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Effect of an industrial expander on the discharge process of a lead microelectrode in 4.5 M sulphuric acid

A. LE MEHAUTE
Laboratoire de Marcoussis, Route de Nozay, 91460, Marcoussis, France

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The presence or absence of an industrial expander is shown to produce a difference in the discharge of a lead microelectrode in concentrated sulphuric acid. The expander acts both before and after passivation, and modifies the concentration and relaxation time of Pb(II) soluble reaction intermediates.

1. Introduction

As is well known, expanders are additives currently used in the negative plates of lead-acid batteries. A number of important advantages accrue from the use of these additives, in particular an improvement in the fast discharge capacity under cold conditions, and better general cycling behaviour. Materials currently used are all wood by-products, and their efficacy is not strongly dependent on the nature of the material.

Consequently, only a single type of product was used in this work, in which expander action on the discharge of lead acid batteries under normal operational conditions, (sulphuric acid of specific gravity ~ 1·27, ambient temperature) was examined.

2. Apparatus

Potentiodynamic measurements were conducted using a Tacussel P.R.T. potentiostat and a Tacussel type 10 A potentiodynamic servocontrol. For pulse measurement, a Tacussel G.I.T.P. impulse generator coupled to a Tacussel P.I.T. potentiostat was used. Faradaic impedance was measured by the Lissajou method, using a Tektronix type 3A3 plug-in unit. The sine-wave generator was a Hewlett–Packard model 203A.

The cell was deareated with 'U' grade argon. (G.I.C.). The electrolyte was a 4·5 M sulphuric acid solution in deionized water. The expander solutions contained 0·24 g l^{-1} of Vanisperce C.B. (Borregaard). A 99.999% pure lead bar (Prolabo) in an epoxy resin jacket, polished with successively finer grits of carborundum paper (Knuth Rotor), was used as a working electrode. Before being used experimentally, the lead electrode was polarized cathodically at 200 mV below its equilibrium potential for several minutes. All potentials are given with reference to the Hg/Hg_2SO_4 couple.

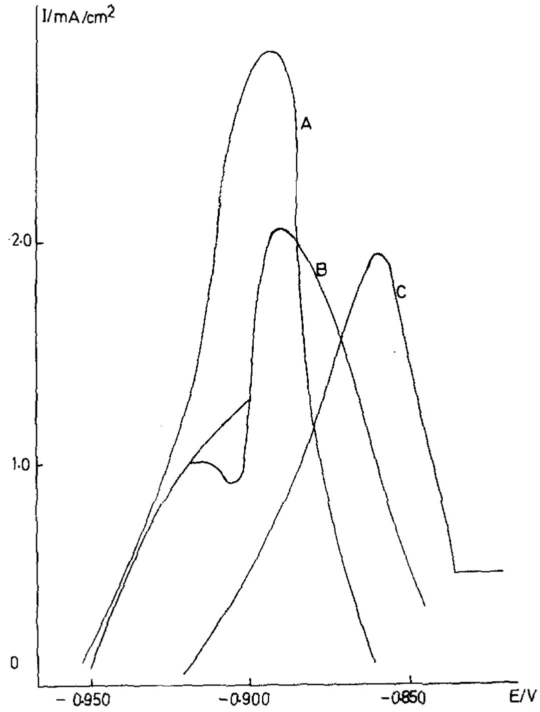
The subscript E is used to indicate the medium containing the expander, the subscript ϕ to indicate the medium without expander.

