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Phase segregation and nanoconfined fluid O₂ in a lithium-rich oxide cathode

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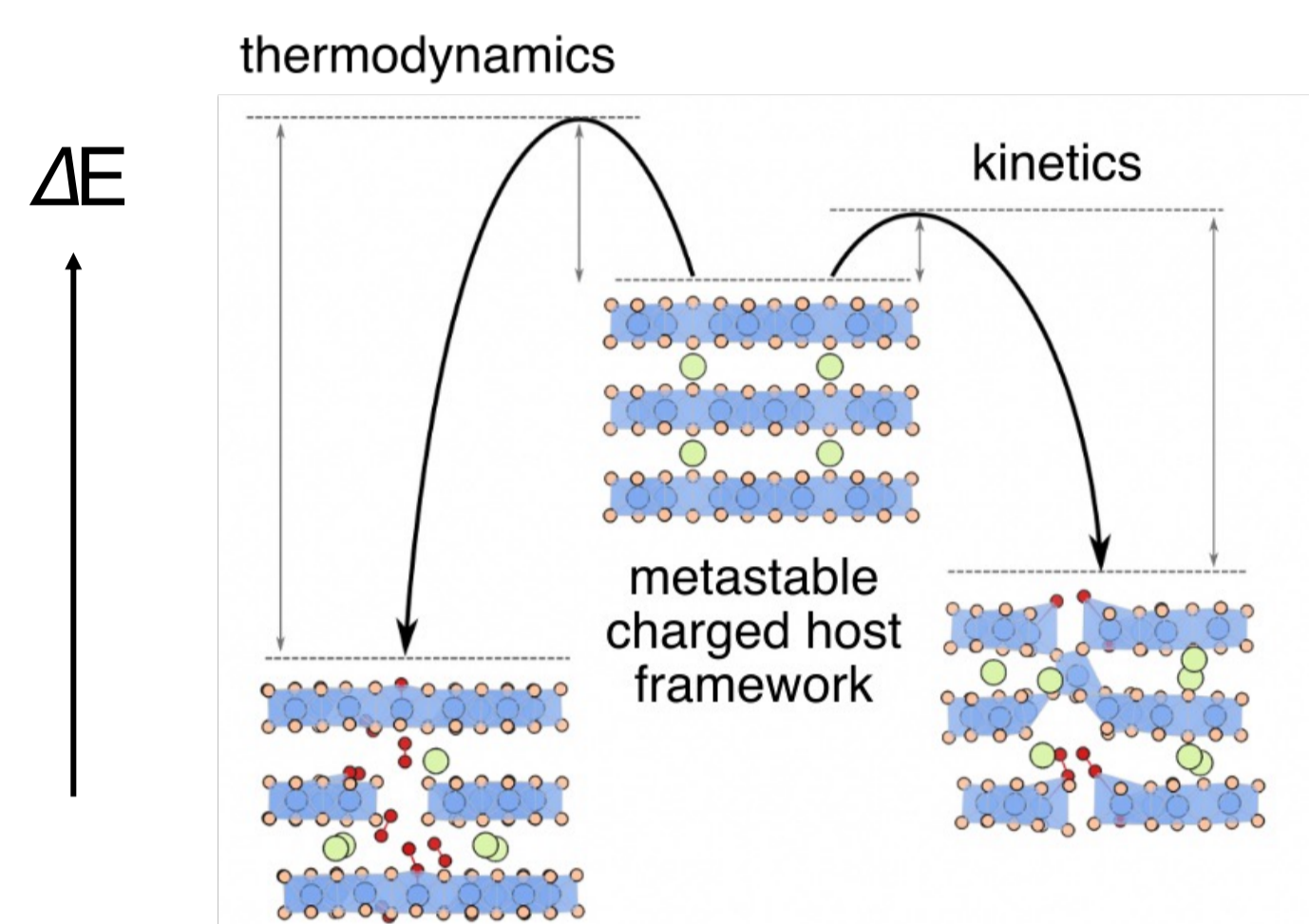
Kit McColl^{a,c}, Samuel W. Coles^{a,c}, Pezhman Zarabadi-Poor^{b,c}, Benjamin J. Morgan^{a,c} and M. Saiful Islam^{a,b,c}

