrated tin oxide proton conducting composites for direct methanol fuel cell applications

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## Abstract

Composite membranes based on sulfonated polyether ether ketone (SPEEK) and hydrated tin oxide ( $\text{SnO}_2 \cdot n\text{H}_2\text{O}$ ) were prepared and characterized. The formation of the composite substantially modified the properties of SPEEK in terms of durability and electrochemical performance. The structural and electrochemical performance of the samples were investigated using scanning electron microscopy (SEM), X-ray diffraction (XRD) analysis, electrochemical impedance spectroscopy (EIS), water and methanol uptake (WU, MU), and direct methanol fuel cell (DMFC) tests. The polymer electrolyte membrane doped with 50 wt%  $\text{SnO}_2 \cdot n(\text{H}_2\text{O})$  possess good proton transport characteristics, reduced methanol uptake and improved stability with respect to a reference unfilled membrane and it is then suitable for application as electrolyte in DMFCs.  
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**Keywords:** SPEEK; Hydrated tin oxide; Composite membranes; Direct methanol fuel cells

## 1. Introduction

Direct methanol fuel cells (DMFCs) are promising devices for a variety of applications by virtue of their efficiency, high-power density, and environmental-friendly nature [1,2]. Nafion® is the most widely used electrolyte for DMFCs [3], although methanol crossover problems, its high cost, and loss of performance above 80 °C limit the large-scale commercialization of DMFCs [4].

A promising polymer that is currently investigated by different authors is polyether ether ketone (PEEK) [5–7], which is a low-cost polymer with good thermal stability and mechanical properties. Proton conductivity for this polymer can be achieved by sulfonation (sulfonated PEEK, SPEEK), and the degree of sulfonation (DS) can be controlled by reaction time and temperature. At low DS, the hydrophilicity of SPEEK is too low to reach the water content needed to ensure values of proton con-

ductivity acceptable for use in fuel cells [8]. Conversely, high DS values imply degradation of the polymer in terms of solubility and mechanical properties [9].

Hybrid organic–inorganic membranes with controlled physico-chemical properties have been investigated to improve thermal and mechanical stability avoiding conductivity losses [6,10]. The development of composite membranes able to operate at  $T \geq 90$  °C represents in fact one of the methods to improve fuel cell performance [11,12].

The approach adopted in the present work consists in preparing composite membranes incorporating a proton conducting oxide,  $\text{SnO}_2 \cdot n(\text{H}_2\text{O})$ , in a SPEEK matrix. An intermediate degree of sulfonation (DS = 0.7) was chosen as a compromise to ensure satisfactory proton conductivity values while avoiding membrane degradation associated with higher DS.

Hydrated tin oxide shows relatively good conductivity values, around  $10^{-3}$  to  $10^{-2}$  S  $\text{cm}^{-1}$  at high relative humidity (RH), and in the temperature range of interest for fuel cell application ( $T = 100$ – $150$  °C) [13,14]. The presence of an inorganic phase in the SPEEK is expected to reduce the conductivity losses due to polymer degradation. The hydrophilic filler was introduced

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at a large content (50 wt%) with the aim of reducing methanol permeability and improving the membrane stability, preventing its water solubilization.

## 2. Experimental

### 2.1. Materials

Polyether ether ketone, Victrex PEEK 450 P, was used as received. Sulfonation was carried out with concentrated sulphuric acid (H<sub>2</sub>SO<sub>4</sub>, Aldrich 96%) at room temperature and achieved sulfonated polyether ether ketone (SPEEK) having degree of sulfonation DS = 0.7 as evaluated by <sup>1</sup>H NMR [8].

Hydrated tin oxide (SnO<sub>2</sub>·*n*H<sub>2</sub>O) was prepared following the method described by Giesekke et al. [15], consisting in alkaline hydrolysis of tin chloride (SnCl<sub>4</sub> Aldrich, 99.995%) by means of ammonia solution (NH<sub>4</sub>OH, Aldrich 25%). The white precipitate obtained was washed with distilled water until no chloride ions were detectable. The sample was then dried at room temperature in air to remove the excess water. The powder samples were characterized and used as-prepared.

