FLEXIBLE HYDROMETALLURGY PROCESS FOR ELECTRIC VEHICLE BATTERY RECYCLING

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Abstract

The electrification of the vehicle fleet has as a direct implication the disposal of lithium-ion batteries. It is noteworthy that such batteries need a suitable destination at the end of their useful life, since they are composed of chemical elements with high added value (such as nickel, cobalt, copper, and lithium) and that cannot be discarded in nature, a since they can generate environmental damage to the ecosystem and to the health of the population. Therefore, the development of effective processes for recycling these batteries is key to the economic and environmental sustainability of vehicle electrification. By recovering critical materials, robust recycling systems reduce raw material demand, greenhouse gas emissions and the environmental impacts associated with mining and refining activities. Within this context, hydrometallurgy has emerged as a promising process for battery recycling, presenting high efficiency, lower processing temperature, generating lower carbon emissions and lower energy consumption. The technique also has a high recovery rate for nickel, cobalt, copper, aluminium, graphite, manganese, iron phosphate and especially lithium, which cannot be recovered by current pyrometallurgy techniques. In this scenario, the present work aims to address economic, environmental and performance aspects of recycled materials, to minimize the emission of waste in nature and generate a flexible process for recycling lithium-ion batteries by hydrometallurgical route. This process will be able to process batteries of different chemistry and geometries in the same recycling batch. In the present work, different types of batteries were characterized, and the physical separation and leaching process recovered more than 90% of the minerals of interest (Ni, Co, Li, Mn, Cu and Al). More details about the project will be explored throughout the article.

Introduction

The search for renewable sources of energy leads to the development of new technologies towards a sustainable future. Among these innovations, the decarbonization by an energy matrix is a challenge in all industrial segments [1,2]. In the case of the automotive sector, there is a growing trend in the use of batteries as a source of energy for electric vehicles [3].

Among the types of batteries, the Li-ion has been used due to the high energy density, non-memory effect, low self-discharge rate, long lifespan, and lightweight equipment [4]. There are three main types of cells of Li-ion batteries for automotive market: Cylindrical, Pouch and Prismatic (figure 1. a, b, and c). These battery cells are grouped together to form a battery module, and then a set of modules form a battery pack (figure 1. d) [5].

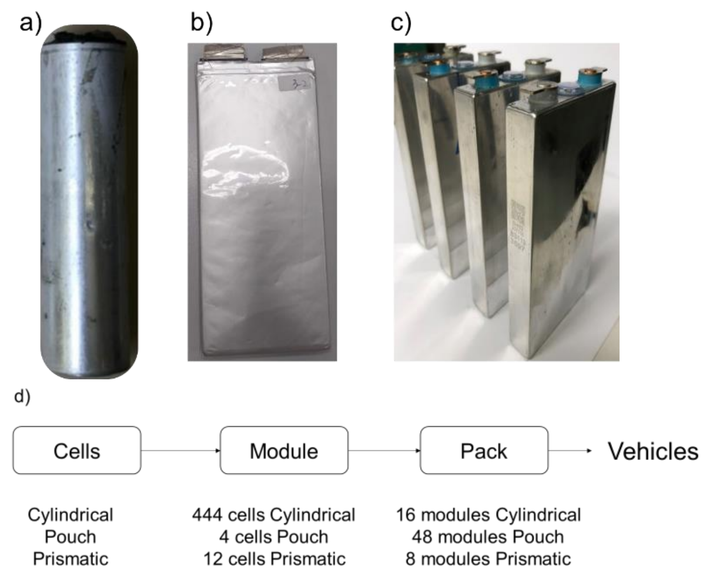

Figure 1. Photo of the types of cells (a) cylindrical (b) pouch (c) prismatic used in electric vehicles and (d) the organization cells, modules, and pack of Li-ion batteries

The estimative is to achieve 30 times of current scenario of electric vehicles until 2030 worldwide, including commercial vehicles, buses, and trucks [6]. It will occur due to the international agreements for reduction of greenhouse gas emissions, affordable and clean energy, and development of sustainable cities, in agreement with the Sustainable Development Goals [4].