3. Potentiodynamic discharge of a polished lead electrode under conditions of semi-infinite diffusion

3.1. *Simple potentiodynamic study*

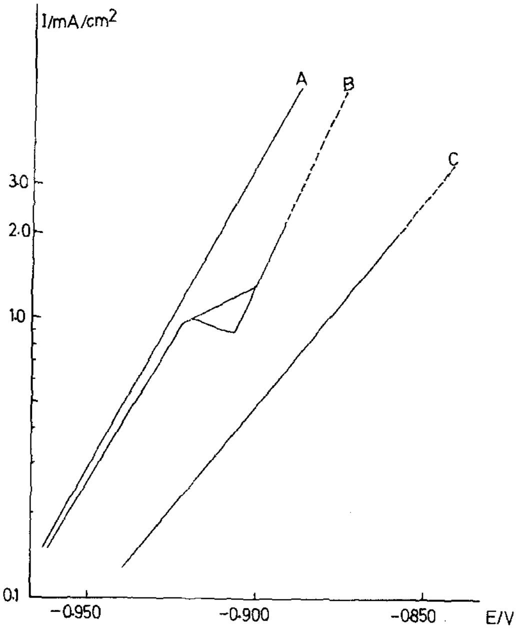
Brennan and Hampson [1–3] observed two separate mechanisms for the oxidation of freshly electropolished lead surfaces using a Tafel slope analysis of potentiodynamic data, confirming the proposals of Archdale and Harrison [4, 5, 9].

According to these authors, a mechanically polished lead electrode is subjected to three-dimensional progressive nucleation at the start of the discharge, whereas electrochemically polished electrodes offer no favoured crystallization sites at the metal solution interface, which constrains the process of nucleation to proceed via a soluble phase. Brennan and Hampson thus associate one of the two mechanisms observed with a process passing through a soluble phase ('dissolution–precipitation'); by extension of the conclusions cited in [4] and [5, 11], the other is a solid-phase



Current-voltage curve showing sweep rate dependence and expander dependence .(A) H_2SO_4 (4.5M) , v=1000mV/mn (B) H_2SO_4 (4.5M),v=200mV/mn .(C) H_2SO_4 (4.5M),expander (0.24g/l), v=200mV/mn . S≈0.67cm^2

Figure 1.



Tafel plot , log i vs potential .(A) H_2SO_4 (4.5M), v=1000mV/mn (B) H_2SO_4 (4.5M) , v=200mV/mn. (C) H_2SO_4 (4.5M) , expander (0.24g/l), v=200mV/mn. S =0.67 cm^2

Figure 2.

process with no soluble Pb(II) intermediate ('nucleation–growth'). The surface redox potentials for the mechanisms are separated by a fixed potential ('nucleation potential') and their respective Tafel slopes are close to 40 and 20 mV dec^{-1} [1].

In our study mechanically polished lead electrodes (apparent area 0·5 cm^2) were potentiodynamically discharged in 4·5 M sulphuric acid.

For potentiodynamic sweep rates greater than 400 mV min^{-1} no special behaviour was observed in the general form of the $I = f(E)$ curve (see Figs. 1 and 2 for linear and logarithmic relationships respectively). The Tafel line for oxidation had a slope of 35 mV dec^{-1}.

For sweep rates less than 400 mV min^{-1}, the phenomenon shown at B appeared on the oxidation curve, i.e. an inflection or intermediate peak, presenting a negative resistance over a range of several millivolts (Figs. 1 and 2). This phenomenon occurs at the discontinuity between the Tafel slopes, which generally shift from 35 to close to 25 mV dec^{-1}, and is located at a potential of about −900 mV.

The above measurements therefore corroborate those in [1], though under slightly different experimental conditions. Two Tafel slopes were observed, which may be attributed to two different mechanisms; in addition, a nucleation potential with current characteristics resembling those previously reported (I(nucleation) ~ 1 mA apparent cm^{-2} [1]) occurred.

3.2. *Polarography using the ring-disc electrode*

Extending the study of phenomenon B, we analysed the response of a high-purity lead ring-disc electrode under a slow potentiodynamic sweep (100 mV min^{-1}), with forced convection (1200 rpm) [6]. Surface preparation involved mechanical polishing, oxidation at 50 mA in a 10 % solution of perchloric acid in deionized water, followed by rinsing in alcohol to remove traces of organics.

