New Method for Preparation of Nanostructured Composites Based on Porous Carbon Materials to Use as Supercapacitor Electrodes

T. A. LARICHEV[1], N. M. FEDOROVA[1], YU. A. ZAKHAROV[1,2], G. YU. SIMENYUK[2], V. M. PUGACHEV[1], V. G. DODONOV[1], E. V. KACHINA[1]

[1]*Kemerovo State University,*
Kemerovo, Russia

E-mail: timlar@kemsu.ru

[2]*Institute of Coal Chemistry and Material Science, Federal Research Center of Coal and Coal Chemistry,*
Siberian Branch, Russian Academy of Sciences,
Kemerovo, Russia

E-mail: galina-simenyuk@yandex.ru

Abstract

The development of alternative power engineering requires the development of highly effective systems for energy storage and transformation. The paper presents a new approach to the solution of a task of preparation of nanostructured composite electrodes for supercapacitors based on highly porous carbon matrixes. The way consists in the thermal (slow or explosive) decomposition of nanocrystals of high-energy compounds pre-generated in matrix pores. A method for preparation of C/CoN_6 composite with a given phase ratio is developed within carried out research. Thermal decomposition of CoN_6 proceeds in explosive or non-explosive modes depending on composite composition and heating mode, as shown. According to X-ray diffractometry, decomposition product in non-explosive mode is Co_2O_3, while in explosive mode – nanoscale cobalt oxide (CoO). The sizes of inhomogeneities formed on the carbon matrix during composite preparation are 7–10 nm, as demonstrated by the study of C/CoN_6 composite using the small angle X-ray scattering (SAXS) technique. Electrochemical properties of the resulting nanocomposite material are studied. The introduction of cobalt oxide into carbon matrix leads to an increase in the resistance and electric capacitance of composite electrodes, as illustrated. Capacitance increase is due to the pseudo-capacitance of cobalt oxides because of reversed redox processes with the involvement of oxide hydroxide phases of cobalt generated during cell charge/discharge.

Keywords: cobalt, cobalt oxides, cobalt azide, porous carbon, nanostructured composites, supercapacitors

INTRODUCTION

In recent years, there has been a growing interest in the development of storage systems of high-capacity electric energy. The development of new types of supercapacitors (ionistors) with high functional characteristics is regarded as one of the promising options [1]. As is known, modern supercapacitors have a high power of energy return and the ability to multiple recharge with reproducible parameters, which provides good prospects of developing advanced hybrid energy storage systems for both mobile and stationary applications based thereon.

Capacitive characteristics, specific capacity, their stability under multiple (thousandfold) charge/discharge cycling, and many other functional characteristics of supercapacitors depend

primarily on properties of electrode materials used therein. Electrode materials based on heterophase nanostructured composites (HNC) consisting of a highly mesoporous electroconductive matrix (a highly porous carbon material (HPCM) and electrochemically active substances with 2D-morphology supported on it with high adhesion, not blocking matrix pores, are regarded as some of the most promising [2, 3]. It is considered that the use of these nanocomposite materials would allow effectively circumventing the limitations of individual substances, e.g., low electrical conductivity and low mechanical strength.

An approach to the development of nanocomposite electrode materials based on the use of high energy compounds (HEC) as precursors for nanoscale species, *i.e.* HPCM fillers seems to be attractive, as believed by us. An additional advantage of this method is the high sensitivity of HEC to the action of physical fields (heat, ionizing radiation, electric and magnetic fields), which allows extending a set of methods for generating filler nanoparticles. At the same time, low energetic and dimensional thresholds of HEC decomposition in the mode of micro-explosions (flares) would allow obtaining filler species of very small sizes and also impregnated resulting from microflares into the matrix material. The latter appears to be sufficiently important from the standpoint of the density of nanoparticle-matrix contacts and the stability of properties, e.g. during long and high-cycle use of these systems as catalysts, electrode material, *etc.*

