Designing an η-Cu_6Sn_5 alloy anode for sodium ion batteries

ENMA490

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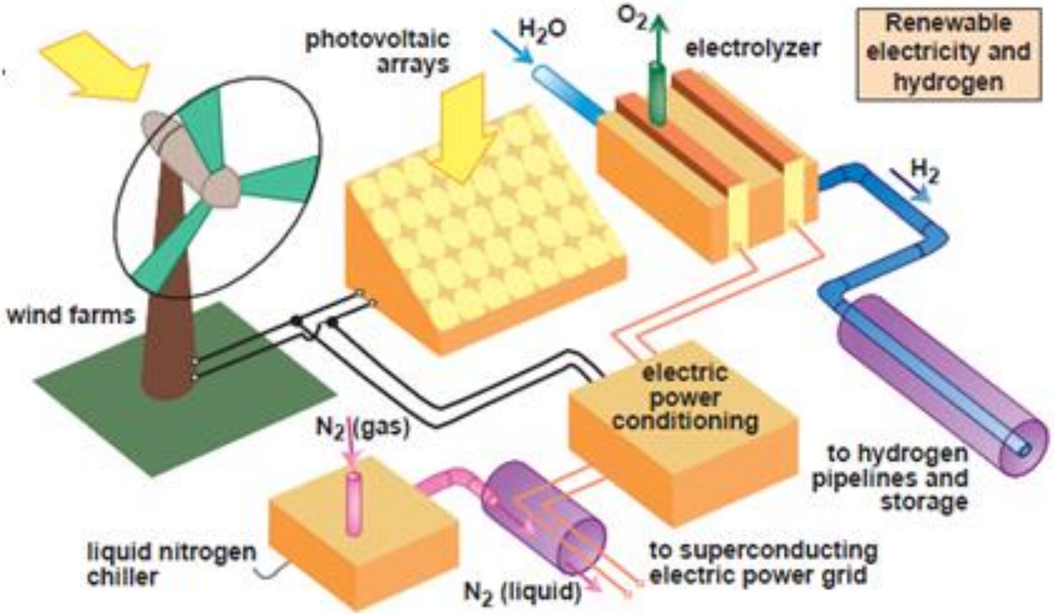
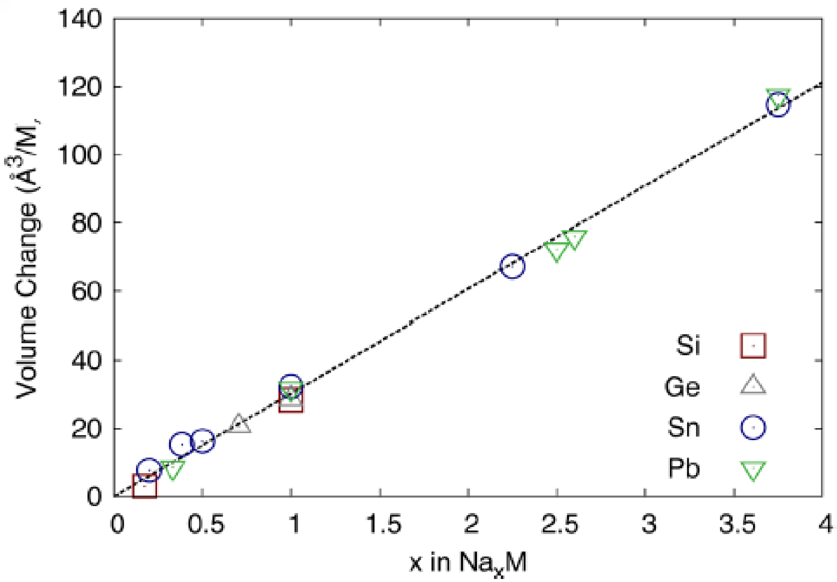
Motivation



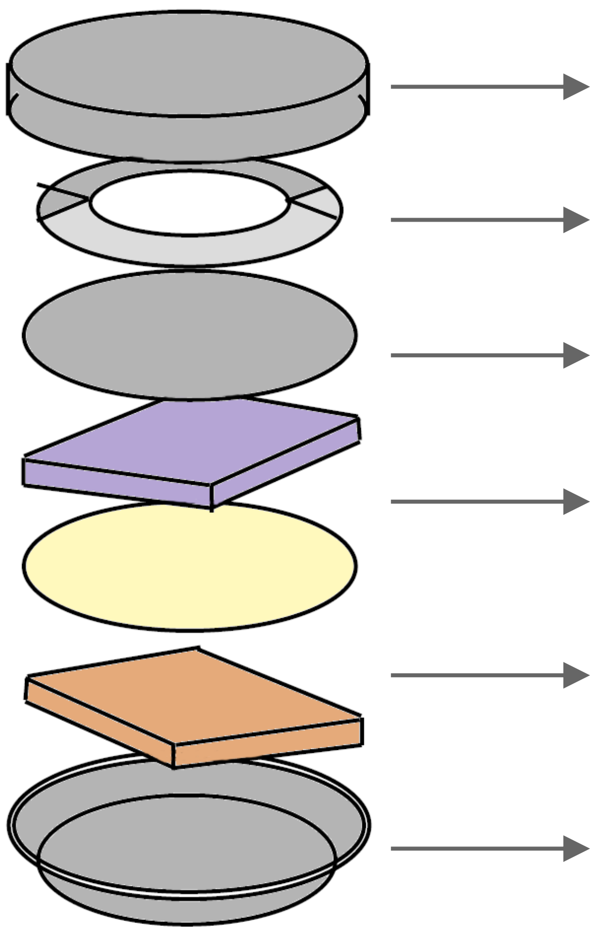
- Grid storage <$100/kWh is needed to make renewables feasible