The number of electric vehicles increased 415% between 2005 and 2015. In 2030, the number of vehicles may achieve around 2 billion, being 20% in China [4,7]. As a result, it is crucial the supply of materials for battery production.

These batteries are composed of critical metals, which are at risk of supply disruption in the short and medium term [8]. As a result, the market supply of Li-ion batteries is insecure. In order to solve the supply disruption, the recycling is a sustainable alternative for the destination and recovery of metals for the production chain [9].

There are two main recycling routes for Li-ion batteries: pyrometallurgical and hydrometallurgical. The pyrometallurgical process involves the use of high temperature (about 1,200°C) to obtain liquid metals and slag phases. For instance, a recycling process occurs in a furnace in three different temperatures. First, the removal of electrolyte is performed at 300°C. Then, at 700°C there is the pyrolysis of plastic. And at 1,200-1,450°C, occurs the smelting and reduction of metallic fractions. However, the pyrometallurgical process has low recovery rates, high CO_2 footprint and high energy consumption [10].

On the opposite, the hydrometallurgical process is performed in aqueous media. a recycling process first dismantling and then milling the Li-ion batteries to prepare the material for leaching. Further, precipitations steps are performed to obtain the products [10].

Comparing both routes, the hydrometallurgical processes have more advantages than pyrometallurgy [11,12]:

- Lower energy consumption;
- Less greenhouse gas emissions;
- Recovery of Li, mainly in high purity;
- Recovery of other metals by hydrometallurgy is higher than pyrometallurgy: 95% against 60%;
- Obtains several products with high purity – over 90%;

The literature reports examples of recycling of Li-ion batteries. For instance, Takahashi et al. (2020) recycled of Li-ion batteries of cell phones by hydrometallurgy with process efficiency close to 90% [13]. Chen and Ho (2018) achieved 95% of efficiency for recycling of Li-ion battery from electronic market by hydrometallurgy [14]. The recovery of lithium in a process designed by Takacova et al. (2016) reached 99% by hydrometallurgy [15].

Despite the vast literature about recycling routes and techniques applied to obtain metallic products from spent Li-ion batteries, as well as patents, none of them report a flexible process to recycle different types of chemistry of Li-ion batteries, whether prismatic, cylindrical or pouch types. Such flexibility is essential in a diverse scenario such as the one presented. Since there is a long period for adoption of certain technology and different battery compositions being tested in the market, a flexible system is something that fits well to the present and future needs of the automotive industry.

The present study aimed to propose a flexible hydrometallurgical process to recycle Li-ion batteries from electric vehicles. The batteries were disassembled and then milled before leaching. All steps occurred in aqueous media, and separation and purification steps were carried out to obtain metallic products.

Recycling process

The process proposed in this article combines different advantages presented in both hydrometallurgy and pyrometallurgy techniques, as shown in fig 2. The high recovery rate of the minerals, the flexibility in processing different types of Li-ion batteries and low cost are the main technological differences.

Three types of Li-ion batteries from electric vehicles were studied: cylindrical (Battery 1), pouch (Battery 2), and prismatic (Battery 3). Modules from cylindrical and pouch batteries were received – 46kg and 9kg, respectively – and disassembled to release the cells. The prismatic battery was received in cell format. The cells were disassembled, separated, and evaluated by gravimetric analysis for characterization.

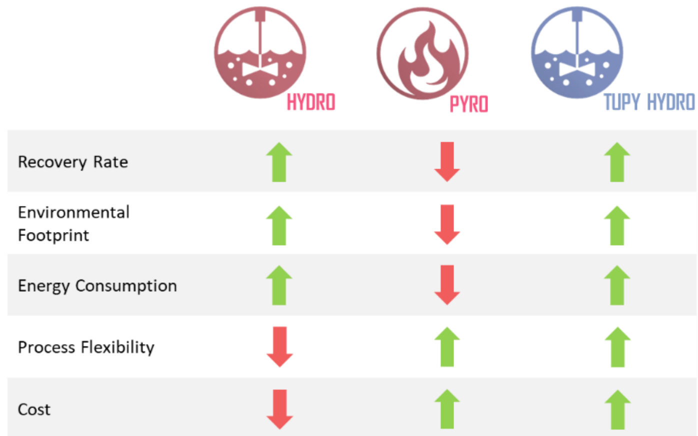

Figure 2. Technology Comparison

The recycling process was designed considering three main steps: milling, to decrease the particle size distribution; leaching, to solubilize the target metals; and separation, to separate the metals and further obtain the products with high added value.

