

Short communication

Electro-catalytic Oxidation of Formaldehyde on Copper Electrode: a New Kinetics Model

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Abstract

Electro-catalytic oxidation of formaldehyde on copper electrode in 100 mM NaOH solution at different concentrations of formaldehyde was studied in the steady state polarization technique. The CV curve shows evidence for two processes occurring at the interface: one is associated with the formaldehyde electro-oxidation leading to formic acid formation on the surface and the other is assigned to the oxidation of formic acid that leads to CO₂ evolutions with low yield. Reaction orders for the faradic current on copper electrode have been determined as 0.21 for the higher and 0.76 for the lower concentration of formaldehyde. Reaction orders for CO₂ evolution during formaldehyde oxidation are 1.4 times higher in each case. Tafel slopes in the range of 140–160 mV are found. This signifies that the first reaction step involving the formation of adsorbed CO₂ is largely determining the overall reaction rate.

Keywords: Formaldehyde, electrocatalysis, steady state, alkaline media.

1. Introduction

Electrooxidation of organic and inorganic compounds have been widely studied on the surface of many different electrodes.^{1–3} In recent years multi-electron oxidation processes, C–C bond cleavage and the generation of lower molecular weight products from organic substrates on copper-based electrodes in alkaline solutions have received considerable attention because of their analytical applications.^{4,5} These include the use of copper metal^{6,7} and copper containing modified electrodes (CMEs), e.g. copper oxide/copper⁸ and copper oxide/carbon paste⁹ modified electrodes. Even though some reports have demonstrated that the anodic oxidation of alcohols^{10,11} is facilitated on these surfaces, no specific study on the use of copper electrodes for the electro-oxidation of formaldehyde has appeared in the literature. The catalytic action of copper has been reported to be the result of Cu(II)/Cu(I) or at very high positive potential, Cu(III)/Cu(II) redox systems.¹²

It is known for more than 70 years that the electrochemical oxidation of formaldehyde in alkaline solutions is accompanied by the evolution of molecular CO₂ on electrodes made of Cu, Ag or Cu.¹³ The faradic reaction

has been studied extensively in view of the influence of the electrode: recent studies of formaldehyde oxidation on polycrystalline Ib-group metal electrodes are reported by Burke et al.^{14–16}

In this paper, continuing our study of electro-oxidation of formaldehyde on copper electrode,¹⁷ we will demonstrate the influence of potential on the CO₂ evolution during the electrochemical oxidation of formaldehyde in alkaline solution and also report on the dependence of the CO₂ evolution on formaldehyde concentration monitored by Tafel plot.

2. Experimental Details

All chemicals used were analytical grade from Merck (Darmstadt, Germany) and were used without further purification. All solutions were prepared with doubly distilled water. Electrochemical measurements were carried out in a conventional three-electrode cell (from Copperis Co., Iran) powered by an electrochemical system comprising an AUTOLAB system with PGSTAT302 N board (Eco Chemie, Utrecht, The Netherlands). A saturated Ag/AgCl (from Metrohm) and platinum wire were ref-

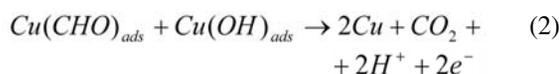
erence and counter electrodes, respectively. All potentials were measured with respect to the Ag, AgCl which was spatially as close to the working electrode as possible by means of a Luggin capillary. Cylindrical copper bars with the purity of 99.9% were fitted into Teflon exposing circular areas having diameters of 4 mm to prepare stationary and working electrodes, respectively. The copper surfaces were polished with sand paper and 0.05 μm alumina to a mirror finish and were subsequently rinsed with distilled water. All experiments were performed at ambient temperature 22 ± 3 °C.

