STUDY OF THE KINETICS OF OXYGEN REDUCTION AT A SINTERED CARBON ELECTRODE WITH A SILVER CATALYST IN ALKALINE MEDIUM

Jaroslav MACENAUER

Department of Physical Chemistry,
Institute of Chemical Technology, 532 10 Pardubice

Received November 17th, 1988
Accepted September 19th, 1989

The present work deals with a model of a hydrogen-oxygen electrochemical cell with a sintered carbon cathode containing a silver catalyst in an alkaline medium. The discharge curves of the cell connected to a variable discharge resistance were measured; their analysis based on a theory of the model cell yielded information about the electrode kinetic parameters.

A theoretical model of the kinetics of electrochemical reactions proceeding in an electrochemical cell with the overall reaction $n_2\mathrm{Ox}_1 + n_1\mathrm{Red}_2 \rightleftharpoons n_1\,\mathrm{Ox}_2 + n_2\,\mathrm{Red}_1$ was proposed in our earlier work[1]. If the reaction takes place only through the electrodes, the increments and decrements of the particular reactants are given by the current, which is determined by the positive charge production per unit time. At the positive electrode with potential E_1, the total production of positive charge per unit time, equal to the difference between the cathodic and anodic partial currents, is consumed in charging the double layer, causing decrease of the electric potential, and in generating the current I flowing through the external current lead. At the negative electrode with potential E_2, the situation is analogous except that the current I flows in the opposite direction. The partial cathodic and anodic currents can be expressed by the known formulae following from the theory of electrode processes. If the electrolyte is well stirred, the kinetic equations together with Ohm's law lead to a system of four differential equations for the two unknown potentials, E_1 and E_2, and two concentration decrements of the oxidant, x, and of the reductant, y:

$$A_1C_1\frac{\mathrm{d}E_1}{\mathrm{d}t} = n_1A_1Fk_1^0\{(a_1 - x)\exp\left[-(E_1 - E_{01})\,\alpha_1n_1F/RT\right] -$$

$$- (b_1 + x)\exp\left[(E_1 - E_{01})(1 - \alpha_1)\,n_1F/RT\right]\} - (E_1 - E_2)/R\,, \qquad (1)$$

$$A_2C_2\frac{\mathrm{d}E_2}{\mathrm{d}t} = n_2A_2Fk_2^0\{(a_2 + y)\exp\left[-\,(E_2 - E_{02})\,\alpha_2n_2F/RT\right] -$$

$$- (b_2 - y) \exp [(E_2 - E_{02}) (1 - \alpha_2) n_2 F/RT]\} + (E_1 - E_2)/R\,, \tag{2}$$

$$n_1 V_1 F \frac{dx}{dt} = n_1 A_1 F k_1^0 \{(a_1 - x) \exp [(- (E_1 - E_{01}) \alpha_1 n_1 F/RT] -$$

$$- (b_1 + x) \exp [(E_1 - E_{01}) (1 - \alpha_1) n_1 F/RT]\}\,, \tag{3}$$

$$-n_2 V_2 F \frac{dy}{dt} = n_2 A_2 F k_2^0 \{(a_2 + y) \exp [- (E_2 - E_{02}) \alpha_2 n_2 F/RT] -$$

$$- (b_2 - y) \exp [(E_2 - E_{02}) (1 - \alpha_2) n_2 F/RT]\}\,. \tag{4}$$

This system is generally not solvable in a closed form. An analytical solution can be obtained under simplifying conditions that the electrode capacities are equal to zero, the ohmic resitance is negligible (hence $E_1 = E_2$), and the back reaction does not proceed. If these conditions are satisfied, the above system of differential equations is reduced to a single one,

$$\frac{dE}{dt} = \frac{RT/F}{\alpha_1 n_1 + (1 - \alpha_2) n_2} \left\{ \frac{A_2}{V_2} k_2^0 \exp\ [(E - E_{02}) (1 - \alpha_2) n_2 F/RT] - \right.$$

$$\left. - \frac{A_1}{V_1} k_1^0 \exp [(E - E_{01}) \alpha_1 n_1 F/RT] \right\} \tag{5}$$

