On the mechanism of electroless plating. I. Oxidation of formaldehyde at different electrode surfaces

J. E. A. M. VAN DEN MEERAKKER

Philips Research Laboratories, Eindhoven, The Netherlands

To elucidate the mechanism of electroless plating solutions with formaldehyde as the reductant, the anodic oxidation of formaldehyde in alkaline medium was studied. The influence of electrode material, pH and potential was investigated. The experimental results can be explained by a mechanism in which methylene glycol anion (CH_2OHO^-) is dehydrogenated at the electrode surface, yielding adsorbed hydrogen atoms. The atomic hydrogen can either be oxidized to water or be desorbed as a gas. Kinetic rate laws for these two reactions are given. Electroless copper, platinum and palladium solutions behave according to the mechanism.

Nomenclature

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E	applied potential
ΔE_a	activation energy of adsorption
ΔE_d	activation energy of desorption ($= -\Delta H + \Delta E_a$)
E_{eq}	equilibrium potential of the reversible hydrogen reaction at a given pH
F	Faraday's constant
$-\Delta H$	heat of adsorption
i^0	apparent exchange current density for the reversible hydrogen reaction
i_0	exchange current density for the reversible hydrogen reaction
k	rate constant for the desorption of hydrogen
L_s	heat of atomization
R	gas constant
T	absolute temperature
v_7	rate of oxidation of hydrogen atoms
v_8	rate of desorption of hydrogen
α	transfer coefficient (≈ 0.5)
η	overpotential ($= E - E_{eq}$)
θ	fraction of the surface covered by hydrogen atoms
Φ_M	work function of metal M
Ψ	potential of the outer Helmholtz layer relative to the bulk of the electrolyte

1. Introduction

Lukes [1] found the following overall reaction for electroless copper solutions with formaldehyde as the reductant:

$$Cu^{2+} + 2HCHO + 4OH^- \rightarrow Cu\downarrow + 2HCOO^-$$
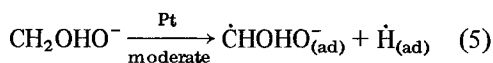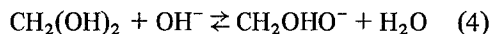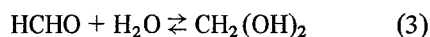$$+ 2H_2O + H_2\uparrow.$$
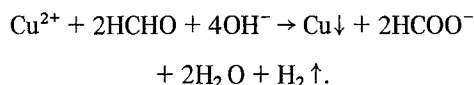
This overall reaction is a combination of the anodic oxidation of formaldehyde and the cathodic reduction of cupric ions at the copper surface. The copper surface is both the anode and the cathode at the same time and attains a potential at which the anodic and cathodic processes equal each other, i.e., a mixed potential. Paunovic [2] showed that the two processes can be studied separately. The anodic reaction occurring in electroless copper solutions is:
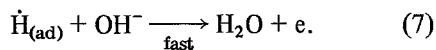
$$2HCHO + 4OH^- \rightarrow 2HCOO^- + 2H_2O + H_2\uparrow + 2e. \tag{1}$$
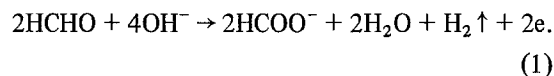
This is not the only possible reaction for the oxidation of formaldehyde to formate. Buck and Griffith [3] found on platinum electrodes:

$$HCHO + 3OH^- \rightarrow HCOO^- + 2H_2O + 2e. \tag{2}$$

They proposed the following mechanism in alkaline medium:

$$HCHO + H_2O \rightleftarrows CH_2(OH)_2 \tag{3}$$

$$CH_2(OH)_2 + OH^- \rightleftarrows CH_2OHO^- + H_2O \tag{4}$$

$$CH_2OHO^- \xrightarrow[\text{moderate}]{Pt} \dot{C}HOHO^-_{(ad)} + \dot{H}_{(ad)} \tag{5}$$

$$\dot{C}HOHO^-_{(ad)} + OH^- \xrightarrow[\text{slow}]{} HCOO^- + H_2O + e \quad (6)$$

$$\dot{H}_{(ad)} + OH^- \xrightarrow[\text{fast}]{} H_2O + e. \quad (7)$$
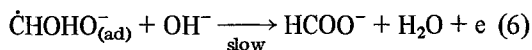
This mechanism explains the possibility of Reaction 2 and holds very well for platinum electrodes. On the other hand it does not explain the hydrogen evolution in electroless copper solutions and on certain other electrodes such as silver [4]. The hydrogen liberated at silver anodes originates from the formaldehyde molecule [5].

