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GRAPHITE PASTES IN THICK FILM SENSORS AREA

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Abstract – Miniature electrochemical sensors can be produced by thick film technology (TFT). The optimal properties of thick film electrode materials are main problems of sensors design. The optimisation of graphite pastes properties for TFT chemical sensor is discussed. The commercial TFT graphite pastes, which are used for common application, are cheap and easily producible, but they are not efficient for electrochemical measurement. These pastes have insufficient sensitivity and they have other bad properties. Graphite pastes, which were designed for special chemical analysis, are technically known, but these pastes are not workable by screen-printing. The first step in rheological properties addition to graphite electrochemical pastes is the goal of this work. This will ensure the pastes printability that will enable the reproducible mass production.

The graphite powder with paraffin wax mixture is the basic component of common chemical graphite pastes. There were examined different properties of these pastes in dependence on graphite powder and binding material content in this work. Finally there are described some measurement with commercial and specially prepared TFT graphite electrodes. All measurements were done using a standard electrochemical couple of potassium ferrocyanide-ferricyanide.

Keywords: electrochemical sensors, graphite paste electrode, thick film electrodes.

1. INTRODUCTION

At the beginning the thick film technology (TFT) was focused on the production of hybrid integrated circuits [1]. The basic use of this technology was in the production of special integrated circuits, small series of non-standards integrated circuits and prototypes [2]. At present time the TFT is partially suppressed in its classical meaning as a tool of preparation of very small electronic details by SMT. Hereby the technological importance of TFT was shifted significantly to military and high reliability applications and unconventional applications. The unconventional applications use the basic ideas of TFT, namely the screen-printing as a method of active layer preparation and they enhance the technology to printing of optically active layers. Obviously an important area is open in unconventional

application for printing of materials, which have chemical activity. This field includes TFT chemical sensors and biosensors [1]. The main advantage is low price and small-scale batch production. In many circumstances they are comparable with classical electrochemical cells. The optimal properties of thick film electrode materials and the optimal technology of TFT sensor production are main problems of sensors design [3]. Therefore the application of TFT to chemical sensors is still in stadium of research and development [4], [5]. Technology of TFT electrochemical sensors grew from classical TFT materials. The first material especially developed for chemical sensors is currently being introduced on the market [6], but majority of materials, which are routinely used for sensor preparation, are not designed for such applications. One of these materials is graphite.

The commercial TFT graphite pastes, which are used for common application, are cheap and easily producible, but they are not efficient for electrochemical measurement. These pastes have insufficient sensitivity and they have other improper properties. It is because of their binding material, which is not water permeable. It can change the electrochemical properties of the graphite grains very significantly. Graphite pastes, which were designed for special chemical analysis, are technically known [7], [8], but these pastes are not workable by screen-printing.

The main goal of this work is the description of graphite paste base suitable for TFT sensors and first step in rheological properties addition to graphite electrochemical pastes. This will ensure the pastes printability that will enable the reproducible mass production.

2. THE GRAPHITE AND THE GRAPHITE PASTE ELECTRODE

Carbon materials (for example glassy carbon, carbon fibres, graphite, graphite paste, etc.) are used in various electrochemical analysis, synthesis and technologies and energy storage devices [7], [10]. Natural carbon has similar microstructures consisting to condensed layers, electron configuration $2s^2 2p^2$, electronegativity 2,5 [9]. Materials from carbide have various crystallite size and extent of microstructural order. Therefore it has important implications for the electron-transfer kinetics [10].

The graphite paste electrodes are prepared from graphite powder, which is mixed with any binder. The binder must not be soluble in measure solution (often in water). Further the binder must be little volatile, viscous; must not be electroactive and must not contain electroactive impurity. For graphite paste electrode these binders are supported: α -bromo naphthalene, ethyl naphthalene, silicone oil, methyl silicone oil and paraffin [7]. The different electrode materials produced from carbon can be used for different potentials. Generally the graphite can be used in range -1,6 to +1,1 V. For example for buffer 0,2 mol/l KNO_3 the limit is in range -0,75 to +1,0 V for glassy carbon, -0,25 to +0,85 V for graphite paste and in range 0 to +0,5 V for graphite impregnated with paraffin [9].

