

Investigation of a Short stack PEM Electrolyzer based on a Nanosized IrO₂ Anode Electrocatalyst

A. Di Blasi^{a*}, S. Siracusano^a, V. Baglio^a, N. Briguglio^a, G. Brunaccini^a,
A. Stassi^a, R. Ornelas^b, V. Antonucci^a, A. S. Aricò^a

^aInstitute of Advanced Technologies for Energy “Nicola Giordano”,
National Council of Research - Salita S. Lucia sopra Contesse, 5 - 98126 Messina, Italy

*tel +39.090.624235, fax +39.090.624247, email: diblasi@itae.cnr.it

^bTozzi Renewable Energy SpA, Via Zuccherificio, 10-48010 Mezzano (RA), Italy

ABSTRACT

A short-stack PEM electrolyzer, consisting of 3 cells of 100 cm² geometrical area, was assembled and performed at 75 °C under atmospheric pressure. The MEAs were realized by using nanosized IrO₂, prepared by a sulfite-complex route, and a Pt/Vulcan X-72 electro-catalysts, as anodic and cathodic electrodes, respectively. After preliminary physico-chemical characterizations (XRD, XRF and TEM) of the IrO₂ catalyst, the short-stack performance was investigated by polarization, impedance spectroscopy and chrono-amperometric measurements. The amount of H₂ produced was 80 l·h⁻¹@ 60 A under 330 W of applied electrical power. The stack electrical efficiency at 60 A and 75 °C was 70 and 81% with respect to the low and high heating value of hydrogen, respectively.

Keywords: PEM electrolyzer, Stack, Hydrogen production, water electrolysis, IrO₂ catalyst, Oxygen evolution reaction.

1 INTRODUCTION

Hydrogen is a promising energy carrier that can be produced by different technologies such as reforming of hydrocarbons including natural gas, liquefied petroleum gas, gasoline, etc., gasification of coal and biomass, electrolysis of water using nuclear, fossil or renewable energy sources, photo electrochemical/photo catalytic splitting of water, thermolysis and thermo-chemical cycles [1-2]. Among these, water electrolysis is a well-established technology and one of the most widely used methods for producing high purity hydrogen. Several processes and devices are currently studied for water electrolysis such as the established alkaline systems, high temperature solid oxide electrolyte and proton exchange membrane-based electrolyzers (PEM). The PEM serves as a solid polymer electrolyte for proton conduction and also as a separator for the gases. Water electrolysis in a proton exchange membrane device is characterized by high efficiencies and suitable current density even at low temperatures. Electrolysis systems based on PEMs have a number of advantages in comparison to the traditional alkaline

electrolyzers, such as ecological cleanliness, considerably smaller mass–volume characteristics and, essentially, a high degree of gases purity. The main disadvantage of PEM electrolysis is the high cost, which is mainly due to the use of noble metal catalysts, perfluorinated membranes etc. The high anode overpotential is the limiting factor for the whole process and, together with the large reversible potential, it mainly contributes to the energy supply necessary to run the PEM electrolyzer. It is therefore important to find an optimal oxygen-evolution electro-catalyst in order to minimize the energy loss. One of the main disadvantages of elemental metals like Pt is, beside the modest specific activity for oxygen evolution, their easy electrochemical sintering at high operating potentials. Several investigations have shown that noble metal oxides, particularly Rutile-type oxides like RuO₂, IrO₂ are considerably better as oxygen-evolution electrodes than the corresponding metals as well as other noble-metals [3-4]. Some of these metal oxides offer high activity, appropriate long-term stability and small efficiency losses due to corrosion or poisoning [5]. One of the main drawbacks of several IrO₂ preparation methods is the presence of chlorine contaminants as residues of chloride-based precursors. In this work, a nanosized IrO₂ anode catalyst for water electrolysis was prepared by using a sulfite-complex route. To our best knowledge, no previous attempts have been made to use sulfur-based precursors for preparation of IrO₂ electrocatalysts for oxygen evolution in a water electrolyzer as well as for other electrochemical purposes. Instead, they have been widely used for preparation of Pt-based fuel cell catalysts [6-7]. This catalysts was used at the anode of a three-cell stack.

