Fabricate PHEV Cells for Testing & Diagnostics

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May 14-18, 2012

DOE Vehicle Technologies Program Annual Merit Review and Peer Evaluation Meeting

Washington, D.C.

Project ID: ES030

Overview

Timeline

- Start: October 2008
- Finish: September 2014
- ~60% Complete

Budget

- Total project funding
  - 100% DOE
- $700K FY12 (ABR)
- $400K No Cost Extension

Barriers

- Development of a safe cost-effective PHEV battery with a 40 mile all electric range that meets or exceeds all performance goals
  - Validation tests of newly developed battery materials are needed in cell formats with at least 0.2 Ah in capacity before larger scale industrial commitment

Partners

- Sandia and Oak Ridge National Labs
- Johnson Controls and Saft
- Media Tech
- A-Pro
- EnerDel
- Howard Battery Consulting
- ConocoPhillips
- Toda America
- Solvay Solexis
- Kureha

Objectives

- Several new battery chemistries are being proposed for PHEV batteries that must be evaluated in cell formats that are larger than a few mAh in capacity.
- To speed the evaluation of novel battery materials, Argonne will fabricate in-house pouch and 18650 cells in its new Cell Fabrication Facility.

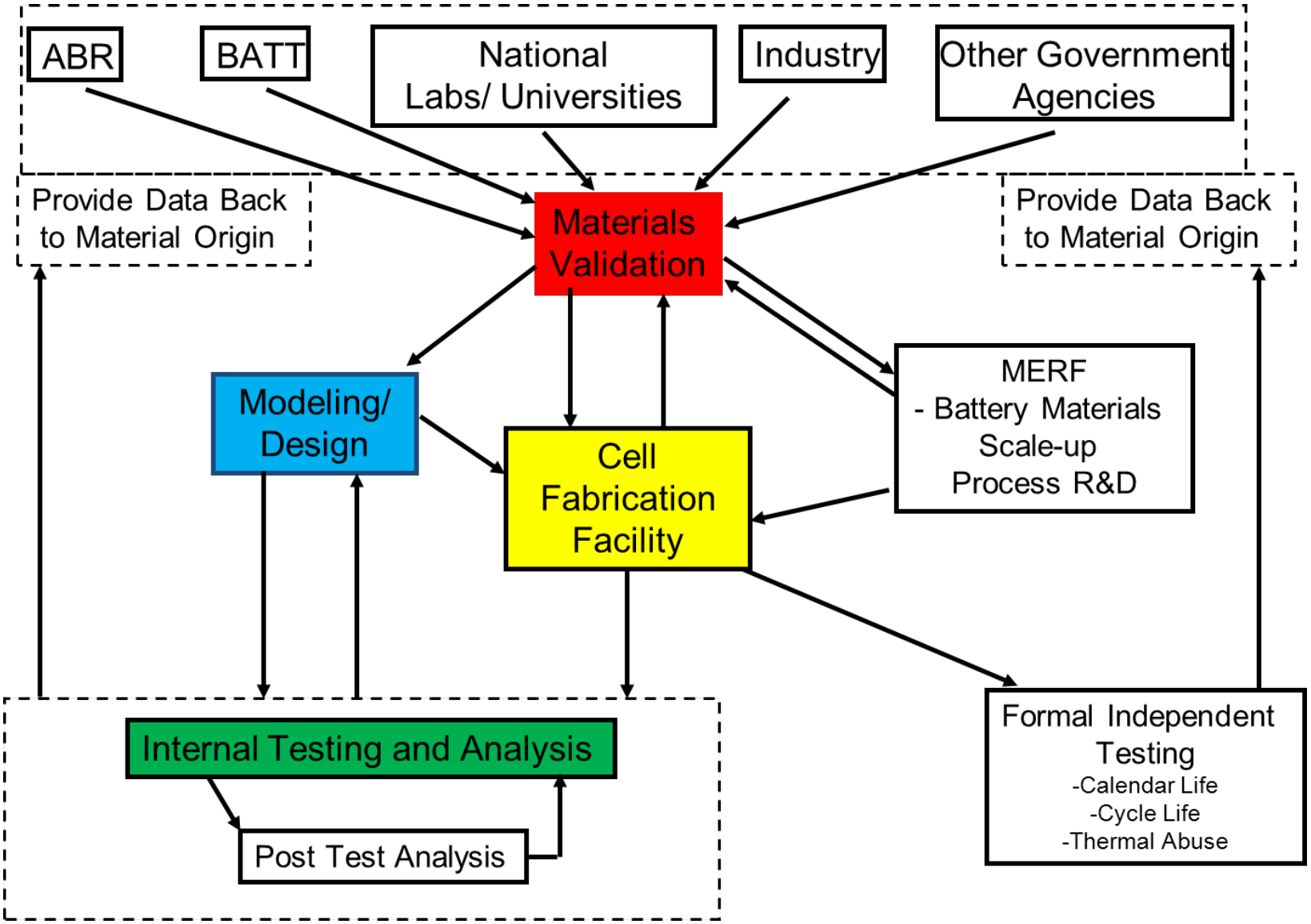
Milestones

All electrode and cell making equipment installed and approved for operation	Feb., 2011
First cell build completed using advanced materials	March, 2011
Completed cell formation/testing lab	June, 2011
Completed installation of high shear planetary mixer (Ross)	October, 2011
Received first scaled-up R&D cathode material from MERF	March, 2012

Approach

- Promising new exploratory materials are often developed in small coin cells, which may not scale up well in large PHEV battery designs. For this reason, industrially relevant cell formats such as pouch cells and 18650's are used for proofing of new materials in the capacity range of 0.2 to 2 Ah in Argonne's new Cell Fabrication Facility (CFF).
- All new materials are evaluated in the Materials Validation effort to obtain material performance data for scaled-up cell design and to prioritize efforts on materials of value to DOE's energy storage programs.
- Partnerships with fellow cell fabrication national labs (Sandia and Oak Ridge) are established to maximize the impact of collective efforts.
- Close working relationships are maintained with the Diagnostic Effort and Argonne's new Post-test Facility during electrode fabrication and end-of-life analysis of cycled cells to elucidate failure mechanisms.
- Collaborations with Argonne's Materials Engineering Research Facility (MERF) are created to aid in scale up of R&D materials.

Cell Fabrication Facility Flow Chart



Argonne's Cell Fabrication Facility Fully Operational

- All equipment installed and training provided by vendor's engineers
- Modifications were made to several pieces of equipment to enhance safety, with final approval to operate all equipment granted in February, 2011
- Argonne now has the capability to coat and hot-roll press electrodes, and to make xx3450 pouch cells and 18650 cells in a dry room environment

ConocoPhillips A12 Graphite and Toda HE5050 NMC Selected for First Cell Build after Validation by ABR

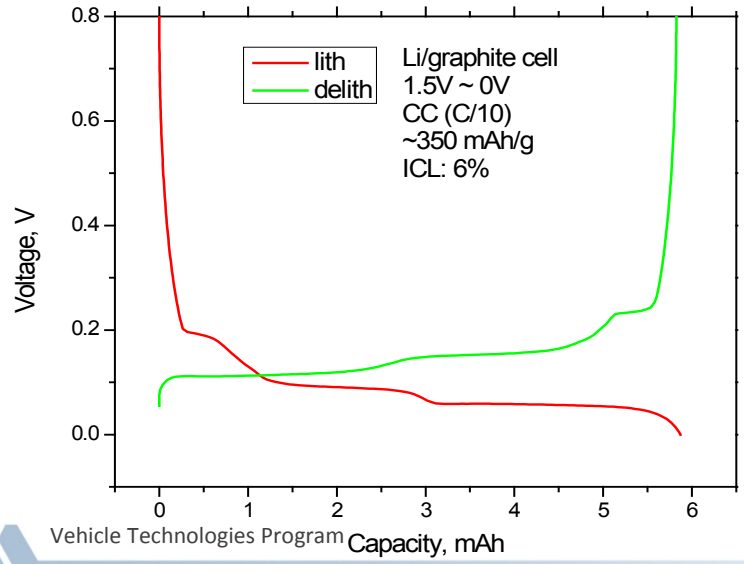
CPreme® A12 is designed for high capacity, which uses a nominal 12-micron, natural graphite core coated with ConocoPhillips proprietary surface treatment and processed for optimum capacity.

