High Energy Density Lithium Battery

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Project ID #
ES231

This presentation does not contain any proprietary, confidential, or otherwise restricted information
Overview

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

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

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

Partners
• National Laboratories
  – Brookhaven; Argonne
• Local Industry
  – Through NYBEST
• Academia
  – Electrolytes – UC Boulder, URI, U Michigan, Army
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
1.1 Demonstrate synthesis and complete characterization of CuF₂. (Dec. 14) **Completed**
1.2 Determine discharge product of CuF₂. (March 15) **Completed**
1.3 Begin cyclability testing of CuF₂. (June 2015) **Completed**
1.4 Demonstrate more than 100 cycles on Sn₂Fe at 1.5 times the volumetric energy density of carbon. (Sept. 15) **Completed**

**Go/No-Go:** Demonstrate cyclability of CuF₂. **Criteria:** Capacity of 200 mAh/g over 10 cycles. (Sept-15) **Completed**

2.1 Determine the optimum composition LiₓVOPO₄. (Dec-15) **Completed**
2.2 Demonstrate VOPO₄ rate capability. (Mar-16) **Completed**
2.3 Demonstrate Sn₂Fe rate capability. (Jun-16) Underway
2.4 Demonstrate CuF₂ 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

- 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$_2$Fe?
      - 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
      - $\Delta G$ Sn/Fe-SnO$_2$: 160 kJ/mole Li
      - $\Delta G$ Si-SiO$_2$: 194 kJ/mole Li
      - $\Delta G$ C-CO$_2$: 2366 kJ/mole Li

\[ \text{Pure Li} \]
Approach and Strategy: Improved Cathodes

• 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$_2$VOPO$_4$ chosen
  – Conversion cathode
    • Destroy and rebuild the crystal structure
    • The system CuF$_2$ – Cu + 2LiF chosen
      – Higher potential than other fluorides
Why the choice of CuF₂ and VOPO₄?

**CuF₂**
- High theoretical energy density of 1874 Wh/kg
  - Compare 1000 Wh/kg and 587 Wh/kg theoretical for complete reaction of LiCoO₂ and LiFePO₄ respectively.
  - Theoretical specific capacity exceeding 500 mAh/g
  - Theoretical potential, 3.5 V, highest amongst the 3d transition metals

**VOPO₄**
- Intercalation cathode
- High energy densities of 1080 Wh/kg and 3.5 kWh/L
  - > 1.5 times that of LiFePO₄
  - Theoretical capacity of ~ 320 Ah/kg (double that of LiFePO₄)
  - Redox potentials at 3.9 V for V⁵⁺/V⁴⁺ and ~ 2.5 V for V⁴⁺/V³⁺
Technical Accomplishments: Barriers being Addressed

• 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
Synthesis of $\text{Cu}_{1-y}\text{Fe}_y\text{F}_2$, $y = 0, 0.2, 0.5$;
- Carbon or $\text{MoO}_3$ composite synthesized by high energy ball-milling of $\text{CuF}_2$ and $\text{FeF}_2$

**XRD Characterization:**
- Fe is soluble in $\text{CuF}_2$ forming a solid solution:
  - Shift in the diffraction peak position
  - Change in lattice parameters
- Both have similar structures.
  - $\text{CuF}_2$ distorted rutile structure
  - $\text{FeF}_2$ rutile structure
- $\text{MoO}_3$ forms a composite: No solid solution.

<table>
<thead>
<tr>
<th></th>
<th>$a$ (Å)</th>
<th>$b$ (Å)</th>
<th>$c$ (Å)</th>
<th>$\beta$ (°)</th>
<th>$V$ (Å³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{CuF}_2$</td>
<td>4.595(3)</td>
<td>4.560(3)</td>
<td>3.295(1)</td>
<td>95.76(1)</td>
<td>68.71(3)</td>
</tr>
<tr>
<td>$\text{Cu}<em>{0.5}\text{Fe}</em>{0.5}\text{F}_2$</td>
<td>4.675(3)</td>
<td>4.642(3)</td>
<td>3.328(1)</td>
<td>90.62(1)</td>
<td>71.39(3)</td>
</tr>
</tbody>
</table>
Milestone 1.2: Discharge products of CuF$_2$/C and Cu$_{0.8}$Fe$_{0.2}$F$_2$/C identified

