Influence of the Ionic Strength and the Nature of Supporting Electrolyte on Electrooxidation of Formaldehyde at Pt and Cu

Rasa Pauliukaite* and Eugenijus Norkus

Department of Catalysis, Institute of Chemistry, A. Goštauto 9, LT-01108 Vilnius, Lithuania

** Corresponding author: E-mail: rasa @chi.lt*

Abstract

The electrooxidation current of methanediol (hydrated formaldehyde) at polycrystalline Pt and Cu decreases with increase in the ionic strength of the solution at constant pH values but increases with increase in pH and formaldehyde concentration. A linear dependence between the oxidation current and the concentration of methanediol anion is obtained, whereas, a non linear dependence is observed between the oxidation current and the total concentration of formaldehyde. The optimum conditions for formaldehyde oxidation were observed when $NaNO_3$, Na_2SO_4, and K_2SO_4 were used as supporting electrolytes in the pH range down to 13.0 and the ionic strength up to 0.5 mol L^{-1}.

**Keywords**: Formaldehyde, methanediol, anodic oxidation, ionic strength, cyclic voltammetry

1. Introduction

The formaldehyde oxidation at Pt electrodes has been studied since the middle of the last century,[1–5] because formaldehyde as a small organic molecule is important in medicine,[2] development of fuel cells,[6,7] and reduction of some metal ions in the processes of their electroless plating.[8–10]

Formaldehyde reacts with water forming methanediol in the aqueous solutions:[2]

$$CH_2O + H_2O \rightleftarrows H_2C(OH)_2 \qquad (1)$$
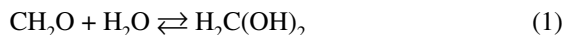
The equilibrium constant of the reaction (1) was found to be $2 \cdot 10^3$ [1] and $2.3 \cdot 10^3$.[11] This fact suggests that formaldehyde is fully hydrated in aqueous solutions. The dissociation (deprotonization) of methanediol occurs in alkaline aqueous solutions:[12]

$$H_2C(OH)_2 \overset{K_a}{\rightleftarrows} H_2C(OH)O + H^+ \qquad (2)$$

or

$$H_2C(OH)_2 + OH \rightleftarrows H_2C(OH)O + H_2O \qquad (3)$$
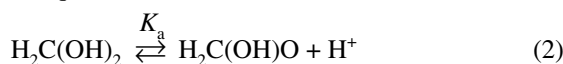
Thus, formaldehyde exists in several forms in aqueous solutions, i.e. free, hydrated (1), and dissociated

(2,3). Hence, it is important to know which form of formaldehyde takes part in the reaction of the anodic oxidation at different metal surfaces since each form has a different oxidation mechanism.

Methanediol and its anion have the different activity in the various chemical and electrochemical reactions, i.e. usually the methanediol anion is supposed to take place in the oxidation reaction in alkaline medium.[3,8–10,13–18] The final product of the formaldehyde oxidation is $HCOO^-$ at Cu[13] and Au,[18] however, it can be oxidised directly to CO_2 in alkaline solutions at Au[16] or Pt[19] micro- or nanoparticles. Hence, the formaldehyde oxidation usually is going to $HCOO^-$ at various electrodes in acidic medium.[4–7,19–24] All formaldehyde forms, free,[25] methanediol[4] or its anion,[13–24] might be oxidized at different electrodes depending on the nature of the electrode and the structure of the metal substrate.

Some interference can be observed at higher potentials, for example from SO_2 in acidic medium.[26,27] However, the formaldehyde oxidation occurs at significantly lower potentials (from +0.2 to +0.6 V), especially in basic medium.

In general, the electrooxidation rate of formaldehyde depends on i) surface structure of the electrode;[4,17,19,21,24] (ii) temperature;[25] (iii) concentration;[25] and (iv) solution pH.[25] The mechanism of the oxidation reaction of formaldehyde depends on the potential range,[13–15] and the oxygen concentration.[25,28]

The equilibrium constant of methanediol deprotonation K_a (2) depends on the ionic strength of the solution and the nature of the cations of supporting electrolyte.[29] Thus, the formaldehyde oxidation may also depend on these factors, moreover, all previous studies were performed either in acid or in hydroxide solutions without respect to ionic strength of the solutions used. In this work the anodic oxidation of formaldehyde at Pt and Cu has been studied in various supporting electrolytes, containing monovalent cations, Li^+, Na^+, and K^+, as well as differently charged anions, Cl^-, NO_3^-, SO_4^{2-}, and PO_4^{3-}. The ionic strength and pH of supporting electrolytes were also varied in order to clarify the influence of these parameters on the electrooxidation of formaldehyde.

