

## MASS TRANSFER COEFFICIENTS IN ELECTROLYTIC CELLS WITH THREE-DIMENSIONAL CATHODES FOR CADMIUM REMOVAL FROM DILUTE SOLUTIONS

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### ABSTRACT

The performance of two electrolytic cells, with three-dimensional cathodes, for cadmium electrodeposition from diluted aqueous solutions is presented. In both cells, a 60 ppi reticulated vitreous carbon (RVC) was used as cathode and a platinized titanium plate as anode. They have shown to be effective for cadmium removal from very diluted solutions. For two liters of solution used the cadmium concentration decreased from 200 down to about 0.1 ppm in a couple of hours, which is adequate for discharge in water ways. The performance of these cells, operated in a potentiostatic mode, was compared through their mass transfer coefficients for cadmium deposition.

### INTRODUCTION

Cadmium is a heavy metal extremely hazardous to human beings. Up to the present, only negative effects to living organisms are known (Kaim and Schwederski, 1994). The main source of cadmium contaminated aqueous effluents is their electroplating industries. These effluents are diluted solutions in the range of 15 to 100 ppm (Cushnie, Jr., 1985). Electrodeposition is an effective method for the recovery and recycling of metals from aqueous process streams. A major goal of the cell design is the achievement of a large area for cadmium deposition, in a compact space; which is obtained by using three-dimensional electrodes or porous electrodes, which have very high electrode area per unit electrode volume and moderately high mass transport characteristics. They have been used for metal removing from dilute aqueous solutions since the 70's (Sioda, 1970; Bennion and Newman, 1972). The reticulated vitreous carbon (RVC), with porous structure and good properties as electrode material (Wang, 1981) offers high performance on electrochemical removal of heavy metals from diluted aqueous solutions, and is

frequently used as cathode material in electrochemical cells.

The object of this technical contribution is the determination of mass transfer coefficients in two electrolytic cells constructed in our laboratory with reticulated vitreous carbon as a three-dimensional cathode, for cadmium removal from dilute aqueous solutions.

### EXPERIMENTAL PROCEDURE

Two flow-by electrolytic cells, named in this work as cell A and cell B, were used for the cadmium electrodeposition experiments. Based on Pletcher *et al.* design (1991), they were constructed in acrylic material; the same hydraulic and electric circuits, were used to both cells.

#### Cell A

The first electrolytic cell was a 30 × 30 × 12 mm reticulated vitreous carbon cathode with 60 ppi (pores per inch) porosity, supplied by Electrosynthesis Co. Inc. (90 – 97% of open volumes), attached with a conductive silver based epoxy resin to a 3.5 mm thick stainless steel plate which served as current feeder; the anode was a platinized titanium plate (30 × 30 × 0.15 mm) and as reference, a saturated calomel electrode (SCE) in a Luggin probe was inserted in the RVC cathode. The anolyte and catholyte compartments were separated by a Nafion<sup>®</sup> 417 cation exchange membrane.

#### Cell B

The second electrolytic cell was constructed with two acrylic blocks (250 × 150 × 25 mm) each. As anode, a platinized titanium plate; a stainless steel plate, which was used as current feeder, 120 × 50 × 1.2 mm each. The cathode, of 60 ppi reticulated vitreous carbon, was attached to the stainless steel plate by a conductive silver based epoxy resin. In some

experiments, a 100 ppi RVC cathode was used. The anolyte and catholyte compartments were separated by a ESC-700, cation exchange membrane (Electrosynthesis). A thin layer of printer silicone rubber material was attached between the RVC and the acrylic surface, to assure that all electrolyte flow passed through the cathode. Silicone rubber gaskets (1 mm) were placed between the two acrylic blocks and firmly attached with screws, to prevent electrolyte leakage. On the upper side of the catholyte compartment one hole (11 mm diameter) was drilled to insert the Luggin probe with a saturated calomel electrode (SCE).

All the potential measurements throughout the experimental work are referred to the SCE ( $E^0 = 0.242$  V vs. SHE).

A schematic view of the cell B is shown in Figure 1.

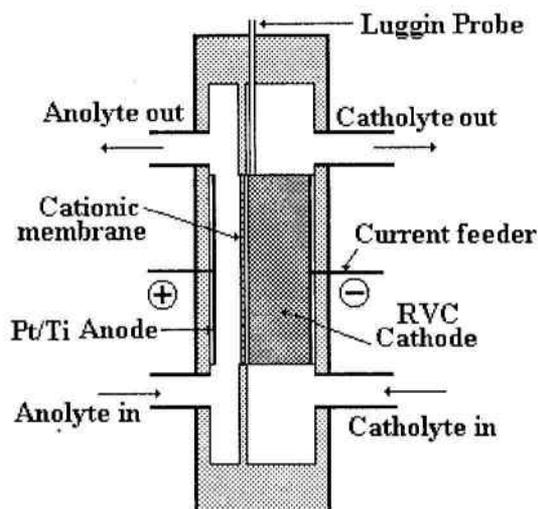


Figure 1 - Schematic view of the B cell.

