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PRE-TREATMENT OPERATIONS ENVISAGING THE PROCESSING OF SPENT LI-ION BATTERIES BY HYDROMETALLURGY

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ABSTRACT
In the recycling of spent batteries by hydrometallurgy, the pre-metallurgical processing is a crucial step to produce a concentrate (black-mass) rich in electrode materials, namely the cathode powders containing the metals Li, Ni, Co and Mn. In this paper, a series of operations including drying, thermal treatment, grinding and sieving were proposed and tested. Drying allowed to remove efficiently the solvent from the electrolyte while thermal treatment was effective in removing the binder and allowing the release of electrode powders during grinding of the electrode sheets. As a result, 98% of the cathode materials containing the valuable metals were recovered in the fine fraction (below 0.5 mm) with low Al and Cu contamination from the foils. These fines constitute a valuable black-mass to be treated by hydrometallurgy.

Keywords: Li-ion-batteries. Recycling. Pre-Treatments. Dismantling. Grinding.

INTRODUCTION
Lithium-ion batteries (LIBs) currently play an important role in energy storage and electric mobility. Due to the exponential growth in materials demand, in the forthcoming years the recycling of metals from end-of-life batteries will be mandatory. Moreover, the correct management of this waste flow also provides environmental protection and materials recovery, allowing economic revenues, especially when considering the cathode metals (lithium, cobalt, nickel, manganese), the graphite from the anode, as well as aluminum, copper, among others.
As far as metallurgical processing is concerned, pyrometallurgy and hydrometallurgy are the two options [1,2]. Pyrometallurgy is a high-temperature process that provides a relatively simple solution for treating LIBs, not requiring many previous steps, and allows heat recovery from the combustion of organic components. These processes targeted cobalt and nickel that are smelted and subsequently refined, normally in hydrometallurgical refining plants. Lithium is lost in slag, regardless of efforts made to develop technology to recover lithium from it. Recently with the rising of lithium demand as well as its market value, hydrometallurgical approach has gained new and increased interest. The material feed in the hydrometallurgical plants is an electrode powder concentrate, usually called black-mass. To obtain such raw material, a series of pre-metallurgical operations are necessary [3,4]. This paper is focused on discussing and presenting results of several pre-treatments of spent Li-ion batteries towards metals recycling by hydrometallurgy.

MATERIALS AND METHODS
To obtain the cells for studying the processing of materials, several spent battery packs from electric vehicles were treated in recycling companies, involving safe discharge and dismantling for separation of materials and components. The resulting battery modules (assembly of groups of cells) were disassembled to obtain the cells to be analyzed in the laboratory. The experimental work involved the removal of electrodes, which were dried at 80ºC in an oven and thermally treated at 400ºC in a muffle furnace. The resulting material was physically processed by grinding in a cutting mill (Retch SM2000) and sieved for granulometric distribution analysis. The materials obtained in the physical

processing were analyzed by ICP-AES, after digestion with aqua-regia, to evaluate the metals distribution in the different fractions.

RESULTS AND DISCUSSION

The cells treated were all pouch-type and from the NCM chemistry (i.e., with a $Li(Ni,Co,Mn)O_2$ cathode). The approach used for the pre-metallurgical treatments was as follows (see Fig. 1):

Pre-treatments:
- The initial step in industrial practice would be the cells opening by a shearing machine. In laboratory tests this operation was replaced by manual opening of the cells.
- Removal of the solvent from the electrolyte by evaporation at 80ºC for 12 h; this operation is important not only in view of the possible recovery of the solvent (usually a mixture of alkyl carbonates) by distillation, but also in view of the subsequent physical processing operations where the solvent may eventually ignite due to heat generated by the mechanical action.
- Thermal treatment at 400ºC for 5 h; this operation is also crucial to remove the binder (usually PVDF) that keeps the electrode powders aggregated and attached to the conductive foils (Al in cathode and Cu in anode).

Physical processing:
- Grinding to allow the particle size reduction and materials liberation.
- Sieving, to separate the fines (the black-mass rich in the electrode powders) and the coarse fraction (rich in the conductive Al/Cu foils, polymeric materials and other scrap).