2. Experimental

2. 1. Chemicals and Solutions

Analytical grade chemicals (Reachim, Russia) and triply distilled water were used to prepare all solutions. The formaldehyde solution was standardised as described elsewhere.[30] The carbonate-free solutions of hydroxides were prepared and standardised according to Brauer.[31]

2. 2. Apparatus and Procedure

Cyclic voltammograms (CVs) were recorded using a programming potentiostat PI-50-1 and a sweep generator PR-8 (Russia) in thermostated three-electrode cell. Either bare or coated with copper Pt plate served as a working electrode; its geometrical area was 1 cm^2. Potential was measured with respect to an Ag/AgCl/KCl$_{sat}$ reference electrode in the Lugin's capillary, but the results were recalculated and are presented below versus standard hydrogen electrode (SHE). The other Pt plate served as an auxiliary electrode and it was separated in the cell with a glass-ceramic filter. The potential sweep rate was 50 mV s^{-1}, and the error of current measurements was ca. ±5%. All solutions were deoxygenated by bubbling Ar-gas through the solution, and all experiments were carried out at 20 ± 1 °C.

Galvanostatic copper deposition on Pt was performed from the solution containing 1.0 mol L^{-1} CuSO$_4$ and 0.5 mol L^{-1} H$_2$SO$_4$ at a current density of 15 mA cm^{-2} for 20 min.

3. Results and Discussions

3. 1. The Influence of the Supporting Electrolyte on Formaldehyde Oxidation

The electrooxidation of formaldehyde was studied at two metal electrodes, Pt and Cu, under the identical conditions; in the most of the cases the concentration of formaldehyde was kept constant and the supporting electrolyte, the ionic strength and the solution pH were varied. The formaldehyde oxidation occurred differently at the both electrodes: the current peak was more positive at Pt than that at Cu, as well as higher oxidation current was observed at Pt (Fig. 1) due to a stronger catalytic effect of Pt substrate on the electrochemical formaldehyde oxidation.[4–10,13–17]
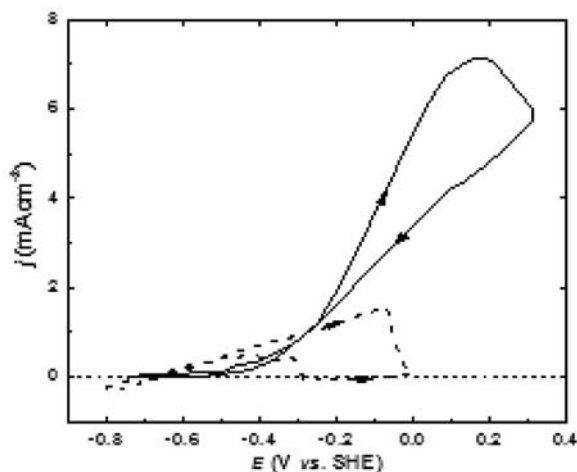

Fig. 1. Cyclic voltammograms of formaldehyde oxidation at Pt (solid line) and Cu (dashed line). Potential sweep rate 50 mV s^{-1}; supporting electrolyte Li$_2$SO$_4$; ionic strength 0.1 mol L^{-1}; and pH 13.0.

