

XRD ANALYSIS OF CHEMICAL COMPOSITION ON LEAD SURFACE MICROELECTRODES

Jan Smejkal

Doctoral Degree Programme (2), FEEC BUT

E-mail: xsmej18@stud.feec.vutbr.cz

Supervised by: Ladislav Chladil

E-mail: chladil@feec.vutbr.cz

Abstract: This work is focused on the observation of changes in the chemical composition on the surface of the negative electrode of the lead-acid battery using an XRD diffractometer. The measurement was performed on thin pasted electrodes with a thickness of about 1mm. After the maturation and molding process, the fully charged negative electrode was gradually discharged and charged at a rate of 0.2 C and 0.3 C. The negative electrode was analyzed at 100 %, 80 %, 60 %, 40 %, 20 % and 0 % SOC states. Chemical changes occurring on the surface of the negative electrode during discharging and charging of the lead-acid battery were measured using X-ray diffractometer Rigaku MiniFlex HR 600.

Keywords: lead-acid, accumulator, negative electrode, X-ray diffractometer, morphology

1 INTRODUCTION

Although the principle of operation of lead-acid batteries has been known for a very long time, this type of battery is again intensively studied. Lead-acid batteries are widely used due to the good availability of the materials used, their recyclability, high electrochemical efficiency, the high number of cycles, and high rate of voltage around 2 V. These properties together with the low production cost make them very attractive for use in the automotive industry, where they can supply high current for motor starters and also in electromobility. Large arrays of lead batteries are used as backup power sources for data and data centers. Lead-acid batteries are also widely used for the long-term storage of energy produced from renewable sources. Today, more than half of the world's lead production is used to make batteries [1].

The degradation mechanisms of accumulators are closely related to the materials used. If one of the undesirable properties is improved, it usually leads to a deterioration of the other properties. One of the most important degradation mechanisms is the PCL phenomena (Premature Capacity Loss). PCL phenomena were formerly known as antimony free effect mainly because the first cases of this degradation mechanism were observed in batteries in which antimony in the lead alloy (Pb-Sb) positive electrode was replaced by a lead-calcium (Pb-Ca) alloy [2]. We currently know three main PCL phenomena, namely PCL 1, PCL 2, and PCL 3. PCL phenomena cause premature loss of capacity and thus reduce the ability to recharge and charge batteries. At the moment, the research team is trying to suppress these negative phenomena as much as possible.

PLC 3 phenomenon was discovered as the last of the phenomena of premature loss of capacity. At the moment when the negative phenomena on the positive mass of the electrode were suppressed, the attention of the research teams turned to the problems related to the negative electrode. To achieve optimal results for the life of a lead-acid battery, we can only achieve this if the positive and negative plates retain their optimal properties. In PLC 3 phenomenon, the negative electrode is sulfated. This phenomenon is often associated with the selective discharge of the negative electrode, which is the result of a combination of the high rate of hydrogen evolution and high efficiency of oxygen recombination. A key parameter for the long life of the electrodes is an even distri-

bution of redox reactions in the entire volume of the electrode during charging and discharging. Even distribution of these reactions prevents the long-term presence of sulfate in certain parts of the electrode, which leads to gradual sulfation and loss of the ability to supply currents at higher loads [3].

According to Dr. Moseley, there are several possible causes of a significant loss of capacitance affecting the negative electrode. One of the causes is the reduction of the active area of the electrode, which is caused by the loss of organic expanders. Organic expanders are destroyed by oxygen, which reaches the negative electrode during the oxygen cycle [4].

Additives such as carbon, glass fibers, or titanium dioxide can be used to suppress the PLC 3 phenomenon. These additives are added to the negative active mass and can reduce and slow down the sulfation of the negative electrode [5, 6, 7].

2 MEASUREMENT

For the experiment of chemical changes on the surface of the negative electrode, it was necessary to create thin electrodes, which were pasted on a lead substrate of circular shape with a diameter of 13 mm. 24 holes were drilled in the lead substrate. These holes allow better adhesion of the active mass to the surface of the lead substrate. To precisely define the reaction area of the electrode, a thin layer of epoxy adhesive was applied to the part of the electrode that did not participate in the chemical processes. 10 g of the mixture was prepared for the measurement and the exact composition of the active mass of the negative electrode is given in Tab. 1. The electrode was then placed in a holder made of PEEK (semicrystalline thermoplastic). Before the measurement, the electrode was placed in the holder so that there were no movements that could adversely affect the measurement. The electrode matured for 5 days in a controlled high humidity environment. The total weight of the active substance of the electrode after maturation was 0.82 g. After maturation, the electrode was placed in a measuring cell with an electrolyte consisting of an aqueous solution of sulfuric acid at a concentration of 27 %. 20 formation cycles were performed in the measuring cell at a supplied current of 13.11 mA.

