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Red Lead as a Key Factor for Higher Efficiency in the Formation of Lead-Acid Batteries

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The Importance of Formation Efficiency

Energy efficiency has become a critical topic for the European battery industry, especially given the energy price increase scenarios since 2022. Environmental protection efforts are also an essential driver toward lower energy consumption in the formation process, as this process step consumes most electrical energy in a battery plant. As the lead-acid industry is expected to keep a significant share of the global battery market, despite current challenges by other battery chemistries, improving the energy efficiency of the lead-acid battery production process remains highly relevant. [1]

The formation of plates in the so-called tank formation process and the direct formation of 2 V cells or 12 V batteries is a crucial production step. It is associated with a significant cost increase, as the EU's electricity prices have increased from about 0.23 € per kWh *(all taxes and levies included) for* non-household consumers in 2021 to more than 0.4 € per kWh in August 2022, averaging 0.284 € per kWh in the second half of 2022. [2] Although energy prices have recovered somewhat after the price surge, the future EU electricity price development and stability remain unclear, given that several factors contributed to the substantial increase in 2022.

In the recent past, several technical improvements aiming at a higher formation efficiency have been made and one good example is the 'closed-loop' formation introduced by Inbatec, which allows for a faster and more effective battery formation. PENOX focuses on bringing additional value to the battery industry by analysing the contribution of red lead and a positive active mass (PAM) with different structural and chemical characteristics on the formation efficiency.

Target and Scope of this Study

In this study, PENOX has investigated the impact of different contents of an industrial grade of Red Lead (RL) in combination with Barton oxide on the formation energy needed to form a cell completely. The Barton oxide had a free lead content of 25 to 27% with a d_{50} particle size of about 3 µm, and the RL had a lead dioxide (PbO_2) content of 25 to 27% and a d_{50} particle size of about 4.5 µm.

The benefits of using RL in formation have been studied in depth, and this first article is focused on the effects of using RL in PAM on formation efficiency and duration.

Reference System and Test Cell

The tested cell group is a 2 V flooded cell with one positive and two negative plates. The positive and negative plates are based on gravity-cast L3 size grids (gravity cast, thickness 1.35 mm). The positive plate is enveloped and has a nominal C20 capacity of 12.5 Ah. The cell design used for this study was chosen for single plate testing of the positive plate under controlled conditions, ensuring that the positive plate limits the test cell's performance.

For capacity and cycle life testing, 300 g of diluted sulfuric acid electrolyte with a density of 1.28 g/cm³ (+/-0.005 g/cm³) at 20 to 22°C was used. Please note that this amount of electrolyte is sufficient for a capacity of 13 Ah. The density at a full discharge of 13 Ah reaches 1.18g/cm³. The theoretical limit at which acid limitation is reported is at a density of 1.2 g/cm³. [3]
The negative plates used for this study were produced by a European manufacturer of automotive batteries. The positive plates were pasted in the laboratory of PENOX, and the pastes were based on Barton oxide and RL. Different PAM paste recipes were used, and the mixes were prepared in an Eirich R01 mixer. Percentages for the content of any compounds in this study are stated in weight-% (%).

Formation Profile

The formation was carried out in an electrolyte with a density of 1.15 g/cm³ at a controlled temperature. The latter was systematically varied between 25°C, 35°C, and 45°C for different tests. The same basic formation profile was used for all investigations, and the formation factor (FF) was systematically varied by modularly adjusting the number of formation steps at the end of the formation profile – see Figure 3 in the Appendix.

The formation factor represents the coulombic efficiency of formation and is calculated by dividing the charge capacity used to form the cell or battery by its nominal capacity. A more accurate comparison would, of course, be to refer to the real capacity. However, in battery manufacturing, the standard nominal capacity is used. It is thus based on capacity values measured in Ah. In contrast, the energy efficiency in formation is based on the amount of energy in Wh required to form a battery completely. The formation energy includes the cell or battery voltage during formation.

The resulting PbO_2 content was analysed in the positive plates. A 'two-shot formation' process was used in this study. This simple process means that the electrolyte was changed after the formation was completed. The diluted sulfuric acid electrolyte used for further testing had a density of 1.28 g/cm³. The formation process used in this study is described in Figure 3 in the Appendix.

While the formation factor was systematically varied by applying a different number of formation steps with reduced current, the current densities and other conditions were kept constant. The latter is important to keep all mass transport-related parameters constant, allowing a better comparison of the results.

After formation, a structural investigation of the cured plates was performed, and the PbO_2 content of the positive formed plates was determined using a standard titration process, with a PbO_2 content target of 85% +/- 3%. Thus, in this study, >88% PbO_2 represents an over-formation, and <82% PbO_2 represents an under-formation.

