



# Performance comparison of long and short-side chain perfluorosulfonic membranes for high temperature polymer electrolyte membrane fuel cell operation

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## ABSTRACT

A new Aquivion™ E79-03S short-side chain perfluorosulfonic membrane with a thickness of 30 μm (dry form) and an equivalent weight (EW) of 790 g/equiv recently developed by Solvay-Solexis for high-temperature operation was tested in a pressurised (3 bar abs.) polymer electrolyte membrane (PEM) single cell at a temperature of 130 °C. For comparison, a standard Nafion™ membrane (EW 1100 g/equiv) of similar thickness (50 μm) was investigated under similar operating conditions. Both membranes were tested for high temperature operation in conjunction with an in-house prepared carbon supported Pt electrocatalyst. The electrocatalyst consisted of nanosized Pt particles (particle size ~2 nm) dispersed on a high surface area carbon black. The electrochemical tests showed better performance for the Aquivion™ membrane as compared to Nafion™ with promising properties for high temperature PEM fuel cell applications. Beside the higher open circuit voltage and lower ohmic constraints, a higher electrocatalytic activity was observed at high temperature for the electrocatalyst-Aquivion™ ionomer interface indicating a better catalyst utilization.

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## 1. Introduction

One of the main challenges of perfluorosulfonic acid ionomer-based polymer electrolyte membrane fuel cells (PEMFCs) for automotive applications is represented by the need to operate at medium or high temperatures (above 120 °C) [1]. In contrast to an internal combustion engine (ICE), which rejects almost half of the heat through the exhaust, a fuel cell has to reject most of the heat through the radiator [2,3]. Since most of the standard perfluorosulfonic acid based membranes are characterized by a limiting operating temperature of 95 °C [4], additional cooling efforts are necessary to keep the operating temperature at a reasonable temperature level. This aspect implies as large size radiator often not compatible with the required compactness of the car as well as an increase of the system complexity and total cost.

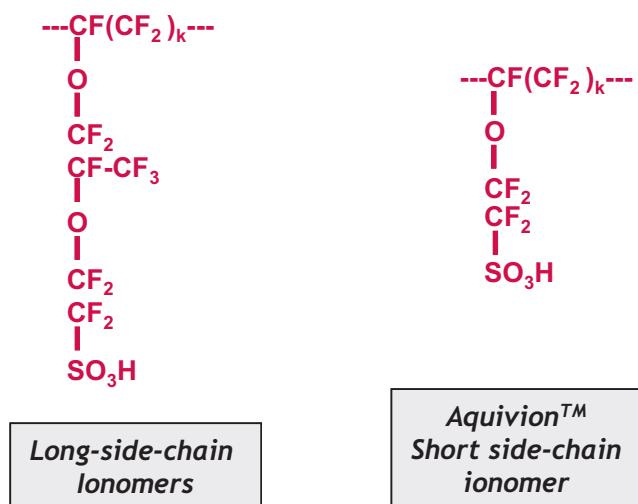
Increasing the operating temperature up to ~130 °C would alleviate this drawback and improve the catalyst behaviour [5–7]. As

an example, high temperature operation will reduce the size of the thermal subsystem [2,3], improve reaction kinetics and increase tolerance to impurities contained in the reactant stream, e.g. CO contained in the hydrogen stream produced by a reforming process, chloride impurities which may be present in water, etc. [1]. Moreover, for stationary purposes, the heat produced by a PEM fuel cell at high temperature (i.e. 130 °C) could be used to produce hot water, as well as for ambient heating and possibly for cogeneration in order to increase the overall system efficiency [8–10]. As well known, phosphoric acid-doped polybenzimidazole membranes can operate up to 180 °C with suitable conductivity [11]. Unfortunately, these membranes are less performing at low temperature and do not allow for a rapid start-up as required for automotive applications. Moreover, the power densities that can be achieved with these membranes appear lower than those obtained with perfluorosulfonic acid (PFSA) membranes. PFSA membranes are characterized by excellent performance, electrochemical stability, suitable mechanical properties and allow rapid start-up. Thus, it appears evident that is necessary to ameliorate the perfluorosulfonic acid membranes to make them able to operate at higher temperatures.

