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SUSTAINABLE LITHIUM RECOVERY FROM LITHIUM-ION BATTERIES: A COMPARATIVE STUDY OF PYRO AND HYDROMETALLURGICAL TECHNIQUES

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ABSTRACT

Different sort of Batteries are used in many diverse applications such as cars, radios, laptops, mobile phones, and watches. They are classified as primary and secondary batteries. The former one is known as alkaline batteries made up of zinc and manganese as primary source and mainly used for household purposes, which directly convert chemical energy into electrical energy. The later one is usually made up of nickel (Ni), cadmium, nickel metal hydride or lithium-ion and it is mainly used in mobile phones, electronic items, cameras etc. The main concern of using batteries is the threat to the environment at the end of their usages. Among all types of batteries, Lithium-ion batteries (LIBs) are gaining world-wide interest owing to their use in almost all modern life devices. In addition, it is of paramount importance to develop new technologies to minimize any environmental impact caused while disposing of such heavy metal bearing residues, since, on the one hand, the metals they contain can affect the environment and, on the other hand, such metals are valuable at an industrial level. In this work, the recoveries of lithium and manganese from the cathodes of exhausted lithium-ion batteries will be investigated using a pyrometallurgical chlorination process, followed by a hydrometallurgical process for the proper solubilization of the lithium, manganese and cobalt chlorides formed. The tests were carried out in isothermal conditions, in alumina reactor so that it will be possible to operate in corrosive atmospheres. The effect of temperature and reaction time on lithium, manganese and cobalt extractions were also considered. The reagents, products and solid residues of chlorination were characterized by atomic absorption spectrometry (AAS) and X-ray diffraction (XRD). The experimental results were being analyzed to assess the efficiency of lithium, manganese and cobalt extractions as LiCl, MnCl and CoCl, respectively. Once these metals were solubilized, lithium was precipitated in the form of carbonate, which is the raw material for the subsequent production of the batteries.

Keywords: Lithium-ion batteries, pyro and hydrometallurgical processes.

INTRODUCTION

A lithium-ion battery is a type of rechargeable battery, which are commonly used in portable electronic devices and electric vehicles and are growing in popularity for military and aerospace applications.[1]

In these batteries, lithium ions move from the negative electrode, through an electrolyte, to the positive electrode during discharge and back during charging. Lithium-ion batteries use an intercalated lithium compound as the material on the positive electrode and typically graphite on the negative electrode. The batteries have a high energy density, no memory effect (except LFP cells – lithium iron phosphate)[2]and low self-discharge. However, they can pose a safety hazard as they contain flammable electrolytes and, if damaged or improperly charged, can lead to explosions and fires.

Chemical, performance, cost, and safety characteristics vary among types of lithium-ion batteries. Portable electronics primarily use lithium polymer batteries (*ie*, with a polymer gel as the electrolyte), a lithium cobalt oxide ($LiCoO_2$) cathode material, and a graphite anode, which together provide a high energy density.[3-4]In the case of Lithium Iron Phosphate ($LiFePO_4$), Lithium Manganese Oxide ($LiMn_2O_4$) or Li_2MnO_3-based Lithium Rich Layer Materials (LMR-NMC) and Cobalt, Manganese, Lithium Nickel Oxide ($LiNiMnCoO_2$ or NMC) may offer longer lives and may have better energy capacity. These batteries are widely used in power tools, medical equipment and other functions. NMC and its derivatives are also widely used in electric vehicles.

Research areas for lithium-ion batteries include extending lifespan, increasing energy density, improving safety, reducing costs, and increasing charging speed,[5]among others. Other research is ongoing in the

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area of non-flammable electrolytes as a way to increase safety based on the flammability and volatility of the organic solvents used in the typical electrolyte. Strategies include aqueous lithium-ion batteries, solid ceramic electrolytes, polymeric electrolytes, ionic liquids, and strongly fluorinated systems.[6-9]

The chemical reactions that occur inside these batteries[10], in the case of the cathode compound Li-CoO , during charging, are shown in Eqs. (1–2). Furthermore, reverse reactions occur during discharge.
2

EXPERIMENTAL AND RESULTS

Figure 1 shows an outline of the reaction system used in the extraction of lithium and other metallic components from exhausted lithium-ion batteries. In Figure 2, the complete reaction system used in the experiments can be seen.

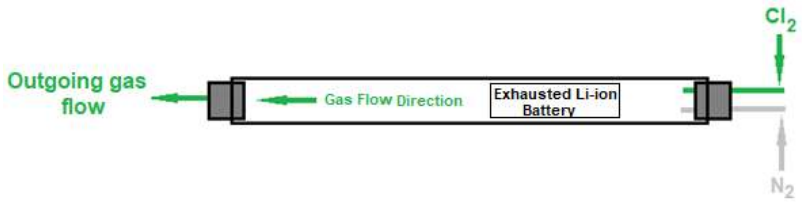

Fig. 1-Outline of the reaction system for generating water soluble metal chlorides.



Fig. 2-Reaction system used in lithium extraction tests from exhausted lithium-ion batteries.

