Hydrometallurgy xxx (2015) xxx–xxx

Contents lists available at ScienceDirect

Hydrometallurgy

journal homepage: www.elsevier.com/locate/hydromet

# Thermal treatment process for the recovery of valuable metals from spent lithium-ion batteries

Yue Yang [a], Guoyong Huang [a], Shengming Xu [a,b,*], Yinghe He [c,**], Xin Liu [a]

[a] Institute of Nuclear and New Energy Technology, Tsinghua University, Beijing 100084, PR China
[b] Beijing Key Lab of Fine Ceramics, Tsinghua University, Beijing 100084, PR China
[c] College of Science, Technology and Engineering, James Cook University, Douglas, Queensland 4811, Australia

ARTICLE INFO

*Article history:*
Received 18 July 2015
Accepted 25 September 2015
Available online xxxx

*Keywords:*
Spent lithium-ion battery
Reducing thermal treatment
Leaching
Valuable material recovery

ABSTRACT

In this paper, a process based on reducing thermal treatment before acid leaching for the recovery of valuable materials from spent lithium-ion batteries is developed. The thermodynamic behavior of the active cathode materials is investigated through analyzing the gases evolved from the thermal treatment with a thermogravimetric–mass spectrometry (TG–MS) instrument. Scanning electron microscopy (SEM) with energy dispersive x-ray (EDX) spectroscopy analyses are also performed on the solid cathode and anode materials to determine their physico-chemical changes from the thermal treatment. The results show that the thermal treatment significantly improves the clean separation of the active materials from the current collectors and the complete removal of the binder and carbonaceous conductor. It also alters the molecular structures of, and partially reduces the transition metals in, the active cathode materials, which increases the leaching efficiency of the transition metals in the subsequent leaching step. After thermal treatment, the leaching efficiency of nickel, cobalt and manganese from the active cathode materials has reached over 98%, 99% and 84%, respectively.



## 1. Introduction

The light weight and reliable lithium ion batteries have been widely used in portable electronic devices (Zhang et al., 2009). Currently, the cheap and safe layered cathode materials $LiMO_2$ (M = Ni, Co and Mn) are one of the most widely used commercial cathode materials in the market (Liu et al., 2012). The expanding demand for high density power sources for hybrid electric vehicles and plug-in hybrid electric vehicles will further increase the consumption of rechargeable batteries. A direct consequence of this large consumption is the accumulation of large quantity of spent lithium ion batteries. These spent lithium ion batteries contain various valuable metals such as copper, aluminum, magnesium, nickel, cobalt and lithium. They are also classified as hazardous solid wastes because they contain toxic heavy metals and corrosive electrolytes (Zeng et al., 2011). Recycling of valuable metals from spent lithium ion batteries helps mitigate both the resource shortage and environmental contamination problems.

Currently, both pyromometallurgical and hydrometallurgical methods have been used in the recycling of spent lithium ion batteries (Kim et al., 2004; Swain et al., 2007; Song et al., 2013; Paulino et al., 2008). Compared to the pyromometallurgy method, hydrometallurgy method is more widely used as it is more environmentally friendly, particularly to the operators, and can achieve a higher rate of metal recovery. In many of the proposed hydrometallurgical recycling processes, the active cathode materials are separated from the cathode current collectors by dissolving the Al foils with NaOH, and the binder, Polyvinylidene Fluoride (PVDF), is removed with N-methylpyrrolidone (NMP) (Weng et al., 2013; Li et al., 2010). The obtained active cathode materials are then leached by either HCl (Wang et al., 2009; Joulie et al., 2014; Li et al., 2009a), $HNO_3$ (Ferreira et al., 2009), $H_2SO_4$ (Zhu et al., 2012; Shin et al., 2005; Chen et al., 2011) or their mixtures (Bok et al., 2004). The valuable metals are separated from the Al in the leaching liquid by solvent extraction with extractants such as D2EHPA, PC-88A, Cyanex 272 and Acorga M5640 (Zhao et al., 2011; Granata et al., 2012; Pranolo et al., 2010; Zhang et al., 1998), followed by ion exchange (Li et al., 2009b) and electrochemical (Freitas and Garcia, 2007) or chemical precipitation processes (Li et al., 2009c).