Apparently, the most promising precursors of this type are the transition and heavy metal azides in view of preparation opportunity as not containing side products, low-dimensional metal species, during their decomposition according to known schemes (a process in vacuo or an inert atmosphere):

$$\mathrm{Me}_x(\mathrm{N}_3)_y \rightarrow x\mathrm{Me} + 3/2y\mathrm{N}_2$$
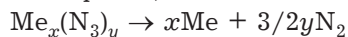
and metal oxides species (during decomposition in air or oxygen atmosphere), relatively low temperatures of thermal decomposition, and high magnitudes of G-values (comparative easiness of carrying out processes in secure modes), and also due to quite low dimensional (about 0.1 µm) and energetic (temperature, dosage rate, and electric field strength) thresholds of carrying out decomposition

processes in the mode of microflares. This may allow generating low-dimensional species of metal or oxide fillers in both the external surface and HPCM pores during their obtaining in various reactions of solid-phase decomposition of metal azides that also proceed depending on conditions in both slow and microexplosive modes.

A fundamental opportunity of creating nanocomposite materials according to this procedure has been earlier demonstrated [4]. The present paper considers the regularities of the generation of the hetero-structural material C/Co_xO_y obtained upon decomposition of cobalt azide in carbon matrix pores and the peculiarities of its electrochemical behaviour.

EXPERIMENTAL

To obtain HNC, porous carbon material Sibunit (TU-145 grade, pore diameter of 10−15 nm, specific pore volume of 0.33 cm^3/g, specific surface of 106 m^2/g according to the BET method) was used as a carbon matrix substrate [5]. Analytically pure $CoCl_2 \cdot 6H_2O$ and NaN_3 were used to prepare reagent solutions.

The introduction of cobalt (II) into the carbon matrix was carried out as follows. A sample of HPCM with a mass of 100 mg was placed into a chemical beaker, an aqueous solution of cobalt (II) chloride with a given concentration was added, and the mixture was kept at room temperature for 1 h. Afterwards, an aqueous solution of sodium azide with a given concentration was poured therein, and the mixture was stirred. The resulting dispersion was air dried for 24 h, after which it was transferred onto filter paper in a Buchner funnel. After rinsing with distilled water, the resulting product was dried under vacuum at a temperature of 25 °C.

Table 1 gives conditions for the preparation of carbon matrixes with introduced cobalt azide. The last number in the sample designation indicates the cobalt content (mass %).

To obtain nanocomposite materials, the resulting carbon matrix was exposed to the thermal treatment. Composite decomposition was carried out in a ceramic crucible un a setup that included a metal capacity, an electric heating element, registering and controlling element Thermodat, two copper − constantan

TABLE 1

Conditions for preparation and experimental sample designations (mass of carbon matrix is 100 g)

Samples	V(CoCl$_2$), mL	C(CoCl$_2$), mol/L	V(NaN$_3$), mL	C(NaN$_3$), mol/L	Calculated cobalt content in the system, mass %
TU-145/CoN$_6$.5	0.17	0.5	0.17	1	4.8
TU-145/CoN$_6$.10	0.36	0.5	0.36	1	9.6
TU-145/CoN$_6$.20	0.21	2	0.21	4	19.9
TU-145/CoN$_6$.40	0.59	2	0.59	4	41.0

thermocouples registering the temperature on the ceramic surface (sample) and on the bottom of the metal capacity.

Thermal decomposition was carried out in the air at a heating rate of ~500 °C/h. Degradation of cobalt azide in non-explosive and explosive modes (the latter − in samples with maximum cobalt content) was registered at a temperature of about 190 °C. Heating was terminated at reaching a temperature of 220 °C. The total duration of thermal treatment in all cases was 6 h. A scheme represents the order of operations during the preparation of HNC (Fig. 1).

