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A Study of the Reduction of Chelated Palladium on Mercury Electrode

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This paper investigates the reduction kinetics and mechanism of Pd(II)-ethylenediamine with cyclic voltammetry and normal pulse polarography techniques. The results indicate that the reduction is an irreversible process. The major kinetic parameters and diffusion coefficients of Pd(II)-ethylenediamine and other Pd(II)-aliphatic diamine complexes are reported. The influences of concentrations, pH values, and ligand structures on the reduction of Pd(II) complex are also discussed. The electrochemical reaction orders with respect to ethylenediamine and Pd(II)-ethylenediamine are found to be 0 and 1, respectively and these reaction orders demonstrate an undissociated complex reduction mechanism. Finally the iodide effect on normal pulse polarography is studied. The increase in current when iodide is added implies that the reduction is via the outer sphere path way.

A palladium deposit is a good substitute for gold in the electronic industry because of its lower cost and excellent chemical, physical, and electrical properties. Among various Pd plating solutions, Pd-diamine system is an important one.[1–4] Although Pd deposition has become a hot topic in recent years, the electrochemical behavior of Pd^{2+} electrolytes has not received wide attentions yet.

Early in 1945 Willis had studied the polarographic reductions of Pd(II) in various complexing agents such as ammonia, ethylenediamine(en), diethylamine, and ethanolamine. He found that the reductions are incompletely reversible two-electron processes.[5] He also found that the half-wave potentials of the reductions of these complexes are more negative as the ligand becomes more basic. Later, Simpson et al. studied the Pd(II) reductions with polarography and obtained the diffusion coefficients of Pd(II) complexes in solutions containing chloride and acetate.[6] Chakravarty also studied polarographic behavior of Pd(II) complexes and discovered that those Pd(II) complexes with ammonia or ethylenediamine as complexing agents are irreversibly reduced.[7] Hirota et al. studied reductions of Pd(II) complexes and found that the more stable the complex the more difficult the reduction.[8] The polarography studies of Gaur revealed that the reduction of Pd(II) in 0.2 M pyridine, 0.1 M HCl is a quasi-reversible process[9,10] (1 M=1 mol dm^{-3}).

The reduction mechanism of $PdCl_4^{2-}$ on some solid electrodes has been studied by some authors. Confusing results were obtained. Watt and Cunningham reported that $PdCl_4^{2-}$ is the species that was reduced.[11] Later in a series of papers published by Harrison and co-workers, $PdCl_2$ was thought to be the species that was reduced, though the prevailing ion in solution is $PdCl_4^{2-}$.[12–17]

For quantative analysis, both direct current polarography and differential pulse polarography have been used to determine Pd(II) concentration.[18–25]

There have been few studies concerning the electrochemical behavior of chelated Pd(II) though it is an important ingredient of palladium plating solution. In this work both the electrode kinetics and reduction mechanism are investigated. First we study the reduction kinetics of Pd(II) chelated with diamines on a mercury drop electrode with cyclic voltammetry(CV) and normal pulse polarography(NPP) techniques. Both kinetic parameters and diffusion coefficients are reported. The influences of concentrations, pH values, and ligand structures on the reduction of Pd(II) complex are discussed. Then we consider the reduction mechanism of $Pd(en)_2^{2+}$. In order to ascertain the reactive species of $Pd(en)_2^{2+}$ reduction, the electrochemical reaction orders with respect to en and $Pd(en)_2^{2+}$ are used as criteria. Finally the iodide effect on NPP is also investigated for a further understanding of the essence of $Pd(en)_2^{2+}$ reduction.

Experimental

A palladium stock solution was prepared by dissolving reagent grade $PdCl_2$ (Wako Co.) in deionized water with sufficient potassium chloride to enhance its solubility and stability. The Pd content was 0.06 M. NaI, KCl, en, 1,2-propanediamine (1,2-pn, Merck), 1,3-propanediamine (1,3-pn, Janssen), 1,4-butanediamine (bn, Janssen), 1,6-hexanediamine (hn, Merck) were all dissolved in deionized water to 2 M. The concentration of Triton X-100 (Merck) solution was 0.1%. The test solutions were prepared by mixing these stock solutions to desired concentrations. Hydrochloric acid and sodium hydroxide were used to adjust the pH value.