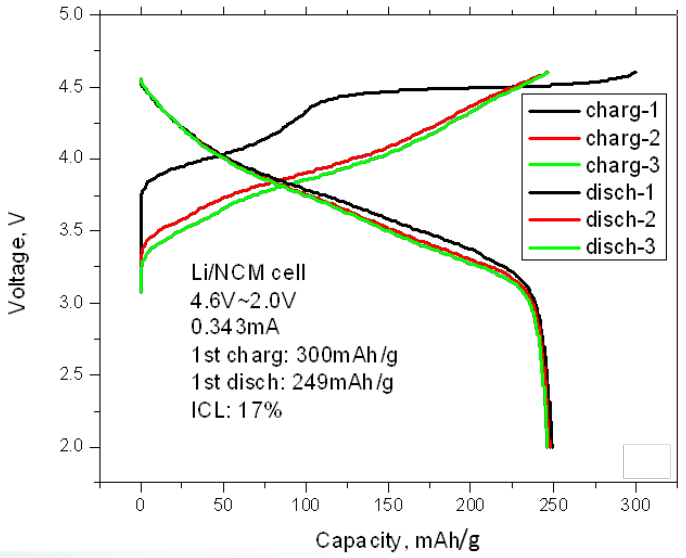
Product	A12
Capacity* mAh/g	360
Efficiency*	94%
BET Surface Area* m2/g	2 - 4
D50* (um)	9 - 12
Optimum Use	Energy Cell
Automotive Application	EV/PHEV

$Li_{1.2}Ni_{0.15}Co_{0.10}Mn_{0.55}O_2$

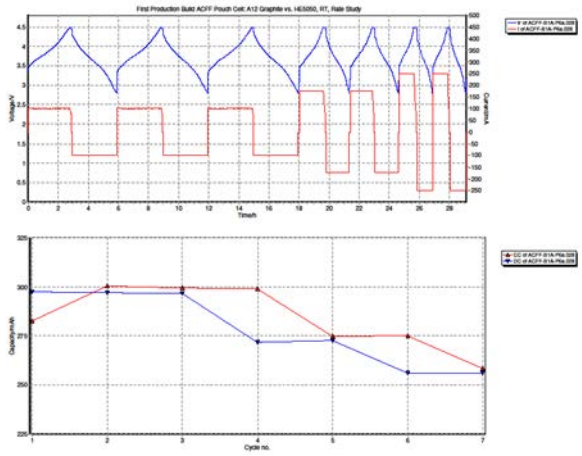
$(0.49Li_2MnO_3 \bullet 0.51LiNi_{0.37}Co_{0.24}Mn_{0.39}O_2)$

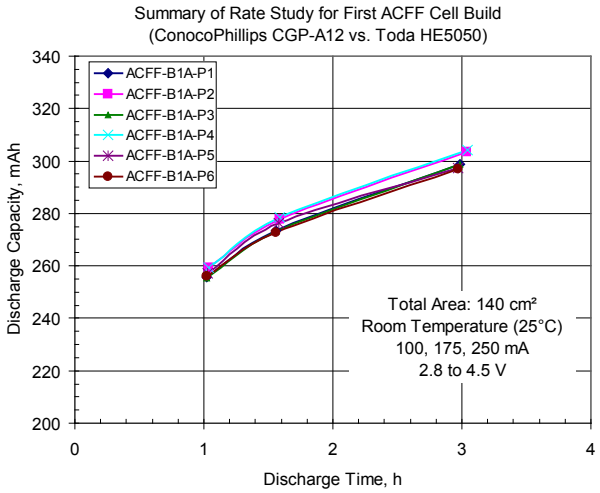
D50	4.9
Tap	1.05
BET	2.63
1st	
charge	320
discharge	270
ICL	13.7

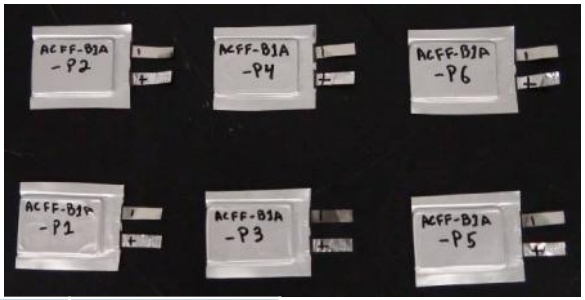




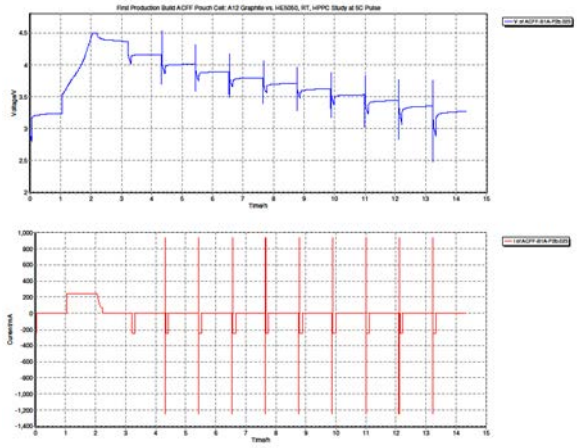
First Cell Build Characterization Cycles

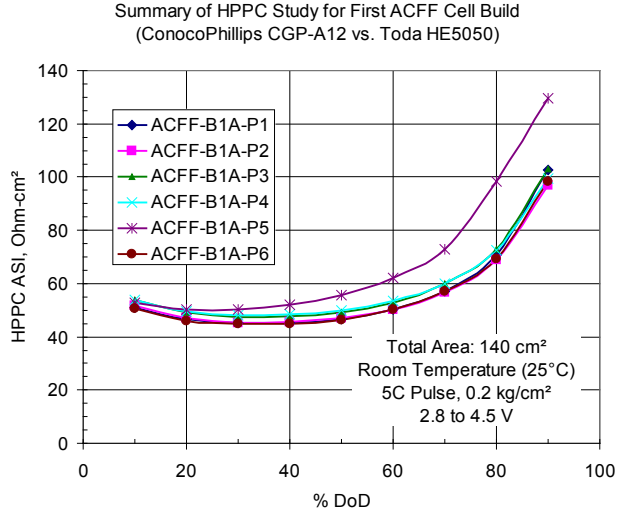


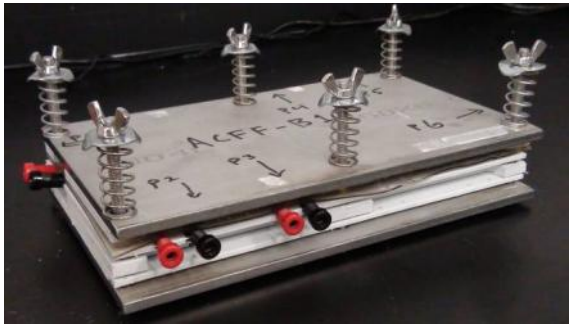




Rate	Capacity – mAh/g
C	146
C/2	163
C/3	172
C/5	183







Cells Delivered for Independent Verification to EADL and Post Test Analysis

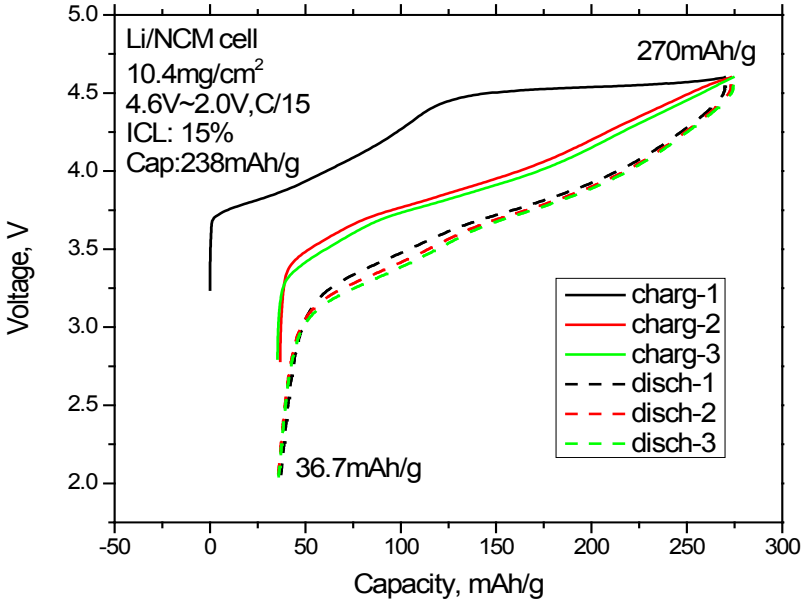
One outlier (P5) was removed from further testing.

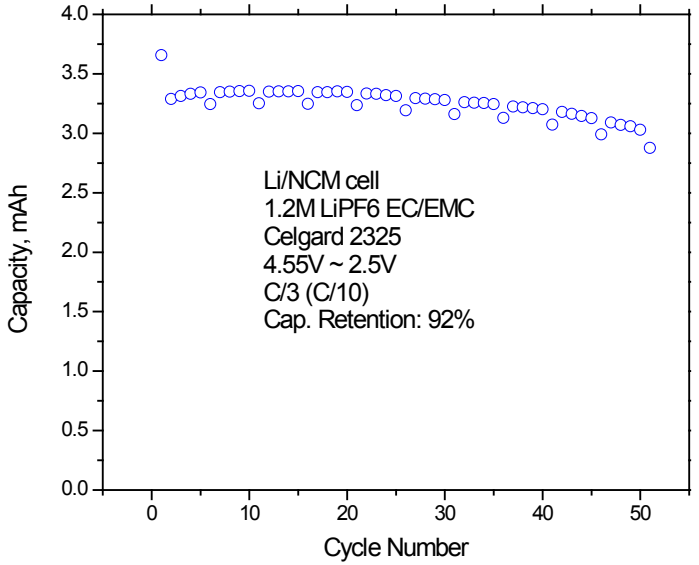
Advanced R&D Cathode for Second Cell Build