In this hydrodynamic regime (1200 rpm), a time lapse (between 15–20 s) appeared between the maximum current observed at the ring and at

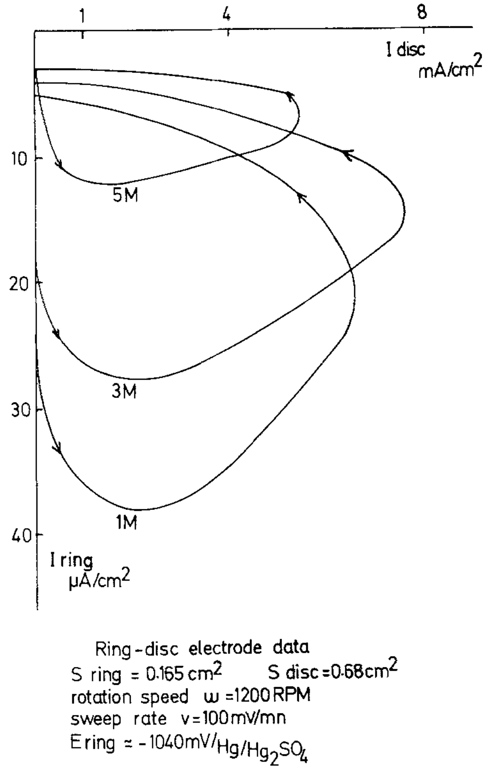


Figure 3.

the disc (Fig. 3). The peak concentration for soluble intermediate Pb(II) species preceded the disc peak.

This maximum concentration was an inverse function of the sulphuric acid concentration: for concentrations close to 5 M, the degree of supersaturation was greater than 4 at the reduction potential imposed at the ring (1040 mV), as shown in Fig. 3. In consequence, the oxidation curves observed under potentiodynamic and forced convection conditions must be subject to variable concentration polarization during the course of discharge.

In the presence of the expander, the ring current was below the detection limit of our apparatus [6]. At the same time, we observed that phenomenon B disappeared (Figs. 1 and 2), and a simple Tafel slope of about 40 mV dec^{-1} was recorded. In contrast, Brennan and Hampson observed a break in the slope with the anodic displacement of the nucleation potential.

The following relationship can be proposed:

$$Q_E > Q_\phi \qquad (1)$$

Where

$$Q_E = \int_{E_0}^{E \text{ nucleation}: E} i\,dt;$$

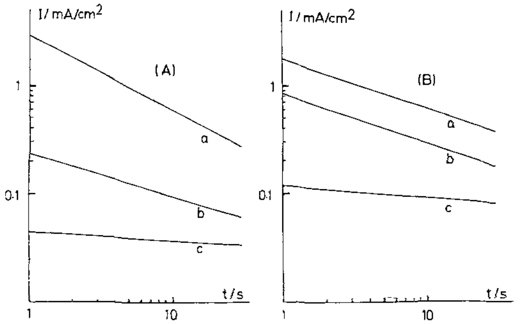
$$Q_\phi = \int_{E_0}^{E \text{ nucleation}} i\,dt$$

assuming that possible sequestration and complexing effects are neglected. The observed delay in crystallization can be attributed to a global reduction in the crystallization rate when an expander is present, or to a geometric limitation of mass transfer, or to a modification of the properties of the diffusion layer. We have attempted below to show which of these various alternatives predominates.

