

Short communication

Electrochemical recovery of cadmium from spent Ni–Cd batteries

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Abstract

In this work, cadmium from spent Ni–Cd batteries is recycled. Ionic cadmium is recovery from acidic solution using a galvanostatic technique. Electrodeposition charge efficiency and deposit morphology depend on current density. Charge efficiency reaches up to 85.0% for a current density between 5.0 and 10.0 mA cm⁻² and decreases with the increase in current density. Pore size decreases with the increase in current density.

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1. Introduction

Rechargeable Ni–Cd batteries have been used since 1950 in applications that require high energy density, long lifetime, and high discharge rates. Ni–MH and lithium batteries also have these properties, but they are more expensive. Therefore, Ni–Cd batteries are used in many countries [1,2]. Ni–Cd batteries pose a risk to the environment and to health [3]. The cadmium present in the negative electrode is a carcinogenic agent. Therefore, Ni–Cd batteries are considered a hazardous residue [4]. As spent Ni–Cd batteries cannot be discarded in domestic garbage or in municipal landfills [5], they are collected by manufacturers for recycling either by pyrometallurgical or hydrometallurgical processes [6–8]. Recycling by pyrometallurgical process is not appropriate due to the emission of toxic gases, which can contaminate the environment. Recycling batteries by a hydrometallurgical process is an alternative solution for the environmental problem. The hydrometallurgical process involves electrochemical and chemical transformations. Electrochemical recycling of cadmium from spent Ni–Cd batteries is viable from the environmental point of view, as it does not produce pollut-

ing residues. Electrochemical recycling of Cd²⁺ from acidic solutions also has scientific interest. The adsorbed hydrogen catalyses metal electrodeposition onto steel, similar to the electrodeposition of ionic zinc from acidic solution. This explains the high charge efficiency obtained for ionic metal recovered from acidic solutions [9]. In the present work, the electrochemical recycling conditions of cadmium from spent Ni–Cd batteries were developed and the relation between current density and deposit morphology was analysed. The materials obtained under different conditions were analysed by X-ray diffraction, scanning electron microscopy (SEM), and energy dispersive X-ray analysis (EDX).

2. Experimental

The battery recycling process requires conditions of selective collection, disassembly, and a sequence of physical and electrochemical transformations. In the selective collection, spent batteries are classified in homogeneous lots. Spent type AA Ni–Cd batteries produced by Toshiba (3.6 V, 600 mAh) were used in this research. In the disassembly, spent batteries are physically separated into their different parts: anode, cathode, steel, separators, and current collectors. On average, the

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total weight of Ni–Cd batteries corresponds to: anode 25%, cathode 34%, and steel, separators and current collectors, 41%.

2.1. Leaching of cadmium electrodes

The anode and the current collectors of spent Ni–Cd batteries are made of cadmium hydroxide. The leaching condition was: 1.0369 g of anode material per 100 ml of H_2SO_4 0.5 mol l^{-1} solution. The suspension was maintained under constant stirring at 298 K. After the dissolution of cadmium hydroxide, the current collector was removed from the solution and the suspension was filtered. The pH and the conductivity of the leaching solution were equal to 0.571 and $362.2 \text{ mS cm}^2 \text{ mol}^{-1}$, respectively. The current collector weighed 0.1467 g. Therefore, the concentration of ionic cadmium in the leaching solution, not taking contamination into consideration, was approximately equal to $0.06080 \text{ mol l}^{-1}$. The leaching solution had a clear green colour due to the presence of ionic nickel from the cathode.

2.2. Electrochemical cell

The working electrode was made with 1020 steel. The electrodes were rectangular steel pieces with a geometric area of 0.20 cm^2 each. The auxiliary electrode was platinum with a geometric area of 3.75 cm^2 . The reference electrode was Ag/AgCl/NaCl. Before each electrochemical experiment, the working electrodes were sanded with 600-grit sandpaper and then rinsed with distilled water. Galvanostatic experiments were performed with a regulated power supply built in the laboratory. The work and auxiliary electrodes were connected to the voltmeter and to a microcomputer through an RS232 interface. The electrolyte solutions were prepared with reagent p.a. and pure water. Solutions were changed after each experiment. All electrochemical experiments were performed at 298 K.

