

The kinetic mechanism of the PbO_2 discharge of the lead/acid positive plates

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Abstract

A kinetic mechanism is proposed for the discharge reaction of positive plates of lead/acid batteries. It includes several steps occurring at different times in each part of the electrode surface. The mechanism takes into account solid-state reactions at the beginning followed by a dissolution/precipitation mechanism. On this basis, experimental data are presented to show that the mechanism implies an intermediate stage in which the product behaves as a continuous film. Finally, data are presented showing that, up to this intermediate stage, the reaction product is a form of PbO that will react later with H_2SO_4 to give PbSO_4 .

Keywords: Lead/acid batteries; Reaction mechanisms; Positive plate discharge; Passivity; Solid-state reactions; Dissolution/precipitation mechanism

1. Introduction

In the past, the kinetic discharge mechanism of the positive and negative plates of lead/acid batteries has been understood on the basis of the double lead sulfate theory proposed by Gladstone and Tribe [1]. For the case of negative plates it seems that the lead sulfate continues to be the product resulting directly from the discharge [2,3]. Nevertheless, the traditional view for the positive plate [2,4] is changing [5–8].

If the positive plates are initially fully charged there is only PbO_2 in the plate. The first step of its discharge must be the nucleation of the discharge product demonstrated by the peak at the beginning of the galvanostatic discharge of a fully charged plate.

A second step will be the growth of the three-dimensional (3D) nuclei of the discharged product. Due to the nucleus ionic structure a reasonable overpotential inside of each one, to force an ionic current through each nucleus, will be required and, thus, promoting its growth. There will be higher current densities at the thinner regions of the nucleus (for a simple hemi-spherical nucleus, at its borders). The non-homogeneous current density distribution on the surface of each nucleus will give rise to a fast transformation of the 3D into a 2D nucleation. Finally, this will produce a continuous film as schematically shown in Fig. 1. All the nucleation based on solid ionic structures are not yet explained by the nucleation theories [9,10]. These theories are essentially developed for nuclei with a high electron conductivity.

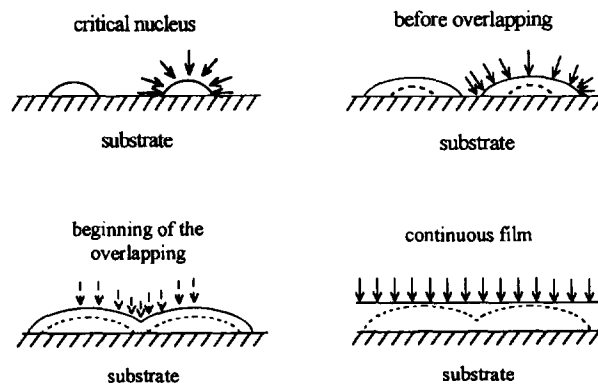
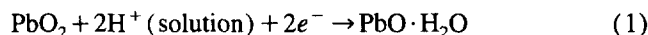


Fig. 1. Schematically representation of the growth of hemispherical nuclei having an ionic structure. The representation takes into account that the ohmic overpotential through each nucleus will give rise to a non-homogeneous distribution of the current density on its surfaces. This non-homogeneous distribution is represented by the number of arrows.

The third step is the growth of the continuous film. Under the situation of a field-assisted growth, the product cannot be PbSO_4 [5]. The reason is clearly shown in Fig. 2. Being considered as a reduction of PbO_2 , the field inside the film will be against the entrance of the SO_4^{2-} ions, but O^{2-} will be able to migrate to the solution side or H^+ migrates in the opposite way



The first product of the PbO_2 discharge must be related to PbO .

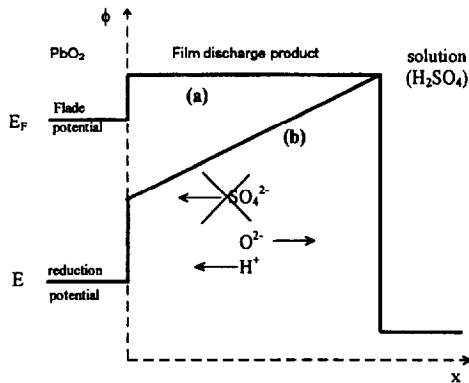


Fig. 2. Inner potential difference (ϕ) vs. position at the PbO_2 /film of the discharge/solution interface: (a) at the Flade potential (zero current density), and (b) at a given potential during a discharge (cathodic current density).

