Research and Development Techniques 1: Potentiodynamic Studies of Copper Metal Deposition

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Summary - The electrochemistry of copper (II) ions in aqueous chloride solution at pH 2 is used to demonstrate the application of voltammetry techniques in characterising electrode processes. The electrolyte used is 1.5 M sodium chloride containing 20 to 50 x 10^{-4} M cupric chloride at 20°C, in which both Cu(II) and Cu(I) ions are stable. A platinum rotating disc electrode (RDE, radius 0.365 cm) is used to provide controlled mass transport under laminar flow conditions. Cyclic voltammetry, at a stationary disc electrode, is used to characterise the general electrochemistry. Four current peaks due to reduction of Cu(II) ions to Cu(I) ions, deposition of Cu from Cu(II) ions, anodic stripping of Cu to form Cu(II) ions and oxidation of Cu(I) ions to Cu(II) ions are seen. Analysis of the Cu(II)/Cu(I) couple indicates a reversible process. A potential sweep rate experiment allows the diffusion coefficient of Cu(I) ions to be calculated. The anodic stripping peak in the cyclic voltammogram is used to estimate the amount of copper deposited. Reduction of Cu(II) to Cu(I) then to Cu is examined at a range of rotation speeds (150-1870 rpm) using linear sweep voltammetry at the RDE. Mass transport data are obtained in the form of limiting current density as a function of the RDE speed, allowing the diffusion coefficients of Cu(II) and Cu(I) ions to be calculated.

Keywords: anodic stripping voltammetry (ASV), charge transfer control, copper deposition, copper stripping, cupric ions, cuprous ions, cyclic voltammetry (CV), Levich equation, linear sweep voltammetry (LSV), mass transport control, Randles-Ševčik equation, rotating disc electrode (RDE).

INTRODUCTION

Electrodeposition and dissolution reactions of copper involving Cu(II)/Cu(I) ions are important to many sectors of industry, including electroplating, electrorefining, marine corrosion and in the manufacture of metallic and semiconductor materials. A range of electrochemical techniques is available[1-3] to characterise the mechanisms involved in copper electrochemistry and the process variables controlling electrode kinetics. The reduction of Cu(II) can be seen as two single-electron steps or as a single two-electron step, depending on the electrolyte composition. In particular, the presence of chloride ions stabilises the Cu(I) species, and the reaction Cu(II) to Cu(I) follows two single-electron steps[4,6], in contrast to the case in chloride-free, acid sulphate media.[5]

The copper chloride electrolyte used in this investigation has a low cost and can be easily discharged to drain. For convenience, the experiments are carried out at room temperature. The stability of both Cu(II) and Cu(I) ions can be examined, providing clear insight into the understanding of the Cu(II) ion reduction mechanism and voltammetry as an electrochemical technique.

In chloride electrolytes, the reactions can be simplified to the reduction of Cu(II) - cupric ions to Cu(I) - cuprous ions (the latter being present as a dichlorocuprous anion).

\[ \text{Cu}^{2+} + 2\text{Cl}^- + \text{e}^- \rightarrow \text{CuCl}_2^-. \] (1)

Reaction (1) is followed by the reduction of Cu(I) ions to copper metal, i.e., the deposition of copper.

\[ \text{CuCl}_2^- + \text{e}^- \rightarrow \text{Cu}^0 + 2\text{Cl}^- . \] (2)

The overall process for copper deposition from Cu(II) ions in chloride electrolyte is obtained by combining reactions (1) and (2).

\[ \text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}^0 . \] (3)

Under controlled conditions, it is possible to observe the forward and reverse reactions for electrode processes (1) and (2). In practice, this means selecting an appropriate range of electrode potential together with a suitable electrolyte composition and controlled flow conditions.

In this work, a cyclic voltammetry technique is used to demonstrate the reversibility of the Cu(II)/Cu(I) redox couple and the reversible, two stage reduction of Cu(II) to Cu(I) in acid (pH 2) chloride. Steady state, linear sweep voltammetry at a rotating disc electrode is used to calculate the diffusion coefficients of Cu(II) and Cu(I) ions. The experiments demonstrate the use of simple electrochemical techniques and show how the deposition of copper can be carried out under controlled hydrodynamic conditions to provide general information on the electrochemistry of the system and to obtain kinetic data.

