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Energy efficiency in metal electrowinning

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The components of the electrical energy requirements for metal electrowinning are reviewed. Various energy saving measures are assessed, including the use of dimensionally stable anodes (DSA) having low oxygen overvoltages. The current–density distribution on parallel electrodes is computed as a function of the electrochemical parameters of the electrode reactions, the ionic resistivity of the electrolyte, and the internal electronic resistivity of the electrodes. The validity of the mathematical model has been experimentally verified using DSA anodes in a copper electrowinning circuit. The energy savings achievable using dimensionally stable anodes are shown to be affected greatly by the internal resistance of the anode substrate. The effects of variation of the kinetic parameters are secondary.

1. Introduction

The electrical energy consumption of the major electrometallurgical processes in use in the United States and Canada is estimated to be 5% of total generated electric energy. The electrowinning of aluminum consumes the major portion (70%) of this, followed by chloro-alkali processes (22%). Hydro-electrometallurgical processes account for the remaining 7–8%.

Several approaches to reducing energy requirements in the electrolytic industries have been developed over the past decade, with the major activity being in the chloro-alkali sector. This paper summarizes the more promising of these possibilities as applied to hydro-electrometallurgy. Particular attention is given to 'depolarization' of the electrode reactions, and to the effects of ohmic resistance.

2. The reversible potential

The voltage of an electrometallurgical cell, which relates to the total energy requirement of the process, may be represented as the sum of four principle components

$$V_A = E_{rev} + \eta_c + \eta_a + V(R_i, R_e, C) \qquad (1)$$

where V_A is the potential applied to the cell,
E_{rev} is the reversible thermodynamic potential of the overall cell reaction,
η_a and η_c are respectively the anodic and cathodic overvoltages, and
$V(R_i, R_e, C)$ denotes all other contributions to the potential including those due to ionic resistance (R_i), electronic resistance (R_e), and concentration polarization (C).

With the exception of E_{rev}, all of the factors on the right-hand side of Equation 1 depend on the current density which is necessary to achieve the desired production rate, and thus on the current efficiency of the process.

The reversible potential is determined by the anodic and cathodic reactions. Since electrowinning only requires cathodic reduction to the metallic product, there is much scope for reducing energy requirements related to the reversible potential by changing the anodic reaction which takes place. In addition, a few metals offer alternatives in the selection of the cathodic process. A series of anodic and cathodic reactions which could take place during representative non-ferrous metal electrowinning processes are recorded in Table 1.

Oxygen evolution is the most common anodic

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Table 1. Possible electrode reactions in electrowinning processes

Anodic reactions		E_0 (V)	*Cathodic reactions*		E_0 (V)
$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$	(A1)	1·23	$Cu^+ + e^- = Cu^0$	(C1)	0·52
$2Cl^- \rightarrow Cl_2 + 2e^-$	(A2)	1·36	$Cu^{2+} + 2e^- = Cu^0$	(C2)	0·34
$H_2SO_3 + H_2O \rightarrow SO_4^{2-} + 4H^+ + 2e^-$	(A3)	0·17	$Ni^{2+} + 2e^- = Ni^0$	(C3)	−0·25
$Fe^{2+} \rightarrow Fe^{3+} + e^-$	(A4)	0·77	$Co^{2+} + 2e^- = Co^0$	(C4)	−0·28
$Cu^+ \rightarrow Cu^{2+} + e^-$	(A5)	0·15	$Zn^{2+} + 2e^- = Zn^0$	(C5)	−0·76

reaction in industrial electrowinning operations in a sulphate medium. The standard electrode potential of this half-cell reaction is 1·23 V (Reaction A1 in Table 1). In a chloride medium, chlorine is generated at the anode by a reaction for which the standard electrode potential is 1·36 V (Reaction A2 in Table 1).

In recent years several hydrometallurgical processes have been developed and proposed in which the generation of oxygen or chlorine is replaced by anodic reactions requiring less energy. One of these is a process which has been developed by the Continental Oil Company for copper electrowinning from a sulphate medium [1, 2]. The anodic reaction in this process is the oxidation of sulphite ions which are formed by the dissolution of sulphur dioxide in the aqueous electrolyte. This half-cell reaction (Reaction A3 in Table 1) has a standard electrode potential of only 0·17 V, a reduction of 1·06 V from the reversible half-cell potential for oxygen evolution. The power consumption for copper electrowinning via this procedure was experimentally found to be 1·0 kW h per kilogram of electrowon metal, approximately half of that for the conventional process (2 kW h per kilogram of copper).

