

Effect of synthesis conditions on the morphological and electrochemical properties of nitrogen-doped porous carbon materials

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Effect of synthesis conditions on the morphological and electrochemical properties of nitrogen-doped porous carbon materials

The microporous carbons samples were obtained on the base of plant feedstock using different modes of carbonization and chemical activation. The effect of N-doped microporous carbon synthesis condition on its morphological properties was investigated by low temperature nitrogen adsorption/desorption and scanning electron microscopy. The impedance spectroscopy measurements performed in 6 M KOH solution allow calculating the carrier concentration and flat band potential of the obtained carbons. Comparative characterization of synthesized carbon materials properties reveals that the sample obtained at weight ratio between activation agent (NaOH) and carbon equals to 0.75 under the condition of double activation procedure has the best preconditions (high value of carrier concentration and flat band potential) for good electrochemical performance.

Keywords: Supercapacitor; N-doped activated carbons; Pseudocapacitance

Introduction

Electric double layer supercapacitors (EDLS) have great perspectives for energy conversion and storage devices, especially for energy recuperation system^[1] due to its high power density, fast charging and discharging with good cycling capability and long lifecycle. Nowadays most of researches are focused on the increasing of both power and energy density of supercapacitors. The searching of the new carbon-based electrode materials is crucially important because energy characteristics of EDL are determined by specific capacitance, operating voltage window and the values of equivalent series resistance^[2]. Activated carbon materials are the most widely used as electrode materials for symmetric supercapacitors due to its developed porous structure and high surface area as well as its low cost^[2,3]. At the same time Faradaic process for the energy storage is the next step to the development of the devices with the improved performance^[4]. Both non-Faradaic double-layer capacitance and pseudocapacitance (associated with

ions electrosorption and redox processes) take place in these systems.

The successful evolution of such a system is determined by the functional properties of electrode materials, in particular, its electrochemical reactivity (determine the possibility of fast surface redox reaction), electrical conductivity (high electron mobility leads to increasing of power density), surface area (high specific surface is crucial for energy density), stable structure (allow hold high rate capability at different modes of charge / discharge). Today the most perspective directions for hybrid systems are the using ultrafine non-stoichiometric transition metal oxides or hydroxides or composite materials based on different carbon nanostructures^[5]. Besides, the functionalized activated carbon is still an attractive electrode material. Doping of carbon with nitrogen allows improving the performance of supercapacitors due to faradaic reaction of the nitrogen-containing functional groups and the increasing of the surface wettability (crucial for aqueous electrolytes)^[4, 6]. The pseudocapacitance properties of N-doped carbon are caused by new valence bonds formation in the near-surface regions of particles^[7]. Doping with the nitrogen can initiate carbon material transformation into n-type semiconductor as a result of direct substitution of C by N or with the formation of the pyridinic or the pyrrolic configurations^[8, 9]. These surface functional groups can improve the rate of redox reaction and provide increasing of pseudocapacitive properties. At the same time the electronic conductivity of the carbon decreases with the increasing of the content of heteroatom so the development of effective strategy to control both electronic and morphological properties of N-doped activated carbon synthesized using agricultural wastes as precursor is necessary for further development of high performance electrode materials for supercapacitors.

Materials and characterization

The microporous carbon was obtained on the base of plant feedstock using

carbonization and chemical activation^[10]. The dry apricot seeds (fraction size of about 0.25-1 mm) were carbonized in the high pressure reactor at 600 and 900 °C. The obtained materials were milled to a fraction size of about 200-250 µm and mixed with sodium hydroxide and distilled water. Weight ratios of m(NaOH)/m(C) values were 0.25, 0.5, 0.75 and 1 under the condition that mass of water equals to the mass of carbon. The resulting mixtures were stirred for 2 hours, dried to the constant weight at 90 °C and annealed in argon atmosphere at 600 °C (heating rate of 10 °C min⁻¹) for 20 min. The obtained powders were mixed with HNO₃ as nitrogen source with the continuous stirring at 50 °C under N₂ flow. The synthesized materials were washed to neutral pH and dried at 90 °C up to constant weight. Average nitrogen content in carbons was about 1.5-2.0 wt%. The activation procedure was repeated for selected samples. The synthesized mesoporous carbons (MC) were marked according to m(NaOH)/m(C) ratio value, the carbonization temperature value and the number of activation procedures. For example, MC-025-600-1 is a material obtained at m(NaOH)/m(C) ratio value equals to 0.25 using carbon prepared at 600 °C with the activation number equals to 1. The conditions of MC samples obtaining are summarized in Table 1.

The specific surface area and pore size distribution of MC samples were analyzed using low temperature nitrogen adsorption / desorption (Quantachrome Autosorb Nova 2200e device). The carbon samples were degassed at 180 °C for 18 h before measuring of morphological characteristics. The specific surface area (S_{BET} , m²/g) value was calculated by multipoint BET method. The total pore volume (V_{total} , cm³/g) was calculated by the number of adsorbed nitrogen. The volume of micropores (V_{micro} , cm³/g) and the values of specific surface of micro- (S_{micro} , m²/g), and mesopores (S_{mezo} , m²/g) were found using t-method. The calculation of pore size distribution was

carried out by NLDFT (non-local density functional theory) method in the approximation of slit-like pores. Electrochemical investigations were carried out in a three-electrode cell with a reference Ag/AgCl electrode, platinum wire as a counter electrode and a working electrode on the pure Ni grid. Working electrode consists of 75% active material and 25% acetylene black as a conductive additive. Electrochemical performance was measured in 6 M KOH as an electrolyte. The specific capacitances were measured at specific currents in a range of 0.08-0.40 A/g. Cyclic voltammetry investigations were carried out at scan rate of 0.5, 1, 2, 3, 4 and 5 mV/s.