Aside from the structural analysis, electrical testing of the initial C5 capacity and capacity evolution was carried out, and the impact of the negative plate was also investigated.

This study follows the strict principle of forming the positive active mass to ideally 85% of PbO_2 with only a low tolerance of the PbO_2 content. PENOX recommends this to avoid overcharging, as this damages the positive plate. Furthermore, an undercharged PAM does not have a fully developed formed structure of the positive electrode. The remaining lead sulfates within the active masses are transformed into sulfuric acid during the operation of the battery in the respective applications. Therefore, depending on the battery technology, there is a second target concerning the maximum lead sulfate content of the positive and the negative plate. This value differs depending on the battery manufacturer. Lead sulfate still contained within the plates after formation will slowly be charged in regular battery operation. The latter increases the acid density of the cell or battery. As the content of lead sulfate tends to vary more for a lower state of formation (i.e., for underformed plates), this can cause inhomogeneous electrolyte densities in different cells. Such variation of the electrode density impacts the open circuit voltage and, thus, the overvoltage controlling the charging process.

Benefits of the use of Red Lead in Formation

Impact of Red Lead on Formation Factor (Coulombic Efficiency)

Red lead is typically mixed with a 'grey oxide', such as Barton or mill oxide. As well known and reported in literature [4], red lead is higher oxidized and will release PbO_2 by contact with sulfuric acid. At the beginning of the formation process, PbO_2 is already formed during the soaking step and thus is available depending on the type and content of the RL. As expected, the initial PbO_2 content in PAM significantly affects the formation efficiency. A shorter formation time leads to a reduced overall charge capacity in Ah. In addition to this, PAM conductivity is increased directly at the beginning of formation when PbO_2 from RL is present. Lead dioxide introduced by RL can also act as a growth template for the porous PbO_2 structure of the PAM, which is created during the formation process. Higher conductivity and lower overvoltage result in a lower average cell- or battery voltage during formation, which equals lower charge energy in units of Wh.

The formation efficiency is higher when the same average PbO_2 content in the formed positive plate is achieved with a lower formation charge. Figure 1 shows the results of this study concerning the impact of the RL content in PAM on formation efficiency. The Coulombic formation efficiency is represented as the minimum formation factor (FF) on the y-axis for the respective Red Lead content in the PAM shown on the x-axis. Please note that the Coulombic efficiency's explicit value is the formation factor's inverse. For instance, a formation factor of 4 means that four times more electric charge in Ah is used in the formation process as can be discharged after the formation. Thus, in this case, the efficiency of storing electrical charge (Ah) in chemical form within the active masses during formation is 25%.

