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A comparison of the electrochemical recovery of palladium using a parallel flat plate flow-by reactor and a rotating cylinder electrode reactor

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ABSTRACT

The production of catalytic converters generates large amounts of waste water containing Pd^{2+}, Rh^{3+} and Nd^{3+} ions. The electrochemical treatment of these solutions offers an economic and effective alternative to recover the precious metals in comparison with other traditional metal recovery technologies. The separation of palladium from this mixture of metal ions by catalytic deposition was carried out using a rotating cylinder electrode reactor (RCER) and a parallel plate reactor (FM01-LC) with the same cathode area ($64\,cm^2$) and electrolyte volume ($300\,cm^3$). The study was carried out at mean linear flow velocities of $1.27 < \nu < 11.36\,cm\,s^{-1}$ ($120 < Re = \upsilon d_e/\nu < 1080$) for the FM01-LC reactor and $20 < \nu < 140\,cm\,s^{-1}$ ($7390 < Re = \upsilon d/\nu < 51{,}700$) for the RCER. The morphology of the palladium deposits at the entrance and at the exit of the electrolyte compartment of the FM01-LC reactor showed the effect of the manifold distributors during the electrolysis; the manifolds generate micro turbulences, increasing the mass transport coefficient in these areas and favouring rapid recovery of palladium ions. More uniform high purity palladium deposits were obtained on the surface of the RCER. The cumulative current efficiency to recover 99% of Pd^{2+} ions in the parallel plate electrode reactor was 35% while the recovery of 97% of Pd^{2+} in the RCER was 62%. The volumetric energy consumption during the electrolysis was $0.56\,kW\,h\,m^{-3}$ and $2.1\,kW\,h\,m^{-3}$ for the RCER and the FM01-LC reactors, respectively. Using a three-dimensional stainless steel electrode in the FM01-LC laboratory reactor, 99% of palladium ions were recovered after 30 min of electrolysis while in the RCER, 120 min were necessary.

1. Introduction

The high catalytic activity and corrosion resistance of palladium metal together with the physicochemical properties of its alloys makes it a very important material for industrial and research applications. The widespread use of such applications has contributed to raising the cost of palladium over the last decade [1]. The increasing environmental and technical difficulties to obtain palladium and other platinum group metals (PGM) from natural sources have emphasized the need to search for new and effective recovery methods. PGM can be recovered from the spent catalysts used in different industrial process [2]. One of these processes, the oxidation of the unburned hydrocarbons to carbon dioxide and water in the presence of oxygen taking place within the catalytic converters of modern automobiles, uses most of the palladium produced worldwide [3]. The process on the PGM alloys supported on an inert monolithic substrate based on zeolites, operates as a three-way catalytic reaction carrying out the oxidation of hydrocarbons and CO to CO_2 as well as the reduction of NO_x to N_2, as indicated in the following reactions:

$$4C_nH_m + (m+4n)O_2 \rightarrow 2mH_2O + 4nCO_2 \tag{1}$$

$$4C_nH_m + (m+2n)O_2 \rightarrow 2mH_2O + 4nCO \tag{2}$$

$$4nCO + 4O_2 \rightarrow 4nCO_2 \tag{3}$$

$$2NO_x + N_2 + xO_2 \tag{4}$$

During the fabrication process of the catalytic converters, high concentrated solutions, typically between 150 and $200\,g\,dm^{-3}$ of palladium and 100 and $150\,g\,dm^{-3}$ of rhodium in concentrated HNO_3, HCl or citric acids, are used. Other metallic ions such as neodymium are used as dispersants to help to impregnate the ceramic zeolite substrate. At the end of the impregnation process the wasted solutions still contain substantial amounts of palladium and rhodium with higher concentrations of neodymium, which is not impregnated on the ceramic substrate and remains in solution. The increasing concentration of neodymium over time after

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several impregnation processes, compared with the concentrations of palladium and rhodium, makes the impregnation efficiency low and eventually a point is reached when the concentration of neodymium is too high that the solution cannot longer be used with new substrates. In order to reuse the remaining palladium and rhodium ions, a separation process from the neodymium ions is necessary. The main general characteristic of these solutions is that they are highly acidic, i.e., 1–5 mol dm^{-3} HNO_3 or HCl, which limits the type of recovery process. The processes implemented to recover Pd^{2+} from acid media in the presence of other metallic ions or from solutions containing palladium only, include: extraction with organic solvents [4–6], ionic exchange resins [7,8], adsorbing on activated carbon [9,10] and the use of supported liquid membranes [11]. The majority of these processes use a number of chemical reactants that require more than one unit operation using sophisticated equipment. These processes result in an increase of the operational cost to remove palladium and might not be suitable with the extremely acidic conditions.

Electrochemical reactors used for metal recovery have seen continuous improvement in design and performance over the last three decades [12–14] and they represent a viable option to selectively recover pure metals in its most valuable metallic form. The recovery of palladium from effluents discharged by the catalytic converters manufacturers can be carried out using a filter-press cell or a rotating cylinder electrode cell. These systems are easy to construct and the operational variables can be accurately controlled [15]. Both types of reactor have been widely used for metal recovery from synthetic and industrial solutions with high current densities and good energy efficiencies [16–20]. The different hydrodynamic and mass transport characteristics involved in the design of these two reactors are important during the metal recovery. The present work aims to compare the efficiencies and the volumetric energy consumption during the recovery of palladium ions using a parallel plate filter-press reactor and the rotating cylinder electrode reactor. The design of both types of reactors favours large mass transport regimes.

