

# Defect-Driven Degradation Mechanisms in Li-Rich Cathodes Materials

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Lithium-rich cathode materials have been looked to as next-generation cathodes primarily for their notably increased capacity, relative to their classical layered oxide counterparts. This excess capacity, exceeding the theoretical utilization of transition metal redox, has recently been attributed to redox participation of the oxygen framework. As such, this increased capacity and oxygen activity is accompanied by severe voltage fade, preventing incorporation of the materials in modern devices. Using a combination of first principles calculations and experimental methodologies, sources of degradation are pinpointed.

Using density functional theory (DFT), oxygen participating in redox is observed to be susceptible to release. This is particularly apparent at surfaces, and oxygen vacancies are seen to facilitate transition metal migration, promoting the formation of a spinel surface layer [1]. Surface oxygen has been successfully stabilized through surface treatments, improving cyclability [2], though x-ray diffraction (XRD) refinement still suggests the formation of oxygen vacancies within the material bulk. Attempting to stabilize bulk oxygen, DFT was applied to determine the potential impact of dopants on the oxygen vacancy formation energy. These calculations suggest 4d transition metals increase the oxygen vacancy formation energy, and experimental doping with Mo into Li-rich NMC was shown to improve capacity retention.

Using operando coherent Bragg diffraction imaging, dislocations were observed to form during cycling. An increased dislocation density is accompanied by the formation of stacking faults, modifying the energetically favorable O3 stacking to intermittently include O1 configurations. Voltage calculations are performed using density functional theory (DFT), linking the formation of stacking faults to the increased voltage fade with delithiation. Voltage fade is observed to be largely reversible with heat treatment of the cycled cathode.

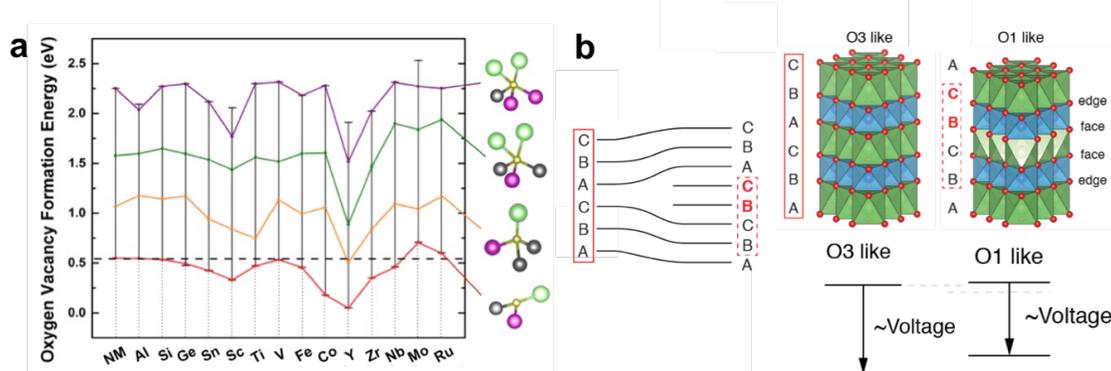


Figure 1. (a) Predicted modification of oxygen vacancy formation energy upon incorporation of dopants; (b) modification to stacking sequence results in notable voltage fade.

## References:

[1] D. Qian, B. Xu, M. Chi, Y.S. Meng, Phys. Chem. Chem. Phys. 16 (2014) 14665-14668.

[2] B. Qiu, M. Zhang, L. Wu, J. Wang, Y. Xia, D. Qian, H. Liu, S. Hy, Y. Chen, K. An, Y. Zhu, Z. Liu, Y.S. Meng, Nat. Commun. 7 (2016).