

Effects of Process Variables on The Electrochemical Recovery of Palladium in A HCl Solution

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Abstract

This study investigated the electrochemical recovery of palladium in a HCl solution that is used for palladium leaching. The high acidity of HCl solution and the low concentration of Pd ions increased the cathodic overpotential and reduced the limiting current density. Lowering the current density produced dense deposits; however, they were under high tensile stress. Raising the temperature affected both the densification and the stress, which enabled the attainment of dense Pd deposits under low stress. Lowering the current density and raising the temperature up to 70°C was recommended for the recovery of palladium as sound bulk Pd deposits. Current efficiency was over 85% at the initial stage of recovery and gradually decreased with the passage of time. The reduction of the Pd ion concentration during the batch-type recovery may decrease the current efficiency, since a low Pd ion concentration results in a low limiting current density.

Key words: electrochemical recovery, hydrochloric acid solution, palladium, deposit morphology, deposit stress, current efficiency

1. Introduction

Palladium is used for a wide variety of: electronics, catalysts, dental materials, etc.^{1,2)} Recovery of palladium from secondary resources is becoming increasingly important, since palladium is one of the mal-distributed platinum group metals.²⁾ Recently, various processes have been studied that recover palladium from a hydrochloric acid leaching solution.³⁾ Traditional chemical recovery processes are generally complex and expensive. Electrochemical recovery of palladium, however, is believed to be a relatively simple and an easily controlled method. Dense and less-stressed deposition is important, since deposit morphology affects the purity of the Pd deposit and high residual stress can cause serious problems, such as the detachment of deposit from cathode during the recovery process. Porous deposit normally obtained over the limiting current density has a high possibility of being contaminated by occluded impurities in

between grains and absorbed hydrogen. The high acidity of the leaching solution can induce severe hydrogen evolution, lowering current efficiency. A Pd deposit can be easily contaminated by hydrogen during the process because of its high capacity for hydrogen absorption.⁴⁾

Electrochemical recovery was attempted as a simple means to obtain sound bulk Pd deposit, without hydrogen contamination, from a strong hydrochloric acid solution. The effects of the preparation conditions were investigated by means of electrochemical reaction examination, deposit morphology observation, and stress measurement.

2. Experimental Procedure

Hydrochloric acid solutions containing palladium were prepared by dissolving PdCl₂ (Wako, 99%) in hydrochloric acid solution of 0.76 M and 6.0 M. The high acid concentration of 6.0 M is similar to that of chemical leaching solution. The electrochemical behavior of palladium in the solutions was examined by using a linear polarization technique in a three-electrode cell: a Ti working electrode of 1.0cm², a

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graphite counter electrode of 6.0cm^2 , and a saturated calomel reference electrode. The cell temperature was controlled automatically with a heating bath. All electrochemical tests were done using EG&G 273 potentiostat. Stress developed during electrodeposition was measured by using an in-situ bending beam method. The working electrode was a Pt(111)-coated glass electrode, $200\ \mu\text{m}$ thick, having an area of 0.5cm^2 . Palladium was galvanostatically deposited on Pt(111). A beam from a He-Ne laser (Melles Griot) was positioned at the backside of the electrode through the optical window of the cell. Since the deposit strain, produced by stress, bends the Pt-coated glass electrode during the deposition, the reflection angle of the laser beam from the electrode is adjusted proportionately to the stress level. The deflection of the reflected laser beam was then converted into an electric voltage signal at a laser beam position detector. The deflection is a degree of the strain that is directly proportional to the stress.⁵⁾ Based on the electrochemical reaction, the morphology and the stress studies, an optimum recovery condition was chosen and the electrochemical recovery of bulk Pd deposit was done in a two-electrode cell with a Ti working electrode of 6.0cm^2 under vigorous stirring. The recovery test was done as a batch-type process without any additional palladium supplement. The current efficiency of the recovery process was calculated by weighing the recovered Pd deposit. The surface morphology and the crystal structure of Pd deposit were also examined using a scanning electron microscope (SirionTM, FEI company) and a x-ray diffractometer (Ru200, Rigaku), respectively.

