

SEALED GAS RECOMBINING LEAD-ACID BATTERIES PART II. ANALYSIS OF REAL SYSTEMS

M. MAJA and N. PENAZZI*

Dpt. di Scienza dei Materiali e Ingegneria Chimica, Politecnico di Torino, Turin (Italy)

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Summary

Our theory on gas recombining lead-acid batteries, previously proposed in Part. I, has been applied to real systems, and various tests have been performed to determine the rate constants of the gas reactions as a function of the active material of the plates. Comparison between experimental and theoretical data shows the validity of the method used to evaluate the battery behaviour. The influence of H₂ and O₂ reactions on plate polarization curves is also discussed.

Introduction

In this second part of our work on recombining lead-acid batteries the theory already discussed in Part I [1] has been applied in a study of various commercial batteries. It is not our aim to compare systems from different manufacturers but to check the theoretical calculations. The results obtained represent a basic background for successive investigations which are now in progress.

After characterizing the batteries, the reaction rate constants for oxygen and the negative active material, and for hydrogen and the positive active material, were measured as proposed in Part I [1].

Starting from these data, the theoretical battery behaviour has been compared with the experimental behaviour. The tests were carried out on two types of battery but the data reported in this paper are for one type only.

Experimental

The gas recombining batteries tested have electrolyte-retaining glass separators and a nominal capacity between 80 and 100 A h. The batteries were initially discharged at $I = 5$ A (I_{20}) to 75% of the total capacity (C_{20})

*Author to whom correspondence should be addressed.

and charged ($V = 14.8$ volt) three times, during which time the opening pressure of the vent plugs was controlled. The nominal capacity, C_{20} , was then determined according to the IEC specifications. The batteries were then prepared for the subsequent tests.

The vent plugs of the cells were replaced by two-way glass valves and two tubes with valves were placed on the battery covers. The gas inlet tube was connected to a gas bottle containing either oxygen, air, or nitrogen. The second tube was connected either to a manometer, for measuring the free volume of the cell, or to gas analysis equipment. Every cell was also equipped with a valved gas outlet at the bottom of the case and with an electronic gas pressure sensor on the cell cover.

At the beginning of the tests, the battery cells were charged, and flushed with nitrogen to test for leaks and to measure the free volume. For this purpose the cells were connected to a water manometer and the relative gas pressure was measured. The gas was then compressed isothermally by reducing the total volume* by a known amount and the pressure was re-measured. The free volume of each cell was calculated by applying the ideal gas law.

The battery was then charged and the open-circuit tests initiated. The cells were first flushed with the same gas mixture (O_2 and N_2) used in the test then the gas outlet valve was closed and the gas pressure in the cells allowed to increase. At a predetermined pressure, the gas inlet valve was closed and automatic logging of the pressure data was started.

After the open circuit tests, the battery was recharged, filled with oxygen, and continuously overcharged under galvanostatic conditions. From time to time the evolved gas was exhausted both for analysis and to prevent an excessive pressure build up. Overcharges at a limited current were run until stable conditions were reached.

When the chemical analysis of the gas, performed by a gas-volumetric method, revealed a high molar fraction of hydrogen ($Y_H > 85\%$) charging was stopped. The pressure measurements were continued in order to record the decay of hydrogen due to its oxidation on the active material of the positive plates.

After the overcharge tests, the cells were filled with O_2 and N_2 mixtures, or with H_2 , and the potentiostatic polarisation curves $I(V)$, both for the negative and for the positive plates, were obtained. The potentials were referred to a standard sulphate electrode (SSE) having a capillary tube with a tip placed on the separators.

Finally, the batteries were disassembled to determine their geometric characteristics and also the mass ratio between the positive and the negative active material. Some negatives were immediately placed in an electrolytic cell, charged and, after washing in doubly distilled water, dipped in 0.01 N

*The total volume of the system is the sum of the free volume of the cell, the volume of the tubes used (which are both constant), and the volume of a branch of the manometer which can be varied by adding water to the other branch.

sulphuric acid. The oxygen reduction of the negative plates in the absence of the positive electrode and of the separators was then studied as described elsewhere [2, 3]. In these tests 0.01 N sulphuric acid was used to reduce the spontaneous hydrogen evolution on lead.

