

Impedance Measurement of Lead-Acid Accumulator in Different State of Charge (SOC) by Difference Method

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Received: 31 October 2013 / Accepted: 8 March 2014 / Published: 14 April 2014

This paper deals with impedance measurements of lead-acid accumulator. New AC difference method (ACDM) was developed to obtain experimental data. The original DC difference method (DCDM) was established earlier at our Power Sources Laboratory of Brno University of Technology [1, 2]. New method in its AC nature is also a close relative to electrochemical impedance spectroscopy (EIS). The DCDM and also the new ACDM are both non-destructive, which means that experimental data can be obtained *in situ*. New method provides more accurate set of information because it can be used in wide frequency range. Unlike the EIS the DCDM method gives us more information about current collector/active mass contact layer and active mass itself. In this paper, the new method was used to compare lead-acid accumulator in different states of charge. Electrodes were analysed with special attention to collector /active mass double layer and to active mass itself. Obtained data contributed to better understanding of involved degradation mechanisms.

Keywords: Impedance, Lead-Acid Accumulator, SoC

1. INTRODUCTION

DC difference method (DCDM) was developed by a team of power sources scientists that was led by Doc. Calabek about twenty years ago. DCDM can be used to distinguish resistivity of interphase collector/active mass from resistivity of active mass itself. Results obtained by this method were published several times. Observation of progressive changes of corrosion layer between collector ribs and active mass of lead-acid accumulator by evaluating resistivity changes is greatest success of this method. This is crucial for evaluation capacity loss effects known as PCL1 and PCL2 [1-6].

The DCDM was significantly extended recently to create brand new AC difference method (ACDM). For measurements alternating current of wide range of frequencies is used. Whilst DC method produces single resistivity value as a result, AC method produces impedance curve in imaginary plane. ACDM can be compared with electrochemical impedance spectroscopy (EIS). ACDM and EIS have a lot of attributes in common. Main differences come out from simple fact that ACDM is two steps method and also that four-point measurement is used. It is true that EIS facilitates four-point measurement either, but four-point measurement is used under specific circumstances e.g. measurements of electrochemical cell separated by membrane.

Furthermore EIS measurements are usually performed on complete electrochemical cell or half-cell. ACDM on the other hand is performed on special experimental electrodes with system of non-continuous parallel ribs. Each rib can be used as an electrode in the measurement. Results provided by ACDM correspond mainly to inner environment of the experimental electrode. For example oxidized layer on the surface of positive electrode collector can be easily observed using this method [7].

Necessity to use our own design experimental electrodes rather than industry produced ones is the main drawback of ACDM. Each collector rib has to have its own voltage and current wires attached. Figure. 1 shows such experimental electrode yet without active mass applied.

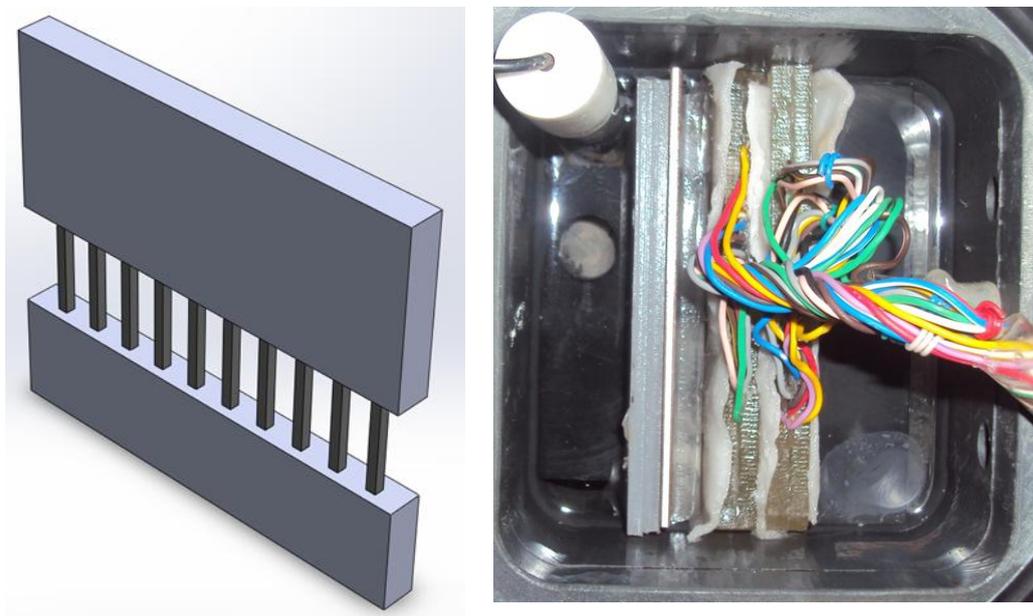


Figure 1. Experimental electrode

Figure. 2 represents impedance scheme of experimental electrode. Impedance $Z_{mi-(i+1)}$ represents active mass impedance between rib i and rib $i+1$, Z_{ki} represents impedance of interphase no. i of collector/active mass, finally impedance Z_{pi} represents wire impedance of rib no. i .

