Fabricate PHEV Cells for Testing & Diagnostics

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May 9-13, 2011

Vehicle Technologies Program Annual Merit Review and Peer Evaluation Meeting

Washington, D.C.

Project ID: ES030

Overview

Timeline

- Start: October 2008
- Finish: September 2014
- ~44% Complete

Budget

- Total project funding
  - 100% DOE
- $1,210K FY10 (ABR)
- $740K FY11 (ABR)
  - Not counting dry room and cell making equipment

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 0.4 Ah in capacity before larger scale industrial commitment

Partners

- Johnson Controls-Saft
- Leyden Energy (Mobius Power)
- 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. The main objective of this task is to obtain trial cells for calendar and cycle life studies in pouch cell or rigid cell (*e.g*. 18650) formats from industrial battery vendors.

- Electrode designs must be developed that are appropriate for PHEV batteries.

- To speed the evaluation of novel battery materials, Argonne will develop the capability to fabricate in-house pouch and 18650 cells in its new dry room facility.

Milestones

Produce graphite and NCA electrodes of varying thickness and test performance	Nov., 2008
Use thickness/performance data to design PHEV battery	Jan., 2009
Identify vendors to make electrodes and pouch/18650 cells for ABR	Jan., 2009
Finalize order of pouch/18650 cells with vendors	April, 2009
Distribute vendor cells to ABR for testing and diagnostics	March, 2010
Complete installation of pouch cell making equipment	March, 2010
All electrode and cell making equipment installed and approved for operation	Feb., 2011
First cell build completed using advanced materials	March, 2011

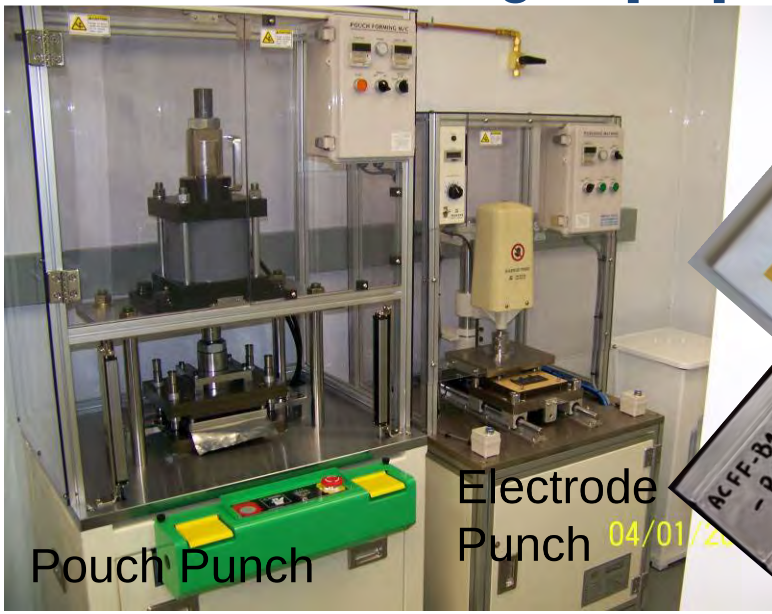
Approach

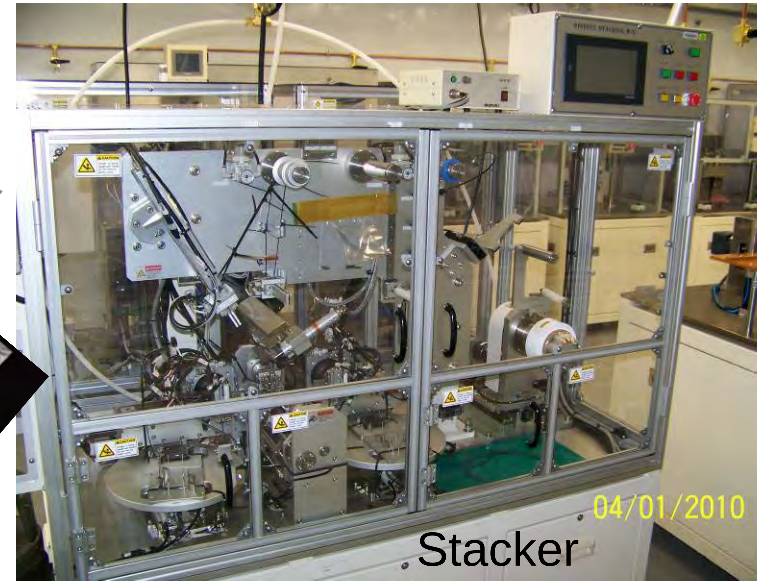
- Promising new exploratory materials are often developed in small coin cells, which may or may not scale up well in large PHEV battery designs. For this reason, pouch cells or rigid cells such as 18650's will be used for proofing of new materials in the capacity range of 0.4 to 2 Ah.
- Subcontracts will be established with battery developers to produce these cells based on screened materials from suppliers and from the ABR and BATT programs.
- Concurrent to the fabrication of PHEV cells by battery developers, Argonne will develop the capability to fabricate pouch cells and 18650 cells in Argonne's new dry room facility.
- Once in-house cells are deemed to be reliable, the developer subcontracts will be reduced.