All CV and NPP experiments were performed on an EG&G Model 384B polarographic analyzer. A mercury drop electrode controlled by mechanical motions (EG&G Model 303A) was used as the working electrode (electrode area 0.009 cm^2). Platinum wire and a silver-silver chloride electrode (SSCE) were used as counter and reference electrodes, respectively. In CV experiments the scan rates ranged from 25 mV s^{-1} to 500 mV s^{-1} while the scan rate was 10 mV s^{-1} with a drop time of 1 second for all NPP experiments. Before the measurements, nitrogen purified through the vanadium (II) chloride scrubbing solution was bubbled into test solutions for 10 minutes to exclude the dissolved oxygen.

All chemicals were reagent grade and used without further purification. The complexes were identified by ultraviolet-(UV) absorption experiments (Hitachi, model 320).[26–28]

Results and Discussion

1. Fundamental Kinetic Studies. First we discuss the reversibility of the $Pd(en)_2^{2+}$ reduction process. Fig. 1 shows the cyclic voltammogram of $Pd(en)_2^{2+}$. Obviously the complex reduction is irreversible. For a totally irreversible system, peak current (I_p) is proportional to the square root of scan rate ($v^{1/2}$) which is not the case for a partially irreversible process. Figure 2 confirms this.

The kinetic parameters and diffusion coefficients were derived from NPP experiments. The normal pulse polarogram of $Pd(en)_2^{2+}$ without the addition of Triton X-100 is shown in Fig. 3(a) which contains a maximum. In order to analyze the polarogram successfully, Triton X-100 was added to suppress the maximum. The result is shown in Fig. 3(b). The addition of Triton X-100 shifts the reduction toward negative direction by about 0.15 V.

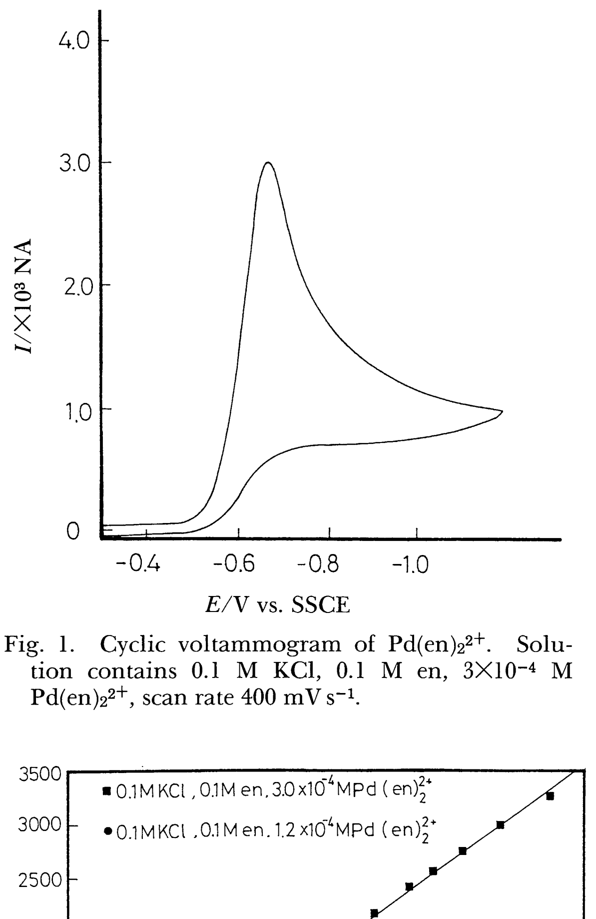

Fig. 1. Cyclic voltammogram of $Pd(en)_2^{2+}$. Solution contains 0.1 M KCl, 0.1 M en, 3×10^{-4} M $Pd(en)_2^{2+}$, scan rate 400 mV s^{-1}.

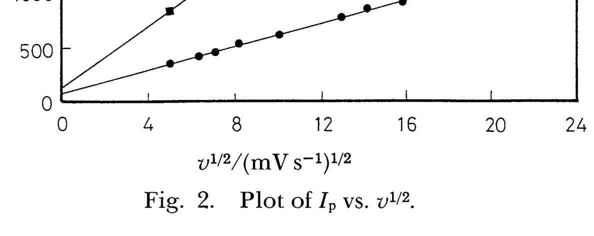

Fig. 2. Plot of I_p vs. $v^{1/2}$.

