New High-Energy Electrochemical Couple for Automotive Applications

K. Amine (PI)

H. Wu, A. Abouimrane, Z. Chen, J. Lu, R. Xu, C.K. Lin and Y.C. Kan

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Project ID: ES208
Overview

Timeline
- Start - October 1st, 2013.
- Finish - September 30, 2015.
- 15% Completed

Barriers
- Barriers addressed
  - High energy (>200wh/kg)
  - Long calendar and cycle life
  - Abuse tolerance

Budget
- Total project funding
  - DOE share: 2500K
- Funding received in FY13: 1250K
- Funding for FY14: $1250 K

Partners
- **Project lead:** Khalil Amine
- **Interactions/ collaborations:**
  - X. Q. Yang (BNL) diagnostic of FCG cathode and SEI of Si-Sn composite anode
  - G. Liu (LBNL) development and optimization of conductive binder for Si-Sn composite anode
  - ECPR: provide baseline cathode material
  - Utah University: provide facility to scale up the baseline Si-Sn composite anode for baseline cell
  - Andy Jansen & Polzin, Bryant (ANL) fabrication of baseline cell
  - Paul Nelson (ANL) design of cell using BatPac
Objectives of the work

- Develop a new high energy redox couple that provide
  - Over 200wh/kg energy density
  - Long cycle life (> 1000 cycle)
  - Excellent abuse tolerance
Relevance

- Objective: develop very high energy redox couple (250wh/kg) based on high capacity full gradient concentration cathode (FCG) (230mAh/g) and Si-Sn composite anode (900mAh/g) with long cycle life and excellent abuse tolerance to enable 40 miles PHEV and EVs.

- This technology, if successful, will have a significant impact on:
  - Reducing battery cost and expending vehicle electrification
  - Reduce greenhouse gases
  - Reduce our reliance on foreign oil
Milestones

- **May 2014**
  - Deliver 12 baseline cells

- **September 2014**
  - Finalize engineering of electrodes based on 50 wt% SiO-50 wt% Sn$_{30}$ Co$_{30}$C$_{40}$ and conductive polymer binder (PFFOMB), fabricate cells and finalize test

- **September 2014**
  - Finalize the optimization of Gen 1 FCG cathode

- **October 2014**
  - Fabricate Gen1 cell based on Gen 1-FCG cathode and 50 wt% SiO-50 wt% Sn$_{30}$ Co$_{30}$C$_{40}$ anode with conductive polymer binder (PFFOMB)
**ANODES**
SiO-Sn\textsubscript{y}Co\textsubscript{1-x}Fe\textsubscript{x}C\textsubscript{z} composite coupled with conductive binder

**ELECTROLYTES**
High voltage electrolytes with additives to stabilize interface of cathode and anode

**CATHODES**
Full Gradient concentration (FCG) LiNi\textsubscript{x}Mn\textsubscript{y}Co\textsubscript{z}O\textsubscript{2} with high concentration of Mn at the surface of the particle

Fluorine based electrolyte with additives:

![Fluorine-based electrolyte](image)

Initial charge & discharge of SiO-SnCoC anode

Conductive binder

Floating test at different voltages of LiNi\textsubscript{0.5}Mn\textsubscript{1.5}O\textsubscript{4}/Li\textsubscript{4}Ti\textsubscript{5}O\textsubscript{12}

Cell using fluorinated electrolyte

Initial charge & discharge of FCG cathode
Approach (cont)

Team configuration

- **LBNL (240K)**
  - Conductive binder optimization

- **ANL (1900K)**
  - Cathode & anode development (Characterization)

- **BNL (360K)**
  - Diagnostic of cathode and anode with in-situ X-ray

DOE Program Manager

- **ANL Cell Fabrication Facility**
- **Khalil Amine**
  - Project Coordinator
- **ANL Material scale up faculty**

- **Ali Abouimrane**
  - Anode Processing
- **Gao Liu**
  - Anode engineering With conductive binders
- **K. Amine**
  - Cathode Development
  - Huiming Wu
  - Cathode processing And cell test
- **Xiao Qing Yang**
  - diagnostic
Recent Accomplishments and Progress

- Scale up 50 wt% SiO-50 wt% Sn_{30} Co_{30}C_{40} anode to 1Kg level for use in baseline cell.
- Acquire 25Kg of LiNi_{0.6}Mn_{0.2}Co_{0.2}O_{4} cathode for use in baseline cell.
- Engineer cathode & anode electrodes using conventional PVDF binder, build a full baseline cell and carry out cycling test.
- Set up CSTR co-precipitation reactor for carrying out full concentration gradient (FCG) cathode development.
- Successfully prepare dense FCG cathode using hydroxide process (2.7g/cc).
- Confirm thermal stability of FCG cathode using Synchrotron soft X-ray at different temperatures.
### Baseline chemistry