3. Results and discussion

3.1. Electrochemical reaction study

Fig. 1 shows the linear polarization curves obtained in the 0.76 M and 6.0 M hydrochloric acid solutions, with 0.10 M PdCl_2 at 40°C . The cathodic currents start to flow at 150 mV and 30 mV in 0.76 M and 6.0 M hydrochloric acid solutions, respectively. It has been reported that Pd ions form chloride complexes in the presence of chloride ions, which are strongly affected by pH and Cl^- concentration.⁶⁻⁸⁾ PdCl_4^{2-} anions are regarded as a major species in solutions of high

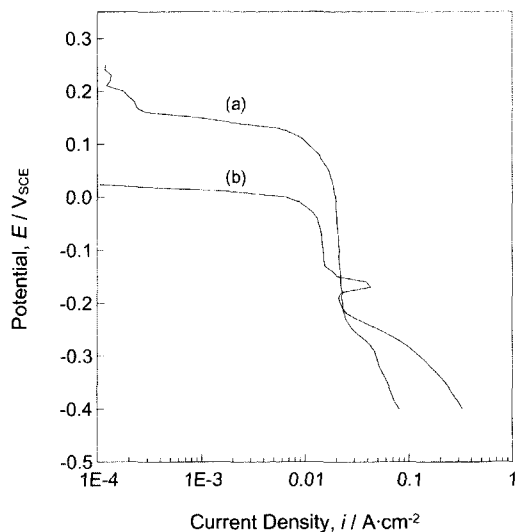
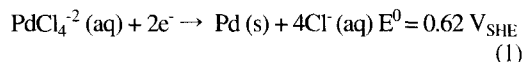


Fig. 1. Linear polarization curves in 0.76 M (a) and 6.0 M (b) HCl solutions with 0.10 M PdCl_2 at 40°C .

chloride concentration and low pH.⁶⁻⁸⁾ The electro-deposition of palladium in a hydrochloric acid solution can be expressed as follows⁹⁾:



The deposition potential in 0.76 M HCl solution was 120 mV higher than that of the 6.0 M HCl solution. The Nernst equation (2) predicts that the higher Cl^- concentration at electrode surface, the lower electrode potential.

$$E = E^0 - \frac{RT}{2F} \ln\left\{\frac{[\text{Cl}^-]^4}{[\text{PdCl}_4^{2-}]}\right\} \quad (2)$$

It can be assumed that the difference of reactant concentration between the electrode surface and the bulk solution is very small at the initial stage of deposition during linear polarization. Then, the surface concentration of Cl^- can be substituted by the bulk one in equation (2). Equation (2) predicts that the high concentration of Cl^- in a 6.0 M HCl solution shifts the deposition potential in a further negative direction than a relatively low concentration of Cl^- in a 0.76 M HCl solution does. The experimental result shown in figure 1 agrees well with the expectation; the potential difference calculated from the Nernst equation was 110 mV. The linear polarograms show that the limiting current regions were followed by a hydrogen absorp-

tion reaction into palladium at -150 mV in 6.0 M HCl and at -250 mV in 0.76 M HCl. Hydrogen evolution after the absorption reaction peak dominates the

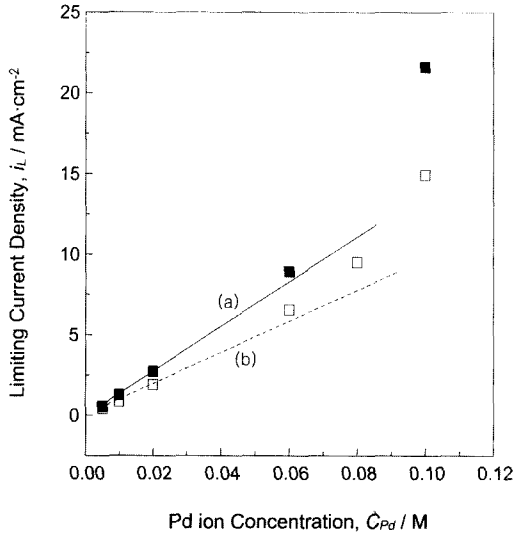


Fig. 2. Limiting current density at -100 mV vs. Pd ion concentration in 0.76 M (a) and 6.0 M (b) HCl solutions.

overall reaction at a more negative potential. This means that hydrogen absorption into palladium takes place at the hydrogen evolution potential, and we cannot avoid hydrogen contamination over the limiting current density.