The cell batteries were milled to separate large particle size parts, and the resulting material was leached in acid conditions under temperature (atmospheric pressure). The conditions of extraction were evaluated considering the yield of 99%. The leach solution was filtered from the solid phase and then the metal ions were separated by hydrometallurgical techniques. The experimental conditions were set considering the purity up to 90% for the products. The recycling process was designed to be flexible, simultaneously processing all types of Li-ion batteries, as shown in fig 3. The experiments were performed in lab scale using 1kg of feed material.

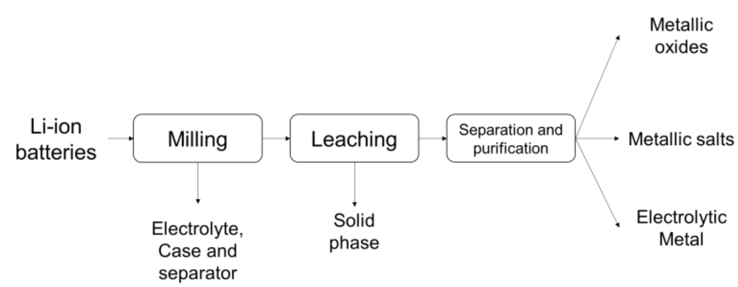

Figure 3. Flowchart proposed for flexible recycling of Li-ion batteries from electric vehicles

Results

The modules from Battery 1 can be split into: cells (56%), aluminium structure (38%) and electronic compounds, like circuit boards and cables (6%). The module from Battery 2 contained 46% of cells, 23% of plastic structure and 12% of internal aluminium structure. The rest of the material corresponds to electronic parts, such as circuits boards, connections, and cables. The information is depicted in Table 1.

Table 1. Composition of Li-ion battery modules

	Battery 1	Battery 2
Battery type	Cylindrical	Pouch
Cells	56%	46%
Structure	38%	35%
Electronic compounds	6%	19%
Mass module	46kg	9kg

* Battery 3 was received in cells.

Table 2 presents the percentage, in mass, of the main components from the evaluated battery cells, which varies according to the type of battery. During the disassembling step, it was observed that the cell components from Battery 3 were more compact than they were in Batteries 1 and 2. For instance, the case of cylindrical and prismatic cells is heavier than pouch, since in both case the structure is made of metallic aluminium with physical resistance. On the other hand, the case of Battery 2 is made of aluminium foils and so they are lighter. The amount of cathode is higher in Battery 1 and 3 than Battery 2, while the opposite was observed for anode material. Fig. 4 presents the data for each battery type.

Table 2. Composition of three types of Li-ion batteries characterized

	Battery 1	Battery 2	Battery 3
Battery type	Cylindrical	Pouch	Prismatic
Case	17%	7%	14%
Polymeric separator	8%	10%	5%
Cathode	39%	32%	40%
Anode	31%	38%	32%
Electrolyte	5%	13%	9%
Mass cell	200g	316g	880g

After module structural characterization, the cell batteries were discharged and then entire ground in knife mills. All types of batteries may be recycled together. Separation by particle size removed the case and polymeric separator. The electrolyte is removed by drying under the effect of temperature and atmosphere. The resulting material of milling process is prepared for extraction step.

The acid leaching is important to solubilize the valuable metals present in the battery. The reaction occurs in batch reactor under stirring with heating and use of acid reagent to solubilize the metals. The process was studied in glass-reactor with temperature control and magnetic stirring. The pH and redox potential were measured during the reaction over time. The reaction achieved 99% of efficiency for extraction of most valuable metals, which is important for economic feasibility.

