

Recycling of nickel–cadmium batteries—Thermogravimetric behavior of electrodes

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Abstract

Although the use of nickel–cadmium batteries is decreasing mainly due to environmental concerns; nickel–cadmium batteries are the only ones that present an established recycling process. On the other hand, the fundamentals of such processes were not well studied. The aim of this work is to investigate the thermal behavior of the electrodes of nickel–cadmium batteries during the conditions used in the recycling process. Tests were carried out using a thermobalance simulating different recycling conditions. Vacuum decomposition of cadmium oxide occurs in two steps. The first step presents a fast rate of decomposition where almost 95% of the reaction is observed. The second step exhibits a low decomposition rate. The same behavior was observed using a reducing agent. Increasing the temperature increases dramatically the rate of cadmium oxide reduction and decomposition.

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1. Introduction

The increase in the consumption of batteries for household appliances and the generation of legislation regulating and promoting the treatment of NiCd household batteries have turned this kind of battery into an increasingly representative material to be recycled.

In the existing pyrometallurgical processes of recycling of NiCd vented batteries, the separation of internal components is very simple. The separation of internal components of sealed batteries is not as simple as for vented batteries. The size and construction of sealed batteries are factors that impede this operation. Thus, the development of processes for the preparation of sealed batteries for distillation treatment is necessary.

Household batteries are composed of some sealed batteries inside a shock resistant plastic case, like batteries for cell phones, notebooks or electric tools. The Inmetco, Sab-Nife and Snam processes have an initial step for combustion of the plastic case.

The Accurec process separates the plastic case of household batteries, but there is no information concerning the specific method used in this operation [1]. Tenório and Espinosa [2] showed the feasibility of the separation of this plastic case. This treatment, besides recovering a recyclable material, is a process which is cheaper than combustion.

The Inmetco process uses carbon as a reducing agent for cadmium oxide and the Sab-Nife process uses carbon to reduce oxygen in the retort. Results obtained by Espinosa and Tenório [3] show that the addition of carbon is not necessary for NiCd sealed batteries. Vacuum or inert gas based processes are called “closed furnace processes”.

To recycle NiCd batteries to obtain cadmium oxide as a product is also possible. These processes use neither vacuum nor inert gas atmosphere and operate at high temperatures with no controlled atmosphere. These processes are known as “open furnace processes”. Cadmium oxide is recovered in the bag house installed at the furnace gas exit. Such was the Inmetco process before 1995 [1].

Metallic cadmium and an iron and nickel alloy are produced in “closed furnace processes”. According to Espinosa and Tenório [3] Cd produced presents up to 100 ppm of cadmium after distillation treatment at 900 °C. Nickel based

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alloy obtained can be used in the production of stainless steel.

Cadmium can be used in the production of new batteries or for electrodeposition.

Pb-acid, NiCd, NiMH and lithium-ion are the main rechargeable household batteries. The Pb-acid battery recycling process is well established and Pb-acid batteries are recycled in several countries around the world. These countries have also developed collection programs for this type of battery. Then, even containing Pb, which is a toxic metal, this kind of battery is still in use and do not represents a great environmental risk, as it presents a high recycling rate and is not disposed in landfills.

The use of NiCd accumulators became more significant in the second half of the 20th century. This use increased dramatically from the 1980s, resulting from the increase in the use of electronic devices. At that time, disposal of household NiCd batteries in landfills became a matter of concern. Estimates of battery disposal indicated that it would be a problem in a short period of time. A 100 days study showed that mercury batteries suffered corrosion in landfills, releasing their contents. Dry cell batteries also showed evidence of corrosion. NiCd batteries were perforated during 100 days, but their contents were not released. It was estimated that a longer period of time would cause the NiCd batteries contents to be transferred to the leachate in the landfill [4].

There are currently several operating systems for recycling of NiCd batteries [1]. On the other hand, collection system for this product is not as established as the system for Pb-acid batteries. In the USA, the Rechargeable Battery Recycling Corporation (RBRC) collects NiCd batteries and ships them to Inmetco for recycling. Since 2000, RBRC also collects other types of batteries for recycling. Besides the accumulators sent by RBRC, Inmetco also receives batteries sent by mail.

In Europe, the European Portable Battery Association (EPBA) collects batteries and promotes collection and separation programs by publicity and conferences.

Household NiCd batteries are being replaced by NiMH and lithium-ion batteries. These batteries, even though considered environmentally less aggressive, do not have a well-established recycling process, such as for NiCd batteries. In addition, such systems present a higher cost for the consumer.

NiCd batteries are the only ones with an established recycling process, except Pb-acid batteries. Although the NiCd batteries are potentially more hazardous than NiMH and lithium-ion, NiCd batteries have a completed life cycle and, consequently, are considered more sustainable.

In addition, adoption of a sustainable growth model for the energy sector is necessary. In this scenario, vented NiCd batteries are still one of the main alternatives, as more recent systems (NiMH and lithium-ion) are still far from presenting the same recycling performance.

