

Recycling of Ni-MH batteries from hybrid vehicles

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July 2019

Abstract

The first Hybrid Electric Vehicles (HEVs) put on the market on the early 2000's are reaching their end-of-life, raising the problem of the nickel-metal hydride batteries packs recycling. This work aims at developing an hydrometallurgical recycling process through a physical and chemical characterization of a Ni-MH module. The module was discharged and manually dismantled. Characterization included mass balance, structural and morphological characterization of the electrodes and the elemental analysis. The module consisted of 30 cylindrical cells and was made of metals (85%), plastics (6%) and NaOH electrolyte (6%). Valuable materials were concentrated in the electrodes. The cathode accounted for 31.8% of a cell weight and consisted of a 3D-mesh supporting the active powder. X-Ray Powder Diffraction analysis showed that the mesh was made of metallic nickel, while the powder corresponded to the Ni(OH)₂ phase. Inductively Coupled Plasma Mass Spectroscopy indicated a composition of 73.3% Ni, 5.1% Co, 0.21% Al, 0.15% Mn and 32.6% OH. The anode accounted for 35.9% of a cell weight and consisted of a nickel 2D-grid, supporting an hydrogen storage alloy of LaNi₅ type and composed of 54.5% Ni, 11.6% Co, 4.2% Al, 6.2% Mn, 6.7% Ce, 5.4% La, 0.6% Pr and 2.1% Nd. The optimal leaching conditions were found to be 1M H₂SO₄, at 25°C, for 3 hours, with a liquid-to-solid ratio of 20 L.kg⁻¹. It allowed to dissolve 100% of Ni, Co and Rare Earth Elements of the anode and the Ni(OH)₂ powder from the cathode. The cathode undissolved metallic nickel can be used directly by the metal industry.

Keywords: Ni-MH batteries, HEVs, recycling, characterization, leaching

1. Introduction

The current economy is based on fossil fuels whose combustion generates anthropogenic greenhouse gases together with atmospheric pollutants, resulting in climate change and harmful consequences for the human health. Due to its strong-oil dependency the transport sector represented on his own, 27% of the European Union greenhouse gases emissions for the year 2016 [1]. Besides the environmental problems this dependency to fossil fuels makes the sector particularly vulnerable to oil price volatility and risks of supply disruption. Therefore, constructors are exploring alternative solutions to develop oil-free vehicles. One of the main options actually considered involves electric motors, however, the actual full electric vehicles present limited autonomy and long battery charging time, making their generalization difficult. A compromise was thus developed, under the form of HEVs, in which the traditional Internal Combustion Engine (ICE) is combined with an electric motor. Nowadays this solution is the most widespread alternative to traditional ICEs, due its affordability when compared to other solutions and no need for specific infra-structures. The

market share of HEVs has been increasing regularly for 20 years and is expected to increase even more in the next years due to stricter and stricter regulation regarding traditional vehicles [2].

One of the most important components in HEVs is the battery, which has traditionally been of Ni-MH type from the apparition of the first models in the early 2000's until today. Despite being considered relatively harmless to the environment the recycling of the battery is essential to decrease the environmental impact of this type of vehicle. Moreover, Ni-MH batteries contain an interesting amount of valuable metals, mainly Ni, Co and Rare Earth Elements (REE).

In Europe, the end-of-life of HEVs batteries is subjected to strict rules regarding collection and recycling efficiency [3]. However, the main industrial processes currently used present various disadvantages; most of them are pyrometallurgical, and thus costly and energy intensive and do not allow the recovery of the rare-earths [4]. Most of the time the quality of the final product is too poor to be used for the manufacturing of new batteries and the metals are down-recycled in the stainless steel industry.

Thus, the challenge is to recover the elements with purity and cost that are competitive with materials coming from primary mining.

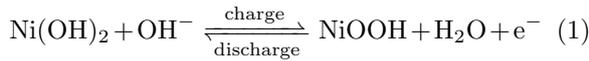
In this thesis a dismantling of a Ni-MH battery module was carried out, followed by physical and chemical characterization of the electrodes, aiming at estimating the economic value of the materials present, and choosing the most appropriate recycling process. Finally the metals extraction by hydrometallurgical process were realized.

2. State-of-the-Art

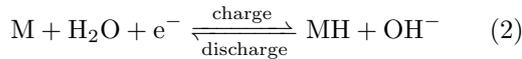
2.1. Ni-MH battery: working principle and applications

Ni-MH cells belong to the category of rechargeable batteries. The cell consists of a cathode, made of nickel, a metal hydride anode and an alkaline electrolyte. The electric insulation between the electrodes is ensured by a separator, generally made of polypropylene or polyethylene fibers [5]. The reactions occurring during the charge-discharge process are described by equations 1 to 3 [6]:

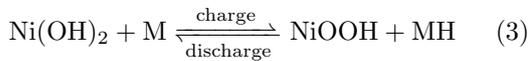
For the cathode:



For the anode:



The overall reaction:



Where M=metal.

