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

Argonne National Laboratory

DOE merit review

June 15^{th} ~20^{th} , 2014

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
- **ECPRO:** 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

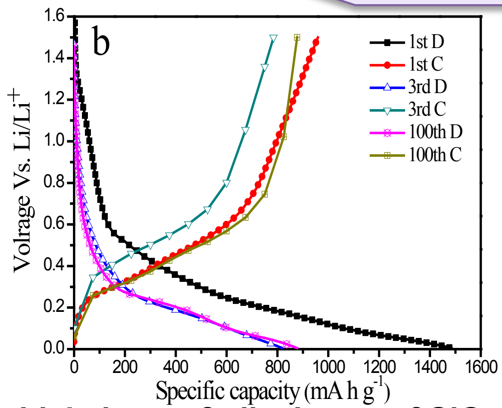
- This technology, If successful, will have a significant impact on:
  - *Reducing battery cost and expending vehicle electrification*
  - *Reduce greenhouse gases*
  - *Reduce our reliance on foreign oil*

Milestones

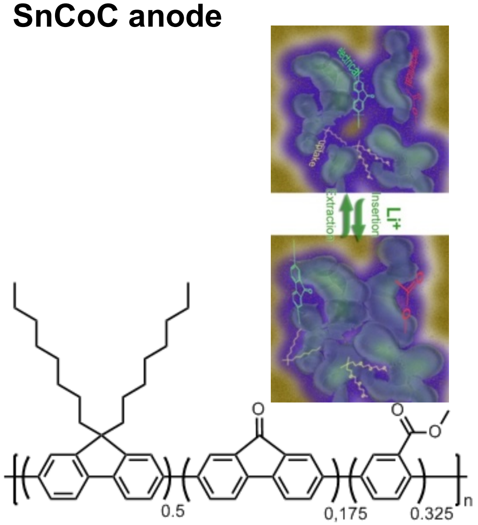
- **May 2014**
  - Deliver 12 baseline cells
- **September 2014**
  - Finalize engineering of electrodes based on 50 wt% SiO-50 wt% $Sn_{30}Co_{30}C_{40}$ and conductive polymer binder (PFFOMB), fabricate cells and finalize test
- **September 2014**
  - Finalize the optimization of Gen 1 FCG cathode
- **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)

Approach

ANODES	ELECTROLYTES	CATHODES
$SiO\text{-}Sn_yCo_{1-x}Fe_xC_z$ composite coupled with conductive binder	High voltage electrolytes with additives to stabilize interface of cathode and anode	Full Gradient concentration (FCG) $LiNi_xMn_yCo_zO_2$ with high concentration of Mn at the surface of the particle

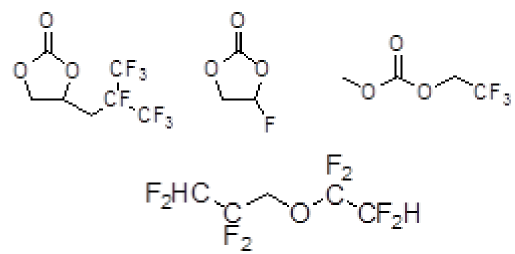


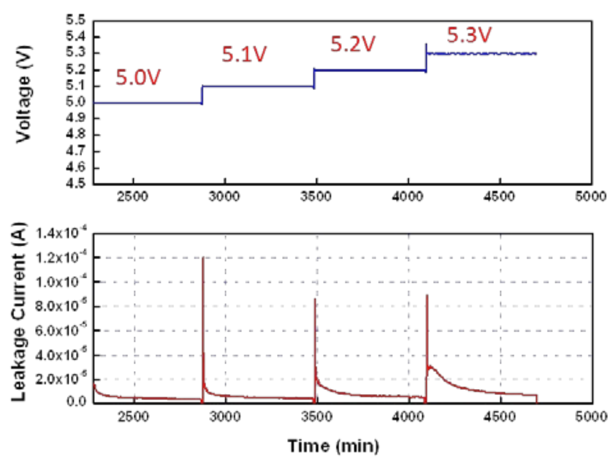
Initial charge & discharge of SiO-SnCoC anode



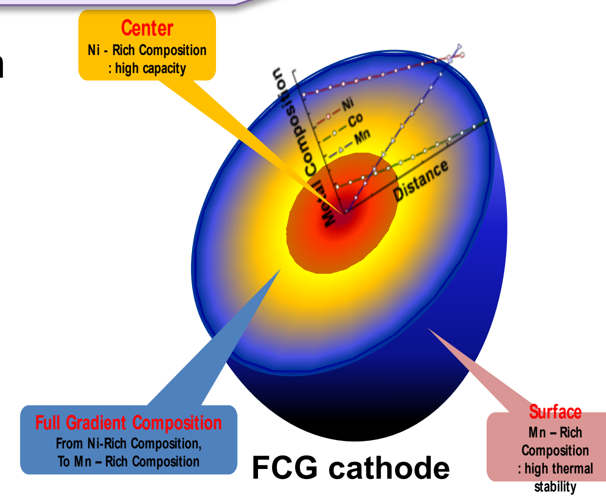
Conductive binder

Fluorine based electrolyte with additives:

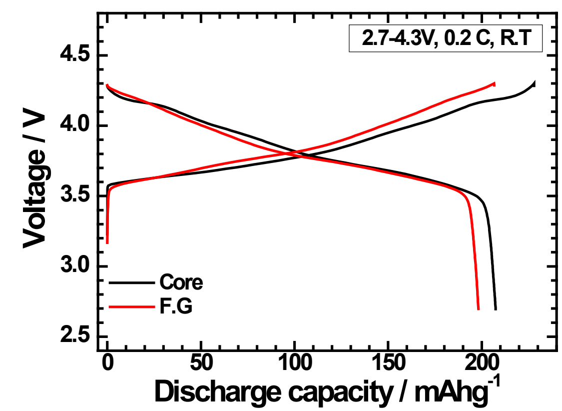




Floating test at different voltages of $LiNi_{0.5}Mn_{1.5}O_4/Li_4Ti_5O_{12}$ Cell using fluorinated electrolyte