- High capacity anodes for sodium ion batteries have short lifetimes
- Introduce an inert alloying element to reduce expansion



Hoffert, et al., *Science* 2002, Chevrier et al., *JECS* 2011

Materials Science Aspects: Sandwich Making



Physics: Kinetics of diffusion, thermodynamic stability of intermetallics

Chemistry: Electrochemistry → deposition, electrolyte optimization

Modeling: Density Functional Theory

Processing: Annealing, anode processing

Experimentation: Electrochemical Impedance Spectroscopy, Galvanostatic Cycling

Characterization: X-ray Diffraction, Scanning Electron Microscopy, Energy Dispersive X-ray Spectroscopy

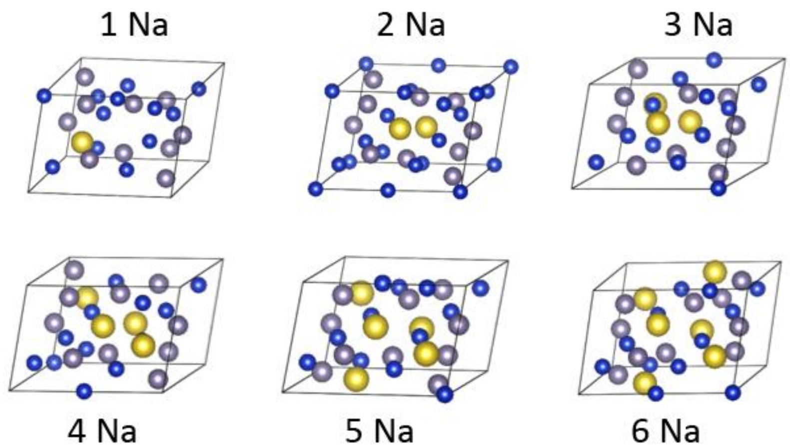
Technical Approach

Technical Approach: DFT

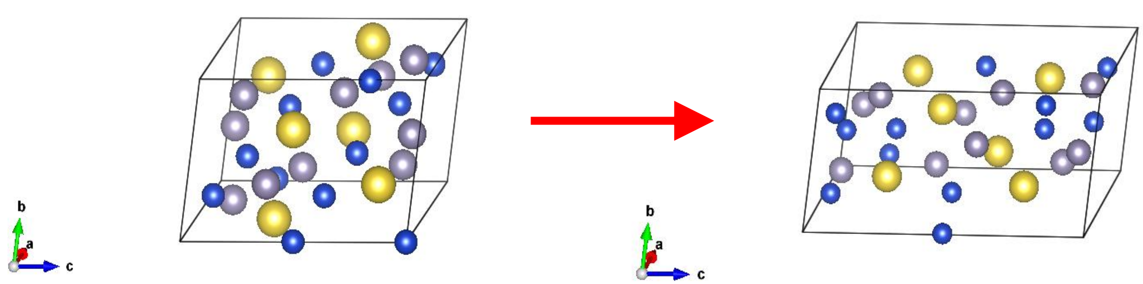
Goals

1. ***Determine the voltage associated with sodiation.***
   - Positive Voltage favors insertion of Na atoms → $V = -\left[\Delta G/(x_2-x_1)*F\right]$

2. ***Determine the number of Na atoms that can be inserted in the $Cu_{12}Sn_{10}$ unit cell.***

