Journal of Applied Electrochemistry **31**: 319–323, 2001.

Electrocatalytic properties of Ti/TiO$_2$ electrodes prepared by the Pechini method

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Received 23 November 1999; accepted in revised form 18 September 2000

Key words: electrocatalysis, factorial design, nitrobenzene, Pechini method, TiO$_2$

Abstract

The effects of three synthesis variables on the electrochemical properties of TiO$_2$ prepared by the Pechini method are described. To minimize the number of experiments, a factorial design was used. It was shown that, in the presence of nitrobenzene, the temperature and the number of layers were the most important variables. The effects of these variables on the cathodic charges measured by cyclic voltammetry were -0.75 and 2.76 mC cm^{-2}, respectively. Explanations of these findings are based on the effect of the conditions of preparation on the morphology and microstructure of the electrodes.

1. Introduction

TiO$_2$ has been widely investigated due to the importance of its electrochemical [1], photochemical [2], catalytic [3] and photoelectrochemical [4] properties. Several authors have described the electrochemical and electrocatalytical properties of this oxide. Beck et al. developed a TiO$_2$ cathode whose surface behaves as a stable redox electron carrier [5, 6]. Recently, TiO$_2$ electrodes have been used as electrocatalyst in the reduction of nitro compounds [1, 7–11]. The mechanism proposed for these reactions [9] involves the reoxidation of Ti^{3+} sites to Ti^{4+}, associated with reduction of the nitro compound molecules adsorbed on the surface. For example, the electroreduction of *o*-nitrophenol to *o*-aminophenol, in acid medium, occurs as follows [9]:

$$6\,\mathrm{Ti}^{3+} + \mathrm{NO_2C_6H_4OH} + 6\,\mathrm{H}^+ \leftrightarrow 6\,\mathrm{Ti}^{4+} + \mathrm{NH_2C_6H_4OH} + 2\,\mathrm{H_2O} \qquad (1)$$

In the aforementioned experiments, TiO$_2$ was prepared by thermal decomposition of a solution of titanium acetyl acetonate in isopropanol.

However, the effect of the preparation variables on the electrocatalytical properties of the TiO$_2$ electrodes is not well documented. Among various methods of preparing oxide electrodes, the Pechini method has been widely used [12–14]. The main advantages of preparing oxide films by this method are the low grain size produced and the possibility of making low-level doped materials. This procedure consists in preparing a polyester polymer by reacting citric acid (CA) with ethylene glycol (EG) in which the metal ions are dissolved. The method has been successfully used in the preparation of films for several applications [12–14]. During the deposition of oxide film on the metallic substrate some preparation variables play an important role, such as the CA/EG ratio and CA/M ratio, where M is the metal salt concentration.

Generally, to optimise the preparation, one variable is altered and all others are fixed. However, the variables may be interactive. To determine these interactions, factorial design can be used [15]. This method consists of changing all variables simultaneously. The number of experiments necessary to describe the independent effects of all variables and the interaction effects among them is k^α, where k is the number of values taken by each variable and α is the number of variables. For example, to investigate the effects of three variables having two different values each (two levels), the total number of experiments is 2^3, that is, eight experiments.

With the above in mind, this work investigates the effects of preparation variables of the Pechini method on the electrochemical properties of TiO$_2$ electrodes using factorial design.

2. Experimental details

Two solutions were prepared with different molar proportions of titanium tetraisopropoxide: 1:2:8 (titanium tetraisopropoxide:citric acid:ethylene glycol) and 1:4:16, while the molar ratio between citric acid and ethylene glycol was maintained constant. The solution was prepared by heating ethylene glycol (Merck) to 60 °C with stirring and then adding the titanium tetraisopropoxide (Hulls AG). Finally, citric acid (Merck) was added, the temperature increased to 90 °C and the solution was stirred at this temperature until it turned clear.

The titanium substrates (surface area 2 cm^2) were polished with emery paper (320 and 400), washed with water followed by isopropanol and, finally, chemically treated in hot oxalic acid [16].

The substrate had both faces coated with the precursor solution. After each layer was deposited, the films were thermally treated at 250 °C for 10 min and then at 450 or 525 °C for 15 min.

