

## First-principles studies of interfacial chemistry in silicon anodes for lithium ion battery applications

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Silicon is a promising alternative to graphite as an anode material for lithium-ion batteries due to its enhanced safety and significantly higher theoretical capacity. Drastic volume changes in silicon during lithiation and delithiation cycles, however, hinder cyclability and capacity retention. Most strategies for improving the cyclability of silicon involve the engineering of interfacial chemistry and nanoscale architectures, and to further these efforts, fundamental insights into lithiation processes at well-defined silicon surfaces are greatly needed.

In this talk, we present an extensive computational study of lithiation of silicon/electrolyte interfaces. Using first principles density functional theory (DFT) calculations, we investigate the thermodynamics and kinetics of lithiation of Si(111), Si(110), and Si(100) surfaces, and we determine voltage/capacity curves for each of these facets. The curves exhibit a distinct, high-voltage feature for the (110) facet of silicon and thereby provide a compact thermodynamic explanation for the experimentally observed anisotropy in lithiation of Si nanowires and micropillars. The atomistic origins of this thermodynamic driving force are traced to a combination of the intrinsic strain-fracture dynamics of the various Si crystal planes and the local strength of Si-Li bonds. We discuss the effects of surface passivation on these lithiation processes, and we close with a comparison of the lithiation characteristics of Si to those of Ge, a related semiconductor material.

Reference: "First Principles Simulations of the Electrochemical Lithiation and Delithiation of Faceted Crystalline Silicon." M. K. Y. Chan, C. Wolverton, and J. Greeley, *Journal of the American Chemical Society* **134** (2012) 14362.