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An Alternative Display of Potentiostatic Measurements. I. Instrumental Design and Verification of Modified Pulse Polarograph

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A modified instrument for the potentiostatic method (modified pulse polarograph) has been developed, which uses techniques of the time-to-voltage converter. The modified pulse mode and the modified differential pulse mode have been tested as tools for quantitative analysis. The determination of kinetic parameters of electrode reactions is presented, together with the characteristics of the modified pulse polarograph.

Modern polarographic methods, especially normal and differential pulse techniques, have been widely used in trace analysis.[1–23] An advantage of using commercial instruments of pulse polarography is in the high signal-to-noise ratio (S/N): the averaging of current signal is synchronized to the a.c. power line. Although signal averagings of this type produce high S/N ratio, available sampling times are restricted, and current-potential curves are slightly distorted.[7]

Recently, the authors have developed a new polarographic technique. The method records the time instead of current or potential and has been successfully introduced in constant-current electrolysis.[24–26] The measurement and the recording of the time have been carried out by the time-to-voltage converter. Introduction of the time-to-voltage converter produces high S/N ratios without sacrifice of the frequency response of the data sampling circuit.

Previously, the authors reported a modified potentiostatic method. This method is based on the measurement of time required to reach a constant sampling current in the potentiostatic method.[27,28] The fundamental concept and the determination of kinetic parameters were reported. However, the complete system has not been developed. The measurement of time was carried out descretely, using a comparator and a digital counter.[27]

In this report, instrumental designs of a modified pulse polarograph, characteristics of modified pulse polarography (MPP), and some applications in the electrode kinetics are presented. The use of the time-to-voltage converter is indispensable to realize the full advantages of the modified potentiostatic method. The development of the modified pulse polarograph simplified the measurement of the instantaneous time-potential-current relation without limitations of sampling time and without distortion of data, attempts at the modified differential pulse polarography (MDPP) are also reported.

Experimental

A three-electrode cell equipped with a saturated calomel reference electrode (SCE: Yanagimoto MR-P$_2$-05-1), a platinum wire electrode (counter electrode) and a dropping mercury electrode (DME: Yanagimoto Type-C) was used; synchronization of DME was done by a electro-mechanical knocker (Fuso Solenoid).

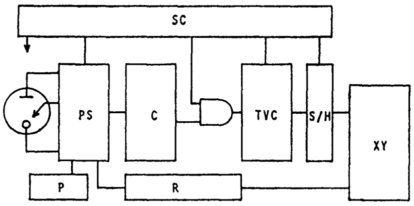

Fig. 1. The block diagram of the modified pulse polarograph. (PS: potentiostat, C: comparator, TVC: time-to-voltage converter, S/H: sample and hold circuit, P: potentiometer, R: ramp generator, SC: sequence controller, XY: x-y recorder).

$[Co(NH_3)_6]Cl_3$ was prepared according to the literature[29] and identified by elemental analysis. The solution was deaerated with pure nitrogen and kept under nitrogen atmosphere. The temperature of the solution was kept constant at 25.0±0.1 °C. All solutions were prepared in twice distilled water; all chemicals were analytical grade.

Apparatus

A new modified pulse polarograph was designed for this study. The polarograms were recorded with this instrument using a Rikadenshi RW-11 x-y recorder. The block diagram and the electronic circuit of the modified pulse polarograph are shown in Figs. 1 and 2. The modified pulse polarograph is constructed with a three-electrode-type potentiostat (PS), comparator (C), time-to-voltage converter (TVC), sample-and-hold

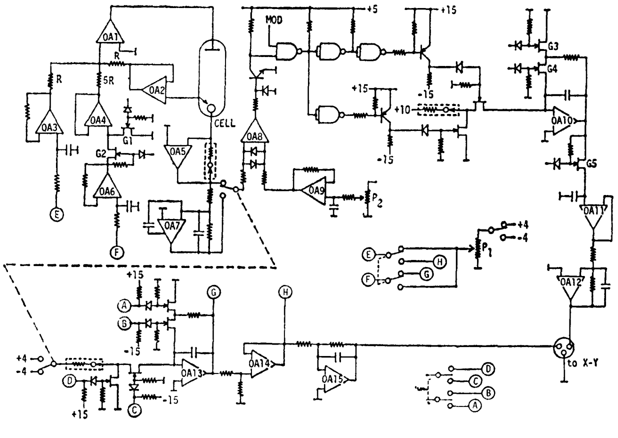

Fig. 2. The electronic circuit of the modified pulse polarograph.

