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Short communication

On the decay of Nafion proton conductivity at high temperature and relative humidity

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Abstract

The irreversible conductivity decay exhibited by Nafion 117 membranes above certain values of temperature and relative humidity (RH) has been investigated by two-probe impedance measurements carried out at 120 °C with the electric field normal to the membrane surface, under controlled applied pressure on the electrodes. The analysis of the evolution of both frequency response and *normal* conductivity during the decay has suggested that the decay arises from changes in the bulk transport properties of the Nafion membrane. This has been confirmed by determining, under stability conditions, the conductivity of membranes pre-treated under decay conditions. The results of these measurements have shown that the decay occurs only if the membrane undergoes an anisotropic deformation along the direction parallel to the electrode surface. Four-probe impedance measurements with the electric field parallel to the membrane surface have also been carried out to determine the membrane *tangential* conductivity before and after the decay. Comparison of *normal* and *tangential* conductivity has indicated that the decay is associated, to a certain extent, with an increase in the conduction anisotropy.

Keywords: Nafion membrane; Proton conductivity; High temperature; High relative humidity; Anisotropic swelling

1. Introduction

Proton exchange membranes made of polyperfluorosulfonic acids are well known for their high chemical inertness, good thermal stability, reasonable mechanical strength and excellent proton conductivity when highly hydrated. Due to these outstanding characteristics perfluorinated membranes, and among them mostly Nafion membranes in hydrogen form, are currently used as solid polymeric electrolytes in fuel cells operated in the temperature range 50–90 °C [1–5].

The upper limit of the working temperature arises to a great extent from the difficulty in maintaining a sufficiently high hydration level of both membrane and membrane–electrode interface at higher temperature. On the other hand, it is known that, depending on the conditions of Nafion pre-treatment, the hydration of samples dipped in liquid water may increase with temperature [6]; this also true for samples equilibrated with water vapour at constant RH values. Therefore, an excessive swelling too could compromise the fuel cell operation above 90 °C at RH values close to 100%. Moreover, increasing temperature above the ionomer glass transition temperature is expected to result in a reduced dimensional stability of the membrane.

Determination of the membrane proton conductivity at controlled temperature and RH is thus essential to understand to which extent changes in the membrane transport properties are responsible for the lack in fuel cell performance above certain temperature and RH values. Increasing attention was indeed focused in last years on the investigation of the conductivity of Nafion membranes above 90 °C [7–21].

We found that the conductivity of Nafion 117 membranes, measured by the impedance technique with the electric field perpendicular to the membrane surface (hereafter *normal* conductivity), shows an irreversible decay at certain critical values of temperature and RH [8]: in particular, the higher RH, the lower the temperature threshold at which the decay occurs. As a possible explanation of this behaviour, it was suggested that the decay is associated with membrane swelling/softening phenomena, which may reduce the effective contact area between electrodes and membrane.

Surprisingly, with the exception of ref. [19], no mention of the conductivity decay was made in subsequent papers dealing with Nafion conductivity at high temperature and RH values. This is probably due to the fact that the decay usually takes

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place only after membrane equilibration for a few hours under critical temperature and RH conditions.

To get a deeper insight into the origin of the conductivity decay, this work deals with the evolution of the frequency response and of the *normal* conductivity of Nafion 117 membranes associated with the decay. Four-probe impedance measurements were also performed with the electric field parallel to the membrane surface to determine the membrane *tangential* conductivity. All measurements were carried out at 120 °C as a function of time at controlled RH and applied pressure on the electrodes.

2. Experimental

Nafion 117 membranes, 180 μm thick, were purchased from DuPont (USA) and used without any pre-treatment in order to reproduce the experimental conditions reported in ref. [8]. The hydration of samples dipped in water at 20 °C was 14 water molecules per sulfonic group.

