

## CARBON NANOTUBES BASED SENSOR FOR HEAVY METALS DETECTION

**Jan Prasek<sup>1</sup>, Martin Adamek<sup>1</sup>, Lukáš Fujcik<sup>1</sup>, Edgar Sotter<sup>2</sup>, Eduard Llobet<sup>2</sup>,  
Carla Bittencourt<sup>3</sup>, Alexandre Felten<sup>3</sup>, Jean-Jacques Pireaux<sup>3</sup>**

1. Dept. of Microelectronics, Brno University of Technology, Udolní 53, 60200 Brno, Czech Republic, phone: + 420 541 146 136, email: prasek@feec.vutbr.cz
2. Dept. Enginyeria Electrònica Elèctrica i Automàtica, Universitat Rovira i Virgili, Avd. Països Catalan 26, 43007 Tarragona, Spain, phone: +34 977 558 502, email: esotter@urv.net
3. LISE, Facultés Universitaires Notre Dame de la Paix, B-5000 Namur, Belgium

*An area of miniature electrochemical sensors for measurement in liquid solutions is described in this paper. The aim of this work is a development of a sensor for trace determination of heavy metals that are dissolved in water solution. A new amperometric sensor substrate was developed to be suitable for measurement using different working electrode material. The sensor is realized using thick film technology. There was prepared several different carbon nanotubes based working electrode materials and deposited on the sensor substrate in this work. All the sensors were measured using cadmium chloride sample solution addition into a potassium chloride buffer solution. Finally the output current response and calibration curves of each sensor are compared and discussed with each other and with graphite based pastes from our previous work.*

**Keywords:** carbon nanotubes, thick film sensor, heavy metals, analysis

### 1. INTRODUCTION

Trace determination of species in living environment is very important in many areas. One group of the species is the group of pollutants that needs to be detected in many branches. Nowadays there are many possibilities of detection of these pollutants and many companies pay much money for research in this field.

One group of the pollutants included in living environment is the group of heavy metals. Heavy metals are very toxic for human life and therefore they need to be monitored in many branches mainly in food industry. Heavy metals are usually reproducible and reliable monitored with use of toxic mercury drop electrodes. One of the possibilities for ecological measurement of heavy metals is use of solid electrodes [1]. These solid electrodes can be integrated into small sensor systems that could be fabricated using thick film technology (TFT) process. At the beginning the TFT was focused on the production of hybrid integrated circuits [2]. The basic use of thick film technology was in the production of special integrated circuits, small series of nonstandard integrated circuits and prototypes [3]. Nowadays the TFT was shifted into the area of nonconventional applications because of its substitution by improved SMT in its original use. The advantage of TFT sensors are low dimensions, good reproducibility, mechanical and electrical properties of electrodes and well accessible and ecological fabrication process [4]. The crucial advantage is low cost of the electrodes (e.g. platinum electrode containing 1 mg of Pt) that enables to use the

electrodes for few numbers of analysis only and high variability of used materials. These materials do not use classical metals only (Pt, Au, Ag) but it is possible to prepare semi-conductive materials, magnetic electrodes and finally it is possible to ensure reproducible nanostructure of electrodes [5], [6]. The aim of this work is to design and compare some carbon based materials of working electrodes that can be screen-printed or drop-coated with possibility of sufficient and reproducible detection limit for heavy metals and with good mechanical properties. For this purpose was designed a special TFT sensor substrate that is suitable for working electrode material varying with eventual possibility of use of different electrochemical systems.

## 2. SENSOR SUBSTRATE DESIGN AND FABRICATION

### 2.1 Design

As a base substrate for electrode material properties measurement a thick film amperometric sensor substrate was designed and presented [7]. The basic shape of the sensor and its' electrode arrangement is shown in figure 1. This sensor uses Ag based paste as a contact material. The reference electrode material is Ag based paste electrochemically covered by AgCl layer [8] after the main sensor fabrication process. Auxiliary electrode material is also Ag based paste. The material of each electrode can be changed by use of other type of paste. The working electrodes materials used for our experiments are described in section below.

