

## New trends in nanoscale compounds for energy storage

**Z.A. Stotsko\*, B.Ya. Venhryn**

Lviv Polytechnic National University, 12 St. Bandera Street, Lviv 79013, Ukraine

\* Corresponding e-mail address: stotsko@polynet.lviv.ua

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### Properties

#### ABSTRACT

**Purpose:** Mechanism of supramolecular complexes C<cavitand> formation and investigation of their electrochemical characteristics were the aim of this paper. Supramolecular complexes were created by inserting an organic receptor into nano/mesopores of activated carbon.

**Design/methodology/approach:** Electrochemical studies of supramolecular complexes C<cavitand> were carried out by means of impedance spectroscopy, cyclic voltammetry and galvanostatic cycling.

**Findings:** The possibility to combine the capacitive storage with faradaic energy generation in one unit is proved. It can be reached by means of active electrode formation as a supramolecular complex C<cavitand>. It is shown that faradaic generation of energy occurs at low positive potentials, whereas the capacitive one at higher potentials. Method of synthesis of blue graphite is developed.

**Research limitations/implications:** This research is a complete and accomplished work.

**Practical implications:** Supramolecular complexes, obtained in this work, could be regarded as promising electrode materials in devices of energy generation, storage and transformation.

**Originality/value:** This work is of urgent importance for physics and chemistry of energy generation, storage and transformation, because it opens new possibilities to new highly effective electrode materials search and enables to reach a high values of functional characteristics.

**Keywords:** Nanoporous carbon; Cavitand; Blue graphite; Faradaic process

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#### Preface

The paper is devoted to an important event both for the materials and manufacturing engineering scientific community, and for the researchers around the world. This event is celebrating the 65th birthday of Prof. Leszek A. Dobrzański. Much can be said about the many-sided activity of Prof. L.A. Dobrzański, his research, teaching, publishing work and his effective organizational activity. His achievements are confirmed by the academic degrees, the positions, and numerous numbers of his students, his colleagues around the world.

It should be noted his international contacts with Ukraine, especially friendly relations with Lviv Polytechnic National University. Prof. L. A. Dobrzański has an impact on the development of material science and engineering in our university and training of specialists in this area. Scientists at Lviv Polytechnic National University use the monographs and scientific publications of Prof. L.A. Dobrzański. Our scientific library has a rich collection of Journal of Achievements in Materials and Manufacturing Engineering issues thanks to his personal assistance.

Journal of Achievements in Materials and Manufacturing Engineering has high scientific rate. And the topical papers of the

authors around the world allow scientists, working in our university, to respond to global challenges in the materials science. Collaboration of the scientists from Lviv Polytechnic National University with the JAMME, and publications their papers in the journal gives them opportunity to present their research to a wide range of scientists around the world.

Prof. L.A. Dobrzański activity towards Ukraine, including our university, is not limited to scientific side. He visited Lviv Polytechnic National University during various public events and conferences. Authority and all his friends in our university treat with respect to Prof. L.A. Dobrzański. We appreciate his scientific achievements, his exceptional organizational skills, his support and goodwill towards colleagues, including Ukrainians. Therefore, our co-operation should be continued, because it has great prospects. We would like to confirm its relevance by this paper.

## 1. Introduction

Present-day interest to studying a new materials for energy storage systems on the base of nanoscale composites is motivated their promising application in various areas of industry (electric car construction and non-traditional energetic impressive success of nanoelectronics and spintronics) [1-2]. But, it should be noted that progress in this field is related with deep problems, which lay in the base of principal contradictions between growing requirements of advanced scheme technical solutions and abilities of up-date technologies of autonomous devices for generation, transformation and accumulation of energy. Main electrochemical systems, existing today in above mentioned branch of technology have been developed more than one hundred years ago. For this reason the progress already reached early is considered as units of supercapacitor technology and energy sources with lithium anode. Supercapacitors, whose principle of operation is based on polarization of volume charge of electric double layer at the boundary between blocking electrode with electrolyte, have a calling to maintain the high specific power and cyclic characteristics. Besides, the specific values of energy capacitance of such devices are limited by low value of differential capacitance, which is notably less than similar parameter of chemical accumulators [3]. The attempts to increase this parameter allowed in seventies of last century to development of new direction in technology of energy storage - creation of so named configuration-hybrid (nonsymmetrical) supercapacitors [4] and functional-hybrid redox- (or pseudo) ionistors [5]. Systems, which have been proposed consist of harmful elements (Pb, Cd) [6], besides they are very rare and very expensive ( $\text{RuO}_2$ ) [4,7]. Both theoretic and experimental studies, which are developed to nowadays yield no clear understanding how to solve the above mentioned problems.

