

Slovak University of Technology in Bratislava
Institute of Inorganic Chemistry, Technology and Materials
Department of Inorganic Technology

Electrochemical characterisation of electrode surfaces in
lead-acid battery with and without activator

Bratislava



prof. Ing. Ján Híveš, PhD.

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1. INTRODUCTION

The lead–acid battery has been used widely as a secondary battery for more than 150 years, since its invention by Planté in 1859. This type of battery is one of the most important electrochemical energy storage systems in use today, but despite the large number of investigations lead electrode reactions are still not completely understood. At anodic potentials lead electrodes in sulphuric acid electrolytes exhibit a wide variety of phenomena which occur both interfacial and in solid state, and their explanation requires proper use of modern theories of surface electrochemistry as well as those of nucleation growth process models.

Sealed lead batteries are presently widely used in various branches, which can be attributed to their relatively high performance characteristic (life time, capacity), the lowest cost in comparison to other battery types, practically no gassing and minimum maintenance. AGM (Absorbed-Glass-Material) battery is designed for repeated deep discharges and high power applications in which maximum run times are needed to very low depths of discharges. The advantages of the lead-acid system are its high-rate discharge capability, good specific energy, high reliability, robustness, low cost in both manufacturing and recycling as the battery is manufactured mainly from a single low-cost raw material [1,2]. AGM batteries are just like flooded lead acid batteries, except the electrolyte is being held in the glass materials, as opposed to freely flooding the plates. Very thin glass fibres are woven into a mat to increase surface area enough to hold sufficient electrolyte on the cells for their lifetime. The fibres that comprise the fine glass fibres glass mat do not absorb nor are affected by the acidic electrolyte they reside in. These materials are wrung out 2-5% after being soaked in acids, prior to manufacture completion and sealing. The AGM battery can now accumulate more acid than is available, and never spill a drop.

A large and growing installed base of lead-acid batteries supply electrical power in critical situations to hospital, banks, mobile telecommunication sites, receiving and transmission utility, and countless other industrial and commercial

installations. The customer testing of their backup-systems does not accurately show battery health in most cases. This mainly due to the fact that only the electrical properties of the battery have been measured using conventional battery test equipment. Two chemical processes, dry out (lost of water) and sulphation (a build over time of lead sulphate on the plates) are two leading causes of battery failure in backup power systems.

In this work, the effect of activator – PowerBatt (Battery Gurus, s.r.o.) - addition into lead-acid battery on the electrode surface properties has been examined by electrochemical methods – cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) together with visual inspection of the electrode surface by scanning electron microscopy (SEM).

2. EXPERIMENTAL PROCEDURES

It is well known that both capacity and the cycle life of lead-acid batteries are dependent on the conditions of plate formation. If the battery is considered as an energy system with its own structure, the process of degradation of its characteristics may be envisaged as a disintegration of this structure. Solid state processes at passive layers formed on lead in sulphuric acid have been studied many times. Lead corrosion appears to be a rather complex phenomenon as the structure and composition of films formed on metal surfaces depend on a large number of variables. It is generally accepted that the nature of the passive film formed on lead electrodes in sulphuric acid solution can be separated into three distinct potential regions.

The passive layer formed at potentials -0.97 to -0.40 V vs. Hg/Hg₂SO₄ ref. electrode consists of PbSO₄ crystals.

The layer produced at potentials -0.40 to $+0.95$ V vs. Hg/Hg₂SO₄ ref. electrode is composed of PbSO₄ and an inner layer involving several basic lead compounds (mainly tetra-PbO and basic lead sulphates), which build up progressively beneath the initial PbSO₄ porous layer structure.

At potentials more positive than $+0.95$ V vs. Hg/Hg₂SO₄ ref. electrode α - and β -PbO₂ become the predominant anodic oxide products.

The negative plate of lead-acid battery consists of two types of structure – primary (skeleton) and secondary (energetic) [3]. The primary structure is strongly affected by the production technology of the negative plate, e.g. phase composition and density of the paste, nature and amount of expander, concentration of the formation electrolyte, current density and temperature of the formation, etc.. The secondary structure of the negative plate appears and disappears at each charge-discharge cycle. It may be expected that both the energetic parameters and cycle life of the plate will depend on the relative proportions of these structures. The preservation of an optimum ratio between these two structures will determine the stability of the operating parameters of the negative plate of the battery [4].

2.1 Cyclic voltammetry

Over the past couple of decades potential sweep techniques, such as cyclic voltammetry, have been applied to an ever increasing range of systems, and at the same time the mathematical description of these techniques has been developed sufficiently to enable kinetic parameters to be determined for a wide variety of mechanisms. It is, however, in the area of preliminary mechanistic investigations that sweep techniques, in particular cyclic voltammetry, are probably most useful. The simplest of these techniques is linear sweep voltammetry (LSV) and this involves sweeping the electrode potential between limits E_1 and E_2 at a known sweep rate, before halting the potential sweep. A generally more useful (and consequently more widely applied) technique is cyclic voltammetry (CV). In this case the waveform is initially the same as in LSV, but on reaching the potential E_2 the sweep is reversed (usually at the same scan rate) rather than terminated. In both LSV and CV experiments the cell current is recorded as a function of the applied potential. The sweep rates used in conventional experiments range from a few mV s^{-1} to a few hundred V s^{-1} .

Our experimental set-up consists of three electrodes. Working electrode was a piece of negative plate from tested battery. A large pieces of graphite electrode was served as counter electrode and $\text{Hg}/\text{Hg}_2\text{SO}_4/\text{K}_2\text{SO}_4(\text{sat.})$ electrode was used as a reference electrode. Apparatus is shown in Fig. 1.

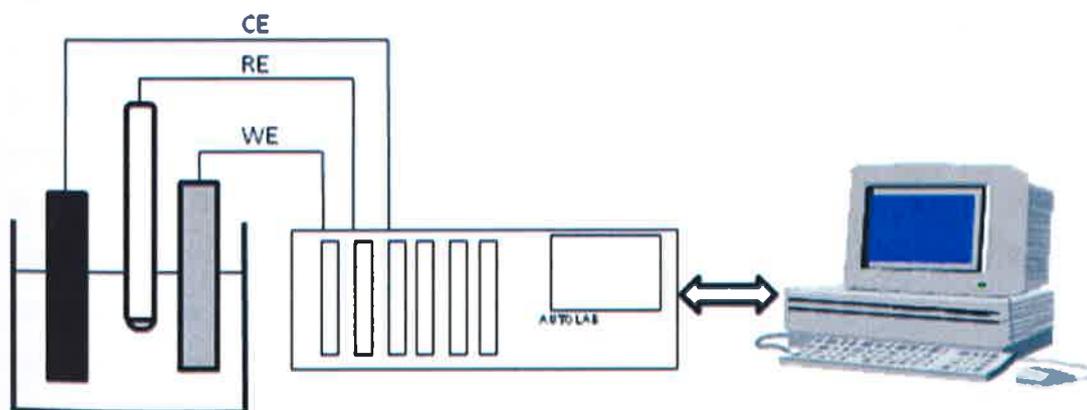


Figure 1. Apparatus for CV experiments, WE-working electrode, RE-reference electrode, CE-counter electrode

The electrochemical measuring system consisted of potentiostat/galvanostat AUTOLAB (EcoChemie) controlled by PC, the CV experiments were managed by electrochemical software GPES.

