New perfluorinated ionomer with improved oxygen permeability for application in cathode Polymeric Electrolyte Membrane Fuel Cell

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ABSTRACT

Proton Exchange Membrane Fuel Cells are considered an alternative to the internal combustion engine for transportation. Despite the existence of relevant demonstrations and few commercial fleets, there are still a series of issues such as the cost of platinum and the durability of the materials which limit a wider application of PEM-FC in automotive. The reduction of Pt load in cathode electrode is the main argument to decrease the cost of PEM-FC, but oxygen reduction reaction (ORR) in the cathode catalyst layer causes the larger overpotential loss of the whole assembly, thus the need of increasing as much as possible the Pt utilization. Herein we report the synthesis, characterization and application of an ionomer used in the cathode catalyst layer; thanks to its higher oxygen permeability the quantity of Pt may be minimized. This ionomer is a modification of commercial Aquivion® PFSA obtained by incorporation of a third monomer (2,2,4-trifluoro-5-trifluoromethoxy-1,3-dioxole, MDO). The results demonstrate a higher oxygen permeability of the new ionomer compared to Aquivion® PFSA E87-05S and Nafion NR212. Furthermore, an improvement of the performance of a PEM-FC in automotive conditions (RH=40-70%) is obtained with the assembly where this ionomer is used as cathode binder.

INTRODUCTION

Fuel cells (FC) are considered the most promising technology for a future clean mobility since they guarantee very high energy efficiency with local emission of solely water vapor. Thus FC are a relevant research topic in all leading automobile manufactures since they are expected to provide an urgent solution to the increasing impact of vehicle pollution [1] and vehicle performance not very far from current internal combustion engines. Among various kinds of fuel cells, polymer electrolyte membrane fuel cells (PEM-FC) are particularly suited to be used for automobiles and portable devices [2] thanks to their flexibility in operating at different load and different temperatures. Currently, membranes and electrode binders are mainly based on perfluorinated sulfonic acids such as Nafion® PFSA [3] (*Chemours*) and Aquivion® PFSA [4,5] (*Solvay Specialty Polymers*).

The challenge of the cost reduction and consequent commercialization of fuel cell vehicles is still open [6]. Only few years ago the main problems related to this technology were associated to the polymer electrolyte membrane durability and can be considered solved today thanks to the introduction of chemically stable grades and chemical scavenger technologies, but the attention has now shifted to the electrodes. This is a complex three-phase system: platinum nanoparticles (which act as catalysts for the reactions) dispersed on carbon (used to increase the available surface) and consolidated by an ionomer, that guarantees the protonic conductivity [7].

The reduction of precious metal load is one of the highest priorities, since Pt catalyst has a significant impact on FC stack cost [8,9]. Platinum catalyzes the oxidation of H_2 at the anode with relatively low overpotential, thus enabling the use of very low loading of catalyst [10]. Higher amount of platinum is necessary in the cathode because the oxygen reduction reaction (ORR) is today the rate determining step, especially when Pt load is reduced to extreme values, the low oxygen concentration of oxygen on Pt surface is even increasing the cathode electrode overpotential [11,12].

Most of the models of electrode structures indicate the Pt nanoparticles surrounded by a thin layer of ionomer, oxygen permeation through this ionomer films has been described to be critical to the performance of low Pt loading cathodes [13,14].

PFSA are relatively permeable to gases, thanks to the perfluoropolymeric structure, but are not optimized to maximize this behavior, since, when used in membrane separators, a certain gas impermeability is key to maximize the fuel cell efficiency through the reduction of gas crossover across the membrane.

The development of a new class of binder materials for a specific use in the catalyst layer, which possesses a high oxygen permeability for lowering the mass transfer resistance at the cathode, is key for the success of PEM-FC technology in automotive application. Only very few examples of polymers have been designed to be specifically

applied as cathode binder with high permeability [15,16]. In literature several solutions based on amorphous ionomers have been reported.

A possible solution is the use of the dioxole structures which hinder polymer chain packing in commercial materials such as Cytop, Teflon AF and Hyflon AD [17,18,19]. These are amorphous fluoropolymers with very high gas permeability [20].

In this work we have synthesized a new ionomer **2** based on Aquivion® PFSA, introducing the 2,2,4-trifluoro-5-trifluoromethoxy-1,3-dioxole (MDO) monomer (Figure 1, left) in the typical perfluorinated structure branched with aliphatic ethers terminated with $–SO_3H$ groups. Aquivion 3 (Figure 1, right) is a commercially available copolymer of the TFE and SFVE, bearing $-SO_3H$ groups on the side chain [21,22].

