

Electrochemical Recovery of Nickel and Cadmium from Spent Ni-Cd Batteries

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Abstract: In compliance with Directives 91/157/CEE and 91/338/CEE about spent batteries with dangerous, the paper proposes some laboratory electrochemical methods for valuable metals recovery like Ni and Cd from Ni-Cd spent batteries. The paper describes quick analyses and control methods for Ni and Cd, by AA spectroscopy, carried out on a novAA 400 G atomic absorption spectrometer - Analytik Jena, with graphite oven, with WinAAS 3.17.0 software for evaluation, control and result presentation, a so-called cookbook, for every element, and a HS 55-1 hydride generator. The components of the deposits were determined by SEM-EDAX electron microscope Inspect S - FEI-Holland.

Keywords: waste metals, toxic metals, spent batteries, electrochemistry recovery of metals

1. Introduction

The production of rechargeable nickel-cadmium batteries began in Europe and in United States in 1950. These types of batteries have been used in applications that require high energy density, long lifetime and high discharge ratios [1,2].

Cadmium is considered one of the most toxic metals with a wide variety of adverse effects. It has an extremely long biological half-life that essentially makes it a cumulative toxin. In 1993 cadmium has been designated by the International Agency for Research on Cancer and the US National Toxicology Program as a human carcinogen [3].

Because Ni-Cd batteries present environmental problems being classified as hazardous waste due to the presence of cadmium, other types of batteries have been developed as an alternative for Ni-Cd batteries: NiMH (nickel-metal hydride) and Lithium-ion batteries. These new types of batteries are acceptable for environment, and technically can substitute Ni-Cd batteries in many applications, but they are more expensive. For this reason and also due to their great stability, Ni-Cd batteries are still largely used in many parts of the world in precision fail-safe electronic equipment (in medical and aviation devices), military and defense applications, portable electronic devices, etc. [1,4].

Recycling of spent Ni-Cd batteries is essential, both from environmental (due to the presence of toxic cadmium) and economical point of view.

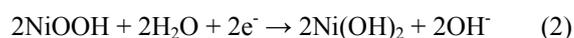
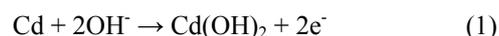
At industrial level, the recycling of spent Ni-Cd batteries is currently done using essentially pyrometallurgical processes, for instance Inmetco (USA), Accurec (Germany), SabNife (Sweden) or Snam-Svam (France). Some hydrometallurgical processes are also

employed, e.g. Batenus (Germany) or TNO (Holand). These are based mainly on solvent extraction by electrowinning, ion exchange or membrane technology [5].

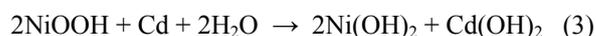
The pyrometallurgical processes are relatively simple, but are not appropriate due to the high energy requirements and the emission of toxic gases in the environment. The hydrometallurgical processes are more environmental suitable and also have some economical advantages such as complete recovery of metals with high purity and low energy requirements.

The hydrometallurgical processes have been investigated in detail by the various researchers [5-7]. Have been reported studies on acidic leaching [8-10], solvent extraction of cadmium and nickel ions [4,11-14], electrodeposition of cadmium [1,8,15], selective precipitation of cadmium [16], recycling of Ni-Cd batteries through vacuum distillation [17]. Also, the biohydrometallurgical methods may be a valuable alternative choice to treat spent batteries [18].

The positive electrode of Ni-Cd batteries is made up of NiOH/Ni(OH)₂ and additives such as graphite and cobalt, and the negative electrode is made of cadmium. The electrodes are isolated by polyethylene, cardboard or polypropylenes separators. The electrolyte is a solution made of KOH and LiOH [1]. The reactions at the two electrodes are as follows:



The general discharge reaction of the Ni-Cd battery can be written:



In this work, nickel and cadmium was recovered from spent Ni-Cd batteries by an acid-leaching operation followed by electrodeposition. The tests have been made without a separation of interesting metals.

The following techniques were used for material characterization: atomic absorption spectrometry (AAS), scanning electronic microscopy (SEM) and energy dispersive spectroscopy (EDAX).

2. Experimental

Spent batteries were disassembled in following more steps: manually cutting procedure, protective plastic coating removal and leaching out the pieces with HCl 9 M. The ratio liquid/solid was 1/8. The time for leaching was 2.5 hours (under stirring) at 120 °C.

