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Studies of the Surface Oxide Layer of Platinum Electrode

By Kunio OHASHI, Kazuo SASAKI* and Shigeo NAGAURA
Faculty of Engineering, Osaka City University, Sumiyoshi-ku, Osaka

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The formation and reduction rates of the oxide layer of the platinum electrode were investigated by triangular-wave voltammetry and chronopotentiometry. A rate equation for the anodic process has been proposed in order to describe the fact that the electrode potential increases linearly with an increase in the surface concentration of oxygen. The cathodic reduction of surface oxide obeys the second-order rate law with respect to the amount of oxide covering the surface.

It has commonly been accepted that, in the electrolysis of an aqueous solution, an oxide layer is formed on the surface of the platinum electrode before any oxygen evolves. The chemical properties of the oxide and the kinetics of this electrode process have been studied by many workers.[1-16]

The present investigation has been carried out by means of chronopotentiometry and triangular wave voltammetry in order to understand the

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* Present address: Faculty of Engineering, Hiroshima University, Hiroshima.

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formation and reduction kinetics of the oxide, in a 1 N sulfuric acid solution. In a previous paper,14) it was pointed out that the formation rate of the oxide can be elucidated by one of the following assumptions, either (a) or (b): (a) the apparent rate constant, k, of the electron transfer step obeys the equation: $k=k_0\exp(-g\theta)$, where θ is the surface coverage of the oxide layer, and g, a constant, or (b) the reaction involves the rate-determining adsorption step of the discharged species, which obeys Elovich's rate equation.17) In this paper, the rate equation previously proposed for the anodic process14) has been re-examined for a wider range of current density. For the cathodic process, a rate equation has been proposed.

Experimental

All the experiments were conducted at 25°C in 1 N aqueous sulfuric acid solutions prepared by mixing distilled water (sepcific resistance$>1\times10^6$ ohm·cm.) and concentrated pure sulfuric acid which had been obtained from the Wako Pure Chemical Ind. Co. (Osaka). For all experiments, the solutions were deaerated by nitrogen gas.

Two kinds of platinum electrode were used. One was a wire electrode of 0.1 cm. in diameter and about 1 cm. long, while the other was the same in platinum, a cross-sectional area of which was exposed. Before each run of measurements, the electrode was cleaned by dipping it in a chromic acid mixture and washed with distilled water. Finally, it was subjected to alternate anodic and cathodic polarizations in the 1 N sulfuric acid solution. A saturated calomel electrode was used as the reference electrode.

Chronopotentiometry.—A series of experiments was carried out by using the chronopotentiometric technique, with a current reversal. An electronic pen-recorder (Model EPR-2TB, Toa Electronics Ltd.; pen speed, 0.5 sec. for the full span; input impedance, 1.8 MΩ) was used to record the potential-time curve at low current densities of about 100 μamp./cm² or less, whereas at higher current densities a cathode ray oscilloscope (Model 502-A, Matsushita Communication Ind. Co., Ltd.; input impedance, 1 MΩ) was employed. The electrolytic current passing through the cell was switched by means of a mercury switching device.

Triangular Wave Voltammetry.—An electronic potentiostat (Model N-EP-2, Nichia Keiki, Sapporo) was used in this experiment. The electrolytic current was recorded by means of the electronic pen-recorder. The maximum sweep rate was limited by the response of the pen-recorder; it was about 0.4 V./sec.

Results and Discussion

The Anodic Chronopotentiogram and the Potential-Current Curve.—A typical chronopotentiogram obtained at the current density of 32 μamp./cm² is shown in Fig. 1. The oxide layer was formed in the region C and reduced in C′. Since the potential-time curve was almost linear in C, the increment of surface oxide with the electrode potential, dq/dE, was determined in this region. The results are listed in Table I in terms of $n\boldsymbol{F}$(dq/dE)[*1].

The transition time in C, τ_a, was always greater than that in C′, τ_c. The ratio of τ_a to τ_c was, for instance, about 1 : 0.8 at the current density of 32 μamp./cm². The cause of this discrepancy is not certain, but this problem will be referred to again at the end of this article.

