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Electrochemical study of novel composite electrodes based on glassy carbon bulk-modified with Pt and MoO_2 nanoparticles supported onto multi-walled carbon nanotubes

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Abstract: This paper reports the preparation and electrochemical study of new glassy carbon electrode (GCE) bulk-modified with synthesized hybrid materials: Pt and MoO_2 nanoparticles deposited on the multi-walled carbon nanotubes (MWCNTs). The results of electrochemical study of commercial GCE and electrodes modified with Pt–MWCNT and MoO_2–MWCNT were obtained by cyclic voltammetry in $K_4Fe(CN)_6$ and NaOH solutions. Morphology and structure of the synthesized hybrid materials were analysed using the method of high resolution transmission electron microscopy, indicating the presence of well dispersed nanoparticles of Pt and MoO_2 over MWCNT network. The results of the electrochemical study show that the capacitance of electrode modified with MoO_2–MWCNT and Pt–MWCNT is 62–65 times higher than the capacitance of the commercial GCE.

Keywords: multi-walled carbon nanotubes; platinum; molybdenum dioxide; cyclic voltammetry.

INTRODUCTION

Carbon nanotubes (CNTs) have many advantages compared to other materials, such as specific shape, small size, high electrical and thermal conductivity.[1,2] Due to the advantages of CNTs, they can be used for applications in electrochemical analyses,[3] as a support for metal catalyst in fuel cells,[4] for the development of electrochemical sensors to detect dyes, ions, phenols, drugs and pesticides.[5,6] The incorporation of metallic nanoparticles, organic molecules, as well inorganic molecules can increase the possibility of use of electrochemical analysis.[7–9]

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The carbon materials, metal oxides and conductive polymers are commonly used as supercapacitor electrode materials.[10] Metal oxides are the most used among all mentioned materials. However, some properties of metal oxides, such as their low stability and low conductivity decrease the capacitive performance of the oxide based electrodes. The certain modifications of morphology and formation of composite electrodes can enhance the capacitive performance of the oxide electrodes.[10] For example, the reduced graphite oxide–MoO_2 composite was used as electrode for lithium-ion batteries.[11] Bhaskar *et al.*[12] synthesized a hybrid composed of spherical flowerlike nanostructures of MoO_2, interconnected by multi-walled carbon nanotubes, for use as a lithium-ion battery anode.

Multi-walled carbon nanotubes (MWCNTs) are well known for their advantages such as good electrical conductivity, high chemical stability, strong adsorptive ability and high thermal capacity.[13,14] Moreover, there are a lot of studies that support the idea that metal nanoparticles are important for the design of the electrochemical sensors platforms.[6,15–18] Therefore, the combinations of metal nanoparticles and materials such as MWCNT are promising solution for obtaining electrodes of superb characteristics. There are few reports about electrochemical behaviour of Pt–MWCNT composite for the determination of pesticide in water sample. Ertan *et al.*[18] developed a voltammetric sensor for simazine determination based on glassy carbon electrode (GCE) modified with platinum nanoparticles involved in a polyoxometalate functionalized multi-walled carbon nanotubes. Ranđelović *et al.*[19] developed an electrochemical sensor based on platinum nanoparticles supported multi-walled carbon nanotubes for clomazone determination. The voltammetric measurements were carried out by differential pulse stripping voltammetry (DPSV).

The most electrochemical sensors based on MWCNT are designed by applying the known mass of dispersed carbon nanotubes to the surface of commercial GCE. Immobilization of MWCNT on the GCE surface are usually accomplished by using an inert organic polymer binder. However, the electrode obtained in this way has a limiting application.

The aim of this paper is to synthesize new composite materials in which modified carbon nanotubes are dispersed within conductive carbon matrix. As such, MWCNTs modified with MoO_2 and Pt nanoparticles are distributed through the volume of GCE in contrast to well-known surface modifications encountered in recent literature. The obtained composite materials have significantly higher mechanical stability and electrical conductivity compared to conventional electrode.

EXPERIMENTAL

Details about chemicals used are given in Supplementary material to this paper.

