MATERIALS FOR CONSTRUCTION OF PLANAR REFERENCE ELECTRODES OF THICK-FILM ELECTROCHEMICAL SENSORS

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This paper covers an area of construction of planar reference electrodes for thick-film electrochemical sensors. Various materials of commercial and own prepared planar reference electrodes were used for electrodes fabrication and compared with classical reference electrode. The focus was on an Ag/AgCl thick-film or electrochemically created layers. Comparison was made in a three-electrode unstirred system using a standard electrochemical solution of potassium ferro-ferricyanide. The results showed a big difference between the electrodes in obtained current responses. The best properties of fabricated electrodes were obtained with commercial thick-film pastes. A big dependence of geometrical arrangement of electrodes in electrochemical cell is showed here too.

Keywords: planar reference electrode, thick-film electrode, thick-film sensor, Ag/AgCl electrode

1. INTRODUCTION

Fast, easy and cheap monitoring of trace elements in environment or biological tissues is nowadays trend. Trace determination is usually performed by big laboratory equipment using spectrometry, fluorescence or voltammetric methods. Voltammetric methods represent one possible solution of their integration into small analytical hand-held devices with appropriate electrode system for fast, easy and cheap on-field analysis. Former analytical methods based on polarography used toxic mercury drop electrodes for such kinds of analyses [1]. Nowadays trend in fast determination of trace elements is focused on use of solid electrodes. Substitution of mercury drop electrode is still aim of science since 1950's [2, 3]. Recently the solid electrodes were used for trace determination of species, e.g. gold nanoparticles modified glassy carbon electrode was used for determination of mercury by anodic stripping voltammetry [4]. Another work reported stripping voltammetry determination of arsenic in real water samples with solid gold-coated diamond thin-film electrode [5].

Commercial solid electrodes are usually created from a big glass body with attached metal wire or plate [6], but the necessity of today's analyses are small-size electrodes. One possibility of miniaturization of solid electrodes is their integration onto a small substrate. Such possibility can be accomplished with use of thick film technology (TFT) [7, 8]. In the beginning, TFT was used for production of hybrid integrated circuits [7], later for prototypes, nonstandard integrated circuits or small series production [8]. Since 1990's with improvement of classical surface mount technology, TFT started to be used in unconventional application. One of these applications is solid electrode system created on standard alumina substrate forming up electrochemical sensor. For example the electrochemical sensor fabricated as a printed thick-film electrode was used for the analysis of trace elements in water [9] or another work reported planar format thick-film ion sensors for biomedical applications [10]. The advantages of mentioned sensor fabricated using TFT are low dimensions, electrical and mechanical properties of electrodes, good reproducibility and well accessible and ecological fabrication process [11]. Unconventional applications of TFT also open wide possibilities of creation of electrodes of sensors and biosensors using chemical active electrode materials.

In last few years, various commercial electrochemical sensors have been developed and presented, e. g. [12, 13]. Besides them, many scientific works reported very good results using different electrochemical thick-film sensors, but nowhere is explained, why the selected topography, electrode materials, etc. was used. Also their influence to output current response of electrochemical sensors is not reported. The aim of presented paper is to check the behavior of output current response of thick-film planar reference electrodes depending on material used for their fabrication. The behavior was tested in a three-electrode system using commercial working and auxiliary electrodes in a standard electrochemical solution of potassium ferro-ferricyanide.

2. THICK-FILM VOLTAMMETRIC SENSOR

For electrochemical trace analysis a TFT voltammetric sensor for which the optimization of reference electrode is suggested to be done was developed. Its topographic design is shown in the Figure 1. A commercial Ag based paste was designed to be used for leads and connector. A reference electrode material was also designed to be based on Ag that can be electrochemically covered by AgCl layer [14] after the main sensor fabrication process. Auxiliary electrode material is suggested to be from a Pt paste but the material of each electrode can be changed by a use of other type of the paste. A real sample of designed thick-film electrochemical sensor is shown in the figure 2.

