

Optimization of Planar Three-Electrode Systems for Redox System Detection

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Numerous analytical, bioanalytical, biochemical and biological instruments have been developed for determination of specific and/or group of compounds, species, cells even organisms, but most of them suffer from the impossibility to miniaturize these instruments in spite of the fact that they have many other advantages. Due to the above-mentioned facts developing and suggesting of simple analytical instruments, methods and procedures with low detection limits and providing on-line and *in situ* monitoring of environment are needed. In this study, we show testing and optimizing of some important features of screen-printed electrodes, which should be considered before their designing, fabrication and applications for low-cost electrochemical analysis *in-situ*, because we found that areas as well as materials of auxiliary and reference electrode can markedly influence of current response and, therefore, markedly influence detection limit of our thick-film three-electrode microsensor. Finally, there was also confirmed, that these three-electrode screen-printed planar electrode systems could be used for high scan rate electrochemical detection of selected species without any significant output current response change in comparison to standard-like non-planar three-electrode system.

Keywords: Electrochemistry; Planar electrode; Electrode system; Sensor; Thick-film electrode; Electrochemical analysis; Voltammetry

1. INTRODUCTION

Bioavailability considerations, contents of hazardous materials and higher anthropogenic activity are one of the tools for a proper assignment of sites potentially and actually at risk as it allows

assessing both the extent (hazard) and probability (risk) environmental contamination [1]. Numerous analytical, bioanalytical, biochemical and biological instruments have been developed for determination of specific and/or group of compounds, species, cells even organisms, but most of them suffer from the impossibility to miniaturize these instruments in spite of the fact that they have many other advantages. Due to the above-mentioned facts developing and suggesting of simple analytical instruments, methods and procedures with low detection limits and providing on-line and *in situ* monitoring of environment are needed [2]. Among very sensitive analytical methods for detection of various analytes including metal ions [3-10], peptides [11-16], proteins [17-29], nucleic acids [30-42] and others [43,44] belong the electrochemical ones [11,45-48]. The classic instruments are consisted of potentiostat/galvanostat with electrochemical cell including three electrodes (working, reference and auxiliary). As the working electrode, hanging mercury drop electrode (HMDE) is commonly used [49]. HMDE can be also modified by biologically active substances to improve sensitivity or selectivity of heavy metal ions detection [48,50-55]. Due to adverse effects of Hg(II) and many restrictions for usage of this metal, carbon electrodes has been found as an alternative [56-63]. As we mentioned above the trend of the analytical techniques is to miniaturize the whole instrument, in which carbon electrodes have much more advantages compared to HMDE [64-67].

The miniaturized planar solid electrode systems (sensors) could be fabricated using several methods. One of them is thick-film technology (TFT), [68,69] which was primarily used for fabrication of hybrid electronic circuits. Due to the improvement of surface mount technology in the end of 1980s, TFT started to be used for some other applications, which opened wide possibilities in fabrication of sensors, biosensors, displays, heater elements, etc. The advantage of standard TFT is a variability of used materials, low-cost production, flexibility, accessibility, non-vacuum and ecological friendly fabrication process, good reproducibility, good compatibility with electronic devices and circuits, good mechanical and electrical resistivity and good thermal conductivity of the substrates. Screen-printed carbon electrodes as a product of TFT belong to the most convincing carbon electrodes to be used for *in situ* environmental analysis [70-74]. Screen-printed electrodes have been successfully used for detection of various gasses [75-80], glucose [81-83], heavy metals [84-90], hydrogen peroxide [91-93], DNA [94-98], methyl parathion [99], phenol in soil sample [100], sildenafil in Viagra tablets [101], and also for blood analysis [102-105].

Common TFT screen-printed three-electrode miniaturized electrochemical voltammetric system is designed as a microsensor with strip electrodes and it is shown in Fig. 1. The microsensor consists of contact part (Fig. 1, on the left) for connector, long enough electrically insulated interconnection part (Fig. 1, in the middle) protecting the connector against the measured sample and three or two-electrode system area (Fig. 1, on the right), which size is usually up to 1 cm². The problem of miniaturized planar electrode systems is in their unknown behaviour in the solution. There are many producers offering small voltammetric screen-printed sensors as DropSens, Rusens Ltd., BVT technologies a.s., BST Bio Sensor Technology GmbH, PINE Research Instrumentation, Windsor Scientific Ltd, etc. These sensors have been used in many applications according to these manufactures, however, the sensor topology design and its influence to output current response or its behaviour in the solution is unknown and one may speculate about their versatility. Therefore, the main aim of this study was investigate the effect of change of geometrical size of the reference and

auxiliary electrodes on the output anodic and cathodic current response and half wave potentials voltage shift in standard electrochemical couple of potassium ferrocyanide and ferricyanide solution. Further, we optimized material to prepare the electrodes. The third part of this study was devoted to comparison of planar electrochemical system (sensor) with standard-like non-planar electrodes arrangement.

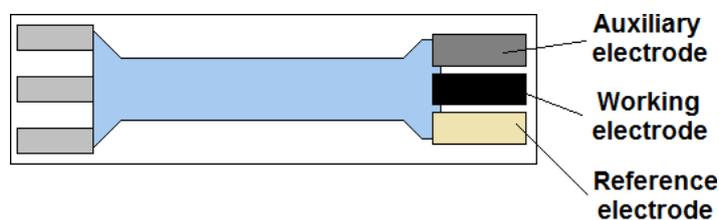


Figure 1. Screen-printed voltammetric sensor topology.

