



# Article Synthesis and Electrochemical Properties of Fe<sub>3</sub>O<sub>4</sub>/C Nanocomposites for Symmetric Supercapacitors

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Abstract: In the work, nanostructured Fe<sub>3</sub>O<sub>4</sub>/C composites based on natural raw materials (beet pulp and corn stalks) are synthesised in various ways. Iron chloride FeCl<sub>3</sub> is used as an activator. The synthesised composites are investigated using the following methods, scanning electron microscopy, X-ray diffractometry, nitrogen adsorption/desorption porometry, magnetometry, impedance and galvanostatic measurements. The presence of nanosized Fe<sub>3</sub>O<sub>4</sub> magnetite in the synthesised carbon structures is disclosed. Based on the magnetic measurements, the particle size of Fe<sub>3</sub>O<sub>4</sub> is on average 50 nm for the sample of the composite synthesised from beet pulp in one step, 30 nm for the sample of the composite synthesised from beet pulp in two steps, 33 nm for the composite synthesised from corn stalks in one step, and 29 nm for the composite synthesised from corn stalks in two steps. It is shown that the two-step synthesis using pre-carbonised raw materials gives the specific capacitance of the composite made with beet pulp at 96 F/g, and for the composite made with corn stalks at 95 F/g. The high coulombic efficiency (>95%) and the stability of the electrical capacitance during long-term cycling make it possible to use Fe<sub>3</sub>O<sub>4</sub>/C composites for the manufacture of supercapacitor electrodes with aqueous electrolytes.

Keywords: nanocomposite; porous structure; iron chloride; supercapacitor; specific capacitance



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## 1. Introduction

The generation and storage of clean and renewable energy has recently been one of the key, yet rather complicated, research topics [1–3]. High demand for green energy generation and its efficient storage is driven by the scarcity of conventional energy sources and the ongoing environmental degradation. While numerous types of renewable energy such as solar, wind and hydropower, are perceived as the new generation of energy sources, electrochemical energy storage, i.e., batteries and supercapacitors are predominant in the energy transmission and storage solutions segments [4–7]. Currently, such devices are being implemented and used in a wide range of industries, from small portable electronics to military and aerospace applications. However, the development of new types and improvement of existing energy storage devices has not passed unnoticed in the scientific circles in various countries.

Among numerous scientific studies, attention should be paid to the key significance of electrochemical devices, which are either called supercapacitors or electrochemical capacitors with a double electrical layer, or ultracapacitors. These are energy storage systems that can be used on their own or in conjunction with modern electrochemical batteries to improve the overall efficiency of the power system, to minimize disturbances to the power grid, as electricity buffers in electric vehicles (efficient collection and return of braking energy and fast charging energy buffering), energy buffers for renewable energy sources, etc. [8–12]. It should be added that the combination of batteries and supercapacitors makes it possible to release a large volume of electric energy rapidly, leading to very high specific power values [13,14]. The supercapacitors have specific power almost five times

higher than the corresponding value for conventional lead–acid batteries [10]. Therefore, if high power consumption is required by any system, supercapacitors are superior to the batteries. In addition, supercapacitors can be incorporated into a hybrid energy storage system along with a battery, which will lead to a reduction in the size of such a system while meeting energy and power requirements, as well as to an enhancement of the battery life of such a power system [15]. In systems that include some portable electronic devices, supercapacitors can be used as the primary power source, as they can be recharged quickly. It is also important that many supercapacitors can operate over a wide temperature range (-40 to +85 °C), while conventional batteries are typically used over a narrower temperature range [16]. Since the electrode materials used in supercapacitors are subject to marginally small phase and/or chemical changes during charge-discharge processes, it is believed that supercapacitors can exhibit very high cycling (lifetime) [13].

The activated carbon (AC) materials are the most widely used materials for making the electrodes of supercapacitors with both aqueous and non-aqueous electrolytes [1,17]. This is due to their well-developed porous structure, good electrical conductivity, low production costs and, above all, they are environmentally friendly. The operational principle of supercapacitors made of AC materials is based on the principle of movement of ions under the influence of an applied electric field (Figure 1). At first, the ions are chaotically scattered in the electrolyte. Under the influence of a potential difference applied to the supercapacitor plates, the ions begin to move towards the electrodes—the cations move towards the cathode and the anions towards the anode. The ions enter the porous AC structure and reach the carbon surface. At this time instant, the surface of the carbon becomes charged with the opposite sign. In this manner, a double electrical layer is formed on the AC material surface of each electrode.



