



FIM-S3 SEMINAR

From Model to Marvel: The Unexpected Complexity of LiNiO_2 in Battery Technology

Wednesday September 11th, 2024 – 11.00 (sharp)

S3 Seminar Room, 3rd Floor, Physics building

Remote link: [Teams](#)

Speaker

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Abstract

After being abandoned due to mechanical and thermodynamic instabilities, layered transition metal oxides with ultra-high Ni content are now experiencing a revival as promising cathode materials for enhancing the energy density of lithium-ion batteries. These materials share many characteristics with pure LiNiO_2 , making it crucial to understand the properties and mechanisms of this model system at an atomic level for developing more complex materials. Our analysis using atomistic simulations delves into LiNiO_2 and its delithiated states, encompassing native defects, structure, thermodynamics, chemomechanics, and kinetics.

The structure and related properties of LiNiO_2 are particularly interesting and challenging due to the presence of dynamic Jahn-Teller distortions in the NiO_6 octahedra. These distortions cause local monoclinic changes, yet our simulations reveal why the material maintains a rhombohedral symmetry on a global scale.[1]

Upon charging, several particularly stable Li orderings ensue.

Employing a cluster expansion approach, we reproduce the experimental phase diagram, accounting for NiLi defects arising from non-stoichiometric synthesis. Their inclusion favors solid-solution behavior, which smooths the voltage curve and aligns well with experimental data.[2]

Exploration of extended defects—stacking faults and dislocations—uncovers comparable energetics and gliding barriers to LiCoO_2 , with NiLi impeding layer gliding notably in fully delithiated states. Dislocations in LiNiO_2 exhibit lower excess energies than in LiCoO_2 , largely due to the compliant alignment of Jahn-Teller distortions, which effectively reduces strain. Dislocations can also attract both Li and O vacancies, potentially affecting material kinetics and acting as precursors for further degradation mechanisms.[3]

Finally, our recent analysis focused on NiLi defects. Our simulations contradict the common belief that NiLi defects are oxidized at low Li content, which is thought to cause local layer constriction and hinder relithiation. We demonstrate instead that NiLi attracts Li vacancies within two lattice sites and can split fast divacancies into slower single vacancies due to a superposition of electrostatic and strain effects. These insights, along with the fact that any NiLi defect obstructs the diffusion of Li ions or Li vacancies, highlight the kinetics of non-stoichiometric LiNiO_2 and support further optimization.[4]

[1] Chem. Mater. 2020, 32, 23, 10096–10103

[2] J. Mater. Chem. A, 2021, 9, 14928–14940

[3] Chem. Mater. 2023, 35, 2, 584–594

[4] Chem. Mater. 2024, 36, 1, 492–500

Host: Deborah Prezzi