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Assessment and reuse of secondary batteries cells

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ABSTRACT

The popularity of portable electronic devices and the ever-growing production of the same have led to an increase in the use of rechargeable batteries. These are often discarded even before the end of their useful life. This, in turn, leads to great waste in material and natural resources and to contamination of the environment. The objective of this study was thus to develop a methodology to assess and reuse NiMH battery cells that have been disposed of before the end of their life cycle, when they can still be used. For such, the capacity of these cells, which were still in good operating conditions when the batteries were discarded, was assessed, and the percentage was estimated. The results reveal that at the end of the assessment process, a considerable number of these cells still had reuse potential, with approximately 37% of all discarded and tested cells being approved for reuse. The methodology introduced in this study showed it is possible to establish an environmentally correct alternative to reduce the amount of this sort of electronic trash.

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1. Introduction

Present day society is facing a paradox it needs to solve quickly: growing production in a market that offers ever more accessible high-tech equipments (faster computers, cellphones with diverse features, sound systems, DVDs, TV sets, among others) associated with great waste of natural resources and contamination of the environment caused by the production process of this equipment and its quick disposal.

Whether due to rapid obsolescence or damage, electronic devices have been disposed of in landfills or other inappropriate sites where the means to reuse them are both rudimentary and precarious. Furthermore, an ineffective policy for regulating such waste creates a situation whereby the actual needs for environmental preservation are not met; harming human health even in those nations considered developed [1].

Among these electronic devices, cellphones have stood out with more than 300 million handsets sold during the last quarter of 2007 and 1114.1 billion being produced that same year. That is a growth of 12.4% compared to 2006 [2]. Taking into account that a handset weighs on average 130 g, that means 148.72 thousand tons of waste. The battery for these cellphones is responsible for approximately half their weight, or practically 75 thousand tons.

Cellphones are powered by several types of rechargeable batteries, and many of these contain toxic substances such as cadmium, nickel, zinc and copper, which can contaminate the environment when incinerated or disposed of in landfills.

The impact of these batteries on common garbage depends on the quantity and their toxicity. The quantity of generated waste is a result of the battery's useful life and its size. The toxicity of this waste depends on the material of which the batteries are made. Countless studies have been conducted aimed at reducing or preventing waste generation associated with the production, use and final disposal of these batteries [3–8].

Rechargeable batteries are what they call secondary. In other words, when the amount of active material is depleted in the cell it is possible to reverse the reaction through the recharging process.

Technological evolution created the need for these rechargeable batteries used in electronic devices to be lighter and more compact and to have greater autonomy. Environmental restrictions regarding the use or disposal of cadmium in landfills, and the concerns about its effects on the environment and health have contributed towards the use of other types of batteries [4]. Thus, NiCd batteries have been replaced by nickel metal hydride (NiMH) and lithium ion (Li-ion) batteries, which are more acceptable in environmental terms and technically they can replace NiCd batteries in many applications [9].

The great majority of mobile telephones sold today use Li-ion batteries. However, there still are many mobile phones, digital cameras, and notebook computers on the market along with other electronic devices that sill use NiMH batteries. However, even NiMH or Li-ion batteries contain toxic substances, which require them to be recycled at the end of their useful life rather than sent to landfills or, according to waste management hierarchy, reused, in an

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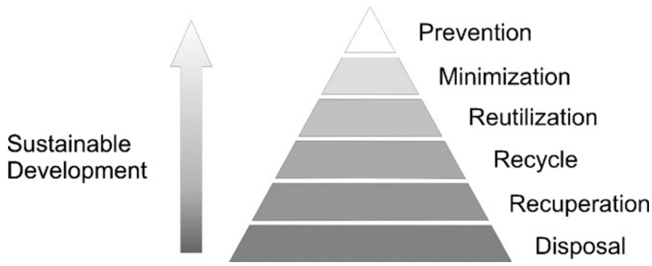


Fig. 1. Residues management hierarch.

attempt to maximize the practical benefit of products and minimize the generation of waste (Fig. 1). Thus, according to the use of rational waste management (Fig. 1), the most favored environmental option is the one at the top of the pyramid. For example, reuse is preferred over recycling, which in turn will have priority over energy recovery, which is preferred over final disposal [10].

