*Int. J. Electrochem. Sci.*, 5 **(2010)** 1507 - 1515

**International Journal of**
**ELECTROCHEMICAL**
**SCIENCE**
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# Electrooxidation of Quercetin at Polycrystalline Pt Electrode

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*Received:* 29 July 2010 / *Accepted:* 19 August 2010 / *Published:* 1 October 2010

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The present paper reports cyclic voltammetry and a.c. impedance spectroscopy studies on electrooxidation of quercetin (3,3’,4’,5,7-pentahydroxyflavone) molecule at polycrystalline Pt electrode surface in 0.1 M sodium acetate – acetic acid buffer in 75 % methanol solution. The significance of this work is demonstrated through the application of a highly-catalytic platinum electrode, which is well-known to be capable of electrochemically oxidizing methanol under similar conditions. In addition, all impedance-derived and associated charge-transfer resistance, and capacitance parameters are discussed, especially in relation to those previously presented for oxidation of quercetin at glassy carbon electrode.

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**Keywords:** Quercetin electrooxidation, $CH_3OH$ electrooxidation, Pt electrode poisoning, impedance spectroscopy

## 1. INTRODUCTION

Flavonoids represent a large group of polyphenol secondary metabolites which are widely distributed in medicinal plants, fruits, teas and health beverages [1]. Many of these compounds exhibit antioxidant properties in a number of biochemical systems.

Quercetin (3,3’,4’,5,7-pentahydroxyflavone, see Fig. 1 below) is a flavonoid, which widely occurs in plants (caper, lovage, broccoli, lettuce, spinach) and food of plant origin (onions, apples, various berries, tea). Its electrochemical behaviour in different media (including identification and analysis of quercetin’s electrooxidation products) [2-11], as well as application in human nutrition systems [12, 13] have successfully been demonstrated (compare e.g. with electrochemical behaviour of rutin[14]. Recently, a new study on the process of electrooxidation of quercetin on glassy carbon electrode has been reported by Zielinska and Pierozynski [15]. There, a combination of cyclic voltammetry and impedance spectroscopy techniques was used to present (for the first time) a quantitative evaluation of the kinetics for successive Faradaic oxidation steps of the so-called *cascade* oxidation process.

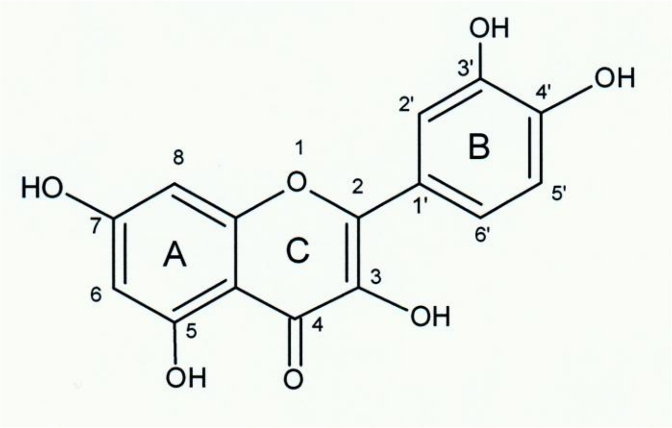

**Figure 1.** Chemical structure of quercetin (3,3’,4’,5,7-pentahydroxyflavone).

In current work, an experimental system from [15] becomes complicated through introduction of exceptionally reactive Pt catalyst surface, which also exhibits a very high electrochemical reactivity towards methanol oxidation reaction, as previously studied at pure Pt, Pt/Ru and Pt/Ir electrode surfaces (see e.g. Refs. 16 through 21). Electrooxidation of methanol at Pt in acidic medium is initiated by the dissociative chemisorption reaction [22-24]:

$$6Pt + CH_3OH \longrightarrow Pt_3COH + 3PtH \qquad (1)$$

Further oxidation leads (as a side reaction) to formation of strongly adsorbed CO species, which is either linearly or bridge-bonded to the Pt surface:

$$Pt_3COH \longrightarrow PtCO + 2Pt + H^+ + e^- \qquad (2)$$

Thus, oxidation of methanol can become self-poisoning by an intermediate product of its anodic oxidation reaction at the electrode surface.

