

## Assembly and Characterisation of Batteries in SoSe 2024

# Lab Assignment 3: Electrochemistry of Lead-Acid Batteries

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# 1 Introduction

In this experiment, the electrochemical basics of lead-acid batteries (LABs) are examined. First, a very basic test cell is build and typical parameters – e.g., internal resistance and capacity – are measured. Subsequently, a second, more complex test cell is build, formed, and measured. Additionally, the influence of the acid density on open-circuit voltage and internal resistance is investigated. Finally, the results for both cells are compared.

## 2 Fundamentals

### 2.1 History

The first experiments in the field of electrochemistry dealing with different electrodes in acid solutions were carried out in 1801. A notable breakthrough was made by the German physician Wilhelm Sinsteden, who created a functional secondary cell using two lead electrodes dipped in diluted sulphuric acid, in 1954. With a specific energy density of  $0.1 \frac{\text{Wh}}{\text{kg}}$  delivering a discharge current for more than 15 min. However, the discovery went unnoticed, so the title of inventor of the LAB officially went to Gaston Planté. In 1859, the French physicist G. Planté described the polarization of electrodes of different materials. During his experiments he found out that the highest differential voltage can be generated by a cell construction made of two lead electrodes, which are separated from each other by an elastomer and immersed in a sulphuric acid.

However, public interest in LABs only came with the invention of the first commercial electric generator in 1869 and the incandescent lamp in 1879. The first production took place in 1871 by the Bréquet Company. However, the quantities produced were severely limited by the manufacturing process, because the formation was very time-consuming and only cells with a relatively low capacity could be build at the time. With new processes simplifying and speeding up the production and enhancing the capacity, the LAB became an important role among secondary cells for decades.

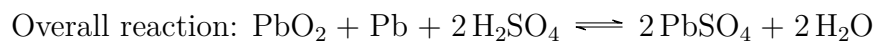
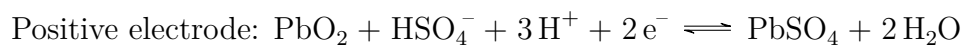
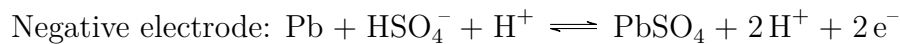
### 2.2 Fundamentals of Electrochemistry

LABs are the oldest rechargeable electrochemical energy storage technology. Till today they are still wildy used as start-lighting-ignition (SLI) batteries in vehicles due to their cheap materials.

A LAB contains of several positive and negative plates, where the active mass (AM) is pasted on grids that work as a current collector. In industrial manufacturing, lead oxide paste is usually applied to a lead grid to create the positive electrode. The negative electrode consists of porous sponge lead. Either the positive or the negative plates can be placed inside envelopes which act as separators and prohibit short circuits on the one hand, but have to provide ionic conductivity on the other hand. At the top of each plate is a lug, which allows to connect several plates of the same polarity with a strap. Intercell connectors build a series connection of multiple cells (a typical SLI battery consists of 6 cells in series).

The electrolyte of LABs is diluted sulphuric acid. It has to provide ionic conductivity but also has to serve as an electrochemical reactant. Batteries with a fluid electrolyte are called flooded or vented LABs. This design allows an interchange of gas and fluid with the surroundings. Previously each cell was closed by a screw-in plug which could be removed for a refill of the cell with distilled water. Nowadays, flooded batteries used for SLI applications have a closed container because the water loss is low and refilling water is no longer necessary.

The main chemical equations within a LAB are:



During discharge the sulphuric acid ions within the electrolyte migrate to the negative electrode and react with the lead to produce the non-conductive, solid product of lead sulphate and hydrogen ions. Two electrons are released during this process. Thereby, a flow of electrons through the external circuit to the positive electrode is enabled.

At the positive electrode lead dioxide reacts with the sulphuric acid and the two electrons to lead sulphate and water is formed as well. During discharge the sulphuric acid contributes two times within this reaction to build lead sulphate at both electrode polarities, which is also referred to as “double-sulphate theory”.

