



# Towards fuel cell membranes with improved lifetime: Aquivion<sup>®</sup> Perfluorosulfonic Acid membranes containing immobilized radical scavengers



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## HIGHLIGHTS

- A novel silica-supported cerium-oxide-based radical scavenger is synthesized.
- This material is loaded as a filler in Aquivion<sup>®</sup> Perfluorosulfonic Acid membranes.
- The loaded membrane show higher stability than radical scavenger-free membrane.
- The composite scavenger mitigates the polymer electrolyte degradation.

## ARTICLE INFO

### Article history:

Received 10 July 2014

Received in revised form

25 August 2014

Accepted 5 September 2014

Available online 16 September 2014

### Keywords:

Radical scavenger

Polymer electrolyte membrane

Fuel cell

Perfluorosulfonic acid

## ABSTRACT

A facile synthesis, based on a wet impregnation technique and a thermal treatment, of a novel silica-supported cerium-oxide-based radical scavenger bearing sulfonic acid functionalities is presented. This material is loaded as a filler in ePTFE reinforced membranes (called R79-02S) prepared starting from Aquivion<sup>®</sup> Perfluorosulfonic Acid (PFSA) dispersions. The aim is to mitigate the peroxy radicals attack to the polymeric membrane under fuel cell operating conditions. These membranes show much longer (7 times more) life-time in Accelerated Stress Tests (AST) and reduced fluoride release (about one half) in Fenton's tests than the radical scavenger-free membrane without any loss in electrochemical performance. Scavenger-free Aquivion<sup>®</sup> PFSA-based membrane durability is about 200 h in AST whereas the same membrane containing the newly developed radical scavenger exceeds 1400 h. These results confirm the stability of the modified membranes and the excellent activity of the composite scavenger in mitigating the polymer electrolyte degradation.

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## 1. Introduction

In the last years, many efforts have been made to analyse, identify and mitigate the causes of early failure of Polymer Electrolyte Membrane Fuel Cells (PEMFC) in order to increase their lifetime [1,2]. Membrane degradation is one of the key factors affecting PEMFC durability [3]. Among the several ionomers (i.e. polymers bearing ionic groups on the side chain) currently available, Perfluoro-Sulfonic Acids (PFSA), thanks to their remarkable chemical resistance given by the strong C–F bonds and ion transport properties under electrochemical operating conditions, are the most promising materials for PEMFC membrane manufacturing [4]. In particular, Aquivion<sup>®</sup> PFSA (Fig. 1) is a perfluorinated ionomer marketed by Solvay Specialty Polymers having the shortest side

chain currently available on the market. This soft difference in its molecular structure imparts to the polymer very peculiar and valuable properties in particular for automotive industry, such as high glass transition temperature (allowing higher operating temperature, reducing the heat to remove and hence the size of the cooling system), high capability to retain water produced at the cathode side, high conductivity and water mobility especially at low humidification level [5]. A higher polymer glass transition temperature as a consequence of enhanced crystalline properties provides increased membrane thermo-stability. This is important during MEA manufacturing using a hot pressing final step and for fuel cell operation at intermediate temperatures [6,7].

Mechanical degradation of the membrane is strongly related to the repetitive swelling/shrinking cycles triggered by changes in humidity and temperature during fuel cell operation especially under automotive conditions. Several physical and chemical modifications have been proposed in order to improve the membrane

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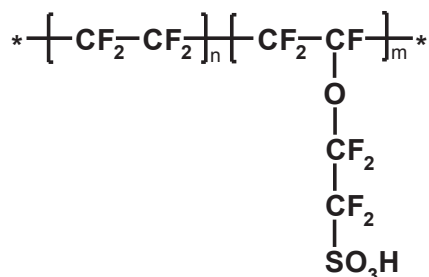


Fig. 1. Chemical structure of Aquivion® PFSA, marketed by Solvay Specialty Polymers.

resistance towards mechanical stress and the most effective are the polymer cross-linking, the incorporation of solid fillers (inorganic oxides or carbon nanotubes) and the membrane reinforcement with an inert matrix such as porous expanded polytetrafluoroethylene (ePTFE), polyimide (PI), polyethylene (PE), polypropylene (PP) or electrospun fibres [8].

Chemical degradation is believed to be initiated by the *in-situ* generation of the highly reactive hydrogen radical ( $\text{H}^*$ ) and the oxygen-centered hydroxy ( $\text{HO}^*$ ) and hydroperoxy ( $\text{HOO}^*$ ) radicals which are able to attack the polymer structure causing the membrane failure [9,10]. Besides the commonly recognized unzipping reaction [11] (currently minimized by removing the undesired carboxylic acid residues), different degradation mechanisms leading to the sulfonic acid [12] or ether group [13] cleavage have been proposed by several authors using different techniques such as Nuclear Magnetic Resonance (NMR) [14], Electron Spin Resonance (ESR) [15] and  $\mu$ -Raman spectroscopy [16,17].

Recent studies highlighted that the addition of even small amounts of Ce [18,19] or Mn [20] as ion, oxide or metal nanoparticle is extremely effective in reducing the degradation rate of PEMFC membrane induced by the reaction with aggressive radicals. These species are identified as radical scavengers. The protective effect of these transition metals relies on the faster reaction rate they have with radicals than the reaction rate radicals have with the polymer membrane [21]. In this regard, the occurrence of a redox mechanism in the scavenger species (e.g.  $\text{Ce}^{4+} + 1\text{e}^- \rightleftharpoons \text{Ce}^{3+}$ ) with potentials matching those of peroxy radicals can influence the capability to mitigate the chemical degradation [22–24].

