Stan Whittingham
SUNY at Binghamton

High Energy Density Lithium Battery

M. Stanley Whittingham
State University of New York at Binghamton

June 9th, 2016

Project ID #
ES231

Overview

Stan Whittingham
SUNY at Binghamton

Timeline

- Project start date: 10-01-2014
- Project end date: 9-30-2017
- Percent complete: 60%

Barriers

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

Budget

- Total project funding
  - DOE $1,265,773
  - Contractor share: Personnel
- Funding received
  - FY15: 398k$
  - FY16: 427k$

Partners

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

Relevance and Objectives of Work

Stan Whittingham
SUNY at Binghamton

- **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

Stan Whittingham
SUNY at Binghamton

1.1 Demonstrate synthesis and complete characterization of CuF_2. (Dec. 14) **Completed**

1.2 Determine discharge product of CuF_2. (March 15) **Completed**

1.3 Begin cyclability testing of CuF_2. (June 2015) **Completed**

1.4 Demonstrate more than 100 cycles on Sn_2Fe at 1.5 times the volumetric energy density of carbon. (Sept. 15) **Completed**

____Go/No-Go: Demonstrate cyclability of CuF_2. Criteria: Capacity of 200 mAh/g over 10 cycles. (Sept-15) **Completed**

2.1 Determine the optimum composition Li_xVOPO4. (Dec-15) **Completed**

2.2 Demonstrate $VOPO_4$ rate capability. (Mar-16) **Completed**

2.3 Demonstrate Sn_2Fe rate capability. (Jun-16) Underway

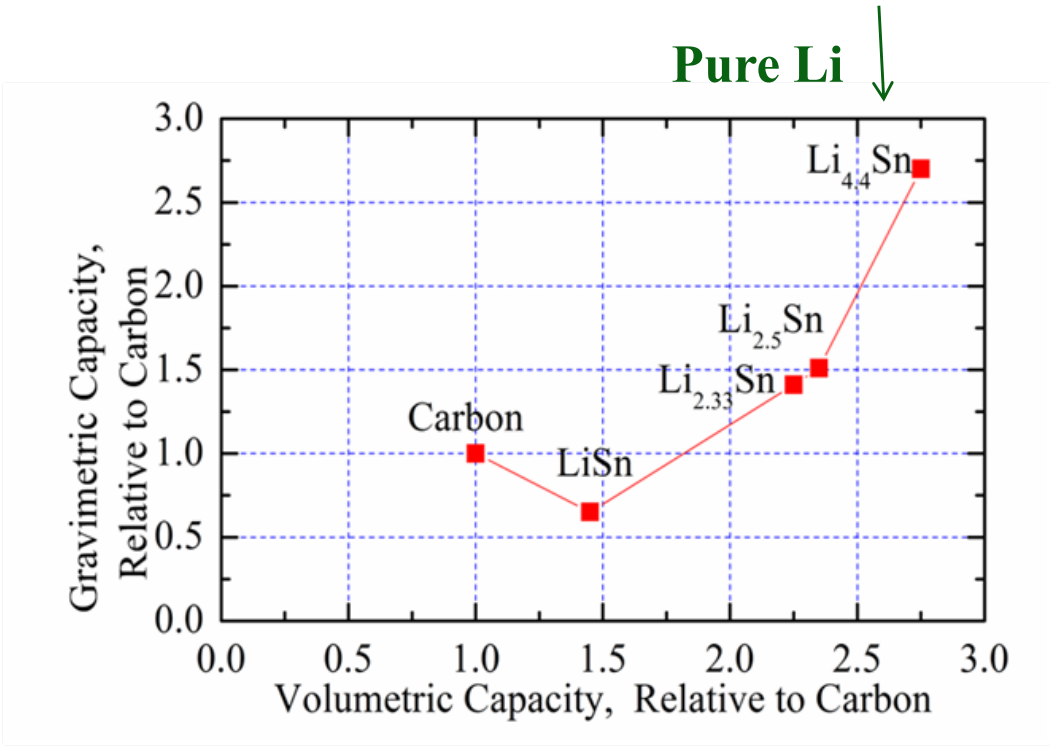
2.4 Demonstrate CuF_2 rate capability. (Sep-16) Underway

____Go/No-Go: Demonstrate lithiation method. Criteria: A cycling cell containing lithium in one of the intercalation or conversion electrodes must be achieved. (Sept-16) Underway

Approach and Strategy: Improved Anodes

Stan Whittingham
SUNY at Binghamton

- Replace intercalation carbon host with conversion reaction material
  - Allows for much higher capacities
    - Carbon – only 350 Ah/kg 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 BMR 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

Stan Whittingham
SUNY at Binghamton

- 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

Stan Whittingham
SUNY at Binghamton

- **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+}

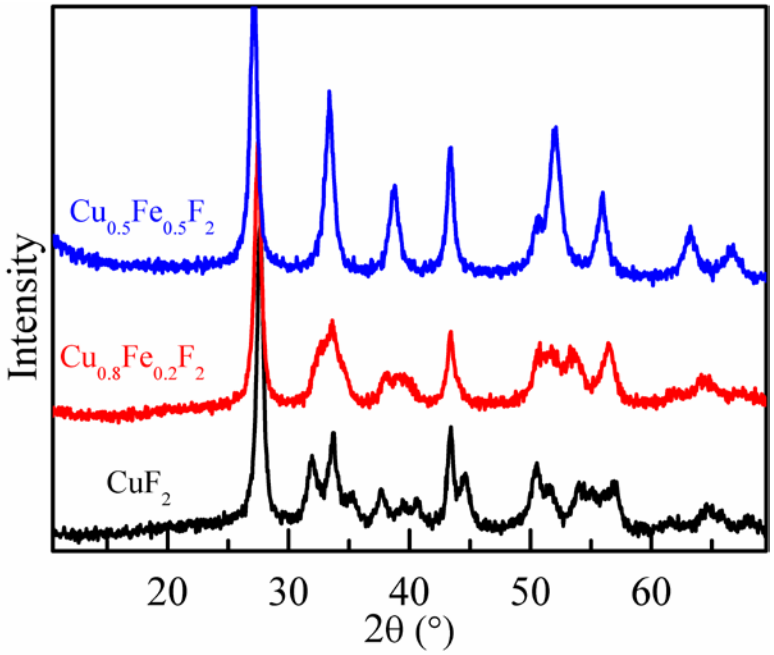
Technical Accomplishments: Barriers being Addressed

