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MASS TRANSPORT DURING LEAD–ACID BATTERY PLATE FORMATION

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Summary

Mathematical equations for mass transport during the formation of the lead–acid battery positive and negative plates have been deduced. It has been shown that both the amount of material transferred between the reaction layer and the bulk of the electrolyte, and also the material flow direction depends on the paste composition and the formation current density. The zone within the plate, where the formation processes occur, is determined by the flow direction and by the maintenance of the electroneutrality of the solution. By measuring the potential of both the positive and the negative plates, with respect to a mercury reference electrode, it has been established that their polarization depends on the difficulties of mass transport through the porous structure of the plate.

Introduction

The processes of lead–acid battery plate formation and the dependence of the active mass performance on the conditions of formation have been studied in many papers [1 - 16], but an investigation of mass transport during formation has not been undertaken.

In some of our previous papers [17 - 20] we have confirmed that lead–acid battery plate formation takes place in two stages. During the first stage PbO_2 and $PbSO_4$ are obtained in the positive plate, and Pb and $PbSO_4$ in the negative plate. The formation proceeds at relatively low potentials; about 1200 mV for the positive plate and about -950 mV for the negative plate (with respect to an Hg/Hg_2SO_4 electrode). During the second stage, already formed $PbSO_4$ oxidizes to PbO_2 and is subsequently reduced to Pb. The potential of the positive plate increases to about 1400 mV, while that of the negative plate reaches approximately -1400 mV. The potentials of the plates during the first stage of formation depend on the pH of the electrolyte as well as on the paste composition.

The present paper is a continuation of our previous work in which the dependence of the potential of the positive and negative plates on the

current density during the first stage of formation is studied. The potential changes are related to the peculiarities of the mass transport during formation.

Experimental

Hand pasted plates (11 A h) for SLI (car; starting, lighting, ignition) batteries were used. The paste was prepared from industrial lead powder with an oxidation degree of 65%, sulphuric acid solution (1.4 sp. gr.) and water. The quantity of H_2SO_4 was 6% with respect to the lead powder, and the quantity of water was selected so that a paste density of 4.2 g cm^{-3} was obtained. The mixing temperature was 30 °C and the mixing time was 40 min. The formation was carried out in an H_2SO_4 (1.05 sp. gr.) solution at a current density of 2.5 - 15 mA cm^{-2} with regard to the plate apparent area. The potential was measured with respect to an Hg/Hg_2SO_4 electrode.

Figure 1(a) shows the dependence of the positive plate potential on the current density, and Fig. 1(b) relates to the negative plate potential. These potentials correspond to the lowest potential values measured during the first stage of formation at each current density. As can be seen from the Figures the positive and negative plate potentials increase in the positive and negative direction, respectively, with increasing current density. This increase
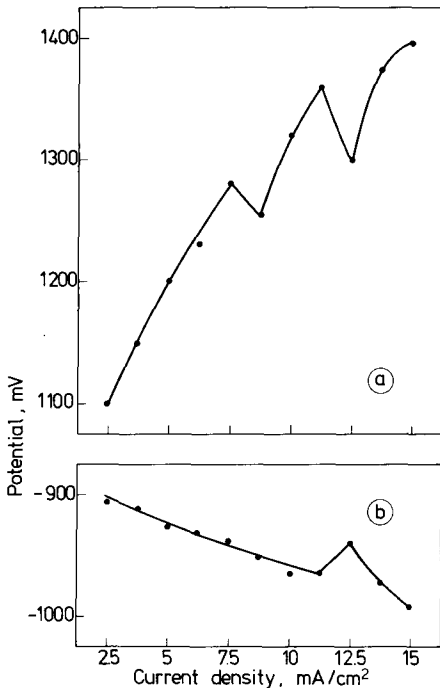

Fig. 1. Dependence of the potential of (a) the positive and (b) the negative plates on the formation current density.

is more pronounced at the positive than at the negative plate. The presence of two minima in Fig. 1(a) and one minimum in Fig. 1(b) is a peculiar feature.

Discussion

The formation processes require detailed discussion in order to explain those minima in the potential plot as a function of the current density. Two papers [18, 20] present general schemes of the processes occurring during the first stage of formation of the positive and negative plates. It can be seen from these schemes that an exchange of ions and water between the bulk of the electrolyte and the reaction layer takes place. The reaction layer is at that site in the plate where the formation reactions occur. Ion and water flows are formed as they enter the reaction layer or leave it. The formation processes take place in the paste which is very porous and the mass transport through it is thereby hampered. We suggest that these difficulties in the transport of substances determine the rate of formation, and attempt to show that the theoretical mass and charge balance is in accord with this hypothesis.

