

## **Investigations of RuO<sub>2</sub> and SnO<sub>2</sub> nanoclusters as potential lithium ion battery electrode materials**

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**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. Actualizing the full potential of using Li-ion batteries in everyday micro- and nano- scale devices, and even electric vehicles demands the development of new stable, safe electrode materials with high electron density. 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 molecular orbital based density functional theory, the voltages for Li ion adsorption on the metal oxide nanoparticles are calculated and the resulting structural changes examined.

**Keywords:** Li-ion batteries, metal oxide nanoparticles, anode coatings, voltages

### **1. Introduction**

Li-ion batteries are considered to be the next generation in battery technology compared to other conventional battery technologies such as Nickel-Cadmium. The development of a wide array of mobile consumer electronics such as notebooks PCs, smartphones, PDAs, pocketsize calculators, camcorders, and portable liquid crystal TVs lead to an ever-present need for the use of batteries, and demand for batteries with longer life cycles. The increase in cyclability of Li-ion batteries will also be very important in transportation applications, such as electric vehicles, and hybrid electric vehicles. In fact, Li-ion are being aggressively researched and implemented, albeit at a rudimentary extent in this area.

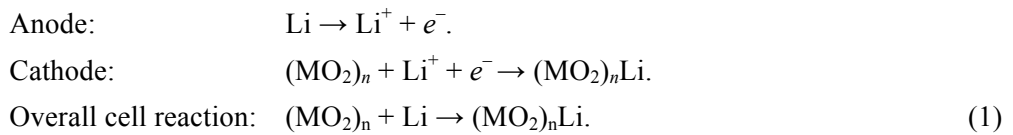
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Of current research interest is the use of nanoscale crystalline thin-film electrode materials in improving the electrochemical performance of Li-ion batteries. Tin (Sn) oxide is one such material, as it has been shown to be a high Li-ion-storage compound. It has twice the gravimetric capacity of carbon, and three times the volumetric capacity of carbon, hence it can store more than twice as much  $\text{Li}^+$  as graphite, the most common commercially available anode. However, it has significantly less cyclability because of structural instabilities in the oxide layer that develop over time.<sup>1,2</sup>

We are also interested in examining  $\text{RuO}_2$  as a possible Li-ion storage compound with desirable capacity and good cyclability.  $\text{RuO}_2$  may be a good candidate for electrode materials due to its low resistivity ( $\sim 40 \mu\Omega \text{ m}$ ), good thermal stability up to  $800^\circ\text{C}$  and chemical stability.<sup>3</sup>

We adopt the approach of the Ceder group<sup>4</sup> to calculate the voltage of the two metal oxides against a  $\text{Li}|\text{Li}^+$  anode, which implies the following cell reactions:



The free energy changes for the cell reaction is used to calculate the cell voltage from the Nernst relationship:<sup>4</sup>

$$E \text{ (V)} = \frac{[G_{(\text{MO}_2)_n}^\circ + G_{\text{Li}}^\circ - G_{(\text{MO}_2)_n\text{Li}}^\circ] \text{ J mol}^{-1}}{xF \text{ (C mol}^{-1}\text{)}}, \quad (2)$$

where  $x$  is the number of electrons involved in the reaction, and  $F$  is the Faraday.

## 2. Computational Methods

Molecular orbital calculations in the framework of Kohn-Sham density functional theory (DFT)<sup>5</sup> has been utilized for all calculations reported. The preferred structure, energetics, and electronic properties of  $(\text{SnO}_2)_6$  and  $(\text{RuO}_2)_6$  clusters were assessed by the recently developed M06 DFT functional of Zhao and Truhlar.<sup>6</sup> The Los Alamos National Laboratory double  $\zeta$  effective core potential (LANL2dz)<sup>7</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. We considered the nanoparticles with chemical formula  $\text{Ru}_6\text{O}_{12}$  and  $\text{Sn}_6\text{O}_{12}$ , respectively.

### 3. Results and Discussions

Several geometric possibilities for Li-ion chemisorption were assessed. The adsorption sites for  $\text{Li}^+$  deposition in both nanoclusters are shown in Figure 1. Both  $\text{Ru}_6\text{O}_{12}$  and  $\text{Sn}_6\text{O}_{12}$  can be considered as hexamers of  $\text{RuO}_2$  and  $\text{SnO}_2$  respectively. The trigonal planar co-ordination of oxygen is more common in  $\text{SnO}_2$  than  $\text{RuO}_2$ ; hence  $\text{RuO}_2$  has a more varied structure than  $\text{SnO}_2$ , giving it more isoforms to consider.

