

UDC 544.7: 544.076.32 + 543.55.054.1

DOI: 10.15372/CSD20170611

# Mesoporous Carbon Matrix-Based $Mn_xO_y/C$ Hybrid Electrode Materials for Asymmetric Supercapacitors

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(Received July 3, 2017; revised August 25, 2017)

## Abstract

With the common purpose of developing functional and cost-effective new electrode materials, including those for supercapacitors, a preparation method was elaborated and electrocapacitive properties of nanostructured composites based on a mesoporous carbon material filled with manganese oxides were examined. Carbon material used as a matrix of nanocomposites was produced by carbonization of oxidized coal at 800 °C under natural conditions. Composites were obtained by reduction of potassium permanganate solutions with carbon matrix at 20–25 °C without the introduction of additional reducing substances. The content of  $Mn_xO_y$  in composites was varied from 1 to 5 mass %. Manganese oxides in nanocomposites were in the X-ray amorphous state, as demonstrated by powder X-ray diffraction technique. Nafion ion exchange membrane was used as a separator, a 6 M KOH solution – as an electrolyte during studying electrochemical properties using Parstat 4000 potentiostat/galvanostat. The electric capacitance of nanocomposite electrodes is higher than that of matrix-based electrode material, as demonstrated by methods of cyclic voltammetry (in potential windows: from –1.5 to 1.5 V; from –1 to +1 V; from 0.1 to 0.8 V), galvanostatic charge–discharge and electrochemical impedance spectroscopy. Internal resistance and total impedance of asymmetric cells with nanocomposite electrodes were less than appropriate values for the symmetric cell with electrodes based on the matrix. The optimum content of manganese in composites was 3 %, as established. Herewith, the reached capacitance for  $Mn_xO_y/C$  nanocomposite hybrid electrode material in a potential window from 0.1 to 0.8 V was 404 F/g when using a 6 M KOH aqueous solution as the electrolyte.

**Keywords:** nanocomposite, mesoporous carbon material, manganese oxides, electrochemical properties, electrode materials, supercapacitor

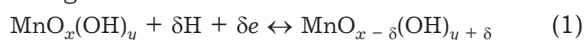
## INTRODUCTION

Development of preparation methods and study of properties of chemically pure nanostructured composites (NC) based on mesoporous carbon materials (MCM) that

have spacial morphology, and also high values of specific surface and porosity is one of the relevant areas of modern material science [1–4]. This is driven by an active introduction of nanoscale and nanostructured materials in many areas of science, technology, and production.

Certain combinations of peculiarities of optical, catalytic, electrophysical, electrochemical, and other properties of components (filler and carbon matrix nanoparticles) should be most apparent in these systems. This has to increase the range, the level of functional characteristics and application range of materials based thereon.

The MCM/Mn<sub>x</sub>O<sub>y</sub> composite that is of great interest as a pseudocapacitive electrode material of supercapacitors (SC) deserves special attention out of this group, since a substantial increase in the range of change of potentials, at which various redox reactions are possible, is probable due to the presence of a large number of oxidation states in manganese [1, 5]. Pseudocapacitance of Mn<sub>x</sub>O<sub>y</sub> is driven by the progression of a reversible electrochemical process resulting in oxide-hydroxide forms of manganese in different valencies:



Nanostructured composites based on MCM that combine the high capacitance of the double electric layer at electrode-electrolyte boundary typical for high porous carbon materials and elevated pseudocapacitance of transition metal oxides and hydroxides driven by the progress of reversible Faraday redox reactions refer to a series of most promising in the field of developing new electrode materials including those for SC. Lately, there have appeared papers on obtaining composite materials based on Mn<sub>x</sub>O<sub>y</sub> applied onto various carbon materials, such as graphite [6], carbon nanotubes [7], carbon nanopens [8], graphene [9], *etc.*

Optimization of preparation conditions and structure of composites that allows reaching the maximum possible degree of coating the surface of carbon materials by filler nano-thick films with minimum blocking of pores remains one of the relevant tasks. The simplification of production technology, a reduction in product costs, an opportunity of controllable production and of a change in the size, shape, and phase composition of filler nanoparticles, an increase in the availability of the active surface of filler particles and matrix for solutions of electrolytes are no less important. Solving these problems would allow reaching record functional characteristics of electrodes and overall, SK.

