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## STUDIES ON THE ELECTROLYTIC WINNING AND ELECTROREFINING OF PALLADIUM

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### ABSTRACT

As the fundamental studies with a view to introduce an electrochemical method into the process of refinery and recovery of palladium, the authors attempted to investigate the mechanism of electrodeposition and find the suitable electrolytic condition for the process of palladium deposition from the solutions containing  $\text{NO}_2^-$  and  $\text{Cl}^-$ .

The effect of the cathode materials and cathode potentials on the current efficiency and the deposition behaviors were examined, and from these results with those of polarization curves, the conditions suitable for the electrodeposition of palladium from this system were determined.

Further, from the effects of composition of electrolyte on the electrodeposition, it was found that adhesive Pd-deposit with high current efficiency could be obtained from the solution having  $\text{NO}_2^-/\text{Pd(II)}$  molar ratio of about 1.

Presence of  $\text{NO}_2^-$  in excess of this ratio was found to reduce the current efficiency of Pd-deposition by participating  $\text{NO}_2^-$  to be reduced to  $\text{NH}_4^+$  in the cathodic reaction.

From the results of visible light absorption spectra of Pd(II)- $\text{NO}_2^-$ - $\text{Cl}^-$  system and polarization curves, the presence of intermediate complex  $[\text{Pd}(\text{NO}_2)_2\text{Cl}_2]^{2-}$  was presumed.

It was concluded from the electrochemical studies on Pd-deposition from the solutions containing  $\text{Cl}^-$  and  $\text{NO}_2^-$  that the complex ion presumed here participated in electrodeposition reaction and that it was the necessary condition for good electrodeposition of palladium.

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## 1. Introduction

In the previous papers (Kammel, et al. 1968 and in print) the results of investigations about the anodic behaviour, especially the anodic dissolution of Pd and Pd-Ag alloy in solutions containing  $\text{Cl}^-$  or  $\text{Cl}^-$  and  $\text{NO}_2^-$ , have been reported. From the data, which were compiled in an E-pH- $\text{Cl}^-$  diagram (Pourbaix diagram) it seemed that some fundamental informations could be extracted for the development of a new electrochemical winning or refining method of palladium.

In this series of experiments the mechanism of electrodeposition of Pd and the most suitable conditions of the new electrolysis process have been studied, using solutions of the Pd(II)- $\text{Cl}^-$ - $\text{NO}_2^-$  system. In the course of the studies also the effects of the electrolyte composition on the cathodic current efficiency of Pd deposition and the existence of complex ions formed in the solution at molar ratio of  $\text{NO}_2^-$  vs. Pd(II) being equal, were investigated.

## 2. Experimental

In these experiments, Pd(99.9%) plates were used as anode and stainless steel plate as cathode materials with surface area of both electrodes being  $2\text{ cm}^2$  in 100 ml of the electrolytic solution. The electrolytic solutions used were fundamentally same as mentioned in the previous paper (Kammel, et al. in print) with the following composition:



These solutions have approximately the same composition and main components as the plating bath published by Yampolski (1963): 5-10 g/l  $\text{PdCl}_2$ , 15-20 g/l  $\text{NaNO}_2$ , 40-50 g/l  $\text{NaCl}$ , 25-30 g/l  $\text{H}_3\text{BO}_3$ , pH 5.6-6.5,  $50^\circ\text{C}$ , current efficiency 40-50%. The experiments performed in the courses of this research work under various electrolysis conditions were carried out at  $25^\circ\text{C}$ .

## 3. Experimental Results and Discussion

### 3. 1. Determination of the Cathodic Potential

In order to obtain the precise information about the optimum electrolytic conditions for the electrodeposition of palladium, the cathodic polarization in  $\text{Cl}^-$  and  $\text{Cl}^-$ - $\text{NO}_2^-$  containing solutions were measured and the results obtained were plotted in Fig. 1.

In solutions containing no  $\text{NO}_2^-$ , electrodeposits of Pd became like as colloidal suspensions at the electrode solution interface and fell down from electrode surface at lower cathodic potentials. Moreover in electrolytes containing  $\text{NO}_2^-$ , the current density was too small in the region till about  $-0.6\text{ v}$  (NCE), but the palladium electrodeposits were almost metallic. Therefore, considering suitable electrolysis conditions, the cathodic potential should be kept at  $-0.7\text{ v}$  (NCE).