It was hardly possible to observe a continuous effect of the cation or the anion influence on the formaldehyde oxidation rate (Fig. 2). However, the lowest currents were obtained in the electrolytes containing Li$^+$ (at Pt) and Na$^+$ (at Cu). Nevertheless, the stronger influence on the oxidation peak current was observed from the anions than that from the cations: the lowest oxidation currents were obtained in the supporting electrolytes containing Cl$^-$ (at Pt) or NO$_3^-$ (at Cu) and the highest ones in the SO$_4^{2-}$-containing supporting electrolyte (at Cu and partially at Pt) as seen from Fig. 2. From one hand this could be explained using Debye-Hückel theory, i.e. the effect of the hydrated ion radius of the electrolyte or so called the secondary kinetic electrolyte effect.[32] If compare the effect of the electrode substrate, the cation effect was stronger expressed at Pt than that at Cu but the influence of the anion was better expressed at Cu electrode than that at Pt under the conditions described above (Fig. 2). From the other hand the formaldehyde oxidation occurs at the potential where formation of the Cu oxide starts and it decreases the oxidation rate since prevents the adsorption of the methanediol anion at the electrode surface.[33] Moreover, the formation pathway and the thickness of the Cu$_2$O layer depends on the anions present in the solution as well as ionic strength,[34] and pH.[33,34] The formaldehyde oxidation rate also depends on the Cu surface nature, i.e. Cu is deposited using chemical or electrochemical plating.[33]
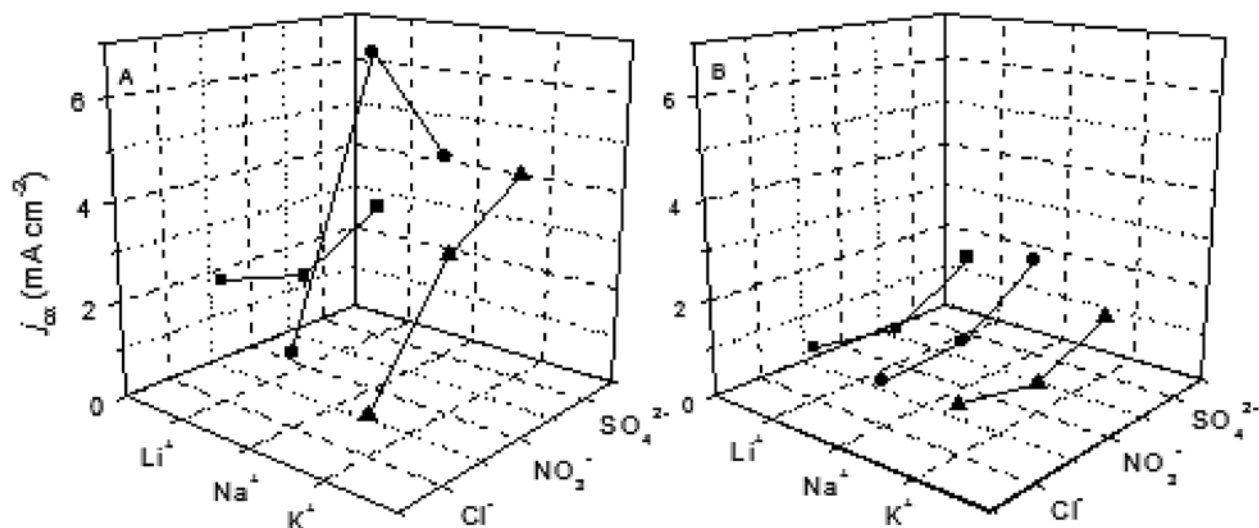
Fig. 2. Dependence of formaldehyde anodic oxidation peak current density at Pt (A) and Cu (B) electrodes on electrolyte composition. Potential sweep rate 50 mV s^{-1}; ionic strength 0.5 mol L^{-1}; and pH 13.0.

The Pt surface oxide formation starts at significantly more positive potentials than the formaldehyde oxidation,[4,5,16,19] therefore, the oxidation current is higher at Pt than at Cu.

One more electrolyte, Na$_3$PO$_4$, was introduced to clarify the influence of the charge of the anion of supporting electrolyte (since the anions had stronger influence than the cations) on the anodic oxidation of formaldehyde. The influence of the anions on the electrooxidation rate of formaldehyde at Pt can be expressed by the following sequence Cl$^-$ < PO$_4^{3-}$ < NO$_3^-$ < SO$_4^{2-}$ (the sequence indicates the growth of the electrooxidation rate in the presence of these anions). In the case of Cu substrate the lowest oxidation peak current was obtained in sodium phosphate, and almost the same peak in chloride and nitrate, however, the highest peak was observed in sodium sulphate. This effect hardly can be related to an anion radius because anhydrous radii of these anions are: 126 pm (Cl$^-$), 125 pm (NO$_3^-$), 223 pm (SO$_4^{2-}$), hence, the radius of a hydrated ion is lower for Cl$^-$ (123 pm) and larger for all other anions studied (129 pm and 230 pm for NO$_3^-$ and SO$_4^{2-}$, respectively).[35] The radius of the hydrated PO$_4^{3-}$ is 250 pm.[36] Thus, the anions show a lower influence on the formaldehyde oxidation directly, and they influence the formation of the surface oxide,[33,34] which further influences the adsorption of methanediol or its anion. Although sulphate causes formation of a thick Cu$_2$O layer at pH 7 but increase in pH conditions a thinner oxide layer,[34] and probably therefore the formaldehyde oxidation rate is quite high at pH 13.0 in supporting electrolyte containing SO$_4^{2-}$.

