Factors affecting the electrochemical behaviour of copper anodes under simulated electrorefining conditions

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Cyclic voltammetry (CV) was used to characterize the behaviour of copper anodes during electrorefining. The method involved cycling the anode potential at a rate of 2 mV s\(^{-1}\) between the open circuit potential of \(-0.35\) V and 0.0 V vs mercury/mercurous sulphate (MSE) reference electrode. Reproducible electrochemical characteristics for pure copper anodes of different shapes, sizes and configurations (vertical vs horizontal) were determined. Passivation time measurements indicated a strong correlation between the CV profile and the ease of anode passivation. The size, shape and geometrical configuration of the anode impact significantly on the electrochemical dissolution and passivation of pure copper. An IBM compatible computer equipped with a data acquisition board was used to acquire, examine, compare, and catalogue the electrochemical data which were presented in the form of a potential–current–time spectrum rather than a conventional cyclic voltammogram. This format enhanced the clarity and readability of the results.

1. Introduction

Anode passivation during copper electrorefining is a serious problem which is sometimes encountered in all refineries. It is believed that various impurities or combinations of impurities contained in the copper anodes have a significant effect on anode passivation and on the morphology and composition of the anode slimes. The problems associated with anode impurities are expected to intensity as anodes become dirtier through expansion of custom smelting activities and the processing of impurity-rich concentrates. Hence, the primary objective of this work was to establish a body of fundamental knowledge on anode passivation that could lead to a passivation index, and hopefully, to a method of analysis of commercial anodes to predict their behaviour during electrorefining. Prior knowledge of the electrochemical characteristics of a particular batch of anodes would allow the adjustment of the electrorefining parameters (current density, temperature, etc.) to lower the energy demand.

Despite the large volume of work already reported on the properties and electrochemical behaviour of copper anodes in acidic copper sulphate solutions, the mechanism of copper anode passivation is still subject to speculation. Some researchers think that the crystallization of nonconductive copper sulphate on the anode surface is the prime cause of anode passivation [1], whereas others conclude that the passivation is due to the formation of a cuprous oxide film [2]. Furthermore, it was reported [3] that the simultaneous formation of CuSO\(_4\cdot5\text{H}_2\text{O}\), CuCl, Cu\(_2\)O and CuO with other slime components contributes to anode passivation. Chen and Dutrizac recently carried out mineralogical studies [4] of passivated and nonpassivated anodes. The surfaces of the nonpassivated anodes consisted mostly of bare copper metal. Although masses of CuSO\(_4\cdot5\text{H}_2\text{O}\) and tiny particles of Cu\(_2\)O were commonly present, they did not cover a large fraction of the anode surface. The anode slimes formed on passivated pure copper consisted of a mixture of copper powder and Cu\(_2\)O, and both phases might contribute to the passivation. Although copper powder was a prominent constituent of the anode slimes formed on pure copper, it was generally absent from commercial anode slimes. The copper powder probably formed by the disproportionation of cuprous ions according to the following:

\[
2\text{Cu}^+ \rightarrow \text{Cu}^0 + \text{Cu}^{2+} \quad (1)
\]

C\(_2\)O was the product of another reaction:

\[
2\text{Cu}^+ + \text{H}_2\text{O} \rightarrow \text{Cu}_2\text{O} + 2\text{H}^+ \quad (2)
\]

Many of the anodes examined were clearly passivated by a thin layer of Cu\(_2\)O on the anode surface. The morphology of the Cu\(_2\)O layer indicated that it formed during electrolysis and that it was not just the accumulation of the spheroidal Cu\(_2\)O particles present in the anode copper. Furthermore, the thickness of the Cu\(_2\)O layer seemed to increase when the anode was held in the passivated state for a prolonged time. This observation correlates with the results of Abe and Goto [2] who showed that the formation of Cu\(_2\)O is inhibited as long as the pure
copper anode continues to dissolve. Garneau et al. [5] noticed that the Cu$_2$O phase became detectable after multiple cyclic voltammetry sweeps, conducted between $-0.34\,V$ and $+0.5\,V$ at a speed of 50 mVs$^{-1}$. The surfaces of most passivated commercial copper anodes [4] were extensively covered either by a thick layer of CuSO$_4$.$5$H$_2$O or by a thin continuous layer of Cu$_2$O. The morphological observations indicated that the copper sulphate crystallizes directly on the surface of the copper metal during electrolysis [6]. The above discussion shows that some uncertainty still exists as to the causes of copper anode passivation and that further study is needed. Hence, the objectives of the present work were:

(i) To develop a reproducible technique using cyclic voltammetry to characterize the behaviour of copper anodes during electrorefining.
(ii) To establish reproducible electrochemical characteristics, using this technique, for pure copper anodes of different sizes, geometries and configurations that could be used later, as a standard, in comparing copper anodes containing different and various amounts of impurities.
(iii) To correlate these electrochemical characteristics with the tendency of the copper anode to passivate.