The fourth stage comes from the fact that the plate is a porous electrode with a high inner surface, where the reaction takes also place. Due to this fact, as the film is thicker in a given region, the current will look for another area having no film or a thinner one. As a consequence the field inside the film will also fall down. Then, the chemical reaction with H_2SO_4 will become possible, because the field is not anymore inhibiting the entrance of the SO_4^{2-} ions. This will be the true reaction that produces the PbSO_4 . This process will be repeated at different times and positions inside the plate. In such a way, that the discharge reaction will move from the regions near to the plate surface to the inner regions.

The partial volume of the formed PbSO_4 will be about two times that of the PbO [11]. The PbSO_4 film will be disrupted to very small particles with a high tendency to recrystallization. The rupture and the recrystallization is the fifth and last stage. This last stage of recrystallization has been described in several papers explaining the dissolution/precipitation mechanisms [2,4]. It must be considered that, for any ex situ measurement, during the preparation of the samples recrystallization may occur over the entire plate surface, because the cut-off of the polarization and the time is sufficient to allow the lead sulfate to recrystallize. Microstructures produced by dissolution/precipitation mechanisms can be observed by scanning electron microscopy (SEM) [2,4].

All these stages make that the reaction is very complicated because the electrode behaves as a multiple electrode. Therefore, the inner potential difference and the current density at each position and time, during a galvanostatic discharge, changes continuously on each point of the electrode surface.

The present work will show the validity of two aspects of the proposed mechanism: (i) an intermediate stage gives rise to a continuous film, and (ii) PbO is an intermediate. The problem of the reaction between the PbO and the H_2SO_4 was avoided by the substitution of the acid solution by distilled water, just before the cut-off of the discharge current.

2. Experimental

The experiments were performed on small portions of actual automotive battery plates. These portions were consti-

tuted by the smaller rectangular area of the plates, delimited by the rods of the grid. They were cut from the plates before the formation process. The rod of the grid was 1.7 mm diameter. The geometrical area of the rectangles was about 1 cm^2 ($1.9 \text{ cm} \times 0.55 \text{ cm}$). Then, all the values per unit area will be given taken into account both sides of the rectangles (2 cm^2) due to the experimental set-up, which will be discussed further. The amount of the PbO and tribasic lead sulfate paste (density 4.1 g cm^{-3}) was about 0.7 g for each positive electrode.

The experimental set-up was a positive plate between two negative plates, all them having identical geometrical areas. The distance between the positive and negative plates was 1 cm in order to keep the acid concentration in the solution constant during the experiments. This set-up can be seen in Fig. 3. The volume of the solution in the cell was 200 cm^3 .

After the assembly, the positive and negative plates were formed in a 0.86 M H_2SO_4 solution under a current density (i_f) of 5.0 mA cm^{-2} (14.3 mA g^{-1} of the original paste) during 48 h. The obtained amount of PbO_2 was about 0.45 g for each plate.

In the present work, one assembly of electrodes was used for each experimental point in the plots. After formation, each electrode was submitted to five stabilization cycles. Stabilization was done under a charge of $2.5 \text{ mA cm}^{-2}/100 \text{ min}$ and under a discharge of $10 \text{ mA cm}^{-2}/20 \text{ min}$, controlled automatically. After stabilization, the electrodes were maintained at 1.8 mA cm^{-2} (8.0 mA g^{-1} of active material) as a floating current density, until the moment of the measurement.

