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Kinetic transitions during Ag and Cu electrorecovery on reticulated vitreous carbon electrodes in flow-by mode

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ABSTRACT

This paper reports on the kinetics of the galvanostatic electrorecovery of copper and silver from sulphate solutions on a reticulated vitreous carbon cathode in flow-by mode. The influence of applied current and flow rate on the electrorecovery rate was systematically studied. Detailed analysis of the electrorecovery kinetics revealed two regimes. The first one was found to be electron-transfer limited, while the second one appeared to be mass transfer limited. From the relevant kinetic rate constants, a current efficiency of 1.03 ± 0.03 for Ag and 0.88 ± 0.01 for Cu electrorecovery was obtained in the first regime. For the second regime, the characteristic mass transport coefficients were determined as $(7.6 \pm 0.3) \times 10^{-3}$ and $(22.6 \pm 0.03) \times 10^{-3}$ cm/s for Ag and Cu, respectively. Analysis of the time and concentration at the kinetic transition was shown to allow for an additional, independent calculation of both the current efficiency and mass transport coefficient, and to confirm that the kinetic transitions occur when the limiting current has been reached.

1. Introduction

Environmental concerns nowadays require the removal of metal ions from industrial wastewaters down to the ppm level. The cathodic removal of these ions has been used for several years, as it allows for the recovery of the considered metal in pure form without having to deal with process sludges. The use of porous electrodes allows for the recovery of metal ions to much lower concentrations as compared to conventional two-dimensional electrodes. Reticulated vitreous carbon (RVC) has naturally become a material of great interest in this field due to its low cost, high surface area, chemical inertness, low resistance to fluid flow and good electrical conductivity [1].

Electrodeposition of metal ions on RVC is already a widely discussed area. Agarwal et al. [2] showed the feasibility of electrorecovery of several metal ions on RVC cathodes from acidic sulphate solution, including copper and cadmium. Copper electrorecovery in particular has been widely used as a model system for testing cells with 3D electrodes. Mass transport properties of potentiostatic electrodeposition of copper from acid sulphate solutions have been characterized by Pletcher et al. [3] in a flow-by cell. These authors also discussed the performance of flow-by cells in batch recycle mode [4] and single pass mode [5]. Recent developments on RVC rotating cylinder cathodes have been discussed by Reade et al. [6]. Nikolic et al. [7] observed the formation of dish-like holes in copper electrodeposits on a copper wire under the influence of hydrogen bubbles. Saleh [8] suggested that hydrogen bubbles generated at a porous cathode could enhance the mass transfer locally.

This paper specifically concentrates on the kinetic details of electrodeposition of Cu and Ag on RVC, using a flow-by cell under galvanostatic conditions in batch recycle mode. The choice of the metallic elements was largely motivated by their presence in wastewaters of the plating industry. Contrary to most of the previous work in the field, our experiments have been carried out from effluents with a relatively high initial metal ion concentration, in the order of 1000 mg/L for Ag and 350 mg/L for Cu, in order to see whether the electrorecovery on porous electrodes would still be feasible at such high initial concentrations. By doing so, the systematic study of the influence of applied current and flow rate revealed for the first time two different kinetic regimes. The first one, when the metal ion concentration in the bulk solution is still relatively high, is limited by electron transfer. When the metal concentration in solution gradually decreases, mass transfer becomes limiting. From the kinetic rate constant of the first regime, current efficiencies for Ag and Cu electrorecovery have been determined. The kinetic rate constant of the second regime allowed for calculating the mass transport coefficient characteristic for Ag and Cu electrorecovery. Finally, a detailed analysis of the time and concentration at the kinetic transition was shown to allow for an

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Nomenclature

List of symbols

C_0	initial concentration in the bulk solution (mol m^{-3})
V_e	volume of the electrode (m^3)
A_e	specific surface of the cathode (m^{-1})
C	concentration in the bulk solution (mol m^{-3})
k_1	kinetic rate constant in the first regime (mol m^{-3} s^{-1})
k_2	kinetic rate constant in the second regime (s^{-1})
q	electric charge (C)
t	time (s)
I	applied current (A)
η	current efficiency (−)
z	number of exchanged electrons (−)
F	Faraday constant (A s mol^{-1})
V	volume of the catholyte (m^3)
k_m	mass transfer coefficient (s^{-1})
D	diffusion coefficient (m^2/s)
δ	thickness of the diffusional boundary layer (m)
$I_{\lim}$	limiting current (A)
C_{trans}	concentration in the bulk solution at the transition (mol m^{-3})
v	mean linear flow velocity (m/s)

additional, independent calculation of both the current efficiency and mass transport coefficient.

