



# Conductivity and hydration of sulfonated polyethersulfone in the range 70–120 °C: Effect of temperature and relative humidity cycling

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## ABSTRACT

Proton conductivity and hydration of sulfonated polyethersulfone (SPES) membranes, with ion exchange capacity of  $1.31 \text{ meq g}^{-1}$ , is determined under different conditions of temperature, in the range 70–120 °C, and relative humidity (RH) in the range 50–90%. Conductivity measurements are performed by the impedance technique, and the impedance data are analyzed on the basis of a simple equivalent circuit in order to compare the evolution of the membrane conductivity with that of the electrical capacitance of the electrode–electrolyte interface during heating and cooling runs.

Temperature cycling at constant RH, as well as RH cycling at constant temperature, give rise to hydration hysteresis and to the concomitant conductivity hysteresis. The highest conductivity ( $4.5 \cdot 10^{-2} \text{ S cm}^{-1}$ ) is measured at 100 °C–90% RH with 8.4 water molecules per sulfonic group. The hysteresis associated with temperature cycling is avoided by filling SPES with zirconium phosphate which makes hydration easier at low temperature.

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## 1. Introduction

Proton transport in most low-temperature proton conductors is water assisted [1] and occurs according two main transport mechanisms: the so-called “vehicle” mechanism [2] where protons migrate attached to a water molecule as hydronium ion, and the Grotthuss mechanism [3] consisting in proton jumps through hydrogen bonds between adjacent water molecules followed by their reorientation. The mobility of the charge carrier depends therefore on the diffusional and/or orientational mobility of the water molecules. In addition, the presence of water favors to a great extent the ionization of the protogenic groups thus determining the concentration of the carriers.

In polymer electrolytes, water forms ionic clusters together with counterions and fixed charges thus giving rise to phase separated systems at the nanometric scale, where the clusters are confined within the hydrophobic polymer matrix [4–7]. Consequently, the proton conductivity of these systems depends not only on carrier concentration and on their mobility but also on cluster connectivity which, in turn, increases with water content [8].

The knowledge of the water content is therefore necessary to rationalize proton conduction. Most hydration and conductivity data reported in the literature for proton conducting polymer electrolytes refer either to samples at room temperature or to samples equilibrated at temperature below 100 °C in liquid water, or in water vapor at 100% relative humidity (RH).

On the other hand, there are only few papers [9–14] reporting conductivity data together with the corresponding material hydration for RH < 100% above room temperature and, in particular, at temperatures above 70 °C which are of interest for polymer electrolyte membrane fuel cells (PEMFCs). The availability of these data would help to understand the problems still hindering PEMFC operation at temperature above 80 °C, that would simplify the PEMFC cooling system, promote the reactions at the electrodes and allow feeding the PEMFC with hydrogen containing CO impurities.

We therefore started investigating proton conductivity and hydration of both sulfonated aromatic polymers and perfluorosulfonic acids at temperature above 70 °C. According to our technique, water uptake at controlled temperature and RH is determined gravimetrically, as described in previous papers [11,12], by using a cell having the same shape and size, as well as the same temperature–RH control system, as those of the conductivity cell in order to reproduce the environment present in the conductivity cell as accurately as possible. This technique, although time consuming, has the advantage to allow determining the polymer hydration at water vapor pressure higher than 1 atm, and in particular at RH values close to 100% for temperature above 100 °C.

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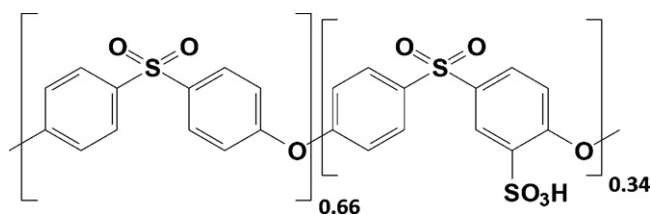


Fig. 1. Repeat unit of SPES with DS=0.34.