Ni-MH cells can be designed in various sizes and shapes and an example of a cylindrical model is shown on Figure 1. In this case, the electrodes are rolled together with the insulator to form a jelly-roll assembly, and inserted in a metallic case which plays the role of battery negative terminal while the top lid corresponds to the positive terminal [7].

The charge transfer reaction at the anode occurs by absorption and desorption of hydrogen. This reaction requires an hydrogen storage alloy. The materials used are A_nB_m metal alloys, where A has a strong affinity to hydrogen and B a poor affinity to hydrogen. Numerous compositions have been developed in order to optimize the performances, but most of the commercial Ni-MH batteries are using AB_5 -type and more precisely LaNi_5 -type alloys. Since pure LaNi_5 presents poor performances and short life cycle, both La and Ni are partially substituted by other metals. Ni is substituted by Co, Fe, Al, Mn, Sn, Cr or Cu and La is replaced by an alloy of rare-earth elements called mischmetal, each substitutes plays a specific role regarding the capacity, corrosion resistance,

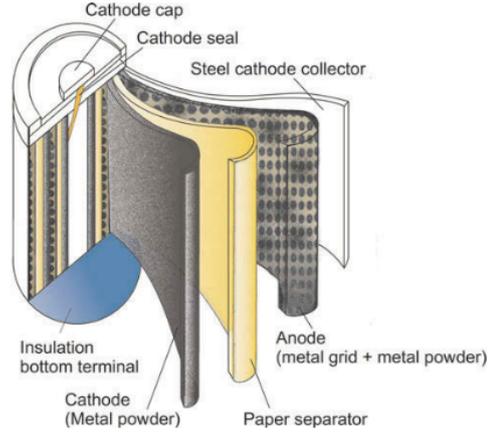


Figure 1: Dissection of cylindrical Ni-MH cell [8].

surface activation, etc. A typical composition is $\text{La}^{0.62}\text{Ce}_{0.27}\text{Pr}_{0.03}\text{Nd}_{0.08}\text{Ni}_{3.55}\text{Co}_{0.75}\text{Mn}_{0.4}\text{Al}_{0.3}$ [6].

Ni-MH batteries are found in various applications, the most known are the portable electronic appliances (cell phones, laptops, GPS units...), but this thesis focuses on HEVs. In HEVs the driving power is provided by two power sources: the traditional ICE and an electric motor. The electric energy is stored using a Ni-MH battery that can be charged either using the combustion engine or regenerative braking, corresponding to the energy of the car's deceleration. Ni-MH batteries are not used for electric vehicles such as Plug-in Hybrid Electric Vehicles and Full Electric Vehicles that can be charged using the electric grid. These applications require a higher energy storage capacity, reason why lithium-ion batteries are preferred due to their higher energy and power density. However, HEVs are working in a specific operating windows in which Ni-MH batteries present a longer lifetime with respect to Li-ion and do not present safety problems [9]. For these reasons 85% of the HEVs sold in 2017 were still equipped with a Ni-MH battery, including Toyota Hybrid Vehicles (Prius I, Prius II, Lexus RX), Honda Insight Hybrid, Ford Escape Hybrid and in some models of GM [10]. Yano & al. estimated to 12.9 years the lifetime of a Ni-MH battery from HEVs and a multiplication by a factor between 50 and 60 between 2010 and 2030 of the end-of life HEVs that will need to be recycled [2].

2.2. Reasons to recycle Ni-MH batteries

The actual trend is to move from linear to circular economy. One of the measures to do so is the development of urban mining, defined as "the recovery of elements and compounds from waste materials and products", to obtain secondary raw materials [11]. Since Ni-MH, are expected to play a key role in the

transition to sustainable mobility they should be integrated in the circular economy. The main raw materials concerned by recycling in Ni-MH batteries are Ni, Co and REE. Recycling of these metals present several advantages:

- it reduces the drawbacks of primary mining (high energy consumption, pollution, land occupation, child labour...) [4, 12].
- it allows to decrease the criticality of the materials.
- it can be profitable from an economic point of view.

The criticality of raw materials is assessed by the European Commission on a regular basis and depends on two parameters: economic importance and supply risk. Ni-MH batteries contain REE and Co, both considered critical raw materials in 2017. Both are used in strategic sectors, difficult to substitute, and their production is concentrated in China for the REE and Democratic Republic of Congo for Co, which are countries with high geopolitical instability.