Nowadays, common membranes adopted in PEM fuel cell are based on Nafion™ (N112, N115, N117, etc.); however, several

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**Fig. 1.** Polymer structure for long-side chain Nafion™ and short-side chain Aquivion™ perfluorosulfonic ionomer membranes.

alternative PSFA membranes with shorter pendant side-chain have been developed by Dow, 3 M, Gore, Asahi glass, Solvay-Solexis, etc. [12–17]. Despite the good performance under conventional operating conditions (60–80 °C), most of them are not suitable for high temperature PEM fuel cells applications especially if they are operated at temperatures above 100 °C. It is well documented in the literature that at a temperature over 100 °C Nafion™ membranes suffer of several drawbacks, including dehydration and excessive swelling. The first drawback causes a decrease of proton conductivity according to the “vehicle” mechanism for proton conduction whereas the latter problem leads quickly the backbone structure to collapse [18].

Recently Solvay-Solexis has developed a new short side chain perfluorosulfonic membrane with the tradename Aquivion™ (Fig. 1) [4]. The E79-03S short-side chain (SSC), chemically stabilized perfluorosulfonic acid membrane has a thickness of 30 μm (dry form) and an equivalent weight of 790 g equiv<sup>-1</sup> [4]. This ionomer is characterized by both larger crystallinity and higher glass transition temperature than LSC polymers at a given equivalent weight [19,20]. In the dry form, a glass transition temperature (T<sub>g</sub>) of 127 °C for Aquivion™ compared to 67 °C for Nafion™ has been observed [4,17,21]. Under humidified conditions, the T<sub>g</sub> increases proportionally due to the plasticizing effect of water [21].

The Aquivion™ membrane appears to be more reliable than Nafion™ to operate at high temperature. In a previous work, we have compared the performance of Aquivion™ and Nafion™ membranes under operation with both low pressure and relative humidity as required for automotive applications [4]. It was observed that the maximum realistic operating temperature was 95 °C for Nafion™ whereas this limit was shifted to 110 °C for Aquivion™ indicating a clear progress beyond the state of the art of perfluorosulfonic membranes [4]. Moreover, the Aquivion™ membrane was assessed at the stack level [4]. In this work, we have focused our efforts on a higher temperature (130 °C) comparison between Aquivion™ and Nafion™, as representatives of a short-side chain ionomer and long-side chain ionomer, respectively. These aspects were addressed to understand if beside the different conductivity characteristics there were also different electrocatalytic properties arising from the presence of a different ionomer at the catalyst–electrolyte interface under such conditions. Since Nafion™ easily dehydrates under high temperature operation, we have overcome this drawback by operating the PEMFC under high pressure and full humidification conditions [22]. An in house prepared nanosized Pt/C electrocatalyst was used and it was elec-

trochemically characterized under operation with the two different ionomers. Each membrane–electrode assembly subjected to this investigation consisted of the same type of ionomer (electrode) and membrane.

## 2. Experimental

### 2.1. Preparation of catalyst

An in-house sulphite complex route synthesis method was adopted for the preparation of the electrocatalyst. A 50% Pt/Ketjenblack catalyst was prepared. It was used both for the anode and cathode manufacturing. The procedure consisted in the following steps: (1) a sulphite complex of Pt in appropriate amount, was decomposed by hydrogen peroxide to form an aqueous colloidal solutions of Pt oxide; (2) then, these particles were adsorbed onto a carbon black to form a PtOx/carbon; and (3) finally, the amorphous oxides on carbon were reduced in a hydrogen stream to form the supported Pt metal particles. The resulting powders were characterized by X-ray diffraction (XRD) to determine the crystallographic structure and transmission electron microscopy (TEM) to evaluate the morphology. As for the carbon support, we have selected Ketjenblack, due to its high purity, high surface area (850 m<sup>2</sup> g<sup>-1</sup>) and suitable surface graphitic index [22]. Moreover, it is noted that the same catalyst was selected for both anode and cathode to minimize the number of variables during this study.

