Chemistry for Sustainable Development **27** (2019) 633–642

UDC 544.076.32(54.05+543.55)

DOI: 10.15372/CSD2019184

Influence of the Conditions for Obtaining Nanocomposite Electrode Materials Mn_xO_y/MCNT on Their Electrocapacity Characteristics

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Abstract

Nanostructured composites Mn_xO_y/multilayered carbon nanotubes (MCNT) with a mass ratio of Mn/MCNT 2 : 98; 5 : 95; 10 : 90 were prepared by the reduction of KMnO4 aqueous solution on the surface of a carbon material (matrix) at a temperature of 25, 60 and 80 °C. Non-ozonized MCNT-1 and ozonized MCNT-2 were used as the carbon matrix. Nanocomposites were studied by means of X-ray phase analysis, small-angle scattering of X-ray radiation, and a complex of electrochemical methods. The influence of the conditions for producing nanocomposites (temperature, ultrasonic radiation) and the filler content on their electrical capacity characteristics was considered. It was determined that the optimal Mn/MCNT ratio was 5 : 95; with an increase in the content of manganese oxides (Mn/MCNT up to 10 : 90) and potential scanning rate higher than 40 mV/s, the electric capacitance of some samples was lower than that of the initial carbon nanotubes. For samples containing non-ozonized nanotubes, the highest capacitance was observed for materials obtained at 80 °C; for ozonized samples, the optimum synthesis temperature was 60 °C. For optimized composition and conditions for the preparation of samples, the specific electric capacitance in asymmetric cells exceeds the specific electric capacitance of the electrodes based on the initial matrices by a factor of 1.5–2.9. Using the methods of galvanostatic charge-discharge and impedancemetry, it was established that electrochemical cells with nanocomposite electrodes have a higher capacitance and low internal resistance. It was discovered that sonication of the reaction medium during the preparation of nanocomposites leads to deterioration in the electrical capacity characteristics and to a noticeable increase in the internal resistance of the cells, especially the active component of the impedance.

Keywords: nanocomposites, manganese oxides, multilayered carbon nanotubes, electrode materials, supercapacitors

INTRODUCTION

Electrochemical systems of energy accumulation, including batteries, supercapacitors (SC) and fuel elements for which the efficiency of energy accumulation, storage and transmission is determined by the processes at the electrode/electrolyte interface, occupy dominating positions among various systems of electric energy accumulation [1]. Supercapacitors are of the keenest interest due to the high specific capacity, power, high rate of charging-discharging processes, long operation life, durability and reliability, they are promising for use in portable consumer electronics, computer systems, backing memory units, in hybrid electric vehicles and other electric vehicles, for the recuperation of braking energy, as uninterruptible power supplies, *etc.* [1–3].

By present, many electrode materials for SC determining the efficiency of these devices have been developed: carbon materials, the compounds of transition metals, conducting polymers [3–5]. The most extensively used material for SC is activated coal possessing rather high specific surface area (S_{sp}). However, the specific charge accumulated at the C/electrolyte interface is limited because not all pores are available for electrolyte ions, so effective surface is always lower than S_{sp}, which causes a decrease in specific capacity and accumulated energy [4, 5]. As a rule, oxide materials possessing high theoretical pseudo-capacity values have low electrical conduction, not very high specific surface, the transport of electrolyte ions proceeds only to the external surface of oxides, so their electrochemical activity is substantially lower than the theoretical value [5].

An advanced approach to an increase in energy density in SC is in the hybridization of electrode materials, that is, the development of composite electrodes [6–10]. The deposition of oxide or hydroxide materials with high pseudo-capacity on the surface of C matrix with the formation of them in the form of isle-like films of nanometer size and nanometer thickness decorating the surface without blocking the pores, that is, with an increase in the specific surface of the active phase of filler in comparison with S_{sp} in the case of homogenous crystallization should enhance their electrochemical activity both because of an increase in S_{sp} and in connection with the dimensional dependence of the oxidation-reduction potential [11, 12]. Moreover, in hybrid materials composed of a carbon matrix and oxides (hydroxides) of transition metals, the conditions may be created for an increase in capacity and energy density of SC based on these composites, as a consequence of a synergetic combination of the capacity of the double electric layer formed on the regions of C matrix surface not covered by nanofilms and a substantial contribution from pseudo-capacity of the oxide nanophases of transition metals, which is due to Faraday oxidation-reduction processes within the potential window under study.

Mixed Mn_xO_y oxides are of great interest [9, 12–16] as a pseudo-capacity electrode material for SC. For instance, the occurrence of several oxidation levels for manganese (from 0 to +7) provides broadening of the range of potential change within which various electrochemical reactions are possible. The capacity of manganese oxides is due mainly to pseudo-capacity, which is connected with the reversible oxidation-reduction transitions with proton and/or cation exchange with the electrolyte, as well as with the transitions between Mn(III)/Mn (II), Mn(IV)/Mn(III) and Mn(VI)/Mn(IV) within the corresponding potential window.

The goal of the present work was to develop the methods to obtain nanostructured composites (NC) based on multilayer carbon nanotubes (MCNT) with the surface decorated with the nanocrystals of manganese oxide, and to study their shape, size and capacity characteristics for the optimization of preparation conditions, composition of the hybrid electrodes of SC and an increase in their electrocapacity characteristics.

EXPERIMENTAL

In the present work, we obtained Mn_xO_y/MCNT NC based on multilayer carbon nanotubes filled with nanometer-sized crystallites of manganese oxide with the Mn/MCNT mass ratio equal to 2 : 98, 5 : 95, 10 : 90. Non-ozonized (MCNT-1) and ozonized (MCNT-2) samples of carbon nanotubes were used as the matrix.

