

## Abstract

Li alloy forming elements such as Sn, Sb, In & Al have attracted significant interest as prospective anode materials due to fact that they have a larger theoretical capacity than graphite, the most popular commercial anode material at present.<sup>1</sup> While tin oxide (SnO<sub>2</sub>) has been studied extensively, tin sulfide (SnS<sub>2</sub>) has been examined to a much lesser extent. Details of the mechanisms by which SnS<sub>2</sub> functions is unclear, although a combination of conversion, and alloying mechanisms have been proposed.<sup>2, 3</sup> We used first principles computational studies to calculate discharge curves for the sorption of lithium in nanoparticle and crystalline systems of (SnS<sub>2</sub>)<sub>n</sub>. These have qualitative agreement with experimental discharge curves for SnS<sub>2</sub> nanosheets. The molecular level analysis of the nanoparticle and crystalline systems reveal that they behave in similar ways at higher Li content. Both of them displayed a transition from conversion to alloying as more Li atoms were added. For the crystalline system, intercalation up to a 2:1 Li:Sn ratio was observed. Beyond a 2:1 Li:Sn ratio, conversion was visible as lithium sulfide began to form as Li infiltrated into the S layers. Beyond a 4:1 Li:Sn ratio, the crystalline system showed clear signs of Sn-Li alloying. Both conversion and alloying are shown to be thermodynamically feasible (i.e., yield positive voltages) for fairly large capacities.

## Computational Methods

### Nanoparticle System

•The preferred structure, energetics, and electronic properties of the (SnS<sub>2</sub>)<sub>8</sub> nanoparticle system were assessed in the DMol3 program in the Materials Studio 6.0 suite utilizing DFT with the Generalized Gradient Approximation (GGA) with the PBE functional.<sup>4</sup>

•The double numerical polarization (DNP) basis set along with the effective core potential were employed.

•The voltage profile and presence or absence of volume expansion of the (SnS<sub>2</sub>)<sub>8</sub> nanoparticle upon Li adsorption were examined, and a bond distance analysis was performed.

•All calculations were performed on Louisiana Optical Network Initiative (LONI) supercomputers.

### Crystalline System

•Periodic DFT calculations were completed using the Vienna Ab initio Simulation Package (VASP),<sup>5</sup> using the PBE form of the GGA<sup>4</sup> in conjunction with the projector augmented wave pseudopotential method.<sup>6, 7</sup>

•A "working cell" of stoichiometric (SnS<sub>2</sub>)<sub>8</sub> was constructed from the optimized SnS<sub>2</sub> unit cell. Li atoms were added to the working cell in succession, and optimized by relaxing the ionic coordinates, cell shape, and volume of the structures with the conjugate gradient method.

•The reference energy for a single Li atom was determined from the Li unit cell energy

Equation 1. Nernst Relationship for voltage calculation:<sup>8</sup>

$$E(V) = \frac{[G_{(MO_2)_n}^\circ + G_{Li}^\circ - G_{(MO_2)_n Li}^\circ]}{xF(C \text{ mol}^{-1})} \text{ mol}^{-1}$$

## Acknowledgements

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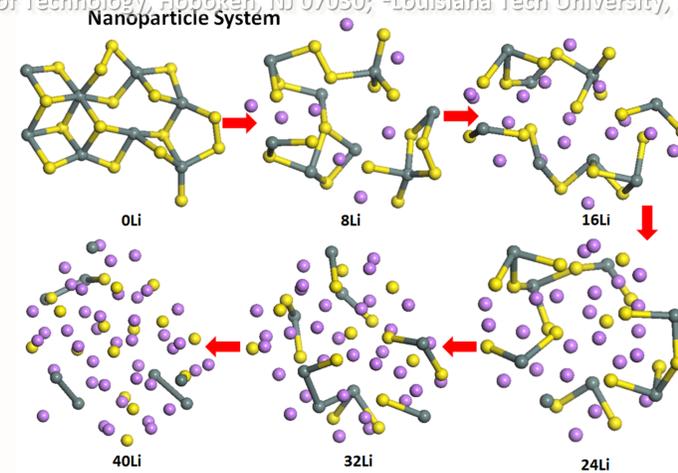


Figure 1: Optimized structures of (SnS<sub>2</sub>)<sub>8</sub> nanoparticles with varying numbers of added lithiums. Sn atoms are gray, Sulfur yellow, and lithium atoms purple.

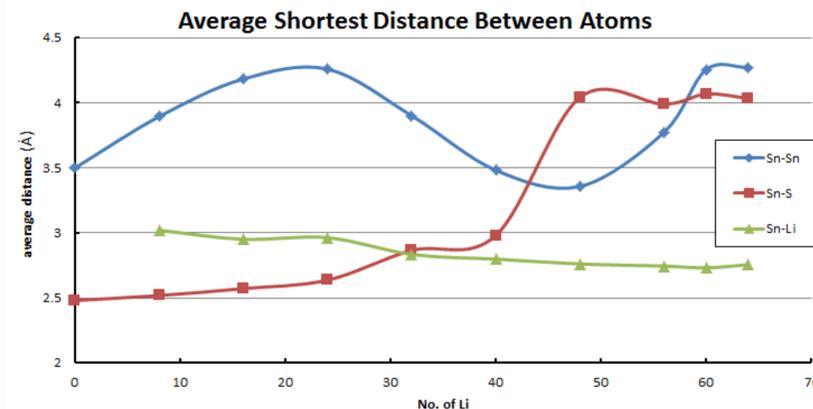


Figure 2: Calculated bond distances between atoms in the Li<sub>x</sub>(SnS<sub>2</sub>)<sub>8</sub> nanoparticle. As Li is added, Sn and S are being pushed apart with concomitant formation of Li-Sn bond (alloying), an effect which accelerates around Li:Sn ratio of 5:1.

