Citation for published version:
Taylor, P, McColl, K, Islam, MS & Morgan, B 2023, 'Oxygen Redox in Polyanion Cathode Materials', CATMAT Phase II kick-off meeting, Birmingham, UK United Kingdom, 16/11/23 - 16/11/23.

Publication date:
2023

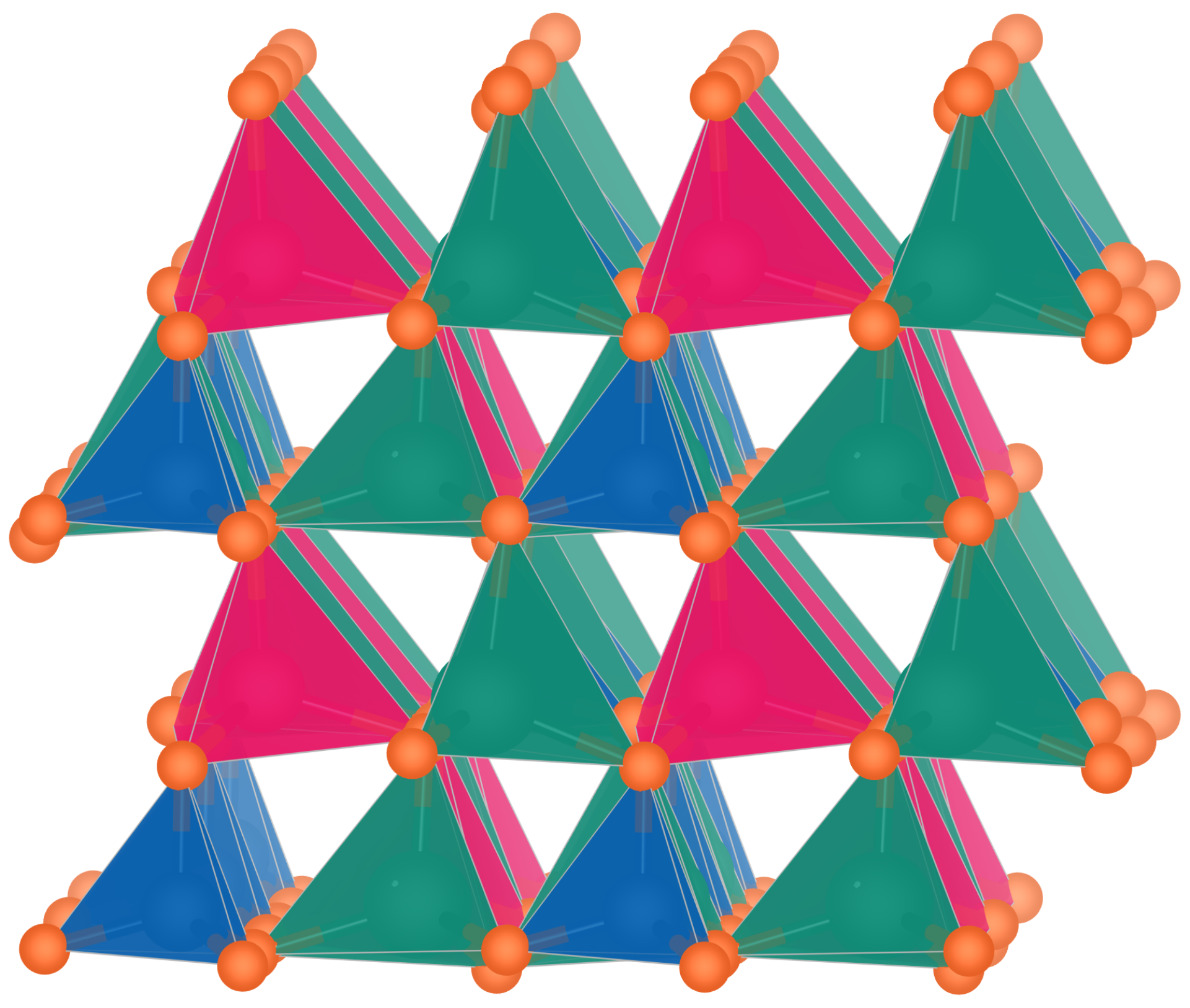
Document Version
Early version, also known as pre-print

Link to publication

Oxygen redox in polyanion cathode materials

Patrick J. Taylor[1,2], Kit McColl[1,2], Saiful Islam[2,3], Benjamin J. Morgan[1,2]

[1] The University of Bath, [2] The Faraday Institution, [3] The University of Oxford