2. EXPERIMENTAL PART

2.1 Chemicals

Solution of 0.05 mol/L potassium ferrocyanide $K_4Fe(CN)_6$ and 0.05 mol/L potassium ferricyanide $K_3Fe(CN)_6$ in 0.1 mol/L KCl in volume ratio 1:1, pH 5.2 and 0.2 M KCl aqueous solution at pH 2 (acidified with HCl) were prepared. All used chemicals of ACS purity were purchased from Sigma-Aldrich Chemical Corp. (USA) unless noted otherwise. Deionized water underwent demineralization by reverse osmosis using the instrument Aqua Osmotic 02 (Aqua Osmotic, Czech Republic) and then it was subsequently purified using Millipore Direct-Q Water Purification System (Millipore Corp., USA, 18 M Ω) – MiliQ water. The pH value was measured using inoLab controlled by the personal computer program (MultiLab Pilot; WTW, Germany).

2.2 Electrochemical measurements

All cyclic voltammetric (CV) measurements were done using potentiostat PalmSens handheld potentiostat/galvanostat (Palm Instruments BV, Netherlands) as suitable set for *in-situ* measurements. The device was connected to a personal computer for measurement setup and response evaluation using PSTrace v2.3 software. Cyclic voltammetric parameters were as follows: potential range -200 to 800 mV, potential step 5 mV, scan rate 10, 20, 40, 80, 160 and 320 mV/s for the experiments with differently sized electrodes and potential range -300 to 600 mV, potential step 5 mV and scan rate 20 mV/s for the experiment with reference electrode (RE) material. The real active size of working electrode (WE) and reference electrode (AE) were calculated from results obtained from measurements of above mentioned simple redox couple Fe(II)/Fe(III) using Randles-Sevcik equation from a peak current, where the measured electrode was connected as the working electrode against standard

platinum AE (6.0343.000, Metrohm, Switzerland) and an Ag/AgCl RE (6.0726.100, Metrohm, Switzerland).

The experiment with RE material was performed against standard gold WE (UMMAUR11, Sycopel Scientific Limited, UK) and platinum auxiliary electrode (UMMPTB11, Sycopel Scientific Limited, UK). RE Theta 403 (Electrochemical detectors, Turnov, Czech Republic) was used as standard RE for comparison. All experiments were done in a 10 ml voltammetric thermostatic cell (25 °C) equipped with thermostat Petite Fleur (Huber GmbH, Germany) at scan rate 20 mV/s and potential range from -300 to 600 mV.

The experiment with planarity was performed in planar and standard-like non-planar configuration. In the planar system configuration all electrodes from one three-electrode planar system were connected. In non-planar system configuration WE from one against RE and AE from second planar electrochemical system in distance of 5 mm was connected. The measurements were done in ferro-ferricyanide solution diluted to concentration of 0.5 mmol/L and scan rate 160 mV/s.

2.3 Electrode system

2.3.1 Fabrication

All TFT electrode systems were screen-printed on alumina substrates using Aurel C880 semiautomatic screen-printer (Aurel Automation, Italy) and fired using BTU fast fire furnace for thick film processing (BTU, USA). The conductive layer was fabricated from AgPdPt based paste (ESL 9562-G). The protective layer was fabricated from dielectric paste (ESL 4917). Auxiliary electrode was fabricated from Pt based paste (ESL 5545). All cermet pastes were obtained from ESL ElectroScience Europe, UK and fired at 850 °C according the recommended values in products datasheets. The working electrodes were screen-printed using special carbon based conductive paste for electrodes of electrochemical sensors (DuPont BQ221) from DuPont Company (DuPont, USA) and cured at 130 °C for 10 minutes according to datasheet. The reference electrodes for the first two and the fourth experiments were screen-printed using special polymer Ag/AgCl paste (DuPont 5874, Ag:AgCl ratio 65:35) and dried at 120 °C for 5 minutes. Reference electrodes for the third experiment were screen-printed using two polymer Ag/AgCl pastes (DuPont 5874, Ag:AgCl ratio 65:35 and DuPont 5870, Ag:AgCl ratio 80:20) and the rest using silver based paste (ESL 9912-K). The electrochemically coated AgCl RE were prepared using electrochemical reoxidation of silver based RE in 0.2 M KCl [106] against platinum auxiliary electrode (UMMPTB11, Sycopel Scientific Limited, UK) and Ag/AgCl RE Theta 403 (Electrochemical detectors, Turnov, Czech Republic), but some of the TFT Ag paste based REs were used as the underlay.

2.3.2 Characterization

LYNX Dynascope stereo microscope (Vision Engineering Ltd, UK) was used for optical characterization of screen-printed electrodes. The electrical inspection was performed using precise digital laboratory multimeter Agilent 34401A (Agilent Technologies, USA). Scanning electron

microscopy (SEM) of fabricated samples was performed by Tescan Mira II microscope (Tescan, Czech Republic) controlled by standard PC equipped with MIRATC software version 3.5.11.0. The beam energy was set to 5 kV and the in-beam secondary electrons detector was used for analysis. The chamber pressure was 9×10^{-3} Pa and the ambient chamber temperature was 25 °C.

3. RESULTS AND DISCUSSION

3.1 Design of the study

In the first part of this study, the change of geometrical size of the reference and auxiliary electrodes and its influence to the output anodic and cathodic current response and half wave potentials voltage shift in standard electrochemical couple of potassium ferrocyanide and ferricyanide solution were investigated. One of them was done for the change of RE geometrical size and the second for the change of AE geometrical size, because these two areas could be changed during the electrode design. The second part of this study was devoted to the experiment for searching of suitable material for RE using the same evaluation method. The third part of this study was devoted to comparison of planar electrochemical system (sensor) with standard-like non-planar electrodes arrangement. Therefore two sets of differently sized electrodes for the first, one set of electrodes for the second and another set of electrodes for the third part of this study were designed and fabricated as it is mentioned in Experimental section.

