

# EFFECT OF CARBONACEOUS MATERIALS ON PERFORMANCES OF CARBON-CARBON AND CARBON-Ni OXIDE TYPES OF ELECTROCHEMICAL CAPACITORS WITH ALKALINE ELECTROLYTE.

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## INTRODUCTION

Carbonaceous materials play the key role in achieving necessary parameters of electrochemical capacitors (EC), because their electrode active mass consists of more than 95% of carbon substances [1]. Double layer capacity determining capacitance and energy store of the capacitor is directly proportional to the electrode surface, wetted with electrolyte. Different types of activated carbon are the most suitable for this purpose. That is why specialists developing EC materials try to increase carbon specific surface as much as possible and to optimize the internal structure of the carbon porous space. Activated carbons possess their own sufficient volumetrical conductivity for electrolyte/collector current interchange.

However, contact resistance between carbon particles in the electrode limits charge/discharge currents of the porous volumetrical system and therefore EC power. It should be also mentioned that the increase of activated carbon specific surface (overactivation) always leads to increase of its specific resistance. Different methods of obtaining of activated carbon optimized volumetrical structure were developed [2,3], but they still do not find industrial application.

Essential improvement of volumetrical conductivity is achieved by introduction of high-conductive fine dispersive additives such as carbon black, graphite, metal powders, graphite fibers, etc. into activated carbon's active mass. Depending on EC power demand, percentage of the introduced additive is in the range of 5 – 40 %.

Fine dispersive carbon substances introduced into active mass of pseudocapacitive electrodes of "hybrid" (asymmetric) capacitors play the most important part in development of volumetrical collector. In this case one electrode is of faradaic type:  $\text{Ni}(\text{OH})_2$ ,  $\text{MnOOH}$ , etc. and active mass own conductivity depends on electrode charge level and here stable conductive skeleton is needed. The latest progressive investigations demonstrate possibility of application of different nanostructured carbon forms, such as single-wall and multi-wall carbon nanotubes [4,5].

As for the industrial application, here high conductive carbon powders and fibers and metal powders used to dominate.

Summarizing the above said, it may be stated, that activated carbons and pseudocapacitive materials in EC electrode structure are responsible for energy store parameters (specific energy), and nonactive high conductive carbon additives are responsible for electrode internal resistance ( EC specific power).

The present article describes results of investigations of carbon materials widely used for creation of volume collector in the EC electrode body. Investigations were carried out with full-size electrodes of NiOxide systems with aqueous solution of KOH.

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## CONDUCTIVITY OF SOURCE MATERIALS AND THEIR DRY MIXTURES.

Before conductivity measuring, carbon materials and their mixtures were dried up to residual moisture content less than 5 %. Sample of investigated material was put into measuring cell, representing dielectric cylinder, closed at both sides by measuring electrodes. Electrode pressure on material sample approximately corresponded to pressure of EC operation and was equal to 8 kgf/cm<sup>2</sup> (minimization of particle contact resistance). Conductivity measuring was carried out by alternating current method – 1 kHz at measuring current density of 2,2...270 mA/cm<sup>2</sup>. There were analyzed 6 samples of each material. In order to reduce current density influence on resistance and for comparability of obtained results for different materials a diagram for extrapolation of “Zero” current density (J=0) was developed.

*Dozen types of materials were analyzed, but this article presents data of typical representatives of conductive materials family. Obtained data are given in Table 1.*

Specific Resistance of Dry Powder Materials.

Table 1

TYPE OF CONDUCTIVE MATERIALS	SPECIFIC RESISTANCE, j = 0, ohm·m
Activated Carbon (SKT)	49 · 10 <sup>-3</sup>
Carbon Black (P- 267)	2,1 · 10 <sup>-3</sup>
ABG-1005 (Superior Graphite)	1,1 · 10 <sup>-3</sup>
2939 APH (Superior Graphite)	2,6 · 10 <sup>-3</sup>
2939 APH-RG (Superior Graphite)	0,9 · 10 <sup>-3</sup>
Ni Powder (Carbonylic Method)	0,75 · 10 <sup>-3</sup>
8% ABG- 1005 + 92% Activated Carbon	35 · 10 <sup>-3</sup>
10% Ni Powder + 90% Activated Carbon	54 · 10 <sup>-3</sup>
15% Carbon Black + 85% Activated Carbon	11 · 10 <sup>-3</sup>

Note: Material dispersivity was for:

- activated carbon < 60 μ (10-20)
- carbon black < 5 μ
- nickel powder < 5 μ
- graphite “Superior Graphite”- delivery state.