Electrochemical impedance spectra were measured at frequencies from 0.01 Hz up to 100 kHz. The measurements were carried out using Autolab PGSTAT12 (ECO CHEMIE Company) with GPES and FRA-2 software. All the measurements were carried out in the same type of three electrodes electrochemical cell with Pt pseudo-reference electrode and Ag/AgCl reference electrode. Impedance measurements were carried out after cyclic voltammetry studies in a constant voltage mode vs Ag/AgCl electrode. The surface morphology of the obtained samples was investigated by Tescan Vega-3 scanning electron microscope (SEM).

Results and discussion

Nitrogen adsorption/desorption isotherms for carbonized at 600 °C carbon samples after one activation procedure (Fig. 1, a) belong to I type of IUPAC classification indicating microporous solids regardless of m(NaOH)/m(C) ratio during activation procedure. Simultaneously total pore volume increases with the increasing of activation agent content (Fig. 1, a). At the same time adsorption/desorption isotherms for materials obtained using two activation procedures have the hysteresis loop that corresponds to bH4-type of IUPAC classification and capillary polymolecular adsorption in micro- and

mesopores (Fig. 1, b). The increasing of hysteresis loop on adsorption/desorption isotherms for the samples carbonized at 900 °C with one activation procedure is observed for increasing of $m(\text{NaOH})/m(\text{C})$ ratios in a range of 0.25 up to 0.75 but material obtained at the maximal concentration of NaOH is characterized by decreasing of capillar condensation probability (Fig. 1, c). The same regularity was observed for the case of double activated samples prepared at 900 °C (Fig. 1, d).

MC samples obtained at 600 °C with one activation procedure are characterized by a microporous structure with an average pore diameter in the range of about 0.7-2.5 nm. The relative content of pores decreases with the increasing of its diameter (Fig. 2, a). The calculated values of specific surface area, average volumes of micro- and mesopores of all the synthesized samples are summarized in Table 1. The values of specific surface area for the sample obtained at 600°C vary in the range of 268-423 m²/g in the case of one activation procedure with the tendency to increasing when NaOH concentration grow. This regularity was also observed for once activated samples obtained at 900°C. The slight decreasing of BET specific surface area for double activated carbons in comparison with once activated samples obtained at the same $m(\text{NaOH})/m(\text{C})$ ratios was observed independently on carbonization temperatures. MC-100-900-1 sample has a maximal (582 m²/g) value of specific surface area.

SEM images of synthesized carbon obtained at 600 °C and 900 °C are presented in Fig. 3 and Fig. 4 respectively. The obtained details of morphological characteristics confirm the BET and pore size distribution results. It is possible to make a general conclusion on increase in the average density of activated carbon and reducing the relative content of its macropores with the temperature increasing from 600 °C up to 900 °C.

The Nyquist plots for the samples obtained at 600 °C and 900 °C after one and two activation procedures were measured at different values of bias potential (Fig. 5, Fig. 6). It is known that electrochemical impedance spectra of porous carbon typically depend on three frequency-dependent processes probability [11]: the mass transfer is unlikely at high-frequencies so only charge transfer at the electrode/electrolyte interface will contribute to system electrochemical response; the ion diffusion in mesoporous channels will be dominant for medium-frequencies and non-homogeneous diffusion in less-accessible sites will be important in low-frequency region.

The Nyquist plots for samples obtained at 600 °C under the condition of one activation procedure consist of a small high-frequency semicircle (the result of limitations on H^+ , Na^+ , OH^- ion transport through the carbon) and a line close to straight at the low-frequency region (corresponds to the double-layer capacitance). It can be concluded that the charge transfer resistance through electric double layer on the electrolyte/electrode interface within the electrode materials is relatively low and doesn't depend on the bias potential. The main reason for observed tendency to decreasing of internal resistance with the increasing of $m(NaOH)/m(C)$ ratio is the enlarging of penetration ability of carbon due to porosity increasing.

The medium frequencies regions are characterized by the 45° Warburg segment that corresponds to diffusion process from the electrolyte into the carbon pores. The tendency to increasing of Warburg segment with the increasing of $m(NaOH)/m(C)$ ratio is observed that indicates an increase in Warburg resistance faced by the electrolyte ions during their transport.

A pure capacitor should demonstrate a vertical line for low frequency region. The deviation from the expected behaviour is an evidence of ion diffusion into the pores of carbon material and the pore size distribution of the porous matrix.

Measuring the electrode capacitance as a function of the applied potential with the next Mott-Schottky analysis allows investigating of the electronic properties of the obtained carbons (the flat band potential position and carrier concentration). The n-type semiconductor properties of the obtained carbon samples were verified from the C^{-2} versus potential curve (Fig. 7, Fig. 8).

