

## **Carbon Paste Electrodes Bulk-Modified with Carbon Nanotubes and Chemically Oxidized Carbon Nanotubes for the Determination of Hydrogen Peroxide**

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**Abstract:** Carbon paste electrodes (graphite/paraffin oil) bulk-modified with multiwalled carbon nanotubes (MWCNT) and chemically oxidized MWCNT (O-MWCNT) were used as sensors for the hydrodynamic chronoamperometric determination of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>). Experimental parameters, such as the type and pH of the supporting electrolyte or the working potential(s) applied were investigated in the batch arrangement.

**Keywords:** Carbon paste electrode; bulk modification; MWCNT; O-MWCNT; hydrodynamic chronoamperometry; hydrogen peroxide.

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## Introduction

Hydrogen-peroxide ( $\text{H}_2\text{O}_2$ ) represents an analyte often detected with carbon based electrodes because of its environmental, industrial and biological importance.  $\text{H}_2\text{O}_2$  has for long time been used in industrial and environmental applications as a powerful oxidant. It is a stronger oxidant than chlorine or permanganate and has the advantage of non-polluting decomposition products [1].  $\text{H}_2\text{O}_2$  is an essential compound in the textile, pulp and paper industry and in some areas of food and medicine [2]. A major application of  $\text{H}_2\text{O}_2$  is in advanced oxidation processes (AOP), which for example include Fenton's reaction, in order to remove pollutants from waste water [3].  $\text{H}_2\text{O}_2$  is product of numerous enzymatic reactions (when some oxidases are applied), and therefore monitoring of its concentration in biological systems is one of the key tasks. It is well known that its direct oxidation at carbon electrodes requires relatively high positive potentials, which in turn causes interferences to many other oxidizable components. Therefore, the main aim is to reduce the overpotential by incorporation a mediator / modifier to the electrode surface or into the electrode bulk [4].

As regards modifiers, especially mediators, it was demonstrated that various metal-oxides are suitable modifiers for both, carbon pastes and carbon inks, in order to prepare carbon paste electrodes (CPEs) and screen printed carbon electrodes (SPCEs). Frequently used metal-oxides are  $\text{MnO}_2$  [5-9],  $\text{Fe}_3\text{O}_4$  [10],  $\text{FeO}$  [11],  $\text{SnO}_2$ ,  $\text{CuO}$ ,  $\text{Fe}_2\text{O}_3$  [12], as well as oxides of platinum group metals. Thus, the electrocatalytic properties of  $\text{RuO}_2$  [4, 13],  $\text{RhO}_2$  [14] and  $\text{PdO}$ ,  $\text{OsO}_2$ ,  $\text{IrO}_2$  and  $\text{PtO}_2$  [15] were exploited in different biosensors for the determination of  $\text{H}_2\text{O}_2$ , glucose and other biologically important compounds. Beside of metal oxides, nowadays different carbon based materials, like carbon nanotubes (in its bare and modified forms), graphenes, as well as fullerenes play important role as modifiers in the contemporary electrode designs.

Carbon nanotubes (CNTs) represent an important group of nanoscale materials since 1991, when being discovered by Iijima [16]. The basic constitution of the nanotube lattice is the C-C covalent bond, as in layers of graphite. Therefore, CNTs are built from  $\text{sp}^2$ -carbon units and present a seamless structure with hexagonal honeycomb lattices, being several nanometers in diameter and many microns in length. As the actual electrode design, among others, there are two very popular groups of CNTs, the so-called multiwalled carbon nanotubes (MWCNTs) and singlewalled carbon nanotubes (SWCNTs), when the former are composed of concentric and closed graphite tubules, each with a rolled graphite sheet, whereas the SWCNTs are made of a single rolled graphite sheet.

Because of their special geometry and unique electronic, mechanical, chemical, and thermal properties, CNTs are nowadays largely used material for the designing of electrochemical sensors and biosensors [17-19].

Due to their properties, MWCNT in its bare or modified forms show electrocatalytic activity towards  $\text{H}_2\text{O}_2$ . In their presence the overvoltage for the oxidation and reduction of hydrogen peroxide significantly decreases [20]. One type of sensor for the determination of  $\text{H}_2\text{O}_2$  can be prepared easily and rapidly by mixing MWCNTs and mineral oil as binding component (so-called carbon nanotubes paste electrode (CNTPE)). The resulting CNTPE retains some properties of the classical carbon paste electrode (CPE) [20, 21]. CNTPE is also suitable for incorporation of different enzymes in composite matrix and therefore for design of highly sensitive biosensors which work is based on detection of  $\text{H}_2\text{O}_2$  as side product of enzymatic reaction [22].

A major problem for developing MWCNT-based sensors and biosensors is their low solubility in most solvents, so different strategies for immobilizing them on the surface of substrate electrodes have been proposed. There are reports for surface modification of glassy carbon electrode (GCE), for determination of  $\text{H}_2\text{O}_2$ , with dispersion of MWCNTs in *Nafion*<sup>®</sup> [23], polyethylenimine [24, 25], polylysine [26], carminic acid [27]. Sensitivity of sensors for  $\text{H}_2\text{O}_2$  can be improved by using MWCNTs in combination with some other components / modifiers. One example is a non-enzymatic amperometric sensor for  $\text{H}_2\text{O}_2$  fabricated by electrodeposition of MWCNTs and polyaniline along with platinum nanoparticles on the surface of a GCE [28]. GCE can be also modified with Ag/MWCNT composite which is prepared by direct electrodeposition of Ag nanoparticles on MWCNTs surface in presence of EDTA [29]. Suitable amperometric sensor for  $\text{H}_2\text{O}_2$  was developed using MWCNTs covalently immobilized with thionine via a carbodiimide reaction. The thionine functionalized MWCNTs were then abrasively transferred onto a paraffin impregnated graphite electrode followed by a coating of a thin film of nafion [30]. Additionally, gold electrode can be successfully modified with suspension of gold nanochains and *Prussian blue* nanorods, which are synthesized with MWCNTs as a template in order to improve analytical performance for  $\text{H}_2\text{O}_2$  determination [31].

