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A Solar Pyro-Metallurgical Process for Li-ion Batteries Recycling: Proof of Concept

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Abstract. Recycling Li-ion batteries is a delicate but strategic operation that can be performed by either pyrometallurgy, hydrometallurgy or a combination of methods. This paper presents, for the first time, an innovative solar pyrometallurgical route that consists in three steps. They are pyrolysis, mechanical separation and smelting. The process is applied to $LiNi_xMn_yCo_{1-x-y}O_2$ (NMC) cathode material. After pyrolysis at 580°C and smelting at 1000°C, the final product is a Ni-based alloy containing Co, Li and Mn.

Keywords: Solar Thermochemistry, Recycling, Li-Ion Batteries, Pyrolysis, Smelting

1. Introduction

The battery market represents a major economic challenge. Global demand for batteries in GWh is expected to increase tenfold between 2020 and 2030. The European market could represent 250 billion euros per year by 2025 (European Commission figures). Moreover, the battery is a strategic issue for the automotive industry: it represents between 30 and 40% of the price of an electric vehicle. The European battery alliance launched by the European Commission in 2017 to build an integrated value chain on European soil is bearing fruit. Fifteen Li-ion battery factory projects have been launched in Europe with a production capacity of 500 GWh by 2030. While it accounted for only a few percent of global battery production in 2019, Europe could be in a position to meet its domestic demand in 2025. But many challenges remain, including battery recyclability, which remains a major challenge for the European industry.

Recycling Li-ion batteries is a delicate operation that is not yet fully automated because there are no standardization norms for the design of battery packs. Recycling presents electrical, thermal and chemical risks that need to be controlled.

After summarizing the strategic metal issues in Li-ion batteries and the current recycling routes, this paper presents the first results of a solar pyro-metallurgical process for the recovery of electrode materials derived from used lithium ion batteries and thus replace a CO_2 emitting energy (combustion) by a renewable non-emitting energy.

2. Strategic metals in Li-ion batteries

A lithium-ion battery (LIB) is composed of five main components: anode, cathode, separator, electrolyte and current collector. The anode is a copper foil coated with graphite; the cathode is an aluminum foil coated with an electrochemically active material. The composition of LIB changes rapidly since LiCoO2 (LCO) was first commercialized in 1991. Today, layered oxides, spinel oxides, and polyanion oxides are the three main types of cathode materials. Cathodes can also be composed of a variety of elements, such as Ni, Mn, and Co. In particular, $LiNi_xMn_yCo_{1-x-y}O_2$ (NMC) is considered the most promising cathode material [1]. More generally, the active material is usually a lithium transition metal oxide $LiMO_2$, (where M stands for Co, Ni, Mn, Al) or NMC (Ni, Mn and Co) and NCA (Ni, Co and Al) materials, with different ratios between particular metals. $LiNi_xMn_yCo_{1-x-y}O_2$ (NMC) is considered the most promising cathode material [1]. A polymeric binder, most often polyvinylidene fluoride (PVDF), improves the adhesion between the Al foil and the active material. Ionic conductivity is provided by an electrolyte such as mixtures of alkyl carbonates and Li salts, such as LiPF6.

The quantities of strategic metals per kWh of storage capacity are as follows,

Lithium: 0.05 - 0.10 kg/kWh

Cobalt: 0.03 - 0.13 kg/kWh

Nickel: 0.39 - 0.48 kg/kWh

Among the components present in li-ion batteries, Co is the most targeted metal for recycling because of its relatively high price. In addition to Co, Li and Ni are also common target elements for recycling.

3. Li-ion batteries current recycling processes

Current recycling process are reviewed in [2]. LIBs must be first classified and most often pretreated through discharge or inactivation, disassembly, and separation after which they can be subjected to direct recycling, pyrometallurgy, hydrometallurgy, or a combination of methods. The three main options are illustrated in Figure 1.

