

SOME PROBLEMS RELATED TO THE REDUCTION CHARGE IN POTENTIODYNAMIC STUDIES OF PASSIVATING FILMS

S.R. BIAGGIO, N. BOCCHI and C.V. D'ALKAINE

Grupo de Eletroquímica - Depto. Química

Universidade Federal de São Carlos-Cx. P. 676

13560 - São Carlos, SP., BRAZIL

Linear sweep voltammetry has been extensively employed in metallic-surface passivating studies¹. It has been used not only aiming at a qualitative view of the studied system, but also aiming at quantitative results, when associated to a passivating film growth model.

Although there are some models applied to potentiodynamic results²⁻⁵, most of them present mathematical relationships involving peak current-density (i_p), peak potential (E_p) and sweep rate (v), while the charge density (q) has not been analyzed systematically. The present work aims to present and analyze charge density results for passivating films grown on tin and zinc electrodes in different aqueous media.

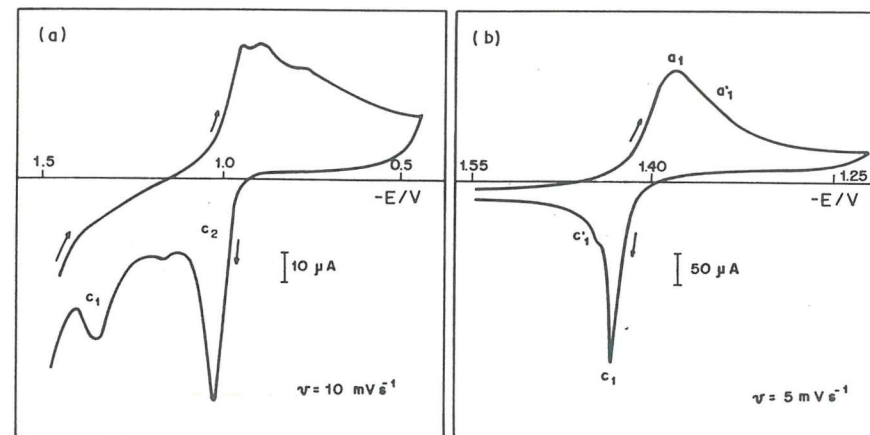


Figure 1. Voltammograms for: a) Sn electrode in $1.0 \text{ mol l}^{-1} \text{ NaClO}_4/1 \times 10^{-3} \text{ mol l}^{-1} \text{ NaOH}$; b) Zn electrode in $1.0 \text{ mol l}^{-1} \text{ NaCl}/5 \times 10^{-2} \text{ mol l}^{-1} \text{ NaOH}$. Reference electrode:NCE; solutions deaerated with N_2 ; T:298K

Figure 1 shows typical voltammograms for tin and zinc electrodes in slightly alkaline solutions; the experimental procedures involved were described elsewhere^{6,7}. Qualitative analyses allowed to conclude that, for the tin electrode, peaks c_1 and c_2 correspond to the reduction processes of Sn(II) in $\text{SnO} \cdot x\text{H}_2\text{O}$ and Sn(IV) in $\text{SnO}_2 \cdot y\text{H}_2\text{O}$, respectively⁶. For the zinc electrode, peaks a_1/c_1 and a_1'/c_1' (the "prime" superscript refers to different stoichiometries and hydration degrees of the oxide)⁷. The anodic peaks for the tin voltammogram are superimposed; therefore, it is convenient to analyze the passivating process through their reduction peaks. To do that the films should be grown in the same anodic conditions ($v_a = \text{constant}$), recording the reduction peaks for different cathodic sweep rates (v_c). It is also important to analyze the total anodic and cathodic-charge ratio (q_t^a/q_t^c), since it allows one to infer about other processes occurring simultaneously with the oxidation and/or reduction of the passivating films. Figure 2 shows the ratio q_t^a/q_t^c obtained for the tin and zinc electrodes in the respective electrolytes for different NaOH concentrations. The constance of the q_t^a/q_t^c values with the OH^- concentration in region I points out that no dissolution process occurs in this pH range. On the

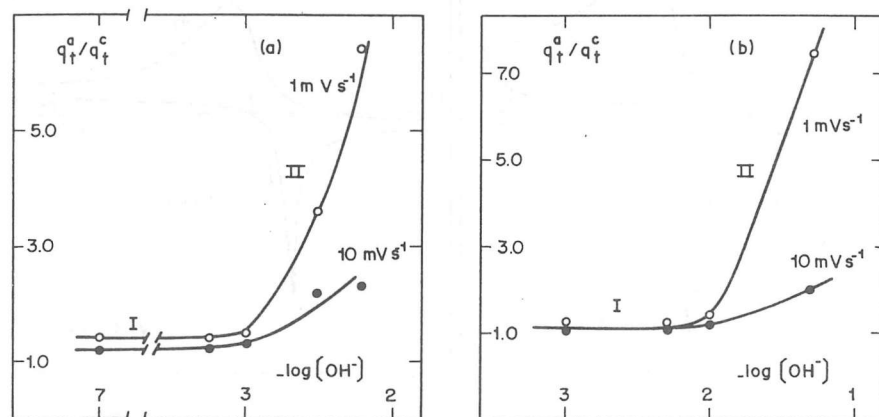


Figure 2. Dependence of the anodic and cathodic-charge ratio on the NaOH concentration (in mol l^{-1}), obtained from voltammograms for $v_a = v_c$: (a) Sn and (b) Zn electrodes.