Wire impedances can be measured prior addition of active mass, but this impedance has character of resistivity or inductive reactivity so it can be neglected.

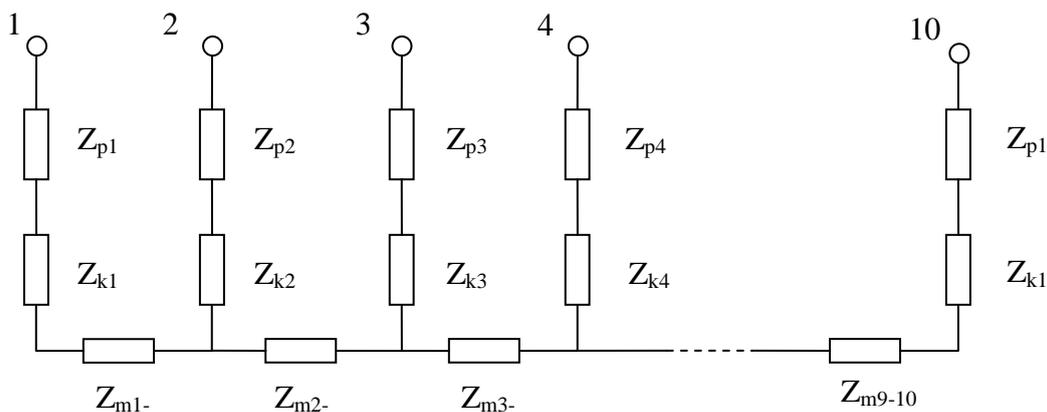


Figure 2. Electrical scheme of experimental electrode

ACDM can be used for independent measurement of Z_{ki} of corrosion interphase of eight inner ribs and for measurement of active mass impedance Z_m .

Measurement is performed in two steps followed by calculation of impedance Z_{ki} . In each step large number of results is obtained for each individual frequency producing impedance curve in imaginary plane. Calculation of Z_{ki} is only possible if data for Z_{ki} evaluation are obtained at precisely same frequencies [9].

1. step: AC current flows through rib i and rib $i+2$. Voltage U_1 is measured between ribs i and $i+1$. From scheme in Figure. 2:

$$U_1 = I(Z_{p_i} + Z_{k_i} + Z_{m_{i,i+1}}), i = 2,3, \dots 8 \tag{1}$$

2. step: Current of same value as in step 1 flows between ribs $i-1$ and rib $i+2$. Voltage U_2 is measured between ribs i and $i+1$ and its value is:

$$U_2 = IZ_{m_{i,i+1}}, i = 2,3, \dots 8 \tag{2}$$

Calculation of Z_k : Impedance of impedance Z_k is then calculated using this formula:

$$Z_k = \frac{(U_1 - U_2)}{I} - Z_p \tag{3}$$

Where Z_p is wire impedance. Value of wire impedance is in order of single ohms and usually can be neglected.

Impedance of active mass Z_m can be calculated using this formula:

$$Z_m = \frac{U_2}{I} \tag{4}$$

2. EXPERIMENTAL PART

Main aim of the experiment presented in this paper was to find out impedance curves Z_k and Z_m for experimental positive electrode of lead-acid accumulator in various states of charge. The cell was compiled with one positive electrode and two negative electrodes prepared from industrial samples. The cell construction was based on flooded design with electrolyte concentration 1.28 g/cm^3 . The cell did not contain any separator however the electrodes were fixed to distance 1.5 mm. Experimental cell

was discharged by 0.25 C₂₀ current. Measurements were performed at 100%, 70%, 35% and 0% SoC. The discharging was interrupted on each SoC state and then the cell was standing for 10 minutes long period because of change of internal parameters. After this procedure ACDM measurement was performed. Then the cell was discharged to the next SoC state etc.

3. RESULTS AND DISCUSSIONS

Figure 3. shows of impedance Z_m . real and imaginary part of impedance are growing with decreasing SoC of experimental cell (SoC 100% means fully charged cell). At lower frequencies was pronounced influence of diffusion. However angle of curve does not correspond with Warburg's impedance (45 angle degrees). We assume that in low frequencies the cell was not stabilized for a sufficiently long period and the measurement is influenced by this phenomenon.

