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Development of Li Ion Sieves Using NaCl-Based Flux Growth Method

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Summary

Selective lithium uptake from sea water and lake brine is an important challenge in energy and environmental science. $H_{1.6}Mn_{1.6}O_4$ with pseudo-spinel type structure is a highly selective adsorbent for Li ions, but it is difficult to prepare large, highly crystalline $H_{1.6}Mn_{1.6}O_4$ crystals with porous structure due to its thermodynamic metastability. Herein we demonstrate simple chemical processes that transform flux-grown, idiomorphic orthorhombic $LiMnO_2$ (o-$LiMnO_2$) cuboids of micrometre size into hierarchically structured $H_{1.6}Mn_{1.6}O_4$ rods. We have optimized the flux growth conditions such as the Mn source, holding temperature, and solute concentration, in order to yield large, single phase o-$LiMnO_2$ particles. The use of MnO under very low solute concentration (1 mol %) and high temperature (1,000 °C) is critical to obtaining the single phase, idiomorphic o-$LiMnO_2$ cuboids. The metastability of o-$LiMnO_2$ is confirmed by *ab initio* density functional theory calculation in comparison with other lithium manganates such as $LiMn_2O_4$ and Li_2MnO_3. The successive calcination and acid treatment allow the transformation of o-$LiMnO_2$ into $H_{1.6}Mn_{1.6}O_4$ rods with porous structure. The resultant $H_{1.6}Mn_{1.6}O_4$ shows high Li^+ adsorption capacity (~5.6 mmol g^{-1}), high Li^+/Na^+ selectivity, and good durability compared with existing $H_{1.6}Mn_{1.6}O_4$ adsorbents.