An estimation of the interfacial energy of the copper–copper sulphate solution interface and of the specific surface of copper powder

K. I. POPOV1, N. D. NIKOĐIĆ2 and Z. RAKOČEVIĆ3

1Faculty of Technology and Metallurgy, Karnegijeva 4, Belgrade, P. O. Box 35-03, YU-11001 Belgrade, ICTM-Institute of Electrochemistry, Njegoševa 12, P. O. Box 815, YU-11001 Belgrade, and 3Vinča Institute of Nuclear Sciences, P. O. Box 522, YU-11001 Belgrade, Yugoslavia

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Abstract: A possible way for the estimation of the interfacial energy of the copper–copper sulphate solution interface is proposed. The estimated value of \((2.7 \pm 0.3) \text{ J cm}^{-2}\) and the derived equations which relate the specific surface of copper powder to the deposition conditions permit an estimation of the specific surface of copper powder. The agreement between the estimated value and literature data is very good.

Keywords: interfacial energy copper–copper sulphate solution, specific surface of copper powder.

INTRODUCTION

The electrodeposition of copper under mixed controlled potentiostatic conditions can be followed by the increase of the surface area for the same quantity of electrodeposited metal. This effect is especially pronounced in the limiting diffusion current density range. The energy \(e_d\) required for the deposition of metal corresponding to the quantity of electricity \(\int I dt\), where \(I\) is the deposition current density and \(t\) deposition time, is given by:

\[ e_d = \eta I dt \]  

where \(\eta\) is the deposition overpotential.

At the same time, the energy required for the formation of a copper surface \(S\), in copper sulphate solution, is given by:

\[ e_d = \gamma S \]  

and equation

\[ \gamma (S_2 - S_1) = (\eta_2 - \eta_1) \int I dt \]  

* Corresponding author. Fax: +381 11 337 03 87. E-mail address: kostad@elab.tmf.bg.ac.yu.
# Serbian Chemical Society active member.
is valid, if the deposition of the same quantity of metal at two overpotentials \( \eta_2 \) and \( \eta_1 \) produces metal deposits surfaces \( S_1 \) and \( S_2 \).

Obviously, Eq. (3) can be rewritten in the form

\[
\gamma = \frac{(\eta_2 - \eta_1)}{(S_2 - S_1)} \int I dt
\]

which can be used for an estimation of the interfacial energy of a copper – copper sulphate solution interface.

EXPERIMENTAL

Electrodeposition of copper was performed potentiostatically from 0.15 M CuSO\(_4\) + 0.50 M H\(_2\)SO\(_4\) onto a stationary platinum wire electrode \((S_0 = 0.45 \text{ cm}^2)\) in an open cell at room temperature \((18.0 \pm 1.0) ^\circ C\).

The polarization curve was determined and different quantities of copper were deposited at different overpotentials using the following procedure: The platinum substrate was covered with a thin copper film by deposition at an overpotential of 300 mV during 2 min. After a relaxation of the diffusion layer for 15 min, the current at an overpotential of 50 mV \( I_{50,0} \) was recorded, being proportional to the electrode surface area 0.45 cm\(^2\). The overpotential was then adjusted to the desired value and deposition was carried out. After the determined quantity of electricity had been reached, the overpotential was decreased to 50 mV and after relaxation of the diffusion layer for 15 min, the current, \( I_{50,0} \), corresponding to the surface \( S \) generated during deposition, was determined. The surface area of the deposit was then calculated using the equation:

\[
S = \frac{S_0 I_{50,0}}{I_{50,0}}
\]

where \( S_0 \) is the original surface area of the electrode, 0.45 cm\(^2\).

During deposition the \( I - t \) dependences were recorded and the quantity of electricity was determined by graphical integration.

RESULTS AND DISCUSSION

The polarization curve for copper deposition is presented in Fig. 1, from which the positions of the deposition overpotentials on the plateau of the limiting diffusion current density can be seen. The results of the interfacial energy determinations are given in Table I.

It can be seen from Table I that good agreement between the results of different determinations is obtained. The calculated average value of the interfacial energy, including the error of the measurements, is \((2.7 \pm 0.3) \text{ J cm}^{-2}\).

