Cyclic Voltammetry of Silver Nanoparticles on Platinum, Gold and Glassy Carbon Electrodes

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The electrochemical behaviour of silver nanoparticles stabilized with polyvinylpyrrolidone is studied in aqueous 0.1M KNO_3 *on platinum, gold and glassy carbon electrodes. The silver nanoparticles are loaded through adsorption from solution onto the electrode surface and cyclic voltammetry experiments are performed onto the loaded electrodes. The data show that the electrode coverage is rather low for all studied electrodes; the interaction between silver nanoparticles and the electrode increases in the order: glassy carbon < platinum < gold. The oxidation of silver nanoparticles leads to a decrease in the particle loading onto the electrode, as expected for a stripping process.*

Keywords: silver nanoparticles, colloidal solutions, cyclic voltammetry, adsorption

Metal nanoparticles are widely used in many fields and with many applications [1,2]. Silver nanoparticles have always been regarded as being relatively easy to synthesize [3-5] and having very desirable general properties [6] or else being useful for specific applications such as electrochemical nitrate sensors [7,8], solar cells [9] or temperature switches [10]. Their study has recently gained a renewed interest, as silver nanoparticles are important from both a theoretical and practical point of view [11]; the electrochemical behaviour of nanoparticles-modified electrodes was recently modeled using various approaches [12-17] and compared to earlier work on stripping voltammetry [18,19].

In this paper we report the cyclic voltammetry behaviour of polyvinylpyrrolidone-stabilized silver nanoparticles in aqueous solutions on platinum, glassy carbon and gold electrodes

Experimental part

The silver nanoparticles were synthesized by the “sacrificial anode” method using a current pulse generator with alternating polarity and a stirrer [20]. 99.999% Ag sacrificial electrodes were used in a solution of deionised water (conductivity < 1 μS/cm) and between 3 and 7 gL^{-1} polyvinylpyrrolidone (PVP) with 55.000 molecular weight. Current densities of about 7 $mAcm^{-2}$ were applied for 3, 5 and 7 h [21] for more details. For cyclic voltammetry experiments in the silver nanoparticles solutions, KNO_3 was added to a final concentration of 0.1 M. All the cyclic voltammetry data were performed at room temperature using an AUTOLAB PGSTAT12 electro-chemical workstation; full IR compensation was usually applied, unless otherwise noted. A silver wire was used as pseudo reference electrode and a platinum sheet as counter electrode; the working disk electrodes were either Pt (0.5 mm diameter), Au (1.5 mm diameter) or glassy carbon (5 mm diameter).

The sizes of the silver nanoparticles ranged between 70 and 120 nm [21]; unless otherwise stated typical experiments involved silver nanoparticle solutions obtained using 7 gL^{-1} PVP; the cyclic voltammetry experiments were performed after a waiting time (with the electrode immersed in the test solution) of ~45 min; the exceptions are noted in the text.

Results and discussions

Cyclic voltammetry of Ag/Ag$^+$ on Pt and Au electrodes

To test whether PVP influences the bulk deposition/stripping of Ag/Ag$^+$ several test experiments were performed in 0.1 M KNO_3 aqueous solution on various electrodes. An example of the influence of PVP on the silver electrodeposition/electrodissolution on platinum is shown in figure 1. While the presence of PVP clearly influences both the silver electrodeposition and dissolution, a clear trend is not apparent, as the changes do not seem to be correlated with the concentration of PVP. A possible strong adsorption of PVP at higher concentrations (> 3 gL^{-1}) may be, at least in part, responsible for such a behaviour (*vide infra*).

On gold however, the situation is somewhat different (fig. 2): while the electrodeposition seems to be barely influenced, the silver stripping shows a second oxidation

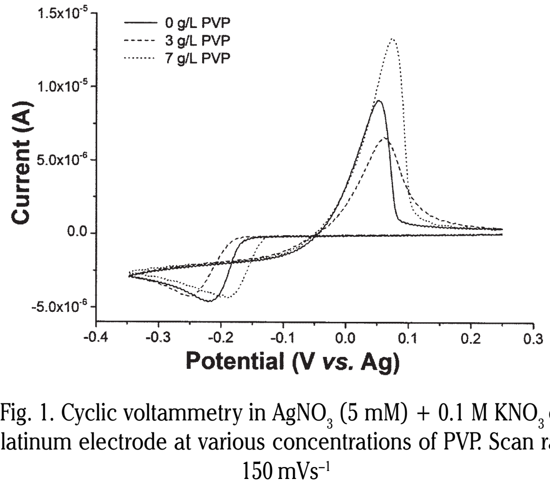

Fig. 1. Cyclic voltammetry in $AgNO_3$ (5 mM) + 0.1 M KNO_3 on platinum electrode at various concentrations of PVP. Scan rate: 150 mVs^{-1}

