

# Electrochemical Properties of the Composites Based on Multiwall Carbon Nanotubes Modified with Nanoparticles of Mixed Cobalt and Nickel Hydroxides

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## Abstract

A simple and reproducible method of chemical deposition was used to modify carbon nanotubes cobalt and nickel hydroxides. Thus the composites containing 5 and 10 wt.%  $\text{Co}_{0.5}\text{Ni}_{0.5}(\text{OH})_2$  (the ratio of hydroxides 1:1) were obtained based on the matrix of multiwall carbon nanotubes: non-functionalized (MWCNT) and functionalized (MWCNT-f). The physicochemical properties of the obtained nanocomposites were investigated with a focus on the characteristics that are relevant for use as the electrode materials of supercapacitors. Electrical capacity characteristics (specific electrical capacitance, internal resistance, etc.) of nanocomposites were determined using cyclic voltammetry and impedancemetry. The effect of matrix functionalization and filler content on the electrochemical characteristics of the composites was considered. It is established that the surface of carbon nanotubes allows the accumulation of the charge in the electrical double layer, in particular at high polarization rates. At low rates, the contribution from the pseudo-capacity component increases on the filler nanoparticles, on the surface of channels in nanotubes, and pore surface in hydroxide aggregates. An increase in the specific electrical capacitance of the composites by a factor of 1.5 to the capacitance of MWCNTs was achieved. The schemes of electrode processes in the nanocomposite are proposed, and the nature of redox peaks on voltammetric curves providing the occurrence of the pseudo-capacity component is revealed. Relying on the analysis of impedancemetry results, the equivalent series resistance and the charge transfer resistance are evaluated. An equivalent circuit of the cell with the working composite electrode is proposed, and its major parameters are calculated.

## 1. Introduction

Nanostructured materials are characterized by high variability of morphology and properties, which determines their broad application in various areas of science and technology. Nanostructured composites based on carbon nanotubes are extensively used, for example, in low-voltage electronics and electrical engineering [1]. Despite the high efficiency of composite electrodes in modern devices for energy generation and accumulation, which has been demonstrated in a large number of studies,

the existing methods of obtaining these materials with high functional properties are expensive, and their multistage synthesis hinders their wide introduction into practice. Therefore, the search for optimal routes to synthesize highly porous composites based on commercially available multiwall carbon nanotubes (MWCNTs) with various fillers possessing improved electrochemical characteristics is a relevant task. Thus, supercapacitors (SC) with electrodes in the form of nanostructured composites (NC) based on MWCNT allow rather efficient charge accumulation due to the formation of an electric double layer (EDL) on the surface of the matrix and occurrence of Red-Ox reactions

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participated by filler nanoparticles [2]. Analysis of the state of studies into the synthesis and properties of these materials shows that the introduction of nanosized particles of transition metal hydroxides into carbon matrices with developed surfaces and high electrical conductivity causes a substantial improvement of electrode characteristics [2]. However, only in limited cases, do the fillers for these hybrid NC electrode materials for SC involve mixed hydroxides (MH) of cobalt and nickel [2, 3], so investigation of the electrical capacity characteristics of this type of NC and studies of the processes of charge accumulation in them remain urgent problems.

Capacity values obtained by us as a result of the introduction of mixed cobalt and nickel hydroxides into MWCNTs exceed the electrical capacity of the initial MWCNT matrix due to electrochemical reactions characteristic of these hydroxides. In this connection, it is of interest to investigate the nature of the occurring processes. In addition, it is important to evaluate the effect of hydroxide filler on the parameters of cyclic voltammetric curves and the spectra of electrochemical impedance and to determine the contribution from oxidation-reduction processes to the total electrical capacitance.

