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Targeted removal of aluminium and copper in Li-ion battery waste solutions by selective precipitation as valuable porous materials

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Abstract

End-of life Li-ion batteries can be a source of valuable materials to rebuild new batteries or for other applications. In this way, we propose to precipitate metals from a dissolution solution of Li-ions batteries (LiBs) as hybrid organic-inorganic materials (metal-organic frameworks, MOFs), well known in many fields due to their specific properties (high porosity, large surface area and sometimes thermal and chemical stability). From raw LiBs containing Al, Cu, Mn, Ni, or Co mainly, a selective precipitation of different metals as MOFs has been possible. The use of a carboxylate ligand allowed complete precipitation of Al from the solution, whereas using a bipyridine ligand changes the selectivity to precipitate Cu as MOFs. This work shows that formation of different MOFs in a multi-metallic solution can be obtained depending on the precipitating agent.

Keywords: Recycling; Lithium-ion battery; Metal Organic Frameworks; Selective precipitation; hydrometallurgy process

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1.   Introduction

Increasing adoption of electrical drive systems and stationary energy storage for renewable energies would lead to a high demand of raw materials for the production of lithium-ion batteries (LiBs).[1] The mining process for extracting metals from ore considerably affects the environment. The recycling of such batteries is now crucial not only to manage our waste, but also to provide a source of precious metals necessary to resynthesize batteries (close loop recycling) or to generate valuable materials for other applications (open loop recycling).[2] Present day state-of art industrial processes are mostly based on pyrometallurgical processes that melts spent LiBs entirely without further pretreatment.[3] The metal phase is then leached with acid solutions after cooling and several chemical precipitations are performed to separate metals as inorganic salts. This method requires a lot of energy and is not efficient to recover all valuable materials especially the lithium. It also generates dust or hazardous gas.[4] Another possibility to recycle batteries relies on hydrometallurgy processes, which consist to dissolve the battery in concentrated acid[5] and then extract metals from the leachate. This method is more efficient to recover metals with low energy consumption, but it produces wastewater containing fluoride that is difficult to treat.[6]

We have recently proposed another possibility with the specific precipitation of metals as valuable materials (Metal Organic Frameworks, MOFs) from simulant battery waste solutions.[7,8] MOFs are hybrid materials resulting from a self-assembly of organic linkers and metal clusters that can be applied in many fields due to their high porosity, large surface area and sometimes aqueous and thermal stability.[9] The main application of MOFs is for the storage or separation of gases[10], but due to the difficulty of their solvothermal synthesis (high temperature, pressure or use of toxic solvent as DMF), they are generally produced at the gram scale, limiting their use for an industrial development.[11] Recently, some methods have been investigated to increase the amount of MOFs production, but these new approaches, such as mechanochemistry, are limited to the synthesis of very few MOFs and the quality of the materials remains poor.[12] We have lately proposed a recycling process to form these MOFs from real spent LiBs. The final cost of a recycling process to precipitate metals as MOFs is higher than recover metals as inorganic salts but the final products will have more

values as porous materials. At the first precipitation step, an Al-MOF, known as MIL-96, can be obtained with high purity (95%) and two other MOFs based on Cu and Ni/Mn can also be obtained in a second precipitation step.[13]

In this work, we propose to use other precipitating agents to obtain MOFs from spent LiBs: BenzeneDiCarboxylate (BDC) and 4,4' BiPyridine (BiPy). Selective precipitation of Al was observed with BDC to obtain MIL-53, a well-known MOF, with very high purity (99%). In contrast, using BiPy resulted in the precipitation of Cu as a Cu-based MOF. This work shows that depending on the precipitating agent; we can achieve total selective precipitation of Al or Cu from dissolved spent LiBs solution under the form of valuable materials.