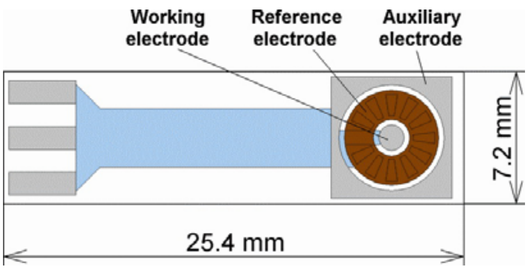

Fig. 1 Topographic design of TFT sensor.

Fig. 2 A real sample of TFT sensor.

3. TFT SUBSTRATE AND REFERENCE ELECTRODES FABRICATION

Reference electrode material properties were measured on a sensor substrate especially done without working and auxiliary electrodes deposited. Sample of the sensor with reference electrode only is shown in the figure 3. The suggested geometrical area of the electrode is 19.3 mm^2.

The TFT substrate was fabricated using standard screen-printing techniques. The conductive layer was fabricated from AgPd based paste (ESL 9635-HG). The covering was fabricated from dielectric paste (ESL 4913-G). The reference electrodes fabricated according to [14] was printed using Ag based paste (ESL 9912-K). All pastes were obtained from ESL ElectroScience, UK.

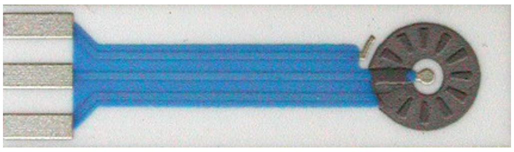

Fig. 3 A real sample of sensor substrate with reference electrode only.

Other TFT materials used for reference electrodes printing were special commercial polymer pastes from DuPont Company. Two DuPont Polymer pastes were used: paste type 5870 (Ag:AgCl ratio: 80:20) and 5874 (Ag:AgCl ratio: 65:35). Pastes were screen-printed and dried at 120 °C for 10 minutes.

The reference electrodes fabricated according to [14] were created using electrochemical deposition on silver based reference electrode substrates using 0.2M KCl electrolyte with a pH 2 (acidified by HCl). Prepared substrates were 50 × electrochemically reoxidized using cyclic voltammetry in range from 0 to 1.2 V in a three-electrode system with the scan rate of 100 mV/sec. The color of electrochemically deposited AgCl layer was brown confirming the results from [14].

4. EXPERIMENTAL

4.1. Chemicals

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

4.2. Experimental method

All the measurements were done using potentiostat Voltalab PST050 (Radiometer analytical, Denmark). The measuring method was cyclic voltammetry (CV) in range of the potential from -300 to 600 mV. The scan rate was set to 20 mV/sec. The measurement setup and response evaluation were done using a standard personal computer.

The experiments were done in a 10 mL voltammetric cell (25°C), using a three-electrode system with a common gold working electrode (UMMAUR11) and platinum auxiliary electrode (UMMPTB11) - both obtained from Sycopel Scientific Limited, UK.

5. Results and Discussion

There were fabricated several samples of each type of reference electrode. Electrodes were measured in 0.05M potassium ferro-ferricyasnide solution in a three-electrode system described above. Reference electrode made of DuPont 5874 paste response example is shown in the figure 4.

From the current response shown in the figure 4 is clear that the current response of each electrode sample is practically reproducible. Very similar results were obtained with the electrodes made of DuPont 5870 paste, as is shown in the figure 5.

In the other hand, the results obtained with electrochemically prepared electrodes, were irreproducible as is shown in the figure 6.

