

Sensing in real-time the hydrogen generated in the water splitting reaction. Design, set up and measurements of a photo-electrochemical cell utilizing a rotating ring-disc electrode as the counter electrode (P-12H)

L. N. Mendiorez^{1*}, P. Steinberg², G. J. A. A. Soler Illia², P. C. dos Santos Claro³, F. A. Viva^{1**}

¹ Departamento de Física de la Materia Condensada e Instituto de Nanociencia y Nanotecnología, Centro Atómico Constituyente, Comisión Nacional de Energía Atómica (CNEA), Av. General Paz 1499, B1650, San Martín, Buenos Aires, Argentina.

² Instituto de Nanosistemas, Universidad Nacional de General San Martín-CONICET, Av. 25 de Mayo 1021 (B1650KNA), San Martín, Argentina

³ Departamento de Química, Universidad Nacional de La Plata. Calle 47 y 115, 1900, La Plata, Buenos Aires, Argentina.

(*) Pres. author: lnmendiorez@gmail.com

(**) Corresp. author: viva@tandar.cnea.gov.ar

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1. Introduction

The search for non-contaminant energy sources is among the main challenges humanity is facing nowadays [1-2]. Sustainable energy sources, such as photovoltaic and eolic, require storing and transport the energy generated [3]. Among the main choices is the production of hydrogen with clean energy [4].

Since Fujishima and Honda, in 1972, showed the possibility to produce hydrogen by illuminating a TiO₂ sample, the photo-electrolysis of water emerged as an option to the conventional electrolysis [5]. Since then, the study of photoactive materials in photo-electrochemical cells (PEC) has been investigated as an interesting way to directly transform the solar energy into hydrogen and oxygen [6]. The PEC is composed by a photo-anode and/or a photo-cathode capable of absorbing light and generating a potential difference capable of driving the reaction forward.

Studies of catalytic material properties are of vital importance for advancing in their development. One key parameter in the material characterization is to verify and quantify the electrode product [6]. The use of photocurrents to directly quantify the studied reaction is complex as a portion may dissipate as heat. Generally, gas chromatography or mass spectrometers are used for the determination and quantification of the reaction products. This means that a sealed PCE has to be used for the products of the reaction to be stored and measured (figure 1.A).

In the present work, we develop a set up for the direct determination of H₂ without the use of an external equipment. A PEC that allows the placement of a rotating ring disk electrode (RRDE) was designed. The detection of small amounts of hydrogen in the counter electrode (CE) is possible through the measurement of currents in the order of μA (figure 1.B). It was confirmed that what is being registered is hydrogen with the use of a differential electrochemical mass spectrometer (DEMS) accumulating the produced gas for 1 h.

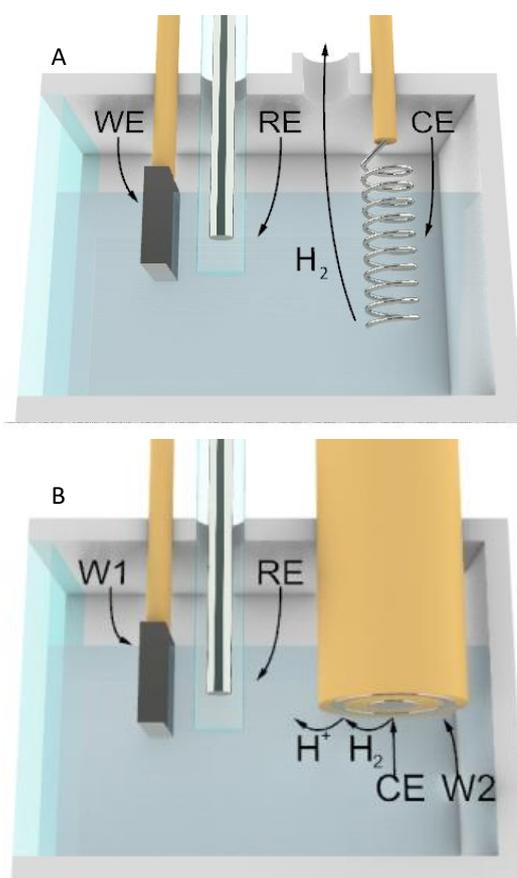


Fig. 1. Cell schematic. A) Typical PEC configuration. B) 4 electrode PEC configuration utilizing the rotating ring-disc electrode. WE, W1, W2 are working electrodes, RE is the reference electrode, CE is the counter electrode.

2. Experimental

2.1 Photo-electrochemical cell Design

The photo-electrochemical cell was made of polypropylene and acrylic, using a CNC machine. The cell included a quartz window for the illumination of the samples. A rotating ring disc electrode was employed as the counter electrode. Moreover, the design contemplated the absence of separated compartments or the need of a membrane to avoid the mixing between the electrode products (figure 1.B).

