

Cite this: *Energy Adv.*, 2022,  
1, 45

# Electrochemical and quantum chemical studies of peculiarities of 2,5-di-Me-pyrazine-di-*N*-oxide oxidation in the presence of methanol at single-walled and multi-walled carbon nanotube paper electrodes

S. I. Kulakovskaya,<sup>\*a</sup> A. V. Kulikov,<sup>ab</sup> T. S. Zyubina,<sup>a</sup> A. S. Zyubin,<sup>a</sup> L. N. Sviridova,<sup>b</sup> E. V. Stenina,<sup>b</sup> A. G. Ryabenko,<sup>a</sup> E. V. Zolotukhina<sup>a</sup> and Yu. A. Dobrovolskiy<sup>a</sup>

The use of methanol (MeOH) in direct methanol fuel cells has increased the interest in the search for new electrode materials and catalysts that allow the oxidation of MeOH to be carried out under conditions that satisfy their practical applications: low cost, stability, and high catalytic activity. In this work, electrochemical and quantum chemical methods were used to study peculiarities of the electrocatalytic system 2,5-di-Me-pyrazine-di-*N*-oxide–methanol at single-walled and multi-walled carbon nanotube (CNT) paper electrodes in comparison with a glassy carbon (GC) electrode in 0.1 M Bu<sub>4</sub>NClO<sub>4</sub> solution in acetonitrile (MeCN). The adsorption energies of MeOH, CH<sub>3</sub>COOH and H<sub>2</sub>O on the CNT surface were determined by quantum chemical modeling; this opened the door for the explanation of effects found in the Pyr<sub>1</sub>–MeOH catalytic system and for the ascertainment of factors affecting the catalytic efficiency of the process at CNT electrodes. We believe that this research will be helpful in using this process in electrocatalysis, sensors and direct methanol fuel cells, since the deactivation of aromatic di-*N*-oxides (as opposed to processes involving noble metals or noble metal oxides) is insignificant.

Received 22nd September 2021,  
Accepted 21st November 2021

DOI: 10.1039/d1ya00005e

rsc.li/energy-advances

## 1. Introduction

The study of methanol oxidation is of particular interest in connection with its use in direct methanol fuel cells (DMFCs).<sup>1,2</sup> In DMFCs, the most commonly used catalysts for methanol oxidation are noble metals and noble metal oxides. However, the high cost of noble metals and the poisoning of catalysts by irreversibly adsorbed carbon monoxide (CO) generated during methanol electrooxidation are driving the search for non-noble metals, metal free materials, and catalysts that are inexpensive, stable and active in catalysis.

Carbon nanomaterials made of reduced graphene oxide, single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs), modified with additives of noble metals (Pt, Ir, Ru, and Pd) or their oxides (IrO<sub>2</sub> and RuO<sub>2</sub>), are used in the electrocatalytic processes of methanol oxidation.<sup>3–8</sup>

An alternative approach could be the use of metal-free materials and organic mediators.

It was shown<sup>9–15</sup> that the aromatic di-*N*-oxide radical cations of phenazine-di-*N*-oxide, pyrazine-di-*N*-oxide (Pyr<sub>0</sub>) and its substituted derivatives, electrochemically generated at GC and Pt electrodes, are carriers of active oxygen that is capable of activating the C–H bond of substrates: alcohols, ethers and cyclohexane. It was assumed that the activation process is accompanied by the formation of a complex of radical cations with a substrate that was confirmed by the registration of radical intermediates by EPR electrolysis at oxidation of phenazine-di-*N*-oxide in MeOH and its deuterated derivatives.<sup>11</sup> The detection of the same radical intermediate in CH<sub>3</sub>OH and CH<sub>3</sub>OD proved the participation of the CH<sub>3</sub> group of alcohol in the formation of the intermediate.

In previous studies,<sup>16–19</sup> in the presence of aromatic di-*N*-oxide, a several-fold increase in the catalytic efficiency of oxidation of organic compounds at SWCNT or MWCNT paper electrodes in comparison with the GC electrode was found. It was noted<sup>16–19</sup> that in the absence of the substrate the oxidation current of phenazine-di-*N*-oxide, 2,3,5,6-tetra-Me-pyrazine-di-*N*-oxide, at SWCNT or MWCNT paper electrodes is by several times

<sup>a</sup> Institute of Problems of Chemical Physics, Russian Academy of Sciences, 142432, Chernogolovka, Moscow Region, Russia. E-mail: kulsi@icp.ac.ru

<sup>b</sup> M.V. Lomonosov Moscow State University, Leninskie Hills, 119991, Moscow, Russia

higher than the oxidation current of the ferrocene (Fc) reference. Quantum chemical modeling of the adsorption energies of Pyr<sub>1</sub>, Fc and MeCN both on the CNT surface and in grooves between two CNTs using the cluster model simulating the surface of conducting and non-conducting carbon nanotubes<sup>20</sup> can explain this effect.

In this work the peculiarities of oxidation of Pyr<sub>1</sub> in the presence of MeOH were studied in 0.1 M Bu<sub>4</sub>NClO<sub>4</sub> solution in MeCN at SWCNT and MWCNT paper electrodes in comparison with the GC electrode using cyclic voltammetry, EPR electrolysis, differential capacitance and quantum chemical modeling. The study of electrocatalytic oxidation of methanol at the electrodes of CNTs in the presence of aromatic di-*N*-oxides as mediators is of interest for using this process in electrocatalysis, sensors and direct methanol fuel cells.

## 2. Materials and methods

Materials and experimental techniques for obtaining cyclic voltammograms, EPR spectra during electrolysis at controlled potentials and dependence of the differential capacitance of the electrical double layer on potentials were described in previous studies.<sup>18,20</sup> The quantum chemical modeling technique was described in detail in our previous work.<sup>20</sup>

## 3. Results and discussion

### 3.1. Quantum-chemical modeling of the adsorption of CH<sub>3</sub>OH, CH<sub>3</sub>COOH and H<sub>2</sub>O on the surface of CNTs

In this paper simulation of the adsorption of MeOH, CH<sub>3</sub>COOH and H<sub>2</sub>O at bundles of CNTs with a diameter of 1.4 nm was

carried out. The C<sub>54</sub>H<sub>18(c)</sub> cluster (structure 1, Fig. 1) was chosen to simulate single-walled conductive (10, 10) CNTs because in our previous work<sup>20</sup> it was shown to be a suitable model. For the modeling of the adsorption of CH<sub>3</sub>OH, CH<sub>3</sub>COOH and H<sub>2</sub>O, on the surface of CNTs, the functional wB97XD<sup>21</sup> was used in the software package GAUSSIAN-09.<sup>22</sup>

**Structures and adsorption energies.** The calculated most stable isomers of H<sub>2</sub>O, CH<sub>3</sub>OH and CH<sub>3</sub>COOH with the carbon cluster C<sub>54</sub>H<sub>18(c)</sub> modeling surface of the isolated conducting carbon nanotubes are shown in Fig. 1 (structures 2, 3, and 4). In complexes C<sub>54</sub>H<sub>18</sub>\*X (X = H<sub>2</sub>O, CH<sub>3</sub>OH, CH<sub>3</sub>COOH) the shortest distance from the C atoms of the CNT to H atoms of the X molecule is 2.6–3.1 Å, and the distance to C or O atoms of the X molecule is 3.2–3.4 Å.

The obtained values of the adsorption energies of H<sub>2</sub>O, CH<sub>3</sub>OH and CH<sub>3</sub>COOH on the carbon cluster C<sub>54</sub>H<sub>18(c)</sub>, modeling surfaces of the isolated conductive (10, 10) carbon nanotubes, are presented in Fig. 1 and Table 1. The adsorption energy decreases from CH<sub>3</sub>COOH (6.3 kcal mol<sup>-1</sup>) to MeCN (5.9 kcal mol<sup>-1</sup>), CH<sub>3</sub>OH (5.1 kcal mol<sup>-1</sup>) and H<sub>2</sub>O (3.0 kcal mol<sup>-1</sup>). An insignificant difference between the obtained values of the adsorption energies of MeCN and MeOH on the CNT surface indicates the possibility of their simultaneous adsorption on the CNT surface.