The membrane *normal* conductivity was measured on Nafion 117 discs, 8 mm in diameter, sandwiched between gas diffusion electrodes (ELAT containing 1 mg cm^{-2} Pt loading) which were pressed on the membrane by means of porous stainless steel discs; the applied pressure was in the range 60–290 kg cm^{-2}. Two-probe impedance measurements were carried out by a Solartron 1260 Impedance/Gain Phase Analyser in the frequency range 0.01–100 kHz at a signal amplitude ≤100 mV by using the cell described in [8]. The impedance data were corrected for the contribution of the empty and short-circuited cell. The membrane resistance was obtained by extrapolating the impedance data to the real axis on the high frequency side.

The membrane *tangential* conductivity was determined by four-probe impedance measurements in the frequency range 10–100 kHz using the above impedance analyser connected to the conductivity cell through a Solartron 1480 multi-channel potentiostat. The cell consists of two platinum foil electrodes (3 cm apart) to feed current, and two platinum wires (0.5 mm in diameter, 1 cm in length and 1 cm apart) to measure the potential drop across the membrane. The four electrodes are arranged on a Teflon disc as schematically shown in Fig. 1. The Nafion membrane (5 cm × 1 cm) is pressed on the electrodes by a second Teflon disc where a rectangular window (0.8 cm × 1.3 cm) allows hydration and swelling of the membrane portion placed between the platinum wires.

In both *normal* and *tangential* conductivity measurements, RH was controlled by using stainless steel sealed-off cells consisting of two communicating cylindrical compartments held at different temperatures. The cold compartment contained water, while the hot compartment housed the membrane under test. RH values were calculated from the ratio between the pressures of saturated water vapour (p) at the temperatures of the cold (T_c) and hot (T_h) compartment: RH = $p(T_c)/p(T_h) \times 100$.

3. Results and discussion

Fig. 2 shows the temperature dependence of the *normal* conductivity at 95% RH for a Nafion 117 membrane that was tightened between ELAT electrodes with a pressure of 60 kg cm^{-2}. At 120 °C, σ starts decreasing and reaches, within about 100 h, a final value that is about five times lower than the initial value at the same temperature. It is clearly seen that the conductivity values measured on heating are not restored on cooling. The decay is also observed when the membrane is sandwiched between smooth platinum electrodes.

The decay evolution as a function of time at 120 °C was investigated by measuring the *normal* conductivity at 100 kHz for membranes that were assembled in the measuring cell with controlled pressure on the electrodes and equilibrated at 90 and 95%

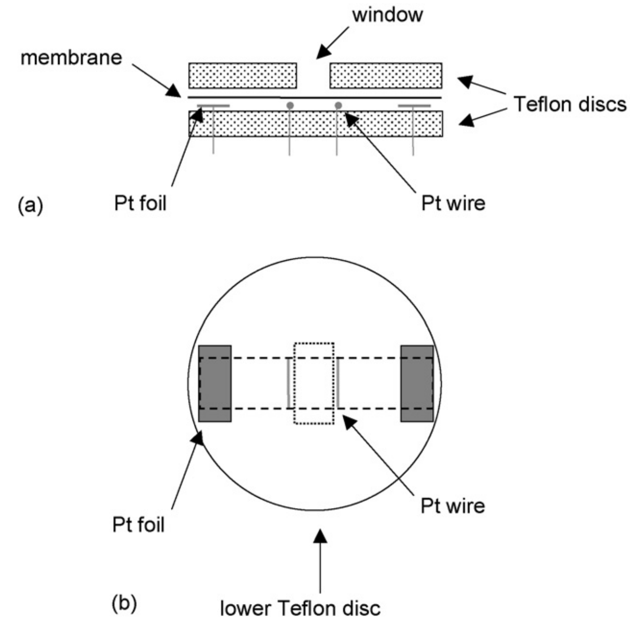

Fig. 1. Schematic representation of the sample holder of the four-probe conductivity cell: (a) cross section, (b) electrode arrangement on the lower Teflon disc (the dashed and dotted lines represent the position of the membrane and of the window of the upper disc, respectively).