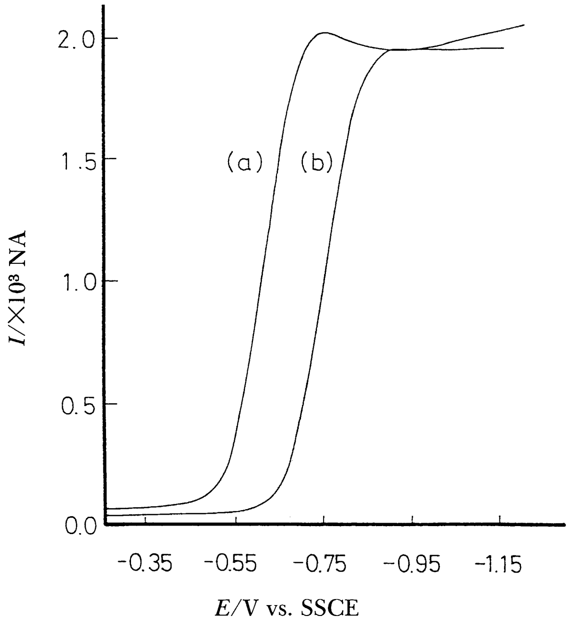

Fig. 3. Normal pulse polarogram of $Pd(en)_2^{2+}$. Solution contains 0.1 M KCl, 0.1 M en, 1.2×10^{-4} M $Pd(en)_2^{2+}$, and (a) no Triton X-100 (b) 0.003% Triton X-100.

The relationship between the diffusion-controlled current(I_d) and bulk solution concentration (C_b) is known as:[29]

$$I_d=\frac{nFAD_o^{1/2}C_b}{\pi^{1/2}(t-t')^{1/2}} \tag{1}$$

where n, F, and A are number of electrons transferred, faradic constant, and electrode surface area respectively, D_o is diffusion coefficient, and t-t' is the NPP sampling time (40 milliseconds). With this equation, the diffusion coefficients can be calculated.

The polarograms were analyzed according to the method proposed by Oldham and Parry for irreversible processes.[30] A plot of log $\{x^2(1.75+x^2)/(1-x)\}$ (where $x=i/i_d$) against electrode potential E should yield a straight line whose slope and intercept can be used to calculate the charge transfer coefficient α and rate constant k. All data reported below were obtained in this way and the effects of concentrations, pH values, and ligand structure will be discussed in the following sections.

1.1. The Effects of Concentrations. The effects of concentrations of $Pd(en)_2^{2+}$ and en upon kinetic parameters and diffusion coefficient were studied. It is found that both concentrations have little influences on these figures in the concentration range of 1.5×10^{-5} to 3×10^{-4} M ($Pd(en)_2^{2+}$) and 0.1 to 0.001

M(en). The αn, $E_{1/2}$, and k^r values are 0.51, −0.75 (V vs. SSCE), and 3.7×10^{-4} (cm s^{-1}) respectively. The diffusion coefficient is 1.1×10^{-5} cm^2 s^{-1} which is somewhat larger than those obtained by Simpson et al.[6] ($4-8\times10^{-6}$ cm^2 s^{-1}, for Pd(II) in solutions containing chloride and acetate) and by Harrison et al.[13] (7×10^{-6} cm^2 s^{-1}, for Pd(II) in chloride solutions).

1.2. The Effects of pH Values. The normal pulse polarograms were also studied in various pH values. Surprisingly different mixing procedures gave different results. Thus it is important to identify the complexes which exist in test solutions. The results in Table 1(a) were obtained from solutions of various pH values which were prepared by adding $PdCl_2^{2-}$, then HCl (or NaOH) to en solution. It is discovered that $Pd(en)_2^{2+}$ was always formed completely since the limiting current observed was the same throughout the pH values studied. The reductions were stable in basic conditions while the half-wave potential shifted negatively with the increase of acidity in acid region. This potential change is attributed to the chloride effect introduced by the addition of HCl since similar results were observed when KCl was used in the experiments instead. It is thus concluded that the accumulation of chloride moves the reduction potential of $Pd(en)_2^{2+}$ toward the hydrogen evolution region and is unfavorable in the electroplating process.