## 2. Experimental

### 2.1. Reagents and materials

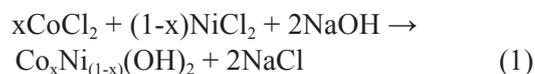
Multiwall carbon nanotubes manufactured at the IC SB RAS were used as a substrate (matrix) to deposit mixed cobalt-nickel hydroxides for the synthesis of nanocomposites. MWCNT characterization showed that the outer diameter of the tubes was 10–20 nm, and the diameter of inner channels was 8–15 nm. The thickness of tube walls composed of 6–14 graphene layers was thus 2–5 nm; the average length of the tubes was about 10  $\mu\text{m}$  [4, 5].

Nanotubes were functionalized through ozonation (OGVK-02K ozonizer, MELP company, St. Petersburg);  $\text{O}_3$  concentration was measured at the inlet and outlet of the reactor with the help of a special ozone meter [4].

For the synthesis of NC  $\text{Co}_x\text{Ni}_{(1-x)}(\text{OH})_2/\text{MWCNT}$  and  $\text{Co}_x\text{Ni}_{(1-x)}(\text{OH})_2/\text{MWCNT-f}(x=0.5)$ , we used the solutions of cobalt and nickel chlorides, and sodium hydroxide as described in detail in [5].

The carbon matrix MWCNT (MWCNT-f) was placed in a weighting bottle and impregnated with

the solutions of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  at a mass ratio of 1:1. After a short time, necessary for matrix impregnation with the substrate (30 min), the solution of NaOH was introduced. Thus the mixed cobalt and nickel hydroxides were formed on MWCNTs surface according to reaction (1):



The process was carried out at a temperature of 98 °C for 20 min, then the product was washed with a small amount of distilled water to liberate NaCl, and dried to a constant weight. It was shown previously [5] that nanocomposites obtained using this procedure contain the solid solutions of cobalt and nickel hydroxides.

### 2.2. Methods of investigation

Electrochemical measurements of the NC were carried out with a two-electrode asymmetric electrochemical cell and a PARSTAT 4000 potentiostat (Princeton Applied Research, USA), using the VersaStudio software package. A Nafion membrane was used as a separator, and KOH solution (30 wt.%) was used as the electrolyte.

In the measurements of electrochemical characteristics of the composites based on MWCNT (MWCNT-f), the NC was used as the working electrode, while the corresponding matrix was used as a counter electrode.

Electrochemical measurements of the MWCNT matrix were carried out using a symmetrical electrochemical cell with electrodes based on MWCNT (MWCNT-f). The mass of each electrode was 10 mg.

Cyclic voltammograms were recorded under variations of the potential sweep rate (10, 20, 40 and 80 mV/s). Cyclic voltammetric curves (CCVA) were measured within the potential window from -1 to 1 V (window width was chosen experimentally to suit the cell).

Capacitance was calculated from the area limited by the CVA curves:

$$C_{\text{cell}} = \frac{q}{U \times m}, \quad (2)$$

where  $C_{\text{cell}}$  is the electrical capacitance of the cell, F/g;  $q$  is the charge accumulated by the cell, Q;  $U$  is the potential difference, V, and  $m$  is electrode mass, g.

The electrical capacitance of the electrode was calculated using Eq. 3:

$$C_{el} = \frac{C_{cell} \times C_0}{C_0 - C_{cell}}, \quad (3)$$

where  $C_{cell}$  is the capacitance of the electrode cell;  $C_{el}$  is the capacitance of the working electrode;  $C_0$  is the capacitance of the counter electrode.

Electrochemical impedance measurements were carried out within the frequency range 10 MHz – 10 kHz, with the amplitude of 10 mV, at zero potential to the open circuit.

### 3. Results and discussion

#### 3.1. Electrochemical properties of MWCNT and MWCNT-f

The curves shown in Fig. 1a were obtained by recording the cyclic voltammograms for the symmetrical cell with electrodes based on the MWCNT matrix. The shape of these curves is nearly rectangular, which points to charge accumulation mainly due to the formation of the EDL at the electrode-electrolyte interface. Insignificant non-linearity within the range of  $\pm 0.4$  V is evidence in favor of the weak contribution from the pseudo-capacitance component, due to the insignificant amount of oxygenated groups on the surface of the matrix.

