



Recovery of valuable metals from mixed types of spent lithium ion batteries. Part II: Selective extraction of lithium



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ABSTRACT

Extensive usage of different kinds of lithium ion batteries (LIBs) may result in a huge amount of complicated waste batteries stream, while insufficient attention has been paid on the selective recovery of lithium from these already complicated wastes. Herein, a novel approach was developed for the selective extraction of Li from mixed types of LIBs (LiCoO₂, LiMn₂O₄, LiFePO₄ and LiCo_{1/3}Mn_{1/3}Ni_{1/3}O₂) using mild phosphoric acid as efficient leaching agent. It can be concluded from leaching results that 100%, 92.86%, 97.57% and 98.94% Li can be selectively extracted from waste cathode materials of LiCoO₂, LiMn₂O₄, LiFePO₄ and LiCo_{1/3}Mn_{1/3}Ni_{1/3}O₂, respectively, while transition metals (Co, Mn, Fe and Ni) can be hardly leached in mild acidic media under optimized leaching conditions. In addition, high selectivity coefficients ($\beta_{Li/Me}$) can be obtained during the extraction of Li from other metals. It can be also discovered from characterization results (SEM, XRD, FT-IR and Raman spectra) that leaching residues are phosphate precipitates, which might be used for the recycling of other metals and preparation of cathode materials. Results from leaching kinetics indicate that the leaching of Li is chemical and internal diffusion controlled reaction, with apparent activation energy (E_a) of 37.74, 21.16, 27.47 and 21.86 kJ/mol for LiCoO₂, LiMn₂O₄, LiFePO₄ and LiCo_{1/3}Mn_{1/3}Ni_{1/3}O₂, respectively. Finally, lithium phosphate with a purity of 98.4% can be obtained and the whole process can be efficient candidate for Li recovery with minor environmental impact and little waste produced.

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1. Introduction

As one of the most promising energy storage devices, lithium-ion batteries (LIBs) have been witnessing an increasing application in electronic/mobile devices and EV/HV due to their excellent electrochemical performances (e.g. high power density, no memory effect) (Amaroli and Balzani, 2011; Di Lecce et al., 2017). With their extensive application, public concerns have been also aroused involved with the huge amount of exhausted LIBs after their end-of-life services around 3 years or 1000 cycles (Wager and Hischer, 2015). It is estimated that global market for LIBs will reach \$ 46.21 billion by 2022 (Richa et al., 2017). On one hand, typical spent LIBs contain a considerable proportion of hazardous substances (e.g. heavy metals, electrolyte) which may present potentially severe impact on eco-system and human-beings with-

out proper disposal (Dunn et al., 2012; Yu et al., 2014). On other hand, these discarded batteries contain certain amount of valuable materials (e.g. nonferrous metals) and their reutilization may result in potentially economic benefits (Newbery and Strbac, 2016). Therefore, the sustainable extraction of valuable materials, especially high value-added metals, from these batteries in environmentally benign way will be significant for the recycling and conservation of strategic metal values, as well as for the alleviation or elimination of potential risks towards eco-system or human-beings (Li et al., 2015; Wang et al., 2014).

Recovery of metals from spent LIBs is attracting an increasing attention and current recycling approaches can be divided into mechanical (Ou et al., 2015), pyro-metallurgical (Hanisch et al., 2015), hydro-metallurgical (Ferreira et al., 2009) and combined method (Winslow et al., 2018). Among them, mechanical method is usually adopted as a pre-treatment step to improve overall yields of different metals (Wang et al., 2016b). An environmentally benign process using mechanical approach (co-grinded with various additives in a hermetic ball milling) was reported for the recovery of Co and Li from spent LIBs with high yields of 98% Co

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and 99% Li under optimized experimental conditions (Wang et al., 2016a). Despite high yield of metals, mechanical recycling of valuable metals from spent LIBs may be always contaminated by impurity metals (e.g. Fe, Al), complicating the subsequent metals separation process. Pyro-metallurgical process is a sophisticated method for metal recovery from minerals with high yield and productivity (Swain, 2017). As investigated by Yang et al. (2016), thermal treatment can significantly improve the separation rate of active materials from current collectors due to the complete removal of binder and carbonaceous conductor and a novel smelting reduction process based on $\text{FeO-SiO}_2\text{-Al}_2\text{O}_3$ slag system was developed by Ren et al. (2017) to recover Co, Ni and Cu from spent LIBs, with yield of 98.83%, 98.39% and 93.57%, respectively. However, it is also acknowledged that pyro-metallurgical process may result in severe secondary contamination. Besides, an increasing attention have been attracted by hydro-metallurgical (include bioleaching) method due to its superiorities in environmentally soundness, high recovery efficiency and product purity, excellent applicability over above approaches (Sun et al., 2017). In our previous studies, both mineral and organic acids were used as leaching agents for the complete dissolution of metals from cathode materials of spent LIBs (Chen et al., 2018, 2015b), and solvent extraction and chemical precipitation were applied for the selective separation and recovery of different metals from leaching solution (Chen et al., 2015a, 2015c). Furthermore, bioleaching can be also effective method for valuable metals recovery from spent LIBs. As reported by Horeh et al. (2016), for example, 100% Cu, 95% Li, 70% Mn, 65% Al, 45% Co, and 38% Ni can be leached using *Aspergillus niger* under optimized conditions. In addition, processes combined two or more recycling methods also attracts an increasing attention for metal recycling (Awasthi and Li, 2017). A typical case is the combination of mechanical separation and vacuum metallurgy method for *in situ* recycling of high value-added products- Li_2CO_3 from spent LIBs without additives as reported by Xiao et al. (2017b). Both hydro-metallurgical and combined approaches, however, may be frustrated by the tedious recycling processes. Therefore, the selective extraction of target metals from a complicated waste stream may be practically important for metal recycling.

