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RECYCLING Ni-MH BATTERIES USED IN MEDICAL DEVICES. PART I - INVESTIGATIONS ON THE CONTENTS OF Ni-MH BATTERIES

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Batteries are an indispensable component of everyday life and a critical component of modern medical devices in diagnostic and monitoring systems or in electrical surgical instruments. We focused on the rechargeable Ni-MH batteries because they have a capacity two or three times higher than NiCd batteries, a high energy density but lower than lithium-ion batteries. NiMH batteries from medical devices were manually disassembled, separated to identify the components and to characterize the materials in each of these. Were used specific methods of analysis (XRF, SEI, EDX, XRD) which will allow finding the optimal technology for the recovery of useful elements.

Keywords: medical devices, Nickel Metal Hydride battery, SEI, EDX.

1. Introduction

Primary batteries (disposable batteries) or secondary batteries (rechargeable batteries) are present in numerous portable medical devices: ventilators, defibrillators (Fig. 1a), pacemakers, insulin pumps - in intensive care units; blood glucose monitors - in diagnostic and monitoring systems; tools for cutting, modeling, fixation, bone dissection, fragmentation and suction of soft tissues - in the electrical surgical instruments (Fig. 1b).

Equally well known are implantable medical batteries; from this category we mention pacemakers, ICDs, neurostimulators. Drug pumps that consist of a pump and a catheter, both of which are surgically placed under the skin (Fig. 3). The pump is a round device that stores and delivers analgesia medication. It is

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placed in the abdomen. The catheter (a thin, flexible tube) is inserted into the spine and connected to the pump).

Fig. 1. Portable batteries in a) BeneHeart D3 Defibrillator - Mindray™ [1]; b) Portable drill for small bones [2]

A cochlear implant (CI) is a surgically implanted neuro-prosthesis (Fig. 4) that provides a person with moderate to profound sensorineural hearing loss with sound perception. With the help of therapy, cochlear implants can enable improved speech understanding in both quiet and noisy environments [6]. A CI bypasses acoustic hearing by directly electrically stimulating the auditory nerve [4]. Through everyday listening and auditory training, cochlear implants allow both children and adults to learn to interpret those signals as speech and sound [4].

Fig. 3. Medicine pump [3]

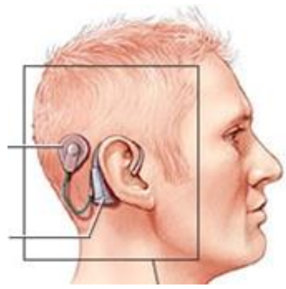

Fig. 4. Cochlear implant (CI) [4]

Batteries are also present on body-applied devices/"patches"; these are small devices (about the size of a smartphone) safe, discreet and dependable that can work 24 hours a day and that replace the need for injections by providing drugs or insulin. The batteries present in the microelectronic pills should not be neglected either; due to the nature of ingestible sensors, they are optimized for passage through hollow organs. This makes them ideal for collecting data throughout the digestive tract, which includes several organs between the mouth and the anus.

From this category we recall digital pills (also known as ingestion sensor) is a form of pharmaceutical dosage that contains an ingestion sensor inside a pill. The sensor starts transmitting medical data after ingested. The technology that makes up the pill, as well as the data transmitted by the pill's sensor, are part of digital medicine. The purpose of the sensor is to determine whether the person is taking their medication (called "compliance"); im0aging pods (images and videos require the most bandwidth for data delivery).

Swallowable capsules containing video cameras are used to generate images of macroscopic structures of hollow organs such as the stomach and small intestine. These battery-powered devices can transmit video at up to 2.7 Mbit/s and are less invasive than other traditional endoscopic imaging devices.

From the large family of rechargeable batteries, we focused on NiMH type batteries. These batteries contain some expensive, scarce and unevenly distributed metals (mainly in the southern hemisphere): Ni, Co, rare earths.

At the level of 2022 [5] Cobalt reserves are concentrated in DPR Congo (3.6 mt, more than 50% of the world's cobalt reserves), Australia (1.4 mt, around 20% of the global share) Cuba – 500.000 t, Philippines – 260.000 t, Russia – 250.000 t, Canada 220.000 t, Madagascar – 100.000 t. Currently, cobalt ores are processed in China (85.000 mt), Finland (12.526 mt), Belgium (6.500 mt), Canada (6.250 mt), Norway (4.400 mt).