2. Experimental details

All experiments were carried out at room temperature from 1 L, 0.5 M sulphuric acid catholyte solutions with an initial nominal concentration (C_o) aimed at, respectively, 5 ± 0.5 mM of Cu^{2+} and 10 ± 0.5 mM of Ag^+. The relative concentrations of the two ions in the catholyte were chosen based on charge equivalency. The anolyte was always 0.5 M sulphuric acid. Metal ion concentrations have been analyzed ex situ with a Varian ICP-OES on 10 mL samples taken from the bulk catholyte during each electrorecovery experiment. The three-dimensional cathode, 35 mm × 35 mm × 6 mm in volume (V_e) was cut from 100 ppi reticulated vitreous carbon (RVC) with a specific surface $A_e = 66\ \text{cm}^2/\text{cm}^3$.

Experiments were performed in a commercial electrochemical filter press cell (Micro Flow cell from Electrocell), shown schematically in Fig. 1(a). The two compartments were separated by a Nafion 350 cationic membrane. A piece of RVC was placed in the centre of the cathodic compartment and compressed onto the stainless steel cathode. The electrical contact made by these collectors generated a current flow perpendicular to the electrolyte flow (flow-by configuration). An upstream flow was imposed to avoid gaseous accumulation in the electrode compartments. The electrochemical cell was inserted into a hydraulic circuit, shown schematically in Fig. 1(b). It comprises two pumps forcing the circulation of the electrolyte in each compartment of the filter press cell. The electrolyte then flows back into a 1 L stirred tank. The pumping rate was adjusted in order to obtain an electrolyte flow varying from 0.26 to 1.0 L/min in the catholyte compartment and constant at 1.2 L/min in the anolyte compartment. The corresponding mean linear flow velocities v, defined as the ratio of volumetric flow rate to the electrode cross-sectional area, therefore varied from 1.3×10^{-2} to 8×10^{-2} m/s in the catholyte compartment. The experiments were carried out under galvanostatic conditions, with the applied current ranging from 0.27 to 1.5 A.

3. Results and discussion

3.1. Kinetic rate constants

Fig. 2 shows a typical evolution of the metal concentration with time, represented on both a linear (a) and a normalised logarithmic (b) scale. Two kinetic regimes can clearly be distinguished. In the first regime, the evolution of the concentration was observed to decrease linearly with time (Fig. 2(a)). It thus follows a zero order kinetics of the form:

$$\frac{dC}{dt} = -k_1 \Rightarrow C = -k_1 t + C_o \qquad (1)$$

with C the concentration in the bulk solution and k_1 the kinetic rate constant of the first regime. In the second regime, a linear decrease of $\ln(C/C_o)$ with time is observed (Fig. 2(b)). This points to a first order kinetics of the form:

$$\frac{dC}{dt} = -k_2 C \Rightarrow \ln\left(\frac{C}{C_o}\right) = -k_2 t \qquad (2)$$

k_2 being the relevant kinetic rate constant for the second regime.

Fig. 3 represents the evolution of the rate constant k_1 with applied current for the 2 metal ions considered. They are seen to increase linearly with current, indicating that the first regime is electron-transfer limited. Indeed, the rate constant for a kinetic regime limited by electron transfer can be rationalised from Faradays' law:

$$q = \eta It \Rightarrow C = C_o - \frac{\eta It}{zFV} \Rightarrow k_1 \equiv -\frac{dC}{dt} = \frac{\eta I}{zFV} \qquad (3)$$

with q the total amount of charge passed at time t, I the applied current, η the current efficiency for electrorecovery, z the number of exchanged electrons, F Faraday's constant and V the volume of the catholyte solution. From Eq. (3), the slope of a linear fit of k_1 vs. I therefore allows to calculate the current efficiencies η. This results in $\eta = 0.88 \pm 0.01$ for Cu and 1.03 ± 0.03 for Ag, the latter error margin being indicative for a 100% electrorecovery efficiency in the case of Ag. We can also point out that, at fixed current densities, k_1 was found to be independent of flow velocity, with average values of

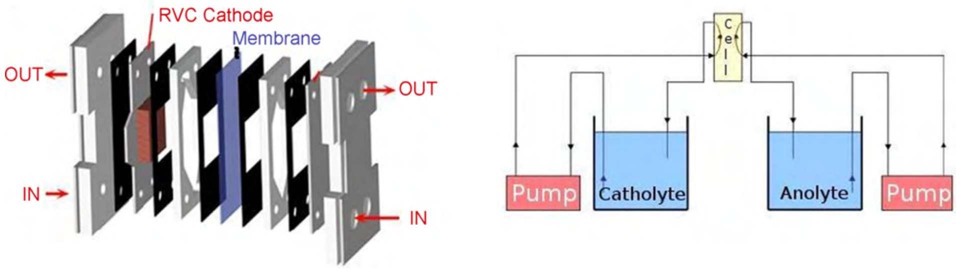

Fig. 1. (a) Schematic of a filter press type electrochemical cell with a porous, three-dimensional cathode, operating in flow-by configuration. (b) Insertion of the cell in the hydraulic circuit.