Hence, one of the alternatives towards a sustainable development in this sector would be the development of specific goals for recycling, including the recycling costs in the products.

Such actions would stimulate not only the implementation of education, collection and recycling systems, but also the devel-

opment of new batteries, recyclable through easier processes, with lower contents of toxic metals.

2. Objective

The objective of this work is to investigate the thermogravimetric behavior of the electrodes of NiCd batteries during the conditions used in the recycling process.

3. Methodology

All thermogravimetric tests were conducted using a Netzsch STA 409 and an alumina crucible.

As the electrodes were the only components of NiCd batteries that contain cadmium, thermogravimetric tests were carried out on both electrodes in order to understand the distillation process of the cadmium contained in these batteries.

Electrodes were manually separated from used batteries and the samples were homogenized in a low rotating speed ceramic mixer. The needed samples were approximately 250 mg. Tests were conducted in order to study the effect of atmosphere on mass loss for both electrodes separated. Three types of tests were conducted: under vacuum, nitrogen atmosphere and by using a reducing agent.

Two additional thermogravimetric tests were carried out. The first one using anthracite as reducing agent; and the second one using a fabric, in which the electrolyte is impregnated, as a reducing agent. These tests were conducted in order to check whether the fabric contained in the batteries could effectively act as the reducing agent.

3.1. Vacuum tests

A vacuum pump and a vacuum meter were attached to the thermoanalysis equipment. Each test was divided in two steps. The first step was conducted under static air, i.e., the furnace was closed, with no gas being injected into the retort. The sample was packaged in an alumina crucible and placed in the microbalance. Heating rate was $50\text{ }^{\circ}\text{C min}^{-1}$ up to $500\text{ }^{\circ}\text{C}$ and $35\text{ }^{\circ}\text{C min}^{-1}$ up to the final temperature.

The furnace, which was equipped with an alumina retort and the highest possible heating rates were used. The sample was kept at the required temperature for 30 min, when there was mass stabilization, i.e., in this time the sample no longer lost mass.

The second step consisted applying a vacuum to the furnace chamber where the sample remained at the test temperature. The mass loss was noted in this step. The test was concluded when the sample no longer lost mass. Temperatures analyzed were 800, 850, 900, 950 and $1000\text{ }^{\circ}\text{C}$ (Table 1).

The first step of the test was to allow evaporation of moisture and elimination of volatile material contained in the sample, besides allowing the decomposition of hydroxides. According to the thermodynamic evaluation presented previously, cadmium oxide does not decompose under the oxidizing atmosphere at the temperatures studied. Hence, there is no cadmium oxide decomposition during this first step. Thus, the second step of test

Table 1
Thermogravimetric analyses under vacuum

Negative electrode		Positive electrode	
Name	Temperature (°C)	Name	Temperature (°C)
V800PC	800	V800PP	800
V850PC	850	V850PP	850
V900PC	900	V900PP	900
V950PC	950	V950PP	950
V1000PC	1000	V1000PP	1000

consists of monitoring the sample mass loss related to cadmium distillation.

The material that remained in the crucible was characterized by scanning electron microscopy coupled to an EDS microprobe.

3.2. Tests under inert gas atmosphere

The procedure adopted in these analyses was similar to that used in vacuum tests. The difference was the injection of nitrogen in the furnace, instead of a vacuum furnace chamber. The test was concluded when the sample no longer lost mass.

Two tests were performed as shown in Table 2.

3.3. Tests using a reducing agent

Load preparation was performed according to the following procedure. About 10 g of material from the negative electrode was packaged in an alumina crucible. The crucible was held at 500 °C for 2 h in a muffle furnace, in order to decompose the hydroxide. Following the cooling, a reducing agent was mixed with the electrode. The reducing agent was added in excess of 20% on the stoichiometric quantity, in order to completely reduce the cadmium oxide. The reducing agent used was anthracite, with 100% particle size up to 0.106 mm and with 83.83% of fixed carbon.

Thermogravimetric tests were carried out according to the following parameters:

- heating rate: 30 °C min⁻¹ up to the test temperature;
- crucible: alumina;
- atmosphere: 35 mL min⁻¹ of nitrogen standard grade.

The tests were stopped when the rate of mass loss observed to be negligible.

In this test, all the mass loss was considered to be caused by Cd distillation, since hydroxide decomposition was performed during sample preparation. The tests were carried out as shown in Table 3.

Table 2
Thermogravimetric tests under nitrogen atmosphere

Sample name	Temperature (°C)
N850PC	850
N950PC	950

Load: negative electrode.

Table 3
Thermogravimetric tests with reducing agent and under nitrogen atmosphere

Name	Temperature (°C)
N650PCC	650
N750PCC	750
N800PCC	800
N900PCC	900
N1000PCC	1000

Load: negative electrode.