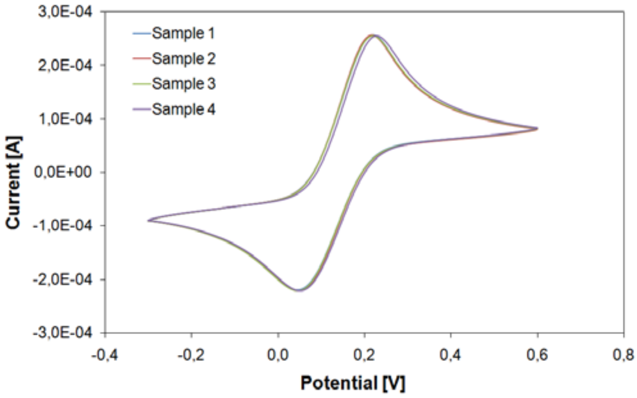

Fig. 4 Output current responses to 0.05M potassium ferro-ferricyanide solution of the reference electrodes made of DuPont 5874 commercial polymer paste.

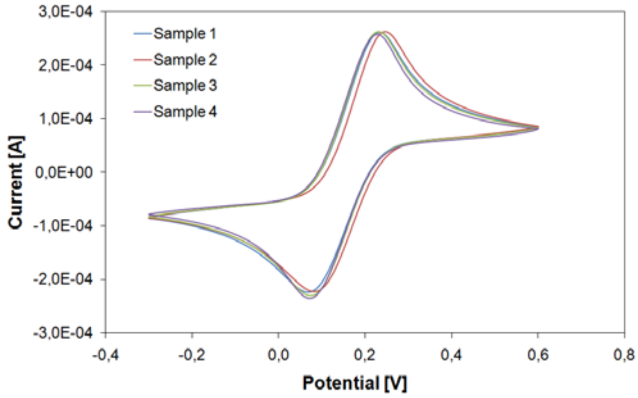

Fig. 5 Output current responses to 0.05M potassium ferro-ferricyanide solution of the reference electrodes made of DuPont 5870 commercial polymer paste.

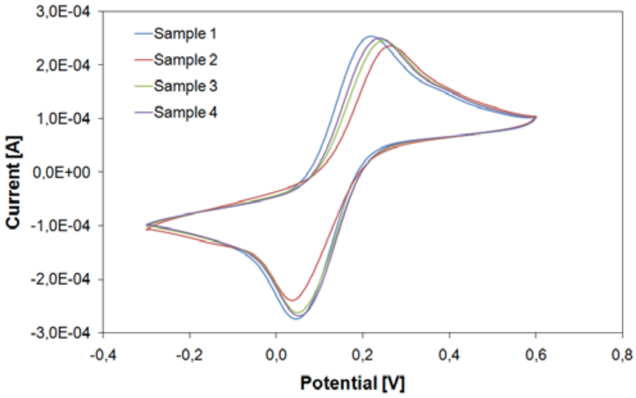

Fig. 6 Output current responses to 0.05M potassium ferro-ferricyanide solution of the electrochemically prepared reference electrodes (according to [14]).

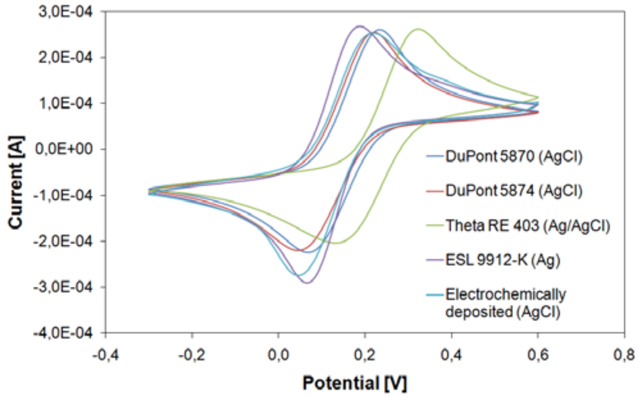

Fig. 7 All measured reference electrodes materials comparison with classical Ag/AgCl electrode.