Mass transport during positive plate formation

The schemes of the chemical and electrochemical processes of positive plate formation [18] are presented in Fig. 2, which allows us to deduce a quantitative flow dependence. Thus, the following equations for the hydrogen ion flow (N_{H^+}), the sulphate ion flow ($N_{SO_4^{2-}}$) and the water flow (N_{H_2O}) can be written:

$$N_{H^+} = \left(\frac{2m}{m+1} - 4\theta \right) n_{Pb^{2+}} \tag{1}$$

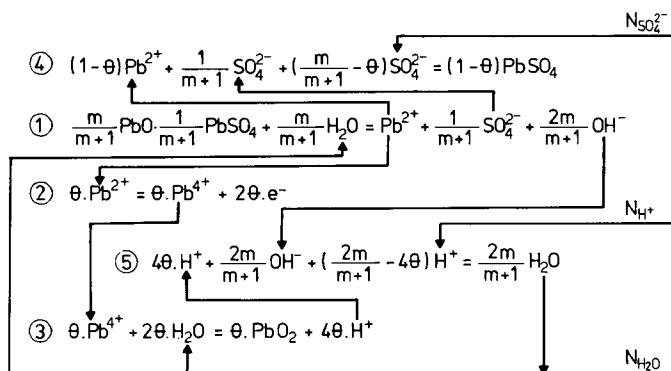Fig. 2. Scheme of the formation reactions of the lead–acid battery positive plate.

$$N_{SO_4^{2-}} = \left(\frac{m}{m + 1} - \theta\right) n_{Pb^{2+}} \tag{2}$$

$$N_{H_2O} = -\left(\frac{m}{m + 1} - 2\theta\right) n_{Pb^{2+}} \tag{3}$$

Here m is a function of the plate paste composition:

$$m = \frac{Q_{PbO} M_{PbSO_4}}{Q_{PbSO_4} M_{PbO}} \tag{4}$$

where Q_{PbO} is the quantity of PbO in the paste, free and combined as basic sulphates, Q_{PbSO_4} is the amount of $PbSO_4$ combined as basic sulphates, while M_{PbO} and M_{PbSO_4} are the molecular weights of PbO and $PbSO_4$, respectively. The calculated values of m for pastes prepared with 0 - 12% H_2SO_4 with respect to the lead powder are given in Table 1. m decreases with increasing H_2SO_4 in the paste.

TABLE 1

H_2SO_4 (%)	0	2	4	6	8	10	12
m	∞	21.3	10.1	6.2	4.5	3.5	2.8

In these equations θ expresses the amount of lead ions that participates in the electrochemical process ($0 < \theta < 1$) and is directly proportional to the current density.

Equations (1), (2) and (3) determine the dependence of the flows on the paste composition (through m), on the current density (through θ) and on the lead ion content of the solution in the paste pores (through $n_{Pb^{2+}}$). These flows can change their signs, which is determined by the bracketed terms in the equations. When positive, the direction of the flow is from the bulk of the electrolyte to the reaction layer, and when negative, the flow is in the opposite direction. As can be seen from the terms in brackets the direction of each flow depends both on m and θ. If each flow is divided by the lead ion flow ($n_{Pb^{2+}}$), specific flows are obtained. The latter depend on the paste composition (m) and on the current density (θ) only:

$$\frac{N_{H^+}}{n_{Pb^{2+}}} = \frac{2m}{m + 1} - 4\theta \tag{5}$$

$$\frac{N_{SO_4^{2-}}}{n_{Pb^{2+}}} = \frac{m}{m + 1} - \theta \tag{6}$$

$$\frac{N_{H_2O}}{n_{Pb^{2+}}} = -\left(\frac{m}{m + 1} - 2\theta\right) \tag{7}$$

