Optimization of copper electrowinning from synthetic copper sulfate solution using a pulsed bed electrode

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Pedro H. Britto-Costa, Luís A.M. Ruotolo *

Department of Chemical Engineering, Federal University of São Carlos, P.O. Box 676, 13565-905 São Carlos, SP, Brazil

ABSTRACT

This paper concludes a series of investigations concerning the use of pulsed bed electrodes (PBEs) for copper electrowinning. In previous papers, the main operational parameters affecting the current efficiency (CE), space–time yield (Y), and energy consumption (EC) were identified and their effects on the performance of the process were analyzed. In light of the results, the fluidized bed time was set at 2 s and it was found that the electrode thickness should be reduced in order to achieve values of CE and EC lower than those obtained in conventional industrial processes using flat plate electrodes. In this work, the electrode thickness was reduced from 3.4 to 2.4 cm and the process was optimized using factorial experimental design and the Derringer desirability method to obtain current density (i), acid concentration (C_{ac}), and pulsed bed time (t_p) values that maximized CE and Y and minimized EC. The best C_{ac} value was 100 mg L^{-1} (a low level), while the optimum i and t_p values were 2600 A m^{-2} and 60 s, respectively (high levels). Use of these values avoided short circuit and minimized copper dissolution during fluidization. The overpotential distribution within the porous cathode was improved using the 2.4 cm electrode, and values of 100% (CE), 102 kg m^{-3} h^{-1} (Y), and 1.7 kWh kg^{-1} (EC) were achieved under the optimized conditions. These values are better than those found for flat plate electrodes.

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1. Introduction

Three-dimensional (3-D) electrodes offer a promising alternative for metal electrodeposition from very dilute solutions, due to their extended surface areas and higher rates of mass transfer (Coeuret, 1980; Coeuret and Paulin, 1988; El-Shakre et al., 1994; Evans et al., 2005; Hadzismajlovic et al., 1996; Jiricny et al., 2002; Martins et al., 2012; Olive and Lacoste, 1979; Ruotolo and Gubulin, 2002). However, little attention has been paid to metal electrowinning from concentrated solutions in hydrometallurgical processes. Although mass transfer is not a process limitation for concentrated electrolytes, the high surface area provided by 3-D electrodes leads to an improved space–time yield (Y). This means that the large electrowinning tankhouses usually found in industrial processes that employ flat plate electrodes could be replaced by a few 3-D reactors, hence decreasing the reactor volume needed to produce the same amount of metal (Evans et al., 2005; Jiricny et al., 2002; Martins et al., 2012; Salas-Morales et al., 1997). The current densities that can be applied for copper electrodeposition using flat plate electrodes typically vary from 250 to 300 A m^{-2}, which therefore requires many plates in order to achieve the desired level of copper production. On the other hand, the extended surface area provided by the 3-D cathode enables the application of current densities up to 3000 A m^{-2} in 3-D reactors (Britto-Costa et al., 2014). Another

advantage is that it is not necessary to remove the electrodeposited metal from the substrate, which is often performed manually in small plants. In the case of particulate bed cathodes, harvesting the electrodeposited metal simply consists of collecting the particles at the end of a process cycle.

Another important issue in electrowinning plants is the release of acid mists that can oxidize electrical contacts, creating additional resistances, or affect the health of the operators (Evans et al., 2005; Jiricny et al., 2002; San Martin et al., 2005; Shakarji et al., 2011; Sigley et al., 2003; Wiechmann et al., 2010). The use of 3-D electrodes enables the acid mist to be easily channeled and expelled outside the process.