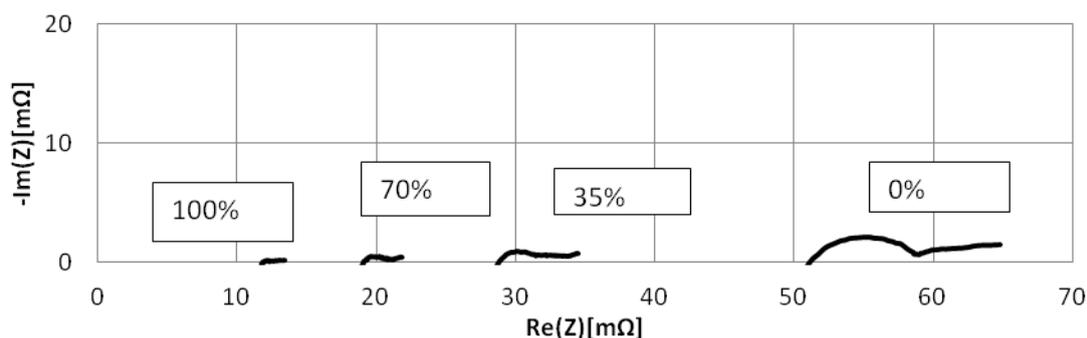


Figure 3. Impedance Z_m of positive electrode, different state of charge

Table 1 shows values obtained by fit of impedance curve with equivalent circuit R_1+R_2/CPE (or serial connection of resistivity R_1 and parallel combination of resistivity R_2 and constant phase element CPE, where α means the angle of rotation in complex coordinates.

Table 1. Values of equivalent circuit of impedance Z_m depending on SoC

SoC [%]	100	70	35	0
R_1 [Ω]	0.01	0.02	0.03	0.05
α [-]	0.6	0.6	0.8	0.6
CPE [$Fs^{(\alpha-1)}$]	131.80	7.03	0.37	0.83
R_2 [$m\Omega$]	0.65	1.82	2.47	8.08
PseudoC [F]*	20.61	0.51	0.09	0.05

*PseudoC is capacitance that would be obtained if C was used instead of CPE

The Table 1 shows:

1) Point in which impedance curve intersects real axis is moving to the right. This change is reflected in rising of table values of R_1 . Reason for this is probably decrease of electrolyte concentration in the active mass pores as accumulator is discharged (there are less ions that can lead electric current in electrolyte and amount of water increases).

2) For fit of semicircle that represents a double layer, RC equivalent circuit can be used or more precise circuit of parallel connection of resistor and CPE, because semicircle is flattened. Increase of size of semicircle with advancing discharge of active mass can be interpreted as active mass resistivity increase because it is R_2 that influences shape of semicircle. How much the semicircle is flattened is given by α , that is approximately 0.6 all the time of experiment. Deviation of α and CPE at 35% SoC is probably a mistake. Pseudo C represents capacitance that would be obtained if C was used instead of CPE in equivalent circuit. It can also be seen that with decreasing SoC the value of capacitance is increasing. This change can be explained by decreasing of size of active electrode surface during chemical reaction of active mass lead dioxide to lead sulfate.

Figure 4. shows impedance Z_k of interphase collector/active mass. Imaginary part of impedance Z_k decreases to zero at low frequencies. This means that no diffusion processes take place at this interphase, or diffusion processes takes a longer time than the lowest frequencies used for measuring. Slight difference in direction of curves at the lowest frequencies could suggest beginning of new semicircle there, but is probably caused by low measuring precision.

