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A multi-layer phase field model to study lithium intercalation in graphite: focusing on the coupling with graphene stacking sequence

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During lithium intercalation in graphite, the active material undergoes phase separation between a succession of several stable phases, known as stages. This staging phenomenon corresponds to the appearance of an ordered sequence of intercalant layers separated by planes of the host-layered material. The stages are defined according to the number of host layers that periodically separates two successive intercalant layers. This phenomenon influences critical properties of graphite like its equilibrium potential, lithium diffusion or lithium insertion kinetics.

Here, thermodynamics and kinetics of stage formation are studied using a multi-layer free energy framework based on mean-field theory, accounting for both intra-layer and inter-layer interactions. More specifically, we go beyond the multi-layer Cahn-Hilliard framework by adding an order parameter to describe the local evolution of the stacking sequence of graphene sheets around lithium islands. The introduction of this order parameter enable the distinction between the liquid-like stage 2L and the stage 2. Key in this approach is the form of the underlying free-energy model and the associated intra- and inter-layers interactions between lithium ions and the host structure.

Following an empirical approach, we show that an inter-layer interaction between the lithium ions and the host-structure is necessary to counterbalance the enthalpy term of the lithium intra-layer energy and allow the formation of islands with intermediate concentrations, characteristics of the liquid-like phases as will be illustrated in the computed phase diagrams. The proposed interactions between the graphite structure and the lithium concentration let the stage 3, now in a dilute liquid-like form 3L, to appear at an average filling fraction around 0.2, a value that is closer to experiments than the value of 0.33 obtained without accounting for the graphene stacking order. Similarly, two stages of periodicity 2 are now solutions of the model. A dilute stage 2L with intermediate filled layers and a graphene staking sequence of the form /AB/BA, where carbon layers are staggered around empty layers, but eclipsed around filled ones and the ordered stage 2 where the graphene stacking sequence is of the form /AA/AA, where carbon layers are eclipsed around both filled and empty layers. This new framework therefore leads to a more complex phase diagram with the presence of the stages 3L, 2L, and 2. Interestingly, with the chosen parameters, the transition between the stages 2L and 2 disappears below 280 K, as reported in the literature.

Introducing the developed free energy model in Cahn-Hilliard's and Allen-Cahn's equations, we can also simulate the evolution of lithium concentration, as well as graphite stacking during spinodal decompositions and follow the emergence and evolution of these stages in a graphite particle. Staggered domains of lithium surrounded by different graphene stacking arise naturally with characteristics typical of stages 1', 3L, 2L, 2 and 1.