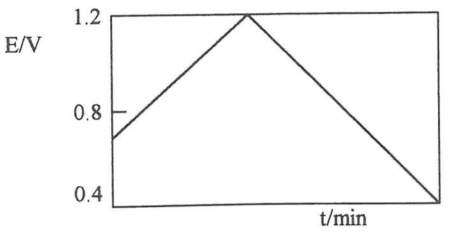

Fig.6: Potential-time program applied to the electrode to study the adsorbed dopamine layer.

The electrode real areas were obtained by measuring the gold oxide monolayer charge, as it has been previously described (20). All charges showed in this work were measured by graphical integration.

As the electrode with the adsorbed dopamine layer was in contact with the atmosphere for a few seconds before putting it in the electrochemical cell, we had to verify that there was no chemical oxidation during this time. Then, we studied the influence of the time during the contact of the electrode with the air on the current-potential response obtained. We did not observe any change for times as long as five minutes. Moreover, we studied the influence of the washing time on the current-potential response obtained. We did not observe any change for times as long as 30 s. (The electrode washing normaly last 5 s.)

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ELECTROCHEMICAL IMPEDANCE SPECTROSCOPIC INVESTIGATION OF Ir-BASED CERAMIC COATINGS CONTAINING CeO_2 UNDER CONDITIONS OF ACCELERATED ANODIC CORROSION

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Abstract

Ti-supported electrodes of nominal composition $Ti/Ir_{0.3}Ti_{(0.7-x)}Ce_xO_2$ ($0 \leq x \leq 0.7$) were prepared by thermal decomposition of the chloride precursor mixtures (450 °C). A systematic study of the corrosion behaviour of these anodes was performed under conditions of accelerated corrosion ($j = 800$ mA cm^{-2}) in acidic medium. Impedance measurements, carried out at regular time intervals, showed to be a very useful technique to accompany the changes occurring at the Ti^o/oxide layer and oxide layer/supporting electrolyte interfaces, during corrosion of the electrodes. The simulation of the impedance spectra through an appropriate equivalent circuit allowed to quantify the parameters.

Key Words: electrocatalysis; oxygen evolution; corrosion; iridium oxide; impedance.

Introduction

The effect of CeO_2 introduction on the service life of the IrO_2/TiO_2 system has been presented elsewhere [1]. It was observed that the gradual substitution of TiO_2 by CeO_2 produces anodes which present a lower service life for the oxygen evolution than the initial system. This rather instability is possibly related to the preferential dissolution of Ce in association with the crystalline structure of these coatings (amorphous phase or low degree of crystallinity). Normally, the service life of an electrode is determined under conditions of accelerated corrosion, imposing a high constant current to the system and measuring the potential vs time response [2]. We have demonstrated [3] that the electrochemical impedance spectroscopy, EIS, can be a useful technique to avaliate the corrosion behaviour of a DSA®. The aim of this study is to utilize the EIS to monitor the variations occurring in the coating layer during the service life of the $IrO_2/TiO_2/CeO_2$ system.

Experimental

Electrode preparation. Ti-supported electrodes of nominal composition $Ti/Ir_{0.3}Ti_{(0.7-x)}Ce_xO_2$ ($0 \leq x \leq 0.7$, changed in 10 mol% steps) were prepared by thermal decomposition (T:450 °C; t_{calc}:1 h; O_2 flux: 5 L min^{-1}) of mixtures of *ca.* 0.14 mol dm^{-3} solutions of $IrCl_3.xHCl.xH_2O$ (Aldrich), $TiCl_4$ (Ventron) and $CeCl_3.7H_2O$ (Pierce) dissolved in 1:1 (*v/v*) HCl (Merck). A detailed description of the experimental procedure used is found in a previous paper published by us [4].

Solution. 1.0 mol dm^{-3} $HClO_4$ (Merck) aqueous solution was used as supporting electrolyte. Experiments were conducted at 32±2 °C.

Technique and instrumentation. Impedance spectra were obtained at regular time intervals during the corrosion experiment, until the end of the service life of the anodes, at constant *dc* potentials (0.9, 1.48 and 1.50 V/rhe). The service life, SL, of the electrodes was taken as the time necessary for complete deactivation of the electrode material (E=6 V/rhe). Impedance measurements were carried out using a PAR model 5210 lock-in amplifier coupled to a PAR model 273A potentiostat, monitored by an IBM, model 55/SX, personal computer.

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Results and Discussion

Electrochemical impedance spectroscopy, EIS, has been proven to be an excellent technique to avaliate the changes occuring at the Ti° support/oxide layer and oxide layer/supporting electrolyte interfaces during corrosion of a DSA® [3], since each process occurs in a characteristic frequency region of the impedance spectrum. Normally, the response of the Ti° support/oxide layer interface appears in the high frequency domain of the complex plane plot, as the beginning of a small semi-circle [5-7]. Its origin is attributed to the TiO_2-film doped with IrO_2, formed during the electrode preparation, especifically during the calcination step (T=450 °C) [8,9].

