RECUPERAREA ARGINTULUI DIN DEŞEURI DE BATERII-BUTON CU OXID DE ARGINT - PARTEA I: CARACTERIZAREA MATERIALULUI ACTIV
RECOVERY OF SILVER FROM WASTE SILVER OXIDE BUTTON CELLS – PART I: CHARACTERIZATION OF ACTIVE MATERIAL

COSMINA CARATA, EUGENIU VASILE * , VALERIU-GABRIEL GHICA, MIRCEA-IONUŢ PETRESCU, GHEORGHE IACOB, MIHAI BUZATU

University POLITEHNICA of Bucharest, 313 Spl. Independenţei, Bucharest, Romania

Global silver mine production fell 2 percent in 2018, registering the third consecutive annual decline. Concurrently, metal demand is increasing; the demand for the photographic industry - the largest consumer - is increasing after the economic shock produced by the appearance of digital formats (Kodak - company under bankruptcy protection procedure between 2012 and 2013 announces increasing sales of films). Demand for contactors and conductors (15%), brazing alloys (7%), catalysts batteries (3%) also increases. Under these circumstances, the concerns to recover silver from all secondary sources become a necessity. Although the amount of silver used is minimal and not a significant contributor to the product cost, due to the huge amount of such batteries continuously produced, the recovery of silver is required. In the present work, button cell batteries with silver content were sectioned, separated (paste from the metal casing) in an ultrasonic bath and the resulting paste was analyzed to identify the constituents in order to subsequently establish the silver recovery technology. The samples were analyzed by SEM (Quanta Inspect F50, with a field emission gun - FEG with 1.2 nm resolution and an Energy Dispersive X-ray Spectrometer - EDX having 133 eV resolutions at MnK_α). XRD data were obtained using a Panalytical X'PERT MPD X-ray diffractometer with a Cu K_α radiation source (λ = 1.5418 Å) in the range 2θ = 10–90º. In the second part of the paper we will study the recovery of silver from active paste by leaching processes in nitric acid (HNO_3) followed by precipitation of silver chloride (AgCl) and finally the melting of AgCl with Na_2CO_3 flux.

Producția globală de argint din producția minieră a scăzut cu 2 la sută în 2018, înregistrând a treia scădere anuală consecutivă. În același timp, cererea de metal este în creștere; cererea pentru industria fotografică - cel mai mare utilizator - este în creștere după șocul produs de apariția formatelor digitale (Kodak - companie aflată sub protecția falimentului între 2012 și 2013 anunță vânzări crescânde de filme). Crește și cererea de contactori și conductori (15%), aliaje de brazare (7%), catalizatori (3%). În aceste condiții, preocuparea de a recupera argintul din toate sursele secundare devine o necesitate. Deși cantitatea de argint folosită este minimă și nu contribuie semnificativ la costul produsului, datorită cantității imense de astfel de baterii produse continuu, recuperarea argintului devine necesară. În lucrarea de față, bateriile tip buton cu conținut de argint au fost secționate, separate (pasta din carcasa metalică) într-o cuvă de ultrasonare și pasta rezultată a fost analizată pentru a identifica elementele constitutive pentru a stabili ulterior tehnologia de recuperare a argintului. Probele prelevate din pasta activă au fost analizate prin SEM (Quanta Inspect F50, cu emisie de câmp - FEG cu rezoluție de 1,2 nm și Spectrometru cu raze X cu dispersie a energiei - EDX având rezoluții de 133 eV la MnK_α). Datele XRD au fost obținute folosind un difractometru cu raze X Panalytical X'PERT MPD cu o sursă de radiație Cu K_α (λ = 1,55418 Å) în intervalul 2θ = 10–90º. In partea a doua a lucrării vom studia recuperarea argintutului din pasta activă prin procese de leşiere în acid azotic (HNO_3) urmate de precipitarea clorurii de argint (AgCl) și în final topirea AgCl cu flux de Na_2CO_3.

Keywords: *used button cells, silver-oxide, recovery, SEM-EDX, XRD*

1. Introduction

The first non-rechargeable battery dates from 1881 (Lead-acid); followed by Zinc-carbon (1898), Zinc-air battery (1932), Mercury oxide-zinc battery (1942), Alkaline battery (1949) [1] and in 1960 Silver-oxide battery (NASA developed silver-zinc batteries for mission-critical applications in spacecraft, including the Apollo command module) [2]. Silver Oxide Battery (SR) is suitable for small and precision electronic devices such as watches and calculators, micro-lamps, hearing aids, cameras and photographic equipment. The larger batteries are generally used in military application (e.g. Mark 7 torpedoes, Alfa class submarines) where price is not the most important factor. These cells have: high-energy density per unit volume; high and stable operating voltage; a flat discharge curve until the end of the discharge time. The storage capacity of a silver-zinc cell is about six times as great as a lead-acid cell of the same size.