Table 1(a). Parameters Calculated from NPP Data in Solutions of 0.1 M KCl+0.001 M en+1.2×10^{-4} M $PdCl_4^{2-}$+0.003% Triton X-100+Various Amounts of HCl or NaOH to Desired pH Values

pH	αn	$-E_{1/2}$	$k^r\times10^{-4}$	$D_o\times10^{-5}$
		V vs. SSCE	cm s^{-1}	cm^2 s^{-1}
3.55	0.56	0.78	1.4	1.1
6.43	0.52	0.77	2.3	1.1
9.92	0.50	0.75	3.9	1.1
11.56	0.51	0.75	3.7	1.1
12.56	0.52	0.75	3.5	1.1

Table 1(b). Parameters Calculated from NPP Data in Solutions of 0.1 M KCl+0.001 M en+0.003% Triton X-100+Various Amounts of HCl or NaOH to Desired pH Values +1.2×10^{-4} M $PdCl_4^{2-}$

pH	αn	$-E_{1/2}$	$k^r\times10^{-4}$	$D_o\times10^{-5}$
		V vs. SSCE	cm s^{-1}	cm^2 s^{-1}
3.55	a)	a)	a)	a)
6.43	0.53	0.77	2.3	1.2
9.92	0.50	0.75	3.9	1.1
11.56	0.50	0.75	3.9	1.1
12.56	b)	b)	b)	b)

a) No $Pd(en)_2^{2+}$ reduction was observed. b) Two-wave polarogram was observed, see Fig. 4(a).

Table 1(b) shows the NPP results obtained from the opposite mixing procedure, i.e., HCl (or NaOH) was added to en solution before the $PdCl_4^{2-}$. Different results were observed in pH 3.55 and 12.56. In acidified solutions the reduction current of $Pd(en)_2^{2+}$ decreased with increasing H^+ concentration and finally the reduction wave disappeared. This phenomenon can be explained by en protonation reported by De Waal and Robb.[31] Since

$$\mathrm{en} + H^+ \rightleftarrows \mathrm{Hen}^+, \tag{2}$$

$$\mathrm{Hen}^+ + H^+ \rightleftarrows H_2\mathrm{en}^{2+}, \tag{3}$$

the major species in an acidified en solution is H_2en^{2+}. After complete protonation, H_2en^{2+} loses its ability to form a complex with Pd(II). This en protonation results in a diminution of free en and then $Pd(en)_2^{2+}$ concentration. Finally in highly acidified solutions, the $Pd(en)_2^{2+}$ reduction current can not be found any more.

This explanation is supported by the UV absorption experiments. The pH 3.55 solution in Table 1(b) showed a λ_{max} of 280 nm with high intensity, which is characteristic of $PdCl_4^{2-}$. Obviously there was no free en to subsititute the chloride of the added $PdCl_4^{2-}$ and consequently no $Pd(en)_2^{2+}$ reduction was observed.

The polarogram in highly basic condition (pH 12.56) in Table 1(b) is presented in Fig. 4(a). A two-wave polarogram was observed. Also shown in Fig. 4(b) is the polarogram of the same solution without en (i.e., the complex in solution is $Pd(OH)_4^{2-}$). From Fig. 4(b) it is apparent that $Pd(OH)_4^{2-}$ is not reduced in the potential range studied. Thus the reduction current in Fig. 4(a) should be attributed to $Pd(en)_2^{2+}$ reduction. In fact the half-wave potential of the first wave is almost the same as that of $Pd(en)_2^{2+}$. This result may be explained qualitatively as follows. As $PdCl_4^{2-}$ was added into a highly alkaline en solution,

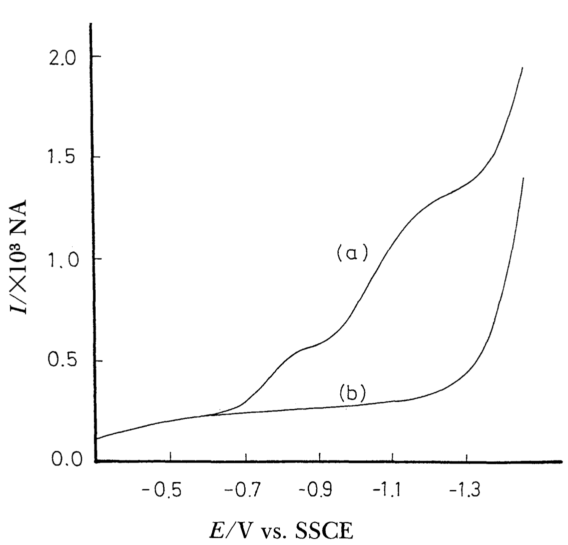

Fig. 4. Normal pulse polarograms of solutions of 0.1 M KCl, NaOH (to pH=12.56), 1.2×10^{-4} M $PdCl_4^{2-}$, 0.003% Triton X-100, and (a) 0.001 M en (b) without en.