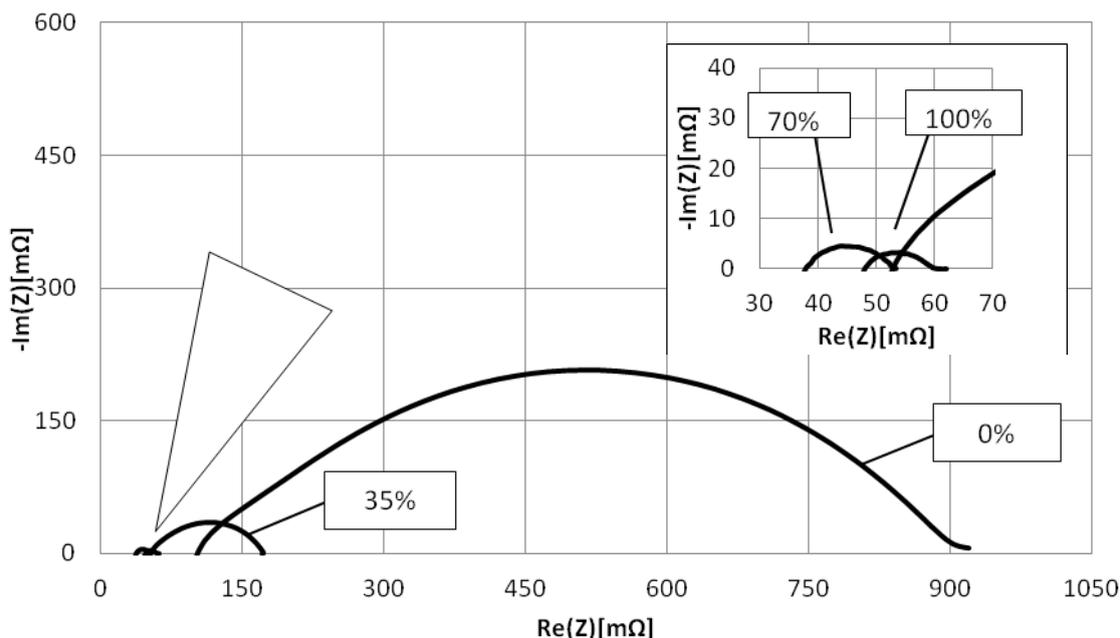


Figure 4. Impedance Z_k of positive electrode for different SoC

Impedance Z_k nonlinearly changes with SoC. The most pronounced change in impedance Z_k can be seen in case of fully discharged accumulator. This change corresponds with continuing transformation of lead dioxide to lead sulphate deep in electrode near to the current collector. This

transformation starts at the end of discharging.

Table 2. Values of equivalent circuit of impedance Z_k depending on SoC

SoC [%]	100	70	35	0
R1[Ω]	0.05	0.04	0.05	0.10
α [-]	0.7	0.7	0.7	0.6
CPE[$Fs(\alpha-1)$]	0.44	0.22	0.06	0.06
R2[m Ω]	0.01	0.02	0.12	0.82
PseudoC[mF]*	26.00	21.00	6.61	6.94

*PseudoC is capacitance that would be obtained if C was used instead of CPE

Impedance Z_k is composed from impedance of interphase of lead collector/positive active mass and from oxidized layer between lead collector and positive active mass (corrosion layer) steadily created during experiment.

Increase of impedance Z_k values can be explained by two mechanisms:

1) Active mass changes to lead sulphate and is discharged so deep that it changes interphase from collector/lead dioxide to collector/lead sulphate that has higher impedance.

2) Collector is covered with mass with higher impedance than in the rest of active mass. This effect is called as PCL-1 in a scientific journals.

Most probable explanation is the first one because impedance Z_k changed rapidly when the cell was fully discharged.

Table 2 shows enumerated impedance Z_k of positive electrode. Impedance curve was fitted with the same equivalent scheme as above.

We expect that the R1 value is composed of wires resistance and electrolyte resistance interphase. We can find that R1 in the beginning of discharge decreases and at the end of discharging grows. It indicates that R1 can contain another mechanism with ohmic character.

Capacitance of interphase collector/active mass is much smaller than in case of active mass. This finding is in good agreement with presumption that Z_k will be lower because of its smaller surface. Capacitance is decreasing with SoC, but contrary from Z_m where the decrease of capacitance was about 4 magnitudes, on Z_k the decrease is only 1 magnitude lower. We can say that the cell interphase area is not significantly affected in a full discharge state [8].

It is apparent that increase of both values of interphase (R_2 and PseudoC) occurs when the accumulator reaches 35% SoC. The interphase area of lead collector/positive active mass is reached when the cell is discharge to 75% of SoC.

Pulse formation experiment

After the function of the new method was verified in the previous experiment the testing started on the electrodes under pulse formation process. The goal was to compare the rates of the active masses. We had to check the existing formation method based on 4 ours of charging and 2 hours of standing with the specific pulse formation profile. The potentials and cell voltage were measured and

evaluated. The experiment was supplemented with impedance measuring.

Four experimental cells contained one positive and negative electrode. New regimes of the formation were propounded because of different formation profile of each electrode. The common property for all pulse profiles was charge of 12 Ah. This value is typical for the standard used method. The charging current was computed based on 90 hours of formation process. The pulse profiles were differed in a current level and pulse length. After the positive pulse followed short depolarization pulse and 3 seconds standing period.

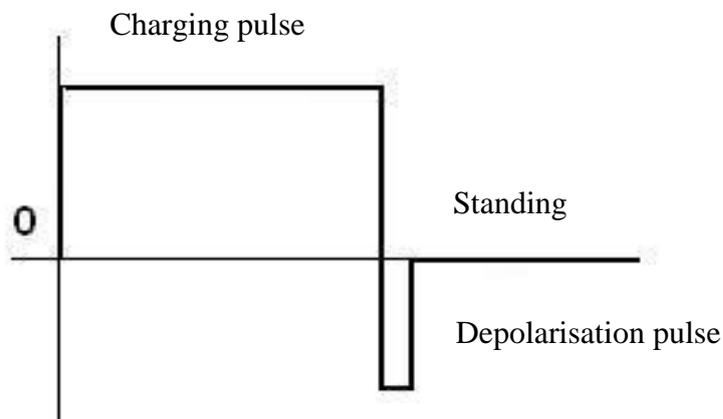


Figure 5. Current profile of the pulse formation

Table 3. Details of applied formation profiles

Cell number	Pulse length [s]	Current level [A]	Standing time [s]
1	4.5	0.3	3
2	12	0.16	3
3	2	0.333	3
4	2	0.333	12

Conditioning cycles started after the formation proces. Due to this the capacities of the cells were measured. The final capacity is one of the primary parameters of active mass formation. This important chart is figured in this section because of the result disscusion.