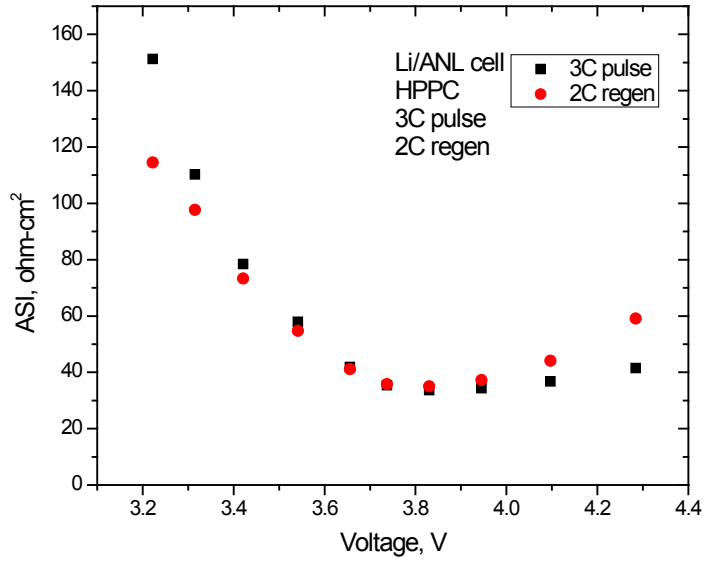
$Li_{1.2}Ni_{0.3}Mn_{0.6}O_{2.1}$ (ABR-HW10101911C)

Contains no Cobalt
Scaled up at MERF

Half cell results of R&D material batch - submitted for Validation (ABR-W. Lu) before cell build







Second Cell Build Cathode Formulation and Process

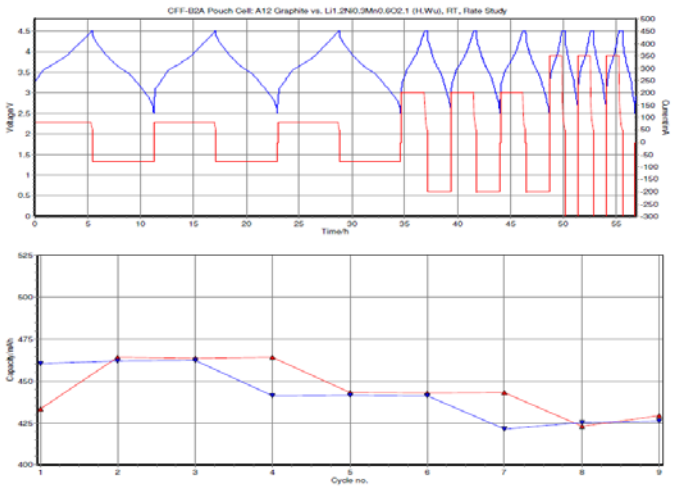
- Cathode Formulation (Dry Composition)
  - 84 wt% $Li_{1.2}$ $Ni_{0.3}$ $Mn_{0.6}$ $O_{2.1}$
    - ABR-HW10101911C
  - 4 wt% Timcal SFG-6 Graphite
  - 4 wt% Timcal Super P®
  - 8 wt% Solvay 5130 PVDF Binder

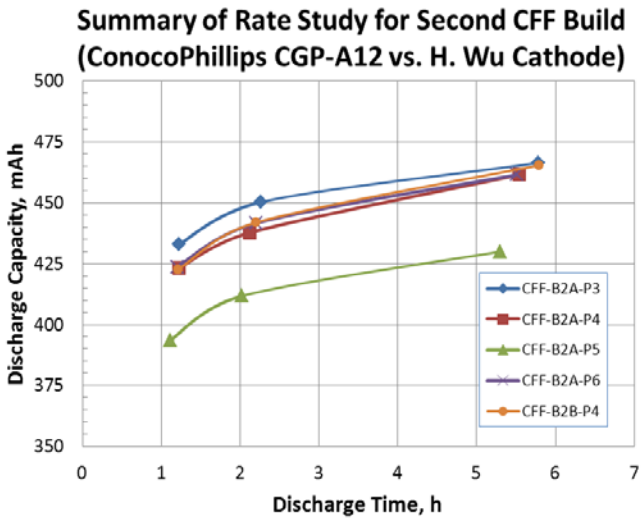
- Cathode Electrode Properties
  - Aluminum Foil Thickness: 20 microns
  - Total Electrode Thickness: ~86 microns
  - Cathode Coating Thickness: ~66 microns
  - Cathode Coating: 15.15 mg/cm²
    (Total Material wt; No Foil)
  - Capacity: 2.75 - 3.07 mAh/cm²
  - Porosity Target: ~36%

- n:p Ratio: 1.17-1.25
- CFF-B2A – outside layers single side coated
- CFF-B2B – outside layers double side coated

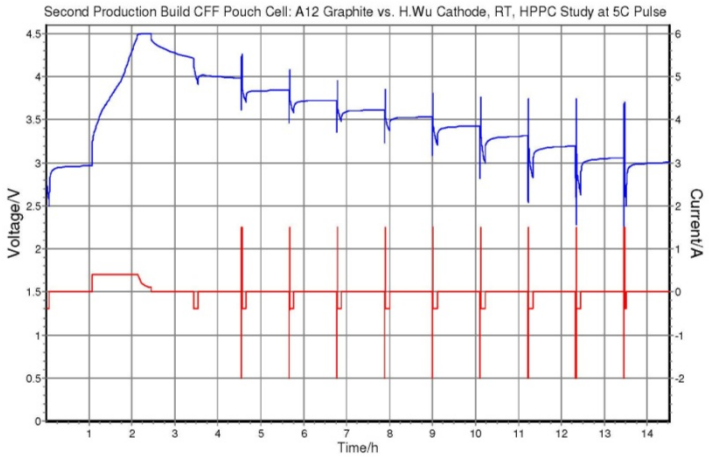
- Cathode Process
  - Mixing
    - 5130 + Extra NMP – Vibratory Mix 10 min
    - Add Super P® and SFG-6 – Vibratory Mix 10 min
    - Add ½ Li1.2 Ni0.3 Mn0.6 O2.1– Vibratory Mix 10 min
    - Add ½ Li1.2 Ni0.3 Mn0.6 O2.1 – Vibratory Mix 10 min
    - Ball Mill Mix for 1 hour
    - Thinky Mix for 3 min
  - De-Gassing
    - 3 mins in vacuum oven
  - Coating
    - 0.5 meters per min coating speed
    - Drying Zone 1 = 85 °C
    - Drying Zone 2 = 115 °C
  - Hot Rolling/ Calendering
    - Rolling Temperature = 80 °C
    - Rolling Speed = 0.5 meter per min

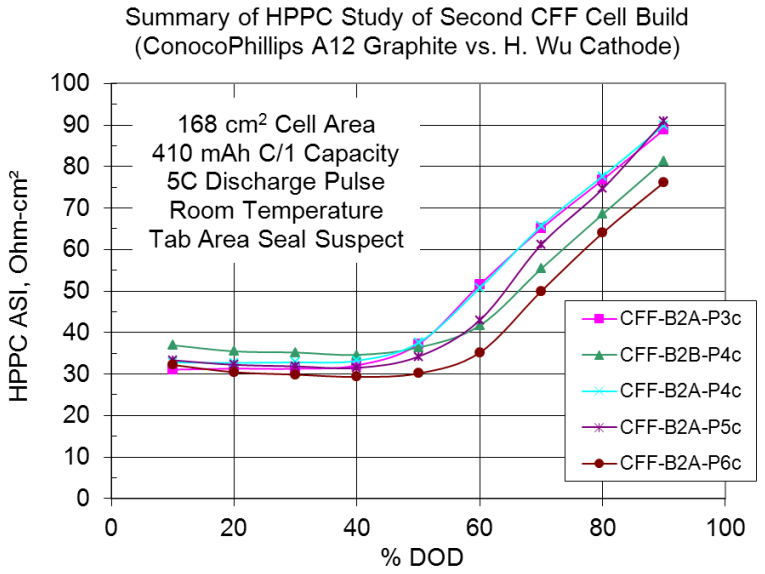
Second Cell Build Characterization Cycles





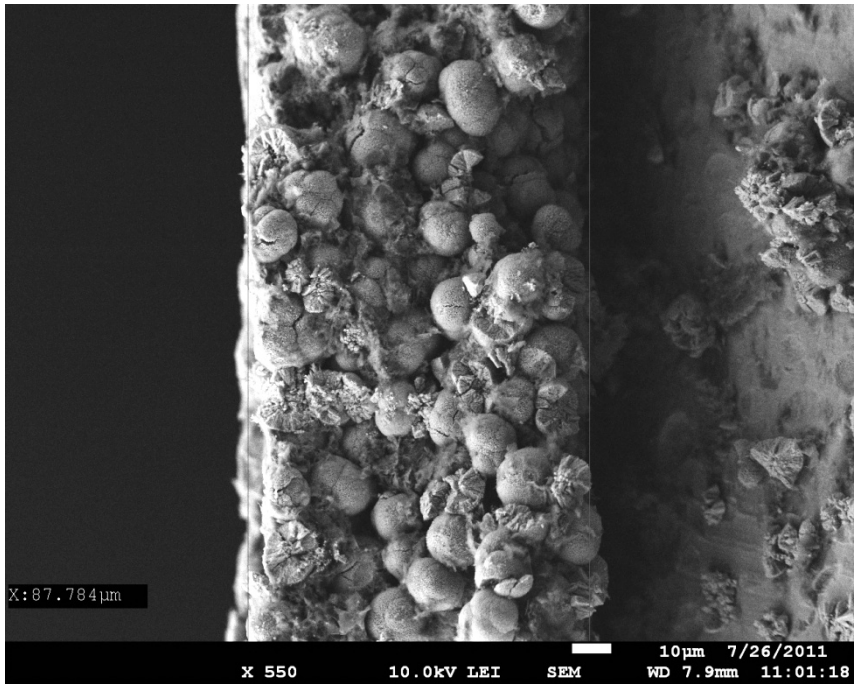
Rate	Capacity – mAh/g
C	196
C/2	205
C/3	209
C/5	217.5



