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# Performance of a PEM water electrolyser combining an IrRu-oxide anode electrocatalyst and a short-side chain Aquivion membrane

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## ABSTRACT

An Ir<sub>0.7</sub>Ru<sub>0.3</sub>Ox nanosized anode electrocatalyst was coupled to an Aquivion short-side chain perfluoro-sulfonic acid membrane (120 μm; EW: 870 g/eq) for operation in a PEM electrolyser. A conventional carbon supported Pt catalyst was used as cathode. An excellent performance, of 4 A cm<sup>-2</sup> at 1.9 V at 90 °C, was achieved for this electrolyser configuration in the presence of a moderate noble metal loading (1.5 mg cm<sup>-2</sup> Ir + Ru; 0.5 mg cm<sup>-2</sup> Pt). The interface of IrRuOx with Aquivion provided a 10% enhancement in performance compared to an equivalent interface with a Nafion membrane of similar thickness but characterized by a larger equivalent weight (EW: 1100 g/eq). The enhanced performance essentially derived from a decrease of polarization resistance. This appeared to be due to better interface characteristics between the electrodes and Aquivion<sup>®</sup> ionomer giving rise to an increased catalyst utilization. Whereas, no significant change in Tafel slope and activation energy was recorded indicating a similar reaction mechanism.

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## Introduction

Several renewable energy plants, such as solar or wind power sources, are characterized by an intermittent behaviour thus requiring the storage of the excess energy that can not be fed into the grid. Among the various technologies of electric energy storage, conversion of excess electrical energy into chemical energy through hydrogen generation by water electrolysis is notable for its high efficiency (80–90%) [1–5]. Proton Exchange Membrane (PEM) water electrolysis technology is a very promising alternative to the more conventional liquid electrolyte alkaline water electrolysis [6–10]. The PEM

electrolysis system allows to achieve higher current densities at higher cell efficiencies and better hydrogen purity than alkaline systems. PEM electrolysis systems can, also, operate in a wide range of load (10–100% of nominal load). The main drawbacks are however associated to the high costs of the titanium bipolar plates, perfluorinated membranes and noble metal electrocatalysts [3,4]. On the other hand, operation at current densities which are typically one order of magnitude larger than alkaline electrolysis (at the same level of efficiency) can provide means to reduce capital costs.

Perfluorosulfonated ion-exchange Nafion<sup>®</sup> membranes are widely used as Solid Polymer Electrolytes (Nafion<sup>®</sup> is a trademark of E.I. du Pont de Nemours for its perfluorosulfonic acid

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polymer membranes). This electrolyte material, which is widely used in fuel cell systems, exhibits excellent electrochemical and mechanical stability, high proton conductivity and low gas permeability. However, despite its wide use, the cost of Nafion<sup>®</sup> is still significantly high. Several perfluorosulfonic acid (PFSA) membranes, alternative to Nafion<sup>®</sup>, with shorter pendant side-chain and higher conductivity have been developed [4,11–14]. Among these polymers, the Aquivion<sup>®</sup> membranes produced by Solvay Specialty Polymers provides good perspectives of cost reduction being obtained through a cost-effective procedure [13]. Moreover, the Aquivion<sup>®</sup> membrane and related ionomer dispersion are characterized by larger crystallinity, higher glass transition temperature and lower equivalent weight than Nafion<sup>®</sup> (870 vs. 1100 g/eq). However, it is appropriate to verify if beside the different conductivity, also different electrocatalytic properties occur at the catalyst–electrolyte interface. In both fuel cell and PEM electrolyzers, the oxygen reaction is the rate determining step. However, different electrocatalysts are used for the oxygen reduction in fuel cell (Pt/C) and oxygen evolution in PEM electrolysis (noble metal oxides). Whereas a similar electrocatalyst i.e. Pt/C is used in fuel cells and PEM electrolysis for the hydrogen process which is relatively fast. The interface between the Aquivion<sup>®</sup> electrolyte and a carbon supported Pt catalyst in fuel cells has been investigated [12,15]. Less attempts have instead been addressed to investigate the interface between mixed oxide catalysts and Aquivion<sup>®</sup> [13,16].