### 3.2. Oxidation of Pyr<sub>1</sub> at GC, SWCNT and MWCNT paper electrodes in MeCN

**In the absence of MeOH.** The oxidation of Pyr<sub>1</sub> at GC, SWCNT and MWCNT paper electrodes was studied in a previous study<sup>20</sup> in 0.1 M Bu<sub>4</sub>NClO<sub>4</sub> solution in MeCN with the use of the methods of quantum-chemical modeling, cyclic voltammetry, EPR-electrolysis and differential capacitance. It was shown<sup>20</sup> that the process of Pyr<sub>1</sub> oxidation at the GC electrode (*E*<sub>ox</sub> = 1.56 V) in 0.1 M Bu<sub>4</sub>NClO<sub>4</sub> solution in MeCN is one-electron, irreversible, and diffusion-controlled and the charge transfer is followed by an irreversible chemical reaction (an EC mechanism) with a rate constant equal to 0.6 s<sup>-1</sup>.

Oxidation of Pyr<sub>1</sub> at MWCNT and SWCNT paper electrodes in 0.1 M Bu<sub>4</sub>NClO<sub>4</sub> solution in MeCN occurs at a potential of 1.78 V,<sup>20</sup> that is, at higher by 220 mV as compared with oxidation at the GC electrode. The process is irreversible and not diffusion-controlled. In contrast to the GC electrode, the oxidation currents of 1 mM Pyr<sub>1</sub> at MWCNT and SWCNT paper

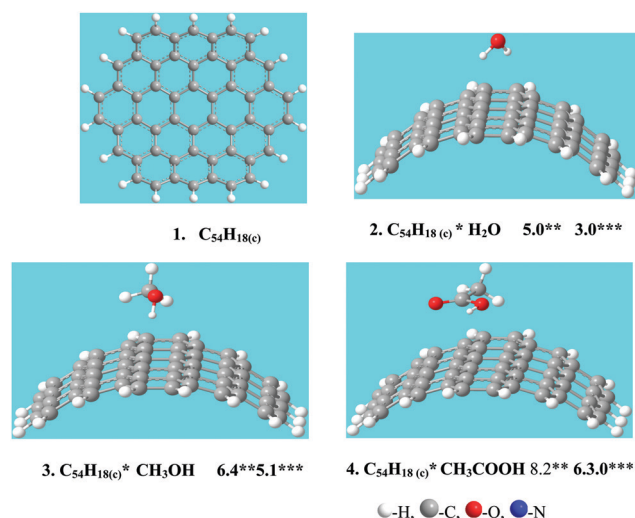


Fig. 1 Structure 1 of the cluster C<sub>54</sub>H<sub>18(c)</sub> modeling surface of single-walled conductive (10,10) CNTs; structures of clusters C<sub>54</sub>H<sub>18(c)</sub>\*X, X = H<sub>2</sub>O, CH<sub>3</sub>OH and CH<sub>3</sub>COOH (structures 2–4). Adsorption energies (in kcal mol<sup>-1</sup>) calculated at different basis sets are given: \*\* – 6-311G(d,p), \*\*\* – 6-311G(d,p) (BSSE).

Table 1 Estimation of the energies of adsorption (*E*<sub>ad</sub>, kcal mol<sup>-1</sup>) of CH<sub>3</sub>OH, CH<sub>3</sub>COOH, H<sub>2</sub>O (this work) and Pyr<sub>1</sub>, Fc и MeCN<sup>21</sup> on the structures modeling single carbon nanotubes. Conducting (c) CNT (10, 10) nanotubes were imitated by the cluster C<sub>54</sub>H<sub>18(c)</sub>. BSSE stands for the basis superposition effect

N	Structure C <sub>54</sub> H <sub>18(c)</sub> *X, X =	<i>E</i> <sub>ad</sub>	<i>E</i> <sub>ad</sub> – BSSE
8	H <sub>2</sub> O	5.0	3.0
9	CH <sub>3</sub> OH	6.4	5.1
10	MeCN	6.8	5.9
11	CH <sub>3</sub> COOH	8.2	6.3
12	Fc	12.6	10.9
13	Pyr <sub>1</sub>	18.2	14.5



electrodes are several times higher than the diffusion oxidation current of 1 mM Fc (as the reference).

**In the presence of methanol.** It should be noted that the data on Pyr<sub>1</sub> oxidation in the absence<sup>20</sup> and presence of MeOH (this paper) at MWCNT and SWCNT paper electrodes were obtained for the first time. Previously,<sup>19</sup> the oxidation of 2,3,5,6-tetra-Me-pyrazine-di-*N*-oxide (Pyr<sub>2</sub>) in the presence of methanol at GC and MWCNT paper electrodes in 0.1 M solution of LiClO<sub>4</sub> in MeCN was studied. It is important that the absence of two methyl groups in the 2,5-di-Me-pyrazine-di-*N*-oxide (Pyr<sub>1</sub>) molecule in comparison with Pyr<sub>2</sub> leads to an increase in its oxidation potential by  $\approx 120$  mV<sup>18,19</sup> and, consequently, to an increase in the reactivity of its radical cation. In this work the study was carried out, in contrast,<sup>19</sup> at both the MWCNT and SWCNT paper electrodes, and a solution of 0.1 M Bu<sub>4</sub>NClO<sub>4</sub> in MeCN was used as a background electrolyte. LiClO<sub>4</sub> is hygroscopic, and forms several crystalline hydrates, the most stable of which is LiClO<sub>4</sub>·3H<sub>2</sub>O. The presence of a trace amount of water as a base in the solvent facilitates the oxidation of organic compounds by the electrochemically generated radical cations of aromatic di-*N*-oxides, proceeding with the elimination of a proton. Therefore, Bu<sub>4</sub>NClO<sub>4</sub> was used as a supporting electrolyte.

In the absence of Pyr<sub>1</sub> no oxidation of MeOH is observed on the CV curves obtained at the GC electrode in 0.1 M Bu<sub>4</sub>NClO<sub>4</sub> solution in MeCN (Fig. 2a). In the presence of 1 mM Pyr<sub>1</sub> with the addition of MeOH a second anodic peak appears at higher anodic potentials (Fig. 2b). The current of the second anodic peak increases with an increase in the MeOH concentration and shifts to the first anodic peak. At a concentration of 0.5 M MeOH, anodic peaks merge.

The study of the dependence of the currents of these peaks on the potential scan rate at a MeOH concentration below 0.1 M shows that, as in 0.1 M LiClO<sub>4</sub> solution in MeCN,<sup>15</sup> the first anodic peak is diffusion (increases directly proportional to the square root of the scan rates; Fig. 3a), and the second anodic peak has a kinetic nature (decreases with an increase of the potential scan rates; Fig. 3a). This dependence of anodic peak current on the scan rate corresponds to the E<sub>1</sub>C<sub>1</sub>E<sub>2</sub> mechanism of the electrode process when two stages of electron transfer are separated by a chemical stage C<sub>1</sub>.<sup>23,24</sup>

The second anodic peak at a MeOH concentration above 0.1 M is proportional to the square root of its concentration (Fig. 2d), weakly depends on the potential scan rate (Fig. 3b) and is proportional to the Pyr<sub>1</sub> concentration (Fig. 3c). According to a previous study,<sup>25</sup> this indicates the catalytic nature of the second anodic peak. The ratio of the catalytic oxidation current of Pyr<sub>1</sub> in the presence of 0.5 M MeOH to the current recorded in the absence of MeOH (the catalytic efficiency of the process) is 6.0. It should be noted that in the presence of 2,3,5,6-tetra-Me-pyrazine-di-*N*-oxide (Pyr<sub>2</sub>) the catalytic efficiency of MeOH oxidation was 4.0.<sup>19</sup> Thus, the catalytic efficiency of the methanol oxidation increased by 1.5 times with an increase of the oxidation potential of di-*N*-oxide.

