

Short communication

Hydrometallurgical recovery of silver from waste silver oxide button cells

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Abstract

In recent years, recycling of household batteries has attracted much attention mainly with respect to environmental aspects in addition to the savings. Small silver oxide primary cells used in electric watches become a waste after their life is over. Recycling procedures are needed to prevent any environmental impact from these wastes and to recover the value inherent in the scrap. Smelting and electrolytic methods are discussed for silver recovery from this battery waste. Acid leaching of waste batteries and precipitation of silver as silver chloride followed by smelting at 1000 °C yields a silver recovery of about 83%. An electrolytic route is studied as an alternative to the smelting operation and involves the electrodeposition of silver with higher purity from a silver thiosulfate complex prepared from silver chloride. The electrolysis is potentiostatically controlled at a potential of –0.400 to –0.600 V (SCE) for avoiding side-reactions such as the sulfiding of silver. Although recovery methods have been identified in principle, their suitability for mixed small battery waste and economic factors have yet to be demonstrated.

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Keywords: Waste silver oxide button cell; Leaching; Silver chloride; Smelting; Potentiostatic electrodeposition; Silver

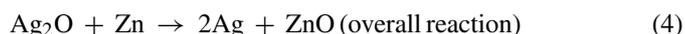
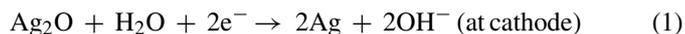
1. Introduction

Primary silver oxide–zinc button cells after use in wrist watches, hearing aids, microlamps, light meters [1], etc. become a waste material that causes environmental concern. The watch manufacturers also face problems in disposing these batteries when they become inactive on long storage. The recovery of silver is an attractive proposition as it would partly meet the demand for the metal in countries such as India. The recovery of silver requires collection, sorting and leaching to get the metal values in solution. The quartz watch industries use silver oxide button cells for their products, and although this button cell constitutes only 3% of the battery market, nearly 1000 million of used button cells are generated annually in India and offer scope for a recovery of around 25 t of silver. Since retailers of these batteries retain spent ones a good amount of used cells can be collected after periodically visiting such shops.

The model SR626SW cell is 6 mm in diameter, 2 mm in height, and weighs about 0.4000 g. The electrodes are separated by a semipermeable ion exchange membrane and the electrolyte is sodium hydroxide. The negative plate (cathode) is made of sin-

tered fine silver oxide (Ag₂O) powder, while the positive plate (anode) is composed of activated zinc with additives such as mercury to avoid corrosion.

The mean composition of the silver oxide button cells is given elsewhere [2]. After battery discharge, the silver oxide is reduced to silver and the zinc is oxidized to zinc oxide, as shown in the Eqs. (1)–(3). The overall reaction is given by Eq. (4).



Various processes have been developed for recycling the spent batteries or, in some cases, for safe disposal. Some processes treat only used button cells while others involve treatment of bulk mixtures containing small cells of different battery chemistries. The used silver oxide batteries can quickly be sorted out by size. Unfortunately, however there is no correlation between the size and the composition of these batteries.

The Mercury Refining Company in the USA accepts most household batteries and these are hand sorted upon arrival. The silver oxide button cells are retorted for mercury reclamation [3].

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The mercury is added to prevent the production of hydrogen that could lead to leakage and shortened shelf-life. Powder from the silver oxide cells is screened and sent to a precious metal refiner. The remaining material is dispatched to a hazardous waste land fill. The spent silver oxide batteries are also processed by smelting in which the impurities are removed as slag to leave a residue for silver recovery [4]. In another method, spent batteries are disassembled into anode and cathode parts, and the valuable materials are recovered [5]. A method based on a cementation technique has been reported [6] where silver is recovered by the addition of copper sulfate solution after nitric acid leaching. All these methods suffer the drawbacks of: (i) emission of toxic gases, which damage the environment; (ii) higher energy consumption; (iii) loss of active materials; (iv) difficulty in dismantling the components of small cells; (v) low purity of the silver metal reclaimed.

