SUMMARY OF EIS RESEARCH OF LEAD-ACID BATTERIES

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ABSTRACT

This is summary of our progression in research of lead-acid batteries using electrochemical impedance spectroscopy (EIS). EIS is non-destructive method that uses impedance measurement in wide range of frequencies to analyse electrochemical systems. This paper also deals with our effort to develop new type of EIS measurement.

1. INTRODUCTION

Lead-acid accumulators are widely used for their properties – cheap price, recyclability and robust design[1] and it seems that these accumulators will be still used in the future. That is why research on this topic is so important and still continuous.

The first lead-acid accumulator was constructed by Gaston Planté in 1859 [2]. From that time it went through various design changes – from flooded types at the beginning to VRLA-regulated ones nowadays. There are also attempts to develop bipolar lead-acid accumulator, but those are not ready for commercial use yet.

2. EXPERIMENTAL

2.1. Electrochemical impedance spectroscopy

Electrochemical impedance measurement of electrochemical systems was rapidly developed for last thirty years. Acquired data can be easily represented as equivalent circuits that consists of electronic elements like resistors, capacitors, inductors and special elements like constant phase element (CPE) and Warburg impedance.

EIS can give us information about corrosion rate of lead alloys in sulphuric acid and about changes in active masses of electrodes. This method is non-destructive, so experiment can continue.

2.2. Four point measurement method

Four point measurement method is used in it's DC form at our department of electrotechnology for about 20 years. It is based on resistance measurement. Now we would like to merge this method with EIS measure principles. New method uses alternating current for measurement in wide range of frequencies. See our experimental electrode at fig 1 and 2:

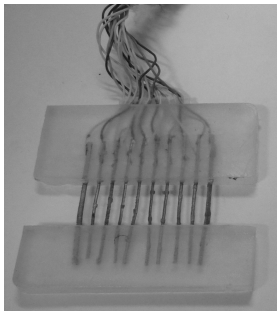
1. step: Measuring alternating current flows through rib i and rib i+2. U_1. Voltage U_1 is measured between ribs i and i+1. From equivalent scheme:

$$U_1 = I\left(R_{pi} + Z_{ki} + Z_{mi,i+1}\right), i = 2,3,\ldots,8 \qquad (1)$$

2. step: Measuring current of the same size as in step 1 flows through rib i-1 and rib i+2. Voltage U2 is measured between ribs i and i+1 and is represented by:

$$U_2 = IZ_{mi,i+1}, i = 2,3,\ldots,8 \qquad (2)$$

At first step we theoretically measure compounded impedance Z_m+Z_k and in second step we measure only impedance of electrolyte Z_m. When we substract these two values we get impedance of corrosion layer[3].



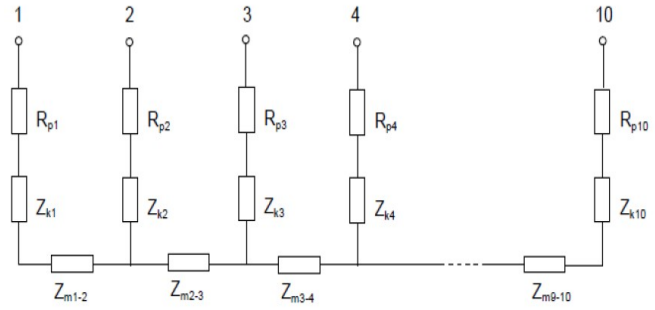


Fig. 1 and 2. Experimental electrode and its equivalent scheme

2.3. World research of lead-acid accumulators impedance measurement

Effort to develop impedance model for lead-acid accumulator begun about year 1950. At first only mathematical models were used. First models of lead-acid accumulator based on electrical elements occurred about year 1980. But nobody probably considers phenomenons like SOC, acid concentration, temperature and other together until 2005 [4]. But only few publications deals with EIS on lead-acid accumulators.

2.4. Experiment

To interpret dependencies of real and imaginary part of impedance we used potenciostat BioLogic VSP. Measurement of positive electrode was made for frequencies form 200 kHZ to 0.1 Hz. Maximal voltage response was set to 30 mV, stabilizing time was set half of period. Results of our measurement are presented at fig 3. Highest frequencies shows positive values of imaginary part of impedance, this we assume is because of inductance of circuit.

Red progression in Fig 3. represents second measure step, theoretically compound of impedance of electrolyte Zm and corrosion layer Zk. From graph is evident that we can apply two RC networks and their time constant differs at least by one digit place.

Diffusion represented by Warburg's impedance occurs again for low frequencies. First two progressions in graph are a bit flat that means that capacity in equivalent diagram should be replaced by capacity element with constant phase.

Blue progression in Fig 3. represents first step of measurement, theoretically electrolyte impedance Zm. From graph is evident that progression is influenced by capacity of double layer and that diffusion occurs at lowest frequencies.

Green progression in Fig. 3 is final dependency of corrosion layer Rk. This progression is represented only by RC network. Progression shows half of circle from highest frequencies to aprox. 12 Hz, where diffusion occurs.

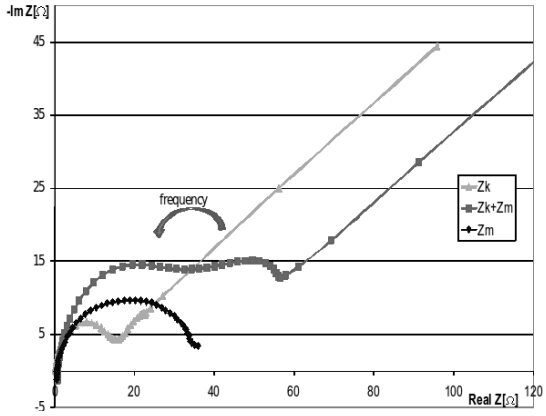


Fig. 3 and 4. Measured data and potenciostat VSP

2.5. TWO-POINT AND FOUR-POINT MEASUREMENT

In two-point measurement we use our experimental electrode and working electrode. In four point measurement we measure among ribs of experimental electrode.

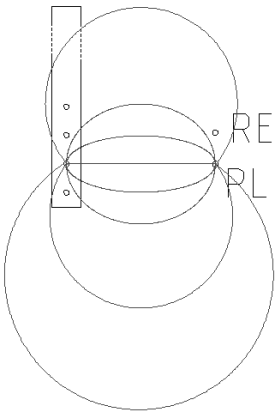


Fig. 5 and 6. Two-point and four-point measurement

Next we want to realize long-term experiment of electrode with uncoated ribs from various metals. And also with electrode with positive active mass. We expect that two-point method as it is seen at fig. 5 will give us information about surface and four-point method will give us information especially about inner part of electrode.

3. CONCLUSIONS

Our experiments shows that both methods seems usable for corrosion rate monitoring. We expect that our two step alternating current method will give us more information about processes then standard two step method.

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