2.2 Electrochemical impedance spectroscopy

EIS technique offers a possibility for a quick and non destructive method for simultaneous evaluation of structural and electrical parameters of electrodes. It might be therefore an appropriate technique for determining the state of health of electrode plates in working lead-acid batteries as well as in control of manufacturing process. EIS initially have been applied to the determination of the double-layer capacitance and in ac polarography, they are now applied to the characterisation of electrode processes and complex interfaces. EIS studies the system response to the application of a periodic small amplitude (tenths of mV) ac signal. These measurements are carried out at different ac frequencies and, thus, the name impedance spectroscopy was later adopted. Analysis of the system response contains information about the interface, its structure and reactions taking place there. Complex plane (Nyquist) plots are the most often used in the electrochemical literature because they allow for an easy prediction of the circuit elements (the vertical axis represents the imaginary component of the impedance and the horizontal axis represents the real part of impedance). However, they do not show all details. Nevertheless, Nyquist plots allow for an easy relation to the electrical model. On the other hand Bode plots contain all the necessary information. That is why Bode plots are mainly used in the circuit analysis. The Bode magnitude plots may be easily predicted from the circuit impedance. The equivalent circuits method is commonly used to fit experimental data. From the shape of the resulting curve, experienced scientists can deduce a great deal of information about the condition of the electrode. A practical way to represent distributed processes such as corrosion on a rough and inhomogeneous electrode is with an element that follows its distribution such as a constant phase element (CPE). The CPE impedance takes the form [5] :

$$Z_{CPE} = (Q(j\omega)^n)^{-1} \quad (1)$$

where coefficient Q is a combination of properties related to both surface and electroactive species. The exponent n ranges between -1 to 1. The value of -1 is characteristic of an inductor, the value of 1 correspond to ideal planar capacitor. The value 0 corresponds to a resistor and the value of 0.5 corresponds to a porous electrode with semi-infinite pores (surface roughness). We can assume that single time constant corresponds to a single $PbSO_4$ layer and two time constants to a composite $PbSO_4$ layer. To analyse measured impedance data a general model of equivalent circuit for an electrode covered with reaction product has been postulated. To cover all possible phenomena at the electrode surface the model should included a parallel $C_1 - (R_2-CPE)$ element representing double layer capacity, charge transfer resistance and constant phase element representing the dielectric properties of the reaction layers, which is equivalent to an pseudo-electrical capacitance, in series with another $C_3 - R_3$ circuit representing double layer capacity and layer resistance in series with ohmic resistance of active material [6]. In some cases also inductance in series with electrolyte resistance R_1 was added. Equivalent circuit which represents surface anode layers on Pb electrode is presented in Fig. 2.

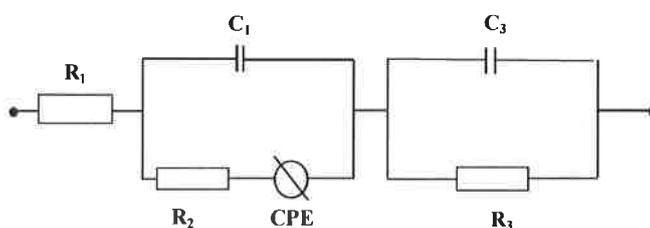


Figure 2. The equivalent circuit used for nonlinear fitting procedure.

Impedance spectra were measured in frequency interval from 10 Hz to 100 kHz, ac amplitude was 5 mV, 61 points were taken within measuring frequency range.

3. RESULTS AND DISCUSSION

3.1 SEM examination

The structure of the negative lead plate sample from the tested battery (obtained from our partner) was subjected to SEM examination. Following figures represent morphology of the original electrode surface.

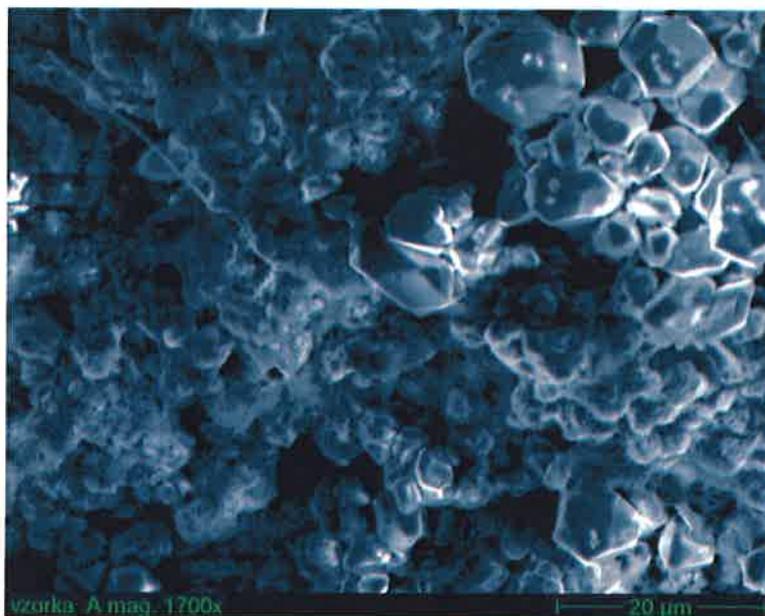


Figure 3. SEM micrograph of tested negative plate. Nicely visible primary (skeleton) structure (left) with PbSO_4 crystals (right).

Elements distribution on the negative plate surface was also investigated by line profile analysis (see following figures).