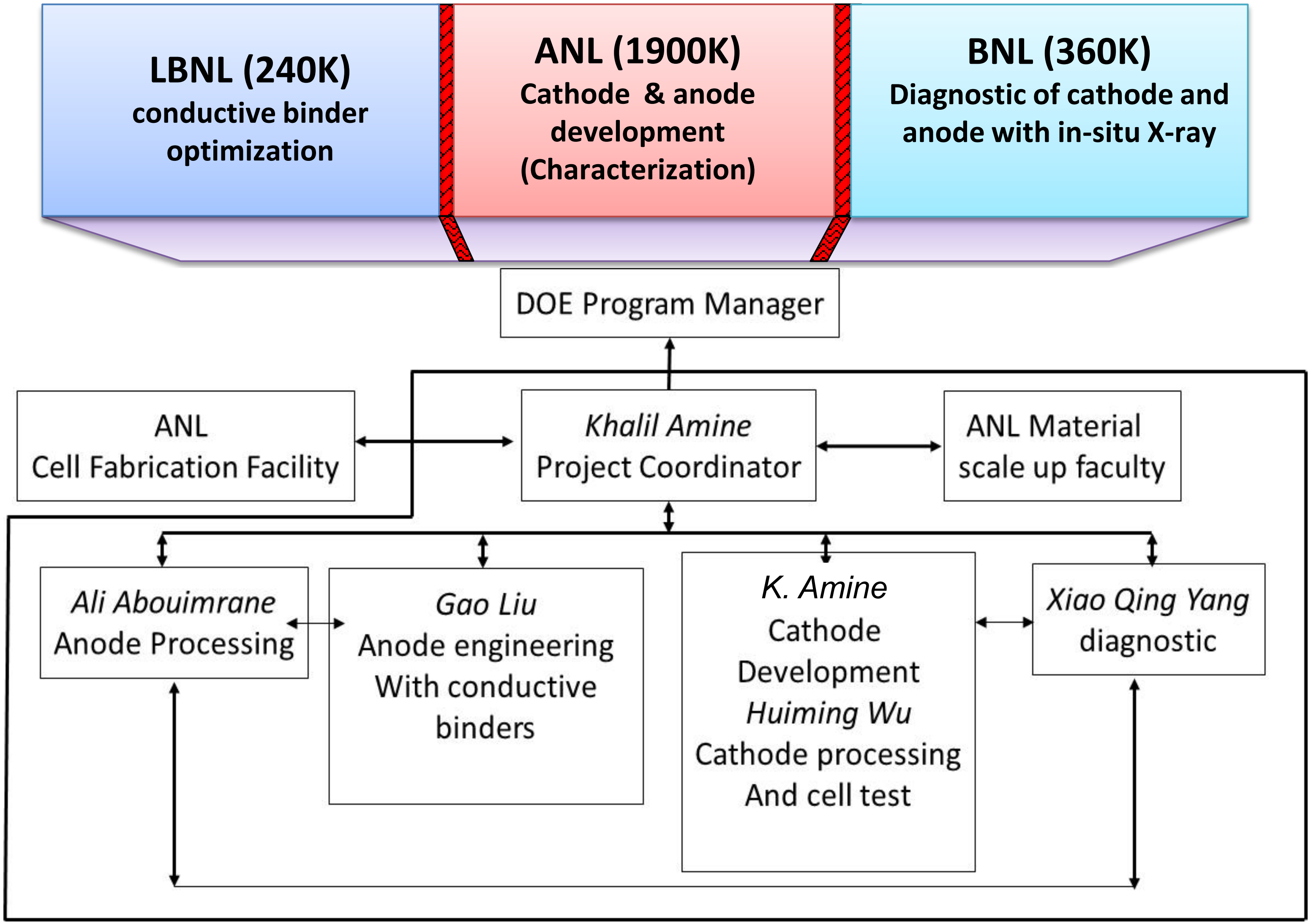
FCG cathode



Initial charge & discharge of FCG cathode

Approach (cont)

Team configuration

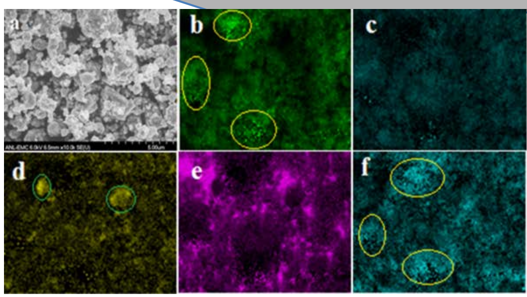


Recent Accomplishments and Progress

- 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.

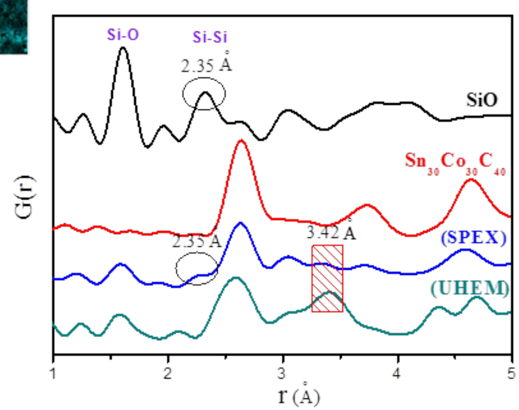
Baseline chemistry

ANODES	ELECTROLYTES	CATHODES
50 wt% SiO-50 wt% $Sn_{30}Co_{30}C_{40}$ coupled with UBE U-Varnish A binder	1.2M $LiPF_6$ in EC:EMC (3:7 wt%) with 10 wt% FEC	$LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$ from ECOPRO

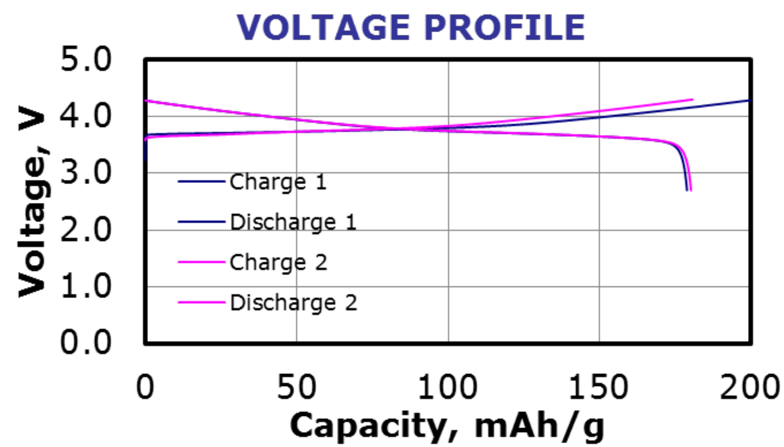


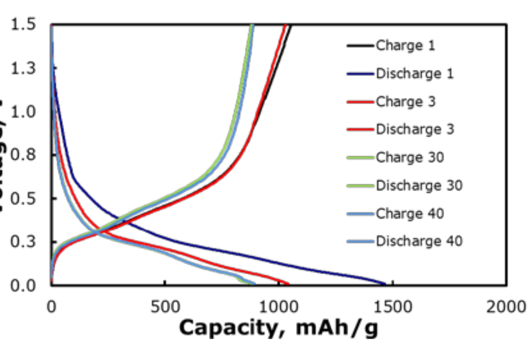
(a) SEM images and EDX elemental mapping of
(b) Si,
(c) O,
(d) Co,
(e) C,
(f) Sn

