Mathematical Modelling of Electrowinning Multiple Metals at a Porous Electrode

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An electrochemical process is being developed for recovering metals from shredded waste electrical and electronic equipment (WEEE) by leaching and electrowinning[1]. In a membrane-divided electrochemical reactor (Fig. 1), chlorine is generated at the anode and used as oxidant in an external leach reactor, in which the scrap is dissolved in an acidic chloride solution.

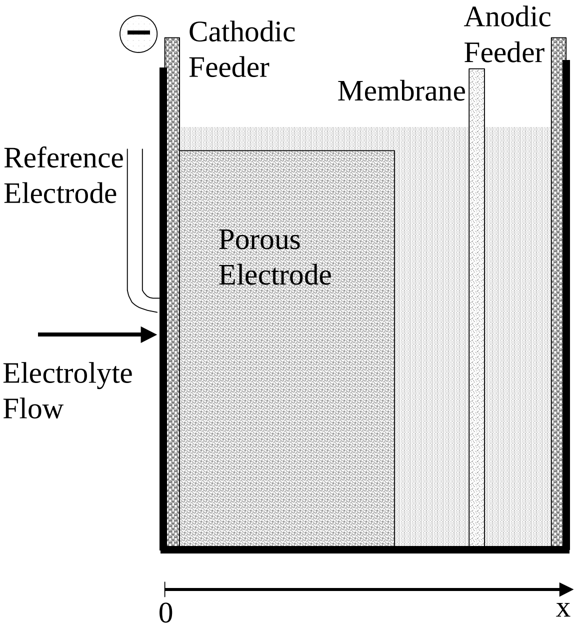

Fig. 1. Schematic of membrane-divided reactor with a porous cathode and Ti / RuO_2 anode.

As the resulting metal concentrations are low, a porous (e.g. graphite felt) cathode with a large specific surface area and high mass transport rates is required to achieve acceptable rates and efficiencies of electrodeposition, the counter reaction to the anodic evolution of chlorine. Hence, as a design tool, a mathematical model was developed to predict potential, concentration, current density and individual current efficiency distributions within the porous cathode, and cell voltages and specific electrical energy consumptions of the electrochemical reactor, as functions of cathode feeder potential, concentrations etc.

The cathodic reactions considered are the simultaneous reduction of metals, such as Ag, Au, Cu and Pb, hydrogen evolution and the reduction of chlorine:

$$MCl_n^{(n-z)-} + ze^- \rightarrow M_{won} + nCl^- \qquad [1]$$

$$2H^+ + 2e^- \rightarrow H_2 \qquad [2]$$

$$Cl_2 + 2e^- \rightarrow 2Cl^- \qquad [3]$$

The rate of reaction [3] needs to be minimised by depleting the dissolved chlorine in the leach reactor, minimising its concentration in the electrolyte fed to the cathode, at which it would cause losses in current efficiencies for metal deposition.

The extended Butler-Volmer equation was used to describe the kinetics of metal ion and chlorine reduction, and Tafel's equation for hydrogen evolution. This involved simplification of the complex reduction mechanism of species such as Au(III) and Cu(II) in chloride media. A fuller model of their reduction will be the subject of a subsequent publication.

Applying Ohm's law to the solution and electrode phases results in the following second order differential equations, relating the local current densities $j(x)$, solution potentials $\phi_s(x)$ and electrode phase potentials $\phi_e(x)$:

$$\frac{d^2\phi_s}{dx^2} = -A_s \frac{j(x)}{\sigma_s} \qquad [4]$$

$$\frac{d^2\phi_e}{dx^2} = A_s \frac{j(x)}{\sigma_e} \qquad [5]$$

where A_s is the electrode specific surface area, and σ_s and σ_e are the effective conductivities of the electrolyte and electrode, respectively. The local current density was assumed to be the algebraic sum of the individual currents due to the reduction of each species i, i.e. interactions were neglected in the first instance:

$$j(x) = \sum_i j_i(x) \qquad [6]$$

The mass balances for each reduced species *i*, relate the local concentrations $c_i(x)$ to the local reaction current densities at electrolyte velocity *u*:

$$unF \frac{dc_i(x)}{dx} = A_s j_i(x) \qquad [7]$$

REFERENCES

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