Figure 1. Structure of supercapacitor with AC materials [12].

Commonly used raw materials for AC material manufacturing are wood, coal, oil derivative waste, peat and polymers. However, in recent years, AC material synthesis has increasingly been carried out using low-cost and available alternative raw materials, primarily agricultural produce waste (including but not limited to fruit seeds, nut shells, rice, corn straw, etc.) and solid waste (sludge, food waste, garden waste, etc.) [18–21]. The production of AC materials from such waste and other by-products is also driven by the economic feasibility of large-scale production. Therefore, biomass waste is suitable for the production of biocarbon, which has a well-developed porous structure, a surface containing various functional groups and mineral components due to the removal of moisture and volatile substances from biomass by heat treatment [22]. However, the conventional methods for obtaining AC materials do not allow one to synthesise an electrode material of the required quality. Therefore, methods for synthesising composites based on carbon materials have become widely used [23–26].

Chemical activation of raw materials for the synthesis of activated carbon (AC) materials is an important method to controllable change in the properties of the resulting AC. One of the methods commonly used for this purpose is the application of metal chlorides, most frequently ZnCl<sub>2</sub> and FeCl<sub>3</sub>, as an activating agent. Activated carbon modified with iron oxides is widely used to solve environmental problems. The main area of application for such carbon composites is the treatment of wastewater and natural water [27–29]. But Refs. [30–33] present the electrochemical properties of carbon obtained from biowastes activated with ferric chloride. Firstly, there is practically no impedance half-circle, which testifies good conductivity of the material and low internal resistance of the cell, and secondly, cyclic voltammograms testify to the electrochemical stability of such carbon in aqueous electrolytes in the cell charging/discharging process. However, the optimal modification methods have not been fully established, because, for instance, the specific capacity of the carbon in the article [30] in an acidic electrolyte is only 57 F/g, while the carbon of [33] already has 252.2 F/g in 0.5 M aqueous  $Na_2SO_4$  solution, although the synthesis methods are very similar. The difference between the carbon tested in [30] and in [33] was solely a difference in raw materials. Thus, in [30], it was the waste from processing coffee beans, while in [33], it was sunflower. In order to optimize the technology for synthesising AC from different types of raw materials for supercapacitors, studies were conducted on carbon materials from beet pulp and corn stalks.

### 2. Sample Preparation and Testing Techniques

The initial raw materials for the synthesis of carbon composites were selected from agricultural processing waste–dry corn stalks and sugar beet pulp.

The carbon composite synthesis was carried out according to the diagrams shown in Figure 2. The raw material was first washed in distilled water at room temperature to a visually clear efflux and dried in an oven in an air atmosphere of 100–110  $^{\circ}$ C until the mass of the raw material stopped changing.



Figure 2. Block diagrams showing one- and two-step organic raw materials-based AC production.

Next, a portion of the raw material was prepared directly for pyrolysis, and another portion was pre-modified with ferric chloride. Dried and crushed beet pulp and corn stalks were filled with an aqueous solution of ferric chloride FeCl<sub>3</sub> using a salt to raw material ratio = 1:10. Raw materials prepared in this manner were stored at room temperature for 48 h, and then dried at 100–110 °C to achieve a constant weight. The next step was pyrolysis, which was carried out in a tubular stainless-steel reactor. The process was carried out at 700 °C for 90 min in an argon atmosphere. The resulting AC was scrubbed three times with hot distilled water. Such samples will be referred one-step synthesis samples (Figure 2).

