J.Serb.Chem.Soc. *65*(9)671-680(2000) UDC 546.562:547.298.1:541.135.52:531.15
JSCS-2790 *Original scientific paper*

Electrochemical behaviour of copper in *N,N*-dimethylformamide + 0.5 M potassium perchlorate solution

V. VOJINOVIĆ,[1] V. KOMNENIĆ,[1] M. PJEŠČIĆ[1] and S. MENTUS[2*]

[1]*Faculty of Metallurgy and Technology, YU-81000 Podgorica and* [2]*Faculty of Physical Chemistry University of Belgrade, Studentski trg 16, YU-11000 Belgrade, Yugoslavia*

(Received 26 February 1999, revised 23 March 2000)

The electrochemical deposition and dissolution of copper in 0.0025 M $CuSO_4$ + *N,N*-dimethylformamide + 0.5 M $KClO_4$ solution was examined by the rotating disc and potentiodynamic methods. Both platinum and copper were used as working electrodes. A wide polarization range –1 to +2 V *vs*. SCE, and several temperatures between 25 and 55 ºC were encompased. The Cu/electrolyte interface was found to be permanently out of equilibrium, as a consequence of the development of a passivating layer. In accordance with the classic theory of a copper electrode in acidified aqueous solutions, the cathodic and anodic Tafel lines of metallic copper define a unique value of the exchange current density, however, their slopes do not correspond to the classic theory.

Keywords: copper, *N,N*-dimethylformamide, electrode kinetics, rotating disc electrode, passivation.

INTRODUCTION

Following the development of copper refinig procedure, many autors have examined the copper electrode from the viewpoint of anodic dissolution in aqueous sulphuric acid solutions.[1–7] Bockris *et al.*[1,2] showed that anodic dissolution in acidified water solutions, discribed by overall reaction:

$$Cu \underset{k_{c1}}{\overset{k_{a1}}{\Leftrightarrow}} Cu^{2+} + 2e^- \quad (1)$$

proceeds through the two following steps:

$$Cu \underset{k_{c2}}{\overset{k_{a2}}{\Leftrightarrow}} Cu^{+} + e^- \text{ (fast)} \quad (2)$$

and

$$Cu^{+} \underset{k_{c3}}{\overset{k_{a3}}{\Leftrightarrow}} Cu^{2+} + e^- \text{ (slow)} \quad (3)$$

In concentrated solultions of copper salts, anodic dissolution is accompanied by passivation, which has been attributed either to oxide formation or to over-

* Corresponding author e-mail: slavko@ffh.bg.ac.yu

saturation of the near-to-electrode electrolyte layer.[7–11] Kiss and Farkas[12] ascertained that the passive layer may be composed of an inner, oxide, layer and an outer, salt, layer.

Burrows *et al.,*[13] using the rotating disc method, also showed that copper deposition from a 0.01 M $CuSO_4$ solution acidified by sulphuric acid proceeds through the above mentioned two steps, with step (3) being slow. The Tafel slopes were determined to be 46 mV for the anodic and 134 mV for the cathodic Tafel line.

In a series of papers,[14–26] copper electrodes were examined in aqueous solutions of either sulphate and chloride mixtures,[14] or chlorides alone. The potentiodynamic *I–E* curve of 0.01 M CuCl in 0.05 M HCl shows one cathodic and two anodic current peaks.[15] The influence of Na^+ and NH_4^+ cations on the crystallization overvoltage was ascertained.[16]

A number of authors,[17–25] examining the anodic dissolution of copper in aqueous chloride solutions, ascertained that concentration polarization prevails, connected to the diffusion of $CuCl_2^-$ and $CuCl_3^{2-}$ ions. Within a relatively narrow Tafel region, Tafel slopes of 50 mV[21] and 60 mV[24] were determined.

