Determining the Relationship Between Crystal Structure and Ionic Conductivity of Solid-State Electrolytes

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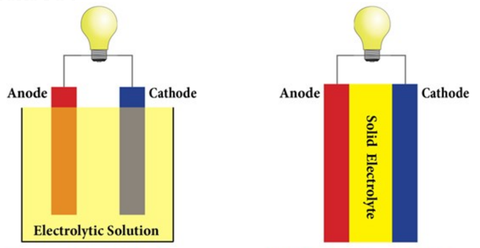
Motivation

- **Li-ion batteries lead the battery market** due to their high ionic conductivity (in the order of 1 [mS cm^{-1}]).
- Traditional Li-ion batteries are made of **organic liquid electrolytes, rendering them flammable**.



- **Superionic conductors**, or solid-state electrolytes or solid-state conductors, are **a safer, non-flammable alternative** to traditional Li-ion batteries.
- However, the **ionic conductivities of solid-state electrolytes are not yet competitive** with those of traditional Li-ion batteries.
- Our research seeks **to develop specific criteria** (based on crystal structure) for **systematically identifying better superionic conductors**.

Background

Ionic Conductivity is the movement of ions through a crystal structure. For superionic conductors, **ions "hop" between interstitial sites.** Best existing ionic conductivities for Li-ion SSC so far:

- Oxide-based in range of 10^{-3} to 1 [mS cm^{-1}]
- **Sulfide-based above 1 [mS cm^{-1}]**

Arrhenius relationship:

- Ionic conductivity (σ)
- Change in energy / **Activation energy (E)**
- Temperature (T)

$$\sigma = Ae^{\frac{-\Delta E}{kT}}$$

Activation energy:

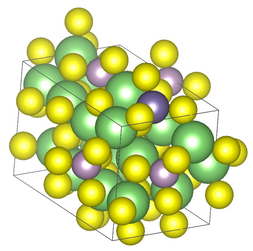
- Def: **Amount** of energy necessary for an ion to "hop" from one interstitial site to another
- Decrease activation energy → increase ionic conductivity → ions move more easily

References

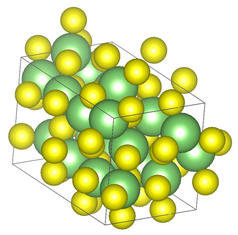
[1] Wang et al.,"Design principles for solid-state lithium superionic conductors". (17 August 2015)
[2] https://chargedevs.com/newswire/toyota-researchers-develop-all-solid-state-li-ion-batteries/
[3] https://fidimag.readthedocs.io/en/latest/nebm.html
[4] http://cmt.dur.ac.uk/sjc/thesis_ppr/node12.html

Methods

- Began with premise from Wang et al. "Design Principles for solid-state lithium superionic conductors" (2015) that **superionic conductors can be mapped to simple frameworks of anions** (bcc, fcc, hcp).



$Li_{10}GeP_2S_{12}$

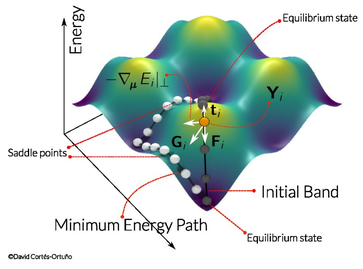


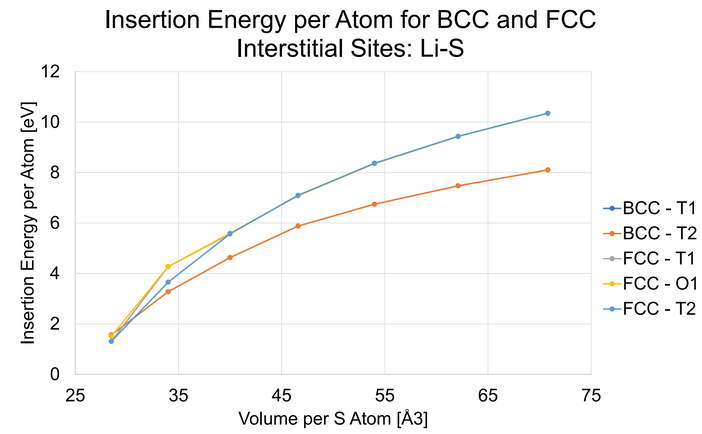
$Li_{10}GeP_2S_{12}$ with Ge & P removed

