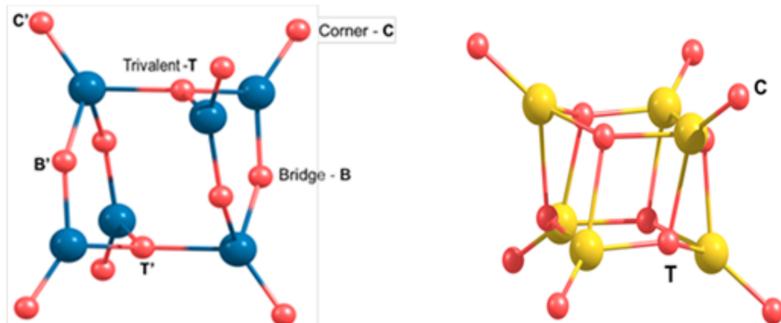


## Abstract

Considerable effort is currently being expended in developing electrode materials in an attempt to improve the cycle life of Li-ion batteries, while preserving high energy and power density of the electrode material. Nanostructured thin films of transition metal oxides have been found to be extremely promising as electrode materials for increasing the energy density of solid-state lithium ion batteries. We present a computational investigation of nanoparticles of RuO<sub>2</sub> as a potential material to achieve this goal. Nanoparticles of SnO<sub>2</sub> are also studied in this work to ascertain the origin of the structural instability of SnO<sub>2</sub> as an electrode material when subjected to charge and discharge cycles in Li-ion batteries. Using density functional theory, the preferred chemisorption sites, as well as voltages for Li ion adsorption on small RuO<sub>2</sub> and SnO<sub>2</sub> clusters are assessed. Furthermore, the structural changes caused by Lithium adsorption/desorption are examined.

## Computational Methods, and RuO<sub>2</sub> clusters

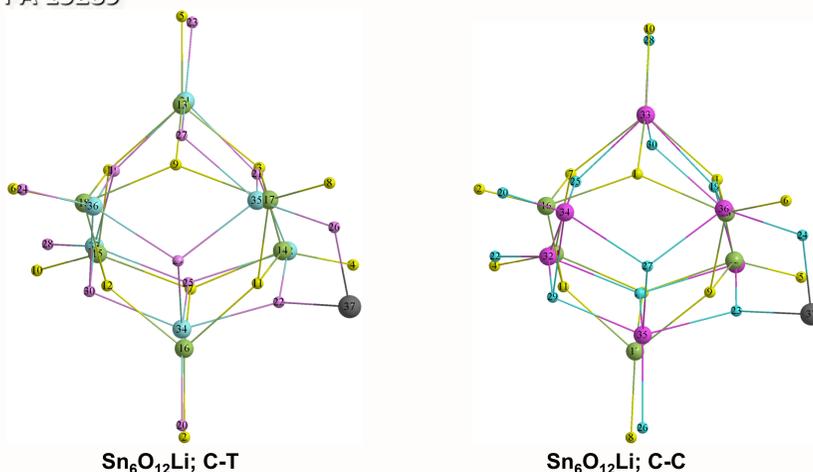
The preferred structure, energetics, and electronic properties of (SnO<sub>2</sub>)<sub>6</sub> and (RuO<sub>2</sub>)<sub>6</sub> clusters were assessed by the recently developed M06 DFT functional of Zhao and Truhlar.<sup>1</sup> The Los Alamos National Laboratory double  $\zeta$  effective core potential (LANL2DZ)<sup>2</sup> basis sets have been employed. Geometries were optimized without any symmetry constraints, and harmonic vibrational frequency calculations were performed at the same level of theory to confirm the structures as minima on their respective potential energy hypersurface. All calculations were performed on LONI computers using the Gaussian 09 suite of programs. Further calculations on the clusters were performed with PBE functional using LANL2dz and DNP basis set.<sup>3</sup>



**Figure 1.** Nanoparticles of RuO<sub>2</sub> (left) and SnO<sub>2</sub> (right) showing the labeling used for various Li adsorption sites. Each nanoparticle has the chemical formula (MO<sub>2</sub>)<sub>6</sub>, where M = Ru or Sn.

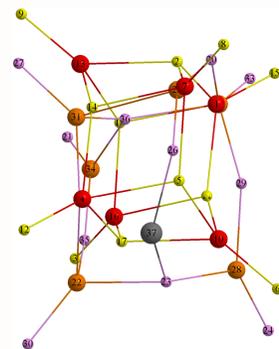
## Objectives

- Determine the preferred structure, energies, and electronic properties of small RuO<sub>2</sub> and SnO<sub>2</sub> clusters.
- Calculate voltages associated with Li ion adsorption
- Use the insights to formulate models for nanoscale metal oxide nanostructured thin films for Li-ion battery application
- Compare the voltages calculated with orbital-based Gaussian basis sets with numerical basis sets
- Examine if Ru/Sn or O environment changes upon Li adsorption.
- Investigate the interaction of lithium with stable RuO<sub>2</sub> clusters of various sizes.
- Consider the possibility of forming hypothetical Li-ion battery cells made of RuO<sub>2</sub> anode and SnO<sub>2</sub> cathode.
- Use insight gained to compare different electrode materials for optimal structural and voltage profiles.

