

A new lead acid cell concept for traction applications

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This paper describes methods for the improvement of the utilization of the positive active material in tubular electrodes. First a lead dioxide matrix with a very high porosity, achieved by means of a granulated grey oxide powder, is described and secondly a special electrode geometry, promoting improved access of electrolyte into the active material and an increased convection of the electrolyte around each separate tube.

1. Introduction

The lead acid battery has been well established for traction use for decades and its use seems to be expanding during the 80's. Efforts are being made all over the world to increase the efficiency of battery operation. Consequently, many recent investigations deal with the structure and the structural changes in the positive material [1-12]. A regular and homogenous structure of the active materials is of great importance for a continuous progress of the electrochemical processes inside the electrodes. The conversion of the active material during discharge causes strains between the particles and a pressure against the surrounding material. Fortunately the active material has a prime porosity, which to a certain extent can eliminate the strains. At the same time, however, the reaction products create a hindrance for the progress of the electrochemical reaction, and can stop it despite the presence of remaining active material.

Investigations [13, 14] show that the active material in the layers nearest the free acid will be discharged first. Especially with high current drains the formation of lead sulphate in the outermost layers is highly marked. It is therefore obvious that a high utilization is promoted by an extra high porosity of the lead dioxide matrix. To increase the porosity in tubular electrodes, two methods are available (a) by mixing the paste or the powder with an additive, which dissolves in the electro-

forming process leaving behind holes and pores in the material or (b) by transferring the lead powder to bigger units, the granules becoming microporous.

This work makes use of such granules and the result is an increase in porosity of about 25%. High porosity improves the supply of fresh electrolyte and this in turn promotes free convection both inside the tubes and in the bulk electrolyte.

Microporous granules are one way to improve the proper function of the electrode process. The geometry of the electrodes is another. This paper introduces a new tubular geometry, - the angular geometry - which also improves the supply of the electrolyte and consequently reduces the acid depletion around each separate electrode. This is, of course, very important in the final stage of the discharge process.

Fig. 1 is an example of an improved traction cell [15]. The envelope around the negative plate serves both as an electronic separator and as a protection against sludge falling from the active material. The energy density of a battery made of these cells could exceed 32 to 34 Wh kg^{-1} at a 3 h regime. The highly increased cycle life due to the tubular plates, compared with the flat plate batteries, is an economic factor of great consequence.

As will be shown later, this design differs from earlier batteries with respect to the shape and the geometrical arrangement of the tubes in the multi-tubular positive plate and to the structure of the lead dioxide material inside the tubes.

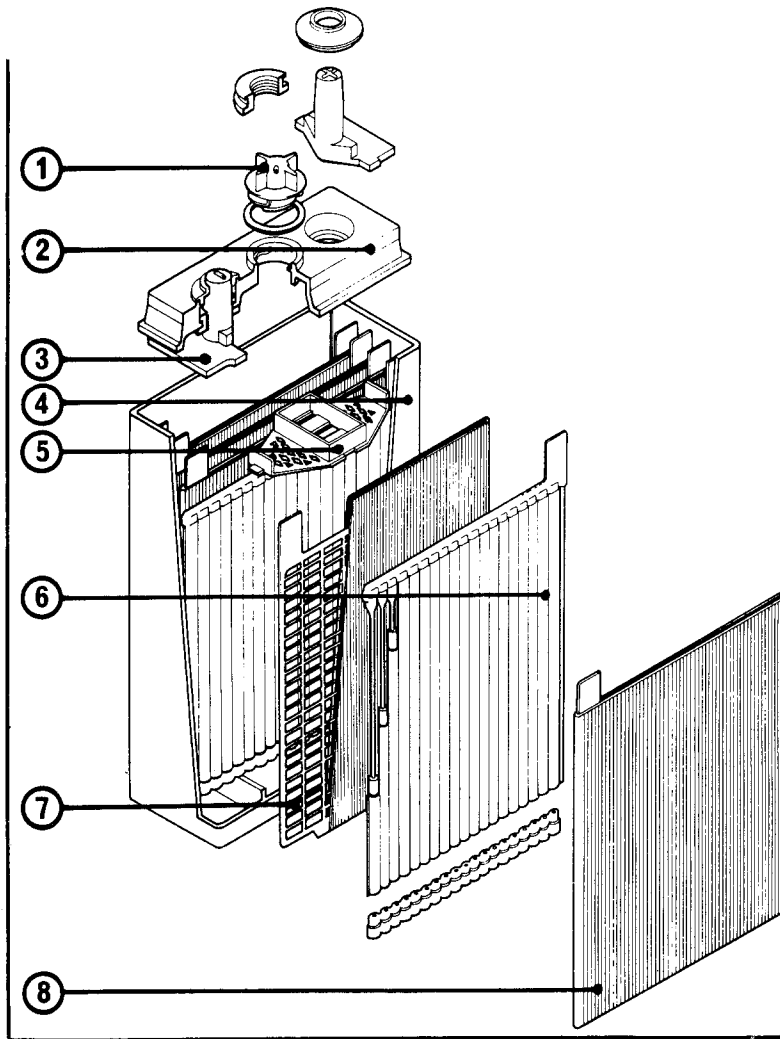


Fig. 1. The components in a modern traction cell manufactured by the Chloride Group, UK. 1. Plug for filling, ventilation and protection. 2. Cover. 3. Low resistance connector and current terminals. 4. Cell box made of hard rubber or plastics. 5. Electrolyte level indicator. 6. Multitubular positive plate. 7. Head grid to hold the active material for the negative plate. 8. Microporous envelopes to separate the negative plate from the positive plate.