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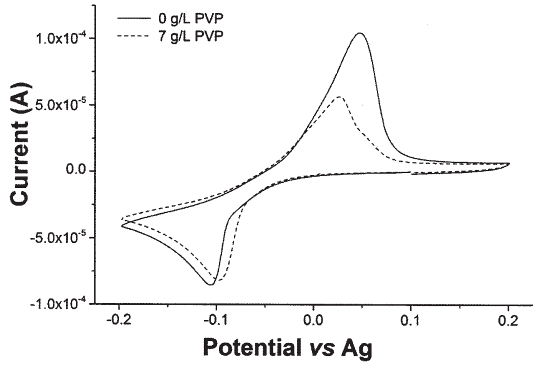

Fig. 2. A comparison between the cyclic voltammograms in AgNO3 (5 mM) + 0.1 M KNO3 aqueous solution on gold electrode in the presence or absence of PVP. Scan rate: 150 mVs^{-1}

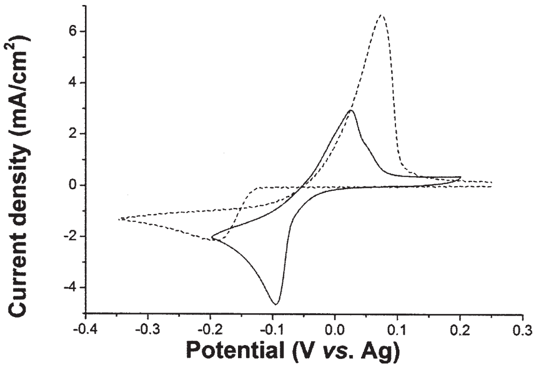

Fig. 3. A comparison between the cyclic voltammograms in 5 mM $AgNO_3$ + 7 gL^{-1} PVP + 0.1 M KNO_3 on gold (solid line) and platinum (dashed line) at 150 mVs^{-1}

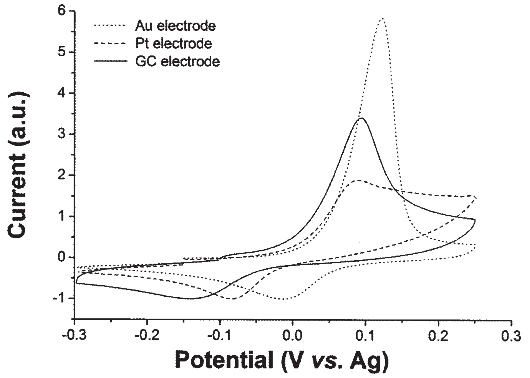

Fig. 4. Cyclic voltammograms of silver nanoparticles (7 gL^{-1} PVP, with 7 h synthesis time) in aqueous 0.1 M KNO_3 on gold, platinum and glassy carbon. The curves were normalized to unity cathode current. Scan rate: 150 mVs^{-1}

shoulder, which suggests the formation of nanoparticles with various sizes onto the gold electrode in the presence of PVP [22]. A comparison between the behaviour on gold and platinum electrodes in the presence of PVP is shown in figure 3. The differences point to a stronger interaction of the electrodeposited silver metal with gold, with the peak potential for silver deposition being positively shifted by more than a hundred millivolts on gold; the catalytic effect (reflected in the positive shift of the deposition potential) of the gold nanoparticles during silver electrodeposition of silver onto carbon paste has been observed before [23].

Cyclic voltammetry of silver nanoparticles

In this section we discuss the behaviour of silver nanoparticles attached onto the electrode surface after various immersing times. Cyclic voltammetry of silver nanoparticles were performed on Pt, Au and glassy carbon (GC) electrodes.

