OPTIMIZATION OF ELECTROCHEMICAL ANALYTICAL DEVICE FOR MEASUREMENTS WITH THICK-FILM ELECTROCHEMICAL SENSORS

Jan Prasek, Martin Adamek, Zdenek Pytlicek

Dept. of Microelectronics, Brno University of Technology, Udolni 53, 60200 Brno, Czech Republic, phone: +420 541 146 175, email: prasek@feec.vutbr.cz

Paper covers an area of electrochemical analytical devices that are made especially for measurements with thick-film electrochemical sensors. There were made several improvements of own designed electrochemical analytical device with rotating vessel in this work. The improvement was done on sensor holder to ensure reproducible sensor placing in the vessel and electronic control part that was optimized for better performance of analytical device prototype. The best current response of the sensor was investigated in dependence on sensor position in the system in potassium ferro-ferricyanide solution. Obtained results have been plotted out in 3D graphs of current response in the set positions. Finally the mass flow optimized sensor response was investigated and compared with a standard one.

Keywords: optimization, electrochemical system, thick-film sensor, flow analysis

1. INTRODUCTION

Electrochemical analysis of species that are dissolved in water solutions is one of the cheapest analyses in this field. Generally the electrochemical analyses are provided by laboratory potentiostats with use of various electrochemical arrangements. Commonly used arrangements are unstirred cells or rotating disk electrodes. The output current signal from unstirred cell is usually low due to current limitation by diffusion. In the other hand the rotating disc electrode (RDE) gives very good signal due to its defined hydrodynamic conditions [1].

The miniaturization of electrochemical analytical systems into small hand-held portable systems is today's trend. Therefore the necessity of use of small electrode systems that can be used with appropriate electrochemical systems is needed. These small electrode systems are represented by sensors. Although the RDE gives very good results, it can't be used with small sensors due to its construction. Other systems with defined hydrodynamic conditions that are capable to work with small sensors are channel cells or wall-jet arrangements [1, 2]. The disadvantages of these systems are in their construction using channels that can be covered by impurities which can affect next analyses.

All of mentioned electrochemical arrangements are designed to be used with solid electrodes, which is in contradiction with classical electrochemical analysis that commonly used mercury drop electrode due to its very good sensing properties [3]. The commercial solid electrodes are usually of high dimensions and cannot be used in small systems. The miniaturized solid electrodes forming the sensor systems can be fabricated using thick film technology (TFT) [4]. The advantage of thick film technology is in low cost fabrication non vacuum process, good reproducibility, mechanical and electrical properties and its flexibility [5]. The main advantage is low cost of fabricated sensors that usually use very small amount of precious metals for contacts, leads and electrodes. Therefore the electrodes can be constructed as disposable sensor for one or few measurements only. The next advantage is the possibility of use of non standard thick-film materials that can be used for sensors with special properties of electrodes. For example the magnetic or semi conducting materials or the materials for realization of defined nanostructure of the electrodes can be used.

This work solves the optimization of new electrochemical analytical arrangement with rotating vessel [6] that was designed especially for use with thick-film electrochemical sensors. The device was designed to ensure reproducible mass transport of the solution to the electrodes. The optimization of the sensor and its position in the rotating vessel with respect to signal noise ratio was studied in this work.

2. DEVICE AND SENSOR OVERVIEW

2.1 Device optimization

In our previous work [6] was shown that the new electrochemical analytical arrangement is working well and can be used for electrochemical analyses. Principle and first steps of sensing properties of the sensor evaluation using this device and its comparison with other systems have been already described [7]. It was shown, that there is a possibility to vary output current response of the sensor in dependence on sensor position in the vessel that can be changed in three axes according to Figure 1. In the previous experiments, the output current noise was not considered well. For better evaluation of the results, there have been redesigned the regulation and measurement unit of the device. The gripping part was also redesigned to ensure reproducible position of the sensor in the vessel. A redesign schema of new analytical device is shown in the figure 2.

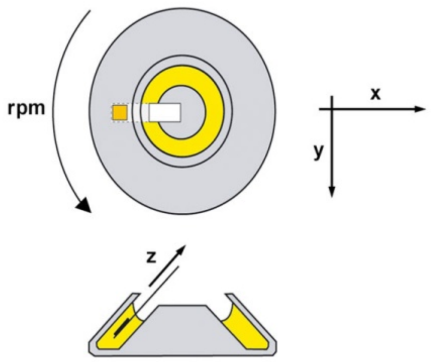

Fig. 1 Possible positions changes in three axes.