HEVs batteries are especially interesting to recycle when compared to batteries of electronic appliances because they allow the recovery of a high amount of material by processing a small number of units. Table 1 shows the quantity of material present in the battery pack of the Toyota Prius [13], as well as the average price of the raw materials over the last 5 years, giving a potential of 100 USD per battery pack if all the Ni, Co and REE were recovered with sufficient purity. Due to the actual low prices of REE, the economic profitability of their recovery is questionable for now, but the situation could be different in a near future due to the high market instability. Moreover, recycling would decrease the European Union dependency towards China and Democratic Republic of Congo for the supply of REE and Co and a maximum collection and recycling rates would reduce the battery acidification and eutrophication potential by 80 to 95%, as well as the Global Warming Potential [13].

	REE	Co	Ni
Mass [g]	2450	1400	8050
Raw material price [USD/kg]	7	30	5
Value [USD]	17.15	42	40

Table 1: Valuable materials content in Ni-MH batteries. Based on [13, 14, 15]

2.3. Recycling processes for Ni-MH batteries

In the EU, the disposal of waste batteries and accumulators is regulated by the Directive 2006/66/EC [3]. The directive is based on the principle of the Extended Producer Responsibility (EPR). Battery manufacturers are considered responsible for the environmental impact of the products they put on the market, and shall bear the costs induced by collection, recycling and disposal (Article 16). This is supposed to incite them to invest on eco-design, reduce waste production at the root and support public collection infrastructures to achieve high collection rate and recycling efficiency. Based on the directive producers cannot refuse to take back the Ni-MH from HEVs at their end-of-life and should inform the consumers about the existing collection facilities. The minimum recycling efficiency is set to 50% by average weight and neither the energy recovery nor the outer-casing can account in the calculation in order to ensure the recovery of the metals present in the electrodes.

In the European Union, the batteries from HEVs are collected together with the end-of-life vehicles. In Portugal this is carried out by Valorcar, a non-profit organization in charge of the EPR for vehicles and batteries, then the treatment of the batteries is carried out by specialized companies. The main European recycling company for Electric Vehicles batteries is SNAM (Société Nouvelle d’Affinage des Métaux). It is a private organization which signed individual agreements with automotive constructors. SNAM has a contract with Toyota Europe since 2011 and with Honda since 2013 which put together represent 90% of the European HEVs market. The company collects and recycles the Ni-MH batteries taken out from end-of-life HEVs, but it is also in charge of the recovery of batteries production waste, batteries under warranty and batteries collected from accidented vehicles.

Recycling processes applied to Ni-MH batteries can be classified into three categories: mechanical treatment, pyrometallurgical processes and hydrometallurgical processes. The most widespread industrial approach to recycle Ni-MH is the pyrometallurgical process while numerous hydrometallurgical routes have been studied in the literature [16, 5, 17, 18].

In Ni-MH batteries, the electrodes, containing the most valuable elements are encapsulated in a plastic or iron case. Therefore, a pre-treatment intending to liberate the electrodes is beneficial for the overall hydro or pyrometallurgical process efficiency. Several studies explored the influence of manual dismantling and mechanical processing [19, 20, 21, 22]. The processes generally used are adapted from mineral processing and include crushing, sieving, magnetic and gravity separation, in or-

der to separate the materials according to their size and physical properties. The advantages of such processes are their simplicity, high efficiency and flexibility [21]. Mechanical treatment is especially interesting in the case of hydrometallurgical process for which it is systematically used. A higher black mass concentration facilitates the leaching by reducing the amount of solvent needed as well as the number of further purification steps [20]. The energy spent to perform the mechanical pre-treatment is compensated by the gain of efficiency on the recycling treatment. However, a mass loss occurs at each step that has to be considered.

Pyrometallurgical processes use high temperature to chemically convert feed material and separate the different components to be recovered [4]. Depending on the nature of the waste it can consist in remelting and spinning, liquid magnesium extraction, electroslag remelting or electrolytic extraction using molten salts [23]. Pyrometallurgical processes are the state of the art for battery recycling at industrial scale because they are easier to implement compared to an hydrometallurgical solution. In Europe the main companies using these processes are SNAM in France, SAFT AB in Sweden and ACCUREC GmbH in Germany, while INCO is the leader for the US market. All these companies use closed furnace processes. The scrap mixture is placed inside a vessel placed in a sealed chamber with outlets for the gases produced by the decomposition of the batteries component. The successive vaporization of the different batteries components starts with water and is followed by organic materials and cadmium if nickel-cadmium batteries are part of the input material. It is obtained by increasing the temperature step by step using heating elements. The residue in the vessel is a mixture of nickel and iron. Depending on the process furnaces can operate under different conditions: atmospheric pressure, low pressure and vacuum [24].