chloride was substituted by either en or OH^- group and consequently there exist both $Pd(OH)_4^{2-}$ and $Pd(en)_2^{2+}$ in the solution. The UV absorption of the solution in Fig. 4(a) shows that the absorption maximum occurs at 365 nm, which is the same as that of the solution in Fig. 4(b), but with a smaller intensity. This observation implies that the solution in Fig. 4(a) contains both $Pd(OH)_4^{2-}$ and $Pd(en)_2^{2+}$ and the UV absorption of $Pd(en)_2^{2+}$ may be covered by that of $Pd(OH)_4^{2-}$.

Now the polarogram can be explained. In the first wave, $Pd(en)_2^{2+}$ is reduced and a limiting current which is controlled by the diffusion of $Pd(en)_2^{2+}$ is achieved. But en released due to $Pd(en)_2^{2+}$ reduction accumulates on the electrode surface and reacts with $Pd(OH)_4^{2-}$ to form more $Pd(en)_2^{2+}$. As a result the reduction current increases again and the surface concentration of $Pd(OH)_4^{2-}$ decreases as the potential increases. Finally another limiting current which is subjected to the diffusion of $Pd(OH)_4^{2-}$ appears.

1.3. The Effects of Ligand Structure. In order to investigate the effects of ligand structure on the complex reduction, we also carried out the CV and NPP experiments of Pd(II) in solutions containing aliphatic diamines with different carbon numbers. The experimental results show that they are all reduced irreversibly and the calculated parameters are summarized in Table 2.

The αn values are almost the same although the half-wave potentials do exhibit some difference between the 5 complexes. This is quite reasonable if we consider the essence of these complexes. Willis[5] reported that Pd(II) complexes have increasing negative half-wave potentials as the ligand becomes more basic. Hirota et al.[8] further pointed out that the reduction is directly related to the stability of the complex. Though the diamines studied here have greater basicity when the length of the carbon chain increases, the half-wave potential does not change significantly. This can be explained in terms of the chelate structure of the complexes. As the carbon number increases, the half-wave potential shifts in the negative direction because of the increasing basicity. However, too long a chain makes the chelate ring unstable and results in the shift of half-wave potential in the positive direction. As a result a maximum occurred at the ligand, 1,3-pn. The same effects were also observed in the rate constants.

Table 2. Parameters Calculated from NPP Data in Solutions of 0.1 M KCl, 0.003% Triton X-100, and 1.2×10^{-4} M $Pd(L)_2^{2+}$

L	αn	$-E_{1/2}$	$k^r\times10^{-4}$	$D_o\times10^{-5}$
		V vs. SSCE	$cm\ s^{-1}$	$cm^2\ s^{-1}$
en	0.51	0.75	3.7	1.1
1,2-pn	0.53	0.73	4.7	1.0
1,3-pn	0.53	0.78	1.7	1.0
bn	0.52	0.74	3.6	0.8
hn	0.51	0.56	83	0.3

The variation of ligand also has an influence upon diffusion coefficient as shown in Table 2. Obviously the complex with a larger volume has a smaller diffusion coefficient, which is consistent with the prediction of the Wilke-Chang equation.[32]

2. Reduction Mechanism Studies. For the reduction of $Pd(en)_2^{2+}$ on mercury electrode, we consider three possible mechanisms as follows:

$$\text{(a) } Pd(en)_2^{2+}+2e^-(Hg)\longrightarrow \text{Pd-amalgam}+2en, \tag{4}$$

$$\text{(b) } Pd(en)_2^{2+}\rightleftarrows Pd(en)^{2+}+en, \tag{5}$$

$$Pd(en)^{2+}+2e^-(Hg)\longrightarrow \text{Pd-amalgam}+en, \tag{6}$$

$$\text{(c) } Pd(en)_2^{2+}\rightleftarrows Pd^{2+}+2en, \tag{7}$$

$$Pd^{2+}+2e^-(Hg)\longrightarrow \text{Pd-amalgam}. \tag{8}$$

Corresponding to these three mechanisms, the current-concentration relationships are:

$$I=K[Pd(en)_2^{2+}],\ \text{for (a)}, \tag{9}$$

$$I=K[Pd(en)_2^{2+}][en]^{-1},\ \text{for (b)}, \tag{10}$$

$$I=K[Pd(en)_2^{2+}][en]^{-2},\ \text{for (c)}, \tag{11}$$

where K is a proportional constant and $[Pd(en)_2^{2+}]$, $[en]$ represent concentrations of $Pd(en)_2^{2+}$ and en respectively. The difference of the electrochemical reaction orders between the three possible mechanisms are listed in Table 3.

