Stan Whittingham
SUNY at Binghamton

High Energy Density Lithium Battery

M. Stanley Whittingham
State University of New York at Binghamton

June 10th, 2015

Project ID #
ES231

Overview

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Timeline

- Project start date: 10-01-2014
- Project end date: 9-30-2017
- Percent complete: 18%

Barriers

- Barriers addressed
  - Higher volumetric energy density
  - Cyclability of conversion electrodes
  - Lower cost
  - Abuse-tolerant safer electrodes

Budget

- Total project funding
  - DOE $1,265,773
  - Contractor share: Personnel
- Funding received
  - FY15: 398k$

Partners

- National Laboratories
  - Brookhaven; Argonne
- Local Industry
  - Through NYBEST
- Academia
  - Electrolytes – UC Boulder, URI

Relevance and Objectives of Work

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- **The primary objectives of our work are to:**
  - Replace the present volume intensive carbon anode
  - Replace the present cathodes with ones where more than one Li reacts per transition metal
  - Lower the cost of materials and approaches
- **The relevance of our work is:**
  - Achieving the above objectives
    - Will increase the volumetric energy density of lithium batteries by > 50%
      - 1 kWh/liter at the cell level
    - Will increase the gravimetric energy density
      - ≥ 300 Wh/kg at the cell level
    - Will lower the cost of tomorrow's batteries

Relevance: Milestones

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1. Demonstrate synthesis and complete characterization of CuF_2. (Dec. 14) **Completed**
2. Determine discharge product of CuF_2. (March 15) **Completed**
3. Begin cyclability testing of CuF_2. (June 2015) **Underway**
4. Demonstrate more than 100 cycles on Sn_2Fe at 1.5 times the volumetric energy density of carbon. (Sept. 15) **Underway**
5. Go/No-Go: Demonstrate cyclability of CuF_2. Criteria: Capacity of 200 mAh/g over 10 cycles. (Sept-15)

Approach and Strategy: Improved Anodes

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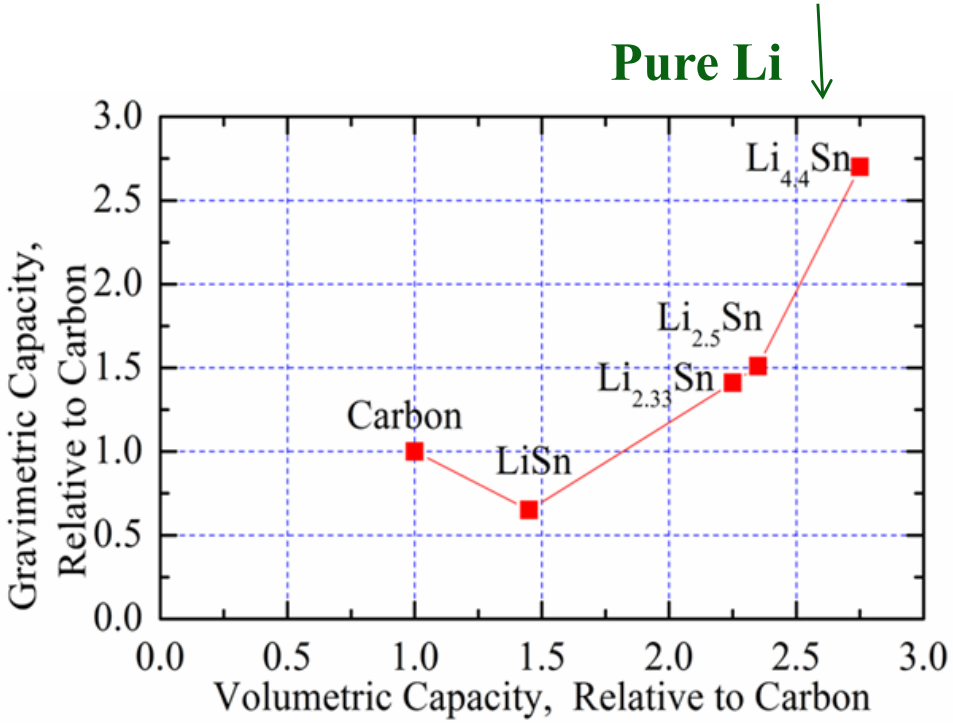
- Replace intercalation carbon host with conversion reaction material
  - Allows for much higher capacities
    - Carbon – only 350 Ah/g and 0.8 Ah/liter
    - Pure lithium anode has around 2.5 times the volumetric capacity
  - Place emphasis on tin-based systems
    - Why Sn_2Fe?
      - 804 Ah/kg and >2000 Ah/liter
      - > 2.5 times that of carbon
    - Protect with carbon coating
      - Initial BATT results promising
    - Safer than carbon and silicon
      - ΔG Sn/Fe-SnO_2 160 kJ/mole Li
      - ΔG Si-SiO_2 194 kJ/mole Li
      - ΔG C-CO_2 2366 kJ/mole Li