Multilayer carbon nanotubes were synthesized by means of pyrolysis of the propane-butane mixture in the presence of catalysts [17]. To remove catalyst admixture, MCNT-1 was treated with a mixture of acids (HCl, HNO_3). The specific surface area of MCNT was 250 m^2/g, the outer diameter of the tubes was 10–20 nm, and the inner diameter was 3–10 nm. To functionalize the surface, carbon nanotubes were treated with ozone. The conditions of MCNT-1 ozonation were described in [11].

Nanocomposites were obtained by the reduction of the solutions of precursor, $KMnO_4$, by active electron-donor centres on the surface of the carbon matrix without introducing additional reducing agents. The synthesis was carried out at a temperature of 25, 60 and 80 °C. In some experiments, NC were obtained under the action of ultrasound (US) in an ST-406 ultrasonic bath (power: 50 W, frequency: 28 kHz).

The procedure of obtaining nanocomposite electrode materials Mn_xO_y/MCNT

Nanocomposite electrode materials NC1 and NC2 based on carbon matrices MCNT-1 and MCNT-2, respectively, with the required mass ratio of components, were obtained as follows: a necessary amount of a 0.01 M $KMnO_4$ solution was poured into a flask 25 mL in volume, then a weighted portion of carbon nanotubes was added to obtain composites with the required components ratio. The samples NC1-5:95-25 °C and NC2-5:95-25 °C were obtained at the mass ratio of Mn/MCNT equal to 5 : 95, at a temperature of 25 °C for 48 h. The samples NC1-5:95-US and NC2-5:95-US were prepared with the action of US during reduction, at the temperature of 34–35 °C in the reaction medium; reaction time was 120 min. The use of US allowed us to enhance the rate of potassium permanganate reduction by carbon nanotubes by a factor of 24. The samples NC2-2:98-60°C; NC1-5:95-60°C; NC2-5:95-60°C; NC2-10:90-60°C were obtained at a temperature of 60 °C for 60 min. The samples NC2-2:98-80°C; NC1-5:95-80°C; NC2-5:95-80°C; NC2-10:90-80°C were obtained at a temperature of 80 °C for 30 min. The time of reaction completion was determined from solution decolouration. Then the samples were washed with distilled water, separated by filtering and kept for 2 h at a temperature of 105–110 °C to the constant mass.

Methods of investigation

Nanostructured composites were studied using various physicochemical methods. Phase compositions were studied by means of X-ray phase analysis (XPA) with a Difrey 401 X-ray diffractometer (Russia) using an iron anode as the source of X-ray radiation with the wavelength of characteristic radiation $\lambda(\mathrm{Fe}K_\alpha) = 1.937$ Å. The functions of the size distribution of nonuniformities (mass) in initial C matrices and in carbon matrix composites were calculated from the spectra of small-angle scattering (SAS) recorded with a KRM-1 instrument (Russia).

Electrocapacity characteristics (specific capacity, internal resistance, *etc.*) of NC obtained in the work were determined in asymmetric cells of SC using a complex of electrochemical analysis methods: cyclic voltammetry (CVA), chronopotentiometry, impedancemetry with a Parstat 4000 potentiostat-galvanostat (USA).

RESULTS AND DISCUSSION

X-ray phase analysis

The diffraction patterns of MCNT and Mn$_x$O$_y$/MCNT nanocomposites with the mass ratio Mn/MCNT equal to 5 : 95 are shown in Fig. 1.

One can see that the diffraction patterns for NC samples and MCNT differ from each other substantially. For NC, broad reflections appear in the region of 44–53° over 2θ; a reflection at ≈60° over 2θ, which is most pronounced for the samples obtained under the action of US and at 60 °C; a clear reflection at 63° over 2θ is detected for all NC. The intensity of the major reflection from the matrix at 53–57° over 2θ decreases substantially. A broad reflection of the matrix at 65–70° over 2θ for all composites has relatively higher intensity, and peaks due to manganese oxides appear on it. A similar situation is observed also for the matrix reflection in the region of 75–85° over 2θ. For the NC1-5:95-25°C composite, reflections at 41.9, 46.2 and 78.4° over 2θ are also pronounced.

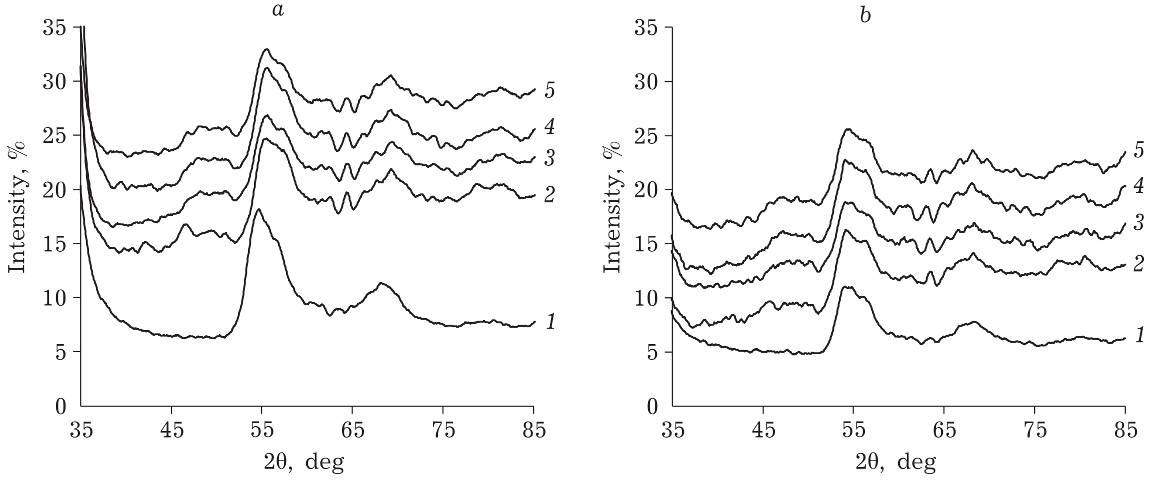

Fig. 1. Diffraction patterns of samples: *a* – non-ozonized MCNT-1 (*1*) and composites (*2* – NC1–5:95-25°C; *3* – NC1-5:95-US; *4* – NC1-5:95-60°C; *5* – NC1-5:95-80°C); *b* – ozonized MCNT-2 (*1*) and composites (*2* – NC2-5:95-25°C; *3* – NC2-5:95-US; *4* – NC2-5:95-60°C; *5* – NC2-5:95-80°C)