## 2. Fundamentals and experimental

The main features of above considered devices allow revealing the deficiencies, which determine the low effectiveness of their work. Understanding these features allow to choose the methods to solve these problems. We suppose that supramolecular

compounds are just such the materials, which have many abilities to solve them.

We use some methods and results of supramolecular chemistry, which, as is known, is the chemistry of molecular ensembles and intermolecular bonds, chemistry beyond the molecules, whose base is interaction of components of host-guest kind with lock-key mean of interaction [8].

Therefore the supramolecular chemistry is a powerful instrument for solving of lot problems of present-day medicine, physics, instrument-making industry, information technologies with colossal potential for creating of desired materials as well of their properties. In particular, crown-ethers, which link alkaline metals by means "lock-key", can be used as such nanoscale compounds.

In order to stabilize the parameters of electrode material in electrolyte solutions and also for modification of energetic diagram of interface between electrode and electrolyte, we propose to create the supramolecular ensemble of hierarchical architecture C<cavitand> according to which molecules of organic receptor of potassium cations are introduced into nano- and mesopores of activated carbon (Fig. 1). Charcoal (BAC- birch activated carbon) was chosen as activated carbon material, which was manufactured by means of carbonization of apricot pits (AP).

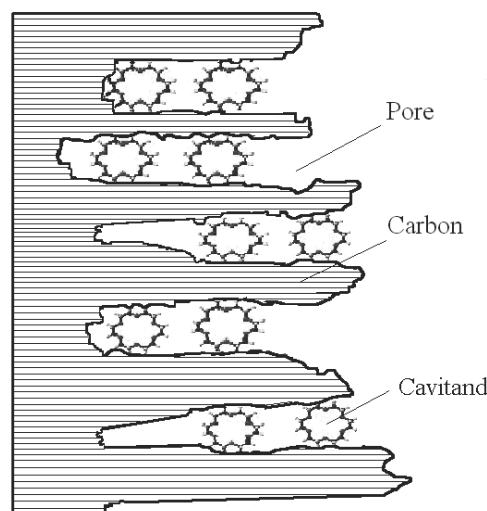


Fig. 1. Supramolecular ensemble C<cavitand>

Process of cavitand introducing has been performed at room temperature in vacuum ( $\sim 10^{-2}$  mm Hg) after preterm desorption of activated carbon in vacuum. Particularly, activated carbon was placed in sealed glass vessel and then all this was put in furnace. The thermal annealing in vacuum was carried out during 2 hours at temperature within 130-140°C temperature range. The seepage of saturated solution of cavitand with  $\text{C}_2\text{H}_5\text{OH}$  as solvent, in vacuum either for  $\tau=15$  or 60 minutes was the final step of process. Upon thermal seepage in vacuum the flushing of activated carbon with  $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$  and following drainage of material to constant mass was done. Mass increase as well as fractal structure effect indicated that crown-ether molecules were intercalated into nano- and mesopores of related activated carbon [9]. 18-crown-ether-6, 12-crown-ether-4, hydrochinon were chosen as supramolecular cavitands.

An electrochemical studies of obtained supramolecular structure has been carried out in three-electrode cell with chlorine-silver reference electrode. Impedance measurements were done within frequency range ( $10^{-2}$  -  $10^5$  Hz) with using measuring equipment "Autolab" ("Eco Chemie", Holland), attached software FRA-2 and GPES. Cyclic voltage-current plots of electrochemical cells were recorded with scanning speed of voltage 0.01 V/s. "Charge-discharge" galvanostatic cycles have been maintained by means of electron galvanostatic device.

