

Electrochemical Characterization of Anodic Passive Layers on Cobalt

*Elida B. Castro, Claudio A. Gervasi and Jorge R. Vilche**

*Instituto de Investigaciones Fisicoquímicas Teóricas y Aplicadas Facultad de Ciencias
Exactas, Universidad Nacional de La Plata, Sucursal 4
C.C.16, (1900), La Plata, Argentina*

Carla P. Fonseca

*Instituto de Química, Universidade Estadual de Campinas, Caixa Postal 1170, (13100)
Campinas - SP, Brazil*

Received: April 30, 1994; August 11, 1994

As propriedades semicondutoras de camadas passivas geradas anodicamente em eletrodos de Co em soluções aquosas quase neutras, variando à vontade o potencial de formação de óxido E_f , foram investigadas usando-se espectroscopia de impedância eletroquímica. A resposta em frequência do sistema é altamente dependente de E_f , de acordo com mudanças na composição da camada passiva. O alto valor de capacitância, que é praticamente independente do potencial operacional par um dado E_f , parece indicar que a contribuição da carga na superfície do metal não pode ser desprezada e, conseqüentemente, a relação de Mott-Schottky não é mais válida. O estudo cinético da reação de transferência de elétrons ferro-ferricianeto em Co passivo conduziu a um mecanismo de transferência de carga tipo banda de valência.

The semiconductor properties of passive layers anodically generated on Co electrodes in nearly neutral aqueous solutions, varying at convenience the oxide formation potential E_f , were investigated using electrochemical impedance spectroscopy. The frequency response of the system is highly dependent on E_f , in accordance with changes in the composition of the passive layer. The high capacitance value which is practically independent of the operational potential for a given E_f , seems to indicate that the charge contribution on the metal surface cannot be neglected and, accordingly, that the Mott-Schottky relation is no longer valid. The kinetic study of the ferro-ferricyanide electron transfer reaction on passive Co pointed out a valence band charge transfer mechanism.

Key words: *cobalt, anodic passive layers, oxide films, electrochemical impedance spectroscopy*

Introduction

Passive films on Co have been studied by different electrochemical¹ and spectroscopic techniques, such as AES², ellipsometry³ and PMR⁴. Although the passive film structure is not a settled matter it is generally accepted that its composition changes with potential³⁻⁵. These changes in the oxide composition affect the ionic transport phenomena and electronic properties of the passive layers.

Recently, some efforts were conducted to determine the electronic and structural properties of the passive films by transient electrochemical and photoelectrochemical meth-

ods⁶⁻⁸. In this respect, electrochemical impedance spectroscopy (EIS) has proved to be a powerful tool for the characterization of oxide layers. Valuable information concerning electronic properties and ionic transport can be obtained from recorded impedance spectra covering a wide frequency range. In this work EIS has been used to analyze different properties of anodic oxide films formed on Co electrodes in slightly alkaline borate buffer solutions. A deep insight on the electronic structure of the film can be attained from impedance data at high frequencies and from the kinetic study of the ferro-ferricyanid electron transfer reaction. Impedance contributions at lower frequencies are

related to the interfacial charge transfer processes which originate ionic transport across the anodic surface film.

Experimental

The experimental setup has been described in a previous publication⁸. The working electrodes consisted of Co discs ("Specpure", Johnson Matthey Chemicals Ltd., geometric area 0.07 cm²) embedded in PTFE holders. The metal surfaces were mechanically polished with 1.0 and 0.3 μm grit alumina-water suspensions and thoroughly rinsed with ultrapure water obtained from a Milli-Ro plus Milli-Q device (Millipore, Bedford, MA). Potentials were measured and referred to in the text against a SCE.

Prior to the electrochemical experiments, the working electrodes were cathodized at potentials located in the net hydrogen evolution reaction region to achieve a reproducible electro-reduced surface. The oxide films were then anodically produced at different oxide formation potentials (E_f), $0.3 \text{ V} < E_f < 1.0 \text{ V}$, for 2 h in 0.1 M H_3BO_3 + 0.05 M $\text{Na}_2\text{B}_4\text{O}_7$. Impedance spectra were carried out in the 1 mHz -100 kHz frequency range using an ISA Zahner IM5d. Impedance measurements started at E_f and continued in decreasing potential steps of 0.02 within the passive region. After each impedance measurement at the operational potential E_m , the electrode potential was held at the initial formation potential (E_f) for 2 min in order to minimize any changes in the thickness and composition of the anodic film. The study of the $\text{Fe}(\text{CN})_6^{4-}$ / $\text{Fe}(\text{CN})_6^{3-}$ charge transfer reaction was accomplished by adding $\text{K}_3\text{Fe}(\text{CN})_6$ and $\text{K}_4\text{Fe}(\text{CN})_6$ to the base solution in which the oxide was previously formed, up to a concentration of 0.1 M for both salts. Electrochemical experiments were performed at 25 °C under purified N_2 gas

