

Electrochemical properties of CoMn/C based on zeolite-like metal-organic frameworks

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Abstract

Herein, we report a systematic investigation of the synthesis methodology, structural characteristics, and electrochemical performance of CoMn/C metal-carbon nanocomposites derived via IR pyrolysis from manganese-substituted metal-organic frameworks (MOFs) exhibiting ZIF-67 topology. The MOF precursors were synthesized utilizing a chemical co-precipitation approach in aqueous media under ultrasonic treatment, with systematic variation of Co:Mn molar ratios ranging from 95:5 to 50:50, employing 2-methylimidazole as the organic linking agent. X-ray diffraction analysis coupled with electron microscopy investigations revealed that manganese incorporation into the cobalt sites is feasible up to a Co:Mn ratio of 70:30 while maintaining the intrinsic ZIF-67 crystalline architecture, concomitantly leading to a systematic reduction in crystallite dimensions from 36 to 21 nm and corresponding morphological modifications. The subsequent IR pyrolysis conducted within the temperature range of 500–700 °C yielded metal-carbon nanocomposites comprising homogeneously dispersed Co, MnO₂, and Mn₃O₄ nanoparticles within a porous carbonaceous matrix. Electrochemical characterization demonstrated optimal specific capacitance values of 336 F/g at 0.25 A/g current density for nanocomposites exhibiting Co:Mn ratio of 80:20, synthesized at the optimal pyrolysis temperature of 600 °C. The resultant materials exhibited exceptional cycling stability, maintaining capacitance retention exceeding 95 % through 1000 charge-discharge cycles, while demonstrating robust performance across a broad potential window up to 1.4 V in 6M KOH aqueous electrolyte. The enhanced specific capacitance values are attributed to the synergistic contribution of double-layer capacitance from the developed porous carbon framework and pseudocapacitive effects arising from reversible redox processes of metallic nanoparticles and their corresponding oxides. These findings elucidate the significant potential of Mn-substituted MOFs as precursors for the fabrication of high-performance electrode materials in symmetric supercapacitor applications, exhibiting superior electrochemical characteristics.

Keywords

metal-organic frameworks, ZIF-67, CoMn/C nanocomposites, supercapacitors, IR pyrolysis, manganese substitution, pseudocapacitance, electrode materials, porous carbon, electrochemical properties, energy storage, cyclic voltammetry

1. Introduction

Metal-organic frameworks (MOFs) constitute a distinctive class of crystalline porous coordination materials characterized by a periodic three-dimensional structure comprising inorganic nodes (metal ions or metal oxide clusters) interconnected via organic bridging ligands. These architectures facilitate the synthesis of functionalized porous materials with precisely controlled chemical compositions, enabling diverse applications across multiple domains.

The structural paradigm of metal-organic frameworks represents a sophisticated advancement in coordination polymer chemistry, wherein metal ions establish systematic coordination bonds with organic linking moieties. Through precise control of synthetic parameters and constituent selection, these frameworks exhibit exceptional surface area characteristics, substantial pore volumes, and remarkable chemical stability.

Comprehensive analysis of the literature pertaining to the synthesis methodologies, structural characteristics, and physicochemical properties of various MOF architectures has established their significant potential for diverse applications, particularly in electrochemical systems [1–3] and electromagnetic radiation absorption [4].

The current scientific literature documents in excess of 20,000 distinct MOF architectures. Within this extensive family, zeolitic imidazolate frameworks (ZIFs), comprising tetrahedral metal centers M ($M = \text{Zn}$ or Co) coordinated with imidazolate ligands (Im), represent a distinguished subcategory of metal-organic frameworks [5, 6]. The characteristic $M\text{--Im--}M$ bond angle ($\sim 145^\circ$) in ZIF structures exhibits remarkable similarity to the Si--O--Si angle observed in conventional zeolites, resulting in analogous tetrahedral topological arrangements [7, 8].

ZIFs demonstrate significant advantages over traditional zeolites and conventional MOFs, synthesizing the beneficial attributes of both material classes. These characteristics include exceptional specific surface area, permanent microporosity, superior thermal and chemical resistance, and abundant catalytically active sites [9–11].

Contemporary research has identified and characterized more than 150 distinct ZIF structures, many of which demonstrate substantial scientific and technological significance [12, 13]. The prototypical ZIF-67 framework, with the chemical composition $\text{Co}(\text{Hmim})_2$ (where Hmim denotes 2-methylimidazole), exhibits a highly ordered cubic crystal structure with lattice parameters $a = b = c = 1.69589 \text{ nm}$ [12, 14]. ZIF-67 demonstrates remarkable porosity characteristics, with specific surface area exceeding $1700 \text{ m}^2/\text{g}$, incorporating abundant active sites and well-defined micropores (diameter: $\sim 0.34 \text{ nm}$). These structural features facilitate enhanced molecular interactions with guest species [15–17]. Furthermore, the framework incorporates numerous coordinatively unsaturated metal sites (CUS), which exhibit exceptional catalytic activity. The derivatization of ZIF-67 through

various synthetic protocols yields metal oxides and metal/carbon composite materials with enhanced functionalities [18–20].

Electrochemical energy systems have emerged as fundamental components in contemporary energy storage and conversion technologies [21–25].

The advancement of energy storage technologies represents a critical imperative in sustainable energy development and transportation systems. Within this context, symmetric supercapacitors (SCs) demonstrate particular significance due to their exceptional power density characteristics and superior cycling stability [26]. These devices exhibit fundamental mechanistic distinctions from conventional capacitors and batteries, utilizing electric double layer formation at the electrode-electrolyte interface to facilitate rapid and reversible charge-discharge processes [27].

The operational principles of symmetric supercapacitors are predicated on the utilization of identical electrode materials, enabling simplified device architecture and symmetrical electrochemical response during operational cycling [28]. Contemporary symmetric supercapacitor systems demonstrate exceptional power density characteristics approaching 5000 W/kg while maintaining operational stability through extensive charge-discharge cycles, substantially exceeding the performance metrics of alternative electrochemical energy storage systems [29].

Device efficiency in symmetric supercapacitors is fundamentally governed by the structural characteristics of the electric double layer at the electrode-electrolyte interface [30]. Optimal charge storage efficiency necessitates precise correlation between electrode material pore architecture and electrolyte ion dimensions [31]. The idealized porous structure exhibits bimodal distribution characteristics, incorporating micropores ($< 2 \text{ nm}$) for surface area maximization and mesopores ($2\text{--}50 \text{ nm}$) for facilitated ionic transport [32].