Nickel reserves are more evenly distributed than Cobalt: Indonesia (21 mt), Australia (21 mt), Brazil (16 mt), Russia (7.5 mt), New Caledonia (7.1 mt), Philippines (4.8 mt), Canada (2.2 mt), China (2.1 mt), USA (0.37 mt). Regarding Nickel production in 2022 (3.3 mt) the classification is different [6]: Indonesia (mine production: 1.6 mt), Philippines (mine production: 330.000 t), Russia (mine production: 220.000 t), New Caledonia (mine production: 190.000 t), Australia (mine production: 160.000 t), Canada (mine production: 130.000 t), China (mine production: 110.000 t), Brazil (mine production: 83.000 t), United States (mine production: 18.000 t).

The rare earths include 17 soft metals, usually gray: the elements Scandium, Yttrium, Lanthanum and those from the lanthanide category, which are divided into light rare earths (lanthanoids) and heavy rare earths. Cerium, Praseodymium, Neodymium, Promethium and Samarium form the lanthanoid group, (Promethium is not found naturally on earth and can only be formed in nuclear reactors); for Lantan and Cerium, the demand is low and the supply in excess. Pr, Nd and Sm are used in the manufacture of strong magnets, resistant to elevated temperatures (military applications).

The heavy rare earths Europium, Gadolinium, Terbium, Dysprosium, Holmium, Erbium, Thulium, Ytterbium and Lutetium are the most sought after, having military applications (Tb and Dy for high temperature magnets used in the manufacture of drones, laser guided weapons) Lu used in medical imaging; Tm and Yb used in X-ray devices; Er and Ho used in medical lasers.

In 2009, China had a market share in the production of rare earths of 97%; this share has decreased constantly - 92% (2010), 63% (2019), 58% (2020). China remains strong in the supply chain and produced in 2022 – 220.000 t. PR reserves are divided as follows [7]: China - 44 mt (about 36% of the world's RE reserves - 2020); Vietnam - 22 mt; Brazil and Russia 21 mt (Russia 12 mt); India – 6.9 mt; Australia 4.2 mt; USA – 2.3 mt. In these conditions, it is necessary to find solutions for the efficient management of Ni-MH battery waste to recover and recycle the valuable metals that these batteries contain (Ni, Co, rare earths).

2. Materials and Methods

The experiments carried out in the laboratory aimed to separate Ni-MH batteries used in the medical field, and to identify the valuable metals present (nickel, cobalt and rare earths); the economic value associated with these metals justifies the research undertaken to find a viable recycling process for used Ni-MH batteries [8]. The authors team has experience in the characterization and recycling of used Li-ion batteries [9, 10]. Ni-MH batteries are of three constructive types: prismatic, cylindrical and button-shaped. The studied batteries are cylindrical (Fig. 5). The cylindrical accumulators are comprising of three layers in the form of a bobbin.

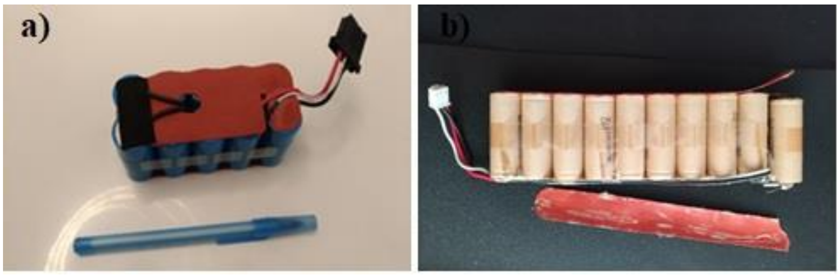

Fig. 5. Two types of Ni-MH batteries used in medical equipment (A and B)

The first layer (the negative electrode) consists of a perforated nickel foil (plate), covered with dark paste composed of hydrogen-absorbing alloys (MH – metal hydride). Two types of alloys are used: AB_2 (hydride-forming element can be for A - Zr, Ti; and for B – Ni, Co, V, Mn, Cr, Al) and AB_5 (A is a mixture of La, Ce, Nd and Pr and B is Ni, Co, Mn and Al). In the case of the studied batteries, the anode is an AB_5-type alloy.

The second layer comprises a separator between the electrodes and the third layer (positive electrode) made of nickel hydroxide (dark past). In Fig. 6 we can see the appearance of a NiMH battery disassembled.

Research was undertaken on two types of Ni-MH batteries used in medical equipment, identified with the names A and B. First, the used Ni-MH battery was manually cut and disassembled into components (steel case, cathode, anode, cathodic paste, anodic paste, separator).