We think that Reaction 7 must compete with the recombination of hydrogen atoms:

$$2\dot{H}_{(ad)} \rightarrow H_2\uparrow. \quad (8)$$

The combination of Reactions 3–6 and 8 results in the overall Reaction 1. Whether Reaction 1 or 2 will proceed on a given metal is determined by the kinetics of Reactions 7 and 8 at the metal surface. It is obvious that the reaction rates are influenced by the adsorption energy of $\dot{H}$ at the surface, the potential at which the oxidation takes place and the pH of the solution.

We measured current–potential curves at various electrode surfaces. To test our hypothesis of the competition between Reaction 7 and 8 we studied the influence of the above-mentioned parameters.

2. Experimental procedures

All solutions were prepared from chemicals of analytical grade and deionized water. Before each experiment nitrogen was bubbled through the solutions to remove the oxygen. All experiments were carried out at $25 \pm 0.1°$ C.

The anodes were at least 99.99% pure. They were polished with emery paper and made free of oxides with suitable etching solutions. To make sure that at the start of the experiment the surface was not oxidized, the anodes were kept for 120 s at a potential of -2.0 V versus a saturated calomel electrode (SCE) in the same solution as was used for the experiment itself.

Current–potential curves were recorded for solutions of 0.1 M HCHO and 0.15 M NaOH (pH = 13.0) in a glass cell (see Fig. 1a). The working electrode was completely surrounded by a platinum sheet as counter electrode. The reference saturated calomel electrode was used in combination with a Luggin capillary whose tip was placed

0.5 mm from the working electrode. The potential of the working electrode was raised stepwise from -1.0 V to 0.0 V versus SCE with the aid of a Wenking 70 TS-1 potentiostat and a Wenking SMP72 scanning potentiometer. The scan rate was 1 step per 10 s, and each step was 10 mV. The current was recorded using a Philips PM8222 recorder.

Potentiostatic oxidation of formaldehyde and analysis of the anolyte were carried out in a two-compartment glass cell (see Fig. 1b). The amount of charge was measured with a Wenking Integrator (SSI 70). During the experiment the amount of hydrogen liberated was measured in a gas burette. After each experiment the concentration of formaldehyde in the anolyte was determined iodometrically [6]. A part of the original solution was kept at the same temperature during the experiment and also analyzed to ensure that side reactions (e.g. Cannizzaro reaction) did not influence the results.
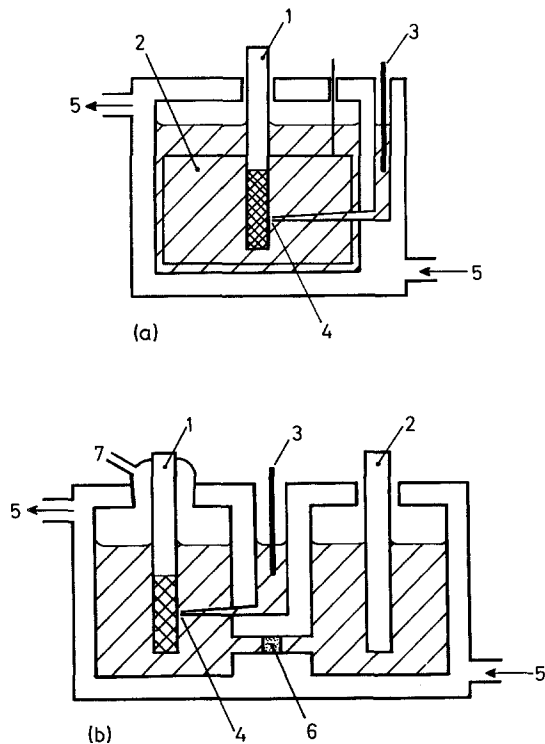

Fig. 1. (a) Cell for current–potential measurements. (b) Cell for analyses during potentiostatic oxidation. 1, Working electrode; 2, platinum counter electrode; 3, reference electrode; 4, Luggin capillary; 5, water from/to thermostat; 6, glass frit; 7, tube to gas burette.