which can be integrated after separation of variables to obtain an equation of the discharge curve. From the kinetic point of view, the total reaction time t_∞ during which the minor reactant concentration drops to zero is important. In contrast to homogeneous reaction kinetics, this time is finite and can be found from the discharge curve for $E \to \infty$ (exhuastion of the reductant) or for $E \to -\infty$ (exhaustion of the oxidant). If we restrict ourselves to one of these two cases, we have either $n_2 V_2 b_2 / / n_1 V_1 a_1 \ll 1$ or $n_1 V_1 a_1 / n_2 V_2 b_2 \ll 1$, and we obtain

$$t_\infty = \frac{V_2}{k_2^0 A_2 \varrho_2} \exp [- (E(0) - E_{02}) (1 - \alpha_2) n_2 F/RT] \tag{6}$$

(rising discharge curve), and

$$t_\infty = \frac{V_1}{k_1^0 A_1 \varrho_1} \exp [(E(0) - E_{01}) \alpha_1 n_1 F/RT] \tag{7}$$

(decreasing discharge curve).

The initial potential $E(0)$ (the potential of the discharge curve for $t = 0$) depends on many parameters; it can be assumed that the dependence of t_∞ on R will be involved in the initial potential of the discharge curve, $E_1(0, R)$, for non-zero values of the resistance R. Since, however, $E_1 \neq E_2$ for $R > 0$, we must introduce $E_2(0, R)$ into Eq. (*6*) and $E_1(0, R)$ into Eq. (*7*). This was verified on theoretical E_1–t curves obtained by numerical solution of the system of equations (*1*)–(*4*) for various resistances R, transfer coefficients α, and initial concentrations of the reactants. The values of t_∞ and $E_1(0, R)$ read from these curves satisfy the equation

$$t_\infty = \frac{V_1}{A_1 k_1^0 \varkappa} \exp\left[\left(E_1(0, R) - E_{01}\right) \alpha_1 n_1 F/RT\right] \qquad (8)$$

which is analogous to Eq. (*7*); the parameter $\varkappa$ is equal to ϱ_1 for low resistances ($R < 10\,\Omega$) and for $\alpha_1 < 0.3$; otherwise $\varkappa = 0.96$. It was shown[1] that the initial potential $E_1(0, R)$ can be introduced into Eq. (*7*) to obtain the expression for the reaction time t_∞ as a function of the parameters A_1, a_1, b_2, R, and V_1:

$$\ln t_\infty = \ln\left[\frac{V_1 n_1 \varkappa^{-1}}{(n_1 A_1 k_1^0)^{\varrho_2} (n_2 A_2 k_2^0)^{\varrho_1}} \left(\frac{a_1}{b_2}\right)^{\varrho_1}\right] + \frac{\alpha_1 n_1 F}{RT} \varrho_2 (E_{02} - E_{01}) + {} \\ + \frac{\alpha_1 n_1 F \varrho_2}{RT} \frac{V_1 n_1 F}{\varkappa} \frac{a_1 R}{t_\infty}. \qquad (9)$$

The quantities A_2, k_2^0 and ϱ_2 refer to the anode compartment of the cell; analogous quantities refer to the cathode compartment. The initial concentrations of the oxidant and reductant are denoted as a_1 and b_2, respectively. Equations (*8*) and (*9*) were verified experimentally on seven cells with a one-electron transfer[2] and on two cells with a two-electron transfer[3].

When we consider the experimental oxygen-hydrogen cell described below, the volumes V_1 and V_2 refer to the oxygen and hydrogen contained in gas volumetric flasks. The gases are used up during recording the discharge curve. Their molar volume concentrations are, on the assumption of ideal behaviour, given as $a_1 = n_{O_2}/V_1$, $b_2 = n_{H_2}/V_2$. If the volumes of the gas burettes are equal and both gases have the same pressure, then $a_1 = b_2$. The gas concentration was varied by the addition of argon to one or both components. Let us assume that an oxygen–argon mixture (partial rates of flow V_{O_2} and V_{Ar1}, $V_{O_2}/V_{Ar1} = m_1$) flows through the gas burette to the cathode, and similarly a hydrogen–argon mixture ($V_{H_2}/V_{Ar2} = m_2$) flows to the anode; then the molar fractions are (on the assumption of ideal behaviour) given as $X_{O_2} = m_1/(m_1 + 1)$ and $X_{H_2} = m_2/(m_2 + 1)$, and the ratio of the molar volume concentrations is given by the equation