Due to non-crystalline nature of activated carbon close to amorphous the measurements were carried out at low frequencies in the range of 0.01-0.1 Hz that allows the effective filling and unfilling of surface states. The positive slopes were observed in all the cases that indicate the n-type semiconductor properties of the carbon samples and can be associated with the valence electrons of nitrogen in π -conjugation [12].

The variation of the C^{-2} value in the potential window from -0.25 to 0.75 V is maximal for the sample carbonized at 600 °C after two activations, and minimal for MC-075-600-1 and MC-100-600-1 that provides the maximal capacitance for these materials. The capacitance and potential are related by Mott–Schottky equation

$$\frac{1}{C^2} = \left(\frac{2}{\varepsilon \varepsilon_0 A^2 e N_D} \right) \left[E - \left(E_{fb} + \frac{kT}{e} \right) \right],$$

where ε and ε_0 are dielectric constant and vacuum permittivity, e is an electron charge, A is BET surface area, N_D is a carrier concentration, E and E_{fb} are electrode potential and flat band potential values, T – an absolute temperature, k – Boltzmann constant. Linear fitting of the low-potential part allows calculating the flat band potential (E_{fb}) and average carrier concentration (N_D) as line interception with the potential axis and from the slope of Mott-Schottky plot respectively.

The small deviation of flat band potential values calculated from Mott-Schottky plots was observed for carbons synthesized at 600 °C after one activation procedure in frequencies range of about 0.01-0.1 Hz. At the same time E_{fb} values for carbon samples

obtained at 900 °C vary in a wide range (Table 1). The lowest carrier concentration in conjunction with the highest flat band potential among the carbons obtained at 600 °C was observed for MC-05-600-1 sample when MC-075-600-2 sample has the highest carrier concentration value and relatively high flat band potential. For carbons obtained at 900 °C MC-075-900-2 sample has the highest value of carrier concentration and the flat band potential. We can make an assumption that samples obtained at weight ratio between activation agent (NaOH) and carbon equal to 0.75 after double activation procedure have the best preconditions (high values of carrier concentration and flat band potential) for using as electrode materials for supercapacitors.

Conclusions

The microporous carbons samples were obtained by chemical activation of previously carbonized plant feedstock with the using of HNO₃ treatment for doping with the nitrogen. It was determined that the increasing of activation agent (NaOH) concentration causes the micropores volume increasing not depends to carbonization temperature. The increasing of carbonization temperature from 600 to 900 °C causes mesopores formation under the same conditions of chemical treatment with the simultaneous compaction of the material at macro-level. The specific surface area values increase with the increasing of activation agent concentration for once activated samples obtained at 600 and 900 °C. The slight decreasing of BET surface area for double activated carbons obtained at the same concentration of activation agent was observed for both carbonization temperatures. MC-100-900-1 sample has a maximal (582 m²/g) value of specific surface area. The small deviation of flat band potential values was observed for carbons synthesized at 600 °C when carbons obtained at 900 °C are characterized by changes of E_{fb} values in a wide range. MC-050-600-1 sample has the lowest carrier concentration that corresponds to the highest flat band

potential from samples obtained at 600 °C. For samples carbonized at 600 °C MC-075-600-2 sample is characterized by the highest carrier concentration in combination with the relatively high flat band potentials that indicates the good opportunity for charge-transfer reactions starting. For carbons obtained at 900 °C MC-075-900-2 sample has the highest carrier concentration and also is characterized by the highest value of flat band potential and, therefore, the preconditions presence for good electrochemical performance as an electrode material for supercapacitors.

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Table 1. The synthesis details and porous structure characteristics of MC samples

Sample	S_{BET} , m^2/g	S_{micro} , m^2/g	V_{micro} , cm^3/g	S_{meso} , m^2/g	V_{total} , cm^3/g	N_{D} , cm^{-3}	E_{fb} , V
MC-025-600-1	268	268	0,06	–	0,06	2.33×10^{20}	-0.40
MC-050-600-1	320	320	0,08	–	0,08	1.20×10^{20}	-0.14
MC-075-600-1	423	423	0,12	–	0,12	9.98×10^{20}	-0.39
MC-100-600-1	408	377	0,16	31	0,18	1.12×10^{21}	-0.39
MC-075-600-2	417	395	0,12	22	0,13	4.03×10^{21}	-0.43
MC-100-600-2	379	289	0,14	90	0,21	1.95×10^{21}	-0.47
MC-025-900-1	168	132	0,07	36	0,10	4.26×10^{20}	-1.39
MC-050-900-1	197	150	0,08	47	0,12	1.43×10^{21}	-2.83
MC-075-900-1	321	215	0,11	106	0,20	1.10×10^{21}	-1.08
MC-100-900-1	582	551	0,23	31	0,25	7.01×10^{21}	-1.36
MC-075-900-2	351	250	0,12	101	0,20	1.52×10^{22}	-0.90
MC-100-900-2	566	520	0,22	46	0,25	2.58×10^{21}	-1.91

