

Physicochemical Characterization of Photoelectrodes of Ti/TiO₂ Prepared by Thermal Oxidation of Titanium

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Abstract

The preparation and study of supported TiO₂ for photocatalytic application in solar cell devices is a relevant research field. Thin films of TiO₂ prepared on Ti by thermal oxidation in a wide range of temperatures (450°C - 900°C) were characterized by electrochemical impedance spectroscopy, potentiometry and amperometry. This material presents photoelectrochemical activity, which depends dramatically of the oxidation temperature and the exposition time at the studied temperatures. The *flatband* potential as well as the donor density and the resistance to the charge transfer were measured. All these parameters are temperature dependent, and the optimal values are observed on the photoelectrodes prepared at 750°C. This result is consistent with the photochemical response reported in the literature for thin films of Ti/TiO₂ prepared under similar conditions.

Keywords

Ti/TiO₂ Photoelectrodes, *Flatband* Potential, Mott-Schottky and Nyquist Diagrams

1. Introduction

Ti/TiO₂ photoelectrode becomes one of the relevant materials in studies related to the application towards clean energy using the solar radiation [1]. The photochemical activity of this material is dramatically dependent on the method applied in the construction of the photoelectrode. Different methods and material have been applied in the construction in this system looking for the best performance and reproducibility of this kind of photoelectrode [2].

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When clean metallic Ti is exposed to air, a very thin film of TiO₂ grows up on the surface. If this system is heated in air atmosphere, the oxide films increases but crystallographic morphological changes take place on the film [3]-[5].

It has been found that current measured in chronoamperometric experiments increases when the material is exposed to visible light. We have found that the thermal treatment of the material leads to a larger photocurrent output when films are prepared at the temperature of 750°C [5].

Electrochemical impedance spectroscopy (EIS) allows us to get information on the number of charge carriers, the *flatband* potential and the resistance to the charge transfer [6]-[9] measured on thin films of TiO₂ of different samples, obtained after the heat treatment at 450°C, 600°C, 750°C and 900°C and the reference material exposed at air at room temperature. It is well known that these set of parameters are of interest in the search of materials with higher photoelectrochemical performance.

The *flatband* potential is related to the space charge layer which is generated when the electrode is dipped into the solution. An electric field arises between the semiconductor surface and the solution. If the electric field increases, the recombination hole-electron in the semiconductor film decreases [8] [10]. The comparison of the *flatband* potential of the different TiO₂ thermally prepared on the Ti surface is a criterion to be considered in the analysis of the performance of the material as an efficient photoelectrode.

We are interested in material with higher yields in connection with the conversion of solar light in chemical energy. In order to accomplish with this target, we expect to prepare photoelectrodes presenting a small resistance to charge transfer, a larger number of charge carriers and a big *flatband* potential should be expected.

The main objective of this study was the characterization of TiO₂ films grown on Ti surface after thermal treatment at different temperatures with the help of the electrochemical impedance spectroscopy and the comparison of the results with other studies performed in our laboratory with the help of amperometry and potentiometry methods as reported previously [5].

2. Experimental

2.1. Photoelectrode Preparation

A set of 11 plates of Ti (Johnson Matthey, 99.7%) of approximately 100 mm² were employed in all experimental conditions. The plates were polished till the surface becomes mirror-like using a 1 μm and 0.3 μm particle size alumina suspension (Bühler). These plates were heated in an oven in atmosphere of air at a rate of 20°C·min⁻¹. As soon the desired temperature was reached, the plates were taken out of the oven. Four of these plates were heated till 450°C, 600°C, 750°C and 900°C and taken out of the oven when the temperature reached the desired value. These temperatures will be referred as quenching temperatures. Another set of three plates were allowed to be heated 30 minutes at 450°C, 600°C and 750°C respectively. Finally, a third set was 3 plates were heated 60 minutes at 450°C, 600°C and 750°C. A reference plate remains without thermal treatment.

The reference and the 10 plates, once cooled, were covered by an epoxy resin leaving a section of 64 mm² for photo-electrochemical experiments.

2.2. Electrochemical Studies

The cell consisting of three electrodes, the photoelectrode as a working electrode (WE) with Pt electrodes symmetrically arranged as counter electrodes and a reference of Hg/HgO were employed in all measurements.