This paper reports conductivity and hydration of sulfonated polyethersulfone (SPES) membranes as a function of temperature and RH. Polyethersulfone (PES) is a high-performance thermoplastic material suitable for the preparation of proton exchange membrane due to its excellent thermal, oxidative and hydrolytic stability; nevertheless there is only a limited number of papers dealing with SPES as polymer electrolyte for use in fuel cells. [15–28].

The SPES membranes investigated in the present work had a degree of sulfonation (DS) of 0.34 (Fig. 1) and an ion exchange capacity of  $1.31 \text{ meq g}^{-1}$ . The membrane conductivity was determined in the range  $70\text{--}120^\circ\text{C}$  at constant RH, and as a function of RH at  $100^\circ\text{C}$ . Measurements were performed by the impedance technique, and the impedance data were analyzed on the basis of a simple equivalent circuit to compare the evolution of the membrane conductivity with the evolution of the electrical capacitance of the electrode–electrolyte interface during heating and cooling runs. The conductivity and the hydration of composite SPES membranes filled with zirconium phosphate (ZrP) were also investigated.

## 2. Experimental

### 2.1. Caution

Chlorosulfonic acid ( $\text{HSO}_3\text{Cl}$ ) is hazardous and should be handled with proper precautions, under a chemical hood with a fume exhaust system.

### 2.2. Chemicals

PES (Victrex,  $\text{MW} = 67,080 \text{ g mol}^{-1}$ ),  $\text{HSO}_3\text{Cl}$  (Sigma Aldrich), sulfuric acid (Carlo Erba 96%) and all other chemicals (Aldrich) were reagent grade and were used as received. Nafion 117 membranes (Ion Power) underwent the following standard treatment: 1 h in boiling 3%  $\text{H}_2\text{O}_2$ , 1 h in boiling 0.5 M  $\text{H}_2\text{SO}_4$ , 1 h in boiling  $\text{H}_2\text{O}$ .

### 2.3. SPES preparation

PES (10 g, 43.1 meq) was added to  $\text{HSO}_3\text{Cl}$  (50 mL) and the mixture was stirred at  $0^\circ\text{C}$  in nitrogen atmosphere for 90 min. After 30 min, the polymer was completely dissolved giving an orange solution. The solution was poured drop by drop, with constant stirring, in 150 mL of sulfuric acid and kept at room temperature for 2 h. It was then poured under continuous stirring into a large excess of ice-cold water. After being allowed to stand overnight the precipitate was filtered and washed several times with cold water to neutral pH. The sulfonated polymer (SPES) was then dried at  $80^\circ\text{C}$  for 1 night. The DS value, evaluated by titration and NMR [29] was DS = 0.34 corresponding to an IEC of  $1.31 \text{ meq g}^{-1}$ .

### 2.4. Membrane preparation

SPES membranes were prepared by solution casting using dimethylformamide (DMF) as solvent. In a typical experiment,

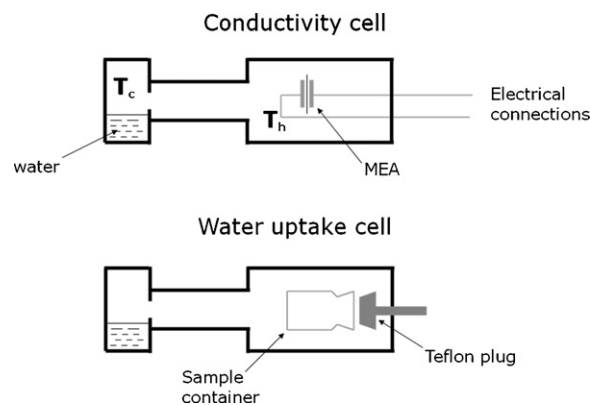


Fig. 2. Schematic representation of the conductivity cell and the water uptake cell.

