Investigations of Rutile-type RuO_2, SnO_2, MnO_2 as potential Lithium-Ion Battery Anode Materials

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Abstract: First principles computational studies were used to understand the molecular mechanism of lithium intercalation in crystalline bulk RuO_2. The calculated discharge curves for lithium in RuO_2 lattice showed qualitative agreement with experimental results for RuO_2 nanoplates. Our molecular level analysis showed that lithium proceeded via an intercalation mechanism until a 1:1 Li:Ru ratio, followed by a phase transition to a new tetragonal structure with higher lithium content, resulting in a recyclable Li:Ru ratio of 3:1. This new structure appeared stable throughout subsequent charging and discharging with lithium, giving different voltages, in agreement with experiment. Having thus validated this approach, we also studied MnO_2 and SnO_2 in a similar manner, as part of ongoing work to understand the suitability of different metal oxides for battery anode materials.

Keywords: Li-ion batteries, metal oxide, anode materials, voltages, LIB

1. Introduction

Lithium-ion batteries have become the rechargeable power sources of choice for a variety of portable electronics applications, biomedical devices, and also electric and hybrid motor vehicles.[1,2] However, especially in the case of electric vehicle applications, there is a great need to increase the gravimetric power capacity and cyclability of the battery. Most current batteries use graphite as an anode and $LiCoO_2$ as cathode. Graphite has a capacity of 372 mAh g^{-1} and typically operates at a voltage of ~0.5 V as the anode.[1,3]

Metal oxides have been studied as electrode materials for Li-ion batteries, as they have been found to be promising in providing higher capacities than standard graphite anodes. RuO_2 may be a particularly good potential material for Li-ion electrode or electrode coating, owing to its good thermal and chemical stability, and low resistivity.[4-6] Balaya et al.[7] conducted an experimental study on the use of RuO_2 nanoparticles for LIB usage, and reported a high capacity of 1130 $mAhg^{-1}$.

The motivation for the present work was provided by the Meda group who deposited crystalline RuO_2 nanoplates of varying thicknesses on stainless steel using chemical vapor deposition. The nanoplates were found to show promise as rechargeable lithium ion battery anode materials. In particular, Meda et al. [unpublished] found that (a) the first discharge curve showed multiple voltage plateaus similar to those published by Balaya et al.,[7] (b) pushing the oxide material to high Li capacities i.e., until the discharge voltage reached 0.5 V, (deep discharge)

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resulted in rapid loss of capacity in subsequent cycles especially for the thicker nanoplates, (c) limiting the discharge voltages to 1.0 V allowed the electrode to be cycled multiple times without loss of capacity, and (d) there were qualitative differences between the first and subsequent discharge curves. Computational studies were undertaken to understand the mechanisms at work in this electrode and, if possible, to explain the observations.

2. Computational methodologies

All calculations reported were done using the Vienna Ab initio Simulation Package (VASP),[8] which is a plane wave Density Functional Theory (DFT) package widely used in computational materials science. The exchange-correlation energy was determined using the Perdew-Burke-Ernzerhof (PBE)[9] form of the generalized gradient approximation (GGA) in conjunction with the projector augmented wave (PAW) method.[10,11] The minimum ground state energies of structures considered were found by relaxing the ionic coordinates, cell shape, and volume of the structures with the conjugate gradient method. Unit cells of RuO_2 and metallic Li were optimized first with appropriate energy cut-offs and the first Brillouin zone sampling with appropriate Monkhorst-Pack[12] k-point meshes. A "working cell" of $(RuO_2)_8$ was constructed from the optimized RuO_2 unit cell such that the (*a*,*b*) plane of the working cell coincided with the (110) crystal plane. The reference energy for a single Li atom was determined from the Li unit cell energy, in keeping with standard practice.

3. Results and Discussions

The RuO_2 working cell with increasing numbers of intercalated lithium atoms were optimized, allowing the geometry, lattice volume, and shape to change. The optimized structures are presented in Figure 1.