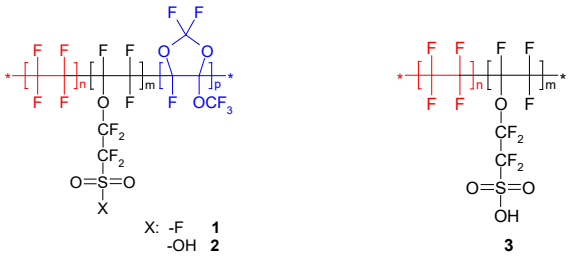


Fig. 1. Chemical structures of the new ionomer (left) and Aquivion® PFSA (right).

Aquivion® is used as polymer electrolyte membrane into the fuel cell as well as in the catalyst layer as binder material. Even if the PEM has to be impermeable to gases and the catalyst binder has to be permeable to oxygen and hydrogen, allowing low mass transport loss to the catalyst, at the moment, the same PFSA is used as binder at the cathode and as constituent of the membrane.

In this paper we describe a variety of physical and electrochemical characterizations for Aquivion® and the new ionomer also in comparison with commercial Nafion. In the first part of the work the intrinsic permeability of the new ionomer was assessed using an electrochemical test on membrane. The second part describes the behavior of the new ionomer as a binder in the cathode catalyst layer, comparing it to the performance of Aquivion®.

The new material demonstrates a higher oxygen permeability compared to commercial Aquivion® and Nafion. As a consequence, an improvement of the performance of the PEM-FC is noted in the polarization curves and a lower transport resistance for the membrane electrode assembly (MEA) containing the new ionomer as cathode binder was observed by impedance spectroscopy analysis.

EXPERIMENTAL

Reagents and Materials – All chemicals are commercially available and used without further purification. The solvents and chemicals were purchased form Carlo Erba and Millipore Corp. Nafion NR212 membrane was purchased from Sigma Aldrich. Pt/C (Decal H500) and IrOx were purchased from Greenerity GmbH and Umicore AG&Co, respectively. Pt/C powder was purchased from Tanaka. Gas diffusion layers (Sigracet 25BC) from SGL Group.

New ionomer polymerization – In a water based emulsion polymerization, perfluorosulfonyl vinyl ether with formula CF_2=$CFO(CF_2)_2$-SO_2F (PSVE), MDO and Fluorolink® PFPE were fed in a 5 liter autoclave stirred at 650 rpm and heated at 70 °C. A water solution of $K_2S_2O_8$ was added to initiate the reaction after having pressurized the system with tetrafluoroethylene (TFE). The pressure was maintained by continuous addition of TFE until the desired reaction conversion was reached.

After 6 hours, a clear and transparent latex was recovered (4.3 kg, solid content: 30 wt%) and coagulated by freeze-thawing. The powder thus obtained (900 g) was carefully washed at room temperature with demineralized water and then dried at 80 °C for 24 h in a ventilated oven.

The composition of the polymer **1**, determined by NMR (dissolving the polymer in C_6F_6) was: TFE 78.0 %mol, PSVE 15.5 %mol and MDO 9.5 %mol. The corresponding equivalent weight (EW) was 899 g/mol.

Conversion of –SO_2F groups in –SO_3H - The polymer powder **1** (100 g) was treated initially in a solution (1 l) of 14 wt% of potassium hydroxide, 30 wt% dimethyl sulfoxide and 56 wt% of demineralized water at 80 °C for 8 hours under stirring. After several washings with demineralized water, in order to remove the excess of base, the polymer was acidified with 1 liter of a 20 wt% nitric acid solution at room temperature for 2 hours. The powder thus obtained was extensively washed with deionized water and eventually dried in a vent oven at 80 °C for 8 hours.

The quantitative transformation to polymer **2** was then confirmed with a FT-IR *Thermo Scientific Zs50R*, monitoring the disappearance of the characteristic -SO_2F peak at 1470 cm^{-1}.

Dispersion preparation - The polymer powder **2** (60 g) was mixed with demineralized water (160 g) in a titanium 250 ml autoclave. The mixture was heated at a temperature above 180 °C and stirred at 750 rpm. After 4 h the mixture was cooled down and the water dispersion was purified by centrifugation (10000 rpm) for 2 hours.

The clear and transparent dispersion had a solid content of 22.7 wt%.

Dispersion Formulation and Membrane Casting - In order to increase the viscosity allowing a homogeneous dispersion casting while introducing additives suitable to preserve the material integrity during membrane preparation, the final dispersion was formulated by mixing the water-based dispersion (34 g) with *n*-propanol (59 g), demineralized water (69 g) and dimethyl sulfone (7.5 g).

