EXAMINATION OF THE THICK-FILM ELECTROCHEMICAL SENSOR ELECTRODES PROPERTIES

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This paper describes a problem of unknown electrochemical behavior of different topologies of thick-film electrochemical sensors. Using DC voltammetry, there were examined the properties of working and reference electrode by output current response and peak potential in this paper. Several electrodes containing different size of electrode area made of Ag, Au and Pt were prepared for this purpose. The influence of working electrode area size of common electrochemical sensor to output current response was measured against commercial Ag/AgCl reference and Pt auxiliary electrode. As we supposed, the results confirm the Levic equation for solid electrodes. The influence of reference electrode area size of common electrochemical sensor to output current response and peak potential was measured against commercial Au reference and Pt auxiliary electrode. The results confirmed presumption that for small sized thick-film sensors, the three-electrode arrangement is more accurate and reproducible than two-electrode system.

Keywords: thick-film electrode, thick-film sensor, solid electrode properties

1. INTRODUCTION

Monitoring of living environment is one of the most discussed problems in these days. Trace determination of species is very important in many areas. One possibility of relative cheap and fast trace determination of some species is use of polarography, which uses toxic mercury drop electrodes [1]. New trend in fast heavy metal determination is focused on using of solid electrodes. Substitution of mercury drop electrode is still aim of science since 1950's [2, 3]. In last years, solid electrodes are used to heavy metal analysis, e.g. thick-film graphite electrodes were used for mercury determination with the stripping voltammetry [4].

Common commercial solid electrodes are made of metal wires or plates attached to glass body with big dimensions [5], but the necessity of low dimensions detectors is nowadays trend. The miniaturized solid electrodes can be produced using the thick-film technology [6]. In the beginning the thick-film technology (TFT) was focused on the production of hybrid integrated circuits [7]. At present, the TFT is used as the tool of preparation of very small electronic devices by SMT - special integrated circuits (for high accuracy and reliable applications), small-lot series of non-standard integrated circuits, prototypes and unconventional applications [6]. The unconventional applications open an important area of printing of chemical active materials. There are TFT chemical sensors and biosensors included. The advantages of TFT chemical sensors and biosensors are small fabrication cost (e.g. platinum electrode containing 1 mg of Pt), low dimensions, good reproducibility, chemical,

mechanical and electrical properties of electrodes and well availability and eco-friendly process.

For electrochemical analysis, there have been developed several commercial thick-film sensors e.g. [8, 9 and 10]. The problem is that many works describe very good results with various commercial or non-commercial electrochemical thick-film sensors in measurement of different species, but there is no explanation about sensors´ topologies and their influence to output response of the electrodes. The aim of this work is to find basic information about behavior of each electrode in a three and two-electrode system and their material and shape influence to output current response and the position of peak potential.

2. EXPERIMENTAL

2.1 Common thick-film electrochemical sensor design

As a common sensor on alumina (25.4 x 7.2 mm) for electrode properties measurement the TFT electrodes were designed and published (fig. 1) [11]. An Ag based paste has been designed for leads and connector. The reference electrode material has been designed also based on Ag that can be electrochemically covered by AgCl layer [12] after the main sensor fabrication process. Auxiliary electrode material is suggested from a Pt paste but the material of each electrode can be changed by a use of other type of the paste. The influence of working and reference electrode to sensor output response is objective of the work to be described below.

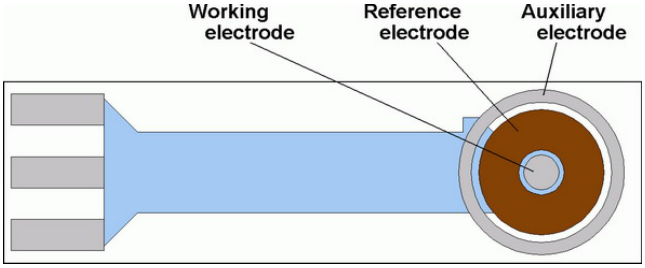

Fig. 1 Standard TFT sensor design [11].