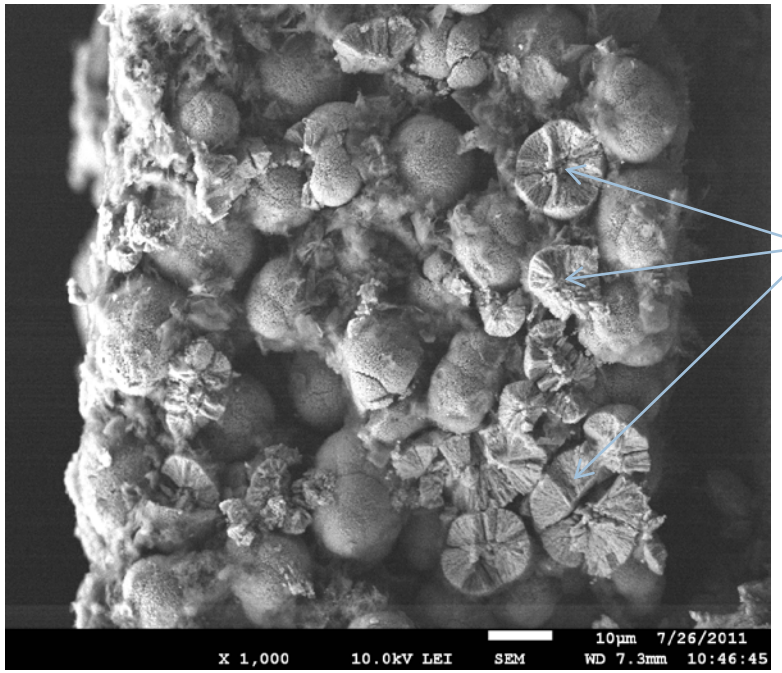


$Li_{1.2}Ni_{0.3}Mn_{0.6}O_{2.1}$ Electrode in Second Cell Build

Cathode powder made in R&D Lab at Argonne



Optimization is needed to increase the strength of the particles to prevent cracking during calendering.



Fractured particles

New Ross Mixer and Formation/Cycling Lab Enhance CFF's Capabilities

2-L High-shear planetary mixer.

Three MACCOR cyclers with 96 multi-range channels each. Exhaust ventilation to ovens provided in case of thermal events.

Third Cell Build Cathode Formulation and Process

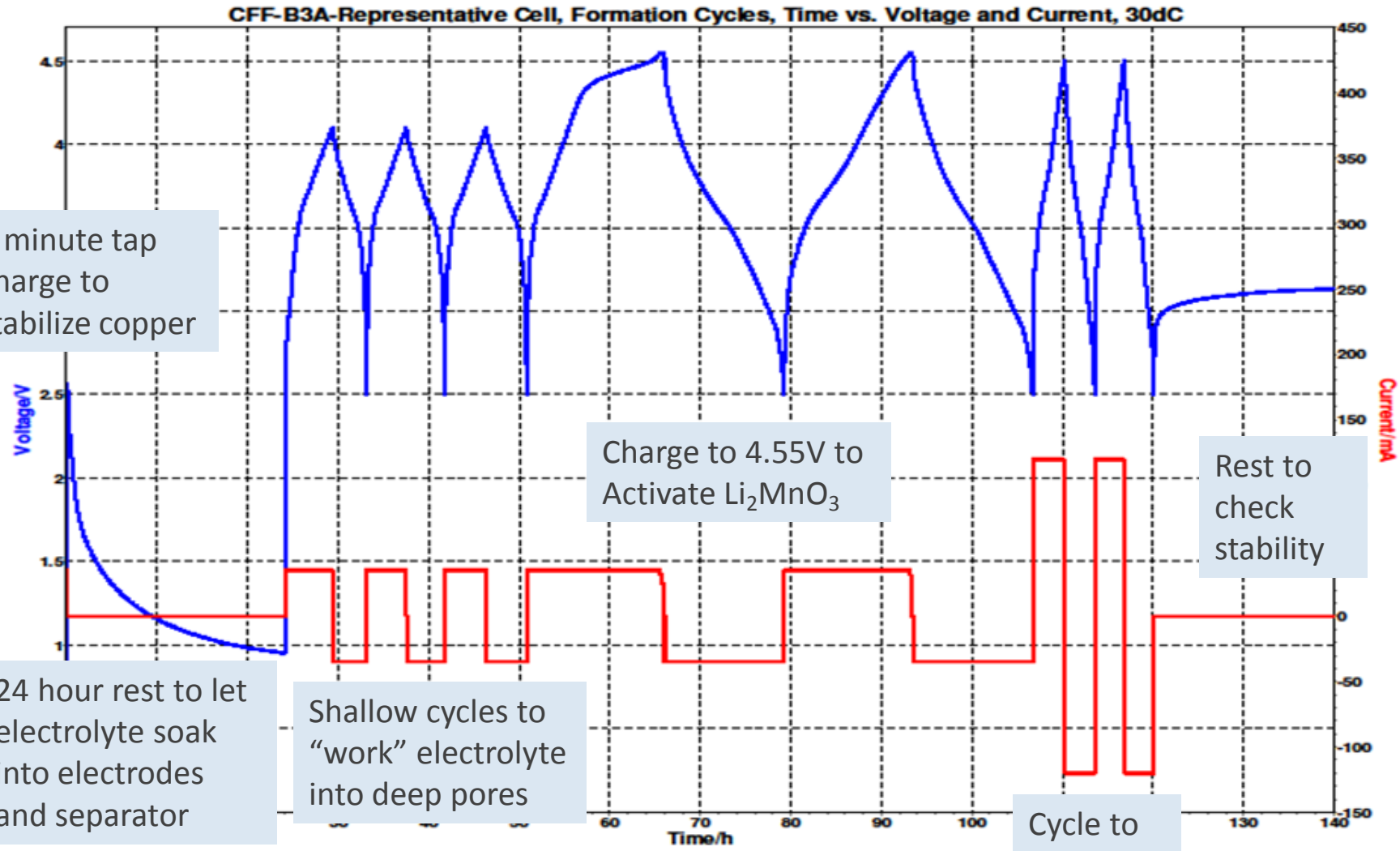
- Cathode Formulation (Dry Composition)
  - 84 wt% $Li_{1.2}$ $Ni_{0.3}$ $Mn_{0.6}$ $O_{2.1}$
    - ABR-HW101217-Blended
  - 4 wt% Timcal SFG-6 Graphite
  - 4 wt% Timcal Super P®
  - 8 wt% Solvay 5130 PVDF Binder

- Cathode Electrode Properties (Single-sided)
  - Aluminum Foil Thickness: 20 microns
  - Total Electrode Thickness: ~93 microns
  - Cathode Coating Thickness: ~73 microns
  - Cathode Coating: 14.8 mg/cm²
    (Total Material wt; No Foil)
  - Capacity: 2.69 - 2.95 mAh/cm²
  - Porosity: 43%

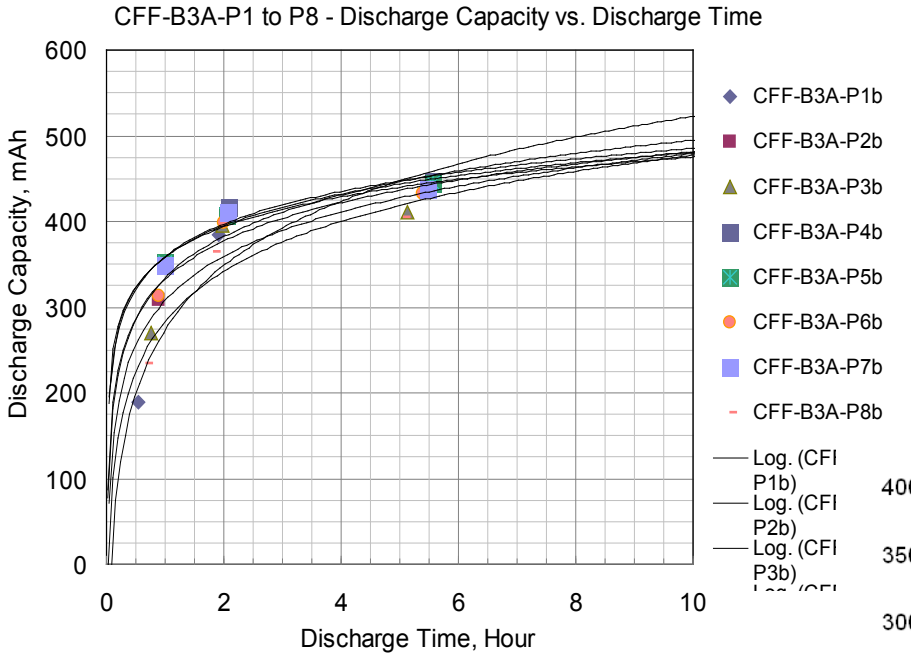
- n:p Ratio: 1.13 to 1.18
- CFF-B3A – outside layers single side coated
- CFF-B3B – outside layers double side coated