2.2 Used sensor

New electrochemical analytical device is designed especially for work with thick-film sensors fabricated on alumina substrate. A real sample of thick-film electrochemical sensor for measurement of dissolved species in aqueous solutions is shown in the Figure 3. A commercial Ag based paste ESL 9912-K was used for leads and contacts. Reference electrode material was also Ag based paste ESL 9912-K that can be electrochemically covered by AgCl layer [8] after the main sensor fabrication process. Working electrode was fabricated from Au based paste ESL 8844-G. For auxiliary electrode a Pt based paste ESL 5545 was used. The material of each electrode can be changed depending on application by use of other type of the TFT paste or special pastes. Dielectric sealing was fabricated from ESL 4917 paste. All used pastes were from ESL ElectroScience, UK.

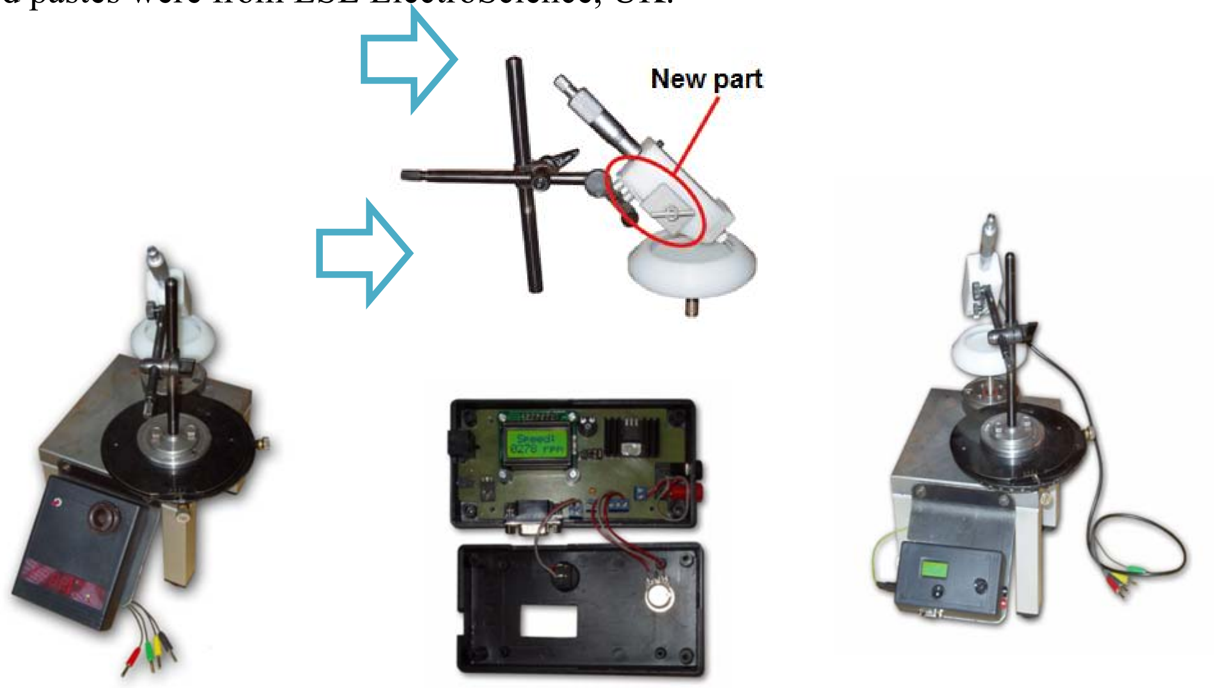

Fig. 2 Redesign of new analytical device for voltammetric measurements.

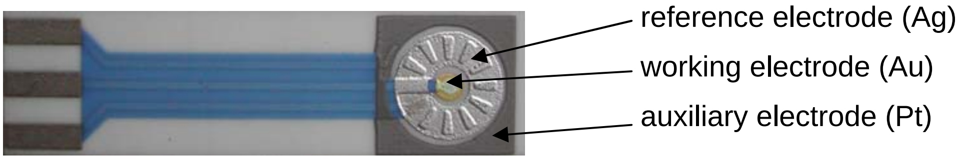

Fig. 3 Real sample of TFT sensor used for measurements.