The morphology and microstructure of the electrodes were determined by X-ray diffraction (Siemens model D5000) with CuK_α radiation, $\lambda = 1.5418$ Å, and scanning electron microscope (Zeiss model DSM 940A).

The electrochemical measurements were performed using a potentiostat/galvanostat (EG&G PARC model 273). A Pt foil and a saturated calomel electrode (SCE) were used as auxiliary and reference electrode, respectively. The experiments were carried out in aqueous solution either free from, or containing, nitrobenzene (NB) at different concentrations. All electrochemical experiments were performed at 25 °C.

3. Results and discussion

The voltammograms for TiO_2 electrodes in H_2SO_4 solution at several concentrations of nitrobenzene are shown in Figure 1. The lower limit potential used was −0.55 V since the oxide layer was observed to detach when the electrode was polarized to more negative values in the absence of NB. In solutions containing NB, no such detachment occurred. Therefore, in order to compare the two conditions, all voltammograms were limited to −0.55 V. Figure 1 shows an increase in cathodic current and a decrease in the anodic peak current as the nitrobenzene concentration increases.

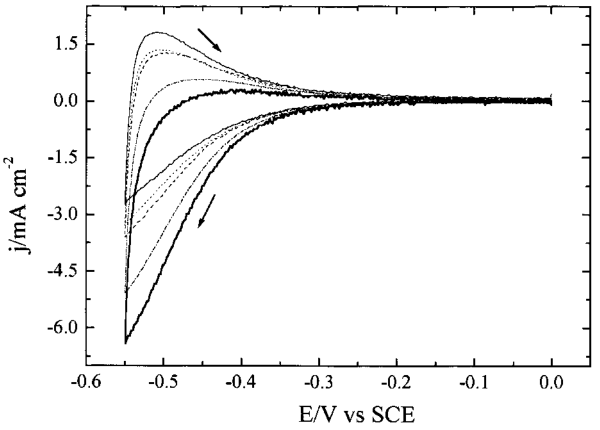

Fig. 1. Cyclic voltammograms for the 10 layer TiO_2 film, obtained from solution 1:2:8, thermally treated at 450 °C. Solution 0.5 mol L^{-1} H_2SO_4, $v = 0.05$ V s^{-1}, $T = 25$ °C. Nitrobenzene concentration: (——) 0 mmol L^{-1}; (······) 2 mmol L^{-1}; (- - - - -) 4 mmol L^{-1}; (—·—·—·—) 6 mmol L^{-1} and (——) 8 mmol L^{-1}.

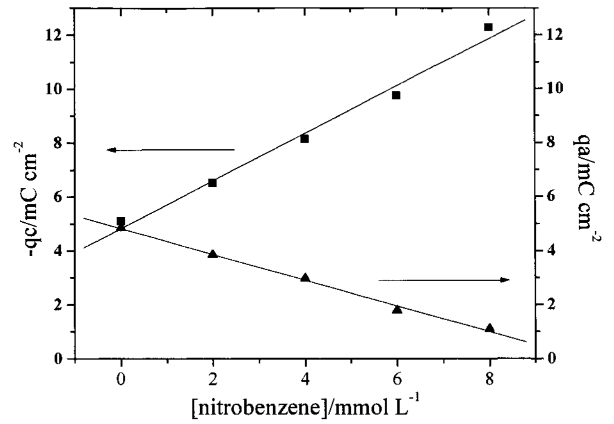

Fig. 2. Variation of (■) cathodic and (▲) anodic charges with nitrobenzene concentration. Electrode obtained from solution 1:2:8, with 10 layers, thermally treated at 450 °C. Solution 0.5 mol L^{-1} H_2SO_4, $v = 0.05$ V s^{-1}, $T = 25$ °C.

Figure 2 shows the values of anodic and cathodic charges calculated from the voltammograms presented in Figure 1. A linear increase in cathodic charge is observed as the NB concentration increases. As can be seen in Figure 2, the anodic charge decreases as the cathodic charge increases. This fact is in agreement with the indirect mechanism presented in Equation 1 [9]. The quantity of reduced titanium sites that can be oxidized during the anodic sweep is small and, therefore, the anodic charge is lower than the cathodic charge.