3. THE PRACTICAL MEASUREMENTS

3.1. Chemicals

Basic electrochemical solution of a 0,05 M potassium ferrocyanide $\text{K}_4\text{Fe}(\text{CN})_6$ and 0,05 M potassium ferricyanide $\text{K}_3\text{Fe}(\text{CN})_6$ and 0,2 M KOH was prepared and used for measurement. The graphite powder (Sigma Aldrich) with grain size of 1 to 2 μm mixed with paraffin wax (Sigma Aldrich) with melting temperature from 52°C to 58°C were used for electrodes preparation.

All chemicals were of high purity and used as received.

3.2. Description of workplace

The base of workplace is analytical chemical workstation AEW2 – 10 (Sycopel Scientific, UK). The instrument is a potentiostat for various electrochemical methods measuring - Open circuit, Potentiostatic, Galvanostatic, Potentiodynamic, Galvanodynamic, Pulse amperometric etc. [11]. The workstation is controlled by computer. The computer gathers and draws a measured data that can be exported into Microsoft Excel that enables other data processing and presentation.

The practical measurements were done in a glass electrochemical cell. In the cell there were silver/silver chloride reference electrode and measured graphite electrode or sensor with graphite working electrode in 15 ml of standard reversible system solution mentioned in subsection 3.1.

3.3. Description of measured graphite electrodes

For experiments, the simple graphite electrode was prepared as a mixture of graphite powder with paraffin wax in various concentrations (0%, 20%, 40%, 60%, 70%) at 70°C. This mixture was pressed into a glass tube.

100% graphite electrode was prepared by graphite powder pressing into the glass tube only. In comparison with classical graphite electrode, there are still spaces between granules of powder. Therefore a reaction surface is bigger and electrode is more absorptive. This electrode is marked as 100%* (in fact the content of graphite was 95 ÷ 99% and the rest is the free space - the electrode is marked on all graphs). Next steps were the electrode grinding using fine grinding paper (400) and the measurement. The section of prepared working graphite electrode is in the fig. 1.

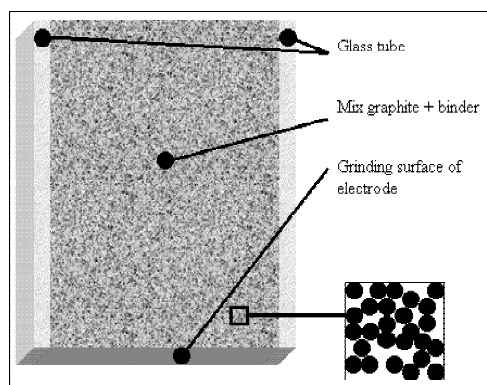


Fig. 1 The section of prepared working graphite electrode.

3.4. TFT sensor

A standard TFT amperometric sensors (fig. 2.) deposited on Al_2O_3 substrate (BVT Technologies, Czech Republic) [14] using the standard commercial graphite paste (sensor type AC1.W4.R1) or special prepared TFT graphite paste (sensor type AC1.W2.RS with various graphite paste types deposited on it) were used for measurements. The sensor type AC1.W4.R1 had the C working, Ag/AgCl (60/40%) reference and PtAu (15/85%) auxiliary electrode. The sensor type AC1.W2.RS had the Pt (100%) working, AgPd (98/2%) reference and Pt (100%) auxiliary electrode. This sensor type is usually used as the sensor for basic electrochemical and bio-electrochemical measurement, e.g. for H_2O_2 , glucose, ferricyanide, pesticide determine and for enzymes deposition. In our case we used this type of sensor as the substrate for three types of graphite pastes that were deposited on its working electrode surface. These pastes are differed from the commercial one in their binding material concentration and they were prepared in our laboratory. Complete sensors' datasheets can be found in [14].

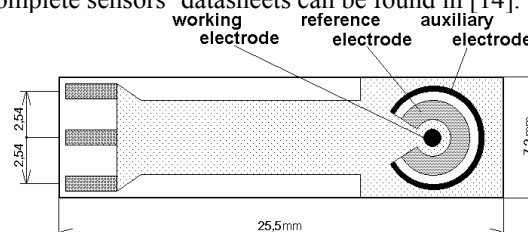
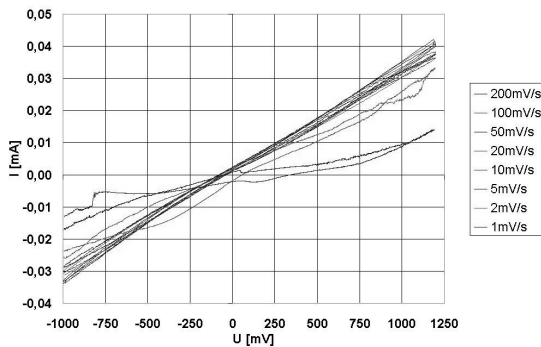


Fig. 2 Standard TFT amperometric sensor.