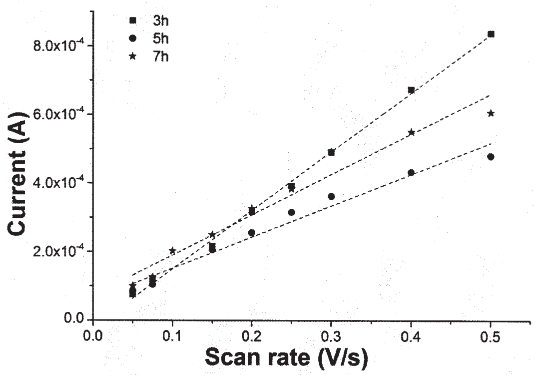

Fig. 5. Scan rate dependence of anodic peak currents for silver nanoparticles (in 7 gL^{-1} PVP + 0.1 M KNO_3 solution for three different synthesis times) oxidation on gold.

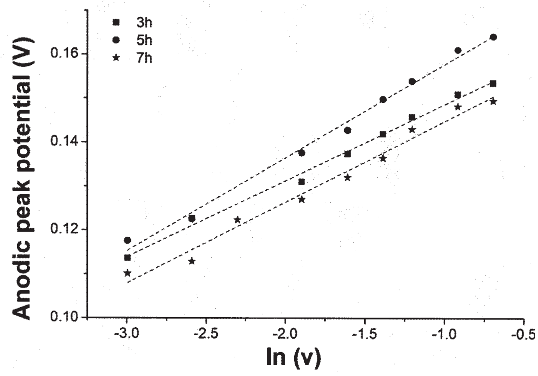

Fig. 6. Scan rate dependence of anodic peak potentials for silver nanoparticles (in 7 gL^{-1} PVP + 0.1 M KNO_3 solution for three different synthesis times) oxidation on gold

Typical voltammograms are shown in figure 4, normalized to reflect the same current on the reduction branch; one notices that the peak potentials are shifted towards more positive potentials in the order GC ≈ Pt < Au. On GC, the results are the least reproducible after immersion times of about 45 min; therefore the discussion using these electrodes will be limited to data obtained after 16 h immersion time.

The peak current for the oxidation process depends linearly on the scan rate, as expected for a surface stripping process [18,19] – an example of such a dependence on gold electrode is shown in figure 5, but the same type of dependence was obtained when using platinum electrodes and, to a lesser degree because of reproducibility issues, glassy carbon ones as well.

The anodic peak potential (E_{pa}) depends linearly with the logarithm of the scan rate (fig. 6). The straight-line slopes on Au from figure 6 are 0.01736 (for 3 h), 0.02125 (for 5 h) and 0.0184 V (for 7 h); on Pt the dependencies are more scattered (due to a lower load in silver nanoparticles and larger background currents), but straight lines can still be reasonably well fitted, yielding slopes close to 0.017 V. All these values are quite close to RT/F (~0.025 V at room temperature), values corresponding to a rather low coverage of the electrode with silver nanoparticles [12], which is however not unexpected since most curves were taken after only 45 min immersion times. For comparison, the same E_{pa} – ln(v) dependence (not shown) corresponding to stripping silver directly electrodeposited onto gold from $AgNO_3$ + 7 gL^{-1} PVP, although having rather scattered and not very reproducible points, yields slopes of ~0.008 V, which are reasonably close to RT/2F,

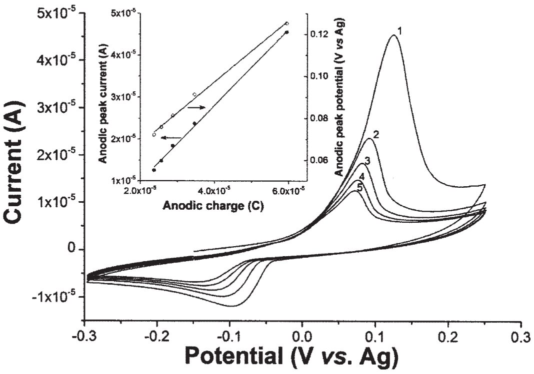

Fig. 7. Successive cycles taken in silver nanoparticles (7 gL^{-1} PVP, 5 h synthesis time) in 0.1 M KNO_3 solution on gold electrode

