

# Synthesis of highly-porous nitrogen-doped carbon materials by pyrolysis of melamine-formaldehyde resin using a hard template

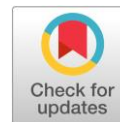
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## Abstract

The use of nitrogen-doped carbon materials as electrodes in supercapacitors is a promising area of research. In this study highly-porous nitrogen-containing carbon materials were obtained by pyrolysis of melamine formaldehyde resin in the presence of nanocrystalline MgO as a hard template that was washed off after the pyrolysis. Magnesium citrate was used as a precursor for the synthesis of the template agent in situ during the pyrolysis of the resin. The obtained materials were characterized by X-ray diffraction, BET nitrogen adsorption method and Raman spectroscopy. The presence of nitrogen in the amount of 4 atomic percent was proved by XPS spectroscopy. The specific surface area was found to increase monotonically from 10 to 1300 m<sup>2</sup>/g with an increase in the content of magnesium citrate in the initial mixture. The samples showed high capacitance of 120 F/g in 1 M H<sub>2</sub>SO<sub>4</sub> electrolyte and can be used in supercapacitors.

## Keywords

nitrogen-doped carbon materials  
template synthesis  
hard template  
highly-porous carbon  
electrode materials  
supercapacitors

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## Key findings

- Nitrogen doped carbon materials were obtained by pyrolysis of melamine formaldehyde resin with the addition of a hard template agent. As a template agent, nanocrystalline magnesium oxide was used, which was obtained by in situ thermolysis of magnesium citrate.
- The hard template method allowed obtaining carbon materials containing 4 at.% of nitrogen having a specific surface area up to 1300 m<sup>2</sup>/g with a high yield of the product.
- The materials have a high specific capacitance values mainly due to the pseudocapacitance ranging from 10–120 F/g in an acidic electrolyte to 3–65 F/g in an alkaline electrolyte.

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## 1. Introduction

Among all advanced devices for the electric energy accumulation, supercapacitors are of interest due to their unique properties, such as a high power density, fast charge-discharge, a large number of cycles and a high charge retention [1]. Carbon materials such as carbon nanotubes [2], graphene [3, 4], activated carbon [5], mesoporous carbon [6], carbon fibres [7, 8], carbon nanosheets [9, 10], etc., are promising electrode materials for space charge storage as electrodes in supercapacitors. Despite all the mentioned advantages of supercapacitors, they have a relatively low energy density compared to other electrochemical devices.

One of the solutions to this problem is an increase in the specific capacity of electrode materials. It is possible by increasing the specific surface area and the number of mesopores, as well as introducing additional functional groups on the surface of the electrodes. In the literature, there are studies on modification of the surface of a carbon material with sulfur [11–13], nitrogen [14, 15], phosphorus [16, 17] and boron [18, 19] atoms.

It is also known that alloying carbon materials with nitrogen atoms increases their charge capacity. This effect can be explained by the presence of nitrogen-containing functional groups on the carbon surface, which increases the capacity of the electrodes through redox reactions [20].

Also, the introduction of nitrogen increases the wettability of the carbon material due to increasing the hydrophilicity of the pores, which enhances the capacity of the electric double layer (EDL) due to an increase in the concentration of electrolyte ions [21], and also improves the contact at the electrode/electrolyte interface along with a decrease in resistance [22]. Doping of the electrode carbon material with nitrogen allows supercapacitors with EDL to work in aqueous electrolytes, which is a promising approach for expanding the application area of these supercapacitors. Working in aqueous electrolytes makes supercapacitors safer, more affordable and increases their operation time.

In the literature, there are two main approaches to the preparation of nitrogen-containing carbon materials: the introduction of nitrogen on the surface of the material by heat treatment with nitrogen-containing gases [23, 24] and the introduction of nitrogen into the material by carbonization of nitrogen-containing precursors [25, 26].

Cui et al. [27] described a method for obtaining melamine-formaldehyde resins (MFR) in various solvents and with various ratios of initial components without the use of a template agent. In their work the authors obtained samples with the maximum specific surface area of 1000 m<sup>2</sup>/g and large pores, which allowed them to regard such carbon materials as adsorbents. The synthesis of carbon material and, both undoped and doped with nitrogen, as well as the comparative characteristics of the obtained samples was reported in the paper [28]. Aniline was used as a source of nitrogen in this work. Electrochemical studies of the materials obtained showed that carbon doped with nitrogen has higher electrochemical capacitance properties than the carbon material itself. The specific capacitances of carbon and carbon doped with nitrogen were 13.56 and 192.12 F/g at a current density of 1 A/g, which means that doping with nitrogen makes it possible to increase the capacitive characteristics by a factor of 14. Liu et al. [29] reported the synthesis of nitrogen-doped carbon materials from melamine, urea and dicyandiamide as nitrogen sources. The samples obtained with the addition of melamine and urea to the carbon materials demonstrated a high reversible specific capacity.