Results and Discussion

The passive state of Co electrodes in borate buffers of pH 8.5 extends from about -0.3 V up to 0.9 V (SCE), at which point transpassive dissolution occurs³. In this potential range a layer of CoO is formed during the initial stages of passivity. At potentials more positive than 0 V an outer layer of Co_3O_4 develops on the CoO film; Co_3O_4 is oxidized to Co_2O_3 at potentials exceeding 0.53 V, and O_2 evolution is detected at approximately 0.6 V².

These changes in the structure and composition of the passive layer according to potential influence the impedance diagrams recorded at different formation potentials E_f . Figure 1 shows impedance plots corresponding to $E_f = 0.3 \text{ V}$ and 0.5 V, the differences in the dynamic response probably being related to changes in the composition of the passive layer with E_f . Impedance spectra when $E_f > 0.6 \text{ V}$ (Fig.2) exhibit low impedance values at $f \rightarrow 0$, probably due to the set up of the oxygen evolution reaction.

As has previously been described for passive Fe⁸, the impedance of the system metal/oxide/solution, discounting

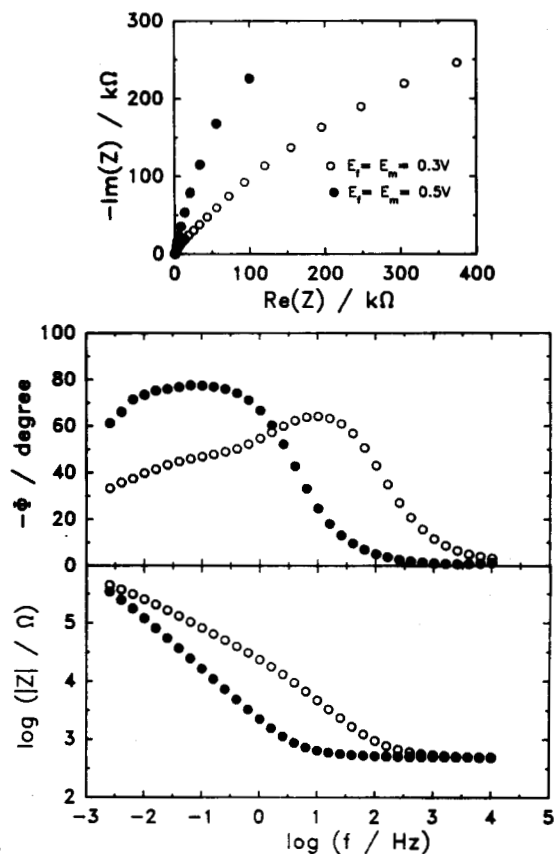


Figure 1. Nyquist and Bode diagrams at $E_m = 0.3 \text{ V}$ (O) and 0.5 V (●) of Co electrodes passivated at $E_f = 0.3 \text{ V}$ and 0.5 V , respectively, in 0.1 M H_3BO_3 + 0.05 M $\text{Na}_2\text{B}_4\text{O}_7$.

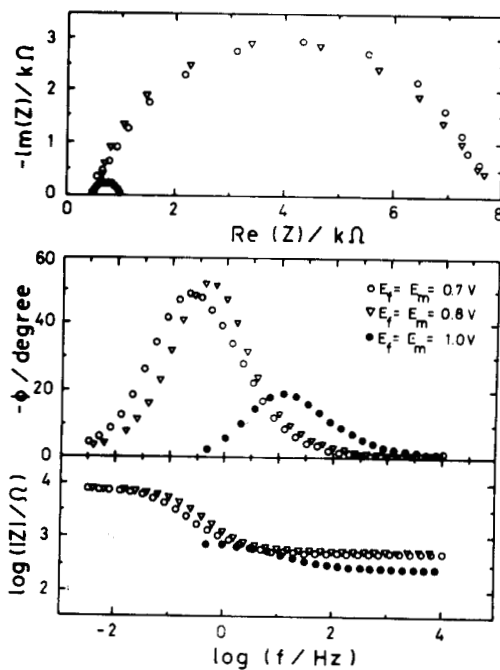


Figure 2. Nyquist and Bode diagrams at $E_m = 1.0 \text{ V}$ (●), 0.8 V (Δ) and 0.7 V (O) of Co electrodes passivated at $E_f = 1 \text{ V}$, 0.8 V and 0.6 V , respectively, in 0.1 M H_3BO_3 + 0.05 M $\text{Na}_2\text{B}_4\text{O}_7$.

the ohmic contribution, includes the sum of three parallel contributions:

$$1/Z = 1/Z_C + 1/Z_I + 1/Z_0 \quad (1)$$

where Z_C denotes the impedance related to the charging of the interfacial capacitances, Z_I the ionic transport through the film, and is consequently associated with the base metal dissolution, and Z_0 the oxygen evolution reaction impedance which should be considered when $E > 0.6$ V.

