

THEORETICAL AND PRACTICAL CONSIDERATIONS ON THE FORMATION OF LEAD/ACID BATTERY PLATES

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Theoretical considerations

There is a large number of publications on the formation of lead/acid battery plates. These contain valuable information on the chemical and electrochemical reactions taking place during the operation. The discrepancies observed in the results and conclusions can be explained by:

- the use of proprietary plates of so-called industrial quality
 - important changes in manufacturing methods, in particular as regards plate porosity and production speed, leading to high-temperature pastes.
- This is not a criticism, and general knowledge on plate behaviour during formation is well founded, but is of a proprietary nature, *i.e.*, many factories and research centres have conducted extensive investigations; not all of this has been made available in the open literature.

Correctly, attention has always been focussed on the positive plates because:

- formation efficiency is low
- battery life is determined by the positive plates.

In simple terms, in the formation of positive plates PbO_2 is obtained mainly from PbSO_4 , *i.e.*, the active mass reacts with the sulphuric acid. This is a rate-limiting step. The sulphation depends on the diffusion of the acid which, in turn, depends strongly on the nature of the plate. The oxidation of the sulphate is very inefficient: the PbSO_4 is a non-conductor, while the presence of PbO_2 favours the evolution of oxygen instead of the oxidation of sulphate. Further, acid diffusion again exerts a significant influence.

The formation of the positive plates is more a complex technical problem of porosity and diffusion than an electrochemical one. Particle size and paste density play important roles, defining capacity and life. Laboratory work seeks for the best formation; industry is looking for fast formation and is satisfied with a practical, acceptable result. The basic electrochemical work generally tries to define an optimal current density, taking into account temperature and electrolyte concentration. Moreover, the final product is identified by chemical analysis, spectroscopy (in particular for the amounts of $\alpha\text{-PbO}_2$ and $\beta\text{-PbO}_2$), and measurements of the electrical performance.

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It appears that the quality of the final product is directly influenced by the initial state of the plate. For example, the particle size and the densities of α -PbO₂ and β -PbO₂ are different and so are their specific surfaces. But this again is already laid down, as a kind of 'memory', in the paste: different types of oxide, paste composition and preparation, curing conditions, etc. This does not mean that the formation current is only a secondary parameter. In fact, the right formation conditions may save many plates originally in a relatively poor state. This may proceed to the point where more attention is paid to formation than to plate preparation.

Electrochemists know that current density is the decisive parameter in plate formation. By adjusting the current, the ratio of α -PbO₂ to β -PbO₂ can be controlled. This ratio is a transient parameter, however, and after a number of cycles the plates contain mainly β -PbO₂. Nevertheless, the performance of the plates depends on the original parameters and these can be identified by the ratio of α -PbO₂ to β -PbO₂. In the author's opinion, however, this ratio is not a convenient parameter for most battery manufacturers, as the crystallographic analysis requires skill and is costly. However, no convenient method has yet been proposed: active mass density does not give sufficient information, surface area (BET) has still to be linked to performance, etc.

When considering the formation of negative plates, the main reaction is the reduction of PbSO₄ together with any PbO that has not reacted. Hydrogen evolution is not a problem as it sets in only when all the active mass has been converted. Side effects are limited to shrinkage of the active mass. The most dangerous impurity is iron (and, occasionally, copper). Problems may arise from the expander: some products are slightly soluble and the carbon black may be released from the plate.

In summary, the general rules for plate formations are:

- negative plates, practically no problems
- positive plates should be formed at the correct current density.

Temperature is a very important processing condition, but should not be used as a control parameter.

A general comment here: very often a situation arises whereby the result is taken as the cause. This inversion is more likely to occur if several parameters are present initially. By varying the processing conditions, the final results may vary widely without it being known whether the initial state is the cause or origin and what is the effect of the operation parameters.

The purpose of this presentation is not to explain what happens — this is well known — but how to achieve well-formed plates. In other words, the aim is a search for quality. This is a major objective of many battery manufacturers. The lead/acid battery has never faced so many technical changes and it is necessary to make provisions for technological changes as well. In this respect, future formation methods are certainly going to be very different. The courage for innovation is sometimes lacking. This is caused partly by the restrictions of the available equipment and also by an absence of good technical advice.

