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## Hydrometallurgical recycling of lithium-ion batteries by reductive leaching with sodium metabisulphite

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## ABSTRACT

The hydrometallurgical extraction of metals from spent lithium-ion batteries (LIBs) was investigated. LIBs were first dismantled and a fraction rich in the active material was obtained by physical separation, containing 95% of the initial electrode, 2% of the initial steel and 22% of plastic materials. Several reducers were tested to improve metals dissolution in the leaching step using sulphuric acid. Sodium metabisulphite led to the best results and was studied in more detail. The best concentration of Na<sub>2</sub>S<sub>2</sub>O<sub>5</sub> was 0.1 M. The metals dissolution increased with acid concentration, however, concentrations higher than 1.25 M are unnecessary. Best results were reached using a stirring speed of 400 min<sup>-1</sup>. The metals leaching efficiency from the active material (Li, Mn, Ni, Co) increased with the temperature and was above 80% for temperatures higher than 60 °C. The dissolution of metals also rose with the increase in the liquid/solid ratio (L/S), however, extractions above 85% can be reached at L/S as lower as 4.5 L/kg, which is favourable for further purification and recovery operations. About 90% of metals extraction can be achieved after only 0.5 h of leaching. Sodium metabisulphite can be an alternative reducer to increase the leaching of Li, Mn, Co, and Ni from spent LIBs.

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### 1. Introduction

Lithium-ion batteries (LIBs) have advantages over other rechargeable batteries, which have made them widely used in portable electronic devices, such as personal computers, video cameras and mobile phones since they were first commercialized in 1991. For that, contribute excellent properties such as high energy and power densities, high battery voltage, long charging-discharging cycles, long lifespan and large operating temperature range (Zhang et al., 1998).

Given concerns about the carbon dioxide footprint, the interest in alternative energy sources has increased and represents a great market for lithium-based batteries, highlighting the electric mobility (electric (EV), plug-in (PHEV) and hybrid (HEV) vehicles) and electrochemical energy storage for renewable energy conversion (solar and wind-powered electric generation) (Goonan, 2012). Electric vehicles are crucial for the sustainable transport systems future and their wide global deployment is necessary to meet

sustainability targets. The EV stock reached 1.26 million in 2015, 100 times more than in 2010 and new registrations of EVs increased by 70% between 2014 and 2015, with over 550,000 vehicles being sold worldwide in 2015 (OECD/IEA, 2016).

Lithium is classified by the American Physical Society (APS) and Materials Research Society (MRS) as an “energy-critical element”, given its role in emerging sustainable energy sources and the fact that it might encounter supply risks and a shortage could significantly affect the adoption of some energy technologies (Hurd et al., 2012). Several countries worldwide are establishing national alternative energy policies that have the potential to considerably increase lithium demand. Moreover, energy storage systems could be beneficiaries of the widespread research and development of LIBs for the transportation sector, which can help make it more affordable (Jaskula, 2014; Diouf and Pode, 2015). Consumer and industrial electronics accounted for about 78% of the global lithium-ion battery market revenues, while transportation applications such as EVs, HEVs and PHEVs accounted for approximately 20%, and grid applications represented about 2%. Moreover, global lithium-ion battery consumption increased by an average of 27% per year from 2011 to 2014 (Jaskula, 2014; Moss et al., 2011).

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The increase in the lithium battery market will result in a growth in the spent battery waste flow, which must be recycled. Batteries recycling is critical not only from an environmental point of view, but they are also an important secondary source of metals, which can be found at very high concentration, sometimes even higher than those found in the ores of those metals (Dorella and Borges, 2007; Jha et al., 2013; Bertuol et al., 2016).

Unlike conventional batteries, in LIBs lithium ions move back and forth between the anode and cathode, forcing electrons to move with them. When the battery discharges, lithium ions exit the graphite anode and migrate through the electrolyte and form chemical compounds with the metal oxide within tiny channels in the physical structure of the cathode. When an opposing voltage is applied, it forces the ions back to their starting point, recharging the battery (Alper, 2002). In general, LIBs consist of a steel and aluminium casing, printed circuit boards, plastic covers, copper and aluminium foils, separators, active electrode materials, carbon, organic binders, organic solvents, salts, additives, etc (Chagnes and Swiatowska, 2015). The anode consists of a copper foil coated with carbon graphite. Similarly, the cathode is comprised of an aluminium foil coated with a mixture of active cathode materials. The active cathodic material is always a lithium containing material, usually an oxide, but its composition can vary. The most common was, for many years, lithium cobalt oxide (LiCoO<sub>2</sub>). The active electrode materials are attached onto the collector foil using a binder, which is commonly polyvinylidene fluoride (PVDF) because of its thermoresistance and nonreactive properties. The separator keeps a space between the anode and the cathode to prevent short circuit from direct contact of the electrodes. The separator is a microporous film usually made of polymers such as polyethylene (PE) or polypropylene (PP) (Alper, 2002; Zhang et al., 2014). Although LiCoO<sub>2</sub> was the active cathode material most used for LIBs, due to the high cost and toxicity of cobalt, Li(Mn,Ni,Co)O<sub>2</sub> has gradually replaced LiCoO<sub>2</sub>. Thus, it makes the waste flow more complex as well as the chemical processes for recovery of the spent LIBs (Chen et al., 2011; Gaines, 2014).