By cyclic voltammetry, Crousier and Pardesuss[26] showed the formation of a CuCl film during the anodic dissolution of copper in an aqueous 3 % NaCl solution; the formation of soluble $CuCl_2^-$ ions preceding the film deposition. Stojanović *et al.*[27] confirmed that copper dissolution in concentrated chloride solution proceeds under diffusion control, and ascertained the influence of the chloride concentration on the dissolution kinetics.

A number of papers reported the results of studies of the copper electrode processes in aprotic solvents. In such solvents, if deaerated in the absence of air, the possibility of oxide film formation during anodic dissolution can be excluded. In a rather old paper (1969), Biallozor[28] examined polarographically the cathodic deposition of copper from its perchlorate salts dissolved in both *N,N*-dimethylformamide (DMF) and acetonitrille (AN). Ten years later, Biallozor and Poletek,[29] using both potentiostatic and galvanostatic methods, examined the anodic dissolution and cathodic deposition of copper from $Cu(ClO_4)_2$ and $Cu(BF_4)_2$ in AN + 0.25 M $LiClO_4$. In a 0.094 M $Cu(BF_4)_2$ solution, Tafel slopes of $b_a = b_c = 155$ mV, and an exchange current density within the limits 1.9–3.5 mA cm^{-2} were found. Under a too slow scan rate, chemical dissolution according to the equation:

$$Cu + Cu^{2+} = 2Cu^+ \tag{4}$$

may become faster than cathodic deposition, as noted earlier by Kratochvil *et al*.[30]

Tsiamis *et al*.[31] examined the voltammograms of $Cu(ClO_4)_2$ in AN, in the presence of complexing agents. They found a pair of well separated peaks corresponding to the steps $Cu^{2+} + e^- \Leftrightarrow Cu^+$ and $Cu^+ + e^- \Leftrightarrow Cu$. The authors attributed the separation of the peaks to the stabilization of the Cu^+ species in solution by complexing.

Sestili *et al.*[32] examined the reduction of Cu^{2+} ions on a Pt-microelectrode in bot AN and DMF. They found the reduction of Cu^{2+} ions to metalic copper in AN to

proceed in two thermodynamically well separated steps, while in DMF only a one-step reduction was observed. Thereby the authors concluded that the intermediate Cu^+ species are thermodynamically stable in AN, but not in DMF. Upon the addition of chloride salts, the number of waves increased, as different species, such as Cu^{2+}, $CuCl^+$, $CuCl_2$, $CuCl_3^-$, $CuCl_4^{2-}$, were formed in the solution.

Biallozor and Lisovska,[33] using both stationary and dynamic galvanostatic polarization of a platinum electrode in 0.025–0.1 M $Cu(ClO_4)_2$ solutions in DMF + 0.25 M $LiClO_4$, within the narrow potential range of 0.07 to –0.04 V *vs*. SCE, established that both the deposition and dissolution of copper proceed as a one-step processes.

Malyszko and Scendo,[34] using cathodically directed polarization of a rotating platinum disc in 0.001 M $Cu(ClO_4)_2$ in DMF + H_2O mixed solvents with 0.5 M $LiClO_4$ added as the supporting electrolyte, within the potential range 0.2 to –0.6 V *vs*. SCE, registered a two-step voltammetric wave, and interpreted it by the formation of stable intermediate Cu^+ species. They examined the kinetics of the electrode in the potential region 0.1 to –0.1 V, in which only the redox couple Cu^{2+}/Cu^+ manifests itself.

As one can see from this literature survey, only two papers[32,33] relate to the electrochemical behaviour of metalic copper in DMF based solutions, and, moreover, the first one considers only the electroanalytical aspect, while the second one is rather old and encompasis only a very narrow potential range, –0.04 to 0.07 V.

In this work, using both the cyclic voltammetry and rotating disc methods over a wide potential range, –1 to +2.0 V *vs*. SCE, at several temperatures between 25 and 55 ºC, and using also AC impedance measurements at the open circuit potential, new data on the electrochemical behaviour of metallic copper in DMF based solutions were obtained.