Synthesis of MoO_2–carbon nanotube composites

MWCNT, 50 mg in mass, was dispersed in 20 mL mixture of ethanol/water (50 vol. %) and 0.5 mL of aniline added. After 90 min of sonication 2 mL of solution containing 16.3 mg of sodium molybdate dihydrate ($Na_2MoO_4\cdot 2H_2O$) was added into suspension. The sonication was continued for the next 5 min and then 0.5 mL of 5 M HNO_3 was added. Finally, the reduction of molybdenum ions to MoO_2 was accomplished by addition 2 mL of 10 mg mL^{-1} of sodium borohydride solution. The suspension was stirred for 30 min and left for the next 24 h, then filtered and washed-out with deionized water to neutral pH. The obtained material (MoO_2–MWCNT) was dried at 90 °C for 3 h.

Synthesis of Pt–carbon nanotube composites

The quantity of 50 mg MWCNT was dispersed in 20 mL mixture of ethanol/water (50 vol. %), then 0.5 mL of aniline was added to suspension and sonicated for 90 min. 2 mL of solution containing 26.7 mg of chloroplatinic acid hydrate ($H_2PtCl_6\cdot H_2O$; Pt, 38–40 %) was added to suspension and sonicated for the next 5 min. After that, 0.5 mL of 5 M HNO_3 was added. For the reduction of ions of platinum to elemental state, 2 mL of 20 mg mL^{-1} sodium borohydride solution was used. The suspension was stirred for 30 min and left for the next 24 h, then filtered and washed-out with deionized water to neutral pH. The obtained material (Pt––MWCNT) was dried at 90 °C for 3 h.

Synthesis of resol resin

Firstly, 3.8 g of phenol was dissolved in 4 mL of 0.3 M NaOH solution and then 5 mL of formaldehyde (36.5 %) was added. Subsequently, solution was heated to 80 °C for the next 6 h. After heating, the mixture was cooled to room temperature and neutralized with H_2SO_4 (30 %). The obtained resin was washed-out with deionized water. A 60 % solution of the resin in tetrahydrofuran was prepared and mildly heated to remove excess water.

Composite electrode preparation

Two types of composite electrode were prepared. For a start, 0.012 g of modified MWCNT was added in 2 mL solution of resin and sonicated to obtain the well-dispersed system. One supsension was prepared with Pt–MWCNT and other with MoO_2–MWCNT. Then the suspensions were placed in polyethylene (PE) mould with diameter of 5 mm. Drying was carried out at room temperature for 12 h, then at 40 °C for 12 h. The temperature was gradually increased to 80 °C for the next 40 h and then increased to 100 °C for 12 h.

The thermal treatment of resol resins, in which MoO_2–MWCNT and Pt–MWCNT were dispersed, was carried out in hermetically sealed reactor under atmosphere which contains a small amount of oxygen (up to 0.03 mL of air was retained within the sealed reactor which total working volume is 1 mL) at temperatures of 1100 °C for 2 h, with a heating rate of 1.25 °C min^{-1}. The reactor is fabricated by DIN 17440 heat-resistant steel. After loading resin (in form of rode) which contains dispersed MoO_2- or Pt-modified MWCNT in reactor, its free volume did not exceed 3 %.

Two materials were obtained, one containing MoO_2–MWCNT and the other containing Pt–MWCNT. The obtained materials were in the form of cylinder with diameter of 3 mm. The first one was designated as MoO_2–MWCNT–GC and the second material as Pt–MWCNT–GC (Fig. S-1 of the Supplementary material).

Electrochemical analysis

The electrochemical analysis was performed using a three-electrode system. The applied electrochemical system consisted of saturated calomel electrode (SCE) as a reference, platinum wire as auxiliary and synthesized materials as a working electrode. Commercial glassy carbon electrode, as well as MoO_2–MWCNT and Pt-–MWCNT modified electrodes, were used as working electrodes.