Independent of the applied potential, as corrosion time, t_{cor}, increases, the semi-circle at high frequencies becomes much better defined. This is a general behaviour and is related to the oxidation of the Ti° support due to the drastic anodic conditions imposed to the electrodes. The evolution of the complex plane plots as a function of the t_{cor} of the electrode of nominal composition $Ti/Ir_{0.3}Ti_{0.3}Ce_{0.4}O_2$, representative of the system, is shown in Fig. 1. The well defined semi-circle in the low frequency domain is related to the faradaic reaction, OER.

Using Boukamp's EQUIVCRT program [10], the experimental data were best simulated by the equivalent circuit, EC, represented by $R_{\Omega}(R_fQ_f)(R_{ct}Q_{dl})$. The f subscript refers to the film properties, the other symbols having their usual meanings. Since DSAs® normally show a high degree of roughness and inhomogeneities two constant phase elements, CPE, instead of capacitances were used to fit the data [11-16]. The use of a CPE replacing the double layer seems to be a good approach for the study of some practical electrodes with different degrees of surface roughness, with physical nonuniformity or with a nonuniform distribution of surface reaction sites [12,17,18].

The impedance of the CPE can be written as [19]

$$Z_{CPE} = \frac{1}{T(j\omega)^n} \qquad (1)$$

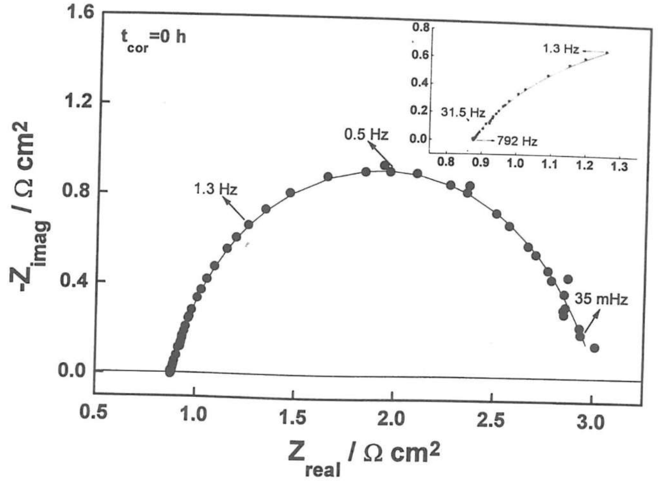
where $T = C_{dl}$ only if n = 1, T is expressed in units of farads per square centimetre per second to the power n, $j = (-1)^{1/2}$ and ω is the angular frequency. n is related to the depression angle, α, by

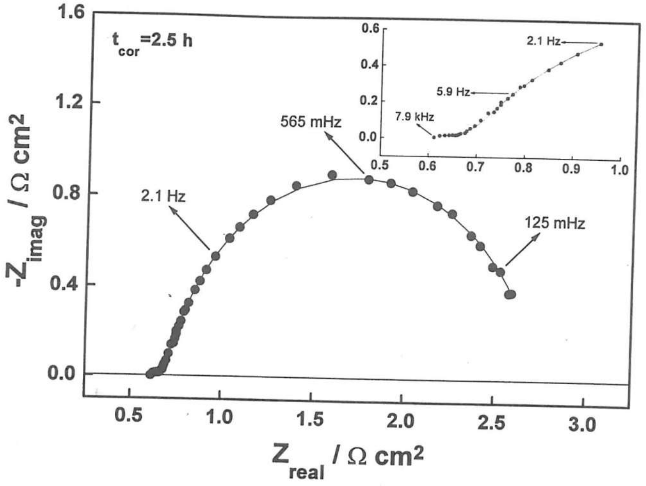
$$\alpha = (1 - n)90^{\circ} \qquad (2)$$

Rammelt and Reinhard [20] showed experimentally that n (or α) unequivocally reflects the roughness of solid electrodes and is independent of the electrode material. Encouraged by these results [20], Piela and Wrona [19] accepted that impedance measurements are capable of providing information on the state of the electrode surface. For $n \approx 1$ ($\alpha \approx 0^{\circ}$) the electrode surface is smooth, whereas for n close to 0.5 ($\alpha \approx 45^{\circ}$) it is extremely rough.