Table 1: Summary of experimental conditions.

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>1.5 M NaCl at pH 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk salt concentration, c</td>
<td>0.0030 M to 0.050 M CuCl₂</td>
</tr>
<tr>
<td>Density, ρ</td>
<td>1.058 g cm⁻³</td>
</tr>
<tr>
<td>Dynamic viscosity, η</td>
<td>0.0115 g cm⁻¹ s⁻¹</td>
</tr>
<tr>
<td>Kinematic viscosity, ν = η/ρ</td>
<td>0.0109 cm² s⁻¹</td>
</tr>
<tr>
<td>Temperature</td>
<td>20°C (293 K)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Electrodes</th>
<th>Pt circular disc Polished down to 0.3 microns on wet alumina</th>
</tr>
</thead>
<tbody>
<tr>
<td>Working electrode</td>
<td>WE surface</td>
</tr>
<tr>
<td>RDE radius, r</td>
<td>0.365 cm</td>
</tr>
<tr>
<td>RDE area, A</td>
<td>0.02 cm²</td>
</tr>
<tr>
<td>Rotation speed (f')</td>
<td>150 to 1870 rpm</td>
</tr>
<tr>
<td>Angular velocity (ω)</td>
<td>2.5 to 31.2 s⁻¹</td>
</tr>
<tr>
<td>Reflux electrode</td>
<td>Ag/AgCl/M NaCl</td>
</tr>
<tr>
<td>Reference electrode</td>
<td>Pt mesh (&gt;2 cm² area)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Process conditions</th>
<th>100 cm³</th>
</tr>
</thead>
<tbody>
<tr>
<td>WE compartment volume</td>
<td>5 to 110 mV s⁻¹</td>
</tr>
<tr>
<td>Potential sweep rate, dE/dt</td>
<td>Hitek 2 A/20V</td>
</tr>
<tr>
<td>Potentiostat</td>
<td>Hitek PPR 101</td>
</tr>
<tr>
<td>Potential programmer</td>
<td>PL3 (Seastall Ltd)</td>
</tr>
</tbody>
</table>

EXPERIMENTAL DETAILS

Table 1 shows the physical properties of the electrolyte. The working electrode was separated from the working electrode by a glass plate. The counter electrode was a platinum mesh (ca. 2 cm²) and a silver-silver chloride (ABB Instrumentation Ltd) reference electrode. All experiments were carried out at 293 K (20°C).

Experimental procedure

The supporting electrolyte consisted of 1.5 M NaCl at pH 2. Solutions with 2, 5, 10, 20, and 50 x 10⁻⁴ M of Cu(II) were prepared by dissolution of CuCl₂, followed by volumetric dilution. All of the reagents used were Analytical Reagent grade (Fisher Chemicals). Prior to each experiment, the working electrode (platinum disc) was manually polished with wet alumina powder on a polishing cloth, followed by rinsing with deionized water until its surface had a mirror finish. The solution was purged with a fast stream of dispersed nitrogen gas for 5 minutes before each experiment to avoid interference from the oxygen reduction reaction. The nitrogen supply was maintained over the surface of the electrolyte during the course of the experiments. In the cyclic voltammetry study of the redox couple Cu(II)/Cu(I), the potential range was from -0.70 to -0.16 V vs. Ag/AgCl (all potentials quoted in this text are versus the silver-silver chloride reference electrode) at a linear potential scan rate of 5 mV s⁻¹. In the rotating disc experiments the potential of the working electrode ranged from -0.70 to -0.60 V at a scan rate of 10 mV s⁻¹.
RESULTS AND DISCUSSION

Cyclic voltammetry

Figure 2 shows a cyclic voltamgram for the reduction of 50 mM CuCl₂ in 1.5 M NaCl at pH 2 at a platinum electrode using a potential scan rate of 5 mV s⁻¹. The I-E curve shows several features. Peak 'A' represents the reduction of Cu(II) to Cu(I) commencing at 0.390 V with an approximate E₁/₂ of 0.280 V. After reaching a maximum, the current decreases as the Cu(II) adjacent to the electrode surface has been consumed and the reaction involves the bulk of the solution diffusing towards the electrode.

