

## New Micro Rotating Mercury Electrode for Voltammetry

by

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### 전류전압법을 위한 마이크로 회전수은 전극

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#### 요 약

수은 표면을 바꾸기 쉽고, 사용하기에 편리한 회전수은전극을 고안하였다. 이 전극은 갈아 닦은 두 유리 부분으로 되어 있다. 그 중 숫 부분의 끝은 백금선 토막을 녹여 넣은 평평한 면으로 막혀 있고 그 옆에 작은 구멍이 하나 뚫여 있다. 암 부분에는 흡이 파여 있고, 모세관(약 1mm 지름)이 붙어 있다. 이 구멍과 흡이 마주치면 두 유리 부분의 수은이 오고갈 수 있고, 사용할 때에는 이 연결을 끊어 수은이 흐르지 못하게 한다. 그러나 백금선 토막이 두 부분을 전기적으로 연결한다. 모세관의 끝은 위를 향하게 굽혀 두어, 노출된 수은 부분이 수용액에 바뀌치지 못하게 한다. 이 노출 수은 표면이 마이크로 전극으로 작용한다. 이 전극은 산성용액에서의 전류법 적정에 매우 유용하며, 전기저항이 작은 마이크로 수은전극이기 때문에 교류 플라토그라피에도 유리하다. 또 정류전극으로서도 매우 편리하다.

#### Abstract

A simple rotating micro mercury electrode is constructed in such a way that the mercury surface can be renewed quite easily with reasonable reproducibility. It consists of a glass capillary of about 1mm diameter connected to a mercury filled tube by means of a ground joint that allows mercury flow at a particular relative position only, and the electrical connection between the two parts is made by a platinum wire fused in the bottom of the latter. Thus the mercury surface exposed at the tip of the capillary replaces the platinum tip of the usual platinum micro electrode; however, the capillary has to be bent so that the tip directs upwards. It has been found to be a convenient electrode in the amperometric titration in strongly acidic media. Furthermore, it has been advantageously used in the alternating-current polarography because of its smaller electrical resistance than the ordinary dropping mercury electrodes. It also can be used as a stationary mercury electrode in fast scanning polarography.

#### Introduction

There are several schemes of using mercury electrode to obtain the diffusion limited current in voltammetry. The rotating electrode developed by Lee<sup>(1)</sup> is rather bulky device and the surface area of its mercury

fluctuates to a considerable degree unless it is used with great care. Arther et al<sup>(2)</sup> developed a fixed mercury-tube electrode with stirring device which is more or less similar to the one described below except the moving part is the solution but not the electrode. The present work is concerned with a rotating mercury

electrode that can be handled in a simple manner, so that it can be used as a rotating micro electrode in all types of voltammetry.

## Experimentals

### 1. Apparatus and Reagents

All polarograms were recorded by means of a Leeds and Northrup Electrochemograph and an alternating-current polarograph constructed in the author's laboratory. Amperometric titrations were carried out with conventional electrical wiring. In the determination of the reproducibility of renewed surface of the electrode, a Sargent Model FS recording polarograph was used. A Sargent Synchronous Rotator of 600 r. p. m. was used for rotating the electrode. All reagents were reagent grade. No attempt was made to keep the temperature of the cell constant.

The electrode assembly is shown schematically in Fig. 1. The electrode is consisted of two parts, A and B, which are connected at the ground joint end. The end of the male part A is closed with a flat bottom through which a small piece of a platinum wire is fused in. There is a small hole C on the ground wall of it. The ground section of the female joint of the part B has a slot that connects the two compartments of the assembled electrode, when it is positioned right against the hole C on the male joint. The open end of capillary section of the part B should be kept upright in order to prevent the displacement of mercury by supporting electrolyte.

### 2. Preparation of the Electrode

As one can see easily, it is essential to have no gas trapped in and or at the top of the mercury column, since it may cause the mercury surface at the open end to become unstable when the electrode is rotated because of the fluctuation of the centrifugal force acting on it. Therefore, the electrode has been filled with mercury using an evacuating apparatus. Thus, the cleaned and dried electrode parts are connected tightly using some lubricant such as silicon grease in such a way that the hole C on the male joint wall and the slot on the female fit together. Then the open end of the male part is immersed in a mercury pool and carefully sucked from the open end of the capillary portion until the slot is just filled with mercury, when the two parts are