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circuit (S/H), and ramp generator (R). The procedure for measurements is controlled by a sequence controller (SC). When a mercury drop begins to grow, it is held at the initial potential E_i set by the potentiometer P_1 (In differential mode, the drop is held at the potential set by the ramp generater.). After the lapse of a preset time period t_w(0.5—11 s), the sequence controller turns the gate G1 off and the gate G2 on. The potentiostat is then connected to the ramp generator, which provides the step voltage ΔE (In the differential mode the step voltage ΔE is provided by the potentiometer P_1.). Simultaneously, the time-to-voltage converter is turned to the ready state by gates G-3 and G-4.

The current signal resulting from potential relaxation (E_i to $E_i+\Delta E$) is fed to a high-speed comparator OA-8. The slice level of the comparator (*i. e.* the constant sampling current, i_s) is set by the potentiometer P_2. The output of the comparater is connected to the gates of the time-to-voltage converter. After 1 s of t_w, the gates G-1 and G-2 are turned to the former state and the DME knocker is started. Simultaneously, gate G-5 stores the output of the TVC in the sample-and-hold circuit (OA-11). Then, gates G-3 and G-4 reset the TVC. The measurement cycle is completed and the sequence is repeated. The values of t are displayed on an x-y recorder as a function of E. The time chart and the relationships between control signals and FET gates are shown in Fig. 3.

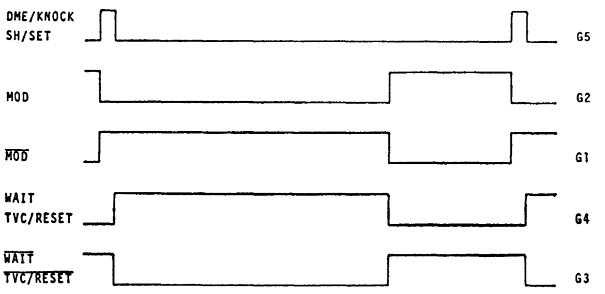

Fig. 3. The time chart of the control sequences and their connection with FET-gates.

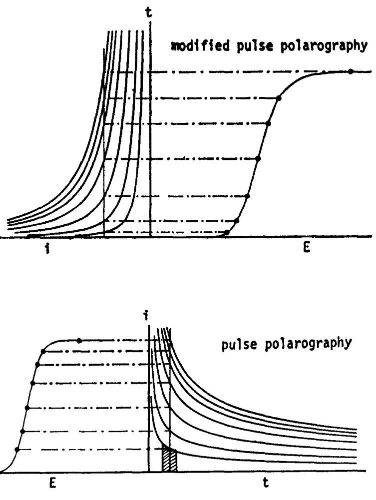

Fig. 4. The relations of current-time curves and the modified pulse and/or the normal pulse polarogram.

The principle of MPP is schematically shown in Fig. 4 together with that of pulse polarography. In MPP, the time required to reach a constant sampling current i_s in potentiostatic measurements is recorded versus the potential. Therefore, the modified pulse polarogram gives the instantaneous time-potential-current relation. On the other hand, in the pulse polarography, the average current in the sampling period is recorded *versus* the potential.

Results and Discussion

System Evaluation. To evaluate the function of the system, modified pulse polarograms of a reversible and an irreversible electrode reactions were measured. Potential-time relations of reversible and irreversible electrode processes were also tested for the case of cathodic reduction, when only the oxidant is present in the solution.

Reversible Case: The potential-time relationships of modified pulse mode are given by

$$E = E_o - \frac{RT}{(\alpha_a+\alpha_c)nF}\ln\sqrt{\frac{D_O}{D_R}} + \frac{RT}{(\alpha_a+\alpha_c)}\ln\frac{\sqrt{t_{diff}}-\sqrt{t}}{\sqrt{t}}, \tag{1}$$

for a reversible electrode process.[27,28] Here E is the electrode potential; E_o, the formal potential; α the transfer coefficient; D, the diffusion coefficient; t, the time; t_{diff}, the time at potentials controlled by diffusion; and R, T and F have their usual meanings. The subscripts a and c indicate the anodic and the cathodic processes, and O and R the oxidant and the reductant.