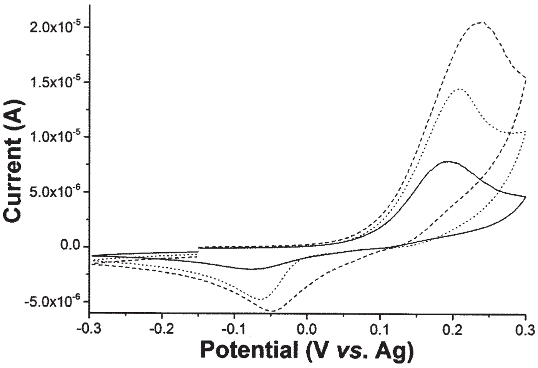

Fig. 8. Cyclic voltammograms of Ag nanoparticles (3 gL^{-1} PVP, 5 h synthesis time) + 0.1 M KNO_3 solution onto platinum for various waiting times in solution: 1 h (solid line), 2 h (dashed line) and 3 h (dotted line). Scan rate: 100 mVs^{-1}

corresponding to large particles and/or high surface coverage [12]; see also [18,19].

The cathodic peaks are always well defined and suggest that the electron transfer is reversible, or at least close to reversible: the ratio between the cathodic and anodic electrical charges during the reduction/oxidation is remarkably constant, being 0.532 ± 0.004 (average between multiple voltammograms taken at scan rates between 150 and 500 mVs^{-1}) on gold electrode. This ratio strongly suggests that the oxidation of silver nanoparticles is accompanied by a loss of material from the electrode (probably due to the solubility of charged nanoparticles and their diffusion away from the electrode): the time scale of the cyclic voltammetry is too fast (even at 50 mVs^{-1}) compared to the time needed for the diffusion/adsorption of silver nanoparticles from the solution to the electrode. Indeed, one can easily notice (fig. 7) that successive cycling in the solution containing silver nanoparticles leads to a decrease of the peak currents and shifting of peak potentials (for both anodic and cathodic peaks) to more negative values; the dependence (inset of fig. 7) of the anodic peak current and potential on the anodic charge (which is proportional to the surface coverage) is linear, as expected [12]. Similar dependencies are actually obtained for the cathodic peaks as well, but with significantly different slopes: the slope of the $I_{pa} – Q_a$ dependence is 0.908 s^{-1} while the one for $I_{pc} – Q_c$ is 0.485 s^{-11}. Similar differences are observed for the dependencies of peak potentials with electrical charge: the slope of the $E_{pa} – Q_a$ dependence is 4676 VC^{-1}, while the one for the $E_{pc} – Q_c$ is 1471 VC^{-1}. Interestingly, the ratio between the cathodic charge in cycle *n* and the anodic charge in cycle (*n*+1) is, on average, 0.85, a value which, given the rather large anodic background current and the likely overestimation of the anodic charge passed in the stripping process (fig. 7), can be considered as close to 1. This almost unit ratio suggests that little to no material is lost during the reduction of oxidized silver nanoparticles and that the material loss is most likely linked to the oxidation/stripping.

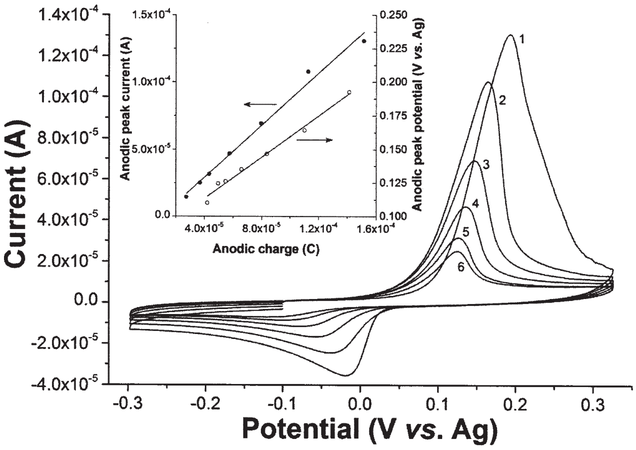

Fig. 9. Successive cyclic voltammograms of silver nanoparticles (7 gL^{-1} PVP, 7h synthesis time) loaded onto GC after 16 h immersion time, in pure 0.1 M aqueous KNO_3. Scan rate: 100 mVs^{-1}.

The cathodic peak potentials (fig. 4) are -0.014 V (on Au), -0.083 V (on Pt) and -0.141 V (on GC); the peak currents also increase in the order GC < Pt < Au; the ratio between the cathodic peak current densities (with GC as unity) are GC:Pt:Au = 1:1.8:6.2. The charge densities values in the anodic stripping peaks (q_{GC} = 1.51, q_{Pt} = 2.68 and q_{Au} = 8.56 mCcm^{-2}) together with the cathodic peak potentials (which vary both in the order Au > Pt > GC) strongly suggest that the gold surface is the “stickiest” surface for the silver nanoparticles [24, 25]. This type of behaviour has been already discussed both theoretically and experimentally and it was shown that the oxidation potential for metal nanoparticles is indeed shifted positively when there is a strong interaction between the nanoparticles and the substrate [26].