The limiting current increased linearly in proportion to the Pd ion concentration at low Pd ion concentrations, as shown in fig. 2. The limiting current can be expressed by equation (3) and is proportional to the bulk concentration (C_{bulk}) of the reactant in a solution at a sufficiently high overpotential.

$$i_L = nFD C_{bulk}/\delta_N \quad (3)$$

A deviation from the linear relationship was observed over 0.060 M $PdCl_2$ in both the 0.76 M solution and the 6.0 M HCl solution, and increased with $PdCl_2$ concentration. The deviation from equation (3) in the high Pd ion concentration seems to be caused by a change of Pd deposit morphology. Fig. 3 shows the change of morphology with Pd ion concentration at the limiting current density. The morphology changed from a flat to a rough surface, with ball-like deposits in high concentration. The ball-like deposits can enlarge

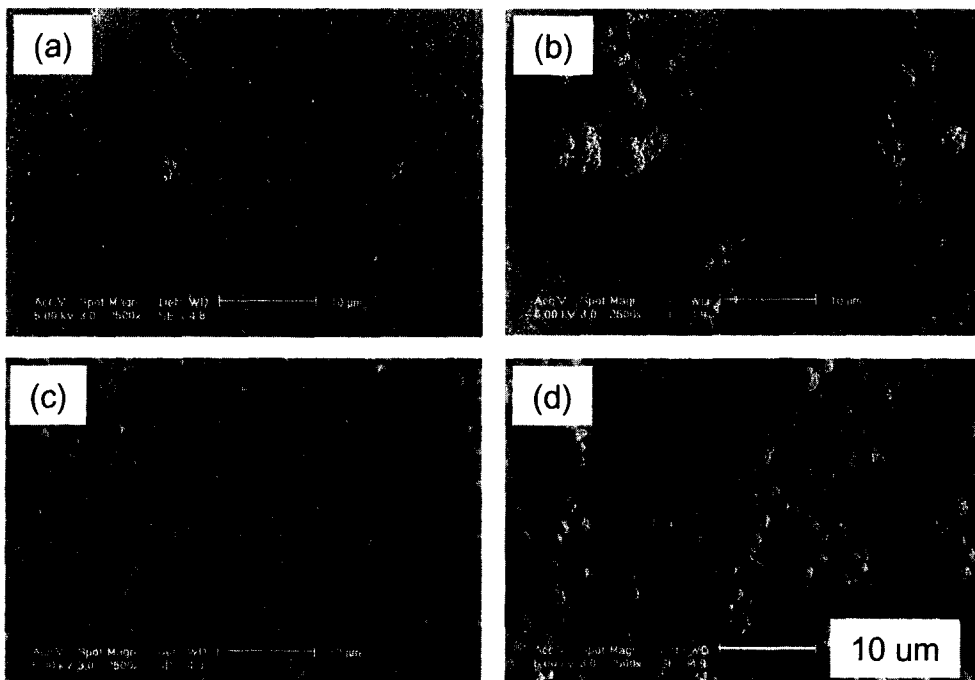


Fig. 3. Palladium deposit morphologies with a variation of Pd concentration in 0.76 M HCl solution at limiting current densities. (X2500) (amount of charge $1.9C$) (a) 0.01 M (b) 0.02 M (c) 0.06 M (d) 0.1 M

the apparent electrode surface and thereby increase the limiting current density. The dependence of the limiting current density on the Pd ion concentration suggests that a batch-type recovery process, without a palladium supplement, can lower the current efficiency, since it decreases the limiting current density. Fig. 2 also shows that the limiting current densities in all the Pd ion concentrations were higher in 0.76 M HCl than in 6.0 M HCl. Although a more detailed explanation should be given by further study, the results indicate that a high acid concentration of leaching solution lowers the efficiency of the electrochemical recovery process, because it decreases the limiting current density.

3.2. Deposit morphology and stress studies

Fig. 4 shows the change in deposit morphology with the current density in 6.0 M HCl solution, containing 0.10 M PdCl₂ at 25°C. At a low current density, the deposit was dense and irregular, as can be seen in fig. 4 (a) and (b). As the current density increases, they

become porous and pyramidal-shaped, as shown in fig. 4 (c), before becoming starfish-shaped, as shown in fig. 4 (d). The extrapolated limiting current density of the deposition, shown in fig. 2, was 10.1 mA/cm². In general, the morphology of metal deposit changes from polycrystalline to powdery, via nodules or dendrites, with increasing current density.¹⁰⁾

