Optimizing Palladium Conversion in Electroless Palladium Plating of Alumina Membranes

By J.N. Keuler, L. Lorenzen, R.N. Sanderson & V. Linkov

Electroless palladium (Pd) plating on alumina membranes was investigated with the aim of obtaining very high Pd conversions and pure Pd films. Interactions among operating variables including Pd source, temperature, reducing agent concentration, stabilizer concentration and buffer pH, require proper choice of these variables to ensure plating solution stability and to maximize the conversion of Pd salt to Pd metal. A preliminary investigation of these variables readily enabled conversions exceeding 80 percent to be obtained after three hr of plating. Near optimal values (>95%) were also achieved within a three-hr reaction period for a very spe-

cific choice of variables. Surface uniformity and purity of the deposited film were excellent. The operating concentration of the stabilizer (Na EDTA) appears to be the most significant consideration in the plating process. Varying Na EDTA concentration results in an optimal region of Pd conversion. Conversions quickly decreased when the system became unstable or if the system had too great a stability.

Pd

Inorganic membranes covered with a thin electroless Pd film are mainly used for hydrogenation/dehydrogenation reactions. Palladium films for organic reactions and hydrogen separation are currently an active area of research.¹⁻³ In this regard, electroless plating has several advantages over other methods for creating such thin metal films. The formation of uniform deposits, either in the bore or on the shell side of tubular surfaces, to obtain dense, nonporous metal films of minimal thickness are important for creating defect-free catalytic membranes. Several other applications exist for electroless Pd thin films, especially in the electronics industry. These include fabrication of printed circuit boards, low resistance ohmic contacts, chip-level interconnects⁴ and selective metal deposition on silicon substrates.5

Several disadvantages of using electroless Pd plating have been mentioned in the literature; these include low deposition rates, using hydrazine as reducing agent,6 difficulty with film thickness control, Pd losses because of bath composition¹ and

Table 1
Solutions Used for Surface Activation

Sensitizing		Activation		
$SnCl_2 \cdot 2H_2O$	1 g/L	$Pd(NH_3)_4(NO_3)_2$		
		1.5 mL, 10% solution/L		
HCl (32%)	1 mL/L			
		HCl (32%) 1 mL/L		





Fig. 1-(a) effect of various Pd salts and reducing agents on mass of Pd plated; (b) effect of various Pd salts and reducing agents on Pd conversion.

film impurities. A further unresolved aspect of this plating process is the Pd conversion achieved. Of the few publications in this regard, Pearlstein achieved 90 percent Pd conversion after 19 consecutive one-hr depositions.⁷ By careful choice of operating conditions and plating chemicals, all of the above-mentioned problems can be addressed, yielding very pure Pd films at a relatively fast rate and with a high percentage of Pd conversion.

Background

Electroless plating is the process of covering a substrate with metal by means of the autocatalytic reduction of metal ions with a reducing agent. It is similar to electroplating; the difference is that a flow of electrons is not supplied by an external source, but rather by the species in the aqueous solution.

Table 2 Composition of Plating Solutions (Values/L)

	Solutions			
	1	2	3	4
$\frac{\text{Pd(NH}_3)_4(\text{NO}_3)_2}{(10\% \text{ solution})}$	25 mL	25 mL	—	—
PdCl ₂	—	—	2.7 g	2.7 g
NH ₄ OH (28%)	200 mL	200 mL	390 mL	390 mL
Disodium EDTA	20 g	20 g	35 g	35 g
Hydrazine (molar ratio to Pd)	0.80	0.80	0.66	0.66
pH 10 buffer	100 mL	100 mL	—	—
Formaldehyde (37%)	—	1.5 mL	—	1.5 mL
Temp (°C)	64	64	64	64

Surface Cleaning

Proper cleaning of the area to be plated prior to activation and plating is essential. Fingerprints, dirt and particles, such as ceramic dust, that exist on the surface or in the pores, will cause nonuniform plating, metal film irregularities or lead to loss in adhesion.

