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

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Motivation for this Work

Battery Types

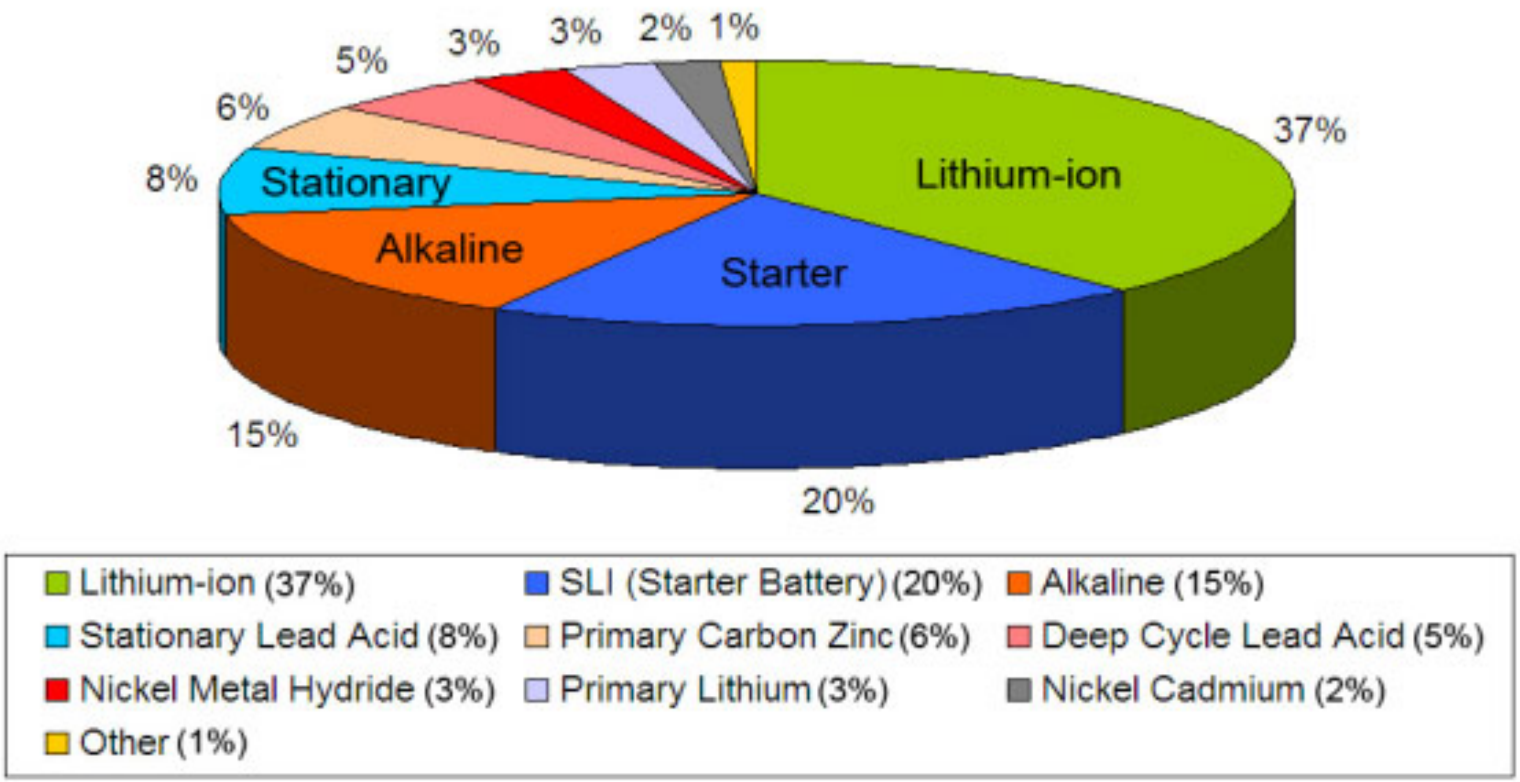
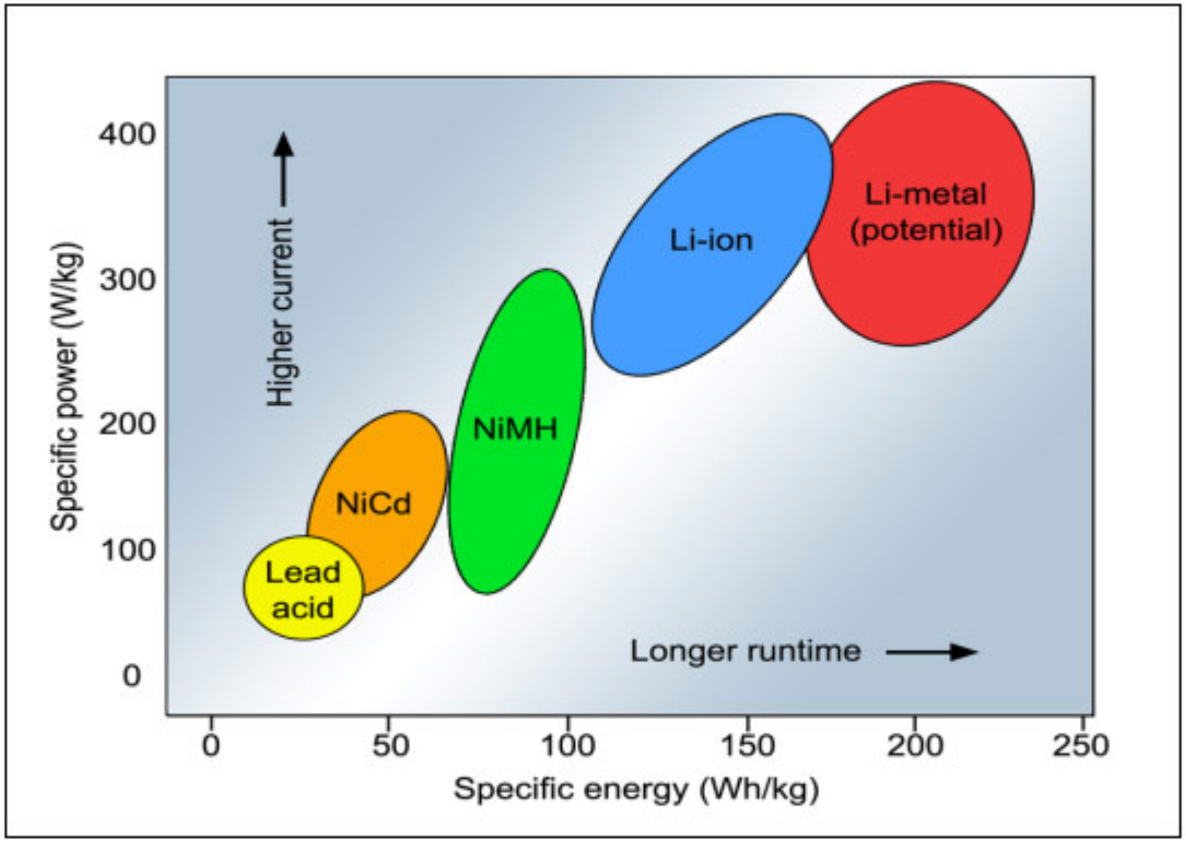