Fig. 5 shows the effect of the current density on the stress of the deposits, shown in fig. 4. The y-axis is the degree of laser beam deflection produced by strain, and it can be considered as indicative of the stress level, since the strain is directly proportional to the stress. A positive value on the y-axis indicates the development of tensile stress on the Pd deposit: the higher the positive deflection of the y-axis, the higher the tensile stress on the deposit. The stress was tensile in nature, except for the highest current density case. The deflection curve can be divided into two stages: an initial sharp rise and a steady growth afterwards. The sharp rise during the initial stage of deposition is due

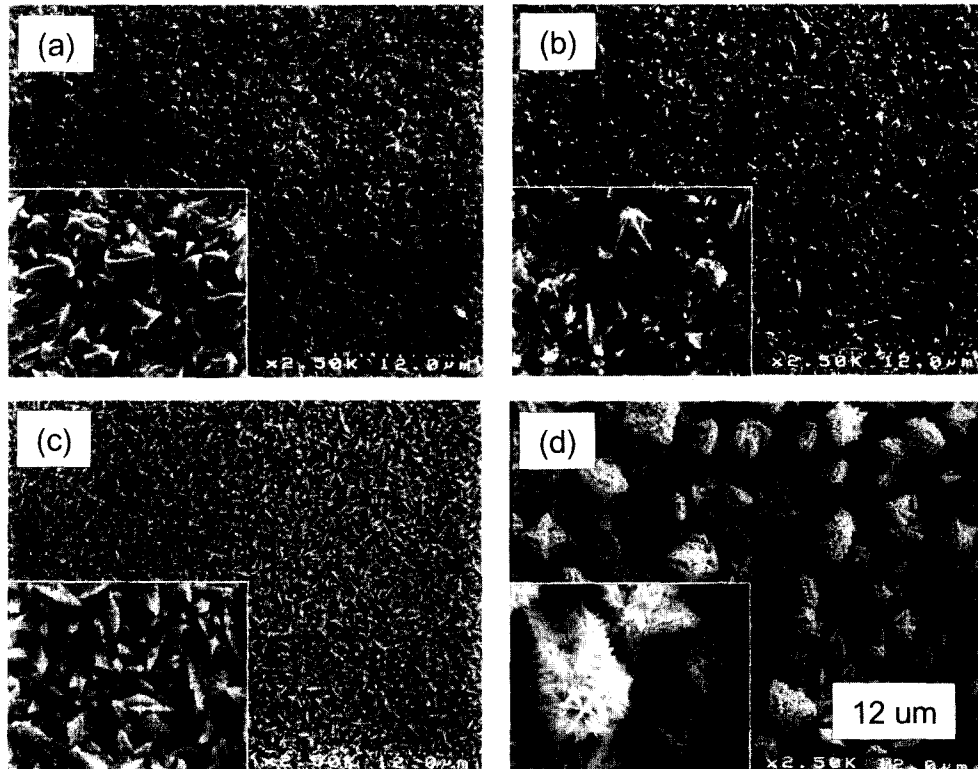


Fig. 4. Change of deposit morphology as a function of current density (mA/cm²) in 6.0 M HCl solution with 0.10 M PdCl₂ at 25°C. (X2.5 K/10.0 K) $i_l = 10.1$ mA/cm² Total charge Q = 2.58C (a) 2.07 (b) 4.43 (c) 8.85 (d) 14.7

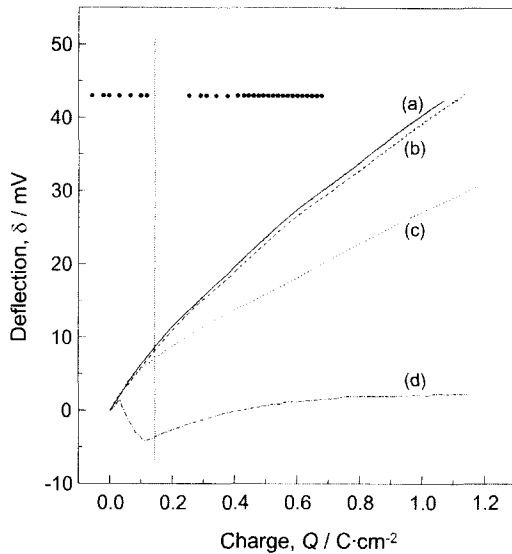


Fig. 5. Deflection vs. deposition charge as a function of current density at 25°C in 6.0 M HCl with 0.1 M PdCl₂. $i_L=10.1 \text{ mA/cm}^2$
 (a) 2.07 (b) 4.43 (c) 8.85 (d) 14.7

to interfacial stress, which is caused by the interaction between the Pt substrate and the Pd deposit¹¹⁾. The interfacial stress, however, diminishes with time, and the volumetric stress, due to deposit growth dominates afterwards.