3. 2. The Influence of pH and Formaldehyde Concentration

Fig. 3a demonstrates the dependence of the oxidation current of formaldehyde at Pt on pH in various nitrate solutions at the same ionic strength, 0.5 mol L^{-1}. The con-

centration of formaldehyde was kept constant and only pH of the solution was varied. The oxidation rate rose with increase in pH due to an augment of the concentration of methanediol.[27] These results confirmed the data obtained by the other authors that usually methanediol anion takes place in the electrochemical oxidation reaction:[13,37]

$$CH_2(OH)O^- + 2OH^- \rightarrow HCOO^- + 2H_2O + 2e^- \quad (4)$$

It should be noted that the reaction (4) is given in the general form without adsorption steps and radical formation as it is discussed elsewhere.[4,16] Interestingly, the highest peak currents were obtained when NaNO$_3$ was used as a supporting electrolyte, in contrary to the probability of the lowest cation size which is for Li$^+$, and it would be naturally to expect the highest currents in LiNO$_3$.

A similar tendency was found at Cu electrode (not shown) only the peak currents were lower than those at Pt. Moreover, quite close oxidation peak current values at Cu were obtained in all three nitrates used as supporting electrolytes, differently form those obtained at Pt electrode (Fig. 3a).

The influence of the concentration of formaldehyde has been investigated as well and the results are presented in Fig. 3b. The ionic strength was kept constant, 0.5 mol L^{-1}, as previously, and the measurements were performed at three different pH values, 12.5, 12.75, and 13.0. The concentration of formaldehyde was recalculated into concentration of methanediol anion using pK_a 13.6.[29] As it was expected the oxidation peak current increased linearly with increase in the methanediol anion concentration; moreover, this increase was non-linear *versus* the total concentration of formaldehyde (not shown). This fact also confirms the presumption that usually methanediol anion takes place in the oxidation reaction.
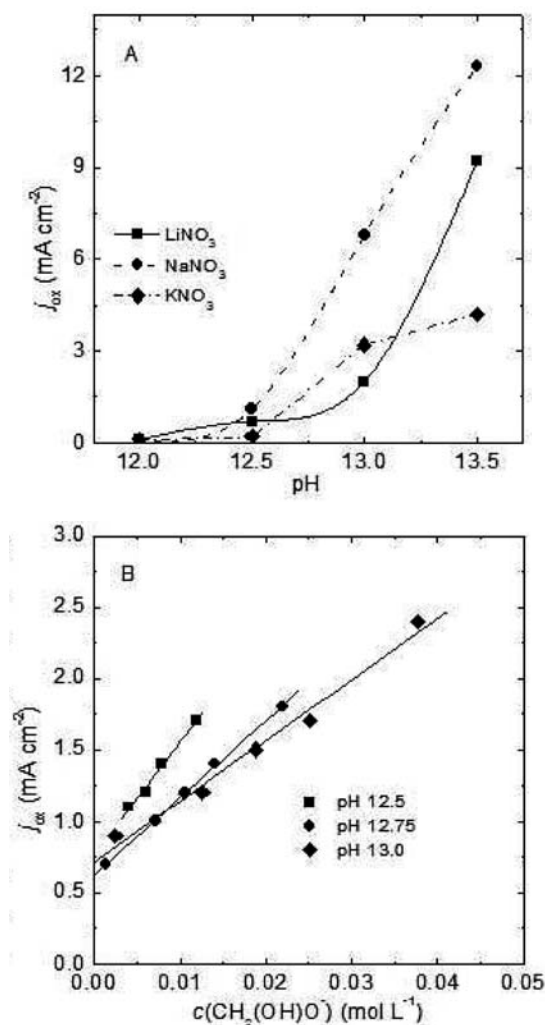
Fig. 3. Dependence of the formaldehyde oxidation peak current density at Pt electrode on pH (A) and concentration of methanediol anion (B). Potential scan rate 50 mV s^{-1}; supporting electrolyte (in B) NaNO$_3$; ionic strength 0.5 mol L^{-1}; formaldehyde concentration (in A) 0.15 mol L^{-1}.
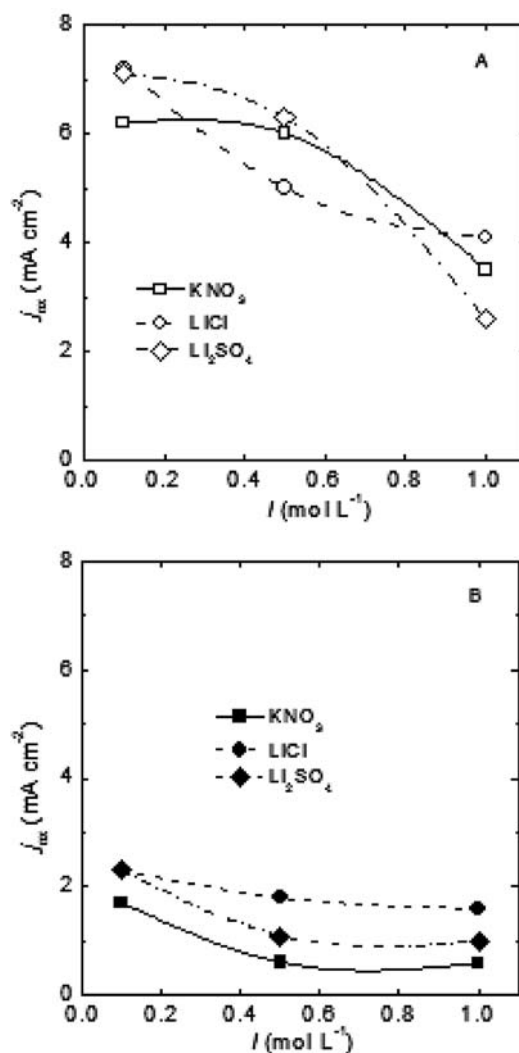