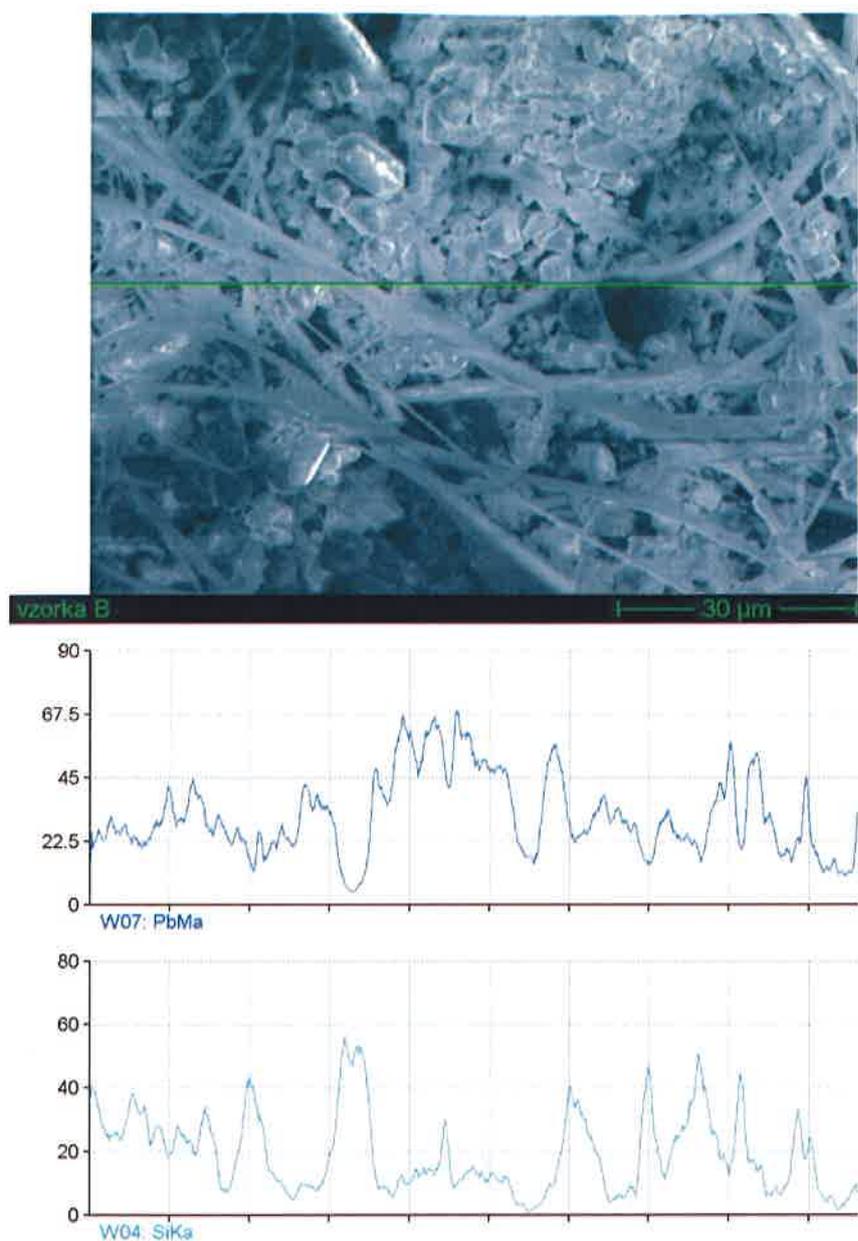


Figure 4. SEM micrograph of tested negative plate with micro porous AGM separator (fibres), primary (skeleton) structure and PbSO_4 crystals. Line profiles of elements (Pb, Si) according to the line marked on SEM picture are placed below SEM micrograph.

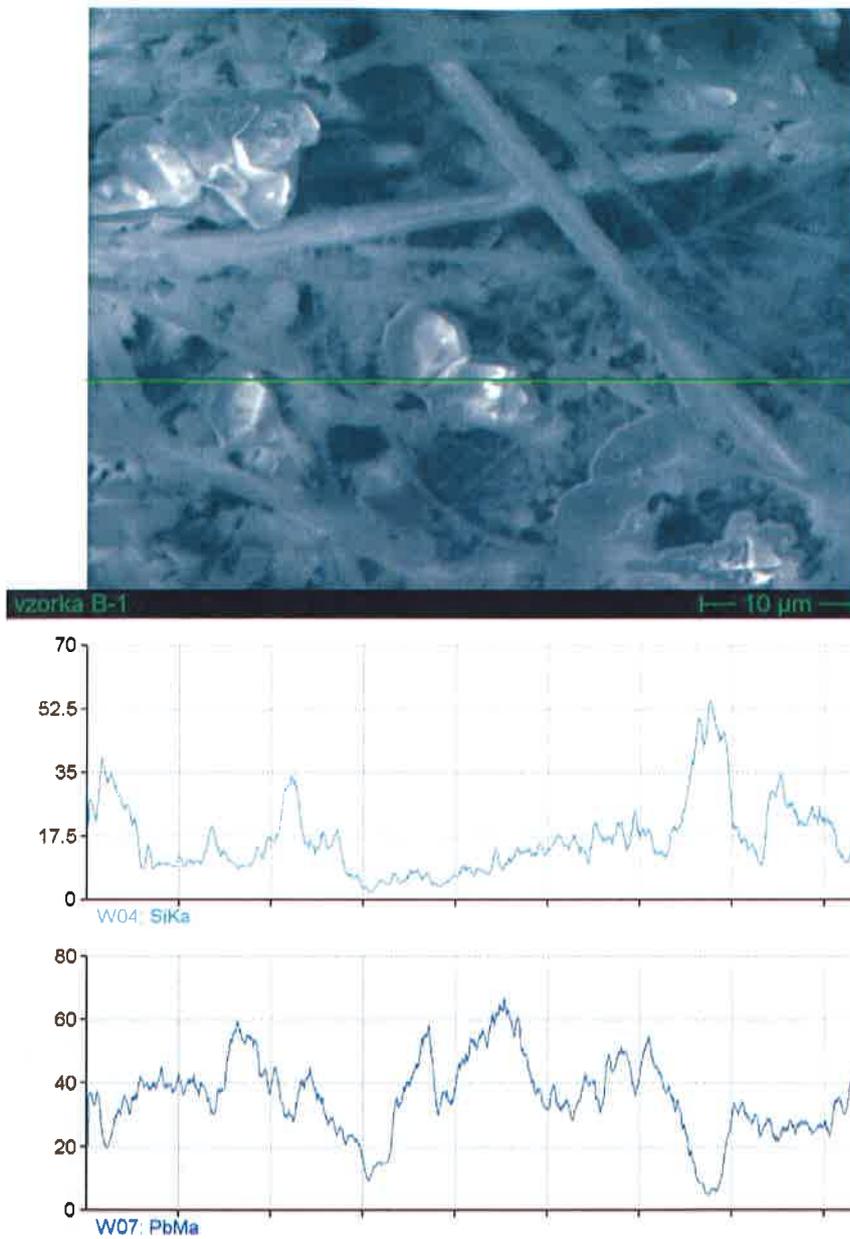


Figure 5. SEM micrograph of tested negative plate with micro porous AGM separator (fibres), primary (skeleton) structure and PbSO_4 crystals. Line profiles of elements (Pb, Si) according to the line marked on SEM picture are placed below SEM micrograph.

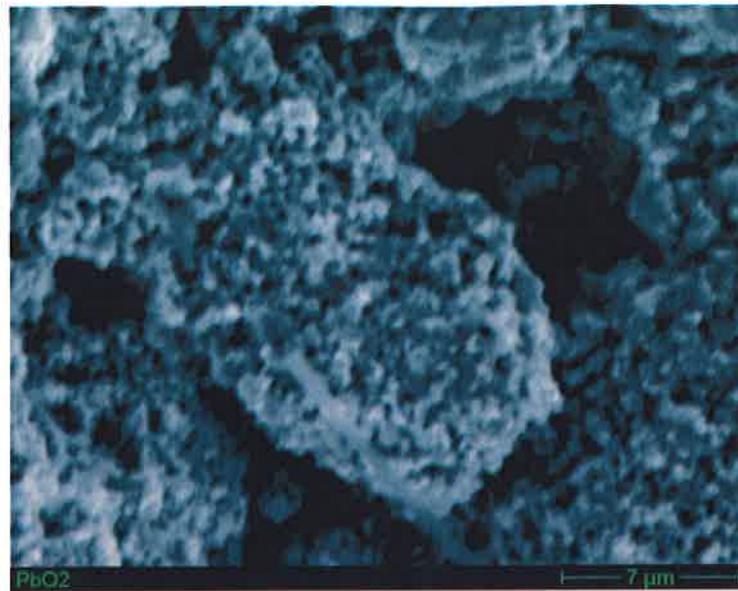


Figure 6. SEM micrograph of the surface of the tested positive plate - PbO_2 .