2.2 Preparation of TiO₂ nanotube

The preparation of TiO₂ nanotubes (NT) over Ti foils (grade 2) were made by electrochemical anodization. An in house vertical electrochemical cell, made from Teflon, was used for exposing a delimited area of the Ti foil. A Pt spring was used as a counter electrode. Either, a potential of 30 V or 100 V was applied between the Ti foil (anode) and the Pt spring (cathode) with a power supply. Before anodization, the Ti foil was cleaned with acetone, methanol and Mili-Q water in an ultrasonic bath for 15 min each, respectively.

A two-step anodization was used. The first one was carried out for 1 hs in a 1 M H₂O and 0.1 M NH₄F solution in ethylene glycol. Afterwards, the nanotubes were removed with scotch tape, followed by a second anodization for 2 h. After the anodization steps, the nanotubes were washed with ethanol and calcined in an oven at 450 °C for 2:30 h.

2.3 Electrochemical measurements

The electrochemical and photo-electrochemical measurements were carried out in the designed cell using 0.1 M Na₂SO₄ as electrolyte. A four electrodes configuration was used for the experiments with an Ag/AgCl as a reference electrode (RE). For the photo-electrochemical measurements, the photo-anode (NT) was set as the working electrode 1 (W1), the ring electrode (Pt) as the working electrode 2 (W2), and the disc electrode (Pt) as the counter electrode (CE) (Figure 1.B). Prior to the photo measurements, a calibration of the rotating ring-disc electrode was carried out, where the disc electrode was set as W1, the ring electrode as W2, and a Pt wire as the CE. For the photo measurements, a Xenon lamp calibrated for AM 1.5 was used.

2.3.1 Counter electrode product identification

In order to employ the W2 current for the quantification of the H₂ produced, a mass spectrometer was used to identify the gaseous product. A sealed cell filled with N₂ with an exit port connected to a differential electrochemical mass spectrometer (DEMS) was employed. A chronoamperometry at 0.5 V vs Ag/AgCl with the photo anode of NT being illuminated was carried out for the period of 1 h. As the amount of gas produces is considerably small, a long accumulation time was used to assure the detection by the DEMS.

3. Results

3.1 Determination of the rotating electrode speed

Chronoamperometries at 0.5 V vs Ag/AgCl with and without illumination at the NT are shown at figure 2.A. The current of the rotating ring electrode at a fixed potential of 0.4 V vs Ag/AgCl at different RPM is shown in figure 2.B.

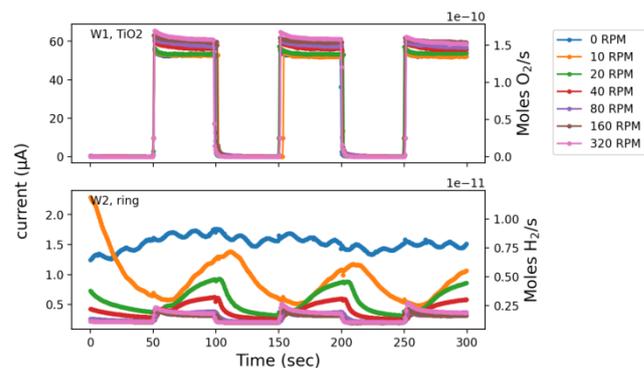


Fig. 2.A. Upper, chronoamperometry of the W1 (TiO₂) at 0.5 V vs Ag/AgCl in 0.1 M Na₂SO₄, with and without illumination. B. Lower, chronoamperometry of the W2 (ring) at 0.4 V vs Ag/AgCl at different rotation speeds.

3.2 Collection efficiency (N) for the H₂ evolution

The relationship of the ring and disk current was analyzed. Chronopotentiometry measurements were carried out in the disk from 10 µA to 100 µA and the current at the ring was measured at a fixed potential of 0.4 V vs Ag/AgCl.

In figure 3 the current of the disk vs the current of the ring employed to determine the collection efficiency from the slope is shown.

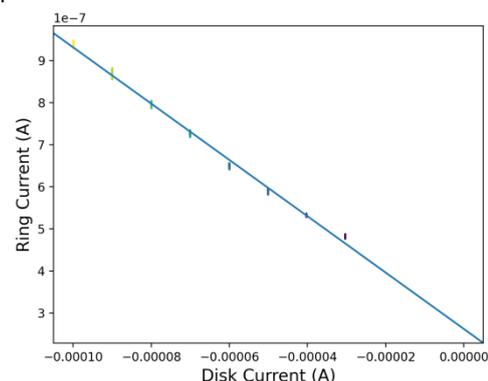


Fig. 3. Ring current vs disk current for a chronoamperometry at 0.4V vs Ag/AgCl, at the ring, at 200 RPM.