3. Results

Current–potential curves of copper, silver, gold, platinum, palladium, nickel, rhenium and cadmium were recorded in the potential range from -1.0 to 0.0 V versus SCE. On nickel, rhenium and cadmium oxidation of formaldehyde was not observed in this potential region. According to Pourbaix [7] these metals are oxidized in this range of pH and potentials. With the other metals clear oxidation peaks for formaldehyde were observed (Figs. 2–6). On copper, silver and gold gas was evolved in part of the potential region. On platinum and palladium no gas evolution took place. The curves of the blank solution (solution of pH 13.0 without formaldehyde) were also recorded. With the exception of copper no peaks were observed. On copper a peak between -0.2 and 0.0 V versus SCE was found. The area under the peak was the same as that of Fig. 2 at the same potential. Obviously this peak is not due to oxidation of formaldehyde, but to the oxidation of the copper surface.

Analysis was combined with potentiostatic oxidation at copper, silver, gold, platinum and palladium electrodes. When hydrogen was evolved, the amount of gas was directly proportional to
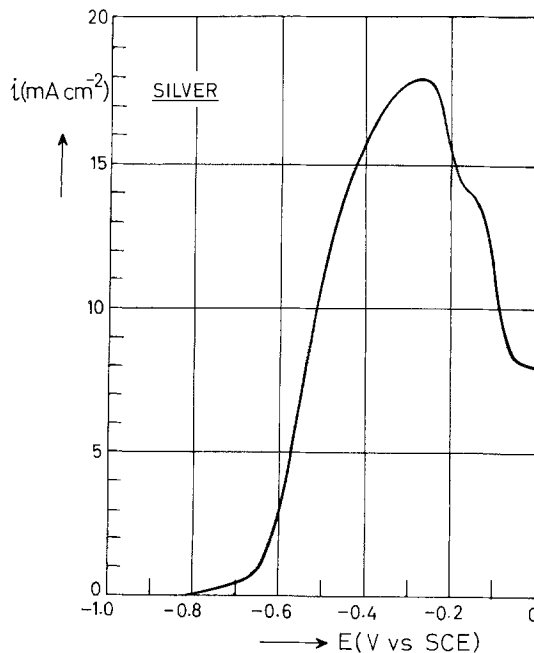

Fig. 3. Current–potential curve for a silver electrode in 0.1 M HCHO + 0.15 M NaOH.

the charge (see Fig. 7 for the silver electrode). From the slope of these lines we calculated the ratio between the amount of hydrogen evolved and the number of electrons (Tables 1–3). This
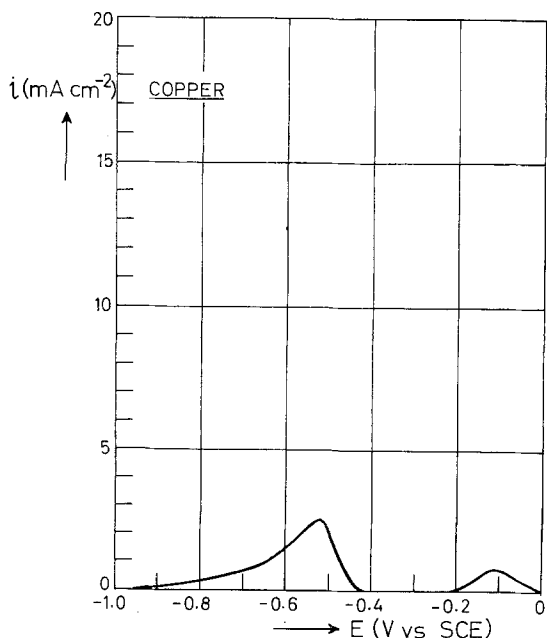

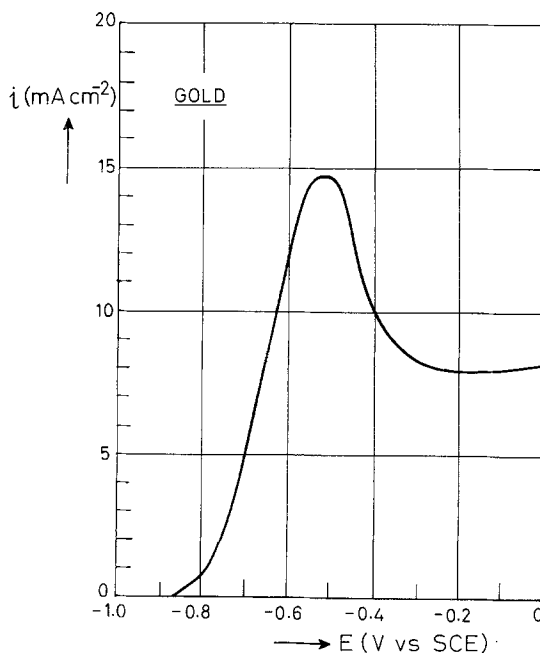Fig. 2. Current–potential curve for a copper electrode in 0.1 M HCHO + 0.15 M NaOH.