Next figure shows negative plate surface after addition of activator. No remarkable changes occurred on the electrode surface as we expected.

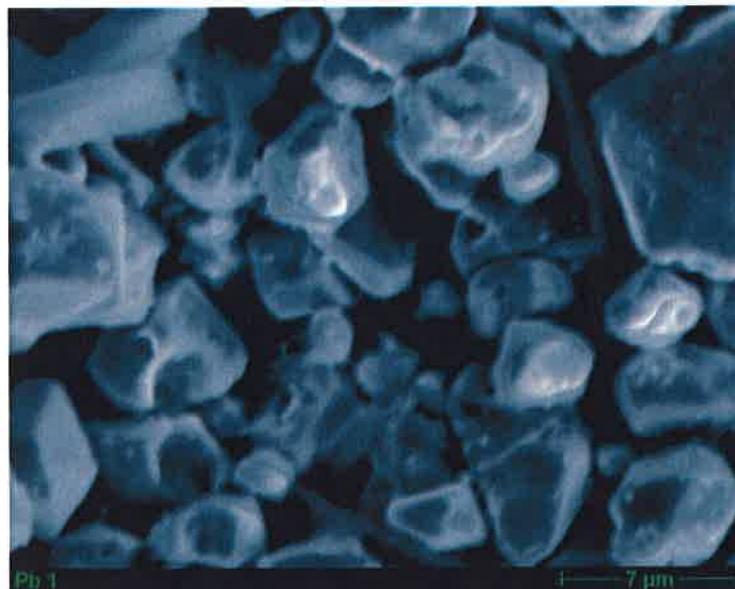


Figure 7. SEM micrograph of tested negative plate after addition of activator. Nicely visible PbSO_4 crystals.

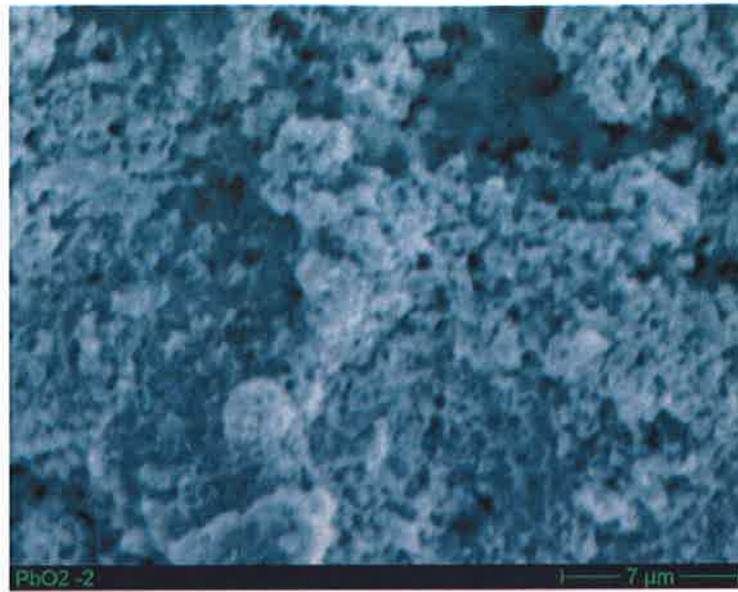


Figure 8. SEM micrograph of tested positive plate after addition of activator.

3.2 Cyclic voltammograms

Fig. 9. represents typical cyclic voltammogram (current-potential curve) of lead electrode (negative plate) at scan rate 100 mV s^{-1} in sulphuric acid environment at 25°C . Potentials are reported vs. reference electrode. Well defined current peaks at A1 and A2 represents the oxidation of metallic Pb to Pb(II) followed by a wide passive current region. At the high anode potential PbO_2 formation can be achieved. The cathodic process occurring in the potential ranges of current peaks C2 and C1 can be associated with the electroreduction of basic Pb(II) compounds (mainly PbO) and PbSO_4 layers, respectively.

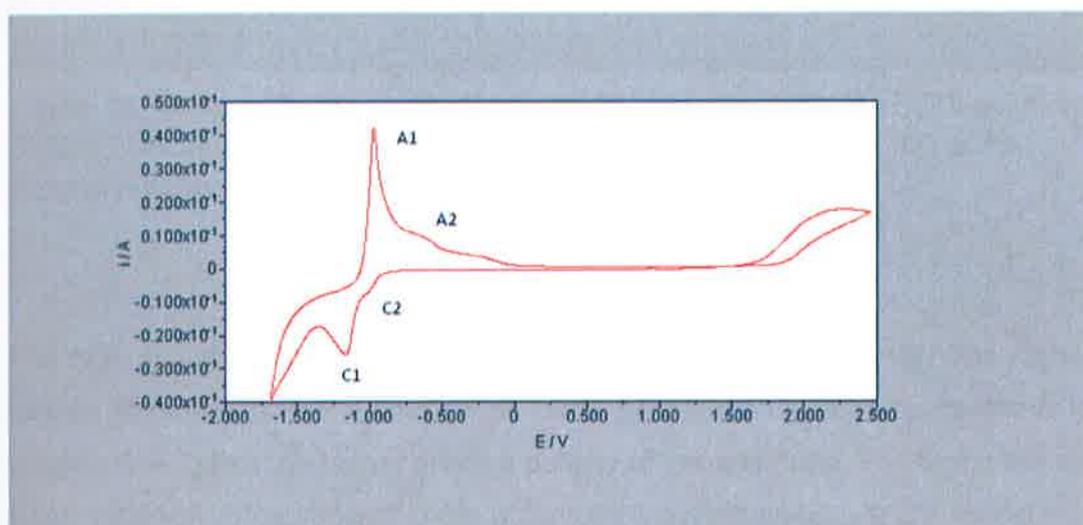


Figure 9. Cyclic voltammogram of original Pb negative plate in H_2SO_4 solution at 25°C . Scan rate 100 mV/s .