The paper presented herein explores the possibilities and limitations of native and chemically oxidised multiwalled carbon nanotubes, MWCNTs and O-MWCNT, respectively, in the role of bulk modifiers in carbon paste electrodes for the hydrodynamic chronoamperometric determination of hydrogen peroxide,  $\text{H}_2\text{O}_2$ .

## Experimental

### *Chemicals, Reagents, Stock, and Standard Solutions*

All chemicals used were of analytical reagent grade and the solutions were prepared in doubly distilled water. The concentration of H<sub>2</sub>O<sub>2</sub> stock solution (p.a., Hemofarm, Vršac, Serbia) was 30%, and it was diluted daily as required. Phosphate buffer solution, pH 7.5, was prepared from the appropriate volumes of stock solutions containing 18.0 cm<sup>3</sup> 0.2 M sodium dihydrogenphosphate (NaH<sub>2</sub>PO<sub>4</sub>·H<sub>2</sub>O, p.a., Sigma-Aldrich) and 84.0 cm<sup>3</sup> 0.2 M disodium hydrogenphosphate (Na<sub>2</sub>HPO<sub>4</sub>·7H<sub>2</sub>O, p.a., Sigma-Aldrich) with the addition of 100.0 cm<sup>3</sup> water. Acetate buffer pH 4.5 – obtained by mixing of appropriate volumes of 0.1 M CH<sub>3</sub>COOH and 0.1 M CH<sub>3</sub>COONa·3H<sub>2</sub>O, while the borate buffer pH 9.18 – was prepared by dissolving of appropriate amount of Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>·10H<sub>2</sub>O in doubly distilled water (4.76 g in 250.0 cm<sup>3</sup>). MWCNTs were synthesized by catalytic chemical vapor deposition at 973 K from acetylene over MgO supported Fe, Co (2.5-2.5 % w/w) catalyst using nitrogen as carrier gas. The synthesized MWCNTs were functionalized by refluxing in conc. HNO<sub>3</sub> for 6 h.

### *Electrochemical Apparatus and Other Instrumentation*

The cyclic voltammetric and hydrodynamic chronoamperometric experiments were performed on an AUTOLAB PGSTAT12 electrochemical analyzer operated via GPES 4.9 software (Ecochemie, The Netherlands). The cell stand included a three-electrode system with a CPE and bulk modified MWCNT-CPEs (5 %, 10 %, and 5%O) as working, a saturated calomel electrode (SCE) (Amel, Italy) as reference, and a platinum (*ibid.*) auxiliary electrode. All potentials are quoted *vs.* SCE reference electrode.

Scanning electron microscopic (SEM) measurements were performed on scanning electron microscope JSM-6460LV (Japan Electron Optics Laboratory, Japan).

### *Preparation of MWCNT-CPEs*

The proper carbon paste-based mixtures were prepared by thoroughly hand-mixing of 0.5 g graphite powder (RW-B type, Ringsdorff, Germany) with 0.2 cm<sup>3</sup> of highly paraffin oil (Pliva, Croatia) and appropriate amount of MWCNTs (5 %, 10 %, and 5%O) (MWCNT-CPEs). All components had been milled manually until the optimal consistency was obtained. The prepared pastes were packed into the piston-driven holders [32] with the surface diameter of 2 mm, thus accomplishing the final CPE configuration.

Whenever needed, the electrode surface was renewed mechanically – by wiping the used carbon paste layer off and by smoothing the new one with a soft tissue.

### ***Measurements and Related Procedures***

#### *Voltammetric Measurements*

*Cyclic Voltammetry (CV).* Basic characterisation of the 5%MWCNT-CPE and 10%MWCNT-CPE was carried out in three different test buffer solutions (acetate, phosphate and borate at pHs 4.5; 7.5 and 9.2) of  $\text{Fe}(\text{CN})_6^{3-/4-}$  by potential cycling from 0.8 to  $-0.8$  V vs. sat. calomel electrode and reversely; typically, with scan rate:: 25, 50, 75, 100, 200, and 300 mV s<sup>-1</sup>.

*Hydrodynamic chronoamperometry.* Four electrodes, CPE and three different bulk modified MWCNT-CPEs (5%, 10%, and 5%O) were compared for H<sub>2</sub>O<sub>2</sub> determination. The investigated working potentials covered the range from 0.6 V to 1.0 V and from -0.8 V to -1.0 V in steps of 0.1 V, while the analyte concentrations were from 44  $\mu\text{g cm}^{-3}$  to 211  $\mu\text{g cm}^{-3}$ , from 44  $\mu\text{g cm}^{-3}$  to 251  $\mu\text{g cm}^{-3}$ , and from 44  $\mu\text{g cm}^{-3}$  to 170.62  $\mu\text{g cm}^{-3}$  for 5%MWCNT-CPE, 5% O-MWCNT-CPE and 10% MWCNT-CPE, respectively. All measurements were carried out in three different buffer solutions as the supporting electrolytes: acetate, phosphate, and borate at pH 4.5, 7.5, and 9.2, respectively.