This work aimed to prepare highly-porous nitrogen-containing carbon materials from MFR using a solid template agent, nanocrystalline MgO, obtained in situ by thermal decomposition of magnesium citrate precursor added to the initial mixture. Obtained materials were characterized and their electrochemical properties – investigated.

## 2. Experimental

### 2.1. Initial reagents

Melamine C<sub>3</sub>H<sub>6</sub>N<sub>6</sub> (Reagent grade), 35% aqueous solution of formaldehyde HCHO (Khimprom, Novosibirsk, Reagent grade, 99,9%), dilute (0.01 M) NaOH water solution, concentrated water solution of hydrochloric acid HCl and dis-

tilled water were used as initial reagents. Magnesium citrate Mg<sub>3</sub>(C<sub>6</sub>H<sub>5</sub>O<sub>7</sub>)<sub>2</sub>·10H<sub>2</sub>O was prepared from citric acid and magnesium oxide as reported earlier [30].

### 2.2. Synthesis and characterization

Magnesium citrate powder was added to the water solution of melamine at the given weight ratios of the reagents C<sub>3</sub>H<sub>6</sub>N<sub>6</sub> and Mg<sub>3</sub>(C<sub>6</sub>H<sub>5</sub>O<sub>7</sub>)<sub>2</sub>·10H<sub>2</sub>O varying from 0 to 1. Then the formaldehyde solution was added to the obtained suspension in the molar ratio C<sub>3</sub>H<sub>6</sub>N<sub>6</sub>:HCHO equal to 1:6, and the mixture was heated for an hour at a temperature of 75–80 °C and pH of 8–8.5. After the solution became viscous, the temperature was increased to 100 °C and kept at this temperature for 12 h until complete polymerization of the melamine-formaldehyde resin (MFR).

Pyrolysis was carried out in a tubular quartz reactor. The samples were placed in a nickel foil boat and heated in an inert argon atmosphere with a rate of 10 K/min up to 900 °C with 1 h dwell. The resulting composites containing carbon and the template agent were treated with HCl solution to remove the magnesium oxide which acted as a hard template. After treatment the samples were dried at 150 °C for 2 h for complete removal of residual moisture.

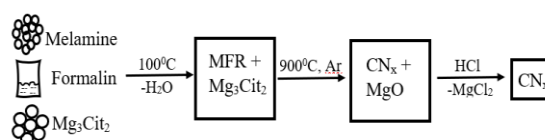
The resulting samples will be further designated as *L-x*, where *x* is the mass fraction of magnesium citrate in the initial magnesium citrate – melamine mixture. Figure 1 shows a schematic diagram of the synthesis process of nitrogen-containing carbon materials using melamine as a carbon and nitrogen source and magnesium citrate as a template agent precursor.

X-ray diffractograms of the samples were obtained on a Bruker D8 Advance diffractometer using Cu K $\alpha$  ( $\lambda = 0.1542$  nm) radiation in the  $2\theta$  angle range from 3° to 85°. The surface characteristics of the obtained carbon materials were evaluated using a nitrogen adsorption/desorption method at 77 K on a Termosorb TPD1200 surface analyzer. The total pore volume was determined from the adsorption value at  $P/P_0$ . The total surface area was estimated using the BET equation.

The surface of the obtained samples was examined using a “HITACHI TM1000” scanning electron microscope.

Raman spectra were recorded in backscattering geometry on a Senterra Raman microscope (Bruker, Germany) at room temperature with laser excitation ( $\lambda = 532$  nm); the spectral measurement range was 500–3500 cm<sup>-1</sup> with a resolution of 3–5 cm<sup>-1</sup>.

X-ray photoelectron spectra (XPS) were recorded on a SPECS spectrometer (Germany) equipped with several isolated vacuum chambers for fast loading of samples, their thermal processing, and analysis.



**Figure 1** Schematic diagram of the process for producing nitrogen-containing carbon material.

The samples for analysis were applied to double-sided conductive adhesive tape. The photoelectron spectra of the samples were recorded in the analyzer chamber at a pressure of  $5 \cdot 10^{-9}$  Torr. The spectra were recorded for each sample using AlK ( $h\nu = 1486.6$  eV) radiation. The binding energy scale of the spectrometer was calibrated against the lines of metallic gold and copper,  $Au4f_{7/2} = 84.0$  eV and  $Cu2p_{3/2} = 932.6$  eV. The spectra of the samples were calibrated against the C1s line, the binding energy of which was assumed to be 284.8 eV.

The electrochemical studies were carried out in a two-electrode planar cell with two identical powder electrodes separated by a hydrophilic porous separator and placed in an electrolyte solution. The measurements by cyclic voltammetry were carried out using a potentiostat IPU-01 at the potential sweep rates of 5, 10, 20, 50 and 100 mV/s in solutions of 1 M  $H_2SO_4$  and 3 M KOH. Galvanostatic charge-discharge curves were obtained on a device Analizator HIT Yarostanmash ACK2.5.10.8 (Russia) at a current density of 0.65 A/g in the voltage range from 0 to 0.8 V in M  $H_2SO_4$ . Impedance spectroscopy was carried out using Electrochemical Workstation ZIVE SP2 in the frequency range from 0.5 to 1 MHz in solutions of 1 M  $H_2SO_4$ .