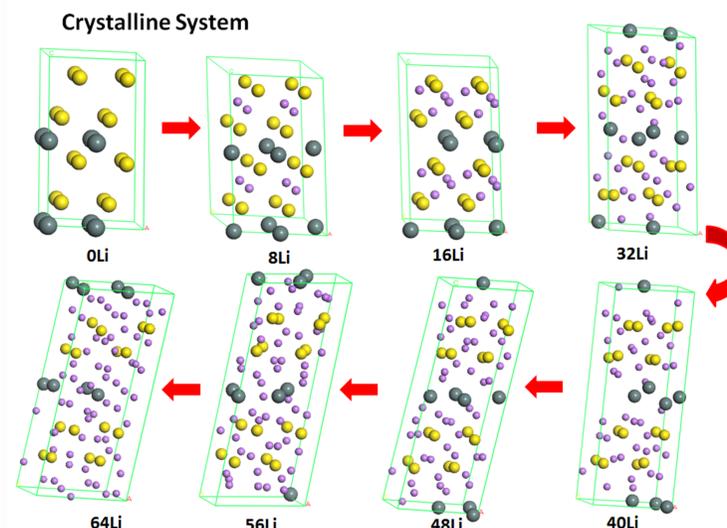


Figure 3: Optimized structures of crystalline (SnS<sub>2</sub>)<sub>8</sub> with varying numbers of intercalated lithiums. Li preferentially occupy the S layers up to Li:Sn ratio of 4:1 (conversion), but shows signs of alloying with Sn at higher Li content.

## Objectives

- Examine structural changes of SnS<sub>2</sub> nanoparticles with addition of Li and the thermodynamic stability of the resulting phases as reflected in voltages relative to Li|Li<sup>+</sup>.
- Examine structural changes of crystalline SnS<sub>2</sub> with addition of Li and the thermodynamic stability of the resulting phases as reflected in voltages relative to Li|Li<sup>+</sup>.
- Compare calculated voltages with experimental results as a function of Li content (capacities) in the electrode.
- Examine if Sn or S environment changes upon Li adsorption.
- Study the thermodynamic stability of the end products of the conversion reaction (Sn and Li<sub>2</sub>S) as a function of Li content (capacities) in the electrode.

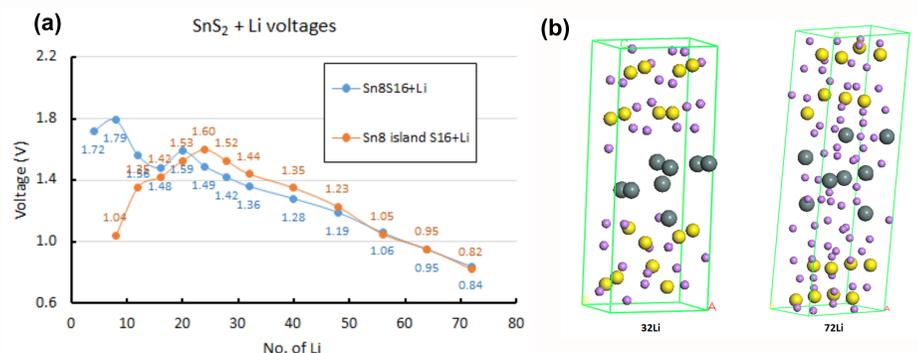


Figure 4: (a) 1<sup>st</sup> discharge curves for crystalline SnS<sub>2</sub> against Li|Li<sup>+</sup>. The blue line represents voltages for the systems shown in Fig. 3. The orange line represents voltages calculated for a (Sn)<sub>8</sub> island in Li<sub>2</sub>S. Starting from the 32 Li system (Li<sub>2</sub>S)<sub>16</sub>(Sn)<sub>8</sub> shown in panel (b), Li atoms were added and removed to access the range of 8 Li to 72 Li. At high Li content, especially beyond 5:1 Li:Sn ratio, Sn-Li alloying becomes apparent.

## Discussion

### Nanoparticle System

- With the addition of successive Li, the voltages of the Sn8S16 nanoparticle decrease.
- Addition of Li atoms appears to swell the nanoparticle and the volume of the (SnS<sub>2</sub>)<sub>8</sub> nanoparticle increases.
- As more Li are added to the (SnS<sub>2</sub>)<sub>8</sub> nanoparticle, the Sn-Sn and Sn-S bond distances increase.
- At high Li concentrations, i.e., beyond 5:1 Li:Sn ratio, average Sn-S distance increases dramatically while Li-Sn distance decreases, indicating alloying.

### Crystalline System

- First 8 Li intercalated (1:1 Li:Sn ratio) into Sn8S16 with minimal distortion.
- Intercalation up to 2:1 Li:Sn ratio causes minor distortion of the crystal structure.
- Conversion to Li<sub>2</sub>S was visible with further addition of Li beyond a 2:1 Li:Sn ratio. At lower Li concentrations, between a 2:1 and 5:1 Li:Sn ratio, the Li atoms reside between the S layers.
- At higher Li content, exceeding the 5:1 Li:Sn ratio, the Li enter into the layer of Sn and Sn alloying becomes visible.

### Conclusion

- Qualitative agreement between experimental and calculated discharge curves.
- Conversion is shown to be thermodynamically feasible.

## References

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