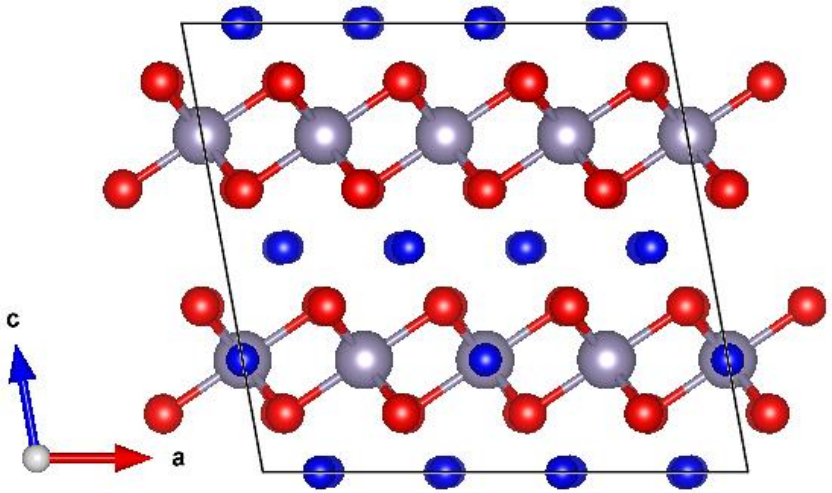
Computational Study of Li_2SnO_3 and Li_2SnS_3*

Jason Howard advisor Natalie Holzwarth

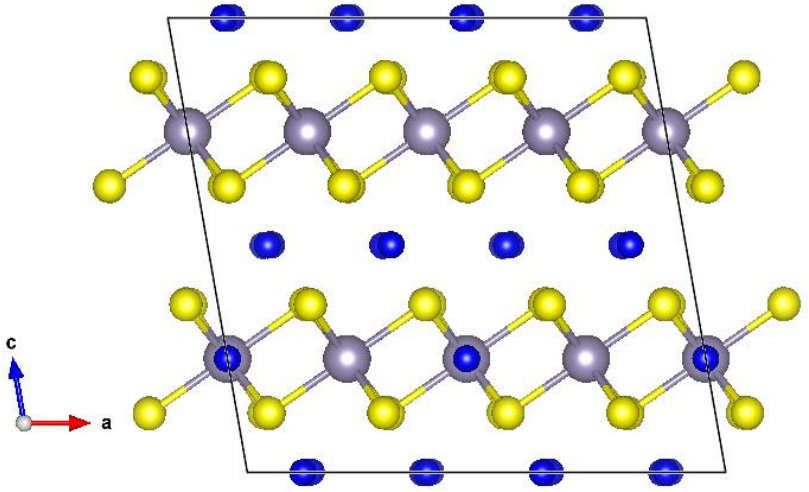
Department of Physics, Wake Forest University, Winston-Salem, NC USA

Li Sn O S

Li_2SnO_3



Li_2SnS_3

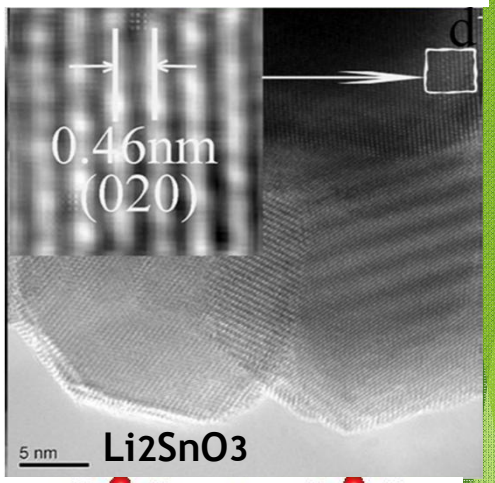


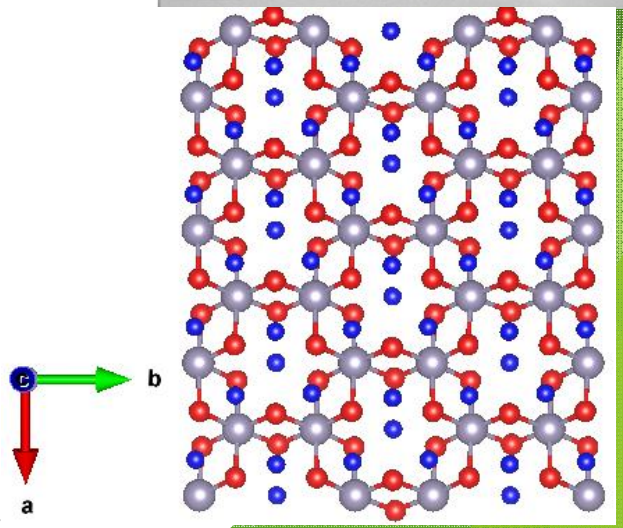
*Supported by NSF grants DMR-1105485 and 1507942 and WFU's Deac computer facility

Background Li_2SnO_3 and Li_2SnS_3

- Close packed layered structures
- AB stacked
- Monoclinic Space group 15 C2/c (#15 in the International Table for Crystallography)
- Oxide material studied as possible anode material 1990's-present
  (Courtney & Dahn, JES **144**, 2943 (1997))
  (Zhang et al., J. Alloy Compd. **415**, 229 (2006))
  (Wang et al., Surf. Interface Anal. **45**, 1297 (2013))
- Sulfide studied as possible electrolyte 2014
  (Brant et al., CM **27**, 189 (2014))
- ionic conductivity, $sulfide\ 1.6 * 10^{-3}\ \frac{S}{cm}(373\ k)$
  $oxide\quad 2 - 3 * 10^{-8}\ \frac{S}{cm}(563\ k)$

Wang et al., Surf. Interface Anal. **45**, 1297 (2013))





WAKE FOREST UNIVERSITY

Overview

- Activation energy for lithium ion migration

  vacancy migration and kick-out mechanism

- Interstitials

- Interfacing with lithium

- Lithiation of bulk –
  change in volume and cell dimensions

  energetics

WAKE FOREST UNIVERSITY

Computational methods

- Density functional theory with LDA
- PAW formalism using datasets generated with ***ATOMPAW*** code (Holzwarth et al. *CPC* **135**, 329 (2001)) http://pwpaw.wfu.edu

- Electronic structure calculations performed using ***QUANTUM ESPRESSO*** . (Giannozzi et al. *JPCM* **21**, 394402 (2009); http://www.quantum-espresso.org, Gonze et al., *CPC* **180**, 2582 (2009)); http://www.abinit.org

- Plane wave expansion for wave functions with Brillouin zone integration mesh of 0.003 bohr^{-3} $|k+G|^2 \leq 64$ Ry

- Ion migration estimated with Nudged Elastic Band (NEB) method. (Hinkleman et al. *JCP* **113**, 9901 & 9978 (2000))

