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Electrowinning of palladium using a modified cyclone reactor

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Abstract

The electrochemical behaviour of palladium in dilute acidic chloride solution was investigated using a rotating disc electrode system and the electrowinning of palladium using a modified electrochemical cyclone cell was also carried out. The effect of several variables such as applied voltage, hydrochloric acid concentration and electrolyte flow rate were studied to obtain the optimum conditions for electrowinning. More than 99% of the palladium in solution was recovered within an hour under the optimum conditions using the cyclone cell and grey powdery deposits were observed at a high applied voltage. The purity of palladium electrowon from the leach liquor was at least 99%.

1. Introduction

Palladium is used extensively in applications such as the manufacture of electronic equipment and catalysis in the chemical. Since palladium is a very expensive metal, its efficient recovery from secondary sources is of considerable importance and there have been increasing demands for the development of new extraction techniques. Recently, these techniques have focused on the recovery of palladium from hydrochloric acid solution, originating from the leaching step of hydrometallurgical processes [1]. Various processes such as solvent extraction, solid–liquid extraction and electroless plating using electroactive polymers, have been studied to recover palladium to a high degree. However, these processes are expensive and/or require complex follow-up treatment [2–4]. Conventional electrowinning has also been used for palladium recovery, but is inefficient and time-consuming [5].

Since leaching solutions contain very small amounts of precious metal in general, enhancement of mass transfer by decreasing the diffusion layer thickness is very important to reduce the time and cost of electrowinning process. Based on the hydrocyclone's principal feature of helical accelerated flow [6–9], an electrochemical cyclone cell was employed for the recovery of metal from dilute solution [7, 8], but the rate of removal of metal was still relatively low.

The purpose of this study is to investigate the electrochemical behaviour of palladium in acidic chloride solution using a rotating disc electrode and also to find optimum conditions for palladium recovery using a modified electrochemical cyclone cell.

2. Experimental details

A titanium disc of 1 cm^2 was mounted in epoxy resin and polished with 3 μm alumina powder for the rotating disc experiments. Electrolytes were prepared by dissolving $PdCl_2$ (Aldrich, 99.999%) in water and the pH was adjusted with hydrochloric acid. A typical three-electrode system (titanium rotating disc electrode, vitreous carbon counter-electrode, and saturated calomel reference electrode) was employed to elucidate the basic electrochemical behaviour of palladium in acidic solution, using EG&G model 273 potentiostat–galvanostat and a EG&G rotator. All potentials are referred to the standard calomel electrode.

An electrochemical reactor, utilizing the principal features of the well-known hydrocyclone, was fabricated for palladium recovery in dilute acidic solution. The schematic arrangement of the cyclone-type cell is shown in Figure 1. A similar cell was employed and tested previously, but the rate of recovery of metal was relatively slow [7, 8]. The cell was modified, especially on the anode side to increase the anode area using a graphite tube as an anode. A titanium cylinder served as cathode, having an inner diameter of 25 mm and a height of 20 mm. Electrolyte flowed not only through the apex at the bottom of the cyclone but also through the graphite tube from which both the inner and outer sides of the graphite tube can be served as an anode in this way. These two electrodes were connected to a d.c. power supply. The solution containing tank was coupled to the cell via a rotary pump to control the flow rate and the flow rate of solution was measured with a flowmeter.

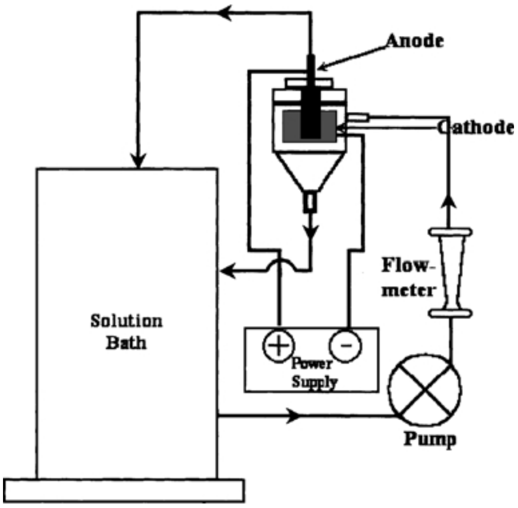

Fig. 1. Schematic of the electrochemical cyclone reactor; arrows indicate electrolyte flow.