A method for obtaining hybrid nanocomposite electrodes based on MCM filled with manganese

oxides was developed by us. Reduction of a potassium permanganate solution with MCM yielded Mn<sub>x</sub>O<sub>y</sub>/C nanocomposites with a manganese content of 1–5 %. Composites were studied by methods of X-ray phase and X-ray fluorescence analyses, cyclic voltammetry (CVA), galvanostatic charge-discharge (GCD, chronopotentiometry), and electrochemical impedance spectroscopy (EIS) in an asymmetric capacitor cell. Hybrid nanocomposite electrode material was used as an operating electrode, and carbon parent material – as a counter electrode.

## EXPERIMENTAL

Naturally oxidized coal of the Shestaki section from the Kuznetsk Coal Basin carbonized in the presence of KOH at 800 °C with a KOH/coal mass ratio of 2 : 1 was used as a mesoporous carbon material [10]. Porous structure parameters were as follows: a specific surface of 1200 m<sup>2</sup>/g, pore volume 0.8 cm<sup>3</sup>/g including a mesopore volume of 0.45 cm<sup>3</sup>/g.

### *Method of obtaining C/Mn<sub>x</sub>O<sub>y</sub> nanocomposites*

A weighed amount of MCM was placed into a 25 mL glass and 5 mL of a KMnO<sub>4</sub> solution was added. Solution concentration was calculated in terms of the sample weight of a carbon material and the required manganese content in the composite. The reaction mixture was carefully stirred and aged for a day to ensure reaction completeness of potassium permanganate reduction, filtered off, rinsed with water, acetone, and air dried.

Nanocomposites were studied by a set of physicochemical research methods, such as X-ray phase analysis (Diffractometer Difrax-401 diffractometer), X-ray fluorescence analysis, and small angle X-ray scattering (X-ray diffractometer KRM-1) in the iron characteristic radiation. Electrochemical measurements were carried out in a two-electrode cell using Parstat-4000 potentiostat/galvanostat with VersaStudio software. Nafion was used as a separator, a 6 M KOH solution – as an electrolyte, the titer of which was checked against a 0.1 M HCl solution. To study properties of electrodes based on the initial matrix there was used the symmetrical cell design with MCM

electrodes accumulating the charge mainly due to the generation of a double electric layer. To explore properties of NC asymmetric cell design was utilized, in which a hybrid nanocomposite electrode material was used as an operating electrode accumulating energy due to an electric double layer (EDL) at the electrode/electrolyte interface, and Faraday redox processes with the participation of manganese compounds in various oxidation states. The original carbon matrix was used as a counter electrode. Electrode material mass was 10 mg. Prior to applying onto current collectors, the electrode materials and the separator were impregnated with an electrolyte solution.

#### *Electrochemical study of nanocomposites as supercapacitor electrodes*

The study by the CVA-method was carried out at a potential scanning rate of 5–80 mV/s in three potential windows: from –1.5 to 1.5 V; from –1 to +1 V; from 0.1 to 0.8 V. Cell capacitance ( $C_c$ ) was determined according to the area [2, 11, 12] limited by volt-ampere curves:

$$C_c = \int I(U)dU/mv\Delta U$$

where  $\int I(U)dU$  is area bounded by the curve ( $A \times B$ );  $m$  is electrode material mass, g;  $v$  is scanning rate, V/s;  $\Delta U$  is potential window. A SC cell is considered as two sequentially connected capacitors:  $1/C_c = 1/C_e + 1/C_0$ , where  $C_e$  is composite electrode capacitance,  $C_0$  is counter electrode capacitance.

To study composite electrode materials by the GCD method a change in cell potential in time at the constant current value of charge ( $I_c = +10$  mA) and discharge ( $I_d = -10$  mA) processes was recorded. Charge/discharge time ( $t_c = t_d$ ) is 10 s; cycle number is 25.