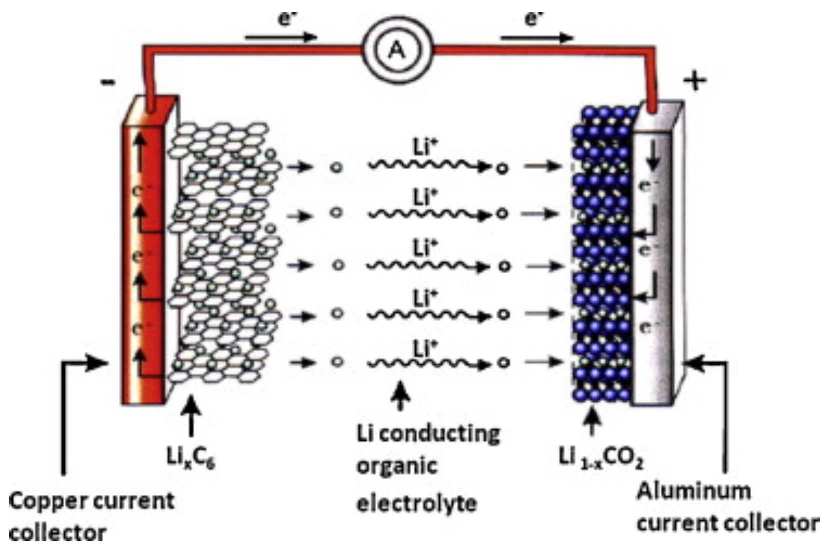
Figure 1*: Revenue contributions by different battery chemistries