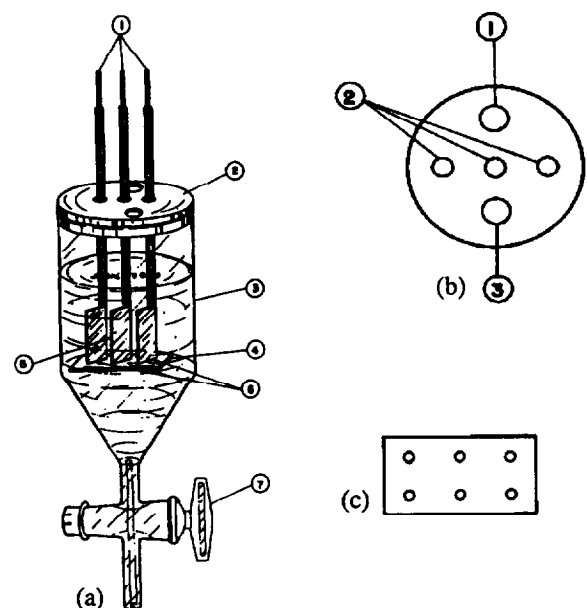


Fig. 3. (a) General view of the experimental set-up: (a-1) connections of the two negatives and the positive plates; (a-2) cover of the cell; (a-3) glass cell; (a-4) polypropylene support for the electrodes; (a-5) positive electrode; (a-6) two negative electrodes; (a-7) stopcock for the acid withdrawal. (b) Details of the cell cover: (b-1) hole for introduction of the water; (b-2) holes for the connections of the electrodes; (b-3) hole for the reference electrode. (c) Details of the polypropylene support assuring rigidity to the plates.

Finally, before the beginning of the potentiostatic or a galvanostatic discharges, the electrodes were maintained, at least for 1 h, at an anodic potential (1.35 V) or a galvanostatic anodic current density (1.8 mA cm^{-2}), respectively. This procedure was adopted to assure a completely charged electrode and at the same time, to have a small oxygen evolution.

Substituting H_2SO_4 by water, during the galvanostatic discharges, the process continued without stopping the discharge current density (i_d). The water was introduced through a tube connected to the remainder hole (see Fig. 3) on the cell cover. At the same time, the acid was drained out at the bottom of the cell. Care has been taken that the electrodes always remained immersed. The operation was considered finished when the liquids coming out from the cell did not present any visible reaction of the SO_4^{2-} anion with a 0.5 M BaCl_2 solution. However, this test was continued for at least 10 min more. Then, i_d was stopped. The whole operation took 40 min.

The mass of the partially discharged active mass (PDAM) was determined by the mass difference between the whole washed and dried plate and the grid. The SO_4^{2-} content in each PDAM was determined by the BaSO_4 gravimetric method. This was done by dissolving portions of the PDAM in a concentrated HCl solution and precipitating with a 0.5 M BaCl_2 [12]. The results are given as the average of three measurements for each PDAM.

All the galvanostatic and potentiostatic measurements were controlled by a PARC Model 173. The equipment was able to maintain the i_d even when the acid solution was completely replaced by the low-conductivity water during the galvanostatic discharges. Also, this equipment was able to maintain the selected electrode potential (E_d) during the potentiostatic discharges.

The working solution was 4.6 M H_2SO_4 and the reference electrode $\text{Hg}/\text{Hg}_2\text{SO}_4, \text{H}_2\text{SO}_4$ (4.6 M).

3. Results and discussions

Due to the proposed objectives, the present discussion will be divided into two parts. In the first part it will be indirectly shown that, during the discharge of an actual positive plate, the discharge product passes through a stage that can be described as a continuous film. In the second part it will be shown that the first product of the discharge is related to a form of $\text{PbO} \cdot \text{H}_2\text{O}$.

3.1. Continuous film

The passivity theories [13] for the growth of a passivating continuous films, allows to show the evolution of the ionic specific resistivity inside a growing film. The theory, for different growth conditions (voltammetric, galvanostatic or potentiostatic), always shows that during film growth the ionic specific resistivity (ρ_i) of the film, during the transient, passes through a minimum or a flat valley.

As a consequence, in a voltammetric sweep it is usually observed that the current passes through a maximum given rise to a peak. The peak corresponds to the minimum in the ρ_i .

On the other hand, in a galvanostatic experiment the potential will first change fast with time, due to the increase of the thickness and the initial fall down of ρ_i . Then, it will reach a linear increase associated with the minimum or the valley of ρ_i . Finally, at the end of the process, a fast change of the potential due to the new increase of ρ_i will appear.

In a potentiostatic experiment, a maximum charge density (q^{max}) is attained because when the ρ_i increases, after the valley, the current becomes so small that the charge becomes constant.

The most interesting point is when the variation of q^{max} is considered as a function of the potentiostatic discharge overpotential (η). From a theoretical point of view [14], if there is the formation of a continuous film, a maximum in the q^{max} versus η plots can be observed.

In this sense, recent experiments of potentiostatic discharges of porous electrodes have shown that the maximum charge of a discharge (q_d^{max}) plotted against the discharge overpotential (η_d), also presents a maximum. This is the case for porous iron electrodes [15] and also for porous $\text{NiO} \cdot \text{OH}/\text{Ni}(\text{OH})_2$ electrodes [16], both in KOH solutions.