300 mg sample was dissolved in 10 mL of solvent. The resulting mixture was stirred for 1 h at room temperature, cast onto a Petri dish, and heated to dryness for 4 h at  $100^\circ\text{C}$ . Finally, the membrane was washed with a 1 M HCl solution at  $80^\circ\text{C}$  for 1 h and then heated at  $100^\circ\text{C}$  for 1 h.

Composite SPES membranes containing 10 wt% ZrP (hereafter SPES/ZrP) were prepared by exchanging the SPES protons with Zr(IV) cationic species and subsequent treatment of the exchanged membrane with phosphoric acid. In particular, a SPES membrane, dried at  $130^\circ\text{C}$ , was first swollen at room temperature in water for 1 h and then equilibrated with a 0.76 M  $\text{ZrOCl}_2$  solution at  $80^\circ\text{C}$  for 15 h. The membrane was rinsed in water at room temperature to eliminate the excess of  $\text{ZrOCl}_2$  solution and then treated with a 1 M  $\text{H}_3\text{PO}_4$  solution at  $80^\circ\text{C}$  for 8 h. The excess of phosphoric acid in the samples was eliminated by washing with a 1 M HCl solution at  $80^\circ\text{C}$ . The membrane was finally rinsed in water at room temperature, dried at  $130^\circ\text{C}$  for 1 h and weighed in order to determine the final weight ( $W_f$ ). The filler weight percentage into the composite membrane was calculated according to the following equation:

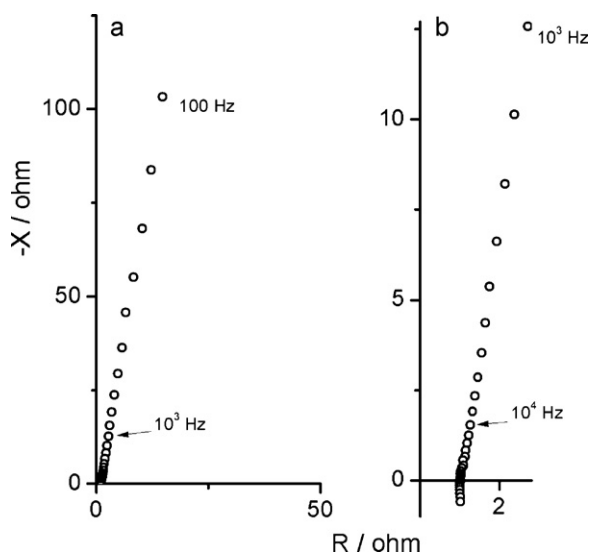
$$\text{ZrP (wt\%)} = 100 \frac{W_f - W_i}{W_f}$$

where  $W_i$  is the weight of the starting SPES membrane dried at  $130^\circ\text{C}$ .

### 2.5. Conductivity measurements

Membranes, 8 mm in diameter and  $90\text{--}100 \mu\text{m}$  thick, were sandwiched between Pt discs or gas diffusion electrodes (Pt-free ELAT) which were pressed on the membrane faces by means of porous stainless steel discs; the applied pressure was  $60 \text{ kg cm}^{-2}$ . The through-plane membrane conductivity was determined as a function of temperature and RH by impedance spectroscopy with a Solartron SI 1260 Impedance/Gain Phase Analyser at a signal amplitude  $\leq 10 \text{ mV}$ . All the conductivity values here reported refer to measurements carried out after the conductivity had reached a constant value for at least 2 h. On the basis of the measurement reproducibility, the relative error on conductivity data was estimated to be not higher than 12%.

RH was controlled by using a stainless steel sealed-off cell consisting of two interconnected cylindrical compartments held at different temperatures (Fig. 2). The cold compartment contained water, while the hot compartment hosted the membrane electrode assembly (MEA). Relative humidity in the hot compartment was calculated from the ratio between the pressures of saturated water vapor ( $p$ ) at the temperatures of the cold ( $T_c$ ) and the hot ( $T_h$ ) compartment:  $\text{RH} = 100 \times p(T_c)/p(T_h)$ .