As the potential becomes more negative, a peak 'B' commences at -0.17 V, corresponding to the reduction of Cu(I) to Cu(0). The shape of peak 'B' is characteristic of a phase change of the reactive species. In contrast to the reduction process in 'A', where the reduction product is CuCl₂, the reduction of Cu(I) forms small nuclei of metallic copper attached to the electrode surface. These nuclei increase the area of the electrode producing a rapid increase in the current. After the peak, the current decreases in an identical manner to the reduction of Cu(II) to Cu(I).

During the reverse scan, a large anodic stripping peak 'C' is observed due to the dissolution of Cu(0) metal to Cu(I) ions. In contrast to processes 'A' and 'B', the Cu(0) reaction is not found on the electrode surface and does not need to be transposed, when the potential changes towards more positive values and metallic copper is no longer thermodynamically stable on the electrode surface. The deposited copper dissolves back into the solution resulting in a drop in the observed current. It should be noted that the reverse and forward curves cross over the same potential value just before the dissolution of copper commences. In contrast to the case of carbon electrodes, there is no nucleation loop as the deposition of copper is thermodynamically favourable at negative potentials from this point due to the use of platinum as an electrode material. In the case of electrode materials such as vitreous carbon, an overpotential of up to 0.2 V from the point in which the dissolution starts would be necessary to induce the formation of copper nuclei during the reduction process.

More positive potentials result in the oxidation of Cu(I) to Cu(II) represented by peak 'D'. After the maximum value, the current decreases in a similar manner to processes 'A' and 'B', due to the depletion of the reactive species on the electrode surface.

Figure 2 shows two electrochemical processes involving soluble/insoluble species, and two processes involving soluble species, each process can be analysed independently by selecting the appropriate technique and potential range. The evaluation of the area under the curve for the dissolution of copper, peak 'B', and the curve for the dissolution of copper, peak 'C', shows that, in both cases, the electrical charge q was 0.0649 C (Fig. 2). During the deposition of Cu(II) to Cu(I), the layer of copper on the electrode surface was visible. Nevertheless, the concentration of copper ions in solution remained constant as the thickness of the layer was 0.12 µm representing only 0.013% of the dissolved copper in the electrolyte solution. Hence, the bulk Cu(II) ion concentration can be considered to remain constant throughout the experiments.

Figure 3 shows a family of cyclic voltammograms for the redox process Cu(II) → Cu(I), corresponding to peaks 'A' and 'D' in Figure 2. The potential was swept from +0.70 V towards negative values and reversed at -0.16 V avoiding the formation of metallic copper. The potential scan rate was controlled at values in the range 10 to 110 mV s⁻¹ at 10 mV intervals. At low scan rates, the reduction product has more time to diffuse towards the bulk solution and the amount available for the oxidation is less resulting in a relatively smaller oxidizing peak. The ratio between cathodic and anodic peak currents I_p/I_w was approximately 0.95 at the lowest scan rate and approximates to 1 at the highest scan rate. A study of peaks 'A' and 'D' shows that both cathodic and anodic currents increase linearly with the square root of the sweep rate ν₁/₂ according to the Randles-Sevčik equation.

\[ I_p = 2.69 \times 10^5 z^2 D^1/2 ν^{1/2} c \]  

(4)

as shown in Figure 4. I_p is the peak current, z the number of electrons, D the diffusion coefficient, ν the potential scan rate and c the concentration. The diffusion coefficients for Cu²⁺ and CuCl₂ species calculated from the slopes of the curves from Figure 4, via equation (4), were (4.2 ± 0.2) x 10⁻⁶ and (4.3 ± 0.2) x 10⁻⁶ cm² s⁻¹. These were obtained using the cathodic and anodic
branches, respectively and are reported in Appendix 2 where they are compared with data obtained as detailed in the following section.