#### ***Scanning Electron Microscopic Measurements***

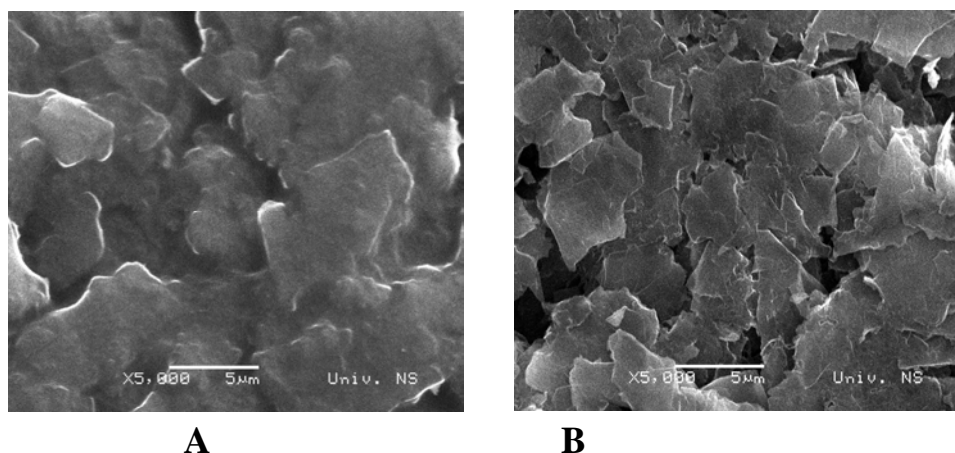
*SEM study of 5%MWCNT-CPE and 10%MWCNT-CPE.* The bulk modified carbon paste electrodes containing two different amounts of MWCNT were examined on a Jeol scanning electron microscope (JSM-6460LV) with an accelerating voltage of 20 kV in low vacuum mode, at the working distance of 20 mm of the targets. The measurements were performed directly without any specific surface pretreatment.

## **Results and Discussion**

### **SEM Characterisation of MWCNT-CPE at different amount of the modifier**

As first, SEM measurements were performed for characterisation of 5%MWCNT-CPE and 10%MWCNT-CPE sensor surfaces (Fig. 1). In both cases, the carbon matrix was formed from paraffin oil and particles of graphite powder of uniform size (5  $\mu\text{m}$ ) which build typical paste particle units, recognizable on the surfaces morphology.

In the case of the micrograph obtained for representative surface area of 5%MWCNT-CPE (Fig. 1A) the basic units are related to each other and build a compact mass of electrode body, while in the case of higher amount of incorporated modifier (10%MWCNT-CPE, Fig. 1B) the basic units are bounded into the paste matrix with less adhesion which can be reflected on the effective dimension of the surface area and on the resistance of the electrode.



**Fig. 1:** Scanning electron micrographs of 5%MWCNT–CPE (A) and 10 %MWCNT-CPE (B) surfaces at magnification of 5000 times.

Based on the micrographs, the different level of association of the basic units in the case of two pastes gave rise to the main difference between 5%MWCNT-CPE and 10%MWCNT-CPE surface morphology, which is also evident from the different macroscopic consistence of the two pastes.

### **Voltammetric Characterisation and Application of 5% MWCNT-CPE**

Cyclic voltammograms obtained in model solution of  $\text{Fe}(\text{CN})_6^{3-/4-}$  showed that different puffer solutions and different pH values influenced the reversibility of the electrode redox process (based on the obtained  $\Delta E_p$  values) on the same electrode (5%MWCNT-CPE). Fig. 2 represents cyclic voltammograms of  $\text{Fe}(\text{CN})_6^{3-/4-}$  obtained at 5%MWCNT-CPE in acetate (A), phosphate (B) and borate (C) buffer solutions as supporting electrolytes. Based on recorded cyclic voltammograms, correlation equations between anodic / cathodic peak intensities and square root of scan rates ( $I_{p,a} \cdot v^{1/2}$  and  $I_{p,c} \cdot v^{1/2}$ ) were constructed. The plots of  $I_{p,a}/I_{p,c}$  versus  $v^{1/2}$  are linear in all three buffer solutions, indicating that the process is diffusion controlled. Basic electrochemical parameters of these correlations are present in the Table I.

**Table I.** Electrochemical characterization of 5%MWCNT-CPE based on cyclic voltammograms of  $Fe(CN)_6^{3-/4-}$  ( $c = 4.76 \cdot 10^{-4}$  M) obtained in acetate, phosphate and borate buffer solutions (pH 4.5, 7.5 and 9.2, respectively).

pH	Anodic process		Cathodic process	
	Equation	r	Equation	r
4.5	$I_p = 2.3[\mu A] + 0.8[\mu A(s\ mV^{-1})^{1/2}] v^{1/2}$	0.999	$I_p = -2.7[\mu A] - 0.7[\mu A(s\ mV^{-1})^{1/2}] v^{1/2}$	-0.999
7.5	$I_p = -3.9[\mu A] + 1.2[\mu A(s\ mV^{-1})^{1/2}] v^{1/2}$	0.985	$I_p = -2.6[\mu A] - 0.4[\mu A(s\ mV^{-1})^{1/2}] v^{1/2}$	-0.982
9.2	$I_p = -0.4[\mu A] + 0.5[\mu A(s\ mV^{-1})^{1/2}] v^{1/2}$	0.985	$I_p = -1.8[\mu A] - 0.3[\mu A(s\ mV^{-1})^{1/2}] v^{1/2}$	-0.993