Numerous studies have been focused on the separation and recovery of transition metals (e.g. Co, Ni, Mn) from spent LIBs and the motivation for selective extraction and recovery of Li is still insufficient (Swain, 2017). Besides, a growing number of portable electronics and HV/EV will be powered by different types of LIBs (e.g. LiFePO_4 and $\text{LiNi}_x\text{Co}_y\text{Mn}_z\text{O}_2$ in HV/EV), using Li as unsubstituted metal (Gu et al., 2017). This indicates that Li will be inevitably followed into waste stream with different metals (Ziemann et al., 2012). However, traditional 'Complete leaching-Transition metals separation-Lithium recovery' recycling model tends to be process tedious, chemical reagent consumed and eco-unfriendly during metal recycling processes (Zhang et al., 2014). Therefore, selective extraction of Li from complicated waste stream with high yield may be necessary. According to Xiao et al. (2017a), a novel method involved with vacuum metallurgy was adopted to recover Li from cathode materials - LiMn_2O_4 , LiCoO_2 , and $\text{LiCo}_x\text{Mn}_y\text{Ni}_z\text{O}_2$ with yield of 81.90%. In our previous study, Li was also selectively leached using mild phosphoric acid with yield over 99% from waste LiCoO_2 (Chen et al., 2017). Therefore, it may be possible for selective extraction of Li from different cathode materials with acceptable yield in mild phosphoric acidic medium.

This work will focus on exploring possibility for the selective extraction of Li from mixed types of spent LIBs. Different types of waste cathode materials, including LiCoO_2 , LiMn_2O_4 , LiFePO_4 and $\text{LiCo}_{1/3}\text{Mn}_{1/3}\text{Ni}_{1/3}\text{O}_2$ obtained after pretreatment, will be used as raw materials (Chen et al., 2015c; He et al., 2015). Leaching experiments were carried out for each kind of waste cathode material to

investigate the leaching behavior of Li and other metals under controlled conditions. Characterization was conducted to analyze the waste cathode materials and leaching residues before and after leaching. Leaching kinetics was also investigated to understand the leaching reaction mechanism of Li in different waste cathode materials. Finally, lithium phosphate can be directly obtained after purification and pH adjustment. It is expected that this recycling process can be an alternative for the selective extraction of Li from complicated cathode materials by a single leaching step with the following features: (1). Short-cut process: Li can be directly leached from waste cathode materials with high yield; (2). Wider applicability: it can be not only capable to recover Li from waste LiCoO_2 , but also capable for different kinds of cathode materials; (3). Mild conditions: all leaching experiments were carried out in mild acidic media.

2. Experimental section

2.1. Materials and reagents

Waste cathode materials including LiCoO_2 , LiMn_2O_4 , LiFePO_4 and $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ were obtained after pretreatment process or leftover materials kindly supplied by Hunan Shanshan Co., Ltd. (Changsh, P.R. China). The detailed pretreatment procedures can be found in Fig. S1 and S2 in Supplementary Materials. Aqua regia (Volume ratio - $\text{HCl}:\text{HNO}_3 = 3:1$) was used for the complete dissolution of cathode material, and Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) was used to determine metal content in waste cathode materials (see Table 1). Leaching reagents used in this study include phosphoric acid (H_3PO_4 , 85%, AR, Tianli Chemical Reagent Co., Ltd.), hydrogen peroxide (H_2O_2 , 30 v/v%, AR, Tianli Chemical Reagent Co., Ltd.). Other reagents used are analytical grade and deionized water was used for preparation of different solutions during the whole experiments.

2.2. Leaching experiments

All leaching experiments were carried out in a 500 mL three-necked and round-bottom flask placed in a water bath to control reaction temperature. A condenser pipe and mechanical stirrer were equipped to control the water evaporation and stirring rate. Leaching reagents (H_3PO_4 and H_2O_2) with different concentrations were prepared with deionized water. Detailed experimental steps and leaching results can be found in Supplementary Materials (see Table S3). In this study, effects of acid concentration (mol/L), retention time (min), reaction temperature ($^\circ\text{C}$) and liquid to solid ratio (mL/g) were investigated to obtain the optimized experimental conditions. Reductant dosage was not taken into consideration for the usage of H_2O_2 as reductant has been studied by previous work, and it can be discovered that that 4 vol% H_2O_2 can be a sufficient amount during the reductive leaching process (Chen et al., 2017). Therefore, 4 vol% H_2O_2 was adopted as optimal reductant dosage during leaching.

2.3. Leaching kinetics

Waste cathode materials are solid particles and the leaching of Li in phosphoric acidic medium is a liquid-solid non-catalytic reaction. It is also reported that solid particles in liquid-solid non-catalytic reaction are unreacted cores, which are abbreviated as "shrinking core model" (Meshram et al., 2016, 2015). According to the change of particle size in the reaction process, "shrinking core model" can be divided into particle size constant shrinkage model (particle size does not change during reaction, that is, there is a solid phase product) and particle shrinkage model (particles

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