- **Density Functional Theory (DFT)**
  - Gives the **ground state energy** of a crystal structure
  - Hohenerg-Kohn Theorem: the external potential $v_{ext}(\mathbf{r})$, and hence the total energy, is a unique functional $E[n(\mathbf{r})]$ of the electron density $n(\mathbf{r})$:

$$E[n(\mathbf{r})] = \int n(\mathbf{r})v_{ext}(\mathbf{r})d\mathbf{r} + F[n(\mathbf{r})]$$

- **Nudged Elastic Band Method (NEB)**
  - Gives the **energy landscape and activation energy** by finding the energy at various points along a path

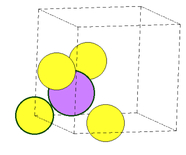




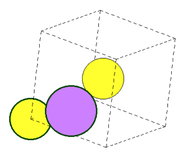
Used **DFT calculations** to **find relationship between activation energy and unit cell volume**.

$$E_{Insertion} = E_{S+Li} - E_{S-sublattice} - E_{Li}$$

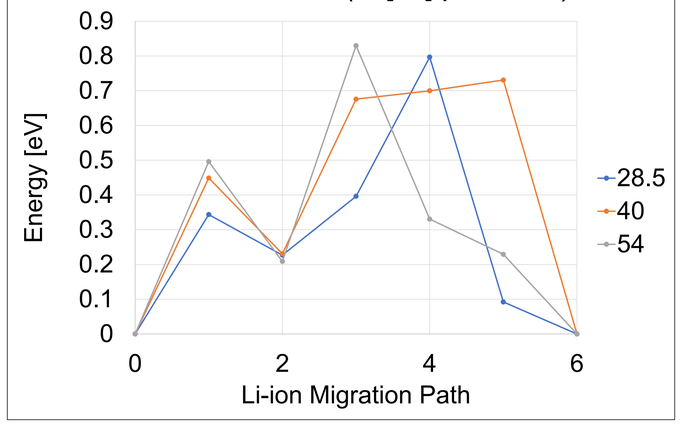
- **With increased volume per S**, the distance between Li-ions and anions in the sub-lattice increases, resulting in **decreased attractive force and a decrease in overall energy**
- **FCC insertion energies are higher** than the BCC curves **because the distance between Li-ions and the sub-anion lattice is smaller**, and thus **the attractive forces are greater**, for each volume than for the BCC cases. Example: For the case where volume = 40 [Å^3] per atom:



FCC, d = 2.351 [Å^3]

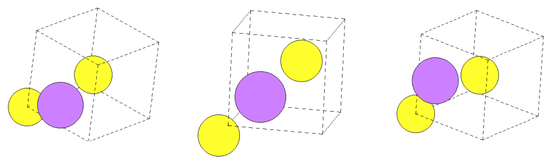


BCC, d = 2.409 [Å^3]

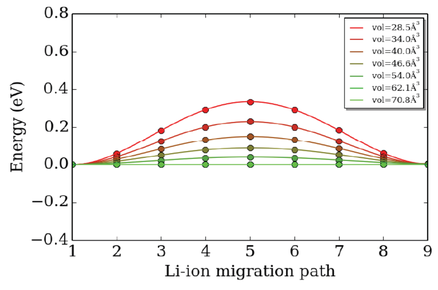


Used **NEB calculations to find energy landscapes**

- **Low energy landscape → high ionic conductivity**
- **Results so far not as expected;** will need to continue refining calculation settings. Should match plots from *Wang et. al.*



Path of Li-ion through BCC S sub-anion lattice



Conclusions & Future Work

- Our plot of Insertion Energy vs. Volume supports *Wang et. al.*'s conclusion that **BCC structures have better ionic conductivity**
- **Will repeat calculations with Na^+ & Mg^{2+} ions and with O^{2-} & Se^{2-} sub-anion lattices** to see if relationships hold true for other ions and anion lattices
- **Will verify relationship** between crystal structure and ionic conductivity by **performing Ab Initio Molecular Dynamics simulations** for various existing superionic conductors

Acknowledgements

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