Toward sustainable electroplating of decorative silver for SMEs in Indonesia

T Widayatno* and Hamid
Department of Chemical Engineering, Faculty of Engineering Universitas Muhammadiyah Surakarta, Surakarta, Indonesia
*Email: tri.widayatno@ums.ac.id

Abstract. Decorative silver electroplating has been a long time conducted by small and medium enterprises (SMEs) in Indonesia. Environmental pollution associated with the electroplating SMEs activities has created serious problems. For example SMEs of silver electroplating has contaminated groundwater which is no longer fit for domestic consumption due to its high level of cyanide contamination. Inefficient process and the use of high concentration of cyanide based electrolyte have been claimed to be the root cause. Therefore, the process of decorative silver electrodeposition in SMEs would be improved by developing an electrolyte with low cyanide concentration, determining onset potential and current densities, and modifying the process and the electrochemical cell so that the process would be more efficient and sustainable. A new electrolyte composed of AgNO₃ and KCN with a ratio of 5:39 were chosen for the experimentation. For this electrolyte, silver would possibly be electrodeposited at potentials ranging from -2.2 V to -2.8 V. Corresponding current densities for silver electrodeposition would be between -2 and 7 mA/cm². To improve the process, a new design of electrochemical reactor has been developed which ensure improvement of the observed electrochemical parameters i.e. the uniform current density distribution, the larger area of anode, and the stability of electrodes distance and position.

1. Introduction
The metallic coating industry has rapidly increased in Indonesia in recent decades. In general, the metallic coating application (i.e. silver, nickel, chrome, etc) is for decorative and functional purposes (e.g. corrosion resistance) [1]. The coating increases the quality of the material surface so that its appearance, wear and corrosion resistance are improved. This is crucial as metals commonly used for imitation jewelry, industrial equipment, and household appliances are easily oxidized and corroded due to exposure to the environment [1, 2].

One of the popular electrochemical coating industries in Indonesia is a silver coating. The silver layer plating has attracted great attention for decades particularly for handicrafts, accessories, and jewelry. This is the most popular decorative application of silver coating in some regions of Indonesia i.e. Kotagede Yogyakarta. Decorative silver electroplating has been long time conducted by small and medium enterprises (SMEs). SMEs have an important role in reducing poverty by creating job opportunities, however, increasing production of SMEs in manufacturing electrodeposited silver has resulted in significant environmental costs [3].

Although local newspapers regularly report these problems, no systematic monitoring has been conducted for tackling the environmental problems and improving health and safety of SME activities
The Ministry of Industry and Trade (MOIT) reported that pollution associated with SME activities, particularly in the electroplating sector, has created serious environmental problems. For instance, in Kotagede, Yogyakarta, where SME activities involving electroplating of silver are concentrated, groundwater is no longer fit for domestic consumption due to its high level of chemical contamination i.e. cyanide [5]. Workers in SMEs and the population near the SMEs' areas of activities are beginning to suffer from serious skin and respiratory problems caused by the pollution from electroplating industries. Hence it is crucial to find out the root cause and to tackle the issues. A traditional and conventional technology used by SMEs has been reported to contribute in process inefficiency and cause the environmental problem [2,6].

A technology for decorative silver plating used by SMEs is still relying on traditional and conventional method and equipment [c.f. Figure 1] which has some issues. A number of drawbacks have been identified such as 1) Inefficient process, 2) Low-quality product, 3) copious waste generation, 4) Frequent replace of the electrolyte, 5) High processing cost [2,6]. Figure 1 shows a simple electrochemical cell used in the process of silver plating in SMEs. The equipment setting implies to an unstable electrode distance and position, a smaller area of anode than cathode, and non-optimal cell geometry. These have been identified to be the causes of some issues that have been previously discussed [7].

![Figure 1. Simple electrochemical cells and equipments for traditional silver electroplating method used by SMEs in Kotagede Yogyakarta [7]](image)

Direct observation to the SMEs practices in the process of silver electroplating has also been carried out [7]. The observation revealed that electrochemical parameters and variables, as well as the operating condition, have not been optimally set. Table 1 shows the electrochemical parameters and operating conditions observed in the silver electroplating carried out by SMEs compared to those in literature.

