

Defect Formation and Many-Particle Dynamics in Li/Na Battery Materials: A Molecular Dynamics Investigation

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The investigation of ion translocation in battery materials moves from a precise account of defect formation and their energetic ranking to the investigation of the importance and defect formation sequences under the effect of temperature. To overcome any sampling shortcomings due to sizable activation energies, several ad hoc techniques were developed, in order to focus on many-particle effects, beyond single defect formation. The investigation was focused on an important class of materials [1-2], LiMPO₄ (M = Mn, Fe) olivine phosphates are materials for battery applications due to their stability, safety, and reliable recharge cycle. Despite continuous experimental and computational investigations, several aspects of these materials remain challenging, including conductivity dimensionality and how it maps onto Li pathways. Based on our finite temperature molecular dynamics “shooting” approach, originally designed to enhance Li hopping probability, we perform a comparative analysis of ion mobility focused on many-particle effects. Therein, we identify main diffusion channels, as well as means of inter-channel couplings, in the form of Li lateral hopping, which markedly impact the overall mobility efficiency as measured by self-diffusion coefficients. This clearly supports the need of many-particle approaches for reliable mechanistic investigations and for battery materials benchmarking due to the complex nature of the diffusion process.

In a further move [3], we are looking at global free energy maps, within which defect formations are investigated as elementary steps of a phase transition that leads to Li sublattice melting as an effect of temperature. Therein, the free energy is explored along its enthalpic and entropic components, to precisely monitor the impact of changed bonding situations due to defects, and how quasi-collective dynamics leads to entropy increase, biasing defect recombination and carrying the system into steady particle translocation dynamics.

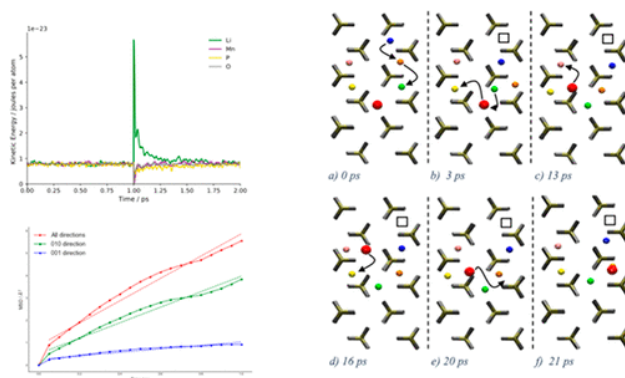


Figure 1: Defect formation along Li diffusion trajectories, resulting in steady diffusion behavior steered accelerated simulations techniques.

[1] S. E. Boulfelfel *et al.*, *Journal Of Materials Chemistry*, 21, 16365 (2011).

[2] T. Flack *et al.*, *J. Phys. Chem. C*, 126, 30, 12339 (2022).

[3] T. Flack, S. A. Jobbins, S. Leoni, *in preparation*.