CATHODIC PRODUCTION OF PALLLADIUM

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Palladium was electrodeposited on a platinum cathode from a number of solutions containing the metal ion and a comlexing agent. The effects of factors such as pH, current density and time of deposition etc have beem described. The results were found to be consistent with the proposed mechanism.

Palladium has long been used in electrodes, most notably as wrought metal in relay contact. As an electrodeposit, Pd is suitable for many of the same functional applications ordinarily filled by the hard acid gold [1].

Considerations of price and availability have until recently favoured gold in these applications and for this reason the technological state of development of Pd electrodeposition has consistently lagged behind that of gold [2].

The rapid escalation of gold price in the late 1970 caused an intensive re-evaluation of Pd vs Au which is still continuing. It seems to be vertually certain that the long-term price trend for gold must be upwards, and for this reason the development of economical alternatives, primarly Pd, has continued unabated. Today nearly all suppliers of plated connectors and major users have accepted Pd as reliable connector contact material, and it has been in practical and increasing use for many years [3]. In addition Pd exhibits a large adsorption capacity for hydrogen and its properties are adequate for use in electrosynthesis [4].

It is surprising that only a few comparative laboratory investigations have been published which give details of the electrolyte composition, deposition parameters and properties of deposits [5-8]. It has been suggested that the low stability of Pd(IV) complexes in aqueous solutions causes the cathodic behaviour of the metal to be relatively simple. Hence only reduction of Pd^{2+} to the metal and phenomena related to the evolution of H on this metal have been considered[9].

EXPERIMENTAL

A stock solution was prepared by dissolving $PdCl_2$ (Merck) in dilute HCl and the exact concentration was checked spectrophotometrically using method of McNevin and Kriege [10,11]. This method depends on the formation of a complex between divalent Pd and EDTA. The extinction coefficient obtained was 6.0×10^{-2} M^{-1} Cm^{-1} which is very similar to the reported value [11]. Other chemicals were Analar grade where possible

The electrodeposition of Pd was carried out using an electrolytic cell. The cathode was made of a platinum plate having an area of 11.52 cm^2, while the anode was made of a platinum wire. A resistance box was connected in series with 12V battery to regulate current. The electrolyte temperature was maintained at 25±1°C. For each experiment 30 ml solution of a known Pd concentration was electrolysed under the appropriate conditions. The pH was adjusted to the appropriate value using ammonium hydroxide solution and the measurements were made using a glass electrode and 632 Metrohm pH meter.

RESULTS AND DISCUSSION

Cathodic Deposition of Palladium

Table 1 shows the results obtained using different complexing agents at different pH's. It is clear from the table that the deposition is generally not affected by pH except in few cases. It is also clear that the best complexing agents are chloride, phosphate, sulphate and citrate. In case of cyanide, there is no deposition and this agrees with earlier studies [12].

It is of interest to notice that the amount deposited in presence of CN^-, I^-, Br^- and Cl^- follows the order $CN^- < I^- < Br < Cl$. This behaviour is in agreement with the fact that the order of decreasing bond strength of the complexes of these ions with Pd is $CN^- > I^- > Br^- > Cl^-$, i.e. in the opposite direction [12].

TABLE 1

EFFECT OF DIFFERENT SUPPORTING ELECTROLYTES ON THE ELECTRODEPOSITION OF Pd
CURRENT DENSITY = 8.68 mA/cm^2 , TIME 15 MIN.

Complexing agent (1 g)	Pd deposited (mg) at pH					
	pH	wt	pH	wt	pH	wt
Acetate	1.5	3.8	3.4	2.7	5.5	2.0
Ascorbic acid	0.6	1.3	1.3	1.9	2.8	1.0
EDTA	1.0	2.0	2.7	2.2	7.5	1.6
Tartaric acid	0.9	2.4	2.5	1.8	4.3	1.6
Iodide	1.9	0.2	4.8	0.4	6.4	2.3
Phosphate	1.4	3.8	3.6	4.6	6.2	4.4
Sulphate	1.5	4.9	4.0	3.3	6.2	4.0
Citrate	1.4	3.3	4.1	4.4	6.1	2.7
Tartarate	1.5	2.6	4.0	3.4	6.0	2.2
Oxalate	1.5	2.0	4.0	2.2	6.3	2.9
Bromide	1.5	3.3	4.1	3.7	6.2	2.8
Floride	1.6	3.5	4.9	3.6	6.0	3.1
Persulphate	1.6	1.4	4.2	1.2	6.0	1.1
Hexamine	1.5	3.5	4.7	3.1	5.9	2.5
Methylthymol blue (0.1g)	1.5	1.1	4.1	1.9	6.3	3.9
Cyanide	0.9	0	-	-	-	-
Chloride NH_4 Cl + NaCl) (5/3g)	1.5	4.2	4.2	5.0	6.7	0.9
Chloride (NaCl)	1.4	1.9	4.6	2.2	6.4	3.5

Mechanism of Deposition

The general reaction mechanism for the electrodeposition is suggested to be [9]:

$$Pd X_2 + 2e = Pd + 2X^- \quad (1)$$

Taking X^- to be Cl^-, for example, it has been shown that reaction (1) goes through two one-electron transferes:

$$Pd Cl_2 + e^- = Pd Cl_2^- \quad (2)$$

$$Pd Cl_2^- + e^- = Pd + 2Cl^- \quad (3)$$

where reaction (2) is assumed to be the rate-determining step for cathodic process [9]. Palladium complexes of the type $[PdCl_4]^{2-}$ and $[PdEDTA]^{2-}$, for example have been reported [10,11]. Reaction (1) will be in competition with the complex formation, i.e.the reaction:

$$Pd X_2 + 2X^- \dashrightarrow [PdX_4]^{-2} \quad (4)$$

Effect of Palladium Concentration

The effect of $[Pd^{2+}]$ in the range of $(0.9\text{-}12)\times10^{-3}$M on the deposition of Pd was studied using chloride and phosphate as complexing agents. In presence of phosphate the deposition current efficiency of deposition increases approximately linearly with increasing $[Pd^{2+}]$ but in presence of chloride the efficiency has a maximum at around 8×10^{-3}M and decreases thereafter. The results are shown in Table 2. The decrease in efficiency in case of chloride may be attributed to the double salt formation [13].