3.3. *Concentration of intermediate species at the interface after potentiodynamic discharge*

The observations given in the preceding section indicate the degree of local supersaturation of free soluble intermediate species as the limiting parameter in discharge. Crystallization models already published [4, 10] can be used in this connection: these show in particular that crystallization must be geometrically delocalized under semi-infinite linear diffusion conditions. Specifically, Pavlov [10] has shown that in a dissolution–precipitation process, opposing gradients of soluble species and of ions leading to insoluble products (sulphate) are created, and therefore that the precipitation rate during discharge passes through a maximum at a certain distance *d* from the electrode. This distance should increase from the beginning to the end of this discharge. If this model is exact, that is, if one assumes that the process is always one of dissolution–precipitation and if longitudinal concentration gradients are ignored, any crystallization must create a screen which would tend to obstruct the surface partially or completely. Pb/PbSO$_4$ layer growth terminates with inhibition of the electrochemical process by the creation of an impermeable film even though the underlaying metal surface remains electrochemically active.

We have confirmed these hypotheses by showing (Fig. 4) that after fast-potentiodynamic discharge (1000 mV min^{-1}) the charge current under a Heaviside potentiostatic cathodic step was a function of the nature of the medium (presence or absence of expander), and of the relaxation time



log i vs logt from potentiostatic charge measurements, after potentiodynamic passivation. $E=-1003\,mV/_{Hg/Hg_2SO_4}$. (A) H_2SO_4 (4.5M) (B) H_2SO_4 (4.5M), expander (0.24g/l). a: 2mn, b: 15mn, c: 60mn

Figure 4.

in the medium in the discharged state. In particular, immediately after discharge (Fig. 4) a curve obtained after an interval of 2 min showed a charge current controlled by the diffusion of an intermediate species:

$$i = 2FC_o\sqrt{(Dt/\pi)} \qquad (2)$$

where C_o is the concentration of the intermediate species and D the diffusion coefficient of these species. The steepest slope ($n = 0{\cdot}6$) (Fig. 4A), represents a very fast relaxation process, whose time constant is of the order of that of the measurements. Our results enable us to establish the following inequalities:

Immediately upon the end of the discharge:

$$(C_o\sqrt{D})_{\mathrm{E}}^{2\,\mathrm{min}} < (C_o\sqrt{D})_{\phi}^{2\,\mathrm{min}} \qquad (3)$$

After partial relaxation of the intermediate species (relaxation time about $\frac{1}{4}$ h):

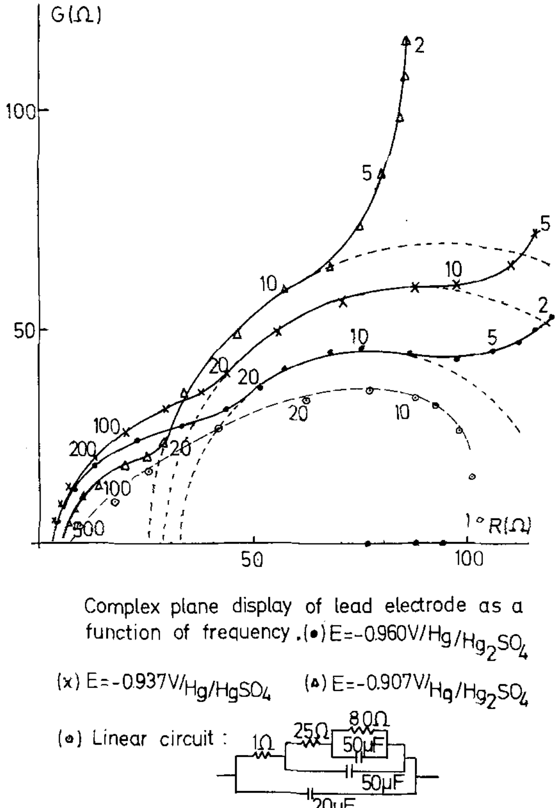
$$(C_o\sqrt{D})_{\mathrm{E}}^{15\,\mathrm{min}} > (C_o\sqrt{D})_{\phi}^{15\,\mathrm{min}} \qquad (4)$$

From Relations 3 and 4, if D is considered invariant during the course of relaxation, it appears that there is an inversion of the concentration values during this period. Thus, not only does the accumulation of intermediate species between the metal and the lead sulphate 'screen' differ when the expander is present or absent, but the relaxation kinetics also differ.