Considering the case of small-sized, rechargeable batteries, prevention is related to their appropriate use and correct charging. This optimizes the amount of energy stored and used during charge and discharge cycles. Minimization is understood as being the rational use of these batteries. For example, shutting the handsets off at night when they are not being used, or even reducing the volume of material employed in battery manufacturing. After prevention and minimization, reuse appears as the next option for reducing waste and it is the focus of this study. In the case of cellphones, the reuse of components, like batteries, would enable them to be used again by means of some sort of improvement or reconditioning, thus avoiding the disposal of material that still has potential for reuse.

Most domestic batteries have been deposited in municipal solid wastes, and sent to sanitary landfills. The environmental impacts caused by these metals from batteries depend on the conditions of these same batteries when discarded, as well as the conditions of the landfill. These factors include: type of housing, charge left in the battery, exposure to lixiviation and oxygen content at the landfill. These can all affect the degree of battery degradation [11].

Furthermore, batteries deteriorate with the chemical action during storage. The design, electrochemical system, temperature and storage duration are factors that affect battery charge retention. A battery gradually increases self-discharging with: an increase in temperature, number of cycles, age and presence of a protection circuit [12,13].

Recycling has also been used in battery waste management. However, this process has been employed to recover metals with high added value [5–8].

The incineration of batteries or their processing in industrial kilns has two worrisome aspects. The first is the release of metals into the air and the second is the concentration of metals in ashes that must be lixiviated. Incineration is only preferable to final disposal (which should be the final option to be considered) [11].

Studies have been conducted with the objective of recycling NiMH batteries since they contain metals with high added value, such as nickel, cobalt and rare earth. Thus, different techniques have been proposed as new hydrometallurgical routes for extracting these metals [6–8]. However, the recycling does not consider the fact that this material is treated as a new kind of miner can still present a potential for application in the way that it is found. Considering this aspect, the study focused on the development and application of a methodology for assessing and reusing discarded NiMH battery cells.

In Brazil there still is no consolidated process for what to do with these batteries. There is a recycling company that receives an average of 200 metric tons per month. All the batteries sent to them have their covers removed and their metals are burned in high-temperature industrial furnaces equipped with gas scrubbers that lower the emission of polluting gases. Metal salts and oxides are obtained in this process, which are used in the industry of refractories, glass, paints, ceramics, and chemicals in general.

Installation costs are very high. A great part of the resources spent with these installations goes to building complicated control equipment and jobs are generated only as it is being built and few permanent jobs are created during its operation.

Every time that we burn batteries or dispose of them in landfills and do not find ways to reuse them, we will have to substitute them. This means that we are going to extract the raw material once again and once again introduce high consumptions of energy to manufacturer them, generate new wastes during its production, etc.

Batteries are sources that store energy, and when correctly used they transfer this energy safely. However, certain conditions can cause an increase in temperature and internal pressure, leading to malfunctions or even explosion. Some of the reasons behind this type of problem in batteries include:

(1) Short circuit on battery terminals.
(2) High charge or discharge rate.
(3) Inverse voltage.
(4) Improper charge of secondary batteries.
(5) Damages to one of the cells of a set.
(6) Damage in some electronic component of the protection circuit.

Of the abovementioned reasons, the fifth is one of the most important in the case of NiMH batteries. Since the nominal voltage of unit cells does not exceed 1.2 V, in order for them to reach higher voltage values they are normally associated in series, thus constituting a battery. Older cellphone batteries were sometimes comprised six such cells. In the more modern handsets, the number has been reduced to three, as shown in Table 1.

