High Energy Density Lithium Battery

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Project ID #
ES231

Overview

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Timeline

- Project start date: 10-01-2014
- Project end date: 9-30-2017
- Percent complete: 80%

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$
  - FY17: 440k$

Partners

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

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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2.1 Determine the optimum composition Li_xVOPO_4. (Dec-15) **Completed**

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

2.3 Demonstrate Sn_2Fe rate capability. (Jun-16) **Completed**

2.4 Demonstrate CuF_2 rate capability. (Sep-16) **Completed**

____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) **Completed**

3.1 Determine cyclability of Sn/Li_xVOPO_4. (Dec-16) **Completed**

3.2 Demonstrate cyclability of Sn/CuF_2. (Mar-17) **Ongoing**

3.3 Choose optimum couple. (Jun-17) **Completed**

3.4 Supply cells to DOE. (Sep-17)

Approach and Strategy: Improved Anodes

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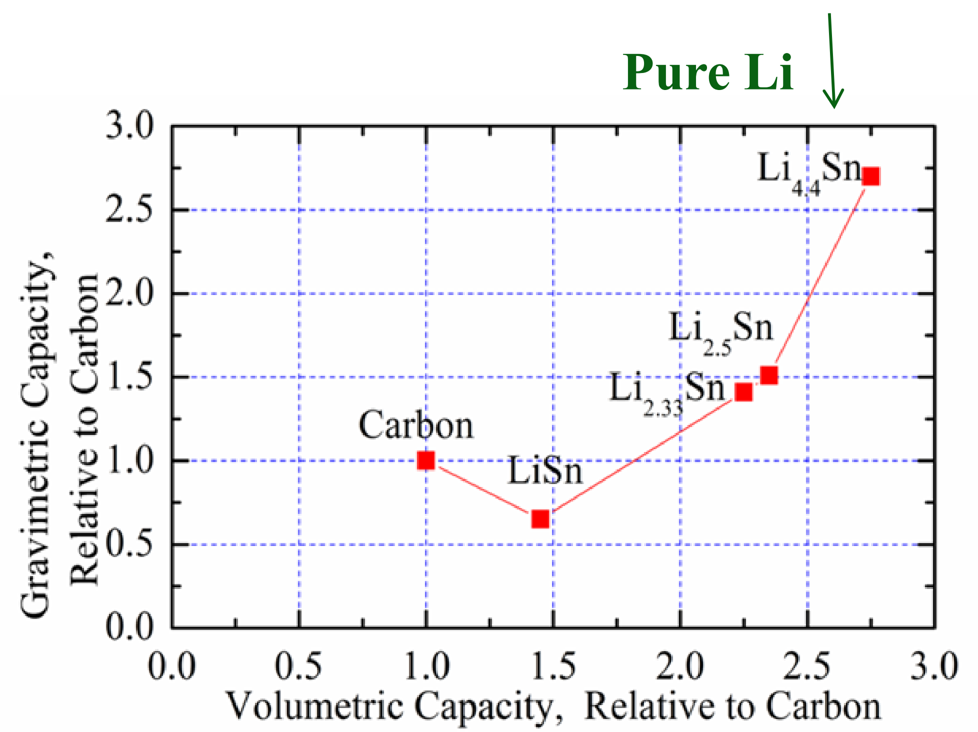
- Replace intercalation carbon host with conversion reaction material
  - Allows for much higher capacities
    - Carbon – only 350 Ah/kg and 0.8 Ah/liter
    - Pure lithium anode has around 2.5 times the volumetric capacity
  - Place emphasis on tin-based systems
    - **Why Sn_2Fe?**
      - 804 Ah/kg 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

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

Milestone 3.3: Choose Optimum Couple

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- **Anode**
  - $SnFe_y$ meets goals
    - 500 cycles completed at up to C rate
    - Two synthetic approaches

- **Cathode**
  - Li_xVOPO_4 chosen
    - 250 Ah/kg achieved over 70 cycles
  - CuF_2 a NoGo without a new electrolyte
    - Cu^+ ion transports through electrolyte to anode