Introduction for this Work

- Highly reactive with much higher energy and power density.
- *No* “memory effect” as in NiCd
- Design flexibility, and safest in use
- Green



Desired Improvements



Graphite $\quad$ 372 mAhg^{-1}

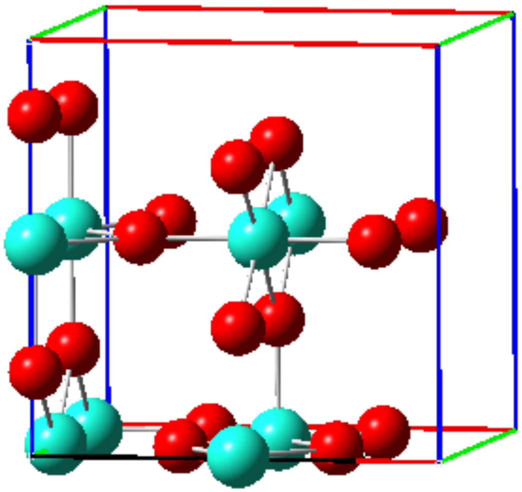
SnO$_2$ $\quad$ 782 mAhg^{-1}

- Produce more energy
- Last longer
- Charge faster
- Reduce cost

- Best metal oxide
- Voltage
- Capacity
- Volume

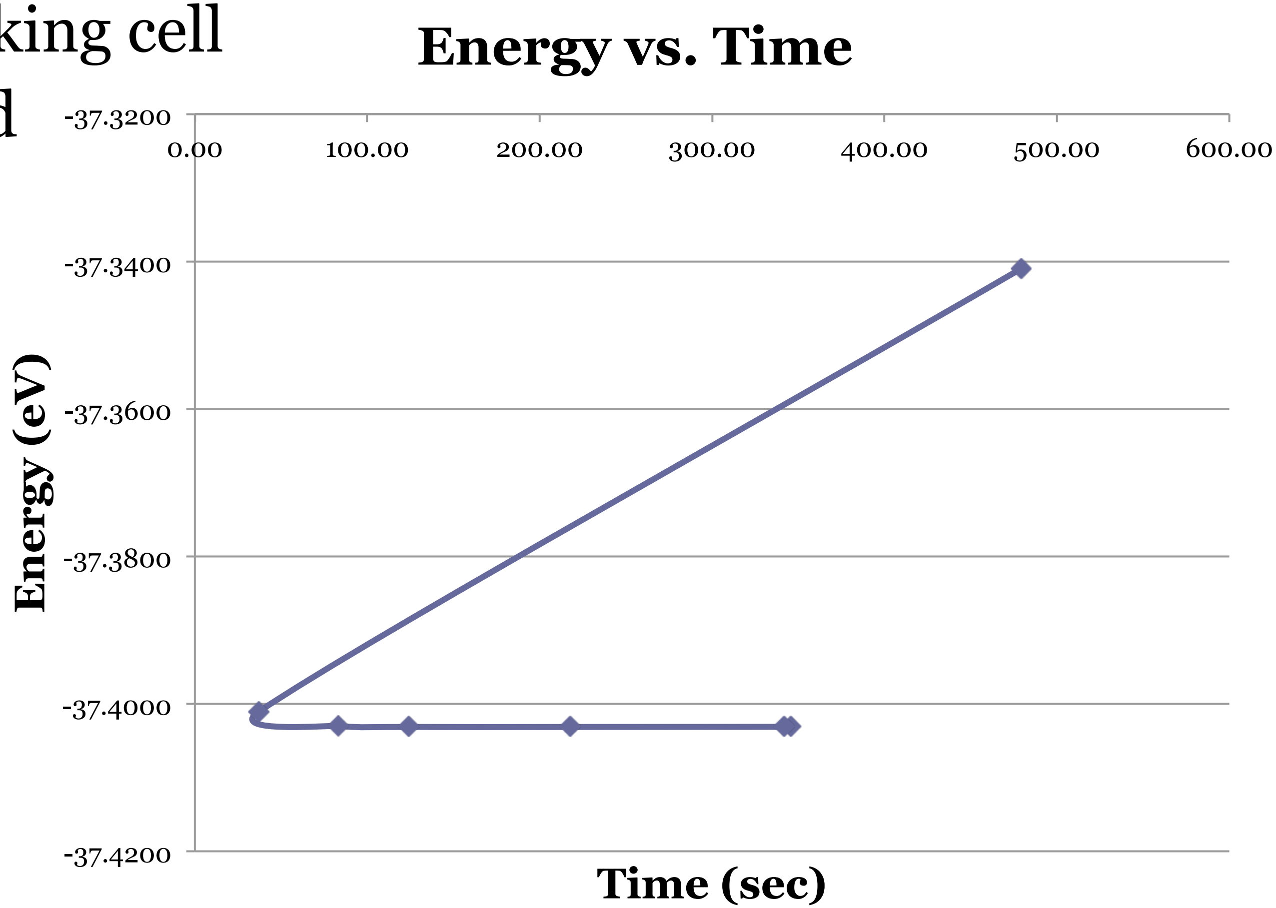
Methods

- VASP (Vienna Ab initio Simulation Package) - Density Functional Theory (DFT).
- Perdew-Burke-Ernzerhof (PBE)[4] functional
- Projector Augmented Wave (PAW) method.
- Allowed the ionic coordinates, cell shape, and volume of the structures to relax
- A "working cell" of $(MO_2)_8$. M=metal; Ru, Sn, Mn



