Laboratory and Pilot Scale Tests of a New Potential-Controlled Method of Copper Industrial Electrolysis

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Copper electrorefining and electrowinning industrial processes are carried out on industrial scale as current-controlled processes practically from the beginning of the commercial exploitation. However, it is the electrode potential which is a driving force of electrochemical process. The copper electrodeposition from industrial electrolytes is in fact a very complex multi-ion process. Consequently, the theoretical analysis of the experimental results should take into account that in concentrated and complex matrix electrolytes migration, convection and diffusion are mass transfer modes. However, there is only very limited number of papers where copper electroreduction from concentrated electrolytes is considered and most of the published theoretical and experimental studies are carried out in diluted electrolytes of relatively simple compositions where only diffusion of copper ions is considered in theoretical analysis. In the present paper some basic aspects of potential-controlled electrolysis of copper in concentrated and industrial electrolytes as a new method of copper electrorefining and electrowinning are presented and discussed. The pilot scale tests results of copper potential-controlled electrolysis are published for the first time. Apart from the possible industrial applications, studies of the electrochemical processes in concentrated electrolytes are very important from the basic research point of view.

Numerous experimental and theoretical studies have been carried out by P. Los and co-workers on laboratory, pilot and industrial scales to recover metal nanoparticles and powders from copper industrial electrolytes and by-products of copper industry. This was subject of a large number of publications and presentations at the conferences.1–14

Potential-controlled copper electrorefining and electrowinning processes have been studied subsequently by the same research group. Current publication is the first in a series where the results of pilot scale copper potential-controlled electrolysis investigations are discussed.

Industrial copper electrowinning and electrorefining processes are carried out (with the exception of e.g. printed circuit board manufacturing) on industrial scale as current-controlled processes. It should be noted that in 2013 global production of refined copper exceeded 20 Mt (metric tons). Although most of the industrial processes of metals electrodeposition are carried out either in concentrated electrolytes or in molten salts, there is only a very limited number of fundamental studies concerning electroreduction of metals from concentrated electrolytes. This paper might help in better understanding of such processes. It is well known that current density is a measure of the electrochemical process rate. Consequently, during the current-controlled (e.g. galvanostatic) electrochemical process a constant rate of electrochemical reaction is imposed, regardless of what processes occur at the electrodes. Current-controlled copper industrial electrowinning process is carried out at a fraction of limiting current density under activation or mixed controll i.e. as a irreversible or quasi-reversible electrochemical process. It is generally known that at higher current densities electrodeposition copper is characterized by poor chemical purity and structure (especially, dendrites and powders formation). One of the reasons of such behavior is that either in the industrial or laboratory copper electrorefining the current density distribution is not uniform when dc current is applied to the electrolytic cell. Current density varies at different cathode – anode pairs of industrial electrolysis cell.14 The uneven distribution of current density at the cathode causes local (non-uniform) distribution in the potential, too. Another important factor is the influence of the non-uniform current distribution at a single electrode, especially cathode on the quality of the electrodeposited copper. Numerical analysis of copper electrodeposition process from diluted copper sulfate and sulfuric acid aqueous solution show substantial non-uniformity of current density along the cathode.15,16 The reasons of the non-uniform potential distribution and its changes with time of the current-controlled i.e. currently conducted industrial copper (and other metals) electrorefining processes are:

- changes in real surface area of the cathodes and anodes
- variation in the distance between the cathode and the anode
- production of compact, adjacent to the surface of the electrode, anode sludge layer
- adsorption of organic inhibitors on the surface of the anode

During copper electrorefining process surface roughness of the cathode might change, too. The latter effect has been very seldom taken into account in the previous investigations of the copper electrodeposition process. However, knowledge of the real (or electrochemical) surface area of the electrode is crucial to understanding any heterogeneous electrochemical process17 as it is pointed out by the IUPAC publication.18

