Phase segregation and nanoconfined fluid O_2 in a lithium-rich oxide cathode

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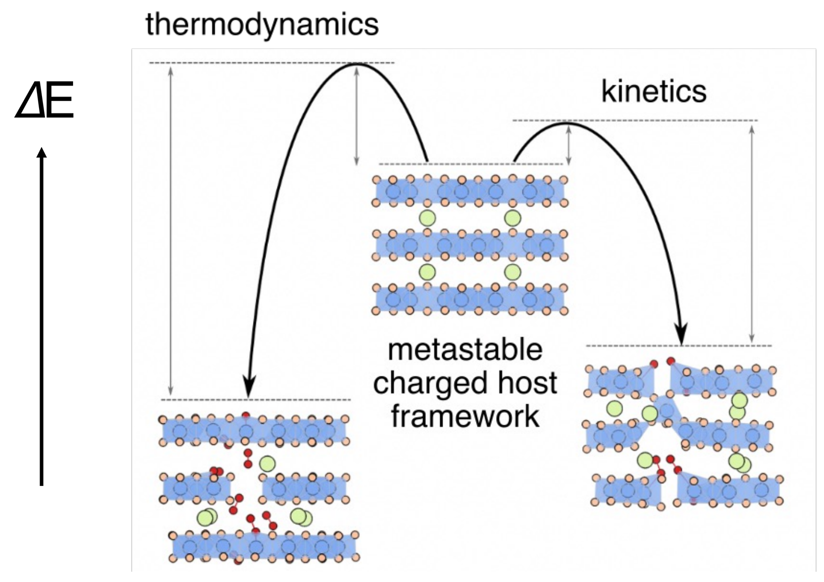
Oxygen-redox cathodes

- Lithium-rich: $Li_{1+x}M_{1-x}O_2$ compositions
- Capacity from cationic and anionic redox
- Voltage hysteresis and voltage fade
- Structural changes during cycling

