Effect of Nb doping on the performance of Li_2RuO_3 cathodes

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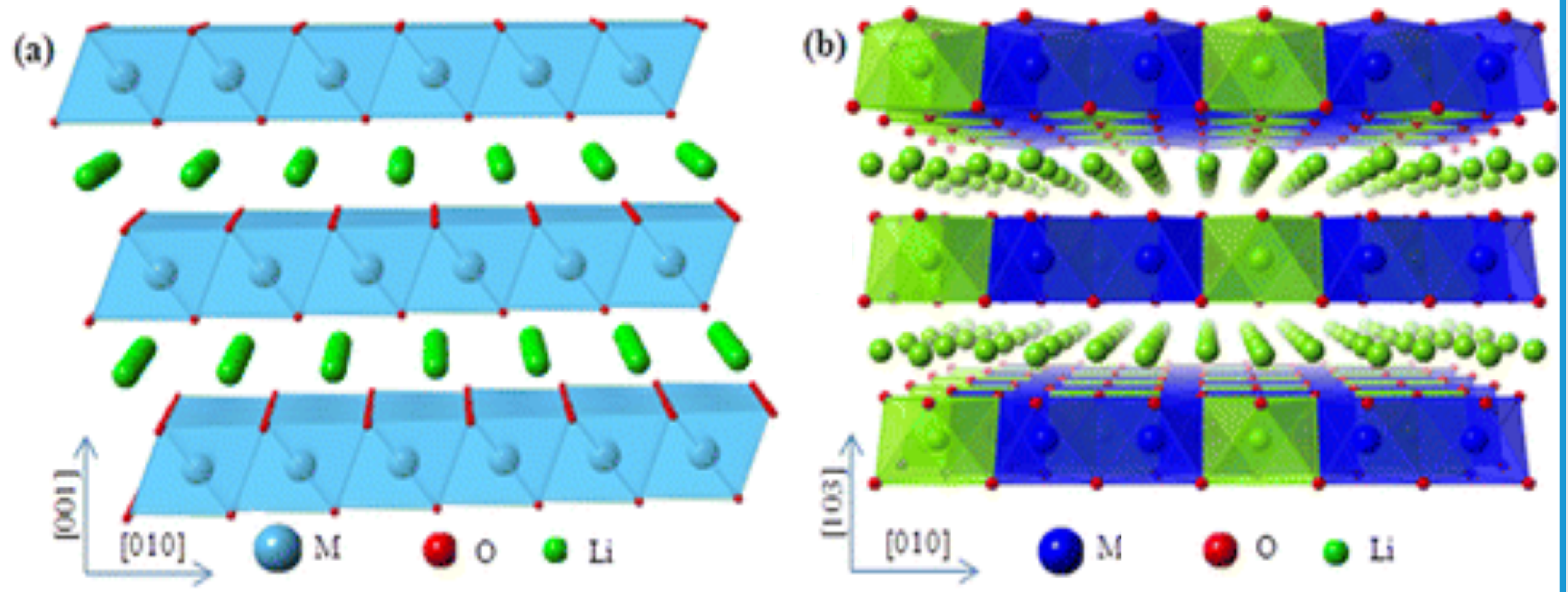
Next Generation Li-ion Battery Technology

Lithium-ion battery technology, having the highest gravimetric and volumetric energy densities of commercialized batteries, has conquered the portable electronic market.[1] It is the battery of choice for powering electric vehicles and potential grid energy storage. Classical positive electrodes for Li-ion technology ($LiMO_2$ compounds) operate mainly through an insertion–disinsertion redox process involving cationic species. Next generation Li-rich layered oxides (Li_2MO_3 compounds) are high-capacity materials where Li entails cumulative cationic ($M^{n+} \rightarrow M^{(n+1)+}$) and anionic ($O_2^- \rightarrow O_2^{2-}$) reversible redox processes, owing to the d–sp hybridization associated with a reductive coupling mechanism.[2]