The table shows, that dry resistance of activated carbon is more than 20 times higher than that of graphites, carbon black and nickel. Nickel powder has minimum resistance, graphite 2939 APH – RG follows next.

More interesting data was found to mixtures: carbon additives reduce specific resistance of the mixture: active material (activated carbon) – current conductive additive, and nickel powder increases resistance ( 54 · 10<sup>-3</sup> ohm·m vs 49 · 10<sup>-3</sup> ohm·m). It testifies that carbon-carbon components have better “package” in electrode volume.

But it should be noted, that ESR of electrode, having minimum resistance in dry state

may be significantly increased during impregnating with electrolyte solution (that is resistance increasing according to n-type in solid phase of active material). It is conditioned by expanding effect of electrolyte film during wetting the surface of electrode particles.

Thus, “dry” conductivity data may serve only as initial estimation during optimization of volume structure of EC electrode.

### **EFFECT OF CARBONACEOUS MATERIALS ON PERFORMANCES OF CARBON-CARBON EC WITH ALKALINE ELECTROLYTE.**

In active material of both electrodes of EC with purely “double electric layer” volume changes do not take place during charge-discharge processes. That’s why it is not expedient to add binder into active material. But that is observed only within the range of safe voltage – for alkaline aqueous electrolytes of 1,12...1,24 V, depending on material purity and current density. Exceeding this voltage causes gassing, electrode swelling and loss of electric contact between particles in electrode volume.

In our case we used paste mixtures of carbon-carbon electrode components with KOH solution of 1,26 g/cc density. Positive and negative electrodes were pasted onto the conductive polymer film, separated by ionoconductive separator, made of special paper, pressed between external collectors of nickel-plated copper with pressure of 8 kgf/cm<sup>2</sup>. The cell was sealed by welding all around the edges of conductive polymer interchanging with the layer of nonconductive polymer. Electrode thickness did not exceed 150 μ, separator thickness was ≈50 μ, active surface dimensions was 128 x 148 mm. Electric capacity was measured within the voltage range of 0,8 V → 0,4 V by constant current method. ESR was measured at frequency of 1 kHz and measuring current value of 1 A. Before test measuring all the cells had been kept during 24 hours under working voltage and additionally had been subjected to 10 charge-discharge cycles. Test temperature was 22-24 °C.

Summarized measured and calculated data are shown in Table 2.

Table 2

PARAMETERS	MATERIALS				
	ABG-1005 8%	2939 APH 8%	2939 APH-RG 8%	Carbon Black 5%	Ni Powder 10%
CAPACITY	90 F	88 F	92,4 F	98 F	104 F
ESR, 1 kHz	0,92 mOhm	1,03 mOhm	0,84 mOhm	0,75 mOhm	1,07 mOhm
ENERGY DENSITY	2,12 kj/kg	2,04 kj/kg	2,29 kj/kg	2,5 kj/kg	2,30 kj/kg
RC-time CONSTANT	83 msec	91 msec	78 msec	70 msec	111 msec
POWER DENSITY	12,8 W/g	11,3 W/g	14,8 W/g	15,2 W/g	10,7 W/g

Analyzing table data one may note, that cells with carbon conductive powders have advantages over metal powders, possessing 1,5 times higher specific power at comparable specific energy level. Carbon black P-267 and graphite 2939 APH-RG have the best indexes. A little bit higher carbon-black indexes are explained by its higher specific surface in comparison with graphite. It provides higher specific sorption of electrolyte and improvement of electrode conductivity according to the conductivity of the second kind.

As to cycle life of EC with above mentioned conductive additives into active mass, consisting of activated carbon, then for all EC types it exceeds 10 000 000 cycles (DOD 30 %), that is quite enough for main spheres of application.

