Investigations of RuO_2 and SnO_2 nanoclusters as potential lithium ion battery electrode materials

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About Me:

- Carnegie Mellon University
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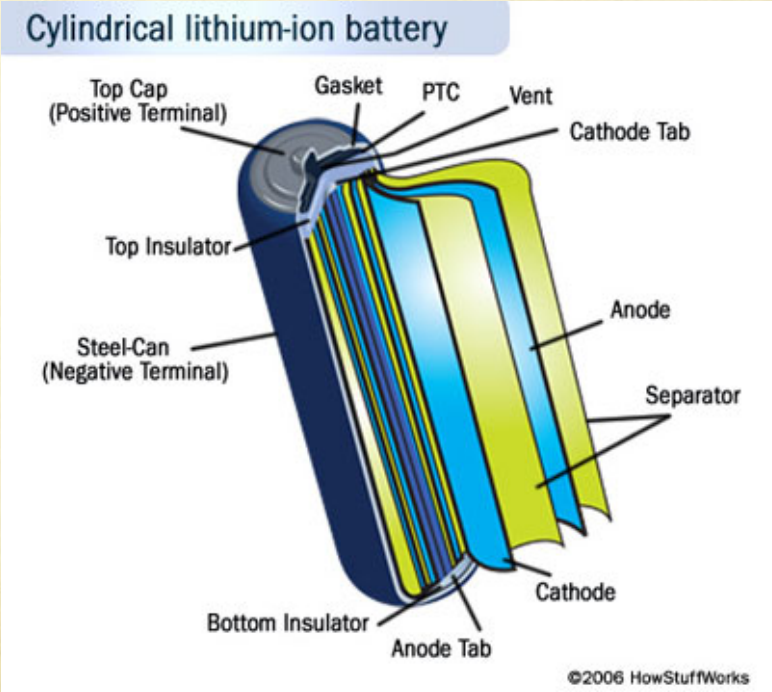
Superiority of Lithium-ion Batteries

- Li-Ion batteries have a higher energy density than Ni-Cad
- Are safely charged and discharged, allowing rechargeability
- Have a longer lifespan that Ni-Cad and self-discharge is slower
- The battery is low maintenance
- Quicker charge times



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Uses of Li-ion Batteries

- Cell Phones
- Laptops
- Heart rate monitors
- Mobile Devices…

- Car Batteries
  - Hybrid Technology
- Generators
  - Consumer
  - Industrial
    - Hospitals
    - Airports…

Effect of metal oxide coating

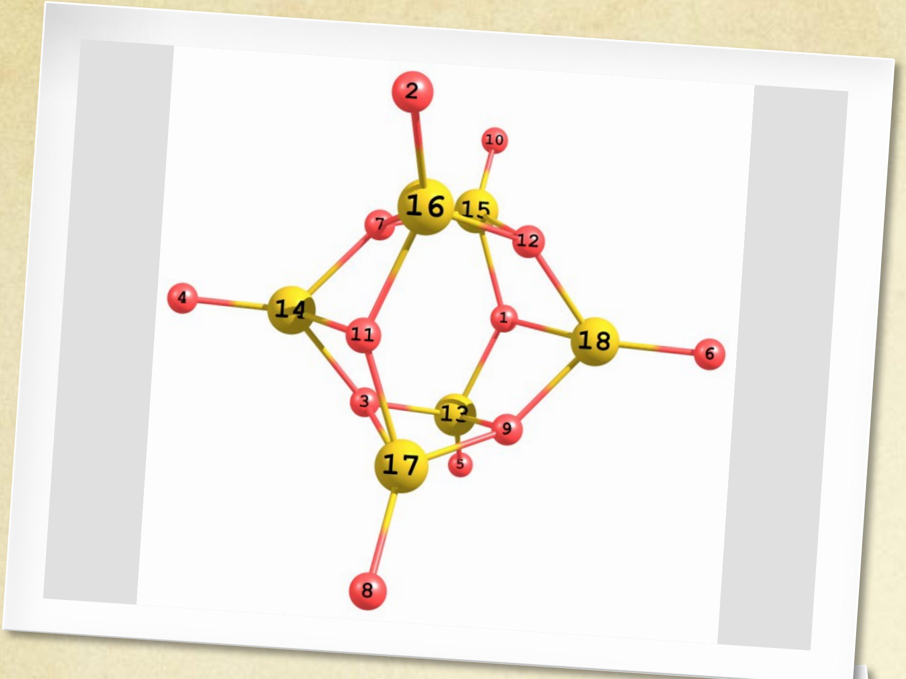
- The use of metal oxide coatings can increase the output voltage of batteries
- Increase stability and longevity
- Increase efficiency