- **Couple:**
  - **$SnFe_y$ // Li_xVOPO_4**

Milestone 2.4: Demonstrate rate capability of CuF_2

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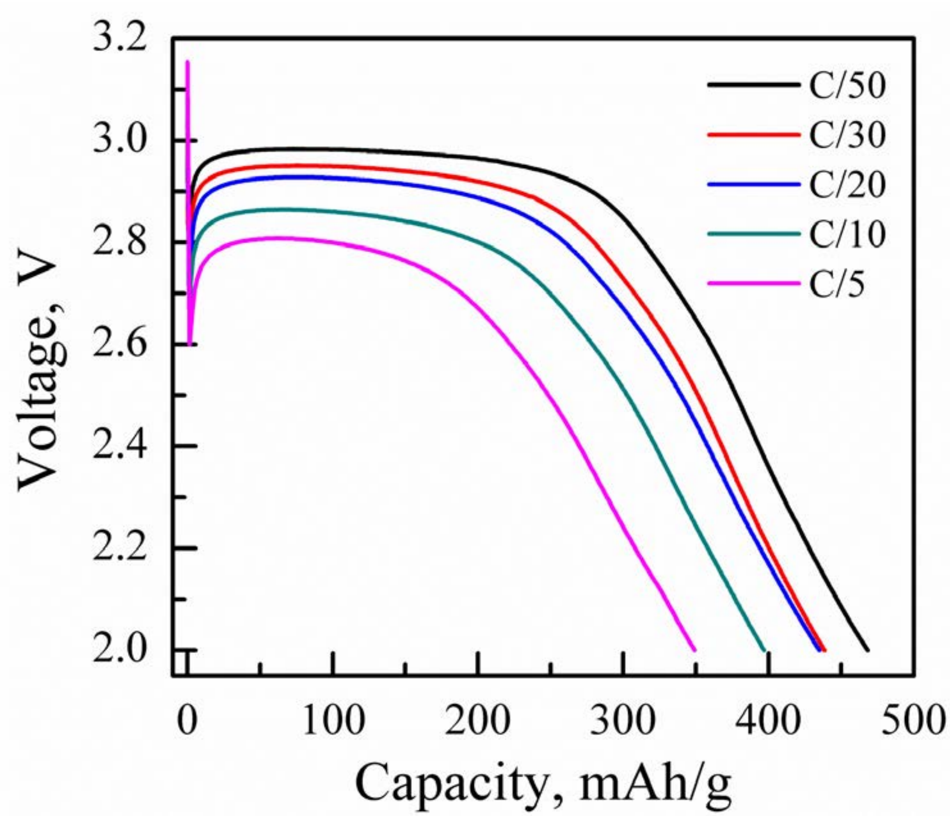
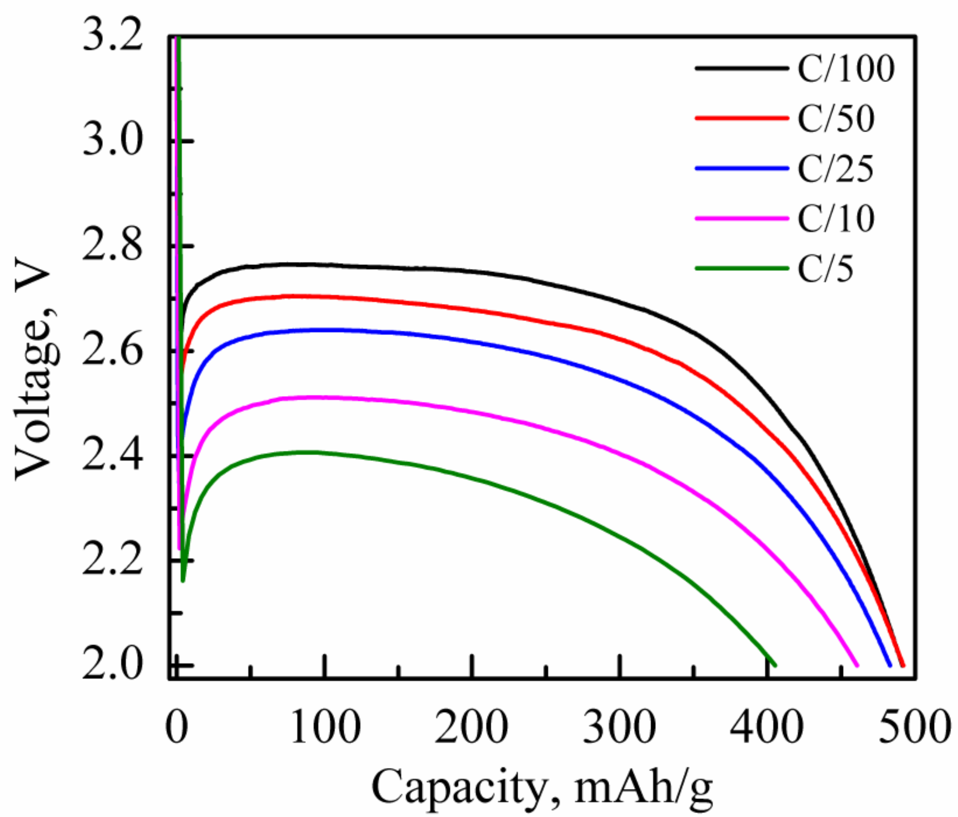
- CuF_2 shows reasonable rate capability
  - Full capacity achieved at low rates
- Addition of $VOPO_4$ increases capacity
  - Reduces voltage and energy density





Capacity vs rate of (left) a Li//CuF_2 cell and (right) a L//CuF_2-$VOPO_4$ cell.