EXPERIMENTAL

The investigations were performed in an argon deaerated three electrode cell. Before use, the *N,N*-dimethylformamide (Merck) was dried for 4 days over dry zeolite 4A, and distilled under reduced pressure at 40 ºC. Anhydrous $CuSO_4$, obtained by heating the crystallohydrate for 3 days at 240 ºC, was added to *N,N*-dimethylformamide + 0.5 M $KClO_4$. Since dissolution proceeded very slowly, and a part of the salt remained undissolved, the effective concentration was determined by diluting a sample solution with a large amount of water and adding KI in excess; the iodine liberated as a cosequence of the reduction $Cu(II) \rightarrow Cu(I)$ was determined by titration with a standard thiosulphate solution.

An EG&G PAR Model 273 Potentiostat/Galvanostat, equiped with a Houston Instruments Model 2000 x-y recorder was used for the DC measurements. For the AC impedance measurements, an EG&G PAR Model 5208 Two-Phase Lock-in Analyzer was added to the previous system.

RESULTS AND DISCUSSION

Figure 1 displays the voltammograms obtained in 0.0025 M $CuSO_4$ + DMF + 0.5 M $KClO_4$ on a rotating platinum disc, using a polarization rate of 50 mV s^{-1} and various rotating frequencies.

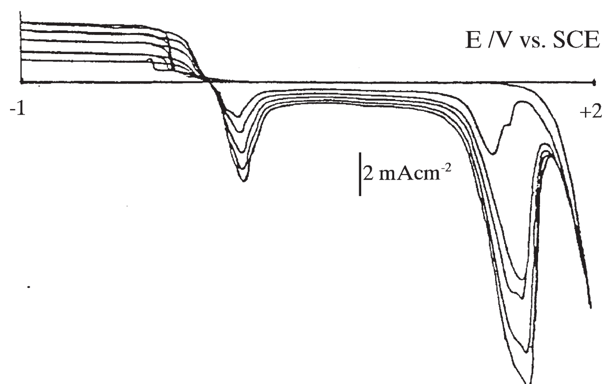

Fig. 1. The voltammograms obtained on a rotating Pt-disc in a 0.0025 M $CuSO_4$ solution in DMF containing 0.5 M $KClO_4$ at 25 ºC, at a scan rate of 50 mV/s, and at rotating frequencies (*f*) of 5, 10, 20, 30 and 40 rps.

On scaning the potential in the cathodic direction, starting from a deep anodic region, it is obvious from Fig. 1 that the current begins to rise at about +0.1 V forming a prewave. The prewave is not connected with any deposit formation, and its height does not depend on the rotation frequency. By extending the cathodic polarization below –0.1 V, the prewave continues to a wide main wave having the form of a plateau. The main wave is related to metallic copper deposition, which was evidenced by chemical analysis of the deposit. The plateau current is linearly related to the square root of the rotation frequency (Fig. 2), which shows that the copper deposition proceeds under mass transfer control.

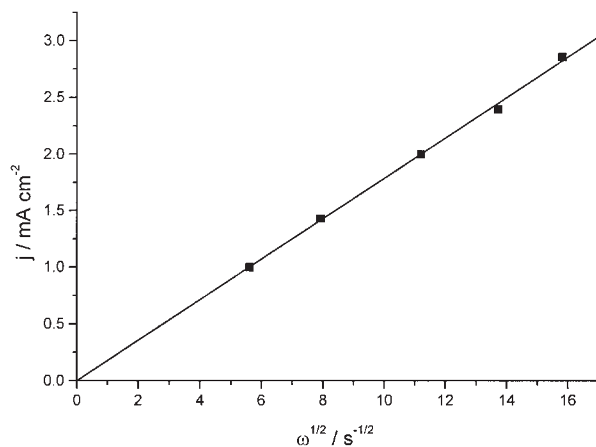

Fig. 2. The diagrams $j_d - \sqrt{\omega}$ ($\omega = 2\pi f$) for cathodic copper deposition from a 0.0025 M $CuSO_4$ solution in DMF containing 0.5 M $KClO_4$ at 25 ºC.