### **EFFECT OF CARBONACEOUS MATERIALS ON PERFORMANCES OF CARBON-Ni OXIDE TYPES OF EC WITH ALKALINE ELECTROLYTE.**

The character of carbonaceous material's influence on asymmetric EC performances of carbon – NiOx system is more complicated than that of carbon-carbon system. It is determined by higher potential of NiOx electrode oxidation and volume changes in electrode active mass during charge-discharge processes:  $\text{Ni(OH)}_2 \leftrightarrow \text{NiOOH}$ .

First of all let's have a look at the morphology structure of agglomerate electrode [6] by way of example of the model shown in Fig. 1.

This is a multiphase system with no fixed connection between its components. As a rule, the active mass of electrode is a mixture of Nickelhydroxide (oxyhydroxide) with conductive of carbon or metal type additive well dispersed mechanically. The NiOx particles when in operation are closely tightened with conductive additive by means of pressing of the electrode block or addition a binder into active mass slurry. Quantity of conductive additive should be chosen pursuing necessity to create a spatially ramified grid providing current transmission from the active material particles to an external collector. In dependence on reciprocal dispersion of conductive additive and active material, the quantity of conductor in the mass may vary from 10% to 70% of the total electrode mass. The conductive particles in the volume of electrode make the so called "chain" structures. As it is seen from the model, the electrical circuit connecting the active mass particles in the solid phase of the electrode, and external collector consists of a long chain of resistors. The current path is through the contact resistance: external collector – volume collectors ( $R_{ki}$ ), then goes through many other resistances: bulk resistance of the conductive particles ( $R_{vi}$ ) and the resistance of contacts between the conductive particles in the volume of the electrode ( $R_{ci}$ ); at the end, there is contact resistance between the conductive particles and active mass particles ( $R_{mi}$ ). Considering this chain, we should take into account the influence of the binder (dielectric) effecting on all the above contact resistances in the circuit and increasing their value ( $R_b$ ). Evidently, the main influence on ESR of the electrode in this circuit is because of *a big number of contact resistances distributed in the bulk of the electrode*. The electrode efficiency at operation in high current density and during service life is determined by the state of the particles of volumetric collector surface. With reference to this, we can point out two main factors effecting principally on reliable operation of Ni-Ox electrode:

1. Electrochemical oxidation of the particles surface of the volumetric collector. Potential of charged NiOx in KOH electrolyte is 0.45 V to 0.5 V vs SHE. This value is sufficient for fast oxidation of carbon materials and appreciable for metal powder. *Even insignificant oxidation of particles surface results dramatically in ESR increasing on electrode*, because we have here a long series circuit of contact resistances between the particles.

2. Electrode swelling. The agglomerate electrode when it even has binder inside, is not a solid structure. Volumetric changes in morphology ( $\alpha$ ,  $\beta$ Ni(OH)<sub>2</sub>;  $\beta$ , $\gamma$ NiOOH) arise thickening of electrode. It is appreciable even in tightly squeezed electrode stacks. Thus, there takes place a mechanical remote of the volumetric conductor particles from the active mass particles, and from each other. Simultaneously, the contact area between the particles diminishes in size and contact resistance gets higher increasing total ESR of the electrode.

Common influence of both the factors significantly limits the performances of operation capability of NiOx electrodes of agglomerate type in asymmetric C/NiOx capacitor. Significantly high initial performances and accelerated failure either in floating mode or in heavy duty cycling mode are expectable.

While choosing an optimum volume collector, tens of various carbon and metal powders were researched. In the report the characteristics of three main representatives are given. They are: Nickel (got by means of carbonyl method), colloidal graphite and refined graphite. Carbon black was not taken into account as the loss of the parameters of EC by ESR appeared soon after several charge – discharge cycles.

The amount of volume collector matched up to the active mass of NiOxide electrode was additionally determined charging by the criteria of minimum ESR and its oxidation resistance. Thus, for the colloidal graphite this quantity is – 12%, for Ni powder – 60%, for the refined graphite – 25%. The design and test results of experimental cells are thoroughly described in previous papers [7]. Now let's describe a cell, by way of example of refined graphite.

#### NiOx electrode.

For electrode manufacturing powder of Ni(OH)<sub>2</sub> was used, produced by H.C.Starck, d50~6 micron, which, afterwards, was mixed with conductive volumetric additive –refined graphite powder, produced by Superior Graphite. The quantity of conductive component varied from 15% to 30%. Solution of thermoplastic polymer in organic solvent was prepared separately. Then, a mixture of dry components Ni(OH)<sub>2</sub> + graphite was added to that solution and mixed one more time.