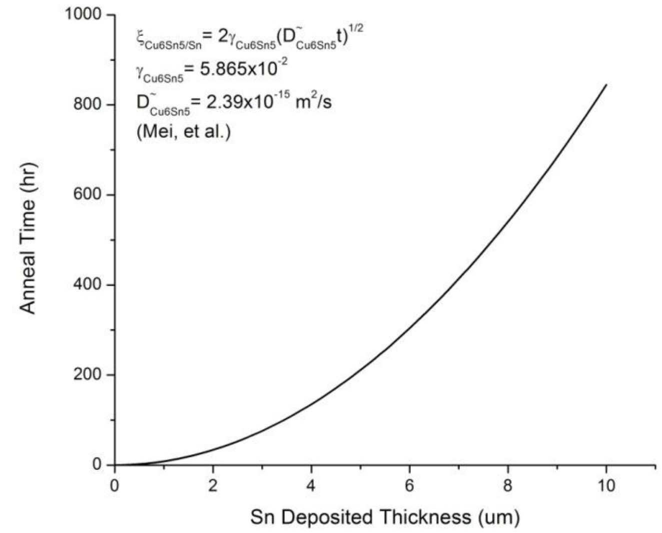


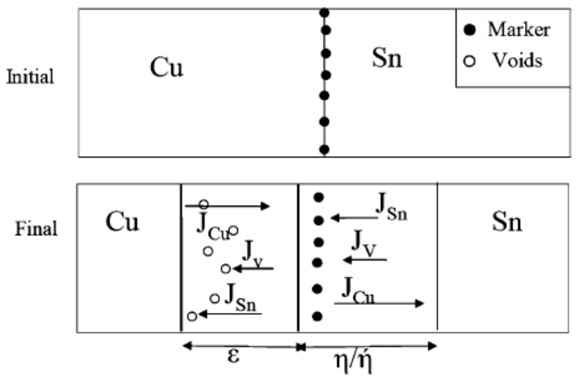
3. ***Relax the sodiated structures and determine the volume expansion.***



Technical Approach: IMC Growth

- Cu_6Sn_5 and Cu_3Sn layers will follow a parabolic growth law
    - Cu_6Sn_5 faster overall rate
- Cu_6Sn_5/Sn interface moves with square root of time
- Calculate annealing time necessary for interface to move completely through Sn
- Assume Cu_6Sn_5 and Cu_3Sn begin growing immediately at Cu-Sn interface





Kumar, et al. (2011)

Technical Approach: Prototyping

- Electrodeposition
  - Deposit Sn on Cu substrate (cathode), Pt anode
  - Faraday's Law of Electrolysis gives deposition time: $t = (N*n*F)/I$ [N= moles dep., n= charges exch., F= Faraday constant, I= current]
  - Electrodeposition Bath:
    - 0.014M Sn(II) Sulfate, 1.93M methanesulfonic acid, 0.05M hydroquinone
    - Methanesulfonic acid provides benefits over conventional acids (sulfuric, etc)
      - Higher solubility of metal salt (tin sulfate)
      - Helps stabilize Sn(II) ions against oxidation
      - Good electrical conductivity
      - Low toxicity, readily biodegradable
    - Hydroquinone greatly reduces the oxidation of the tin ions in the solution
      - Oxidation of Sn(II) to Sn(IV) results in formation of insoluble tin salts (sludging), removing tin from solution and reducing its ability to deposit