The equivalent series resistance of the cell was calculated [13] according to the voltage drop in the steep initial portion of SC cell discharge curve according to the formula  $ESR = U'/I_d$  [13].

Cell capacitance was counted by formula

$$C = -I_d(t_2 - t_1)/(U_2 - U_1)m$$

where  $U_1$  and  $U_2$  are potential values at discharge time  $t_1$  and  $t_2$ , respectively,  $m$  is electrode material mass, g.

The systems under study were also studied by the EIS technique [14]. Impedance hodographs

(Nyquist diagrams) were constructed; there was assessed the impedance of electrochemical cells and capacitance versus current frequency.

## RESULTS AND DISCUSSION

Nanostructured MCM/Mn<sub>x</sub>O<sub>y</sub> composites were obtained by reduction of KMnO<sub>4</sub> on the surface of mesopores and on the external surface of carbon matrix without the introduction of additional reducing agents. The reduction occurred because of a high reducing ability of MCM due to the presence on their surface of functional groups (carboxyl, hydroxyl, phenol, lactone *etc.*) and reducing the capacity of nanoscale carbon.

According to the literature data [1, 11, 15], both MnO<sub>2</sub> and Mn<sub>2</sub>O<sub>3</sub>, and also their mixtures may form during reduction of KMnO<sub>4</sub>. This may be driven by different experimental conditions and/or different chemical composition of surface carbon functional groups. Manganese (IV) oxide (MnO<sub>2</sub>) is mainly formed in a relatively acid medium (pH < 3) and/or in the presence of COOH groups. Manganese (III) oxide (Mn<sub>2</sub>O<sub>3</sub>) is stable under neutral conditions, and in acid medium, it disproportionates and manganese MnO<sub>2</sub> and soluble Mn<sup>2+</sup> salts are formed.

Reduction of KMnO<sub>4</sub> introduced in the amount of 1–2 % (hereinafter, in terms of Mn) by carbon matrix proceeds instantly, as established under our experimental conditions. Total reduction occurs in 5–10 min in introducing 3–5 mass % of KMnO<sub>4</sub>.

#### *X-ray diffraction study of hybrid electrode materials*

There are no clear reflexes in diffraction patterns of NC, therefore, it is hard to assess the phase composition of components. Apparently X-ray amorphism of NC is driven by the presence of manganese compounds (mainly, oxides) in different oxidation degrees and phase states, and also their high dispersion, to 1–5 nm.

According to X-ray fluorescence analysis data, manganese lines are relatively strong; their intensities increase in direct proportion to manganese content in a sample.

### Study of electrode materials via the cyclic voltammetry method

In asymmetric SC cells, a counter electrode accumulates a charge mainly due to EDL; in the main electrode (hybrid electrode material) the charge accumulation occurs both due to EDL at the interface of MCM/solution uncoated area with oxides and due to the pseudocapacitance of manganese oxides ( $\text{Mn}_2\text{O}_3$  and  $\text{MnO}_2$ ) and oxygen-containing groups in the electrode surface. The content of these groups may increase due to the oxidation of the surface of MCM at the reduction of  $\text{KMnO}_4$ . However, when applied to the surface of MCM of nanoparticle fillers (including manganese oxides), a reduction in the specific surface of the matrix due to partial blocking of micro- and

mesopores. The main goal is to maximally cover the surface of MCM with extremely thin (nanothick) films of electrochemically active filler while maintaining high values of the parameters of the porous structure. It is therefore necessary to find optimum preparation conditions and compositions of hybrid electrode materials that allow significantly increasing pseudocapacitance and minimizing the blocking of pores.

Experimental CVA curves in a symmetric cell, and also an asymmetric one with working  $\text{Mn}_x\text{O}_y/\text{C}$  electrodes containing the determined optimum manganese content of 3 mass % are given in Fig. 1. It can be seen that in asymmetric cells, there are pseudocapacitive peaks driven by reversible redox reactions of manganese compounds in different oxidation states. Peak positions depend on potential scanning rates and potential window sizes.