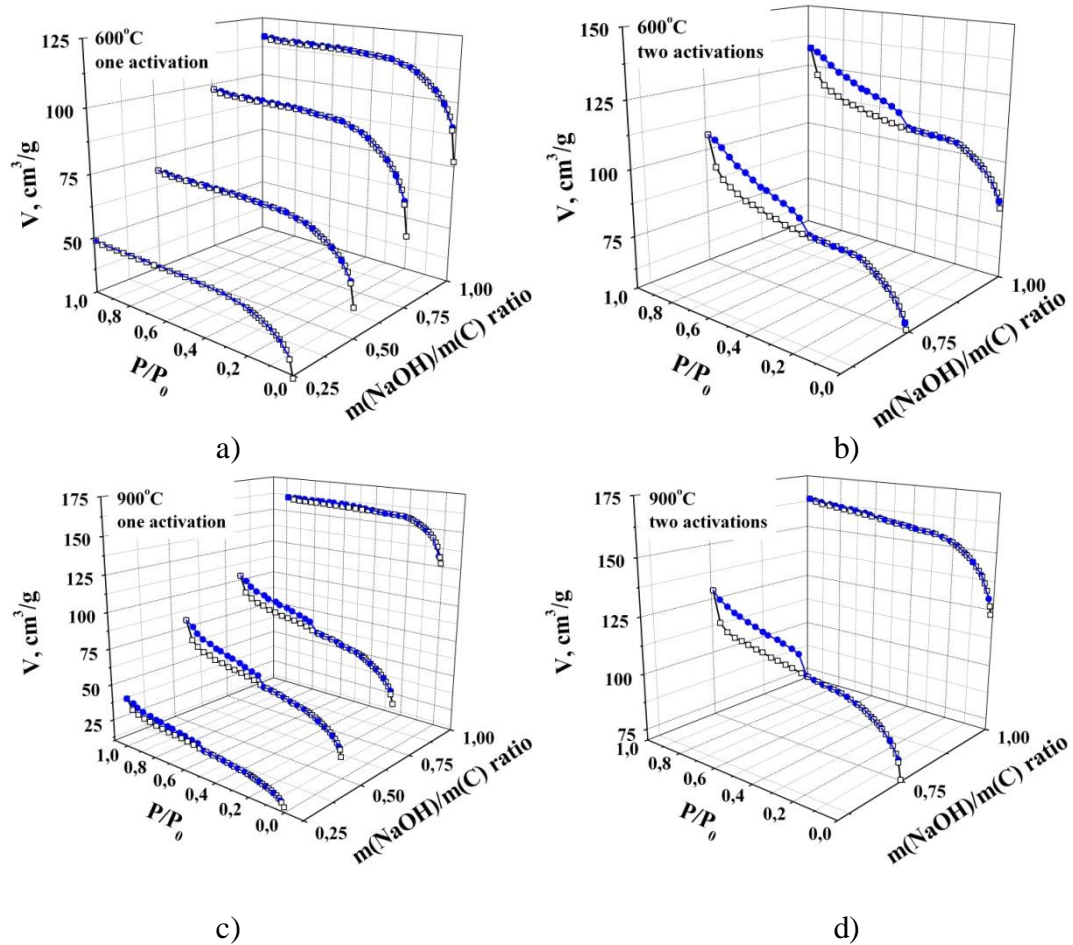


Figure 1. Nitrogen adsorption/desorption isotherms for MC samples carbonized at 600 and 900°C after one (a, c) and two (b, d) activation procedures respectively.