The above limitation of the current density of current-controlled copper electrodeposition process is removed when the process is carried out under potential controlled regime. As it was shown in our previous studies12–14 high quality and purity of copper deposits are obtained using potential-controlled electrolysis even at the potentials where limiting current density is achieved. In the current study a very rare results obtained in the industrial electrolytes are presented at the very high negative potentials which in turn leads to the very high cathode current densities of copper electroreduction. One of the most important factors influencing the potential-controlled process in concentrated electrolytes at diffusion control regime is related to the natural convection at the electrodes resulting from the buoyancy forces. According to the reference [16] at the initial stages of copper electrodeposition diffusion and migration are the main ion-transport phenomena. However, due to the electrochemical reaction (e.g. copper electrodeposition at the cathode and copper dissolution at the anode in the electrorefining process) the buoyancy force becomes dominant and causes the electrolysis to achieve the steady-state which is related to the natural convection. There are number of theoretical approaches which show that the mass transport of electroactive species in concentrated electrolytes might be further complicated by e.g. the influence of the formation of the space charge distribution in the vicinity of the electrode which might affect the thickness of the local diffusion layer.19,20 The influence of the migration of indifferent electrolyte on the buoyancy forces should be analyzed properly, too.20 Consequently, the local concentrations profiles of non-electroactive ions may have strong effect on the value of the limiting current density.21,22 In the present paper a basic properties of the concentrated electrolytes in the copper electrodeposition process will be experimentally tested and analyzed.
Experimental

The electorefining and electrowinning of copper in laboratory scale was studied by chronoamperometry. All measurements were carried out using AUTOLAB GSTST30 system. General Purpose Electrochemical System version 4.5 was the program used for data acquisition. The measurements were conducted in two electrodes configuration. Copper plates of high purity (99.99% Cu, Good Fellow, Great Britain) of surface about 2 cm² were used as the cathodes. The auxiliary electrode (acting also as the reference electrode) was a copper plate of (99.99% Cu, Good Fellow, Great Britain) of surface about 20 cm². The cell temperature was maintained at 25°C.

In the pilot scale installation, tests were performed in electrolytic cell made of PVC-U of internal dimensions 500 mm × 700 mm × 400 mm using a industrial rectifier (Munk, Netherlands) connected to electrolytic cell via coaxial cable. The rectifier (output rating: 0–24 V and 0–600 A) with voltage and current control mode, was equipped with system of data logging (all electrical parameters: voltage, current, time, electrical charge can be stored every second). The external device providing circulation and heating of electrolyte solution equipped with a pump and a heater was connected to the electrolytical cell. The heater was connected to the bath in such a way that the heated solution was pumped into the bath through a hole positioned at the bottom, while the suction was executed on the opposite side from a position at the upper edge of the cell. Copper plates of high purity were used as the cathodes as well as anodes in the electorefining tests. The surface of the cathode was 0.19 m² and the anodes 0.38 m². In electrowinning measurements the lead anodes of surface of 0.38 m² were employed. The distance between the cathode and the anode was 5 cm.

The electrolytes identical to refinery electrolyte of composition similar to those used e.g in KGHM PM copper refinery (Poland) were investigated. The average composition of such industrial electrolyte1–6 is the following: 1–44 g dm⁻³ Cu, 170–200 g dm⁻³ H₂SO₄, and numerous impurities such as Ni, As, Fe (>1000 mg dm⁻³), Cd, Co, Bi, Ca, Mg, Pb, Sb (between 1 mg dm⁻³ and 1000 mg dm⁻³) and Ag, Li, Mn, Pb, Rh (<1 mg dm⁻³) and also 1–10 parts per million of leveling and grain-refining agents (e.g. animal glue and thiourea). The electrolytes were stored longer than one month and consequently, one may assume that active animal glue and thiourea concentrations are negligible.

Scanning electron microphotographs were recorded on JOEL JSM 6490 LV (Japan) instrument equipped with EDS.

