Electrowinning of Silver from Non-circulated Silver Nitrate Electrolyte using Graphite Electrode Recovered from Spent Zinc Carbon Batteries as Anode*

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Abstract

The electrowinning of silver from non-circulated aqueous silver nitrate electrolytic bath was investigated using cylindrical graphite rods recovered from spent zinc-carbon batteries (TigerHead Brand, Guangzhou-China) as anode and a slab of ultrapure silver metal as cathode. The effects of current density and temperature on product quality, current efficiency, and specific energy consumption were also investigated at voltages ranging from 1.2 to 2.5 V. Visual examination of electrodeposited product at the cathode was combined with analysis of the cathodic product by X-Ray Diffraction (XRD) and Scanning Electron Microscopy-Energy Dispersive X-Ray Spectroscopy (SEM/EDS), followed by measurement of current efficiency and specific energy consumption. The results indicated that graphite rods recovered from spent zinc-carbon batteries are effective at functioning as anodes for the electrowinning of silver from non-circulated nitrate baths, even at room temperatures. Increasing the current density resulted in an increase in current efficiency, increase in energy consumption and deterioration in electrodeposited product quality, evidenced by the formation of dendrites. Utilisation of voltages above 2.0 V resulted in physical deterioration of the cylindrical graphite at the anode. Analysis by XRD revealed distinct and well-defined peaks of silver metal with minor impurities at high current densities. Finally, high concentrations of silver metal (above 99.0 wt%) were revealed by SEM/EDS with minor contamination of aluminium and gold at an applied potential of 1.8 V and silver ion concentration of 30.0 g/l.

Keywords: Electrowinning; Current Density; Current Efficiency; Energy Consumption; Dendrites

1 Introduction

Rapid growth in the electrical and electronic industry has resulted in increased demand for the precious groups of metals. Silver is an extremely important metal owing to its various useful properties and its economic value. Silver is used in four major areas, including the industrial, photography, jewellery and coin sectors.

Industrially, silver finds application in the preparation of utensils, formation of ceramics and polishing/manufacturing of mirrors (Afzal et al., 2016). Moreover, silver is used for monetary, decorative and jewellery purposes and in X-ray photography, medicine (Ag₂O, AgNO₃, Argyrols), bactericide, antiseptic, oil and water purifier (Ag₃PO₄) (Afzal et al., 2016). Silver is also applied as a conductor and corrosion resistant metal in tableware, electric components, circuits, stable electrodes, medals and batteries (Cox et al., 2005; Harper and Siegel, 2003; Kazmi and Abbas, 2001). The global demand for silver has been escalating progressively as a result of the increasing consumption of electronic and electrical equipment (EEE) (Vats and Singh, 2015; Cayumil et al., 2016).

Some zinc-carbon batteries are constructed with cylindrical graphite rods as cathode material (Dankwah *et al.*, 2015). These primary cells are non-

rechargeable and, accordingly, are used and discarded after reaching their end of life (Dankwah et al., 2015). Recent power fluctuations in Ghana have resulted in the generation of millions of endof-life zinc-carbon batteries that are indiscriminately disposed of into the environment (Dankwah et al., 2015). In an attempt to address the menace posed by this category of the waste stream, Dankwah et al. (2015) synthesised spherical samples of spinel ZnMn₂O₄ from samples of spent zinc-carbon batteries using end-of-life polypropylene as reductant. Pattaweepaiboon et al. (2024)investigated the upcycling of electrode materials from spent zinc-carbon/alkaline batteries into rechargeable lithium-ion battery application. Gromov et al. (2004) studied electrolysis of silver in 84-95 wt % sulphuric acid with addition of 40 g/l of silver sulphate at electrolyte temperature of 40 °C. They performed a semi-commercial test of the method for electrochemical recovery of silver from silver coatings on copper, brass, aluminium, and steel. Metallic silver with 99.9 wt % purity was obtained with average recovery degree of 99.0 %. Afzal et al. (2016) investigated the electrogravimetric recovery of silver from aqueous solutions and its precursors using stainless steel anode and aluminium cathode. They reported a maximum recovery of 96.5 wt% silver. Accordingly, in this research, the electrowinning of silver from non-circulated silver nitrate solution was

investigated using cylindrical graphite rods (recovered from spent zinc-carbon cells) as anode.

2 Materials and Methods Used

2.1 Materials

Cylindrical samples of graphite rods (Fig. 1) were recovered from spent zinc-carbon batteries (TigerHead Brand, Guangzhou-China). These were used as the anode material for the electrolytic cell (Fig. 2), which consists of cylindrical beaker (Pyrex) of volume 0.5 l. A sample of silver spoon (Fig. 3) was used as the cathode for the electrodeposited silver metal.