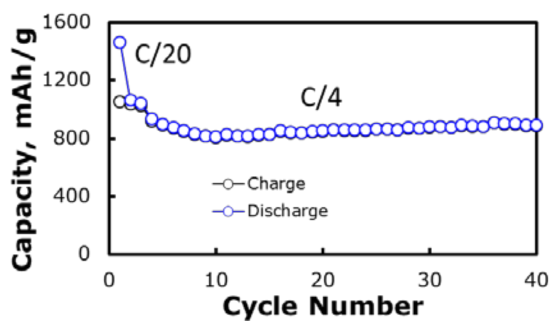
PDF of anode

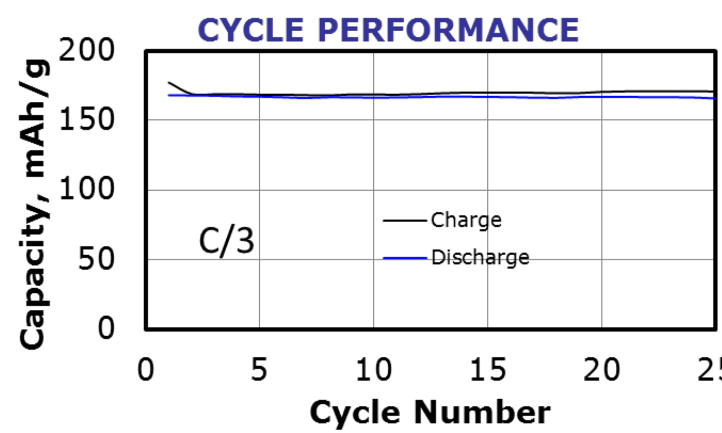


EDAX & PDF of anode showing possible alloying between Si and Sn





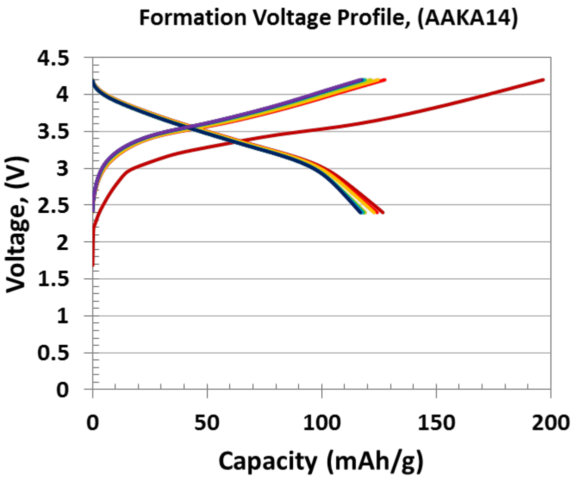




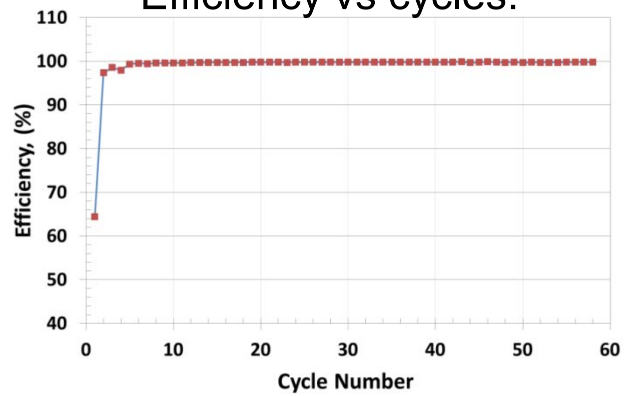
Baseline cell Chemistry and design

- **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/cm^3
    - 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/cm^3
    - Porosity: ~36%
- **Separator:**
  - Celgard® 2325 PP/PE/PP Tri-Layer
- **Electrolyte:**
  - Tomiyama Pure Chemicals -1.2M $LiPF_6$ in EC:EMC (3:7 wt%) with 10 wt% Solvay FEC
- Coin Cell work done in 2032 sized cells

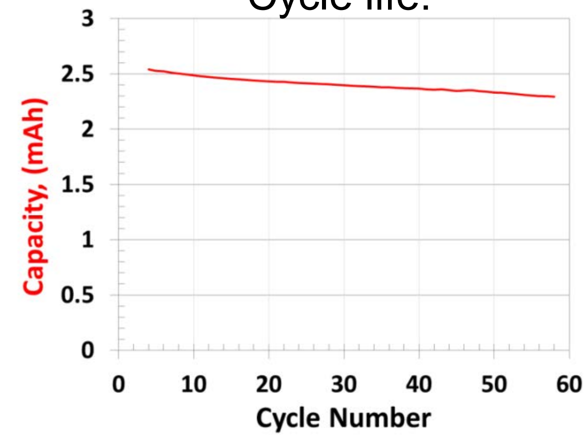
Initial result of baseline cell using button cells

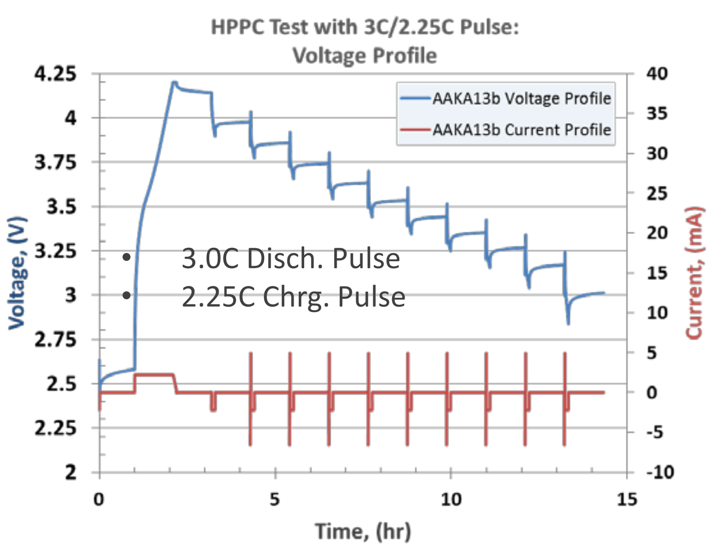


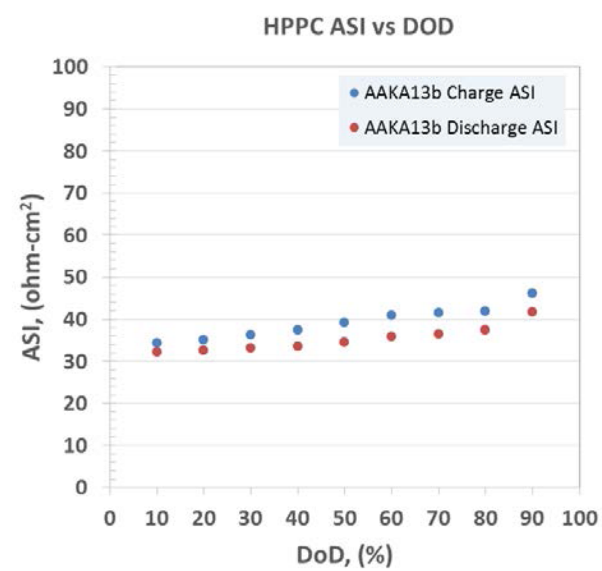
Efficiency vs cycles:



Cycle life:



