COVER LETTER

To: Dr Snežana Gojković

Editor,

Journal of the Serbian Chemical Society

Dear Editor,

I am sending revised manuscript, which title is **“Electrochemical study of novel composite electrodes based on glassy carbon bulk-modified with Pt and MoO2 nanoparticles supported onto multi-walled carbon nanotubes“**.

The cover letter contains comments of authors on the questions of reviewer.

**MAJOR REMARKS:**

**1) Table I:**

**The observed increase of the separation between the anodic and cathodic peak (ΔEp) for MoO2-MWCNT-GC (0.125 V) and Pt-MWCNT-GC (0.145 V) compared to that of commercial GC (0.115 V) points out to the conclusion that the MoO2-MWCNT and Pt-MWCNT modified electrodes possessed somewhat lower electrical conductivity than commercial GC. Please comment in the text.**

The Authors would explain increased peak to peak separation (ΔEp) for MoO2-MWCNT-GC and Pt-MWCNT-GC compared to that of commercial GC as a result of kinetics constraints (related to electron transfer) at mentioned electrodes. Namely, kinetics of electrode process of Fe(CN)63-/4- reduction/oxidation is slightly more favourable at comercial GC electrode. However, peak current intensity (Ip) is significantly higher in the case of fabricated electrodes MoO2-MWCNT-GC and Pt-MWCNT-GC which could be conected with their higher electrical conductivity. In support of this claim is the fact that measured ohmic resistance of comercial GC is higher compared to that of the electrodes fabricated in our lab.

**2) Electroactive surface area, Table II, Fig. 5:**

**Table II shows that the electroactive surface areas of Pt-MWCNT-GC and MoO2-MWCNT-GC were 26 and 2 times larger than that of commercial GC, respectively. However, it can be calculated from Fig. 5 that the slopes of the Ipc vs. v1/2 dependencies of Pt-MWCNT-GC, MoO2-MWCNT-GC and commercial GC, from which their electroactive surface areas in Table II were supposedly determined, stand in the proportion 4.4 : 3.3 : 1. How is this possible?**

**Please double-check the analysis and provide correct electroactive surface area values in Table II.**

Thank you for this comment. Unfortunately, an error within Table II was occured during the manuscript preparation (decimal notation of concentration value). This has been corrected now.

**3) Please show the CV’s of Pt-MWCNT-GC, MoO2-MWCNT-GC and commercial GC recorded in 6 M NaOH at scan rates 5-100 mV s–1, based on which their C vs. v dependencies in Fig. 6 were plotted.**

The CV’s of commercial GC, MoO2-MWCNT-GC and Pt-MWCNT-GC recorded in 6 M NaOH are presented in Supplementary material to this paper.

**4) Capacitance performance of composite electrodes:**

**a) Please discuss or at least speculate the origins of the significantly improved areal capacitance of MoO2-MWCNT-GC (619 mF cm–2) and Pt-MWCNT-GC (591 mF cm–2) with respect to that of commercial GC (9.5 mF cm–2).**

Thank you very much for raising this interesting topic. In accordance with your request the Authors could give the following opinion, having in mind that we avoided speculation in the manuscript due to further research that should reveal some crucial points in this complex investigation.

It seems that oxygen groups were not involved in additional pseudocapacitive processes with NaOH, and the charge storage that we measured can be contributed to ion electrosorption and specific textural characteristics of materials. As can be seen from provided cyclic voltammograms none of the materials exhibit distinguishable redox peaks at any sweep rates (cathodic and anodic humps were not observed on CVs). It is often observed for the CV recorded in acid.

Porosity and textural characteristics of materials can also be connected with 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 desolvated 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 for providing a pseudofaradic contribution. Pt and chemical species of generated during carbonization of resin containing MoO2 (maybe carbides, non-stoichiometric oxides of Mo, or even elemental Mo) can be efficient electrocatalysts for water decomposition according to equation:

H2O + e ⮀ OH- + H

The adaptable surface functionality and nanotexture of carbons offers wide opportunities for developing supercapacitors able to fulfill the industry requirements.

**b) It seems reasonable to assume that MWCNTs contribute to the total capacitance of the prepared composite electrodes with a pseudocapacitance component arising from their surface functional groups. Please comment.**

MWCNTs were dispersed in the resin which was subsequently cured and carbonized at 1100 ˚C under atmosphere which contain small amount of oxygen (up to 0.03 mL of air was retained within the sealed reactor which total working volume is 1 mL). MWCNTs should ensure acceptible mechanic stablity of final product and contribute to its electric conductivity as well. Mentioned contribution of MWCNT to the total capacitance is very likely to occur.