2 EXPERIMENTAL

An IrO₂ electrocatalyst was synthesized through the sulfite-complex route. IrCl₄·xH₂O (STREM Chemicals, Inc.) was used to prepare the Na₆Ir(SO₃)₄ precursor. In this process, all chlorides were replaced by sulfite anions in the Ir-complex. Iridium tetrachloride was dissolved in distilled water and the pH of the solution was adjusted to 7 by adding Na₂CO₃ (Aldrich). Subsequently, NaHSO₃ (Aldrich)

was added to the solution to obtain a precipitate of $\text{Na}_6\text{Ir}(\text{SO}_3)_4$, which was filtered, washed with distilled water up to a complete disappearance of chloride residues as confirmed by X-ray fluorescence analysis. The precipitate was dried in an oven at 80 °C. The Ir-sulfite complex was suspended under stirring in distilled water and then decomposed by adding drop-wise a 40% H_2O_2 solution (Carlo Erba) at a temperature of 80 °C, which resulted in a vigorous gas evolution. The colloidal IrO_x was filtered, washed with distilled water, and dried in an oven at 80 °C. The resulting amorphous dry powder was subjected to a thermal analysis, in order to individuate a proper thermal treatment. Accordingly, the IrO_x amorphous catalyst was calcined in air at 400°C for 1 h, using a heating ramp of 5 °C min^{-1} . The resulting powder was characterized by X-ray diffraction to determine the crystallographic structure. Catalyst morphology was investigated by Transmission Electron Microscopy (TEM) using a Philips CM12 instrument. X-ray fluorescence analysis (XRF) was carried out by a Bruker AXS S4 Explorer spectrometer operating at a power of 1 kW and equipped with a Rh X-ray source, a LiF 220 crystal analyzer and a 0.12° divergence collimator. XRD was performed on the dry catalyst powder by a Philips X-Pert diffractometer that used $\text{CuK}\alpha$ as radiation source. This diffractometer operated at 40 kV and 20 mA, with a scan rate of 0.5 2θ min^{-1} and angular resolution of 0.005° 2θ . The diffraction pattern was fitted to Joint Committee on Powder Diffraction Standards (JCPDS).

A Nafion 115 (Ion Power) membrane was used as the solid polymer electrolyte. The IrO_2 oxygen evolution catalyst was directly deposited onto one side of the Nafion 115 by a spray-coating technique. Inks were composed of aqueous dispersions of catalyst, deionized water, Nafion solution (5% Aldrich) and Ethanol (Carlo Erba); the anode catalyst loading was 3 mg cm^{-2} . A Ti mesh (Franco Corradi, Italy) was used as backing layer. A commercial 30% Pt/Vulcan XC-72 (E-TEK, PEMEAS, Boston, USA) was used as the catalyst for the H_2 evolution. The cathode electrode was prepared by directly mixing in an ultrasonic bath a suspension of Nafion ionomer in water with the catalyst powder. The obtained cathode paste was spread on carbon cloth backings (GDL ELAT from E-TEK) with a Pt loading of 0.6 mg cm^{-2} . The ionomer content in both electrodes was 33 wt.% in the catalytic layer after drying.

The active area of each MEA was 100 cm^2 . MEAs were assembled in a short stack of 3 cells connected in series by tightening at 7 N·m using a dynamometric wrench. A squared geometry and a design used in fuel cell applications were selected for this stack instead of the circular design which has been widely adopted for PEM electrolyzers [8]. The stack hardware, including end-plates and bipolar plates, was supplied by DANA Corp.. Bipolar plates were of stainless steel 904L - 1.4539. This material was preferred due to its high resilience to electrochemical corrosion in acidic environment.

