Tin Sulfide as a Battery Anode

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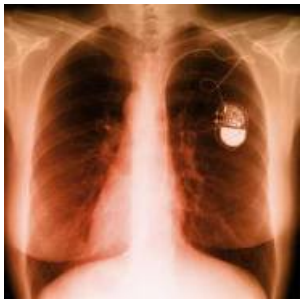
Motivation

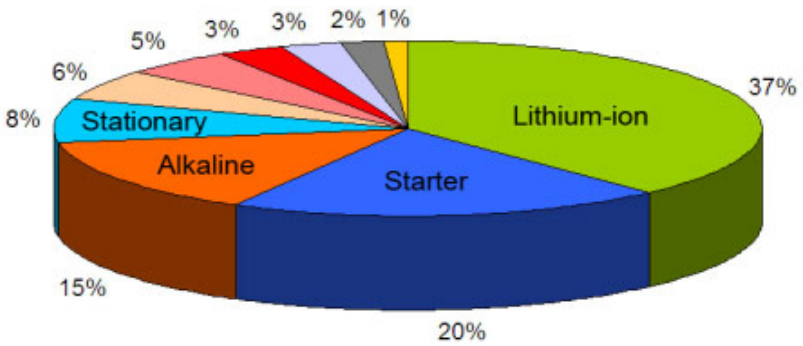


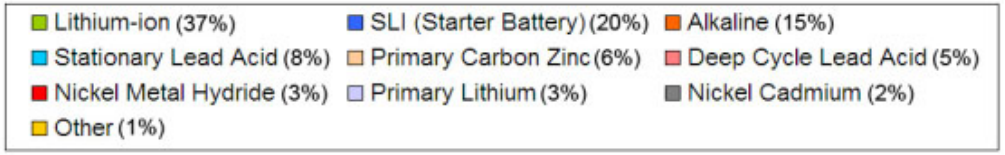
- Lithium ion batteries are currently the most advanced and powerful rechargeable batteries for consumer electronic products.

- As the technology industry rapidly expands there is an insatiable demand for longer-lasting and faster-charging batteries.

Why Lithium?

- Lighter than other materials
- Most commercially viable chemistry for PHEVs
- Highly reactive with much higher energy and power density
- No “memory effect” as in NiCd
- Design flexibility and safest in use
- Environmentally friendly





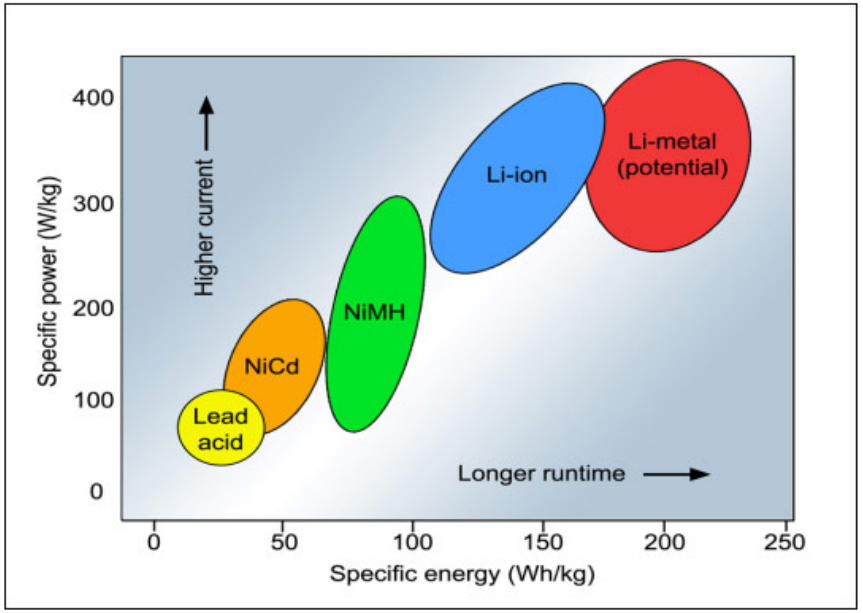
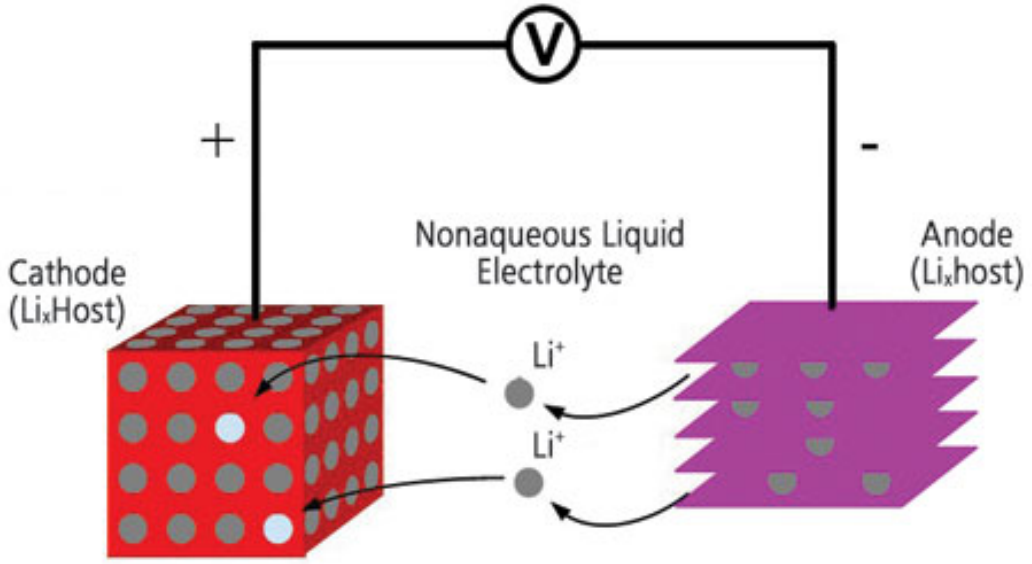