Oxygen-redox cathodes

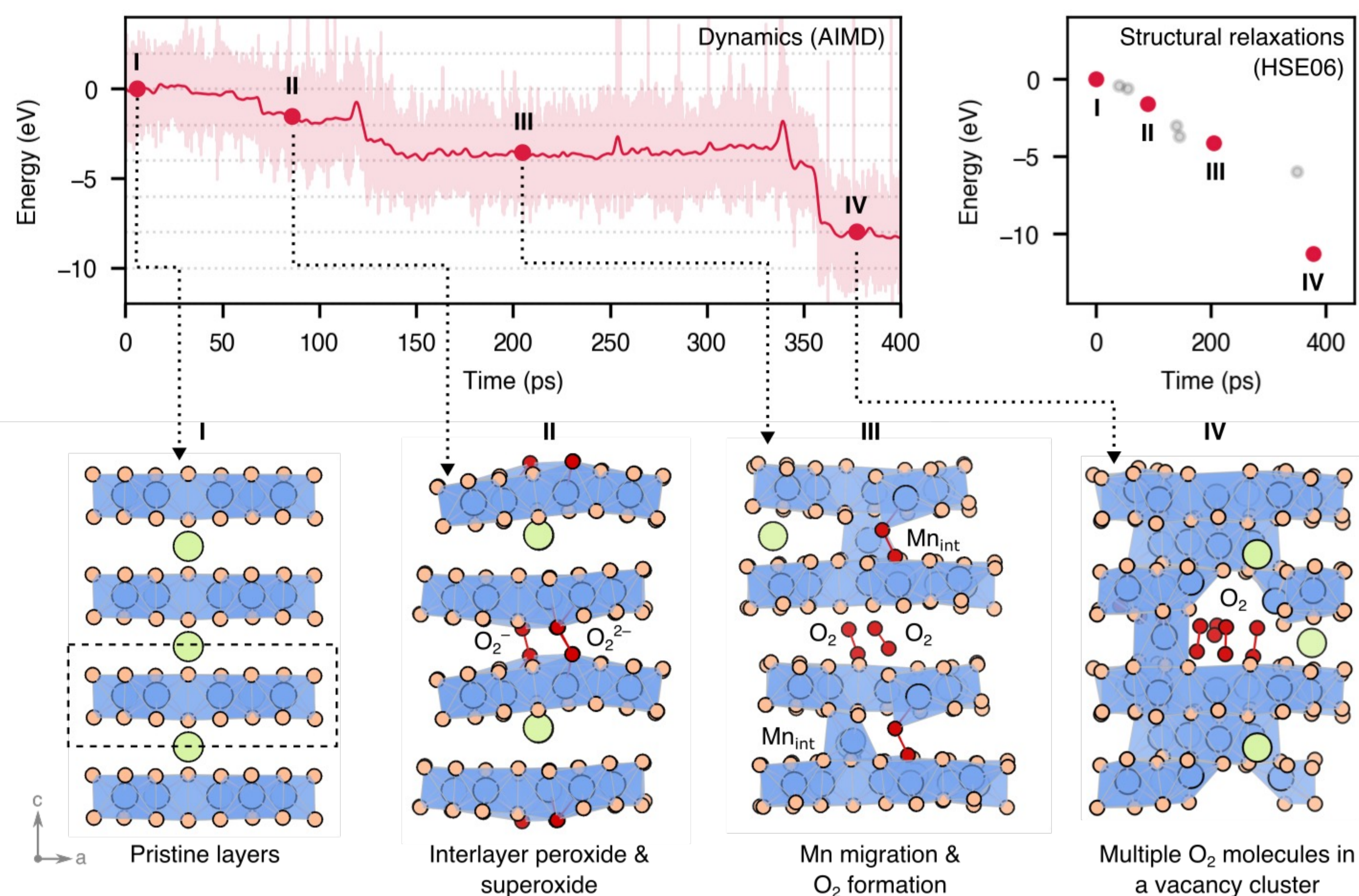
- Lithium-rich: Li_{1+x}M_{1-x}O₂ compositions
- Capacity from cationic and anionic redox
- Voltage hysteresis and voltage fade
- Structural changes during cycling