During the reverse, anodic polarization, the cathodically deposited copper begins to dissolve anodically when the potential attains roughly 0.0 V. However, above 0.2 V passivation inhibits the dissolution forming a current peak, and higher overvoltages, above 0.9 V, are necessary for dissolution to continue (the second peak). Above approx. 1.6 V, dissolution is complete and a current jump appears. This current jump also appears in the same manner in the absence of the copper salt, and, therefore, it may be attributed to solvent oxidation.

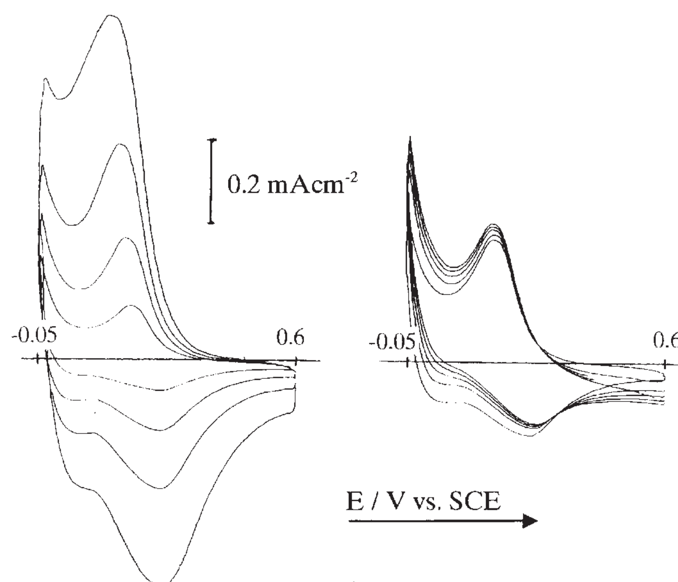

Fig. 3. The voltammograms obtained on a platinum electrode in a 0.0025 M $CuSO_4$ solution in DMF containing 0.5 M $KClO_4$ at 25 ºC in the potential interval from +0.6 to –0.05 V; left: the influence of scan rate: after steady state was attained on the stationary electrode, the scan rates were adjusted in the sequence 200, 100, 50 and 20 mV s^{-1}; right: the influence of the rotation frequency: the rotation frequencies were adjusted in the sequence: 0, 5, 10, 20 and 30 rps at a constant scan rate of 50 mV s^{-1}.

The cathodic prewave starting at + 0.1 V on bare platinum is observable only if a copper salt is present in the electrolyte. Therefore, according to a report of the behaviour of the Cu^{2+}/Cu^{+} redox pair in DMF + H_2O mixtures,[34] this prewave may be attributed to the reduction $Cu^{2+} \rightarrow Cu^{+}$. It is, however, worth mentioning that the prewave under consideration is connected to a process leading to electrode passivation. Namely, by cycling the potential within a reduced range, namely between 0.6 and –0.1 V, at a scan rate slower than 20 mV s^{-1}, a progressive diminishing of the current during each subsequent polarization cycle can be observed.

Under particular conditions, namely after multiple repetition of the polarization cycles within the range 0.6 to –0.05 V at the high scan rate of 100 mV s^{-1}, the *I–E* curve may attain a time-independent form. In Fig. 3 (left), several potentiodynamic *I–E* curves, recorded after steady state was attained, are presented. If scan rates lower than 20 mV s^{-1} were applied, the non-stationary nature of the potentiodynamic curves became expressed, and repetition of the polarization cycles caused a progressive decrease of the peak heights.

The current peak heights in Fig. 3 (left) depend non-linearly on both the scan rate and the square root of the scan rate, but the dependence on scan rate is closer to a linear one.

Figure 3. (right) shows the voltammograms recorded at a constant scan rate of 50 mV s^{-1} with various rotation frequencies. It can be seen that both the anodic and cathodic currents are practically independent of rotation frequency.

