Analytical Studies Using the Convection Electrode. VIII. A. C. Polarography with the Pushed-out Mercury Drop Convection Electrode

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A series of investigations[1] using the rotating-disk convection electrode as an electrode of d. c. polarography has been carried out by the authors. In a previous paper[2] it was reported that the pushed-out mercury drop convection electrode (PMDCE) has a sensitivity about twenty times larger than the dropping mercury electrode (DME) and, also, that it could be used even in a strongly alkaline or an acidic medium and could be reused many times with a good reproducibility.

On the other hand, it is already known that the sensitivity of the a. c. polarographic method is better than that of the d. c. polarographic method for the reversible reaction, and, also, that in a buffer or an acidic medium it is not necessary to remove dissolved oxygen.[3] Therefore, the application of the convection electrode to the a. c. polarographic method can be expected to obtain a much higher sensitivity.

In the present paper, the results of a. c. polarographic studies using cadmium(II) as a depolarizer are reported. The relations between the concentration of the depolarizer and the summit current, and between the stirring rate of the rotating disk and the summit current or the summit potential are discussed in especial detail.

Experimental

Apparatus.—The electrolytic cell, the electrode and the rotating apparatus are the same as have been described in the previous paper,[2] but the position in which the electrode is set is different.

The Shimadzu model RP-2BF polarograph is employed for the measurements of d. c. and a. c. polarograms.

Reagents.—A cadmium solution is prepared from chemicals of reagent grade, extra pure, without further purification. Also, a hydrochloric acid solution is of reagent grade, extra pure.

Procedure.—About 30 ml. of the solution of cadmium in 1 M hydrochloric acid are poured into the electrolytic cell.

While dissolved oxygen remains in the solution, the a. c. polarogram is recorded immediately after the solution is poured into the cell.

As dissolved oxygen is removed from the solution, a hydrogen gas stream is passed constantly through the solution at the rate of about 4 bubbles per second for 1 hr., and then the a. c. polarogram is recorded.

The procedure for each polarographic measurement, i. e., the renewal of the mercury drop as the electrode, is the same as has been described in the previous paper.[2]

The polarograms are recorded with a chart speed of about 2 cm./min., a rate of change of applied potential of about 100 mV./min., and a superposed alternating voltage of 20 mV.

All the measurements are performed at 15± 0.5°C.

Results

The Reproducibility of the Summit Current.—Typical current-voltage curves for cadmium are shown in Fig. 1. The reproducibility of

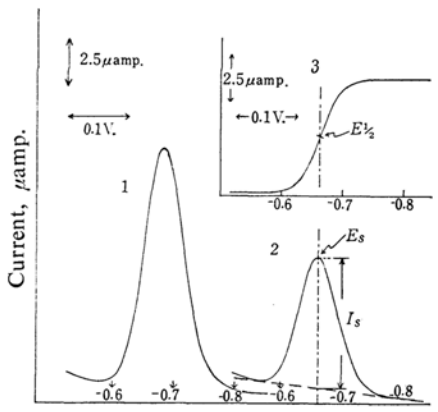

Fig. 1. Current-voltage curves of 1×10^{-4} M cadmium in 1 M HCl.
1 A. C. polarogram at the PMDCE in the presence of dissolved oxygen
2 A. C. polarogram at the PMDCE in the absence of dissolved oxygen
3 D. C. polarogram at the PMDCE

1) T. Ozaki and T. Nakayama, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **81**, 98 (1960); T. Ozaki and T. Nakayama, ibid., **82**, 46 (1961).
2) J. Suzuki and T. Ozaki, This Bulletin, **37**, 230 (1964).
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3) K. Itsuki and M. Nagao, ibid., **8**, 825 (1959); K. Itsuki and M. Nagao, ibid., **9**, 836 (1960).

TABLE I. REPRODUCIBILITY OF THE SUMMIT CURRENT i_s (μamp.)
(Stirring rate: 800 r. p. m.)

Concn. C, mol./l.	Oxygen dissolved		Oxygen removed	
	Average values of i_s	Average deviation %	Average values of i_s	Average deviation %
1×10^{-4}	13.175	0.76	7.067	1.41
5×10^{-5}	6.660	1.08	3.514	1.22
1.5×10^{-5}	2.085	1.68	—	—
7×10^{-6}	0.905	1.50	—	—
2×10^{-6}	0.254	1.66	—	—

TABLE II. REPRODUCIBILITY OF THE SUMMIT POTENTIAL E_s (V. vs. SCE)
(Stirring rate: 800 r. p. m.)