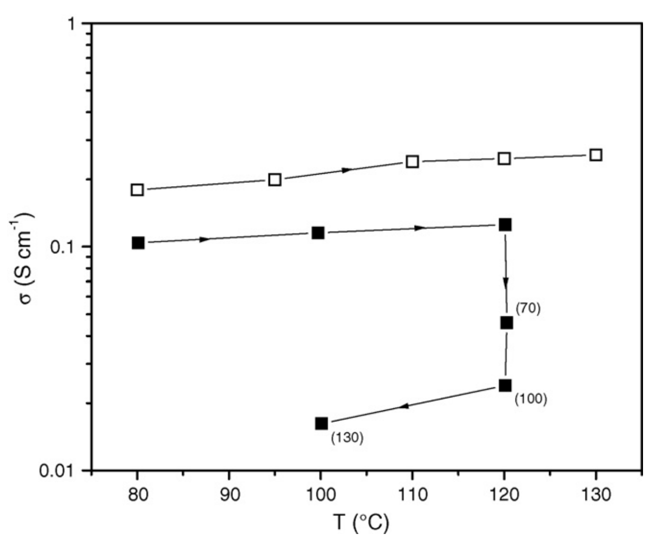

Fig. 2. *Normal* (■) and *tangential* (□) conductivity of Nafion 117 membranes as a function of temperature at 98% RH. Figures in brackets represent the time 'h' elapsed since the decay beginning; arrows indicate the direction of temperature changes.

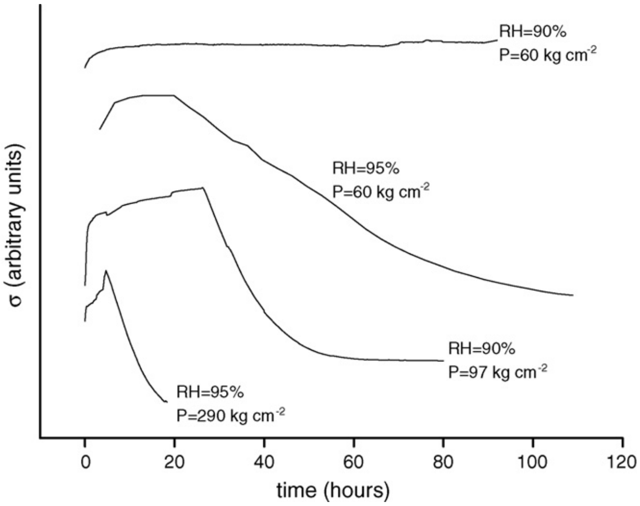

Fig. 3. *Normal* conductivity at 100 kHz and 120 °C as a function of time for Nafion 117 membranes at the indicated RH and pressure (P) on the electrodes. The curves were arbitrarily shifted along the σ axis.

RH. A few impedance measurements, carried out at regular time intervals, showed that the membrane conductivity obtained from the extrapolation of the Nyquist plot has the same time dependence as that determined at 100 kHz. From Fig. 3 it is seen that, with a pressure of 60 kg cm^{-2}, the conductivity becomes unstable when RH is increased from 90 to 95%, while at 90% RH the conductivity decay is observed when the pressure rises from 60 to 97 kg cm^{-2}. Moreover, at 95% RH, an increase of pressure from 60 to 290 kg cm^{-2} speeds up the decay to a great extent.

These findings are consistent with the hypothesis [8] that the conductivity decay is associated to some extent with membrane swelling phenomena, determined by a combined action of increasing temperature and hydration. However, the fact that a higher pressure on the electrode facilitates the decay in terms of shorter time and lower RH values can hardly be explained on the basis of reduced effective contact area between electrodes and membrane, as suggested in ref. [8].

Information on the modification of the electrode–membrane interface can be obtained by analysing the Nyquist plot of the membrane–electrode assembly in the frequency range 0.01–100 kHz. To this aim it is assumed that (i) the resistance of the Nafion 117 membrane is given by the high frequency extrapolation of the Nyquist plot to the real axis (Z') and (ii) at the lowest frequency values the impedance changes are dominated by the frequency response of the electrode–membrane interface.

Figs. 4 and 5 show some Nyquist plots collected at 120 °C and 95% RH for a membrane tightened at 60 kg cm^{-2} between ELAT electrodes. It can be observed that the position of the high frequency portion of the Nyquist plots keeps nearly unaltered within the first 16 h, but shifts to higher Z' values for longer equilibration times. Correspondingly, the membrane conductivity decreases from 0.12 S cm^{-1} to a final value of 0.025 S cm^{-1} (Fig. 6).