The determination of cobalt content in the samples obtained was carried out by the method of inductively coupled plasma optical emission spectroscopy using iCAP 6500 DUO spectrometer in the radial mode of plasma observation, on an analytical line of 228.616 nm. To transfer into a solution, a solid analysed sample
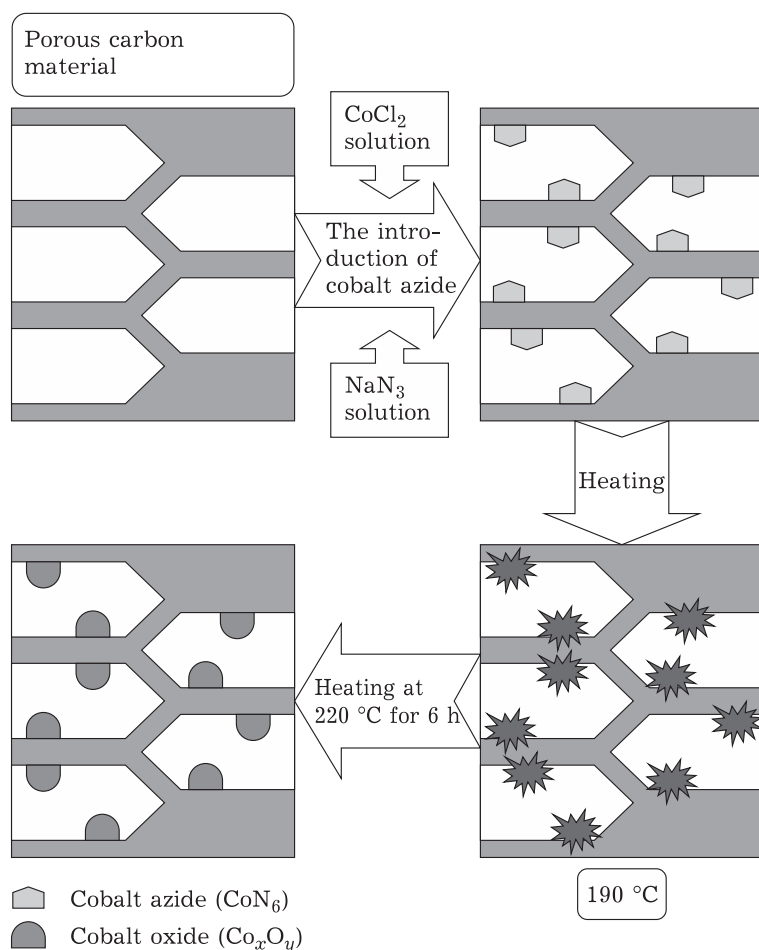

Fig. 1. Scheme for synthesis of nanocomposite electrode materials.

was exposed to treatment with aqua regia.

X-ray diffraction measurements were performed using Difray 401X-ray diffractometer in the iron radiation ($\lambda_{K_\alpha} = 1.9373$ Å) with integrated energy dispersive Amptek detector.

Measuring the intensity of small angle X-ray scattering (SAXS) is performed using KPM-1 diffractometer for transmission in the iron characteristic irradiation by the method for counting pulses at the points in the range of $0.002-0.35$ Å^{-1}. Particle size distribution functions in the approximation of homogeneous spheres were calculated according to SAXS curves [6].

Electrochemical studies were carried out using Parstat 4000 potentiostat/galvanostat in a two-electrode cell with stainless steel electrodes and a Nafion separator. A 6 M KOH solution was used as electrolyte liquor.

RESULTS AND DISCUSSION

Table 2 gives determination results of cobalt content in C/Co_xO_y composites. From the presented data it follows that the used procedure allows obtaining HNC with given ratios of components.

Figure 2 presents the typical X-ray diffraction patterns of two HNC samples. Products of explosive decomposition of cobalt azide are cobalt oxide (II) (line at 46.4, 54.0, and 80.0°) and cobalt metal (lines at 56.2, and 66.0°). Spinel (cobalt oxide (Co_3O_4), lines at 36.6,

TABLE 2

Calculated and experimentally determined cobalt contents in nanostructured materials

Samples	Cobal content, mass %	
	Experimental	Calculated
TU-145/CoO$_x$.5	4.3	4.8
TU-145/CoO$_x$.10	8.7	9.6
TU-145/CoO$_x$.20	18.4	19.9
TU-145/CoO$_x$.40	35.5	41.0

46.8, 57.2, and 77.0°) is the main product during non-explosive decomposition. Thus, cobalt oxidation during rapid azide decomposition is incomplete, unlike oxidation during slow thermal degradation, *i.e.* the composition of HNC filler may be regulated. The size of Co_3O_4 crystallites assessed from the broadening of X-ray reflexes is $4-6$ nm; CoO − about 20 nm.