**Fig. 3.** (a) Nyquist plot for a SPES membrane collected at 120 °C–75% RH with ELAT electrodes; (b) magnification of the high frequency region of the same plot.

### 2.6. Water uptake determination

Water uptake at controlled temperature and RH was determined by using the cell sketched in Fig. 2. This cell has the same size and shape as the conductivity cell and differs from that mainly because the MEA holder is replaced by a glass container hosting the membrane sample ( $\approx 0.5$  g). The cell is equipped with a device which allows to close the sample container with a Teflon plug without opening the cell. After a suitable equilibration time (usually a day) at the desired temperature and RH, the sample container is closed, extracted from the cell and weighed. The water content ( $\lambda$ , number of water molecules per sulfonic group) is determined on the basis of the weight of the polymer dried at 130 °C taking into account the amount of water trapped in the sample container at the temperature and RH of the experiment. The error on the determination of  $\lambda$  is estimated to be  $\pm 0.3$  at most.

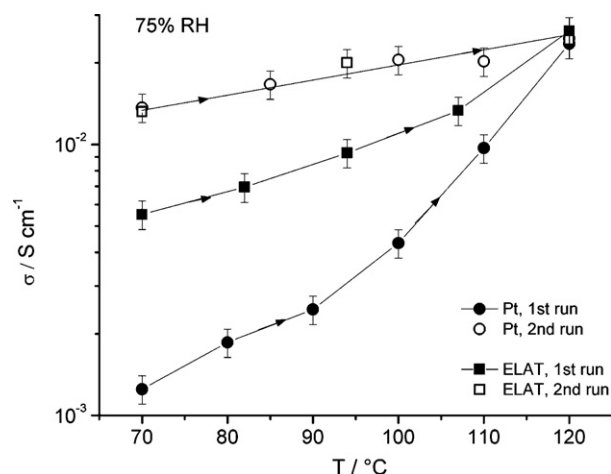
In order to prove the reliability of the RH control on the basis of  $T_c$  and  $T_h$  values, the amount of water trapped in the empty sample container was determined gravimetrically for  $T_h$  in the range 80–140 °C and  $T_c$  in the range 75–136 °C so as to generate RH values between 65% and 90%. The difference between RH values calculated from  $T_c$  and  $T_h$  ( $RH_T$ ) and those determined gravimetrically ( $RH_w$ ) turned out to be in the range 0.4–2.5 RH units with an average value of 1.6, being in all cases lower than the sum of the absolute errors estimated for  $RH_T$  and  $RH_w$  (average values 1.1 and 1.7, respectively).

## 3. Results and discussion

### 3.1. Conductivity and hydration vs. temperature

The conductivity of SPES membranes was determined as a function of temperature at 75% RH by using either Pt discs or Pt-free ELAT electrodes. Two heating runs were carried out in the range 70–120 °C, and after the first run the membranes were allowed to cool for at least one day in the conductivity cell. This kind of measurements was also carried out on composite SPES/ZrP membranes with ELAT electrodes. As an example Fig. 3 shows a typical Nyquist plot ( $Z''$  vs  $Z'$ ) collected for a SPES membrane with ELAT electrodes at 120 °C. Similar plots were obtained with Pt electrodes.

For negative  $Z''$  values, the Nyquist plot consists in a linear region, tilted by about 80° with respect to the  $Z'$  axis, which is



**Fig. 4.** Conductivity of SPES membranes as a function of temperature measured with Pt or ELAT electrodes during two heating runs.

typical of a blocking electrode–electrolyte interface whose frequency response is represented by a constant phase angle element [30]. The extrapolation of the linear region to the  $Z'$  axis provides the membrane resistance ( $R$ ). At the highest frequencies some points of Nyquist plot lie below the  $Z'$  axis due to the inductance of the measuring circuit.