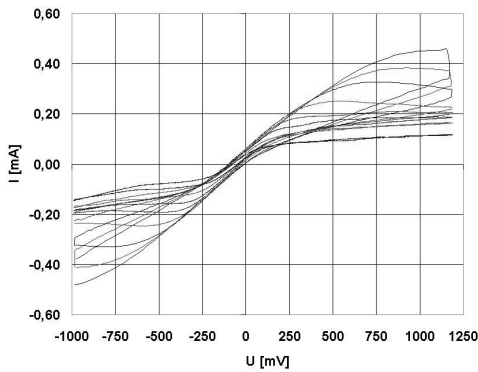
2.3. Results and discussion

The determination of standard measuring method was the first step before measurement starting. The potentiodynamic method, where a potential between the working electrode and the reference electrode is linearly changed with pre-select scan rate over defined range and corresponding current in time is measured and recorded, was used for measurements [12], [13]. Measurements were done in the model reversible system mentioned in subsection 3.1 in the potential range <-1000; 1200> with all electrodes and sensors mentioned in subsections 3.3. and 3.4. Chosen measurement method was used for all electrodes measurements. The electrode with concentration of 100%* graphite was very absorptive and it was changing its volume

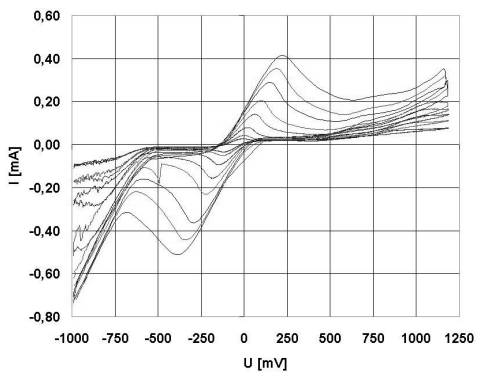
during measurement. The result examples are shown in fig. 3.



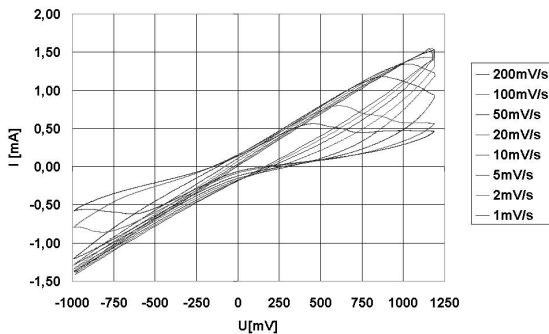
a, The working electrode with 20% of graphite,



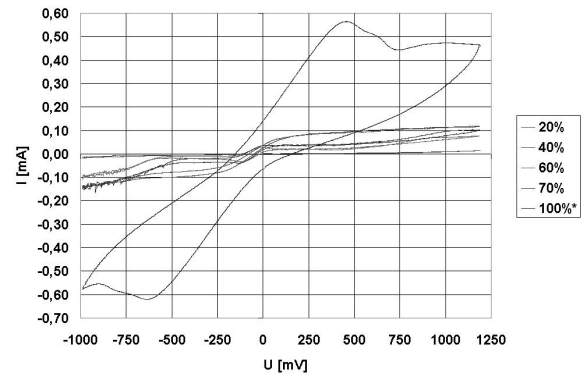
b, The working electrode with 40% of graphite,



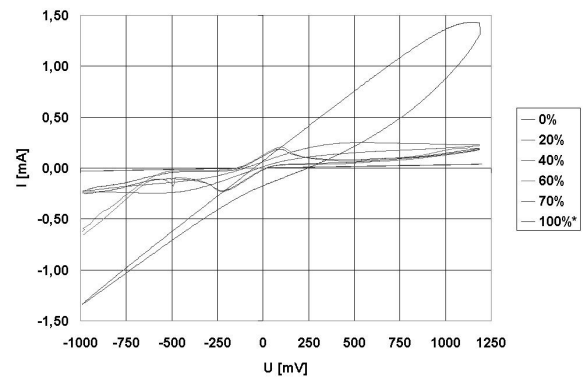
c, The working electrode with 60% of graphite,