First we carried out the NPP experiments without the addition of Triton X-100 to avoid the interference which may be introduced by surface active materials such as gelatin, Triton, etc. Figures 5 and 6 are the $\log I$ vs. $\log C$ plots derived from NPP experiments under various $Pd(en)_2^{2+}$ and en concentrations. These figures show that the electrochemical reaction orders with respect to $Pd(en)_2^{2+}$ and en are 1 and 0 respectively. Hence according to Table 3 we conclude that the reduction mechanism is mechanism (a), i.e., $Pd(en)_2^{2+}$ is reduced to Pd-amalgam directly (Eq. 4).

The influence of Triton X-100 on the reduction mechanism of $Pd(en)_2^{2+}$ was also investigated through NPP analyses. One of the polarograms is shown in Fig. 3(b). It seems that Triton X-100 shifts the reduction toward negative direction and has little effect upon its shape except in the region where diffusion becomes important. The electrochemical reaction orders with respect to $Pd(en)_2^{2+}$ and en in the presence of Triton X-100 were also calculated from $\log I$ vs. $\log C$ plots and were found to be 1 and 0 respectively.

Table 3. Electrochemical Reaction Orders for Different Reduction Mechanisms

Electroactive species	Electrochemical reaction order	
	$[Pd(en)_2^{2+}]$	[en]
$Pd(en)_2^{2+}$	1	0
$Pd(en)^{2+}$	1	−1
Pd^{2+}	1	−2

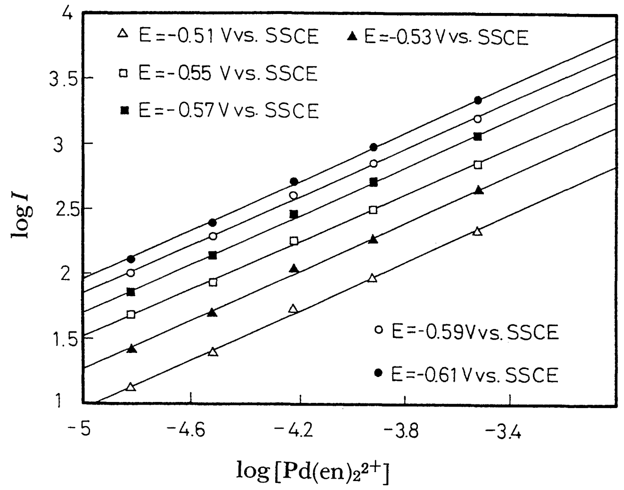

Fig. 5. Plot of $\log I$ vs. $\log[\mathrm{Pd(en)_2}^{2+}]$. Solutions contain 0.1 M KCl, 0.1 M en, and various $\mathrm{Pd(en)_2}^{2+}$ concentrations.

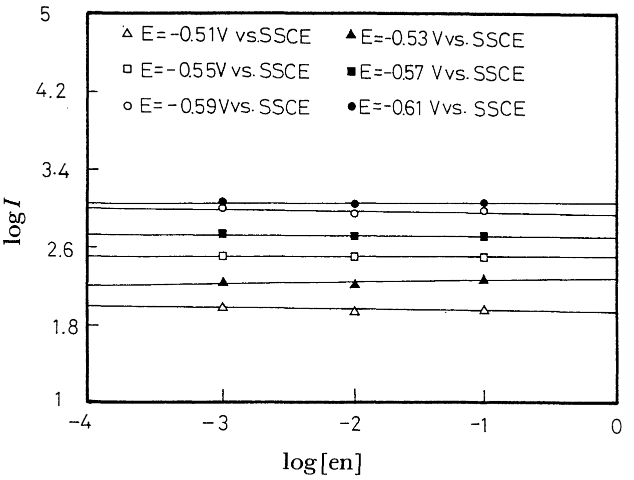

Fig. 6. Plot of $\log I$ vs. $\log[\mathrm{en}]$. Solutions contain 0.1 M KCl, 1.2×10^{-4} M $\mathrm{Pd(en)_2}^{2+}$, and various en concentrations.