The substrate with electrode topology have been designed to be compatible with electrochemical analytical devices – Micro Flow System [8] and Rotating Vessel [13, 14] that are commonly used in our laboratory to ensure the reproducible conditions during the measurement under flowing electrolyte.

2.2. Test electrodes design and fabrication

For the influence of working and reference electrode to sensor output response investigation, a special substrate with different size of working electrode area was designed and fabricated (fig. 2). The size of electrode diameter was from 1.2 (marked 1 in the fig. 2) to 3.8 mm (marked 14 in the fig. 2).

The TFT electrodes were fabricated using screen-printing techniques. The TFT materials used for electrodes preparation were Au, Pt for working electrodes experiments and Ag for reference electrodes experiments. The conductive layer was ESL 9912-D paste and dielectric layer ESL 4913-G paste. For the working electrodes

the ESL 5545 paste (Pt) and ESL 8844-G paste (Au) and for reference electrode the ESL 4913-G paste (Ag) were used (all pastes were ESL ElectroScience, USA).

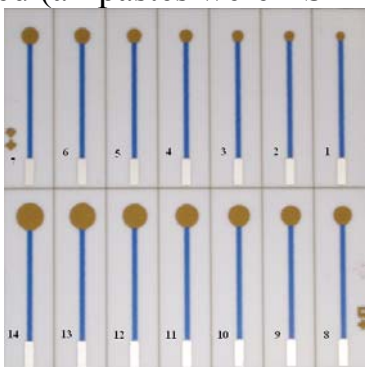

Fig. 2 Sample of fabricated Au working electrodes with different area size (the numbers are used for electrode identification in graph *x* axis values).

2.3 Chemicals

All of used chemicals were purchased from Sigma Aldrich (St. Louis, USA), unless noted otherwise. Solution of a 0.05 mol/L potassium ferrocyanide $K_4Fe(CN_6)$, 0.05 mol/L potassium ferricyanide $K_3Fe(CN_6)$, 0.2 mol/L KOH, 0.1 mol/L KCl and 10 mmol/L $CdCl_2$ were prepared using 18 MΩ redistilled and deionized water (taken from Direct-Q Water Purification System, Millipore).

2.4 Experimental method

Cyclic voltammetry (CV) in range of the potential from -300 to 600 mV with scan rate of 20 mV/sec was performed using the Voltalab PST050 (Radiometer analytical, Denmark). The device was connected to a personal computer for measurement setup and response evaluation.

Electrochemical experiments were carried out in a 10 mL voltammetric cell, at room temperature (25°C), using a three or two-electrode configuration system using a common Ag/AgCl reference electrode (Theta 403, Elektrochemické detektory, Turnov, Czech Republic) and Pt auxiliary electrode (Sycopel Scientific Limited, UK).

3. Results and Discussion

In every experiment, there were fabricated and measured four samples of each electrode area size and material and the results were averaged for better evaluation.

3.1 Working electrodes experiment

First of all, there was made an experiment for working electrode area size and its basic materials (Pt and Au) influence to output current response. The comparison of dependence of output current response to working electrode area size for both electrode materials is shown in the figure 3. The figure shows that there are almost no current response differences between Pt and Au material.

Furthermore it is clear that the difference of maximum output current responses are for both electrode materials worst in case of larger electrode area size (samples 10 to 14). But the percentage current deviation from the average value is worst in case of lower electrode area sized electrodes (samples 1 to 10). From this fact it is clear that

the higher electrode area is the more accurate and higher is the response. It also confirms the Levic equation for solid electrodes [1, 2] (the bigger the electrode area size is the higher is the response).

