

Fundamentals of lead-acid cells. XVI. Phase formation at porous lead electrodes at low temperatures

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The oxidation and reduction of porous lead electrodes in 5 M H₂SO₄ at -30°C are reported. It is shown that the formation of ice crystals is an important factor in the behaviour of the porous lead electrode under these conditions.

1. Introduction

The behaviour of the lead-acid battery cell at low temperature is important technologically since it is the ability to deliver charge at high potentials under cold conditions which forms an important and searching criterion on which lead-acid cells are to be judged. It is accepted [1] that the electrode which limits cell discharge under low-temperature (7-10°C) conditions is the negative one. It is partly for this reason that organic expander (lignosulphonates and related compounds) is added to the negative electrode.

We have already reported on the behaviour of solid lead (negative) electrodes in sulphuric acid [2, 3]; we now report an extension of these measurements to porous electrodes.

2. Experimental

The apparatus, cells and porous electrodes (containing the conventional expander materials [4]) with which potentiostatic step experiments were made have already been described. The temperature in the present experiments was controlled by immersing the cell in a methanol bath thermostatted to ± 1°C using a Townson and Mercer refrigerator unit.

3. Results and discussion

Fig. 1 shows a typical oxidation transient, recorded on the porous Pb electrode at -30°C. This is markedly different from those recorded on the

planar electrode under similar conditions [2]. Further comparison with other oxidation transients recorded on porous electrodes at ambient temperature also shows some differences [3], although the current in the transient again rises as $t^{1/2}$ (Fig. 2). Comparison with corresponding ambient temperature results [3] indicates that significantly lower currents are obtained at -30°C.

Fig. 2 also shows that the $i-t^{1/2}$ plots intercept the current axis at $t = 0$, indicating the pre-existence of nuclei for the growth of PbSO₄. These nuclei probably result from the BaSO₄ addition made to the above material [3]. The magnitude of the currents at zero time moreover indicates that the suitability of such a site for nucleation depends on the potential. It is also expected that the low solubility of PbSO₄ at -30°C will also have a significant effect, by increasing the tendency for PbSO₄ to form as a solid phase at the electrode.

In an earlier paper [4] the $i-t^{1/2}$ behaviour of the porous electrode was explained in terms of de Levie porous electrode theory [5]. The $i-t^{1/2}$ behaviour at the porous electrode is the counterpart of the $i-t$ behaviour at a solid electrode [5]. Consequently, we can conclude that the formation of PbSO₄ occurs by an instantaneous nucleation and 2D growth process. This is equivalent to the passivation process already discussed in the case of the solid electrode [2].

In the latter regions of the current decay curve in Fig. 1, there is an abrupt change in the $i-t$ relationship. The change was more gradual at lower overpotentials. This feature is substantially

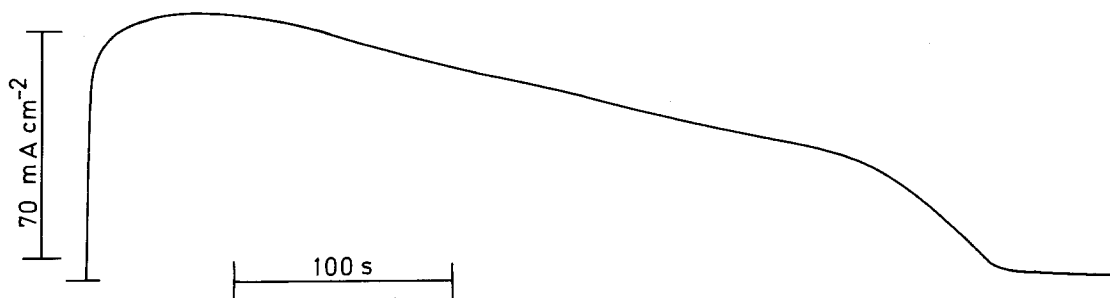


Fig. 1. A typical oxidation transient on porous lead at -30°C in $5\text{ M H}_2\text{SO}_4$. Initial potential -1050 mV ; final potential -780 mV .

different from that observed for a porous electrode containing no lignosulphonate at ambient temperature [4]. This current decay did not conform to any simple relationship, except that at low overpotentials and intermediate times some $i-t^{1/2}$ behaviour was observed, although this may well be a chance correlation. This accelerated current decay rate has a significant effect in reducing the charge required to passivate the electrode (the capacity), as shown in Table 1.