The texture as well as the porosity of the materials can affect the values of capacitance. The radii of the certain ions can also influence the values of capacitance. Therefore, the composites containing carbon nanotubes dispersed in a carbon matrix can be important for the development of new capacitors. It should be mentioned that higher electrical charge is built up at graphitic edge surfaces that orirginate of MWCNT.

**c) The roles of MoO2 and Pt nanoparticles in the charge transfer mechanism at the surface of corresponding composite electrodes must be addressed in the text.**

The Authors previous studies revealed good electrocatalytic performances of MoO2 and Pt nanoparticles-MWCNs hybrid materials. Hence, main idea here was to examine electrocatalytic effect of imobilized nanoparticles onto electrochemical characteristics of final composite electrodes. It should be noted also that MoO2 attached to MWCNT after carbonization step at 1100˚C is probably reduced to elemental form or generates non-stoichiometric oxides and carbides. All these species are known for their good electrocatalytic performances.

Moreover, 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 proces at electrodes. On the other side, accumulation of charge and electrosorption is responsible for high capacitance.

In accordance with this explanation, the changes have been made in the text.

**5) Please specify, compare and comment the capacitance retentions of MoO2-MWCNT-GC, Pt-MWCNT-GC and commercial GC at a scan rate of 100 mV s–1 with respect to their initial capacitances obtained at 5 mV s–1. The required results should be presented in percentages.**

As can be seen from Fig. 5 the MoO2 modified electrodeshows the highest capacitance at all values of scan rates. The maxium value of capacitance of this electrode is 1.179 F cm-2 at value of scan rate of 0.005 V s-1.

If compare the capacitances of commercial GC, MoO2-MWCNT-GC and Pt-MWCNT-GC at scan rate of 0.005 V s-1 (0.0143, 1.179, 1.069, respectively) with thier 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, MoO2-MWCNT-GC and Pt-MWCNT-GC of scan rate of 0.005 V s-1 and 0.1 V s-1 are 31.5 %, 23.5 %, 26 %, respectively.

In accordance with this explanation, the changes have been made in the text.

**6) Lines 268-271: “The resluts of cyclic voltammetry in the potassium ferrocyanide solution indicate that the Pt and MoO2 modified electrodes have higher values of the cathode and the anode current peaks compared to the commerical glassy carbon electrode. Therefore, the electrodes exerts high electrical conductivity.” This conclusion is not supported by experimental evidence. Please revise the statements.**

The statements have been revised.

**7) Figs. 4-6: Axis titles, tick labels and legend text in Figs. 4-6 must be increased to make graphs more readable. Thicker solid lines and larger symbols would also be required in order to improve the quality of the figures.**

The Figures are made in accordance with the requirements of Journal, but their sizes in the paper were visually reduced. This has been improved now.

**MINOR REMARKS:**

**8) Please use consistently either “cm3” or “ml” as volume units throughout the paper.**

The units of volume throughout the paper are uniform now (mL is used).

**9) Please specify the manufacturers of all chemicals and materials used in this study in a separate subsection in the Experimental.**

Chemicals which were applied are presented in Supplementary material to this paper.

**10) Line 99: Please define the abbreviation “PE”.**

It has been corrected.

**11) Please describe processes that occurred during the thermal treatment of MoO2-MWCNT and Pt-MWCNT modified resol resin at 1100 °C in a hermetically sealed reactor.**

The electrode materials were carbonized in a custom made hermetically sealed reactor fabricated by DIN 17440 heat-resistant steel under atmosphere which contain small amount of oxygen (up to 0.03 ml of air was retained within the sealed reactor which total working volume is 1 ml). After loading resin (in form of rode) which contains dispersed MWCNT and MoO2 or Pt nanoparticles in reactor, free volume did not exceed 3%. Small amount of residual oxygen, as well as oxygen from functional groups in resin during carbonization step could produce specific structure 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.

Pt and chemical species of Mo generated during carbonization of resin containing MoO2 can be efficient electrocatalysts for water decomposition.

The chemical species formed during carbonization of resin containing MoO2 are carbides or non-stoichiometric oxides of Mo or even elemental Mo. All these species are known for their good electrocatalytic performances.

In accordance with this explanation, the changes have been made in the text.

**12) Fig. 1 must be cited in the text.**

Fig. 1 is the original scheme drawn by Authors. In the new version of the paper, Fig. 1 is presented in Supplementary material to this paper (Fig. S-1).