The formulated dispersion had the following composition: polymer: 20 wt%, water: 40.5 wt%, *n*-propanol: 35 wt% and dimethyl sulfone; 4.5 wt%.

Dispersion casting was carried out using a *Zehntner doctor blade* ZUA 2000 and a *Zehntner ZAA 2300* automatic film applicator on a tempered glass support. After deposition, the film underwent a 3 steps heating cycle in a vent oven: 1 hour at 65 °C, 1 hour at 90 °C and 1 hour at 190 °C. The membrane is then peeled off from the glass using demineralized water and dried in a vent oven at 80 ° C.

Membrane thickness was 49 ± 5 µm.

Membrane electrode assembly (MEA) preparation for Oxygen crossover test - MEAs were produced using commercial Aquivion E87-05S (EW: 870 g mol^{-1}, thickness: 50 µm), Nafion NR212 (EW: 1100 g mol^{-1}, thickness: 50 µm) and new ionomer membrane as membrane separators. For the cathode catalyst layer was used a commercial Pt/C with a loading of 0.45 mg_{Pt} cm^{-2}. The anode catalyst layer was made in-house with IrO_x loading of 0.1 mg_{IrOx} cm^{-2}. The latter was produced using 22 g of a commercial Aquivion D83-06A (6 wt% of polymer) and 4 g of IrOx, stirred with a magnetic bar for 30 minutes in a flask and 1 hour in an ultrasonic bath. The anode layer then was produced using a film depositor *Elcometer 4340* and then heated at 90 °C for 2 hours. The electrode was obtained by hot pressing the catalyst layer with wet-proofed carbon fiber paper (*SGL 25BC*) with microporous layer (MPL) as gas diffusion layer (GDL) at 200 °C and 8 barA.

Membrane electrode assembly (MEA) preparation for electrochemical characterization - A commercial Aquivion® membrane E98-05S (EW: 980 g mol^{-1}, thickness: 50 µm) was used as electrolyte membrane. The anode catalyst layer is a commercial Pt/C with loading of 0.45 mg_{Pt} cm^{-2}.

The cathode catalyst layer has been prepared by using the new ionomer dispersion previously described as binder and, for comparison, a commercial Aquivion® dispersion D83-24B was used. The preparation is the same for both ionomers dispersions: 5 g of water based dispersion (20 wt%), 2 g of Pt/C, 7.9 g of *iso*-propanol and 7.9 g of *n*-

propanol were mixed and stirred to obtain a uniform paste. The cathode electrode was produced by casting the pastes with a film depositor *Elcometer 4340* and then heated at 90 °C for 2 hours to remove the solvents.

X-Ray diffraction - X-ray diffraction (XRD) data were collected using a PANalytical X' Pert MPD PRO powder diffractometer equipped with an X'Celerator detector, exposing samples to Cu-Kα X-ray radiation. Samples were mounted in a sample holder with amorphous Silica window and analyzed in the range 5-80° 2θ at 40 KV-40 mA.

Morphological characterization and EDS Microanalysis - The morphological characterization was performed using the FE-SEM Jeol JSM 7610F and the EDS microanalysis was performed using an X-Max 50 mm2 Silicon Drift detector from Oxford Instruments.

Thermogravimetric (TGA) analysis- Thermogravimetric analysis (TGA) was performed with a Perkin Elmer TGA 8000 instrument in the temperature range 30-800°C, with heating rate 10°C/min and air as purge gas at 30 ml/min.

O_2 Permeability Measurement of Membranes - Gas permeability through a PFSA membrane has been measured in the literature using a number of techniques [23,24], including volumetric method [25], time-lag study [26] and gas chromatography [27]. In this work the oxygen permeability of the membrane is measured using an electrochemical test [28] under realistic PEM fuel cell operating conditions. The oxygen permeability (P_{O2}) was assessed from the oxygen-crossover-rate limited oxygen reduction reaction (ORR) at the cathode, as expressed by the formula:

$$P_{O_2} = \frac{i_{ORR} \cdot \delta_{mem}}{4F \cdot p_{O_{2,an}}}$$

where i_{ORR} is the oxygen reduction reaction current, δ_{mem} is the membrane thickness, F is the Faraday constant (96487 C mol^{-1}) and $p_{O2,\,an}$ is the oxygen pressure.

