

Analysis of Electrode Surface Lithiation Using DFT

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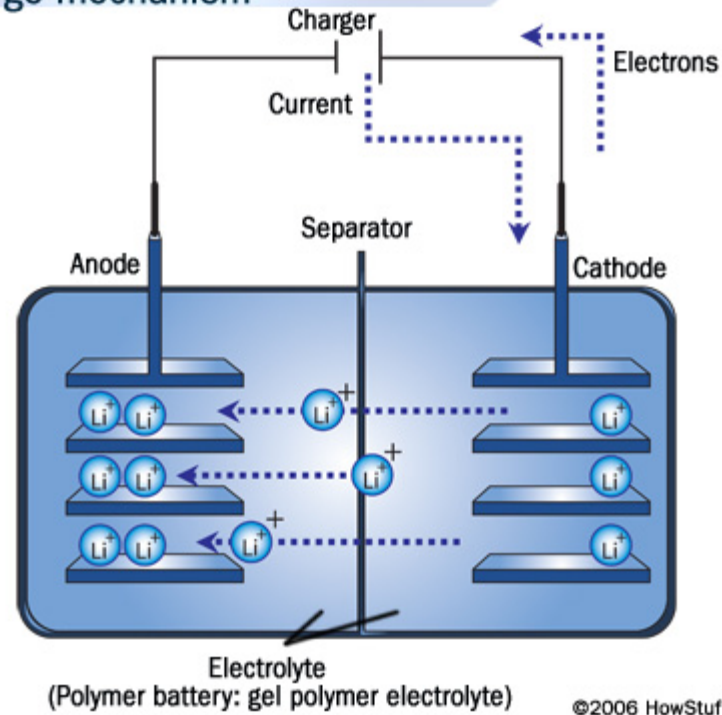
Introduction

- Investigated the process of adding lithium to thin slabs and nanoparticles of ruthenium oxide.
- Used Density Functional Theory (DFT) to calculate the energy change associated with lithiation.
- Calculated volume change in electrode materials.



Lithium-ion battery structure

Lithium-ion rechargeable battery Charge mechanism



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Methods

- Vienna Ab Initio Simulation Package (VASP) uses an iterative process to find minimum energy.
 - Calculates total energy, moves the atoms, and recalculates.
 - Continues to move atoms until local minimum energy is found.
 - Sometimes necessary to test multiple starting configurations to find true lowest energy.
- Energy converted to voltage by use of the Nernst equation.
 - Start with total energy of lithiated system.
 - Subtract out energy of starting unlithiated system and energy of lithium atoms in bulk form.
 - Divide by number of lithium atoms to get the voltage of the lithiation process.

$$E - E_0 - n * E_{Li} / n$$

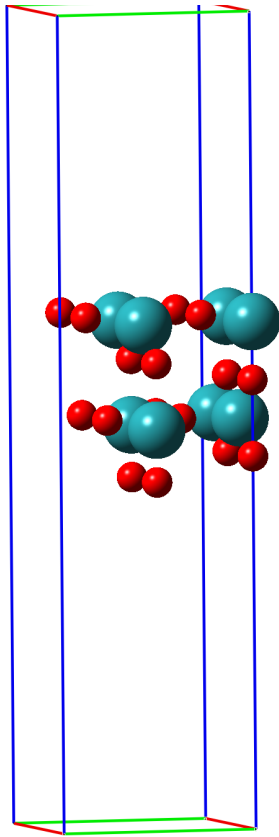


Structure of systems

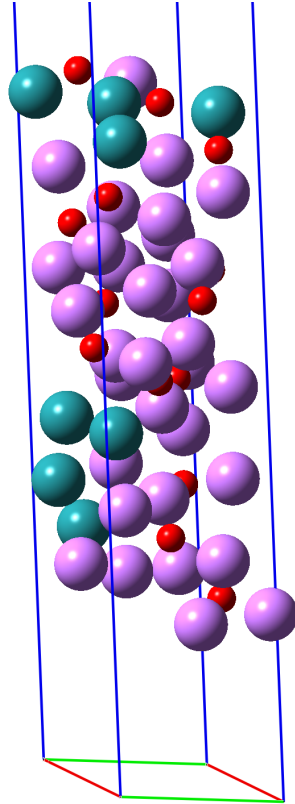
- Three different geometries tested.
 - Uniform slab with exposed surfaces.
 - Ruthenium island surrounded by lithium oxide with exposed surfaces.
 - Ruthenium oxide nanoparticle.