Fig. 4. Dependence of formaldehyde anodic oxidation peak current density at Pt (A) and Cu (B) electrodes on ionic strength in different electrolytes: KNO$_3$ (squares), LiCl (balls), and Li$_2$SO$_4$ (diamonds). Potential scan rate 50 mV s^{-1}; pH 13.0.

3. 3. The Influence of the Ionic Strength

The electrochemical investigation of the influence of the ionic strength on the anodic formaldehyde oxidation was performed for the first time. Three ionic strength values were chosen and they were applied to all supporting electrolytes used (Fig. 4): lithium, sodium and potassium chlorides, nitrates and sulphates, and sodium phosphate.

In the most of the cases the formaldehyde oxidation current decreased with increase in the ionic strength of the solution as seen in Fig. 4. However, there are some cases where the oxidation peak current increased or remained constant with increase in the ionic strength of the solution, and the specific effect of some anion or cation was observed, e.g. the oxidation rate of formaldehyde was growing with increase in the ionic strength in LiNO$_3$–LiOH solution. Such an influence of the ion nature could be explained by the Debye-Hückel theory or the secondary

kinetic electrolyte effect based on the radius of an ion: the larger radius of cation in the sequence Li$^+$, Na$^+$ and K$^+$, the less increase in oxidation rate although the ionic strength is increasing.[32]

From the other hand, the influence of the ionic strength on the formaldehyde oxidation current also depended on a specific concentration, activity, which had changed with the ionic strength due to changes in size of the hydrated ions, according to the Debye-Hückel theory. The value of the activity coefficients usually (exceptions LiCl and LiNO$_3$) diminished with the increase in ionic strength in the sequence of the increase of ion radius.[37,38] Thus, the influence of the ionic strength probably was related to the secondary kinetic electrolyte effect:[32] apparently, the electrolyte ions stopped the reaction of the formaldehyde hydration (1), because the oxidation current usually was higher at low ionic strength and it decreased

with further increase in the ionic strength (Fig. 4). This effect was most visible in the solutions were the supporting electrolyte was potassium nitrate, all chlorides and sulphates at both electrodes. Hence, in other nitrates and sodium phosphate electrolytes at Pt electrode the primary kinetic electrolyte effect was more expressed and the oxidation current of formaldehyde increased with increase in the ionic strength (not shown).