The results obtained can be verified in the following way. It is well known that at deposition overpotentials larger than some critical value, a compact deposit is not formed, rather a powdered one characterized by a very large surface area.\(^3\)\(^4\)

Hence, for \( S_2 \gg S_1 \)

\[
S_2 = \frac{(\eta_2 - \eta_1)}{\gamma} \int I dt
\]

On the other hand, the quantity of electrodeposited metal \( m \) is given by

\[
m = \frac{(A/nF)}{\gamma} \int I dt
\]
assuming a current efficiency of 1, where \( A \) is the atomic mass of the deposited metal, \( n \) is the number of electrons involved in the metal deposition reaction and \( F \) is the Faraday constant. The specific powder surface \( S_{sp} \) from Eqs. (5) and (6) is obviously:

\[
S_{sp} = \frac{S_{m}^{2}}{m} = \frac{(\eta_{2} - \eta_{1})mF}{\gamma A}
\]

(7)

TABLE I. The estimated values of the interfacial energy for the interface copper – copper sulphate solution

<table>
<thead>
<tr>
<th>Number of measurements</th>
<th>( I/t )/A s</th>
<th>( \eta_{2} )/mV</th>
<th>( \eta_{1} )/mV</th>
<th>( S_{2} )/cm(^2)</th>
<th>( S_{1} )/cm(^2)</th>
<th>( \gamma /l ) cm(^{-2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>8.64</td>
<td>600</td>
<td>400</td>
<td>1.03</td>
<td>0.450</td>
<td>2.98</td>
</tr>
<tr>
<td>2.</td>
<td>8.64</td>
<td>600</td>
<td>400</td>
<td>1.30</td>
<td>0.450</td>
<td>2.40</td>
</tr>
<tr>
<td>3.</td>
<td>8.64</td>
<td>650</td>
<td>400</td>
<td>1.54</td>
<td>0.450</td>
<td>2.40</td>
</tr>
<tr>
<td>4.</td>
<td>8.64</td>
<td>600</td>
<td>400</td>
<td>1.11</td>
<td>0.450</td>
<td>2.62</td>
</tr>
<tr>
<td>5.</td>
<td>8.64</td>
<td>650</td>
<td>400</td>
<td>1.41</td>
<td>0.450</td>
<td>2.25</td>
</tr>
<tr>
<td>6.</td>
<td>8.64</td>
<td>650</td>
<td>300</td>
<td>1.41</td>
<td>0.480</td>
<td>3.25</td>
</tr>
<tr>
<td>7.</td>
<td>8.64</td>
<td>600</td>
<td>450</td>
<td>1.11</td>
<td>0.540</td>
<td>2.27</td>
</tr>
<tr>
<td>8.</td>
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<td>400</td>
<td>1.30</td>
<td>0.550</td>
<td>2.88</td>
</tr>
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<td>9.</td>
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<td>400</td>
<td>1.19</td>
<td>0.550</td>
<td>2.70</td>
</tr>
<tr>
<td>10.</td>
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<td>650</td>
<td>400</td>
<td>0.970</td>
<td>0.540</td>
<td>2.51</td>
</tr>
<tr>
<td>11.</td>
<td>4.32</td>
<td>650</td>
<td>400</td>
<td>0.95</td>
<td>0.510</td>
<td>2.46</td>
</tr>
<tr>
<td>12.</td>
<td>12.96</td>
<td>650</td>
<td>400</td>
<td>1.80</td>
<td>0.770</td>
<td>3.15</td>
</tr>
<tr>
<td>13.</td>
<td>12.96</td>
<td>600</td>
<td>400</td>
<td>1.69</td>
<td>0.770</td>
<td>2.82</td>
</tr>
<tr>
<td>14.</td>
<td>12.96</td>
<td>650</td>
<td>400</td>
<td>1.875</td>
<td>0.814</td>
<td>3.05</td>
</tr>
</tbody>
</table>

According to Calusaru\(^5\) the specific surface of copper powder is 500 – 3000 cm\(^2\) g\(^{-1}\) depending on the deposition conditions. From the difference in the actual deposition
overpotential and the overpotential of the beginning of the limiting diffusion density plateau (0.80 V), the value of $\gamma$ determined in this way as 2.7 J cm$^{-2}$, the atomic mass of copper, the number of electrons 2 and $F = 96485$ C mol$^{-1}$, it is easy to calculate using Eq. (7) that $S_p = 1100$ cm$^2$ g$^{-1}$, which is in fair agreement with the findings of Calusaru.$^5$

It is obvious that using this value of the interfacial energy and Eq. (7) the specific surface of copper powder can be calculated for each deposition conditions if the deposition overpotential and the overpotential of dendritic growth initiation from the electrolyte under consideration are known. In this way, it can be seen that one of the most important characteristics of copper powder is related to the deposition overpotential and hence to the deposition conditions.

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