Cyclic voltammograms recorded in the symmetrical cell with the electrodes based on functionalized MWCNT-f are presented in Fig. 1b. In comparison with the CVA curves of pure MWCNT, these curves exhibit more substantial non-linearity in the region of 0.7–0.9 V in the anode and cathode semi-cycles, which points to a more noticeable contribution of the pseudo-capacitance component into the total electrode capacitance. In addition to charging accumulation due to the formation of

the EDL, the charge is also accumulated due to Red/Ox-reactions proceeding with the participation of oxygen-containing groups, which are introduced additionally during ozonation. The presence of O-containing groups in the initial MWCNT matrix and an increase in their number after functionalization were confirmed previously by means of thermogravimetric (TG) investigation and CNHO-analysis [5].

#### 3.2. Electrochemical properties of NC $Co_xNi_{(1-x)}(OH)_2$ /MWCNT and $Co_xNi_{(1-x)}(OH)_2$ /MWCNT-f

The accumulation of electrical charge on NC was observed in asymmetric cells. CVA curves for NC (Fig. 2) containing mixed hydroxides contain peaks that change the nearly rectangular shape characteristics of MWCNT. For  $NCCo_{0.5}Ni_{0.5}(OH)_2$ /MWCNT, two groups of anode-cathode peaks are observed within the potential range 0.4–0.9 V, which are due to the electrode reactions participated by cobalt and nickel hydroxides. The  $E_a/E_c$  potentials for the indicated peaks are (V): 0.55/0.35 and 0.75/0.60 at the scanning rate of 40 mV/s. An increase in the rate causes a regular increase in the peak current and the shifts of the peaks to the anode and cathode regions, respectively (Fig. 2).

CVA curves obtained for  $Ni(OH)_2$  electrode in the alkaline electrolyte (5M KOH) are presented in [6]. A pair of anode-cathode maxima arising as a result of the Red/Ox reaction



is observed at  $E_a/E_c$ : 0.48/0.39 V ( $v = 10$  mV/s).

The region of oxygen evolution for this electrode system starts at the potential of 0.62 V and corresponds to the process:

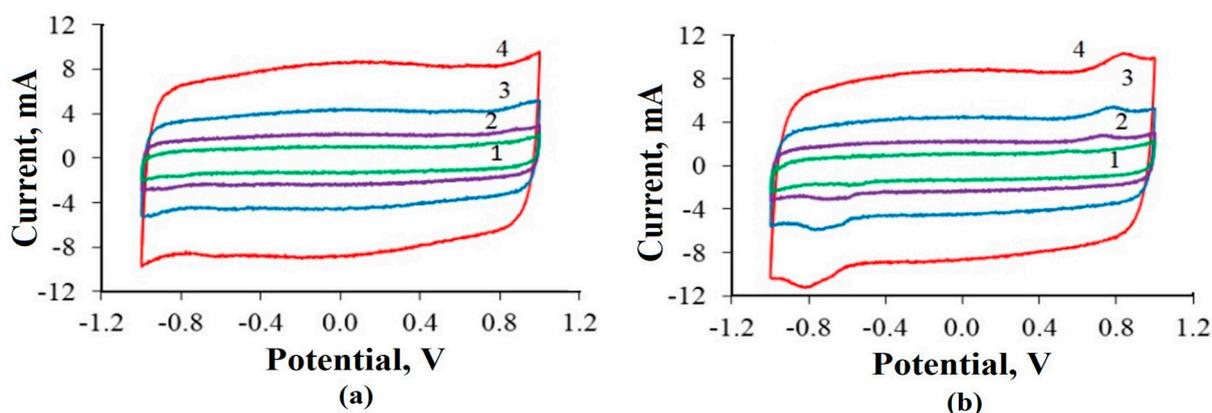
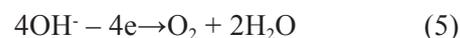


Fig. 1. CVA curves for symmetrical cells with the electrodes made of MWCNT (a) and MWCNT-f (b), at scanning rates: 1 – 10 mV/s; 2 – 20 mV/s; 3 – 40 mV/s; 4 – 80 mV/s.

