STUDIA UBB CHEMIA, LX, 3, 2015 (p. 141-150)
(RECOMMENDED CITATION)

Dedicated to prof. dr. I. C. Popescu
on the occasion of his 70th anniversary

GALVANOSTATIC GRAPHITE ELECTROACTIVATION FOR HYDROGEN PEROXIDE ELECTROSYNTHESIS BY MULTI-SEQUENCE AND AUTO-ADAPTIVE TECHNIQUES

CODRUŢA AURELIA VLAIC[a], SORIN-AUREL DORNEANU[b,*]

ABSTRACT. Electrochemical oxidation/reduction of carbonaceous electrodes represents a simple and inexpensive way for in-situ electroactivation (EA), increasing the electrocatalytic activity toward hydrogen peroxide electrosynthesis (HPE). In this context, our previous results obtained by cyclic hydrodynamic voltammetry (CHV) and an original potentiostatic multi-sequence electroactivation technique (MSET) revealed that the graphite anodization followed by the surface partial reduction has a positive effect upon the HPE efficiency. Unfortunately, CHV is not suitable for industrial approaches and the use of MSETs in potentiostatic mode induces prohibitive electrical energy consumptions during the EA steps. In order to overcome these drawbacks, in this work, new galvanostatic MSETs were designed and tested in hydrodynamic controlled conditions using a Pt/graphite wall-jet ring disk electrode system. The galvanostatic approach diminished significantly the electrical energy used for graphite EA (under 30 % from the global consumption) and improved HPE efficiency up to 35 % compared to the unmodified graphite. The best results were obtained when original auto-adaptive protocols were used. Finally, in the attempt to eliminate the energy waste during the EA steps, we proposed the use of a symmetrical divided reactor with periodic inversion of the electrodes function and the feasibility of this idea was also tested with very promising results.

Keywords: *hydrogen peroxide electrosynthesis, graphite electroactivation, wall-jet ring disk electrode, auto-adaptive techniques*

---

[a] *Technische Universität Ilmenau, Electrochemistry and Electroplating Group, Gustav-Kirchhoff-Str. 6, 98693 Ilmenau, Germany*

[b] *Babes-Bolyai University, Faculty of Chemistry and Chemical Engineering, 11 Arany Janos str., RO-400028, Cluj-Napoca, Romania*

[*] *Corresponding author: dorneanu@chem.ubbcluj.ro*

INTRODUCTION

Hydrogen peroxide (H_2O_2) represents a potential energy carrier and is also widely used in almost all industrial areas, particularly in the chemical industry and environmental protection. At industrial scale, the H_2O_2 is mainly produced by the anthraquinone oxidation process (AOP), but this multi-step technology requires complex equipments and significant energy input, and generates large amounts of waste [1]. Moreover, the transport, storage, and handling of bulk H_2O_2 involve hazards and escalating expenses. In this context, during the last decades, significant efforts have been dedicated to develop efficient and on-site/in-situ H_2O_2 production technologies, which can considerably reduce the cost for synthesis, separation, transport, storage and handling [2]. A first alternative to the AOP involve the direct synthesis of H_2O_2 from H_2 and O_2 using plasma reactors [3] or various catalysts [4, 5]. These methods allow a decentralized production of H_2O_2 in continuous mode but their implementation is difficult due to the potential risk of H_2/O_2 gas mixture explosion. Another extremely studied alternative is the hydrogen peroxide electrosynthesis (HPE) by the partial electroreduction of O_2. For the HPE process, diverse models of electrochemical cells were proposed: divided [6-8] or undivided [9-11] batch reactors, filter-press [12], flow-trough [13] or wall-jet [14] micro-reactors, H_2/O_2 fuel cells [15, 16] or solid polymer electrolyte electrolyzer [17]. In the great majority of the above cited studies, the cathode was made of modified or unmodified carbonaceous materials, in different forms, like compact (bare or plate), porous, reticulated, felt, granular, powder or gas diffusive composite membranes. Comparing to the other cathodic materials, the compact graphite electrodes present major advantages (facile production at low costs, high electrical conductivity and mechanical robustness), allowing the design of small scale plants for on-site and in-situ wastewater treatment and drinking water disinfection. In order to counteract the low specific surface of compact graphite, consistent studies were dedicated to increase it electrocatalytic activity toward HPE by physical, chemical or electrochemical modification [18, 19].