<i>Ingredients</i>	<i>Lead powder</i>	<i>Demineralized water</i>	<i>Sulfuric acid</i>	<i>Borosilicate</i>	<i>Barium sulphate</i>
Quantity (g)	8.42	0.92	0.51	0.02	0.13

Table 1: Exact composition of the active mass of the negative electrode

Before measurement, the active substance of the electrode was instilled with an electrolyte, which consists of an aqueous solution of sulfuric acid with a concentration of 33 %. The electrode was then covered with a 12 μm thick polyamide foil. The foil is attached to the holder with a rubber ring to prevent air from entering the active material of the electrode (see Fig. 2).



Figure 1: On the left there is a picture of the detail of the lead substrate. On the right there is a picture of the complete test electrode covered with polyamide foil.

The analysis of the surface of the active substance took place in a three-electrode circuit. The electrode was immersed in an electrolyte consisting of a 33% aqueous sulfuric acid solution. After the formation cycles, the fully charged electrode was gradually discharged. The discharge was performed

med by the galvanostatic method in five steps at a supplied current of 18.86 mA for 1 hour with a potential limitation $E_M = -0.8$ V vs. MSRE. The electrode was discharged at a rate of 0.2 C and subsequently analyzed in XRD at 100 %, 80 %, 60 %, 40 %, 20 %, and 0 % SOC (State of Charge). Charging was also performed by the galvanostatic method in five steps at a supplied current of 18.86 mA for 1 hour with a potential limitation $E_M = -1.3$ V vs. MSRE. For a speed of 0.3 C, the same setting was used for the experiments, only a current of 31.43 mA was supplied for 31 minutes. Chemical composition on the surface of the negative electrode during charging and discharging was observed using X-ray diffractometer Rigaku MiniFlex HR 600. Diffractograms were measured over a range of 10-100° at step 0.01, IHS 5, divergence slit of 0.625, and $k\beta$ filter 0.03.

3 RESULTS AND DISCUSSION

During the discharge, in each of the states 100 %, 80 %, 60 %, 40 %, 20 %, and 0 % SOC, the chemical composition on the surface of the active mass of the negative electrode was measured by XRD. The results of the chemical composition can be seen in Fig. 2.

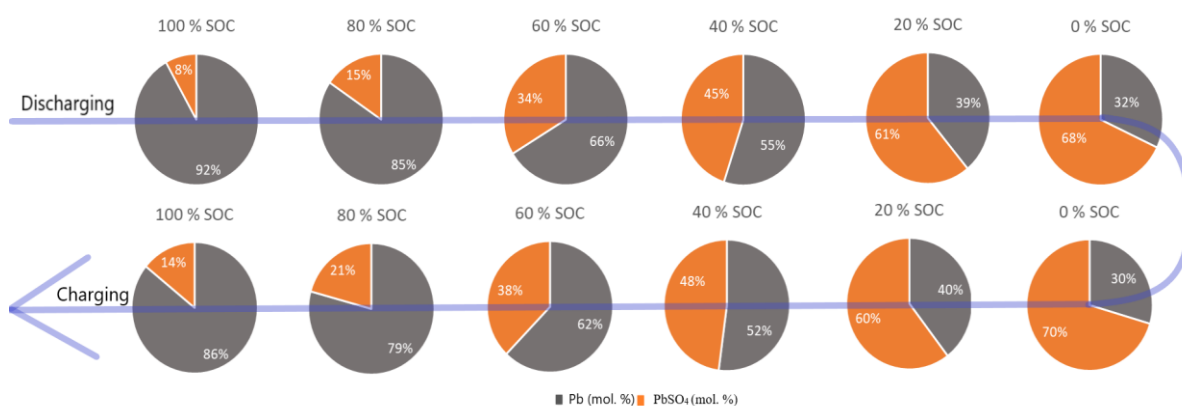


Figure 2: Chemical composition on the surface of the active mass of negative electrode at different SOC at a rate 0.2 C for discharging and charging.

It can be seen that when the electrode is fully charged, the electrode contains 8 mol. % lead sulfate. In the fully discharged state, the electrode contains almost 32 mol. % metallic lead. The composition on the surface of the electrode in the fully charged and discharged state indicates that at almost 40 mol. % of active material does not convert during cycling. It is also possible to observe the prior dissolution of the metal lead when discharging between 80 % and 60 % SOC. There was a decrease in the lead on the surface of the electrode by 18 mol. %, in contrast, in the last part of the discharge from 20 % to 0 % SOC there was a decrease of only 8 mol. %. This half-decrease in lead describes a two-stage discharge. In a two-stage discharge, lead ions first begin to dissolve into the electrolyte, forming a supersaturated solution and precipitating large amounts of sulfate on the electrode surface.