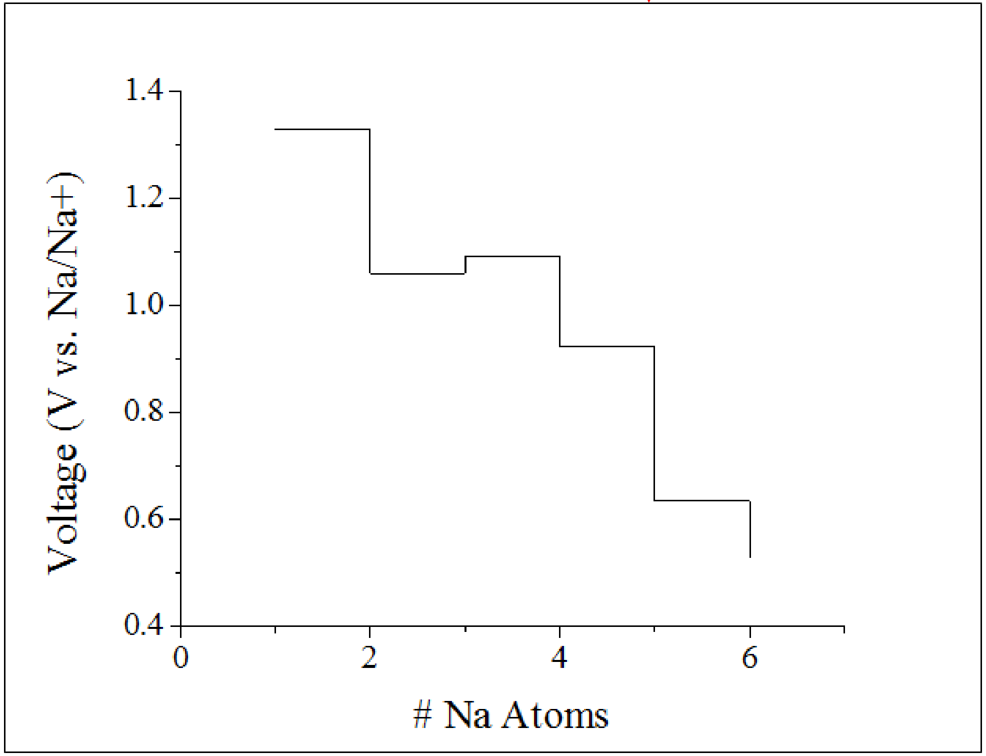
Results

DFT Modeling

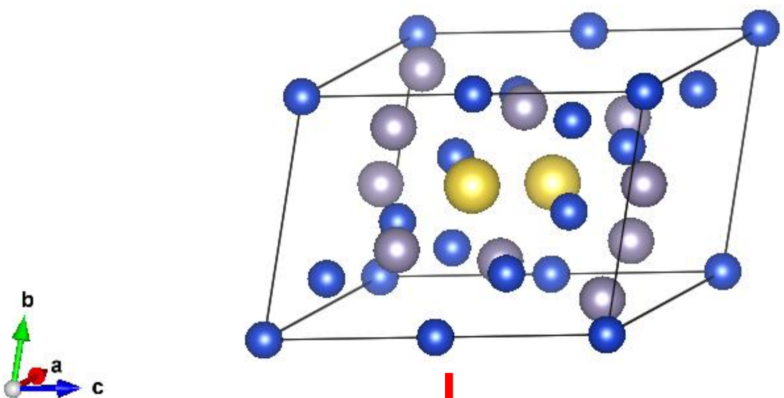
- $V_{theory} = -(E_{defect} + xE_{Na} - E_{perfect})/x =$

-1.306 eV   - 83.48 eV

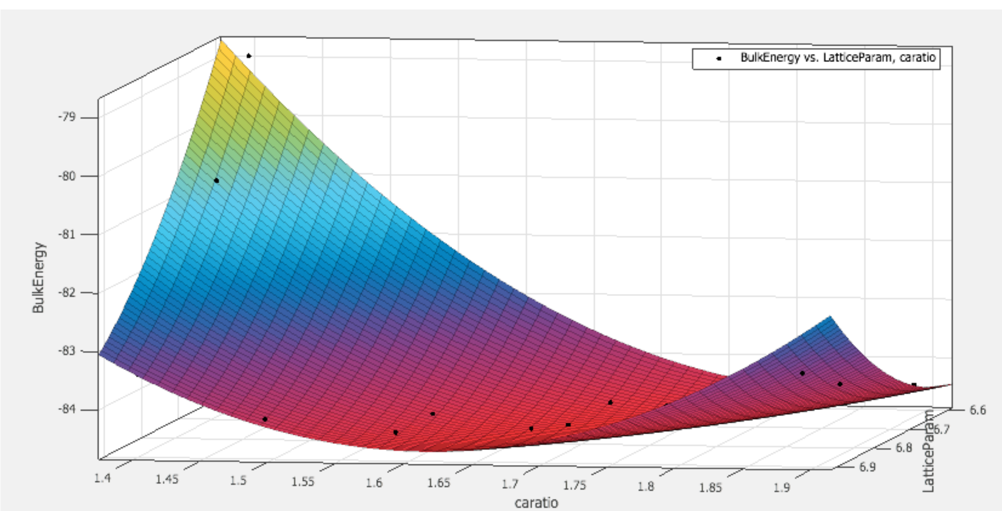
Na-CuSn structure Bulk E (eV)	# Na Atoms
-83.51	1
-82.98	2
-82.82	3
-81.95	4
-80.12	5
-78.81	6

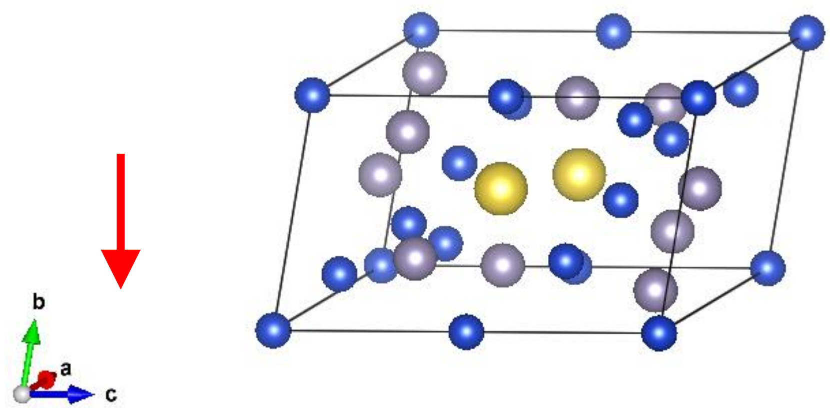


DFT Modeling



- NaSn5 is first to form in pure Sn anodes
- Na_2-$Cu_{12}Sn_{10}$ Volume = 405.95 Angstroms^3
- Relaxed Na_2-$Cu_{12}Sn_{10}$ Volume = 483.11 Angstroms^3
- 19.01% Volume Expansion via DFT
- 30.14% Volume Expansion from Sn-->NaSn5 from reported theoretical values