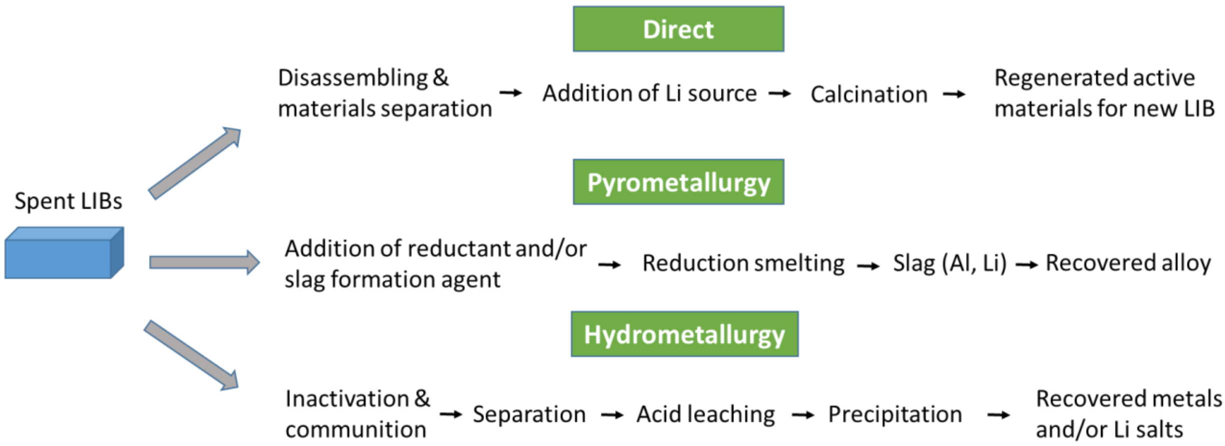

Figure 1. *The three main LIB recycling processes, adapted from [2].*

Direct methods involve cathode material removing for reuse or reconditioning. They require disassembly of LIB to obtain useful battery materials. Methods to renovate used batteries into new ones are also requiring battery disassembly to replace battery components.

Pyrometallurgy uses thermal energy to convert metal oxides of the LIB materials to metals or metal compound. After pretreatment, the battery materials are processed by smelting (reductive melting) under vacuum or inert atmosphere. The treatment results in converting the metal oxides to a mixed metal alloy containing cobalt, nickel, copper, iron, and slag containing lithium and aluminum. The composition of the product depends on the battery composition.

In hydrometallurgical processes aqueous solutions are to extract and separate metals from LIBs. Acids such as H_2SO_4 and H_2O_2, HCl, HNO_3 and organic acids are used to extract the pretreated battery materials (Al and Cu current collectors are previously removed). Then, metal containing components are precipitated selectively as salts using pH variation or extracted using organic solvents.

Combination of methods integrate generally a heat tretament step (for example pyrolysis) and hydrometallurgy steps [3].

In this context of fast variation of LIBs composition, pyrometallurgical processes would face negligible challenges from evolving battery design because of their low requirements on pre-treatment [1]. This recycling route is considered as energy-intensive and, consequently, CO_2-emitted when using fossil fuel as energy source. Nevertheless, this drawback disappears if renewable energy is involved in the thermal process. The following section presents the first results of LIB recycling using an innovative solar pyrometallurgical process.

4. Solar recycling process

4.1 A three-step process

The solar recycling process consists in three steps; two of them involve solar heating of the materials as illustrated in Figure 2.

Step 1. Thermal pre-treatment by pyrolysis at 580°C, which is a technology currently recommended in the battery recycling industries for the removal of binder and organic impurities as well as the separation of electrode materials and copper/aluminum foils.

Step 2. Mechanical separation of cathode and anode materials from the current collectors, copper foil for the anode and aluminium foil for the cathode.

Step 3. Carbothermal reduction (smelting) at 1000°C to separate the transition metals in metallic form. A mixture of pyrolysed cathode material (containing the metals to recover) with carbon is processed. The graphite recovered from the anode is used as the reducing agent.