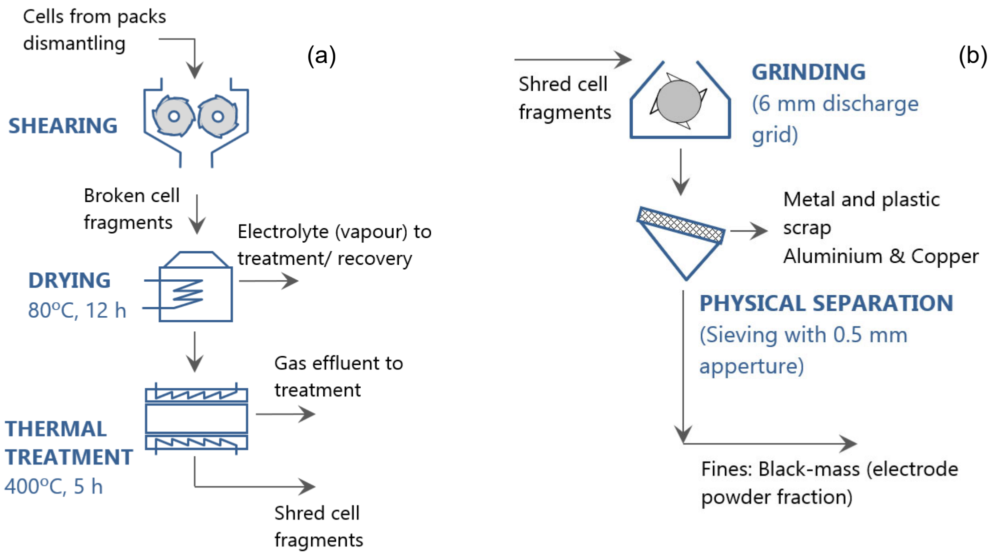

Fig. 1. Schematic diagram of the pre-metallurgical treatments in the recycling of spent LIBs: (a) Pre-treatments; (b) Physical processing.

Drying and Thermal treatment

Drying proved to be very effective for removing the alkyl carbonate organic solvent (Table 1). Regarding the removal of the binder by thermal treatment, the cathodic electrode was successfully disaggregated, and the resulting aluminum foils were almost clean. On the contrary, the anodic powder (graphite) was not removed with the same efficiency, essentially due to the partial oxidation of the copper support foils, which made the disaggregation process more difficult.

Grinding and sieving

To evaluate the real effect of binder removal on electrode disaggregation, grinding tests in a cutting mill were performed on sheets of pre-treated electrode samples (dried and thermal treated). The resulting particle size distribution as well as the chemical analysis of the fractions allowed the evaluation of the best particle size for the effective separation of the black-mass from the metal scrap essentially composed of the collecting foils (Fig. 2). The range 0.3-0.5 mm seems adequate for maximum electrode recovery with minimum Cu and Al contamination. Recovery of fines with 98% of the cathode materials (containing Li, Ni, Co and Mn metals) was achieved, with only 10-15% Cu and 1-2 % Al present in the initial material. The black-mass produced by the process has therefore a good purity and is a suitable raw-material to be used as feed for a hydrometallurgical process to recover metals from spent LIBs.

Table 1. Average weight loss and removal efficiency in the drying and thermal treatment operations, applied to electrode sheet samples.

Operation	Conditions	Weight loss (wt%)	Efficiency (%)
Drying	80ºC, 12 h	5.9 %	Solvent removal: 95%
Thermal treatment	400ºC, 5 h	Cathode: 9 % Anode: 13 %	Cathode disaggregation: 85 % Anode disaggregation: 50 %

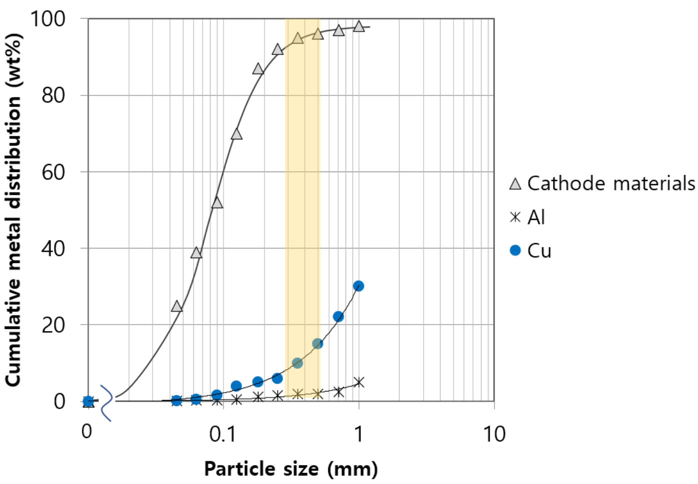

Fig. 2. Cumulative metal distribution in size fractions of grinded electrode sheets using a cutting mill with 6 mm discharge grid, in samples previously dried and treated at 400ºC for 5 h.

CONCLUSIONS

Pre-metallurgical treatments by drying, thermal treatment, grinding and sieving were tested and proved to be suitable for the production of a black-mass concentrate containing 98% of the cathode materials (with Li, Ni, Co and Mn) and relatively low contamination of Cu and Al from the foils.

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