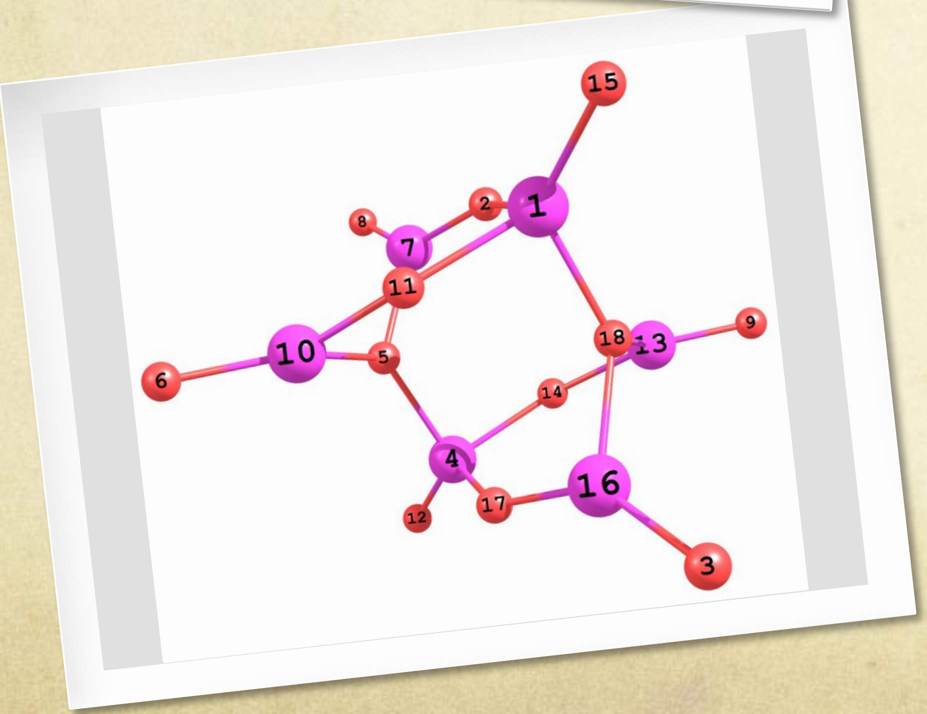
Will allow for:

- Better Hybrid and Electric Car technology
- Longer lasting mobile devices
- Greener battery technology
- More compact cells

Ruthenium and Tin Oxide electrode coatings

- Studied $(SnO_2)_6$ and $(RuO_2)_6$ as possible coatings
  - Optimized Ru and Sn oxide structures and added Li to observe structural and energy changes
- Tin oxide has been extensively studied for use
  - Low cost
  - Promising Lithium-ion adsorption voltages
- The problem with tin oxide coatings is that charging and discharging result in large conformational changes that destabilize the coating, which results in a very short life cycle
- Due to the tin oxide coating instability tin nano-particles were explored
- Ruthenium was studied as a replacement because:
  - Ru has low resistivity (about 40 $\mu\Omega$ m)
  - Good thermal stability up to 800 °C
  - Chemically stable.





