STRATEGIES FOR COUNTERACTING HYDROGEN EVOLUTION AND WATER LOSS IN DEEP CYCLE LEAD-ACID BATTERIES

INDUSTRIAL BATTERY SOLUTIONS
MICRO-POROUS SEPARATORS - WOVEN & NON-WOVEN GAUNTLETS

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HYDROGEN EVOLUTION: GASSING AND WATER LOSS PROBLEM

- Watering is the most common battery maintenance action required from the user.
- Automatic and semi automatic watering systems are among the most popular lead acid battery accessories.
- Lack of proper watering leads to quick degradation of the battery (corrosion, sulfation....).
- In many cases contamination of the cells can accrue when low purity water is used for refilling.

Limiting water losses significantly:
- extends the life time of the battery
- lowers the maintenance effort

High maintenance efforts related to water refills are often listed among the biggest disadvantages of lead-acid batteries. Furthermore, if a battery is operated with high water loss it leads to its fast destruction. Slowing down water losses allows to limit the maintenance work needed, making the operation of the battery less dependent on the user.
• Hydrogen evolution overpotential in lead acid batteries

• Metals as catalysts of hydrogen evolution

• Antimony as hydrogen evolution catalyst – vicious cycle of water losses

• Importance of high end of charge voltage – stibine generation

• Hydrogen evolution inhibitors - breaking the viscous cycle of water losses

• Separators as source of hydrogen evolution inhibitors

This presentation starts with recognizing that a lead-acid battery is able to reach more than 2V open circuit voltage only thanks to the very high hydrogen evolution overpotential on lead electrodes preventing gassing in a fully charged battery. Later it will be shown that the presence of metal contaminants, particularly in the active mass of the negative electrode, destroys this condition leading to excessive gassing. The vicious cycle of antimony poisoning will be discussed and the role of hydrogen inhibitors and stibine generation in preventing this detrimental process will be outlined. In the final stage the practical role of the separator as source of hydrogen evolution inhibitors will be discussed.
In acidic electrolytes voltage above 1.23 V is enough to split water into oxygen and hydrogen. This makes lead-acid batteries thermodynamically unstable however the system works successfully with typical open circuit voltage more than 2 V. This is possible due to outstandingly high overpotential slowing down hydrogen evolution (gassing) on metallic lead surfaces. Cleanliness of negative electrodes and inhibiting hydrogen evolution on their surface are key to successful operation of lead-acid batteries, particularly those of deep cycle kind containing antimony alloy PbSb positive electrodes.

The 2V Pb/PbO₂ cell has an outstandingly high voltage for a water based system, exceeding the thermodynamic water decomposition potential. This is possible due to high overpotential for water splitting on Pb surface.

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Most metals other than lead allow less hindered hydrogen evolution leading to higher gassing rates in batteries if such metals contaminate the negative electrode. The figure on the left compares the hydrogen bubble formation at surface of lead and few other metals under the same reductive condition chosen to be similar to the potential of a negative electrode at the end of its charging process. On the right hand side the so called Tafel plot for hydrogen evolution reaction is shown illustrating the same phenomena in a more scientific way.
HYDROGEN EVOLUTION: REACTION (HER) CATALYSTS - ANTIMONY

RELEASE OF SB

PREMATURE BATTERY FAILURE

INCREASE CORROSION RATE ON THE POSITIVE PLATE

SB DEPOSITS ON NEGATIVE ELECTRODE

INCREASE OF CHARGE NEEDED TO FULLY RECHARGE THE BATTERY

PREMATURE BATTERY FAILURE

DECREASE OF HYDROGEN EVOLUTION REACTION OVERPOTENTIAL

OTHER / EXTERNAL METAL IMPURITIES DEPOSITED IN THE NEGATIVE PLATE

DECREASE OF HYDROGEN EVOLUTION REACTION OVERPOTENTIAL

INCREASE OF CHARGE NEEDED TO FULLY RECHARGE THE BATTERY

PREMATURE BATTERY FAILURE

INCREASE CORROSION RATE ON THE POSITIVE PLATE

SB DEPOSITS ON NEGATIVE ELECTRODE

RELEASE OF SB
Because of its inherent presence in commonly chosen lead alloys, antimony is a particularly important contaminant, which is a hydrogen evolution reaction catalyst when compared to lead. Antimony can be released from lead-antimony positive electrode grids (or spines) due to corrosion processes. If it reaches the negative electrode it may deposit in the active material and lead to accelerated gassing. This in result, due to larger amount of current passing through the battery in the charging process, leads to faster positive plate corrosion and even more antimony released into the electrolyte.