All experiments were performed under potentiostatic conditions, and samples were withdrawn periodically to measure the Pd concentration by atomic absorption spectroscopy (GBC904 AA) or inductively coupled plasma spectroscopy (ICP-1000IV, Shimadzu).

3. Results and discussion

3.1. *Cathodic polarization behaviours*

Electrodeposition of palladium in acidic chloride media occurs as follows:
Cathode

$$Pd^{2+} + 2e^- = Pd \quad E^\circ = 0.743\,V \tag{1}$$

$$2\,H^+ + 2\,e^- = H_2 \quad E^\circ = -0.241\,V \tag{2}$$

Anode

$$H_2O = \frac{1}{2}O_2 + 2\,H^+ + 2\,e^- \quad E^\circ = 0.988\,V \tag{3}$$

$$2\,Cl^- = Cl_2 + 2e^- \quad E^\circ = 1.117\,V \tag{4}$$

where E° is the standard state potential. Figure 2 shows the cathodic polarization curves with variation of rotation speed at 20 °C. The limiting current density for palladium deposition was observed around −0.13 V with a small potential range of 0.1 V. A small hump was developed at approximately −0.3 V which is probably due to the formation of palladium hydride [10, 11]. Limiting current densities for palladium deposition are plotted against square root of rotation speed: the plot shows good linearity and obeys the Levich equation well [12],

$$i_l = 0.62\,nFD^{2/3}\nu^{-1/6}\omega^{1/2}C_b \tag{5}$$

Here i_l is the limiting current density, n is the number of electrons transferred in Reaction 1, F is the faradaic constant, D is the diffusivity, ν is the kinematic viscosity, ω is the electrode rotation speed, and C_b is the bulk concentration of palladium. The diffusion coefficient of palladium calculated from the slope of the inset graph in Figure 2 is 8.956×10^{-6} cm^2 s^{-1}, which is similar to reported values [11].

Figure 3 illustrates the temperature dependence of the electrodeposition of palladium. The equilibrium potential increases with temperature according to the Nernst equation. An Arrhenius plot was made and an activation energy of 12.22 kJ mol^{-1} was obtained which indicates diffusion control. The cathodic polarization behaviour was almost independent of pH as shown in Figure 4.

3.2. *Electrowinning of Pd using a modified cyclone cell*

Electrowinning of palladium using a modified cyclone cell was performed at 20 °C. Figure 5 shows the effect of

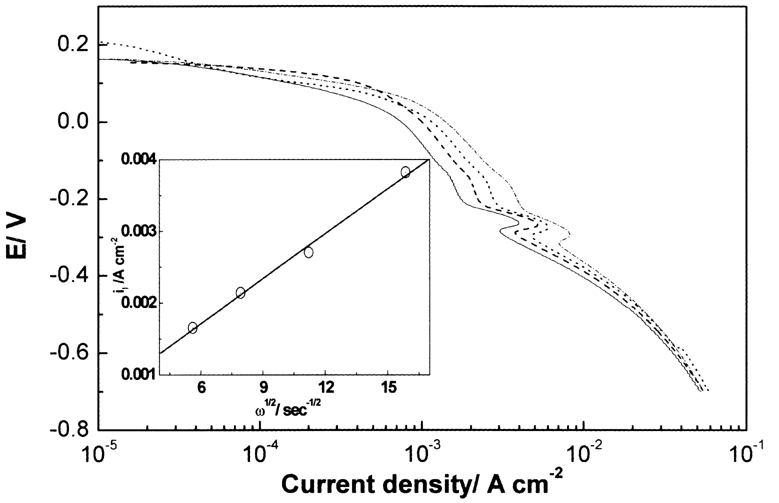

Fig. 2. Cathodic polarization curves with a variation of the rotating speed; C_{pd}^{2+} = 200 ppm, pH 1, 20 °C. ω: (——) 300, (– – – –) 600, (- - - -) 1200 and (– · – · – · –) 2400 rpm.