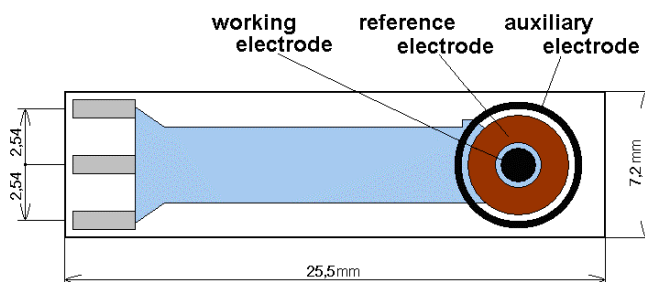


Fig. 1: Thick film amperometric sensor design.

The main advantage of this solution is a possibility of working electrode material change during the fabrication process and compatibility with electrochemical analytical devices – Micro Flow System [9] and Rotating Vessel [10] that are commonly used in our laboratory to ensure the reproducible conditions during the measurement by reproducible stirring.

### 2.2 Fabrication

The TFT amperometric sensor was fabricated (fig. 2) using a standard TFT process. The TFT materials used for electrodes and conductive layer was ESL 9912-D paste and for dielectric layer ESL 4913-G paste.

The next fabrication process was deposition of AgCl layer on the TFT silver reference electrode. The layer was made by electrochemical reoxidation by an anodic

potential sweep in 0,2M KCl solution at pH 2 (acidified with HCl) [8]. The reference electrode area of the sensor covered by AgCl layer is shown in the figure 3.



Fig. 2: The TFT amperometric sensor with graphite working electrode without AgCl layer deposited over the reference electrode.

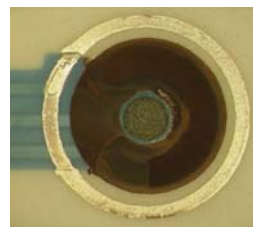


Fig. 3: Detail of the electrode part of the sensor with deposited AgCl layer on the reference electrode.

### 3. WORKING ELECTRODES MATERIAL PREPARATION

In our previous work [11] were made several graphite based pastes that were deposited onto the TFT amperometric substrate and tested for detection of heavy metals. A 0,01M  $\text{CdCl}_2$  solution was used as a measuring sample an added into the 10ml 1M KCl buffer solution. The obtained results – the sensitivity and detection limit – were not very satisfied and therefore was decided to do some test with use of carbon nanotubes based TFT pastes.

Eight different funtionalised pastes containing multi wall nanotubes (MWNT) [12] were prepared. The MWNTs were approximately 50  $\mu\text{m}$  long, their inner diameters range is between 2 and 7 nm, their outer diameters between 3 and 15 nm, and they had a purity superior to 60 %. These data were indicated by the provider (NAMUR, Belgium).

#### *Paste type N1*

Not funtionalised MWNTs

#### *Paste type N2*

MWNTs with 10%  $\text{O}_2$  at the surface

#### *Paste type N3*

MWNTs with 20%  $\text{O}_2$  at the surface

#### *Paste type N4*

MWNTs with 20%  $\text{O}_2$  + Co + Fe + Al at the surface

#### *Paste type NA*

MWNTs - Plasma AA - 15min at 15W

#### *Paste type NB*

MWNTs - Ferrocene - 15min at 15W

#### *Paste type NC*

MWNTs - Ferrocene - 5min at 50W

#### *Paste type ND*

MWNTs - Plasma AA - 30min at 50W

The depositing pastes were prepared by dispersing MWNTs in glycerol (25 $\mu\text{g}$  in 1ml). The problem was that these pastes are not suitable for screen printing. Therefore they were drop-coated using precision drop-coating equipment (JBE1113 Dispenser, I&J FISNAR Inc., USA). A drop-coating method was employed for the deposition of MNWTs over the sensors Ag working electrode on the test substrate (fig. 1) and dried at 125 $^\circ\text{C}$  for 15 minutes. An example of the deposited layer is in the figure 4.