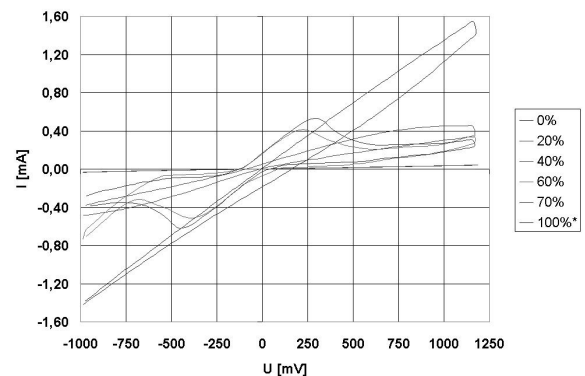
d, The working electrode with 100%* of graphite,
Fig. 3 The results of standard measurements for working electrodes with various scan rates and constant concentrations of graphite.



a, The scan rate 1mV/s



b, The scan rate 20mV/s



c, The scan rate 200mV/s

Fig. 4 The results of standard measurements for working electrodes with various concentrations of graphite and constant scan rate.

From the graphs in figure 3 the new graph with output signal electrodes dependence demonstration for constant scan rates and various concentration of graphite was created (fig. 4).

The graphs 3 and 4 are showing that:

- Optimal concentration of graphite for this electrode type is about 60% and higher.
- Optimal scan rate for this electrode type is in limit between 10 to 100 mV/s.
- Though the redox couple is in classical electrochemical systems reversible, the behaviour with graphite paste electrode is irreversible.

For last proposition survey, the graphs of peaks voltage differences were created. For reversible systems the difference between peaks is 112mV and scan rate independent. The graphs were made for electrode with graphite concentration of 60% and 70% (fig. 5 and 6). The graphs show that the dependence of peaks voltage differences on scan rate is logarithmic.

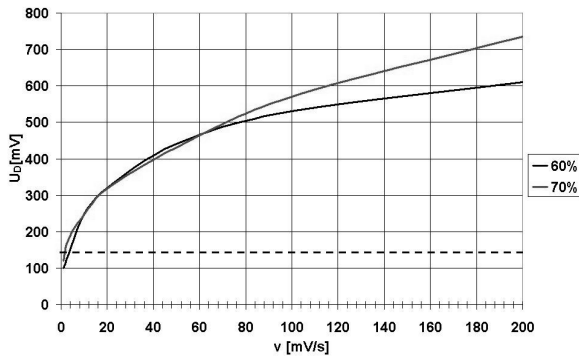


Fig. 5 The dependence of peaks voltage differences on scan rate for working electrodes with constant concentrations of graphite (60% and 70%). Dashed line is theoretical curve for reversible system.

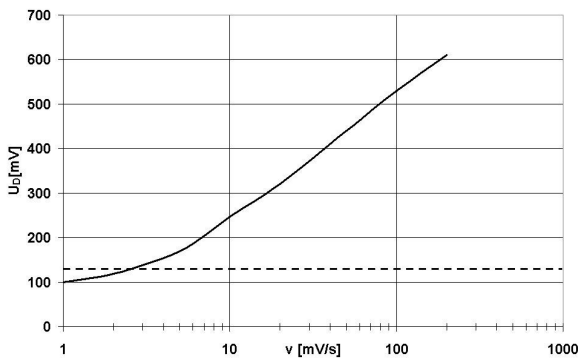
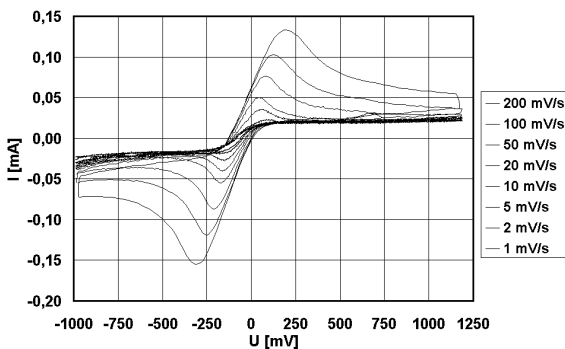
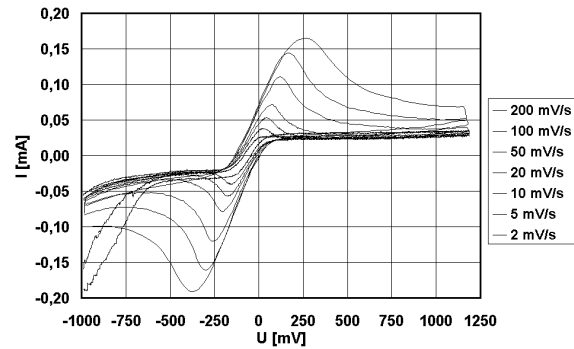


Fig. 6 The dependence of peaks voltage differences on scan rate for working electrodes with 60% of graphite. Dashed line is theoretical curve for reversible system.