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<sub>2</sub> delivers near theoretical discharge capacity; Fe substitution improves reversibility**

**Initial discharge capacity:**
- **CuF<sub>2</sub>** 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 2<sup>nd</sup> cycle
- Fe substitution, Cu<sub>1-y</sub>Fe<sub>y</sub>F<sub>2</sub> improves the electrochemical performance
  - Improved reversibility
    - Around 300 mAh/g in the 5<sup>th</sup> cycle
Go/NoGo: Demonstrate cyclability of CuF₂
Capacity of over 200 mAh/g over 10 cycles achieved

- Effort focused on the solid solution Cu₁₋ₓFeₓF₂ 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 CuF₂ or CuF₂/oxide mixtures
- 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$_2$Fe/C anode

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 1$^{st}$ 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

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

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

Zhixin Dong et al, Advanced Science, 3_1500229_2016
Synthesis approaches beyond mechanical grinding

- **Modified polyol approach**
  - Carbon free Sn\(_2\)Fe and Sn\(_5\)Fe
  - By controlling temperature and reactants ratio

- **Sn\(_2\)Fe and Sn\(_5\)Fe**
  - Good capacity retention
  - Capacity exceeds graphite
  - Excess 1\(^{st}\) cycle capacity
Milestone 2.1: Determine the optimum composition of \( \text{Li}_x\text{VOPO}_4 \)

- **Hydrothermal synthesis provides diffraction pure material**
  - However, this material contains protons.
- **Solid State reactions at 700 - 800° C**
  - Provides pure \( \varepsilon \)-LiVOPO\(_4\) phase*
    - Higher capacity than \( \varepsilon \)-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 \( \varepsilon \)-VOPO\(_4\) phase gives \( \varepsilon \)-LiVOPO\(_4\) phase, not \( \alpha \)-LiVOPO\(_4\) phase.*
- 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$_4$

- 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
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$_2$Fe/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.
Collaboration and Coordination with other Institutions

• **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

- **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$_2$Fe**
  - 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 (3$^{rd}$ year)**
  - Neither electrode presently contains Li
Proposed Future Work

- **Copper Fluoride, CuF₂**
  - Cyclability
    - Determine impact of electrolyte
      - Is solubility of copper species a solvable issue?
    - Determine rates of reaction
    - Determine optimum composition of CuF₂ composite

- **Vanadyl Phosphate, LiVOPO₄**
  - Determine long-term cyclability over both redox plateaus

- **Anode: Tin-Iron-Carbon Composite, Sn₂Fe**
  - Increase cycling performance to 500 cycles
  - Incorporate into full cells with cathode
Summary

• **Sn-Fe Conversion Anodes**
  – Sn$_2$Fe has more than 50% higher volumetric capacity than carbon
    • Carbon plays a critical and active role in mechanochemical material
    • Chemically synthesized Sn$_2$Fe cycles, but with lower capacity
      – Found good cycling for Sn$_5$Fe

• **CuF$_2$ Conversion Cathodes**
  – Synthesized and characterized copper fluoride material
    • Pure CuF$_2$ formed, as well as solid solution Cu$_{1-y}$Fe$_y$F$_2$
      – 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
Calculation of capacity of Sn-Fe-C composite:
Volumetric energy density exceeds carbon

- **Gravimetric capacity:**
  - Measured reversible capacity of 600 Ah/kg of total composite
  - $\text{Sn}_2\text{Fe}$ contributes 804 Ah/kg
  - Remainder contributed by carbon
    - Must be $\text{C}_2\text{Li}$
      - 1100 Ah/kg
    - Theoretical capacity of 760 Ah/kg for total composite
      - If $\text{C}_6\text{Li}$ 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

- **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 $\frac{1}{2}$ Fe$_2$O$_3$
  - -705.5 kJ/mole for oxidation of Sn$_2$Fe to SnO$_2$ and Fe$_2$O$_3$
  - -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$_2$Fe 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