The deposit plated at the highest current density, $1.46 i_L$ exhibited a steep negative deflection, which indicated compressive stress, during the initial stage. It changed to a positive deflection after a few minutes with almost negligible values. Hydrogen absorption into palladium leads to the expansion of the palladium lattice parameter.¹²⁾ As shown in fig. 1, a severe hydrogen absorption reaction occurred at over the limiting current density in the 6.0 M HCl solution. Therefore, hydrogen should be codeposited at a high current density over i_L and expand the lattice parameter of palladium. The expansion of the lattice parameter by hydrogen should thus explain the negative deflection produced by compressive stress during the initial stage.

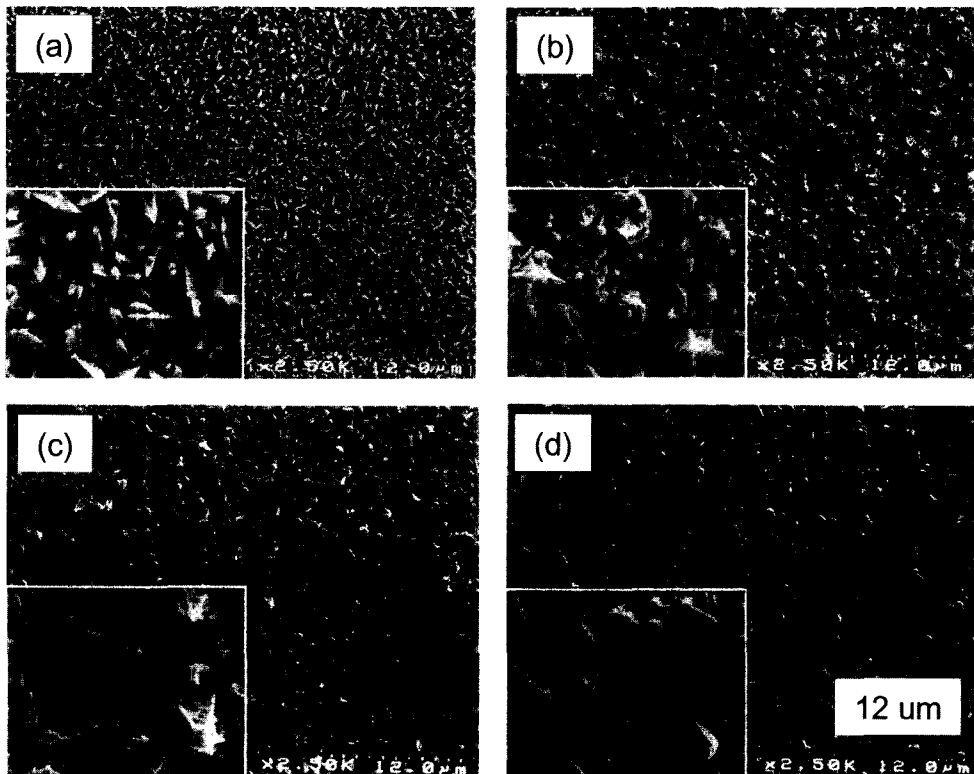


Fig. 6. Change of deposit morphology with temperature in 6.0 M HCl solution with 0.10 M PdCl₂. (X2.5K/10.0K) $i=8.85 \text{ mA/cm}^2$, Total charge $Q=2.58\text{C}$ (a) 25°C (b) 40°C (c) 55°C (d) 70°C

One distinct relationship between morphology and stress was that the dense deposit exhibited high tensile stress states, and the stress was reduced as the morphology transformed to a porous structure with increasing current density. There have been various theories to explain the origin of the stress.¹³⁻¹⁷⁾ Regardless of the origin of the stress, the tensile stress indicates the contraction of a newly deposited layer on the substrate or on the previously deposited metal layer itself. In view of this, it is reasonable to assume that the porous deposit should have lower stress values, as compared to the case where they are dense and compact.