The solution of $K_4[Fe(CN)_6]$ (0.015 M) in 0.1 M KCl was used to test electrochemical characteristics of the obtained materials. The capacitance of the electrodes was tested in 6 M solution of NaOH. Electrochemical analysis was performed by the cyclic voltammetry for different scan rates: 0.01, 0.025, 0.05, 0.1, 0.15, 0.2 and 0.25 V s^{-1}.

RESULTS AND DISCUSSION

Characterization of composite materials

The morphology and structure of modified carbon nanotubes (CNTs) were analyzed using the method of high resolution transmission electron microscopy (HRTEM). Fig. 1a shows the HRTEM micrograph of Pt-–MWCNT. It can be clearly seen that Pt nanoparticles are well dispersed and successfully deposited on MWCNT. As a result of observing a large number of samples, it was concluded that Pt nanoparticles form aggregates of about 10 nm in size that adhere to the CNT surface. The measurements of the electron diffraction shown in Fig. 1b, revealed that it is a centred cubic lattice of Pt nanoparticles, with a distance between crystallographic planes (111) of 0.225 nm. Further structural analysis showed that Pt nanoparticles are polycrystalline, with crystallographic planes described by indices (111), (220) and (222).

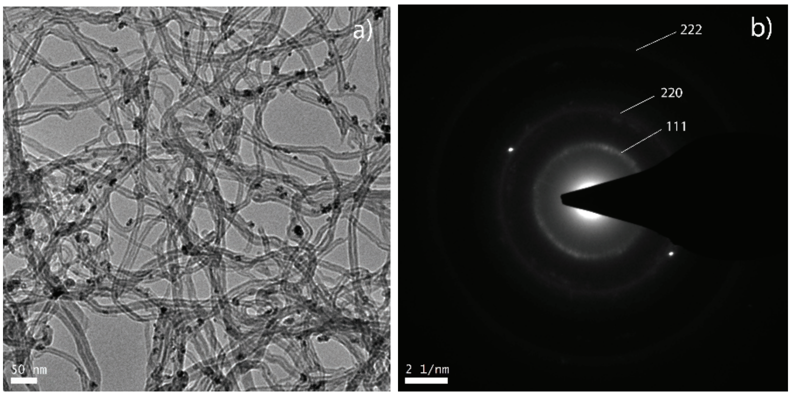

Fig. 1. a) HRTEM micrograph of Pt-MWCNT; b) the electron diffraction of Pt nanoparticles.

Fig. 2a shows the HRTEM micrograph of MoO_2 nanoparticles deposited on the MWCNT surface. The fibrous morphology of MWCNTs with discrete dark spots attributed to MoO_2 nanoparticles can be clearly observed. This arrangement of nanoparticles was achieved by *in situ* reduction of dissolved Na_2MoO_4 in suspension containing dispersed MWCNT:

$$Na_2MoO_4 + NaBH_4 + 2HCl \rightarrow NaBO_2 + MoO_2 + 2NaCl + 3H_2$$

The dimensions of MoO_2 nanoparticles are from 7 to 50 nm with *d*-spacing between crystallographic planes of 0.35 nm, measured by the HRTEM method. Fig. 2b shows the results of electron diffraction (SAED) of MoO_2–MWCNT sample. The appearance of several concentric circles confirmed the crystalline nature of the deposited MoO_2. The diffraction rings, viewed from the inside to out, corresponded to the (–111), (–211) and (–212) planes of monoclinic MoO_2 phase.