A cell's capacity is determined by the amount of active material in contains and it is expressed by the total amount of electricity involved in the electrochemical reaction defined in Coulomb (C) or Ampere hour (Ah) [14].

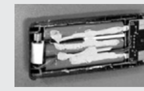
A cellphone's energy consumption depends on how it is used. They operate in three modes: talk, standby and off. Each of these modes requires different amounts of energy. The maximum amount of energy is consumed in talk mode, when the telephone is receiving or transmitting voice signals. It consumes less energy in standby mode, and even when the cellphone is turned off, some energy is consumed [15].

Nickel metal hydride batteries were developed in 1989 and commercialized primarily in Japan in 1990. Such systems have high electrochemical capacity, as well as safety. The life cycle for these batteries, or, the number of times they can be recharged, is approximately 500, and after this, their efficiency in terms of energy storage capacity gets very low and is associated with the increase in internal impedance [16].

Internal impedance of batteries is related to charge retention capacity and it is influenced by a series of factors like temperature, depth of discharge, charge status, storage time, construction factors, and therefore, it is difficult to be measured. The ideal model uses a resistance connected in series to an inductance and a parallel capacitance. The resistance can be measured indirectly by reading the voltage on the battery terminals divided by the current that circulates through them. This is often used as an indicative parameter of battery charge status because the inductive and capacitive effects are almost always disregarded since the battery is a direct current device [17,18].

However, the time needed for batteries to reach the end of their life cycle depends on the frequency in which they are recharged. For

Table 1
Evolution of the number of cells per NiMH battery used in cellphones.

Voltage (V)	7.2	6.0	4.8	3.6
No. cell/battery	6	5	4	2
Example				

cellphone batteries, this frequency depends on their charge capacity, handset energy consumption and how the user conducts the charging process. When charging is carried out in an appropriate manner, the amount of stored energy is optimized per recharge cycle.

However, many people change cellphones more than once per year in search of a better performing handset with more features and a modern design. Like most of these handsets, their batteries end up being retired before the end of the life cycles. However, considering a life cycle of 350 charge and discharge cycles (when average energy capacity becomes 80% less) [16], according to the frequency of weekly recharging, batteries would have an average life cycle of more than two years in the case of three recharges per week, greater than three years with two recharges per week, and greater than six years if only recharged once per week, as can be seen in Fig. 2.

The objective is to keep from throwing them away by finding ways so that more battery cells can be reused when they still have reusage potential instead of sending them to their final disposal (landfill). Fig. 3 shows a schematic drawing with the life cycle of the materials where it is indicated that a greater quantity of materials

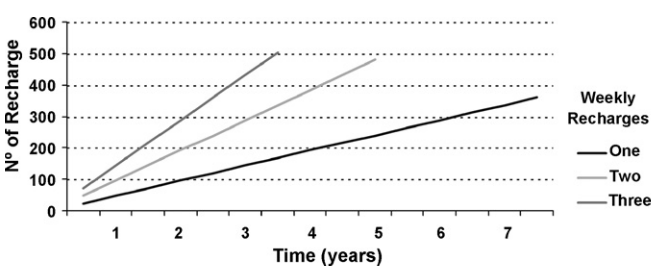


Fig. 2. Time used × number of recharges per week for NiMH batteries.