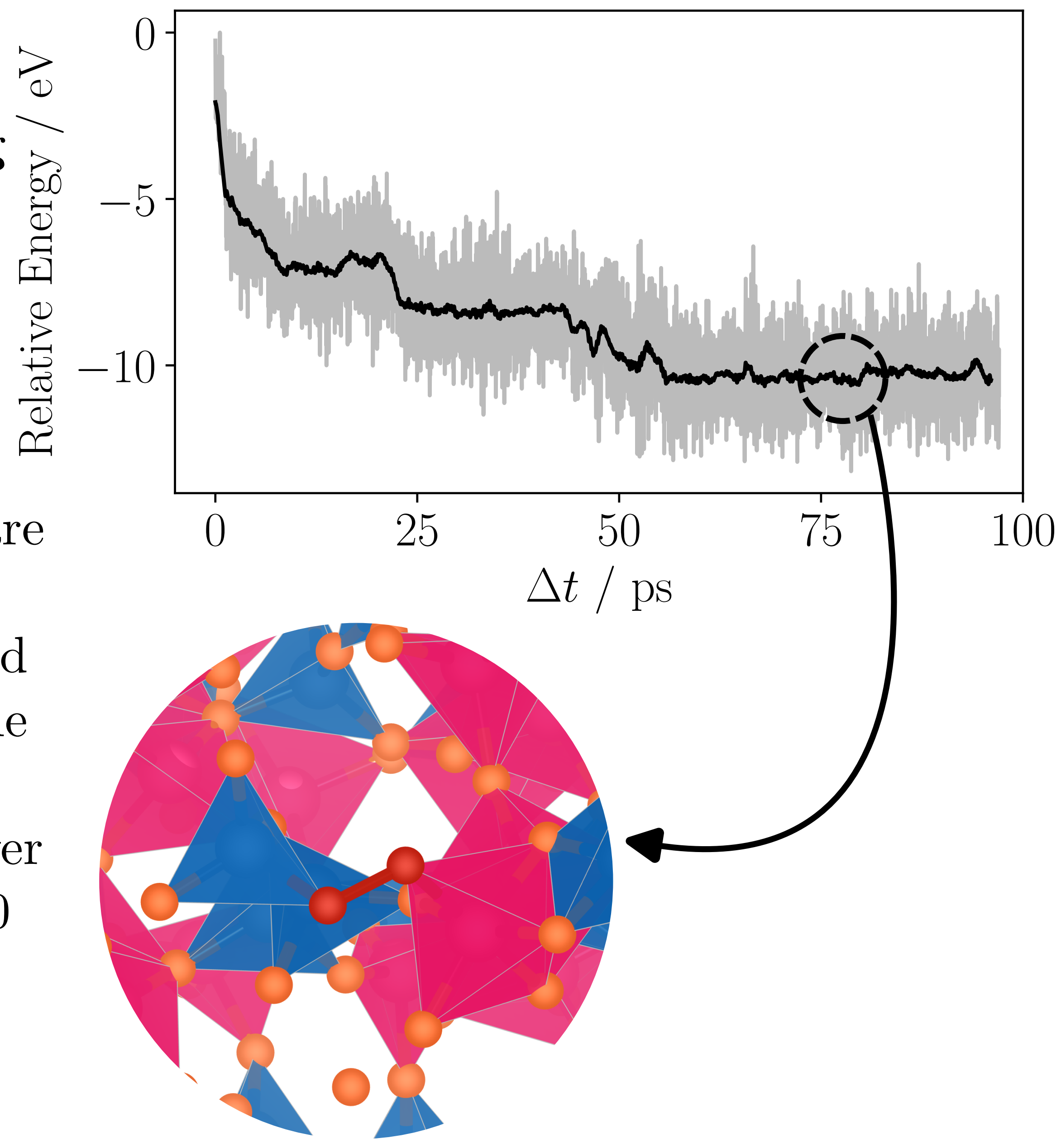


Aims

- Investigate oxygen redox processes in a model (Li-ion) polyanion cathode material (Li_2FeSiO_4) using **density functional theory** and *ab initio* **molecular dynamics**.
- Compare these processes to the lithium-rich layered systems and determine the extent to which the mechanism of oxygen redox is **transferable** between materials.