Content of polymer binder in composition of a dry electrode was 5...10%. Electrode film was formed out of the mixture of components in organic solvent by means of casting, which after drying (removing of solvent) was rolled by dry method to the desirable thickness (150...200 microns). As a result form-stable, self-supported electrodes were obtained. Then these electrodes were subjected to formation during two charge - discharge cycles in the solution of electrolyte, consisting of 40% KOH and 10g/l LiOH.

#### Carbon electrode.

Activated carbon cloth of 1-1.1 mm. thickness was used as the initial material for the most of experiments. Ribbon, made of carbon cloth, was soaked in the solution with 40% KOH and 10g/l LiOH for 72 hours, and afterwards, was cut into electrodes of the appropriate dimensions. Electrolyte surplus was removed by pressing.

#### Cells.

An electrode block, which included a positive NiOx electrode, a separator, made of special paper (60 microns), and a negative electrode, was placed between two sheets of conductive plastic of 50...60 microns thickness. The upper and lower plastic sheets were welded along the edges through the isolating layer with an exception of the area which was used preliminary as a ventilation outlet.

The assembled cell was put between two metal collectors and pressed to the level of

operating pressure for reducing contact resistance of assembling parts between power covers of the clamping unit.

#### Testing.

Assembled cells were cycled in the most severe mode: “Continuous day cycling”. This is uninterruptable (without pauses) cycling during 8 hours in voltage window 1,5 – 1,1 V. The upper level of charging voltage – 1,5 V is critical value for the system C – NiOx in aqueous electrolyte. Here formation of some quantity of atomic oxygen on NiOx electrode takes place, which oxidize electrode components more rapidly. Typical test cyclogram is shown in Fig. 2. Quantity of such cycles during the day is  $\approx 1400$ .

Changes of ESR and capacity during cycling are shown in Figure 3. High stability of volume collector out of refined graphite (2939 APH – RG) in critical test conditions were observed.

For comparison the test data of EC with volume collector out of colloidal graphite and powdered nickel are shown in Fig. 4. ESR of EC with refined graphite was increased by 56 % after 36000 cycles and with nickel powder by 81 % already after 1400 cycles. Resistance of EC colloidal graphite increased 4,5 times compared to initial values already during 500<sup>th</sup> cycle.

Capacity loss for EC with graphite 2939 APH – RG was 13 % during the 36000<sup>th</sup> cycle, while with nickel powder – 43 % during  $\approx$  the 1000<sup>th</sup> cycle and with colloidal graphite – 32 % during the 500<sup>th</sup> cycle.

Carried out testing confirmed the supposition about the degradation mechanism of proposed electrode model (Figure 1). Obviously, the less dimensions of particles of volume collector (colloidal graphite) and more active its surface (nickel powder), the faster oxidation processes taking place on the surface of these particles. It provokes avalanche type growth of contact resistances and accelerated failure of EC due to high ESR and capacity loss during operation.

### **CONCLUSIONS.**

1. For electrochemical capacitors of the system carbon-carbon in spite of the fact that the electrode body consists of conductive activated carbon, it is always necessary to use high conductive additives, *preferably of carbonaceous type*. Concrete additives type plays secondary part during operation of such EC type in safe voltage interval.
2. For electrochemical capacitors of the carbon-NiOxide system with aqueous KOH solution it is expedient to use carbonaceous graphite materials with expanded structure and modified surface. In this case quantity of contact resistances is decreased in chain structure of volume collector and its stability to electrochemical oxidation is increased. It provides long service life of EC even in critical operation conditions.

The greatest demand now and in the future during development and production of electrochemical capacitors lies in the sphere of high conductive microfibers with modified surface against oxidation.

## REFERENCES.

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Appendix: Figures 1 – 4.