3. EXPERIMENTAL

All measurements have been carried out using cyclic voltammetry in range of the potential from -100 to 350 mV. Measurement with scan rate of 25 mV/sec was performed using the Voltalab PST050 (Radiometer analytical, Denmark). The device was connected to a personal computer for measurement method setup and response evaluation.

As an electrochemical standard solution a 5 mmol/L potassium ferrocyanide $K_4Fe(CN_6)$ and 5 mmol/L potassium ferricyanide $K_3Fe(CN_6)$ was prepared using 18 MΩ deionised and redistilled water taken from Direct-Q Water Purification System (Millipore). All used chemicals were from Sigma Aldrich (St. Louis, USA).

Electrochemical experiments were carried out in rotating vessel cell (18 ml of solution) at room temperature (25°C), using a three-electrode system configuration.4. RESULTS AND DISCUSSION

3.1 Rotation speed experiments

First measurements were done to know the level of the noise during change of rotation speed. The rotation speed was changed from 0 to 450 rpm. The dependence of output current response and its corresponding noise level measured at potential around 300 mV on the change of rotation speed is shown in the Figure 4.

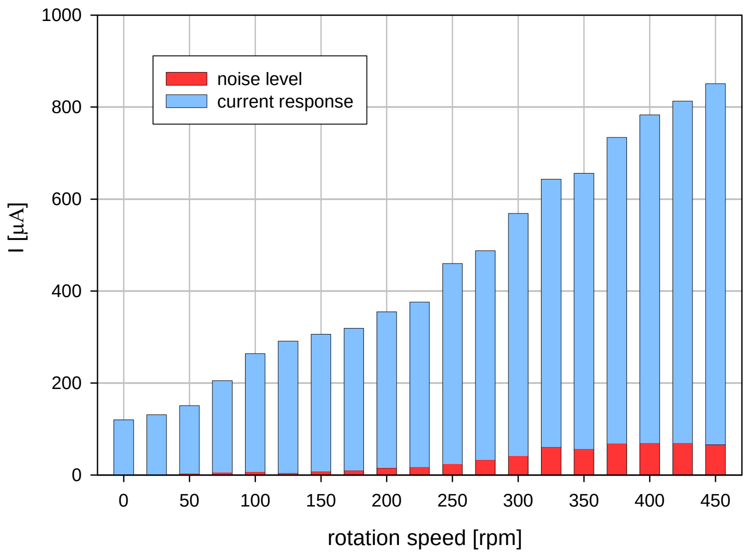

Fig. 4 Dependence of output current response and its corresponding noise level on the change of rotation speed.

From the Figure 4 is clear that the best current response with low level of noise was achieved at 125 rpm. Therefore this value was selected for other experiments.

3.2 Sensor position experiments

Two different position of the sensor electrode system were done. In the first one the sensor electrode system was oriented outside and the second one to the centre of the vessel. All of measurements were done at the three levels of *z* axis (0, 1, 2 mm). En example of best results obtained for first position of the sensor electrode system is shown in the Figure 5. The second position is represented by Figure 6.

From the results is clear that better results can be achieved with sensor oriented to the centre of the vessel. In suitable position can be achieved very good signal/noise ratio. Suitable working area is marked by red arrows in the Figure 5 and 6.

3.3 Mass flow along the sensor optimization

The last experiment was done with modified sensor edges (see Fig. 7 left) to ensure better mass flow along the electrodes with minimum turbulences. The electrode part of the sensor was oriented outside the vessel. From comparison of unchanged and modified sensor response (see Fig. 7 right) is clear that with use of modified senor was achieved higher current response but the noise was also increased. It concludes that the presumption of lover noise level with modified sensor was not confirmed.

