Quantifying the affinity difference between lithium and close identity ions using ETS-10 titanosilicate and supported with density functional theory

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Abstract

Separating lithium from multicomponent aqueous streams is critical to ensure the continuous supply of lithium for battery applications. The properties of lithium and other cations present in such aqueous streams, such as potassium, are similar, rendering their separation challenging. As a result, conventional methods for separating these ions often require large quantities of hazardous solvents and are energy intensive. Continuous ion exchange and ion chromatography could be sustainable and environmentally benign alternatives. The adoption of these separations requires development of selective sorbent materials, and fundamental understanding of ion-sorbent interactions are needed to facilitate rationale sorbent material design.

We examine the thermodynamics of ion exchange for Li^+ and K^+ using modified microporous titanosilicate, ETS-10. Ion exchange isotherms were measured for Li^+ and K^+ in dilute aqueous solution using the sodium form of ETS-10, Na-ETS-10. Equilibrium uptake data were analyzed by using a modification of the Langmuir isotherm equation that accounts for ion exchange: the desorption of a cation from the ETS-10 framework together with adsorption of the cation of interest (i.e., Li^+ or K^+) to the framework. Equilibrium constants for the ion exchange of Na^+ with cation i, $K_{i,Na}$ (where i = Li^+ or K^+) and the exchange capacity of Na^+ with cation i, $Q_{i,e}$, were determined. K_{K^+} is 6-fold greater than K_{Li^+}, reflecting the more favorable exchange of K^+ into Na-ETS-10 compared to Li^+. This affinity difference is corroborated by density functional theory (DFT) calculations of ion affinity to the ETS-10 framework. Energy differences from DFT were interpreted using a thermochemical cycle to account for hydration and solvation of cations, thus enabling comparison of experiment and theory. DFT-derived energy differences also revealed the binding affinity difference of the various sites of ETS-10 among Li^+, Na^+, and K^+. These studies provide a foundation to tune the composition of the porous material and measure the selectivity based on exchange isotherms. Selectivity studies are extended to examine separation of lithium from divalent ions, simulating complex aqueous lithium sources, as well as to explore the role of framework substitution in ion affinity.