Thus, if there is a reaction stage with the formation of a continuous film in the positive plate then, there must be a maximum in the q_d^{max} versus η_d plots during potentiostatic discharge.

The Fig. 4 shows the i_d versus time plots at different η_d for the positive plates of lead/acid batteries under potentiostatic discharges.

The variation of the charge density (q_d) as a function of time is plotted in Fig. 5 for the same experiments presented in Fig. 4. Fig. 5 shows the presence of maxima in the charge

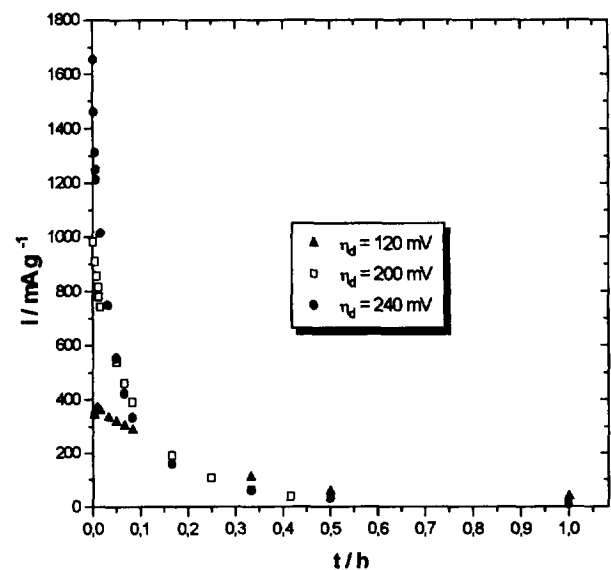


Fig. 4. Current densities (i_d) vs. time (t) for the initial part of potentiostatic discharges of positive plates in 4.6 M H_2SO_4 solution: (▲) $\eta_d = 0.12$ V; (□) $\eta_d = 0.20$ V, and (●) $\eta_d = 0.24$ V.

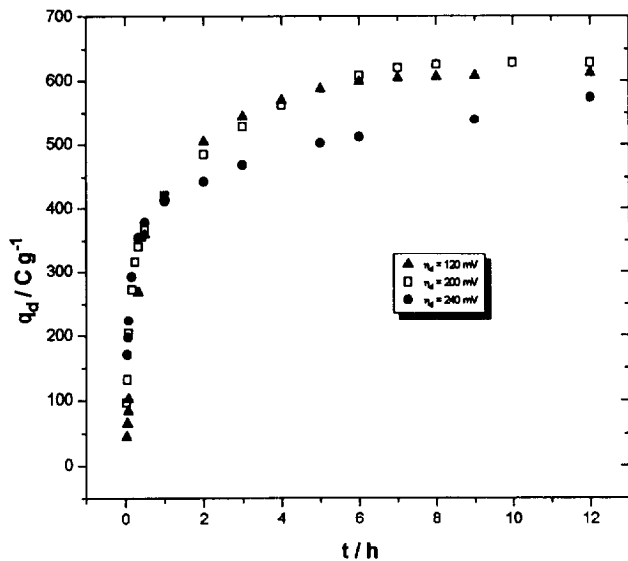


Fig. 5. Charge density of discharge (q_d) vs. time (t) for the same experiments presented in Fig. 4: (\blacktriangle) $\eta_d = 0.12$ V; (\square) $\eta_d = 0.20$ V, and (\bullet) $\eta_d = 0.24$ V.

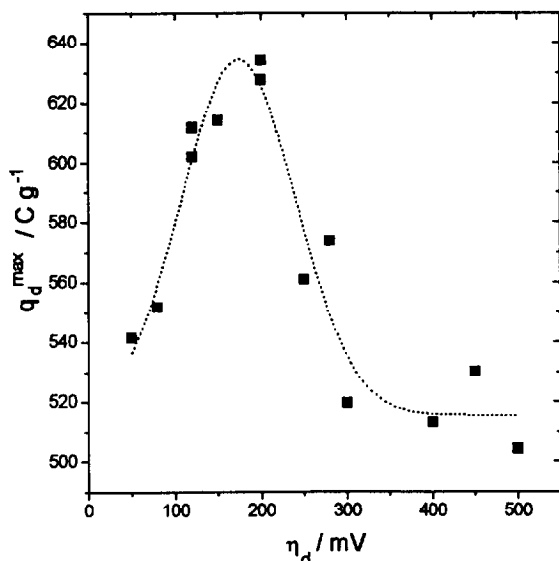


Fig. 6. Representation of the maximum charge density of a discharge (q_d^{\max}) as a function of the overpotential for a potentiostatic discharge (η_d) at a 4.6 M H_2SO_4 concentration.

density of the discharges (q_d^{\max}), as was suggested by the theoretical approach.

q_d^{\max} versus η_d plot is presented in Fig. 6. It is evident that the q_d^{\max} passes through a maximum as foreseen by the theory for the growth of a continuous film. This is evident in the sense that, as the result of the nucleation and growth of the nuclei, there is a stage of formation and growth of a continuous film.