### 2.2. Catalyst characterization

XRD was carried out using a Philips X-pert 3710 X-ray diffractometer with Cu K $\alpha$  radiation operating at 40 kV and 30 mA. The peak profile of the (2 2 0) reflection in the face centered cubic structure of Pt was analysed by using the Marquardt algorithm and it was used to calculate the crystallite size by the Debye–Scherrer equation. TEM analysis was made by first dispersing the catalyst powder in isopropyl alcohol. A few drops of these solutions were deposited on carbon film-coated Cu grids and analysed with a FEI CM12 microscope.

### 2.3. Aquivion™ preparation

The Aquivion™ SSC ionomer was obtained from a free radical copolymerization of the sulfonyl fluoride vinyl ether (SFVE) monomer with the tetrafluoroethylene (TFE) in aqueous media by using a fluorinated surfactant in emulsion or micro-emulsion conditions. A TFE pressure between 9 and 11 bar of TFE was typically used for obtaining a polymer with EW of 790 g equiv<sup>-1</sup>. The reactivity of TFE was sensitive to pressure changes. This parameter is fundamental when the molar composition needs to be controlled. The latex was stripped for removing the residual monomers and then coagulated by freezing–thawing (or eventually by addition of electrolytes). The polymer powder (with the functional groups in –SO<sub>2</sub>F form) was then washed in water several times and dried at high temperature. The precursor polymer powder, after drying, was pelletized and melt-extruded into films in a screw extruder at a temperature at least 30 °C above the complete melting of the polymer as determined by differential scanning calorimetry (DSC). The film was then hydrolyzed with a process comprising a first step in hot, strong bases (usually potassium hydro-oxide or sodium hydroxide) and a second step in strong acid.

### 2.4. Membrane electrode assemblies (MEAs) preparation

Two different membrane–electrode assemblies, were prepared by using Aquivion™ or Nafion™ membranes and ionomers. As

for the membrane, the experimental Aquivion™ E79-03S short-side chain perfluorosulfonic membrane with a thickness of 30 μm (dry form) and an equivalent weight of 790 g equiv<sup>-1</sup> [4] was used. Whereas, for comparison, a standard N112 Nafion™ membrane with similar thickness (50 μm) was used in parallel experiments.

Both membranes here investigated for high temperature and high pressure operation were non-reinforced films, i.e. extruded products. As above mentioned, Aquivion™ PFSA membrane was a melt-extruded product based on the unique Short Side Chain (SSC) copolymer of Tetrafluoroethylene and a Sulfonyl Fluoride Vinyl Ether of low molecular weight produced by Solvay-Solexis. The ionomer dispersion used for electrode manufacturing in the Aquivion-based MEA had the same structure/composition of the membrane; it was in acid form and contained as solvents 20% water, 40% 1-propanol and 40% 2-propanol.

For both MEAs, the electrodes were prepared according to the procedure described in a previous paper [22]; they consisted of carbon cloth backings, diffusion, and catalytic layers. In the present work, the catalytic layers were composed of 33 wt% ionomers (Nafion™ or Aquivion™ ionomer solutions) and 67 wt% catalyst with Pt loading of 0.3 mg cm<sup>-2</sup>. MEAs were formed by a hot-pressing procedure and subsequently installed in a fuel cell test fixture.