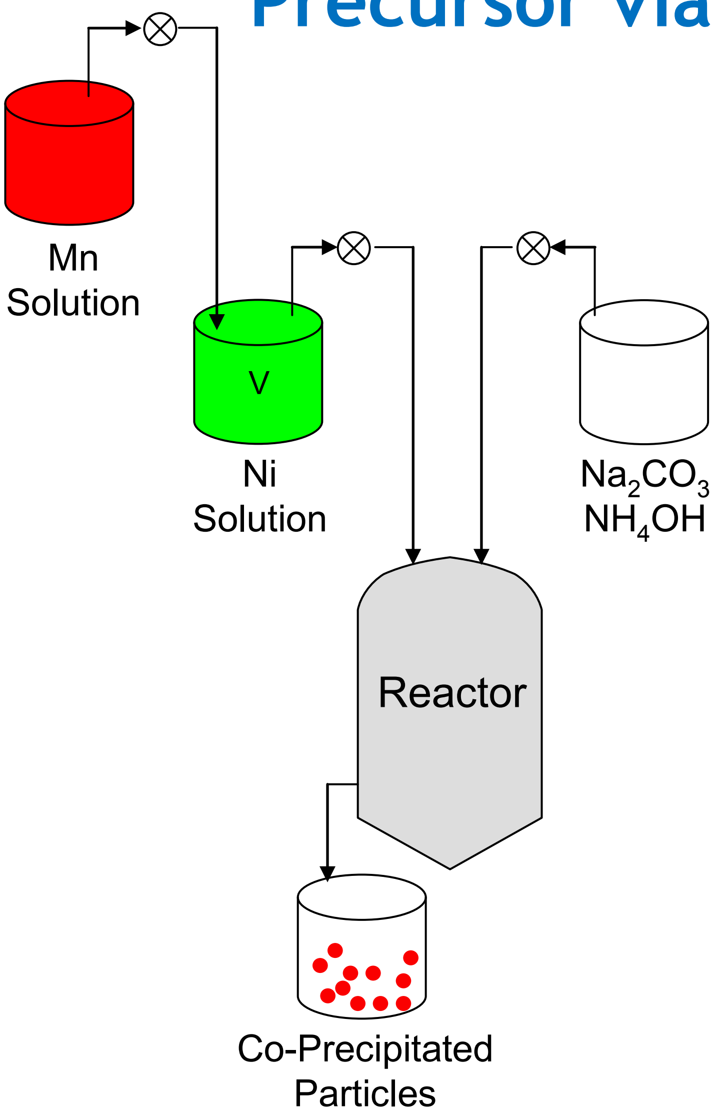




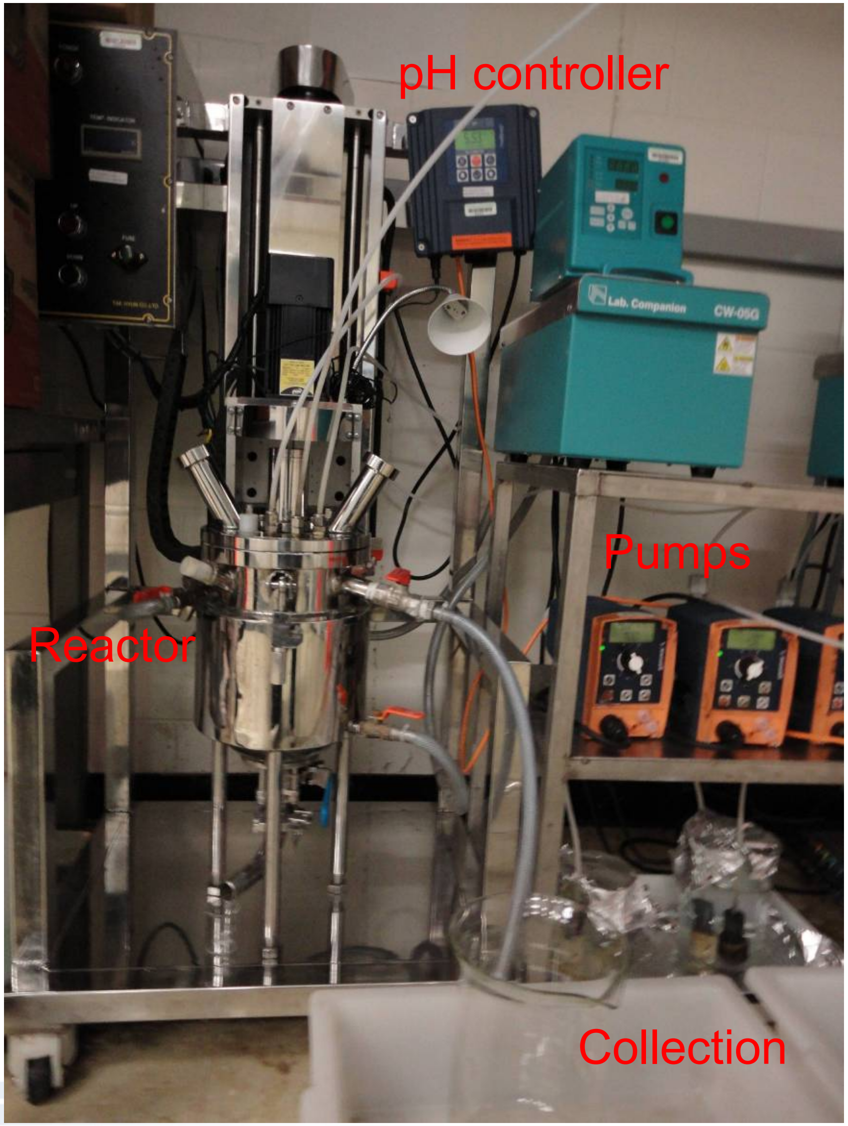
Usable Energy and power of baseline cell based on BatPac Design

Deliverable	Device	Battery Performance (Cell Level)			
		Usable Specific Energy (Wh/kg)	**Energy Usable Density** (Wh/l)	**Power at SOCmin** (W/kg,10 sec)	**Technology Info**
baseline	**20Ah Cell** **40Ah Cell** BatPac Design	**(~216)** **(~271)**	**(~511)** **(~650)**	**(~1880)** **(~1177)**	Si-Sn Composite And NMC (6:2:2)

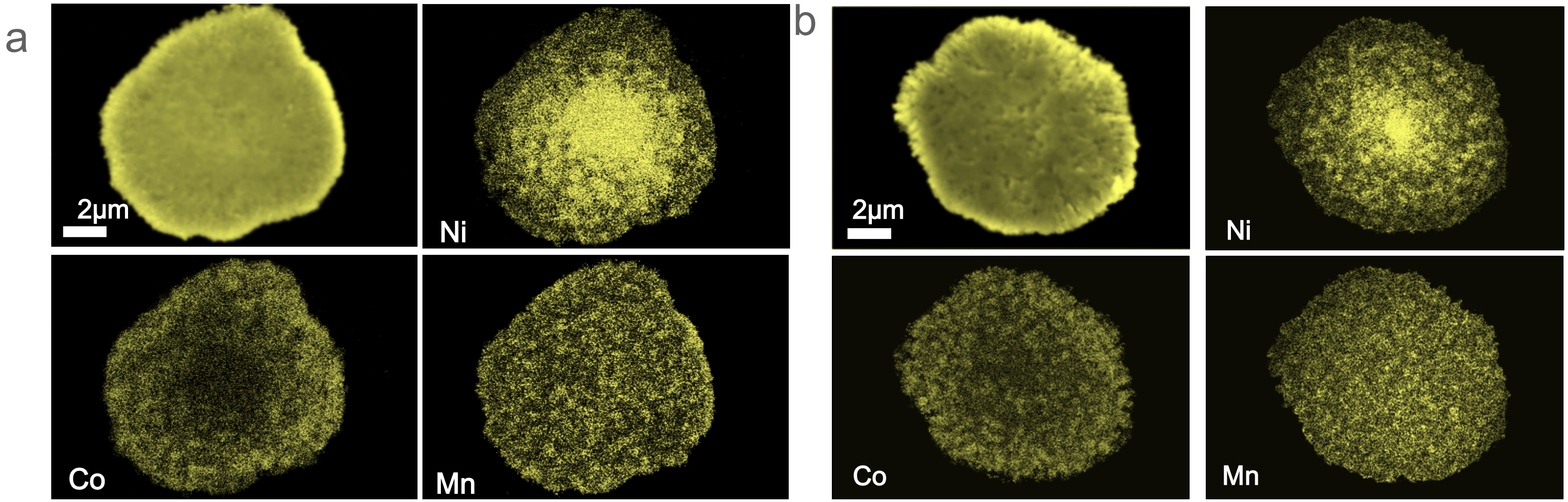
Synthesis of Full Gradient Concentration (FCG) Precursor via CSTR Co-precipitation