3.2 Electrodes design and fabrication

Design of new three-electrode systems used for all experiments came out from the planar voltammetric electrochemical three-electrode screen-printed electrochemical system (sensor) with strip electrodes, which is shown in Fig. 1. The size of the sensor substrate was chosen to be compatible with standard size of printed electrodes used in our laboratory [60], which dimension (7.2×25.4 mm) is given by dividing of the standard alumina substrate used in TFT (2×2 " in this case) to equal electrode substrates.

To investigate the effect of geometrical size of the reference and auxiliary electrodes and its influence to the output anodic and cathodic current, fourteen different electrode systems, where one of the electrodes (RE or AE) was changed, were designed as strip electrodes. Working electrode was designed with a fixed geometrical electrode area for all cases because the response is given mainly by the active area of the WE as follows from Cottrell equation for current coming through the system with solid electrodes. All strip electrode systems were designed to fit onto one alumina substrate with the size of 2×2 inch. Finally the limiting size for each three-electrode system area was approximately 7×7 mm. The geometrical size of WE and unchanged electrode (RE or AE depending on the experiment) were designed to be 6.75 mm^2 large. The geometrical areas of variable-sized electrodes (RE or AE depending on the experiment) were designed to differ from 1.12 to 6.75 mm^2 , which means that the ratio against WE differed in range from 1:6 to 1:1. The electrodes were designed to be spaced 0.4 mm

and the strip electrode length was 4.5 mm. WE was placed in the middle between RE and AE. All designed electrode systems are shown in Fig. 2a. The designed geometrical areas of AE and RE and their ratio against WE are summarized in Tables 1 and 2, respectively. There were fabricated ten sets containing fourteen changed electrode systems and used for measurements according to Fig. 2a. The same electrodes design was used for variable REs or AEs design, but the RE and AE electrodes positions were swapped during the printing process. Fabricated substrate containing fourteen deposited electrode systems with various AE is shown in Fig. 2b.

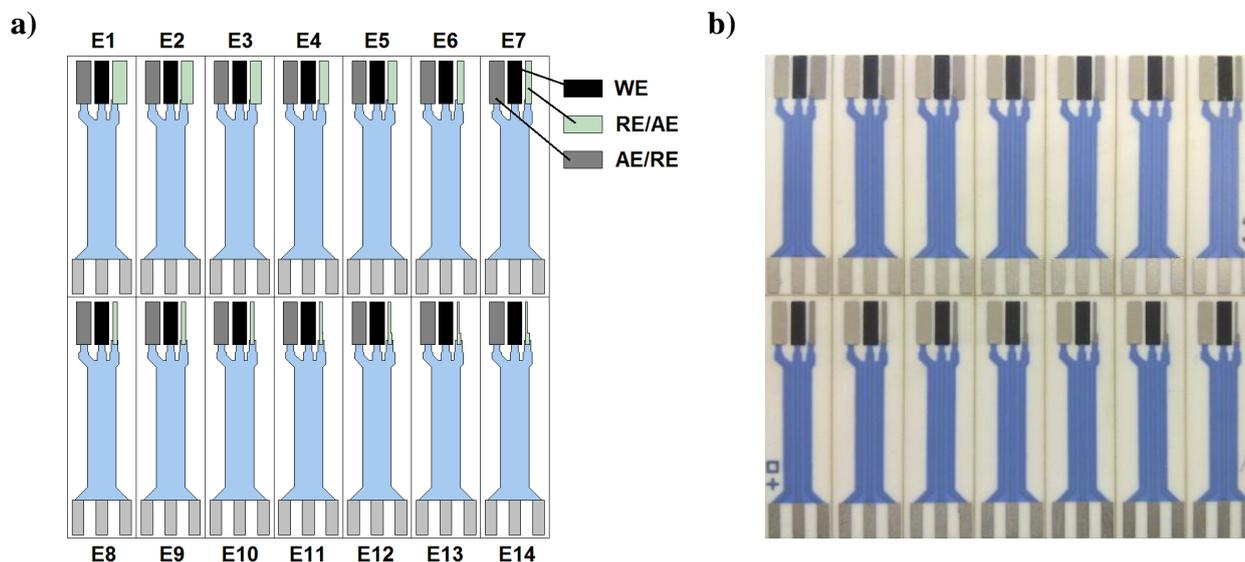


Figure 2. (a) strip electrodes Designed. (b) with printed electrodes on alumina substrate after fabrication.

Table 1. Designed electrode areas for RE geometrical size changing.

	E1	E2	E3	E4	E5	E6	E7	E8	E9	E10	E11	E12	E13	E14
RE/WE ratio	1/1 (1)	4/5 (0.8)	3/4 (0.75)	2/3 (0.67)	3/5 (0.6)	1/2 (0.5)	2/5 (0.4)	1/3 (0.33)	8/27 (0.3)	1/4 (0.25)	2/9 (0.22)	1/5 (0.2)	8/45 (0.18)	1/6 (0.17)
Geometrical area of RE [mm ²]	6.750	5.400	5.063	4.500	4.050	3.375	2.70	2.250	2.000	1.680	1.500	1.350	1.200	1.120

$$WE=AE=6.75 \text{ mm}^2$$

Table 2. Designed and measured electrode areas for AE geometrical size changing.

