A photoelectrochemical cell for the study of the photosensitive materials used in solar-hydrogen energy

P Ardelean¹, E Indrea¹, T D Silipas¹, C Ardelean², Gh Mihaiescu¹, Ramona-Crina Suciu¹, Simina Virginia Dreve¹, Z Moldovan¹, Marcela Corina Rosu¹

¹National Institute for Research and Development of Isotopic and Molecular Technologies, 65-103 Donath, 400293 Cluj-Napoca, Romania

²Technical University of Cluj-Napoca, Department of Automatization and Computers, 26-28 Gheorghe Baritiu, 400027 Cluj-Napoca, Romania

E-mail: petru.ardelean@itim-cj.ro

Abstract. It was built a versatile photoelectrochemical cell devoted to the comparative study of the photosensitive materials used as photoelectrodes in solar-hydrogen production. The experimental arrangement makes possible a relative evaluation of the electrodes properties by the measurement of the electric parameters, giving directly I = f (U) for the cell electric circuit with and without an external electrical bias. It also gives a direct measurement of the volume of the evolved gases, and an on-line analysis of the gases by the coupled gas chromatograph, or of-line, by a mass spectrometer.

1. Introduction

Considerations concerning the emission of greenhouse gases and their influence on the global warming, goes to a conclusion that it is necessary to develop technologies for the generation of new clean sources of energy [1, 2, 3] to supplement and ultimately to replace the fossil fuels. It must be taken into account also the fact that the fossil fuels have not a promising future: 40 years for the oil and about 62 years for the natural gases.

As it seems, hydrogen will replace fossil fuels as energy carrier [4, 5]. The production of hydrogen from the splitting of water, using solar energy, so called solar-hydrogen, is very convenient from both environmental and economic considerations [1, 6]. The solar-hydrogen technologies exhibits some important advantages: the process requires supplies of only solar energy and water, the associated infrastructure is simple and does not have any moving parts, maintenance being minimal, the necessary infrastructure is simple and the process does not cause pollution [1]. The difficulty consists in the development of a special class of new photosensitive materials for an efficient and clean conversion of solar energy.

TiO₂ (titania) is a promising candidate for the development of photoelectrodes for solar-hydrogen production due to its advantages [7, 8, 9]. It is less expensive than other photosensitive materials and titania reserves are abundant. Also TiO₂, unlike others materials, has outstanding resistance to corrosion and photocorrosion in aqueous solutions [1] and this could ensure that its functional properties remain unchanged over a very large period of time.
The main disadvantage of this material consists in the necessity of increasing its low value of energy conversion efficiency from ~ 0.5% obtained initially [7] to an acceptable value (around 10%). This low value is due to its low photosensitivity given by the relatively large band gap ~3eV [9] and consequently its poor absorption of visible light [1, 10]. So, its functional properties must be optimized in order to modify the band gap at a convenient value between 1.8 ÷ 2.2 eV [1].

In this direction intensive research, in many laboratories, is dedicated to increase its visible light sensitivity [9, 10]. That is because it is considered that the performance electrodes are expected to be obtained by the modification of TiO$_2$ rather than on the development of new valence semiconductors [1]. Encouraging results [11, 12] were obtained, but also some skepticism [1] was reported. However, the incorporation of aliovalent ions [11, 13] results in a reduction of band gap. Also the properties of TiO$_2$ can be modified by varying the defect chemistry (and the related electronic structure) [1, 14].

2. Description

In our laboratory there is an interest for the development of the materials with desired properties in order to be used as higher performance photosensitive materials. Our work on titania is mainly aimed at the optimizations of its functional properties. In this purpose, it was built a photoelectrochemical cell provided with some facilities and included in an experimental arrangement in order to allow a comparative study of TiO$_2$ and TiO$_2$ based materials properties.

The experimental arrangement figure 1, include: the photoelectrochemical cell F, a gas chromatograph GC, a variable DC stabilized power supply P, a digital voltmeter V and a digital miliamperimeter M, and a light source S.

![Figure 1](image1.png)

**Figure 1.** The experimental arrangement of the photoelectrochemical cell. F the photoelectrochemical cell; GC the gas chromatograph; P the power supply; K the three way valve system; S the light source; I the quartz window; T the Nafion proton transfer membrane; R electrolyte reservoirs; CT calibrated tubes.

![Figure 2](image2.png)

**Figure 2.** The photoelectrochemical cell.

The parts of the photoelectrochemical cell (figures 1 and 2) are given in the following part. The frame, is a two-compartment Plexiglas reactor provided with a quartz window I, and having a Nafion proton transfer membrane T on the separation wall. The separation of the cell in two compartments allows to use of two different electrolytes in the performed studies and this make possible to provide a small chemical bias assisting the studied processes. The cover of the frame
is provided with two calibrated tubes with stopcocks CT on the lines of the collected gases, which allows the measurement of the volume of the produced gases. The cover is also provided with two electrolyte reservoirs R to supply the content of the two compartments cell as the electrolyte is consumed in the cleavage process (and to maintain the electrolyte levels in the calibrated tubes), and with two electric feedthroughs connected to the photoanode and respectively to the photocathode which allows to connect the electrodes (the anode and the cathode) to the external electrical circuit (figure 1). The photoanode and the photocathode could be easily fixed and taken down from the supports, and the supports positions could be adjusted by screwdrivers. The measurement of the electrical parameters of the circuit could give important data concerning the electrode material properties. As it can be observed from figure 1, there are two ways to perform the measurements of the electrical parameters. It is known that, without a bias supply, the efficiency of the cell is very low. So we can use in performing the measurements an external variable DC electrical supply (position „up“ of the double electric switcher SW) and we can use only one electrolyte. We can use also two different electrolytes in the two compartments (NaOH at anode and H₂SO₄ at cathode) and we have an „internal“ chemical bias instead an external one (position „down“). The measurement of the electrical parameters of the circuit could be visualized on PC as curves I = f(U), (I being the measured current intensity in mA and U the value of the voltage in V), or as tables, and they are useful for appreciating the parameters of electrodes materials. The exit of the two calibrated tubes for gas collection is connected by a three way valve system K to the gas chromatograph or, to a sampling ampoule. In this way the gas could be analyzed directly by the chromatograph or could be sampled and analyzed off-line by a mass spectrometer.