3.2. PbO as an intermediate

Fig. 7 shows the plots of the equivalent charge density ($q_{\text{PbSO}_4, \text{exp}}$) versus the charge density of the discharge, for galvanostatic discharges. The $q_{\text{PbSO}_4, \text{exp}}$ is the equivalent

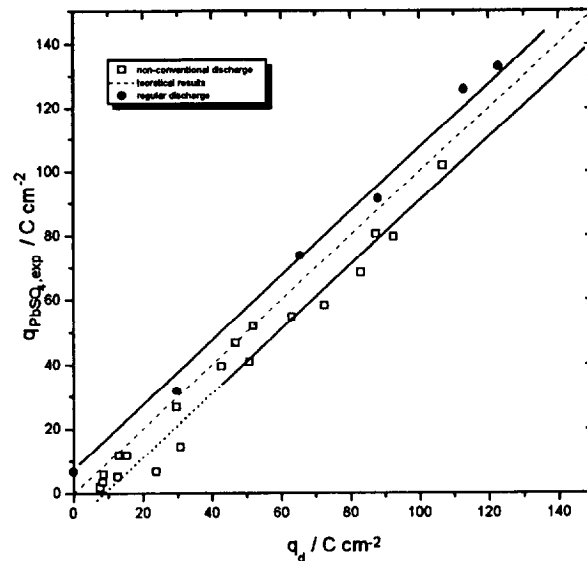


Fig. 7. Equivalent charge density ($q_{\text{PbSO}_4, \text{exp}}$) corresponding to the experimental determined PbSO_4 mass, measured as SO_4^{2-} ions in the active mass, vs. the charge density of the discharge. (\bullet) regular discharge; (\square) non-conventional discharge, and (---) theoretical results.

charge density that corresponds to the experimental determined mass of PbSO_4 . This last one was measured as SO_4^{2-} ions in the active mass. Each result corresponds to a different time of discharge and to different plates.

The data in Fig. 7 are representing two cases. The first one, when there is no elimination of the H_2SO_4 from the solution (regular experiments). The second one when, before to cut off the i_d , the H_2SO_4 solution is replaced by water (non-conventional experiments). For comparison, the dashed straight line in Fig. 7 represents the results as if all the charge has been used to give only PbSO_4 (theoretical results).

It is clearly seen in the Fig. 7 that the plotted results for the regular experiments present a constant shift to higher values than the theoretical ones. This shows that, as it is well known [17], at the end of the formation process of a plate, there is always an amount of lead sulfate that has not been oxidized. This amount will depend on the formation conditions.

Let now to consider Fig. 7 showing the results obtained when the H_2SO_4 is replaced by distilled water, before the cut-off of the current. In this case, the amount of PbSO_4 equivalent charge ($q_{\text{PbSO}_4, \text{exp}}$) presents a constant shift to values that are lower than those theoretically obtained. The amplitude of the experimental error is lower than the shift of these results with relation to the normal experiments. The difference between the values of the $q_{\text{PbSO}_4, \text{exp}}$ from the regular experiment and that from the non-conventional, which is also practically constant, was 16.6 C cm^{-2} . On the other hand, it must be considered that during the replacement of H_2SO_4 by water, some amount of PbO will be formed (mainly at the end of the replacement). Therefore, one should consider that the detected difference does not come from this fact.

Considering that during all the time of the H_2SO_4 replacement by water only PbO (which will give a maximum contribution by this way) has been formed, it is possible to

calculate the maximum acceptable value for the difference between the $q_{\text{PbSO}_4, \text{exp}}$ of the regular and the non-conventional experiments. Since the time for the replacement is 40 min and the used i_d is 4 mA cm^{-2} , the corresponding equivalent charge in $q_{\text{PbSO}_4, \text{exp}}$ would be 9.6 C cm^{-2} . This result will be an overestimation of the actual one because during some time, at the beginning of the replacement, there will be H_2SO_4 in the pores and micropores of the plate. Even so, this result is lower than the found difference between the experiments (16.6 C cm^{-2}). Then, the observed difference must have another explanation. The discharge of PbO_2 must produce, during the nucleation, the overlapping of the nuclei and the growth of the continuous film, the formation of PbO and not of PbSO_4 . The PbSO_4 will be formed only after the end of the third step of the proposed mechanism.