It was shown that the dependence of the CV curves of Pyr<sub>1</sub> oxidation at the GC electrode in 0.1 M Bu<sub>4</sub>NClO<sub>4</sub> solution in

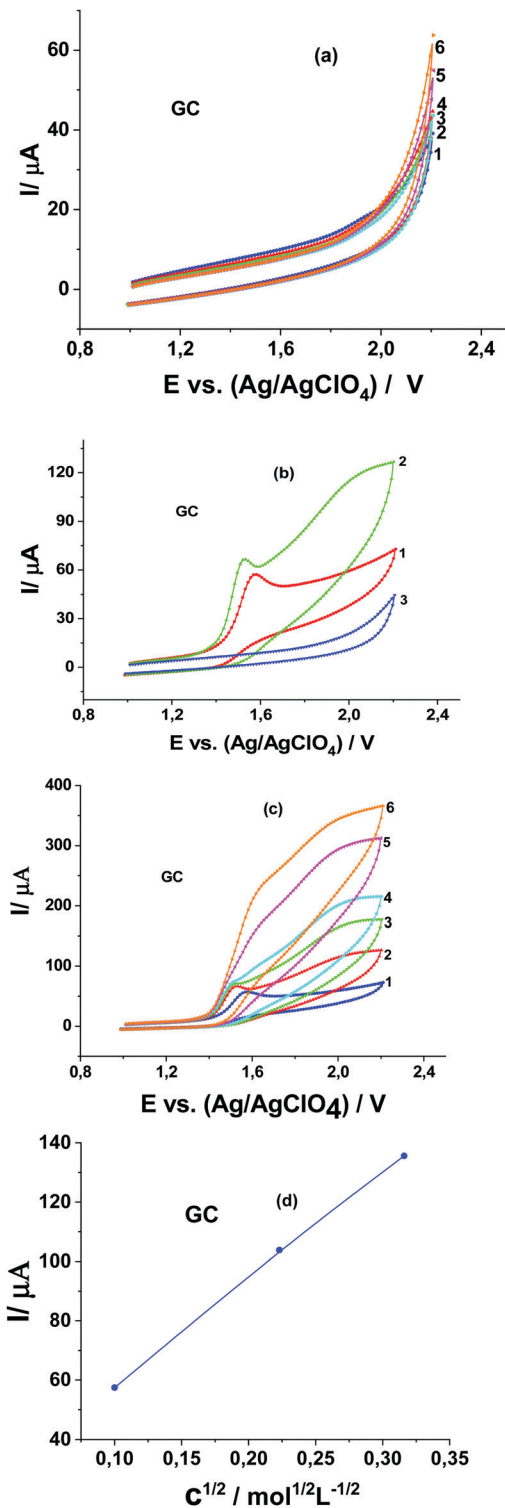


Fig. 2 CVs of 0.1 M Bu<sub>4</sub>NClO<sub>4</sub> solution in MeCN at the GC electrode at a potential scan rate of 20 mV s<sup>-1</sup> in the presence of MeOH: (a) (1) 0, (2) 0.01, (3) 0.05, (4) 0.1, (5) 0.5, and (6) 1.0 M; (b) (1) 1 mM Pyr<sub>1</sub>, (2) 1 mM Pyr<sub>1</sub> and 0.01 M MeOH, and (3) 0.01 M MeOH; (c) 1 mM Pyr<sub>1</sub> and MeOH: (1) 0, (2) 0.01, (3) 0.05, (4) 0.1, (5) 0.5, and (6) 1.0 M; and (d) dependence of the anodic peak current on the square root of the MeOH concentration.

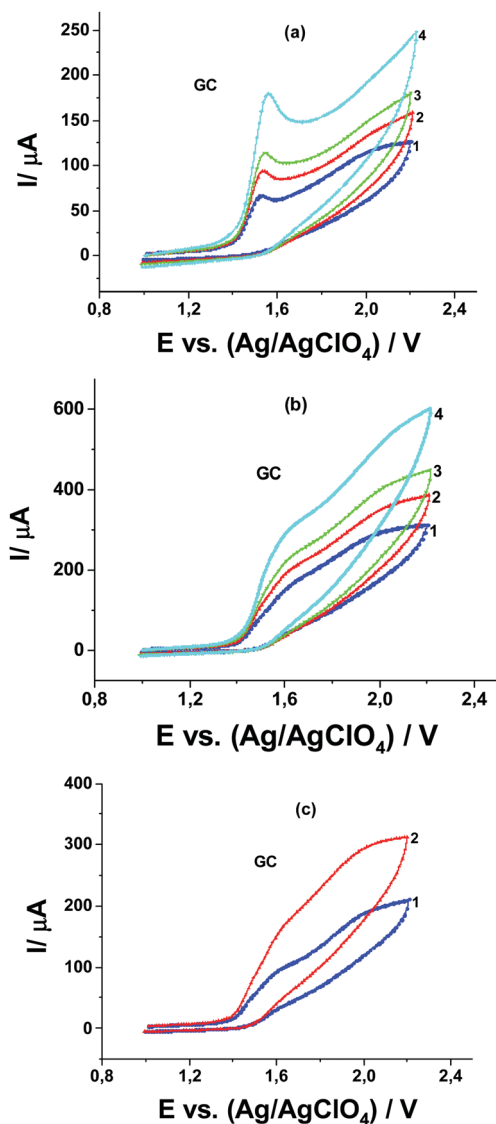


Fig. 3 CVs of 0.1 M  $\text{Bu}_4\text{NClO}_4$  solution in MeCN at the GC electrode in the presence of: (a) 1 mM  $\text{Pyr}_1$  and 0.01 M MeOH at potential scan rates of: (1) 20, (2) 50, (3) 80, and (4) 200  $\text{mV s}^{-1}$ ; (b) 1 mM  $\text{Pyr}_1$  and 0.5 M MeOH at potential scan rates of: (1) 20, (2) 50, (3) 80, and (4) 200  $\text{mV s}^{-1}$ ; and (c) 0.5 M MeOH and  $\text{Pyr}_1$ : (1) 0.5 mM and (2) 1 mM at a potential scan rate of 20  $\text{mV s}^{-1}$ .

MeCN on the MeOH concentration and the potential scan rate are identical to those obtained in ref. 15 in 0.1 M  $\text{LiClO}_4$  solution in MeCN. Therefore, the nature of the background cation does not affect the electrocatalytic oxidation of MeOH in the presence of  $\text{Pyr}_1$  at the GC electrode.

Previously,<sup>15</sup> it was established that the EPR spectra of radical cations pyrazine-di-*N*-oxide and its substituted derivatives were not found in the presence of MeOH in 0.1 M  $\text{LiClO}_4$  solution in MeCN. The EPR spectra of radical cations could have been detected during electrolysis at the Au electrode in deuterated methanol at a temperature close to the freezing point of the solvent at  $-85^\circ\text{C}$ .<sup>15</sup> The EPR spectrum of the radical cation of  $\text{Pyr}_1$  in 0.1 M  $\text{LiClO}_4$  solution in  $\text{CD}_3\text{OD}$  is presented in Fig. 4b and c. The registration of the EPR spectrum of the radical