From the other hand, the dependence of the formaldehyde oxidation current on the ionic strength of the solution at Cu electrode can be attributed to the simultaneous formation of Cu oxides. As it was mentioned above, the formation of the surface oxide layer depends strongly on the anions of the supporting electrolyte as ionic strength.[34] Nevertheless, the surface oxide hardly interfered the formaldehyde oxidation at Pt because formaldehyde electrooxidation occurs at lower potential than than of platinum oxides formation as described above. However, there are some data reported in literature that the Pt surface oxide can also interfere some oxidation process, for example oxidation of sulphur dioxide in acidic medium.[26,27]

The dependence of the formaldehyde electrooxidation on the ionic strength of the solution can be used improving the development of fuel cells. Since formaldehyde is a small molecule, which can be easy oxidised,[2] is used for the development of the fuel cells like methanol, ethanol and similar small molecules.[6,7] The optimal ionic strength value is up to 0.5 mol L^{-1}, the higher values lead to decrease of the oxidation currents.

4. Conclusions

A linear dependence between the oxidation current and the concentration of methanediol anion was obtained. In contrary, a non linear dependence was observed between the oxidation current and the total concentration of formaldehyde up to pH 13.0. Additionally, a linear increase on the oxidation current was obtained with the increase in solution pH at a constant formaldehyde concentration. The $CH_2(OH)O^-$ oxidation rate depended on the cation radius of supporting electrolytes studied: the larger cation radius, the less increase in oxidation rate despite the augmentation the ionic strength of the solution. The formaldehyde oxidation rate diminished with the growth of the ionic strength of the solution in most of the cases studied of due the secondary kinetic electrolyte effects related to the changes of a hydrated ion size at Pt and additionally due to simultaneous formation of the surface oxides formation at Cu.

The highest oxidation currents were obtained when sodium nitrate, sodium and potassium sulphates were used as the supporting electrolytes at Pt. Moreover, the oxidation current rose up with the increase in the ionic strength of the solution in these supporting electrolytes. However, the best conditions of electrooxidation of formaldehyde were when

pH was down to 13.0 and a higher quantity of protonised methanediol was present in the solution, and the optimal ionic strength was up to 0.5 mol L^{-1} when the kinetic electrolyte effects had less influence. This information might be advantageous for development of the fuel cells and/or electroless copper plating baths.

5. Acknowledgement

6. References

1. P. Greenzaid, Z. Luz, D. Samuel, *J. Am. Chem. Soc.* **1967**, *89*, 749–752.
2. J. F. Walker, *Formaldehyde*, 3rd ed., Robert E. Krieger Publishing: New York, 1975.
3. J. E. A. M.van den Meerakker, *J. Appl. Electrochem.* **1981**, *11*, 395–401.
4. P. Olivi, L. O. S. Bulhoes, B. Beden, F. Hahn, J. M. Leger, C. Lamy, *Electrochim. Acta* **1996**, *41*, 927–932.
5. A. Karantonis, D. Koutsaftis, N. Kouloumbi, *Chem. Phys. Lett.* **2006**, *422*, 78–82.
6. J. B. Joo, P. Kim, W. Kim, J. Kim, J. Yi, *Catal. Today* **2006**, *111*, 171–175.
7. K. Bergamaski, A.L.N. Pinheiro, E. Teixeira-Neto, F.C. Nart, *J. Phys. Chem. B* **2006**, *110*, 19271–19279.
8. Z. Jusys, A. Vaskelis, *Langmuir* **1992**, *8*, 1230–1231.
9. Z. Jusys, R. Pauliukaite, A. Vaskelis, *Phys. Chem. Chem. Phys.* **1999**, *1*, 313–318.
10. R. Pauliukaite, G. Stalnionis, Z. Jusys, A. Vaskelis, *J. Appl. Electrochem.* **2006**, *36*, 1261–1269.
11. A. Calusaru, L. Crisan, J. Kuta, *J. Electroanal. Chem.* **1973**, *46*, 51–59.
12. Barnes, D.; Zuman, P.; *J. Electroanal. Chem.* **1973**, *46*, 323.
13. Jusys, Z.; *J. Electroanal. Chem.* **1994**, *375*, 257.
14. A. Vaskelis, E. Norkus, R. Juskenas, E. Matulionis, G. Stalnionis, *Galvanotechnik* **1995**, *86*, 2114–2118.
15. Z. Jusys, A. Vaskelis, *Electrochim. Acta* **1997**, *42*, 449–454.
16. N. M. Ristic, M. Kotorcevic, C. M. Lacnjevac, A. M. Jokic, M. M. Jaksic, *Electrohim. Acta* **2000**, *45*, 2973–2989.
17. R. Stadler, Z. Jusys, H. Baltruschat, *Electrohim. Acta* **2002**, *47*, 4485–4500.
18. M.V ten Kortenaar, Z. I. Kolar, J. J. de Goeij, M.; G. Frens, *J. Electrochem. Soc.* **2001**, *148*, E327–E335.
19. S. Park, Y. Xie, M. J. Weaver, *Langmuir*, **2002**, *18*, 5792–5798.
20. M.V. ten Kortenaar, Z. I. Kolar, J. J. M. de Goeij, G. Frens, *Langmuir*, **2002**, *18*, 10279–10291.
21. E. Mishina, A. Karantonis, Q. K. Yu, S. Nakabayashi, *J. Phys. Chem. B* **2002**, *106*, 10199–10204.
22. A. Miki, S. Ye, T. Senzaki, M. Osawa, *J. Electroanal. Chem.* **2004**, *563*, 23–31.