Significant advances in symmetric supercapacitor development have been achieved through systematic modification of ZIF-67-derived electrode materials. The resultant metal-carbon nanocomposites exhibit specific surface areas ranging from 1500 to $1700 \text{ m}^2/\text{g}$ with corresponding pore volumes of $0.69\text{--}0.75 \text{ cm}^3/\text{g}$. Controlled thermal processing of ZIF-67 facilitates the formation of hierarchically porous metal-carbon nanocomposites with optimized metal nanoparticle distribution, critical for enhanced capacitive performance [33]. These materials demonstrate exceptional specific capacitance values reaching 413 F/g at 0.5 A/g current density [34], with further optimization potential through systematic modification of compositional and synthetic parameters [35]. In aqueous electrolyte systems, these materials maintain stable operational voltage windows within $0.8\text{--}1.0 \text{ V}$, determined by electrolyte electrochemical stability limitations [36].

Current investigations into modified ZIF-67 structures for supercapacitor applications demonstrate substantial progress in performance optimization. Recent

developments in Co-Mn oxide polyhedral structures derived from ZIF-67 precursors exhibit enhanced electrical conductivity through morphological optimization, demonstrating exceptional cycling stability exceeding 10,000 cycles while achieving specific capacitance values of 850–900 F/g at 1 A/g current density [37].

Particular attention has been directed toward the formation of nitrogen-doped carbon architectures through controlled pyrolysis of Mn-modified ZIF-67, facilitating the development of interconnected conductive networks and enhanced charge transfer characteristics [38].

Advanced synthetic methodologies, incorporating single-step co-precipitation protocols with ultrasonic modification, enable the preparation of carbonate-containing bimetallic layered structures with optimized morphological characteristics, ensuring reproducible material properties and enhanced electrochemical performance metrics [39].

Experimental investigations confirm that controlled pyrolysis of modified ZIF-67 structures facilitates the formation of nitrogen-doped carbon nanopolyhedra, exhibiting enhanced specific capacitance and superior cycling stability in supercapacitor electrode applications [40]. The implementation of ultrasonic-assisted single-step co-precipitation methodologies represents a promising approach for the synthesis of manganese-substituted ZIF-67 structures, which upon pyrolytic treatment yield highly effective electrode materials for symmetric supercapacitor applications, establishing new paradigms in high-performance energy storage device development.

2. Experimental

The synthesis of Mn-substituted MOFs with ZIF-67 structure was carried out by chemical precipitation in aqueous medium. The following initial components were used: organic linker 2-methylimidazole (2-MeIm, produced by “NOVOCHIM”), cobalt nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) as a source of cobalt ions, manganese chloride tetrahydrate ($\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$) as a source of manganese ions, and bidistilled water ($\text{pH} = 5.5$; electrical conductivity 0.2 mS/m) as the reaction medium. The molar ratio of 2-MeIm/ H_2O /metal nitrates was 8/223/1. The Co:Mn ratios varied in the range of 95:5, 90:10, 80:20, 70:30, 50:50.

The synthesis process included dissolving 2-methylimidazole in three-quarters of the total volume of bidistilled water in the main flask. In parallel, metal salts were dissolved in the remaining quarter of the water volume in the required ratio for 15 min. Then, the metal salts solution was added to the 2-methylimidazole solution under constant stirring at room temperature (23–25 °C). After a 20-minute exposure until turbidity appeared, the resulting solution was subjected to ultrasonic treatment (~500 W) for 20 min. The subsequent exposure was 12 h, after which the precipitate was separated by centrifugation at 4000 rpm, washed with bidistilled water and ethanol, then dried at a temperature of ≤ 70 °C to constant weight.

Metal-carbon nanocomposites were obtained by IR pyrolysis of synthesized MOFs in a MILA-5000 furnace under nitrogen atmosphere. The temperature varied in the range of 500–700 °C, heating rate was 50 °C/min, holding time was 5 min. Cooling was carried out in nitrogen flow for 45–50 min.

The structure of metal-organic frameworks and metal-carbon nanocomposites obtained by pyrolysis of Me-substituted MOFs was studied at room temperature using a DIFRAY 401 X-ray diffractometer and CrK_α radiation. Based on X-ray phase analysis results, calculations of average coherent scattering region sizes were performed using Debye–Scherrer equations for both obtained MOFs and metal-containing phases in nanocomposites. Phase composition identification was carried out by comparing obtained diffractograms with reference spectra from the database. The analysis considered the features of the equipment used, particularly the inability to register the first three peaks in diffractograms due to the use of CrK_α radiation and the specific detector features in the DIFRAY diffractometer.

The electrochemical characteristics of synthesized metal-carbon nanocomposites were studied in symmetrical experimental cells using a two-electrode scheme. Titanium foil with a thickness of 50 μm , pre-etched in aqua regia and washed in water and ethanol, was used as current collectors. To apply the electrode material, a suspension of nanocomposite powder in ethanol was prepared using ultrasonic treatment. The suspension was applied to the prepared current collectors using a capillary. The mass of the studied material on the current collectors was determined by the difference between the mass of titanium foil before application and after complete drying of the applied nanocomposite powder layer with an accuracy of 0.0001 g. Ashless paper filters impregnated with 6M KOH aqueous electrolyte were used as separators. The resulting cell was packed in polyethylene and hermetically sealed. Material testing was conducted using a two-electrode scheme with a P-40X device (Elins company). Studies were carried out in potentiostat mode (cyclic voltammetry) and galvanostat mode (galvanostatic charge-discharge measurements).

3. Results and discussion

During the research, MOFs with ZIF-67 structure were synthesized with partial substitution of cobalt with manganese, and metal-carbon nanocomposites based on them were obtained by IR pyrolysis. Special attention was paid to studying the effect of cobalt substitution degree with manganese on the structural and electrochemical properties of the obtained materials, as well as optimizing synthesis conditions to achieve maximum specific capacity indicators.