- Cathode Process
  - Mixing with Ross Mixer (at 25 mm Hg)
    - 5130 + Extra NMP – Ross Mix 10 min
      - Planetary 45 rpm/Shear 2000 rpm
    - Add Super P® – Ross Mix 10 min
      - Planetary 45 rpm/Shear 2000 rpm
    - Add SFG-6 – Ross Mix 10 min
      - Planetary 45 rpm/Shear 2000 rpm
    - Add ½ $Li_{1.2}$ $Ni_{0.3}$ $Mn_{0.6}$ $O_{2.1}$– Ross Mix 10 min
      - Planetary 45 rpm/Shear 2000 rpm
    - Add ½ $Li_{1.2}$ $Ni_{0.3}$ $Mn_{0.6}$ $O_{2.1}$ – Ross Mix 10 min
      - Planetary 45 rpm/Shear 2000 rpm
    - Ross Mix for 2 hour
      - Planetary 25 rpm/Shear 0 rpm
  - Coating
    - 0.5 meters per min coating speed
    - Drying Zone 1 = 83 °C
    - Drying Zone 2 = 110 °C
  - Hot Rolling/ Calendering
    - Rolling Temperature = 80 °C
    - Rolling Speed = 0.5 meter per min

Modified Cell Formation to Enhance Electrolyte Wetting



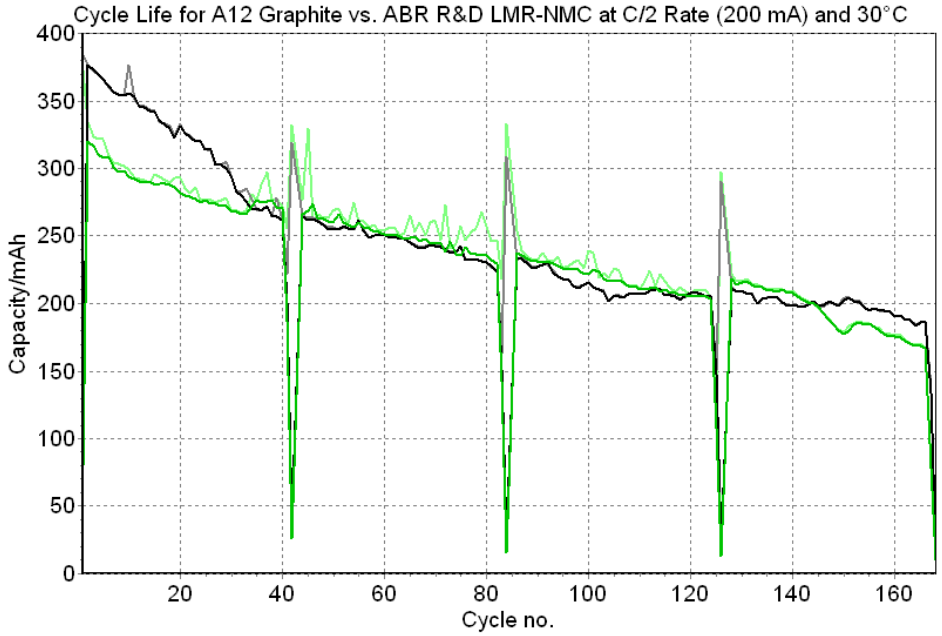
Third Cell Build with R&D Cathode Showed Problems with Coulombic Efficiency



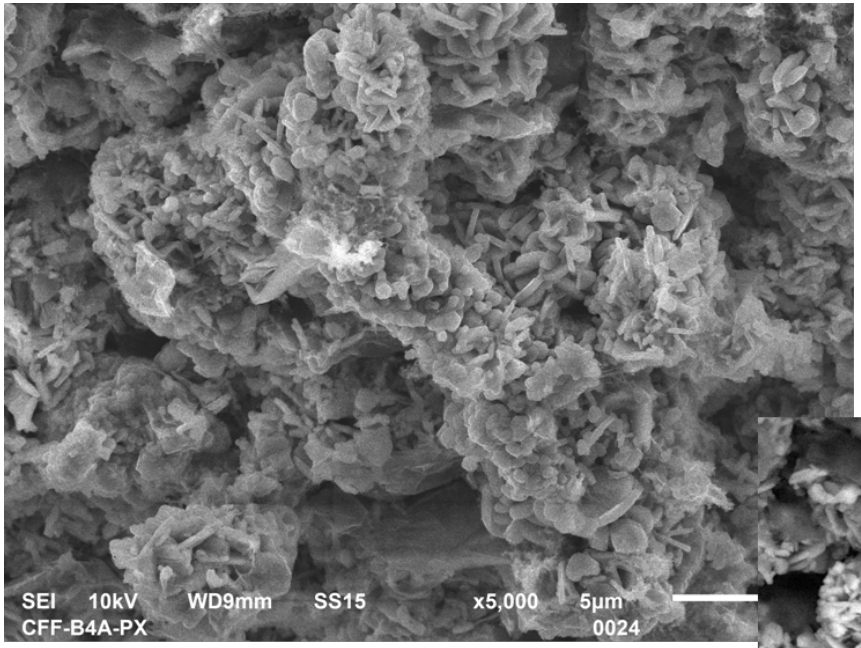
Rate	Capacity – mAh/g
C	150
C/2	193
C/3	203
C/5	215

This R&D cathode batch also had problems with particles cracking during calendering, which may be the cause of “noisy” cycling.

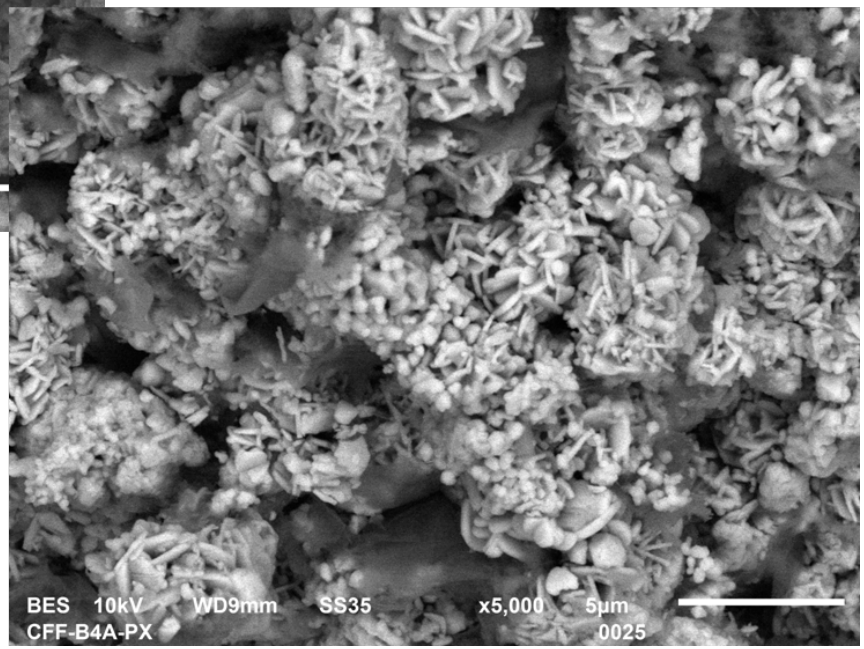
Discharge and Charge capacities for two representative cells.



Fourth Cell Build is a More Skilled Repeat of First Cell Build



The Toda HE5050 is made by a process that yields rosettes instead of spheres.



No signs of particle cracking during calendering.

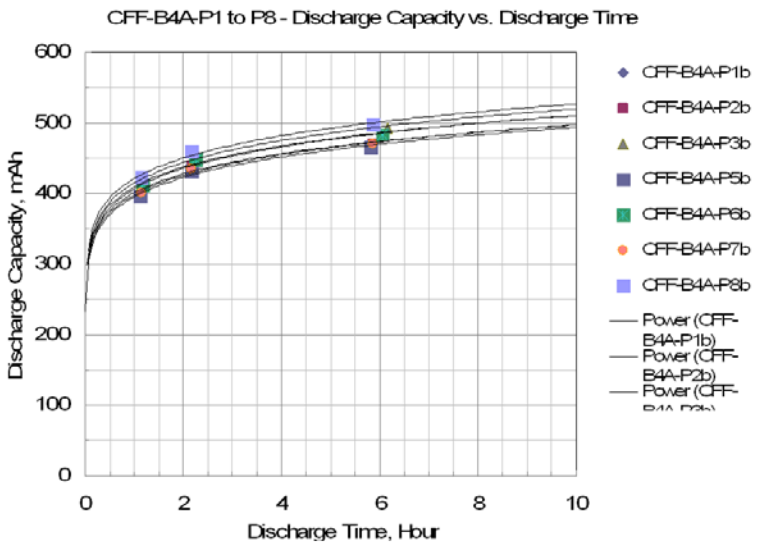
Photos from Post Test Facility.