The conversion of the latter (PtCO) adsorbate to form the final product, $CO_2$ (see an overall $CH_3OH$ oxidation reaction at Pt in equation 3 below) requires further attack on the adsorbed carbon species by an oxygen-containing group. This process is usually slow and strongly dependent on the nature of that species [22].

$$CH_3OH + H_2O \longrightarrow CO_2 + 6H^+ + 6e^- \qquad (3)$$

## 2. EXPERIMENTAL

### *2.1. Solutions and chemical reagents*

All solutions were prepared from analytical grade chemicals, including: methanol, sodium acetate and acetic acid (POCH – Polish Chemical Compounds, Poland), and quercetin (Extrasynthese, Genay, France). A stock solution of quercetin in methanol was prepared and the concentration of quercetin in the solution was verified by the UV [25] spectroscopy measurements. In addition, superior quality water of 18.2 MΩ cm resistivity was supplied by a Direct-Q3 UV ultra-pure water purification system from Millipore. For all experiments, a supporting electrolyte was 0.1 M sodium acetate - acetic acid buffer in 75 % $CH_3OH$, and quercetin concentration was $2.5x10^{-4}$ M. The experiments were carried-out at pH values 5.0 and 6.5.

### *2.2. Equipment, experimental methodology and electrodes used*

A low volume (*ca.* 1 ml) electrochemical cell made all of Teflon was used during the course of this work. The cell comprised three electrodes: a polycrystalline Pt working electrode (2 mm diameter, 99.999 % Pt disc), an Ag/AgCl (3.5 M KCl) reference (RE) and a Pt (0.5 mm diameter coiled Pt wire) counter electrode (CE). Prior to each experiment, the cell was taken apart, rinsed with Millipore ultra-pure water and methanol. The Pt working electrode was carefully hand-polished before each experiment with 3 and 1 micron polycrystalline diamond suspensions (Metalogis, Poland), using BAS (MF-1040) polishing cloth. Then, the electrode was thoroughly rinsed with ultra-pure water and finally with methanol.

All a.c. impedance and cyclic voltammetry measurements were conducted at room temperature by means of the *Solartron* 12608W Full Electrochemical System, consisting of 1260 frequency response analyzer (FRA) and 1287 electrochemical interface (EI). The voltammetric polarisations were conducted over controlled ranges of the working-electrode potential, for potentials positive to the $H_2$ reversible potential. For impedance measurements, the generator provided an output signal of known amplitude (5 mV) and the frequency range was typically swept between $1.0x10^5$ and $5.0x10^{-2}$ Hz. The instruments were controlled by *ZPlot 2.9* or *Corrware 2.9* software for Windows (Scribner Associates, Inc.). Presented here results were obtained through analysis of representative series of experimental data (usually 3-5 impedance measurements were conducted at every studied potential value). Data analysis was performed with *ZView 2.9* or *Corrview 2.9* software package, where the impedance spectra were fitted by means of a complex, non-linear, least-squares immitance fitting program, *LEVM 6* [26].

## 3. RESULTS AND DISCUSSION

### *3.1. Electrooxidation of quercetin on polycrystalline Pt electrode at pH 5.0*

The process of electrochemical oxidation of quercetin at glassy carbon (GC) electrode proceeds via the *cascade* mechanism [2, 15], which initially leads to oxidation of catechol 2xOH groups in ring

B, followed by oxidation of the three remaining OH groups, located in rings C and A (see Fig. 1 below).

The cyclic voltammetric behaviour of quercetin at the polycrystalline Pt electrode in 0.1 M acetate-acetic acid buffer solution (in 75 % methanol) at pH 5.0 is shown in Fig. 2 below.