Results and Discussion

In our previous study it has been shown that due to the complexity and coupling of the mass transfer processes at the copper cathode immersed in the industrial electrolyte the responses of the electrochemical systems might be different for potential- and current-controlled electrolysis.14 The results show that at higher current densities when the mass transfer control influences strongly the electrochemical processes current-controlled electrolysis becomes “unstable” and reproducibility of the measurements is quite low. This might be observed for current densities which gives the steady-state potentials of approximately −0.40 V versus copper reference electrode. The comparison of current-potential curves for potential-controlled and current-controlled laboratory scale copper electrolysis confirmed that the electrochemical window of pure copper deposition is wider of approximately 200 mV in the case of potential-controlled electrolysis than in the case of current controlled electrolysis (potentials were not corrected for ohmic drop iR). It was shown that both registered current-potential curves are very close up to the potential of approximately −0.30 V i.e. when the copper electrodeposition process is controlled predominantly by the charge transfer process (activation control).

Fig. 1 shows that in the industrial electrolytes of different copper concentrations a steady-state current is achieved in less than 20 s of electrolysis. Steady-state currents are achieved due to the convective-diffusion mode of mass transport.16,19,23–26 The potential of −0.50 V vs copper reference electrode immersed in the studied electrolyte has been chosen in Fig. 1 because limiting current is achieved at this potential for all copper concentrations. Longer times of observation might cause electrodeposition (particularly at higher current densities) of large copper crystallites which might change the electrochemical surface area of copper cathode and consequently to the variations of current electrolysis. That is why the observations are limited to 60 s in this case.

Table 1 shows the experimental values of the steady-state chronoamperometric currents (see Fig. 1) for different copper concentrations in industrial electrolytes and different applied potentials are presented. The gray colored regions mark the conditions where impure copper is obtained due to the co-deposition of arsenic at the cathode. From the obtained results it is very clear that using potential-controlled electrolysis in laboratory scale experiments pure copper can be obtained at the cathode at the very low copper concentrations and at the very negative applied potentials even at limiting current densities. Figures 2a and 2b present the voltammetric curves registered in the industrial electrolytes of different concentrations of copper. Fig. 2b shows the results from Fig. 2a but after ohmic drop correction (ac impedance measurements were used to establish the ohmic resistance of the system). Figs. 2a and 2b enable proper understanding of data from Table 1, especially the limiting currents potentials for all range of copper concentrations can be identified.

According to the above discussion in the case of industrial (concentrated) copper electrolyte one should analyze mass transport flux on the basis of the gradient of electrochemical potential27 i.e. the activities28 of the electroactive ions should be taken into account as well as migration. In the latest paper of Hong Zhao and co-workers26 the influence of migration on the value of limiting current has been confirmed at high molar concentrations of copper ions even at 9M concentrations of supporting electrolyte. Consequently, applied in many publications (see e.g.29) the equation describing limiting current (1) should not be used for the estimation of neither mass transfer coefficient nor thickness of the diffusion layer.

$$I_{lim} = nFDc^*/\delta$$  [1]

where: $I_{lim}$ – limiting current density, $n$ – number of electrons, $F$ – faradic constant, $D$ – diffusion coefficient, $c^*$ – bulk concentration of electroactive ions; $\delta$ – thickness of the diffusion layer; $D\delta$ – mass transfer coefficient $k_m$.

It is interesting to note that when the above equation is applied to the data from Table 1 the mass transfer coefficients, $k_m$ varies between 0.00031 cm/s and 0.00055 cm/s and assuming the copper diffusion coefficient in industrial electrolytes at room temperature as approximately 0.000005 cm²/s the thickness of diffusion layer varies from

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Figure 1. Chronoamperometric curves of laboratory scale copper electorefining at $E = −0.50$ V for different copper ion concentrations: (a) 2, (b) 5, (c) 7, (d) 10, (e) 14, (f) 22, (g) 29, (h) 37 and (i) 44 g/L.
Cu electrolysis conditions. It should be added, that in the vanostatic) copper electrolysis processes are very sensitive to changes in different copper concentrations the relationship between limiting current density and copper concentrations is not linear (as it is predicted by equation 1).