Despite the great research efforts invested in recent years, there are still significant issues to be addressed in the recovery of valuable metals from spent lithium ion batteries. Firstly, scale up of the dissolution of the binder PVDF in the cathode materials with organic solvent is difficult and expensive. Secondly, separation of the Al foils from active materials in the cathode assembly by dissolving it with NaOH generates a large amount of waste aqueous alkaline solution with some aluminum lost in the leaching liquid that cannot be recovered efficiently (Xu et al., 2008). Thirdly, metal ions at high charge states in the spent cathode materials are difficult to be leached without the use of a significant amount

* Correspondence to: S. Xu, Institute of Nuclear and New Energy Technology, Tsinghua University, Beijing 100084, PR China.
** Corresponding author.
*E-mail addresses:* smxu@stinghua.edu.cn (S. Xu), yinghe.he@jcu.edu.au (Y. He).

http://dx.doi.org/10.1016/j.hydromet.2015.09.025
0304-386X/

of reducing agent. $H_2O_2$ is the most commonly used reducing agent in most proposed hydrometallurgical approaches to reduce the metal ions from a high charge state to a low state (Kang et al., 2010). The quantity of $H_2O_2$ used in this approach makes the recovery of the valuable metals from spent lithium ion batteries expensive. Finally, copper as the current collectors in the anode is usually considered not worth recycling and therefore wasted.

A commercial lithium ion battery consists of a cathode, an anode, a separator, and electrolyte. The cathode assembly mainly consists of Al foils (collector), active cathode materials, carbon black, and a binder PVDF, and the anode mainly consists of Cu foils (collector), graphite and a binder PVDF. Ideally, maximum amount of materials should be recovered in minimum number of steps and minimum amount of reagents. As applied to the spent lithium ion battery materials, the process must facilitate the complete separation of the powdery active materials from the current collector metal foils and the binder PVDF. It should also promote better recovery of the valuable transition metals from the active materials, which is usually by leaching. A thermal treatment of the waste cathode assembly at a reasonably elevated temperature in a slightly reducing atmosphere is an apparent and logical candidate that satisfies the above objectives.

In this paper, a process including a reducing thermal treatment and leaching is developed to recover Al foils, Cu foils and transition metals from spent lithium ion batteries. Experimental investigations are designed to examine the thermodynamic behaviors of the cathode materials and the effects of thermal treatment on the separation of the active materials from the current collectors, decomposition of PVDF and the leaching of the transition metals in the subsequent leaching process. The optimum thermal treatment and leaching conditions in terms of maximum material recovery with minimum reagent and energy consumption are also established.

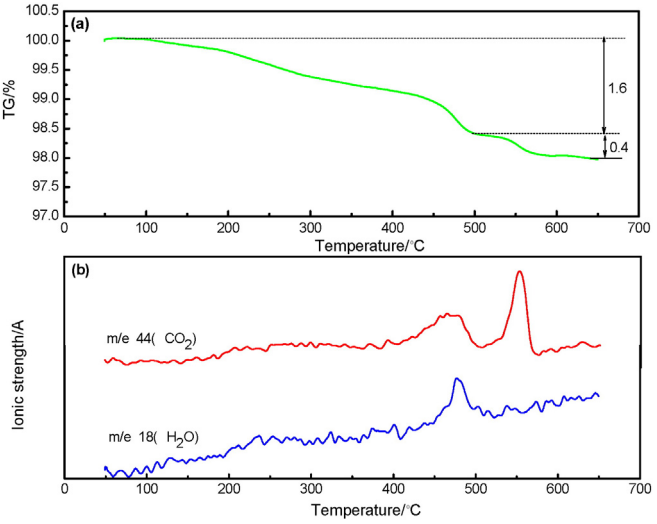


**Fig. 2.** TG and MS intensity curves showing devolatilization of cathode materials.

## 2. Experimental

### 2.1. Separation of active materials from current collectors

The cathode assemblies were out-of-spec waste products of laminated battery production supplied by Brunp Recycling Technology Co., Ltd of China. The cathode assemblies were cut into 2 cm * 2 cm squares then placed in the middle of a tube furnace (Ke Jing, OTF-1200X). The furnace was purged with a high purity nitrogen (>99.999%) at a rate of 150 $cm^3$/min for 30 min to completely remove the air. The nitrogen flow rate was then adjusted to 30 $cm^3$/min and the furnace heated to the desired temperature at a rate of 10 °C·$min^{-1}$.