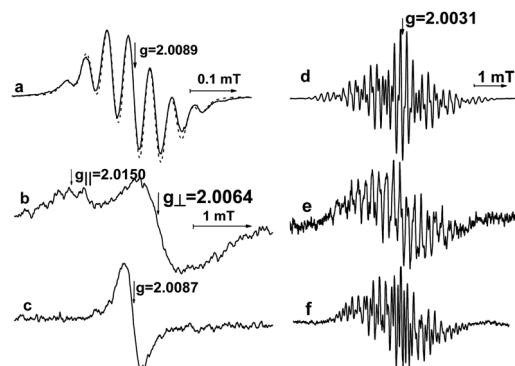


Fig. 4 EPR spectra recorded during electrolysis of 1 mM  $\text{Pyr}_1$  solution in the presence of 0.1 M  $\text{LiClO}_4$  at different temperatures and potentials.<sup>15</sup> (a) In MeCN at  $-45^\circ\text{C}$  and +1.6 V, the dotted line is simulation using a Bruker software Symfonia taking into account hyperfine splitting on all nuclei of  $\text{Pyr}_1$ :  $a_N = 0.047$  mT (2),  $a_{H_1} = 0.042$  mT (2), and  $a_{H_2} = 0.113$  mT (6); the numbers in parentheses are the numbers of equivalent nuclei, the half-width at half-height of the Lorentz line is 0.012 mT, (b) in  $\text{CD}_3\text{OD}$  at  $-97^\circ\text{C}$  and +1.8 V, (c) in  $\text{CD}_3\text{OD}$  at  $-85^\circ\text{C}$  and +1.7 V, (d) in  $\text{CH}_3\text{OH}$  at  $-35^\circ\text{C}$  and  $-0.9$  V, (e) in  $\text{CH}_3\text{OD}$  at  $-35^\circ\text{C}$  and  $-0.9$  V, and (f) in  $\text{CD}_3\text{OD}$  at  $-35^\circ\text{C}$  and  $-0.8$  V. The spectrum (a) was recorded at the Pt electrode, and the other spectra were obtained at the Au electrode.

cation of  $\text{Pyr}_1$  in 0.1 M  $\text{LiClO}_4$  solution in  $\text{CD}_3\text{OD}$  confirms that the  $\text{Pyr}_1$  structure remains unchanged during the alcohol catalytic oxidation. The registration of the EPR spectra of the  $\text{Pyr}_1$  radical anion at  $-35^\circ\text{C}$  during electrolysis at a controlled potential after alcohol catalytic oxidation at positive potentials (Fig. 4d–f) is further evidence that the structure and concentration of  $\text{Pyr}_1$  remain unchanged after the catalytic process. Since the nature of the background cation does not affect the electrocatalytic oxidation of MeOH in the presence of  $\text{Pyr}_1$ , these data can be used as evidence for the invariability of the structure and concentration of  $\text{Pyr}_1$  in the catalytic process in 0.1 M  $\text{Bu}_4\text{NClO}_4$  solution in MeCN in the presence of MeOH.

In the absence of  $\text{Pyr}_1$  at CV curves recorded at SWCNT and MWCNT paper electrodes in 0.1 M  $\text{Bu}_4\text{NClO}_4$  solution in MeCN in the presence of MeOH from 0.01 to 1.0 M, as in the case of the GC electrode, the MeOH oxidation is not observed (Fig. 5a and b). The oxidation current of  $\text{Pyr}_1$  at SWCNT and MWCNT paper electrodes in 0.1 M  $\text{Bu}_4\text{NClO}_4$  solution in MeCN increases with the addition of MeOH from 0.01 to 1.0 M, and an increase of the anodic current shifts to lower positive potentials (Fig. 5c and d).

Unlike oxidation at the GC electrode, at the CV curves of  $\text{Pyr}_1$  oxidation at SWCNT and MWCNT paper electrodes in 0.1 M  $\text{Bu}_4\text{NClO}_4$  solution in MeCN in the presence of MeOH, one anodic wave is observed. This can be explained by the adsorption of  $\text{Pyr}_1$  molecules on the surface of SWCNT and MWCNT paper electrodes, which leads to a 220 mV shift towards higher positive potentials of the  $\text{Pyr}_1$  oxidation potential as compared to the oxidation potential of the unadsorbed  $\text{Pyr}_1$  molecules on the GC electrode. This shift results in the merging of the first and second anodic waves of  $\text{Pyr}_1$  oxidation at SWCNT and MWCNT paper electrodes in the presence of MeOH.





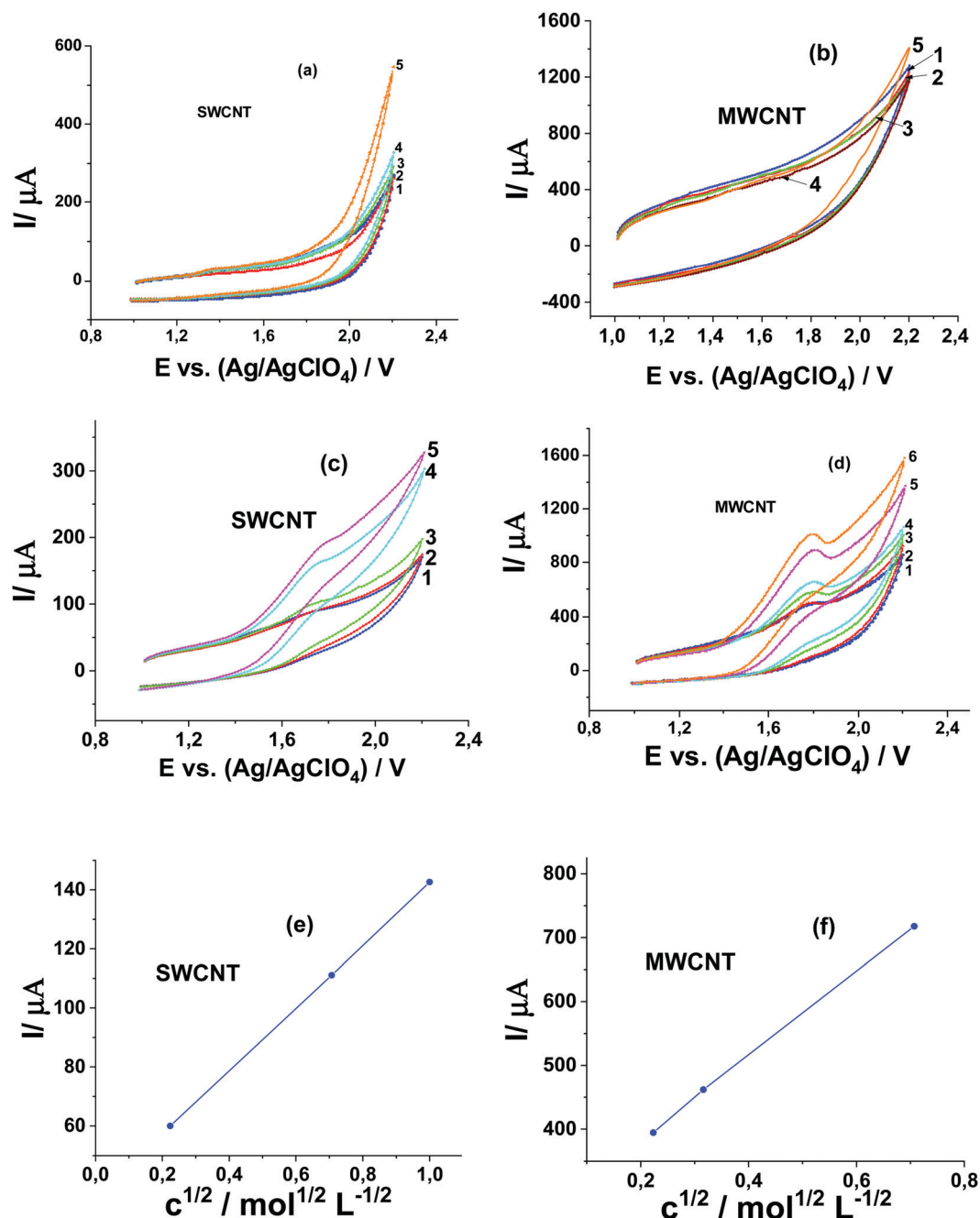


Fig. 5 CVs of 0.1 M Bu<sub>4</sub>NClO<sub>4</sub> solution in MeCN at a potential scan rate of 20 mV s<sup>-1</sup> in the presence of MeOH: (1) 0, (2) 0.01, (3) 0.05, (4) 0.1, and (5) 0.5 M at (a) SWCNT and (b) MWCNT paper electrodes, (c) at the SWCNT paper electrode in the presence of 1 mM Pyr<sub>1</sub> and MeOH: (1) 0, (2) 0.01, (3) 0.05, (4) 0.5, and (5) 1.0, (d) at the MWCNT paper electrode in the presence of 1 mM Pyr<sub>1</sub> and MeOH: (1) 0, (2) 0.01, (3) 0.05, (4) 0.1, (5) 0.5, and (6) 1.0 M; and dependence of the anodic peak current on the square root of the MeOH concentration at (e) SWCNT and (f) MWCNT paper electrodes.