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

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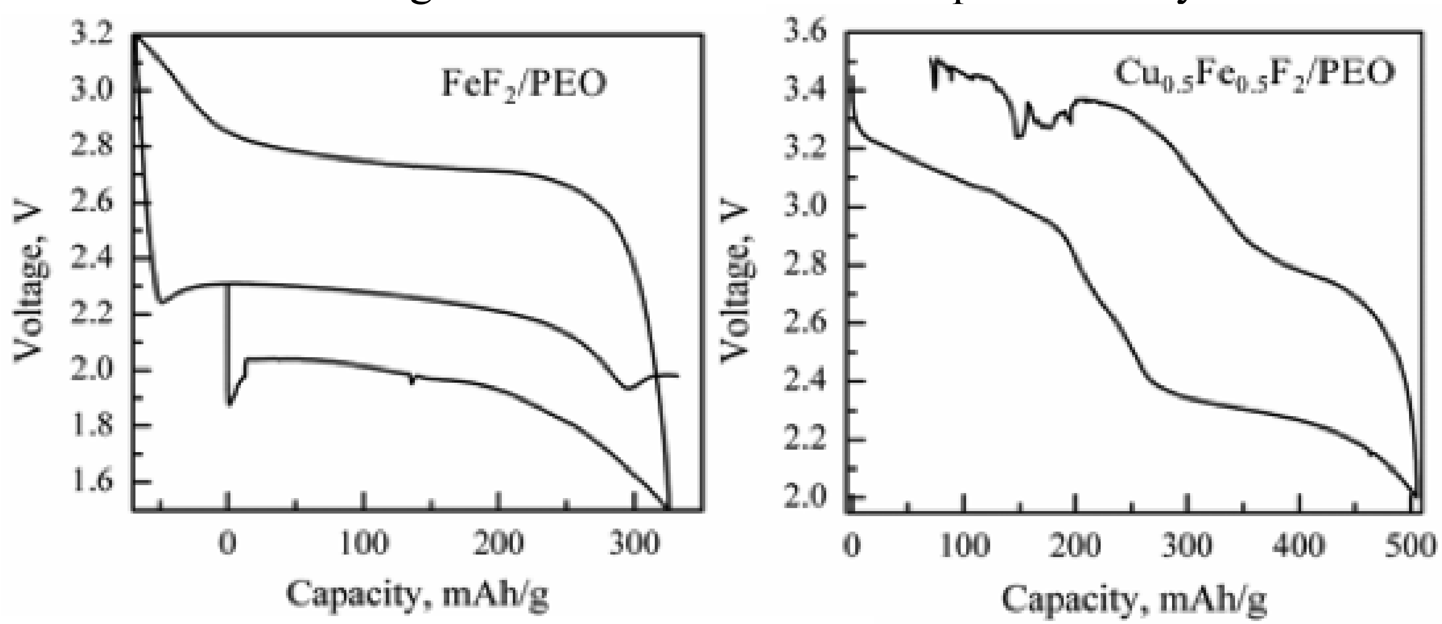
- Proof of principle test underway
  - Can a solid electrolyte allow the extended cycling of CuF_2 systems?
    - PEO based electrolyte chosen
      - FeF_2 cycles reversibly
      - $Cu_{0.5}Fe_{0.5}F_2$: initial discharge capacity comparable to organic liquid electrolytes
      - However stability issues at copper redox charging voltage
      - Cu metal observed on anode
      - Now looking at other alternative solid/liquid electrolytes



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

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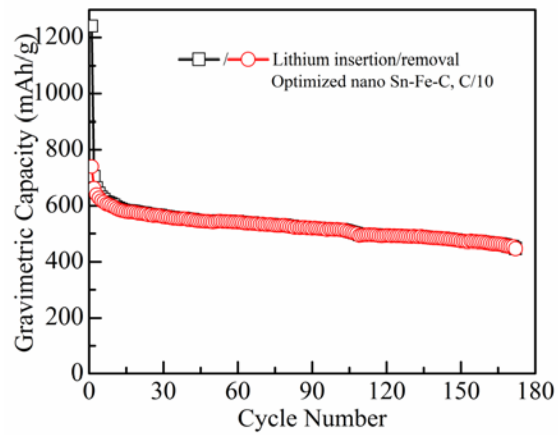
Mechanochemical synthesis

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



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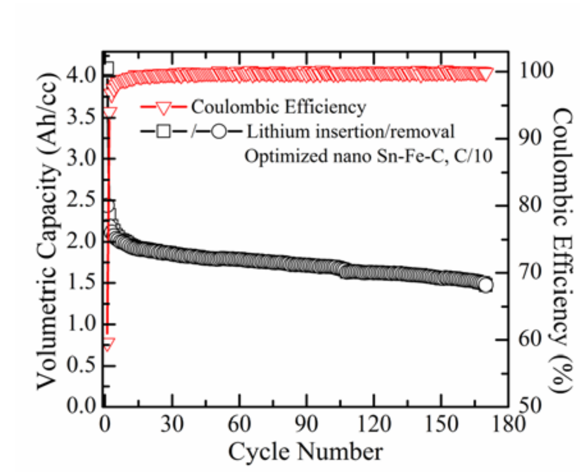

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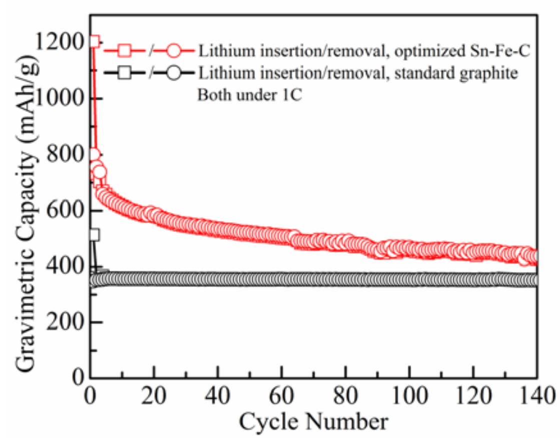
- **C rate**
  - Capacity retention
  - Exceeds graphite
  - Exceeds milestone of 1.5 x volumetric capacity of graphite



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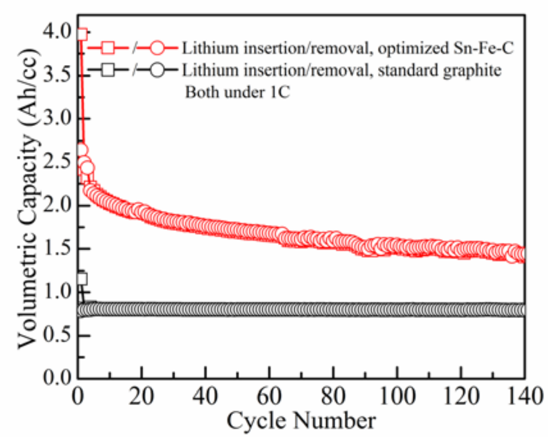

(d)