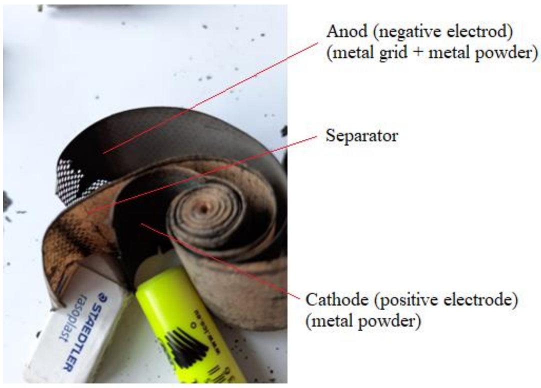

Fig. 6. Structure of Ni-MH cylindrical cell

The collected metallic components were then investigated (XRF analysis, optical microscopy, electron microscopy (SEI, EDX), X-ray diffraction. The first analyzes were conducted to identify the materials found in used and disassembled Ni-MH batteries, using a Genius Explorer 5000 (Skyray Instruments Explorer) X-ray fluorescence (XRF) spectrometer. This instrument allows the fast (2 - 60 seconds) and precise (minimum detection limits ~ 5 ppm) identification of a wide spectrum of elements (atomic number from 12 to 95 (element from magnesium (Mg) to uranium (U); it can be simultaneous analysis 40 items.

Next, samples from the cathode and anode of Ni-MH batteries were analyzed by scanning electron microscopy using a Quanta Inspect F50, with a field emission gun (FEG) with 1.2 nm resolution and an energy dispersive X-ray Spectrometer - EDX with resolutions of 133 eV at MnKα).

3. Results and discussions

The XRF analyzes performed under similar conditions (Testing time 60 s; Volt 45; Curr 40; Mode Ni alloy) on the anode grid of samples A and B indicated a high concentration of Ni - 99.90%; the presence of Co and Fe was also recorded on the spectrum. XRF spectra performed on the two anodic metal grids are presented in Fig. 7 (A and B).

The chemical composition of the anodic grid, obtained after the XRF analysis of the two samples (A and B) is presented in Table 1; Table 2 shows the chemical compositions of the anodic paste for the two samples.

Table 1

Chemical composition anode grid (A) and (B)

Chemical composition anode grid (A)		**Chemical composition anode grid (B)**	
Element	Content (Avg)	Element	Content (Avg)
Fe (%)	57.79	Fe (%)	44.31
Co (%)	1.02	Co (%)	0.37
Ni (%)	40.43	Ni (%)	53.11