As seen in fig. 4, a dense Pd deposit could be obtained by means of low current density deposition. Even though the deposit at a higher current density exhibited lower values of stress, deposition at a high current density over i_L has several drawbacks, as porous structure with high possibility of impurity occlusion and most probably hydrogen contamination from severe hydrogen evolution. Therefore, ways to reduce the stress level while maintaining a dense morphology should be sought for a dense bulk Pd deposit with lower stress.

Fig. 6 shows the effect of deposition temperature on the morphology of deposits prepared at the current density of 8.85 mA/cm^2 . The current density was chosen because it showed the lowest stress level, except for the case of the highest current density over i_L . It can be seen that the deposits prepared at 40°C , 55°C and 70°C show dense structures compared to the deposit prepared at 25°C . The increase of temperature can be regarded as having a similar effect of increasing the limiting current density through the improvement of mass transport in solution. The temperature of deposition affected stress greatly. Fig. 7 shows the effect of deposition temperature on the stress. The deflection drastically decreases as the temperature rises from 40°C to 70°C . The reduction of deflection indicates the reduction of tensile stress. The mechanism by which tensile stress is lowered by temperature is not clear, but it is thought that one effect of raising the temperature is enhanced diffusion of surface adatoms to stable sites, where they produce less stress. Jinxian Yu et al. reported that the diffusion rate of surface adatoms during Zn deposition accelerates exponentially with

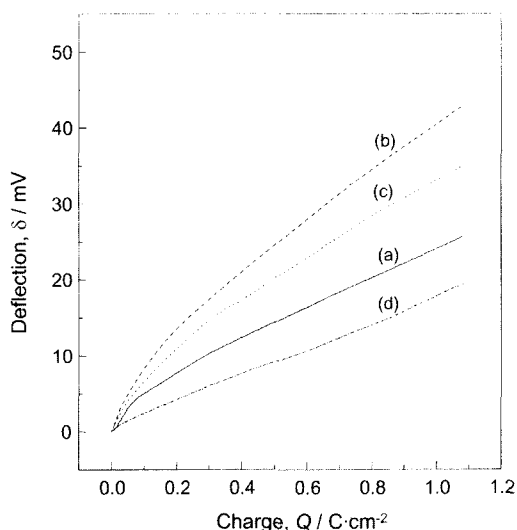


Fig. 7. Deflection vs. deposition charge as a function of temperature in 6.0 M HCl with 0.10 M PdCl₂ at 8.85 mA/cm^2 . (a) 25°C (b) 40°C (c) 55°C (d) 70°C

increasing temperature and causes the adatoms to diffuse and reach stable sites.¹⁸⁾

It should be noted, however, that the tensile deflection measured at 40°C and 55°C are significantly higher than that measured at 25°C . The increase in temperature resulted in the densification of the deposit, as seen in fig. 6 (b), (c), and (d). The densification is expected to increase the stress for the reasons discussed previously. The more rise in the deposition temperature enhances both the densification and the stress relief of the deposits. As the temperature becomes high as 70°C , the stress relief effect overwhelms the densification effect resulting in the significant reduction in stress as observed in fig. 7.

3.3. Electrochemical recovery of bulk Pd deposit

Electrochemical recovery of the bulk Pd deposit was done by means of a batch-type process that utilized no further supplement of palladium during the process. The foregoing electrochemical reaction, the deposit morphology and the stress studies suggested that a dense and less-deformed Pd deposit could be produced using low current density and high temperature. The current density should be determined by considering deposit structure, deformation, and recovery rate. The recovery condition chosen was a $0.6i_L$ current density

(34.7 mA/cm^2) at 70°C , with vigorous agitation. The stirring was expected to raise the recovery rate by increasing the limiting current density in the batch-type recovery process.

Fig. 8 and 9 show the effect of the recovery process

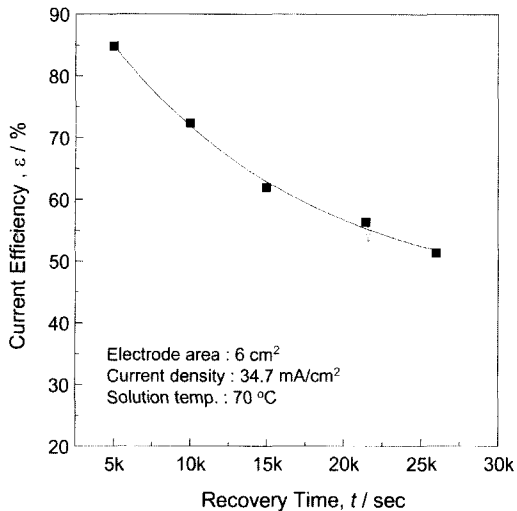


Fig. 8. Current efficiency vs. electrochemical recovery time in 6.0 M HCl with 0.10 M PdCl₂.