The pattern of change in SAXS spectra for HNC with a matrix is consistent with the ideas about the morphological composition of composite materials: the values of the extrema at the curves of the size distribution of inhomogeneities are higher for a composite containing cobalt oxides; moreover, with an increase in its content, the difference in the maxima increases, and maxima positions remain almost unchanged. Thus, there is the generation of a nanoscale fraction of species in matrix pores, the more pronounced, the higher
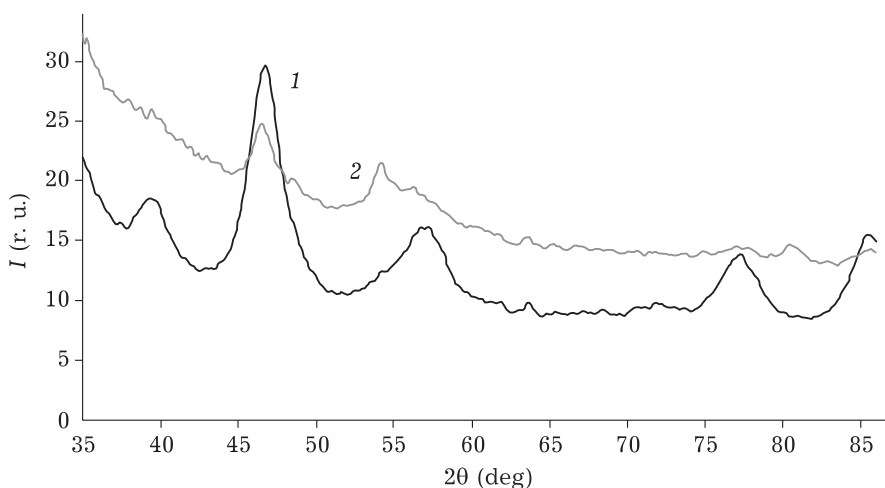

Fig. 2. Diffraction patterns of HNC samples obtained at different modes of thermal decomposition of CoN$_6$: *1* − TU-145/Co$_x$O$_y$.20 (non-explosive thermal decomposition), *2* − TU-145/Co$_x$O$_y$.40 (explosive thermal decomposition).
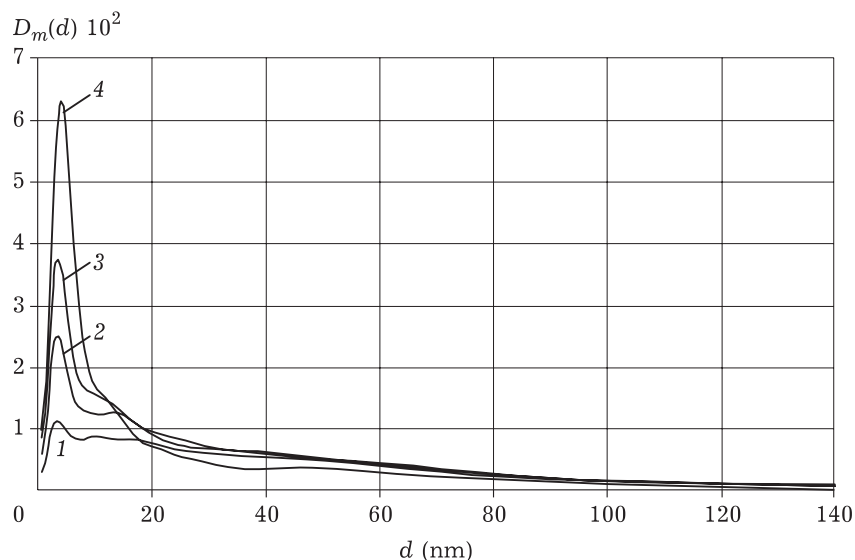
$D_m(d)\ 10^2$