In this context, our previous results [20] obtained by cyclic hydrodynamic voltammetry (CHV) and by an original potentiostatic multi-sequence electroactivation technique (MSET) revealed that the compact graphite anodization followed by the partial reduction of its surface induces an increase of around 50 % in HPE efficiency comparing to the value evaluated on unmodified graphite. Unfortunately, CHV is not suitable for industrial approaches and, using the MSET in potentiostatic mode, the amount of electricity used for electroactivation (EA) steps was around 100 times larger than that employed for HPE.

In order to overcome these drawbacks, in the present work, new galvanostatic MSETs were designed and tested in hydrodynamic controlled conditions using a Pt-graphite wall-jet ring disk electrode (WJRDE) system. In this manner, the electrical charge (Q_{EA}) used for graphite EA diminished below 30 % from the global charge consumption (Q_G), and HPE efficiency increased up to 35 % against the unmodified graphite, the best result being obtained using original auto-adaptive MSETs. Supplementary, in the attempt to eliminate the energy waste during the EA steps, we propose a symmetrical divided reactor with periodic inversion of the electrodes and compartments functions and the feasibility of this new design was also tested at the WJRDE scale with very promising results.

RESULTS AND DISCUSSION

Constant current HPE tests

Because the graphite activation by potentiostatic MSETs had relative modest results upon HPE global efficiency, we decide to test similar protocols, but in galvanostatic conditions, taking into account that the galvanostatic approach is more feasible for potential industrial applications.

The necessity of graphite surface periodic activation was proved by two preliminary long duration HPE experiments (results not shown) at a constant current value and a volume flow rate (V_F) of 1.42 mL/min. In the first test, imposing a disc current (I_d) of -13 μA (corresponding to the maximal HPE efficiency evaluated by CHV), the recorded ring current (I_r) slowly decreased and, consequently, the current efficiency (CE) diminished from 57% to 54% after one hour. Similarly, during the second experiment, carried out at I_d = -15 μA (value corresponding to the beginning of 4 electrons oxygen reduction process), the initial CE value of 64 % decreased rapidly to 46% and 39 % after 50 min. and 100 min, respectively. The CE values were calculated using the following equation:

$$CE\,(\%) = 100 \cdot I_r / (I_d \cdot N) \qquad (1)$$

where N is the collection efficiency of the WJRDE ensemble.

In both cases, the CE decrease can be explained by the disk potential (ε_d) shift to negative values due to the continuous modification of graphite surface in an air saturated strong alkaline solution [21], which favors the total O_2 reduction via the 4 electrons pathway.

Galvanostatic EA/HPE using fixed parameters MSETs

These new galvanostatic experimental protocols were designed in the idea of periodical graphite EA during the HPE process using a train of rectangular current pulses with constant intensities and durations, fixed by user. For each EA/HPE cycle, the applied signal includes three current pulses, corresponding to the already mentioned processes: anodisation step (AS), partial reduction step (PRS) and H_2O_2 production step (PS).

During the first set of measurements, performed at V_F = 1.42 mL/min, we tried to establish the best experimental parameters for the EA sequences. Currents of +100 and +150 μA (I_{AS}) were imposed trough the graphite disc electrode during the AS and of -100 and -150 μA (I_{PRS}) for the PRS, respectively. Different ratios between AS duration (T_{AS}) and PRS duration (T_{PRS}) were also tested: 2:2, 3:1, 4:2 and 2:1.5 (s:s) in order to reach the optimum EA potentials. Based on these experiments, we found that the best combination consisted in an AS of 2 s at +100 μA followed by a PRS of 1.5 s at -100 μA. Starting from these parameters, we initiated an optimization study concerning the duration of PS (T_{PS}) through 30 consecutive cycles for each experiment. Different T_{PS} values of 20 s, 60 s and 120 s wee tested and the best results were obtained for a T_{PS} of 60 s, the recorded signals being presented in Figure 1.