Analysis of the synthesized materials structure by XRD showed that at Co:Mn ratio of 90:10, substituted MOFs with a structure similar to the original ZIF-67 can

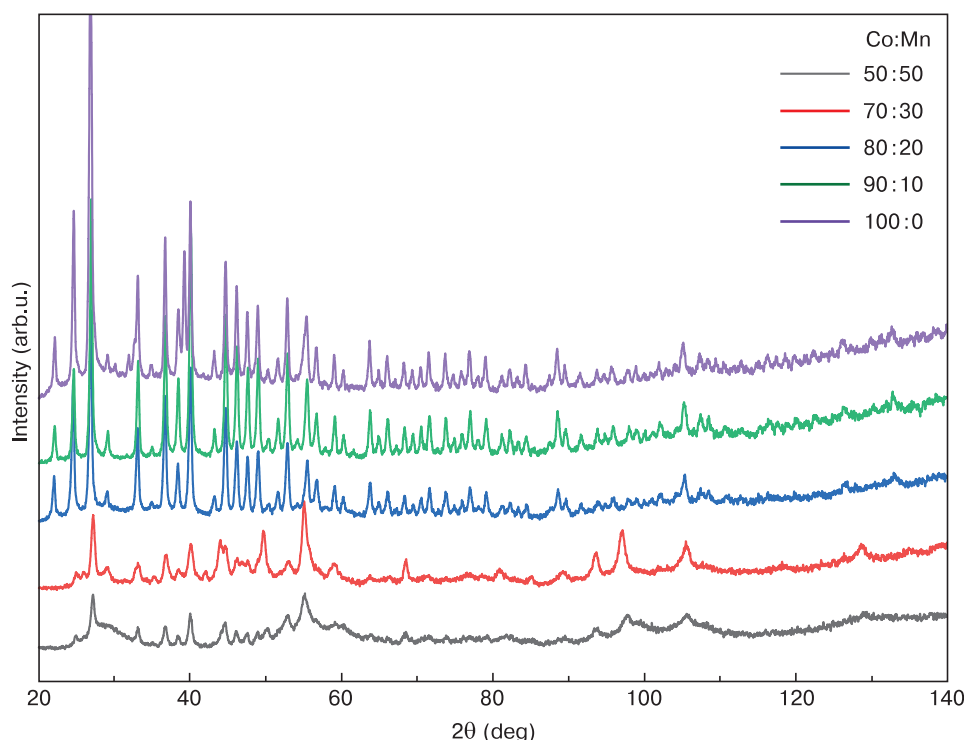


Figure 1. Diffraction patterns of synthesized samples with different Co:Mn ratios

be obtained. Characteristic changes in the diffraction pattern are observed: decrease in peak intensity, shift of maxima, and appearance of new reflections (Fig. 1). The decrease in intensity and some relative broadening of diffraction peaks upon manganese introduction is associated with partial substitution of cobalt atoms in the MOF structure, which leads to changes in some bond angles and lengths, and consequently, irregular changes in interplanar distances.

Detailed study of the substitution degree effect on the structure of Mn-substituted MOFs revealed that at Co:Mn ratio = 80:20, the ZIF structure is preserved, but there is a further decrease in the reflection intensities and their shift, which clearly indicates the incorporation of Mn into the MOF structure (Fig. 2). It is important to note that at this metal ratio, the crystallinity of the material and the main structural characteristics of the original ZIF-67 are preserved, making this composition particularly interesting for further research.

When increasing the substitution degree to 70:30 and above, significant structure amorphization is observed, manifested in the disappearance of some reflections and a significant decrease in the intensity of others (see Fig. 2). This effect may be related to reaching the solubility limit of manganese in the ZIF-67 structure and the beginning of formation of separate manganese-rich phases. Calculations showed that with the increase in manganese content from 0 to 30 %, the size of coherent scattering regions (CSR) of MOF decreases from 36 to 21 nm, indicating a decrease in crystallite sizes with increasing manganese content in the structure.

Figure 3 shows diffractograms of CoMn/C metal-carbon nanocomposites with different Co:Mn ratios. The

main reflections correspond to crystalline phases Co (111), Co (200), and Co (220). Asterisk (*) marks peaks corresponding to MnO_2 phase, square markers ($\square$) indicate Mn_3O_4 reflections. The C (002) peak corresponds to the carbon matrix of the composite. With increasing manganese content (from ratio 100:0 to 50:50), a decrease in the intensity of metallic cobalt reflections is observed, along with the appearance and growth of manganese oxide peak intensities, as well as changes in the ordering degree of the carbon matrix, which is reflected in the C (002) peak profile changes. The obtained results indicate the formation of a heterogeneous composite structure where cobalt and manganese oxide nanoparticles are distributed in a porous carbon matrix. The increase in manganese content leads to changes in the phase composition and morphology of the resulting material.

Figure 4 shows the results of X-ray phase analysis of CoMn/C metal-carbon nanocomposites with different metal ratios (100:0, 90:10, 80:20, 50:50). Graph (Fig. 4a) shows the characteristic Co(111) peak, which has maximum intensity for pure cobalt (about 2000 pulses) and consistently decreases with increasing manganese content in the samples. Graph (Fig. 4b) demonstrates the formation region of manganese oxide phases, where MnO_2 and Mn_3O_4 peaks are clearly observed, with their intensity increasing proportionally to the manganese content in the composite. Graph (Fig. 4c) presents a wide range of diffraction angles (20–50 deg), reflecting the change in the amorphous component profile of the composite with varying composition. Graph (Fig. 4d) illustrates the dependence of crystallite sizes (CSR) of different phases (Co, MnO_2 , Mn_3O_4) on the relative manganese content in the range from 0 to 50 %.