All experiments were carried out at 25°C. A 6 M KOH (p.a.) aqueous solution was the electrochemical media. Measurements under light irradiation were carried out employing a dichroic lamp of 250 W (Zurich MR16) settled at 16 cm of the photoelectrode surface.

2.2.1. EIS Studies

The equivalent circuit shown in **Figure 1** was used for evaluating the charge transfer resistance (R_{ct}) in all the studied samples. The ohmic resistance R_{Ω} as well as the capacitance C of the material is also shown in **Figure 1**.

The R_{ct} values were obtained from each photoelectrode taking at the repose potential an impedance spectrum in the range 100 kHz to 1 MHz. These results were fitting using a standard soft for this sort of calculations.

The analysis of the Mott-Schottky plot [11] [12] can be applied to measure the *flatband* potential. The space charge layer C_{sc} is the usual parameter to be measured in this kind of studies. As reported in the literature, a

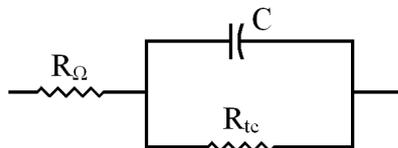


Figure 1. Equivalent circuit for EIS.

C_{sc}^{-2} plot versus the applied potential (V) to the photoelectrode lead to the typical Mott-Schottky plot. Equation (1) can be used to interpret the experimental results,

$$\frac{1}{C_{sc}^2} = \frac{2}{e_0 N_d \varepsilon \varepsilon_0} \left(\bar{V} - V_{fb} - \frac{kT}{e_0} \right) \quad (1)$$

In Equation (1), e_0 is the elemental charge, N_d is the donor density, ε is the dielectric constant of TiO_2 , ε_0 is the permittivity in the vacuum, V is the applied potential, V_{fb} is the *flatband* potential, k is the Boltzmann constant and T is the temperature of the solution.

A linear dependence between C_{sc}^{-2} and V should be expected. The donor density is obtained from the slope of this plot. The value kT/e_0 is normally smaller than the difference $V - V_{fb}$ ($kT/e_0 = 0.03$ V at 298 K) and it can be ignored in standard studies. Therefore, the *flatband* potential is obtained by extrapolation of the linear plot to $C_{sc}^{-2} = 0$.

The C_{sc} is measured as the imaginary component (Im) in impedance measurements at the frequency f (in Hertz) using an electrode of area A , as given by Equation (2),

$$\frac{1}{C} = \frac{1}{2\pi \cdot f \cdot |\text{Im}| \cdot A} \quad (2)$$

Spectrochemical impedance measurements were carried out employing an impedance analyzer Zahner IM6. An external overvoltage of 5 mV was chosen and applied in all experiments performed with this equipment.

2.2.2. Current and Potential Measurements on the Photoelectrode

The measurements were carried out in short circuited conditions irradiating the photoelectrode against an electrode of Pt. Both electrodes were dipped in the electrolyte solution. The photocurrent was measured with a microamperimeter Kipp and Zoner (AL4 model).

A similar set of experiments were carried out in open circuit conditions with the photoelectrodes in darkness and under irradiation. These experiments were used for characterizing the photoelectrodes and for measuring the photoactivity of the materials under studies. These potential difference against the Hg/HgO electrode was recorded with a potentiostat PAR model 263 A.

3. Results

3.1. Potentiometry and Amperometry Results

The potential of the photoelectrodes in darkness and under irradiation as well as the output photocurrent is listed in **Table 1**, where the results in darkness and under irradiation are shown. Experimental conditions can be read in **Table 1** legend.

As seen in this Table, excluding the reference, the response of the photoelectrodes depend on the quenching temperature and the time of heating of the material at a given temperature. Even though the behavior is strongly dependent how the material was handled (temperature quenching and time of heating at a given temperature during 30 and 60 minutes), the best photochemical answer is observed in the material prepared at 750°C. This behavior is consistent with previous results obtained in our laboratory [13].

An interesting behavior can be observed in **Table 1**. In fact, the potential in darkness depends dramatically on the temperature program applied to the material whereas the potential measured under light irradiation is almost independent on the quenching temperature applied on the same material. The thermal treatment induces morphological changes on the surface [4]-[6], being these changes responsible of the voltage measured in darkness, but the similar values observed under irradiation can be attributed to the TiO_2 , which is the photo active material.