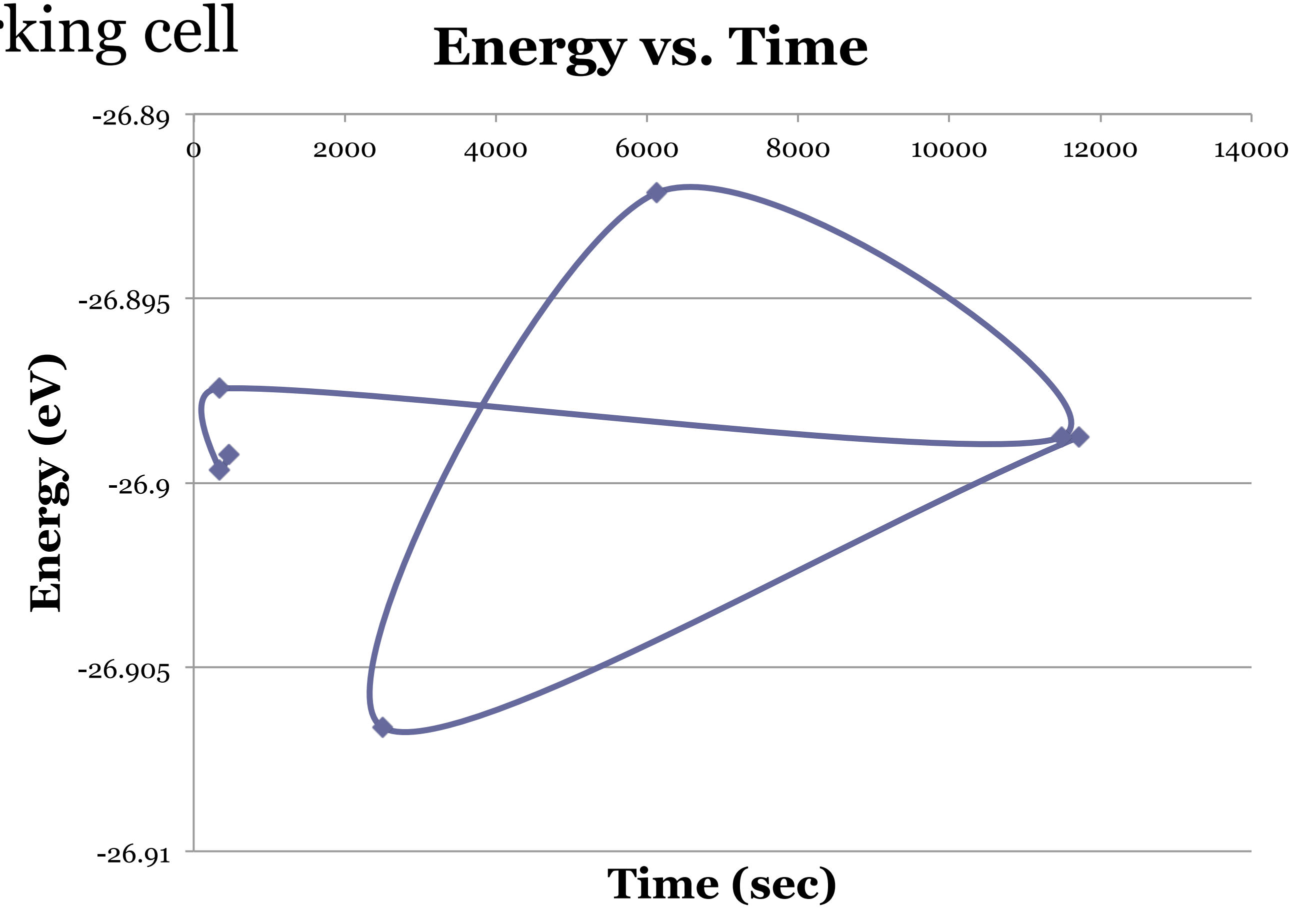
K-POINTS Convergence

- 7 X 7 X 7 k-points
- Time vs. Accuracy
- Working cell
- Good



K-POINTS Convergence

- 7 X 7 X 7 k-points
- Time vs. Accuracy
- Working cell
- Bad



Nernst Equation

