

Characterization of Palladium Electrodeposition in Ammonia-free

In-Chan Oh*, Jong-Kyu Park**, Young-Min Byoun***

*T&I Chem,39, Gajwa-ro 84beon-gil, Seo-gu, Inchen. 22824, Korea

**SBP Surtech, Jeongseojin-ro, Seo-gu, Incheon, 22689, Korea

***Metal & Machinery Team, Korea Conformity Laboratories(KCL), 85 Dambang-ro, Namdong-gu, Incheon,21591, Korea
e-mail:82bym@kcl.re.kr

비암모니아 Palladium 도금 특성 연구

오인찬*, 박종규**, 변영민***

*(주)티앤아이켄

**에스비피 선택

***한국건설생활환경시험연구원

Abstract

Electrodeposition of palladium provides excellent chemical and low-contact resistance with good electrical properties, such as different types of electrical contacts in the electronics industry. The conventional palladium plating process utilizes ammonia-based electrolytes. Ammonia was added continuously in small quantities to maintain the optimum pH range. In addition, the unpleasant and annoying odor of the evaporating ammonia necessitates the use of a ventilator. A further disadvantage is that the brass substrate is corroded by the ammonia vapor, and the corrosion products can contaminate the bath, thereby changing the technological properties of the deposited plating for the worse. Ethylenediamine has been proposed as an alternative to ammonia; however, palladium electrodeposition occurs as microcracks via hydrogen evolution.

In this study, the effects of palladium electrolyte on ethylenediamine as a complexing agent and the properties of various additives are investigated to improve the current density and control the internal stress in the palladium electrodeposition that occurs on a brass substrate. Therefore, complexing agents such as 3-pyridine sulfonic acid, sodium nicotinate, butyne 1-4 diol, and sodium allylsulfonate, are selected as additives, to serve as an alternative to ammonia in the palladium electrolyte. The properties of electrodeposited palladium with various additives were examined. The effect of additives on palladium electrolytes can be classified as dense surfaces without defects such as microcracks. As complexing agents, particularly, a palladium electrolyte using sodium nicotinate has relatively improved surface roughness and properties. The palladium electrolyte was optimized under ammonia-free conditions by the addition of sodium nicotinate.

1. Introduction

Electrodeposition of palladium provides an excellent chemical, stability, and low-contact resistance with good electrical properties, and it is mainly used as a plating for connectors and leadframes for electronics industries such as the automotive industry, decorative industry, and in nuclear fuel [1, 2]. As the price of gold and platinum has increased, palladium has constantly garnered increasing attention as an effective alternative. Therefore, palladium is increasingly becoming important [3].

The electrodeposition of palladium depends on various process conditions such as palladium ion, current density, temperature, and pH, which are affected during electrodeposition [4]. Particularly, the additives used in palladium electrodeposition affect the properties of electrodeposited metals, such as surface morphology, phase,

grain size, and roughness [5]. Accordingly, it is important to understand the effects of additives on palladium electrodeposition.

Palladium electrolytes can be classified into ammoniacal, chelated, and acid systems. Ammoniacal systems use ammonia as a complexing agent [6]. Currently, the most widely used palladium electrolyte for industrial and commercial Pd electrodeposition is the ammoniacal system [7].

Palladium electrolytes contain ammonia as a complexing agent to maintain pH values and relatively high temperatures [8]. However, this causes numerous problems owing to evaporation during the process. The problems are the evaporation of alkaline ammonia, which deteriorates the stability of the palladium-ammonia complex ion and causes hydrogen embrittlement (HE) issues and ammonia

may cause respiratory problems in humans, such as headaches and skin irritation, when inhaled or in contact with the skin, leading to a harmful working environment [10-12]. Despite the research on palladium electrolytes with ammonia-free systems, the problems could not be solved owing to the presence of ammonia.

The purpose of this study is to elucidate the effect of ethylenediamine as a complexing agent, and as an alternative to ammonia. Various additives were used to improve current efficiency and reduce internal stress due to microcracks on the electrodeposition of palladium to examine their mechanical and electrochemical properties such as surface morphology, roughness, and corrosion resistance. Thereafter, the results of this study are discussed.

2. Experimental

Brass substrates (99.9 % purity, 50 mm × 50 mm × 0.4 mm) were used for electrodeposition using direct current. Platinum was used as the electrolyte anode. The electrodeposition of palladium in ammonia-based catalysts was performed using conventional palladium under composition and electrolyte conditions, as summarized in Table 1. Palladium electrolytes in ammonia-based were electrodeposited from palladium (II) chloride ($\text{Pd}(\text{NH}_3)_4\text{Cl}_2$) as a source of palladium as follows: temperature, 45 ± 2 °C; current density, 0.7 A/dm^2 ; pH, 8.0 ± 0.2 ; deposition time, 12 min; and agitation using a magnetic stirrer. Table 2 summarizes the composition and procedure of electrodeposited palladium in ammonia-free used in this study. The ammonia-free electrodepositions of palladium electrolytes were performed using palladium (II) sulfate (PdSO_4) as a source of palladium. To study the effect of additives on electrodeposited palladium, palladium electrolytes of the additives synthesized with 3-pyridine sulfonic acid 2.0 – 3.0 g/L, sodium nicotinate 1.0 – 2.0 g/L, butyne 1-4 diol 1 – 2 g/L, and sodium allylsulfonate 1.0 – 0 g/L are as follows: temperature 55 ± 2 °C, current density 0.7 A/dm^2 , pH 6.5 ± 0.2 , deposition time 12 min, and under the same agitation condition.