Cathode theoretical specific capacities

Industry standard: $LiMO_2$
120 - 200 mAh g^{-1}

Lithium-rich: Li_2MO_3
250+ mAh g^{-1}



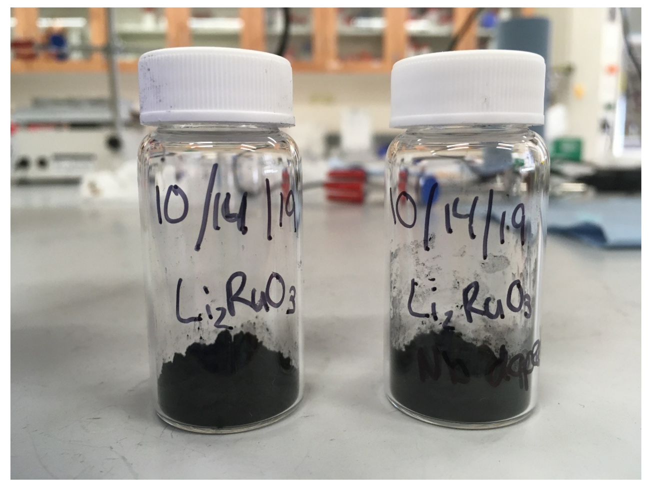
J. Phys. Chem. Lett. 2013, 4, 8, 1268-1280

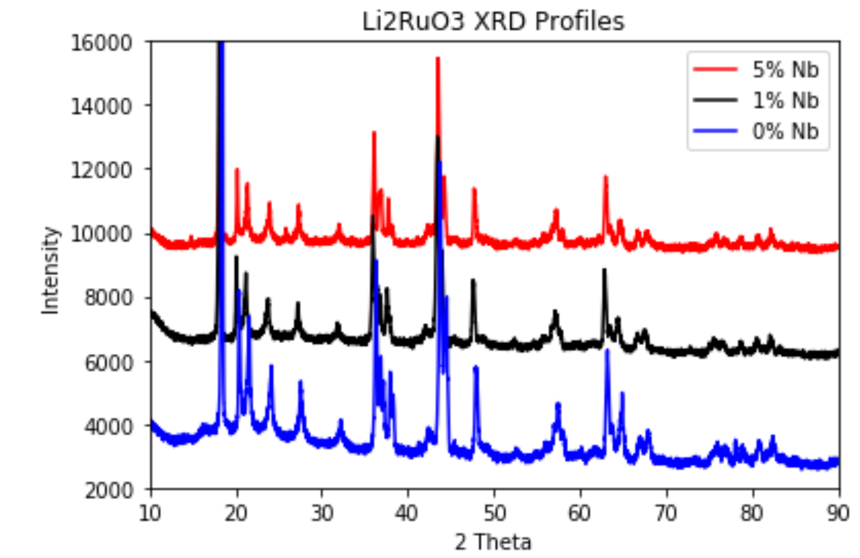
[1] Sathiya, M. (2014). Origin of voltage decay in high-capacity layered oxides. ***Nature Materials***

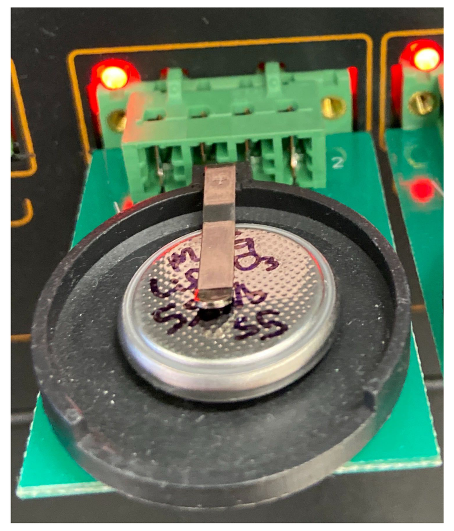
[2] Sathiya, M. (2013). Reversible anionic redox chemistry in high-capacity layered-oxide electrodes. ***Nature Materials***

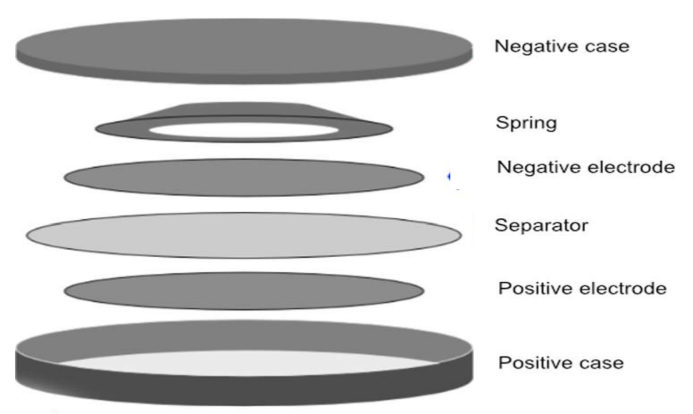
Material Synthesis and Electrochemical Cycling