Figure 3 presents the exemplary SEM/EDX results obtained at different conditions of electrolysis (see Table I). The results confirm that high purity copper can be obtained at the laboratory scale experiments even at the very low copper concentrations and very high current densities. Presented results show that potential-controlled electrolysis is a new process which is characterized by a series of advantages apart from higher economical effectivity related to much higher current densities in the electrowinning process and better recovery of pure copper by electrowinning process. The most important advantage of potential-controlled electrolysis is that current density might change according to the changes of actual conditions of the industrial electrolysis. Consequently, a high purity copper is obtained by potential-controlled electrolysis even when such fundamental conditions of copper electrodeposition process varies as copper concentration, temperature, concentration of additives (e.g. animal glue and thiourea) etc. Presently used in the industry, current-controlled (galvanostatic) copper electrolysis processes are very sensitive to changes of copper electrolysis conditions. It should be added, that in the current-controlled processes cathode-anode pair potential difference might change during a whole copper cathode manufacturing cycle in the range from $-200 \text{ mV}$ to $-450 \text{ mV}$.

According to our knowledge, this study is an important step in better understanding of the copper electrolysis in industrial (concentrated) electrolytes as well as in further development of industrial practices which are shortly described in the Introduction. Consequently, potential-controlled copper electrolysis is a new (from fundamental point of view) copper electrowinning and electrowinning processes which enable manufacturing of high purity and quality copper even at the very low copper concentrations (current processes claim that commercial purity of copper can be obtained only for copper concentrations higher than 15–20 g/L) and very high current densities as high as limiting current density. Such laboratory results enabled to scale up the tests and the studies were continued in a pilot scale copper electrowinning and electrowinning electrolysis. It should be stressed that in pilot tests the real industrial electrolyte, either lead or copper anodes as well as copper and stainless steel cathodes were used. Reproducibility of the pilot scale potential-controlled copper electrowinning is illustrated in Fig. 4. Reproducibility of the registered current time curves registered at the initial 5 minutes of electrolysis is very high e.g. at $-2150 \text{ mV}$ potential applied between the copper cathode and pair of lead anodes currents densities registered after 2.5 minutes and 5 minutes are respectively 302 A/m² and 300 A/m². Standard deviations of these parameters are respectively 3 A/m² and 5 A/m².

Table II presents the parameters of pilot scale potential-controlled electrowinning of copper performed for 1 h duration at 60 °C. The

| E/V  | 46g/L | 44g/L | 37g/L | 29g/L | 22g/L | 14g/L | 10g/L | 7 g/L | 5g/L | 2g/L | 1g/L |
|------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| −0.10| 75.1  | 78.0  | 78.1  | 41.8  | 36.2  | 22.9  | 18.1  | 9.0   | −     | −     | −     |
| −0.15| 102.9 | 139.8 | 125.3 | 65.5  | 54.2  | 33.4  | 20.8  | 9.9   | −     | −     | −     |
| −0.20| 303.5 | 293.3 | 264.0 | 264.2 | 199.0 | 168.0 | 81.0  | 23.8  | 10.9  | −     | −     |
| −0.25| 404.6 | 396.9 | 350.8 | 334.8 | 242.8 | 195.7 | 88.0  | 44.0  | 24.3  | 10.8  | −     |
| −0.30| 493.5 | 494.1 | 422.2 | 387.8 | 269.0 | 212.1 | 95.7  | 41.2  | 24.0  | 11.0  | −     |
| −0.35| 579.5 | 578.0 | 466.9 | 405.1 | 280.9 | 217.4 | 96.6  | 83.9  | 45.4  | 24.7  | 11.6  |
| −0.40| 651.0 | 644.5 | 497.8 | 418.6 | 288.1 | 222.3 | 96.0  | 80.0  | 45.1  | 25.5  | 11.7  |
| −0.45| 702.0 | 691.5 | 510.5 | 426.8 | 292.4 | 229.0 | 94.7  | 86.4  | 44.8  | 26.8  | −     |
| −0.50| 734.0 | 729.0 | 526.0 | 431.5 | 297.4 | 237.3 | 99.0  | 93.9  | 48.3  | 29.1  | −     |
| −0.55| 758.0 | 762.5 | 543.5 | 449.4 | 309.5 | 266.4 | 104.0 | 98.6  | 53.8  | 37.3  | −     |
| −0.60| 783.5 | 814.0 | 603.0 | 534.6 | 359.0 | 333.9 | 121.3 | 118.9 | 72.2  | 46.9  | −     |

Table I. The experimental values of the steady-state chronoamperometric currents densities registered for copper laboratory electrowinning process for different copper concentrations industrial electrolytes and different applied potentials. Accuracy of current density determination is ca 3%.

