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**LA THÈSE A ÉTÉ
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THE EFFECTS OF AMMONIUM LIGNOSULPHONATE
AND TEMPERATURE ON THE ELECTROCRYSTALLISATION
OF LEAD SULPHATE ON LEAD ELECTRODES

by

(C) Deborah Ann Rennie, B.Sc.
Carleton University

A thesis submitted to
the Faculty of Graduate Studies and Research
in partial fulfilment of
the requirements for the degree of
Master of Science

Department of Chemistry

Carleton University
Ottawa, Ontario, Canada

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on the Electrocrystallisation of Lead Sulphate on
Lead Electrodes"

submitted by Deborah Ann Rennie, B.Sc.

in partial fulfilment of the requirements for
the degree of Master of Science

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ABSTRACT

The influence of ammonium lignosulphonate as a battery expander on the formation of lead sulphate films on lead amalgam and solid lead electrodes, at ambient and subzero temperatures was investigated. Linear potential sweeps and potentiostatic pulse measurements were used on the lead amalgam electrode at 20°C. The lead sulphate film formed via 3-dimensional nucleation and growth. The expander adsorbed onto the clean amalgam surface and inhibited the nucleation and growth processes until more positive potentials were reached. The expander increased the anodic current and charge required for passivation. Evidence was obtained for an optimum concentration of expander between 7.89 and 17.45 ppm.

Linear potential sweeps and scanning electron microscopy were employed on the solid lead electrode at temperatures from 20° to -20°C. The expander did not influence the anodic current, nor the charge passed. The expander adsorbed onto the electrode surface blocking sites that would promote Pb^{2+} dissolution. The rate of lead dissolution was reduced, which in turn decreased the rate of crystal growth. The expander had a minor influence on the nucleation rate. Lower temperatures decreased lead dissolution and lead sulphate crystal growth rate.

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GLOSSARY

A	electrode area
C_O	bulk concentration of oxidized species
C_R	bulk concentration of reduced species
ϵ	capacitance of parallel plate capacitor
D_O	diffusion coefficient of oxidized species
d	plate separation on a parallel plate capacitor
E_a	activation energy
E_e	equilibrium potential
E^0	standard electrode potential
E	potential of working electrode
E_p	anodic peak potential on a linear potential sweep
F	Faraday's constant
i	current density
i_o	exchange current
i_p	anodic peak current on a linear potential sweep
i_m	maximum current on a potentiostatic pulse transient
K	dielectric constant
k_f	rate constant for forward reaction
k_b	rate constant for backward reaction
k_1	lateral growth rate
k_2	vertical growth rate
k^0	standard rate constant
L	thickness of deposit

M	molecular weight
n	number of electrons transferred
n_a	number of electrons in rate determining step
N_0	number of nuclei formed at $t=0$
Ox	oxidized species
Red	reduced species
R	universal gas constant J/mole/k
R_1	resistance
S	true surface coverage
S_x	extended surface coverage
S_i	surface coverage for instantaneous nucleation
S_p	surface coverage for progressive nucleation
T	temperature in degrees kelvin
t	time
t_m	time at which i_m occurs
Z	nucleation rate
ϵ_0	permittivity of free space
α	transfer coefficient
η	overpotential
ρ	density of deposit
ρ_i	resistivity in Ω cm
ν	sweep rate

1 INTRODUCTION

1.1 LITERATURE REVIEW

The lead acid battery is one of the most prevalent electrical power sources in use today because of its wide commercial and industrial uses (1). The lead acid battery was invented in 1859 by Planté and the literature which includes many books, monographs and review articles published since then is vast (1-9).

When the battery is manufactured, a proprietary paste of lead monoxide in sulphuric acid is applied to the lead alloy grids contained within the battery. The battery is then charged to generate the electrochemically active materials of lead dioxide on the positive plate, and spongy lead on the negative plate.

The operation of the lead acid battery is based upon the double-sulphate theory as proposed by Gladstone and Tribe in 1882 (10). According to this theory, the discharge product on both plates is lead sulphate. The electrochemical reactions that occur during discharge are as follows (9): At the positive plate, the lead dioxide reacts with the sulphuric acid to form lead sulphate and water,

At the negative plate, lead is oxidized to produce lead sulphate,

The net reaction is therefore,

1.1.1. LEAD SULPHATE FORMATION ON THE NEGATIVE PLATE

The oxidation of lead in sulphuric acid results in the formation of a relatively insoluble film consisting primarily of lead sulphate that tends to passivate the electrode surface. The composition of the film depends upon the applied potential (11-16). At potentials negative to -400mV (versus mercury/mercurous sulphate) the layer is composed only of lead sulphate crystals. At more positive potentials the anodic layer contains the higher oxides of lead as well as lead sulphate. One of the disadvantages of the lead acid cell is the formation of a passivating lead sulphate layer(s) which is responsible for the limitation of the discharge capacity of the lead acid battery, especially at subzero temperatures. The investigation of this system is therefore desirable.

The exact mechanism of the formation of lead sulphate has often been disputed in the literature and two different mechanisms have been suggested (17-29), the solid state

(or nucleation and growth) and dissolution-precipitation. Generally speaking, in the solid state mechanism, anions from the solution react with the metal directly at the electrode surface without the metal cations entering the solution. In the dissolution-precipitation mechanism, the metal dissolves as ions until a certain critical concentration is reached near the anode interface, inducing precipitation on the electrode, which blocks the metal surface (17). It is generally concluded (18, 24, 25, 27, 30-32) that in low overpotential regions prior to the equilibrium potential of the Pb/PbSO₄ system -950mV, the electrochemical process that occurs is the reversible Pb²⁺ dissolution, namely,

4

The possibility of Pb²⁺ complexation with the sulphate anions cannot be ruled out (33, 34) but the existence and participation of these complexes in the formation of lead sulphate has yet to be established or investigated. As the potential is made more positive than the equilibrium potential, the lead sulphate formation takes place via a three dimensional nucleation and growth mechanism (21, 24, 25, 27, 35, 36). Here, crystals nucleate on the electrode surface followed by the growth across and away from the surface, that is, in three dimensions.

1.1.2 INFLUENCE OF AN EXPANDER ON THE LEAD SULPHATE FORMATION

It is well known that the addition of an organic additive or expander, to the paste of the negative plate improves both the cycle life and the discharge rate at low temperatures (18, 37-40). There are three materials that are commonly used either separately or in combination: lampblack, BaSO_4 and derivatives of lignosulphonic acid (henceforth referred to as lignin). Lignin gives the best expander action, and lampblack the poorest (2, 5). BaSO_4 is often used in conjunction with lignin (2, 5) however, lignin remains the conventional expander. The amount of lignin added to the paste is usually very small, and a 1 to 2% addition can cause an increase in capacity of the negative plate by as much as 100% (2, 9). Lignin is a naturally occurring anionic polymer with a coiled structure of great complexity (41, 42). Its chemical characterization is extremely difficult due to the tendency to undergo self-condensation reactions of an unknown nature (42).

The essential requirement for an organic material to act as an expander is its surface active properties. The adsorption of surface active compounds exhibits a substantial influence on the kinetics of electrode processes. The expander adsorbs onto both the metallic lead surface and onto the surface of the lead sulphate crystals

themselves (2, 3, 5, 18, 37, 39, 41, 43-51). Sharpe (46) compared the adsorption of expander onto lead powder and onto lead sulphate crystals. He found that the degree of adsorption was greater onto lead powder than lead sulphate. However, this doesn't necessarily apply to metallic lead.

The adsorption of lignin onto the electrode surface modifies the electrocrystallisation of lead sulphate (43). During the discharge cycle, the expander alters the size and shape of the lead sulphate crystals as a result of the adsorption onto both lead and lead sulphate (45). Disagreement exists in the literature with regard to exactly how the structure is changed. Some authors claim that smaller lead sulphate crystals are formed (1, 37, 39, 48, 51, 52), while others suggest the formation of larger crystals (45, 49, 53).

The discharge capacity is equivalent to the amount of lead sulphate generated (53) since this film will eventually cover the electrode surface and limit further discharge. This means that the size of the crystals are important in determining the amount of lead sulphate that can be generated on the surface of the negative plate. If there are a small number of large crystals, the volume of lead sulphate is greater and the discharge capacity is increased (45, 53, 54). If the crystals are small and numerous, the discharge capacity is reduced since the amount of lead

sulphate formed is less.

The expander causes an increase in the discharge capacity of the negative plate (18, 37, 39, 44, 45, 51, 55). However, the exact mechanism of the expanders is not explained and the literature is very vague on how the discharge capacity is increased. The possible causes of enhanced discharge are: the lead surface is left free of lead sulphate for a longer period of time; the crystals are larger; or the rate of Pb^{2+} dissolution is higher. The presence of expanders results in crystals that are less densely packed (1, 37, 38, 45) consequently increasing the porosity of the final lead sulphate layer (37, 40, 50, 51, 56, 57). A more porous film increases the discharge capacity by allowing channels through which the metallic lead surface can continue to dissolve as Pb^{2+} ions. It can be summarized that the effect of the expander lies essentially in increasing the oxidation current during the discharge cycle (18, 19), and the total charge passed upon passivation of the electrode (18, 39, 41, 57). The reduction of the lead sulphate film is inhibited (39, 41, 47, 48, 54). The existence of an optimum concentration of 20 ppm of the expander lignosulphonate has been reported by Mahato on cycled lead electrodes (41). Beyond that concentration, the expander had an inhibitory effect on the reactions involved.

It is clear that the exact nature of the expander action has yet to be resolved fully. More research in this important area is obviously needed.

1.1.3 EFFECT OF TEMPERATURE ON THE LEAD SULPHATE FORMATION

Temperature plays an important role in determining the capacity of the battery that can be delivered. Below -17.8°C it becomes nearly impossible to charge batteries fully, and the percentage of available capacity at the lower temperatures decreases as the required rate of discharge increases (2).

Chang et. al. (58) observed that a reduction in temperature from 25° to -40°C increased the separation between the oxidation and reduction potentials which suggested that the formation of lead sulphate was more irreversible at low temperatures. There was less current and charge passed upon passivation. Their results were confirmed by Hampson and Lakeman (26) who also concluded that at -30°C the film was more porous. In addition, they observed a decrease in the charge of the reduction peak which confirmed the work of Willihnganz (59) who reported that lowering the temperature made the rechargability of the battery more difficult.

The addition of an expander to the negative plate at subzero temperatures inhibits lead sulphate crystal growth thereby improving the discharge capacity (38, 60, 61) but,

the exact interpretation of the mechanism of crystal growth was not explained in the literature. It could be interpreted that the nucleation rate was hindered giving fewer nuclei that could still grow into larger crystals; or the growth of the crystals themselves was inhibited, or both effects were taking place simultaneously. However, the work of Simon et. al. (38) suggested that the presence of the expander inhibited the nucleation, and not the crystal growth since the film had a definite crystalline structure. In the absence of expander, they could not detect the film's structure and this suggests the existence of extremely small crystals that produced a very thin, or amorphous, passivating layer which results when the nucleation rate is very high. When the nucleation rate is low, fewer nuclei are present that grow to give a crystalline film similar to the case in expander free solutions. It appears that the expander may adsorb onto active nucleation sites, thus inhibiting the nucleation process so the fewer crystals that did form would grow larger.

