

## FACTORS AFFECTING THE FORMATION OF LEAD/ACID TUBULAR POSITIVES

### II. RESTING AND EXTREME CONDITIONS

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#### Summary

The first-cycle discharge capacity of tubular positive plates was determined as a function of formation conditions. "Infinite acid volumes" were used and formation conditions were more extreme (up to 152 h, 70 °C, s.g. 1.320 and paste densities from 3.2 to 5.5 g cm<sup>-3</sup>) than those examined in a previous paper. In addition, the effect on capacity of resting periods during the formation cycle was evaluated. The data are presented in both tabular and graphic form, and it is shown that a computer-based polynomial curve-fitting routine can be satisfactorily used to interpolate and, to some extent, to extrapolate such data.

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#### Introduction

In a previous paper [1] we reported on the manner in which formation conditions affected the first-cycle discharge capacity of tubular type lead/acid positive plates. That paper contained a review of published literature relating to the behaviour of the tubular positive element of the lead/acid battery. Since then, only very few additional publications have come to light. Though not recent, the work of Sundberg [2] is of interest in discussing the way in which the electrochemical parameters are influenced by the design and geometry of the active material retainer. Both cylindrical and elliptical geometries are discussed. A much more recent paper by Voss [3] considers (though without providing actual results) the parameters of importance in the formation of both positive and negative plates. The factors considered as desirable by Voss are similar to those reported here and in our previous paper [1]. We are also aware of two further studies of relevance. Rogatchev *et al.* [4] have studied the corrosion rate of the spines in tubular

positive plates and the manner in which the corrosion rate depends on current density and active mass thickness, while Lindholm [5] has again emphasised the effect of design of the element on capacity.

The conditions of our previous study [1] were contained within the envelope: specific gravity 1.060 - 1.270 g cm<sup>-3</sup>, temperature 10 - 50 °C, fill density 3.8 - 5.2 g cm<sup>-3</sup> with formation current density 0.53 - 0.84 A dm<sup>-2</sup> (based on the internal area of the tube), and formation times of 36 - 72 h. Inspection of the data in the previous paper showed that, as the formation conditions were varied, the capacity value passed through a maximum in certain conditions, while in others it continued to rise to the limit of the parameter investigated. In the latter case, we have extended the range of the investigation to see whether the trend persisted.

In the work reported here we have (a) extended the above range of formation parameters and (b) included formation procedures with one or more "rest" periods.

The formation conditions reported here firstly extend the formation duration up to 152 h; well beyond that normally used. It is generally considered in the battery industry [6] that such long formations are beneficial. The range of electrolyte specific gravities used was extended to 1320, since it is frequently alleged that high specific gravities are conducive to higher capacities [6]. However, it should be noted that in contrast to flat plate manufacture where the unformed positive paste is mainly PbO (70%) with PbSO<sub>4</sub> as a smaller constituent (15 - 20%), the composition of a tubular positive (in its pickled or sulphated state) before formation is usually of the order of 70 - 80% PbSO<sub>4</sub>, the other constituents being the unreacted oxides. The sulphated tubular positive would therefore be expected to generate substantial amounts of sulphuric acid on formation, thus effectively and progressively raising the s.g. of the formation acid. The range of formation temperature was extended to 70 °C but, as expected on the basis of earlier results, this showed no increase in capacity values. Finally, pastes of both lower and higher densities than hitherto were examined, ranging from 3.2 to 5.5 g cm<sup>-3</sup>.

The second major extension of the previously reported work involved the introduction of "rest" periods into the formation schedule. This procedure is widely used in the battery industry, indeed, some plants even include discharge periods within the overall formation procedure. The rationale behind these is firstly to promote the oxidation of any particles of elemental or "residual" lead contained in the paste. In as much as the amount of free lead varies from plant to plant (from about 5 - 15% depending on the method of oxide production) the importance of this aspect varies. The second purpose underlying the use of rest periods (related to self-discharge) or discharge periods (as an electrochemical operation) during formation is to open up the mass of active material, thus rendering it more accessible to acid and thereby bringing forward this effect which takes place at the first and succeeding discharges (cycling) of a plate in service. Structural transformations of the PbO<sub>2</sub> electrode during cycling, which forms part of

this process, have been reviewed by Burbank *et al.* [7] and later by Simon *et al.* [8].