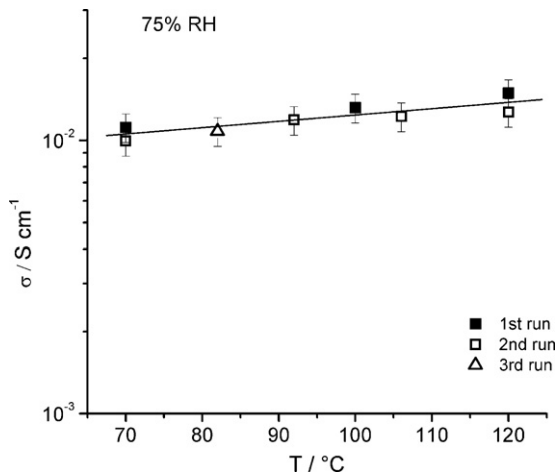
Fig. 4 shows the temperature dependence of the SPES conductivity ( $\sigma = d/(SR)$ , where  $d$  and  $S$  are the thickness and the area of the membrane, respectively). For both kinds of electrodes, the conductivity of the first heating run is lower than that of the second run at temperature below 120 °C. However, with increasing temperature, the conductivity of the first run approaches that of the second run and, within the experimental error, becomes equal to it at 120 °C. Moreover, while the differences between the conductivity of the first and the second run are larger for the measurements carried out with Pt electrodes, the conductivity values determined in the second run are independent of the type of electrode but only depend on temperature. In all cases, at 120 °C,  $\sigma$  lies in the range 0.024–0.026  $S\text{ cm}^{-1}$ .

It can be pointed out that the dependence of SPES conductivity on temperature at constant RH differs to a great extent from that reported for Nafion 117 under the same conditions [31]: in this case the conductivity is weakly dependent on temperature already in the first heating run, going from 0.06 to 0.07  $S\text{ cm}^{-1}$  in the range 80–120 °C.

A behavior similar to that of Nafion 117 was instead observed for the SPES/ZrP membrane for which nearly coincident conductivity values were found during three heating runs (Fig. 5). The conductivity of this membrane is however slightly lower than the second run conductivity of neat SPES since ZrP is less conductive than SPES.

To get an insight into the physical origin of the different temperature dependence of the SPES conductivity during the first and the second heating run, the hydration of a SPES membrane was determined at 75% RH as a function of temperature. It was found that, with increasing temperature from 70 to 120 °C, the water content goes from 15.3% to 17.7% of the weight of anhydrous SPES, the corresponding  $\lambda$  values being 6.5 and 7.5, respectively. However, when the membrane is cooled to 70 °C the water content keeps nearly unchanged (18.2 wt%,  $\lambda = 7.7$ ). The higher conductivity of the second heating run is therefore associated with a larger polymer hydration.

Similar determinations showed that the water content of the composite SPES/ZrP membrane is nearly independent of temperature: 18.2 wt% at 70 °C, 17.7 wt% at 120 °C, 18.2 wt% after cooling the membrane from 120 to 70 °C. The corresponding  $\lambda$  values cannot be



**Fig. 5.** Conductivity of a SPES/ZrP membrane as a function of temperature measured with ELAT electrodes during three heating runs.

calculated because the hydration of the filler is unknown. Nevertheless it can be concluded that the presence of the filler makes water uptake easier at low temperature thus avoiding the conductivity hysteresis observed for neat SPES.

While hydration data account nicely for the different temperature dependence shown by the conductivity of SPES and SPES/ZrP during the two heating runs, they do not provide a straightforward explanation for the different conductivities measured for SPES with Pt and ELAT electrodes during the first heating run.

Taking into account that different conductivity values could also arise to some extent from different effective contact areas between membrane and electrodes, it was of interest to analyze the impedance data in order to get information on the evolution of the electrode–membrane interface during heating and cooling runs.