1.1.4 DIFFICULTIES INHERENT WITH SOLID ELECTRODE SURFACES

Much of the previous research has focussed on the behaviour of the negative plate with and without the addition of expanders especially at ambient temperatures and it is rather astounding that there are very few reliable quantitative investigations at lower temperatures (26, 38,

40, 58, 59, 62). At ambient temperatures the studies have employed solid lead electrodes without expander (12, 13, 16, 21, 23-28, 30, 31, 35, 41, 58, 63, 64) and with expander added (18-20, 29, 39, 45, 47, 48, 65-67); pasted lead electrodes without expanders (41, 59, 62, 68) and with expanders (37, 38, 40, 43, 44, 50, 56, 57, 61); and finally lead amalgam electrodes with expander (39, 54). A major problem associated with the above studies is that it is difficult to compare the experimental data obtained from electrodes with different surfaces. Complications arise from the pretreatment of the solid electrode because it is essential to have well-defined electrode surfaces (28, 32, 69, 70) in order that valid kinetic conclusions can be made. The presence of both roughness, pits, defects and asperities on the solid lead surface strongly influenced the experimental results (28, 69). In general, smooth electrodes without surface heterogeneity gave low values of the oxidation peak current, whereas rough surfaces gave high values (28). In addition, internally consistent data has been very difficult to obtain because the individual kinetic measurements in one experiment were controlled by the irreproducible variations on the electrode surface (28). A procedure commonly reported in the literature to get reproducible surfaces involves cycling the electrode in the

desired potential region until a constant current response is obtained (41, 48, 63, 66). However, cycling the electrode adds a further complication because it strongly modifies the electrode surface by the irreversible deposition of the thick deposit of insoluble, or what is referred to as "hard" lead sulphate crystals which largely affect the oxidation peak in the lead/lead sulphate potential region (28, 64). The use of lead amalgam electrodes offers a superior technique over solid electrodes to give reproducible surfaces because they offer fresh, smooth well-defined electrode surfaces free from surface defects. They have a disadvantage in that they are not suited for low temperature studies because the lead freezes out near 0°C (71).

1.2 RESEARCH AIMS

From the preceeding literature survey, it is quite apparent that the studies on the various aspects of the lead acid system is copious. However, there are a few major drawbacks with the reported investigations.

- i) Most of the reported studies deal with the technological aspects of the battery, its manufacture, variety of uses, etc. and not on the fundamental electrochemical processes, that is, the kinetics and mechanism of lead sulphate formation, the structure of the passive film, and the role of battery expanders on the formation of lead sulphate.
- ii) The use of organic additives to improve the discharge

capacity is well documented, but there is no satisfactory explanation for the mechanism of the expander, that is, exactly how it improves the discharge capacity.

iii) The use of the additives improves the cycle life and discharge capacity at low temperatures, and it is rather astounding that the literature published in this area of practical importance is extremely scarce, especially relating to the use of expanders at subzero temperatures.

It is obvious that there is a necessity to investigate the nature of the electrode processes in the presence and absence of expanders at ambient and subzero temperatures. This dissertation focusses on these important areas of research. First, the use of lead amalgam electrodes at ambient temperatures as an "ideal system" to determine the effect of the expander on the nucleation and growth of the lead sulphate film. A concentration dependence could identify the existence of an optimum concentration of expander. The phase diagram of lead in mercury (71) shows that at 0°C the lead will separate out from the mercury, thus, the lead amalgam would not be suitable for subzero temperature investigations. In addition a lead amalgam is obviously not too relevant to conditions in a real battery. Therefore, a solid lead electrode was used for the low temperature work. It was desirable to identify how

lowering the temperature affected the optimum concentration of the expander. Finally, it was necessary to elucidate how the expander influences the lead sulphate formation and its varying crystallographic morphology on the lead surface.

1.3 THEORETICAL ASPECTS

A review and inclusion of the theoretical aspects is presented here because these equations and theoretical considerations are relevant to the understanding of the thesis. Its inclusion in this section also facilitates the understanding of this work by any reader.

In studies of electrode processes, proper measurements and analysis of electrode potentials, currents and their time dependence enables one to understand the mechanisms and kinetics of electrochemical reactions.

The simple electron exchange between ions in the electrolyte and the electrode can be represented as:

where k_f is the rate constant for the forward reaction, and k_b is the rate constant for the backward reaction. At equilibrium, the system is characterized by the Nernst equation which links the electrode potential to the bulk concentrations of the reactants and products:

$$E_e = E^\circ + \frac{RT}{nF} \ln \left[\frac{C_O}{C_R} \right] \quad 6$$

where E_e is the equilibrium potential, E° is the standard electrode potential, C_O and C_R are the bulk concentrations of the oxidized and reduced species respectively.

For irreversible reactions, when the current flows through an electrochemical cell, the potential of the working electrode, E , differs from the equilibrium value E_e , and the difference between them is defined as the overpotential η :

$$\eta = E - E_e$$

The overpotential is the extra potential that must be applied to the electrode reaction to make it proceed. If $\eta = 0$, the forward and reverse reactions are occurring at equal and opposite rates in both directions. In this case, no net current flows, and the electrode is in its equilibrium state.

The net current density, i , can be expressed in terms of the exchange current, i_0 , through the Butler-Volmer equation:

$$i = i_0 \left[\exp \left(\frac{(1-\alpha)nF\eta}{RT} \right) - \exp \left(\frac{-\alpha nF\eta}{RT} \right) \right]$$

The terms in the square brackets represent the anodic and cathodic contributions to the net current.

For overpotentials smaller than 5 mV, the Butler-Volmer equation can be simplified to give:

$$i = \frac{i_0 n F \eta}{RT}$$

For larger values of η , either negative or positive, one of the bracketed terms in equation 8 becomes negligible.

For example, at large negative overpotentials:

$$\exp \left[\frac{-\alpha n F \eta}{RT} \right] \gg \exp \left[\frac{(1-\alpha) n F \eta}{RT} \right]$$

and thus:

$$i = -i_0 \exp \left[\frac{-\alpha n F \eta}{RT} \right] \quad 10$$

taking logarithms of both sides of equation 10 gives:

$$\ln(i) = -\ln(i_0) - \frac{\alpha n F \eta}{RT} \quad 11$$

which can be solved explicitly for η :

$$\eta = \frac{RT}{\alpha n F} \ln(i_0) - \frac{RT}{\alpha n F} \ln(i) \quad 12$$

Since only η and i are variables for a given electrode system, the equation can be written as:

$$\eta = a + b \ln(i) \quad 13$$

This relationship is known as the Tafel equation, and it is used to plot $\log(i)$ as a function of η for the evaluation of kinetic parameters. In general, the plot results in an anodic branch with a slope of $(1-\alpha)nF/2.3RT$, and a cathodic branch whose gradient is equivalent to $-\alpha nF/2.3RT$. These Tafel slopes can be employed to determine whether the reaction proceeds via a single or multistep electron transfer mechanisms. For example, for a simple one electron transfer reaction at 25°C, α is equivalent to 0.5, and b is then 0.118V, which is the corresponding Tafel slope.

1.3.1 ELECTROCRYSTALLISATION

Many important electrode reactions involve the formation of a solid phase either as a result of the reduction of ions in solution (metal deposition), or by the oxidation of the electrode and the subsequent reaction with anions to form an anodic film. Electrocrystallisation is the phenomenon that describe the electrode processes of these types.

1.3.2 TWO DIMENSIONAL GROWTH

Fleischmann and Thirsk have theoretically developed models to describe the process of two dimensional nucleation and growth of discrete centres (72, 73). The models treat two limiting cases, instantaneous, and linear progressive nucleation. Instantaneous nucleation occurs when all the nuclei form simultaneously, while in the case of progressive nucleation, the nuclei form linearly in time at a constant rate of nucleation. This constant rate of growth corresponds to the deposition being proportional to, and occurring at the perimeter of the growing nucleus.

In the initial stages of the growth of nuclei to form crystals, the nuclei are able to grow freely, independent of one another. As the growth continues, there is less available surface on the electrode in which the growth can take place. This causes the nuclei to impinge upon one another resulting in overlapping of the growing nuclei. The growth ceases upon impingement but continues unaltered

everywhere else. The problem of overlap is accounted for by the Avrami equation (74)

$$S = 1 - \exp(-S_x) \quad 14$$

where S is the true surface coverage, and S_x is the extended surface coverage which is the amount of surface that would have been covered by the growing nucleus had it not come into contact with another growing nucleus.

Experimentally, the surface coverage is proportional to the charge and the extended surface coverage is proportional to the current. As derived from the Avrami equation, these quantities are given by:

$$\text{2D instantaneous: } S_i = 1 - \exp(-N_o \pi k_1^2 t^2) \quad 15$$

$$\frac{dS_i}{dt} = 2N_o \pi k_1^2 t (\exp(-N_o \pi k_1^2 t^2)) \quad 16$$

$$\text{2D progressive: } S_p = 1 - \exp\left[\frac{-2\pi k_1^2 t^3}{3}\right] \quad 17$$

$$\frac{dS_p}{dt} = 2\pi k_1^2 t^2 \exp\left[\frac{-2\pi k_1^2 t^3}{3}\right] \quad 18$$

where S_i and S_p are the surface coverages for instantaneous and progressive nucleation respectively, $\frac{dS_i}{dt}$ and $\frac{dS_p}{dt}$ are the rate of surface coverages for instantaneous and progressive nucleation respectively, N_o is the number of

nuclei formed at $t=0$ for instantaneous nucleation, Z is the nucleation rate, k_1 is the lateral growth rate and t is the time.

1.3.3 THREE DIMENSIONAL GROWTH

The electrocrystallisation of a new phase on a foreign substrate may involve in its early stages the formation of three dimensional nuclei. Armstrong and co-workers (8) have extended the two dimensional model of Fleischmann and Thirsk to be applicable to the case of three dimensional nucleation and growth of discrete centres. In their model, the growth centre was represented as a right circular cone rather than a flat circular disc for the two dimensional model. The growth could occur in two directions, parallel to the electrode surface with a rate constant k_1 , and perpendicular to the surface with a rate k_2 . The current response due to the progressive nucleation and growth of a three dimensional deposit is given by (8):

$$i = nFk_2 \left[1 - \exp \left[\frac{-\pi M^2 k_1^2 Z t^3}{3 \rho^2} \right] \right] \exp \left[\frac{-\pi M^2 k_1^2 Z t^3}{3 \rho^2} \right] \quad 19$$

where i is the current, n is the number of electrons transferred, F is Faraday's constant, k_2 is the vertical growth rate, M is the molecular weight, k_1 is the lateral growth rate, Z is the nucleation rate, t is the time, and ρ is the density of the deposit. Equation 19 can be represented in non-dimensional or "reduced variable" form.

The reduction of variables is achieved through consideration of the maximum current, i_m , and the time to this maximum, t_m in the experimental transients. The theoretical reduced variable form is expressed as:

$$\frac{i}{i_m} = 4 \left[1 - \frac{1}{2} \left(\frac{t}{t_m} \right)^3 \right] \left[\frac{1}{2} \left(\frac{t}{t_m} \right)^3 \right] \quad 20$$

where for three dimensional electrocrystallisation:

$$i_m = \frac{n F k_2}{4} \quad 21$$

$$t_m = \left[\frac{3 \rho^2 \ln(2)}{\pi M^2 k_1^2 Z} \right]^{1/3} \quad 22$$

Thus, the experimental potentiostatic pulse transients can be analyzed to give values of the parameters k_2 and $k_1^2 Z$ from i_m and t_m .