3. Results and Discussion

3.1. Oxidation of formaldehyde on Cu

In the previous work we were studying electro-oxidation of formaldehyde in two concentration ranges (>10 mM and <7 mM). Our results indicated that the concentration is a good tool to investigate the oxidation of formaldehyde. In the previous work we indicated that the reaction between Cu(III) and formaldehyde is a low-yield process and the rate determining step for the electro-oxidation of formaldehyde on the Cu electrode. The redox Cu couple Cu(II)/Cu(III) has played a mediator role on heterogeneous catalytic oxidation of formaldehyde. In the redox system HCHO is firstly oxidized to HCOOH in an alkaline medium, and then HCOOH is oxidized to CO_2 .¹⁷ Subsequently, HCOOH is converted to CO_2 at higher potential, leading to the appearance of a new anodic peak assigned to CO_2 evolution.¹⁷

The following discussion will proceed along the mechanism as given by the reactions (1), (2) and (3):



Since these are experimentally well distinguishable, these reactions are certainly not elementary reactions, and further refinements have been suggested, e.g. formation of $\text{CH}(\text{OH})\text{O}^-_{\text{ad}}$ as a chemisorbed intermediate.

3.2. Reaction Order and Tafel Slopes

On Cu electrode the onset potential and the half-wave potential of formaldehyde oxidation are about 50 mV more positive than on copper electrodes, as can be seen from a comparison of Fig. 1A and B. The current efficiencies in this experiment are around 30% in both cases for 1 mM CH_2O . So, a slight influence of the electrode structure is visible, though none was observed by Adzic et al.¹⁸

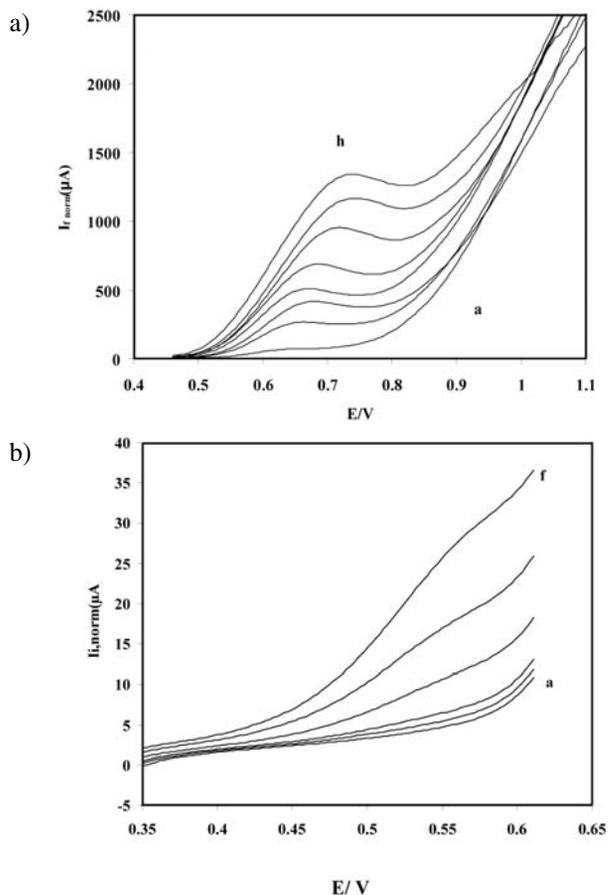


Figure 1: Oxidation of formaldehyde at different concentrations **a:** high concentrations (a: 10, b: 20, c: 25, d: 30, e: 35, f: 40 g: 45 and h: 50 mM) **b:** Low concentrations (a: 0.5, b: 0.7, c: 1, d: 3, e: 5, f: 7 mM) sweep rate 10 mV/s.

The concentration dependence of i_f (faradic current) and i_i (ion current) of formaldehyde oxidation on copper is shown in Fig. 2. The faradic current increases with higher concentrations and so do the ion currents of CO_2 evolution. The current efficiencies of CO_2 evolution from formaldehyde oxidation on copper show a significant dependence on the formaldehyde concentration, as is shown in Table 1. For low concentrations (0.5–7 mM), the current efficiency is about 25–40%, whereas for high concentrations (10–50 mM) up to 80% are observed.

3.3. Modeling the Reaction Kinetics of formaldehyde Oxidation

In order to facilitate the discussion, in the following we derive values for the Tafel slopes and reaction orders with plausible assumptions.

