Extraction and recovery of critical metals using eco-friendly processes to secure lithium-ion batteries resources

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論 文 名　：Extraction and recovery of critical metals using eco-friendly processes to secure lithium-ion batteries resources
(環境に優しいプロセスを使用したリチウム電池資源確保のためのレアメタル金属の抽出と回収)

区　　分　：甲

論　文　内　容　の　要　旨

The demand for the critical metals (Li, Co, Ni, and Mn) has been continuously growing in recent years. Especially, the electric vehicles (EVs) industry has presented a booming scene in the context of governments of all countries pursuing new energy sources to achieve “carbon neutrality” goals. The lithium-ion batteries (LIBs), as the main battery type for EVs, have unprecedented attractive. The prosperity of the LIBs industry has also led to the development of its upstream resources (primary mineral resources) and downstream resources (secondary resources—waste LIBs). Prices of Co and Li_2CO_3 have been rising sharply in the past several years. However, around the entire battery industry, whether extracting these critical metals from its upstream resource—minerals or recovering these critical metals from its downstream resource—waste LIBs, an eco-friendly, sustainable, and economical technology is a challenging issue. To address this problem, the present thesis is devoted to the development of eco-friendly processes in the field of solvent chemistry to extract and recover these critical metals required for LIBs.

In the Chapter 2, a novel extraction system by dissolving [Omim][TTA] in a different ionic liquid (IL) [Omim][NTf_2] instead of hazardous organic diluents was developed to selectively extract the critical metal—Li(I) from salt lakes (primary resources). The newly developed functionalized ionic liquid (FIL) system shows a high extraction ability and enables the extraction of Li(I) at a lower pH condition. The extraction performance of the FIL extractant was enhanced by dissolving it in an ionic liquid diluent, because the active component TTA anion was enhanced. The extraction mechanism was examined by slope analysis and UV-vis measurement, which indicated that one molecule of FIL interacts with one Li(I) ion and forms a 1:1 complex. Moreover, the FIL showed a high selectivity toward Li(I) in the presence of high concentrations of interfering ions such as Na(I) and K(I). Using a countercurrent extraction process at a phase ratio of $V_o : V_a = 1 : 1$, the Li(I) recovery from salt lakes reached 88.2% in 2-3 stages and the extraction efficiency reached 97.3% at a phase ratio of

$V_o : V_a = 3 : 1$. The $SF_{Li/Na}$ at a phase ratio ($V_o : V_a = 1 : 1$) in this study was 227, which is the highest value among the FILs previously reported which were used without the addition of another extractant for collaborative extraction. Overall, the ionic liquid extractant [Omim][TTA] shows a good prospect in the industrial operation for the recovery of Li(I) from salt lakes.

The Chapter 2 is about the successful extraction of Li from the primary resource—salt lakes. In the Chapters 3 and 4, we recovered critical metals such as Co, Ni and Mn from secondary resources—waste LIBs using eco-friendly and efficient aqueous biphasic system (ABS) technology.

In the Chapter 3, the selective recovery of Co(II), Ni(II), and Mn(II) from a spent LIB model solution using novel ABSs comprising biocompatible components was demonstrated. In the first step, an ABS of $[N_{4444}]HSO_4$, Na_2SO_4, and H_2O mixed with Phe successfully transferred Co(II) and Ni(II) to the IL-rich phase while Mn(II) stayed in the salt-rich phase. In the second step, the IL-rich phase was mixed with methanesulfonic acid (MSA) and NaCl to form a new ABS ($[N_{4444}]HSO_4$–NaCl–MSA–H_2O), which enabled effective separation of Co(II) and Ni(II): Ni(II) was stripped to the salt-rich phase and Co(II) was enriched in the IL-rich phase as $[CoCl_4]^{2-}$. Finally, Co(II) was stripped from the IL-rich phase by adding Na_2SO_4 and simultaneously regenerating the ($[N_{4444}]HSO_4$) IL. A reusability test showed that the performance of the regenerated IL was relatively stable over a three-cycle experiment. An eco-friendly ABS with remarkable metal separation performance was developed in this chapter without using any hazardous reagents or toxic organic solvents. The insights might further be explored to recover critical metals from an actual LIB waste.

In the Chapter 4, we integrated the leaching and separation of Co from an actual spent LIBs cathode material using biocompatible amino acids. The new ABS (Ser - PPG 400- H_2O) was first applied to the recovery of metals from waste batteries. In the first step (leaching), under a relatively mild temperature (70 °C) and a solid-liquid ratio of 10/1 (g/L), the leaching efficiency of each metal (Co, Ni, Mn, Li, Al, Cu and Fe) is higher than 80% by using serine as a leaching agent. Especially, the leaching efficiency of Co reached 98%. The mechanism of Ser leaching for the metals from the waste LIB cathode was also discussed. Amino acids are attractive as amphoteric substances that exhibit excellent reducing properties at a certain pH. Then in the second step (separation of Co using ABS), the Co was selectively extracted with the extraction efficiency of 97% and the purity of over 95% by adding thiocyanate to the ABS system. The amino acids have excellent prospects in the field of spent battery recycling due to their eco-friendly and low-price advantages.