

Synthesis of lithium ion-sieves using biogenic birnessite as a precursor

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Lithium (Li) is regarded as one of the most important elements in advanced industries, and its concentration in geothermal water is around 10 mg/L at the maximum corresponding to about 50 times larger than in seawater [1]. In the present work, synthesis of lithium ion-sieve was investigated using biogenic Mn oxides. Biogenic Mn oxides were produced by a Mn-oxidizing fungus, *Paraconiohyrium sp.* WL-2 strain at pH 6.5 [2].

After biogenic birnessite was suspended in LiCl solution, the solid phase was obtained by evaporation at 80 °C for 24 hours and then calcined at 450 °C for 4 or 8 hours. The calcined product was washed with 0.1 mol/L HCl to exchange with Li⁺ to obtain a sorbent as a template for Li⁺ ions. To compare with biogenic birnessite, several types of synthesized Mn oxides, that is, acidic birnessite, ramsdellite, Mn₃O₄, cryptomelane, were investigated as the starting materials in the same manner.

Based on XRD results, LiMn₂O₄ was detected in three products of five before acid washing, that is, derived from biogenic birnessite, acidic birnessite and ramsdellite. The minimum calcination time was required to obtain a pure LiMn₂O₄ phase using biogenic birnessite as a starting material. XRD peaks assigned to LiMn₂O₄ were maintained even after Li⁺ ions were extracted by acid washing.

While products from acidic birnessite sorbed little Li⁺, the products from biogenic birnessite and ramsdellite sorbed Li⁺ more effectively. Some release of Mn²⁺ was observed during sorption of Li⁺ ions on the product derived from ramsdellite. Products derived from biogenic birnessite showed the most effective performance to sorb Li⁺ ions.

Very alkaline condition is required to synthesize ramsdellite, while biogenic birnessite can be produced around neutral pH values. Therefore, biogenic birnessite is a promising geomimetics as starting materials for synthesis of the effective lithium ion-sieves.

[1] Yoshinaga, T. *et al.* (1982) *Proc NZ Geotherm Workshop Pt 2*, 329–332. [2] Sasaki, K. *et al.* (2008) *Mater. Trans.* **49**, 605–611.

Sorption of Sr²⁺ on hydroxyapatite from calcined fish bones at different temperatures

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Hydroxyapatite was produced by calcination of fish bones at different temperatures (400–1100 °C). Higher calcination temperatures reduced the organic matter content but also provided better crystallized hydroxyapatite and larger crystal sizes with less lattice strain. Higher calcination temperatures also decreased the specific surface area and increased the ion-exchange capacity hydroxyapatite. Sorption of Sr²⁺ as a surrogate for radionuclides was investigated with hydroxyapatite calcined at different temperatures. These results demonstrated that lattice strain affects ion-exchange properties at nano-domain level relatively more as compared to its effects on the surface area.

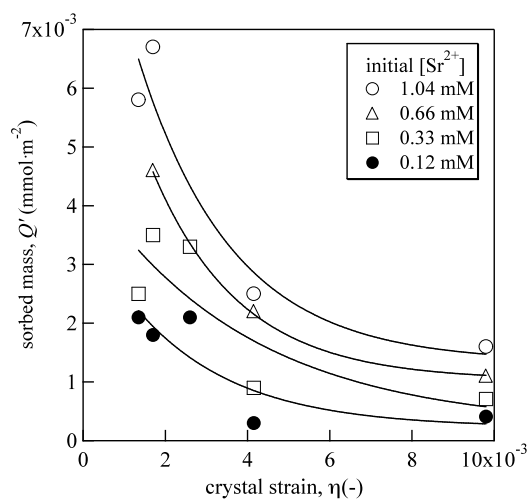


Figure 1: Sorption capacity of Sr²⁺ on hydroxyapatite with different lattice strain.