Electrodeposition

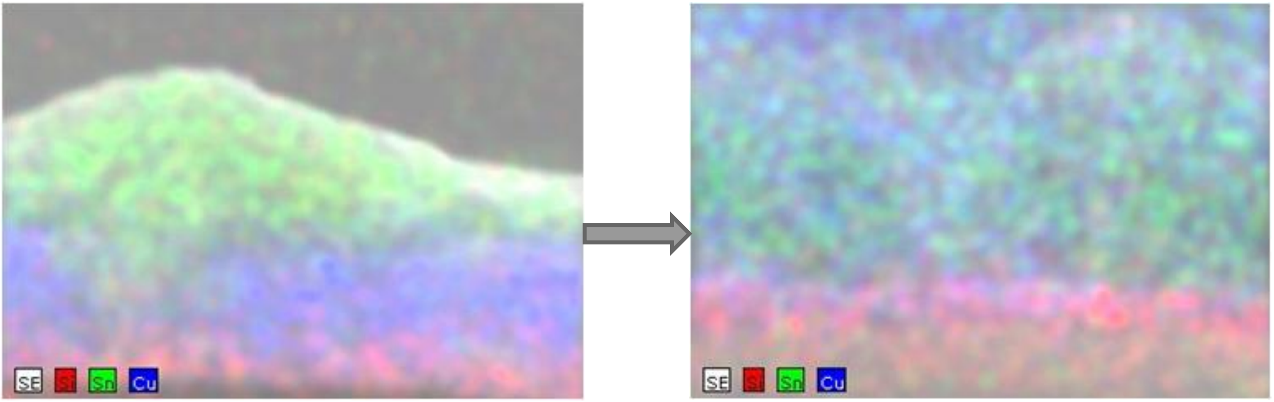
Sample	Cu mass (g) (est.)	Desired Sn mass (g)	Deposition current (mA)	Deposition time (min)	Deposited Sn mass (g)
1	0.0091	0.0141	5.0	90	0.0134
3	0.0091	0.0141	5.0	66	0.0077
5	0.0093	0.0144	5.0	90	0.0117
6	0.0092	0.0143	5.0	90	0.0061
7	0.0076	0.0007	0.5	40	0.0001

Origin of discrepancies:

- Error in mass measurement
- Sn(II) ion oxidation
- Sn(II) ion transport and depletion
- Competing reactions

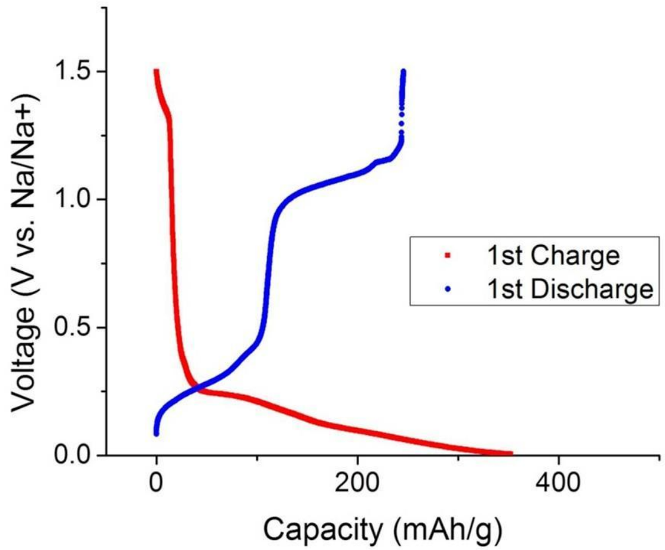
XRD and SEM/EDS

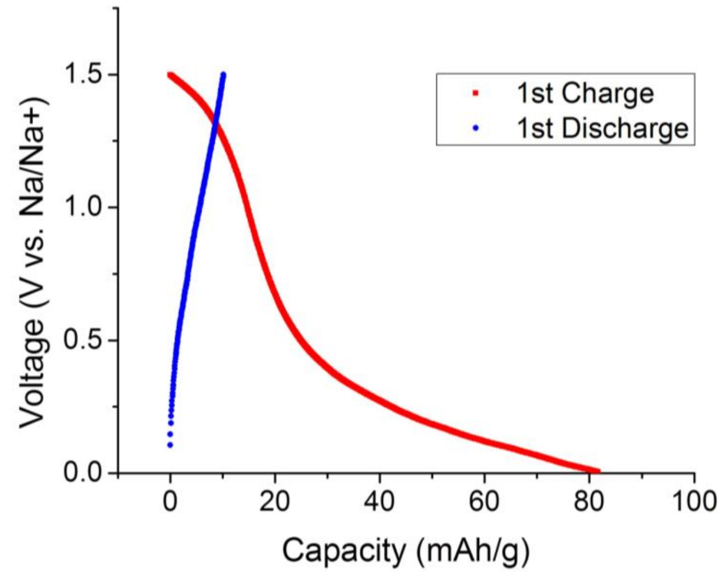
Sample	Annealing time(hrs)	Sn	Cu	Cu3Sn	Cu6Sn5
1A	20	X	X	X	
3	20	X	X	X	X
5	20	X	X	X	X
6	20	X	X	X	X
1a	120	X	X	X	
3a	120	X	X	X	X
5a	120	X	X	X	
6a	120	X	X	X	X
6b	120	X			
7	12		X	X	
Si3 (Control)	0	X	X		
Si5	2.116		X	X	
Si6	2.116		X	X	