4. Transient analysis of the transfer impedance

4.1. *Alternating-signal analysis; free diffusion conditions; electrode equilibrium*

Frequency analysis of the faradaic impedance [8, 13] at different depths of discharge complements the previous discussion by throwing some light on the kinetic behaviour of the interfacial process.



Complex plane display of lead electrode as a function of frequency. (●) $E=-0.960\,V/Hg/Hg_2SO_4$

(x) $E=-0.937\,V/_{Hg/HgSO_4}$ (▲) $E=-0.907\,V/_{Hg/Hg_2SO_4}$

(○) Linear circuit :

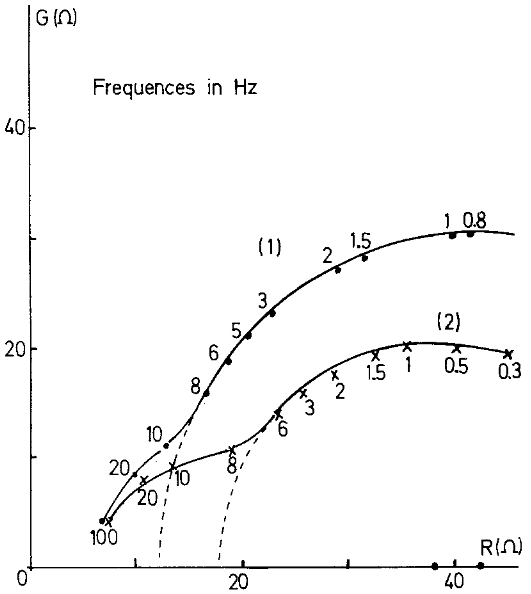
$S=0.67\,cm^2$. ω=0 RPM. H_2SO_4 (4.5M).

Figure 5.

In the frequency domain 1 Hz–1 kHz (Fig. 5) under semi-infinite linear-diffusion conditions, our observations show that it is possible to consider the interface kinetics as a series association of two first order processes that are weakly coupled (Fig. 7). In this simple form, the time constants are local and are estimated at 200 and 16 ms on a charge electrode.

The state of discharge of the surface only slightly modifies equivalent circuit A (Fig. 7), but influences considerably the properties of circuit B, whose time constant increases with the degree of discharge of the electrode.

The fully discharged state corresponds to a strong accumulation of species at the interface, without modification of the process whose time constants are less than 40 milliseconds.



Complex plane display of electrode as a function of frequency. (1) H_2SO_4 (4.5M) + Expander (0.24g/l). (2) H_2SO_4 (4.5M)

$S = 0.67\,cm^2$ $\omega = 2000$ RPM

$E = -0.960\,V/Hg/Hg_2SO_4$

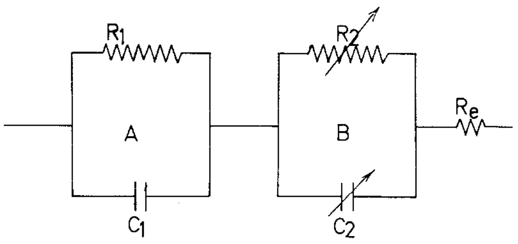
Figure 6.

4.2. *Sinusoidal-signal analysis; forced convection conditions; electrode equilibrium*

The expanders must clearly modify the above type of phenomenon; nevertheless, in the domain of intermediate frequencies (I.F.) analysed, and under semi-infinite linear-diffusion conditions, it proved impossible to demonstrate clearly a variation in the impedance spectrum which could be attributed solely to the presence of the expander.

On the other hand, an analysis made under forced convection (2000 rpm min^{-1}) showed (Fig. 6) a modification of the impedance spectra in the I.F. and low frequency (L.F.) domains, compared with that for semi-infinite linear-diffusion conditions. In particular this shows that in the I.F. domain the equivalent-circuit representation of the interface (Fig. 7) does not represent the association of two simple kinetic steps in the real electrochemical process.