The theoretical capacity of the electrode is 16.85 C , and results for a similar lignosulphonate-containing electrode at ambient temperature give $\sim 10\text{ C}$ [4]. At -30°C , capacities are significantly lower, especially when it is remembered that the Pb/PbSO_4 rest potential in $5\text{ M H}_2\text{SO}_4$ is $\sim -935\text{ mV}$ at -30°C . At ambient temperature, the discharge of a porous electrode was described as two competing processes [4]: passivation and pore plugging by product PbSO_4 . At -18°C , Winsel [6] has suggested that, at high discharge

rates, these two processes are accelerated by the presence of ice crystals, in addition to the PbSO_4 . Such ice crystals would be formed when the isothermal dilution of the pore liquid causes its concentration to coincide with the solidus curve of the $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ phase diagram [7]. If the pore electrolyte falls to a concentration of $\sim 3.5\text{ M}$ at -30°C , ice crystals will form with a volume about eight times larger than that of the PbSO_4 which is generated simultaneously.

It is considered therefore that discharge at -30°C effects electrolyte depletion in the pores of the electrode, and this causes the formation of ice crystals which accelerate the passivation and pore plugging processes. This 'ice passivation' is reflected in the sudden change in decay rate of the $i-t$ transient shown in Fig. 1.

Fig. 3 shows a typical double-layer charging transient for the porous electrode at -30°C . This figure shows that the current decays as $t^{1/2}$ as is to be expected for a transient arising from a porous electrode containing semi-infinite pores; it is interesting that this behaviour is still valid at -30°C . The $i-t^{1/2}$ plot shows that the intercept occurs at shorter times than for the same electrode at $\sim 22^{\circ}\text{C}$ [4], because of the even greater ohmic

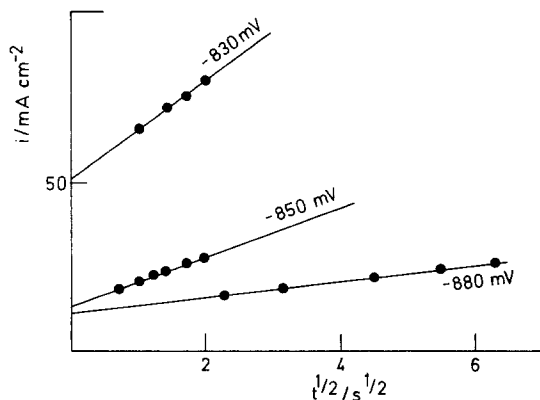


Fig. 2. Typical $i-t^{1/2}$ plots from transients represented by Fig. 1. Initial potential -1050 mV ; final potential as shown on the curve.

Table 1. The variation of electrode capacity with oxidation potential at -30°C

E (mV)	Capacity (C)
-880	3.9
-870	3.4
-860	2.9
-830	2.2
-810	2.0
-800	1.8

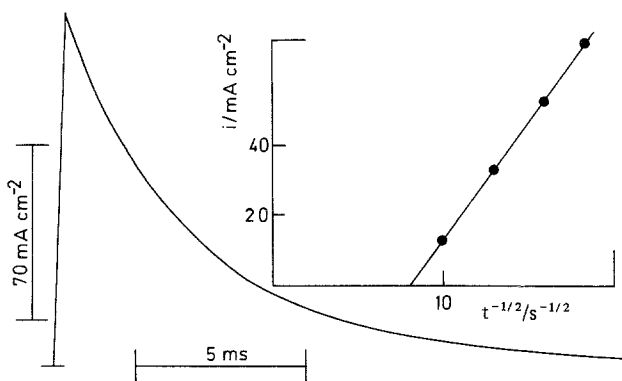


Fig. 3. Double-layer charging transient for the porous electrode corresponding to a potential step from -1050 mV to -1200 mV in 5 M H_2SO_4 at -30°C . Inserted curve: $i-t^{-1/2}$ correlation.

resistance of the electrode preventing an infinite current density at zero time. The double-layer capacitance was found to be only 2% of the ambient temperature value. The fall in double-layer capacitance with temperature has been observed elsewhere [5], and in this case arises from stronger adsorption forces, and perhaps even from the possibility of ice crystals at the interface if significant reaction occurs in the double-layer charging region.

On reduction of a passivated porous Pb electrode at -30°C , rising transients were not observed at potentials more positive than -1080 mV. At ambient temperature, rising transients were observed at overpotentials of ~ 20 mV. This low-temperature behaviour is confirmed by

the potential sweeping experiments on the planar electrode [3], where the reduction peak was shifted substantially towards the hydrogen evolution region as a consequence of lowering the temperature.