The CPE exponents, n, corresponding to the semi-circle of the OER (low frequencies), present values close to one for freshly prepared electrodes, indicating $Q_{dl} \equiv C_{dl}$. As the corrosion time, t_{cor}, increases, these values diminish, tending to 0.8 at the end of the electrodes service life. This means the electrode surface becomes rougher, which is reasonable since the active layer is severely corroded and eroded (see SEM analysis section of ref. [1]).

As expected, the solution resistance values, R_{Ω}, remained practically constants between 0.7 and 1.2 Ω cm^2.





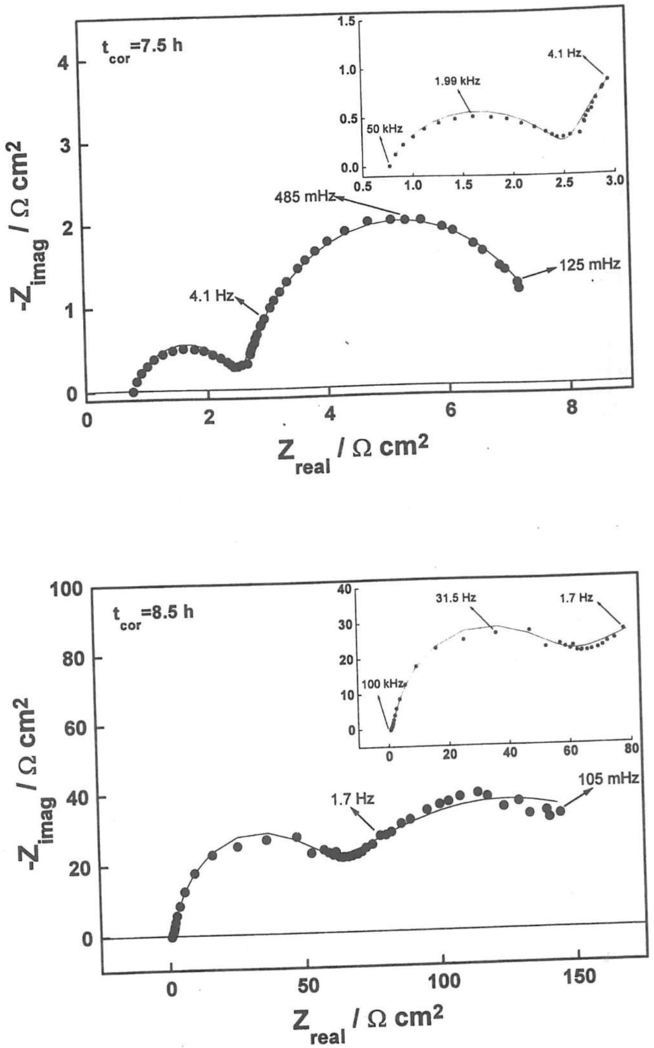


Figure 1. Impedance spectra in the complex plane as a function of the corrosion time of the electrode of nominal composition $Ti/Ir_{0.3}Ti_{0.3}Ce_{0.4}O_2$. E=1.50 V/rhe. (●) Measurement and (—) Simulation.

The double layer capacitance of freshly prepared electrodes, C_{dl}, as a function of electrode composition is shown in Fig. 2a. The higher the electrode CeO_2 content the higher the C_{dl}, reflecting the increase in the active surface area of these electrodes, in agreement with the anodic charge, q_a, values [21]. After the corrosion investigation, C_{dl}-values decrease significantly (Fig. 2b), attesting an almost complete colapse of the active layer.

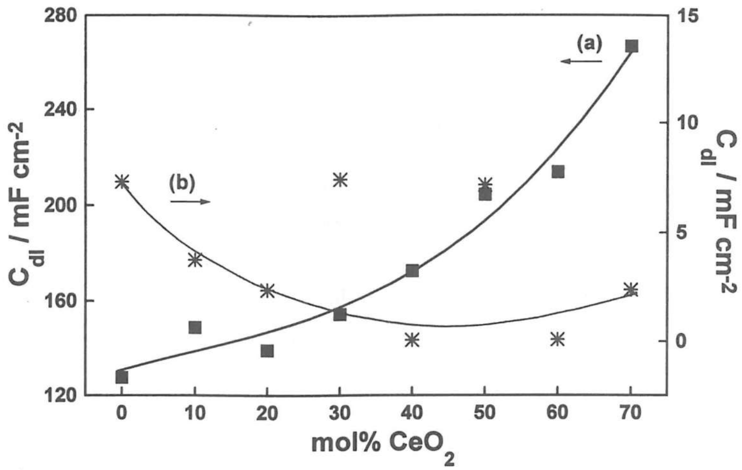


Figure 2. Double layer capacitance, C_{dl}, as a function of electrodes of nominal composition $Ti/Ir_{0.3}Ti_{(0.7-x)}Ce_xO_2$ before (a) and after (b) the corrosion investigation. E=1.48 V/rhe.