To determine the optimal amount of Nb dopant, several compositions were synthesized through a solid state reaction. Dry precursors (RuO_2, Li_2CO_3, Nb_2O_5) were mixed in stochiometric ratios, with 10% excess Li_2CO_3 to account for material volatilization. After several grinding and heating steps the samples were characterized with XRD. Samples containing 1 mol% Nb and 5 mol% Nb were tested against a control of pure Li_2RuO_3. These samples were mixed with 10 wt% PVDF binder and 10 wt% SP carbon cast over aluminum foil, assembled into coin cells against Li metal, and cycled at C/10.







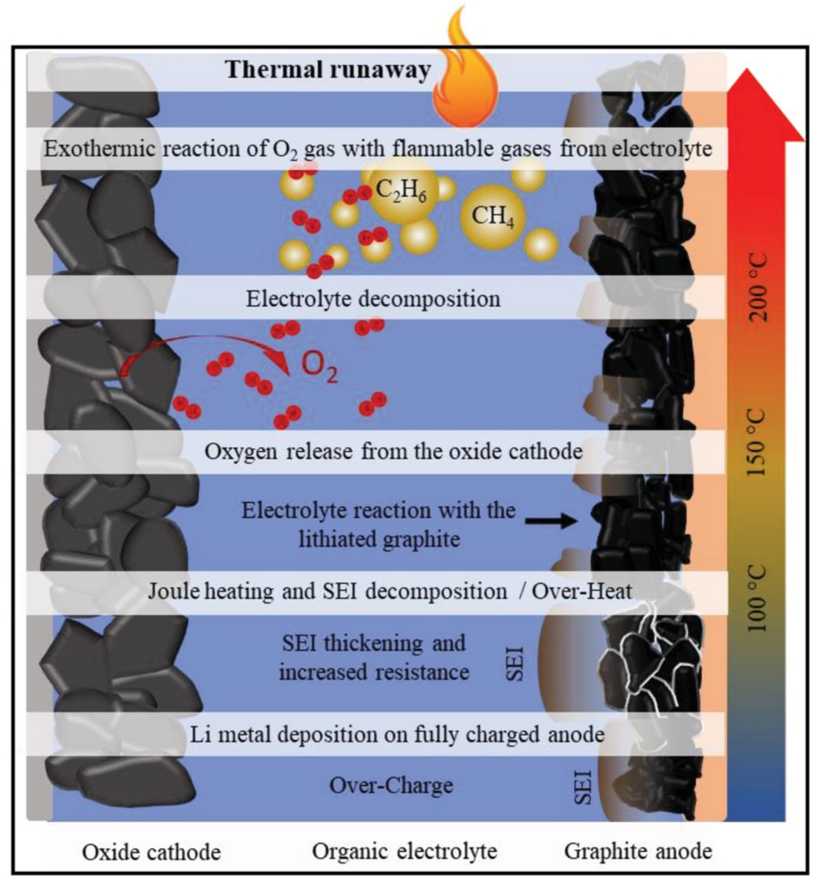