Zhixin Dong et al, Advanced Science, 3_1500229_2016

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

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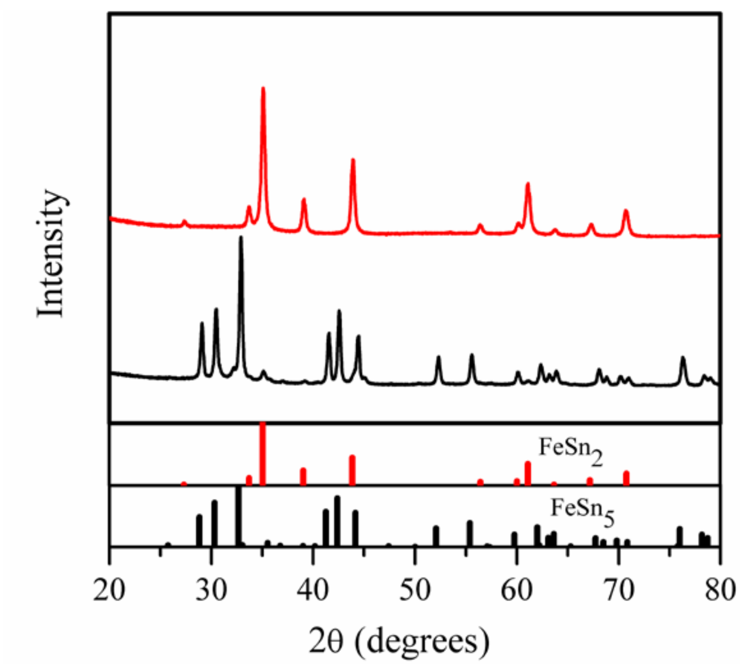
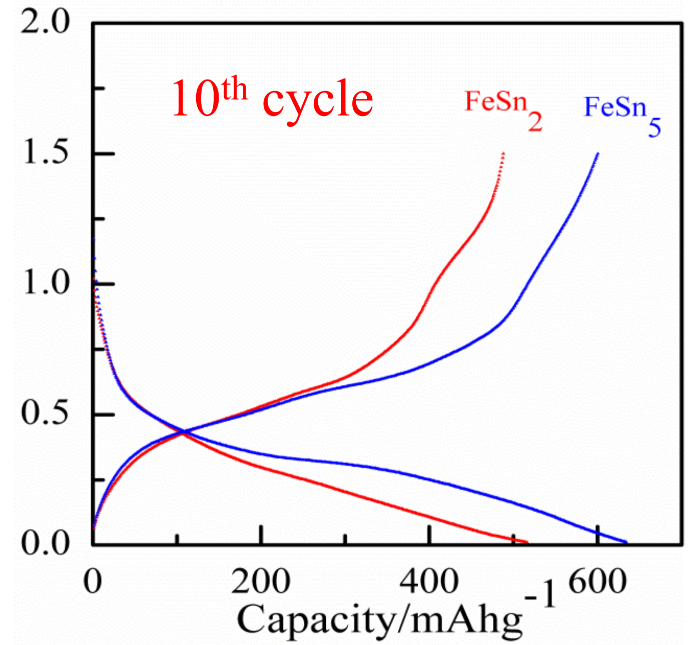
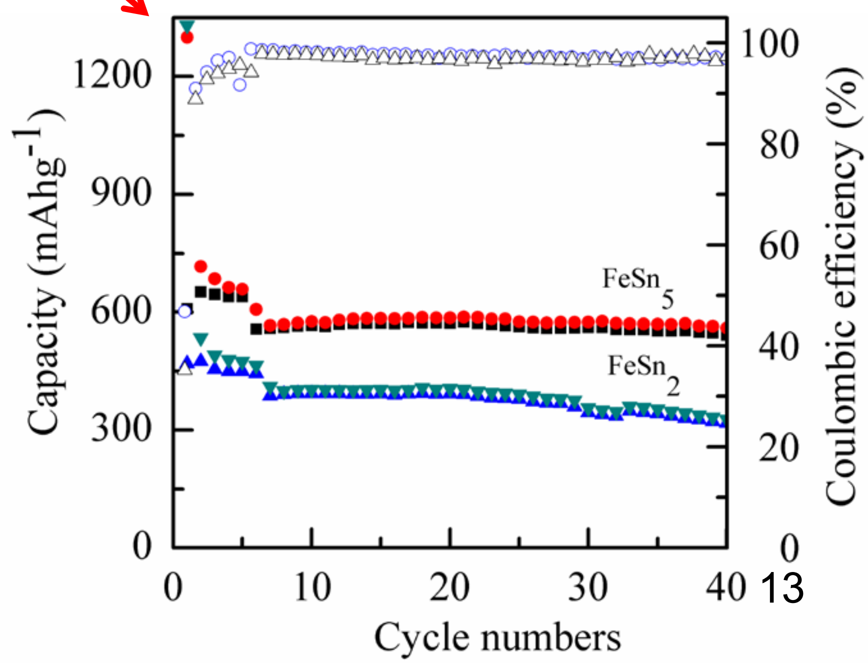
Synthesis approaches beyond mechanical grinding