Subsequently, the electrode was charged at a rate of 0.2 C. Charging was also performed by the galvanostatic method in five steps at a supplied current of 11.35 mA for one hour with a potential limitation $E_M = -1.3$ V vs. MSRE. At 0 % SOC during the charge cycle, the electrode contained 30 mol. % lead. This amount of lead correlates with discharge results. The electrode was again measured at 0 %, 20 %, 40 %, 60 %, 80 % a 100 % SOC. Up to 40 % SOC, the electrode was made of lead sulfate. From 60 % SOC, the electrode was already largely lead. At full charge, there was 14 mol. % of lead sulfate on the electrode, which is 6 mol. % more than at 100 % SOC at discharging cycle.

In Fig. 3 we can observe a comparison of the molar proportion of lead and lead sulfate when charging and discharging the electrode at a rate of 0.2 C. When charging and discharging the electrode,

there were no significant variations in the proportion of Pb and PbSO₄ and the course of representation of elements on the surface of the electrode was almost linear.

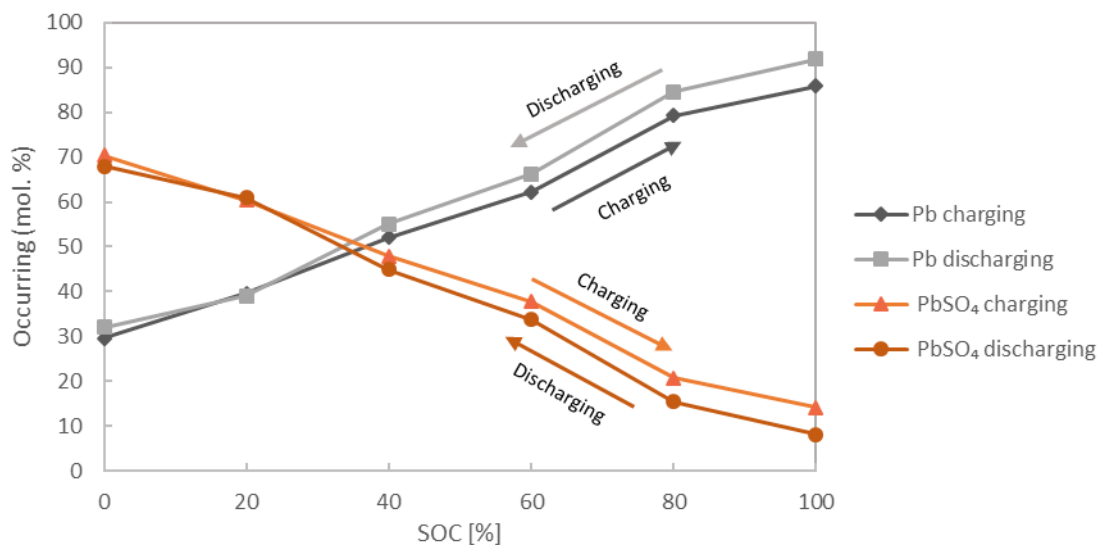


Figure 3: Representation of the surface composition of the active substance at different SOC at a rate 0.2 C during charging and discharging.

At a higher discharge rate of 0.3 C, it can be observed that in the fully charged and discharged state there is a significantly higher amount of active material on the electrode surface, which does not convert from lead to sulfate and vice versa when cycling the negative electrode. Even though a smaller amount of active material was used at a higher charging and discharging speed, almost the same charge was delivered at both speeds.