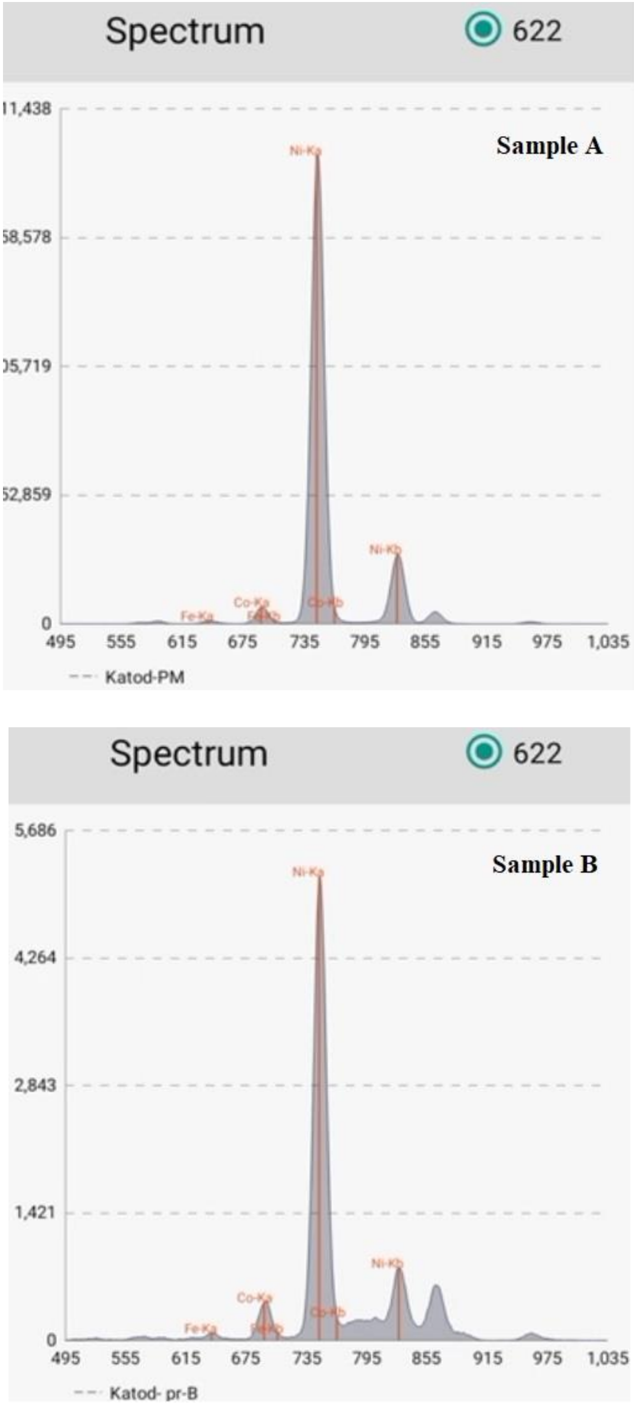

Fig. 7. XRF spectra performed on the two anodic metal grids taken from samples A and B

Table 2

Chemical composition anode paste (A) and (B)

Chemical composition anode paste (A)		**Chemical composition anode paste (B)**	
Element	Content (Avg)	Element	Content (Avg)
K (%)	3.16	K (%)	2.22
Mn (%)	1.44	Mn (%)	0.31
Fe (%)	13.58	Fe (%)	1.09
Ni (%)	27.30	Ni (%)	20.30
La (%)	12.76	La (%)	1.95
Ce (%)	19.20	Ce (%)	-
Nd (%)	4.88	Nd (%)	11.06
Pr (%)	-	Pr (%)	-
Pm (%)	-	Pm (%)	-
Sm (%)	-	Sm (%)	16.86

In both samples, in anode paste, in addition to the presence of Fe and Ni, the presence of rare metals (Ce, La, Nd in sample A, Sm, Nd, La in-sample B) was identified. Cathode (A and B paste) is made from a pressed paste based on nickel hydroxide.

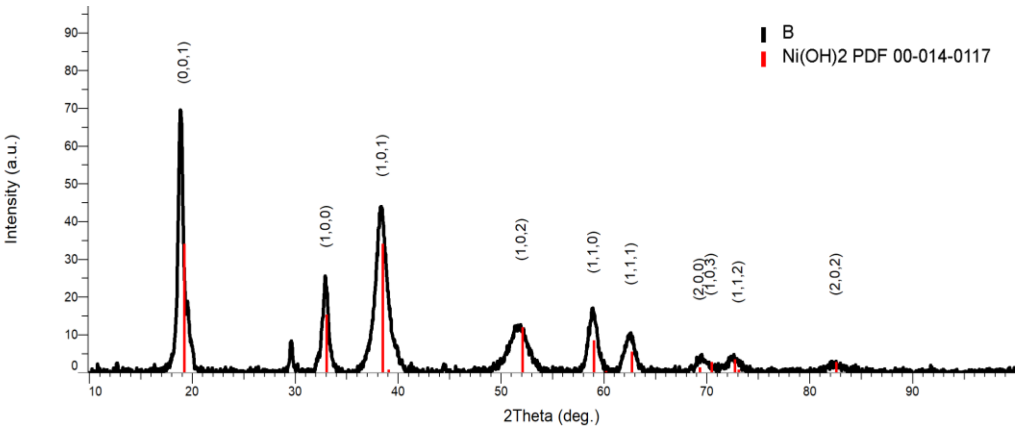

Fig.8. X-ray diffraction on cathode of Ni-MH batteries

The X-ray diffraction analysis was conducted using the D8-Discover diffractometer, Bruker, Germany, with Cu primary radiation (λ = 1.540598 Å), parallel geometry and 1D LynxEye detector (Bruker, Germany) on the secondary side. The diffractograms were obtained with an angular increment of 0.04°, at a scanning speed of 1 s/step. The identification of the crystallographic phases was conducted using the ICDD PDF 2 Release 2022 database.

Electron microscopy analyzes (SEI and EDX) were performed on samples taken from the anodic paste of the two samples to confirm the presence of rare earths, and to record their morphology and distribution.

Sample A (Anode): Grid + paste)

The surface of the grid, covered with a thin film of black paste (AB_5) with rare earth content, are presented in Figs. 9-10.

