THE INFLUENCE OF PRINTING PROPERTIES OF SCREEN PRINTED ELECTRODES ON SENSITIVITY MEASURED WITH CYCLIC VOLTAMMETRY

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Abstract: *Disposable screen printed electrodes are widely used for environmental monitoring such as water quality test, heavy metals detection and gas pollutants. (Hayat et al, 2014; Li et al, 2012) Screen printed electrodes used for electrochemical detection consist of three electrodes: auxiliary, working and reference electrode. The working electrode is the principal electrode on which electrochemical reactions are performed, while the reference and auxiliary electrodes are used to complete the electronic circuit. (Hayat et al, 2014) To produce efficient screen printed electrodes the modification of the electrode surface or altering of the geometry of electrode can be done. Researchers mostly modify the surface of the electrode, but on the other hand, there are many properties that can be changed and optimized at the beginning, in the process of screen printing.*
In the presented research the influence of the modification of the working electrode area and conductive ink thickness on the final electrochemical activity was evaluated. Besides that, a modification of conductive printing ink was done using carbon nanotubes. Finally, electrochemical activity of all samples was analyzed with potassium ferricyanide $K_3[Fe(CN)_6]$. It was found that the highest impact on electrochemical activity has conductive ink thickness. Working electrode area also affects the electrochemical activity, but less, while modification of conductive ink with the addition of carbon nanotubes does not have significant influence. The main reason for that was immersing of nanotubes into the ink and consequently, the specific surface of the modified working electrode remains comparable to non-modified one.

Key words: screen printed electrodes, printing properties, cyclic voltammetry

1. INTRODUCTION

Disposable screen printed electrodes (SPE) are widely used for environmental monitoring such as water quality test, heavy metals detection and gas pollutants. (Hayat et al, 2014; Li et al, 2012) Screen printed electrodes used for electrochemical detection consist of three electrodes: auxiliary (AE), working (WE) and reference (RE) electrode (Figure 1). A RE is mostly printed with silver printing ink, while AE and WE can be printed also with different conductive printing inks (carbon, gold etc.). The WE is the principal electrode on which electrochemical reactions are performed, while the RE and AE are used to complete the electronic circuit (Hayat et al, 2014).

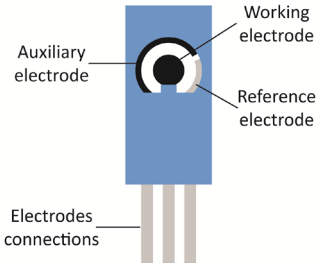


Figure 1: Screen printed electrode

There are two main strategies to produce efficient SPEs (Mohamed, 2016): (1) modification of electrode by depositing several substances or (2) altering the geometry of electrode or used printing inks. For the detection of a target analyte, researchers mostly use modified commercially available SPEs (DropSens, Metrohm Autolab, Gamry etc.). (Menart et al, 2017; Gusmão, 2017; López-López, 2017) That way, the most important property of the SPE is its modification. But on the other hand, there are many properties that can be changed and optimized at the beginning, in the process of screen printing. The sizes of all three electrodes, the conductive ink, the thickness of the conductive ink and consequently the conductivity of the electrodes can all be variables.

Researchers focus on both, modification of commercially available electrodes and also on altering the geometry. Jadav (Jadav et al, 2018) presents a development of silver/carbon screen printed electrode for determination of vitamin C in fruit juices. In his article he presents the whole process from formulation of conductive ink and screen printing process to analysis of electrochemical performance of screen printed electrode. Jewell and co-authors (Jewell et al, 2016) present the interactions between printing ink solvent, printed ink conductivity and process consistency. Oppositely to the printing process and used materials Garcia (Garcia et al, 2010) and Prasek (Prasek et al, 2012) focus on the geometry of the screen printed electrodes. Garcia with co-authors was focused on changing design parameters (the area of WE and AE, the distance between them and the overlap length between them). They found out that the only key parameter that influences the performance of the sensor is the area of the WE. Prasek was changing the geometrical size of RE and AE and found out that areas and materials of those two electrodes can markedly influence detection limit of the sensor.
In the first part of the presented research, the influence of WE area, the carbon ink thickness (and consequently the conductivity) on the final electrochemical behaviour by using cyclic voltammetry was analysed. In the second part of the research, the influence of addition of carbon nanotubes (CNT) into carbon ink was researched. The electrochemical performance of all SPEs was analysed with cyclic voltammetry. Cyclic voltammetry technique enables the study of the modified SPEs performance, by using a ferricyanide solution, being the redox couple peaks intensities (e.g. $K_3Fe(CN)_6/K_4Fe(CN)_6$) frequently used as sensitivity indicators (Sharma et al, 2010; Couto et al, 2016). For the cyclic voltammetry, 2.5 mM potassium ferricyanide $K_3[Fe(CN)_6]$ in 0.1 M KCl solution was used and cyclic voltammogram for each SPE was scanned. By altering the WE area, conductive carbon ink thickness and with modification of conductive carbon ink with CNT the enhancements in the sensor sensitivity could be achieved.