The main alternative to pyrometallurgical processes are hydrometallurgical processes. Their advantage over pyrometallurgical treatments is the possible recovery of REE in addition to the base metals and a higher purity of the final product. They are complex processes, with numerous steps and parameters, leading to dozens of possible combinations. Almost all hydrometallurgical processes require a mechanical pre-treatment to liberate the electrodes material from the casing [25]. Then, a typical treatment starts with the leaching of the material in order to selectively dissolve the metals of interest [4]. The leaching of Ni-MH powder is carried out using inorganic acids, among which sulfuric acid H_2SO_4 and hydrochloric acid HCl were the most studied. The chemical reactions involved in the leaching using H_2SO_4 are described by equa-

tions ?? and 5, while the ones involved in the leaching with HCl are described by equations 6 and 7 [25]:

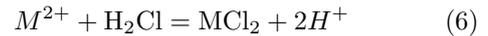
Sulfuric acid leaching:



Where $M=Ni, Co, Mn, Zn$



Hydrochloric acid leaching:



Where $M=Ni, Co, Mn, Zn$



The main experimental factors influencing the leaching efficiency are the leaching agent, the solid-to-liquid ratio, the leaching time and the temperature that need to be optimized. Higher temperature, higher acid concentration and low solid-to-liquid ratio were reported to give the best results, however this lead to higher acid and energy consumption which is detrimental from an economic point of view [26, 27]. After leaching, REE and metals must be recovered: several options are available, including selective precipitation, solvent extraction, electrochemical processes and adsorption, or a combination of several methods.

The most common methods are solvent extraction and selective precipitation. In solvent extraction leach liquor is put in contact with an organic phase and metallic ions are selectively transferred from the liquor to the organic phase [25]. Then metal ions are recovered from the organic phase by stripping or scrubbing. Recovery yields superior to 90% are often reached with this method. Recovery by selective precipitation can be carried out using $NaOH$, KOH and oxalic acid. A comparison with selective precipitation carried out by Provazi & al. showed that solvent extraction enabled higher recovery yields than selective precipitation [28]. However, solvent extraction is a complex process involving numerous operations. Their optimization includes the determination of the different steps, their relative order as well as the reagents to be used. Then the organic to acid ratio, pH and number of stages required to reach acceptable purity must be determined too [29].

From an industrial point of view some recyclers, together with electric car manufacturers, developed combined processes known as "pyrohydrometallurgical processes". This processes aim at overcoming the drawbacks of traditional industrial pyrometallurgical processes and obtain a final product with sufficient quality to be used again in

the battery industry. Two processes were developed recently by Umicore/Rhodia and Honda, in which the REE-containing slags from the pyrometallurgical process are recovered and sent to a hydrometallurgical plant to extract the REE [30].

3. Experimental methodology

The experiments were carried out using a spent Ni-MH pack from an hybrid vehicle provided by Valcar. The pack consisted of three identical modules whose specifications are given in Table 2. The

Cell type	Voltage[V]	Capacity[Ah]	Number of cells
Ni-MH	36.0	13	30

Table 2: Specifications of the Ni-MH module used for the experiments

experimental methodology followed the flow-chart of Figure 2. It was divided into four main steps: discharge, physical treatment, characterization and hydrometallurgical treatment.

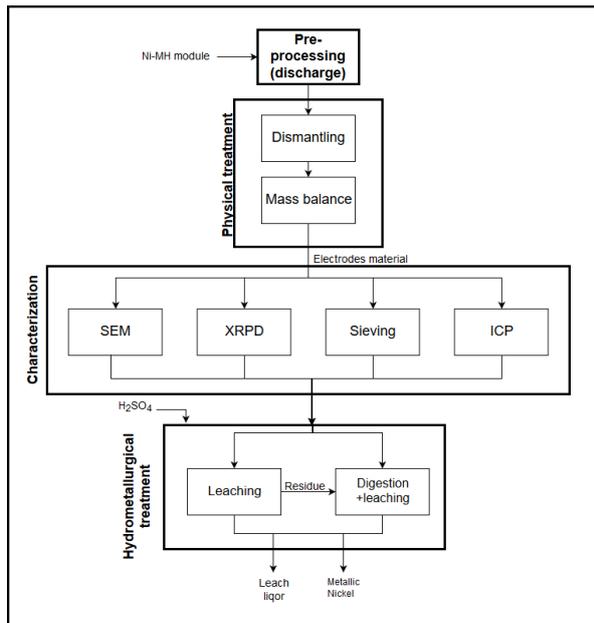


Figure 2: Experimental methodology

First, one Ni-MH module was discharged for 48 hours with a domestic oil-heater, equivalent to a constant resistance. Then, the module was manually dismantled, the cells were opened using a cutting disk, the electrodes were unrolled and separated. All the components were measured and weighed in order to carry out a mass balance.

In a second time the electrodes were characterized. The phases were determined using X-Ray Powder Diffraction (XRPD) and the morphology using Scanning Electron Microscopy (SEM). The

particles size of the electrodes active material was determined by wet sieving and laser diffraction spectroscopy, and the elemental composition was determined by Inductively Coupled Plasma Mass Spectroscopy (ICP).