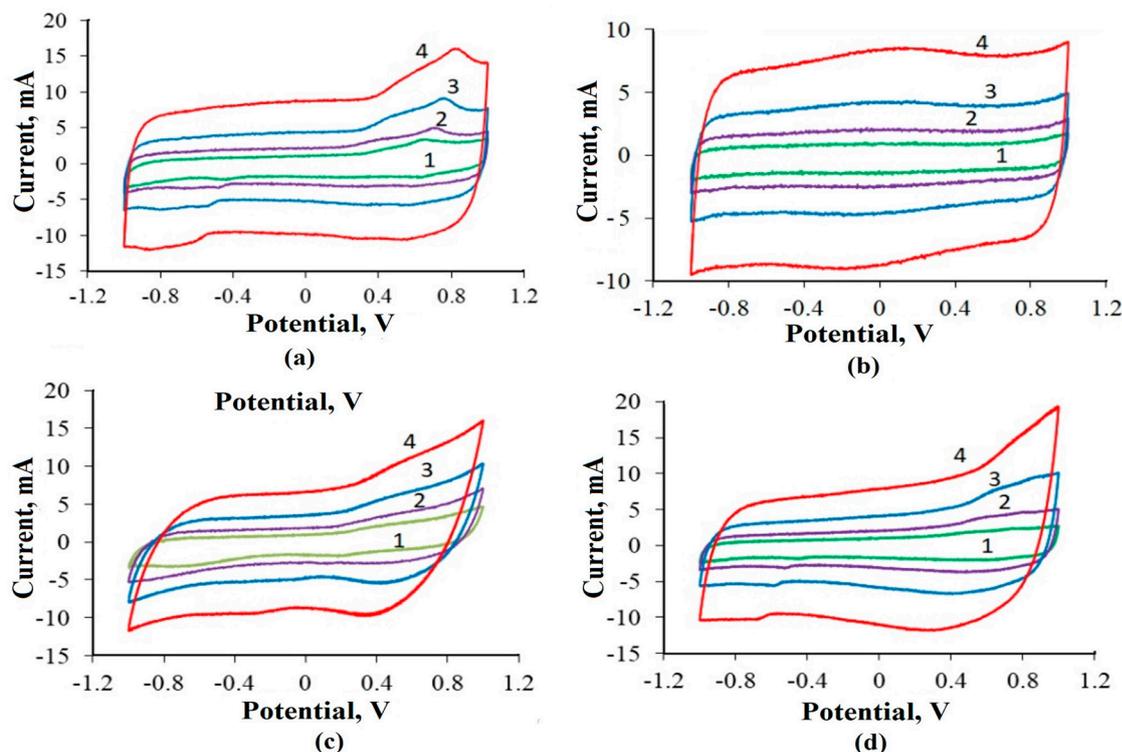


Fig. 2. CVA curves for asymmetric cells with the electrodes made of the corresponding matrix and NC  $\text{Co}_{0.5}\text{Ni}_{0.5}(\text{OH})_2/\text{MWCNT}$  (5 wt.% MH) (a) and  $\text{Co}_{0.5}\text{Ni}_{0.5}(\text{OH})_2/\text{MWCNT-f}$  (5 wt.% MH) (b);  $\text{Co}_{0.5}\text{Ni}_{0.5}(\text{OH})_2/\text{MWCNT}$  (10 wt.% MH) (c) and  $\text{Co}_{0.5}\text{Ni}_{0.5}/\text{MWCNT-f}$  (10 wt.% MH) (d), at the potential scanning rates: 1 – 10 mV/s; 2 – 20 mV/s; 3 – 40 mV/s; 4 – 80 mV/s.