The measurement procedure consists in a first step of conditioning for 4 hours in H_2/air at a cell temperature of 75 °C and a relative humidity of 65 %; after that, the system is purged in N_2 at the same temperature. The measure is then carried out in a 25 cm^2 active area single cell at a 60 °C, feeding N_2 (cathode) and O_2 (anode) at pressure of

120 kPa, O_2 flow rate of 1000 sccm, N_2 flow rate of 500 sccm and potential of 1V using an *AutoLab PGSTAT30* potentiostat/galvanostat equipped with the program Nova 2.1.

Polarization and Electrochemical Impedance Spectroscopy (EIS) characterization – The fuel cell performance was measured with polarization curve and electrochemical impedance spectroscopy in a 25 cm^2 active area single cell.

Polarization curves were performed on a test station of *Fuel Cell Technology (Albuquerque NM)* setting the following parameters: potentiostatic mode, voltage range 1-0.4 V, voltage step 0.01 V/s repeated at three different relative humidity condition and temperature (66 °C - 120 % RH, 75 °C - 70% RH, 90 °C - 43 % RH) feeding H_2 (650 sccm) at the anode and air (1300 sccm) at the cathode. The electrochemical impedance spectroscopy measure was performed with *AutoLab PGSTAT 30 potentiostat/galvanostat* with the program Nova 2.1 setting the following parameters: 60 and 120 % of relative humidity, cell temperature of 60 °C feeding H_2 (1000 sccm) at the anode and air (1000 sccm) at the cathode side, repeated at two different current density (0.025 A cm^{-2} and 1.2 A cm^{-2}).

RESULT AND DISCUSSION

Physical Characterizations- Crystallinity and texture of ionomer **2** have been investigated through X-Ray Diffraction (XRD) analysis. Diffraction profile of the new ionomer **2** and commercial Aquivion® PW87S (powder having EW of 870 g/mol) are presented in Figure 2a. Accordingly to the two-phase model, the semicrystalline Aquivion shows two peaks positioned at 17 (broad) and 18 (sharp) °2Θ corresponding to the scattering of amorphous phase and diffraction of crystallites whereas the new ionomer shows an unique peak at 17 °2Θ attributable to the amorphous region. Although it isn't the unique parameter, the lack of crystallinity is expected to play an important role in influencing the higher oxygen permeability of the new ionomer **2**.

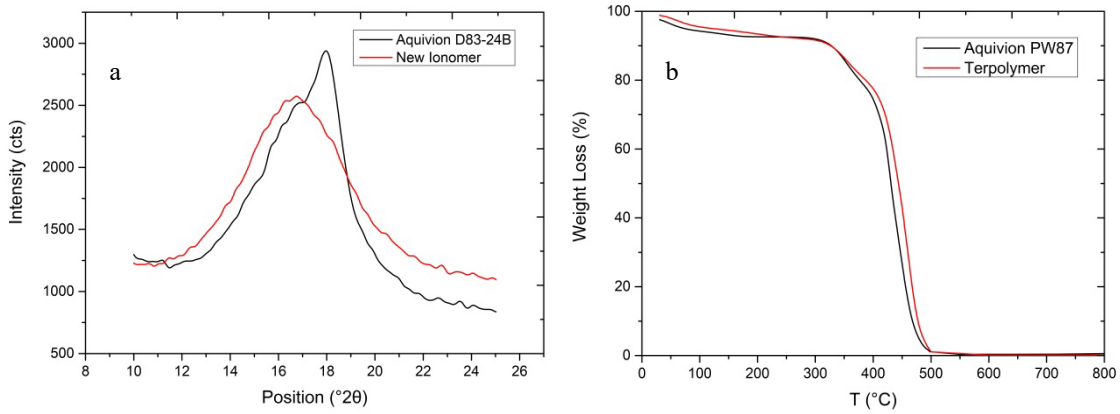


Fig. 2. XRD pattern (a) and Thermogravimetry analysis (b) (air, heating rate: 10 °C/min) of new ionomer in comparison with commercial Aquivion PW87S.

Thermal stability of ionomer is a crucial parameter in view of electrode fabrication and membrane lamination during MEA assembly. Figure 2b shows the ThermoGravimetric Analyses (TGA) in air of the new ionomer **2** and Aquivion PW87S as reference. Thanks to the perfluorinated structure both ionomers, after the initial loss of moisture at about 100°C, have similar behavior showing heat stability more than enough to stand the typical thermal treatment of MEA manufacturing.

O_2 Permeability Measurement of Membranes- The oxygen permeability of Aquivion® E87-05S, Nafion NR212 and the new ionomer **2** membrane were measured by coupling such membranes with a Pt/C cathode and a IrOx anode and feeding N_2 and O_2 at the cathode and at the anode, respectively. According to Zhang *et al.*[28], in this configuration the oxygen crossover limiting current can be measured by the oxygen reduction reaction at the cathode and then transformed in oxygen permeation. Results are shown in figure 3, where is illustrated the oxygen permeability as a function of the relative humidity.