3.3.1. Low formaldehyde Concentrations

At low formaldehyde concentrations, CO_2 evolution from formaldehyde oxidation is comparatively small, with

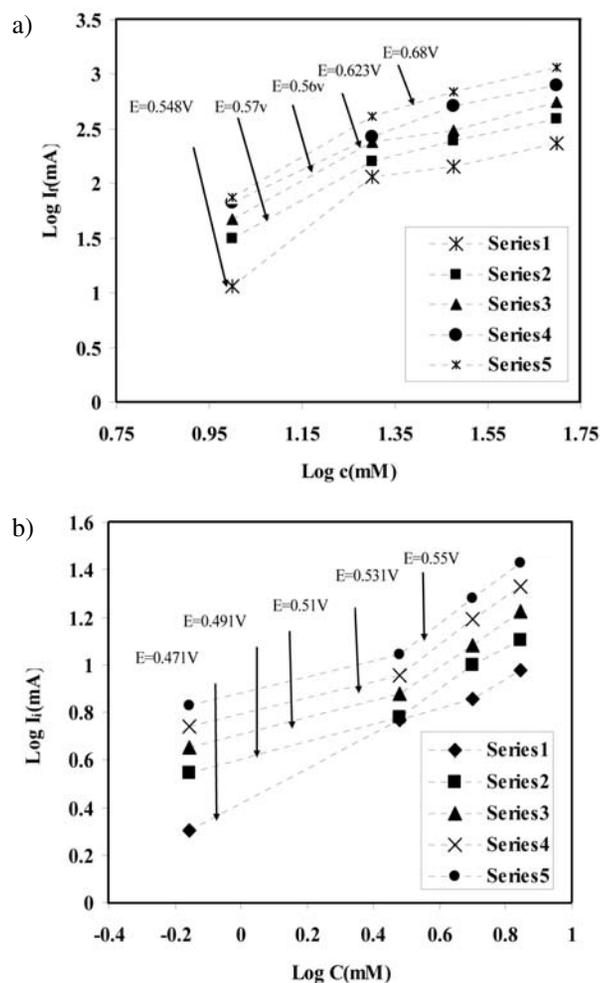


Figure 2: Reaction orders for formaldehyde oxidation. Currents taken at five different potentials (data from Figure 1) **a:** Reaction order for high concentrations (a: 10, b: 20, c: 30, d: 50). **b:** Reaction order for concentrations (a: 0.7, b: 3, c: 5, d: 7).

a current efficiency below 30%. Therefore, the overall reaction is mainly determined by reactions (1) and (3).¹⁷ Steady state coverage of adsorbed CO₂ is then established. Assuming Langmuir conditions, the corresponding reac-

tion rates are given by:

$$r_1 = k_1^0 e^{\alpha FE/RT} c(1-\theta) \quad (4)$$

where r , reaction rate; k^0 , standard heterogeneous rate constant; α , transfer coefficient; F , Faraday constant; E , potential; R , gas constant; T , absolute temperature; c , concentration; θ , fractional coverage.

$$r_3 = k_3^0 e^{\alpha FE/RT} \theta \quad (5)$$

Here, k_1^0 and k_3^0 are the rate constants at an arbitrarily chosen reference potential.

(a) We first assume that the reverse of reaction (1) is negligible, *i.e.* its rate is slow compared to that of reaction (3). Assuming, for simplicity, identical transfer coefficients $\alpha_1 = \alpha_3 = \alpha$ of 0.5 for both reactions, we obtain from $r_1 = r_3$:

$$\frac{\theta}{1-\theta} = \frac{k_1^0 c}{k_3^0} \quad (6)$$

and

$$\theta = \frac{k_1^0 c / k_3^0}{1 + (k_1^0 c / k_3^0)} \quad (7)$$

Since in both reactions (1) and (3) one electron is transferred, we obtain for the faradic current:

$$\frac{i_f}{F} = (r_1 + r_3) = (k_1^0 c(1-\theta) + k_3^0 \theta) e^{0.5FE/RT} \quad (8)$$

$$2r_1 = 2k_1^0 c(1-\theta) e^{0.5FE/RT} \quad (9)$$

From this we obtain a theoretical Tafel slope of 120 mV/dec. For the reaction order $\ln i_f / \ln c$, the concentration dependence of θ – Eq. (7) has to be taken into account.