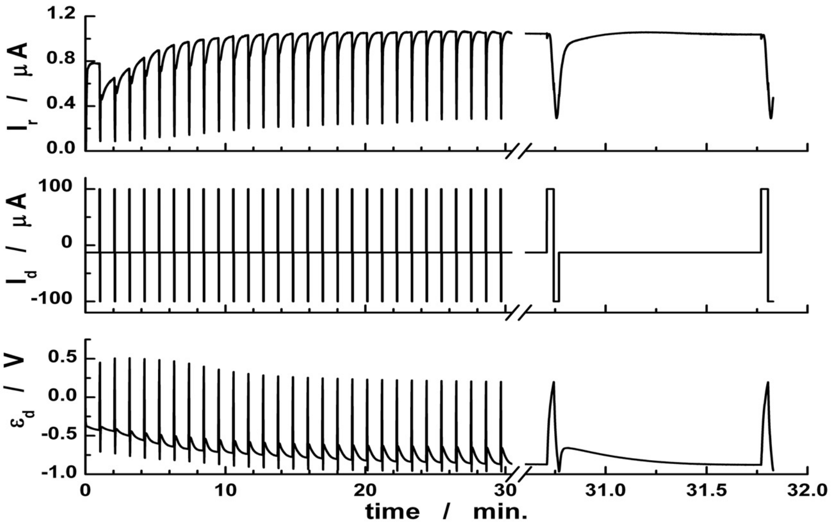

Figure 1. The influence of the disk applied current (I_d) on the recorded disc potential (ε_d) and ring current (I_r) for 30 cycles of galvanostatic EA and HPE. (T_{AS} = 2 s; I_{AS} = +100 μA; T_{PRS} = 1.5 s; I_{PRS} = -100 μA; T_{PS} = 60 s; I_{PS} = -13 μA)

It can be noticed that, at the end of the first four cycles of EA/HPE, ε_d did not decrease enough to reach the adequate potential value (near -0.8 V) for partial reduction of the active centers. As a consequence, during the cycles 2 to 4, the CE of HPE is inferior to that obtained in the first PS, corresponding to the unmodified graphite electrode. Starting from the fifth cycle, the ε_d reached adequate negative values for partial reduction and the I_r values increased largely, proving the HPE efficiency enhancement due to this original technique of graphite galvanostatic EA.

From another point of view, it is worth to note that, comparing to potentiostatic MSETs, the values of Q_{EA} decreases at reasonable values, representing around 30 % from the Q_G value. Moreover, the HPE efficiency increases with approx. 35 % in respect to the values evaluated on unmodified graphite electrode.

The downside of these EA protocols consists in the fact that, after more than 20 consecutive cycles, the ε_d values during the PRS and PS became too negative and, consequently, the HPE efficiency started to diminish due to the total oxygen reduction and the subsequent reduction of the electrosynthetized H_2O_2. In order to overcome this inconvenient, we designed new EA galvanostatic protocols, described below.

Galvanostatic EA/HPE using auto-adaptive MSETs

The previous results showed that the galvanostatic EA of graphite using a fixed time MSETs did not allow us to control rigorously, in each step, the evolution of ε_d values during the long time experiments. This fact is caused by the continuous modification of the electrode surface and, consequently, the EA and HPE parameters must be permanently readjusted. Aiming to accomplish these requirements, the initially designed LabView application, based on programmable fixed time sequences, was modified in order to allow an auto-adaptive control of steps duration. Practically, for each programmed sequence, the experimenter can set both the maximal duration and one limitative (maximal or minimal) value for other three recorded electrical parameters (ε_d, I_d or I_r). Depending on the electrochemical system evolution, the software detects the occurrence of the first limitative condition (time or the selected electrical parameters), stops the current sequence and jumps to the next programmed sequence.