Results and discussion

The data reported below refer to a nominal 100 A h battery. Each cell contained eleven negatives and ten positives and the mass ratio of positive to negative active material was about 1.4. The cell volume above the plates was estimated to be about 560 ml while measurements showed that the free volume varied between 510 and 550 ml per cell. A mean value of 525 ml was used in the calculations.

The decay in gas pressure for cells initially filled with pure O_2 and an O_2-N_2 mixture is shown in Fig. 1(a). These curves represent the kinetic law of oxygen reduction on the active material of the negative plates provided that the spontaneous hydrogen evolution on lead can be neglected. Figure 2(a) shows two pressure decay curves for hydrogen oxidation at the positive active material. Figure 3(a) refers to O_2 on a single negative plate from a disassembled battery treated as described above. The results have been analysed by calculating the derivatives $\ln(|dP/dt|)/dt$ (Figs. 1(b) - 3(b)).

In the case of oxygen reduction, the values of $\ln(|dP/dt|)/dt$ are constant during the measurement period, suggesting that the current, I_1 , for spontaneous hydrogen evolution on the negative plates is negligible. From the theoretical curves of the derivatives as a function of time, Fig. 4 (calculated as described in Part I [1]), however, it can be deduced that unless the

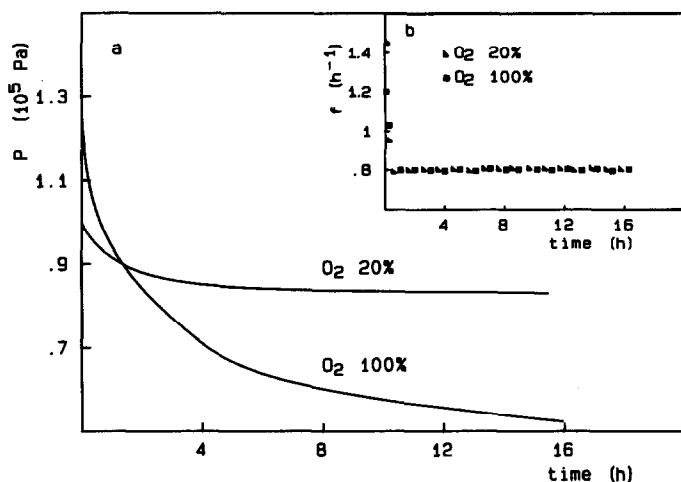


Fig. 1. (a) Pressure decay curves for two cells initially filled with different N_2-O_2 mixtures. $T = 300$ K; (b) corresponding values of f calculated from the pressure data.

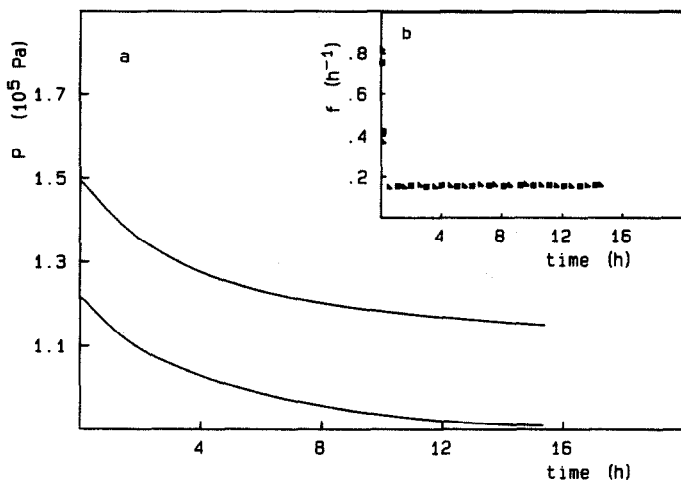


Fig. 2. (a) Hydrogen pressure decay curves for two initially different pressures, $T = 300$ K; (b) corresponding values of f calculated from the pressure data.

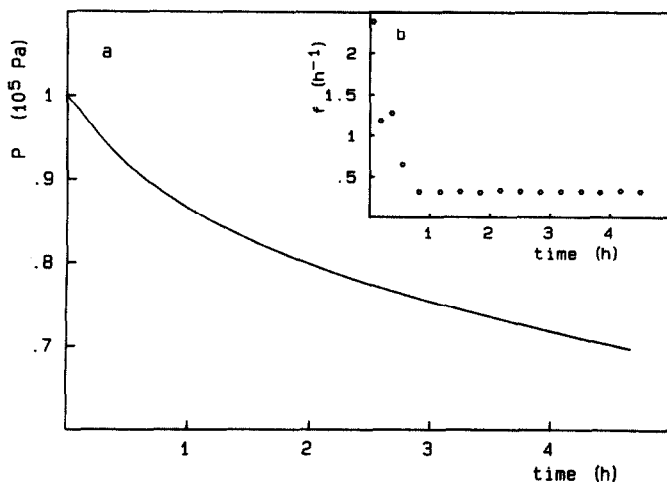


Fig. 3. (a) Pressure decay curve for a single negative plate in a sealed container initially filled with oxygen, $T = 300$ K; (b) corresponding values of f calculated from the pressure data.