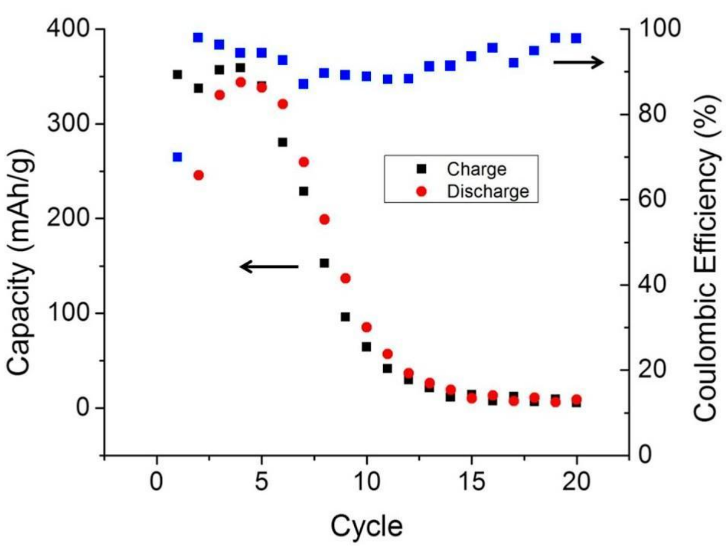


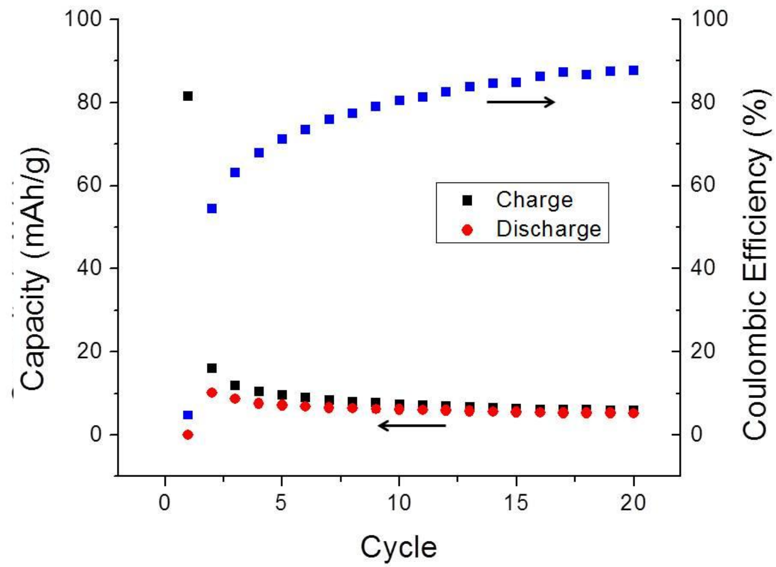
- Initial deposition:
  - Based fabrication on stoichiometry, found that sufficient annealing would take long period of time
- IMC interface movement:
  - Predicted total consumption of Sn thin layer
  - XRD identification of only Cu_3Sn likely due to excess Cu

Battery Cell Testing









Conclusions

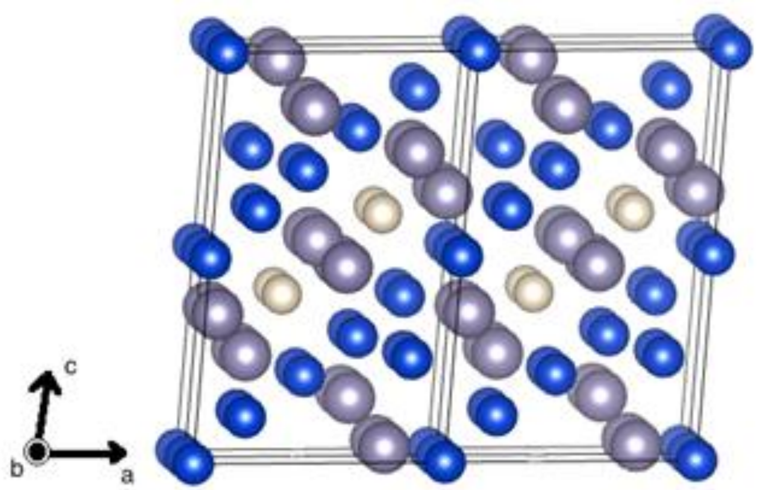
- First principles calculations indicate that Na can insert into η-Cu_6Sn_5 with a capacity of at least 82 Ah/kg and 62.6% volume expansion.