Using the new designed auto-adaptive protocol, we started an optimization study, fixing T_{PS} at 60 s and I_{PS} at -13 μA, and setting different limitative ε_d values: maximum of +0.5 V or +0.6 V for the AS ($\varepsilon_{AS,\ MAX}$) and minimum of -0.7 V, -0.8 V or -0.9 V for the PRS ($\varepsilon_{PRS,\ MIN}$). In order to accelerate the EA processes, I_{AS} and I_{PRS} were fixed at increased values of +150 and -150 μA, respectively. Based on this set of experiments, we conclude that the best limitative ε_d values were +0.5 V for $\varepsilon_{AS,\ MAX}$ and -0.8 V for $\varepsilon_{PRS,\ MIN}$. From the obtained results, presented in Fig. 2, a progressive enhancement of the HPE efficiency up to 35 % was estimated. Moreover, this auto-adaptive protocol allows the reduction of the Q_{EA} value at around 20 % from Q_G. In order to validate these optimized parameters, the experiment was repeated in duplicate for 20 and 30 successive cycles, the obtained values being quasi-identical.

Considering the favorable results obtained by the auto-adaptive galvanostatic EA, supplementary long duration experiments (100 cycles) were carried out for the T_{PS} optimization, values of 60, 80, 100, 120 and

140 s being tested. The obtained results, summarized in Table 1, reveal that the optimal T_{PS} value is 100 s, when the global current efficiency (CE_G) reaches a reasonable value of 67 % and the percent of Q_{EA} against Q_G ($Q_{EA/G}$) decreases to 14 %. CE_G and $Q_{EA/G}$ were calculated as:

$$CE_G = 100 \cdot Q_R /(Q_G \cdot N) \qquad (2)$$

$$Q_{EA/G} = 100 \cdot Q_{EA} / Q_G \qquad (3)$$

were Q_R is the integral electric charge recorded for the ring electrode.

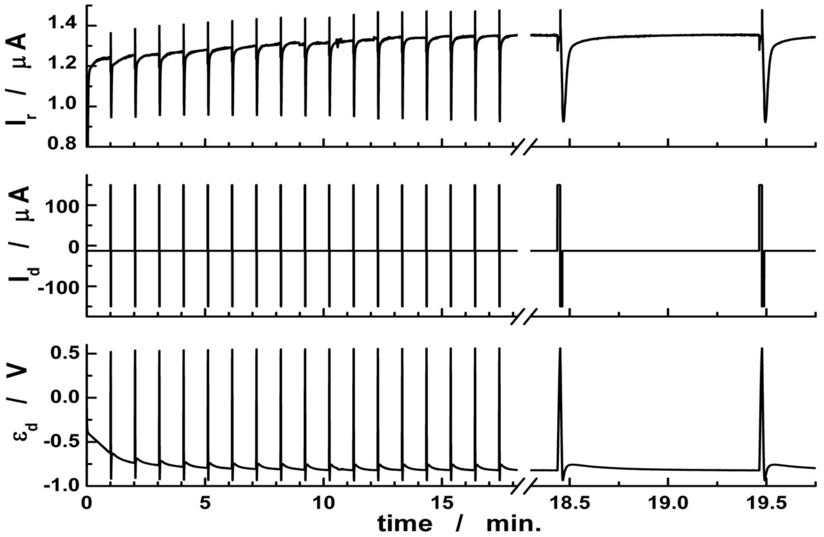

Figure 2. The evolution of I_r, I_d and ε_d during 20 cycles of galvanostatic auto-adaptive EA and HPE. (V_F = 1.42 mL/min.; $\varepsilon_{AS, MAX}$ = +0.5 V; $\varepsilon_{PRS, MIN}$ = -0.8 V; T_{PS} = 60 s; I_{AS}.= +150 µA; I_{PRS}.= -150 µA; I_{PS}.= -13 µA)

Table 1. Influence of T_{PS} over global current efficiency (CE_G) and EA charge percentage ($Q_{EA/G}$) during the auto-adaptive galvanostatic EA and HPE