1.3.4 EXPERIMENTAL TECHNIQUES

The experimental techniques employed in this study to examine the nature of the electrochemical behaviour involved can be classified into linear potential sweep and potentiostatic pulse perturbations.

1.3.4.1 LINEAR POTENTIAL SWEEP PERTUBATION

In this technique the potential applied to the working electrode is initially held at a potential where the phase formation reaction does not occur. The potential is then varied linearly with time at a sweep rate ν through the region where the phase formation takes place, reversed, and

swept at the same rate to the initial potential. The current response is recorded as a function of potential. The behaviour of an electrochemical system can be observed over a wide potential range on a single voltammogram, and analyzed in terms of the peak current, i_p , and the peak potential, E_p , at which the peak current occurs. The reaction intermediates and products will be evident as peaks on the voltammogram, and are capable of being identified by the potentials at which they are oxidized or reduced. Therefore, the major use of linear potential sweeps is the qualitative elucidation of reaction mechanisms. However, it must be emphasized that quantitative kinetic data can only be accurately obtained from the analysis of a single sweep, and not after the electrode has been cycled many times between the set potential limits.

The theories of linear potential sweeps were first investigated by Randles (75) and Sevcik (76) for reversible systems, and later extended by Delahay (77) to include irreversible systems. The theoretical relationships relating the experimental parameters of peak current, i_p , and peak potential, E_p , to the sweep rate v , under diffusion controlled conditions are given by Delahay (78):

- 1) for a reversible charge transfer reaction where the electron transfer rate is sufficiently high to maintain Nernstian equilibrium at the electrode surface:

$$i_p = (3.67 \times 10^5) n^{3/2} A D_o^{1/2} C_o \nu^{1/2}, \text{ at } 25^\circ\text{C} \quad 23$$

E_p is independent of sweep rate.

ii) for an irreversible charge transfer in which the reaction rate is sufficiently slow compared to the sweep rate where the process is unidirectional:

$$i_p = (3.01 \times 10^5) n(\alpha n_a)^{1/2} A D_o^{1/2} C_o \nu^{1/2}, \text{ at } 25^\circ\text{C} \quad 24$$

$$E_p = E^\circ - \frac{RT}{\alpha n_a F} \left[0.78 + \ln \left[\frac{D_o^{1/2}}{k^o} \right] + \ln \left[\frac{\alpha n_a F \nu}{RT} \right]^{1/2} \right] \quad 25$$

where A is the electrode area in cm^2 , D_o is the diffusion coefficient of species O in cm^2/sec , C_o is the concentration of the bulk species O in mol/cm^3 , ν is the sweep rate in V/sec , n_a is the number of electrons in the rate determining step, and n is the number of electrons transferred. As seen from the above equations, for an irreversible system i_p is proportional to C_o and $\nu^{1/2}$, whereas E_p is a function of sweep rate. In addition, E_p shifts in the negative direction by $30/\alpha n_a$ mV for each tenfold increase in sweep rate.

1.3.4.2 POTENTIOSTATIC PULSE PERTUBATION

This electrochemical technique involves an initial perturbation in potential from a region where no electrode reaction occurs to a constant potential where the reaction proceeds. The current response is monitored as a function of time. For a diffusion controlled process, the current

response due to the perturbation is given by the Cottrell equation:

$$i = \frac{nFD_o^{1/2}C_o}{\pi^{1/2}t^{1/2}} \quad 26$$

that is, the current falls as $t^{-1/2}$. A plot of i as a function of $t^{-1/2}$ should be linear and pass through the origin. This graph is often employed as a diagnostic test for diffusion control.

The response of the potential pulses as described earlier gives rise to falling i - t transients which are observed when both the reactant and product are soluble in solution. In the case of electrocrystallisation of anodic passivating films, the i - t profiles consist of a rising portion which is a clear indication of a nucleation step, then the current falls as the growing nuclei overlap on the electrode surface. The i - t transients are analyzed in terms of the current and time maxima as discussed in section 1.3.2 depending upon the type of nucleation, that is, two or three dimensional.

II EXPERIMENTAL

II.1 CHEMICAL REAGENTS

All solutions were prepared using triply distilled water obtained after distillation from an alkaline potassium permanganate solution. Two concentrations of sulphuric acid (ARISTAR, 98.0%) were used. For the lead amalgam work the average concentration of the acid was 1.29 ± 0.04 molal. However, this concentration of solution would freeze at -20°C , therefore, for the solid lead studies the concentration was increased to 4.26 ± 0.11 molal. The organic additive employed was ammonium lignosulphonate (Lignosol C-16, Lignosol Chemicals Ltd., Quebec) and its composition is given in Table 1. The concentration of ammonium lignosulphonate ranged from 0 to 76 ppm.

Oxygen was purged from the electrolytes by bubbling purified nitrogen (79) for 20 minutes prior to and during an experiment. The solution temperature was 20°C for the lead amalgam and ranged from 20° to -20°C for the solid lead studies.

II.2 PREPARATION OF LEAD AMALGAM

The lead amalgam of 1.26% by weight of lead was prepared by dissolving lead beads (99.999%, Cominco of Canada Ltd.) in ultrapure mercury (99.9998%, Alfa Inorganics). Approximately 1 ml of a very dilute perchloric acid solution (1 drop perchloric acid to 2 mls water) was kept over the amalgam to maintain it free of organic contaminants. The

TABLE 1 - A Typical Chemical Analysis of the
Ammonium Lignosulphonate Used.

H ₂ O	5.0%
Ash	1.7%
Total sulphur	7.5%
Organic sulphur	7.3%
Calcium	<0.1%
Sodium	traces
Organic nitrogen	1.4%
Nitrogen (ammonia)	1.8%
Methoxyl	8.2%
Impurities	
(Mg, Fe, Mn, Zn, Cu, heavy metals)	traces
Equivalent weight	>320

amalgam was rinsed free of the perchloric acid with copious quantities of triply distilled water immediately prior to use.

11.3 ELECTROCHEMICAL CELL FOR LEAD AMALGAM STUDIES

The electrochemical cell was of conventional three-electrode configuration. The cell body of 20 mls capacity and the lid were cylindrical and machined from Teflon. The lid held three modified Pasteur pipettes. One pipette was used to bubble nitrogen through the solution; the second was employed to dislodge used amalgam drops from the capillary tip by squirting the solution in the cell at them. The third pipette was located in the centre. It was drawn to a very fine tip and acted as a Luggin capillary to reduce the uncompensated solution resistance between the working and reference electrodes. The uncompensated solution resistance of the order of 7 Ω was determined by observing at what value of ohmic compensation the potentiostat would oscillate. Figure 1 illustrates the geometrical orientation of the Luggin capillary, the syringe and solution squirter.

11.3.1 ELECTRODES FOR LEAD AMALGAM

The working electrodes were small sessile amalgam drops extruded on the tip of an upturned syringe. The syringe was a 50 μ l Hamilton gas-tight syringe (Model #1705). The needle was removed and the end of the glass syringe drawn to a very fine tip of an inner diameter of 331 μ m as measured by a

Figure 1 - Approximate geometric arrangement of the
(a) tip of the syringe,
(b) the Luggin capillary and,
(c) the solution squirter used to dislodge used
amalgam drops.

Three stages in the extrusion of a drop are
illustrated. The geometry of the drop is true
to scale as depicted.

travelling microscope. Prior to an experiment, the syringe tip was thoroughly cleaned in aqueous potassium hydroxide, dilute nitric acid, followed by a thorough rinse in triply distilled water, and further cleansing in a nitrogen plasma (Harrick model PDC-3XG plasma cleaner) for 20 minutes to remove any traces of contaminants possibly present on the glass surface. After cleansing the tip, it was rendered hydrophobic to avoid solution creepage into the tip by soaking for 15 minutes in a solution of a few drops of dimethyldichlorosilane (99% Aldrich Chemical Co.) in 15 ml of carbon tetrachloride (JT Baker Chemical Co., reagent grade). The tip was then rinsed by immersion for 15 minutes in clean carbon tetrachloride. The syringe was then dried in a 110°C oven for 24 hours. Once the tip was filled with the lead amalgam it was inserted into the cell body through a hole in the bottom of the cell. The plunger of the syringe was controlled by a micrometer (Moore and Wright, Sheffield, England) which was securely attached to the body of the syringe. The Teflon tip on the plunger was cut away to expose its stainless steel tip. This allowed electrical contact to be made with the amalgam.

The reference electrode used in both the amalgam and solid lead electrode studies was a mercury/mercurous sulphate couple ($\text{Hg}/\text{Hg}_2\text{SO}_4$) in the sulphuric acid/additive solution of the same concentration, and all potentials are quoted

with respect to it. It was prepared in 5 mm glass tubing which could fit inside the Pasteur pipette that acted as the Luggin capillary. The tubing was closed at one end leaving a very small hole exposed. The bottom of the tube contained loosely packed reagent grade mercurous sulphate (BDH Chemicals Ltd.) to a depth of 3-4 mm. The tube was then dipped into the electrolyte to wet the mercurous sulphate. Ultrapure mercury was added on top of the mercurous sulphate. A platinum wire was inserted into the mercury for electrical contact. The electrode was left soaking in the solution overnight in a sealed vessel. At the end of each day's experiments, the reference electrode's potential was verified against a saturated calomel electrode (Fischer Scientific) to account for the possibility of any small drifts in potential. The potentials of each day's experiments were then corrected for the small potential drifts which were less than 2 mV.

The counter electrode was a cylindrical platinum gauze that completely surrounded the syringe tip and Luggin capillary.

11.3.2 MEASUREMENT OF DROP SIZE

A novel, convenient and accurate method was used to measure the area of the lead amalgam drops which involved observing the double layer capacitance of the electrode/electrolyte interface as a function of micrometer travel. When a drop was dislodged, the amalgam would break off inside

the capillary of the tip. While the amalgam was still inside the tip the capacitance was constant, and it increased sharply as the drop began to form on the tip (See Figure 1). Therefore, a plot of capacitance versus micrometer travel demonstrated two linear segments in which the inflection point corresponded to the capacitance of a hemisphere of amalgam which could be conveniently converted to the area of the spherical sessile drop. A calibration curve was constructed for each solution used. Fresh amalgam drops were used for individual measurements and were all of the approximate area ($4.5 \times 10^{-3} \text{ cm}^2$) in order to give a consistent geometry of the drop and the capillary tip. The sessile drops were assumed to be sections of a sphere.

11.3.3 ADSORPTION OF THE EXPANDER ONTO THE LEAD AMALGAM SURFACE AS A FUNCTION OF TIME

The double layer capacitance of a drop measured as a function of time at -1100 mV in 17.45 ppm of expander decreased as illustrated in Figure 2. A decrease in the double layer capacitance with time in the presence of an expander has been reported previously and was attributed to the adsorption of expander layers on the electrode surface (18, 44, 47). Because the expander was found to adsorb onto the lead amalgam surface, it was necessary to wait a sufficient period of time to allow the adsorption to reach its equilibrium value before the electrochemical perturbations

Figure 2 - The double layer capacitance as a function of time for a fresh amalgam drop in 17.45 ppm of the expander. The capacitance was measured at -1100 mV versus $\text{Hg}/\text{Hg}_2\text{SO}_4$.

were carried out. Therefore, for the expander containing solutions, upon extrusion of a drop, the drops were maintained at -1100 mV to allow the maximum quantity of expander to adsorb. As seen from Figure 2, a period of 3 minutes is sufficient for the adsorption to occur.