### 3. Results and Discussion

#### 3.1. X-Ray diffraction

The X-ray diffraction patterns of a composite prepared from the mixture of 30 wt.% melamine and 70 wt.% magnesium citrate by heat treatment at 900 °C in an inert argon atmosphere are presented in Figure 2. After the heat treatment at 900 °C the sample shows diffraction peaks corresponding to nanocrystalline MgO. The values of the grain size of magnesium oxide were estimated using a Scherrer equation:

$$d = \frac{K \cdot \lambda}{\beta \cdot \cos\theta} \quad (1)$$

where  $d$  is the grain size (or more correctly, the coherent domains size),  $\lambda$  is the X-ray wavelength ( $\lambda_{Cu} = 0.154$  nm);  $\theta$  is the diffraction reflections angle;  $K$  is the constant equal to 0.9. The estimation shows that the grain size of MgO in the composite is nearly 7 nm. After treatment of the composite with a solution of hydrochloric acid, all reflections attributed to magnesium oxide vanish due to a complete removal of the oxide from the resulting mesoporous carbon material. A strong low-angle X-ray scattering can be explained by the presence of mesopores in the carbon material under study.

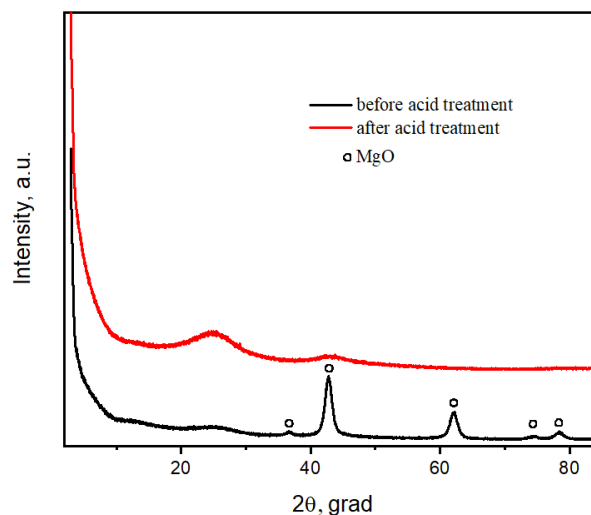
#### 3.2. Nitrogen adsorption studies

Figure 3 shows the dependence of the specific surface area on the mass fraction of magnesium citrate in the initial mixture. As can be seen from Figure 3, the product of pyrolysis of pure MFR has a small specific surface area. With an increase in the content of magnesium citrate in the initial

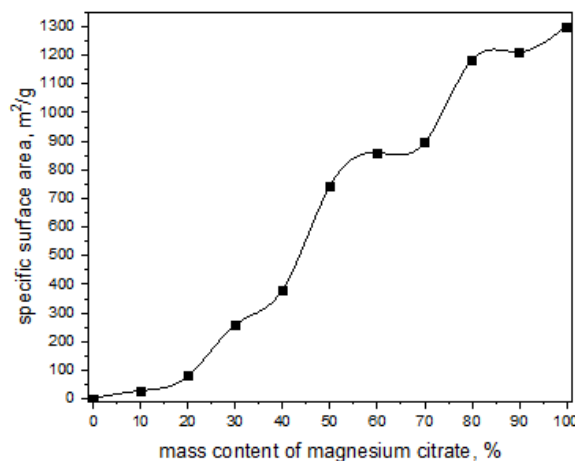
mixture, the specific surface area of carbon materials increases and reaches a maximum value of 1304  $m^2/g$  for pure magnesium citrate. The increase in the specific surface area occurs due to the increase in the content of nanocrystalline magnesium oxide, which, in turn, plays the role of a template agent responsible for the formation of pores in the final product.

However, despite the high specific surface area of the composite obtained from pure magnesium citrate, the product mass yield (i.e., the mass ratio of the pyrolysis product after MgO removal to the total mass of the carbon and nitrogen in the initial mixture) from this precursor is very small, around 4%. It is seen in Figure 4 which shows the mass yield of the carbon as a function of the magnesium citrate in the initial mixture.

One can see that the yield of the final carbon material depends on the mass content of magnesium citrate in the initial mixture. With the addition of magnesium citrate, the yield of the product increases and reaches a maximum at about 50–70% of magnesium citrate.



**Figure 2** X-ray diffractogram of a L-70 composite containing 30 wt.% melamine and 70 wt.% magnesium citrate obtained by pyrolysis at 900 °C, before (black line) and after treatment with hydrochloric acid (red line).



**Figure 3** The variation of the specific surface area of the obtained materials on the content of magnesium citrate in the initial mixture.