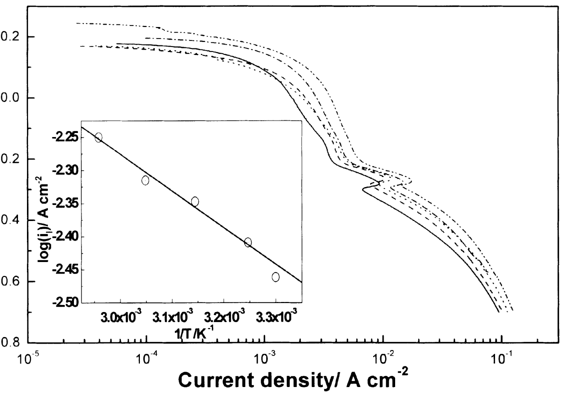

Fig. 3. Cathodic polarization curves with a variation of the solution temperature; $C_{pd}^{2+} = 200$ ppm, pH 1, $\omega = 900$ rpm. Temperature: (——) 25, (- – – –) 35, (- - - -) 45, (–·–·–·–) 55 and (–··–··–··–) 65 °C.

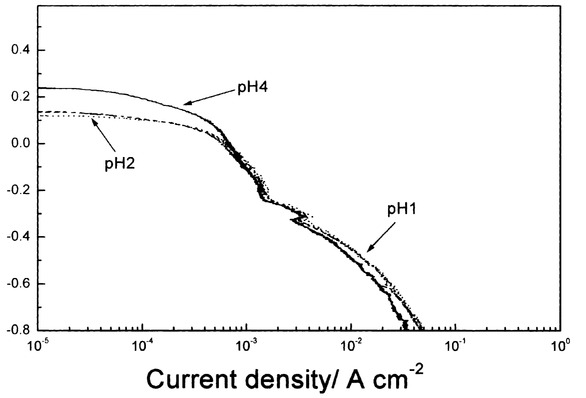

Fig. 4. Cathodic polarization curves with a variation of pH; $C_{pd}^{2+} = 200$ ppm, 20 °C, $\omega = 900$ rpm.

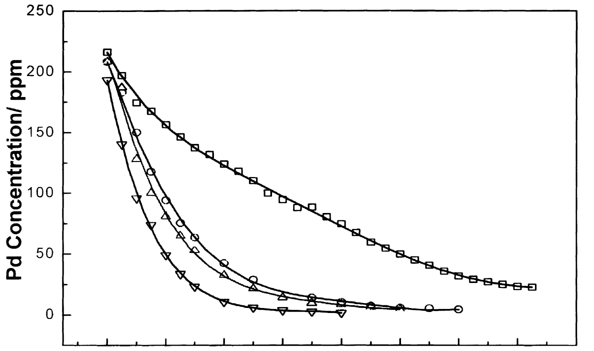

Fig. 5. Effect of flow rate on the recovery of the palladium; $C_{pd}^{2+} = 200$ ppm, applied voltage 2 V, pH 1, 20 °C. Key: (□) 0.6, (○) 1.8, (△) 2.4 and (▽) 3.0 m s^{-1}.

flow rate, which was correlated in terms of linear velocity at an applied potential of 2 V and pH of 1. Here the linear velocity is defined as the ratio of the flow rate to the cross sectional area of the cell inlet. The concentration of palladium drops exponentially for high flow rates due to the turbulent nature of the flow, while a linear shape appears for the laminar flow case of 0.6 m s^{-1}, and the rate of removal of palladium increased with flow rate.