3.4. Reducing agent

Mass loss tests were performed with the anthracite used in the reduction tests and with the fabric which is the carrier for the electrolyte. These tests were conducted in order to evaluate whether the fabric could act as a reducing agent. In the manual dismantling step, since part of the fabric remains attached to the negative electrode, so the fabric sample was obtained by manual separation from the negative electrode paste using tweezers. Tests were carried out under the following conditions:

- crucible: alumina;
- final temperature: 900 °C;
- heating rate: 5 °C min⁻¹;
- atmosphere: 30 mL min⁻¹ of O₂ and 65 mL min⁻¹ of Ar.

4. Results and discussion

Three types of thermogravimetric test using depleted sealed NiCd batteries were performed, under vacuum, nitrogen atmosphere and by using a reducing agent. These tests were performed in order to study Cd distillation under different conditions.

4.1. Vacuum tests

4.1.1. Negative electrode

Fig. 1 shows the curve obtained in test V950PC. Curves from other tests exhibited a similar shape. A two-step pattern can be clearly identified in Fig. 1. One can also notice that there was

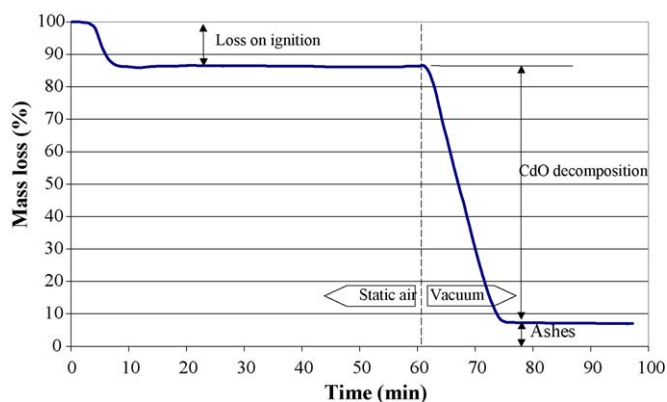


Fig. 1. Thermogravimetric curve of test V950PC ($T=950$ °C, vacuum).

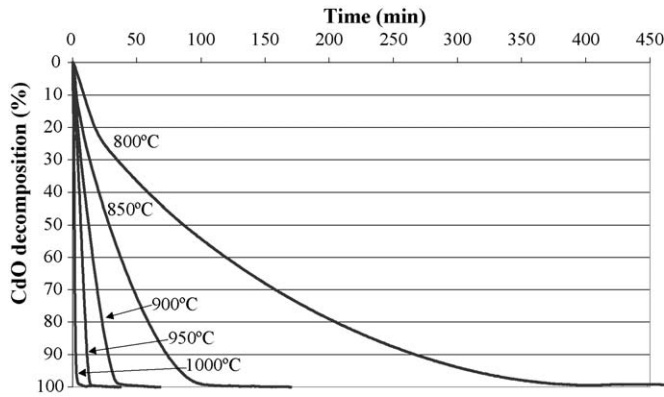


Fig. 2. Cd elimination percentage in the negative electrode in function of time.

not a complete mass loss, since ashes remain in the crucible at the end of the test.

In the first step, there was no cadmium evaporation and mass loss occurred mainly by $\text{Cd}(\text{OH})_2$ decomposition. In the second step CdO decomposition is considered to occur, generating cadmium vapor. Thus, in order to study cadmium distillation or removal, the second step was isolated in all tests. So, part of the curve related to the first step was ignored and the mass loss was considered 100%. This approach was carried out as the sample no longer lost mass, even at temperatures of 1000 °C. This indicated that the residue contained no volatile material.

Fig. 2 shows the Cd elimination percentage as a function of time for all tests performed under vacuum. Curves from tests carried out at 800 and 850 °C can be divided in three distinct steps. First, an enhanced mass loss, followed by a reduction in the mass loss rate. When this mass loss approaches 100%, the mass loss rate fell dramatically.

In the tests above 900 °C only two steps could be identified, one with an enhanced mass loss rate, up to almost 100%, followed by a dramatic reduction in this rate.

The time at which the last step was identified was plotted against the test temperature and the curve is shown in Fig. 3. One can observe that the Cd elimination rate at temperatures above 900 °C is modestly affected by temperature increase. On the contrary, at temperatures up to 900 °C, the time for Cd elimination increased significantly with temperature reduction.

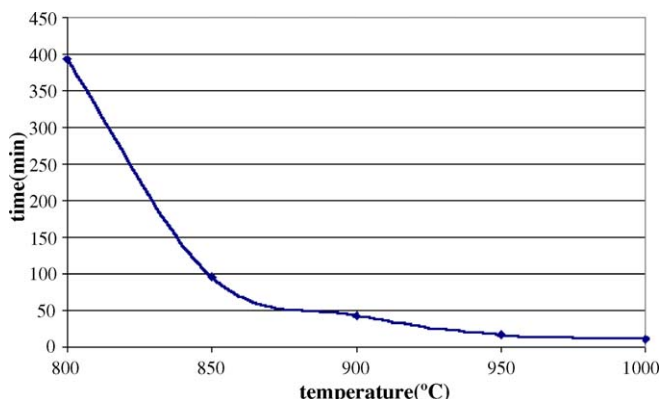


Fig. 3. Time variation for cadmium elimination as function of test temperature.