Thermodynamics and Kinetics

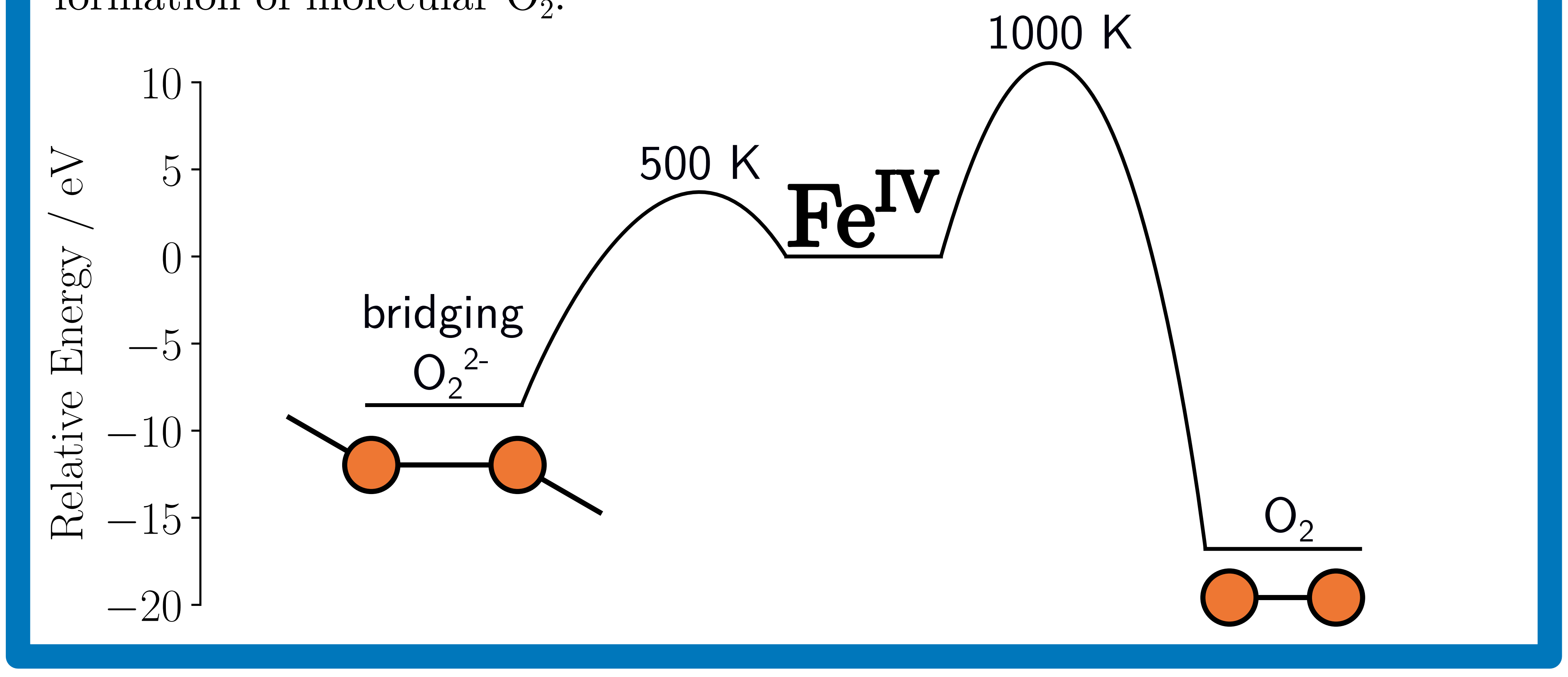
- We have calculated that $FeSiO_4$ is **thermodynamically unstable** (~ 0.2 eV/atom above the convex hull) with respect to decomposition into Fe_2O_3, SiO_2 and O_2 trapped in the bulk.
- As has been suggested in the lithium-rich layered systems, we thus expect the thermodynamic product of oxygen redox to be **bulk molecular O_2**.
- We have sampled the kinetically accessible states of $FeSiO_4$ with *ab initio* molecular dynamics simulations at 500 and 1000 K.



- We observe **low-energy configurations containing oxygen dimers**, in which some of the Fe^{IV} ions have been reduced to Fe^{III}.