Fourth Cell Build Cathode Formulation and Process

- Cathode Formulation (Dry Composition)
  - 86 wt% Toda HE5050
  - 4 wt% Timcal SFG-6 Graphite
  - 2 wt% Timcal Super P®
  - 8 wt% Solvay 5130 PVDF Binder

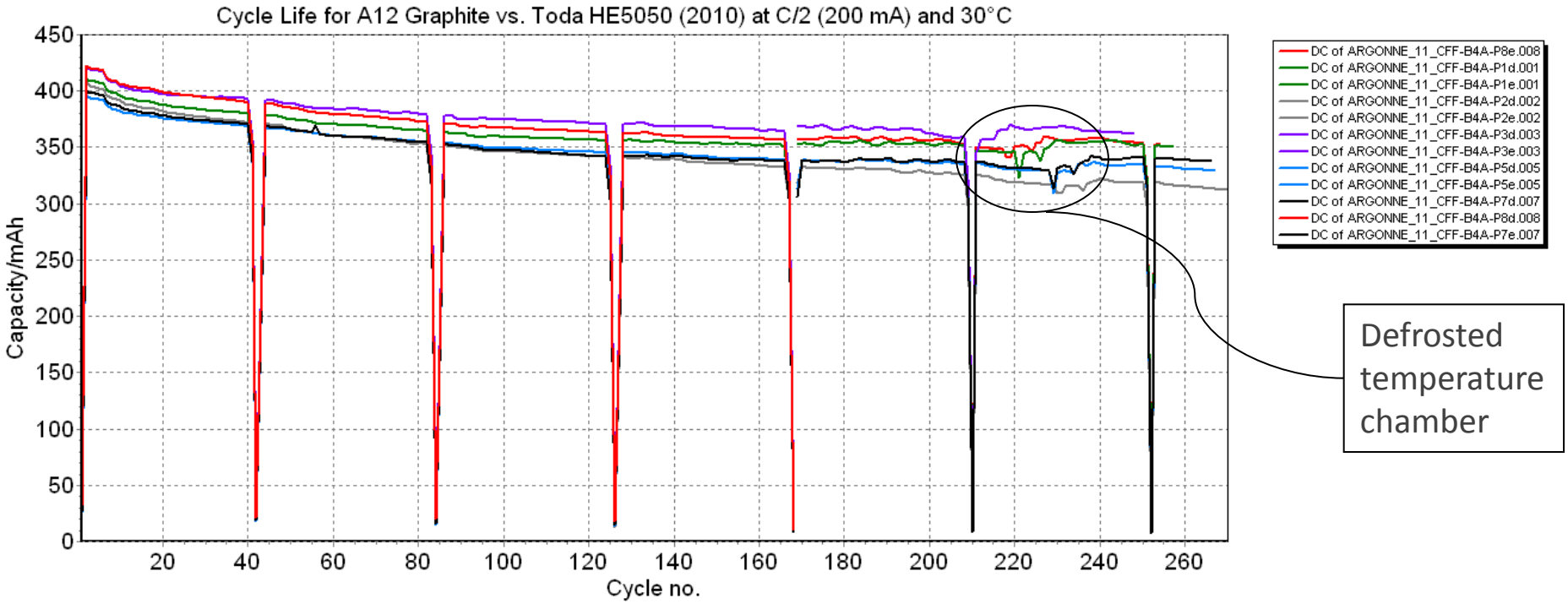
- Cathode Electrode Properties (Single-sided)
  - Aluminum Foil Thickness: 20 microns
  - Total Electrode Thickness: ~83 microns
  - Cathode Coating Thickness: ~63 microns
  - Cathode Coating: 14.3 mg/cm²
    (Total Material wt; No Foil)
  - Capacity: 2.58 - 3.06 mAh/cm²
  - Porosity: 38%

- n:p Ratio: 1.02 to 1.15



Rate	Capacity – mAh/g
C	198
C/2	213
C/3	217
C/5	227

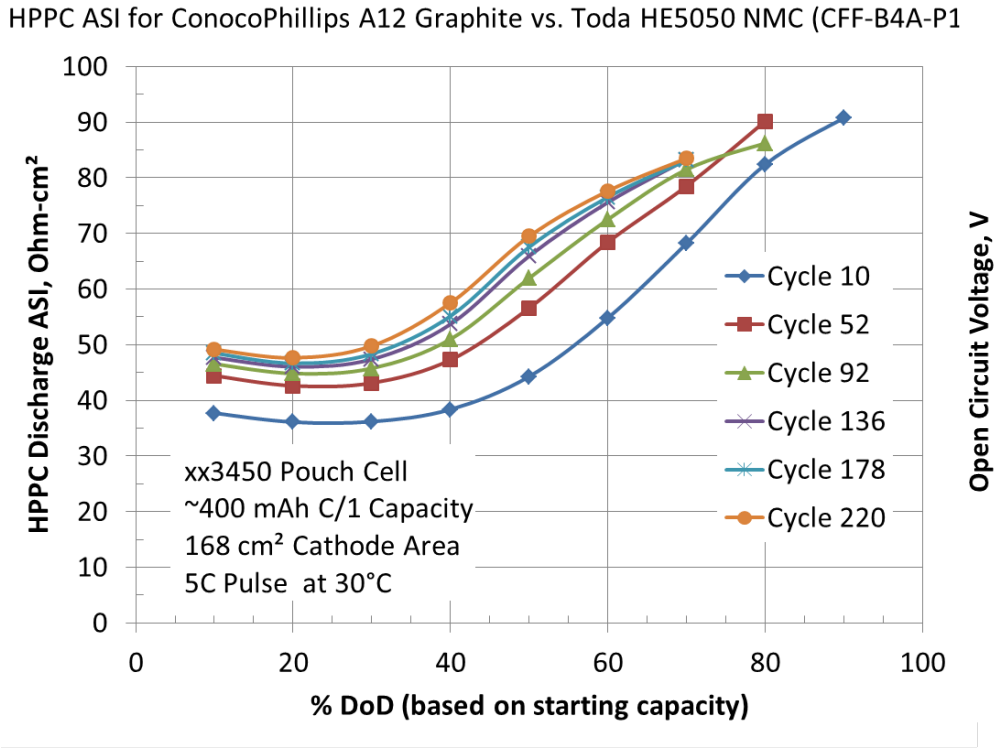
Cycle Life for Fourth Cell Build
(No Additive, C/2 Rate, 2.5 to 4.4 V)

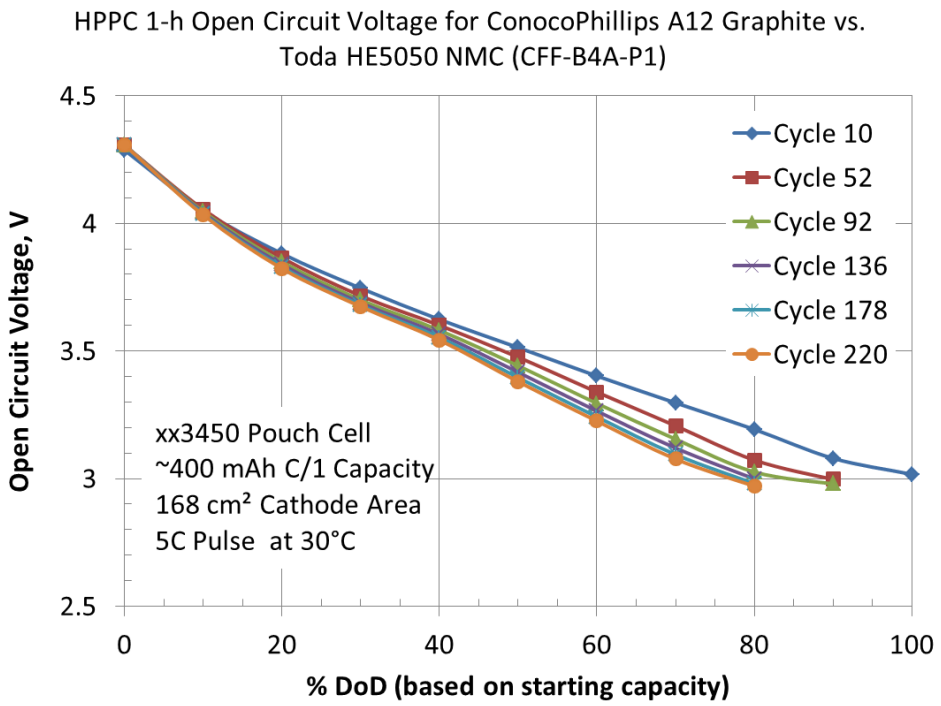


Based on Diagnostic results, upper voltage was limited to 4.4 V to enhance life.

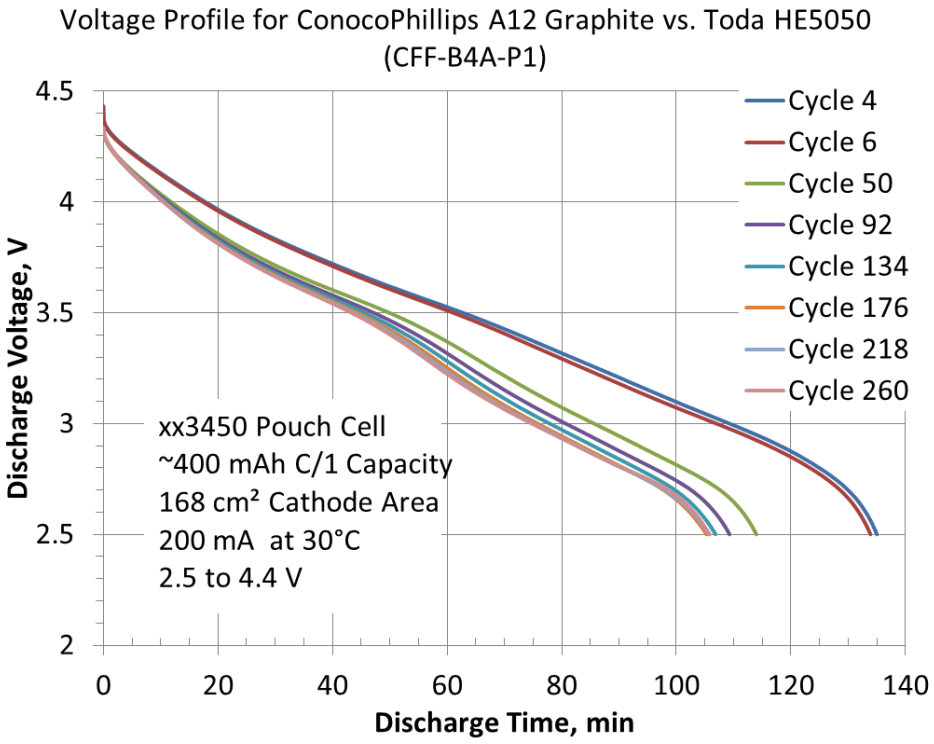
No electrolyte additives were used; will include additives in future cells.