The hydraulic circuit was constructed with PVC pipes and valves. The anolyte and catholyte, from two 2 liter reservoirs, circulated independently by two peristaltic pumps. The catholyte reservoir was fitted with a nitrogen bubbler to remove the dissolved oxygen. The catholyte flow was controlled by a measuring cylinder.

All electrochemical experiments were controlled by an EG&G PAR model 273A potentiostat/galvanostat connected to microcomputer with the M270 software and the anode-cathode potentials were monitored with a Keithley model 617 electrometer.

The electrolyte was prepared from analytical grade  $3 \text{ CdSO}_4 \cdot 8\text{-H}_2\text{O}$  and  $0.5 \text{ M Na}_2\text{SO}_4$  in deionized water. The catholyte composition was  $0.5 \text{ M}$  sodium

sulfate, pH 2, adjusted with sulfuric acid, containing the specified concentration of cadmium sulfate. In some experiments the concentration of  $\text{Cd}^{2+}$  required for the electrodeposition was adjusted by addition of 50mL of cadmium concentrated solution. The anolyte solution was always  $0.5 \text{ M}$  sodium sulfate, with pH 2. For all experiments, two liters of catholyte were purged with nitrogen and eventually pre-electrolyzed at  $-550 \text{ mV}$ , for the reduction of oxygen and to avoid the negative effect of dissolved oxygen on the cadmium removal (Pletcher, 1991).

The analysis for cadmium ions were carried out with a Perkin Elmer 3300 atomic absorption spectrophotometer.

## RESULTS AND DISCUSSION

In previous work (Dutra *et al.*, 2000), studies of polarization curves for the cadmium ions reduction onto a vitreous carbon rotating disk electrode were conducted. It has been shown that the cadmium ions reduction starts around  $-800 \text{ mV}$ . Figure 2 shows polarization curves for a 100 ppi RVC cathode on the cell B, with 60 ppm of cadmium ions, for two different linear flow solution velocities. The adequate potential range for cadmium ion removal from acidic aqueous solution is  $-820$  to  $-900 \text{ mV}$ . After this plateau, intensive hydrogen evolution occurs, interfering with the cadmium deposition and blocking the RVC cathode pores.

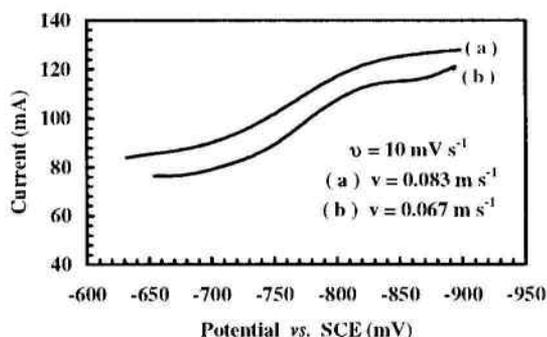


Figure 2 - Polarization curves for cadmium ions reduction in the flow-by cell B with a RVC cathode of 100 ppi. Cadmium ion concentration: 60 ppm.

The electrolysis experiments in both flow-by cells were carried out with 60 ppi RVC cathodes. Figure 3 shows the plot of normalized concentration of  $\text{Cd}^{2+}$  vs. time. With the cell A,  $\text{Cd}^{2+}$  concentration could be reduced from 202 ppm down to less than 0.1 ppm in 60 minutes, with a relatively high current efficiency (41%)

and 3.5 kWh·kg<sup>-1</sup> of energy consumption. With cell B, the cadmium concentration decay, from 209 ppm to below 0.1 ppm required 83 minutes, with a current efficiency of 15.9 % and an energy consumption of 14.4 kWh·kg<sup>-1</sup>.

Table I shows the performance of the two flow-by cells according to the best cadmium electrodeposition experiments of Figure 3.

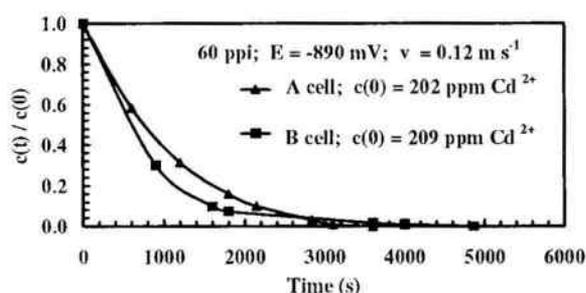


Figure - 3 Normalized concentration of Cd<sup>2+</sup> vs. time for 60 ppi RVC cathodes in A and B flow-by cells.