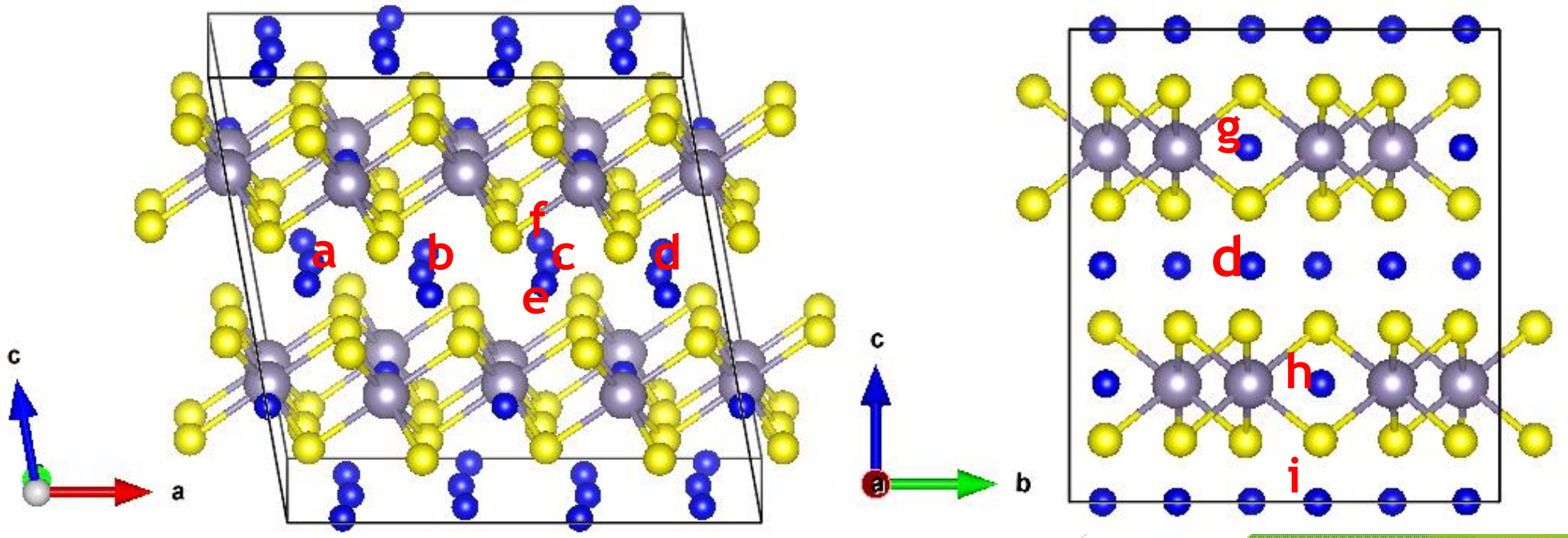
- Visualization software: ***Xcrysden***, ***VESTA***

- Plotting **xmgrace, gnuplot**

WAKE FOREST UNIVERSITY

Calculating Ea via vacancy mechanism

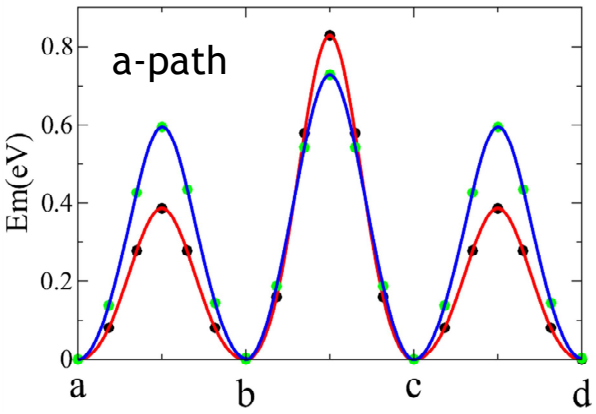
- Choose paths of migration:
  a-path: A – B – C –D b-bath: E – C – F c-path: G – D – H – I
- Relax vacancy structures
- Run NEB calculations between images

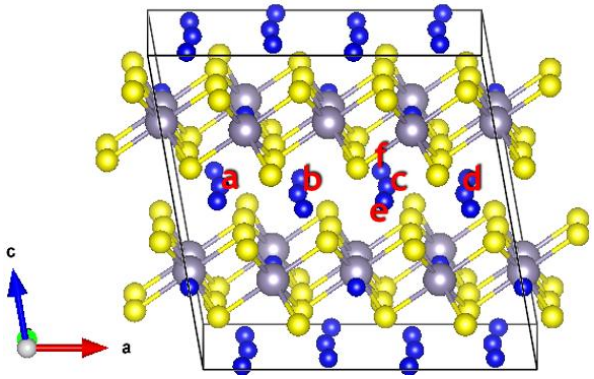


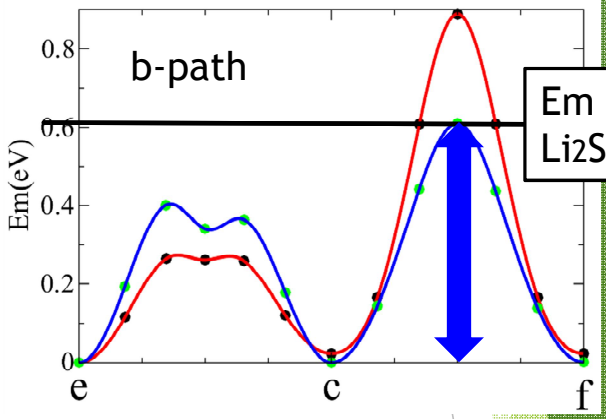
NEB results, extracting Em

(oxide)

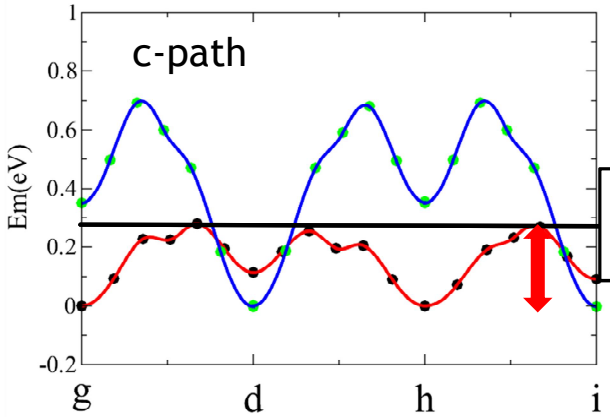
(sulfide)