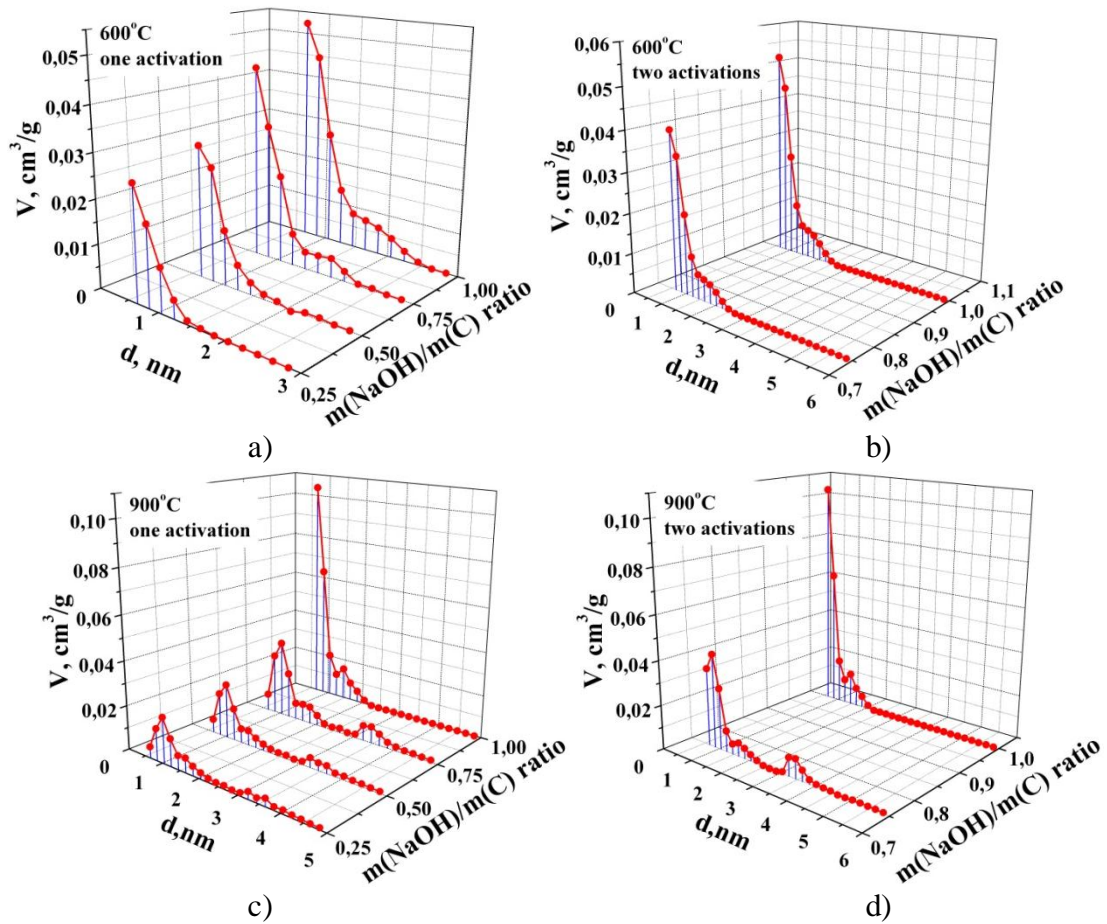


Figure 2. Pore size distribution curves calculated by NLDFT model on carbon slit pores for MC samples carbonized at 600 °C and 900 °C after one (a, c) and two (b, d) activation procedures.

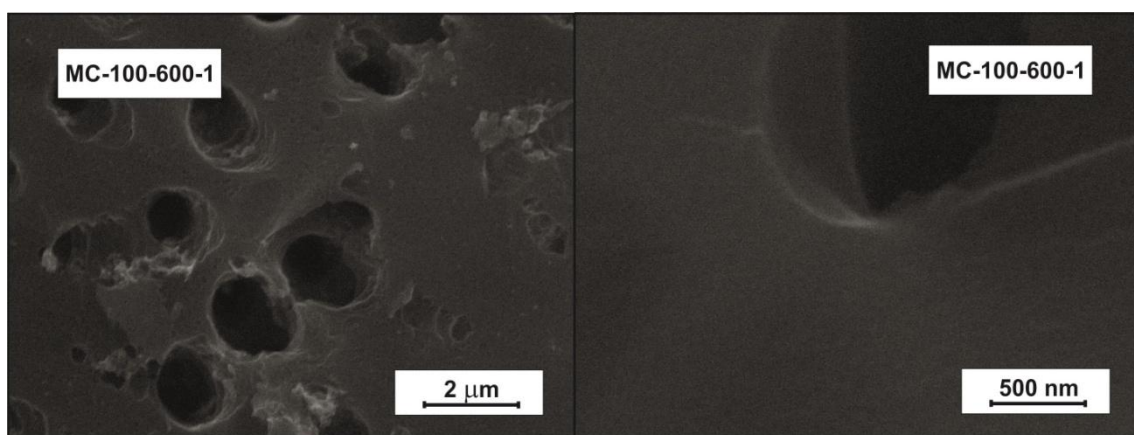


Figure 3. SEM images of MC samples carbonized at 600 °C.

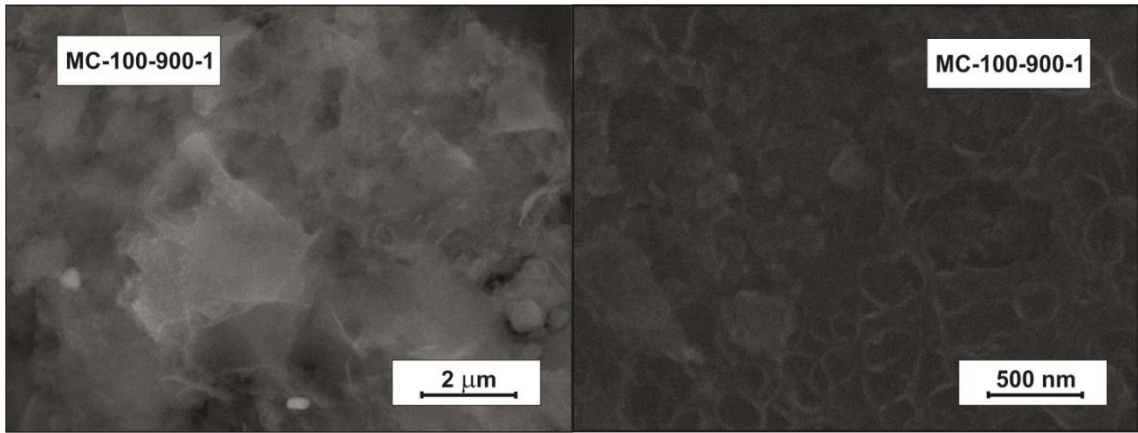


Figure 4. SEM images of MC samples carbonized at 900 °C.

