# Purification of Palladium by AC Electrodissolution and Electrodeposition

A. D. Styrkas\* and D. A. Styrkas\*\*

\* Institute of Solid-State Physics, Russian Academy of Sciences, Chernogolovka, Moscow oblast, 142432 Russia \*\* Department of Physics, University of Surrey, Guildford, UK Received February 19, 1999

**Abstract**—A technique is proposed for purifying palladium by ac electrodissolution in acidic solutions followed by dc or ac electrodeposition. It is shown that ac electrodeposition ensures a more effective purification than does conventional cathodic deposition.

## **INTRODUCTION**

Effective purification of substances often requires combining a few methods, including conversion of one compound into another. In this respect, noble metals differ somewhat from other substances in that the production of their compounds requires considerable effort and high temperature (for example, C. Claus, who was the first to identify ruthenium, converted it into a soluble state by melting with nitrates and alkalies) [1, 2], which often leads to additional contamination.

Elecrochemists have recently focused their attention on the anodic dissolution of noble metals [3-6]. This approach is however complicated by passivation of the metal surface [7-10], which notably reduces its efficiency.

An applied alternating current assists in breaking down passivating films and, hence, dissolving noble metals in hydrochloric acid, as demonstrated by the examples of rhodium [11–14], gold [15], and other platinum metals [16]. AC electrodissolution appears more attractive than high-temperature sintering [1], chlorination [2], or melting [17]. Room-temperature ac electrodissolution introduces no contaminants and, occasionally, as, e.g., in the case of Pt, makes it possible to obtain compounds surpassing the starting metal in purity.

The objective of this work was to improve the purity of palladium by electrodissolution in chloride solutions, followed by metal extraction using either conventional cathodic deposition or a new approach—ac electrodeposition of the metal.

#### THEORETICAL ANALYSIS

AS electrodissolution is successfully employed in the inorganic synthesis of high-purity soluble salts of noble metals [18], in analytical chemistry [11], and in extracting metals from industrial waste or low-grade ore [16].

An alternating current passing through an electrode results in alternating anodic and cathodic polarization cycles. Anodic polarization is accompanied by metal oxidation, dissolution, and passivation [12]. Concurrently, it gives rise to oxidation of the substances present in the solution or resulting from electrode reactions and capable of oxidizing at the set potential. Cathodic polarization causes reduction of the oxide film to metal, which then can be oxidized again. Concurrently, it leads to reduction of the dissolved substances, including the metal ions produced over the preceding anodic half-period. These can be reduced to a lower valence ions or metal and deposited on the cathode. Thus, at the metal-electrolyte interface, electrode processes corresponding to the set potential may occur; since the potential varies with time, so do the rates of these processes. If the anodic and cathodic processes were symmetric, the net effect would be zero and the current would not change the solution composition. Actually, there is asymmetry between electrode processes. The net rates of dissolution-ionization and complex formation,

 $M^0 \xrightarrow{ne} M^{n+} \xrightarrow{H_2O, Cl^-} [M^{n+}(H_2O)_{6-m}Cl_m^-]^{(n-m)+}$ , and those of the reverse processes—complex dissociation and reduction—depend on the rates of partial electrode reactions. As the dissolution products accumulate in the electrolyte, the reaction rate drops, by virtue of the law of mass action, and the reduction rate rises. Clearly, a state can be reached in which the net dissolution rate is zero because of the increased rate of electrodeposition.

In some cases, the passage of an alternating current may reduce the impurity concentration. For example, if, after Pt deposition in the form of  $K_2PtCl_6$ , the deposit is subjected to the additional action of an alternating current, the purity of the product will be higher than that of the starting material [18]. The passage of an alternating current may also reduce the impurity concentration owing to forced recrystallization. During the cathodic half-period, the Pt<sup>4+</sup> ions are reduced to Pt<sup>2+</sup>,

which form complexes with a higher solubility. The deposit dissolves again, and the divalent ions find themselves in the solution. During the anodic half-period, they are again oxidized to  $Pt^{4+}$ , and  $K_2PtCl_6$  precipitates. This forced recrystallization results in purification of the material.

A similar redox "recrystallization" accompanies oxidation and reduction of ions to metal in the process of alternating polarization but, in the latter case, the metal, rather its salt, undergoes recrystallization.