This process must present a spectrum of distributed parameters – associated with mass transport – even if as a whole it can be approximated by the circuit shown (Fig. 7) when the electrode is in the semi-infinite linear-diffusion mode. In the low frequency domain we have shown that the expander introduces a variation of the time constants of the slowest processes ($6 < f < 0{\cdot}3$ Hz). At these frequencies, and under our experimental conditions, the kinetic behaviour can be considered as similar to that of a parallel R.C. circuit. The presence of the expander is characterized by the diminution of the time constant of a process which we attribute to crystallization ($\tau_E \simeq 0{\cdot}19$ s; $\tau_\phi \simeq 0{\cdot}32$ s) and which is associated with an increase in the resistance component ($R_E = 30$; $R_\phi = 20$) and a decrease in the faradaic capacity. This could correspond, as we shall see, to a more marked confinement of the species to the interfaces when the medium contains an expander.



Model circuit diagram of lead-sulphuric acid (interface). Rotation speed: $\omega = 0$. $S = 0.67\,cm^2$

$R_1 \gg 100\,\Omega$. $C_1 \ll 150\,\mu F$. $R_2 \simeq 25\,\Omega$. $30\,\mu F \ll C_1 \ll 100\,\mu F$

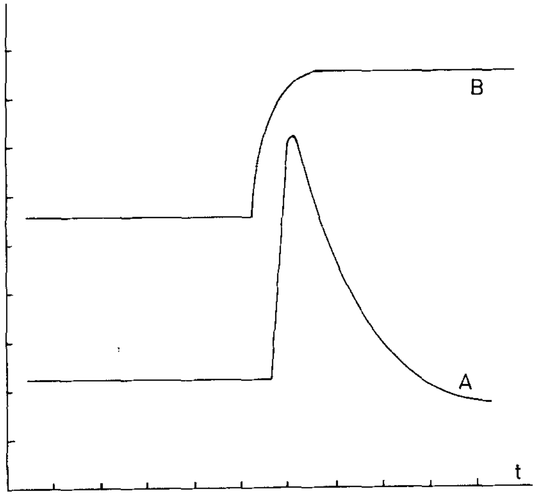
Figure 7.

4.3. *Pulse analysis under various equilibrium conditions*

Pulse analysis by small Heaviside anodic potentiostatic steps (Fig. 8) provided confirmation of the preceding conclusions. It is observed that in (4·5 M) H_2SO_4 electrolyte in the semi-infinite linear-diffusion mode, the only accessible capacities are faradaic (Fig. 10).

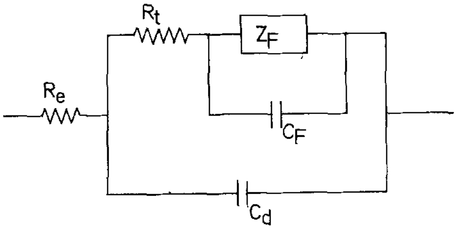
The small time constants observed require a R.C. series equivalent circuit presenting a low transfer resistance ($\tau \simeq 0{\cdot}1$ ms, $R < 1\ \Omega$). An equivalent circuit compatible with these analyses (4.1, 4.3) is shown in Fig. 9, where C_F represents the localized space charge in the crystallization zone [10].

Fig. 10 shows the diminution of faradaic capacity when the electrolyte contains expanders.



Transient response to anodic Heaviside function.
H_2SO_4 (4.5M), expander (0.24g/l).
Horizontal axis : 100μs/division
Vertical axis : 1mA/division(A) and 1mV/division(B)

Figure 8.