The comparison of all measured types of reference electrodes with classical commercial Ag/AgCl reference electrode (Theta 403, Electrochemical detectors, Turnov, Czech Republic) is shown in the figure 7. The results showed that the results obtained with both commercial DuPont pastes are very similar although the Ag/AgCl ratio is different. The comparison with classical Ag/AgCl reference electrode showed that the current response is comparable. Different situation was obtained in comparison of half-wave potentials, where was observed the potential shift in range of ~ 100 mV. The half-wave potentials of the electrochemically fabricated reference electrodes were similar to half-wave potentials of the DuPont polymer pastes. The current differed just in the peak current of the reduction process.

Mentioned results led us to decision that the DuPont pastes are the best solution for construction of planar reference electrodes of TFT sensors because of very good and reproducible response.

In the beginning of the measurements an unexpected problem was appeared. As is shown in the figure 8 the geometrical position of electrode system in the electrochemical cell had big influence to output current response. Reference electrode is usually designed to be placed as close as possible to the working electrode to obtain negligible voltage loss between working and reference electrode in two-electrode system, but our results showed that it shouldn't be due to high current loss in the three-electrode system. For all measurements, the same distances and electrodes position in the cell had to be therefore ensured. From other experiments was observed that this problem is not appeared with use of classical commercial reference Ag/AgCl electrodes. From these results is clear that these types of solid planar TFT electrodes can assure reproducible results just in case, where is not possible to change distances between the electrodes. This condition is satisfied by the planar electrode system of the TFT sensor.

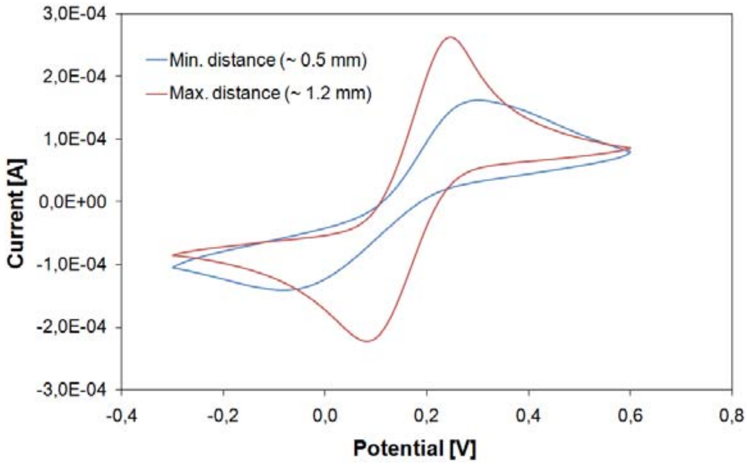

Fig. 8 Electrode distance change influence to output current response of the reference electrode.

6. CONCLUSIONS

In this work, there were fabricated and compared several Ag/AgCl screen-printed and electrochemically prepared planar reference electrodes. The results showed that the results obtained with both commercial DuPont pastes are very similar although the Ag/AgCl ratio is different. The comparison with classical Ag/AgCl reference electrode showed that the current response is comparable. Different situation was obtained in comparison of half-wave potentials, where was observed the potential shift in range of ~ 100 mV. The half-wave potentials of the electrochemically fabricated reference electrodes were similar to half-wave potentials of the DuPont polymer pastes. The current differed just in the peak current of the reduction process. Mentioned results led us to decision that the DuPont pastes are the best solution for construction of planar reference electrodes of TFT sensors because of very good and reproducible response.

During the experiments was observed the problem of irreproducible current response caused by change of electrode distances during the electrodes replacement. From other experiments was observed that this problem is not appeared with use of classical reference Ag/AgCl electrodes. From these results is clear that these types of solid planar TFT electrodes can assure reproducible results just in case, where is not possible to change distances between the electrodes. This condition is satisfied by the planar electrode system of the TFT sensor.

7. ACKNOWLEDGEMENT

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8. REFERENCES

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