11.4 ELECTROCHEMICAL CELL FOR SOLID LEAD STUDIES

The electrochemical cell employed was of the conventional three electrode configuration. The main cell body of 60 mls capacity constructed of pyrex glass was surrounded by a glass temperature thermostatted jacket. The lid to the cell was machined from a piece of Teflon to fit snugly into the main cell body. A long hollow cylinder extended from the centre of the lid into the cell and supported the working electrode. This cylinder had a small lip at the end that enabled the working electrode to be inserted into the solution in the same configuration each time giving a constant geometrical orientation. In addition, the lid held three modified Pasteur pipettes which served in a similar manner as described for the lead amalgam cell, that is, for nitrogen supply and as a Luggin capillary. The third pipette was sealed and inserted well into the electrolyte to contain a thermocouple to monitor the temperature.

The uncompensated solution resistance of the order of 4 Ω was measured in the same manner as was done for the lead amalgam system. The cell body and lid are shown photographically

in Figure 3 and can be compared with an illustration given in Figure 4. The orientation of the Luggin capillary, the thermocouple, bubbler and counter electrode with the working electrode is photographed in Figure 5.

11.4.1 SOLID LEAD ELECTRODES

The solid lead working electrodes were constructed from a 1 mm lead wire (99.9997, JMC Puratonic England). The electrode design that will be described was novel and required several trials before a suitable configuration was found. Electrical contact to the lead wire was achieved by soldering the lead to a small piece of brass with low temperature solder.

It was found experimentally that erratic performance of the electrode began to occur long before it had been microtomed to its minimum length, and meaningful current readings could not be obtained. It was suspected that the crystal structure of the lead had been altered due to the heat from soldering. This was verified by adequate heat sinking of the lead wire near the solder junction and rapid soldering. The wire/brass combination was supported by casting in SCOTCHCAST. It was observed through irregular experimental behaviour of the electrode that if the seal between the lead and SCOTCHCAST was not excellent, solution would have crept between the two. To avoid this, previous to casting the lead wire was coated with a very thin layer of ARALDITE, a hard epoxy

Figure 3 - A photograph of the electrochemical cell for the solid lead electrode showing
(a) the nitrogen bubbler,
(b) the Pt gauze counter electrode,
(c) the working electrode, and,
(d) the Luggin capillary

Figure 4 - Illustration of the solid lead electrochemical cell depicting
(a) the Luggin capillary,
(b) the working electrode,
(c) the Pt gauze counter electrode and,
(d) the nitrogen bubbler.
The geometry is accurate as shown.

Figure 5 - A photograph of the orientation of
(a) the nitrogen bubbler,
(b) the Luggin capillary,
(c) the working electrode,
(c) the thermocouple holder, and,
(d) the Pt gauze counter electrode

resin. This produced an excellent seal around the wire. When the wire/brass combination was cast in the SCOTCHCAST, 1/4" of brass was left exposed for the connection of electrical circuitry connections. The SCOTCHCAST was machined to an outer diameter of 0.279". The average area of the working electrode surface was $7.2472 \times 10^{-3} \text{ cm}^2$.

11.4.2 PREPARATION OF ELECTRODE SURFACE

A serious problem associated with solid electrodes is that they do not offer fresh, reproducible surfaces with well-defined geometry. They contain various surface defects and structures which make consistent electrochemical data extremely difficult to obtain. A common method used to achieve reproducible surfaces is to cycle the electrode until a constant current response is attained. However, this leaves the surface of the electrode covered with a film which renders the electrode surface poorly defined. Therefore, in the present study, an original approach was employed to obtain fresh, reproducible surfaces. Prior to each electrochemical perturbation, the lead electrode was cut with a glass knife in a microtome as reported previously in this laboratory (80) until the surface of the lead appeared mirror-smooth, and highly reflective. Immediately after microtoming, the electrode was dipped in dilute nitric acid to clean the surface from any organic contaminants that may have resulted from microtoming. The electrode was rinsed

well with triply distilled water, and transferred directly into the solution at a potential of -1100 mV for 3 minutes. A wide variety of rinsing procedures were tried with different combinations of acid/water mixtures and degreasing with organic solutions. The procedure decided upon gave the most reproducible results. The electrode was potentiostatted at -1100 mV because it was found that there was no advantage in using more negative potentials plus it was sufficiently negative to maintain the lead in an unoxidized state. The 3 minute wait was sufficient to allow the limiting quantity of expander to adsorb onto the electrode surface and gave the most reproducible results from a large number of empirical experimental trials.

The counter electrode was a platinum gauze that was wrapped around the cylinder on the cell lid. The reference electrode was the mercury/mercurous sulphate couple employed with the lead amalgam experiments.

11.5 ELECTRONIC INSTRUMENTATION

The potentiostat employed to supply a constant potential to the working electrode was a Stonehart BC 1200 Model used in conjunction with a PAR model 175 potential programmer. A 10:1 voltage divider was used on the output from the PAR for added precision. This allowed the potentials to be set within ± 0.1 mV. The potential was monitored by a Hewlett-Packard model 5465A digital multimeter. A Hewlett-

Figure 6 - The electronic circuit diagram indicating RE, the reference electrode, WE, the working electrode, and CE, the counter electrode.

Packard model 331UB function generator supplied a 3.84 mV rms sinusoidal signal to the working electrode. The in-phase and out-of-phase components of admittance were measured using a PAR model 128A Lockin Amplifier. The current response to the electrochemical perturbations were recorded on a Nicolet 3091 digital oscilloscope. Permanent hard copies were plotted on a Hewlett-Packard model 7047A x-y-t plotter. A circuit diagram of the electronic system is given in Figure 6.

11.6 CLEANING PROCEDURES

The rigorous cleaning procedures were designed to remove trace impurities, especially organic contaminants which may have been adsorbed onto the surfaces of the glassware. The use of soaps or detergents was rigorously avoided. All parts of the cells were soaked for a prolonged period of time in concentrated sulphuric acid, followed by a prolonged soak in aqueous potassium hydroxide. They were rinsed thoroughly with copious quantities of triply distilled water and left to air dry overnight in a closed container. Immediately prior to use, they were exposed to a nitrogen plasma for 20 minutes.

11.7 SCANNING ELECTRON MICROSCOPY

A model JSM-U3 scanning electron microscope (SEM) was used to observe different crystal morphologies of the lead sulphate film found in solutions containing 0, 15, 40 and 60 ppm of ammonium lignosulphonate solutions. For each

solution the electrode was removed at various points during the positive sweep, that is, the rising portion, at the peak, midway down the falling side, and after complete passivation. At any given point, the electrode was removed and immediately rinsed by gently dipping in a beaker of triply distilled water. A thin section of the electrode was sliced off with a clean razor blade, and stored in a small petrie dish under vacuum in a desiccator until the SEM's were recorded. Special care was taken not to disturb the lead sulphate film in any way. All slices were taken at 20°C.

III RESULTS

III.1 LEAD AMALGAM

III.1.1 DOUBLE LAYER CAPACITANCE

The double layer capacitance of an amalgam drop in solution measured at -1100 mV decreased as a function of time in the presence of the expander as shown in Figure 2. The decrease from $17 \mu\text{F cm}^{-2}$ for 0.0 ppm to $8 \mu\text{F cm}^{-2}$ for 76.60 ppm of expander is a result of the presence of an adsorbed layer of the expander onto the electrode surface (18, 44, 47). The time dependence of the double layer capacitance as a function of time was proportional to $t^{-1/2}$ indicating that the adsorption of the expander onto the clean amalgam surface was controlled by diffusion.

The decrease in the double layer capacitance can be explained by treating the electrode/electrolyte interface as a parallel-plate capacitor whose capacitance C , is given by:

$$C = \frac{\epsilon_0 k A}{d} \quad 27$$

where ϵ_0 is the permittivity of free space, k is the dielectric permittivity, A is the area of the plates, and d is the separation between the plates. The permittivity of organic molecules is less than that of water (81), plus organic layers are thicker than water layers, therefore, from equation 27 it is obvious that the capacitance should decrease in the presence of the expander.

Similar results for the behaviour of the double layer capacitance as a function of time were determined for the solid lead electrode.

111.1.2 POTENTIAL STEP PERTUBATION

A sample transient in which the potential was stepped from -1100 to -874 mV in a solution containing 7.67 ppm of expander is given in Figure 7. The falling currents before the maximum gave linear i versus $t^{-1/2}$ plots signifying that these currents are due to lead dissolution. Therefore, lead dissolution precedes the lead sulphate film formation.

Potential step transients can be analyzed in terms of the parameters of i_m and t_m given in equations 21 and 22 respectively, and plotted in a non-dimensional form as depicted in Figure 8. As the concentration of the expander increased, the transient broadened and the tail became longer. This trend was also observed in the formation of thick layers of $PbCl_2$ on a lead amalgam electrode (55).

The semi-log plot of the maximum current, i_m , as a function of potential is given in Figure 9. It can be seen that an increase in the expander concentration lowers the maximum current observed at any particular potential. In the low overpotential regions, there is not a large change in i_m values with different concentrations of expander. However, the effect on i_m is more severe at higher overpotentials and higher concentrations of expander.

Figure 7 - A sample potential step transient where the potential was stepped from -1100 mV to -874 mV in 7.89 ppm of the expander. Note the large lead dissolution current before the onset of electrocrystallisation.

Figure 8 - Potentiostatic current-time transients plotted in non-dimensional form. The numbers at the end of the curves are the expander concentrations in ppm. The curve for 0.0 ppm is not shown because it is essentially the same as for 0.72 ppm. A single curve for the rising portion of the transient was shown rather than separate curves for each concentration since these parts of the transients were very close to one another.

Figure 9 - A semi-logarithm plot of the maximum current, i_m , as a function of potential, E , for the potentiostatic transients. The numbers beside the curves represent the expander concentrations.

The semi-log relationship between the time at which the maximum time, t_m , occurs and potential is illustrated in Figure 10. As the concentration of the expander is increased, t_m is shifted to longer times and to more positive potentials. Table 2 lists the slopes $dE/d\log i_m$ and $dE/d\log t_m$ for the steep portions of the curves of solutions containing 0.0 and 0.72 ppm of expander. This high potential dependence of i_m and t_m at low overpotentials are typical of electrocrystallisation and have been previously reported for both two dimensional and three dimensional systems (82).

III.1.3. LINEAR POTENTIAL SWEEP PERTUBATION

Figure 11 depicts a linear potential sweep in 1.29 $\pm$ 0.04 molar sulphuric acid in the absence of expander. The potential was swept at 20 mV s⁻¹ in a positive direction from -1100 mV to -850 mV, reversed, and swept negatively back to -1100 mV. The anodic peak in the region of -940 mV to -820 mV is due to the formation of a lead sulphate film, and the cathodic peak is from the reduction of lead sulphate. The potential region of film formation is consistent with earlier results on solid lead electrodes (12, 25, 27, 31, 65, 83). The separation between the two peaks of 100 mV, and their different shapes indicate the film formation and reduction proceed irreversibly.

These sweeps in the absence of expander often exhibited a sharp transition or "kink" separating the regions of lead

Figure 10 - A semi-logarithm plot of t_m as a function of potential, E , for the potentiostatic transients. The numbers beside the curves represent the expander concentrations.

