Development of Palladium Electrolyte for Maskless Electrochemical microfabrication Process

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Abstract — A development of a new palladium electrolyte required for use in a maskless electrochemical microfabrication process, Enface, is presented. Prior works showed that a specific conductivity (~2.7 S/m) of electrolytes is crucial to achieve pattern replication. Selection of appropriate electrolyte based on physicochemical properties is crucial to design a process that is theoretically and practically achievable. The electrolyte was electrochemically characterised to determine onset deposition potential and current densities. In this paper, physicochemical properties i.e. pH and conductivity of palladium electrolyte with composition and concentration ranged between 0.014 – 0.013 M were investigated. The electrochemical experiments were carried out in an unagitated vertically-cylindrical cell with nickel pattern deposited on copper disk as working electrode. The pattern feature was 5 mm x 4 mm and 5 mm x 2 mm. The diameter of the copper disk was 1 cm. A nickel disk with diameter of 1 cm was used as counter electrode. Platinum wire was used as a pseudo reference electrode. The experiments were carried out at stagnant condition. The result suggested that an ammoniacal palladium solution was preferable for the experimentation. The spectroscopy analysis confirmed that the palladium was present in the form of $Pd(NH_3)_4Cl_2$ as major species and $PdCl_2(H_2O)_2$ with concentration ratio 4:1. According to the conductivity, the electrolyte of 0.019 M $PdCl_2$ + 0.188 M NH_4Cl was chosen for use in the experiments. The solution contains 2 g/L as Pd metal and 10.08 g/L NH_4Cl exhibiting pH of 2.74 ± 0.31 and conductivity of 2.35 ± 0.11 S/m. At these physicochemical properties, electrodeposition of palladium was expected to occur and pattern replication could possibly be achieved. Polarisation curves obtained from electrochemical characterisation experiments showed that the potential for palladium electrodeposition was in the range of -0.3 to -0.45 V vs Pt wire. For the fully exposed anode, the potentials corresponded to current densities of between 0 and -2.57 mA/cm².

Key words – Electrodeposition, Enface technology, Pattern transfer, Palladium plating, Maskless patterning process..

I. INTRODUCTION

Palladium has been broadly used in microelectronic contacts as a top layer coating due to its distinctive physicochemical and electrical properties (i.e. good gold wire bondability) [1]. Palladium has been used to substitute gold leadframe so that the Pd-plated leadframe has replaced lead containing solder [2]. Since 1970's palladium has become technically vital in the development of microfabricated devices to perform the same functionality or even better [3, 4]. In addition, the use of palladium significantly reduces the metalisation cost of microdevices as the price per volume of palladium is less expensive than gold [5, 6].

Owing to a rapid increase in the functional application of palladium coating, Pd layer plating has attracted a great attention in recent decades [3]. A number of researches have been devoted to investigate the process of Pd electrodeposition [3]. An electrolyte formulation including its physicochemical properties and electrochemical parameters are crucial to obtain a palladium deposit with excellent properties to define its desirable functionality [7, 8].

A technology for metalisation of microdevices (e.g. microfabrication) still relies on photolithography of each substrate. In spite of the popularity and continous development of this technology, a number of drawbacks have been identified such as it is expensive due to a multistage process, uses a large amount of water and chemical that generates copious waste, and requires clean room [9-12]. Therefore, an alternative option to obtain a functional metal pattern without photolithography of each individual work piece has been proposed. The technology was named Electrochemical nano and micro-fabrication by Flow and ChEmistry (Enface). This technology is based on maskless electrochemical method which has been thoroughly discussed in a number of publications [10, 11, 13-18].

In this paper, a study on palladium electrolyte for use in Enface process will be presented. Previous works on copper and nickel deposition indicated that pattern replication was achieved at a specific conductivity (~2.7 S/m) of electrolyte. Therefore, a development of a new palladium electrolyte is required. The investigation focused on how to obtain an electrolyte to meet the required physicochemical properties, and the electrochemical characterisation of the electrolyte to determine onset deposition potential and applied current densities.