The previous chart shows that the initial capacity of the first three cell sis about 1.5 Ah. The best formation profile was got in in the first case because the highest final capacity which is not so stable, but in the global point of view the capacity stayed the same in the lifecycle. The capacity of the second cell is quiet smaller, but without any variance. Drop down of the capackity was the same as the first cell.

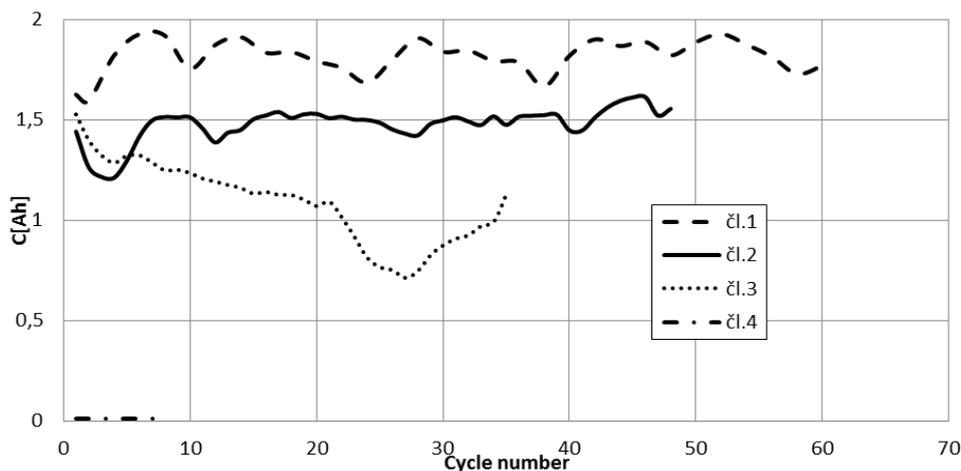


Figure 6. Capacity profile during conditioning cycles

The third cell had a little bit higher capacity than second cell, but after a few cycles this value felt down. The last cell had really small capacity and the final voltage (1.6 V) was achieved in a short time.

The capacity of the fourth cell correspond with a data from formation itself. Potential are shwon in figures compared with referent electrode which has potential in face of standard hydrogen electrode equal to 0.64 V. The following charts show voltage and pontential at the end of the charging pulse or standing. Higher predicative information has the voltage (pontential) during charging. It say us information about total electrode polarisation. If the polarisation is lower (difference of the pontetials from steady state), the charging capability is better. The speed of electrolysis grows with a electrode polarisation. We have found the similar beahvour in [8].

The voltage drop (potentials) during standing reflects diffusion processes which take place in concentration gradients compensation.