	E1	E2	E3	E4	E5	E6	E7	E8	E9	E10	E11	E12	E13	E14
AE/WE ratio	1/1 (1)	4/5 (0.8)	3/4 (0.75)	2/3 (0.67)	3/5 (0.6)	1/2 (0.5)	2/5 (0.4)	1/3 (0.33)	8/27 (0.3)	1/4 (0.25)	2/9 (0.22)	1/5 (0.2)	8/45 (0.18)	1/6 (0.17)
Geometrical area of AE [mm ²]	6.750	5.400	5.063	4.500	4.050	3.375	2.700	2.250	2.000	1.680	1.500	1.350	1.200	1.120

$$WE=RE=6.75 \text{ mm}^2$$

To study suitable material for RE, the same topology design of electrode system area was used, but RE with area of 6.75 mm^2 was implemented. For this purpose, there were fabricated four sets of REs with variable material of the electrode. First two sets were fabricated using special commercial Ag/AgCl DuPont pastes and the third and fourth set from silver based ESL paste. The fourth set was then successfully electrochemically coated by AgCl layer according to Lanz et al. [106]. For the comparison of planar system configuration behaviour with three-electrode standard-like non-planar system configuration, the same topology design of electrode system area with all three electrode sizes designed to be 6.75 mm^2 large was also used. The DuPont 5874 paste was used for RE fabrication.

3.3 Electrodes surfaces morphology characterization

Fabricated electrodes surfaces were examined using scanning electron microscopy. All surfaces structures with magnification of $20\text{k}\times$ are shown in Fig. 3. The WE structure is shown in Fig. 3a. It is clear that the WE surface is not covered homogeneously by carbon particles, but the surface is porous and with very small crystallinity. This protruded morphology ensures that the active surface is larger than the designed geometrical area that was confirmed by measurement, where the WE area was measured and calculated using Randles-Sevcik equation for peak current as 7.54 mm^2 large. It would be expected that the active area would be much higher than the designed one, but the real active area of polymer pastes is in general affected by approximately 40-70 wt% of inactive polymer filling (approx. 65% in case of BQ221 paste), which partially covers the active electrode material surface. The RE surface structure made of DuPont 5874 paste shown in Fig. 3b consists of $0.5 \mu\text{m}$ big grains forming rough and crystalline morphology, thus, the active electrode area is estimated to be higher than the designed one. The AE surface structure shown in Fig. 3c made of high porous structure of melted platinum grains with diameter of about $1 \mu\text{m}$ also ensures that the active electrode area is little bit larger than the designed one.

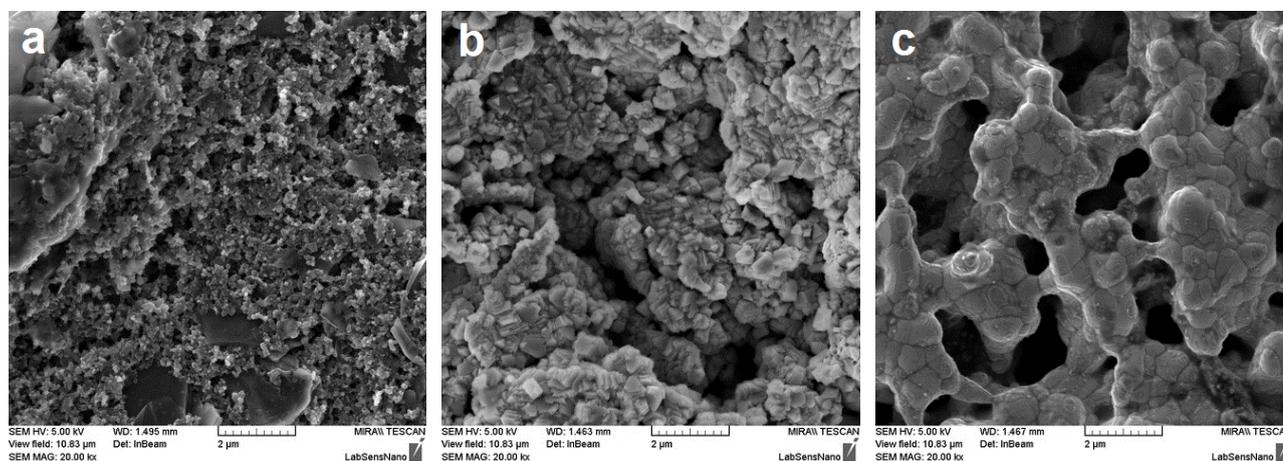


Figure 3. SEM characterization of screen-printed electrodes: a) working electrode (DuPont BQ221), b) reference electrode (DuPont 5874), c) auxiliary electrode (ESL 5545).

This was also confirmed by measurement and calculation from Randles-Sevcik equation for peak current. The measured sizes of the electrodes are shown in Table 2. It clearly follows from the results obtained that the surface of all screen-printed materials structures are in accordance with the reference structures, which means that the pastes were screen-printed properly. Based on the optical and electrical measuring of screen-printed electrodes it was clear that we obtained standard quality of printed layers without any short-circuits between the electrodes.

3.4 REs with various surfaces

After that we characterized printed electrodes differing in areas of their RE, we tested the influence of various areas on the cathodic and anodic current responses of standard electrochemical couple of potassium ferrocyanide and ferricyanide solution measured by CV. Various scan rates as 10, 20, 40, 80, 160 and 320 mV/s were used and current responses were detected. The obtained cyclic voltammograms are shown in Fig. 4. The influence of areas of RE on both measured responses can be found in Table 3. We linearly plotted dependence of cathodic and/or anodic currents on scan rates and found equations and coefficients of determination. Based on the results it can be concluded that anodic currents were larger than cathodic, but the process was reversible due to the difference of peak potentials less than 50 mV.