Figure 1*: Revenue contributions by different battery chemistries

*Frost & Sullivan (2009)

Research

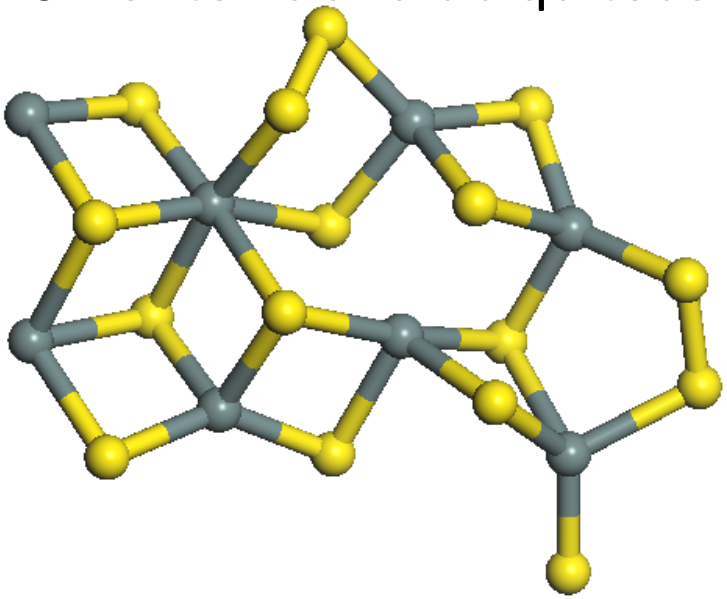
- Investigate lithium sorption in different materials using computational chemistry
- Determine the ability of new materials to serve as rechargeable lithium battery anodes



Why Tin Sulfide?

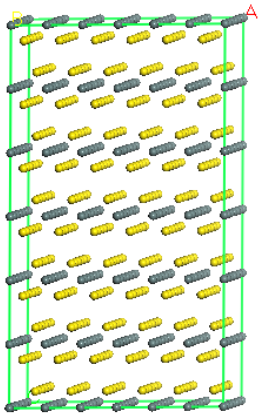
- Battery anodes are of particular interest as the anode material has principal influence on the performance of lithium ion batteries.
- Explore tin sulfide as potential battery anode material
  - Low cost
  - High theoretical specific capacity
  - Nontoxic and ubiquitous

converged Sn_8S_{16} cluster



Momma, Toshiyuki, Nobuhiro Siraishi, Atsuhito Yoshizawa, Tetsuya Osaka, Aharon Gedanken, Junjie Zhu, and Lena Sominski. "SnS2 anode for rechargeable lithium battery." 29 January 2001. *Journal of Power Sources.* 23 June 2014.

Crystal Structure



- Layered, hexagonal crystal structure
- Consists of 2 layers of close packed sulfur anions with tin cations between them in octahedral coordination
- (0 0 1) plane configuration

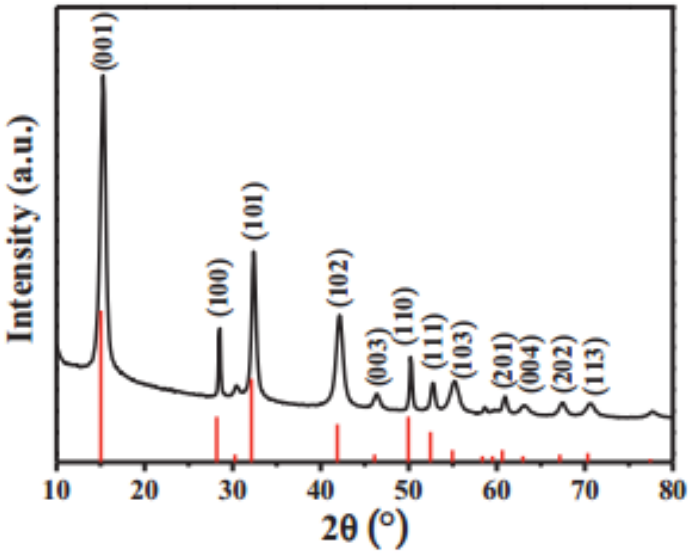
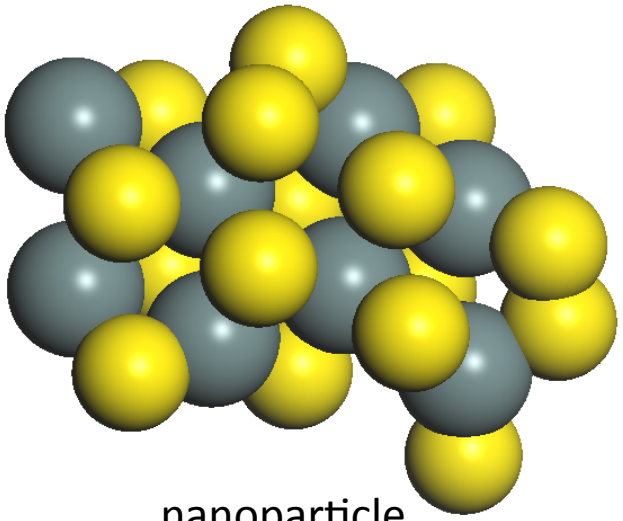