Reactor Setup



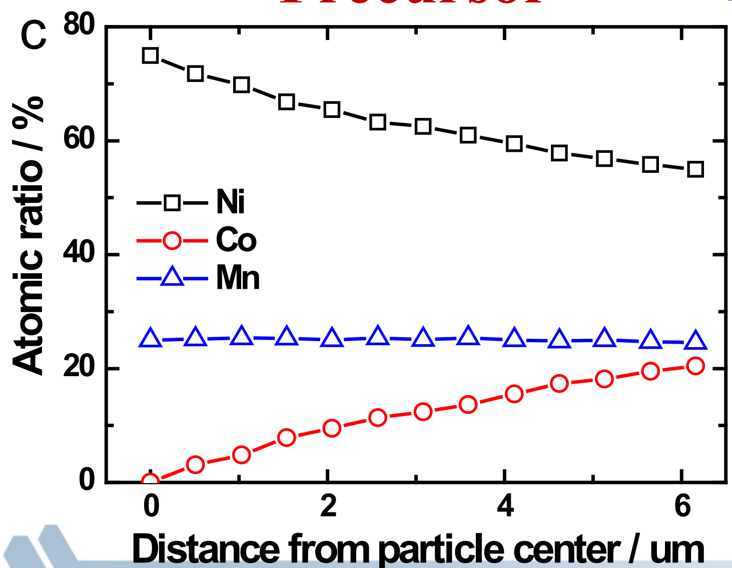
Cross section EPMA of precursor and (FCG) from Carbonate Process

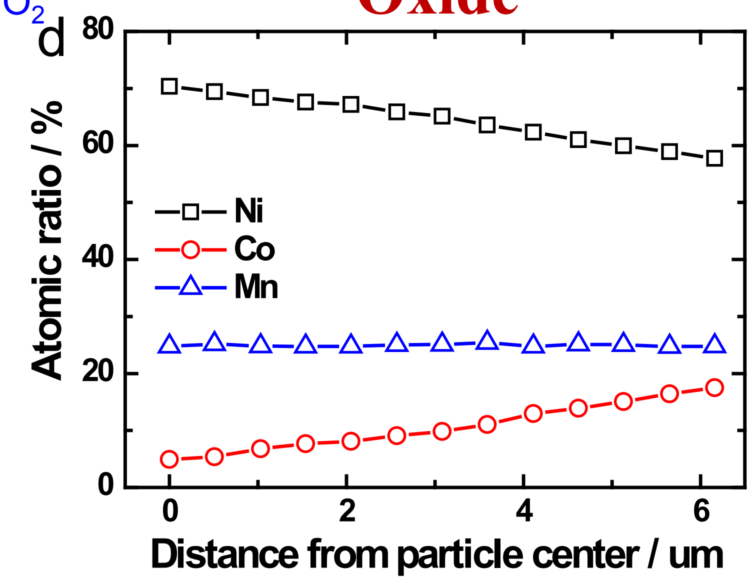


Precursor

$Li[Ni_{0.65}Co_{0.15}Mn_{0.25}]O_2$

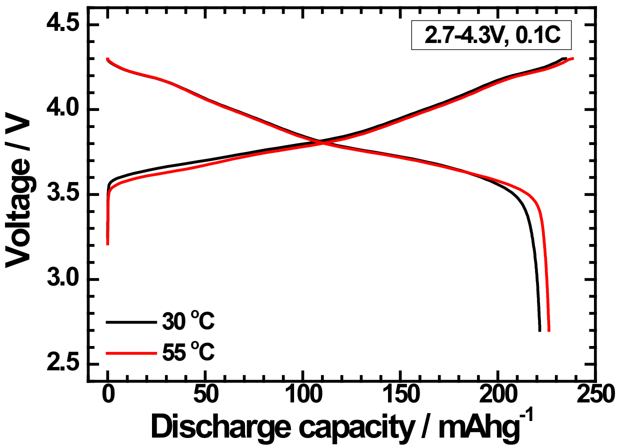
Oxide



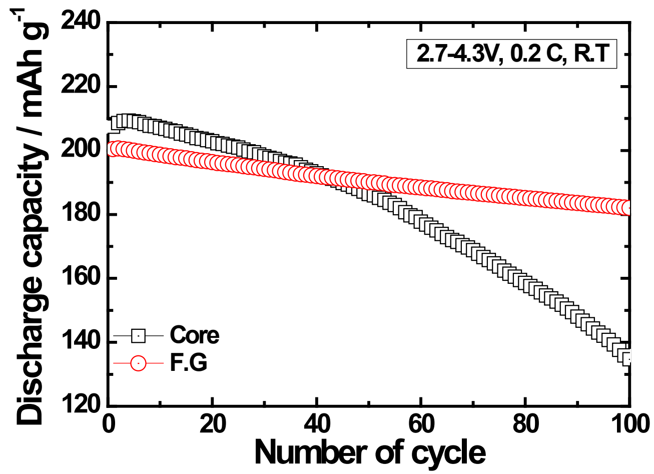


Tab density: 2.2g/cc

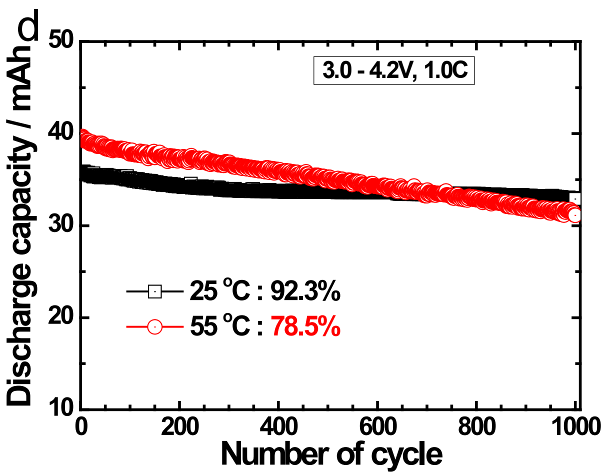
Electrochemical performance of FCG cathode