Another electrometallurgical process which has been developed for copper electrowinning is the electrolysis of cuprous sulphate from a water–acetonitrile mixture [3, 4]. A substantial power saving is expected using this process since the anodic reaction is oxidation of cuprous ions to cupric ions ($E_{\mathrm{rev}} = 0{\cdot}15$ V) instead of oxygen evolution ($E_{\mathrm{rev}} = 1{\cdot}23$ V). The cathodic reaction is the reduction of cuprous ions to metallic copper. This method, therefore, involves $Cu^+ \rightarrow Cu^{2+} + e$ as the anodic reaction and $Cu^+ + e \rightarrow Cu$ as the cathodic reaction, resulting in a reversible cell potential of − 0·37 V. Electrical energy consumption is claimed to be 10% of that for the conventional sulphate process.

Several hydrometallurgical methods have been developed for direct leaching of metal sulphides with ferric chloride [3–7]. The leaching medium normally contains ferric ions which are reduced to ferrous ions during the leaching process. Metal recovery in the subsequent electrowinning step can take advantage of this by using selective anodic re-oxidation of the ferrous ions to the ferric state as the anodic reaction. The oxidation of ferrous ions has a lower electrical energy requirement (Reaction A4 in Table 1) than the conventional chlorine evolution reaction (Reaction A2 in Table 1).

In summary, it is technically possible to reduce substantially the electrical energy requirements for most metal electrowinning processes by the reduction of the reversible potential through suitable modification of the electrode reactions. Modified anodic reactions are the most promising. The only cathodic reaction alternatives developed to date for the reduction of total energy requirements are copper electrowinning from cuprous ions in water–acetonitrile mixture or in strong chloride electrolyte [3, 8, 9].

3. Electrode overvoltages

The second term in Equation 1, η_c, is the cathodic overpotential. This term is normally small (approximately 100 mV) for deposition of metals such as copper, zinc, cadmium, and nickel. Thus, the cathodic overpotential does not contribute substantially to electrical energy requirements.

The anodic overvoltage is a major contributor to energy inefficiency. The anodic process in metal

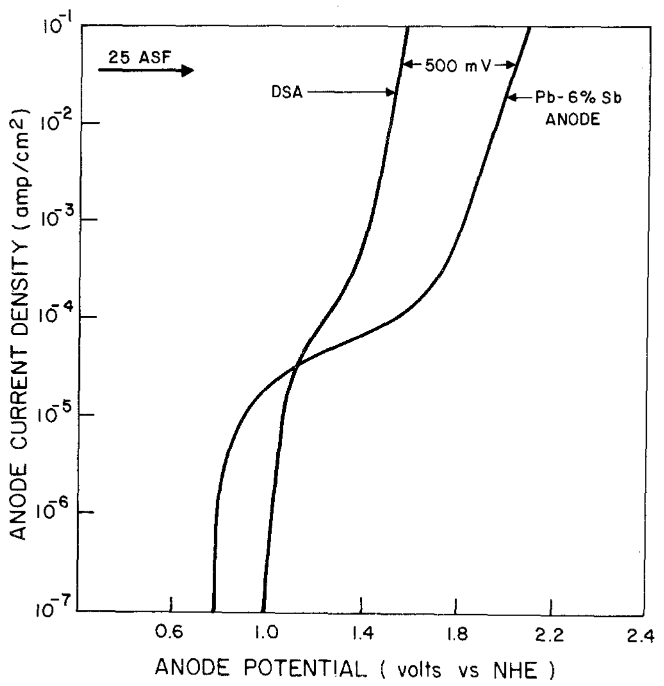

Fig. 1. Polarization measurements for the oxygen evolution reaction on a TiO_2/RuO_2 dimensionally stable anode (DSA) and a conventional lead/antimony anode. The electrolyte was $200\,g\,l^{-1}$ sulphuric acid at 25° C.

electrowinning from a sulphate medium is the evolution of oxygen, a reaction which is well known for its irreversibility. The most commonly used insoluble anode is lead, and the PbO_2 surface on this material exhibits one of the largest oxygen overpotentials known. The anodic polarization curve for a lead–6% antimony anode is shown in Fig. 1: the overpotential can be as high as 1 V. This is a major component of the energy requirement for metal electrowinning.