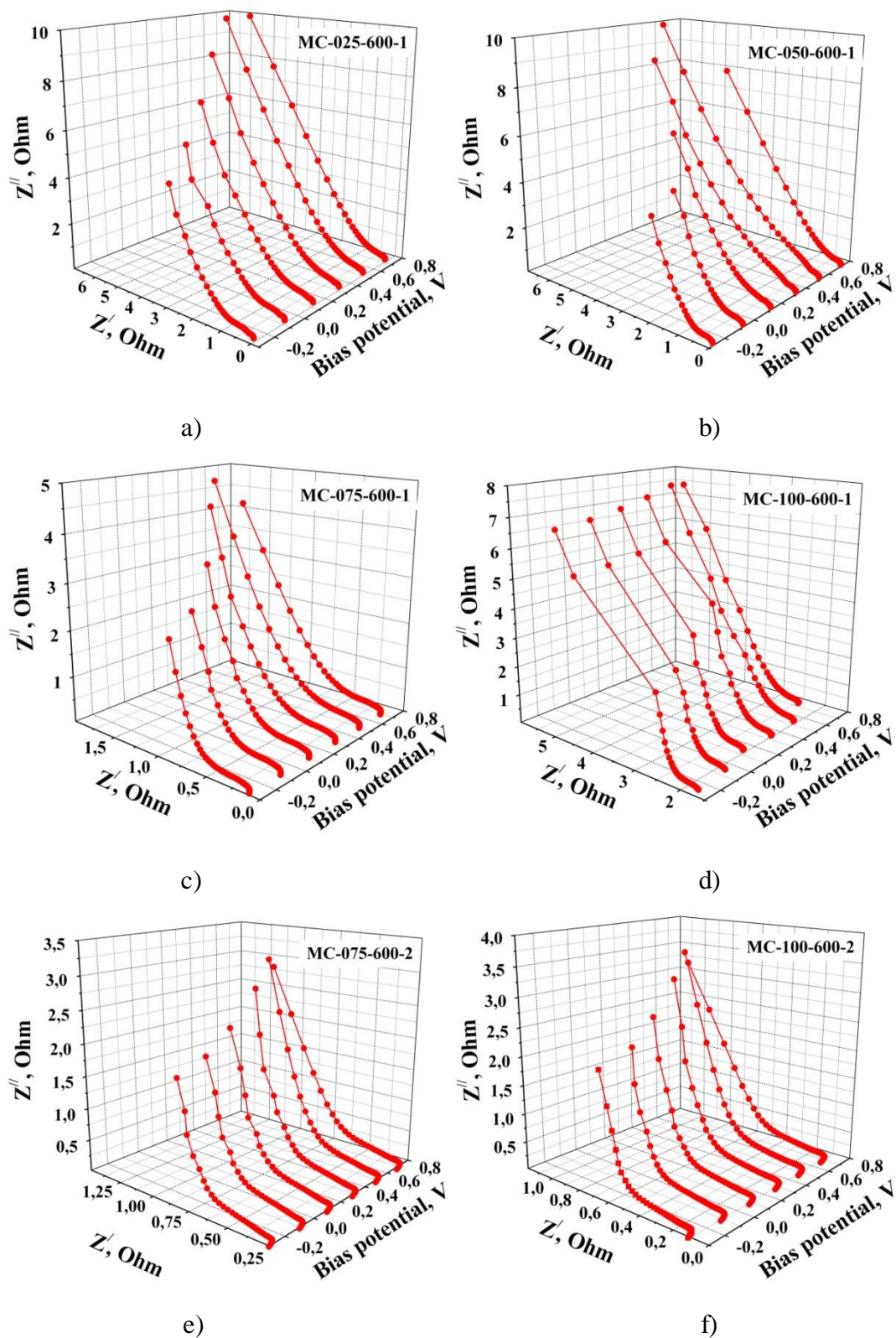


Figure 5. Nyquist plots of MC samples carbonized at 600 °C after one (a, b, c, d) and two (e, f) activation procedures.