A typical current-potential curve obtained at the sweep rate of 0.2 V./sec. is illustrated in Fig. 2. The curve shows two peaks in the region A, where the ionization of chemisorbed hydrogen occurs.7)

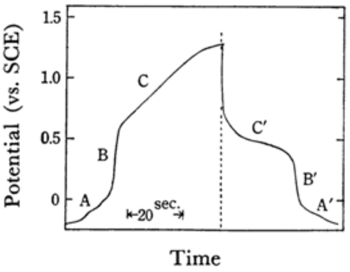

Fig. 1. Chronopotentiogram of platinum electrode in 1 N sulfuric acid solution.
Current density: 32 μamp./cm²

TABLE I. THE VALUES OF $n\boldsymbol{F}$(dq/dE) AT VARIOUS CURRENT DENSITIES

Current density mamp./cm²	$n\boldsymbol{F}$(dq/dE) μF/cm²
0.032	1.5×10^3
0.23	1.3
0.45	1.3
0.91	1.2
2.2	1.3
8.9	1.1
22	1.1

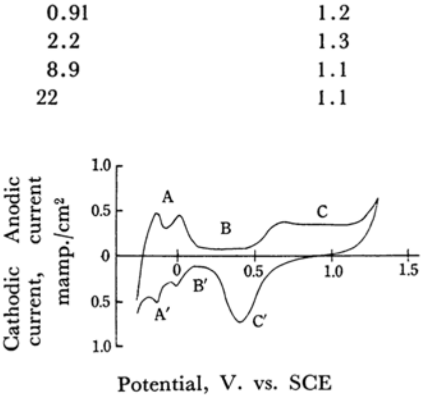

Fig. 2. Current-potential curve obtained by the potential sweep experiment with platinum electrode in 1 N sulfuric acid solution.
Sweep rate: 0.2 V./sec.

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[*1] The value of q is in mol./cm². The number of electrons, n, involved in the reaction concerned was assumed to be 2.

The regions denoted by C and C′ correspond to those denoted by the same notations in Fig. 1. The amount of charge (Q_H) required in A was graphically determined to be 4.0×10^2 μcoul./cm.^{2} while that (Q_O) required in C′ was 8.2×10^2 μcoul./cm^2. Thus, the ratio Q_H/Q_O was almost 1/2. This value coincides with that obtained by Will and Knorr,7) who suggested a one-to-one correspondence between hydrogen and oxygen atoms on the surface of the platinum electrode.

The Rate Equation for the Anodic Process.—The anodic formation rate of the surface oxide obeys the following equation, as was pointed out in a previous paper.14)

$$i_a = n\boldsymbol{F}k_a \exp\left(\beta n\boldsymbol{F}E/\boldsymbol{R}T-\lambda_a q\right) \tag{1}$$

where i_a is the anodic current density; k_a and λ_a, constants; q, the amount of oxygen deposited to form the oxide layer (in mol./cm^2), and where the other symbols have their usual significance. The electrode potential, E, referred to the normal hydrogen electrode (NHE), was used in Eq. 1 instead of the overpotential.

Since in the experimental conditions $\mathrm{d}i_a/\mathrm{d}t=0$ in the chronopotentiometry, Eq. 1 may be simplified as follows;

$$\mathrm{d}q/\mathrm{d}t = \frac{\beta n\boldsymbol{F}}{\lambda_a\boldsymbol{R}T}\cdot\frac{\mathrm{d}E}{\mathrm{d}t} \tag{2}$$

This equation indicates that $\mathrm{d}q/\mathrm{d}E$ should be constant, regardless of the current density. In fact, the experimentally-determined values of $n\boldsymbol{F}(\mathrm{d}q/\mathrm{d}E)$ were approximately constant even though the current densities employed were in a wide range, as may be seen in Table I. The slight decrease in $n\boldsymbol{F}(\mathrm{d}q/\mathrm{d}E)$ with an increase in the current density may be caused by another reason.*2

In Eq. 1, there is an additional exponential term describing the current dependence upon the amount of surface oxide deposited. Such a form of rate equation has often been found in the chemisorption process,18,19) in which the activation energy, ε, of chemisorption increases linearly with an increase in the surface coverage, θ, of adsorbed species, as is shown by:

$$\varepsilon = \varepsilon_0 + r\theta$$

Since the surface coverage, θ, can be given by q/q_s, in which q_s is the amount of oxygen at the full coverage, the following equation can be written in analogy to Eq. 1:

$$i_a = n\boldsymbol{F}k_a \exp\{(\beta n\boldsymbol{F}E - r\theta)/\boldsymbol{R}T\} \tag{3}$$

A rate equation of this form has also been applied to some electrode processes involving the chemisorption of reactant or intermediate product.20)

Although Eq. 1 is analogous to Eq. 3 in form, it is hard to say whether the process concerned is the chemisorption of oxygen or the surface oxide formation.