The reason for the decrease in the yield of carbon during the pyrolysis of MFR in inert atmosphere is the elimination of low molecular weight hydrocarbons and nitrogen-containing gases, such as ammonia, amines, etc., at high temperatures. Pyrolysis of pure MFR is accompanied by a nearly 90% weight loss. Magnesium citrate starts to decompose at relatively low temperatures with formation of amorphous phases of magnesium organic salts [30] and the escape of  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . At temperatures above  $400\text{ }^\circ\text{C}$  in inert atmosphere magnesium salts transform to nanocrystalline  $\text{MgO}$  and organic anions decompose with formation of highly-dispersed carbon and elimination of hydrocarbons and  $\text{CO}$ . As a result, the pyrolysis of pure magnesium citrate is accompanied by a nearly 95% weight loss. One would expect the mass yield of the final product to decrease from 11 to 4 wt.% with the increase in the magnesium citrate content in the initial compositions. Surprisingly, the dependence of the mass yield on the concentration has a strong maximum at 50–70 wt.% magnesium citrate in the initial mixture. The increase in the mass yield is important for practical applications. This effect requires additional, more detailed study and might be explained by an influence of the reaction of the magnesium citrate decomposition on the kinetics of the MFR pyrolysis.

### 3.3. Scanning electron microscopy

Morphology of the nitrogen-doped carbon materials was investigated using scanning electron microscopy (SEM); a typical SEM image is shown in Figure 5. It is seen that the sample consists of strongly aggregated particles of carbon material 3–10  $\mu\text{m}$  in size. Each particle is a highly-porous pseudomorphosis of the initial polymeric matrix that retained its shape after the pyrolysis and subsequent acid treatment.

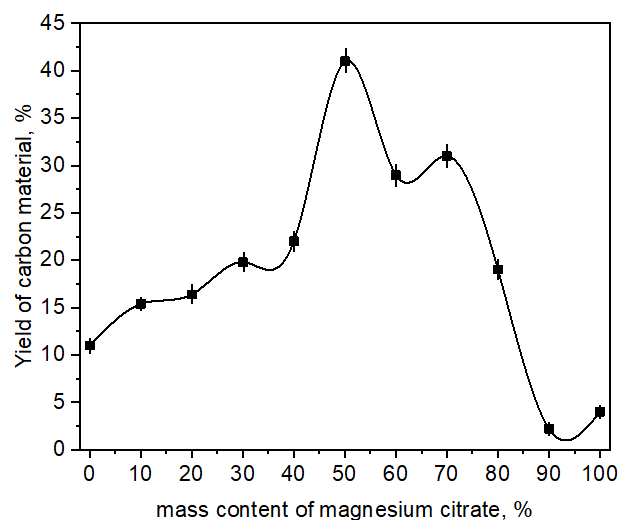
### 3.4. Raman and XPS spectroscopy data

The samples of nitrogen doped carbon were examined by Raman spectroscopy to determine the structure of the material. The Raman spectra are shown in Figure 6.

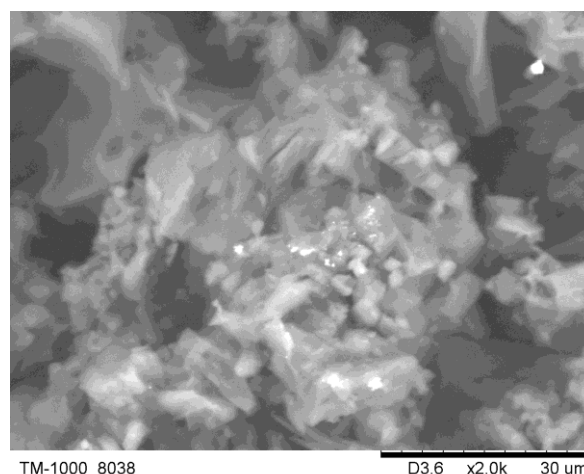
Peaks centered at  $1340\text{ cm}^{-1}$  (including the unresolved  $\text{D}_3$ ,  $\text{D}_1$ , and  $\text{D}_4$  bands),  $1600\text{ cm}^{-1}$  (including the unresolved G and  $\text{D}_2$  bands), and  $2680\text{ cm}^{-1}$  can be assigned to the D, G, and 2D bands, respectively. The presence of the D-band indicates the defectiveness of the material and also displays the degree of structural disorder. The  $\text{D}_3$  band demonstrates a high intensity, indicating that the carbon materials are mainly amorphous. The G-band characterizes carbon bonds in the plane of the  $\text{sp}^2$  vibrational mode; this parameter reflects the degree of crystallization of the material. The 2D band is related to the graphene layers in the material under study [31]. The presence of peaks at Raman shifts of  $2680\text{ cm}^{-1}$  and  $2940\text{ cm}^{-1}$  is caused by the presence of a small impurity of graphene-like fragments in the obtained material [32].