23. C. F. Mai, C.H. Shue, Y.C. Yang, L. Y. O. Yang, S. L. Yau, K. Itaya, *Langmuir*, **2005**, *21*, 4964–4970.

24. H. Yang, T. Lu, K. Xue, S. Sun, G. Lu, S. Chen, *J. Molec. Cat. A* **1999**, *144*, 315–321.

25. M. Beltowska-Brzezinska, J. Heitbaum, *J. Electroanal. Chem.* **1985**, *183*, 167–181.

26. P. W. T. Lu, R. L. Ammon, *J. Electrochem. Soc.* **1980**, *127*, 2610–2616.

27. C. Quijada, E. Morallón, J. L. Vázquez, L.E.A. Berlouis, Electrochim. Acta 2000, 46, 651–659.

28. A. J. Motheo, E.R. Gonzalez, G. Tremiliosi, P. Olivi, A. R. de Andrade, B. Kokoh, J. M. Leger, E. M. Belgsir, C. Lamy, *J. Braz. Chem. Soc.* **2000**, *11*, 16–21.

29. E. Norkus, R. Pauliukaite, A. Vaškelis, E. Butkus, Z. Jusys, M. Krenevičiene, *J. Chem. Res. (S)* **1998**, 320–323.

30. I.M. Kolthoff, R. Belcher, V.A. Stenger, *Titrimetritsheskii analiz* (in Russian), Vol. 3., Gos. Nautshn. Techn. Izd. Khim. Lit.: Moscow 1961.

31. G. Brauer, *Handbuch der Präparativen anorganischen Chemie*, Vol. 3, 3rd ed., F. Enke: Stuttgart 1981.

32. K.A. Connors, *Chemical Kinetics. The Study of Reaction Rates in Solution*, VCH: New York, 1990.

33. A. Vaškelis, E. Norkus, I. Stalnionienë, G. Satlnionis, *Electrochim. Acta* **2004**, *49*, 1613–1621.

34. J. O. Zerbino, L. M. Gassa, *J. Solid State Electrochem.* **2003**, *7*, 177–182.

35. K. G. Wagner, R. Gruetzmann, *AAPS J.* **2005**, *7*, E668–E677.

36. R. E. W. Hancock, C. Egli, R. Benz, A.J. Siehnel, *J. Bacteriol.* **1992**, *174*, 471–476.

37. P. Olivi, L.O.S. Bulhões, B. Beden, F. Hahn, J.M. Léger, C. Lamy, *J. Electroanal. Chem.* **1992**, *330*, 583–594.

38. Kaye&Laby online; *Tables of Physical & Chemical Constants. Chapter 3: Chemistry.* http://www.kayelaby.npl.co.uk /chemistry/3_9/3_6_9.html.

Povzetek

Hitrost elektrooksidacije metandiola (hidratiranega formaldehida) na polikristalinični platini ali bakru pada z naraščajočo ionsko močjo raztopine pri konstantni vrednosti pH in narašča z rastočo vrednostjo pH in koncentracijo metandiola. Oksidacijski tok je linaerno odvisen od koncentracije metandiolnega aniona vendar odvisnost od celokupne koncentracije formaldehida kaže nelinearno zvezo. Optimalne pogoje oksidacije formaldehida dosežemo z uporabo $NaNO_3$, Na_2SO_4 ali K_2SO_4 kot nosilnega elektrolita pri ionski moči do 0.5 in pH pod 13.