



Recycling of spent lithium-ion battery cathode materials by ammoniacal leaching

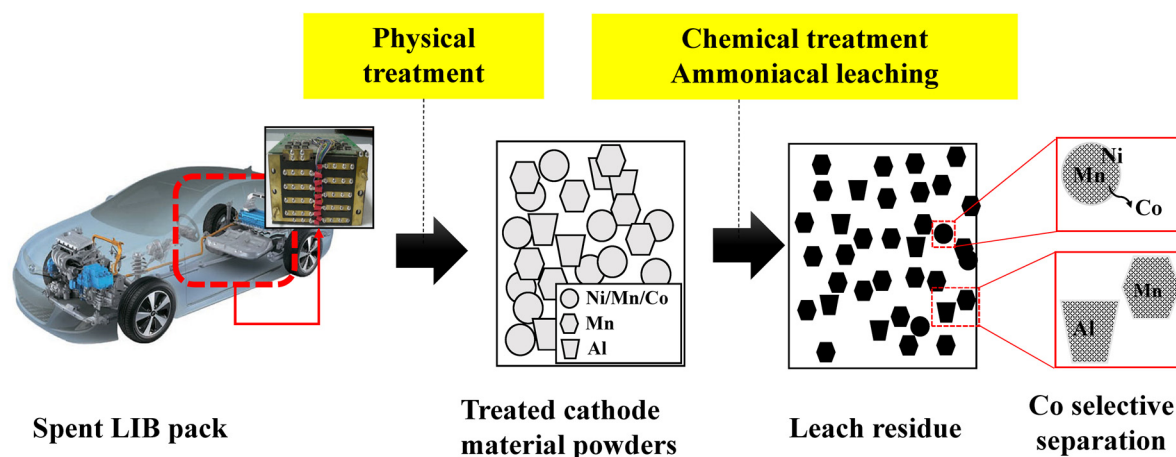


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GRAPHICAL ABSTRACT



HIGHLIGHTS

- Ammoniacal leaching is used to recover spent Li-ion battery cathode materials.
- Leaching agents consist of ammonia, ammonium sulfite and ammonium carbonate.
- Ammonium sulfite is a reductant and ammonium carbonate acts as pH buffer.
- Co and Cu can be fully leached while Mn and Al are not leached.
- Co recovery via ammoniacal leaching is economical compared to acid leaching.

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ABSTRACT

As the production and consumption of lithium ion batteries (LIBs) increase, the recycling of spent LIBs appears inevitable from an environmental, economic and health viewpoint. The leaching behavior of Ni, Mn, Co, Al and Cu from treated cathode active materials, which are separated from a commercial LIB pack in hybrid electric vehicles, is investigated with ammoniacal leaching agents based on ammonia, ammonium carbonate and ammonium sulfite. Ammonium sulfite as a reductant is necessary to enhance leaching kinetics particularly in the ammoniacal leaching of Ni and Co. Ammonium carbonate can act as a pH buffer

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so that the pH of leaching solution changes little during leaching. Co and Cu can be fully leached out whereas Mn and Al are hardly leached and Ni shows a moderate leaching efficiency. It is confirmed that the cathode active materials are a composite of LiMn_2O_4 , $\text{LiCo}_x\text{Mn}_y\text{Ni}_z\text{O}_2$, Al_2O_3 and C while the leach residue is composed of $\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$, LiMn_2O_4 , Al_2O_3 , MnCO_3 and Mn oxides. Co recovery via the ammoniacal leaching is believed to gain a competitive edge on conventional acid leaching both by reducing the sodium hydroxide expense for increasing the pH of leaching solution and by removing the separation steps of Mn and Al.

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1. Introduction

Lithium-ion batteries (LIBs) offer several advantages including high power density, high energy density, high potential, long storage life, low self-discharge rate, and a wide operating temperature range [1]. The LIBs are widely used in mobile phones, laptops, video cameras, and other modern life appliances [2]. They now become more important because of usage as electric vehicle power sources [3]. The world's production of LIBs reached 2.05 billion in 2005 and 5.86 billion in 2012 respectively [4]. It is anticipated that the production and consumption of LIBs will increase steadily in the forthcoming years.

The LIBs, of which main components are anode, cathode, electrolyte, and separator, consist of lithium transition metal oxides, organic chemicals, carbons and polymers [1]. While the anode is basically a composite of carbon powder and polymer binder, the cathode is a composite of conducting carbon, polymer binder, and lithium transition metal oxides such as LiCoO_2 , LiMn_2O_4 , LiNiO_2 , and $\text{LiCo}_x\text{Mn}_y\text{Ni}_z\text{O}_2$. These anode and cathode active materials are respectively coated on Cu and Al foils, which act as current collectors [5,6].