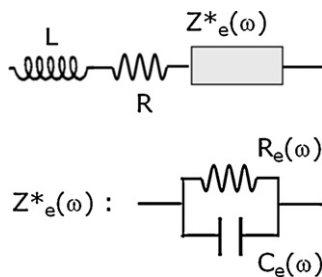
The simplest equivalent circuit, consistent with the Nyquist plot of Fig. 3, is made of a series-combination of a resistance ( $R$ ), arising from the bulk transport properties of the membrane, a constant-phase-angle impedance ( $Z_e^*$ ) associated with the electrode–membrane interface, and the inductance ( $L$ ) of the measuring system (Fig. 6). The impedance ( $Z^*$ ) of the circuit is given by the following equation:

$$Z^* = R + i\omega L + Z_e^* \quad (1)$$

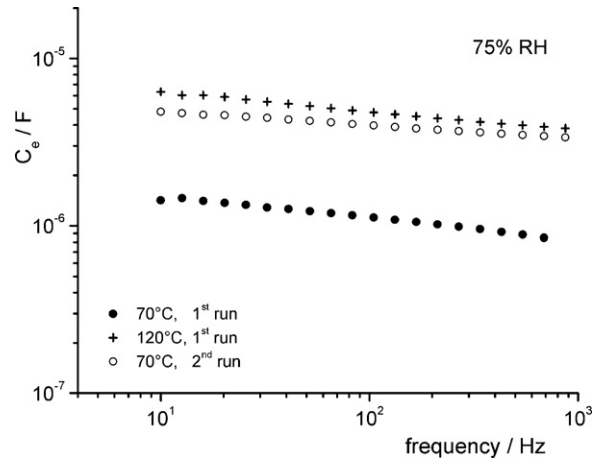
Putting  $Z^* = Z' + iZ''$  and  $Z_e^* = Z_e' + iZ_e''$ , Eq. (1) can be separated into the following equations:

$$Z' = R + Z_e' \quad (2)$$

$$Z'' = \omega L + Z_e'' \quad (3)$$



**Fig. 6.** Equivalent circuit for SPES membranes sandwiched between blocking electrodes.  $R$ : membrane resistance;  $L$ : inductance of the measuring circuit;  $Z_e^*(\omega)$ : impedance of the electrode–membrane interface;  $R_e(\omega)$ ,  $C_e(\omega)$ : resistive and capacitive parallel components of  $Z_e^*(\omega)$ , respectively.



**Fig. 7.**  $C_e$  as a function of frequency for SPES/Pt calculated through Eq. (6) at 70 °C and at 120 °C.

If  $Z_e^*$  is considered as a parallel combination of a resistance ( $R_e$ ) and a capacitance ( $C_e$ ), both frequency dependent, and if it is taken into account that the electrodes are blocking, then it can reasonably be assumed that  $C_e$  is roughly proportional to the effective contact area between membrane and electrode.  $C_e$  is defined as

$$C_e = -\frac{Z_e''}{\omega(Z_e'^2 + Z_e''^2)} \quad (4)$$

Combination of Eqs. (2)–(4) allows to express  $C_e$  as a function of  $R$ ,  $L$ ,  $Z'$  and  $Z''$ :

$$C_e = -\frac{Z'' - \omega L}{\omega[(Z' - R)^2 + (Z'' - \omega L)^2]} \quad (5)$$

The inductance  $L$ , determined by measuring the impedance of the short-circuited cell, is estimated around 0.1  $\mu\text{H}$ . Since  $Z''$  increases in absolute value with decreasing  $\omega$ , the term  $\omega L$  becomes negligible, in all cases, at frequency below about 10 kHz. In addition, due to the shape of the Nyquist plot,  $Z''^2$  grows more rapidly than  $(Z' - R)^2$  as frequency decreases. Then, when  $Z''^2 \gg (Z' - R)^2$ , Eq. (5) can be simplified as follows:

$$C_e = -\frac{1}{\omega Z''} \quad (6)$$

Eq. (6) turned out to be valid in all cases for frequencies below about 1 kHz. The  $C_e$  values calculated with this approximation are shown in Fig. 7 for the system SPES/Pt. It can be seen that, on a log–log scale,  $C_e$  depends linearly on frequency ( $f$ ) as expected for a constant-phase-angle element of equation  $Z_e^* = q(i\omega)^{-p}$ , where  $\omega = 2\pi f$  and  $p$  and  $q$  are constant, with  $0 < p < 1$  [30].