II. FUNDAMENTAL

Chemistry of complexed metal: In many cases, a metal may requires complexation to ensure the desired electrodeposition process takes place. Complexed metals are formed by coordination bond of ions or molecules, so called ligands, and the metal. For noble metals, their simple salts

often have too positive reduction potential, poor stability, and may not be easily dissolvable in solutions. Due to highly positive reduction potential, when a less noble metal is introduced to the more noble metal solution e.g. as an electrode, an immersion deposition may occur as a result of displacement reaction. The unexpected immersion plating tends to produce non-adherent and powdery deposits. In addition, due to the displacement reaction the less noble metal may contaminate the electrolyte. In the case of unstable solution, metals may easily precipitate. Henceforth, the complexation of the metals with suitable ligands is essential not only for increasing the stability and solubility but also negatively shifting the reduction potential [19, 20].

Selecting suitable ligands is crucial to design a process that is theoretically and practically achievable [3], as too strong metal-ligand interaction leads to a practically impossible deposition process. The ligand formation is commonly characterised by stability constant (β_x) which is defined as follows:

$$M^{z+} + xL \leftrightarrow ML_x^{z+} \tag{1}$$
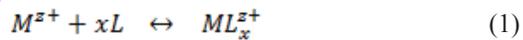
$$\beta_x = \frac{[ML_x^{z+}]}{[M^{z+}][L]^x} \tag{2}$$

β_x is a degree of the stability of the corresponding metal complex. A small value of β_x indicates a poorly stable metal complex, whereas a high stability of the complex indicated by a large equilibrium constant [21].

Electrodeposition from aqueous solution: Electrodeposition is a process involving a reduction reaction of a dissolved metal in an electrolyte solution which occurs at an electrode surface. It is usually carried out in a system comprising working electrode, counter electrode, reference electrode, electrolytic solution, and external power supply. A general reduction reaction of metal is shown in equation (3)

$$M^{n+}{}_{solution} + ne^- \rightarrow M^0{}_{lattice} \tag{3}$$
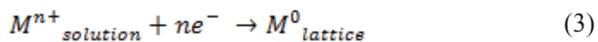
The metal ions e.g. Mn+ is reduced to a solid state (M^0) and deposited on to the working electrode. The reduction reaction is driven by a deviation of the electrode potential from its equilibrium value which is known as the overpotential (η).

Electrochemical deposition takes place via several complex processes:
- Mass transfer of metallic ions from bulk solution to the electrode/solution interface
- Electro-active ions are adsorbed onto electrode surface
- Charge transfer reaction at the electrode surface
- Nucleation of the product (metal) and is incorporated into growing lattice at the electrode surface [22]

Kinetic of Charge Transfer Process: electrodeposition is driven by an electrical charge applied to the working electrode to flow the current. This is due to the electrode potential is shifted from its equilibrium value. The potential deviation, so called the overpotential (η), serves as the driving force for the reaction to take place. The overpotential is defined as:

$$\eta = E - E_e \tag{4}$$

E is applied potential and E_e is equilibrium potential.

Nernst's equation shows that the reaction at the electrode surface depends on the value of the overpotential. If the overpotential is negative ($E<E_e$), to re-establish the equilibrium, a reduction reaction takes place. In this case, the ratio of $\frac{c_{Oxd}}{c_{Red}}$ decreases. The cathodic current flows to supply the electron (ne^-). On the other hand, oxidation reaction occurs due to the flow of anodic current when more positive potential (E>Ee) imposed to the working electrode.

In particular cases, a slow kinetic of the electron transfer reaction controls the overall rate of the electrodeposition. To analyse this case, some assumptions are taken into account to simplify the system:
- No other reaction involves, only simple electron transfer reaction takes place
- Mass transfer rate is significantly faster than the rate of the reaction.
- No concentration difference between reactant at the electrode surface and in the bulk of solution.

When any value of overpotential is applied to drive the electrochemical reaction, the net current density response (*i*) can be defined as:

$$j = \vec{j} + \overleftarrow{j} \tag{5}$$

Where, *j* is a current density which is a normalised form of current respect to an electrode area. $\vec{i}$ is partial cathodic current density and $\overleftarrow{i}$ is partial anodic current density. Butler-Volmer equation (eq 6) is developed to represent the relationship of the overpotential and the current density.

$$j = j_0 \left[exp\left(\frac{\alpha_A nF\eta}{RT}\right) - exp\left(\frac{-\alpha_C nF\eta}{RT}\right) \right] \tag{6}$$

j_0 is the exchange current density, α_A and α_C are anodic and cathodic charge transfer coefficients respectively. The exchange current density is obtained when equilibrium partial current density is achieved where the anodic and the cathodic partial current densities are equal. The exchange current density depends on the electrochemical reaction and the electrode material and surface [22]. The relationship between α_A and α_C is as equation (7)

$$\alpha_A + \alpha_C = 1 \tag{7}$$

Butler-Volmer equation shows that the current density is affected by several parameters i.e. the overpotential, the charge transfer coefficient, the temperature, and the exchange current density. Thus, at higher overpotentials, the current density increases results in an increase in the rate of electrochemical reaction.

