

Graphite Electrode Elastic Properties upon Li Intercalation

First-principles calculations reveal a *three-fold increase* in the Young's modulus of graphite as it is lithiated ($C \rightarrow LiC_6$). A linear expression is determined that describes the approximate stiffness of Li intercalated graphite as a function of loading which may lead to greatly improved continuum models of electrode deformation and failure.

Keywords: Graphite, anode, lithium ion battery, elastic properties, first-principles, computations

Background

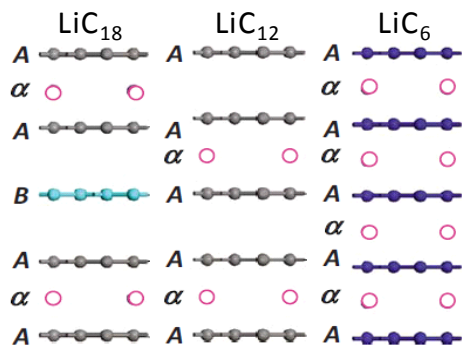
There is widespread interest in improving the performance and capacity of Li-ion batteries. Graphite is the standard anode material in these devices. As such, there is a critical need for an in-depth understanding of fundamental graphite properties at the varying operating conditions of a device. Upon charging of the battery, lithium diffuses into the graphite anode particles forming lithiated graphite intercalation structures ($C \rightarrow LiC_6$), accompanied by a 10% increase in volume.[1] The accumulated internal stress, due to repeated Li diffusion in and out of the anode can lead to structural failure. In simulations of the structural failure modes and diffusion induced deformation, it is often assumed that the intrinsic mechanical properties of the graphite anode are independent of Li

concentration. First-principles calculations were carried out to determine the Young's modulus (E) and Poisson's ratio (μ) for graphite at Li loading levels representative of the phases formed during the cycling of a Li ion battery.[2]

Computed Results

The lithium graphite intercalation compounds (Li-GIC) are illustrated in Figure 1 (left). Structurally, the Li filled interlayer spaces increase by ~10%, whereas at low loading levels the unfilled interlayer spaces undergo slight contraction. The calculated Li-GIC structures are consistent with experimental measurements.[3,4]

The dramatic changes in structure and bonding in graphite during Li intercalation may be



	Average Polycrystalline	
	Young's Modulus (E)	Poisson's Ratio (μ)
Graphite	32.47	0.32
LiC ₁₈	28.57	0.39
LiC ₁₂	58.06	0.34
LiC ₆	108.67	0.24
Li	2.00	0.34

Figure 1. (Left) Atomic structure side-view of Li-intercalation compounds: LiC₁₈, LiC₁₂ and LiC₆ (Open circles represent Li atoms); (Right) Computed Young's Modulus and Poisson's Ratio for graphite, the Li-intercalation compounds, and lithium for comparison. (Adopted from Reference 1)

expected to have a significant effect on the mechanical properties. The magnitude of the effect and correlation with loading levels is important for the development of engineering-scale models of electrode deformation and fracture. The computed polycrystalline Young's modulus (E) and Poisson's ratio for the Li-GICs, along with graphite and metallic lithium are presented in Figure 1 (right). The E for the Li-GICs is found to increase by more than a factor of 3 in going from C→LiC₆. Comparison with the E values for graphite and lithium indicate that this increase is not a linear combination of the reference data. In fact, based on the computed results, the Li-GIC Young's modulus is found to follow an approximate linear relationship in Li concentration,

$$E(\chi_{\text{Li}}) = 19.25 + 82.23\chi_{\text{Li}};$$

suitable for use in continuum-scale models of electrode deformation.

Significance

First-principles computations have become a valuable source for elastic coefficients, which can be used in lieu of experimental data with a high level of confidence. In particular, the mechanical properties of battery materials can be predicted under wide-ranging conditions providing insight into the underlying physical mechanisms leading to stress, deformation and eventual structural failure. Given the widespread application of graphite as a lithium ion battery anode, an understanding of the change in its elastic response during lithium intercalation is a critical step in improving the accuracy of engineering models of electrode mechanics.

First-principles calculations can play a valuable role in battery materials discovery, analysis and optimization through the prediction of the atomic structure, stability, and properties such

as elastic constants for electrode materials as demonstrated here for the case of lithiated graphite.

MedeA modules used for this application

The present calculations were performed with the MedeA platform using the following integrated modules of the MedeA software environment

- MedeA framework including crystal structure builder, surface builder, and analysis tools
- MT module
- JobServer and TaskServers
- VASP and its graphical user interface as integrated in MedeA

References

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