There is little published quantitative information however on the effect of such rest periods on battery performance. The monograph of Bode [9] which is otherwise so informative does not refer to the practice, though brief mention of it is made by Vinal [10]. It is clearly of importance to have some information on it, and the formation operations reported below incorporated either one or two rest periods, of duration from two to four hours, at various stages in the overall formation schedule.

## Experimental

The apparatus used has been previously described [1] and the paste was from the same batch as used in our earlier work. To obtain the lower fill densities, the paste was mixed with a filler (a commercially available diatomaceous earth). The test discharge to determine the plate capacity was carried out using electrolyte SG 1.275 - 1.285 (at 15 °C), the test temperature being controlled to 30 °C ± 1 °C.

## Results and discussion

The results of the conventional (without rest) data are shown in Tables 1 and 2, and for the purpose of discussion, the trends apparent within the Tables will be considered in sequence.

TABLE 1  
Capacity (A h kg<sup>-1</sup>) of the formed plates\*

Run number	Current density (A dm <sup>-2</sup> )	Duration (h)	Formation input (A h kg <sup>-1</sup> )	Paste density (g/cm <sup>3</sup> )	Formation s.g.	Capacity (A h kg <sup>-1</sup> )
19	0.63	48	565	4.13	1.260	124.9
168	0.63	72	811	4.25	1.260	138.9
58	0.63	48	561	4.00	1.060	129.3
167	0.63	72	811	4.25	1.060	128.6
163	0.63	48	532	4.25	1.160	118.8
166	0.63	72	811	4.25	1.160	134.6
172*	0.63	86	858	4.61	1.025	125.4
173	0.63	86	858	4.61	1.110	132.1
174*	0.63	86	858	4.61	1.290	133.4
58	0.63	48	561	4.00	1.060	129.3
46	0.63	48	584	4.07	1.115	135.6
19	0.63	48	565	4.13	1.260	124.6
94	0.46	48	369	4.13	1.060	124.1
64	0.46	72	583	4.00	1.060	138.3
178	0.46	152	1194	3.94	1.060	120.3
179	0.46	152	1028	4.58	1.285	125.0

\*Formation at 23 °C.

TABLE 2

Capacity ( $A h kg^{-1}$ ) of the formed plates\*

Run number	Formation input ( $A h kg^{-1}$ )	Paste density ( $g/cm^3$ )	Formation s.g.	Formation $T$ ( $^{\circ}C$ )	Capacity ( $A h kg^{-1}$ )
75	556	4.03	1.060	30	138.4
202	540	4.05	1.060	60	131.1
205	545	4.02	1.060	70	125.6
73	468	4.79	1.060	30	101.2
204	463	4.80	1.060	60	98.9
207	460	4.81	1.060	70	98.5
16	531	4.01	1.260	30	133.0
208	540	4.04	1.260	60	122.1
212	549	4.05	1.260	70	113.1
139	574	3.88	1.110	35	146.2
140	587	3.79	1.110	35	150.8
141	411	5.42	1.110	35	82.1

\*All formed at  $0.63 A dm^{-2}$  for 48 h.

The effect on capacity of extending formation time (and current density during that time) can be seen by inspection of the data in Table 1. Conditions for the attainment of maximum capacities vary from 48 h (SG  $1.060 g cm^{-3}$ , c.d.  $0.63 A dm^{-2}$ ) to 72 h (SG  $1.060 g cm^{-3}$ , c.d.  $0.46 A dm^{-2}$ ) but always occur within these times. In the same manner, formation current density affects the optimum time, though there is no simple connection between them.

The effect of specific gravity appears to be relatively straightforward, with capacity inversely proportional to specific gravity down to SG values of 1.060 where the relationship breaks down due to shortfall of  $SO_4^{2-}$  ions.

With regard to fill densities, Tables 1 and 2 show that very low densities give exceedingly high capacities when this is expressed in terms of  $A h kg^{-1}$ .

Turning to the effect of rests during the formation cycle, results are shown in Figs. 1 - 3\*. It is seen that the effect of resting is beneficial (compared with uninterrupted formation) provided the rest(s) are implemented neither too early (when the formation process is running at high coulombic efficiencies) nor too late in the formation cycle when it can be counter-

\*Figs. 1 to 4. Capacity of positive (after 1st discharge) (vertical axis) vs. formation charge (horizontal axis). Both parameters expressed as  $A h kg^{-1}$  active material. The graphs also show the effect of fill density since, on each line, there are at least three data points corresponding (left to right) to high, medium and low fill densities. The figures thus show the effect of fill density on capacity. Fill densities are: low,  $4.0 - 4.2 g cm^{-3}$ ; medium,  $4.3 - 4.5 g cm^{-3}$ ; high,  $4.5 - 4.9 g cm^{-3}$ .