### 2.5. Electrochemical studies

Electrochemical studies in PEM were performed in a H<sub>2</sub>-O<sub>2</sub> 5 cm<sup>2</sup> single cell at a temperature of 130 °C, with a pressure of 3 bar abs. and a R.H. of 100%. The oxygen and hydrogen flow rates were fixed at 2 and 1.5 times, respectively, the stoichiometry value corresponding to 1 A cm<sup>-2</sup>. The Pt loading was 0.3 mg cm<sup>-2</sup>. Single cell performance was investigated by steady-state galvanostatic measurements. The cell was connected to a fuel cell test station including an HP6060B electronic load and an AUTOLAB Metrohm Potentiostat/Galvanostat equipped with FRA and a 20A current booster for AC-impedance spectroscopy and electrochemical diagnostics. For cyclic voltammetry (CV) studies under pressurised PEMFC configuration, humidified and diluted hydrogen was fed to the anode that operated as both counter and reference electrode, whereas, humidified nitrogen was fed to the cathode (working electrode). The sweep rate was 50 mV s<sup>-1</sup>. The electrochemical active surface area was determined by integration of CV profile in the hydrogen adsorption region after correction for double layer capacitance. Data were not corrected for hydrogen cross-over. The time tests in PEMFC were carried out at 130 °C by using the same configuration above discussed with both cell and humidifiers pressurized (3 bar abs.) and maintained at the same temperature.

## 3. Results and discussion

The XRD pattern of the Pt/C catalyst is shown in Fig. 2. The catalyst showed cubic structure for Pt (fcc) and hexagonal structure for carbon support. XRD analyses indicated the occurrence of a small crystallite size of about 1.8 nm for the 50% Pt/Ketjenblack catalyst. The crystallite size was calculated by using the Debye–Sherrer equation. TEM analysis (Fig. 2, inset) showed proper metal particle dispersion and good homogeneity. The TEM micrographs also showed that essentially round Pt particles were present on the surface of the carbon support. The mean particle size derived by TEM (~2 nm) was essentially similar to that obtained by XRD. From geometrical considerations, by assuming spherical metal particles (as envisaged from TEM), the theoretical metal surface area (MSA/m<sup>2</sup> g<sup>-1</sup>) for this Pt electrocatalyst can be derived from the

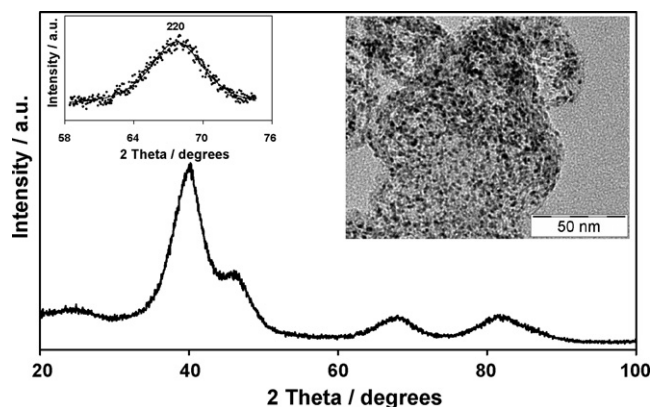


Fig. 2. XRD patterns of Ketjenblack carbon-supported 50 wt% Pt electrocatalyst; The insets show the least-square fitting of the diffraction peaks related to the (220) reflection of the Pt fcc structure and a TEM micrograph of the sample.

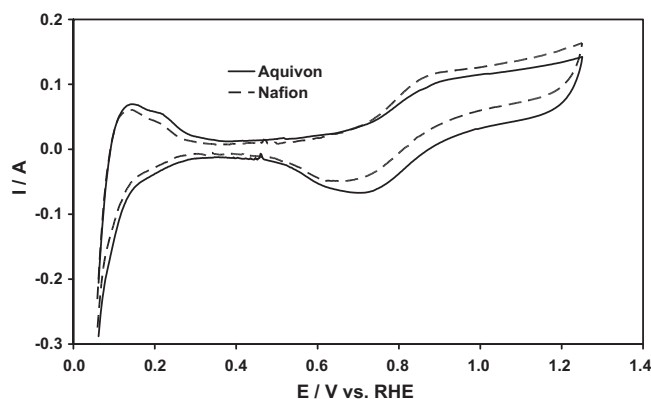


Fig. 3. In situ cyclic voltammetry of the Pt/C-ionomer interface with diluted H<sub>2</sub> feed at counter and reference electrode and N<sub>2</sub> feed at the working electrode. Sweep rate 50 mV s<sup>-1</sup>.

following equation [23]:

$$MSA = \frac{6 \times 10^3}{\rho d} \quad (1)$$

where  $\rho$  (g cm<sup>-3</sup>) is the density of Pt (21.46 g cm<sup>-3</sup>) and  $d$  (nm) is the average particle size (~2 nm). Accordingly, a theoretical metal surface area of ~140 m<sup>2</sup> g<sup>-1</sup> is obtained.