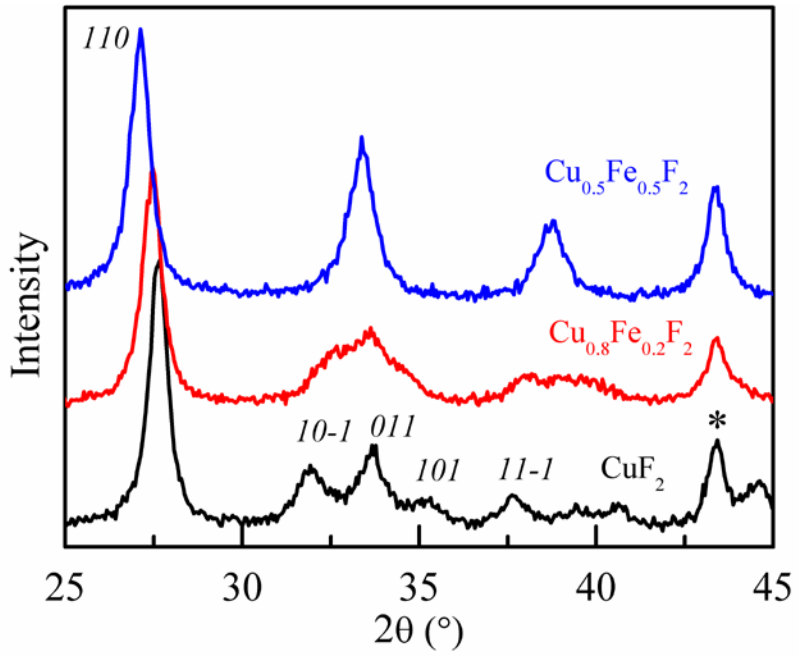
Stan Whittingham
SUNY at Binghamton

- **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
- **Low Safety and Abuse-tolerance**
  - Find an anode that reacts with lithium faster
  - Find thermally stable electrodes under all states of charge

Milestone 1.1: CuF_2 synthesized and characterized: it forms a solid solution with FeF_2

Stan Whittingham
SUNY at Binghamton





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

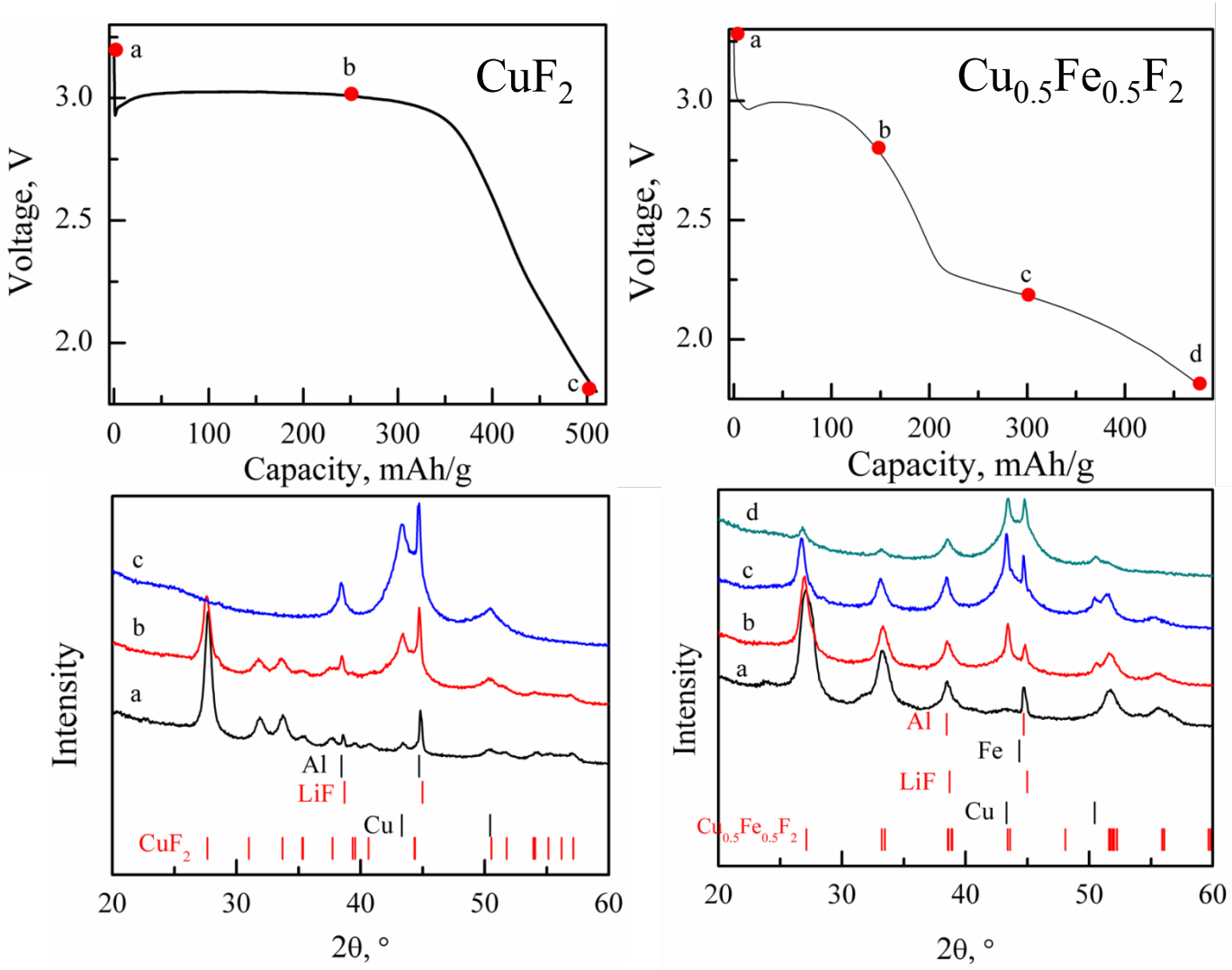
XRD Characterization:

- 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 1.2: Discharge products of CuF_2/C and $Cu_{0.8}Fe_{0.2}F_2$/C identified

Stan Whittingham
SUNY at Binghamton



CuF_2

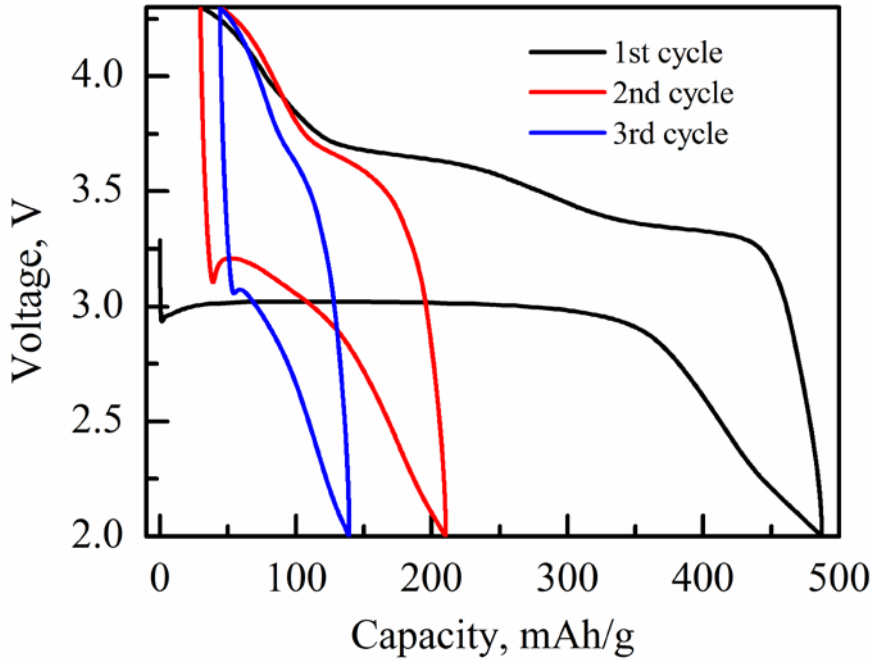
- Reaction complete at 1.8 V
- CuF_2 converted to Cu and LiF

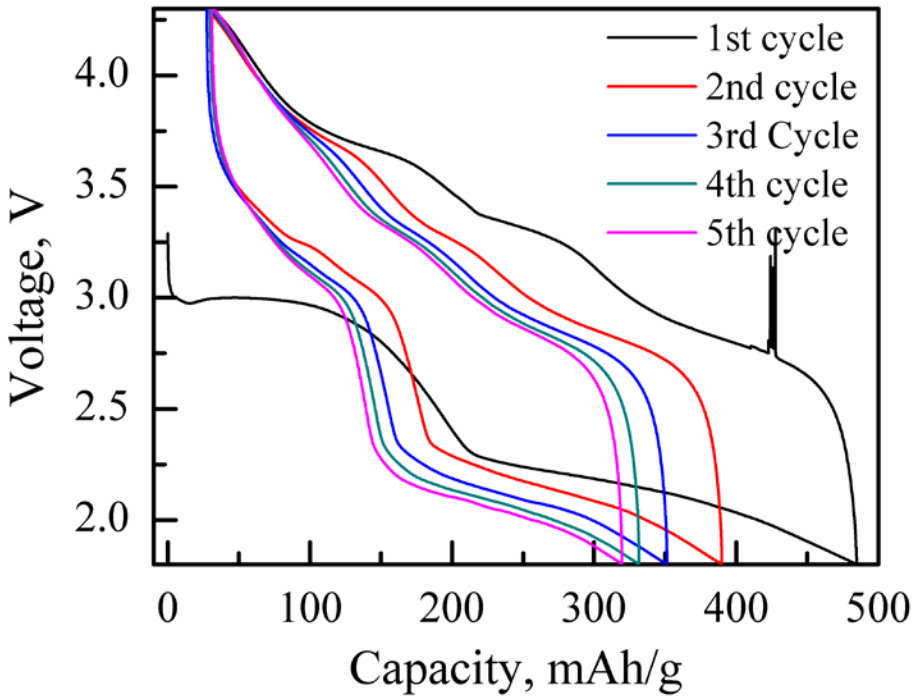
$Cu_{0.5}Fe_{0.5}F_2$

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

Milestone 1.3: CuF_2 delivers near theoretical discharge capacity; Fe substitution improves reversibility