TABLE 2

EFFECT OF [$PdCl_2$]ON THE ELECTRODEPOSITION OF Pd.
CURRENT DENSITY = 4.3 MA/cm^2 , pH = 4.4,
TIME = 15 MIN.

[$PdCl_2$]x 10^{-3} M	Deposition of Pd in presence of			
	Phosphate		Chloride	
	Pd(wt)	C.E.	Pd(wt)	C.E.
0.86	0.18	0.7	0.88	3.5
1.56	0.49	2.0	1.5	6.0
2.59	1.0	4.0	-	-
3.3	1.2	4.8	5.0	20.1
5.8	2.9	11.7	-	-
6.5	2.3	9.2	7.0	28.1
8.8	7.3	29.3	-	-
9.6	6.5	26.1	6.7	26.9
12.0	10.4	41.8	4.0	16.1

TABLE 3

EFFECT OF pH ON THE ELECTROPOSITION OF Pd
[$PdCl_2$] = 4.3 mA/cm^2 , time = 15 min.

pH	Pd deposited in presence of			
	Phosphate		Chloride	
	Pd(Mg)	CE	Pd(Mg)	CE
0.00	3.7	14.9	3.1	12.5
0.22	4.5	18.1	5.8	23.3
1.00	3.8	15.3	6.2	24.9
2.53	3.9	15.7	6.6	26.5
4.00	3.3	13.3	3.6	14.5
6.00	2.3	9.2	-	

Effect of pH

The general effect of pH on deposition for different baths is shown in Table 1, while the effect of a wider range of pH is shown in Table 3. The results reveal that the best depostion is achieved at pH 2.5. This pH dependence is attributed to different forms of complexes which differ in their stability.

Effect of Current Density

Table 4 illustrates the effect of current density (c.d) on the amount of Pd deposited in the presence of phosphate and chloride solutions.

TABLE 4

EFFECT OF CURRENT DENSITY (c.d.) ON THE ELECTRO-DEPOSITION OF Pd.
$[PdCl_2]$ = 3.3 x 10^{-3} M, time = 15 min. pH = 4.4

c.d. (mA/cm^2)	Pd deposited (mg) in presence of	
	Phosphate	Chloride
1.3	0.53	-
2.6	0.88	2.0
4.4	1.2	2.4
5.6	1.4	-
7.8	1.6	-
8.7	2.3	3.7
9.5	2.5	-
10.4	1.2	2.0
11.3	1.8	-
13	2.6	3.6
15.6	2.3	-
34.7	4.2	4.9
43.4	3.5	-

TABLE 5

EFFECT OF $[PO_4^{3-}]$ ON THE ELECTRODEPOSITION OF Pd
$[PdCl_2]$ = 3.3 x 10^{-3} M, c.d. = 4.3 mA/Cm^2 ,
time = 15 min., pH = 4.0

wt of phosphate (g)	pd deposited (mg)
0.02	2.9
0.10	2.8
0.30	2.9
0.80	1.9
1.0	1.0
1.5	1.2

The palladium concentration was 3.3x10^{-3} m and pH 4.4. The time of deposition was 15 min. It is apparent that the deposition is independent of c.d at least in the range 10.42 mA/cm^2 to 43.4 mA/cm^2. The current effeciency is higher at low current density and it decreases at high c.d. This may be due to the formation of nonadherent Pd over the cathode surface. It is also clear that chloride is better as complexing agent than phosphate. This is probably due to the ease of discharging chloride complexes as compared with phosphate complexes.

Effect of Phosphate and Chloride Concentrations

Table 5 shows the effect of [phosphate], as complexing agent on the deposition of Pd, while table 6 shows the effect of $[NH_4Cl]$/ [NaCl] on the deposition. It is obvious that there is no effect of phospahte in the range of 0.02-0.3 M but the deposition decreases thereafter. This means

TABLE 6

EFFECT OF $[Cl^-]$ ON THE ELECTRODEPOSTION OF Pd.
$[Pd\ Cl_2]$ = 3.3 x 10^{-3} M, c.d. = 4.3 mA/cm^2 ,
time = 15 min., pH = 4.0

NH_4 Cl / NaCl (g)	Pd deposited (mg)
0.63/0.37	3.1
1.25/0.75	4.0
2.5/1.5	4.4
5.3/3	4.0

that at high [phos-phate], other competing reactions are occuring at the cathode. In presence of chloride, the deposition increases marginally with $[Cl^-]$ indicating that the reaction mechanism is rather simple.

Effect of Time

It was found experimentally that the Pd deposited in the presence of phosphate increase from 1.4 mg at 5 min., to 4.4 mg at 45 min. The corresponding current effeciency decreases from 17% to less than 4% at 60 min. This is understandable because of the depletion od the metal/metallic complex species with time.

Effect of Stirring

It was observed that the rate of deposition increases with increasing the speed of a magnetic stirrer. Thus, under fixed conditions, the amount of deposition increases from ~ 2 mg in case of unstirred to 4.5 mg for a stirred solution. Stirring enhances the transport of the reducible species and countracts the effect of depletion. It is also possible that stirring helps in removing adsorbed gases on the cathode leading to a better deposition.

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