It should be considered that for practical catalyst-ionomer interfaces, the effects of metal-support interaction, the lack of triple-phase boundary in small micropores, the uneven distribution of the ionomer and ionomer dry-out in the catalytic layer can significantly reduce the catalyst utilization. To get information on the effect of the two different ionomers (LSC and SSC) on Pt utilization we have carried out in situ a cyclic voltammetry analysis (Fig. 3). The electrochemical active surface area (ELSA) of the cathode was determined by integration of CV profile in the hydrogen adsorption region after correction for the double layer capacitance. The electrochemically active surface area was larger in the case of Aquivion™ ionomer than in the case of Nafion™. The gain in terms of electrochemical active surface area for the cathode in the MEA equipped with Aquivion™ membrane was close to 30% compared to Nafion™. In fact, the ECSA changed from 66 m<sup>2</sup> g<sup>-1</sup> for the cathode equipped with Nafion™ ionomer to 84 m<sup>2</sup> g<sup>-1</sup> for that containing Aquivion™ ionomer. A similar effect was also recorded for the anode being the electrode manufactured in the same way.

Since the catalyst was the same for both MEAs as well as the weight content of ionomer in the catalytic layer, this increase of

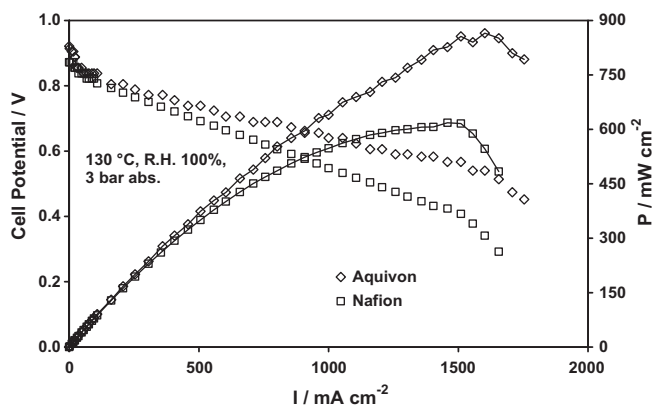


Fig. 4. Comparison of the polarization behaviour for Aquivion™ and Nafion™-based MEAs at 130 °C, 100% R.H., 3 bar abs. H<sub>2</sub>–O<sub>2</sub>.

electrochemical active surface area, could be explained in terms of:

- (i) The smaller equivalent weight for Aquivion™ increases the triple phase boundary region as it would be played by a liquid electrolyte.
- (ii) A different interaction between the ionomer and the catalysts at the three-phase reaction zone may occur.
- (iii) A better filling of the catalyst micropores by the Aquivion™ ionomer micelles leads to an increase of the availability of platinum sites.

Beside these aspects, it should be considered that Aquivion™ suffers less than Nafion™ of ionomer dry out constraints under harsh conditions [4]. The catalyst utilization is 60%, in each electrode, in the case of Aquivion™-based MEA whereas the utilization reaches 47% for Nafion™-based MEA. Accordingly, the increase of Pt utilization in the presence of the SSC ionomer with respect to the LSC ionomer in each electrode is about 13%. It is pointed out that this result is observed for a Pt/C catalyst with fine nanosized particles approaching the physical limit to maintain a crystalline structure. A catalyst with a crystallite size lower than 1.5 nm is partially amorphous being more than 50% of the atoms on the surface [23]. Probably, such difference is less exacerbated for a catalyst with larger particle size or on a lower surface area carbon consisting of a lower amount of micropores.