**13) Capacitance calculation, Table III:**

**The presented equation (Eq. 3) for calculation of the areal capacitance from cyclic voltammograms is incorrect. Instead, it should be:**

**C = (∫IdE)/(2·ΔE·v·S)**

**where ∫IdE is** **the total area enclosed by the voltammogram, which is obtained by integration of the anodic and cathodic branch, I is the current, E is the potential and ΔE = E2 – E1 is the applied potential window.**

**Please provide the correct equation and double-check the capacitance values**

**presented in Table III.**

The equation 3 has been corrected. The values of capacitance in Table III were already accurate.

**14) Line 11: Instead of “papir” should be “paper”.**

It has been corrected.

**15) Line 35: Instead of “can increases” should be “can increase”.**

It has been corrected.

**16) Line 38: Instead of “such as low stability, low conductivity” consider “such as their low stability and conductivity,”.**

It has been corrected.

**17) Line 41: Instead of “grapihte” should be “graphite”.**

It has been corrected.

**18) Line 47: Instead of “studdies” should be “studies”.**

It has been corrected.

**19) Line 56: Instead of “carried out” should be “were carried out”.**

It has been corrected.

**20) Line 62: Instead of “a new composite materials” should be “new composite materials”.**

It has been corrected.

**21) Line 63: Instead of “distribudted” should be “distributed”.**

It has been corrected.

**22) Line 65: Instead of “litterature” should be “literature”.**

It has been corrected.

**23) Line 68: Instead of “Synthesis of MoO2 carbon nanotube” consider “Synthesis of MoO2-carbon nanotube composites”.**

It has been corrected.

**24) Line 70: Instead of “solution contained” should be “solution containing”.**

It has been corrected.

**25) Line 78: Instead of “Synthesis of Pt carbon nanotube” consider “Synthesis of Pt-carbon nanotube composites”.**

It has been corrected.

**26) Line 80: Instead of “aniline added” should be “aniline was added”.**

It has been corrected.

**27) Lines 80-81: Instead of “solution contained” should be “solution containing”.**

It has been corrected.

**28) Lines 83-84: Instead of “2 ml of solution 20 mg ml-1 of sodium borohydride was used”**

**consider “2 ml of 20 mg ml-1 sodium borohydride solution was used”.**

It has been corrected.

**29) Line 89: Instead of “solution 0.3 M NaOH” should be “0.3 M NaOH solution”.**

It has been corrected.

**30) Lines 96-97: Instead of “0.012 g modified MWCNT modified” should be “0.012 g of modified MWCNT”.**

It has been corrected.

**31) Line 101: Instead of “Termical” should be “Thermal”.**

It has been corrected.

**32) Line 102: Instead of “dispresed” should be “dispersed”.**

It has been corrected.

**33) Line 105: Instead of “containig” should be “containing”.**

It has been corrected.

**34) Line 145: Instead of “dimension” should be “dimensions”.**

It has been corrected.

**35) Line 147: Instead of “MoO2MWCNT” should be “MoO2-MWCNT”.**

It has been corrected.

**36) Line 210: Instead of “concentracion” should be “concentration”.**

It has been corrected.

**37) Line 212: Instead of “potassium ferocyanide” consider “ferrocyanide ions”.**

It has been corrected.

**38) Line 214: Instead of “geometirc” should be “geometric”.**

It has been corrected.

**39) Line 233: Instead of “The processes on this two electrodes are qausi-reversibile” should be “The processes on these two electrodes are quasi-reversible”.**

It has been corrected.

**40) Line 236: Instead of “composte” should be “composite”.**

It has been corrected.

**41) Line 238: Instead of “electrochemicaly” should be “electrochemically”.**

It has been corrected.

**42) Line 266: Instead of “easliy dispresed” should be “easily dispersed”.**

It has been corrected.

**43) Line 268: Instead of “resluts” should be “results”.**

It has been corrected.

**44) Line 270: Instead of “commerical” should be “commercial”.**

It has been corrected.

**45) Lines 271-272: Instead of “the capacitance of the composite electrodes is very high” consider “the capacitance of the composite electrodes** **is higher than that of commercial GC”.**

It has been corrected.

**46) Line 285: Instead of “Mo2” should be “MoO2”.**

It has been corrected.

**47) Lines 295 and 297: Instead of “молибден диоксида депонованим” should be “молибден-диоксида исталоженим”.**

It has been corrected.

Sincerely,

Jelena Čović,

Ph. D. Student

Department of Chemistry, Faculty of Science and Mathematics, University of Niš, 18000 Niš, Višegradska 33, Serbia

e-mail: covic.jelena91@gmail.com