2. Preparation and properties of granulated oxide

The granules in this project were made in a simple spray process [16]. The original mixture is lead powder (red lead, grey oxide) and water. The ratio of powder to water was generally 4:1. The choice of binder was most important, because the binder and procedure of granulation have a great effect on shrinkage and dimension control. The binder used here was poly(vinylalcohol), 0.8 to 1.5% of the dry powder weight. The powder/water slurry was pumped through a forming die under a pressure of 1 to 1.5 MPa into a conical chamber, where the temperature range was about 150 to 300° C. The granules formed were spherical to oval with deep cavities (Figs. 2 and 3). The particle size of the granules can be varied according to the

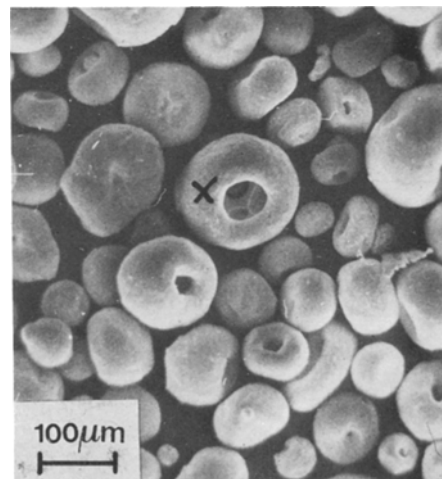


Fig. 2. Granulate made of a mix of 75% grey oxide and 25% red lead.

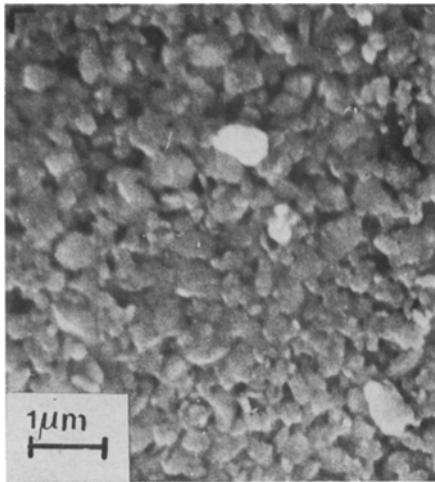


Fig. 3. A small unit of the surface (X-marked in Fig. 2) showing the microporosity of the particles.

requirements. The main product, however, always had a particle size between 50 and 250 μm. A typical result of a sieve analysis is

% > 250 μm	0.6
> 180	19.2
> 120	52.3
> 100	69.3
> 60	87.2

The apparent (fill) density after free falling was

about 2.5 to 2.7 g cm⁻³ and after a short time of vibration 2.7 to 2.9 g cm⁻³. The difference in filling properties of milled powder and granulated oxide is remarkable. A method of filling ordinary lead oxide powder and red lead has been developed [17]. The equipment provided with a vibrating frame works with high precision. It is made for single tubular electrodes in laboratory cells. The standard deviation in filling weight of individual tubes is, according to the author, always less than 1%. Some results are given in Fig. 4.

The points B, C, D, E and M (= tube of brass) on the upper line are valid for tubes with a smooth inner surface, while A, F and GS represent tubes with a rough inner surface. The result of this weight test is of importance when investigating the real behaviour of the active material under different experimental conditions.

The points Bg and Dg are the same spherical tubes as B and D on the upper line. The positions of Bg and Dg are the filling results of 10 tubes each using granulated red lead and free running. The point TOg represents the oval tube filled in the same way as Bg and Dg.

This means that the possibilities of preparing a lead dioxide matrix with a particular, high macroporosity and regular structure are most favourable when using granulated material.

When examining the individual granules in a

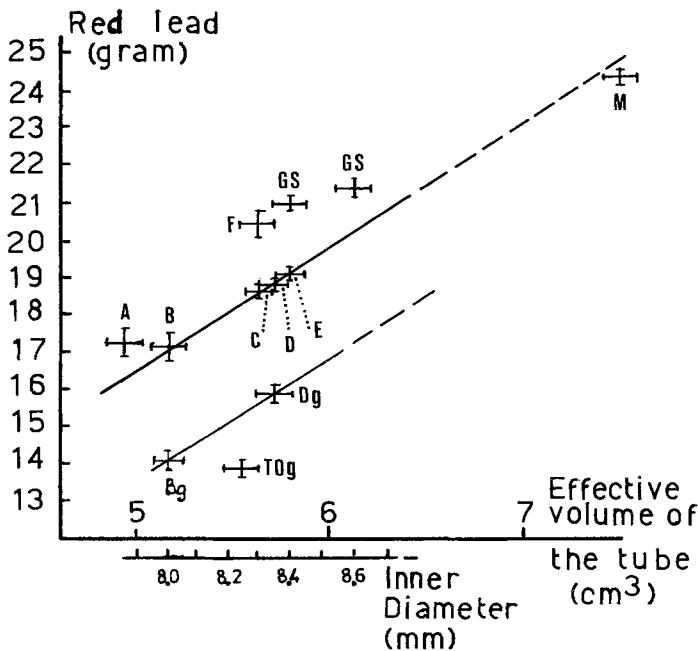


Fig. 4. The upper straight line shows cylindrical tubes with a smooth inner surface and a vibration time of 2 min. The lower line represents tubes Bg(= B) and Dg(= D) filled with granules of red lead without vibration.