The  $C_e$  values calculated for  $f = 100$  Hz at the beginning of the first and the second heating run, as well as at the end of the first heating run, are listed in Table 1 for the systems SPES/Pt and SPES/ELAT. In both cases  $C_e$  increases significantly during the first heating run and decreases to a little extent when the membrane is cooled to 70 °C. The  $C_e$  increase is due to the fact that during the first run the membrane becomes progressively more capable of being deformed so that the contact surface with the electrode increases.

**Table 1**  
 $C_e$  values for SPES/Pt and SPES/ELAT calculated at 100 Hz through Eq. (6).

Heating run	Temperature (°C)	$C_e$ ( $\mu\text{F}$ )	
		Pt	ELAT
First	70	1.12	0.34
First	120	4.76	15.1
Second	70	3.98	11.9



**Table 2**

Conductivity ( $\sigma$ ) and hydration ( $\lambda$ ) at 100 °C for RH changing according to the sequence: 50% → 90% → 63%.

% RH ± 1.6	$\sigma \pm 12\%$ (S cm <sup>-1</sup> )	$\lambda \pm 0.3$
50	$3.3 \cdot 10^{-3}$	5.5
60	$4.9 \cdot 10^{-3}$	6.1
70	$9.3 \cdot 10^{-3}$	7.0
80	$2.1 \cdot 10^{-2}$	7.6
90	$4.5 \cdot 10^{-2}$	8.4
76	$2.3 \cdot 10^{-2}$	7.6
63	$1.1 \cdot 10^{-2}$	6.9

In addition, at the beginning of the first heating run, the capacitance of the SPES/Pt interface is larger than that of SPES/ELAT interface, while the opposite is found at the end of the run. This behavior is explained by considering that, although porous ELAT has a larger surface than flat Pt, at low temperature the membrane sticks better to the smooth surface of Pt than to the porous surface of ELAT.

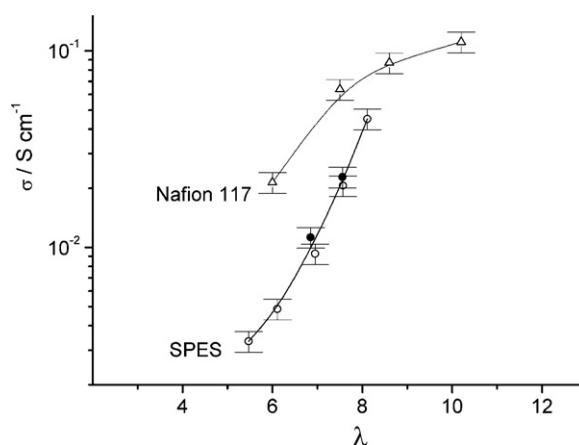
Comparison between conductivity and capacitance data for SPES/Pt and SPES/ELAT shows that the smaller capacitance changes are associated with the larger conductivity changes. Since the changes in the electrode capacitance do not reflect the corresponding changes in membrane conductivity, it must be concluded that the different conductivity trends observed during the first heating run with Pt and ELAT electrodes do not arise from changes in the effective contact area between membrane and electrodes but rather from the different hydration levels the membrane can reach at low temperature when pressed between porous (ELAT) and non-porous (Pt discs) electrodes.