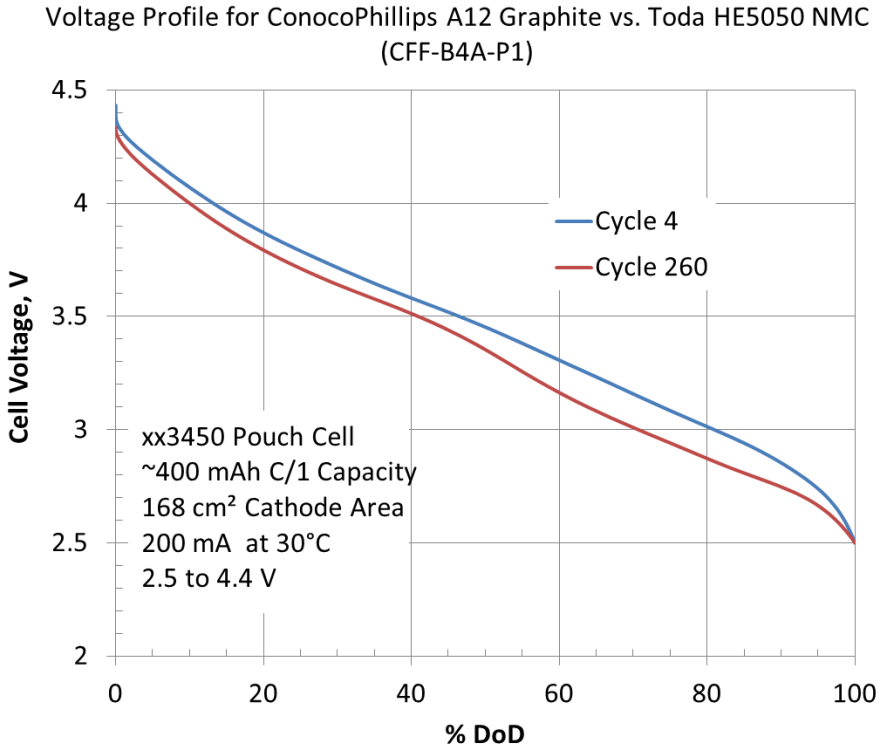
HPPC Analysis Shows Gradual Rise in Impedance (after 50 cycles) and Some Voltage Fade





Cycle Life Analysis Shows Modest Signs of Capacity Loss and Voltage Fade after 50 cycles





On-going and Future Cell Builds (Future Plans)

Cathodes:

- ABR Cathode from MERF
  - $Li_{1.25}\ Ni_{0.3}\ Mn_{0.62}\ O_2$
  - Received 1 kg (of 10 kg batch)
  - 20 L reactor can make 1 kg/h
- Reformulated Toda HE5050
- 5 Volt Spinel from NEI
  - For high voltage electrolyte studies
- Toda NCM 523
  - Baseline Electrode Build for Argonne, SNL, ORNL

Anodes:

- A12 Graphite from ConocoPhillips
- Silicon (still being sourced)

Binders:

- Polyamide/imide
- Cellulose
- Brown algae
- Solvent-less binders

Continue collaborations with other facilities and projects with an emphasis on solving Voltage Fade problem.

Gain more experience making 18650 cells.

Collaborations with Other Institutions

- The CFF maintains an Electrode Library of various electrodes that outside organizations may request samples. To date, electrodes were sent to Wildcat Discovery Technologies, Army Research Lab, JPL, UIUC, ORNL, LBNL, INL, NREL, and BNL.
- Argonne's CFF personnel coordinate their efforts with fellow electrode and cell making national labs (Sandia and Oak Ridge), and with Materials Validation, Diagnostics, Post Test Facility, and MERF (scale-up).
- While Argonne's CFF was being installed, outside companies were contracted to make electrodes and cells for several ABR Program tasks. These companies include Johnson Controls, Saft, Leyden Energy (Mobius Power), and EnerDel. Great advice was also provided by several of these companies in setting up the facility and making electrodes and cells.
- Rick Howard of Howard Battery Consulting was contracted to train Argonne staff on making electrode slurries and coatings.
- Numerous discussions were made with materials suppliers regarding their material properties and applications. The relevant companies in this work shown include ConocoPhillips, Toda America, Solvay Solexis, and Kureha.

Summary

- Several high energy **composite structure cathode materials** from e.g., Toda Kogyo, Argonne R&D, Materials Engineering Research Facility (MERF), were received and characterized. The validation results were transferred to the **Cell Fabrication Facility** (CFF) for production. Initial cycling data is very promising with many cells reaching hundreds of cycles.

- Completed installation of facilities to fabricate and test Li-ion prototype cells.
  - Installed 18650 and pouch cell making equipment
  - Installed custom electrode coating and hot roll press.
  - Installed high shear planetary mixer from Ross.
  - Setup of Cell Formation and Cycling Lab.
  - First cell builds showed good improvement in capacity and rate.

Rate	Capacity of Cell Builds (mAh/g cathode)			
	1	2	3	4
C	146	196	150	198
C /2	163	205	193	213
C/3	172	209	203	217
C/5	183	217	215	227

Contributors and Acknowledgments

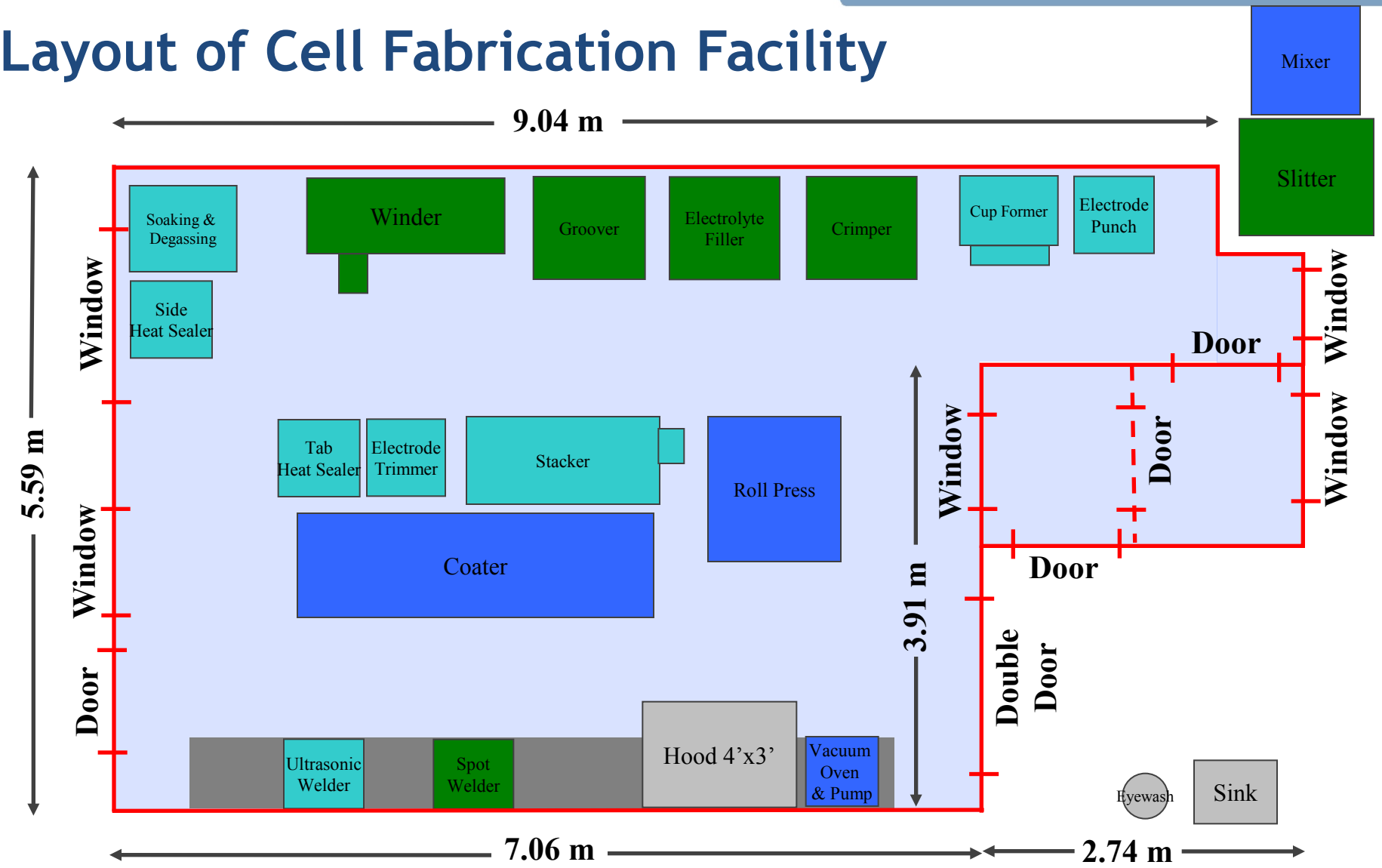
- Sun-Ho Kang (Argonne)
- Dennis Dees (Argonne)
- Ira Bloom (Argonne)
- Wenquan Lu (Argonne)
- Nancy Dietz (Argonne)
- Daniel Abraham (Argonne)
- Kevin Gering (INL)
- Jon Christophersen (INL)
- Huiming Wu (Argonne)
- Jeff Chamberlain (Argonne)
- Pete Roth (SNL)
- Khalil Amine (Argonne)
- Paul Nelson (Argonne)
- Gary Henriksen (Argonne)
- Dan Preuss (Argonne)
- Chris Orendorff (SNL)
- Kyle Fenton (SNL)
- David Wood III (ORNL)
- Claus Daniel (ORNL)
- Johnson Controls
- Saft
- Leyden Energy (Mobius Power)
- Media Tech
- A-Pro
- EnerDel
- Howard Battery Consulting
- ConocoPhillips
- Toda America
- Solvay Solexis
- Kureha

