Analytical Studies Using the Convection Electrode. VII. The Use of the Pushed-out Mercury-drop Electrode

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The "rotating disk" convection electrode of platinum wire has previously been devised as a new polarographic electrode by one of the present authors, and the current-voltage curves for the oxidation of iodide and the reduction of cadmium and thallum(I) have been studied. However, the platinum wire electrode, like the other solid electrodes, showed a poor reproducibility.[1] Therefore, using a mercury-coated platinum wire, polarographic waves for the reduction of cadmium and thallium(I) have been investigated and well-reproducible waves obtained.[2] In a neutral or almost neutralized medium, good results were achieved, but in a strongly alkaline or acidic medium, coated mercury on the platinum wire is often detached from the wire during the electrolysis and, in this case, the electrode loses its function as a mercury electrode. Consequently, the polarographic applications of this electrode were found to be limited to a narrow range of pH.

In order to correct these weak points, the authors prepared an electro-deposited mercury-drop electrode.[3] It has a small cup-shape vessel at the end of a glass tube and a small mercury drop electro-deposited on the tip of platinum wire sealed at the bottom of the vessel. The electro-deposited mercury-drop is never detached, even in strongly alkaline or acidic solutions. However, this electrode is difficult to construct and to manipulate, and, also, it takes much time to deposit a mercury drop electrolytically. In order to improve these points, the "pushed-out" mercury-drop

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[1] T. Ozaki and T. Nakayama, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **81**, 98 (1960).

[2] T. Ozaki and T. Nakayama, ibid., **82**, 46 (1961).

[3] T. Ozaki, *Bull. of Educ. Fac. of Shizuoka Univ.*, **11**, 133 (1960).

convection electrode (PMDCE) has recently been invented by the authors as a new polarographic electrode. This is much easier to construct and to manipulate than the electrodes mentioned above.

In the present paper, polarographic studies using this electrode on various depolarizers, i. e., cadmium, thallium(I) and lead, are reported, and the following points, among others, are examined: (1) the reproducibility of limiting currents or half-wave potentials, (2) the relation between the concentration and the wave height, (3) the relation between the stirring rate of the rotated disk and the wave height, and (4) the half-wave potential and its shift. The results are discussed in detail.

Experimental

Apparatus. — A Shimadzu RP-2 type polarograph was employed for the measurement of all the current-voltage curves. The curves were recorded with a chart speed of about 2 cm./min. and a rate of change of applied potential of about 100 mV./min. A rotating apparatus of a Shimadzu "rotated platinum electrode" was also used in all experiments. It can be rotated at 600, 800, 1000 or 1200 r. p. m. by shifting the gears. The rotated disk was fixed to the axis of the rotator. The disk was made of hard polyvinyl chloride resins and pulley shape.

Cell and Electrode. — The cell and the electrode used in this experiment are shown in Fig. 1. The cell was made of hard glass, while the electrode tube is composed of three parts: (A) a small cup-shape glass vessel (0.2 cm. in inside diameter, 0.3 cm. in outside diameter, and 0.4 cm. deep), (B) a glass capillary for inserting mercury, into A, and (C) a glass tube connecting it with the large mercury reservoir.

Small amounts of mercury are pushed-out into vessel A through B by the pressure caused by raising the mercury reservoir. When the reservoir is lowered, the mercury in vessel A is separated from the mercury in C and, accordingly, a mercury drop is formed in the vessel and the mercury remaining in the capillary B moves back to C.

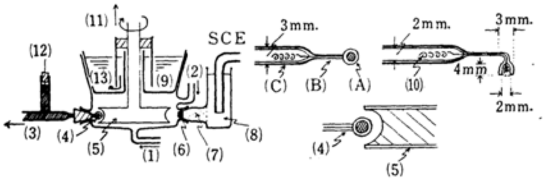

Fig. 1. Polarographic cell and electrode.