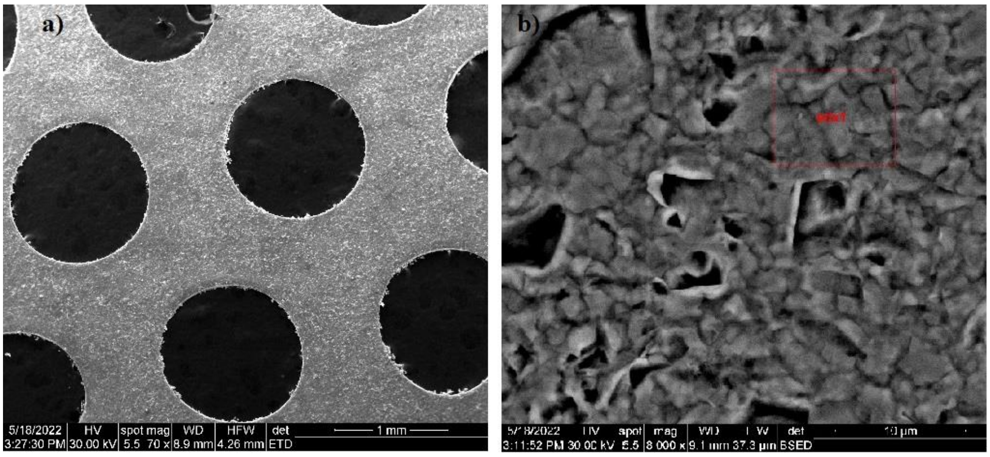

Fig. 9. Sample A - SEI image on the surface of the anodic grid (a); location of EDX analysis (b)

EDX analysis (Fig.10), collected information from under the rare earth film and established the composition of the Nickel alloy: Ni between 79.15 - 79.61; Fe between 18.26 - 18.43; Co between 0.13 - 0.41.

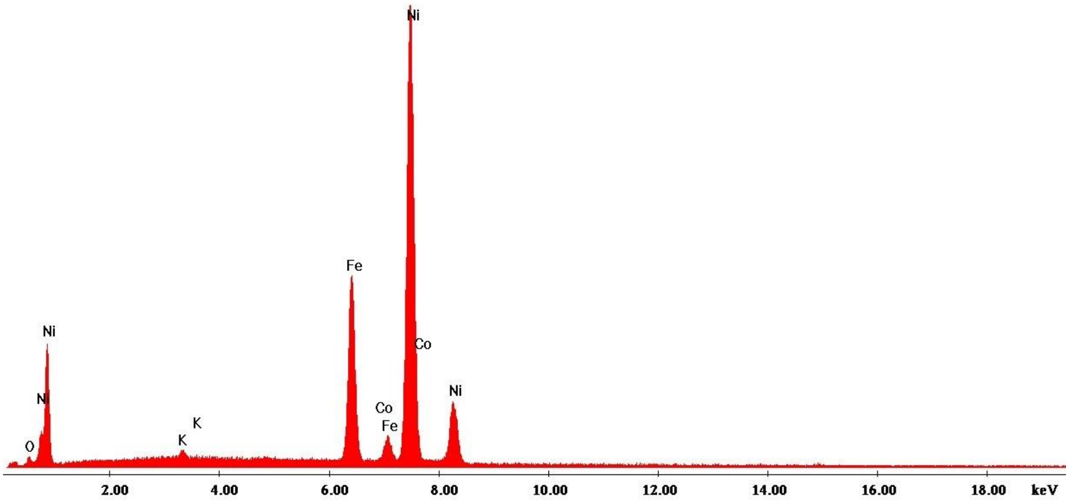

Fig. 10. EDX analysis of the anodic grid (Nickel alloy); sample A

On the surface of the grid, particles of rare metals (shiny) separated from the black paste are caught (Fig.11) With the help of EDX analysis, lanthanides (La, Ce, Sm) were identified (Fig.12).

