# Entropy Sinks the Convex Hull in Sodiated Black Phosphorus

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The development of Na-ion batteries (NIBs) is one route to practical, utility-scale energy storage with improved scalability and energy security, relative to Li-ion batteries (LIBs), especially within Europe and Canada. However, the intercalation-based graphite negative electrodes that provide LIBs such exceptional lifetime are fundamentally incompatible with NIBs, because Na intercalation in graphite is endergonic. Black phosphorus is structurally analogous to graphite, but does electrochemically intercalate Na, making it a potential alternative. Insertion electrodes (of which intercalation electrodes are a subset) are known to have a significant entropy contribution due to the large number of possible geometric configurations. The purpose of this work is to evaluate the significance of configurational entropy for DFT energy calculations of sodiated black phosphorus (NaxP) electrodes. For these calculations, B86bPBE-XDM(Z) is used to include accurate representation of the interactions between adjacent black phosphorus layers, as well as intercalated Na atoms. Experimental measurements, such as temperature-dependent electrode potentials and isothermal microcalorimetry, are used to measure the entropy during sodiation of NaxP, for $x \leq 0.5$. The results show that including configurational entropy decreases the energy of some stoichiometries below what is expected for the convex hull based on a single Na configuration. The implications of this work suggest new computational approaches are needed for properly determining the true convex hull of insertion and intercalation electrodes, which make up the vast majority of battery electrode materials.