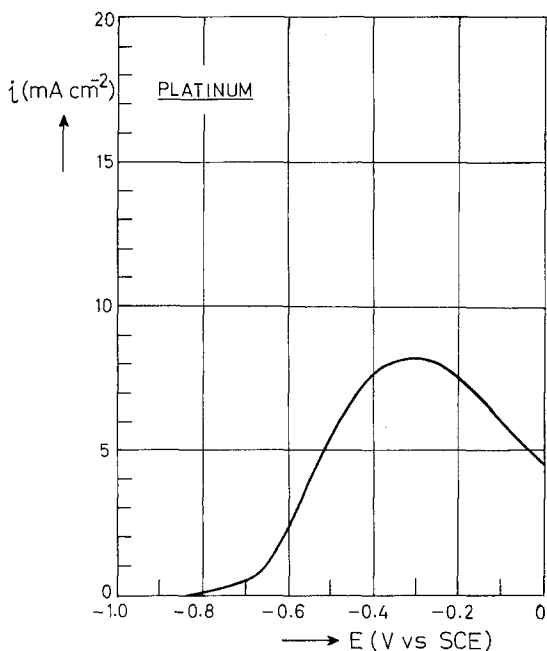Fig. 4. Current–potential curve for a gold electrode in 0.1 M HCHO + 0.15 M NaOH.

Fig. 5. Current–potential curve for a platinum electrode in 0.1 M HCHO + 0.15 M NaOH.

Fig. 7. The amount of hydrogen evolved as a function of the charge for a silver electrode in 0.1 M HCHO + 0.15 M NaOH at (a) − 0.4 V and (b) − 0.2 V versus SCE.

ratio should be zero for Reaction 2 and 0.5 for Reaction 1. From the changes in the formaldehyde concentration we also calculated the ratio of the formaldehyde used and the number of electrons
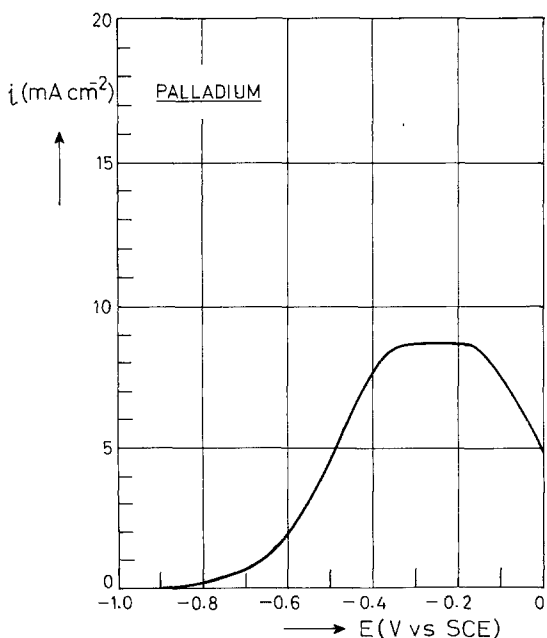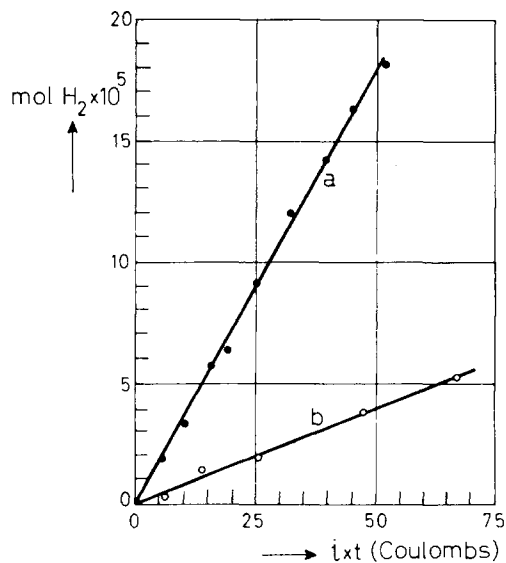
(Tables 1–3). This ratio should be 0.5 for Reaction 2 and 1.0 for Reaction 1. Assuming that a third reaction took place (oxidation to carbonate), we calculated the percentage of the current which was due to each of the three reactions. From Tables 1–3 it follows that, within experimental error, the total from Reactions 1 and 2 yields 100%. So oxidation of formaldehyde in alkaline medium and in the potential region under investigation gives formate as the final product. Further oxidation to carbonate does not take place on copper, silver, gold, platinum and palladium.