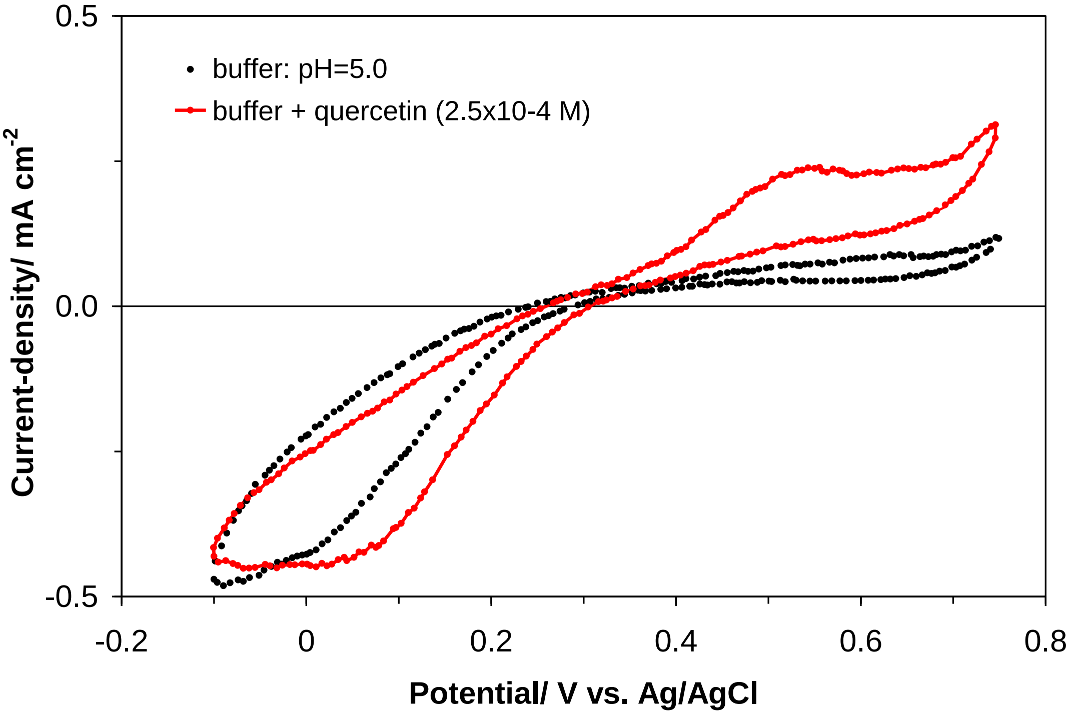

**Figure 2**. Cyclic voltammograms for polycrystalline Pt electrode in 0.1 M acetate-acetic acid buffer solution (in 75 % methanol), in the absence and presence of $2.5 \times 10^{-4}$ M quercetin, recorded for the third consecutive voltammetric scan at pH 5.0.

In the absence of quercetin, a very broad, but fairly-well defined anodic oxidation peak (centred at *ca*. 600 mV vs. Ag/AgCl) is clearly present in the CV profile. This voltammetric feature is assigned to the process of $CH_3OH$ electrooxidation, which proceeds on the surface of polycrystalline Pt disc electrode [18, 20, 24]. Then, a reversal of the voltammetric sweep leads to partial reduction (and supposedly also desorption) of the surface electrodeposited products of $CH_3OH$ oxidation, which is evidenced by the formation of a very broad reduction peak, over the potential range: -0.1-0.3 V.

On the other hand, introduction of $2.5 \times 10^{-4}$ M quercetin to the methanol-based buffer solution leads to the appearance of a very broad and large anodic oxidation peak, over the potential range 0.3-0.7 V (see the corresponding voltammogram in Fig. 2). The above-mentioned anodic peak is centred at *ca*. 530 mV vs. Ag/AgCl and is designated to the surface electrooxidation of the catechol 2xOH group (ring B). When this CV profile is compared to that recently reported for quercetin, but studied on the GC electrode (see *peak 1* in Fig. 2a of Ref. 15), a significant voltammetric shift of the peak's centre (by over 200 mV) towards the more positive potentials can be observed for the oxidation process taking place on the Pt electrode.

The a.c. impedance behaviour of the initial stage of quercetin oxidation on the Pt electrode, at pH 5.0 is presented in Fig. 3 and Table 1 (for both studied pH values) below.