Post 1990s, the Li-ion battery became a serious competitor to the Silver Oxide Battery, but the latter features some advantages, namely: smaller sizes than Li-ion (at equivalent energy density); longer life-cycle; free of thermal leaks; safety – non-flammable; eco-friendly recyclable. Among the disadvantages should be mentioned: high price due to the presence of silver; it may contain mercury, which requires special measures for recycling.

* Autor corespondent/*Corresponding author*,
E-mail: eugeniuvasile@yahoo.com

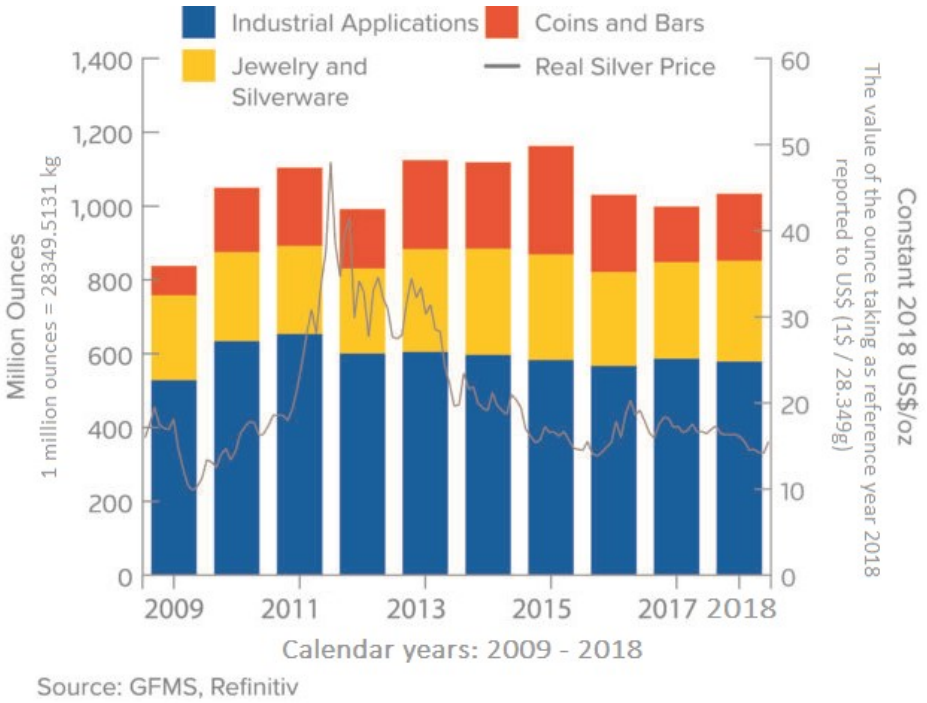


Fig. 1 - Silver supply and demand / *Oferta și cererea de argint [5].*

Until 2004, all silver-oxide batteries contained up to 0.2% mercury; the mercury was incorporated into the zinc anode to inhibit corrosion in the alkaline environment [3]. In 2004, Sony started producing the first silver-oxide batteries without added mercury (Hg) [4].

Global silver (Ag) mine production fell 2 percent in 2018, registering the third consecutive annual decline to 855.7 Moz (24.25 tons). Mexico, Peru, China, Russia and Chile were the world's top five producers of silver, accounting for a collective 60.5% or 556.9 Moz (15.75 tons) in 2018. In the same time, silver jewelry demand moved 4 percent higher in 2018 to 212.59 Moz (6.024 tons). Global demand for silverware jumped by 6 percent last year to 61.1 Moz (1.73 tons). Figure 1 presents the main applications of silver [5].

The recovery of silver is an attractive issue. Silver scrap supply fell by 2 percent to 151.3 Moz. Lower silver prices accounted for the bulk of the decline.

The recovery process of silver requires collection, sorting and different metallurgical treatment. In Figure 2 is present a flowchart for recovery of silver from used silver oxide button cells.