A factorial design, with three factors at two levels, was used to evaluate the effects of the preparation variables on the electrochemical properties of the electrodes. The electroactivity of the TiO_2 electrodes was evaluated using as response their cathodic charges at constant nitrobenzene concentration and sweep rate in H_2SO_4 medium. Table 1 presents the variables and their levels. Table 2 shows the design matrix and the results obtained for the cathodic charges. It shows whether a variable takes its high (+) or low (−) value in each experiment, which were carried out in duplicate in order to estimate the error.

The calculated effects of the variables and the effects of the interactions among them are presented in Table 3, for the tests performed in the absence and in the presence of 2 mM NB. It is important to state that what is presented in Table 3 are the effects of the variables, that is, the change in the response (cathodic charge) when the level of the variable is shifted from low to high level.

Table 1. Preparation variables for the TiO_2 electrodes

Variables	Level (−)	Level (+)
Solution (*C*)	1:4:16	1:2:8
Temperature (°C) (*T*)	450	525
Number of layer (*L*)	2	10

Table 2. Design matrix and cathodic charges (response) measured in 0.5 mol L^{-1} H_2SO_4 solution in the absence or in the presence of 2 mmol L^{-1} of NB

Experiment	*C*	*L*	*T*	Cathodic charge /mC cm^{-2}	
				0 mM NB	2 mM NB
1	−	−	−	−1.02	−2.10
2	+	−	−	−0.88	−2.03
3	−	+	−	−3.43	−4.82
4	+	+	−	−5.22	−6.51
5	−	−	+	−0.79	−2.22
6	+	−	+	−0.44	−2.10
7	−	+	+	−2.26	−4.52
8	+	+	+	−2.46	−3.71

$v = 0.05\ V\ s^{-1}$, $T = 25\ °C$

Examining Table 3, and considering the errors, it may be noted that the average values of the cathodic charge increase in the presence of nitrobenzene. The number of layers (*L*) and temperature (*T*) exert the most significant effects. The important interactions are between number of layers and temperature ($L \times T$) and between solution concentration and temperature ($C \times T$). A negative sign for an effect means that, in this case, the cathodic charge value decreases when the level is changed from low to high.

The effect of the number of layers, *L*, is probably related to a surface area change and not to a true mass change effect. This is supported by the analysis of the surface microstructure of films with different masses (Figure 3). Figure 3 shows the micrographs of electrodes prepared with two (Figure 3(a)) and 10 (Figure 3(b)) deposited layers. It can be seen that the electrode with 10 layers has wider and deeper cracks, compared to the electrode with two layers. This suggests that the surface area is greater for the 10 layer electrode. Otherwise, it is not possible to normalize the charges obtained in terms of the total mass, because this parameter is related to the layer volume and not to the layer surface area. The increase in the number of cracks when the electrode has 10 layers may be related to the stress generated during each thermal treatment as the polymer decomposes.

Table 3. Effects of the preparation variables on the cathodic charges for the Ti/TiO_2 electrodes measured in 0.5 mol L^{-1} H_2SO_4 solution in the absence or in the presence of 2 mmol L^{-1} of NB

Cathodic charge/mC cm^{-2}		
NB Concentration/mM	0	2
Average	2.06	3.49
C	0.37	0.19
L	2.56	2.76
T	−1.15	−0.75
CL	0.62	0.29
CT	−0.45	−0.62
LT	−0.81	−0.84
CLT	−0.34	−0.60
Error	±0.117	±0.370