The linear dependence of the anodic peak of Pyr<sub>1</sub> oxidation on the square root of the concentration of MeOH at SWCNT and MWCNT paper electrodes (Fig. 5e and f) at a MeOH concentration above 0.05 M corresponds to the catalytic nature of this peak.<sup>25</sup> The ratio of the catalytic current at 0.5 M MeOH to the diffusion current of ferrocene (as the reference) is 16. Thus the catalytic efficiency of

MeOH oxidation at SWCNT and MWCNT paper electrodes is ~2.7 times higher than at the GC electrode.

It should be noted that in contrast to the GC electrode, on which the catalytic current (*I*<sub>a</sub>) increases proportionally to the concentration of Pyr<sub>1</sub> (Fig. 3c), at SWCNT and MWCNT paper electrodes, it increases by a factor of 1.3 (Fig. 6a and b) with a two-fold magnification of the Pyr<sub>1</sub> concentration.

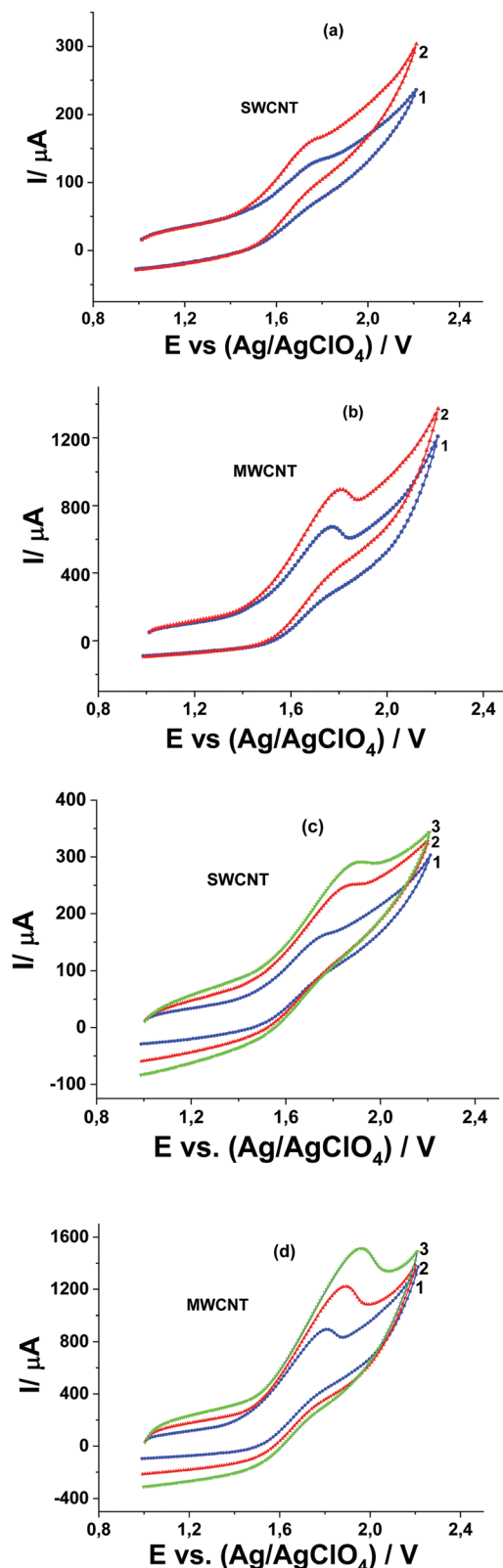


Fig. 6 CVs of 0.1 M  $\text{Bu}_4\text{NClO}_4$  solution in MeCN in the presence of 0.5 M MeOH and  $\text{Pyr}_1$ : (1) 0.5 mM and (2) 1 mM at a potential scan rate of  $20 \text{ mV s}^{-1}$  at (a) SWCNT and (b) MWCNT paper electrodes and in the presence of 1 mM  $\text{Pyr}_1$  and 0.5 M MeOH at potential scan rates of: (1) 20, (2) 50, and (3)  $80 \text{ mV s}^{-1}$  at (c) SWCNT and (d) MWCNT paper electrodes.

This can be explained by the fact that in the absence of MeOH the oxidation current of  $\text{Pyr}_1$  is several times higher than the oxidation current of Fc as a reference and weakly depends on the  $\text{Pyr}_1$  concentration.<sup>20</sup> Since the adsorption energy of  $\text{Pyr}_1$  ( $14.5 \text{ kcal mol}^{-1}$ , Table 1) on the CNT surface significantly exceeds the adsorption energies of MeCN and MeOH, the presence of MeOH in solution will not affect the adsorption of  $\text{Pyr}_1$  on the CNT surface and retains a weakly dependent anodic current of  $\text{Pyr}_1$  oxidation on its concentration.

The adsorption of  $\text{Pyr}_1$  at the MWCNT paper electrode in 0.1 M  $\text{Bu}_4\text{ClO}_4$  solution in MeCN was studied in a previous study<sup>20</sup> by measuring the C,E-dependence of the differential double layer capacitance of the electrode on potential. It was found that the differential double layer capacitance of the electrode recorded in 0.1 M  $\text{Bu}_4\text{ClO}_4$  solution in MeCN at the MWCNT paper electrode is not changed when 1 mM  $\text{Pyr}_1$  is added to the solution (Fig. 7). It has been established by quantum chemical modeling<sup>20</sup> that the preferred arrangement is the parallel arrangement of the planar part of the  $\text{Pyr}_1$  molecule adsorbed on the surface of carbon nanotubes. It is known<sup>26</sup> that the differential double layer capacitance of the electrode does not decrease at the flat arrangement of the adsorbed aromatic molecules on the electrode surface. With the addition of 0.5 M MeOH to the solution of 1 mM  $\text{Pyr}_1$  in 0.1 M  $\text{Bu}_4\text{ClO}_4$  solution in MeCN the differential double layer capacitance of the electrode decreases. This indicates the formation of the adsorption layer on the surface of the MWCNT paper electrode, including  $\text{Pyr}_1$ , MeOH and MeCN molecules. This conclusion is confirmed by quantum chemical modeling (Fig. 1 and Table 1).

Studying the influence of  $\text{CH}_3\text{COOH}$  and water (as a basis) on the potential and current of the catalytic wave of  $\text{Pyr}_1$  oxidation at GC, SWCNT, and MWCNT paper electrodes in the presence of MeOH makes it possible to establish the mechanism of the electrode process. A decrease of the catalytic

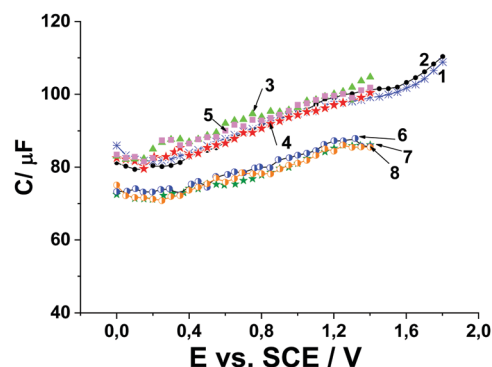


Fig. 7 Dependences of the differential capacitance  $C$  of the MWCNT paper electrode at a potential  $E$  of 0.1 M  $\text{Bu}_4\text{ClO}_4$  solution in MeCN in the presence of  $\text{Pyr}_1$ : 0 (curves 1 and 2) and 1 mM (curves 3–5), 1 mM  $\text{Pyr}_1$  and 0.5 M MeOH (curve 6–8). Curves 1 and 2 were recorded just after recording the cyclic voltammetry curves, and curves 3, 4 and 5 are settled curves.