SPEEK-based composite membranes containing 50 wt% SnO<sub>2</sub>·*n*H<sub>2</sub>O were prepared dissolving the polymer in dimethylacetamide (DMA, 98% Aldrich) and adding SnO<sub>2</sub>·*n*H<sub>2</sub>O. The suspension was heated and stirred, then cast onto a Teflon plate and heated at 60 °C to dryness. Pure SPEEK membranes were prepared following the same procedure for sake of reference. For DMFC tests, Nafion membranes (thickness 170 μm), prepared as previously described [16], were used as a reference for the composite membranes, due to the fact that pure SPEEK membranes could not survive in the DMFC test operating conditions.

The thickness of the dried membranes were in the 150–200 μm range. Before each measurement, the membranes were treated with 5 M H<sub>2</sub>SO<sub>4</sub> for 15 h at room temperature to remove residual casting solvent which presence might negatively affect conductivity [17,18], and then washed with deionized water.

### 2.2. Methods

The solvent uptake was measured as a function of temperature in the 20–80 °C range. Pieces of 1 cm<sup>2</sup> were cut from the membranes, dried overnight at 80 °C and weighted.

Powder of SnO<sub>2</sub>·*n*(H<sub>2</sub>O) was pressed uniaxially into pellets (13 mm diameter and 0.4 mm thickness) at 106 MPa. The pellets were dried overnight at 80 °C and weighted. Pellets and membranes were then exposed to saturated water or absolute methanol vapor pressure and weighted after 1 h at each temperature value. Solvent uptake (SU) was calculated as reported in the literature [8], using the following equation:

$$SU (\%) = \left[ \left( \frac{W_{\text{swollen}}}{W_{\text{dry}}} \right) - 1 \right] \times 100 \quad (1)$$

where SU is expressed in percentage units,  $W_{\text{swollen}}$  the weight of the membrane exposed to the solvent, and  $W_{\text{dry}}$  is the weight of the dry membrane. In the text we referred to water uptake

(WU) values or methanol uptake (MU) values when the solvent is water or methanol, respectively.

The overall uptake of solvent molecules per sulfonic acid group (SO<sub>3</sub>H) in the membranes, i.e.  $\lambda$ , was calculated using Eq. (2). For the calculation of  $\lambda$  of the composite membrane, this equation takes into account the solvent amount (either water or methanol) adsorbed by the tin oxide phase, which was subtracted assuming an additive behavior of the polymer and the inorganic phase:

$$\lambda = \frac{n_{\text{solvent}}}{n_{\text{SO}_3\text{H}}} = \frac{SU (\%)_{\text{membrane}} / MW_{\text{solvent}}}{((\%wt_{\text{SPEEK}} - \%wt_{\text{SnO}_2}) - (SU (\%)_{\text{SnO}_2} / 2)) / EW_{\text{SPEEK}}} \quad (2)$$

where  $MW_{\text{solvent}}$  is the molecular weight of the solvent,  $\%wt_{\text{SPEEK}}$  and  $\%wt_{\text{SnO}_2}$  the weight percentage of SPEEK and tin oxide in the membranes, respectively, and  $EW_{\text{SPEEK}}$  is the equivalent weight of the SPEEK.

SEM images were acquired using FE-SEM, LEO mod. Supra 35, being 2 kV the electron beam energy.

Simultaneous thermogravimetric and differential thermal analyses (TG-DTA) were carried out in the 25–500 °C range, using a thermobalance (STA 409, Netzsch), in air flow (80 mL min<sup>-1</sup>) with a heating rate of 5 °C min<sup>-1</sup>.

X-ray diffraction (XRD) analysis was performed using a Philips X'Pert MPD powder diffractometer equipped with a Cu K $\alpha$  radiation source and graphite monochromator.

The proton conductivity of the membranes was measured by electrochemical impedance spectroscopy (EIS) measurements using a Multichannel Potentiostat VMP3 (Princeton Applied Research). An applied voltage of 20 mV and a frequency range of 500 KHz to 10 Hz were used. The composite membranes were sandwiched between commercial electrodes (E-Tek ELAT HT 140E-W with a platinum loading of 5 gm<sup>-2</sup>) and the proton conductivity was recorded as a function of temperature at saturated water vapor pressure (100% RH), using a homemade apparatus. The resistance of the membranes, hence their conductivity, was calculated by a linear fit of the impedance spectra in their linear portion. From the resistance values we obtained the conductivity ( $\sigma$ ) value using Eq. (3):

$$\sigma = \frac{d}{RA} \quad (3)$$

where  $R$  is the resistance,  $d$  the distance between electrodes and  $A$  is the electrode area.

