Low-temperature fluid-induced $\beta$-phase propagation: an energy-efficient pathway for recovering Li from $\alpha$-spodumene

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Lithium-ion batteries exhibit very high energy density and are currently the dominant technology for powering electric vehicles. They drive the worldwide growth of Li production and, consequently, supply chain diversification is a major concern. Li-Cs-Ta pegmatites are the most important mineral-based source of lithium, where spodumene is often the main carrier phase. Although numerous approaches have been proposed to recover lithium from spodumene, most are highly energy intensive involving an initial heat treatment at temperatures exceeding 1000°C to convert natural $\alpha$-spodumene to its $\beta$ form, a tetragonal stuffed silica derivative where ion exchange with interstitial lithium can be achieved in a second stage such as an acid bake at $\approx$ 250°C. The high temperatures required for completing the phase transition are not dictated by thermodynamics but rather sluggish kinetics, and extrapolation of high-pressure results indicate that the $\beta$ form is stable below 500°C at atmospheric conditions.

Here we report the progress of experiments designed to investigate factors that can promote the phase transformation at low temperature as a means of identifying an energy-efficient Li recovery process. The results of dynamic treatment, where $\alpha$-spodumene was progressively heated from room temperature up to 900°C, indicate that the initial rate of the $\alpha$-$\beta$ transition is significantly faster for cm-sized crystals when compared to finely-ground powder. Raman spectral imaging reveals that the propagation of the $\beta$-phase in the crystals is initiated below 650°C and follows trails of entrapped alkali-rich fluids (Fig. 1) that initially enhance the transition kinetics until their release along defects. Consequently, the lower rate of transformation observed for the fine powder results from breaching the fluid inclusions in the grinding step. From these observations, $\alpha$-spodumene crystals were exposed to alkali hydroxide melts to induce the phase transition and simultaneously exchange with interstitial lithium from the newly-formed $\beta$-phase. Following specific temperature-time pathways within a narrow window between 400 to 500°C, decomposition of millimeter-sized $\alpha$-spodumene crystals with excellent Li fractionation from Na and K was achieved within less than 30 minutes. This low-temperature single-stage approach leads to major reduction in energy consumption compared to the conventional two-stage process.