The catalyst providing the highest intrinsic activity for the oxygen evolution reaction (OER) appears to be RuO<sub>2</sub> [3]. However, in acidic media, pure RuO<sub>2</sub> is subjected to erosion during O<sub>2</sub> evolution and loses its activity rapidly. To improve the stability of RuO<sub>2</sub>, inert oxide components like TiO<sub>2</sub>, Ta<sub>2</sub>O<sub>5</sub>, SnO<sub>2</sub> or ZrO<sub>2</sub> are added to form mixed oxides [17–20]. Beside RuO<sub>2</sub>, also IrO<sub>2</sub> is an excellent electrocatalyst for the OER [21–25], IrO<sub>2</sub> is known for being one of the most resistant materials under O<sub>2</sub> evolution conditions in strong acidic environments; yet, its activity is slightly lower than RuO<sub>2</sub> and its cost higher [24]. Mixed oxides, like Ir<sub>x</sub>Ru<sub>1-x</sub>O<sub>2</sub>, appear to provide a good compromise in terms of activity and stability for the OER in acidic electrolyte. However, the IrRuOx electrocatalysts have been essentially validated using Nafion<sup>®</sup> ionomers [26–28]. To our best knowledge, no efforts have been addressed to investigate the electrocatalytic behaviour of the mixed IrRu-oxide in the presence of Aquivion<sup>®</sup> for the oxygen evolution.

The objective of the present study is to investigate the electrochemical properties of the electrolysis cell based on a mixed IrRu-oxide anode electrocatalyst in combination with the Aquivion<sup>®</sup> short side-chain perfluorosulfonic acid (PFSA) membranes and ionomer dispersion.

The electrocatalyst has been evaluated in a single cell polymer electrolyte water electrolyser by linear sweep voltammetry and electrochemical impedance spectroscopy.

A comparison of the electrochemical properties for the electrocatalyst interface with Aquivion<sup>®</sup> and Nafion<sup>®</sup> has been carried out. Ac-impedance spectroscopy has allowed to deconvolute the effects of ohmic drop from the polarization resistance which is essentially affected by the catalyst-ionomer electrolyte interface. The analysis of Tafel slope

and activation energy for the different catalyst ionomer interfaces has allowed to get insights into the reaction mechanism.

## Experimental

### Preparation of Ir<sub>0.7</sub>Ru<sub>0.3</sub>Ox and Pt/C electrocatalysts

Adams fusion method [15,16] was used to prepare an Ir<sub>0.7</sub>Ru<sub>0.3</sub>Ox electrocatalyst. Dry salts containing metal precursors (IrCl<sub>4</sub>·xH<sub>2</sub>O and RuCl<sub>3</sub>·xH<sub>2</sub>O, Strem Chemicals) and NaNO<sub>3</sub> (Aldrich) were treated in a furnace at 500 °C for 10 min. The fused salt-oxide product was cooled down, washed, filtered and dried in an oven at 80 °C for all night. A pre-leaching procedure in HClO<sub>4</sub> (0.1 M, 80 °C, 30 min) was used to completely remove the impurities providing a crystalline nanosized IrRu-oxide.

The hydrogen evolution catalyst of the MEAs was prepared according to a sulphite complex route [29] allowing to obtain 30% Pt/Vulcan XC-72 catalyst.

### Catalyst characterization

XRD was performed on the Ir<sub>0.7</sub>Ru<sub>0.3</sub>Ox catalyst powder by a Philips X-Pert diffractometer equipped with a CuK $\alpha$  radiation source. This diffractometer operated at 40 kV and 20 mA, with a scan rate of 0.5 2 $\theta$  min<sup>-1</sup> and angular resolution of 0.005° 2 $\theta$ . The diffraction patterns were fitted to Joint Committee on Powder Diffraction Standards (JCPDS).

The morphology of the electrocatalyst was investigated by TEM using a FEI CM12 instrument. The specimen was prepared by ultrasonic dispersion of the catalyst in isopropyl alcohol and subsequently depositing a drop of the suspension on a carbon-coated Cu grid.

Scanning Electron Microscopy (SEM) with Energy Dispersive X-Ray (EDX) analysis was carried out by a FEI XL30 SPEG microscope. The instrument was operated at 25 kV and the EDX probe was used to determine the bulk elemental composition of the samples.

### Aquivion<sup>®</sup> preparation

The Aquivion<sup>®</sup> SSC ionomer membrane (E87-12S) with 120  $\mu$ m thickness and EW of 870 g/eq was obtained from a free radical copolymerization of the Sulfonyl Fluoride Vinyl Ether (SFVE) monomer with the tetrafluoroethylene (TFE). The polymer in –SO<sub>2</sub>F form was melt-extruded into films at a temperature higher than the melting temperature of the polymer. The film was then hydrolysed first in hot, strong bases and a subsequently in strong acid, before washing with demi water.

### Membrane-electrode assemblies (MEAs) preparation

Two types of membrane-electrode assemblies were prepared by using Aquivion<sup>®</sup> (E87-12S) or Nafion<sup>®</sup> 115 membranes and ionomers. The ionomer dispersion (D83-06A) used for electrode manufacturing in the Aquivion<sup>®</sup>-based MEA had similar structure/composition of the membrane; it was in acid form and contained as solvents 20% water, 40% 1-Propanol and 40%

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