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Improvement of the performance of porous electrodes using ionic conducting particles: application to silver recovery

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Experimental measurements are reported for a complex conducting porous electrode system consisting of electronic and ionic conducting particles. A very large value of the ionic conductivity within the electrode is its main characteristic. The complex conducting electrodes and traditional graphitic granular electrodes were used separately to recover silver from a silver plating rinse water. The former displayed excellent performance. A packed-bed reactor composed of the complex conducting electrodes has been successfully tested on a plating line.

Nomenclature

a	specific interfacial area of the electrode bed
c	concentration of reactants
c_0	initial concentration of reactants
F	Faraday constant
I	cell current
i_0	exchange current density
L	thickness of electrode bed
p	electric power
Q	volume flow rate
R	universal gas constant
r	percentage recovery of silver
s	space velocity (i.e. the number of dm^3 solution per dm^3 volume of electrode per hour)
S	normalized space velocity (i.e. the number of dm^3 solution whose concentration could be reduced tenfold per dm^3 volume of electrode per hour)
T	absolute temperature
U	cell voltage
α_a	transfer coefficient for anode
α_c	transfer coefficient for cathode
ε	porosity or void fraction of bed
$\bar{\eta}$	average current efficiency
κ	effective conductivity of solution
κ_0	intrinsic conductivity of solution
v	square root of dimensionless exchange current
σ	effective conductivity of conducting solid matrix

1. Introduction

Porous electrodes have several uses in electrochemical technology [1]. The behaviour of the packed-bed electrode, in particular, has been analysed theoretically by several authors [2–4]. A major drawback of porous electrodes is the excessive potential drop in the electrolyte [5]. The reason is that the effective conductivity of the solution within the pores is small, so that the electrode reaction penetrates the electrode matrix poorly. To enhance the performance of porous electrodes, various improvements have been sought. For example, for three-dimensional packed-bed electrode geometry, Kreysa and Reyvaan have made a detailed analysis and developed a new metal-containing waste water purification process [6]. In the following study, the research focuses on increasing the ionic conductivity within a packed-bed electrode.

In a packed-bed cell with parallel current and electrolyte flow the 'penetration depth' of current has an important role. It limits the flow length [6]. Newman and Tiedemann [3] pointed out that the penetration depth is characterized by the expression

$$\frac{L}{v} = \left[\frac{RT\kappa\sigma}{(\alpha_a + \alpha_c)ai_0F(\kappa + \sigma)}\right]^{1/2} \tag{1}$$

In analysing a three-dimensional electrode based on the one-dimensional model, Kreysa [7] obtained a similar result.

In general, $\sigma \gg \kappa$, so that Equation 1 becomes

$$\frac{L}{v} = \left[\frac{RT\kappa}{(\alpha_a + \alpha_c)ai_0F}\right]^{1/2} \tag{2}$$

It is thus clear that the penetration depth increases with increase in κ. Now, κ is related to the bulk solution conductivity, k_0, and the porosity, ε, according to [4], as follows

$$\kappa = \kappa_0\varepsilon^{1.5} \tag{3}$$

In view of the above, the present study attempts to improve the performance of porous electrodes (i) by increasing the porosity, ε, and (ii) by adding ionic conducting particles to the electrodes. The latter

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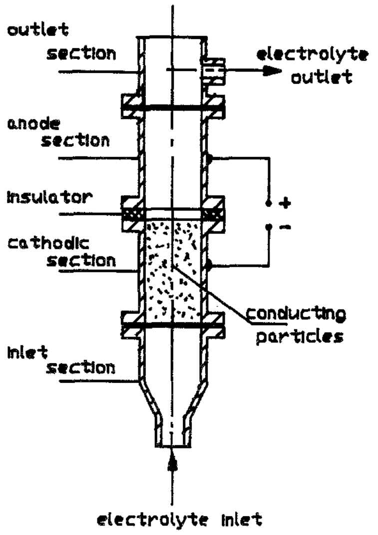

Fig. 1. Scheme of the reactor.

strategy (ii) produced notable improvements. Moreover, for the sake of comparison, we have also tested the performance of traditional granular graphitic electrodes.

2. Experimental details

2.1. *Apparatus*

The reactor employed is shown in Fig. 1. It consisted of an inlet section, an anodic section, a cathodic section and an outlet section. The anodic and cathodic sections were both made of 70 mm diameter stainless steel tube of length 260 mm. The inlet and outlet sections were made of PVC.