2. Experimental details

Copper rods measuring 20 cm long by 5 cm in diameter and containing various amounts of oxygen, silver, selenium and nickel were prepared for CANMET by the Noranda Technology Centre. Samples of commercial anodes were obtained from Noranda's CCR Division, from Falconbridge's Kidd Creek Division and from the Hudson Bay Mining and Smelting Co. (HBMS). A listing of the synthetic and commercial anodes used in this study is presented in Table 1. Typical impurity concentrations of the commercial anodes are presented in Table 2. Additional pure copper rods were prepared at CANMET by melting hydrogen-reduced pure cathode copper in vacuum-sealed silica tubes. These rods were 8 cm in length and 1.6 cm in diameter. Twenty-two pure copper anodes of different sizes and geometries were examined, ranging from a thin wire (surface area 0.05 cm$^2$) to a circular anode with a surface area of 2.27 cm$^2$. A listing of the pure copper anodes of different shapes, surface areas and configurations is presented in Table 3.

Anodes were prepared either by cutting rectangular sections from the cast rods or by slicing the laboratory rod samples into round pieces. The copper anodes were mounted in acrylic such that only a single face was exposed to the electrolyte. Electrical contact was achieved by drilling through the back of the acrylic mount into the copper. A brass rod was threaded into the copper and this served as the external electrical contact. The brass rod was insulated from the electrolyte by a tight-fitting sleeve of Tygon tubing which was sealed into the acrylic mount using silicone rubber. Most of the anodes were assembled in a vertical configuration although some were also mounted horizontally such that the slimes produced during electrorefining stayed on the surface of the anode. Thus the effect of these slimes on the electrochemical behaviour of the anode could be determined.

Cyclic voltammetry (CV) studies were performed using a conventional water-jacketed cell with a copper working electrode, a platinum counter electrode and a mercury/mercurous sulphate reference electrode. A Luggin capillary, the tip of which was set at a distance of 1 cm from the surface of the working electrode, was used to minimize uncompensated resistance effects. This configuration gave reproducible cyclic voltammograms and thus objective (i) of this study was achieved. A PAR 173 potentiostat-galvanostat, equipped with plug-in module M376, was used as a potentiostat allowing the anode to be maintained at various programmed potentials with respect to the reference electrode. A PAR 175 universal programmer provided various potentiodynamic voltage vs time programs. Initially the $I/V$ profiles were recorded using a Hewlett-Packard X–Y recorder. Later, the $I/V$ profiles were recorded via an analog to digital Keithley MetraByte DAS-16 board. The acquired data were analysed, graphically examined, directly compared and presented as plotter-generated graphs.

Most of the CV experiments were conducted in aqueous solutions containing 40 gdm$^{-3}$ Cu as CuSO$_4$ and 160 gdm$^{-3}$ H$_2$SO$_4$ at 65°C as these conditions approximate those used in commercial electrorefining operations. The effect of copper ion concentration on the electrochemical characteristics

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight percent in anode</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CCR</td>
</tr>
<tr>
<td>Ag</td>
<td>0.29</td>
</tr>
<tr>
<td>Se</td>
<td>0.12</td>
</tr>
<tr>
<td>O</td>
<td>0.13–0.15</td>
</tr>
<tr>
<td>As</td>
<td>0.02–0.07</td>
</tr>
<tr>
<td>Pb</td>
<td>0.066</td>
</tr>
</tbody>
</table>

Table 1. Anodes characterized by cyclic voltammetry in this study

* Pure Cu
* Cu–0.1% Ag
* Cu–0.1% Se
* Cu–0.1% O
* Cu–0.1% Ag + 0.1% Se
* Cu–1.0% Ag
* Cu–1.0% Se
* Cu–1.0% O
* Cu–0.3% Ni + 0.3% O
* CCR Commercial Anode
* Kidd Creek Commercial Anode
* HBMS Commercial Anode

Table 2. Typical concentrations of major impurities contained in the commercial anodes used in this study

* Pure Cu
* Cu–0.1% Ag
* Cu–0.1% Se
* Cu–0.1% O
* Cu–0.1% Ag + 0.1% Se
* Cu–1.0% Ag
* Cu–1.0% Se
* Cu–1.0% O
* Cu–0.3% Ni + 0.3% O
* CCR Commercial Anode
* Kidd Creek Commercial Anode
* HBMS Commercial Anode