This study describes laboratory treatment of waste silver oxide button cells for the recovery of silver metal, by both smelting and electrolytic routes. An attempt is made to promote the electrodeposition of silver potentiostatically from a silver-thiosulfate complex that is prepared from silver chloride to avoid side reactions.

2. Experimental

2.1. Characterization of active material from spent cells

Spent silver oxide button cells of the maxell type and specification SR626SW were used in this investigation. The cells were cut open manually and the active material was collected, dried and powdered. The active material was characterized by X-ray diffraction phase analysis.

2.2. Analysis of waste silver oxide button cells by nitric acid leaching

The active material collected from scrap button cells of weight 10.3842 g was leached with nitric acid solution of concentration ranging from 50 to 200 g l⁻¹ in a closed glass reactor of 500 ml capacity. Stirring was provided with a variable speed mechanical stirrer and the temperature was maintained at 30–75 °C. The solid:liquid ratio was kept at 1:3.4 during leaching. The concentration of silver and the impurities were determined in the leached solution both by chemically means and also by atomic absorption spectrophotometry.

2.3. Silver separation

For the precipitation of silver as silver chloride, 20.2 g of waste button cells was leached in nitric acid. The leached solution was then boiled with a little active charcoal for removing any organic material arising from the small rubber gasket present in the cell and filtered. The silver present in the leach solution was separated as insoluble silver chloride precipitate by adding a 0–15 wt.% stoichiometric excess of 25% sodium chloride solution in a slight acid medium.

2.4. Silver recovery by smelting

A 30 g sample of silver chloride was smelted with sodium carbonate flux at 1000 °C in a clay crucible to obtain silver metal. The silver separated from the slag in the crucible was immediately poured into a graphite mould.

2.5. Silver recovery by electrolysis

The silver thiosulfate complex electrolyte with 12.5 g l⁻¹ silver was prepared by dissolving 6.644 g of silver chloride in 400 ml of 240 g l⁻¹ sodium thiosulfate solution. This complex catholyte was electrolyzed in a poly vinyl chloride cylindrical cell divided by a cation exchange membrane [7]. A rotating cylindrical electrode (RCE) made up of stainless steel and rotated at 400 rpm was used as the cathode. Its potential was controlled between -0.400 and -0.750 V using a potentiostat (PAR model: 371, EG&G with 10 A/10 V capacity). The anolyte was 1 M sodium hydroxide solution and a cylindrical nickel electrode was used as the anode. Current, potential and the cell voltage were monitored by means of a digital multimeter. Experiments were carried out at room temperature. The rotation speed of the RCE was monitored with a hand tachometer. The silver in the catholyte was analyzed periodically by atomic absorption spectrophotometry (AAS). A saturated calomel electrode (SCE) was used as the reference electrode. All potentials are quoted with respect to this reference electrode unless otherwise stated.

2.6. Characterization of silver metal

The silver metal recovered was analyzed chemically for its purity. It was also characterized both by X-ray diffraction phase analysis and scanning electron microscopy.

3. Results and discussion

3.1. Silver oxide button cell

A cross-sectional view of the waste silver oxide–zinc button cell is shown in Fig. 1. The overall composition of a waste silver oxide button cell is shown in Table 1. A typical X-ray diffraction

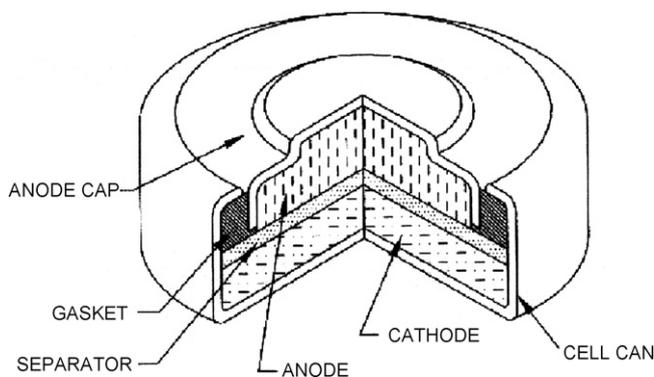


Fig. 1. Cross-sectional view of silver oxide-zinc button cell.