Table 3. Equations and coefficients of determination for cathodic and anodic currents depending on the various surfaces of REs in measured scan rate range.

Cathodic current			Anodic current		
Surface [mm ²]	Equation of linear plot	R ²	Surface [mm ²]	Equation of linear plot	R ²
1.120	y = 698.21x + 69.028	R ² = 0.9907	1.120	y = 823.43x + 57.001	R ² = 0.9893
1.200	y = 691.44x + 69.029	R ² = 0.9925	1.200	y = 827.69x + 58.208	R ² = 0.9886
1.350	y = 667.45x + 66.747	R ² = 0.9909	1.350	y = 781.60x + 58.283	R ² = 0.9881
1.500	y = 668.73x + 64.592	R ² = 0.9922	1.500	y = 790.40x + 56.839	R ² = 0.9887
1.680	y = 673.99x + 68.258	R ² = 0.9929	1.680	y = 811.98x + 57.169	R ² = 0.9883
2.000	y = 668.46x + 69.870	R ² = 0.9915	2.000	y = 796.80x + 56.797	R ² = 0.9890
2.250	y = 682.12x + 64.098	R ² = 0.9916	2.250	y = 791.18x + 54.769	R ² = 0.9900
2.700	y = 648.34x + 73.185	R ² = 0.9871	2.700	y = 754.65x + 60.316	R ² = 0.9884
3.375	y = 666.46x + 66.509	R ² = 0.9913	3.375	y = 769.95x + 57.136	R ² = 0.9888
4.050	y = 699.94x + 67.542	R ² = 0.9926	4.050	y = 812.66x + 58.033	R ² = 0.9911
4.500	y = 705.20x + 67.319	R ² = 0.9914	4.500	y = 815.64x + 56.307	R ² = 0.9922
5.063	y = 742.19x + 72.327	R ² = 0.9916	5.063	y = 868.11x + 60.526	R ² = 0.9914
5.400	y = 726.04x + 64.765	R ² = 0.9946	5.400	y = 826.09x + 60.289	R ² = 0.9915
6.750	y = 722.90x + 61.685	R ² = 0.9942	6.750	y = 814.03x + 58.222	R ² = 0.9921

Considering cathodic currents only, the highest current responses expressed by the highest slopes of the dependencies obtained were found at RE with area 5.063 mm². After similar evaluation

of anodic currents, we found that the highest responses were detected using RE with area 5.063 mm², which well corresponds with the cathodic currents and shows stable surface and electrochemical behaviour of these electrodes in a solution. In our following experiments, we used RE with area 5.063 mm².