Approach and Strategy: Improved Cathodes

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- Replace materials that react with ≤ 1 Li per transition metal
  - E.g. $LiFePO_4$ and $LiCoO_2$
- By materials that can react with up to 2 Li per transition metal
- Two-pronged approach
  - Intercalation cathode
    - Essentially retain the crystal structure
    - The system $VOPO_4$-$LiVOPO_4$-Li_2VOPO_4 chosen
  - Conversion cathode
    - Destroy and rebuild the crystal structure
    - The system CuF_2 – Cu + 2LiF chosen
      - Higher potential than other fluorides

Approach and Strategy: Improved Cathodes

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- **Why the choice of CuF_2 and $VOPO_4$?**

- **CuF_2**
  - High theoretical energy density of 1874 Wh/kg
    - Compare 1000 Wh/kg and 587 Wh/kg theoretical for complete reaction of $LiCoO_2$ and $LiFePO_4$ respectively.
    - Theoretical specific capacity exceeding 500 mAh/g
    - Theoretical potential, 3.5 V, highest amongst the 3d transition metals

- **$VOPO_4$**
  - Intercalation cathode
  - High energy densities of 1080 Wh/kg and 3.5 kWh/L
    - > 1.5 times that of $LiFePO_4$
    - Theoretical capacity of ~ 320 Ah/kg (double that of $LiFePO_4$)
    - Redox potentials at 3.9 V for V^{5+}/V^{4+} and ~ 2.5 V for V^{4+}/V^{3+}

Technical Accomplishments: Barriers being Addressed

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- **Low Volumetric Energy Density of Li batteries**
  - Volumetric capacity of today's Li-ion batteries limited by carbon anode and less than 1 Li/transition metal
  - Find anode material with double the volumetric capacity of carbon
  - Find cathode material that reacts with approaching 2 Li
- **Cyclability of conversion electrodes**
  - Efficiency of known conversion reactions too low
- **High cost of lithium batteries**
  - Reduction of Materials and manufacturing costs
  - Find anode material with double the volumetric capacity of carbon
  - Find
- **Low Safety and Abuse-tolerance**
  - Find an anode that reacts with lithium faster
  - Find thermally stable electrodes under all states of charge

Milestone 1 – CuF_2 synthesized and characterized: forms solid solution with FeF_2. Composite with MoO_3.

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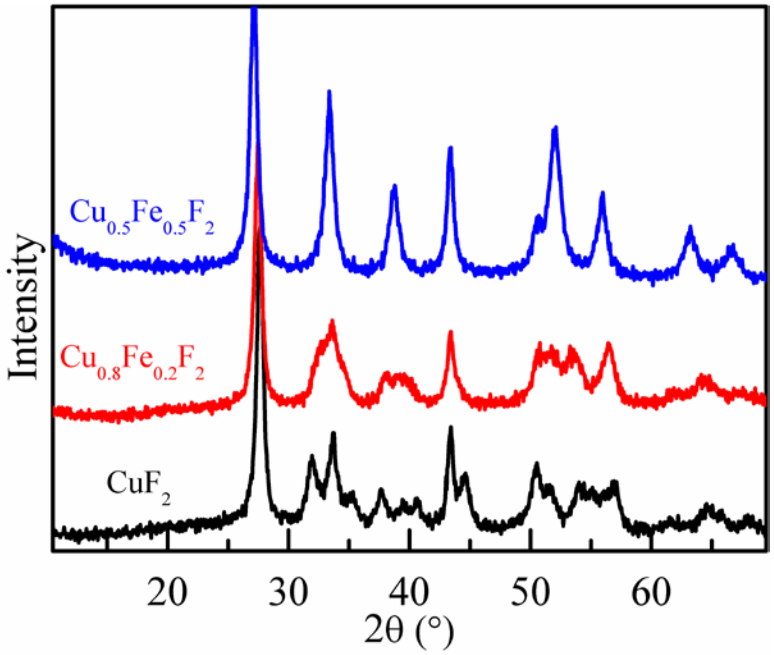