(1), (2)	Inlet pipe of H_2 gas
(3)	To mercury reservoir
(4)	Electrode (PMDCE)
(5)	Rotating disk (stirrer)
(6)	Sintered glass
(7)	Agar bridge
(8)	Sat. KCl solution
(9)	Water
(10)	Mercury coated platinum wire
(11)	To synchronous motor
(12)	Cathode
(13)	Outlet of H_2 gas

The electric connection of a mercury drop in vessel A with the mercury in C was made by mercury-plated platinum wire (0.01 cm. in diameter). The platinum wire prevents a mercury drop from falling out of A.

The solution containing the supporting electrolyte has a tendency to penetrate into the vessel. Therefore, the inside of the vessel is coated with silicone film.

The capillary B is constructed so finely as to separate the mercury drop in vessel A from the mercury in C in order to avoid the diffusion of an amalgamated metal from A to C.

The mercury drop prepared as mentioned above does not fall out of the vessel even under such severe experimental conditions as in 1 M sodium hydroxide or 1 M hydrochloric acid or at the rate of rotation of 1200 r. p. m.

Reagents.—Each solution of thallium(I), cadmium and lead was prepared from chemicals of an extra pure reagent grade without further purification. The other chemicals used are all of extra pure reagent grade.

Procedure. — The mercury drop is renewed in each polarographic measurement. The procedure is as follows.

Before the measurement of a current-voltage curve, the mercury reservoir is raised to the height of about 27 cm. A few mercury drops are made to fall out of vessel A because of the pressure created by raising the reservoir. When the last of these drops falls, the reservoir is brought down to the height of about 5 cm. The fall of mercury drops then stops, and, in vessel A, a mercury drop is formed. After that, a polarogram is recorded. The mercury drop can be renewed as the electrode by repeating the above process.

Dissolved oxygen is removed by passing H_2 gas through the solution or by adding small amounts of a sodium sulfite solution.

0.3 ml. of a 1 M sodium sulfite solution freshly prepared is added to 50 ml. of a 0.1 M potassium chloride solution containing thallium(I) or cadmium ions as depolarizers. A reduction wave is measured after 15 min. Also, after 50 ml. of 1 M sodium hydroxide or hydrochloric acid containing a lead depolarizer is poured into the electrolysis cell, a hydrogen gas stream is passed, at the rate of about 4 bubbles per second for about 1 hr., through the solution to remove the dissolved oxygen. These lead sample solutions are electrolyzed by the constant bubbling of hydrogen gas (by using gas-inlet pipe (2) in Fig. 1).

All the measurements were carried out at 16.5±0.5°C.

Results

The Reproducibility of the Limiting Currents. — A mercury drop is pushed out into the vessel of the electrode before each measurement, so its surface area must always be kept

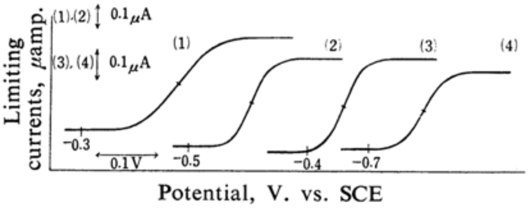

Fig. 2. Typical current-voltage curves of thallium, cadmium and lead (HCl and NaOH).
(1) 5×10^{-6} M Tl^+ in 0.1 M KCl
(2) 5×10^{-6} M Cd^{2+} in 0.1 M KCl
(3) 5×10^{-6} M Pb^{2+} in 1 M HCl
(4) 5×10^{-6} M Pb^{2+} in 1 M NaOH

constant. To test the reproducibility of the area, the limiting currents were measured with various depolarizers. Typical current-potential curves are shown in Fig. 2, while some of these results are given in Table I. The curves oscillated slightly, but this had no effect upon the results.

On the other hand, the limiting currents obtained by the renewal method of the electrode proposed by Marple et al.⁴⁾ are shown in Table II (the applied voltage and the time for the renewal were −0.4 V. vs. SCE and 5 min. respectively).

As is shown in Tables I and II, reproducibility with the PMDCE was slightly poor in comparison with the method of Marple et al.,⁴⁾ but it is considered that the surface area of the mercury drop can be kept fairly constant, because good reproducibilities of the limiting currents can always be obtained within a range of error of 2%.

The Reproducibility of Half-wave Potentials. — The half-wave potentials of various depolarizers were determined by the ordinary method; the results are listed in Table III. As is shown in Table III, the half-wave potentials have a good reproducibility.