### 3. Results and discussion

In result of incorporating of supramolecular receptors the densities of supromolecular ensembles (SE), created in such the way, were measured by means of picnometric method and it was found the significant difference of their values from one for initial carbon material (Table 1). It is seen that density of SE on the base of AP coal notably increases both for 18-crown-ether-6 (24%) and hydrochinon (40%). It is the evidence of more significant excess Gibbs energy at hydrochinon sorbtion compared to 18-crown-ether-6. Most probably that it is caused by stronger hydrophobic entropy bounding of hydrochinon molecules by carbon receptor.

Porous structure of carbon materials is studied by means of X-ray small angle scattering method. We have used this method in order to obtain the scattered intensities for materials under investigation. X-ray small angle scattering data were obtained over scattering range  $2\theta=0.2-4.0$  degree with using the special collimation system both for initial and scattered beams. In order to reduce the parasite scattering from crystal-monochromator, the special slit system was arranged before sample at the distance within 3.5-4.0 cm range. The similar system was installed also before receiving slit of detector that allowed us to reduce the background scattering. Using the LiF perfect crystal and mentioned above the collimation system permitted us to carry the investigation within small angle region, starting from  $2\theta=0.2-0.25$  degree. The resolution of detector was estimated to be 0.03 degree. The scattered intensities have been measured in transmission regime with step  $\Delta 2\theta=0.05$  degree and exposition 100 s.

Analysis of obtained angular dependences of scattered at small angles intensities was carried out with using the integral Porod law:

$$Q = \int_0^\infty sI(s) ds \text{ - Porod's integral invariant;}$$

$$K_p = \lim_{S \rightarrow \infty} \{S^3 I(S)\} \text{ - constant, which is proportional to total surface area of pores;}$$

$$S = \frac{\pi w}{\rho_m} \cdot \frac{K_p}{Q} \text{ - specific surface area of pores;}$$

$$w = 1 - \frac{\rho_m}{\rho_s} \text{ - porosity; } R_p = \frac{3Q}{\pi K_p} \text{ - effective poroe's radius;}$$

$\rho_m$ ,  $\rho_s$  - picnometric and structure densities, respectively.

From these formulas we have obtained the parameters, which are the characteristics of porous structure (Table 1).

As is seen from table 1 the variation of active surface area S significantly depends on organic content seepage duration. It is important that a notable reduction of S at 15 min regime of treatment in vacuum is observed not depending on kind of both

inorganic and organic receptor, whereas at seepage over 60 min the increase of surface area occurs.

Table 1. Parameters of porous structure for initial materials as well as for their based supramolecular complexes

Material	$K_{p3}$ $\text{\AA}^{-3}$	$Q_2$ $\text{\AA}^{-2}$	$\rho_m$ , $\text{g/cm}^3$	$\rho_s$ , $\text{g/cm}^3$	$R_p$ , $\text{\AA}$	$S$ , $\text{m}^2/\text{g}$
AP	2.89	57	0.77	1.08	19	598
AP <18-crown-ether-6> ( $\tau=15$ min)	1.57	71	0.72	1.32	43	438
AP <hydrochinon> ( $\tau=15$ min)	1.60	380	0.72	1.48	226	95
BAC	0.49	45	0.72	1.40	88	228
BAC <18-crown-ether-6> ( $\tau=15$ min)	0.74	112	0.61	1.40	145	190
BAC <hydrochinon> ( $\tau=15$ min)	0.67	159	0.30	1.23	226	334
BAC <18-crown-ether-6> ( $\tau=60$ min)	1.43	33	0.61	1.30	22	1200
BAC <12-crown-ether-4> ( $\tau=60$ min)	1.78	33	0.60	1.30	18	1530