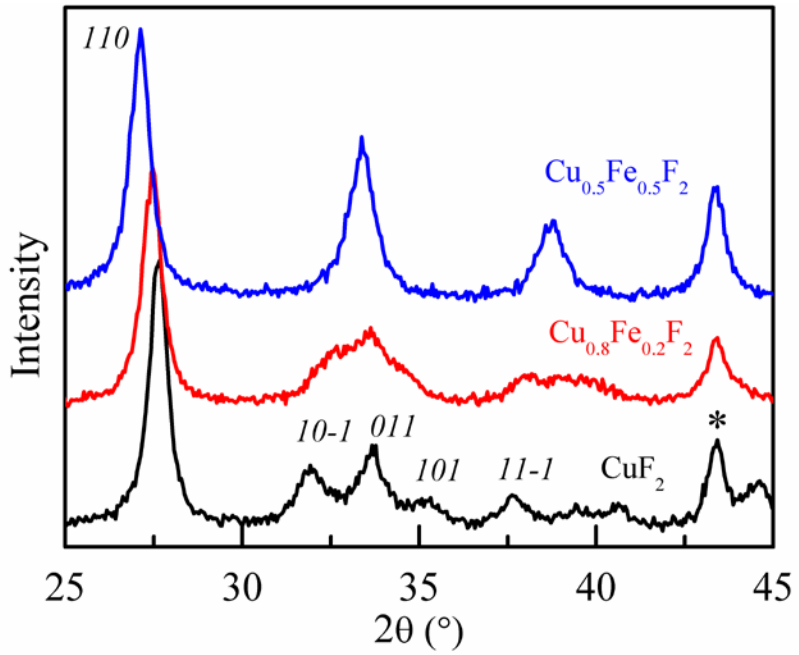

Synthesis of $Cu_{1-y}Fe_yF_2$, y= 0, 0.2, 0.5;

- Carbon or MoO_3 composite synthesized by high energy ball-milling of CuF_2 and FeF_2

XRD Characterization:

- Fe is soluble in CuF_2 forming a solid solution:
  - Shift in the diffraction peak position
  - Change in lattice parameters
- Both have similar structures.
  - CuF_2 distorted rutile structure
  - FeF_2 rutile structure
- MoO_3 forms a composite: No solid solution.

	a (Å)	*b*(Å)	*c*(Å)	*β*(°)	*V*(Å³)
CuF_2	4.595(3)	4.560(3)	3.295(1)	95.76(1)	68.71(3)
$Cu_{0.5}Fe_{0.5}F_2$	4.675(3)	4.642(3)	3.285(1)	90.62((1)	71.39(3)

Milestone 2 – Discharge products of CuF_2/C and $Cu_{0.8}Fe_{0.2}F_2$/C identified

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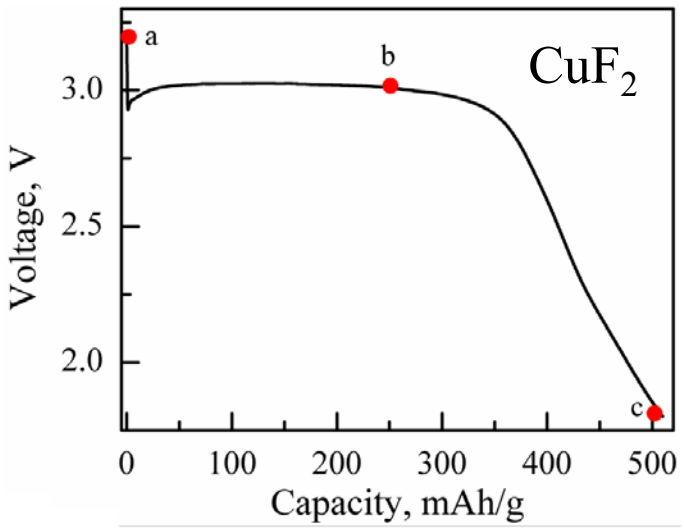