After the characterization leaching in H_2SO_4 was performed for the anode active material and for the cathode separately. A factorial experiment was carried out in order to study the influence of the acid concentration, leaching temperature, presence of H_2O_2 and liquid-to-solid ratio. This was done by analyzing the leach liquor composition by ICP. The first tests did not succeed in dissolving totally the cathode material, therefore an alternative strategy was tempted, consisting in a digestion of the material at $150^\circ C$ for 1 hour, using concentrated H_2SO_4 in various amount, followed by leaching in distilled water for 3 hours. After the leaching tests the residues were recovered to be weighed and analyzed by XRPD.

4. Results

4.1. Discharge

Because the power of the heater used to carry out the discharge was very high compared to the power of the module the discharge took longer than expected due to a recuperation phenomenon. The voltage at the module terminal dropped to 0 V in 3 min. However, after removing the heater the voltage started to increase again and after two hours 93% of the initial value was recovered. In an ideal circuit this recuperation phenomenon would not be observed since all the cells would have the same voltage difference at their terminals. However, in practice some cells are more damaged, with smaller voltage and higher resistance to the current. If the variation of resistance between two neighboring cells is too important, the cells with higher resistance are susceptible to experience an inversion of the polarity when a load is applied, leading to a total voltage close to 0 V, as it was observed during the experiment. When the circuit is open a readjustment of the charges occurs through the cells and an increase of the total voltage is observed.

4.2. Dismantling and mass balance

An exhaustive list of the components of the Ni-MH module is presented in Figure 3 with the corresponding labels. The module was constituted of 30 identical Ni-MH cells (C), assembled in 10 columns, of 3 cells each, and connected in series by means of metallic connectors (D). The cathode and the anode, separated by a polymer sheet, were rolled together in a jelly-roll structure forming the electrode roll (C3). From the center to the exterior, the layers followed the sequence: separator, cathode, separator, anode.

The steel case (C1) corresponded to the negative

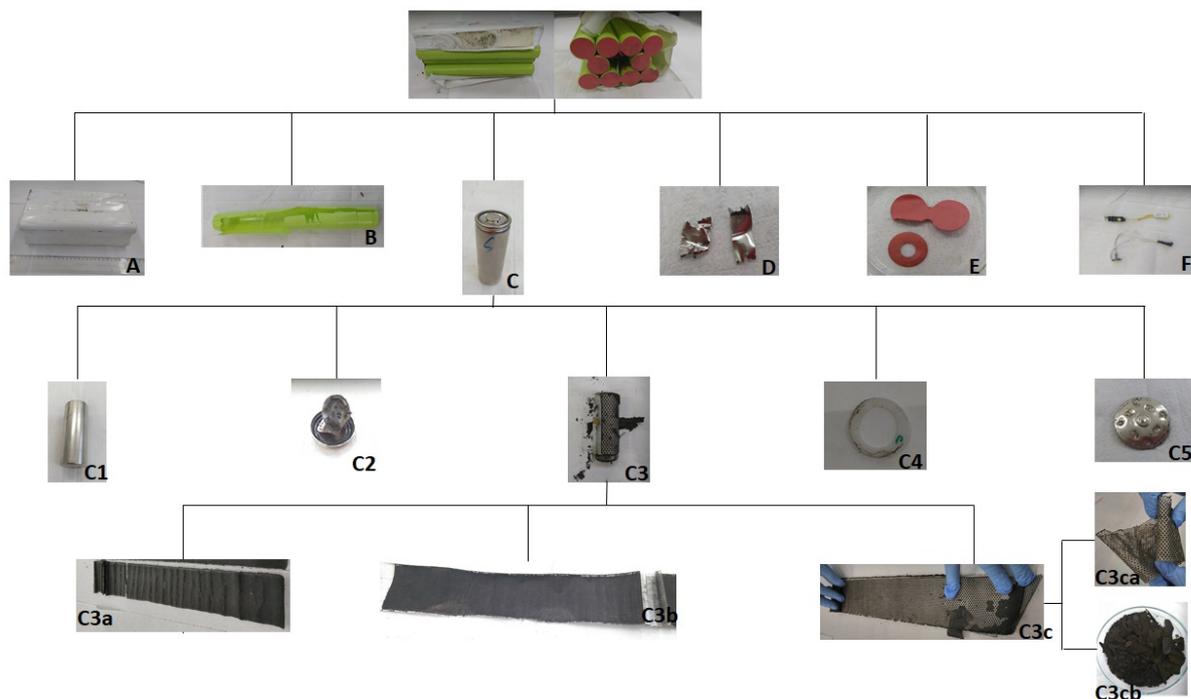


Figure 3: Components of a the Ni-MH module separated by manual dismantling: A) White plastic label, B) Green plastic label, C) Battery cell, D) Metallic connectors, E) Cardboard insulators, F) Cables, C1) Steel case C2) Cathode collector, C3) Electrode roll, C4) PVC sealant, C5) Anode collector, C3a) Cathode, C3b) Separator, C3c) Anode, C3ca) Anode grid, C3cb) Anode paste.

pole. The electric connection with the anode was made by the current collector (C5). The positive pole (C2) corresponded to the top case, connected to the cathode. The mass balance carried out indicated that in one single cell, the cathode accounted for 31.8% of the weight, the anode for 35.9%, the polymeric separator for 9.5% and the electrolyte for 6.3%. The whole module was found to be mainly made of metals (85%), then plastics and cardboard accounted for 6% and the electrolyte for 6%. The 3% remaining were shared between the electric circuits and the mass loss during the dismantling.