After the thermal treatment, the active cathode materials could be easily separated from the current collector by gravity separation method based on great differences of densities of the two materials (Dorella and Mansur, 2007). Pure Al products could be recovered by a simple washing of water.

The same procedure is used for the recovery of copper from the anode assembly.

### 2.2. Leaching

Thermally treated active cathode materials were leached in sulfuric acid solutions of different concentrations in a 500 ml, three-necked and round-bottomed flask. The flask was placed in a water bath with a stirrer (Chao Yue, DF-101S) and was coupled with a condenser. The leaching process was conducted at 90 °C and an agitation speed of 500 rpm under the conditions of changing leaching time (t), liquid–solid ratio

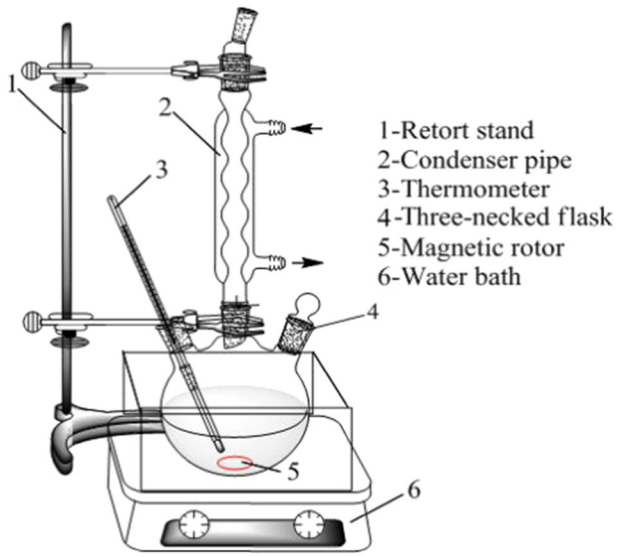


**Fig. 1.** Schematic diagram of leaching apparatus.

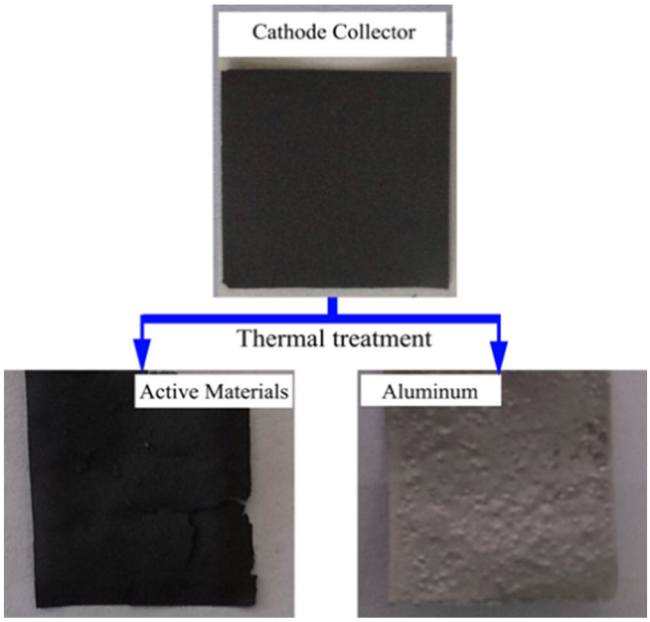


**Fig. 3.** Separation of active materials from Al foils.

Please cite this article as: Yang, Y., et al., Thermal treatment process for the recovery of valuable metals from spent lithium-ion batteries, Hydrometallurgy (2015), http://dx.doi.org/10.1016/j.hydromet.2015.09.025