For this reason, the term "surface oxide" has been used in the present article without any specification of its physico-chemical nature.

The Rate Equation for the Cathodic Process.—Since no rate equation has been strictly confirmed so far, the following equation will be assumed for the time being;

$$i_c = n\boldsymbol{F}k_c q^m \exp\left(-\alpha n\boldsymbol{F}E/\boldsymbol{R}T+\lambda_c q\right) \tag{4}$$

where i_c is the cathodic current density, and k_c and λ_c are constants. In contrast to Eq. 1, the variable, q, which describes the surface concentration of oxygen is included in both the pre-exponential and the exponential terms in order to see the effect of this variable. In addition, the number of the reaction order, m, was introduced.

The time derivative of Eq. 4 is:

$$\frac{\mathrm{d}i_c}{\mathrm{d}t} = i_c\left\{\left(\frac{m}{q}+\lambda_c\right)\frac{\mathrm{d}q}{\mathrm{d}t} - \frac{\alpha n\boldsymbol{F}}{\boldsymbol{R}T}\cdot\frac{\mathrm{d}E}{\mathrm{d}t}\right\} \tag{5}$$

For the chronopotentiometric experiment, where the current is kept constant, Eq. 5 can be written as:

$$\frac{\mathrm{d}E}{\mathrm{d}t} = -\frac{\boldsymbol{R}T}{\alpha n\boldsymbol{F}}\left\{\frac{m}{\tau_c-t}+\frac{\lambda_c i_c}{n\boldsymbol{F}}\right\} \tag{6}$$

by using the relations of $n\boldsymbol{F}q=(\tau_c-t)\cdot i_c$ and $i_c=-n\boldsymbol{F}\,\mathrm{d}q/\mathrm{d}t$. The slope, $\mathrm{d}E/\mathrm{d}t$, at the midpoint of the cathodic transition wave is:

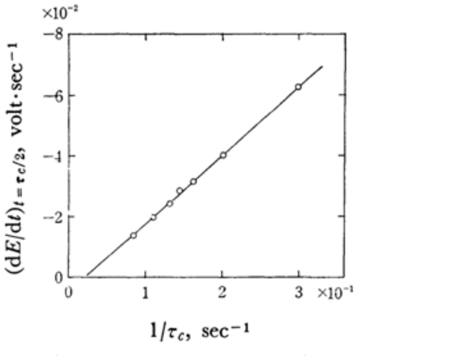

Fig. 3. Slope at the midpoint of the cathodic transition wave plotted against the reciprocal of the transition time (examination Eq. 7). The current density was kept at 1.8×10^2 μamp./cm^2 and the potential at which the anodic current as was reversed to cathodic one was changed.

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*2 This behavior may be related to the fact that τ_a was greater than τ_c. If a part of the oxide dissolves chemically from the electrode surface, the value of $\mathrm{d}q/\mathrm{d}E$ should decrease with an increase in the current density.

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$$\left(\frac{\mathrm{d}E}{\mathrm{d}t}\right)_{\tau_c/2} = -\frac{\boldsymbol{RT}}{\alpha n\boldsymbol{F}}\left\{\frac{2m}{\tau_c}+\frac{\lambda_c i_c}{n\boldsymbol{F}}\right\} \qquad (7)$$

Eq. 7 is examined in Fig. 3, where the slope of the potential-time curve determined at $\tau_c/2$ is plotted against the reciprocal of the transition time. The linearity is very good. It must be noted that the straight line crosses an ordinate near the point of origin. This shows a small value of λ_c (about 2% of λ_a). Therefore, the exponential contribution of q in Eq. 4 is negligible, and the term can safely be dropped. The slope of Fig. 3 should give $2m\boldsymbol{R}T/\alpha n\boldsymbol{F}$. Assuming $n=2$,[*3] α/m is found to be 0.13.