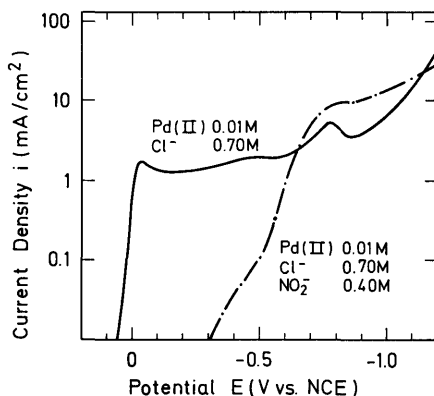
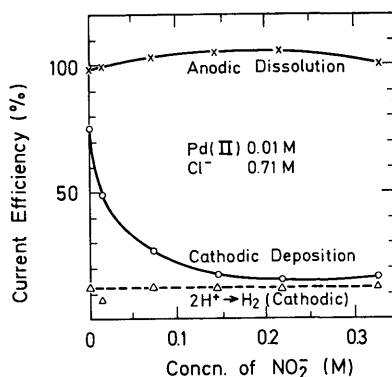


Fig. 1 Cathodic Polarization Curve

### 3. 2. Effects of NO<sub>2</sub><sup>-</sup> Concentration on Current Efficiency

The influence of various NO<sub>2</sub><sup>-</sup> concentrations on the current efficiency for the palladium deposition was examined, and the results obtained with solutions containing relatively low Pd(II) concentration are shown in Fig. 2.


 Fig. 2 Efficiency vs. Concentration of NO<sub>2</sub><sup>-</sup>  
 [Case of lower Concentration of Pd(II)]

From the dependence of the current efficiency of the anodic dissolution of Pd and of the cathodic hydrogen gas evolution it can be seen that both electrode processes are almost independent of the NO<sub>2</sub><sup>-</sup> concentration in the solutions investigated. However, the current efficiency for the cathodic deposition of Pd decreases markedly with increasing NO<sub>2</sub><sup>-</sup> concentrations. Considering the overall cathodic efficiency (deposition of Pd and hydrogen evolution) the experiments performed reveal that it is far smaller than 100%. It is supposed that this observation can be related to the simultaneous cathodic reduction of NO<sub>2</sub><sup>-</sup>.

To confirm the reduction of NO<sub>2</sub><sup>-</sup> the relation between the NO<sub>2</sub><sup>-</sup> content and

the current efficiency on the deposition of Pd was examined also in solutions with higher concentration of Pd(II) and the results are illustrated in Fig. 3.

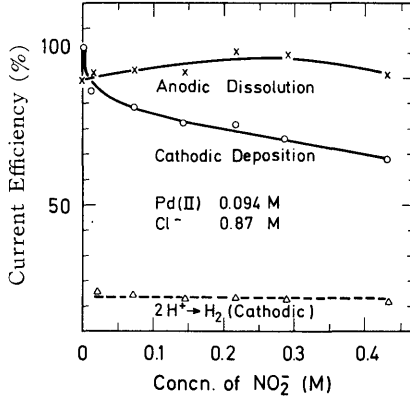


Fig. 3 Efficiency vs. Concentration of  $\text{NO}_2^-$   
[Case of higher Concentration of Pd(II)]

Though also in this case the cathodic current efficiency was decreasing gradually with the  $\text{NO}_2^-$  concentration, the degree of the current efficiency decrease was smaller than in the case of lower Pd(II) concentration in the solutions. From these results it can be assumed that the decrease of current efficiency for the deposition of Pd can be related due to the superposition of the  $\text{NO}_2^-$  reduction.

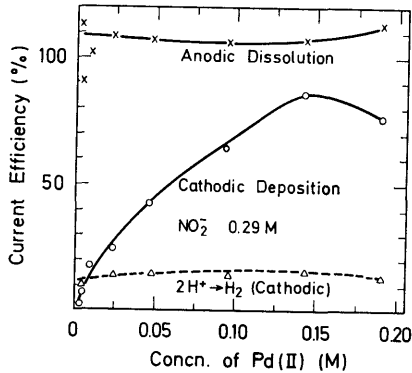


Fig. 4 Efficiency vs. Concentration of Pd(II)

In order to confirm this cathodic reduction mechanism a series of experiments were performed to determine the influence of the Pd(II) concentration in the electrolyte on the current efficiency at constant concentration of  $\text{NO}_2^-$ . From the results shown in Fig. 4 it can be seen that the current efficiency of the cathodic palladium deposition is increasing with the concentration of Pd(II). On the other hand the current efficiency of anodic dissolution of palladium remains almost constant at approximately 100% and also the cathodic hydrogen evolution is nearly

constant with variations 10~15%. From these results it might be presumed that the various concentrations of Pd(II) and  $\text{NO}_2^-$  in the electrolyte have only some negligible influence on the anodic palladium dissolution, but the ratio of Pd(II)-to  $\text{NO}_2^-$ -concentration effects distinctly the current efficiency of the palladium deposition. Furthermore the results reveal that it might be possible to suppress the simultaneous cathodic reduction of  $\text{NO}_2^-$  and accordingly to increase the current efficiency of the palladium deposition by increasing the Pd(II) concentration of the electrolyte.