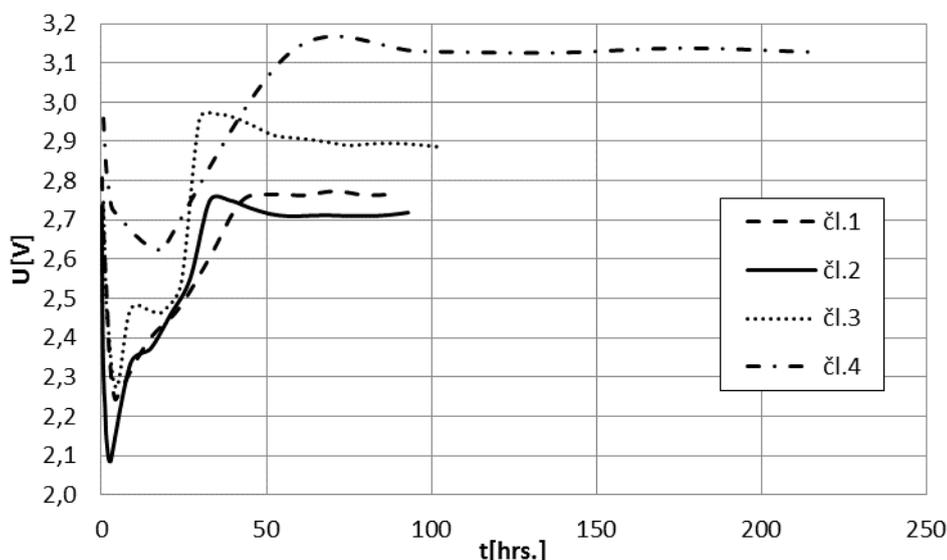


Figure 7. Cell voltage at the end of charging

Figure 7 shows voltage courses at the end of applied formation pulse. The final voltage values corresponds with charging current levels (pulse length respectively) when the cells with a lower charging current reaches lower final voltage. There is a sensible voltage drop at the beginning, which takes place in the first formation stage when the internal resistance is step down. The current net was created and lead sulphate was changed as well. The lead sulphate is reduced on positive respectively negative active mass in the second stage. The third formation stage occurs when the cell voltage will grow up over gassing voltage (2.5 V) and supplied energy in charging is consumed for electrolysis. It is evident that the voltage in the fourth cell is higher than 2.6 V and the cell had high internal resistance and the formation process was ineffective. The idea was confirmed by the zero capacity test. Similar results were observed in [5].

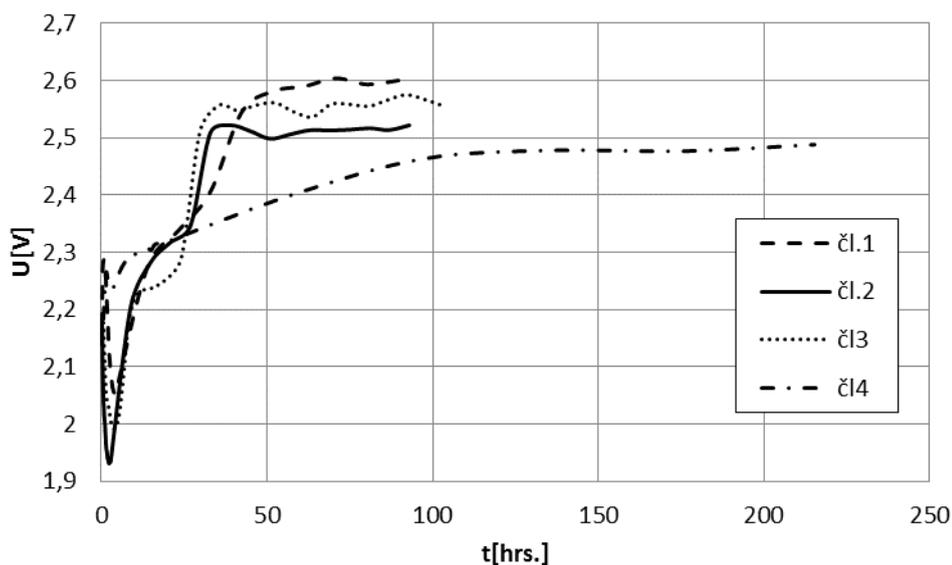


Figure 8. Cell voltage at the end of standing

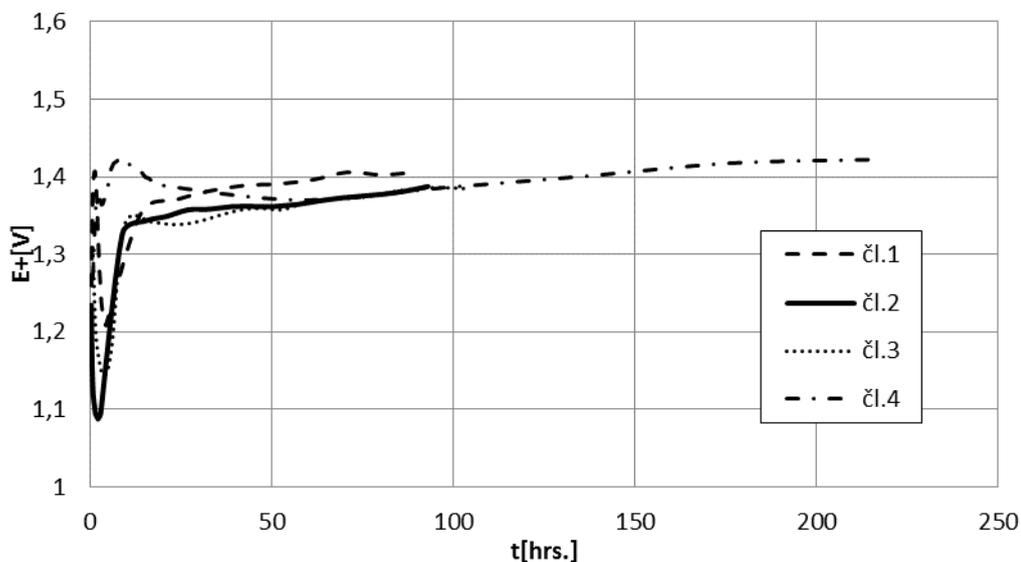


Figure 9. Potential of the positive electrode during standing

Next figure shows cell voltage at the end of one pulse cycle. We can say that there is a big difference between the cells. Voltage drop and rise is apparent corresponding to all formation stages. The voltage drop during standing is given by the speed of diffusion processes which compensates concentration drift of the electrolyte or by the oxygen and hydrogen outflow from the cell system. On account of the long standing on cell number 4 his voltage is the lowest [8].