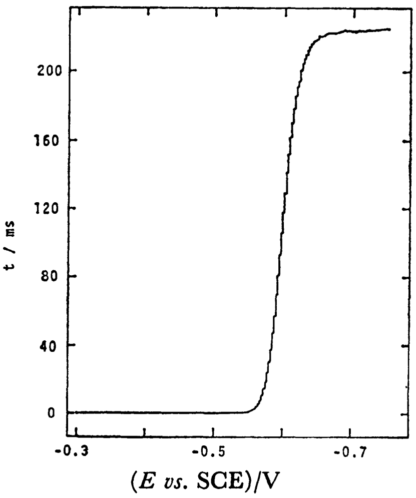

Fig. 5. An example of modified pulse polarogram. (1 mM $Cd(NO_3)_2$†† in 1 M $NaNO_3$ containing 2 μM LEO, i_s = 10 μA, t_w = 2 s, m = 1.063 mg s^{-1}).

The modified pulse polarogram of cadmium ion is shown in Fig. 5 as an example of a reversible process. Equation 1 shows the linear relation between E and $\ln\{(\sqrt{t_{diff}}-\sqrt{t})/\sqrt{t}\}$. Such plots of the Cd(II)/Cd(Hg) system are shown in Fig. 6. The data points lie very close to the least-square line drawn through them. Furthermore, the slope of the least-square line is almost

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†† 1 M = 1 mol dm^{-3}.

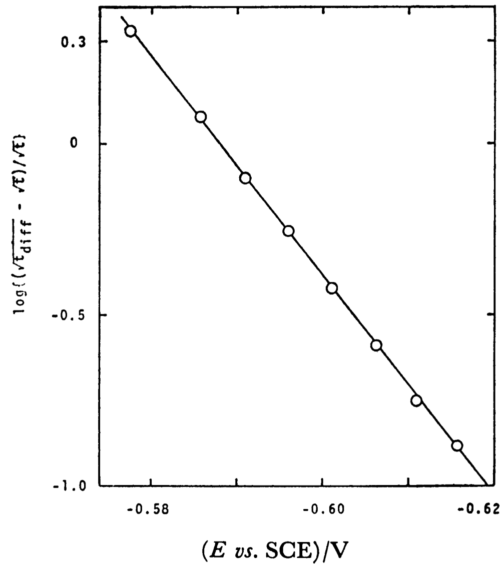


Fig. 6. The plots of $\log\{(\sqrt{t_{\rm diff}}-\sqrt{t})/\sqrt{t}\}$ *vs.* E. (1 mM $Cd(NO_3)_2$ in 1 M $NaNO_3$ containing 2 μM LEO $i_s=30$ μA, $t_w=4$ s, $m=0.6656$ mg s^{-1}).

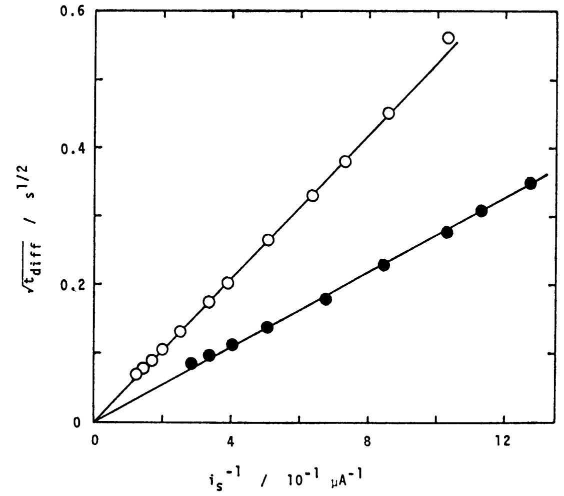


Fig. 8. The plots of $\sqrt{t_{\rm diff}}$ *vs.* reciprocal of i_d. (○: 0.8 mM $Cd(NO_3)_2$ in 1 M $NaNO_3$, $t_w=4$ s, $m=0.6656$ mg s^{-1}; ●: 1 mM $[Co(NH_3)_6]Cl_3$ in 0.9 M $NaNO_3$ containing 0.1 M acetate buffer (pH 5.0) and 2 μM LEO, $t_w=3$ s, $m=1.05$ mg s^{-1}).

equal to RT/nF.

