NEW APPROACH TO ELECTROCHEMICAL MICROTRANSUDERS FABRICATION

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Abstract

Fabrication and electrochemical characterization of disposable working electrodes/transducers of electrochemical sensors is described in this work. The aim was to find the best electrochemical properties of screen-printed electrode substrates modified with multiwalled carbon nanotubes (MWCNTs) based active layers. Two types of platinum electrode contacts were investigated and the suitable thickness of deposited MWCNTs active layers was studied. Fabricated electrodes were characterized optically using scanning electron microscope, mechanically using profilometer and electrochemically in a standard redox couple of potassium ferro/ferricyanide employing cyclic voltammetry. The reversibility of the electrode system, size of electroactive surface area, influence of spray-coated layer thickness and platinum electrode contact size on the current response were investigated. It was found that more stable and electrochemically suitable behaviour was achieved using the electrodes with bigger platinum contact and lower thickness of deposited active layers. The electrochemical experiments also confirmed that the electroactive size of the electrode surface is at least two times larger than the designed geometrical size.

Keywords: Electrode, Transducer, Voltammetry, Carbon nanotubes

1. INTRODUCTION

Easy, fast and reliable detection of species in environment under field conditions or in vitro/vivo online biodetection is one of the most discussed problems in these days. In general, small handheld, usually electrochemical, systems using miniaturized sensors are therefore developed [1, 2]. The main problem of electrochemical sensors miniaturization is reduction of their geometrical size in comparison to standard electrodes resulting in lower current response. This problem could be solved by creation of some 3D structures on the geometrically reduced electrode which could increase the active size of the electrode several times. Such electrode system could be used as a base for high sensitive intelligent sensors and biosensors [3].

Carbon nanotubes (CNTs) have been under scientific investigation more than fifteen years. Their unique properties, including high electrical conductivity, chemical stability and mechanical strength, predestine them for various applications. Among them, usage in electrochemical detection of biologically significant compounds is especially attractive due to their electrocatalytic properties and ability to improve oxidative signals. CNTs based electrochemical sensors generally have higher sensitivity, lower limit of detection, and faster electron transfer kinetics in the comparison with traditional carbon electrodes. Moreover the mixture made of CNTs and suitable vehicle can form the porous working electrode of high electrochemically active surface [4-11].

In this work the standalone multiwalled carbon nanotubes (MWCNTs) based spray-coated working electrodes/transducers of electrochemical sensors were optimized with respect to the accurate electrochemical behaviour of deposited layers.
2. MATERIALS AND METHODS

2.1 Electrode substrates fabrication

Electrode substrates were fabricated on a 0.65 mm thick alumina using standard thick-film technology also known as screen-printing. Two types of thick-film platinum electrode contacts were investigated (Figure 1) and the suitable thickness of spray-deposited MWCNTs/DMF active layers was studied. The contact layer was made of platinum paste ESL 5545 and the protective layer from ESL 4917 paste (both ESL ElectroScience, United Kingdom).

![Fig. 1 Two types of thick-film contacts design: Pt(mk) left and Pt(+) right](image)

2.2 Active layers deposition

Active layers were fabricated using spray-coating of MWCNTs dispersed in DMF over stencil template. The diameter of round electrode/active layer was chosen to be 3 mm. There were fabricated two series of samples on Pt(+) and Pt(mk) contact respectively in five amounts of deposited MWCNTs/DMF solution – 1, 2, 3, 4 and 5 ml. Fabricated sample of electrode on Pt(+) contact is shown in Figure 2.

![Fig. 2 Fabricated MWCNTs based electrode on Pt(+) contact](image)

2.3 Chemicals

Aqueous solution of potassium chloride (KCl) with concentration of 0.1 mol·L\(^{-1}\) and solution of 2.5 mmol·L\(^{-1}\) potassium ferrocyanide and 2.5 mmol·L\(^{-1}\) potassium ferricyanide in 0.1 mol·L\(^{-1}\) KCl in volume ratio 1:1 were prepared. All of used chemicals were purchased from Sigma Aldrich (USA). All solutions were prepared with deionised water of resistivity not less than 18.2 MΩ·cm\(^{-1}\).

2.4 Electrodes characterization

Voltammetric measurements were carried out using the μ-Autolab III (Metrohm Autolab B.V., The Netherlands) potentiostat/galvanostat connected to a personal computer and controlled by NOVA software version 1.9. The potential range was from −0.25 V to +0.7 V and scan rate was 50 mV·s\(^{-1}\). All measurements were conducted at room temperature (25°C) using a three-electrode configuration with the standard Ag/AgCl reference electrode type 6.0726.100 and platinum auxiliary electrode type 6.0343.000 (both from Metrohm AG, Switzerland).