$$a_1/b_2 = \frac{p_1 m_1}{p_2 m_2} \frac{m_2 + 1}{m_1 + 1} = n\,, \tag{10}$$

where p_1 and p_2 denote pressures of the cathode and anode gases, respectively. The parameter n can be varied experimentally.

EXPERIMENTAL

The experimental set-up consisted of an apparatus for the preparation of oxygen–argon and hydrogen–argon mixtures, the model cell, and a measuring equipment. The gases were taken from pressurized bottles with a maximum pressure of 15 MPa, which was reduced to 0·15 MPa and stabilized by means of manostats. The rates of flow were measured by calibrated capillaries and the corresponding pressure loss was measured by volume-calibrated tubes with a floating bubble for the purpose of calibration. For the preparation of gas mixtures, the rates of flow of both gases were measured before mixing. The whole apparatus was kept at a temperature of 303 K.

The cylindrical model cell (Fig. 1) was made of poly(methylmethacrylate) and its middle compartment was filled with 5M-KOH. The bases of the cylinder were formed by the cathode and anode, whose active surface was in contact with nickel current collectors. The other side

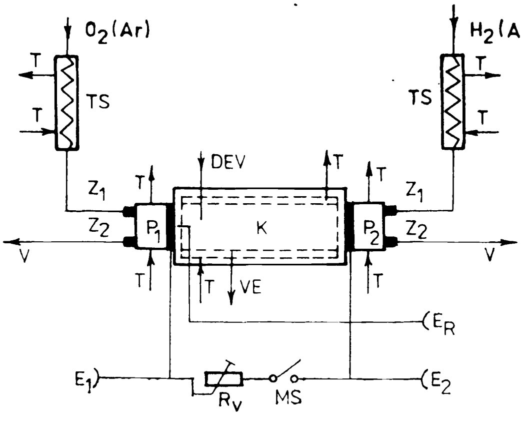

FIG. 1

The model cell. O_2(Ar) inlet of oxygen or its mixture with argon; H_2(Ar) inlet of hydrogen or its mixture with argon; P_1, P_2 gas burettes for O_2 and H_2 or their mixtures with Ar; K electrolyte chamber; Z_1, Z_2 valves of the gas burettes; TS thermostated glass spirals; V gas outlet; DEV inlet for electrolyte or distilled water; VE outlet of electrolyte or distilled water; T thermostat; R_v calibrated resistance set; MS mechanical switch; E_1, E_2 measuring points for the potential difference EMN (electrodes are black); E_R Hg/HgO reference electrode of each electrode was joined with an easily removable gas burette of changeable volume, provided with valves at the inlet and at the outlet. Both the electrolyte chamber and the gas burettes were kept at a temperature of 303 K.

The measuring equipment recorded automatically the time dependences of the electromotive force at the points E_1 and E_2 by using a K 200 recorder (VEB Carl Zeiss, Jena) of $10^{10}\,\Omega$ input resistance. The obtained discharge curves of the oxygen-hydrogen cell were used to determine the discharge time t_∞ corresponding to 1/4 of the curve height[2,3]. Another K 200 apparatus recorded the potential of the oxygen electrode against Hg/HgO reference electrode in 0·1M-NaOH (E_R = 0·165 V; the measuring points are denoted as E_1 and E_R). The cell was discharged through a variable resistance (a calibrated resistance set XL 6, Metra Blansko).