2.3. Characterisation techniques

The following techniques were used for material characterisation: scanning electron microscopy, X-ray diffraction, and energy dispersive X-ray analysis. The following instruments were used in measurements: JEOL JXA, model 8900RL equipped with an energy dispersive X-ray detector, Rotaflex-Rigaku model 200B diffractometer.

3. Results and discussion

3.1. Characterisation of cadmium electrodes

The surface and the bulk of the anodes of spent Ni–Cd batteries were analysed by SEM, EDX, and X-ray diffraction. A typical SEM of a discharged anode surface from spent Ni–Cd batteries is shown in Fig. 1A. Fig. 1B gives an enlargement of

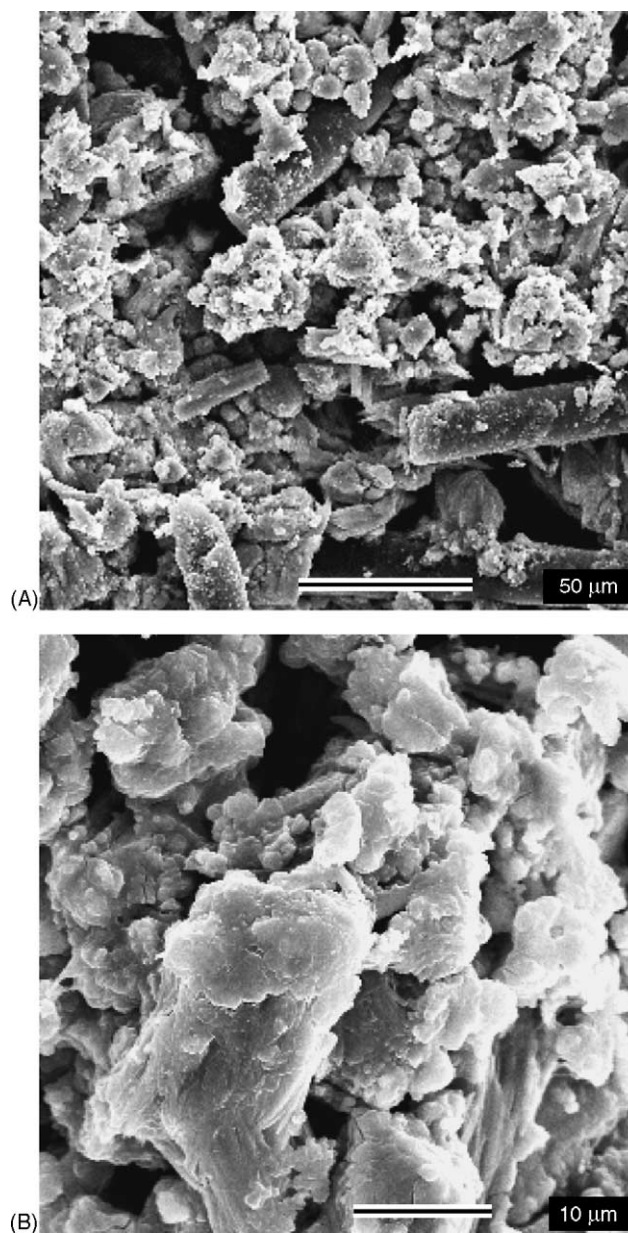


Fig. 1. Typical scanning electron microscopy for discharged anode of the spent Ni–Cd battery. (A) 500 \times ; (B) 2000 \times .

the central parts of Fig. 1A. Macropores and micropores can be seen in the microphotograph of the surface of the electrodes. The macropores assure the diffusion of the solution to areas where the electrochemical reactions occur. The micropores afford a larger reaction area on the electrode. EDX analysis (Fig. 2) shows that the anode surface is contaminated with Ni and Co from the positive electrode and K from the electrolyte. The X-ray diffraction of the bulk of the discharged anode is shown in Fig. 3. In comparison with JCPDS cards, it was found that the relative intensities of the diffracted X-ray peak nearly resemble those tabulated for cadmium hydroxide [10].