The research undertaken on the recovery of silver from used button batteries with silver oxide was divided into two parts. The current study focuses on the process of separation and recovery of active material and its characterization while the next part will aim at analyzing the samples obtained after the operations: leaching with nitric acid (HNO_3); precipitation of silver chloride (with NaCl or KCl); melting of silver chloride (with Na_2CO_3 flux) in order to obtain metallic silver.

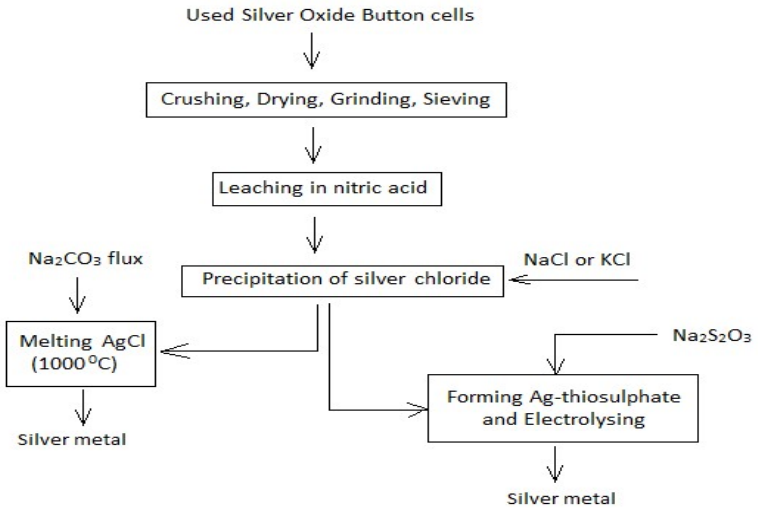


Fig. 2 - Flowchart for silver recovery from used silver oxide button cells / *Schema procesului de recuperare a argintului din baterii-buton cu oxid de argint uzate.*

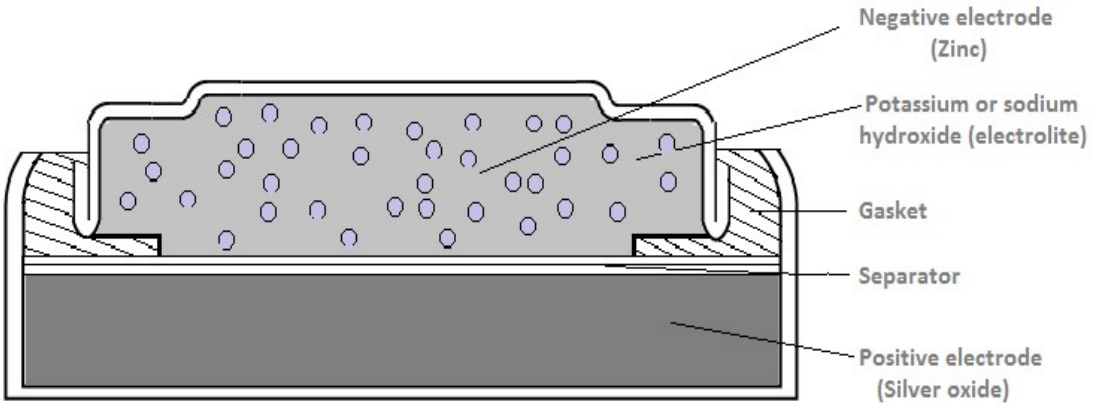


Fig. 3 - Section through a silver oxide-zinc button-type battery / *Secţiune printr-o baterie tip buton cu oxid de argint-zinc.*

2. Materials and Methods

A Silver Oxide button cell (also called silver-zinc battery), comprise a positive electrode (silver oxide - Ag_2O), a negative electrode (zinc, Zn) and an alkaline electrolyte – e.g. potassium hydroxide (KOH) or sodium hydroxide (NaOH) (Fig.3).

While battery is in use, take place the redox reaction [6]:

Cathode:

$$Ag_2O(s) + H_2O(l) + 2e^- \rightarrow 2\,Ag(s) + 2HO^-(aq) \quad (1)$$

Anode:

$$Zn(s) + 2HO^-(aq) \rightarrow ZnO(s) + H_2O(l) + 2e^- \quad (2)$$

Total reaction [6]:

$$Ag_2O(s) + Zn(s) \rightarrow 2Ag(s) + ZnO(s) \quad (3)$$

Because the solution is not involved in the net reaction, the amount of electrolyte is small, and the whole assembly can be very compact.