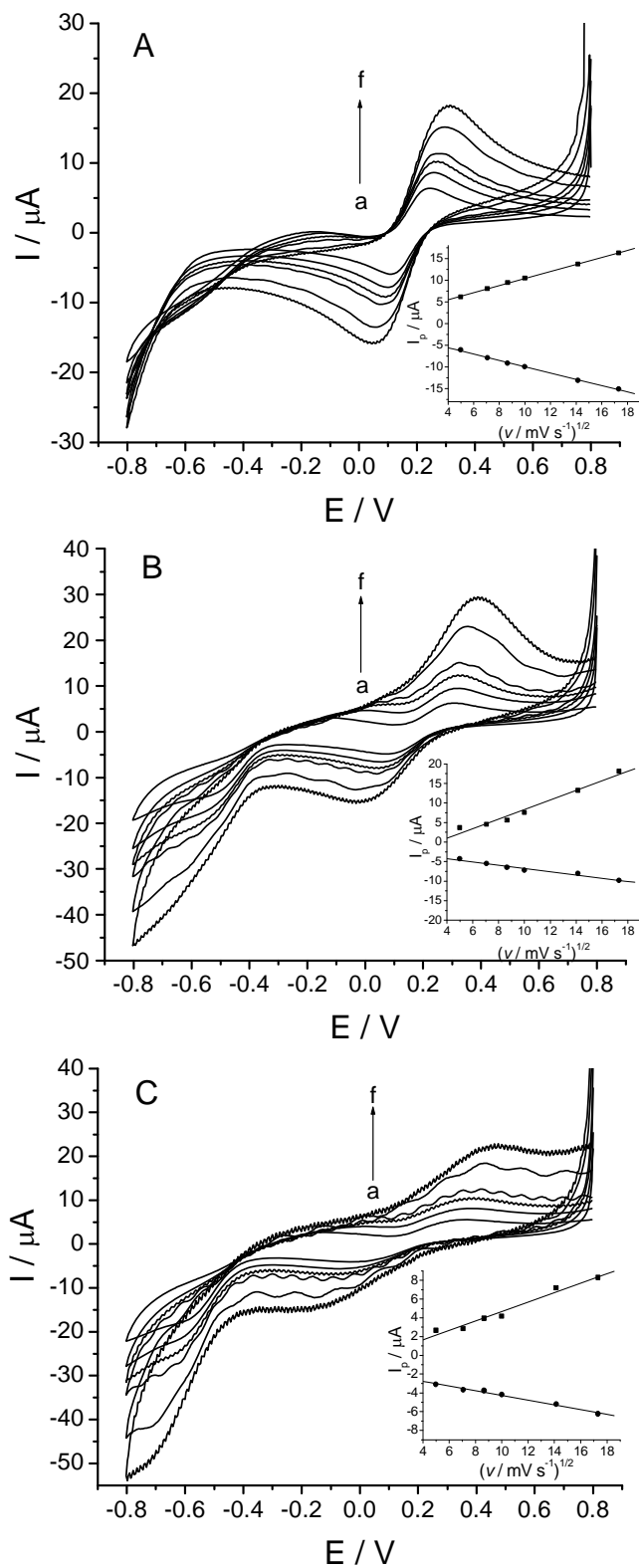
After electrochemical characterisation by cyclic voltammetry, 5%MWCNT-CPE was tested for hydrodynamic chronoamperometric determination of  $H_2O_2$  (Fig. 3). Hydrodynamic chronoamperometric responses obtained at the same experimental conditions, by injecting the appropriate volumes of  $H_2O_2$  solution into the acetate, phosphate and borate buffer supporting electrolyte, were compared. The applied working potentials were in the range from 0.6 to 1.0 V and -0.8 to -1.0 V, and typical hydrodynamic chronoamperometric signals of  $H_2O_2$  together with appropriate calibration curves (insets) are shown in Fig. 3. As can be seen, the electrode response depends on pH value of supporting electrolyte and working potential.

In the positive potential range, the most intensive signals of  $H_2O_2$  were obtained in borate buffer solution pH 9.2, but in negative potential range there are no characteristic staircase signals of  $H_2O_2$  analyte. In acetate and phosphate buffer, hydrodynamic chronoamperometric signals of  $H_2O_2$  are more than 5× higher at negative working potentials than at positive ones. Although, the analytical signals of  $H_2O_2$  are more intensive in negative potential range, the noise is higher at such polarisations of the electrode. Selected parameters of hydrodynamic chronoamperometric determination of  $H_2O_2$  at 0.7 V and -0.8 V by 5%MWCNT-CPE in acetate, phosphate and borate buffer solutions are elaborated in Table II.

Comparison of the hydrodynamic chronoamperometric signals of  $H_2O_2$  obtained at 0.7 V in phosphate buffer solution on 5%/MWCNT-CPE with those obtained by bare CPE (not shown here), the signal intensities are 2.5 times higher for modified one, which additionally confirmed the need of such type of carbon paste electrode modifications.