TABLE 2 - Potential Dependences of the
Transient Maximum Parameters,
 i_m and t_m

Concentration of expander in the solution (ppm)	$dE/d\log i_m$ (mV dec ⁻¹)	$dE/d\log t_m$ (mV dec ⁻¹)
0	8.70 ± 0.01	-8.20 ± 0.01
0.72	9.11 ± 0.04	-7.53 ± 0.04

Figure 11 - A linear potential sweep, at $20 \text{ mV} \cdot \text{s}^{-1}$ in 1.29 ± 0.04 molal sulphuric acid with no expander added. The potential was swept positively from -1100 mV to -800 mV , reversed and swept negatively back to -1100 mV . Only the potential range from -1040 mV to -870 mV has been shown.

dissolution and nucleation and growth. The lead dissolution region showed a rising curve that broke sharply at the onset of nucleation and growth. The kink was not evident on the transients from any solutions containing expander.

The linear potential sweep in the absence of the expander can be compared to a similar one done at 20 mV s^{-1} in 7.89 ppm of expander shown in Figure 12. The current on the reverse sweep has been expanded by a factor of 10. The significant differences in this sweep are the increase of 10 times in the anodic peak current, the positive shift in the potential of the anodic peak, the presence of the small anodic peak on the reverse sweep, and the smaller reduction current that is independent of potential even out to the region of hydrogen evolution.

The profile of the linear potential sweeps in Figures 11 and 12 demonstrate features of an electrocrystallisation process. The current rises gradually due to the dissolution of Pb^{2+} ions, then rises more sharply upon nucleation and growth. The electrode surface is being covered by a growing film, therefore, eventually the periphery available for further growth will be diminished and the current will decrease. The charge required for passivation ranged from 20 to 964 mC cm^{-2} for 0.0 to 76.60 ppm of expander which is much larger than that necessary for a monolayer of lead sulphate of $325 \text{ } \mu\text{C cm}^{-2}$ as quoted by Hampson and Lakeman

Figure 12 - A linear potential sweep at 20 mV s⁻¹ in 7.89 ppm of expander. The potential was swept positively from -1100 mV to -800 mV, reversed, and swept negatively to -1700 mV, again reversed and swept negatively back to -1100 mV. Only the potential range from -1100 mV to -800 mV is shown. The current on the reverse sweep has been expanded by a factor of 10. Note the small reduction current that is independent of potential, and the small anodic peak on the reverse sweep.

(26, 65). These observations indicate the presence of a thick deposit of lead sulphate which forms via a three dimensional nucleation and growth mechanism, and this is consistent with earlier studies on cycled lead electrodes (21, 24, 25-27, 29).

The behaviour of the region of lead dissolution which is characterized by the low current domain prior to the onset of nucleation and growth, was studied by performing slow sweeps (10 mV s^{-1}) and examining the current as a function of potential as shown in Figure 13. The slopes $dE/d\log i$ for 0.0 and 17.45 ppm are $27.37 \pm 0.43 \text{ mV dec}^{-1}$ and $30.26 \pm 0.46 \text{ mV dec}^{-1}$ respectively. These slopes are very close to that expected ($29.58 \text{ mV dec}^{-1}$) for a reversible two electron process. Therefore, the lead is dissolving reversibly as Pb^{2+} ions both in the absence and presence of the expander.

The log-log dependence of the anodic peak current, i_p , as a function of sweep rate ν , in Figure 14 enables one to draw conclusions regarding the effect of the expander on the controlling mechanism of the lead sulphate formation. Table 3 gives the slopes $d\log i_p/d\log \nu$ for the different solutions. The slopes for 7.89, 17.45, and 76.60 ppm of expander are less than one half meaning that the reaction is diffusion controlled. For 0.0 and 0.72 ppm, the slopes larger than one half signify that the reaction is not controlled by diffusion,

Figure 13 - Tafel relationships of the logarithm of the anodic current as a function of potential from the low current region prior to the onset of nucleation and growth on the lead amalgam. The numbers at the end of the lines represent the expander concentrations in ppm. The least squares lines are indicated.

Figure 14 - A log-log plot of the anodic peak current, i_p , as a function of sweep rate, v , on the lead amalgam. The symbols are $\square$ for 0.0 ppm, $\triangle$ for 0.72 ppm, $\bullet$ for 7.89 ppm, $\blacksquare$ for 76.60 ppm.

TABLE 3 - Potential Dependences of Sweep Rate,
Peak Potential, and Anodic Peak
Current.

Concentration of expander in the solution (ppm)	$dE_p/d\log v$ (mV dec ⁻¹)	$d\log i_p/d\log v$
0.0	$15.08 \pm .01$	$0.81 \pm .15$
.72	$9.92 \pm .04$	$1.00 \pm .21$
7.89	$8.82 \pm .02$	$0.35 \pm .03$
17.45	$24.02 \pm .002$	$0.40 \pm .008$
76.60	$42.14 \pm .002$	$0.43 \pm .02$

but by electrocrystallisation, or by both processes (84).

An interesting feature to note is that the curves for 17.45 and 76.60 ppm lie below 7.89 ppm. This suggests the existence of an optimum concentration of expander as reported by Mahato (41) who found 20 ppm as the optimum concentration on a cycled lead electrode, and beyond that the expander exhibited an inhibitory effect, that is, it adversely affected the reactions involved.

The linearity of the semi-log relationship between the sweep rate, v , and peak potential, E_p , in Figure 15 indicates that the formation of the lead sulphate is proceeding irreversibly in the absence and presence of expander. An increase in the concentration of expander shifts E_p to more positive potentials. Table 3 lists the values of the slopes $dE_p/d\log v$ as calculated from linear regression. The steep slopes for 0.0, 0.72, and 7.89 ppm are characteristic of rate control by electrocrystallisation. The slope of 42.14 ± 0.002 for 76.60 ppm is greater than $29.58 \text{ mV dec}^{-1}$ which would have been expected for a two electron diffusion controlled process. This larger slope at the higher expander concentration is further evidence of the expander's inhibitory effect, namely increasing the irreversibility of the reaction by an increased overpotential.

The optimum concentration of the expander was determined from the plot of anodic current as a function of concentration

Figure 15 - A semi-logarithm plot of sweep rate, V , as a function of peak potential, E_p . The numbers beside each line represent the expander concentrations in ppm. The steepness of the slopes at low expander concentrations are characteristic of electrocrystallisation. The least squares lines are indicated.

in Figure 16 to be near 7.89 ppm where the current reaches a maximum.

The area under the anodic peak gives the charge required for passivation. Figure 17 depicts a further effect of the expander, that is, to increase the charge as the expander concentration increased. The charge reached a maximum near 17.45 ppm then approached a steady state. This suggested that 17.45 ppm was the smallest concentration to give a maximum expander effect.

The relationship between the peak potential and the expander concentration is given in Figure 18. The presence of the expander shifts the peak potential to more positive values.

The resistance of the passive film was measured by allowing the potential to sweep positively from -1100 mV to -800 mV to form the lead sulphate film, and then maintained at -800 mV. Figure 19 shows the decrease in the resistance of the film with increasing concentrations of expander. The resistances have units of $\Omega \text{ cm}^2$ which is equivalent to the product of the resistivity of the film and its thickness:

$$R_1 = \rho_1 \frac{L}{A}$$

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where R_1 is the resistance; ρ_1 is the resistivity in $\Omega \text{ cm}$, L is the thickness of the film and A is the cross-sectional area. Therefore, if the resistance decreases, then either

Figure 16 - A plot of the oxidation current as a function of the expander for fixed sweep rates of 10 and 500 mV s⁻¹ on the lead amalgam. In both cases the curves reach a maximum at 7.89 ppm indicating the presence of an optimum concentration of expander.

Figure 17 - A semi-logarithm plot of the charge, Q , as a function of expander concentration for the sweep rates of 10 and 20 mV s^{-1} on the lead amalgam. The symbols are $\bigcirc$ for 10 mV s^{-1} and $\square$ for 20 mV s^{-1} .

Figure 18 - A plot of the anodic peak potential, E_p , as a function of the expander concentration for the lead amalgam. The sweep rate was 50 mV s^{-1} . Note the absence of the plateaus.

Figure 19 - The resistance of the lead sulphate film measured as a function of the expander concentration. The average area₂ of the lead amalgam drops was $4.47 \times 10^{-3} \text{ cm}^2$.

the resistivity is decreasing because of pores in the film, and/or because the thickness of the film is less.

III.2 SOLID LEAD ELECTRODE

III.2.1 LINEAR POTENTIAL SWEEP PERTUBATION

A typical linear potential sweep at 20°C with no expander is illustrated in Figure 20. The potential was swept positively from -1100 mV to -750 mV, reversed and swept negatively back to -1100 mV. The large oxidation peak in the potential region of -925 mV to -800 mV is due to the formation of the lead sulphate film and the subsequent partial reduction of the film at -990 mV. The potentials and currents are consistent with the results for experiments using a lead amalgam electrode, however, the reduction peak is much smaller on the solid lead.

The expander did not seriously affect the profile of the sweeps in either the anodic or cathodic peak's current or potential. Lowering the temperature did not alter the shapes of the transients. The reduction peak decreased and disappeared completely at 0°C both in the presence and in the absence of the expander.

III.2.2 SWEEP RATE DEPENDENCE

A sweep rate dependence in which the rate was varied between 5.6 and 1000 mV s^{-1} was determined for 0.0 and 15.01 ppm of expander solutions at temperatures of 20°, 0°, and -20°C. The log-log dependences of i_p with sweep rate

Figure 20 - A linear potential sweep on the solid lead electrode where the potential was swept positively from -1100 mV to -760 mV, reversed and swept negatively back to -1100 mV. Only the potential range from -1080 mV to -760 mV is shown. Note the smaller reduction peak compared to that on the lead amalgam.

are illustrated in Figures 21 and 22 for 0.0 and 15.01 ppm respectively for temperatures of 20° and -20°C. Linear relationships were obtained and linear regression was used to calculate the slopes $d\log i_p / d\log v$ in Table 4. At 20°C for both 0.0 and 15.01 ppm of expander, the gradients were greater than one half which meant that the lead sulphate film formation was not diffusion controlled. Slopes greater than one half have been observed for other electro-crystallisation reactions (11, 21, 26, 85, 86), and are consistent with a surface controlled process where nucleation events may be coupled with adsorption, diffusion and dissolution, and uncompensated solution resistance effects. At 10°C and below, the slopes with and without expander decreased towards one half.

Figures 23 and 24 demonstrate the semi-log relationship between the anodic peak potential and sweep rate for 0.0 and 15.01 ppm of expander respectively. The linear relationship means that lead sulphate formation proceeds via an irreversible charge transfer mechanism. However, the presence of the small reduction peak suggests that the reaction is not totally irreversible. The combination of increasing the concentration of expander and lowering the temperature shifted E_p to more positive potentials.

The sweep rate dependence shows that the scatter on the data points is large. However, since this relationship is

Figure 21 - A log-log plot of the anodic peak current, i_p , as a function of sweep rate, v , for 0.0 ppm of expander on the solid lead electrode. The relationships for two representative temperatures of 20° and -20°C are illustrated together with the least squares lines. Note the smaller current at the lower temperatures.

Figure 22 - A log-log plot of the anodic peak current, i_p , as a function of sweep rate, V , for 15 ppm of expander on the solid lead electrode. The relationships for two representative temperatures of 20° and -20°C are shown together with the least squares lines. Note the smaller current at the lower temperatures.