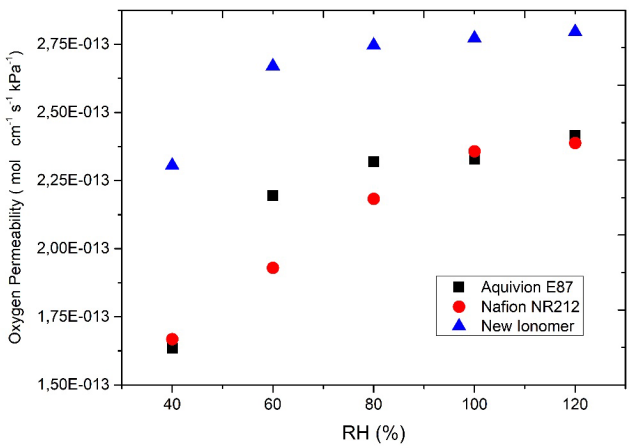


Fig. 3. Oxygen permeability of Aquivion E87-05S, Nafion NR212 and the new ionomer as a function of relative humidity.

As expected, oxygen permeability increased with the relative humidity for all samples. The new ionomer showed an improved permeability compared to Aquivion® and Nafion in the investigated RH window. In particular, in full humidification conditions the new material has 20% higher oxygen permeability than commercial ionomer membranes. This confirmed the fact that the presence of MDO monomer in the polymer structure increases the oxygen permeability of the membrane thanks to the higher free-volume induced by its steric hindered cyclic structure.

Morphological Characterization – In order to confirm the higher oxygen permeability of the new ionomer when used as an electrode binder, a MEA containing Aquivion E98-05S membrane, commercial Pt/C at the anode and Pt/C consolidated with ionomer **2** has been assembled. SEM images of the cross-section of the MEA and GDL at different magnification are shown in Figure 4a and 4b. The central zone corresponds to the polymer membrane Aquivion E98-05S the cathode catalyst layer (containing the new ionomer, platinum and Carbon). The outer layer corresponds to the carbon of the gas diffusion layer.

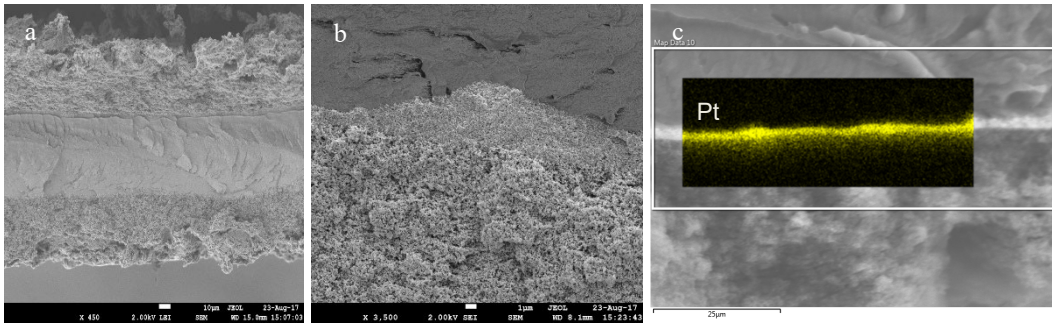


Fig. 4. SEM micrograph (a) and magnification (b) of the MEA produced using the new ionomer as binder in the cathode catalyst layer and EDX micro analysis (c) of the cathode catalyst layer to study the homogenous distribution of platinum

Since the good adhesion of the different layers the MEAs manufactured in this way are comparable with the ones produced with Aquivion® commercial dispersions and thus the electrochemical behavior of these MEAs can be considered reliable and representative of a typical MEA containing Aquivion membrane and ionomer in the electrodes.

The homogeneity of Pt distribution within the cathode layer has been confirmed through an EDX analysis inside the region highlighted in figure 4c . The study was focused in particular on the K_α signal of Platinum.

The good distribution of the Platinum catalyst inside the cathode layer is comparable with the one achievable with Aquivion.

Polarization curves - Performance of the MEA thus prepared was then tested with polarization curves recorded at different relative humidity. The MEA containing the new ionomer **2** was compared to a MEA having a commercial Aquivion D83-24B (EW: 830 g mol^{-1}) as cathode binder.

The first measure was carried out at full humidification condition (RH=120%) with a cell temperature of 66 °C; results are shown in figure 6.

