Overview

Timeline
- Project start date: Nov. 15, 2012
- Project end date: Jul. 22, 2016
- Percent complete: 86%

Barriers
- Barriers addressed
  - Specific Energy
  - Life
  - Cost

Budget
- Total project funding
  - DOE share $1,147,684
  - Contractor share $123,042
- Funding received in FY14
  - $499,990
- Funding for FY15
  - $499,909

Partners
- XG Sciences - Project lead
- A123 System
- Georgia Institute of Technology
- Collaborators
  - Argonne National Laboratory
  - Ashland Specialty Ingredients
  - Daikin America
  - JSR Micro
  - Lawrence Berkeley National Laboratory
  - Lubrizol
  - Sandia National Laboratory
  - Zeon Chemicals
  - Solvay
Relevance

Overall Objectives:

• Demonstrate XG SiG™ Si-graphene nano composite next generation Li-ion anode:
  – 600 mAh/g (*Specific Energy Barrier*),
  – 85% 1st cycle efficiency and
  – 1000 cycles with 75% capacity retention (*Life Barrier*)

• Stabilize and optimize the XG SiG™ anode pilot production (*Cost Barrier*)

• Develop a scalable dispersion and coating process with desired electrode properties

• Validate the XG SiG™ technology in commercial grade 2 Ah prototype Li-ion cells
EV Everywhere program defines a cell specific energy target of greater than 350 Wh/kg with 1000 cycles

Project Objective #1: Improve XG SiG™ anode performance
   a. 600 mAh/g (Energy Barrier),
   b. 85% 1st cycle efficiency, and
   c. 1000 cycles with 75% capacity retention (Life Barrier)
EV Everywhere targets cutting battery costs to $125/kWh

- This has been one of the biggest challenges for Si-based anodes due to poor scalability and prohibitive process cost.
- XGS’ XG SiG™ manufacturing process specifically addresses the cost issue in three ways:
  - Use of a low cost Si precursor,
  - Producing XG SiG™ in an existing manufacturing plant,
  - Automation and modular design of the production system making the XG SiG™ process less labor intensive
- Cost models show that XG SiG™ can achieve a competitive price as compared with graphite which is required for the commercial acceptance for PHEVs and EVs.
### Milestones

<table>
<thead>
<tr>
<th>Tasks</th>
<th>2014</th>
<th>2015</th>
<th>2016</th>
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<tbody>
<tr>
<td></td>
<td>Q1</td>
<td>Q2</td>
<td>Q3</td>
</tr>
<tr>
<td>1. Improve EC performance of XG SiG™</td>
<td></td>
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<tr>
<td>2. Optimize pilot production</td>
<td></td>
<td></td>
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<tr>
<td>3. Characterize materials/electrodes/cells</td>
<td></td>
<td></td>
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<td>4. Optimize dispersion</td>
<td></td>
<td></td>
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<tr>
<td>5. Optimize electrolyte/additives</td>
<td></td>
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<tr>
<td>6. Design/build 2Ah prototype cells</td>
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</tr>
</tbody>
</table>

**MS 1**: Demonstrate XG SiG™ silicon anode material in full cells:
- 600mAh/g, 85% 1st cycle efficiency, 500 cycles with 70% retention

