

Ion-Exchange Properties of Metal Phosphates and
Its Application for Recovery of Lithium from Seawater

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Summary

Sea water is a good source of lithium, which is a most important material to resolve many energy problems in the near future. We reported in the last period, that the lithium selectivity was greatly enhanced by a partial replacement of the Zr^{4+} site with Cr^{3+} or Fe^{3+} ion for the ion-exchange properties of $HZr_2(PO_4)_3$.

In this study, various metal ions Zr^{4+} , Ti^{4+} , Fe^{3+} , Al^{3+} and In^{3+} were substituted for $H_3Cr_2(PO_4)_3$. $Li_{3-x}M_xCr_{2-x}(PO_4)_3$ (L-MCP) [M:Zr, Ti, Fe, Al and In, $0 \leq x \leq 2$] compounds were prepared by conventional solid state reactions, heating a mixture of $LiCO_3$, Cr_2O_3 , H_3PO_4 , and other metal oxides in a stoichiometric ratio at $1000^\circ C$. The ion-exchange experiments on L-MCP or H-MCP [$H_{3-x}M_xCr_{2-x}(PO_4)_3$] were carried out by a batch method. Subsequently, it was revealed that $H_{2.5}Ti_{0.5}Cr_{1.5}(PO_4)_3$ showed high lithium selectivity in buffer solution. This material has been applied to recover lithium from Oita sea water with high concentration factor, 6400 l/kg.

We measured 7Li NMR for various compositions of $H_xLi_{1-x}Zr_2(PO_4)_3$ [$0 \leq x \leq 1$] at room temperature to explain the Li^+ behavior in the solid materials. When $x=0$, the compound $LiZr_2(PO_4)_3$ had two kinds of Li-sites, as confirmed by NMR. One is -1.35 ppm [site(1)], another is -0.60 ppm [site(2)]. According to the progression of $Li^+ \rightarrow H^+$ ion exchange in HNO_3 solution, site(1)- Li^+ decreased faster than site(2)- Li^+ , and site(2)- Li^+ did not show signs of weakening until site(1)- Li^+ had vanished on the NMR spectrum. On the other hand, when $H^+ \rightarrow Li^+$ ion exchange in buffer solution containing 5 mM Li^+ , only site(2)- H^+ was replaced with Li^+ rapidly.