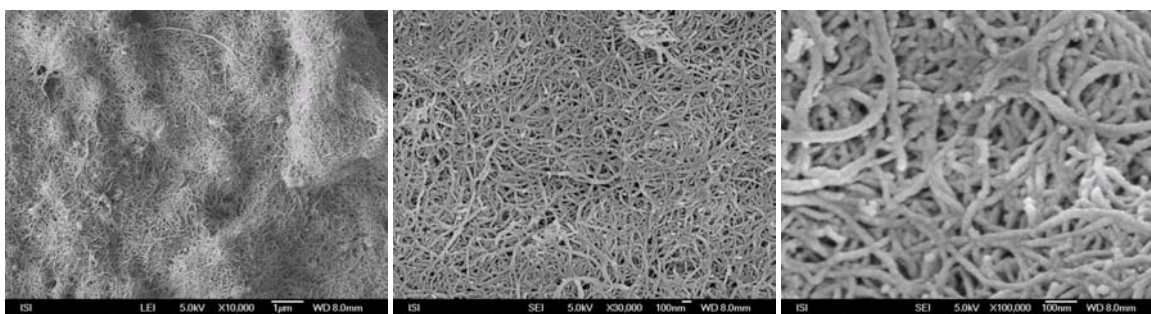


Fig. 4: SEM paste type NA analysis.

#### 4. CHEMICALS

The buffer solution used for measurement was 10ml 1M KCl. As a heavy metal sample was used 0,01M CdCl<sub>2</sub>. All the chemicals were used as received.

#### 5. EXPERIMENTAL METHOD

All the measurements were done using Polarographic analyzer PA4 device (Laboratorni pristroje Prague, Czech Republic) in two electrodes system using a stirred cell and a classical Ag/AgCl reference electrode. The stirring was ensured using a buffer solution bubbling by NO<sub>2</sub>.

The measurement method was differential pulse voltammetry in range of potential from 0 to -1,1V with scan rate of 10mV/sec.

#### 6. RESULTS AND DISCUSSION

All the measurements were done using method and arrangement mentioned above - additions of 0,01M CdCl<sub>2</sub> into 10ml of 1M KCl buffer solution.

In the figure 5, there are shown examples of the nanotubes based sensors current responses to heavy metals additions.

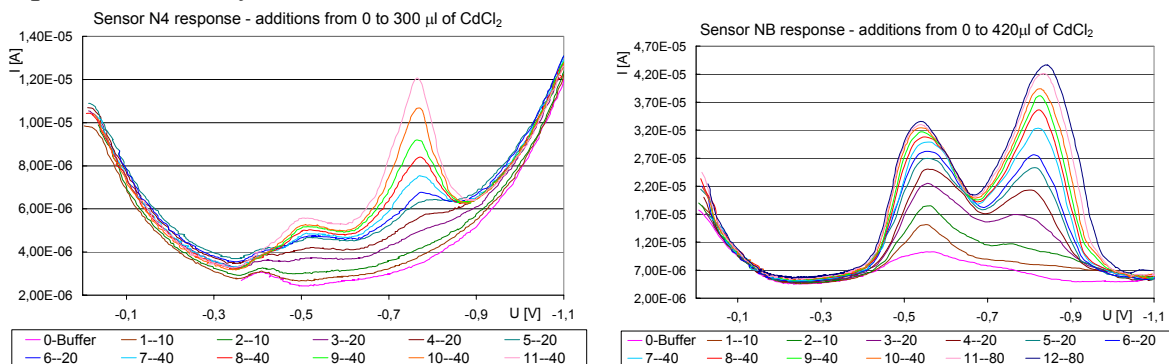


Fig. 5: Examples of sensor type N4 (left) and sensor type NB (right) output current responses to additions of 0,01M CdCl<sub>2</sub>. The units of amount of CdCl<sub>2</sub> additions mentioned in legends are µl.

From the plots of sensors current responses it is obvious that the current response of the best sensor from set N1-N4 is four time lover than the current response of the best sensor from newer set NA-ND. It increases the sensitivity of the sensor but it would be a problem for such potentiostats that do not have the possibility of current offset (than the measurement has to be done at low sensitivity degree and the current

change with heavy metals additions is not visible). This problem can be solved by use of buffer solution with lower conductivity (e.g. 0,1M KCl).

The correspondent current responses were red in the peak maximums of measured curves and plotted out into a calibration curve. The achieved calibration curves of all measured sensors (only for sensors with visible response to heavy metals additions) were plotted out into the calibration curves graph (fig. 6).