Stan Whittingham
SUNY at Binghamton



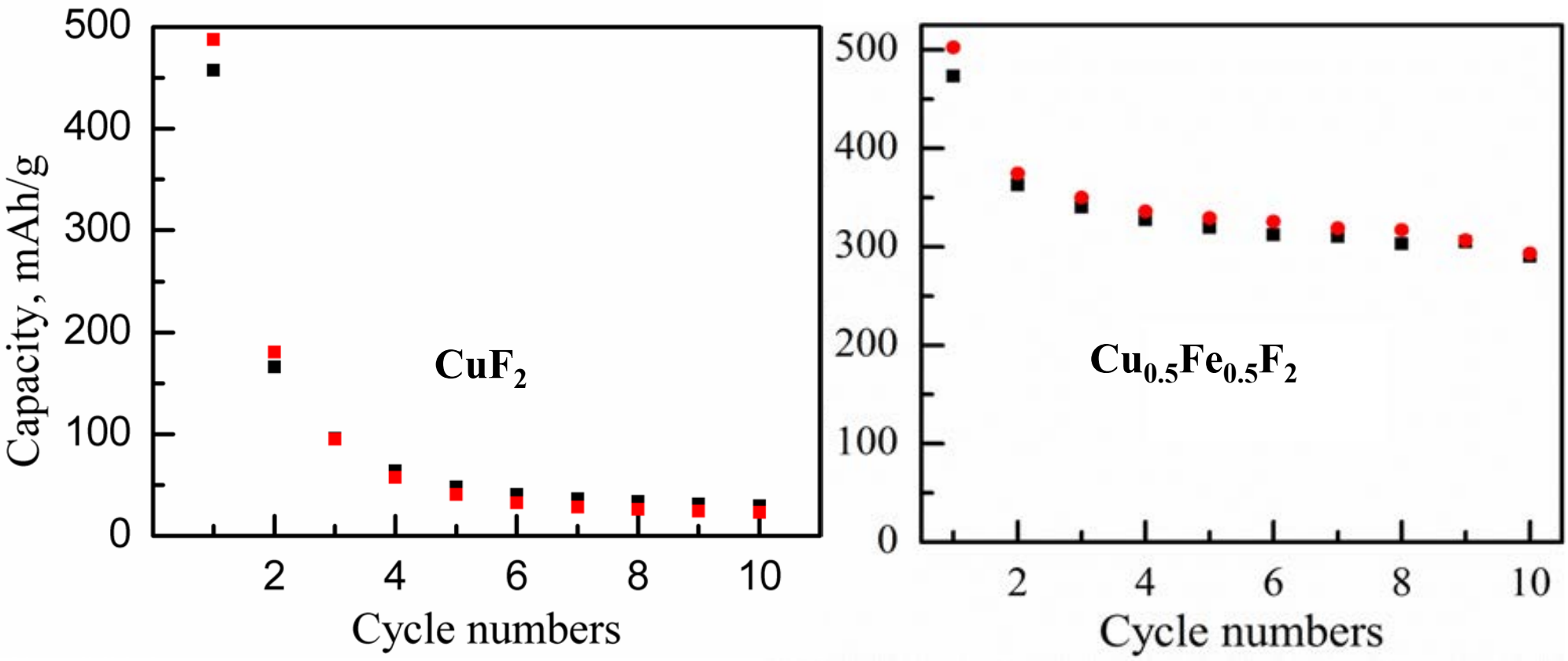


Initial discharge capacity:

- CuF_2 delivers close to the theoretical capacity of 528 mAh/g
  - Best first cycle recharge reported
  - But, fast capacity fade thereafter
    - Around 150 mAh/g in the 2nd cycle
- Fe substitution, $Cu_{1-y}Fe_yF_2$ improves the electrochemical performance
  - Improved reversibility
    - Around 300 mAh/g in the 5th cycle

Go/NoGo: Demonstrate cyclability of CuF_2 Capacity of over 200 mAh/g over 10 cycles achieved

Stan Whittingham
SUNY at Binghamton

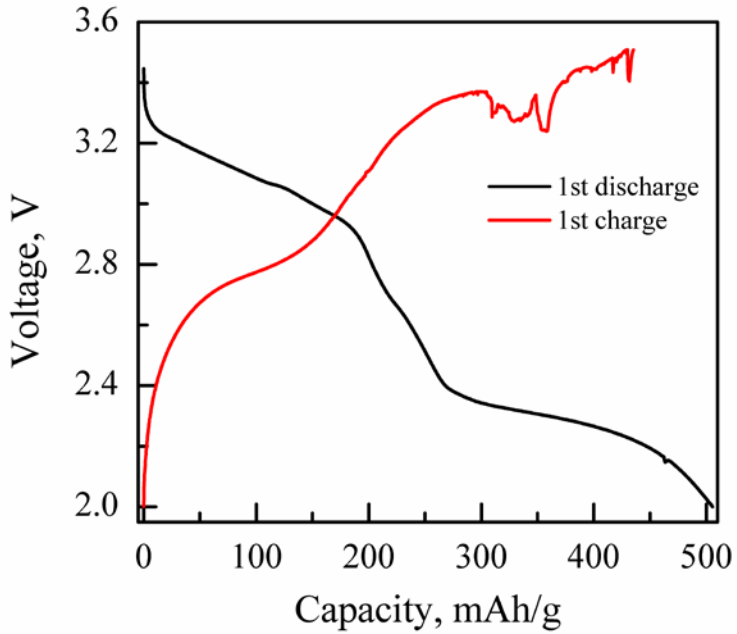


- Effort focused on the solid solution $Cu_{1-y}Fe_yF_2$ composite with carbon
  - Capacity is 290 mAh/g, exceeding the Go/No-Go target of 200 mAh/g
    - Best reported in literature
- Much superior to pure CuF_2 or CuF_2/oxide mixtures

Milestone 2.4: Is cuprous dissolution on charging a show-stopper for long-term cycling?