The time at potentials controlled by diffusion, $t_{\rm diff}$, is represented as

$$\sqrt{t_{\rm diff}}=\frac{nFA\sqrt{D_{\rm O}}c_{\rm O}^{\circ}}{\sqrt{\pi}\,i_{\rm d}} \tag{2}$$

for both the reversible and the irreversible processes, where A is the electrode area at t_w; $c_{\rm O}^{\circ}$, the concentration of the bulk of the solution and i_d, the diffusion current.

Equation 2 shows the linear relation between $\sqrt{t_{\rm diff}}$ and $c_{\rm O}^{\circ}$ or $1/i_d$. In this report, the time data are corrected for the effect of the expansion of DME during measurements. The correcting factor of the time data is $1/(1-t/t_w)^{2/3}$ which is the reciprocal of relative surface area at t_w+t. The linear relations between $\sqrt{t_{\rm diff}}$ and $c_{\rm O}^{\circ}$ or reciprocal of i_d were tested for the reduction of Cd(II) and $[Co(NH_3)_6]^{3+}$. The plots of $\sqrt{t_{\rm diff}}$ *versus* $c_{\rm O}^{\circ}$ and $\sqrt{t_{\rm diff}}$ *versus* $1/i_d$ are shown in Figs. 7 and 8, respectively. Those plots gave excellent linear relations up to 300 ms of the $t_{\rm diff}$ values, indicating that the instrument works satisfactorily.

Irreversible Case: The potential time relations for an irreversible electrode process are given by[27,28]

$$E=E_{\rm o}+\frac{RT}{2\alpha_{\rm c}nF}\ln\frac{16t_{\rm diff}(k_{\rm s})^2}{3D_{\rm O}}-\frac{RT}{2\alpha_{\rm c}nF}\ln\frac{1.75+t/t_{\rm diff}}{1-\sqrt{t}/\sqrt{t_{\rm diff}}}, \tag{3}$$

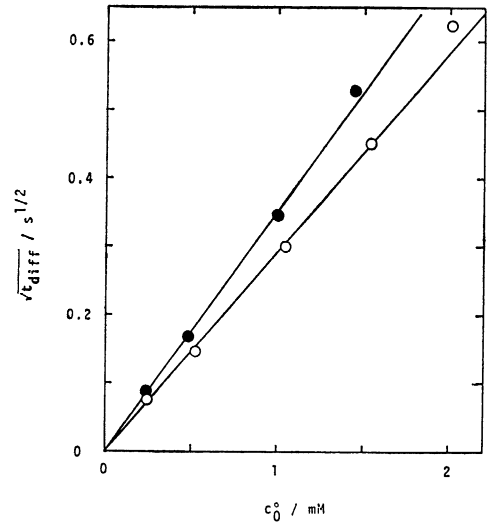


Fig. 7. The plots of $\sqrt{t_{\rm diff}}$ *vs.* the bulk concentration. (●: $[Co(NH_3)_6]Cl_3$ in 0.9 M $NaNO_3$ containing 0.1 M acetate buffer (pH 5.0) and 2 μM LEO, $i_s=8$ μA, $t_w=3$ s, $m=1.05$ mg s^{-1}; ○: $Cd(NO_3)_2$ in 1 M $NaNO_3$ containing 2 μM LEO, $i_s=15$ μA, $t_w=2$ s, $m=0.6656$ mg s^{-1}).