value of the hydrogen current, I_1 , is less than $100 \mu\text{A}$ for each cell, $\ln(|dP/dt|)/dt$ would vary with time. Other authors report a greater value of I_1 but our previous work [2 - 4] demonstrated the marked influence of impurities on this current. The low value found for I_1 could also indicate that H_2 evolution on negative plates is inhibited by O_2 reduction.

Therefore, the values of these derivatives can be taken as the kinetic constants, K_H and K_O , for the H_2 and O_2 reactions. Their values are, for the system under study, equal to 0.15 h^{-1} and 0.8 h^{-1} , respectively, corresponding to a current density of about 0.05 and $0.53 \text{ mA cm}^{-2}/10^5 \text{ Pa}$.

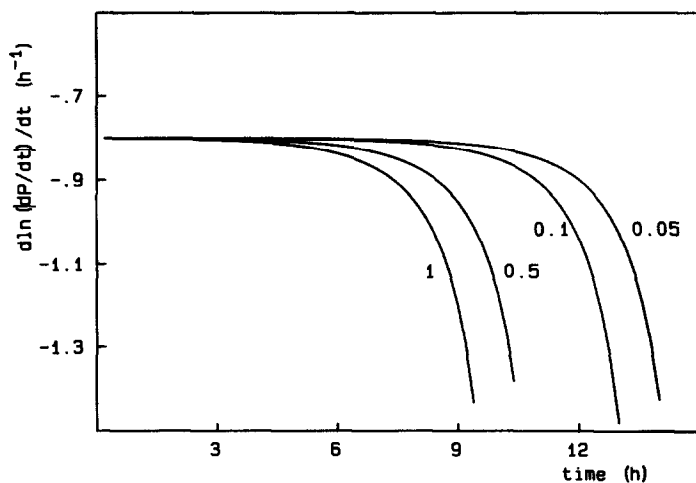


Fig. 4. f vs. t curves calculated for various values of the spontaneous hydrogen current I_1 (in mA), $T = 300$ K, $P = 100$ kPa, $K_O = 0.8$ h $^{-1}$, $K_H = 0.15$ h $^{-1}$, $V = 525$ ml.

The value of K_H has also been evaluated from the following expression:

$$(dP/dt)_{t=0} = (3I/4F - 3K_O\bar{N}_O - 3K_H\bar{N}_H/2) \times RT/V \quad (1)$$

where \bar{N}_H and \bar{N}_O are the numbers of moles of H_2 and O_2 at $t = 0$, I is the current, P the internal pressure, V the cell free volume and T the temperature.

The derivative, dP/dt , was determined during the overcharge tests, just after degassing at a pressure corresponding to the N_H and N_O values at that instant, Fig. 5.

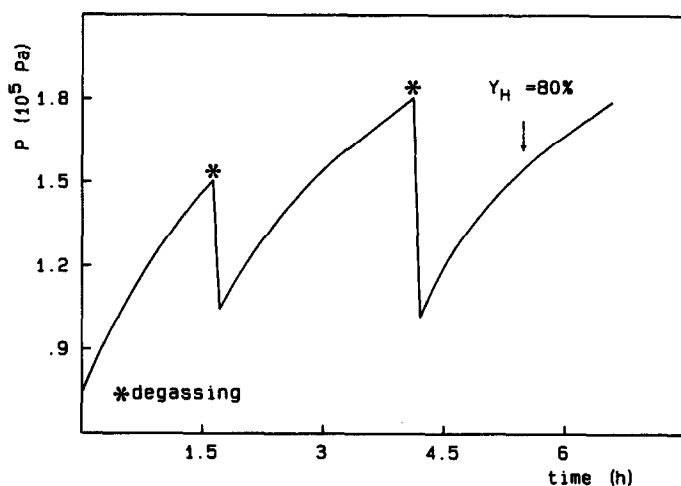


Fig. 5. Gas pressure vs. time for a sealed cell in overcharge at 0.8 A, $T = 300$ K. The gas was periodically released and part of it collected to determine its composition.

