First Principles Calculation of Lithiation Voltage at Electrode Surfaces

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Abstract

First principles density functional theory calculations were used to study the surface and near-surface lithiation of RuO_2 electrode materials. For the RuO_2 system, comparing the calculated discharge curve with previous results showed that lithiation near the surface of a RuO_2 slab was similar to lithiation of bulk RuO_2, but slightly more energetically favorable, with near-surface lithiation being more favorable than adsorption to the outer surface. In addition, near-surface lithiation appeared to show the same mechanism as bulk lithiation, and volume expansion was within the typical range for lithiation of metal compounds. Voltage remained positive after the addition of lithium in excess of a 10:1 Li:Ru ratio, indicating that the surface region has a very high theoretical capacity.

Methods

All computational work was done using the Vienna Ab initio Simulation Package (VASP)[1] for plane wave density functional theory (DFT) calculations. Most aspects of the calculations were similar to the methods of Hassan et. al.;[2] the Perdew-Burke-Ernzerhof (PBE)[3] generalized gradient approximation was used with the projector augmented wave[4] method. Energies were minimized by relaxing ionic coordinates, cell shape, and volume with the conjugate gradient method. The plane wave energy cut-off for all calculations was fixed at 500 eV, and an automatically generated Monkhorst-Pack[5] k-point mesh was used. The "working cell" of $(RuO_2)_8$ differed from that of Hassan et. al. by the inclusion of a surface exposed to vacuum along the (1,1,0) surface.

a. b.

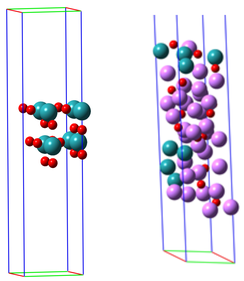

Figure 1: The working cell
a. 0 Li
b. 32 Li

Lithiation sites were selected by an algorithm that finds points with maximized open space, subject to the constraint that they must have a specified number of metal atoms within a specified distance to ensure that they are placed within the slab interior.[2] An alternate algorithm which placed lithium on the outside surfaces of the slab was considered, but gave consistently less favorable energies.

For comparison, a nanoparticle of $(RuO_2)_{10}$ was generated and analyzed by the same methods. For the nanoparticle, lithium placement on the outside surface was more energetically favorable.

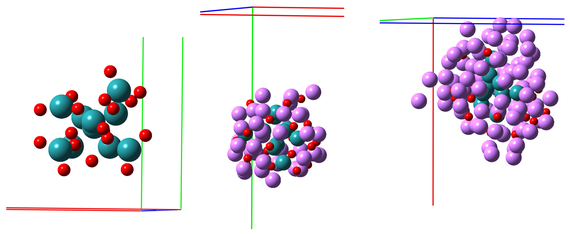

Figure 2: $(RuO_2)_{10}$ nanoparticle.
a. 0 Li
b. 40 Li
c. 80 Li

Experimental[6] and computational[2] evidence shows that RuO_2 undergoes conversion reactions to form islands of Ru surrounded by Li_2O. To study the end-point of the conversion reaction, cells containing an Ru_8 island surrounded by 16 Li_2O was created, representing the stoichiometry of the slab at full conversion.

a. b. c.

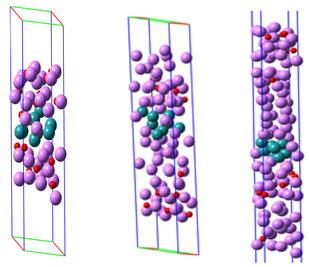

Figure 3: Lithiated island structures
a. 32 Li
b. 64 Li
c. 88 Li

Results

The island structure was found to have lower energy than the initial slab (and therefore higher voltage) for all Li:Ru ratios exceeding 1:1. Most of the additional Li's beyond the conversion limit (4:1 ratio of Li:Ru) were stored in the interface between the Ru island and the oxide, a result consistent with previous calculations for bulk Li.[2] The average volume expansion was 10.0 Å^3 for each additional Li, which is smaller than the 14.8 Å^3 per Li usually seen in binary Li-M alloys.[7] The slab data was compared with the bulk system[2] and with the results obtained for the nanoparticle.

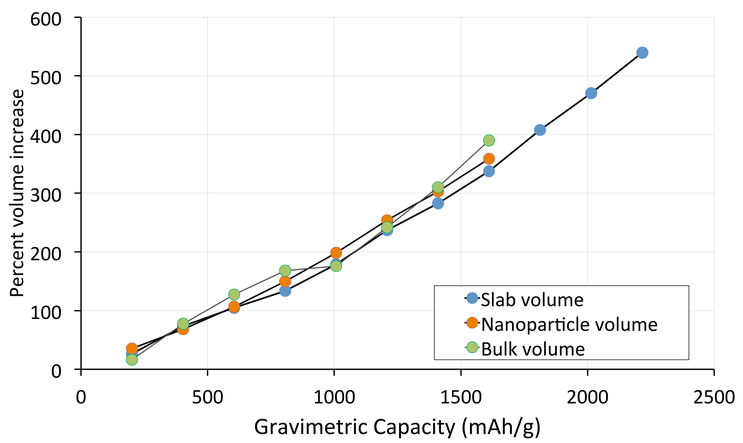

Figure 4: Percent volume increase as a function of gravimetric capacity

The voltage relative to pure lithium of an optimized system with *n* lithium atoms was calculated using the equation

$$E - E\downarrow 0 - n * E\downarrow Li \,/ n$$

where *E* is the total energy of the system, E_0 is the energy of the unlithiated system, and E_{li} is the energy of a lithium atom in bulk crystalline lithium (all energies are measured in electron volts). Figure 5 compares this calculated voltage with that found for bulk RuO_2,[2] and the $(RuO_2)_{10}$ nanoparticle, as well as experimental results.[2]

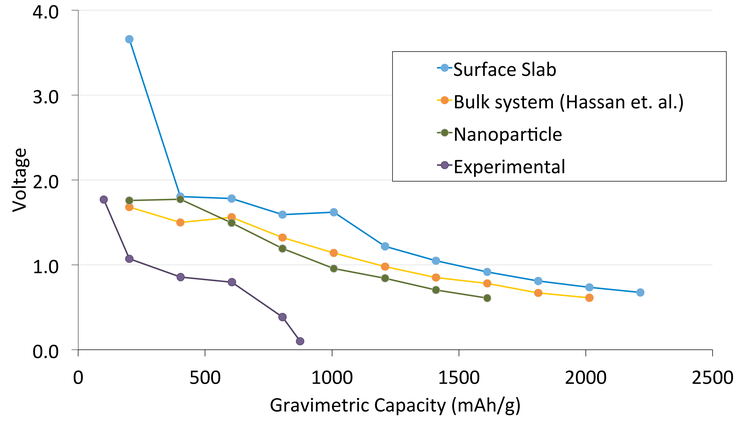

Figure 5: Voltage as a function of gravimetric capacity

Voltage approached zero but remained positive with respect to pure lithium at Li:Ru ratios exceeding 10:1.

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Images generated with: GaussView, Version 5, Dennington, Roy; Keith, Todd; Millam, John. *Semichem Inc.*, Shawnee Mission, KS, 2009.

Acknowledgements

This work is supported by the National Science Foundation under cooperative agreement EPS-1003897 with additional support from the Louisiana Board of Regents.