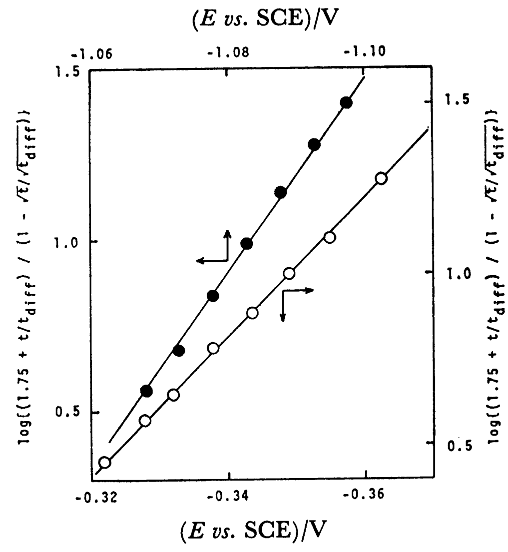
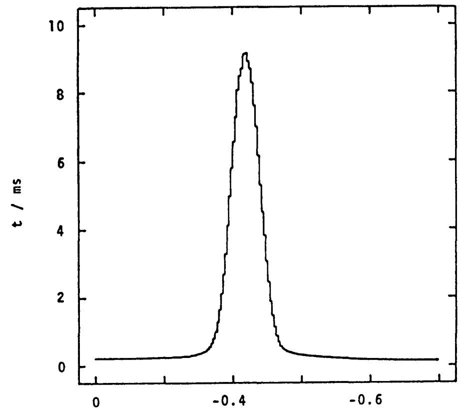


Fig. 9. The plots of $\log\{(1.75+t/t_{\rm diff})/(1-\sqrt{t}/\sqrt{t_{\rm diff}})\}$ *vs.* E. (○: 1 mM $[Co(NH_3)_6]Cl_3$ in 0.9 M $NaNO_3$ containing 0.1 M acetate buffer (pH 5.0) and 2 μM LEO, $i_s=8$ μA; ●: 1 mM $NiCl_2$ in 0.1 M KCl containing 2 μM LEO, $i_s=18$ μA; $t_w=3$ s, $m=1.05$ mg s^{-1}).

where, k_s is the formal standard rate constant. The linear relation of E and $\ln\{(1.75+t/t_{\mathrm{diff}})/(1-\sqrt{t}/\sqrt{t_{\mathrm{diff}}})\}$ has been tested for the reduction waves of $[Co(NH_3)_6]^{3+}$ and Ni(II). These plots, shown in Fig. 9, gave good linear relations.

The above mentioned results of the system evaluation for reversible and irreversible cases were quite satisfactory. The logarithmic plots shown in Fig. 6 can be utilized for the diagnostic criteria of reversibility. The working curve, $\sqrt{t_{\mathrm{diff}}}$ *versus* c_O°, will give a fundamental concept of quantitative analysis.



(*E vs.* SCE)/V

Fig. 10. A display of modified differential pulse polarogram of 600 μM $TlNO_3$ in 1 M KNO_3. (i_s=3.0 μA, t_w=6 s, m=0.539 mg s^{-1}, ΔE=100 mV).

Modified Differential Pulse Polarography. A new method, modified differential pulse polarography, has been successfully introduced. The measurement is carried out by measuring the time required to reach a constant sampling current; the principle of electrolytic method of MDPP is similar to that of the differential pulse polarography. Characteristics of modified differential pulse polarogram were studied using Tl(I)/Tl(Hg) and Cd(II)/Cd(Hg) systems. Figure 10 shows a modified differential pulse polarogram of 600 μM $TlNO_3$ in 1 M KNO_3. The slope of the log-log plots of peak-height and bulk concentration was 2.0. The empirical relation between the peak height t_p of modified differential pulse polarogram and the bulk concentration can be written as