The porous electrodes, consisting of granular particles, were packed in the cathodic section. The anodic section was lined with a layer of graphite in order to prevent corrosion. In addition, an electrical heater was placed around the anodic and cathodic sections to control the temperature of the reactor.

The experimental flow circuit is shown in Fig. 2.

2.2. *Procedure*

The electrolyte consisted of distilled water plus a silver-plating solution containing cyanide, in which the silver concentration was made up according to need then analysed by spectrophotometry, using bromopyrogallol red as the colour reagent.

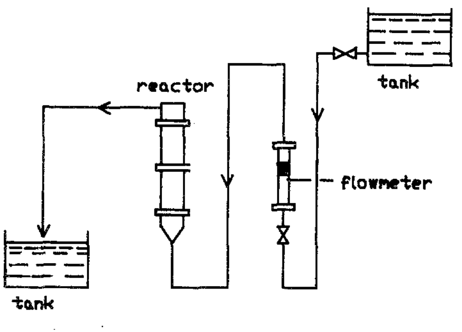

Fig. 2. Flow circuit.

Table 1. Results for graphitic sphere electrodes with $T = 40 \pm 0.5°C$, $Q = 30\,cm^3\,min^{-1}$, $c_0 = 38.3\,mg\,dm^{-3}$ and $s = 4.68\,h^{-1}$

	Cell current, I (mA)					
	100	200	300	500	700	900
c (mg dm^{-3})	36.0	22.8	15.7	10.8	10.3	8.4
S (h^{-1})	0.314	2.10	3.07	3.73	3.80	4.06
r (%)	6.0	40.5	59.0	71.8	73.1	78.1

3. Results

3.1. *Graphitic sphere electrodes*

The graphitic particles had a mean diameter of 3.7 mm and produced a packed-bed of 38% porosity with a specific surface area of 10.3 cm^{-1}. After packing the spheres into the cathodic section (in which the bed thickness was 100 mm) the electrode performance was determined.

In the test, the cell current was adjusted to the required value and the reactor was operated for 2 h at each current value. At the end of this period, the silver content, c, in the reactor effluent was measured and the recovery percentage r ($r = 1 - c/c_0$) was calculated. The data obtained are given in Table 1.

3.2. *Coil electrodes of copper wire*

In order to increase the conductivity of the porous cathode, an electrode consisting of copper coils of 0.2 cm diameter was used. The small coils were packed into the cathodic section in which the bed thickness, L, was also 100 mm. For this packed-bed, $\varepsilon = 80\%$, and $a = 4.4\,cm^{-1}$. In this test, other parameters were the same as above. The experimental data obtained are given in Table 2.

3.3. *Complex conducting electrodes*

The complex conducting electrodes consisted of two types of conducting particles, i.e. electronic and ionic (ion-exchange resin beads) conductors. The purpose of adding ionic conducting particles was to increase the ionic conductivity within the electrode. In the test, L, Q, T, and the other parameters were the same as above.

The experimental results are given in Table 3. Obviously, the performance is superior to that for graphitic sphere and coil electrodes.

Table 2. Results for copper coil electrodes with $c_0 = 48.7\,mg\,dm^{-3}$ and $s = 4.68\,h^{-1}$

	Cell current, I (mA)						
	30	50	100	200	300	400	500
c (mg dm^{-3})	40.9	39.1	21.1	21.0	19.9	15.2	16.8
S (h^{-1})	0.83	1.03	2.95	2.95	3.08	3.58	3.41
r (%)	16.0	19.7	56.9	56.9	59.1	68.8	65.5

Table 3. Results for complex conducting electrodes with $c_0 = 42.8\,mg\,dm^{-3}$ and $s = 4.68\,h^{-1}$

	Cell current, *I* (*mA*)			
	100	200	300	500
c (mg dm^{-3})	4.3	3.0	3.2	3.3
S (h^{-1})	4.68	4.84	4.81	4.80
r (%)	90.0	93.0	92.5	92.3

4. Discussion

The different performances of the above electrode systems can be explained by the penetration depth, L/v, which determines how thick an electrode can be effectively utilized.