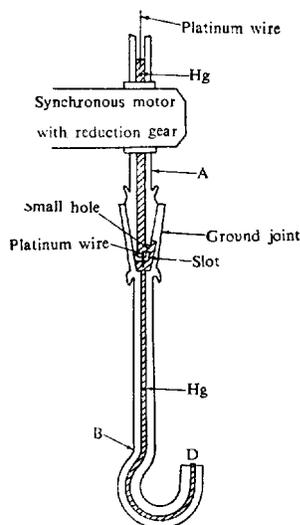


Figure 1. Electrode Assembly

turned opposite to separate the slot and the hole far apart. After evacuating the capillary section as far as possible, they are brought together again to allow the mercury rise up to the bent portion of the capillary. After turning the two parts opposite again to cut the mercury column, the electrode assembly is detached from the evacuating apparatus and tightly hooked together by means of a rubber ring or springs. With the electrode in position, the upper tube A is filled with mercury up to an appropriate level for practical use. Then the two parts are turned back to allow the mercury flow down filling the entire portion of the capillary section. When a mercury drop forms at the end of the capillary, cut the mercury column again by turning the two parts. The mercury drop thus formed can be cut off either by means of a razor blade in the presence of the supporting electrolyte at the tip or by rotating the electrode in the cell to be studied. The mercury surface can be renewed in a similar manner after letting the mercury flow out by a desired amount.

## Results and Discussion

The polarograms obtained by using the rotating electrode tend to be quite irregular in the sense that they have maxima and minima. Probably, it may have been caused by creeping of the electrolyte into the capillary as proposed previously.<sup>(2),(3),(4)</sup> Such irregu-

larities can be easily eliminated by adding some surface active agent such as gelatine to the electrolyzing solution. When the electrode is used after electrolyzing a solution of which the reaction product is soluble in mercury, there appears a hump at the beginning of the diffusion limited current, which is similar in nature with the one reported by Arthur et al<sup>(2)</sup>. In such cases, an anodic wave appears at the

beginning part of the polarographic wave, too, and the gradient of the rising portion of the wave is steeper than with a new electrode surface. This fact should be borne in mind when the electrode is to be used in the alternating current polarography (see Fig. 2). As expected, with the reaction product soluble in mercury, the graph of  $E$  vs.  $\log(i/i_d - i)$  was a straight line, and its slope increased with the concentration of the reacting species in the electrolyte, as shown in Table 1.

In order to check the reproducibility of the exposed surface area of the electrode in renewing, the peak height of the fast scanning polarogram was measured with the electrode not rotated, which is supposed to be proportional to its effective surface area<sup>(5)</sup>. The results obtained with the surface renewed by cutting off the mercury droplet by rotating the electrode in the solution are shown in Table 2. As shown in Fig. 3, which compares the ordinary dropping mercury electrode and the present electrode in amperometric titration, the latter gives better result when used as the indicating electrode, besides the simplicity of its manipulation.

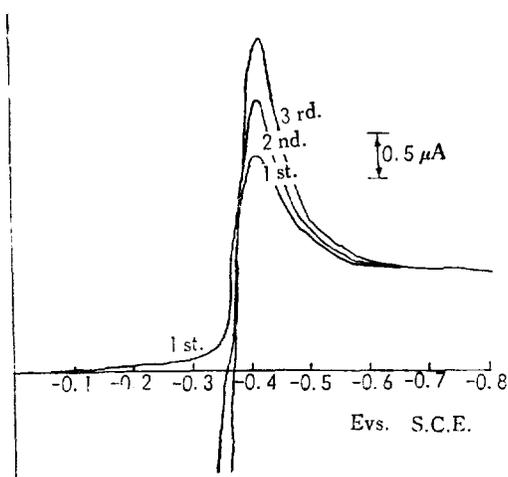


Figure 2. (a)

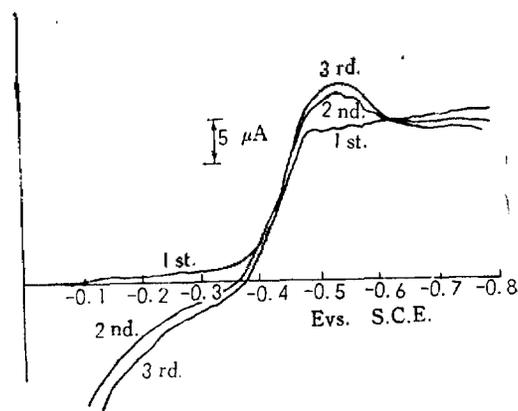


Figure 2. (b)