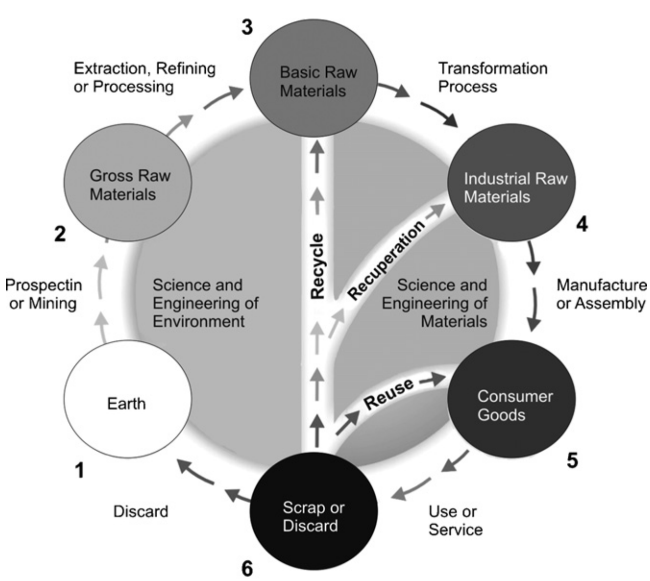


Fig. 3. Graphic representation of materials life cycle.

should preferably be reused (path 6–5) instead of being sent to their final disposal (landfill—path 6–1).

Considering these aspects, the study focused on the development of a methodology for assessing and reusing discarded NiMH battery cells. For such, the capacity of these cells, which were still in good operating conditions when the batteries were discarded, was assessed, and the percentage was estimated.

2. Materials and methods

With the objective of studying small rechargeable batteries that are being discarded before the end of their useful lives, 237 BMS-3 1000 mAh–3.6 V NiMH batteries (with three cells each) were gathered, donated by private individuals or by authorized cellphone companies. The percent of NiMH batteries (in comparison with Li-ion) that give a better extent of its usefulness is shown in Table 2, witch shows the most common models of NiMH and Li-ion batteries collected during the years 2006 and 2007 for this study. Of the 1121 batteries received, 456 were Li-ion and 656 NiMH, which correspond to approximately 41.5% and 58.5%, respectively. When analyzing the quantity and models received, we could notice that, compared to Li-ion, most of the batteries were very old, especially of NiMH, which also shows that it is not very common for the authorized cellphone companies to send their phones to the manufacturer.

A methodology was developed for assessing cells (considered reusable) that is basically comprised four phases as shown in Fig. 4. The first phase was to disassemble the batteries. A work station was organized for this that was comprised a well-illuminated work bench with tools to force the joints at the most fragile points of the housings in order to remove the cells as well as the printed circuit boards (PCB) in the batteries. In this phase of disassembly, care was taken to avoid an accidental short circuit with the cell carcass and to avoid any damage to the same.

After disassembling the batteries and removing the cells, the latter entered the second phase of the assessment process. Here, an analysis was conducted of the superficial aspect of the cells' positive and negative poles, identifying terminals presenting signs of leaks, oxidized layers or deformation due to high internal pressure through visual inspection. The detection of any of these aspects characterized the cell as degraded making it impossible to study its reuse.

Cells approved by visual inspection entered the third phase of the assessment process, where remaining voltage was measured. They were then classified, identified and separated according to the respective voltage value as: high (1.25–0.85 V), medium (0.84–0.5 V), low (0.49–0.06 V) and zeroed (0.05–0 V). Cells with voltage values between 0.05 and 0 V were rejected. During this phase, the battery's PCB was also removed.

Fig. 5 shows cells retrieved of disassembly batteries (first phase) on A, cells rejected (second phase) on B and the remaining voltage of the cells approved in the second phase being measured with multimeter on C (third phase).

Considering that after several charge and discharge cycles, batteries with low charge retention capacity have high internal resistance. A monitoring of the voltage on the battery terminals

Table 2
Most common models of NiMH and Li-ion batteries collected.