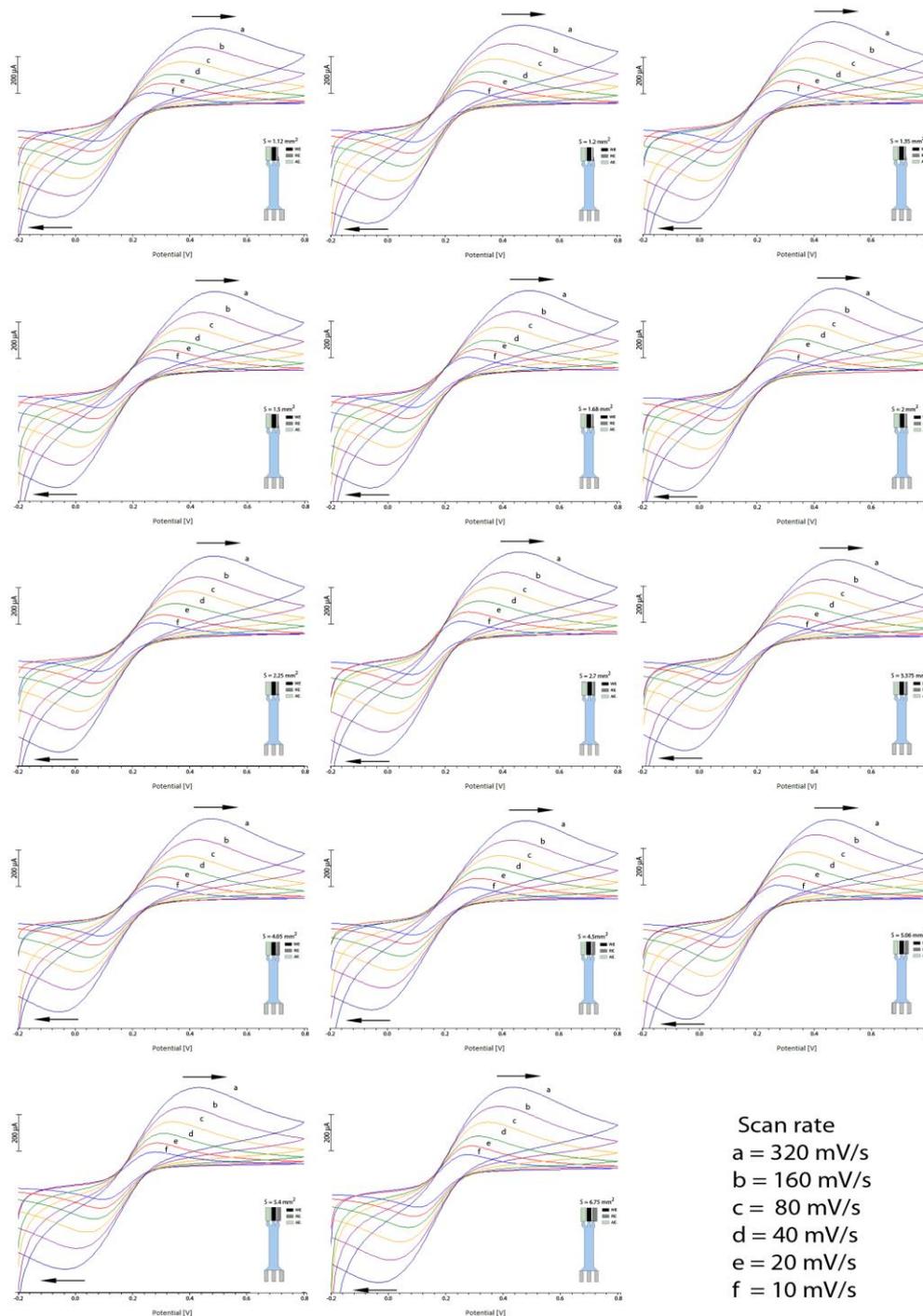


Figure 4. Cyclic voltammograms of potassium ferro-ferricyanide system measured by tested differently sized REs using six scan rates. In the bottom inset: shape of the screen printed electrode.

3.5 AEs with various surfaces

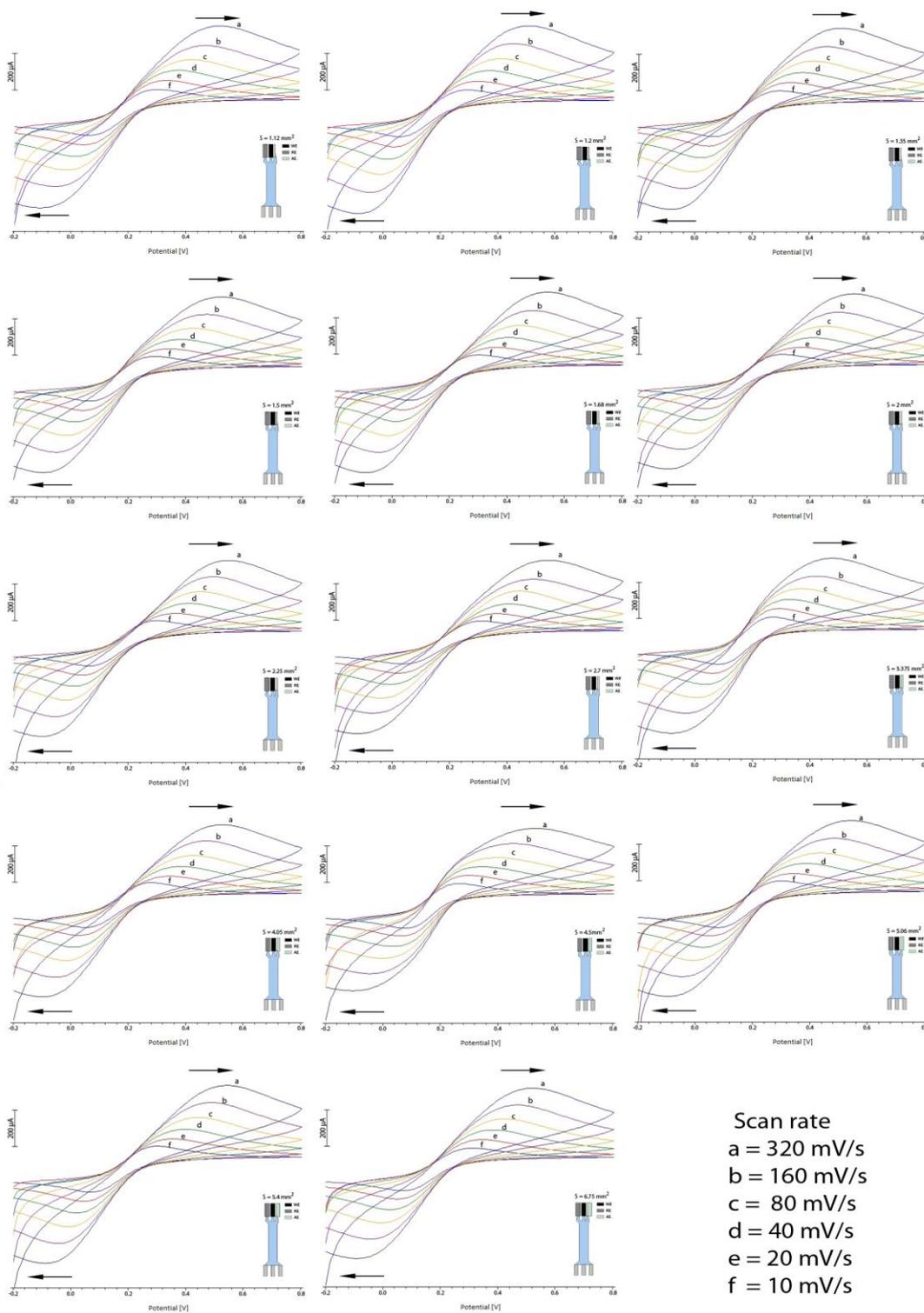


Figure 5. Cyclic voltammograms of potassium ferro-ferricyanide system measured by tested differently sized AEs using six scan rates. In the bottom inset: shape of the screen printed electrode.