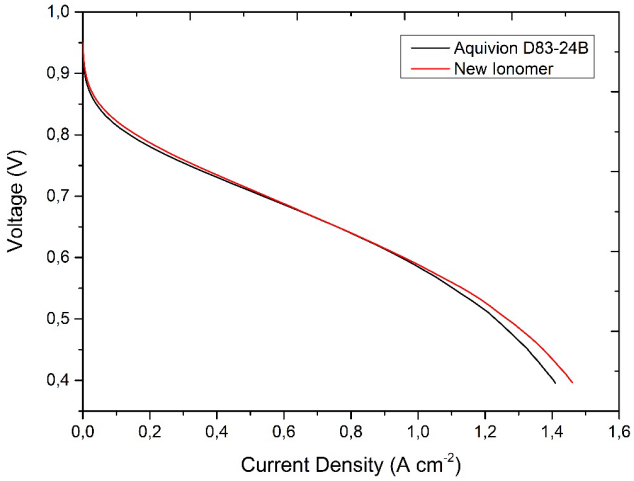


Fig. 5. Polarization curve at full humidification condition (RH=120%) and cell temperature of 66 °C.

From the I-V curve is clear that at full humidification condition the performance of the new ionomer used as binder in the cathode layer has a negligible influence on the oxygen reduction reaction. This can be explained considering that at very high relative humidity the material is completely soaked of water, so the oxygen transport is already favored from the presence of the water channels in a swollen matrix.

The measure was then repeated in drier condition with a relative humidity of 70% and a cell temperature of 75 °C; results are shown in figure 6a.

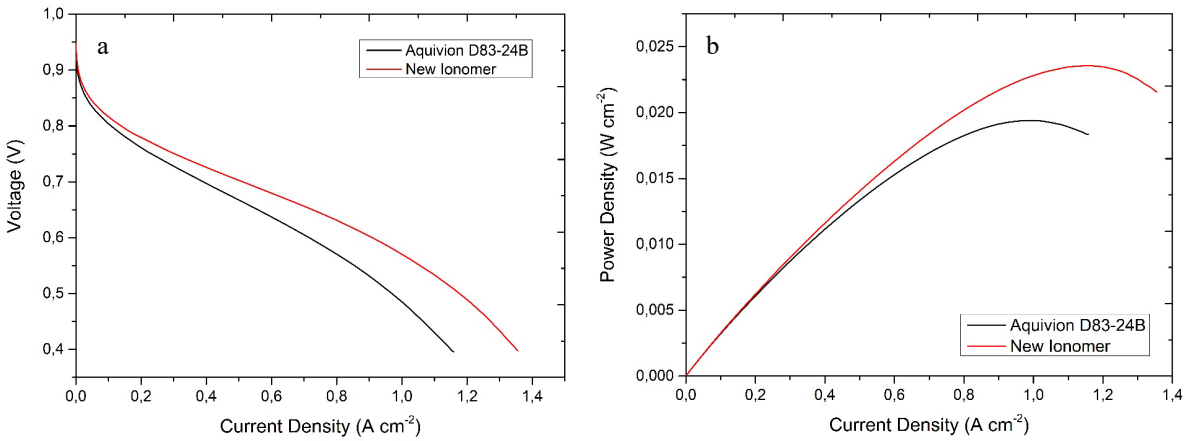


Fig. 6. Polarization curve (a) and power density (b) in dry condition (RH=70%) and cell temperature of 75 °C.

In this case there is a net improvement of the performance (also calculated as power density produced, figure 6b) for the sample having the new ionomer as cathode binder. The different behavior results in the mass transfer region of the polarization curve, a proof of the improvement in the oxygen permeability of this new material.

Finally, the last measure was performed in the driest condition, at a relative humidity of 43% and a cell temperature of 90 °C. Results are shown in figure 7a.