A number of researches have been devoted to investigate the process of silver electrodeposition [8,9]. An electrolyte formulation, electrochemical parameters, operating condition and cell geometry are crucial to achieve more efficient and more environmentally friendly process [10]. There are several alternative options taken into account in this study: 1. the environmentally friendly process can be achieved by using low concentration of cyanide or by removing use of cyanides electrolyte. 2. The efficient process can be achieved by applying optimum electrochemical parameters and operating condition. 3. Electrochemical cell geometry has to be modified to ensure uniform current distribution.

In this paper, the process of silver electroplating improved by developing an electrolyte with low cyanide concentration, determining onset potential and current densities from the electrolyte, and modifying the electrochemical cell will be presented. Electroplating Process efficiency could be improved by thorough and comprehensive analysis and evaluation of SME practice based on the best practice of electrochemical method. The improvement of decorative electroplating process by SMEs have to take into account the principles and fundamental aspects of electrochemistry.
Table 1. Observed Parameters of Electroplating Process of decorative silver by SMEs [7] Compared to the literature [8]

| No | Parameter                             | Observed SMEs Practices            | Literature                                          |
|----|---------------------------------------|-------------------------------------|-----------------------------------------------------|
| 1  | Applied Current/current densities     | Not monitored                       | 0.5 – 1.5 A or 1.5 – 3 A/dm²                         |
| 2  | Applied Potentials                    | 30 V                                | 4 – 6 V                                             |
| 3  | Cell Geometry                         | Simple without considering current distribution | Well-designed consider uniform current distribution |
| 4  | Electrode area                        | Commonly cathode area> anode area    | Anode area must be > cathode area                   |
| 5  | Electrodes distance                   | Always change, moved by operator    | Relatively stable and steady                        |
| 6  | Electrodes position                   | Always change, moved by operator    | Relatively stable and steady                        |
| 7  | Types of Electrodes used              | Anode: stainless steel, cathode: work piece (Cu coated by thin nickel ) | Anode: pure metallic silver, cathode: work piece (Cu coated by thin nickel ) |
| 8  | Electrolyte composition and concentration | Initially according the standard, no systematic monitoring afterward | According to standard, and constantly monitored     |
| 9  | Electrolyte make up/replacement       | According to the operator feeling   | Carefully estimated                                 |
| 10 | Method                                | Potentiostatic                      | Galvanostatic                                        |

2. Theory

Electroplating or electrodeposition is a process of metal deposition through a nonspontaneous reduction reaction of dissolved metallic ions to form deposited metal on an electrode surface (cathode) in an electrolytic solution. It typically requires a set of electrochemical system composed of an external power supply, an electrolyte, cathode, anode, and reference electrode (optional). The equipment is set to be a system as shown in Figure 2. In order to achieve efficient process, the electroplating has to be carried out at the most appropriate electrochemical parameters and geometry of the cell [10]. The reduction reaction will take place as overpotential applied to the system so that the condition deviates from its equilibrium. The deviation leads to electrical current flow between the two electrodes and the reduction reaction begins to occur [11].

Figure 2. Scheme of typical electrochemical system for metal electroplating use [7]

Kinetics of the electrochemical reaction has been formulated by Nernst equation. According to Nernst’s equation, the electrode surface reaction is determined by the value of overpotential. When negative overpotential (E<E<ek) imposed to the working electrode, a reduction reaction occurs to achieve a new equilibrium condition. The cathodic current flows to supply the electron (ne⁻) for the
reaction which is in the polarization curves represented by current densities. Based on Butler-Volmer equation, the current density depends on a number of parameters i.e. the temperature, the overpotential, the exchange current density, and the charge transfer coefficient. Therefore, the current density increases at higher overpotentials which represent the increase of the electrochemical reaction rate [11].

