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Recovery of lithium and cobalt from spent lithium ion batteries (LIBs) using organic acids as leaching reagents: A review

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ABSTRACT

Environmental restrictions and economic benefits have obliged countries to promote recycling processes from secondary resources like spent lithium ion batteries (LIBs) instead of using primary ones. In spite of the developments have been made on industrial scale for the technologies involved in recycling processes, most of these technologies suffer from lack of efficiency and echo-friendliness. To reduce the footprints of the recycling processes, several efforts are made. A major development area is the use of organic acids which are considered as promising agents for leaching of valuable metals from spent LIBs. In this review paper, we provided an overview of the recent status of the recycling technologies of spent LIBs using organic acids. For this purpose, necessity of green processes and advantage of organic acids in recycling of spent LIBs is discussed. To fully understand the effect of these agents, production, origin, application, and structure of organic acids that have been used in recovery of metals from spent LIBs are also addressed. Afterwards, recycling processes using organic acids, and benefits and drawbacks of using them are summarized and possible complexes formed by these agents are proposed. Eventually, development of different reducing agents, ultrasonic agitation, and evolution and future prospect of green processes in recycling of spent LIBs is reviewed.

1. Introduction

Changes in the life style of human beings, global developments, competition between different manufactures and short life span of electrical and electronic equipment (EEE) have put a greater demand on EEE (Akcil et al., 2015; Faraji et al., 2018; Gomes et al., 2017; Priya and Hait, 2017). It is anticipated that 24–46 % of all vehicles in the USA will be replaced by electrical vehicles by 2030 (Dunn et al., 2012; Wang et al., 2014a). It is reported that, annual production of waste electrical and electronic equipment (WEEE) was 43.8 million tons in 2015 and it is expected to reach 49.8 million tons in 2018 which highly emphasizes proper management of such wastes (Nekouei et al., 2018).

Batteries, printed circuit boards (PCBs), liquid crystal displays (LCDs), cathode ray tubes (CRTs), hard disk drives (HDDs), refrigerators and cell phones are the integral parts of a typical WEEE (Zhang and Xu, 2016). These wastes contain precious metals such as indium, gold, silver, lithium, cobalt, nickel, copper and rare earth elements (REEs) (Akcil et al., 2015; Zhang et al., 2017). Lithium ion batteries contain Fe, C, Al, Cu, Li, Co and Ni as valuable materials and $LiPF_6$ as hazardous material. Currently, lithium ion batteries (LIBs) hold 0.3–0.4 wt. % of WEEE (Innocenzi et al., 2017). Due to the higher voltage per cell, wide range of operating temperature and desirable discharge resistance, LIBs are widely used in electric vehicles (EVs), hybrid electric vehicles (HEVs), plug-in hybrid electrical vehicles (PHEVs), personal computers (PCs), cameras, mobile phones and solar and wind energy storage devices (Li et al., 2012; Liang et al., 2017; Ordoñez et al., 2016).

Due to the presence of strategic metals such as cobalt (5–20 wt. %) and lithium (5–7 wt. %) in spent LIBs (Xu et al., 2008) they are found as an important secondary resource for the extraction of such valuable metals (Bigum et al., 2017; Chagnes and Pospiech, 2013; Jandová et al., 2012; Puca et al., 2017). From another point of view, presence of these metallic contaminations would affect the environment and threaten life on the planet (Jagannath et al., 2017; Wei et al., 2018). Thus, the management of spent LIBs in different countries is highly crucial (Wang et al., 2014b; Zeng et al., 2015a). It is outlined that 500 thousand tons of spent LIBs will be produced in 2020, which is equal to 25 billion units of spent LIBs (Zhang et al., 2016). Based on the US Department of Transportation (USDT), due to the drastic increase in the production of electrical vehicles using LIBs, it is anticipated that the required lithium for production of LIBs in 2025 would become more than the worldwide lithium reserve and resources (Gaines and Nelson, 2010; Meshram

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et al., 2014; Wanger, 2011). It should be noted that 35% of lithium (Martin et al., 2017) and 25% of cobalt (Bernardes et al., 2004; Winslow et al., 2018) produced across the world is used in the LIB industry.

Despite of large investments on the recycling industry made by the governments on a global scale, only around 32 wt. % of the spent LIBs in 2017 were recycled (Jiang et al., 2015). Lack of effective regulations, weak collection systems and old technologies for recycling of spent LIBs are the important reasons for inefficient management of these waste batteries in China (Zeng et al., 2015a). Traditional methods of waste disposal, including landfilling, stabilization and incineration, have disadvantages such as penetration of metallic contaminations to the soil and groundwater, emission of toxic gases to the atmosphere, and high maintenance and operation costs; especially in incineration plants (Guo et al., 2016; Liu et al., 2017; Pietrelli et al., 2005). Besides, loss of valuable metals in aforementioned methods is another factor that should be considered (Zand and Abduli, 2008).

To solve this intractable problem, some countries have established strict regulations. For example, the USA inhibits landfilling of spent LIBs by considering them as hazardous materials (Bahaloo-Horeh and Mousavi, 2017; Wang et al., 2014b). Similarly, recycling of at least 50% of waste batteries has been obliged by the European union (EU) (Dewulf, 2010; Hao et al., 2017). Life cycle assessment of spent LIBs showed that each 100 ton of spent LIBs, requires 8.7×10^5 kg material and 9×10^3 kJ energy to be recycled (Rocchetti et al., 2013). On the other hand, spent LIBs recycling reduces energy consumption and greenhouse gas emissions, and also leads to the conservation of 51.3% of the natural resource as compared to landfilling (Boyden et al., 2016).

