A critical investigation of the effect of hygrothermal cycling on hydration and in-plane/through-plane proton conductivity of Nafion 117 at medium temperature (70–130 °C)

Mario Casciola, Anna Donnadio*, Paola Sassi

Chemistry Department, University of Perugia, via Elce di Sotto 8, 06123 Perugia, Italy

HIGHLIGHTS

► Proton conductivity of Nafion 117 from 70 to 130 °C under controlled relative humidity.
► Membrane hydration under the environmental conditions of conductivity measurements.
► Effect of temperature and relative humidity cycling on hydration and through-plane/in-plane conductivity.
► Determination of activation energy for conduction at constant hydration.

ABSTRACT

Hydration, in-plane and through-plane conductivity of Nafion 117 membranes are investigated in the temperature range 70–130 °C and in the relative humidity (RH) range 50–90% upon cycling RH, at constant temperature, and cycling temperature at constant RH. Both temperature and RH cycling result in hysteresis of conductivity and hydration. During the RH cycle, conductivity changes at decreasing RH are faster than hydration changes, thus indicating the presence of water molecules contributing weakly to conductivity. During the temperature cycle, the in-plane conductivity shows a hysteresis loop where, as expected, the more hydrated state is the more conductive state as well. However, under the same conditions of temperature and RH, the through-plane conductivity exhibits an anomalous behaviour where the lower conductivity is associated with the higher hydration level. Upon temperature cycling, through-plane and in-plane conductivity show different temperature dependence during heating but the same dependence during cooling. This behaviour is attributed to irreversible structural changes occurring during heating when the membrane is pressed between the electrodes in the through-plane conductivity cell. The possible influence of the through-plane conductivity hysteresis on the performance of a PEM fuel cell in the range 70–130 °C is also discussed.

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1. Introduction

Perfluorosulfonic acid membranes, and among them mostly Nafion membranes, are currently used as solid polymeric electrolytes in fuel cells (PEMFCs) [1–8] due to their outstanding properties in terms of high chemical inertness, good thermal stability and excellent proton conductivity when highly hydrated.

PEMFCs are operated in the temperature range 50–90 °C, but working temperatures above 90 °C are desirable since they would simplify the PEMFC cooling system, promote the reactions at the electrodes and allow feeding the PEMFC with hydrogen containing CO impurities.

Understanding to what extent the polymer electrolyte limits fuel cell operation at temperatures above 90 °C needs the investigation of membrane properties, such as conductivity and hydration, at those temperatures. While several papers deal with membrane conductivity above 90 °C [9–37], there is only a limited number of papers reporting membrane hydration above 90 °C at the environmental conditions under which the conductivity data were collected [32–37]. The knowledge of hydration is however of fundamental importance, since the water content is responsible for different membrane properties including proton conductivity, swelling and mechanical stability.

In a recent paper [32] we described a simple gravimetric method allowing the determination of water uptake up to 140 °C

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even at relative humidity (RH) close to 100%. This method was used to investigate the relation between the conductivity and the hydration of sulfonated polyethersulfone membranes in the temperatures range 70–120 °C. It was also shown that cycling temperature and RH results in conductivity and hydration hysteresis so that the conductivity and the hydration at a certain temperature and RH value depend on the history of the changes the membrane underwent in terms of temperature and RH.

On the basis of the above results it was of interest to perform a similar investigation on Nafion 117 membranes. The present paper reports the effect of cycling RH at constant temperature and of cycling temperature at constant RH on the hydration and proton conductivity of Nafion 117. The determination of conductivity as a function of temperature at constant hydration allowed the calculation of the activation energy of conduction in the range 70–130 °C. Most conductivity measurements were performed by applying the electric field parallel to the membrane surface (in-plane conductivity), while a few measurements were carried out with the electric field perpendicular to the membrane surface (through-plane conductivity). The results obtained by through-plane and in-plane measurements are compared and discussed in terms of membrane structural changes occurring under the different measurement conditions.