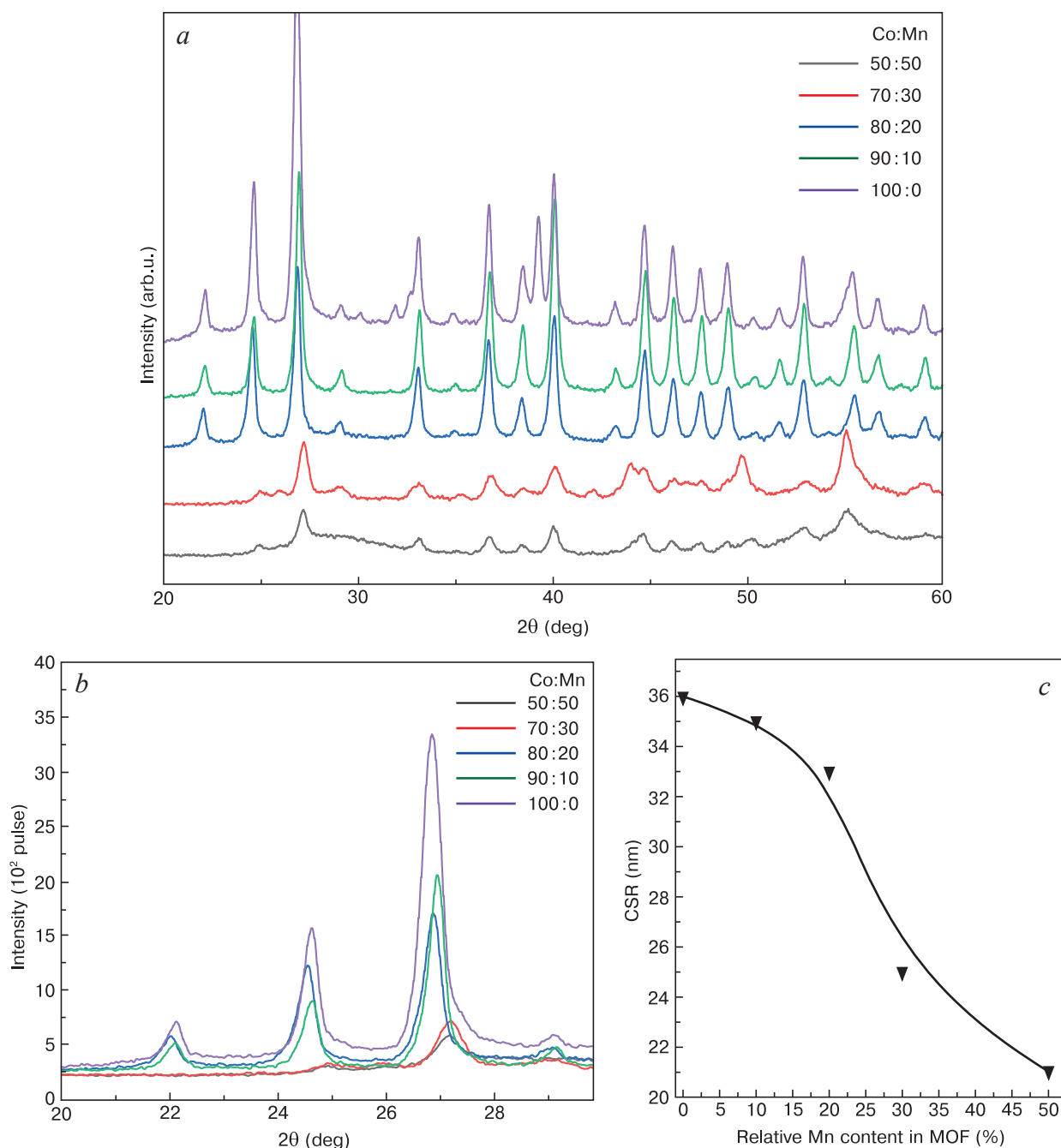


Figure 2. Enlarged areas of diffractograms of MOF with different relative Mn content (*a*, *b*); influence of relative manganese content on the average CSR size of Mn-substituted MOFs (*c*) (calculated using Scherrer formula)

Crystallite sizes vary from 4 to 24 nm, with a nonlinear pattern of change observed as the manganese proportion increases. The obtained data indicate a significant influence of metal ratios on the phase composition and structural characteristics of the forming composites, which is manifested in changes in diffraction peak intensities, emergence of new crystalline phases, and transformation of crystallite sizes.

Investigation of the morphology of synthesized materials by scanning electron microscopy (SEM) revealed several important structural features of Mn-substituted metal-organic frameworks. Analysis of SEM images showed that crystal size heterogeneity is characteristic

for all studied samples (Fig. 5). The samples contain both large crystals with sizes around 3 μm and smaller particles of about 1 μm in size. It is important to note that the observed crystal sizes significantly exceed the crystallite sizes determined by XRD method, which indicates the polycrystalline nature of individual particles.

With increasing degree of cobalt substitution by manganese, significant changes in crystal morphology are observed. In the sample with Co:Mn ratio = 90:10 (Fig. 5a), well-faceted crystals with relatively smooth surface are formed. As manganese content increases to ratio 80:20 (Fig. 5b) and further to 70:30 (Fig. 5c), gradual morphology changes occur – crystals become more amorphous,