Many cleaning procedures for ceramics exist in the literature.⁸⁻¹⁰ Four cleaning steps usually precede surface activation (alkaline clean, rinse, etch and rinse again). Etching is optional and depends on the surface roughness of the specimen. When glass, plastic or non-porous ceramic is plated, etching is required. For good metal adhesion, plastics are etched with strongly oxidizing chromic acid solution or chromic acid-sulfuric acid solution.¹¹ The etchant chemically modifies the surface, making it hydrophilic and physically roughening it to ensure mechanical locking and chemical bonding of metal to plastic. Etching of ceramic and glass is done with sodium hydroxide¹² or fluorides.⁹⁻¹⁰ Etching is usually not needed when cleaning porous materials.^a

Surface Activation

Plating on most metals does not require catalytic activation.¹¹ Exceptions are stainless steels and titanium, which need to be etched first, and materials (such as lead) that poison the electroless reaction. These exceptions, as well as nonconductors (ceramics, plastics) must be pretreated to create the catalytic surface required for controlled electroless plating.





Table 3
Plating Solutions Used for Additional
Experimentation
(Values/L)

27.5 g
200 mL
Varied from EDTA:Pd molar ratio of 6 to 50
Varied from hydrazine:Pd molar ratio of 0.4 to 0.88
100 mL
Varied from 59 to 77 °C

The catalysts for electroless plating not only act as plating initiators, but have a considerable effect on the smoothness, coverage, adhesion and surface quality of the deposited metal film.

Catalyzing the inactive surface is done using a combination of tin and palladium. Two processes are commonly used:¹⁶

- 1. The older, two-step immersion procedure, consisting of a sensitizing step (SnCl/HCl), followed by an activation step with PdCl/HCl.
- 2. The "exchange process," requiring a catalyzation step with PdCl/SnCl/HCl/HCI (colloids), then acceleration with NaOH or HCl.

In recent years, methods have been developed using organic solvents and ligands instead of tin^{4,17} for stabilizing the Pd colloids. These processes involve fewer steps and display superior selectivity compared to the conventional Pd/Sn catalyzing processes. Moreover, there are fewer adhesion problems compared to those encountered with a Pd/Sn catalyst on Si-OH-containing surfaces (silicon, silica and glass).

Several mixed PdCl/SnCl catalyst solutions are listed in the literature.^{16,18} Pd-Sn catalysts are colloids with the core made from Pd and Sn, surrounded by Sn(II) as Cl⁻ and OH⁻ complexes. Accelerators are used to expose the catalytic Pd core by removing the Sn. A method for evaluating catalysts for electroless plating was proposed by Horkans.¹⁹

The two-step procedure deposits more Pd on the surface than does the exchange process, ensuring a very even metal film over a large surface area after plating. The two-step process also deposits less tin,¹⁹ which is important in obtaining the very high-purity Pd film necessary for catalytic membranes.

Choice of Chemicals

A limited choice of reductants is available for electroless plating (dialkylamine borane,²⁰borohydride, hypophosphite,⁷ formaldehyde and hydrazine²¹). Very little has been published on the use of borohydride and boranes for the electroless plating of Pd. This option was not considered for this study, because boron is codepsoited with Pd. Formaldehyde is not a good reducing agent²² because of the small potential

^a Examples include Vycor¹³ glass, Corning, Inc., Corning, NY, porous stainless steel,¹⁴ and Membralox,¹⁵ U.S. Filter Corp, Warrendale, PA.

Table 4 Pd Conversions for pH 9 & 11 Buffers (EDTA:Pd molar ratio = 6)

		Hydrazine	
Buffer pH	Temp (°C)	(molar ratio)	Conversion %
9	59	0.4	19.5
11	59	0.4	19.0
9	59	0.72	38.7
11	59	0.72	35.7
9	71	0.4	43.0
11	71	0.4	45.5

Table 5
$E_{Pd^{+2}/Pd}$ for various EDTA:Pd
Molar Pation at 25 °C

EDTA:Pd Molar Ratio	0	6	20	40
$E_{Pd^{+2}/Pd}(V)$	0.83	0.2601	0.2446	0.2357

difference between the oxidation and reduction reactions that acts as the driving force. Hypophosphite is commonly used, but deposits usually contain in excess of 1.5 percent phosphorus,⁶ thereby reducing film quality. Problems with surface adhesion of Pd, using hypophosphite, can be encountered in films exceeding 5 mm.²³ Hydrazine was judged the most suitable and was chosen as our reducing agent.

