Will Lead-Based Anodes Ever Be Replaced in Aqueous Electrowinning?

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Lead anodes have been employed in commercial aqueous electrowinning for close to a century. In the past three decades, several attempts have been made to replace lead anodes with other materials. For the most part, the use of other anodes, particularly coated titanium anodes (CTAs), has been limited to niche electrowinning applications. This article will review electrowinning processes that employ coated titanium anodes and evaluate metal electrowinning systems from a coated titanium anode perspective, including recent attempts at replacing lead-based anodes. Finally, a general economic evaluation of CTAs and lead anodes will be presented and areas for future research will be identified that could hasten the replacement of lead-based anodes in aqueous electrowinning systems.

INTRODUCTION

The electrowinning of metals from aqueous solutions has been practiced for over a century. It is the main recovery method for zinc and plays a significant role in gold, silver, copper, nickel, and cobalt recovery. The anode used in each of these systems is mainly dependent on the electrolyte composition. Generally, lead-based anodes are used in electrowinning processes that employ acidified sulfate electrolytes. Where the electrolyte is alkaline (gold), stainless steel is often utilized. When electrolytes contain significant quantities of chloride ion (nickel), coated titanium anodes (CTAs) are the norm.

Lead-based anodes dominate the aqueous electrowinning market as sulfate-based applications dwarf the other processes in terms of the number and size of the plants involved. Lead-alloy anodes are widely used because they possess many desirable characteristics, as shown in Table I. The main disadvantages of lead anodes are elevated power consumption, corrosion products fouling the cathode deposit, and generation of a hazardous by-product.

If lead-alloy anodes are to be replaced, the alternative anodes must be economically justifiable. As lead is one of the cheaper metals, replacement anodes are typically going to cost more on a material basis. Therefore, the replacement anode technology must offer economic advantages such as reduced power consumption, manpower (no sludge generation), and chemical additions, and/or longer lifetimes.

How would you…

…describe the overall significance of this paper?

This paper provides an overview of electrowinning anodes, why lead anodes are still used, technical hurdles that exist, and economics of alternative anodes.

…describe this work to a materials science and engineering professional with no experience in your technical specialty?

This paper gives an overview of attempts to replace lead-based anodes in aqueous electrowinning systems. It provides examples where replacement has occurred, and is a summary of challenges that need to be overcome. A simplified analysis is given indicating that the replacement of lead-based anodes with coated-titanium anodes is feasible at high energy prices.

…describe this work to a layperson?

In processes that recover metal by electrodeposition, lead anodes are often used. This paper looks at alternatives to lead anodes and the economic and technical challenges that must be faced.

ELECTROWINNING SYSTEMS EMPLOYING COATED TITANIUM ANODES

Currently, CTAs are employed in two industry electrowinning applications: electrowinning in chloride-based solutions and recovery of metals from dilute solutions.

Electrowinning from chloride-based solutions is primarily used at certain refineries to recover nickel, cobalt, and copper. The Kristiansand, Norway[1] and Niihama, Japan[2] refineries are examples of plants that utilize CTAs. The anode reaction in the electrowinning cells is chlorine gas evolution. The chlorine gas is captured and recycled to the matte leaching portion of the plant. These plants use CTAs since they have very low chlorine overpotentials and can exhibit long lifetimes in chlorine evolution applications.[3] Lead-based anodes, on the other hand, corrode quickly in chloride-based electrolyte and thus are not acceptable for this application.

The recovery of metals by electrowinning dilute solutions uses CTAs in cylindrical cells developed by Electrometals Technologies Limited, Queensland, Australia. Coated titanium anodes are employed because they offer the ability to operate at higher current densities and do not generate sludge, which can contaminate the product and foul the system. EMEW® cells are currently used to recover copper from rod line pickling solutions,[4] copper from electrorefinery bleed streams,[5] and silver from alkaline cyanide solutions.[6]

Previous Attempts to Replace Lead-Alloy Anodes

While CTAs are being utilized in niche applications, commercial production from sulfate-based electrolytes is still dominated by lead-based alloys. Over the past three decades, several attempts have been made to develop a CTA technology for sulfate-based electrowinning processes. The most significant technologies in terms of size of commercial testing have been standard CTAs and hybrid lead/coated titanium anodes such as MOL™.