There are different approaches for recycling of spent LIBs. Nonetheless, in order to save the echo-system, to guarantee the human health and to manage the waste sustainability, it is crucial to find environmentally friendly methods for recycling of spent LIBs. Recently, some attempts have been made to introduce efficient and echo-friendly methods for recycling of spent LIBs. Among them, use of organic agents in leaching of lithium and cobalt from spent LIBs have attracted much more attention. However, there is little information about origin, structure and effect of each organic acid on recovery of lithium and cobalt from spent LIBs. In this review paper, we are trying to provide the readers with the comprehensive record of widespread use of organic agents as both leaching and reducing agents for recycling processes of LIBs.

2. Structure of LIBs

A conventional LIB comprises of a cathode, an anode, a separator, electrolyte solution, collectors (aluminum and copper foils), protective shells, and containers (Gratz et al., 2014). Fig. 1 shows the schematic drawing of a LIB and Table 1 illustrates the contribution of each section (Horeh et al., 2016). Cathode is an aluminum foil coated with cathode active materials which are mainly lithium containing components (mostly oxide) and different active metals (Zeng et al., 2014). The cathode active materials are made of various compounds such as $LiMPO_4$ (M = Co, Mn, Fe), $LiMO_2$ (M = Co, Ni, Mn) and in some cases LiV_3O_8 and $Li_3V_2(PO_4)_3$ (Chagnes and Pospiech, 2013; Etacheri, 2011; Gratz et al., 2014; Ordoñez et al., 2016). Despite the development of new cathode materials, $LiCoO_2$ is still the most common cathode active material because of the high specific energy density it provides and its stability (Kang et al., 2006; Stephan, 2006; Zeng et al., 2014). Based on Table 1, cathode not only has the most contribution in the structure of spent LIBs, but also it contains valuable metals such as lithium and cobalt which makes it the most valuable part of spent LIBs for recycling. Anode is a copper foil covering with carbon graphite; however, there have been some attempts for introducing new anode materials such as $Li_4Ti_5O_{12}$ (Ordoñez et al., 2016), Mn_3O_4 (Wang et al., 2010), Sn nanoparticles (Yu et al., 2009), Fe_2O_3 nanoflakes (Reddy et al., 2007), CuO nano composites (Wangm et al., 2010).

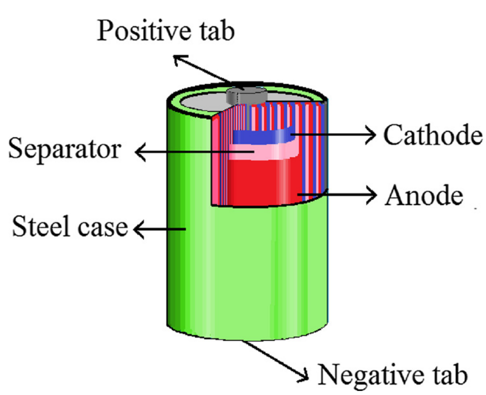

Fig. 1. Shape and components of LIBs.

Table 1
Contribution of different sections in spent LIBs (Horeh et al., 2016).

Battery components	The contribution (%)
Cathode	35
Anode	18
Plastic	6
Electrolyte	11
Case	26
Loss	4

Polyvinylidene fluoride (PVDF) is used to bind cathode and anode materials onto the aluminum and copper foils, respectively (Gratz et al., 2014; Li et al., 2013). It is worthwhile mentioning that the environment of the LIBs is reactive and a thermal and electrical resistance material as PVDF can act more efficient than any other materials (Zeng et al., 2014). Direct contacts of the electrodes lead to short circuiting, thus, either polyethylene (PE) or polypropylene (PP) is used to separate cathode and anode foils (Zeng et al., 2014). The electrolyte of LIBs is a mixture of lithium salts ($LiPF_6$, $LiAsF_6$, $LiClO_4$, $LiCF_3SO_3$, $Li(SO_2CF_3)_2$ and $LiBF_4$) and organic solvents (dimethyl carbonate or ethylene carbonate and diethyl carbonate) (Gong et al., 2013; Zeng et al., 2014). The chemical reactions in LIBs in which cathodes and anodes are made of $LiCoO_2$ and graphite are (Zhang et al., 1998):

$$6C + xLi^+ + xe^- \leftrightarrow C_6Li_x \text{ (Cathodic reaction)} \quad (1)$$

$$LiCoO_2 \leftrightarrow Li_{(1-x)}CoO_2 + xLi^+ + xe^- \text{ (Anodic reaction)} \quad (2)$$

3. Necessity of green recycling processes and economic feasibility

Since spent LIBs are considered as valuable waste, sustainable, eco-friendly and cost effective approach for recycling of them is required. To recycle spent LIBs, there have been various approaches including pyrometallurgy, hydrometallurgy and biohydrometallurgy. In pyrometallurgy the organic electrolyte and binders are burnt off and then the metals are dissolved using two furnaces (Cheret and Santen, 2007; Sun and Qiu, 2012). Electrolyte and plastic containers are eliminated in the first furnace, and molten metals and alloys are formed in the second furnace (Cheret and Santen, 2007). By melting the scrapes, cobalt, nickel and copper would effectively be recovered while other components such as lithium will be lost in the form of slag and gas (Georgi-Maschlera et al., 2012). Though, this method is feasible, it needs high temperatures (500–1000 °C), does not recover organic compounds, consumes lots of energy, emits large amount of toxic gases, results in production of non-pure alloys and requires additional refinements (Garcia et al., 2017; Joulié et al., 2017; Xu et al., 2008).

In hydrometallurgy approach, different processes are involved to dissolve, separate and concentrate valuable metals in an aqueous