4.1. *Electrodes: system 1* (*graphitic*) *and system 3* (*complex*)

The two electrode systems have the same electronic conducting material, i.e. graphite, and the same specific interfacial area, a. Thus, they have the same σ and i_0. Suppose that the α_a and α_c are also the same, then Equation 2 becomes

$$(L/v)_1 = B(\kappa_1)^{1/2} \qquad (4)$$

$$(L/v)_3 = B(\kappa_3)^{1/2} \qquad (5)$$

where $B = [RT/(\alpha_a + \alpha_c)ai_0F]^{1/2}$ and from Equation 3 $\kappa_1 = \kappa_0\varepsilon_1^{1.5}$. In the above experiments, κ_0 was about $0.78 \times 10^{-3}\,\Omega^{-1}\,cm^{-1}$, and $\varepsilon_1 = 0.38$. Hence, $\kappa_1 = 0.18 \times 10^{-3}\,\Omega^{-1}\,cm^{-1}$.

For the electrode system 3, the pores within the electrode were occupied by the ionic conducting particles. If we neglect the porosity of the ionic conducting particles in the pores, i.e. take $\varepsilon_3 = \varepsilon_1$, and suppose that Equatiton 3 is suitable for this case, then $\kappa_3 = 0.38^{1.5}\kappa_0'$.

Because there is no standard method for measurement of the conductivity of ion-exchange resin, we quote the conductivity of the corresponding ion-exchange membrane as the value of κ_0', i.e. $10^3\,\Omega^{-1}\,cm^{-1}$ [8]. Thus $\kappa_3 = 0.23 \times 10^3\,\Omega^{-1}\,cm^{-1}$.

Substituting κ_1 and κ_3 into Equations 4 and 5, we obtain

$$\begin{aligned}(L/v)_1 &= 0.13\,B\\(L/v)_3 &= 15.2\,B\\&= 117(L/v)_1\end{aligned}$$

Therefore, the performance of the electrode system 3 is much superior to that of electrode system 1.

4.2. *Electrode sytem 2* (*copper coil*)

By using a similar procedure, we obtain

$$(L/v)_2 = 3(L/v)_1$$

However, since a_2 is much smaller than a_1 ($a_2 = 4.4\,cm^{-1}$, and $a_1 = 10.3\,cm^{-1}$ and, therefore, the total interfacial area of the electrode, A_2, is much smaller than A_1. Hence, the performance of the electrode system 2 is not obviously improved.

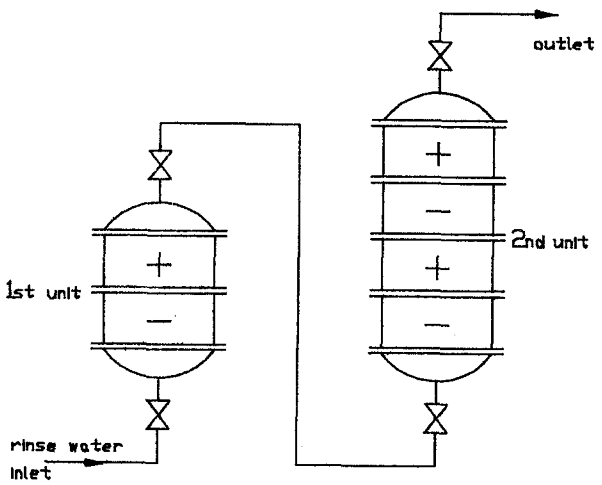

Fig. 3. Configuration of anodes and cathodes.

5. Application

An industrial trial was carried out on a cyanide-based silver plating line in a factory. In the plating line, there were two 800 dm^3 baths which utilized one 250 dm^3 rinsing tank. The experiment was performed for 25 days.

5.1. *Apparatus and flow circuit*

5.1.1. Reactor. The reactor consisted of three cells, which were assembled into two units. The first unit consisted of the first stage cell. The second unit consisted of the second and third stage cells. The configuration of the anodes and cathodes is shown in Fig. 3.

The diameter of the reactor was 700 mm, and the length of each anodic and cathodic section was 200 mm. The cathodic sections, in which the complex conducting particles were packed, were made from stainless steel. The thickness of the bed was 190 mm.

The shell of the anodic section was made from glass fibre reinforced plastic. The anodic body was made from a graphite disc of 695 × 140 mm diameter

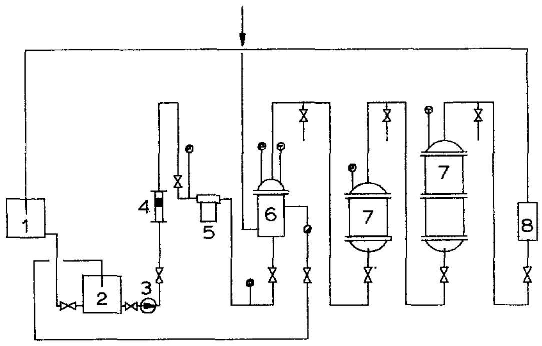

Fig. 4. Experimental flow circuit. Key: (1) rinse tank, (2) tank, (3) pump, (4) flowmeter, (5) filter, (6) heater, (7) reactor, (8) activated carbon filter.