On the other hand, in all cases a progressive contraction of the impedance plot is observed with the passing of time (Figs. 4a and 5a). At frequencies below about 100 Hz, this contraction is also associated with an increase of the parallel–equivalent capacitance of the membrane electrode assembly, $C_p(\omega) = -Z''/2\pi f(Z'^2 + Z''^2)$, f being the frequency of the applied signal. As an example Fig. 6 shows C_p values at 0.01 Hz as a function of time. It is clearly seen that the beginning of the conductivity decay is concomitant with a steep increase in the C_p values.

Both the contraction of the Nyquist plot and the corresponding increase in the low-frequency parallel capacitance seem to indicate an increase, rather than a decrease, in the effective contact area between electrodes and membrane. This is probably due to the above mentioned swelling phenomena, occurring at high temperature and RH values, that should force the membrane surface to a progressively better adaptation on the rough surface of the ELAT electrodes. On the basis of these considerations it should be inferred that, contrary to what was suggested in the previous work [8], the conductivity decay arises mainly from changes in the bulk transport properties of the Nafion membrane.

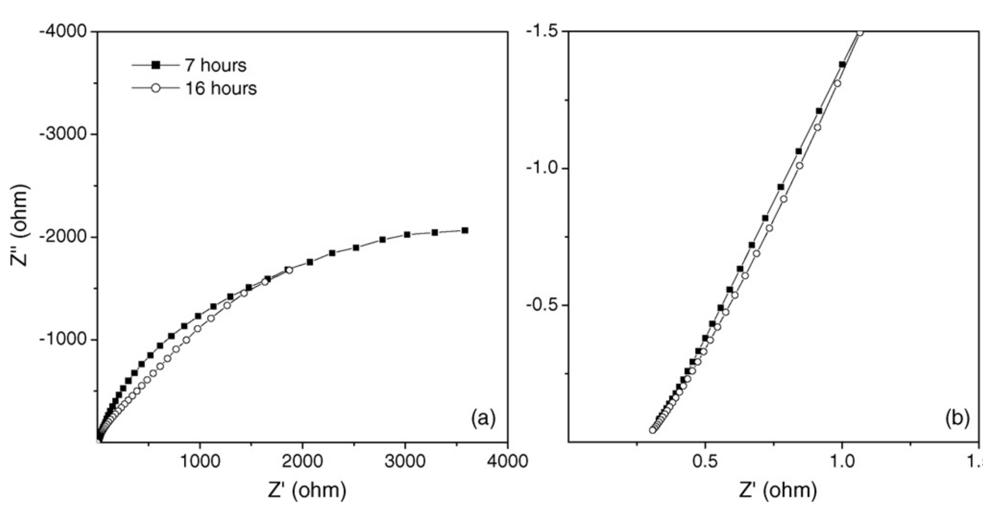

Fig. 4. (a) Nyquist plots collected in the frequency range 100 kHz–0.01 Hz at the indicated times after the beginning of the experiment; (b) detail of the high frequency region of the Nyquist plots. *Conditions*: 120 °C, 95% RH, 60 kg cm^{-2} pressure on the electrodes.