The oxygen and hydrogen electrodes were prepared by the published method[25,26]. The oxygen electrode consisted of two layers: the gas layer of square density 100 mg/cm^2 was prepared from teflonized carbon black (acetylene black P-1042, G.D.R., containing 35% PTFE), and the active layer was a mixture of teflonized carbon black (12 mg/cm^2) and a powdered catalyst (18 mg/cm^2) containing 80% of active carbon HS-4 (MCHZ Ostrava) and 20% of silver deposited from a solution of $AgNO_3$ by reduction with hydrazine[4]. The electrode was sintered at 350°C at a pressure of 20 MPa; it had the shape of a disc of 45 mm diameter and about 1 mm thickness.

Pressure bottles with medicinal oxygen and electrolytic hydrogen were supplied by Technoplyn, Prague, and the gas purity was checked analytically. Pressure bottles with argon were supplied by MCHZ Ostrava.

The discharge curves of the cell were recorded as functions of the parameters a_1/b_2 and R. The former was determined according to Eq. (*10*), which was simplified by the choice of equal pressures in both cell compartments. For a chosen value of a_1/b_2, both mixtures flowed through the gas volumetric flasks, which were closed at the inlet and at the outlet just before the beginning of the experiment. To obtain discharge curves with a chosen R value, constant ratio of a_1/b_2 was chosen so that the condition $n_1 V_1 a_1/n_2 V_2 a_2 \ll 1$ was satisfied and Eq. (*8*) could be used. This was achieved by adjusting the ratio of argon to oxygen.

RESULTS AND DISCUSSION

The discharge curves of the oxygen-hydrogen cell were first measured at constant external resistance for $n < 1$, the oxygen in the gas burette being mixed with argon. Hydrogen in the other gas burette was of 99·99% purity. To check the reproducibility of the measurements, five discharge curves were recorded at $R = 15\,\Omega$ and different n values, the curve for $n = 0{\cdot}29$ being recorded three times with no apparent deviations (Fig. 2).

To evaluate the kinetics of the oxygen reduction, we studied the discharge curves under conditions at which Eq. (*8*) holds good. The ratio of a_1/b_2 was kept constant below 0·3. A set of discharge curves for several R values is shown in Fig. 3; the parameter $a_1/b_2 = 0{\cdot}15$. To check the long-term stability of the electrodes, these measurements were repeated 15 times during a month, while the electrodes were constantly immersed in 5M-KOH in the cell. Each set of measurements was evaluated by regression analysis to give the slope and regression coefficient of the dependence of $\log t_\infty$ on $E_1(0, R)$ (Fig. 4). Thirteen regression coefficients are in the interval 0·995 – 1·00, evidence for the validity of Eq. (*8*) for the oxygen-hydrogen cell. The product of $\alpha_l n_l = (2{\cdot}303RT/F)\,S$, where S denotes the slope of the mentioned dependence, can also be evaluated. The same equation can be used to determine the rate constant of the electrochemical oxygen reduction under the given conditions, provided that the standard potential of the oxygen electrode, E_{01}, is known.

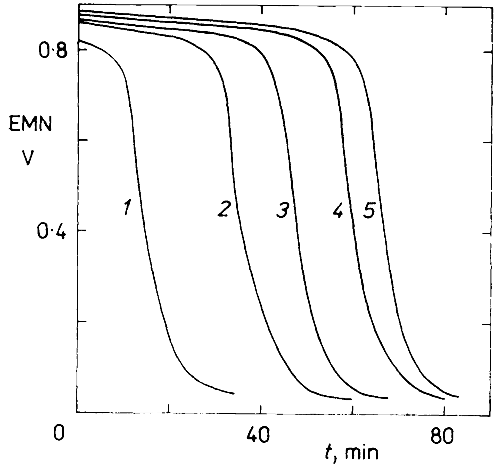

FIG. 2

Cell discharge curves for constant $R = 15\,\Omega$, 303 K, $V_1 = V_2 = 26{\cdot}11\,\text{cm}^3$; curves *1*–*5* correspond to $n = 0{\cdot}17$, 0·29, 0·38, 0·44, and 0·47, respectively; EMN is the potential difference between the electrodes during discharge