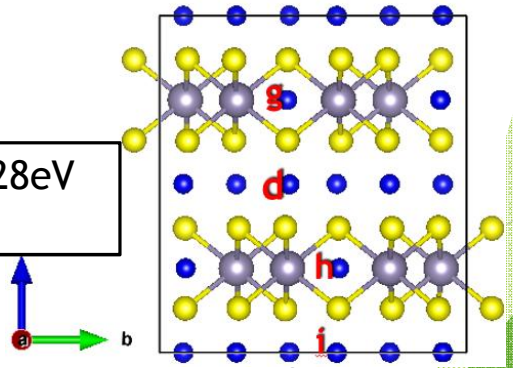




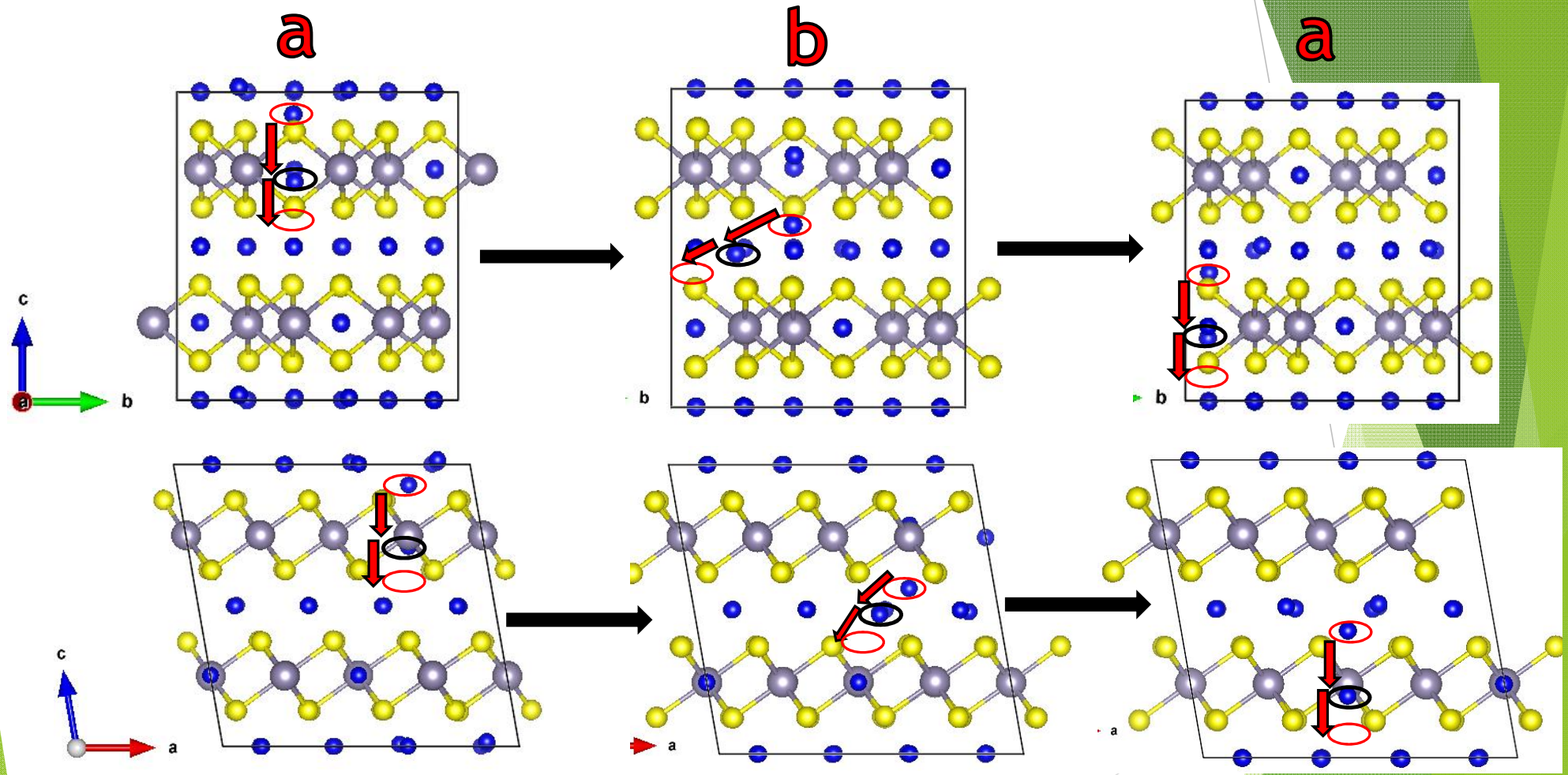
Em = 0.61eV
Li_2SnS_3



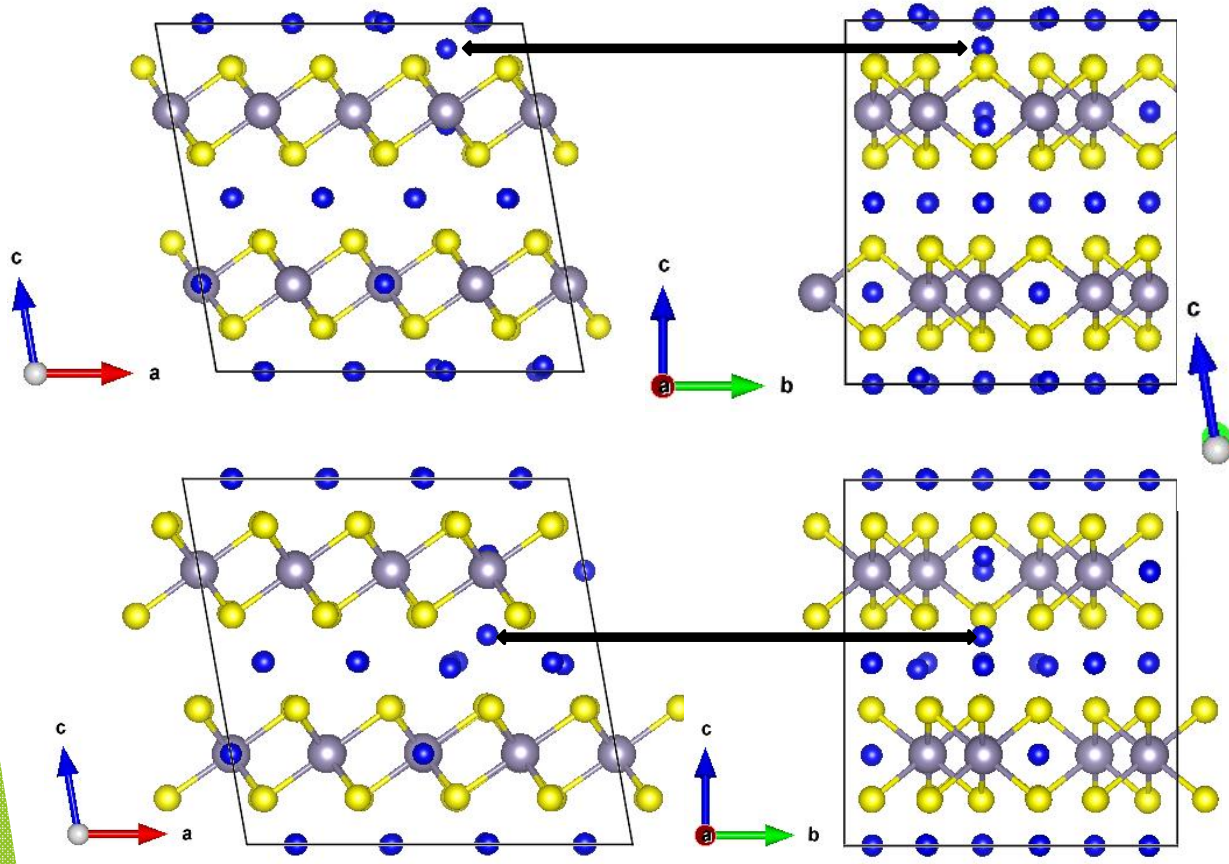
Em = 0.28eV
Li_2SnO_3



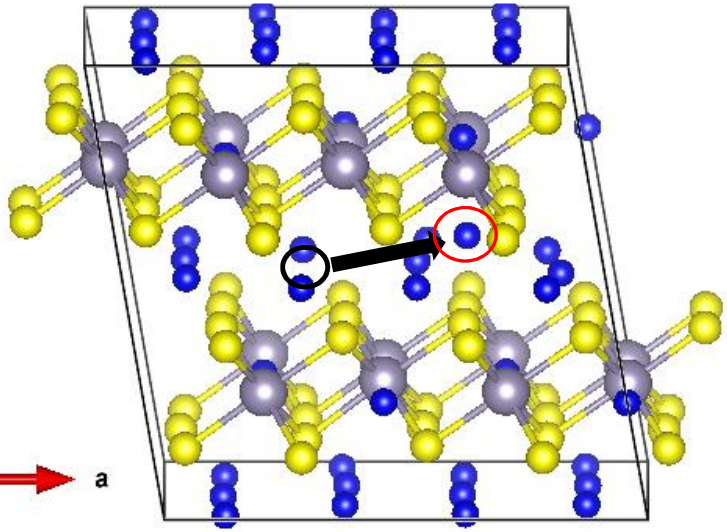
kick-out mechanism for Li-ion conduction