There are different beginning differences of the pulse regimes on potential on the positive electrode. All the voltage courses in standing are the same except the cell number 1 from the 60 hours. Potential of the positive electrode number 4 is much higher during charging. Formation proces is faultily and the electrode has higher internal resistance and the oxygen is developer. Following figures show the impedance of the positive mass.

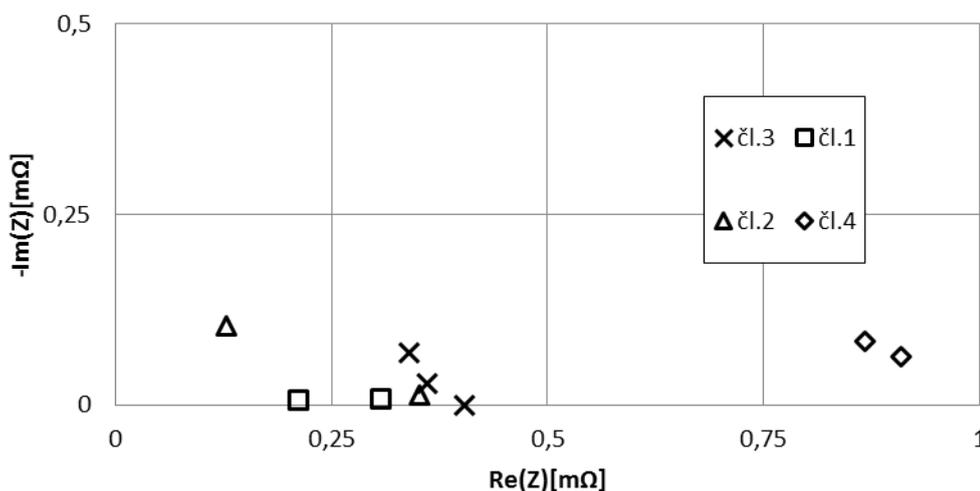


Figure 10. Z_m of the positive electrode after formation

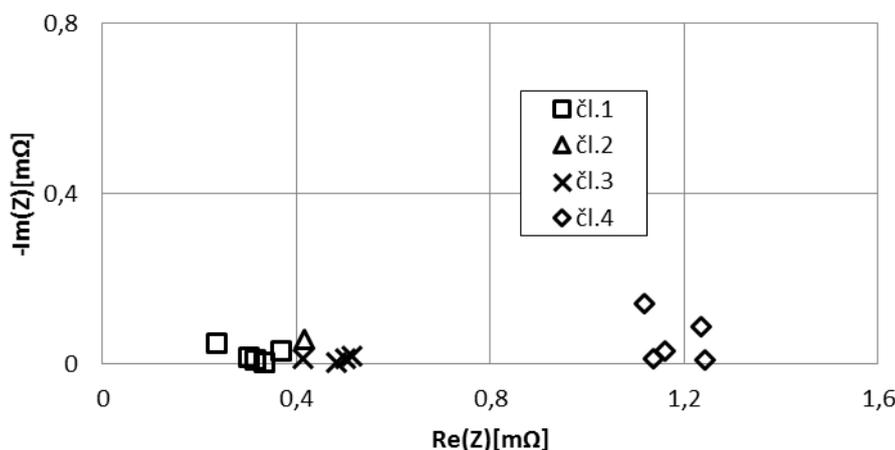


Figure 11. Z_m of the positive electrode after conditioning cycles

Previous two figures comes up to impedance Z_m of the positive active mass after formation and conditioning cycles. The impedance after formation grows up with a cell number and it corresponds with a capacity chart. Interesting is figure 11 where the impedance of the third cell is higher during conditioning cycles. There is a clear semicircle in a complex which can be represented by the parallel

RC element. The properties of active mass were changed during conditioning cycles and it is according with capacity figure.

