Mesh-on-Lead Anodes for Copper Electrowinning

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ELTECH System Corporation has developed and patented a Mesh-on-Lead™ (MOL™) (Mesh-on-Lead and MOL are trademarks of ELTECH Systems Corporation) anode for primary copper electrowinning operations. Over the past five years, ELTECH has demonstrated the MOL concept with full-scale anodes at several premier commercial tankhouses. During these demonstrations MOL anodes exhibited numerous performance advantages relative to standard Pb-Ca-Sn anodes, including reduced power consumption due to lower oxygen evolution overpotential, improved cathode quality, minimized lead sludge generation, eliminated cobalt addition as a result of stabilized lead substrate, and improved current efficiency due to reduced short circuiting.

INTRODUCTION

Lead anodes of various alloys have been utilized since the inception of copper electrowinning mainly because they are inexpensive and moderately robust. The principal problem associated with standard lead anode operation centers on the fact that the anodes are consumed during electrolysis. The corrosion of the lead anode, and its associated lead oxide by-product, results in numerous quality issues that all tankhouses must deal with daily. These include: lead anode lifetime variance from 1.5 to 10 years depending on the quality of the lead anode and the tankhouse/electrolyte operation, varying current distribution due to changing electrode thickness and flatness, requirements for cobalt sulfate addition to the electrolyte to control lead anode corrosion rate, pitting corrosion along the liquid/air interface, lower copper quality due to the inclusion of lead oxide from the anode surface, and the resultant lead-oxide sludge that must be removed from the cells and handled with environmental constraints.

Various dimensionally stable anode (DSA® [DSA is a registered U.S. trademark of ELTECH Systems Corporation]) concepts have been attempted over the years for copper electrowinning. All-titanium anode structures with titanium-clad copper conductor bars, adapted from the chlor-alkali industry, were first attempted in the 1970s. These anodes were expensive and easily damaged in operation by dendritic shorts, resulting in the loss of large areas of the titanium structure. The next-generation technology was the activated lead electrode developed in the mid-1980s.[1,2] This patented technology employed catalyzed titanium sponge pressed into the surface of the lead substrate. The anodes performed well technically but were too expensive and not amenable to repair in the field.

In the late 1990s, ELTECH Systems Corporation developed an innovative hybrid anode[3] for copper electrowinning tankhouses. This hybrid anode is called Mesh on Lead (MOL). As shown in Figure 1, the MOL anode consists of titanium mesh, coated with an electrocatalyst, attached to a standard lead anode. Using the existing lead anode as a current distributor in combination with the stability of a DSA coating and the repairability of titanium mesh,[4] an economically viable alternative anode can be produced.

MOL ADVANTAGES

Over the past five years, MOL anodes have been demonstrated on a full-scale basis in commercial tankhouses to prove the advantages of this technology over standard Pb-Ca-Sn anodes. During these demonstrations the following advantages have been proven:

- Power savings of 12–17%
- Stabilization of the base lead substrate
- Elimination of cobalt sulfate addition
- Improved cathode quality (<1 ppm lead)
- Enhanced current efficiency (up to 5%)

POWER SAVINGS

The main technological advantages of a MOL anode come from the electrocatalytic coating on the titanium mesh. The coating has a lower overpotential for the evolution of oxygen than the lead dioxide formed on the Pb-Ca-Sn anodes.[5] This advantage is clearly seen in Figure 2, where plots of cell voltage versus current density from short-term

Figure 1. A photograph of a Mesh-on-Lead anode prior to testing.

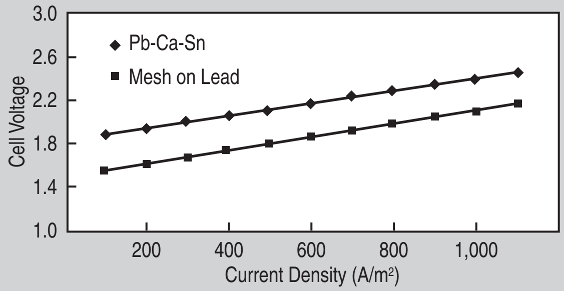

Figure 2. The current-potential curves for lead and DSA mesh-on-lead anodes in commercial copper electrowinning electrolyte containing cobalt at 42°C with 2.5 cm electrode gap.

laboratory experiments for MOL and Pb-Ca-Sn anodes in commercial copper electrowinning electrolyte are presented. The differential between anode potentials for MOL and Pb-Ca-Sn is 250–350 mV depending on the electrocatalytic coating used for the MOL anode and the condition of the lead anode. The anode potential differential between MOL and lead anodes translates directly to a lower operating voltage for a copper electrowinning cell. In turn, the lower cell voltage means power savings to a copper electrowinning facility. For example, a MOL cell operating 300 mV less than a lead cell, for which the cell voltage is typically about 2.0, would represent a power savings of ~15% since power is directly proportional to voltage.

