New Micro Rotating Mercury Electrode for Voltammetry

by

Q. WON CHOI

Department of Chemistry, College of Liberal Arts and Sciences, Seoul National University
(Received July 21, 1967)

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[13] is rather bulky device and the surface area of its mercury fluctuates to a considerable degree unless it is used with great care. Archer et al[14] 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.

**Experimental**

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 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, (7), (9), (10). 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.\(^{(3)}\) 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\(^{(3)}\). 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)](image-a)

**Figure 2. (a)**

![Figure 2. (b)](image-b)

**Figure 2. (b)**

![Figure 2. (c)](image-c)

**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: \(1.25 \times 10^{-4}\) M \(Pt^{2+}\) in 0.1 M KCl containing 0.01% gelatine.

\(b\): Rotated mercury electrode: \(1.00 \times 10^{-3}\) M \(Pt^{2+}\) in 0.1 M KCl containing

\(c\): Two successive AC polarograms with rotated mercury electrode without renewing: \(10^{-3}\) M Cd\(^{2+}\) in 0.1 M KCl, superimposed AC was 280 cps, 10mV peak. Potential shift between the polarograms is artificial.
Figure 3. Amperometric Titration Plots. 0.5068 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.

<table>
<thead>
<tr>
<th>Concentration MM</th>
<th>Diffusion constant μA/mL</th>
<th>E1/2 vs. SCE (volts)</th>
<th>Slope volt</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05</td>
<td>11.0</td>
<td>0.415</td>
<td>0.0350</td>
</tr>
<tr>
<td>0.125</td>
<td>10.7</td>
<td>0.418</td>
<td>0.0369</td>
</tr>
<tr>
<td>0.250</td>
<td>10.8</td>
<td>0.421</td>
<td>0.0382</td>
</tr>
<tr>
<td>0.500</td>
<td>10.8</td>
<td>0.424</td>
<td>0.0430</td>
</tr>
<tr>
<td>1.00</td>
<td>11.1</td>
<td>0.432</td>
<td>0.0454</td>
</tr>
<tr>
<td>2.50</td>
<td>11.8</td>
<td>0.445</td>
<td>0.0595</td>
</tr>
<tr>
<td>5.00</td>
<td>11.5</td>
<td>0.471</td>
<td>0.0999</td>
</tr>
</tbody>
</table>

average = 11.2, σ = 4.6%

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.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Peak Current μA</th>
<th>Deviation from average, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.53</td>
<td>-2.0</td>
</tr>
<tr>
<td>2</td>
<td>2.53</td>
<td>-2.0</td>
</tr>
<tr>
<td>3</td>
<td>2.67</td>
<td>+3.6</td>
</tr>
<tr>
<td>4</td>
<td>2.60</td>
<td>+0.8</td>
</tr>
<tr>
<td>5</td>
<td>2.57</td>
<td>+0.4</td>
</tr>
<tr>
<td>6</td>
<td>2.58</td>
<td>0.0</td>
</tr>
<tr>
<td>7</td>
<td>2.58</td>
<td>0.0</td>
</tr>
</tbody>
</table>

Acknowledgment

Acknowledgment is made of the technical assistance of H. S. Lim and H. S. Lee. The author wishes to thank the Research Institute of Mining and Metallurgy for supporting the project in part.

Literature Cited

(1) T. S. Lee, J. Am. Chem. Soc. 74, 5001 (1952)


(3) C. A. Streuli and W. D. Cooke, ibid., 25, 1961 (1953)

(4) D. Rosie and W. D. Cooke, ibid., 21, 1360 (1957)