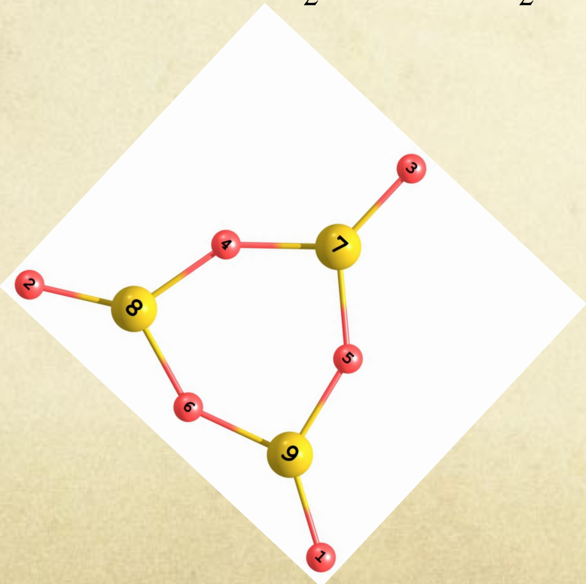
Sn_6O_{12} and Ru_6O_{12} Optimized Structures

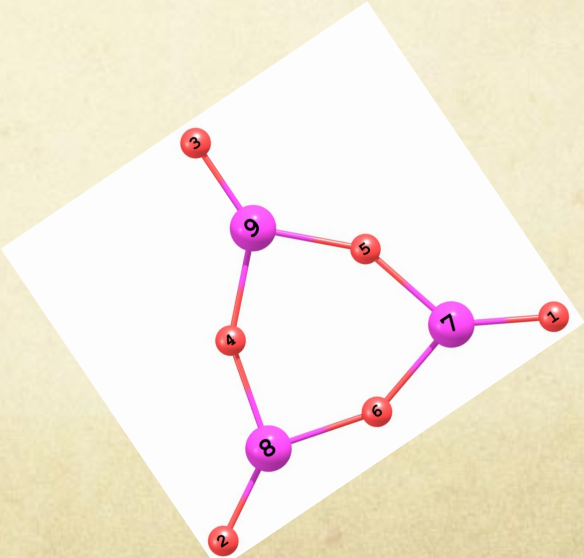
Yellow = Sn

Purple = Ru

Objectives

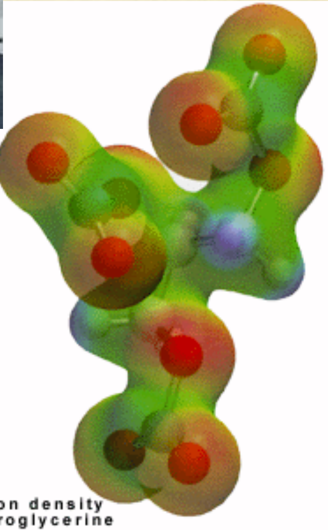
- Determine the preferred structure, energies, and electronic properties of small RuO_2 and SnO_2 clusters.
- Calculate voltages associated with Li ion adsorption
- Examine if Ru/Sn or O environment changes upon Li adsorption
- Consider the possibility of forming hypothetical Li-ion battery cells made of RuO_2 and SnO_2 electrodes





Computational Method

- Used Gaussian 09 to optimize structures
- Method: Density Functional Theory
  - Density Functional Theory is a method for obtaining electronic structure and properties of molecules from the total electron density rather than the wave function.
  - LA-SiGMA senior investigator John Perdew at Tulane is a pioneer and major contributor in this field.
- Functional: M06
  - The M06 functional was developed in Minnesota in 2006 by Don Truhlar's research group.
- Confirmation of local minimum by frequency calculations showing no imaginary frequencies.