$v = 0.05\ V\ s^{-1}$, $T = 25\ °C$

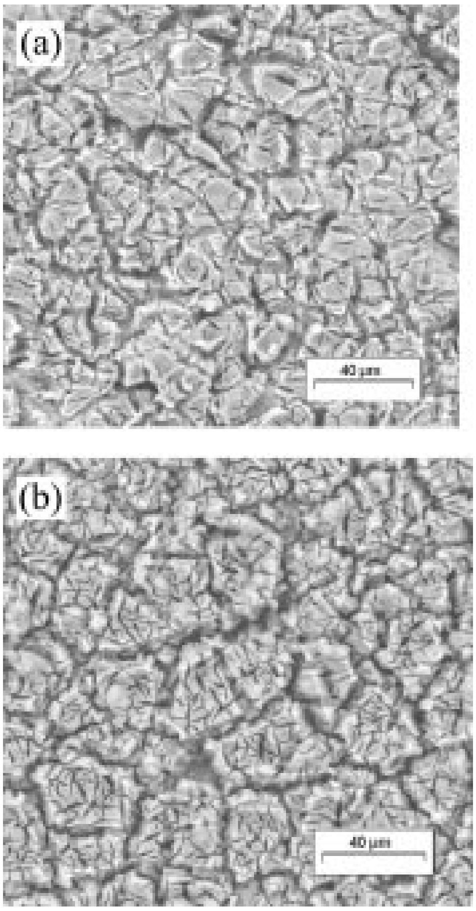

Fig. 3. Micrographs of TiO_2 electrodes prepared using solution 1:2:8 (M:CA:EG) at 450 °C: (a) 2 layers and (b) 10 layers.

The morphology and microstructure of the electrodes explain the effect of temperature. The films thermally treated at 525 °C show a higher proportion of rutile phase than those treated at 450 °C (Figure 4). The effect of the rutile phase on the electronic and electrochemical properties of TiO_2 has been previously discussed. Tang et al. [17] measured the conductivity of TiO_2 films in both anatase and rutile phases, prepared by sputtering and showed that anatase films are more conductive than rutile films, irrespective of the preparation conditions. Wahl et al. [2] observed that during the reduction of oxygen on rutile TiO_2, the reduction potential is displaced 0.1 V in the more negative direction, compared to that measured on anatase. As well as the occurrence of a significant amount of rutile phase, a reduction in the surface area also takes place as the thermal treatment is performed at a higher temperature, as can be seen in Figure 5, which shows micrographs of all electrodes prepared at 525 °C. Comparing this figure with Figure 3, an increase in island size and a decrease in the crack width is evident. Thus, the decrease in charge on the electrodes prepared at 525 °C may be related to both the presence of the rutile phase and the decrease in surface area.