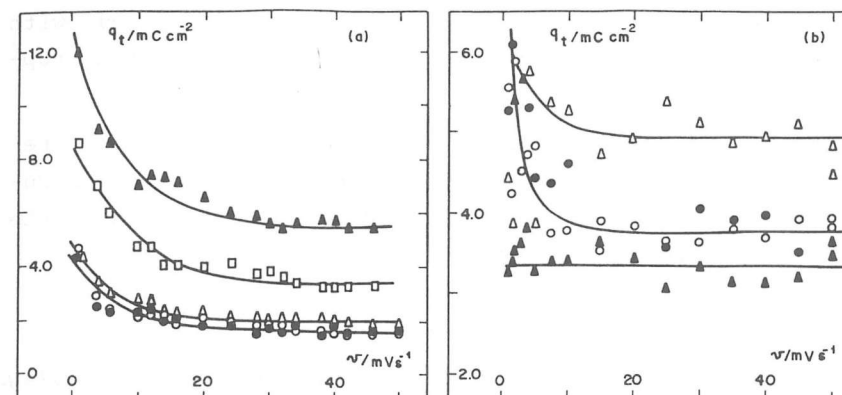


Figure 3. Dependence of the total charge on the sweep rate for:
a) peak c_2 for Sn electrode in O neutral, \bullet 6×10^{-4} , Δ 1×10^{-3} , \square 3×10^{-3} , \blacktriangle 6×10^{-3} mol l^{-1} NaOH;
b) peak c_1 for Zn electrode in O 1×10^{-3} , \bullet 5×10^{-3} , Δ 1×10^{-2} , \blacktriangle 5×10^{-2} mol l^{-1} NaOH.

other side, the fact that $q_t^a/q_t^c > 1$ in the same region points out that another phenomenon is occurring and, therefore, must be taken into account. This becomes more evident when the dependence of the q_t^c on v_c for the films grown always in the same conditions (Figure 3) is analyzed. Contrarily to what would be expected, i.e. $q_t^c = \text{constant}$, q_t^c decreases as v is increased for all the OH^- concentrations, even for those of region I of Figure 2. These results seem to indicate a breakdown process of the passivating films when the current, during the cathodic potential sweep, is inverted. The rupture of the passivating films has been already pointed out as one of the processes which lead to transpassivation⁸. In this case, the rupture is understood as occurring when the electrostriction tension exceeds the critical rupture tension. In the present case, the rupture phenomenon could be thought as due to the internal tension of the film, since the electric field passes through zero during the cathodic sweep. In other words, the electrostriction tension would be decreased below a critical value, when the internal tension due to

the higher partial molar volume of the film (compared with the one of the metal) would prevail, thus causing the rupture.

Returning again to the analysis of Figure 2, region II points out that, in the correspondent OH^- concentrations, dissolution, rupture and/or more growth of the film with posterior rupture processes could exist.

REFERENCES

1. D.D. MacDonald, *Transient Techniques in Electrochemistry*, New York, Plenum, 1977, p.290.
2. S. Srinivasan and E. Gileadi, *Electrochim. Acta*, **11**, 321 (1966).
3. A.J. Calandra, N.R. de Tacconi, R.Pereiro and A.J.Arvia, *Electrochim. Acta*, **19**, 901 (1974).
4. H. Kozłowska and B.E. Conway, *J. Electroanal. Chem.*, **95**, 1 (1979).
5. C.V. D'Alkaine and J.M. Cordeiro, In: *Advances in Lead-Acid Batteries* (K.R. Bullock and D. Pavlov, Eds.). Pennington, The Electrochemical Society, 1984.v.84-14 p. 190-200.
6. S.R. Biaggio, *Ph.D.Thesis*, São Paulo University, IFQSC, São Carlos (1986).
7. N. Bocchi, *Ph.D.Thesis*, *ibid*, (1986).
8. N. Sato, *Electrochim. Acta.*, **16**, 1683 (1971).

ELECTROCHEMICAL STUDY OF ISOCYANIDE DERIVATIVES OF FERROCENE AND OF THEIR COMPLEXES WITH THE $\{\text{Cr}(\text{CO})_5\}$ CENTRE

T. EL-SHIHI, F. SIGLMÜLLER, R. HERRMANN

Organisch-Chemisches Institut der Technischen Universität
München, Lich.4, D-8046 Garching, F.R.G.

M.F.N.N. CARVALHO and A.J.L. POMBEIRO*

Centro de Química Estrutural, Complexo I,
Instituto Superior Técnico, Av. Rovisco Pais,
1096 Lisbon Codex, Portugal

INTRODUCTION

Within our broad interest on the study of the redox and electronic properties of coordination compounds by electrochemical methods,⁽¹⁾ we embarked upon the investigation of the redox behaviour of series of ferrocene derivatives, FcX [where Fc stands for $\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\eta^5\text{-C}_5\text{H}_4\text{X})$], with different types of substituents (X);⁽²⁾ the latter may ligate an aromatic ring through, for instance, a sp^3 or an unsaturated sp^2 hybridized C atom, and some homo- and hetero-annular disubstituted ferrocenes have also been investigated. However, in this preliminary communication, we wish to report the results we have obtained with a type of substituents we are particularly interested⁽³⁻⁵⁾ from a coordination point of view: that with the isocyano functional group.

In the ferrocene derivatives under study, CNR [**1**; $\text{R}=\text{Fc}$ (**a**), CH_2Fc (**b**) or $\text{CH}(\text{Men})\text{Fc}$ (**c**) where $\text{Men}=(1\text{R}, 2\text{S}, 5\text{R})$ -2-isopropyl-5-methylcyclohexyl], the isocyano group is prone to coordination to a metal centre and the derived ferrocenyl-isocyanide complexes $[\text{Cr}(\text{CO})_5(\text{CNR})]$ (**2**) can be prepared by reaction of the former with $[\text{Cr}(\text{CO})_5(\text{thf})]$.