Concn. C, mol./l.	Oxygen dissolved		Oxygen removed	
	Average values of E_s, V. vs. SCE	Average deviation, %	Average values of E_s, V. vs. SCE	Average deviation, %
1×10^{-4}	−0.684	0.17	−0.661	0.18
5×10^{-5}	−0.683	0.09	−0.661	0.13
1.5×10^{-5}	−0.687	0.14	—	—
7×10^{-6}	−0.685	0.12	—	—
2×10^{-6}	−0.680	0	—	—

the summit current for the various concentrations of cadmium was investigated; the results are listed in Table I. As the table shows, the summit current has a good reproducibility. The summit current in the presence of dissolved oxygen in the electrolytic solution is larger than the corresponding current in the absence of dissolved oxygen.

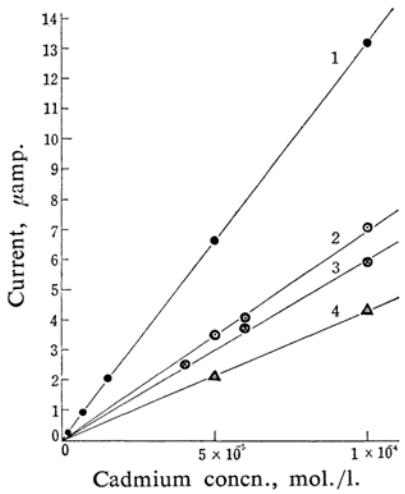

Fig. 2. Relations between the current and Cd^{2+} concentration.
1 At the PMDCE (in the presence of dissolved oxygen, a. c. polarographic method)
2 At the PMDCE (in the absence of dissolved oxygen, a.c. polarographic mothod)
3 At the PMDCE (d. c. polarographic method)
4 At the DME (in the presence of dissolved oxygen, a. c. polarographic method)

The Reproducibility of the Summit Potential.—The summit potential of each concentration was determined by the ordinary method; the results are shown in Table II. As the table shows, the good reproducibility of the summit potential can always be obtained within a mean error of 0.2%. Also, it can be seen that the summit potential in the presence of dissolved oxygen is slightly shifted to a more negative position than the corresponding potential in the absence of dissolved oxygen and that in both cases (in the presence or absence of dissolved oxygen) the potential is not affected by the concentration of cadmium.

The Relation between the Concentration of Cadmium and the Summit Current.—The relation between the concentration and the current is shown in Fig. 2. It can be seen

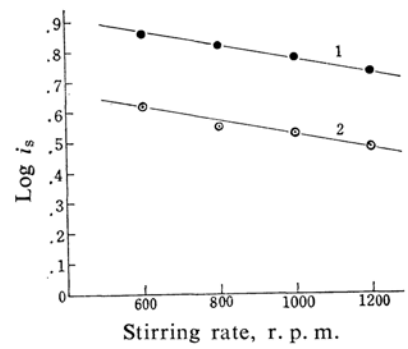

Fig. 3. Relations between the stirring rate and the summit current of 5×10^{-5} M Cd^{2+} in 1 M HCl.
1 In the presence of dissolved oxygen
2 In the absence of dissolved oxygen

Table III. Relation between the stirring rate r (r. p. m.) of the rotating disk and the summit potential E_s V. vs. SCE)

r	600	800	1000	1200	Remark
E_s	−0.679	−0.683	−0.687	−0.687	Oxygen dissolved
	−0.658	−0.661	−0.658	−0.660	Oxygen removed

Table IV. Relation between the superposed alternating voltage ΔE (mV.) and the summit potential E_s (V. vs. SCE). (Stirring rate: 800 r. p. m.)

ΔE	10	20	30	Remark
E_s	−0.683	−0.683	−0.684	Oxygen dissolved
	−0.662	−0.661	−0.660	Oxygen removed

Table V. Influence of the rate of polarization P (mV./min.) on the summit current i_s (μamp.) and the summit potential E_s (V. vs. SCE) (Stirring rate: 800 r. p. m.)

C mol./l. \ P	100		200		Remark
i_s, E_s	E_s	i_s	E_s	i_s	
1.5×10^{-5}	−0.687	2.100	−0.687	2.906	Oxygen dissolved
5×10^{-5}	−0.661	3.514	−0.663	4.285	Oxygen removed

from the figure that a linear relation is obtained between the concentration and the current.

The Effect of the Stirring Rate on the Summit Current.—The effect of the stirring rate of the rotating disk on the summit current was investigated; the results are shown in Fig. 3. From the figure, it can be seen that the current decreases exponentially with the increase in the stirring rate.

The Effect of the Stirring Rate on the Summit Potential.—The dependence of the summit potential on the stirring rate was investigated. The results are listed in Table III. In the oxygen-dissolved solution, the potential is slightly shifted toward a negative position with the increase in the stirring rate (600~1200 r. p. m.), but in the case of the oxygen-free solution, the stirring rate has no effect on the summit potential.