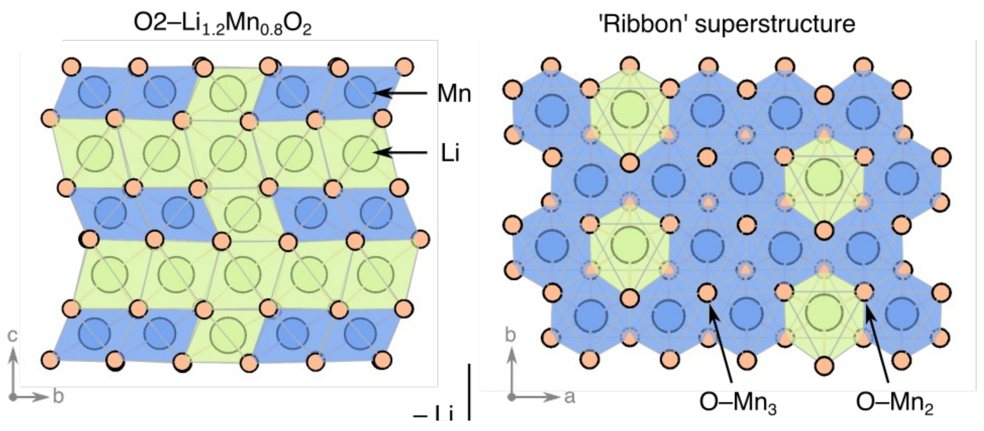
Modelling O-redox

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



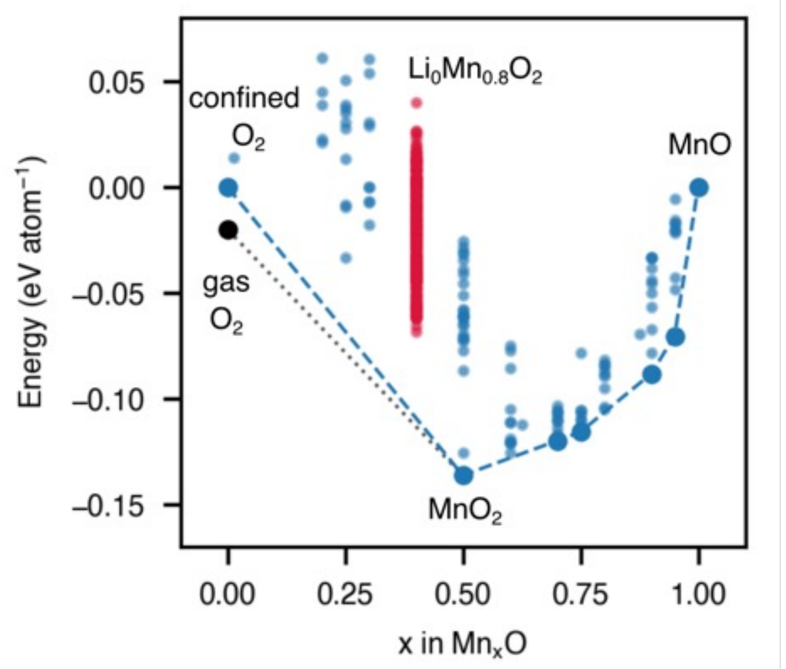
$Li_{1.2}Mn_{0.8}O_2$

- O2 stacking, ribbon superstructure