Under our experimental conditions, the oxygen peak is in the region of 0.90–0.98 V. So, it is necessary to shift the values of the oxidation-reduction potential (ORP) for reaction 4 by  $\approx 0.35$  V to the anode region. Because of this, the corresponding ORP for nickel hydroxide should be observed on the CVA curves for NC (Fig. 2) at the regions of 0.84 V and 0.75 V.

In addition, the authors of [7] stress the possibility of separate oxidation/reduction processes with the participation of  $\alpha$ - and  $\beta$ -hydroxides of nickel and the formation of the corresponding pairs of anode/cathode peaks. The schemes of electrode processes are:



The potentials of peaks in the alkaline electrolyte with respect to the silver chloride reference electrode ( $v = 50$  mV/s) in 0.5 M NaOH are equal to  $(E_a/E_c)(\text{V})$ : 0.35, 0.65/0.30 and 0.45, respectively. The region of oxygen evolution in the experiments [7] starts at a potential higher than 0.75 V. Therefore, under the conditions of our measurements peak potentials should be  $(E_a/E_c)$ , V: 0.55 and 0.85/0.5 and 0.65; comparison shows that the

data obtained from our observation of MWCNT-based composites are in agreement with the literature data for electrodes containing nickel hydroxide on carbon substrates.

Mixed cobalt-nickel hydroxide is a component of the NC electrodes [5], so a set of reactions marked with (\*) in the list of reactions presented in Table 1 based on data reported in [8] also may be characteristic of the system under investigation. Potential values were recalculated taking into account the position of the region of oxygen evolution ( $\Delta E = 0.45$  V) because the authors of [8] used a mercury oxide reference electrode.

Thus, the entire diversity of electrode processes schematically presented in Table 1, along with the above-considered reactions for nickel hydroxide (4-6), may be expected for NC containing mixed cobalt and nickel hydroxides.

The most clearly pronounced peaks on CVA curves recorded by us are those within the potential region of 0.4–0.9 V, which corresponds to reactions 4\* and 7\* (Table 1). Thus, the peak for reaction 4\* in the region of -0.05 V concerning the mercury oxide reference electrode should appear under our conditions in the potential region of 0.4 V; for reaction 7\*, its peak in the region of 0.25 V should be observed under our conditions,

**Table 1**

Electrochemical processes and the values of electrode potentials measured with respect to the Hg/HgO electrode [8], in comparison with the values calculated for the experimental conditions of the present work

No.	Electrode pair	Electrode reaction	Potential with respect to Hg/HgO, V	Calculated potential, V
1	CoO/Co <sub>3</sub> O <sub>4</sub>	3CoO + 2OH <sup>-</sup> → Co <sub>3</sub> O <sub>4</sub> + H <sub>2</sub> O + 2e	-0.37	0.08
2	Co(OH) <sub>2</sub> /Co <sub>3</sub> O <sub>4</sub>	*3Co(OH) <sub>2</sub> + 2OH <sup>-</sup> → Co <sub>3</sub> O <sub>4</sub> + 4H <sub>2</sub> O + 2e	-0.19	0.26
3	CoO/CoOOH	CoO + OH <sup>-</sup> → CoOOH + e	-0.17	0.28
4	Co(OH) <sub>2</sub> /CoOOH	*Co(OH) <sub>2</sub> + OH <sup>-</sup> → CoOOH + H <sub>2</sub> O + e	-0.05	0.40
5	CoO/CoO <sub>2</sub>	CoO + 2OH <sup>-</sup> → CoO <sub>2</sub> + H <sub>2</sub> O + 2e	0.20	0.65
6	Co <sub>3</sub> O <sub>4</sub> /CoOOH	*Co <sub>3</sub> O <sub>4</sub> + OH <sup>-</sup> + H <sub>2</sub> O → 3CoOOH + e	0.22	0.67
7	Co(OH) <sub>2</sub> /CoO <sub>2</sub>	*Co(OH) <sub>2</sub> + 2OH <sup>-</sup> → CoO <sub>2</sub> + 2H <sub>2</sub> O + 2e	0.25	0.70
8	Co <sub>3</sub> O <sub>4</sub> /CoO <sub>2</sub>	*Co <sub>3</sub> O <sub>4</sub> + 4OH <sup>-</sup> → 3CoO <sub>2</sub> + 2H <sub>2</sub> O + 4e	0.48	0.93

with a shift by 0.45 V, in the region of 0.70 V, which corresponds to the experimental data.