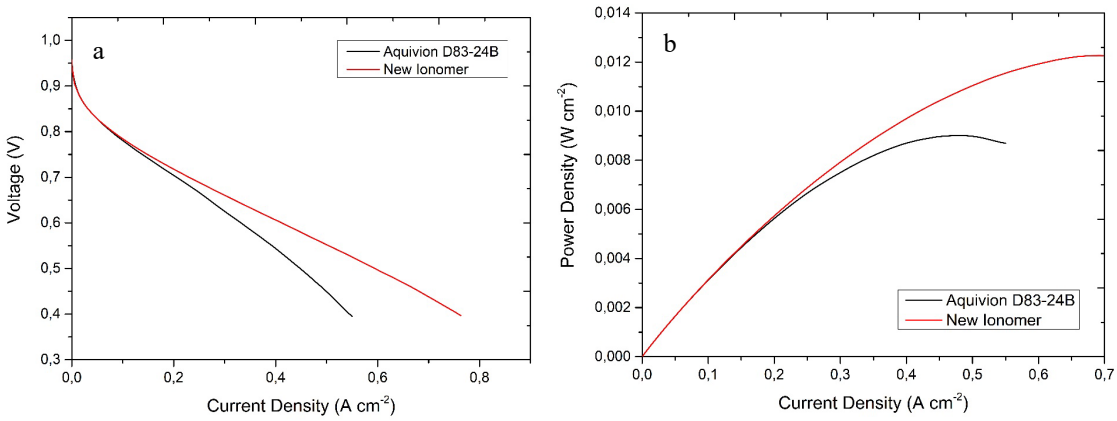
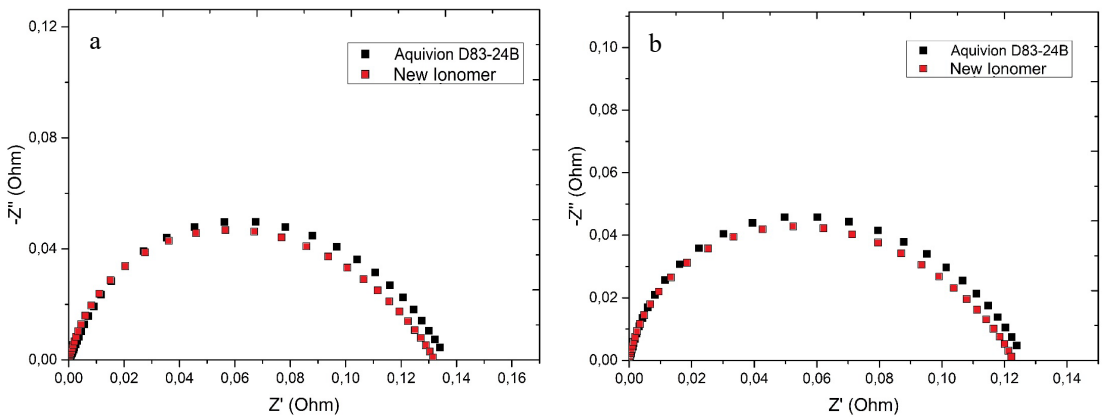


Fig. 7. Polarization curve (a) and power density (b) in super dry condition (RH=43%) and cell temperature of 90 °C.

Also in this case, there is a sharp improvement in the performance for the sample having as cathode binder material the new ionomer (also calculated as power density produced, figure 7b), in particular again in the mass transfer region (high current density).

Electrochemical Impedance Spectroscopy - As for the polarization curve, we tested the MEAs having the new ionomer **2** and Aquivion® D83-24B as cathode binder. In particular, we studied the charge transfer resistance (related to kinetic/activation processes) and the mass transfer resistance (related to transport processes). The curves were referred to the origin because the ohmic contribution of the membrane and the other components is the same for all samples, being used the same membrane and the same cell components being the only difference the ionomer in the cathode electrode.

The charge transfer resistance was characterized at two different relative humidity conditions (RH= 70% , RH=120% in figure 8a and 8b), cell temperature of 60 °C and current density of 0.025 A/cm^2. The charge transfer resistance corresponds to the diameter of the semicircle shown in the Nyquist diagram. As shown in the figures, the charge transfer resistance of the two samples are nearly the same in both relative humidity conditions. This follows the results obtained in the polarization measurements, in which the difference between Aquivion and the new ionomer are not linked to charge transfer kinetic processes. Instead when we characterized the mass transfer resistance, the behavior of the samples is very different. At high current density the Nyquist diagram shows indeed two semicircles: the first is again linked to kinetic/activation process and the second, observed only at high current density, to the oxygen transport process.