3 RESULTS AND DISCUSSION

3.1 Physico-chemical characterization of the anode catalyst

Figure 1a shows the XRD patterns of the powder calcined at 400°C / 1 h and the amorphous IrO_x . The sample was characterized by the presence of broadened peaks indicating the occurrence of nanosized particles and possibly also an underlying amorphous matrix by comparison with the colloidal IrO_x pattern. The diffraction peaks in the calcined sample were assigned to a crystalline IrO_2 phase with a tetragonal structure. The presence of nanosized crystalline particles makes the IrO_2 treated at 400°C appropriate for the oxygen evolution reaction both in terms of specific activity (crystalline structure) and surface area. To study the morphology of the catalyst, a TEM analysis was carried out on the IrO_2 powder calcined at 400°C (Fig. 1b). The catalyst showed the presence of large agglomerates. Each of these agglomerates consisted of very small and homogeneously distributed crystalline domains probably embedded in an amorphous matrix. The inset shows the crystalline lattice of primary IrO_2 particles. The lattice lines for each primary particle were used to determine the size of the crystalline domains that was about 2.9 nm. Thus, the nucleation of nanosized IrO_2 crystals in the amorphous matrix appears favoured with respect to the typical particle growth occurring during a thermal sintering. Probably, this phenomenon is promoted by the presence of sulfur impurities, due to the Ir-precursor used in this preparation procedure.

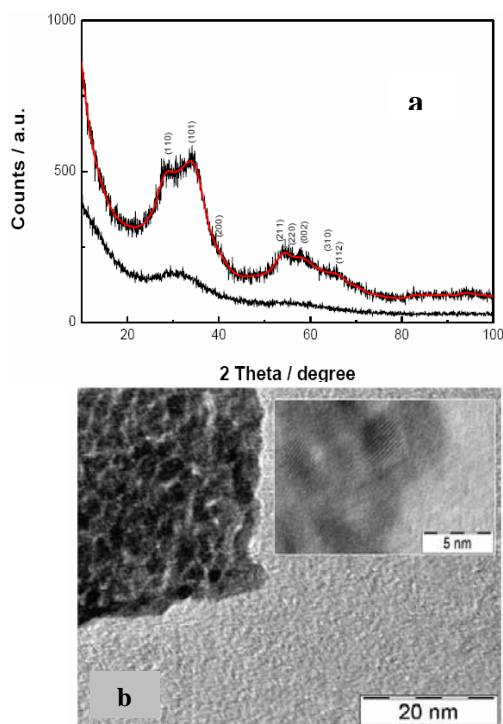


Figure 1: a) X-Ray diffraction patterns of colloidal IrO_2 (bottom) and IrO_2 powder calcined at 400°C (top); b) TEM Micrographs of IrO_2 catalyst calcined at 400°C ; (JCPDS card, IrO_2 15-870 P 42/nm).

3.2 Electrochemical characterization in a short stack

A short stack consisting of three cells connected in series based on large area (100 cm^2) MEAs was investigated (Fig. 2). A commercial stainless steel-based stack hardware for fuel cell systems was adapted for the electrolysis process. Special stainless steel bipolar plates were selected due to the high resistance to water and electrochemical corrosion. Ti mesh current collectors were used as backing layers between the electrodes and bipolar plates. Yet, a fine tuning of the current collector thickness was not possible due to the limited choice of Ti meshes. An appropriate matching of the thickness of current collectors and gaskets is necessary to reduce contact resistances. An optimum temperature of 75°C , compatible with the system auxiliaries, was selected to maintain a constant temperature through the stack during operation.