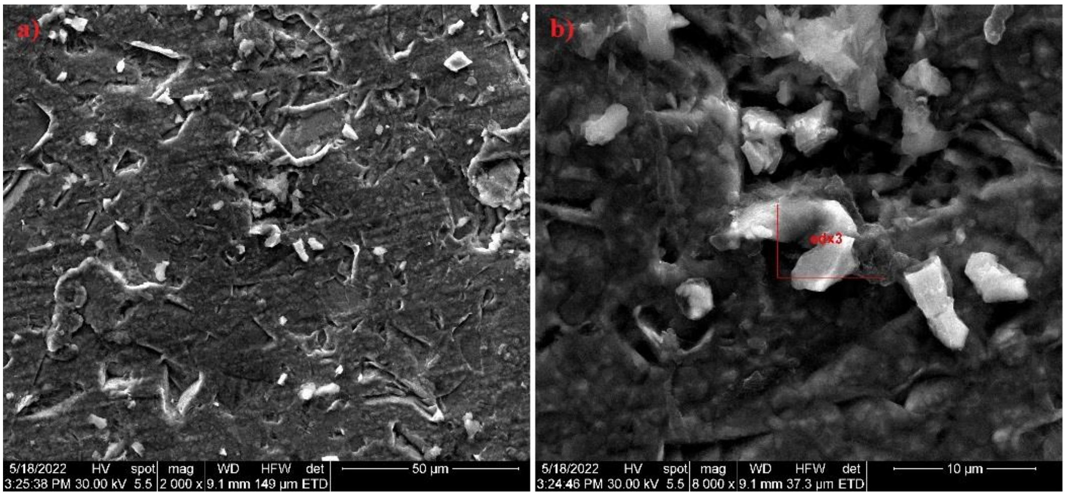

Fig. 11. Sample A- SEI image on the surface of the anodic paste (a); location of EDX analysis (b)

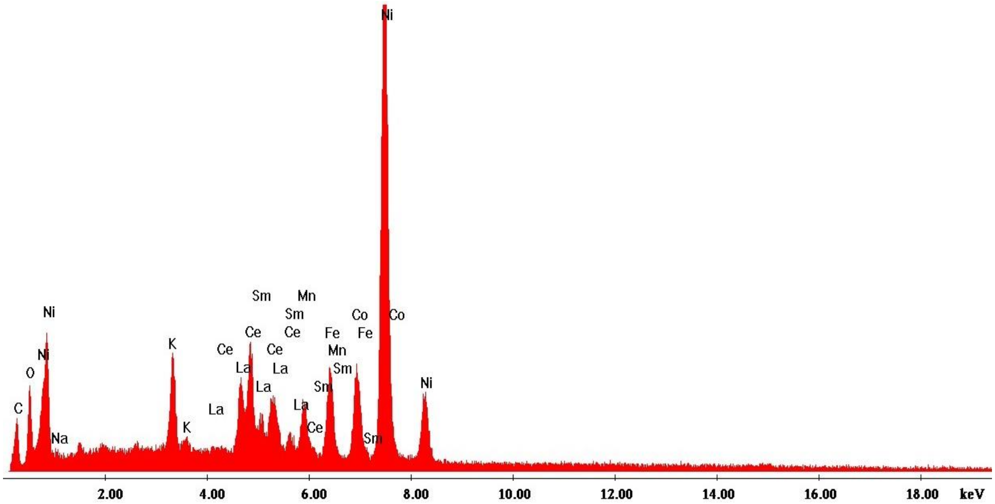

Fig. 12. Sample A - EDX analysis of the anodic paste sample A; lanthanides (La, Ce, Sm) were identified

Next, the anodic paste detached from the grid was analyzed. At x1000 magnifications, we can see that the paste is composed of relatively homogeneous particles (from a dimensional point of view) of RE: La, Ce, Sm, (Figs. 13, 14). In the analysis of rare earths performed on the anode of sample A, previous XRF analysis identified La, Ce and Nd, but following the EDX analysis, which is a micro-compositional analysis performed on a specific area, the presence of Nd does not emerge, instead the appearance of Sm is noted.

This is a first indication that, in this sample, the material from which the anodic paste was made is not very homogeneous, the analyzed material being composed of agglomerated particles with micron sizes, as can be seen in Fig. 13.

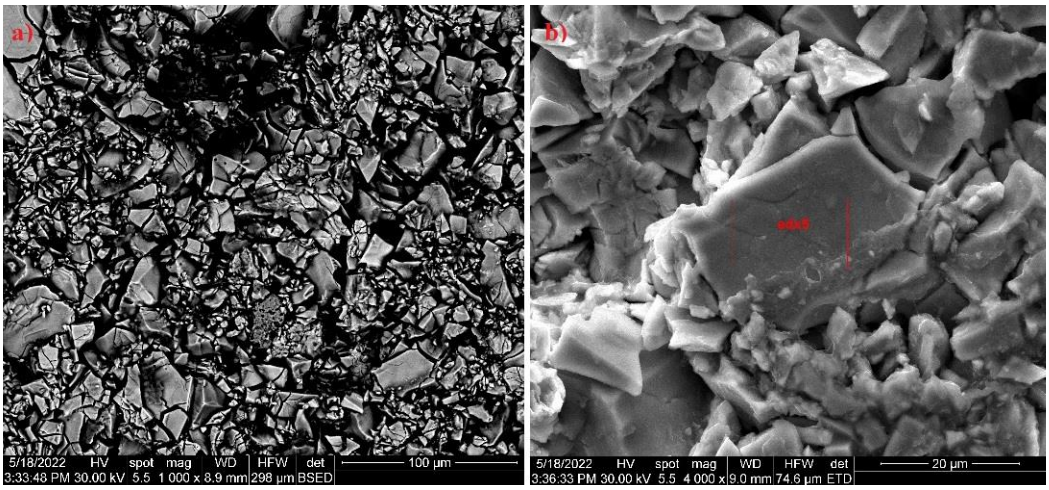

Fig.13. Sample A - SEI image taken in the depth of the anodic paste-(a); location of EDX analysis-(b)