Interstitials



vacancy interstitial pair defect



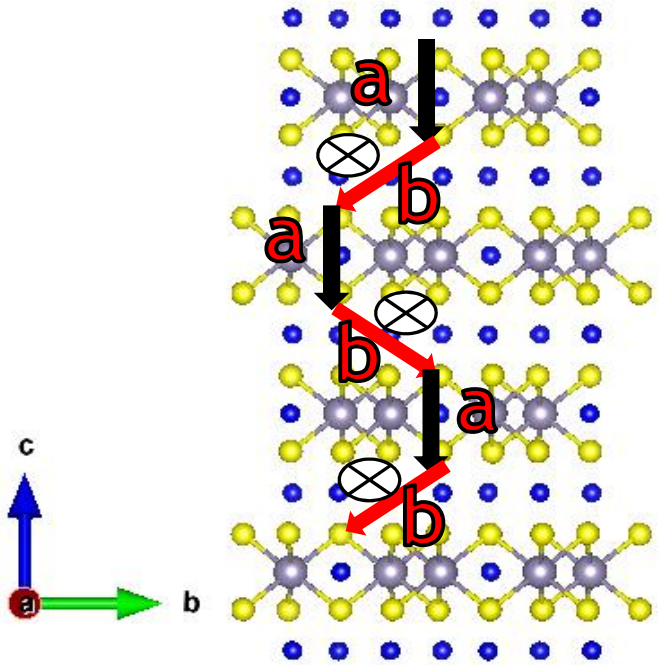
For the vacancy interstitial defect

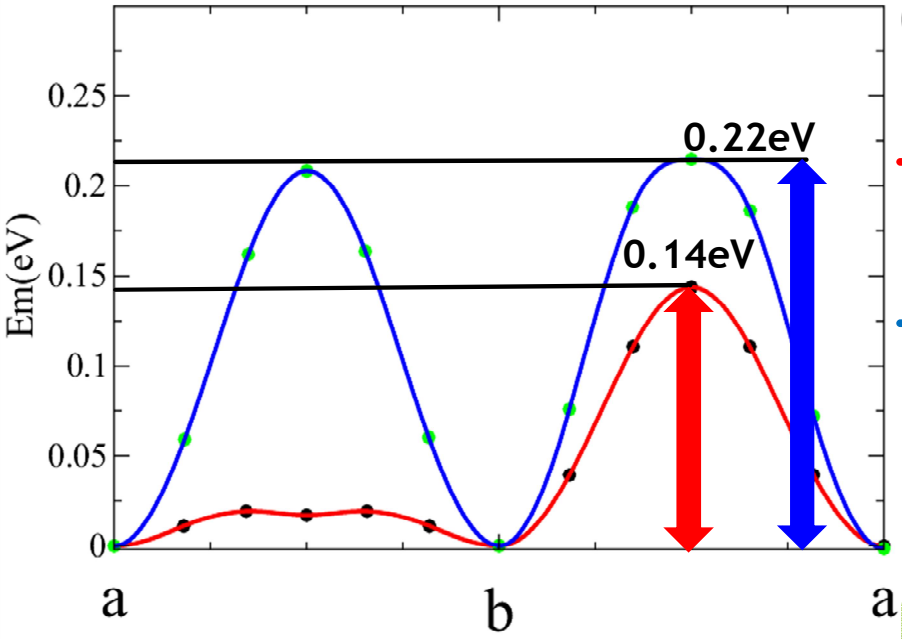
$$Edefect - Eperfect = Eformation$$

$1.25eV$ (Li_2SnO_3)

$0.96eV$ (Li_2SnS_3)

NEB results, Em for kick out





oxide

sulfide

$$Em \leq Ea \leq Em + \frac{1}{2} * Ef \qquad Ef = 1.25\,(oxide),\ 0.96(sulfide)$$

Li2SnO3	Em	Em + $\frac{1}{2}$ *Ef
vacancy	0.28	0.91
Kick-out	0.14	0.77

- Experiment
  L.P.Teo, et al. Ionics (2012) 18:655-665

  0.69 - 0.91 eV

Li2SnS3	Em	Em + $\frac{1}{2}$ *Ef
vacancy	0.61	1.07
Kick-out	0.22	0.68

- Experiment
  J. A. Brant, et al.. ACSJCa|JCA10.0.1465/W

  0.59 eV

Overview

- Activation energy for lithium ion migration

  vacancy migration and kick-out mechanism

- Interstitials

- Interfacing with lithium

- Lithiation of bulk –

  change in volume and cell dimensions

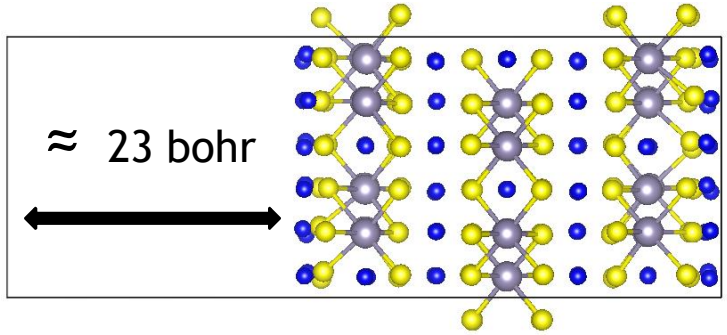
  energetics

- Modeling interfaces with Li help to understand behavior with excess Li at surface
- Can provide insight in to electrolyte or anode functionality
- As electrolyte Li_2SnS_3 would need to have stable interface with Li
- As proposed anode, Li interface calculations are to help understand decomposition process

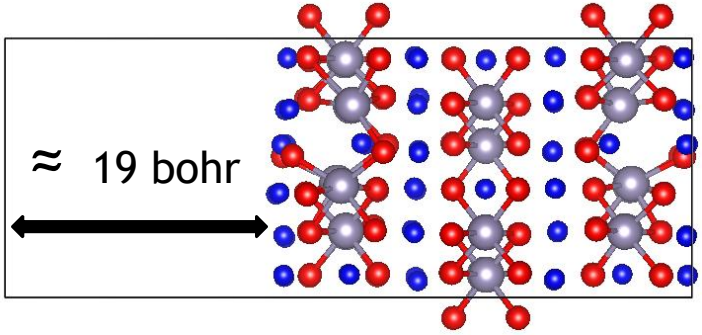
Interfacing with lithium

- Preparation - surface vacum calculation
  Six extra lithium left on each surface, 24*(Li_2SnO_3) + 12*Li

Li_2SnS_3 Vacuum Volume ≈8300 bohr^3



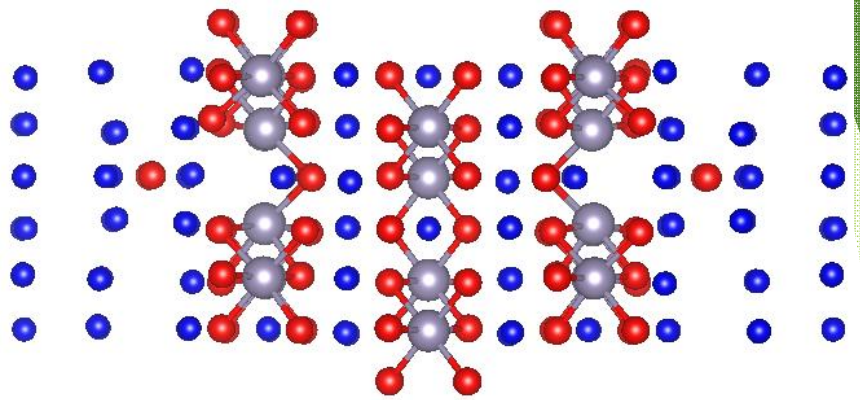
Li_2SnO_3 Vacuum Volume ≈4500 bohr^3



Li_2SnO_3 - Li interfaces

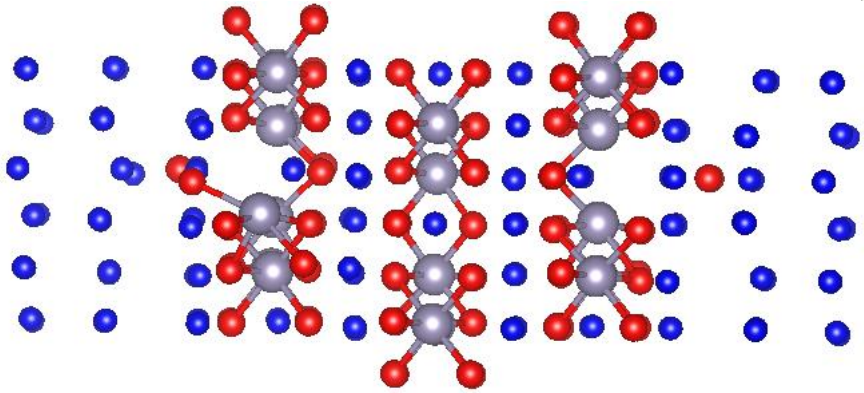
VC-relax, cell-do free “Z”