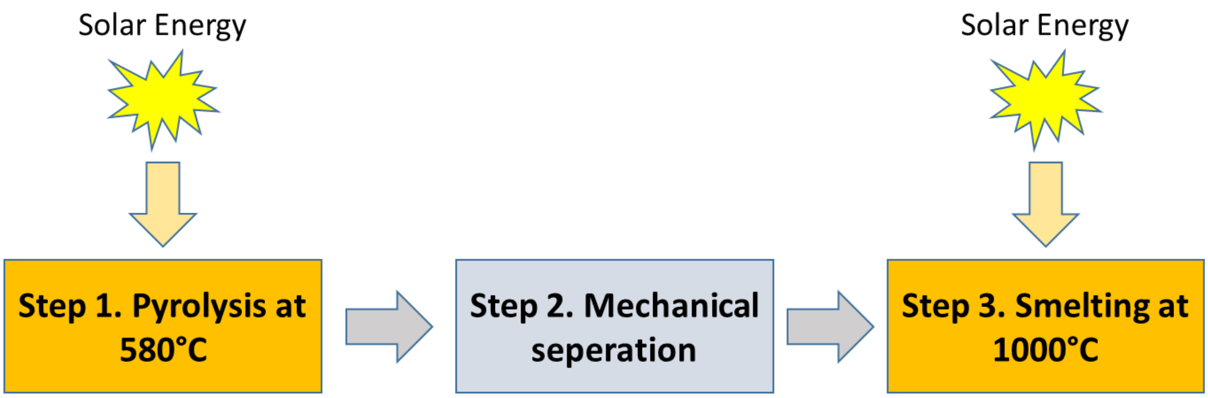

Figure 2. *The solar process for LIB material recycling.*

4.2 Experimental setup

The experimental setup is illustrated in Figure 3 and the system in operation in Figure 4.

The solar concentrator is a 1.5 kW solar furnace working in the beam-down mode (Fig. 3a). The samples are placed in a crucible placed in a cavity in order to get a homogeneous temperature (Fig. 3b). The assembly is put in a chamber in which pressure and atmosphere composition can be controlled. Both steps 1 and 3 are performed under argon gas in the same chamber in sequence. A PID controller enables managing the operation temperature by moving the position of the shutter blades.