Modelling O-redox

- How can we obtain realistic structures?
- Kinetically-viable structural rearrangements
- Thermodynamic ground-state structures
- Disorder & nanoscale structural changes

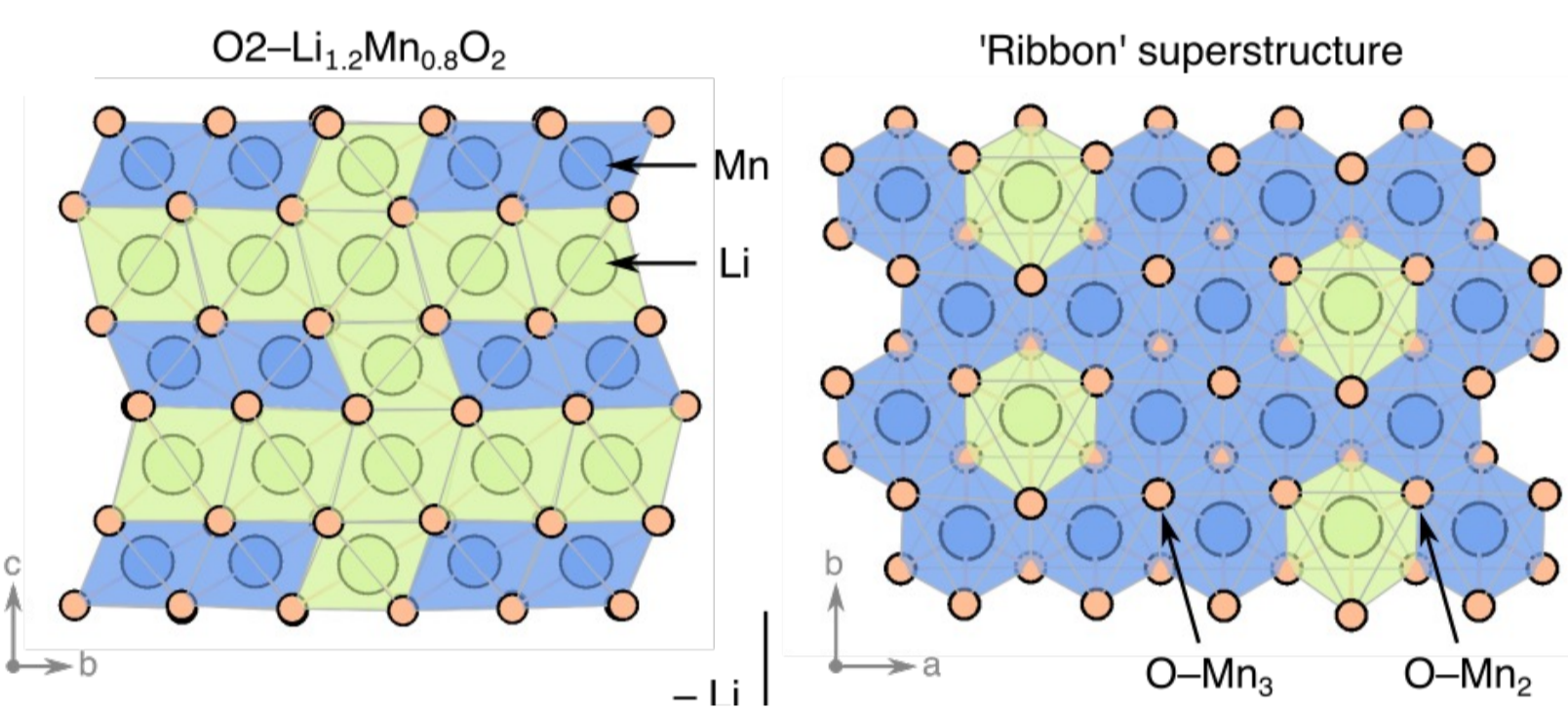


Kinetically viable structural changes: ab initio molecular dynamics



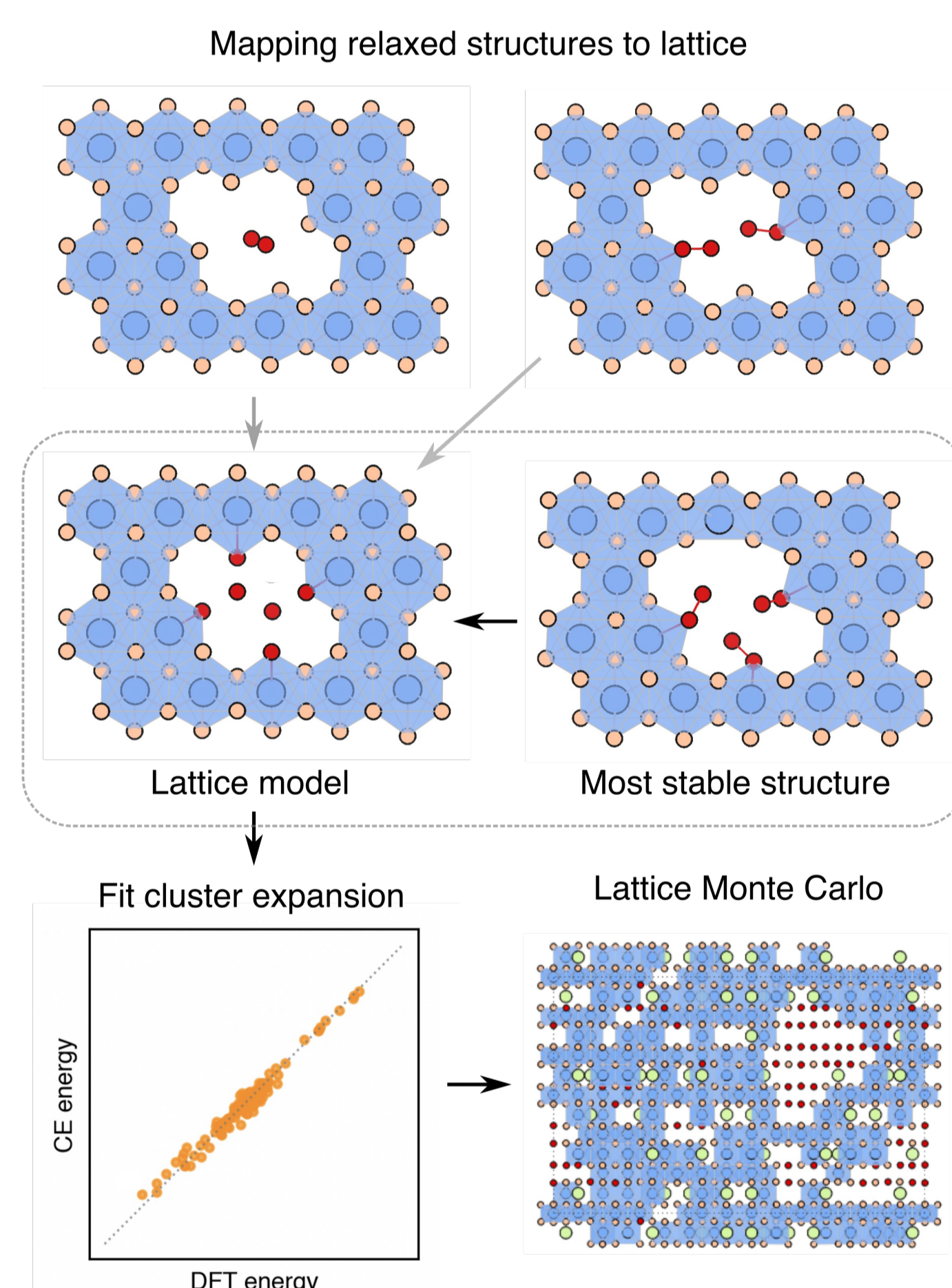
Li_{1.2}Mn_{0.8}O₂

- O₂ stacking, ribbon superstructure