The Relation between the Concentration of Depolarizers and the Limiting Currents. — The

TABLE I. REPRODUCIBILITY OF THE LIMITING CURRENTS (i_l) OBTAINED WITH THE PMDCE (STIRRING RATE: 800 r. p. m.)

	Depolarizer	Cd^{2+}	Tl^+	Pb^{2+}(NaOH)	Pb^{2+}(HCl)
i_l	Average*, μamp.	4.807	4.055	4.762	5.564
	Mean deviation, %	1.07	1.36	0.71	0.57

* Average value of 5∼6 data

TABLE II. REPRODUCIBILITY OF THE LIMITING CURRENTS (i_l) OBTAINED BY USING THE METHOD OF MARPLE ET AL.⁴⁾ (STIRRING RATE: 800 r. p. m.)

	Exp. No.	1	2	3	4	5	Average, μamp.
i_l	Cd^{2+}, 5×10^{-6} M	0.203	0.206	0.203	0.206	0.201	0.203
	Tl^+, 5×10^{-6} M	0.197	0.199	0.198	0.199	0.199	0.199

Mean deviation (%) —— Tl^+: 0.49, Cd^{2+}: 0.59

TABLE III. REPRODUCIBILITY OF HALF-WAVE POTENTIALS ($E_{1/2}$, V. vs. SCE) (STIRRING RATE: 800 r. p. m.)

	Depolarizer*	Cd^{2+}(KCl)	Tl^+(KCl)	Pb^{2+}(NaOH)	Pb^{2+}(HCl)
$E_{1/2}$	Average	−0.610	−0.479	−0.784	−0.467
	Mean deviation	0.07	0.21	0.10	0.17

* The concentration of each depolarizer is 1×10^{-4} M.

TABLE IV-1. RELATION BETWEEN CONCENTRATION (C) AND THE LIMITING CURRENTS (i_l) (STIRRING RATE: 800 r. p. m.)

Depolarizer C, mol./l.	Cd^{2+}(KCl)		Tl^+(KCl)	
	i_l, μamp.	$(i_l/C)\times10^{-4}$	i_l, μamp.	$(i_l/C)\times10^{-4}$
1×10^{-4}	4.807	4.81	4.055	4.06
5×10^{-5}	2.276	4.55	1.903	3.81
2×10^{-5}	0.886	4.43	0.851	4.26
5×10^{-6}	0.205	4.10	0.195	3.90
1×10^{-6}	0.044	4.40	—	—
5×10^{-7}	0.021	4·20	—	—

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4) T. L. Marple and L. B. Rogers, *Anal. Chem.*, **25**, 1351 (1953).

Table IV-2. Relation between concentration (C) and the limiting currents (i_l) (stirring rate: 800 r. p. m.)

Depolarizer C, mol./l.	Pb^{2+} (NaOH)		Pb^{2+} (HCl)	
	i_l, μamp.	i_l/C, $\times 10^{-4}$	i_l, μamp.	i_l/C, $\times 10^{-4}$
1×10^{-4}	4.762	4.76	5.564	5.56
5×10^{-5}	—	—	2.865	5.73
2×10^{-5}	0.973	4.87	1.100	5.50
5×10^{-6}	0.243	4.86	0.256	5.12
1×10^{-6}	0.047	4.70	0.051	5.10
5×10^{-7}	0.023	4.60	0.029	5.80

Table V. Effect of stirring rate on half-wave potentials (V. vs. SCE)

Depolarizer*	Stirring rate, r. p. m.			
	600	800	1000	1200
Cd^{2+} (KCl)	−0.610	−0.610	−0.610	−0.611
Tl^{+} (KCl)	−0.478	−0.479	−0.481	−0.480
Pb^{2+} (NaOH)	−0.782	−0.784	−0.785	−0.783
Pb^{2+} (HCl)	−0.466	−0.467	−0.468	−0.468

* Each concentration of these depolarizers is 1×10^{-4} M.