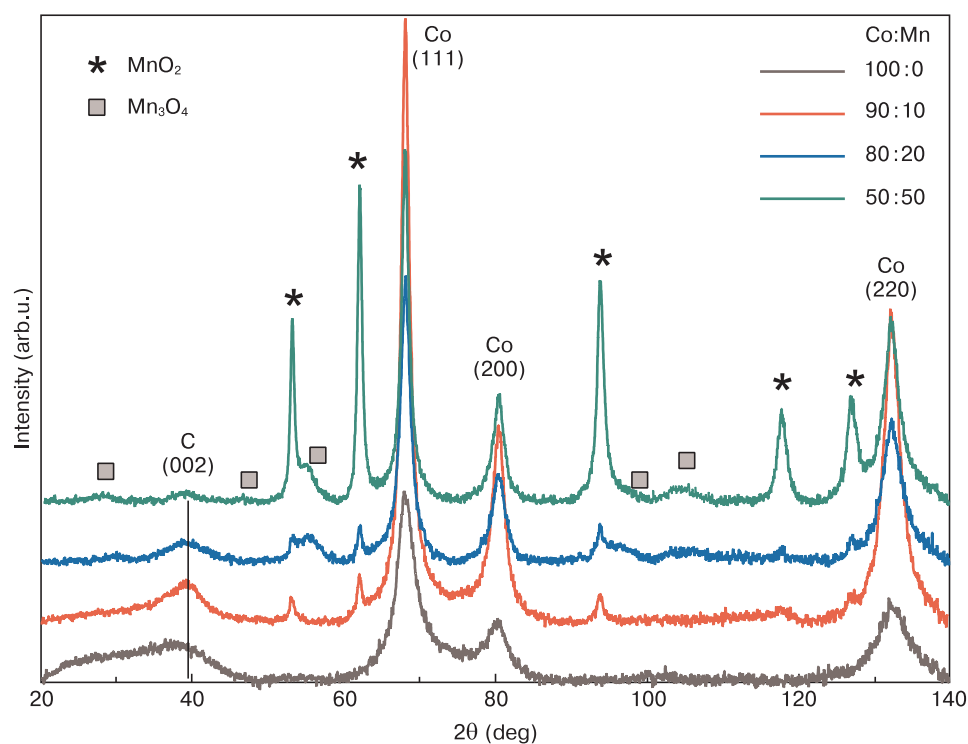


Figure 3. Diffractograms of CoMn/C nanocomposites with different metal ratios

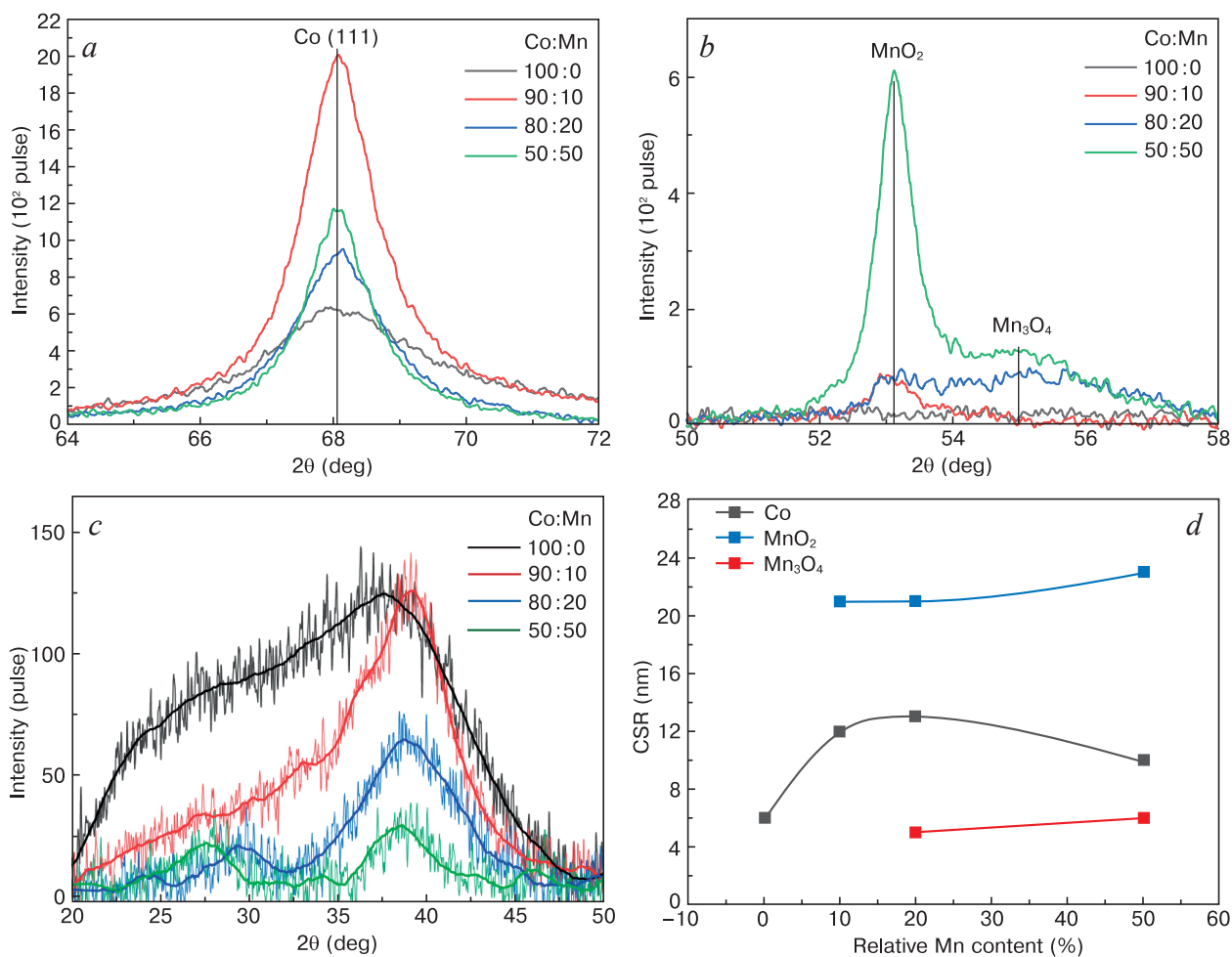


Figure 4. Enlarged fragments of diffractograms of CoMn/C nanocomposites: region of Co (111) plane peak (a), region of MnO₂ (200) plane peak (b), graphite (002) plane peak (c), average CSR size of nanoparticles (d)