In order to investigate the nature of nitrogen atoms in the structure of the obtained materials, XPS spectra were

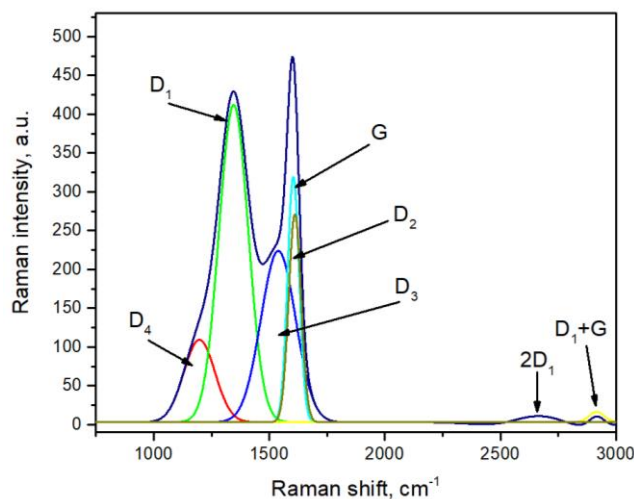
recorded for the sample L-70. The spectra are presented in Figure 7. From the comparison of the intensities of  $\text{C}1\text{s}$  and  $\text{N}1\text{s}$  peaks it was found that the atomic ratio of  $\text{N}/\text{C}$  is equal to 0.04. This value is much lower than the stoichiometric  $\text{N}/\text{C}$  ratio in the initial compositions, which is equal to 0.67.



**Figure 4** Mass yield of the carbon as a function of the magnesium citrate in the initial mixture.



**Figure 5** Scanning electron microscopy image of L-70 sample.



**Figure 6** The Raman spectrum of L-70 sample and its decomposition into components (descriptions are given in the text).

The main reason for the diminishing of the nitrogen content seems to be a relatively easy escape of nitrogen-containing products from the resin structure during the pyrolysis due to lower values of the binding energy of C-N bonds compared to C-C bonds.

The complex spectrum of the N1s region after deconvolution using the XPS Peak package can be described as a superposition of three peaks corresponding to the electronic states of nitrogen: pyridinic-N (398.2 eV); pyrrolic-N (400.3 eV); graphitic-N (or quaternary-N) (401 eV). Such spectra are typical of other nitrogen-doped carbon materials [33]. According to the qualitative analysis, the relative concentrations of pyridinic-N, pyrrolic-N and graphitic-N are 20%, 35% and 45%, respectively.

### 3.5. Electrochemical properties

#### 3.5.1. Cyclic voltamperometry

To investigate the possibility of using the obtained N-doped carbon materials in supercapacitor applications, cyclic voltammogram (CVA) study was carried out using the samples under study as electrodes in symmetric cells with different electrolytes. Figure 8 shows the CVA curves obtained in acidic and basic electrolytes.

Specific capacitance per unit mass of carbon material  $C_m$  was calculated using the following formula:

$$C_m = \frac{1}{(U_2 - U_1) \cdot m \cdot v} \int_{U_1}^{U_2} I(t) dU, \quad (2)$$

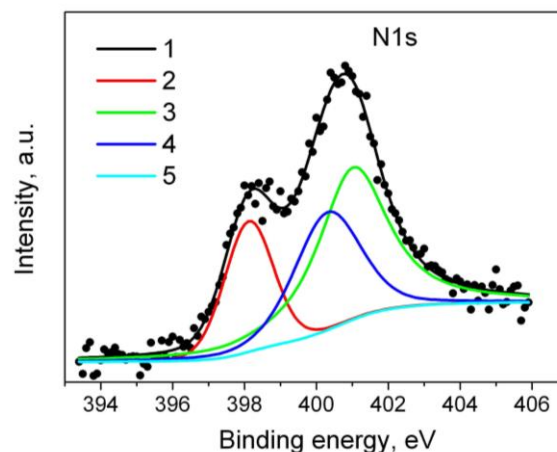
where  $I$  is the current value (A);  $U_1$  and  $U_2$  are the voltage limits between which the voltage scan is performed (V);  $v$  is the potential sweep rate (V/s);  $m$  is the total mass of carbon material on two electrodes (g).

Tables 1 and 2 show the results of voltammetry of the obtained series of samples in acidic and alkaline electrolytes at different potential sweep rates. The specific capacity of the samples in acidic electrolyte has a fairly high value, exceeding 100 F/g. It can also be observed that with an increase in the mass content of magnesium citrate in the initial mixture, the specific capacity increases, goes through a flattened maximum in the range from 30 to 90 wt.% magnesium citrate and strongly decreases for the sample L-100. Similar trend is observed for the capacitance values obtained in 3M KOH alkaline electrolyte. The comparison shows that the specific capacitance values obtained in an acidic electrolyte are 2–3 times higher than those obtained in an alkaline electrolyte.