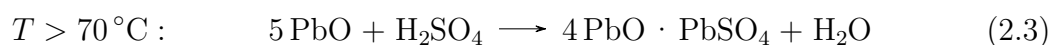
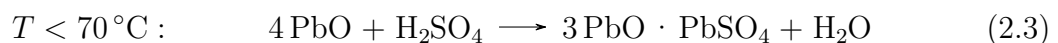
The electrochemical processes at the electrodes are reversed during the charge process. If the battery is almost fully charged, the majority of the lead sulphate will have been converted back to lead and lead dioxide and further charging will increase the evolution of hydrogen at the negative electrode and oxygen at the positive electrode, which is also referred to as gassing. Gassing occurs because the cell voltage of a lead-acid battery is greater than the water decomposition voltage of 1.23 V. With traditional cell designs, this will result in a loss of water from the cell electrolyte solution.

The voltage of a single cell is slightly more than 2 V. Commercially use LABs are mostly operated between 2.66 V and 1.75 V. Theoretically, it is possible to completely discharge a LAB and thereby completely converting all active materials on both sides of the cell into lead sulphate. Then the polarity of the cell would be arbitrary switched for the next charging, since the same material would be present on both sides. In practice, this state cannot be achieved, since the lead sulphate covers the entire surface and no further reaction can take place.

## 2.3 Industrial Production

An industrially manufactured plate always consists of a grid and the active material. The grid can consist of different alloys and gives the electrode shape and strength. Furthermore, electric conductivity and resistance against sulphuric acid is of importance. The base material for the active material is lead dust, which consisting of (70 ... 75) % lead oxide and (30 ... 25) % metallic lead powder. It is produced in modern grinding plants, where the ground lead dust particles are oxidized by air supply. Furthermore, the lead dust can be heated at (250 ... 470) °C resulting in the oxidation of PbO and PbO<sub>2</sub> to Pb<sub>3</sub>O<sub>4</sub>. The end products are characterized by specifying the amount of PbO and the amount of bound PbO<sub>2</sub>.

When producing a positive or negative paste, the individual components are added to the mixing process in a specific order. Lead dust is used as the starting material for both plates plate. In addition, a small amount of reinforcing fibres is added to the positive active mass to allow a better adhesive force during pasting. Additional expanding agents such as carbon black, barium sulphate (BaSO<sub>4</sub>) or organic components are added to the negative active mass, to prevent that the sponge lead loses its porous structure through recrystallization and sulphation. After all the solids have been added to the mixer, the liquid components are added in the form of water and sulphuric acid. Depending on the heat generated in the mixer, the lead oxide reacts to form tribasic lead sulphate (2.3) or tetrabasic lead sulphate (2.3):



By controlling the water and sulphate content, the density can be adjusted to the LABs needs. The lower the density of the paste, the higher the later porosity of the active material. Therefore, the capacity increases which also increases the efficiency, but at the same time enables active material losses during cycling and thus shortens the battery life time. The mixing process is complete in less than 30 minutes. The mass is then pasted to the grid.

The plates are cured under moderate temperatures and a defined atmosphere. In the first step a high humidity of > 95 % RH at 40 °C is kept for 18 h to form tribasic lead sulphate. During the second curing step the plates have dried, and residual lead content was reduced at temperatures being increased from (50 ... 60) °C over a period of 24 h. The humidity is decreasing during the second step from > 95 % RH until approximately 10 % RH due to opening a vent of the curing box.

After drying the plates they are used to build the complete battery. Either the positive or the negative plates can be placed inside envelopes which act as separators and prohibit short circuits on the one hand, but have to provide ionic conductivity on the other hand. At the top of each plate a lug is connecting it to other plates. They are put into the case of a battery and connected with intercell connectors to build a series connection of multiple cells.