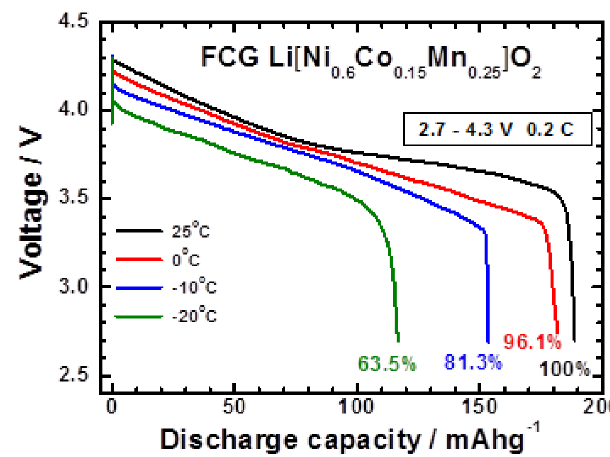
Initial cycling at 30°C and 55°C



cycling performance of core $LiNi_{0.6}Co_{0.15}Mn_{0.25}O_2$ at 30°C and 55°C

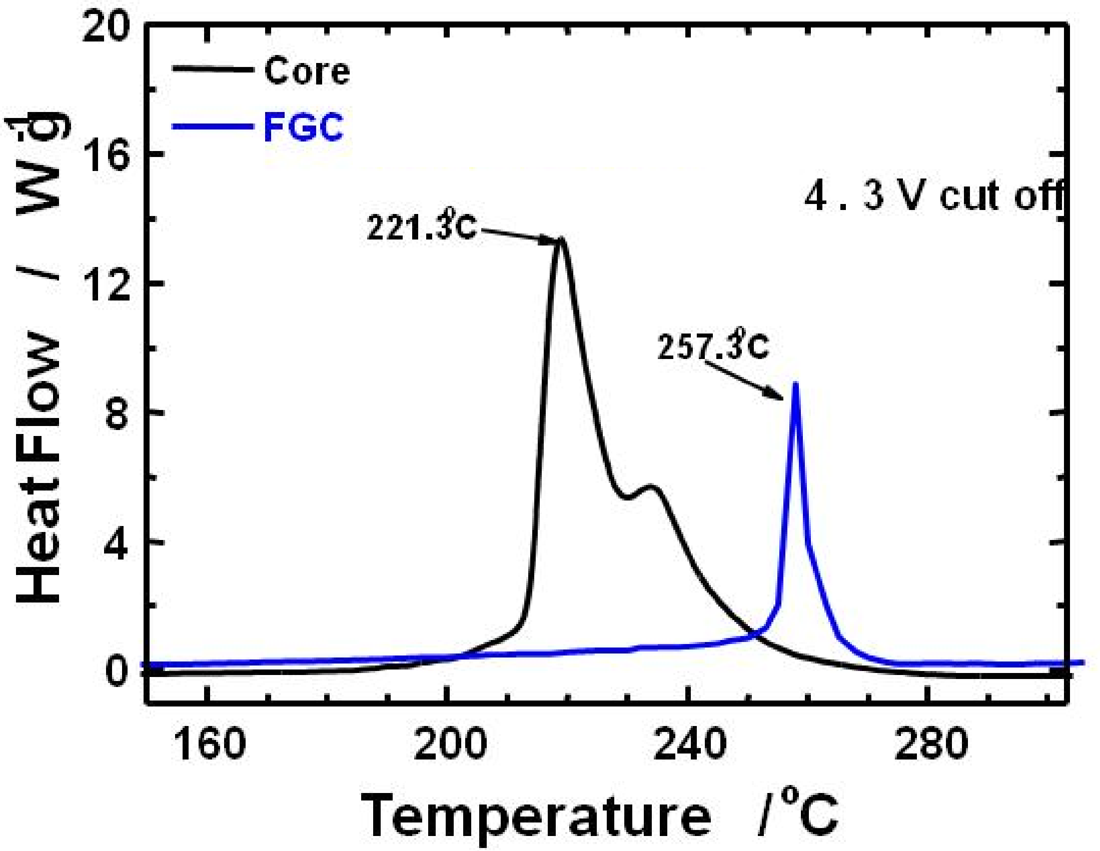


cycling performance of FCG at 30°C and 55°C



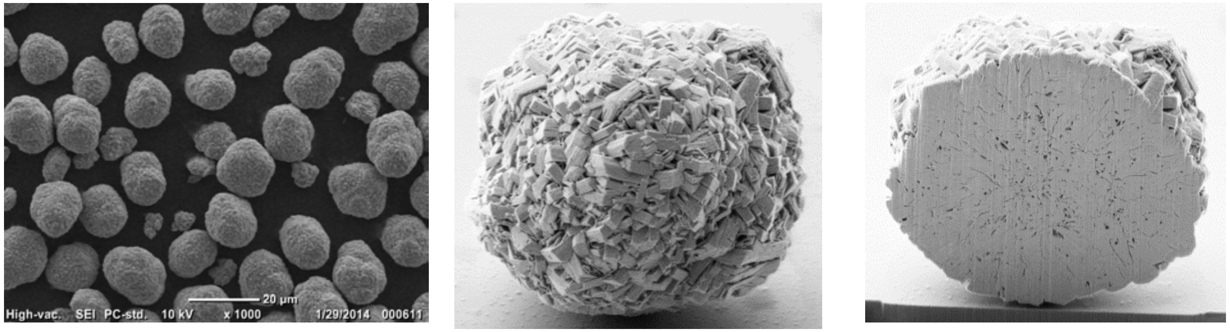
Low temperature performance of FCG

DSC of Charged FCG and $LiNi_{0.6}Co_{0.15}Mn_{0.25}O_2$ (Core) Having the Same Composition