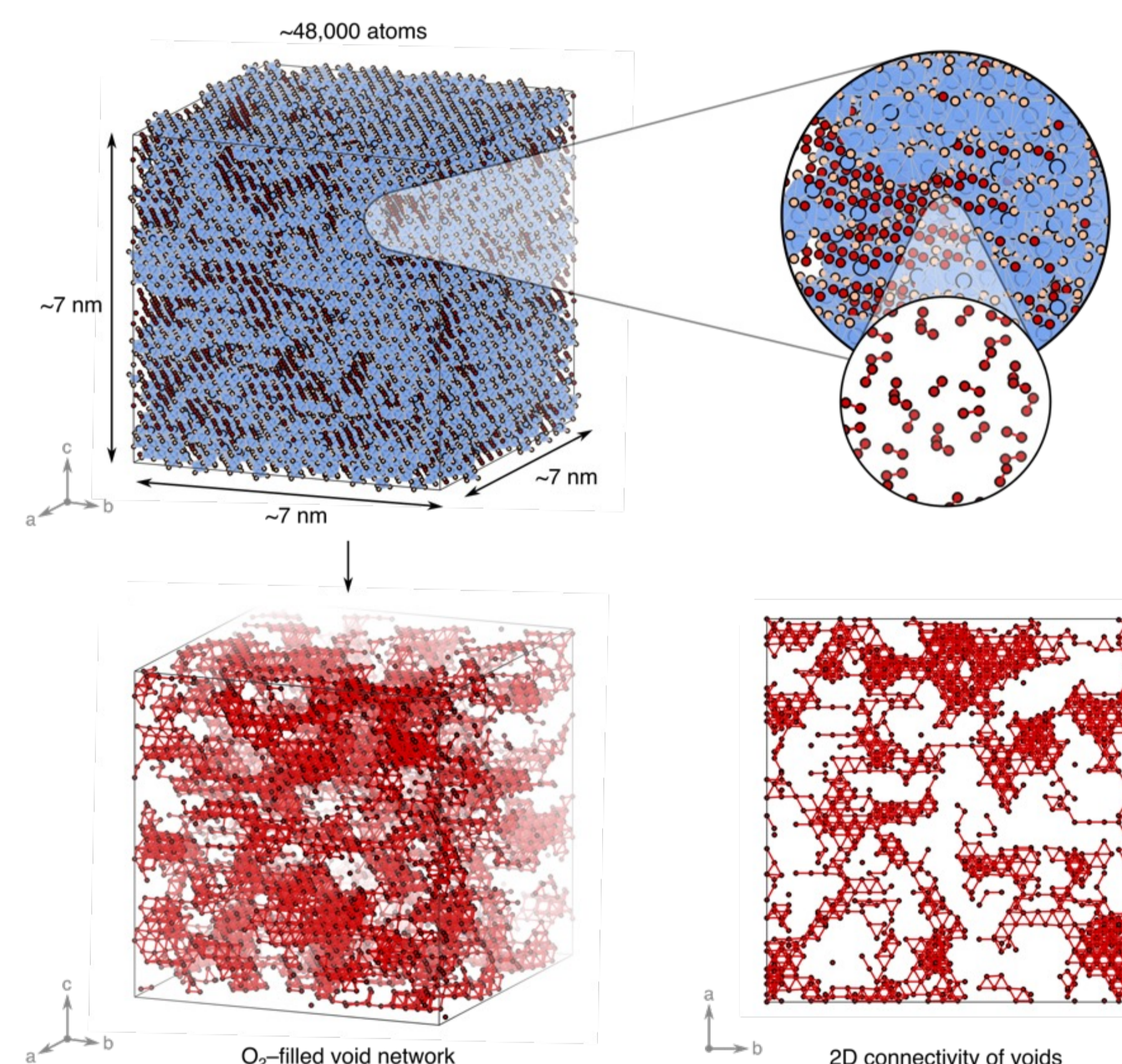
Cluster expansion

- Lattice representation of O₂ molecules
- Equivalent lattice configurations: sample for a ground-state structure