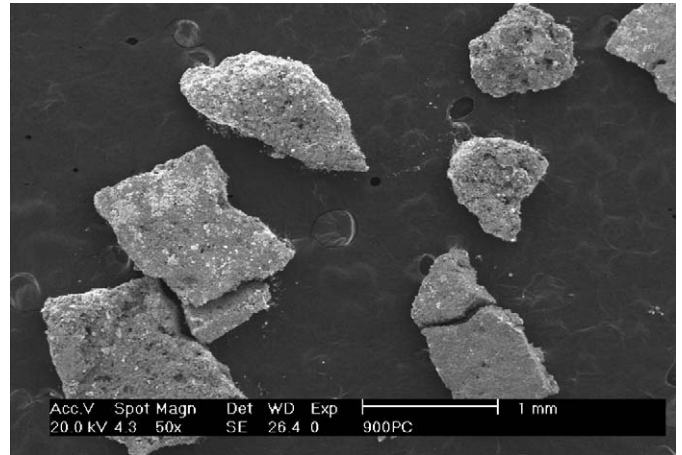


Fig. 4. Particles of material remaining inside the crucible after test V900PC.

4.1.1.1. Scanning electron microscopy and EDS. Residues remaining in the crucible were characterized by scanning electron microscopy and the composition of some particles was analyzed by EDS. Fig. 4 shows particles of material remaining in the crucible at the end of test V900PC. The amount of material was not enough for chemical analysis either by atomic absorption spectrophotometry or by X-ray fluorescence. Hence, microprobe analysis through EDS detector coupled to the scanning electron microscope was chosen as the analysis method.

A darker matrix and a lighter fine precipitate can be noted in Fig. 4. Fig. 5a shows the precipitate found on the particles presented in Fig. 4. A lighter precipitate was found only on the particle surfaces. The spectrum obtained by analysis through EDS of the matrix in Fig. 5a is exhibited in Fig. 5b.

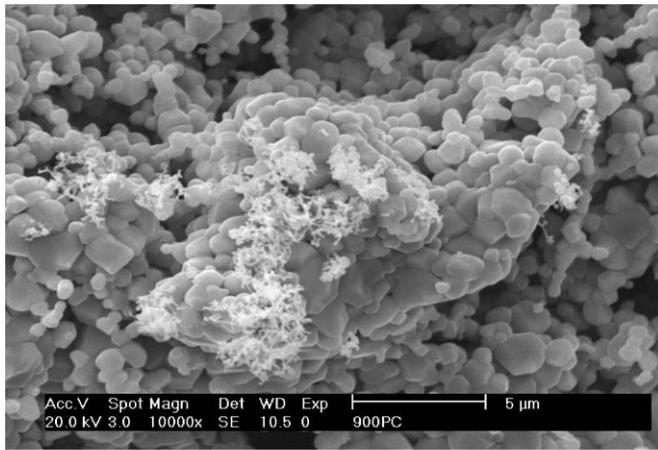
Gold sputtering was performed on the sample surface to allow observation by SEM. Only nickel and cobalt were identified in the EDS spectra. Gold is also present in the spectra due to the sputtering. The area presenting a higher concentration of light precipitates (Fig. 5a) was analyzed through EDS, but the result was similar to that of the matrix. The precipitate was too fine and since the EDS detector only presents good precision for areas greater than 1 μm the precipitate composition was not analysable.

4.1.2. Positive electrode

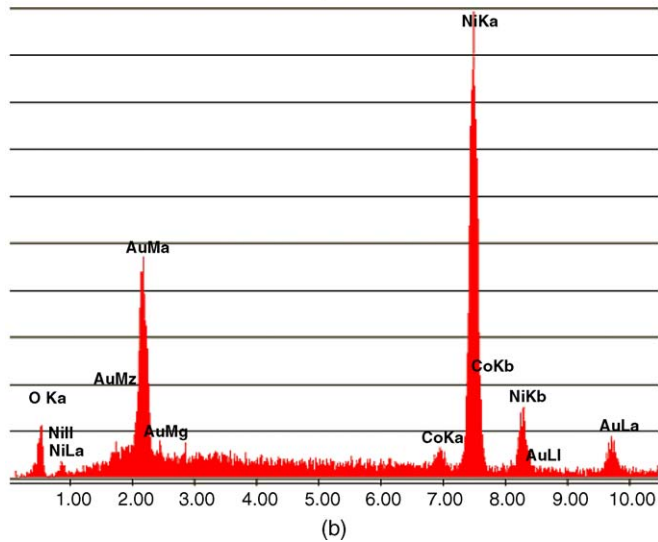
Tests carried out with the positive electrode showed curves with similar shapes and a clear identification of two steps in the test was possible (under static air atmosphere and under vacuum). Fig. 6 shows the curve obtained in test V1000PP.

