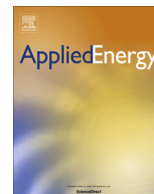




Contents lists available at ScienceDirect

Applied Energy

journal homepage: [www.elsevier.com/locate/apenergy](http://www.elsevier.com/locate/apenergy)

## Enhanced performance and durability of low catalyst loading PEM water electrolyser based on a short-side chain perfluorosulfonic ionomer

Stefania Siracusano<sup>a</sup>, Vincenzo Baglio<sup>a</sup>, Nicholas Van Dijk<sup>b</sup>, Luca Merlo<sup>c</sup>, Antonino Salvatore Aricò<sup>a,\*</sup>

<sup>a</sup> CNR-ITAE, Via Salita S. Lucia sopra Contesse 5, 98126 Messina, Italy

<sup>b</sup> ITM Power (Research) Ltd, Unit H, Sheffield Airport Business Park, Europa Link, Sheffield S9 1XU, UK

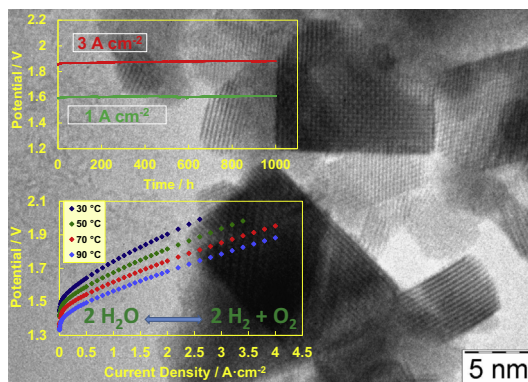
<sup>c</sup> Solvay Specialty Polymers Italy SpA, viale Lombardia, 20, 20021 Bollate, Italy

### HIGHLIGHTS

- Current density  $>3 \text{ A}\cdot\text{cm}^{-2}$  is achieved in electrolysis cells with efficiency  $>80\%$ .
- A 4-fold reduction of noble metal loading is demonstrated in electrolysis cells.
- Degradation rate  $<5 \mu\text{V}/\text{h}$  is achieved in a 1000 h durability test at  $1 \text{ A}\cdot\text{cm}^{-2}$ .
- Degradation associated to a change in Lewis acidity characteristics is observed.

### GRAPHICAL ABSTRACT

Tripling current density ( $>3 \text{ A}\cdot\text{cm}^{-2}$ ) with respect to the state of the art of commercial PEM electrolyser can be achieved also in the presence of a significant reduction, about 4-fold, of the total noble metal loading ( $0.5 \text{ mg}\cdot\text{cm}^{-2}$ ) while achieving high efficiency ( $>80\%$ ) and proper durability.