The figure on the right shows water loss in a common 8 V deep cycle (golf car) battery. It is seen that water losses are accelerated with the number of cycles performed by the battery. It is also noticeable that the type of separator used strongly influences the rate at which water is electrolyzed into gas. Processes determining the rate of water losses will be explored in more detail further in this presentation.

Though not discussed here in detail other metals catalysing hydrogen evolution such as earlier shown Cu, Pt, Ni and other transition metals may further accelerate the viscious cycle by promoting gassing.
Vicious Cycle

Release of SB

SB Deposits on Negative Electrode

Increase of Charge Needed to Fully Recharge the Battery

Decrease of Hydrogen Evolution Reaction Overpotential

Increase Corrosion Rate on the Positive Plate

Hydrogen Evolution Reaction (HER) Catalysts - Antimony - 3/4
In order to control water losses and gassing in a lead-acid battery prone to antimony poisoning it is essential to break the antimony vicious cycle. This can be effectively done by blocking the hydrogen evolution reaction with inhibitors that would deactivate the areas of the electrode contaminated for instance with antimony. Further in the specific and particularly important case of antimony, the contamination may be reduced by removing antimony in form of stibine. However this very beneficial process can only occur if the battery is charged to a high enough voltage.

**Hydrogen evolution:** $2H^+ + 2\bar{e} \rightarrow H_2 \uparrow$ (water loss)

**Stibine Generation:** $Sb^0 + 3H^+ + 3\bar{e} \rightarrow SbH_3 \uparrow$

(effective below -300mV vs Pb/PbSO$_4$)
(corresponding to 2.5 V cell voltage)
STIBINE GENERATION VS. HYDROGEN EVOLUTION

Hydrogen evolution: \[ 2H^+ + 2\bar{e} \rightarrow H_2 \uparrow \] (water loss)
Stibine Generation: \[ Sb^0 + 3H^+ + 3\bar{e} \rightarrow SbH_3 \uparrow \]

High enough end-of-charge voltage is supports the health of the battery...

Fact 1: Stibine generation occurs at cell potentials over about 2.5V/cell and leads to partial self cleaning of the negative plate.
Fact 2: If gassing occurs with high rates the battery may not reach high enough end-of-charge potential for stibine generation.
Fact 3: At high levels of Sb poisoning the battery will not be able to fully recharge - charging current will be used for gassing.

This page emphasizes the importance of stibine generation for self-cleaning of the negative electrodes and summarizes the most important conditions which need to be fulfilled for the process to occur.
The plot on the right shows experimental evidence that stibine generation can effectively occur only at high enough cell voltage. For this experiment a test cell composed of one negative electrode placed between two positive ones was built (image on the left). The cell was deliberately poisoned with 150 mg of Sb(III). After a full recharge the cell was put under constant voltage conditions. As it can be seen for voltages below 2.5 V a relatively high but steady float current is observed related to the gassing of the cell. When the cell was polarized to 2.6 V the float current was initially very high and proportional gassing was observed, but later the current as well as the gassing diminished which is attributed to removal of antimony from the plate in the stibine generation reaction.

This data underline the importance of high enough (preferably over 2.5 V per cell) end-of-charge voltage as a means to prevent antimony poisoning of lead batteries.
Stibine generation alone cannot solve the entire problem of water losses in a lead-acid battery. Hydrogen evolution reaction inhibitors can effectively block the gassing reaction and help the battery operate at high cell voltages with diminished water losses. A proposal of the molecular mechanism for hydrogen evolution reaction inhibition is shown in the left figure. On the right side experimental data showing that hydrogen evolution reaction is accelerated when lead electrodes are contaminated with antimony, but than can be slowed down when inhibitors are introduced to the electrolyte.


Antimony Poisoning in lead-acid Batteries  
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2000 Norderstedt (F.R.G.) (Received September 29, 1986)
Studying hydrogen evolution reaction with respect to its catalysis and inhibition in voltammetry tests on lead metal electrodes is not sufficient to understand the entire complexity of water loss prevention in lead-acid batteries. A good compromise between such experiments and full scale battery testing are single plate experiments, in which actual battery electrodes and separators are used to build a minimal size 2 V cell. Date presented further were obtained in single plate experiments.
The utilized test cell design and the charge discharge cycle for the test adapted from the standard BCI test procedure for golf car batteries are presented above.