Disodium EDTA was used as a stabilizer because it forms a highly stabile palladium complex. Ammonium chloride can also act as a stabilizer when using PdCl for the metal salt.

Experimental Procedure

Ceramic membranes used in this study were supplied by Potchefstroom University. The membranes consisted of $\sqrt{-Al_2 O_3}$ (70%) and ZrO₂ (29%) stabilized with Y₂ O₃ (1%), leading to excellent mechanical properties and chemical stability. The tubular membranes had a 12-mm outer diameter, wall thickness of about 0.8 mm and nominally the following properties: 210-nm pore size, 48.5 percent porosity and 4.0 m²/g surface area.



Fig. 4—EDTA: Pd molar ratio required for plating solution stability.

Five different variables were investigated for their effect on palladium conversion: Tetra-ammine palladium chloride or tetra-ammine palladium nitrate, solution temperature, buffer pH and the concentrations of hydrazine and Na₂ EDTA. Plating temperature was controlled to ± 0.5 °C from the predetermined temperature of the water bath. The volume of the plating solution (22 mL per experiment) and the surface area to be plated, were kept constant. Plating was performed in glass vials precleaned with 6-percent HNO₃. The palladium solution was allowed to stabilize for at least 8 hr prior to plating. Both hydrazine and palladium solutions were preheated to the predetermined temperature amd mixed, then the membrane (ends sealed with TeflonTM) was added to the solution.

Surface Cleaning

A simple cleaning procedure for the membranes, similar to that used by Collins,¹⁵ was performed. Membranes were sectioned into 5-cm lengths, using a diamond saw. Cleaning comprised

- treatment for 1 min in a 0.1 wt% NaOH ultrasonic bath (room temperature)
- ultrasonic treatment for 2 min in deionized water
- rinsing in isopropanol for 10 min
- rinsing in deionized water for a further 10 min
- drying at 110 °C for 8 hr.

Surface Activation

The two-step procedure (although now not much in use) was chosen for reasons mentioned in the background section.

The solutions used for surface activation are listed in Table 1. They are similar to those used by Shu.¹⁴ A fresh sensitizing solution was prepared for each catalyzation. The activation solutions generally have an indefinite shelf life.²³ All solutions were, however, used within two weeks. In both cases, metal salts were dissolved in deionized water prior to adding HCl, resulting in a colloidal solution (which favors high tin surface concentrations). Apparently, lower tin surface concentrations can be obtained by changing the mixing order of the sensitizing solution.¹⁹ Dissolving the tin salt in concentrated HCl, then diluting, results in a true solution and a lower tin surface concentration.



Fig. 5-Effect of temperature on Pd conversion.



Fig. 6—Effect of EDTA on Pd conversion at various temperatures.



Fig. 7-Effect of EDTA on Pd conversion at various temperatures.

Membrane pieces, 5 cm in length, were sealed with Teflon[™] at the ends and only the outer surface was treated. The following four procedural steps were repeated 10 times, resulting in a brown, evenly distributed catalytic layer over the entire surface:

- 2 min in sensitizing solution
- 30 sec in deionized water
- 2 min in activation solution
- 30 sec in deionized water

The membranes were then dried at $110 \,^{\circ}$ C, cut into 8-mm lengths, scrubbed and washed again in deionized water to remove ceramic dust. Further drying was done at $110 \,^{\circ}$ C before beginning electroless plating.

Choice of Palladium Salt For Maximum Conversion

For the experiments described in Fig. 1a, plating was carried out for 2 hr, using solutions 1 to 4, as described in Table 2. The membrane was then removed, washed with deionized water and dried at 110 °C between one and two hr. The plating and drying processes were repeated several times. Palladium is reduced in the following manner:

 $Pd(ammine complex)^{+2} + 2e^{-} \rightarrow Pd^{0} \qquad (1)$

Solution 3 was prepared in the same manner as Collins.¹⁵ The addition of one to two mL/L formaldehyde are claimed to produce higher quality films.¹³ In this study, a white gelatinous precipitate was formed in the solution.