Brand	Model	Quantity	Brand	Model	Quantity
Nokia	BLB-3	24	Nokia	BBH-1H	32
Nokia	BLC-2	30	Nokia	BBH-1S	27
Nokia	BL-6C	22	Nokia	BMS-3	295
Nokia	BL-5C	64	Nokia	BMC-3	95
Nokia	BL-4C	23	Nokia	BMC-2	30
Siemens	V30145-K1310-X215	41	Ericsson	BKB 193 104 4,8V	28
Siemens	V30145-K1310-X250	38	Ericsson	BKB 193 104 4,3V	25
Motorola	AANN4285B	34	Ericsson	BKB 193 085	40
Motorola	NN4815B	30	Ericsson	BKB 193 (123-105)	29
Motorola	SNN5571A	41	Ericsson	BKB 931 C30 R3C	30
Motorola	SNN5749A	19	Siemens	V30145-K1310-X222	25
LG	LGIP-411A	20			
LG	LGIP-A1000E	36			
LG	LGIP-G830	28			
Sony Ericsson	BKB193 174/11	15			
Total		465			656

makes it possible in a simple and quick way to analyze the battery charging state. 1.25 V is the cell's voltage without charge and 1.2 V is the most common voltage. Once as the cycling increases, this voltage level of the cells tends to decrease, it can be used to evaluate the state of the cells in the next step of the assessment process. Therefore, in the fourth phase, cells that still had medium or high charges were discharged to then be tested in two charge and discharge cycles [18].

The charging method used was of constant current. The currents used were limited in order to avoid an excessive increase in temperature and to not exceed the oxygen recombination reaction rate since this is harmful to the cells and could degrade them. The values of the currents and duration of the cycles were defined so as to apply not very deep charges and discharges in order to offer a greater life cycle to the cells. It was taken into consideration that the greater levels of capacity could be reached with 150% input charge and the maximum life cycle is reached with 120% of input charge, but with less capacity due to the insufficiency of the input charge.

In the first cycle, "fast charge and discharge" was used. In the charge phase, charge current (I_c) was adjusted at 60% of battery