The above-described considerations suggest that the main processes causing the formation of the pseudo-capacitance component during polarization of the electrodes made of NC Co<sub>x</sub>Ni<sub>(1-x)</sub>(OH)<sub>2</sub>/MWCNT are electrochemical reactions (6), (7), 4\* and 7\*. The anode and cathode peaks corresponding to these reactions are overlapping as a consequence of the close potential values, so a total broad peak is observed in the region from 0.4 to 0.9 V. In some cases (Fig. 2b), too, broad relatively weak maxima are detected on CVA curves in the region of more negative potentials, therefore, there is the possibility for processes 2\*, 6\*, 8\* to take place, but to a substantially lower extent.

### 3.3. Electrochemical impedance spectroscopy

The data obtained by means of impedancemetry in the potentiostatic mode (frequency range from 10<sup>-2</sup> to 10<sup>4</sup> Hz, E = 0 V to the open circuit potential) are shown in Fig. 3.

The spectra of electrical impedance of initial, ozonized MWCNT and all the composites under study are shifted along the abscissa axis as a consequence of the active cell resistance R<sub>s</sub>, which is a sum of the resistance of electrodes, electrolyte and the (MWCNT)/electrolyte interface; all the spectra are characterized by the presence of a depressed-semicircle in the region of higher frequencies, then a sharp increase in -Z<sub>im</sub> values follows (Fig. 3). For the initial MWCNT matrices, the radius of the semicircle is substantially smaller. With an increase in the mass fraction of the filler, almost proportional changes of the boundary values Z<sub>re</sub> and Z<sub>im</sub> of the semicircle occur, which confirms its

correspondence to the charge transfer processes: Faraday-type and those related to the double layer (R<sub>ct</sub> and C<sub>dl</sub>), proceeding with the participation of metal oxides/hydroxides introduced into MWCNT matrix. Within the medium frequencies, a weakly pronounced transition region is observed, which is likely to correspond to the diffusion of ions in the volume of the electrolyte filling the pores with complicated configurations in the composite and may be described by Warburg impedance W.

One can see in the results presented above that the introduction of the filler into MWCNT matrix causes a substantial increase in electrical conductivity; quite contrary, the functionalization of nanotubes does not lead to any significant changes in the impedance of the electrochemical system.

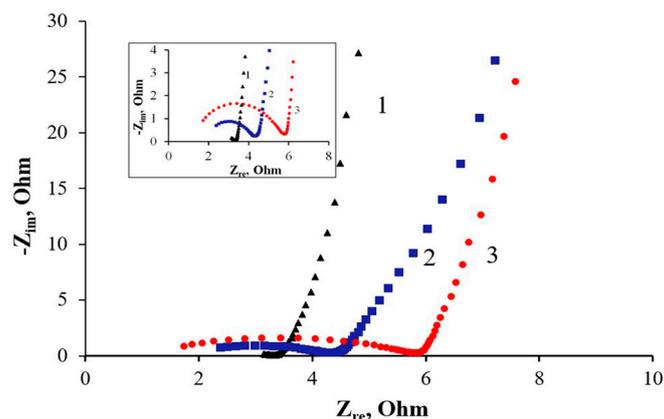


Fig. 3. Nyquist plot for SC cells based on MWCNTs and NC on this basis: 1 – symmetrical cell with electrodes based on MWCNT; 2–3 – asymmetric cells with working electrodes based on NC with the composition Co<sub>0.5</sub>Ni<sub>0.5</sub>(OH)<sub>2</sub>/MWCNT (5 and 10 wt.% MH, respectively) and counter electrodes based on MWCNTs.