Membrane electrode assemblies (MEAs) were fabricated using commercial electrodes E-TEK, A-6 ELAT/SS/PtRu60-3-30PTFE/0.8N, custom 3 mg cm<sup>-2</sup> loading using 60% HP Pt:Ru alloy (1:1) on Vulcan, 30 wt% PTFE with 0.8 mg cm<sup>-2</sup> Nafion (anode), and A-6 ELAT/SS/Pt40-2-30PTFE/0.8N custom 2 mg cm<sup>-2</sup> loading using 40% HP Pt on Vulcan, 30 wt% PTFE with 0.8 mg cm<sup>-2</sup> Nafion (cathode).

MEAs were prepared by hot pressing using SPECAC hot press. Membrane and anodic electrode were placed in a teflon sheet and pressed for 2 min at 80 °C applying 0.39 MPa. After

that, the cathode was put on the other side of the membrane. Proper electrode/membrane/electrode interfacial adhesion was achieved pressing the sandwich at 100 °C under a load of 0.98 MPa for 5 min.

Fuel cell experiments were carried out in a 5 cm<sup>2</sup> single cell (ElectroChem), in a homemade fuel-cell test station. The test station was equipped with independent temperature control of the reactant gas (O<sub>2</sub>), methanol solution, and single cell. Flow rate of the gas was regulated using mass-flow controller (MKS PR4000, 500 sccm), the total pressure of the gas was controlled using a back-pressure regulator. Flow rate of methanol solution (2 M) was monitored by a KNF's Model FEM 1.08 Liquid Metering Pump with control board (1 mL min<sup>-1</sup>).

All experiments were performed fixing at 0.2 MPa the total pressure in the cell and at 100 °C the cell temperature.

Polarization data were recorded using a Multichannel Potentiostat VMP3 (Princeton Applied Research).

### 3. Results and discussion

#### 3.1. Characterization of SnO<sub>2</sub>·n(H<sub>2</sub>O)

The procedure used to synthesize SnO<sub>2</sub>·n(H<sub>2</sub>O) allowed to obtain nanosized particles. Fig. 1 shows the typical SEM micrograph of the as-prepared SnO<sub>2</sub>·n(H<sub>2</sub>O) powder. As typical morphology for hydrated compounds, the powder was made of soft agglomerates. Numerous SEM observations allowed to measure the unit particles in the nanometric size range (5–15 nm). Such a small particle size is expected to ease the formation of homogeneous composite membranes.

To study the thermal evolution of SnO<sub>2</sub>·n(H<sub>2</sub>O) thermogravimetric (TG) and differential thermal analysis (DTA) were carried out on the precursor. Fig. 2 shows the TG and DTA curves of the sample. It is known that hydration water of SnO<sub>2</sub>·nH<sub>2</sub>O can be classified into different classes as a function of the water/oxide bond strength [13,14]. The main weight loss (about 12% of the total loss), observed in the 50–150 °C range in the TG curve, can

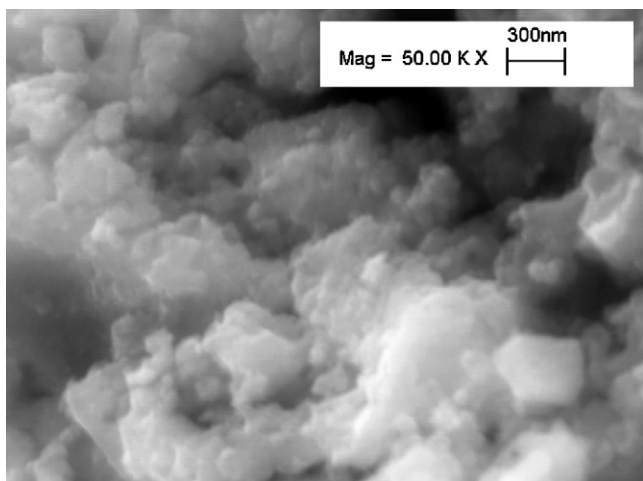


Fig. 1. SEM micrograph of the as-prepared SnO<sub>2</sub>·n(H<sub>2</sub>O) powder.