T_{PS} (s)	60.00	80.00	100.00	120.00	140.00	Auto
Q_G (mC)	98.66	140.02	151.15	176.93	221.28	132.79
Q_R (mC)	4.55	7.05	11.11	10.90	13.96	10.18
Q_{EA}(mC)	20.66	36.02	21.15	20.93	39.28	15.72
$Q_{EA/G}$ (%)	20.94	25.73	**13.99**	11.83	17.75	**11.84**
CE_G (%)	41.94	45.77	**66.85**	56.03	57.34	**69.72**

A supplementary test using the galvanostatic auto-adaptive EA and HPE was performed at $\varepsilon_{AS,\ MAX}$ = +0.6 V and $\varepsilon_{PRS,\ MIN}$ = -1.0 V, and limiting the PS at T_{PS} = 500 s or until ε_d decrease under -0.8 V. In these conditions, as indicated in the last column of Table 1, CE_G reaches an improved value of ~70 % and the $Q_{EA/G}$ decreases below ~12 %, proving the feasibility on this original protocol for graphite EA and HPE.

Galvanostatic electroactivation using symmetrical rectangular signal

As pointed before, the galvanostatic auto-adaptive EA and HPE protocols present many advantages, but a small quantity of electricity is still wasted for the EA steps. In order to overcome this drawback, we intend to design and use a symmetrical divided reactor with periodic inversion of the electrodes functions. This approach was based on the idea that, when one electrode is anodised, simultaneously, on the other electrode occurs the partial reduction of surface and, afterwards, the HPE process could take place. Subsequently, switching simultaneously the electrodes polarities and electrolytes flows, the processes would interchange, allowing a periodic reactivation of the graphite electrode without energy wasting. In order to confirm the feasibility of this new design, several tests were accomplished using the WJRDE system and a symmetrical rectangular signal. Practically, pulses of equal duration but with different symmetric (positive and negative) current values were applied to the disc electrode, at two values of V_F (1.5 and 10 mL/min.). An example of recorded data for V_F = 10 mL/min is presented in Figure 3.

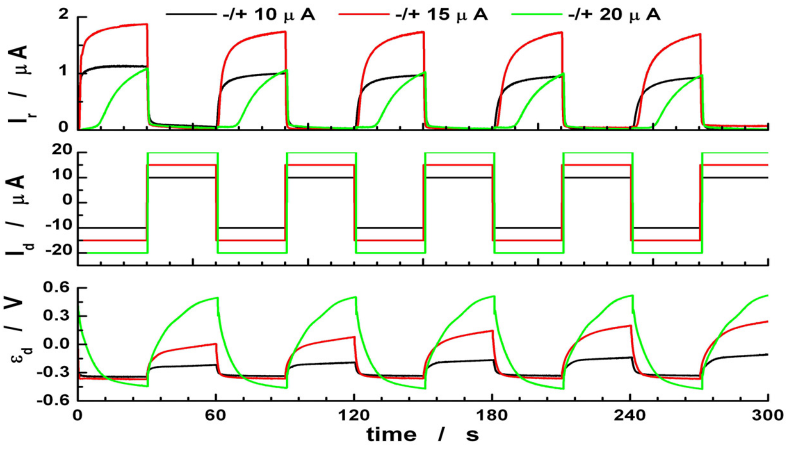

Figure 3. Example concerning the evolution of I_r, I_d and ε_d recorded with the WJRDE system at V_F = 10 mL/min. for symmetrical current pulses

Reference data were also recorded in asymmetric mode (without activation), meaning that the disc current was switched only between 0 and the negative value. The calculated values of CE for different experimental conditions are centralized in Table 2.

