Machine learning resolves the mechanism of charge transport and the phase transition in $LiMn_2O_4$

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The transition toward sustainable energy storage demands battery technologies built from sustainable materials. Manganese and iron-based cathodes offer promising alternatives yet contain Jahn-Teller active centers that fundamentally influence charge transfer kinetics. Despite their technological importance, the coupling between Jahn-Teller dynamics and electronic transport in these systems has not been systematically characterized. $LiMn_2O_4$ (LMO) serves as an ideal model system to investigate this interplay. At elevated temperatures, LMO adopts a cubic spinel structure where Mn^{3+} ions exhibit dynamic Jahn-Teller distortions with continuously reorienting distortion axes. Upon cooling, cooperative ordering of these distortions drives a phase transition to an orthorhombic structure.

We combine machine-learned interatomic potentials (MACE) with density functional theory, nudged elastic band (NEB) calculations and ab initio molecular dynamics (AIMD) to systematically investigate the relationship between Jahn-Teller dynamics and polaron transport. PerQueue, a modular workflow manager, enables the systematic orchestration of these calculations across diverse Jahn-Teller configurations. Our NEB calculations reveal that polaron migration barriers depend sensitively on the Jahn-Teller state, while MACE-driven molecular dynamics simulations access the extended timescales required to establish a direct mechanistic link between Jahn-Teller dynamics and polaronic transport. Since the MACE potential is trained on energies and forces alone, the electronic state is not directly available in the MACE trajectories and is instead tracked through the local octahedral distortion with a Gaussian and a von Mises mixture model. Both are fitted on AIMD frames, where the site magnetic moment provides an unambiguous label, and assign the oxidation state and the Jahn-Teller orientation of every site at every time step.

Our results demonstrate that Jahn-Teller dynamics governs both polaron transport kinetics and the macroscopic phase transition in LMO, with implications for other battery materials containing Jahn-Teller active centers.

References

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