It is obvious that the electrode material has a considerable influence on the competition between Reactions 1 and 2 (see Table 1). On platinum and palladium the adsorbed atomic hydrogen is oxidized via Reaction 7. On copper, however, the hydrogen atoms recombine and escape as a gas via Reaction 8. On silver and gold both reactions take place, and, as would be expected from the given mechanism, a more anodic potential favours Reaction 2 (see Table 2). The influence of the pH (see Table 3) is also in agreement with the proposed mechanism.

4. Discussion

From the results it follows that in the potential region investigated formaldehyde is oxidized to formate. We think that this oxidation proceeds

Fig. 6. Current–potential curve for a palladium electrode in 0.1 M HCHO + 0.15 M NaOH.

Table 1. Influence of electrode material on the oxidation of formaldehyde. Solution: 0.1 M HCHO, 0.15 M NaOH; pH = 13.0

Metal	Potential (mV vs SCE)	$\dfrac{\text{mol } H_2 \times F}{it}$	$\dfrac{\text{mol HCHO} \times F}{it}$	Reaction 1 (%)	Reaction 2 (%)
Cu	− 600	0.50	1.01	100	0
Au	− 500	0.34	0.83	68	34
Ag	− 400	0.34	0.84	68	32
Pt	− 400	0.00	0.50	0	100
Pd	− 400	0.00	0.49	0	102

Table 2. Influence of potential on the oxidation of formaldehyde. Solution: 0.1 M HCHO, 0.15 M NaOH; pH = 13.0

Metal	Potential (mV vs SCE)	$\dfrac{\text{mol } H_2 \times F}{it}$	$\dfrac{\text{mol HCHO} \times F}{it}$	Reaction 1 (%)	Reaction 2 (%)
Ag	− 400	0.34	0.84	68	32
	− 200	0.08	0.59	16	82
Au	− 700	0.38	0.89	76	22
	− 500	0.34	0.83	68	34
	− 200	0.00	0.50	0	100

Table 3. Influence of pH on the oxidation of formaldehyde. Metal: Au; potential: − 700 mV versus SCE

pH	$\dfrac{\text{mol } H_2 \times F}{it}$	$\dfrac{\text{mol HCHO} \times F}{it}$	Reaction 1 (%)	Reaction 2 (%)
12.5	0.42	0.92	84	16
13.0	0.38	0.89	76	22
13.5	0.19	0.69	38	62

via dehydrogenation of methylene glycol anion (CH_2OHO^-), yielding adsorbed hydrogen atoms, as discussed in the introduction. Hydrogen atoms have indeed been detected as intermediates in the anodic oxidation at a palladium membrane [8]. The dehydrogenation step explains the catalytic nature of electroless copper solutions.

The competition between oxidation and recombination of the atomic hydrogen explains the fact that a more anodic potential and a higher pH favour Reaction 2 over 1. The influence of the anode material can be explained by the kinetics of the two reactions:

$$\dot{H}_{(ad)} + OH^- \rightarrow H_2O + e \qquad (7)$$

$$\dot{H}_{(ad)} + \dot{H}_{(ad)} \rightarrow H_2\uparrow. \qquad (8)$$
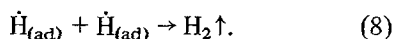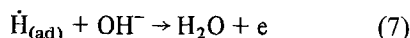
The rate of Reaction 7 is given by:

$$v_7 = \frac{i_0 \exp\left[\alpha F(\eta - \Psi)/RT\right]}{F}. \qquad (9)$$

So

$$v_7 = \frac{i_0 \exp\left(-\alpha F\Psi/RT\right) \exp\left(\alpha F\eta/RT\right)}{F}. \qquad (10)$$

At high electrolyte concentrations (> 0.1 M) a change in the overvoltage does not essentially change Ψ [9]. In this case the term involving Ψ can be incorporated into the i_0 term to give i^0, the apparent exchange current density. Equation 10 then becomes:

$$v_7 = \frac{i^0 \exp\left(\alpha F\eta/RT\right)}{F}. \qquad (11)$$

We list mean values of i^0, as given by Kita [10], in Table 4.