Table 2. HPE current efficiency (%) evaluated in different experimental conditions using galvanostatic pulses of equal duration

Pulse shape	Pulses intensity (μA)*					V_F (mL/min)	Pulse width (s)
	10	13	15	20	25		
Symmetric	55.5	68.5	58.4	43.6	-	1.5	60
Asymmetric	61.5	-	66.6	66.9	65.2	10	30
Symmetric	71.5	-	85.1	38.5	-	10	30
Symmetric	-	-	89.7	-	-	10	60

* +/- for symmetric or 0/- for asymmetric pulses

The data included in Table 2 indicate that, at V_F = 1.5 mL/min., a maximal CE value of 68.5 % was obtained for symmetrical current pulses of ±13 μA. The increase of V_F at 10 mL/min. enhances the CE of HPE on inactivated graphite (asymmetric mode) up to 66.9 % for current pulses of -20 μA. At the same V_F of 10 mL/min., the CE for the HPE process attained maximum values of 85.1 % and 89.7 % when symmetrical current pulses of ±15 μA were applied for durations of 30 and 60 s, respectively. These very promising results encourage us to implement this protocol on a pilot scale reactor.

CONCLUSIONS

In order to increase and maintain the HPE efficiency on compact graphite electrodes, we designed new techniques for in-situ galvanostatic EA. These protocols include two essential sequences, corresponding to the electrode surface oxidation followed by a partial reduction step. All the measurements were performed in hydrodynamic controlled conditions using a Pt/graphite WJRDE system, that allow the instant monitoring of the experimental parameters and process efficiency. The necessity of periodic EA was confirmed by two preliminary HPE experiments at constant current values, both of them revealing a permanent and significant CE decrease after a prolonged electrolyze. Consequently, several multi-sequence electroactivation techniques were designed and tested in galvanostatic conditions. For the beginning, trains of rectangular pulses of fixed currents and periods were applied to the disc electrode as exciting signal. Using this type of EA/HPE protocol, the amplitude and duration of the current pulses were optimized in order to maximize the HPE efficiency. At the best combination of experimental parameters (pulses of +100, -100 and -13 µA for durations of 2, 1.5 and 60 s, respectively), the values of $Q_{EA/G}$ decreases under 30 % and the HPE efficiency increases with approx. 35 % beside the unmodified graphite.

Because the protocols based on rectangular pulses of fixed currents and periods did not allow a rigorous control of the ε_d evolution during the prolonged experiment, the experimental parameters must be permanently re-adjusted. For solving this problem, the initially designed Labview application was modified in order to allow an auto-adaptive control of steps duration. Using this new protocol, after an intensive optimization study, $Q_{EA/G}$ can be diminished below 12 % while CE_G can increase up to 70 %.

Finally, in the attempt to eliminate the energy waste during the EA steps, we proposed a symmetrical divided reactor with periodic inversion of the electrodes and functions. The feasibility of this new design was tested using the WJRDE system and symmetric current pulses. In these conditions, the preliminary results indicate the possibility to increase of HPE efficiency up to 90 %, without inutile energy consumption.

For future developments, the best experimental parameters will be transferred on a micro-pilot scale electrochemical reactor in order to validate the very promising obtained results. Moreover, due to the extreme flexibility of the new developed multi-sequence techniques, these will be implemented for other electrochemical processes that require similar protocols such as electrodeposition, electrosynthesis etc.

EXPERIMENTAL SECTION

All the electrochemical measurements were carried out in controlled hydrodynamic conditions, using the experimental setup described in detail in our previous work [20]. Briefly, it includes a wall-jet cell (WJC) equipped with a Pt/graphite ring-disc electrode (RDE), a peristaltic pump (Reglo Analog, Ismatec, Switzerland) and a fully computer controlled home-made bipotentiostat. All designed and used applications for data acquisition and experiment control were elaborated using the LabView 8.5 software. In the WJC, the distance between the injector and disc electrode was fixed at 1 mm in order to achieve a planar laminar flow. The collecting efficiency (N) was evaluated using a 10 mM $K_4[Fe(CN)_6]$ solution in 1 M NaOH as supporting electrolyte and values of 0.11 and 0.13 were obtained at V_F of 1.42 and 10 mL/min., respectively. For HPE experiments, an air saturated ([O2] ~ 8 ppm) 1 M NaOH aqueous solution was pumped in the WJC at V_F of 1.42 or 10 mL/min. Before each set of experiments, the RDE surface was polished on waterproof emery paper of 1200 grit (Struers, Denmark) and intensively washed with doubly distilled water. In order to reduce the background value of I_r, the Pt ring electrode was pre-oxidized at +0.8 V for 10 s before each experiment. All measurements were performed at room temperature (25 ± 1 ^oC).