At first we consider the changes of energy storage processes upon seepage over 60 min for BAC<18-crown-ether-6> and BAC<12-crown-ether-4>. The data on galvanostatic charge-discharge cycles (Fig. 2) permit to establish about twice increase of specific capacitance at perfect Coulomb effectiveness for BAC<18-crown-ether-6> that is notably higher than observed increase of active surface area (table 1). On other hand there is a slight increase of specific capacitance for BAC<12-crown-ether-4> (10-15%) although the increase of S- value is the same as for BAC<18-crown-ether-6>. The shape of cyclic voltammogram, measured at potential sweep rate 0.01 V/s (Fig. 3) explains the capacitive energy storage mechanism. The similar behavior of cyclic voltammogram is observed also for BAC<12-crown-ether-4>.

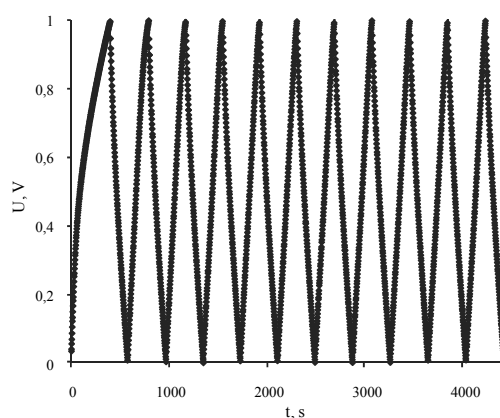


Fig. 2. Galvanostatic charge-discharge cycles for supramolecular ensemble BAC<18-crown-ether-6>

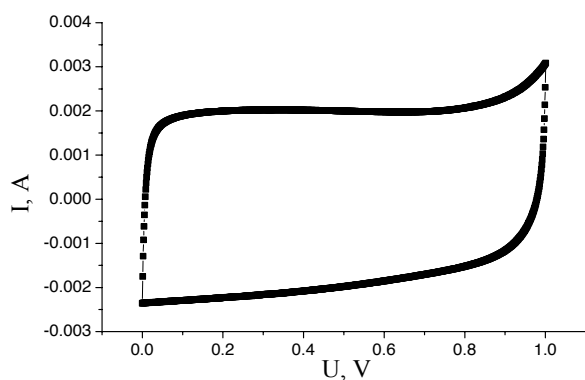


Fig. 3. Cyclic voltammogram for supramolecular ensemble BAC<18-crown-ether-6>

Taking into account the fact that potential of opened circuit in respect to reference chlorine-silver electrode is  $-0.3$  V for BAC<18-crown-ether-6> and  $-0.4$  V for BAC<12-crown-ether-4>, the intervals of voltage scanning for plotting of volt-farade dependences were  $-0.8 \div +0.2$  V and  $-0.9 \div +0.1$  V respectively. Nyquist diagrams for these intervals are shown in Fig. 4.