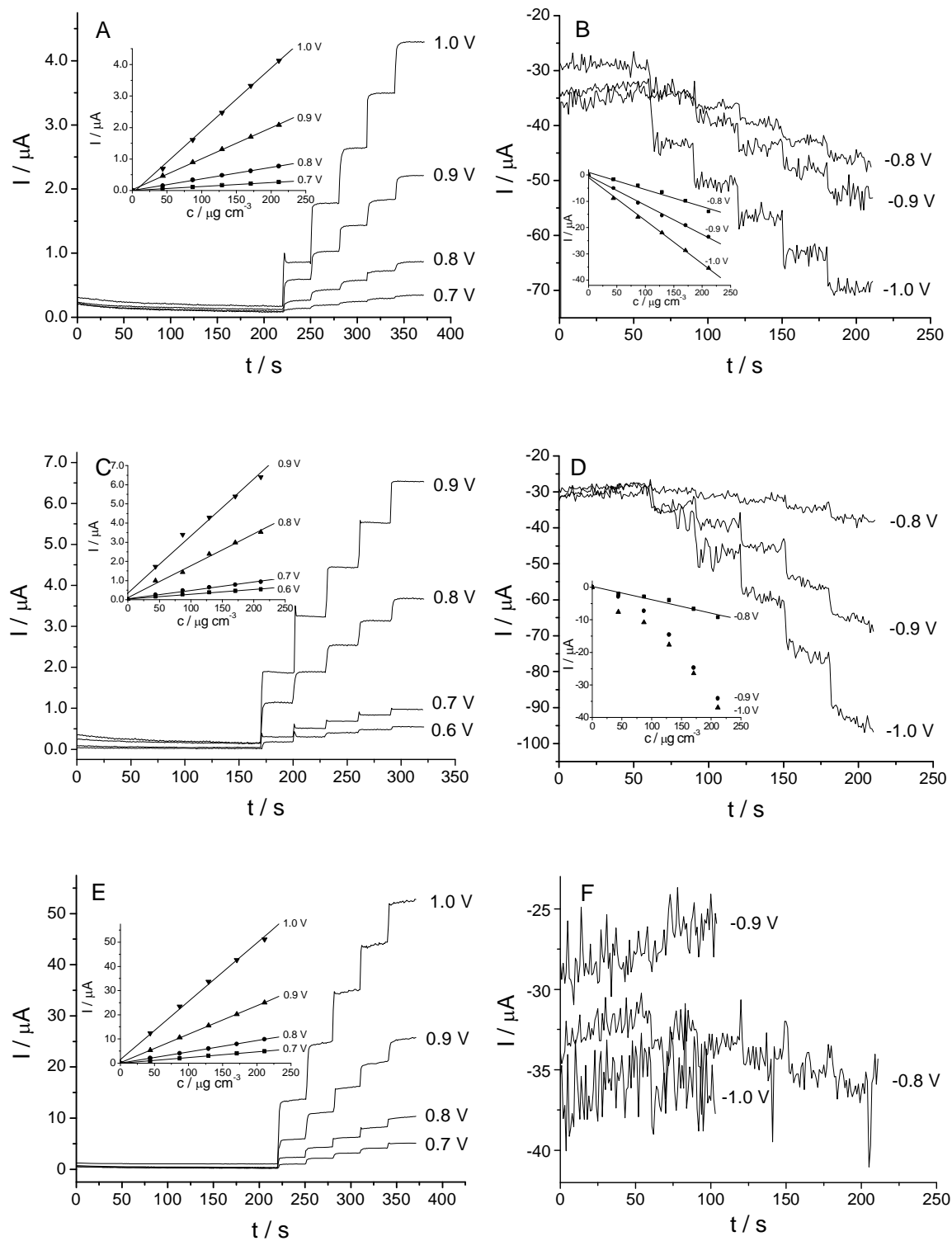
### Voltammetric Application of 5%O-MWCNT-CPE

The applicability of 5%O-MWCNT-CPE for hydrodynamic chronoamperometric determination of  $H_2O_2$  was investigated, and the representative signals are shown in Fig. 4. They are more intensive compared with signals obtained at 5%MWCNT-CPE, but their shape



**Fig. 2:** Cyclic voltammograms of  $Fe(CN)_6^{3-/4-}$  ( $c = 4.76 \cdot 10^{-4} M$ ) test system obtained at 5%MWCNT-CPE in acetate buffer pH 4.5 (A), phosphate buffer pH 7.5 (B) and borate buffer pH 9.2 (C) solutions with appropriate  $I_p-v^{1/2}$  correlations (insets). Scan rates (from a to f): 25, 50, 75, 100, 200 and 300  $mV s^{-1}$ .





**Fig. 3:** Hydrodynamic chronoamperometric signals of  $H_2O_2$  obtained at 5% MWCNT-CPE at positive (A, C, E) and negative (B, D, F) working potentials in acetate buffer pH 4.5 (A, B), phosphate buffer pH 7.5 (C, D) and borate buffer pH 9.2 (E, F) solutions and appropriate calibration curves (insets).

indicates that the O-MWCNT modifier is not the favored one in the acetate (positive and negative polarisations) and borate (negative polarisations) buffer solutions. In the case of phosphate buffer solutions pH 7.5 the staircase signals showed high sensitivity of the electrode to H<sub>2</sub>O<sub>2</sub> analyte, see in Table III.

**Table II:** Selected analytical parameters of hydrodynamic chronoamperometric determination of H<sub>2</sub>O<sub>2</sub> at 0.7 V and -0.8 V by 5%MWCNT-CPE in acetate, phosphate and borate buffer solutions (pH 4.5, 7.5 and 9.2, respectively).

pH	0.7 V		-0.8 V	
	Equation	r	Equation	r
4.5	$I = 4.9[\text{nA}] + 1.3[\text{nA } \mu\text{g}^{-1}\text{cm}^3] c$	0.999	$I = 1.0[\mu\text{A}] - 0.07[\mu\text{A } \mu\text{g}^{-1}\text{cm}^3] c$	-0.986
7.5	$I = 0.05[\mu\text{A}] + 0.004[\mu\text{A } \mu\text{g}^{-1}\text{cm}^3] c$	0.993	$I = 0.3[\mu\text{A}] - 0.04[\mu\text{A } \mu\text{g}^{-1}\text{cm}^3] c$	-0.979
9.2	$I = -0.07[\mu\text{A}] + 0.02[\mu\text{A } \mu\text{g}^{-1}\text{cm}^3] c$	0.999	-	-