4.3. Characterization

Optical microscopy The cathode was brittle, and its structure was not visible to the naked eye. The image on Figure 4 was observed with an optical microscope. The cathode was $780\mu\text{m}$ thick and was made of a metallic wire of $80\mu\text{m}$ average diameter, forming polygonal 3D meshes of various sizes from $280\mu\text{m}$ to $965\mu\text{m}$ diameter. The metallic mesh plays at the same time the role of substrate for the active powder and of electric conductor. On the contrary, the anode was made of a 2D flexible grid, covered on both sides by the active material which detached easily. The grid presented a regular circular pattern of 2 mm diameter.

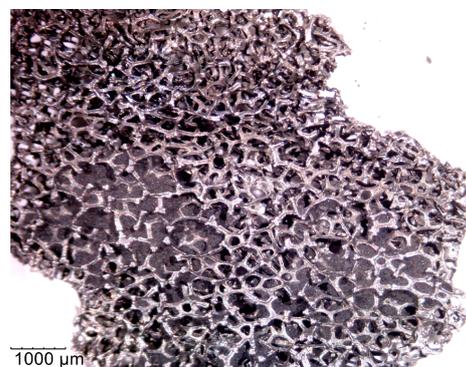


Figure 4: Cathode 3D structure observed with an optical microscope.

XRPD XRPD of the anode support grid indicated a metallic nickel Ni^0 phase. The diffractograms of the anode paste were very similar to the ones reported by Cabral & al. and Larsson & al. and were identified as a LaNi_5 structure with some peaks deviations. The deviation corresponded to the partial substitution of La by other rare-earth elements and of Ni, by Co, Al, and Mn [31, 5]. Regarding the cathode, the metal mesh corresponded to Ni^0 . The peaks were narrow, indicating a high crystallinity of the material. The active powder was under the form of $\text{Ni}(\text{OH})_2$, corresponding to the

phase in discharged conditions [31]. The broadening of the peaks indicated poor crystallinity and structural disorder.

SEM Both anode and cathode were analyzed by SEM. The cathode free active powder showed in Figure 5 presented a spherical morphology with a diameter from $3.5 \mu\text{m}$ to $20.7 \mu\text{m}$. EDS indicated the presence of Ni, Co, Na, O, Au and Pd. Au and Pd were added during sample preparation to make it conductive while Ni and O are concordant with the $\text{Ni}(\text{OH})_2$ phase identified by XRPD. Co is a common additive in nickel hydroxide powders, since it prevents the formation of $\gamma\text{-Ni}(\text{OOH})$ phase that causes volume expansion of the electrode and is associated to a degradation of the cell performances [32]. Na came from the NaOH electrolyte.

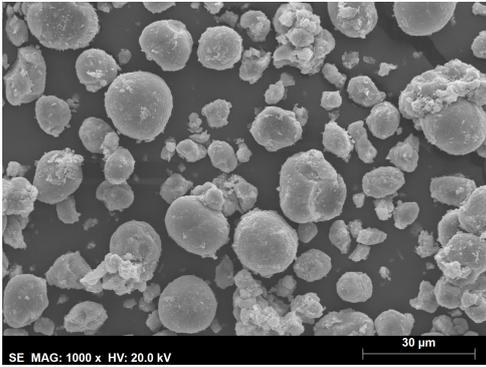


Figure 5: SEM micrograph of the cathode active material

Regarding the anode, Figure 6 showed a flat structure with no relief. The elemental composition of the region was determined using EDS. C was present in a non-neglectable quantity despite never being mentioned elsewhere in the literature. Some carbon might have been added to the anode paste to enhance the electric conductivity of the paste in the absence of 3D conductive grid. Assuming an LaNi_5 -type alloy, EDS gave the following stoichiometry: $\text{Ni}^{3.38}\text{Co}^{0.77}\text{Mn}^{0.5}\text{Al}^{0.14}\text{La}^{0.41}\text{Ce}^{0.53}\text{Nd}^{0.17}\text{Pr}^{0.08}$.

The composition is similar to the one of materials already reported in the literature, however the A:B ratio was found to be 1.21:4.79 instead of 1:5 [5, 6]. This could be explained by either an overstoichiometric material or by a local variation of the material composition. The partial substitution of La by other lanthanoids and of Ni by Co, Al and Mn intends to increase the lifetime and the performances of the cell [6]. The chemical composition needs to be confirmed with more precise methods, which was done using ICP .