Support from David Howell and Peter Faguy of the U.S. Department of Energy's Office of Vehicle Technologies is gratefully acknowledged.

Technical Back-up Slides

The following slides are available for the presentation and included in the DVD and Web PDF files released to the public.

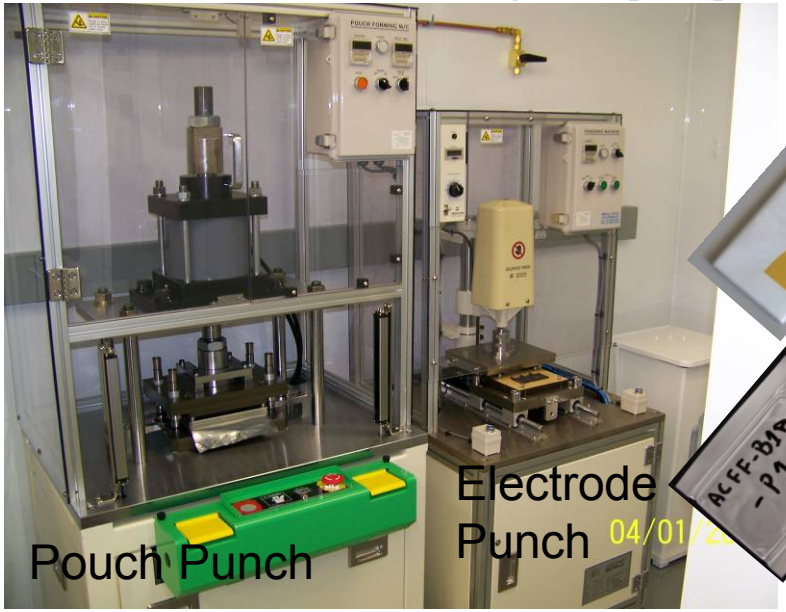
Layout of Cell Fabrication Facility

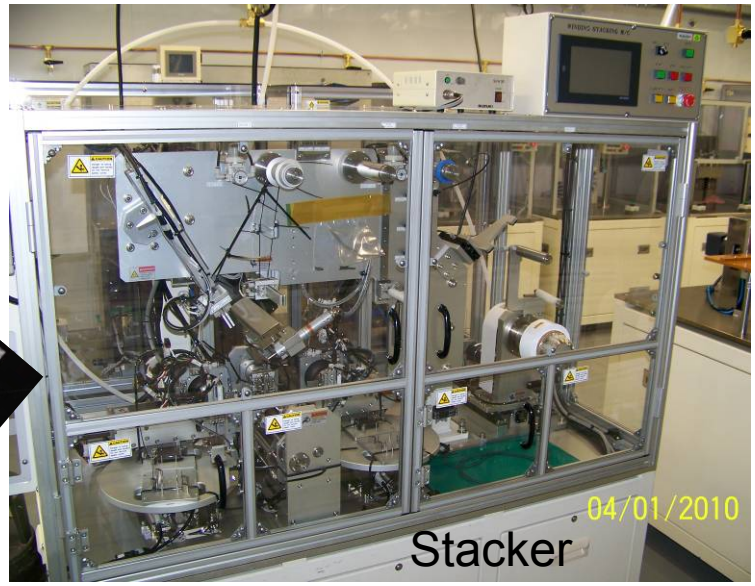


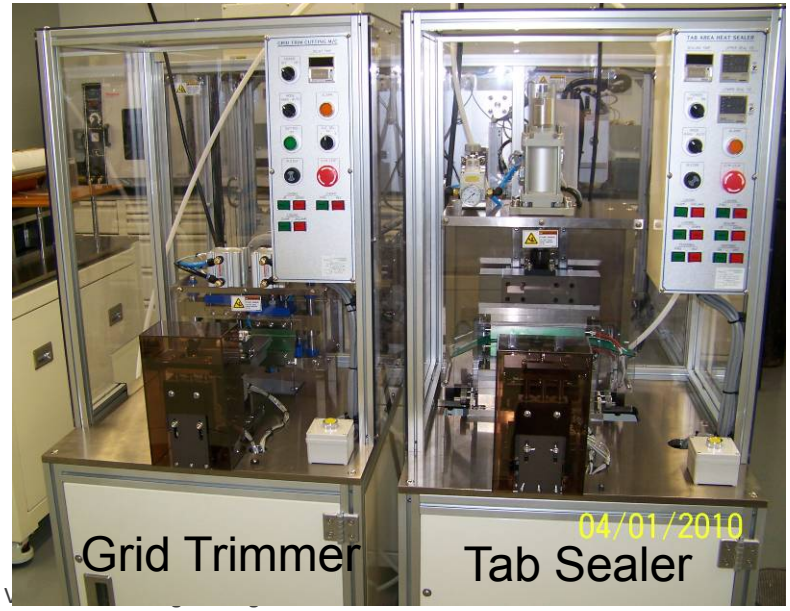
Argonne's Dry Room Cell Fabrication Facility

(Interior Dimensions)

Pouch Cell Making Equipment Installed in Dry Room







First Cell Build: Anode Formulation and Process

- Anode Formulation (Dry Composition)
  - 89.8 wt% Conoco Phillips: CGP-A12 Graphite
  - 4 wt% Timcal Super P®
  - 6 wt% Kureha KF-9300 PVDF Binder
  - 0.17 wt% Oxalic Acid

- Anode Electrode Properties
  - Copper Foil Thickness: 10 microns
  - Total Electrode Thickness: ~96 microns
  - Anode Coating Thickness: ~86 microns
  - Anode Coating: 11.5 mg/cm²
    (Total Material wt; No Foil)
  - Capacity: 3.4 – 3.6 mAh/cm²
  - Target Porosity: 33%-37%

- Anode Process
  - Mixing:
    - 9300 + Extra NMP – Vibratory Mix 10 min
    - Add Super P® – Vibratory Mix 10 min
    - Add ½ A12 – Vibratory Mix 10 min
    - Add ½ A12 + Oxalic Acid – Vibratory Mix 10 min
    - Ball Mill Mix for 1 hour
    - Thinky Mix for 3 min
  - De-Gassing
    - 3 mins in vacuum oven
  - Coating
    - 0.3 meter per min coating speed
    - Drying Zone 1 = 83 °C
    - Drying Zone 2 = 115 °C
  - Hot Rolling/ Calendering
    - Rolling Temperature = 80 °C
    - Rolling Speed = 0.5 meter per min

First Cell Build: Cathode Formulation and Process

- Cathode Formulation (Dry Composition)
  - 86 wt% Toda HE-5050 NCM
  - 4 wt% Timcal SFG-6 Graphite
  - 2 wt% Timcal Super P®
  - 8 wt% Solvay 5130 PVDF Binder

- Cathode Electrode Properties
  - Aluminum Foil Thickness: 20 microns
  - Total Electrode Thickness: ~88 microns
  - Cathode Coating Thickness: ~68 microns
  - Cathode Coating: 14.5 mg/cm²
    (Total Material wt; No Foil)
  - Capacity: 2.8 – 3.3 mAh/cm²
  - Porosity Target: 40%-45%

- n:p Ratio: 1.08-1.25

- Cathode Process
  - Mixing
    - 5130 + Extra NMP – Vibratory Mix 10 min
    - Add Super P® and SFG-6 – Vibratory Mix 10 min
    - Add ½ HE-5050 – Vibratory Mix 10 min
    - Add ½ HE-5050 – Vibratory Mix 10 min
    - Ball Mill Mix for 1 hour
    - Thinky Mix for 3 min
  - De-Gassing
    - 3 mins in vacuum oven
  - Coating
    - 0.4 meters per min coating speed
    - Drying Zone 1 = 83 °C
    - Drying Zone 2 = 105 °C
  - Hot Rolling/ Calendering
    - Rolling Temperature = 80 °C
    - Rolling Speed = 0.5 meter per min