-14716.9205 Ry, **ref 0 eV**



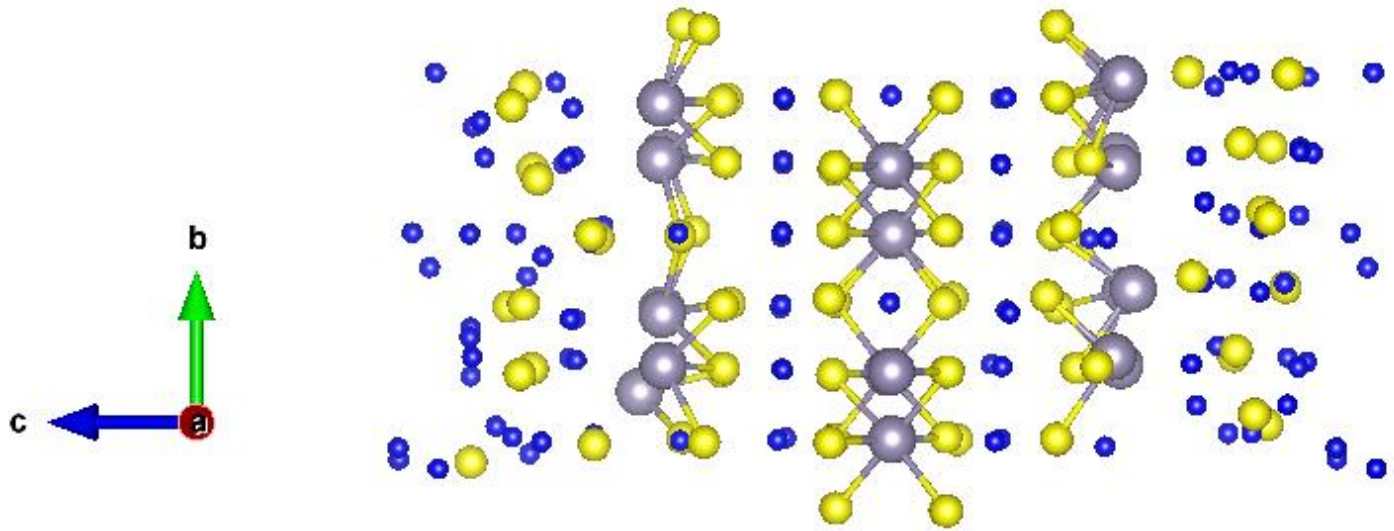
MD 300k 38 fs → VC-relax, cell-do free “Z”

-14716.8014 Ry, **+ 1.62 eV**



Li_2SnS_3 -Li interfaces

Unconverged



Overview

- Activation energy for lithium ion migration

  vacancy migration and kick-out mechanism

- Interstitials

- Interfacing with lithium

- Lithiation of bulk –
  change in volume and cell dimensions

  energetics

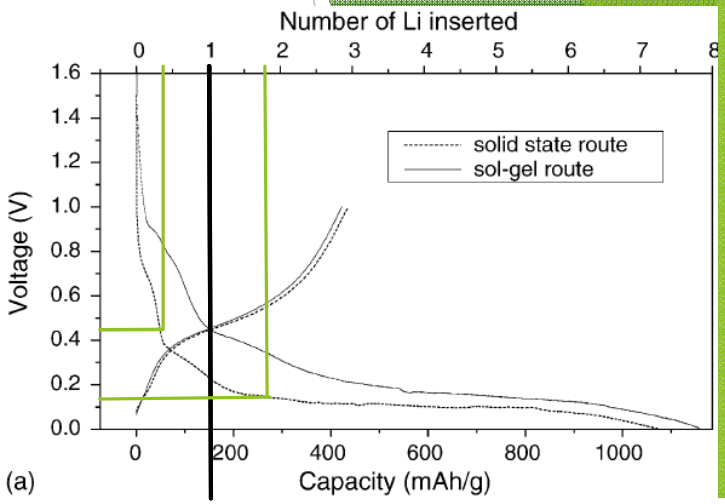
- Goal is to better understand decomposition process for Li_2SnO_3

Lithiation of Li_2SnO_3

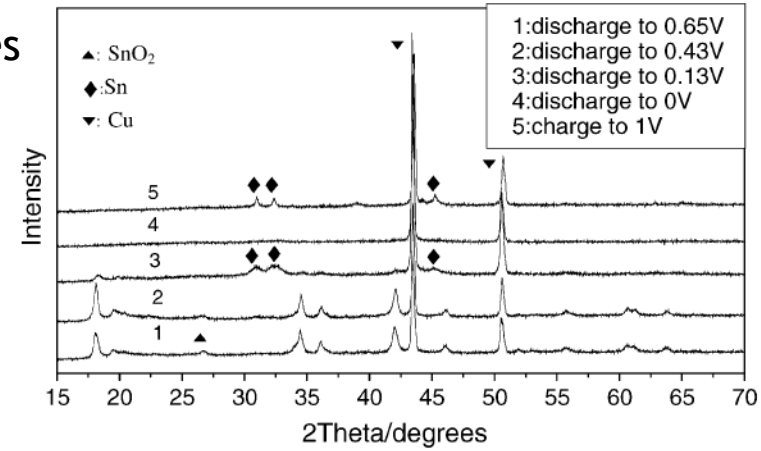
- Li_2SnO_3 has been studied as electrode (**Courtney, Zhang, Wang**)

1. $Li_2SnO_3 + 4*Li \rightarrow 3*Li_2O + Sn$
2. $3*Li_2O + Sn + 4.4*Li \leftrightarrow 3*Li_2O + Li_{4.4}Sn$

- First cycle irreversible
- Decomposition Occurs between 0.4 – 1.75 Li inserted per Li2SnO3 (Zhang et al., J. Alloy Compd. **415**, 229 (2006))
- Residual lithium oxide matrix said to stabilize further cycles
- I studied beginning of decomposition

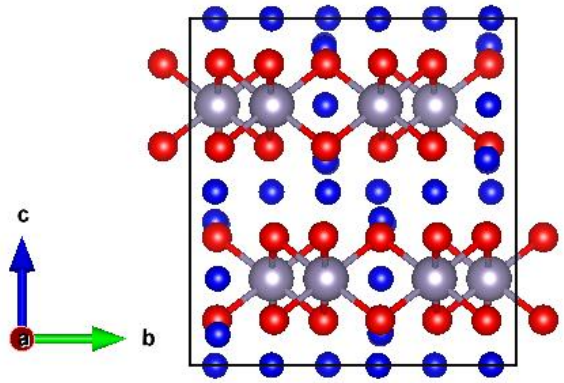


(Zhang et al., J. Alloy Compd. **415**, 229 (2006))

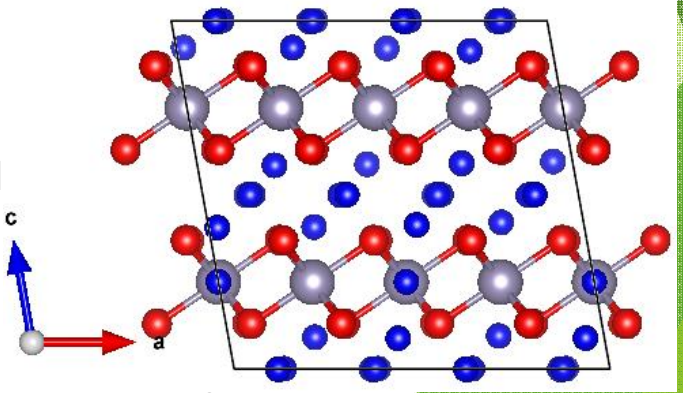


Modeling Lithiation up to 1 Li inserted per formula unit Li_2SnO_3

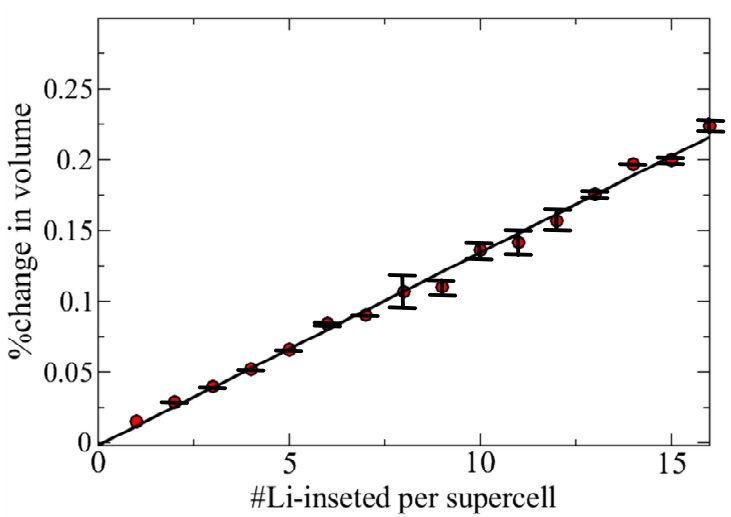
- Assumption – Li will populate interstitial points first
- Run VC-relax no symmetry = true for 1-16 interstitials filled
- Choose interstitials to fill via random number generator(random.org)
- Run multiple trials avg data
- Interpret data from energetics, %volume change, change in cell dimensions