Ruthenium Oxide Slab $(\text{RuO}_2)_8$

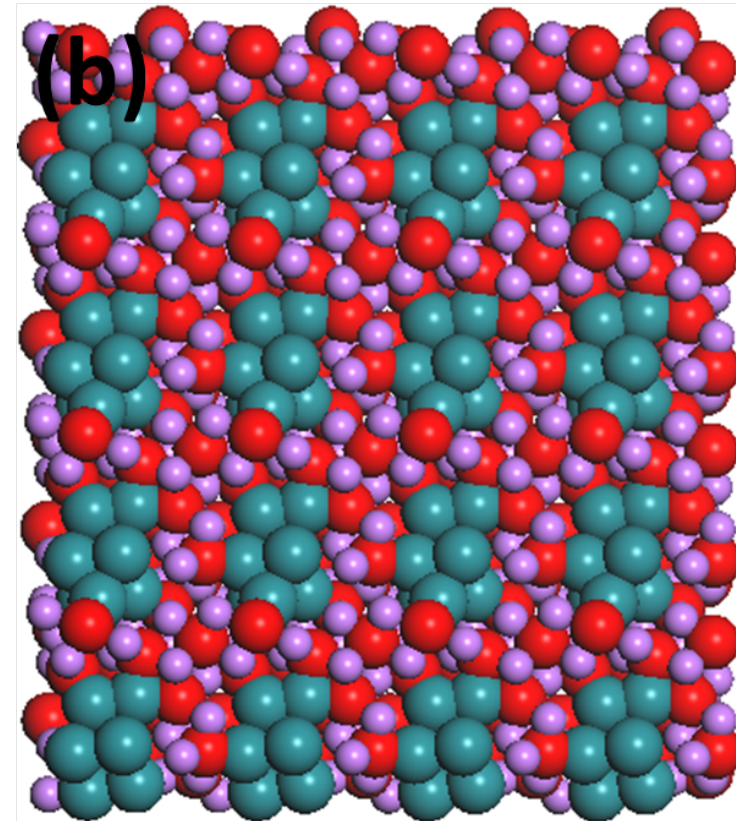
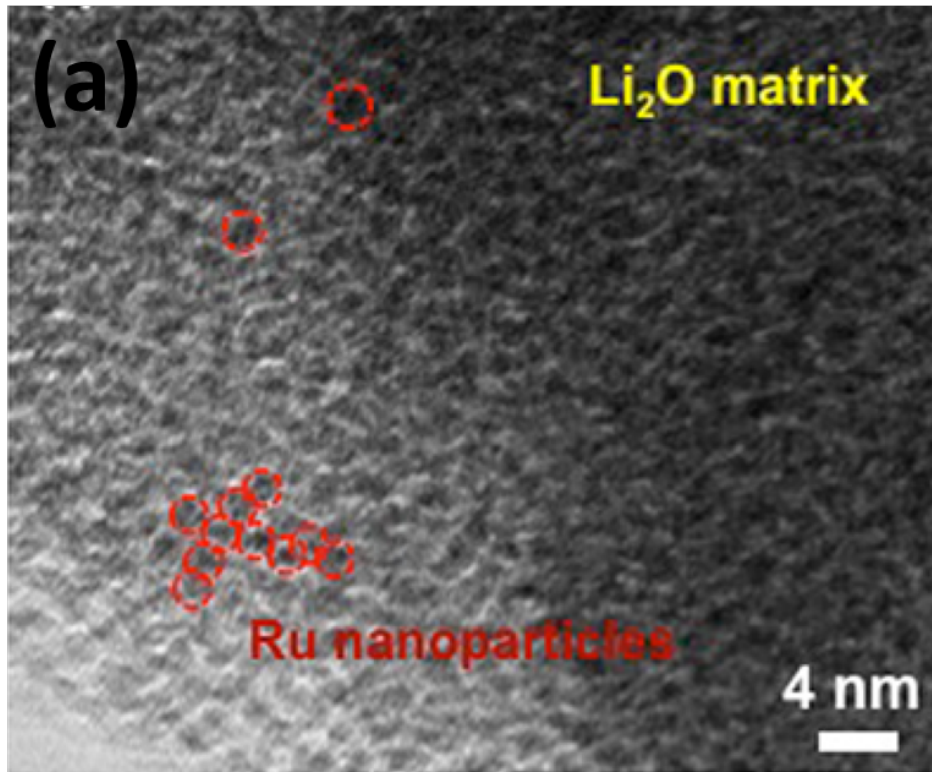