Fig. 1. XRD patterns of SnS_2-200-10.5 (the bottom of the image indicates the JCPDS data (JCPDS: 23-0677) for SnS_2).

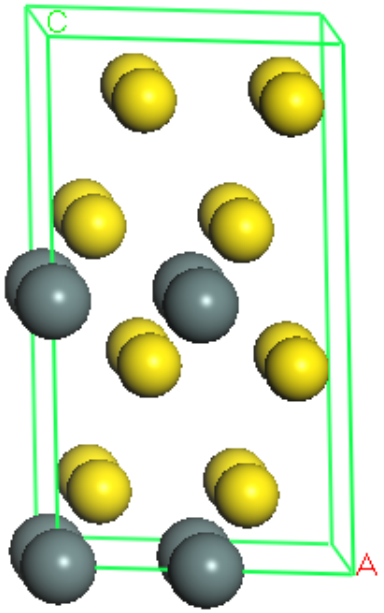
Kim, Tae-Joon, Chunjoong Kim, Dongyeon Son, Myungsuk Choi,and Byungwoo Park. "Novel SnS2 - nanosheet anodes for lithium-ion batteries." 27 February 2007. *Journal of Power Sources.* 25 June 2014.

Objectives

- Examine structural changes of nanoparticle and crystalline SnS_2 upon Li adsorption.
  - Study differences between intercalation, conversion, and alloying
- Calculate voltages as a function of Li content along with capacity and compare with experiment



nanoparticle

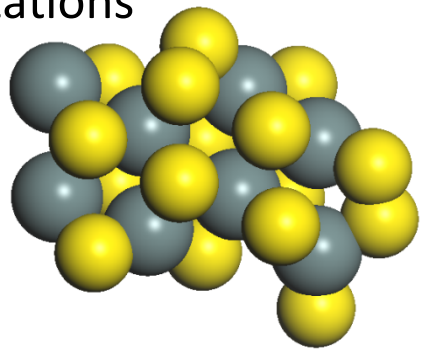


Crystalline system

Approach

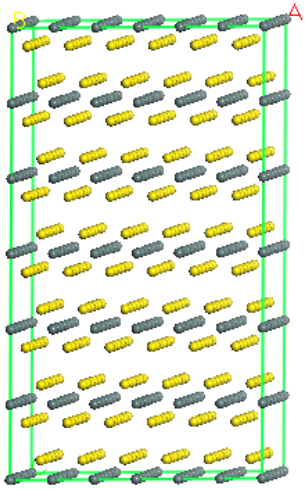
- Computational studies of Li adsorption on tin sulfide nanoparticles
  - Materials Studio 6 DMol3 used for computations
    - PBE GGA functional, DNP basis set