It was noticed that longer immersion times do not necessarily yield larger electrode loads; in fact the anodic charge density for the first cycle on GC electrode is significantly smaller for 16 h compared to just 45 min immersion time (0.77 mCcm^{-2} compared to 1.51 mCcm^{-2}) – a possible competitive adsorption of PVP present in solution may be responsible for such a behaviour, as it is known that PVP adsorbs rather strongly onto glassy carbon [27,28]. A similar behaviour is observed also on Pt electrode, with an increase in the peak current after 1 and 2 h immersion time, followed by a decrease after 3 h immersion time. It was suggested that nanoparticle agglomeration onto the electrode surface may also influence in time the shape of the voltammogram. However, the oxidation peak potential should shift positively as the nanoparticle size increases [22,29], while the shift in figure 8 is negative when going from 2 to 3 h immersion time, suggesting rather a loss in coverage with silver nanoparticles [12] (fig. 7).

The fact that the shape of the voltammogram is actually related to the surface coverage can be clearly seen from figure 9, which shows the successive scans for the oxidation in pure 0.1 M aqueous KNO_3 of silver nanoparticles loaded onto GC: the larger the surface coverage, the more anodic the oxidation potential and the higher the oxidation peak. In this case the loss of material during oxidation should be quite irreversible, as the electrolyte solution does not contain any silver nanoparticles which may be further adsorbed in time on GC; similar behaviour was observed for silver nanoparticles loaded onto GC in phosphate buffer [30]. Again, linear dependencies of $I_{pa} – Q_a$ and $E_{pa} – Q_a$ are obtained, as expected, but while the slope of the $I_{pa} – Q_a$ straight-line (0.967 s^{-1}) is quite similar to the one obtained on gold, the slope of the $E_{pa} – Q_a$ straight-line (615 VC^{-1}) is very different from that obtained on gold; no attempts have been made at this stage to account for these differences, as a more detailed study is in progress. Again, the ratio between the cathodic charge in cycle n and the anodic charge in cycle (n+1) on GC is closer to 1, but its value averages only ~0.7, compared to the 0.85 value obtained on gold. It is actually possible that some material loss may occur during the reduction process as well, but again the rather large background currents on GC preclude a clear answer.

Conclusions

The electrochemical behaviour of silver nanoparticles stabilized with polyvinylpyrrolidone is studied in aqueous 0.1 M KNO_3 on platinum, gold and glassy carbon electrodes. The electrochemical behaviour is typical of adsorbed nanoparticles, with the anodic stripping peaks well described by existing theories and corresponding to low coverage of the electrodes with nanoparticles. The strength of the interaction between silver nanoparticles and the substrate is shown to increase in the order: glassy carbon < platinum < gold. The electrochemical oxidation of silver nanoparticles leads to a decrease in the particle loading onto the electrode, with a good correlation between the peak currents and the degree of coverage, within the framework of existing theories.

Acknowledgements: Nicoleta Dobre is grateful to the University "POLITEHNICA" of Bucharest for financial support through project DocInvest (ID 76813).

References

1. FEDLHEIM D.L., FOSS C.A., Metal Nanoparticles: Synthesis, Characterization, and Applications, Marcel Dekker, New York, 2001

2. TAN Y., LI Y., ZHU D., Noble Metal Nanoparticles, in: Nalwa H.S. (Ed.) Encyclopedia of Nanoscience and Nanotechnology, vol. 8, American Scientific Publishers, 2012, p. 9.

3. HEILMANN A., WERNER J., SCHWARZENBERG D., HENKEL S., GROSSE P., THEIB W., Thin Solid Films, **270,** (1–2), 1995, p. 103.