The papers concerning the modification of raw materials with KOH, for Instance [34], have shown the effectiveness of two-step carbonisation-activation in AC material produc-

tion. This idea was also used to obtain AC materials with ferric chloride modifier. The raw materials for modification were corn stalks and beet pulp carbonised in an inert atmosphere at 400 °C for 90 min. The carbonised corn stalks and beet pulp were soaked in an aqueous ferric chloride solution, held for 24 h, and then dried in an oven at the temperature of 100–110 °C. In the next step, we subjected the ferric chloride-modified raw material to pyrolysis at 700 °C in an argon atmosphere for 90 min. The resulting AC material was scrubbed three times with hot distilled water. The AC material was then dried until the carbon mass stopped changing. Such samples will be referred to two-step synthesis samples (Figure 2).

A scanning electron microscope REMMA-102-02 (SELMI, Sumy, Ukraine) with a low-vacuum chamber and an energy-dispersive microanalysis system was used to obtain images of synthesised carbon composites.

Magnetic measurements were carried out using a vibration magnetometer based on the method described in [35]. The magnetometer was calibrated by the comparison method. Pure non-porous nickel with a density of  $\rho = 8.9$  g/cm<sup>3</sup> was used as a standard. The magnetisation curves of the samples under study were recorded in magnetic fields from -300 kA/m to +300 kA/m. The content of the magnetic phase in the synthesised composites was calculated from the measurement of the specific saturation magnetisation. For the correct determination of the saturation magnetisation, the study should be performed in strong magnetic fields sufficient for complete saturation. In our case, a magnetic field of 800 kA/m was used.

The parameters of the porous structure of the studied samples were estimated by the isothermal processes of nitrogen adsorption/desorption at its boiling point (T = 77 K). The adsorption/desorption isotherms were obtained using a NOVAtouch LX2 (Anton Paar QuantaTec, Boynton Beach, FL, USA). All synthesised samples were degassed in a vacuum at 473 K before measuring the isotherms, and the duration of degassing was 12 h.

X-ray diffractograms of the AC materials were obtained using a DRON-3 diffractometer (NPO Burevestnik, Saint Petersburg, Russia) in Cu K $\alpha$  radiation ( $\lambda$  = 0.1542 nm), monochromatized by reflection from the (002) plane of the pyrographite monocrystal. Diffractograms were measured in continuous detector scanning mode at a rate of 2 degrees/min. Processing of the diffraction spectra (smoothing, background subtraction, determining the positions and widths of half maxima, breaking the composite maxima into separate components) was carried out using the DHN\_PDS Program Package for Powder Diffraction Version 2.0 suite.

The obtained carbon types were ground in a ceramic bowl and sieved on screens. A fraction of 40–63  $\mu$ m was used to make supercapacitor electrodes. The supercapacitor electrodes were made from both AC from corn stalks and beet pulp, as well as from AC material types dried after modification. Polyvinylidene fluoride (PVDF) was used as the binding agent. The active electrode mass was obtained by mixing carbon material with PVDF, which was previously dissolved in dimethyl sulfoxide. The mass ratio of AC to PVDF was 19:1. The active mass was applied to the nickel mesh and pressed using a hydraulic press with a force of 500 N/cm<sup>2</sup>. The electrode dimensions were 0.5 × 1.5 cm<sup>2</sup>. The finished electrodes were dried in an oven at 100 °C. The electrolyte was a 30% aqueous solution of potassium hydroxide KOH.

Impedance spectra and cyclic voltammograms of the fabricated supercapacitors were measured using an AUTOLAB PGSTAT-100 (Metrohm AG, Herisau, Switzerland) impedance spectrometer. Impedance spectra were measured in the frequency range from  $10^{-2}$  to  $10^{5}$  Hz. Modelling of the obtained Nyquist diagrams was carried out with electrical equivalent circuits using Zview 3.4 software. The parameters of the elements in the electrical equivalent circuits were determined with an accuracy of not higher than 10%.

#### 3. Results and Discussions

Scanning electron microscope images of the synthesised carbon nanocomposites are shown in Figure 3a–d.



**Figure 3.** SEM images of beet pulp carbon composite using a one-step synthesis (**a**) and using a two-step synthesis (**b**), corn carbon composite using a one-step synthesis (**c**) and using a two-step synthesis (**d**).

From the obtained images it can be seen that all the synthesised composites are quite homogeneous; moreover, elements showing the macroporous structure of the original biowastes are also observed.