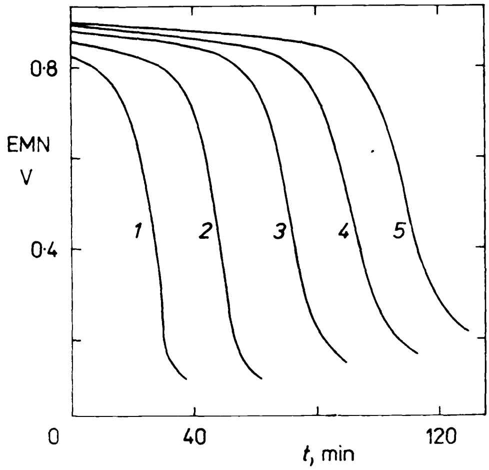

FIG. 3

Discharge curves for constant $n = 0{\cdot}15$ at 303 K, $V_1 = V_2 = 26{\cdot}11\,\text{cm}^3$; curves *1*–*5* correspond to $R = 20$, 40, 60, 80, and 100 Ω, respectively. Tenth day of measurements; the calculated parameters are given in Table I

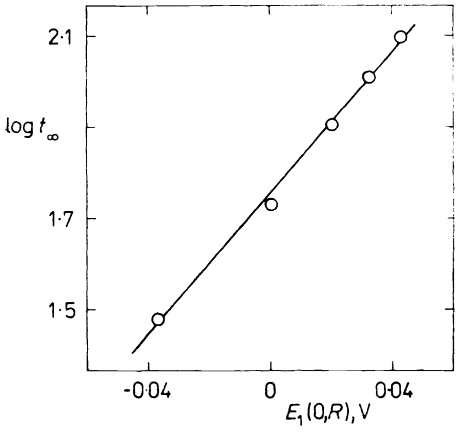

FIG. 4

Linearization of Eq. (*8*) for the O_2-H_2 cell. Parameters: $n = 0{\cdot}15$; $V_1 = V_2 = 26{\cdot}11\,\text{cm}^3$; $R = 20$, 40, 60, 80, and 100 Ω; 303 K. Tenth day of measurements

According to Frumkin[12,13], oxygen is weakly adsorbed on the active carbon surface and can gradually form more stable surface oxides, while the electrochemical activity is due to the weakly bonded oxygen, in accord with Garten and Weiss[14,15]. An important property of active carbon as active material for the oxygen electrode in alkaline medium is its catalytic activity for decomposition of hydrogen peroxide. The potential of the oxygen electrode is controlled by the number of active centres with adsorbed oxygen and their catalytic activity with respect to the decomposition of hydrogen peroxide[4,16,17]. The measured potentials of carbon electrodes operating on oxygen differ from the theoretical value for the reaction $O_2 + 2\,H_2O + 4\,e \rightleftharpoons 4\,OH^-$ (standard potential $E_{01} = +0{\cdot}401$ V). According to Berl[19] and other authors[20,21], the reduction in alkaline medium proceeds with the formation of peroxide: $O_2 + H_2O + 2\,e \rightleftharpoons HO_2^- + OH^-$, $E_{01} = -0{\cdot}076$ V. The latter value, given by Berl, is similar to that given by Yablokova and Bagotskii[22]; and it leads, based on Eq. (*8*), to values of the rate constant for oxygen reduction given in Tables I and II.

Březina et al.[5] studied the reduction of oxygen at a silver electrode in 0·1M-KOH by using cyclic voltammetry; they concluded that the reaction proceeds via hydrogen peroxide and is kinetically controlled by transfer of the first electron. The charge transfer coefficient was determined as $\alpha = 0{\cdot}5$. Later Březina and Hofmanová-Matějková[6] studied the reduction of oxygen on carbon paste and smooth carbon electrodes in KOH solutions. The electrochemical kinetic parameters depended on the mode of preparation of the electrode. The charge-transfer coefficient on a smooth carbon electrode was equal to 0·5 and the rate constant of the electrode reaction at the O_2/H_2O_2 standard potential was $k^0 = 5\,.\,10^{-5}\ \text{cm s}^{-1}$. The rate of the electrode reaction was controlled (as in the case of Ag, Pt, and Hg electrodes[5,8-10]) by transfer of the first electron forming a superoxide anion, whose existence was assumed in voltammetric studies[11]. The electrode kinetic parameters obtained on carbon paste electrodes bonded with paraffin oil were less reproducible, the value of α was in the range 0·6–0·7 and k^0 was of the order of $10^{-4}\ \text{cm s}^{-1}$. Yeager et al.[18,23,24] proposed a reaction mechanism in alkaline medium, consisting of five follow-up reactions, and concluded that the overall reaction rate is controlled by one-electron transfer involving adsorbed radicals.