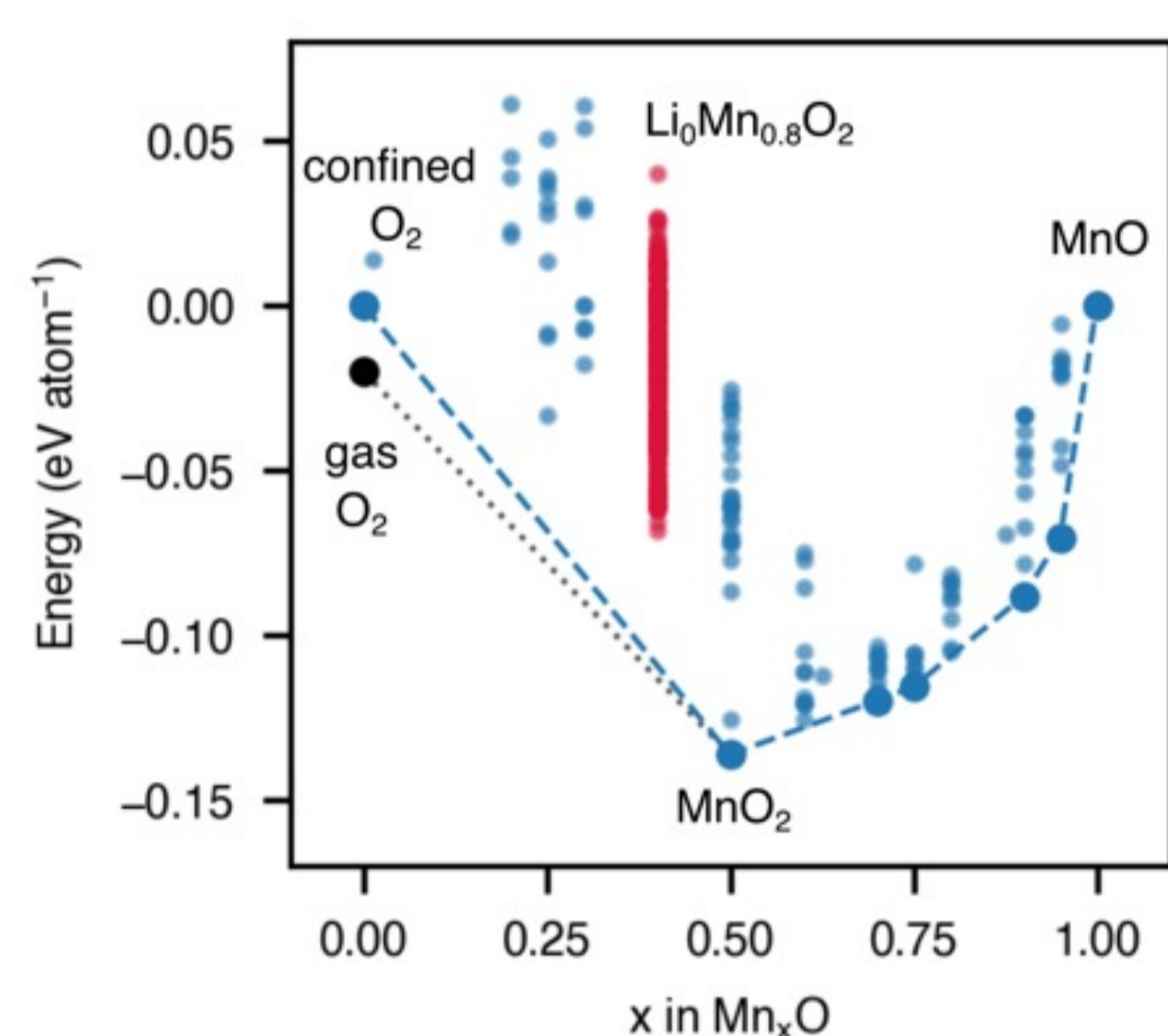
Thermodynamic ground state structure: lattice Monte Carlo

- Simulated annealing: obtain ground-state structures
- Nanovoids containing confined O₂ molecules