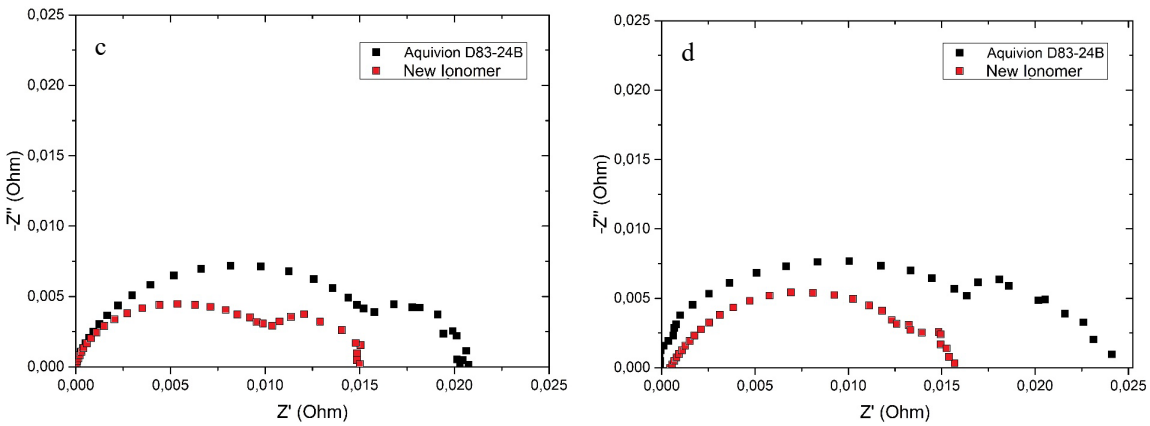


Fig. 8. Impedance measure at 0.025 A cm^{-2}, cell temperature of 60 °C and relative humidity of 70% (a) and 120% (b) for the two MEAs having as cathode binder Aquivion D83-24B and the new ionomer. Impedance measurement at 1.2 A cm^{-2}, cell temperature of 60 °C and relative humidity of 120% (c) and 70% (d) for the two MEAs having as cathode binder Aquivion D83-24B and the new ionomer. Membrane is Aquivion E98-05S.

The measurements were again carried out at two different relative humidities (RH= 120% , RH= 70% in figure 8c and 8d), cell temperature of 60 °C and current density of 1.2 A/cm^2.

As evidenced from those figures, we can observe two important aspects. First of all, analyzing the mass transfer resistance (the diameter of the second semicircle in the Nyquist diagram) it was observed that in full humidification conditions the resistance of the two samples are nearly the same (about 0.005 Ohm, figure 8C); whereas in dry condition the mass transfer resistance for the sample having the new ionomer as cathode binder is lower (about 0.0025 Ohm, figure 8D). This is a confirmation that this new ionomer has a better oxygen diffusion than commercially available and usually employed PFSA ionomers. The second important observation in the EIS measurements, is that the different mass transport processes for the two sample affect the kinetic processes. Indeed, for both measurements the diameter of the first semicircle is smaller for the new ionomer than for Aquivion D83-24B ionomer; this behavior can be explained as a more efficient utilization of Pt induced by a better oxygen transfer from the bulk to the surface of the catalyst. This parameter is considered of paramount importance in order to reduce the Pt loading in the next generation PEM-FC.

CONCLUSIONS

In this study we report the synthesis, characterization and application in PEM-FC of a new ionomer with improved oxygen permeability to be used as binder for the cathode catalyst layer. The new ionomer is obtained as a modification of the structure of the commercial Aquivion®, adding a third monomer (MDO) during

polymerization. Oxygen permeation through ionomer is a key factor for enabling the reduction of catalyst load in cathode side electrode of PEM-FC thus reducing the cost of the electrochemical package.

The permeability of the material containing 78 mol% of TFE, 15.5 mol% of PSVE and 9.5 mol% of MDO (EW about 900 g/mol) was initially measured with an electrochemical test, comparing it to commercial Aquivion E87-05S and Nafion NR212. The results showed an improved permeability for the new ionomer at every relative humidity tested. Then the new material was tested in situ in single cell assembly, as binder in the cathode catalyst layer, comparing the performance with a commercial Aquivion D83-24B binder. The behavior was tested by recording polarization curves and electrochemical impedance spectroscopy under different temperature and relative humidity. The polarization curves showed an improvement of the performance of about 20% (measured as maximum power density produced) for the sample having the new ionomer as cathode binder, in particular in dry conditions (RH=70%). The electrochemical impedance spectroscopy was used to characterize the charge transfer resistance and mass transport resistance of the electrodes. Results showed that the charge transfer resistance for the new binder and commercial Aquivion® at low current density is the same, proof of the fact that the new material does not modify the kinetic processes. The mass transport resistance measured at high current density is lower for the new ionomer compared to commercially available Aquivion D83-24B thanks to an increased oxygen transport ability inside the electrode.

ACKNOWLEDGEMENTS

The authors are gratefully to Dr. D. Aurilia, Dr. D. Ferrari and P. Vanotti for physical characterizations (SEM/EDX, XRD and TGA).

The research leading to these results received support from the European Union's Horizon 2020 research and innovation programme for the Fuel Cells and Hydrogen 2 Joint Undertaking under grant agreement No 671465 "Volumetriq- Volume Manufacturing of PEMFC Stack for Transportation and In-Line Quality Assurance".

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