# Modeling phase transformations in Mn-rich cathodes with charge-informed machine-learning interatomic potentials

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## Background

- Mn-rich disordered rocksalt cathodes **(DRX)** materials are promising **earth-abundant** materials for Li-ion batteries, with the potential to scale sustainable energy storage solutions to TWh/year.
- The degree of **cation orderings** can change upon battery cycling, which affects the electrochemistry (e.g., voltage profile) [1].
- There are significant challenges in modeling the structure vs. electrochemistry from *ab-initio* considering their **compositional complexity**, substantial **site disorder** and the state with **partial disorder** with quantum accuracy.

## Methodology

- **Cluster expansion** as a lattice model to capture the cation-disordered states. The CE casts the energy from *ab-initio* calculation as a function of the occupancy of atoms on a set of predefined sites [2, 3]:

$$E(\boldsymbol{\sigma}) = \sum_{\beta} m_\beta J_\beta \left\langle \Phi_{\boldsymbol{\alpha}\in\beta} \right\rangle_\beta + \frac{E_0}{\varepsilon_r}, \quad \Phi_{\boldsymbol{\alpha}} = \prod_{i=1}^{N} \phi_{\alpha_i}(\sigma_i). \tag{1}$$

- **CHGNet** is a graph neural network (GNN) based machine-learning interatomic potential (MLIP) [4]:

$$E_{\text{tot}} = \sum_i \phi_E(v_i^n), \quad \boldsymbol{f}_i = -\frac{\partial E_{\text{tot}}}{\partial \boldsymbol{x}_i}, \quad m_i = \phi_m(v_i^{n-1}) \tag{2}$$

- **Potential energy surface samplings** with r$^2$SCAN-DFT:

**Relaxation from existing datasets (e.g. MP)**

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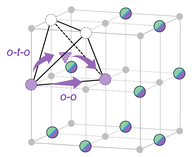
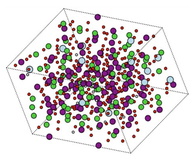
ENCUT = 680 eV
EDIFF = 1e-6

**Transition states sampling**




**MLIP-MD Trajectories**



- **Monte Carlo Simulations** were implemented at $T = 1273$ K to simulate the cation-disordered structure (including short-range order effect [5])
- **Molecular Dynamics** were implemented at $T = 1273$ K for 2 ns to simulate the phase transformation from the DRX to $\delta$-phase (partially disordered + spinel-like ordering)
- **Equilibrium voltage profiles** from thermodynamics were evaluated using

$$\bar{V}(x_1, x_2) \approx -\frac{E_{\text{Li}_{x_1}\text{TMO}_2} - E_{\text{Li}_{x_2}\text{TMO}_2} - (x_1 - x_2)E_{\text{Li}}}{F(x_1 - x_2)}. \tag{3}$$

where $E_{\text{Li}}$ is the internal energy of the bcc Li metal, $E_{\text{Li}_x\text{TMO}_2}$ represents the internal energy of the (de)lithiated structures.

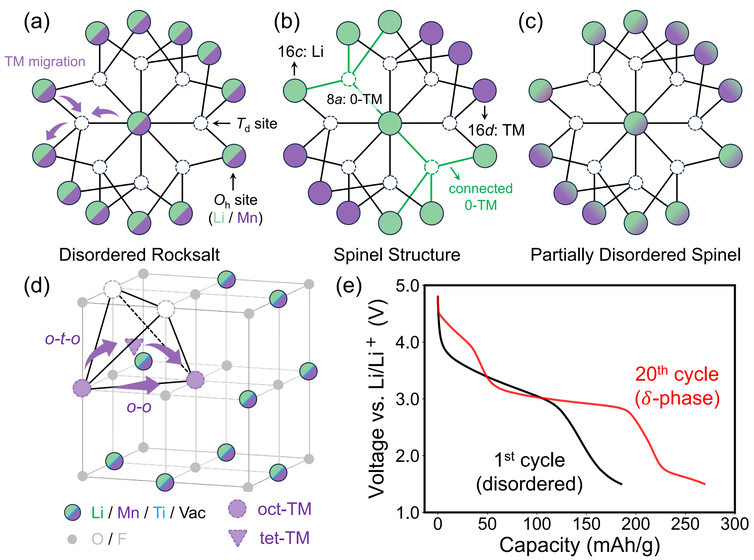
## References

[1]Z. Cai et al., Nature Energy **9**, 27–36 (2023).
[2]P. Zhong et al., PRX Energy **2**, 043005 (2023).
[3]L. Barroso-Luque et al., Journal of Open Source Software **7**, 4504 (2022).
[4]B. Deng et al., Nature Machine Intelligence **5**, 1031–1041 (2023).
[5]P. Zhong et al., Chemistry of Materials **32**, 10728–10736 (2020).
[6]J. Reed et al., Electrochemical and Solid-State Letters **4**, A78 (2001).