III. METHODOLGY

Electrolyte Formulation: Since palladium is a noble metal, the electrolyte requires to be specifically designed based on theoretical and practical consideration. Hence, thermodynamics and electrochemistry of palladium play important role in a further development of Pd electrolyte

formulation [3]. A First palladium electrolyte was formulated by Henry around 1855 using a complexing agent of nitrate. An ammonia-complexed palladium electrolyte was later introduced [3]. The two electrolytes were used to deposit palladium onto a copper sheet [3].

The standard potential of Pd^{2+}/Pd^0 according to reaction (8) was reported in the range of +0.915 and +0.979 V [3]

$$Pd^{2+}_{(aq)} + 2e^- \rightarrow Pd_{(s)} \qquad (8)$$
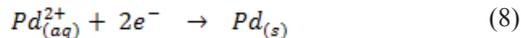
This highly positive standard potential implies that palladium deposition from an aqueous electrolyte of non-complexed Pd is facile leading to displacement reaction. If less noble metal i.e Cu is used in the system, Pd^{2+} is easily reduced to Pd^0. The simultaneous electrodeposition and displacement process produce a powdery and non-adherent palladium deposit [3]. In addition, the non-complexed palladium and the simple salt of Pd i.e. $Pd(SO_4)^{2-}$ also tends to be unstable as its stability constant is low (Table I) [3]. The low stability constant also suggests that non-ligated or simple salt palladium is not easily dissolvable in the solution [3]. Therefore, complexation of palladium is required to lower the reduction potential and to increase its stability and solubility.

Studies showed that palladium tends to form a complex molecule with a ligand in the solution instead of forming pure single palladium ion [3, 23]. Various complexing agents have been use to formulate palladium electrolytes e.g. 1, 2 ethylenediamine, 1, 3 diaminopropane, chloride (Cl^-), and NO_2 [3, 21]. Thermodynamics and electrochemistry of the complexed palladium have been comprehensively examined. The thermo-electrochemical data including the stability constant (log β_x) and standard reduction potential (E^0) are presented in Table I. It suggests that NH_3 is the better choice of ligand for palladium. $Pd(NH_3)_4^{2+}$ complex is formed producing an electrolyte that is highly stable with sensible reduction potential [3].

TABLE I
STABILITY AND ELECTROCHEMICAL DATA OF PALLADIUM COMPLEXES [3]

Formula (Aqueous)	log β_x	E^0 (V)
Pd^{2+}	<3	+0.915
$Pd(SO_4)^{2-}$	3.16	+0.82
$PdCl_4^{2-}$	12.20	+0.62
$Pd(en)_2^{2+}$	26.90	-0.79
$Pd(NH_3)_4^{2+}$	30.50	0.00
$Pd(CN)_4^{2-}$	51.60	-1.52

Where,

$$Log\beta_x = Log \frac{[PdL_x^{z+}]}{[Pd^{2+}][L]^x} \qquad (9)$$

In general, based on the sources of palladium and complexing agents, the palladium electrolytes can be categorised into ammoniacal systems, chelated systems, and acid systems [24]. Ammoniacal systems use ammonia as a ligand, whereas chelated systems use aliphatic diamines. Strong acid such as hydrochloric acid may be used as

complexing agent in a very acid system [24]. The most popular commercially available electrolyte is a solution based on $PdCl_2$ as palladium source and NH_3 as complexing agent [21, 23]. The combination of $PdCl_2$, NH_3 (ligand), and NH_4OH (pH buffer) forms palladium complex of $[Pd(NH_3)_4Cl_2]$ and $[Pd(NH_3)_2Cl_2]$ [23]. Currently, ammoniacal palladium electrolyte is the most widely used for industrial and commercial application [3, 21].