According to the X-ray diffraction databases, the 2θ region under consideration should contain the reflections from the basic crystallographic configurations characteristic of manganese oxides: MnO of orthorhombic and cubic systems; Mn_2O_3 with orthorhombic, hexagonal and cubic lattices; MnO_2 (hexagonal, cubic, orthorhombic, tetragonal lattices) and Mn_3O_4 (cubic, orthorhombic and tetragonal lattices). So, many reflections expected for manganese oxides, especially for

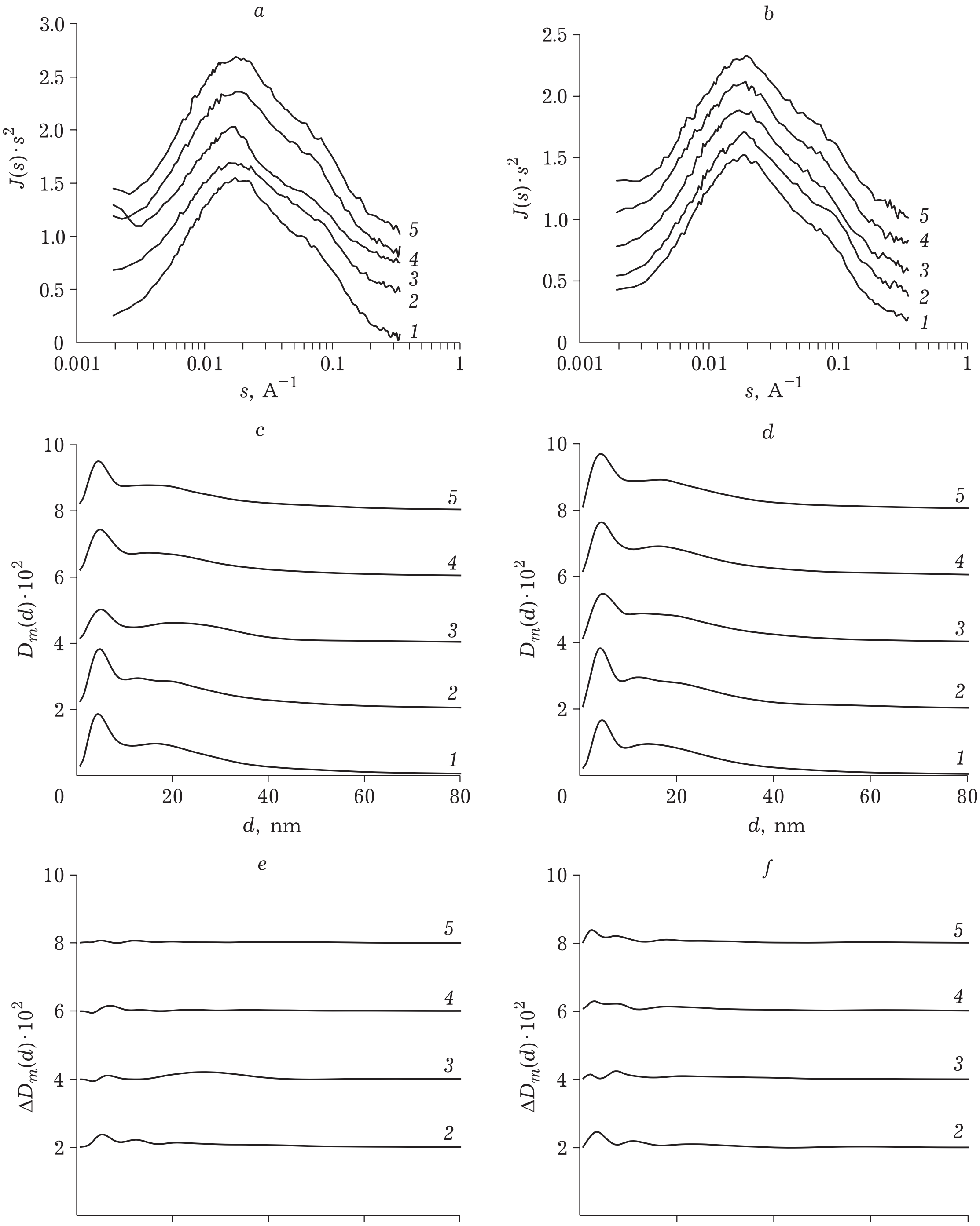

Fig. 2. Experimental SAS spectra (*a*, *b*), the functions of the size distribution of nonuniformities (*c*, *d*) and differential functions (*e*, *f*): *a*, *c*, *e* – non-ozonized MCNT-1 (*1*) and composites (*2* – NC1-5:95-25°C; *3* – NC1-5:95-US; *4* – NC1-5:95-60°C; *5* – NC1-5:95-80°C); *b*, *d*, *f* – ozonized MCNT-2 (*1*) and composites (*2* – NC2-5:95-25°C; *3* – NC2-5:95-US; *4* – NC2-5:95-60°C; *5* – NC2-5:95-80°C).

mixed oxide Mn_3O_4 appear within the angle range under investigation.