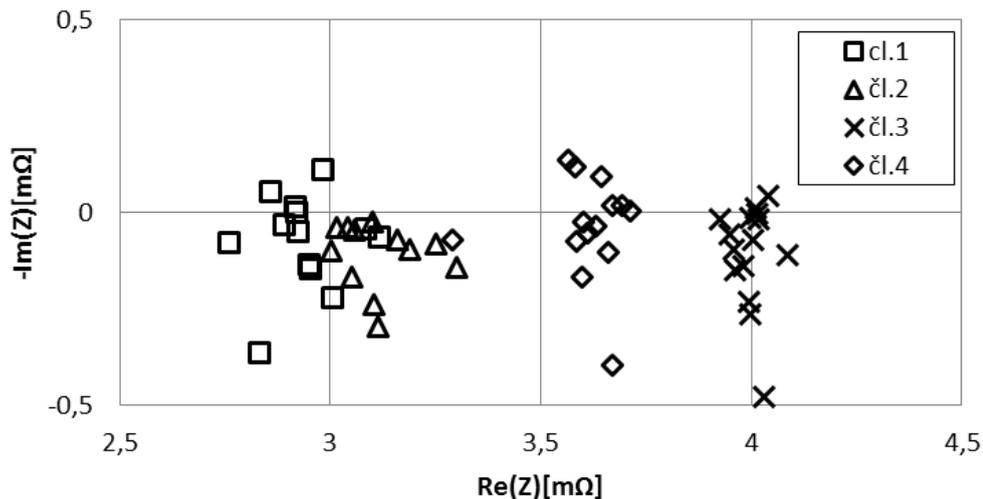


Figure 12. Z_k of the positive electrode after formation

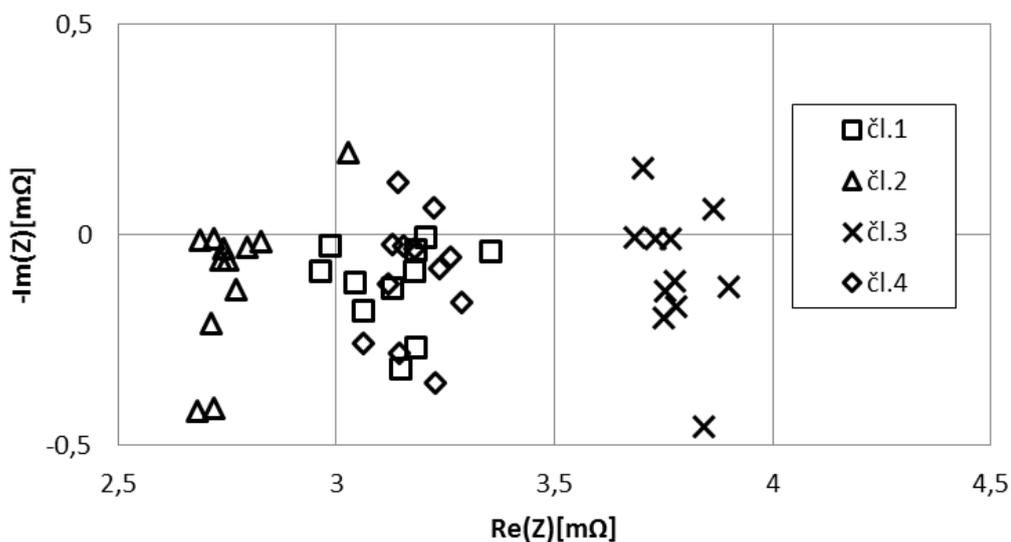


Figure 13. Z_k of the positive electrode after conditioning cycles

The results are pretty surprising namely of several reasons. There are divergences between impedances of the interfaces in a real and mainly in a complex component. In case of electrodes 2 and 3 the impedance do not break even complex component while in case of electrode 1 and 4 the complex component is clearly evident. We compared the experimental results with theoretical values from [1, 2, 3, 4].

Table 4. Z_k compensatory circuit components for the positive electrode

SoC [%]	Cell 1 - formation	Cell 1 - conditioning	Cell 4 - formation	Cell 4 - conditioning
R1[m Ω]	38	32	68	46
α [-]	0.72	0.68	0.62	0.65
CPE[Fs(α -1)]	0.32	2.7	0.24	0.44
R2[m Ω]	14	3.5	125	32
PseudoC[mF]*	38	313	26	46

*PseudoC is capacitance that would be obtained if C was used instead of CPE

Obvious is a decrease of impedance R_1 and R_2 during conditioning cycles. The exception is electrode number 3, where took place the ascent distinct of the real part of the impedance from 60 m Ω to 160 m Ω . This ascent is interesting because the capacitive component not appear in the results. Due to a higher potential of positive electrode along charging pulse of the cell 1 and 4 was in progress corrosion of current collector. This big corrosion layer has influence on capacitance part of impedance. The capacity PseudoC after conditioning cycles grown up which reflects with a rising of the corrosion layer. This is due to macropore surfaces as well [5].

This experiment has shown interesting results. New formation regimes do not show itself by big differences in an impedance of the active mass, but they influenced the interface collector/active mass. We can approve this due to this new difference method. This method was not used out of our working compartment and the obtained results are unique.

ACKNOWLEDGEMENT

This work was supported by the EU CZ.1.05/2.1.00/01.0014 and by the specific research of the Brno University of Technology No. FEKT-S-11-7. Publication of the results was financially supported by the project Popularization of BUT R &D Results and Support of Systematic Collaboration with Czech Students, no.CZ.1.07/2.3.00/35.0004.

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