It is known [5] that the composites under investigation are chaotically located regions of hydroxide-modified MWCNT with different conductivities and different relaxation times after the action of the exciting signal. A decrease in the total resistance of the cell after the introduction of the filler is connected with an increase in the interface area, an increase in the effective density of the composites [5] and changes in the resistance of MWCNT/electroactive filler/electrolyte interfaces formed in the composites, in comparison with the MWCNT/electrolyte interface. The appearance of the characteristic pseudo-capacitance component in the NC is connected with the latter.

Within the low frequency region, an almost vertical increase in the reactive component of the impedance – Zimmans the circuit includes additional capacity elements connected with the features of cell design: the limited volume of the electrode material, a small amount of electrolyte, and high filling density, which causes additional diffusion limitations. Indications for similar effects in the cells of similar structure, in particular those containing MWCNT, can be found in the literature [9–12].

To model the electrochemical behavior of cells based on MWCNT, a circuit presented in Fig. 4 is proposed. In this circuit,  $R_s$  is the total active resistance of the cell: electrolyte, current-collecting electrodes, separator membrane;  $R_{ct}$  is the charge transfer resistance; ( $C_{dl}$  the capacitance of the electric double layer;  $W$  is Warburg diffusion impedance;  $C_{pseudo}$  is pseudo-capacitance of the electrode material, corresponding to electrochemical (Faraday) processes that take place with the participation of the oxide-hydroxide filler and, to a small extent, functional groups on MWCNT surface.

Mathematical modeling of the spectra of electrochemical impedance was carried out in agreement with the circuit. Modeling results in comparison with experimental data are shown in Fig. 5.

One can see in the Fig. 5 and in the values of modeling error, calculated using the ZSimpWin-software (Echem Software, Michigan, USA), that the presented equivalent circuit provides a satisfactory accuracy in the description of the electrochemical properties of the system composed of two

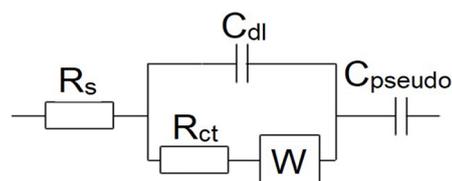


Fig. 4. Equivalent circuit for asymmetric electrochemical cells with working electrodes based on  $\text{Co}_{0.5}\text{Ni}_{0.5}(\text{OH})_2/\text{MWCNT}$  nanocomposites.

composite electrodes made of MWCNT filled with metal hydroxides.

According to the data shown in Table 2, the studied electrode materials are characterized by the close electrochemical properties, and clearly expressed reactive constituent of impedance, which includes the charge transfer resistance and pseudo-capacity. The processes of hydroxide transformation according to the presented equations (6), (7), 4\* and 7\* proceed with decelerated charge transfer. Results of impedancemetry correspond to the data obtained by means of CVA, in particular, those concerning the presence of the pronounced pseudo-capacitance component along with the double-layer capacity of the nanocomposite.

#### 4. Conclusion

Electrochemical transformations proceeding in symmetrical and asymmetric cells based on MWCNT, MWCNT-f,  $\text{NiCo}_x\text{Ni}_{(x-1)}(\text{OH})_2/\text{MWCNT}$  with potential cycling are a result of a combination of the Faraday and double-layer processes. The nature of anode and cathode peaks on the CVA curves for MWCNT and NC containing nickel hydroxides is established. For nickel and cobalt hydroxides, reduction-oxidation reactions corresponding to the scheme  $\text{M}(\text{OH})_2 \leftrightarrow \text{MOOH}$  are observed. In addition, the MWCNT matrix also contributes to the formation of the electrochemical response. The spectra of electrochemical impedance for all the studied composites look like semi-circles in the region of relatively high frequencies, and then a sharp increase in the imaginary part of impedance follows. An equivalent circuit of electrochemical cells with the electrodes based on the composites made of MWCNT is proposed.