According to the data reported in [6], the reduction of Mn-containing compounds by the carbon matrix leads mainly to the formation of the oxides of tri- and/or tetravalent manganese Mn_2O_3 and MnO_2. Manganese is able to form oxides in which it exhibits different oxidation degrees with different types of lattices, so the identification of its oxide phases, especially those in the nanometer-sized state, on the basis of X-ray diffraction data is difficult. One may state only the multiphase nature of the products and the fact that ozone treatment of MCNT matrices does not have substantial effect on their phase composition. Further on, it is planned to study the obtained NC by means of X-ray electron spectroscopy, which will allow us to evaluate the valence state of manganese in oxides.

Small-angle scattering of X-ray radiation (SAS)

The experimental SAS spectra for initial MCNT-1, ozone-treated MCNT-2 and composites based on them with the Mn/MCNT mass ratio equal to 5 : 95 are presented in Fig. 2, *a*, *b*. One can see that the scattering profiles for NC repeat the profiles of the matrices, especially for ozonized samples. For non-ozonized samples – for NC1 obtained under the action of US radiation – a maximum is observed in the region of nonuniformities of relatively large size. This maximum is not observed for other NC and the initial MCNT-1 matrix. On the basis of the recorded SAS spectra, the functions of the size distribution of nonuniformities (see Fig. 2, *c*, *d*) and differential functions (see Fig. 2, *e*, *f*) were calculated.

One can see that the profiles of the size distribution of nonuniformities in NC and the initial matrices differ only slightly, and at the same time the intensities of SAS spectra are higher for NC. This is the evidence in favour of the fact that the inner surface of carbon nanotube channels and their outer surface are decorated with the layer of the filler nanoparticles. The first maximum of the functions of the size distribution of nonuniformities appears at ≈4.0 nm, which corresponds to the average values of the inner diameter of multilayer nanotubes. Partial filling of the channels of C tubes with the nanoparticles of manganese oxides leads to an increase in the intensity of SAS spectra in the angle range corresponding to this size range because of the higher electron density in Mn_xO_y than in carbon.

Electrochemcial investigation of nanocomposite materials in a SC cell

Electrochemical studies were carried out by means of CVA, galvanostatic charging-discharging and impedancemetry. Investigation of initial MCNT as electrode materials was carried out in the cells of symmetrical design in which the working electrode and counter-electrode are identical. Nanocomposite electrode materials were analyzed using a cell with asymmetric structure, in which the working electrode is made on the basis of NC, while counter-electrode is the initial matrix. Potential scanning was carried out within the range – 1 to + 1 V at different potential scanning rates within the range 10–160 mV/s. A 6 M KOH solution was used as the electrolyte. It was prepared directly before assembling the cell. Solution titre was determined with respect to the 0.1 M HCl solution. Nafion was used as a separator. The experimental procedure and the cell structure were described in [8, 13].

Cyclic voltammetry (CVA)

Non-ozonized samples. The CVA curves of initial non-ozonized MCNT-1 and NC1 based on the former with the mass ratio of Mn/MCNT equal to 5 : 95, with scanning rates 10, 20, 40 and 80 mV/s, are shown in Fig. 3.

One can see that several pseudo-capacity peaks are observed in the mentioned potential window for the asymmetric cells with NC electrodes. The positions of these peaks depend on the conditions of NC preparation and the rate of potential scanning. It should be stressed that with an increase in scanning rate to 160 mV/s the peaks are still observed but their intensity decreases. Therefore, electrochemical transformations of manganese compounds occur partially, the access of electrolyte ions to manganese oxides is provided, and the fine state of manganese oxides does not lead to a complete kinetic inhibition of electrochemical reactions.

Specific capacities of electrodes calculated from the areas of CVA curves are presented in Fig. 3, *f*. One can see that the capacities of NC electrodes are substantially higher than the capacities of electrodes based on initial MCNT-1, especially at low scanning rates. The highest capacity is that of the composite electrode material obtained through the reduction of $KMnO_4$ by the MCNT-1 matrix at 80 °C. Composite electrodes obtained at 60 °C and under the action of US exhibit slightly lower capacity.