Table I. Comparison of Anode Characteristics

Category	Lead-Based Anodes	Coated-Titanium Anodes
Material Cost	Inexpensive	Expensive
Lifetimes	2–8 years	1–3 years in copper electrowinning
Cathode Quality	Can produce high-quality products Need anode or electrolyte additives Corrosion products are main impurity	Can produce higher-quality products No observed corrosion products
Robustness	Excellent Withstands short circuits Self-healing oxide Tolerates impurities	Moderate Damaged by shorts No self-healing Susceptible to fouling
Dimensional Stability	Moderate	Excellent
Oxygen Overpotential	600–800 mV	300–500 mV
End-of-Life Disposal	Hazardous sludge Recyclable	Precious metal oxide coating typically consumed Titanium can be recycled

Information regarding the development and testing of CTAs based on standard technology (e.g., coated mesh welded to titanium-clad copper bars) is mostly proprietary. It is known that CTAs were investigated in the 1970s.[7,8] In general these anodes suffered from three problems: high initial cost of the titanium structure, susceptibility to significant shorting damage,[9] and relatively short lifetimes (~1 year). These problems made the replacement of lead-alloy anodes uneconomical.

In the past 5–10 years, another hybrid anode has been developed combining a lead substrate and coated titanium mesh.[9,10] This concept was called the mesh-on-lead or MOL anode (MOL and Mesh on Lead are trademarks of Industrie De Nora, Milano, Italy). Coated titanium mesh was spot-welded to a standard Pb-Ca-Sn anode for copper electrowinning service. MOL anodes have demonstrated the ability to operate in a cobalt-free electrolyte[11] and exhibited a 3+ year lifetime in a commercial tankhouse while saving an average of 208 mV over that life.[12] It appears that the MOL anode technology is not economical as it has not been commercially installed according to a recent copper electrowinning operating data survey.[13]

SULFATE-BASED ELECTROWINNING SYSTEMS AND CTAs

Of the attempts to replace lead-based anodes with CTAs, almost all have been in copper electrowinning systems. The main technical reason for this is electrolyte purity. Since conventional copper electrowinning electrolytes are produced by solvent extraction, the concentration of manganese in the electrolyte is significantly lower than in zinc electrowinning (10–200 mg/L vs. 2,000–5,000 mg/L). As such, the likelihood of MnO_2 deposition on CTAs is lower. Minimal deposits and the large market size appear to be likely reasons for so much CTA development for this area.

While significant research and development has occurred on CTAs for copper electrowinning, very little has been published regarding the causes for anode failure. Reference is given to electrochemical dissolution (wear) of ruthenium-based coating and passivation,[14] but no concrete discussion is given in the open literature.

While conventional zinc electrowinning appears unlikely to replace lead anodes soon because of the electrolyte's manganese concentration,[15,16] a flowsheet using solvent extraction like at the Skorpion mine in Namibia may be a candidate.[17,18] At Skorpion, manganese is added after purification to insure protection of the lead anodes. As manganese does not need to be present in systems employing solvent extraction, CTAs could provide these systems with potential economic benefits as discussed later.

Sulfate electrolytes for nickel electrowinning are also typically produced by solvent extraction. The solutions are thus fairly pure with minimal impurities, which can lead to anode depositions. While nickel electrowinning has not been a focus for CTA development, it appears to be a likely candidate. The removal of lead anodes could be operationally beneficial with reduced diaphragm fouling by lead sludge, reduced power consumption, and reduced lead contamination of the cathode.

Cobalt electrowinning would be a difficult process for CTAs due to the formation of CoOOH during electrolysis.[19] The formation of a non-conducting deposition on CTAs would lead to surface blinding and early anode failure. For CTAs to have a chance to replace lead anodes in cobalt electrowinning, a coating that can inhibit or withstand CoOOH would have to be invented. Such development seems unlikely to be pursued since the market size and thus the likely return on investment is small.

ECONOMIC EVALUATION

The previous discussions show that it is at least technically feasible for lead-based anodes to be replaced by CTAs for sulfate-based electrolytes produced by solvent extraction for zinc, copper, and nickel electrowinning. As is usually the case in mature process systems, material replacement is a question of return on investment.