In general:

$$Z_C = \frac{1}{j\omega C} = \frac{1}{j\omega} \left(\frac{1}{C_{ox}} + \frac{1}{C_H} \right) \quad (2)$$

where $j = (-1)^{1/2}$, $\omega = 2\pi f$, C_H is the Helmholtz layer capacitance, and C_{ox} corresponds to the oxide capacitance. The latter term can be given by different mathematical expressions, so that in the case of very thin films, and in the absence of surface states at the oxide/solution interface⁹:

$$C_{ox} = C_{sc} + C_M \quad (3)$$

where C_{sc} is the space charge layer capacitance, and C_M is the contribution due to the metal surface charges.

As Z_I is the impedance associated with the base metal dissolution process, the interfacial reactions occurring at both the metal/oxide and oxide/solution interfaces, must be taken into account as these reactions are coupled to the ionic transport in the film. Assuming homogeneous electric field in the oxide layer and a constant film thickness for a given E_f , Z_I can be expressed in terms of the theoretical model previously proposed for Fe passive films⁸:

$$Z_I = \sigma \omega^{-1/2} (1 - j) + \frac{R_\infty R_0 (1 + j\omega\tau)}{R_\infty + R_0 (1 + j\omega\tau)} \quad (4)$$

The first term in Eq. 4 accounts for the diffusion and migration of defects throughout the film, as proposed by Chao *et al.*⁹, and the second term, which predominates at higher frequencies, is related to the interfacial reactions¹⁰ whose parameters R_∞ , R_0 and τ depend on the potential.

Taking into account the ohmic contribution R_Ω , the total impedance at potentials preceding the oxygen evolution region is given by:

$$Z_T = R_\Omega + \frac{Z_C Z_I}{Z_C + Z_I} \quad (5)$$

where Z_C and Z_I correspond to Eqs. 2 and 4.

Optimum-fit results using this model are shown in Fig. 3.

Experimental impedance diagrams measured at potentials in the oxygen evolution reaction range were simulated (Fig. 4) in terms of the theoretical transfer function presented in Eq. 1, where Z_C and Z_I correspond to the contri-

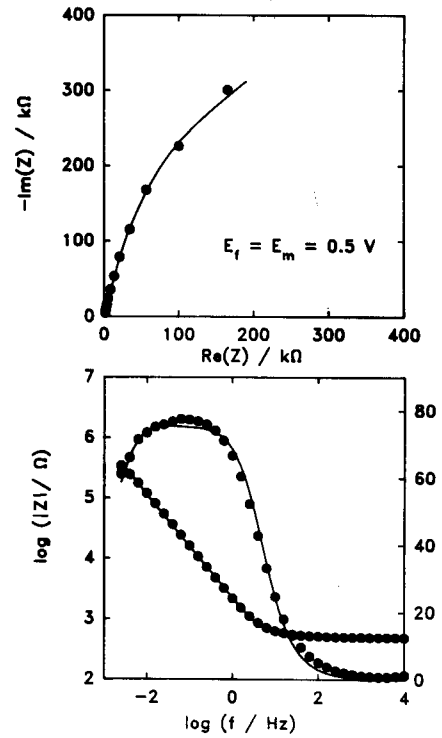


Figure 3. Simulated and experimental impedance diagrams, at $E_m = 0.5$ V, of Co electrodes passivated at 0.5 V.