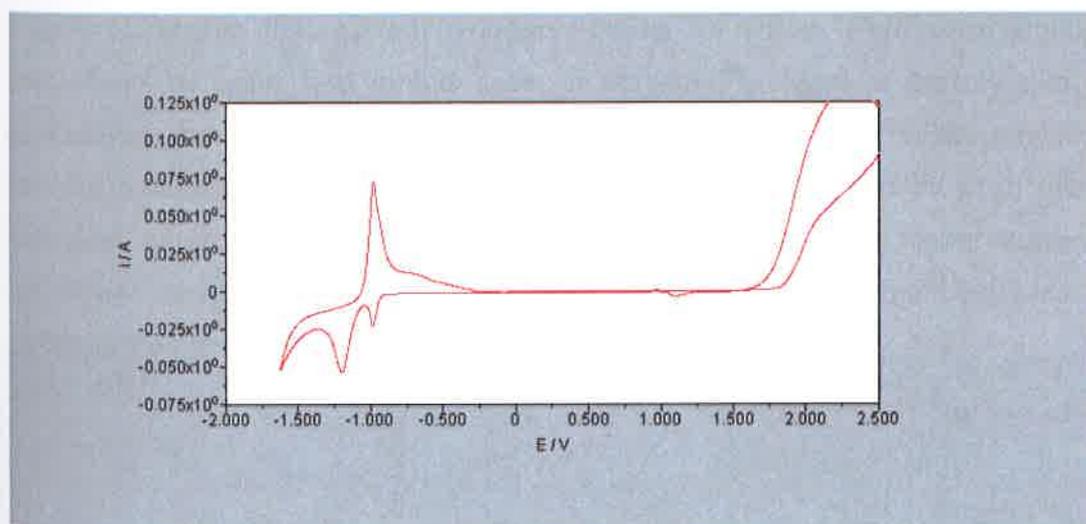


Figure 10. Cyclic voltammogram of original Pb negative plate in H₂SO₄ solution at 25 °C after activator addition. Scan rate 100 mV/s.

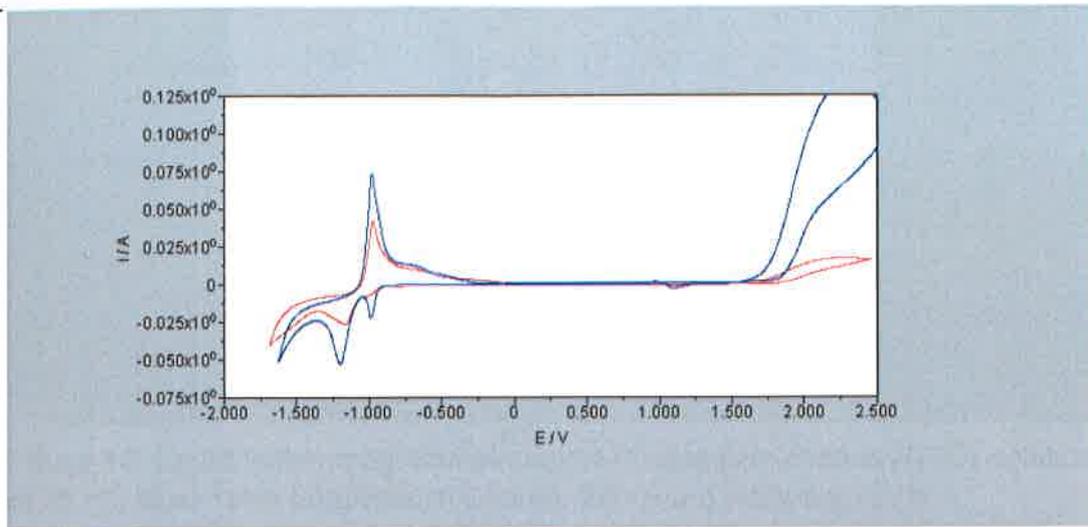


Figure 11. Cyclic voltammogram of original Pb negative plate in H₂SO₄ solution at 25 °C before (red) and after (blue) activator addition. Scan rate 100 mV/s, reverse potential $E_{rev} = 2.5$ V vs. ref. electrode.

The high activity of the electrode surface can be seen from Fig. 11. The higher current densities of the electrode at same polarisation potentials compare to original one, mean the higher surface activity of the electrode. The same results were obtained in the case of lower polarisation potentials ($E_{rev} = 2$ V vs. ref. el.) as one can see from Figs. 12 and 13.

Figure 12 shows that current oxidation peaks for Pb to Pb(II) are slightly influenced by scan rate in the case of original Pb negative battery plate, pasivation phenomena occurred. After activator addition into H₂SO₄ solution current oxidation peaks for Pb to Pb(II) are strongly influenced by scan rate, diffusion control on the electrode surface takes place. Also higher current densities, compare to original one, were obtained at the same polarisation potentials which means higher surface activity in this case.

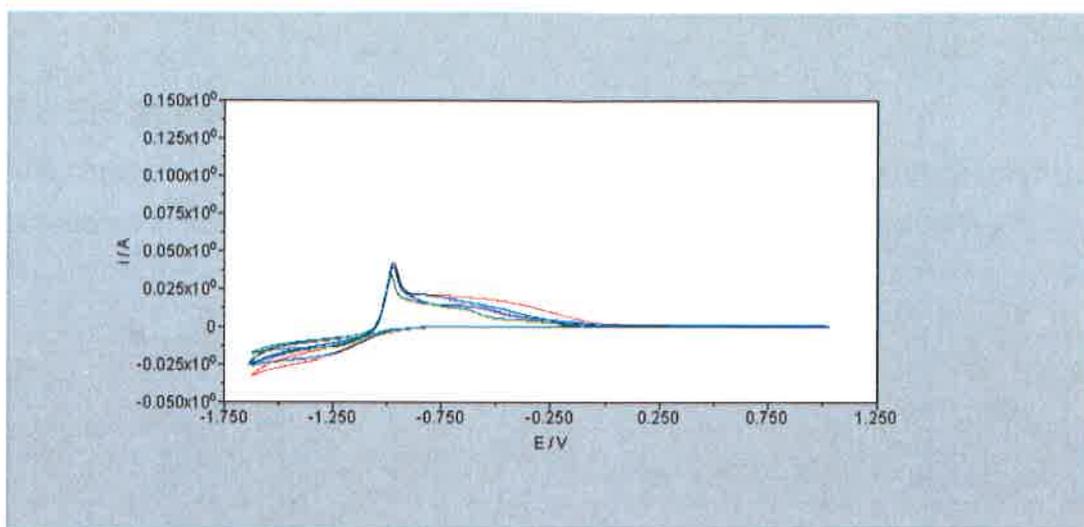


Figure 12. Cyclic voltammograms of original Pb negative plate in H_2SO_4 solution at $25\text{ }^\circ\text{C}$. Scan rates 50(green), 100(blue), 200(cyan), 400(red) mV/s.

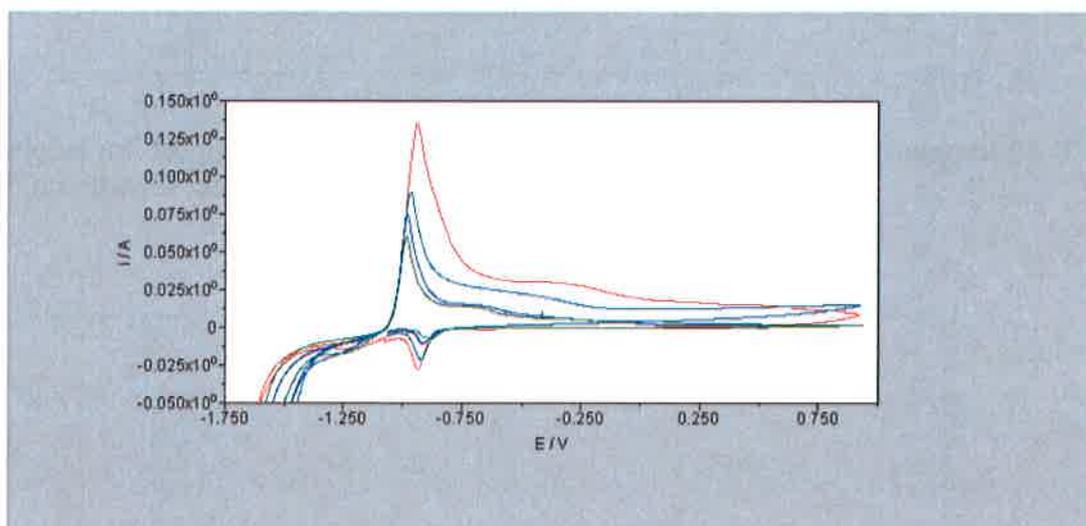


Figure 13. Cyclic voltammograms of original Pb negative plate in H_2SO_4 solution at $25\text{ }^\circ\text{C}$ after activator addition. Scan rates 50(green), 100(blue), 200(cyan), 400(red) mV/s.