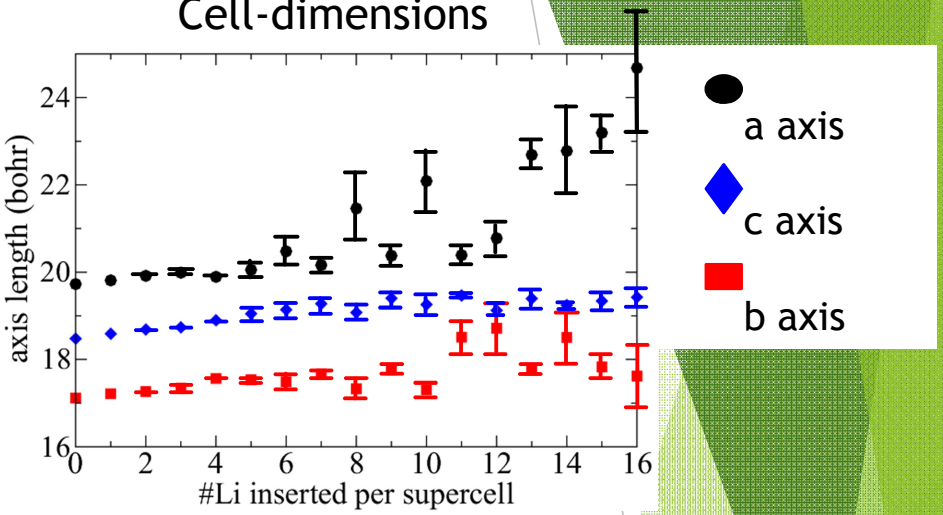
Unrelaxed structures
All 16 interstitials filled

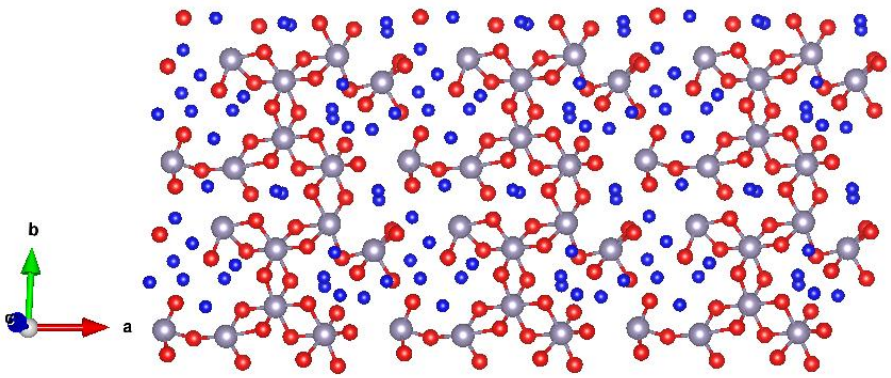


Volume expansion change in cell-dimensions

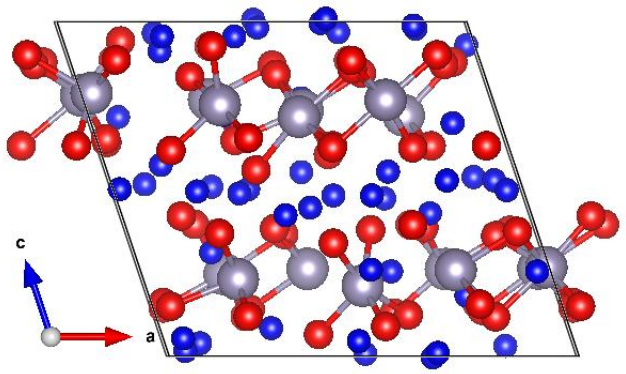


Cell-dimensions

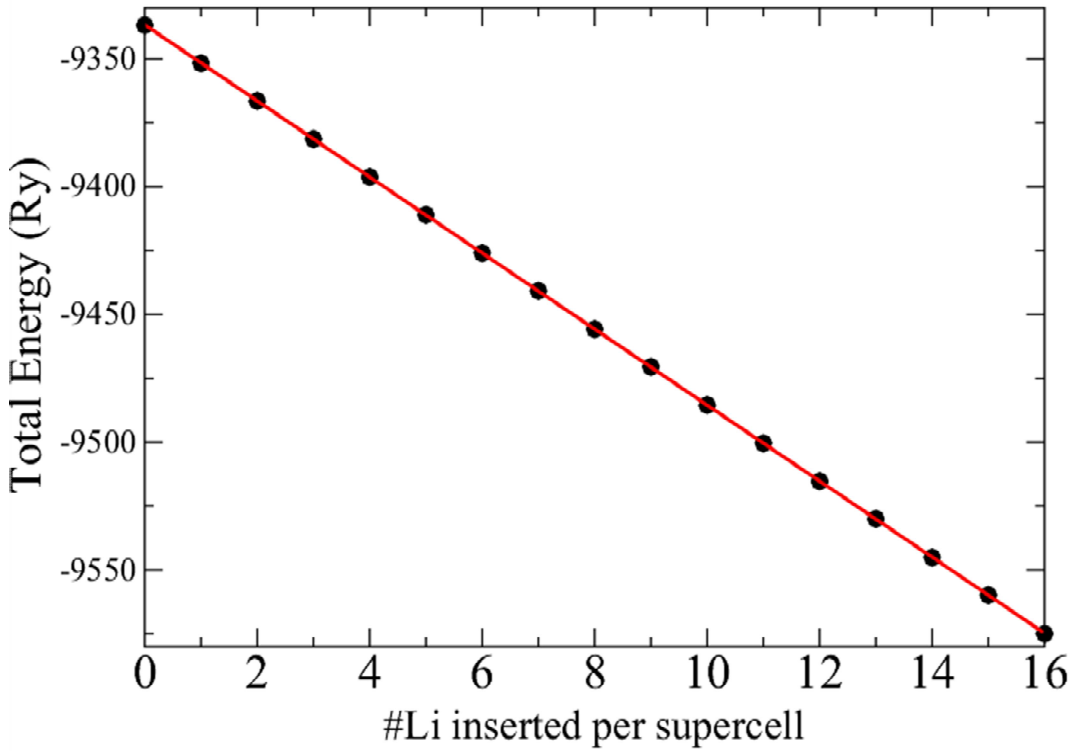




15 Li inserted



Energetics


Total Energy (Ry)
-9350
-9400
-9450
-9500
-9550
0
2
4
6
8
10
12
14
16
#Li inserted per supercell