The effect of applied voltage is shown in Figure 6(a) at a solution velocity of 3 m s^{-1} and pH of 1. The initial concentration of palladium was approximately 200 ppm similar to the process recovering the Pd from spent catalysts in actual commercial operation. In the case of 1.5 V, the recovery of palladium is 75% after 2 h while it reaches close to 99% at 2 V and 3 V within an hour. Comparing the latter two cases, the initial rate of recovery of palladium is much faster in the case of 3 V; the overall recovery becomes almost the same after 40 min. After 40 min hydrogen evolution increases. The percentage current efficiency for palladium deposition can be calculated from the following equation and is represented in Figure 6 (b).

$$\frac{I_{\mathrm{Pd}}}{I_{\mathrm{sys}}} = \frac{nF\Delta CV}{M_{\mathrm{Pd}}\Delta t} \times \frac{2}{I_{\mathrm{sys}\_t} + I_{\mathrm{sys}\_t+\Delta t}} \times 100 \qquad (6)$$

where I_{Pd} is the current for palladium recovery, I_{sys} is the total current averaged measured at neighbouring two points during recovery, $n = 2$, $F = 96\,487$ C mol^{-1}, M_{Pd} is the molar weight of palladium, Δt is the time interval between sampling, ΔC is the concentration difference for each sampling step, and V is the volume of solution in bath. In the cases of 1.5, 2 and 3 V, the initial current efficiencies for recovery of palladium are 49, 37, and 16%, respectively. Despite the fact that these values

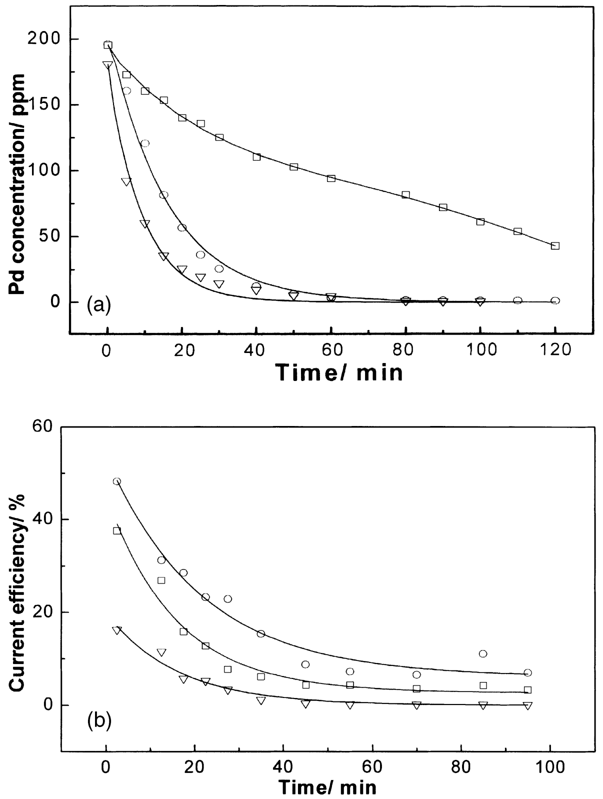

Fig. 6. (a) Effect of applied voltage on the recovery of palladium; (b) current efficiency during electrowinning; $C_{pd}^{2+} = 200$ ppm, linear solution velocity 3 m s^{-1}, pH 1, 20 °C. Key: (□) 1.5, (○) 2.0 and (▽) 3.0 V.

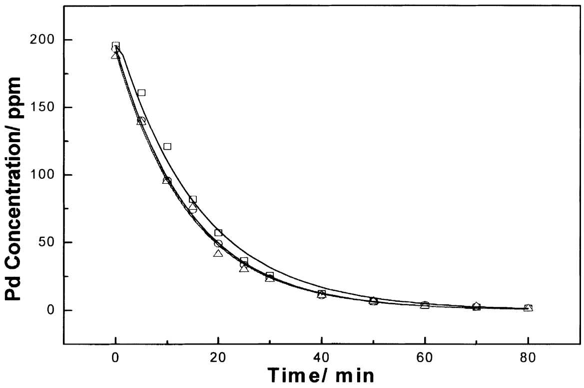

Fig. 7. Effect of pH on the recovery of palladium; $C_{\mathrm{pd}}^{2+} = 200$ ppm, linear solution velocity 3 m s^{-1}, applied voltage 2 V, 20 °C. Key: (□) pH 1, (○) pH 2 and (△) pH 4.