Equation 1. Nernst Relationship for voltage calculation:

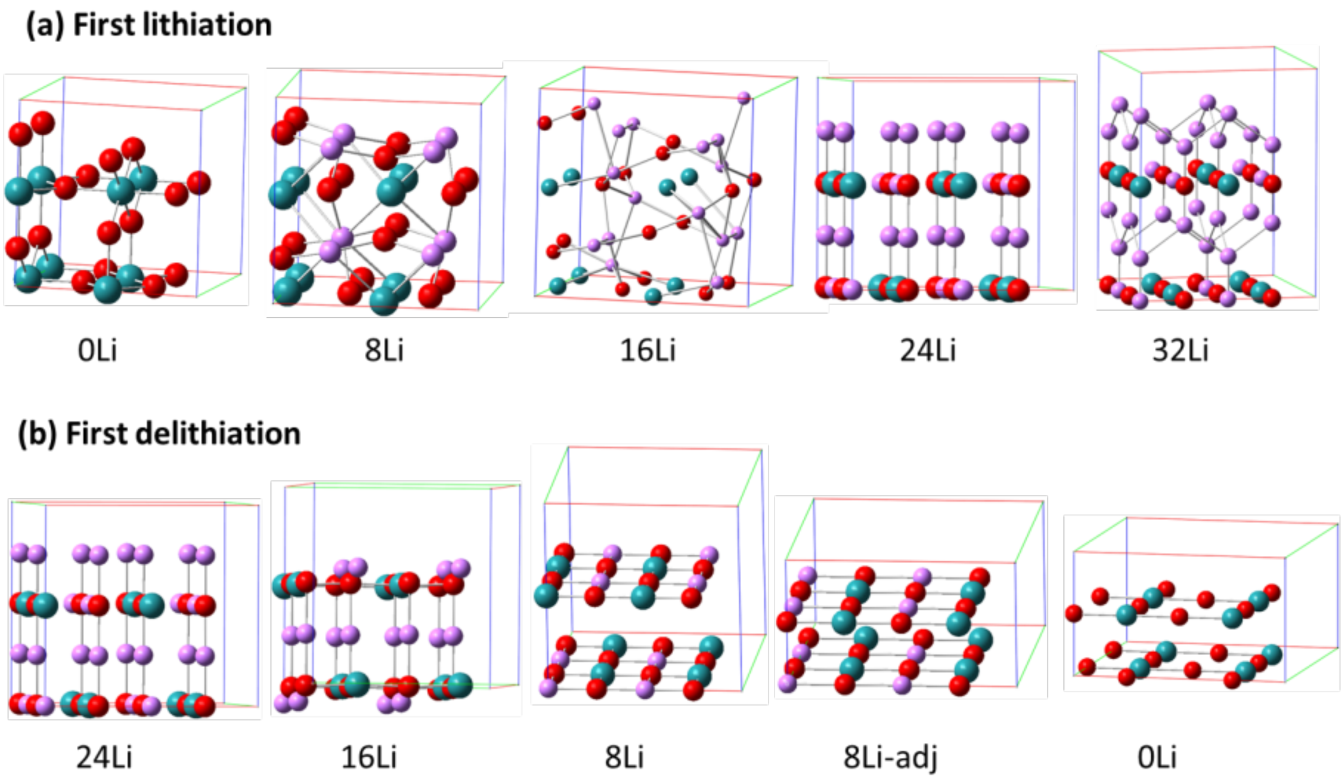
$$E\,(\mathrm{V}) = \frac{\left[G^{\circ}_{(\mathrm{MO_2})_n} + G^{\circ}_{\mathrm{Li}} - G^{\circ}_{(\mathrm{MO_2})_n\mathrm{Li}}\right]\mathrm{J\ mol^{-1}}}{xF\,(\mathrm{C\ mol^{-1}})}$$