Table 1. Difference of potential measured in the photoelectrode in darkness and under irradiation (open circuit) versus Hg/HgO and photocurrent measured under irradiation at closed circuit with a counter-electrode of Pt. In the first column 450.30 means 450°C and 30 minutes of heating at this temperature. A similar nomenclature is applied to all experimental conditions in this column.

| Photoelectrode | Experimental conditions | | | |
|----------------|-------------------------|---------------------|------------|---------------------------------------|
| | $V_{ca, dark}$ (V) | $V_{ca, light}$ (V) | ΔV | I_{light} ($\mu A \cdot cm^{-2}$) |
| Reference | -1.056 | -1.056 | 0 | -- |
| 450°C | -0.456 | -0.605 | 0.149 | 5.94 |
| 450.30 | -0.444 | -0.668 | 0.224 | 6.72 |
| 450.60 | -0.566 | -0.661 | 0.095 | 7.50 |
| 600°C | -0.312 | -0.547 | 0.235 | 7.97 |
| 600.30 | -0.116 | -0.626 | 0.510 | 12.19 |
| 600.60 | -0.527 | -0.636 | 0.109 | 19.06 |
| 750°C | +0.137 | -0.663 | 0.800 | 41.56 |
| 750.30 | +0.097 | -0.667 | 0.764 | 13.13 |
| 750.60 | +0.070 | -0.662 | 0.732 | 10.63 |
| 900°C | -0.068 | -0.622 | 0.554 | -- |

Moreover, the largest output photocurrent is obtained from the material prepared at 750°C. Except for the reference and the photoelectrode prepared at 900°C; these results are reproducible, even though the measurements were carried out several days after their preparation.

The behavior of these magnitudes show that the photoelectrode quenched at 750°C presents the optimal photocurrent. These results can be correlated with the optimal thickness and the ratio of the anatase/rutile crystalline forms on the films as seen by X-ray diffraction and SEM studies reported in earlier studies [5].

A small current intensity (1 mA) is recorded in the blank and the photoelectrode prepared at 900°C. However, these values decay to negligible values ($<1 \mu A$) in a few minutes. Some instability is observed which can be associated to morphological changes on the electrodes, *i.e.*, if the mirror-like Ti electrode is dipped alone into the solution, there are visual changes in the reflectance of the surface, but when is connected to the Pt counter electrode, the visual appearance of the surface changes, and a dark-grayish tonality is developed. This behavior is not observed on the other photoelectrodes, which show stability and reproducibility as reported in the literature [5].

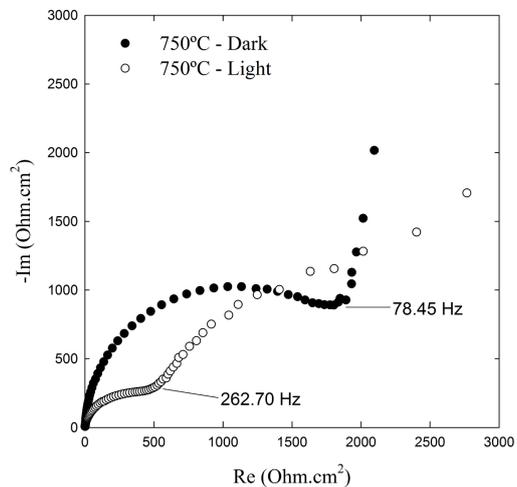
The thickness or amount of the TiO₂ on the surfaces should increase regularly with the time of heating leading to a better performance of the photoelectrochemical behavior. At 750°C, the photocurrent is the highest observed in our experiments, but it decreases by a factor 3 to 4 with the heating time of this photoelectrode.