Demonstration cells with MOL anodes have exhibited power savings at multiple tankhouses throughout North America. Power savings and duration of testing at four tankhouse demonstrations are presented in Table I. The commercial cell demonstrations exhibited average power savings of 12–17% over test durations of 12–16 months.

LEAD STABILITY

Besides producing power savings, the lower oxygen overpotential of a MOL anode also stabilizes the lead substrate. During standard service a lead anode will form a surface layer of lead dioxide. Flakes of this oxide will detach from the surface resulting in lead contamination of the cell and copper cathode. With an attached electrocatalytic mesh, the MOL structure stabilizes the lead substrate by maintaining the electrode potential below the thermodynamic potential at which lead sulfate converts to lead dioxide.

The stabilization of the lead substrate has been demonstrated in numerous tankhouses by monitoring the accumulation of lead sludge at the bottom of a MOL cell and a cell with standard lead anodes. During one three-month test period, a lead cell accumulated around 100 kg of sludge material while a MOL cell had less than 1 kg, some of which may have entered the cell from the incoming contaminated electrolyte. In addition, full-scale MOL cells have been operated for 12–16 months without cell cleaning or effect on cathode quality. Stabilizing the lead substrate produces several benefits, including extending the useful life of the lead substrate from 1.5–10 years for a traditional lead anode to a projected 10–20 years, minimizing corrosion at the liquid/air interface, decreasing downtime since cell cleaning will essentially be eliminated, and greatly reducing the generation of lead sludge, a hazardous material.

COBALT-FREE OPERATION

Another advantage of stabilizing the lead substrate through lowering the oxygen overpotential is the ability to operate without the addition of cobalt to the commercial electrolyte. It is well known in the industry that cobalt lowers the operating potentials of lead anodes and minimizes their corrosion. Unfortunately, cobalt has to be replenished, as it is lost to bleed streams, filter back wash, and electrolyte drag out. Standard copper electrowinning practice is to routinely add cobalt sulfate to the electrolyte to maintain the desired concentration. With MOL anodes, cobalt is not needed to stabilize the lead substrate. This results not only in a significant cost savings but also allows a higher electrolyte bleed rate to control other impurities, such as iron, that affect current efficiency.

MOL anodes have produced London-Metals-Exchange-grade copper from “cobalt-free” (e.g., no cobalt added) electrolyte both in commercial and laboratory-scale testing. The commercial-scale testing was conducted at a facility with full-size anodes and cathodes over a three-month period. During this test the MOL anodes displayed stability of the base lead. Besides the commercial-scale experiment, cobalt-free testing has been conducted on a continuous basis in ELTECH’s laboratory pilot cell facility. MOL anodes have operated in cobalt-free electrolyte for approximately nine months with no appreciable corrosion to the lead substrate.

CATHODE QUALITY

By eliminating the generation of lead-oxide flakes, MOL anodes remove a major source for lead contamination of the copper cathode. Lead is one of the two major impurities of electrowon copper cathode, the other being sulfur from the electrolyte. Lead is incorporated into the cathode through physical entrapment of lead-oxide flakes. By stabilizing the lead surface, the MOL anode eliminates the production of lead-oxide flake and thus produces copper with fewer lead impurities. This has been established at several tankhouses throughout the last five years. In one of the larger demonstrations over five months of testing, four MOL cells produced a median lead concentration of 0.8 ppm while four cells with new lead anodes produced a median value of 1.6 ppm. It is unknown what lead concentration could be achieved if an entire commercial circuit converted to MOL anodes. However, the three months of full-scale cobalt-free testing resulted in median lead concentrations of 0.4 ppm at current densities of 215 Am^{-2}and 320 Am^{-2}.