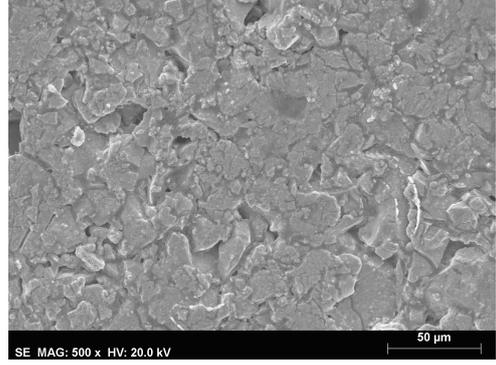


Figure 6: SEM micrograph of the anode active material

Granulometry The results of the anode active powder diffraction spectroscopy showed two sizes of particles. 50% of the material was inferior to $25 \mu\text{m}$ and 90% was inferior to $120 \mu\text{m}$.

Wet sieving of the cathode performed after crushing showed two sizes of material too. The finer fraction had a diameter inferior to $100 \mu\text{m}$ and represented 75% of the electrode weight. This fraction corresponded to the $\text{Ni}(\text{OH})_2$ black powder liberated by water and crushing. Laser diffraction indicated that 90% of the nickel hydroxide powder was comprised between $11 \mu\text{m}$ and $17 \mu\text{m}$. The coarse fraction represented 25% of the cathode weight and had a diameter higher than $250 \mu\text{m}$. The visual aspect was the one of the crushed metal mesh with some residual hydroxide powder. It was therefore concluded that nickel hydroxides represented at least 75% of the cathode weight.

ICP After complete dissolution of a material in aqua regia ICP is able to determine the concentration of the different metals in solution. These concentrations were used to determine the initial solid material composition using equation 8:

$$\text{wt}\% = \frac{\text{metal concentration}[\text{mg/L}] \times V_{\text{final}}[\text{L}]}{\text{sample weight} [\text{mg}]} \quad (8)$$

The average weight composition determined for the anode is presented in Table 3. The sum of all the

	Ni	Co	Al	Mn	Ce	La	Pr	Nd	Sum
wt%	53.9	11.4	1.9	5.5	13.6	9.7	1.8	5.0	102.6

Table 3: Chemical composition of the anode material determined by ICP

elements around 100% indicated that the material was completely dissolved by aqua regia. However, when looking at the A:B atomic ratio a value of 1:6 which is too far from theoretical values [6]. Regarding the cathode, hydroxyl groups coming from

Ni(OH)₂ and Co(OH)₂ should not be forgotten in the composition. Since O and H concentrations were not measured by ICP their content had to be calculated. In order to do so an assumption must be made regarding the distribution of Ni and Co between the metallic and hydroxide phases. To be coherent with the granulometry results it was assumed that Ni(OH)₂ represented 80% of the cathode weight and that Ni⁰ represented 20%. The same assumption was made for Co despite Co(OH)₂ phase not being detected by XRPD. Since Co accounted for approximately 5% of the electrode composition it was too low to be detected by XRPD. The composition obtained for the cathode is given in Table 4.

	Ni	Co	Al	Mn	Fe	OH	Sum
wt%	73.3	5.1	0.21	0.15	0.04	32.6	111.4

Table 4: Chemical composition of the cathode material determined by ICP.

4.4. Hydrometallurgical treatment

Anode First the calculation of the anode leaching yields were made using the composition determined in Table 3. However, using these values led to leaching efficiencies systematically highly superior to 100% for La and Ce and were comprised between 115% and 140%. Two phenomena might have occurred. The first one is some interference between the emission spectra of La and Ce that are very similar. The second one is an interference coming from the media. The first analysis were carried out in aqua regia while the leaching tests were performed using a solution of H₂SO₄ leading to a difference of viscosity that may affect the ICP results. Since no residue was recovered at the end of the leaching test it was assumed that the final yields were 100%. And the initial composition of each sample was recalculated from the metals present in the liquor at the end of the experiments. The average composition is given in Table 5. It gave a lower content of Ni and Co and higher content of La and Ce. With this second method, the atomic A:B ratio is closer from the theoretical value of 1:5. From the average atomic composition the formula of the hydrogen storage alloy was: Ni_{3.27}Co_{0.69}Mn_{0.37}Al_{0.25}La_{0.32}Ce_{0.4}Nd_{0.13}Pr_{0.04}. This formula was almost the same as the one obtained by EDS and lead to B:A ratio of 5.2:0:8 which is closer from the theoretical value. Therefore this composition was used rather than the previous one for the leaching yields calculations.