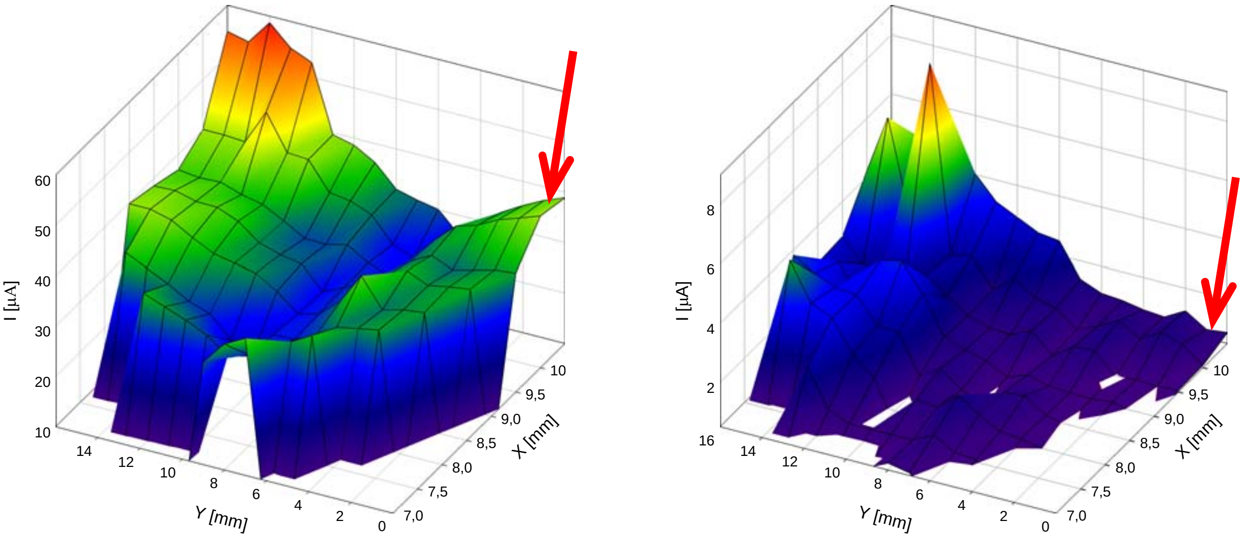

Fig. 5 Sensor oriented outside of the rotating vessel current response (left) and corresponding noise level (right) for the $z = 0$.

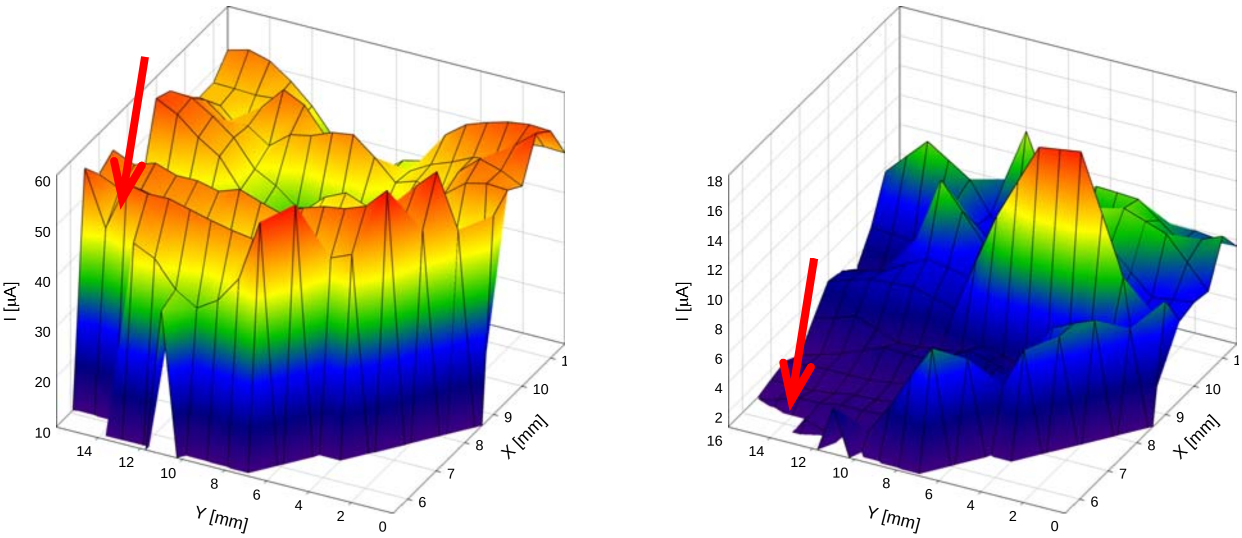

Fig. 6 Sensor oriented to the centre of the rotating vessel current response (left) and corresponding noise level (right) for the $z = 0$.