In order to homogenize the electrolyte each compartment of the cell is provided with a magnetic core glass stirrer. The radiation is generated by a homemade light source S which is provided with a mercury-arc lamp and it can give a beam intensity which can be regulated (by distance modification) between 75 mW/cm² and 1 mW/cm².

3. Experimental results and discussions

In figure 3 it is given the current-voltage characteristics obtained with an external electrical supply. The anode is an ITO (In₂O₃:SnO₂) substrate with deposited nanocristaline TiO₂ based electrode, synthesized via wet-chemical techniques, by screen-printing, and the cathode was a Pt plane spiral wire. In both compartments electrolyte with pH = 13.5 was used. The curves a and b are obtained with and respectively without light beam. As it can be observed, the influence of the light beam becomes more important as U increases. So, the difference between the I values with and respectively without light beam, starts from 5% at 4 V and it increases at 20% at 8 V remaining afterwards at a value over 10%. After the system reaches the equilibrium (~ 40 minutes) the correspondence between the intensity of the current and the production of hydrogen is in close relationship. For example at U = 8.5 V for an current intensity of 38.9mA, which correspond to 2.43 x 10¹⁷ electrons/s, will be expected a number of 1.216 x 10¹⁷ H₂ molecules/s (0.272 cm³/min). As the measured hydrogen production rate was 0.24 cm³/minute, it results that about 88% of hydrogen molecules are detected. The small discrepancy is due probably to some gas leakage. A chromatogram of the gas obtained from the cathode compartment is given in figure 4. Argon was used as carrier gas. It is observed that O₂ and N₂ are also present, from residual air, and theirs concentrations go lower in time. In the mass spectrum of a sample taken from the evolved gas in the cathode compartment, an isotope effect was observed. As it is known, in the water splitting, an isotope effect takes place. So, the H₂O molecules are easier split than HDO. In this case the value of HD/H₂ observed in mass spectra is ~70 ppm, HDO/H₂O being as it knows ~150 ppm in the natural water, the isotope effect being more pronounced that it was expected.

In the case of working with internal chemical bias (position down of the electric switcher S), the observed open circuit voltage was 0.7 V and the short circuit current was 11 mA/cm².
active area of the electrode was 6.25 cm². The concentration of the electrolytes was 1 mol/l NaOH in the anode compartment and 1 mol/l H₂SO₄ in the cathode compartment. The measurements were performed after the system reaches equilibrium (~ 40 min). The work is in progress.

Figure 3. The current-voltage characteristics with external electrical supply: a with the light beam, b without the light beam.

Figure 4. The chromatogram of the gas obtained from the cathode compartment.

4. Conclusions
A two-compartment photoelectrochemical cell was constructed and tested with a nanocrystalline titania as anode and a plane spiral Pt wire cathode, devoted to the comparative study of the titania based materials necessary as photoelectrodes. The electrodes supports, permits a facile replacement of the electrodes and position adjustment. The experimental arrangement allows a comparative study of the electric properties of titania based materials under chemical bias or with an external electrical bias as well as a measurement of the volume of the evolved gas and its analysis.

References
[1] Nowotny J, Bak T, Novotny M K and Sheppard L R 2007 Int. J. Hydrogen Energy 32 2609-29
[2] Friedli H, Lotscher H, Oescher H and Siegenthaler U 1996 Nature 324 237-9
[3] Russ M 1994 Series of Umweltechnik (Aachen: Shaker) pp 1-180
[4] Nowotny J and Sheppard L R 2007 Int. J. Hydrogen Energy 32 2607-8
[5] Veziroglu T N 1998 Int. J. Hydrogen Energy 23 1077-8
[6] Veziroglu T N 2008 Int. J. Hydrogen Energy 33 1-2
[7] Fujishima A, Kohayakawa K and Honda K 1975 J. Electrochem. Soc. 122 1487-9
[8] Nozic A J 1975 Nature 257 383-6
[9] Nowotny J, Sorrell C C, Sheppard L R and Bak T 2005 Int. J. Hydrogen Energy 30 521-44
[10] Bak T, Nowotny J, Rekas M and Sorrel C C 2002 J. Hydrogen Energy 27 991-022
[11] Khan S U M, Al-Shahry M and Ingler W B 2002 Science 297 2243-4
[12] Nazeeruddin M K and Gratzel M 2001 J. Photochem. Photobiol. A: Chem. 145 79-86
[13] Nakamura R, Tanaka T and Nakato Y 2004 J. Chem. Phys. B 108 10617-20
[14] Bak T, Nowotny J and Sorrell C C 2003 J. Phys. Chem. Solids 64 1069-87.