The stability of $Pd(NH_3)_4^{2+}$ is sufficient to prevent spontaneous metal reduction and oxidation reactions, but it still allows electrodeposition of the metal to take place. Therefore, the ammoniacal palladium solution was selected for the experiments of palladium electrodeposition.

A range of palladium electrolyte composition and concentration in which the conductivity was about 2.7 S/m was firstly investigated. Standard conductance equation was used to estimate the conductivity of some ammoniacal palladium solutions. The calculated conductivities of the solutions are presented Table II.

TABLE II
CALCULATED CONDUCTIVITIES FOR THE PALLADIUM SOLUTIONS CONTAINING DIFFERENT CONCENTRATIONS OF Pd^{2+} AND NH_3

Composition		Calculated
$PdCl_2$ (M)	NH_4Cl (M)	Conductivity (S/m)
0.014	0.136	2.32
0.019	0.188	3.21
0.023	0.224	3.83

The palladium electrolytes were prepared from palladium chloride ($PdCl_2$ ReagentPlus® grade, 99 %) and ammonium chloride (NH_4Cl 99.99% trace metals basis) obtained from Sigma-Aldrich. The chemicals were dissolved in to deionised (DI) water system (18 MΩ) (a Millipore Puritee).

The electrolyte solution was prepared in 500 mL using the following procedure due to solubility issue of palladium chloride:
- Dissolution of n gram $PdCl_2$ in 500 ml DI water
- Addition of m gram NH_4Cl (99.99 %) into the 500 ml DI water
- Slowly heating up the solution to 50 °C
- Continuously stirring the solution until the palladium and ammonium chloride was completely dissolved
- Cooling of the solution to room temperature

To identify the chemistry of palladium complexes in the solution, ultraviolet-visible (UV-Vis) spectroscopy analysis was carried out. The analysis was carried out using a Unicam 8700 series spectrometer (Philips) so that the species of palladium complex in the solution can be identified. Refer to literature, the species was determined by using the recorded absorption peaks and corresponding wavelengths.

Apparatus: The polarisation experiments were carried out in a 0.5 L unstirred vertically-cylindrical cell. The cell has a dimension of 10 cm diameter and a depth of 8 cm constructed of transparent polyvinyl chloride (PVC). Two polytetrafluoro

ethylene (PTFE) electrode holders were located on each side for mounting the tool (anode) and the substrate (cathode). An electrode gap was adjusted to an approximately 300 μm by screw action. An external power supply was connected to electrode through a copper rod in the core of the electrode holder, and the electrode disks are mounted to the electrode holder by a screw. The cell was filled up with approximately 500 ml of electrolyte to ensure the electrodes were completely immersed in solution. A reference electrode was prepared by inserting platinum wire into PTFE holder. The reference electrode was located orthogonally on the other side of this cell. This cell has been thoroughly described in previous publication [25].

Electrode preparation: a variety of deposited nickel pattern on copper disc (d = 1 cm) was used as working electrode. The counter electrode was a nickel disc (d = 1 cm). A Pt wire was the reference electrode. The deposited nickel on copper was always freshly produced from a 0.19 M nickel sulfamate using the similar reactor. The experiments were performed with a variation of pattern feature sizes on the tool including fully exposed anode, 5 x 4 mm^2, and 5 x 2 mm^2 (*c.f.* Figure 1).

a)   b)   c)
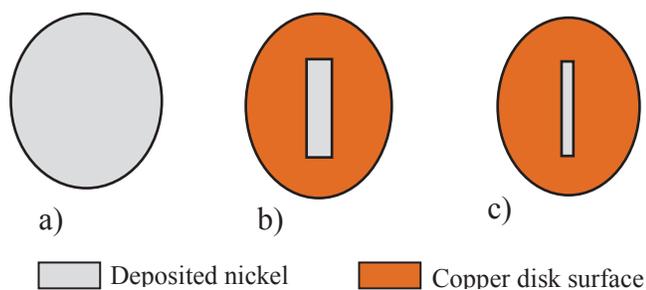
▭ Deposited nickel   ▮ Copper disk surface

Figure 1 designed millimetre scale pattern with feature sizes of a) fully exposed b) 5 mm x 2 mm, c) 5 mm x 1mm

Instrumentation: a PGSTAT30 potentiostat (Autolab) was utilised for all electrochemical characterisation experiments. Potential-current density data were acquired by using a computer supported by General Purpose Electrochemical System (GPES) software version 4.9. The polarisation data was interpreted using spreadsheet software (i.e. Microsoft excel).

pH and conductivity were measured using an S47 SevenMulti^{TM} dual pH and conductivity meter from Mettler-Toledo. The measurement was carried out at room temperatures (18 – 22 ^{o}C).