## 2.4 Formation

When formatting the plates, the reaction speed of the electrochemical processes depends primarily on the current density. If you were to carry out a formation with a very small current over a period of more than two weeks, you could get very close to the theoretical specific capacity of  $241 \frac{\text{Ah}}{\text{kg}}$  of  $\text{PbO}$ . In industrial production, the entire forming process is shortened to (15 ... 30) h for economic reasons. The shortening of the formation time is accompanied by a reduction in capacity and increased energy consumption during formation. At the same time, the increase in the forming current leads to increased gas formation and heat development in the container. The electrolysis causes energy losses and the increase in temperature degrades later performance of the battery. Ultimately, one tries to find the most efficient and profitable formation current:

- The temperature of the electrolyte stays in a range of (30 ... 50) °C.
- The voltage does not increase too much to minimize gassing.
- The formation current must be high enough to allow finishing all chemical processes.

One of the simplest profiles for formation is the constant current formation. Thereby, the forming current is kept constant throughout the entire process, regardless of the electrolyte, temperature and the battery voltage.

After formation, the electrolyte concentration of all batteries will be adjusted to  $1.29 \frac{\text{g}}{\text{cm}^3}$  at 100 % *SoC* and all cells are filled to an equal level. After the acid adjustment, all batteries would need a final charging step to mix the acid and to finalize the formation process. However, most companies skip this step and the end used is finishing the formation during his or her first recharge.

## 2.5 Electrolyte Concentration

The concentration of the electrolyte affects both the open-circuit voltage (OCV) and the internal resistance ( $R_{in}$ ) of the battery. There is an almost linear relationship between the acid concentration and the OCV, shown in 1.

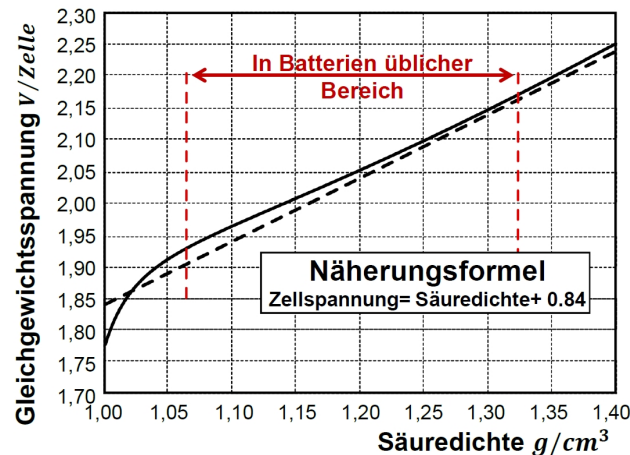


Figure 1: OCV of an LAB as a function of acid density

When discharging, the sulphuric acid inside the battery is used up and the equilibrium voltage is reduced. As an approximation, it can be assumed that the OCV is approximately equal to the acid concentration plus 0.84. There is an optimal concentration for the internal resistance at which the conductivity is maximum and thus the performance of the cell is maximum.

## 2.6 Current Dependency

The capacity of LABs is highly dependent on the discharge current. Larger currents drastically reduce the capacity. This behaviour can be described empirically by the Peukert equation:

$$I^n \cdot t = \text{const.}$$

The Peukert number  $n$  has a value between 1 and 1.5, depending on the technology. The higher the Peukert number, the higher the current dependence of the batteries capacity. The equation must be parametrised by measurements for each battery type. For example, measurements with different discharge currents and thereby discharging times are made. With two measurement points the Peukert number  $n$  can be determined. If  $n$  is known, the capacity that can be drawn at any discharge current can be estimated with  $C = I \cdot t$ .

### 3 Pre-Tasks

#### 15 P Task 1: Fundamentals

- (a) Why are Planté plates no longer used in modern LABs? 3 P
- (b) Determine the weight per cent of sulphuric acid with an electrolyte concentration of  $1.2 \frac{\text{g}}{\text{cm}^3}$  and  $1.4 \frac{\text{g}}{\text{cm}^3}$  respectively. 6 P
- (c) Calculate the theoretical capacity of your laboratory cell (used in the second experiment), assuming that the positive electrode consists entirely of lead oxide. The lead plates used in the experiment each weigh about 163 g. Assume that the material can be completely converted for the reaction. 6 P