After that we optimized all of reference electrodes, which had marked influence on current response of standard electrochemical couple of potassium ferrocyanide and ferricyanide solution, we followed with the studying of the influence of various areas of auxiliary electrode (AE) on the cathodic and anodic current responses of standard electrochemical couple of potassium ferrocyanide and ferricyanide solution measured by CV. Various scan rates as 10, 20, 40, 80, 160 and 320 mV/s were again used and current responses were detected. The obtained cyclic voltammograms are shown in Fig. 5. Detected responses were measured and summarized in Table 4. We linearly plotted dependence of cathodic and/or anodic currents on scan rates and found equations and coefficients of determination. From the point of view of electrochemical process itself, we analysed well defined and reversible redox system with well-defined peaks. Considering cathodic currents only, the highest current responses expressed by the highest slopes of the dependencies obtained were found at AE with area about 5 mm². After similar evaluation of anodic currents, we found that the highest responses were detected using RE with area 5.400 mm² followed by area of 5.063 mm². These results well corresponds with those obtained with various areas of REs. It is obvious that area of 5.063 mm² seems to be very suitable for fabrication of both AE and RE, which is also very good for easy fabrication of the electrodes.

Table 4. Equations and coefficients of determination for cathodic and anodic currents depending on the various surfaces of AEs in measured scan rate range.

Cathodic current			Anodic current		
Surface [mm ²]	Equation of linear plot	R ²	Surface [mm ²]	Equation of linear plot	R ²
1.120	y = 687.49x + 66.064	R ² = 0.9884	1.120	y = 815.07x + 54.362	R ² = 0.9888
1.200	y = 690.57x + 64.045	R ² = 0.9907	1.200	y = 815.74x + 54.955	R ² = 0.9880
1.350	y = 697.92x + 62.458	R ² = 0.9910	1.350	y = 821.17x + 53.562	R ² = 0.9881
1.500	y = 679.56x + 61.880	R ² = 0.9910	1.500	y = 802.25x + 53.955	R ² = 0.9882
1.680	y = 692.65x + 59.560	R ² = 0.9933	1.680	y = 806.08x + 54.760	R ² = 0.9887
2.000	y = 684.15x + 62.554	R ² = 0.9922	2.000	y = 800.94x + 55.808	R ² = 0.9888
2.250	y = 662.67x + 60.671	R ² = 0.9918	2.250	y = 773.89x + 52.293	R ² = 0.9894
2.700	y = 686.73x + 66.877	R ² = 0.9903	2.700	y = 806.31x + 55.796	R ² = 0.9901
3.375	y = 680.77x + 70.055	R ² = 0.9894	3.375	y = 805.76x + 57.367	R ² = 0.9897
4.050	y = 696.34x + 68.520	R ² = 0.9904	4.050	y = 813.33x + 57.185	R ² = 0.9902
4.500	y = 667.02x + 70.077	R ² = 0.9871	4.500	y = 775.11x + 59.801	R ² = 0.9896
5.063	y = 735.66x + 67.530	R ² = 0.9931	5.063	y = 840.44x + 59.533	R ² = 0.9901
5.400	y = 725.79x + 66.175	R ² = 0.9914	5.400	y = 843.86x + 56.987	R ² = 0.9905
6.750	y = 726.45x + 60.689	R ² = 0.9915	6.750	y = 825.02x + 54.409	R ² = 0.9915

3.6 Testing of various RE materials

Under the optimized AE and RE areas, we were interested in the issue how various materials for fabrication of reference electrodes could influence current response of standard electrochemical couple of potassium ferrocyanide and ferricyanide solution measured by CV. DuPont 5870 (AgCl),

DuPont 5874 (AgCl), electrochemically deposited AgCl and pure Ag based TFT paste (ESL 9912-K) were tested. We independently fabricated four same electrodes and tested their behaviours. Voltammograms measured using reference electrode made of DuPont 5874 paste are shown in Fig. 6a. Voltammograms obtained were repeatable, therefore, selected material and areas of electrodes were suitable for this redox system. Similar promising results were obtained with the electrodes made of DuPont 5870 paste, as it is shown in Fig. 6b. On the other hand, the results obtained with electrochemically prepared electrodes were of worse repeatability (Fig. 6c). Pure silver based TFT REs were of poor repeatability. Based on the results obtained it can be concluded that the best behaviour was detected at electrodes made of DuPont 5874 followed by DuPont 5870 and electrochemically deposited AgCl.

Moreover, the comparison of all measured types of reference electrodes with standard Ag/AgCl reference electrode (Theta 403, Electrochemical detectors, Turnov, Czech Republic) was done to find, whether the results are comparable with commercial standard. Cyclic voltammograms of all tested RE are shown in Fig. 6d.