As previously mentioned a silver oxide battery uses two types of electrolytes: potassium hydroxide and sodium hydroxide. Potassium hydroxide batteries are used primarily in LCD watches with backlights, and sodium hydroxide batteries are used primarily in digital watches. Using potassium hydroxide as the electrolyte allows silver oxide batteries to operate even under heavy draining conditions and also at lower temperatures [7].

Various processes have been developed for recycling the used batteries due to environmental issues and for economic reasons. There are recycling processes that process a mix of batteries of different types while other processes only process used silver oxide button cells sorted beforehand. One of the important problems considered for this type of batteries was the removal of the mercury present in their components. The mercury was incorporated into the zinc anode to inhibit corrosion in the alkaline environment. Sony started producing the first silver-oxide batteries without added mercury in 2004 [4].

Since 1996, the United States has banned the use of mercury in batteries, and in the European Union the maximum allowed quantity is 5 ppm.

The chemical composition of the silver oxide button cells is constantly changing.

In 2006, for example, the SR26SW cathode was made of sintered fine silver oxide (Ag_2O) powder and the anode was composed of activated zinc with additives (mercury) to avoid corrosion [8]. Composition of used silver button was: zinc (10.4 wt%); silver (39.3 wt%); steel case (42.4 wt%); mercury (0.8 wt%); NaOH (7.1 wt%); paper/plastic (6 wt%); water (2.6 wt%); remainder (0.4 wt%). X-Ray diffraction showed that silver is present mostly in the form of metal with a little Ag_2O, while zinc is present as ZnO [8].

In 2010 the composition of waste silver button SL11205W was [9]: steel case (55.25 wt%); battery paste (37.1 wt%); membranes and plastics (4.25 wt%); electrolyte (3.1 wt%); remainder (0.3 wt%) and chemical composition of cell powder was: Ag (62.09 wt%); Zn (13.55 wt%.); Hg (0.54 wt%); C (2.48 wt%).

From 2013-2014 the metal content of powder obtained from used silver oxide zinc button cell batteries had content in: silver about 30% and zinc 10% [10, 11].

We analyzed model type RENATA (Watch393BL1, Watch 329 BL1) or similar; cells use as chemical system: Zinc / Monovalent Silver Oxide, high drain (weight ≈ 1 g). Renata Watch 393BL1 batteries made in Switzerland, the technology is with AgO, capacity range 37 mA / h, diameter 7.9 mm, height 5.4 mm; voltage 1.55 V, weight approx. 1 g.

2.1. Active paste extraction

First, the used silver oxide button cells were cut manually and the active material collected, as shown in Figure 4, was manually separated from the steel shell and then investigated.

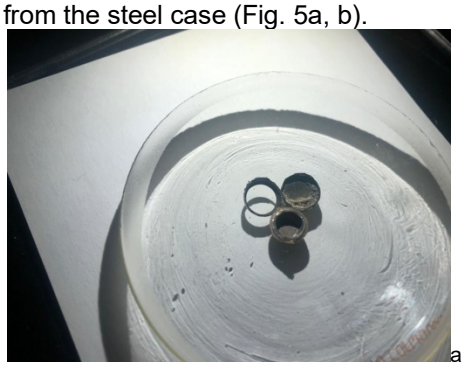
Then, the manually dismantled batteries were treated in an ultrasonic cleaning machine (Emmi 12-HC). The technical specifications of the cleaning machine were as follows: housing – stainless steel, cleaning frequency = 45 kHz; volume = 1.2 l; heating temperature = 20 – 80 ºC; bath dimension 200x100x65 mm; maxim power = 100 W; ultrasonic power = 50/75/100 W.

Fig. 4 - The used silver oxide-zinc cell button battery and powder containing silver, manganese and zinc / *Baterie-buton uzata cu celule din zinc-oxid de argint și pulbere conținând argint, mangan și zinc.*

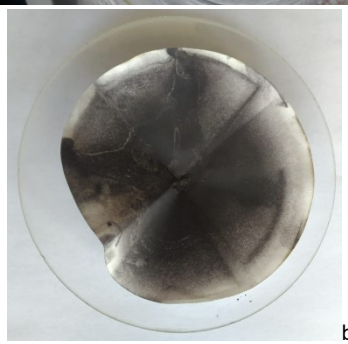
The ultrasonic cleaning machine uses cavitations bubbles induced by high frequency pressure (sound) waves to agitate a cleaning liquid. The cavitations bubbles can increase in dimension, till a critical dimension, when bubbles reach implosion.