Stan Whittingham
SUNY at Binghamton

- Proof of principle test underway
  - Can a solid electrolyte allow the extended cycling of CuF_2 systems?
    - If yes, then we will search for an appropriate liquid electrolyte
  - PEO based electrolyte chosen
    - Initial discharge capacity comparable to organic liquid electrolytes
    - However stability issues at copper redox charging voltage
      - Now looking at other alternative solid/liquid electrolytes



Milestone 1.4: Synthesis optimization of Sn_2Fe/C anode

Stan Whittingham
SUNY at Binghamton

Reaction: SnO ground together with Ti powder and carbon at RT

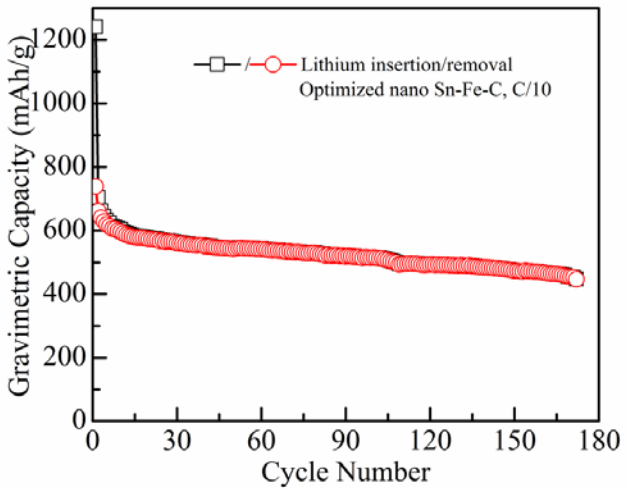
- **Ratio of components and grinding time critical**
  - Carbon
    - Source of carbon not important, carbon black or graphite
      - Graphite leads to slightly higher capacities
    - Need 10:1 carbon:tin atom ratio
      - 5:1 carbon:tin leads to larger amounts and greater crystallinity of tin metal
        - Results in lower capacity retention and lower Coulombic efficiency
  - Titanium
    - Optimum is a Ti/Sn ratio of 0.25
      - Lower amounts lead to an increased 1st cycle excess capacity
  - Grinding time and media
    - 8 hours was the optimal ball-milling time
    - Hard steel balls are needed as soft balls lead to chromium contamination
    - Carbon is needed to prevent the melting of the tin

Full details: Zhixin Dong et al, Advanced Science, 3_1500229_2016

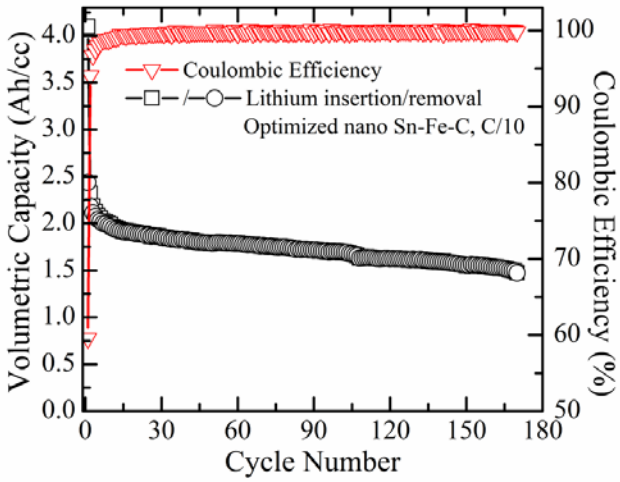
Milestones 1.4 and 2.3: Sn-Fe-C anode showed excellent cycling for 140+ cycles at both C/10 and C rates

Stan Whittingham
SUNY at Binghamton

- **C/10 rate**
  - Capacity retention
  - Coulombic efficiency

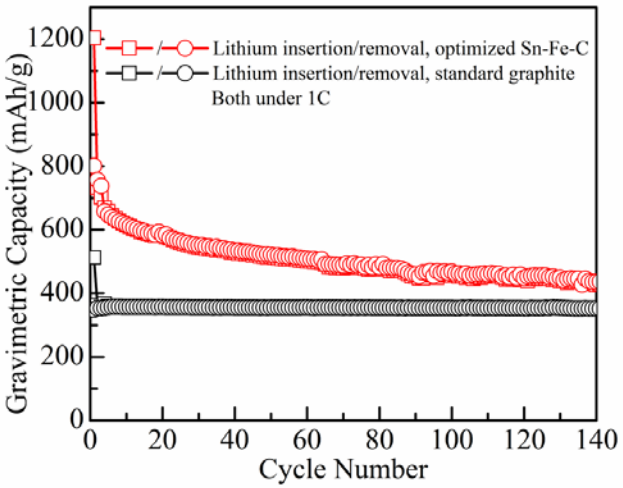


(a)

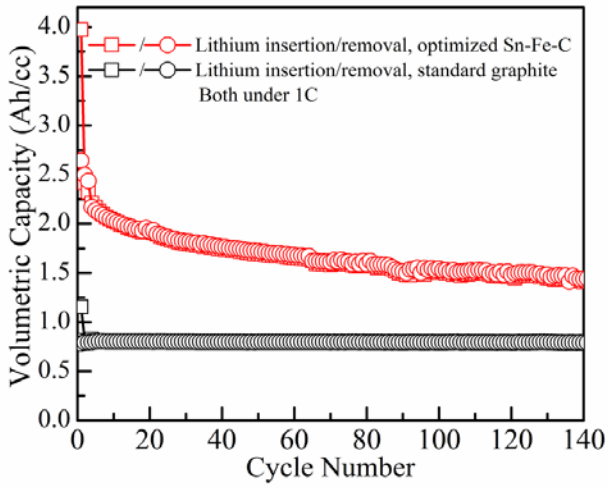


(b)

- **C rate**
  - Capacity retention
  - Exceeds graphite
  - Exceeds milestone of 1.5 x volumetric capacity of graphite



(c)



(d)

