Journal of Electrochemical Science and Technology

jecst.kecs.or.kr

Mercury Ion Monitoring in Mercury Plating Bath by Anodic Stripping Voltammetry

Mijung Park, Sumi Yoon, and Woonsup Shin*
Department of Chemistry, Sogang University, Seoul, 04107, Korea

ABSTRACT

Anodic stripping voltammetry (ASV) is successfully applied in mM level detection of mercury ion in an electroplating bath which is currently used in preparing a cathodic electrolyzer. Glassy carbon electrode is used for the detection and the optimum condition obtained is 10 s deposition at -1.4 V vs. Ag/AgCl and stripping by scanning from -1.4 to +0.4 V vs Ag/AgCl at 50 mV/s. By applying the method, the mercury ion concentration in the electroplating bath could be successfully monitored during the plating.

Keywords : Mercury ion detection, Mercury ion monitoring, Anodic stripping voltammetry, Hg plating bath

Received : 9 August 2016, Accepted : 2 September 2016

1. Introduction

Mercury electroplating is mainly used in making a thin mercury film electrode for analytical purposes. Platinum and glassy carbon are the main surfaces to make the thin Hg film since those do not easily form the alloy of mercury, amalgam [1-4]. The main application of the film is the determination of heavy metal ions in ppm or ppb level by anodic stripping voltammetry (ASV). Normally, once the mercury is electroplated on a metallic surface, it forms amalgam with the metal and the surface properties are dramatically changed. Among them silver amalgam electrode (SAE) is the most popular and it is applied in the electrochemical determination of metal ions, organic, and biological compounds [5-9].

Since mercury is toxic, the uses of mercury film and amalgam electrodes are limited in laboratory purposes and industrial or large scale mercury electroplating is rare. Recently, our lab developed a preparation method of dental amalgam composition on a surface of copper electrode by alternative electroplating of mercury and silver-tin for making a cathodic electrolyzer [10]. In this case, the amount of mercury deposited on the surface should be critically controlled. In the plating bath, the concentration of mercury ion is normally in the range of mM level. Therefore, we developed a method to follow the concentration of mercury ion in the bath during the plating. ASV is successfully applied in monitoring mM level concentration although the technique is normally used in detecting ppm or ppb concentration level of metal ions.

2. Experimental Section

2.1 Materials and Instruments

$Hg(OAc)_2$ is purchased from Sigma Aldrich, USA, Na_2EDTA and $K_4P_2O_7$ are from Jin Chemicals, Korea, and 0.5 μm alumina powder for polishing is from Buehler Ltd., UK. Distilled and deionized water by Millipore purification system was used throughout the experiments. Cyclic voltammetry and anodic stripping voltammetry were performed using CHI 1232a potentiostat (CH Instruments, USA). Electrochemical measurements were made in a glass cell (15 mL) equipped with a glassy carbon disc working electrode (3 mm diameter) and Ag/AgCl reference electrode, and a platinum coil counter electrode.

*E-mail address: shinws@sogang.ac.kr

2.2 Procedures of Hg ion detection

The glassy carbon disc electrode was polished by 0.5 µm alumina slurry and sonicated for 3 min in ethanol/water (1/1) solution, followed by N_2-blow drying. The sample solution was under Ar atmosphere during electrochemical measurements. In ASV measurement, after the several trials, the optimized condition was 10 s electrodeposition at -1.4 V vs. Ag/AgCl followed by the stripping from -1.4 to +0.4 V vs. Ag/AgCl at 50 mV/s. The plating solution is 13 mM $Hg(OAc)_2$ in 0.2 M Na_2EDTA and 0.4 M $K_4P_2O_7$ and the aliquots sampled during the plating were diluted 3 times by 0.2 M Na_2EDTA and 0.4 M $K_4P_2O_7$ solution prior to the determination. After the measurement, the electrode surface was cleaned and conditioned by cycling between -0.4 to +0.4 V vs. Ag/AgCl to ensure the reproducible measurements in the next runs.

3. Results and Discussion

3.1 Electrochemical responses of mercury ion on glassy carbon electrode in the plating bath condition

The glassy carbon electrode was chosen as a sensing electrode because it has considerably less mercury memory effect compared to other electrode materials tested such as gold and conducting polymer modified glassy carbon electrode. The mercury deposition and stripping potentials vary a lot depending on solution and experimental conditions. In case of stripping, the peak potentials were reported in a wide range of -0.3 V ~ +0.5 V vs. Ag/AgCl [11-14]. Therefore, the voltammetric behavior in the plating

Fig. 1. Cyclic voltammogram of 1 mM $Hg(OAc)_2$ in 0.2 M Na_2EDTA and 0.4 M $K_4P_2O_7$ solution (red) and the background (blue) at a scan rate of 50 mV/s.

solution we are interested in should be well-studied and the applying potential and potential range of the scan should be determined.