All the facts observed are consistent with the concept, developed previously for acidified water solutions,[1–3] that the Cu^{+} ion appears to be an intermediate species in the processes of copper deposition and dissolution. Similar to the case of a copper electrode in aqueous solutions, in DMF step (2) also appears to be the slow in DMF, since the prewave current in Fig. 1 does not depend on the rotation frequency. However, the case under consideration is specific in that the appearance of intermediate species leads to passivation of the electrode. We suppose that the intermediate Cu^{+} ions are retained on the electrode surface in the form of a compex with solvent molecules. Complexation is required to explain the electrochemical inactivity of the adsorbed ions. To resolve the actual structure of the passivation layer, the methods of molecular structure analysis must be employed.

It is worth mentioning that a bare Cu surface undergoes a permanent passivation even under open circuit conditions. Namely, if a freshly polished copper electrode is dipped into the solution under investigation, the complex impedance diagram recorded immediately upon submergence corresponds to a reversible process, with approximately zero charge transfer resistance. However, after 10 min, the complex impedance correponds to a slow activation controleed process, having a charge transfer resistance of the order of 100 Ω cm^{2}. After one hour in contact with the electrolyte, the copper/electrolyte interface shows a purely capacitive behaviour. That may be explained by a chemical dissolution (Eq. (4)) characteristic of copper metal in a solution containing Cu^{2+} ions.[29,30] As assumed, the thus formed Cu^{+} ions most probably remain at the surface complexed in a certain way with the solvent molecules.

In Fig. 3 (right), the electricity corresponding to the cathodic process for zero rotation frequency amounts to 1.2 mC cm^{-2}. This value exceeds by about 6 times the amount of 0.22 mC cm^{-2}, required to form a monolayer of adsorbed monovalent atoms on platinum.[35] That means that the thickness of the passivation layer on a copper/electrolyte interface corresponding to steady state, is considerably larger than a monolayer thickness.

Passivation in the region of the open circuit potential seems to be an overall characteristic of non-noble metal electrodes in aprotic solvents (see for instance zinc deposition from a DMF based solution.[36]).

Figure 4 shows the voltammograms obtained with a freshly polished platinum disc, at a rotation frequency of 10 rot s^{-1} and at a scaning rate 5 mV s^{-1}, over a reduced potential range, 0.3 to –0.6 V. The copper deposition current starts in this case at potentials more negative than 0.0 V, adding itself to the prewave current considered above. In accordance to Fig. 1, the process becomes exclusively diffusion controlled below –0.3 V. At the observed concentration, the limiting deposition current is considerably higher than the prewave current and their ratio increases with increasing rotating frequency. If, after cathodic deposition, reverse polarization is applied, an anodic current peak, starting at approx. 0.0 V, can be observed, which corresponds to the anodic dissolution of metallic copper. Upon exceeding 0.2 V, the dissolution rate decreases as a consequence of passivation. The next cathodic polarization cycle, labeled in Fig. 4 by a double arrow, is characterized by a more ex-

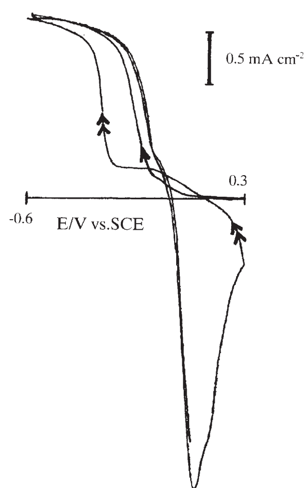

Fig. 4. The voltammograms obtained on a rotating Pt-disc in a 0.0025 M $CuSO_4$ solution in DMF containing 0.5 M $KClO_4$ at 25 ºC, in the potential interval from 0.3 V to –0.6 V, at a scan rate of 5 mV s^{-1} and at a rotation frequency 10 rps. The first and the second polarization cycle are marked by a one-fold and a two-fold arrow, respectively.

pressed cathodic prewave, as well as by an increased overvoltage for metal deposition. If cathodic polarization did not exceed –0.3 V, the cathodic deposit may be dissolved completely up to 0.2 V, before passivation attenuates the dissolution.