The addition of cobalt salts to copper electrowinning electrolytes has been found to reduce the oxygen overpotential by about 100 mV, as cobalt catalyses the oxygen discharge reaction [10]. Unfortunately, this approach cannot be used for zinc electrowinning because cobalt interferes with the zinc deposition process. Another approach which seems more attractive is the use of dimensionally stable anodes (DSA). A typical anodic polarization curve for oxygen evolution on a DSA anode is shown in Fig. 1. A 500 mV reduction in the oxygen overvoltage could be achieved. These anodes are rapidly replacing the traditionally-used graphite anodes in the chlorine industry. Their activity is chiefly due to the presence of noble-metal oxides such as IrO_2 or RuO_2 in the electrode coating. Ruthenium dioxide exhibits the lowest oxygen and chlorine overvoltages of any material investigated so far.

Dimensionally stable anodes are normally fabricated by thermal decomposition of a solution of noble-metal chlorides such as $RuCl_3$ or $IrCl_3$, together with a valve-metal compound containing titanium or tantalum, to produce a mixed oxide. Multiple coatings are applied to a valve-metal substrate, usually titanium. The resulting electrode activation can give substantial reductions in the energy requirements for the overall cell reaction. However, the benefit is not in general as great as that which would be expected from considerations of the electrode overvoltages alone. The limited electronic resistivity of the valve metals, and their relatively high cost, results in a limitation on the cell-voltage reduction which is economically achievable. The benefits of the anode overvoltage reduction are partially lost due to the high voltage drop which develops in the valve-metal substrate. This effect is represented by the last term of Equation 1, and its magnitude is estimated in the following section.

4. Contribution of ohmic resistance

Voltage losses in electrowinning cells result from both the resistance of the electrolyte to the passage of ions, and from the resistance of the electrodes themselves to electronic currents. For an electrowinning circuit with its normally planar, parallel electrodes, the former quantity may be estimated as

$$V_{IR} = I\rho_e d/LW \qquad (2)$$

where I is the current passing between anode and cathode,
ρ_e is the resistivity of the electrolyte, modified to take account of the contribution of evolved gases, if any,
d is the electrode spacing, and
L and W are respectively the electrode height and width.

The effect of electronic resistance can be readily estimated if it is assumed that the current density has a constant value i, independent of height in the electrowinning cell. Considering the anode defined by Fig. 2, the voltage drop across the element of height dx is

$$dV = \rho_a I_x dx/t_a W \qquad (3)$$

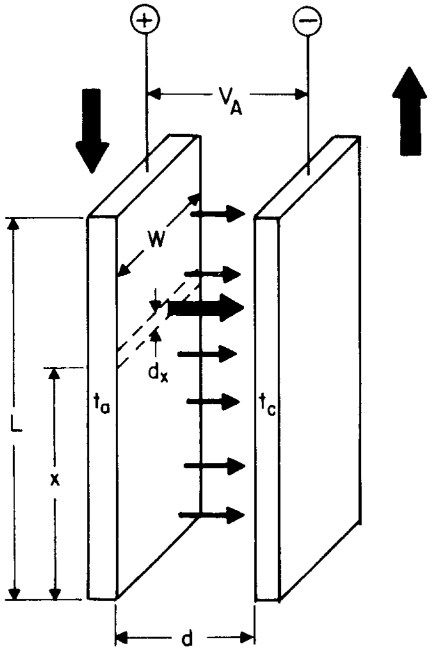

Fig. 2. Schematic representation of the current flow between parallel, planar anode and cathode elements.

where ρ_a is the electrical resistivity of the anode material, and
I_x is the total current flowing down the electrode at height x.

I_x is readily derived as the total current flowing from the anode below height x:

$$I_x = n_a i(t_a + W)x, \qquad (4)$$

where n_a is the number of sides (1 or 2) of the anode which receive current.

Substituting this expression into Equation 3 and integrating from 0 to x yields the total potential drop from the bottom of the anode to a height x

$$\Delta V = i\frac{n_a\rho_a}{2}\frac{(t_a + W)}{t_a W}x^2. \qquad (5)$$

The maximum potential drop occurs at $x = L$. Substituting, and noting that in general $W \gg t_a$,

$$\Delta V_{\max} \simeq i\frac{n_a\rho_a}{2}\frac{L^2}{t_a}. \qquad (6)$$

This result shows that the potential drop over the height of a current-carrying electrode depends on the square of the height.

In fact, the current density in an electrowinning cell is not independent of height in the cell, but tends to decrease with increasing distance from the terminal by which current is applied. This effect can be accounted for by a more rigorous analysis.