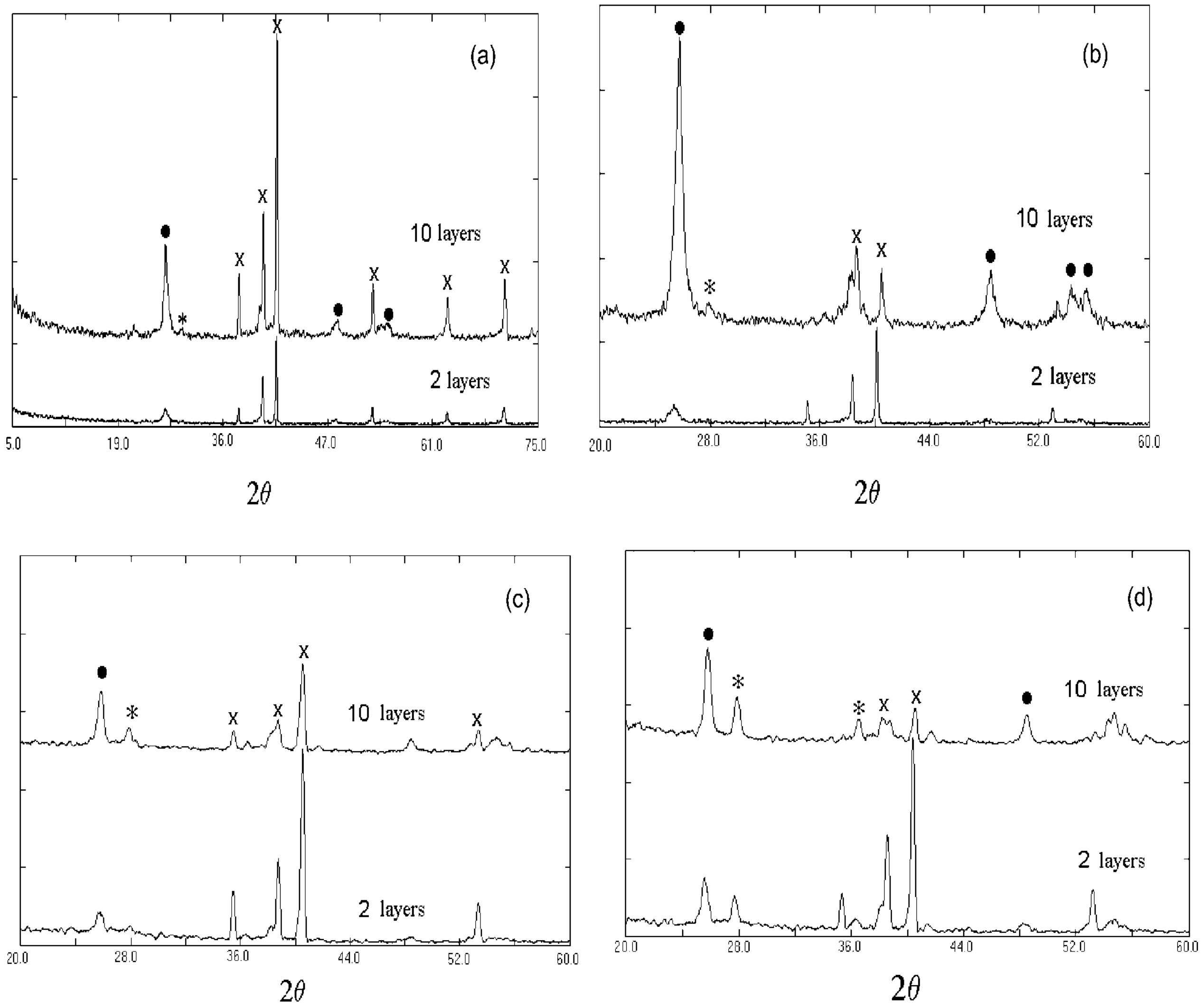

Fig. 4. X-ray diffractograms for TiO_2 films: (a) solution 1:4:16 (M:CA:EG) treated at 450 °C; (b) 1:4:16 (M:CA:EG) treated at 525 °C; (c) 1:2:8 (M:CA:EG) treated at 525 °C and (d) 1:2:8 (M:CA:EG) treated at 525 °C. Key: (●) anatase, (∗) rutile and (×) titanium.

An interesting result obtained by the use of factorial design is the interaction between variables which can be understood as the synergetic effect between them. In the present case, it was observed that the $C \times L$ interaction effect has a significant value only in the absence of nitrobenzene. Otherwise, $C \times L$, $C \times T$ and $L \times T$ interaction effects were significant in the presence of NB. These results means that to optimise the electrode response it is necessary to change simultaneously both variables. It is, however, very difficult to propose a mechanistic interpretation for these results.

The effect of the preparation variables on the cathodic charge can be visualised by constructing a cube figure (Figure 6), representing the eight experiments carried out, according to Table 2. The electrocatalytic activities of the prepared electrodes were evaluated on the basis of their cathodic charge at a constant nitrobenzene concentration (2 mmol L^{-1}) and sweep rate (0.05 V s^{-1}) in H_2SO_4 medium.

The experimental error of the measurements, in this case, is ± 0.370 mC cm^{-2}. As can be seen in Figure 6, as the calcination temperature is increased from 450 °C to 525 °C a decrease in the cathodic charge (Q_c) is observed for all samples investigated. An increase in Q_c is observed for all samples, when the number of deposited layers is 10. When the resin composition is changed from 1:4:16 to 1:2:8 there is also an increase in Q_c. The best response is obtained for the electrode prepared under the following conditions: 10 layers, calcination temperature of 450 °C and using the 1:2:8 (AC:EG:M) resin composition.

4. Conclusions

The results showed the influence of the preparation variables on the electrocatalytical reduction of nitrobenzene on TiO_2 electrodes. The use of factorial design allowed the effects of these variables and the interaction between them to be calculated by performing eight experiments. The results showed the most important variables to be the number of layers and the temperature. These findings were explained in terms of morphological and microstructural characteristics of the electrodes.