Since, in the potential sweep experiment, the sweep rate is constant and $\mathrm{d}i_c/\mathrm{d}t$ is zero at the point of the cathodic current peak, the following equation can be obtained from Eq. 5:

$$\frac{1}{i_{max}} = \frac{\boldsymbol{RT}}{\alpha(n\boldsymbol{F})^2 v}\left\{\frac{m}{q_{max}}+\lambda_c\right\} \qquad (8)$$

where v is the sweep rate in V./sec. ($v=-\mathrm{d}E/\mathrm{d}t$ for the cathodic potential sweep) and where the subscript *max* denotes the values of each quantity observed at the current peak.

It was observed that the peak current value decreases with the decrease in the amount of oxide layer deposited anodically. In Fig. 4, the reciprocal of the peak current, $1/i_{max}$, is plotted against $1/q_{max}$. The value of q_{max} is the amount of oxide yet remaining unreduced until the potential of current peak is reached. Each q_{max} value was obtained by the graphical integration of the current-potential curve. The straight line intersects the ordinate at the point of origin, thus confirming the negligible value of λ_c. From the slope, α/m was found to be 0.13.

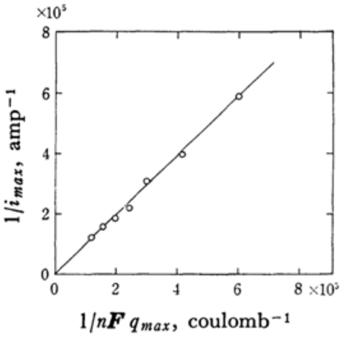

Fig. 4. The reciprocal of the peak current (i_{max}) is plotted against the reciprocal of the amount of oxide yet remained at the potential of current peak (examination of Eq. 8).
Sweep rate: 0.1 V./sec.
Electrode area: 7.8×10^{-3} cm²

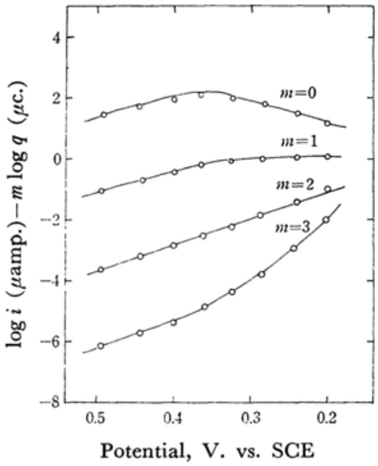

Fig. 5. The determination of the number of reaction order.
Sweep rate: 54 mV./sec.
Electrode area: 0.41 cm²

The reaction order, *m*, can be determined from the potential sweep experiment. The results obtained are shown in Fig. 5, where ($\log i_c - m\log q$) is plotted against the electrode potential. Four curves correspond to the arbitrary values of $m=$ 0, 1, 2 and 3 respectively. A straight line was obtained over the whole range of the cathodic reduction (C′ in Fig. 2) only when $m=2$. Accordingly, it can be concluded that the cathodic process is a second-order reaction with respect to the surface concentration. Therefore, the proper rate equation for the cathodic process becomes:

$$i_c = n\boldsymbol{F}k_c q^2 \exp(-\alpha n\boldsymbol{F}E/\boldsymbol{R}T) \qquad (9)$$

Another indication that the reaction order should be of the second-order was obtained by the following examination.

If the exponent of the amount of the oxide is unity instead of two, the following equation can be written as in Eq. 9, under the conditions of the potential sweep experiment, i. e., $\mathrm{d}E/\mathrm{d}t=-v=$ constant:

$$i_c = n\boldsymbol{F}k_{c,\mathrm{I}}\, q \exp\left\{-\frac{\alpha_{\mathrm{I}} n\boldsymbol{F}}{\boldsymbol{RT}}(E_{t=0}-vt)\right\} \qquad (10)$$

where the I subscript refers to the first-order reaction and where $E_{t=0}$ denotes the potential at which the direction of the potential sweep is reversed. By writing Eq. 10 as;

$$i_c = n\boldsymbol{F}k_{\mathrm{I}} q \exp\left(\frac{\alpha_{\mathrm{I}} n\boldsymbol{F}}{\boldsymbol{RT}}vt\right) \qquad (10')$$