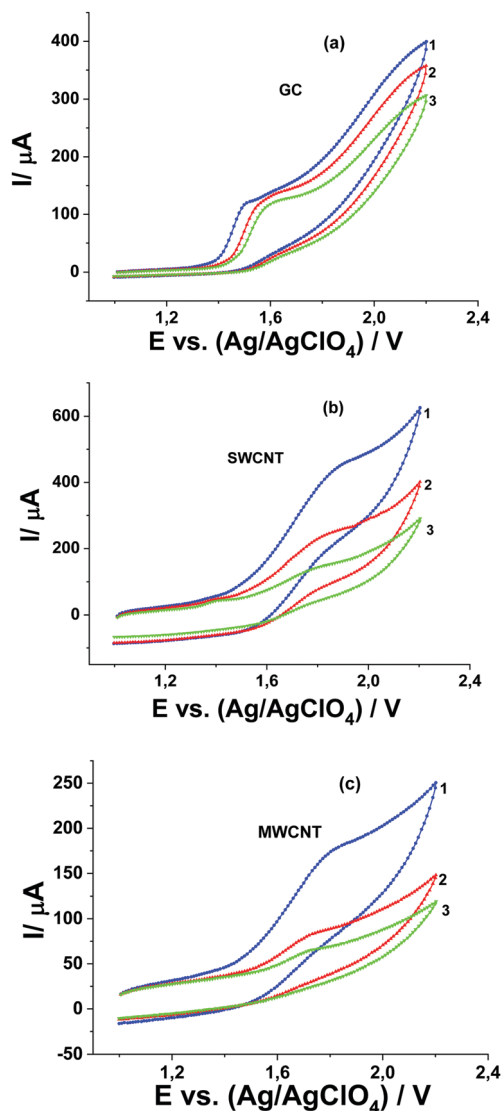


Fig. 8 CVs of 1.0 mM Pyr<sub>1</sub> and 0.5 M MeOH in 0.1 M Bu<sub>4</sub>NClO<sub>4</sub> solution in MeCN in the presence of CH<sub>3</sub>COOH: (1) 0, (2) 1.0, and (3) 2.0 M at (a) (GC), (b) SWCNT and (c) MWCNT paper electrodes at a potential scan rate of 50 mV s<sup>-1</sup>.

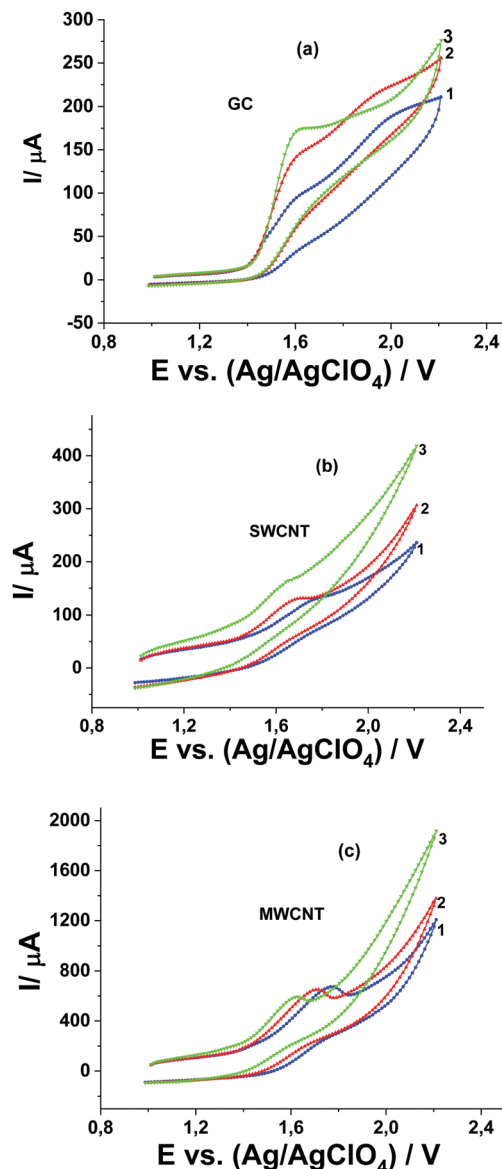


Fig. 9 CVs of 0.5 mM Pyr<sub>1</sub> and 0.5 M MeOH in 0.1 M Bu<sub>4</sub>NClO<sub>4</sub> solution in MeCN in the presence of H<sub>2</sub>O: (1) 0, (2) 0.5, and (3) 2.0 M at (a) (GC), (b) SWCNT and (c) MWCNT paper electrodes at a potential scan rate of 20 mV s<sup>-1</sup>.

current and the shifts of the catalytic wave and the first oxidation wave of Pyr<sub>1</sub> towards higher positive potentials (Fig. 8a–c) are observed at the GC electrode with the addition of 1.0 and 2.0 M CH<sub>3</sub>COOH to solution 1.0 mM Pyr<sub>1</sub> and 0.5 M MeOH in 0.1 M Bu<sub>4</sub>ClO<sub>4</sub> solution in MeCN. It should be noted that with the addition of 2.0 M CH<sub>3</sub>COOH, the catalytic current at the GC electrode decreases by 1.4 times and at SWCNT and MWCNT paper electrodes by 3.8 and 3.1 times, respectively (Fig. 9).

The shift of the catalytic wave at the GC electrode to potentials of the anodic wave of Pyr<sub>1</sub> oxidation (Fig. 8a) is recorded with the addition of 0.5 and 2.0 M H<sub>2</sub>O to a solution of 0.5 mM Pyr<sub>1</sub> and 0.5 M MeOH in 0.1 M Bu<sub>4</sub>ClO<sub>4</sub> solution in MeCN (Fig. 8a). This indicates that the oxidation potentials of the reaction product of the radical cation with MeOH and the initial di-*N*-oxide are close. At SWCNT and MWCNT paper

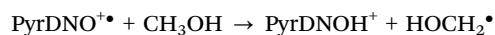
electrodes the influence of the addition of H<sub>2</sub>O is less pronounced.

The difference in the manifestation of the inhibiting effect of CH<sub>3</sub>COOH and of the catalytic effect of H<sub>2</sub>O at SWCNT and MWCNT paper electrodes as compared with the GC electrode can be explained by the performed quantum chemical modeling and the determination of the adsorption energies of MeCN<sup>20</sup> and MeOH, CH<sub>3</sub>COOH and H<sub>2</sub>O (this work) on the CNT surface (Table 1). The adsorption energy of CH<sub>3</sub>COOH (6.3 kcal mol<sup>-1</sup>) on the CNT surface is sufficient to displace MeCN with an adsorption energy of 5.9 kcal mol<sup>-1</sup> from the electrode surface. As a result of the adsorption of CH<sub>3</sub>COOH, its concentration on the CNT surface increases and the



inhibiting effect is more pronounced compared to the GC electrode. The adsorption energy of  $\text{H}_2\text{O}$  ( $3 \text{ kcal mol}^{-1}$ ) on the CNT surface (Table 1) is much lower than the adsorption energy of MeCN and therefore its catalytic effect is less pronounced compared to the GC electrode. A similar difference in the manifestation of the inhibiting effect of  $\text{CH}_3\text{COOH}$  and of the catalytic effect of  $\text{H}_2\text{O}$  at SWCNT or MWCNT paper electrodes as compared with the GC electrode was observed in ref. 17–19. Quantum chemical modeling has provided an explanation for this effect. The effect of acid and water additions on the catalytic process indicates that the catalytic process is accompanied by proton elimination.

