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Recovery of critical metals from spent Li-ion batteries: Sequential leaching, precipitation, and cobalt–nickel separation using Cyphos IL104

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ABSTRACT

This study presents a novel recycling scheme for spent Li-ion batteries that involves the leaching of lithium in hot water followed by the dissolution of all transition metals in HCl solution and their separation using the ionic liquid Cyphos IL104. The parametric studies revealed that >84 % Li was dissolved while the cathode material was leached at 90 °C for 2 h. Approximately 98 % Li from the non-acidic solution was directly precipitated as Li_2CO_3 at a Li^+:CO_3^{2-} ratio of 1:1.5. The transition metals from the Li-depleted cathode mass were efficiently (>98 %) dissolved in 3.0 mol·L^{-1} HCl at 90 °C for a 3 h leaching process. Manganese from the chloride leach liquor was selectively precipitated by adding $KMnO_4$ at a 1.25-fold higher quantity than the stoichiometric ratio, pH value 2.0, and temperature 80 °C. The remaining co-existing metals (Ni and Co) were separated from the chloride solution by contacting it with a phosphonium-based ionic liquid at an equilibrium pH value of 5.4 and an organic-to-aqueous phase ratio of 2/3. The loaded ionic liquid was quantitatively stripped in 2.0 mol·L^{-1} H_2SO_4 solution, which yielded high-purity $CoSO_4 \cdot xH_2O$ crystals after evaporation of the stripped liquor. Subsequently, ~99 % nickel was recovered as nickel carbonate [$NiCO_3 \cdot 2Ni(OH)_2$] from the Co-depleted raffinate by the precipitation performed at Ni^{2+}:CO_3^{2-} ratio of 1:2.5, pH value of 10.8, and temperature of 50 °C. Finally, a process flow with mass and energy balances yielding a high recovery rate of all metals in the exhausted cathode powder of spent LiBs was proposed.

1. Introduction

The unique characteristics of specific energy density (up to 265 W h·kg^{-1}), specific power storage (up to 340 W·kg^{-1}), and life-span (up to 1200 cycles) have made lithium-ion batteries (LiBs) the dominant entity of the rechargeable battery market (Ilyas et al., 2021; Wagner, 2006). LiBs' consumption has drastically grown in the recent past and is estimated to exceed 700 GWh by 2030 (Natarajan and Aravindan, 2018), as modern society gradually shifts to electric vehicles (Porvali et al., 2019). Hence, the raw materials used in LiBs' production (including lithium, cobalt, and nickel) may face a supply crunch by the mid of the next decade (Chen et al., 2019). In fact, they are already listed to be the energy-critical elements by the European Union, the US Department of Energy, the American Physical Society, the Materials Research Society, etc. (European Commission, 2017; US-DoE, 2011).

Besides the foreseeable shortage of primary raw materials, the burgeoning quantity of spent batteries (LiBs) poses significant environmental issues (Munir et al., 2020). Landfill disposal of spent LiBs without proper treatment can severely contaminate the soil and underground water, whereas, the electrolyte may emit harmful gases (like HF) by reacting with water (Pathak et al., 2017). Moreover, the undischarged power storage in spent batteries may explode, resulting in hazardous emissions of Cl_2, H_2, and HF due to the burning of organic electrolytes (Zheng et al., 2018). There is hence an urgent need to find an appropriate management strategy for spent LiBs (Meshram et al., 2020). Moreover, the associated benefit of recycling critical metals from this - waste stream in a circular economy perspective has gained great attention (Munir et al., 2020; Pathak et al., 2021).

Direct smelting of discharged batteries is a simple recycling practice. However, secondary waste (slag) generation, high-energy consumption (reaching up to 1450 °C), and loss of lithium with molten silicates have been identified as the major drawbacks (Agrawal et al., 2012). Despite

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