The graph of achieved calibration curves for all measured sensors is shown in the figure 5. The current peak values were recounted into current density because of different electrodes dimensions for better evaluation and comparison. The dimensions differences are caused by different working electrode fabrication process.

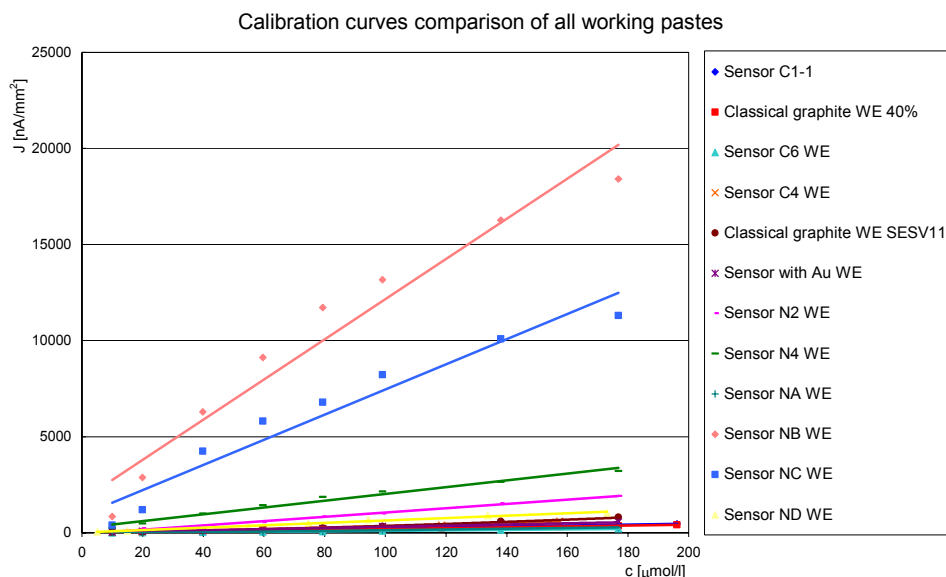


Fig. 6: The comparison of calibration curves of all measured types of sensors.

From the figure 6 it is obvious that the responses of some sensors based on carbon nanotubes (Nx type) are much better than the sensors based on graphite (Cx) that was measured in our previous work [11]. This material also has much better response than the sensor with gold working electrode and classical commercial graphite electrode SESV11 (Electrochemical Detectors, Trutnov, Czech Republic) which has four times larger working electrode area than Nx type sensor. The achievable detection limit with sensors Nx type is  $5 \cdot 10^{-6}$  mol/l. This limit could be increased by the electrochemical cell modification or by the change of measurement method. Main problem of nanotubos based sensors are the mechanical properties of the working electrode layer. Therefore it is necessary to improve the mechanical properties of these pastes to ensure the possibility of use of reproducible stirred electrochemical cells - Micro Flow System [9] or Rotating Vessel [10], that are commonly used in our laboratory.

In comparison of sensor type Nx sets can be seen better improvement between older and newer sets. It can be seen that from older set, the sensors N2 and N3, that were doped with oxygen, had much better response than the sensor without doping (N1) or different doping (N4). The newer sensors types NB and NC have much better

responses than the older ones. Therefore it could be expected that this sensors doped with oxygen would have better response. This will be a task for next experiments.

## 7. CONCLUSION

The utilization of the thick film sensor with carbon nanotubes based working electrode was shown in this paper. All the sensors were compared with sensors that have graphite working electrode using the detection of dissolved cadmium in water solution. The achievable detection limit with sensors Nx type is  $5 \cdot 10^{-6}$  mol/l. The current response of the sensors with nanotubes (Nx) based working electrode is ten times better than the response of the sensors with graphite based working electrodes (Cx). In comparison of Nx type sensors is better the newer set and it can be expected, that the current response could be improved by nanotubes doping by oxygen as it was in case of first set of Nx sensors. Finally it is obvious that for heavy metals detection the nanotubes based sensors are better than the classical commercial graphite electrodes, TFT graphite based electrodes and TFT gold electrodes.

## 8. ACKNOWLEDGEMENT

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