For small coverages, *i.e.* Henry conditions, $(1-\theta)$ is roughly 1, and a reaction order of 1 is obtained. On the

Table 1: Reaction kinetics under different conditions

	$\square_{CO_{ad}}$	Tafel slope of i_f	Tafel slope of i_f (mV)	Reaction of i_f (mV)	Reaction of i_f (mV)
Low concentration (1) + (3) (1)eq ^b + (3)rds ^c	Small	120	∞^a	3.1	2
	High	120	∞	1...0	2 × RO(i_f)
	Small	40	30	1	2
	High	40–120	30... ∞	1...0	2 × RO(i_f)
Experimental value		130–150	≈200	0.76	1.07
High concentration (1) + (2) (1)eq + (2)rds	Small	40	120	1	1
	High	<120–... ∞	<120–... ∞	1...0	1...0
	Small	30	30	2	2
	High	30–... ∞	30–... ∞	0	0
Experimental value		130–150	≈200	0.21	0.32

^a $\rightarrow \infty$ very large values (no dependence on potential) ^b eq, reaction is at equilibrium ^c rds, rate determining step.

contrary, at higher coverages approaching 1 the reaction order will be zero.

(b) Alternatively, one could assume that reaction (1) is in equilibrium and that reaction (3) is the rate determining step. In this case, we obtain for Langmuir conditions

$$\frac{\theta}{1-\theta} = k_1^0 e^{F/RT} c = k_1 c \quad (10)$$

and

$$\theta = \frac{k_1 c}{1 + k_1 c} \quad (11)$$

when k_1^0 is the equilibrium constant at the arbitrary potential of zero.

The overall rate is given by

$$\frac{i_f}{F} = 2r_3 = 2k_3^0 e^{0.5FE/RT} \theta \quad (12)$$

For Henry conditions we obtain

$$\frac{i_f}{F} = 2k_3^0 K_1^{0.5FE/RT} c \quad (13)$$

and thus a Tafel slope of 40 mV/dec and a reaction order of 1 will result.

In the limit of high coverages, i.e. $K_1 c \geq 1$, we get

$$\frac{i_f}{F} = 2k_3^0 \quad (14)$$

and a Tafel slope of $b = 120$ mV/dec and a reaction order of 0.

As long as the current efficiency for CO_2 evolution from formaldehyde oxidation is small, the steady state coverage of adsorbed CO_2 is mainly governed by reactions (1) and (3). The ion current i_i for CO_2 is then given by:

$$\frac{i_i}{k^*} = r_2 = k_2 \theta^2 \quad (15)$$

where θ is given by Eq. (7) for case (a); for case (b) it is given by Eq. (11).

The reaction order of the ion current is twice that of the faradic current, and 2 for Henry conditions.

For the simple case of equal transfer coefficients for reactions (1) and (3), there is no potential dependence of reaction (2), but in practice, they will differ and the potential dependence will be given by $2(\alpha_1 - \alpha_3) \alpha_2^{\text{app}}$ at low coverages. Since the reaction intermediate CO_{ad} is rather unstable, i.e. its free enthalpy is rather large, the activated state of reaction (1) resembles the intermediate more than the product, and the transfer coefficient α_1 is probably larger than 0.5¹⁹; similarly, the activated state of reaction (3) is close to the product, i.e. the intermediate, the transfer coefficient α_3 will be smaller than 0.5, and the difference should be positive.

At higher potentials, diffusion limitation leads to a decrease of the apparent transfer coefficient, therefore, the steady state coverage of CO_{ad} should decrease as well as the rate of CO_2 formed in reaction (3).

Our experiments have always shown a dependence of the ion current on the potential. This might be due to this difference of the transfer coefficients. Note that a difference of only 0.2 (e.g. $\alpha_1 = 0.6$ and $\alpha_3 = 0.4$) will lead to an apparent transfer coefficient of $\alpha_2^{\text{app}} = 0.4$ and thus a Tafel slope of 150 mV/dec will result.

If the difference of α_1 and α_3 is negligible, at low potentials r_2 should be comparable to r_3 and the current efficiency should increase with decreasing potentials.

3.3.2. High Formaldehyde Concentrations

At higher formaldehyde concentrations, the CO_2 coverage will be larger and therefore r_2 and the current efficiency as well. Formaldehyde oxidation will be influenced by reaction (2) and, in the extreme case, be determined only by the reaction rates of Eqs. (1) and (2).