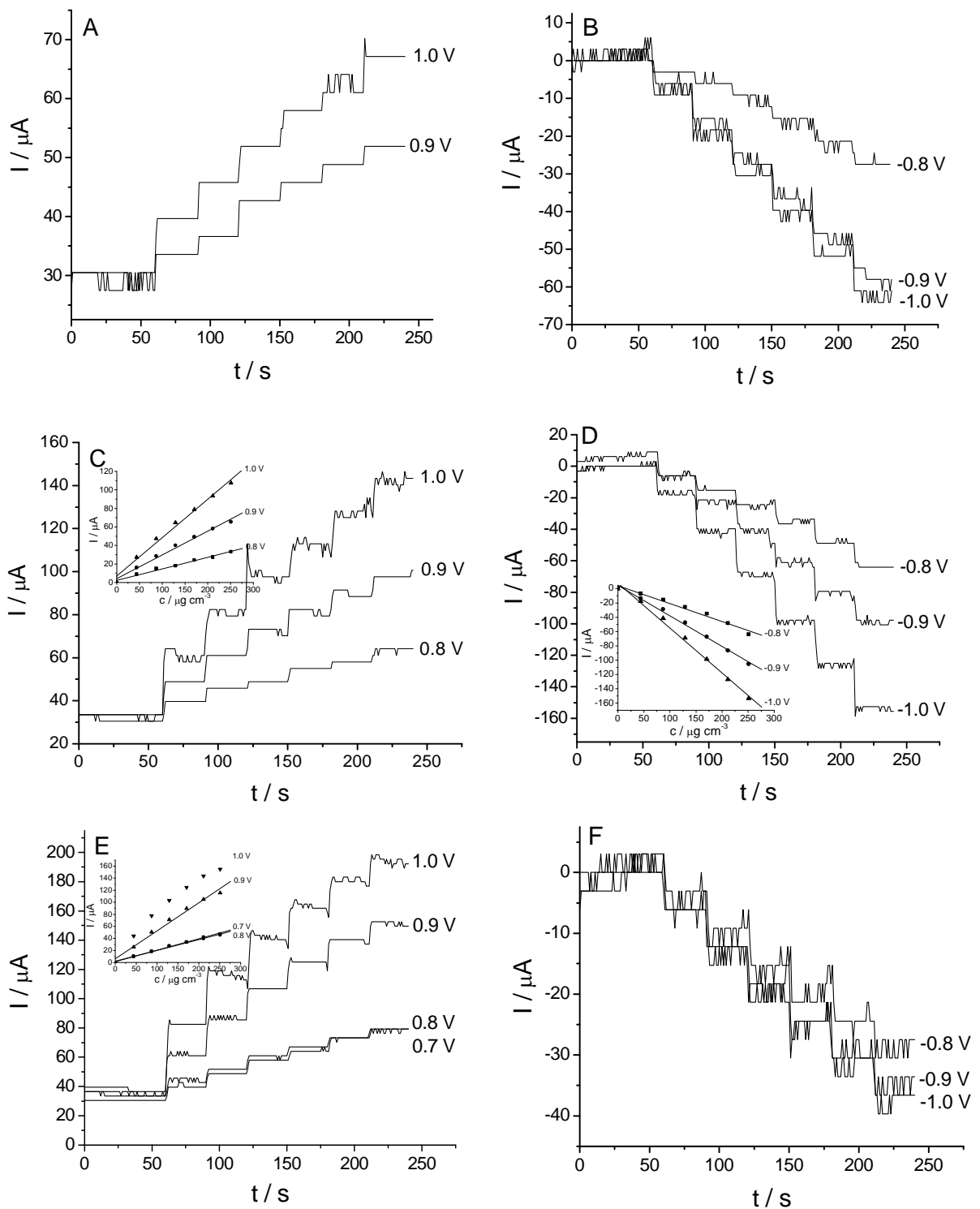
**Table III:** Selected analytical parameters of hydrodynamic chronoamperometric determination of H<sub>2</sub>O<sub>2</sub> at 0.8 V and -0.8 V by 5%O-MWCNT-CPE in acetate, phosphate and borate buffer solution (pH 4.5, 7.5 and 9.2, respectively).

pH	E <sub>amp</sub> = +0.8 V		E <sub>amp</sub> = -0.8 V	
	Equation	r	Equation	r
4.5	-	-	-	-
7.5	$I = 2.3 [\mu\text{A}] + 0.1[\mu\text{A } \mu\text{g}^{-1}\text{cm}^3] c$	0.992	$I = 4.0[\mu\text{A}] - 0.2[\mu\text{A } \mu\text{g}^{-1}\text{cm}^3] c$	-0.989
9.2	$I = 2.2 [\mu\text{A}] + 0.2[\mu\text{A } \mu\text{g}^{-1}\text{cm}^3] c$	0.996	-	-

Probably, with the fine tuning of oxide layer quality on MWCNT surface during the chemical oxidation with conc. HNO<sub>3</sub> or other oxidation agents it will be possible to prepare working electrode modifier with appropriate performances for trace level determination of H<sub>2</sub>O<sub>2</sub>.

### Voltammetric characterisation and application of 10%MWCNT-CPE

As first, the electrochemical characterisation of 10%MWCNT-CPE was performed by cyclic voltammetry in the presence of Fe(CN)<sub>6</sub><sup>3-/4-</sup> test system in three different buffer solutions: acetate, phosphate and borate (Fig. 5).



**Fig. 4:** Hydrodynamic chronoamperometric signals of  $H_2O_2$  obtained at 5%O-MWCNT-CPE at positive (A, C, E) and negative (B, D, F) working potentials in acetate buffer pH 4.5 (A, B), phosphate buffer pH 7.5 (C, D) and borate buffer pH 9.2 (E, F) solutions and appropriate calibration curves (insets).

Signals obtained at this electrode are with higher intensity, but the reversibility of the redox process (based on the obtained  $\Delta E_p$ ) is higher in the case of 5%MWCNT-CPE. Additionally, better linearity of the plots of  $I_{p,a}/I_{p,c}$  versus  $v^{1/2}$  is obtained when the CPE with lower amount of MWCNT was applied. Electrochemical characterisation of 10%MWCNT-CPE is shown in the Table IV.