It should be added that organic raw materials often contain various additional atoms in addition to carbon, the type and amount of which depends on the type of raw material. These atoms combine with oxygen or carbon atoms during high-temperature synthesis and can form water-insoluble particles. Therefore, such particles do not dissolve during water rinsing and remain in the synthesised carbon material. However, as can be seen from Figure 3, such additional (non-carbon) particles are practically absent in any of the synthesised composites.

X-ray diffraction methods were used to analyse the internal structural features of the synthesised samples. X-ray diffractograms of the obtained samples are shown in Figure 4c–f. As can be seen, wide scattering maxima are observed in the diffractograms of all materials, indicating the amorphous structure of the samples [36–38]. For comparative sake, the positions of polycrystalline graphite reflections corresponding to three-dimensional (002) and two-dimensional (100), (110) diffraction from graphene layers (Figure 4b) are given, and red lines (Figure 4a) correspond to  $Fe_3O_4$  magnetite. In addition, all diffractograms show a number of small peaks of crystalline phases, which are most likely associated with impurity elements present in the initial raw material. In the work [39], it was established that the raw materials (beet pulp and corn stalks) do not contain  $Fe_3O_4$  magnetite particles. Therefore, they are introduced into the carbon structure during activation with ferric chloride.



**Figure 4.** X-ray diffractogram of beet pulp carbon composite using a one-step synthesis (**c**) and using a two-step synthesis (**d**), corn carbon composite using a one-step synthesis (**e**) and using a two-step synthesis (**f**). For comparison, the lines of  $Fe_3O_4$  magnetite (**a**) and polycrystalline graphite (**b**) are shown.

During the carbonisation of raw materials in the presence of iron salts, processes occur that lead to the formation of iron oxides and the development of porosity [40,41].

First of all, Fe<sup>3+</sup> ions are hydrolysed to Fe(OH)<sub>3</sub> at a temperature of 350 °C:

$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3 + 3H^+$$
(1)

When further heated in an inert atmosphere, the hydroxide is dehydrated and converted to  $Fe_2O_3$  hematite at 400 °C:

$$Fe(OH)_3 \rightarrow FeO(OH) \rightarrow Fe_2O_3$$
 (2)

At higher temperatures (from 500 °C to 700 °C),  $Fe_2O_3$  hematite is reduced to  $Fe_3O_4$  magnetite by amorphous carbon and CO gas:

$$3Fe_2O_3 + C(CO) \rightarrow 2Fe_3O_4 + CO(CO_2)\uparrow$$
(3)

A number of studies [42,43] have reported that FeCl<sub>3</sub> promotes the development of pores in carbon-containing materials. Unfortunately, the mechanism of FeCl<sub>3</sub> activation is not well understood. But, for example, the reduction reaction given in Equation (3) can promote the development of pores in samples of synthesised nanocomposites by converting C into CO and removing carbon in the form of CO or CO<sub>2</sub>, resulting in certain cavities within the material structure.

Nitrogen adsorption/desorption isotherms are shown in Figure 5. All the isotherms can be classified as type II isotherms [44]. The isotherms of composites synthesised in one step are characterised by a discrepancy between the adsorption and desorption curves. The main reason for this behaviour may be the irreversible retention of adsorbate molecules in pores whose size is close to the size of the adsorbate molecules. The isotherms of composites synthesised in two steps are characterised by the presence of a hysteresis loop, which can be classified as type H4. This behaviour of the isotherm is typical for porous solids with slit-like pores [45].



**Figure 5.** Nitrogen adsorption/desorption isotherms of beet pulp carbon composite (**a**) using a one-step synthesis (1) and using a two-step synthesis (2), corn carbon composite (**b**) using a one-step synthesis (1) and using a two-step synthesis (2). The red curves correspond to adsorption and the blue curves to desorption of nitrogen.

To calculate the parameters of the porous structure of the synthesised composites, the obtained isotherms were analysed using the Quantachrome TouchWin version 1.22 software. To do this, we used the multipoint BET method [45], which approximates the experimental data with a straight line in the range of relative pressures  $P/P_0 = 0.05 \div 0.35$ . The calculation data are given in Table 1.