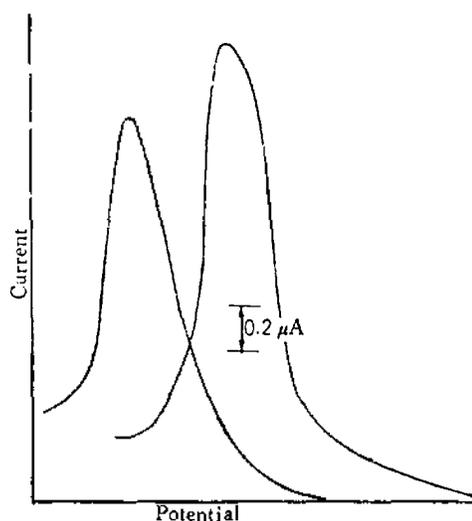


Figure 2. (c)

**Figure 2. Anodic Current and Wave Shape Variation with Repetitive Use of Electrode. Scan Rate, 0.2 volt/min.; 16°C**

a: Hanging MDE;  $1.25 \times 10^{-6} M$   $Pb^{++}$  in 0.1M KCl containing 0.01% gelatine.

b: Rotated mercury electrode;  $1.00 \times 10^{-3} M$   $Pb^{++}$  in 0.1M KCl containing

c: Two successive AC polarograms with rotated mercury electrode without renewing;  $10^{-6} M$   $Cd^{++}$  in 0.1M KCl; superimposed AC was 280 cps, 10mv peak. Potential shift between the polarograms is artificial.

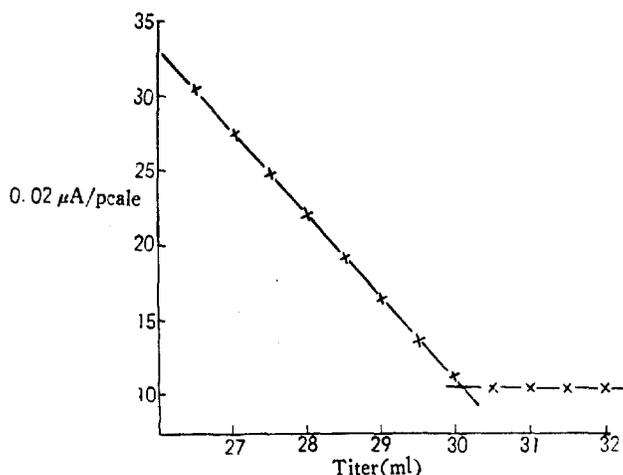


Figure 3. (a)

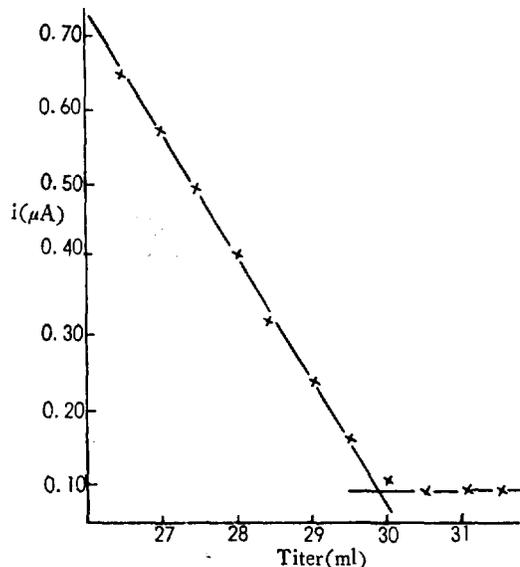


Figure 3. (b)

Figure 3. Amperometric Titration Plots. 0.50968 g Bi/1 solution with 0.6035 g EDTA/1 solution; pH=12, applied potential  $-0.20$  volt vs. SCE. Theoretical end point 30.09 ml.

a. Rotated mercury electrode, b. DME

Table 1. Polarographic Behavior of Pb(II) at Rotated Mercury Electrode; 600 rpm, 0.01% Gelatine in 0.1M KCl; Scanning Rate 0.2 volt/min. 15°C.

Concentration MM	Diffusion current constant $\mu a/mM/l$	$E'_{1/2}$ vs. SCE (-) volt	Slope volt
0.05	11.0	0.415	0.0350
0.125	10.7	0.418	.0360
0.250	10.8	0.421	.382
0.500	10.8	0.424	.0430
1.00	11.1	0.432	.0454
2.50	11.8	0.445	.0595
5.00	11.5	0.471	.0920

average=11.2,  $\sigma=4.6\%$

### Acknowledgment

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Table 2. Peak Height of Fast Scanning Polarogram with Successively Renewed Electrode surface. 1.00 mM Cd(II) in 0.2M KCl; Scanning rate 1.0 volt/min.

Run No.	Peak current $\mu a$	Deviation from average, %
1	2.53	-2.0
2	2.53	-2.0
3	2.67	+3.6
4	2.60	+0.8
5	2.57	+0.4
6	2.58	0.0
7	2.58	0.0

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