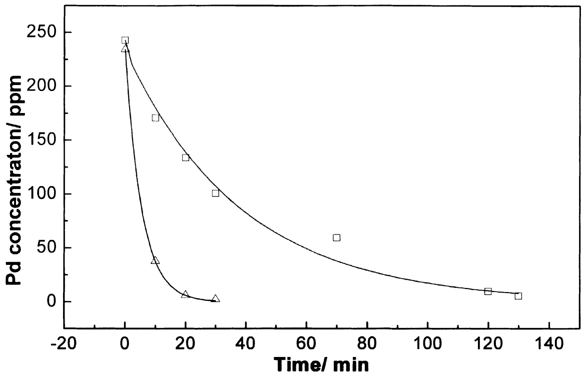

Fig. 8. Recovery of palladium from leach liquor; linear solution velocity 3 m s^{-1}, applied voltage 2 V, pH 1, 20 °C. Key: (□) 1 and (△) 2 V.

continuously decrease with time as the palladium concentration decreases, the current efficiency remains the same order as above during electrowinning. From these results, the optimum applied voltage would be 2 V, considering the energy consumption, since the recovery rate of palladium would be slow at lower concentrations of palladium.

At a relatively high cell voltage, the deposits are powdery and grey in colour. However, under conditions of cell voltage lower than 1.5 V, metallic films are obtained. In general, increase in flow rate leads to a higher mass transfer but erosion of the metal deposit takes place, and powdery deposits are observed similarly to this study [13, 14].

At low concentration, at most 200 ppm, the rate of reaction is apparently controlled by the diffusion of palladium ions to the cathode, which is confirmed by the independence of the reaction rate from the hydrogen ion concentration as shown in Figures 4 and 7.

3.3. *Practical application; recovery from leaching solution*

Leaching solution from spent catalysts containing about 250 ppm of palladium was tested with the electrochemical cyclone reactor and the results are presented in Figure 8. Concentrations of the other species are listed in Table 1. The solution velocity and pH were 3.0 m s^{-1} and 1.0, respectively. When all the electrolysis conditions were the same, the recovery of palladium and deposition morphologies were similar to those of previous experiments. In the case of 2 V, 99% of palladium was recovered within an hour, while it took at least twice the time to reach the same concentration in the case of 1 V. From the chemical analysis shown in Table 1, the purities of recovered palladium were above 99%.

4. Summary

The electrochemical behaviour of palladium was investigated using a rotating disc electrode and the electrowinning of palladium was carried out using a modified cyclone reactor in dilute acidic chloride solution. The diffusion coefficient and activation energy were obtained from rotating disc electrode experiments and found to be 8.96×10^{-6} cm^2 s^{-1} and 12.22 kJ mol^{-1}, respectively. The optimum applied voltage in the cyclone cell is 2 V on the basis of energy consumption. Increasing the electrolyte flow promotes the rate of removal of palladium significantly and 99% of palladium was recovered within an hour under optimum conditions. The purity of Pd electrowon from the leach liquor exceeds 99%, which shows that this is a potential process for precious metal recovery from dilute solution.

Acknowledgements

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Table 1. Chemical analysis of leaching solution and recovered palladium (wt %)

	Al	Fe	Ni	Cu	Co	Ti
Leaching solution	0.0763	0.0428	0.0927	0.0438	0.0432	0.0409
2 V	0.0720	0.0087	0.0040	0.0240	0.0018	–
	Purity of recovered Pd: 99.90 wt %					
1 V	0.0170	0.0074	0.0034	0.0280	0.0011	–
	Purity of recovered Pd: 99.94 wt %					

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