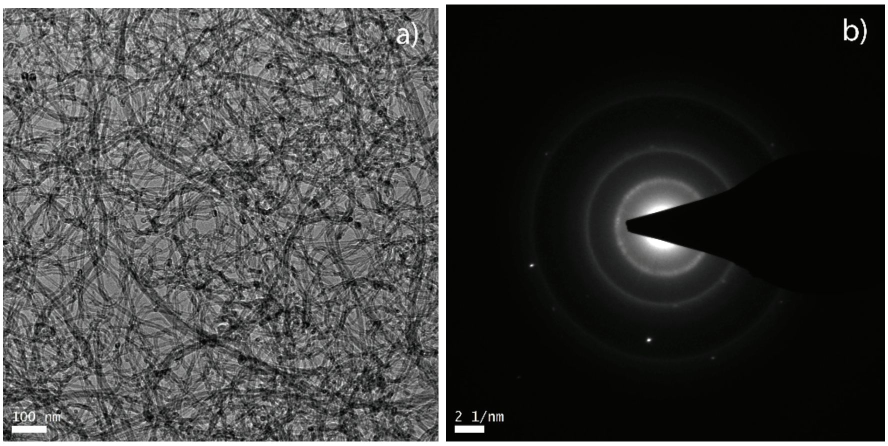

Fig. 2. a) HRTEM micrograph of MoO_2–MWCNT; b) the electron diffraction of MoO_2 nanoparticles.

This morphology is crucial for the electrocatalytic properties of MoO_2–MWCNT based materials. The combination of MoO_2 nanoparticles, which provide electrocatalytic and adsorption activity due to their large surface area and MWCNT, whose application as a carrier is a reliable way to improve the electrical conductivity, allows efficient electron transfer and good electrochemical performance.

Electrochemical study

In order to examine the electrochemical properties of commercial glassy carbon and composite electrodes with Pt and MoO_2 active nanoparticles deposited on MWCNT and dispersed in glassy carbon based matrix were characterized by the cyclic voltammetry in $K_4Fe(CN)_6$ and NaOH solutions.

Potassium ferrocyanide was chosen as benchmark redox system due to its well-known „surface sensitive" electrochemical response for carbon material. Electrochemical responses of 15 mM $K_4Fe(CN)_6$ at commercial and composite electrodes were obtained for different scan rates: 0.01, 0.025, 0.05, 0.1, 0.15, 0.2 and 0.25 V s^{-1}. Fig. 3 shows the obtained cyclic voltammograms.

As can be seen from Fig. 3, the commercial GCE shows well defined anodic and cathodic peaks of the $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ redox pair. On the other hand, Pt–MWCNT–GC and MoO_2–MWCNT–GC electrodes give much higher current intensities, but peaks are less pronounced, which indicates higher value of capacitive current and unfavourable kinetics of electrode process on modified electrodes.

The important parameter values used to characterize electrochemical reversible processes at GCE were obtained by comparing the cyclic voltammograms at 0.05 V s^{-1} in 15 mM $K_4Fe(CN)_6$. The electrochemical parameters were collected and presented in the Table I.