As mentioned above, the original state of the plate is the important factor. No two companies use exactly the same material and even within a given company, the product tends to vary in a seasonal fashion. If improvements in plate making are not yet sufficiently advanced, formation conditions, at least, should be adapted to meet these product variations. In particular, efforts must be directed towards achieving major improvements in temperature control (particularly cooling), appropriate electrolyte density, modulated current (including pulse and discharge steps), and automated handling. Increased efficiency, both in time and energy, must be obtained.

Before addressing practical aspects, a brief comment is called for concerning the more usual way of defining the formation method:

- fill the cells, install the plates
- charge n times the capacity (in $A\ h\ kg^{-1}$ active mass)
- divide the total number of $A\ h$ by the time available: this gives the formation current and size of the rectifier
- make some minor modifications (if the equipment allows).

No attention is given, however, to an assessment of the plate quality, the optimum electrolyte density and temperature, and the final application of the battery! This is probably painting too black a picture, but, unfortunately there are a large number of companies where formation is the factory bottle-neck and processing time is a very important parameter.

Practical aspects

Plates for dry-charged automotive batteries

The formation of automotive plates can be achieved through the tackleless operation, *i.e.*, the plates are installed in tanks with contact bars. A widely adopted design is one with a double row of slots for the positive and negative plates where, depending on the thickness of the plates, up to four plates per slot may be installed. One tank may hold as many as $2 \times 13 \times 4$ double positive plates, or a total of 432 single positive and negative plates, *i.e.*, sufficient for some seven batteries. The number of tanks in series depends on safety considerations; eighty is a good maximum.

The electrical contact between the plates and the bars is established by passing a current so that the positive plates are first polarized negatively. A cold weld is established between the metallic lead of the bar and that of the lugs. After a certain time, the cells are discharged through a resistance for a few minutes in order to lower the voltage. The current is then switched on again but with the reverse polarity, *i.e.*, the positive plates (now firmly contacted) will be oxidized and the negatives will be welded to the bars and reduced to the required metallic spongy lead.

Three important processing parameters are:

- electrolyte density
- electrolyte temperature
- current profile.

In fact, the electrolyte temperature is the limiting parameter and for this reason the size of the rectifier depends on the climatic conditions. A unit of 400 A appears to be adequate in moderate climates and 300 A is advised for warm climates. If the tanks are cooled sufficiently, use of a 600 A rectifier will accelerate the process.

If four plates are installed per slot, however, acid diffusion becomes the rate-limiting factor. New ways of current modulation are then required. Plate polarization has to be kept low for improved efficiency and the formation current should not be greater than the acid diffusion. Decreasing the temperature lowers the plate polarization, but delays the acid diffusion. Therefore, the use of a higher electrolyte density is preferred. With conventional formation equipment, the best efficiency and acceptable plate quality is obtained with a specific gravity of 1.05 kg l^{-1} and an electrolyte temperature of 45°C .

The formation current should be calculated from the plate area, but the latter is difficult to define if several plates stick together in one slot. Such an arrangement may be considered as one very thick plate. Thus, the weight of the active mass may be used instead of the plate area. It is sufficient to consider only the positive mass for further calculations. A practical value of the maximum current density is $\sim 30 \text{ A kg}^{-1}$ and, depending on the quality and the thickness of the plates, about $420\text{--}540 \text{ A h kg}^{-1}$ are necessary. This will lead to a formation cycle of 24 h, including removing the formed plates, installing new ones, and the reverse charge.

Except for an occasional bad contact, the main defects are caused by too high temperatures, too high current densities and, of course, poor plate quality. It is worthwhile mentioning that the formation of the so-called tetrabasic active mass: $4\text{PbO}\cdot\text{PbSO}_4 = 4\text{BS}$ is much more difficult than the formation of the tribasic one: $3\text{PbO}\cdot\text{PbSO}_4\cdot\text{H}_2\text{O} = 3\text{BS}$.