Curves of the Figure 3 and figures from Table I show that the cadmium decay in the cell B was faster than in cell A by 1600 seconds (27 minutes), when 90% of cadmium ions were deposited on the cathode. In the cell A, 90% of cadmium deposit was reached only after 2150 seconds (36 minutes) of electrolysis; after that, the cadmium decay in the cell A changed, to turn faster than in cell B, reaching, in 3600 seconds (60 minutes), a cadmium removal from the solution of 99%. On the other hand, this same value of cadmium removal has only been reached after 4000 seconds (67 minutes) of electrolysis in the cell B. For both cells, the current efficiency for 90% of cadmium removal was nearly the same (45% for the cell A and 42% for cell B). A huge difference in current efficiency occurred at the end of the electrolysis, in the range in which cadmium removal attained 90% until the residual concentration of 0.1 ppm. At that time, the current efficiency in the cell B dropped to 15.9%; but in the cell A, it dropped only from 45% to 41%.

Table I - Cadmium electrodeposition performance in A and B flow-by cells.

Cell	Cd <sup>2+</sup> conc. (ppm)	t <sub>90%</sub> * (s)	t <sub>99%</sub> † (s)	Current efficiency ‡ (%)	Cd <sup>2+</sup> residual concentration (ppm)
A	202	2150	3100	45	0.1
B	209	1600	4000	42	0.1

\*Time to remove 90% Cd<sup>2+</sup>; † Time to remove 99% of Cd<sup>2+</sup>; ‡ Current efficiency to 90% removal.

Usually, the electrodeposition requires batch operation with electrolyte recirculation to provide good

mass transport conditions in the electrochemical cell. The product of mass transfer coefficient,  $k_m$ , by specific surface area,  $A_e$  (the active area/unit volume of electrode),  $k_m A_e$ , rules the cell performance during the electrodeposition. It may be obtained by a mathematical model valid for plug-flow batch cells operated under mass transport control (Pletcher and Walsh, 1990), according to the following equation:

$$c(t) = c(0) \exp\left[\frac{-k_m A_e V_e t}{V_R}\right] \quad (1)$$

where,  $c(t)$  is a cadmium ion concentration as function of time during controlled potential electrolysis;  $c(0)$  the initial cadmium ion concentration;  $V_e$  and  $V_R$ , the electrode and electrolyte volumes, respectively. Thus, the concentration should decay exponentially with time.

The equation above may be rewritten in terms of the factor  $k_m A_e$ , for estimating it from the slope of the semi-log plot of normalized concentration against time. If the plot of  $\ln[c(t)/c(0)]$  against time is linear, an exponential decay is expected, corresponding to a first order decay, according to the following equation:

$$k_m A_e = \frac{-\ln[c(t)/c(0)]}{V_R} \quad (2)$$

Figure 4 shows a semi-log plot of the same experiments of Figure 3. The linear plot confirms that the decays of cadmium concentration were exponential with time (Figure 3), as well as the behavior of both flow-by cells is like a simple batch process, where all the electrode surface was operating under mass transfer control.

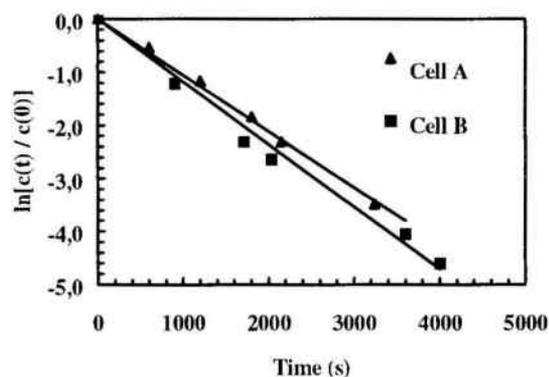


Figure 4 - Semi-log plot of normalized concentration of Cd<sup>2+</sup> as a function of time in the flow-by cells A and B with 60 ppi RVC cathodes.

Close-ups of the two different areas with cadmium deposit on the 100 ppi RVC cathode in the flow-by B

cell with a cadmium deposit equivalent to  $110 \text{ } \Gamma \text{ g.cm}^{-2}$  is shown in the Figures 5 and 6.

It can be seen that, in the flow-by cell, cadmium deposit occurred preferentially at the entrance of the electrolyte. The more densely covered area in Figure 5 is due to the  $\text{Cd}^{2+}$  ion concentration drop throughout the electrode length (Figure 6). The deposition on preferential areas is due to the non-uniform potential distribution throughout the electrode thickness. The structure of the deposited cadmium seems to be mostly nodular, a characteristic of the mass transfer control mechanism.