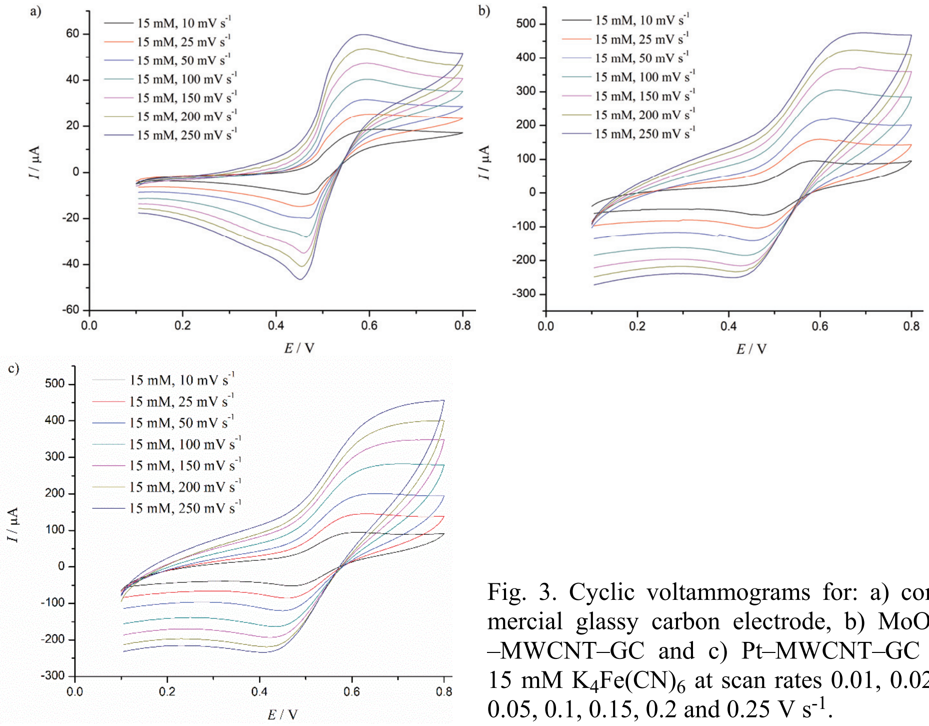

Fig. 3. Cyclic voltammograms for: a) commercial glassy carbon electrode, b) MoO_2–MWCNT–GC and c) Pt–MWCNT–GC in 15 mM $K_4Fe(CN)_6$ at scan rates 0.01, 0.025, 0.05, 0.1, 0.15, 0.2 and 0.25 V s^{-1}.

TABLE I. Electrochemical parameters obtained from cyclic voltammogrames for: commercial glassy carbon electrode (GCE), MoO_2-MWCNT GC and Pt-MWCNT GC

Electrode	E_{pa} / V	E_{pc} / V	ΔE_p / V	$E_{1/2}$ / V	I_{pc} / μA
Commercial GC	0.585	0.470	0.115	0.527	–29.47
MoO_2–MWCNT–GC	0.6	0.475	0.125	0.537	–123.8
Pt–MWCNT–GC	0.620	0.475	0.145	0.547	–115

The electrochemical behaviour in the potassium ferrocyanide solution shows that the oxidation peak has changed from 0.585 V for GCE, to 0.6 V for the MoO_2–MWCNT modified electrode and to 0.620 V for the Pt–MWCNT modified electrode. The reduction peak position has also shifted from 0.470 V for the commercial glassy carbon electrode to 0.475 V for both modified electrodes. The value of the cathode current peak has varied from –29.47 μA for the commercial glassy carbon electrode, to –123.8 μA for the MoO_2-modified electrode and to –115 μA for the Pt modified electrode. The half-wave potential $E_{1/2}$ was determined from the anodic (E_{pa}) and the cathodic (E_{pc}) potentials of the peaks, using the expression:

$$E_{1/2} = (E_{pa} + E_{pc})/2 \tag{1}$$

The parameter, ΔE_p, is also related to the kinetics of electrode process and its theoretical value for a given system should be 57 mV. Any deviation from this value represents a measure of system deviation from ideal reversibility. This indicates that the most favourable kinetics has the commercial GCE, for which ΔE_p is 0.115 V. The value of ΔE_p for the MoO_2-modified electrode is 0.125 V and for the Pt modified electrode is 0.145 V.

The electroactive surfaces of electrodes were calculated using the Randles–Sevcik equation:

$$I_p = 2.69\times10^5 AD^{1/2}n^{3/2}v^{1/2}C \tag{2}$$

where I_p is the peak current (μA), A is the surface area of the working electrode (cm^2), D is the diffusion coefficient of the electroactive species (cm^2 s^{-1}) n is the number of exchanged electrons, v is the scan rate (V s^{-1}) and C is the bulk concentration of the electroactive species (mol dm^{-3}).[20] The value of the diffusion coefficient of ferrocyanide ions at 295 K is 6.5×10^{-6} cm^2 s^{-1}.

The values for the electroactive and the geometric surface of commercial GCE, MoO_2–MWCNT–GC and Pt–MWCNT–GC were calculated and presented in Table II. As can be seen, the Pt-modified electrode possesses the largest electroactive surface area compared to the commercial glassy carbon electrode and the MoO_2 modified electrode.

TABLE II. The values for the electroactive surface area of electrodes for the geometric surface area of 0.071 cm^2

Electrode	Electroactive surface area, cm^2
Commercial GC	0.0130
MoO_2–MWCNT–GC	0.0345
Pt–MWCNT–GC	0.0447

Fig. 4 shows the dependences of the cathodic current peak (I_{pc}) *versus* the square root of scan rate ($v^{1/2}$).