0 Li

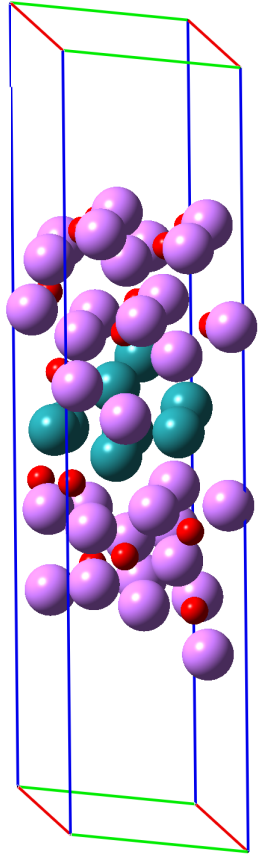


32 Li

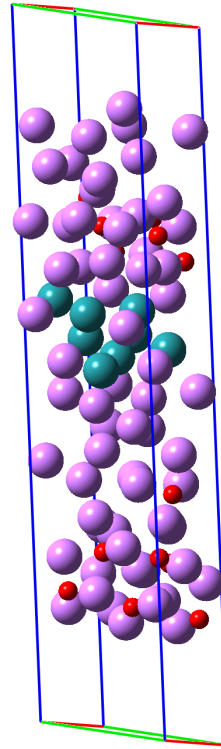




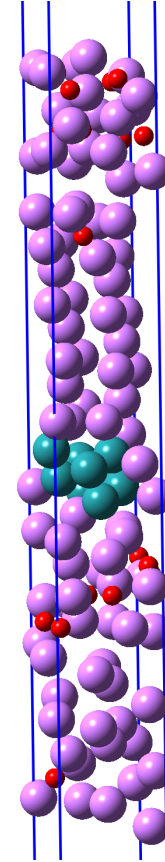
Island Structures with interfacial storage



