



A sustainable process for metal recycling from spent lithium-ion batteries using ammonium chloride



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ABSTRACT

In this paper, a sustainable process to recover valuable metals from spent lithium ion batteries (LIBs) in sulfuric acid using ammonium chloride as reductant was proposed and studied. Being easily reused, ammonium chloride is found to be efficient and posing minor environmental impacts during the overall process. By investigating the effects of a wide range of parameters, e.g., H₂SO₄ concentration, NH₄Cl concentration, temperature, leaching time, and solid-to-liquid mass ratio, the leaching behaviour of Li, Ni, Co, and Mn was systematically investigated. And the leaching mechanism and kinetics were determined by mineralogically characterization of residues at various reaction times and by fitting using different kinetic models. With this research, it is possible to provide a win-win solution to improve the recycling effectiveness of spent LIBs by using waste salt that is easily reused as the reductant.

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1. Introduction

Rapid development of mobile phone, energy storage device and electric vehicles, leads to an ever-increasing demand of rechargeable lithium-ion batteries (Gao et al., 2017; Wu et al., 2018). Meanwhile, the amount of waste LIBs substantially climbed due to the rapid increase in the consumption of LIBs (Lv et al., 2018). Richa et al. has estimated that 0.33–4 million metric tons of LIBs are projected to enter the waste stream from electric vehicles between 2015 and 2040 (Winslow et al., 2018). The waste will lead to the issues in supply chains, resource, and environment (Mishra and Gostu, 2017). For example, some of waste LIBs are not completely discharged, which may catch fire or explode under improperly handle. Sol-vent electrolyte lithium hexafluorophosphate (LiPF₆) and some of the heavy metals contained within the batteries are dangerous to leach into solution and soil (Natarajan et al., 2018; Winslow et al., 2018). Besides, LIBs contains many valuable metals such as cobalt and lithium. As a result, it is highly required to recycle spent LIBs in an environmentally friendly and economic way (Helbig et al., 2018; Lv et al., 2018; Sun et al., 2017).

Nowadays, spent LIBs are usually processed by using either pyrometallurgical or hydrometallurgical methods, to recover valuable metals or other components. Pyrometallurgical methods usually carried out under harsh reaction conditions, during which toxic gases would be released and some metals like Li and Al can hardly be recovered (Li et al., 2017; Xiao et al., 2017; Zeng et al., 2014). Thus, a growing number of studies have focused on the hydrometallurgical processes, because of its high extraction efficiencies of valuable metals, especially Li, controlled environmental influence, and low energy consumption (Chagnes and Pospiech, 2013; Peng et al., 2018). A hydrometallurgical process mainly consists of leaching, purification, and fabrication procedures. In the leaching procedure, reductants are usually needed to be added into the inorganic/organic acid (Joulié et al., 2017; Meshram et al., 2015; Senčanski et al., 2017) or ammonia-based alkaline (Ku et al., 2016; Wang et al., 2017a) leaching reagents to enhance the leaching process. The most common reductant used in experiments is H₂O₂, because of its lower redox potential and no introduction of impurities. However, the instability of hydrogen peroxide leads to some issues in leaching process, storage, and transport (Meng et al., 2017). Recent studies have attempted to investigate alternative reductants, like Na₂S₂O₅ (Vieceli et al., 2018), NaHSO₃ (Meshram et al., 2015), glucose (Pant and Dolker, 2016), ascorbic acid (Nayaka et al., 2018), etc. These alternatives are more stable than H₂O₂. However, all of these reductants cannot be directly or simply regenerated and reused. Besides, the

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productive processes of raw materials also need to be considered from the environmental and life cycle assessment perspective. For example, the commercial anthraquinone oxidation (AO) process for producing H_2O_2 generates substantial organic by-product wastes, which are necessary to remove. The separation of product from these waste organics requires high investment in equipment and high temperature (Campos-Martin et al., 2006).

Fortunately, no reductant is needed when leaching with HCl, this is because that the NCM could be reduced by Cl^- in this system (Takacova et al., 2016). Barik et al. (2016) used HCl as leaching reagent to recover valuable metals from spent cathode, and over 99% of Li, Co, and Mn in the cathode were extracted into the solution. Wang et al. used HCl as leaching reagent with 99% of Li, Ni, Co, and Mn leached from the mixture contained spent $LiCoO_2$, $LiMn_2O_4$, and NCM cathode materials (Wang et al., 2009). However, when using HCl barely as the leaching reagent, the volatility and corrosion of HCl with concentration of 2–4 M should not be ignored.

Therefore, to achieve a similar reaction performance, chloride components, like ammonium chloride, sodium chloride, could be introduced into non-HCl acidic systems as a reductant, without causing the above-mentioned volatility and corrosive problems. Besides, it was reported that more than 2.4 million m^3 waste water containing ammonium chloride was discharged in China in 2013 (Li et al., 2016), and a lot of waste NH_4Cl water produced in extracting cobalt production need to be solved through concentration and crystallization (Guideline on Available Technologies of Pollution Prevention and Control for Cobalt Smelting Industry (on Trial), 2015, Ministry of Ecology and Environment of the People's Republic of China). If the waste ammonium chloride can be reused in industrial production, it will reduce environment pollution and increase profit.