3.3 Mass spectrometer determination

The chronoamperometry at 0.5 V vs Ag/AgCl under illumination to accumulate H₂ for the mass spectrometer analysis is shown in figure 4.A. Figure 4.B shows the signal obtained for the gas sample injected in the mass spectrometer corresponding to the m/z 2 (H₂).

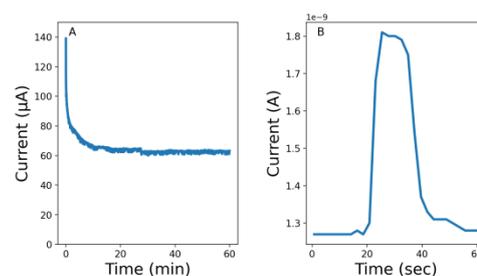


Fig. 4. A. Chronoamperometry of a NT at 0.5 V vs Ag/AgCl under illumination. B. Response of the mass spectrometer for the m/z 2 after accumulating for 1 h.

3.4 Photo-electrochemical measurements utilizing the N

A chronoamperometry with and without illumination was used to validate the value of N and compare the currents of the NT with the current of the ring Pt electrode (figure 5).

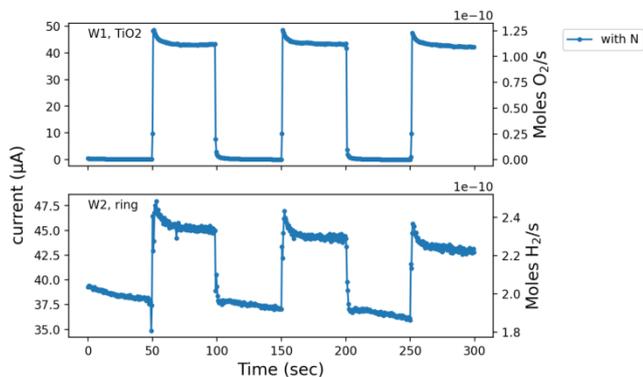


Fig. 5. Upper, chronoamperometry of the W1 (TiO₂) at 0.5 V vs Ag/AgCl in 0.1 M Na₂SO₄, with and without illumination. Lower, chronoamperometry of the W2 (ring) at 0.4 V vs Ag/AgCl at 200 RPM applying the N obtained.

4. Discussion

For this work, a non-typical 4 electrodes arrangement was used to quantify the photo electrolysis product at the cathode.

The experimental conditions, namely applied potential and RPM, for the rotating ring electrode were determined. For the potential selection, cyclic voltammetry was carried out and a potential more positive than the H⁺ generation peak was chosen to ensure all H₂ that reach the ring was oxidized. The potential selected was 0.4 V vs Ag/AgCl. For the RPM selection, chronoamperometry with and without illumination was carried out at different rotation speeds (figure 2). The RPM was chosen so that the measurement in the ring electrode corresponds to the reaction occurring at the NT.

The mass spectrometer showed that the generated gas in the CE (disk) was only H₂ (Figure 4). This indicated that there is no mixing between the electrode products or the presence of any other possible side reaction.

The N of the rotating ring-disc electrode for the evolution of H₂ was calculated. The collection efficiency was obtained from the relationship between the ring and disk currents (equation 1).

$$N = \frac{-I_R}{I_D} \quad (1)$$

Figure 3 shows the measurements carried out for the N value calculation from the rotating ring-disc electrode for the H₂ reaction. The N value obtained was 0.007. The fact that N is so low ensure that current flowing at the CE is, predominantly, produced by the W1.

Photo-electrochemical experiments were carried out for several NT samples. With the use of the set up and the designed PEC, the sensing of the electrode currents allowed us to follow, in real-time, the evolution of H₂ (figure 5). The current value calculated for the CE (disk), where the

H₂ is formed, by using the W2 current is in agreement with the current measured for W1. This result confirms that the current measured in W2 can be directly related to the H₂ produced at the CE.

5. Conclusions

A 4 electrodes photo-electrochemical cell was designed for the measurement of H₂ in real-time. The generation of H₂ in the CE was corroborated with a mass spectrometer. Furthermore, the current of the CE was verified to correlate with the current for the W1 arising from the generation of O₂. Illumination of a NT sample at 0.5 V vs Ag/AgCl produced 2.3 x 10⁻¹⁰ moles/sec of H₂ corresponding to a current of 45 µA.

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