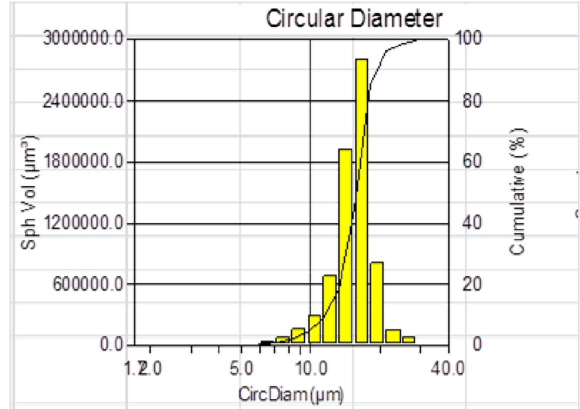


FCG average composition: $LiNi_{0.6}Co_{0.15}Mn_{0.25}O_2$

Characteristics of FCG Precursor Made From Hydroxide Process

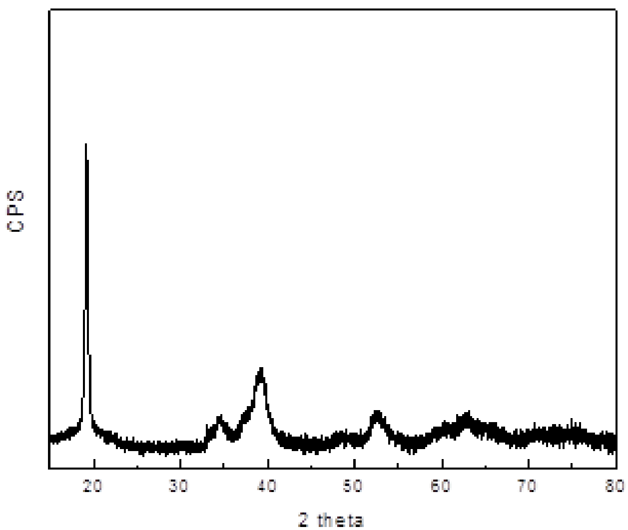


SEM of $Ni_{0.6}Co_{0.2}Mn_{0.2}(OH)_2$



Minimum:	1.71
Maximum:	30.28
Mean:	15.61
Std Dev.:	3.29
D10:	11.64
D50:	15.79

Particle distribution of $Ni_{0.6}Co_{0.2}Mn_{0.2}(OH)_2$



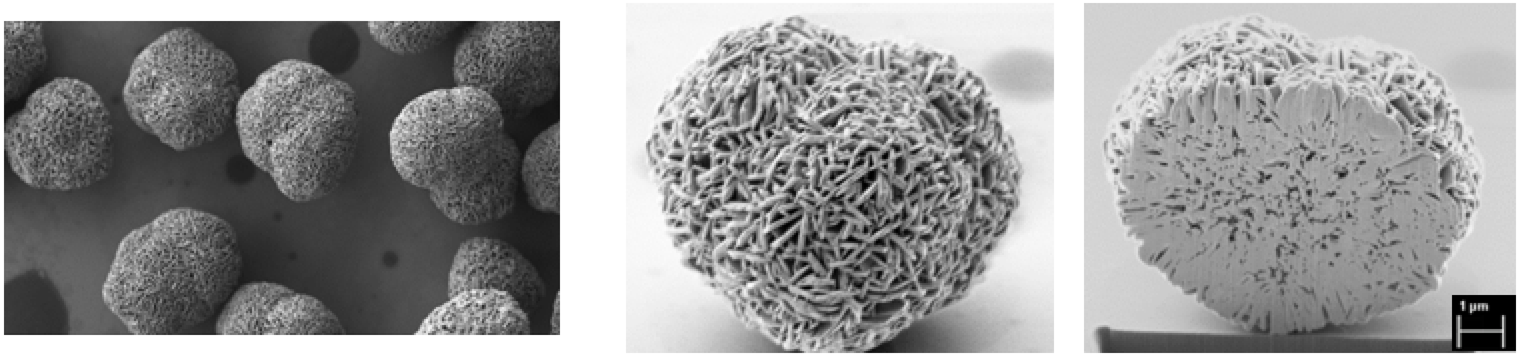
X-ray of $Ni_{0.6}Co_{0.2}Mn_{0.2}(OH)_2$

1. High Tap density=2.2 g/cc

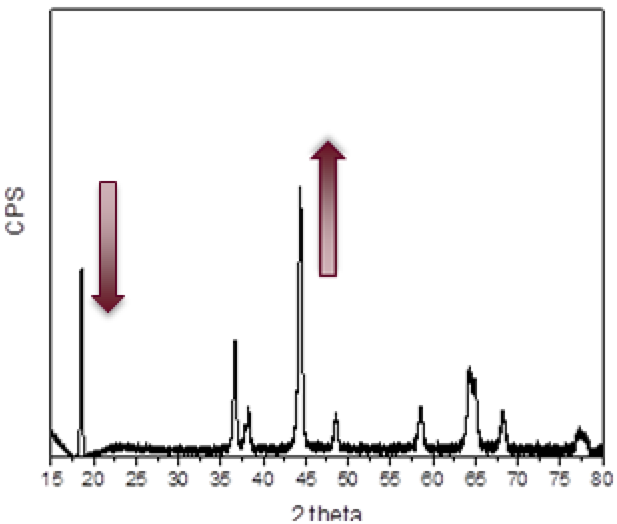
3. Good particle distribution: D50=11.64 um

4. Average composition is : $Ni_{0.6}Co_{0.2}Mn_{0.2}(OH)_2$
   outer is about: $Ni_{0.46}Co_{0.23}Mn_{0.41}(OH)_2$
   inner is about : $Ni_{0.8}Co_{0.1}Mn_{0.1}(OH)_2$

Characteristics of FCG Gradient Cathode Made From Hydroxide Process



SEM of $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$



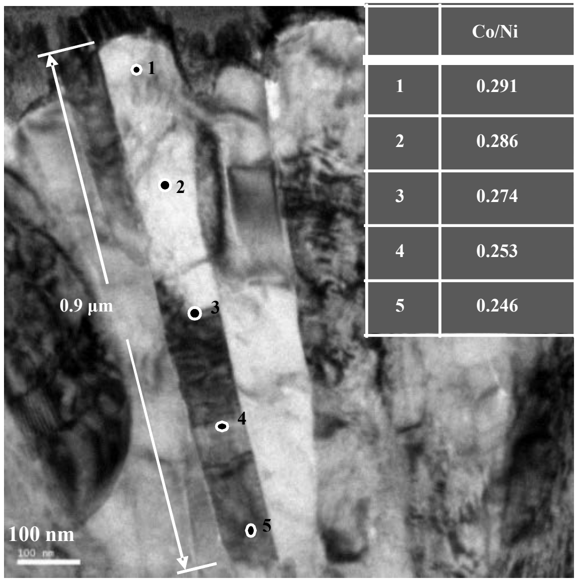
X-ray of $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$

1. High Tap density=2.7g/cc

3. particle distribution: D50=11.64 um (unchanged)

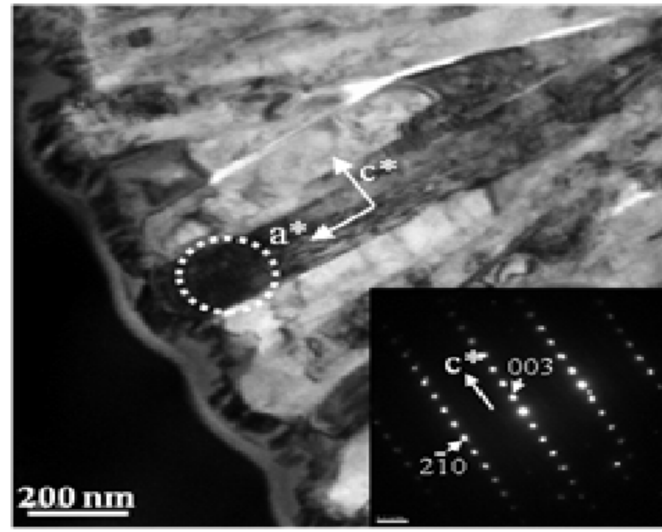
4. Average composition is : $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$
   outer is about: $LiNi_{0.46}Co_{0.23}Mn_{0.41}O_2$
   inner is about : $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$

TEM of Full Gradient Concentration Cathode made from Hydroxide Process



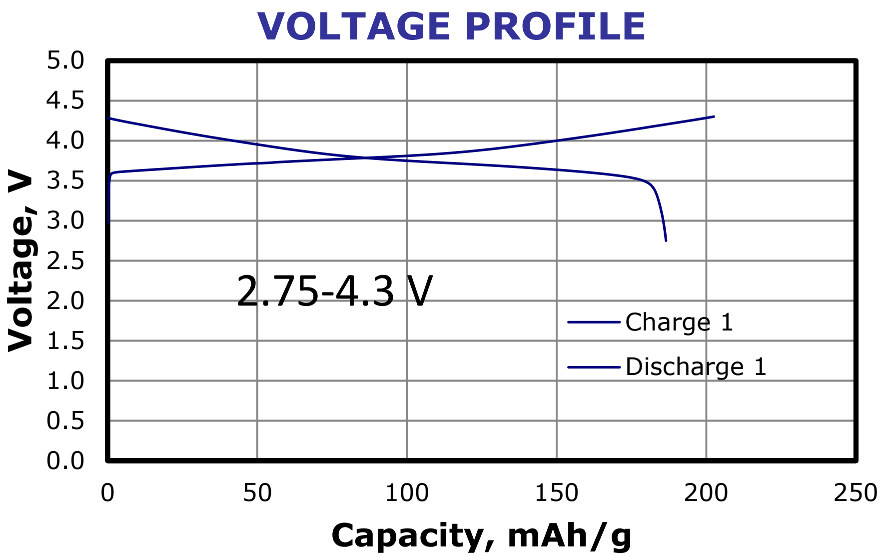
	Co/Ni
1	0.291
2	0.286
3	0.274
4	0.253
5	0.246