The cell potential at a height x where the current density is i_x can be written as

$$V_a(x) - V_c(x) = E_{\text{rev}} + \eta_a(i_x) + \eta_c(i_x) + V_{IR}(i_x) + V_{\text{res}}(i_x). \qquad (7)$$

The right-hand side of this equation is a single-valued function of i_x and known parameters, except for $V_{\text{res}}(i_x)$ which takes account of the effects of mass transfer limitations in solution and of gas blocking. This latter term is not considered in the following analysis. The potentials $V_a(x)$ and $V_c(x)$ are measured with respect to the contact point on the cathode (at $x = L$) which is taken to be zero potential.

The terms on the left-hand side of Equation 7 are determined by the applied voltage, the current density in the cell as a function of height, and the physical parameters of the electrode. In parallel with the derivation of Equations 3–5 above, it can be shown that

$$V_a(x) = V_A - \int_x^L \frac{\rho_a}{Wt_a}\left[\int_0^{x'} n_a(W+t_a)i_{x''}\,dx''\right]dx' \qquad (8)$$
$$\simeq V_A - \frac{n_a\rho_a}{t_a}\int_x^L\int_0^{x'} i_{x''}\,dx''\,dx'.$$

A similar result may be derived for $V_c(x)$.

The anodic and cathodic overpotentials in Equation 7 may be approximated by the Tafel equations, and the ohmic factor by

$$V_{IR} = i\rho_e d.$$

Combining these results yields the required expression which defines the current density as a function of height, i_x

$$V_A - [(n_a\rho_a/t_a) + (n_c\rho_c/t_c)]\int_x^L\int_0^{x'} i_{x''}\,dx''\,dx' \qquad (9)$$
$$= E_{rev} + b_a\log_{10}(i_x/i_{oa}) + b_c\log_{10}(i_x/i_{oc}) + i_x\rho_e d.$$

In this expression ρ_c is the electronic resistance of the cathode material and n_c is the number of sides of the cathode which are receiving current (1 or 2). b_a and b_c are respectively the Tafel slopes for the anodic and cathodic processes while i_{oa} and i_{oc} are respectively the exchange current densities for these processes. The other quantities have been previously defined.

The current distribution along the electrodes, and the corresponding potential drop, is calculated by solving Equation 9 for i_x as a function of height using an iterative technique. Representative values of the maximum potential drop calculated from this model for a dimensionally stable anode are compared in Table 2 with values calculated from equation 6. The overall electrode dimensions were taken to be $L = 98$ cm by $W = 5$ cm.

It is apparent from Table 2 that a lower potential drop is obtained using the rigorous model which takes into account the current–potential interaction along the anode. The magnitude of this drop is approximately 100 mV for the 0·159 cm titanium substrate at an average current density of 60 mA cm^{-2}. It can be concluded that the 500 mV reduction in oxygen overvoltage claimed for the DSA's may not be economically realizable, due to the high resistivity of the valve-metal substrate. 80% of this reduction may be the maximum which can be obtained in practice.

5. Sensitivity to the kinetic parameters

The current distribution along parallel electrodes of an electrowinning cell was calculated using Equation 9 for a range of values of the anodic exchange current density and Tafel slope. In each case, the total applied potential required to generate an average current density of 60 mA cm^{-2} was determined. This value, and the difference in current density between the top and the bottom of the cell, are recorded in Table 3. The overall electrode dimensions, resistivity factors, and cathode electrochemical parameters were taken to be the

*Table 2. Comparison of 'exact' (Equation 9) and approximate (Equation 6) results for the voltage along a 98 cm titanium electrode**

Thickness of titanium substrate (cm)	*Maximum potential drop* (mV) (*Equation 6*)	*Maximum potential drop* (mV) (*Equation 9*)
0·635	47	30
0·476	63	40
0·318	95	58
0·159	189	105

* Resistivity parameters used were $\rho_a = 72 \times 10^{-6}$ Ω cm (measured), $\rho_c = 1{\cdot}7 \times 10^{-6}$ Ω cm (assumed), $\rho_e = 1{\cdot}33$ Ω cm (measured). The kinetic parameters were taken as $i_{oa} = 2{\cdot}6 \times 10^{-6}$ A cm^{-2} (measured), $i_{oc} = 1{\cdot}0 \times 10^{-4}$ A cm^{-2} (estimated), $b_a = 0{\cdot}069$ V decade^{-1} (measured), and $b_c = 0{\cdot}035$ V decade^{-1} (estimated).