After acid-leaching, the amount of residue was removed by filtration. The leaching solution had a clear green color due to the presence of nickel ions. The pH of the solution was found to be less than unity. The chemical composition of Ni and Cd in the leach solution was quantitatively analyzed by atomic absorption spectrometry.

AA spectrometry has been achieved with a novAA 400 G type spectrometer - Analytik Jena - Germany, equipped with an graphite furnace, WinAAS 3.17.0 software for evaluation, control and result presentation, a so-called cookbook, for every element, and a HS 55/1 hydride generator [19].

After filtration of paper and carbon residues, the each 20 ml leach liquor for studies was treated with saturated solutions of sodium hydroxide and sodium citrate (Aldrich) to pH=4.9 (sample after treatment has 28 ml). The organic complex reagent help to stabilize and buffer the liquor electrolyte. The citrate complex was found to be the most efficient reagent for stabilizing the metallic ions [8].

Electrochemical recovery of nickel and cadmium was carried out in a 50 cm³ BEC/EDI X51 V001 three-electrode electrochemical cell. The working electrode was manually manufactured of flat copper plate ($S_{\text{work}}=3 \text{ cm}^2$). Before each experiment, the copper electrodes are roughen with HNO₃ 30% and then rinsed with distilled water. The auxiliary electrode was platinum with geometric area of 50 mm². A saturated calomel electrode (SCE) was used as the reference electrode. Electrodepositions have been studied on various potential intervals and rates of registration by Voltalab 80 PGZ 402 apparatus from Radiometer Copenhagen, equiped with VoltaMaster 4, 7.0 software. For each sample 10 cycles have been ran. All electrochemical experiments were performed at 25°C.

A Scanning electron microscope (SEM) Inspect S – FEI Company equiped with an energy dispersive detector EDAX Genesis XM 2i was used for deposits characterization.

3. Results and discussion

The concentrations of cadmium and nickel ions in the obtained leach solution have been analyzed by atomic absorption spectrometry. Calibration curves have been

plotted using standard solution of Ni(NO₃)₂ 1g/L and Cd(NO₃)₂ 1g/L. The experimental results for the two major metal ion concentrations are following: 8375 ppm Cd and 4488.5 ppm Ni.

The leaching solution was divided in equal volumes before starting the electrodeposition tests. Each solution was treated with saturated solution of NaOH and sodium citrate for pH adjustment.

The electrodeposition of cadmium and nickel from the leaching solutions with pH=4.9, was conducted by varying the applied potential in the range -200 to -1300 mV at different scan rates. After several tests, it has been noticed that the electrodeposition carried out between (-1000 mV) – (-1300 mV) is the most efficient.

In figures 1 and 2 are presented the voltammograms for electrodeposition process of the metal from two solutions at the same potential interval and scan rate of 50 mV/s, and 10 mV/s respectively.

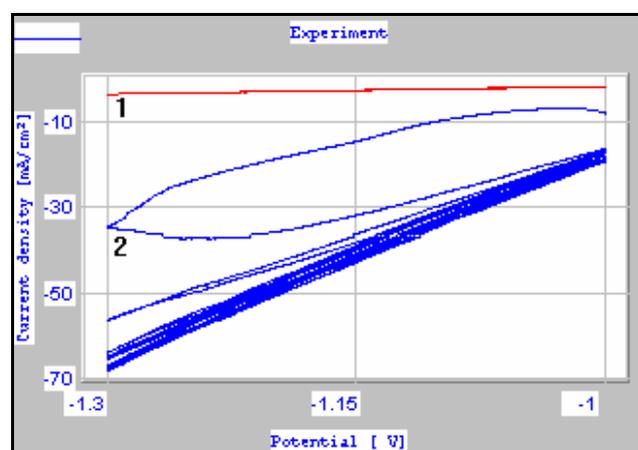


Figure 1. Voltammograms for sample 1, at potential (-1000)-(-1300) mV, scan rate = 50 mV/s
1 – electrolyte support HCl 2N; 2 – sample 1