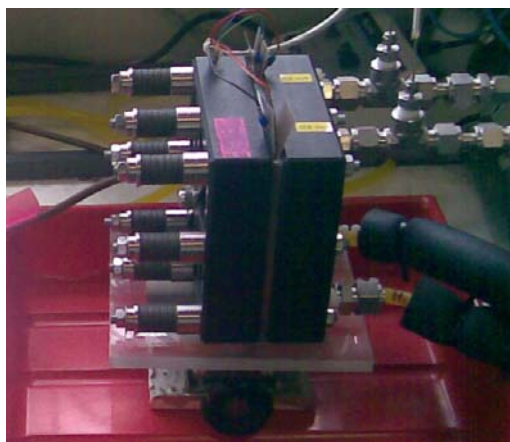


Figure 2: SPE stack electrolyzer under operation

Polarization curves for stack and cells were carried out in the galvanostatic mode by recording the respective terminal voltages. Fig. 4a and b shows the polarization curves for the entire stack and each cell. The current density of each cell was normalized by the electrode area (100 cm^2). The stack showed an onset potential of 4.15 V for water splitting and a terminal voltage of 5.3 V at 60 A (Fig. 3a). By comparing the behaviour of the three cells (Fig. 3b), it was clearly observed that the cell 1 and 3 close to the end-plates performed better than the central cell 2. However, even for the best cells, the recorded terminal voltage at 0.6 A cm^{-2} was about 150 mV larger than that recorded for the small single cell. The different cell behaviour can be clearly understood by analyzing the results of the ac-impedance spectra. The Nyquist plots for each cell in the stack are

reported in Fig. 4. The central cell #2 showed a larger series resistance than the other cells and an increase of the imaginary component $-iZ''$ of the impedance response associated to a capacitive behaviour at high frequencies. Both aspects reflected the occurrence of a large contact resistance between the electrode backing layers and the bipolar plates for this cell.

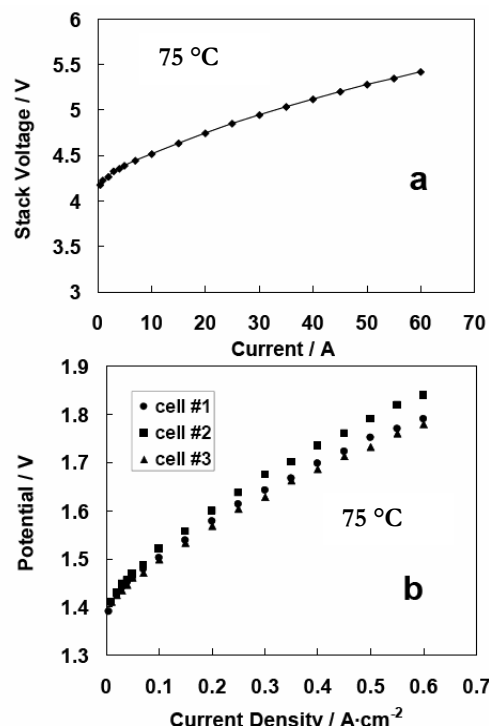


Figure 3: Polarization curves of: a) PEM stack electrolyzer; b) stack cells (active area MEA: 100 cm^2).

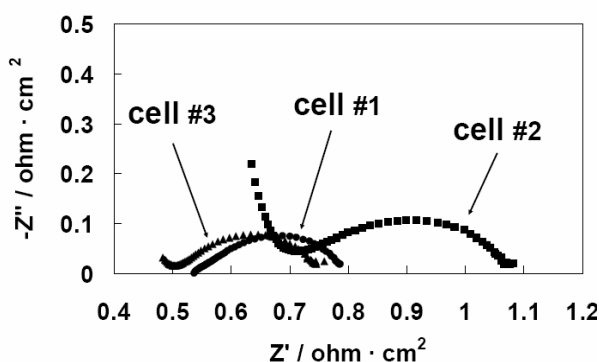


Figure 4: Impedance Spectroscopy at 1.55 V and 75°C for single cells of the PEM stack electrolyzer.