![Figure 2](image-url)
Figure 3. SEM pictures and EDS results of copper deposition for 300s at: a) $E = -0.55\, \text{V}$, $c = 44\, \text{g/L}$, b) $E = -0.50\, \text{V}$, $c = 7\, \text{g/L}$, c) $E = -0.45\, \text{V}$, $c = 2\, \text{g/L}$.

exemplary current potential curves for those processes are given in Figure 5. The increase of current density during low cathode potential (high current density) electrolysis at $-0.60\, \text{V}$ is due to the increase in real surface area of the cathode. The high purity and structure of the copper cathode deposit obtained even at the very high current densities is confirmed by SEM/EDX results presented in Figure 6. Neither dendrites nor copper powders are observed during the process.

The above positive results are confirmed when much longer, 12 hours electrolysis were performed. The parameters of the potential-controlled copper electrorefining conducted at $E = -0.40\, \text{V}$ and $E = -0.55\, \text{V}$ are presented in Table III. Current-time curves registered during electrolysis are presented in Figure 7 and SEM/EDX results of cathode surface in Figure 8.

Higher than 100% current efficiencies presented in Tables II and III result from the fact that copper electroreduction/oxidation is a two stage process where copper(I) and copper(II) ions are involved.

Table II. Parameters of pilot scale copper electrorefining performed for 1 hour at various potentials. Copper concentration: 44g/L.

| $E$    | Average cathodic current density, A m$^{-2}$ | Current efficiency, % | Energy consumption, kWh/t |
|--------|--------------------------------------------|-----------------------|--------------------------|
| -0.30 V| 253                                        | $102.1 \pm 0.2^*$     | 248                      |
| -0.40 V| 429                                        | $101.5 \pm 0.2^*$     | 333                      |
| -0.50 V| 585                                        | $101.0 \pm 0.1^*$     | 417                      |
| -0.60 V| 752                                        | 99.8 $\pm 0.1$        | 507                      |

Figure 4. The results of pilot scale copper electrowinning reproducibility – copper concentration 44g/L, temperature 42$^\circ\text{C} \pm 1$ $^\circ\text{C}$, flow of the electrolyte 4.0 $\pm 0.2$ l/min, cathode surface 0.186 m$^2$, distance between cathode-anode: 5 cm.
Figure 5. Current-time curves recorded for pilot scale electrolysis for 1h at 60°C at: a) \( E = -0.50 \) V, b) \( E = -0.60 \) V. Copper concentration: 44g/L.

Usually, current efficiency of the electrorefining process is calculated assuming that only copper(II) ions are reduced at the cathode and two electrons are involved in such process. It has been observed in our potential-electrolysis copper electrorefining studies that considerable amount of the current is used for the reduction at the cathode of copper(I) ions created by the anodic dissolution of the copper anode.

As in the case of short term (1h) of pilot copper electrorefining electrolysis at higher negative cathode potentials (high current densities) current is increasing with time (Figure 7) because of cathode surface roughness. It is interesting to note that such an increase in cathode current density due to the increase of cathode surface roughness might be an indicator that the cathode potential should be decreased for a certain period of time to obtain smoother cathode surface. Such control of the cathode quality and structure is impossible in the current industrial process. The increase of the current due to the increase of real surface area of the cathode is the example how the current of the potential-controlled electrolysis follows the changes in the process parameters. As noted earlier in this paper such behavior is very favorable for the industrial electrorefining and electrowinning processes where many parameters might change during the whole cycle of the copper cathode manufacturing. The higher than 99.995% purity of the copper cathode obtained in the long term pilot scale tests have been confirmed by the cathode samples analysis which have been carried out in the external London Metal Exchange (LME) analytical laboratory.