The first series of measurements in the present work was carried out with a single oxygen electrode in 5M-KOH at 303 K and the results are given in Table I. The tenth measurement is shown graphically in Fig. 3 and its evaluation based on linearized Eq. (*8*) is illustrated in Fig. 4; the parameter $n = 0{\cdot}15$.

The second series of measurements was done for $n = 0{\cdot}22$. This increased n value was without influence on the results, in agreement with the theory. We used seven oxygen electrodes prepared in the same way; the results of measurements are given in Table II. When the two series of measurements are compared, it can be seen that the electrochemical parameters are nearly identical. A certain scatter of the results

TABLE I

Results of measurements on a single oxygen electrode in 5M-KOH at 303 K. Parameters: n = 0·15, u section of the linearized Eq. (*8*), S its slope, r regression coefficient

Measurement No.	u	S, V^{-1}	r	$\alpha_1 n_1$	k_1^0 . 10^3, cm s^{-1}
1	1·753	7·804	0·998	0·469	1·97
2	1·684	6·919	0·984	0·416	1·98
3	1·685	9·124	0·995	0·549	2·90
4	1·711	8·559	0·996	0·515	2·48
5	1·750	8·588	0·999	0·516	2·28
6	1·730	8·770	0·999	0·527	2·46
7	1·749	8·215	0·997	0·494	2·14
8	1·742	8·729	0·998	0·525	2·38
9	1·752	8·636	0·997	0·519	2·29
10	1·754	8·345	0·995	0·502	2·16
11	1·752	7·527	0·989	0·452	1·89
12	1·729	8·385	0·998	0·504	2·31
13	1·749	8·199	0·996	0·493	2·14
14	1·738	8·192	0·996	0·492	2·19
15	1·762	7·810	0·995	0·470	1·94
αn_1 = 0·496 ± 0·009			k_1^0 = (2·23 ± 0·07) . 10^{-3}, cm s^{-1}		

TABLE II

Measurement results for seven electrodes prepared by the same procedure: n = 0·22. Other data as in Table I

Measurement No.	u	S, V^{-1}	r	$\alpha_1 n_1$	k_1^0 . 10^3, cm s^{-1}
1	1·721	10·257	0·994	0·617	3·26
2	1·780	9·045	0·993	0·544	2·03
3	1·771	9·055	0·991	0·544	2·36
4	1·800	8·479	0·999	0·510	1·99
5	1·842	10·699	0·996	0·643	2·67
6	1·879	8·381	0·997	0·504	1·63
7	1·769	7·435	0·998	0·447	1·78
$\alpha_1 n_1$ = 0·544 ± 0·028			k_1^0 = (2·28 ± 0·23) . 10^{-3}, cm s^{-1}		

in Table II is conceivable, since it is the result of measurements on different electrodes (although prepared in the same way). It seems that the value of $\alpha_1 n_1$ is sensitive to the mode of electrode preparation.

The proposed method enabled us to determine the rate constants for the electroreduction of oxygen to peroxide at the given electrode type. If we assume the reaction $O_2 + H_2O + 2\,e \rightleftharpoons HO_2^- + OH^-$, involving transfer of two electrons, then the charge transfer coefficient drops to one half with respect to the found values of $\alpha_1 n_1$ (Tables I and II). Such values, however, are at variance with the results of other authors. The difference may be due to differences in the electrode type and preparation.