In this paper, ammonium chloride was adopted as a new reductant to achieve high leaching efficiencies of Ni, Co, Mn, and Li from the spent cathode materials in the sulfuric acid. The effect of leaching agent concentrations, reductant concentrations, solid-to-liquid mass ratio (S/L mass ratio), temperature, and leaching time on the leaching efficiencies of various valuable metals were systematically investigated. Then the leaching mechanism and kinetics were determined by mineralogically characterization of residues at various reaction times and by fitting using the unreacted contraction nuclear model. On one hand, the ammonium chloride is a stable (easy to transport and store) and cheap reductant corresponding to the H_2O_2 . It can be obtained from factory waste, which has a huge stock and is urgent to be disposed. Therefore, this is a win-win solution. On the other hand, the recycling of chlorine during the leaching procedure was also proposed. Although, there is still a lot of work need to be done on this technology, it has great potential to be applied in the future.

2. Material and methods

2.1. Materials and reagents

The cathode scraps were supplied by a local spent LIBs recycling company (Ganzhou highpower technology Co., Ltd) in China. A complete dissolution of cathode scrap was carried out in aqua regia to determine the chemical composition using ICP-OES (iCAP 6300 Radial, Thermo Scientific). The contents of Li, Co, Ni and Mn in scrap were 6.15%, 10.70%, 26.08%, and 14.58%, respectively. The XRD patterns of the cathode scrap shown that $Li(Ni_{0.5}Co_{0.2}Mn_{0.3})O_2$ is the major phase (Fig. 1). Sulfuric acid was used as the leaching reagent with ammonium chloride used as the reductant. All chemical reagents (H_2SO_4 , HCl, HNO_3 , NH_4Cl , NaOH) were of analytical

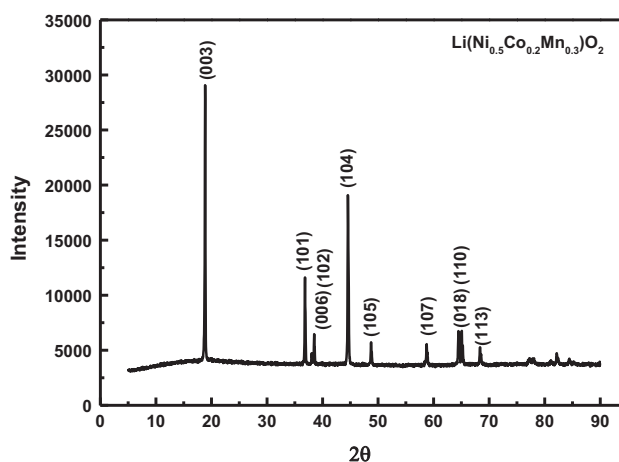


Fig. 1. XRD patterns of cathode materials.

grade from Alfa Aesar Chemical Co. Ltd and all solutions were prepared with ultrapure water (Milli-pore Milli-Q).

2.2. Leaching of cathode scraps

The leaching experiments were carried out in a 250 mL round-bottom flask, equipped with condensing unit to reduce the influence from evaporation, magnetic stirrer, and a sensor based temperature controller (DF-101SZ, Gongyi, Yuhua Equipment Co., Ltd). A given mass of scraps was added to a 100 mL solution containing sulphuric acid and the reductant. The residue was dried at 80 °C in a drying cabinet (DHG-9070A, Shanghai Yiheng Equipment Co., Ltd). To investigate the leaching kinetics, 0.5 mL of liquid sample was taken out from the leachate at a certain reaction time, to get the local leaching efficiency of each metal. The leaching efficiencies of metals from the cathode scraps were determined as follows:

$$x = C_{M,t} \times V / m_M \times 100\% \quad (1)$$

where x (%) is the leaching efficiency of metal M ($M = Co, Ni, Mn, Li$), $C_{M,t}$ (g/L) is the concentration of M ions in the leachate, m_M is the mass of M in the initial scraps, and V (L) is the volume of the leachate.

2.3. Characterization

The cathode scrap was characterized by X-ray diffraction (X'pert PRO, PANalytical) with Cu $K\alpha$ radiation and the data was collected from 5 to 90°. The concentrations of Li, Ni, Co, and Mn ions in leachate were analysed by ICP-OES (iCAP 6300 Radial, Thermo Scientific). The morphology and the surface composition of scrap were characterized using a mineral liberation analyzer (MLA 250, FEI) equipped with an energy dispersive spectrometer (EDS, EDAX GenesisSiLi) and a scanning electron microscope (SEM, Quanta 250).

3. Results and discussion

3.1. Leaching metals from spent LIBs

The reaction between NCM cathode scraps and H_2SO_4 in the absence of reductant like NH_4Cl was described as Eq. (2). The calculation demonstrates that the reaction is thermodynamically feasible. For the absence of the Gibbs free energy of NCM, the data of $LiCoO_2$, $LiNiO_2$ and $LiMnO_2$ (Yokokawa et al., 1998) were used to calculate a possible range of ΔG_{298K}^θ (Eq. (2)). The Eqs. (3)–(6)

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