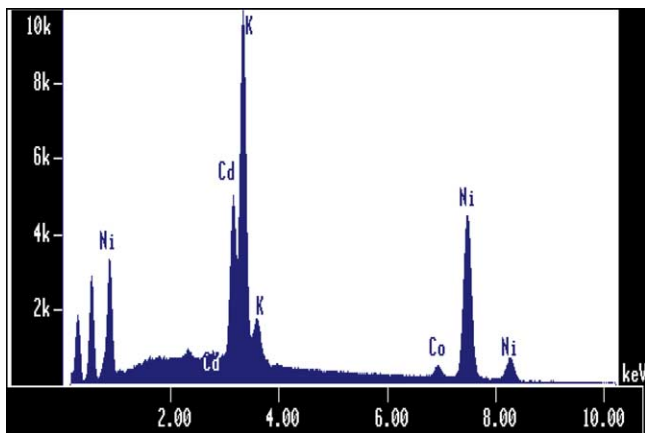


Fig. 2. Typical energy dispersive analysis of X-ray for discharged anode of the spent Ni–Cd battery.

3.2. Electrochemical recycling of cadmium

Cadmium electrodeposition was carried out at different current densities. Independent of the current density applied in the interval between 1.0 and 50.0 mA cm⁻², a transient potential was observed as soon the current was turned on. The transient potential was slower for low current density. It is associated with hydrogen evolution and the formation of active cadmium sites by nucleation. The current density decreased with the increase in deposit surface area. As a result, the potential led to lower cathodic values with increasing electrodeposition time. Fig. 4 shows a typical chronopotentiometric plot for Cd²⁺ electrodeposition in acidic solution. The hydrogen evolution reaction and cadmium electrodeposition occur at the same time. The increase in hydrogen evolution on metallic cadmium reduced charge efficiency ($\alpha = Q_{\text{deposition}}/Q_{\text{applied}}$), as shown in Fig. 5.

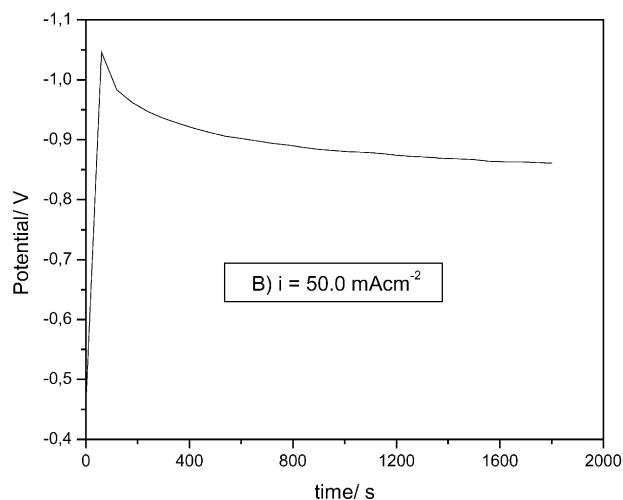
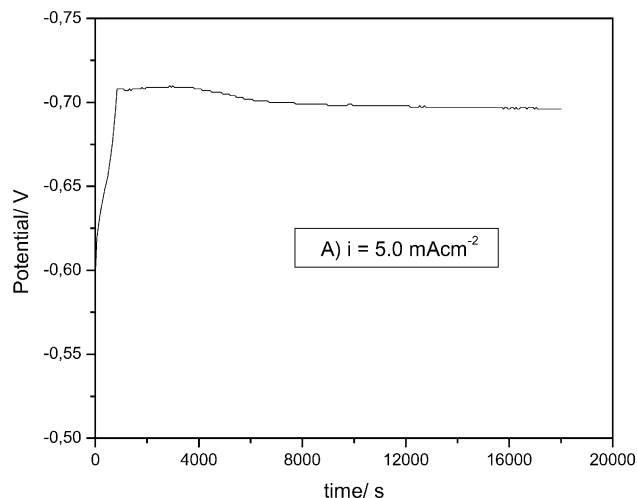


Fig. 4. Chronopotentiometric plot for ionic cadmium electrodeposition in acidic solutions, H₂SO₄ 0.5 mol l⁻¹, 298 K, without stirring; $q_{\text{applied}} = 90.0 \text{ C cm}^{-2}$. (A) $i = 5.0 \text{ mA cm}^{-2}$; (B) $i = 50.0 \text{ mA cm}^{-2}$.