Procedures: Palladium would be deposited on top of the nickel deposit pattern. In the first stage, the chosen electrolyte was electrochemically characterised to determine its onset deposition potential and applied current densities. Linear sweep voltammetry (LSV) measurement with a low scan rate (2 mV/s) was carried out to record the steady state cathodic polarisation data. The two potential limits (V_1 and V_2) were set in the cathodic region where V_2 was more negative than V_1.

The electrochemical investigation was carried out by performing polarisation experiments in the unstirred cell using

the patterned tool. The substrate was a deposited nickel pattern (with various feature sizes) on a 1 cm diameter copper disk. A resist-patterned nickel disk with different feature sizes was used as anode for each experiment. The deposited nickel feature on the substrate was arranged as accurately as possible to face the exposed area of the anode. The potential was measured against the reference electrode of platinum wire.

The potential-current density data was then analysed to determine onset potential and applied current density for palladium electrodeposition.

IV. RESULT AND DISCUSSION

The physicochemical properties of all previously prepared electrolyte solutions were experimentally measured. The results of the measurement showed that the solution containing 0.019 M PdCl$_2$ and 0.188 NH$_4$Cl was preferable for use in further experiments. As shown in Table II the conductivity of the chosen electrolyte was relatively as low as the desired value. The measured pH of the solution is also presented in Table III.

TABLE III
COMPOSITION AND PHYSICOCHEMICAL PROPERTIES OF PALLADIUM ELECTROLYTE AT 20 ± 2 ^{O}C

Composition	Conductivity (S/m)		pH
	Calculated	Measured	
0.019 M PdCl$_2$ + 0.188 M NH$_4$Cl - 2 g/L as Pd metal - 10.08 g/L NH$_4$Cl	3.21	2.35 ± 0.11	2.74 ± 0.31

UV-Vis spectroscopic analysis has been carried out to identify the formation of palladium complexes. The species of palladium complexes were determined by observing absorbance peaks and corresponding wavelengths. The spectroscopic data are shown in Table IV

TABLE IV
UV-VIS SPECTROSCOPIC DATA FOR PALLADIUM SOLUTION

Solution	λ_{max} (nm)	Absorbance	Species
0.0189 M PdCl$_2$ + 0.188 M NH$_4$Cl	296.8	2.8	Pd(NH$_3$)$_4$Cl$_2$ [26]
	418.0	0.7	PdCl$_2$(H$_2$O)$_2$ [27]

According to the data available in the literature [26, 27], based on the wavelength and absorbance peak, the palladium was identified to be in the form of Pd(NH$_3$)$_4$Cl$_2$ [26] as main species and PdCl$_2$(H$_2$O)$_2$ [27]. The concentration ratio between the two species is 4:1 (based on their absorbencies).

Polarisation experiments have been carried out for the selected palladium electrolyte. Figure 2 shows the polarisation curve for the reduction of palladium in the electrolyte of

18.9 mM PdCl$_2$ and 188 mM NH$_4$Cl on fully exposed anode without pattern feature.
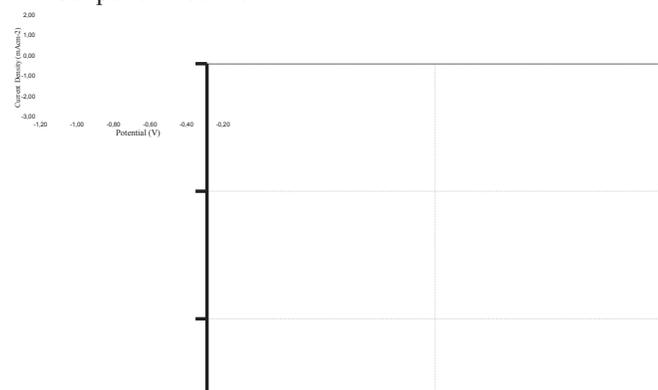

Figure 2. Polarisation Curve for the reduction of palladium on fully exposed nickel anode

In this polarisation experiment, the potential was swept toward cathodic region started from OCP to -1.20 V vs. platinum wire (reference electrode) at scan rate of 2 mV/s. As can be seen from the curve, reduction current is observed to commence at a potential around -0.32 V. The cathodic current increases rapidly until the potential reaches -0.45 V where cathodic current peak is observed. This potential wave was thought to correspond to the reduction of palladium complex ion [Pd(NH$_3$)4]$^{2+}$ to palladium metal. The peaks were possibly due to the restriction of mass transfer of palladium ions from the bulk solution to the electrode surface as the electrodes gap was narrow.