$$\sqrt{t_p} = p\cdot c_O^\circ. \tag{4}$$

Here, p is the proportionality constant. The plots of

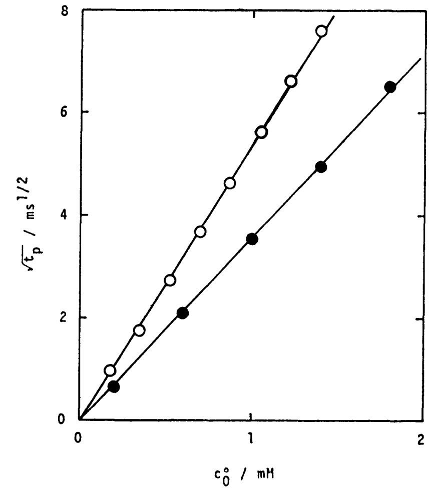


Fig. 11. The plots of $\sqrt{t_p}$ *vs.* the bulk concentration. (●: $TlNO_3$ in 1 M $NaNO_3$, t_w=6 s, ΔE=100 mV, ○: $Cd(NO_3)_2$ in 1 M $NaNO_3$, t_w=6 s, ΔE=100 mV, m=0.539 mg s^{-1}).

$\sqrt{t_p}$ *vs.* c_O° of Tl(I)/Tl(Hg) and Cd(II)/Cd(Hg) systems are shown in Fig. 11. The data points gave a good straight line which through the origin. These plots can be utilized as the working curve of quantitative analysis.

The theoretical treatment of modified differential pulse polarography will be discussed elsewhere.

Application to the Determination of Kinetic Parameters. Kinetic parameters of electrode reactions can be determined from the following relations:[27,28)]

$$\frac{\sqrt{t}}{\sqrt{t_{\mathrm{diff}}}}\,\frac{1+\sqrt{D_O/D_R}\,\gamma}{1-(c_R^\circ/c_O^\circ)\gamma} = \sqrt{\pi}\,\lambda\sqrt{t}\exp(\lambda^2 t)\mathrm{erfc}(\lambda\sqrt{t}), \tag{5}$$

$$\gamma = \frac{k_a}{k_c} = \exp[(\alpha_a+\alpha_c)(E-E_o)nF/RT], \tag{6}$$

$$k_c = \frac{\sqrt{D_O}}{1+\sqrt{D_O/D_R}\,\gamma}. \tag{8}$$

Introducing the values of $\alpha_c+\alpha_a$ and E_o from the references,[27,28)] the value of γ in Eq. 6 can be calculated. Since the value of $\sqrt{t/t_{\mathrm{diff}}}$ is measurable, the left hand side of Eq. 5 is calculated from experimental data. Then, the parameter λ can be obtained at various potentials. In these calculations, the function $\phi(\lambda\sqrt{t})$ and the inverse function of $\phi(\lambda\sqrt{t})$ can be calculated by a computer.[30,31)]

The rate constants k_a and k_c are calculated from

TABLE 1. KINETIC PARAMETERS OF ELECTRODE REACTIONS OBTAINED AT 25.0 °C

(E_0 *vs.* SCE)/V	α_c	α_a	k_s/cm s^{-1}	Ref.
$Zn(NO_3)_2$ in 0.3 M $NaNO_3$ +1 mM $HClO_4$+2 μ M LEO				
−0.999	0.31	0.63	8.4×10^{-3}	This work
−0.998	0.32	0.62	8.7×10^{-3}	27, 28
$Cu(NO_3)_2$ in 1 M $NaNO_3$+5 mM HNO_3+0.001% PAA				
0.022	0.23	0.73	2.2×10^{-2}	This work
0.022	0.24	0.73	2.9×10^{-2}	27, 28
$[Co(NH_3)_6]Cl_3$ in 0.9 M $NaNO_3$+0.1 M acetate buffer				
−0.250	0.58	0.42	1.5×10^{-3}	This work
−0.249	0.71	0.29	1.9×10^{-3}	27, 28

Eqs. 6 and 7 using the value of λ obtained above. The kinetic parameters are determined from the relations

$$k_a = k_s \exp\left\{\frac{\alpha_a nF}{RT}(E-E_o)\right\}, \tag{8}$$

$$k_c = k_s \exp\left\{\frac{-\alpha_c nF}{RT}(E-E_o)\right\}, \tag{9}$$

using a least square method.[27,28,30,31] Kinetic parameters of the electrode reactions of Cu^{2+}, Zn^{2+}, and $[Co(NH_3)_6]^{3+}$ were determined. The obtained values of k_s, E_o, and α_c are listed together with literature values in Table 1. The results are in good agreement with the literature values.

In conclusion, it should be mentioned that the modified pulse polarograph developed has advantages in the easy measurement of the instantaneous potential-current-time relationship.