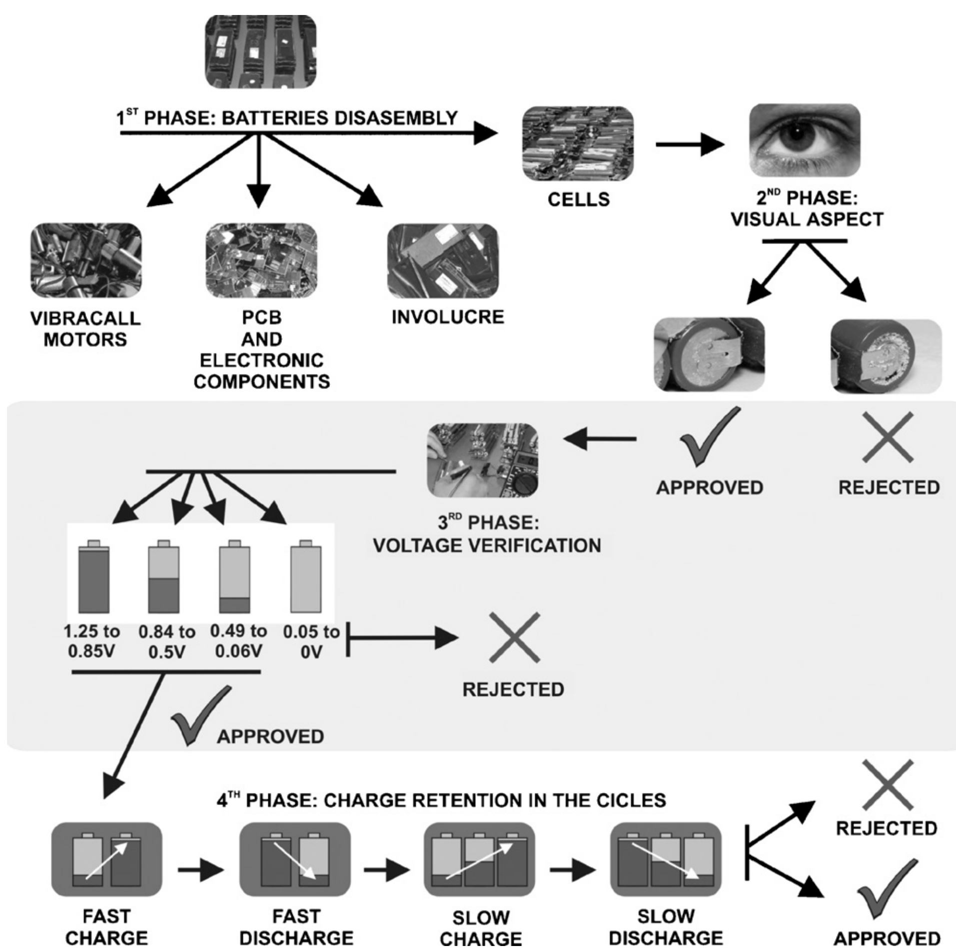


Fig. 4. Phases of the assessment process for cells considered reusable.

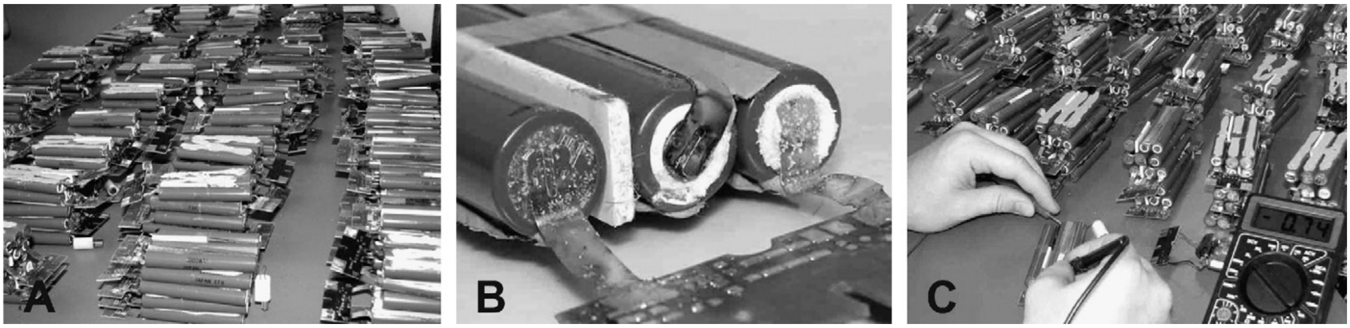


Fig. 5. Cells retrieved of disassembly batteries (first phase) on A, cells rejected (second phase) on B and the remaining voltage of the cells approved in the second phase being measured with multimeter on C (third phase).

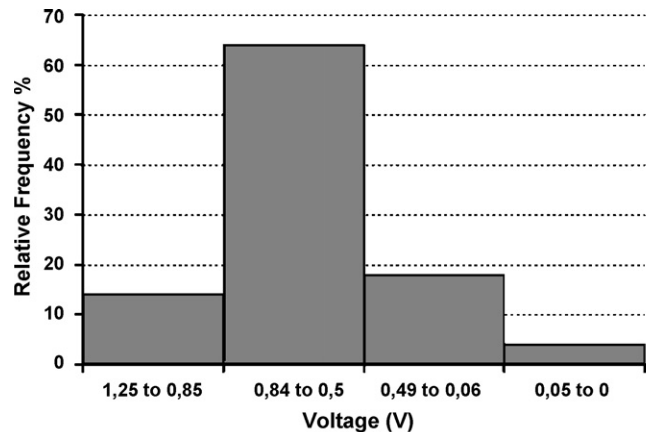


Fig. 6. Proportion of remaining voltage values in cells (third phase of the assessment process).

capacity for 1 h. The voltage was checked in each cell and the readings were recorded on a spreadsheet. Those with voltage values under 50% of nominal voltage (1.2 V) were discarded. In the "fast discharge" phase, discharge current (I_d) was adjusted at 50% of capacity for 30 min. The voltage in each cell was then checked and the readings recorded on the same spreadsheet. Cells with voltage values under 20% of nominal voltage were discarded. In the second cycle, "slow charge and discharge" was used. In the charge phase, I_c was adjusted at 40% of battery capacity for 3 h. After that, I_c was reduced to 20% of capacity for another 20 min and the voltage was measured in each cell. Measured voltage values were recorded and cells with voltage values under 90% of nominal voltage were discarded. In the "slow discharge" phase, I_d was adjusted at 30% of battery capacity. The discharge was maintained for 90 min. After that, the voltage was checked again in each cell and the readings were recorded on the same spreadsheet. Those with voltage values under 25% of nominal voltage were discarded.