Type of Nanocomposite	S, m <sup>2</sup> /g	V, cm <sup>3</sup> /g	<d>, nm</d>
AC from beet pulp, 1-step synthesis	359.6	0.167	1.86
AC from beet pulp, 2-step synthesis	738.2	0.361	1.96
AC from corn, 1-step synthesis	413.1	0.269	2.6
AC from corn, 2-step synthesis	889.8	0.591	2.66

Table 1. Parameters of the porous structure of synthesised nanocomposites.

As can be seen from Table 1, the two-step synthesis results in an increase in the specific surface area and specific volume by about half, regardless of the type of initial raw material. At the same time, the average pore size remains virtually unchanged.

Magnetic measurements have shown that the synthesised nanocomposite samples have magnetic hysteresis. The corresponding hysteresis loops are shown in Figure 6.

The coercive force  $H_c$  and specific saturation magnetisation  $\sigma_s$  were calculated from the hysteresis loops. These data are shown in Table 2.

Table 2. Magnetic characteristics of synthesised nanocomposites.

Type of Nanocomposite	$\sigma_s$ , $A \cdot m^2 \cdot kg^{-1}$	H <sub>c</sub> , kA/m	Fe <sub>3</sub> O <sub>4</sub> Content, Mass %
AC from beet pulp, 1-step synthesis	3.03	11.3	3.79
AC from beet pulp, 2-step synthesis	2.39	5.5	2.99
AC from corn, 1-step synthesis	1.42	6.6	1.78
AC from corn, 2-step synthesis	0.42	5.3	0.53



**Figure 6.** Hysteresis loops of beet pulp carbon composite (**a**) using a one-step synthesis (1) and using a two-step synthesis (2), corn carbon composite (**b**) using a one-step synthesis (1) and using a two-step synthesis (2).

Based on the results of measuring the saturation specific magnetisation of synthesised nanocomposites, the content of magnetic moment carrier particles, magnetite, can be determined. For the calculation, it is necessary to know the value of the saturation specific magnetisation of magnetite particles. The saturation specific magnetisation of massive magnetite is 92  $A \cdot m^2 \cdot kg^{-1}$  [46]. The value of the specific saturation magnetisation of magnetite particles required for the calculation was chosen taking into account the phenomenon of a decrease in the magnetisation of small particles with a decrease in their size [47]. According to the data on the dependence of coercive force on particle diameter in  $Fe_3O_4$  dispersions [48,49], for the measured values of coercive force, the size of magnetic moment carriers is on average 50 nm for the sample of the composite synthesised from beet pulp in one step, 30 nm for a sample of the composite synthesised from beet pulp in two steps, 33 nm for the composite synthesised from corn stalks in one step, and 29 nm for the composite synthesised from corn stalks in two steps. Accepting from the above sources that the indicated particle sizes correspond to an average value of the specific saturation magnetisation of 80  $A \cdot m^2 \cdot kg^{-1}$ , the percentage of magnetite in the composites was determined (Table 2).

Galvanostatic charge/discharge cycles were carried out on the manufactured symmetric supercapacitors. Figure 7 shows a typical charge-discharge curve for supercapacitors. The specific capacitance of the carbon material was determined from the formula [50]:

$$C = \frac{2I\Delta t}{m\Delta U} \tag{4}$$

where: I is the discharge current,  $\Delta t$  is the discharge time, m is the active mass of one electrode,  $\Delta U$  is the discharge voltage.

As a result of the analysis, it was found that one-step modification yields not very high capacitance values in alkaline electrolyte—for nanocomposites from beet pulp the value is 41 F/g, and for nanocomposites from corn stalks it is 72 F/g. In contrast, a two-step synthesis using pre-carbonised raw materials boosted the specific capacitance of beet pulp nanocomposites to 96 F/g, and that of corn stalk nanocomposites to 95 F/g. Coulombic efficiency in both cases was higher than 95 percent. The current density during the study of charging and discharging processes was 1 A/g.

Since composites made in two-step process show higher capacitance, further studies were carried out on the properties of supercapacitors made from these materials.



Figure 7. Typical charge-discharge curve for manufactured supercapacitors.

