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Practical Application of Advanced Lithium Ion Adsorbent

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Summary

A demand for lithium is forecasted to increase by up to 60%, from 102,000 tons to 162,000 tons of Li_2CO_3 equivalent, in the next 5 years with the application on batteries occupying a large percentage (40,000 t) of this growth. Lithium is found in lakes and brines, and exists in several minerals such as spodumene, petalite, lepidolite, and amblygonite. Seawater is also considered as a great source of lithium, although the concentration of lithium is 0.17 ppm. Until now lithium has been produced mostly from brines which contain 300～1,600 ppm. The current resource of lithium in brines is *ca.* 52.3 million tons of lithium equivalent; lithium from mineral resources is 8.8 million tons. Uyuni (Bolivia) brine's lithium reserve is estimated to be 5.4 million tons, but it contains saturated levels of Na^+, Cl^- and SO_4^{2-}, and high Mg^{2+}. New process scheme "Recovery of lithium from brine" needs to be developed. Spinel-type manganese oxide ($Li_{1.33}Mn_{1.67}O_4$) is a suitable material for its remarkably high selectivity for lithium ions in the aqueous phase, but it has a relatively low chemical stability against lithium insertion-extraction reaction. During acid treatment Mn(III) in $Li_{1.33}Mn_{1.67}O_4$ will be turned into Mn(IV) and Mn(II) in disproportion. Mn(IV) remains in the spinel skeleton and Mn(II) is dissolved in an acidic solution to trigger the spinel structure collapse gradually. The purpose of this study is to improve the chemical stability of $Li_{1.33}Mn_{1.67}O_4$ for the recovery of lithium from brine. A series of metaloxide-coated lithium ion adsorbents was synthesized by an impregnation method in pH under control, adding different metal-hydroxide precursors (Al, Mg and Ni) on spinel $Li_{1.33}Mn_{1.67}O_4$ followed by oxidation at 400°C. It was recognized by X-ray diffraction that the spinel-type structure was maintained after heating. Loaded metal-oxide contents were 7.1 wt% of Al, 5.2 wt% of Mg and 11.8 wt% of Ni, respectively. The influence of metallic species on chemical stability of resulting materials using 0.25 mol/L H_2SO_4 for 90 min was investigated by inductively coupled plasma spectroscopy. As a result, alumina-coated $Li_{1.33}Mn_{1.67}O_4$ showed lower manganese dissolution (25% decrease) and similar lithium extraction, compared with that of the raw $Li_{1.33}Mn_{1.67}O_4$. It is revealed that the impregnation method and the pH adjustment are important in the region forming metal oxide oligomers as precursors.