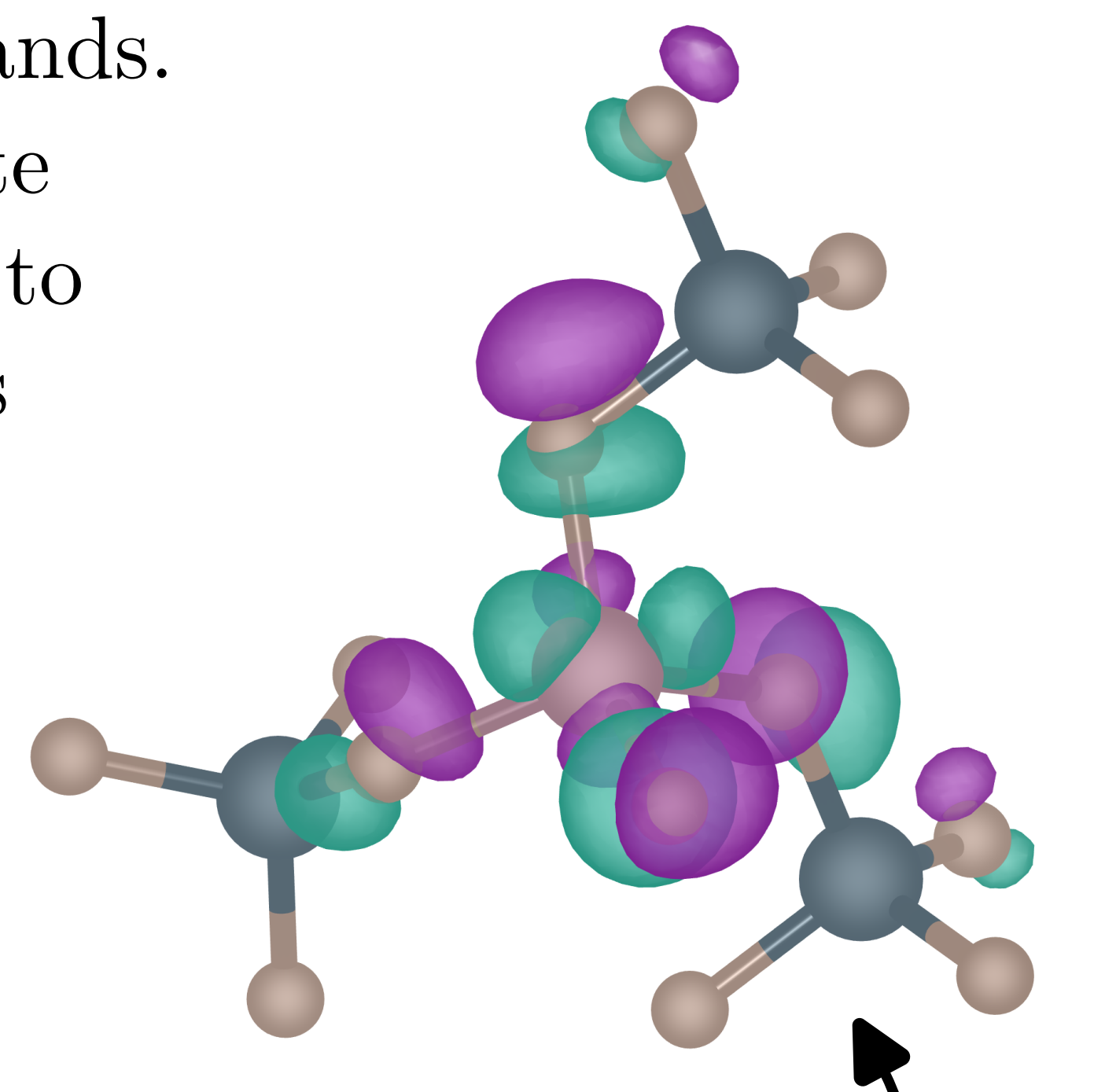
- The **lowest energy** configurations we collected are those containing **trapped molecular oxygen** (sampled at 1000 K), as opposed to the peroxides bridging between cation polyhedra seen at lower temperature (sampled at 500 K).