scanning electron microscope (Fig. 3) one easily sees the microporous surface of the granules. This is of the greatest importance for the utilization of the inner parts of each granule.

The test cells, in which the positive electrodes were made up of tubes filled with granulated substance, have shown the useful properties of this material. For example

- a high *in situ* strength
- a good cycle life
- an improved capacity output
- a high charge acceptance

In addition, because of the macropores, it is easy for the gas bubbles arising during formation and charging, to leave the material, and new fresh acid can rapidly replace the bubbles. One problem was discovered when starting the experimental work. The contact between the lead spines and the electroformed layer nearest the spine could sometimes be broken. This phenomenon could, however, be rectified by means of two operations: (a) after the free running into the tubes, the plates were vibrated for some seconds with an oscillator for 50 p s^{-1} ; (b) the schedule of the formation process was changed in such a way that an improved corrosion of the spine could be obtained during the first two hours of the process.

3. The electrode geometry

Most of the work to develop good tubular electrodes has been concentrated on the material and wall structure of the envelope surrounding the active material. The structure must provide high permeability for electrolyte and gas, low electric resistance, good resistance against oxidation attack, high tensile strength, low deformability, resistance to external abrasion, etc. The shape of the envelope, the tube, is usually spherical, occasionally also rectangular or oval. Weaved and felted multitubes is a commonly used construction because of lower production costs and easier handling in the production process.

The electrode geometry and an optimal cell size are most important for the proper and regular formation of the electrochemical reaction layers through the electrode during its operation. Anomalous distributions of the discharge product and a high polarization resistance are important factors which govern the discharge efficiency of the

porous electrode. It is already shown that one can avoid these phenomena when using granulated material.

Almost all types of tubes manufactured by different companies have a macrostructure well adapted to an ample percolation of electrolyte through the walls into the pore system of the active material. The access of electrolyte around the separate tubes may, however, be strongly limited at a certain stage of the discharge process, especially when the electrodes are thick and the plates are tightly packed.

It is therefore important to create an electrode geometry, which is able to supply the active material with sufficiently strong electrolyte from outside the wall. Spherical tubes have, for this purpose, a good geometry.

An angular geometry with oval shaped tubes seems to be a successful solution to the problem of the electrolyte supply during a prolonged discharge period. And for traction use the advantages are pronounced.

Fig. 5 illustrates the new configuration. The tubes have an elongated, preferably almost elliptical cross-section and are turned so that the plane through the major axis of the cross-section forms an angle of 35 to 40 degrees to the central plane of the plate. The contact with each adjacent tube will under these circumstances be along a straight line (the small figure below). The figure to the right is a conventional plate with spherical tubes.

The arrangement of the tubes of different shapes is given in Fig. 6.

(1) Spherical tubes with an inner diameter of 8.4 mm, distance $B = 9.4$ mm, (2) oval tubes, $b = 5.5$ mm and (3) oval tubes in angular geometry with $B = 9.4$ mm and $\alpha = 36^\circ$. The number of tubes on a grid of a starter battery size (L) will be: 15 for (1), 11 for (2) and 17 for (3). Assuming a cell with 6 positive plates of (1) and (3), then the number of plates for (2) decreases to 10. The ratio of active material, using granulated powder will be: (1): (2): (3) = 1440: 1650: 1530 or 1: 1.14: 1.06 when the apparent density is about 2.70 g cm^{-3} . This ratio is, however, not significant for the capacity output of the cell configurations. The main reason for this irregularity is divergences in the current distribution. Because of acid depletion in the pore system and a decrease of the pore diameter due to lead sulphate formed during dis-

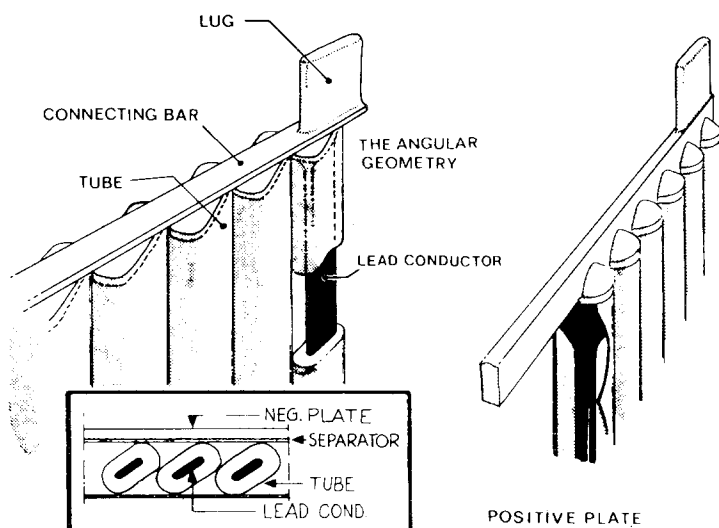


Fig. 5. Oval tubes in angular geometry and ordinary spherical tubes as commonly used.

charge, the electrolyte resistance increases and the result will be an anomalous distribution through the active material and a premature decrease of the cell voltage. The combination of an angular geometry and a high porosity is to a certain extent a good way to overcome these problems.