After establishing tetra-ammine palladium nitrate without additional formaldehyde as the best option for high Pd conversion, further experimentation employed the solution described in Table 3. Plating was carried out in 22 mL of solution for three hr. The solution was slightly shaken every 10 min to improve homogeneity. Inductively coupled plasma (ICP) discharge analysis showed that a time of three hr was sufficient for a nearly complete plating reaction. The membranes were then removed from the glass vial, washed with deionized water and dried for two hr at 200 °C. Conversion was determined by the mass ratio of the Pd plated on the membrane to the Pd initially present in the solution; the mass of the latter had also been recorded, ensuring high accuracy.

Ammonium hydroxide is used to provide stability and OH⁻ for oxidation. The volume (mL/L) was kept constant, because Athavale reported that volumes above 100 mL/L had little effect on Pd deposition (conversion).⁶

Results and Discussion The Effect of Pd Salt On Percent Pd Conversion

As seen from Fig. 1b, in the presence of formaldehyde, the conversion was very low and decreased to zero after two plating sessions, making formaldehyde unsuitable as a reducing agent in the absence of an osmotic driving force. The precipitate is probably a polymerized form of tetraformal trisazine.²⁴ The intermediate is formed according to the following reaction:²⁴



Fig. 8-Effect of hydrazine concentration on Pd conversion at different EDTA



Fig. 9—Effect of EDTA on Pd conversion at various hydrazine concentrations.

$$4 \text{ HCHO} + 3\text{H}_2\text{NNH}_2 \rightarrow \begin{array}{c} & & \\ N & N & N \\ & & | & | & | & +4\text{H}_2\text{O} \\ N & N & N \\ & & & \\ \end{array}$$
(2)

Both the tetra-ammine complexes of palladium chloride and palladium nitrate produce films that grow fairly linearly in thickness with time if fresh solution is used every two hr (see Fig. 1a). This linear time dependence is very favorable for controlling film thickness. The chloride salt gives lower conversions; the nitrate form was preferred.

Effect of pH on Conversion

Plating was done in an alkaline solution, because hydrazine is a better reducing agent in an alkaline rather than acidic medium:

$$N_{2}H_{4} + 4OH^{-} \rightarrow N_{2} + 4H_{2}O + 4e^{-} E = +1.16 V$$
 (3)

$$N_{2}H_{5}^{+} \rightarrow N_{2}^{+} + 5H^{+} + 4e^{-}$$
 $E = +0.23 V$ (4)

Operating in the pH buffer range of 9 to 11 had little effect on the conversion of the metal ion (see Table 4), but is necessary to maintain the correct potential difference for the oxidation and reduction reactions.

The use of higher or lower pH buffers resulted in decomposition of the plating solution either at high temperatures or at high hydrazine concentrations. This phenomenon can be clearly seen in Fig. 2. Experiments done outside the pH buffer range of 9 to 11 caused a sudden decrease in Pd conversion. Pd is then no longer deposited on the membrane alone, but also on the surface of the glass vial and onto Pd nuclei formed in the solution itself. The solution turns black and no Pd ions are available for plating. Figure 3 shows the comparison between the Pd conversions, in buffer pH 9 and 11, at various EDTA concentrations. Slightly better conversion results are obtained with a pH 9 buffer. Below an EDTA to Pd molar ratio of 20, decomposition took place. Optimum conversion is obtained with pH buffer values of 9 to 11.

It was previously found that the pH does have a large influence on the stability of the Pd complex.²⁵ The pH determines the degree of ionization of EDTA. The fully ionized chelate anion (EDTA⁻⁴) forms the strongest metal chelate (Pd-EDTA) complex. Chelating agents require high alkalinity to be very effective.²⁵ In the pH range of 9-11, EDTA⁻³ and EDTA⁻⁴ dominate and are capable of strong metal bonding.