After leaching, solid-liquid filtration is important to separate the inert material from the leach solution. The non-leached material may be used treated and then used as raw material for other industries. By the same token, the liquor obtained in the leaching reaction is rich in different valuable metals. For this reason, separation and purifications steps are required using hydrometallurgical techniques.

For instance, Fig. 5 shows a difference between a metallic salt without and with purification treatment. The unit operation increased the purity from the products until over 90%. Different products may be obtained by separation of the metals from leach solution: metallic oxides, metallic salts (such as carbonates and chlorides) and electrolytic metal. The recovery efficiency of the proposed route is at least 90% of cathode material.

As reported by Makuza et al. (2021), Assefi et al. (2020) and Kwon and Sohn (2020), the pyrometallurgical process will not recover the critical metals present in Li-ion batteries. Moreover, lithium will not be recovered, which is a massive impact to the battery market. Also, the capital investment is extraordinary due to the high energy consumption and off-gas treatment. For this reason, a hydrometallurgical route is an alternative to ally high extraction efficiencies and to meet the sustainable development goals [16][17][18].

Allied to all of this, the new generation of Li-ion batteries with more complex metallic contents will require flexible recycling process. The present manuscript reports an innovative process to receive all types of batteries used in electric vehicles.

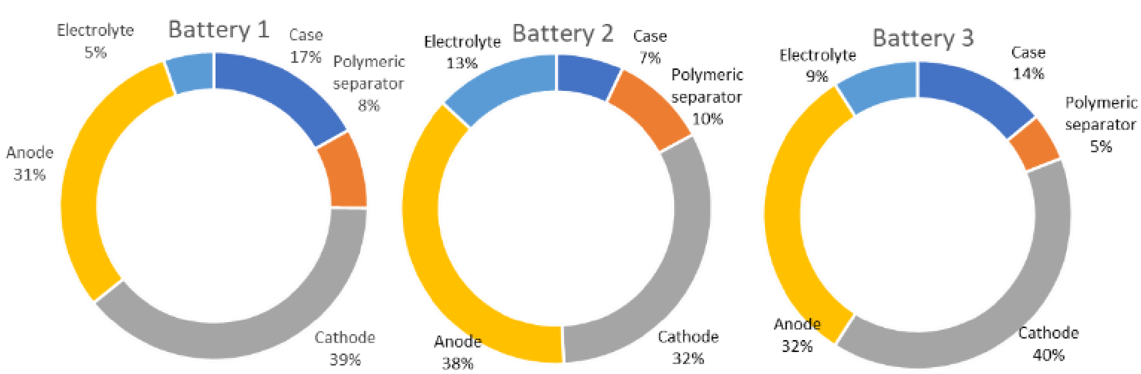

Figure 4. Composition of battery cells of cylindrical (Battery 1), pouch (Battery 2) and prismatic (Battery 3) types

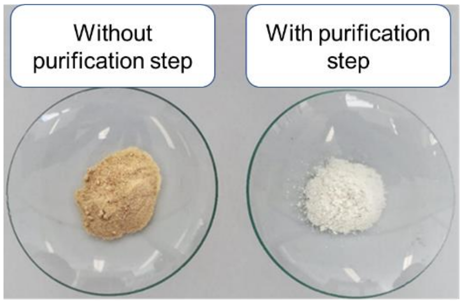

Figure 5. Differences among the materials without and with purification step to obtain high pure product

Conclusions

According to the results obtained, it may be concluded that:

- The proposed flexible recycling method can simultaneously process different types of Li-ion batteries;
- The leaching efficiency from the most valuable elements was up to 99% for all types of Li-ion batteries;
- Separation after leaching resulted in high purity end products;
- The proposed process achieved up to 90% global efficiency;
- The proposed process is efficient and has lower environmental impacts than the pyrometallurgical route;
- The designed process is innovative and will be patented.

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