Table 1
Composition of waste silver oxide button cell

Components	Weight (%)
Zinc	10.4
Silver	30.3
Steel case	42.4
Mercury	0.8
NaOH	7.1
Paper/plastic	6.0
Water	2.6
Remainder	0.4

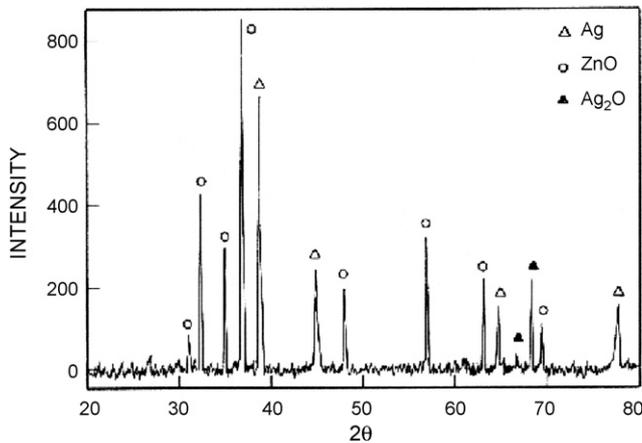


Fig. 2. X-ray diffraction pattern of active mass of waste silver oxide button cell.

pattern of the active mass of the waste silver oxide button cell is given in Fig. 2. Silver is present mostly in the form of metal with a little Ag_2O , while zinc is present as ZnO . It is observed that the relative intensities of the X-ray diffraction peaks for the presence of silver, silver oxide and zinc oxide in the active mass are found to match well with their standard values.

3.2. Flowchart for silver recovery

The flowchart for the recovery of silver from waste silver oxide cells is shown in Fig. 3. It includes the unit operations followed in the two different routes, namely, smelting and electrolysis. Acid leaching of the spent cells and precipitation of silver as silver chloride in the leach solution are common steps for both routes. Silver chloride can be directly smelted to metallic silver, or it can form a silver thiosulfate complex employing sodium thiosulfate solution that on electrolysis produces silver metal.

3.3. Nitric acid leaching

The effect of nitric acid concentration on the leaching of waste button cells for the extraction of silver is shown in Fig. 4. Increase in nitric acid concentration is found to improve the leaching of silver up to 200 g l^{-1} . At low concentrations of nitric acid, the leaching efficiency of silver is found to decrease due to the formation of its hydroxides with increasing pH. Hence, the optimum nitric acid concentration is fixed at 200 g l^{-1} .

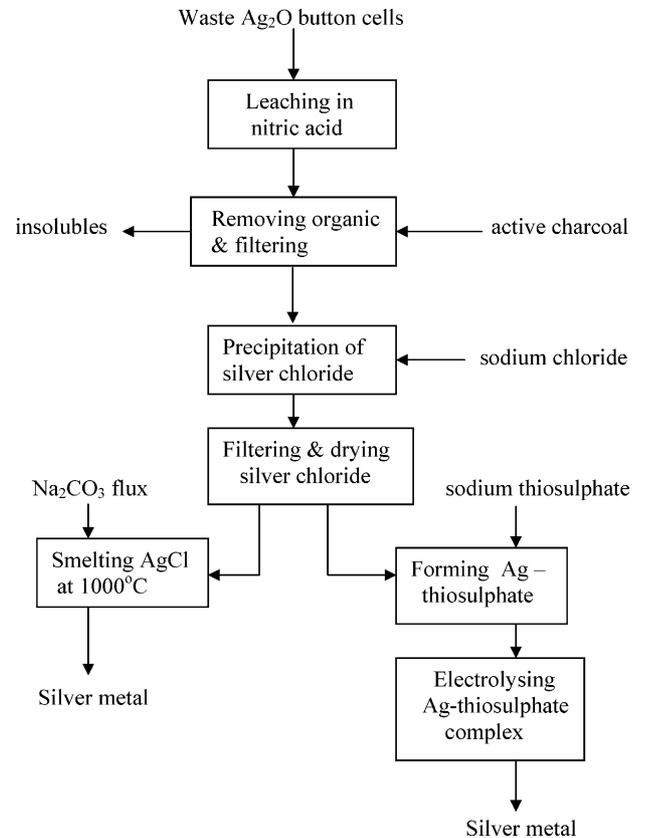


Fig. 3. Flowchart for silver recovery from waste silver oxide button cells.