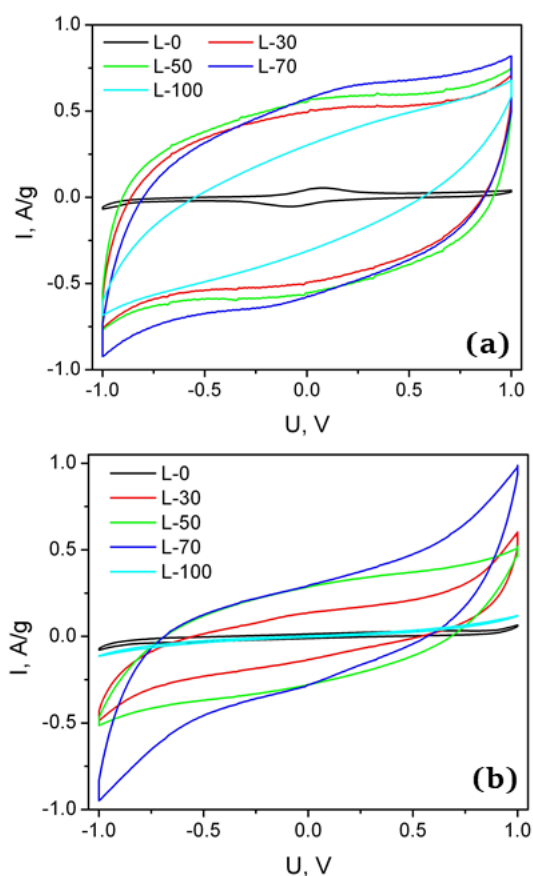
It is known [34] that the specific capacitance of highly porous materials is defined by contributions of the double charge layer,  $C_{DL}$ , and the pseudocapacitance  $C_{ps}$ . The latter is the result of Faradaic effects, i.e. electrochemical processes proceeding on the electrodes which are defined by the diffusion of the reagents or products to the electrode surface and depends on the sweep rate. In order to separate the  $C_{ps}$  contribution into the overall capacitance, one can use the relation [35, 36]:

$$C_m = C_{DL} + \alpha \cdot v^{-1/2}, \quad (3)$$

where the second term on the right-hand side corresponds to the contribution of the pseudocapacitance. According to Equation (2), the dependence of  $C_m$  on  $v^{-1/2}$  should be linear, and the double layer capacitance  $C_{DL}$  can be found from the intersection of this curve with the  $C_m$  axis. Figure 9 shows such dependences for some nitrogen-doped carbon materials obtained in acidic and basic electrolytes.



**Figure 7** XPS spectra of N1s for L-70 sample. Points are experimental data, lines are calculated spectrum (1) obtained by superposition of contributions of pyridinic-N (2), pyrrolic-N (3), graphitic-N (4) and the background (5).



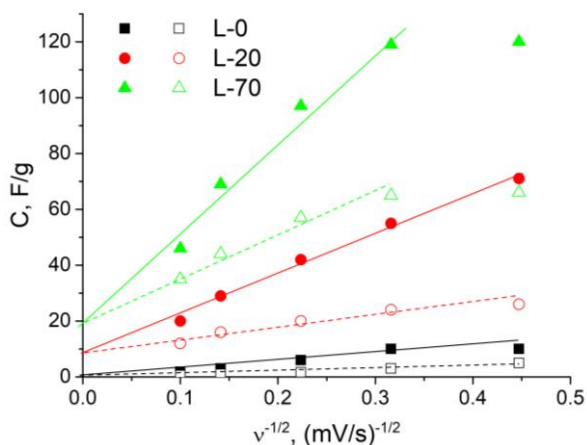
**Figure 8** Cyclic voltammograms of the samples under study obtained for the samples under study in water solutions of 1 M  $H_2SO_4$  (a) and 3 M KOH (b).

**Table 1** Specific capacity of the obtained samples at potential sweep rates of 5, 10, 20, 50 and 100 mV/s in 1 M H<sub>2</sub>SO<sub>4</sub> electrolyte.

Sample	Specific capacity, F/g, at potential sweep rate, mV/s				
	5	10	20	50	100
L-0	10	10	6	3	1.8
L-10	56	50	40	30	20
L-20	71	55	42	29	20
L-30	111	100	95	75	52
L-40	117	108	88	65	48
L-50	120	112	108	82	64
L-60	121	120	114	96	60
L-70	118	115	111	81	58
L-80	120	119	97	69	46
L-90	110	108	119	91	63
L-100	61	47	56	30	18

**Table 2** Specific capacity of the samples at potential sweep rates of 5, 10, 20, 50 and 100 mV/s in 3 M KOH electrolyte.