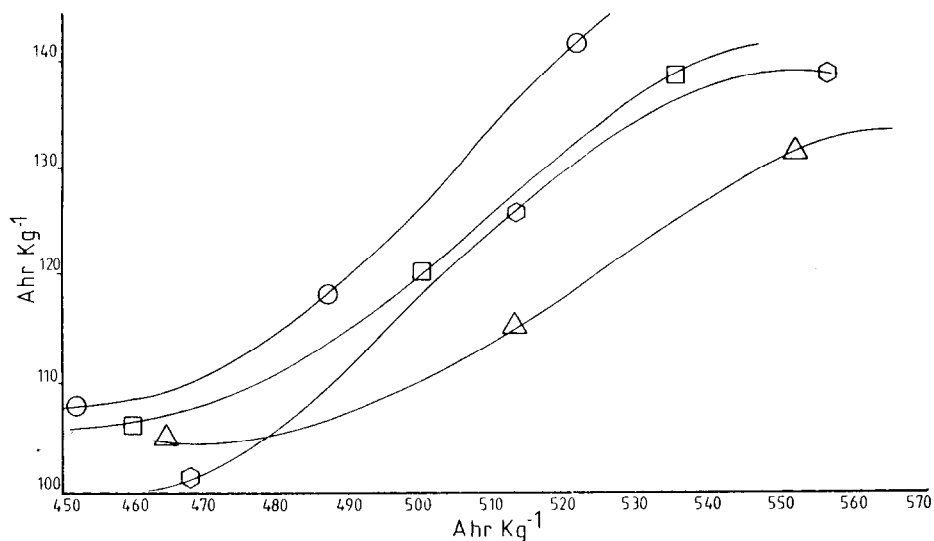


Fig. 1. Formation at 30 °C, sp. gr. 1.060, current density 0.63 A dm<sup>-2</sup> based on superficial plate area.  $\circ$ , no rests;  $\diamond$ , rests after 12 h;  $\square$ , rest after 24 h;  $\triangle$ , rest after 36 h. All rests 4 h duration. The group of four different symbols on the left represents high fill density, that in the centre, medium, those on the right low fill density.

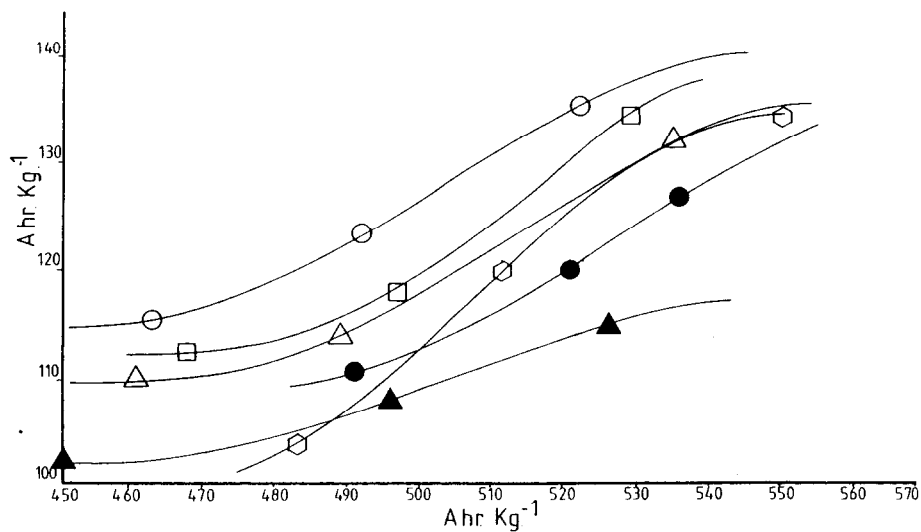


Fig. 2. As Fig. 1, but sp. gr. 1.160. Symbols as Fig. 1, but additionally  $\bullet$  indicates 4 h rest after 24 h, formation temperature 15 °C;  $\blacktriangle$ , no rest, formation temperature 15 °C.