3.2. Nyquist Diagrams

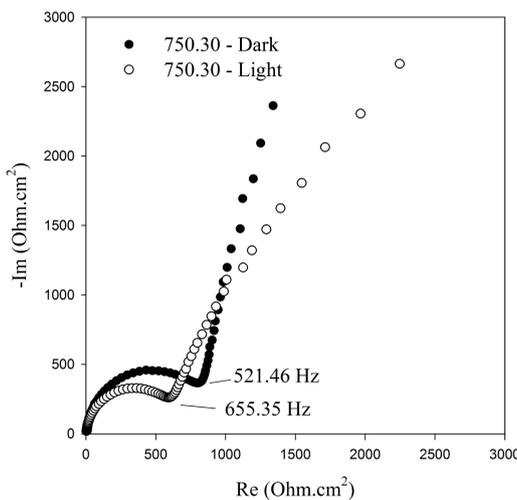
Nyquist diagrams obtained on the photoelectrodes prepared at 750°C are shown in **Figure 2**. As seen in these plots, at higher frequencies the typical loops are observed. At lower frequencies a diffusional behavior can be observed but not depicted in these Figures, because we are only interested in the parameters associated with the charge transfer processes. The diffusional contribution is only observed in the photoelectrode prepared at 750°C which presents a lower charge transfer resistance in comparison with the other electrodes listed in **Table 2**.

Nyquist diagrams shown dramatic differences when the measurements are carried out in darkness and under illumination. A significant decreasing the charge transfer resistance in the illuminated photoelectrode is recorded, as consequence of the catalytic effect of the TiO₂ under irradiation.

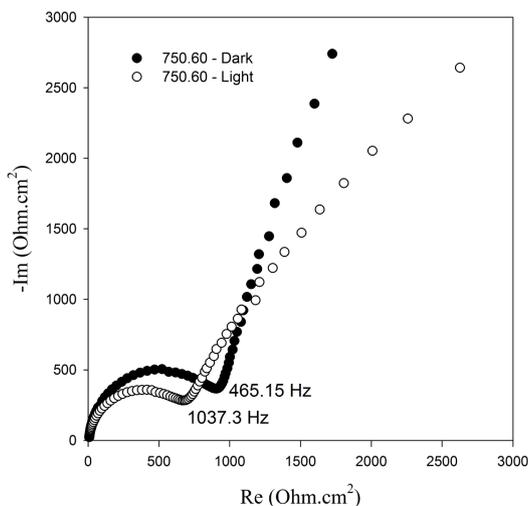
In **Table 2** are resumed the experimental results measured in these set of experiments. All the R_{ct} listed in this Table show an important decrease when the photoelectrodes are irradiated. These parameters are temperature dependent as can be observed for all photoelectrodes analyzed in this study. Even though the photocatalytic effect of light is observed in all samples, the effect is more important in the photoelectrode prepared at 750°C.



(a)



(b)



(c)

Figure 2. Nyquist diagrams obtained using photoelectrodes prepared at 750°C and different times of heating: (a) quenching at 750°C, (b) maintained at 750°C during 30 minutes and (c) maintained at 750°C during 60 minutes.

Table 2. Experimental results of charge transfer resistance (R_{ct}) and degree of fitness (n) obtained in darkness and under light illumination for all samples. The nomenclature employed in the first column is the same as described in **Table 1**.

| Photoelectrode | Experimental results in darkness and under irradiation | | | |
|----------------|--|-------------------|--|--------------------|
| | $R_{ct, \text{dark}} (K\Omega \cdot \text{cm}^2)$ | n_{dark} | $R_{ct, \text{light}} (K\Omega \cdot \text{cm}^2)$ | n_{light} |
| Reference | 2.88 | 0.951 | 0.734 | 0.939 |
| 450 | 450.16 | 0.964 | 83.731 | 0.961 |
| 450.30 | 915.20 | 0.981 | 57.315 | 0.971 |
| 450.60 | 324.04 | 0.962 | 26.378 | 0.952 |
| 600 | 875.65 | 0.890 | 41.286 | 0.913 |
| 600.30 | 502.40 | 0.962 | 28.206 | 0.934 |
| 600.60 | 406.33 | 0.957 | 23.739 | 0.943 |
| 750 | 2.14 | 0.976 | 0.463 | 0.936 |
| 750.30 | 0.986 | 0.953 | 0.703 | 0.959 |
| 750.60 | 1.04 | 0.970 | 0.762 | 0.961 |

As seen in **Table 1**, the photocurrent output increases with the temperature, being higher on the photoelectrodes prepared at 750°C, meanwhile, as observed in **Table 2**, the R_{ct} value is the most small. As can be seen the **Table 1**, the parameter $n \approx 1$ suggests that the model depicted in **Figure 1** fits reasonably well the experimental results.