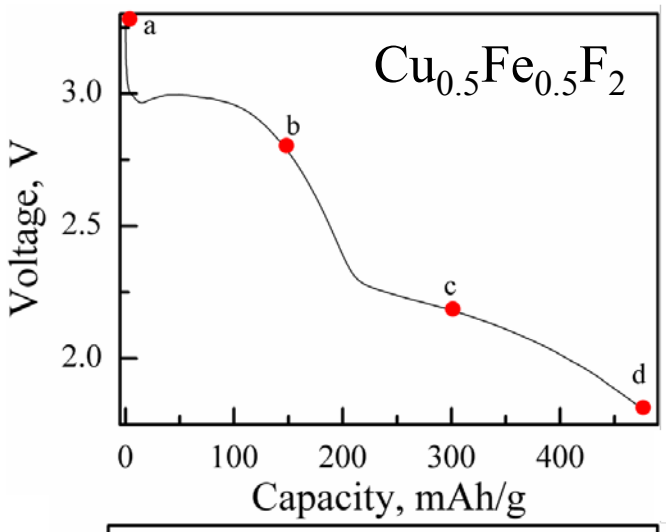

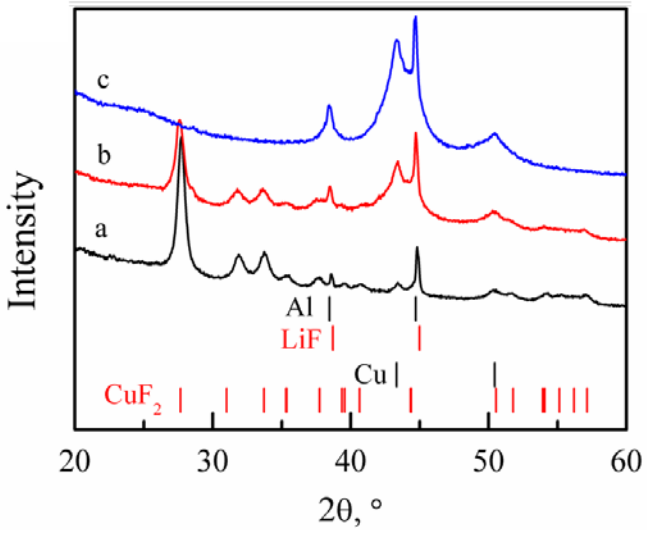

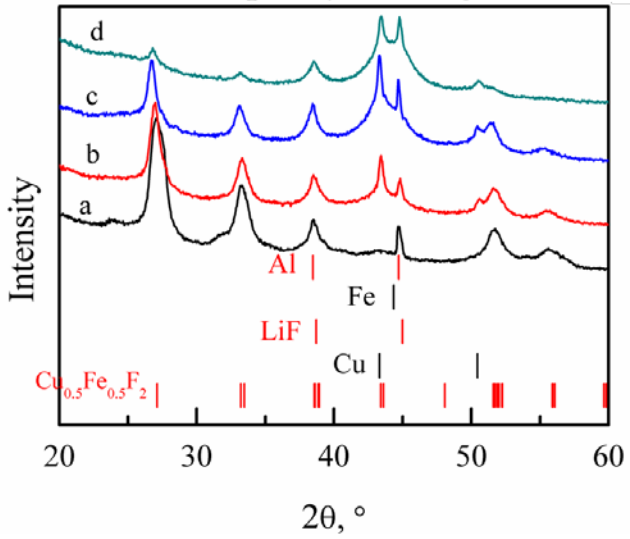

CuF_2

- Reaction complete at 1.8 V
- CuF_2 converted to Cu and LiF

$Cu_{0.5}Fe_{0.5}F_2$

- Not complete at 1.8V
- Forms LiF and Cu
- Peaks of Fe phase overlap with LiF phase, so cannot be identified

Milestone 3 – Cycling shows close to theoretical capacity for CuF_2; MoO_3 composite does not cycle well

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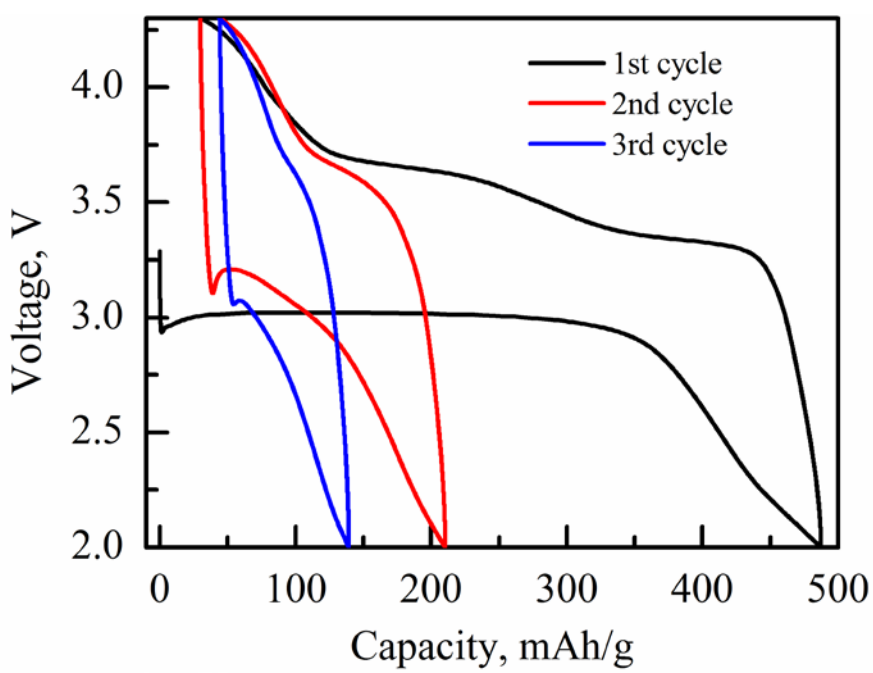