With regard to the values of the constant K_O for complete cells and single negative plates, Figs. 1(b) and 3(b), it has been found that their ratios are not equal to the ratio between the corresponding areas, the difference ranging from 10% to 15%. Moreover, the current density for O_2 reduction is lower than that calculated by Thompson [5] and measured by Thompson [5] and Mahato [6].

It is our opinion that these discrepancies can be ascribed to the different values of the ratio between the active area of the plates and the diffusion layer thickness. More work is needed to determine the real values of these quantities.

The curves presented in Figs. 1(b) - 3(b) also demonstrate that K_H and K_O decrease rapidly over the first 30 min of the pressure decay and assume constant values, as the theory forecasts. The idea expressed by some authors concerning the inhibition due to sulphate ions cannot account for this phenomenon as it involves both H_2 and O_2 .

Such a sharp deviation from the kinetic law occurring under all experimental conditions, even if the test is repeated without charging the battery, may be due to a physical process needing some time to establish or to a slow change of the conditions under which the reactions run.

The reaction between the gas and the active material produces water, which diffuses into the sulphuric acid electrolyte to dilute it and to generate heat. Thus it seems likely that the increased local temperature, and the counter diffusion of the water, decrease the kinetic constants of the reaction with time until stable conditions are arrived at. This hypothesis is currently being tested experimentally.

The possibility of modeling the system using measurements of the parameters K_H and K_O and knowing the free volume of the cells, has been verified by comparing the theoretical and the experimental behaviour of the system under various conditions. Some examples obtained under dynamic and stable conditions are shown in Fig. 6 and Table 1. It can be seen that there is good agreement in both cases.

Finally, the calculated molar fraction values of H_2 , O_2 , and N_2 , during overcharge of a battery initially filled with air are plotted in Fig. 7 as a function of the number of times the safety vents were opened at a regulated

TABLE 1

Pressure values at which stable conditions are reached for various values of I
 $T = 300$ K, battery initially filled with air.

I (A)	P (10^5 Pa)	
	Measured	Calculated
0.300	1.08	1.17
0.400	1.28	1.30
0.600	1.57	1.56
0.800	1.80	1.82

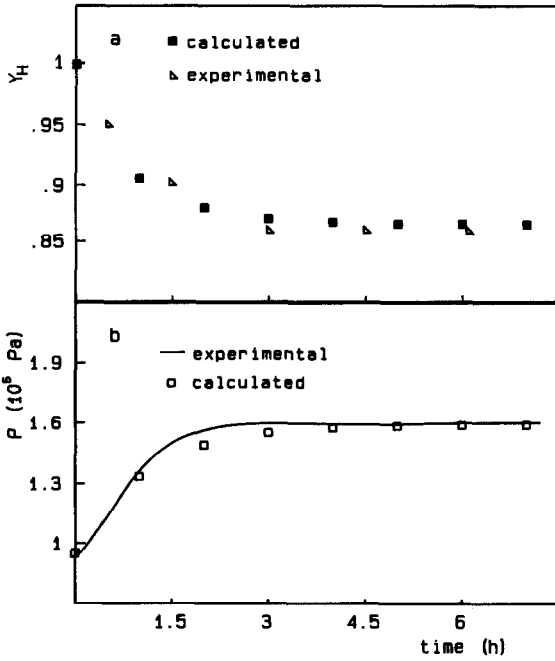


Fig. 6. Comparison between experimental and calculated data for gas composition (a) and pressure (b) under dynamic conditions for a cell in overcharge, $T = 300$ K, $I = 0.6$ A, $P_H = 0.95 \times 10^5$ Pa.