4. FERRARI M., GRATTON L.M., MADDALENA A., MONTAGNA M., TOSELLO C., J. Non-Cryst. Solids, **191,** (1–2), 1995, p. 101.

5. UNG T., GIERSIG M., DUNSTAN D., MULVANEY P., Langmuir, **13,** (6), 1997, p. 1773.

6. SIBBALD M.S., CHUMANOV G., COTTON T.M., J. Electroanal. Chem., **438,** (1–2), 1997, p. 179.

7. FAJERWERG K., YNAM V., CHAUDRET B., GARÇON V., THOURON D., COMTAT M., Electrochem. Commun., **12,** (10), 2010, p. 1439.

8. DHANYA S., SAUMYA V., RAO T.P., Electrochim. Acta, **102,** (0), 2013, p. 299.

[9] KALFAGIANNIS N., KARAGIANNIDIS P.G., PITSALIDIS C., PANAGIOTOPOULOS N.T., GRAVALIDIS C., KASSAVETIS S., PATSALAS P., LOGOTHETIDIS S., Sol. Energy Mater. Sol. Cells, **104,** (0), 2012, p. 165.

10. GUO L., NIE J., DU B., PENG Z., TESCHE B., KLEINERMANNS K., J. Colloid Interface Sci., **319,** (1), 2008, p. 175.

11. IVANOVA O.S., ZAMBORINI F.P., Journal of the American Chemical Society, **132,** (1), 2009, p. 70.

12. WARD JONES S.E., CHEVALLIER F.G., PADDON C.A., COMPTON R.G., Anal. Chem., **79,** (11), 2007, p. 4110.

13. BRAININA K.Z., GALPERIN L.G., GALPERIN A.L., J Solid State Electrochem, **14,** (6), 2010, p. 981.

14. BRAININA K.Z., GALPERIN L.G., KIRYUHINA T.Y., GALPERIN A.L., STOZHKO N.Y., MURZAKAEV A.M., TIMOSHENKOVA O.R., J Solid State Electrochem, **16,** (7), 2012, p. 2365.

15. BRAININA K.Z., GALPERIN L., VIKULOVA E., STOZHKO N., MURZAKAEV A., TIMOSHENKOVA O., KOTOV Y., J Solid State Electrochem, **15,** (5), 2011, p. 1049.

16. BRAININA K.Z., GALPERIN L., PIANKOVA L., STOZHKO N., MYRZAKAEV A., TIMOSHENKOVA O., J Solid State Electrochem, **15,** (11-12), 2011, p. 2469.

17.WARD JONES S.E., CAMPBELL F.W., BARON R., XIAO L., COMPTON R.G., J. Phys. Chem. C, **112,** (46), 2008, p. 17820.

18. BRAININA K.Z., Talanta, **18,** (5), 1971, p. 513.

19. BRAININA K.Z., VYDREVICH M.B., J. Electroanal. Chem., **121,** (0), 1981, p. 1.

20. MA H., YIN B., WANG S., JIAO Y., PAN W., HUANG S., CHEN S., MENG F., ChemPhysChem, **5,** (1), 2004, p. 68.

21. DOBRE N., PETICA A., BUDA M., ANICAI L., VISAN T., U.P.B. Sci. Bull., Series B, accepted**,** 2013, p. 1.

22. BRAININA K.Z., GALPERIN L.G., VIKULOVA .V., GALPERIN A.L., J Solid State Electrochem, **17,** (1), 2013, p. 43.

23. GONZÁLEZ-GARCIA M.B., COSTA-GARCIA A.N., Biosens. Bioelectron., **15,** (11–12), 2000, p. 663.

24. BARNES E.O., COMPTON R.G., J. Electroanal. Chem., **693,** (0), 2013, p. 73.

25. KRISTINA T., ROBERT G.P., CHRISTOPHER B.-M., RICHARD G.C., Nanotechnology, **24,** (29), 2013, p. 295502.

26. BRAININA K.Z., GALPERIN L.G., VIKULOVA E.V., J Solid State Electrochem, **16,** (7), 2012, p. 2357.

27. ČENAS N.K., POCIUS A.K., KULYS J.J., Bioelectrochem. Bioenerg., **11,** (1), 1983, p. 61.

28. COX J.A., KULESZA P.J., J. Electroanal. Chem., **175,** (1–2), 1984, p. 105.

29. TOH H.S., BATCHELOR-MCAULEY C., TSCHULIK K., UHLEMANN M., CROSSLEY A., COMPTON R.G., Nanoscale, **5,** (11), 2013, p. 4884.

30. GIOVANNI M., PUMERA M., Electroanalysis, **24,** (3), 2012, p. 615

Manuscript received: 21.10.2013