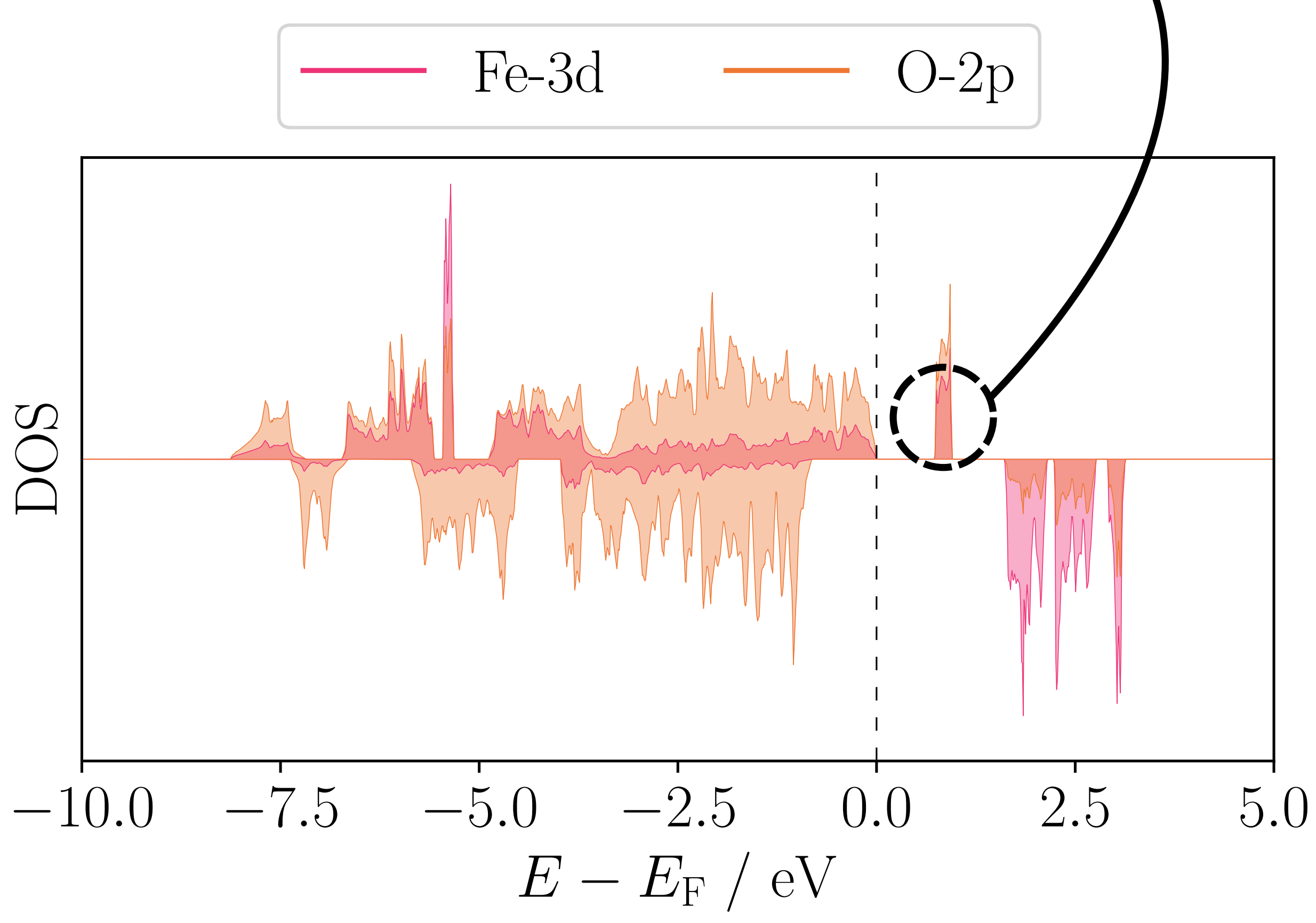
- The reduction of Fe^{IV} to Fe^{III} by peroxide formation is reminiscent of the **ligand to metal charge transfer** process observed in the disordered rock-salts. Our results suggest that this is an **intermediate step** towards the formation of molecular O_2.



Electronic Structure

- Delithiation of Li_xFeSiO_4 is known to occur in two distinct two-phase processes, from x=2 to x=1 and from x=1 to x=0.
- The projected electronic density of states for $FeSiO_4$ exhibits a redox state above the Fermi level that has substantial overlap with **both Fe and O states**.
- We have visualised these redox states by plotting the **Wannier isosurface** associated with the relevant bands.
- The oxidation state of the Fe according to the Wannier centres is **Fe^{IV}**, but there is **significant covalency** as evidenced by the shape of the isosurface.





Conclusions

- Despite the kinetic stability imparted by a rigid polyanion framework, the **ultimate product of oxygen redox in Li_2FeSiO_4 is molecular oxygen trapped in the bulk.**

- Extraction of the second lithium per formula unit oxidises Fe^{III} to Fe^{IV}, which (owing to substantial covalency) constitutes a **joint cationic and anionic redox process**.

- Fe^{IV} is a **metastable intermediate** which is reduced back to Fe^{III} upon oxygen dimerisation.

- Our results suggest that the oxygen redox process in polyanion systems has **significant overlap** with the equivalent mechanism in the lithium-rich layered and disordered rock-salt systems.