**Mechanism of  $\text{Pyr}_1$  oxidation in the presence of MeOH at GC, SWCNT and MWCNT paper electrodes in MeCN.** Previously<sup>15</sup> quantum chemical modeling of the reaction of the radical cation of unsubstituted pyrazine-di-*N*-oxide ( $\text{PyrDNO}^{\bullet+}$ ) with MeOH by the mechanism of hydrogen atom abstraction with the formation of the protonated pyrazine-di-*N*-oxide ( $\text{PyrDNOH}^+$ ) and the  $\text{HOCH}_2^{\bullet}$  radical,



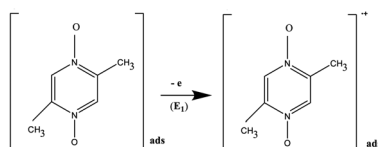
was performed. It was found that the adduct  $[(\text{CH}_3\text{OH})\text{PyrDNO}^{\bullet+}]$  was formed with a noticeable gain in energy equal to  $16.495 \text{ kcal mol}^{-1}$ , and the equilibrium constant of its formation was  $7 \times 10^6 \text{ M}^{-1}$ . H-atom abstraction from MeOH by the  $\text{PyrDNO}^{\bullet+}$  radical cation is impossible because the product, the complex of the  $\text{HOCH}_2^{\bullet}$  radical and the  $\text{PyrDNOH}^+$  cation, has a negligibly small lifetime and virtually zero activation energy for its transformation to the original adduct. It should be noted that the EPR spectrum of the  $\text{HOCH}_2^{\bullet}$  radical was not found. Thus the oxidation of aromatic di-*N*-oxides in the presence of methanol at the GC electrode was interpreted by the  $\text{E}_1\text{C}_1\text{E}_2\text{C}_2$  mechanism of a two stage electrode process with the catalytic current recorded at the second electrode stage.

Based on the obtained experimental data and quantum chemical modeling the following mechanism of  $\text{Pyr}_1$  oxidation at SWCNT and MWCNT paper electrodes in MeCN in the presence of MeOH is proposed.

### $\text{E}_1$ – first electrode stage

*At the GC electrode.* At the first electrode stage ( $\text{E}_1$ ),  $\text{Pyr}_1$  is oxidized to the radical cation. This process is one-electron, irreversible, and diffusion-controlled. The charge transfer is followed by an irreversible chemical reaction.

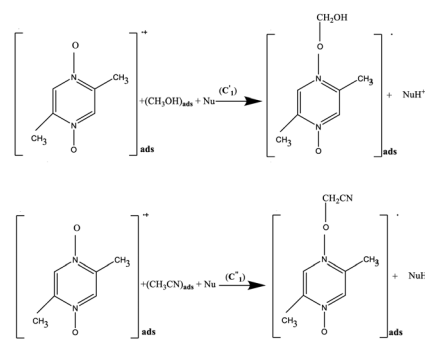
*At SWCNT and MWCNT paper electrodes.* At the first electrode stage ( $\text{E}_1$ ),  $\text{Pyr}_1$ , adsorbed on the CNT surface, is oxidized to the radical cation. This process is irreversible and not controlled by diffusion.



### $\text{C}_1$ – first chemical stage

*At GC, SWCNT and MWCNT paper electrodes.* At the first chemical stage ( $\text{C}_1$ ), two competitive chemical reactions of the electrophilic addition of the oxygen atom of  $\text{Pyr}_1$  radical cations to the C–H bonds of MeCN and MeOH occur. The reactions are accompanied by proton elimination and the formation of radical intermediates (complexes with an N–O–C structure). Compounds of this structure and methods for their preparation are known.<sup>27–33</sup>

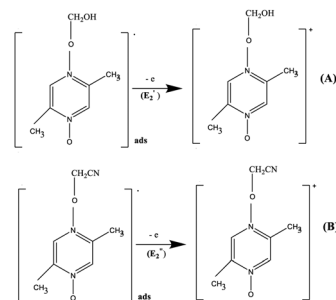
*At SWCNT and MWCNT paper electrodes.* The chemical stage proceeds with the participation of the  $\text{Pyr}_1$  radical cations, as well as MeCN and MeOH, adsorbed on the surface of the SWCNT and MWCNT paper electrodes.



### $\text{E}_2$ – second electrode stage

*At the GC electrode.* At the second electrode stage ( $\text{E}_2$ ), the radical intermediates are oxidized to the cations.

*At SWCNT and MWCNT paper electrodes.* The radical intermediates adsorbed on the surface of the SWCNT and MWCNT paper electrodes are oxidized to the cations of (A) and (B).



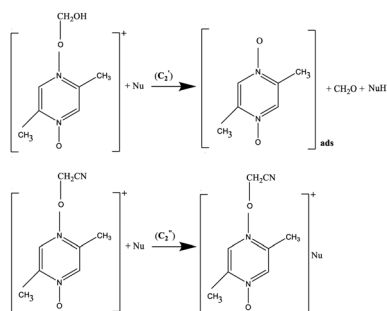
### $\text{C}_2$ – second chemical stage

*At GC, SWCNT and MWCNT paper electrodes.* The second chemical stage ( $\text{C}_2$ ) corresponds to the interaction of the cations of (A) and (B) with a nucleophile or a base (a water admixture in the solution). It is assumed that the cation (A) decomposes at the stage ( $\text{C}'_2$ ) with the formation of the initial aromatic di-*N*-oxide and the product of two-electron oxidation of MeOH (formaldehyde). The regenerated aromatic di-*N*-oxide is immediately oxidized at the electrode to a radical cation, and the cycle is repeated; the catalytic current of the total





two-electron oxidation of MeOH is recorded. In a competitive chemical stage ( $C_2'$ ), the cation (**B**) is attached to a base or a nucleophile to form an adduct.<sup>20</sup>



## 4. Conclusions

In this work, electrochemical and quantum chemical methods were used to study the peculiarities of the behavior of the electrocatalytic system of 2,5-di-Me-pyrazine-di-N-oxide – methanol at single-walled and multi-walled carbon nanotube paper electrodes in comparison with a glassy carbon (GC) electrode. The cluster model describing the surface of conducting carbon nanotubes (10, 10) was used to simulate the adsorption of MeOH, CH<sub>3</sub>COOH, and H<sub>2</sub>O on the surface of CNTs. The observed effects in the catalytic system are explained by quantum chemical modeling of the non-covalent interaction of the components of the studied system with the CNT surface. It is concluded that, in the course of the catalytic process at SWCNT and MWCNT electrodes, in contrast to the GC electrode, the adsorption of the components of the catalytic system on their surface is of decisive importance. This research may be helpful in using this process in electrocatalysis, sensors and direct methanol fuel cells.

This work was performed in accordance with the state task, state registration no. AAAA-A19-119061890019-5.

## Conflicts of interest

There are no conflicts of interest to declare.

## Acknowledgements

Calculations were performed at the Computer Center, Institute of Problems of Chemical Physics, RAS.