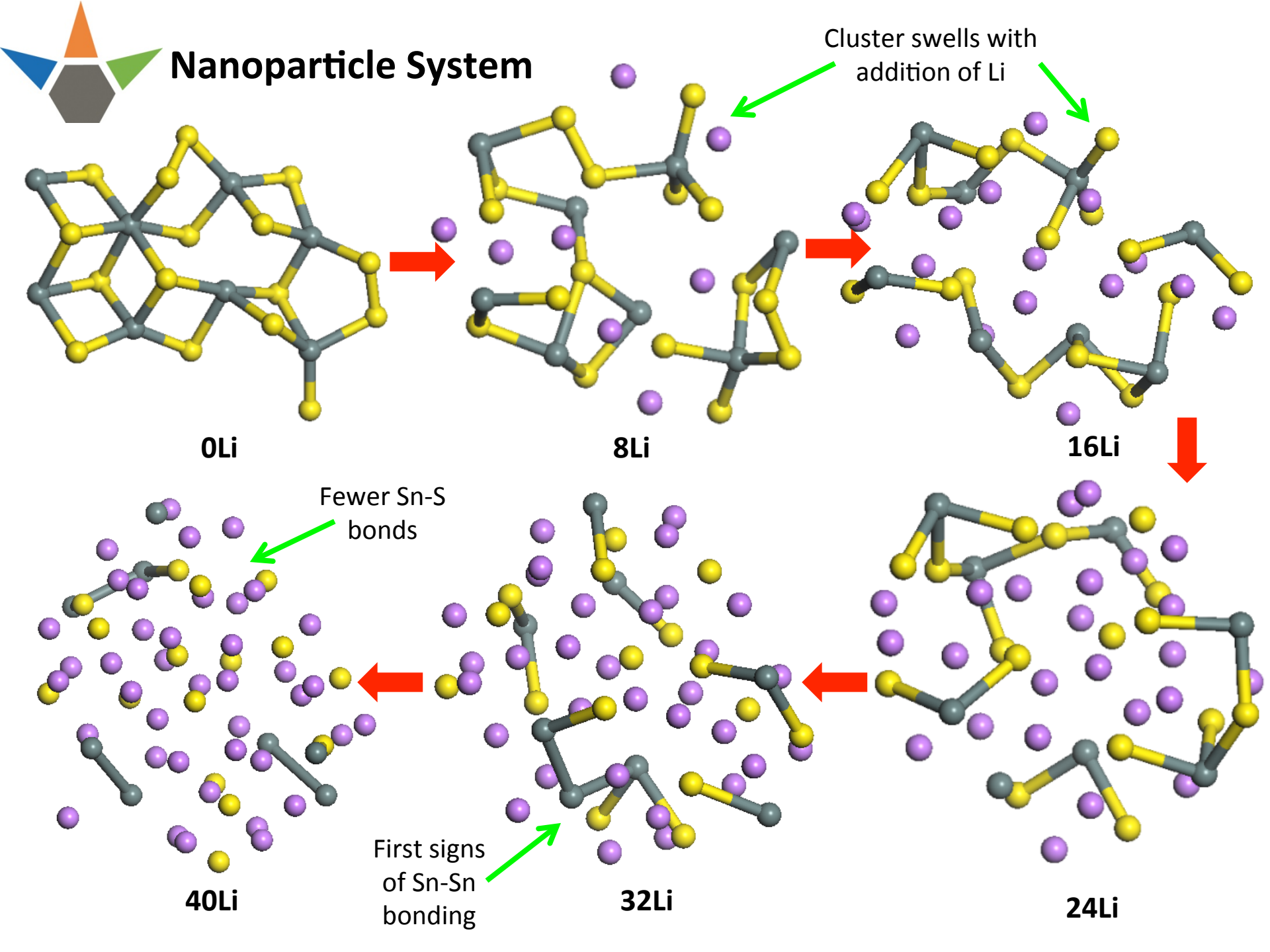
MATERIALS STUDIO



- Computational studies of Li adsorption on tin sulfide periodic crystalline systems
  - VASP (Vienna *ab initio* simulation package)
    - PBE GGA functional, plane wave basis set, Monkhorst-Pack k-point sampling

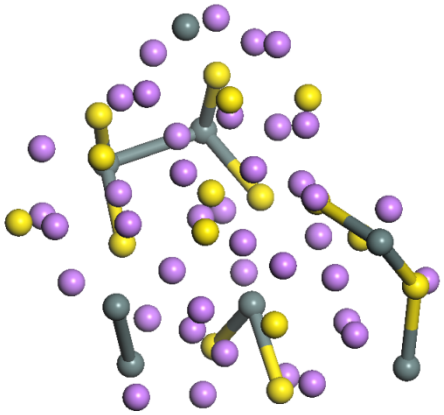
b-initio VASP ackage ienna imulation




Nanoparticle System
Cluster swells with addition of Li
0Li
8Li
16Li
24Li
32Li
40Li
Fewer Sn-S bonds
First signs of Sn-Sn bonding