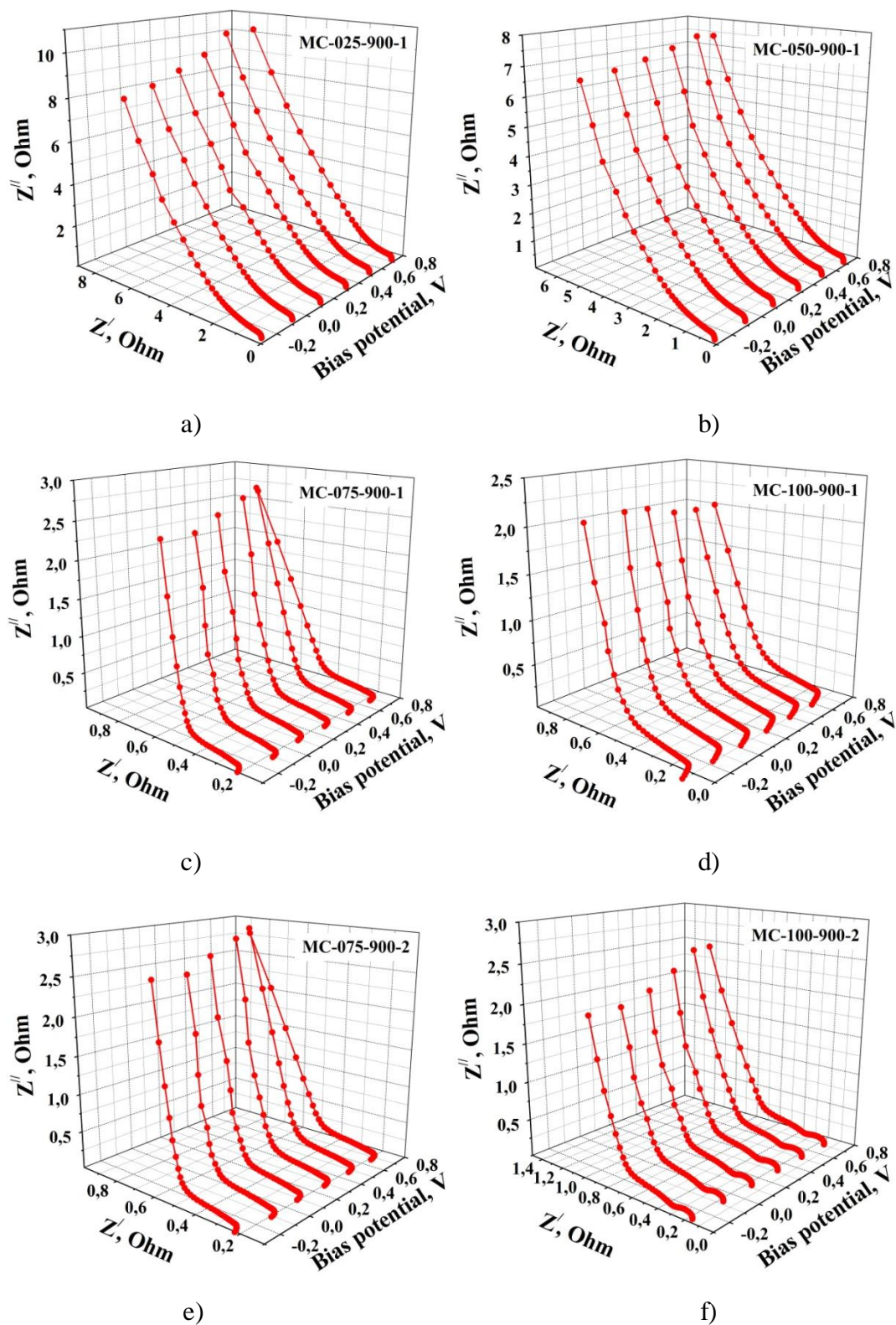


Figure 6. Nyquist plots of MC samples carbonized at 900 °C after one (a, b, c, d) and two (e, f) activation procedures.