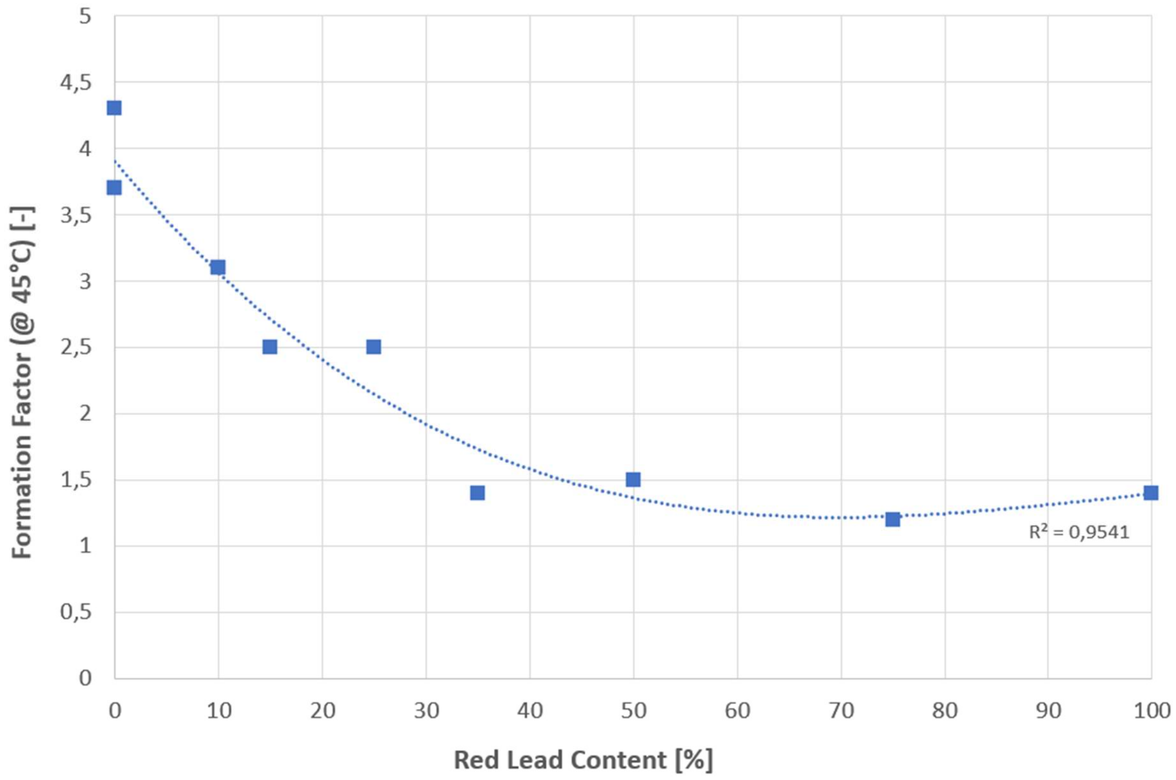

Figure 1: Impact of the RL content in unformed PAM on formation efficiency: Minimum required formation factor for different RL contents required to achieve a complete formation, i.e., a PbO_2 content of ≥ 85%.

Due to the PbO_2 content of RL in the leady oxide mix of the cured plates, these plates have an improved intrinsic electric conductivity that increases with a higher PbO_2 content. The conductivity of the semiconductor type of PbO_2 is high and overall in the range of 10^5 S/m (metallic lead has a conductivity of 4.8 x 10^6 S/m). The different crystallographic forms, mainly the alpha- and beta-PbO_2, have slightly different conductivity. [5]

The experimental results in Figure 1 show that:

- up to an RL addition of around 30% in the leady oxide mix, the required minimum formation factor for complete formation is reduced nearly linearly with an increasing content of RL.
- For a ca. 30 – 50% RL dosage, there is still an additional benefit regarding a formation factor (FF) reduction.
- RL addition rates beyond 50% will not further improve coulombic formation efficiency.

A content of 100% RL in PAM requires a higher FF for complete formation than a content of 75% RL, as it does not support 4BS curing and instead results in a mixed 1BS/3BS structure. The content of mono-basic lead sulfate (1BS) is attributed to a negative impact on the formation process. Please note that 100% of red lead is used in a traditional process that, in the experience of PENOX, is still maintained for submarine batteries and some Motive Power (i.e., traction) applications.

Impact of Red Lead on Formation Duration

The impact of the RL content in PAM on formation time, running the formation profiles similar to Figure 3, was analysed, and Figure 2 gives an overview of the findings. It shows the formation duration for each formation factor used in this study.