The passivation appearing during anodic dissolution is most probably due to the same reason as the one appearing during cathodic polarization. Namely, Cu^+ ions appearing in step (2), remain adsorbed in the form of a complex with solvent molecules.

If an virgin copper electrode is subjected to anodic dissolution within the potential interval 0.0 to 0.2 V, the peak current can exceed by two order of magnitude that corresponding to cathodically deposited copper on a Pt cathode. This fact excludes the presumption that supersaturation by copper salts might cause anodic passivation above 0.2 V. If cyclic polarization of a bare copper electrode is performed within the potential range 0.1 to –0.25 V, a progressive decrease of the anodic current can be observed, indicating a progressive passivation, accompanied by a progressive increase in the overvoltage required for metal deposition. Prolonged polarization cycling may lead to complete attenuation of all electrode processes within the potential range mentioned.

The amount of charge consumed for cathodic deposition, if corrected for the charge relating to the prewave current, practically equals to the charge consumed for anodic dissolution. This indicates that the loss of copper *via* Cu^+ ion diffusion during anodic dissolution is negligible.

The Tafel plots of the voltammograms obtained at the low polarization rate of 5 mV s^{-1} within the range –0.3 to 0.2 V, at various temperatures, after correction for diffusion limitations, are presented in Fig. 5. The potential range of Tafel-like behaviour is relatively narrow, as a consequence of the high value of the exchange current density. The intrinsic characteristics of the Tafel lines at a given temperature is that they intersect mutually at a point corresponding to the open circuit potential, thus defining a unique value of the exchange current density.

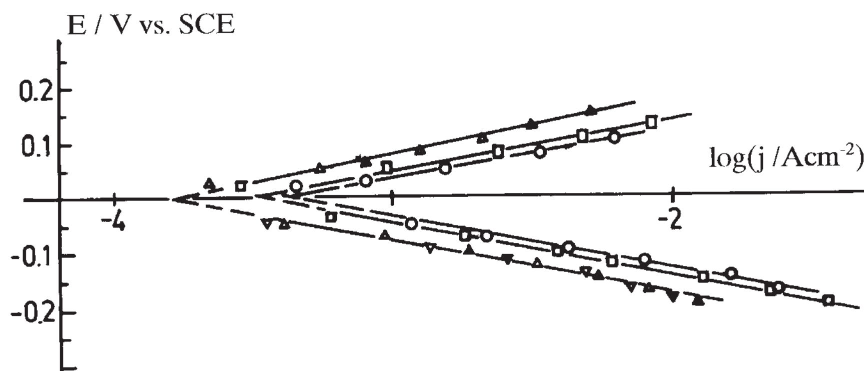

Fig. 5. Tafel plots of the voltammograms obtained on a rotating platinum disc in a 0.0025 M $CuSO_4$ solution in DMF containing 0.5 M $KClO_4$ at temperatures 25, 45 and 55 ºC. The scan rate and rotating frequency were 5 mV s^{-1} and 10 rps, respectively.

Since the results obtained in the system under investigation do not oppose the mechanism proposed by Mattson and Bockris,[1] with a slow step (3), and with negligible losses due to Cu^+ diffusion, the rate equation may be expressed in fhe following simple form:

$$j = j_0\left[\exp\left(\frac{\alpha_a E}{RT}\eta\right) - \exp\left(\frac{-\alpha_c E}{RT}\eta\right)\right] \quad (5)$$

where:

$$j_0 = 2Fk_{c3}\left(\frac{k_{a3}\,k_{a2}}{k_{c3}\,k_{c2}}\right)^{\frac{\beta_3}{2}} c_{Cu^{2+}}^{\frac{2-\beta_3}{2}} \quad (6)$$

$$\alpha_a = 2 - \beta_3$$

$$\alpha_c = \beta_3$$

and where β_3 presents the symmetry factor of reaction (3). However, the Tafel slopes in this case (Table I) do not correspond to the ones for $\beta_3 = 0.5$ (46 and 135 mV) which is probably caused by the participation of Cu^+ ions in the adsorption processes leading to a screening of the electrode surface.