Table VI. Effect of the rate of polarization on the limiting currents (i_l, μamp.) and half-wave potentials ($E_{1/2}$, V. vs. SCE)

Depolarizer	Rate of polarization, mV./min.					
	$E_{1/2}$	i_l	$E_{1/2}$	i_l	$E_{1/2}$	i_l
Cd^{2+} (KCl)$^{1)}$	−0.611	0.870	−0.611	0.886	−0.609	0.938
Tl^{+} (KCl)$^{2)}$	−0.488	3.918	−0.479	4.042	−0.463	4.349
Pb^{2+} (NaOH)$^{3)}$	—	—	−0.782	1.515	−0.777	1.866
Pb^{2+} (HCl)$^{4)}$	−0.458	2.825	−0.460	2.880	−0.463	2.988

Stirring rate: 800 r. p. m.
1) 2×10^{-5} M 2) 1×10^{-4} M 3) 3×10^{-5} M 4) 5×10^{-5} M

relations between the limiting currents and concentration are shown in Table IV. It can be seen from Table IV that a satisfactory proportionality between the limiting currents and concentration is obtained.

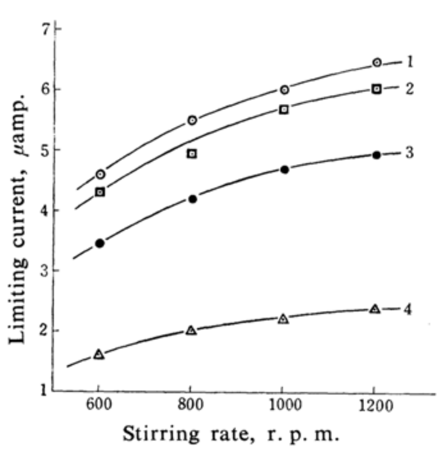

Fig. 3. The effect of stirring rate on limiting currents.
1: 1×10^{-4} M Pb^{2+} in 1 M HCl
2: 1×10^{-4} M Cd^{2+} in 0.1 M KCl
3: 1×10^{-4} M Pb^{2+} in 1 M NaOH
4: 5×10^{-5} M Tl^{+} in 0.1 M KCl

The Effect of the Stirring Rate on Limiting Currents. — The dependence of the limiting currents on the stirring rate of the rotating disk was investigated by using a cadmium, thallium(I) or lead solution respectively. The results are shown in Fig. 3. It can be seen that no linear relation between the limiting currents and the stirring rate is obtained, although the currents decrease gradually with the increase in the stirring rate.

The Effect of the Stirring Rate on the Half-wave Potentials. — The effect of the stirring rate on the half-wave potentials of cadmium, thallium(I) and lead was investigated; the results are shown in Table V. It can there be seen that the change in the stirring rate of 600∼1200 r. p. m. has no effect on the half-wave potentials.

The Effect of the Rate of Polarization. — It was observed with a stationary mercury-plated platinum electrode by Marple et al.[4] that the half-wave potential was shifted toward positive potentials as the rate of polarization was increased from 37 mV. to 222 mV. per minute.

Therefore, the effect of the rate of polarization was investigated with the PMDCE. The results are given in Table VI. It can be seen from Table VI that the limiting currents are increased with the increase in the rate of polarization and that, at the same time, the half-wave potentials are slightly shifted toward positive potentials, as Marple et al.[4] observed, in the cases of thallium(I) and lead (in 1 M sodium hydroxide). However, no change in the half-wave potential is observed on the other ions.

A comparison with the Dropping Mercury Electrode (DME). — The limiting currents obtained with the PMDCE (1200 r. p. m.) for thallium(I), cadmium, and lead (in 1 M hydrochloric acid and in 1 M sodium hydroxide) were, respectively, about eighteen, fifteen, sixteen and fourteen times as large as the corresponding diffusion currents obtained by the DME. The capillary of the DME used had an m value of 0.92 mg./sec. and a drop time of 5.1 sec./drop at -0.8 V. vs. SCE in a 0.1 M potassium chloride solution.