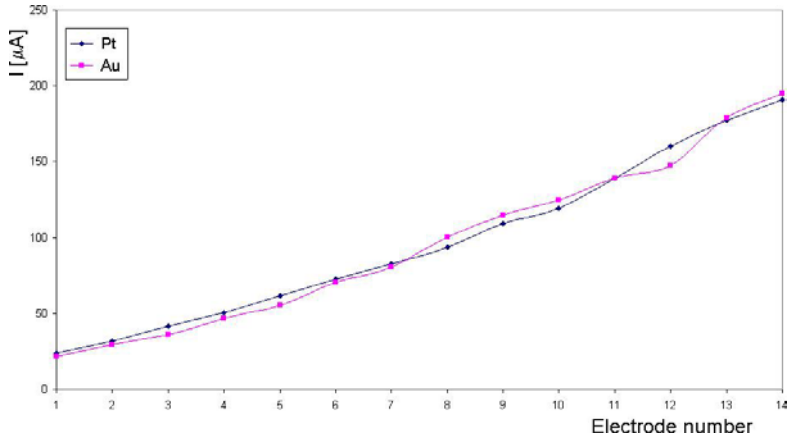

Fig. 3 The comparison of average output current responses for Pt and Au electrodes.

In case of peak potential position we obtained comparable results for both electrode materials too. The peak potential difference was for both electrode materials in range of 30mV for all measured sizes of the electrodes. This value is relative low and for many applications satisfied. Example of peak potential shifts for Pt electrode sets is shown in the figure 4.

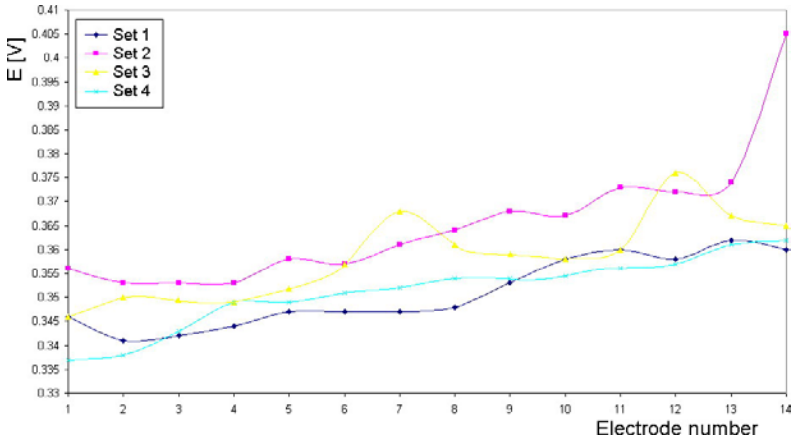

Fig. 4 Peak potential changes for all four sets of Pt electrodes.

From both experiments is also clear that for this electrochemical arrangement is no significant difference between Pt and Ag electrodes and there is no need to make future experiments with both electrode materials.

3.2 Reference electrodes experiment

For this experiment were used two prepared sets of Ag electrodes connected in three-electrode system as in previous experiments. For two-electrode arrangement two prepared sets of Ag reference electrodes were connected against our prepared thick-film Au working electrode (1.4 mm diameter) that is usually used as sensor's working electrode on our sensors [11].

As we supposed, in three-electrode system was almost no difference in output current responses and peak potential position. The conclusions are similar to ones we

have obtained in previous experiment (subsection 3.1). In this case the working electrode area size (higher than of 3mm^2) had almost no influence to output current response with relative error up to 2%. Peak potential difference was lower than 20mV for all electrodes (higher than of 3mm^2) with maximum relative error of 0.9%.

In two-electrode system, we obtained very different results that satisfied our presumptions. In case of output current response the current changes differ up to 10 µA that corresponded to maximal relative error of 38%. The peak potential comparison is shown in the figure 5. From the results it is clear that the peak potential is in some cases shifted by more than 100 mV with relative error higher than 100%. The important is that although the electrodes sizes ratio between working and reference electrode is low, there is possible to read and evaluate the output current responses.