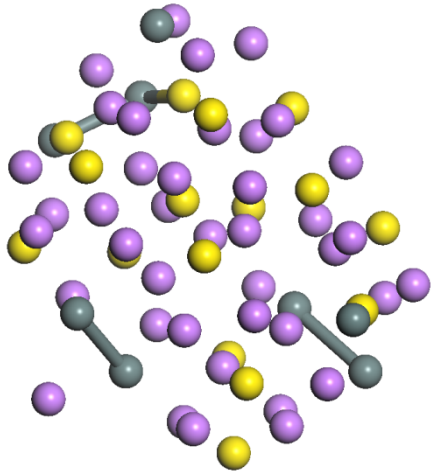
Optimization Steps

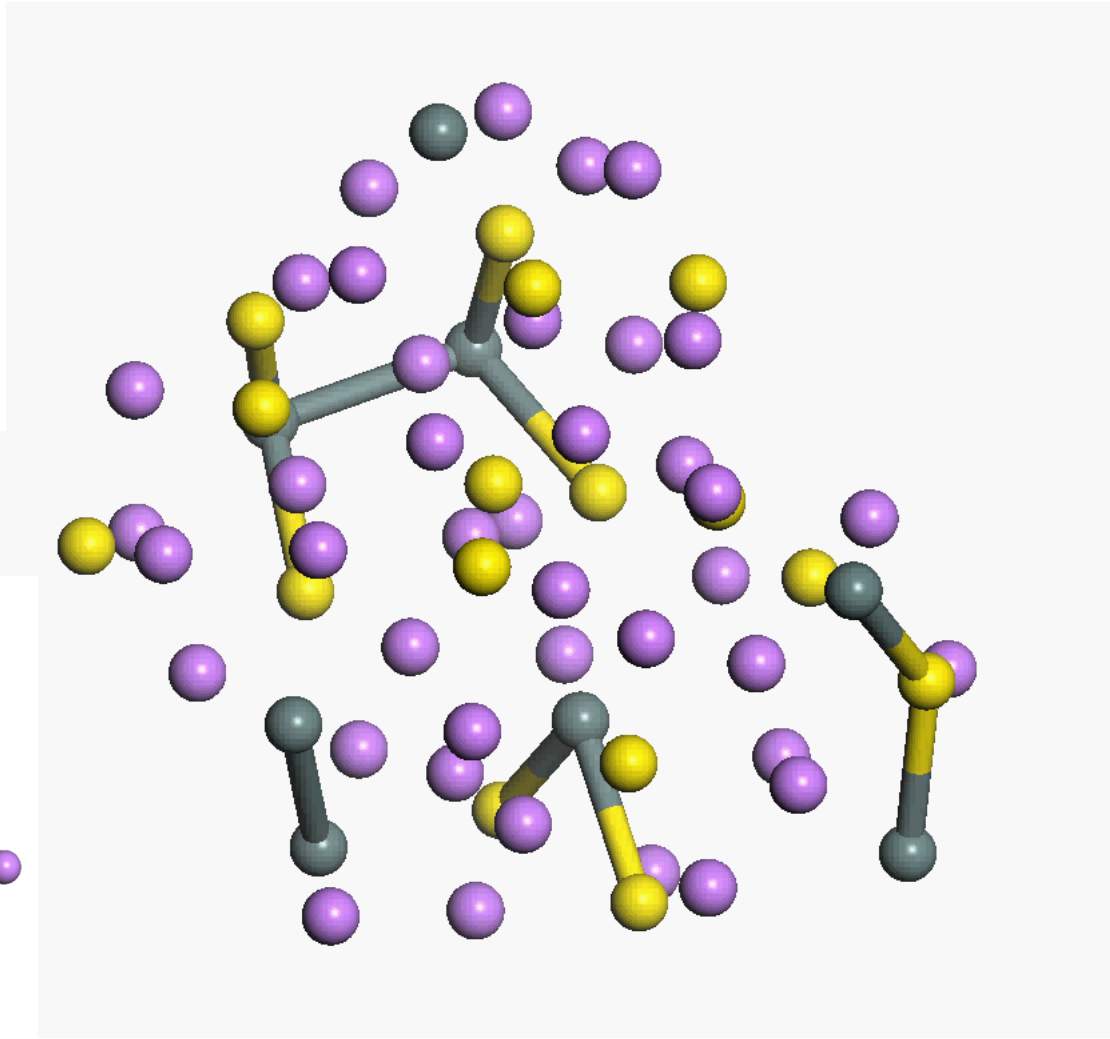
input



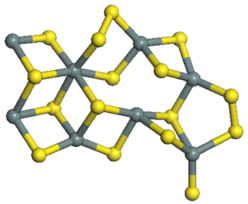
40Li

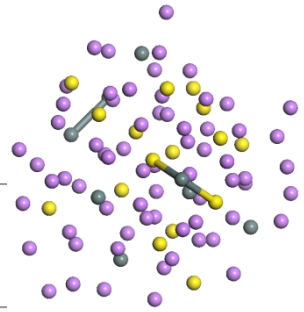
converged

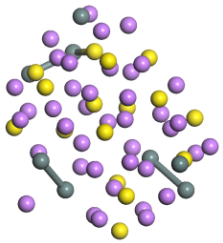




Cluster Bond Distances