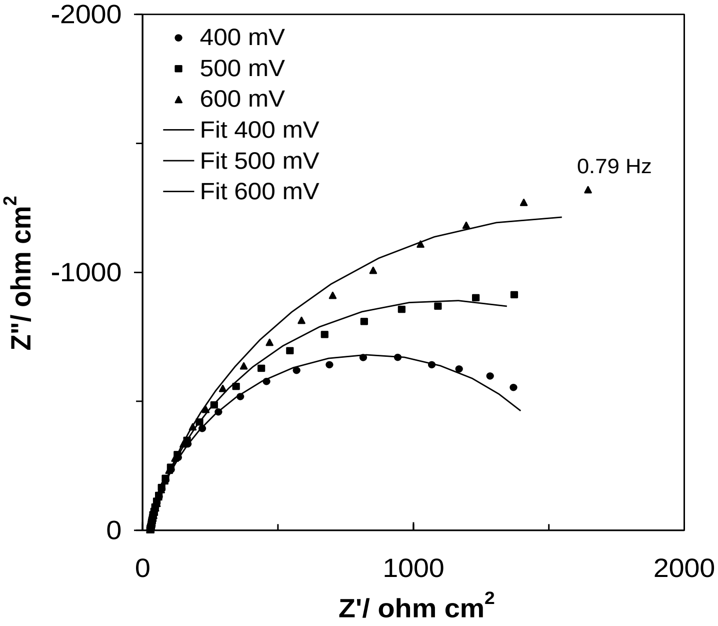

**Figure 3.** Complex-plane impedance plots for the initial electrooxidation step of quercetin on polycrystalline Pt electrode surface, in contact with 0.1 M acetate-acetic acid buffer (in 75 % methanol) solution at pH 5.0, recorded at 293 K for the stated potential values. The solid lines correspond to representation of the data according to the equivalent circuit shown in Fig. 4c of Ref. 15.

Here, for all studied potentials the impedance spectra exhibit a single, distorted partial semicircle, which is associated with the Faradaic oxidation process of the 2xOH catechol moiety (ring B). Thus, the impedance-derived reaction charge-transfer resistance parameter ($R_{F1}$) at potentials close to that of the capacitive peak observed over the potential range 350-700 mV vs. Ag/AgCl oscillates around 2,000 Ω cm$^2$ (with the minimum of *ca.* 1,640 Ω cm$^2$ recorded at the potential of 400 mV, see Table 1). These values are dramatically higher (over 500 times) than those previously recorded for quercetin at the GC electrode, at similar conditions in Ref. 15 (see Table 1 there). This spectacular change in the reaction kinetics (combined with the voltammetric shift of the CV profile) is related to the fact that electrooxidation of quercetin on the Pt electrode very likely proceeds via a *reactive layer* generated upon the oxidation of methanol species (as also suggested in Ref. 24). Thus, quercetin molecules are forced to compete for adsorption sites along with other surface-adsorbed species. The above phenomenon makes a good illustration of how the surface-poisoning effect (see equations 1 and 2 above) could affect the catalytic properties of one of the best known electrochemical catalyst material.

**Table 1.** Resistance and capacitance parameters for the process of electrooxidation of quercetin at polycrystalline Pt electrode, obtained by finding the equivalent circuit (simple, CPE-modified Randles equivalent circuit), which best fitted the impedance data (as shown in Fig. 4c in Ref. 15). The electrolyte was 0.1 M sodium acetate – acetic acid buffer solution in 75 % $CH_3OH$ (at pH 5.0 and 6.5) and the concentration of quercetin was 2.5x$10^{-4}$ M.