The electron density of nitroglycerine

Location of Li adsorption

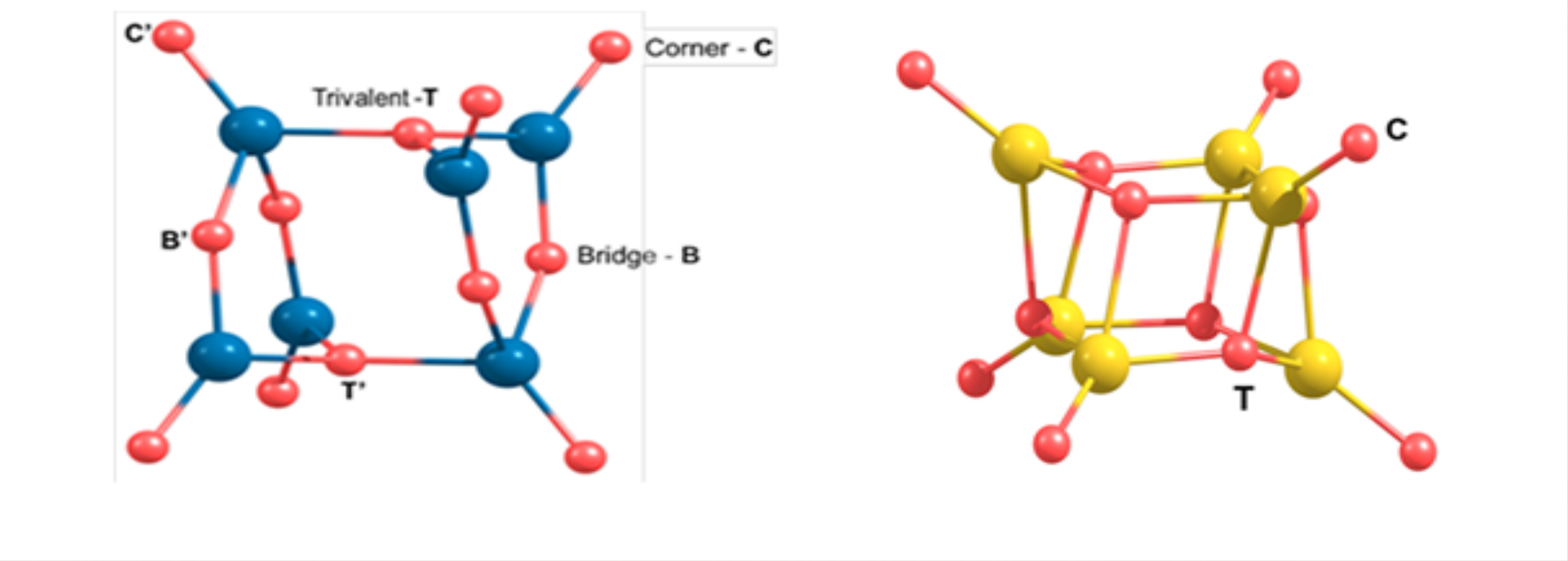
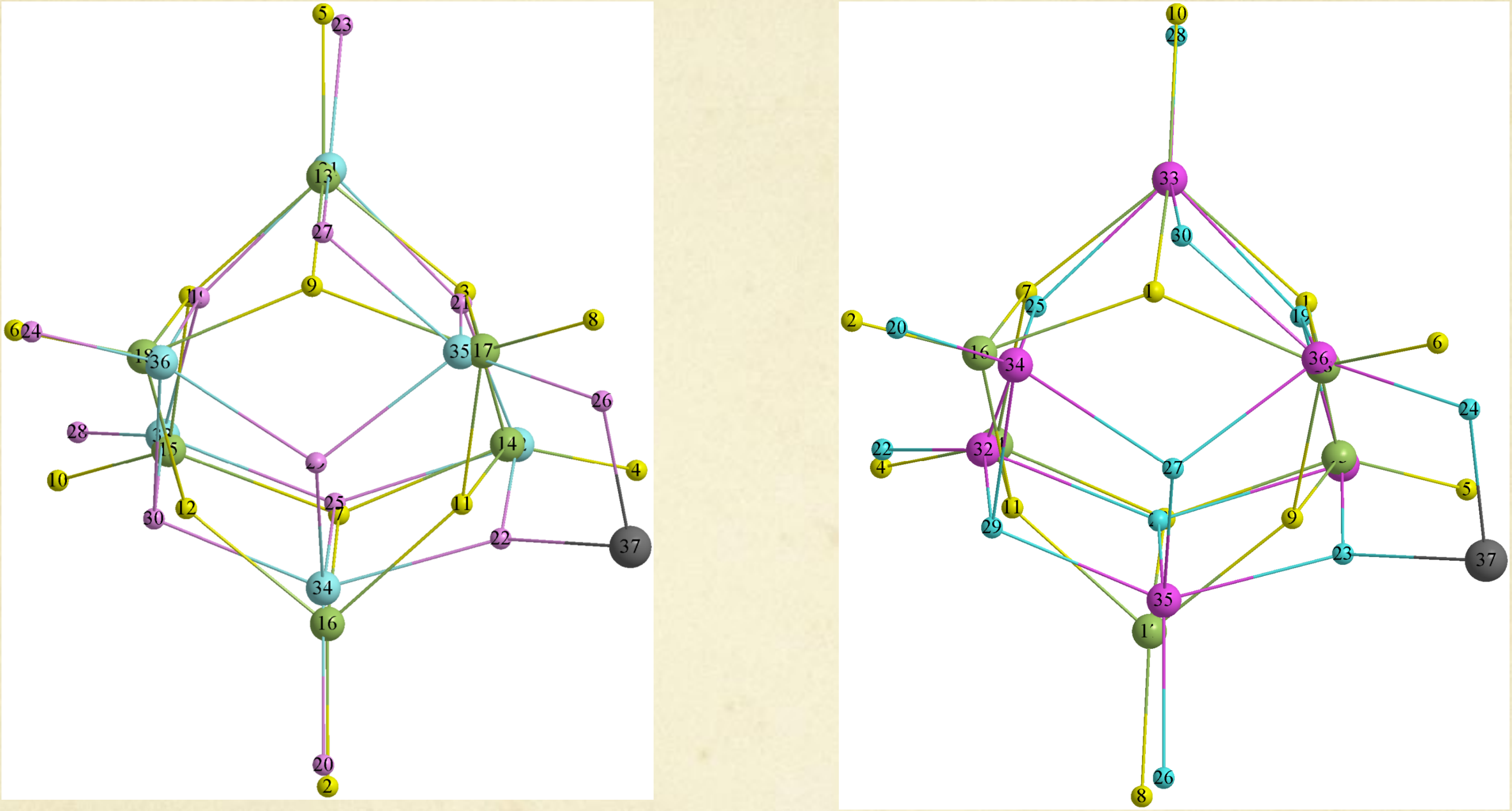