The relationships between the specific flows (eqns. (5) - (7)), m and θ are shown in Figs. 3, 4 and 5. It can be seen from the Figures that under some formation conditions (m and θ) the flow is directed into the reaction layer (that part of the surface is marked by +), and out of the layer under other conditions (marked by —). The curve "a" in each Figure corresponds to the values of m and θ which give a zero flow. Under such formation conditions the flow direction is reversed. These conditions may be determined by zeroing eqns. (1), (2) and (3). This dependence, which characterizes the formation conditions (m and θ) of zero flow, is shown in Fig. 6. Curve 1
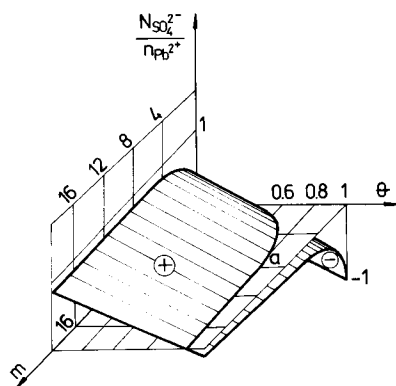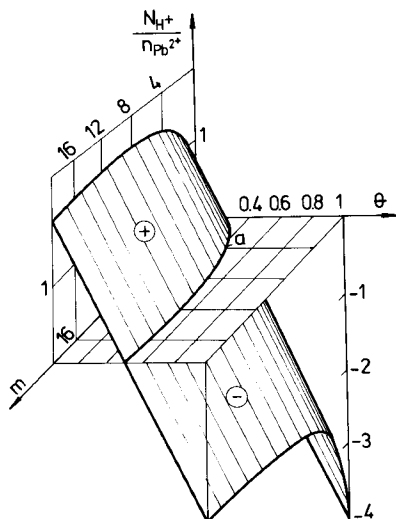
Fig. 3. Dependence of the specific hydrogen ion flow on m and θ.

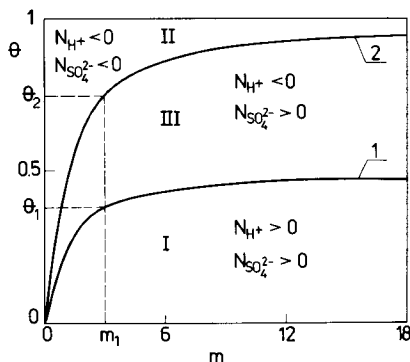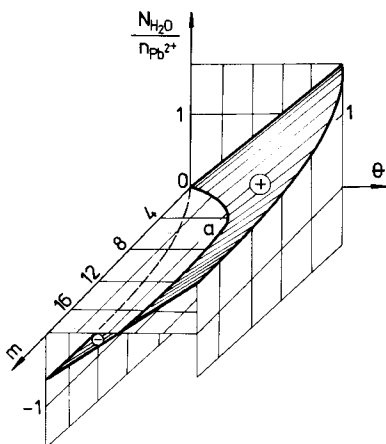Fig. 4. Dependence of the specific sulphate ion flow on m and θ.

Fig. 5. Dependence of the specific water flow on m and θ.

Fig. 6. Dependence of θ on m.

corresponds both to the hydrogen ion and to the water flows, and curve 2 to the sulphate ion flow. These curves are the "a" curves from Figs. 3 - 5.

It can be seen from Fig. 6 that three types of flow direction, depending on the formation conditions, are possible.

Water rapidly penetrates into the paste and does not participate in maintaining the electroneutrality of the solution. Water flow will therefore not be considered when these three cases are examined below.

(a) The flows of hydrogen and sulphate ions from the electrolyte to the reaction layer are positive, i.e.,

$$N_{H^+} > 0 \tag{8}$$

$$N_{SO_4^{2-}} > 0 \tag{9}$$

As the H^+ and SO_4^{2-} ions move in the same direction, it can be assumed that a resultant flow of H_2SO_4 ($N_{H_2SO_4}$) occurs. This is equal to:

$$N_{H_2SO_4} = \frac{1}{2} N_{H^+} = \left(\frac{m}{m+1} - 2\theta \right) n_{Pb^{2+}} \tag{10}$$

The difference ($\Delta N_{SO_4^{2-}}$) between the total quantity of sulphate ions that enter the reaction layer ($N_{SO_4^{2-}}$) and the sulphate ions ($N_{H_2SO_4}$) combined as H_2SO_4 is:

$$\Delta N_{SO_4^{2-}} = N_{SO_4^{2-}} - N_{H_2SO_4} \tag{11}$$

After substituting eqns. (2) and (10) in eqn. (11) we get:

$$N_{SO_4^{2-}} = \theta n_{Pb^{2+}} \tag{12}$$

Thus, the sulphate ions, which are not combined as H_2SO_4 carry $2\theta n_{Pb^{2+}}$ negative charges. When they penetrate the layer, their charges compensate the positive charges obtained by the electrochemical reaction, i.e., these sulphate ions maintain the electroneutrality of the solution in the reaction layer pores.