#### **EXPERIMENTAL**

We examined dissolution of palladium-containing powders and massive palladium electrodes—wires 0.5 mm in diameter and plates 2.5 mm in width and 0.3 mm in thickness. The electrodes were immersed in solution using a micrometer screw. The instant in time when the electrode and solution were brought in contact was determined using an ohmmeter. The current density was reduced to the apparent electrode surface.

Clearly, electrodissolution of powders presents a problem since it is more difficult to pass a current through particles. We used powders of spent silicate or asbestos hydrogenation catalysts containing 0.02–0.3 wt % Pd. The powders were dissolved in U-shaped electrolyzers [19], which could be connected in parallel or in series to ensure the required capacity. The current density was calculated using the cross-sectional area of the electrolyzer at the powder–electrolyte interface. If cooling was needed, the electrolyzers were mounted in a thermostated container with distilled water.

The solvent used was concentrated HCl (reagent grade). The solutions for the cathodic deposition of palladium and preparation of  $K_2PdCl_4$  contained sodium and ammonium phosphates, ammonium chloride, and aqueous ammonia (all of reagent grade) [20].

The electrolyte temperature during electrolysis was maintained with a stability of  $\pm 2^{\circ}$ C.

The ac (50 Hz) current density was set using LATR autotransformers.

To isolate individual dissolution products (for analysis and preparation of the electrolyte for the cathodic deposition of the metal from the phosphate bath), the solution was boiled down on a glycerol bath at 120°C; the dry residue was withdrawn out under a water-jet air pump in the dry HCl flow.

#### **RESULTS AND DISCUSSION**

The kinetic curves of palladium dissolution are displayed in Figs. 1–3. Similar to other platinum metals, palladium dissolves in acids. The dissolution is preceded by an induction period necessary for the removal of the passivating film (Fig. 1). The films were found to contain only trace levels of chlorides. The induction period shortens if the metal is preannealed in hydrogen or subjected to preliminary cathodic polarization



**Fig. 1.** Time variation of the Pd dissolution rate; [HCl] = 11.6 N,  $t = 45^{\circ}\text{C}$ ,  $j = 3.5 \text{ A/cm}^2$ ; (1) starting Pd, (2) after hydrogen annealing, (3) after preliminary cathodic polarization.







Fig. 3. Pd dissolution rate vs. temperature; [HC1] = 11.6 N,  $j = 3.2 \text{ A/cm}^2$ .

(Fig. 1, curves 2, 3). The dissolution rate saturates at a level determined by the current density and electrolyte convection regime. The curve obtained after cathodic prepolarization, shows a maximum (Fig. 1, curve 3),



**Fig. 4.** Time variation of sample weight for electrodes 1 and 2 during long-term ac electrolysis.

which is due to the active heating upon oxidation of the hydrogen absorbed by palladium. Hydrogen annealing produces no such effect: at high temperatures, the hydrogen solubility is fairly low, and cooling of the metal after annealing is typically performed in flowing  $CO_2$ . Cathodic palladium accumulates larger amounts of hydrogen. Pd also catalyzes hydrogen oxidation, accompanied by a significant thermal effect, which causes the foil to curl. After the induction period, the dissolution rate rises and then saturates (Fig. 1) at a level determined by the current density (Fig. 2), elec-

Impurity contents of the (a) starting palladium, (b)  $K_2PdCl_4$ precipitate, (c) cathodic deposit from the phosphate bath, and (d) palladium black after long-term ac electrolysis (n = 2, P = 0.9)

Impurity	Weight percent impurity			
	а	b	с	d
Cu	0.008	0.001	0.005	0.002
Ag	0.007	0.001	0.001	Not found
Au	0.001	0.001	0.001	Not found
Mg	0.003	0.003	0.003	0.003
Al	0.005	0.002	0.001	0.001
Si	0.005	0.002	0.004	Not found
Sn	0.001	Not found	Not found	Not found
Pb	0.005	0.002	0.004	Not found
Sb	0.002	0.001	Not found	0.001
Fe	0.01	0.003	0.005	0.003
Pt	0.01	0.008	0.01	0.005

trolyte temperature (Fig. 3), and electrolyte composition [16, 19].