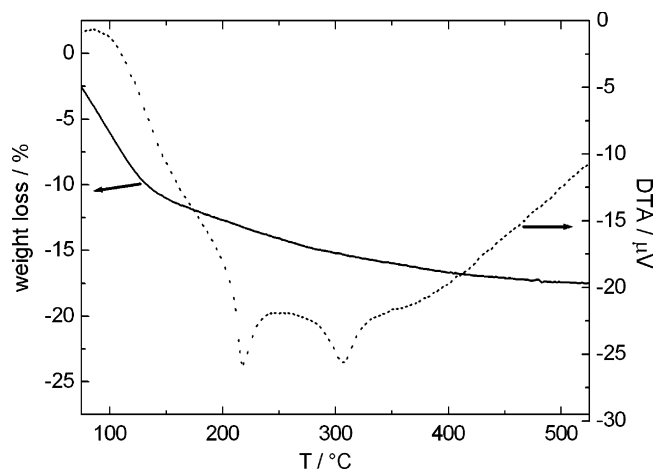


Fig. 2. TG curve (solid line) and DTA curve (dotted line) of the SnO<sub>2</sub>·n(H<sub>2</sub>O) powder.

be attributed to the loss of physisorbed water. The DTA curve showed also two distinct peaks with their maxima at 200 and 320 °C, which can be attributed to the desorption of chemisorbed water [15].

#### 3.2. Morphological and structural characterization of the composite membranes

Fig. 3 shows the SEM micrograph of the SPEEK/SnO<sub>2</sub> 50:50 wt% composite membrane. The membrane showed high homogeneity, being the filler well distributed in the SPEEK matrix. The particle size of the inorganic phase is larger than the size of the SnO<sub>2</sub>·n(H<sub>2</sub>O) precursor, due to aggregation phenomena. As previously observed with different systems, the size of the aggregates increases with increasing the filler loading in the membrane [19–21].

Fig. 4 shows the comparison between the XRD patterns of the as-prepared SnO<sub>2</sub>·n(H<sub>2</sub>O) powder and of the SPEEK/SnO<sub>2</sub> composite membrane. The XRD pattern of a pure SPEEK membrane (not shown) is typical of an amorphous structure. Regarding the tin oxide XRD pattern, broad peaks revealed an

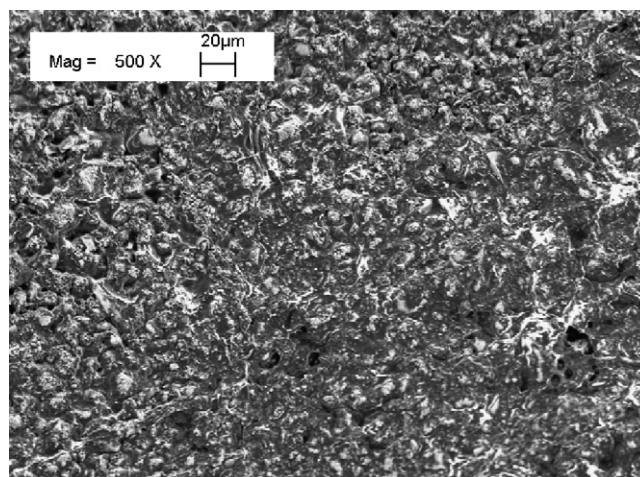


Fig. 3. SEM micrograph of the SPEEK/SnO<sub>2</sub> composite membrane.