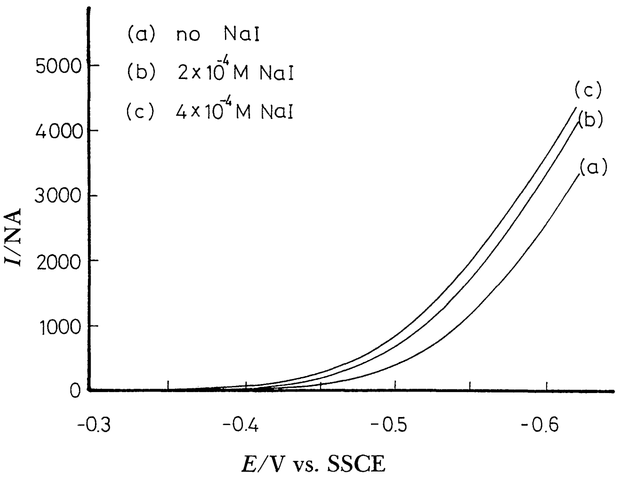

Fig. 7. Iodide effect on NPP experiments. Solutions contain 0.1 M KCl, 0.1 M en, 3×10^{-4} M $\mathrm{Pd(en)_2}^{2+}$, and different amounts of NaI.

Based on these results we know that Triton X-100 does not alter the reduction mechanism of $\mathrm{Pd(en)_2}^{2+}$.

We also studied further the nature of the discharge complex in double layer by adding iodide into electrolyte. Because of its ability to be adsorbed strongly on mercury surface and its electrochemical inactivity,[33-36] iodide is commonly used to distinguish between the inner sphere and outer sphere mechanisms for reductions of positively charged complexes. For an inner sphere mechanism, the transition state will be formed at the inner Helmholtz Plane (IHP). The presence of iodide which is strongly adsorbed on the surface will lead to a competition for adsorption sites which should raise the energy of the transition state and produce a lower reaction rate. But if an outer sphere reaction pathway is involved, the addition of iodide should produce rate changes only if there is an alternation in the potential at the outer Helmholtz Plane (OHP). This will result in a surface concentration increase because of the greater electrostatic attraction caused by iodide adsorption. Consequently a current increase is expected.

The iodide effects on normal pulse polarograms of $\mathrm{Pd(en)_2}^{2+}$ are shown in Fig. 7. An increase in current was observed which implies that $\mathrm{Pd(en)_2}^{2+}$ reduction should proceed via the outer sphere mechanism. That is, the complex does not enter the inner Helmholtz Plane.

Conclusions

Both CV and NPP data show that $\mathrm{Pd(en)_2}^{2+}$ reduction is an irreversible process. The reduction is independent of both $\mathrm{Pd(en)_2}^{2+}$ and en concentrations. The half-wave potential is −0.75 V (vs. SSCE, in the presence of 0.003% Triton X-100) and diffusion coefficient is 1.1×10^{-5} cm^2 s^{-1}.

Different mixing procedures give different complexes which have been identified by UV absorption experiments. If Pd(II) is added to en solution before pH adjustment, $\mathrm{Pd(en)_2}^{2+}$ is always formed completely. When Pd(II) is added to an acidified en solution, the $\mathrm{Pd(en)_2}^{2+}$ reduction current decreases and finally no $\mathrm{Pd(en)_2}^{2+}$ reduction can be observed. On the other hand, adding Pd(II) to an en solution of high $\mathrm{OH^-}$ concentration results in a two-wave polarogram. The two waves are controlled by the diffusion of $\mathrm{Pd(en)_2}^{2+}$ and $\mathrm{Pd(OH)_4}^{2-}$ respectively.

The reduction of different Pd-diamine complexes depends on the coordinated ligands. A compromise of basicity and chelate ring size results in a maximal half-wave potential at $\mathrm{Pd(1,3\text{-}pn)_2}^{2+}$.