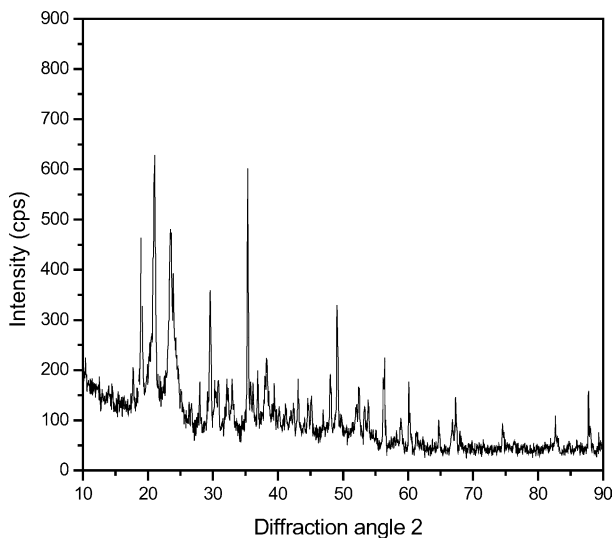


Fig. 3. Typical X-ray diffraction for discharged anode of the spent Ni–Cd battery, cadmium hydroxide JCPDS Card No. 40-0760.

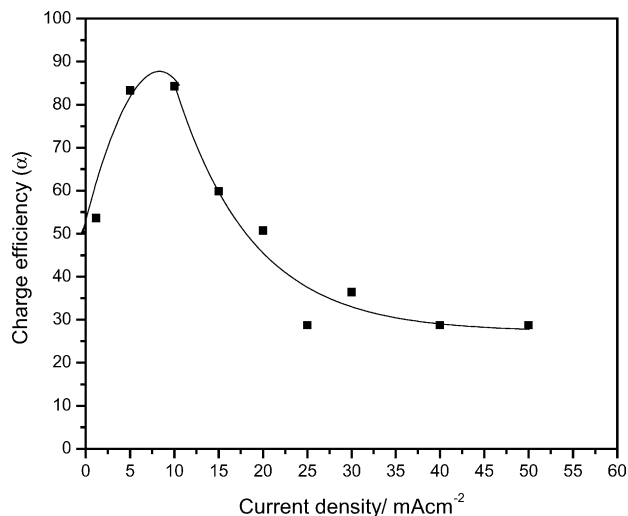


Fig. 5. Charge efficiency in function of the current density for cadmium electrodeposition, acidic solutions, H₂SO₄ 0.5 mol l⁻¹, 298 K, without stirring; $q_{\text{applied}} = 90.0 \text{ C cm}^{-2}$.

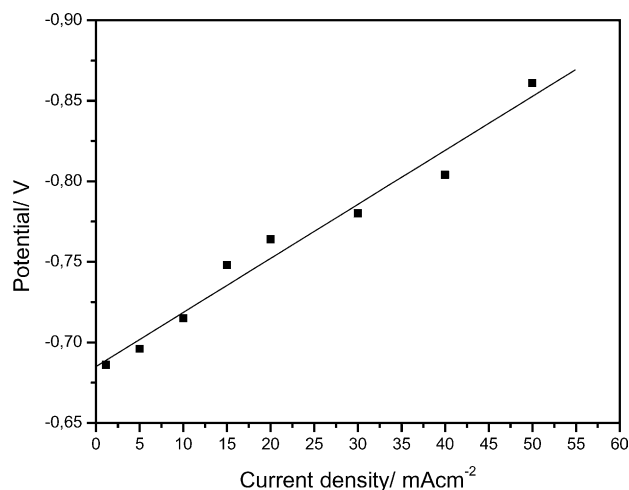


Fig. 6. Patamar potential in function of the current density for cadmium electrodeposition in acidic solutions, H_2SO_4 0.5 mol l^{-1} , 298 K, without stirring; $q_{\text{applied}} = 90.0 \text{ C cm}^{-2}$.