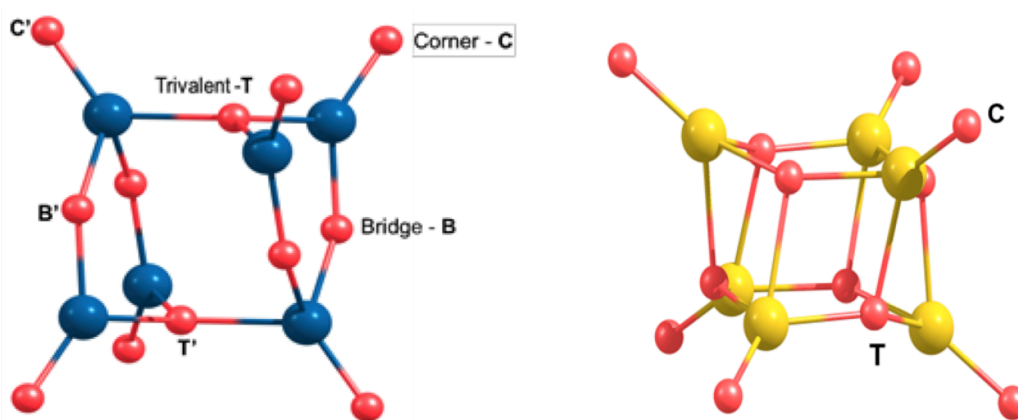
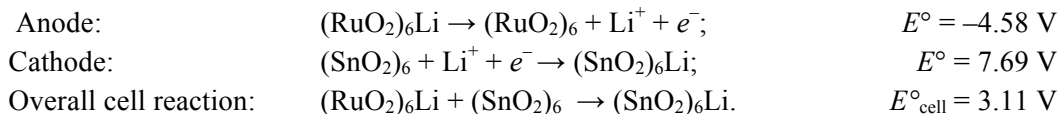


Figure 1: Nanoparticles of  $\text{RuO}_2$  (left) and  $\text{SnO}_2$  (right) showing the labeling used for various Li adsorption sites. Each nanoparticle has the chemical formula  $(\text{MO}_2)_6$ , where  $\text{M} = \text{Ru}$  or  $\text{Sn}$ .

For the  $(\text{RuO}_2)_6$  cluster, we found that Li adsorption on its surface favors the corner (C and C' in figure 2) and trivalent (T and T') sites. The placement of Li in the center of the cluster is highly unfavorable, and the Li atom gets pushed out from the cluster during optimization. We have calculated the voltages for the net reaction in an electrochemical process using Eq. (2), which implies that the reference is the  $\text{Li}|\text{Li}^+$  anode. For Li adsorption on the C-T sites in each case, the voltages are calculated to be 4.58 V for  $\text{Ru}_6\text{O}_{12}$ , compared to 7.69 V for  $\text{Sn}_6\text{O}_{12}$ .

While the voltage for  $\text{Ru}_6\text{O}_{12}$  is not as high as that of  $\text{Sn}_6\text{O}_{12}$ , the obtained value for  $\text{Ru}_6\text{O}_{12}$  suggest that it could be a prospective anode coating material especially due to its stability, and potential to suffer less from capacity fading/poor cyclability. In fact, from the results obtained thus far, one could construct a hypothetical cell with nanostructured metal oxide electrodes as follows:



#### 4. Summary and Future work

The interaction of Li ions with transition metal oxide thin film nanoparticle surfaces is being studied with density functional theory. The high unfavorability of Li placement in the middle of the  $\text{Ru}_6\text{O}_{12}$  cluster appears to be a promising result because intercalation of  $\text{Li}^+$  leading to large structural change is a problem in Sn and Sb anodes.

We are studying these small nanoclusters as models for nanoscale domains, we intend to increase the size and geometry of the cluster. To this end, we are currently examining the results of our Gaussian basis sets calculations against double numerical basis sets with polarization (DNP) as implemented in DMol3 module of the Materials studio suite of program. This will allow us to assess the reliability of GGA(PBE)/DNP level of theory, and afford us the ability to extend our cluster size to as large as 200 atoms. We hope to gain enough insight into the energetics and electronic properties of these systems to be able to develop a methodology to compare many different potential electrode materials for optimized structural and voltage properties for lithium ion oxidation/reduction.

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