LIST OF SYMBOLS

k_i^0	electrode reaction rate constant
n_i	number of transferred electrons
α_i	charge transfer coefficient
E_i	electrode potential
$E_i(0)$	initial electrode potential for $t = 0$, $R = 0$
$E_i(0, R)$	initial electrode potential for $t = 0$, $R > 0$
E_{0i}	standard electrode potential
A_i	electrode surface area
C_i	electrode specific capacity
a_i	initial concentration of the oxidant of i-th redox system
b_i	initial concentration of the reductant of i-th redox system
V_i	volume of space adjacent to the cathode or anode
$\mathbf{R}$	gas constant
R	electrical resistance
n_{O_2}	number of mols of oxygen
n_{H_2}	number of mols of hydrogen
m_1	ratio of volume rates of flow of oxygen and argon
m_2	ratio of volume rates of flow of hydrogen and argon
EMN	potential difference between cathode and anode during discharge
F	Faraday's constant
n_i	charge number of redox system
t_∞	total reaction time
n	ratio of molar volume concentrations of oxygen and hydrogen
X_{O_2}	molar fraction of oxygen mixed with argon
X_{H_2}	molar fraction of hydrogen mixed with argon
$\varkappa$	numerical factor

REFERENCES

1. Tockstein A., Macenauer J.: Collect. Czech. Chem. Commun. *49*, 2857 (1984).
2. Macenauer J.: Collect. Czech. Chem. Commun. *49*, 2867 (1984).
3. Macenauer J.: Collect. Czech. Chem. Commun. *51*, 493 (1986).
4. Yeager E.: *Technical Report No. 12.* Western Reserve University, Cleveland, Ohio 1960.

5. Březina M., Koryta J., Musilová M.: Collect. Czech. Chem. Commun. *33*, 3397 (1968).
6. Březina M., Hofmanová-Matějková A.: Collect. Czech. Chem. Commun. *38*, 3024 (1973).
7. Březina M., Hofmanová A.: Collect. Czech. Chem. Commun. *38*, 985 (1973).
8. Březina M., Wedell M.: Collect. Czech. Chem. Commun. *49*, 2320 (1983).
9. Lodmaa V. R., Past V. E., Chaga M. E.: Elektrokhimiya *2*, 927 (1966).
10. Bagotskii V. S., Yablokova I. I.: Zh. Fiz. Khim. *27*, 1663 (1953).
11. Březina M., Hofmanová-Matějková A.: J. Electroanal. Chem. *44*, 460 (1973).
12. Frumkin A. N.: *Sbornik Trudov Konferentsii po Adsorptsii*, p. 53. Izd. Moskov. Univ., Moscow 1957.
13. Burshtein R. Kh., Frumkin A. N.: Dokl. Akad. Nauk SSSR *32*, 327 (1951).
14. Garten V. A., Eppinger K.: Aust. J. Chem. *12*, 394 (1959).
15. Weiss D. E.: in: *Proc. Conf. Carbon, 5th, Univ. Park, Penna, 1961* (publ. 1962).
16. Davtyan O. K.: Zh. Fiz. Khim. *38*, 1594 (1964).
17. Tkach I., Davtyan O. K.: Zh. Fiz. Khim. *35*, 2727 (1961).
18. Yeager E., Kozawa A.: *Technical Report No. 17.* Western Reserve University, Cleveland, Ohio 1964.
19. Berl W. G.: Trans. Electrochem. Soc. *83*, 253 (1943).
20. Bianchi G., Caprioglio G., Mazza F., Mossini T.: Electrochim. Acta *4*, 232 (1961).
21. Witherspoon R., Urbach H., Yeager E., Hovorka F.: *Technical Report No. 4.* Western Reserve University, Cleveland, Ohio 1954.
22. Yablokova I. E., Bagotskii V. S.: Dokl. Akad. Nauk SSSR *85*, 599 (1952).
23. Yeager E., Krouse P., Rao K. V.: Electrochim. Acta *9*, 1057 (1964).
24. Yeager E., Kozawa A. in: *Extended Abstracts of Battery Division*, Vol. 9, Abstract No. 1. Electrochem. Soc., Washington 1964.
25. Smrček K., Wedell M., Mrha J., Musilová M.: Collect. Czech. Chem. Commun. *48*, 2165 (1983).
26. Musilová M., Wedell M., Mrha J., Smrček K.: Collect. Czech. Chem. Commun. *48*, 394 (1983).

Translated by K. Micka.