Figure 1. Nanoparticles of RuO_2 (left) and SnO_2 (right) showing the labeling used for various Li adsorption sites. Each nanoparticle has the chemical formula $(MO_2)_6$, where M = Ru or Sn.

Li adsorption results

- Li^+ adsorption on Ru_6O_{12} appears to favor corner and trivalent sites
- Complexation with Li could result in disruption of O and Ru/Sn bond network
- T-T' highly unfavorable in Ru_6O_{12} , and the cluster distorts to push Li to the periphery
- Sn_6O_{12} cluster prefers C-C and T-T positions; adsorption at the C-T site reverts back to C-C position
- Ru cluster experience a greater conformational change with Li adsorption compared to Sn clusters

$Sn_6O_{12}Li$

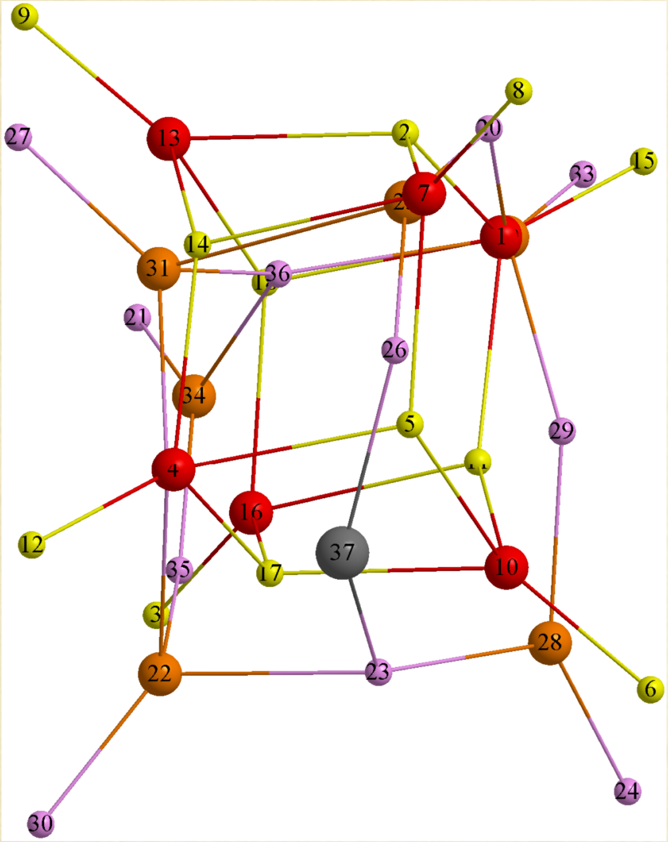


$Sn_6O_{12}Li$; C-T

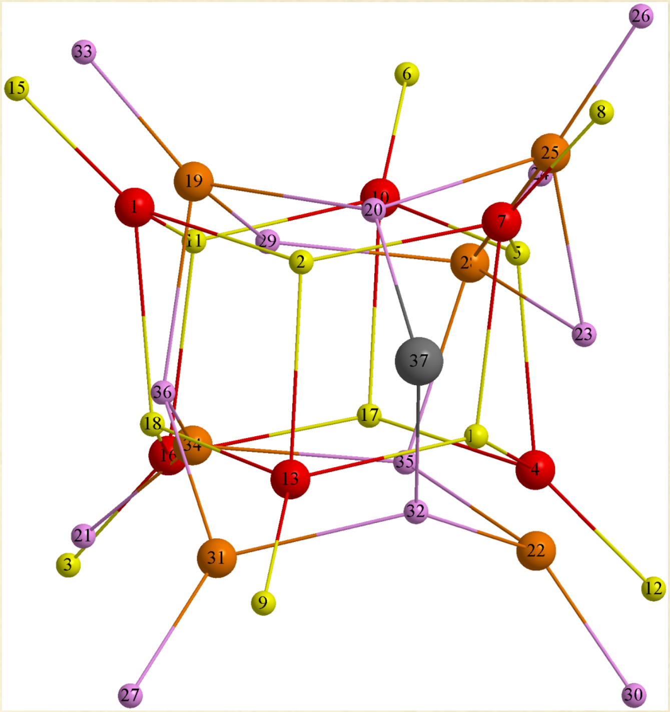
$Sn_6O_{12}Li$; C-C

The oxygen atoms in the pristine nanoclusters are in yellow, while those in Li-adsorbed clusters are in lilac. Sn atoms are represented in light green and light blue for the cluster and complex respectively.

$Ru_6O_{12}Li$



$Ru_6O_{12}Li$; C-T



$Ru_6O_{12}Li$; B-B'