## References

- X. Li and A. Faghri, Review and advances of direct methanol fuel cell (DMFCs) part 1: Design, fabrication, and testing with high concentration methanol solutions, *J. Power Sources*, 2013, **226**, 223–240.
- Y. Feng, H. Liu and J. Yang, A selective electrocatalyst-based direct methanol fuel cell operated at high concentrations of methanol, *Sci. Adv.*, 2017, **3**, e1700580.
- T. Radhakrishnan and N. Sandhyarani, Three dimensional assembly of electrocatalytic platinum nanostructures on reduced graphene oxide – An electrochemical approach for high performance catalyst for methanol oxidation, *J. Hydrogen Energy*, 2017, **42**, 7014–7022.
- Y. Gan, H. Huang and W. Zhang, Electrocatalytic oxidation of methanol on carbon-nanotubes/graphite electrode modified with platinum and molybdenum oxide nanopaticles, *Trans. Nonferrous Met. Soc. China*, 2007, **17**, 214–219.
- S. Wang, X. Wang and S. P. Jiang, PtRu Nanoparticles supported on 1-aminopyrene functionalized multi-walled carbon nanotubes and their electrocatalytic activity for methanol oxidation, *Lungmuir*, 2008, **24**, 10505–10512.
- Y. Zhao, X. Yang, J. Tian, F. Wang and L. Zhan, Methanol electro-oxidation on Ni@Pd core-shell nanoparticles supported on multi-walled carbon nanotubes in alkaline media, *Int. J. Hydrogen Energy*, 2010, **35**, 3249–3257.
- H. An, L. Pan, H. Cui, D. Zhou, B. Wang, J. Zhai, Q. Li and Y. Pan, Electrocatalytic performance of Pd nanoparticles supported on TiO<sub>2</sub>-MWCNTs for methanol, ethanol, and isopropanol in alkaline media, *J. Electroanal. Chem.*, 2015, **741**, 56–63.
- H. Zhang, X. Han and Y. Zhao, Pd-TiO<sub>2</sub> nanoparticles supported on reduced graphene oxide: green synthesis and improved electrocatalytic performance for methanol oxidation, *J. Electroanal. Chem.*, 2017, **799**, 84–91.
- S. I. Kulakovskaya, V. M. Berdnikov, A. Y. Tikhonov, L. B. Volodarskii and V. E. Maier, A cyclic voltametric study of the mechanism responsible for the oxidation of organic compounds on a glass-carbon electrode in the presence of aromatic *N,N'*-dioxides as organic mediators, *Russ. J. Electrochem.*, 1993, **29**, 40–45.
- S. I. Kulakovskaya, V. M. Berdnikov, A. A. Vasilenko, A. Y. Tikhonov and L. B. Volodarskii, The mechanism of electrochemical activation of the C–H bond during oxidation of organic compounds in the presence of aromatic *N*-oxides as the intermediates, *Russ. J. Electrochem.*, 1996, **32**, 784–790.
- S. I. Kulakovskaya, A. V. Kulikov, V. M. Berdnikov, N. T. Ioffe and A. F. Shestakov, Electrochemical and EPR study of the C–H bond activation. Electrocatalytic oxidation with participation of radical cation of phenazine-di-*N*-oxide, *Electrochim. Acta*, 2002, **47**, 4245–4254.
- S. I. Kulakovskaya, A. V. Kulikov and A. F. Shestakov, Radical cation of pyrazine-di-*N*-oxide as a mediator in electrocatalytic oxidation of organic compounds, *Russ. J. Electrochem.*, 2004, **40**, 1035–1044.
- S. I. Kulakovskaya, A. V. Kulikov and A. F. Shestakov, Substituted pyrazine-di-*N*-oxides as the mediators of catalytic oxidation of organic compounds, *Russ. J. Electrochem.*, 2007, **43**, 1156–1163.
- S. I. Kulakovskaya, A. V. Kulikov and A. F. Shestakov, Electrochemical and EPR-study of the mechanism of organic



- compound oxidation in the presence of mediators – radical cations of substituted pyrazine-di-*N*-oxydes, *Russ. J. Electrochem.*, 2007, **43**, 1234–1242.
- 15 S. I. Kulakovskaya, A. V. Kulikov and A. F. Shestakov, Electrochemical and EPR Studies of the Oxidation Mechanism of Pyrazine-di-*N*-oxides in the Presence of Methanol and its Deuterated Derivatives, *Russ. J. Electrochem.*, 2012, **48**, 1023–1036.
  - 16 S. I. Kulakovskaya, A. G. Krivenko, N. S. Komarova, A. V. Kulikov and A. F. Shestakov, Electrochemical and EPR study of the mechanism of oxidation of phenazine-di-*N*-oxide in the presence of cyclohexanol on glass carbon and single-walled carbon nanotube electrodes, *Russ. J. Electrochem.*, 2014, **50**, 1–12.
  - 17 S. I. Kulakovskaya, A. V. Kulikov, L. N. Sviridova and E. V. Stenina, Electrochemical and electron paramagnetic resonance study of the mechanism of oxidation of phenazine-di-*N*-oxide in the presence of isopropyl alcohol at glassy carbon and single-walled carbon nanotube electrodes, *Electrochim. Acta*, 2014, **146**, 798–808.
  - 18 S. I. Kulakovskaya, A. V. Kulikov, L. N. Sviridova and E. V. Stenina, Electrochemical and electron paramagnetic resonance study of the mechanism of oxidation of 2,3,5,6-tetra-Me-pyrazine-di-*N*-oxide as a mediator of electrocatalytic oxidation of isopropyl alcohol at glassy carbon and single-walled carbon nanotube electrodes, *J. Electroanal. Chem.*, 2017, **795**, 81–89.
  - 19 S. I. Kulakovskaya, A. V. Kulikov, L. N. Sviridova, E. V. Stenina, A. G. Ryabenko and V. G. Basu, Comparative electrochemical and electron paramagnetic resonance study of the mechanism of oxidation of 2,3,5,6-tetra-Me-pyrazine-di-*N*-oxide as a mediator of electrocatalytic oxidation of metanol at glassy carbon and multi-walled carbon nanotube paper electrodes, *J. Adv. Electrochem.*, 2018, **4**(1), 162–167.
  - 20 S. I. Kulakovskaya, A. V. Kulikov, T. S. Zyubina, A. S. Zyubin, D. V. Konev, L. N. Sviridova, E. V. Stenina, A. G. Ryabenko and E. V. Zolotukhina, Role of non-covalent interactions at oxidation of 2,5-di-Me-pyrazine-di-*N*-oxide at glassy carbon, single-walled and multi-walled carbon nanotube paper electrodes, *Carbon trends*, 2021, **4**, 100057, DOI: 10.1016/j.cartre.2021.100057.
  - 21 J.-D. Chai and M. Head-Gordon, Long-range corrected hybrid density functionals with damped atom–atom dispersion corrections, *Phys. Chem. Chem. Phys.*, 2008, **10**, 6615–6620.
  - 22 M. J. Frisch, G. W. Trucks and H. B. Schlegel, *et al.*, *Gaussian 09, Revision B.01*, Gaussian, Inc., Wallingford CT, 2010.
  - 23 R. S. Nicholson and J. Shain, Theory of stationary electrode polarography. Single scan and cyclic methods applied to reversible, irreversible, and kinetic systems, *Anal. Chem.*, 1964, **36**, 706–723.
  - 24 R. S. Nicholson and J. Shain, Theory of stationary electrode polarography for a chemical reaction coupled between two charge transfers, *Anal. Chem.*, 1965, **37**, 178–189.
  - 25 Z. Galus, *Fundamentals of Electrochemical Analysis*, New York, Harwood, 1976.
  - 26 A. N. Frumkin and B. B. Damaskin, Adsorption of organic compounds at electrodes, in *Modern Aspects of Electrochemistry*, ed. J. O. M. Bockris and B. E. Conway, London, Butterworth, 1964, vol. 3, pp. 149–223.
  - 27 V. A. Golubev, R. V. Miklyush and E. G. Rozantsev, Metod sinteza ketoefirov *N*-oksipiperidina, (Method of synthesis of ketoether of *N*-oxypiperidine), *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1972, **3**, 656–658.
  - 28 V. A. Golubev and R. V. Miklyush, Novyi preparativnyi metod okisleniya aktivirovannoi metilenovoi gruppy do karbonil'-noi, (New preparative method of the oxydation of methylene group to carbonyl), *Zh. Org. Khim.*, 1972, **8**, 1356–1357.
  - 29 A. R. Katritzky, The preparation of some substituted pyridine 1-oxides, *J. Chem. Soc.*, 1956, 2404–2408.
  - 30 T. Okamoto and H. Tani, Synthesis of 2- and 4-cyanopyridines, *Chem. Pharm. Bull.*, 1959, **7**, 130–131.
  - 31 T. Okamoto and H. Tani, Reaction mechanism in aromatic heterocyclic compound. The reactions of *N*-alkoxy-pyridinium derivatives (1), *Chem. Pharm. Bull.*, 1959, **7**, 925–930.
  - 32 A. R. Katritzky and E. Lunt, *N*-oxides and related compounds-XXXV. Reactions of *N*-alkoxy-pyridinium and quinolinium cations with nucleophiles, *Tetrahedron*, 1969, **25**, 4291–4305.
  - 33 R. Eisenthal and A. R. Katritzky, The ring-opening of *N*-methoxypyridinium perchlorate by hydroxide ion, *Tetrahedron*, 1965, **21**, 2205–2213.