Modern production equipment working at high speed gives high paste and plate temperatures leading to 4BS and this is a further reason for using low density acid for formation. Although this will give strong plates, the initial capacity is low. Each company should define the optimum amount of acid and water experimentally as a function of the oxide quality. It is advantageous to keep the amount of free lead in the oxide between 25 and 30 wt.%; lower lead contents give poor paste adhesion, higher values cause formation problems.

A beneficial approach in tackless formation is the use of cassettes. They greatly simplify handling, reduce lead dust in the atmosphere (and on the floor) and, generally, carry only two plates per slot. This allows the use of a 300 A rectifier and formation within 16 h, with some cooling of the tanks. Optimum operating conditions in terms of current profile and electrolyte density can be established quite easily. This method opens up new means of increasing overall efficiency and tailoring the quality of the plates. Results obtained so far are very encouraging.

Plates for dry-charged industrial cells

Two types of positive plates are encountered in industrial batteries:

- flat, pasted plates
- tubular plates.

They both have their advantages, but the pasted plates present more disadvantages.

Tubular plates are usually powder filled, but some companies use a paste or a slurry. Whether sulphation (or 'pickling') is carried out is not especially important, since upon installation in the tanks the oxide will react with the sulphuric acid. This will heat up the electrolyte and decrease the acid strength. This is not always taken into account, e.g., when short or tall plates are installed. Neither is it very important if the positive plates are formed against dummies nor together with their negative plates.

As 4BS is generally not present in tubular plates, formation can be carried out at high electrolyte densities. The low rate of acid diffusion, however, limits the maximum current. The absence of α -PbO₂ simplifies the formation programme, in particular for traction cells which will receive sufficient charge and cycles in actual use. It is important that only a few percent. of PbSO₄ remains in the plates: the presence of PbO is not considered to be a handicap. In the case of stationary cells, the plates must be cycled to some extent to avoid sulphation. Moreover, porosity is increased and, consequently, a high power capability is achieved.

Flat, pasted plates are still best formed in more dilute acid and at moderate current levels in order to increase the strength of the plates. Industrial plates can also be formed by the tackless procedure; it may be advantageous to improve the contact area between the lugs and the bars. The use of red lead eases the formation as it does not sulphate and, therefore, improves the current efficiency. Depending on the desired quality, formation may be carried out between 16 and 48 h. A great effort is required to achieve uniformity.

Container formation

Automotive batteries

Success in the container formation of automotive batteries depends to a large extent on the quality of the separator. High temperatures (> 65 °C), high overcharge, and oxygen evolution can be very destructive. Plates should be clean to reduce the risk of short circuits arising through adhering particles of dried paste. The one-step formation programme is a good method for maintaining the temperature within limits. Acid diffusion is not so much a problem as is the lack of acid and care should be exercised when processing so-called compact batteries with very thin separators. In general, the results are satisfactory and the greater part of the positive active mass is of the β -PbO₂ type.

For this formation procedure, a 12 - 15 A rectifier for some sixteen 12 V batteries is the most common equipment. If possible, temperature sensors

should be used for current modulation. Efficiency can be very good; a value of 350 - 370 A h kg⁻¹ of unformed mass may be sufficient. The duration will be between 24 and 36 h. The number of formation lines can be quite impressive and some type of processor is necessary to keep track of the actual situation. The available equipment is, generally, sufficiently sophisticated to meet future demands, and most of it can also be used for the final charging of the filled batteries before shipment. An interesting aspect is that this equipment can be used for sealed batteries as well.

General comments can be made on the performance of container-formed automotive batteries compared with dry-charged ones. Tank-formed plates contain a higher percentage of β -PbO₂ and therefore yield a slightly higher initial capacity but container formation may give better life. The final result depends greatly on the freshness of the battery and on its conditioning before installation. Certainly, container formation is much more economical and avoids many environmental problems.

Industrial cells

Although inventory control seems difficult, container formation of industrial batteries — both motive power and stationary — presents the same advantages as for automotive batteries. Of course, the formation programme should be studied very carefully. As a rule the duration will be of the order of five days. Special rectifiers are necessary that allow discharge with feed-back of the energy into the main supply.