2. METHODS

SPEs were firstly designed in accordance with Dropsens potentiostat dimensional requirements. Three SPEs with different WE area (diameter of 2, 3 and 4 mm) were designed (Figure 2). After that, multi-layer screen printing followed. Firstly, contacts (electrodes connections) and RE were printed with silver printing ink (SC), then AE and WE electrode with carbon printing ink (PE) and at the end dielectric printing ink. For SPEs printing, the printing inks, printing and curing conditions as presented in Table 1 were applied. As a printing material, synthetic paper Monotex L 175 BG 254 g/m^2 (Feron, Germany) was used.

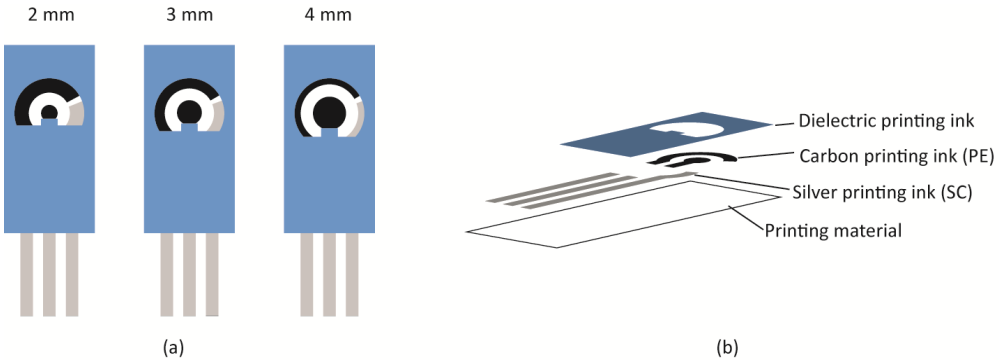


Figure 2: Samples of SPE with 2, 3 and 4 mm WE diameter (a) and multi-layer SPE (b)

Table 1: Used printing and curing conditions

Abbreviation	Printing ink	Producer	Ink type	Mesh count [lines/cm]	Curing conditions
PE	PE-C200 Carbon resistive ink	Applied Ink Solution, US	Carbon printing ink	77-55	5 min @ 120 °C
SC	CRSN 2442, SunTronic Silver 280	Sun Chemical	Silver printing ink	120-31	10 min @ 120 °C
Dielectric	CFSN6057 SunTronic Dielectric 681	Sun Chemical	Dielectric printing ink	90-45	600 mJ/m^2

2.1 The influence of WE area, ink thickness and sheet resistance on cyclic voltammetry

In the first part of the research, the variation of WE area and WE printing ink thickness was analysed. All samples had contacts and RE printed using silver conductive ink SC, while WE and AE were printed with PE ink in two thicknesses (PE ink was printed in one or in two layers) (Figure 2 (b)). After curing, the thickness of the dry ink was measured using micrometre (Lorentzen & Wettre, Sweden). The resistance of conductive ink lines was measured using LCR-300 Voltcraft multimeter and sheet resistance was calculated for both thicknesses.

2.2 The influence of carbon nanotubes on cyclic voltammetry

In the second part of the research, the influence of CNT addition into PE ink on electrochemical activity was analysed. 0.4 % of multi-walled carbon nanotubes (Sigma-Aldrich, USA) were added to the PE carbon ink. The printing and curing were applied under the same conditions as PE ink (see Table 1).