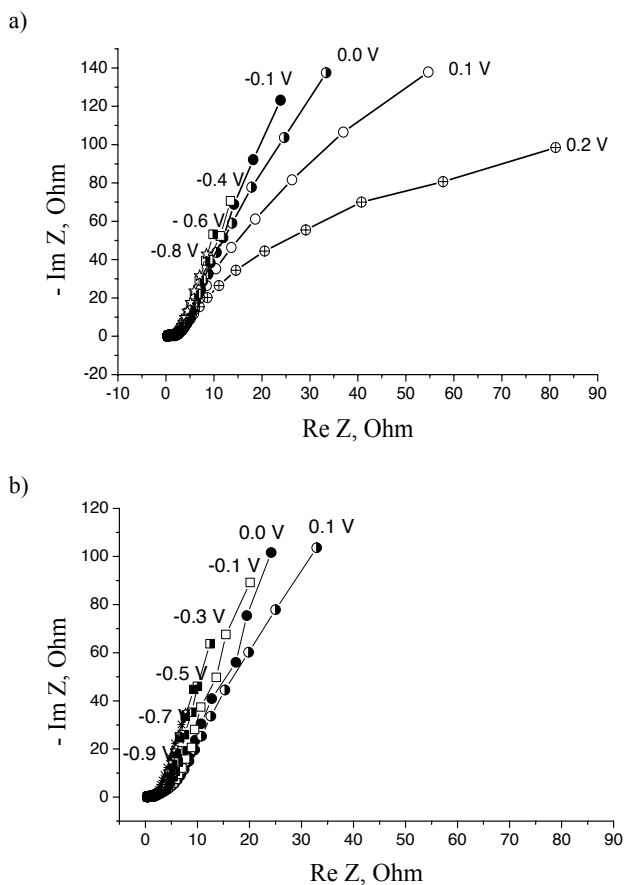


Fig. 4. Nyquist diagrams for supramolecular ensemble BAC<18-crown-ether-6> a) and BAC<12-crown-ether-4> b)

From computer parametric identification of five-chains de Levie model [10] follow the next results (Fig. 5).

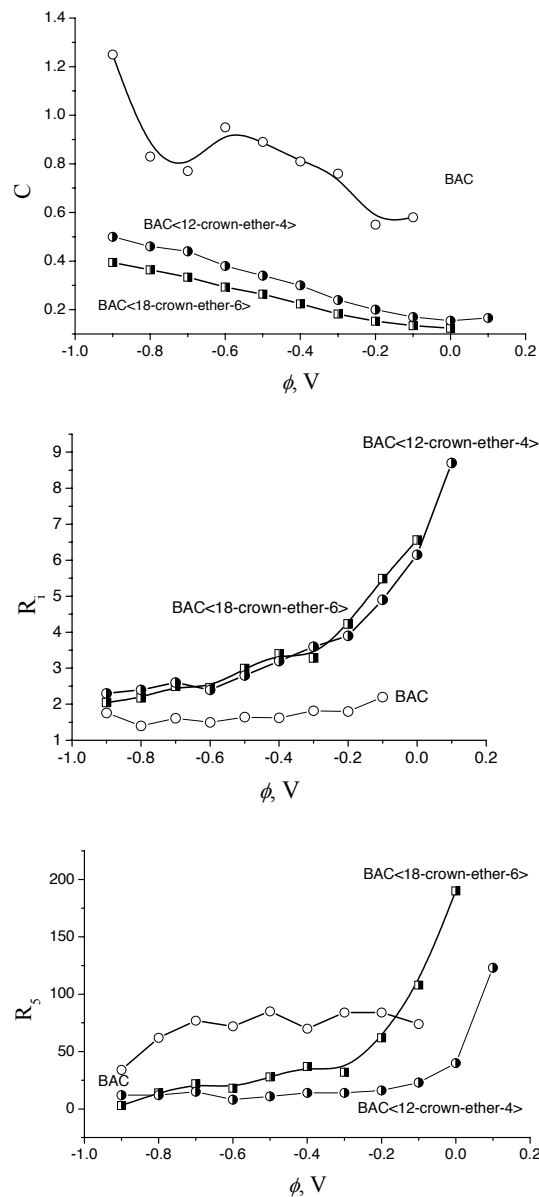


Fig. 5. Parameters of five-chains de Levie model for supramolecular ensemble BAC<18-crown-ether-6>

Notably that at the ends of cathode potential intervals  $+0.1 \div +0.2$  V for BAC<18-crown-ether-6> the corresponding Nyquist diagrams can be described by Rendels-Ershler model circuits similar to Faraday processes. Such feature is not observed for BAC<12-crown-ether-4> and for  $+0.1$  V the process reveals nonfaraday mechanism that was expected since  $K^+$ -cation is not identified by BAC<12-crown-ether-4>.

The next step was to form and then investigate the electrochemical system  $-Zn \parallel KOH \parallel C<18-crown-ether-6>+$ .

Results on galvanostatic cycling within potential values intervals 0-1.24 V and 0.4-1.24 V are shown in Fig. 6 and Fig. 7 respectively. So in the first interval (0-0.4 V) the value of specific capacitance for AP<18-crown-ether-6> is equal  $\sim 10000$  F/g, whereas in another interval (0.4-1.24 V) it is 154 F/g. For another supramolecular ensemble (BAC<18-crown-ether-6>) this value equals  $\sim 13350$  F/g, while in second region (0.4-1.24 V) it is 80 F/g.