The density of the filling acid can be calculated, so no final correction is necessary. The sulphation of the positive plate is an important parameter. Cells have to be cooled; a waterbath with flow control is more efficient than a spray. Optimum temperature is 35 °C; excursions of the electrolyte temperature up to 45 °C are permissible.

The highest formation current is of the order of 12 A kg⁻¹ of positive mass ($C/7$ of the C_5 capacity). Total charge is some 600 A h kg⁻¹, discharge is of the order of 120 A h kg⁻¹. This means rectifiers of 50 - 300 A h can be used. The total safe working voltage varies; a maximum of 80 - 100 cells in series is possible. Good rectifier energy efficiency is important. Average energy consumption is some 20 kV A up to a maximum of 100 kV A. With 25 lines, some 3000 cells can be formed each week.

Due to the compact installation of the plates, the limiting factor is acid depletion and diffusion. In general, the formation of the negative plates presents no problems, but the quality of the positive plates is extremely important, in particular if cells are to be stored. Good cells will not need any further charge for two to four months. Aerosol emission is strongly reduced if plugs are installed on the cells.

The most satisfactory fact of container formation is the great uniformity of the cells. It is easy to achieve less than 0.1% losses. Compared with pre-charged cells, the risk of insufficient conditioning is absent. The greatest disadvantage is the transportation and handling of filled cells. No difficulties have been encountered with container formation of low-antimony alloys; in

fact, as very little handling is involved, it is the best procedure for soft and thin plates.

The choice of formation technique enables the optimum ratio of α - and β - PbO_2 to be attained. High PbO_2 contents are, of course, necessary. The most important parameter is a very low PbSO_4 concentration at the end of formation; typical values are less than 3 wt.% for the positive plates and 1 wt.% for the negatives.

Sealed batteries

Since the term 'maintenance free' has been used often for automotive batteries with low water consumption, the term 'sealed' better describes those batteries that require no water additions. Whether sealed units are of the gelled or absorbed electrolyte type, these batteries are made with lead-calcium alloys (with one exception where pure lead sheet is employed). Lead-calcium certainly is a very interesting alloy, but some precautions are necessary during its processing. The formation conditions should be such that no layer of α - PbO exists at the grid/active-mass interface.

Generally, the plates are tank formed and the drying of the positive plates should be done quite carefully. Cells with gelled electrolyte can be container formed, but with a change of electrolyte. This avoids drying of the plates, but requires the handling of large amounts of acid.

Since the state of the plates can easily be verified with tank formation, cells or batteries with pre-charged plates are generally more uniform. As equipment for tank formation is available, the execution does not present any problems, but the programmes for antimony alloys are not applicable. The formation conditions depend greatly on plate quality. Process time and energy requirements are essentially the same as for standard plates, but the programme stages are quite different, in particular as regards discharging the positive plates. The first part is an important step in avoiding a passivating layer. The main difference is the absence of a coralloid structure and the difficulty in recharging (due to the absence of the catalytic activity of antimony for the formation of PbO_2). Both result in reduced cycle life. Of the three adverse properties of antimony-free plates, namely,

- premature failure
- lower initial capacity
- shorter cycle life (and less overall energy output)

the first two can be avoided by proper formation programmes.

There is no great difference in the methods for the formation of automotive and industrial plates. With the thicker and heavier industrial plates, the main problem is to reduce all the PbSO_4 without too much discharging or cycling. A solution to the speeding up of the formation process can be expected from the use of pulsed current. To date, very good results have been obtained, but further optimization is both possible and necessary.

An important part of the formation of sealed batteries is the first charge after (re-)filling of the cells. A precisely defined amount of electrolyte has to be added; the safety valves are not installed at this point. Any charge lost

will have to be made up, and some overcharge is necessary to create voids for the passage of the oxygen from the positive to the negative plates. This is easier with absorbed electrolyte than with gelled acid. A short time after the end of this charge, the safety valves should be fitted firmly. Any leakage of atmospheric oxygen will burn the negative plates. The correct charge and discharge conditions, as specified by the manufacturer, should be observed very carefully.