| Table III. Parameters of pilot scale long lasting copper electrorefining at various potentials. Copper concentration: 44g/L. |
|------------------|------------------|------------------|------------------|
| \( E \)         | Time/h | Current density, A m\(^{-2}\) | Current efficiency,% | Energy consumption, kWh/t |
| \(-0.40 \) V    | 12     | 392             | 102.0 ± 0.2*     | 331                 |
| \(-0.55 \) V    | 11     | 626             | 101.0 ± 0.1*     | 453                 |
| *due to important contribution of \( \text{Cu(I)} \)\(^+\) \( 1e \)\(^-\) = \text{Cu}^0 \) reaction in the potential-controlled electrorefining process – Cu(I) ions are created at the copper anode dissolution process.

Figure 7. Current-time curves of pilot scale copper electrorefining recorded at 60°C and at: a) \( E = -0.40 \) V for 12h, b) \( E = -0.55 \) V for 11h. Copper concentration: 44g/L.

Figure 6. Cathodes photographs, SEM images and EDS results of copper deposit obtained after 1h pilot scale copper electrorefining at 60°C at: a) \( E = -0.50 \) V, b) \( E = -0.60 \) V.
Copper electrowinning and electrefining are complex multi-ion processes realized in concentrated electrolytes with migration, convection and diffusion as mass transfer modes. Literature review shows that there are very limited number of theoretical and experimental publications where concentrated electrolytes and especially, industrial copper electrolytes are used. In the present paper some basic aspects of potential-controlled electrolysis of copper in concentrated and industrial electrolytes as a new method of copper electrorefining and electrowinning are presented and discussed. Laboratory experimental results showed that the potential window for obtaining pure copper at the cathode is much wider in the case of potential-controlled in comparison to current-controlled electrolysis.

Potential-controlled copper electrolysis is a new copper electrorefining and electrowinning processes which enable manufacturing of high purity and quality copper. Electrowinning of copper can be carried out at the very low copper concentrations even below 1 g/L which might simplify existing copper recovery from by-products and spent electrolytes of copper industry. On the other hand potential-controlled industrial electrorefining of copper can be potentially realized at the very high current densities (as high as limiting current densities) even above 500 A/m² and cathodic current efficiencies above 98% with a purity of copper even higher than 99.995%.

The most important advantage of potential-controlled electrolysis is that current density might change according to the changes of actual conditions of the industrial electrolysis. Consequently, a high purity copper is obtained by potential-controlled electrolysis even when such fundamental conditions of copper electrodeposition process as copper concentration, temperature, concentration of additives (e.g. animal glue and thiourea) change with time and site of the electrolytic cell. Presently, the current-controlled (galvanostatic) copper electrolysis processes are very sensitive to changes of the copper electrolysis conditions.

According to the laboratory and pilot scale results presented in this paper, potential-controlled electrolysis is potentially a new, very effective method of industrial copper electrorefining and electrowinning especially for high current densities copper electrorefining and very low copper concentration electrowinning processes. Potential is a driving force of electrolysis and by fixing its value at the electrode one might control the purity and structure of the product even at the very low concentration of copper in industrial electrolytes. Using potential-controlled copper electrorefining and electrowinning possible co-deposition of the cathodic by-products might be avoided in a much wider range of current densities than in the present galvanostatic (current-controlled) industrial process.

Acknowledgments

The authors are grateful for financial support of this study by Nanometallurgy SA, Wroclaw, Poland.