After the corrosion study, depending on the electrode composition, the CPE exponents of the semi-circle at high frequencies present values between 0.7 and 1.0. This element also was attributed to a capacitance, especifically to the interlayer film capacitance, C_f. The increase of n has been attributed to the fact the TiO_2 film formed at the Ti^o/oxide layer interface becomes more stoychiometric as t_{cor} increases. The higher the electrode CeO_2-content, the higher the n-value (the TiO_2 film approaches an ideal dielectric).

C_f-values are shown as a function of electrode composition in Fig. 3a. These values, independent of CeO_2 concentration, remain practically constants around 50 μF cm^{-2}. This value is typical of the TiO_2, which is 60 μF cm^{-2} [22], confirming an anodic TiO_2 film really grows at the Ti^o/oxide layer interface of the electrodes.

On the other hand, the interlayer film resistance values, R_f (Fig. 3b), show a clear increase for the electrodes with ≥ 40 mol% CeO_2, whose TiO_2 films are supposed to be thicker due to the higher instability (erosion/corrosion) of these coating layers.

The charge transfer resistance values, R_{ct}, of the electrodes after the corrosion study show sligthly higher values as the electrode CeO_2 content increases (see Fig. 4), supporting the supposition made earlier [1] that Ce dissolution brings about the catalytic component (Ir) from the electrode surface.

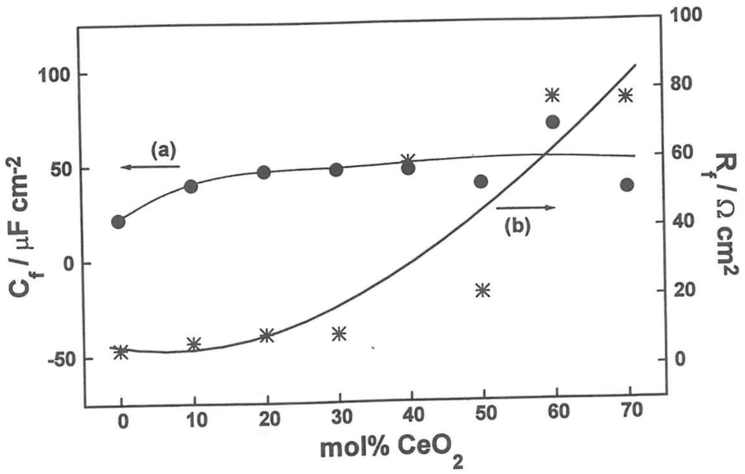


Figure 3. Capacitance, C_f, (a) and resistance, R_f, (b) of the interlayer Ti°/OL as a function of electrodes of nominal composition $Ti/Ir_{0.3}Ti_{(0.7-x)}Ce_xO_2$ after corrosion investigation. E=1.48 V/rhe.

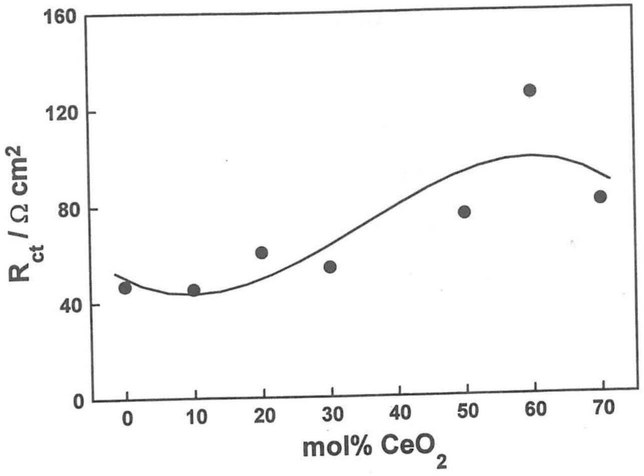


Figure 4. Charge transfer resistance, R_{ct}, as a function of electrodes of nominal composition $Ti/Ir_{0.3}Ti_{(0.7-x)}Ce_xO_2$ after corrosion investigation. E=1.50 V/rhe.

Final Comments

Electrochemical impedance spectroscopy measurements show that high CeO_2 content electrodes (CeO_2 > 30 mol%), after corrosion study, present high R_f and R_{ct}, suggesting a thick TiO_2 film has been grown at the Ti°/oxide layer interface of these anodes. The higher R_{ct} values for the OER confirms the low Ir content remaining on the surface of these electrodes.

Acknowledgements

V. A. Alves wishes to acknowledge the FAPESP foundation (Brazil) for a fellowship received. L. A. da Silva acknowledges financial support received from CAPES. J. F. C. Boodts acknowledges financial support received from FAPEMIG, PADCT II and CNPq.

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