The thickness of the active material inside the oval tube is 4.5 mm and the distance to the spine(s) about 1.3 mm. The free electrolyte space (lined area, Fig. 6) is about 30% larger than the same space surrounding the spherical tubes (1). As a consequence the following contributions can be achieved:

(a) acid depletion in the pore system will be limited because of a flow of fresh electrolyte from the outside reservoir through the macropores of the granulated active material,

- (b) the free convection of the electrolyte increases,
- (c) the risk of overheating diminishes.

4. Experimental details

Several hundred experimental cells have been made for testing the function of the granulated oxide in comparison to the ordinary milled powder, for example grey oxide and red lead.

The cell dimensions regarding length and width have varied, while the height was always adapted to the dimensions of an ordinary negative plate to a starter battery. Because of that the tubes were cut into pieces of 130 mm. The shape of the tubes was mostly oval and in certain cases circular. They were always of the double wall type, i.e. an inner sleeving of braided glass fibres surrounded by a perforated PVC wrapping. The lead conductors, the spines, were taken from factory made grids, containing 4.5 to 5.0% of antimony. The separation was of conventional type and the negatives usually dry charged plates from different factories. The electrolyte, in complete charged condition, was 4.9 mol dm^{-3} sulphuric acid.

The test equipment were standard power sources for constant current/voltage, digital multimeters and high impedance recorders, especially when measuring the individual electrode potentials. The reference electrode was a new type of Cd/CdSO₄ electrode in a pH-buffered sulphuric acid solution. The life test was carried out in an equipment with automatic control of

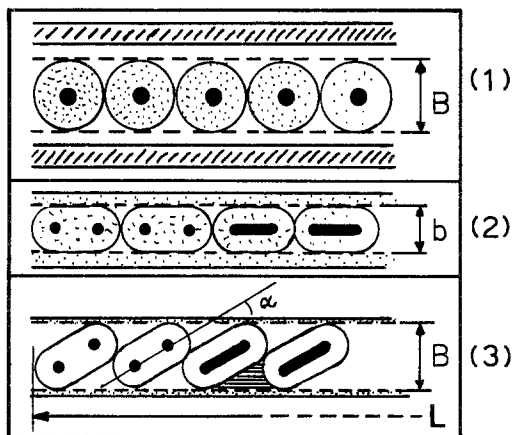


Fig. 6. Some configurations of tubular plates used in the investigation.

predetermined values of currents and voltage limits. The condition of the cells was continuously monitored on 12-channel recorders. In this report it is not the intention to describe all series of experiments. It is of interest to show the most representative results which will lead to important improvements of the lead acid battery.

This is discussed in the next section, which also includes the details of the cell components in each reported series.

5. Results and discussion

5.1. Single cells with one (1) positive tubular electrode and two (2) negatives

The distance between the positive and the negative was 4.0 mm, so that there was an abundance of electrolyte. There was no need of separators because of separate holders for each electrode.

The test was performed with 3 cells with granulated material in the tubes (= G-tube) and 3 cells with standard milled powder (P-tube) – in this case filled with 75 wt % of grey oxide and 25 wt % of red lead. The apparent density, $3.18 \pm 0.02 \text{ g cm}^{-3}$, was the same for each electrode. It could be achieved by periodic vibration of the G-tubes and only a slight vibration of the P-tubes.

Fig. 7 shows the progress of the mean electrode potential for each kind of positive electrode. The result indicates a high utilization of the granulated material; here about 25% longer discharge time at the 1 h rate down to 1.5 V.

Fig. 8 is an illustration of the first nine cycles and the changes in capacity output depending on the amplitude of the discharge. Points 1 and 2

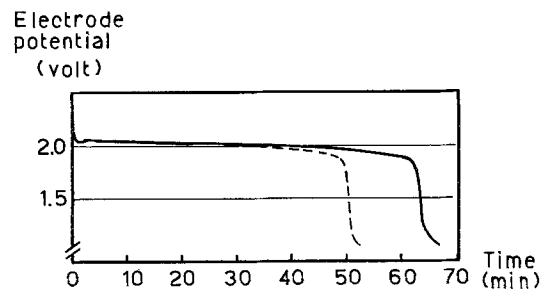


Fig. 7. The mean electrode potential vs a Cd-reference electrode. Discharge.