Table 2

Parameters of the equivalent circuit for various electrode materials, obtained by means of modeling

Sample	$R_s$ , Ohm	$C_{dl}$ , $\mu\text{F}$	$R_{ct}$ , Ohm	$W(Y_0)$ , $\text{S}\cdot\text{sec}^{1/2}$	$C_{ps}$ , F
5% $\text{Co}_{0.5}\text{Ni}_{0.5}(\text{OH})_2/\text{MWCNT}$	2.26	27.4	1.92	0.409	0.106
10% $\text{Co}_{0.5}\text{Ni}_{0.5}(\text{OH})_2/\text{MWCNT}$	1.69	21.6	3.82	0.489	0.116

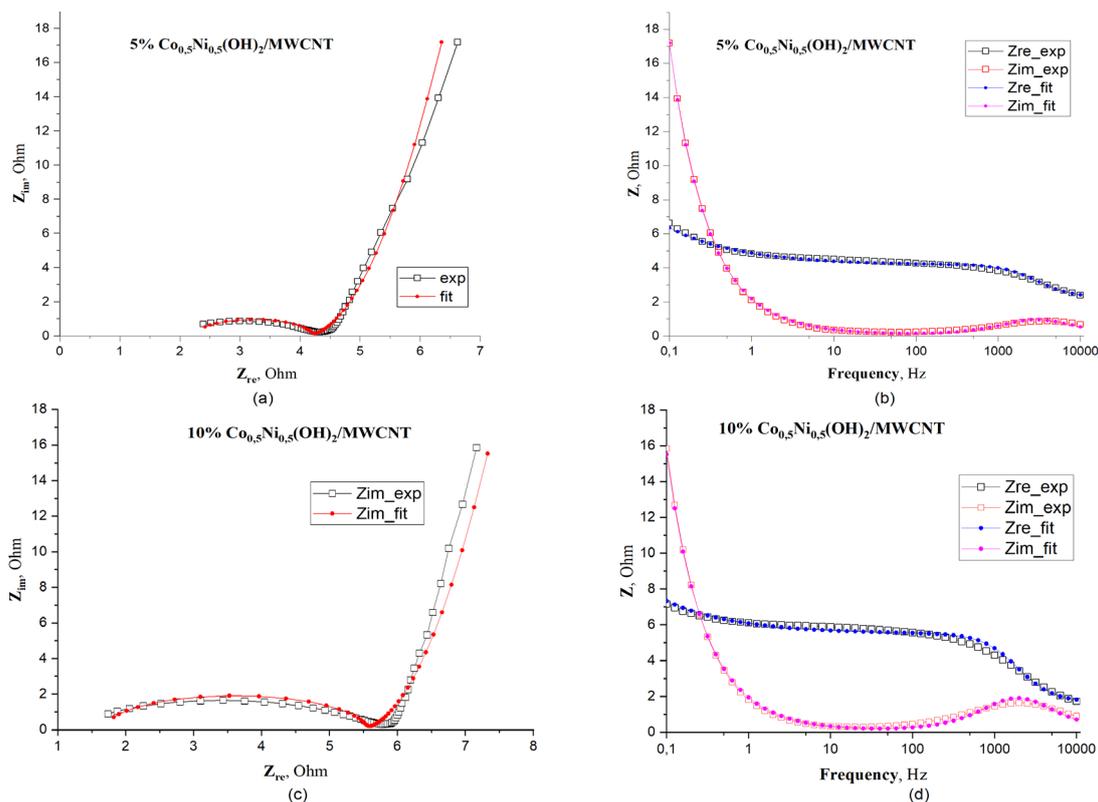


Fig. 5. Comparison of the experimental Nyquist (a, c) and Bode (b, d) dependences with the results of modeling for electrochemical cells with the working electrodes based on NC with different MH-filler content: 5 wt.% (a, b); 10 wt.% (c, d).

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