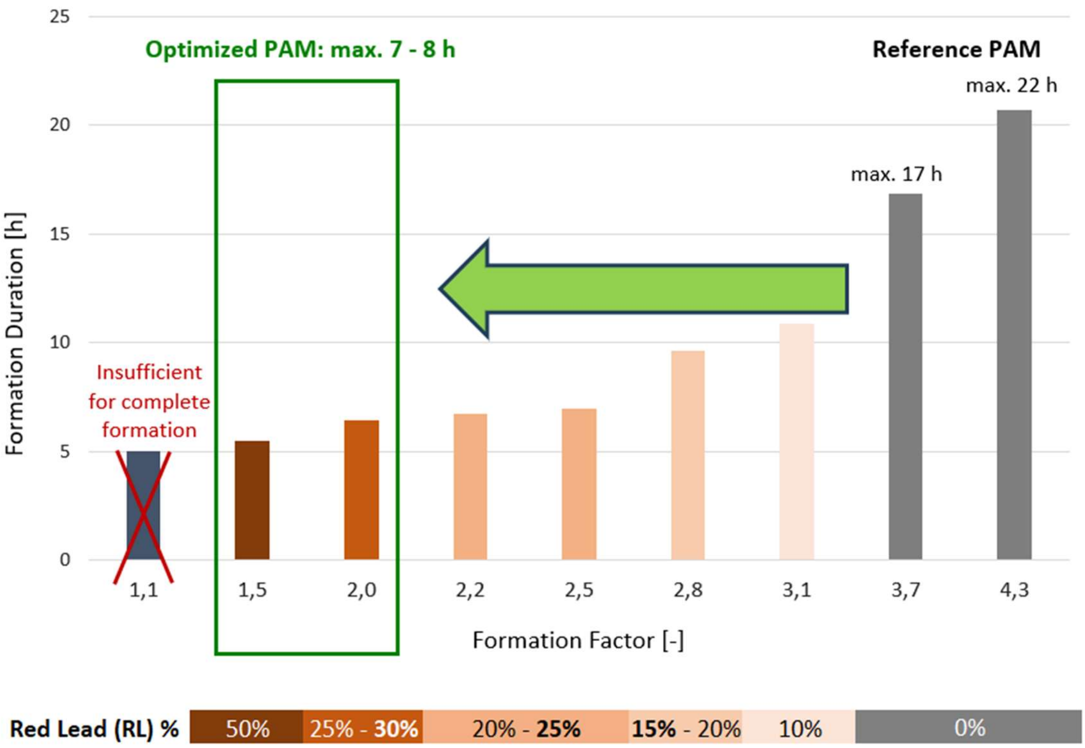

Figure 2: Impact of RL on formation time. Formation duration per formation factor (PENOX – flooded LA Technology).

Reducing the formation factor from about 3.7 for the reference cells to about 2 is made possible by the use of RL. The modular formation program used for this study allows for a significant formation time reduction from about 17 h to a maximum of 7 h or more than 50%.

Even with the optimised test cells, a formation factor of 1.1 is insufficient to achieve the target of 85% PbO_2 for a complete formation. This is unsurprising, as this formation factor would be in the same range as a standard charging factor (CF) for cells or batteries based on flooded technology (e.g., 2V PzS Motive Power after 70% DoD, using an IUIa charging profile). The discharged positive active mass (PAM) of such MP cells contains about 20 % of PbO_2 at 80% DoD. Furthermore, the negative plate contains a minimum of 10 to 15% spongy elemental lead.

In contrast, an unformed cell, even with 50% RL (PENOX industrial grade), contains only about 13% of PbO_2. Furthermore, the unformed negative plate contains less than 3 % elemental lead (free lead) without a conductive network of spongy lead. Thus, it is understandable that the formation process runs at a lower efficiency than charging a discharged battery from 20% SoC to 100% SoC.

Impact of Red Lead on Carbon Dioxide Emissions

The impact of RL on carbon dioxide emissions was also investigated as part of this study, and the associated calculations were done with data based on the German energy mix with about 400 g of carbon dioxide per kWh of electricity. [6]

It was found that even an addition of 10% of RL already leads to a significant reduction of around 20% in total CO_2 emissions. Increasing the RL content from 10% to 25% reduces CO_2 emissions significantly. At 25% RL content, total CO_2 emissions per plate are reduced by almost 50% vs the reference without RL.

At 50% and higher RL addition rates, there is no further relevant decrease in the total CO_2 emissions per plate.

These results on the impact of RL on carbon dioxide emissions of formation will be discussed in more detail in the second article of this series on formation efficiency.

Conclusion and Recommendations

Red Lead (RL) added to the leady oxide mix of the positive active mass (PAM) allows for a significant formation factor reduction. The effect of RL addition is not linear. Thus, an optimum content can be observed depending on the plate technology, the plate group design, and the respective battery technology.

Even a small addition of 10% RL to PAM already enables a formation factor reduction from 3.7 (reference) to 3.1 in this study, representing a significant reduction in coulombic formation efficiency of more than 15%.

An increase of the RL content in PAM to 25% allows for a further formation factor reduction to 2.0, which equals a substantial increase in formation efficiency of almost 50% versus the reference cells without RL.

When the RL content in PAM is increased to 50%, an even lower formation factor of 1.5 can be achieved. This equals a reduction of 60% versus the reference cells without RL. In PENOX's experience, such high RL content is used primarily in thicker industrial grids and for industrial tubular technology. For automotive technologies, the RL content of interest is well below 50% and typically between 10% and 20%.

Please note that 100% RL content does not allow for a well-developed 4BS structure, and PENOX does not recommend using such high content of RL, as this, in terms of energy efficiency, is not the optimum solution. In this study, we observed a slight increase in the formation factor resulting from mono-basic lead sulfate (1BS) in the cured active mass structure.

Please note further that the experimental data indicates that adding a minimum of 10% up to 30% RL significantly improves formation efficiency. PENOX considers this range to be optimum in terms of formation efficiency and optimal to reduce the carbon dioxide footprint. The economic optimum is more challenging to analyse, as several factors differ strongly by region and are essential for the result. In general, using RL is becoming increasingly attractive with higher electricity prices, and an additional driver is the ability to reduce the process time.

Further Findings of Related Study and Outlook: Upcoming Publications

In 2022 and 2023, PENOX studied the influence of active material structure on formation efficiency, comparing tribasic (3BS) and tetrabasic (4BS) cured positive active masses (PAM).