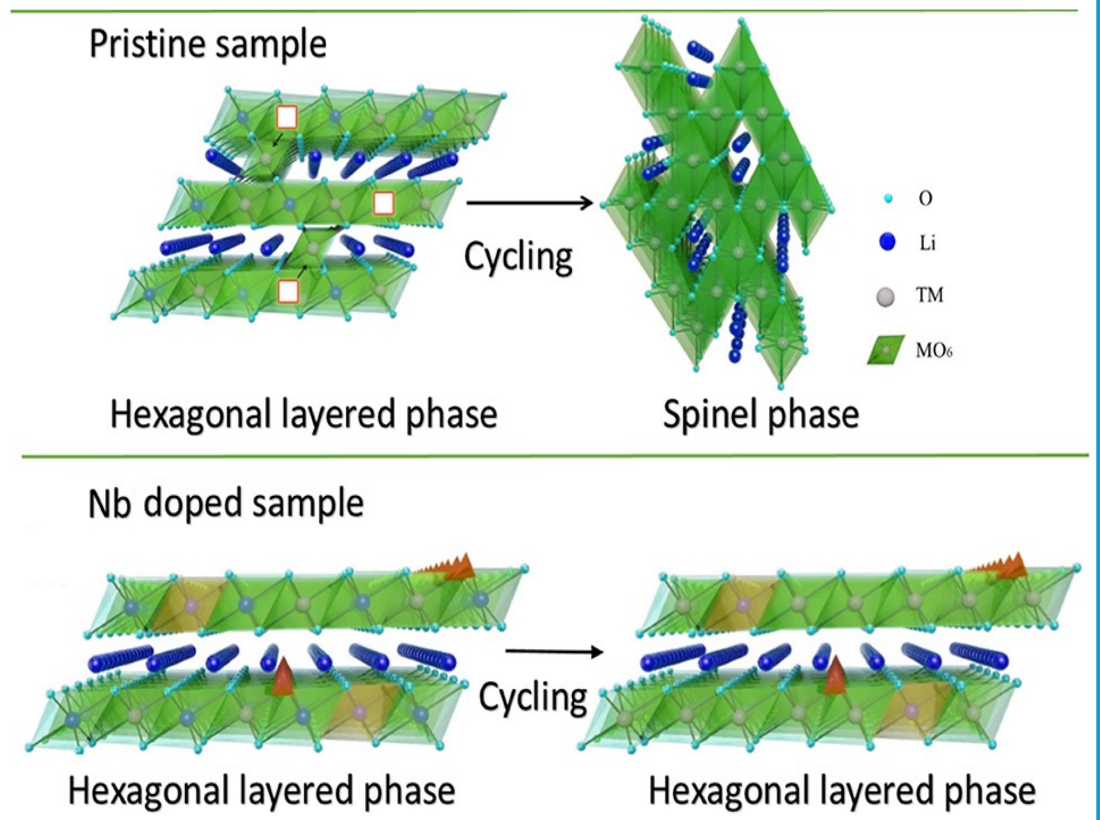
State of the Art Cathodes

Li-rich cathodes undergo structural rearrangement at high potential that evolve O_2, lead to voltage fade, poor electrochemical kinetics, and safety concerns including thermal runaway. Nb dopant has a superior oxygen dissociation energy and was proposed to stabilize the structure.

Dissociation energies

Nb – O : 727 kJ mol^{-1}
Ru – O : 528 kJ mol^{-1}
Co – O : 368 kJ mol^{-1}
Ni – O : 392 kJ mol^{-1}





Sharifi−Asl, Soroosh, et al. (2019) Oxygen Release Degradation in Li−Ion Battery Cathode Materials: Mechanisms and Mitigating Approaches. ***Advanced Energy Materials***