This process was aimed at separating active paste from the steel case. All experiments were performed at room temperature (no need additional heat sources). Purified water and acetic acid (CH_3COOH) 0.5 M were used as the cavitating medium (solvent).

The working parameters were: Power 100W; ultrasound time 180 minutes. The position of cell in the basket of ultrasonic bath was maintained at 15 mm from the ultrasonic generator. Stirring produces large forces that help the detachment of active paste from the steel case (Fig. 5a, b).



a



b

Fig. 5 - Steel case after cleaning operation (a); recovery of the active paste by filtering the acetic acid solution after the ultrasound operation (b) / *Carcasa din oțel după operația de curățare (a); recuperarea pastei active prin filtrarea soluției de acid acetic după operația de ultrasonare (b).*

The active material was characterized by X-ray diffraction phase analysis and scanning electron microscopy.

3. Results and Discussions

3.1. Characterization of the obtained powder (Active mass)

In 2006, analyzing batteries type SR626SW, in typical X-ray diffraction presented in Figure 6, silver was found present mostly in the form of metal with a little Ag_2O, while zinc was found present as ZnO [8].

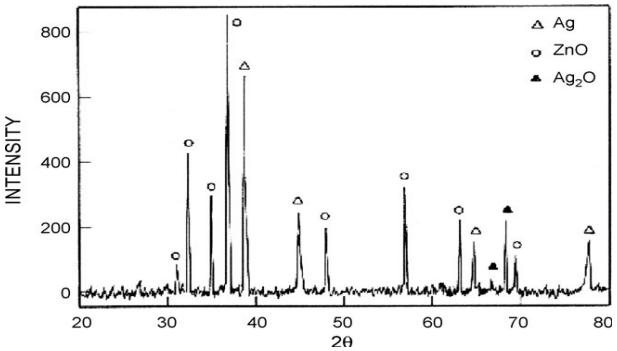


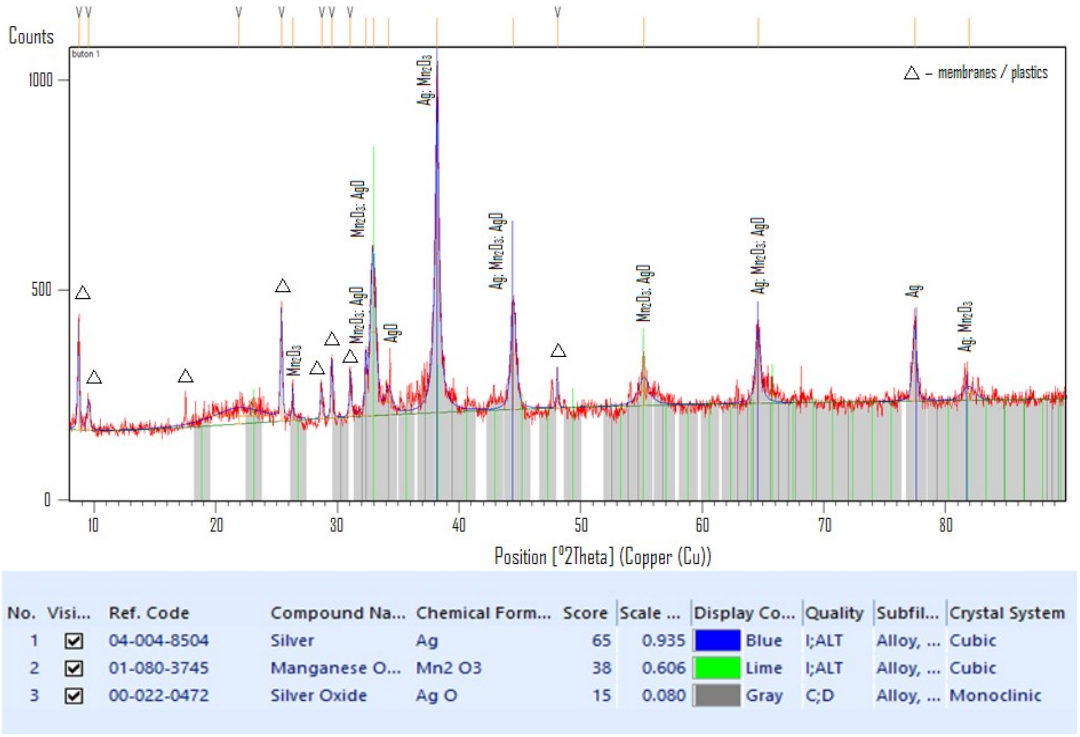
Fig. 6 - X-ray diffraction pattern of active mass of used silver oxide button cell [8] / *Spectrul de difracție cu raze X a masei active a bateriei uzate tip buton cu oxid de argint*

Now, following the analysis performed with the X-ray diffractometer (Fig. 7), the presence of silver (in the form of Ag and AgO), manganese (Mn_2O_3), membranes and plastics was revealed.