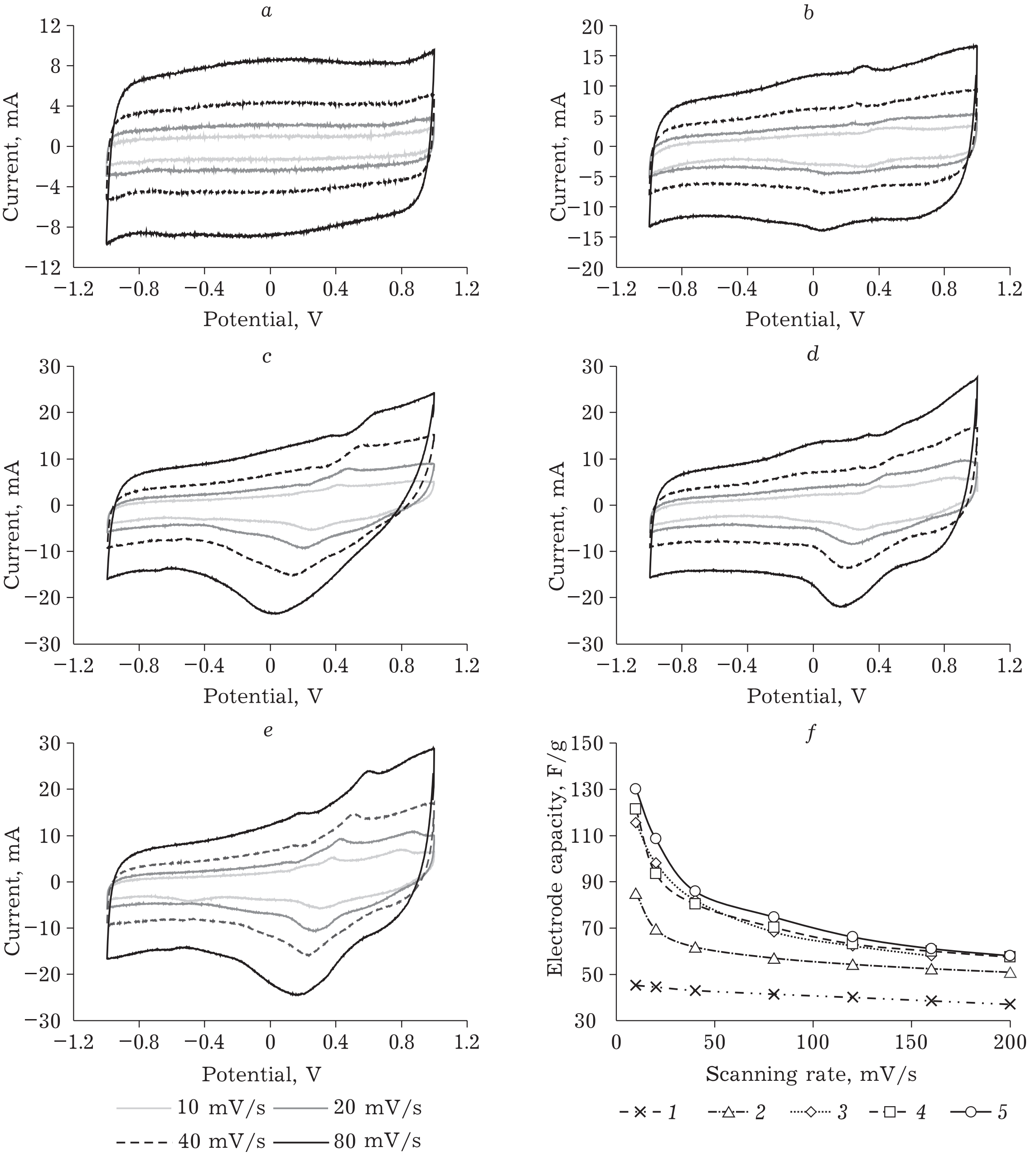

Fig. 3. CVA curves: *a* – symmetrical SC cell with electrodes based on MCNT-1; *b*–*e* – asymmetric cell with nanocomposite working electrodes prepared at a temperature of 25 (*b*), 35, US (*c*), 60 (*d*), 80 °C (*e*); *f* – dependences of electrode capacity on the potential scanning rate (*1* – MCNT-1; *2* – NC1-5:95-25°C; *3* –NC1-5:95-US; *4* – NC1-5:95-60°C; *5* – NC1-5:95-80°C).

In the case of non-ozonized matrix, the least efficient method turned out to be NC preparation at room temperature, however, even under non-optimized conditions the capacity of the composite electrode is nearly two times as high as the capacity of initial non-ozonized tubes. At the scanning rate of 10 mV/s, the capacities of composite electrodes are 1.8–2.9 times higher than the capacity of initial non-ozonized MCNT-1.

Ozone treated samples. For asymmetric cells with nanocomposite electrodes based on ozonized MCNT-2, with manganese content in composites Mn/MCNT-2 = 5 : 95, the lowest capacity was also observed when manganese oxides were deposited on carbon surface at 25–35 °C, under the action of US and without it. The highest capacity was that observed for the electrode material obtained at 60 °C. Thus, at the scanning rate of 10 mV/s, the capacities of composite electrodes are 1.9–2.6 times higher than the capacity of initial ozonized MCNT-2. It should be stressed that the capacity of non-ozonized samples NC1 is higher than that for ozonized NC2, while the capacity of initial MCNT-1 is only slightly lower than the capacity of MCNT-2; the reason is that ozonation causes an increase in the amount of oxygen-containing groups able to participate in Faraday processes.

The effect of manganese concentration in NC2 composites and preparation temperature (60 and 80 °C) on their capacity characteristics was studied. The CVA curves of asymmetric cells are presented in Fig. 4. The capacities of electrode materials at different potential scanning rates were calculated from these curves (Fig. 5.)

One can see that the optimal components ratio in NC Mn_xO_y/MCNT-2 corresponds to Mn/MCNT-2 = 5 : 95. The composites with the components ratio Mn/MCNT-2 equal to 2 : 98 exhibit slightly lower capacity (1.2–1.4 times lower). In this situation, CVA curves clearly exhibit pseudo-capacity peaks, which are due to the oxidation-reduction interconversions of the oxide – hydroxide phases of manganese within the given potential window from –1 to +1 V. With an increase in manganese content in the composites