CURRENT EFFICIENCY

Probably the most interesting of all the advantages observed during the

Table I. Average Power Savings and Duration of Testing at Four Tankhouses in North America

	Average Power Savings	Testing Duration (months)
Tankhouse 1	12%	12
Tankhouse 2	14%	14
Tankhouse 3	17%	15
Tankhouse 4	12%	16

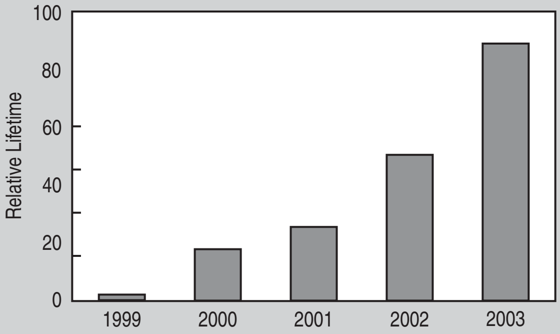

Figure 3. The coating lifetime improvement for a RuO_2-based coating shown by plotting relative lifetime by year. Lifetime is based on laboratory-accelerated testing.

demonstrations of MOL anodes was an improvement in current efficiency of 0–5% at multiple tankhouses. This improvement is believed to result from a decrease in short circuiting in a cell equipped with MOL anodes. It is well known that premier tankhouses can minimize short circuiting utilizing traditional lead anodes. In these operations MOL anodes would not be expected to increase current efficiency. However, more typical operations would be expected to observe a 1–3% improvement in current efficiency. This advantage will be a substantial economic benefit to mining operations that are limited by tankhouse capacity.

ANODE LIFETIME

While the last five years of testing have demonstrated the MOL anode advantages, they have also indicated the importance of anode lifetime. As shown in Table I, the test cells lasted for 16 months or less before a loss of electrocatalytic advantage over lead anodes. A major focus of ELTECH's development has thus been on creating an anode with an economic lifetime.

The lifetime of a coated titanium material is governed by several factors. The first is the stability of the electrocatalytic coating itself. Loss of the coating can occur by mechanical means (e.g., through abrasion/erosion, which is rare) or through chemical means by species in the electrolyte. For example, high fluoride concentrations are known to undercut the coating and thus de-bond it from the substrate. Traditionally oxygen-evolving DSA coatings contain high amounts of IrO_2, like those used in the electrogalvanizing industry.[6] While an IrO_2 coating may afford long lifetimes at the relatively low current densities of copper electrowinning, such coatings are cost prohibitive and do not provide sufficient power savings. RuO_2-based electrodes, on the other hand, have very good power savings but typically have very short lifetimes under oxygen-evolution conditions. RuO_2-based coatings have a stability limit imposed by the electrochemical oxidation of the Ru^{+4} component to higher oxidation states. The fundamental requirement in developing coatings for oxygen evolution using RuO_2 is to decrease the electrochemical dissolution (i.e., stabilize the ruthenium). For the chlorine reaction, the principal use of RuO_2 coatings for the past 35 years, this is often achieved with the addition of TiO_2. However, when used for oxygen evolution, the wear rate is high resulting in relatively short lifetimes. Development efforts at ELTECH have sought other methods to stabilize RuO_2 coatings. These efforts have been successful and led to extended lifetimes of RuO_2-based oxygen-evolving coatings in accelerated testing, as shown in Figure 3.

As the stability of the coating is improved, the ultimate lifetime of the anode is limited by passivation of the titanium surface at the substrate/coating interface. Passivation occurs due to the growth of a resistive TiO_2 layer at the interface resulting in voltage escalation, which effectively terminates the anode's use. Under extreme conditions, this layer can be observed microscopically in cross sections but its effects on voltage usually occur with very thin layers (approximately tens of nanometers) due to the high resistance of TiO_2. This layer can be detected, not only by the increase in voltage, but also by the use of electrochemical impedance spectroscopy.[7] In the case of electrowinning with a MOL electrode, total passivation is not expected. As the anode begins to passivate the voltage differential between the active mesh and the underlying lead substrate will decrease until the point at which the lead becomes active. Experience in commercial tankhouses indicates that this will occur as the voltage differential drops to 40–70 mV. This actually is a built-in safety factor for the MOL technology. In other applications involving all-titanium structures, passivation effectively shuts down the process until the anode is replaced. For electrowinning, though, copper production can continue unabated until the mesh is replaced, although the risk of lead contamination will increase in cobalt-free electrolyte.

CONCLUSION

The aforementioned advances in coating technology are being evaluated in various tankhouses. If these prove successful, a large-scale commercial demonstration of the MOL anode technology will occur in 2004.

References

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