The polarization curves for the two different PEM single cells equipped with the Nafion™ and Aquivion™ membranes are reported in Fig. 4. Polarizations were carried out at 130 °C (3 bar abs.; 100% R.H.). An open circuit voltage (OCV) of 921 mV was registered for the Aquivion-based MEA that was significantly higher than that recorded with Nafion-based MEA (872 mV). This behaviour could be attributed principally to an increase of the hydrogen cross-over effect in Nafion™ at this temperature [4]. In fact, the decrease of OCV for the Nafion-based with respect to the Aquivion-based MEA could be attributed to an increase in membrane swelling at high temperature [4]; this usually causes an increase of the hydrogen cross-over through the electrolyte and, thus, a mixed potential at the cathode. The increase of hydrogen cross-over with the temperature has been previously reported [24]. It should be also mentioned that Nafion™ has a lower glass transition temperature than Aquivion™ [21]. The latter is also characterized by improved mechanical and crystalline properties [4].

A maximum power density of about 870 mW cm<sup>-2</sup> was obtained with Aquivion™. This value was significantly better compared to the power density of 620 mW cm<sup>-2</sup> measured with Nafion™ membrane. The voltage efficiency at the maximum power den-

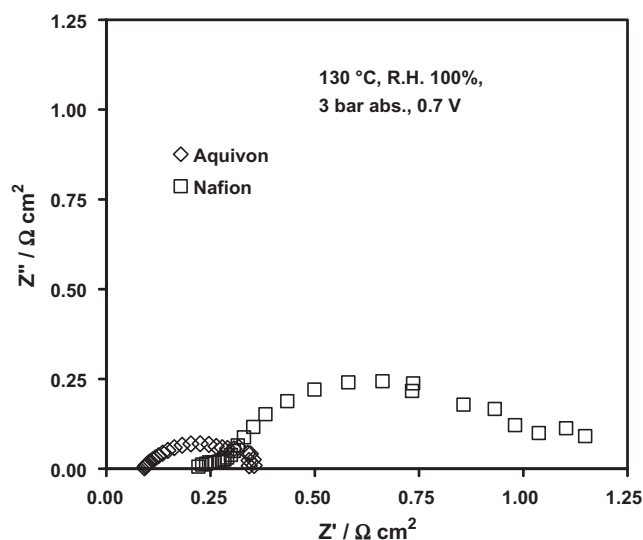
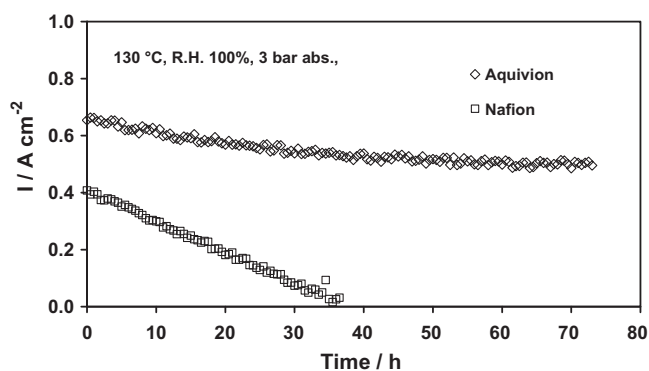


Fig. 5. Comparison of the ac-impedance spectra for Aquivion™ and Nafion™-based MEAs at a cell voltage of 0.7 V at 130 °C, 100% R.H., 3 bar abs. H<sub>2</sub>–O<sub>2</sub>.

sity is also larger for Aquivion™ (0.57 V) than Nafion™ (0.4 V). A larger electrochemical active surface area and a lower cross-over for Aquivion™ vs. Nafion™-based MEAs may provide a suitable explanation for the better performance in the first case. Moreover, a higher conductivity of Aquivion™ vs. Nafion™ was already reported [17]; the latter aspect can be mainly interpreted in terms of lower equivalent weight.