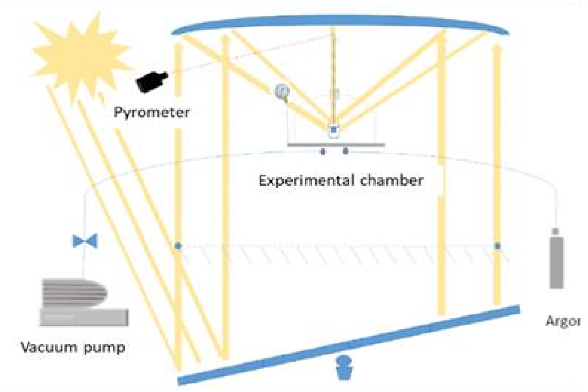

Fig. 3a **Fig.3b**

***Figure 3**. The experimental setup, the chamber and the crucible located inside a graphite cavity.*

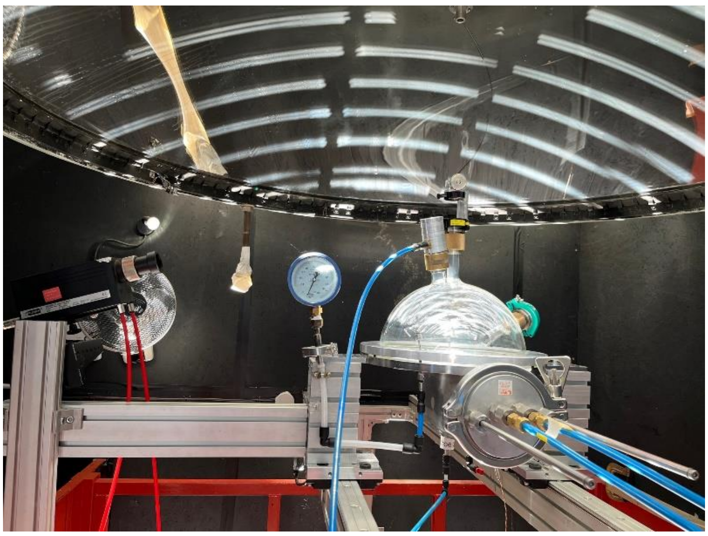

***Figure 4**. The experimental setup during a run.*

4.3 Protocol and experimental results

4.3.1. Protocol

The LIB collectors are provided by SNAM Company, they are NMC type for the cathode and graphite for the anode. The collector foils are cut is small chips of approximately 3x3 mm in size and placed in an alumina crucible to be pyrolysed (Step 1). Both cathode and anode foils are pyrolysed. After separation of the metallic foils and the pyrolysis product from the cathode, the “black mass”, (Step 2), is mixed with the graphite recovered from the anode to be smelted (step 3). Both initial LIB material and final product composition is determined by ICP-OES. The metal composition of starting NMC material is given in Table 1.

Table 1. *Composition in main components of interest of the starting NMC LIB material.*

Element	Co	Ni	Li	Mn	C	Al	Cu
wt %	5.43	44.59	6.72	2.30	5.80	10.43	<0.005

For pyrolysis and smelting argon flow rate is 3.5 sl/h.

4.3.2. Experimental results

The pyrolysis step was performed during 30 minutes. The selectivity of the separation of the collector components is very sensitive to the pyrolysis temperature. For example, pyrolysis of cathode material at 570 an 580°C results in a variation of the component (black mass and aluminum foil) of 73.5 and 84% respectively. At 600°C, the metal collector becomes brittle. Consequently, the recommended pyrolysis temperature is 580-590°C. Several samples were pyrolysed in order to obtain enough material for step 3. The composition of the cathode pyrolysis products is illustrated in Table 2. Carbon and aluminum have been eliminated. The variations of the composition of the other components are in the range of uncertainty of the measurements.

Table 2. *Composition in main components of interest of the cathode pyrolysis product after separation.*

Element	Co	Ni	Li	Mn	C	Al	Cu
wt %	3.47	49.06	5.93	2.44	0	0.16	<0.05

The smelting process is achieved during 30 minutes at 1000°C by mixing the black mass from the cathode with the pyrolysed product (graphite) of the anode. The product looks like a metal bead. It is a Ni-based alloy which composition in given in Table 3.

Table 3. *Composition in main components of interest after solar smelting of the cathode pyrolysis product.*

Element	Co	Ni	Li	Mn	C	Al	Cu
wt %	5.28	74.24	6.78	3.56	0	0.92	<0.05

Table 3 proves that recovery of strategic metals by solar pyrometallurgy can be achieved.

Figure 5 plots the XRD pattern of the product after solar smelting. It indicates that Ni is in the metallic form. The product is a Ni-based alloy.

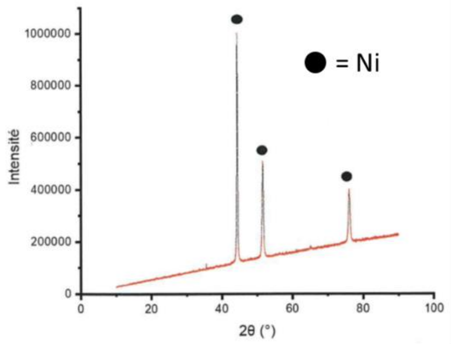

Figure 5. *XRD pattern of the product after solar smelting.*

5. Conclusion

We demonstrated that a 3-step solar pyrometallurgical process can achieve recycling of strategic metals of LIBs. The results must be confirmed by additional experiments at variable temperature, in particular concerning the smelting step. Reaction mechanisms and upscaling issues are also one of the targets of future works.

Data availability statement

All the data have been presented in the paper except XRD patterns.

Author contributions

Gilles Flamant: Conceptualization, data curation, funding acquisition, methodology, writing-original draft; Soukayna Badre-Eddine: Investigation, methodology; Françoise Bataille: Supervision, writing-review and editing; Nicolas Coppey: Investigation, data curation.

Competing interests

The authors declare that they have no competing interests.

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