TABLE 4 - Potential Dependences for the Sweep Rate
Dependence - Solid Lead

Concentration of expander in the solution (ppm)	Temperature °C	$d \log i_p / d \log V$
0	20	0.84 ± .11
	0	0.54 ± .16
	-20	0.58 ± .15
15	20	0.84 ± .15
	0	0.77 ± .23
	-20	0.58 ± .13

Figure 23 - A semi-logarithm plot of the sweep rate, v , as a function of peak potential, E_p , for 0 ppm on the solid lead electrode at two representative temperatures of 20° and -20°C. The symbols are ○ for 20°, and □ for -20°. The least squares lines are indicated. Note the shift to more positive potentials at the lower temperature.

Figure 24 - A semi-logarithm plot of the sweep rate, v , as a function of peak potential, E_p , for 15 ppm on the solid lead electrode at two representative temperatures of 20° and -20°C . The symbols are ○ for 20° and □ for -20° . The least squares lines are indicated. Note the shift to more positive potentials at the lower temperature.

linear over the experimentally accessible range, it is convenient to use a single sweep rate to represent the line. This will allow for a more detailed investigation of the influence of the expander and temperature on the formation of lead sulphate. If the chosen rate is too slow, then the currents will be small, and the signal to noise ratio will be poor. If the rate is too high, uncompensated solution resistance effects will distort the profile of the sweeps. Therefore, a midrange sweep of 40 mV s^{-1} was chosen. To improve the reproducibility, six sweeps were recorded for each solution at each temperature. The values were averaged and the 95% confidence intervals calculated.

III.2.3 SINGLE SWEEP RATE

The effect of the expander on the anodic peak current is demonstrated in Figure 25 for three representative temperatures of 20° , 0° , and -20°C . Increasing the concentration of the expander did not have a significant effect on i_p . In contrast to the behaviour on the lead amalgam electrode or on cycled lead electrodes (41), no evidence for an optimum concentration of the expander was provided from the data on the solid lead electrode.

The charge passed during passivation did not exhibit any dependence upon the concentration of the expander. For each temperature, an average charge was calculated for all the solutions from 0.0 to 63.73 ppm of expander. The results

Figure 25 -

A plot of the anodic peak current, i_p , as a function of the expander concentration on the solid lead electrode for three representative temperatures of 20°, 0°, and -20°C. The average error bar is indicated. Note the absence of an optimum concentration of the expander.

are tabulated in Table 5. The charge decreased as the temperature was lowered.

The influence of the expander on the anodic peak potential is illustrated in Figure 26 for three representative temperatures of 20°, 0°, and -20°C. The interesting feature demonstrated is the two plateaus shown. These plateaus were observed for each temperature studied, however, they were not present in the lead amalgam studies. Upon initial addition of the expander, E_p rises to the first plateau. At a concentration of 30 ppm, E_p rises to the second plateau. The value of E_p remained constant at this level as the expander concentration increased. Temperature did not influence the plateaus. A positive shift in the peak potential with a decrease in temperature is also shown in this Figure.

The activation energy, E_a , of a reaction can be determined from the Arrhenius equation:

$$\ln(k) = \ln(A) - E_a/RT \quad 29$$

where k is a specific rate constant, and A is a frequency factor that is independent of temperature. Thus, if a plot of $\ln(k)$ versus the inverse of temperature is linear, the intercept will equal $\ln(A)$ and the gradient will be equivalent to $-E_a/R$, and the reaction is said to display Arrhenius behaviour. Figure 27 shows the Arrhenius plot of

TABLE 5 - The Average Charge Passed upon
Passivation of the Solid Lead
Electrode as a Function of
Temperature

Temperature °C	Charge Passed mCcm ⁻²
21.7	29.7 ± 5.1
10	22.4 ± 2.6
0	17.4 ± 2.6
-10	14.8 ± 2.1
-20	11.3 ± 1.9

Figure 26 - The relationship between the anodic peak potential, E_p , and the expander concentration of the solid lead electrode at three representative temperatures of 20°, 0°, and -20°C. The rise to the two plateaus is clearly illustrated at expander concentrations of 5 and 30 ppm. The average error bar is indicated.

Figure 11 - An Arrhenius plot of the natural logarithm of the anodic peak current, i_p , as a function of the inverse of temperature. Only points for 0 and 61 ppm are shown since all the solutions demonstrated a similar dependence. The least squares line is indicated. The symbols are $\circ$ for 0 ppm and $\blacksquare$ for 61 ppm. The average error bar is indicated.

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$\ln(i_p)$ as a function of the inverse of temperature. Only 0.0 and 63.73 ppm are depicted as representative points. All solutions gave linear relationships and they were superimposable upon one another. The energy of activation was calculated and plotted as a function of expander concentration in Figure 28. The activation energy apparently does not depend upon the concentration of the expander. This suggests that the mechanism of lead sulphate formation has not been altered by the expander. The average activation energy was $12.76 \pm 0.88 \text{ kJ mole}^{-1}$.

In order to investigate the effect of the expander on the dissolution of lead, Tafel plots of the logarithm of the current as a function of potential in the low current region prior to the onset of nucleation and growth were determined as illustrated in Figure 29. The potential dependences of $dE/d\log i$ are given in Table 6. For all solutions, the gradients are close to $29.58 \text{ mV dec}^{-1}$ indicating a reversible two electron dissolution of the lead. Increasing the concentration of the expander shifts the lines to more positive potentials. It should be emphasized that these shifts result in three groups corresponding to the concentrations of the plateaus in Figure 26.

At a constant potential of -915 mV in the dissolution region, the current was plotted as a function of expander concentration. Figure 30 shows that the current decreases

Figure 28 - A graph of the activation energy as a function of the expander concentration. The average error bar is indicated.

Figure 29 - A Tafel plot of the anodic current, i , as a function of potential, E , in the dissolution region prior to the onset of nucleation and growth on the solid lead electrode. For the higher expander concentrations, only 30 and 60 ppm are shown as representative curves. Note the three potential regions corresponding to the concentrations of the two plateaus. The symbols are Δ for 0 ppm, $\square$ for 10 ppm, $\blacktriangle$ for 20 ppm, $\blacksquare$ for 30 ppm, and $\circ$ for 60 ppm.

TABLE 6 - The Potential Dependences of the Tafel Relationships in the Dissolution Region

Concentration of expander in the solution (ppm)	$dE/d\log i$ (mV dec ⁻¹)
0	31.44 $\pm$.003
10	28.97 $\pm$.004
20	32.71 $\pm$.003
30	31.81 $\pm$.002
40	27.17 $\pm$.003
50	31.14 $\pm$.005
60	30.77 $\pm$.001

Average 30.57 $\pm$.003

Figure 30 - A plot of the current, i , as a function of expander concentration at a constant potential of -915 mV in the Pb^{2+} dissolution region on the solid lead electrode.

as the expander is increased. Similarly, at a constant current density of 1.2 mA cm^{-2} , in the dissolution region, the potential was plotted as a function of increasing expander concentration as shown in Figure 31. Evidence for the existence of the two plateaus is clearly indicated, and the potential regions of these plateaus correspond to those from E_p in Figure 26.

In order to study the influence of the expander on the nucleation and growth of the lead sulphate film, during a linear potential sweep the potential was reversed on the rising current prior to the oxidation peak. Upon scan reversal, the current formed a nucleation loop (87) and the typical transient is depicted in Figure 32. When the sweep is reversed before the maximum, further nucleation is stopped and the return current loop is due to the growth of the crystals. The separation between the point where the return loop crosses the potential axis (the crossing potential, E_x), and the point where the front slope extrapolates to the potential axis is an approximate measure of the nucleation overpotential (88). The above measurements give information of the crossing potential as a function of expander; the nucleation overpotential versus the expander; and the growth kinetics as a function of expander.

Table 7 shows the results of the influence of the

Figure 31 - The relationship between potential and $\text{expander concentration}$ at a constant current density of 1.2 mA cm^{-2} in the dissolution region on the solid lead electrode. Note the two plateaus which correspond to the same concentration regions as the E_p plateaus.

Figure 32 - A sample nucleation loop transient in 40 ppm of the expander. Note the crossing over of the current of the return loop as indicated by the arrows. The sweep rate was 40 mV s^{-1} .

TABLE 7 - The Influence of the Expander on the Potential Dependence of E_x and on the Nucleation Overpotential

Concentration of expander in the solution (ppm)	Crossing Potential (mV)	Nucleation Overpotential (mV)
0	-932.1 ± 5.7	31.1 ± 6.2
10	-935.8 ± 1.7	44.8 ± 4.1
20	-931.2 ± 1.4	49.9 ± 1.7
30	-911.2 ± 1.9	41.0 ± 4.8
40	-923.8 ± 3.0	49.7 ± 2.3
50	-913.9 ± 2.5	39.3 ± 2.6
60	-918.7 ± 4.5	40.9 ± 2.6

expander on the crossing potential, and on the nucleation overpotential. There is a slight positive shift of 14 mV in the crossing potential, E_x , as the expander concentration is increased. The addition of the expander increased the nucleation overpotential by about 12 mV. However, further additions did not have any other effect.

The potential dependences of the growth kinetics in the various expander concentrations are shown in Figure 33 as well as in Table 8. The slopes are all very close to $29.58 \text{ mV dec}^{-1}$, which is in agreement with the potential dependences in the dissolution region. Moreover, the curves are moved to more positive potentials with the increase in the expander. It should be emphasized that the shift again results in three groups of lines corresponding to the concentration of the plateaus as seen earlier.

III.3 SCANNING ELECTRON MICROSCOPY

The microtomed and etched lead surface prior to any electrochemical perturbation is shown in Figure 34. For a solid electrode, the lead surface represented is good since it is reasonably flat and well-defined. Some cracks are evident, but since solid lead is crystalline and rather soft, microtoming could cause some of the crystal grains to separate creating crevices and pits between them. The small pits could be the result of etching the electrode in nitric acid, or they could be due to gas bubbles that were

Figure 33 - A plot of the logarithm of the current as a function of potential for the return current loop of a nucleation loop transient. For the higher expander concentrations only 30 and 60 ppm were shown as representative curves. Note the three potential regions corresponding to the E_p plateaus. The symbols are Δ for 0 ppm, $\square$ for 10 ppm, $\blacktriangle$ for 20 ppm, $\blacksquare$ for 30 ppm, and $\circ$ for 60 ppm.

TABLE 8 - The Potential Dependences of the
Growth Kinetics of the
Return Loop

Concentration of
expander in the
solution
(ppm)

$dE/d\log i$
mV dec⁻¹

0	28.75 ± .0009
10	32.95 ± .0007
20	33.87 ± .0006
30	30.54 ± .0004
40	32.33 ± .0001
50	29.07 ± .0007
60	33.67 ± .0005

Average 31.60 ± .001

Figure 34 - The microtomed and etched surface of the solid lead electrode prior to any electrochemical perturbation. 1500x magnification.

trapped in the lead during the casting process.

Figure 35(a) represents the electrode surface in 0.0 ppm on the rising portion of the sweep. The morphology is characterized by large platelet crystals and some needle-like crystals. The distribution of crystals is not uniform over the electrode surface, and this reflects the different activities of the different crystal faces exposed, or of the different active sites on the electrode surface.

The electrode surface on the falling part of the sweep is depicted in Figure 35(b). The crystals have grown larger and seem to form a thicker, denser film which is not completely uniform over the surface. Cracks appear in the deposit, but it is not certain whether they resulted from the crystals growing together, or from drying in the desiccator.