It was found by electrolysis tests with solutions containing no  $\text{NO}_2^-$  that the apparent current efficiency for the palladium deposition was high, but to a certain extent superimposed a cementation of palladium and deposits of palladium started to diffuse into solution like colloidal suspensions. From these results it becomes evident, that it is necessary to add  $\text{NO}_2^-$  into electrolytic solution for the suitable deposition of palladium as well as for the anodic palladium dissolution.

From the above mentioned results it was assumed that the best electrolysis conditions in this system might be expected within the range of the molar ratio Pd(II) vs.  $\text{NO}_2^-$  of about 1.

### 3. 3. Reduction of $\text{NO}_2^-$

Concerning the product generated during the cathodic reduction of  $\text{NO}_2^-$ , the electrolysis conditions with only  $\text{NO}_2^-$  as well as Pd(II) and/or  $\text{Cl}^-$  containing electrolytes are illustrated in the E-pH diagram of the system  $\text{N}_2\text{-H}_2\text{O}$  (Pourbaix) as shown in Fig. 5. The plotted data reveal that  $\text{NH}_4^+$  should be the most stable under equilibrium conditions, and moreover,  $\text{NH}_4^+$  was identified in the electrolytic solution by chemical analysis. These results confirm that  $\text{NO}_2^-$  might be reduced to  $\text{NH}_4^+$  by the cathodic reaction.

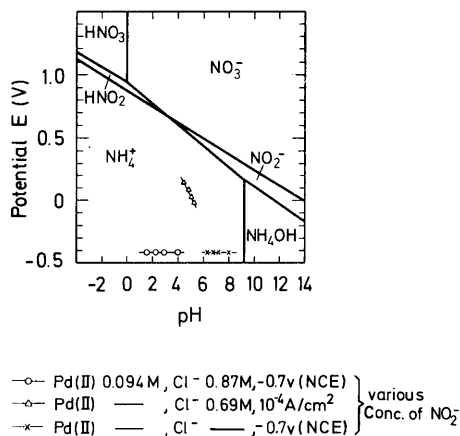


Fig. 5 Potential-pH (Pourbaix)-Diagram of the System  $\text{N}_2\text{-H}_2\text{O}$

Moreover, to ensure the effects of the  $\text{NO}_2^-$  concentration on the electrodeposition, the cathodic polarization curves were measured and plotted for various  $\text{NO}_2^-$  concentrations, expressed as  $\text{NO}_2^-/\text{Pd(II)}$  ratio with constant  $\text{Pd(II)}$  contents, in Fig. 6.

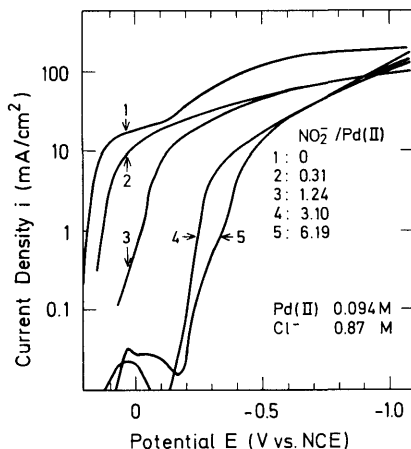


Fig. 6 Cathodic Polarization Curve

The polarization curves indicate the tendency that the cathodic potential is shifting with increasing  $\text{NO}_2^-/\text{Pd(II)}$  ratios to more negative values and the curves become more and more characteristically different from the others. From these cathodic polarization curves the effect of  $\text{NO}_2^-$  on cathodic reaction seemed to be remarkable.