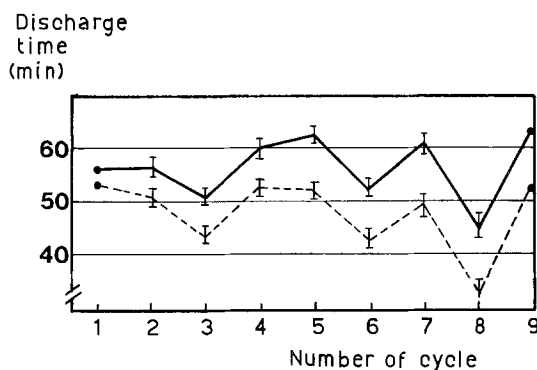


Fig. 8. The variation of the capacity depending on the discharge conditions. Discharge current 56 mA g^{-1} . Dashed line represents P-tubes and the full line represents G-tubes.

show the initial capacities after formation and charging to 150% of the previous capacity value. Thereafter the cells were discharged deeply just to the reverse polarity, and again charged in a normal way. Point 3 shows now a lower output. Points 4 and 5 show again increasing capacities for each group. The discharge was continued to a very low value again and charged with low current to about 200%. The following discharge is about the same as for cycle 3. The points 7, 8 and 9 are the results of the same procedure as above. Point 8 is very low for both groups because of an extreme previous discharge. This was run to a reverse polarity of 2.5 V. The charge was then done with low current to about 300%. It is interesting to note that the electrodes recovered very rapidly after this maltreatment of the active material and the corrosion layer.

The cycle process was then continued in a more normal manner; charging with 1A to 150% of the previous capacity value, and discharge with 1A to a cell voltage of 1.50 V. The result was increasing capacities up to 25 to 30 cycles and for P-tubes from 0.83 to 1.17 Ah, for G-tubes from 1.05 to 1.42 Ah, which means a very high degree of utilization at 1 h rate; 65 mAh g^{-1} and 79 mAh g^{-1} respectively. The reason is the abundance of acid and no separation between the electrodes. However, the factor of interest is the more favourable capacity output for G-tubes.

This series was thereafter subjected to a cycling process of 100 cycles and then stopped for examining the electrodes. When scrutinizing the active material, it was a pleasure to see that the 'balls' of the granules still had their original shape. Only a

Table 1. Values of the positive material used

Cell number	Calculated amount of lead dioxide (g)	Apparent density (g cm ⁻³)	Amount of electrolyte (cm ³ g ⁻¹)	Type of material
1	75.5	2.72		
2	74.8	2.69		
3	75.0	2.70	1.20	Granulated *G material
4	75.2	2.71		
5	83.6	3.01		
6	85.0	3.06		
7	86.1	3.10	1.18	Grey oxide + 25 wt% of P red lead
8	83.9	3.02		

*G = granules, P = standard powder in the tubes.

small amount had lumped together in the layer nearest the lead spine.

5.2. Single cells with five (5) oval tubes as in configuration 2, Fig. 6 on a grid with double spines for each tube

The negatives were 2.0 mm thick dry charged starter battery plates and the separator a 2.0 mm Porvic type. The electrode pack, 1 positive, 2 negatives, was tight packed in the cell container.

Table 1 gives the basic values of the positive material used.

The values of the fill weights are almost perfect for the G-cells. P-plates contain about 13 wt% more active material than the G-plates. The electroformation was performed in such a manner that an eventual difference in charge acceptance could be verified. The initial density of the electrolyte was 1.20 g cm⁻³. The current density during the periods of formation was 30 mA g⁻¹ for all the cells. The schedule of operation and some basic results are given in Table 2.

Table 2. Operation schedule and some basic results

	Cell 1	Cell 2	Cell 5	Cell 6
1. First charge after the sulphating procedure				
Charging current (A)	2.48	2.48	2.73	2.73
Input (Ah)	7.44	7.44	8.19	8.19
2. First discharge				
Discharge current (A)	2.00	2.00	2.00	2.00
Current density (mA g ⁻¹)	26.5	26.7	23.9	23.5
Output (Ah)	1.61	1.55	1.28	1.45
3. Second charge				
Input (Ah)	18.6	18.6	19.1	19.3
4. Second discharge				
Discharge current (A)	2.00	2.00	2.20	2.20
Current density (mA g ⁻¹)	26.5	26.7	26.3	25.9
Output (Ah)	4.32	4.24	4.04	4.16
5. Third charge				
Input (Ah)	22.3	22.3	24.8	24.8
6. Third discharge				
Discharge current (A)	2.00	2.00	2.20	2.20
Current density (mA g ⁻¹)	26.5	26.7	26.3	25.9
Output (Ah)	6.00	5.92	5.65	5.32
7. Final formation to 300% of the theoretical value				

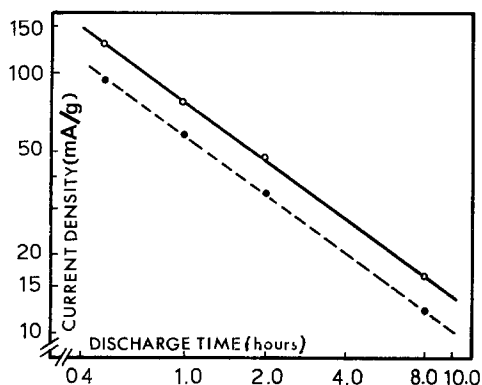


Fig. 9. The log-log diagram according to the equation $I^n t = C$ in the area of linearity. Full line represents G-material and dashed line represents P-material.