The following simplified economic evaluation includes differences in material costs versus some expected operational savings. It should be stressed that the simplified analysis is only for discussion purposes. Several items are not included in both costs and savings. For example, labor and manufacturing costs of anodes are not included. Labor savings for not having to remove lead sludge are not included. Potential changes in current efficiency are not factored in as well. A detailed analysis of all items is beyond the scope of this overview. Also, each plant interested in making replacements should perform its own detailed analysis factoring in

Table II. Simplified Economic Evaluation of Replacing Lead Anodes with CTAs

	Zinc	Copper	Nickel
Materials Costs[a] ($)			
Lead Alloy Anodes[b]	992	125	167
Coated Titanium Anodes	2,022	1,124	1,124
Cost Differential (CTA-Pb Alloy)	1,030	999	957
Average Power Savings (mV)	385	210	245
Current Density (A/m^2)	500	350	250
Annual Power Savings ($)			
Scenario 1 ($0.05/kWh)	273	58	48
Scenario 2 ($0.10/kWh)	547	116	97
Scenario 3 ($0.15/kWh)	820	174	145
Other Savings ($)			
Cobalt Savings ($/y)	N.A.	271	N.A.
Projected Anode Lifetime			
Lead Alloy Anodes	3.8	5	2
Coated Titanium Anodes	2.3	3.3	5.0
Net Present Value (15% discount rate) ($)			
Scenario 1 ($0.05/kWh)	(825)	(21)	(191)
Scenario 2 ($0.10/kWh)	163	233	(86)
Scenario 3 ($0.15/kWh)	1,152	486	207
Internal Rate of Return (%)			
Scenario 1 ($0.05/kWh)	–25	14	4
Scenario 2 ($0.10/kWh)	22	23	10
Scenario 3 ($0.15/kWh)	57	31	26

a. Material costs were calculated in U.S. dollars based on spot prices in June 2008 of $0.80/lb Pb, $15/lb Ti, $3.70/lb Cu, $10/lb Sn, $45/lb Co, $17.50/troy ounce Ag, and $450/troy ounce Ir.

b. For zinc electrowinning, a Pb-0.75%Ag anode of 9 mm thickness, 1,800 mm length, and 900 mm width was chosen. For copper electrowinning, a Pb-Ca-Sn anode of 6 mm thickness, 1,000 mm length, and 900 mm width was taken. For nickel electrowinning, a Pb-Ca-Ag (0.5%) anode was selected with a thickness of 6 mm, 970 mm length, and 630 mm width.

all costs and benefits.

A summary of the simplified economic evaluation for zinc, copper, and nickel electrowinning is presented in Table II.

Electrode Material Costs

As electrowinning processes use different lead alloys and anode sizes, a typical composition and size (see Table II) for each system was chosen. Regardless of the system, each titanium anode consisted of two 2-mm-thick pieces of expanded metal mesh with 50% void area of the same length and width as the lead anode being replaced. The mesh would be attached to four titanium-clad (1 mm thick) copper bars (16 mm diameter) of the same length as the anode. The catalytic coating was assumed to be an oxide coating with a composition of 70% Ir and 30% Ta and a coating loading of 15 g Ir/m^2 of projected area on both sides of the mesh.

The material cost listed in Table II should not be construed as a selling price as it does not include manufacturing costs and profit margins. For the economic calculations, calcium (in Pb-Ca-Sn) and tantalum (in the Ir-Ta oxide coating) were assumed to have minimal cost impacts and were ignored. A copper header bar was not included in the material costs as it would be the same for each anode type in a given electrowinning system.

Operational Savings

The largest operational savings that will occur when lead anodes are replaced by CTAs will result from reduced power consumption. Power savings is related to the overpotential reduction, current density employed, and power cost. For this economic evaluation, conservative average voltage savings of 385 mV, 210 mV, and 245 mV were chosen for zinc, copper, and nickel electrowinning, respectively. Current densities of 500 A/m^2, 350 A/m^2, and 250 A/m^2 were used, respectively, for zinc, copper, and nickel electrowinning calculations. Three power cost scenarios were evaluated: $0.05/kWh, $0.10/kWh, and $0.15/kWh.

In copper electrowinning, if CTAs are used then cobalt no longer needs to be added to the circuit. In this analysis, a cobalt addition rate of 475 g of cobalt per tonne of copper plated and an 88% current efficiency were used[13] to determine the amount of cobalt that could be saved per anode.

Anode Lifetime and Recoating

The final consideration needed for an economic evaluation of lead alloy and CTAs is lifetime. For lead anodes, the average lifetime reported in two recent plant surveys were used for zinc[20] and copper electrowinning.[13] In nickel electrowinning, the lead alloy lifetime was chosen based on industrial information.[21]

For CTAs, a lifetime in copper electrowinning was chosen based on the most recent reported industrial demonstration.[12] The lifetimes in zinc and nickel were calculated assuming a linear relationship between current density and lifetime with the copper electrowinning lifetime as the reference point. The reader should remember that the lifetime in zinc electrowinning assumes the electrolyte is produced by solvent extraction and manganese is maintained at a minimal concentration. As the CTAs can be recoated and the titanium re-attached to the existing conductor bars, it was assumed the titanium would be recoated two times before new mesh and conductor bars were installed. The cost of re-coating was assumed to be equal to the material cost of iridium in the replaced coating.

