

# EFFECT OF pH ON PHOTOVOLTAGE BEHAVIOR OF TiO<sub>2</sub> PHOTOANODES

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**Abstract** - An important requirement in a photoelectrochemical cell to water splitting is to reach the photo-voltage required to drive the oxidation and reduction reactions to produce oxygen and hydrogen without any other external energy supply. In this work, it was studied the effect of pH on the photo-voltage of photoelectrochemical cell. Open circuit photo-voltage as a function of aqueous electrolyte pH has been investigated using the TiO<sub>2</sub> photoanode connected with a stainless steel photocathode. The open circuit photo-voltage measurements were made from 1 to 14 pH units, showing a decrease of photo-voltage values with increasing pH.

**Keywords**- Photo-voltage, pH, interface, electrolyte, semiconductor.

## I. INTRODUCTION

Hydrogen is an energy carrier and fuel of high energy density by weight. It may be used in different applications including fuel cells using different kinds of polymeric membranes to generate energy efficiently without pollutant release [1-4]. Hydrogen can be obtained by different mechanisms [5-9], the photodissociation of water process to produce hydrogen and oxygen is a promising and ecologically friendly method of hydrogen generation, that implies an important conversion reaction of radiant energy into chemical free energy. The use of semiconductor electrodes in photoelectrochemical cells for water dissociation allows absorption of energy photons of the electromagnetic spectrum, giving rise to the generation of electron – hole pairs for conducting oxidation and reduction reactions at the electrode-electrolyte interface [10-13]. The first photoelectrochemical experiment was performed in 1839 by Becquerel, who demonstrated that a voltage and an electric current were produced when was illuminated a silver chloride electrode immersed in an electrolytic solution and connected to a counter electrode [14]. The origin of this photovoltaic phenomenon called the "Becquerel effect" was understood until 1954, when Brattain & Garrett launched the modern era of photoelectrochemistry, it became apparent that the Becquerel effect was due to the establishment of a semiconductor-electrolyte junction at the interface [15].

For direct photoelectrochemical decomposition of water to occur, the semiconductor system must generate sufficient voltage upon irradiation to split water, the band-edge potentials at the surfaces must straddle the hydrogen and oxygen redox potentials, the charge transfer from the surface of the semiconductor to the solution must be selective for water splitting rather than corrosion [10]. This is an endoergic reaction, with an increase in Gibbs free energy  $\Delta G_{(H_2O)}^0 = 237.141 \text{ kJ/mol}$  equivalent to 2.46 eV/molecule. So that the water splitting reaction takes place, the threshold energy ( $E_t$ ) should be surpassed.  $E_t = \frac{\Delta G_{(H_2O)}^0}{2N_A}$  that is, 1.23 eV, the energy difference between the Fermi levels for both processes, which correspond to the minimum energy difference that must exist between the band edges of a semiconductor. For a semiconductor to be effective in this process, the lower edge of the conduction band must be located at a more negative position than the reduction potential ( $H_2/H^+$ ), and upper edge of the valence band must be more positive compared to the water oxidation potential ( $H_2O/O_2$ ) [11], [16], [17].

All phenomena associated with photoelectrochemical systems are based on the formation of a semiconductor – electrolyte junction. A thermodynamic equilibrium is established by electronic and ionic exchange processes at the interface, electric charges of opposite sign (electrons, holes) accumulate on both sides creating an electric field. In this process, the pH of the electrolyte solution is a determining factor. According to [18], [19] variation of pH of an electrolyte shift the energy positions of bands of the semiconductor at a rate of 59 meV per unit of pH. All these represent chemical reactions, which are accompanied by the transfer of an electric charge across

the interface; this in aftermath allows finely tuning the driving force of the processes occurring in the system [20].

This paper is concerned with the characteristics of a process of photoelectrochemical water splitting from variations in the pH in the electrolyte solution, in order to determine their effect on the behavior of system to produce hydrogen and the generation of photo-voltage of the photoelectrodes made from TiO<sub>2</sub> (Degussa P25) y TiO<sub>2</sub> nanoparticles synthesized by using of green chemistry process.

## II. EXPERIMENTAL PROCEDURE

### A. Fabrication of TiO<sub>2</sub> photoelectrodes

TiO<sub>2</sub> films were supported on stainless steel 304 substrates (SS 304 – area 5-5 cm<sup>2</sup>) by Doctor Blade technique [21], [22], using commercial TiO<sub>2</sub> nanoparticles (Degussa P25 - consisted of 70% anatase and 30% rutile). Stainless steel substrates were cleaned with soap water, acetone and ethanol for 10 minutes before use to degrease the sheet and ensure adhesion of the film [23]. 0.3 g of TiO<sub>2</sub> were mixed with a 1 ml of solution of water and Acronal (ratio 50% v/v) to ensure proper adhesion of the films on the substrates. The suspension was magnetically stirred and dispersed by ultrasound during 20 minutes before applied onto the surface of the substrate. The thickness of the deposited suspension layer was 0.05 mm (50 μm), the thickness of film was controlled by the amount of deposited suspension and the layer numbers supported, films with the same number of layer were elaborated by repeating the deposition three times accompanied by a step of drying between each layer. The films were dried under ambient conditions and then annealed at 300° C for 30 minutes to remove the solvent.