The first discharge shows a higher capacity for the G-cells in spite of lower current density for the P-cells. The conclusion is that the material has consumed a larger part of the amp hours fed than in the case of the P-material. Calculated on the mean value of the total electrode material one finds 21 mAh g^{-1} for G-material and 16 mAh g^{-1} for P-material. Accordingly, the activation and resistance polarization seem to be higher for P-material.

Regarding the following operations in this stepwise formation, and for instance the second and third discharge, the capacity difference apparently is about 5 to 10% higher for the G-cells. When the cells were then conditioned and prepared for regular capacity tests a more marked difference could be seen (Fig. 9).

There is no doubt about the superior properties of the granulated material compared to standard milled powder, when the base material is the same for both of them, i.e. grey oxide, red lead or a mixture of them. It is interesting to observe some values for different discharge times (Table 3).

Considering the cell construction – only one positive plate – these values probably will be

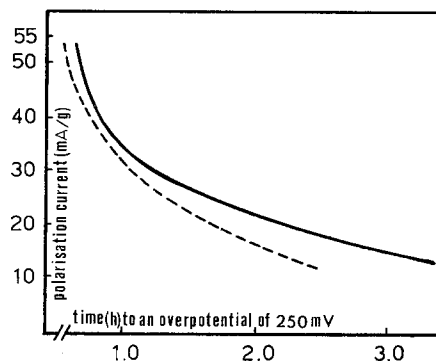


Fig. 10. Curves for the charge acceptance. Full line: cells with granules. Dashed line: cells with ordinary milled powder.

slightly lower when testing a full scale cell containing 5 to 10 positive plates. This will be tested in the near future with a traction battery of 120 V, where the cell contains 11 positive and 12 negative plates.

The first attempt (Table 2) to show the differences in charge acceptance during the formation process was not quite decisive. A direct method was therefore used. After 24 cycles the eight experimental cells were charged and discharged according to the schedule:

1. *Charging* with a current density of 53 mA g^{-1} from the open circuit potential (OCP for the positive vs Cd-reference electrode) to a polarization potential of + 250 mV. Time and polarization were registered on recorders.
 2. Pause for 5 min.
 3. Discharge with 133 mA g^{-1} (about 1/2 h discharge rate) to 1.70 V vs reference.
 4. Pause for 10 min.
 5. *Charging* with 40 mA g^{-1} ; otherwise as for point 1.
 - 6, 7 and 8. The same as for 2, 3 and 4.
 9. *Charging* with 30 mA g^{-1} (see point 1).
 - 10, 11 and 12. The same as for 2, 3 and 4.
 13. *Charging* with 13.3 mA g^{-1} (see point 1).
- The results are given in Fig. 10. It is quite clear

Table 3. Values for different discharge times

Discharge time (h)	Current density (mA g^{-1})		Degree of utilization (%)	
	G-material	P-material	G-material	P-material
1/2	126	92	28	21
2	45	33	40	29
5	22.5	16.7	50	37

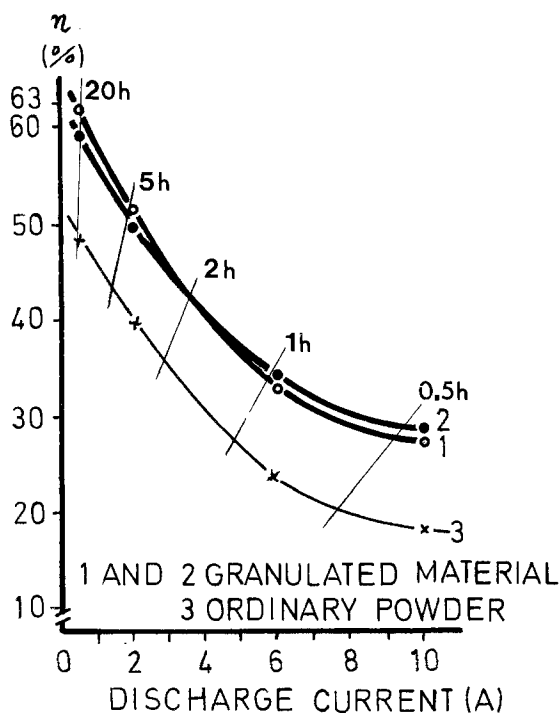


Fig. 11. The degree of utilization of granulated material against ordinary milled powder.

that a marked difference in charge acceptance exists between the two materials. The increased divergence towards lower charging currents is self-evident. A suitable charging current for G-cells could be a value of 30 mA g^{-1} , which means a charging time of about 5 h for a full scale battery.

Finally Fig. 11 illustrates the degree of utilization for these cells. In the diagram there are also straight lines for 0.5 to 20 h discharge. For example at a discharge rate of about 2 h the degree of utilization is 42% for G-plates and 34% for P-plates.

