

Effect of Initial Black Mass Composition on Valuable Metal Recovery Efficiency in Hydrometallurgical Recycling of Lithium-Ion Batteries

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The rapid growth of electric vehicles has increased the importance of recovering valuable metals such as lithium (Li), nickel (Ni), and cobalt (Co) from end-of-life lithium-ion batteries (LIBs). Although it is known that metal recovery efficiency varies depending on battery dismantling and thermal treatment conditions, the mechanisms responsible for these variations remain insufficiently understood. This study investigates the effect of initial black mass (BM) composition on valuable metal recovery during hydrometallurgical recycling process of LIBs. The objective is to clarify the factors that govern metal extraction efficiency by comparing black masses produced from different starting conditions of LIBs, that is, with or without disassembling the LIBs.

An automotive LIB employing an NCM811 cathode, graphite anode, and LiPF₆-based electrolyte was used as the model system. Two types of black mass were prepared by heat treatment at 750 °C for 1 h in air: (i) cathode-derived BM obtained from disassembling LIB and (ii) cell-derived BM produced by heating the entire cell. Following thermal treatment, particles smaller than 1 mm were collected and subjected to hot-water extraction and subsequent acid leaching using 1 mol/l sulfuric acid or 1 mol/l citric acid. Quantitative elemental analysis was carried out by XRF, ICP-OES, and AAS. Chemical states and phase compositions were investigated by X-ray diffraction (XRD) and X-ray absorption fine structure (XAFS) analyses, while particle size distributions were evaluated by laser diffraction.

Hot-water extraction revealed that a portion of lithium existed as water-soluble compounds, such as Li₂CO₃ and LiOH, generated during heat treatment. The cathode-derived BM exhibited a higher lithium extraction ratio than the cell-derived BM, suggesting the formation of water-insoluble lithium compounds through reactions involving electrolyte residues and aluminum components in the full-cell system resulting in the generation of water insoluble lithium salts such as Li₃PO₄ and lithium aluminum oxides.

Significant differences were observed during acid leaching. For both sulfuric and citric acid systems, the cell-derived BM showed substantially higher Ni and Co recovery than the cathode-derived BM. Sulfuric acid consistently achieved higher extraction efficiencies than citric acid. XRD analysis demonstrated that the cathode-derived BM contained significant amounts of NiO, whereas metallic Ni was the dominant Ni-containing phase in the cell-derived BM. In addition, Li₂CO₃ and LiAlO₂ were detected in both samples, while Li₃PO₄ originating from electrolyte decomposition was uniquely observed in the cell-derived BM.

The XAFS results further confirmed the difference in chemical states. Quantitative analysis of Ni valence showed that the cathode-derived BM consisted predominantly of NiO, whereas the cell-derived BM was primarily metallic Ni with only a minor portion of Ni oxide. These findings indicate that graphite from the anode acted as a reductant during heat treatment, promoting the reduction of transition-metal oxides to metallic species. Because metallic Ni and finely dispersed particles are more readily dissolved under the present leaching conditions, this reduction process contributed significantly to the enhanced metal recovery observed for the cell-derived BM.

Particle size analysis supported this interpretation. The cathode-derived BM contained a large fraction of coarse particles exceeding 100 μm, while the cell-derived BM was dominated by particles around 10 μm. The finer particle size is attributed to suppression of cathode particle sintering by carbothermal reduction reactions involving graphite during heat treatment.

Overall, the initial chemical state and morphology of black mass strongly influence hydrometallurgical recovery efficiency. Reduction of transition-metal oxides to metallic phases and simultaneous particle refinement during heat treatment markedly improve valuable metal extraction efficiency. Furthermore, sulfuric acid provided higher recovery than citric acid, mainly due to its lower pH and superior ability to dissolve metallic and oxide phases under the tested conditions.

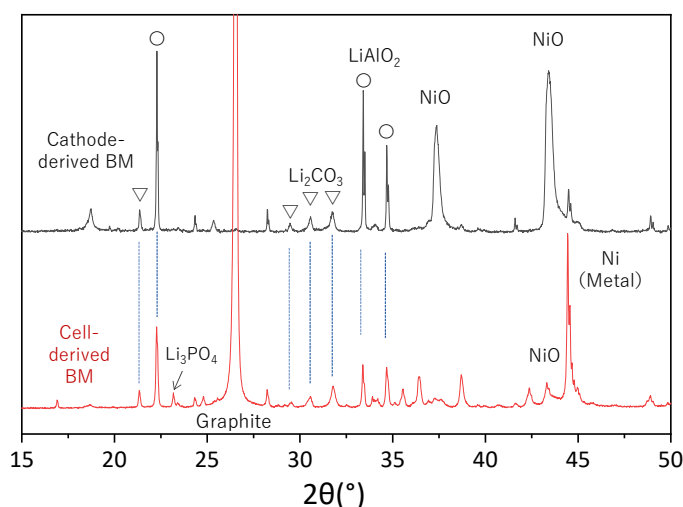


Figure 1 XRD patterns of Black Mass (BM)