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References

1) G. C. Barker and A. W. Gardner, *At. Energ. Res. Establ. AERE Harwell C/R*, 2297 (1958).

2) G. C. Barker and A. W. Gardner, *Fresenius' Z. Anal. Chem.*, **173**, 79 (1960).

3) E. P. Parry and R. A. Osteryoung, *Anal. Chem.*, **36**, 1366 (1964).

4) E. P. Parry and R. A. Osteryoung, *Anal. Chem.*, **37**, 1634 (1965).

5) G. D. Christian, *J. Electroanal. Chem.*, **22**, 333 (1969).

6) H. E. Keller and R. A. Osteryoung, *Anal. Chem.*, **43**, 342 (1971).

7) J. H. Christie, J. Osteryoung, and R. A. Osteryoung, *Anal. Chem.*, **45**, 210 (1973).

8) N. Klein and Ch. Yarnitzky, *J. Electroanal. Chem.*, **61**, 1 (1975).

9) R. Kalvoda and A. Trojanek, *J. Electroanal. Chem.*, **75**, 151 (1977).

10) V. I. Boduy, I. V. Kotlova, and U. S. Lyapilov, *Zavod. Lab.*, **28**, 1042 (1963).

11) J. H. Christie and R. A. Osteryoung, *J. Electroanal. Chem.*, **49**, 301 (1974).

12) A. A. A. M. Brinkman and J. M. Los, *J. Electroanal. Chem.*, **7**, 171 (1964).

13) A. W. Fonds, A. A. A. M. Brinkman, and J. M. Los, *J. Electroanal. Chem.*, **14**, 43 (1967).

14) A. A. A. M. Brinkman and J. M. Los, *J. Electroanal. Chem.*, **14**, 269 (1967).

15) K. B. Oldham, *Anal. Chem.*, **40**, 1024 (1968).

16) J. P. van Dieren, B. G. W. Kaars, J. M. Los, and B. J. C. Wetsema, *J. Electroanal. Chem.*, **68**, 129 (1976).

17) J. H. Christie, L. L. Jackson, and R. A. Osteryoung, *Anal. Chem.*, **48**, 561 (1976).

18) J. H. Christie, L. L. Jackson, and R. A. Osteryoung, *Anal. Chem.*, **48**, 242 (1976).

19) M. Krizan, H. Schmidtpott, and H. Strehlow, *J. Electroanal. Chem.*, **80**, 345 (1977).

20) M. Krizan, *J. Electroanal. Chem.*, **80**, 337 (1977).

21) C. Peker, H. Herlem, and J. Bodoz-Lambling, *Fresenius' Z. Anal. Chem.*, **224**, 204 (1967).

22) A. Lagrou and F. Verbeek, *J. Electroanal. Chem.*, **19**, 413 (1968).

23) E. Timmerman and F. Verbeek, *J. Electroanal., Chem.* **12**, 158 (1966).

24) Y. Kato, A. Yamada, N. Yoshida, K. Unoura, and N. Tanaka, *Rev. Polarog. (Kyoto)*, **23**, 62 (1977).

25) Y. Kato, A. Yamada, N. Yoshida, K. Unoura, and N. Tanaka, *ACS/CSJ Chemical Congress*, ANAL-74 (1979).

26) Y. Kato, A. Yamada, N. Yoshida, K. Unoura, and N. Tanaka, *Bull. Chem. Soc. Jpn.*, **54**, 175 (1981).

27) N. Tanaka, A. Kitani, A. Yamada, and K. Sasaki, *Sci. Repts. Tohoku Univ. Ser. I*, **55**, 201 (1972).

28) N. Tanaka, A. Kitani, A. Yamada, and K. Sasaki, *Electrochim. Acta*, **18**, 675 (1973).

29) J. Bjerrum and J. P. MacReynolds, *Inorg. Synth.*, **2**, 216 (1946).

30) A. Yamada, and N. Tanaka, *Sci. Repts. Tohoku Univ. Ser. I.*, **53**, 110 (1970).

31) A. Yamada and N. Tanaka, *Anal. Chem.*, **45**, 167 (1973).