### 3.2. Conductivity and hydration vs. RH

The conductivity of a SPES membrane, that had undergone two heating runs between 70 and 120 °C, was also determined at 100 °C as a function of RH. Before measurements, the membrane was equilibrated for two days at 100 °C–50% RH. Two measurement runs were performed: RH was changed from 50% to 90% in the first run and from 90% to 63% in the second run. Concomitantly, the conductivity increased from  $3.3 \cdot 10^{-3}$  S cm<sup>-1</sup> to  $4.5 \cdot 10^{-2}$  S cm<sup>-1</sup> and then decreased to  $1.1 \cdot 10^{-2}$  S cm<sup>-1</sup> (Table 2). It can be observed that the latter conductivity value, obtained at 63% RH, is about twice the value found at RH = 60% during the first run. These conductivity values compare favorably with those recently reported in ref.26 for SPES with similar DS and, in spite of the lower DS, are similar to those of highly sulfonated SPEEK under the same conditions [31].

Water uptake determinations were also carried out under the same conditions of temperature and RH as those of conductivity measurements. Table 2 shows that  $\lambda$  goes from 5.5 to 8.4 for RH increasing in the range 50–90% while decreases to 6.9 when RH is lowered to 63%: the latter  $\lambda$  value is slightly higher than the value ( $\lambda = 6.1$ ) found at 60% RH during the first run. The difference between these  $\lambda$  values, although close to the sum of the errors on their determination, must be considered still significant since it reflects the weight increase of the same sample at RH around 60% after equilibration at 90% RH. Thus, both conductivity and hydration show some hysteresis when RH is decreased below 90%. However, when  $\sigma$  is plotted against RH, points collected in the two measurement runs gather around the same curve (Fig. 8), thus proving that changes in conductivity are fully explained by changes in hydration.

Finally, it was of interest to compare SPES with Nafion as far as the dependence of  $\sigma$  on  $\lambda$  is concerned. To this aim conductivity and hydration of Nafion 117 samples were determined at 100 °C with RH increasing in the range 50–90%. Fig. 8 shows that, the  $\lambda$  value being the same, Nafion is always more conductive than SPES in spite of its lower IEC (0.9 vs. 1.31 meq g<sup>-1</sup>); however the difference



**Fig. 8.** SPES and Nafion 117 conductivity as a function of hydration at 100 °C; open and solid symbols refer to measurements performed at increasing and decreasing RH, respectively.

in conductivity decreases as  $\lambda$  increases. According to Kreuer [7] this is due to the fact that, in comparison with perfluorosulfonic polymers, sulfonated aromatic polymers are characterized by lower acidic strength of the sulfonic group and by less pronounced phase separation into hydrophobic and hydrophilic domains leading to narrower and more branched water channels.

## 4. Conclusion

The conductivity and hydration of SPES membranes (DS = 0.34) was determined under different conditions of temperature and RH. The conductivity turned out to be stable up to at least 120 °C–75% RH and the maximum value reported in this paper,  $4.5 \cdot 10^{-2}$  S cm<sup>-1</sup> at 100 °C–90% RH, is already of some interest for application in polymer electrolyte fuel cells.

Temperature cycling at constant RH, as well as RH cycling at constant temperature, gave rise to hydration hysteresis and to the concomitant conductivity hysteresis: in particular, at 70 °C–75% RH the SPES/ELAT conductivity increases from  $5.5 \cdot 10^{-3}$  to  $1.3 \cdot 10^{-2}$  S cm<sup>-1</sup> after equilibration at 120 °C–75% RH, while at 100 °C–60% RH the conductivity nearly doubles after equilibration at 100 °C–90% RH.

The results here reported seem to indicate that the maximum hydration and conductivity that a SPES membrane can reach at a certain temperature and RH depend to some extent on the highest temperature and RH values at which the membrane was equilibrated. The SPES conductivity is therefore expected to be susceptible of improvement after suitable membrane treatments, for example, at temperature-RH above 120 °C–75%, respectively.

It was also shown that the hydration and conductivity hysteresis associated with temperature cycling can be avoided by filling SPES with zirconium phosphate which makes hydration easier at low temperature.

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