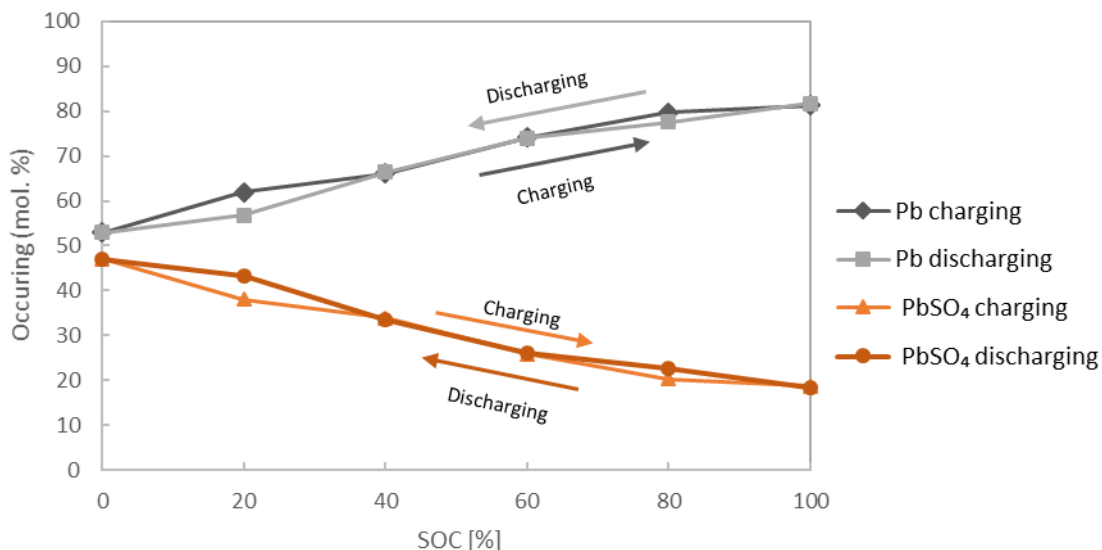


Figure 4: Representation of the surface composition of the active substance at different SOC at a rate of 0.3 C during charging and discharging.

4 CONCLUSION

As can be observed from the measured results, there is almost 40 mol. % on the negative electrode of the active substance in which no material is converted during cycling. The addition of a carbon additive to the active substance could help to reduce the percentage of unused material, and thus

contribute to increasing the capacity of the lead-acid battery. Furthermore, during discharging, there was a negative phenomenon of preferential dissolution of lead at the beginning of the discharging cycle. The preferential dissolution of lead leads to an increase in sulfates on the surface of the electrode and then in the entire volume of active mass. During charging, the conversion of lead to sulfate was almost linear. Only in the range of 60 % - 80 % SOC did the conversion of lead to sulfate accelerate. Furthermore, it was possible to observe that the electrode can absorb an equally large charge at a higher charging and discharging speed, even though there was a lower amount of active material on its surface, which is converted into charged or discharged form.

One step to better understand the operation of the negative electrode in lead-acid batteries could be to compare the behavior and chemical composition on the electrode surface at different battery cycling speeds. The next step could be to analyze the chemical composition of the negative electrode surface with added additives such as glass fibers or carbon. These additives could significantly contribute to the elimination of the negative properties described above occurring in the cycling of the negative electrode.

ACKNOWLEDGEMENT

This work was supported by the specific graduate research of the Brno University of Technology No. FEKT-S-20-6206.

REFERENCES

- [1] MOUBAYED, Nazih, Janine KOUTA, Ali EL-ALI, Hala DERNAYKA a Rachid OUTBIB. Parameter identification of the lead-acid battery model. *2008 33rd IEEE Photovoltaic Specialists Conference* [online]. IEEE, 2008, **2008**(33), 1-6. ISBN 978-1-4244-1640-0. ISSN 0160-8371. Dostupné z: doi:10.1109/PVSC.2008.4922517
- [2] HOLLENKAMP, A.F. When is capacity loss in lead/acid batteries 'premature'?. *Journal of Power Sources* [online]. 1996, **59**(1-2), 87-98 [cit. 2021-02-10]. ISSN 03787753. Dostupné z: doi:10.1016/0378-7753(96)02306-3
- [3] LAM, L.T., H. CEYLAN, N.P. HAIGH, T. LWIN a D.A.J. RAND. Influence of residual elements in lead on oxygen- and hydrogen-gassing rates of lead-acid batteries. *Journal of Power Sources* [online]. 2010, **195**(14), 4494-4512 [cit. 2021-02-11]. ISSN 03787753. Dostupné z: doi:10.1016/j.jpowsour.2009.12.020
- [4] MOSELEY, Patrick. ALABC 2000 - the way ahead. *Journal of Power Sources* [online]. USA, 2001, (95), 218-223 [cit. 2021-02-11].
- [5] BODEN, D.P., D.V. LOOSEMORE, M.A. SPENCE a T.D. WOJCINSKI. Optimization studies of carbon additives to negative active material for the purpose of extending the life of VRLA batteries in high-rate partial-state-of-charge operation. *Journal of Power Sources* [online]. 2010, **195**(14), 4470-4493 [cit. 2021-02-25]. ISSN 03787753. Dostupné z: doi:10.1016/j.jpowsour.2009.12.069
- [6] BAČA, P., P. KŘIVÍK a S. VACULÍK. Negative Lead-Acid Battery Electrodes Doped with Glass Fibres. *International Journal of Electrochemical Science* [online]. 2015, , 2206-2219 [cit. 2021-02-21]. Dostupné z: https://www.researchgate.net/publication/282822951_Negative_Lead-Acid_Battery_Electrodes_Doped_with_Glass_Fibres
- [7] MICKA, K., M. CALÁBEK, P. BAČA, P. KŘIVÁK, R. LÁBUS a R. BILKO. Studies of doped negative valve-regulated lead-acid battery electrodes. *Journal of Power Sources* [online]. 2009, **191**(1), 154-158 [cit. 2021-02-24]. ISSN 03787753. Dostupné z: doi:10.1016/j.jpowsour.2009.01.014