ACKNOWLEDGMENTS

The authors wish to thank for the financial support provided from programs co-financed by The SECTORAL OPERATIONAL PROGRAMME HUMAN RESOURCES DEVELOPMENT, Contract POSDRU 6/1.5/S/3 – "Doctoral studies: through science towards society".

REFERENCES

1. J.M. Campos-Martin, G. Blanco-Brieva, J.L.G. Fierro, *Angewandte Chemie - International Edition*, **2006**, *45*, 6962.
2. Y. Liu, X. Quan, X. Fan, H. Wang, S. Chen, *Angewandte Chemie - International Edition*, **2015**, *54(23)*, 6837.
3. Y. Yi, J. Zhou, H. Guo, J. Zhao, J. Su, L. Wang, X. Wang, W.Gong, *Angewandte Chemie - International Edition*, **2013,** *52*, 8446.
4. R. Dittmeyer, J.-D. Grunwaldt, A. Pashkova, *Catalysis Today*, **2015**, *248*, 149.
5. J.K. Edwards, S.J. Freakley, R.J. Lewis, J.C. Pritchard, G.J. Hutchings, *Catalysis Today*, **2015**, *248*, 3.
6. E.L. Gyenge, C.W. Oloman, *Journal of Applied Electrochemistry*, **2001**, *31*, 233.
7. G.A. Kolyagina, V.L. Kornienkoa, Yu. A. Kudenkob, A.A. Tikhomirovb, S.V. Trifonovb, *Russian Journal of Electrochemistry*, **2013**, *49(10)*, 1004.
8. G.A. Kolyaginz, V.L. Kornienko, *Russian Journal of Electrochemistry*, **2014**, *50(8)*, 798.
9. L. Zhou, Z. Hu, C. Zhang, Z. Bi, T. Jin, M. Zhou, *Separation and Purification Technology*, **2013**, *111*, 131.
10. Y. Sheng, Y. Zhao, X. Wang, R. Wang, T. Tang, *Electrochimica Acta*, **2014**, *133*, 414.
11. G. Xia, Y. Lu, H. Xu, *Electrochimica Acta*, **2015**, *158*, 390.
12. M. Giomo, A. Buso, P. Fier, G. Sandona, B. Boyec, G. Farnia, *Electrochim. Acta,* **2008**, *54*, 808.
13. Q. Li, C. Batchelor-McAuley, N.S. Lawrence, R.S. Hartshorne, C.J.V. Jones, R.G. Compton, *Journal of Solid State Electrochemistry*, **2014**, *18(5)*, 1215.
14. P. Ilea, S.A. Dorneanu, I.C. Popescu, *Journal of Applied Electrochemistry*, **2000**, *30*, 187.
15. E. Lobyntseva, T. Kallio, N. Alexeyeva, K. Tammeveski, K. Kontturi, *Electrochimica Acta,* **2007**, *52*, 7262.
16. T. Murayama, S. Tazawa, S. Takenaka, I. Yamanaka, *Catalysis Today*, **2011**, *164(1)*, 163.
17. J. Choi, S.H. Hwang, J. Jang, J. Yoon, *Electrochemistry Communications*, **2013**, *30*, 95.
18. A.R. Khataee, M. Safarpour, M. Zarei, S. Aber, *Journal of Electroanalytical Chemistry*, **2011**, *659(1)*, 63.
19. I. Kocak, M.A. Ghanem, A. Al-Mayouf, M. Alhoshan, P.N. Bartlett, *Journal of Electroanalytical Chemistry*, **2013**, *706*, 25.
20. Vlaic, S. A. Dorneanu, P. Ilea, *Studia UBB Chimia*, **2011**, *LIV(2)*, 167.
21. R. Berenguer, J.P. Marco-Lozar, C. Quijada, D. Cazorla-Amorós, E. Morallón, *Carbon*, **2009**, *47*, 1018.