3.3 EIS spectra

The complex-plane impedance plots (Nyquist diagrams and Bode diagrams) are presented in following figures for Pb negative plate of the tested battery.

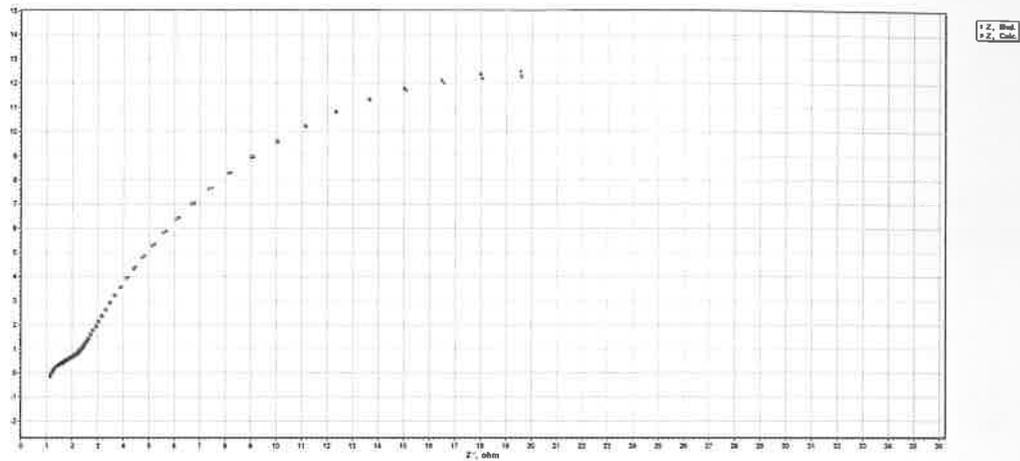


Figure 14. Nyquist plot of original Pb negative plate in H_2SO_4 solution at $25\text{ }^\circ\text{C}$. Experimental data and calculated data are marked in the figure.

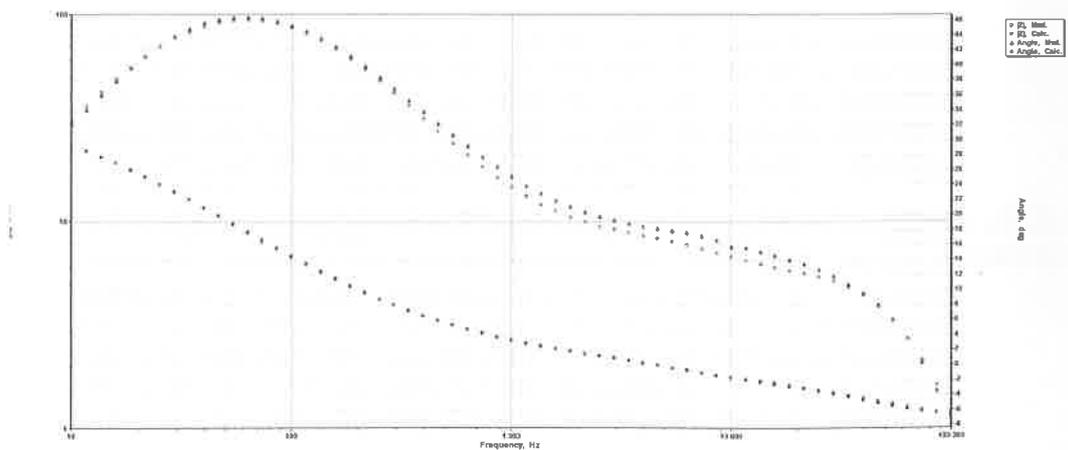


Figure 15. Bode plot of original Pb negative plate in H_2SO_4 solution at $25\text{ }^\circ\text{C}$. Experimental data and calculated data are marked in the figure.

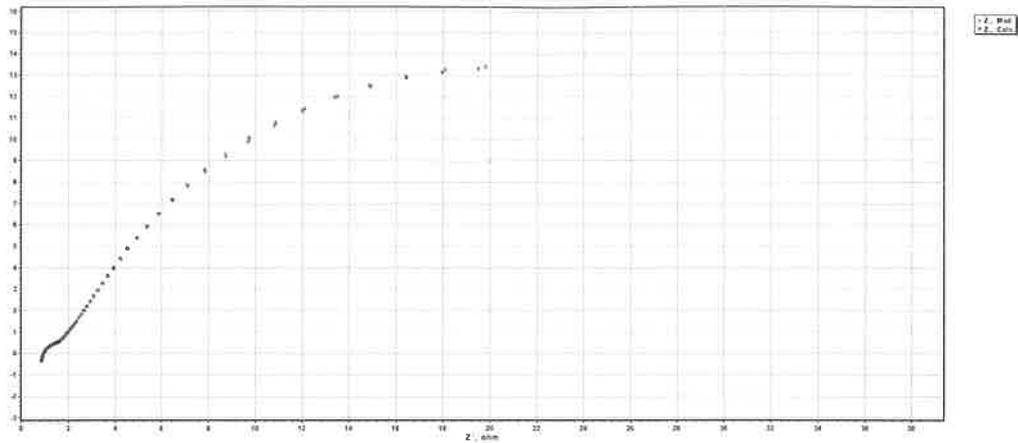


Figure 16. Nyquist plot of original Pb negative plate in H_2SO_4 solution at $25\text{ }^\circ\text{C}$ **after** activator addition. Experimental data and calculated data are marked in the figure.