Pd is known to form compounds with different valences, 2+ and 4+, which can convert to one another at the electrode via oxidation of Pd<sup>2+</sup> to Pd<sup>4+</sup> during the anodic half-period and reduction of Pd<sup>4+</sup> to Pd<sup>2+</sup> in the process of cathodic polarization, thereby reducing the efficiency of the current. Intermediate-valence compounds are typical of noble metals. They can accumulate, attaining considerable concentrations. The formation of mirrorlike deposits on the electrolyzer wall upon rapid cooling of the solution resulting from ac electrolysis seems to be associated with disproportionation of such compounds.

The ac electrodissolution of palladium in HCl eventually yields  $H_2PdCl_4$ , a compound readily soluble in water, alcohols, and other protic solvents.

According to chemical analysis data,  $K_2PdCl_4$  precipitated by KCl (n = 3 determinations, confidence level P = 0.95) contains 32.06 wt % Pd (nominal content, 32.64 wt %) and 43.61 wt % Cl (43.44 wt %).

If the surface of Pd is free from oxides after reduction, it dissolves at the anode with 100% current efficiency. At potentials above +1 V (relative to SCE), the efficiency drops again because of the formation of a stable passivating film, preventing ac dissolution. The method under consideration is based on the nonlinearity and asymmetry of the current-voltage curves in the cathodic and anodic branches at sufficiently high polarizations. For this reason, the effects of the cathodic and anodic half-periods do not cancel out. The activation of the passivated metal is achieved by producing pure metal on the surface during the cathodic half-period. During the anodic half-period, part of this metal dissolves.

The method also has considerable potential for other applications; e.g., ac electrodissolution can be used to extract noble metals from low-grade ore and industrial waste.

To test its potentialities, we used a spent hydrogenation catalyst containing 3.0 wt % C and silicate waste containing 2.6 wt % Fe, 0.1 wt % Ti, and 0.1 wt % V. The nominal amount of Pd in the sample was 3.10 g; 3.03 g was extracted. The impurity concentrations in the product differed little from those in Pd (table, column a). Ti and V were not detected.

As pointed out above, the accumulation of Pd ions in solution must reduce, by virtue of the law of mass action, the dissolution rate and raise the rate of the reverse process—precipitation of Pd. This was checked in experiment by examining Pd dissolution (Fig. 4). Two identical Pd electrodes 0.3 mm in thickness and 2.5 mm in width, fabricated from the same Pd platelet, were dipped, using a micrometric screw, one 10.0 mm (electrode 1) and the other 10.2 mm (electrode 2) into a cell. The current (50 Hz) through the cell was stabilized at 2 A. Initially, the dissolution rates were identical and both increased as Pd ions gradually accumulated in solution. With time, the dissolution rate of electrode 1 became faster, and the difference gradually increased. After 3 h, Pd black appeared at the edges of both electrodes. Eventually, the weight of electrode 2 began to rise owing to the growing Pd black coating, while the weight of electrode 1 continued to decrease. Thus, the accumulation of the dissolution products reversed the process at electrode 2; as a result, electrodeposition dominated over dissolution.

A natural question is how these changes influence the purity of the metal. As mentioned above, the passage of an alternating current may reduce the impurity concentration [18]. It might be expected that the similar "redox recrystallization" of the metal would improve its purity.

The purity of the compounds obtained and Pd deposit was determined by spectroscopic analysis. In all of the compounds (table, column b), the impurity concentrations were no higher than those in the starting metal (table, column a). Upon dissolution, the impurity content on metal basis either remained unchanged or decreased. Thus, dissolution introduced no additional contaminants, in contrast to high-temperature methods, which notably reduce the purity of compounds and require additional purification.

As apparent from the table, electrodeposition also somewhat reduces impurity concentration (table, column c); ac processing ensures, in some instances, finer purification (table, column d). It was found that the concentrations of a few impurities in the metal obtained by ac electrodeposition of palladium black were lower than those in the starting Pd by a factor of 2 or more.

### CONCLUSION

The dissolution of powder and massive palladium and a spent catalyst in acidic solutions was studied.

The results demonstrate that ac electrodissolution of Pd and its waste is a promising technique for preparing pure compounds.

Subsequent ac electrodeposition reduces the impurity concentration by a factor of 2 or more.

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