Fig. 1 Samples of Graphite Rods recovered from Spent Zinc Carbon Batteries



Fig. 2 Set-up of the Electrowinning Bath for the Experimental Investigation

2.2 Electrolyte Preparation

The electrolytic solution was prepared at concentrations of 20, 25, and 30 g/l Ag⁺ by dissolving appropriate amounts of AgNO₃ (> 99% purity, procured from Sigma Aldrich) in doubledistilled water. Power supply to the electrolytic bath was through a YiHua 305 precision adjustable 30V-5A variable regulated DC Power Supply.



Fig. 3 Sample of Silver Spoon utilised as Cathode for the Electrolytic Cell

2.3 Methods Used

This investigation adopted a non-circulated electrolytic approach for the electrodeposition of metallic silver at the cathode in order to avoid the mass transport limitations. Afzal et al. (2016) observed that stirring causes convection of ions in the direction of working electrode and suggested that optimisation of the stirring was essential for attaining smooth and maximum recovery of metals. They proposed an optimum stirring rate of 400 rpm for the attainment of metallic, shinning and scratchable silver electrodeposit at the cathode. Mi-Sook et al. (2006) and Clinio (2006) reported an optimum stirring rate of 600 rpm for the electrodeposition of silver and platinum group metals (PGM), respectively. However, this investigation sought to investigate the possibility of producing metallic silver that is both shiny and scratchable, in the absence of stirring.

The electrowinning process was conducted at applied voltages of 1.2, 1.5, 1.8, 2.0, 2.2 and 2.5 V for 30, 45, 60, 75 and 90 min. The current density for each electrolytic process was calculated using the current selected by the DC power supply equipment at each applied voltage, based on the conductivity of the electrolyte. For each set of parameters, the mass of silver electrodeposited at the cathode was calculated from the difference between the mass of cathode before and after the electrowinning process. The current efficiency (CE, %) and the specific energy consumption (SEC, kWh/kg) for each experimental run were then calculated from equations (1) and (2), respectively:

$$C.E. = \frac{m_a}{m_t} \times 100\% \tag{1}$$

$$SEC = \frac{26.8 \times n \times U}{S \times M_{Ag}} \, kWh/kg \tag{2}$$

where

ma	=	actual mass deposited at the
		cathode
mt	=	theoretical mass (in accordance
		with Faraday's law)
n	=	number of electrons
U	=	applied cell potential (V)
S	=	current efficiency (C.E./100)
M_{Ag}	=	atomic mass of silver
-		

The effect of applied cell potential on the graphite anode and on the nature of metal electrodeposited at the cathode as well as on the current efficiency and specific energy consumption was assessed.



The electrodeposited metal at the cathode was analysed by X-ray diffraction (Rigaku MiniFlex 600C Benchtop XRD) analyser and scanning electron microscopy SEM (ZEISS EVO MA 15) coupled with energy dispersive X-Ray spectroscopy (EDS) analyser.

3 Results and Discussion

3.1 Nature of Metal Electrodeposited at the Cathode

Fig. 4 illustrates the nature of metal electrodeposited at the cathode at applied cell potential of 1.8 V. It shows a well compacted material with virtually no signs of dendrite formation.





Fig. 4 Sample of Silver Metal Electrodeposited at the Cathode at an applied Potential of 1.8 V

At an applied cell potential of 2.5 V there was evidence of dendrite formation in the electrodeposited metal along with physical degradation of the graphite anode as illustrated in Fig. 5.



Fig. 5 Illustration of Dendrite Formation and Anode Degradation at High Current Densities and Applied Potential of 2.5 V

The results in this investigation demonstrate that, even without stirring, metallic, shiny and scratchable silver can be electrodeposited at the cathode at appropriate applied potentials, as indicated in Fig. 4. These results are comparable to those reported by Gromov *et al.* (2006), Clinio (2006) and Afzal *et al.* (2016). It is apparent from this investigation that the optimum applied potential for silver electrowinning at room temperature is 1.8 V.

Fig. 6 shows the nature of metals electrodeposited at other electrodes.







Fig. 6 Nature of Silver Metal Electrodeposited at the Cathode at an applied Potential of a) 1.2 V, b) 1.5 V and c) 2.0 V

3.2 Analyses of Electrodeposited Metal

3.2.1 SEM-EDS Analyses

SEM micrographs of the electrodeposited silver metals in Fig. 4 and Fig. 5 are shown in Fig. 7 and Fig. 8, respectively. Fig. 7 shows the formation of irregularly shaped particles along with minor regions of dendrites to the extreme left. However, Fig. 8 indicates the reverse scenario where the whole morphology is dominated by several regions of metallic silver dendrites.