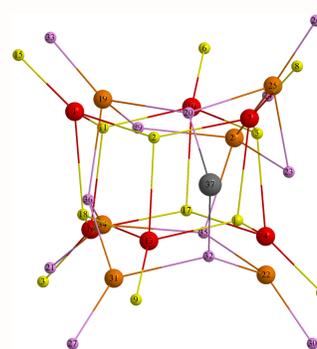


Sn<sub>6</sub>O<sub>12</sub>Li; C-T

Sn<sub>6</sub>O<sub>12</sub>Li; C-C



Ru<sub>6</sub>O<sub>12</sub>Li; C-T



Ru<sub>6</sub>O<sub>12</sub>Li; B-B'

**Figure 2.** Geometric displacement encountered by metal nanoparticles upon Li adsorption. 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. Red and orange depict Ru atoms in MO<sub>2</sub> and MO<sub>2</sub>Li respectively.

**Table 1.** Comparison of structural changes in Ru<sub>6</sub>O<sub>12</sub> and Sn<sub>6</sub>O<sub>12</sub> nanoparticles as a result of Li adsorption. Total atom displacements  $D$ , average displacements  $\langle d \rangle$ , and standard deviations  $\sigma$  are shown, in Angstroms.

	Ru <sub>6</sub> O <sub>12</sub> B-B'	Ru <sub>6</sub> O <sub>12</sub> C-B	Ru <sub>6</sub> O <sub>12</sub> C-B'	Ru <sub>6</sub> O <sub>12</sub> C-T	Ru <sub>6</sub> O <sub>12</sub> C-T'	Sn <sub>6</sub> O <sub>12</sub> T-T	Sn <sub>6</sub> O <sub>12</sub> C-T	Sn <sub>6</sub> O <sub>12</sub> 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
$\sigma$	1.00	0.56	1.15	0.90	1.12	0.87	0.86	0.90

**Equation 1.** Nernst Relationship for voltage calculation:<sup>4</sup>

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

**Table 2.** Potential difference of hypothetical cell constructed from (RuO<sub>2</sub>)<sub>6</sub> Li impregnated anode and (SnO<sub>2</sub>)<sub>6</sub> cathode, in reference to Li|Li<sup>+</sup> standard.

Anode:	(RuO <sub>2</sub> ) <sub>6</sub> Li → (RuO <sub>2</sub> ) <sub>6</sub> + Li <sup>+</sup> + e <sup>-</sup> ;	E° = -4.58 V
Cathode:	(SnO <sub>2</sub> ) <sub>6</sub> + Li <sup>+</sup> + e <sup>-</sup> → (SnO <sub>2</sub> ) <sub>6</sub> Li;	E° = 8.21 V
Overall cell reaction:	(RuO <sub>2</sub> ) <sub>6</sub> Li + (SnO <sub>2</sub> ) <sub>6</sub> → (SnO <sub>2</sub> ) <sub>6</sub> Li.	E° <sub>cell</sub> = 3.63 V

**Table 3.** Comparison of the raw energies (in Hartrees) and voltages (in Joules/Coulomb) obtained using PBE functional with LANL2DZ basis set and DNP basis set.

	PBE/LANL2dz		PBE/DNP <sup>3</sup>		$\Delta V$
	Energies (Hartrees)	Voltages(J/C)	Energies (Hartrees)	Voltages(J/C)	
Sn <sub>6</sub> O <sub>12</sub>					
C-T	-930.09088	5.67	-930.70209	4.60	1.08
C-C	-930.09088	5.67	-930.70221	4.60	1.07
Ru <sub>6</sub> O <sub>12</sub>					
C-T	-1472.95450	4.61	-1480.54516	3.92	0.69
B-B'	-1472.95218	4.55	-1480.55059	4.07	0.48
C-B'	-1472.93888	4.19	-1480.55085	4.08	0.11
C-B	-1472.93692	4.13	-1480.53469	3.64	0.50
C-T'	-1472.94906	4.47	-1480.55979	4.32	0.15

## Results and Discussion

- Li<sup>+</sup> adsorption on Ru<sub>6</sub>O<sub>12</sub> appears to favor corner and trivalent sites.
- Complexation with Li could result in disruption of O and Ru/Sn bond network (see Figure 2).
- T-T' highly unfavorable in Ru<sub>6</sub>O<sub>12</sub>, and the cluster distorts to push Li to the periphery. This appears to be a promising result because intercalation of Li<sup>+</sup> leading to large structural change is a problem in Sn and Sb anodes.
- Future calculations will examine whether this behavior persists as more Li<sup>+</sup> ions adsorb and also for larger (RuO<sub>2</sub>)<sub>n</sub> clusters.
- Sn<sub>6</sub>O<sub>12</sub> 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.
- Our DNP results are comparable to the orbital based Gaussian basis set calculation.

## Future Work

- Use numerical basis sets in probing reactions with larger clusters with sizes up to 100 atoms.
- Examine the trend towards bulk crystalline structure within the larger clusters by comparing the larger clusters with experimental crystal structures of oxoruthenates.
- Employ structural and electronic information obtained in studying catalytic reactions occurring on the surface of these clusters, and in developing forcefields for MD simulations.
- Propose new materials for Li-ion batteries with better energy and power density.

## References

- Zhao, Y.; Truhlar, D. *Theor.Chem. Acc.* **2008**, *120*, 215.
- Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 270.
- Delley, B. *J. Chem.Phys.* **1990**, *92*, 508.
- Mueller, T.; Hautier, G.; Jain, A.; Ceder, G. *Chemistry of Materials* **2011**, *23*, 3854.

## Acknowledgements

This material is based upon work supported by the National Science Foundation under the NSF EPSCoR Cooperative Agreement No. EPS-1003897 with additional support from the Louisiana Board of Regents.