2.3 Cyclic voltammetry

After printing, an electrochemical activity using cyclic voltammetry was analysed. The electrochemical performance of all SPEs was analysed using 100 µl of 0.1 M KCl solution containing 2.5 mM potassium ferricyanide $K_3[Fe(CN)_6]$ and cyclic voltammogram for each screen printed electrode (with different WE area, WE conductive ink thickness and CNT addition) was scanned. Cyclic voltammograms were scanned using Dropsens µStat 300 Bipotentiostat with the parameters presented in Table 2.

Table 2: Cyclic voltammetry parameters

Parameter	Value
Current range	auto
E_{begin}	0.22 V
E_{vtx1}	-0.15 V
E_{vtx2}	0.5 V
Estep	0.002 V
Scan rate	0.05 V/s
n scan	1

The important parameters for a cyclic voltammogram are the peak potentials and peak currents. (BASi, 2018) So, at the end, the final comparison of the cyclic voltammograms peak currents of the samples printed with different WE area and different ink thicknesses as well the influence of the CNT addition in PE ink was checked.

3. RESULTS AND DISCUSSION

3.1 The influence of WE area, ink thickness and sheet resistance on cyclic voltammetry

The final area of a WE and its conductivity (which is a consequence of ink thickness) influence the final signal of cyclic voltammetry. The actual areas of WEs of different diameters are presented in Table 3. In Table 4 the final ink thicknesses of the WEs printed once (1 × PE) and twice (2 × PE) and corresponding sheet resistances of the samples are presented.

Table 3: Diameters and actual areas of samples WE electrodes

WE diameter [mm]	WE actual area [mm^2]
2	3.061
3	7.169
4	12.863

Table 4: Printing ink thicknesses of WE and AE and corresponding sheet resistances

Sample	Thickness [µm]	Sheet resistance [Ω/sq]
1 × PE	21	137
2 × PE	28	46

In Figures 3, 4 and 5 cyclic voltammograms of 2.5 mM potassium ferricyanide $K_3[Fe(CN)_6]$ in 0.1 M KCl for different WE diameters (2, 3 and 4 mm) and for different WE ink thicknesses (1 × PE and 2 × PE) are presented. When changing the potential from 0.22 V to -0.15 V and through 0.5 V back to the starting potential the current that is produced presents electrochemical properties of the analyte. The maximum current achieved during the cyclic voltammetry scanning (one or more peaks) has to be as high as possible, which can be regulated also with WE area and its conductivity. In Figures 3, 4 and 5 it can be seen that the peaks are getting higher with larger WE diameter. The difference between the minimum and maximum current peaks at 1 × PE samples is 7.93 µA when using SPE with 2 mm diameter of WE, when the diameter is 3 mm the difference is 20.27 µA, and when using the largest, 4 mm diameter WE the difference increases to 29.88 µA. When analysing samples with higher thicknesses and conductivities (2 × PE) the peaks are getting even higher. After comparison of the influence of WE diameter and ink thickness on cyclic voltammetry, it is clearly seen that the final conductivity of the WE influences the cyclic voltammetry more that the WE diameter itself.