Discussion

Sensitivity. — Table VII lists the values of sensitivity, "S" ($S=i_l/nC$), which derived by Kolthoff and Jordan[5] to characterize the convection electrode, at the PMDCE; the values of $S/D^{2/3}$ (D: diffusion coefficient) are shown in column 4 of this table. If the limiting currents are completely controlled with convection, the S values of these depolarizers should be of the same value, because all measurements were carried out under the same hydrodynamic conditions. As is shown in Table VII, however, at the PMDCE the S values of these depolarizers are not equal, while the $S/D^{2/3}$ values agree well with one other. Therefore, it is found that the limiting currents change proportionally with two-thirds the power of the diffusion coefficient. Apparently both diffusion and convection contribute to the currents; i. e., the limiting currents depend on the diffusion coefficient and, at the same time, on the convection coefficient.[5]

The Relation between the Stirring Rate and the Limiting Currents. — The relation between the limiting currents and the speed of the rotation of the stirrer can generally be expressed by this equation:[6]

$$i_l=pr^a$$

where p is a constant, r is the number of rotations per minute of the stirrer, and a is a constant which is generally comprised between 0.4 and 1 and which depends on the geometric factors of the electrolytic cell, the stirrer and the electrode.

This relation was investigated with the PMDCE in the cases of cadmium, thallium(I) and lead. A logarithm of limiting current was plotted against a logarithm of the stirring rate of the stirrer. These plots are shown in Fig. 4, where the plots of various depolarizers give straight lines. The values of a in the above equation can be determined with the slope of a line in Fig. 4. The value of a

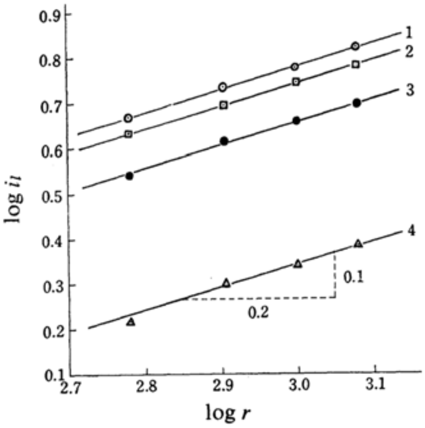

Fig. 4. The relation between logarithm of stirring rate (r) and logarithm of limiting currents (i_l).

1 : 1×10^{-4} M Pb^{2+} in 1 M HCl
2 : 1×10^{-4} M Cd^{2+} in 0.1 M KCl
3 : 1×10^{-4} M Pb^{2+} in 1 M NaOH
4 : 5×10^{-5} M Tl^{+} in 0.1 M KCl

TABLE VII. COMPARISON OF S VALUES AND $S/D^{2/3}$ VALUES OF VARIOUS DEPOLARIZERS. (STIRRING RATE : 800 r. p. m.)

Depolarizer	Supporting electrolyte	S*	$S/D^{2/3}$
Cd^{2+}	0.1 M KCl	2.49×10^4	6.7×10^7
Tl^{+}	0.1 M KCl	5.10×10^4	6.9×10^7
Pb^{2+}	1 M NaOH	2.95×10^4	6.5×10^7
Pb^{2+}	1 M HCl	3.08×10^4	6.6×10^7

* μamp./equiv. per liter

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[5] I. M. Kolthoff and J. Jordan, *J. Am. Chem. Soc.*, 76, 3843 (1954).

[6] P. Delahay, "New Instrumental Methods in Electrochemistry," Interscience Publishers, New York (1953), pp. 217-249.

obtained is 0.50. This shows that the limiting currents change in proportion to the square root of the stirring rate.

Accordingly, the limiting currents at the PMDCE change linearly with the square root of the stirring rate and, at the same time, with two-thirds the power of the diffusion coefficient.[3] If it is assumed that the velocity of the stream on the surface of the electrode, which can hardly be measured, is proportional to the rate of the rotation of the disk, it seems that the limiting currents with the PMDCE conform to the equation of the limiting currents for the rotating disk electrode derived by Levich,[7] which is as follows:

$$i_l = knFACD^{2/3}\omega^{1/2}\nu^{-1/6}$$

where i_l = limiting currents, C = bulk concentration, ω = angular velocity of electrode, and ν = kinematic viscosity.