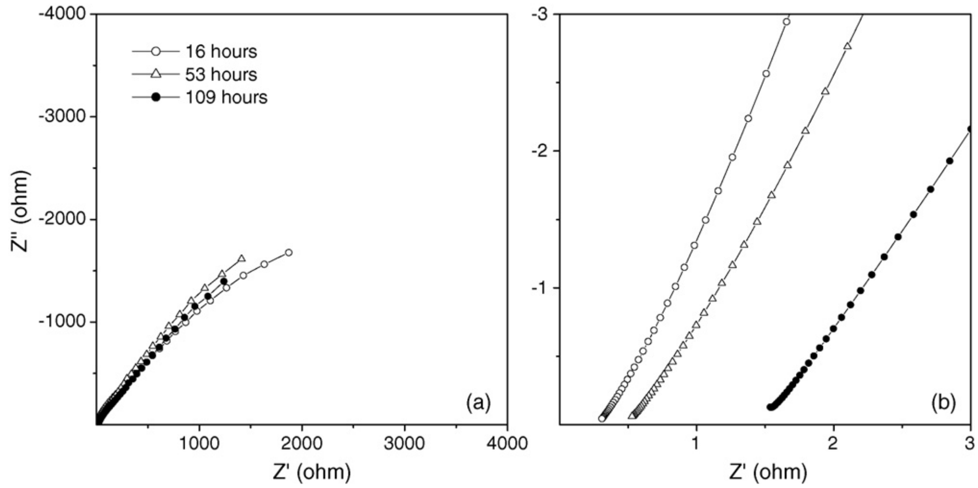

Fig. 5. (a) Nyquist plots collected in the frequency range 100 kHz–0.01 Hz at the indicated times after the beginning of the experiment; (b) detail of the high frequency region of the Nyquist plots. *Conditions*: 120 °C, 95% RH, 60 kg cm^{-2} pressure on the electrodes.

The above conclusion seems, however, to contradict the fact that neither the ion exchange capacity, nor the proton conductivity of Nafion 117 membranes turned out to be significantly altered after a 3-day treatment in autoclave at 140 °C and 100% RH [8]. To overcome this contradiction it can be pointed out that, while in the autoclave the membrane is free to swell, in the conductivity cell the membrane is constrained between the electrodes and forced to swell mainly parallel to them. To prove that the different type of swelling is responsible for different bulk transport properties, the following experiments were performed: (i) in situ conductivity measurements on membranes that were allowed to swell without any constraint at 120 °C and 98% RH, (ii) ex situ conductivity measurements on membranes that had previously been conditioned at 120 °C and 95 or 30% RH under pressure between two smooth platinum sheets.

In the first case, impedance measurements were carried by the four-probe technique as described in the experimental section. Due to the presence of a window of suitable size in the Teflon disc that presses the membrane over the electrodes, the portion of the membrane placed between the potential probes was able to swell without constraints. In the frequency range 10 Hz–10 kHz the frequency response was purely resistive with phase angle lower than 0.25°, in absolute value, and changes in the impedance modulus lower than 0.5%. As expected from ref. [8] the *tangential* conductivity did not show any decay during at least 100 h. Measurements were then extended in the temperature range 80–130 °C. A comparison of *normal* and *tangential* conductivity data (Fig. 2) shows the absence of any decay in the *tangential* conductivity. In particular, even at 130 °C and 98% RH the conductivity turned out to be stable for at least 100 h.

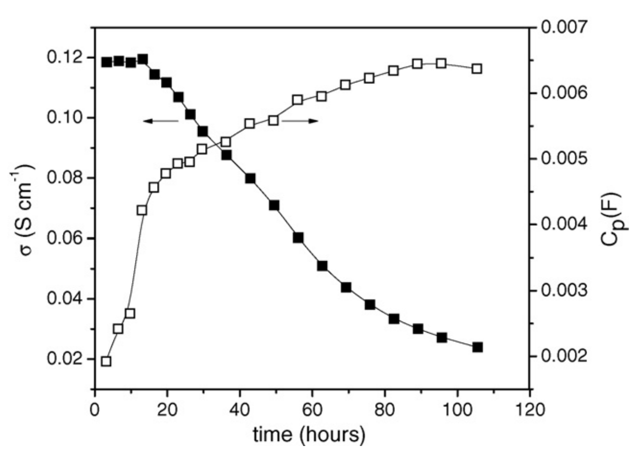

Fig. 6. *Normal* conductivity (σ, ■) and parallel–equivalent capacitance at 0.01 Hz (C_p, □) as a function of time for a Nafion 117 membrane. *Conditions*: 120 °C, 95% RH, 60 kg cm^{-2} pressure on the electrodes.