$$Capacity\left[\frac{Ah}{kg}\right] = \left(\frac{ze^{-}}{yA_m^{alloy}}\right) * F * \left(\frac{3600kg}{1000hr}\right)$$

- Volume expansion for the 2 Na atom system is 10% less than for pure Sn anodes, indicating that η-Cu_6Sn_5 anodes may have improved lifetime due to reduced expansion.
- Further fabrication and electrochemical characterization required to experimentally confirm DFT results.

Future Work

- Utilize Nudged Elastic Band (NEB) method to determine energy barriers for Na insertion into η-Cu_6Sn_5.
- Perform similar first principles calculations for ε-Cu3Sn to compare to experimental results.



- Optimize Cu/Sn ratio for substrate to obtain η-Cu_6Sn_5.
- Explore other deposition methods (sputtering, PLD).
- Assemble and test half-cells with the η-Cu_6Sn_5 anode.

Acknowledgements

UMD:

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Dr. Ganesh

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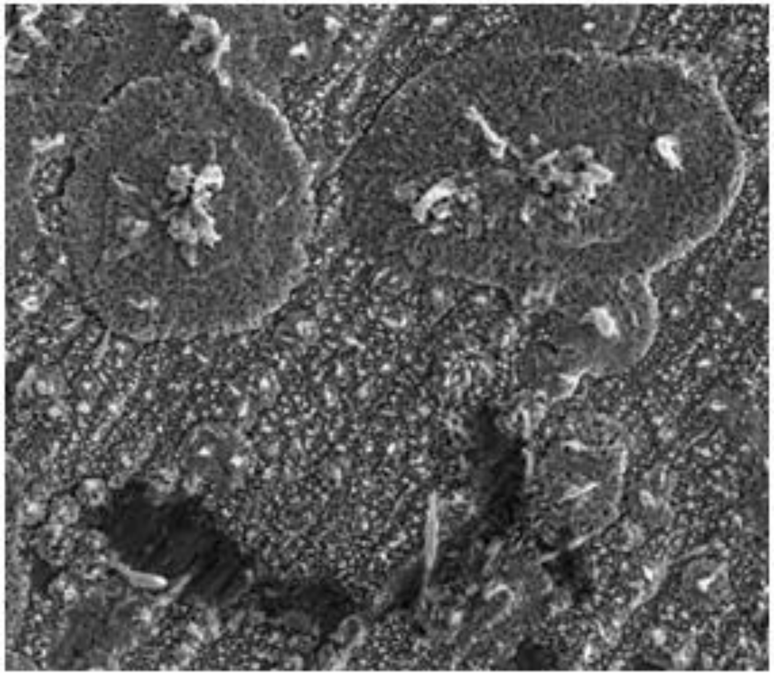

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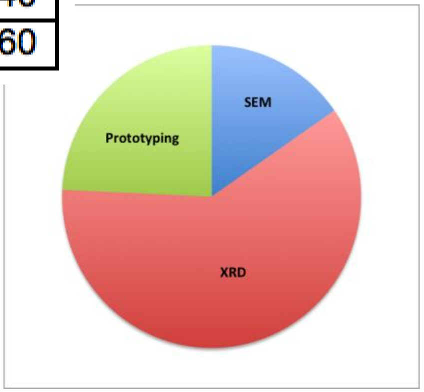
Thank You