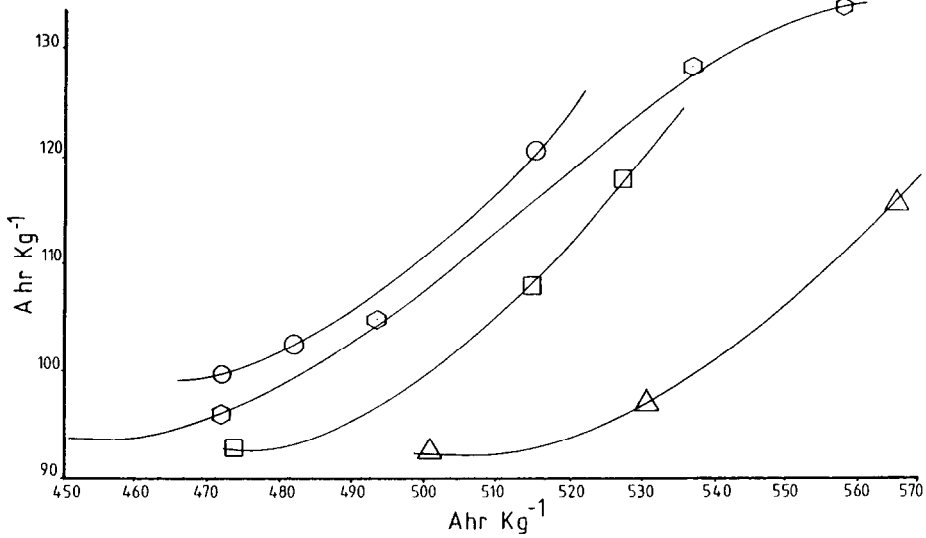


Fig. 3. As Fig. 1, but sp. gr. 1.260. The upper two data points (○) are for high fill density pastes.

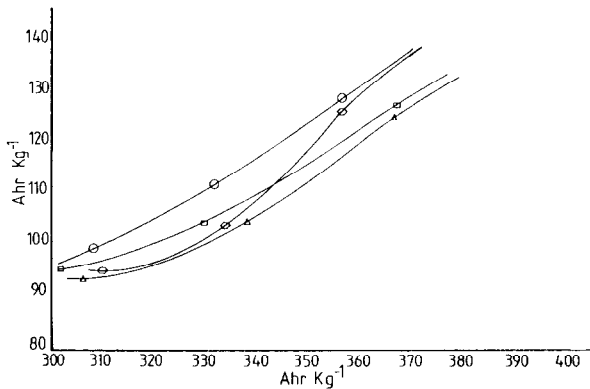
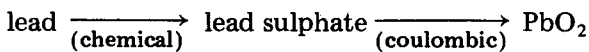


Fig. 4. As Fig. 1, but current density  $0.42 \text{ A dm}^{-2}$ .

productive not only in terms of discharge capacity but also in terms of time wasted. The presence or absence of rests does not appear to affect the ranking in respect of formation acid gravity or formation temperatures employed. It is also seen (Fig. 4\*) that the lower the formation current density, the less useful is the resting procedure and this one would expect in terms of the consecutive reaction sequence:



since a high formation rate leads more quickly to acid depletion in the pores of the positive active material as a result of diffusion limitation.

\*Please see p. 392.

The primary value of the results both in this work and the previous publication, is to demonstrate, using the most closely defined conditions yet reported, how the initial capacity of a tubular positive plate varies as a function of those formation conditions.

Because of this, it might be expected that the form of the capacity plots was inherently simpler than that of similar plots obtained under conditions where the acid temperature rose during the process of formation or other parameters varied. If it is accepted that the curves are now as simple and free from side effects as possible, it is right to ask whether they can be fitted to any simple mathematical relationship. If this were possible a number of benefits would arise. Description of the curved plot in mathematical terms is a useful simplification for the battery scientist or designer to interpolate and (perhaps with less confidence) to extrapolate the data, thereby eliminating the need for costly and time-consuming experimentation. At a more fundamental level, it is possible that with such a quantitative description of the formation data, further insights into battery theory might be obtained.

We have taken the data from the present and previous studies [1] and attempted curve-fitting procedures to them. The model was an "Nth Order" curvilinear least-mean squares regression fitting [11]. The program allowed various orders of equation to be tested and, in general, 3rd order polynomials were found to give the best fit. The upper limit to the order of equation which may be used is, of course, limited by the number of data points. However, in some cases, a lower order (3rd) polynomial was found to give a better fit than a 4th order expression.