If spent LIBs are simply disposed by dumping them in landfill, soil contamination resulting from the leakage of organic electrolytes as well as heavy metals in the batteries will become a serious environmental concern [7]. Aside from their potentially hazardous nature, valuable materials from spent LIB wastes need to be recycled with considering their limited resources. Therefore, the recovery of the major components in the spent LIBs appears beneficial to prevent environmental pollution and raw material consumption [8,9].

From an environmental and health viewpoint, hydrometallurgical treatment could be a favored technology for recycling of metals from LIBs compared with pyrometallurgical processes because it offers such advantages as low energy consumption, no air emissions, and complete recovery of valuable components with high purity [4,10]. It is widely known that valuable metals such as Ni, Mn, Co, Al and Cu from the spent LIBs can be leached out by using acids such as hydrochloric acid and sulfuric acid. In particular, Co is the most extensively studied metal for recycling because of its relatively high price. Furthermore, separation of materials containing Co is particularly important from an environmental and health viewpoint as Co is classified as carcinogenic, mutagenic and toxic to reproduction [6]. The majority of Co can be leached out with hydrochloric acid or sulfuric acid and its leaching efficiency increases further in the presence of reducing agent such as hydrogen peroxide [1,5,8,11,12].

However, this acid leaching incurs an extra cost for regulating the pH of leaching solution to separate Co from Ni and Mn as a precipitated form. For example, when sodium hydroxide was sequentially added to an acidic leach liquor containing Ni, Mn and Co, Wang et al. observed that the precipitation of Ni, Mn and Co began at a pH value of 2, 1 and 3 and was completed at a pH value of 8, 12 and 10, respectively [13]. Therefore, a large amount of sodium

hydroxide would be necessary to increase the pH from a very low value to as high as 12. Moreover, the selective precipitation of each metal becomes difficult because the pH range for metal precipitation is overlapped between Ni, Mn and Co. Therefore, the spent LIBs leached with acidic medium undergo various steps of separation and recovery techniques such as solvent extraction, selective precipitation and electrochemical method [2,5,13–17]. For example, Chen et al. separated and recovered Mn, Ni, Cu and Co in a series of solvent extraction and precipitation steps. Mn and Ni were respectively precipitated with KMnO_4 , NaOH and Na_3PO_4 while Cu and Co were respectively extracted with Mextral® 5640H and Mextral® 272P [15].

By contrast, alkaline leaching employing ammoniacal solutions based on ammonia, ammonium carbonate, ammonium chloride or other alkaline reagents is known to show different leaching behavior for Ni, Mn, Co and Cu from acidic leaching. Bhuntumkol et al. investigated the leaching behavior of nickel oxides in acid and ammoniacal solutions [18]. The leaching behavior of Mn-containing ores with ammoniacal medium was also studied by some research groups [19–23]. Senanayake et al. compared the leaching behavior of Zn–Mn–C batteries between ammoniacal and sulfuric acid solutions [24]. They attributed the higher and lower leaching efficiency of Zn and Mn in ammoniacal solutions to the formation of soluble $\text{Zn}(\text{NH}_3)_4^{2+}$ and the inability of Mn to form a soluble complex ion, respectively. Rokukawa carried out extraction of Ni, Co, Cu, Mn, and Fe from cobalt crusts and ocean manganese nodules, and obtained the highest leaching efficiency of Ni, Co and Cu using combined ammonium carbonate and ammonium sulfite as leaching agent [20,25].

In this paper, the leaching behavior of Ni, Mn, Co, Al and Cu is investigated with ammoniacal medium for cathode active materials, which are separated from a commercial LIB pack in hybrid electric vehicles. We adopted ammoniacal leaching agents based on ammonia, ammonium carbonate and ammonium sulfite. The effects of leaching agent composition, leaching time and temperature are examined herein.

2. Experimental

2.1. Materials and methods

LIB cathode active materials were obtained from a commercial, spent LIB pack in hybrid electric vehicles (Hyundai Motor Company). The flowchart of treatment process of spent LIBs is illustrated in Fig. 1. The physical treatment procedure involves discharging, dismantling, separating, drying, crushing, grinding, sieving and grain size separation in sequence. After a spent LIB pack was connected to a discharger, the pack was discharged to less than 0.1 V, and then, the pack proceeded with the dismantling process. Dismantled cells from the pack were forced to be short-circuited to release residual electrical charge. The discharging step is necessary before dismantling to avoid the potential danger of short-circuit or self-ignition of battery rolls when anode and cathode are put

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