TABLE I. Kinetic parameters of the copper electrode in a 0.0025 M $CuSO_4$ solution in DMF containing 0.5M $KClO_4$

T/K	j_0/mA cm^{-2}	b_c/mV	b_a/mV	E_e/V *vs*. SCE
298	0.166	98	100	–0.001
318	0.339	100	95	0.004
328	0.436	99	90	0.007

CONCLUSIONS

From a 0.0025 M solution of $CuSO_4$ in DMF containing 0.5 M $KClO_4$, the deposition of copper on a rotating disc electrode proceeds under diffusion control over the wide potential range of –0.3 to –1 V *vs*. SCE. The cathodically deposited copper dissolvs anodically in the potential range 0.0 to 1.6 V, with a wide potential window, 0.2 to approximately 1.2 V, within which electrode passivation hinders the anodic process.

The use of a virgin copper electrode enabled the conclusion to be reached that the copper electrode in the medium under investigation undergoes permanent passivation, and that both the deposition and dissolution of metallic copper proceed under permanent competition with the passivation process. It was asumed that all the passivation processes are due to the adsorption of intermediate Cu^+ ions complexed with solvent molecules.

The Tafel lines of both the cathodic and the anodic processes of metallic copper intersect mutually at the open circuit potential, enabling it to be concluded that the Mattson-Bockris mechanism,[1] developed for acidified aqueous solutions, can also be applied here. The disagreement of the values of the Tafel slopes to this mechanism is probably due to the adsorption of Cu^+ intermediate ions in an electroinactive form. A temperature change within the range 25 – 55 ºC does not influence the mechanism of the electrode processes.

ИЗВОД

ЕЛЕКТРОХЕМИЈСКЕ ОСОБИНЕ БАКРА У РАСТВОРУ *N,N*-ДИМЕТИЛ ФОРМАМИД + 0,5 M $KClO_4$

В. ВОЈИНОВИЋ,[1] В. КОМНЕНИЋ,[1] М. ПЈЕШЧИЋ[1] и С. МЕНТУС[2]

[1]*Металуршко-технолошки факултет у Подгорици, 81000 Подгорица и* [2]*Факултет за физичку хемију, Београдски универзитет, Студентски трг 16, 11000 Београд*

Електрохемијско издвајање и растварања бакра у раствору 0,0025 M $CuSO_4$ + *N,N*-диметил формамид + 0,5 M $KClO_4$ испитивано је помоћу ротирајуће електроде и потенциодинамичком методом. Као радна електрода коришћена је платина као и сам бакар. Испитивањима је обухваћен широки интервал потенцијала, –1 до 2 V према ЗКЕ, као и интервал температура 25 – 55 ºC. Нађено је да је граница Cu/електролит стално у неравнотежном режиму због константног спорог грађења пасивног слоја. Као и у воденим растворима, Тафелове праве катодног и анодног процеса секу се на потенцијалу отвореног кола, дефинишући јединствену вредност струје измене, међутим њихови нагиби не одговарају класичној теорији бакарне електроде у воденим растворима.