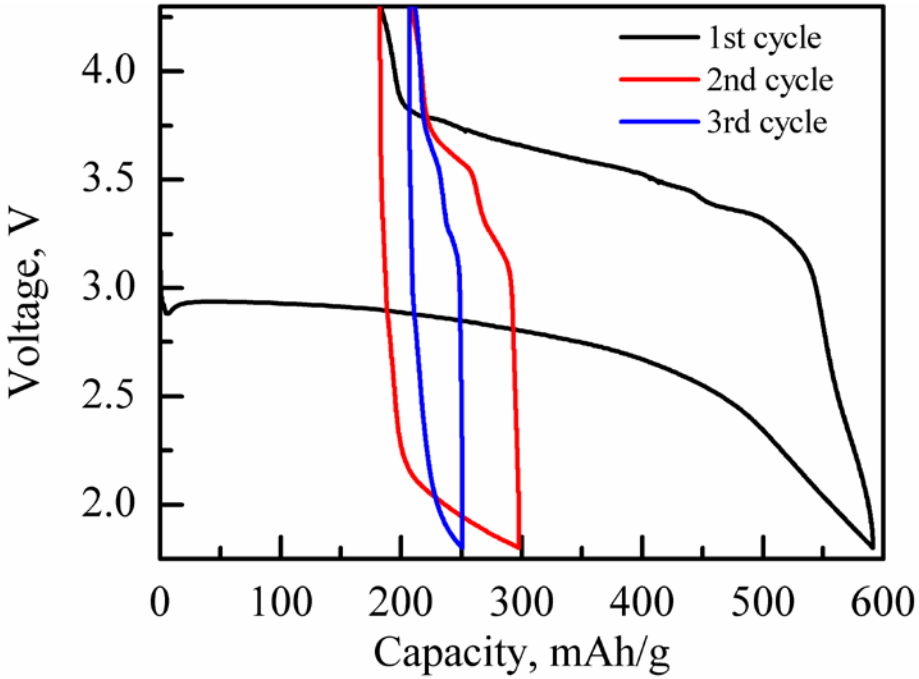

Initial discharge capacity:

- CuF_2 shows close to the theoretical capacity of 528 mAh/g
  - More extended cycling underway
- CuF_2/MoO_3 composite shows higher first discharge capacity
  - Consistent with prior primary battery report
  - Cyclability does not warrant further study

Milestone 4. Demonstrate 1.5 times the capacity of carbon in the Sn_2Fe – What is the role of carbon?

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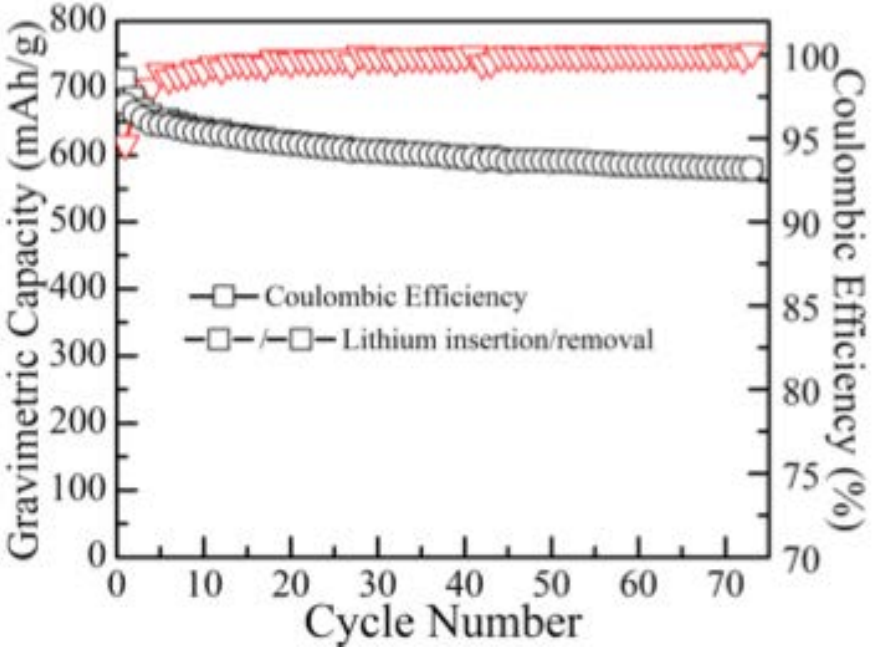
- **Earlier results showed capacity exceeding that of Sn_2Fe**
  - Theoretical capacity of Sn_2Fe is 804 mAh/g
  - Carbon must contribute to capacity
    - Formation of LiC_2 can explain capacity
    - Study initiated to determine role of carbon