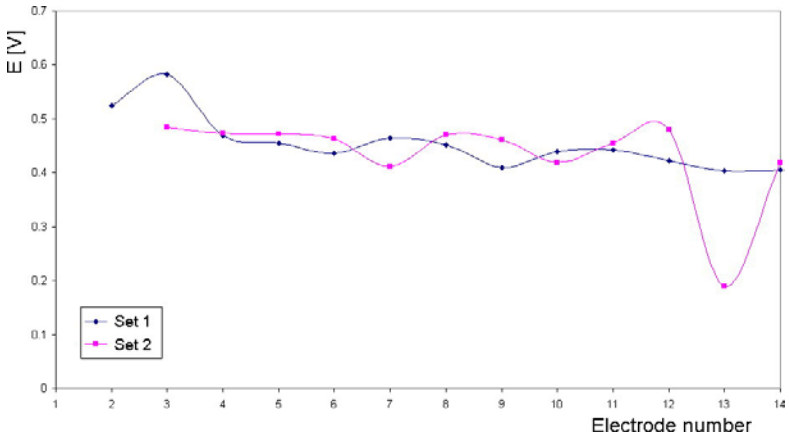

Fig. 5 Comparison of peak potential in two-electrode system.

The responses of three and two-electrode system are easily compared in the fig. 6.

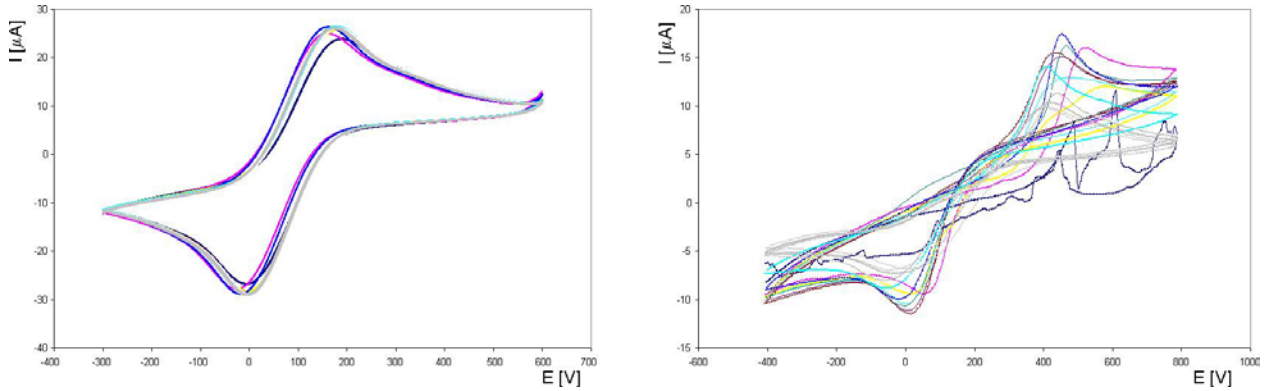

Fig. 6 Comparison of three-(left)/two-(right) electrode system responses.

From the results is clear that for proper measurement is necessary to use three-electrode system. Two-electrode system is possible to be used with very high ratio of electrode area size between working and reference electrode (WE<<RE ~ 1:50) only as it is described in literature [1, 2]. If we ensure the needed ratio WE<<RE in case of small size thick-film electrochemical sensor, the working electrode area size has to be decreased, so we could obtain very low current response only. Therefore the two-electrode system is for thick-film sensors with low dimensions inappropriate.

4. CONCLUSIONS

For the influence of working and reference electrode to sensor output response investigation, the special substrate with different size of working electrode area was designed and fabricated. Influence of working electrode area size to output current response confirmed the Levic equation for solid electrodes. The maximum peak potential difference was 30mV. This value is relative low and for many applications satisfied. During measurements there was found no significant difference between Pt and Au electrodes and for next experiments is possible to use any of them. Influence of reference electrodes area size to output current and peak potential shift experiment was done for three and two-electrode system. The three-electrode system was almost independent on size of electrode area. In other hand, two-electrode system is influenced very much by ratio between working and reference electrode. Therefore the two-electrode system is for thick-film sensors with low dimensions inappropriate.

5. ACKNOWLEDGEMENT

Funding for this work was provided by the Czech academy grant agency under the contract GAAV 1QS201710508, Czech grant agency under the contract GACR 102/06/1624 and Czech Ministry of Education in the frame of Research Plan MSM 0021630503 MIKROSYN.

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