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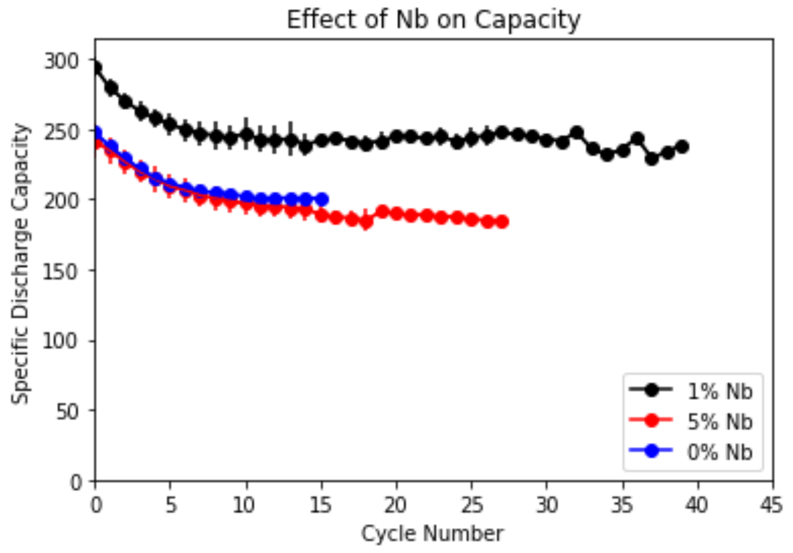
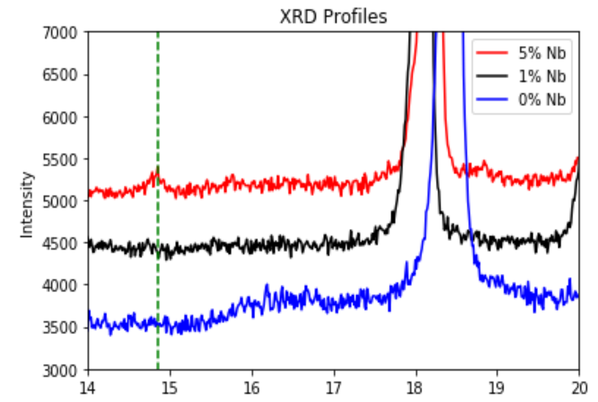
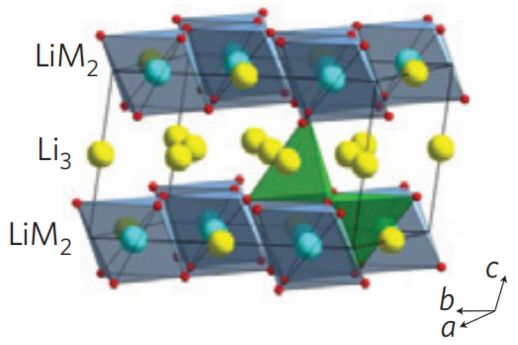
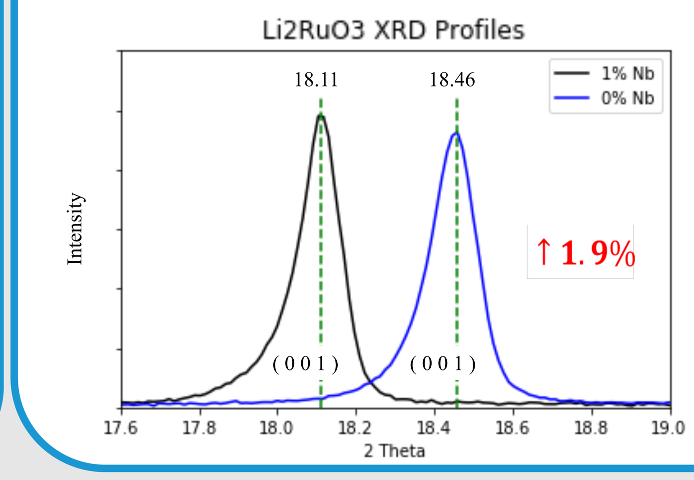
Structure-Performance Relationships in Nb-doped Li_2RuO_3

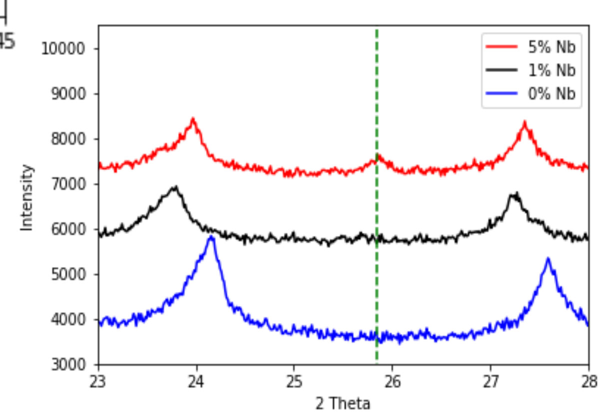
Batteries with doped with 1 mol% Nb exhibit higher capacity, yet it is unclear whether they can retain this capacity for more cycles than undoped cells. Literature values for Li_2RuO_3 state that reversible capacity decreases from 240 mAh/g to ~140 mAh/g after 100 cycles. An inactive impurity, Li_3NbO_4, in 5 mol % Nb cells may lead to similar performances to undoped cells.

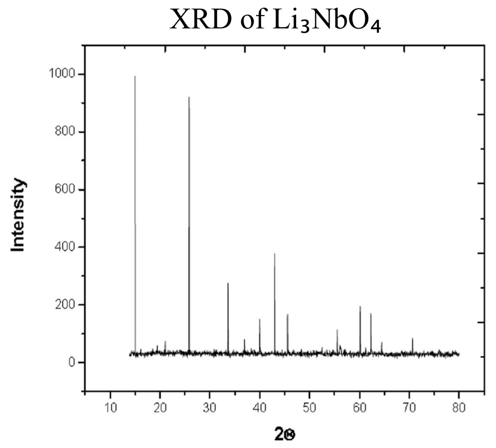












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Acknowledgements

The Marbella Group

Left to right: Mateo, Amrita, Sapna, Julia, LEM, Karlie, Drew, Eli, Richard

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