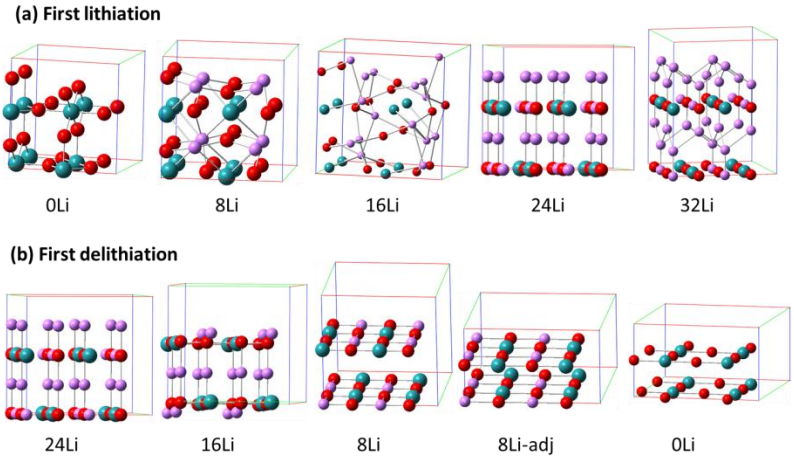

Figure 1: Optimized structures of $(RuO_2)_8$ with varying numbers of intercalated lithiums. Ru atoms are dark green (teal), oxygen red, and lithium atoms purple.

It is evident from the top row of Figure 1 that the first 8 Li added (reaching Li:Ru ratio of 1:1) are intercalated into the RuO_2 lattice with minimal distortion. Increasing the Li:Ru ratio to 2:1 causes significant distortion of the crystal structure. Approaching the 3:1 ratio causes the lattice structure to undergo a phase change from its original rutile to a new tetragonal structure *during optimization*. This leads to a higher capacity, as it opens up the

structure and allows for the intercalation of more lithium. The crystalline phase change appears to be irreversible. As the bottom row of Figure 1 shows, removing Li from the 3:1 ratio does not cause the crystal structure to revert back to its original structure. Increasing Li content to 4:1 results in a distorted tetragonal structure and the corresponding voltage drops to about 0.20 V.

The voltages associated with the addition of lithium atoms were calculated as the free energy change associated with the addition according to the Nernst relationship for voltage calculation relative to a $Li|Li^+$ standard, but with the assumption that $\Delta G° \approx \Delta E$:[13]

$$\mathcal{E}(V) = \frac{[E^o_{(RuO_2)_n} + E^o_{Li} - E^o_{(RuO_2)_n Li}]Jmol^{-1}}{xF(Cmol^{-1})} \quad (1)$$

where E's are the optimized energies, F is the Faraday constant, x is the number of moles of electrons involved.

The voltage and capacity of the metal oxide as a function of number of Li added is presented in Figure 2. Note that the "reactant" $(RuO_2)_8$ for the first discharge is the rutile structure on the top row left of Figure 1 while for subsequent discharges, it is the tetragonal lattice shown on the bottom right.