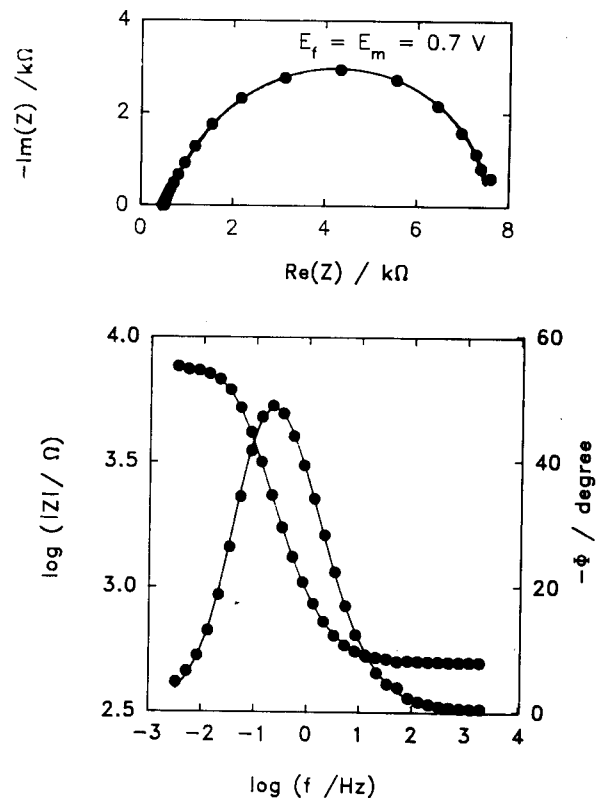


Figure 4. Simulated and experimental Nyquist and Bode diagrams, at $E_m = 0.7$ V, of Co electrodes passivated at 0.7 V.

butions described above and Z_O is assumed to behave like a resistive component, i.e., $Z_O = R_O$.

Figure 5 shows C vs. E_f plots resulting from values obtained by non-linear fit procedures. In the potential range of 0.5 V to 1 V capacitance values on the order of 10^{-4} F cm^{-2} were found, whereas at approximately 0.4 V a sudden transition to values of about 10^{-5} F cm^{-2} is evident.

C^{-2} vs. E_m plots corresponding to the oxide film produced at $E_f = 0.4$ V are depicted in Fig. 6. It is worth noting that only the oxides formed at $E_f < 0.4$ V exhibit a nearly Mott-Schottky type dependence of C on the potential. Furthermore, at $E_f > 0.5$ V the capacitance is independent of E_m . Therefore, it can be concluded that a change in the oxide composition occurs at E_f more positive than 0.4 V, with these Co oxides behaving like dielectric layers of nearly constant thicknesses. Thin semiconductor layers exhibiting high values of the Debye length, L_D , can give rise to this type of dependence of C on the potential¹¹. Changes in the oxide composition have also been reported from ellipsometry measurements³, which led to the conclusion that an oxide layer of nearly constant thickness is produced on Co in neutral borate buffers at potentials more positive than 0.5 V.

Figure 7 shows a Tafel type diagram corresponding to the charge transfer reaction of the redox couple $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ on a Co electrode passivated at $E_f = 0.6$ V. The potential of a zero current is coincident with the normal equilibrium potential of the redox couple, $E_{\text{redox}} = 0.23$ V. According to Fig. 7, the value of the cathodic transfer coefficient approaches $\alpha_c = 0$, and the anodic limiting current resembles similar data corresponding to Pt electrodes. Thus, this electrochemical behavior can be assigned to a process under diffusion control in solution.

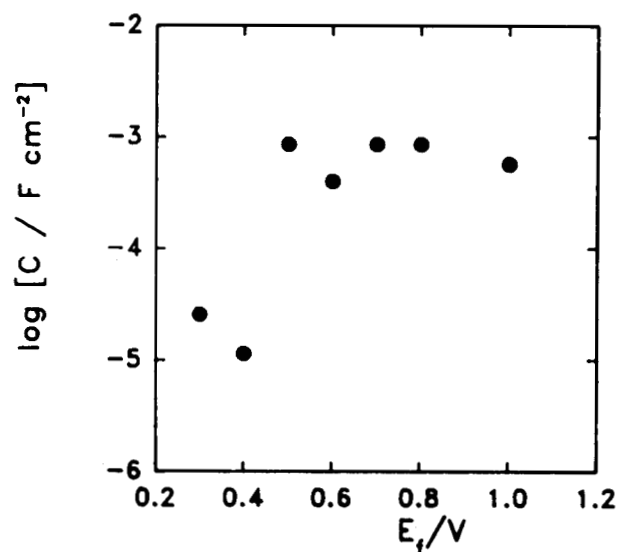


Figure 5. $\log(C)$ vs. E_f plot corresponding to Co electrodes passivated in 0.1 M H_3BO_3 + 0.05 M $\text{Na}_2\text{B}_4\text{O}_7$.