Positive electrodes showed a different behavior compared to the negative electrode in a TG test. There was a mass gain instead of mass stabilization at the end of first step. The positive electrode had a number of metallic elements in its composition, including nickel. Thus, the mass gain was considered to result from oxidation of metals present in the sample.

A second process of mass loss was observed when the vacuum step was used in the chamber. In this case, the oxidation process was interrupted by a decrease in the oxygen potential in the furnace atmosphere. Consequently, the cadmium oxide which



(a)



(b)

Fig. 5. (a) Detailed image of lighter precipitate found on the particles exhibited in Fig. 4. (b) Matrix EDS.

is present in the sample began to decompose and generate Cd vapor. This process explains how the sample increases in mass and subsequently lost mass.

Since studying Cd distillation was the goal, only the second steps of all tests were plotted in the same figure. It was hypoth-

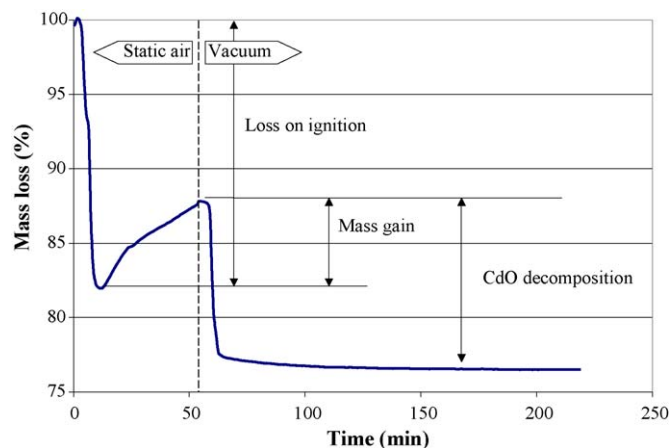


Fig. 6. TG curve of test V1000PP.

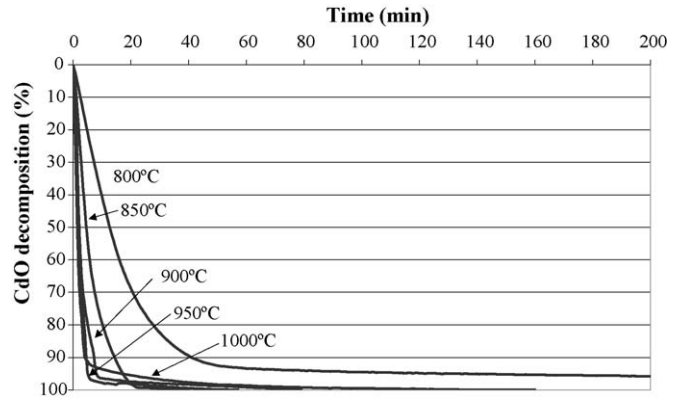


Fig. 7. Cd elimination percentage in the positive electrode.

esized that all volatile material was eliminated during the test, since there was no mass loss at the end of test. Thus, mass loss related to the second step of the test (performed under vacuum) was considered to be 100%. The resulting curves are shown in Fig. 7.

Mass loss curves presented in Fig. 7 show a stepwise process. Each curve can be divided into two parts. The first part of the curve is characterized by an enhanced mass loss in a short period of time, while the second part is characterized by a significantly slower mass loss.

Time for this behavioral change in the mass loss is plotted against test temperature in Fig. 8. The time spent in the rapid mass loss region is short at test temperatures above 900 °C. This time increased significantly for the tests performed at 850 and 800 °C.

Comparing the curves presented in Fig. 8 one can notice that at temperatures above 900 °C, the time to complete the rapid mass loss was similar. However, at test temperatures of 850 and 800 °C, this step one order of magnitude faster for the negative electrode than for the positive electrode. Thus, at temperatures below 900 °C, the time for the negative electrode should be considered the Cd distillation time.

This discrepancy in the Cd distillation rate is caused not only by a smaller amount of Cd in the positive electrode, but also by the greater surface area, of the positive electrode material, compared to the negative electrode material.

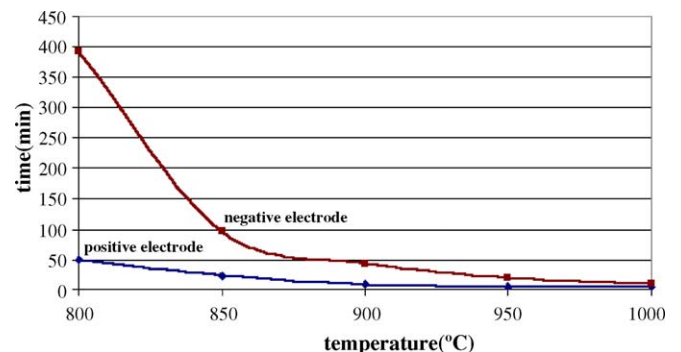


Fig. 8. Time variation for Cd elimination against test temperature. Comparison of results for negative and positive electrodes.