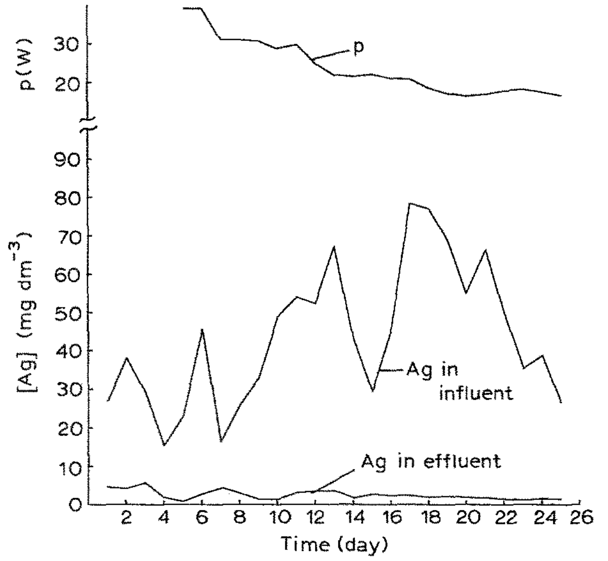

Fig. 5. Operational performance for the reactor installed in a plating line.

through which 85 holes of 50 mm diameter were bored.

During operation, the aqueous stream flowed through the porous cathode (complex conducting particles), then out from the holes of the anode.

The flow capacity of the reactor was 150 dm^3 h^{-1}.

5.1.2. Flow system. The experimental flow system is shown in Fig. 4. In operation, the rinse water flows from rinse tank 1 to tank 2, it is then forced by pump 3 to flow through flowmeter 4, filter 5 and heater 6, then into reactor 7, where the silver is recovered. Flowing out of the reactor 7, the water flows through an activated carbon filter 8, and finally returns to the tank 1.

Table 4. Results of the industrial trial. ($I_1 = I_2 = I_3 = 2\,A$, $s = 0.68\,h^{-1}$)

Item	*Interval*	*Average*
Time (day)	1–25	–
U_1 (V)	6.5–2.5	3.0
U_2 (V)	4.9–2.8	2.9
U_3 (V)	5.5–3.1	3.3
p (W)	39.0–16.4	23.8
Ag c_0 (mg dm^{-3})	15.3–78.5	43.7
c (mg dm^{-3})	5.7–1.22	2.5
CN$^-$ c_0 (mg dm^{-3})	36.8–266	–
c (mg dm^{-3})	28.0–284	–
r (%)	–	94.0
S (h^{-1})	–	0.72

5.2. *Results*

5.2.1. Operational performance. Setting $Q = 150\,\text{dm}^3\,\text{h}^{-1}$, $T = 40 \pm 5°\text{C}$ and an identical cell current, $I_1 = I_2 = I_3 = 2\,\text{A}$, the apparatus was continuously operated for a month (25 days). The data are given in Table 4, and Fig. 5.

During the experiment, the apparatus was operated for 5–7 h each day, and four samples of the influent and effluent were collected. The Ag and CN$^-$ content of each sample was measured and their average value was calculated.

In Fig. 5, the power, p, consumed in the electrolysis process is also given as a daily average value. This is calculated from the current, I, and the voltage, U, of each cell, which were recorded four times each day.

The data in Table 4 show that the recovery efficiency of silver is high and the power consumed in the electrolysis process is small. Thus, adding ionic conducting particles to porous electrodes is an effective way of improving their performance.

The average current efficiency on the basis of a 7 h day operation was calculated to be 26%.

5.2.2. Energy consumption. The data in Fig. 5 show that currents were determined after the fifth day of the operation. From the fifth to the 25th day of the operation, on the basis of the records of c_0, c, I and U each day (no average), the recovered silver, energy consumption of the reactor, the effective operation time, and the winter steam consumption (according to the collected condensate) are given as follows:

effective operation time	115.3 h
silver recovered	756.5 g
energy consumption of the reactor	2.477 kWh
steam consumption	~ 100 kg day^{-1}

Thus, the specific energy consumption was calculated to be (a) electric energy = 3.274 kWh kg^{-1} and (b) steam = 2.64×10^3 kg kg^{-1}.

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