Cyclic voltammograms of 1 mM Hg^{2+} containing plating solution and the background solution are shown in Fig. 1. In the background solution, the open circuit potential (OCP) was 0.0 V vs. Ag/AgCl and the hydrogen starts evolving near -1.1 V vs. Ag/AgCl. In the plating solution, the mercury ion starts to deposit on glassy carbon electrode from -0.6 V vs. Ag/AgCl during the negative scan and the stripping is shown at near 0 V vs. Ag/AgCl during the positive scan.

3.2 ASV Analysis of mercury ion in standard solutions and real samples

The stripping peak currents at different concentrations of mercury ion in the plating solution were compared at deposition potentials of -1.0, -1.2, -1.4 V vs. Ag/AgCl and the stripping currents deposited at -1.4 V vs. Ag/AgCl showed the best linearity versus the concentration. The 10 s deposition time was found to be enough for the stable responses. The scan rate of 50 mV/s was enough fast without the distortion of the voltammetric responses. The stripping from -1.4 V to 0.4 V vs. Ag/AgCl was immediately followed by the deposition. Therefore, the optimized ASV condition for the current system was set to be 10 s deposition at -1.4 V vs. Ag/AgCl followed immediately by positive scanning from -1.4 V to +0.4 vs. Ag/AgCl at 50 mV/s.

The standard solutions are prepared in 0, 1, 3 and 5 mM of $Hg(OAc)_2$ in the plating condition of 0.2 M Na_2EDTA and 0.4 M $K_4P_2O_7$ solution and stripping peaks are shown in Fig. 2, left. It shows sharp stripping peaks and the currents near 0 V vs. Ag/AgCl is linear to the concentration of mercury ion in the solution as shown in Fig. 2, right. It is used for the calibration line for the mercury ion determination in the plating bath.

The same ASV measurement was applied to the real electroplating solutions. Because the base copper electrode is electroplated repeatedly in mercury and silver-tin baths, the mercury plating solution may contain impurities of Ag, Sn and Cu ions. The mercury ion measurements in the electroplating solution before and after the plating are shown in Fig. 3. Because the concentration of mercury ion is larger than 20 mM in the solution, before the measurement, the aliquots were taken and diluted 10 times by the solution of 0.2 M Na_2EDTA and 0.4 M $K_4P_2O_7$. The
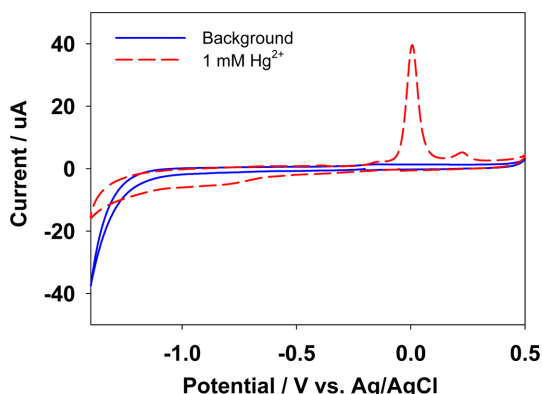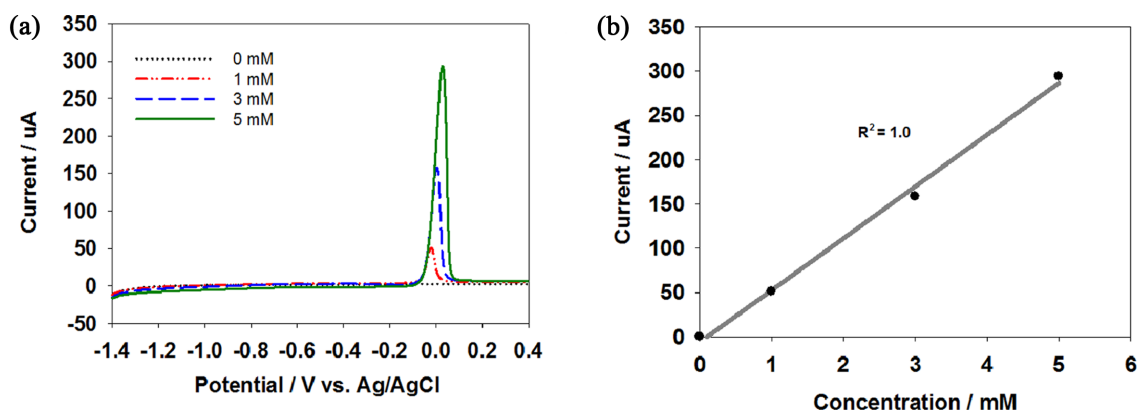
Fig. 2. (a) The ASV responses of 0, 1, 3 and 5 mM Hg^{2+} in 0.2 M Na_2EDTA and 0.4 M $K_4P_2O_7$ solution scanned from -1.4 V to +0.4 V vs. Ag/AgCl at a scan rate of 50 mV/s. (b) Calibration plot of stripping peak current vs. mercury ion concentration.
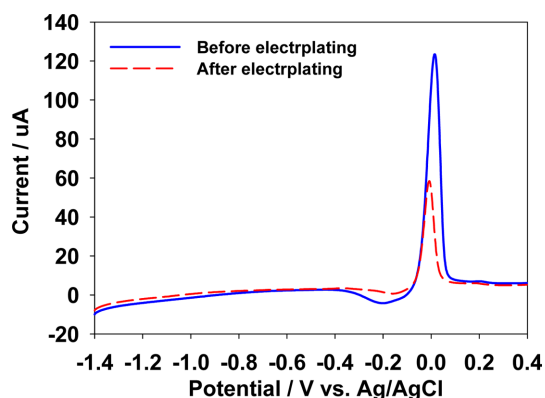

Fig. 3. The ASV of 1/10th diluted Hg^{2+} plating solutions before (blue) and after the plating (red). The experimental conditions are the same as in Fig. 2.