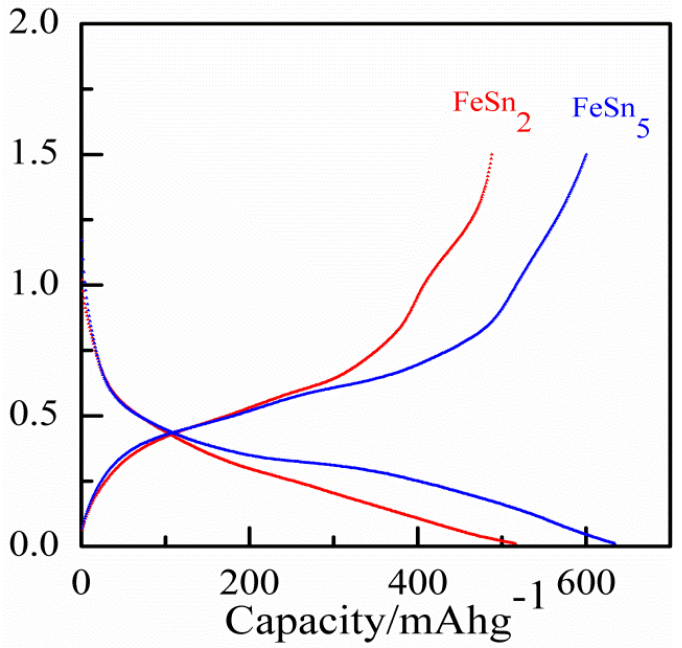
Zhixin Dong et al, Advanced Science, 3_1500229_2016

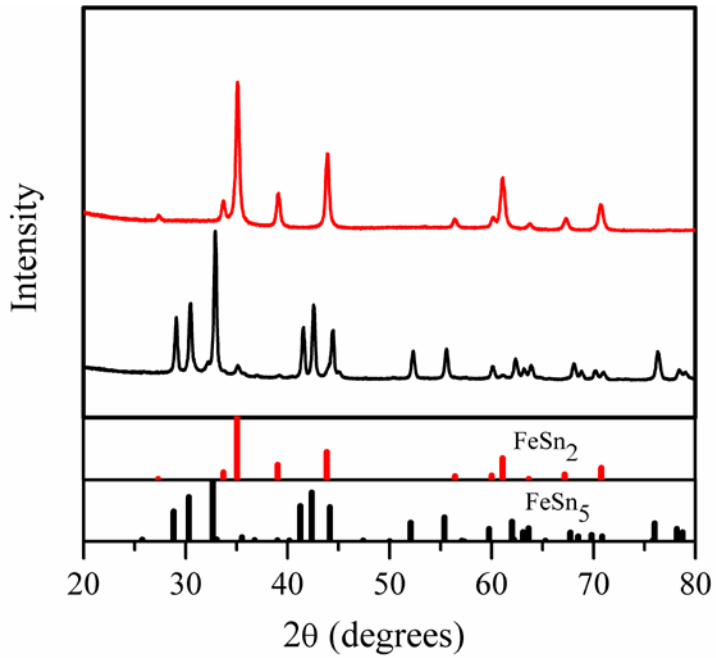
Milestone 2.3: Other Sn-Fe anode compositions, synthesis approaches and 1st cycle excess capacity

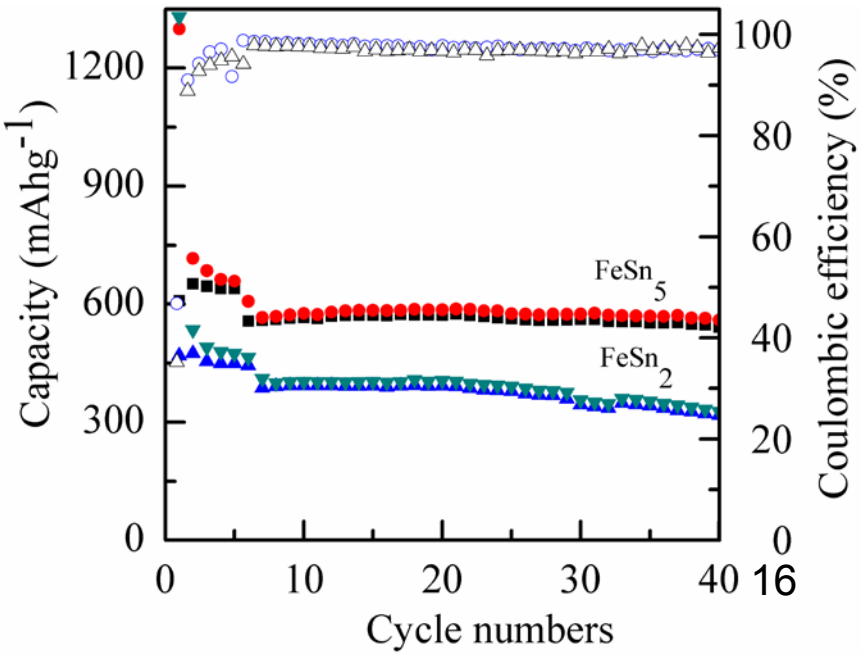
Stan Whittingham
SUNY at Binghamton

Synthesis approaches beyond mechanical grinding

- **Modified polyol approach**
  - Carbon free Sn_2Fe and Sn_5Fe
  - By controlling temperature and reactants ratio
- **Sn_2Fe and Sn_5Fe**
  - Good capacity retention
  - Capacity exceeds graphite
  - Excess 1st cycle capacity