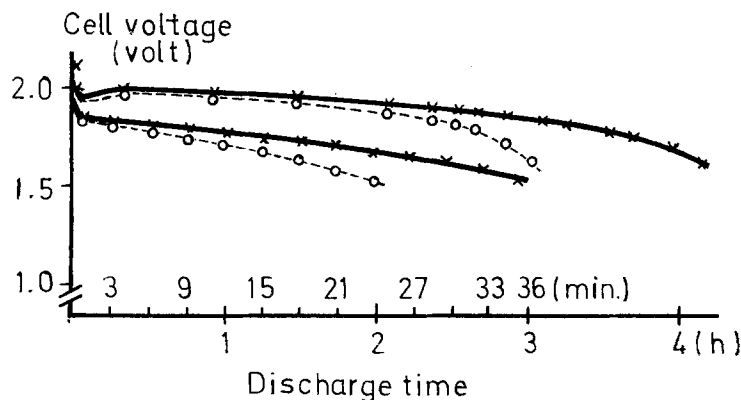


Fig. 12. Discharge at about 1/2 and 4 h rate. Current density 120 resp. 27 mA g^{-1} . The two upper curves for 4 h rates. Dashed lines for conf. (1). Full lines for conf. (3).

5.3. Cells with the positive electrodes in angular geometry

The intention of this series of six test cells was to show a probable capacity difference between the oval tubes in angular geometry, configuration (3) in Fig. 6, and spherical tubes as commonly used, configuration (1).

The cell pack contained two positives and three negatives of standard starter battery type, thickness 2.0 mm. Three cells with the positives of configuration (1) had 15 tubes on each grid and single spines with a diameter of 3.0 mm and another three cells of configuration (3) with 17 tubes on each grid and double spines, each with a diameter of 1.8 mm. The separation was 1.8 mm. Accordingly the pitch is the same for (1) and (3), i.e. 15 mm (Fig. 6) and because of that the comparison of the discharge data are valuable. The configuration (2) has also certain advantages, but due to the drawbacks noted above, i.e. acid depletion and overheating during the cycle process, it will be left out in this comparison.

The tubular plates were filled with granulated material of the same quality as used before. The ratio of the active material of (1):(3) is 1:1.06. In this special case the mean apparent density of the electroformed material was 2.80 g cm^{-3} .

The electroformation was performed to about 300% of the theoretical value and to the electrolyte density of 1.28 g cm^{-3} . After 2 to 3 conditioning cycles and a careful control of the electrolyte level and density some discharge tests were performed.

Fig. 12 shows the cell voltage as a function of the discharge time at 3 h and 1/2 h rate. Regarding the curves for 3 h rate one finds a normal decline for the spherical tubes just before 3 h,

Table 4. Some discharge values according to Fig. 12.

Current (mA g ⁻¹)	Discharge time (h)	Specific capacity (mAh g ⁻¹)	Capacity (Ah/plate)	Degree of utilization (%)
27				
AG	4.2	113	28.8	50.4
ST	3.1	84	20.2	37.5
120				
AG	0.6	72	18.3	32.0
ST	0.4	48	11.5	21.4

AG means Angular Geometry, configuration (3), Fig. 6.
ST Spherical Tubes, configuration (1), Fig. 6.

while the angular electrodes continue an additional hour to the same final voltage (about 1.6 V).

The same behaviour, but more pronounced, appears at the 1/2 h rate. Obviously it depends on a more rapid acid depletion for the tubes in configuration (1). Table 4 illustrates some important figures taken from the above performed discharges.

The great difference in capacity between the two configurations is also a consequence of 6% more active material in the AG-plate, but the thin oval tubes forming this particular electrode geometry and, to a certain extent, also the two spines in each tube are the principal contributions to the achieved results. The high degree of utilization is the combined effect of the high porosity matrix and the different properties caused by the geometry.

6. The service life

In general, it is said that a very high porosity shortens the electrode life owing to broken connections between the particles and a breakdown of the particles (granules) to a nonactive sludge. This risk is always present, and probably all previous efforts have failed due to these phenomena. It has therefore been an important task to control the changes of the granular structure from time to time during a life test. It was already mentioned one observation after 100 cycles. The result was satisfactory.

A hard life test was performed on cells according to Tables 5 and 6.

After electroformation in a usual way and adjustment of the acid to 1.28 g cm⁻³, the test of the service life was performed according to the

Table 5. Oval tubes of configuration (2), 11 tubes on each plate; 2 plates/cell. Apparent density 2.70 g cm⁻³ for cells 1 to 4, 3.40 g cm⁻³ for cells 5 and 6. Amount of electrolyte: 1.1 cm³ g⁻¹, positive material for cells 1 to 4; 1.2 cm³ g⁻¹ for cells 5 and 6. Electroformation in acid of the density 1.20 g cm⁻³

Cell number	Positive material	Active material (g PbO ₂)	Separation thickness (mm)
1	Granules	332	1.8
2	Granules	332	2.0
3	Granules	332	2.0
4	Granules	333	2.0
5	Powder	419	1.8
6	Powder	420	2.0

following schedule:

1. Fully charged cells.
2. Discharge at about 3 h rate (9.0 A) to a cell voltage of 1.50 V.
3. Direct automatic change to charge with 6.0 A; input 133% of the nominal capacity.
4. Direct discharge as for point 2.

The test was carried out in the same equipment with automatic control as mentioned before. The condition of the cells was continuously monitored on a 12-channels recorder.