2.   Experimental

Dissolution of wastes: 15 g of crushed battery wastes were dissolved in 150 mL of three different acidic solutions: HCl (37 %):H_2O (1:1), HNO_3 (67 %):H_2O (1:3.5 in volume) or H_2SO_4 (96 %)/H_2O_2(30 %)/H_2O (1:0.3:5 in volume) at room temperature for 24 h in a beaker. Plastics and carbon materials were separated by filtration and centrifugation. The different dissolution solutions were analyzed by ICP-OES. Concentrations (g/L) of elements were for the HCl solution: 16.0(Mn), 7.9(Cu), 4.8(Al), 4.0(Ni), 1.8(Li), 1.1(Co); for the HNO_3 solution: 11.3(Mn), 7.5(Cu), 4.8(Al), 3.7(Ni), 1.6(Li), 0.9(Co); and for the H_2SO_4:H_2O_2 solution: 15.0(Mn), 7.0(Cu), 4.7(Al), 3.8(Ni), 1.7(Li), 1.0(Co).
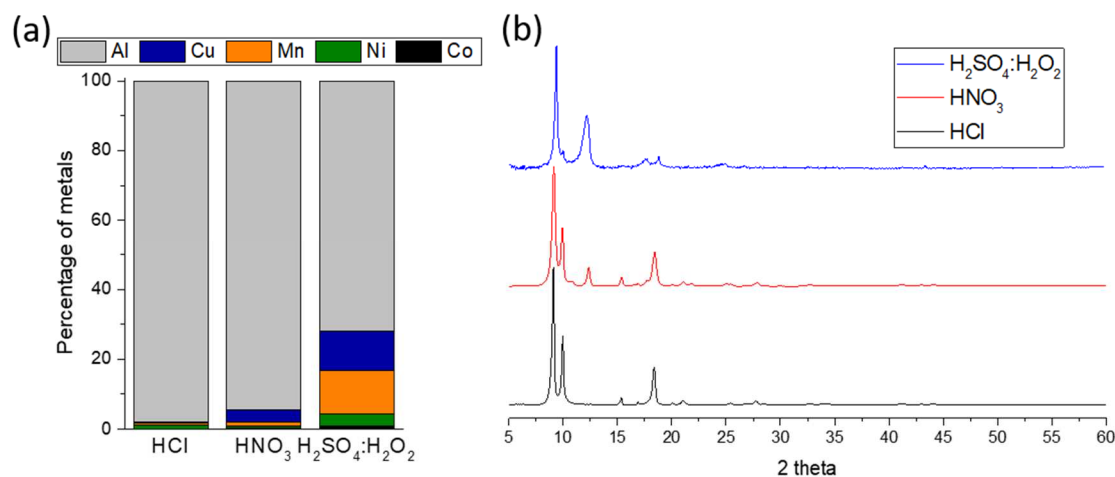
Precipitation of metals as materials: 16 mg of BDC (98 % purity) or 15 mg of BiPy (for synthesis purity) were dissolved in 1 mL of DMF and 1 mL of the acidic dissolution solution was then added. The mixture was heated at 90 °C during 24 hours. A precipitate was then observed and recovered by centrifugation.

3.   Results and discussion

3.1 BDC ligand

The dissolution solutions (in HCl, HNO_3 or H_2SO_4:H_2O_2) were then mixed with a solution of DMF (ratio 1:1) containing the BDC ligand. After a heat treatment at 90 °C during 24 hours a white
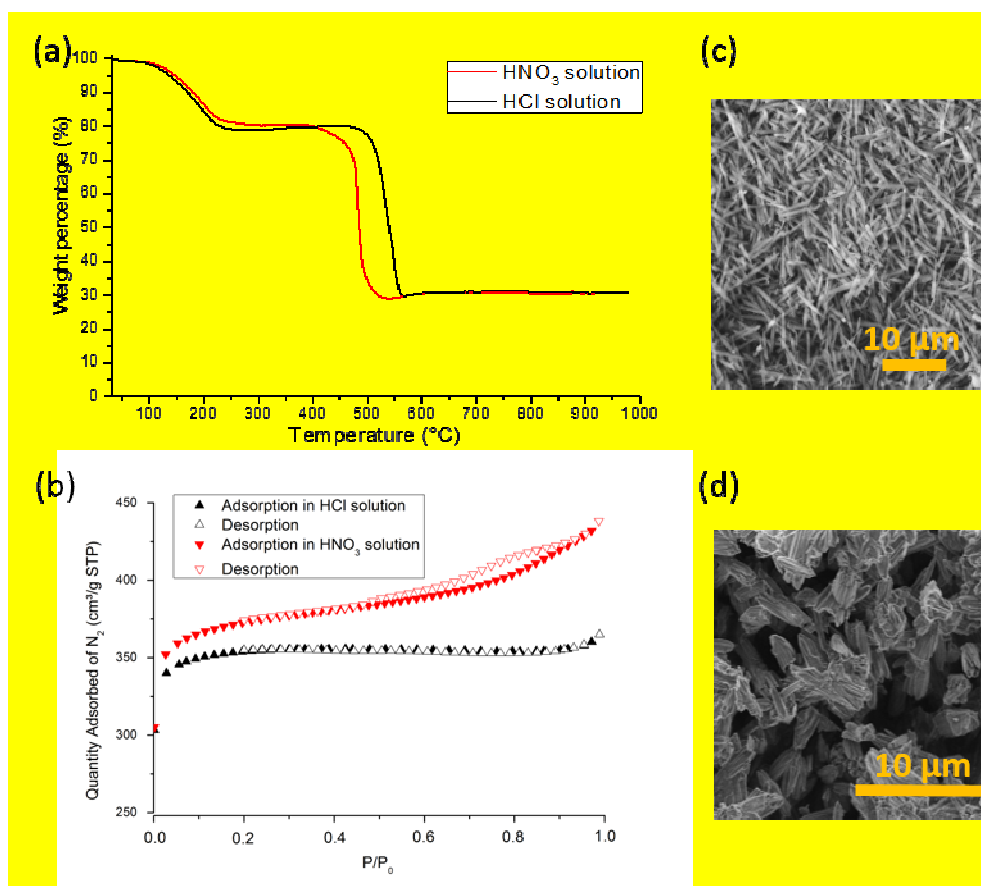
powder was formed. The quantity of materials obtained after precipitation is similar for HCl and HNO$_3$, whereas a very small amount of material was recovered with the H$_2$SO$_4$:H$_2$O$_2$ solution.