on current efficiency and deposit morphology. Current efficiency was over 85% at the initial stage of recovery and gradually decreased to 52% after 26000 seconds of the deposition. The Pd ion concentration in the solution was decreased to 57 % of the initial value after 26000 seconds of the deposition. The conductivity and pH of the 6.0 M HCl solution containing 0.10 M PdCl₂ were about 0.96 S/cm and -1.0 at 25°C, respectively, and were hardly changed during the recovery experiments as shown in figure 10. This indicates that conductivity and pH have no effect on the observed decrease in the current efficiency. If the fitting line at low concentrations in fig. 2 is valid at high concentrations, a 50% reduction of Pd ion concentration should be accompanied by a 50% decrease of the limiting current density. This means that the recovery process needs a periodical supplement of Pd source for keeping the high current efficiency. The absence of surface roughening with ball-like deposits in fig. 9 makes it appropriate to explain the decrease of current efficiency in fig. 8. The decrease in the limiting current density indicates a decrease in the current efficiency by increased side reactions and it can cause a change in

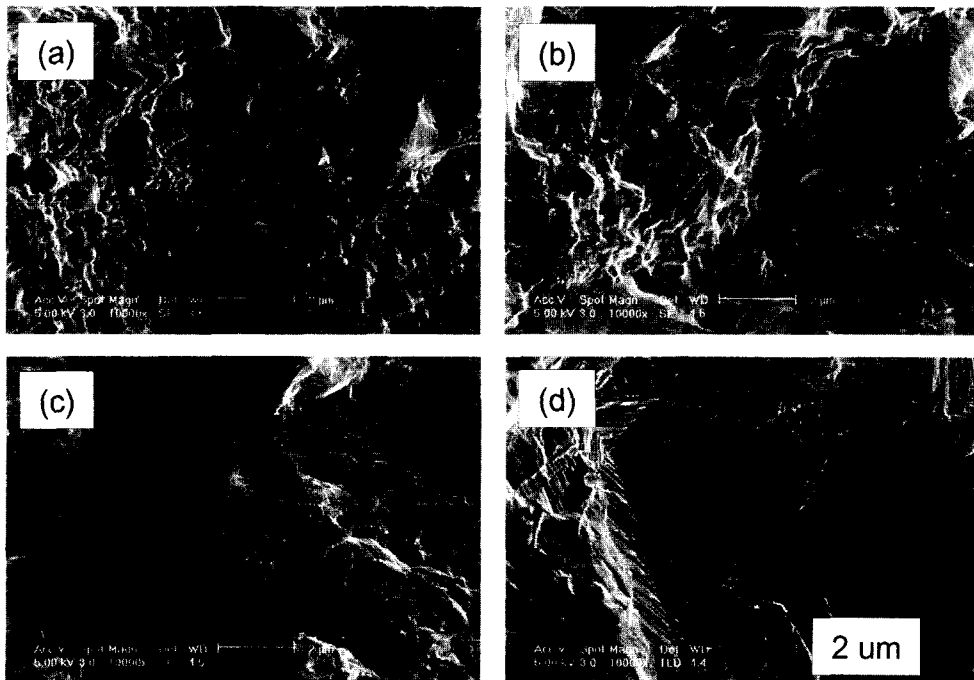


Fig. 9. SEM images of bulk Pd deposits as a function of electrochemical recovery time in 6.0 M HCl solution with 0.10 M PdCl₂. (X10.0K) (current density 34.7 mA/cm^2 , 70°C) (a) 5000 sec (b) 10000 sec (c) 15000 sec (d) 26000 sec

deposit morphology. The morphology at 5000 seconds of deposition in fig. 9 (a) was similar to the dense irregular morphology seen in fig. 4 (a). The dense surface morphology changed from irregular to starfish-like grains during the recovery period. The predominant morphology after 26000 seconds of deposition was the starfish-like pentagonal compact layers stacked up like a pagoda.