The low value for the constant difference between the regular discharge and that eliminating the acid, must be due to the fact that the only parts that will have no sulfate will be those areas that were intervening in the first, second or third steps of the discharge. This is because the field inside the film in these areas is inhibiting the entrance of the SO_4^{2-} ions. Those areas in the fourth and fifth steps must have sulfate. The detected difference (16.6 C cm^{-2}) must be compared with the total capacity under the same discharge conditions. This total capacity was 115 C cm^{-2} . The areas that are in the first, second or third steps are, then, a very small part of the total area of the micro and macropores. All this is in agreement with the proposed mechanism of the discharges and shows that the reaction mechanism passes through a stage with the presence of PbO .

4. Conclusions

A general model is proposed for the discharge mechanism of the PbO_2 positive plates. It includes several steps:

- (i) the nucleation and the overlapping of the nucleus passing from a 3D to a 2D nucleation;
- (ii) the formation of a layer with a continuous thickness;
- (iii) the growth of this layer and the consequent reduction of the field through it;
- (iv) the reaction with the sulfuric acid after the reduction of the field inside the film and its disruption, and
- (v) the recrystallization of the disrupted film.

On the basis of this proposed general sight about the discharge mechanism, it is shown that this process passes through a stage in which the product is a continuous film. This is done using some aspects of the passivity theories for the continuous film growth under potentiostatic conditions.

On the other hand, the results presented here are clearly indicating that the first product of the discharge of the PbO_2 is some form of PbO . As a consequence, to give the final product (the PbSO_4), this intermediate must react with H_2SO_4 . This will happen only when the field inside the PbO film becomes small enough, due to its thickening and the consequent redistribution of the current.

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References

- [1] J.H. Gladstone and A. Tribe, *The Chemistry of Secondary Batteries*, London, 1883.
- [2] K. Asai, M. Tsubota, K. Yonezu and K. Ando, *J. Power Sources*, 7 (1981) 73.
- [3] C.V. D'Alkaine, M.C. Lopes and A. Carubelli, *J. Appl. Electrochem.*, submitted for publication.
- [4] Z. Takehara and K. Kanamura, *Electrochim. Acta*, 29 (1984) 163.
- [5] C.V. D'Alkaine, *Conf. UNESCO Workshop Theory and Practice of Lead/Acid System, Dresden, Germany, 1991*.
- [6] D. Pavlov, *J. Power Sources*, 42 (1993) 345.
- [7] C.V. D'Alkaine, A. Carubelli, H.W. Fava and A.C. Sanhueza, *J. Power Sources*, 53 (1995) 289.
- [8] C.V. D'Alkaine and L.M.M. Souza, submitted for publication.
- [9] C. Saravanan, P. Sunthar and E. Bosco, *J. Electroanal. Chem.*, 375 (1994) 59.
- [10] B. Bhattacharjee and S.K. Rangarajan, *J. Electroanal. Chem.*, 366 (1994) 271.
- [11] H. Bode, *Lead-Acid Batteries*, Wiley, New York, 1977.
- [12] M.A. Santana, *M.Sc. Thesis*, 1988, Chemistry Postgraduation Program, UFSCar, São Carlos (SP), Brazil.
- [13] C.V. D'Alkaine, *Trends Corr. Res.*, 1 (1993) 91.
- [14] C.V. D'Alkaine and M.N. Boucherit, *J. Electrochem. Soc.*, submitted for publication.
- [15] C. Caldas, *Ph.D. Thesis*, 1995, Material Science and Engineering Postgraduation Program, UFSCar, São Carlos (SP), Brazil.
- [16] M.B.J. Freitas, *Ph.D. Thesis*, 1996, to be submitted to the Chemistry Postgraduation Program, UFSCar, São Carlos (SP), Brazil.
- [17] P.R. Impinnisi, *Ph.D. Thesis*, 1995, Chemistry Postgraduation Program, UFSCar, São Carlos (SP), Brazil.