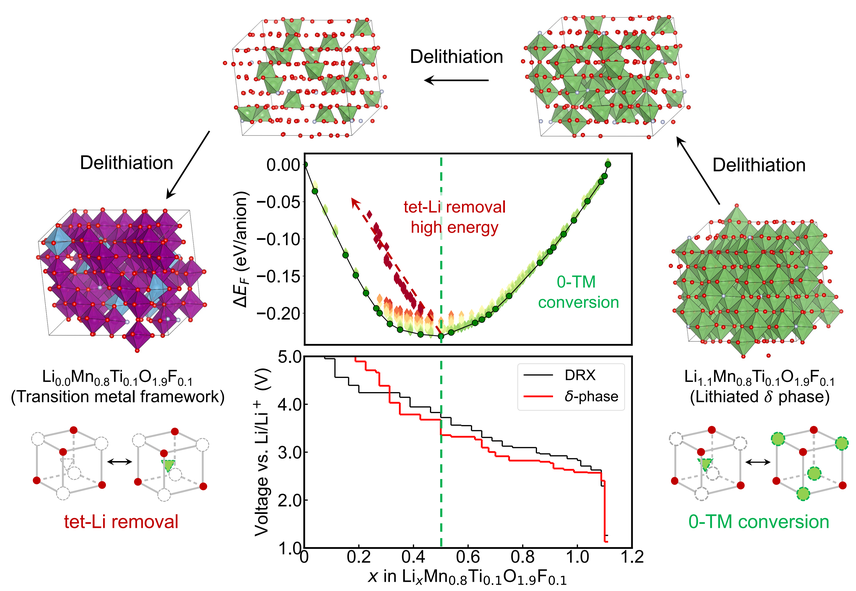
smol
Statistical Mechanics on Lattices

CHGNet

## Cation orderings vs. electrochemistry

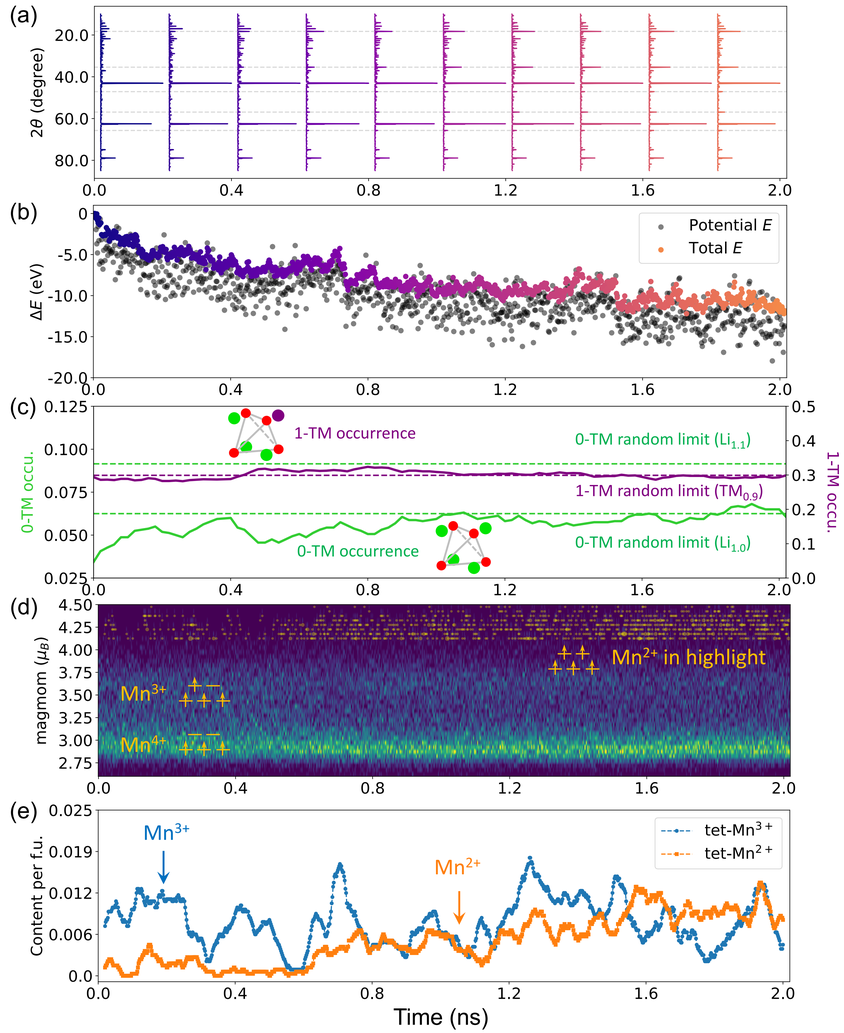



## Equilibrium Intercalation Voltage Profiles




- The transition metal (TM) sites in the MD structure after 2 ns of MD simulation were coarse-grained into their nearest octahedral site to form **the TM framework**.
- **0-TM conversion** for Li removal in low-V region $4\text{Li}_{\text{oct}}$ (0-TM) $\rightarrow 3\square_{\text{oct}} + 1\text{Li}_{\text{tet}}$ (delithiation in spinel)
- Both lithiation/delithiation pathways were considered by searching the low-E sites for Li intercalation.

## Structure and charge evolution from charge-informed MD simulations




## Conclusion

- We successfully modeled the **phase transformation in complex oxides** using **charge-informed MLIP-MD** and rationalized the relation between structure change and electrochemistry.
- **No two-phase reaction has been observed for the $\delta$-phase**, which exhibits (1) systematically lower average voltage around 3 V and (2) high voltage features around 4 V in the charged states compared to that of the DRX phase.
- We discovered that contrary to the previous belief attributing $Mn^{2+}$ ions to phase transformation due to their low migration barriers [6], **the emergence of $Mn^{2+}$ is correlated to the formation of spinel-like ordering** (ns-scale phenomenon) rather than a local hopping (ps-scale). Instead, $Mn^{3+}$ is the initial majority of migrating ions that drive the transformation.