Measures the voltage for adding Li to a metal oxide cluster

$$\underbrace{\mathrm{MO_2} \quad + \quad \mathrm{Li}}_{\text{“Reactants”}} \quad \longrightarrow \quad \underbrace{\mathrm{MO_2Li}}_{\text{“Product”}}$$

$$\Delta\mathrm{Energy} = \mathrm{E_{product}} - \mathrm{E_{reactants}}$$

Optimized Structures of $(RuO_2)_8$

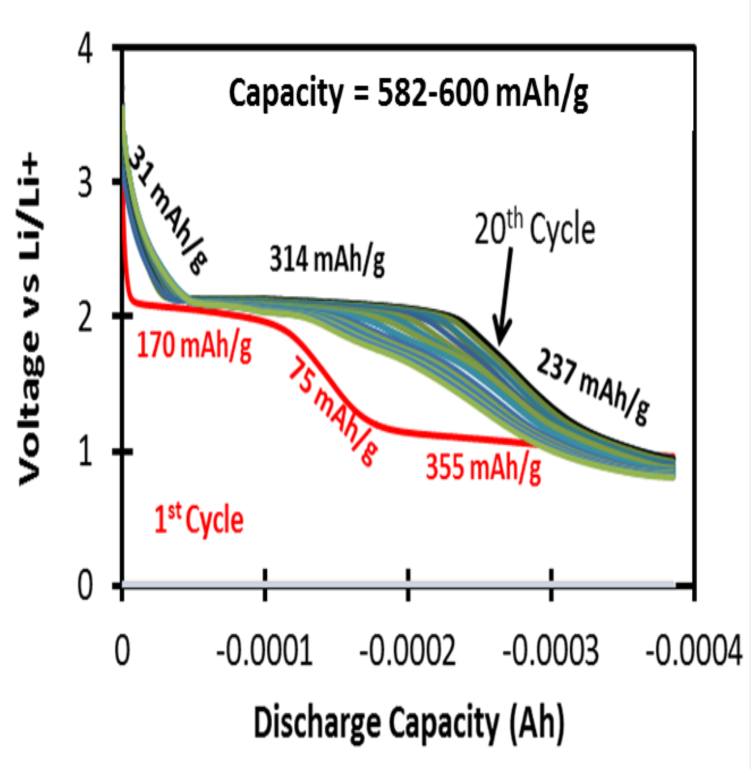


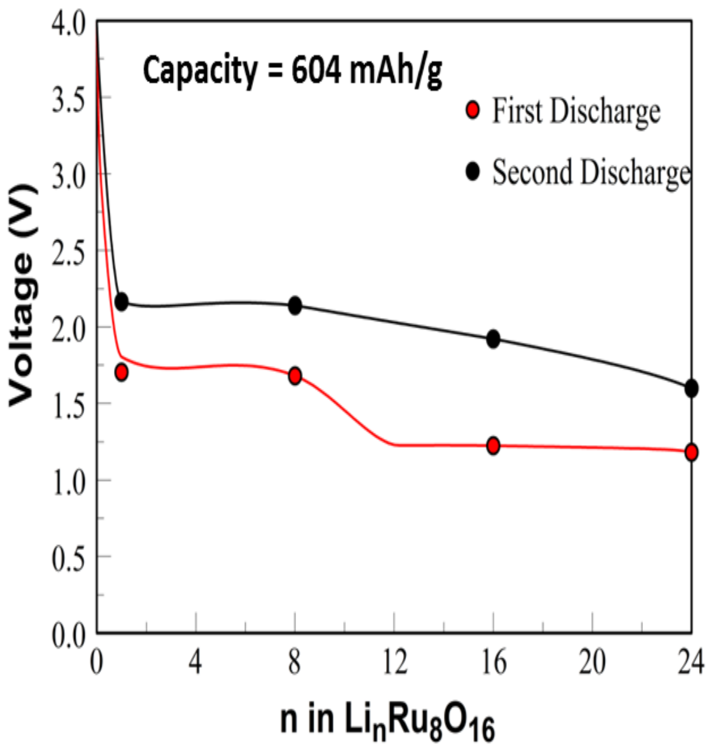
Ruthenium (Ru) - dark green   Oxygen (O) – red   Lithium (Li) - purple