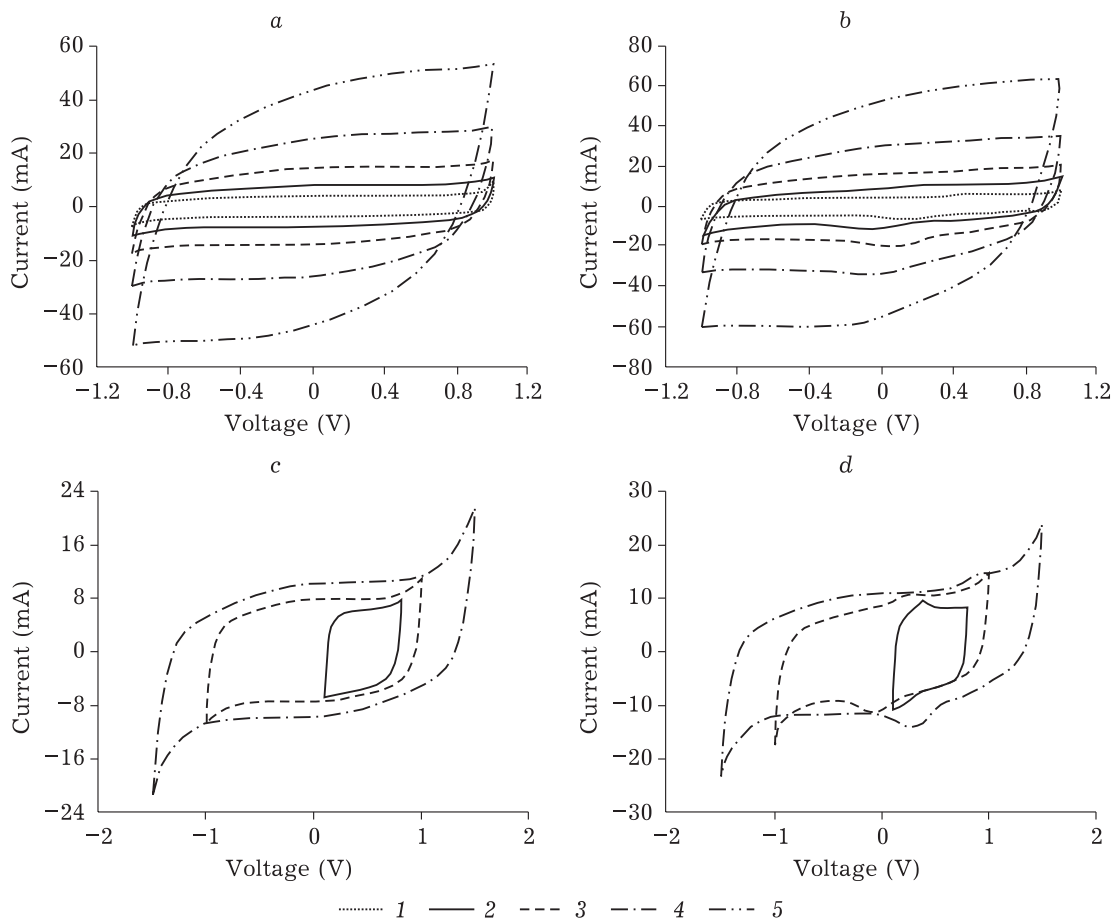


Fig. 1. Cyclic voltammetry (CVA) curves of symmetric (a, c) SK cell with electrodes based on the initial C-matrix and asymmetric (b, d) SK cell with a working electrode based on nanostructured  $\text{C}/\text{Mn}_x\text{O}_y$  composite (3 mass %) in a potential window from  $-1$  to  $+1$  V at the specified potential scanning rate (5 (1), 10 (2), 20 (3), 40 (4), 80 (5)  $\text{mV/s}$ ) and in different potential windows (c, d) at potential scanning rate of  $10$   $\text{mV/s}$ .