- **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





1st cycle



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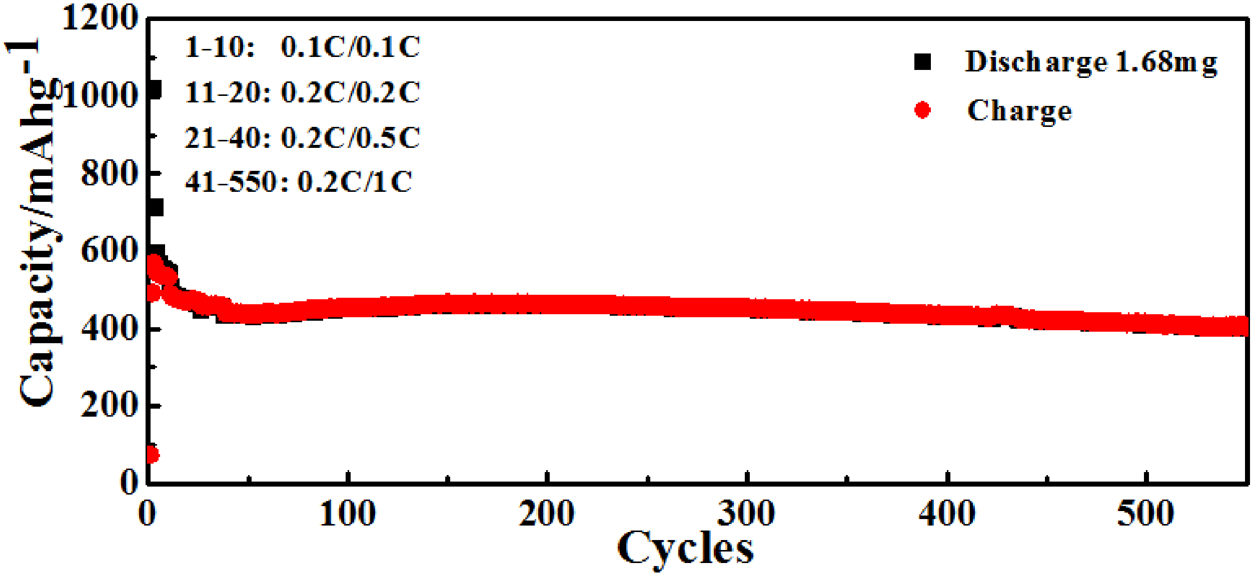
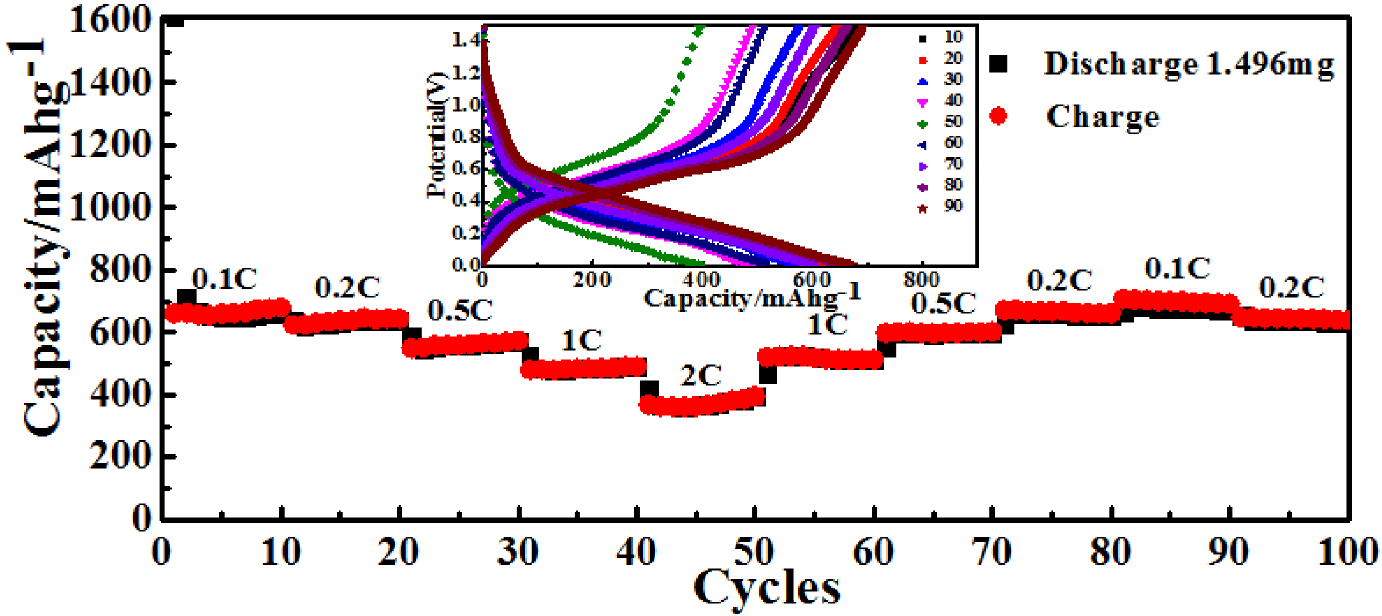
Polyol Sn_2Fe/Sn_5Fe