### ARTICLE INFO

#### Article history:

Received 7 March 2016

Received in revised form 25 August 2016

Accepted 5 September 2016

Available online xxx

#### Keywords:

Hydrogen

PEM water electrolysis

Iridium-ruthenium oxide electrocatalyst

Polymer electrolyte membrane

Low noble metal loading

Short-side chain ionomer

### ABSTRACT

Water electrolysis supplied by renewable energy is the foremost technology for producing “green” hydrogen for fuel cell vehicles. In addition, the ability to rapidly follow an intermittent load makes electrolysis an ideal solution for grid-balancing caused by differences in supply and demand for energy generation and consumption. Membrane-electrode assemblies (MEAs) designed for polymer electrolyte membrane (PEM) water electrolysis, based on a novel short-side chain (SSC) perfluorosulfonic acid (PFSA) membrane, Aquivion<sup>®</sup>, with various cathode and anode noble metal loadings, were investigated in terms of both performance and durability. Utilizing a nanosized  $\text{Ir}_{0.7}\text{Ru}_{0.3}\text{O}_x$  solid solution anode catalyst and a supported Pt/C cathode catalyst, in combination with the Aquivion<sup>®</sup> membrane, gave excellent electrolysis performances exceeding  $3.2 \text{ A}\cdot\text{cm}^{-2}$  at 1.8 V terminal cell voltage ( $\sim 80\%$  efficiency) at  $90^\circ\text{C}$  in the presence of a total catalyst loading of  $1.6 \text{ mg}\cdot\text{cm}^{-2}$ . A very small loss of efficiency, corresponding to 30 mV voltage increase, was recorded at  $3 \text{ A}\cdot\text{cm}^{-2}$  using a total noble metal catalyst loading of less than  $0.5 \text{ mg}\cdot\text{cm}^{-2}$  (compared to the industry standard of  $2 \text{ mg}\cdot\text{cm}^{-2}$ ). Steady-state durability tests, carried out for 1000 h at  $1 \text{ A}\cdot\text{cm}^{-2}$ , showed excellent stability for the MEA with total noble metal catalyst loading of  $1.6 \text{ mg}\cdot\text{cm}^{-2}$  (cell voltage increase  $\sim 5 \mu\text{V}/\text{h}$ ). Moderate degradation rate (cell voltage increase  $\sim 15 \mu\text{V}/\text{h}$ ) was recorded for the low loading  $0.5 \text{ mg}\cdot\text{cm}^{-2}$ , MEA. Similar stability characteristics were observed in durability tests at  $3 \text{ A}\cdot\text{cm}^{-2}$ . These high performance and stability characteristics were attributed to

\* Corresponding author.

E-mail address: [arico@itae.cnr.it](mailto:arico@itae.cnr.it) (A.S. Aricò).

the enhanced proton conductivity and good stability of the novel membrane, the optimized structural properties of the Ir and Ru oxide solid solution and the enrichment of Ir species on the surface for the anodic catalyst.

© 2016 Elsevier Ltd. All rights reserved.

## 1. Introduction

The increasing use of renewable energy sources is helping to reduce the carbon footprint of the electricity grid but their intermittent nature is expected to cause significant energy management issues as the proportion of energy generation by renewables increases. One of the main problems that a future energy system must address is the excess of renewable energy which cannot be transferred to the grid when demand is low and thus must be curtailed by the grid operators. This problem can be conveniently addressed by converting the intermittent surplus of electrical energy into hydrogen and storing the energy chemically. The hydrogen can be directly used as fuel in transportation.

Electrolysis of water using renewable energy sources is one of the most promising chemical processes to produce “green” hydrogen economically with the high purity needed for fuel cell based electric vehicles [1–3].

The three main technologies currently used in the electrolysis sector are differentiated by their electrolyte, namely: alkaline electrolyzers, solid oxide electrolyzers and polymer electrolyte membrane (PEM) electrolyzers [4–12].

The key features of PEM electrolysis are the high current densities at low applied cell voltages, high efficiency (even at low temperatures), excellent dynamic behaviour, rapid start-up/response and high resistance to duty cycles [6,7,13–18]. This makes polymer exchange membrane water electrolysis (PEMWE) ideal for either grid stabilization or direct coupling with renewable energy sources [13–16]. PEM electrolyzers are environmentally friendly systems with an increased level of safety (e.g. there is no recirculation of caustic electrolyte). In addition, these systems have a very high power density by both mass and volume with the capability to operate under high differential pressure. High differential pressure helps reduce compression requirements for the produced hydrogen gas [2,8] while avoiding safety and cost implications associated with high pressure oxygen. These devices can provide the highest degree of hydrogen gas purity ( $\gg 5$  N) with extremely low traces of carbon monoxide and other detrimental contaminants as required by fuel cell-based electric vehicles and specified in the industry standard ISO1487-2 [19].