The sulphuric acid and sulphate ions flow (eqns. (10) and (12)) from the bulk of the electrolyte to the reaction layer are enhanced when the reaction layer is on the surface of the plate, where PbO_2 will be formed. The conditions under which both flows are positive are defined in area I of Fig. 6. This area corresponds to low values of θ (low current density) and high values of m (low amount of H_2SO_4 used in the paste preparation). The experimental results [18] show that, when the pastes are made from 0, 2, 4 and 6% H_2SO_4 and the formation is carried out at low current density, PbO_2 is formed on the surface of the plate.

(b) The flows of hydrogen and sulphate ions from the reaction layer to the bulk of the electrolyte are negative, i.e.,

$$N_{H^+} < 0 \tag{13}$$

$$N_{SO_4^{2-}} < 0 \tag{14}$$

The resultant flow of H_2SO_4 ($N_{H_2SO_4}$) leaving this layer is:

$$N_{H_2SO_4} = N_{SO_4^{2-}} = \left(\frac{m}{m+1} - \theta\right) n_{Pb^{2+}} \tag{15}$$

The difference (ΔN_{H^+}) between the total quantity of hydrogen ions (N_{H^+}) and the hydrogen ions that leave the reaction layer bonded as sulphuric acid ($N_{H_2SO_4}$) is:

$$\Delta N_{H^+} = N_{H^+} - 2N_{H_2SO_4} \tag{16}$$

After substituting eqns. (1) and (15) in eqn. (16) we get:

$$\Delta N_{H^+} = -2\theta n_{Pb^{2+}} \tag{17}$$

The electroneutrality of the solution, as can be seen from eqn. (17), is maintained by the hydrogen ions.

The resultant flow of H_2SO_4 (eqn. (15)) would be directed towards those parts of the plate where the pH is highest, *i.e.*, inside the paste where PbO_2 is formed. The conditions for this are defined within area II of Fig. 6. This area corresponds to low values of m (large amount of H_2SO_4 used for the paste preparation) and high values of θ (high current density).

The experimental results [18] confirm this conclusion. When the pastes were made with more than 6% H_2SO_4 and formation was at 10 mA cm^{-2}, PbO_2 was formed inside the paste.

(c) The flows of hydrogen and sulphate ions have different directions, *i.e.*,

$$N_{H^+} < 0 \tag{18}$$

$$N_{SO_4^{2-}} > 0 \tag{19}$$

In this case there is no resultant flow of H_2SO_4. The hydrogen ion flow cannot enter the paste because the H$^+$ ions will charge the solution positively and alter the electroneutrality. Therefore the hydrogen ion flow has to be directed into the bulk of the electrolyte. This movement is enhanced when the reaction layer is on the surface of the plate. The movement of sulphate ions from the bulk of the electrolyte is facilitated at this site as well. Therefore, PbO_2 would be formed on the surface of the plate. Area III of Fig. 6 gives the conditions under which the flows have different directions, *i.e.*, average values of m and θ.

If a paste of a known composition (ex. m_1) is formed at a given current density (θ_1), the hydrogen ion flow and the water flow become equal to zero and no exchange of hydrogen ions and water between the reaction layer and the bulk of the electrolyte occurs. The hydrogen ions and water needed for the formation reactions (Fig. 2) are produced in the reaction layer. At θ_1 (corresponding to 8.75 mA cm^{-2} in Fig. 1) the difficulties due to the transport of hydrogen ions and water through the porous paste disappear, polarization is reduced and, consequently, the potential of the plate will be lower (Fig. 1(a)).

A similar potential decrease will be observed when the current density (at θ_2) reaches a value at which the sulphate ion flow is equal to zero. This occurs at a current density of 12.5 mA cm^{-2} (Fig. 1(a) and (b)).