Three-dimensional cathodes also permit the use of fewer anode plates, compared to processes carried out using flat plate electrodes. For example, a porous particulate cathode had an estimated surface area of 920 cm^2, while the counter-electrode had a surface area of 90 cm^2 (Britto-Costa et al., 2014). In conventional electrowinning processes, the most commonly used anode is composed of PbO$_2$, which has the disadvantage of being unstable and therefore requires the addition of chemical additives to the electrolyte in order to increase its operational lifetime (Lupi and Pilone, 1997; Moats et al., 2003; Muresan et al., 2000). However, the use of additives does not prevent anode corrosion and care must be taken to prevent lead contamination of the electrodeposited metal (Lafront et al., 2010; Moats et al., 2003; Moskalyk et al., 1999). Since the use of 3-D cathodes can avoid the need for large anodes, the replacement of PbO$_2$ by dimensionally stable anodes (DSA®) based on titanium–iridium or titanium–ruthenium

* Corresponding author. Tel.: +55 16 3351 8706; fax: +55 16 3351 8266.
E-mail address: pluis@ufscar.br (L.A.M. Ruotolo).

oxides, or platinized titanium, could become economically viable. A further advantage is that the replacement of PbO$_2$ by DSA® anodes eliminates the need for chemical additives (Lupi and Pilone, 1997; Muresan et al., 2000).

Particulate 3-D electrodes have been used previously for metal electrodeposition in applications involving the treatment of effluents in which metal concentrations are very low (Britto-Costa and Ruotolo, 2011; Hadzismajlovic et al., 1996; Olive and Lacoste, 1979; Pletcher et al., 1991; Ruotolo and Gubulin, 2002). The high conductivity of the solid phase, together with high mass transfer coefficients, enables packed bed cathodes to operate at high current efficiency (Britto-Costa and Ruotolo, 2011; Ruotolo and Gubulin, 2002). Unfortunately, when the metal concentration is high (as in the case of electrowinning processes), metal deposition results in very fast clogging of the electrode pores (Hadzismajlovic et al., 1996; Ruotolo and Gubulin, 2002). The use of fluidized bed electrodes for metal electrodeposition offers a way of overcoming this problem, because clogging of the electrode can be avoided by maintaining the conducting particles in a fluidized state using an upward flow of electrolyte (Coeuret, 1980; Hadzismajlovic et al., 1996; Hutin and Coeuret, 1977; Kazdobin et al., 2000; Sabacky and Evans, 1979). However, for this type of electrode, the reaction rate is very sensitive to the fluid dynamic conditions because the conductivity of the solid phase depends on the frequency of collisions between the particles, which is mainly determined by the bed expansion (Hadzismajlovic et al., 1996; Hutin and Coeuret, 1977). In some cases, when the local difference between the solid and liquid phase potentials is positive, zones of metal dissolution can occur inside the fluidized cathode (Coeuret, 1980; Hutin and Coeuret, 1977). For these reasons, the pulsed bed electrode (PBE) has emerged as a promising alternative. This electrode benefits from the high current efficiency provided by the packed bed electrode, while avoiding electrode clogging by fluidization of the cathode (Argondizo, 2001; Coeuret and Paulin, 1988; Garfias-Vasquez et al., 2004). In this type of electrode, the packed bed is periodically fluidized by applying regular flow rate pulses generated by mechanical or electrical devices (Argondizo, 2001; Garfias-Vasquez et al., 2004), or by using special valve setups (Coeuret and Paulin, 1988). Another advantage of the use of PBEs is the continuous mixing of particles during the pulse, which enables the particles to grow uniformly.

This study describes a PBE electrochemical reactor for copper electrowinning using copper concentrations typically found in industrial hydrometallurgical processes. The operational parameters considered were the acid concentration, current density, and packed bed time. The system was designed as a single compartment reactor, with no membrane separating the catholyte from the anolyte, which minimizes capital expenditure (Tonini et al., 2013). The flow rate pulses were generated by controlling the rotation of a centrifugal pump using a logic module and a frequency inverter. Considering the state of the art, there have only been a few reports on the use of PBEs for metal electrodeposition, most of which concern the recovery of metals from dilute solutions during the treatment of effluents (Argondizo, 2001; Coeuret and Paulin, 1988). There has only been one study of the use of the PBE in hydrometallurgy (Coeuret and Paulin, 1988), but the system used for pulse generation was very different to that used in the present work. As far as we know, there have been no papers published concerning the use of membraneless PBEs or the pulsed flow rate technique proposed here.