The commercial glassy carbon electrode shows a linear dependence of the cathodic current peak as a function of the square root of scan rate for the system $[Fe(CN)_6]^{3-/4-}$, which indicates the reversibility of the electrode process.

The tested MoO_2 and Pt composite electrodes have lower values of correlation coefficients than the commercial glassy carbon electrode, indicating a deviation from linear dependence. The processes on these two electrodes are quasi-reversible, which implies a lower value of the constant of the electrode reaction rate. Moreover, the possibility of adsorption of electrochemically active species on the surface of the electrode cannot be excluded. This is due to the formation of surface functional groups onto the composite electrodes during the synthesis and thermal treatment. Namely, small amount of the residual oxygen, as well as the oxygen from functional groups in resin during carbonization step could produce specific structure, texture and chemical composition of final material. MWCNTs provide mechanical stability of electrode and contribute to electric conductivity, while Mo species and Pt enhances electrochemical characteristics of materials.

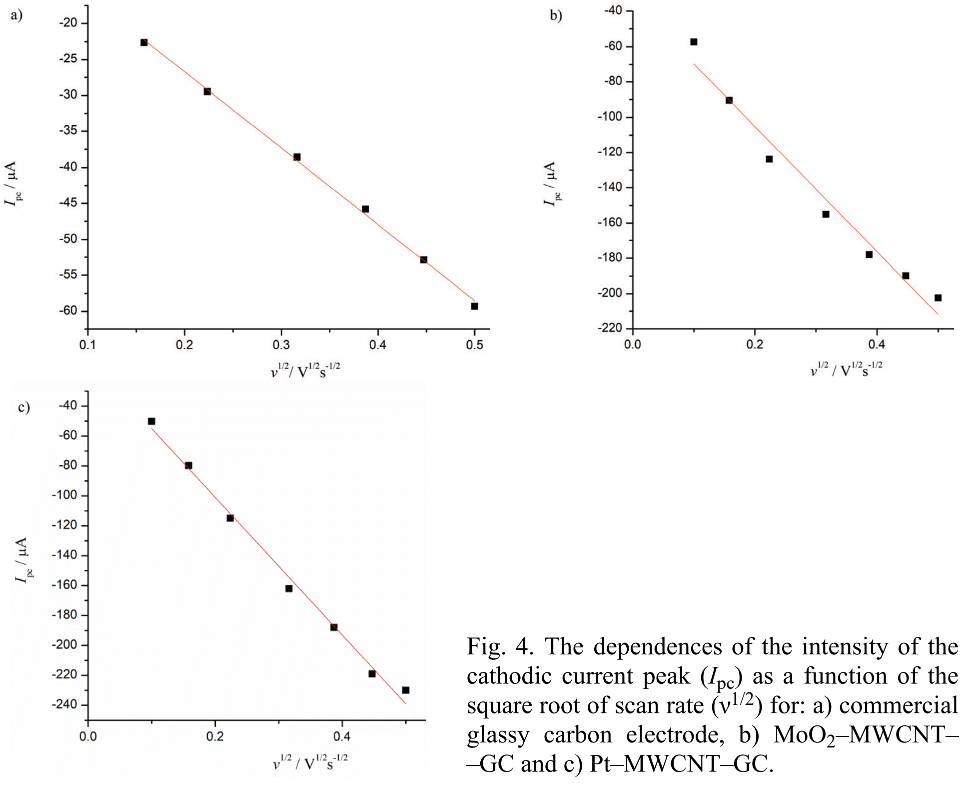

Fig. 4. The dependences of the intensity of the cathodic current peak (I_{pc}) as a function of the square root of scan rate ($\nu^{1/2}$) for: a) commercial glassy carbon electrode, b) MoO_2–MWCNT–GC and c) Pt–MWCNT–GC.