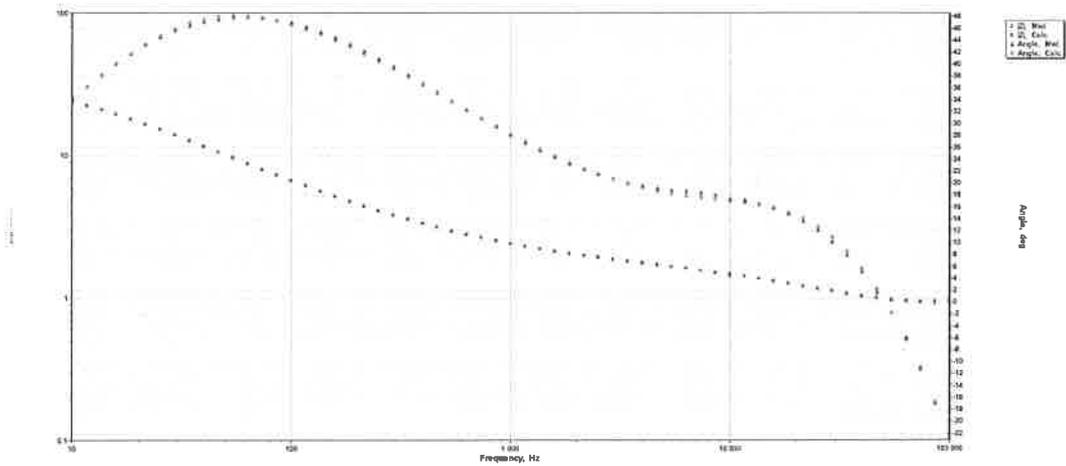


Figure 17. Bode plot of original Pb negative plate in H_2SO_4 solution at $25\text{ }^\circ\text{C}$ **after** activator addition. Experimental data and calculated data are marked in the figure.

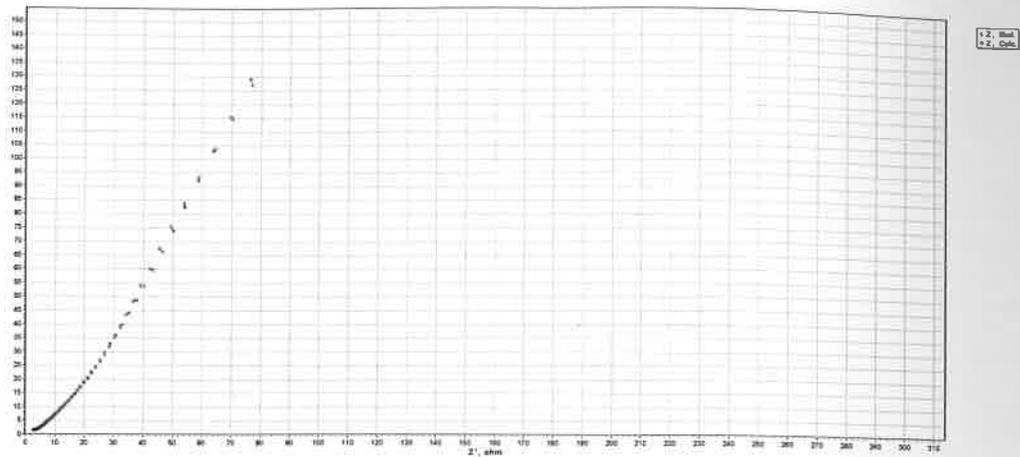


Figure 18. Nyquist plot of original Pb negative plate in H_2SO_4 solution at $25\text{ }^\circ\text{C}$ **one day** after activator addition. Experimental data and calculated data are marked in the figure.

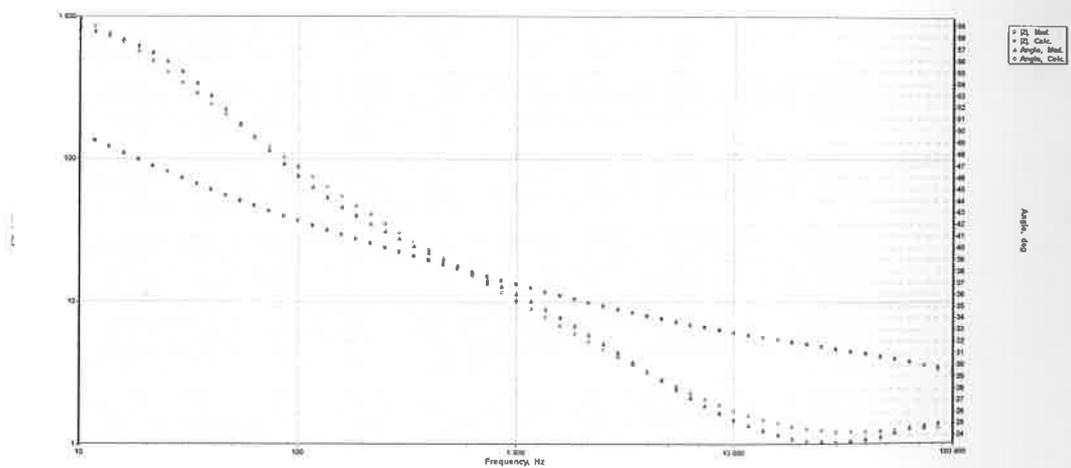


Figure 19. Bode plot of original Pb negative plate in H_2SO_4 solution at $25\text{ }^\circ\text{C}$ **one day** after activator addition. Experimental data and calculated data are marked in the figure.

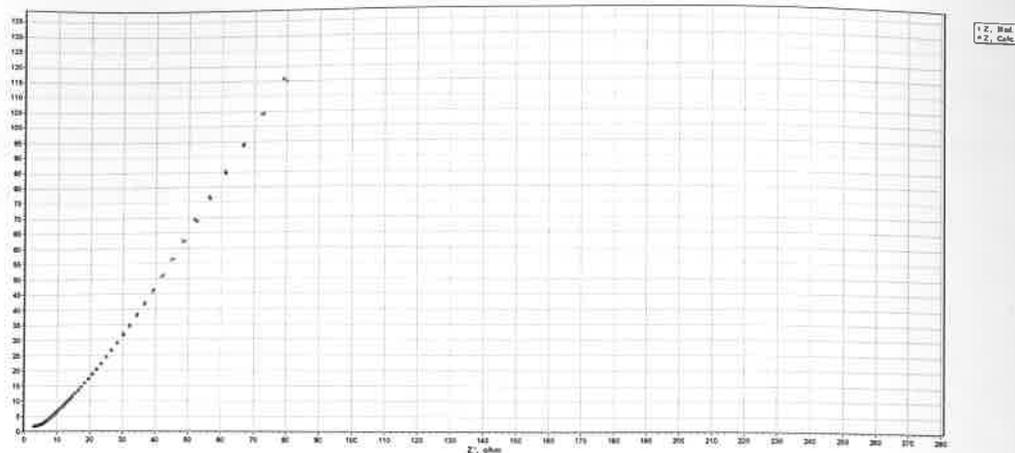


Figure 20. Nyquist plot of original Pb negative plate in H_2SO_4 solution at $25\text{ }^\circ\text{C}$ **seven days** after activator addition. Experimental data and calculated data are marked in the figure.