Fig. 7 SEM Micrograph of Electrodeposited Metal at the Cathode



Fig. 8 SEM Micrograph of Electrodeposited Dendritic Metal at Applied Potential of 2.5 V

Details of point-by-point surface analyses of the micrograph are discussed in Fig. 9-Fig. 13. Fig. 9 shows that the region of analysis (2778) is dominated by silver (99.08 wt%) with minor amounts of aluminium (0.92 wt%). The situation appears to be not different in Fig. 10 for Region 2779, with the compositions of 98.26 wt% Ag, 1.02 wt% Al and 0.72 wt% Au. It is clear from the forgoing discussions that the purity of the electrodeposited metal at the cathode is very high, when cylindrical graphite electrodes (recovered from spent zinc-carbon batteries) are used as anodes for silver electrowinning from aqueous silver nitrate electrolytic bath. In particular, we notice a metal purity of 100 wt% Ag at Regions 2780 and 2781 as illustrated in Fig. 11 and Fig. 12, respectively. With Region 2882 displaying a composition of 99.28 wt% Ag and 0.72 wt% Al, it is clear that the average purity of the electrodeposited metal at the cathode is higher than 99 wt% Ag.





Ag	99.08	96.43
SUM	100	100

Fig. 9 SEM/EDS of the Electrodeposited Metal at the Cathode (Region 2778)



Element	Mass [%]	Atom [%]
Al	1.02	3.98
Ag	98.26	95.64
Au	0.72	0.38
SUM	100	100

Fig. 10 SEM/EDS of Electrodeposited Metal at the Cathode (Region 2779)





Element	Mass [%]	Atom [%]
Ag	100	100
SUM	100	100

Fig. 11 SEM/EDS of the Deposited Silver Metal (Region 2780)





Element	Mass [%]	Atom [%]
Ag	100	100
SUM	100	100

Fig. 12 SEM/EDS of the Electrodeposited Silver Metal (Region 2781)



Element	Mass [%]	Atom [%]
Al	0.72	2.80
Ag	99.28	97.20
SUM	100	100

Fig. 13 SEM/EDS of the Electrodeposited Silver Metal (Region 2782)

3.2.2 Line Scan Analyses

Line scan analyses of the micrographs are shown in Fig 14 and 15. Analysis of the elements along the line in Fig. 14 (0-8000 μ m apart) indicates that the electrodeposited metal is once again dominated by silver and some aluminium and oxygen. The situation is not very different from Fig. 15, although oxygen is absent in this case.



Fig. 14 Line Scan Analysis of the Electrodeposited Silver Metal (Line 1)





Fig. 15 Line Scan Analysis of the Electrodeposited Silver Metal (Line 2)

Ultrapure silver metal is utilised in a range of applications as listed under Section 1, particularly as a contact material in all areas of electrical engineering (Ivanovic *et al.*, 2012). Its utilisation as a contact material is based largely on its nobility and consequently, its ability to preserve contact resistance (Ivanovic *et al.*, 2012). Obviously, the presence of impurity elements like Al, O, etc., could affect this aspect of its utilisation.

3.2.3 X-Ray Diffraction Analyses of Electrodeposited Metal

Results of XRD analysis of the electrodeposited metal are shown in Fig. 16. Sharp and well-defined peaks of silver metal can be seen from the figure with minor contamination from the alloy GaHoSn₂. The electrodeposited metal (silver-3C, syn) crystallises out as a *face-centred-cubic* (*fcc*) structure along the crystallographic axes (111), (200), (220), (311), and (222) at 20 values of 38.373° , 44.507°, 64.578°, 77.548°, and 81.705° , respectively. The lattice parameter (a = b = c) of the crystallised structure is approximately 4.07236 Å.



Fig. 16 XRD Analysis of the Deposited Silver Metal

3.3 Effect of Processing Parameters

3.3.1 Effect of Concentration of Silver Ions [Ag⁺] on Current Efficiency



The effect of concentration of silver ions on the current efficiency of the electrowinning process is shown in Fig. 17. An increase in the concentration of silver ions from 20 g/l to 30 g/l results in an increase in the current efficiency of the process from 94.48% to 96.36%. An increase in the concentration of silver ions results in the release of more mobile Ag^+ ions in solution. This will result in a more conducting electrolyte.