3.3. Mott-Schottky Plots (MS)

Plots of $1/C_{sc}^2$ versus the applied potential V are shown in **Figure 3**. In all cases V was measured against a Hg/HgO electrode. The slopes in all cases are positive as expected for a semiconductor type n [11].

The slopes and the intercepts of MS plots are also temperature dependent as seen in these Figures. New sets of photoelectrodes were prepared to perform these experiments as described in section 2.1.

As usual, experiments were performed in a wide range of frequencies, but those showing a reasonable electrochemical behavior were selected as relevant in the construction of MS diagrams.

Experimental results are resumed in **Table 3**. It can be observed that the donor density (N_d) decrease as the temperature increases. The comparison between those experimental results listed in **Table 1** are not parallel as expected in a simplified analysis, *i.e.* larger N_d values should imply an increase in the current output (I_{light}).

The *flatband* potentials do not show a significant difference below 750°C, but at this temperature a much higher value is measured.

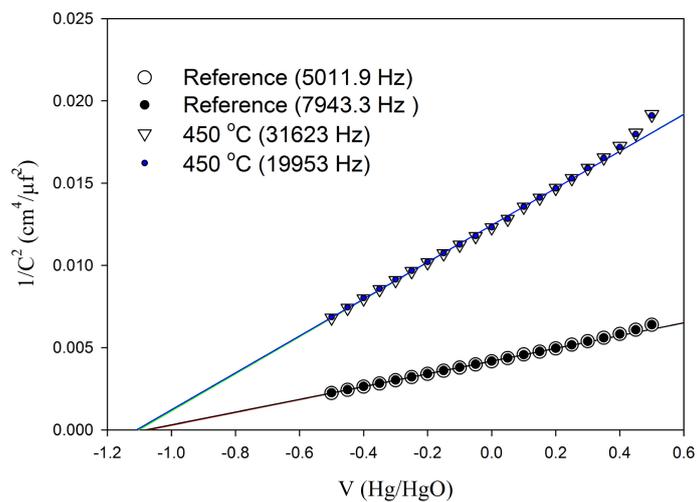
The information presented in **Table 3** can be correlated to the film thickness (w) of the space charge layer (SCL) as well as to structural changes on the TiO₂. The film thickness of the SLC can be estimated by Equation (3), as proposed in the literature [12], assuming that the SLC is fully depleted at high anodic potentials, where the layer behaves as a capacitor. This assumption allows us to correlate its capacity with the ϵ_r of the TiO₂.

$$w = \left(\frac{2\epsilon_0\epsilon_r}{e_0N_d} \right)^{\frac{1}{2}} \left(\bar{V}_{int} - V_{fb} - \frac{kT}{e_0} \right)^{\frac{1}{2}} \quad (3)$$

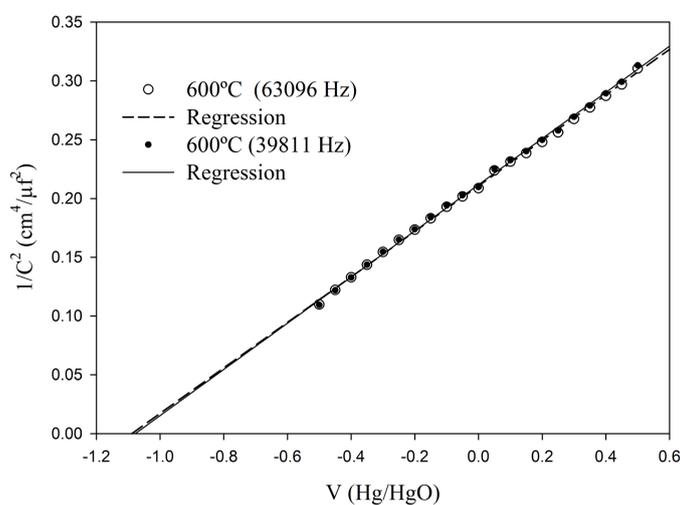
V_{int} is the potential in the erfase between the support and the TiO₂. A rough estimation can be obtained is this value is assumed smaller than V_{int} , as observed on other systems [14].