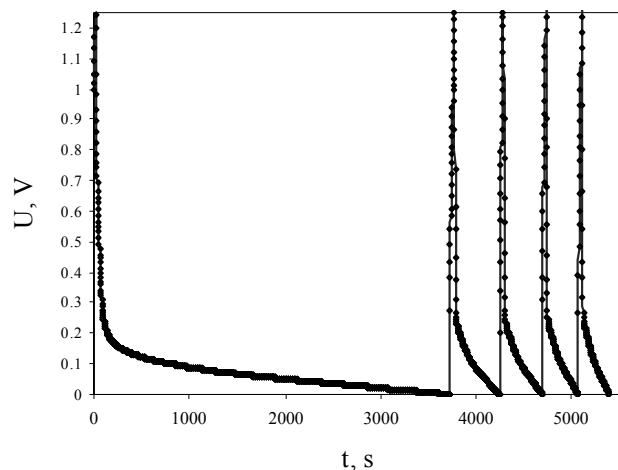


Fig. 6. Cathode-anode galvanostatic cycles for AP<18-crown-ether-6> within potential region 0-1.24 V

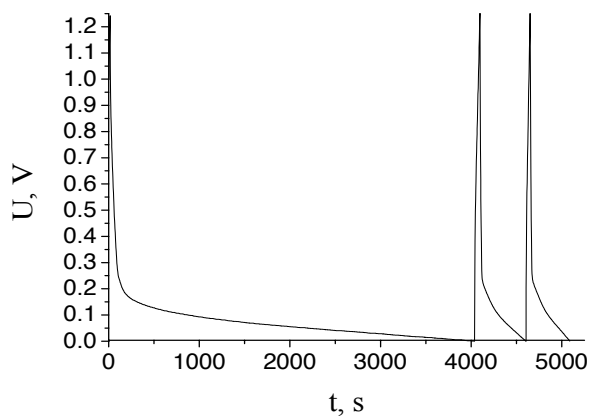


Fig. 7. Cathode-anode galvanostatic cycles for BAC<18-crown-ether-6> within potential region 0-1.24 V

In order to study the ultrasonic effect on storage properties of carbon supramolecular ensembles of C<18-crown-ethers>, materials under investigation were sonicated with using piezoelectric ultrasonic generator. It was found that upon ultrasonic irradiation the specific capacitance for BAC<12-crown-ether-4> increases more than by 20%. For supramolecular ensemble BAC<18-crown-ether-6> the significant change of specific capacitance was

not observed. Analysis of cyclic voltammograms shown that ultrasonic modification in first case causes the significant growth of redox-processes, while as for supramolecular ensemble BAC<18-crown-ether-6> the changes are slight (Fig. 8). Therefore, a molecular identifying stabilizes the system in respect to ultrasonic irradiation.

