High Energy Density Lithium Battery

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Project ID #
ES231

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Overview

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
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. 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$_2$Fe 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

- 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\textsubscript{2}Fe?
      - 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
      - $\Delta G$ Sn/Fe-SnO\textsubscript{2} 160 kJ/mole Li
      - $\Delta G$ Si-SiO\textsubscript{2} 194 kJ/mole Li
      - $\Delta G$ C-CO\textsubscript{2} 2366 kJ/mole Li

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

- Replace materials that react with $\leq 1$ 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
**Approach and Strategy: Improved Cathodes**

- **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
  - Find

- **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 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.

Milestone 1 – CuF$_2$ synthesized and characterized: forms solid solution with FeF$_2$. Composite with MoO$_3$.

<table>
<thead>
<tr>
<th></th>
<th>$a$ (Å)</th>
<th>$b$ (Å)</th>
<th>$c$ (Å)</th>
<th>$\beta$ (°)</th>
<th>$V$ (Å$^3$)</th>
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<tbody>
<tr>
<td>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>Cu$<em>{0.5}$Fe$</em>{0.5}$F$_2$</td>
<td>4.675(3)</td>
<td>4.642(3)</td>
<td>3.285(1)</td>
<td>90.62(1)</td>
<td>71.39(3)</td>
</tr>
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</table>
Milestone 2 – Discharge products of CuF₂/C and Cu₀.₈Fe₀.₂F₂/C identified

**CuF₂**
- Reaction complete at 1.8 V
- CuF₂ converted to Cu and LiF

**Cu₀.₅Fe₀.₅F₂**
- Not complete at 1.8V
- Forms LiF and Cu
- Peaks of Fe phase overlap with LiF phase, so cannot be identified
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
Earlier results showed capacity exceeding that of Sn$_2$Fe

- Theoretical capacity of Sn$_2$Fe 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

- 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

- 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
Milestone 4. Synthesis optimization of Sn-Fe-C anode
LiC₆ vs LiC₂ - does ball-milling activate the carbon?

- **Impact of high energy ball milling on graphite electrochemistry**
  - Crystallinity of graphite reduced
    - Fe₃C 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 LiC₂
Response to 2014 Reviewers’ Comments

New Project – No Comments
Collaboration and Coordination with other Institutions

- **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

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$_2$Fe**
  - Long term cycling
  - Cost effective synthesis methods
    - Mechanochemical method
      - Find collaborator to determine viability of mechanochemical manufacturing

- **Lithium incorporation in full cell (3$^{rd}$ year)**
  - Neither electrode presently contains Li
Proposed Future Work

• 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$_2$Fe
  – Improve cycling performance over 100-200 cycles
Summary

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$_y$F$_2$
      - 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$_y$F$_2$ 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$_2$Fe 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
Technical Back-Up Slides
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 CO₂
  - -519.6 kJ/mole for Sn to SnO₂
  - -371.1 kJ/mole for Fe to ½ Fe₂O₃
  - -705.5 kJ/mole for oxidation of Sn₂Fe to SnO₂ and Fe₂O₃
  - -850.7 kJ/mole for oxidation of Si to SiO₂

- Free energy of oxidation per lithium stored:
  - -2366 kJ/Li for a carbon anode
  - -160 kJ/Li for a Sn₂Fe 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