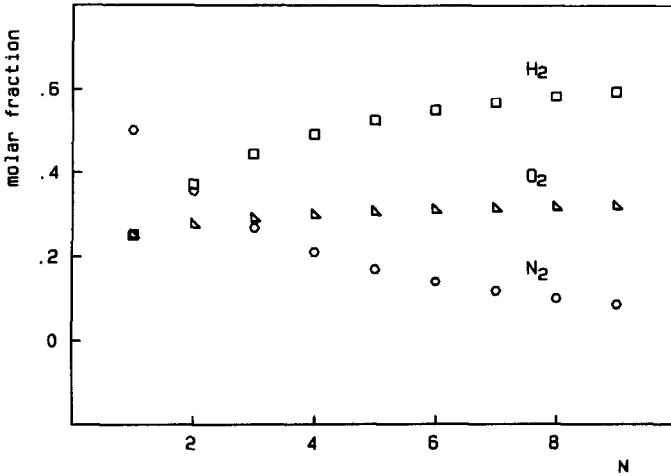


Fig. 7. Gas composition vs. the number of safety vent openings, N , during overcharge. The free volume of the battery initially contained air, $T = 300$ K.

pressure of 1.5×10^5 Pa. After a certain number of gas releases, the nitrogen is completely expelled and the cells become filled with hydrogen ($Y_H = 0.66$) and oxygen ($Y_O = 0.33$) alone. If, after overcharge, the battery is left at open circuit, oxygen is consumed at a higher rate than is the hydrogen so that,

TABLE 2

Values of pressure and hydrogen molar fraction for a cell of an open-circuit battery after overcharge

Time at o. c. (h)	Pressure (10^5 Pa)	Y_H
0	1.5	0.667
0.2	1.4	0.695
0.4	1.3	0.722
0.6	1.22	0.748
0.8	1.15	0.771
2	1.09	0.794

during the rest period, Y_H increases and the pressure decreases with time, Table 2.

Tests performed using a battery which had been deeply discharged about 20 times produced similar results to those obtained using batteries just purchased.

The expression:

$$I = 4FK_O\bar{N}_O + 2FK_H\bar{N}_H \quad (2)$$

gives the current at which the internal pressure in the battery does not change [1] and can be used to evaluate the float current. By means of the characteristic curve of the system, the float voltage is also obtained.

From the data collected, one can evaluate the maximum float current in air, ranging between 0.002 and 0.004 A per A h of cell capacity. These values agree very well with those published by some manufacturers. The value of K_H , on the other hand, does not agree with the conclusions of some authors [7], according to which H_2 recombination is immeasurably small, and with the values of Badger [8] who found a ratio K_O/K_H much greater than that measured by us. This is discussed below.

Figure 8 shows polarization curves for different gaseous compositions present in the free volume of the cell. The curves clearly show the marked influence of O_2 and the negligible effect of H_2 . The cathodic branch of the curves indicates that there is a change in the predominant electrochemical reaction occurring at the negative plates.

At low currents the cathodic reaction corresponds to a charging of the negative plates, *i.e.*, to reduction of lead sulphate formed by the reaction of lead, oxygen, and sulphuric acid. At high currents hydrogen evolution occurs. The transition between the two reactions takes place when the oxygen current reaches its limiting value. The data obtained agree well with those calculated using expression (2).

Regarding the positive plates, it seems that the hydrogen has no influence: there is only a negligible shift of the curves towards more negative potential values. This is probably due to the oxygen evolution curve which overlays the charge curve of the positive plates.

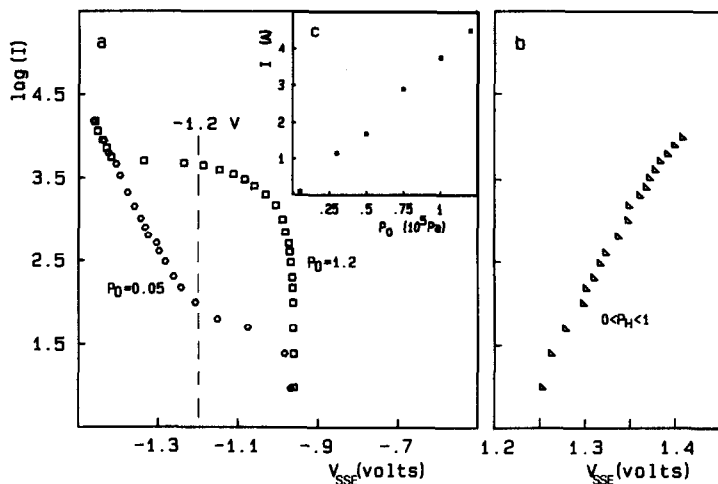


Fig. 8. (a), (b): Polarization curves of the negative and positive plates of a cell (current, I , in mA); (c) influence of the oxygen partial pressure P_O on the O_2 reduction current (in A) at -1.2 V.