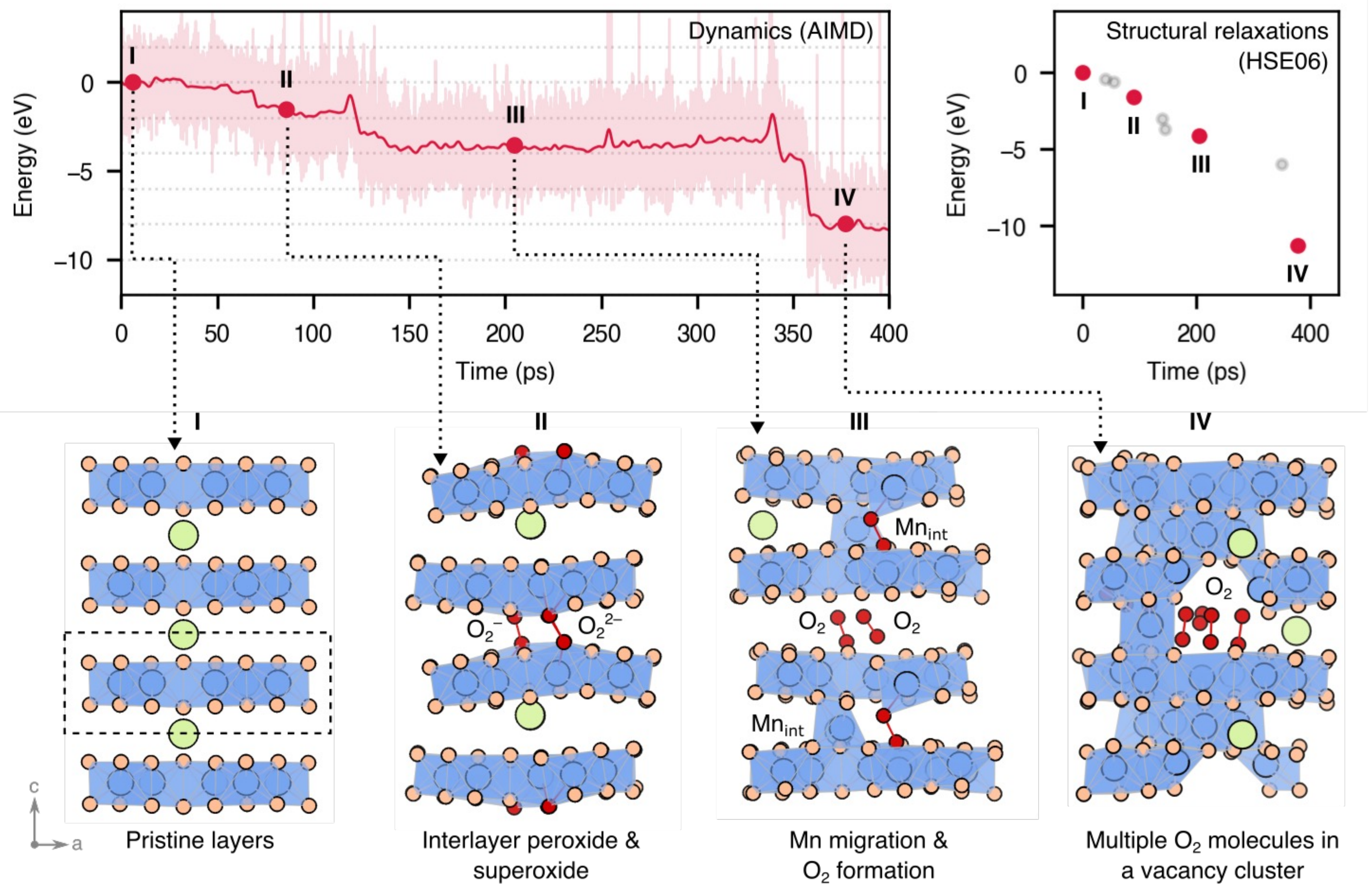


Phase segregation

- $Mn_{0.8}O_2 \rightarrow$ two-phase mixture of $MnO_2 + O_2$

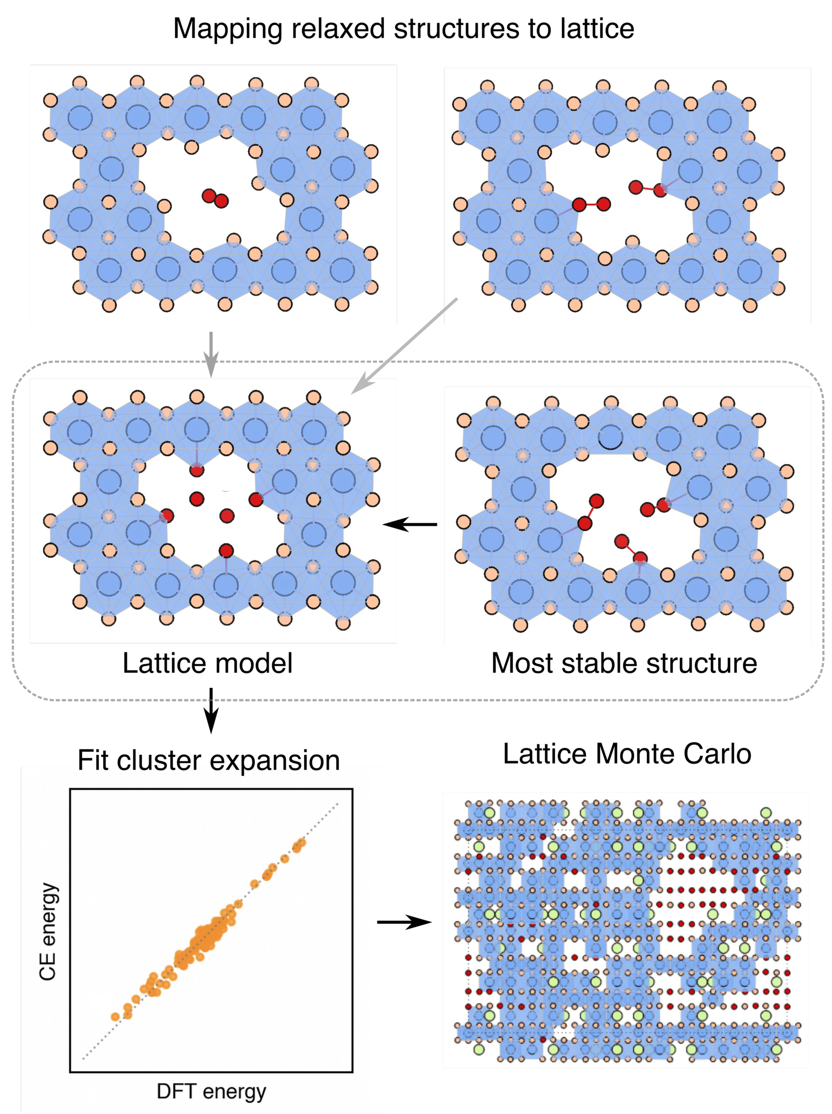


Kinetically viable structural changes: ab initio molecular dynamics



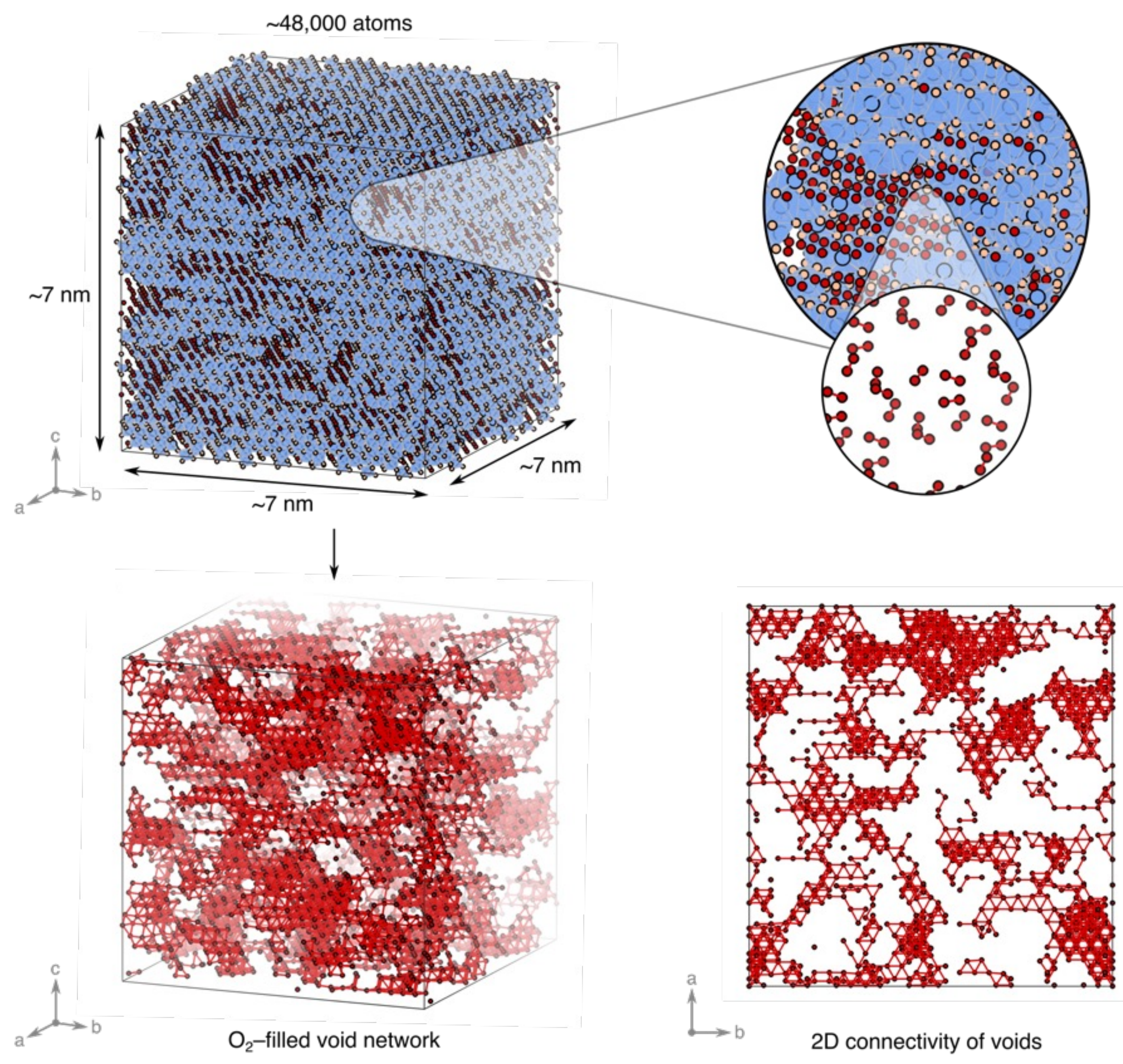
Cluster expansion

- Lattice representation of O_2 molecules
- Equivalent lattice configurations: sample for a ground-state structure