Recycling of spent lithium batteries generally involves mechanical treatment, hydrometallurgical treatment, association of thermal pre-treatment and hydrometallurgical methods or pyrometallurgical treatment. Mechanical treatments include crushing and physical separation methods to liberate and separate specific components and recover the black mass (active electrode material) that contains valuable metals, such as cobalt, nickel, manganese and lithium. In the hydrometallurgical treatments, after a mechanical/physical processing, the metals from the black mass are dissolved in aqueous solutions containing reagents (usually acids). The resulting metal rich solution is treated by precipitation, solvent extraction or ion exchange to recover metals. However, these processes produce wastewater that can be treated. By the pyrometallurgical route, spent LIBs are generally processed without mechanical treatment. Plastic covers and all the organic electrolyte and binder are decomposed or combusted, thus, these processes are often associated with stringent treatment/filtration standards for gas emissions. Other drawback of pyrometallurgical processes is that metals such as aluminium, manganese and lithium are lost in the slag. Therefore, for many authors, the efficiency of pyrometallurgical processes is often considered lower than hydrometallurgical processes (Chagnes and Swiatowska, 2015; Li et al., 2010; Meshram et al., 2014; Freitas et al., 2010). Some alternative thermal treatment processes have been developed. A thermal process for regeneration of LiCoO<sub>2</sub> at 900 °C with solid states synthesis was studied by Nie et al. (2015). A reducing thermal treatment before acid leaching for recovery of metals from LIBs was studied by Yang et al. (2016) and a method using oxygen-free roasting and wet magnetic separation to in situ recycling of materials from LIBs was proposed by Li et al. (2016). However,

from an environmental and health point of view, hydrometallurgical treatments are considered more suitable than pyrometallurgical treatments since offer advantageous such as low energy consumption, no air emissions and higher recovery of elements with high purity grade (Li et al., 2015).

Several LIBs leaching studies were performed using inorganic acids, such as HCl (Li et al., 2015; Joulié et al., 2014; Wang et al., 2009; Contestabile et al., 2001; Guo et al., 2016), H<sub>2</sub>SO<sub>4</sub> (Joulié et al., 2014; Meshram et al., 2015a, 2015b; Kang et al., 2010), HNO<sub>3</sub> (Joulié et al., 2014; Lee and Rhee, 2002, 2003). Recently, many studies involving the use of organic acid have been developed, for example using citric acid (Chen et al., 2015; Chen and Zhou, 2014; Nayaka et al., 2015), succinic acid (Li et al., 2015), DL- malic acid (L- and D- enantiomers) (Li et al., 2010) and the use of Na<sub>2</sub>CO<sub>3</sub> and Na<sub>3</sub>PO<sub>4</sub> was also proposed as precipitants in the treatment of the effluent from the LIBs recycling process (Guo et al., 2017). However, in most of the studies, acids were used combined with hydrogen peroxide, which is used as a reducer.

Although some studies using different reducers have been performed (Chen et al., 2015, 2016; Meshram et al., 2016), hydrogen peroxide is still the reducer most widely used in the leaching of spent LIBs. The aim of using a reducing agent during the leaching of spent batteries is to promote the reduction of some elements present in their composition that are more easily dissolved when they are in a more reduced form. However, hydrogen peroxide has some drawbacks, since it easily decomposes and thus the efficiency of its use is normally low. Based on this, the main objective of this study was to test different reducers (Na<sub>2</sub>SO<sub>3</sub>, Na<sub>2</sub>S<sub>2</sub>O<sub>5</sub> and iron scrap) during the leaching of spent lithium-ion batteries with sulphuric acid, as well as to compare their effect with that of H<sub>2</sub>O<sub>2</sub>, in order to present alternative approaches for the treatment of LIBs. A more detailed evaluation was carried out using sodium metabisulphite (Na<sub>2</sub>S<sub>2</sub>O<sub>5</sub>), a commercial reducer widely used in the industry, such as in leather tanning, water dechlorination, rubber industry, chemical synthesis and in industrial waste water treatment plants. Moreover, the effect of some variables, such acid and reducer concentrations, the leaching time and temperature and the liquid to solid ratio, on the metals dissolution was also evaluated.

## 2. Materials and methodology

### 2.1. Sampling and physical separation

Two hundred and seventy-nine laptop batteries were classified by their brands and models and their average weight was determined. In order to obtain a sample, 40 batteries were selected taking into consideration their representativeness (amount among the several brands and models) in the initial set. These 40 batteries were dismantled using pliers, and their plastic case, microcontroller board and connectors were removed. Six lithium-ion cells were contained in each battery and their residual voltage was measured for safety precautions. Cutting the cell cases can produce strong heating, given their internal short circuit or self-ignition (even with a residual charge) when cathode and anode are in contact in the dismantling (Nan et al., 2005). Therefore, some practices are recommended to prevent flames and explosions hazardous, such as refrigeration during the cutting, using NaCl solution for discharge, or water and electric iron powder to promote the short circuit and discharge of the cells (Zhang et al., 2014; Contestabile et al., 2001; Nan et al., 2005; Fan et al., 2016; Li et al., 2016). Thus, in this work a cryogenic treatment was performed previously to crush the cells by their immersion in liquid nitrogen for 4–6 min. The cells were then shredded in a grab shredder (Erdwich EWZ 2000) using a 6 mm bottom discharge grid.

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