Cyclic voltammetry at a rotating disc electrode
Figure 5 shows a typical family of I-V curves for the reduction of 2 mM Cu(II) to Cu(I) at rotation frequencies from 150 to 1870 rpm (2.5 to 31.2 Hz; 16-192 rad s⁻¹). the potential was scanned from +0.70 to -0.50 V at a scan rate of 10 mV s⁻¹. For the lowest rotation rate, 130 rpm (α = 0.16); the reduction of Cu(II) ions to Cu(I) ions, process A, starts at approximately the same potential as in the cyclic voltammogram shown in Figure 2. The reduction process is observed as a constant current plateau region rather than a peak, since the continuous rotation of the electrode maintains a constant supply of Cu(II) ions to the surface of the disc.

As the electrode potential becomes more negative, the reduction of Cu(I), process B, appears at a potential of approximately -0.24 V Cu(I) species on the electrode surface are reduced to Cu(0), generating another plateau region, which is less well defined as it is affected by a secondary reaction, hydrogen evolution. It should be noted that at this potential the processes A and B take place at the same time, the rotation of the electrode brings Cu(II) ions from the bulk of the solution to the electrode surface which is immediately reduced to Cu(I) ions and then to Cu(0) metal in the solution conditions, the reduction of Cu(II) ions appears as a single step of two electrons and the current of the step B of Figure 5 is approximately twice the size of the current in process A. The two plateau regions are characterised by a limiting current value, which is proportional to the rate at which the reactant species reach the electrode surface. Under these conditions the reaction rate is limited by the rate of mass transport and the limiting current value can be predicted by the Levich equation,

\[ I = \frac{2.69 \times 10^{-5} nF^2D^{0.5}v^{1/2}c^{0.5}}{w^{1/6} \eta^{1/2}} \]

where \( I \) is the limiting current, \( n \) the Faraday constant, \( \omega \) the rotation rate and \( \eta \) the kinematic viscosity of the electrolyte. At higher rotation frequencies, \( \omega > 150 \text{ rpm} \), \( \eta \approx 3 \times 10^{-5} \text{ m² s}^{-1} \), the I-E curves have a similar shape and the supply of electroactive species to the electrode surface is faster resulting in higher limiting currents; the stagnant diffusion layer adjacent to the electrode surface reduces its thickness as the rotation rate increases. Figure 6 shows the limiting current values plotted against \( \omega^0 \) for the process A', B' and A minus B' from Figure 5, where A corresponds to the reduction of Cu(II) ions to Cu(I) ions, B corresponds to the total current of the reduction of Cu(II) ions to Cu(I) metal which appears as one single step of two electrons and A minus B' corresponds to the current for the process Cu(I) to Cu(0). The linear correlation between \( I \) and \( \omega^0 \) shows that in these reduction processes the mechanisms are mass transport controlled. Similar curves to those presented in Figure 5 were obtained for concentrations of 5, 10, 20 and 50 x 10⁻³ M Cu(II) and their corresponding plot of \( I \) vs. \( \omega^2 \) shows that they are completely mass transport controlled.

The diffusion coefficients values for Cu⁺ and the CuCl₂ ion obtained from cyclic voltammetry at a stationary disc electrode and from linear sweep voltammetry at a rotating disc electrode for species are comparable. Table 2 lists the diffusion coefficient values for CuCl₂ and Cu²⁺ species determined by electrochemical techniques both from this work and from the literature. The majority of the literature \( D \) values for CuCl₂ in aqueous chloride media near room temperature are in the range of (4.1 ± 10) x 10⁻⁶ cm² s⁻¹, in agreement with the values obtained in the present work. Electroanalytical literature cited in the past has contained values for diffusion coefficients, as high as (14.2 x 10⁻⁶ cm² s⁻¹)⁻¹. The diffusion coefficients values for Cu⁺ from this work and from the literature are within the range (4.1 ± 1.4) x 10⁻⁴ cm² s⁻¹.

Effect of Cu(II) concentration and electrode rotation frequency on the limiting current
Figure 7 shows a family of curves for \( I \) vs. \( \omega^2 \) for the reduction of Cu(II) to Cu(I) at different Cu(II) concentrations. The limiting currents increase proportionally to the concentration. For example, at constant rotation frequency of \( \omega = 4 \text{ Hz} \), the limiting current of a 50 mM solution is 10 times the limiting current at a 5 mM solution.

