Hessisches Kompetenzzentrum
für Hochleistungsrechnen

Diffusion in Layered Transition Metal Oxides



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Clusters
Lichtenberg II Cluster Darmstadt

Software
LAMMPS, VASP

Additional Software
Pacemaker

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Introduction

Layered transition-metal oxides of the $LiMO_2$ family (with M typically Co, Ni, or Mn) are widely used as cathodes in high-voltage, rechargeable lithium-ion batteries. During charge, lithium leaves the cathode and is stored at the anode; discharge reverses this process. Fast charging and high power density depend on how quickly lithium can move inside the cathode, which is governed by lithium diffusivity and ionic conductivity. Even for $LiNiO_2$, extracting reliable diffusion coefficients across different states of charge is difficult because ordering tendencies, local migration barriers, and method-related limitations are tightly entangled. Real materials also contain defects, especially Ni-on-Li antisites, which can reshape diffusion pathways and change the effective mobility. This work therefore targets an atomistic assessment of lithium diffusion in LiNiO across lithium content, with attention to how typical defects influence transport.

Methods

We aimed to compute lithium diffusion coefficients for pristine LixNiO2 over a wide lithium-content range and to quantify how Ni-on-Li antisites modify diffusion. Direct molecular dynamics at room temperature is inefficient because lithium hops have high barriers, so simulations would need to be extremely long or artificially accelerated and extrapolated, both with large uncertainties. Instead, we combined first-principles energetics with an efficient long-time kinetic model. Density functional theory was used to characterize lithium hop energetics via nudged elastic band calculations, providing energies for local

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minima and transition configurations. These data were used to fit a cluster expansion using the icet toolkit. Only lithium and vacancies were treated as configurationally active, while the Ni–O framework defined a fixed lattice. The trained model then supplied configuration-dependent energies and barriers for kinetic Monte Carlo simulations that sample lithium hopping over long times. Lithium motion was tracked via mean-squared displacement from ensembles of independent runs, enabling comparison of diffusion trends as a function of lithium content and ordering.

Results

A key requirement was a transition-state representation that remains compatible with a lattice-based description while still capturing how local lithium and vacancy arrangements modify migration barriers. This ruled out approaches that require explicit, independent transition-state sites, which dramatically increase model complexity and proved unstable in practice. The successful solution was an anchored transition-state representation, in which the two lattice sites involved in a hop are temporarily marked so that the cluster expansion can distinguish transition configurations from stable ones. This approach preserves detailed balance by construction, avoids enlarging the configurational space, and still allows local environments to influence barrier heights in a physically meaningful way. Interaction ranges for the cluster expansion were determined by systematic cross-validation to balance accuracy and model complexity. Once the cutoffs were fixed, the resulting parameter set was used to compute configuration-dependent event energetics for kinetic Monte Carlo simulations. Proof-of-concept kMC runs were carried out for selected lithium contents using a monolayer model. While this geometry is not physically ideal given the interaction range of the cluster expansion, it is sufficient to validate the workflow and probe qualitative diffusion trends.

Discussion

Across compositions, a clear pattern emerged. Lithium mobility is high in vacancy-rich, disordered configurations where many uncorrelated hops are available. As lithium content increases and Li–vacancy ordering becomes thermodynamically favorable, diffusion slows markedly because accessible pathways are reduced and motion becomes increasingly correlated. In such cases, mean-squared displacement curves often show an initial increase followed by a plateau as ordering develops, making it difficult to extract a single, well-defined diffusion coefficient within limited simulation times. Despite this limitation, the simulations robustly distinguish “fast, vacancy-rich” regimes from “ordering-limited” regimes and demonstrate that the methodology captures the essential coupling between diffusion and ordering. This establishes a solid foundation for quantitative diffusivity calculations once larger, more representative models are employed. The main runtime bottleneck is event handling: after each hop, the code rebuilds the full event list, including events far from the executed jump. This is unnecessary because

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only the local environment around the origin and destination changes. The next step is a local-update kinetic Monte Carlo scheme using a precomputed neighbor list for all lattice sites. Events will be stored per site and updated only for the affected sites within the interaction cutoff, reducing per-step overhead from scaling with system size to roughly constant cost per hop. We will also improve structure initialization: starting from random configurations wastes time before reaching representative states, so we will initialize from equilibrated Metropolis Monte Carlo samples. With these changes, multilayer models can be reintroduced so that the simulation thickness comfortably exceeds the interaction range, reducing finite-size artifacts. Finally, the cluster expansion will be extended to explicitly include off-stoichiometry and Ni-on-Li antisites in the lithium layer, enabling diffusion predictions closer to experimental conditions and a quantitative assessment of how these defects block, reroute, or facilitate transport.

Publications

Reference

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