Once the capacity of the cells studied were 1000 mAh, the currents used were: 600 mA in the fast charge, 500 mAh in the fast discharge, 400 and 200 mAh in the slow charge and 300 mAh in the slow discharge. After being submitted to the charge and recharge cycles, the tested cells, characterized for reuse, were labeled with the qualification they obtained in the tests and packed. Special attention was given to the negative and positive poles, which were protected with insulation tape, to be reused or stored.

3. Results and discussion

According to the results shown in Table 3 of the 237 disassembled batteries (711 cells) in the second phase of the assessment process, 11 batteries were rejected by visual inspection with their 3 cells presenting oxidation or leaks; 136 batteries had at least one damaged cell (oxidation or leak), and 90 batteries were approved. Therefore, of the 771 cells, 442 were approved and 269 were rejected, which corresponds to approximately 62.2% and 37.8%, respectively, of the total number analyzed.

We observed that in terms of approval estimates, the number of cells considered approved in the second phase of the assessment process was greater than the number of batteries. Since a battery is comprised several associated cells in series, if one cell presents a defect, the performance of the battery will be unsatisfactory and it shall be rejected. This result further reinforces this study's proposal which is that many of the batteries discarded by users because they presented possible problems were comprised cells in good conditions, that is, material with potential for reuse.

Table 3
Relation between the quantity and relative frequency of approved and rejected batteries and cells in the second phase of the assessment process.

	Batteries		Cells	
	Quantity	Relative frequency (%)	Quantity	Relative frequency (%)
Approved	90	38.0	442	62.2
Rejected	147	62.0	269	37.8

Fig. 6 shows that in the third phase of the assessment process, when the remaining voltage was tested in those cells approved in the second phase of the assessment process, only 18 of the 442 cells approved in the first screening (4% of the 442 cells) had remaining voltage values between 0.05 and 0 V and were therefore rejected, whereas most (64%) of the cells had remaining voltage values between 0.84 and 0.5 V.

After measuring the remaining voltage, the 424 approved cells underwent charge and discharge cycles to check their charge retention capacity (fourth phase). Of these, 17 cells were rejected because they did not reach the minimum voltage value established during the cycles. We can see in Fig. 7 that of the 407 remaining cells approximately 64.6% had voltage greater than or equal to 0.7 V and were approved, whereas approximately 35.4% of the cells were rejected for having voltage values less than 0.7 V. In this phase of the study, the approved cells were classified and identified according to their voltage.

A cost analysis of the treatments given to the batteries in the end of their life cycle is important, but the consequent of environment impact must therefore be studied too. The difficulty of this analyses elapses of the complex interaction among theses treatments (reuse, recycle, recuperation and final disposal) and the environment, and the relatively large quantity of uncertainties presents in this kind of evaluation.

The damages caused on the environment can be classified in three categories: damages to the human health (number and dura-

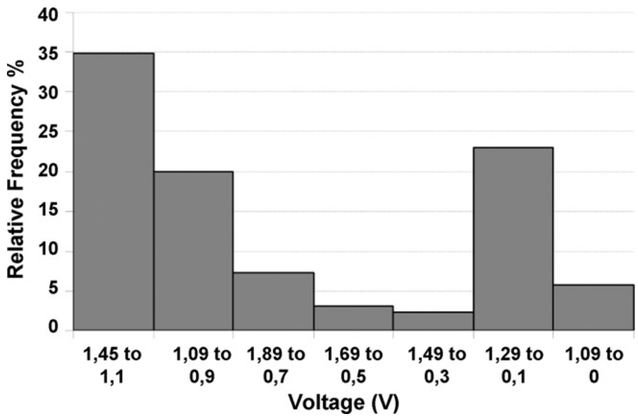


Fig. 7. Relative frequency of charge retention in charge and discharge cycles (fourth phase of the process).