In light of the high interest of the battery industry in carbon dioxide footprint, PENOX is preparing a comprehensive overview of the contributions of RL and the new Red Lead Plus (RL+) in the formation process.

Appendix

I) Formation Profile

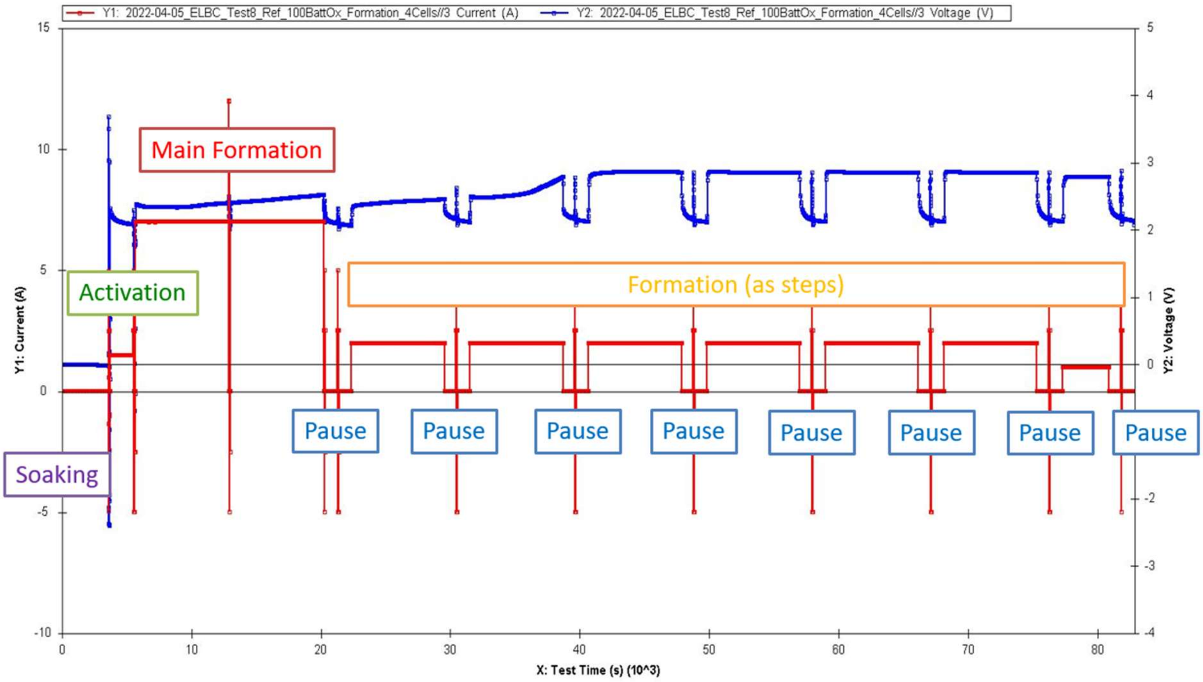

Figure 3: Basic formation profile used, with the different formation steps marked to show the distinct parts of the formation process.

References:

[1] EUROBAT Battery Innovation Roadmap 2030, Version 2.0, June 2022, https://www.eurobat.org/campaigns-and-initiatives/battery-innovation-roadmap-2030/

[2] Eurostat (online data code: NRG_PC_204), https://ec.europa.eu/eurostat/databrowser/view/NRG_PC_204/default/table?lang=en

[3] D. Pavlov, Lead-acid Batteries: Science and Technology; A Handbook of Lead-acid Battery Technology and its Influence on the Product, Bulgarian Academy of Sciences, Elsevier, P. 129ff, 2011

[4] Bode, Lead-acid Batteries, John Wiley & Sons, Inc., P. 17, 1977

[5] D. Pavlov, Lead-acid Batteries: Science and Technology; A Handbook of Lead-acid Battery Technology and its Influence on the Product, Bulgarian Academy of Sciences, Elsevier, P. 353ff, 2011[6] Statista, https://www.statista.com/statistics/1290224/carbon-intensity-power-sector-germany/, Value for 2022

About the Author:

Micha Kirchgessner holds the R&D Electrochemical Laboratory Manager position at PENOX in Ohrdruf, Germany. Responsibilities include implementing and developing new test methods, planning test series in the context of basic research, developing new battery additives, and providing technical support to customers from the battery industry. He joined PENOX in 2013 and was previously responsible for the R&D chemical laboratory. Before joining PENOX, he worked for five years as IP Manager and R&D Engineer at EXIDE Technologies in Büdingen, Germany. Micha holds an M.Sc. in Chemical Engineering from the Karlsruhe Institute of Technology (KIT).