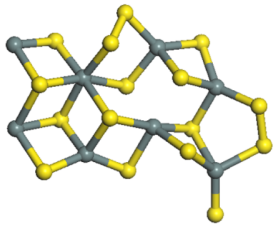






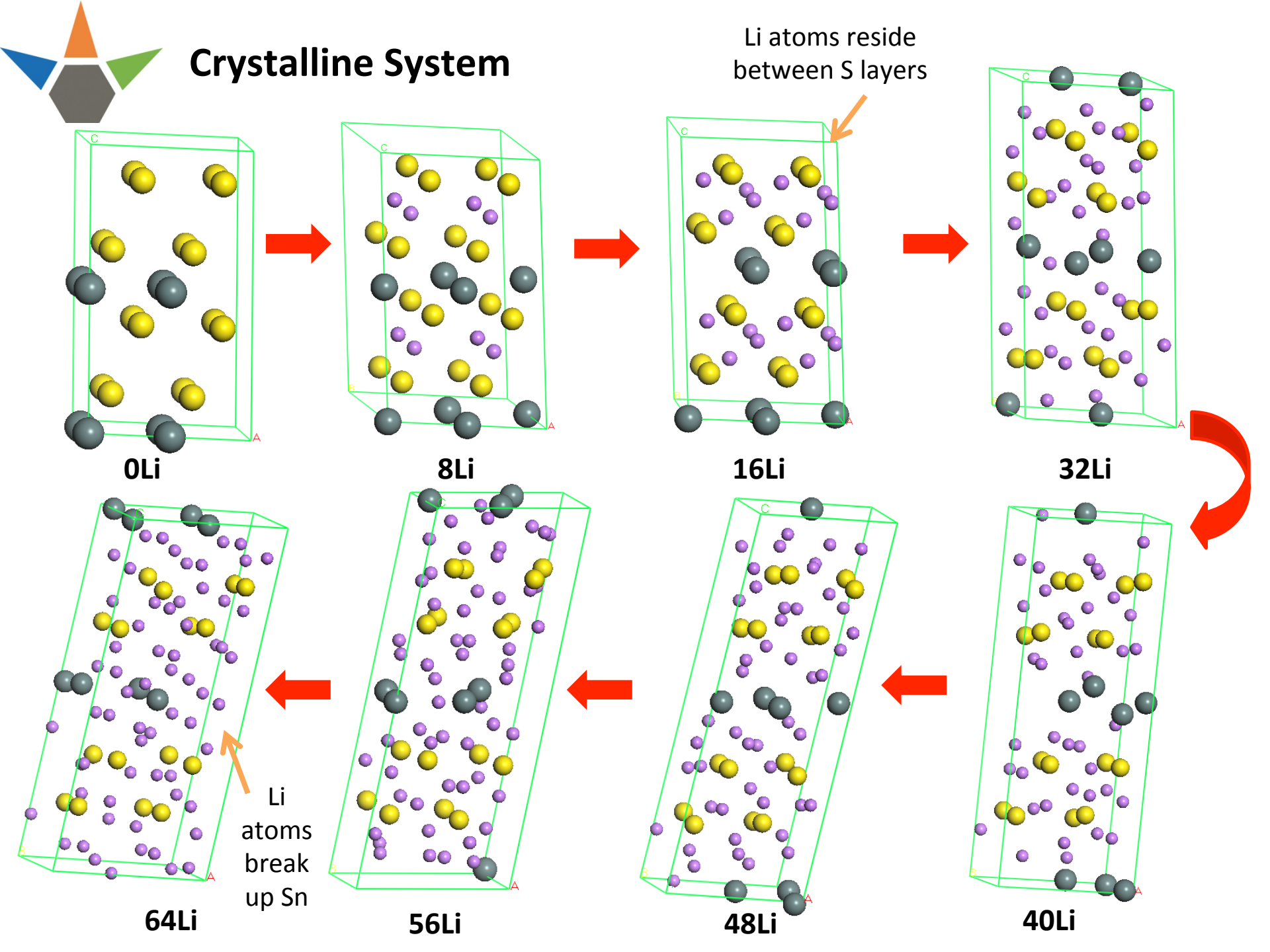
- Calculated bond distances between atoms in the $Li_X(SnS_2)_8$ nanoparticle.
- As Li is added, Sn and S are being pushed apart with concomitant formation of Li-Sn bond (alloying)