In the second series of experiments, measurements of *normal* conductivity were carried out under stability conditions (i.e. 120 °C, 90% RH and electrodes pressed at 60 kg cm^{-2}) on membranes that had previously been treated under decay conditions, thus avoiding that an excessive membrane swelling could affect the conductivity determination. In particular, Nafion 117 samples were tightened between two square platinum sheets (1 cm × 1 cm) at a pressure of 97 kg cm^{-2} and the resulting sandwich was conditioned for 4 days at 120 °C and 95% RH. The conductivity of these membranes turned out to be, on average, 0.013 S cm^{-1}, i.e. about eight times lower than the conductivity of the untreated membranes under the same conditions (Table 1). On the basis of these results it was of interest to measure the *tangential* conductivity too after the membrane treatment under decay conditions. To this aim the central portion of (5 cm × 1 cm) strips of Nafion 117 was tightened between the above square platinum sheets and the strips were used for four-probe measurements. At 120 °C and 90% RH the *tangential* conductivity was 0.061 S cm^{-1}. Taking into account the ratio *tangential*/*normal* conductivity before (1.8–2) and after (∼5) the decay, it is clear that the decay of the *normal* conductivity is associated to a certain extent with an increase of the anisotropic character of the conductivity of Nafion 117.

On the other hand, both the *normal* and *tangential* conductivity of membranes that had been tightened between platinum sheets at 60 kg cm^{-2}, but conditioned under stability conditions

Table 1
Tangential and *normal* conductivity at 120 °C and 90% RH for Nafion 117 membranes that were pressed between platinum sheets at the indicated temperature (*T*), pressure (*P*) and RH values

Pre-treatment			σ (S cm^{-1}) at T = 120 °C, RH = 90%	
T (°C)	RH (%)	*P* (kg cm^{-2})	*Tangential*	*Normal*
*	*	*	0.18	0.10
120	95	**		0.075
120	30	60	0.16	0.079
120	95	97	0.061	0.013

* No pre-treatment.
** No pressure applied.

(i.e. 120 °C and RH = 30%), were close to those of untreated membranes (Table 1). These results show that Nafion 117 membranes undergo irreversible modifications when pressed under those temperature and RH conditions that give rise to the conductivity decay.

The increase of the anisotropic character of conductivity appears to be associated with the anisotropic deformation taking place, under certain conditions of temperature and RH, when the membrane is constrained between the electrodes and forced to swell mainly in the direction parallel to them. The resulting shear stress should bring about a partial alignment of the conduction pathways along the stress direction as it was recently shown for polystyrene–4-vinylpiridine copolymers doped with phosphoric acid [22].

To prove that an anisotropic deformation is necessary for the occurrence of the conductivity decay, membranes were conditioned under decay conditions (i.e. 120 °C, 95% RH, 64 kg cm^{-2}) in such a way to avoid deformation to a great extent. This was achieved by sandwiching a (5 cm × 1 cm) strip of Nafion 117 between two Teflon discs, 3 cm in diameter. Under the applied pressure the discs got deformed around the two major strip sides thus hindering membrane swelling. After equilibration for 4 days at the above temperature and RH values, the *tangential* conductivity was measured at 120 °C and 90% RH. Subsequently, the *normal* conductivity was determined under the same conditions on a disc, 1.0 cm in diameter, which was cut out from the central portion of the strip. Both *tangential* (0.14 S cm^{-1}) and *normal* (0.08 S cm^{-1}) conductivity values turned out to be by only 20% lower than those of the untreated membrane (Table 1), thus confirming that no significant conductivity decay occurs when the membrane is not allowed to swell anisotropically.

4. Conclusion

Two-probe and four-probe impedance measurements, under different conditions of RH and pressure applied on the electrodes, were performed to get an insight into the physical origin of the conductivity decay exhibited by Nafion 117 membranes above certain values of temperature and RH. It was shown that the decay occurs only when the membrane is forced to swell anisotropically along the plane parallel to the membrane surface.

On the basis of these results we suggest that conductivity measurements as a function of temperature, at controlled RH and applied pressure on the electrodes, can be used to have information on the membrane dimensional stability under temperature and RH conditions that are of interest for fuel cell operation but hardly accessible with the standard equipment for testing mechanical properties.

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