The morphology change was accompanied by an alteration of the dominant lattice plane, as shown in

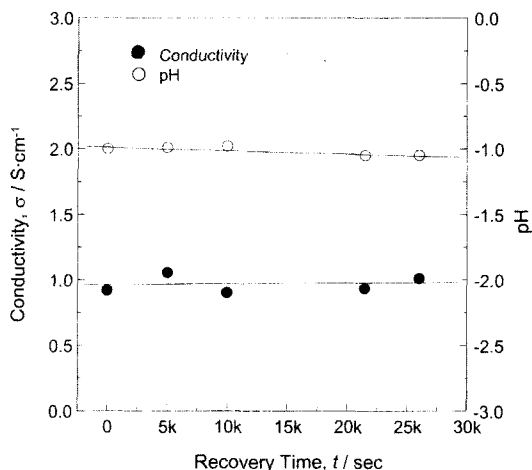


Fig. 10. Change of conductivity and pH of 6.0 M HCl solution with 0.10 M PdCl₂ during electrochemical recovery.

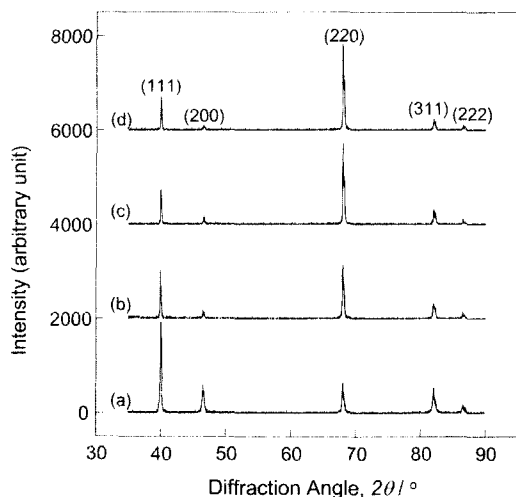


Fig. 11. X-ray diffraction patterns of bulk Pd deposit surfaces as a function of electrochemical recovery time. (a) 5000 sec (b) 10000 sec (c) 15000 sec (d) 26000 sec

fig. 11. The recovered bulk Pd deposit was a cubic close packed structure, with a lattice parameter of 3.89 Å. The dominant lattice plane of the deposit surface changed from Pd(111) to Pd(220) during the recovery process. Although a growth mode of metal deposition is much more complicated, the growth mode is generally confined to the plane having the lowest normal growth rate.¹⁹⁾ Under idealized conditions, these would be the planes having a close-packed structure. The Pd(111) plane has a close-packed structure. It would be the lowest normal growth plane at the initial stage. The morphology change from an irregular to a starfish-like compact layer indicates that the dominant deposit layer of the irregular compact layer is Pd(111) plane, while the dominant deposit layer of the starfish-like pentagonal compact layer is the Pd(220) plane. Pd(220) is not a close-packed plane and can be formed more easily than the Pd(111) plane at a high current density or, in this case, at a low limiting current density, caused by the decrease of Pd ion concentration during the recovery. The decrease of Pd ion concentration resulted in a change of growth mode, from a close-packed to a non-close-packed structure, during the recovery.

4. Conclusions

Electrochemical recovery of palladium in a hydrochloric acid solution was investigated by means of linear polarization, deposit morphology observation, and stress measurement. The high acidity of the HCl solution and the low concentration of Pd ion increased the cathodic overpotential with severe hydrogen evolution and lowered the limiting current density. The morphology and stress of the Pd deposits could be controlled by means of changing the current density and the solution temperature. Increasing the current density changed the morphology of the Pd deposit, from dense and irregular to porous and starfish-like. Lowering the current density produced dense deposits; however, they were under high tensile stress. Raising the temperature affected both densification and stress, enabling the attainment of dense Pd deposits under low stress. Lowering the current density and raising the temperature up to 70°C was recommended for the electrochemical recovery of palladium as sound bulk Pd deposits.

During the batch-type recovery process, the current efficiency was over 85% at the initial stage of recovery and gradually decreased. The reduction of the Pd ion concentration during the process not only decreases the current efficiency, but also changes the dominant deposit structure, because a low Pd ion concentration results in a low limiting current density.

List of symbols

- E^0 : formal potential of an electrode
 E : electrode potential
 R : gas constant
 T : temperature
 F : faraday constant
 n : stoichiometric number of electrons involved in an electrode reaction
 i_L : limiting current density
 D : diffusion coefficient
 C : concentration
 δ_N : Nernst diffusion layer thickness

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