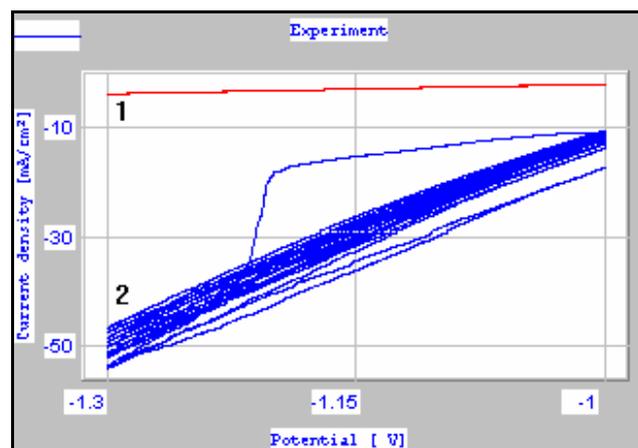


Figure 2. Voltammograms for sample 2, at potential (-1000)-(-1300) mV, scan rate = 10 mV/s
1 – electrolyte support HCl 2N; 2 – sample 2

Regarding to potential interval and scan rates according to the voltammograms from Fig. 1 and Fig. 2, the macroscopic aspect of deposits obtained on the copper electrodes are presented in Fig. 3.

A higher and compact electrodeposit it has been observed at 10 mV/s scan rate then at 50 mV/s scan rate.

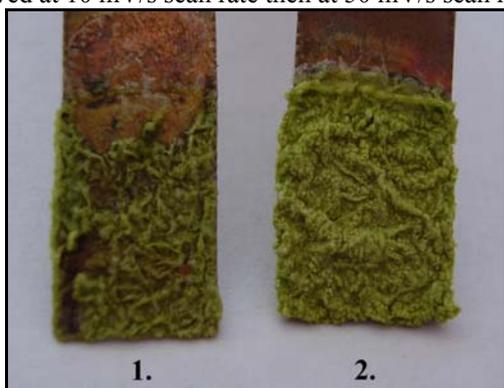


Figure 3. Macroscopic aspect of electrodeposition for samples 1 (50 mV/s) and sample 2 (10 mV/s)

Also, an experiment at a scan rate of 1 mV/s it has been made. A thicker electrodeposit has been obtained, but it is very spongy and inadherent. At the electrode removing from the electrolyte solution, a part of this deposit it has detached (Fig. 4).



Figure 4. Macroscopic aspect of electrodeposition for samples 3 (1 mV/s)

The surface of the deposit obtained at 50 mV/s scan rate was characterized by SEM and EDAX analyses (Fig. 5 and Fig. 6).

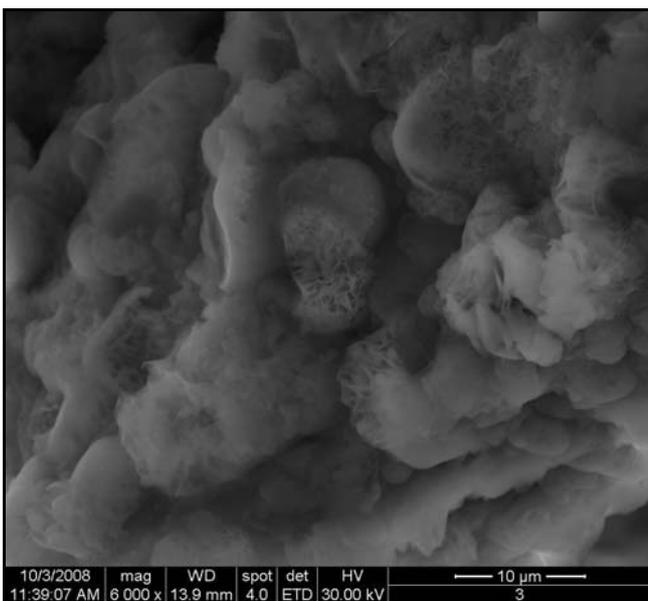


Figure5. Typical scanning electron microscopy (SEM) of electrodeposition (sample 1)

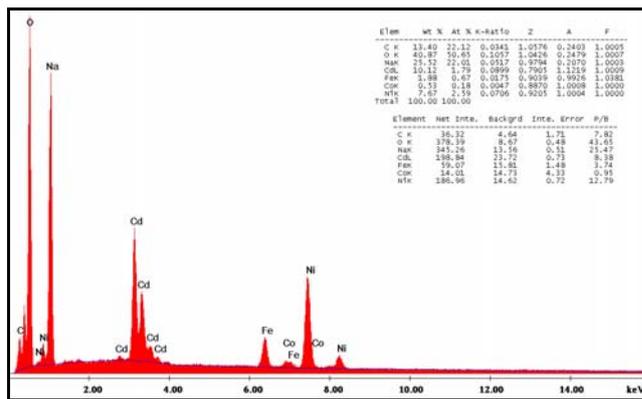


Figure 6. EDAX diagram of deposit for sample 1

The SEM and EDAX analyses for the surface of the deposit obtained at 10 mV/s scan rate are presented in Fig. 7 and Fig. 8.