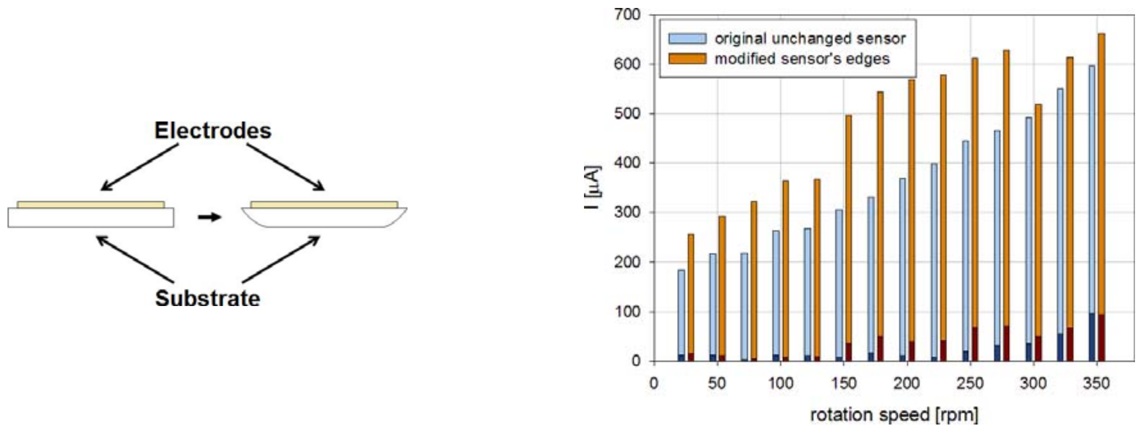

Fig. 7 Modification of sensor's edges (left) and comparison of unchanged and modified sensor response (right).

4. CONCLUSIONS

There was made new electrochemical analytical device optimization in this work. The response was clearer and the rotation speed was easier to control. Reproducible gripping of the sensor in fixed position in the vessel was added.

For the experiments the rotation speed of the vessel 125 rpm was chosen due to high output current response with low level of noise at this value.

During the investigation of the best sensor position in the vessel were studied two different orientations of the sensor – sensor electrodes oriented outside of the vessel and sensor electrodes oriented to the centre of the vessel. In both cases was found that the best results were achieved when the sensor was put in its deepest position (z axis = 0). From the comparison of both sensors orientation is clear that better results in all xy range can be achieved with sensor electrodes oriented outside of the vessel, although the position with best ratio signal/noise was found in sensor electrodes to the centre orientation.

The last experiment was done with modified sensor edges to ensure better mass flow along the electrodes with minimum turbulences. From comparison of unchanged and modified sensor is clear that with use of modified sensor was achieved higher current response but the noise was also increased. It concludes that the presumption of lover noise level with modified sensor was not confirmed.

5. ACKNOWLEDGEMENT

Funding for this work was provided by the Czech academy grant agency under the contract GAAV KAN208130801 and Czech Ministry of Education in the frame of Research Plan MSM 0021630503 MIKROSYN.

6. REFERENCES

[1] Rieger, P. H. Electrochemistry. Prentice-Hall, second edition, USA: 1987, 514 p.

[2] Bard, A. J.; Faukner, L. R. Electrochemical methods, Fundamentals and applications. John Wiley & Sons, Inc., USA: 718 p.

[3] Vydra, F.; Šťulík, K.; Juláková, E. Rozpouštěcí polarografie a voltametrie. SNTL, Prague 1977, 256 p.

[4] Haskard, M., Pitt, K.: *Thick-film Technology and Application*, Electrochem. Pub. LTD, GB 1997.

[5] Harsanyi, G.: *Sensor technologies and Applications*, Department of Electronics technology, Technical University of Budapest, Budapest.

[6] Prasek, J.; Adamek, M.; Hubalek, J.; et al. *Sensors* 2006, n. 11, pp. 1498 – 1512.

[7] Prasek, J.; Adamek, M. Novel device for thick-film electrochemical sensors and biosensors measurement. Electronics ET'2006. Sozopol, Bulgaria, 2006. p. 15 – 20.

[8] Lanz, M., Schürch, D., and Calzaferri, G. *Journal of Photochemistry and Photobiology A: Chemistry*, 120, 1999, pp. 105-117.