#### 15 P Task 2: Formation and Operating Behaviour

- (a) Which secondary reaction takes place during formation? Give the full reaction equation and assign the released gases to their corresponding electrodes. 3 P
- (b) You have three possible formation currents – 250 mA, 500 mA, and 1000 mA – as well as three different forming times – 5 min, 10 min, and 15 min. Prepare an experimental procedure to derive a trend for the capacitance with as few measurements as possible for both variables and create a corresponding test matrix. 8 P
- (c) Visualise the expected voltage curve during discharge. Label all individual voltage drops. 4 P

#### 20 P Task 3: Experimental Procedure

- (a) Create a list of all the materials, tools and devices needed for the individual experiments. 6 P
- (b) Calculate the required volume of  $1.4 \frac{\text{g}}{\text{cm}^3}$  sulphuric acid mixed with water to achieve an electrolyte concentration of  $1.2 \frac{\text{g}}{\text{cm}^3}$  in your electrolyte. 6 P
- (c) For both experiments, briefly describe the exact procedure. Please note that 3P2N cells are assembled in this year's course and that the instructions given in section 4 might not contain all the exact details and necessary measures to be taken for a safe execution of the experiments. 8 P



## 4 Experimental Procedure

### General Safety Instructions

Wearing a lab coat, gloves, and protective goggles at all times is mandatory in the laboratory. One has to also wear long pants with closed shoes. With gloves on, you must not touch your clothes or face! All work must be carried out carefully. At the beginning of the lab work, students must be informed about safety instructions such as body shower and eye shower. Special care has to be taken when working with chemicals and hazard symbols must be taken into account. Always wash your hands carefully when leaving the lab. If you have any questions, please contact the supervisor at any time.

### Special Safety Instructions (Pb, H<sub>2</sub>SO<sub>4</sub>, HHO)

Lead is toxic and should not be touched with bare hands. Always wear gloves when cutting and positioning the lead electrodes. Lead electrodes are made of fine prose lead sponge, invisibly spreading everywhere in the lab. Therefore, better not touch anything in the lab. If lead does come into contact with the skin, wash your hands immediately. If you are wearing gloves you must not touch your clothes or face.

Sulphuric acid is highly corrosive and should be handled with extreme caution. Sulphuric acid on the skin causes severe redness and irritation and should be rinsed off immediately under running water for at least 10 min. In the event of contact with clothing, all soiled or soaked clothing must be removed immediately. To create diluted sulphuric acid, acid must be added to the water. Since the reaction of concentrated sulphuric acid with water generates a lot of heat, it must be diluted only by pouring it into water, and not adding water to the acid. Otherwise, it may splash and burn bystanders. Diluted sulphuric acid is not as corrosive as pure sulphuric acid. However, it should still be handled with caution, hands should be washed after exposure and clothes might be getting holes if you spill acid (don't wear your favourite pants).

When forming the cells, oxyhydrogen (HHO, "Knallgas") is produced, so all experiments must be carried out in a fume hood or climate chamber. Open fire is strictly prohibited!

## List of Provided Materials, Tools, and Devices

- voltage source, cables, and clips
- multimeter and sulphuric-acid measurement device
- resistor ( $2\text{ k}\Omega$ )
- beakers and rubber spacer
- lead electrodes
- plate envelopes, spacers, and cell case
- spanners, paper towels, and miscellaneous tools
- chemicals:
  - sulphuric acid ( $1.4\frac{\text{g}}{\text{cm}^3}$ )
  - water
  - lead sheet

## Experiment 1: Building a basic LAB

1. Verify that all active items are present before beginning assembling.
2. Cut two lead electrodes of the same size from the lead sheet.
3. Carefully polish the electrodes with a paper towel.
4. Stir the sulphuric acid (30 %) container to avoid acid stratification. Fill one beaker with 200 ml of sulphuric acid (30 %) each.
5. Attach the rubber spacers to the edge of the beakers and bend two of the electrodes upright to attach them with clips.
6. Connect the lead stripes to the switched off voltage source and connect two multi-meters in parallel.
7. Set the current limit to zero, turn on the voltage source, and set the voltage to the highest value.
8. Increase the current limit until the desired current is obtained. Choose one of the formation criteria from your test matrix generated in the pre-tasks.
9. Turn off the voltage source when the formation is over and wait until the OCV stabilizes.
10. Measure the OCV and the internal resistance of the cell.
11. Connect the cell to the 2 k $\Omega$  resistor and record the voltage during discharge. The end-of-discharge voltage is 1.75 V.  
  