The shapes of the characteristic curves in Fig. 8, lead us to consider the test proposed by Badger [5] to determine the efficiency of gas recombination. This test is based on measurements of charge acceptance currents of a battery flushed first with nitrogen followed by a reactive gas. If the reactive gas is oxygen, the differences between the charge acceptance currents correspond to the limiting oxygen current which, according to expression (2), depends on the kinetic constant of oxygen reduction.

By contrast, if the flushing gas is hydrogen, the corresponding charge acceptance currents do not give information about the hydrogen reaction on lead dioxide, because of the slight effect this gas has on the characteristic curves of positive plates. For this reason the author found a low kinetic constant for hydrogen oxidation.

Applying the test proposed by Badger to O_2 reduction, a K_O value greater than that calculated from the pressure decay curves was deduced. On the other hand Table 1 shows good agreement between the measured and calculated data using a K_O value obtained from the pressure decay curves.

This discrepancy could possibly be related to the difference in the extent of the reacting area of the plates according to the experimental conditions.

Conclusions

From the analysis of the gas pressure decay in a gas recombining lead-acid battery filled initially with oxygen or hydrogen and maintained at open circuit, it is possible to determine the kinetic constants relative to reactions of the gas with the active material of the plates.

For the system considered, these constants correspond to a current density of $0.53 \text{ mA cm}^{-2}/10^5 \text{ Pa}$ for the oxygen reduction and $0.050 \text{ mA cm}^{-2}/10^5 \text{ Pa}$ for hydrogen oxidation.

The determination of these parameters provides a sufficiently good evaluation of the battery behaviour under charge, float charge or storage. The results obtained suggest that further research should be focussed on three major topics:

- (i) the trend of the $P(t)$ curves at the beginning of decay;
- (ii) the influence of the experimental operating conditions on the reacting areas;
- (iii) the conditions resulting in spontaneous H_2 evolution at the negative plates, and the high value of the H_2 molar fraction in the gas at an overall pressure greater than atmospheric.

List of symbols

F	Faraday's constant ($26.8 \text{ A h (g eq.)}^{-1}$)
f	$= \text{dln}(dP/dt)/dt \text{ (h}^{-1}\text{)}$
I	Charge current (A)
I_1	Current intensity for H_2 evolution at open circuit (A)
$K_{\text{H}}, K_{\text{O}}$	Kinetic constants for the reactions of H_2 and O_2 with the active materials (h^{-1})
$N_{\text{H}}, N_{\text{O}}$	Number of H_2 and O_2 moles present in the free volume of the cell at time t
$\bar{N}_{\text{H}}, \bar{N}_{\text{O}}$	Number of H_2 and O_2 moles present in the free volume of the cell at time zero
P	Cell internal pressure at time t (Pa)
P_{H}	Hydrogen partial pressure (Pa)
P_{O}	Oxygen partial pressure (Pa)
R	Gas constant ($82.05 \text{ ml atm K}^{-1} \text{ mol}^{-1}$)
t	Time (h)
T	Temperature (K)
V	Free volume of the cell (ml)
$Y_{\text{H}}, Y_{\text{O}}$	H_2 and O_2 molar fractions

References

- 1 M. Maja and N. Penazzi, *J. Power Sources*, 25 (1989) 99.
- 2 A. Arlanch, G. Clerici, M. Maja and N. Penazzi, in L. J. Pearce (ed.), *Power Sources 10*, Paul Press Ltd., London, 1985, p. 495.
- 3 M. Maja, N. Penazzi and P. Spinelli, *Proc. 6th Eur. Symp. on Corrosion Inhibitors, Ferrara, Italy, September 1985*, Centro Stampa Università, Ferrara, p. 427.
- 4 M. Maja and N. Penazzi, *J. Power Sources*, 22 (1988) 1.
- 5 J. Thompson and S. Warrell, in J. Thompson (ed.), *Power Sources 9*, Academic Press, London, 1983, p. 97.
- 6 B. K. Mahato, E. Y. Weissman and E. C. Laird, *J. Electrochem. Soc.*, 121 (1974) 13.
- 7 J. S. Symanski, B. K. Mahato and K. R. Bullock, *J. Electrochem. Soc.*, 135 (1988) 548.
- 8 J. Badger, *Rept. 50th IBMA Convention, Chicago, IL, Oct. 27 - 29, 1987*, IBMA Inc., Largo, FL, 1987.