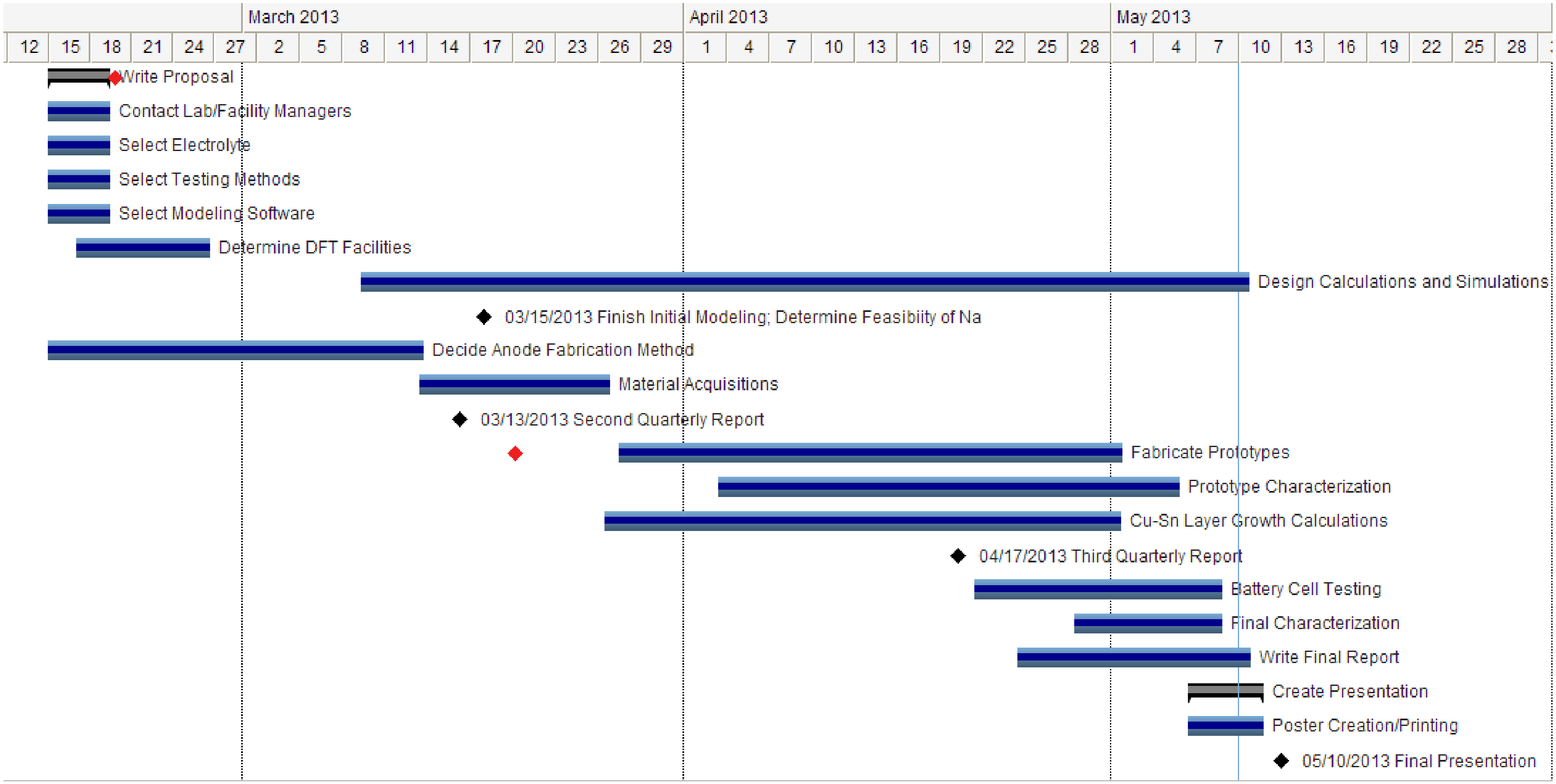
Budget and Resources

Purpose	Item	Cost/unit ($/unit)	Units	Cost ($)
Characterization	SEM in the Fablab	$ 22.00	5	$ 110.00
	X-Ray Diffraction	$ 64.00	4	$ 256.00
	X-Ray Diffraction	$ 55.00	5	$ 275.00
	Electron Probe Microanalysis	$ 25.00	1	$ 25.00
Modeling	XSEDE Allocation for VASP	$ -	1	$ -
Prototyping	Alumina Boat (50 x 40 x 18 mm)	$ 5.00	3	$ 15.00
	Beaker (400 ml)	$ 3.24	1	$ 3.24
	Hydroquinone Electrolyte (100 g)	$ 24.09	1	$ 24.09
	3M Electroplating Tape 470	$ 24.34	1	$ 24.34
	Thermal Evaporation	$ 61.00	2	$ 122.00
	Stir Bar	$ 5.78	1	$ 5.78
	Stopper	$ 18.95	1	$ 18.95
		Total		$ 879.40
		Remaining		$ 620.60

Calculation	Service Units Used
Bulk Energy of $Cu_{12}Sn_{10}$	118
Relaxations of Na Insertion	119
Relaxation of 2 Na Structure	1583
Relaxation of 6 Na Structure	6127
Total Used	7947
Remaining	92053



Timeline


March 2013
April 2013
May 2013
12 15 18 21 24 27 2 5 8 11 14 17 20 23 26 29 1 4 7 10 13 16 19 22 25 28 1 4 7 10 13 16 19 22 25 28
Write Proposal
Contact Lab/Facility Managers
Select Electrolyte
Select Testing Methods
Select Modeling Software
Determine DFT Facilities
Design Calculations and Simulations
03/15/2013 Finish Initial Modeling; Determine Feasibiity of Na
Decide Anode Fabrication Method
Material Acquisitions
03/13/2013 Second Quarterly Report
Fabricate Prototypes
Prototype Characterization
Cu-Sn Layer Growth Calculations
04/17/2013 Third Quarterly Report
Battery Cell Testing
Final Characterization
Write Final Report
Create Presentation
Poster Creation/Printing
05/10/2013 Final Presentation