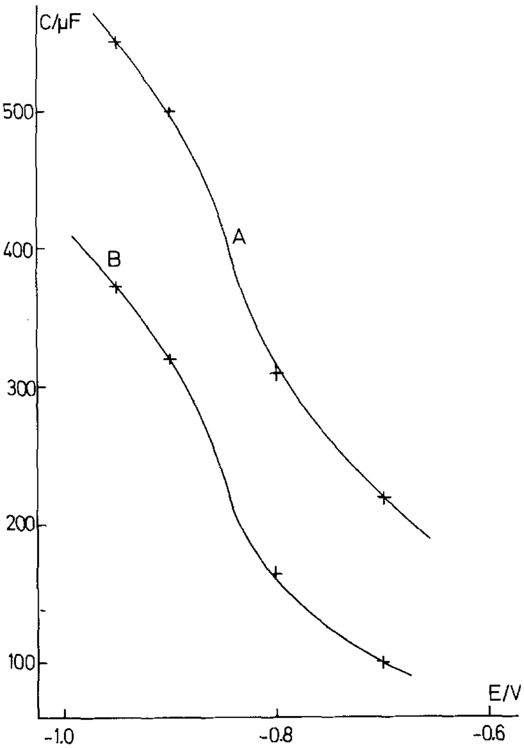
Model circuit diagram according to our analysis. R_e : electrolyte resistance
R_t : transfert resistance
C_F : faradaic capacity
C_d : double-layer capacity
Z_F : faradaic impedance

Figure 9.

The impedance Z_F, which represents that for the kinetic process of recrystallization (excluding transfer), cannot be directly accounted for by the linear circuit in Fig. 7. Fig. 5 shows a linear simulation of the crystallization process.

5. Discussion

Some kinetic data for the oxidation of a mechanically polished lead surface in concentrated sulphuric acid has been obtained in the above work.



Faradaic capacity data vs potential.
(A) H_2SO_4 (4.5M) .(B) H_2SO_4 (4.5M) expander (0.24g/l)

Figure 10.

Analysis of potential sweep data indicates that two distinct mechanisms occur; depending on electrode polarization the two submechanisms are separated by a 'nucleation potential'.

Analysis of lead ring-disc electrode data showed that the nucleation potential in the neighbourhood of −900 mV must correspond to a maximum concentration of divalent soluble intermediates, presumably Pb(II).

The presence of these two mechanisms can be attributed to a large variation in concentration polarization in the vicinity of the electrode when a limit of metastable supersaturation is exceeded, under the non-steady state conditions considered here.

In circumstances where two different types of process occur, in particular under potentiodynamic conditions, the difference cannot be due to a change in electron transfer rate. If, as we suggest, the nucleation potential corresponds to the point of maximum supersaturation of soluble intermediates, it determines the limits of the two domains which can be called 'dissolution' and 'precipitation'. In the domain of low potential the concentration polarization increases because of the large time constant of crystallization; after precipitation begins, concentration polarization decreases.

Since the concentration polarization is a stationary phenomenon associated with transients, we may exclude any steady state assumption. The process may be schematized by: (a) = electron transfer; (b) = transport ionic species; and (c) = crystallization. Each step of the mechanism may be modified by the presence of expanders.

Initial analysis of transient phenomena assumed semi-infinite linear-diffusion conditions (cyclic voltammetry and impedance in unstirred solution). In this case, the passivation observed did not result from slow electron transfer: below the $PbSO_4$ barrier layer, the lead surface stays electrochemically active and immediately after discharge the charge current is controlled by the diffusion of intermediate species.

It was observed that overpotential depended on the accumulation of ionic species between the lead surface and the $PbSO_4$ layer. Time constants for relaxation processes are different in the presence and absence of expanders. The retention time for accumulated ionic species was 15–30 min with expanders, whereas without expanders it was only a few minutes.

The very large time constant in the presence of expanders indicates that there are strong interactions between expander molecules and the ionic intermediates. The well-known ion exchange properties of lignosulphonate at neutral pH may be associated with these interactions, although the necessity of large local pH variations has not been demonstrated in the present work.