Fig. 2, a presents the generalized graph of the dependence for the capacitance of electrode materials on potential scanning rate for a symmetric cell and asymmetric SC. It can be seen that at potential scanning rates of 5–20 mV/s, capacitances of all hybrid electrode materials under study are higher than the capacitance of electrode material based on the initial C-matrix. The highest capacitance is observed for C/Mn<sub>x</sub>O<sub>y</sub> hybrid electrode with a manganese content of 3 mass %. However, capacitance drops sharply at high potential scanning rate due to the kinetic inhibition of electrochemical redox processes with the participation of manganese oxides. There is even a more significant decrease in capacitance at high potential scanning rates, as EDL capacitance drops significantly due to a decrease in specific surface and volume of meso- and macropores of carbon matrix. At manganese content of 1 and 2 %, electrode materials are more stable at high potential scanning rates (20–80 mV/s), however, the contribution of the pseudocapacitance of manganese oxides is insufficient to achieve the maximum capacitance. Thus, the optimum manganese content in composites is 3 mass %. Pseudocapacitance contribution increases with an increase in manganese content and peaks are more clearly visible in the curves. Peak positions depend on potential scanning rates and potential window sizes.

Figure 2, b presents histograms of the capacitance of electrode materials versus potential window sizes: a) from 0.1 to 0.8 V ( $\Delta U = 0.7$  V); b) from -1 to +1 V ( $\Delta U = 2$  V); c) from -1.5 to +1.5 V ( $\Delta U = 3$  V). It can be seen that at 10 mV/s, capacitances of hybrid electrode materials based on composites in all the studied potential windows is higher than the capacitance of the electrode material based on the initial C-matrix. The highest capacitance is observed for Mn<sub>x</sub>O<sub>y</sub>/C composite electrode with 3 mass % Mn: 404 F/g in a potential window 0.1–0.8 V; 209 F/g (in a window from -1 to +1 V); 265 F/g (in a window from -1.5 to +1.5 V). This is driven by the presence of pseudocapacitive oxidation peaks for manganese (III) compounds in this region during the discharging process and reduction of manganese (IV) derivatives during discharge.

The optimum manganese content in composites should vary depending on MCM types and the method of applying Mn<sub>x</sub>O<sub>y</sub> due to strong effects of the porous structure of matrixes, the morphology of nanocrystallites of manganese compounds, the nature of their adhesion to MCM, and the accessibility of them and matrix surface for electrolyte ions.

#### Study of charge-discharge characteristics of electrode materials at a constant current

Figure 3 presents curves of a symmetric electrochemical cell with C-matrix based

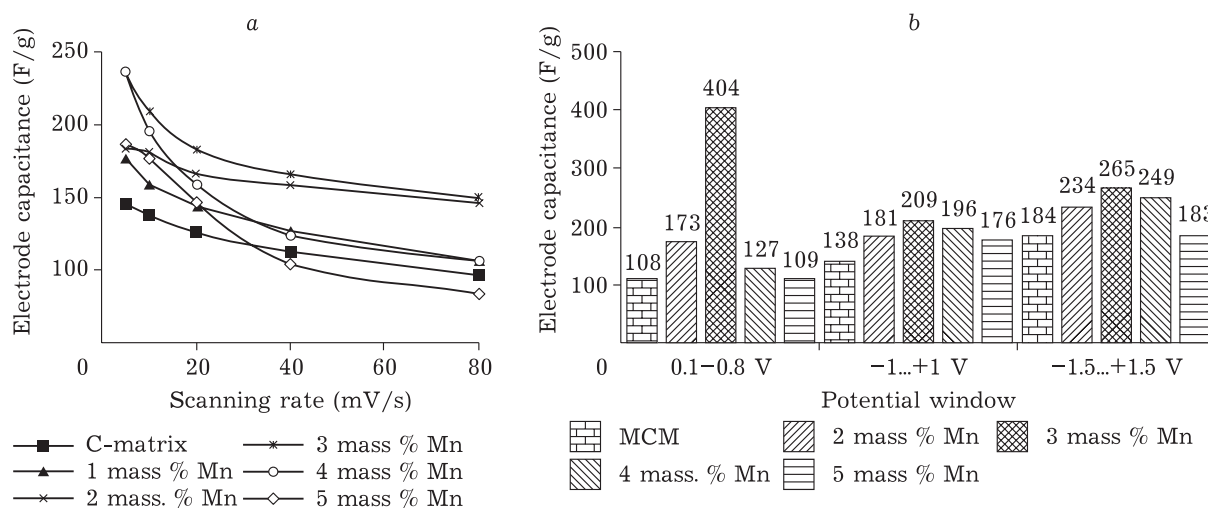


Fig. 2. Capacitance of electrode materials versus scanning rate in a potential window from -1 to +1 V (a) and potential window size at potential scanning rate of 10 mV/s (b).