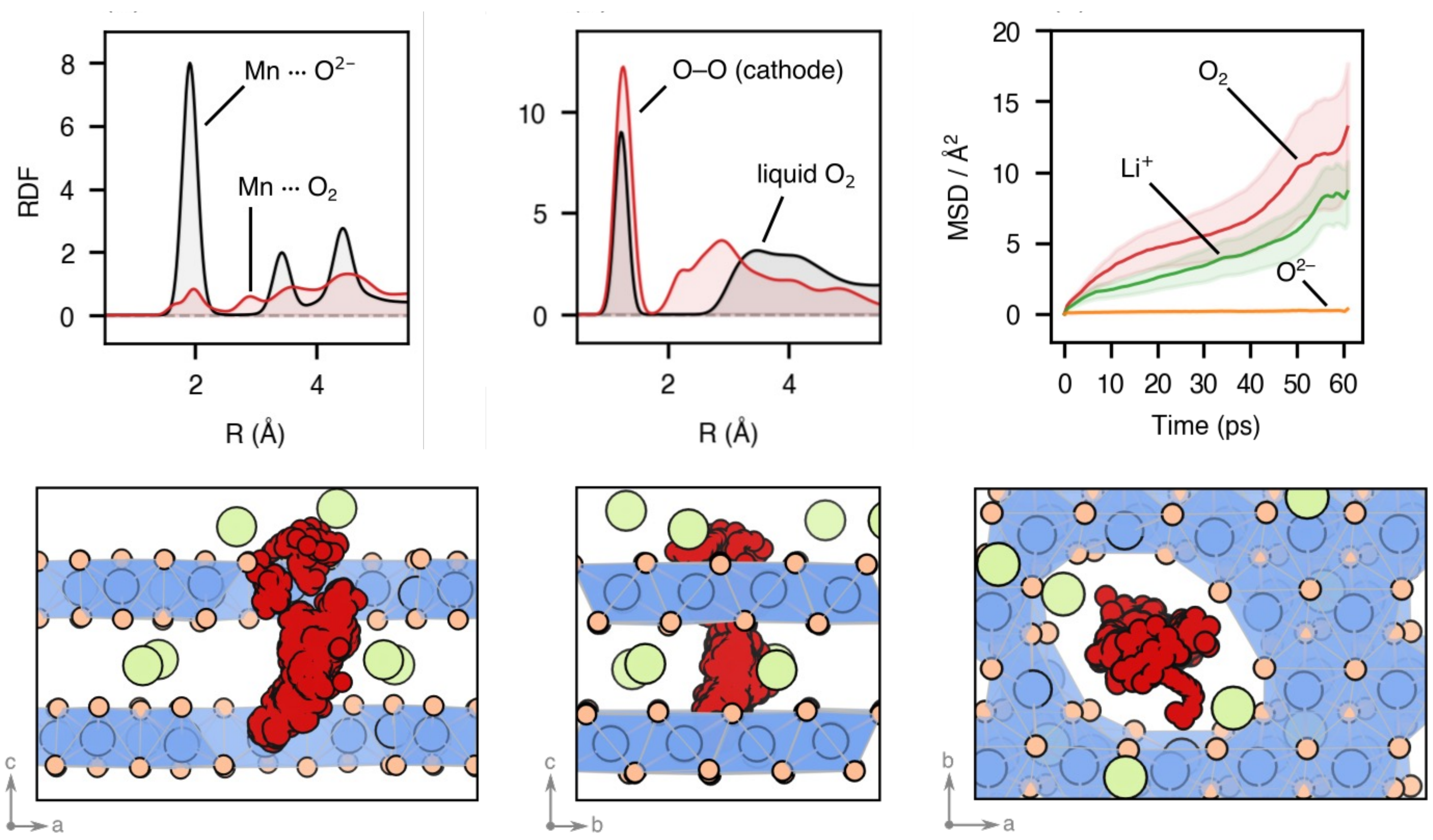
Thermodynamic ground state structure: lattice Monte Carlo

- Simulated annealing: obtain ground-state structures
- Nanovoids containing confined O_2 molecules



Nanoconfined fluid O_2

- Confined O_2 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 O_2 can diffuse through the structure, linking bulk O_2 formation and surface O_2 loss

Preprint

Phase segregation and nanoconfined fluid O_2 in a lithium-rich oxide cathode. K. McColl et al., ChemRxiv.(2023)

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