**MS 2**: Demonstrate 600mAh/g, 85% 1st cycle efficiency, 1000 cycles with 70% retention

**MS 3**: Demonstrate XG SiG™ manufacturing process readiness

**MS 4**: Demonstrate electrode coating ready for prototype cell builds 2~3 L slurry preparation

**MS 5**: Select final electrolyte / additive

**MS 6 & 7**: Demonstrate XG SiG™ performance in 2Ah cells
# Status of Current Term Milestones

<table>
<thead>
<tr>
<th>Milestone ID</th>
<th>Description</th>
<th>Status</th>
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<tbody>
<tr>
<td>2</td>
<td>Demonstrate 600mAh/g, 85% FCE, 1000 cycles with 70% retention</td>
<td>Cell demonstrated 600 mAh/g; 88% FCE; 1000 cycles with ~85% capacity retention</td>
</tr>
<tr>
<td>3</td>
<td>Demonstrate XG SiG™ manufacturing product and process variable limits</td>
<td>Manufacturing product and process variable limits were defined and implemented resulting in improved and stable material quality</td>
</tr>
<tr>
<td>5</td>
<td>Select final electrolyte / additive</td>
<td>XGDA-3 electrolyte, xGnP Grade R-10 graphene nanoplatelet additive</td>
</tr>
<tr>
<td>7</td>
<td>Demonstrate XG SiG™ performance in 2Ah cells</td>
<td>2Ah cells demonstrated &gt; 1000 cycles</td>
</tr>
</tbody>
</table>
Approach to Performance Improvement

**Milestone:** 600mAh/g, 85% FCE, 75% capacity @ 1000 cycles

**Status:** Demonstrated XG SiG™ material 600 mAh/g, >85% FCE and >75% capacity retention at 1000 cycles targets

- Employ material modification to target more stable SEI layer
  - Si precursor
  - Composite formulation
  - Composite manufacturing process

- Reduced Si fracture
- Reduced Li⁺ reaction
- Optimized graphene nanoplatelet support
Approach to Manufacturing Process Improvement

**Milestone:** Demonstrate XG SiG™ manufacturing process readiness

**Status:** XG SiG™ manufacturing product and process variable limits were defined and implemented resulting in improved and stable material quality

- Define process capability
- Define XG SiG™ Product capability
  - Relate key performance to manufacturing metrics
- Demonstrate Manufacturing Process Control
Milestone: Selection of Electrolyte and Additives

Status: XGDA-3 electrolyte, xGnP Grade R-10 selected based on performance

- Identify:
  - Appropriate candidate electrolytes/ electrolyte additives,
  - Appropriate candidate conductive additives and loadings,
- Characterize applicable electrolytes and conductive additives
  - Single layer pouch cells and coin cells
- Select the best performing combination for 2Ah Cell Build
Approach to demonstrating SiG™ in 2Ah cells

**Milestone:** Demonstrate XG SiG™ performance in 2Ah cells

**Status:** 2Ah Cells meet program objectives; 600 mAh/g; 88% FCE (Half Cell); 1000 cycles with ~85% capacity retention

- Formulate optimized SiG™, electrolyte, binder, conductive additive, etc.
- Coat and characterize coatings at A123 Systems
- Build and characterize 2Ah Cells
Technical Progress

XG SiG™ met MS 2 target in 63 mAh pouch cells

Demonstrated XG SiG™ material 600 mAh/g, 85% FCE and 70% capacity retention at 1000 cycles targets in small format cells

**Improvement tied to:** (a) modified Si precursor, (b) optimized formulation, and (c) manufacturing process modifications

- **Anode**
  - 90% Active + 6% PAA binder + 4% conductive additive
  - Active: lab and plant XGS Gen 3 (600 mAh/g, > 88% FCE)
  - Conductive additive: lab and plant xGnP-10
  - Loading: 2.5 mAh/cm² and 3.8 mAh/cm²
  - Anode density: 1.55 g/cc for full coin cell

- **NCA cathode**
  - 2.27 mAh/cm² for 2.5 mAh/cm² Gen 3 anode
  - 3.45 mAh/cm² for 3.8 mAh/cm² Gen 3 anode

- **Full cell & Test condition**
  - Gen3 SiG anode: NCA cathode = ~1.1
  - Test protocol: 1C Cycling, Voltage as indicated

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*Phases of testing*

**Phase I**
- Phi (Y2) - 38 mAh Gen3 pouch cell (3.25~4.2V) (Plant Gen 3.0 #510)
- Phi (Y3) - 63m Ah pouch cell (3.2~4.2V)
- Phi (Y3) - 1.7mA coin cell (3.25~4.1V)
- Phi - 35m Ah pouch cell (3.25~4.1V)