Fig. 17 Effect of Concentration of Silver Ions on the Current Efficiency of the Process

The results compare favourably with those of Gromov *et al.*, (2004) who utilised silver ion concentration of 27.7 g/l, and Patcharawit *et al.*, (2023), who utilised concentrations 17.71 g/l and 33.36 g/l. These results are, however, superior to the conventional Merrill-Crowe Process for gold and silver recovery from cyanide solutions, where lower recovery and lower metal purity were reported by Patcharawit *et al.*, (2023).

3.3.2 Effect of Applied Cell Potential on Current Efficiency

The silver electrowinning process was conducted by varying cell potentials from 1.2 V to 2.5 V. The effect of applied cell potential on the current efficiency of the process is shown in Fig. 18. It is clear from Fig. 18 that increasing the applied cell potential from 1.2 V to 2.5 V will lead to increase in the current efficiency of the electrowinning process from 89.77% to 96.89%. However, increasing the applied potential beyond 2.0 V resulted in physical degradation of the graphite anodes, as elucidated in Fig. 19 for an electrolytic process at applied potentials of 1.5 V and 2.5 V. Degradation of the graphite electrode results in shrinking of its thickness at the sections that were immersed in the electrolyte.



Fig. 18 Effect of Applied Potential on Current Efficiency of the Process



Fig. 19 Nature of Graphite Anode after Electrowinning at Applied Potential of a) 1.5 V and b) 2.5 V

In Fig. 20, we notice a black suspension of fine carbon particles in an otherwise colourless $AgNO_3$ electrolyte after electrowinning at an applied potential of 2.5 V.





Lebed *et al.* (2013) observed the formation of insoluble anodic products and attributed it to the oxidation of Ag^+ to Ag^{2+} , which paints the anolyte black at applied potentials beyond 1.5 V. The anode material was made of gold. They were able to demonstrate that formation of an anode deposit

during silver electrowinning was not influenced by the nature (AgNO₃, Ag₂SO₄) and concentration of the electrolyte (50-170 g/L), or by the composition of the insoluble anode. Much lower concentrations of electrolyte were utilised for the current investigation and we are unable to confirm the formation of the anode deposit at all applied potentials. Accordingly, the black colouration of the electrolyte is attributed exclusively to the degradation of the graphite electrode at potentials in excess of 2.0 V.

3.3.3 Effect of Current Density on Current Efficiency and Specific Energy Consumption

Fig. 21 illustrates the effect of cathodic current density on the current efficiency and the specific energy consumption during the electrowinning of silver from nitrate solutions. It is apparent from Fig. 21 that an increase in cathodic current density results in an increase in both current efficiency and specific energy consumption. Optimisation of the current density of the electrowinning process is therefore important.



Fig. 21 Effect of Current Density on Current Efficiency and Specific Energy Consumption of the Process

3.3.4 Effect of Concentration of Silver Ions [Ag⁺] on Specific Energy Consumption

The variation of specific energy consumption as a function of the concentration of silver ions (Ag^+) in the electrolyte is shown in Fig. 22. Clearly, running the electrowinning process at higher concentrations of Ag^+ is beneficial as it decreases the specific energy consumption of the process. Combining this with the observed effect on current efficiency (as illustrated in Fig. 17), better outcomes are expected for optimised current density and higher concentrations of Ag^+ in the electrolyte. However, the process works at practically all concentrations of silver.





4 Conclusions and Recommendations

The electrowinning of silver from aqueous silver nitrate electrolytic bath was investigated in this research at varying applied cell potential, current density, and concentration of silver ions $[Ag^+]$ in the electrolyte. Major findings of the investigation are summarised as follows:

- i. Graphite rods recovered from spent zinc carbon batteries are effective at functioning as anodes for the electrowinning of silver from noncirculated nitrate baths, even at room temperatures.
- Increasing the current density resulted in an increase in current efficiency, increase in energy consumption and deterioration in electrodeposited product quality, evidenced by the formation of dendrites.
- Utilisation of voltages above 2.0 V resulted in physical deterioration of the cylindrical graphite at the anode.
- iv. Increasing the concentration of silver ions [Ag⁺] from 20 g/l to 30 g/l resulted in an improvement in the current efficiency from 94.5% to 96.4% while the specific energy consumption decreased from 0335 kWh/kg to 0.323 kWh/kg, respectively.
- Analysis by XRD revealed distinct and well defined peaks of silver metal that crystallised out in a face-centred cubic (fcc) structure.
- vi. High concentrations of silver metal (above 99.0 wt% Ag) were revealed by SEM/EDS with minor contamination of aluminium and gold.



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