Milestone 4. Synthesis optimization of Sn-Fe-C anode
Impact of graphite content

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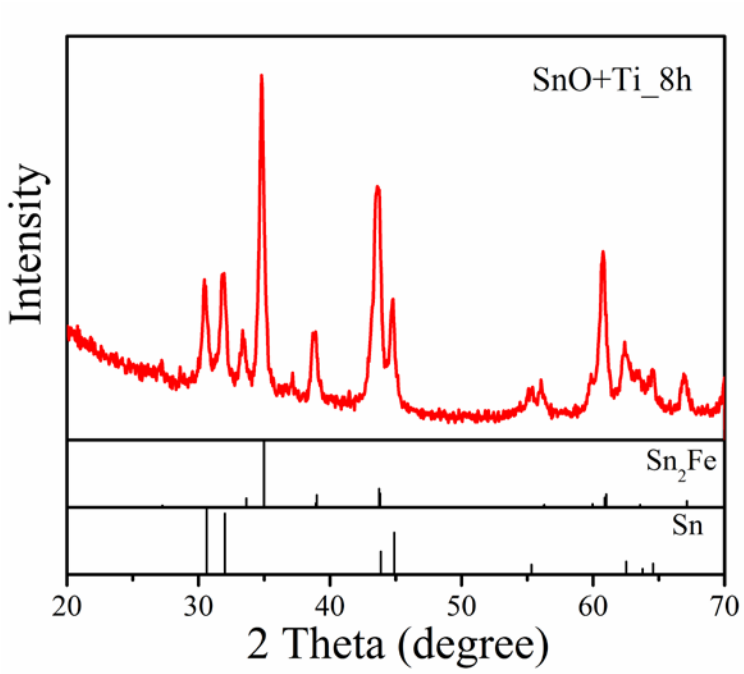
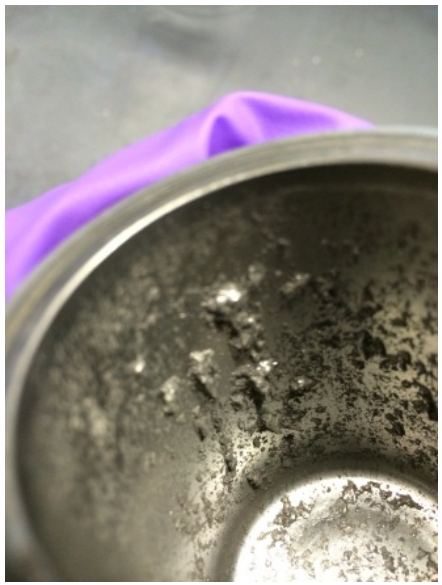
- **Carbon essential to mechanochemical synthesis**
  - Tin melts at the high temperature caused by high energy ball milling.
  - Fails to react completely leaving globules of tin.





Milestone 4. Synthesis optimization of Sn-Fe-C anode
Impact of carbon type and amount

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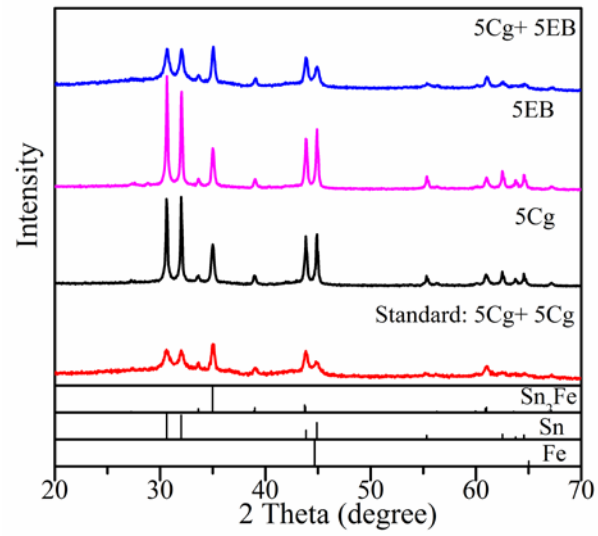
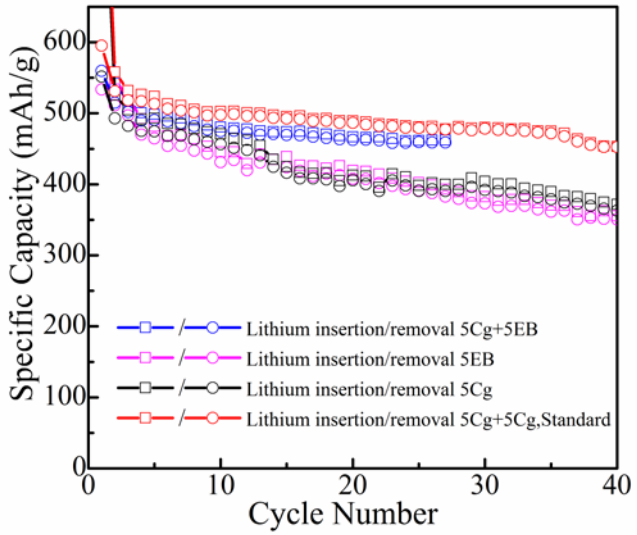
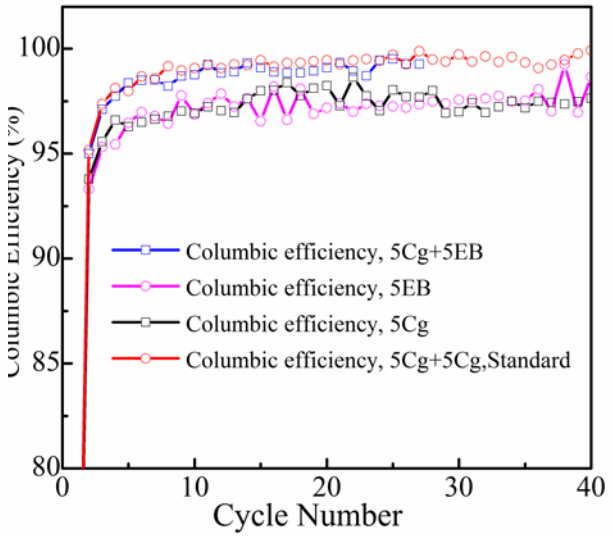
- **Past standard synthesis used a 10:1 ratio of graphite:tin**
- **Replacing graphite partially by carbon black had no impact on capacity retention, however amount of carbon critical**
  - 5:1 carbon:tin leads to larger amounts and greater crystallinity of tin metal
  - 5:1 carbon:tin results in lower capacity retention and lower coulombic efficiency.
  - Conclusion: need 10:1 ratio, and source of carbon not important