The effect of temperature on the acid leaching for the recovery of silver from the waste button cells is shown in Fig. 5. The extraction of silver is found to increase with rise in temperature and is only marginal beyond $50\text{ }^\circ\text{C}$.

3.4. Precipitation of silver chloride

The addition of sodium chloride solution is found to be effective in separating silver selectively from the other metal values

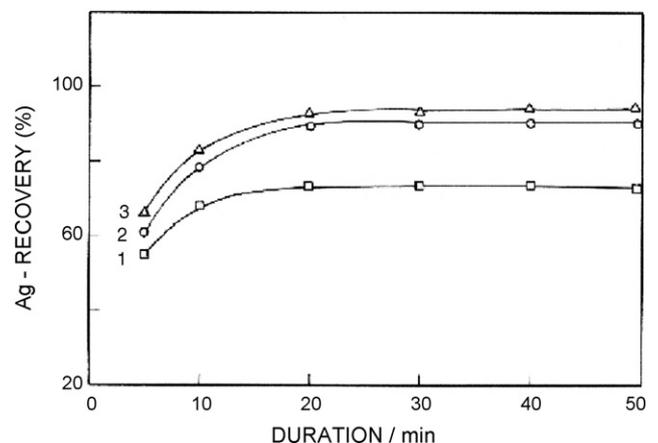


Fig. 4. Effect of HNO_3 concentration on silver oxide button cell leaching at: (1) 100 g l^{-1} , (2) 200 g l^{-1} , (3) 250 g l^{-1} .

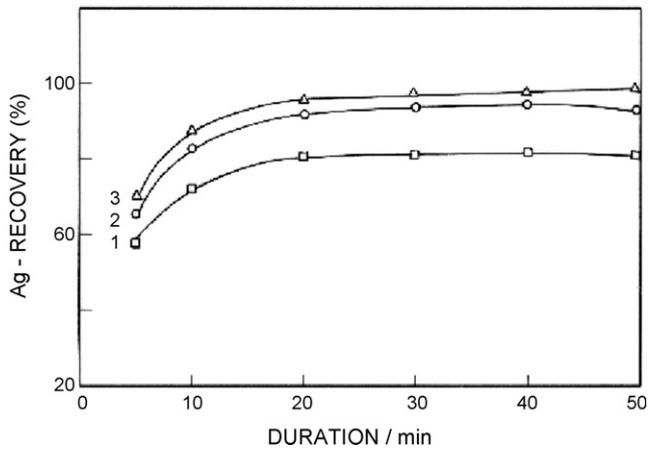


Fig. 5. Effect of temperature on leaching of silver oxide button cell with $200 \text{ g l}^{-1} \text{ HNO}_3$ at: (1) 30°C , (2) 50°C , (3) 70°C .

present in the leachate as silver chloride precipitate shown by:

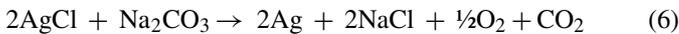


The effect of a stoichiometric excess of sodium chloride solution on the precipitation of silver as silver chloride from the leach solution is shown in Table 2. The silver present in the leach solution could almost all be recovered (99.6%) as silver chloride precipitate on the addition of a 5 wt.% stoichiometric excess of 25% sodium chloride solution. At a higher stoichiometric excess of sodium chloride, the silver recovery is found to be low due to the formation of silver chloride precipitate and its redissolution as a soluble silver chloride complex.

The X-ray diffraction pattern of the silver chloride separated from the leach solution is found to be in good agreement with the diffraction lines of standard silver chloride Fig. 6. This indicates that the precipitate consists only of pure silver chloride.