Nanoparticles/carbon matrix/electrolyte solution form three phases contacts which are responsible for specific electrochemical behaviour of electrodes. On the one side, there are kinetics limitations related to electron transfer hindrances during redox process at electrodes. On the other side, accumulation of charge and electrosorption is responsible for high capacitance as described further below.

The cyclic voltammetry method in electrochemically inert electrolyte solutions is suitable for measuring the capacitance of a material. For this reason, a series of experiments in 6 M NaOH electrolyte were performed (Fig. S-2 of the Supplementary material).

The capacitance of electrode, C (F cm^{-2}), was calculated using following formula:

$$C = \frac{\int_{E_1}^{E_2} I \mathrm{d}E}{2\Delta E v S} \quad (3)$$

where

$$\int_{E_1}^{E_2} I \mathrm{d}E$$

is the total area enclosed by the voltammogram, which is obtained by integration of the anodic and cathodic branch, I is the measured current, ΔE is the potential divergence (E_2–E_1), v is scan rate, S is the geometric surface.[21]

The calculated values of capacitance for scan rate of 0.02 V s^{-1} for all three electrodes, are summarized in Table III.

TABLE III. Values of capacitance for scan rate of 0.02 V s^{-1}

Electrode	Capacitance, F cm^{-2}
Commercial GC	0.0095
MoO_2–MWCNT–GC	0.619
Pt–MWCNT–GC	0.591

The MoO_2 modified electrode shows a higher value of capacitance than the Pt modified electrode and the commercial glassy carbon electrode. As can be seen in Table III, the value of capacitance of commercial glassy carbon electrode is very low.

Fig. 5 shows the graphical dependence of capacitances as a function of the values of scan rate for all three electrodes, with values of scan rate of 0.005, 0.01, 0.02, 0.05 and 0.1 V s^{-1}.

As can be seen from Fig. 5, the MoO_2 modified electrode shows the highest capacitance at all values of scan rates. The maximum value of capacitance of this electrode is 1.179 F cm^{-2} at value of scan rate of 0.005 V s^{-1}.

If the capacitances of commercial GC, MoO_2–MWCNT–GC and Pt–MWCNT–GC at scan rate of 0.005 mV s^{-1} (0.0143, 1.179, 1.069, respectively) are compared with their capacitances at scan rate of 0.1 V s^{-1} (0.0045, 0.277, 0.278, respectively), it can be concluded that the capacitances at scan rate of 0.1 V s^{-1} are lower than the capacitances at initial scan rate of 0.005 V s^{-1}. The percentages of previously mentioned capacitance values of commercial GC, MoO_2–MWCNT–GC and Pt–MWCNT–GC of scan rate of 0.005 and 0.1 V s^{-1} are 31.5, 23.5 and 26 %, respectively.

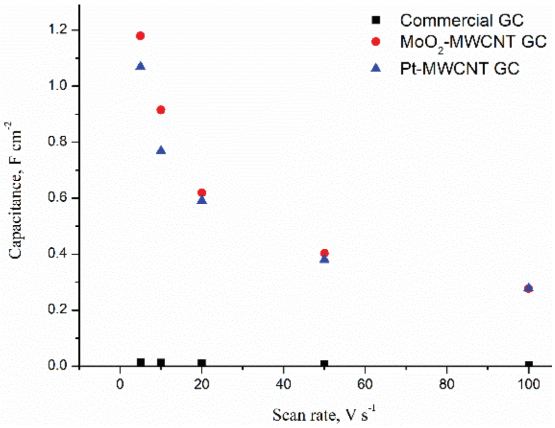

Fig. 5. The dependence of the capacitances as a function of the values of scan rate for: commercial glassy carbon electrode, MoO_2–MWCNT–GC and Pt–MWCNT–GC.

According to the results obtained, it seems that oxygen groups were not involved in additional pseudocapacitive processes with NaOH, and the charge storage can be contributed to ion electrosorption and specific textural characteristics of materials. As can be seen from provided cyclic voltammograms (Fig. S-2) none of the materials exhibit distinguishable redox peaks at any sweep rates (cathodic and anodic humps were not observed on CVs).