**Phase II Year 1**
- Phi (Y2) - 28mAh Gen3 pouch cell (3.25~4.2V) (Lab Gen 3.0 #901)

**Phase II Year 2**
- Phi (Y2) - 38 mAh Gen3 pouch cell (3.25~4.2V) (Plant Gen 3.0 #810)
Technical Progress

Evaluation of New Si – Precursors

- Alternative Commercial Si Precursors Obtained
  - Si-2 is standard Si-precursor for reported work
- Improved Cycling Performance (Half Cell)
  - Si-3 and Si4 show inherent improved performance to Si-2
  - Anode Capacity of 850 mAh/g
- Crystal Size
  - The Si raw materials have different peak curve areas, indicating different particle or crystallite sizes
- Surface oxidation
  - Si – 5 provides an opportunity to evaluate impact of oxygen content on XGS SiG Materials
Technical Progress

Production material shows good consistency in 1st Cycle Efficiency and capacity retention in support of MS 3 - Manufacturing process readiness

- Anode FCC: 600 mAh/g
- 97%: 3% CMC/SBR
- Anode loading: 3.3 mg/cm²
- Anode density: 1.62 g/cc
- Protocol: CCCV/ CC, 1C
Technical Progress

Electrolyte / electrolyte additive selection was performed in combination with several partners. Coin cell testing considered: FCE, Capacity retention

XGDA-3 was selected for use in 2Ah cells
Technical Progress

Anode conductive additive selection was performed in combination with several sources. Coin cell testing considered: FCE, Capacity retention

Grade R-10 xGnP graphene nanoplatelets were selected for use in 2Ah cells.
SiG coating quality improved for 2Ah cell build

- Modified dispersion protocol and drying condition => No streaks or flaking

- Dry adhesion improved by 2X over the first coating trial.
- Electrode passed all QC checks.

![Graph showing dry adhesion comparison between 1st and 2nd coating trials.](image)
Technical Progress

2Ah Cell Build – Cell Design

- Anode
  - Slurry: 90% Gen3 SiG + 4% R10 conductive additive + 6% PAA
  - Loading: 5.68 mg/cm² per side
  - Electrode density: 1.55 g/cc
  - Thickness: 83um total

- NCA cathode
  - Loading: 27.7 mg/cm² double side

- Cell capacity
  - 2.11 Ah (without aging)
  - 1.83 Ah (with aging)

- A / C = 1.1
Technical Progress

2Ah Cell Build – Cell Build

1st cycle: +C/40, -C/40, 4.2-3.0V, 100% DOD, RT
HT aging: +C/10 to 100% SOC, aging for 3 days, degas/seal
Qualification: -C/10; +C/10, -C/10, then +C/5, -C/5, DCR, ACR check at 50% SOC, RT

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<th>Cell ID</th>
<th>1st Chg (Ah)</th>
<th>1st Dis (Ah)</th>
<th>1C Chg (Ah)</th>
<th>ICL(%)</th>
<th>f-DCR (mΩ)</th>
<th>1st n-Disl (Ah)</th>
<th>2nd n-Disl (Ah)</th>
<th>% Ret</th>
<th>5A (Ah)</th>
<th>5A (Wh)</th>
<th>Avg V</th>
<th>DCR (mΩ)</th>
<th>n-ICL (%)</th>
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</table>

Average
20.79
2.360
25.798
26.101
10.701

- Stabilized cell capacity @C/10 (4.2~3.0V)
  + 2.35 Ah
  + 11.8% over design max. (2.11 Ah)
Technical Progress

2Ah Cell Build – Cycling

+\(C/2\), -\(C/2\), 4.2-3.25 V, 100% DOD, RT

Discharge \(\Delta SOC\) vs Cycle Number

<table>
<thead>
<tr>
<th>Cell ID</th>
<th>C rate</th>
<th>Voltage range (V)</th>
<th>EOL (75%)</th>
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<tbody>
<tr>
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<tr>
<td>XXO854400006/11</td>
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<td>4.2-3.25</td>
<td>&gt; 1176</td>
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</table>