In the presence of 15 ppm of expander, the morphology of the film formed on the rising portion of the sweep is shown in Figure 36(a). Unlike the behaviour in the absence of the expander (Figure 35(a)), the film consists of smaller and fewer crystals which are distributed more uniformly on the electrode surface. The underlayer has a granular appearance with some cracks in it.

On the falling part, there were even fewer and smaller crystals as demonstrated in Figure 36(b) compared to Figure 35(b). The crystals have not grown together to form

Figure 35(a) - The crystal morphology on the rising current of a linear potential sweep in 0 ppm of expander. 1500x magnification.

Figure 35(b) - The crystal morphology on the falling current of a linear potential sweep in 0 ppm of expander. 1500x magnification.

Figure 35(a)

Figure 35(b)

Figure 36(a) - The crystal morphology on the rising
current of a linear potential sweep
in 15 ppm of expander. 1500x magnification.

Figure 36(b) - The crystal morphology on the falling
current of a linear potential sweep
in 15 ppm of expander. 1500x magnification.

Figure 36(a)

Figure 36(b)

a dense, thick layer and this resulted in a porous film. The larger crystals appeared in patches over the electrode surface, and there is no dendritic growth from the larger crystals. The underlayer has a fine, granular appearance.

The electrode surface in 40 ppm of expander on the rising portion of the sweep is given in Figure 37(a). The film is still characterized by fewer crystals compared to the solution containing no expander (Figure 35(a)) which is consistent with the behaviour observed in 15 ppm of expander. Some striations from microtoming are evident.

As shown in Figure 37(b), there are no large crystals in 40 ppm of expander on the falling part of the sweep, and the layer is granular. There are some cracks in the layer and some striations from microtoming.

Since the large crystals which are evident in these scanning electron micrographs (SEM's) never form a dense or compact film, there must be a contribution towards the passivation of the electrode from a thinner, underlying layer which is probably the granular layer.

Similar SEM's were recorded at -20°C for comparison, but these did not indicate any crystalline structure in any of the solutions with and without expander. This could be due to the slow kinetics of the lead sulphate formation at -20°C .

Figure 37(a) - The crystal morphology on the rising
current of a linear potential sweep
in 40 ppm of expander. 1500x magnification.

Figure 37(b) - The crystal morphology on the falling
current of a linear potential sweep
in 40 ppm of expander. 1500x magnification.

Figure 37(a)

Figure 37(b)

III.3.1 EFFECT OF CYCLING THE ELECTRODE

To examine the possibility of a long term effect of the expander, the electrode was cycled from the beginning of hydrogen evolution (-1700 mV) through the region of lead sulphate formation, then recycled until a constant anodic current response was attained. A SEM was taken of the surface at $3000\times$ magnification for 0, 40, and 60 ppm of expander, and are given in Figures 38, 39, and 40 respectively. In the absence of expander, the crystals are square and not tightly packed. Upon addition of 40 ppm of the expander, the square crystals have grown to form dendrites and the underlying layer is dense and tightly packed. No dendritic crystals were observed in 60 ppm of the expander, and the dense underlayer which was observed in 40 ppm covered the electrode surface. It is worth mentioning that the oxidation current increased upon addition of expander when the sweep began at -1700 mV, which is different from the behaviour observed from -1100 mV where the expander had no effect on the anodic current. The current response at 60 ppm of expander was less than that at 40 ppm suggesting an optimum concentration of the expander between 40 and 60 ppm.

Figure 38 - Effect of cycling on the lead sulphate
crystal structure in 0 ppm of expander.
3000x magnification.

Figure 39 - Effect of cycling on the lead sulphate
crystal structure in 40 ppm of expander.
3000x magnification.

Figure 38

Figure 39

Figure 40 - Effect of cycling on the lead sulphate crystal structure. 60 ppm of expander. 3000x magnification.

IV DISCUSSION

IV.1 LEAD AMALGAM

IV.1.1 POTENTIAL STEP PERTUBATION

It has been shown that the lead sulphate layer forms via a three dimensional nucleation and growth mechanism. Therefore, the i - t transients from the potential step dependence can be analyzed using the equations for i_m and t_m , that is:

$$i_m = nFk_2/4 \quad 21$$

$$t_m = \left[\frac{3\rho^2 \ln 2}{\pi M^2 k_1^2 A} \right]^{1/3} \quad 22$$

The decrease in the double layer capacitance demonstrated that the expander adsorbs onto the electrode surface of the amalgam. The expander can also adsorb onto the lead sulphate crystals themselves. Therefore, the expander could influence either the nucleation rate, the growth rate, or the Pb^{2+} dissolution or some combination of the three. Consider the shape of the reduced variable plots in Figure 8 which the rising portions of the curves all superimpose, but the tails are different. Prior to t_m nucleation is occurring and beyond that, it is only the growth of the crystals that occurs. Therefore, the expander is influencing, or slowing the rate of crystal growth since the tails of the transients are vastly different in expander containing

solutions. This conclusion is consistent with the results shown in Figures 9 and 10 when the expander is present since i_m is lower at a constant potential and proportional to k_2 , the vertical growth rate, and t_m is longer at a constant potential and proportional to $(2k_1^2)^{-1}$. If k_2 decreases i_m must decrease, similarly if k_1 decreases t_m must increase. The growth rate will be decreased if the expander blocks active sites on the electrode, and on the lead sulphate film where further incorporation of Pb^{2+} ions would have occurred.

From Figures 9 and 10, the expander has a greater dependence on t_m than i_m . A one decade change in i_m corresponds to a one decade change in k_2 , whereas, a one decade change in t_m corresponds to a three decade change in $2k_1^2$ as seen from Equations 21 and 22. Therefore, the expander could influence both the nucleation rate and the lateral growth rate. At a given potential, for example -855 mV, there is a 1.5 to 1 ratio of $\Delta \log t_m$ to $\Delta \log i_m$. Thus the change in $\log t_m$ is greater than a change in $\log i_m$ by a factor greater than 2 which would be consistent with the expected change if only k_1 and k_2 were altered, that is, assuming $k_1 = k_2$. Now, if $k_1 = k_2$ and the nucleation rate played no role, then t_m should be 1.5 times greater than i_m . But t_m is more than 1.5 times larger than i_m , therefore

the increase is due to the nucleation rate being lowered, but not as profoundly as k_1 and k_2 .

IV.1.2 LINEAR POTENTIAL SWEEP PERTUBATION

The addition of the expander resulted in a small anodic peak on the reverse sweep as shown in Figure 12. Interpretation of this phenomenon involved a preliminary experiment investigating the double layer charging on a mercury drop in the presence of the expander which indicated a desorption or re-orientation of the adsorbed expander film in the same potential region as the small anodic peak. If desorption, or re-orientation is occurring, then the bare portions of the electrode that are being generated could allow further oxidation of the lead resulting in the small anodic peak.

The lead sulphate film formation consists of three processes which are lead dissolution, nucleation and growth. The sweep rate dependence (Figure 14 and Table 3) has shown that for the expander containing solutions the film formation is controlled by diffusion. The influence of the expander on i_m and t_m has demonstrated that the expander retards the nucleation and more significantly, the growth of the film. Therefore, since the nucleation and growth processes are not controlled by diffusion, this leaves the lead dissolution to be diffusion controlled. The fact that the Tafel relationships do not change in the expander signifies that the mechanism of Pb^{2+} dissolution has not been altered by the

expander. However, in the absence of the expander, the film formation is not controlled by diffusion, but by electro-crystallisation, and thus, the nucleation and growth are not seriously inhibited.

The addition of the expander resulted in a significant increase in the anodic peak current as illustrated in Figure 12. The presence of an optimum concentration of expander near 8 ppm was clearly observed. This concentration is almost half of what Maltato (41) observed on cycled lead electrodes. This difference can be attributed to changes in the state of the electrode surfaces in the two cases. The surface of a cycled electrode cannot be defined whereas, in the present work, the lead amalgam gave reproducible and well-defined surfaces. The inhibitory effect of the expander was clearly demonstrated by larger slopes at high expander concentrations in Figures 14 and 15. The shift to more positive potentials in E_p , i_m , and t_m indicates that the expander is blocking the electrode surface by delaying the passivation. This issue will be more fully discussed in the solid lead section.

The charge required for passivation is larger in the presence of the expander, but the rate of growth of the lead sulphate film decreased as the expander concentration was increased. Since the total charge is a summation of the components from dissolution and nucleation and growth, the

increase in the charge passed indicates that there will be more Pb^{2+} ions diffusing into the solution away from the electrode. Fewer Pb^{2+} ions will be incorporated into the lead sulphate film, thereby reducing the charge efficiency into the film.

A decrease in the resistance of the lead sulphate film as observed in Figure 19 corresponds to an increase in the porosity consistent with what has been reported in the literature (38, 43, 45, 48, 89). The porosity will increase if there are empty spaces in the deposit which will form if the growth is not enough to cover the electrode surface completely. This incomplete growth is a result of the inhibition of the crystal growth rate by the expander.

The section on the lead amalgam studies has demonstrated that the expander is inhibiting the growth rate of the lead sulphate film. It also has a less significant effect, namely to reduce the rate of nucleation.

IV.2 SOLID LEAD ELECTRODE

IV.2.1 ABSENCE OF EXPANDER

Similar to the lead amalgam work, the charges required for passivation at all temperatures were too large for two dimensional monolayer formation. Therefore, the lead sulphate layer forms via a three dimensional nucleation and growth mechanism. The SEM's in Figures 35(a) and 35(b) show a thick deposit, but this deposit has too many crevices

to have caused the passivation. Therefore, there must be a thinner layer formed underneath the large crystals to have caused the passivation.

On the linear potential sweep in Figure 20 the large anodic peak and small cathodic peak, plus the large potential separation of 120 mV between them indicates that the lead sulphate film formation proceeded under irreversible conditions. At room temperature, electrocrystallisation is controlling the film formation, however, diffusion is becoming the controlling step at lower temperatures as evidenced from Table 4.

When the temperature is reduced i_p decreases, which means that the rate of film formation is slower. Also, there is less charge passed upon passivation, thus the amount of lead sulphate formed is less. The absence of the reduction peak at 0°C indicates that the lead sulphate film is reduced very slowly at lower temperatures. This confirms the fact that at low temperatures the rechargability of the battery is less efficient.

IV.2.2 PRESENCE OF EXPANDER

It was surprising that no evidence was found for an enhancement of the anodic current from the expander on the solid lead electrode as was observed on the lead amalgam. The results indicate unambiguously that the expander does not have a strong influence on the rate of the initial

formation of the lead sulphate film since neither i_p nor the charge required for passivation depended upon the expander. *

The mechanism for film formation was not altered by the presence of the expander. Evidence for this was obtained from the sweep rate dependence since the slopes of $d \log i_p / d \log v$ did not change upon addition of the expander. If the mechanism changed, the dependence of i_p with sweep rate would have been altered since a different reaction would have taken place.