SystemStability

A response surface, using a smooth spline to plot it, was compiled indicating system stability (Fig. 4). The molar ratio of EDTA to Pd, on the z-axis, represents the value at which stability can be guaranteed for a specific temperature and hydrazine concentration. Values on and above the curve indicate stability, while those below the curve show probable instability. Increases in temperature and hydrazine concentration require a sharp increase in EDTA concentration to guarantee stability. An unstable system is highly unfavorable and will always lead to low conversions.

Combined Effect of Temperature

& EDTA Concentration on Pd Conversion

Plating solution temperature and EDTA concentration are interactive parameters. From Fig. 5 it can be seen that the temperature and EDTA concentrations must be chosen concurrently to achieve maximum conversion. Figure 5 also shows that low EDTA:Pd molar ratios (6 and 14) cause bath depletion at high temperatures (above 66 °C) and a decline in Pd conversion. Pd conversion from stable solutions increases as expected with increasing temperature;²⁷ for example, the case where the EDTA to Pd molar ratio is 30. The figure also clearly shows the generally higher conversion at a higher EDTA concentration.

According to Fig. 6, the EDTA:Pd salt molar ratio has one of three effects. These are best illustrated by the T=71 °C and T=77 °C curves. First, at low EDTA to Pd molar ratios (concentrations), conversion is low because of bath decomposition. Second, an increase in concentration increases stability and conversion. Third, when the EDTA concentration is too high, there is a decline in conversion, presumably because of too great a stability. EDTA to Pd molar ratios between 20:1 and 40:1 and T \geq 65 °C result in conversion levels greater than 80 percent (at the given hydrazine and buffer pH values).

Lower hydrazine concentration (Fig. 7) shows a trend similar to that shown in Fig. 6. The stability limit is achieved at lower EDTA concentrations (14 molar ratio or lower). In the stable region, higher temperatures always result in higher conversions. Maximum conversion at this lower hydrazine concentration is lower than that shown in Fig. 6, proving that hydrazine concentration has a definite effect on palladium conversion.

Both temperature and EDTA concentration have an effect on potential difference. An increase in temperature leads to an increase in $E_{pd}^{+2/}_{pd}$, according to the Nernst equation, while increasing EDTA concentration reduces the potential.¹⁴ It can be concluded that large potential differences will cause decomposition of the plating solution. This was observed at the lower EDTA:Pd molar ratio (value of 6) seen in Fig. 5, for T > 65 °C, where decomposition took place. EDTA is a very good stabilizing agent for Pd, with a stability constant of log K_{PdEDTA} equal to 18.5.²⁸ EDTA effectively reduces the Pd potential (Table 5), stabilizes the Pd ion and results in a slower reaction rate, high stability and high Pd conversion. This extra stability brought on by the higher EDTA concentration shifts decomposition of the plating solution to higher temperatures (Fig. 5).

Combined Effect of Hydrazine & EDTA on Pd Conversion The complete autocatalytic reaction is:

 $2Pd(NH_{2})_{4}^{+2} + N_{2}H_{4} + 4OH^{-} \rightarrow 2Pd^{0} + 8NH_{3} + N_{2} + 4H_{2}O$ (5)

Stoichiometry predicts that a 0.5 hydrazine to Pd molar ratio is required for complete reaction. This was not found in practice, however. Conversion increased with increasing hydrazine concentration (Fig. 8), beyond the expected stoichiometric value. This was not in agreement with results obtained by Rhoda.²⁷ He obtained the expected stoichiometric value. This is probably because of the higher operating temperatures we used, resulting in increased hydrazine decomposition. The exception in this figure, where conversion declines, is because of bath decomposition. No instability was encountered with hydrazine to Pd molar ratios of 0.56 and 0.4. Higher molar ratio values did cause decomposition below an EDTA to Pd molar ratio of 14. Figure 9 clearly indicates an increase in conversion with an increase in hydrazine concentration at EDTA:Pd molar ratios above 14. Fig-



Fig. 10-Effect of EDTA and hydrazine concentrations on Pd conversions.

ure 10 confirms this. The curves in Fig. 10 have similar shapes, but the higher hydrazine concentration causes a shift to higher EDTA concentrations required for stability.