- Shows capacity of 1.2 Ah/cc after 500 cycles, 1.5 that of graphite at C rate





Milestone 2.1: Determine the optimum composition of Li_xVOPO_4

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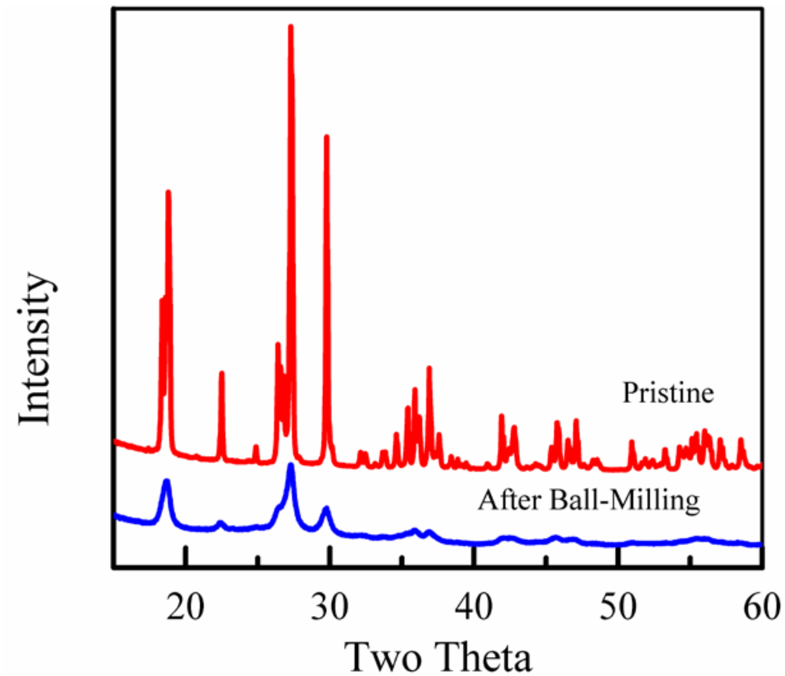
- **Hydrothermal synthesis provides diffraction pure material**
  - However, this material contains protons.
- **Solid State reactions at 700 - 800° C**
  - Provides pure ε-$LiVOPO_4$ phase*
    - Higher capacity than ε-$VOPO_4$ phase
    - Contains a source of lithium
    - Stable in air
  - Grinding 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 2.2: Demonstrate rate capability of $LiVOPO_4$

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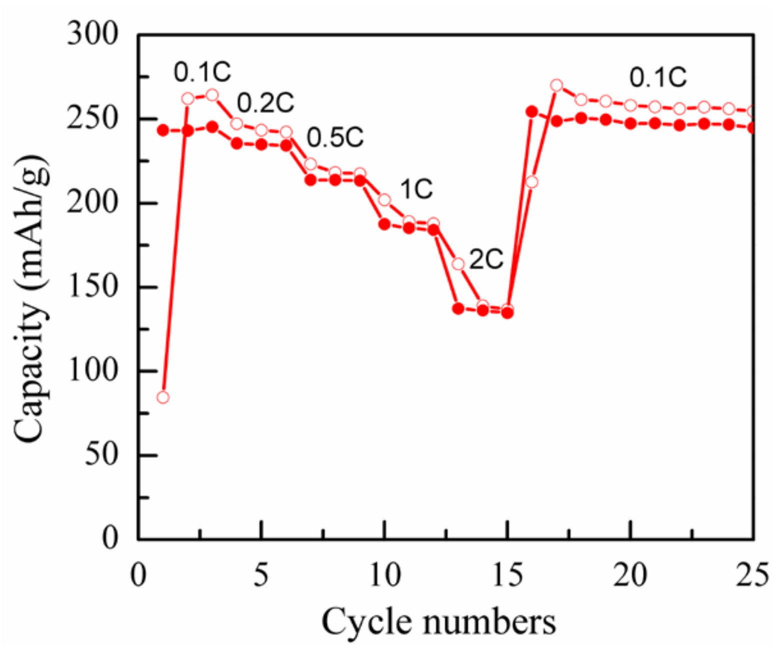
- $LiVOPO_4$ ball milling with carbon:
  - Leads to higher cycling capacity
  - Improves the rate capability
    - 80% of the practical capacity at 0.1 C can be retained at 1 C
    - Capacity is recovered after high rate
      - Good reversibility
    - Rate capability milestone achieved



Milestones 3.3: $LiVOPO_4$ chosen as cathode for full cell 250 mAh/g achieved at C/5

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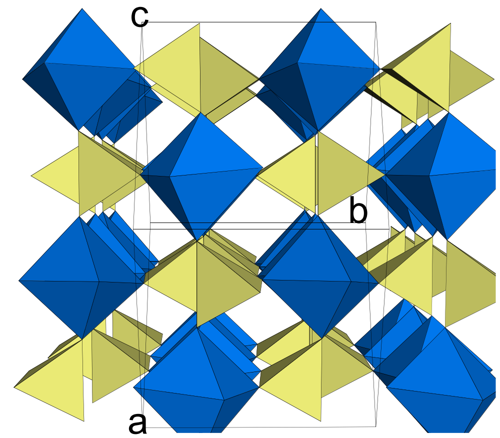
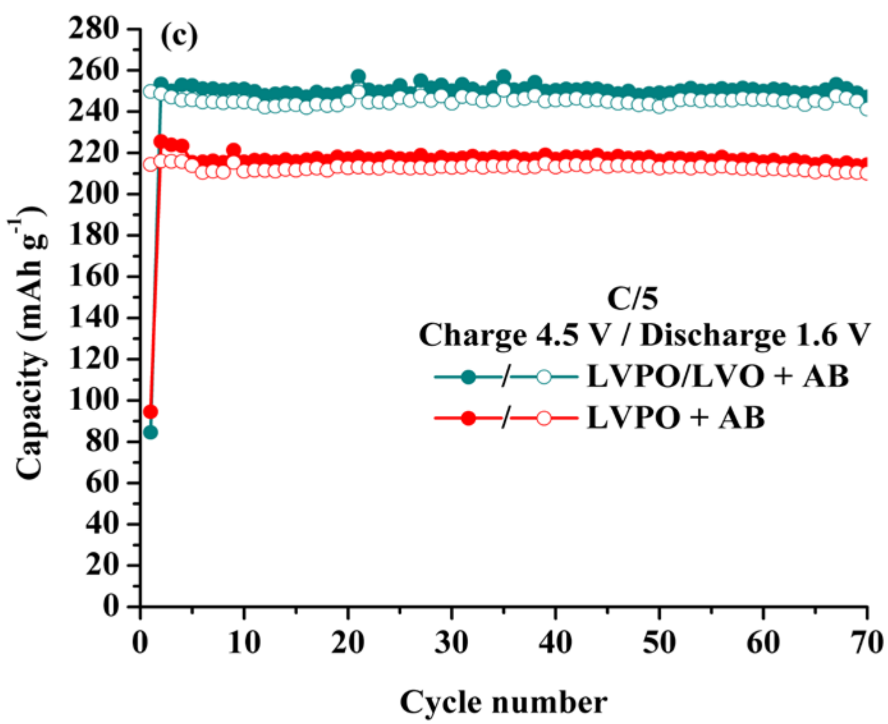
- $LiVOPO_4$ ball milled with carbon:
  - Gives improved electronic conductivity
  - Capacity improved by a Li_3VO_4 coating
    - Leads to higher and stable cycling capacity
      - 250 mAh/g achieved at C/5 rate
      - Highest reported for any phosphate