Figure 1. (a) Metal composition and (b) PXRD of materials obtained in the three different waste solutions

The different materials were then digested in a piranha solution (H$_2$SO$_4$/H$_2$O$_2$ in 3:1 ratio) prior analysis by ICP-OES to determine their metal composition (**Figure 1-a**). In all conditions, the obtained powders are mainly composed of Al. Only with HCl and HNO$_3$, the selectivity in the precipitation of Al was observed with, respectively, a powder composed of 98 % and 95% of Al. In the case of H$_2$SO$_4$:H$_2$O$_2$ impurities of Mn and Cu (28 %) co-precipitate with Al. For this reason, further analysis will only be discussed with MOFs obtained from HCl and HNO$_3$ solutions. No more Al is observed in the leachate. PXRD patterns of all these materials (**Figure 1-b**) are very similar to a previously reported MOF: MIL-53 (Al), with different ratios of guest molecules inside the pores.[14,15] MIL-53 (Al) has a very particular structural flexibility in response to a stimulus (temperature, pressure, presence/absence of guest molecules …) conducting to a reversible change in the crystalline structure (pore diameters, unit cell parameters and even symmetry of the crystal structure). Here the obtained materials are a mixture of such phases (Figure S1) with different guest molecules inside the pore cavities (no particular heat treatment prior analysis). Due to these properties, MIL-53 (Al) has shown interesting performance in the separation of alkylaromatics[16] or for gas separation (e.g. CO$_2$/CH$_4$).[17]

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TGA analyses are in accordance with a material composed as [Al(III)(OH)(BDC)] and correspond to MIL-53 (Al) (**Figure 2-a**).
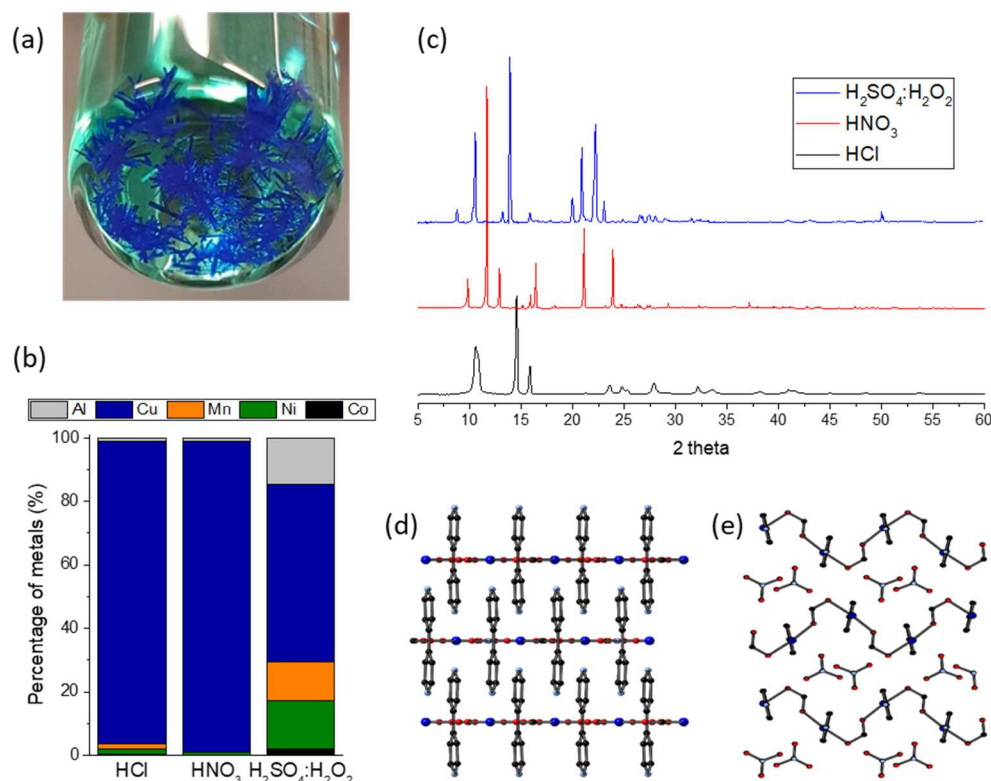