The principal drawback of PEM electrolysis is the high capital cost due to the PFSA membrane, the high loadings of noble metal electrocatalysts, titanium bipolar plates and expensive coatings [10,20–23]. The industry standard membrane in a PEMWE is Nafion<sup>®</sup>, a perfluorosulfonated ion-exchange ionomer. This membrane has a relatively low resistivity, excellent electrochemical stability with very good mechanical properties. However, its high cost, limited operating temperature range and significant ionic resistance, a direct result of the necessity for relatively high membrane thicknesses (120–170  $\mu\text{m}$ ) to reduce gas cross-over at high pressure, drive the search for alternative membranes. In this work, a short-side chain perfluorosulfonic ionomer, Aquivion<sup>®</sup>, produced by a cost effective procedure [24,25], was used to enhance the performance and reduce the cost of PEM electrolysis. The Aquivion<sup>®</sup> ionomer is characterised by both greater crystallinity and higher glass transition temperature than Nafion<sup>®</sup> [24]. These properties reduce the gas cross-over and improve the thermal stability, respectively [24]. This novel type of membrane can be thinner,

reducing the ohmic losses at high current densities while keeping hydrogen gas cross-over at very low levels.

The other major source of increased voltage (loss of efficiency) is the slow oxygen evolution reaction. The most active and stable catalysts for the oxygen evolution reaction (OER) in PEMWEs are based on noble metal oxides [26–37]. RuO<sub>2</sub> is the most intrinsically active electrocatalyst but it is prone to dissolution if not bound within a solid solution with stable oxides [8,38]. IrO<sub>2</sub> is the catalyst most commonly used for the OER due to its long-term stability compared to pure RuO<sub>2</sub> [26,32,39–46]. The stability of RuO<sub>2</sub> can be greatly enhanced by alloying it with IrO<sub>2</sub> [47–49] and segregation of iridium on the surface which is promoted by specific catalyst annealing procedures.

To ensure widespread commercial uptake of the technology, the costs need to come down without affecting performance or durability. A major obstacle is the need to use the expensive noble metal catalysts mentioned above, Ir and Pt, in large amounts due to the harsh electrochemical environment and the sluggishness of the electroodic processes. As no practical alternatives are envisaged to replace these materials with non-noble metal catalysts, the most appropriate solutions to decrease capital costs are to increase significantly the operating current density and to decrease the noble metal loading to sustainable levels.

The purpose of this work is to develop an enhanced PEM electrolysis device characterised by a significant decrease of the noble metal content and an increase of the current density with respect to the state-of-the art. Membrane-electrode assemblies (MEAs) based on a novel Aquivion<sup>®</sup> membrane, specifically designed for water electrolysis, with enhanced Ir<sub>0.7</sub>Ru<sub>0.3</sub>O<sub>x</sub> and Pt/C catalysts have thus been developed and assessed in this work in terms of performance and durability using low catalyst loadings. In this work, we are showing that tripling the electrolysis current density (3 A·cm<sup>-2</sup>) with respect to a state of the art of commercial PEM electrolyser can be achieved in the presence of a significant reduction, about 4 times, of the total noble metal loading (from 2 to 0.5 mg·cm<sup>-2</sup><sub>MEA</sub>) while maintaining a very high conversion efficiency (>80%). This is made possible in our context by the use of improved electro-catalysts and short-side chain perfluorosulfonic ionomer enhancing the reaction rate at the electrode-electrolyte interface. Good stability of these systems for operation at 3 A·cm<sup>-2</sup> is recorded using durability tests of 1000 h whereas most literature reports deal with endurance tests up to 1 A·cm<sup>-2</sup> [8]. Assessment of stability characteristics at high current densities is of fundamental interest to evaluate the reliability of such systems for real-life operation. To allow for a proper comparison of the results achieved with different systems, a new approach to express the stability factor for assessing the durability of the electrolysis cell, valid in all situations, is here proposed. The degradation mechanisms have been investigated using both *ex-situ* characterizations and *in-situ* methods to analyse surface, structure, chemical and morphological changes and their impact on the electrochemical behaviour. We have identified for the first time that a relevant factor influencing the degradation rate in the PEM water electrolysis is associated to a change of the Lewis acidity characteristics for the Ir and Ru cations. This modifies their ability to promote water chemisorption and dissociation on the anode catalyst surface (the rate determining step of the overall process).

Download English Version:

<https://daneshyari.com/en/article/4916448>

Download Persian Version:

<https://daneshyari.com/article/4916448>

[Daneshyari.com](https://daneshyari.com)