This system consists of a horizontal furnace, equipped with an alumina reactor where the exhausted batteries are inserted. At the beginning of the operation, the temperature range used was 400 to 500 °C, under a continuous flow of nitrogen so that the referred battery was destroyed in the absence of oxygen and humidity. Once this temperature was reached, a flow of chlorine gas was passed through the reactor for the proper transformation of the elements present (*ie*, Li, Co and Mn) into the respective water-soluble chlorides.

The first zone, between 400 and 500 °C, presents a mass gain that is a consequence of LiCl generation due to partial chlorination of LiCoO from the cathode, as shown in reaction 3:
2

In the second region, between 500 and 650 °C, a significant increase in mass gain is observed, which can be attributed to the continuation of reaction (3) and to the chlorination of LiMn O:
2 4

During the passage of chlorine through the reactor, a continuous flow of nitrogen was also kept avoiding any reaction of the unreacted lithium compound with the humidity and oxygen, perhaps present, inside the reactor. This chlorine flow was stopped after 15 minutes of reaction, enough time for the complete formation

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of the referred chlorides. Once the chlorination reactions have been finished, the furnace was turned off and remained so until the complete cooling of the reactor.

Once at room temperature, the inside of the furnace was washed with water for complete solubilization of the formed chlorides. Once in solution, the extraction of metals was evaluated by analyzing their concentrations by atomic absorption spectrometry. Table 1 shows the percentages of lithium, manganese and cobalt extraction according to the temperatures used.

Table 1-Metal extraction according to the used temperature.

Extraction of Lithium, Cobalt and Manganese, %		
Temperature, the W	400	600
I read	95	98
Mn, Co	-	94 & 97

The resulting leachate was treated with sodium carbonate solution to precipitate lithium carbonate (Li_2CO_3), as shown in reaction 5, the only insoluble carbonate among the others present. This lithium carbonate was thoroughly washed with hot water to free it from other soluble carbonates.

The other elements present in the aqueous phase were separated according to their chemical characteristics.

This treatment process can be applied to recover lithium from cathode materials of various chemical compositions and therefore to a wide variety of commercially available lithium-ion batteries.

The gaseous emanations leaving the reactor were collected in a sodium hydroxide solution for the proper formation of sodium hypochlorite, as shown in reaction 6 and, with this, to avoid environmental contamination.

Figure 3 shows the physical aspects of the metal salts that make up lithium-ion batteries from their precipitation processes from aqueous leachate.

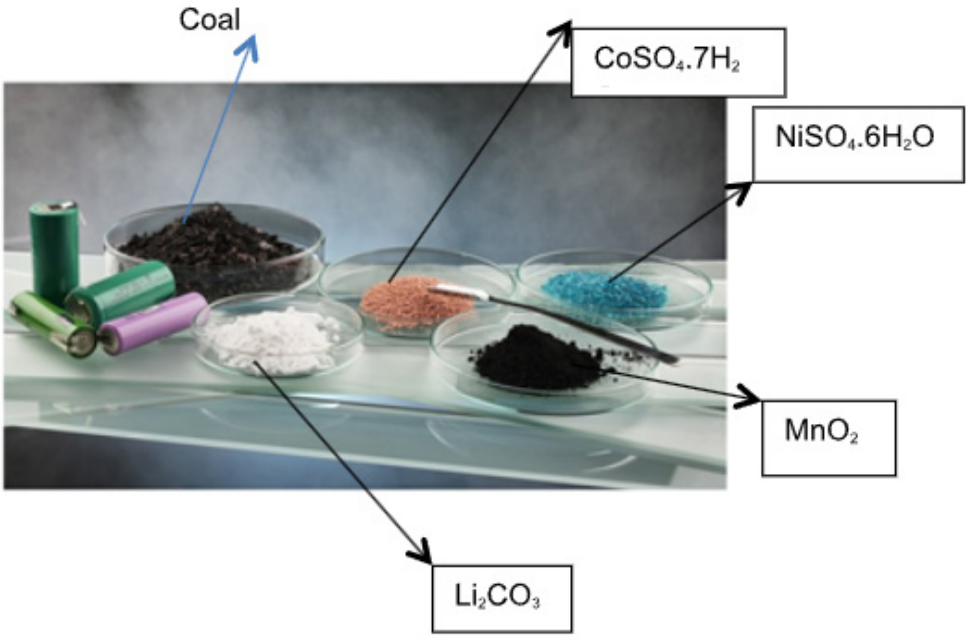

Fig. 3-Physical aspects of the constituent compounds of lithium-ion batteries after selective precipitation processes.

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CONCLUSIONS

Experimental results showed that the pyrometallurgical process of chlorination, followed by aqueous leaching, is an efficient route to extract lithium, manganese and cobalt at moderate temperatures. The results indicated that the chlorination of mixed oxides from exhausted lithium-ion batteries gives the following products: LiCl at 400 °C, LiCl and MnCl$_2$ at 500 °C and LiCl, MnCl$_2$ and CoCl$_2$ at 600 °C, with LiCl selectively extracted at 400 °C. Finely, we do believe that the metals extraction efficiencies might be enhanced by extending the chlorination time.

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