The activation energy did not depend upon the expander as shown in Figure 28 which again confirms that the expander does not alter the reaction mechanism. The lead sulphate formation is controlled by nucleation and growth. Both nucleation and growth should depend on temperature but the exact dependences are uncertain. Usually it has been found that nucleation rates for many electrocrystallisation systems are temperature insensitive (90). However, the small activation energies in the order of 12.76 ± 0.88 kJ/mole implies that their rate determining steps are weakly dependent upon temperature. It is believed that the rate determining step is the desolvation of the metal ion in solution and the simultaneous incorporation into either the growing crystal, or into the critical cluster leading to a stable nucleus (91, 92). Since hydration energies are

* Footnote: There is a possibility that complexation between

the dissolving Pb^{2+} ions and the ammonium lignosulphonate molecules can occur. However, the likelihood of this occurring is rather small or improbable for a number of reasons. First, if Pb^{2+} - ammonium lignosulphonate complexes were forming, then there would not have been sufficient expander molecules present to adsorb onto the electrode surface to cause a substantial decrease in the double layer capacitance. Secondly, the anodic current on the lead amalgam would not have increased to such an extent as shown in Figure 12 as the expander concentration increased if the Pb^{2+} ions were bound as a complex species. Finally, the magnitude of the lead sulphate film formed by calculation of the charge under the anodic peak of a linear potential sweep (see Figure 12 and Table 5) would not have been possible on either the solid lead or lead amalgam electrode surfaces if the Pb^{2+} ions were consumed in the complexation.

low, this is consistent with a small activation energy. These ideas are supported by experimental work in homogeneous precipitation where the activation energies ranged from 0 to 21 kJ mole⁻¹ (93). It was suggested (93) that since the activation energy was small, it could be interpreted in terms of a temperature insensitive process on the surface or in the interfacial layer. Therefore, the expander may block sites for nucleation or incorporation, but it has no effect on the desolvation step.

The expander is not altering the mechanism of the lead sulphate formation. But it is clear from the positive shifts in potential, that the expander plays a distinct role on the film formation. The positive shift in E_p is consistent with a slower reaction that requires extra potential to drive it to an appreciable rate. Since the formation of the film is controlled by dissolution, nucleation and growth, the shift in potential could be due to:

- (i) inhibition of Pb^{2+} dissolution which provides material for incorporation into the growing lead sulphate film,
- (ii) adsorption of the expander onto active sites that would promote the nucleation of lead sulphate crystals, or
- (iii) adsorption of the expander onto sites for incorporation of Pb^{2+} into the lead sulphate crystals, slowing the growth rate. Thus the influence of the expander on each of

dissolution, nucleation, and growth must be examined to elucidate the mechanism of the expander.

The potential dependence $dE / d \log i$ of the Tafel plots in the dissolution region (Table 6), do not change with expander. This means that the expander has not altered the mechanism of lead dissolution, that is, the lead is still dissolving reversibly as Pb^{2+} ion. However, the positive shift in potential with expander means that the expander is affecting the lead dissolution in some manner. The decrease in the current as a function of expander concentration at a constant potential of -915 mV (Figure 30) indicates that the rate of lead dissolution decreases as the expander blocks the electrode surface. In the absence of expander, the electrode surface is bare, and therefore the rate of lead dissolution is at a maximum. As the expander concentration increases, the electrode becomes covered or blocked, consequently the current decreases and so does the rate of dissolution of lead.

The influence of the expander on the nucleation process was found to be minimal as seen from the small increase in the nucleation overpotential of 12 mV, and the small positive shift of the crossing potential of 14 mV. There is some inhibition of the nucleation since the SEM's in the nucleation region (Figures 36(a) and 37(a)) demonstrate that in the

presence of the expander, fewer crystals were formed, which implies fewer nuclei, hence a reduced rate of nucleation.

The growth of the lead sulphate crystals is hindered in the presence of the expander because the SEM's in the growth region showed smaller crystals which were less densely packed and a lack of dendrites in Figure 36(b). In 40 ppm, there was an absence of the large square platelets indicating severe inhibition of the crystal growth. In the nucleation loop experiments the potential dependence of the return loop of (30.57 ± 0.003 mV) confirms that the growth of the lead sulphate deposit is being supplied by the diffusion of Pb^{2+} ions. Dissolution is controlled by diffusion and since the lead dissolution is feeding the growth of the crystals, the growth rate must also be diffusion controlled. Therefore, if the dissolution is slower at a given potential and expander concentration, then the crystal growth must be correspondingly slower as well.

The above discussion has demonstrated that the expander plays a major influence in the dissolution and growth processes and a minor effect on the nucleation events. The E_p plateaus observed on the solid lead electrode and the fact that they were absent on the lead amalgam, offers an explanation for the manner in which the expander is reducing the rate of lead dissolution, and hindering crystal growth. The plateaus could be explained as a result of either a

layer-by-layer adsorption of the expander, or by blocking of population sites of certain activities. This would force the dissolution, nucleation, or lead sulphate lattice incorporation to occur on less active sites. The layer-by-layer postulate is unlikely because the nature of the solid lead surface, that is, the surface asperities, would not allow the expander to adsorb in well-defined layers. This is supported by the fact that no plateaus were observed on the lead amalgam where the expanders should have been able to form well-defined layers. The plateaus appear at the same expander concentration regardless of temperature which suggests that they are associated with something that is independent of temperature, namely the electrode surface structure. In the investigation of the dissolution region, plateaus were seen when the potential as a function of expander was plotted at a constant current density (Figure 31). This means that the plateaus are associated with dissolution, and not nucleation and growth. Therefore, the more plausible explanation for the plateaus is the blocking of two different kinds of sites, for example, kink sites (more active) and ledges (less active), by the expander, forcing the dissolution to occur on less favourable sites. On average, each microtomed lead surface would

have a relatively large and constant number of surface defects, thus it would always require the same quantity of expander to block the sites of a certain activity.

IV.2.3 EFFECT OF TEMPERATURE

The sweep rate dependence demonstrated that diffusion became the rate controlling step at lower temperatures. Since the rate of Pb^{2+} dissolution is controlled by diffusion, then the dissolution process is temperature dependent. Dissolution of Pb^{2+} ions promotes the growth of the lead sulphate crystals. Thus, if the rate of dissolution decreases with a lower temperature, the crystal growth will be reduced.

IV.2.4 EFFECT OF CYCLING

To understand the effect of the expander further, the solid lead surface was cycled beginning from hydrogen evolution, -1700 mV, through the potential region of lead sulphate. The linear potential sweeps demonstrated an increase in the anodic current upon addition of the expander, and an optimum concentration between 40 and 60 ppm. The SEM's taken showed dendrite formation in expander solutions up to 40 ppm and an absence of them in 60 ppm. Dendrites form when the growth rate in one direction is less than that in another direction. This indicates some inhibition of the growth rate in the presence of the expander in agreement with all earlier results. The total

absence of dendrite formation in 60 ppm indicates a dramatic inhibition of the growth rate. It is interesting that an increase in current was observed when the sweep began at hydrogen evolution, -1700 mV, and not at -1100 mV, a more positive potential. These results imply that the potential of -1700 mV has somehow "activated" the surface so the expander blocking action would be more effective. This is similar to the behaviour on the lead amalgam surface. Hydrogen evolution tends to roughen the electrode surface. It is known that ammonium lignosulphonate does not act uniformly in deep charge and discharge storage batteries which often have gas evolution. In cases of deep charge/discharge the expander tends to decompose with a concentration gradient from the top to the bottom of the battery. These stand-by or reserve lead acid batteries are of great importance for storing charge in load-levelling in various Hydro Company operations. They are also useful in the event of blackouts by Electricity Generating Stations. Hospitals and institutions that have large installation of computers depend on them (94). It should be noted that this phenomenon does not occur with S.L.I. (S-starting, L-lighting, I-ignition) batteries used in automobiles.

IV.3 COMPARISON OF LEAD AMALGAM AND SOLID LEAD ELECTRODES

There are some striking differences in the behaviour of the expander observed on the lead amalgam and solid lead

electrodes. First, the expander has significantly decreased the reduction of the lead sulphate film on the lead amalgam whereas, on the solid lead surface, the effect is much less pronounced. Secondly, and perhaps more interesting, is the effect of the expander on the anodic peak current and peak potential. On the lead amalgam, the expander increased the current, but it did not do so on the solid lead, and the potential plateaus were only observed on the solid lead electrode. The interpretation of this behaviour can be explained as follows. It has been shown that the expander can adsorb onto both the lead amalgam and solid lead surfaces. The principal difference between the two systems is the nature of the electrode surface. The lead amalgam has a very smooth surface (homogeneous) and therefore the expander can adsorb as a uniform layer. However, the solid lead surface is heterogeneous, thereby, the expander cannot adsorb in uniform layers. On the lead amalgam, the expander hinders the growth of the lead sulphate film and to some extent the nucleation. This inhibition is not severe at low concentrations of the expander, therefore passivation can take place at less positive potentials. At high concentrations of the expander, the presence of the thick organic layer is more inhibiting thus forcing the passivation to proceed at more positive potentials.

On the solid lead surface, the expander cannot block the surface as effectively and the inhibition will not be as great, so at all concentrations there will still be favourable sites on which the reaction can take place.

The Tafel slopes on both surfaces show a 30 mV dec^{-1} dependence of the lead dissolution. This means that for every 30 mV the current can increase by a factor of 10. Dissolution occurs at an exponential rate until diffusion takes over and the curve levels off. So if the potential was to increase by 60 mV , the currents would increase 100 times! Figures 17 and 25 demonstrate that for the same range of expander concentration, that is, 0 to 65 ppm , the severe blockage of the surface by the expander shifted the potential to more positive values by approximately 50 mV on the lead amalgam, whereas on solid lead the shift is only in the order of 20 mV . Therefore, because the expander can block the lead amalgam surface more effectively, the passivation is forced to proceed at much higher potentials where there is a higher rate of lead dissolution, thus increased currents. In both cases, the electrode surface will eventually be covered by the lead sulphate film, stopping the dissolution, and passivating the electrode so the current falls, resulting in the oxidation peak.

The severe blocking of the lead amalgam surface is the cause for the absence of the reduction peak. The presence of the thick organic layers make it more difficult to electrochemically reduce the film. On the solid lead surface, there will always be sites in which the reduction of the film can occur even in high expander concentrations.

V SUMMARY

V.1 LEAD AMALGAM ELECTRODE

The major influence of the expander on the formation of the lead sulphate film was the inhibition of the nucleation and growth processes. It appeared that the growth rate was inhibited more than the nucleation rate. However, on the basis of these results, unequivocal conclusions cannot be made with respect to which process, or both was more influenced. Evidence was found for an optimum concentration of the expander between 7.89 and 17.45 ppm, and beyond that concentration the presence of the expander severely inhibited the lead sulphate formation.

V.11 SOLID LEAD ELECTRODE

There was no evidence found for an optimum concentration of the expander, and if it did exist, it was not well defined. The principal effect of the expander was to block two different sites of different surface activities that promote lead dissolution, or sites for further lattice incorporation of Pb^{2+} ions into the growing lead sulphate film. The expander reduces the frequency with which these sites can occur, but it does not make the energy or kinetics of the film formation more difficult, that is, it does not alter the mechanism of the lead sulphate formation.

The results did not show that the expander enhances or has a major influence on the initial formation of lead

sulphate. However, if the potential of the linear potential sweep began at -1700 mV the expander did enhance the reaction. The expander action that has been well documented in the literature with respect to lead acid batteries must be associated with gas evolution. This idea needs to be investigated further to clarify how the presence of hydrogen evolution changes the pattern of expander action.

The important electrochemical results concerning the influence of the expander on the nucleation and growth processes has been verified by scanning electron microscopy. The SEM'S offer a clearer understanding as to the morphology of the crystal growth in the presence of the expander.

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