Investigation of Oxygen Reduction Reaction on a rotating Ag/GC disk electrode in an acidic solution

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The electrochemical reduction of molecular oxygen is important especially for devices such as metal air batteries, fuel cells and air cathodes in many industrial electrocatalytic processes [1]. Even though oxygen reduction reaction (ORR) appears to be simple, it is quite complex. Finding an appropriate mechanism of oxygen reduction reaction, without having kinetic parameters and intermediate species at hand, is an impossible task. In view of the fact that this reaction is one of the important reactions, we tried to overcome this problem through computing the kinetic parameters by means of Ag/GC rotating disc electrode in 1.0 M H₂SO₄ solution. The rotation rates of the Ag/GC electrode are varied from 200 to 2500 rpm.

The current-potential curves for this electrode are shown in Fig.1 and Fig.2 shows typical K-L plots.

![Figure 1](image1.png)

Figure 1. Oxygen reduction on Ag/GC in O₂ saturated 1.0 M H₂SO₄ at a scan rate of 5 mV/s.

![Figure 2](image2.png)

Figure 2. K-L plots for oxygen reduction on Ag/GC electrode in 1.0 M H₂SO₄ at various potentials.
An equation for the complete \( i-E \) response is derived using the Nernst diffusion layer approach. The result for a reduction reaction is given in Eq. (1) [2]:

\[
\log \left( \frac{i_L}{i_0} \right) = \text{Const} + \log(C^*) - \frac{\alpha A n F}{E} \quad (4)
\]

\[
i_L - i_0 = 2.3RT
\]
This equation can be used to put i-E data from several rotation rates on to a single linear plot and the transfer coefficient can be found from the slope of the curve. The Tafel slopes and the corresponding rotation rates are given in Table 1.

<table>
<thead>
<tr>
<th>Rotation rate (rpm)</th>
<th>200</th>
<th>400</th>
<th>900</th>
<th>1600</th>
<th>2500</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tafel slope from -0.2 to -0.5 V</td>
<td>0.0597</td>
<td>0.0571</td>
<td>0.0540</td>
<td>0.0595</td>
<td>0.0597</td>
</tr>
</tbody>
</table>

Using n = 4 for the overall reduction to water, the transfer coefficient $\alpha_1$ for the Tafel slope was 0.25. The transfer coefficient can also by found evaluating the data in the mixed control region in Fig. 1. Using Tafel equation $\alpha_2$, is calculated to 0.1.

Based on relative equations we show that the reaction order changes from 0.39 to 0.31 over a potential range from -0.36 to -0.56 V with a maximum of 0.7 at a potential of -0.4 V. This indicates that the general rate equation for the reduction reaction is a function of the adsorption of oxygen to the electrode surface.

According to information, we proposed a second electrochemical step and a final chemical step, i.e. an ECE mechanism in accord with Damjanovic’s statement for oxygen reduction in acidic medium.

Keywords: Oxygen Reduction Reaction, Reaction order, Transfer coefficient, K-L plot.

Reference