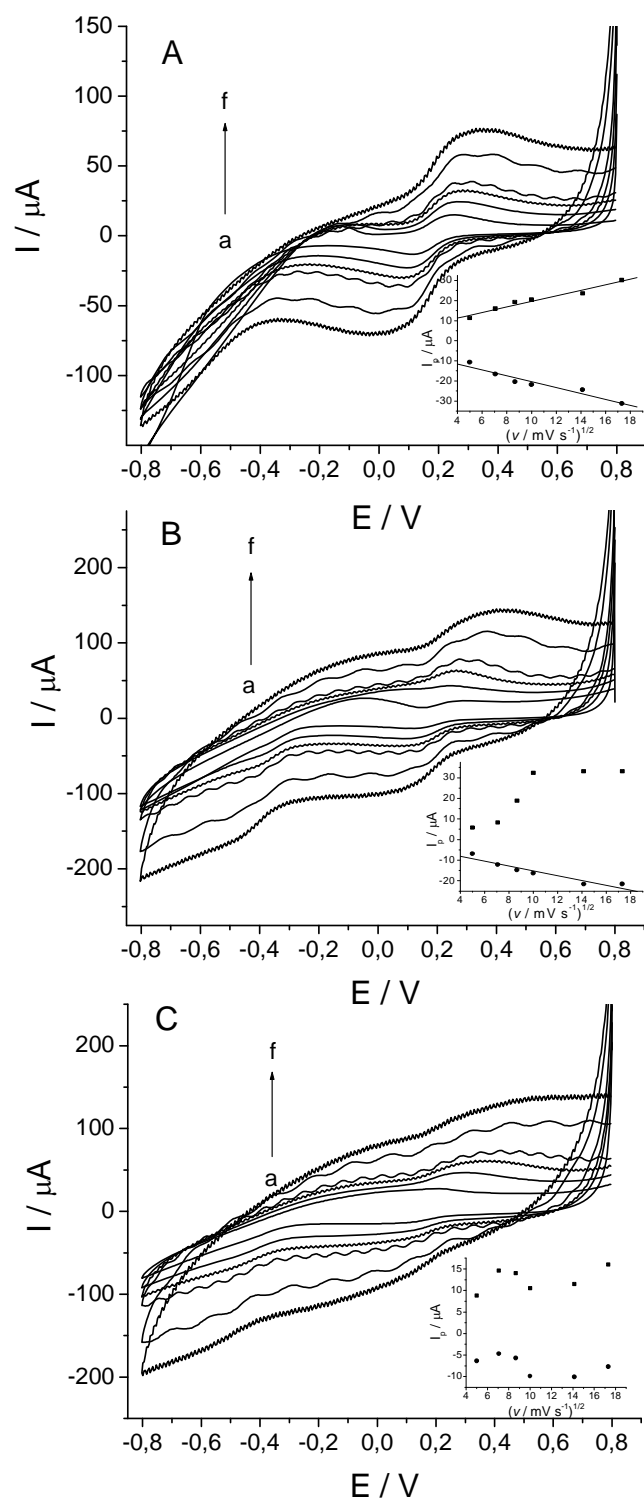
**Table IV:** *Electrochemical characterization of 10%MWCNT-CPE based on cyclic voltammograms of  $Fe(CN)_6^{3-/4-}$  ( $c = 4.76 \cdot 10^{-4} M$ ) obtained in acetate, phosphate and borate buffer solutions (pH 4.5, 7.5 and 9.2, respectively).*

pH	Anodic process		Cathodic process	
	Equation	r	Equation	r
4.5	$I_p = 5.8[\mu A] + 1.4[\mu A(s\ mV^{-1})^{1/2}] v^{1/2}$	0.980	$I_p = -5.7[\mu A] - 1.5[\mu A(s\ mV^{-1})^{1/2}] v^{1/2}$	-0.965
7.5	$(I_p = -3.1[\mu A] + 2.4[\mu A(s\ mV^{-1})^{1/2}] v^{1/2})$	(0.865)	$I_p = -3.4[\mu A] - 1.2[\mu A(s\ mV^{-1})^{1/2}] v^{1/2}$	-0.948
9.2	-	-	-	-