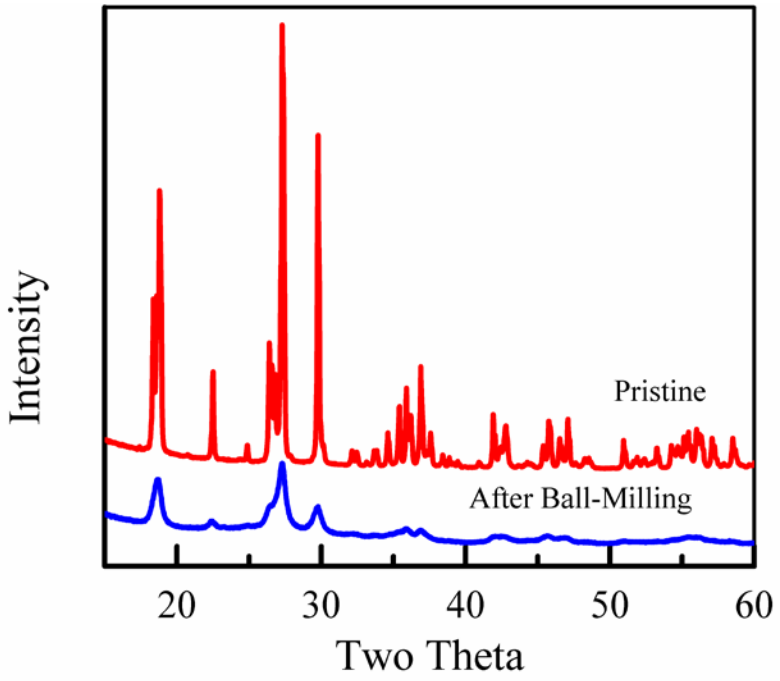




Milestone 2.1: Determine the optimum composition of Li_xVOPO_4

Stan Whittingham
SUNY at Binghamton

- **Hydrothermal synthesis provides diffraction pure material**
  - However, this material contains protons.
- **Solid State reactions at 700 - 800° C**
  - Provides pure ε-$LiVOPO_4$ phase*
    - Higher capacity than ε-$VOPO_4$ phase
    - Contains a source of lithium
    - Stable in air
  - Grinding with carbon
    - Gives a conductive coating
    - Reduces particle size to around 200 nm
      - Characterized by broad diffraction peaks

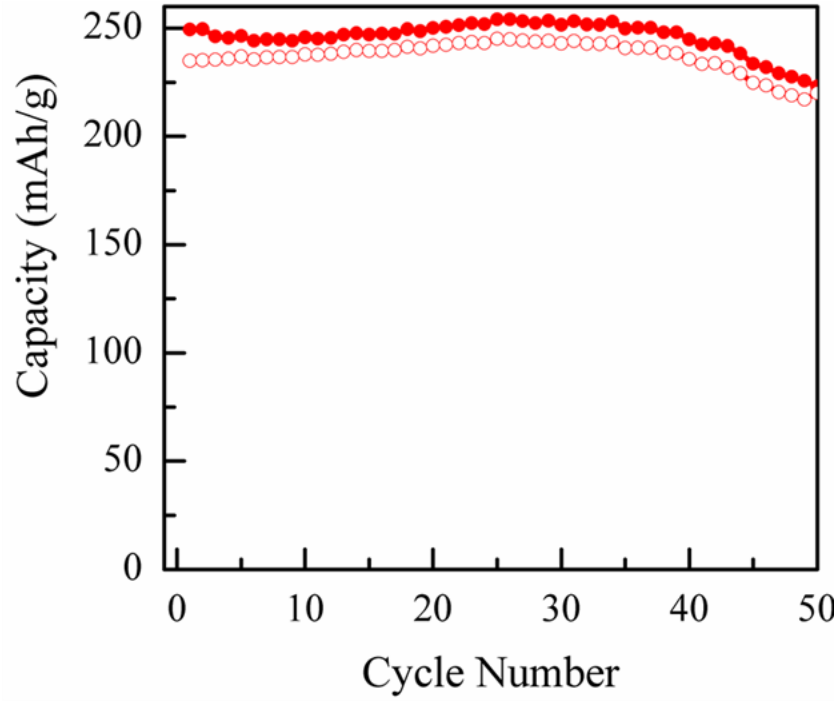


*Nomenclature used is based on that of $VOPO_4$ phase; thus ε-$VOPO_4$ phase gives ε-$LiVOPO_4$ phase, not α-$LiVOPO_4$ phase.

Milestones 2.1: Achieve 50 cycles exceeding 200 mAh/g

Stan Whittingham
SUNY at Binghamton

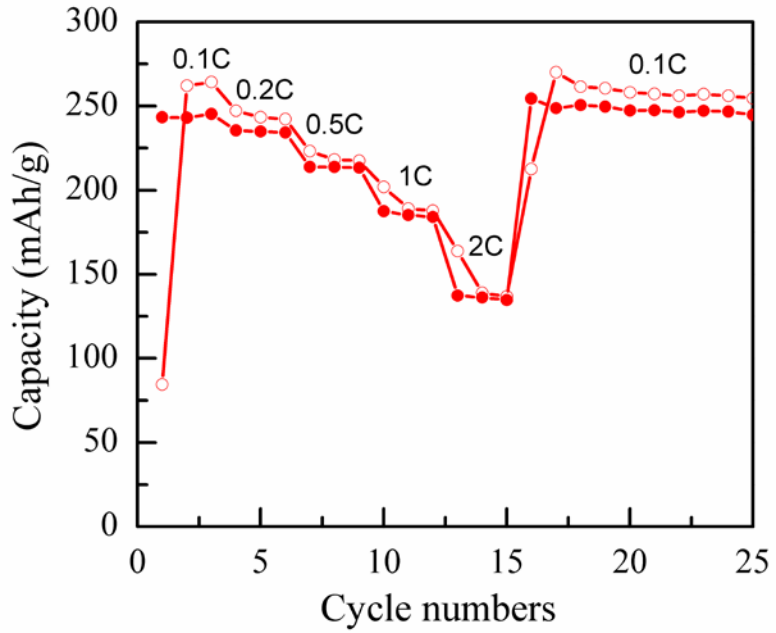
- $LiVOPO_4$ ball milled with carbon:
  - Gives improved electronic conductivity
  - Gives smaller particle size of around 200 nm
    - Leads to higher cycling capacity
      - Achieved milestone of 50 cycles above 200 mAh/g



Milestones 2.2: Demonstrate rate capability of $LiVOPO_4$

Stan Whittingham
SUNY at Binghamton

- $LiVOPO_4$ ball milling with carbon:
  - Leads to higher cycling capacity
  - Improves the rate capability
    - 80% of the practical capacity at 0.1 C can be retained at 1 C
    - Capacity is recovered after high rate
      - Good reversibility
    - Rate capability milestone achieved
  - Extended cycling underway