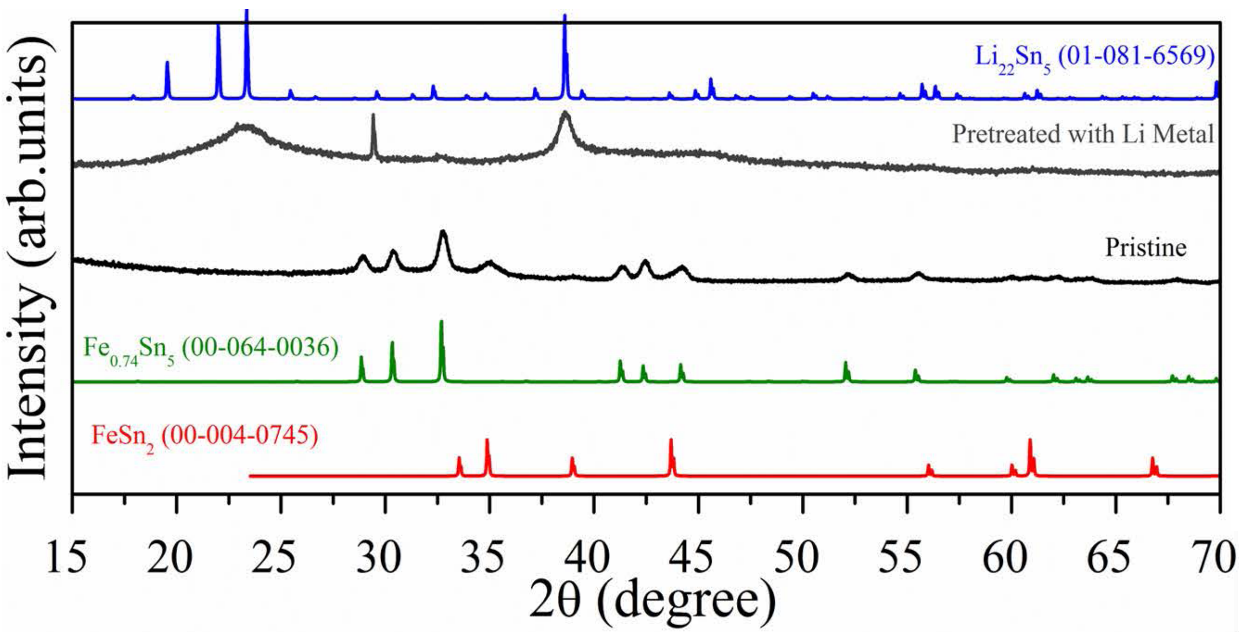


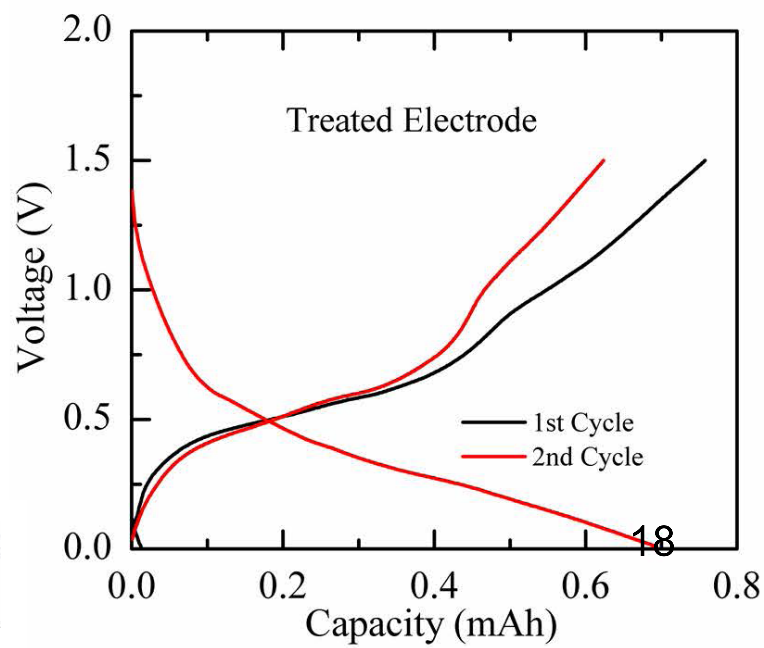
Go/No-Go: Demonstrate lithiation method:

Criteria: A cycling cell containing lithium in one of the intercalation or conversion electrodes must be achieved.