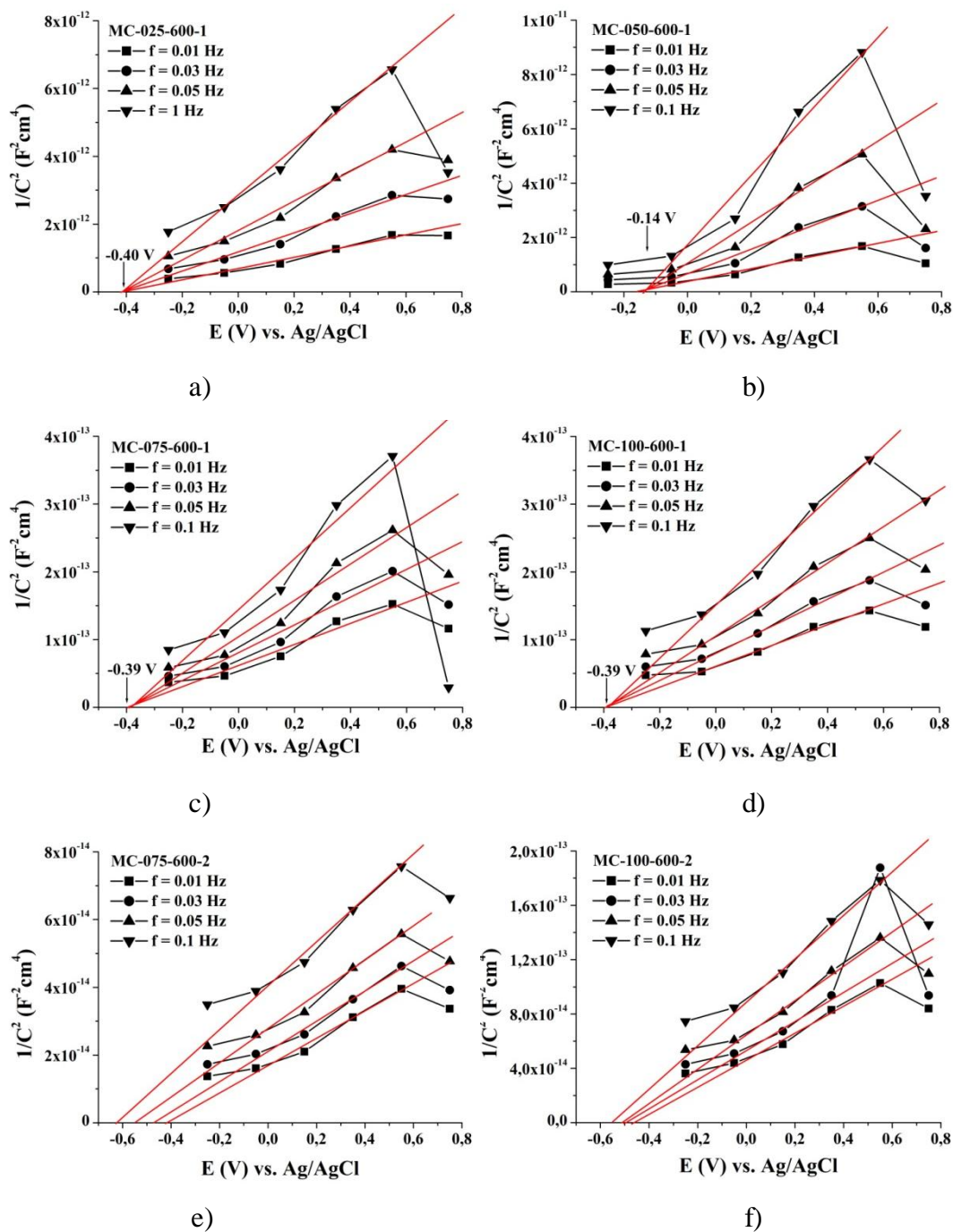


Figure 7. Mott-Schottky plots of MC samples carbonized at 600 °C after one (a, b, c, d) and two (e, f) activation procedures.

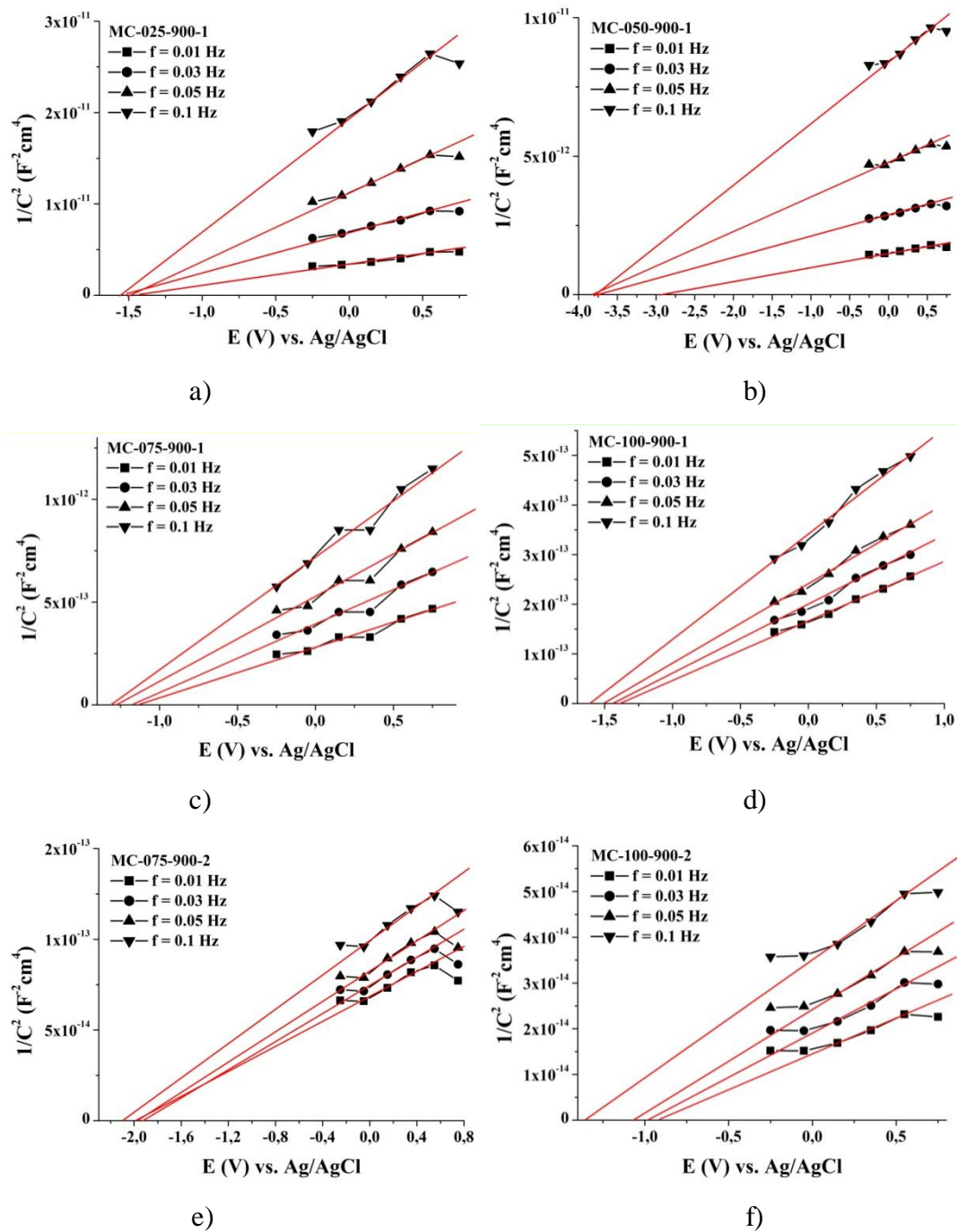


Figure 8. Mott-Schottky plots of MC samples carbonized at 900 °C after one (a, b, c, d) and two (e, f) activation procedures.