The best conditions for the anode leaching were considered the ones that minimized both the acid and the energy consumption while giving a max-

	Ni	Co	Al	Mn	Fe	Ce	La	Pr	Nd	Sum
wt%	46.8	10.3	1.8	5.2	-	14.2	11.3	1.3	4.7	98.3

Table 5: Chemical composition of the anode material determined by mass balance.

imum leaching yields. They corresponded to 1M H₂SO₄, with L/S=20 L.kg⁻¹ at room temperature, for one hour and allowed to dissolve 100% of Ni, Co and REE. Increasing the concentration to 2M decreased the leaching time to 30 min, while lower concentration did not allow complete dissolution while the addition of 1 wt% H₂O₂ did not have any relevant effect.

Cathode Complete dissolution of the cathode was never achieved, even for the strongest conditions (2M H₂SO₄ at 90°C). XRPD of the residue allowed to determine that the Ni(OH)₂ phase which is known to be very reactive dissolved completely after 3 hours at room temperature in 1M H₂SO₄, while the Ni⁰ phase required much stronger conditions to start dissolving. Like for the anode it was verified that increasing the temperature and the acid concentration was increasing the leaching yields. However the Ni⁰ could never be dissolved completely. Since the Ni⁰ residue is quite pure it can be sold directly as secondary raw material for the metal industry. Therefore the best recycling strategy would consist in performing a leaching in mild conditions (1M at room temperature for 3 hours) to selectively dissolve the Ni(OH)₂ powder and separate it from the Ni⁰ mesh.

Digestion of the cathode Performing a digestion at 180°C before water leaching aimed at assessing the possibility of dissolving the metallic nickel while reducing the acid consumption. Leaching yields between 53.1 and 61.7% were obtained for Ni and between 71.7% and 83.6% for Co with this method. When compared to the single-step leaching tests carried out for the same amount of acid the results were systematically worse. Moreover total dissolution of Ni⁰ was never achieved, meaning that it would required strongest conditions, most probably higher temperature which it is not worth from an economic point of view. Moreover once dissolved in the acid, the Ni would need complex treatments to be extracted and recovered under metallic form. Therefore the solution consisting to dissolving only the Ni(OH)₂ phase and recovering directly the Ni⁰ one appears to be preferable.

4.5. Intrinsic material value

The electrodes material composition, together with the module mass balance allowed to quantify the

elements present in the initial battery pack, constituted by three identical Ni-MH modules. The results are presented in Table 6. Based on the raw material average price over the last five years the value of the materials present in the pack was evaluated. The most valuable material is Ni, due to the

Metal	Ni	Co	REE	Steel
Mass kg	9.2	1.018	2.076	0.996
Cost [USD/kg]	5	30	7	1
Value [USD]	46	30.54	14.5	1.00
Total [USD]	91.04			

Table 6: Value of the materials present in the Ni-MH battery pack

high amount present in the battery, followed by Co, which has the highest price. For the REE the price was the one of mischmetal, corresponding to the material used for the anode fabrication. Nowadays the price of REE is low, however, due to the almost complete dependency towards China and the complicated geopolitical situation between China and the USA, the uncertainty regarding the prices is high. In case a crisis similar to the one of 2011 occurred, the REE price could be multiplied by 10, making the recycling of Ni-MH batteries more interesting. The evaluation gave a value of 91.04 USD of material present in one car battery pack. As a comparison, the cost of an HEV Toyota Prius is between 2,300 USD and 2,590 USD, meaning that the raw materials account for 3.5-3.9% of the total cost.

5. Conclusions

The discharge and manual dismantling of a Ni-MH module from an HEV was carried out. A mass balance was performed, indicating that the module was made at 85% of metal, 6% of plastics and 6% of NaOH electrolyte. Then characterization of the electrodes material was performed, including optical microscopy, SEM, XRPD, laser diffraction spectroscopy and ICP. The cathode was found to be made of a metallic Ni⁰ 3D-mesh, accounting for 20% of the weight and at 80% of a Ni(OH)₂ spherical powder. ICP indicated a composition of 73.3% Ni, 5.1% Co, 32.6% OH and traces of Al and Mn. The anode consisted of a 2D Ni⁰ grid, coated with an hydrogen storage alloy of LaNi₅ type composed of 54.5% Ni, 11.6% Co, 4.2% Al, 6.2% Mn, 6.7% Ce, 5.4% La, 0.6 % Pr and 2.1% Nd. The optimum leaching conditions for both electrodes were found to be 1M H₂SO₄ at room temperature for 3 hours. These conditions allowed the complete leaching of the anode and of the Ni(OH)₂ of the cathode. The Ni⁰ cathode residue can be sold directly. The value of the material present in a battery pack was estimated to 91.04 USD. In future works the recovery of

the leach metal should be study, either by selective precipitation or by solvent extraction. Moreover the way to implement industrially an hydrometallurgical recycling process should be studied together with an economic assessment of the feasibility.

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