Similarly, Figure 8 shows a family of curves of \( I \) vs. \( \omega^0 \) for the reduction of Cu(II) to Cu(I).

### Table II: Diffusion coefficients for Cu(II) and CuCl₂ ions

<table>
<thead>
<tr>
<th>Species</th>
<th>( D_{Cu(II)} ) [10⁻⁶ cm² s⁻¹]</th>
<th>( D_{CuCl_2} ) [10⁻⁶ cm² s⁻¹]</th>
<th>Electrolyte conditions technique etc.</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(II)</td>
<td>4.1 ± 0.2</td>
<td>4.2 ± 0.2</td>
<td>Cyclic voltammetry (Figure 3), Pt, 293 K</td>
<td>This work</td>
</tr>
<tr>
<td>CuCl₂</td>
<td>5.6</td>
<td>5.3</td>
<td>RDE, 5 mM CuSO₄, pH 3.0, Pt, 293 K</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>7.4 ± 0.1</td>
<td>11.8</td>
<td>RDE, 10 mM CuSO₄, pH 3.0, Pt, 293 K</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>5.7</td>
<td>0.8 M NaSO₄, pH 3.5</td>
<td>Chronopotentiometry (Figure 4), Pt, 293 K</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td>7.5 ± 0.01</td>
<td>14.2 ± 0.06</td>
<td>Chronopotentiometry (Figure 4), pH 3.0, Pt, 293 K</td>
<td>14</td>
</tr>
<tr>
<td></td>
<td>7.8 ± 0.001</td>
<td>13.3 ± 0.03</td>
<td>RDE and Chronopotentiometry, CuSO₄ infinite dilution, 0.5 M H₂SO₄, 293 K</td>
<td>14</td>
</tr>
<tr>
<td></td>
<td>7.35 ± 0.18</td>
<td></td>
<td>RDE and Chronopotentiometry, CuSO₄ infinite dilution, 0.5 M H₂SO₄, 293 K</td>
<td>18</td>
</tr>
<tr>
<td>CuCl₂</td>
<td>5.3</td>
<td>5.9</td>
<td>CuCl₂, 0.1 to 10 M NaCl at 296 ± 1 K</td>
<td>19</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>0.5 to 2 M in x M HCl at 298 K</td>
<td>CuCl₂, 0.1 to 2 M in x M HCl at 298 K</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>CuCl₂, see water 298 K</td>
<td>CuCl₂, see water 298 K</td>
<td>21</td>
</tr>
</tbody>
</table>
ions at a series of rotation frequencies. The slope of the curves increases with the rotation rate. The relationship between the limiting current and concentration can be expressed as:

$$I_L = k_w n A D c$$  \(6\)

where, \(k_w\) is the mass transport coefficient.

Appendix 2 shows the slopes of the curves of Figure 8 and the values of the mass transport coefficients calculated for the reduction of Cu(I) ions to Cu(0) ions and 

$$c$$ Bulk reactant concentration (mol cm$^{-3}$) 

$$D$$ Diffusion coefficient \(\text{cm}^2 \text{s}^{-1}\) 

$$E$$ Electrode potential (V) 

$$f$$ Faraday constant \(96485 \text{ C mol}^{-1}\) 

$$I$$ Current \(\text{A}\) 

$$I_p$$ Peak current (in cyclic voltammetry) \(\text{A}\) 

$$j$$ Current density \(\text{A cm}^{-2}\) 

$$k_w$$ Mass transport coefficient \(\text{cm} s^{-1}\) 

$$r$$ Radius of rotating disc electrode \(\text{cm}\) 

$$n$$ Number of electrons 

$$\alpha$$ Rotation rate of RDE \(\text{rad s}^{-1}\) 

$$\nu$$ Kinematic viscosity of electrolyte \(\text{cm}^2 \text{s}^{-1}\) 