Prelithiation of Sn_yFe:

- Achieved using Stabilized Lithium Metal Powder (SLMP) or lithium metal
  - Fabricated electrode was shorted by bringing it into direct contact with lithium metal/SLMP or by mixing it with SLMP
  - $Li_{22}Sn_5$, formation confirmed by X-ray diffraction
- Electrochemical testing of the pre-lithiated electrode
  - Greatly reduces the initial irreversible excess capacity





Go/No-Go: Demonstrate lithiation method: Milestone 3.1: Determine cyclability of Sn/Li_xVOPO_4.

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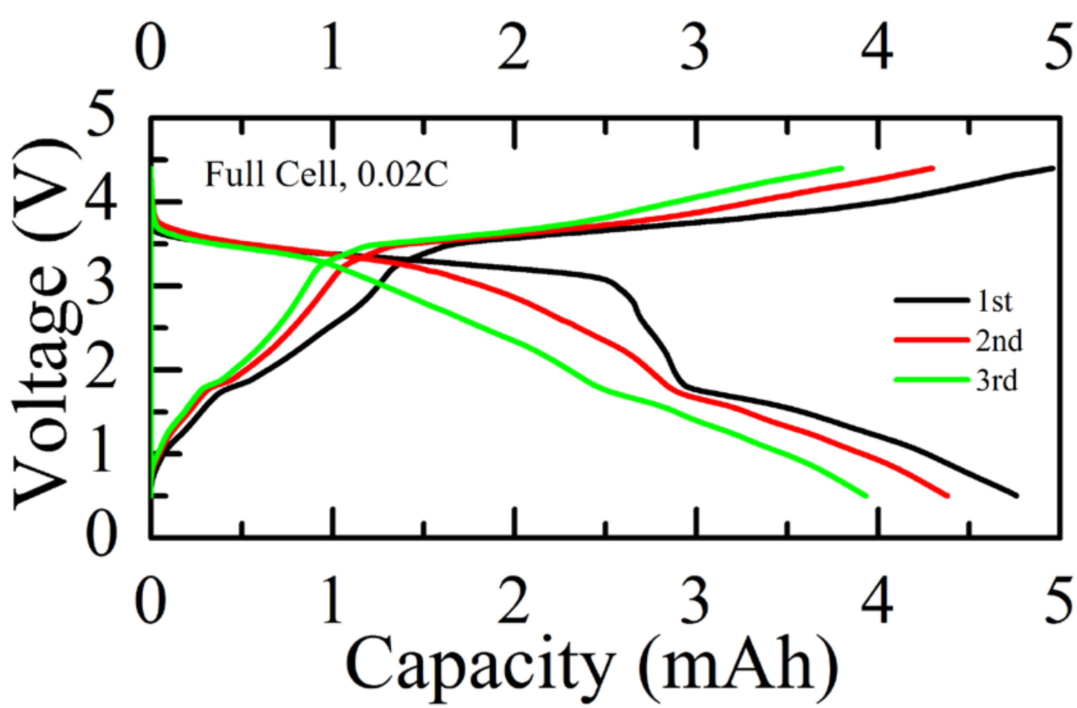
Criteria: A cycling cell containing lithium in one of the intercalation or conversion electrodes must be achieved.

Functional cell constructed of prelithiated Sn_yFe and $VOPO_4$:

- Initial results obtained
  - Meets 4 mAh cell goal for Milestone 3.4
- Will do extended cycling of full cell
- Will test both prelithiated electrodes against carbon



Response to 2016 Reviewers' Comments

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No reviewer comments.

Collaboration and Coordination with other Institutions

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- **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

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- **Lithium incorporation in full cell**
  - Neither electrode presently contains Li
- **$VOPO_4$ intercalation cathode**
  - Long-term stability of structures when two Li are intercalated
- **Sn_yFe**
  - Long term cycling in full cell
- **CuF_2 conversion cathode**
  - Transport of Cu^+ ions through the electrolyte
  - Not ready for full cell testing

Proposed Future Work

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- **Anode: Tin-Iron-Carbon Composite, Sn_2Fe**
  - Complete characterization of SnFe anodes
- **Vanadyl Phosphate, $LiVOPO_4$**
  - Extend the cyclability beyond 70 cycles
- **Full Cell Sn_2Fe//$LiVOPO_4$**
  - Evaluate extended cycling
  - Demonstrate several lithiation processes
- **Copper Fluoride, CuF_2**
  - Maintain low level effort to identify possible elctrolytes

Any proposed future work is subject to change based on funding levels

Summary

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- **Sn-Fe Conversion Anodes**
  - Sn_2Fe has more than 50% higher volumetric capacity than carbon
    - Synthesized by two different techniques
    - Coulombic efficiency around 99.5%
    - More than 500 cycles achieved vs Li
- **$LiVOPO_4$ Intercalation Cathodes**
  - $LiVOPO_4$ cycles well over V^{4+}/V^{5+} and V^{4+}/V^{3+} redox couples
    - Capacities exceed 250 Ah/kg
      - Achieved over 70 cycles
- **Sn-Fe/$LiVOPO_4$ Chosen as cell couple**
  - Initial cycling accomplished
    - Range of lithiation methods identified
- **CuF_2 Conversion Cathodes**
  - Limited cycling achieved
    - Cu^+ ions transport through liquid and solid electrolytes
  - Need new electrolyte and further research

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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 of mechanochemical Sn_2Fe/C composite:**
  - **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