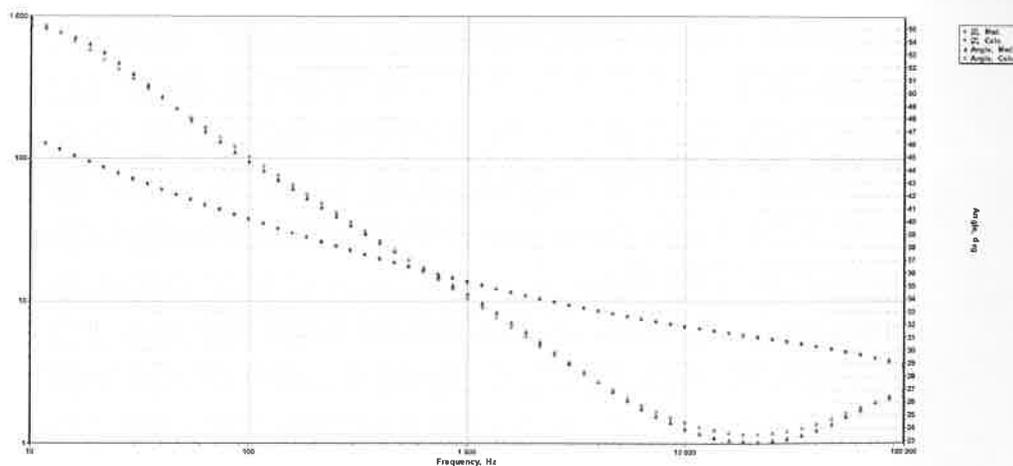


Figure 20. Bode plot of original Pb negative plate in H_2SO_4 solution at $25\text{ }^\circ\text{C}$ **seven days** after activator addition. Experimental data and calculated data are marked in the figure.

The impedance spectra were fitted by using the equivalent circuit in Fig. 2, and the values of the equivalent circuit elements obtained are presented in following figures. Data obtained show that the properties of the surface layers changed dramatically after activator addition. The most important parameter characterising surface irregularities (n) is decreasing, which means increase of surface roughness of primary skeleton. Double layer capacity of interface layer

is increasing after activator addition in two magnitudes of order. This observation supports the theory that activator addition can increase surface reactivity. Furthermore, this is consistent with the CV results, which showed higher current densities of the electrode at same polarisation potentials, the reactivity of the electrode surface increased.

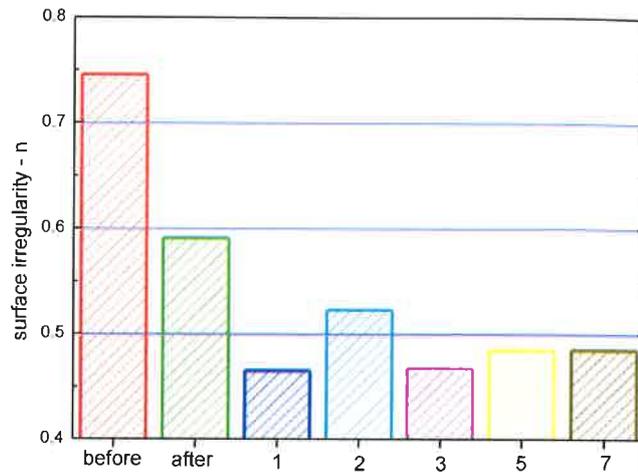


Figure 22. The surface irregularities of the Pb negative plate in H_2SO_4 solution at 25 °C. Before means before activator addition, after means immediately after activator addition, number represents days after addition.

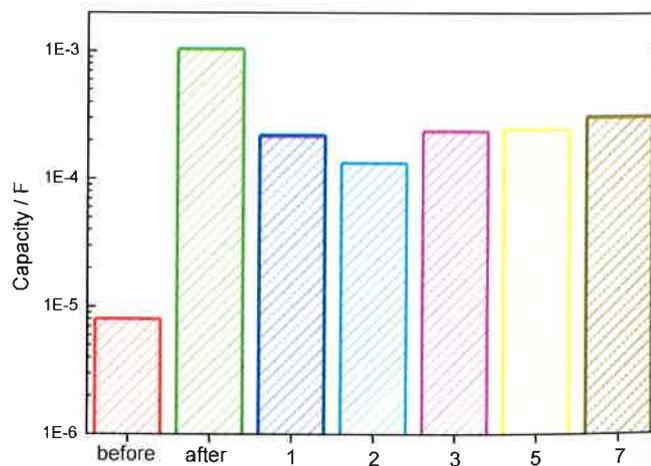


Figure 23. The capacity of active material Pb negative plate in H_2SO_4 solution at 25 °C. Before means before activator addition, after means immediately after activator addition, number represents days after addition.

Measured EIS spectra of positive plate battery electrode (PbO_2) did not show any remarkable changes in its shape, activity of the electrode is still very high.

Measured EIS spectra of negative plate battery electrode (Pb) did not show any changes in its shape after activator addition in several weeks.

4. CONCLUSIONS

The electrochemical behaviour of negative (Pb) and positive (PbO₂) battery plate was studied in the wide range of polarisation potentials before and after activator – PowerBatt - addition. The investigation was performed in H₂SO₄ solution by means of cyclic voltammetry and electrochemical impedance spectroscopy technique. Samples were taken from the plates for SEM analysis. SEM imaging showed the primary (skeleton) structure serving as a current collector and mechanical support of the lead. The secondary (energetic) structure participates mainly in the charge-discharge processes and is represented as PbSO₄ crystals on the electrode surface (Fig. 3). No remarkable changes occurred on the electrode surface after the activator – PowerBatt - addition to the solution as we expected (Figs. 7 and 8).

Cyclic voltammograms show low peak current densities of oxidation peaks for Pb to Pb(II) in the case of the original negative battery plate (Fig. 12). The activator – PowerBatt - addition increased current densities (about two times) of the measured peaks it follows high electrochemical surface activity in this case (Fig. 13).

The EIS spectra of the negative battery plate show totally different behaviour in the case of the activator – PowerBatt - addition. The impedance spectrum of the original negative plate is characterised with two semicircles corresponding to the composite PbSO₄ – oxide layer (Figs. 14 and 15). Development of the parameter n which is used to characterise surface irregularities is shown on Fig. 22. It is decreasing from 0.75 to approx. 0.5 a typical value for highly porous electrode. Double layer capacity of the interface layer is increasing after the activator PowerBatt addition in two magnitudes of order (Fig. 23). This observation supports the theory that the activator – PowerBatt - addition to the solution can increase surface reactivity. Furthermore, this is consistent with the CV results, which showed the higher peak current densities of the electrode at

same polarisation potentials, the electrochemical activity of the electrode surface increased.

Measured EIS spectra of positive plate battery electrode (PbO_2) did not show any remarkable changes in its shape, the electrochemical activity of the electrode is still very high.

Measured EIS spectra of negative plate battery electrode (Pb) did not show any changes in its shape after activator – PowerBatt - addition in several weeks.

Finally, all electrochemical techniques used for characterisation of the electrode electrochemical surface activity support positive influence of the activator – PowerBatt - addition on the electrochemical activity of the electrode plates in the tested battery. The activator – PowerBatt - can be recommended as an additive to keep electrodes electrochemically active in proposed concentration range.

REFERENCES

1. Parker CD., J. Power Sources 100, 18-28(2001).
2. Hejabi M., Oweisi A., Gharib N., J. Power Sources 158, 944-948(2006).
3. Pavlov D., Iliev V., J. Power Sources 7, 153-164(1981/82).
4. Iliev V., Pavlov D., J. Power Sources 15, 39-52(1985).
5. MacDonald J.R., J. Electroanal. Soc. 223, 25-50(1987).
6. De Marco R., Lowe A., Sercombe M., Singh, Electrochim. Acta 51, 2088-2095(2006).