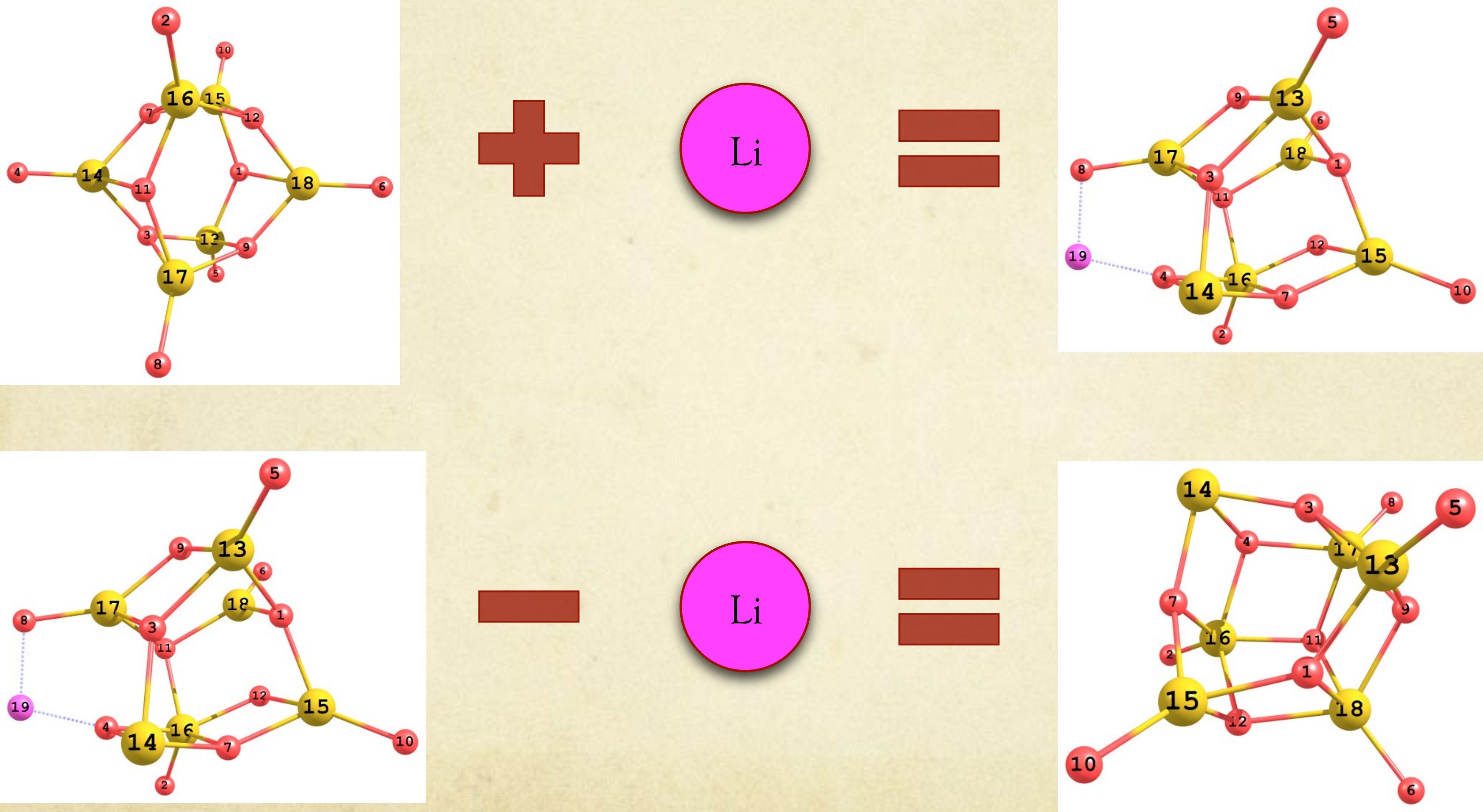
The oxygen atoms in the pristine nanoclusters are in yellow, while those in Li-adsorbed clusters are in lilac. Red and orange depict Ru atoms in MO_2 and MO_2Li respectively.

A Look at Ru/$Sn_6O_{12}Li$

Table 1. Comparison of structural changes in Ru_6O_{12} and Sn_6O_{12} nanoparticles as a result of Li adsorption. Total atom displacements *D*, average displacements $\langle d \rangle$, and standard deviations σ are shown, in Angstroms.