4.1.2.1. *Scanning electron microscopy and EDS.* Similarly to the procedure used in the tests with negative electrode, samples of material remaining inside the alumina crucible following the thermogravimetric test were analyzed through the EDS detector coupled to the scanning electron microscope. Fig. 9 shows a general view of particles at the end of test V950PP.

The aspect and size of particles of the material remaining in the crucible at the end of the tests with the positive electrode (Fig. 9) and with the negative electrode (Fig. 4) are similar. Since the negative electrode is basically composed of cadmium hydroxide, one can conclude that the remaining particles came from contamination occurring during the manual dismantling process of batteries, when the two kinds of electrodes were separated.

Fig. 10 shows a lighter precipitate on the particle surface. Particles larger than $2\ \mu\text{m}$ were found, and qualitative analysis of the composition using EDS was possible (Fig. 10b). Fig. 10c shows the EDS spectrum of the matrix in Fig. 10a. Gold peaks identified in all spectra are related to sputtering used for sample preparation. This sputtering prevented quantitative analysis, and all microprobe analyses were qualitative.

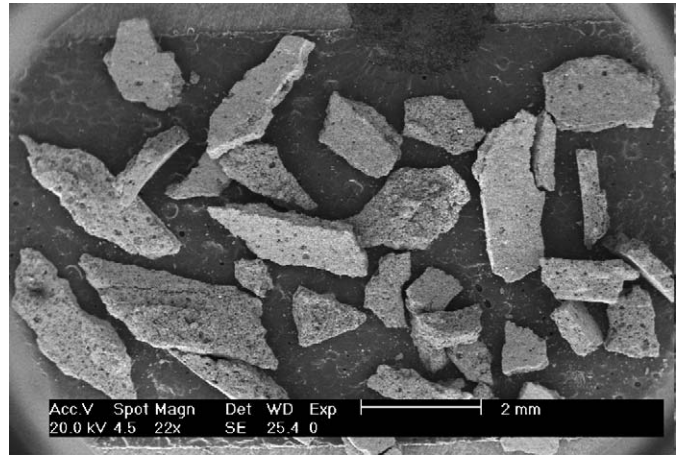
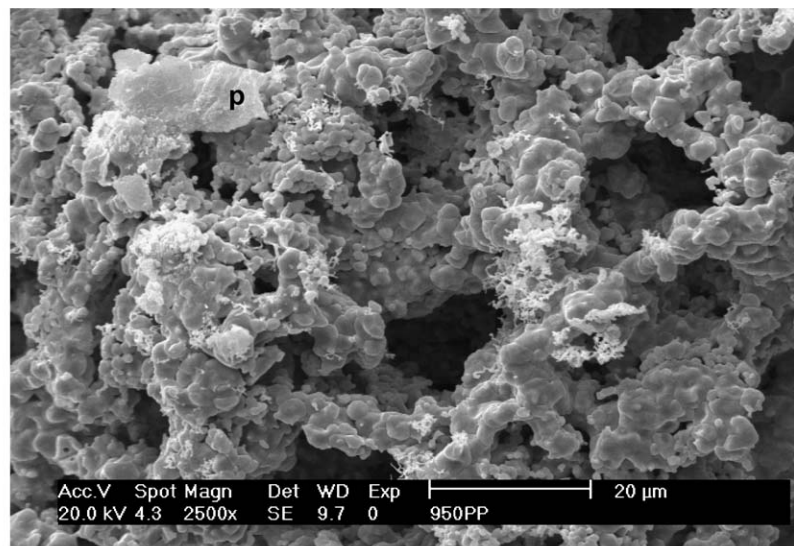
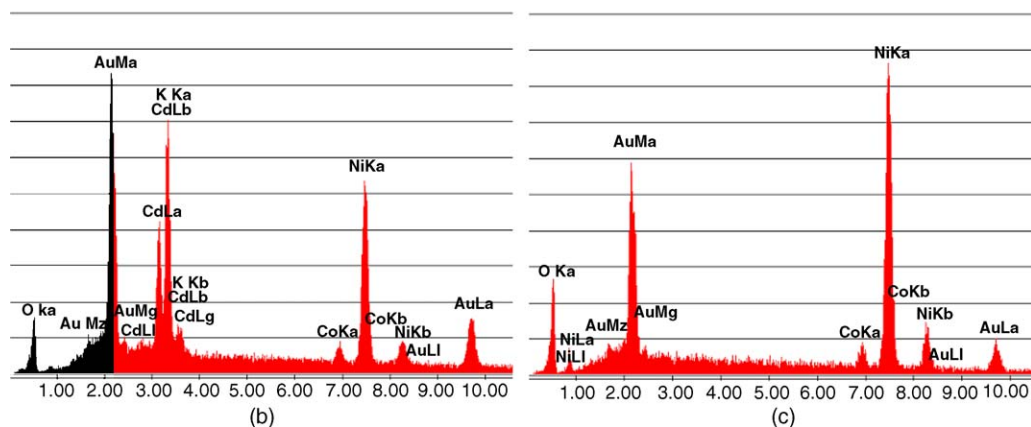


Fig. 9. Particles of material remaining in the crucible at the end of test V950PP.