CONCLUSIONS

The voltammetry experiments show that the first step in the reduction of Cu(I) ions to Cu(0) ions is a reversible process and follows the Randles-Shevko equation. The stabilisation of Cu(0) in chloride media allows the observation of the reduction of Cu(I) to Cu(0) ions (and the reverse process) in rotating disc electrode experiments. The reduction current follows the Levich equation, indicating that the processes are mass transport controlled. The diffusion coefficients calculated from cyclic voltammetry at a stationary disc and from rotating disc electrode techniques are similar for Cu(I) ions. The values of the diffusion coefficients calculated here are comparable to those reported in the literature although reported diffusion coefficients vary over a large range depending on the authors and the experimental conditions. The amount of electroactive species deposited during the reduction of Cu(I) to Cu(0) was negligible in comparison with the concentration of the bulk solution. The use of a platinum electrode shows that there is no need to impose an overpotential on the electrode, in order to deposit Cu(0), as a result no nucleation loop is observed as in the case of other electrode materials, such as vitreous carbon.

ACKNOWLEDGEMENTS

The authors are grateful to Professor Derek Fletcher (University of Southampton) for early discussions on the electrochemistry of Cu(I)/Cu(0) in chloride electrolytes.

List of Symbols

Symbol | Meaning | Units
--- | --- | ---
$A$ | RDE area \((\pi r^2)\) | cm$^2$
$c$ | Bulk reactant concentration | mol cm$^{-3}$
$D$ | Diffusion coefficient | cm$^2$ s$^{-1}$
$E$ | Electrode potential | V
$f$ | Faraday constant | 96 485 C mol$^{-1}$
$I$ | Current | A
$I_p$ | Peak current (in cyclic voltammetry) | A
$j$ | Current density | A cm$^{-2}$
$k_w$ | Mass transport coefficient | cm s$^{-1}$
$r$ | Radius of rotating disc electrode | cm
$n$ | Number of electrons |
$\alpha$ | Rotation rate of RDE | rad s$^{-1}$
$\nu$ | Kinematic viscosity of electrolyte | cm$^2$ s$^{-1}$

REFERENCES

Appendix 1: Tables of Voltammetry Data

'\(\alpha\)' (corresponding to Figure 7): Cu(II) \(\rightarrow\) Cu(I)

\[
\begin{array}{cccccc}
\text{(\text{mM} \text{ s}^{-1})^{1/2}} & \text{2mM} & \text{5mM} & \text{10mM} & \text{20mM} & \text{50mM} \\
4.0 & 0.122 & 0.305 & 0.58 & 1.14 & 3.04 \\
6.0 & 0.180 & 0.460 & 0.87 & 1.72 & 4.56 \\
8.0 & 0.236 & 0.605 & 1.14 & 2.58 & 5.84 \\
10.0 & 0.292 & 0.750 & 1.43 & 2.86 & 7.32 \\
12.0 & 0.350 & 0.895 & 1.72 & 3.42 & 8.64 \\
14.0 & 0.406 & 1.045 & 2.00 & 4.00 & 9.90 \\
16.0 & & & & & 10.95 \\
\end{array}
\]

'B' (corresponding to Figure 8): Cu(II) \(\rightarrow\) Cu(I)

\[
\begin{array}{cccccc}
\text{(\text{mM} \text{ s}^{-1})^{1/2}} & \text{2mM} & \text{5mM} & \text{10mM} & \text{20mM} & \text{50mM} \\
4.0 & 0.256 & 0.610 & 1.190 & 2.30 & 6.04 \\
6.0 & 0.368 & 0.915 & 1.730 & 3.46 & 9.06 \\
8.0 & 0.480 & 1.210 & 2.300 & 4.58 & 11.92 \\
10.0 & 0.592 & 1.500 & 2.900 & 5.78 & 14.80 \\
12.0 & 0.712 & 1.800 & 3.470 & 6.92 & 17.68 \\
14.0 & 0.820 & 2.095 & 4.045 & 8.08 & 20.40 \\
16.0 & & & & & 22.40 \\
\end{array}
\]