Response to 2015 Reviewers' Comments

Stan Whittingham
SUNY at Binghamton

AMR 2015 reviewer comments were overall very positive and supportive of this step-out project. They recognized that the project was in its very early stages and noted several challenges that should be addressed:

- **Cathode CuF_2.** The dissolution/migration and aggregation of copper species from the CuF_2 cathode that effect the cyclability of CuF_2, also suggest that structural changes should be investigated:
  - The cyclability of CuF_2 has been determined and is reported here.
  - Proof of concept experiments are underway to determine if complete cyclability is obtained if dissolution of Cu^+ is eliminated. This is being done using a solid electrolyte. Initial results are reported here.
- **Anode Sn_2Fe/C.** Here more data was requested to show full cycling curve, dissolution of the SEI, and high irreversible capacity.
  - The full cycling curve is shown now in the presentation. The coulombic efficiency of this anode is over 99.9% after the first few cycles. The initial excess capacity is being investigated.

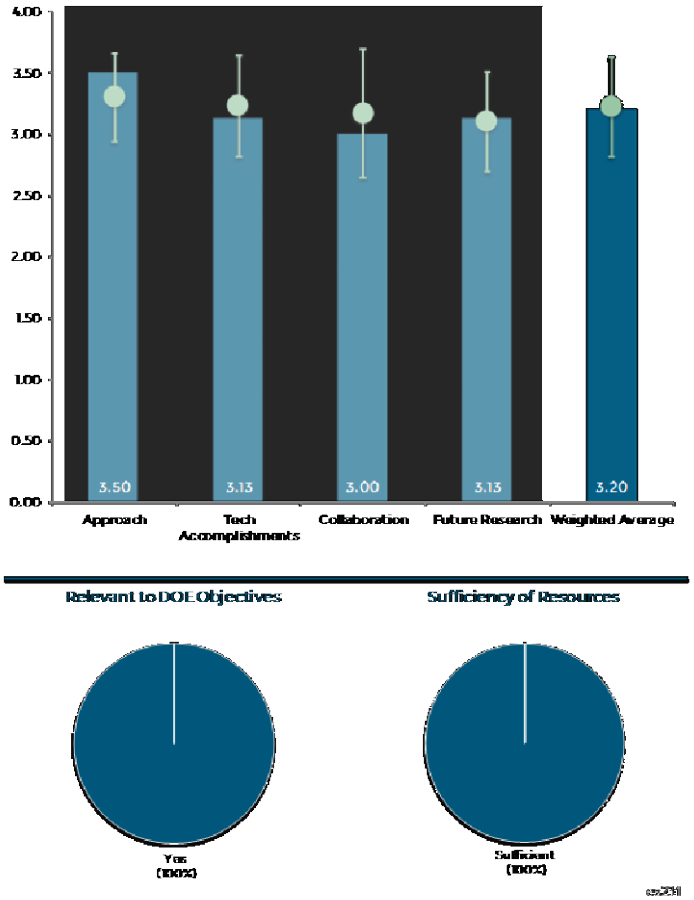


Figure 2-48 High Energy Density Lithium Battery: Stanley Whittingham (Binghamton University) - Electrochemical Energy Storage

Collaboration and Coordination with other Institutions

Stan Whittingham
SUNY at Binghamton

- **Brookhaven and Argonne National Laboratories**
  - Synchroton: Ex-situ and in-situ synchrotron X-ray diffraction, PDF (pair distribution function) and XAS (X-ray absorption) studies
  - Center for Functional Nanomaterials @ BNL: TEM studies

- **Academia**
  - Working with DOE funded electrolyte efforts (will use their improvements)
    - U. Colorado and U. Michigan on solid electrolytes
    - U. Rhode Island and Army on liquid electrolytes and 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

Stan Whittingham
SUNY at Binghamton

- **CuF_2 conversion cathode**
  - Cyclability of electrode
    - Dissolution of copper species
- **$VOPO_4$ 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
    - Find alternative synthesis approaches
- **Lithium incorporation in full cell (3rd year)**
  - Neither electrode presently contains Li

Proposed Future Work

Stan Whittingham
SUNY at Binghamton

- **Copper Fluoride, CuF_2**
  - Cyclability
    - Determine impact of electrolyte
      - Is solubility of copper species a solvable issue?
    - Determine rates of reaction
    - Determine optimum composition of CuF_2 composite
- **Vanadyl Phosphate, $LiVOPO_4$**
  - Determine long-term cyclability over both redox plateaus
- **Anode: Tin-Iron-Carbon Composite, Sn_2Fe**
  - Increase cycling performance to 500 cycles
  - Incorporate into full cells with cathode

Summary

Stan Whittingham
SUNY at Binghamton

- **Sn-Fe Conversion Anodes**
  - Sn_2Fe has more than 50% higher volumetric capacity than carbon
    - Carbon plays a critical and active role in mechanochemical material
    - Chemically synthesized Sn_2Fe cycles, but with lower capacity
      - Found good cycling for Sn_5Fe

- **CuF_2 Conversion Cathodes**
  - Synthesized and characterized copper fluoride material
    - Pure CuF_2 formed, as well as solid solution $Cu_{1-y}Fe_yF_2$
      - Substituted retains capacity much better
    - Working on alternative electrolytes
    - Will work with other CuF_2 efforts

- **$LiVOPO_4$ Intercalation Cathodes**
  - $LiVOPO_4$ cycles well over V^{4+}/V^{5+} and V^{4+}/V^{3+} redox couples
    - Initial capacities exceed 200 Ah/kg

Stan Whittingham
SUNY at Binghamton

Technical Back-Up Slides

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

Stan Whittingham
SUNY at Binghamton

- **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

Stan Whittingham
SUNY at Binghamton

- **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