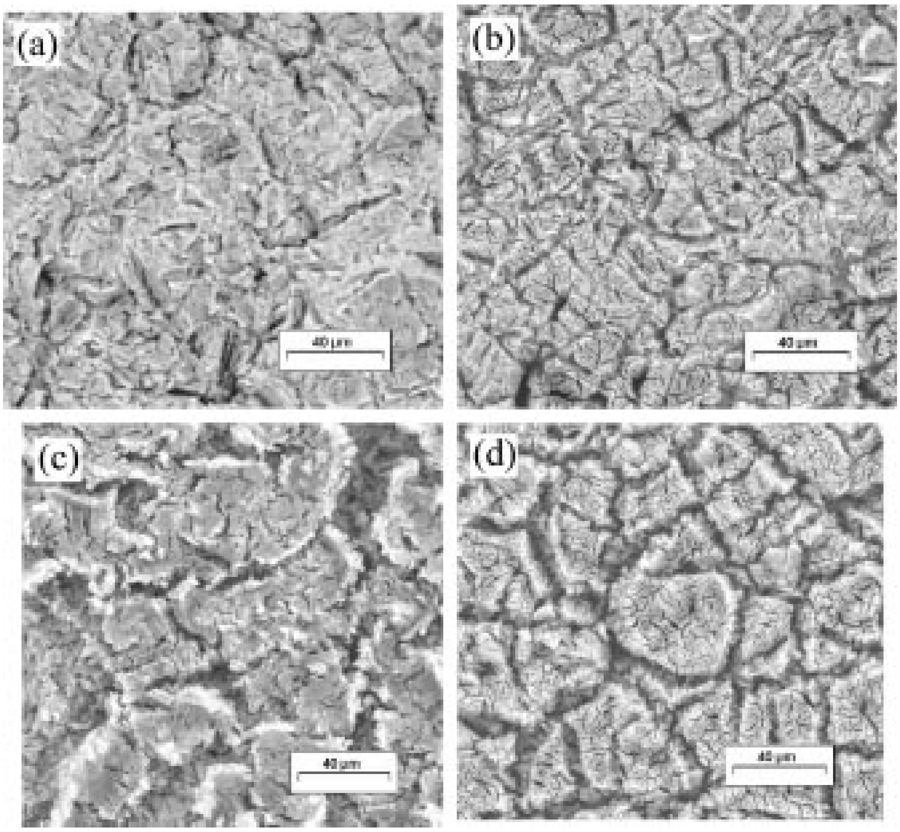

Fig. 5. Micrographs of TiO_2 electrodes prepared at 525 °C: (a) solution 1:4:16 (M:CA:EG), 2 layers; (b) solution 1:2:8 (M:CA:EG) , 2 layers; (c) solution 1:4:16 (M:CA:EG), 10 layers and (d) solution 1:2:8 (M:CA:EG), 10 layers.

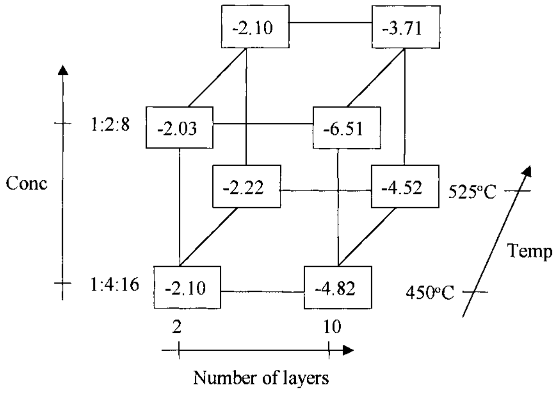

Fig. 6. Geometric representation of the effects of preparation variables on the cathodic charge in the presence of 2 mmol L^{-1} nitrobenzene. Voltammograms measured in 0.5 mol L^{-1} H_2SO_4 solution at $T = 25$ °C. $v = 0.05$ V s^{-1}.

Acknowledgements

The authors acknowledge CNPq, PADCT-III, PRONEX and FAPESP (Brazilian Government Research Agencies) for their financial support. The authors acknowledge Tim Roberts for his assistance with the English text revision.

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