| E/ mV | $R_{F1}$/ Ω $cm^2$ | x$10^6$ $C_{dl}$/ F $cm^{-2}$ $s^{\varphi-1}$ | φ |
|---|---|---|---|
| **pH 5.0** | | | |
| 350 | 2,169 ± 24 | 53.6 ± 0.7 | 0.892 ± 0.002 |
| 400 | 1,642 ± 15 | 54.7 ± 0.7 | 0.887 ± 0.002 |
| 450 | 1,856 ± 23 | 54.6 ± 0.9 | 0.884 ± 0.003 |
| 500 | 2,184 ± 41 | 58.7 ± 1.3 | 0.871 ± 0.004 |
| 600 | 3,070 ± 69 | 68.8 ± 1.3 | 0.852 ± 0.004 |
| 700 | 1,816 ± 25 | 92.4 ± 1.5 | 0.853 ± 0.003 |
| **pH 6.5** | | | |
| **E/ mV** | **$R_{F2}$/ Ω $cm^2$** | **x$10^6$ $C_{dl}$/ F $cm^{-2}$ $s^{\varphi-1}$** | **φ** |
| 300 | 2,019 ± 18 | 71.5 ± 0.7 | 0.875 ± 0.002 |
| 400 | 2,874 ± 39 | 78.4 ± 0.8 | 0.865 ± 0.002 |
| 450 | 5,533 ± 111 | 87.1 ± 0.7 | 0.856 ± 0.002 |
| 550 | 4,839 ± 115 | 108.2 ± 1.0 | 0.845 ± 0.002 |
| 600 | 2,256 ± 23 | 110.4 ± 0.8 | 0.854 ± 0.001 |
| 700 | 1,077 ± 9 | 111.5 ± 1.1 | 0.865 ± 0.002 |

Furthermore, a capacitance dispersion effect (represented by distorted partial semicircles) is observed in all Nyquist plots of Fig. 3. Thus, a CPE-modified (constant phase element) equivalent circuit model (see Table 1 for details) was used to represent the electrochemical behaviour of quercetin throughout this work. The CPE behaviour is normally observed in case of inhomogeneous surfaces, displaying surface defects and porosity of the material [27, 28]. For instance, for a series RC connection, a deviation from the purely capacitive ($90^o$ phase-angle) behaviour is observed, which is determined by a dimensionless φ parameter, where $0 \leq \varphi \leq 1$. In the present study, the recorded CPE behaviour is likely due to inhomogeneous distribution of current caused by increasing surface inhomogeneity for the Pt electrode. The above could be a result of extended potentiostatic impedance measurement. Values of a dimensionless φ parameter oscillated in this work between 0.850 and 0.890 (see Table 1). The double-layer capacitance ($C_{dl}$) parameter (see Table 1 again) for the experiments performed at pH 5.0 oscillated around 50-60 μF $cm^{-2}$ $s^{\varphi-1}$ (which is relatively close to 20 μF $cm^{-2}$, a commonly used $C_{dl}$ value in literature for smooth and homogeneous surfaces [29, 30]). Considerably increased $C_{dl}$ value (over 90 μF $cm^{-2}$ $s^{\varphi-1}$), recorded at the potential of 700 mV, could imply a significant contribution to the capacitance parameter from electrosorption of OH species at Pt.

### *3.2. Electrooxidation of quercetin on polycrystalline Pt electrode at pH 6.5*

The electrochemical behaviour of quercetin at pH 6.5 is quite similar to that reported for pH 5.0. However, a characteristic anodic peak for the catechol moiety oxidation is somewhat less pronounced at this pH value and the peak's centre is shifted by about 100 mV towards the lower potential range (from *ca*. 530 mV at pH 5.0 to about 430 mV for pH 6.5), as shown in Fig. 4 below.