	Ru_6O_{12} B-B’	**Ru_6O_{12} C-B**	**Ru_6O_{12} C-B’**	**Ru_6O_{12} C-T**	**Ru_6O_{12} C-T’**	**Sn_6O_{12} T-T**	**Sn_6O_{12} C-T**	**Sn_6O_{12} C-C**
D	21.5	14.4	23.2	25.4	29.0	10.9	11.1	18.9
$\langle d \rangle$	1.19	0.80	1.29	1.41	1.61	0.61	0.62	1.05
σ	1.00	0.56	1.15	0.90	1.12	0.87	0.86	0.90

The reversibility of lithium adsorption by Sn_6O_{12}



Voltages

- Voltages were calculated from energies obtained by optimizing the pertinent structures
- This calculation was done using the following equation*:

Nernst Relationship for voltage calculation:

$$E\,(\mathrm{V}) = \frac{\left[G^{\circ}_{(\mathrm{MO_2})_n} + G^{\circ}_{\mathrm{Li}} - G^{\circ}_{(\mathrm{MO_2})_n\,\mathrm{Li}}\right]\mathrm{J\ \ mol^{-1}}}{xF\,(\mathrm{C\ \ mol^{-1}})}$$

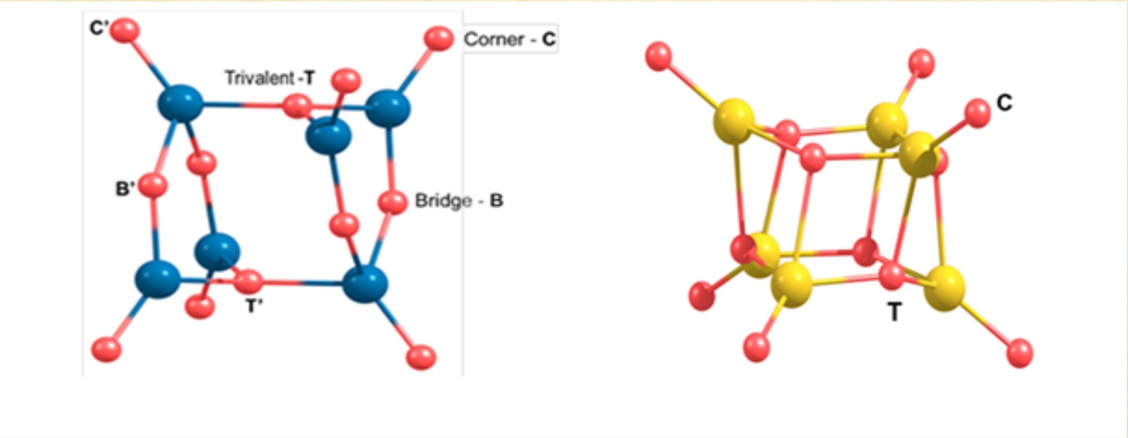
*in reference to Li | Li⁺ standard

The Following Hypothetical cell can be created using the voltage data.

Anode:	$(RuO_2)_6Li \rightarrow (RuO_2)_6 + Li^+ + e^-$;	$E° = -4.58$ V
Cathode:	$(SnO_2)_6 + Li^+ + e^- \rightarrow (SnO_2)_6Li$;	$E° = 8.21$ V
Overall cell reaction:	$(RuO_2)_6Li + (SnO_2)_6 \rightarrow (SnO_2)_6Li$.	$E°_{cell} = 3.63$ V

Summary

- RuO_2 nanoparticles suffer large geometry changes when Li adsorbs, and SnO_2 nanoparticles suffer smaller changes, but if these changes are reversible, and only affects the surface of the nanoparticle without destabilizing its attachment to the electrode surface, then geometry changes are not necessarily that bad.
- Ru clusters experience a greater conformational change with Li adsorption compared to Sn clusters
- Sn_6O_{12} cluster prefers C-C and T-T positions; adsorption at the C-T site reverts back to C-C position



Future Work

- Propose new materials for Li-ion batteries with better energy and power density
- Determine whether RuO_2 clusters maintain their original structure after discharge
- Experimentally, it will be very hard to make nanoparticles as small as the ones we have studied. So we will look at larger particles to see if our current observations will hold.
- Examine the trend towards bulk crystalline structure within the larger clusters by comparing the larger clusters with experimental crystal structures of oxoruthenates.
- Explore structural changes due the adsorption of multiple lithium ions.
- Observe lithium adsorption to large metal oxide structures.

Acknowledgments

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Going to miss you Guys :-D