Activation or mass transport can affect the electrodeposition process. The relation between the potential and the current density follows the Tafel equation when it is activation controlled. The potential is independent of current density when electrodeposition is controlled by mass transport [11]. This behaviour is verified for electrodeposition of ionic metal on plane electrodes. However, for porous electrodes, the control of the kinetic reaction changes with the position on the electrodes. The kinetic reaction can be controlled by mass transport inside the pores and by activation on the electrode surface. There is dual control. In addition, due to the water decomposition reaction, cadmium hydroxide films precipitated onto the deposit. This superficial film inhibits current passage and increases the resistance of the deposit, as confirmed by experiments [12]. Because of this behaviour, for constant charge density, the cathodic potential increased linearly with the increase in current density, as can be seen in Fig. 6. The relation between potential and current density can be written as follows:

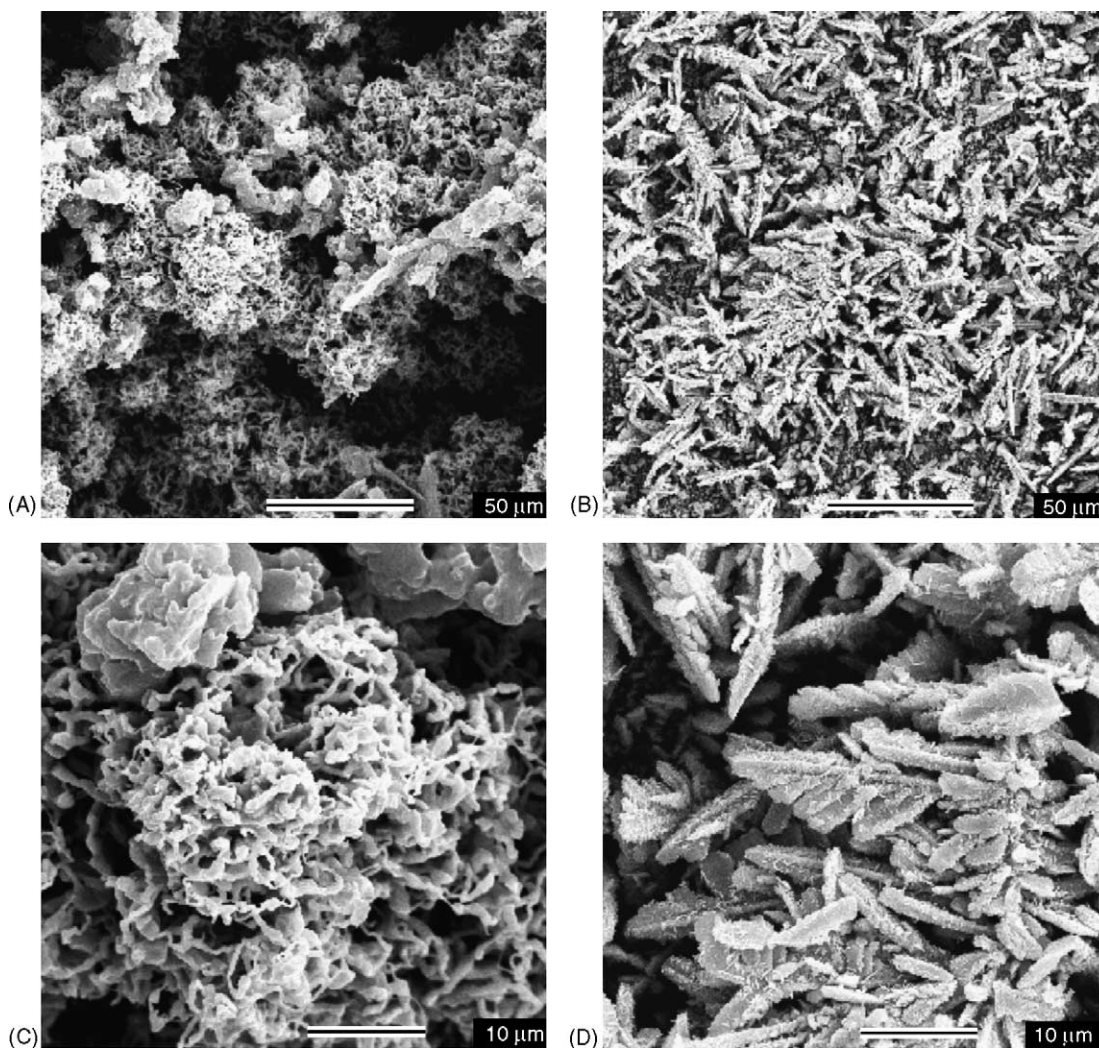


Fig. 7. Typical scanning electron microscopy for cadmium electrodeposit. (A) $i = 5.0 \text{ mA cm}^{-2}$ and magnification factor 500 \times ; (B) $i = 50.0 \text{ mA cm}^{-2}$ and magnification factor 500 \times ; (C) $i = 5.0 \text{ mA cm}^{-2}$ and magnification factor 2000 \times ; (D) $i = 50.0 \text{ mA cm}^{-2}$ and magnification factor 2000 \times ; $q_{\text{applied}} = 90.0 \text{ C cm}^{-2}$.

$$\eta = E_R + R_i \quad (1)$$

where η is the cathodic potential for i applied, E_R is the rest potential, i is the cathodic current density applied, and R is the resistance of the deposit.

3.3. Morphology of cadmium electrodeposit

The density of the applied current affects not only charge efficiency of deposition but also the morphology of the deposit. The crystallisation process begins with the growth of nuclei. The rate and the direction of nucleus growth affect the morphology of the deposit. For low current densities, the nucleus growth rate perpendicularly to the electrode surface is larger than in other directions. In this case, can be seen large microporosity in the crystal agglomerates and large macropores between the agglomerates. For high current densities, the nucleus growth rate in the direction parallel to the electrode surface is larger than that in other directions. In this case, microporosity decreases and the macropore extension between the agglomerate is smaller. The morphology of the cadmium electrodeposit can be seen in Fig. 7.