In Fig. 5 we have compared the ac-impedance spectra at an intermediate cell potential, i.e. 0.7 V, where the effect of activation control, mainly determined by the catalyst–electrolyte interface characteristics, is still present and there are also minor effects of the cross-over with respect to the OCV condition. From this comparison, it is observed that the series (ohmic) resistance i.e. high frequency intercept is only 0.11 Ω cm<sup>2</sup> for the Aquivion™ at 130 °C with high pressure and full humidification. In the case of Nafion it is about twice, i.e. 0.23 Ω cm<sup>2</sup>. The ohmic (series) resistance of a PEMFC is mainly determined by the membrane properties whereas a minor contribution to the ohmic characteristics is given by the electrodes and cell hardware. By considering that the membrane thickness is slightly different (30 μm vs. 50 μm) for Aquivion™ and Nafion™, if we normalize the series resistance by the membrane thickness, resistivity values of 46 Ω cm and 36 Ω cm for the Nafion™ and Aquivion™ based MEAs, respectively, are obtained.

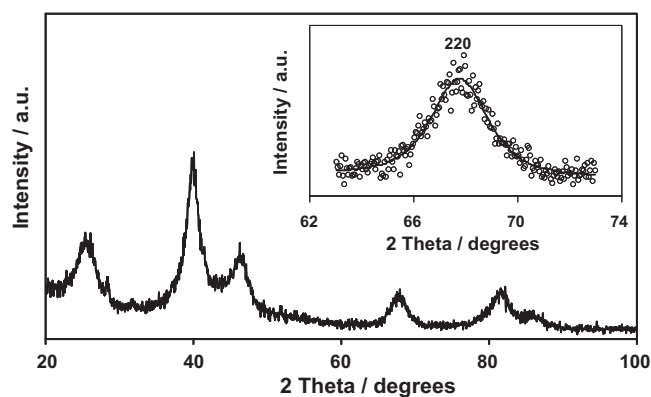
This indicates better hydration and higher conductivity for the Aquivion™ membrane vs. Nafion™ on account of the smaller EW (790 vs. 1100 g equiv<sup>-1</sup>). It was previously reported that an extruded Solvay-Solexis short-side chain ionomer of EW 790 g equiv<sup>-1</sup> was characterized by a larger uptake of liquid water at high temperature compared to Nafion™ ionomer with EW 1100 g equiv<sup>-1</sup> [14]. The main difference that is envisaged for the impedance spectra relates with the significantly lower polarization resistance for Aquivion™ than Nafion™-based MEA (0.26 Ω cm<sup>2</sup> vs. 0.93 Ω cm<sup>2</sup>). It is considered that at 0.7 V, the polarization resistance mainly reflects the electrocatalytic properties than diffusion limitations which are predominant at high current densities and lower cell voltages. Thus, these results clearly indicate that there is not only the effect of larger ionic conductivity but also an impact on electro-catalytic properties played by the short-side chain ionomer-catalyst interface. At high cell potential (i.e. in the region that may be of major interest to operate under suitable efficiency conditions), the electro-catalytic effect may be predominant. This evidence represents a new insight to achieve a better



**Fig. 6.** High temperature time-test for Aquivion™ and Nafion™-based MEAs at a cell voltage of 0.7 V at 130 °C, 100% R.H., 3 bar abs. H<sub>2</sub>–O<sub>2</sub>.

understanding of the behaviour of PSFA membranes especially at high temperature. It may be envisaged that such an effect appears related to the better triple-phase boundary and the lower extent of ionomer dry-out for Aquivion™. Yet, in our opinion, it should not be discarded the effect of super-acidity or proton activity at the electrode–electrolyte interface. Protons are involved in the oxygen reduction reaction. Their availability at the catalyst–electrolyte interface is thus important. In the case of ionomer dry-out, clear mass transport constraints were recorded in PEFC polarization curves [4,22]. Under high temperature operation, the super-acidity may compensate for a lower water availability which generally causes a decrease of proton transport towards the interface. Interestingly, the Pt-oxide reduction peak in the cyclic voltammograms is shifted towards higher potentials in the case of Pt-Aquivion™ interface vs. Pt-Nafion™ (Fig. 3) as it occurs in the case of an increase of specific activity [22].

