Potential Step Reduction of the Surface Oxide of Platinum Electrodes

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In previous papers,[1,2] we reported that the cathodic reduction of the surface oxide of a platinum electrode obeys a second order rate law with respect to the fractional coverage of the oxide. An empirical rate equation we proposed for the reaction concerned was

$$i = n\boldsymbol{F}kq^2 \exp(\alpha n\boldsymbol{F}E/\boldsymbol{R}T) \qquad (1)$$

where q is the quantity of the surface oxide to be reduced expressed in g atoms per square centimeter. Two constants in this equation were determined as $k=1.3\ \text{cm}^2\ \text{mol}^{-1}\ \text{sec}^{-1}$ at 1.3 V SCE and $\alpha=0.26$.

The discussions therein made were mainly based on the results of cyclic voltammetry and chronopotentiometry. In this paper, we shall describe the results obtained by a potential step method.

Basic Concept. Generally, when an electrode reaction accompanied by a simultaneous detachement of an ad-layer at the electrode surface obeys one of the following rate equations

$$i = n\boldsymbol{F}k \exp(\alpha n\boldsymbol{F}E/\boldsymbol{R}T + \gamma q) \qquad (2)$$

$$i = n\boldsymbol{F}kq \exp(\alpha n\boldsymbol{F}E/\boldsymbol{R}T) \qquad (3)$$

or

$$i = n\boldsymbol{F}kq^2 \exp(\alpha n\boldsymbol{F}E/\boldsymbol{R}T) \qquad (1)$$

then the current transient at a constant electrode potential should obey one of the following equations, respectively.

$$1/i = \gamma t/nF + 1/i_0 \qquad (2a)$$

$$i = i_0 \exp(-At); \qquad i_0 = nFAq_0 \qquad (3a)$$

or

$$1/q = At + 1/q_0 \qquad (1a)$$

where A stands for $k \exp(\alpha n\boldsymbol{F}E/\boldsymbol{R}T)$ and q_0 is the total quantity of the surface oxide to be reduced (g atom/cm^2).

These equations will be examined in the following part of this paper.

Results. In order to confirm the validity of Eq. (1) and hence Eq. (1a), we carried out a series of experiments in 1 N sulfuric acid solutions. A potentiostaic rectangular pulse (repeating frequency: 1 cps, duty ratio: 1) was applied to the working electrode by means of NS-2 model pulse generator of Nichia-Keiki Co. The current transient was photographed using a 50 MC synchroscope (Model 502-A, Matsushita Communication Ind. Co.). Anodic pulse level was kept at 1.2 V against a saturated calomel reference electrode and the cathodic potential was varied between 0.2 to 0.4 V. A cross section of a 1 mm platinum wire sealed in a soft glass tube was used as the working electrode.

In Fig. 1, a typical current transient observed when the potential was stepped down from 1.2 to 0.4 V is shown. It was confirmed that Eq. (1a) best fitted for this curve. This is shown in

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[1] K. Ohashi, K. Sasaki and S. Nagaura, This Bulletin, **39**, 2066 (1966).

[2] K. Sasaki and K. Ohashi, *Electrochim. Acta*, **12**, 366 (1967).

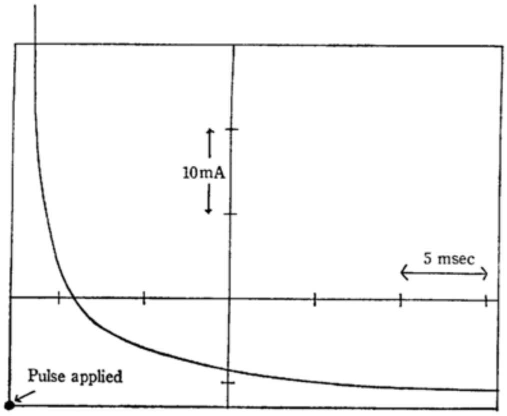

Fig. 1. The transient current for the reduction of surface oxide electrode potential stepped down from 1.2 V to 0.4 V SCE.

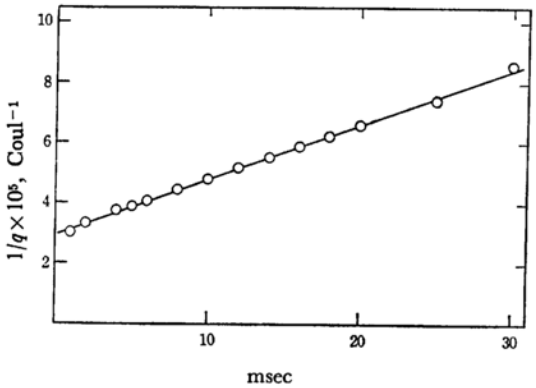

Fig. 2. Examination of Eq. (1a).

Fig. 2 where the reciprocal of the amount of the surface oxide to be reduced is plotted against time. According to Eq. (1a), the slope of the curve must be $k\exp(\alpha n\boldsymbol{F}E/\boldsymbol{R}T)$ so that the logarithmic expression of the slope is

$$\ln s = \ln k + \alpha n\boldsymbol{F}E/\boldsymbol{R}T \qquad (4)$$

Accordingly, the transfer coefficient α should be determined from the determination of the slope at various cathodic potentials. The rate constant k will also be determined from the intersect of the $\ln s$ *vs.* E curve. This is shown in Fig. 3. The two constants determined from Fig. 3 were $\alpha=0.25_5$ and $k=2.8\,\text{cm}^2/\text{mol sec}$ at 1.3 V SCE, respectively. These are in good agreement with the values mentioned in the first of this paper.

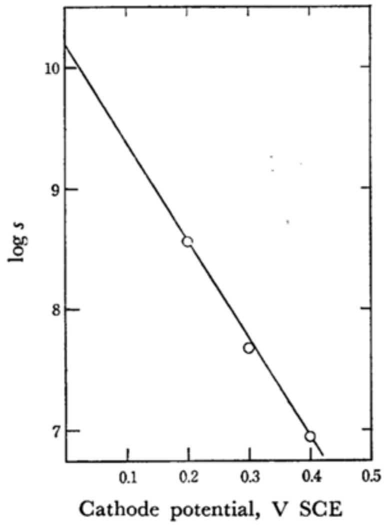

Fig. 3. Graphic representation of Eq. (4).

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