XRD data were obtained using a Panalytical X'PERT MPD X-ray diffractometer with a Cu Kα radiation source (λ = 1.5418 Å) in the range 2θ = 10–90°.

It is known that in the first models of silver - zinc oxide batteries, the voltage remained constant until the end of the battery life. This was a good feature, but sometimes it could cause inconvenience not knowing when the discharge suddenly appeared, (there case of batteries that supply critical medical devices). Thus, the need arose to generate a voltage drop at the final stage of discharge. This was achieved by mixing the silver particles with manganese dioxide. Any metal oxide having a lower standard oxidation-reduction potential than silver oxide as the main positive active material may be used for this purpose (MnO_2, HgO, CuO, and PbO_2). In this case, Manganese (III) oxide (Mn_2O_3) was used. Probably through using this Mn_2O_3 into the anode, two step-potential can be obtained at the final stage of the discharge of the positive electrode.

Then, the samples were analyzed by scanning electron microscopy using a Quanta Inspect F50, with a field emission gun (FEG) with 1.2 nm resolution (shown in Figure 8) and an Energy Dispersive X-ray Spectrometer (EDXS) having 133 eV resolutions at MnKα (Shown in Figure 9).



No.	Visi...	Ref. Code	Compound Na...	Chemical Form...	Score	Scale ...	Display Co...	Quality	Subfil...	Crystal System
1	☑	04-004-8504	Silver	Ag	65	0.935	Blue	I;ALT	Alloy, ...	Cubic
2	☑	01-080-3745	Manganese O...	Mn2 O3	38	0.606	Lime	I;ALT	Alloy, ...	Cubic
3	☑	00-022-0472	Silver Oxide	Ag O	15	0.080	Gray	C;D	Alloy, ...	Monoclinic

Fig. 7- The X-ray diffraction pattern of active positive electrode; the peaks are corresponding to Ag, AgO and Mn_2O_3 phaces / *Spectrul de difracție cu raze X al electrodului pozitiv activ; maximele de difracție corespund fazelor Ag, AgO si Mn_2O_3.*

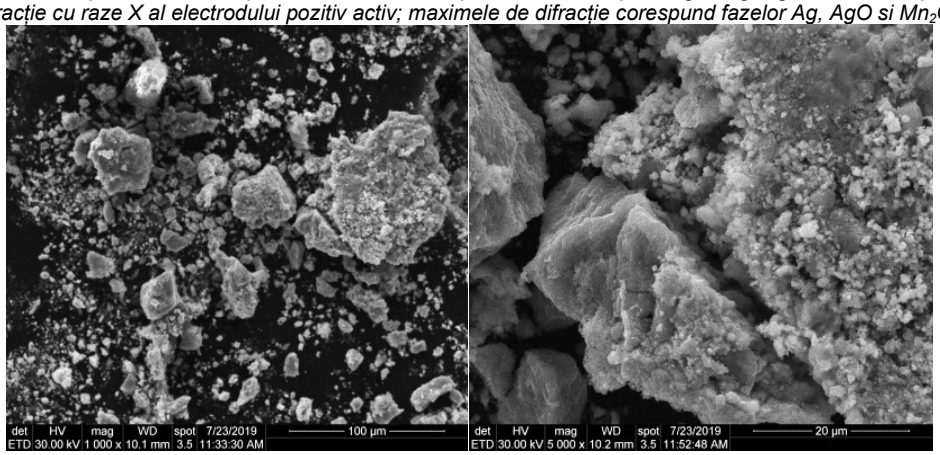


Fig. 8 **-** Scanning electron microscopy images of active positive electrod / *Imagini de microscopie electronică de baleiaj ale electrodului pozitiv activ.*