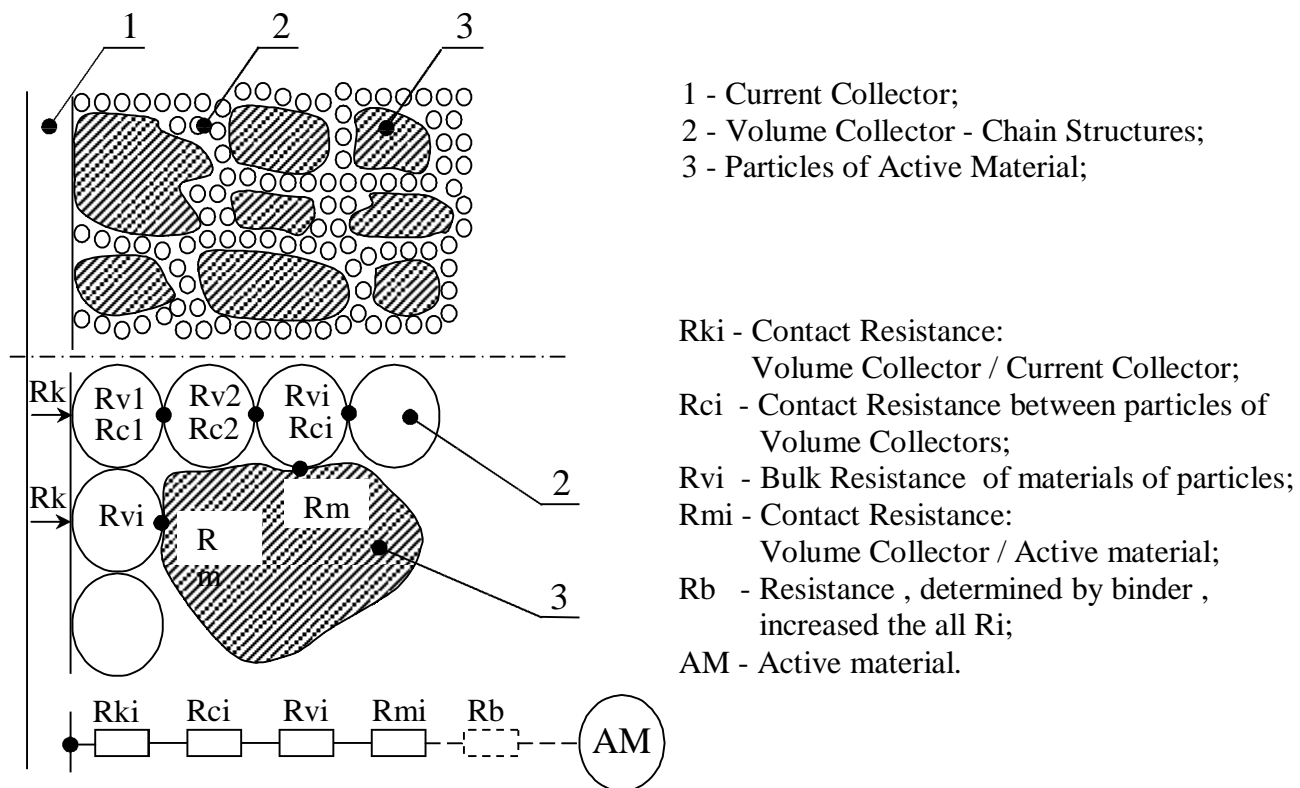


Fig. 1. Simplified model of agglomerate electrode.