'B minus \(\alpha\)' (by calculation): Cu(II) \(\rightarrow\) Cu(I)

\[
\begin{array}{cccccc}
\text{(\text{mM} \text{ s}^{-1})^{1/2}} & \text{2mM} & \text{5mM} & \text{10mM} & \text{20mM} & \text{50mM} \\
4.0 & 0.134 & 0.305 & 0.610 & 1.16 & 3.00 \\
6.0 & 0.188 & 0.455 & 0.860 & 1.74 & 4.50 \\
8.0 & 0.244 & 0.605 & 1.160 & 2.30 & 6.08 \\
10.0 & 0.300 & 0.750 & 1.470 & 2.92 & 7.48 \\
12.0 & 0.362 & 0.905 & 1.750 & 3.50 & 9.04 \\
14.0 & 0.414 & 1.050 & 2.045 & 4.08 & 10.50 \\
16.0 & & & & & 11.45 \\
\end{array}
\]

Appendix 2: Specimen Calculations

Diffusion coefficient of Cu(II) ions from cyclic voltammetry at a stationary disc electrode, using the Randles-Sevcik equation.

Slope of cathodic \(I_0\) vs. \(v^{1/2}\): \(0.01136 \text{ A V}^{1/2} \text{ s}^{-1/2}\)

Cathodic: \(D_{\text{cat,ar}} = (4.1 \pm 0.2) \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}\)

Anodic: \(D_{\text{an,ar}} = (4.2 \pm 0.2) \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}\)

Diffusion coefficient of Cu(II) ions from linear sweep voltammetry at an RDE using the Levich equation.

\[
\begin{array}{cccc}
\text{[Cu(II)] / mM} & D_{\text{Cu(II)}} / 10^{-6} \text{ cm}^2 \text{ s}^{-1} & D_{\text{Cu(II)}} / 10^{-6} \text{ cm}^2 \text{ s}^{-1} & D_{\text{Cu(II)}} / 10^{-6} \text{ cm}^2 \text{ s}^{-1} \\
& \text{'A'} & \text{'B'} & \text{'B minus A'} \\
2 & 4.3 \pm 0.2 & 4.3 \pm 0.2 & 4.3 \pm 0.2 \\
5 & 4.6 \pm 0.2 & 4.6 \pm 0.2 & 4.6 \pm 0.2 \\
10 & 4.4 \pm 0.2 & 4.4 \pm 0.2 & 4.4 \pm 0.2 \\
20 & 4.4 \pm 0.2 & 4.5 \pm 0.2 & 4.5 \pm 0.2 \\
50 & 3.9 \pm 0.2 & 4.2 \pm 0.2 & 4.5 \pm 0.2 \\
\end{array}
\]

Mass transport coefficient for Cu(II) reduction from limiting current vs. concentration plot of linear sweep voltammetry data at an RDE.

\[
\begin{array}{cccc}
\text{f/rev min}^{-1} & \text{a/\text{rad s}^{-1}} & \text{a/\text{rad s}^{1/2}} & \text{Cu(II)} \rightarrow \text{Cu(I)} \\
\text{Slope of} & \text{Slope of} & \text{Cathodic} & \text{Anodic} \\
I_0 \text{ vs. } c & k_w & I_0 \text{ vs. } c & k_w \\
& & \text{mA cm}^{-2} \text{ cm}^{-1} & \text{mA cm}^{-2} \text{ cm}^{-1} \\
153 & 16 & 4 & 60.2 & 1.5 \\
344 & 36 & 6 & 90.4 & 2.2 \\
611 & 64 & 8 & 116.4 & 2.9 \\
955 & 100 & 10 & 145.9 & 3.6 \\
1375 & 144 & 12 & 172.6 & 4.3 \\
1490 & 156 & 14 & 198.4 & 4.9 \\
\end{array}
\]

\[
\begin{array}{cccc}
\text{Cu(II)} \rightarrow \text{Cu(0)} \\
\text{Slope of} & \text{Cu(II)} \rightarrow \text{Cu(0)} \\
I_0 \text{ vs. } c & k_w \\
& \text{mA cm}^{-2} \text{ cm}^{-1} \text{ s}^{-1} \\
59.7 & 1.5 \\
90.0 & 2.2 \\
121.7 & 3.0 \\
149.6 & 3.7 \\
180.9 & 4.5 \\
210.1 & 5.2 \\
\end{array}
\]