The simplified expression leads to an approximate linear dependence between w and $(V_{fb}/N_d)^{1/2}$. Assuming that the geometric area of the photoelectrode is constant, the increase of the TiO₂ films should be proportional to the relative increase of the TiO₂ mass with the quenching temperature (see **Table 3**).

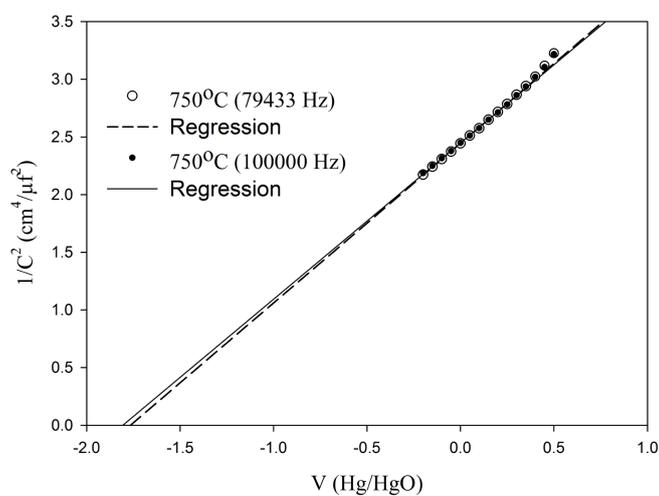
This proportionality between these variables allows us to estimate the dielectric constant of the film, assuming that the natural thickness of the film is of the order 10 - 20 nm. Therefore, taking a value of 15 nm, an applying the Equation (3) assuming that $|V_{int}/N_{fb}| < 1$, a value of $\epsilon_r = 230$ is obtained. Weber *et al.* [13] reported values of 300 - 1000 for ϵ_r in defect-doped TiO₂. In **Table 3** are shown the estimated values of the film thickness. It can



(a)



(b)



(c)

Figure 3. Mott-Schottky plots obtained at different temperatures and frequencies: (a) reference at 25 °C and at 450 °C, (b) at 600 °C, and (c) at 750 °C. The lines were obtained by lineal regression. The frequencies are given in brackets.

Table 3. Donor density (N_d) and flatband potential (V_{fb}) measured in the studied samples. The thickness of SCL of the film is estimated as described in the text.

| Sample | Experimental results and estimated thickness of the SCL | | | |
|-----------------------|---|-------------------------------|---|------|
| | N_d (cm ⁻³) | $ V_{fb} $ (V. vs. Hg/HgO) | Increase of TiO ₂ mass (%) from TG (ref. 5) | w/nm |
| Reference (5011.9 Hz) | 3.02×10^{20} | 1.07 | 0 | 15 |
| 450°C (31,623 Hz) | 1.04×10^{20} | 1.10 | 0.0675 | 45 |
| 600°C (63,096 Hz) | 1.04×10^{18} | 1.09 | 0.0862 | 160 |
| 750°C (100,000 Hz) | 8.67×10^{17} | 1.80 | 0.2339 | 226 |

be seen that the donor density decreases with the thickness as observed in by R. van de Krol *et al.*, [15]. The donor density behaves in a similar way as the value reported by Spagnol *et al.* working on TiO₂ nanotubes (on stainless steel) *i.e.*, at 145 nm, a value of $N_d = 1.4 \times 10^{18}$ cm⁻³ is reported.

Studies performed on films of anatase on indium-tin oxide showed that the donor density decreases with the thickness. Values of 2.9×10^{19} , 7.9×10^{18} and 4.1×10^{16} cm⁻³ have been evaluated for thickness of 40, 80 and 120 nm respectively (See reference [15]), employing a dielectric constant of 55 for anatase.

4. Conclusions

Photoelectrodes of Ti/TiO₂ prepared by thermal treatment at different temperatures and at different time of heating (450°C, 600°C, 750°C and 900°C) show different behavior in darkness and under light illumination. The photoactivity of the semiconductor measured by the charge transfer resistance, the flatband potential and the number of charge carriers are also temperature dependent as well as the temperature and the heating time at a given temperature.

Under the present experimental conditions, the electrodes prepared at 750°C showed the best photoresponse under irradiation, which could be applied in the design photoelectrochemical devices in PEC.

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