The hydrogen produced by the electrolysis process was measured by a digital flow-meter after proper water removal from the stream. Fig. 5 shows the amount of electrical power consumed in the electrochemical process as a function of the H_2 produced. A power of about 330 W

was supplied to the device to produce 80 l h⁻¹ of hydrogen at room pressure. The electrical efficiency was calculated with reference to both the low (LHV) and high (HHV) heating values of hydrogen (Fig. 6). Several PEM electrolyzer developers as well as manufacturers of commercial alkaline electrolyzers [8-9] refer the electrical efficiency to the HHV since water is used in these devices in the liquid form.

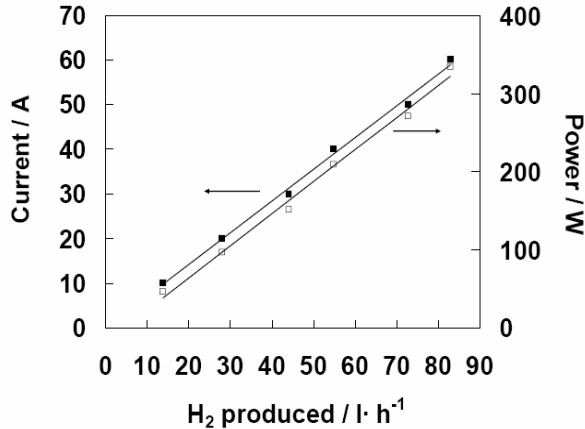


Figure 5: current and supplied electrical power vs. H₂ produced at 75 °C of the PEM stack electrolyzer.

However, the plot in Fig. 6 shows in our case that, at very low current density, the efficiency exceeds 100% if referred to the HHV corresponding to a thermoneutral potential of about 1.48 V at 80 °C ($\Delta H \sim 286 \text{ kJ mol}^{-1}$).

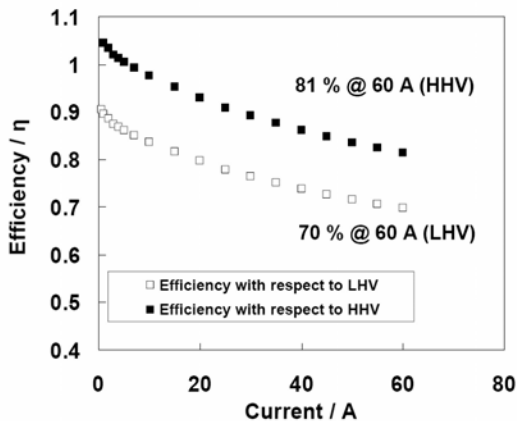


Figure 6: Stack electrical efficiency at 75 °C with respect to LHV and HHV

The onset of hydrogen production in fact occurs at potentials lower than 1.41 V. On the contrary, the electrical efficiency is always lower than 1, even at low current densities, as expected for an irreversible process, if the reversible potential of 1.25 V corresponding to the LHV ($\Delta H \sim 242 \text{ kJ mol}^{-1}$) is considered. The formation of a small amount of water vapour at 80 °C requires to take also under consideration the enthalpy change associated to the water

vaporization. At 60 A, the electrical efficiency vs. LHV was about 70% and 81% vs. HHV for the short stack electrolyzer (Fig. 6). These values are not significantly different from those reported in the literature for circular design-based PEM stack electrolyzers [8].

4 CONCLUSION

A short stack PEM electrolyzer based on a nanosized IrO₂ anode electrocatalyst was investigated. The peculiarity of this catalyst was the presence of 2-3 nm crystalline IrO₂ particles embedded in an amorphous matrix. This characteristic probably reduced the sintering phenomena and represented a good compromise between the specific activity determined by the occurrence of a crystalline structure and a suitable surface area due to a small particle size. The electrochemical diagnostic analysis carried out on the stack indicated that further reduction of the ohmic contact resistance between the bipolar plates and the electrode backing layer is necessary to improve the performance. The achieved efficiencies are comparable to the state of art of PEM electrolyzer based on a circular geometry.

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