3.5. Smelting of silver chloride

Table 3 shows the effect of the amount of sodium carbonate flux on the recovery of silver metal from silver chloride by smelting according to:



The addition of 50 wt.% of sodium carbonate flux is found to be beneficial in increasing the recovery of silver to the extent of 83%. Further increase in the addition of sodium carbonate flux affects the recovery as the silver separated tends to mix with the slag in the form of very fine droplets. The X-ray diffraction pattern of the smelted silver is given in Fig. 7(a) and is found

Table 2
Effect of NaCl on AgCl precipitate formation

Stoichiometric excess of sodium chloride (wt.%)	Silver recovery as silver chloride (%)
0	90.0
5	99.6
10	91.5
15	89.6

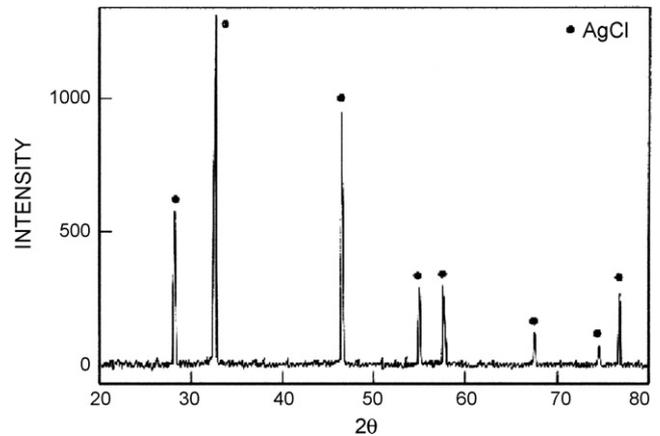


Fig. 6. X-ray diffraction of silver chloride precipitate.

Table 3
Effect of Na_2CO_3 flux on AgCl for silver recovery by smelting

Addition of sodium carbonate (total wt.%)	Silver recovery (%)
10	70.0
20	75.4
50	83.1
80	83.3
100	83.5

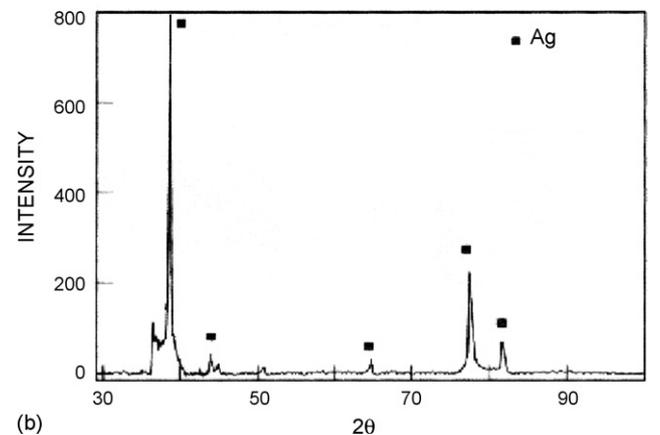
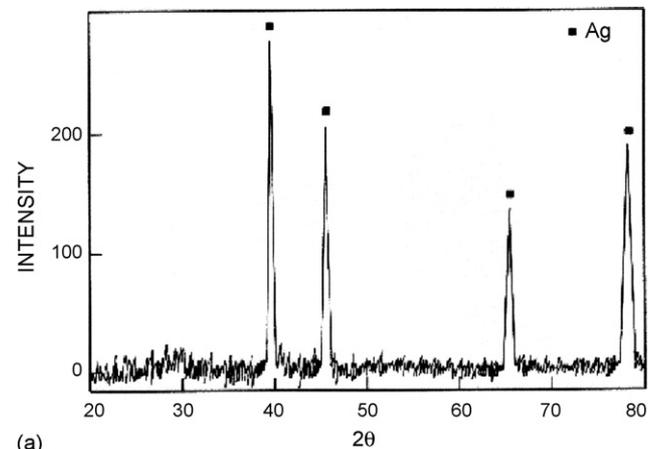


Fig. 7. X-ray diffraction of silver by: (a) smelting of 30 g of AgCl with 30 g of Na_2CO_3 at 1000°C , (b) electrowinning from 12.5 g l^{-1} silver as silver thiosulfate at -0.600 V cathode potential.