Mass transport during negative plate formation

When the chemical and electrochemical reactions during the first stage of negative plate formation reported earlier [19, 20], and the same reasoning as above, are used for the negative plate, we can again denote the flows of hydrogen ions ($N_{H^+}^-$), sulphate ions ($N_{SO_4^{2-}}^-$) and water ($N_{H_2O}^-$) as follows:

$$N_{H^+}^- = \frac{2m}{m+1} n_{Pb^{2+}} \tag{20}$$

$$N_{SO_4^{2-}}^- = \left(\frac{m}{m+1} - \theta \right) n_{Pb^{2+}} \tag{21}$$

$$N_{H_2O}^- = - \frac{m}{m+1} n_{Pb^{2+}} \tag{22}$$

The hydrogen ions and water flows (eqns. (20), (22)) have opposite directions and depend only on the paste composition (m). These two flows cannot change their direction of movement, so that the flow of hydrogen ions always enters the reaction layer and the water flow always leaves it. Only the sulphate ion flow depends on the current density as well as on the paste composition (eqn. (21)). This dependence is identical to that of the positive plate (eqn. (2)).

The specific flows $N_{H^+}^-/n_{Pb^{2+}}$ and $N_{H_2O}^-/n_{Pb^{2+}}$ are given in Figs. 7 and 8. The dependence of the specific sulphate ion flow ($N_{SO_4^{2-}}^-/n_{Pb^{2+}}$) is the same as that given in Fig. 4.

From eqns. (20) - (22) it follows that only the sulphate ion flow can be zero. Therefore, in the potential *versus* current density dependence of the negative plate only one minimum is observed. This minimum is determined by the decrease of polarization when $N_{SO_4^{2-}}^- = 0$. As can be seen from Fig. 1(b), such a minimum exists at 12.5 mA cm^{-2}. Because the composition of the positive and negative plate pastes is identical (the same value of m for both plates) the minimum is at the same current density (Fig. 1) as is seen from eqns. (2) and (21).

Mass transport during the second stage of formation

The first stage of positive plate formation is completed when the PbO and the basic sulphates of the paste are converted to PbO$_2$ and PbSO$_4$ [17, 18]. The oxidation of PbSO$_4$ to PbO$_2$ occurs during the second stage of formation and the equations describing the flows (eqns. (1) - (3)) can also
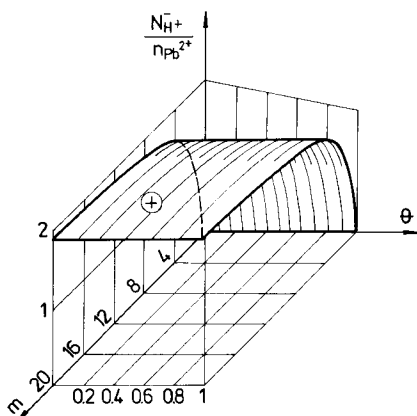
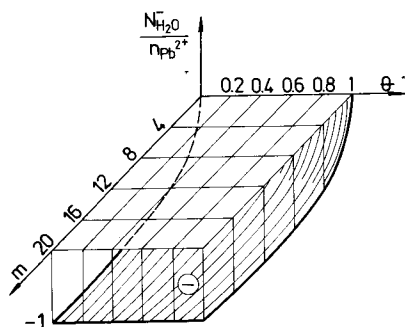Fig. 7. Dependence of the specific hydrogen ion flow of the negative plate on m and θ.

Fig. 8. Dependence of the specific water flow of the negative plate on m and θ.

be used to explain the mass transport during the second stage, when m equals zero. Thus, from eqns. (1) - (3) we get:

$$N_{H^+} = -4\theta n_{Pb^{2+}} \tag{23}$$

$$N_{SO_4^{2-}} = -\theta n_{Pb^{2+}} \tag{24}$$

$$N_{H_2O} = 2\theta n_{Pb^{2+}} \tag{25}$$

It can be seen from eqns. (23) - (25) that during the second stage of positive plate formation the flows cannot reverse their directions.

The hydrogen and sulphate ions (eqns. (23), (24)) leave the reaction layer and a resultant flow is formed from H_2SO_4 and hydrogen ions towards the bulk of the electrolyte. The movement of the hydrogen ions maintains the electroneutrality of the solution in the layer. The water (eqn. (25)) necessary for the formation of PbO_2 enters the reaction layer.