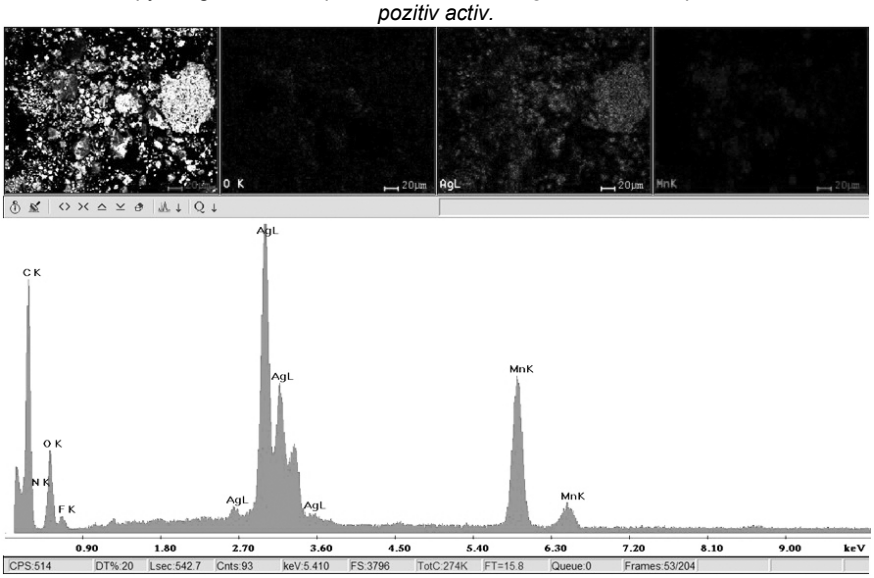


Fig. 9 - SEM image, EDX analysis maps with the distribution in the matrix of the constituent elements, and enery dispersive X-Ray spectrum for Cathode paste / *Imagine SEM, hărți de analiză EDX cu distribuția în matrice a elementelor constitutive și spectru EDX pentru pasta catodică.*

The anodic paste was analyzed microstructurally by SEM-EDX spectrometry analysis. Figure 10 shows the anodic paste with zinc filaments that have a nanometric size around 85.7 nm, and Figure 11 shows the EDX spectrum with the identified elements.

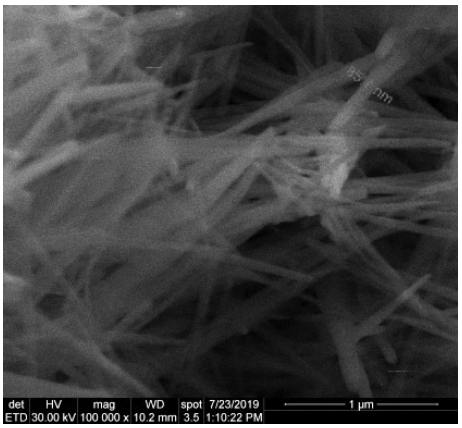


Fig. 10 - Scanning electron microscopy image with Zn filaments of nanometric size - / *Imagine de microscopie electronică de baleiaj cu filamente de Zn de dimensiuni nanometrice.*

In the analyzed batteries, we consider that the content of AgO and Mn_2O_3 should be around these values. From figure 7 which analyzes the positive electrode (active paste) it is observed that Ag represents 52.10%, Mn_2O_3 = 32.20 %, AgO = 12.70 % and membranes and plastics.

4. Conclusions

The presence of silver in silver oxide-zinc batteries justifies the research undertaken to promote some technologies for the recovery of this precious metal, both economically and environmentally. Ultrasonication in acetic acid medium (0.5M) of used silver oxide-zinc cell batteries allows the separation of the active paste from the steel housing and subsequently the recovery of silver paste. Scanning Electron Microscopy and X-ray diffraction investigations allowed the exact identification of the components of active mass: Ag, AgO; Mn_2O_3; Zn, it is observed that Ag = 55.10%, Mn_2O_3 = 32.20 % and AgO = 12.70 %. Researches will continue to recover metallic silver. The paste containing Ag will be