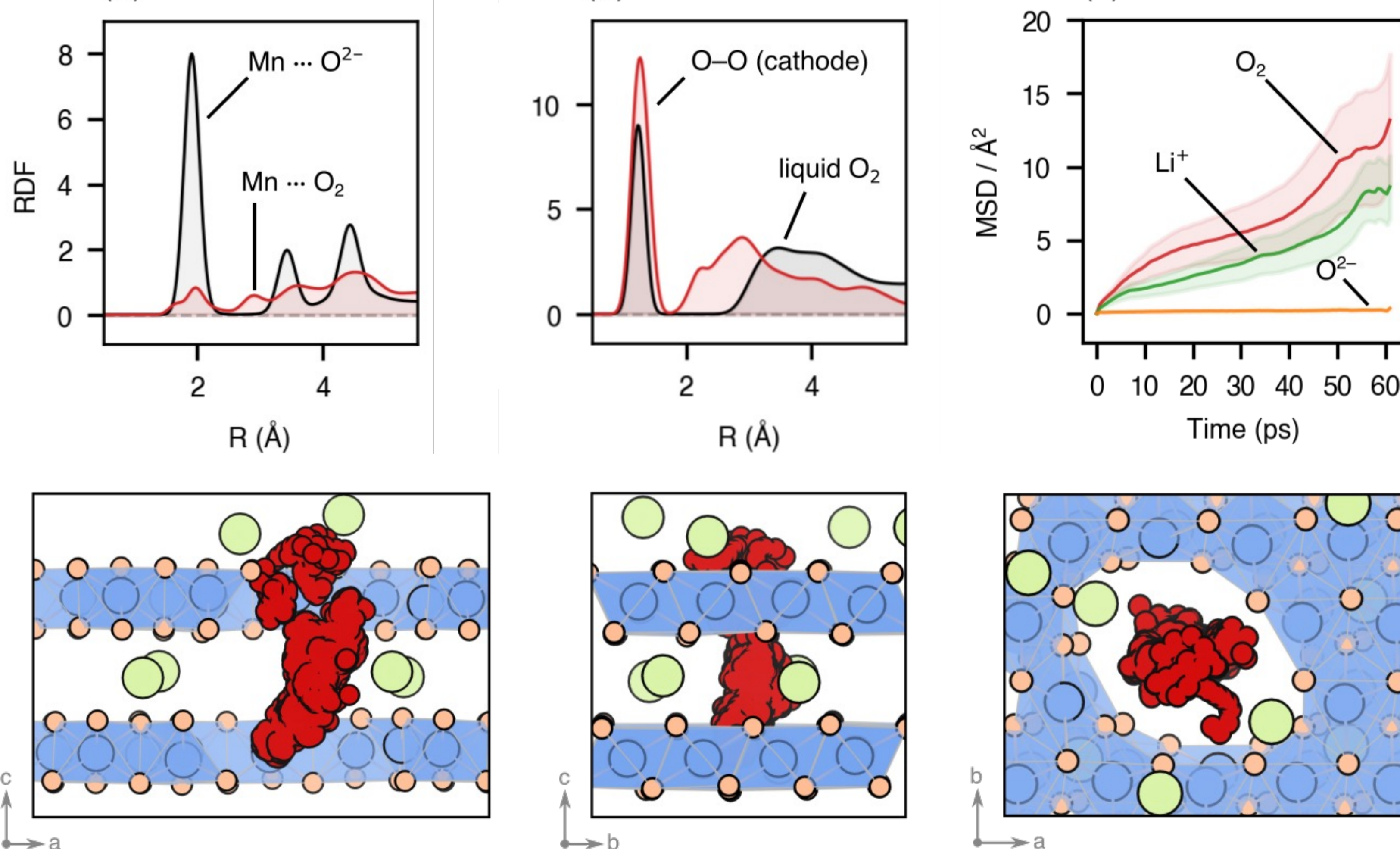
Phase segregation

- Mn_{0.8}O₂ → two-phase mixture of MnO₂ + O₂



Nanoconfined fluid O₂

- Confined O₂ in the voids is a supercritical fluid and can diffuse over long distances, through the bulk



Methods

- AIMD**
- AIMD with PBE+U (VASP) to sample structural changes
 - 300K, 600K, 900K simulations in 120 atom unit cell
 - HSE06 relaxations (CRYSTAL) along AIMD trajectory

- Cluster expansion**
- CE fit: ICET with ~400 HSE06-relaxed structures
 - AIMD step prevents ambiguous structure mapping
 - LASSO+RFE fit: CV RMSE of <22 meV atom⁻¹

Conclusions

- Combination of AIMD and cluster expansion obtain kinetically viable and thermodynamically stable O-redox structures
- Phase segregation forms nanovoids
- Fluid O₂ can diffuse through the structure, linking bulk O₂ formation and surface O₂ loss

Preprint

Phase segregation and nanoconfined fluid O₂ in a lithium-rich oxide cathode.
 K. McColl et al.,
 ChemRxiv.(2023)