Even if radical scavengers are added in small amount (few molar percent with respect the  $-\text{SO}_3\text{H}$  group) and thus there is no a dramatic effect on membrane conductivity, some drop in PEMFC electrochemical performance is expected. Moreover, being a fuel cell an open system, radical scavenger leaching can result in electrocatalyst poisoning and shortening of the expected membrane lifetime. In this regard, it is necessary to immobilize the scavenger inside the membrane to avoid dissolution during operation.

In this paper, we present the synthesis and characterization of a novel silica-supported cerium-based radical scavenger bearing sulfonic acid functionalities and its introduction in ePTFE reinforced membranes (called R79-02S) prepared starting from suitable Aquivion® PFSA dispersions. These membranes showed much longer lifetime in Accelerated Stress Tests (AST) and reduced fluoride release in Fenton's tests than the radical scavenger-free congeners without any loss in electrochemical performance.

## 2. Experimental

### 2.1. Preparation and physico-chemical characterization of Ce-based scavenger supported on sulfonated silica

Ce-oxide scavenger supported on sulfonated silica was synthesized in-house. A simple wet impregnation technique was employed.

In a closed vessel  $\text{SiO}_2$  (EH5 from Cabot),  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  and  $(\text{NH}_4)_2\text{SO}_3 \cdot \text{H}_2\text{O}$  were suspended in water. The reactant ratio was silica:Ce-salt: $(\text{NH}_4)_2\text{SO}_3 \cdot \text{H}_2\text{O} = 8:1.5:0.5$ . The slurry was stirred at  $80^\circ\text{C}$  for 16 h until a gel was obtained. This was heated from room temperature to  $150^\circ\text{C}$  in 1 h, maintained constant at  $150^\circ\text{C}$  for 2 h, then heated from  $150^\circ\text{C}$  to  $300^\circ\text{C}$  in 1 h and kept constant at  $300^\circ\text{C}$  for 2 h. The obtained powder was cooled down from  $300^\circ\text{C}$  to room temperature in 1 h. The specific thermal treatment was a key aspect to achieve the desired dispersion properties for Ce species and to anchor properly sulphur moieties on the silica surface. The powder was then washed with 0.5 M  $\text{H}_2\text{SO}_4$  solution at  $70^\circ\text{C}$  until no change in the amount of Ce and S content was determined by X-Ray Fluorescence (XRF) analysis in the solution from the washing treatment. The material was dried under vacuum at  $80^\circ\text{C}$  for 2 h and then ground in a planetary ball mill for 2 h at 200 rpm.

XRF analysis of the catalysts was carried out by a Bruker AXS S4 Explorer spectrometer to determine the elemental composition of the as prepared sample and after washing with diluted sulphuric acid solution. X-ray diffraction (XRD) powder pattern for the material was obtained on a Philips X'Pert X-ray diffractometer using a  $\text{Cu}/\text{K}\alpha$  source operating at 40 kV and 30 mA. Transmission electron microscopy (TEM) analysis was carried out by first dispersing the catalyst powder in isopropyl alcohol. A few drops of this solution were deposited on a carbon film-coated Cu grid and analysed with a FEI CM12 microscope. Scanning Electron Microscopy (SEM) with Energy Dispersive X-Ray (EDX) analysis was carried out by a FEI XL30 SFEG microscope. The instrument was operated at 25 kV and the EDX probe was used to determine the bulk elemental composition of the sample.

### 2.2. Preparation of Aquivion® PFSA dispersion containing Ce scavenger supported on sulfonated silica

Ce scavenger supported on sulfonated silica (1 g) was suspended in 1-propanol (50 g) and the mixture was sonicated in an ultrasonic bath at room temperature for 2 h to obtain a complete dispersion of the solid. The amount of alcoholic dispersion required to obtain the desired radical scavenger loading was added dropwise to a stirred mixture of a commercially available Aquivion® PFSA dispersion D79-25BS (100 g), 1-propanol (36 g) and *N*-ethylpyrrolidinone (15.5 g). After 15 min of stirring at room temperature a clear and transparent mixture was obtained. The same procedure was used for the ionomer solution not containing any scavenger and for that containing Ce nitrate salt.

### 2.3. Preparation of reinforced membranes

Expanded PTFE support (Tetratex 3101 purchased from Donaldson Inc., USA) was mounted on a PTFE circular frame having an internal diameter of 100 mm and then was immersed in the ionomer mixture described above at room temperature for 2 min. The specimen was then heat treated in a vent oven at  $65^\circ\text{C}$  for 1 h, at  $90^\circ\text{C}$  for 1 h and from  $90^\circ\text{C}$  to  $190^\circ\text{C}$  in 1 h. The membranes thus obtained were transparent and colourless indicating the full and homogeneous occlusion of porous support with the ionomer. The thickness of resulting membranes was  $25 \pm 5 \mu\text{m}$ .

### 2.4. Fenton's test

Pre-weighted membrane samples (0.3 g) was added to a plastic vessel equipped with a water cooled condenser and containing a solution of  $\text{H}_2\text{O}_2$  (15% w/w, 200 g),  $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  (0.05 g) and  $\text{H}_2\text{SO}_4$  (0.5 M, 0.025 g). The system was allowed to react for 4 h at a constant temperature of  $75^\circ\text{C}$  then the membrane sample was removed and the solution was cooled-down till room temperature.

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