Figure 2. (a) TGA; (b) Nitrogen physisorption measurements at 77 K; (c) SEM image of the MOF obtained in the HCl waste solution and (d) SEM image of the MOF obtained in the HNO$_3$ waste solution

A first loss of 20 wt.% is observed between 100 and 240 °C and is attributed to some residual solvent molecules (water and/or DMF) prior to the degradation of the framework at 430 °C for HNO$_3$ and at 490 °C for HCl with the decomposition of the organic ligand (50 % weight loss). An inorganic residue of Al$_2$O$_3$, representing 30 % of the initial weight, is observed in both cases showing some additional impurity of Al$_2$O$_3$.

Nitrogen physisorption experiments at 77 K (**Figure 2-b**) have been performed on these two materials after a heat treatment at 300 °C for 24 h to remove all solvents before the outgassing of samples under high vacuum. The material obtained in HCl presents a type I isotherm suggesting that the MOF is mainly

composed of micropores whereas the other material obtained in HNO_3 exhibits a type IV isotherm, suggesting a mesoporous material. BET surface areas of these materials are very close (1384 $m^2.g^{-1}$ for HCl and 1445 $m^2.g^{-1}$ for HNO_3).

Figure 3. (a) Photograph of crystals obtained in HNO_3 solution; (b) Metal composition; (c) PXRD of materials obtained in the three waste dissolution solutions; (d) View of the structure [010]; (e) Projection of the structure [001]

Finally, SEM images have revealed homogeneous needle shape particles of 6 µm length in HCl (**Figure 2-c**) whereas in HNO_3, particles are smaller in length (3-4 µm) but thicker (**Figure 2-d**).

3.2 Bpy ligand

A similar protocol was used with the BiPy ligand as precipitating agent. Precipitation of a blue/green powder in HCl and H_2SO_4:H_2O_2 was observed instead of blue needle shape crystals in HNO_3 (**Figure 3a**). ICP-OES has revealed than materials are mainly composed of Cu with high purity in HCl and HNO_3

(95 and 99 % respectively) whereas the selectivity for Cu is lower in the case of $H_2SO_4:H_2O_2$ (56 % Cu, 15 % Al, 15 % Ni and 12 % Mn) (**Figure 3-b**). No more Cu is observed in the leachate.

PXRD patterns of these three materials are different for each conditions. A poor crystalline pattern was observed in the case of HCl with some peaks between 20 and 45° corresponding to $CuCl_2$, whereas in other conditions crystalline patterns were observed (**Figure 3-c**). Single X-ray resolution of crystals obtained in HNO_3 has revealed a material already reported and characterized in the literature[18], of formula $[Cu(BiPy)\mu OOCH(NO_3)]$ (**Figure3-d/e**). This material has revealed abilities for the catalysis of cyanosilylation of aldehydes.

Conclusions

A method is proposed to selectively remove Al or Cu from the dissolution solution of LiBs by using different precipitating agent: a carboxylate (BDC) or a bipyridine (BiPy) ligand. With BDC, a material called MIL-53 (Al) has been obtained whereas with BiPy, a Cu-MOF can be obtained. This original work shows, that from raw batteries, it is possible to obtain crystalline compounds with interesting properties and that selective precipitation can occur by changing the nature of the precipitating agent. From these results, we also can imagine forming more interesting or complex hybrid materials from such solutions by adding other structural molecules with the precipitating agent or use other precipitating agent to precipitate other metals in solution than Al or Cu (e.g. Mn, Co, Ni). Future works will be to develop a greener protocol to avoid toxic solvent, as DMF used for this proof of concept.

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Graphical abstract :