Sample	Specific capacity, F/g, at potential sweep rate, mV/s				
	5	10	20	50	100
L-0	5	3	1.6	1	0.6
L-10	22	24	23	22	20
L-20	26	24	20	16	12
L-30	32	28	24	16	12
L-40	60	54	28	22	16
L-50	62	58	40	25	10
L-60	61	55	34	24	14
L-70	64	60	54	43	32
L-80	66	65	57	44	35
L-90	15	12	8	4	2
L-100	1	0.8	0.4	0.1	0.08

**Figure 9**  $C_m$  vs  $v^{-1/2}$  dependences for some samples under study: filled and open symbols are experimental data obtained in 1M H<sub>2</sub>SO<sub>4</sub> and 3M KOH electrolytes, respectively, lines are linear dependences corresponding to Equation (2) for acidic (solid lines) and basic (dotted lines) electrolytes.

The analysis of the data shows that Equation (2) satisfactorily describes experimental data at the scan rates above 10 mV/s. The values of  $C_m$  obtained at smaller scan rates deviate from the theoretical dependence, and more sophisticated approaches should be used to explain this effect. Both contributions,  $C_{DL}$  and  $C_{ps} \approx \alpha v^{-1/2}$ , have maxima for L-

70 sample. At low scan rates the pseudocapacitance gives the main contribution to the overall capacitance, whereas the maximum value of the double layer capacitance is less than 20 F/g. According to the data reported in the literature [34, 37], Faradaic processes in nitrogen-doped carbon materials are accompanied by the proton transfer. Therefore,  $C_{sp}$  values in acidic electrolytes are higher than in basic ones.

The maxima on the concentration dependences of  $C_{DL}$  and  $C_{ps}$  are caused by two factors: the increase in the specific surface area and the decrease in the total concentration of nitrogen in carbon materials. Both capacitances,  $C_{DL}$  and  $C_{ps}$ , are defined by the concentration of active surface centers. The estimation of the specific capacitance normalized per unit surface of the electrode material  $C_s$  [F/m<sup>2</sup>] using the equation

$$C_s = \frac{C_m}{S_{sp}}, \quad (4)$$

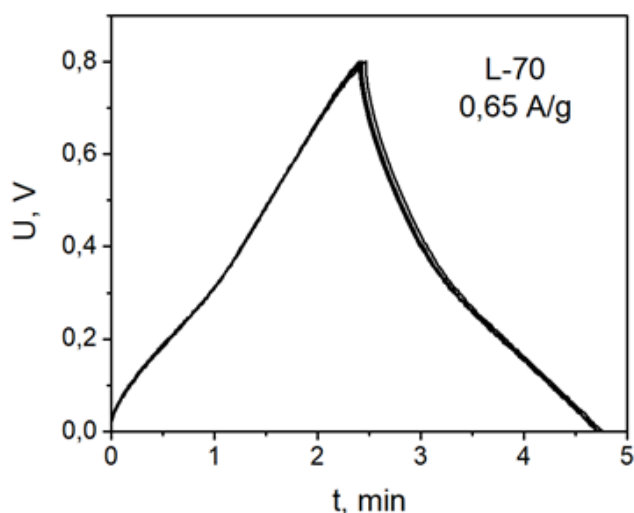
where  $S_{sp}$  [m<sup>2</sup>/g] is the specific surface area of the material, shows that the value of  $C_s$  in the samples under study depends on the electrolyte used and has a maximum of 0.10 F/m<sup>2</sup> for the L-80 sample. Comparison with the literature data shows that this value is lower than the pseudocapacitance values for nitrogen-doped carbon materials [37], which may be explained by a relatively low surface concentration of nitrogen in the samples under study. To increase this concentration, the pyrolysis should be done in the atmosphere of nitrogen or ammonia. Relatively low values of the double layer capacitance  $C_{DL}$  in the samples under study compared to the data reported for activated carbons [34, 38] seem to be caused by an influence of the surface nitrogen centers on the adsorption activity of adjacent carbon atoms. As a result, only a part of carbon atoms participates in the formation of the surface double layer, and the pseudocapacitance gives main contribution into total  $C_m$  and  $C_s$  values.

### 3.5.2. Galvanostatic charge-discharge

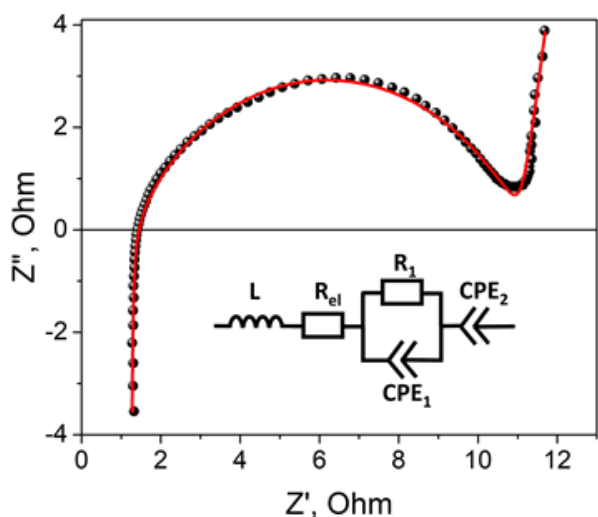
The results of galvanostatic charge-discharge tests of sample L-70 at a current density of 0.65 A/g are shown in Figure 10. The curves have a symmetrical triangular type behavior, which indicates the terminal electrical capacitance of the double layer. A small hump can be observed on the charge and discharge curves, by which one can judge the presence of Faraday reactions, which are caused by the presence of heteroatoms in the structure [39]. The specific capacitance calculated from the discharge curve is 112 F/g, which is almost identical to the integrated area CV curves at the voltage sweep rates of 10 to 20 mV/s.