Fig. 3. Size-mass distribution functions of inhomogeneities: *1* − pure TU-145 matrix; *2* − TU-145/Co$_x$O$_y$.5; *3* − TU-145/Co$_x$O$_y$.10; *4* − TU-145/Co$_x$O$_y$.20.

cobalt concentration in the samples. Herewith, the filler particle sizes are close to the assessed ones from broadening of X-ray reflexes (Fig. 3).

Figure 4 gives cyclic voltammetry (CV) curves of asymmetric cells of a supercapacitor with the nanocomposite-based working electrode and with the counter electrode based on TU-145 source matrix.

From on the curves obtained, the values of specific capacities and internal resistance of cells were calculated. Table 3 gives the results. A decrease in electrical conductivity observed
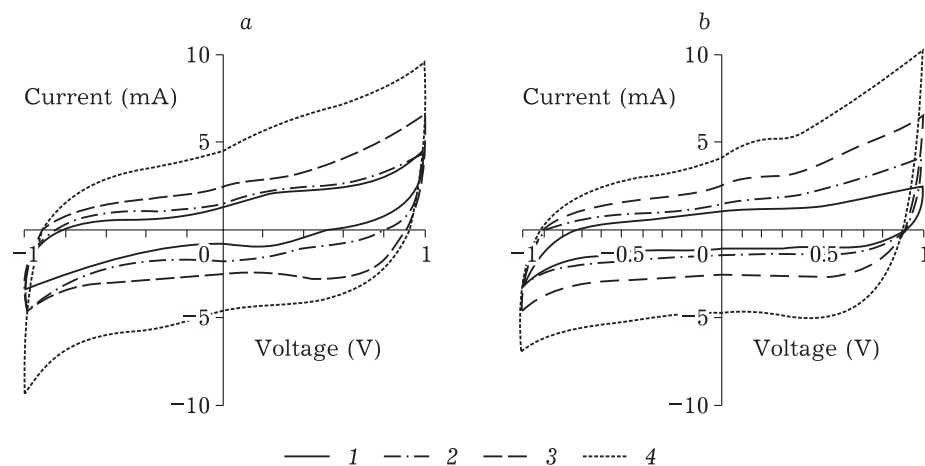

Fig. 4. Cyclic voltammetry (CV) curves for asymmetric supercapacitor cell. The working electrode is TU-145/Co$_x$O$_y$.10 (*a*) and TU-145/Co$_x$O$_y$.40 (*b*) nanocomposite with the counter electrode based on the parent matrix TU-145.

TABLE 3

Working electrode materials internal resistance

Material of working electrode	Interrnal resistance, Om	Cell capacity, F/g	Working electrode capacity, F/g
TU-145	28	6.9	13.8
TU-145/Co$_x$O$_y$.10	30	7.7	17.4
TU-145/Co$_x$O$_y$.40	37	7.5	16.5

during introducing Co_xO_y into matrixes is due to the lower electrical conductivity of carbon materials. The capacity increase is driven by the contribution of the pseudo capacity of cobalt oxides because of redox processes with the involvement of oxide hydroxide phases of cobalt generated during cell charge/discharge. It is worth noting that the determined values of internal resistance and cell capacity are also typical for electrode materials based on Sibunit type matrix. These results point to an opportunity to develop electrode materials for supercapacitors based on the carbon matrix commercially produced and thermolysis products of cobalt azides.

CONCLUSION

It was possible to experimentally confirm an opportunity to develop nanocomposite electrode materials for supercapacitors *via* the method of thermal decomposition of metal azides in a porous carbon matrix resulting from the research carried out. The selection of decomposition temperature mode allows obtaining either Co_3O_4 or CoO species and cobalt metal. The dimensional characteristics of the produced nanoparticles ensure remaining the porous structure of the carbon matrix.

Acknowledgements

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