[Table 1] Composition and electrolytic conditions condition of electrodeposited palladium in ammonia-based

Composition	g/L (ml/L)	pH	Temp (°C)	Time (min)	Current density (A/dm ²)
NH_4Cl	100 – 110				
$(\text{NH}_4)_2\text{SO}_4$	30–35	8.0	45 ± 2	12	0.7
NH_4OH	10–15	±			
$\text{Pd}(\text{NH}_3)_4\text{Cl}_2$	7–9	0.2			

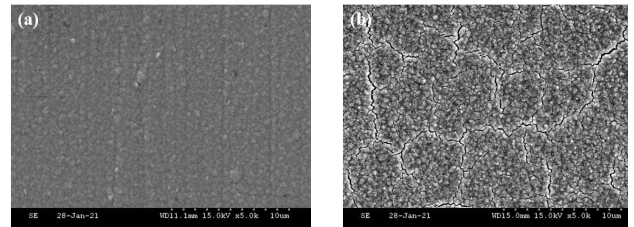
[Table 2] Composition and electrolytic conditions condition of palladium electrodeposition in ammonia-free.

Composition	g/L (ml/L)	pH	Temp (°C)	Time (min)	Current density (A/dm ²)
$\text{C}_6\text{H}_6\text{O}_7$	100–110				
KH_2PO_4	30–35				
$\text{C}_2\text{H}_8\text{N}_2$	10–15	6.5	55 ± 2	12	0.7
PdSO_4	7–9	±			
(1) $\text{C}_3\text{H}_7\text{NO}_3\text{S}$	2.0–3.0	0.2			
(2) $\text{C}_6\text{H}_4\text{NNaO}_2$	1.0–2.0				
(3) $\text{C}_8\text{H}_8\text{O}_2$	1.0–2.0				
(4) $\text{C}_3\text{H}_7\text{NaO}_3\text{S}$	1.0–2.0				

3. Results and discussion

3.1 Characterizations of Pd plating in ammonia

Figure 1 shows the surface morphology of the electrodeposited palladium layer in ammonia-based and ethylenediamine as ammonia in non-additives. The surface of the palladium electrolyte in ammonia-based was observed to be homogeneous in size and uniform (Fig. 1(a)), whereas that of the palladium electrolyte in ethylenediamine as a complexing agent had droplets and microcracks (Fig. 1(b)).



[Fig. 1] Surface morphology images of palladium electrodeposition layers; (a) ammonia-based, and (b) ethylenediamine

3.2 Characterizations of Pd plating in ammonia-free

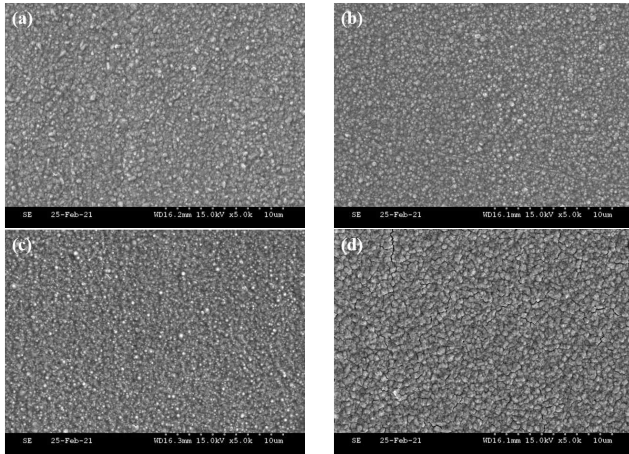
The surface morphologies were examined using scanning electron microscopy (SEM). Fig. 2 shows the micrographs of palladium layers in ammonia-free obtained from electrolytes with various additives such as 3-pyridine sulfonic acid, sodium nicotinate, butyne 1-4 diol, and sodium allylsulfonate.

As observed, when palladium electrolytes adding complexing agents was observed that the surface condition changed from an almost smooth with adding 3-pyridine sulfonic acid, sodium nicotinate, butyne 1-4 diol. It was indicated that the internal stress in the palladium electrolyte reduced from appropriate complexing agents and the uptake of low hydrogen evolution.

Figure 3 shows the potentiodynamic polarization curves for the brass substrate and palladium layers in ammonia free with various additives. The cathode polarization curve is related to the evolution of hydrogen gas (H_2),

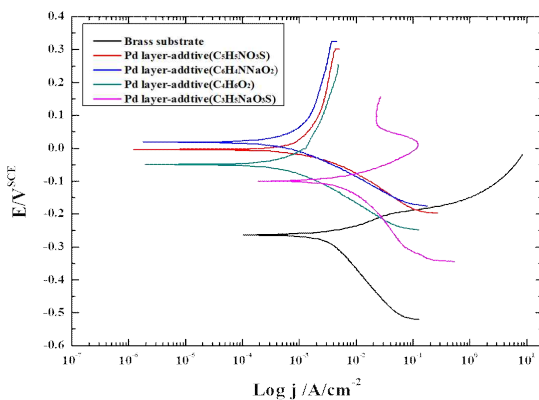
whereas the anodic polarization curve is the most important feature associated with corrosion resistance.