### 3.5.3. Impedance spectroscopy

The impedance plot obtained for the electrochemical cell is presented in Figure 11. The impedance data were successfully fitted by the equivalent circuit (see Figure 11) including the inductance contribution  $L$  due to the terminals, the resistance of the electrolyte,  $R_e$ , and the electrode impedance which consists of active resistance  $R_1$  connected in parallel to the constant phase element  $CPE_1 = Y_1 \cdot (i\omega)^{\alpha_1}$  and another constant phase element  $CPE_2 = Y_2 \cdot (i\omega)^{\alpha_2}$ .



**Figure 10** Galvanostatic charge-discharge curves of sample L-70 in water solutions of 1M H<sub>2</sub>SO<sub>4</sub> at a current density of 0.65 A/g.



**Figure 11** The impedance plot obtained for the electrochemical cell and the equivalent circuit used for the data interpretation. Points are experimental data, line is the fitting curve.

It was found that the resistances of the electrolyte  $R_e$  and the electrode resistance  $R_1$  are equal to 1.2 Ohm and 9.9 Ohm, respectively. Capacitance contributions are determined by CPE<sub>1</sub> and CPE<sub>2</sub> values, which are equal to  $2.9 \cdot 10^{-4} \cdot (\omega)^{0.68}$  and  $8.1 \cdot 10^{-2} \cdot (\omega)^{0.90}$ , respectively. The exponent  $\alpha_2$  for CPE<sub>2</sub> contribution is close to unity. It means that the CPE<sub>2</sub> may be regarded as a slightly non-ideal capacitance (for which the parameter  $\alpha$  should be equal to 1).

#### 4. Limitations

This work demonstrated that solid template approach may be used for synthesis of highly-porous nitrogen-containing carbon materials from MFR. Nevertheless, many aspects of the work should be considered in more detail. To increase the nitrogen concentration in the materials under study the synthesis should be repeated in a nitrogen-containing atmosphere to minimize the nitrogen loss during pyrolysis. Other precursor salts could be tested as solid templates instead of magnesium citrate. Possibly, the use of other salts

could allow one to increase further the mass yield of the carbon materials. In the present study we have discussed only the role of the specific surface area. In future, it would be desirable to investigate the influence of the pore size distribution on the properties of the materials. Electrochemical studies also require carrying out additional experiments aimed to establish correlations between concentration of the nitrogen, double layer capacitance and pseudocapacitance. Moreover, the decrease in the pseudocapacitance observed at low voltage sweep needs more thorough investigation and theoretical explanation.

#### 5. Conclusion

In this work carbon materials doped with nitrogen were obtained for the first time by the hard template method followed by pyrolysis of melamine-formaldehyde resin (MFR). Nanocrystalline magnesium oxide used as a template agent was obtained by in situ thermolysis of magnesium citrate added to the melamine precursor. X-ray diffraction phase analysis revealed that the size of the resulting magnesium oxide is 7 nm and the carbon matrix is amorphous. By the method of BET nitrogen adsorption, the specific surface area of all samples was estimated, and it was found that with an increase in the content of magnesium citrate in the initial mixture the specific surface area of final carbon materials increases from 2 m<sup>2</sup>/g for pure MFR to 1304 m<sup>2</sup>/g for the pure magnesium citrate. The mass yield of carbon material depends on the magnesium citrate content in the initial mixture, and at 50–70 wt.% magnesium citrate it is several times higher than that in the materials obtained from pure components. According to the Raman spectroscopy and XPS spectroscopy data, the surface concentration of nitrogen is 4% and the carbon occurs mostly in an amorphous state with small amount of graphene fragments. The samples under study show excellent capacitance characteristics relative to their specific surface area. In 1 M of H<sub>2</sub>SO<sub>4</sub>, the specific capacity of the samples obtained from the precursors with a mass content of magnesium citrate from 30–90% exceeds 110 F/g. In 3 M KOH, the samples show lower values of specific capacity. The capacitance of the samples is mainly due to the contribution of the pseudocapacitance rather than the double layer capacitance in agreement with the earlier data for nitrogen-containing carbon materials [37]. Finally, it can be concluded that the materials obtained by the hard template pyrolysis of MFR are promising electrode materials for supercapacitors with aqueous electrolytes.

#### • Supplementary materials

No supplementary materials are available.

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## ● Conflict of interest

The authors declare no conflict of interest.

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