Fig. 4. The monitoring of mercury ion concentration during the plating. The fitted line is exponential and coefficient of determination is 0.99. The volume of the plating bath is 900 mL.

measurements based on the calibration plot in Fig. 2 are 2.3 mM for the 1/10th diluted initial sample and 1.2 mM for the 1/10th diluted sample of the solution after the plating. Therefore, the concentration of mercury ion in the plating solution is decreased by 11 mM. It gives an estimation of 9.9 mmol plated mercury on the electrode since the plating solution is 900 mL. In case of amalgam electrode the amount of mercury deposited on the surface is difficult to measure directly and the current method is only valuable method to quantify the deposited amount.

3.3 Monitoring of mercury ion during the electroplating

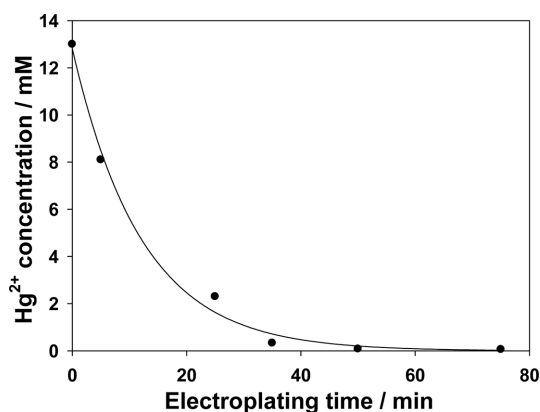The same method was applied to the plating bath

where the total amount of mercury in the bath is deposited on the electrode. The initial concentration was around 13 mM. The aliquots were sampled roughly every 10 min. The decrease of mercury ion concentration is clearly seen and it fits to exponential decay (Fig. 4). It is observed that most mercury ions are consumed after 50 min and this information is used for setting the electroplating condition to improve the reproducibility.

4. Conclusions

ASV measurements are valid in mM concentration of mercury ion and it is a valuable tool to quantify the

amount of mercury deposited on the surface or during the amalgam formation. The concentration change during the plating could be successfully followed by the developed method and it helps in setting the plating conditions.

Acknowledgements

References

[1] J. E. Anderson and D. E. Tallman, *Anal. Chem.*, **1976**, *48*, 209-212.

[2] U. Eisner, J. A. Turner and R. A. Osteryoung, *Anal. Chem.*, **1976**, *48*, 1608-1610.

[3] M. A. Baldo, S. Daniele, M. Corbetta and G. A. Mazzocchin, *Electroanalysis*, **1995**, *7*, 980-986.

[4] U. Tamer, T. Oymak and N. Ertaş, *Electroanalysis*, **2007**, *19*, 2565-2570.

[5] V. V. Ales Danhel, K. K. Shiu, B. Yosypchuk, J. Barek and K. Peckova, *Electroanalysis*, **2009**, *21*, 303-308.

[6] I. Jiranek, K. Peckova, Z. Kralova, J. C. Moreira and J. Barek, *Electrochim. Acta*, **2009**, *54*, 1939-1947.

[7] P. Kapturski and A. Bobrowski, *J. Electroanal. Chem.*, **2008**, *617*, 1-6.

[8] A. N. de S. Dantas, D. De Souza, J. E. S. de Lima, P. de Lima-neto and A. N. Correia, *Electrochim. Acta*, **2010**, *55*, 9083-9089.

[9] B. Yosypchuk and L. Novotny, *Talanta*, **2002**, *56*, 971-976.

[10] Manuscript in preparation

[11] J. Wang, J. Lu, Ü. A. Kirgöz, S. B. Hocevar and B. Ogorevc, *Anal. Chim. Acta*, **2001**, *434*, 29-34.

[12] N. Y. Stojko, Kh. Z. Brainina, C. Faller and G. Henze, *Anal. Chim. Acta*, **1988**, *371*, 145-153.

[13] B. C. Janegitz, L. C. S. Figueiredo-filho, L. H. Marcolino-junior, S. P. N. Souza, E. R. Pereira-filho and O. Fatibello-filho, *J. Electroanal. Chem.*, **2011**, *660*, 209-216.

[14] J. Gong, T. Zhou, D. Song and L. Zhang, *Sensors Actuators B. Chem.*, **2010**, *150*, 491-497.