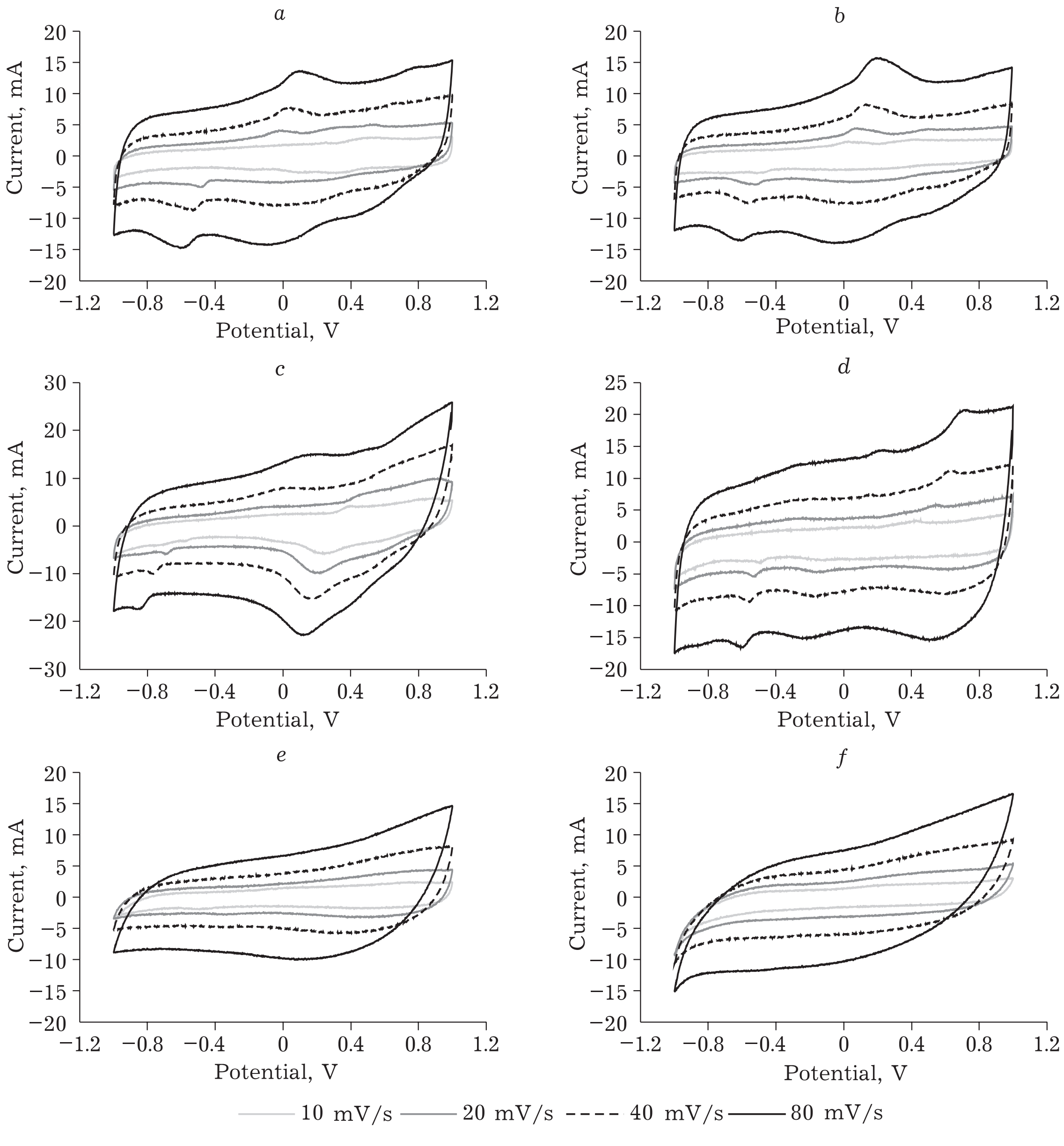

Fig. 4. CVA curves of asymmetric cells with working electrodes based on NC: *a* – NC2-2:98-60°C; *b* – NC2-2:98-80°C; *c* – NC2-5:95-60°C; *d* – NC-5:95-80°C; *e* – NC2-10:90-60°C; *f* – NC2-10:90-80°C.

(Mn/MCNT-2 = 10 : 90), capacity characteristics worsen, pseudo-capacity peaks are almost non-pronounced, and total specific capacity decreases. This is especially evident for the sample obtained at a temperature of 60 °C: at the potential scanning rate of 40 mV/s, its capacity is comparable with the capacity of the initial matrix, while at the potential scanning rate of 80 mV/s it is even lower by a factor of 1.1 in comparison with the initial MCNT-2 matrix. The charge in the cathode region decreases substantially (see Fig. 5, *a*).

Investigation of charging-discharging at the constant current

Chronopotentiometric studies were carried out for all symmetrical cells with electrodes based on MCNT-1 and MCNT-2 and for asymmetric cells with working electrodes based on NC Mn_xO_y/MCNT-1 and Mn_xO_y/MCNT-2, with current strength (±10 mA) and discharging/charging time 10 s. The internal resistance and capacity of electrodes were calculated on the basis of charging-discharging curves. The results are presented in Table 1.

One can see that the capacity of asymmetric cells with composite electrodes is higher than the capacity of symmetrical cells with initial MCNT-1 and MCNT-2. It was also discovered that the internal resistance of the cells decreases by a factor of 1.5–2 when NC materials are used as the working electrodes. Exceptions are NC1-US and NC2-US obtained with the action of ultrasound; quite contrary, the internal resistance of the cell with these samples increases. This may be due to an increase in defect content in MCNT structure during ozonation, subsequent destruction under the action of US. Results agree with the CVA data: the highest capacity is exhibited by the composites obtained at a temperature of 60 and 80 °C.

Electrochemical impedance spectroscopy

The data obtained in the studies of SC cells by means of impedancemetry (in the potentiostatic mode) within frequency range 10^{-2} to 10^4 Hz are presented in Fig. 6.

One can see that the values of impedance components and hence the values of full impedance are lower for asymmetric cells with composite electrodes than for symmetrical cells with electrodes based on MCNT-1 and MCNT-2. The lowest value, first of all for the active component, was observed for asymmetric cells with composite electrodes NC1-5:95-25°C and NC2-5:95-25°C. In the case when NC obtained under the action of US are used as working electrodes, the active component of the impedance increases noticeably, especially in the region of the charge transfer resistance, which is most tangible for ozonized systems NC2-US. Therefore, the data obtained using a set of electrochemical methods are in good agreement with each other. The cells with NC electrodes have higher capacity than symmetrical cells based on initial MCNT-1 and MCNT-2.