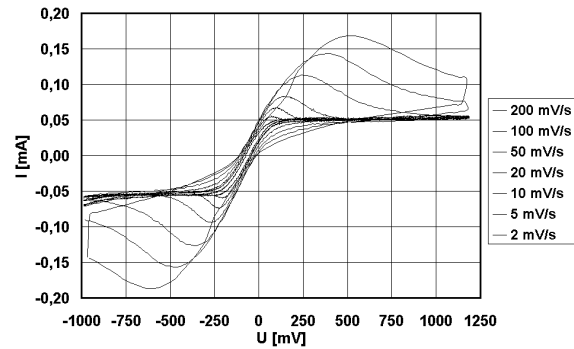
Next the various graphite pastes, which were deposited on standard amperometric sensor type, were measured. The result examples are shown in fig. 7 and 8.



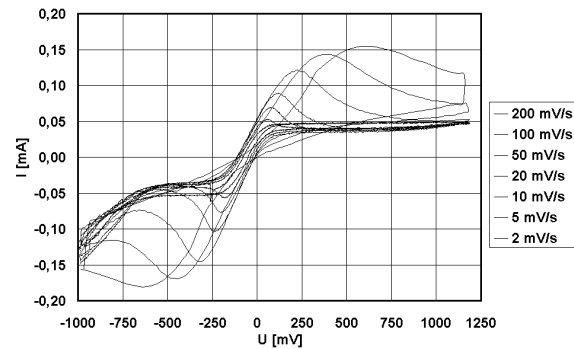
a, The sensor type AC1.W4.R1 with commercial graphite paste,



b, The sensor type AC1.W2.RS with graphite paste type 1,



c, The sensor type AC1.W2.RS with graphite paste type 2,



d, The sensor type AC1.W2.RS with graphite paste type 3,

Fig. 7 The results of standard measurement for sensor type AC1 with various deposited graphite pastes.

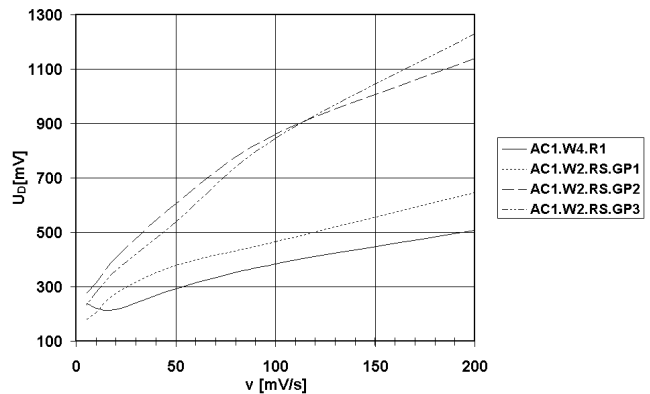


Fig. 8 The dependence of peaks voltage differences on scan rate for various graphite pastes deposited on standard amperometric sensor type AC1.

3. CONCLUSION

The base of graphite paste electrodes with various concentration of graphite powder with paraffin wax was prepared. The measurement was made in a model reversible system, alkaline solution of potassium ferricyanide and potassium ferrocyanide mixture. There were examined different properties of these pastes in dependence of graphite powder and binding material content in this work. As optimal concentration of graphite for electrode preparation is appeared to be the concentration of about 60% and higher and optimal scan rate is appeared to be in limit between 10 and 100 mV/s. However the reversible electrochemical redox couple was used the resulting signal was irreversible. The logarithmic dependence of peaks voltage differences on scan rate was appeared.

Next the various graphite pastes deposited on standard amperometric sensor type AC1 were measured. The results showed that the graphite pastes deposited on standard amperometric sensor have dependence of peaks voltage on differences on scan rate too but the dependence is more linear than in case of graphite paste electrodes.

In this work the next step will be measurement of peaks voltage differences on graphite paste parameters dependence.

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