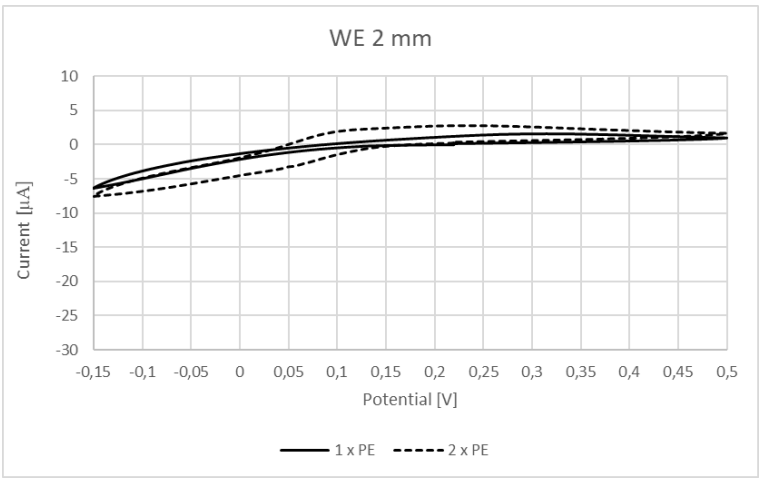


Figure 3: Cyclic voltammograms of SPE with 2 mm WE diameter in two thicknesses

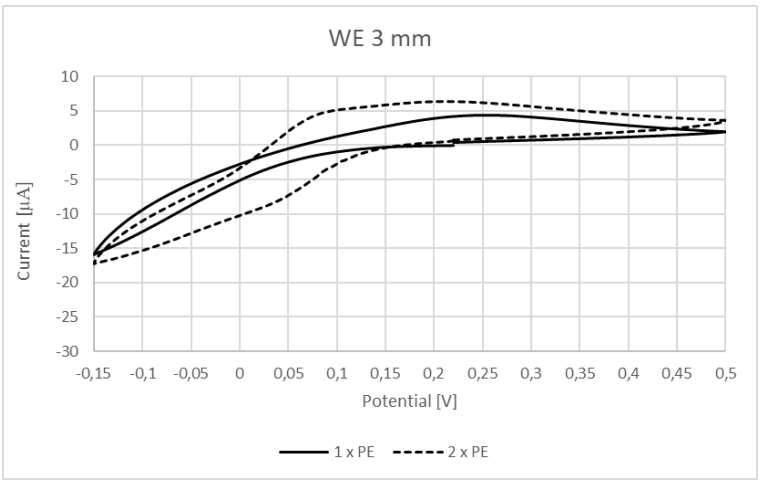


Figure 4: Cyclic voltammograms of SPE with 3 mm WE diameter in two thicknesses

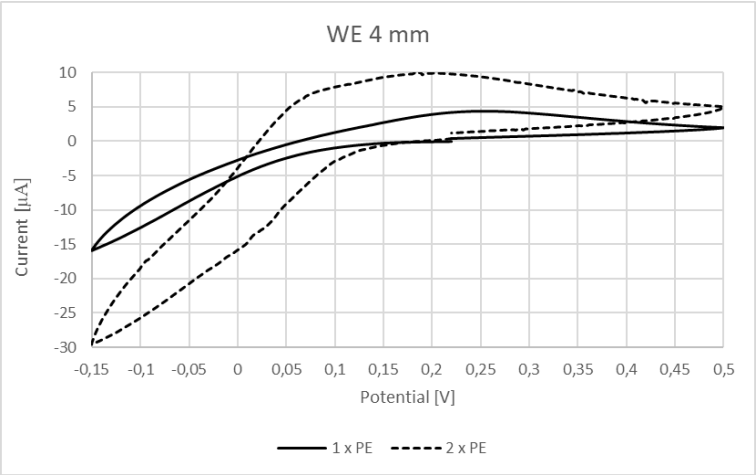


Figure 5: Cyclic voltammograms of SPE with 4 mm WE diameter in two thicknesses

3.2 The influence of carbon nanotubes on cyclic voltammetry

The functionalization of the SPE WEs is often used to enhance the final response of cyclic voltammetry. While comparing the different graphical properties on the final cyclic voltammetry response, the functionalization of WE was one of the variables changed during the experiment. Regarding literature, the functionalization is often done with nanotubes addition, so it was expected to get a better response in comparison to SPEs printed without CNT. But when cyclic voltammograms were scanned for samples with CNT (1 × PE + CNT) the current peaks were comparable to those without CNT (1 × PE) as presented in Figure 6.