Some of the more successful examples obtained using this approach are shown in Fig. 5. The goodness of fit (interpolation) is seen to be excellent, and an extrapolation apparently giving reasonable data values also results. It was found that best results were given when the data points for lower capacity (charge or discharge) formed a "convex" rather than a "concave" envelope. Presumably this allows the polynomial to converge more readily. The specific equations used to fit the data in Fig. 5 are shown on the graph.

From the present work, a number of conclusions emerge. In the first place, the value of "resting" in building up first-cycle capacity values is confirmed and it is seen that the timing and duration of such rests is an important parameter in this respect. Though the morphological effect of resting lies outside the scope of this work, it is interesting to note that SEM studies [12] have been successful in showing structural changes caused by this regime. Related to "resting" during formation is pulse formation, and a recent publication by Penchev *et al.* [13] where this technique was used, makes startling claims for increased capacity resulting from the method.

Turning to the computer-fitting of the capacity data, it is interesting to show that such data can be represented by a third-order polynomial over both the rising and descending portion of the whole curve. To what extent such an approach might be used with confidence for both interpolation and extrapolation must await a further study where more data points (relating

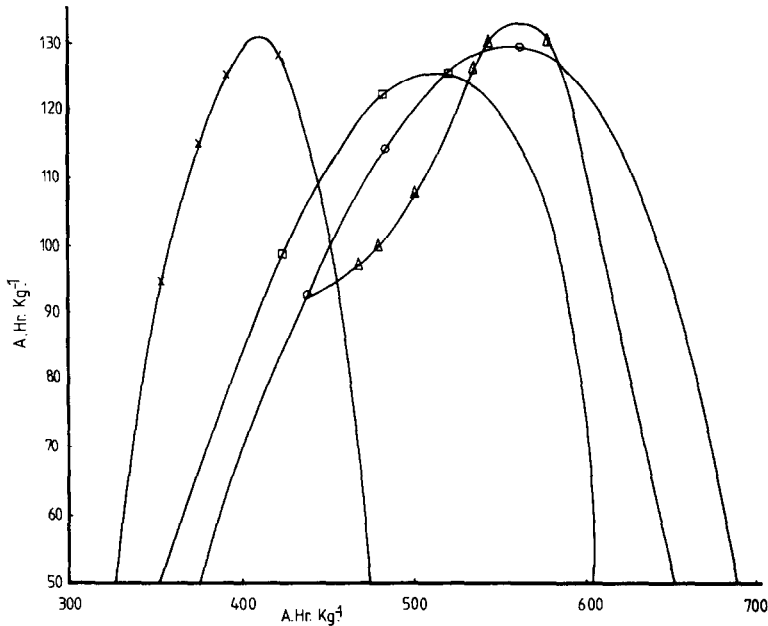


Fig. 5. As Figs. 1 - 4, but demonstrating how the computer-based polynomial curve-fitting routine can simulate experimental data. Lines are computer-derived, points are experimentally determined.  $\times$ , formation at 20 °C, sp. gr. 1.060, formation at 0.53 A dm<sup>-2</sup>. Equation for best fit is:  $Y = 2.36 \times 10^{-6} - 4.97X + 2.68 \times 10^{-2} X^2 - 3.38 \times 10^{-5} X^3$ .  $\square$ , As above, but formation at 0.42 A dm<sup>-2</sup>. Equation for best fit is:  $Y = -4.01 \times 10^{-6} - 1.43X + 7.00 \times 10^{-3} X^2 - 7.4 \times 10^{-6} X^3$ .  $\circ$ , As above, formation at 0.63 A dm<sup>-2</sup>. Equation for best fit is:  $Y = 2.3 \times 10^{-6} - 1.1X + 5.29 \times 10^{-3} X^2 - 5.14 \times 10^{-6} X^3$ .  $\triangle$ , As Fig. 3, equation for best fit is:  $Y = -5.5 \times 10^{-4} + 17.01X - 0.1X^2 + 1.99 \times 10^{-4} X^3 - 1.3 \times 10^{-7} X^4$ .

to a single set of conditions) can be tested against the model and, quite possibly, a model such as we have used here, might find a place within a larger computer program, as used in modelling whole battery behaviour. A somewhat different approach, though showing numerically similar optimum values, has recently been published by Horvath [14] and the assimilation of these different approaches into a unified treatment must now be an important goal for battery designers.

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