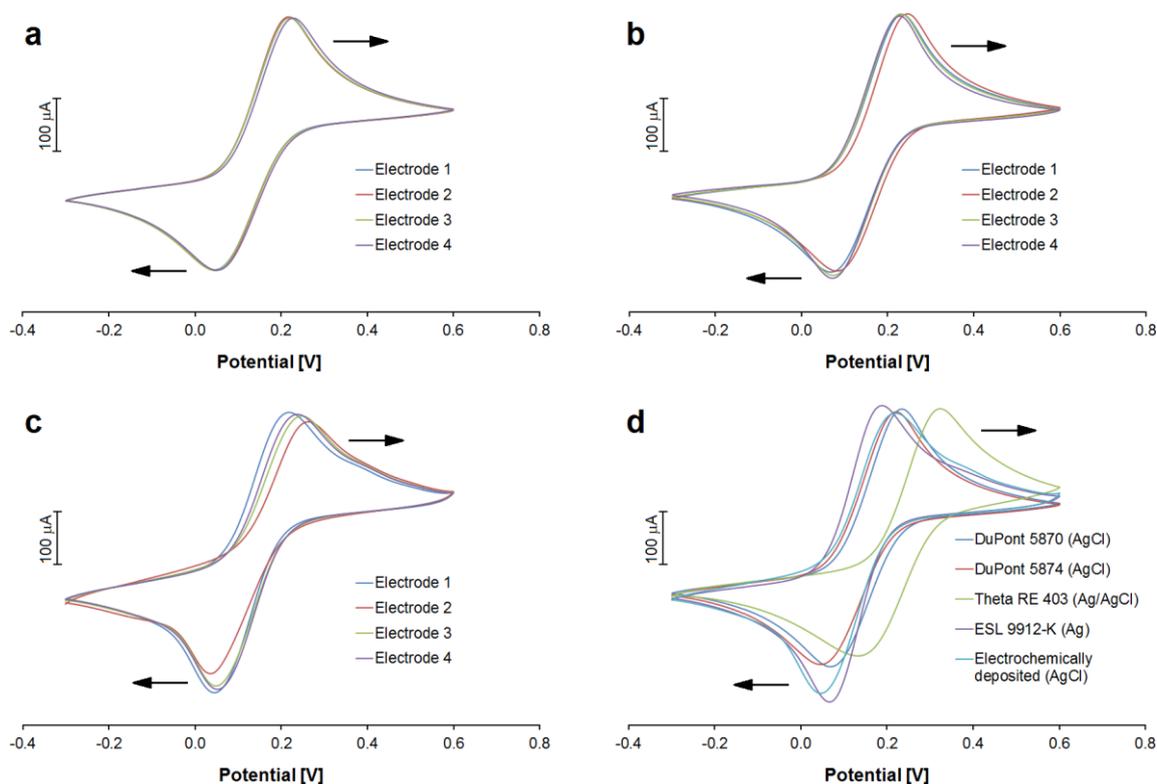


Figure 6. RE output current responses to 0.05M potassium ferro-ferricyanide solution. a) DuPont 5874 commercial polymer paste. b) DuPont 5870 commercial polymer paste. c) Electrochemically coated reference electrodes. d) Tested materials comparison with standard Ag/AgCl electrode and pure silver based TFT paste.

The results showed that behaviour of commercial DuPont pastes are very similar although the Ag/AgCl ratio is different. The comparison with standard Ag/AgCl reference electrode showed that the

current response is comparable. However, potentials of the measured peaks were shifted using DuPont made electrodes compared to commercial standard for more than 100 mV. The potentials measured using electrochemically fabricated reference electrodes were similar to potentials measured using DuPont polymer pastes made electrodes. It clearly follows from the results obtained that DuPont pastes are the best solution for construction of planar reference printed electrodes because of very good and reproducible response.

3.7 Testing of planarity influence to output current response

After the optimization of electrode sizes and suitability of RE materials we wondered if there will be any influence of planar system to output current response. We assumed that there could be some diffusion limitation of planar stationary system at low concentrations and high scan rates due to smaller bulk of free Fe(II) and Fe(III) ions around the planar electrodes. Therefore we compared our planar electrode system with standard-like non-planar system configuration, where just our WE from planar system was used on one side against planar AE and RE on the second side in distance of 20 mm. Comparison of both systems response to 0.5 mmol/L potassium ferro-ferricyanide solution is shown in Fig. 7. The results showed that no significant output current response change was observed for selected scan rate of 160 mV/s. It clearly follows from our results obtained that planar electrochemical systems could be also used for fast determination of low concentrations of species that are generally detected using non-planar system configuration.

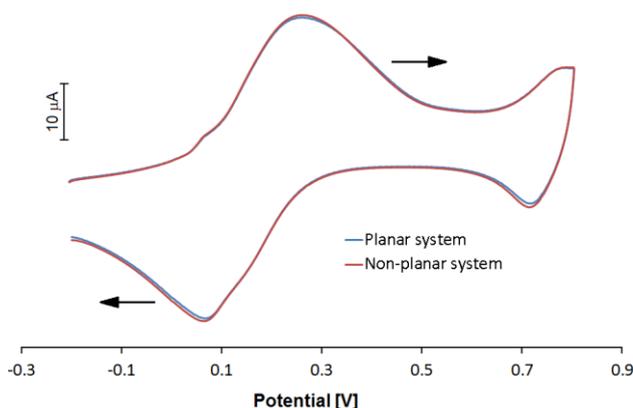


Figure 7. Planar electrode system configuration output current response comparison to non-planar electrode system configuration.

4. CONCLUSIONS

The trend of the analytical techniques is to miniaturize the whole instrument due to many advantages of small devices including portability, low costs and demands on service and operations, sufficient sensitivity and selectivity [64,65]. In this study, we show testing and optimizing of some

important features of screen-printed electrodes, which should be considered before their designing, fabrication and applications for electrochemical analysis, because we found that areas as well as materials of auxiliary and reference electrode can markedly influence of current response and, therefore, markedly influence detection limit of the sensor. Finally, there was also confirmed, that these three-electrode screen-printed planar electrode systems could be used for detection of 0.5 mmol/L of ferro-ferricyanide solution at the scan rate 160 mV/s without any significant output current response change in comparison to standard-like non-planar three-electrode system predicting for presented electrodes sizes no diffusion limits impacting the low concentration determination.

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