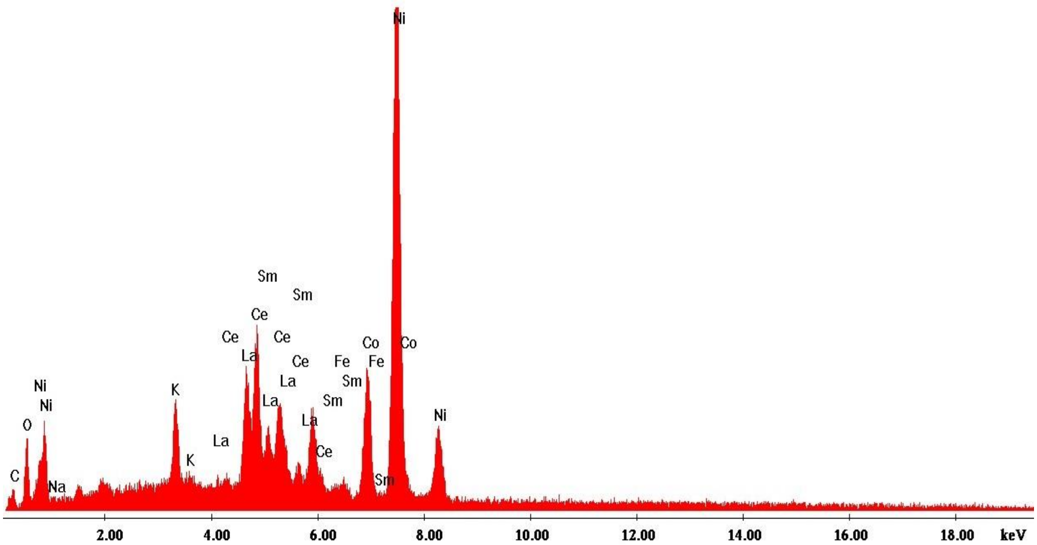

Fig. 14. Sample A - EDX analysis of the anodic paste; lanthanides (La, Ce, Sm) were identified

The samples taken from the second type of Ni-MH battery (B) analyzed show significant differences compared to the first one (A).

Sample B (Anode): Grid + paste)

The surface of the nickel grid, covered with a thin film of black paste (AB_5) with rare earth content. EDX analysis, collected information from under the rare earth film and established the composition of the Nickel alloy: Ni between 93.65 - 94.74; Fe between 4.56 – 4.91; the composition is different from that recorded for sample A (Fig.15, 16).

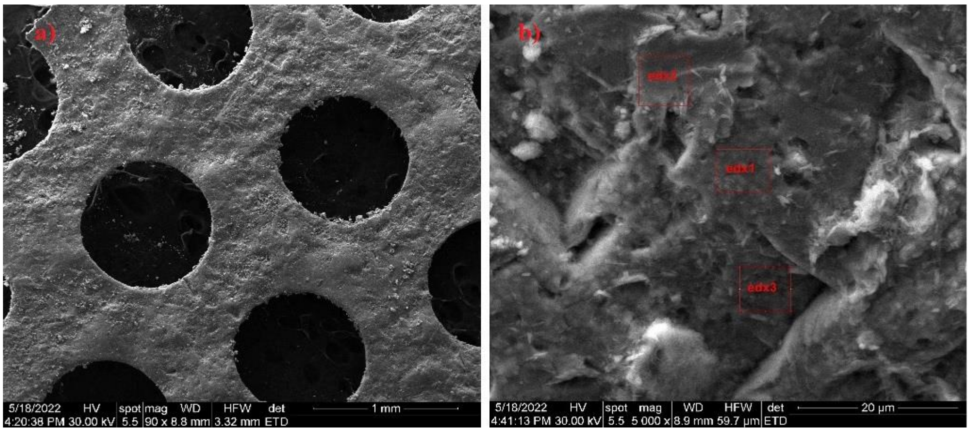

Fig. 15. Sample B - SEI image on the surface of the anodic grid (a); location of EDX analysis (b)