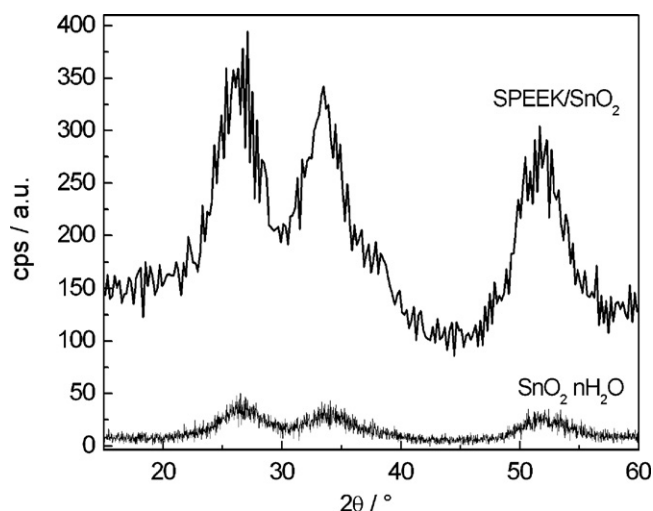


Fig. 4. XRD patterns of the  $\text{SnO}_2 \cdot n(\text{H}_2\text{O})$  powder and SPEEK/ $\text{SnO}_2$  composite membrane.

amorphous-like state of the oxide, due to its hydration water. Sharpening of the peaks, without any detectable shift, was observed in the XRD pattern of the composite membrane. It has been previously reported that the peaks of  $\text{SnO}_2 \cdot n(\text{H}_2\text{O})$  sharpened after heating, as a result of crystallization [14]. In the case of SPEEK/ $\text{SnO}_2$  composite membranes, the sharpening of the peaks can be ascribed to a change of the hydration grade of the oxide in the membrane with respect to the precursor powder, due to coordination of the oxide water molecules with the polymer sulfonic acid groups, as previously observed also for SPEEK/hydrated tungsten oxide composite membranes [6].

### 3.3. Electrochemical and water uptake characterization of the composite membranes

Fig. 5 shows the Arrhenius plots of the conductivity of the composite membranes and of the unfilled SPEEK reference

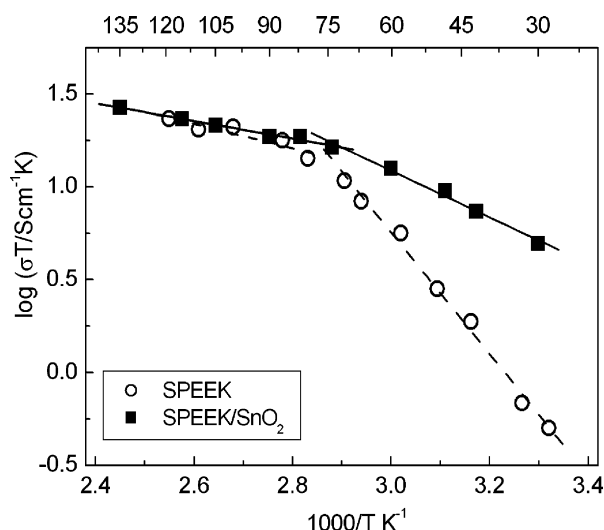


Fig. 5. Arrhenius plots of the unfilled SPEEK and SPEEK/ $\text{SnO}_2$  composite membranes at 100% RH.

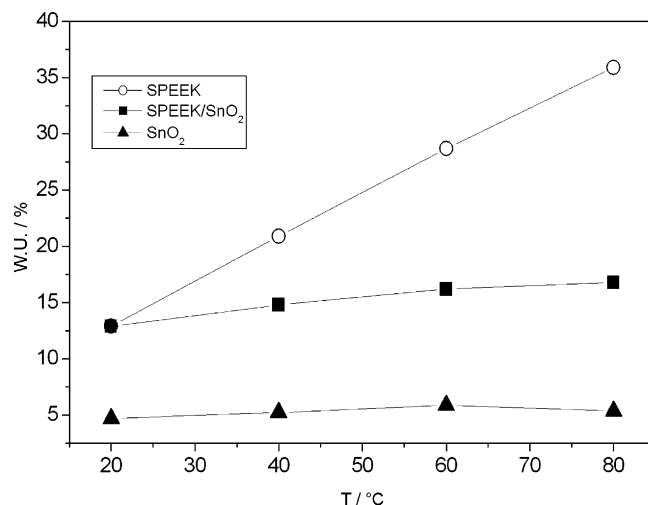


Fig. 6. Water uptake (WU) as a function of temperature, measured at 100% RH for composite SPEEK/ $\text{SnO}_2$  membrane and individual components.