**ANODES**
50 wt% SiO-50 wt% Sn<sub>30</sub>Co<sub>30</sub>C<sub>40</sub> coupled with UBE U-Varnish A binder

**ELECTROLYTES**
1.2M LiPF<sub>6</sub> in EC:EMC (3:7 wt%) with 10 wt% FEC

**CATHODES**
LiNi<sub>0.6</sub>Mn<sub>0.2</sub>Co<sub>0.2</sub>O<sub>2</sub> from ECOPRO

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**EDAX & PDF of anode**
showing possible alloying between Si and Sn

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**VOLTAGE PROFILE**

**CYCLE PERFORMANCE**

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**Graphs and Diagrams**

- Voltage profile
- Cycle performance
- Capacity vs. cycle number
- EDAX and PDF images of anode
- Elemental mapping of Si, O, Co, C, Sn
Baseline cell Chemistry and design

• **Anode:**
  - 90 wt% SiO-SnCo-C; 5 wt% Timcal C-45; 5 wt% UBE U-Varnish A
  - Total Electrode Thickness: 13 microns
  - Cu Foil Thickness: 10 microns
  - Total Electrode Loading: 2.41 mg/cm³
  - Porosity: ~45%

• **Cathode:**
  - 90 wt% ECOPRO NCM 622; 5 wt% Timcal C-45; 5 wt% Solvay 5130 PVDF
  - Total Electrode Thickness: 77 microns
  - Al Foil Thickness: 20 microns
  - Total Electrode Loading: 14.83 mg/cm³
  - Porosity: ~36%

• **Separator:**
  - Celgard® 2325 PP/PE/PP Tri-Layer

• **Electrolyte:**
  - Tomiyama Pure Chemicals -1.2M LiPF₆ in EC:EMC (3:7 wt%) with 10 wt% Solvay FEC

• Coin Cell work done in 2032 sized cells
Initial result of baseline cell using button cells

**Formation Voltage Profile, (AAKA14)**

**Efficiency vs cycles:**

**Cycle life:**

**HPPC Test with 3C/2.25C Pulse:**
Voltage Profile

- 3.0C Disch. Pulse
- 2.25C Chrg. Pulse

**HPPC ASI vs DOD**
- AAKA13b Charge ASI
- AAKA13b Discharge ASI
# Usable Energy and power of baseline cell based on BatPac Design

<table>
<thead>
<tr>
<th>Deliverable</th>
<th>Device</th>
<th>Battery Performance (Cell Level)</th>
<th>Technology Info</th>
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<tbody>
<tr>
<td>baseline</td>
<td>20Ah Cell</td>
<td>Usable Specific Energy (Wh/kg)</td>
<td>Si-Sn Composite</td>
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<tr>
<td></td>
<td>(~216)</td>
<td>Usable Energy Density (Wh/l)</td>
<td>And NMC (6:2:2)</td>
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<td></td>
<td>(~271)</td>
<td>Power at SOCmin (W/kg, 10 sec)</td>
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<td>40Ah Cell</td>
<td>(~511)</td>
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<td></td>
<td>(~650)</td>
<td>(~1880)</td>
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<tr>
<td></td>
<td>BatPac Design</td>
<td>(~1177)</td>
<td></td>
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Synthesis of Full Gradient Concentration (FCG) Precursor via CSTR Co-precipitation

Mn Solution

Ni Solution

V

Na₂CO₃, NH₄OH

Reactor

Co-Precipitated Particles

pH controller

Pumps

Reactor

Collection
Cross section EPMA of precursor and (FCG) from Carbonate Process

Precursor $\text{Li}[\text{Ni}_{0.65}\text{Co}_{0.15}\text{Mn}_{0.25}]\text{O}_2$

Oxide

Tab density: 2.2g/cc
**Electrochemical performance of FCG cathode**

Initial cycling at 30°C and 55°C

Cycling performance of FCG at 30°C and 55°C

Low temperature performance of FCG
DSC of Charged FCG and LiNi$_{0.6}$Co$_{0.15}$Mn$_{0.25}$O$_2$ (Core) Having the Same Composition

FCG average composition: LiNi$_{0.6}$Co$_{0.15}$Mn$_{0.25}$O$_2$
Characteristics of FCG Precursor Made From Hydroxide Process

1. High Tap density = 2.2 g/cc

2. Good particle distribution: $D_{50} = 11.64 \, \mu m$

3. Average composition is: $\text{Ni}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}(\text{OH})_2$

4. Outer is about: $\text{Ni}_{0.46}\text{Co}_{0.23}\text{Mn}_{0.41}(\text{OH})_2$

5. Inner is about: $\text{Ni}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}(\text{OH})_2$

X-ray of $\text{Ni}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}(\text{OH})_2$

Particle distribution of $\text{Ni}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}(\text{OH})_2$

1. High Tap density = 2.2 g/cc

3. Good particle distribution: $D_{50} = 11.64 \, \mu m$

4. Average composition is:
   - Outer is about: $\text{Ni}_{0.46}\text{Co}_{0.23}\text{Mn}_{0.41}(\text{OH})_2$
   - Inner is about: $\text{Ni}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}(\text{OH})_2$
Characteristics of FCG Gradient Cathode Made From Hydroxide Process