The evolution of oxygen also takes place during the second stage and this stage of the positive plate formation can be represented by the following reactions:

$$PbSO_4 + 2H_2O = PbO_2 + H_2SO_4 + 2H^+ + 2e^- \tag{26}$$

$$2H_2O = O_2 + 4H^+ + 4e^- \tag{27}$$
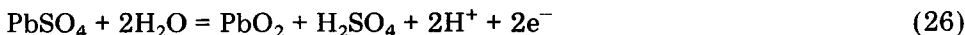
The first stage of the negative plate formation is completed when PbO and the basic sulphates are transformed. Reduction of $PbSO_4$ to Pb takes place during the second stage. The flows during this stage can be obtained from eqns. (20) - (22) with $m = 0$:

$$N_{H^+}^- = 0 \tag{28}$$

$$N_{SO_4^{2-}}^- = \theta n_{Pb^{2+}} \tag{29}$$

$$N_{H_2O}^- = 0 \tag{30}$$

From eqns. (28) - (30) it follows that during this stage only the sulphate ions (eqn. (29)) leave the reaction layer and enter the bulk of the electrolyte. This flow also maintains the electroneutrality of the solution. The negative plate formation processes are accompanied by the evolution of hydrogen. The reactions describing the second stage of the negative plate formation are:

$$PbSO_4 + 2e^- = Pb + SO_4^{2-} \tag{31}$$

$$2H^+ + 2e^- = H_2 \tag{32}$$

The overall reactions for the second stage of the formation of a cell consisting of a positive and a negative plate are:

$$2PbSO_4 + 2H_2O = PbO_2 + Pb + 2H_2SO_4 \tag{33}$$

$$2H_2O = O_2 + 2H_2 \tag{34}$$
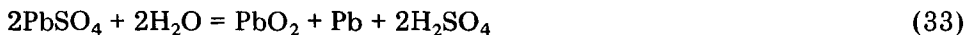
As a result of the formation processes and the electrolysis of water, the electrolyte density in the cell increases [19]. This second electrochemical process, the electrolysis of water (eqn. (34)), reduces the current yield of the formation of the positive and negative active masses.

List of symbols

N_x = Flow of "x"
N_y = Flow of "y"
m = $(Q_{PbO} \times M_{PbSO_4})/(Q_{PbSO_4} \times M_{PbO})$
Q_x = Quantity of "x" in the paste
M_x = Molecular weight of "x"
θ = Current density

References

1 V. H. Dodson, *J. Electrochem. Soc.*, *108* (1961) 401.
2 A. C. Simon and E. L. Jones, *J. Electrochem. Soc.*, *109* (1962) 760.
3 W. O. Butler, C. J. Venuto and D. V. Wisler, *J. Electrochem. Soc.*, *117* (1970) 1339.
4 J. Burbank, *J. Electrochem. Soc.*, *113* (1966) 10.
5 J. Burbank and E. J. Ritchie, *J. Electrochem. Soc.*, *116* (1969) 125.
6 J. Armstrong, I. Dugdale and W. J. McCusker, *Power Sources 66*, Pergamon Press, Oxford, 1967, p. 163.
7 J. R. Pierson, *Electrochem. Technol.*, *5* (1967) 323.
8 G. Sterr, *Electrochim. Acta*, *15* (1970) 1221.
9 E. F. Bordt, V. V. Novoderejkin and Z. S. Kudzevich, *Sb.Rab. HIT*, *7* (1972) 65.
10 E. F. Bordt, V. V. Novoderejkin and G. A. Kolikova, *Sb.Rab. HIT*, *7* (1972) 48.
11 E. F. Bordt, G. A. Kolikova, V. V. Novoderejkin and M. A. Dasojan, *Sb. Rab. HIT*, *7* (1972) 48.
12 E. F. Bordt, V. V. Novoderejkin, G. A. Kolikova and M. A. Dasojan, *Sb. Rab. HIT*, *8* (1973) 10.

13 J. Armstrong, *Lead–Acid Batteries*, Lead Development Association, London, Oct., 1967.
14 A. C. Simon and S. M. Caulder, *J. Electrochem. Soc., 118* (1971) 659.
15 E. Maier, *Electrochim. Acta, 27* (1982) 1627.
16 J. M. Stevenson and A. T. Kuhn, *J. Power Sources, 8* (1982) 385.
17 D. Pavlov, G. Papasov and V. Iliev, *J. Electrochem. Soc., 119* (1972) 8.
18 D. Pavlov and G. Papasov, *J. Electrochem. Soc., 127* (1980) 2104.
19 D. Pavlov, V. Iliev, G. Papasov and E. Bashtavelova, *J. Electrochem. Soc., 121* (1974) 854.
20 D. Pavlov and V. Iliev, *J. Power Sources, 7* (1981 - 82) 153.