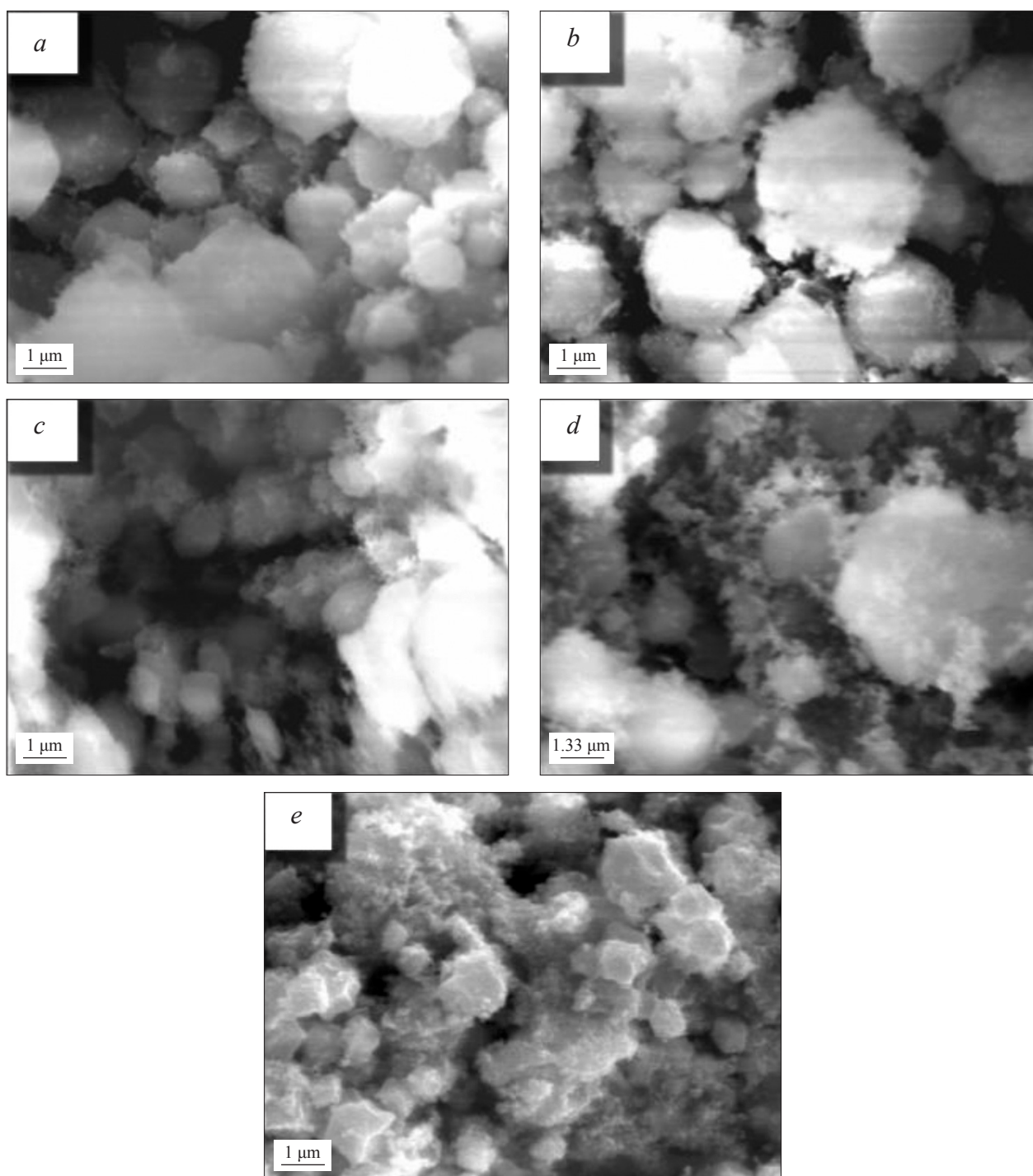


Figure 5. SEM images of MOF with Co:Mn ratio = 90:10 (a), 80:20 (b), 70:30 (c), 50:50 (d), 90:10 pyrolyzed at 600 °C (e)

and their surface is covered with characteristic coating of filamentous and fibrous formations. The formation of these surface structures can be explained by disruption of regular ZIF-67 crystal lattice construction due to manganese atoms incorporation. At maximum substitution degree (Co:Mn = 50:50) (Fig. 5d), the most pronounced development of surface filamentous structures is observed, indicating significant distortion of the original crystal structure.

Of particular interest are the results of studying the material morphology after pyrolysis at 600 °C. SEM

images of the pyrolyzed sample with an initial Co:Mn ratio of 90:10 (Fig. 5e) demonstrate partial destruction of the original crystalline structures with the formation of amorphous porous carbon material. Some crystals retain their original geometric outlines and shape, although they undergo noticeable size reduction due to thermal destruction of the organic component of MOF. Such morphology transformation during pyrolysis plays a key role in forming the developed porous structure of the resulting metal-carbon nanocomposites, which in turn determines their high electrochemical characteristics.

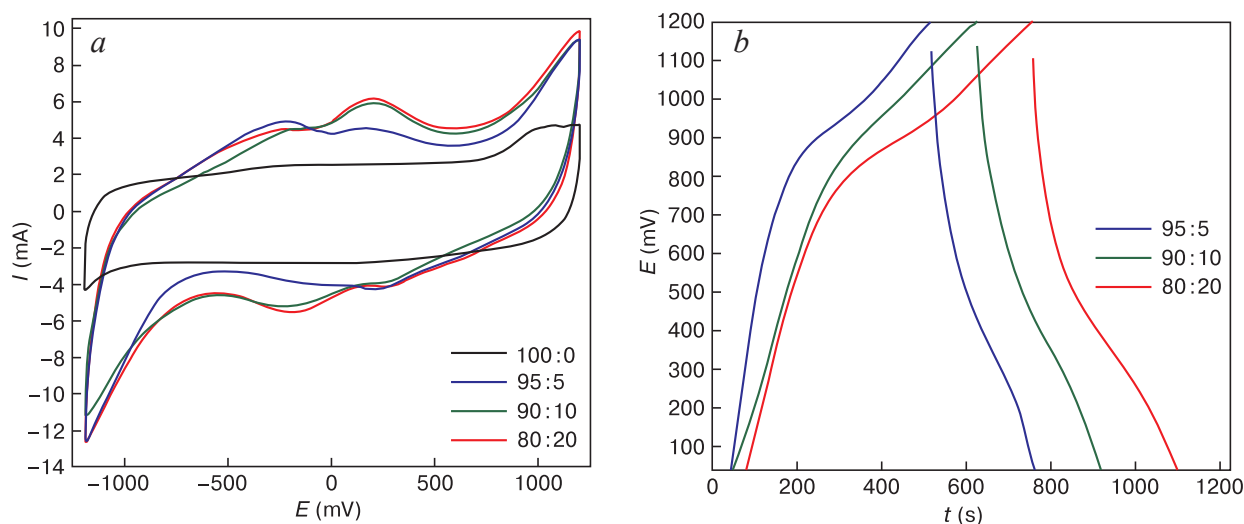


Figure 6. Electrochemical characteristics of electrode materials: (a) cyclic voltammograms; (b) galvanostatic charge-discharge curves

The observed changes in morphology with increasing degree of substitution and subsequent pyrolysis correlate well with XRD data and electrochemical characteristics of materials, confirming the optimality of the chosen Co:Mn = 80:20 metal ratio and thermal treatment temperature of 600 °C for obtaining effective electrode materials.

Figure 6 shows the results of electrochemical studies of synthesized nanocomposites using cyclic voltammetry (CV) and galvanostatic charge-discharge methods. Cyclic voltammograms (Fig. 6a) were obtained in the potential range from -1000 to +1000 mV at a potential scan rate of 50 mV/s in 6M KOH solution.

The shape of CV curves has a mixed character, combining features of both double-layer and pseudocapacitive charge storage components. The rectangular shape of voltammograms in the low potential region, particularly noticeable for the sample with minimal active component content (black curve), is characteristic of the double-layer charge storage mechanism. The charge-discharge currents for this sample are in the range from -2 to +2 mA, corresponding to a specific capacitance of about 98 F/g.

With increasing electroactive component content (blue, green, and red curves), there is a significant increase in current characteristics up to ± 8 mA and the appearance of characteristic redox peaks in the potential region of +400 mV (anodic) and -300 mV (cathodic), indicating an increasing contribution of Faradaic processes. The potential difference between anodic and cathodic peaks (ΔE) is about 700 mV, indicating quasi-reversible electrode processes. The integral area of CV curves increases in the sample series by approximately 4 times, indicating a proportional increase in specific capacitance up to 322–336 F/g for the optimal composition at 1.4 V.

Galvanostatic charge-discharge curves (right part of the figure) were obtained at a constant current density of 0.25 A/g in the potential range of 0–1400 mV. The curves demonstrate a non-linear shape with Coulombic efficiency of about 98 %, indicating high reversibility of electrochemical processes and significant contribution of the

pseudocapacitive component. The charge-discharge time increases from 300 s for the initial sample to 800–1000 s for modified composites.

With increasing current density up to 1 A/g, a decrease in specific capacitance to 242 F/g is observed, which is associated with kinetic limitations of Faradaic processes. The contribution of the double-layer component becomes more noticeable, which is manifested in more linear charge-discharge curves at high currents.

The observed slight slope of charge-discharge curves indicates the presence of internal material resistance. High symmetry of charge-discharge curves and small IR-drop value (50–70 mV at discharge current) indicate good transport properties of the electrode material and efficient organization of its conductive structure, which provides internal resistance of about 1.5–2.0 Ohm.