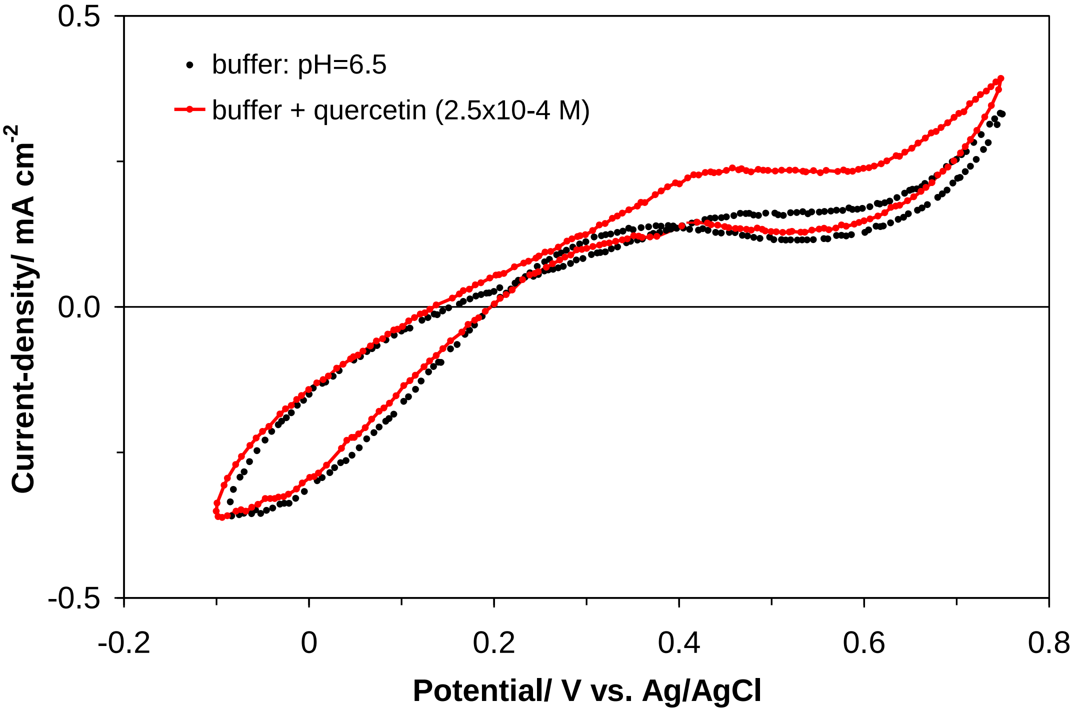

**Figure 4.** Cyclic voltammograms for polycrystalline Pt electrode in 0.1 M acetate-acetic acid buffer solution (in 75 % methanol), in the absence and presence of $2.5x10^{-4}$ M quercetin, recorded for the third consecutive voltammetric scan at pH 6.5.

This voltammetric behaviour is similar to that observed at the GC electrode in Ref. 15, between the pH values of 5.0 and 7.5. The derived reaction resistance ($R_{F2}$) parameter at pH 6.5 (see Table 1 again) shows an analogous *"Pt-to-GC relationship"* to that observed at pH 5.0. Thus, the obtained $R_{F2}$ parameter values vary from *ca*. 1,100 to 5,500 Ω $cm^2$ over the potential range: 300-700 mV and as such are at least 2 orders of magnitude higher than those reported for quercetin (at both 5.0 and 7.5 pHs), at the glassy carbon electrode in Ref. 15. In addition, the double-layer capacitance values recorded at pH 6.5 were somewhat higher (*ca*. 70-90 μF $cm^{-2}$ $s^{\varphi-1}$) than those derived at more acidic pH and did tend to quite rapidly increase (reaching about 110 $\mu$F cm$^{-2}$ s$^{\varphi-1}$), over the potential range 550-700 mV vs. Ag/AgCl (see Table 1 for details). The above-observed behaviour is very likely associated with an onset of the Pt surface electrooxidation process (see the cyclic voltammetric profiles over the potential range: 0.60-0.75 V in Fig. 4). Interestingly, the impedance behaviour reported at pH 6.5 in methanol-based buffer solution was purely capacitive (a straight line was produced throughout the studied frequency range in the Nyquist impedance plots) at 450 and 500 mV potentials.

## 4. CONCLUSIONS

The a.c. impedance and cyclic voltammetry investigations described in this work demonstrated that the kinetics of the process of quercetin electrooxidation at polycrystalline Pt electrode (with respect to the initial step of the *cascade* oxidation process) became significantly inhibited (over two orders of magnitude), as compared to those recently reported for the glassy carbon electrode. The above is realized through partial blocking of active Pt sites by electroactive species formed during simultaneous electrooxidation of methanol. It can also be supposed that under these experimental conditions, the remaining two Faradaic oxidation reactions (concerned with electrooxidation processes of 3-hydroxy group in ring C and 5,7-dihydroxy group in ring A) take part at much more positive potential range (beyond 800 mV vs. Ag/AgCl), where significant surface electrooxidation of Pt already takes place.

The above-presented study makes a good example of how dramatically the catalytic properties of an outstanding catalyst material could become altered through an interference with electroactive side reaction processes.