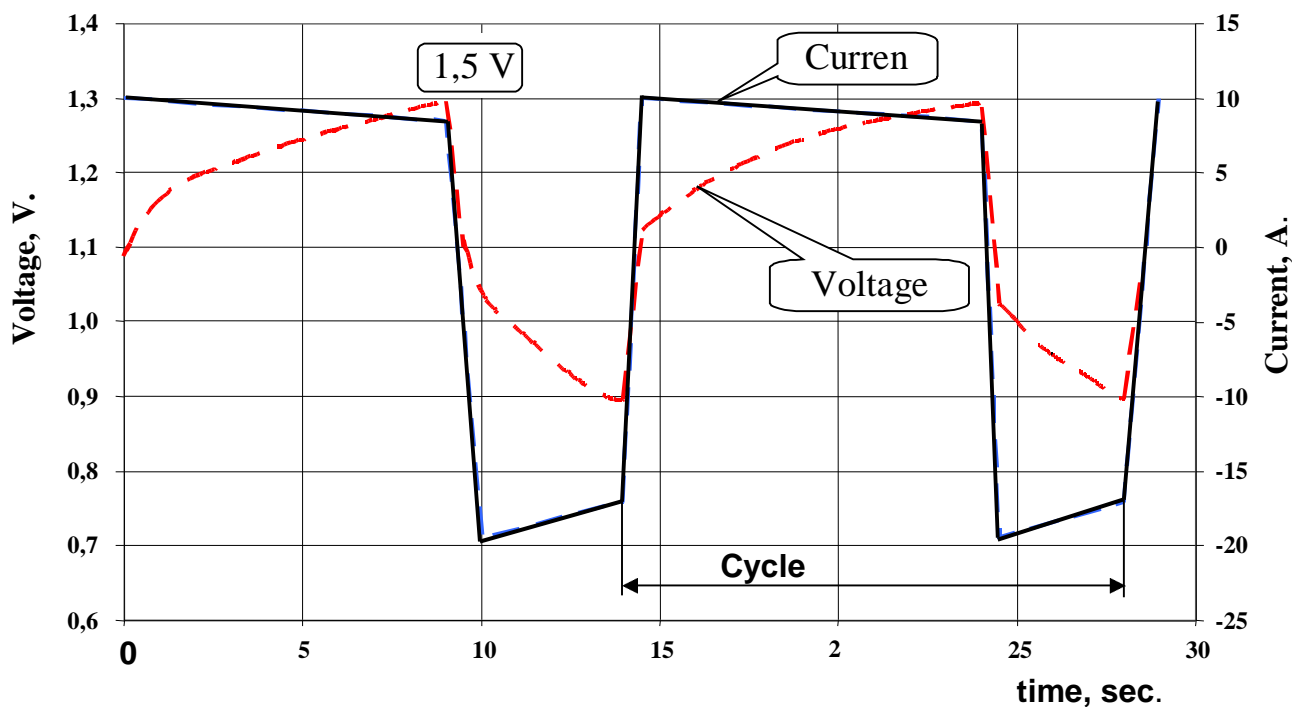


Fig. 2. Cycling diagram in day-cycling mode.