Time tests at high temperature are reported in Fig. 6. The cells were operated at a constant voltage of 0.7 V at 130 °C with a pressure of 3 bar abs. and 100% R.H. The performance of Aquivion™ was larger than Nafion™ as previously observed in the polarization curves. Beside this aspect, it can be observed that a linear decay with time is initially observed in both cases. Yet, the slope was significantly lower for the Aquivion™-based MEA. After a few days, the latter reached an almost steady state current whereas the performance of the Nafion-based MEA decreased down to the zero current. This different behaviour is very likely related to the fact that the cross-over is significantly larger in the presence of Nafion™ as envisaged from the low OCV in the polarization curve. Cross-over and membrane dry-out may determine a dramatic performance decay in the case of Nafion™. The Aquivion™ membrane is characterized by lower ionomer and membrane dry-out characteristics as well as by better mechanical properties and higher thermal stability due to the higher glass-transition temperature [21]. However, a small decay with time under such harsh operating conditions was also recorded for the Aquivion™-based MEA. This was in contrast to what observed at lower temperature (110 °C) and lower R.H. values (33%) where a steady-state behaviour was substantially achieved [4]. One effect may be due to membrane swelling at higher temperatures especially in the presence of the large level of humidification used here. This was selected to allow for such membrane comparison. However, XRD analysis also indicated a significant change of particle size especially for the cathode catalyst (from 1.8 to 4.2 nm) after the time test (Fig. 7). This indicates that dissolution and re-precipitation phenomena (Ostwald ripening) may have occurred significantly in the first hours of operation under such conditions [25–27]. However, after several hours, the particle growth effect mitigates any further particle sintering with time and it allows to achieve a steady-state performance. It is worth to consider that beside the electrochemical



**Fig. 7.** XRD pattern of the cathode after high temperature operation. The inset shows the least-square fitting of the diffraction peaks related to the (2 2 0) reflection of the Pt fcc structure.

potential the catalyst degradation is promoted by the high temperature and high water content as it occurs in the presence of full humidification [22]. Moreover, a fine nanosized Pt catalyst, even if characterized by high surface area, may be less stable under these conditions with respect to a Pt or Pt-alloy consisting of larger particles [28].

In the case of Nafion™, the low glass transition temperature and poor mechanical properties at high temperature may cause an increase of membrane swelling with time with consequent increase of hydrogen cross-over. As discussed before, this leads to a mixed potential at the cathode. Hydrogen and oxygen may react directly on the platinum cathodic sites. This reaction is extremely exothermic and it produces a local heating that, with time, can destroyed the membrane backbone structure or cause a strong catalyst sintering. This latter effect, even if less dramatic, may also contribute to the catalyst sintering effect at the cathode also in the case of the Aquivion-based MEA. Although, the OCV is larger for Aquivion™, it is lower than that recorded for the MEA based on the same membrane under conventional or less critical operating conditions [4] indicating the occurrence of cross-over at 130 °C. However, it should be mentioned that under practical operation conditions a lower relative humidity generally mitigates such effect [4] being the membrane swelling not only determined by temperature but also by the water content.

#### 4. Conclusion

An experimental Aquivion™ E79-03S short-side chain and a long-side chain Nafion™ perfluorosulfonic membranes characterized by an equivalent weight of 790 and 1100 gequiv<sup>-1</sup>, respectively, were investigated under operation at high temperature in a pressurised PEMFC under full humidification conditions. The tests were performed at a temperature of 130 °C that represents the target for automotive applications. The Aquivion™-based MEA membrane appeared significantly more performing under these conditions. Beside the lower ohmic resistance, a lower cross-over and a better electro-catalytic activity was observed for the Aquivion™ under these conditions. These enhanced properties were explained by the larger crystallinity, higher glass transition temperature and lower equivalent weight of Aquivion™. The first two properties assure better mechanical properties whereas the latter produces higher conductivity and an increase of catalyst utilization. Moreover a significantly lower decay was recorded for the Aquivion™ membrane-based MEA during an endurance test essentially related to the lower dry-out and cross-over effects. However, a sintering effect for the nanosized Pt particles in the cathode electrocatalyst was recorded which may be in part promoted by

the hydrogen cross-over and recombination with oxygen at the cathode–electrolyte interface.

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