Figure 7 shows comparative characteristics of materials with different pyrolysis temperatures in charge-discharge cycles. Galvanostatic charge-discharge curves (Fig. 6a) demonstrate nonlinear behavior for all studied samples, with the longest discharge time characteristic for materials obtained at 600 °C. The curve shapes indicate the presence of pseudocapacitive processes in the studied materials. The dependence of specific capacitance on synthesis temperature (Fig. 7b) shows that at 500 °C the specific capacitance is about 235 F/g, reaches a maximum value of 322 F/g at 600 °C, and decreases to 216 F/g when temperature increases to 700 °C. The observed capacitance decrease at high temperature (700 °C) may be due to reduced specific surface area of the material, increased nanoparticle size, decreased number of active centers, changes in carbon matrix structure, and coarsening of the nanocomposite powder fraction. The obtained results indicate that the optimal pyrolysis temperature for achieving maximum specific capacitance is 600 °C, which provides the best balance between material structural characteristics and its electrochemical properties.

Figure 8 shows cyclic voltammograms (CV) for CoMn/C nanocomposites. Graph (Fig. 8a) shows curves

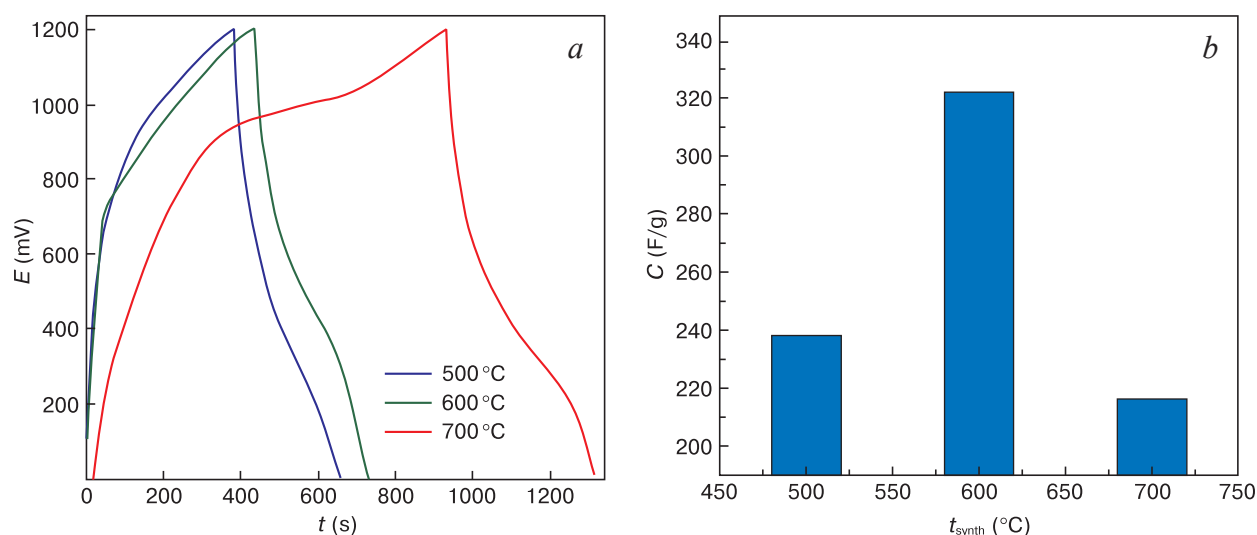


Figure 7. Comparative characteristics of materials with different pyrolysis temperatures in charge-discharge cycles (*a*); effect of synthesis temperature on specific capacity of CoMn/C nanocomposites obtained from Mn-substituted MOFs (*b*)

with different potential limits, demonstrating characteristic redox peaks in the potential range from 0 to 1.8 V. The shape of voltammograms indicates the occurrence of reversible Faradaic processes. Graph (Fig. 8*b*) illustrates the effect of voltage sweep rate on CV behavior, where a regular increase in current characteristics is observed with increasing potential sweep rate. The presence of well-defined redox peaks and their shift with changing sweep rate indicates the pseudocapacitive nature of charge storage in the studied materials. The preservation of CV shape at different sweep rates indicates good reversibility of electrochemical processes and stability of nanocomposite structure under cycling conditions.

Figure 9 shows the results of electrochemical studies of CoMn/C nanocomposite obtained from Mn-substituted MOF. Figure 9*a* demonstrates charge-discharge

dependencies at different specific currents. The curves have a nonlinear character, indicating the presence of pseudocapacitive charge storage processes associated with reversible redox reactions on the electrode material surface. Figure 9*b* shows the dependence of specific capacitance on current density for the CoMn/C nanocomposite. At the minimum current density of 0.2 A/g, the maximum specific capacitance value of about 335 F/g is achieved. With an increase in current density to 1.0 A/g, there is a natural decrease in capacitance to 240 F/g, which is due to kinetic limitations of electrochemical processes at high charge-discharge rates. Such behavior is characteristic of pseudocapacitive materials and indicates a significant contribution of Faradaic processes to the charge storage mechanism.

Based on the conducted research, results were obtained regarding the cyclic stability of synthesized materials.

