Strategic metals extraction from LIBs cathode materials by supercritical CO2 assisted by functional copolymers as CO2-philic complexing agents

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Résumé

Li-ion batteries (LIBs) are the mainstream power source of electric vehicles (EVs) due to their excellent performance and mature technology. Consequently, LIBs are highly demanded and produced to electrify the current vehicle market. The global EVs stock is growing fast with less than 1,600,000 to more than 17,400,000 in 2015 and 2021, respectively.(1) Metals contained in LIBs (Ni, Co, Li, etc.) are becoming strategic resources which are considered as critical materials by the European governments and other countries worldwide.(2) Recycling these metals while restricting secondary pollution produced by the current hydrometallurgical processes due to wastewater generation, energy and chemicals consumption, is an innovation challenge.(3) Supercritical CO2 (scCO2) extraction assisted by complexing copolymers is a promising process to recover LIB valuable metals. CO2, besides being non-toxic, abundant and non-flammable, allows an easy separation of metal-complexes by depressurization, limiting the wastewater production.
However, extraction of metals using CO2 is not obvious because of the apolar character of CO2. Therefore, to allow scCO2 metal extraction, complexing agent soluble in CO2 and/or surfactants to form reverse micelles are required to solubilize the metal cations. In this context, CO2-soluble functional copolymers have been synthetized by Reversible Addition-Fragmentation chain Transfer (RAFT) copolymerization with a phosphonic acid derivative as metal complexing unit (vinyl benzyl phosphonic diethyl ester, VBPDE) and a fluorinated CO2-philic monomer (1,1,2,2-tetrahydroperfluorodecyl acrylate, FDA). In its acid form, poly(VBPDA-*co*-FDA) copolymer previously proved its ability to complex cobalt cation.(4)

The scCO2 extraction conditions such as pressure, temperature, functional copolymer concentration, and the presence of additives are varied to optimize the metals extraction from LiCoO2 cathode material.

Most metal extraction studies reported in the literature concern the decontamination of

*Intervenant

solid or liquid effluents where the metal is already in its cationic form. For recycling metals from spent LIBs, a leaching step has first to occur in scCO2 to form metal cations and then these cations can undergo complexation. Recently, micro-emulsion systems based on TBP-HNO3 mixtures have been used for metal leaching and extraction of rare earths elements. In this study, functional copolymers are playing the triple role of leaching agent, complexing agent and surfactant (Figure 1), corresponding to an unprecedented inorganic acid free process. Leaching, complexation and extraction proof of concept has been performed. Optimization is in progress for quantitatively extracting cobalt and lithium using this innovative dry extraction process.

Figure 1. Metal recycling from spent LIBs by scCO2 using copolymers.

Mots-Clés: strategic metals, Li, ion batteries, metal recycling, supercritical CO2 extraction, complexing polymers