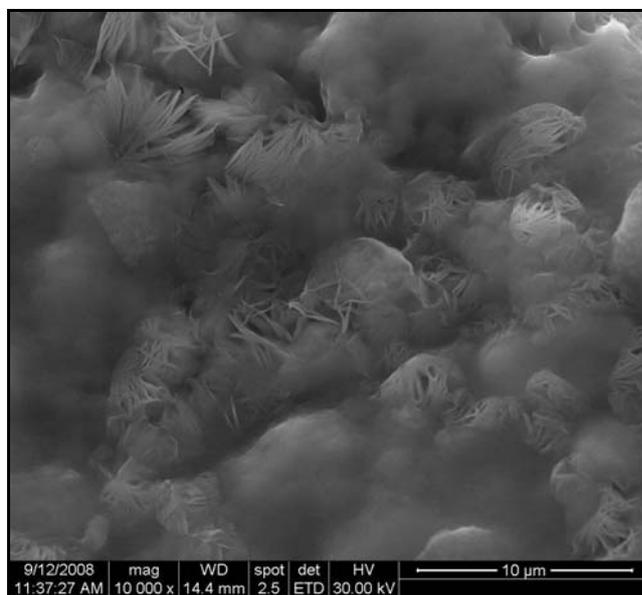


Figure7. Typical scanning electron microscopy (SEM) of electrodeposition (sample 2)

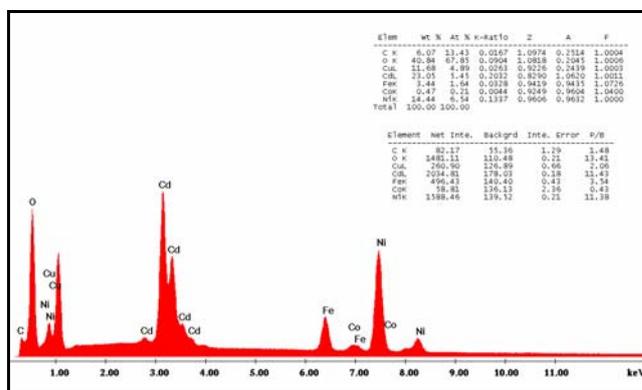


Figure 8. EDAX diagram of deposit for sample 2

It has been observed from EDAX diagrams (Fig. 6 and Fig. 8) that a large amount of cadmium, then nickel was detected in electrodeposits. Besides cadmium and nickel,

the presence of iron and cobalt is also observed in the EDAX spectra.

It has been obtained 10.12 % Cd and 7.67 % Ni in the deposit resulted at scan rate of 50 mV/s, respectively 23.05 % Cd and 14.44 % Ni in the deposit obtained at 10 mV/s.

4. Conclusions

Cadmium and nickel have been recovered from spent batteries by an acid-leaching process followed by an electrochemical technique.

Relatively larger and more uniform deposits on the surface of the working electrode can be observed at potentials between (-1000) and (-1300) mV and scan rate of 10 mV/s. At a rate of 50 mV/s the process occurs more randomly, as if the layers have not enough time to cover each other. At a rate of 1 mV/s a part of deposit detached from the electrode (sample 3).

EDAX analyses show that in the case of electrodeposits obtained at scan rate of 10 mV/s, the amounts of Cd and Ni in deposit are higher than at 50 mV/s.

This work will be continued with other experiments for selective recovery of nickel and cadmium from Ni-Cd spent batteries. Several methods like selective precipitation or solvent extraction will be used for metals recovery. Other acids and other electrochemical conditions will be tested for leaching liquors processing of spent Ni-Cd batteries. Also, we focus on the recovery of Ni from the spent Ni-MH batteries.

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