1176 cycles @86.9%
2Ah Cell Build – Cycling

+C/2, -C/2, 4.2-3.25 V, 100% DOD, RT

Discharge (Ah) vs Cycle Number

<table>
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<td>4.2-3.25</td>
<td>&gt; 825</td>
</tr>
<tr>
<td>XXO854400006/11</td>
<td>1C</td>
<td>4.2-3.25</td>
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</table>
Technical Progress

2Ah Cell Build – Cycling

$+C/2$, $-C/2$, $4.2-(2.7\sim3.25)\ V$, $100\%\ DOD$, RT

<table>
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<tr>
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Discharge (Ah) vs Cycle Number
### Responses to Previous Year Reviewers’ Comments

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<tr>
<th>2015 Reviewer Comments</th>
<th>Response</th>
</tr>
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<tbody>
<tr>
<td>The path to both scale-up and cycle life is not clear.</td>
<td>XG Sciences currently operates a ~50 Ton/year plant for XG SiG™. Scale-up to 250 Ton/year plant is planned but outside the scope of this project. Cycle life has been improved but additional work is still necessary. Pathway to improved cycle life focuses on enhancing Si/graphene interface to provide additional protection from electrolyte reactions.</td>
</tr>
<tr>
<td>There are still significant technical barriers to overcome in this project.</td>
<td>Agreed. Additional technical developments are needed in order for high capacity silicon anodes to be able to meet automotive requirements. While this project has made progress, more work is needed especially in capacity retention and swelling.</td>
</tr>
<tr>
<td>Need to see more information on volumetric energy density and rate capabilities of this material.</td>
<td>The cells used in this program are not optimized for volumetric or gravimetric energy density. Thus reporting this information would not accurately represent commercial capabilities or performance. XG SiG 2Ah cell capacity retention as a function of C-rate is shown here.</td>
</tr>
</tbody>
</table>
Collaboration & Remaining Challenges

• Collaborations and Coordination
  • XG Sciences – Prime
  • A123 Systems – Subcontractor
  • Georgia Institute of Technology – Subcontractor
  • Argonne National Laboratory (A. Jansen)
  • Ashland Specialty Chemicals
  • Daikin America
  • Lawrence Berkeley National Laboratory (G. Liu)
  • Sandia National Laboratory (C. Orendorff)
  • JSR Micro
  • Lubrizol
  • Zeon
  • Solvay

• Remaining Challenges
  • Further improve capacity retention performance over larger voltage window
  • Improve initial (1st 100 cycles) capacity retention performance
## Proposed Future Work

<table>
<thead>
<tr>
<th>Barrier</th>
<th>Proposed work</th>
<th>Objective (MS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific Energy,</td>
<td>• Optimize SiG Formulation utilizing newly identified potential Si-Precursors&lt;br&gt;• Improved cycle life observed in half cells&lt;br&gt;• Reduce overall electrode expansion through tailored crystal size</td>
<td>Demonstrate: 600 mAh/g, 85% FCE, 85% Cap retention @1000 cycles &lt;50% expansion</td>
</tr>
<tr>
<td>Life</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Specific Energy,</td>
<td>• Improve SiG graphene conductive coating&lt;br&gt;  - Optimization of graphene XGS coating process to improve coverage and SEI formation protection&lt;br&gt;  - Small Business Voucher Program Underway w/ LBNL&lt;br&gt;  - DE-FOA-0001417, SBIR/STTR FY 2016 Phase I proposal submitted</td>
<td>Objective: Improved voltage window performance, 850 mAh/g, 85% FCE, 75% Cap retention @500 cycles</td>
</tr>
<tr>
<td>Life</td>
<td></td>
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</table>
Summary

- XG Sciences has met program objectives
  - Goals met for Si anode performance based on 2Ah cycling.
  - Further improvements in voltage window are desirable
- All material developments
  - Transferred to high capacity plant production, material at numerous cell customers.
- Slurry and coating developments
  - Transferred to A123 Systems and numerous other cell manufacturers.

<table>
<thead>
<tr>
<th>2015 Program Objectives</th>
<th>2015 Program Accomplishments</th>
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