Using the inequality:

$$Q_E > Q_\phi \tag{1}$$

and supposing that the cathodic capacity preceding the nucleation potential Q can be written in the linear form: $C_o\delta$, where C_o is the mean concentration of ionic species, then

$$(C_o\delta)_E > (C_o\delta)_\phi \tag{5}$$

where δ has the dimensions of thickness. If we suppose the faradaic capacity to be proportional to the concentration of accumulated ionic species [12], we obtain (cf. 4.3):

$$(C_o)_E < (C_o)_\phi \tag{6}$$

thus

$$(\delta)_E \gg (\delta)_\phi. \tag{7}$$

Hence our analysis concludes that a formal increase of the thickness δ occurs in the presence of expander.

No definite conclusions can be obtained about the nature of the interaction between intermediate species and the expander molecules. The interaction may be of a physical nature, (affecting the hydrodynamic properties at the vicinity of the electrode), or chemical interactions may be involved. A particular difficulty is the fact that the variation of the diffusion coefficient D is not known in concentrated H_2SO_4. Nevertheless, the increase of time constant for elimination of soluble intermediates appears to indicate that the expander must introduce a delay line in the kinetic process, suggesting a change in D. This conclusion is in accord with Brennan and Hampson's observation that a reduction in diffusion in other acid media containing expanders occurs.

Without expander, a.c. measurements show that passivation must be consequent to an accumulation of species at the interface without modification of faster processes, such as electron transfer. During the course of discharge, some modifications in the slowest processes analysed occur. These modifications can be schematically given by the equivalent circuit of two coupled processes (Fig. 7). The first, of small time constant, is not affected during the course of discharge, while the second represents the crystallization process. The modification does not seem to correspond to a diminution in crystallization rate, but rather should be considered as a consequence of the geometric limitations of transport. Difficulties of reproducibility, do not allow any conclusions to be reached concerning the effect of expanders on the coupled processes.

In the second type of analysis, transients were conducted under convective diffusion conditions (rotating ring-disc electrode).

The correlations between potential sweep analysis and polarographic ring-disc electrode experiments are given above: in addition for the ring-disc electrode, we have:

$$(I\ \text{ring})_E \ll (I\ \text{ring})_\phi. \tag{8}$$

If we suppose, for all potentials cathodic to the nucleation potential, that the ionic species are stored in the hydrodynamic layer, we can write:

$$\left(N_0 \frac{D}{\delta'} C'_0\right)_E \leqslant \left(N_0 \frac{D}{\delta'} C'_0\right)_\phi \qquad (9)$$

where N_0 is the collection efficiency, D the diffusion coefficient, C'_0 the mean concentration of intermediates, and δ' the hydrodynamic layer thickness.

If we suppose both fluids to be Newtonian, we may write [7]

$$\delta' = 0{\cdot}643\omega^{-1/2} \times \nu^{1/6} D^{1/3} \qquad (10)$$

where ω is the rotation speed and δ the kinematic viscosity.

Since N_0 depends only on the geometric characteristics of the electrode,

$$\left(\frac{D^{2/3}}{\nu^{1/6}} C'_0\right)_E \leqslant \left(\frac{D^{2/3}}{\nu^{1/6}} C'_0\right) \qquad (11)$$

this relation characterizes the behaviour of the expander under polarographic conditions and forced convection.

Under the same hydrodynamic conditions impedance faradaic analysis shows that the time constant of the slowest phenomenon (i.e. crystallization) is modified by the presence of expanders (Fig. 6), showing, in particular, a slightly decreased time constant with an increase of the resistive component and a decrease of the capacitive component.

Thus we may conclude that stages (b) and (c) are modified in the presence of expanders. Analysis using Heaviside functions indicates an equivalent circuit as shown in Fig. 9. The circuit is simulated in Fig. 2.

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