Table 4
Effect of cathode potential on silver recovery

Cathode potential (–V)	Duration (min)	Current density (AM ^{–2})	Current efficiency (%)	Silver deposit nature	Purity of silver (%)
0.400	120	51–14	95.3	Shiny foil	99.95
0.500	110	75–10	86.8	More foil + powder	99.89
0.600	50	124–97	79.5	Grey powder	99.81
0.750	32	208–160	67.9	Dark grey powder	96.72

to match well with the diffraction lines of standard silver. The dispersion of silver in the slag and the diffusion of silver metal particles into the pores of the clay crucible employed are major obstacles in achieving a high recovery of silver in the smelting process. The purity of the silver is listed in Table 5. Loss of silver by smelting of purified silver chloride produced from different sources has been reported [8] together with discussion of a purification step for the silver chloride.

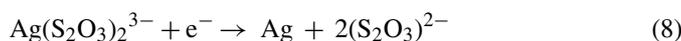
3.6. Silver electrowinning

The electrolyte for the electrowinning of silver is silver-thiosulfate complex which is prepared from the silver chloride as follows:

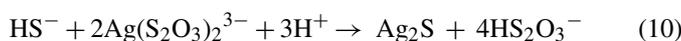


Even though 1 mol of silver chloride reacts with 2 mol of sodium thiosulfate solution for the dissolution of silver chloride into the soluble silver-thiosulfate complex, the sodium thiosulfate concentration should be present in excess in order to react with silver ions, and ensure maximum performance and to obtain complete dissolution of silver chloride. The silver chloride:sodium thiosulfate weight ratio is kept at 0.05:1.

The electrolytic recovery of silver from a sodium thiosulfate bath offers advantages over other techniques of silver recovery in that the silver obtained is relatively pure, clean and, easier for re-use and resale. In addition, the silver-depleted liquor may be recycled for the subsequent dissolution of silver chloride. Also, it can be adapted to a wide range of silver concentrations by means of adequate process control. The rate of reaction is relatively easy to control [9]. The silver-thiosulfate complex is electrolysed to deposit silver at the cathode and evolve oxygen at the anode. The possible cathodic reactions are:



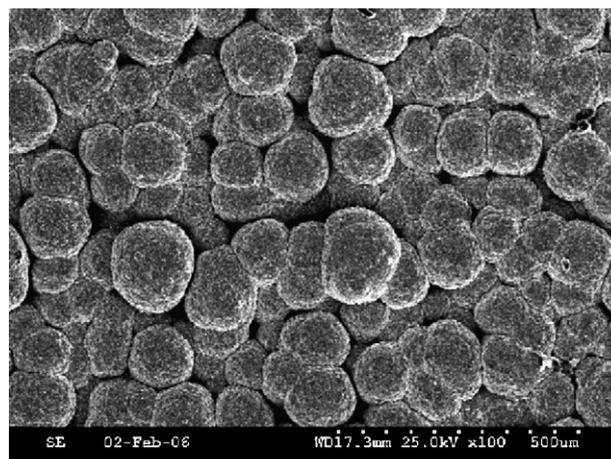
The precipitation of silver sulfide from the electrolyte is also possible by Eq. (10).



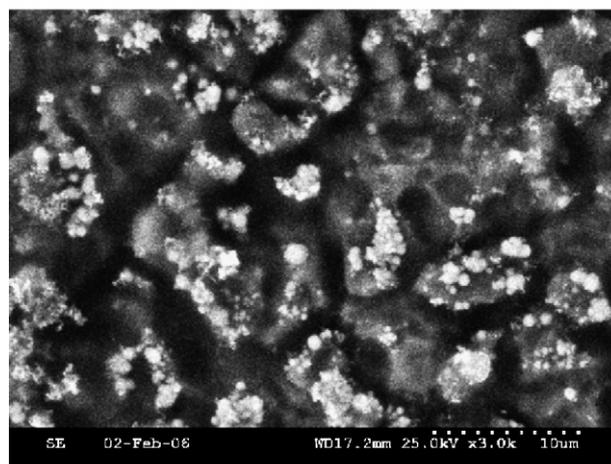
The control of cathode potential becomes necessary to avoid sulfiding. The minimum cathode potential at which silver will deposit is reported [10] to be –0.400 V. Silver can be deposited without any sulfiding up to a cathode potential of –0.600 V, above which sulfiding is likely to occur and thereby affect the purity of the silver deposit and the current efficiency.