Island with 32 Li



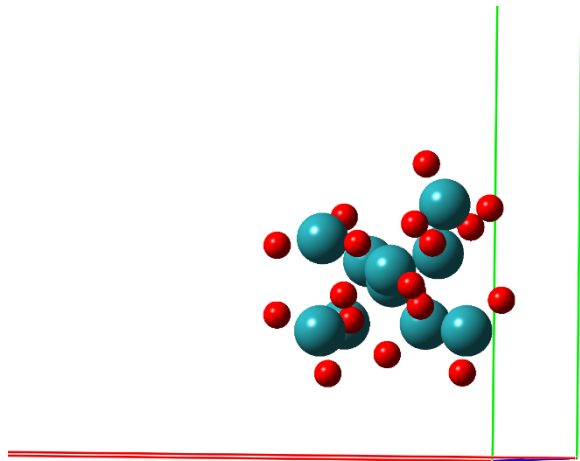
Island with 64 Li



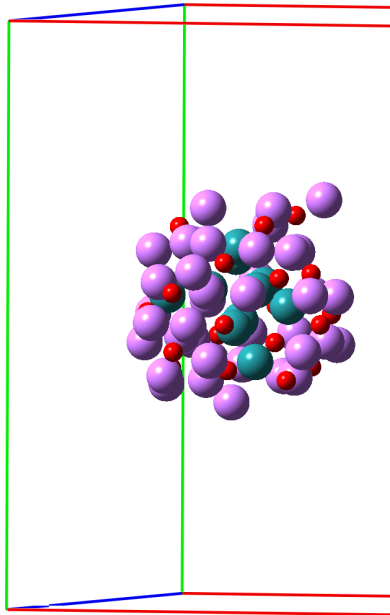
Island with 88 Li



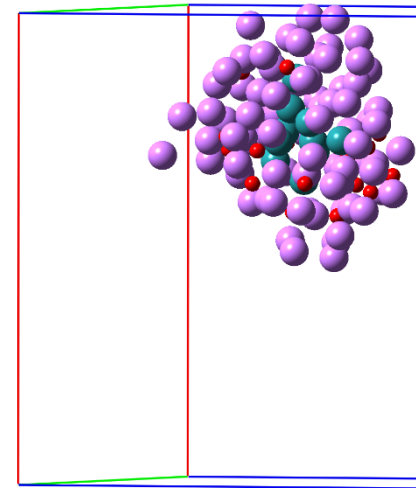
Nanoparticle $(\text{RuO}_2)_{10}$



Nanoparticle with 0 Li



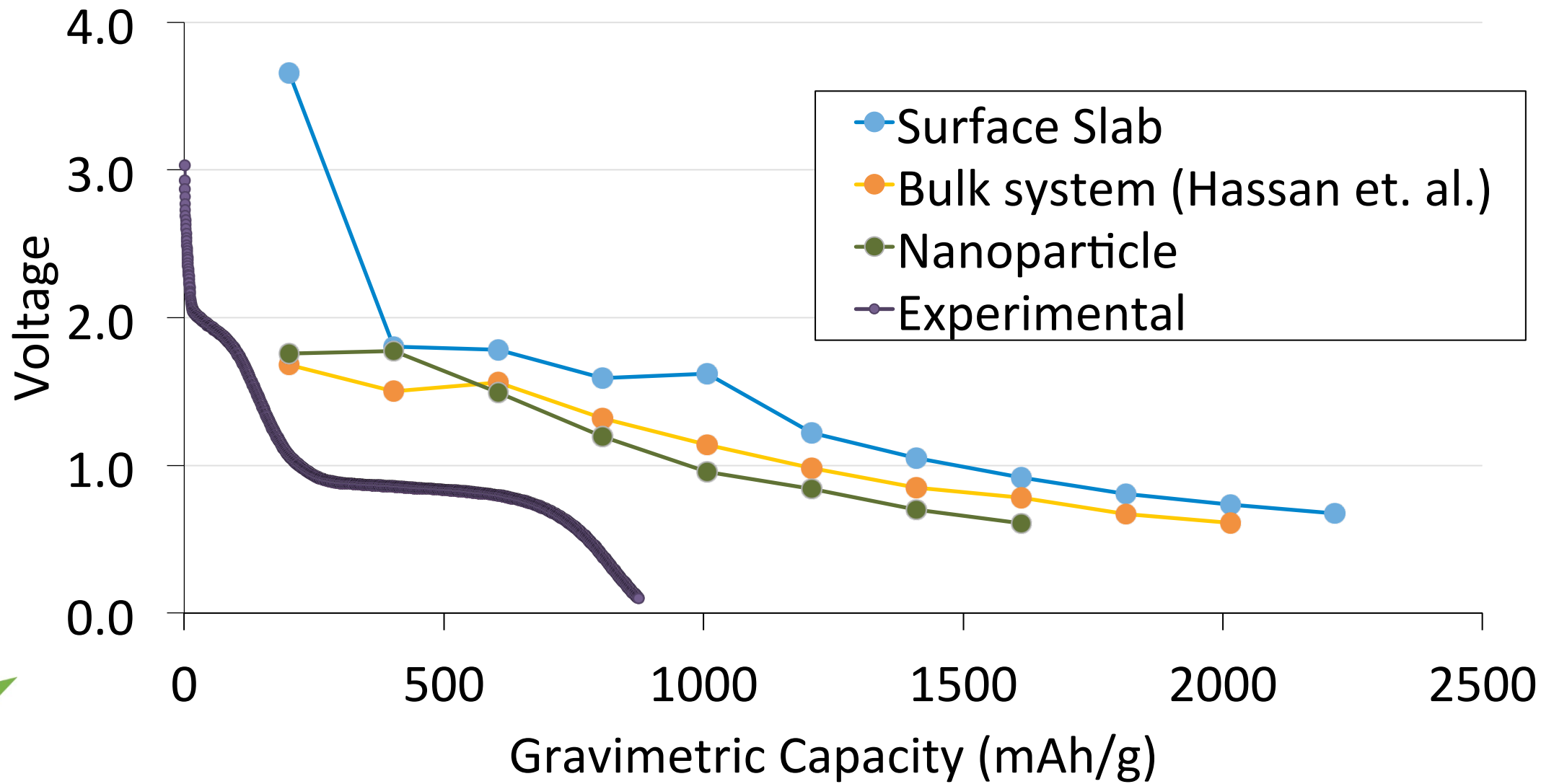
Nanoparticle with 40 Li



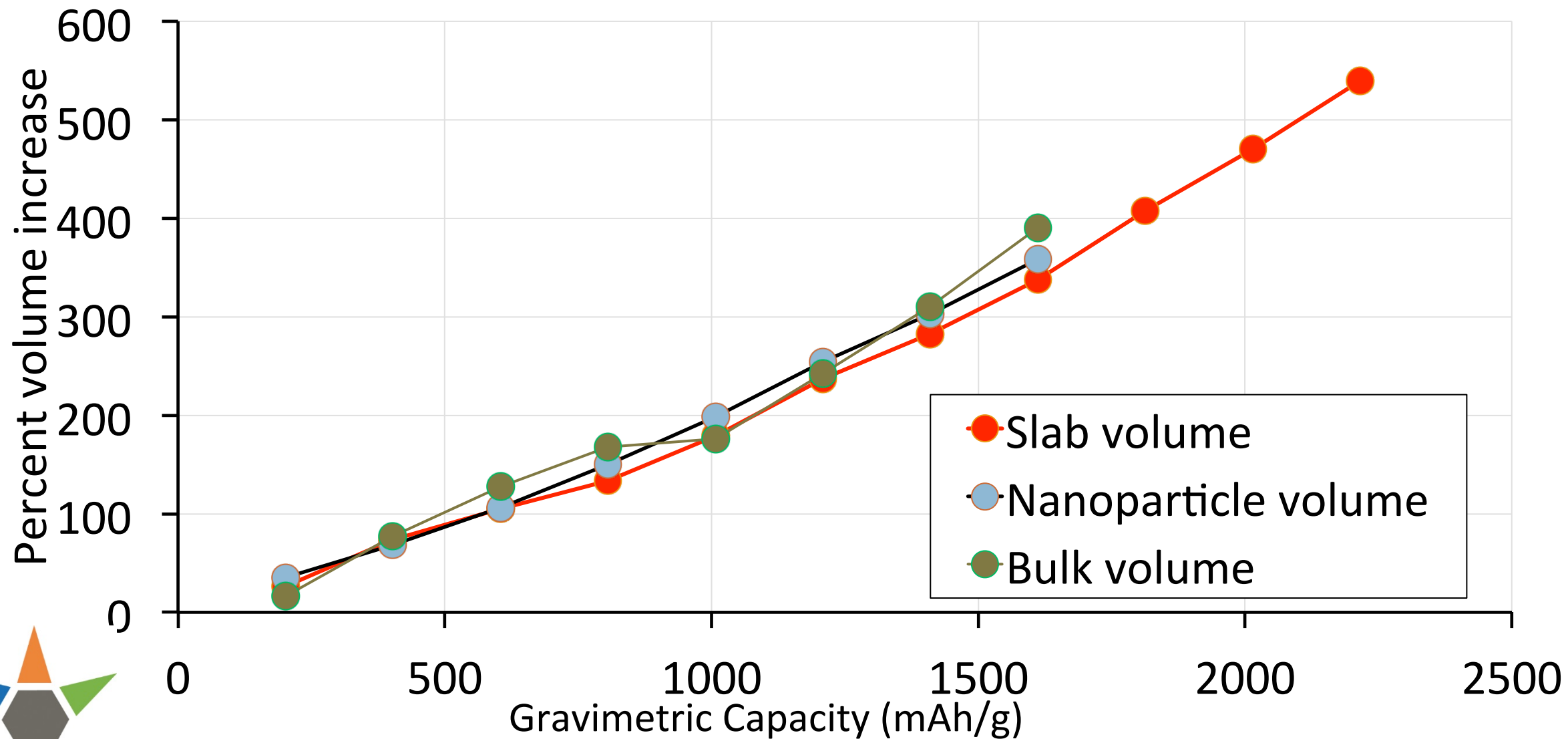
Nanoparticle with 80 Li



Lithiation voltage

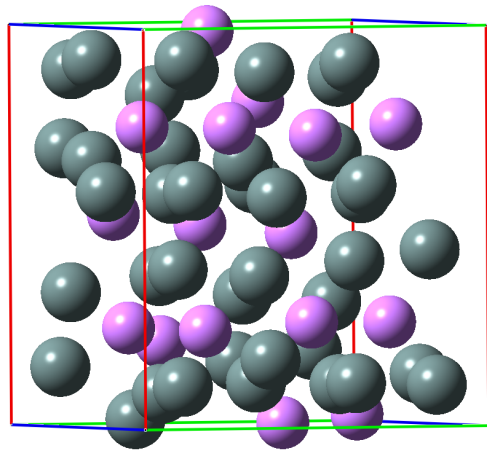


Percent volume increase

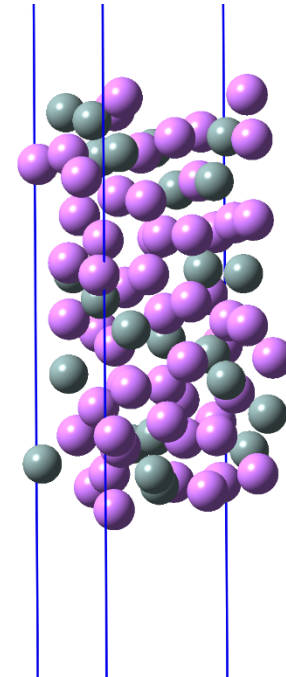


Additional work

Similar calculations in progress for SnO_2 , Sn, Si, and NiSn.



Sn with 16 Li



Si with 56 Li



Conclusion

- Investigation of near-surface lithiation of RuO_2 found that it operated by the same mechanisms as bulk lithiation.
- Theoretical gravimetric capacity was high, and volume expansion was similar to bulk volume expansion.



Acknowledgement

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