*Note: The discharge should last (20 ... 40) min. During this time, you can continue with the next experiment.*
12. Take the cell and reverse the polarity of the electrodes.
13. Repeat the formation and capacity determination with the reversed polarity.
14. Reverse the polarity one last time and carry out the formation and determination of the capacity again.

## Experiment 2: Building a Commercially Used LAB

1. Prepare 600 ml of sulphuric acid with a density of  $1.2 \frac{\text{g}}{\text{cm}^3}$ . Allow the acid to cool down as you continue.
2. Take matching positive and negative electrodes (3P2N, see table 1).
3. Put the positive plates into separator sheets.
4. Merge the negative and the positive electrodes together.
5. Use spacers around the electrodes to fill the gap between electrodes and cell case.
6. Insert the test cell into the cell case and close the test cell with the cover and the plugs.
7. Fill in the sulphuric acid until the current collectors are slightly covered. Determine how much acid you filled into the test cell.
8. Connect the test cell to the testing equipment within a climate chamber.
9. For formation, use a constant current of  $3 \cdot I_{20}$  (see table 1) for (33 ... 47) h at room temperature ( $25^\circ\text{C}$ ).

*Note: The formation takes too long for this lab assignment. Consequently, all of the following points need to be worked on at the beginning of the next appointment.*

10. Measure the inner resistance, the OCV, and the acid density after formation.
11. The electrolyte concentration of all cells needs to be adjusted to  $1.29 \frac{\text{g}}{\text{cm}^3}$  at 100 % SoC. Use the electrolyte with a density of  $1.4 \frac{\text{g}}{\text{cm}^3}$ .
12. Measure the inner resistance, the OCV, and the acid density again after the adjustment.
13. The cells are now ready for further testing.

Table 1: Formation criteria dependent on cell layout

Cell Type			Formation		
Layout	Size	$C_N$	$I_{\text{form}}$	Criterion	$t_{\text{form}}$
Small-size cell	2P1N	10 Ah	1.5 A	$7 \cdot C_N$	46.7 h
Middle-size cell	3P2N	20 Ah	3.0 A	$6 \cdot C_N$	40 h
Complete cell	7P8N	70 Ah	10.5 A	$5 \cdot C_N$	33 h

## 5 Evaluation

### **10 P** Form

- general layout
- formal quality of diagrams, tables, and figures
- clearness and comprehensibility
- correct indication of sources

### **5 P** Introduction and Summary

### **25 P** Experimental Procedure

- detailed report of the exact procedure for each experiment
- description of all relevant observations
- recording of all deviations from the originally planned procedure
- if applicable: drafts and photographs of the experimental setups

### **60 P** Evaluation

- General Requirements:
  - if necessary: theoretical derivations and explanations
  - preparation and visualisation of the measurement data
  - interpretation of the findings and comparison with theory/simulation
  - discussion of possible sources for errors

**10 P**

- Focus on Experiment 1:

30 P

- Determine the theoretical capacity of the cell.
- Discuss why your laboratory cell has a significantly lower capacity than theoretically possible.
- Calculate the capacity that can be expected from your laboratory cell with a Peukert number of 1.16 and a two-hours discharge current.
- Why does the electrolyte become cloudy when the polarity is reversed during formation?
- What influence did the polarity reversal have on the capacity of the cell? Explain the effect. Create a trend curve for the polarity reversals.

- Focus on Experiment 2:

20 P

- Plot current, voltage, and capacity during the formation of the test cell. Describe and discuss the effects.
- How does the acid density change during formation? Describe and discuss the effect.