Cadmium or potassium peaks were identified in the EDS spectrum of the lighter precipitate. In the cadmium distillation tests, material remaining in the crucible always contained residual cadmium (approximately 20–100 ppm), which indicated that



(a)



(b)

(c)

Fig. 10. (a) Detailed image of Fig. 9 evidencing precipitated material (light, marked with letter “p”) on the sample matrix (dark). (b) EDS spectrum of the lighter precipitate marked with letter “p”. (c) Matrix EDS spectrum.

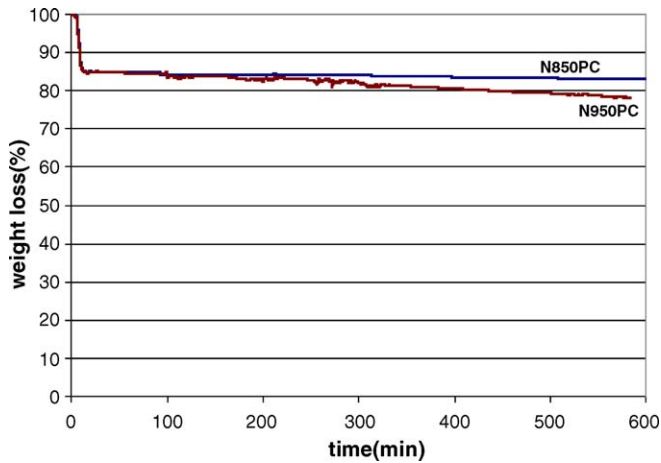


Fig. 11. TG curve of tests N850PC and N950PC.

possibly cadmium was not completely eliminated during the distillation process. Thus, cadmium could be part of the composition of the lighter precipitates.

Potassium also is part of the composition of the separated positive electrode, due to contamination from the potassium hydroxide electrolyte, which is in direct contact with the electrode. Thus, potassium could also be part of the composition of this lighter precipitate.

Only nickel, cobalt and oxygen peaks are found in the EDS spectra of the matrix (Fig. 10c), indicating that nickel and cobalt oxides present in the positive electrode did not decompose during the vacuum distillation process without a reducing agent.

4.2. Tests under nitrogen atmosphere

Tests with final temperatures of 800, 850, 900, 950 and 1000 °C with material from the negative electrode (richer in Cd) were carried out. Fig. 11 shows the TG curves obtained in the thermoanalysis tests at 850 and 950 °C.

One can notice that following the initial mass loss, related to cadmium hydroxide decomposition, the sample mass loss is virtually interrupted in test N850PC and the mass loss rate is very low in test N950PC, compared to vacuum tests. This behavior shows that cadmium oxide decomposition does not occur under standard grade nitrogen atmosphere without a reducing agent.

One explanation could be the oxygen content in the nitrogen used. This content would not allow a sufficiently low oxygen partial pressure in order for the cadmium oxide decomposition to occur at a rate comparable to the rate in vacuum tests.

It is hypothesized that organic compounds provide reducing agents in order to allow the cadmium oxide decomposition to occur without the addition of a reducing agent when the load is composed of milled batteries. This hypothesis is supported by the results obtained in thermogravimetric tests with a negative electrode under nitrogen atmosphere alone.

4.3. Tests with a reducing agent

Hydroxide decomposition was carried out in a muffle furnace before performing the thermogravimetric tests, in order to pre-

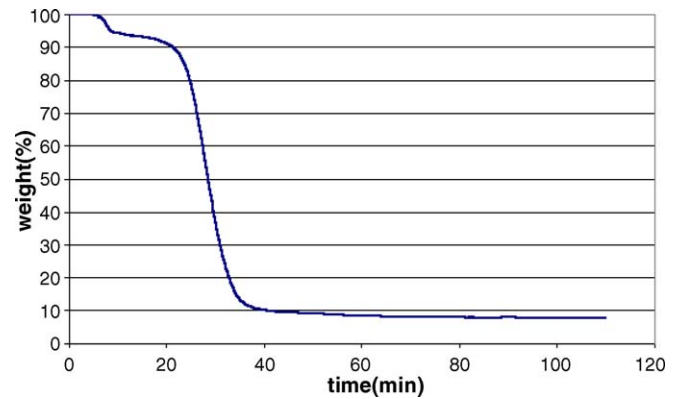


Fig. 12. TG curve of test N900PCC.

vent concomitant CdO and hydroxide decomposition. Material from the negative electrode was packaged in an alumina crucible and heated in a muffle furnace at 500 °C for 2 h. Reducing agent, in excess of 20%, was added to this material, in order to reduce the Cd oxide. This material was used in the thermogravimetric tests.

The curves obtained in these tests have a similar shape. Fig. 12 shows the curve obtained in the test N900PCC. An initial small mass loss during sample heating can be observed. This mass loss was related to moisture loss and decomposition of some remaining hydroxide. Subsequently, the sample loses most mass in the second step. Some ashes remained in the crucible, at the end of the test.