The Relation between the Superposed Alternating Voltage and the Summit Current or the Summit Potential.—The relations between the superposed alternating voltage and the current or potential were investigated. The results are given in Fig. 4 and Table IV respectively. As the figure and the table show, the current is proportional to the superposed alternating voltage, but the potential is not affected.

The Effect of the Rate of Polarization.—The effect of the rate of polarization on the summit current or the summit potential was investigated; the results are listed in Table V.

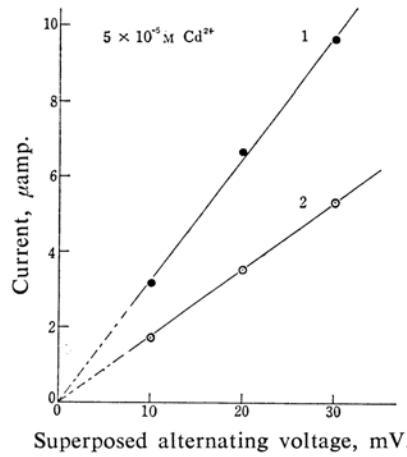

Fig. 4. Relations between the superposed alternating voltage and the summit current.
1 In the presence of dissolved oxygen
2 In the absence of dissolved oxygen

The change of the rate of polarization has no effect on the potential, but the current increases with the increase in the rate of polarization.

A Comparison with the DME.—The summit current obtained with the PMDCE (in the presenceof dissolved oxygen at the stirring rate of 600 r. p. m.) for 1×10^{-4} M cadmium is about thirty times as large as the corresponding diffusion current obtained with the DME using the d. c. polarographic method; moreover, it is about three times as large as the summit current

TABLE VI. COMPARISON OF E_s OR $E_{1/2}$ VALUES WITH THE DME AND THE PMDCE

Electrode \ $E_{1/2}$, E_s	$E_{1/2}$	E_s	
	Oxygen removed	Oxygen dissolved	Oxygen removed
DME	−0.653	−0.655	−0.656
PMDCE*	−0.662	−0.683	−0.661

* Stirring rate of the rotating disk : 800 r. p. m.

obtained with the DME using the a. c. polarographic method.

The capillary of the DME used has an m value of 0.93 mg./sec. and a drop time of 4.9 sec. in a 1 M hydrochloric acid solution at −0.80 V. vs. SCE.

Discussion

Half-wave Potential and Summit Potential.—In order to compare the half-wave potential and the summit potential with the PMDCE or with the DME, a series of investigations was performed; the results are shown in Table VI. When these values of the half-wave potential and of the summit potential are compared, it can be seen that they agree well each other, except for the summit potential with the PMDCE in the presence of dissolved oxygen. In the absence of dissolved oxygen, both the half-wave potential and the summit potential with the PMDCE are slightly shifted to a more negative position than the corresponding half-wave potential and summit potential with the DME. This effect is considered to be due to the fact that the rate of mass transfer becomes larger than the rate of electron transfer because of the convection. This agrees with the results of Jordan.[4]

The Stirring Rate and the Summit Current.—As is shown in Fig. 3, the summit currents decrease with the increase in the stirring rate in the presence or absence of dissolved oxygen.

As has been pointed out by Jordan,[4] Kolthoff and Jordan,[5] and Delahay,[6] at the convection electrode the rate of mass transfer becomes larger than the rate of electron transfer because of the effect; i. e., the effective thickness of the diffusion layer becomes smaller with the increase in the velocity of convection, which depends on the stirring rate. Therefore, the electrode reaction becomes quasi-reversible.[4] Namely, it is considered that the decrease in the summit current with an increase in the stirring rate is caused by the decrease in the reversibility.

The Influence of Dissolved Oxygen.—It is commonly known in the case of an acidic or a buffer medium that the summit current is not affected by dissolved oxygen. In the present investigation, this phenomenon has been observed with the DME for cadmium in 1 M hydrochloric acid solution. However, the summit current obtained with the PMDCE in the presence of dissolved oxygen is increased more than in the absence of such oxygen. This is considered to be a special feature of this electrode, but it has not yet been explained.

Summary

A. C. polarography with the PMDCE has been investigated, using cadmium in 1 M hydrochloric acid.

A satisfactory proportionality between the summit current and the concentration is obtained in the range from 1×10^{-4} to 2×10^{-6} M, and the summit current obtained with the PMDCE (in the presence of dissolved oxygen at the stirring rate of 600 r. p. m.) for the cadmium depolarizer is about thirty times as large as the corresponding diffusion current obtained with the DME.

The a. c. polarogram obtained with the PMDCE shows a gradual decrease in the summit current as the stirring increases; this decrease is considered to be due to the quasi-irreversibility at the electrode reaction because of the increase in the rate of mass transfer caused by the convection. The relation between the summit current and the stirring rate is exponential in the range from 600 to 1200 r. p. m.

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