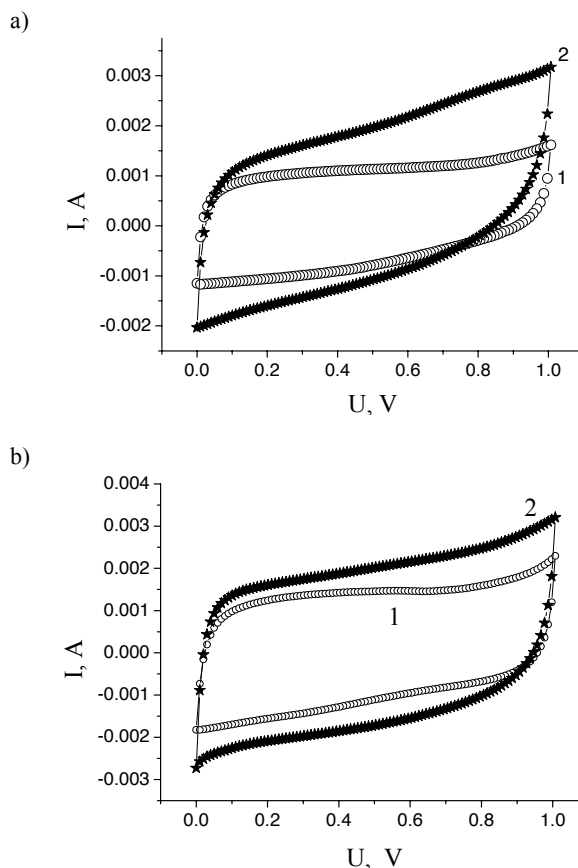


Fig. 8. Cyclic voltammograms for supramolecular ensemble BAC<12-crown-ether-4> -a) and for BAC<18-crown-ether-6> -b) (1 - initial; 2 - upon irradiation)

The notable changes, caused by ultrasonic irradiation, are in fair correlation with corresponding changes of impedance spectra (Fig. 9).

As is seen in this figure for both cases the ultrasonic irradiation leads to successful result- decrease both active and reactive component of capacitance.

Another important branch in this field is studying and application of such promising material as blue graphite, in which the carbon layers alternate with acid anions and acid molecules layers [11]. The special methods were used in order to fabricate these materials. We have studied blue graphite and obtained results permitted us to consider it as promising for use in energy storage devices. Especially it was shown that parameters of such material can be improved by means of combination of PbO-electrode with blue graphite one.

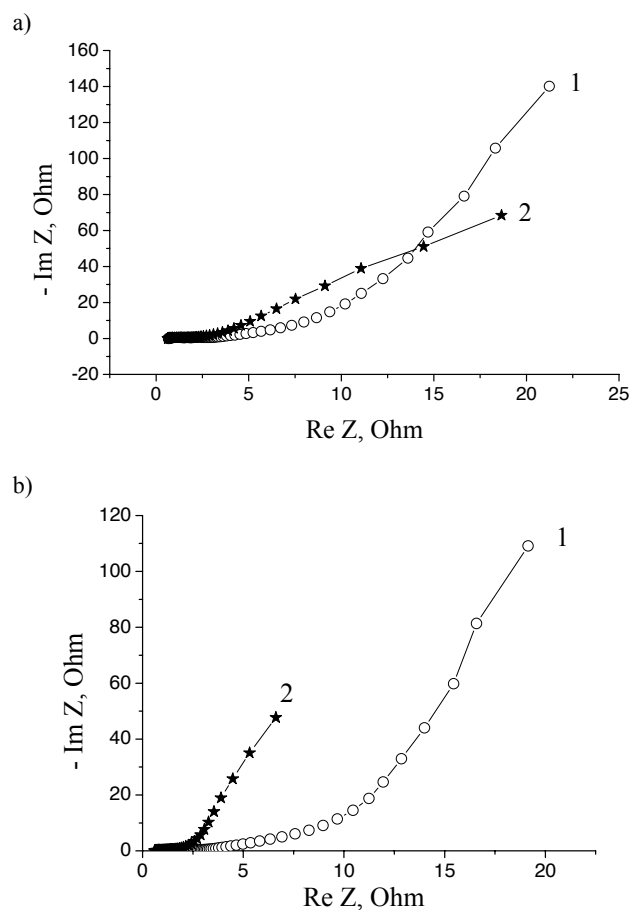


Fig. 9. Nyquist diagrams for supramolecular ensemble BAC<12-crown-ether-4> - a) and for BAC <18-crown-ether-6> - b) (1- initial; 2- upon irradiation)

## 4. Conclusions

1. Therefore, the obtained results allowed us to establish that ultrasonic irradiation of supramolecular ensembles BAC 12 crown-ether-4 and BAC 18-crown-ether-6 provides the increase of both specific energy and power in reverse processes of energy storage.

2. It was found that upon ultrasonic irradiation the specific capacitance for BAC<12-crown-ether-4> increases more than by 20 %.

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