2. Experimental

2.1. Chemicals

Nafion 117 membranes, 180 μm thick, were purchased from Ion Power (USA). Before use, all membranes were boiled in 3% (v/v) hydrogen peroxide, 1 M sulphuric acid and water, 1 h for each treatment. Sulphuric acid and hydrogen peroxide were supplied by Carlo Erba.

2.2. Techniques

The membrane through-plane conductivity was measured on Nafion 117 discs, 8 mm in diameter, sandwiched between gas diffusion electrodes (Pt free ELAT) which were pressed on the membrane by means of porous stainless steel discs; the initial applied pressure was 60 kg cm^{-2} and was not controlled during the experiment. Two-probe impedance measurements were carried out by a Solartron 1260 Impedance/Gain Phase Analyser in the frequency range 0.01 Hz–100 kHz at a signal amplitude ≤100 mV by using the cell described in ref.14. 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 in-plane conductivity was determined by four-probe impedance measurements in the frequency range 10 Hz–100 kHz using an Autolab, PGSTAT30 potentiostat/galvanostat equipped with an FRA module. 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. The Nafion membrane (5 cm × 0.5 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 (further details are reported in Ref. [14]).

In both in-plane and through-plane 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 (Tc) and hot (Th) compartment: RH = p(Tc)/p(Th) × 100.

Water uptake at controlled temperature and RH was determined by using the cell described in Ref. [32]. This cell has the same size and shape as the conductivity cell used for through-plane conductivity measurements and differs from that mainly because the MEA holder is replaced by a glass container hosting the membrane sample (≈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 ($λ$, 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 $λ$ is estimated to be ±0.3 at most.

Water uptake determinations were also carried out for membranes kept under pressure between ELAT discs. More specifically 15 stacked membrane discs, 10 mm in diameter, were sandwiched between a couple of gas diffusion electrodes (Pt free ELAT) which were pressed on the membranes by means of porous stainless steel discs; the initial applied pressure was 60 kg cm^{-2} and was not controlled during the experiment.

According to Ref. [32], the error on the RH control is estimated to be lower than 2 RH units for both conductivity and water uptake cells.

Infrared spectra were recorded using a Bruker TENSOR27 spectrometer equipped with a Deuterium Triglycine Sulphate (DTGS) detector. ATR spectra were collected with a Gateway ATR accessory from SPECAC, using a six reflection horizontal ATR sampling system equipped with a ZnSe crystal. The sample was placed on top of the ZnSe crystal at room temperature and each ATR spectrum was the average of fifty scans, measured with a resolution of 2 cm^{-1} in the 400–4000 cm^{-1} range.

3. Results and discussion

3.1. Conductivity and hydration at 70 °C

The in-plane conductivity of Nafion 117 was initially investigated as a function of RH at 70 °C. A first set of measurements was carried out at increasing RH from 50 to 90% with steps of 10 RH units. The conductivity increased with RH ranging from 0.035 S cm^{-1} to 0.12 S cm^{-1}. At the end of the measurements RH was decreased to 50% and, after one day equilibration, a second set of measurement was started again. Fig. 1 shows that the logarithm of conductivity depends linearly on RH and that the conductivity changes reversibly with RH.

The water uptake ($λ$) of a Nafion sample was also determined at 70 °C as a function of RH: $λ$ values range from 5.2 to 9.5 with RH increasing from 50% to 90%, respectively (Fig. 2). Subsequently, the same Nafion sample was conditioned for one day at 70 °C − 50% RH and the water content was determined again: the $λ$ value was 7.0, significantly higher than that found at the beginning of the experiment at the same RH value. This was surprising because, under the same conditions of temperature, RH and equilibration time, the conductivity of the second set of measurements turned out to be coincident with that of the first set, within measurement errors (Fig. 1). Further RH increase to 90% gave the same $λ$ value measured at the end of the first set of measurements.

These results suggested to further investigate the long term evolution of both hydration and in-plane conductivity after decreasing RH from 90% to 50%. To this aim two Nafion samples,