Energetics

- For each calculation I can write the process as

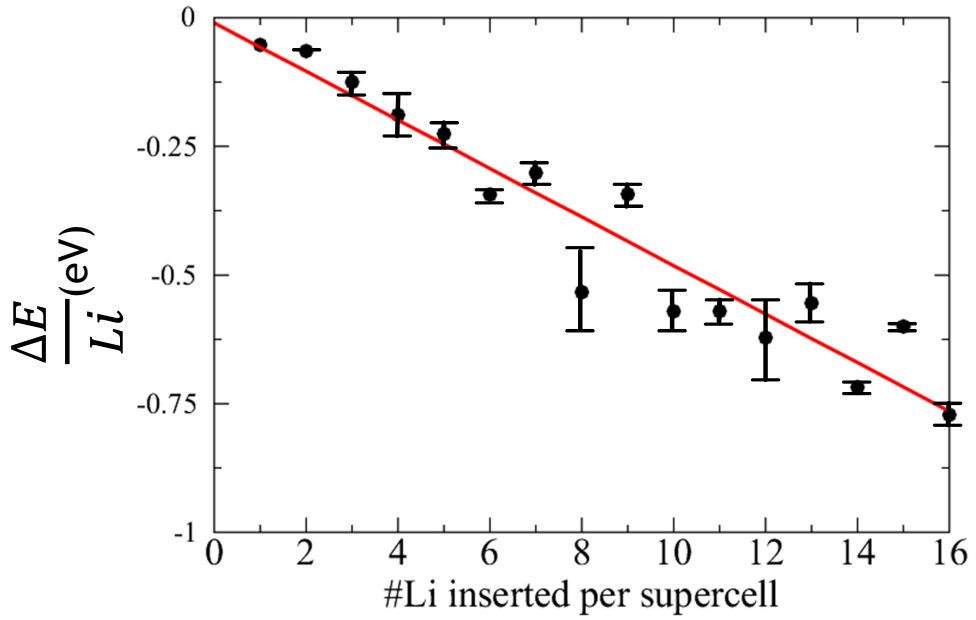
$16 * Li_2SnO_3 + x * Li \rightarrow Li_x[16 * Li_2SnO_3]$, x being the # Li inserted per supercell

I analyzed $\frac{\Delta E}{x} = \frac{E(Li_x[16*Li_2SnO_3]) - E(16*Li_2SnO_3 + x*Li)}{x}$

This shows the insertion process is favorable

And is becoming more so as the #Li inserted

Increases



Conculsions

- Kick out mechanism is likely mechanism for Li-ion conduction
- Experimental samples (**Brant**, **Teo**) measured for Ea not likely to have significant populations of native vacancy interstitial defects
- Li_2SnO_3 – Li interfaces appear to be stable
- Li_2SnS_3 – Li interfaces appear to be unstable
- Bulk Li_2SnO_3 becomes semi-unstable at ≈0.5 Li per formula unit
- Lithiation of Li_2SnO_3 becomes more favorable as the #Li inserted increases

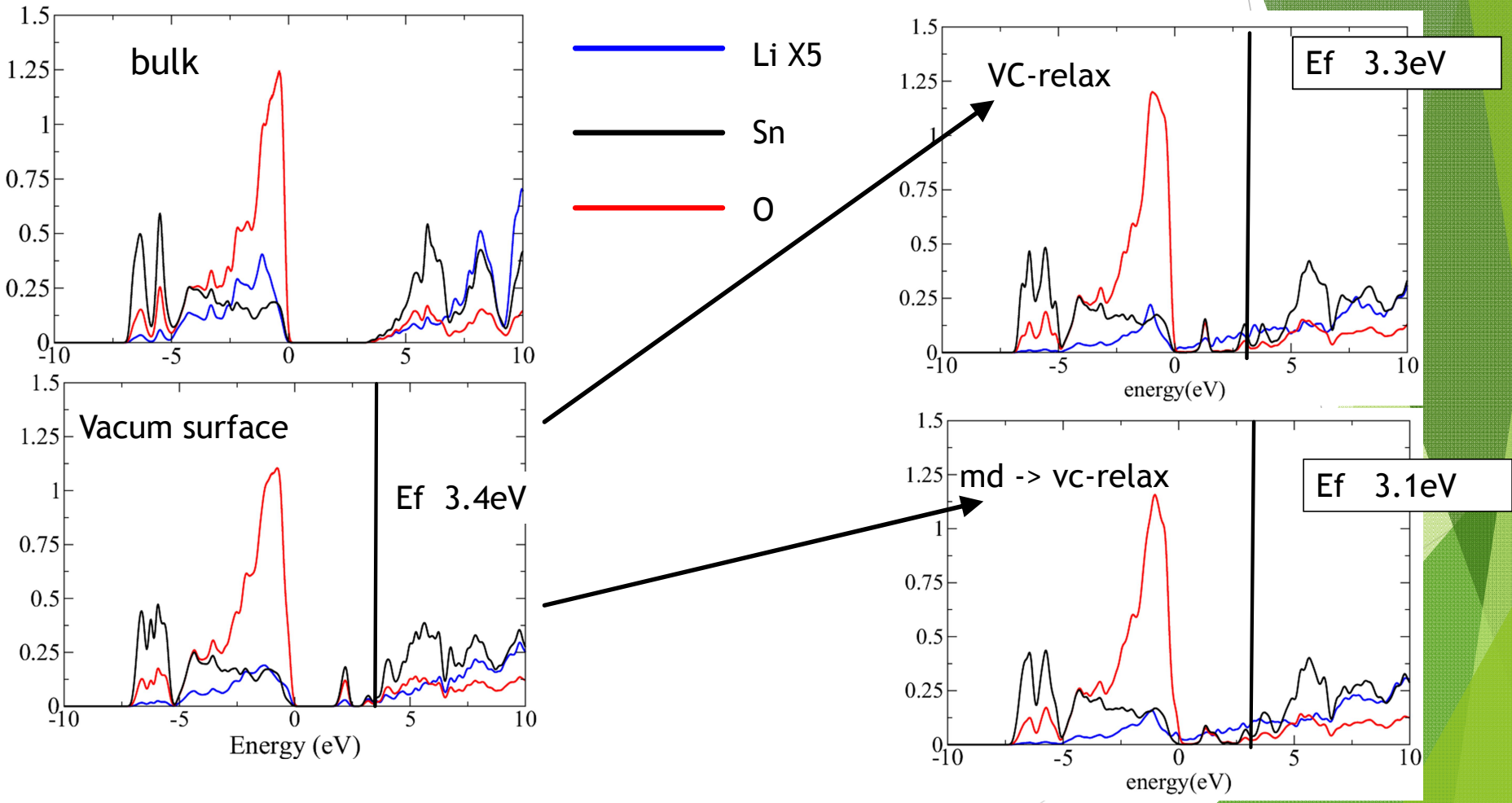
Acknolwedgements

The computational portion of this work was supported by NSF grant DMR-1105485 and 1507942. Computations were performed on the Wake Forest University DEAC cluster, a centrally managed resource with support provided in part by the University.

References

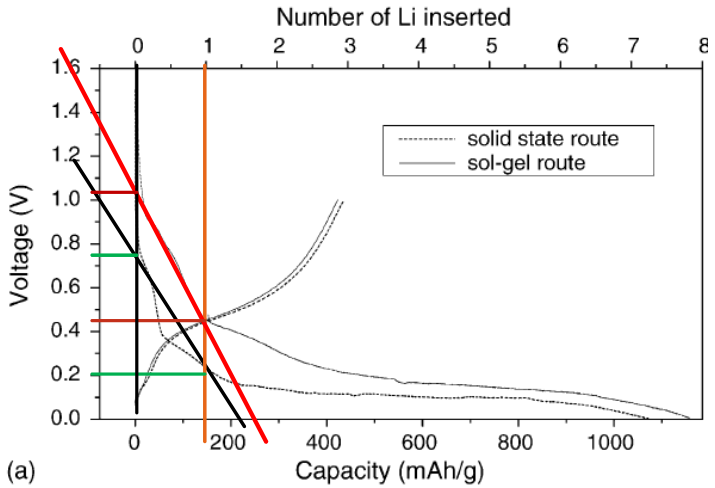
- I.A.Courtney, et al. “Electrochemical and Situ X-Ray Diffraction studies of Reaction of Lithium with Tin Oxide composites”. J. Electrochem. Soc, Vol. 144, No.6, June 1997
- J. A. Brant, et al. “Fast Lihtium Ion Conduction in Li_2SnS_3 : Synthesis, Physicochemical Characterization, and Electronic Structure”. ACSJCa| JCA10.0.1465/W
- L.P.Teo, et al. “Conductivity and dielectric studies of Li2SnO3”. Ionics (2012) 18:655-665
- D.W.Zhang, et al. “Li_2SnO_3 derived secondary Li-Sn alloy electrode for lithium-ion batteries” . Jorunal of Alloys and Compounds 415 (2006)229-233
- Q.Wang , et al. “Preparation of Li_2SnO_3 and its application in lithium-ion batteries”. Surf. Interface Anal, 2013, 45, 1297-1303
- M.K. Aydinol, K. Cho, et al. “*Ab initio* study of lithium intercalation in metal oxides and metal dichalcogenides”. Phys, Rev B. vol 56, no. 3 july 15 1997

