



New perfluorinated ionomer with improved oxygen permeability for application in cathode polymeric electrolyte membrane fuel cell



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HIGHLIGHTS

- A new amorphous ionomer with improved oxygen permeability was synthesized.
- The ionomer is modification of Aquivion PFSA with a steric hindered monomer (MDO).
- Oxygen permeability through ionomer is important for reduction of catalyst loading.
- A 20% increase of oxygen bulk permeability has been demonstrated.
- Ionomer showed an improvement of performance and lower mass transport resistance.

ABSTRACT

Proton Exchange Membrane Fuel Cells (PEM-FC) 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 durability of the materials and the cost of platinum which limit a wider application in this field. To this regard, better utilization and consequently loading reduction of Pt in electrodes is of outstanding importance. Herein we report the synthesis, characterization and application of an ionomer 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). Results on cast membrane demonstrate a 20% higher oxygen permeability of the new ionomer compared to Aquivion PFSA E87-05S and Nafion NR212 at 100% RH. 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. In particular polarization curve at 70% RH shows improvement of 20% of power density peak and electrochemical impedance confirms higher oxygen permeability due to lower mass transport resistance than Aquivion.

1. 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

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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 H₂ 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 and, 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 and oxygen permeation through this ionomer films has been described to be critical to the performance of low Pt loading cathodes [13,14].

PFSAs 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 [17–19]. These are amorphous fluoropolymers with very high gas permeability [20].

In this work we have synthesized a new ionomer **2** based on Aquivion PFSAs, introducing the 2,2,4-trifluoro-5-trifluoromethoxy-1,3-dioxole (MDO) monomer (Fig. 1, left) in the typical perfluorinated structure branched with aliphatic ethers terminated with –SO₃H groups. Aquivion **3** (Fig. 1, right) is a commercially available copolymer of tetrafluoroethylene (TFE) and perfluorinated vinyl ether, bearing –SO₃H groups on the side chain [21,22].

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 PFSAs are 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

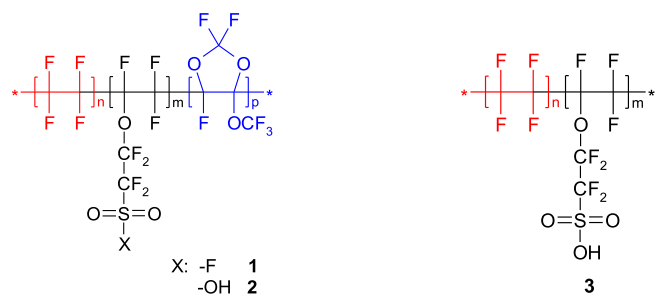


Fig. 1. Chemical structures of the new ionomer (left) and Aquivion PFSAs (right).

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.

2. Experimental

2.1. Reagents and materials

All chemicals are commercially available and used without further purification. The solvents and chemicals were purchased from 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.

2.2. New ionomer polymerization

In a water based emulsion polymerization, perfluorosulfonyl vinyl ether with formula CF₂=CFO(CF₂)₂-SO₂F (PSVE), MDO and Fluorolink PFPE were fed in a 5 L autoclave stirred at 650 rpm and heated at 70 °C. A water solution of K₂S₂O₈ 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 h, 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 C₆F₆) was: TFE 78.0 %mol, PSVE 15.5 %mol and MDO 9.5 %mol. The corresponding equivalent weight (EW) was 899 g/mol.

2.3. Conversion of –SO₂F groups in –SO₃H

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 h under stirring. After several washings with demineralized water, in order to remove the excess of base, the polymer was acidified with 1 L of a 20 wt% nitric acid solution at room temperature for 2 h. The powder thus obtained was extensively washed with deionized water and eventually dried in a vent oven at 80 °C for 8 h.

The quantitative transformation to polymer **2** was then confirmed with a FT-IR *Thermo Scientific Zs50R*, monitoring the disappearance of the characteristic –SO₂F peak at 1470 cm⁻¹.

2.4. 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 h.

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

2.5. 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:

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