It is clear that a discharge current of 9.0 A causes large differences in current densities to the test groups. The cells 1 to 4 are therefore impressed with 27 mA g⁻¹; 5 to 6 with 21.5 mA g⁻¹; 7 to 10 with 19 mA g⁻¹ and 11 to 12 with 16 mA g⁻¹. The service life is of course dependent upon this treatment.

The result (Fig. 13) makes clear that the heavy load for the cells 1 to 4 causes a more rapid capacity drop in the interval 600 to 700 cycles

Table 6. Spherical tubes of configuration (1) 15 tubes on each plate; 2 plates/cell. Apparent density 2.80 g cm⁻³ for cells 7 to 10; 3.40 g cm⁻³ for cells 11 and 12. Amount of electrolyte 1.11 cm³ g⁻¹, positive material for cells 7-10; 1.2 cm³ g⁻¹, for cells 11 and 12. Acid 1.20 g cm⁻³ for electroformation

Cell number	Positive material	Active material (g PbO ₂)	Separation thickness (mm)
7	Granules	477	1.8
8	Granules	476	1.8
9	Granules	476	2.0
10	Granules	475	2.0
11	Powder	572	1.8
12	Powder	572	2.0

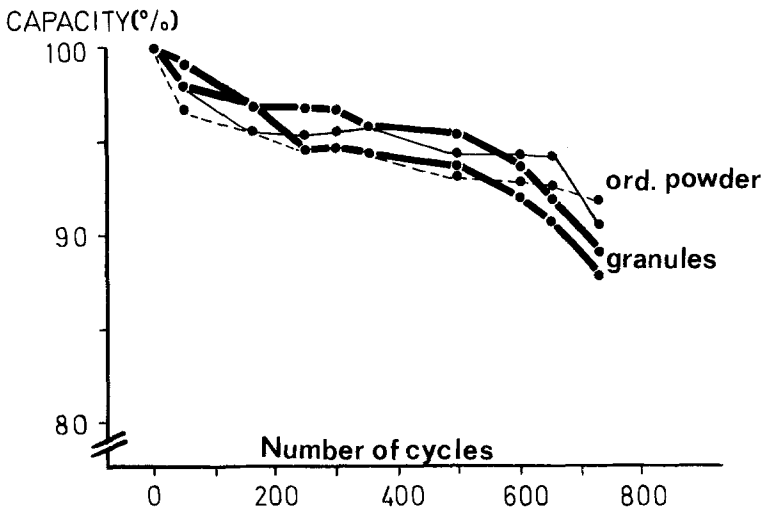


Fig. 13. The life test of 12 experimental cells. Discharge at 3 h rate and charge to about 130% of the output.

than for the other groups. But according to the hard test and the fact that the capacity after 730 cycles still had a value of about 87 to 88% of the initial capacity, it can be stated that granulated material is fully comparable to the other materials concerning strength and activity in the cycle life. When the electrodes thereafter were investigated with optical and scanning electron microscope the original structure of the granules had disappeared, and the material of all tubes had almost the same appearance.

7. Conclusions

The results reported in this paper indicate a practicable and rather easy way to produce a better lead acid battery for traction use. Because of the exceptional properties of the granulated positive material, i.e. free flowing, high strength and high degree of utilization of each separate particle, in combination with the angular geometry it is possible to increase the energy density with about 15 to 20% at a 2 h rate in a full scale lead acid cell.

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References

- [1] Lead-Research Digest, No 31-1973, ILZRO Ind.
- [2] A. C. Simon, Presentation at the 85th Convention of BCI, April/May 1973.
- [3] J. Burbank and E. J. Ritchie, *J. Electrochem. Soc.* **117** (1969) 125.
- [4] S. M. Caulder and A. C. Simon, *ibid.* **121** (1974) 1546.
- [5] J. L. Weininger and C. R. Morelock, *ibid.* **122** (1975) 1161.
- [6] S. M. Caulder, J. S. Murday and A. C. Simon, *ibid.* **120** (1973) 1515.
- [7] A. C. Simon, S. M. Caulder and J. T. Stemmler, *ibid.* **122** (1975) 1161.
- [8] W.O. Butler, C. J. Venuto and D. V. Wisler, *ibid.* **117** (1970) 1339.
- [9] C. W. Fleischmann, *ibid.* **127** (1980) 664.
- [10] D. Pavlov and G. Papazov, *ibid.* **127** (1980) 2104.
- [11] P. Casson and N. A. Hampson, *J. Electroanal. Chem.* **92** (1978) 191.
- [12] *Idem*, *ibid.* **93** (1978) 1.
- [13] A. Lindholm, Presentation at the 23rd ISE Meeting, Stockholm, August/September, 1972. A revised and extended paper will be published in *J. Power Sources*, January 1984.
- [14] D. Simonsson, *J. Electrochem. Soc.* **120** (1973) 151.
- [15] Lead Development Association; Special Reprint Electric Vehicles, An Investigation By Commercial Motor, February 1977.
- [16] John H. Perry, 'Chemical Engineers Handbook', McGraw-Hill Book Company, New York (1973).
- [17] T. Eriksson, Laboratory method for filling tubular electrodes, Internal Report AGA IC-6045 (1976).