The effect of cathode potential on silver recovery from the silver-thiosulfate complex solution in a divided cell is pre-

sented in Table 4. The current efficiency for the silver deposition decreases gradually from 95.3 to 67.9% when the cathode potential is changed from –0.400 to –0.750 V. The high current efficiency observed at low cathodic potentials is due to silver deposition only as shown by Eq. (8), while low current efficiency at high potentials is due to sulfiding via the side-reactions represented by Eqs. (9) and (10). The nature of the deposit and the purity of the silver metal obtained changes at higher cathodic potentials, i.e., the deposit transforms from shiny foils into dark grey powder. As the cathode potential increases so obviously will the current density with decrease in duration. The current is found, however, to decrease gradually during the electrodeposition of silver because the silver concentration in the electrolyte is depleted with time. The optimum time required for maxi-



(a)



(b)

Fig. 8. Scanning electron micrograph of silver by electrowinning from 12.5 g l^{–1} silver as silver thiosulfate at cathode potential of: (a) –0.600 V, (b) –0.750 V.

Table 5
Purity level of silver metal obtained by different routes

Element	Composition (%)	
	Smelting	Electrolysis
Silver	99.130	99.810
Iron	0.357	0.044
Zinc	0.152	0.047
Nickel	0.201	0.010
Mercury	0.004	0.001
Sulphur	–	0.088
Lead	0.156	–

imum recovery of silver at each cathode potential is also given in Table 4. It is found to decrease with increase in cathodic potential as the rate of deposition is obviously higher at enhanced current. On the other hand, the nature of silver deposit is a subject of concern at higher potentials where the silver deposit becomes powdery and dark grey in colour.

From this study, it is observed that silver recovered above -0.600 V will be contaminated with sulfide. The current efficiency for silver deposition at -0.600 V is 79.5% and the metal has 99.81% purity. Though lower cathode potentials give rise to higher current efficiency, the space-time yield is lower. The loss in current efficiency of silver during deposition may be attributed to occurrence of sulfiding as a side-reaction [11] and redissolution of metal via corrosion or anodic contact [12]. The X-ray diffraction pattern of the silver recovered at -0.600 V by electrowinning is presented in Fig. 7(b). The scanning electron micrograph given in Fig. 8(a) shows that the silver electrodeposited at -0.600 V cathode potential has a uniform grain size. A scanning electron micrograph of silver electrodeposit from the same complex at a cathode potential of -0.750 V is given in Fig. 8(b). It is observed the silver particles are capsulated by black silver sulfide layers due to sulfiding as a side-reaction in the electrodeposition process. The purity level of silver produced by electrolysis at -0.600 V is very high as shown in Table 5 and the inclusion of some sulfur may be a consequence of the employment of a thiosulfate bath.

For the treatment of large weights of waste silver oxide button cells for silver recovery, the smelting route is preferred but there will be a great loss of silver. In the treatment of spent button cells with low weights, however, the electrolytic method is definitely more suitable with minimum loss of silver.

4. Conclusions

The waste silver oxide button cells used in electric watches with silver contents of around 30 wt.% has been studied for the

recovery of silver metal by different routes, e.g., smelting and electrowinning. The separation of silver as silver chloride from the spent active material of the batteries is a common operation in both smelting and electro winning operations. Smelting of silver chloride obtained with a sodium carbonate flux at 1:1 weight ratio provides a quick recovery of silver, but with lower purity, and a marginal loss of the metal in the slag. Electrolysis of the silver thiosulfate complex prepared from the silver chloride yields silver metal with maximum purity of 99.81%. Rotation of the cathode for the enhanced mass transfer of silver in the electrolyte and control of its potential between -0.400 and -0.600 V (SCE) are required for efficient electrodeposition of silver by avoiding side-reactions such as the sulfiding of silver. X-ray diffraction and scanning electron microscopy studies throw much light on the purity and morphology of the silver deposit obtained in the electrowinning operation.

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