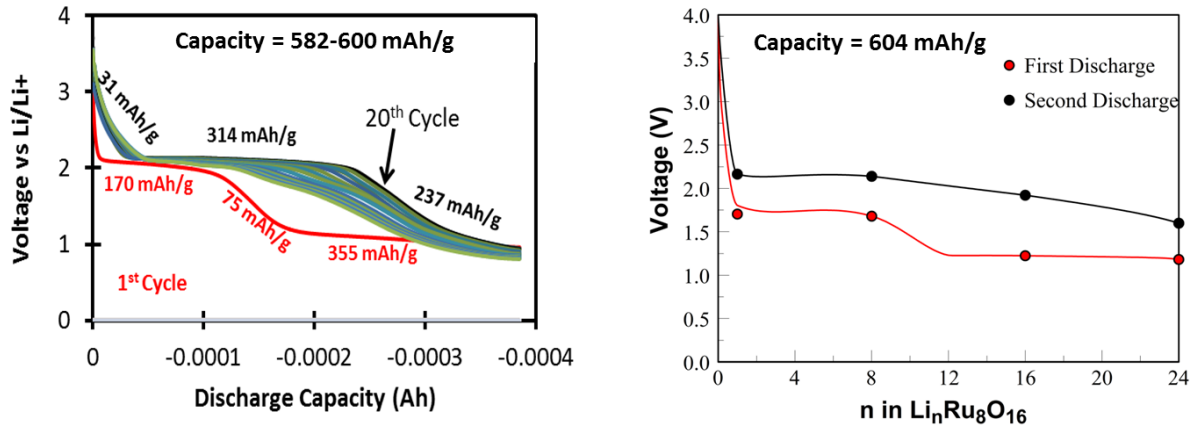

Figure 2: (a) Experimental discharge curves for 850nm RuO_2 nanoplates from Meda et al. for 20 discharge cycles [to be published]. (b) Calculated voltage profiles for the first and second discharges (this work). The curves are interpolations through the computed points which are shown as symbols.

The experimental and calculated discharge curves are qualitatively similar, and there is almost quantitative agreement between the voltages in the case of the first discharge curve. We interpret the first plateau in the first discharge curve at about 2.0 V as intercalation of Li into the original rutile lattice. The constant voltage as increasing amounts of Li are accommodated shows that the incoming Li are occupying sites which are energetically equivalent. The drop in voltage beyond this point is an indication that intercalation of additional Li is less favorable but still thermodynamically preferred. Thus the voltage plateau at ~1.0 V represents intercalation into the new tetragonal crystal structure. As stated previously, the addition of additional lithium, beyond a 1:1

ratio, disrupted the original crystal structure, eventually causing a phase change at a 3:1 ratio to the new tetragonal structure. The voltage of this is lower than that for the original intercalation. This new structure is stable for subsequent charge/discharge cycles, but results in higher voltages for the reduction of lithium atoms in the crystal lattice. Thus the calculated second discharge curve represents the intercalation of Li into a tetragonal lattice which is able to easily accommodate a Li:Ru ratio of 3:1 without dropping below 1.0 V.

4. Summary and Future Work

This work presents preliminary results of our experimentally motivated computational investigations on the performance of RuO_2 as a lithium ion battery anode material. Our methodology has yielded semi-quantitative agreement between the experimental and calculated discharge curves, and provided plausible explanations the experimental observations. This experimentally validated computational approach is presently being extended to SnO_2 and MnO_2 to ascertain if rutile structures other than RuO_2 exhibit the same lithium intercalation mechanism.

5. Acknowledgments

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6. References

[1] Armand, M.; Tarascon, J. M. *Nature* **2008**, *451*, 652.
[2] Kang, B.; Ceder, G. *Nature* **2009**, *458*, 190.
[3] Wu, Y. P.; Rahm, E.; Holze, R. *Journal of Power Sources* **2003**, *114*, 228.
[4] Zheng, J. P.; Cygan, P. J.; Jow, T. R. *Journal of The Electrochemical Society* **1995**, *142*, 2699.
[5] Soudan, P.; Gaudet, J.; Guay, D.; Bélanger, D.; Schulz, R. *Chem. Mater.* **2002**, *14*, 1210.
[6] Krusin-Elbaum, L.; Wittmer, M.; Yee, D. S. *Applied Physics Letters* **1987**, *50*, 1879.
[7] Balaya, P.; Li, H.; Kienle, L.; Maier, J. *Advanced Functional Materials* **2003**, *13*, 621.
[8] Kresse, G.; Furthmüller, J. *Physical Review B* **1996**, *54*, 11169.
[9] Perdew, J. P.; Burke, K.; Ernzerhof, M. *Physical Review Letters* **1996**, *77*, 3865.
[10] Blöchl, P. E. *Physical Review B* **1994**, *50*, 17953.
[11] Kresse, G.; Joubert, D. *Physical Review B* **1999**, *59*, 1758.
[12] Monkhorst, H. J.; Pack, J. D. *Physical Review B* **1976**, *13*, 5188.
[13] Bard, A. J.; Faulkner, L. R. *Electrochemical Methods: Fundamentals and Applications.*; John Wiley & Sons: New York, 1980.