The relation between i_l and ν has not yet been investigated experimentally. This result is very similar to that obtained by Galus et al.[8] or by Galus and Adams.[9]

Half-wave Potentials. — Table VIII summarizes the half-wave potentials at the PMDCE and DME. As is shown in Table VIII, the half-wave potentials of various depolarizers at the PMDCE are slightly more negative than the corresponding half-wave potentials of DME. It seems probable that the rate of mass transfer becomes large as compared with the rate of electron transfer, as has been reported by Jordan,[10] or that δ_0, the effective thickness of the diffusion layer, is smaller, as has been pointed out by Delahay,[6] because of the convection effect caused by increasing the stirring rate. Table V shows the effect of the stirring rate on the half-wave potential; the results indicate that the half-wave potential is not affected by the stirring rate. It seems probable that a change in δ_0 can be almost disregarded in the range of a given stirring rate, as the relationship of the half-wave potential to δ_0 is of an exponential function.[3]

The effect of the concentration of reducible material on the half-wave potential is shown in Table IX. For cadmium, the half-wave potential is nearly the same at every concentration, but with the others, the half-wave potentials are shifted slightly toward positive potentials with the decreasing concentration of depolarizers. Such a shift can be found

TABLE VIII. COMPARISON OF HALF-WAVE POTENTIALS AT DME AND PMDCE (STIRRING RATE: 800 r. p. m.)

Electrode	Depolarizer			
	Cd^{2+} (KCl)	Tl^{+} (KCl)	Pb^{2+} (NaOH)	Pb^{2+} (HCl)
DME, 4×10^{-4} M	−0.60	−0.46	−0.76	−0.44
PMDCE, 1×10^{-4} M	−0.61	−0.48	−0.78	−0.47

TABLE IX. EFFECT OF DEPOLARIZER CONCENTRATION ON HALF-WAVE POTENTIALS (STIRRING RATE: 800 r. p. m.)

Depolarizer	Concentration, mol./l.)			
	1×10^{-4}	5×10^{-5}	5×10^{-6}	5×10^{-7}
Cd^{2+} (KCl)	−0.611	−0.609	−0.610	−0.613
Tl^{+} (KCl)	−0.479	−0.470	−0.462	—
Pb^{2+} (NaOH)	−0.783	—	−0.780	−0.776
Pb^{2+} (HCl)	−0.467	−0.461	−0.458	−0.456

TABLE X. EFFECT OF STIRRING RATE ON THE SLOPE (mV.)

Stirring rate r. p. m.	Depolarizer					
	Cd^{2+} (KCl)		Pb^{2+} (NaOH)		Pb^{2+} (HCl)	
	mV.	n	mV.	n	mV.	n
600	32.3	1.78	29.0	1.98	29.0	1.98
800	33.3	1.72	29.6	1.94	29.7	1.93
1000	33.3	1.72	30.0	1.91	32.3	1.78
1200	35.0	1.64	33.3	1.72	32.4	1.77

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[7] V. G. Levich, *Acta Physicochim.*, **17**, 257 (1942).

[8] Z. Galus, C. Olson, H. Y. Lee, and R. N. Adams, *Anal. Chem.*, **34**, 164 (1962).

[9] Z. Galus and R. N. Adams, *J. Am. Chem. Soc.*, **84**, 2061 (1962).

[10] J. Jordan, *Anal. Chem.*, **27**, 1708 (1955).

reported also by Arthur et al.[11]

Plot of the Applied Potential against log $i/(i_l-i)$. — The logarithm of quantity (i/i_l-i) was plotted against the applied potential at the PMDCE. These plots for thallium, cadmium and lead how perfectly straight lines. Table X shows both the values of the slope (mV.) and the number of electrons, n calculated from it.

The data given in Table X show that the values of n decrease with an increase in the stirring rate. It is considered that the increase in the mass transfer due to the convection gives the increase in quasi-irreversibility.[10]

Summary

The limiting currents with the PMDCE depend on the factors of both convection and diffusion. The PMDCE is easy to prepare and to manipulate, and it has an excellent sensitivity. It can be used even in a strongly alkaline or acidic medium and can be reused many times with good reproducibility. Therefore, various applications to analytical chemistry can be expected.

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[11] P. Arthur, J. C. Kamyathy, R. F. Maness and H. W. Vaughan, ibid., **27**, 895 (1955).