4. Conclusions

The anodes of spent Ni–Cd batteries were analysed by SEM, EDX, and X-ray diffraction. the macropores and micropores can be seen in the microphotograph of the electrode surface. EDX analysis showed that the anode surface is contaminated with Ni, Co, and K. According to X-ray diffraction measurements of the bulk of the discharged anode, it is composed of cadmium hydroxide.

In the interval between 1.0 and 50.0 mA cm⁻², there is a transient potential associated with hydrogen evolution and the formation of active cadmium sites by nucleation. The increase in hydrogen evolution on metallic cadmium reduces charge efficiency. Maximum charge efficiency is equal to 85.0%. In porous electrodes, the electrodeposition mechanism of ionic cadmium from acidic solution changes with the position on the electrodes. Control by activation and mass transport can occur in the same process. Therefore, the cathodic potential increases linearly with the increase in current density. The rate and the direction of nucleus growth affect the morphology of the deposit. Micropore and macropore size decreases with the increase in current density.

References

- [1] C.J. Rydh, M. Karlström, *Resour. Conserv. Recycl.* 34 (2002) 289.
- [2] C.J. Rydh, B. Svärd, *Sci. Total Environ.* 302 (2003) 167.
- [3] T. Osawa, E. Kobayashi, Y. Okubo, Y. Suwazono, T. Kido, K. Nogawa, *Environ. Res. Sect. A* 86 (2001) 51.
- [4] M.P. Waalkes, *J. Inorg. Biochem.* 79 (2000) 241.
- [5] CONSELHO NACIONAL DO MEIO AMBIENTE (CONAMA), Resolution n. 257, June 30, 1999, Diário Oficial da União (DOU) July 22, 1999.
- [6] M. Bartolozzi, G. Braccini, S. Bonvini, P.F. Marconi, *J. Power Sources* 55 (1995) 247.
- [7] P. Ammann, *J. Power Sources* 57 (1995) 41.
- [8] A.M. Bernardes, D.C.R. Espinosa, J.A.S. Tenório, *J. Power Sources* 130 (2004) 291.
- [9] M.B.J.G. Freitas, M.K. de Pietre, *J. Power Sources* 128 (2004) 343.
- [10] Joint Committee on Power Diffraction Standards (JCPDS), Card No. 40-0760.
- [11] K.J. Vetter, *Electrochemical Kinetics: Theoretical and Experimental Aspects*, first ed., Academic Press, New York, 1967.
- [12] M.B.J.G. Freitas, R. Bonfá, C.V. D'Alkaine, in: *Proceedings of the Interfinish Latino-Americano-EBRATS*, São Paulo, Brazil, 1997, p. 59.