The corrosion potential (E_{corr}) and corrosion current density (i_{corr}) of the brass substrate and palladium layers in ammonia-free with various additives were determined by extrapolating the linear sections of the anodic and cathodic Tafel lines [13].



[Fig. 2] Surface morphology images of palladium electrodeposition layers in ethylenediamine with various additives; (a) 3-pyridine sulfonic acid, (b) sodium nicotinate, (c) butyne 1-4 diol, and (d) sodium allylsulfonate.

Table 3 lists the corrosion potential (E_{corr}), corrosion current density (i_{corr}), Tafel slope (β_a), cathodic Tafel slope (β_c), and corrosion current density (i_{corr}) of the specimen obtained from the polarization curves. The anodic and cathodic Tafel slope (β_a , β_c) decrease from 154.4 mV and 33.0 mV for the brass substrate to 11.1 mV and 12.2 mV after adding complexing agents, respectively. Therefore, this indicates that the addition of complexing agents prevents chloride penetration to the surface and subsequently decreases the corrosion potential (E_{corr}) and corrosion current density (i_{corr}). Particularly, the addition of sodium nicotinate resulted in significantly enhanced corrosion resistance.



[Fig. 3] Potentiodynamic polarization curves of substrate and palladium electrodeposition in ethylenediamine with various additives.

[Table 3] Tafel analysis for brass substrate and palladium electrodeposition in ethylenediamine with various additives.

Specimen	E_{cor} (mV)	β_a (mV/decade)	β_c (mV/decade)	i_{corr} (A/cm ²)
Brass substrate	-0.257	33.0	154.4	2.317×10^3
Pd layer (C ₆ H ₄ N ₂ NaO ₂)	0.024	11.1	12.2	0.052×10^3
Pd layer (C ₄ H ₆ O ₂)	-0.003	14.2	12.5	0.071×10^3
Pd layer (C ₃ H ₅ NaO ₃ S)	-0.049	27.2	19.6	0.105×10^3

4. Conclusions

In this study, ammonia-free palladium electrolytes were operated with additives as complexing agents, and their properties, such as surface morphology and corrosion resistance were examined. Additives as complexing agents significantly enhanced surface morphology and corrosion resistance. The following characteristics were confirmed:

1. Microcracks were observed in the palladium electrolyte without the complexing agent, which revealed that the low stability constant due to the low pH promoted hydrogen evolution.
2. The effect of additives as complexing agents was observed to stabilize the palladium electrolyte with low hydrogen evolution. In addition, the palladium layers formed a dense and uniform morphology without defects such as microcracks and pores.
3. The addition of sodium nicotinate to an ammonia-free palladium electrolyte significantly improved the smooth and corrosion resistance, indicating that the increased hydrodynamic conditions and appropriate polarization of the working electrode (complexing agent) may be key parameters for significantly improving the metal deposition rate and properties of the palladium layer in ammonia-free. Therefore, all the experimental results obtained in this study, such as sodium nicotinate, as a complexing agent.

References

[1] M. Konoe, Japan patent., 86 52 (1984) 389.
 [2] Y.A. Pokhitonov, V.N. Romanovskii, Radiochemistry., 47 (2005) 1–13.
 [3] R. Le Penven, W. Levason & D. Pletcher, J. Appl. Electrochem., 20(3) (1990) 399.
 [4] J.W. Dini, Electrodeposition, Noyes Publications,

- New Jersey, (1994) 145.
- [5] P. Wikinson, Trans. Inst. Met. Fin. 60 (1982) 152
- [6] M. Schlesinger, and M. Paunovic, Modern Electroplating, 4th Edition, Electrochemical Society Series, John Wiley and Sons, Inc. New York (2000) 139-199.
- [7] Ch. J. Raub, Platinum Metals Rev., 26, (4) (1982) 158-166.
- [8] M. Enyo and P. C. Biswas. J, Electroanal. Chem., 335 (1992) 309-319.
- [9] P. Manolatos and M. Jerome, Electrochimica Acta, 41(3) (1996) 359-365.
- [10] Fang-zu Yang, Shu-kai Xu, Ling Huang, Electrodeposit. Trans. IMF, 76(6) (1996) 238-240.
- [11] M. Schlesinger, and M. Paunovic, Modern Electroplating, 4th Edition, Electrochemical Society Series, John Wiley and Sons, Inc. New York (2000) 139-199.
- [12] S. Nouraei, and S. Roy, Journal of the Electrochemical Society, 155(2) (2008) 97-103
- [13] Y. G. Ko, K. M. Lee, K. R. Shin, D. H. Shin, Kor. J. Met. Mater, 48 (2010) 724-729.