tion of diseases); damages to the ecosystem quality (the effect on species diversity); damages to the resources (surplus energy needed in future to extract lower quality mineral resources).

Costs with collection, separation, taking apart, assessment, and selection of discarded batteries can be estimated:

Collection: this stage calculates the expenses with transporting the batteries from their collection point to the location where they will be separated and depends on distances, quantity of batteries, and transportation frequency.

Separation: in this stage the batteries are separated by types and models and it depends on the level of mixture or quality of the pre-selection done by consumers and if the collection points offered different compartments for different types of battery, such as primary, NiMH, Li-ion, and NiCd.

Disassembly: during this stage it is estimated that in 1 h a trained person is capable of taking apart and removing the cells of 25 batteries. It depends of the quantity of batteries and number of workers involved and their skill in carrying out this service.

Assessment: in this stage an analysis is done of the superficial aspect, remaining voltage measuring, as well as the charging and discharging cycles. It depends on labor costs and amount of electric energy used. In Brazil the electric energy rate for low voltage groups is equivalent to 0.13 US$ $kW\,h^{-1}$.

Selection: in this stage the cells are selected that can make up new batteries for various applications. The criteria used are the capacity to be reused and requirements for new applications depending on computerized selection and checking specifications in database, e.g. voltage, load current and profile, duty cycle, temperature requirements, service life, physical requirements, shelf life, environmental conditions, safety and reliability.

Labor costs are very relative and vary from country to country. Labor is cheap in countries where a considerable part of the population have informal jobs. In countries where labor costs are high, it would be best to automate some stages. We intend to bring about a new way to look at it with this study, making society and the manufacturers aware as to the need to conserve resources based on the proposal of reusage.

It is important to underscore that every time a battery is discarded, a new battery needs to be manufactured to replace it. Since a considerable number of cells with capacity for reuse are being treated as waste, the methodology developed for assessment and reuse is feasible. With its use, it is possible to minimize economic waste due to diverse phases that involve the cell production process (insertion of electrodes and separators wound in a spiral shape inside a nickel-plated steel tube, addition of an electrolyte, configuration of the top and labeling) and the environmental waste caused by the extraction of the raw material and contamination of the environment as a result of early disposal.

4. Conclusions

The results obtained in this study reveal a degree of uncertainty regarding the quality of discarded batteries. The condition of these batteries when received is generally unknown; however, even though many batteries can be considered damaged, we see that this was being associated with the presence of cells with defects. This revealed the need to develop a methodology to assess and reuse these cells.

Although the cells of some batteries have been rejected in several phases of the assessment process they underwent, many of these cells revealed great potential capacity for reuse.

Since on average 62% of the cells were approved in the second phase of the assessment process, and of these, on average 96% were approved in the third phase, and of the remaining cells, 67.3% were rejected after the cycles, at the end of the assessment process, approximately 37% of all tested cells (which had been discarded) were considered approved for reuse.

The methodology introduced in this study permitted the selection of cells from discarded batteries that were still in conditions to be reused and showed it is possible to establish an environmentally correct alternative to reduce the quantity of this type of electronic trash as well as optimize raw material use, when taking into account that for each discarded battery a new battery needs to be manufactured for replacement.

As a next phase, we hope to continue studying the internal resistance variations of the cells in the charge and discharge cycles in order to further refine the assessment process, as well as also apply this methodology to assess the reuse of other types of rechargeable batteries, such as the Li-ion.

Acknowledgement

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