membrane. In the region between 25 and 75 °C, the proton conductivity ( $\sigma$ ) values of the composite membrane were always larger than the values measured for the unfilled SPEEK membrane. In particular, at 25 °C,  $\sigma$  of the composite membrane was one order of magnitude larger than the  $\sigma$  of the unfilled SPEEK (composite:  $0.016 \text{ S cm}^{-1}$ ; unfilled SPEEK  $0.0017 \text{ S cm}^{-1}$ ). This difference decreased with increasing the temperature and eventually was null at 75 °C. This behavior is also reflected by the activation energy ( $E_a$ ) values that in the 25–75 °C region were found to be 0.249 and 0.659 eV for the composite and the unfilled SPEEK membrane, respectively. Above 75 °C,  $\sigma$  values as well as  $E_a$  values were similar for the two samples up to 130 °C ( $\sigma = 0.040 \div 0.066 \text{ S cm}^{-1}$ ,  $E_a \sim 0.1 \text{ eV}$ ).

It has been reported for Nafion that the activation energy is strongly dependent on the membrane water content. In a dry membrane the activation energy is in the 0.4–0.5 eV range, whereas the activation energy of a highly swollen membrane is 0.1 eV, which is close to the value of  $E_a$  for bulk water conductivity [22].

The water uptake (WU) values of the composite membrane and of the individual components was then investigated as a function of temperature. WU values were recorded at 100% RH from 20 to 80 °C, temperature effect at which the filler effect in terms of  $\sigma$  and  $E_a$  became negligible. Data are shown in Fig. 6. The water uptake of the oxide was low and almost independent from the temperature, while larger values, almost linearly increasing with temperature, were determined for the unfilled SPEEK sample. The WU values of the composite membrane were intermediate between those of the two components. The  $\lambda$  values (the number of water molecules per sulfonic acid group of SPEEK) calculated considering an additive behavior of the components, are shown in Fig. 7.  $\lambda$  of the composite membrane was larger than the  $\lambda$  value of the SPEEK membrane below 60 °C, temperature at which the  $\lambda$  values of the two samples became the same. This behavior is in agreement with the larger conductivity values observed for the SPEEK/ $\text{SnO}_2$  membrane at lower temperatures, indicating that at larger  $\lambda$  values corresponded larger  $\sigma$  values [18].

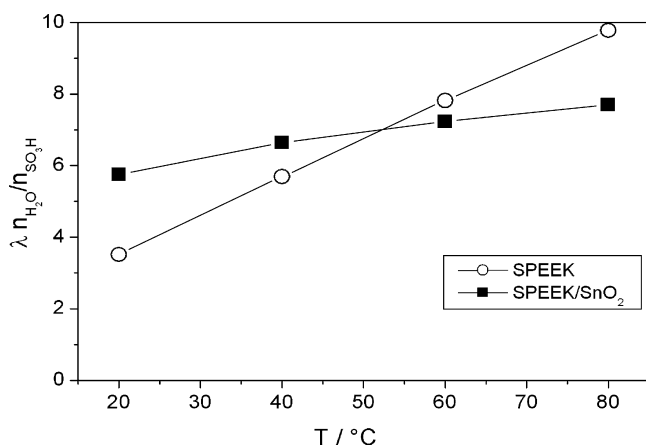


Fig. 7.  $\lambda$  (i.e.  $n_{\text{H}_2\text{O}}/n_{\text{SO}_3\text{H}}$ ) as a function of temperature, calculated from the water uptake values.

The overall reduced swelling of the composite membrane can be explained assuming that the filler induces morphological modification of the membrane and that the oxide hydration water molecules generate a connection between the polymer sulfonic acid moieties, creating different hydrophilic paths that favor proton transfer [19]. The effect becomes negligible at higher temperature when a decrease in the interactions between polymer chains is known to favor a greater hydration of the polymer [18]. The improved performances reported for several Nafion based composite membranes have been indeed attributed to modifications of the polymer structure [23–25].