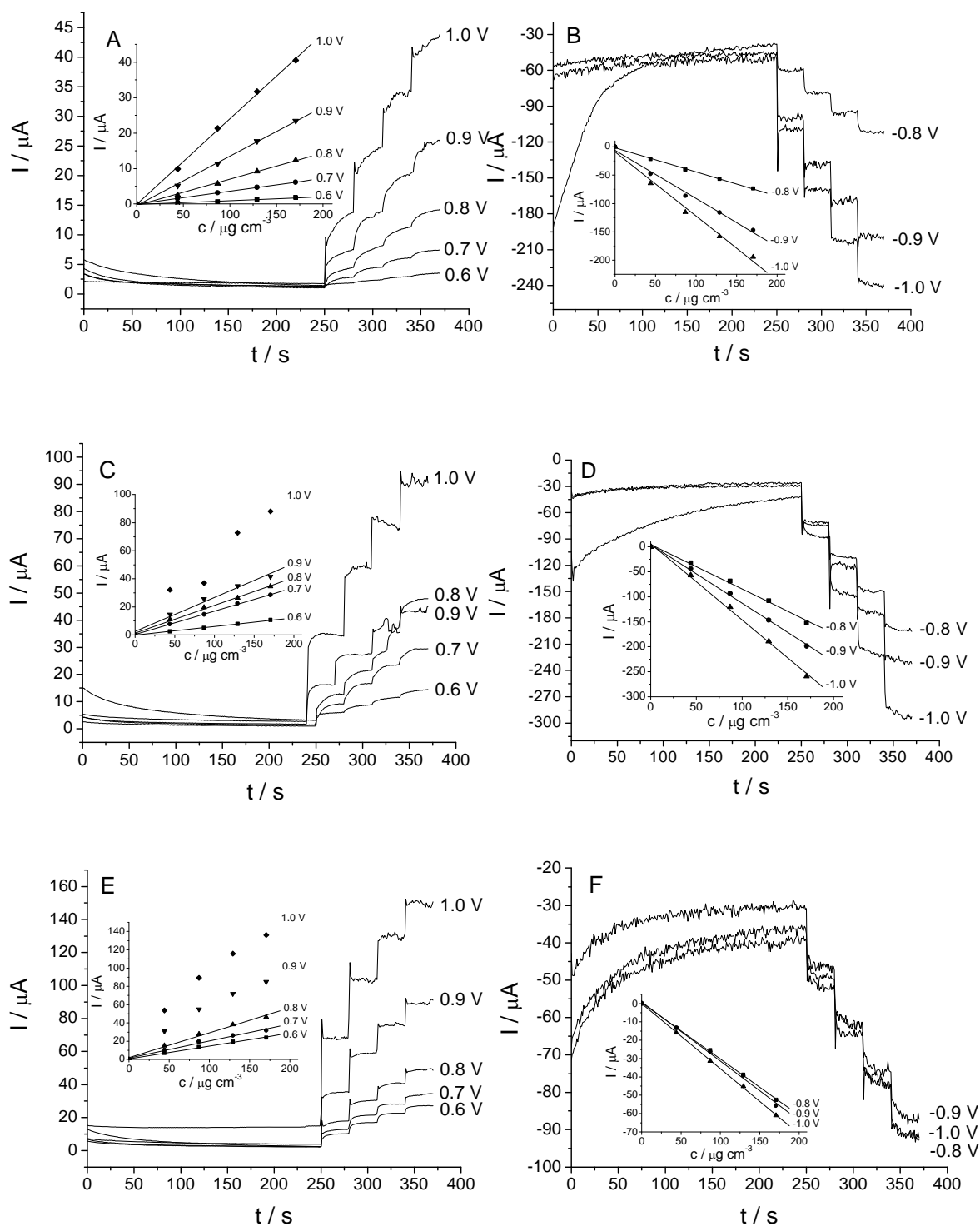
Hydrodynamic chronoamperometric signals of  $H_2O_2$  obtained at 10%MWCNT-CPE in acetate, phosphate and borate buffer solutions are shown in Fig. 6, and some selected analytical parameters are presented in Table 5. As can be expected, based on previously recorded cyclic voltammograms for  $Fe(CN)_6^{3-/4-}$  model solutions at different pHs, the  $H_2O_2$  signals are more intensive in comparison with 5%MWCNT-CPE, but the steps have not exact staircase form in all investigated systems (making it difficult to evaluate the data). In the case of acetate and phosphate buffer solutions, signals of  $H_2O_2$  are up to 10 times higher, and in the case of borate buffer solution as supporting electrolyte, signals are about 2 times higher in comparison with signals obtained on 5%MWCNT-CPE in parallel systems. Further investigations are planned to get deeper insight into the behavior of the 10%MWCNT-CPE electrode in the case of  $H_2O_2$  determination.

Comparing the cyclic voltammetric and hydrodynamic chronoamperometric results obtained on 10%MWCNT-CPE with those obtained by 5%MWCNT-CPE it can be concluded that different amounts of MWCNT influenced the voltammetric responses of the bulk modified carbon paste electrodes.

Further experiments are planned for the optimisation of MWCNT-CPE preparation in its bulk- and surface modified configurations for highly sensitive determination of  $H_2O_2$ , as well as other target analytes.



**Fig. 5:** Cyclic voltammograms of  $\text{Fe}(\text{CN})_6^{3-/4-}$  ( $c = 4.76 \cdot 10^{-4} \text{ M}$ ) test system obtained at 10%MWCNT-CPE in acetate buffer pH 4.5 (A), phosphate buffer pH 7.5 (B) and borate buffer pH 9.2 (C) solutions with appropriate  $I_p-v^{1/2}$  correlations (insets). Scan rates (from a to f): 25, 50, 75, 100, 200 and  $300 \text{ mV s}^{-1}$ .



**Fig. 6:** Hydrodynamic chronoamperometric signals of  $H_2O_2$  obtained at 10%MWCNT-CPE at positive (A, C, E) and negative (B, D, F) working potentials in acetate buffer pH 4.5 (A, B), phosphate buffer pH 7.5 (C, D) and borate buffer pH 9.2 (E, F) solutions and appropriate calibration curves (insets)

**Table V:** Selected analytical parameters of hydrodynamic chronoamperometric determination of  $H_2O_2$  at 0.7 V and -0.8 V by 10%MWCNT-CPE in acetate, phosphate and borate buffer solutions (pH 4.5, 7.5 and 9.2, respectively).

pH	$E_{amp} = +0.7$ V		$E_{amp} = -0.8$ V	
	Equation	r	Equation	r
4.5	$I = -0.04[nA] + 0.04[nA \mu g^{-1} cm^3] c$	0.999	$I = -1.7[\mu A] - 0.4 [\mu A \mu g^{-1} cm^3] c$	-0.999
7.5	$I = 0.2[\mu A] + 0.2[\mu A \mu g^{-1} cm^3] c$	0.999	$I = 4.7[\mu A] - 0.9 [\mu A \mu g^{-1} cm^3] c$	-0.997
9.2	$I = 1.6[\mu A] + 0.1[\mu A \mu g^{-1} cm^3] c$	0.993	$I = 0.4[\mu A] - 0.3 [\mu A \mu g^{-1} cm^3] c$	-0.999

## Conclusions

Initial measurements were performed at carbon paste electrodes (graphite/paraffin oil), bulk-modified with multiwalled carbon nanotubes (MWCNT) and chemically oxidized MWCNT (O-MWCNT), for the hydrodynamic chronoamperometric determination of hydrogen-peroxide in different buffer solutions from acidic to basic media.

Based on the type and amount of incorporated MWCNT-based modifiers different properties of the sensors are obtained. In prospect, further experiments are planned and the respective tests should include the optimisation of MWCNT-CPE preparation, as well as a deeper insight into the voltammetric behavior and applicability of the MWCNT-based carbon paste electrodes.

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