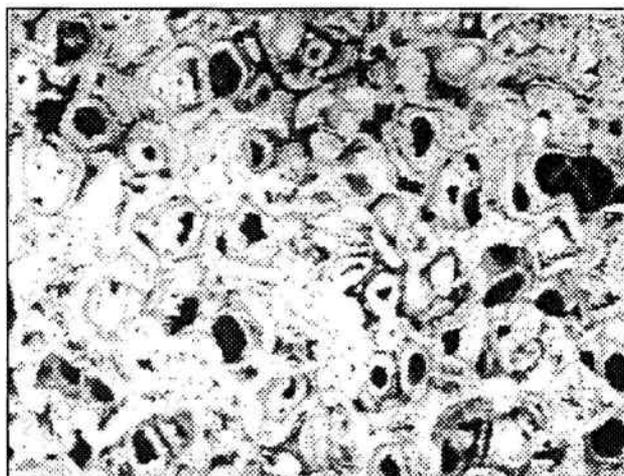


Figure 5 - Micrograph of the cathode area near the entrance of the electrolyte, in the Flow-by cell B with 100 ppi RVC cathode after cadmium deposition; magnification: 55X.

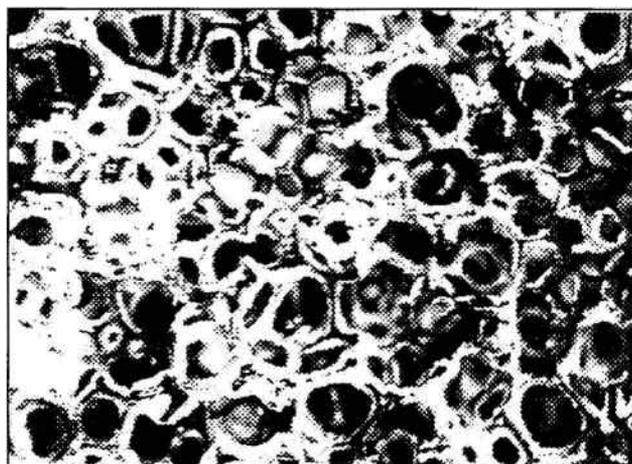


Figure 6 - Micrograph of the central cathode area. Flow-by cell B with 100 ppi RVC cathode after cadmium deposition; magnification: 55X.

Table II shows the main parameters for the flow-by cells with A ( $30 \times 30 \times 30 \text{ mm}$ ) and B ( $120 \times 50 \times 12 \text{ mm}$ ) cathodes; with the  $k_m A_e$  factors and the mass

transfer coefficients for cadmium ions, as obtained from cadmium electrodeposition experiments.

Table II - Cathode dimensions and main parameters of cells A and B, for the cadmium electrodeposition experiments.

60 ppi RVC				
Cathode (mm)	$V_c$ ( $10^{-5} \text{ m}^3$ )	$V_c/V_R$	$k_m A_e$ ( $\text{s}^{-1}$ )	$k_m$ ( $\text{m s}^{-1}$ )
$30 \times 30 \times 30$	1.05	0.0053	0.21	$8.7 \times 10^{-5}$
$120 \times 50 \times 12$	6.9	0.0345	0.04	$1.5 \times 10^{-5}$

The specific surface area,  $A_e$ , for a 60 ppi RVC cathode was  $2400 \text{ m}^{-1}$ , according to the Electrosynthesis Co. Inc..

Data from Table II shows better results with the small RVC cathode. Better performance was achieved by the flow-by cell A. Although the performance of cell B should be improved, the magnitude of its data is comparable to those of Walsh (1993).

Cell performance may be improved by using a RVC cathode with smaller porosity as well as increasing the mean linear flow velocity of the electrolyte.

## CONCLUSIONS

Both flow-by cells were efficient for cadmium removal from dilute solutions, using a 60 ppi RVC cathodes with dimensions of  $30 \times 30 \times 30$  and  $120 \times 50 \times 12 \text{ mm}$  respectively.

A mass transport coefficient of  $8.7 \times 10^{-5} \text{ m s}^{-1}$  was reached using a 60 ppi RVC cathode ( $30 \times 30 \times 30 \text{ mm}$ ). Residual cadmium concentration of 0.1 ppm was achieved after 60 minutes electrolysis, with 41% of current efficiency and an energy consumption of  $3.5 \text{ kWh.kg}^{-1}$ .

The performance of the cell B should be improved for better general efficiencies.

Further study with real waste water from electroplating industries shall be conducted, before scaling up these cells tested for cadmium aqueous solutions, without the usual contaminants.

## ACKNOWLEDGEMENTS

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