and by integrating, using the relation $-n\boldsymbol{F}\mathrm{d}q/\mathrm{d}t = i_c$,

$$i_c = n\boldsymbol{F}k_{\mathrm{I}} q_0 \exp\left(\frac{k_{\mathrm{I}}}{P_{\mathrm{I}}}\right)\exp\left\{x-\frac{k_{\mathrm{I}}}{P_{\mathrm{I}}}\exp(x)\right\} \qquad (11)$$

where q_0 is the total amount of oxide to be reduced and where the other notations are:

$$P_{\mathrm{I}} = \frac{\alpha_{\mathrm{I}} n\boldsymbol{F}v}{\boldsymbol{RT}} \quad \text{and} \quad x = P_{\mathrm{I}}t$$

[*3] Cf. the reaction scheme proposed below.

Since $di_c/dt=0$ at the current peak,

$$P_{\mathrm{I}}t_{max} = \ln\frac{P_{\mathrm{I}}}{k_{\mathrm{I}}} \tag{12}$$

By introducing Eq. 12 into Eq. 11, one can obtain an expression of the peak current, i_{max}:

$$i_{max}=n\boldsymbol{F}q_0\,P_{\mathrm{I}}\exp\left\{\frac{k_{\mathrm{I}}}{P_{\mathrm{I}}}-1\right\} \tag{13}$$

Assuming $k_{\mathrm{I}}P_{\mathrm{I}}\ll 1$[*4]

$$i_{max}=\frac{\alpha_{\mathrm{I}}(n\boldsymbol{F})^2q_0v}{e\boldsymbol{RT}} \tag{14}$$

From the last equation, the transfer coefficient, α_{I}, can be determined by using the peak value of the current as determined experimentally. Once α_{I} is obtained, k_{I} is determined using Eq. 12.

If, however, the rate is second-order with respect to the surface concentration, Eq. 9 can be expressed in terms of time, i. e.,;

$$i_c = n\boldsymbol{F}k_{\mathrm{II}}q^2\exp\left(\frac{\alpha_{\mathrm{II}}n\boldsymbol{F}vt}{\boldsymbol{RT}}\right)$$

After similar treatment, as has been done with the equations from 11 to 14, the following relation are obtained:

$$i_c = n\boldsymbol{F}k_{\mathrm{II}}\left[\frac{P_{\mathrm{II}}q_0}{k_{\mathrm{II}}q_0\{\exp(x)-1\}+P_{\mathrm{II}}}\right]^2\exp(x) \tag{15}$$

$$P_{\mathrm{II}}t_{max} = \ln\left(\frac{P_{\mathrm{II}}}{k_{\mathrm{II}}q_0}\right) \tag*{(16)*4}$$

and by inserting Eq. 16 into Eq. 15:

$$i_{max} = \frac{\alpha_{\mathrm{II}}(n\boldsymbol{F})^2q_0v}{4\boldsymbol{RT}} \tag{17}$$

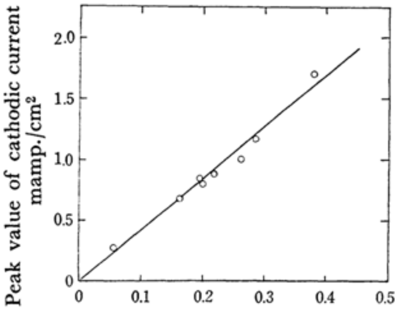

Fig. 6. Plot of cathodic peak current against sweep rate.

The α_{II} and k_{II} parameters can be determined by means of Eqs. 17 and 16. Equation 14 or 17 shows that the peak value of the current should be proportional to the sweep rate. This is confirmed in Fig. 6.

The values of kinetic parameters determined for the first- and second-order reactions are listed in Table II, where α_{I} and α_{II} were determined from Fig. 6 using either Eq. 14 or 17. The validity of the drived equations, 11 and 15, is examined in Fig. 7. It can easily be seen that the curve drived from Eq. 15 coincides with the experimental curve depicted for the sake of comparison. In the foregoing examination, the value of α/m was found to be 0.13, which is just half as much as the value of $\alpha_{\mathrm{II}}=0.26$ determined for the second-order reaction (see Table II). This may, again, give the value of m to be two. The apparent rate constant, k_c, in Eq. 9 was determined as 5×10^{13} cm²/mol. sec. at 0 V. (vs. NHE).