electrodes and asymmetric cells with a working electrode based on  $\text{Mn}_x\text{O}_y/\text{C}$  nanocomposite with 3 mass % Mn, the optimum in composition.

Capacitances and internal resistance of cells were calculated according to experimental data. They were as follows:  $\sim 54 \text{ F/g}$  and  $\sim 8 \Omega$  for S-matrix and  $\sim 71 \text{ F/g}$  and  $\sim 6 \Omega$  for the asymmetrical cell.

Thus, the results obtained by CVA and GCD methods are in agreement among themselves: in both cases, the capacitances of an asymmetric cell are higher than symmetric cell capacitance. The capacitance of electrode materials calculated by the formula ( $1/C = 1/C_1 + 1/C_2$ ) for a symmetric cell was  $108 \text{ F/g}$ ; for  $\text{Mn}_x\text{O}_y/\text{C}$  with 3 mass % Mn hybrid electrode material in an asymmetric cell –  $207 \text{ F/g}$ , which was close enough to the values obtained from CVA curves at high potential scanning rates.

### Impedance spectroscopy

As it can be seen from Nyquist diagrams presented in Fig. 4, a, the highest resistance at both high frequencies ( $10^4\text{--}10^2 \text{ Hz}$ , kinetic region) and low frequencies ( $10\text{--}10^{-2} \text{ Hz}$ , straight sections (diffusion region)) are observed for matrix; with increasing manganese content in NC from 1 to 3 mass %, resistance decreases and increases again later. The total impedance of cells versus frequency is of the same nature (Fig. 4, b). Herewith, the values of active resistance component ( $4\text{--}7 \Omega$ ) are close enough to total impedance quantities in a region of 0.1 Hz for the appearance of the reactive component.

As it follows from the data of the frequency dependence of electrodes presented in Fig. 4, b, the nature of the effect of the introduced  $\text{Mn}_x\text{O}_y$  corresponds to CVA and chronopotentiometry results. The influence of  $\text{Mn}_x\text{O}_y$  appears in the low-frequency region, thus, the rate of redox processes that determine pseudocapacitance is much lower than the EDL formation rate. This generally corresponds to existing ideas about electrode processes.

Ascertaining the causes for good accordance of the values of specific capacitance of MCM obtained in CVA, GCD, and impedance measurement experiments and at the same time notable differences in the values of capacitance of nanocomposite materials requires further research.

### CONCLUSION

A facile method for preparation of nanostructured  $\text{C}/\text{Mn}_x\text{O}_y$  composites to develop electrode materials of supercapacitors has been elaborated. It consists in the direct reduction of an aqueous potassium permanganate solution with mesoporous carbon matrix leading to decorating matrix surface with X-ray amorphous  $\text{Mn}_x\text{O}_y$  species under optimum conditions.

The study of the resulting composites *via* cyclic voltammetry technique in different potential windows has demonstrated that the capacitance of electrodes generated therefrom is higher than that in the initial matrix. The highest capacitance ( $404 \text{ F/g}$ ) has been reached with manganese content in composites of 3 mass % in a potential window from 0.1 to 0.8 V, in