Decorative silver electrodeposition conducted by SMEs in Indonesia is commonly used to produce bright silver coating for imitation jewelry. In general, a number of silver electrolytic baths with various concentrations and compositions to obtain bright silver are used. Typical silver electrolytes used for decorative purposes are shown in Table 2.

| No | Components       | Concentration (g/l)/parameters |
|----|------------------|-------------------------------|
| 1  | AgCN             | 31 – 55                       |
| 2  | KCN (free)       | 35 – 50                       |
| 3  | KCN (total)      | 50 – 80                       |
| 4  | Ag (metallic)    | 20 – 45                       |
| 5  | K₂CO₃            | 15 – 90                       |
| 6  | Anode            | Pure silver                   |
| 7  | Potentials (V)   | 4 – 6                         |
| 8  | Current densities (A/dm²) | 0.5 – 1, 1.5 - 3               |
| 9  | Temperature (°C) | 20 - 28                       |

It can be seen in Table 2 that typical silver electrolytes contain a high concentration of cyanide (50 – 80 g/l). Due to the present of AgCN, and KCN, a complex of KAg(CN)₂ is formed in the solution. Such cyanide baths have been used for more than 100 years application, as it is the most stable electrolyte to consistently produce high-quality silver deposit [9]. The process in cyanide has current efficiencies that are close to 100%. Thus, use of high purity silver anodes (≥ 99.98%) is preferred [8]. However, the cyanide bath possesses extremely high risks due to its toxicity [9]. So it is vital to reduce the use of cyanide.

3. Experimental

In this study, more environmentally friendly process of silver electroplating would be achieved by using low concentration of cyanide. Therefore, a new silver electrolyte with low cyanide concentration would be formulated. Several compositions with a specific ratio of AgNO₃ and KCN were analyzed using steady-state polarization experiments. Ratio of AgNO₃: KCN that offers higher current densities would be chosen for further experimentation. The electrolytic solutions were prepared using analytical grade of AgNO₃ and KCN obtained from Sigma-Aldrich.

The process efficiency would be improved by determining optimum electrochemical parameters and operating condition using polarization experiments. The electrochemical polarisation experiments for the chosen electrolyte carried out at various temperatures in a vertical cylindrical glass electrochemical cell (volume of 250 ml). All polarization experiments were conducted in the laboratory of chemical engineering Universitas Muhammadiyah Surakarta. The experiments were carried out in a two electrodes electrochemical system. The system consisted of a silver rod anode and a cathode of thin deposited nickel on copper plate. A range of potentials between 0 V and 3 V were supplied by a power supply of Sanfix SP3050 applied to the system with a potential interval of 0.1 V. Corresponding currents were recorded when steady state condition has been reached (for around 1 minute). The cell potentials and the corresponding current densities were then plotted into a graph to produce polarization curves. Using these curves, applied potentials and current densities at which the silver electrodeposition would be optimally achieved could be determined.
Since uniform current distribution is crucial to obtain a high coating quality, a new design of electrochemical cell for the process of silver deposition was developed. The new design considered electrode area (anode), distance and position of electrodes, as well as geometry of the cell that allows uniform current distribution.

4. Results and Discussion
A new formulation of silver electrolyte with low cyanide concentration has been developed. The electrolyte composed of AgNO$_3$ and KCN with a ratio of 5:39 were chosen for the experimentation. This has been discussed in the previous publication [12]. Polarization experiments for the chosen electrolyte have been carried out in the previously described electrochemical system. The polarization curves obtained from the experiments at different temperatures are shown in Figure 3.

![Figure 3](image_url)

**Figure 3.** The polarization curves for the chosen electrolyte in the electrochemical cell previously described at various different temperatures

It can be seen in Figure 3 that cathodic current begins to flow at potential of around -1.0 V. This is an indication that there has been electrochemical reaction taking place. However at potential between -1.0 and -2.2 V, no silver deposit on the cathode surface was observed. This indicates that the current flow at potential between -1.0 and -2.2 V was consumed by competing reaction(s). The polarization curves show that silver would possibly be electrodeposited at potentials ranging from -2.2 V to -2.8 V indicated by a sharp increase of the current densities. Corresponding current densities for silver electrodeposition would be between -2 mA/cm$^2$ and 7 mA/cm$^2$. At cell potential greater than -2.8 V, gas evolution was clearly noticeable. Figure 1 also shows that temperatures do not significantly affect the current densities at lower applied cell potentials, however at higher potential cells the effect of temperature becomes more obvious [13].