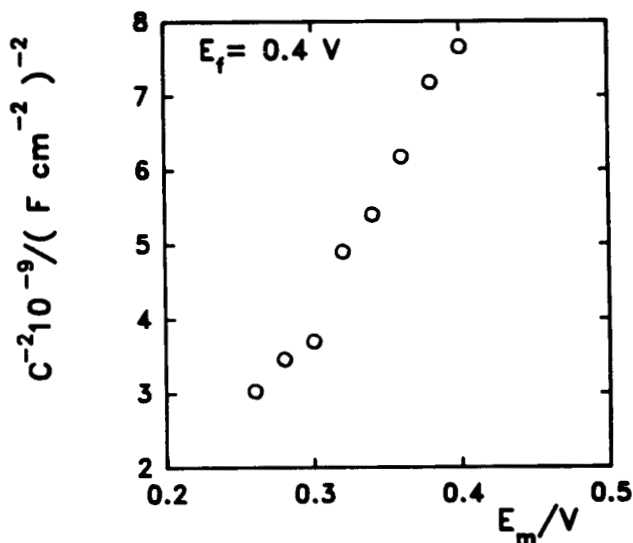


Figure 6. Mott-Schottky plot of Co passive layers formed at $E_f = 0.4$ V.

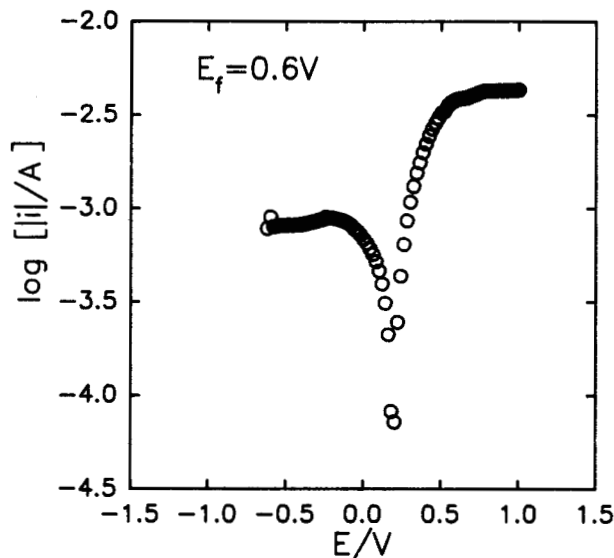


Figure 7. Tafel type plot corresponding to the charge transfer reaction of the redox couple $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ on Co electrodes passivated at $E_f = 0.6$ V.

A charge transfer mechanism involving the valence band seems to be compatible with a Tafel diagram like the one depicted in Fig. 7, although more experimental data are required.

Conclusions

The impedance spectra of Co passive layers can be interpreted in terms of two parallel contributions associated with both the electronic and the ionic currents. The first term is related to charging processes and to charge transfer reactions where the species in solution participate. The second contribution accounts for the base metal dissolution coupled to the ionic transport across the film.

The electronic properties of oxide layers formed at $E_f < 0.5$ V differ from those of oxides produced at more positive potentials. The former behave like n-type semiconductors, while the latter are found to be similar to dielectrics or very thin semiconducting films, L_D probably being smaller than the oxide thickness.

Acknowledgments

This research project was financially supported by the Consejo Nacional de Investigaciones Científicas y Técnicas, the Comisión de Investigaciones Científicas de la Provincia de Buenos Aires, the Fundación Antorchas, and the CNPq. Part of the equipment used in the present work was provided by the DAAD and the Alexander von Humboldt-Stiftung.

References

1. N. Sato and T. Ohtsuka, *J. Electrochem. Soc.* **125**, 1735 (1978).
2. G.T. Burstein and D.H. Davies, *Corros. Sci.* **20**, 989 (1980).
3. K. Kudo, N. Sato and T. Ohtsuka, *Passivity of Metals* (R.P. Frankenthal and J. Kruger, eds., The Electrochemical Society Inc., Princeton N.J., 1978), p. 918.
4. G. Larramona and C. Gutierrez, *J. Electroanal. Chem.* **293**, 237 (1990).
5. G. Simmons, E. Kellerman and H. Leidheiser, *J. Electrochem. Soc.* **123**, 1276 (1976).
6. J.R. Vilche, K. Jüttner, W.J. Lorenz, W. Kautek, W. Paatsh, M.H. Dean and U. Stimming, *J. Electrochem. Soc.* **136**, 3773 (1989).
7. U. Köning, P. Meisterjahn and J.W. Schultze, *Werkstoffe und Korrosion* **42**, 179 (1991).
8. E.B. Castro and J.R. Vilche, *Electrochim. Acta* **38**, 1567 (1993).
9. C.Y. Chao, L.F. Lin and D.D. Macdonald, *J. Electrochem. Soc.* **129**, 1874 (1982).
10. R.D. Armstrong and K. Edmonson, *Electrochim. Acta* **18**, 937 (1973).
11. S.U.M. Khan and W. Schmickler, *J. Electroanal. Chem.* **108**, 329 (1980).