The working potential or "electrochemical window" of a supercapacitor is determined by the electrochemical stability of the electrolyte. Among other electrochemical methods, the cyclic voltammetry method can be considered the most efficient method for determining the "electrochemical window". For smooth electrodes, it is believed that the decomposition processes of electrolyte components start to run intensively when the surface current density is  $0.5 \text{ mA/cm}^2$  [51]. In the case of porous electrodes, there is no such criterion, so it is believed that the electrolyte component decomposition processes begin to occur when the current in the system goes up rapidly. The presence of Faraday electrochemical processes in the system is manifested in the form of voltammogram peaks [52].

Figure 8 show cyclic voltammograms of supercapacitors, electrodes of which were manufactured from carbon nanocomposites synthesised in two steps. The tests were carried out for different scanning speeds. As can be seen in both figures, the shape of the obtained curves indicates mainly the capacitance nature of the electrochemical system behaviour with a good ionic response [53].



**Figure 8.** Cyclic voltammograms for supercapacitors made from beet pulp (**a**) and corn stalks (**b**) carbon composites synthesised in two steps.

Increasing the scan rate to 50 mV/s leads to the acceleration of charge-discharge processes, which reduces the availability and movement of electrolyte ions inside the electrode material. At the same time, the effective interaction between the electrolyte ions and the electrode is significantly reduced due to the electrode material resistance, which is reflected in the deviation of the cyclic voltammogram from a rectangular shape [54,55].

We do not observe clear current peaks in all curves, which indicates the absence of parasitic capacitances and the absence of undesirable electrochemically active impurities in the electrochemical systems of manufactured supercapacitors. The obtained shape of the curves allows us to conclude that practically only adsorption and desorption of K+ cations and OH- anions occur on the surface of electrodes in the set potential range.

To confirm the electrochemical stability of the obtained nanocomposites, long-term tests of the fabricated supercapacitors were carried out. The results of the change in specific capacitance depending on the number of charge-discharge cycles are shown in Figure 9.



**Figure 9.** Dependence of specific capacitance on the number of charge-discharge cycles for supercapacitors made from carbon composites made from beet pulp (1) and from corn stalks (2).

It is known that supercapacitors based on  $Fe_3O_4$  nanoparticles do not have stable electrochemical parameters at a large number of charge-discharge cycles [56]. As shown in Figure 9, the specific capacitance of the corn stalks nanocomposite practically does not decrease, while for the beet pulp nanocomposite the decrease for 8000 cycles was of the magnitude of 3%.

The Impedance spectra of the tested supercapacitors are shown as Nyquist diagrams and Bode diagrams (Figure 10). All curves have a typical appearance for the dominant process of electric double layer formation at the carbon electrode/electrolyte interface. The Nyquist diagrams at high frequencies look like straight lines at an angle close to 90° to the axis of the real component of the complex resistance, while the Bode diagrams show a phase angle of about  $-80^{\circ}$  at a frequency of  $10^{-2}$  Hz. According to [57], such behaviour of a supercapacitor may be due to the presence of Faraday processes, the contribution of which may be as high as 5–10%. However, studies by Frackowiak and Beguin in [58] showed that quasi-reversible Faraday processes of electrochemical reduction of oxygencontaining surface groups in alkaline electrolytes appear in Nyquist diagrams only at sufficiently low frequencies of the order of  $10^{-3}$  Hz. Therefore, for our chosen frequency range ( $10^{-2}-10^5$  Hz), the influence of such Faraday processes can be neglected.

This conclusion is confirmed by the calculation of the specific capacitance at  $10^{-2}$  Hz using the following formula [50]:

$$C = -\frac{1}{2\pi f Z''} \tag{5}$$

A value of 94.5 F/g in terms of specific value is obtained for the beet pulp nanocomposites, and 91.6 F/g for the corn stalks nanocomposites. These values are quite close to those obtained using Equation (4) for galvanostatic charging/discharging.