(a) Assuming Henry conditions, we obtain with $r_1 = r_2$

$$r_1 = \frac{i_f}{F} = k_1^0 e^{\alpha_1 FE/RT} c \quad (16)$$

$$r_2 = \frac{i_i}{k^*} = k_2 \theta_2 = k_1^0 e^{\alpha_1 FE/RT} c \quad (17)$$

This results in a Tafel slope $b = 120$ mV/dec (for $\alpha_1 = 0.5$) and a reaction order of 1 for both, r_1 and r_2 . In the case of Langmuir conditions, the reaction order will be smaller.

In any case, the reaction order of reaction (2) is twice that of reaction (3), since reaction (2) is proportional to u_2 whereas reaction (3) is proportional to θ . Therefore, when the reaction is mainly determined by Eqs. (1) and (3), the reaction order for i_i is nearly twice that of i_f . This ratio becomes smaller with higher contribution from reaction (2).

(b) Next, we shall again consider the case that reaction (1) is in equilibrium and reaction (2) is the rate determining step. The rate of CO_2 formation is then given by

$$r_2 = k_2 \theta^2 = k_2 \left(\frac{k_1 c}{1 + k_1 c} \right)^2 \quad (18)$$

In the limiting case of $\theta \rightarrow 0$:

$$r_2 = k_2 k_1^2 c^2 \quad (19)$$

The reaction order will be 2 for both CO_2 evolution and faradic current, the Tafel slope 30 mV/dec.

On the other hand, when $\theta \rightarrow 1$, $r_2 = k_2$ and the reaction order is 0. In this case, the Tafel slope will become very large.

3. 4. Comparison With the Experimental Results

Our experimental Tafel slopes between 130 and 150 mV/dec are in accordance with those of 110 mV/dec at higher concentrations reported by Enyo,²⁰ and point to Eq. (1) as being rate determining.

The reaction order for the faradic current of 0.76 at low concentrations is close to 1, as expected from Henry conditions. The value of 0.21 at high concentrations, which is in accordance with that of Enyo,²⁰ points to a saturation of the surface, as expected from the calculation assuming Langmuir conditions. It should be noted, however, that a full coverage of the copper surface with CO₂ is highly unlikely. Saturation therefore means saturation of active sites of the surface, and a formal ‘full coverage’ order refers to those active sites. Alternatively, a Frumkin isotherm including the coverage dependence of the adsorption enthalpy might be better suited for an exact description, but is too complicated for our simple treatment.

The reaction orders found for CO₂ evolution from formaldehyde oxidation are much larger although not twice that of the faradic current. This is because even at low concentrations the rate of reaction (2) is not really negligible, and the reaction order is between the limiting values in Table 2.

Table 2: Dependence of current efficiencies on formaldehyde concentration in 100 mM NaOH

Current efficiency	Concentration (mM)
25	0.5
40	1
60	5
68	10
80	50

Error: 10%

4. Conclusions

Steady state polarization studies of formaldehyde oxidation were investigated on Cu electrode. The steady state polarization data shows evidence for two processes occurring at the interface: one is associated with the formaldehyde electro-oxidation leading to formic acid formation on the surface and the other is assigned to the oxidation of formic acid that leading to CO₂ evolutions with low yield. In addition, the kinetics of the reaction was explained using steady state polarization technique.

5. Acknowledgements

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6. References

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Abstract

V tehniki polarizacije v ravnotežnem stanju smo preučevali elektrokatalitsko oksidacijo formaldehida na bakrovi elektrodi v 100 mM NaOH raztopini pri različnih koncentracijah formaldehida. Iz CV krivulje vidimo, da gre za dva procesa na fazni meji: eden je povezan z elektrooksidacijo formaldehida, pri kateri na površini nastaja mravljična kislina; drugega smo pripisali oksidaciji mravljične kisline, pri čemer se z nizkim izkoristkom razvija CO₂. Red reakcije za faradični tok na bakrovi elektrodi smo določili kot 0,21 za višjo in 0,76 za nižjo koncentracijo formaldehida. Red reakcije za razvijanje CO₂ med oksidacijo formaldehida je v obeh primerih 1,4-krat večji. Ugotovili smo Tafelov naklon v območju 140–160 mV. To pomeni, da prva reakcija, kjer nastaja adsorbirani CO₂, pretežno določa skupno reakcijsko hitrost.