Commissioning and putting batteries into service

Formation is the first step in obtaining a high-quality battery. The means by which dry-charged batteries are put into service is the second step. It seems logical that after all the care required to obtain high-quality plates, the filling and initial charging should also be carried out in a careful manner. The fault very often lies with the manufacturer who states that the batteries are ready for use and no special care is required!

It might be supposed that there is some kind of 'reorganization' within the battery. Plates are generally formed in low density acid and dried, but in service a higher density acid is employed, and the grid/active-mass interface, which is affected by the drying process, has to be re-established. Surprisingly, very little attention is often paid to this. This is due to time and cost restraints.

The same basic principles — diffusion and temperature — play an important role. Upon filling with acid, the active mass reacts and PbSO_4 is formed (in general from the remaining PbO). If this product is not eliminated as fast as possible, the battery will start its active life with a serious handicap. Thus, the provision and application of detailed instructions are of great importance to both the manufacturer and the user. As this aspect has been neglected, no special attention has been paid to the supply of necessary equipment. The cost of this equipment is not very high, and a good charger is essential when processing such batteries. The problem is much reduced in the case of container-formed batteries: freshness and an optimal state of charge should, however, be standard.

A final word on 'breaking-in': a new battery is as delicate as a newly-born baby: it should not be strained too much; neither very deep discharges (e.g., capacity checks) nor heavy overcharges should be applied. Limiting the actual work of the battery guarantees that sufficient energy remains available for those occasions where it is really needed. In fact, oversizing the battery presents the most economical solution: 10 or 15% more capacity may increase life by 50%. Finally, it is important that batteries be kept properly charged. This is a study in itself, and it is to be expected that electronics will take over where individuals have failed.

Storage

Unfortunately batteries have to be stored. The high costs of inventory can be avoided by the 'just in time' technique. The quality of the plates and of the formation process are prime conditions for good shelf life and, if the commissioning is done as indicated above, the influence of storage on the battery performance can be eliminated.

Dry-charged batteries

A certain loss in capacity takes place, but is totally recuperated by a correct charge. As no sulphation occurs, the reaction should be totally reversible. This is still a strong point in favour of dry-charged batteries of all types.

Wet-charged batteries

The self-discharge reactions are of the same type as those experienced in ordinary discharge, although of different origin. Probably the largest loss is a result of local action between the grid and the active mass, both in the positive and negative plates. Impurities play an important role.

The only solution is to recharge regularly and not to wait until the batteries are run down. Industrial cells with high percentage antimony alloys should be recharged after two to four months. It does not appear that the self discharge of container-formed plates is any greater than that of tank-formed ones. For automotive batteries, six months' storage is appropriate.

Experience has shown that wet batteries can be stored extremely well on float charge: performance may be improved, but corrosion problems have been encountered, especially if pre-charged cells are filled and placed on float without a topping-up charge.

Sealed batteries

The main problem with sealed batteries is the presence of sulphate within the microfibre separator. On charge, this is transformed to Pb and PbO₂, both excellent conductors. Micro-shorts occur and the battery exhibits irregular behaviour. Even though the manufacturers state a shelf life of nine months, sealed batteries should not be left unattended for more than two months, particularly in the case of absorbed-electrolyte types. This storage problem is not encountered with flooded cells, although a low quality separator may be attacked by the PbO₂. Some effects are of a long-term nature and it is not always easy to link the various causes with a poor result.

Equipment

The cost of the formation equipment is only part of the total operating cost. A careful analysis is necessary, not only of the obvious items, but also of the flexibility. By applying basic rules, and in searching for optimum performance, new methods must be introduced. In fact, it is practically impossible to define any equipment before the formation method has been chosen and tested. Minor modifications before, or after, the formation process may greatly simplify the overall problem.

An important aspect is the sealed battery. Container formation offered the best solution, and now tank formation becomes a necessity. In new, modern processing methods with automatic plate handling, more sophisticated formation techniques must be found and provisions made for environmental compatibility. This is of particular interest for both the very large and the very small company.