SEM of LiNi$_{0.6}$Co$_{0.2}$Mn$_{0.2}$O$_2$

1. High Tap density = 2.7 g/cc

3. Particle distribution: D$_{50}$ = 11.64 µm (unchanged)

4. Average composition is: LiNi$_{0.6}$Co$_{0.2}$Mn$_{0.2}$O$_2$
   - Outer is about: LiNi$_{0.46}$Co$_{0.23}$Mn$_{0.41}$O$_2$
   - Inner is about: LiNi$_{0.8}$Co$_{0.1}$Mn$_{0.1}$O$_2$

X-ray of LiNi$_{0.6}$Co$_{0.2}$Mn$_{0.2}$O$_2$
TEM of Full Gradient Concentration Cathode made from Hydroxide Process

TEM image along with energy-dispersive X-ray spectroscopy (EDS) data for a single elongated CCG primary particle

TEM image and the corresponding electron diffraction pattern from a CCG primary particle, illustrating the crystallographic alignment of the primary particle in the radial direction.
Initial Electrochemical Performance of FCG Gradient Cathode from Hydroxide Process

**VOLTAGE PROFILE**

- Initial Electrochemical Performance of FCG Gradient Cathode from Hydroxide Process
  - 2.75-4.3 V
  - Charge 1
  - Discharge 1

**CYCLE PERFORMANCE**

- Cycle life: it is very stable at C/3 with 50 cycles at room temperature

**Initial cycle: Charge: 202.5 / Discharge: 186.6 mAh/g with 92.1% efficiency at C/5**
The thermal stability of NCA and FCG charged to 4.5V using synchrotron soft X-ray at different temperatures.

- The FCG sample shows less oxygen release than bulk NCA samples.

The first cycle capacity of NCA and FCG at 4.5V is around 230mAh/g. The FCG sample showed much better thermal stability.
Responses to Previous Year Reviewers’ Comments

This project is new and was not reviewed last year
Collaborations

• X.Q. Yang of BNL
  - Diagnostic of FCG and SEI of Si-Sn composite electrodes using soft & hard X-ray.

• G. Liu (LBNL)
  - Development and optimization of conductive binder for Si-Sn composite anode

• H. Wu (ANL)
  - Optimize the synthesis of FCG cathode

• A. Abouimrane (ANL)
  - Development of SiO-Sn_yCo_{1-x}Fe_xC_z anode

• J. Lu & Z. Chen (ANL)
  - Characterization of cathode, anode and cell during cycling using In-situ techniques

• ECPRO: Baseline cathode material

• University of Utah: Facility to scale up the baseline Si-Sn composite anode for baseline cell

• A. Jansen & B. Polzin (ANL)
  - Design & fabrication of baseline cell

• Y.K. Sun (ANL/Hanyang University): Technical discussions
Remaining Challenges and Barriers

• Reduce irreversible loss of SiO-SnyCo1-xFexC

• Demonstrate 1000 cycles of SiO-SnyCo1-xFexCz using conductive binder

• Improve further FCG cathode capacity to 220~230mAh/g at high voltage 4.4V and 4.5V

• Demonstrate 250wh/kg at the cell level using improved FCG cathode and SiO-SnyCo1-xFexCz anode.
Future work

• Optimize the ratio of SiO-SnyCo1-xFexC and graphite to reduce irreversible loss

• Optimize SiO-SnyCo1-xFexC electrode with conductive binder to improve cycle life

• Investigate the stability of SEI in SiO-SnyCo1-xFexC and explore additive that provide stable passivation film.

• Synthesize FCG gradient materials with different surface Mn concentration as well as different gradient concentration slopes to determine the detailed effects of the composition profile on cathode capacity and stability.

• Explore further coating FCG cathode with AlF3 to improve cycle life at 4.4 and 4.5V.

• Investigate performance of FCG with high voltage fluorinated electrolyte
Summary

- Baseline cell based on NMC (6:2:2) / 50 wt% SiO-50 wt% Sn₃₀Co₃₀C₄₀ carbon was fabricated and tested.
- Set up of CSTR Co-precipitation reactor for making FCG cathode was successfully implemented.
- Synthesis of FCG using hydroxide process was successfully carried out and spherical particles with very high tap density of 2.7g/cc was obtained which can lead to high loading at the electrode level and increase the energy density of the cell.
- High thermal stability of FCG cathode was demonstrated using synchrotron soft X-ray at different temperatures.
Publications and Presentations

1- Cathode Material with Nanorod Structure “An Application for Advanced High-Energy and Safe Lithium Batteries”
Hyung-Joo Noh, Zonghai Chen, Chong S. Yoon, Jun Lu, and Khalil Amine,*

2- Formation of a Continuous Solid-Solution Particle and its Application to Rechargeable Lithium Batteries
Hyung-Joo Noh , Seung-Taek Myung , Hun-Gi Jung , Hitoshi Yashiro , Khalil Amine *,
and Yang-Kook Sun