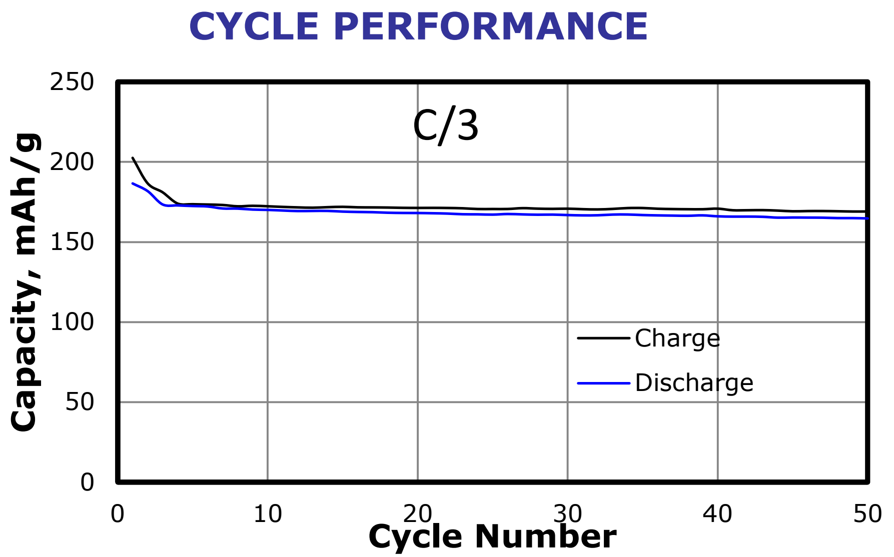
TEM image along with energy-dispersive X-ray spectroscopy (EDS) data for a single elongated CCG primary particle



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

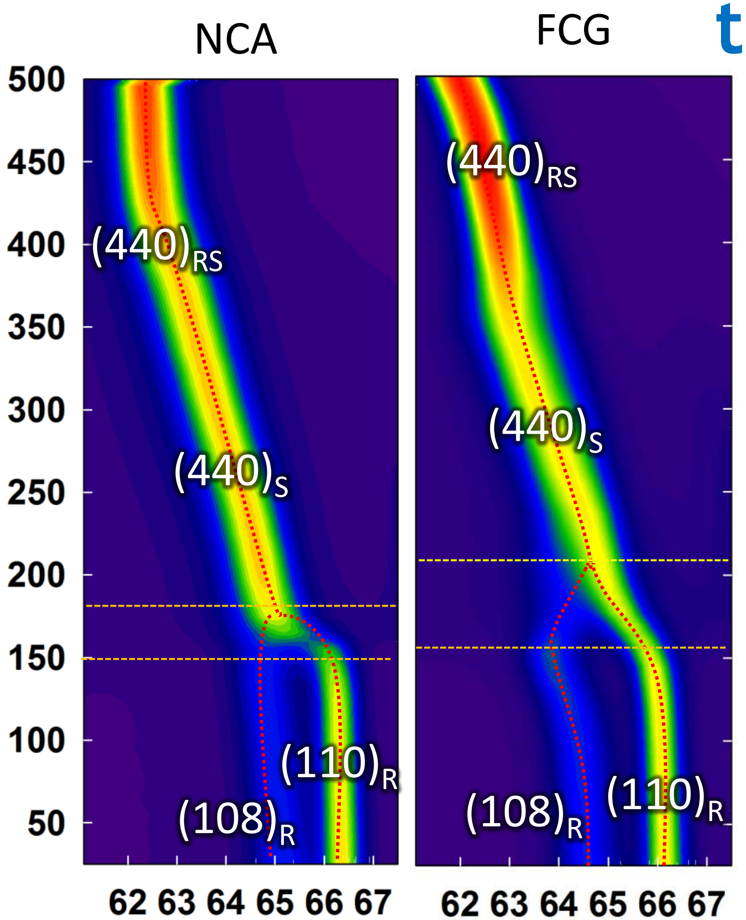




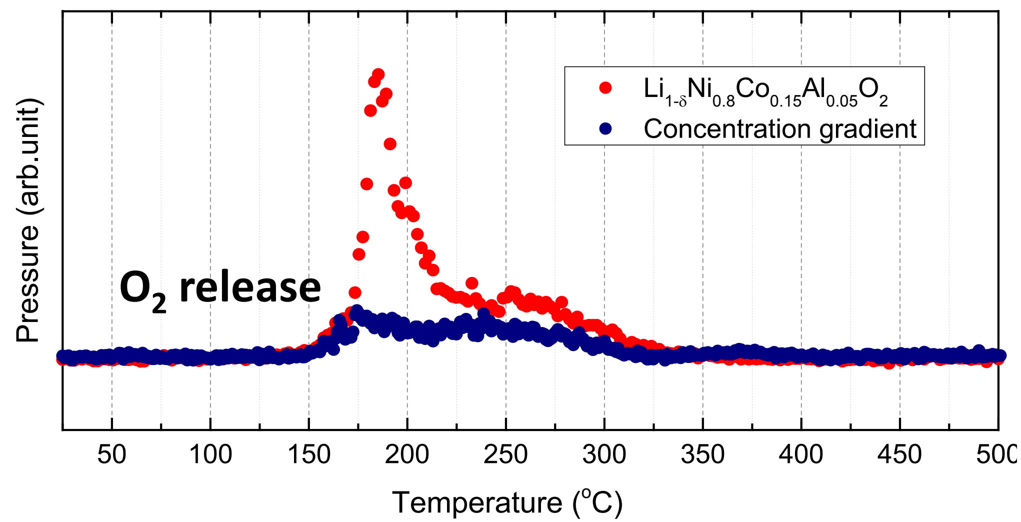
Initial cycle: Charge: 202.5 / Discharge: 186.6 mAh/g with 92.1% efficiency at C/5

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

Thermal stability of NCA and FCG charged to 4.5V using synchrotron soft X-ray at different temperatures



Synchrotron soft X-ray at different temperature.



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

The fist 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-$Sn_yCo_{1-x}Fe_xC$
- Demonstrate 1000 cycles of SiO-$Sn_yCo_{1-x}Fe_xC_z$ 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-$Sn_yCo_{1-x}Fe_xC_z$ anode .

Future work

- Optimize the ratio of $SiO\text{-}Sn_yCo_{1-x}Fe_xC$ and graphite to reduce irreversible loss
- Optimize $SiO\text{-}Sn_yCo_{1-x}Fe_xC$ electrode with conductive binder to improve cycle life
- Investigate the stability of SEI in $SiO\text{-}Sn_yCo_{1-x}Fe_xC$ 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 AlF_3 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% $Sn_{30}Co_{30}C_{40}$ 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,*

Chem. Mater. 2013, 25, 2109−2115

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

Adv. Funct. Mater. 2013, 23, 1028–1036