Thus, we developed procedures to obtain nanocomposite electrode materials based on non-

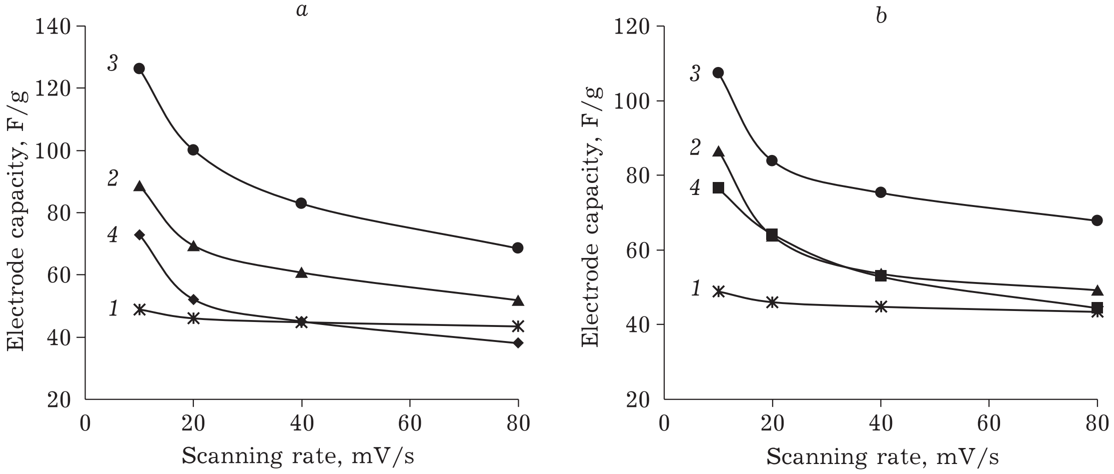

Fig. 5. Dependences of specific electric capacity of electrodes on the rate of potential scanning. Nanocomposite electrodes were obtained at a temperature of 60 (*a*) and 80 °C (*b*). *1* – capacity of electrodes based on MCNT-2 in a symmetrical cell; *2–4* – capacities of the working composite electrodes in asymmetric cells with working electrodes based on NC with the mass ratio of Mn/MCNT-2 equal to 2 : 98 (*2*), 5 : 95 (*3*), 10 : 90 (*4*).

TABLE 1

Capacity and internal resistance of SC cells with electrodes based on non-ozonized MCNT-1, ozonized MCNT-2 and composites based on them

Materials for the working electrode / counter-electrode	Capacity, F/g	Internal resistance, Ohm
MCNT-1/MCNT-1	10	13
MCNT-1/MCNT-1	11	14
NC1-5:95-25°C/MCNT-1	11	6
NC1-US/MCNT-1	12	14
NC1-5:95-60°C/MCNT-1	14	6
HNC1-5:95-80°C/MCNT-11	16	7
NC2-5:95-25°C/MCNT-2	13	7
NC2-US/MCNT-2	12	22
NC2-5:95-60°C/MCNT-2	15	8
NC2-5:95-80°C/MCNT-2	14	10

ozonized MCNT-1 and ozonized MCNT-2 containing manganese oxides, with clearly pronounced pseudo-capacity. The optimal conditions for obtaining the composites and the components ratios Mn/MCNT were determined. The obtained composites have high capacity and are of interest for the development of electrode materials for SC.

CONCLUSION

Nanocomposites based on non-ozonized MCNT-1 and ozonized MCNT-2 (matrices) with the outer and inner surfaces decorated with nanometer-thick crystallites of manganese oxides with different phase and chemical composition were obtained by the reduction of the aqueous solutions of $KMnO_4$ directly by the carbon matrix, without the introduction of additional reducing substances. The effect of manganese oxide content and reaction temperature from 25 to 80 °C on the properties of resulting composites was studied. It was established that the optimal mass ratio of Mn/MCNT-2 is equal to 5 : 95. The optimal temperature was 60 °C for NC based on MCNT-2 and 80 °C for NC based on MCNT-1. An increase in manganese oxide content to the ratio Mn/MCNT-2 = 10 : 90 in the composites causes a decrease in capacity, especially at high potential scanning rates, as a result of blocking the surface of MCNT-2 by the nanoparticles of manganese oxides. For the samples optimized with respect to composition and synthesis conditions, specific electric capacity in the asymmetrical SC cells exceeds the specific electric capacity of electrodes based on initial matrices by a factor of 1.5–2.9.

