Computational Study of Li$_2$SnO$_3$ and Li$_2$SnS$_3$*

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Background Li$_2$SnO$_3$ and Li$_2$SnS$_3$

- 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))
- Sulfide studied as possible electrolyte 2014
  (Brant et al., CM 27, 189 (2014))

- Ionic conductivity,  
  sulfide $1.6 \times 10^{-3}$ S/cm (373 k)
  oxide $2 - 3 \times 10^{-8}$ S/cm (563 k)
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
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](http://pwpaw.wfu.edu)
- Plane wave expansion for wave functions with Brillouin zone integration mesh of \( 0.003 \text{ bohr}^{-3} |k + G|^2 \leq 64 \text{ Ry} \)
- Ion migration estimated with Nudged Elastic Band (NEB) method. (Hinkleman et al. JCP 113, 9901 & 9978 (2000))
- Visualization software: Xcrysden, VESTA
- Plotting xmgrace, gnuplot
Calculating Ea via vacancy mechanism

- Choose paths of migration:
  a-path: A - B - C - D  
  b-path: E - C - F  
  c-path: G - D - H - I

- Relax vacancy structures

- Run NEB calculations between images
NEB results, extracting $E_m$

- **a-path**
  - $E_m = 0.61\text{eV}$ for Li$_2$SnS$_3$ (oxide)

- **b-path**
  - $E_m = 0.28\text{eV}$ for Li$_2$SnO$_3$

- **c-path**
kick-out mechanism for Li-ion conduction
For the vacancy interstitial defect

\[ E_{\text{defect}} - E_{\text{perfect}} = E_{\text{formation}} \]

- 1.25\( eV \) (\( \text{Li}_2\text{SnO}_3 \))
- 0.96\( eV \) (\( \text{Li}_2\text{SnS}_3 \))
NEB results, Em for kick out

0.22 eV

0.14 eV

oxide

sulfide
\[ Em \leq Ea \leq Em + \frac{1}{2} \times Ef \]

\[ Ef = 1.25 \text{ (oxide)}, \ 0.96 \text{ (sulfide)} \]

<table>
<thead>
<tr>
<th>Li2SnO3</th>
<th>Em</th>
<th>Em + ( \frac{1}{2} \times Ef )</th>
</tr>
</thead>
<tbody>
<tr>
<td>vacancy</td>
<td>0.28</td>
<td>0.91</td>
</tr>
<tr>
<td>Kick-out</td>
<td>0.14</td>
<td>0.77</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Li2SnS3</th>
<th>Em</th>
<th>Em + ( \frac{1}{2} \times Ef )</th>
</tr>
</thead>
<tbody>
<tr>
<td>vacancy</td>
<td>0.61</td>
<td>1.07</td>
</tr>
<tr>
<td>Kick-out</td>
<td>0.22</td>
<td>0.68</td>
</tr>
</tbody>
</table>

- **Experiment**
    - 0.69 - 0.91 eV
  - J.A. Brant, et al. ACSJCa JCA10.0.1465/W
    - 0.59 eV
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  vacancy migration and kick-out mechanism

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  change in volume and cell dimensions

  energetics
• Modeling interfaces with Li help to understand behavior with excess Li at surface

• Can provide insight into electrolyte or anode functionality

• As electrolyte Li$_2$SnS$_3$ 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 vacuum calculation
  Six extra lithium left on each surface, $24 \times (\text{Li}_2\text{SnO}_3) + 12 \times \text{Li}$

**Li$_2$SnS$_3$ Vacuum Volume $\approx 8300$ bohr$^3$**

**Li$_2$SnO$_3$ Vacuum Volume $\approx 4500$ bohr$^3$**
Li$_2$SnO$_3$ - Li interfaces

VC-relax, cell-do free “Z”

-14716.9205 Ry, ref 0 eV

MD 300k 38 fs $\rightarrow$ VC-relax, cell-do free “Z”

-14716.8014 Ry, $+1.62$ eV
Li$_2$SnS$_3$ - Li interfaces

Unconverged
Overview

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  vacancy migration  and kick-out mechanism

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  energetics
• Goal is to better understand decomposition process for Li2SnO3
Lithiation of Li$_2$SnO$_3$

- Li$_2$SnO$_3$ has been studied as electrode (Courtney, Zhang, Wang)
  
  1. Li$_2$SnO$_3$ + 4Li $\rightarrow$ 3Li$_2$O + Sn 
  2. 3Li$_2$O + Sn + 4.4Li $\rightarrow$ 3Li$_2$O + Li$_{4.4}$Sn

- First cycle irreversible

- Decomposition Occurs between 0.4 - 1.75 Li inserted per Li$_2$SnO$_3$ (Zhang et al., J. Alloy Compd. 415, 229 (2006))

- Residual lithium oxide matrix said to stabilize further cycles

- I studied beginning of decomposition
Modeling Lithiation up to 1 Li inserted per formula unit Li$_2$SnO$_3$

- 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

- a axis
- c axis
- b axis

15 Li inserted
Energetics

![Graph showing the total energy (Ry) as a function of the number of Li inserted per supercell. The graph displays a linear decrease in energy as the number of Li increases.](image)
Energetics

- For each calculation, I can write the process as

\[ 16 \times Li_2SnO_3 + x \times Li \rightarrow Li_x[16 \times Li_2SnO_3], \quad x \text{ being the # Li inserted per supercell} \]

I analyzed \[ \frac{\Delta E}{x} = \frac{E(Li_x[16 \times Li_2SnO_3]) - E(1 \times Li_2SnO_3 + x \times Li)}{x} \]

This shows the insertion process is favorable.

And is becoming more so as the #Li inserted increases.
Conclusions

• 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$_2$SnO$_3$ - Li interfaces appear to be stable

• Li$_2$SnS$_3$ - Li interfaces appear to be unstable

• Bulk Li$_2$SnO$_3$ becomes semi-unstable at ≈0.5 Li per formula unit

• Lithiation of Li$_2$SnO$_3$ becomes more favorable as the #Li inserted increases
Acknowledgements

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References


• Q. Wang, et al. “Preparation of Li2SnO3 and its application in lithium-ion batteries”. Surf. Interface Anal, 2013, 45, 1297-1303

Density of States Li$_2$SnO$_3$ interfaces

- **bulk**
- **Vacum surface**

**Energy (eV)**

- Li X5
- Sn
- O

**Vacum surface**

- **Ef 3.4eV**

**VC-relax**

- **Ef 3.3eV**

**md -> vc-relax**

- **Ef 3.1eV**
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
Vacuum extra six on surfaces

Bulk

Energy (eV)

-10 -5 0 5 10

Ef 1eV

Li X 5
Sn
S

Energy (eV)

-10 -5 0 5

1.5 1.25 1 0.75 0.5 0.25 0

0.75 0.5 0.25 0
θ(b-c)
θ(a-b)
θ(a-c)