Cluster Atom Analysis

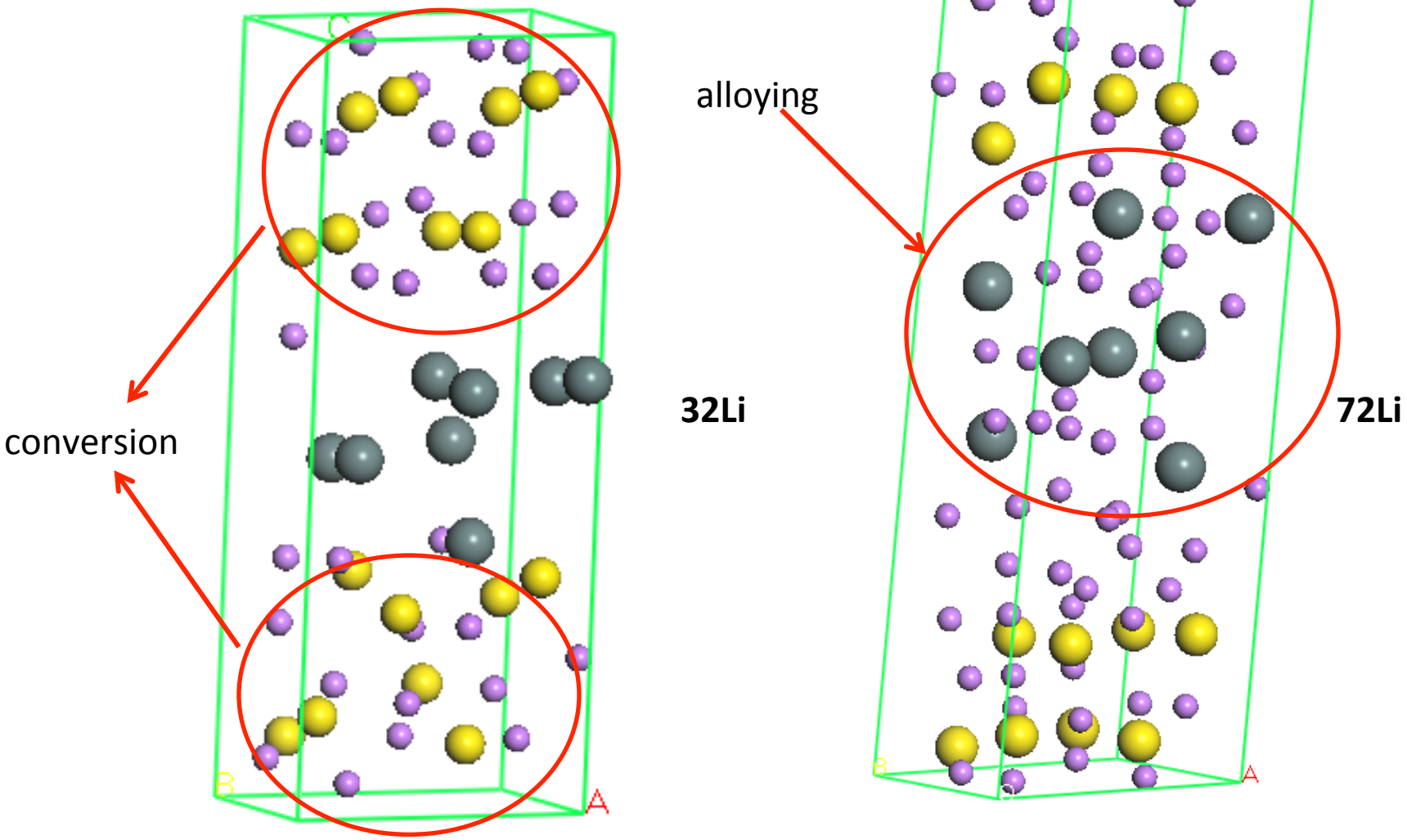


- As more Li is added the number of Sn-S decreases while the number of Sn-Li increases
- Around an 8:1 Li:Sn ratio the number of Sn-Sn and Sn-S bonds drastically decreases

Crystalline System

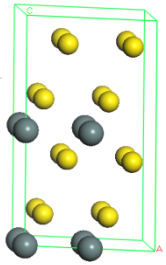


Sn8 island S16

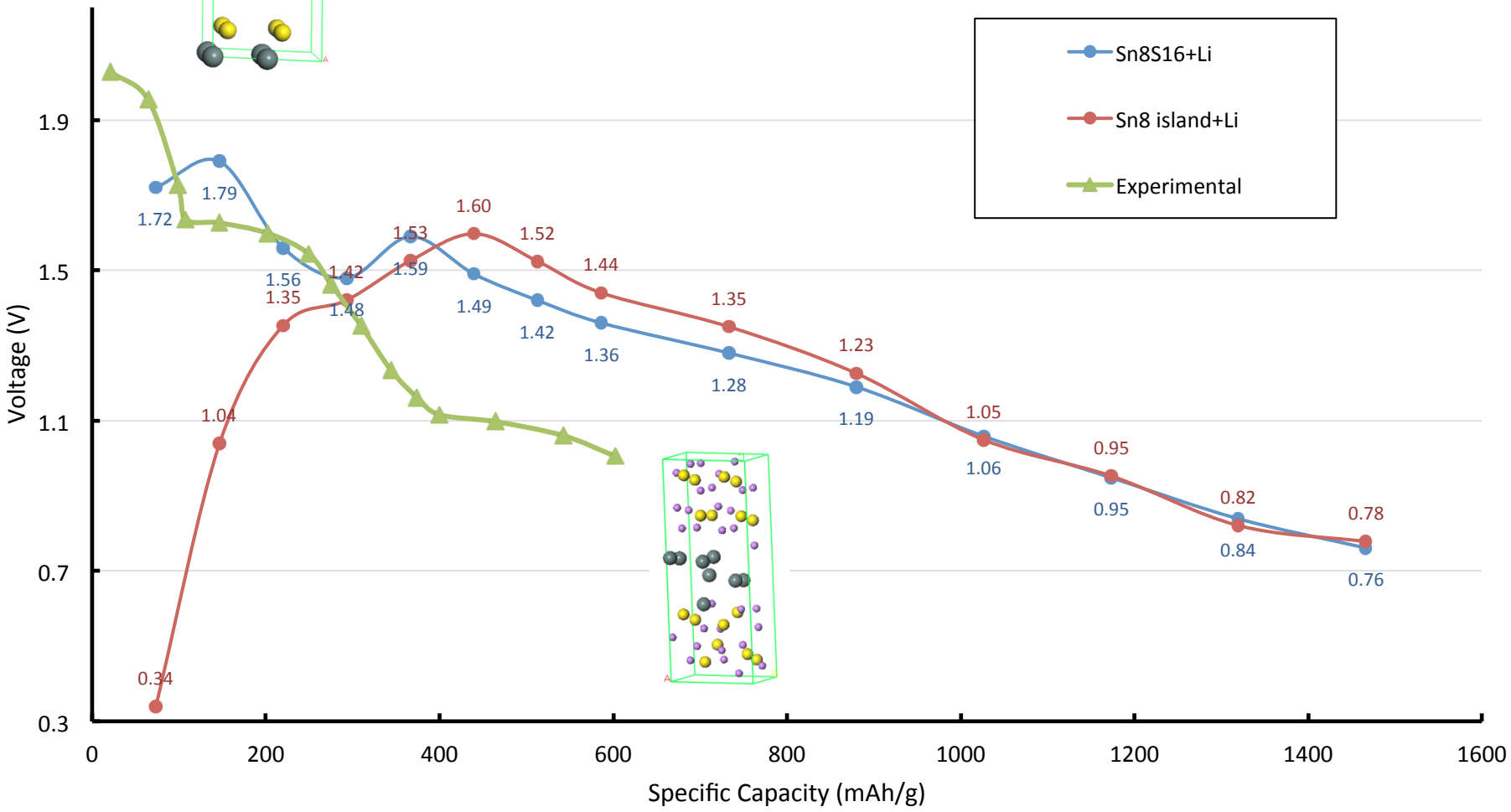


- Starting from the 32 Li system $(Li_2S)_{16}(Sn)_8$, Li atoms were added and removed to access the range of 8 Li to 72 Li.