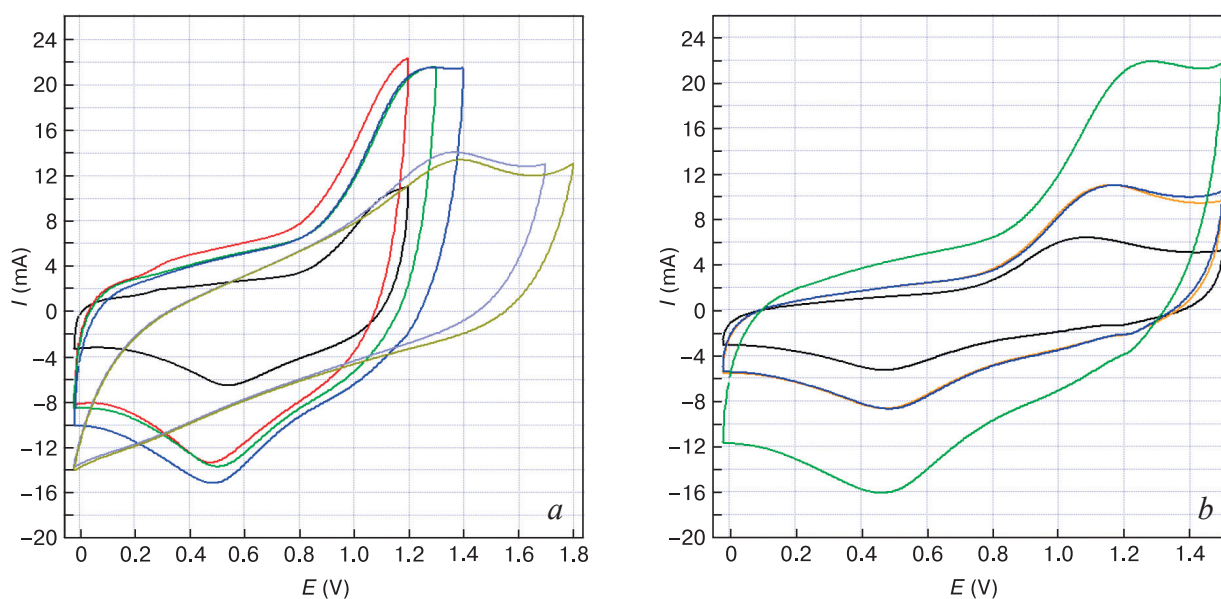


Figure 8. CVA for CoMn/C nanocomposites with different potential limits (*a*), influence of voltage sweep rate on CVA behavior (*b*)

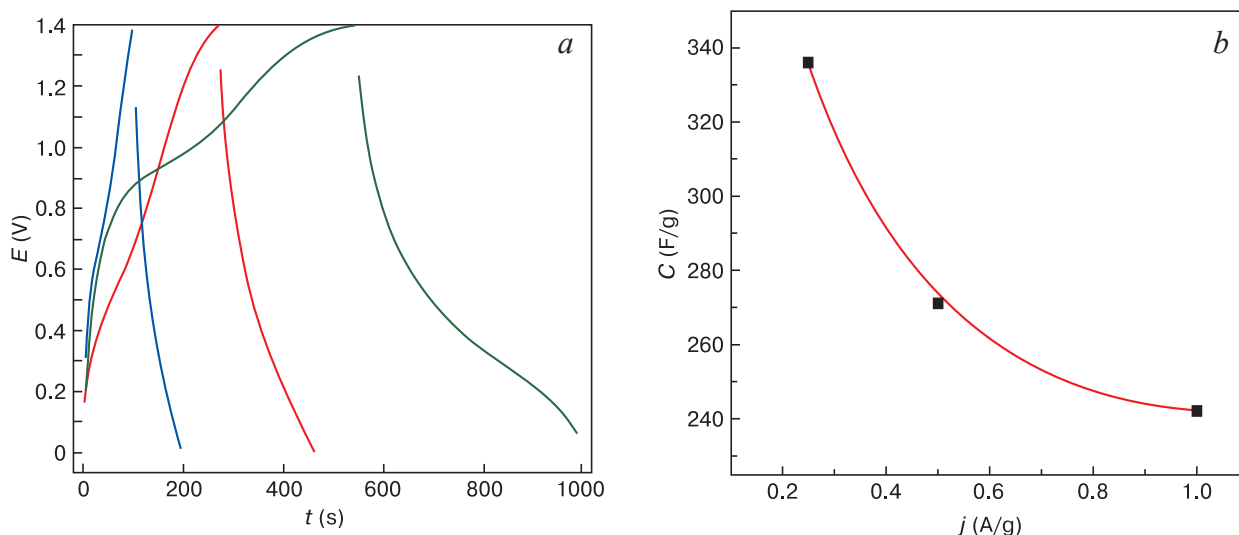


Figure 9. Comparative characteristics of CoMn/C 600 nanocomposite in charge-discharge cycles at different specific currents (a), influence of specific current on specific capacity (b)

Galvanostatic studies at a current density of 1 A/g showed high stability of electrochemical characteristics – after 1000 charge-discharge cycles, more than 95 % of the initial capacity is retained. Analysis of charge-discharge curves showed that their shape remains practically unchanged throughout the cycling, indicating no degradation of the material structure.

Investigation of the operating voltage range influence showed that the material operates stably in a wide potential window from -0.8 to $+0.8$ V versus Ag/AgCl. The increase in voltage range leads to a proportional growth in specific capacity without significant reduction in characteristic stability, which is an important advantage for practical application in supercapacitors.

The high specific capacity values of CoMn/C nanocomposites are due to the synergistic effect from the combination of double-layer capacity of the carbon matrix and pseudocapacitance associated with reversible redox reactions of metal nanoparticles and their oxides. Presumably, the presence of manganese may contribute additionally to the pseudocapacitive component due to its ability to exist in various oxidation states.

Thus, the conducted studies have shown that partial substitution of cobalt with manganese in the ZIF-67 structure is an effective way to improve the electrochemical characteristics of the resulting metal-carbon nanocomposites. The optimal Co:Mn ratio is 80:20, and the pyrolysis temperature is 600°C . Under these conditions, maximum specific capacity values are achieved while maintaining high stability characteristics. The obtained results open up prospects for developing new electrode materials for supercapacitors with improved characteristics based on manganese-substituted MOFs.

Conclusion

As a result of the conducted research, a method for synthesizing CoMn/C metal-carbon nanocomposites based on manganese-substituted metal-organic frameworks with ZIF-67 structure was successfully developed and optimized. It was established that cobalt substitution with manganese is possible up to a ratio of 70:30 while maintaining the crystal structure of the original ZIF-67, with a regular decrease in crystallite size from 36 to 21 nm observed. X-ray phase analysis and electron microscopy methods showed that increasing manganese content leads to significant changes in particle morphology and the appearance of characteristic filamentary formations on their surface. The optimal metal ratio of Co:Mn = 80:20 was determined, ensuring the formation of a stable structure with high electrochemical characteristics. Metal-carbon nanocomposites containing Co, MnO_2 , and Mn_3O_4 nanoparticles uniformly distributed in a porous carbon matrix were obtained by IR pyrolysis. The optimal pyrolysis temperature was established at 600°C , at which a maximum specific capacity of 336 F/g is achieved at a current density of 0.25 A/g. The synthesized materials demonstrate high cyclic stability, retaining over 95 % capacity after 1000 charge-discharge cycles, and can effectively operate in a wide potential range up to 1.4 V in 6M KOH aqueous electrolyte. It is shown that high specific capacity values are due to the synergistic effect of the double-layer capacity of the developed porous carbon matrix and pseudocapacitance associated with reversible redox reactions of metal nanoparticles and their oxides. The presence of manganese contributes to increasing

the pseudocapacitive component due to a wider range of oxidation states compared to cobalt. The obtained results demonstrate the promise of using Mn-substituted

metal-organic frameworks for creating highly efficient electrode materials for symmetric supercapacitors with improved electrochemical characteristics.

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