The same hypothesis applied in the vacuum tests was used here, which means all of the volatile material was evaporated during the test and the material remaining in the crucible does not present volatile material. Thus, the mass loss was considered to be 100%. The resulting curves of all tests from this step are shown in Fig. 13.

One can notice that the mass loss rate is very similar in the tests performed at the maximum temperatures of 900 and 1000 °C. A reduction in the mass loss rate can be noted at lower temperatures. In the test N650PCC, even though the sample loses mass, the distillation rate is too low to afford a com-

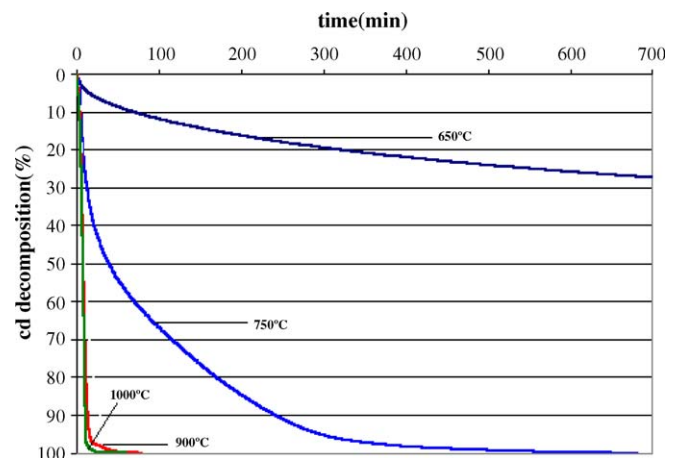


Fig. 13. Mass loss related to CdO decomposition and Cd evaporation.

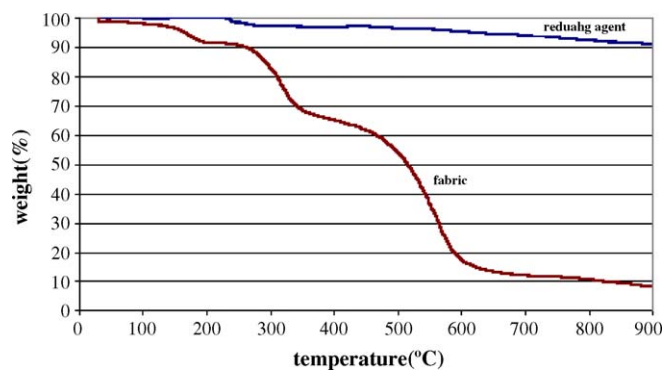


Fig. 14. TG curve of tests using anthracite and fabric.

mercial value. In the test N750PCC, Cd elimination approaches 100%, but the time needed is one order of magnitude greater than in the tests carried out at higher temperatures.

4.3.1. Reducing agents

Two thermogravimetric tests were performed in order to check whether the fabric contained in the batteries could act as a reducing agent. One of the tests was carried out with the reducing agent used in previous tests (anthracite with particle size below 0.106 mm and with 83.83% fixed carbon). Another test was performed using the fabric. Fig. 14 shows the curves obtained in TG tests with anthracite and with the fabric.

Mass loss was greater in the fabric sample compared to anthracite used in the tests, as can be noted in mass loss curves under an oxidizing atmosphere. Using anthracite shows a steady mass loss with heating and a small loss of volatile material. On the other hand, loss of volatile material is significant in the tests using fabric.

In addition, at temperatures above those in which the volatile material is evolved, the combustion process is accelerated with material from fabric than from anthracite.

Volatile material released from the fabric should be basically composed of potentially reducing gasses. This effect should be taken into account, as it indicates that the fabric can be a better reducing agent than anthracite. Consequently, reduction process

always occur in the material milled and loaded in the furnace, even without an exogenous reducing agent.

In the tests conducted in the thermobalance, since the material was virtually free of fabric after manual separation process, there was no reducing effect caused by the fabric.

However, under an inert gas atmosphere, the CdO decomposition reaction should proceed similarly to the process under vacuum. Although there was an inert atmosphere, a purge gas has a certain oxygen content, since it was a standard grade. This means that CdO decomposition occurred during the heating step up to the time at which the reaction oxygen potential and atmospheric oxygen were the same.

5. Conclusions

1. The vacuum decomposition of cadmium oxide occurs in two steps. The first step represents a fast rate of decomposition where almost 95% of the reaction is observed. The second step exhibits a slow decomposition rate. The same behavior was observed using a reducing agent.
2. Increasing the temperature increases dramatically the rate of cadmium oxide reduction and decomposition. Above 900 °C the first step is complete in a few minutes.
3. The fabric used to absorb the electrolyte can act as a reducing agent.
4. The velocity of decomposition and reduction of the negative electrode is greater than the observed for the positive electrode. This behavior was attributed to the small amount of cadmium oxide concentration and also to the higher surface area of the negative electrode material.

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