## References

1. C. Manach, A. Scalbert, C. Morand, C. Remesy, L. Jimenez, *Am. J. Clin. Nutr.*, 279, (2004), 727.
2. A. M. O. Brett, M.E. Ghica, *Electroanalysis*, 15, (2003), 1745.
3. H.R. Zare, M. Namazian, N. Nasirizadeh, *J. Electroanal. Chem.*, 584, (2005), 77.
4. D. Zielinska, L.J. Nagels, M.K. Piskula, *Anal. Chim. Acta*, 617, (2008), 22.
5. J.B. He, G.P. Jin, Q.Z. Chen, Y. Wang, *Anal. Chim. Acta*, 585, (2007), 337.
6. I.E. Mulazimoglu, E. Ozkan, *E-Journal Chem.*, 5(3), (2008), 539.
7. A. K. Timbola, C.D. de Souza, C. Giacomelli, A. Spinelli, *J. Braz. Chem. Soc.*, 17(1), (2006), 139.
8. A. Zhou, S. Kikandi, O.A. Sadik, *Electrochem. Commun.*, 9, (2007), 2246.
9. A. Osman, D.P. Makris, P. Kefalas, *Process Biochem.*, 43, (2008), 861.
10. R. Lei, X. Xu, F. Yu, N. Li, H.W. Liu, K. Li, *Talanta*, 75, (2008), 1068.
11. G.P. Jin, J.B. He, Z.B. Rui, F.S. Meng, *Electrochim. Acta*, 51, (2006), 4341.
12. M.K. Piskula, K. Nemeth, *Crit. Rev. Food Sci. Nutr.*, 47, (2007), 397.
13. W. Wiczkowski, J. Romaszko, A, Bucinski, D. Szawara-Nowak, J. Honke, H. Zielinski, M.K. Piskula, *J. Nutr.*, 138, (2008), 885.
14. H.R. Zare, R. Samimi, M.M. Ardakani, *Int. J. Electrochem. Sci.*, 4, (2009), 730.
15. D. Zielinska, B. Pierozynski, *J. Electroanal. Chem.*, 625, (2009), 149.
16. R.G. Freitas, E.P. Antunes, E.C. Pereira, *Electrochim. Acta*, 54, (2009), 1999.

17. A. Santasalo, F.J. Vidal-Iglesias, J. Solla-Gullon, A. Berna, T. Kallio, J.M. Feliu, *Electrochim. Acta*, 54, (2009), 6576.
18. Z.B. Wang, Y.Y. Chu, A.F. Shao, P.J. Zuo, G.P. Yin, *J. Power Sources*, 190, (2009), 336.
19. G. Wu, L. Li, B.Q. Xu, *Electrochim. Acta*, 50, (2004), 1.
20. S.B. Han, Y.J. Song, J.M. Lee, J.Y. Kim, K.W. Park, *Electrochem. Commun*., 10, (2008), 1044.
21. A.A. Hathoot, M. Abdel-Kader, M. Abdel-Azzem, *Int. J. Electrochem. Sci.*, 4, (2009), 208.
22. B.E. Conway, B.V. Tilak, *Adv. Catalysis*, 38, (1992), 1.
23. A. Hamnett, in *Interfacial Electrochemistry, Theory, Experiment and Applications*, A. Wieckowski (Ed.), Marcel Dekker, Inc., New York, Chapter 47, (1999), 843.
24. S. Andreescu, D. Andreescu, O.A. Sadik, *Electrochem. Commun*., 5, (2003), 681.
25. A. Adrian, A.A. Franke, L.J. Custer, C. Arakaki, S.P. Murphy, *J. Food Compos. Anal.*, 17, (2004), 1.
26. J.R. Macdonald, *Electrochim. Acta*, 35, (1990), 1483.
27. T. Pajkossy, *J. Electroanal. Chem*., 364, (1994), 111.
28. B.E. Conway, in: E. Barsoukov, J. Ross Macdonald (Eds.), *Impedance Spectroscopy. Theory Experiment and Applications*, Wiley-Interscience, John Wiley & Sons Inc., Hoboken, NJ, Chapter 4.5.3.8, (2005), 494.
29. A. Lasia, A. Rami, *J. Applied Electrochem*., 22, (1992), 376.
30. L. Chen, A. Lasia, *J. Electrochem. Soc*., 138, (1991), 3321.