(Примљено 26. фебруара 1999, ревидирано 23. марта 2000)

REFERENCES

1. E. Mattson, J. O'M. Bockris, *Trans. Faraday Soc.* **55** (1959) 1586
2. J. O'M. Bockris, M. Enyo, *Trans. Faraday Soc.* **58** (1962) 1187
3. W. H. Smirl, in *Comprehensive Treatise of Electrochemistry* Vol. 4. Plenum Press, New York, 1981

4. K. Kinoshita, D. Landolt, R. H. Muller, C. W. Tobias, *J. Electrochem. Soc.* **117** (1970) 1246
5. H. P. Leckie, *J. Electrochem. Soc*. **117** (1970) 1478
6. M. L. Elias, *Metal Progress* (1981) 36
7. L. Kiss, A. Bosquez, M. L. Varsany, *Acta. Chim. Acad. Sci. Hungaricae* **108** (1981) 396
8. A. Rusin, B. P. Yur'ev, O. V. Potokova, *Sb. Rab. Khim. Istochnikam Toka*, (Collection of Papers on Chem. Power Sources (Russ.)) **10** (1975) 57
9. K. Azuma, T. Nakamura, M. Karachi, *Nippon Kogyo Kaishi* 94 (1978) 347
10. C. Clero, R. Alkire, *J. Electrochem. Soc.* **138** (1991) 25
11. A. H. Moreira, A. V. Benedetti, P. L. Cabot, P. T. A. Sumodjo, *Electrochim. Acta* **38** (1993) 981
12. L. Kiss, J. Farkas, *Acta Chim. Acad. Sci. Hungaricae* **66** (1970) 395
13. J. R. Burrows, J. A Harrison, J. Thompson, *J. Electroanal. Chem.* **58** (1975) 241
14. J. Crousier, J. Bimaghra, *Electrochim. Acta* **34** (1989) 1205
15. J. Crousier, L. Pardessus, *Electrochim. Acta* **33** (1988) 1039
16. A. Moreau, *Electrochim. Acta* **26** (1981) 497
17. T. Hurlen, *Acta Chim. Scand.* **15** (1961) 1231
18. A. L. Bacarella, J. C. Griess, *J. Chem. Soc.* **120** (1973) 459
19. N. Szabo, Z. Szabo, *Z. Phys. Chem.* **166A** (1973) 228
20. R. K. Astakhova, B. S. Krasikov, *Zh. Prikl. Khim.* **44** (1974) 363
21. S. Cooper, J. H. Bartlett, *Acta. Chim. Scand.* **130** (1978) 109
22. M. Braun, K. Nobe, *J. Electrochem. Soc.* **126** (1979) 1668
23. H. P. Lee, K. Nobe, *J. Electrochem. Soc.* **133** (1985) 2035
24. H. Lal, H. R. Thirsk, *J. Electrochem. Soc.* **100** (1953) 2638
25. J.-P. Diard, J.-M. Le Canut, B. Le Gorrec, C. Montella, *Electrochim. Acta* **43** (1998) 2469
26. J. Crousier, L. Pardesuss, *Electrochim. Acta* **33** (1988) 8
27. M. Stojanović, D. Šepa, M. Vojnović, *6th Yugoslav Meeting on Electrochemistry*, Dubrovnik 1989, Book of Papers, p. 214
28. S. B. Biallozor, *Elektrokhimiya* **5** (1969) 1831
29. S. G. Biallozor, D. Poletek, *Elektrokhimiya* **15** (1979) 472
30. B. Kratochvil, K. R. Berty, *J. Electrochem. Soc.* **121** (1974) 851
31. C. Tsiamis, S. Cambanis, A. D. Jannakoudakis, *J. Electroanal. Chem.* **252** (1988) 109
32. L. Sestili, C. Furlani, A. Ciana, F. Garbssi, *Electrochim. Acta* **15** (1970) 225
33. S. G. Biallozor, B. A. Lisovska, *Elektrokhimiya* **15** (1979) 634
34. J. Malyszko, M. Scendo, *J. Electroanal. Chem.* **269** (1989) 113
35. E. Gileadi, *Electrode Kinetics for Chemists, Chemical Engineers and Material Scientists,* VCH Publishers Inc., New York-Weinheim - Cambridge, 1993, p. 263
36. S. G. Biallozor, E. T. Bandura, *Electrochim. Acta* **32** (1987) 891.