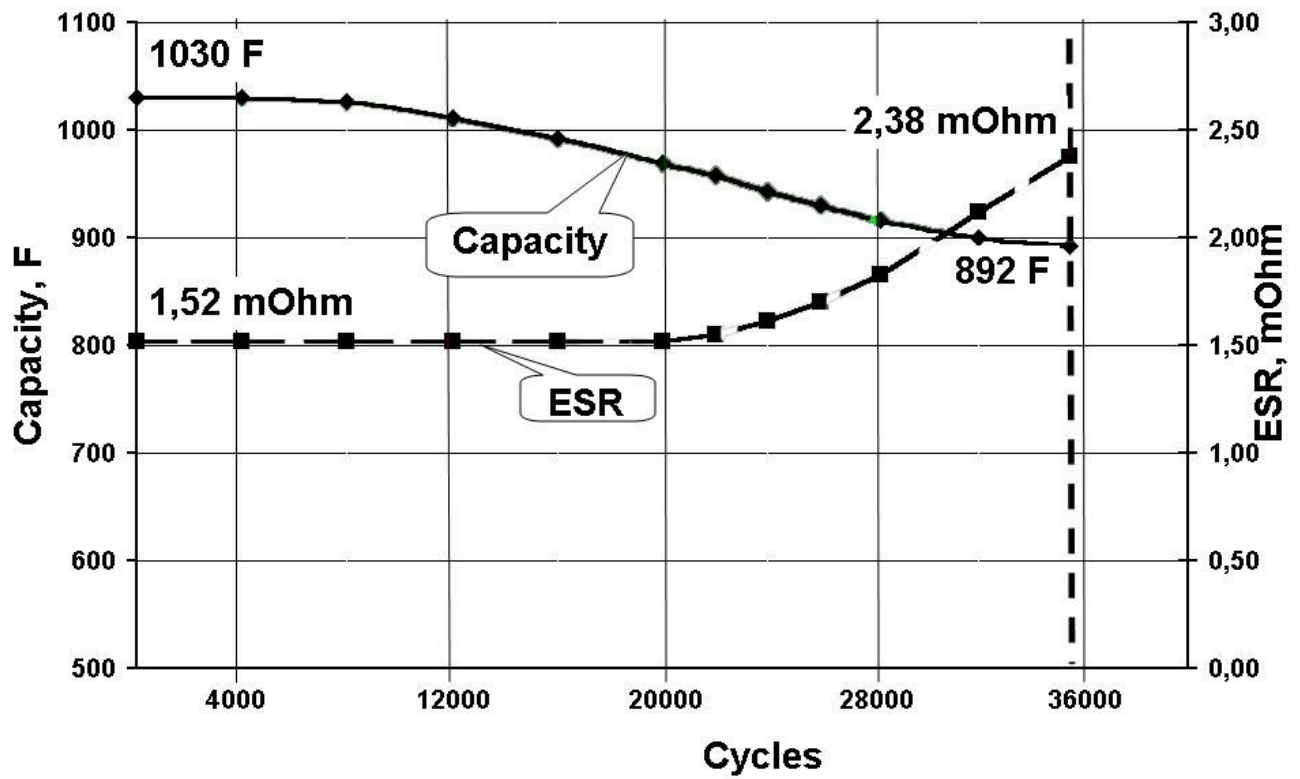


Fig. 3 Changing Capacity and ESR VS Cycles, Capacitor C/NiOX, 25% 2939APH-RG, 1400 cycles/day + 650 hours of floating.

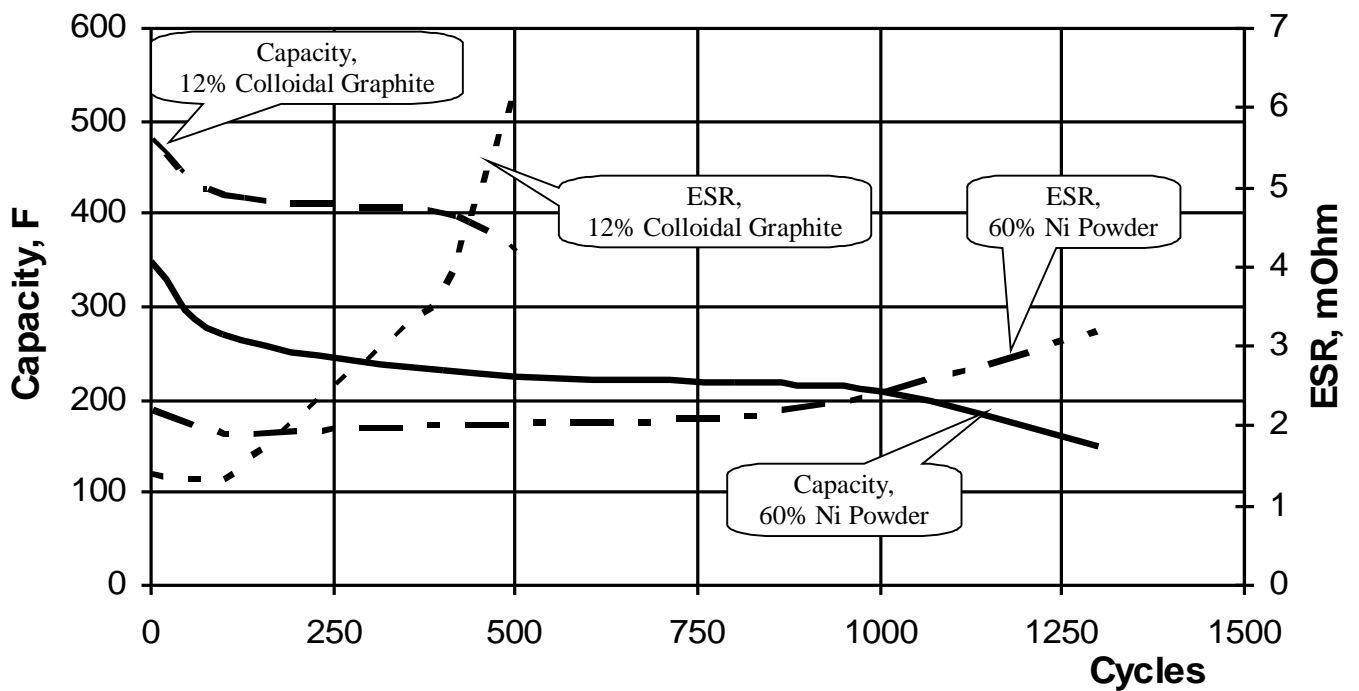


Fig. 4 Changing of Capacity and ESR in cycling.