Table 3. Variation of current density with height in an electrowinning cell as a function of the kinetic parameters of the anodic process

	Applied potential (V)			Δi(mA cm^{-2})		
i_{oa}(A cm^{-2})	b_a(V decade^{-1}) = *0·035*	*0·069*	*0·120*	*0·035*	*0·069*	*0·120*
2·6 × 10^{-5}	1·512	1·630	1·805	5·14	4·96	4·76
2·6 × 10^{-6}	1·545	1·696	1·927	5·16	5·00	4·77
2·6 × 10^{-7}	1·583	1·768	2·045	5·12	4·98	4·77

same as in the example of Table 2 with t_a = 0·635 cm.

The results in Table 3 reflect the fact that a higher applied potential (cell voltage) is required to maintain a particular value of the current for anodic reactions with high Tafel slopes or low exchange current densities. This clearly reflects the effects of these parameters in the second term on the right-hand side of Equation 9. The current variation along the electrode decreases with increasing Tafel slope. This is because anode reactions having higher Tafel slopes are less sensitive to the reduction in applied voltage which occurs with increasing depth in the cell. Varying exchange current density has no significant effect on the current distribution.

The maximum potential drop calculated from Equation 9 for the values of i_{oa} and b_a which are presented in Table 3 was about 30 mV. This drop showed no significant dependence on the values of the electrochemical parameters for the cell conditions assumed. This is because the difference in current density between the top and bottom of the cell, at a given total applied current, is a relatively weak function of the parameters assumed and the corresponding differences in potential drop are negligibly small.

In general, the magnitude of the current-density change with depth in an electrowinning cell is determined primarily by the resistivity of the anode substrate. Decreasing the thickness of a titanium substrate from 0·635 cm to 0·159 cm results in an increase in the current density variation Δi from 4·9 to 14·5 mA cm^{-2}. This compares with an increase of Δi from 4·8 to 5·1 mA cm^{-2} for a change in the anodic Tafel slope b_a from 0·12 to 0·035 V decade^{-1}.

6. Experimental verification

Electrolysis experiments were carried out to verify the model which is summarized in Equation 9 using full-height industrial DSA's (L = 100 cm)

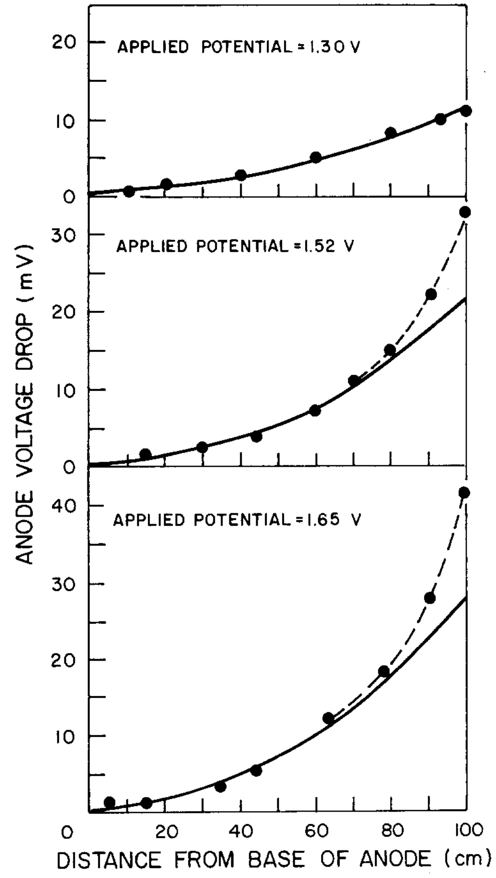

Fig. 3. Variation of anode potential with height in a copper electrowinning cell. Points are experimentally determined, while solid curves are calculated from Equation 9.

under copper electrowinning conditions. Measurements were made of the anode voltage as a function of electrode height, at various current densities. Results are recorded in Fig. 3, in comparison with values calculated using Equation 9. There was some discrepancy between the model and the experimental results particularly at high applied potentials and near the top of the anode. The agreement was excellent for low applied potentials on the lower part of the anode. The discrepancy is attributed to the contributions of mass transfer limitations and gas blocking effects (final term of Equation 7). Such effects are expected to be important at high current densities and near the top of the anode, as was observed.

The good agreement between the calculated potential drop as a function of electrode height and the experimental results obtained at low applied potential substantiates the model which is presented here. Further improvements are being made, to include the final term of Equation 7.

7. Conclusion

There are several intriguing possibilities for achieving substantial improvements in the energy efficiency of industrial electrowinning processes. The most promising of these are reduction of the reversible potential by judicious selection of the overall cell reaction, and overvoltage reduction through anode activation. Strict attention to cell design is necessary, however, to ensure that efficiency gained by electrode activation is not lost through ohmic heating of the electrodes.

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