At more negative potentials, another smaller potential wave is observed at a potential around -0.80 V. This wave may be associated to hydrogen adsorption on to the deposited palladium [28]. Hydrogen evolution was found to occur at potential greater than -1.0 V vs. Pt wire.

This result showed that electrodeposition of palladium from the newly developed electrolyte in an unagitated system is achievable. The potential reduction for palladium is in the range between -0.30 V and -0.45 V vs. platinum wire. Applied current densities corresponding to the potential are in the range of 0.0 to -2.7 mA/cm^2.

Polarisation experiments were also carried out for two different pattern features. Figure 2 shows the potential-current density curve for reduction of palladium from the newly developed electrolyte on various pattern feature sizes.
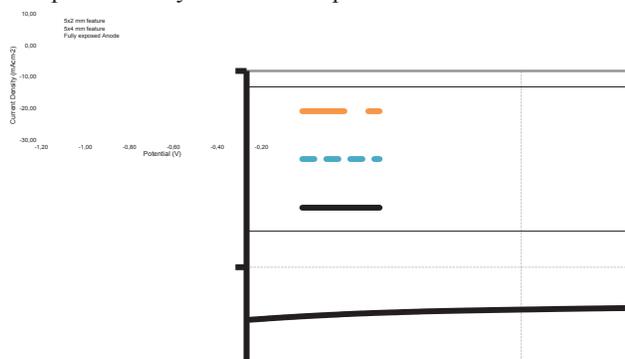

Figure 3. Polarisation Curves for the reduction of palladium and the effects of pattern features

The curves were obtained from the polarisation experiment on fully exposed anode, a feature of 5 x 4 mm^2, and a feature of 5 x 2 mm^2.

As shown in Figure 3, the polarisation curves of three different features exhibit similar trend. The curves are characterised by two cathodic current waves which correspond to palladium reduction and hydrogen adsorption. The curves also show that the pattern feature size significantly affects applied current density of palladium deposition. However, it has a slight effect to the overpotential as the cathodic potential peaks are slightly shifted to more positive region.

Figure 3 also shows that the current densities increase on smaller feature sizes. Since the current densities were calculated based on the active area, the increase is possibly caused by the decrease of the electro-active area on the anode as a result of the smaller feature size. In addition, a diffusional mass transfer of palladium ions through diffusion layer towards the electrode surface might be enhanced at smaller electro-active area due to a hemispherical diffusion. The enhancement of mass transfer led to an increase in the current densities. This finding is in agreement with literature [29- 31]. The increase of current density of palladium reduction due to the pattern feature sizes is shown in Table V.

TABLE V
THE EFFECT OF PATTERN FEATURE SIZE ON CURRENT DENSITY

No	Feature Sizes	Area (mm^2)	Cathodic Potential Peak (V vs Pt wire)	Current density (mA/cm-2)
1	fully exposed	0.78	-0.453	-2.57
2	5mm x 4 mm	0.20	-0.403	-9.48
3	5mm x 2 mm	0.10	-0.422	-22.80

After each polarisation experiment, black and powdery palladium deposits were found to cover both working electrode and counter electrode. This might be due to The displacement reaction. The anode surface was also found to be rough as a sign of metal dissolution.

V. CONCLUSIONS

A new palladium electrolyte for use in Enface system has been systematically developed. Based on the conductivity value, an electrolyte of 0.019 M PdCl$_2$ and 0.188 NH$_4$Cl has been chosen.

Steady state polarisation data for the chosen electrolyte indicates that the electrolyte has been shown to be capable of depositing palladium.

The polarisation data at various feature sizes of pattern shows that that the current densities increase when the feature becomes smaller. Reduction potential of palladium has been observed to be in the range of -0.3 to -.45 V. The corresponding current densities for palladium deposition depend on the feature size.

For the fully exposed anode, the applied current densities are in the range of -0.0 to -2.57 mA/cm^2.

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