### 3.4. Stability and methanol permeability of the composite membranes

It is well known that one of the main drawbacks for membranes prepared with SPEEK with high sulfonation degree is their water solubility. Therefore, the stability of the composite membranes in saturated water vapor pressure conditions was investigated. Fig. 8 shows the  $\sigma$  values measured at 100 °C and

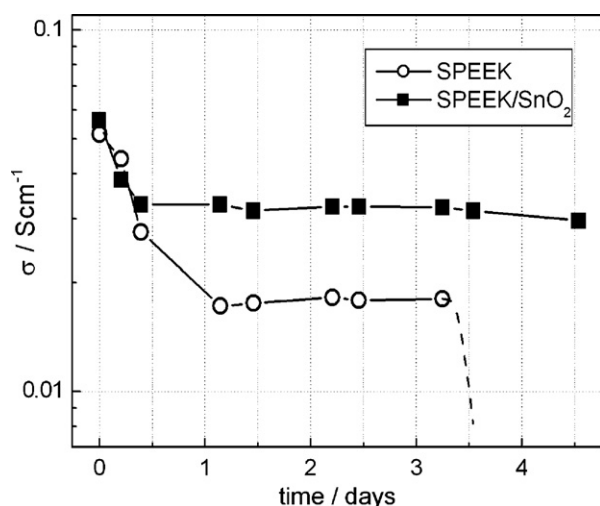


Fig. 8. Proton conductivity as a function of time, measured at 100 °C and 100% RH.

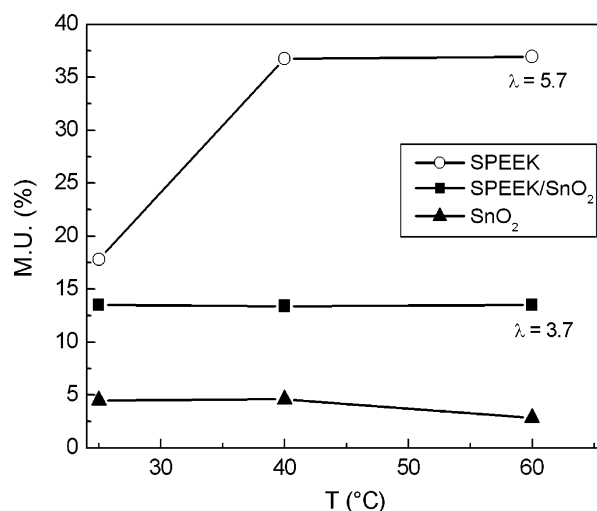


Fig. 9. Methanol uptake as a function of temperature for composite SPEEK/SnO<sub>2</sub> membrane and individual components. Calculated  $\lambda_{\text{MeOH}}$  values are shown.

100% RH as a function of time, for both unfilled and filled samples. The  $\sigma$  of the unfilled SPEEK membrane decreased with time in the first day of exposure to 0.02 S cm<sup>-1</sup>, then remained constant up to 3 days, and finally drastically dropped, showing a complete degradation of the membrane. On the other hand, the conductivity of the composite membrane was the same as the unfilled membrane at the beginning of the test and decreased with the same rate for about 12 h, after which the conductivity value, larger than the value measured for the unfilled membrane at the stability plateau, was stable over 4 days. After this time, the measurements were stopped. The reduced swelling and higher morphological stability of the composite resulted in improved membrane performance in terms of durability.

The influence of the filler on the methanol permeability was also investigated evaluating the membrane methanol uptake (MU). Fig. 9 shows the MU values as a function of temperature. Values increased along the series SnO<sub>2</sub>· $n$ (H<sub>2</sub>O) < composite membrane < unfilled membrane.  $\lambda_{\text{MeOH}}$  values, i.e.  $n_{\text{CH}_3\text{OH}}/n_{\text{SO}_3\text{H}}$ , are always lower for the composite. As the consequence of these methanol uptake data, the SPEEK/SnO<sub>2</sub> composite membranes are then expected to possess a lower methanol permeation rate when exposed to methanol aqueous solution in a DMFC [26].