Porosity and textural characteristics of materials can also relate to observed high capacitance. The respective sizes of ions and pores may also strongly influence the values of capacitance, especially under high operating current densities. The certain ions (depending on their radii) could penetrate in the pores. The open mesoporosity of nanotubes and their good electrical conductivity permit a good charge propagation in the carbon framework. For all these reasons, composites where nanotubes are homogeneously dispersed in a carbon matrix of certain textural characteristics could represent an interesting breakthrough for developing a new generation of (super)capacitors. It is also known that higher electrical charge is built up at graphitic edge surfaces (originating from MWCNT) under an electrochemical polarization.

The reversible chemisorption of hydrogen by water electrodecomposition on a negatively polarized carbon electrode is also an interesting way of providing a pseudofaradic contribution. Pt and chemical species of generated during carbonization of resin containing MoO_2 (maybe carbides, non-stoichiometric oxides of Mo, or even elemental Mo) can be efficient electrocatalysts for water decomposition according to equation:

$$H_2O + e^- \leftrightarrows OH^- + H$$

The adjustable surface functionality and nanotexture of presented composites offers wide opportunities for developing supercapacitors able to fulfill high performance requirements.[22]

CONCLUSION

Using a simple process of the suitable precursors reduction in the suspension of carbon nanotubes, the nanoparticles of Pt and MoO_2 can be deposited onto their surface to obtain electrocatalytically active hybrid materials which can be easily dispersed in the resol resin. After the carbonation of these materials composites with good electrical conductivity and interesting electrochemical characteristics can be obtained. The results of cyclic voltammetry in the potassium ferrocyanide solution indicate that the Pt and MoO_2 modified electrodes have higher values of the cathodic (E_{pc}) and the anodic (E_{pa}) peaks compared to the commercial glassy carbon electrode. Additionally, the capacitance of the composite electrodes is higher than that of commercial GC and this suggests that they can be used for energy storage, production of batteries or supercapacitors. From the obtained results it can be seen that the highest capacitance has MoO_2–MWCNT glassy carbon electrode (0.619 F cm^{-2}), which is about 65 times higher than the capacitance of the commercial glassy carbon electrode. The capacitance of Pt–MWCNT glassy carbon electrode is about 62 times higher than the capacitance of the commercial glassy carbon electrode.

SUPPLEMENTARY MATERIAL

The additional data are available electronically at the pages of journal website: http://www.shd.org.rs/JSCS/, or from the corresponding author on request.

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ИЗВОД

ЕЛЕКТРОХЕМИЈСКО ИСПИТИВАЊЕ НОВИХ КОМПОЗИТНИХ ЕЛЕКТРОДА БАЗИРАНИХ НА СТАКЛАСТОМ УГЉЕНИКУ ЗАПРЕМИНСКИ МОДИФИКОВАНОМ Pt И MoO_2 НАНОЧЕСТИЦАМА ИМОБИЛИСАНИМ НА ВИШЕСЛОЈНИМ УГЉЕНИЧНИМ НАНОЦЕВИМА

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У овом раду су описане припрема и електрохемијско испитивање нове електроде од стакластог угљеника која је модификована синтетизованим хибридним материјалима: наночестицама платине и молибден-диоксида исталоженим на вишеслојним угљеничним наноцевима. Комерцијална електрода од стакластог угљеника и електроде модификоване наночестицама платине и молибден-диоксида исталоженим на вишеслојним угљеничним наноцевима испитиване су цикличном волтаметријом у растворима $K_4Fe(CN)_6$ и NaOH. Морфологија и структура синтетизованих хибридних материјала анализирани су методом трансмисионе електронске микроскопије високе резолуције, чији резултати указују на присуство добро диспергованих наночестица платине и молибден-диоксида преко мреже вишеслојних угљеничних наноцеви. Резултати електрохемијске анализе показују да је капацитивност електрода модификованих MoO_2–MWCNT и Pt–MWCNT око 62–65 пута већа од капацитивности комерцијалне стаклене угљеничне електроде.

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