### 3. 4. Absorption Spectra of Electrolytic Solutions

From the above mentioned results and from previous investigations (Kammel et al. in print) it was assumed that  $\text{Pd(II)}$  and  $\text{NO}_2^-$  are forming a complex ion in the electrolytic solution. In order to get more precise information the absorption spectra in the range of the visible light were observed with solutions having

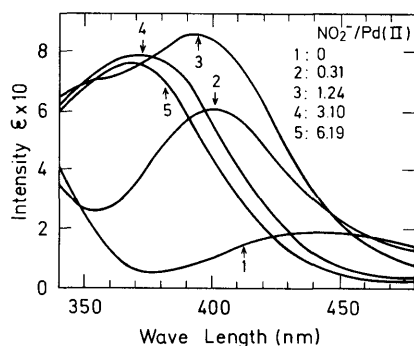


Fig. 7 Absorption Spectra of  $\text{Pd(II)-Cl-NO}_2^-$  System

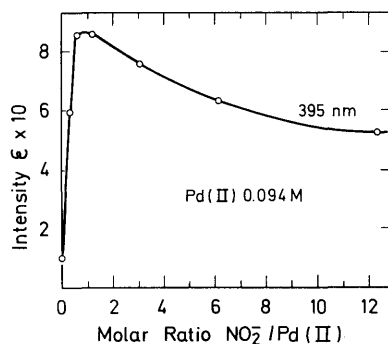


Fig. 8 Absorption Intensity vs. Molar Ratio

various values of molar  $\text{NO}_2^-/\text{Pd(II)}$  ratio. From the curves compiled in Fig. 7 it can be seen that the peak of absorption is shifting to shorter wave length with increasing  $\text{NO}_2^-$  contents resp.  $\text{NO}_2^-/\text{Pd(II)}$  ratio, and reaches finally an almost constant value of about 365 nm. The peak of curve 1 corresponds to the existence of  $\text{PdCl}_4^{2-}$  and the peak of curve 5 to that of a palladium complex ion containing Pd(II),  $\text{NO}_2^-$ , i.e.  $\text{Pd}(\text{NO}_2)_4^{2-}$ . The other peaks between curves 1 and 5 show that  $\text{Cl}^-$  and  $\text{NO}_2^-$  are mixed to coordinate to Pd(II).

To estimate more definite value about the composition of the intermediate complex ion, the dependence between molar ratio of  $\text{NO}_2^-/\text{Pd(II)}$  and absorption intensity data was given in Fig. 8. From the curve a pronounced knick point can be observed near molar ratio of 1, examining the relation for intermediate wave length between peaks 1 and 5 (395 nm in Fig. 8). From these results it can be elucidated that a Pd(II) ion is coordinated by a  $\text{NO}_2^-$  ion and  $\text{Cl}^-$ , and is forming the following complex ion:

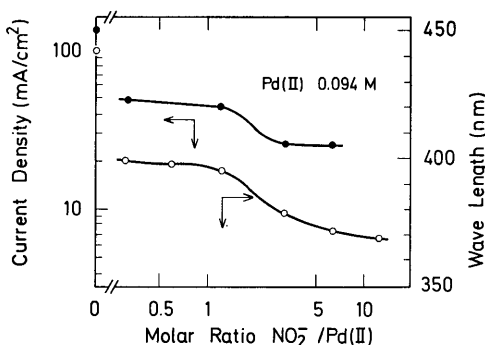
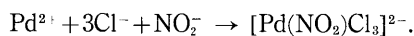


Fig. 9 Cathodic Current or Absorption Perk vs. Molar Ratio

Moreover, from plotting the wave length for the peak of absorbance and the current density at a constant potential in the polarization curve against the molar ratio of  $\text{NO}_2^-/\text{Pd(II)}$ , as shown in Fig. 9, it might be clear, that flat parts of both curves appeared at molar ratio nearly between 0.3 to 1 and that there is satisfactory correspondence between the absorption spectra and the polarization data.

#### 4 Conclusion

The experimental results about the electrolytic winning and refining of palladium in solutions containing Pd(II),  $\text{Cl}^-$  and  $\text{NO}_2^-$  show that the  $\text{NO}_2^-$  content is increasing the efficiency and extending the region of anodic palladium dissolution, but excess  $\text{NO}_2^-$  concentration decreases the current efficiency for the cathodic palladium deposition because of the simultaneous cathodic reduction of  $\text{NO}_2^-$  to  $\text{NH}_4^+$ .

However, metallic palladium could be deposited with high current efficiency from the solution of the system with molar ratio  $\text{NO}_2^-/\text{Pd(II)}$  of about 1, and



from the absorption spectra and the polarization data it might be deduced that Pd(II),  $\text{NO}_2^-$  and  $\text{Cl}^-$  are forming a complex ion of the type  $[\text{Pd}(\text{NO}_2)\text{Cl}_3]^{2-}$  in the solution, which is suitable for the electrodeposition of Pd.

The studies reveal, that under the optimum electrolysis conditions palladium can be dissolved and deposited with high current efficiencies and indicate the fundamental possibility to a new electrochemical method for the electrowinning or refining of palladium.

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