Density of States Li2SnO3 interfaces

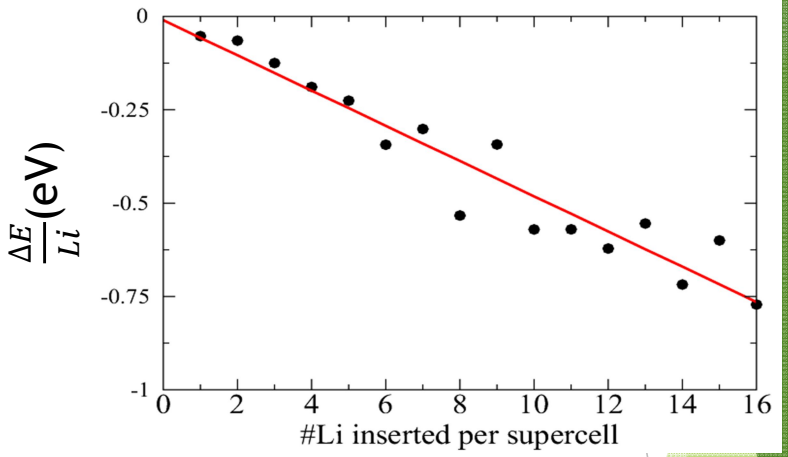


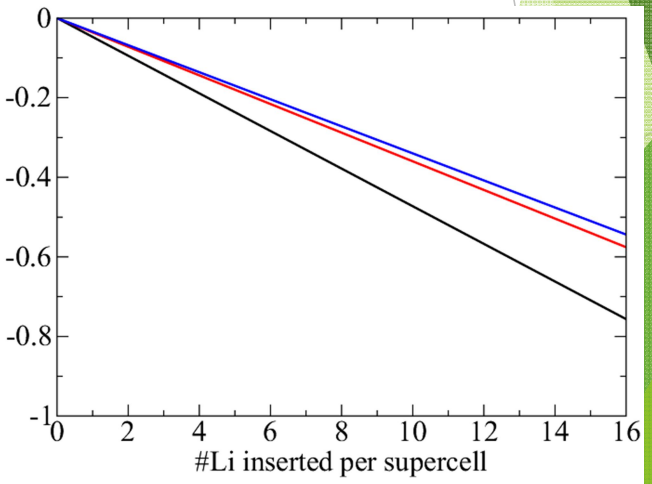
Relating energetics to experiment

- In analyzing my data I found a relationship to a first order approximation to the experimental Voltage vs capacity slope



(Zhang et al., J. Alloy Compd. **415**, 229 (2006))

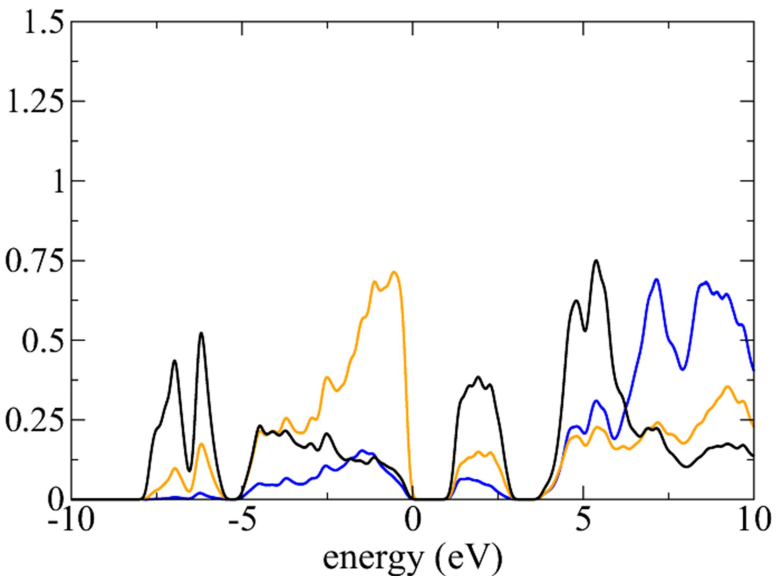




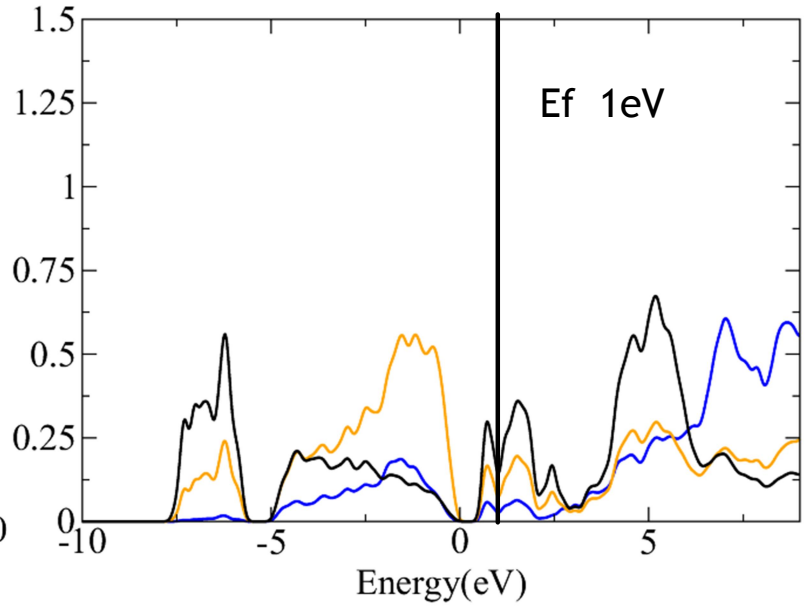
If I subtract the y-intercepts to the fits above I get a fit representing an approximation to the change in Voltage as function of Li inserted

My curve appears to approximate the change in voltage as function of Li inserted for this experiment

Bulk



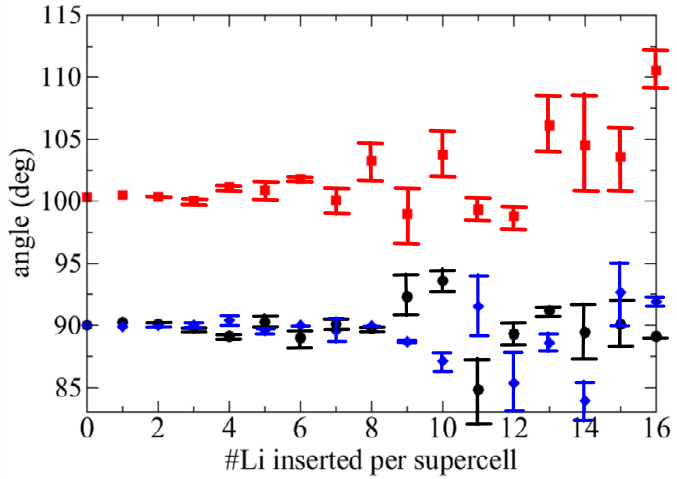
Vacum extra six on surfaces



Li X 5

Sn

S


115
110
105
100
95
90
85
angle (deg)
0
2
4
6
8
10
12
14
16
#Li inserted per supercell

θ(b-c)

θ(a-b)

θ(a-c)