References

1. O. Gladysz and P. Los, Electrochimica Acta, 54, 801 (2008).
2. A. Lukomska, A. Plewka, and P. Los, Journal of Electroanalytical Chemistry, 633, 92 (2009).
3. A. Lukomska, A. Plewka, and P. Los, Journal of Electroanalytical Chemistry, 637, 50 (2009).
4. P. Los, A. Lukomska, A. Plewka, and D. Wilson-Poli, Cuprum Czasopismo Naukowo-Techniczne Górnicze Rud, 1(50.51), 60 (2009).
5. A. Lukomska, A. Plewka, and P. Los, Chemik, 6, 315 (2009).
6. A. Lukomska, A. Plewka, and P. Los, Conference Proceedings GDMB – Copper 2010, Hamburg, Germany, I, 425 (2010).
7. P. Los, A. Lukomska, and A. Plewka, Polish Patent, No. 212864 (2012).
8. P. Los, A. Lukomska, and A. Plewka, PCT Patent application, No.PCT PL 2010/000022.
9. P. Los, A. Lukomska, and S. Kowalska, Rudy Metali, I, 42 (2012).
10. O. Gladysz and P. Los, Journal of Applied Electrochemistry, 41, 713 (2011).
11. P. Los, A. Lukomska, and S. Kowalska, “A new technology to recover copper and other metals from by-product and wastewaters of copper industry,” in Conference Proceedings Copper Metallurgy, p.389, S. Instytut Metalu Niezelaznych, Eds., Gliwice, Poland, (2011).
12. P. Los, A. Lukomska, S. Kowalska, and O. Bartosiewicz, Ochrona przed korozja, 2, 39 (2012).
13. P. Los, A. Lukomska, S. Kowalska, and M. Masalski, Potentiostatic electrowinning as a method of metals recovery from industrial wastewaters in Conference Proceedings 8th International Conference On Non-ferrous Ore Processing p.174, KGHM Cuprum Sp. z o.o. CBR Eds. (2012).
14. P. Los, A. Lukomska, S. Kowalska, M. Masalski, and M. Kwartnik, “Potential-controlled electrolysis as a new method of copper electrorefining and electrowinning – discussion of some basic aspects,” in Conference Proceedings Copper 2013 Chile V, 27 (2013).
15. N. J. Aslin, D. Stone, and W. Webb, Current Distribution in Modern Copper Refining, available at the website: www.isaprocess.com/EN/Downloads/Pages/TechnicalPapers.aspx.
16. G. I. Bauer, A. Coupled Finite Element Approach for Electrochemical Systems, Ph.D. Thesis Technische Universität München, Munich, Germany pp, 101 (2012).
17. P. Los, A. Rami, and A. Lasia, *Journal of Applied Electrochemistry*, 23, 135 (1993).
18. S. Trasatti and O. A. Petrii, *Pure & Applied Chemistry*, 63(5), 711 (1991).
19. M. H. Chang, *Electrochimica Acta*, 45, 3959 (2000).
20. A. P. Grigin, L. A. Reznikova, N. N. Tomashova, and A. D. Davydov, *Russian Journal of Electrochemistry*, 40(6), 723 (2004).
21. A. P. Grigin, L. A. Reznikova, N. N. Tomashova, and A. D. Davydov, *Russian Journal of Electrochemistry*, 36(5), 472 (2000).
22. V. M. Volgin and A. D. Davydov, *Russian Journal of Electrochemistry*, 44(4), 459 (2008).
23. C. Ponce-de-Leon, C. T. J. Low, G. Kear, and F. C. Walsh, *Journal of Applied Chemistry*, 39(11), 1261 (2007).
24. A. Filzwieser, K. Hein, and G. Mori, *JOM*, 4, 28 (2002).
25. K. Doblhofer, S. Wasle, D. M Soares, K. G. Weil, G. Weinberg, and G. Ertl, *Zeitschrift für Physikalische Chemie* 217, 479 (2003).
26. H. Zhao, J. Chang, A. Boika, and A. J. Bard, *Analytical Chemistry* 85, 7696 (2013).
27. A. J. Bard and L. R. Faulkner, *Electrochemical Methods, Fundamentals and Applications*, 2nd ed., (John Wiley&Sons Inc., New York, USA), (2001).
28. M. Gieron, P. Zaprzalski, and S. Ruta, Patent application, No.PCT/EP 2012/070568 (2012).