### B. Procedure in Photoelectrochemical cell

The photoelectrochemical system used in this study involved a TiO<sub>2</sub> photoanode, a stainless steel cathode and aqueous electrolyte. Both electrodes in contact with the same electrolyte formed the photocell. Electrical connection between photoanode and cathode was made using a copper wire without application of any external bias. The dynamic of the PEC during light-on period was measured with a multimeter. The UV light source had a 380 nm wavelength. This source was placed 10 cm away from the photoelectrochemical cell, in front of the working electrode surface (photoelectrode). The experimental procedure involved the measurements of the open-circuit photo-voltage during successive light-on regimens in this experiments the medium pH was varied to determinate the dependence of E<sub>oc</sub> for TiO<sub>2</sub> electrodes on pH of the electrolyte solution. The open - circuit was measured using the two-electrode method; sulfuric acid and sodium hydroxide were used to adjust the solution values in the range from 1 to 14.

## III. RESULTS

According to figure 1, the photo-voltage generated into the cell using the TiO<sub>2</sub> photoanode decreased as the electrolyte solution become more alkaline, in this case, the maximal value for the photo-voltage in the PEC was 50 mV by using an acid electrolyte with pH 1. Comparing the results obtained in this investigation to the results obtained by [24], it is observed a similar behavior regarding electrolyte pH effect over the photo-voltage, where although the photo-voltage values are different, it was reported a reduction of photo-voltage values with the pH increase. The dependence of photo-voltage upon pH electrolyte solution is associated with the semiconductor/electrolyte interface, the band edges positions of TiO<sub>2</sub> and most of oxide semiconductors change with solution pH, according its Nerstian pH dependence [25],[26]. With the increase of pH electrolyte, the band edges of conduction and valence band shift to higher energies on the energy scale, this is, to more cathodic potentials on the electrode potential scale, by around 59 mV per pH unit [25], [27].

The photo-voltage obtained did not reach the maximum values that until now have been reported for TiO<sub>2</sub> photoanodes into a PEC water splitting without an external bias, 0.7 – 0.9 V [28]. According to [11] the major source of energy loss is associated with ohmic resistances of the external and internal circuits in the PEC, including electrodes, electrolyte, electrical leads, electrical connections, and measurement and control equipment. In this case, the concentration of electrolyte solution was in a too low concentration, some references establish that the minimal resistances with Cl<sup>-</sup> are between 3 and 4 M concentrations [11], The behavior of the photo-voltage is an indicative of the process for separation and recombination of charge carriers in the semiconductor [29], so low values on photo-voltage are an indicative of recombination process into de bulk of the semiconductor.

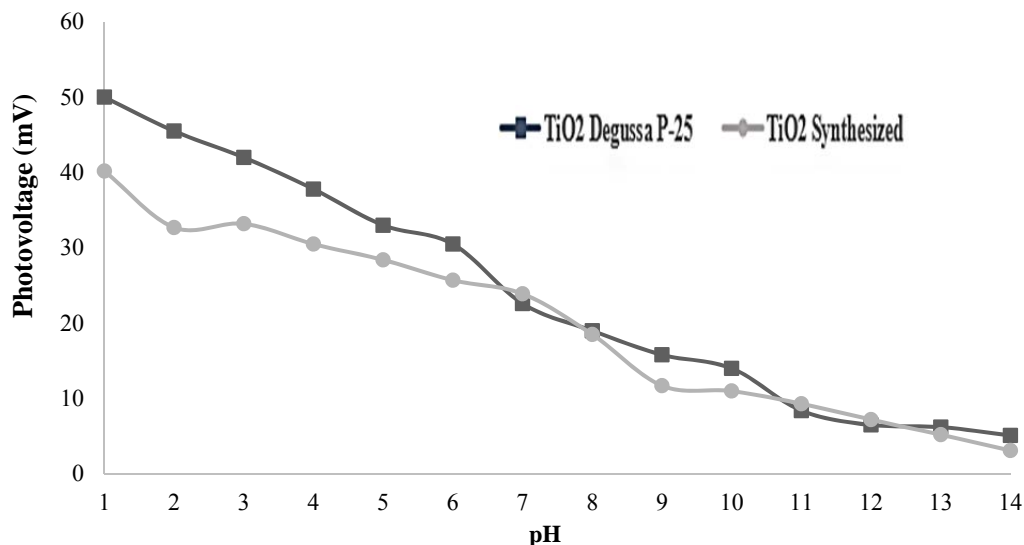


Figure 1. Photo-voltage behavior according electrolyte pH using TiO<sub>2</sub> photoanodes

#### IV. CONCLUSION

The results obtained in this work show that the maximum photo-voltage value in the photoelectrochemical cell using TiO<sub>2</sub> photoanode and without bias applied is 50mV, this photo-voltage reached is far below that the required voltage to water splitting. These results are associated with the interface semiconductor film – electrolyte behavior, and the band edge positions.

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