- Minimal distortion 1:1
- Significant distortion 2:1
- Phase change 3:1

- Phase change allowed more Li intercalation
- Phase change is irreversible

Experimental Discharge Curves

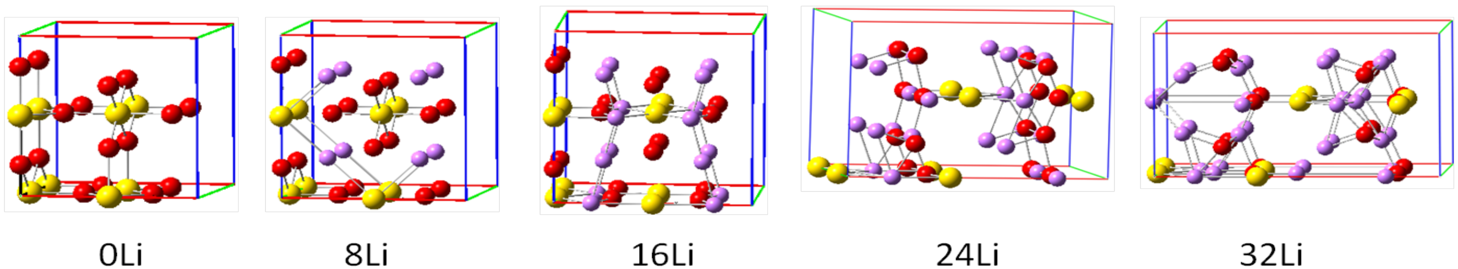




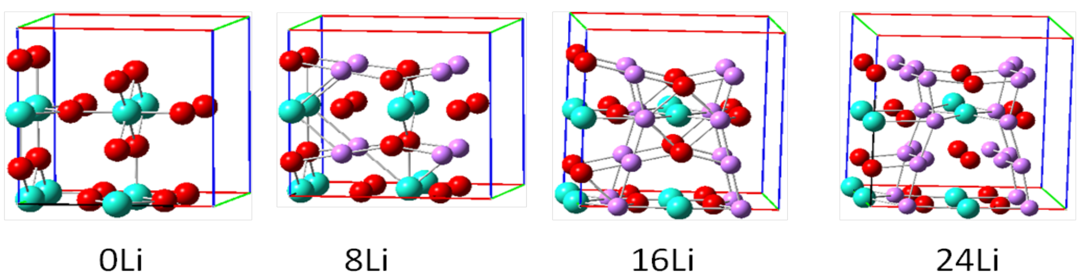
- First plateau in the first discharge represents intercalation of Li into original rutile structure
- Second discharge interpreted as intercalation of Li into the new tetragonal structure resulting after phase change
- Agreement between experimental and calculated curves