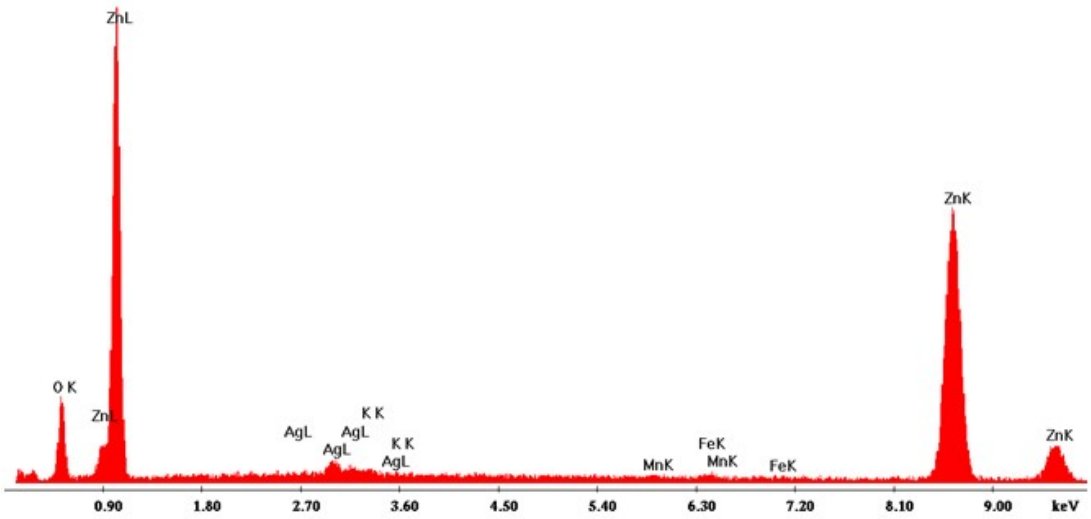


Fig. 11 - EDX spectrum for Anode paste / *Spectrul EDX pentru pasta anodică*

The optimal battery operation is achieved by adjusting the proportion of negative active material (zinc) and positive active materials (Ag, AgO, Mn_2O_3).

Must most likely be satisfied, a double inequality according to the model [12]:

$$[Zn]_{min} > [Ag, AgO]_{max}$$
$$[Zn]_{max} < [Ag, AgO+Mn_2O_3]_{min}$$

According to the data from the specialized literature [10, 11] we can conclude that the amount of Ag in silver oxide-zinc batteries is 30 wt. %, also the Zn amount is 10 wt. %, steel case 43 wt. %, electrolyte 7 wt. %, plastic / paper 7 wt. % and remainder 3 wt. %.

leached in nitric acid, HNO_3 and after the precipitation of silver chloride (AgCl) the melting of AgCl with Na_2CO_3 flux will allow obtaining of metallic silver. Another possible option could be the electrolyzing of Ag-thiosulphate (AgS_2O_3) complex).

REFERENCES

[1] R.A. Huggins, Primary, Non-rechargeable Batteries, Energy Storage, Springer, Cham, 2016.
[2] Zpowerbattery. Available online: https://www.zpowerbattery.com/why-silver-zinc-microbatteries/ (accessed on 14 March 2020).
[3] J. Natsuki, T. Natsuki, Y. Hashimoto, A review of silver nanoparticles: synthesis methods, properties and applications, International Journal of Materials Science and Applications, 2015, **4** (5), 325-332.

[4] AZO Materials. World's First Environmentally Friendly Mercury Free Silver Oxide Battery Commercialized by Sony, Posted September 29th, 2004. Available online: https://www.azom.com/article.aspx?ArticleID=2651 (accessed on 21 March 2020).
[5] Silver Institute. Available online: https://www.silverinstitute.org/scrap-supply/ (accessed on 22 March 2020).
[6] T.R. Compton, Battery Reference Book Third Edition, Newnes, Oxford, MA, 2000, 20/3.
[7] Maxell. Available online: https://biz.maxell.com/en/primary_batteries/sr_coin.html (accessed on 22 March 2020).
[8] N. Sathaiyan, V. Nandakumar, P. Ramachandran, Hydrometallurgical recovery of silver from waste silver oxide button cells, Journal of Power Sources, 2006, **161**, 1463–1468.
[9] S, Aktas, Silver recovery from spent silver oxide button cells, Hydrometallurgy, 2010, **104**, 106–111.
[10] N. Sathaiyan, Reclamation of Mercury from Used Silver Oxide Watch Batteries, Advances in Chemical Engineering and Science, 2014, **4**, 1-6.
[11] Umesh Jadhav, Hong Hocheng, Extraction of silver from spent silver oxide–zinc button cells by using Acidithiobacillus ferrooxidans culture supernatant, Journal of Cleaner Production, 2013, **44**, 39-44.
[12] Y. Uetani, A. Shimizu, K. Kajita, O. Yumimoto and S. Kuwano, Silver oxide cell and its manufacture, U.S. Pat. No. 4247606, January 27, 1981

****