The electrochemical reaction orders with respect to $\mathrm{Pd(en)_2}^{2+}$ and en are 1 and 0 respectively and won't be altered by the addition of Triton X-100. The addition of iodide increases the reduction current of $\mathrm{Pd(en)_2}^{2+}$. From these two results, we conclude that the $Pd(en)_2^{2+}$ reduction process can be described as follows:

$$Pd(en)_2^{2+}\ (bulk) \rightleftarrows Pd(en)_2^{2+}\ (OHP),$$

$$Pd(en)_2^{2+}\ (OHP) + 2e^-\ (Hg) \longrightarrow \text{Pd-amalgam} + 2en.$$

References

1) S. Yoshimura, S. Chida, E. Sato, and N. Kubota, *Met. Finish.*, **84**, 39 (1986).
2) J. A. Abys and H. S. Trop, U.S. Patent 4486274 (1984).
3) R. J. Morrissey, U.S. Patent 4278514 (1981).
4) R. J. Morrissey, U.S. Patent 4406755 (1983).
5) J. B. Willis, *J. Am. Chem. Soc.*, **67**, 547 (1945).
6) R. B. Simpson, R. L. Evans, and H. A. Saroff, *J. Am. Chem. Soc.*, **77**, 1438 (1955).
7) B. Chakravarty and D. Banerjea, *J. Inorg. Nucl. Chem.*, **16**, 288 (1961).
8) M. Hirota, Y. Umezawa, M. Nakamura, and S. Fujiwara, *J. Inorg. Nucl. Chem.*, **33**, 2617 (1971).
9) J. N. Gaur, S. C. Baghel, and R. S. Sharma, *Inorg. Chim. Acta*, **30**, 65 (1978).
10) R. S. Sharma and J. N. Gaur, *Bull. Electrochem.*, **2**, 485 (1986).
11) G. W. Watt and J. A. Cunningham, *J. Electrochem. Soc.*, **110**, 716 (1963).
12) M. F. Bell and J. A. Harrison, *Electroanal. Chem. Interfacial Electrochem.*, **41**, 15 (1973).
13) J. A. Harrison, R. P. J. Hill, and J. Thompson, *Electroanal. Chem. Interfacial Electrochem.*, **47**, 431 (1973).
14) J. A. Harrison and J. Thompson, *Electrochim. Acta*, **18**, 829 (1973).
15) J. A. Harrison, H. B. Sierra Alcazer, and J. Thompson, *Electroanal. Chem. Interfacial Electrochem.*, **53**, 145 (1974).
16) J. N. Crosby, J. A. Harrison, and T. A. Whitfield, *Electrochim. Acta*, **26**, 1647 (1981).
17) J. N. Crosby, J. A. Harrison, and T. A. Whitfield, *Electrochim. Acta*, **27**, 897 (1982).
18) R. F. Wilson and R. C. Daniels, *Anal. Chem.*, **27**, 904 (1955).
19) B. K. Puri and A. Kumar, *Analyst*, **108**, 1345 (1983).
20) R. Sreenivasulu, V. S. R. Rao, and K. H. Reddy, *Analyst*, **110**, 411 (1985).
21) G. M. Rafi and A. Paul, *Curr. Sci.*, **51**, 350 (1982).
22) T. C. Childers, P. Moncuse, J. J. Reiss, and S. K. Vohra, *Am. Lab.*, **1984**, 37.
23) A. Varma, *Talanta*, **28**, 701 (1981).
24) R. J. Magee and I. A. Beattie, *Anal. Chim. Acta*, **28**, 253 (1963).
25) W. H. Douglas and R. J. Magee, *J. Electroanal. Chem.*, **5**, 171 (1963).
26) G. Anderegg, *Inorg. Chim. Acta*, **111**, 25 (1986).
27) L. Rasmussen and Chr. K. Jorgensen, *Acta Chem. Scand.*, **22**, 2313 (1968).
28) A. J. Cohen and N. Davidson, *J. Am. Chem. Soc.*, **73**, 1955 (1951).
29) A. J. Bard and L. R. Faulkner, "Electrochemical Methods, Fundamentals and Applications," Wiley (1984).
30) K. B. Oldham and E. P. Parry, *Anal. Chem.*, **40**, 65 (1968).
31) D. J. A. De Waal and W. Robb, *Int. J. Chem. Kinet.*, **6**, 309 (1974).
32) R. H. Perry and D. Green, "Perry's Chemical Engineers' Handbook," 6th ed, McGraw-Hill (1984).
33) M. J. Weaver and F. C. Anson, *Inorg. Chem.*, **15**, 1871 (1976).
34) M. J. Weaver and F. C. Anson, *J. Am. Chem. Soc.*, **97**, 4403 (1975).
35) F. C. Anson, M. G. Finn, and A. Yamada, *Inorg. Chem.*, **16**, 2124 (1977).
36) M. J. Weaver and T. L. Satterberg, *J. Phys. Chem.*, **81**, 1772 (1977).