Fig. 4 shows that on potentiostatic reduction, a current transient is substantially different from results obtained at room temperature [4]. In the low-temperature case, there is a rapid rise in current as the double layer charges, followed by a substantial fall, and a subsequent slow rise in current. This rising electrocrystallization transient is substantially slower than its ambient temperature counterpart. Also, the current rise follows an $i-t^{3/2}$ relationship, as shown in Fig. 5. The current rise is shallow, and the $i-t^{3/2}$ plots intercept the current

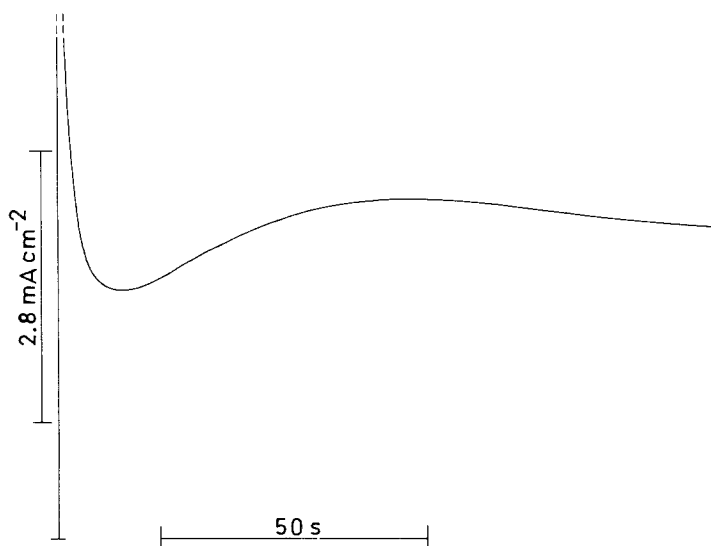


Fig. 4. A typical reduction transient on porous lead at -30°C in 5 M H_2SO_4 . Initial potential -800 mV; final potential -1100 mV.

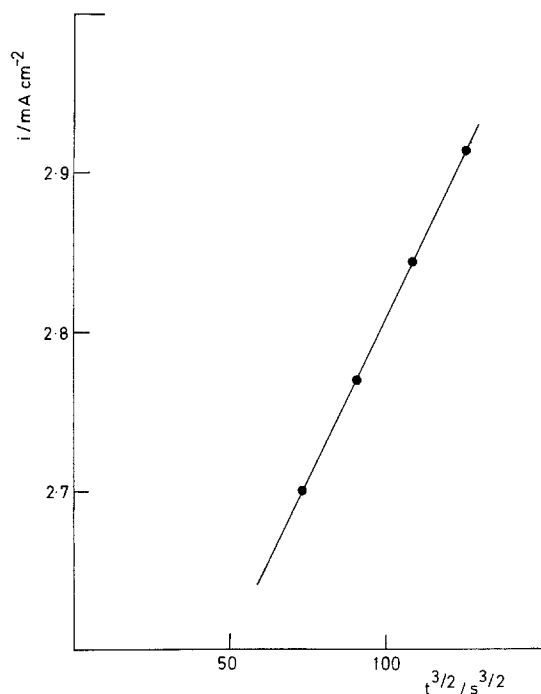


Fig. 5. The rising portion of Fig. 4 expressed as an i versus $t^{3/2}$ plot.

axis at zero time. Therefore, Pb nucleation centres exist before the nucleation and growth phase and subsequent growth of lead occurs at a relatively low rate. The pre-existence of nucleation centres is not surprising in view of the porous nature of the PbSO_4 film. However, rising transients were never recorded after a potentiostatic reduction step on the sulphated solid Pb electrode at -30°C . Therefore, significantly less nucleation centres must be available for Pb growth on the porous Pb electrode. This would be the case if the pores of the electrode were plugged with PbSO_4 (and ice crystals), preventing the reaction penetrating to the inner native surface.

The current rise in the transient as $t^{3/2}$ can be explained in the light of the porous electrode theory already discussed [5], which would lead to an $i-t^3$ relationship at a solid electrode. Armstrong *et al.* [8] have demonstrated this relationship

for progressive nucleation and 3D growth, although this model predicts a current which rises asymptotically to a current maximum. These authors also demonstrated that the current would fall if the electrode was being progressively passivated. This is clearly not the case here, and the fall in current is difficult to explain on the basis of this model.

It is possible that the 'progressive nucleation and 3D growth' is an artefact due to the progressive dissolution of ice crystals of relatively large volume as the electrolyte concentration increases. The observed transient is, therefore, characteristic of a complex phenomenon resulting from the reduction of PbSO_4 to Pb, the dissolution of ice crystals, and the hydrogen evolution reaction. The $i-t$ relationship of the falling transient did not fit any simple mathematical equation, and a substantial current at long times was recorded as the result of the hydrogen evolution reaction. It is probable that hydrogen bubbles in the electrode caused some current decay by a pore blocking mechanism.

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