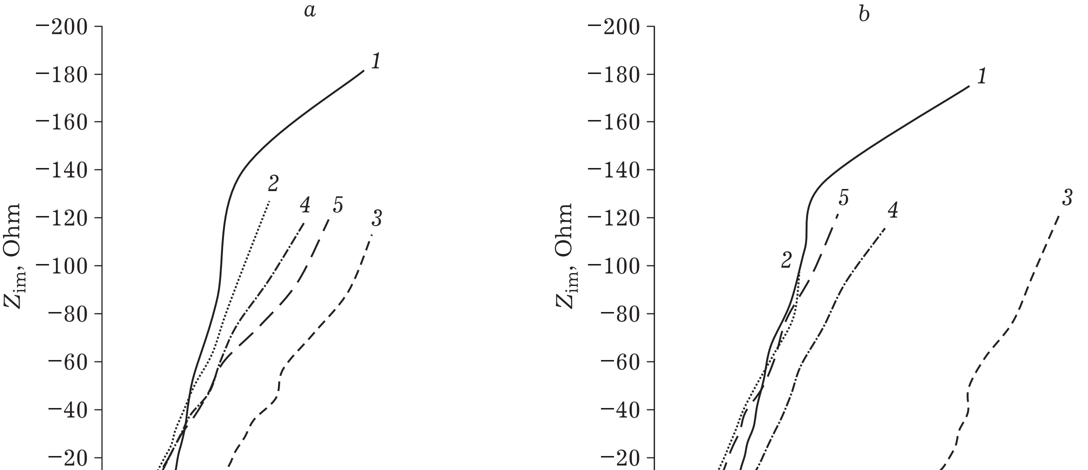

Fig. 6. Nyquist diagrams for SC cells on the basis of non-ozonized MCNT-1 (*a*) and ozonized MCNT-2 (*b*) and NC on their basis: *1* – symmetrical cells with electrodes based on initial matrices; *2*–*5* – asymmetric cells with working electrodes based on NC obtained at a temperature of, °C: 25 (*2*); US, 35 (*3*); 60 (*4*); 80 (*5*).

The maximal capacity (131 F/g) was achieved with the nanocomposite electrode based on MCNT-1 obtained at 80 °C, with a scanning rate of 10 mV/s. It was established by means of galvanostatic charging-discharging and impedancemetry that electrochemical cells with nanocomposite working electrodes have higher capacity and low internal resistance, which is in agreement with the data of CVA.

Acknowledgements

The work was carried out with support from the Integrated Programme of Fundamental Research SB RAS (Project No. V.46.3.1) using the equipment of the Shared Equipment Centre at the FRC CCC SB RAS.

The authors thank Cand. Sci. in Technology A. S. Chichkan (IC SB RAS) and Cand. Sci. in Chemistry E. S. Mikhailova (Institute of Coal Chemistry and Chemical Materials Science FRC CCC SB RAS, Kemerovo) for the submitted samples of ozonized and non-ozonized multilayer carbon nanotubes.

REFERENCES

1 Yun S., Zhang Y., Xu Q., Liu J., Qin Y., *Nano Energy.* 2019. Vol. 60. P. 600–619.

2 Zhang L., Hu X., Wang Zh., Sun F., Dorrell D. G., *Renew. and Sust. Energy Rev.* 2018. Vol. 81. P. 1868–1878.

3 Raza W., Ali F., Raza N., Luo Y., Kim K.-H., Yang J., Kumar S., Mehmood A., Kwon E. E., *Nano Energy.* 2018. Vol. 52. P. 441–473.

4 Miller E. E., Hua Y., Tezel F. H., *J. Energy Storage.* 2018. Vol. 20. P. 30–40.

5 Wang G., Zhang L., Zhang J., *Chem. Soc. Rev.* 2012. Vol. 41. P. 798–828.

6 Chen Y., Zhang X., Xu Ch., Xu H., *Electrochim. Acta.* 2019. Vol. 309. P. 424–431.

7 Simenyuk G. Y., Zakharov Y. A., Puzynin A. V., Barnakov Ch. N., Manina T. S., Ismagilov Z. R., Vladimirov A. A., Ivanova N. V., Pugachev V. M., Dodonov V. G., *Mater. and Manufacturing Proc.* 2016. Vol. 31, No. 6. C. 739–744.

8 Larichev T. A., Fedorova N. M., Zakharov Yu. A., Simenyuk G. Yu., Pugachev V. M., Dodonov V. G., Kachina E. V., Mikhailova E. S., *Chemistry for Sustainable Development.* 2018. Vol. 26, No. 6. P. 619–624.

9 Simenyuk G. Yu., Zakharov Yu. A., Nechaeva T. S., Pugachev V. M., Ismagilov Z. R., *Chemistry for Sustainable Development.* 2017. Vol. 25, No. 6. P. 603–609.

10 Zakharov Yu. A., Kachina E. V., Fedorova N. M., Larichev T. A., Simenyuk G. Yu., Pugachev V. M., Dodonov V. G., *Chemistry for Sustainable Development.* 2018. Vol. 26, No. 6. P. 625–633.

11 Simenyuk G. Yu., Zakharov Yu. A., Pugachev V. M., Dodonov V. G., Trosnyanskaya T. O., Nechaeva T. S., Ilkevich L. V., Mikhailova E. S., Ismagilov Z. R., *Chemistry for Sustainable Development.* 2018. Vol. 26, No. 6. P. 609–618.

12 Simenyuk G. Yu., Zakharov Yu. A., Pavelko N. V., Dodonov V. G., Pugachev V. M., Puzynin A. V., Manina T. S., Barnakov Ch. N., Ismagilov Z. R., *Catal. Today.* 2015. Vol. 249. P. 220–227.

13 Wang X., Chen L., Zhang Sh., Chen X., Li Y., Liu J., Lu F., Tang Y., *Colloids and Surf. A: Physicochem. Eng. Aspects.* 2019. Vol. 573. P. 57–66.

14 Guo W., Yu Ch., Li Sh., Wang Zh., Yu J., Huang H., Qiu J., *Nano Energy.* 2019. Vol. 57. P. 459–472.

15 Xie Y., Yang Ch., Chen P., Yuan D., Guo K. MnO_2-decorated hierarchical porous carbon composites for high-performance asymmetric supercapacitors, *J. Power Sources.* 2019. Vol. 425. P. 1–9.

16 Toupin M., Brousse T., Bélanger D., *Chem. Mat.* 2004. Vol. 16. P. 3184–3190.

17 Chichkan A. S. Utilization of associated petroleum gases by means of catalytic decomposition of light hydrocarbons witht eh formation of carbon nanomaterials and hydrogen (Abstract of Thesis for Cand. Sci. in Technology). Tyumen, 2013. 20 p.