Impedance data were modelled with Zview 3.4 software using an electrical equivalent circuit based on a linear model of de Levy with the addition of an R4C4 coupler, which corresponds to the resistance and capacitance of the space charge region in the AC [59,60]. The calculated parameters of the elements in the electrical equivalent circuits are shown in Table 3. The contribution of pores of a certain size to the formation of an electrical double layer corresponds to a certain RC cell. In the circuit shown in the insert in Figure 10a, the resistance R1 corresponds to the internal resistance of the supercapacitor, R2 and C2 are the electrolyte resistance and capacitance in the mesopores, and R3 and C3 are the electrolyte

resistance and capacitance in the micropores. In modelling the impedance of the studied carbon nanocomposites in aqueous electrolyte, a capacitive phase constant element (CRE1) was also used [61]. It simulates the distributed capacitance resulting from the presence of vacancies or impurity defects that provide conductivity to the carbon material at room temperature. The C3/C2 ratio for composites from beet pulp is 2.35, and for composites from corn stalks it is 2.67, indicating the main influence of micropores in shaping the capacitance of the electrical double layer. Similar conclusions were made in [62], where the C3/C2 ratio was about 2.75.



**Figure 10.** The Nyquist (**a**) and Bode diagrams (**b**,**c**) for supercapacitors made of carbon composites from beet pulp (1) and corn stalks (2). The insert (**a**) shows the electrical equivalent circuit for the supercapacitor.

Table 3. Parameters of elements in electrical equivalent circ	uits.
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Type of Nanocomposite	R1, Ohm	CPE1-T	CPE1-P	R2, Ohm	C2, F	R3, Ohm	C3, F	R4, Ohm	C4, F
AC from beet pulp, 2-step synthesis	0.87	0.19	0.71	0.49	0.31	1.38	0.73	0.27	$6.48  imes 10^{-5}$
AC from corn stalks, 2-step synthesis	0.72	0.19	0.67	0.94	0.26	2.26	0.56	0.19	$8.78  imes 10^{-5}$

Another parameter that can be calculated from the model applied is the relaxation time of the charging/discharging process of a porous structure with different pore sizes, in which an electrical double layer is formed. The relaxation time can be calculated using the following formula [50]:

 $\tau =$ 

$$C \cdot R$$
, (6)

where C is the electrical capacitance, R is the resistance.

The lower the value of  $\tau$  is, the faster the supercapacitor charges and discharges. For commercial supercapacitors  $\tau = 0.5 \div 3.6$  s [50]. If we carry out calculations for our model, we obtain the values shown in Table 4.

Table 4. Relaxation time of pore charge/discharge in AC materials.

Type of Nanocomposite	Relaxation Time for Mesopores, $\tau = C2 \cdot R2$	Relaxation Time for Micropores, $\tau = C3 \cdot R3$
AC from beet pulp, 2-step synthesis	0.15	1.01
AC from corn stalks, 2-step synthesis	0.24	1.27

As shown by data in Table 4, the charging/discharging process of mesopores is very fast compared to the charging/discharging of micropores. However, even if we consider the total charging/discharging time of the porous structure of the synthesised nanocomposites, both nanocomposites are suitable for the manufacture of supercapacitors that can operate under fast charging/discharging conditions.

#### 4. Conclusions

The proposed two-step modification method showed good prospects for using ferric chloride as an activator to obtain carbon nanocomposites from natural raw materials that can be used to produce supercapacitor electrodes.

X-ray diffraction studies showed the presence of  $Fe_3O_4$  nanoparticles in all synthesised carbon materials. Magnetic measurements made it possible to estimate the size of these nanoparticles from 29 nm to 50 nm, depending on the type of initial raw material and the method of composite synthesis.

The specific electrical capacitances of the nanocomposites synthesised in two steps determined by two different methods were almost identical, indicating that Faraday processes have little effect on the formation of an electrical double layer on the carbon surface. This is also confirmed by measurements of cyclic voltammograms. An important advantage of supercapacitors made from synthesised nanocomposites over supercapacitors made from pure Fe<sub>3</sub>O<sub>4</sub> nanoparticles is their stability of electrical capacitance during long-term cycling.

Modelling of impedance data made it possible to estimate the effect of meso- and micropores on the capacitance of the supercapacitor, as well as to calculate relaxation times during charging/discharging of these pores. It was found that the synthesised nanocomposites have a porous enough structure that the supercapacitors made from them can be used in devices and circuits that require rapid storage and release of electrical energy.

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