Net Present Value and Internal Rate of Return

Using the aforementioned inputs, the net present value (NPV) and internal rate of return (IRR) were calculated for CTAs used as a replacement for lead anodes. The analysis was performed for a 7 year, 10 year, and 13 year period for zinc, copper, and nickel, respectively. All costs and savings were assumed to occur at the end of the year in which the value occurred. These periods of time were chosen so the re-coating cycle of the CTAs (new anodes + re-coats) corresponded to the full utilization of lead anodes.

The NPV and IRR are presented in Table II for the three power cost scenarios. It becomes apparent in this simplified economic evaluation that at higher power costs, CTAs could become an attractive replacement option to lead-based anodes in all three systems.

A closer examination of copper electrowinning replacement economics reveals that the economies are particularly interesting due to current cobalt prices. However, cobalt prices are projected to decrease as large copper-cobalt operations start up in Africa in the next 3–5 years. If cobalt prices were to drop to $25/lb, none of the scenarios presented for copper electrowinning would be attractive at a 15% discount rate.

The zinc and nickel electrowinning economics indicate that CTAs would only replace lead anodes if the power costs were relatively high. This simplified economics does not include the possibility of a premium price for cathodes with low lead content. In both nickel and zinc electrowinning, lead from the anode dissolves into the electrolyte and deposits on the cathode. The removal of lead anodes from the electrowinning cells would result in a decrease in lead contamination of the cathode. The author has been told that nickel electrowon using a Pb-Ca-Ag anode and CTAs contains 20 ppm and 3 ppm lead, respectively.[21] It is unclear if lower lead content in zinc and nickel cathodes would warrant a selling price premium and thus was not added to this economic analysis.

AREAS FOR FUTURE RESEARCH

To improve the economics of CTAs, two properties need to be improved: power savings and lifetime per dollar of material cost.

Power savings (e.g., lower oxidation overpotential) is mostly controlled by coating composition and coating microstructure. RuO_2-based coatings typically exhibit a lower overpotential relative to IrO_2-based coating.[14] However, RuO_2-based coatings tend to electrochemically dissolve during oxygen evolution. It has been reported that a stabilized ruthenium coating lasted 3+ years in a commercial demonstration, but details of the coating's composition were not given.[12] Another method to reduce IrO_2 overpotential is to increase its nanocrystallinity by decreasing the curing temperature used in the thermal decomposition process,[22] but this may lead to shorter lifetimes.[23]

Increasing the ratio of lifetime to materials cost would also improve CTA economics. For the economic analysis performed, the material cost related to the iridium coating was 70% of the total CTA cost. Substituting another metal oxide for iridium would be of interest. Historically ruthenium has been much cheaper than iridium and the recent spot price of ruthenium is approximately half that of iridium. Hence, a stabilized ruthenium coating could be economically attractive. Recently, the author's group has produced Ru-Ir oxide-coated titanium samples that exhibited 2–3 times longer life in the laboratory than Ru-Pd oxide-coated titanium[24] indicated in the patent literature for copper electrowinning. This indicates further improvement could be achieved.

IrO_2-based coatings often fail by passivation caused by the growth of a nonconducting film between the titanium substrate and metal oxide coating. Thus, a longer life with the same amount of coating could be achieved by improving the passivation resistance of the substrate. Recently, the author's laboratory showed that a passivation improvement can be achieved by thermal oxidation of the titanium substrate prior to coating.[25] Simple methods such as thermal oxidation of the substrate should be investigated further.

CONCLUSIONS

Lead alloys are the workhorse material for electrowinning anodes in aqueous-based systems. Coated titanium anodes are used in niche applications where chloride concentrations are high and/or lead corrosion is of particular concern. The replacement of lead-based anodes by CTAs appears to be technically feasible for electrolytes produced by solvent extraction for copper, nickel, and zinc electrowinning. A simplified economic analysis indicates that high energy prices may drive the replacement of lead-based anodes with CTAs. With increasing concerns about global energy supply and greenhouse gas emissions, energy prices may increase in the future, leading to the utilization of CTAs. However, applications such as conventional zinc electrowinning appear unlikely to convert to titanium anodes unless the complete removal of lead from the system is mandated.

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