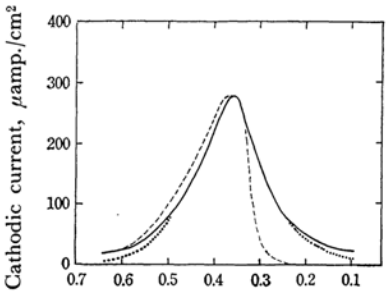

Fig. 7. Cathodic current-potential curves for the reduction of surface oxide;
—— Experimental curve sweep rate: 5.4×10^{-2} V./sec.)
---- Calculated from Eq. 11
······ Calculated from Eq. 15

Vetter[5] once suggested that hydrogen peroxide might be produced during the cathodic reduction of the surface oxide of the platinum electrode. According to him, the number of electrons, n, involved in the anodic oxide formation must be two per atom of oxygen deposited, whereas n is unity if the cathodic reduction product is hydrogen peroxide. Hence, in this case the quantity of charge observed in the anodic oxide formation should be twice as much as that in the cathodic reduction. Although Vetter's assumption was not based upon

TABLE II. NUMERICAL VALUES OF PARAMETERS REQUIRED IN THE CALCULATION OF EQS. 11 AND 15
Apparent rate constants, k_{I} and k_{II}, refer to 1.30 V. (SCE), at which the direction of the potential sweep was reversed. The value of q_0 was found as 5.1×10^{-9} mol./cm².

	m	α	k_{I} or k_{II}		v
1st order	1	0.18	1.9×10^{-6}	(sec⁻¹)	0.054 (V./sec.)
2nd order	2	0.26	1.3	(cm²sec⁻¹mol⁻¹)	

[*4] The validity of this assumption was confirmed by the derived result, $(k_{\mathrm{I}}/P_{\mathrm{I}})=1.4\times10^{-7}/v$. A similar assumption made in deriving Eq. 16 was confirmed by the result, $(k_{\mathrm{II}}q_{\mathrm{I}}/P_{\mathrm{II}})=3.2\times10^{-10}/v$.

any direct proof of the formation of hydrogen peroxide, its formation has recently been confirmed by Peters and Mitchell,[21] and also by Bianchi and Mussini.[22] They observed that hydrogen peroxide is produced with a high current efficiency during the cathodic reduction of the dissolved oxygen on the platinum electrode. Although Liang and Juliard[23] reported that no hydrogen peroxide was detected in the same system, this discordant finding, in our opinion, might have arisen from the different surface states of the electrode used.

Since, at the platinum electrode, the cathodic reduction of the dissolved oxygen and the surface oxide take place voltammetrically in one step,[24,25] the mechanism of the cathodic reduction of these two species will be quite similar. Therefore, it is probable that hydrogen peroxide will be produced intermediately during the reduction of surface oxide. If this is the case, the second-order rate law observed by the authors seems to favor the elucidation of the hydrogen peroxide formation. This problem, together with the reactions of dissolved oxygen and hydrogen peroxide, will be discussed elsewhere.[25]

The discrepancy found between τ_a and τ_c can be attributed partly to the intermediate formation of hydrogen peroxide. The reaction scheme may be written, for instance,[*5] as:

$$\rightarrow 2\mathrm{PtO} + 2\mathrm{H}^+ + 2e \rightarrow 2\mathrm{Pt} + \mathrm{H_2O_2} \qquad \text{(I)}$$

$$\mathrm{Pt} + \mathrm{H_2O_2} \rightarrow \mathrm{PtO} + \mathrm{H_2O} \qquad \text{(II)}$$

If a part of the hydrogen peroxide formed by the bimolecular step (step I) diffuses away from the platinum surface without oxidative decomposition (step II), τ_c must be less than τ_a.

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[23] C. C. Liang and A. L. Juliard, *J. Electroanal. Chem.*, **9**, 390 (1956).

[24] J. J. Lingane, ibid., **5**, 441 (1963).

[25] K. Sasaki, K. Ohashi, M. Ioi and S. Nagaura, to be published in *J. Chem. Soc. Japan*.

[*5] The reactions scheme presented here is the simplest one among the several possible reaction paths.