Graphite-Cg Ethylene Black-EB

Milestone 4. Synthesis optimization of Sn-Fe-C anode LiC_6 vs LiC_2 - does ball-milling activate the carbon?

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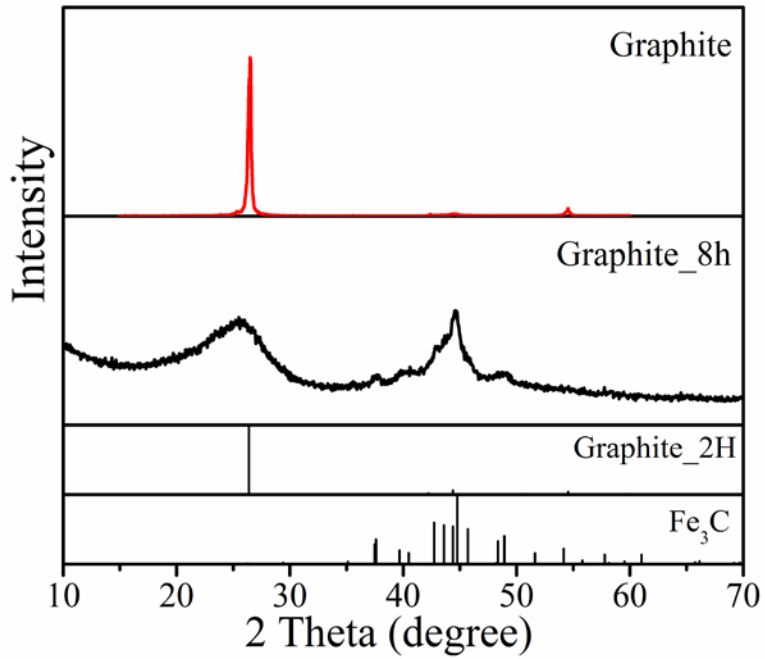
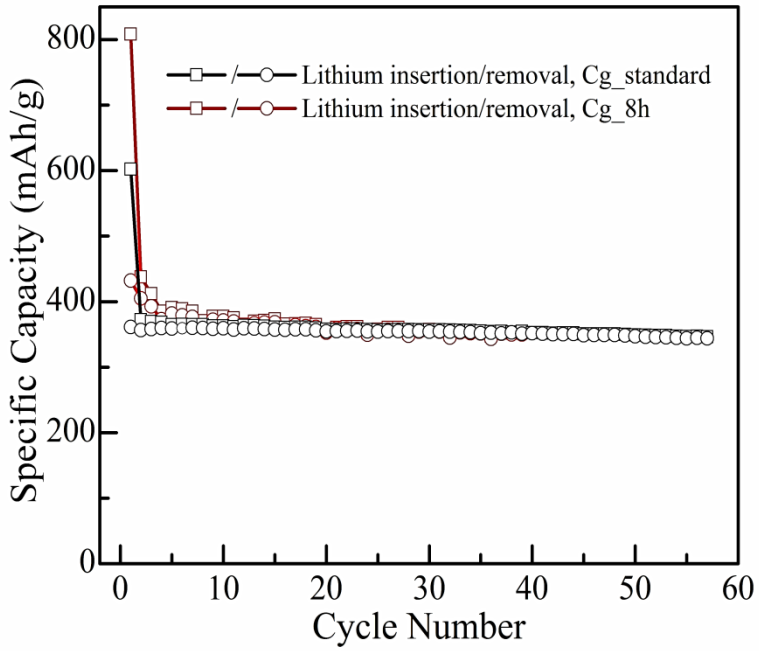
- **Impact of high energy ball milling on graphite electrochemistry**
  - Crystallinity of graphite reduced
    - Fe_3C impurity phase might form
  - First cycle excess capacity is increased significantly (doubled)
    - Attributed to creation of defects in graphite structure
  - Electrochemical capacity of graphite not significantly increased by high energy ball milling
  - Conclusion: tin needed to activate carbon to LiC_2