### 3.5. Direct methanol fuel cell performance of the composite membranes

To check the functioning of the composite membrane in a real device, the electrochemical performance of the membranes was tested in a DMFC single cell, acquiring polarization curves. Fig. 10 shows the polarization and power curves for the SPEEK/SnO<sub>2</sub> composite membrane in a DMFC test at 100 °C, compared with a recast Nafion membrane. As already mentioned, Nafion is the most widely used electrolyte for DMFCs, even though it exhibits high methanol permeation rate as well as a drop in proton conductivity at temperatures larger than 80 °C. The  $I$ - $V$  curves clearly showed the improved performance of

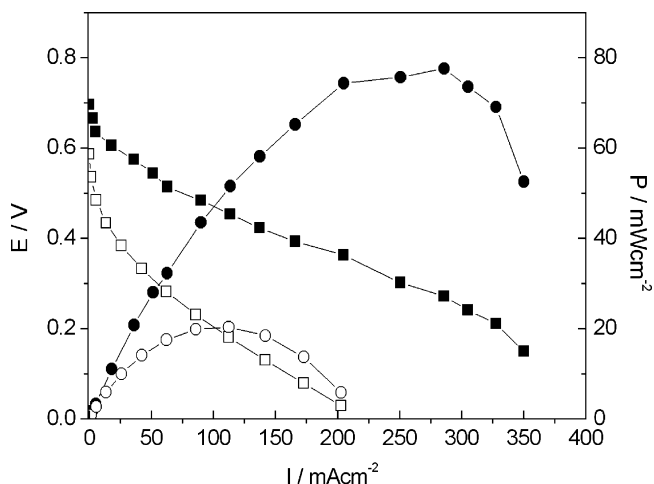


Fig. 10. Polarization (■: SPEEK/SnO<sub>2</sub>; □: Nafion) and power density curves (●: SPEEK/SnO<sub>2</sub>; ○: Nafion) of the composite membrane and an unfilled recast Nafion membrane, measured at 100 °C, oxygen feed, MeOH 2 M.

the composite membrane with respect to the Nafion membrane. The open circuit voltage (OCV) for the composite membrane (0.70 V) was larger than that of unfilled SPEEK (0.65 V) and reference Nafion (0.59 V). The polarization curve of the unfilled SPEEK membrane is not shown due to its lower stability in terms of proton conductivity as a function of time. This finding shows that the use of a SPEEK membrane allowed to reduce the methanol crossover with respect to Nafion, as already evidenced in previous works [27]. Moreover, the presence of tin oxide allowed a further reduction of the methanol crossover as expected from the MU values.

In the whole voltage range investigated, the current values of the SPEEK/SnO<sub>2</sub> membrane were always larger than the values obtained with the Nafion membrane. In particular, the composite membrane reached a maximum current density value of 350 mA cm<sup>-2</sup> (with respect to 200 mA cm<sup>-2</sup> for unfilled Nafion). The maximum power density value reached at 100 °C with the composite membrane was 80 mW cm<sup>-2</sup> at a current density of about 300 mA cm<sup>-2</sup>, whereas the maximum power density value of the reference unfilled Nafion membrane at the same temperature was 20 mW cm<sup>-2</sup>, at a current density of about 120 mA cm<sup>-2</sup>. The improvement of the polarization curve of the SPEEK/SnO<sub>2</sub> composite membrane reflected the drop in conductivity of the unfilled Nafion membrane above 90 °C and the enhanced stability of the composite membrane at 100 °C.

These results converge to indicate that filling SPEEK membranes with hydrated tin oxide allowed to improve the membrane stability, as well as to decrease its methanol permeability. These features led to an enhancement of cell performance of the composite membrane with respect to our reference Nafion recast membrane, pointing out that SPEEK/SnO<sub>2</sub> membrane is a promising electrolyte for DMFCs.

#### 4. Conclusions

Polymer electrolyte membranes doped with an inorganic proton conductor were successfully prepared. Our strategy to

improve the performance of both SPEEK and hydrated tin oxide consisted in the combination of the two materials at the same content. The composite membrane showed good proton transport characteristics, without any loss in conductivity due to the presence of a large amount of the inorganic phase. The presence of the oxide led to a decrease in the methanol permeability of the membrane, as well as to increase the membrane stability avoiding SPEEK degradation due to its water solubility. In fact, doping a SPEEK-based material with 50 wt% of hydrated tin oxide allowed the preparation of a proton-conducting membrane having low water swelling, low methanol permeability, large and stable proton conductivity, that exhibited good performance in a direct methanol fuel cell at 100 °C.

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