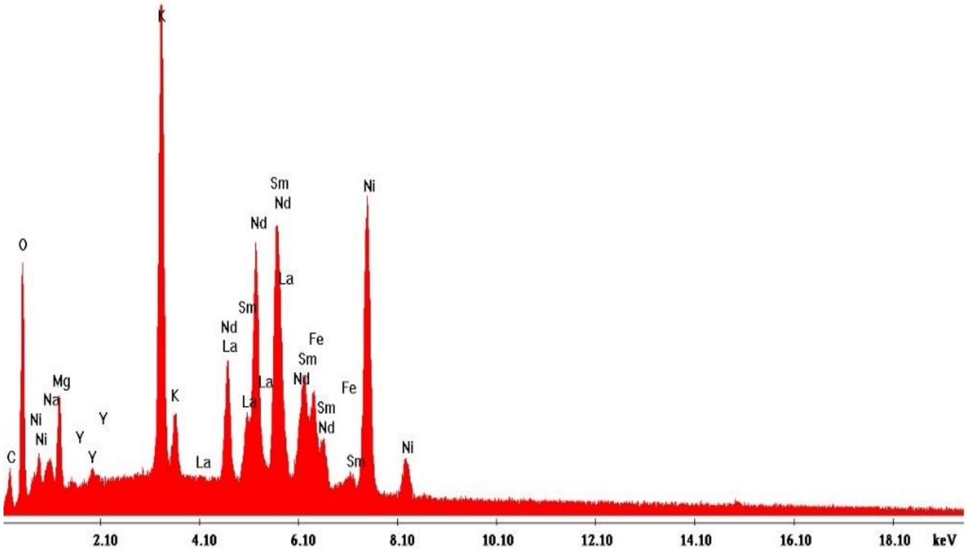

Fig. 16. Sample B - EDX analysis of the anodic paste; lanthanides (La, Nd, Sm) were identified

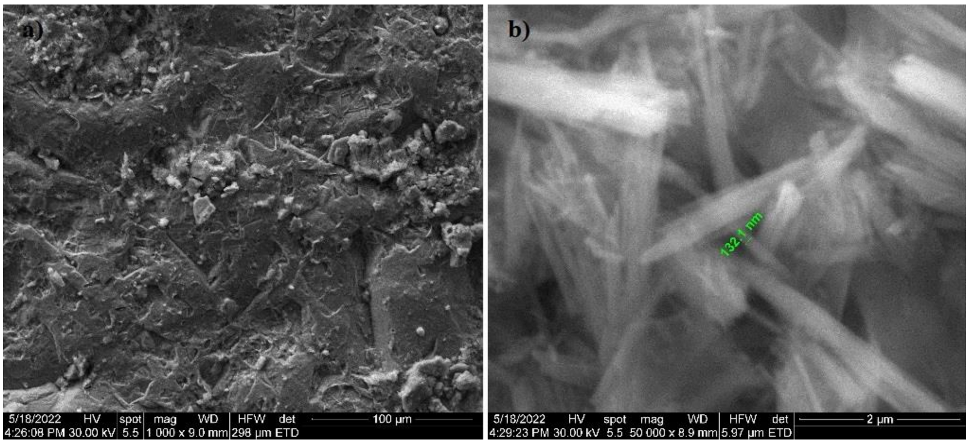

Fig. 17. Sample B - SEI image taken in the depth of the anodic paste (a); nanotube (b)

With the help of EDX analysis other lanthanides (La, Nd, Sm) were identified and compared to those identified in sample A. The material of the black paste in sample B is more homogeneous (nanometric dimensions) than in sample A (micron dimensions), as observed in Fig. 17b, so that the point analyzes performed by EDX on the rare earths completes data obtained through XRF.

Rare earth nanotubes (132.1 nm) detached from the black paste are trapped (Fig.17) on the grid surface.

4. Conclusions

The composition of the analyzed Ni-MH batteries differs (composition, structure of the anode and cathode). The chemical composition of RE differs from one manufacturer to another and from one destination to another (in the case of the same manufacturer). In the paper, the composition and structure of the constituent elements of used NiMH batteries were determined. The experimental research shows that the RE used to make Ni-MH batteries are from the lanthanoids category (light rare earths) and are in the anode of the Ni-MH battery. The XRF analysis must be completed with at least one other chemical analysis, EDX in our case, to identify which specific elements of the lanthanide group are present in the anode of Ni-MH batteries. The presence of RE in the anode of Ni-MH batteries can be in the form of micron size powder (less homogeneous) or in the form of nanotubes (homogeneous, high quality).

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