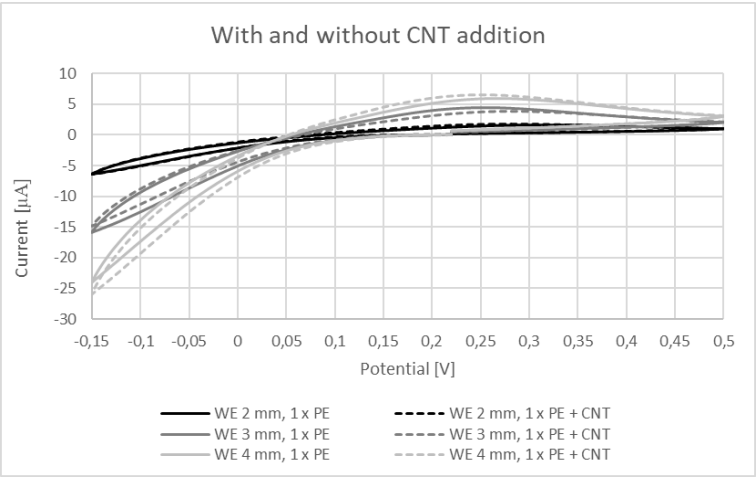
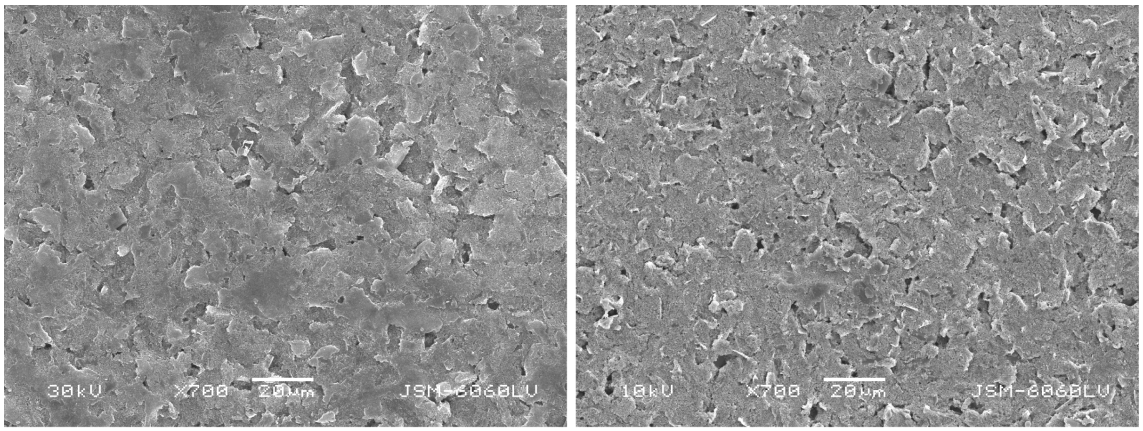


Figure 6: Cyclic voltammograms of SPE with different diameters of non-functionalized (1 × PE – solid line) and with CNT functionalized (1 × PE + CNT – dashed line) ink WE

While the results of cyclic voltammetry of non-functionalized and with CNT functionalized SPE were so comparable the surface of the both WE were scanned at scanning electron microscopy – SEM. In Figure 7 we have presented the surfaces of both and it is seen that the surface roughness is very similar, which can be attributed to the very small size of CNT (in comparison to conductive ink thickness) which were immersed into the ink and not remained at the surface of the WE. Consequently, the surface area changed just a little in comparison to non-functionalized SPE and the final response did not increase significantly.



(a) (b)

Figure 7: 700 × magnification of non-functionalized (1 × PE) – (a) and functionalized (1 × PE + CNT) – (b) surface of WE

4. CONCLUSIONS

Screen printing process offers many possibilities for printing SPE. The variations in thickness, conductivity and WE area can be easily achieved. Besides that, the functionalization of the ink can be freely done (for example with incorporation of chemical functionalized materials into the ink). In the presented research there are presented all the aforementioned properties and the final evaluation with cyclic voltammetry analysis was conducted. It was shown, that the conductivity of the WE (i.e. printing ink thickness) influences the cyclic voltammetry response much more than the WE diameter (even though also the diameter of the WE contributes the current change). Regarding WE functionalization, it was shown that CNT that are mixed into the printing ink sink into the ink and do not remain at the surface of WE. Consequently, the final response of WE printed with added CNT is just comparative to those without CNT. In the future analysis, the functionalization of the very top of the surface should be done and it is expected that with CNT on the top of WE surface would enlarge the specific area of the WE and consequently increase the response of the cyclic voltammetry.

5. ACKNOWLEDGEMENTS

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