Response to 2014 Reviewers' Comments

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New Project – No Comments

Collaboration and Coordination with other Institutions

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- **Brookhaven and Argonne National Laboratories**
  - Ex-situ and in-situ synchrotron X-ray diffraction, PDF (pair distribution function) and XAS (X-ray absorption) studies
- **Academia**
  - Working with DOE funded electrolyte efforts (will use their improvements)
    - U. Colorado on electrolytes
    - U. Rhode Island on electrolyte additives
- **Industry**
  - As this is a new project working through NYBEST to disseminate information
- **NYBEST** (New York Battery and Energy Storage Technology Consortium)
  - Building collaborations between Industry, Academia, and Government

Remaining Challenges and Barriers

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This Project has only completed the first 6 months

- **CuF_2 conversion cathode**
  - Cyclability of electrode
- **$VOPO_4$ intercalation cathode**
  - Long-term stability of structures when two Li are intercalated
- **Nano-Sn_2Fe**
  - Long term cycling
  - Cost effective synthesis methods
    - Mechanochemical method
      - Find collaborator to determine viability of mechanochemical manufacturing
- **Lithium incorporation in full cell (3rd year)**
  - Neither electrode presently contains Li

Proposed Future Work

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- **Copper Fluoride, CuF_2**
  - Cyclability
    - Determine impact of partial substitution of part of copper
    - Determine impact of electrolyte
      - Is solubility of copper species a key issue?
        - solvable?
    - Determine rates of reaction
- **Vanadyl Phosphate, $VOPO_4$**
  - Determine optimum synthesis approach
  - Determine long-term cyclability over both redox plateaus
- **Anode: Tin-Iron-Carbon Composite, Sn_2Fe**
  - Improve cycling performance over 100-200 cycles

Summary

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Project started October 2014

- **Enhanced Cathodes**
  - Synthesized and characterized copper fluoride material
    - Pure CuF_2 formed, as well as solid solution $Cu_{1-y}Fe_yF_2$
      - Lattice parameter is a function of the Fe content
    - Products of electrochemical reduction determined
      - For pure CuF_2 only copper and lithium fluoride observed
      - For $Cu_{1-y}Fe_yF_2$ some rutile phase remains
    - Discharge capacity exceeding 300 mAh/g attained
  - Parallel Effort beginning on $VOPO_4$
    - Initial capacities exceed 200 Ah/kg

- **Enhanced Anodes**
  - Sn_2Fe effort transferred from previous BATT funded project
    - Carbon plays a critical role
    - On target to be substantially better than carbon anodes
      - Anticipate up to double volumetric capacity of carbon

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Technical Back-Up Slides

Calculation of capacity of Sn-Fe-C composite:
Volumetric energy density exceeds carbon

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- **Gravimetric capacity:**
  - **Measured reversible capacity of 600 Ah/kg of total composite**
  - **Sn_2Fe contributes 804 Ah/kg**
  - Remainder contributed by carbon
    - Must be C_2Li
      - 1100 Ah/kg
      - Theoretical capacity of 760 Ah/kg for total composite
    - If C_6Li then theoretical capacity is 490 Ah/kg
- **Volumetric capacity:**
  - **Approaches 1.6 Ah/cc, based on above value of 600 Ah/kg**

Safety of Sn and Si anodes relative to carbon:
On complete combustion to the oxide

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- **Free energy of formation of oxide:**
  - **-394.36 kJ/mole for C to CO_2**
  - **-519.6 kJ/mole for Sn to SnO_2**
  - **-371.1 kJ/mole for Fe to ½ Fe_2O_3**
  - **-705.5 kJ/mole for oxidation of Sn_2Fe to SnO_2 and Fe_2O_3**
  - **-850.7 kJ/mole for oxidation of Si to SiO_2**
- **Free energy of oxidation per lithium stored:**
  - **-2366 kJ/Li for a carbon anode**
  - **-160 kJ/Li for a Sn_2Fe anode**
  - **-193 kJ/mole for a Si anode**

Assumptions: 6 C/Li and 4.4 Li/Sn or Si
Even if substantial amounts of carbon are used with the Sn and Si anodes, they will still generate less heat than graphite alone