Voltages



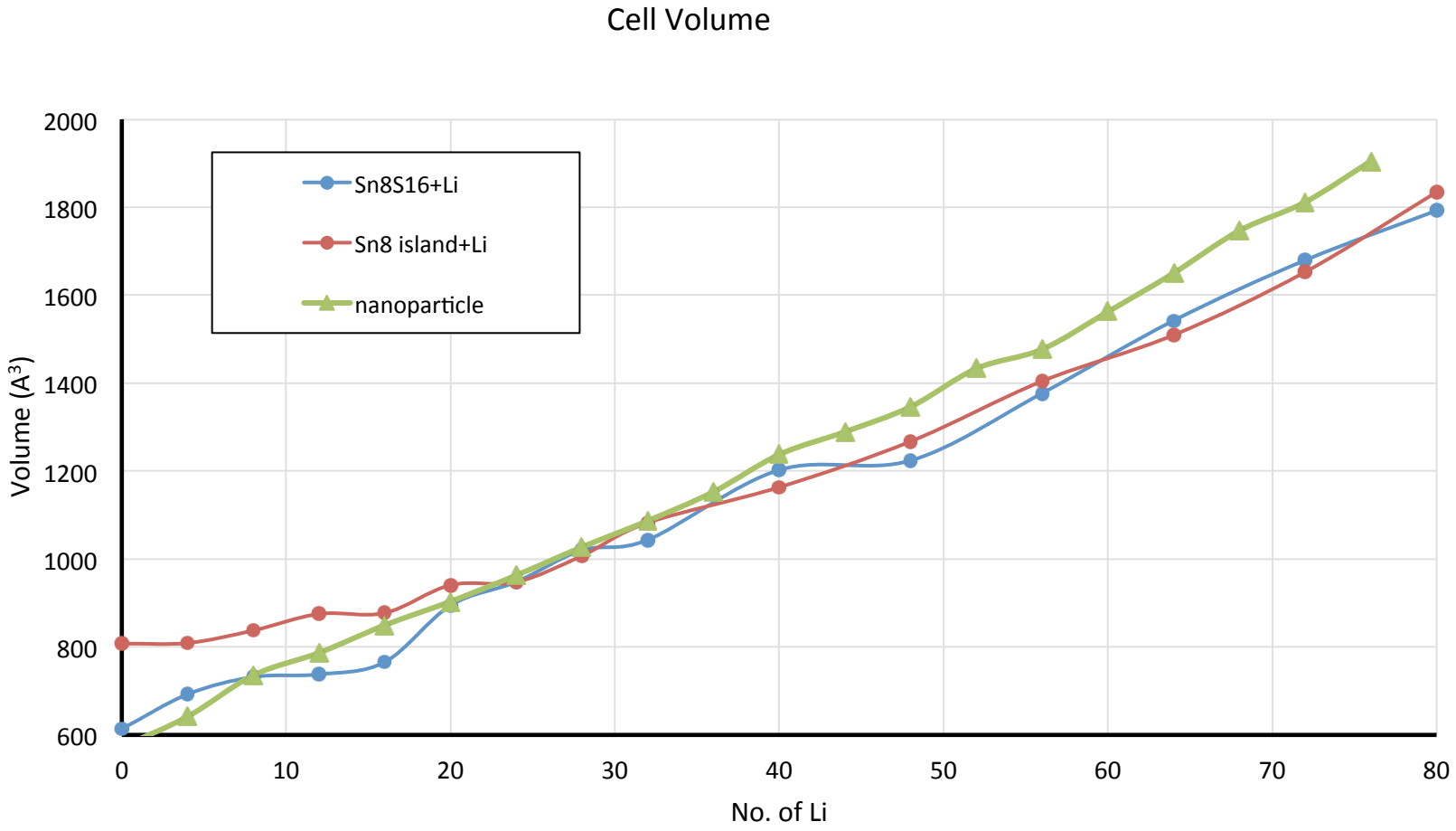
SnS_2 + Li voltages



Nernst Equation

$$E(\mathrm{V}) = \frac{\left[G^{\circ}_{(\mathrm{MO}_2)_n} + G^{\circ}_{\mathrm{Li}} - G^{\circ}_{(\mathrm{MO}_2)_n \mathrm{Li}} \right] \mathrm{J\ mol^{-1}}}{xF(\mathrm{C\ mol^{-1}})}$$

Volume Expansion



Conclusions

- For nanoparticles and crystalline systems as Li content increases, mechanism changes from adsorption/intercalation to conversion to alloying.
- Qualitative agreement between experimental and calculated discharge curves.
- The volume expansion trends of the nanoparticle and crystalline system are similar