**Cycling procedure (BCI adapted):**

1) Constant current charge at 7 A till 2.57 V
2) Constant voltage charge (float) 7 h at 2.57 V
3) Discharge 14 A till 1.67 V

1 negative between 2 positive golf car plates. Separated with the test separators.
Executing the experiment a charge discharge curve was collected for the constructed single plate 2 V test cell following a BCI golf car cycling procedure scaled to fit the single plate 2 V cell.

CC charge: 7 A till 2.57 V
CV charge (float): 2.57 V, 7 h
CC discharge: -14 A till 1.67 V
To estimate the gassing rate of the cell, the current at the end of the constant voltage (float) phase of the tests cycle was recorded for each consecutive cycle. To accelerate the test, antimony was added artificially to the cell by dissolving antimony-(III)-sulphate in the electrolyte. Cells would typically respond with an increase of the end of float current. The exemplary data in the plot on the right show results obtained for an inactive separator not containing hydrogen evolution inhibitors and a rubber separator known from market experience to be effective in limiting the water losses of deep cycle batteries. These two results can be considered as references for a cell with no particular resistance against antimony poisoning and water loss and a cell which is state-of-the-art resistant to antimony poisoning showing good water loss suppression.
WATER LOSS SUPPRESSION IN LEAD-ACID BATTERIES

1. Common hydrogen evolution inhibitors added to the electrolyte are not really effective

When testing substances identified in laboratory tests as effective hydrogen evolution inhibitors in the single plate 2 V tests cell, it was noticed that they do not appear effective. It was concluded that when added once into the electrolyte at the beginning of the test, these molecules get destroyed (likely in an oxidation process) and do not offer effective protection against gassing. Therefore it is concluded that the molecules need to be released gradually and continuously throughout the life of the battery.

**Background:**
Many surfactants and benzaldehydes are known to be effective HER inhibitors identified in laboratory scale experiments.

**Explanation:**
These molecules added once in the beginning of the experiment most likely get oxidised in contact with the positive plate during charge and are destroyed.
When testing substances identified in laboratory tests as effective hydrogen evolution inhibitors in the single plate 2 V tests cell, it was noticed that they do not appear effective. It was concluded that when added once into the electrolyte at the beginning of the test, these molecules get destroyed (likely in an oxidation process) and do not offer effective protection against gassing. Therefore it is concluded that the molecules need to be released gradually and continuously throughout the life of the battery.

2. Sources of hydrogen evolution inhibitors must be placed close to negative plate

- Inactive Separator
- Rubber Separator – inside (close to the negative electrode)
- Rubber Separator – outside (behind the positive electrode)

Explanation:
Hydrogen evolution inhibitors cannot reach the negative plate. If they pass in vicinity of the positive plate during charge, they will be destroyed.
Knowing the nature of hydrogen evolution inhibitors and understanding the importance of the mechanism in which the inhibitor molecules are delivered to the negative electrodes, tests with inhibitor containing powders were conducted. Such laboratory designed powders have shown effectiveness in suppressing gassing and water losses, well matching rubber separators.

3. A method to test hydrogen evolution inhibitor additives

- Rubber Separator
- Inert Separator with Powder Additive 1
- Inert Separator with Powder Additive 2

**Explanation:**
Same powder would not appear active unless distributed evenly close to the surface of the negative plate.
In the last step substances such as tested in the previous slide were incorporated into Amer-Sil PVC separators. Depending on the formulation of the prototype they have shown some (prototype 1) and up to excellent (prototype 2) ability to suppress water losses in the 2 V tests cell.

AMER-SIL can now design separators containing HER inhibitors that are slowly released during the life of the battery to counteract Sb poisoning and help minimize water losses in order to extend the life of the battery.

<table>
<thead>
<tr>
<th>Test Type</th>
<th>Cycle (#)</th>
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<tbody>
<tr>
<td>Inactive Separator</td>
<td></td>
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<tr>
<td>Rubber Separator</td>
<td></td>
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<tr>
<td>PVC Separator Prototype 1</td>
<td></td>
</tr>
<tr>
<td>PVC Separator Prototype 2</td>
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</tbody>
</table>

End of Flot Current (A)

4. Tests of Amer-Sil prototypes of water loss preventing separators
TAKE HOME MESSAGES

High enough end of charge voltage is an effective condition for stibine generation and retarding Sb poisoning of negative plates in Pb-Sb alloy batteries.

HER inhibitors need to be continuously delivered to the negative plate and are not stable in contact with the positive plate (oxidize).

Amer-Sil has designed PVC-Silica separator prototypes able to deliver HER inhibitors to the negative plate in order to minimize gassing and increase the end of charge voltage of the battery.
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