The rate of Reaction 8 is given by:

$$v_8 = k\theta^2 \exp\left(-\Delta E_d/RT\right). \qquad (12)$$

The rate constant k is of the order of 5×10^{15} mol cm^{-2} s^{-1} [11]. The activation energy of desorption

Table 4.

Metal	$L_s^\dagger$	$\Phi_M^\ddagger$	$-\Delta H$	$\log i^{0\,\ddagger}$
Cu	81	4.46	25.8	−6.7
Au	84	4.46	26.5	−5.4
Ag	68	4.44	24.0	−5.7
Pt	135	4.52	33.8	−3.4
Pd	91	4.49	27.0	−2.7

$\dagger$ From [11].
$\ddagger$ Mean values of [10].

Table 5. Calculated and observed values for the extent of Reaction 2

Metal	pH	Overpotential (V vs RHE)	Reaction 2 (% calculated)		Reaction 2 (% observed)
			$\theta = 0.01$	$\theta = 1.0$	
Cu	13.0	0.41	10	0	0
Au	13.0	0.31	41	0	22
	13.0	0.51	97	0	34
	13.0	0.81	100	55	100
	12.5	0.28	35	0	16
	13.5	0.34	64	0	62
Ag	13.0	0.61	71	0	32
	13.0	0.81	99	1	82
Pt	13.0	0.61	100	100	100
Pd	13.0	0.61	100	98	100

(ΔE_d) equals the heat of adsorption $(-\Delta H)$ plus the activation energy of adsorption (ΔE_a). The latter is small $(\approx 0.5\ \text{kcal mol}^{-1})$ [11] compared with the heat of adsorption $(\Delta E_d \approx -\Delta H)$. So Equation 12 becomes:

$$v_8 = k\theta^2 \exp(\Delta H/RT). \qquad (13)$$

Stevenson [12] has shown that $-\Delta H$ can be calculated from the heat of atomization (L_s) and the work function (Φ_M) of the metal:

$$-\Delta H = \tfrac{1}{6}L_s + 46.12(2.10 - 0.355\Phi_M)^2. \qquad (14)$$

In Table 4 the calculated values are given and they are in a fair agreement with observed values as given by Bond [11].

With the given mechanism, the percentage of Reaction 1 or 2 can be calculated using Equations 9–14. The percentage of Reaction 2 for instance must be $100v_7/(v_7 + v_8)$. Assuming that θ lies between 0.01 and 1.0 we can calculate limiting values for the extent of Reaction 2. The observed

values lie between the calculated values very well (see Table 5).

It has been shown that in electroless copper solutions Reaction 1 proceeds, and that the proposed mechanism can explain why this reaction proceeds. The mechanism also predicts that electroless solutions of platinum and palladium with formaldehyde as the reductant must operate without hydrogen evolution. We made up such solutions, and although they were unstable no gas evolution was observed at all.

5. Conclusions

The proposed mechanism explains the anodic behaviour of formaldehyde on different electrode surfaces, and the influence of pH and potential on it. As the anodic oxidation of formaldehyde and the cathodic reduction of metal ions are independent processes in electroless plating solutions, the proposed mechanism will also be

valid for electroless reactions. Electroless copper, platinum and palladium solutions behave as the mechanism predicts.

References

[1]   R. M. Lukes, *Plating* 51 (1964) 1066.
[2]   M. Paunovic, *ibid* 55 (1968) 1161.
[3]   R. P. Buck and L. R. Griffith, *J. Electrochem. Soc.* 109 (1962) 1005.
[4]   W. Vielstich, 'Brennstoffelemente', Verlag Chemie GmbH, Weinheim (1965) pp. 87–91.
[5]   H. Hoyer, *Z. Naturforschg.* 4a (1949) 335.
[6]   J. F. Walker, 'Formaldehyde', 3rd edn, Reinhold, New York (1964) pp. 489–490.
[7]   M. Pourbaix, 'Atlas d'Equilibres Electrochimiques', Gauthier-Villars, Paris (1963).
[8]   N. V. Korovin and B. N. Yanchuk, *Sov. Electrochem.* 7 (1971) 354.
[9]   P. Delahay, 'Double Layer and Electrode Kinetics', Interscience Publishers, New York, London, Sydney (1965) p. 158.
[10] H. Kita, *J. Electrochem. Soc.* 113 (1966) 1095.
[11] G. C. Bond, 'Catalysis by Metals', Academic Press, London and New York (1962) Chapters 5, 6, 8 and Appendix I.
[12] D. P. Stevenson, *J. Chem. Phys.* 23 (1955) 203.