Electrode surface was characterized optically using scanning electron microscope MIRA II (TESCAN, Czech Republic) and mechanically using DektakXT profilometer (Bruker, USA).
3. RESULTS AND DISCUSSION

3.1 Optical characterization of the electrodes

Successfully fabricated electrodes with spray-coated MWCNTs active layers were characterized optically using SEM. SEM microimages of fabricated electrodes are shown in the Fig. 3.

From the SEM image of Pt contact shown in the Fig. 3A is clear that the electrode contact surface is very porous. MWCNTs/DMF active layer spray-coated over the Pt(+) contact (Fig. 3B) show that the pores of the Pt layer are homogenously covered. From the SEM images of fabricated Pt(+) contact/Al₂O₃ substrate crossing shown in Fig. 3C is clear that 1 ml of spray coated suspension leave visible step between the
contact and the substrate, which almost disappear with 5 ml of spray coated suspension (Fig. 3D). Other images of active electrode surface taken on Pt contact and pure alumina substrate confirmed worse coverage of alumina substrate by electrode material. This fact led to losing of active layer adhesion during the measurement and thus the destruction of the electrode. This problem was observed namely on small Pt(mk) contact where the larger electrode area is deposited over Al₂O₃ substrate.

3.2 Mechanical characterization of the electrodes

Thickness and roughness of deposited layers was investigated using profilometer. Obtained surface profiles of clear Pt(+) substrate and Pt(+) substrate with spray-coated MWCNTs/DMF active layer (5 ml) is shown in the Fig. 4. The porosity of Pt(+) contact and its thickness of ~8 μm is clearly visible. The spray-coated MWCNTs/DMF layer thickness was measured to be ~7 μm over all diameter of the electrode (3 mm). The profile MWCNTs/DMF active layer also confirmed the higher roughness of the electrode surface which corresponds with larger electroactive area of the electrode as it was expected from Fig. 3B. It could be expected that more porous structure representing larger electroactive surface area exhibits faster electron transfer rates [12]. Moreover the Pt(+) contact/Al₂O₃ substrate crossing is more visible than in the case of optical inspection.

![Fig. 4 Surface profiles of free Pt(+) substrate and Pt(+) substrate with spray-coated MWCNTs/DMF active layer (5 ml)](image)

3.3 Electrochemical characterization of the electrodes

Fabricated electrodes were characterized electrochemically in a standard redox couple of potassium ferro/ferricyanide employing cyclic voltammetry as is described in subsection 2.4. The reversibility of the electrode system, influence of spray coated layer thickness and platinum electrode contact size on the current response were investigated.

The electrochemical cyclic voltammograms of electrodes with small Pt(mk) contact and large Pt(+) contact are shown in the Fig. 5. From the Fig. 5 is clear that large Pt(+) contact gives more stable and accurate response. This is probably given by better adhesion of MWCNTs active layer to the platinum contact and, for that reason, better current propagation from the CNTs to the electrical circuit. Next experiments also confirmed, that more stable and repeatable behaviour was achieved using the electrodes with bigger
platinum contact and lower thickness of deposited active layers due to better current response of supporting electrolyte. The electroactive surface area of the electrode was determined from anodic peak current using Randles-Sevcik equation. It was found that the electroactive electrode size is at least two times larger than the designed geometrical size.

Fig. 5 Cyclic voltammograms recorded at 50 mV/sec in 2.5 mM potassium ferro/ferricyanide solution for different active layer thickness (from 1 to 5 ml) achieved at:
small contact Pt(mk) (A) and large contact Pt(+) (B)
4. CONCLUSIONS

In this work, two types of platinum electrode contacts and the suitable thickness of deposited MWCNTs active layers as the working electrodes/transducers of electrochemical sensors were investigated. From the SEM microimages and surface profile analysis is clear, that we obtained rough and highly porous electrode surface with large electroactive surface area. Moreover during the electrochemical experiments the reversibility of the electrode system, size of electroactive surface area, influence of spray-coated layer thickness and platinum electrode contact size on the current response were studied. It was found that more stable and electrochemically suitable behaviour was achieved using the electrodes with bigger platinum contact Pt(+) and lower thickness of deposited active layers. The electrochemical experiments also confirmed that the electroactive size of the electrode surface is at least two times larger than the designed geometrical size.

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LITERATURE