2. Experimental

2.1. Electrochemical cell

A typical three-electrode glass cell of 50 cm^3 capacity for the working electrode compartment was used to study the electrochemical characteristics of the spent solutions containing rhodium, palladium and neodymium ions before the use of the parallel and rotating cylinder reactors. The working electrode was a stainless steel plate 303 (AI304) grade of 0.07 cm^2. The counter and reference electrodes were a platinum wire and Ag/AgCl(sat), respectively. The working electrode was polished with silicon carbide sand paper grade 600 and 1200 consecutively followed by polishing with microcloth felt (Buehler®) with decreasing particle size of powder alumina (1.0, 0.3 and 0.05 μm). The electrode was finally rinsed with deionised water and left in an ultrasonic bath for 5 min. Linear sweep voltammetry and constant potential electrolysis were applied via a potentiostat–galvanostat EcoChemie Autolab (PGSTAT20) coupled to a PC fitted with a General Purpose, Electrochemical Software (GPES) Version 4.5.

2.2. Reactants and procedure

The electrolyte solution was a mixture of $Rh(NO_3)_3$ and $Pd(NO_3)_2{\cdot}2H_2O$ standards (Johnson Matthey) and Nd_2O_3 (Rhodia Electronics & Catalysis) at concentrations of 100, 500 and 1200 mg dm^{-3}, respectively, in 1 mol dm^{-3} HNO_3 supporting electrolyte at 298 K temperature. The solutions were deoxygenated with nitrogen for 10 min before each experiment. The volume of electrolyte treated in each electrochemical reactor was 300 cm^3 and the working electrode area in each case was 64 cm^2, maintaining the same ratio electrode area to solution volume at 0.213 cm^2 cm^{-3} in the two reactors. During the electrolysis at constant potential the electrode was maintained at −0.10 V *vs.* Ag/AgCl. The cell voltage was measured with a high impedance digital voltmeter. All the experiments were carried out in duplicate and the electrolysis time was 2 h. An aliquot of 1 cm^{-3} was taken from the electrolyte every 10 min to analyse the concentration of the dissolved metal ions. The concentrations were determined by ion plasma (±5% accuracy) coupled to a mass spectrometer detector (ICP-MS) using a model 7500 Agilent.

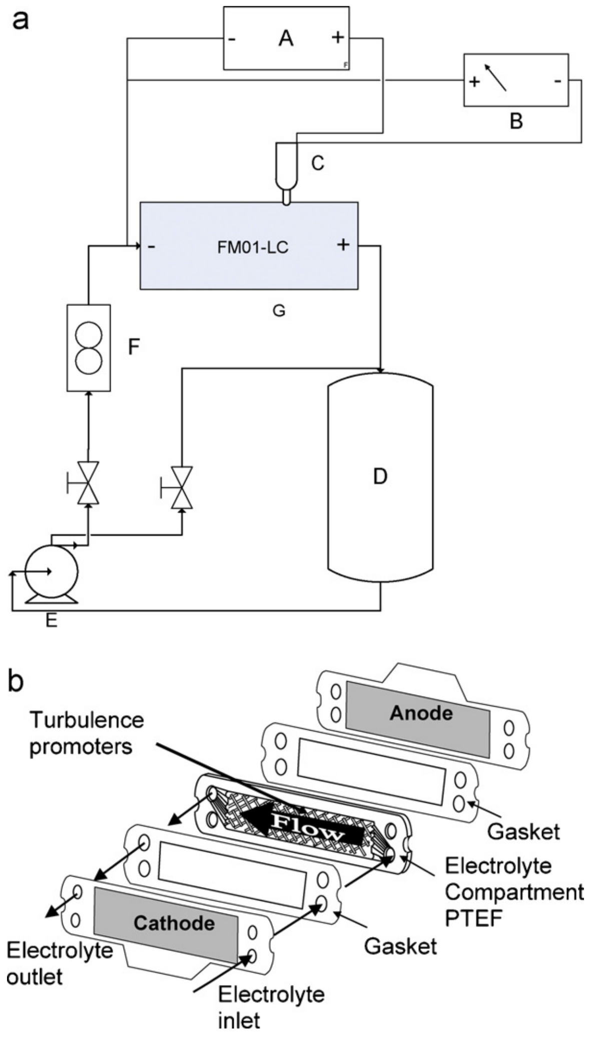

Fig. 1. (a) Electrical and electrolytic circuit used for the parallel plate reactor (0.3 dm^3): (A) potentiostat, (B) digital voltmeter, (C) reference electrode Ag/AgCl (KCl sat), (D) storage tank for the electrolyte, (E) pump, (F) flowmeter, and (G) reactor FM01-LC. (b) Expanded view of the one compartment FM01-LC reactor.

2.2.1. Electrolysis in the FM01-LC reactor

The parallel plate cell reactor FM01-LC is very versatile and can be used in divided or undivided configuration with an interelectrode gap that can be varied between zero, using lantern blade electrodes, and 0.5 cm to allow space for turbulence promoters or a three-dimensional electrode. The geometric characteristics and full description of this cell has already been given by several authors [15–17]. Fig. 1a and b shows the electrical and electrolytic circuit and an expanded view of the undivided reactor, respectively. A