Excess hydrazine is required for optimum conversion, because hydrazine catalytically decomposes in solution. This subject is extensively covered in the literature.^{24,29} Thermal decomposition increases with increasing temperature and the presence of the metal catalyst. Decomposition proceeds mainly by the following reaction:

$$3N_2 H_4 \rightarrow 4NH_3 + N_2 \tag{6}$$

Small amounts of hydrogen are also formed according to:

$$N_{2}H_{4} \rightarrow N_{2} + 2H_{2}$$
(7)

The latter reaction becomes more probable with increasing pH.²⁹ To obtain maximum conversion and sufficiently high stability, 40 to 60 percent excess hydrazine is recommended.

FilmPurity

High-purity films were obtained. Energy dispersive X-ray analysis (EDAX) showed only Pd, and small amounts of Al and Zr. The presence of aluminum and zirconium is not surprising, because they form part of the underlying membrane material.

Findings

- 1. Tetra-ammine palladium nitrate was found to be the best Pd salt with which to achieve high Pd conversions. The use of hydrazine as the reducing agent produces the purest Pd films.
- 2. Plating is done in an alkaline solution with a pH buffer between 9 and 11. The stabilizer (EDTA) and reducing agent perform best in this pH range, while higher and lower pH buffers tend to cause bath instability and rapid conversion decline.
- 3. Excess hydrazine (40-60 percent above stoichiometry) is required to compensate for thermal decomposition of the hydrazine and to ensure high conversions.
- 4. Decomposition of the plating solution occurs more readily when the hydrazine concentration and temperature in-

crease; in this case, solutions require high EDTA concentrations to remain stable.

- 5. The effect of EDTA concentration is non-linear—too high a value results in too stable a complex, while too low a value shows insufficient stability. Both cause a reduction in conversion.
- 6. Pd conversions in excess of 95 percent were obtained, within three hr, using tetra-ammine palladium nitrate as Pd salt under the following conditions: T=77 °C, hydrazine to Pd molar ratio = 0.72:1, EDTA to Pd molar ratio = 30 to 40:1 and buffer pH = 11.
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About the Authors



Johan Keuler is a graduate student at the University of Stellenbosch. He obtained a B.Eng. with distinction at Stellenbosch in 1995. Some of the undergraduate awards he received include: The SA Institute for Chemical Engineers' prize for the best final-year chemical engineering student at Stellenbosch and the AECI prize for the best firstyear student.



Professor Leon Lorenzen is professor and chair of the Department of Chemical Engineering at the University of Stellenbosch, Banhoek Road, Stellenbosch 7600, South Africa. He joined the department in 1990 after several years' industrial experience in the gold and uranium industries, as well as two years' experience in the aerospace industry. He holds a B.Eng. in chemical

engineering, an M.Eng., and PhD (Eng.) in metallurgical engineering from the University of Stellenbosch and a postgraduate diploma in systems engineering. He has published as author or co-author 21 papers in international symposia. Prof. Lorenzen teaches high-temperature thermodynamics, electrochemical engineering, mineral processing, project and technology management. His research interests include all aspects of hydrometallurgy, especially leaching, waste processing and reactive processes using membranes, resins and activated carbon.



Dr. Ronald D. Sanderson is the director of the Institute for Polymer Science at the University of Stellenbosch. He obtained a B.Sc. and B.Sc. Hon. at the University of Cape Town (South Africa) and a PhD at the University of Akron. He has published as author or co-author 90 publications in international journals and holds 18 patents. His main interests are

membranes, separation, reactors and polymers.



Dr. Vladimir Linkov completed his undergraduate studies in Russia and his PhD in 1995 at the Institute for Polymer Science, University of Stellenbosch. He has published several papers and is currently part of a research team at the SASOL Centre for Chemistry at the University of Potchefstroom (South Africa).

Note: Correspondence regarding this paper should be addressed to Professor Lorenzen.