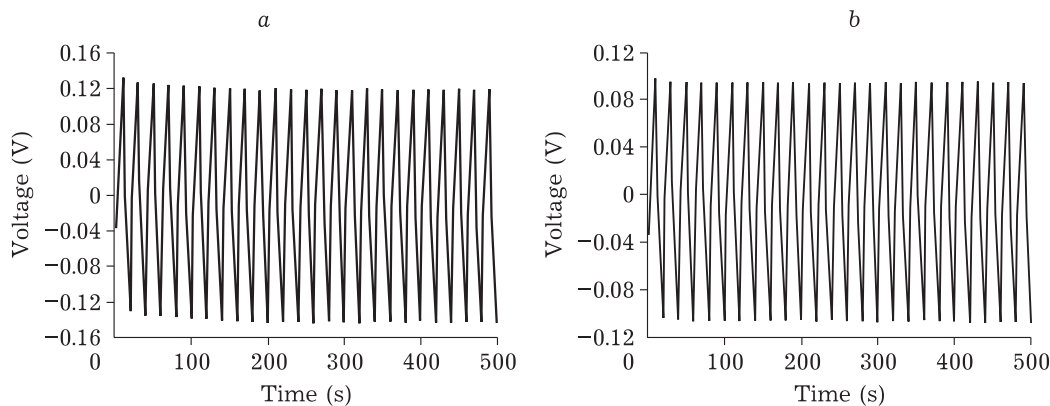


Fig. 3. Galvanostatic charge/discharge (GCD) curves of symmetric (a) and asymmetric (b) cells at a constant current strength.

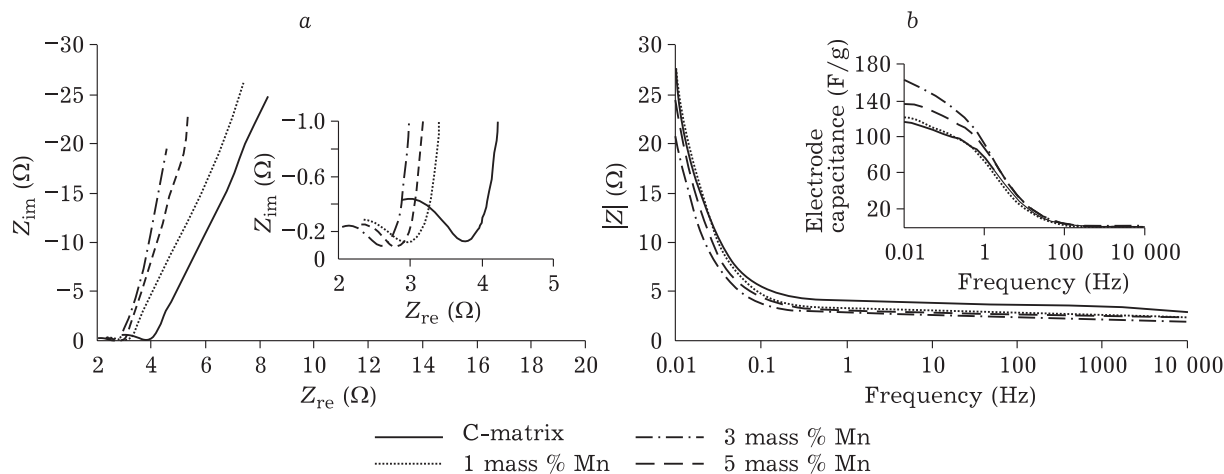


Fig. 4. *a* – Nyquist diagram for symmetric and asymmetric cells with electrodes with different manganese content (the high frequency region in the inset); *b* – dependences of full impedance of the cell and the electrode capacitance (the inset) on the frequency.

which main pseudocapacitive peaks in charge and discharge curves become apparent.

Galvanostatic and impedancemetry data are in agreement with cyclic voltammetry findings. An increase in manganese content in composites from 1 to 3 mass % during carrying out measurements in all modes leads to increasing capacitance; it reduces with a further increase in manganese content. This is driven by the fact that blocking pores increases and the size of  $Mn_xO_y$  species grows during increasing filler content. Consequently, the specific surface area of composites and electrochemical activity of manganese oxides decrease.

A cause for increasing the total electric capacitance of composites is related to pseudocapacitance contribution due to redox processes with the involvement of  $Mn_xO_y$ , which is observed in the low-frequency region and also to a decrease in the active component of electrode resistance.

The resulting nanocomposites are of interest for the use as materials of a working electrode of supercapacitors owing to the combination of a relatively high capacitance with a low cost of raw materials and simplified preparation technique.

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