In a previous study, Britto-Costa et al. (2014) investigated the effects of variables such as packed bed and fluidized bed times, temperature, current density, and acid concentration on the process efficiency. After all these variables had been optimized, the best current efficiency (CE) and energy consumption (EC) values obtained were 76.7% and 2.5 kWh kg^{-1}, respectively. Although the energy consumption was comparable to values found in industrial processes using flat plate electrodes, it should be possible to make further improvements using strategies to increase the current efficiency and reduce the energy consumption. The present work therefore investigates the main variables

affecting copper electrowinning, using an electrode with a thickness ~30% lower than that used in the previous work. The electrode thickness was reduced from 3.4 to 2.4 cm in an attempt to improve current penetration within the porous cathode and avoid anodic zones. The effects of acid concentration, current density, and packed bed time on CE, EC, and Y were studied using a central composite rotatable design (CCRD). Optimization of the parameters was performed using the desirability method in order to maximize CE and Y, while minimizing EC. The operational variables investigated were selected because the acid concentration influences the local particle-solution potential within the three-dimensional cathode, and therefore affects the local kinetics, while the packed bed time and current density have strong interaction effects with the acid concentration, influencing current penetration and determining whether metal dissolution will occur. In all the experiments, the fluidized bed time was maintained constant at the previously optimized value (Britto-Costa et al., 2014). Scanning electron microscopy (SEM) was used to analyze the morphology of the anode, before and after the electrowinning processes, as well as the electrodeposited copper.

2. Experimental

The pulsed bed electrochemical reactor used for copper electrowinning has been described in detail elsewhere (Britto-Costa et al., 2014). Briefly, the reactor shown in the Graphical abstract consisted of three rectangular acrylic plates assembled using bolts and nuts. The dimensions of the particulate cathode were 2.4 cm (thickness) and 4.5 cm (width). The bed heights were 8 and 12.5 cm during the packed and fluidized states, respectively.

The same electrode was used in the previous work (Britto-Costa and Ruotolo, in press), but with a thickness of 3.4 cm. Equilateral 1.0 mm cylindrical copper particles were used to form the porous cathode. Stainless steel 316 and a Ti/Ti$_{0.7}$Ru$_{0.3}$O$_2$ DSA® (DeNora, Brazil) were used as the current feeder and counter-electrode, respectively. The current density was calculated considering the area of the current feeder (4.5 cm × 8.0 cm).

An important characteristic distinguishing this reactor from many others used for metal electrodeposition is that it did not have two compartments with a membrane separating the catholyte from the anolyte (it was a membraneless reactor). There was only one separator, composed of a polyethylene mesh covered with a polyamide fabric, which was placed between the porous cathode and the counter-electrode to prevent short circuit. Advantages of this reactor configuration, compared to membrane reactors, include low cell potential, low energy consumption, ease of maintenance, and low capital expenditure because the use of expensive membranes is avoided.

The flow rate pulses were generated using a frequency inverter acting on the centrifugal pump rotation and, consequently, on the flow rate. The frequency inverter (MicroMaster MM55, Siemens) was controlled by a logic module (LOGO! 230RC, Siemens) that determined the time during which the bed remained in the packed (low frequency rotation) and fluidized (high frequency rotation) states.

2.1. Copper electrowinning

The copper electrowinning was carried out galvanostatically using a constant current source (Genesys™ 1500 W, Lambda). The cell potential (E_{cell}) was recorded every 2 s using a data acquisition system. A complete description of the experimental setup used for copper electrowinning has been provided previously (Britto-Costa et al., 2014). The schematic view of the complete experimental system is shown in the Graphical abstract.

The electrolyte was prepared using deionized water, technical grade copper sulfate, and sulfuric acid. The copper concentration ranged from 35 to 40 g L^{-1} (Cu^{2+}) and the acid concentration ranged from 100 to 180 g L^{-1}, in line with the concentrations typically used in the copper