To improve the electroplating process, a new design of electrochemical reactor has been developed. It consists of three compartments which allow parallel silver electroplating process (Figure 4). This design would improve the observed electrochemical parameters number 3, 4, 5, and 6 (c.f. Table 1) as it ensures the uniform current density distribution, the larger area of anode, and the stability of electrodes distance and position.
5. Conclusion
A new formulation of silver electrolyte with low cyanide concentration has been developed. The electrolyte composed of AgNO$_3$ and KCN with a ratio of 5:39 were chosen for achieving more sustainable decorative silver electroplating. A range of applied potentials between -2.2 and -2.8 V was determined for silver electrodeposition using the chosen electrolyte. Applied current densities corresponding to the applied potential are between -2 mA/cm$^2$ and 7 mA/cm$^2$. A new geometry of an electrochemical cell for the silver electrodeposition has been designed which promises the uniform current density distribution, the larger area of an anode, and the stability of electrodes distance and position as well as parallel use of the three compartments.

References
[1] Mawadah, A. 2008. Thesis, Program Studi Fisika, Fakultas Sains dan Teknologi, Universitas Islam Negeri Syarif Hidayatullah, Jakarta. Online access on http://repository.uinjkt.ac.id/dspace/bitstream/123456789/15695/2/ADE%20MAWADAH-FST.pdf
[2] Istiyono, E., R Yosi Aprian Sari, and Banu Setyo Adi, 2008, Inoteks, Volume 12 No. 2. online access (27/04/2014): http://staff.uny.ac.id/sites/default/files/132048515/6_Inoteks_Elektroplating.pdf
[3] Ivone De Carlo, 2012. Dinamika Kerajinan dan Batik, Vol. 32, No. 2, Desember 2012
[4] Maksum, F, 2013, Manado Tribun News. accessed online 31 Maret 2018 on http://manado.tribunnews.com/2013/08/27/bahaya-sianida-bagi-manusia-dan-lingkungan
[5] BLH Propinsi DI Yogyakarta. 2014. Laporan tahunan 2014. Accessed online 31 Maret 2018 on https://blh.jogjaprov.go.id/po-content/uploads/Laporan-Tahunan-2014.pdf
[6] Lies Susilaning Sri, Hastuti .2012. Seminar Nasional Teknik Kimia Soebardjo Brotohardjono IX, 21 Juni 2012, Surabaya. accessed online (27/04/2014) on

Figure 4. Schematic diagram of the new electrochemical cell (a) top view and (b) side view (cross sectional view)
http://eprints.upnjatim.ac.id/4147/1/C3.pdf

[7] Widayatno, T. and Hamid. 2016. Proceeding of Simposium Nasional RAPI XV – 2016 FT UMS, Surakarta, Indonesia.

[8] Schlesinger, M. and Paunovic, M., (2010), Modern Electroplating, 5th Edition, p. 131-138, Electrochemical Society Series, John Wiley and Sons, Inc. New York

[9] Liu, A., Ren, X., An, M., Zhang, J., Peixia Yang, Bo Wang, Yongming Zhu & Chong Wang. 2014. SCIENTIFIC REPORTS 4 : 3837 DOI: 10.1038/srep03837

[10] Widayatno, T. 2016. ARPN Journal of Engineering and Applied Sciences 11 (8), 5183 - 5189

[11] Bard, A. J. and Faulkner, L. R., (2001) Electrochemical Methods: Fundamentals and Applications, 2nd edition, 22 – 43, John Wiley and Sons, Inc.

[12] Widayatno, T., Hamid, Ibnu Ari Swasemba, dan Miftah Khairi Zufron, 2015. Simposium Nasional RAPI XIV - 2015 FT UMS

[13] Stern,M. And A.L.Geary. 1957. Electrochemical Polarization, J. Electrochem. Soc. 1957 volume 104, issue 1, 56-63. doi: 10.1149/1.2428496

Acknowledgments
Research funding from Ministry of Research technology and Higher Education through the scheme of Hibah Bersaing in the year of 2015-2016 is acknowledged by authors.