Optimized Structures of $(SnO_2)_8$ and $(MnO_2)_8$

(a) SnO_2



(b) MnO_2

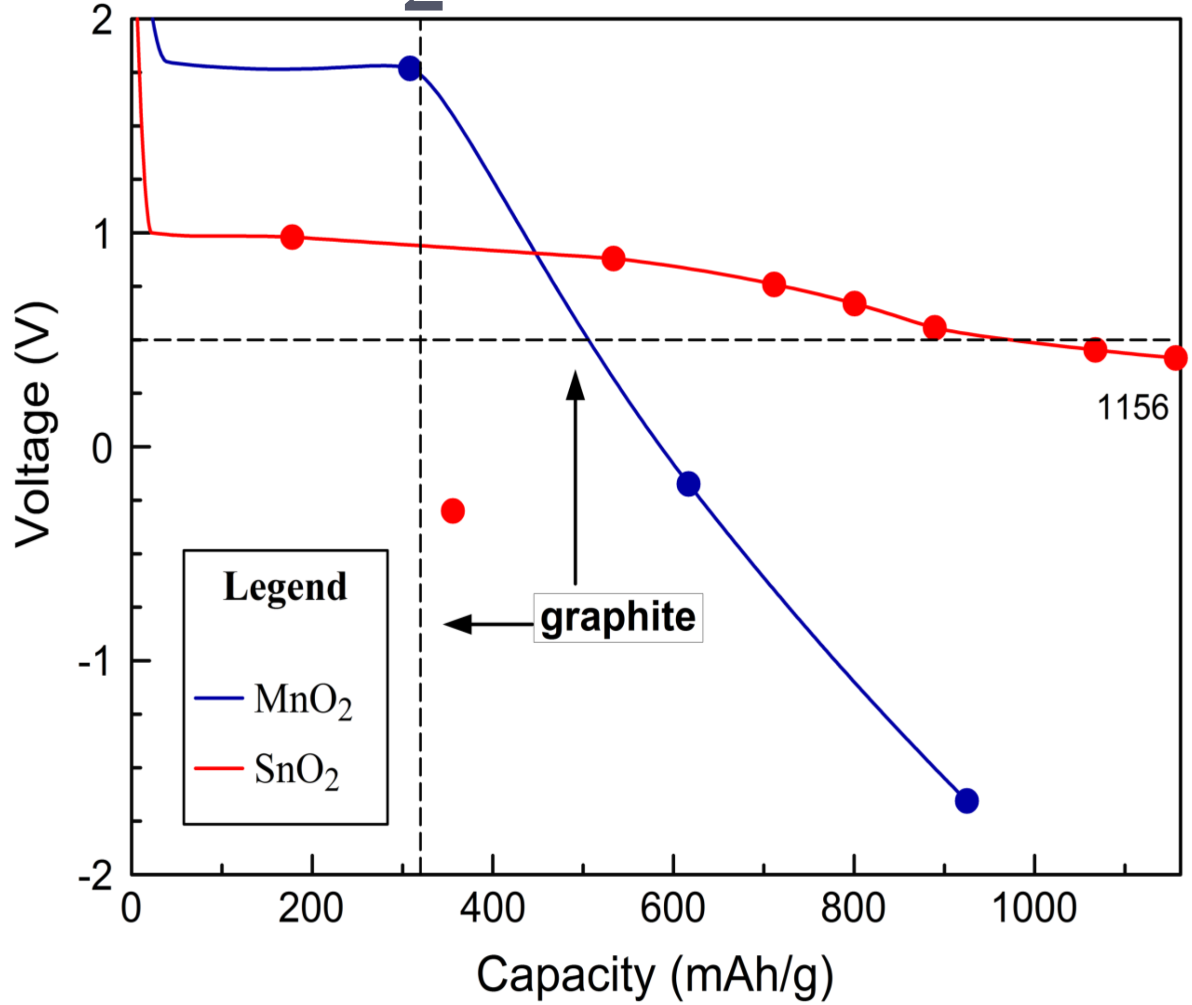


Tin (Sn) – yellow   Oxygen (O) – red   Manganese (Mn) – aqua   Lithium (Li) - purple

- Further work
- Same rutile structure as Ru

Discharge curves for MnO_2 and SnO_2

- MnO_2 does not seem promising
- Capacity drops below 0.5V at 16 Li for Mn
- SnO_2 does seem promising
- Has more capacity before dropping below 0.5v for SnO_2



Conclusion

- RuO_2 seems very promising but expensive
- Phase change occurred during first cycle
- Phase change allowed more capacity and is irreversible
- Researching other to find better materials


MEANT FOR
EVIL;
GENESIS 50:20

Acknowledgements

- **Dr. Ayorinde Hassan**
- **Dr. Ramu Ramachandran**
- **Dr. Collin Wick**
- **Mrs. Holly Payton**
- **Ms. Alicia Boudreaux**

- **National Science Foundation:**
  EPS 1003897
  EPS 1006891

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Q & A