Argonne's Cell Fabrication Facility Fully Operational

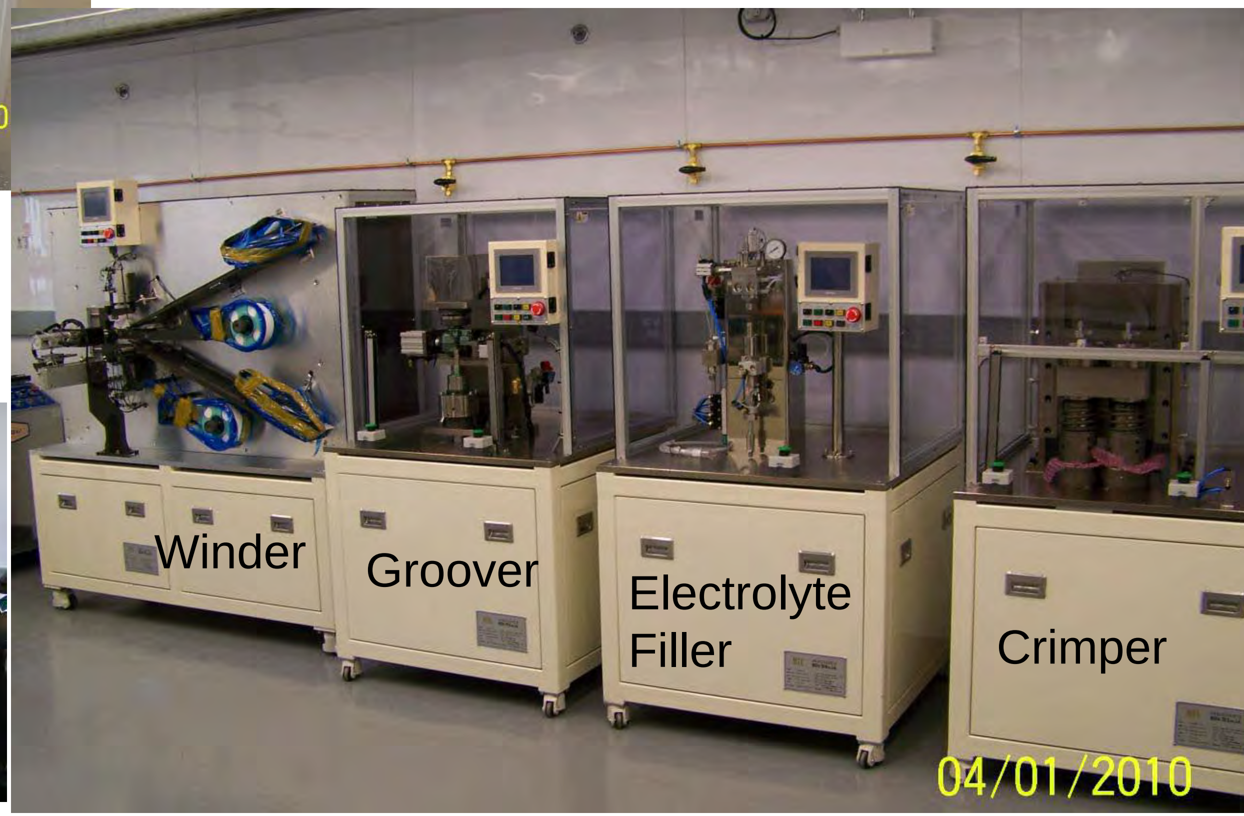
- All equipment installed and training provided by vendor's engineers
- Modifications were made to several pieces of equipment to enhance safety, with final approval to operate all equipment granted in February, 2011
- Argonne now has the capability to coat and hot-roll press electrodes, and to make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

Pouch Cell Making Equipment Installed in Dry Room

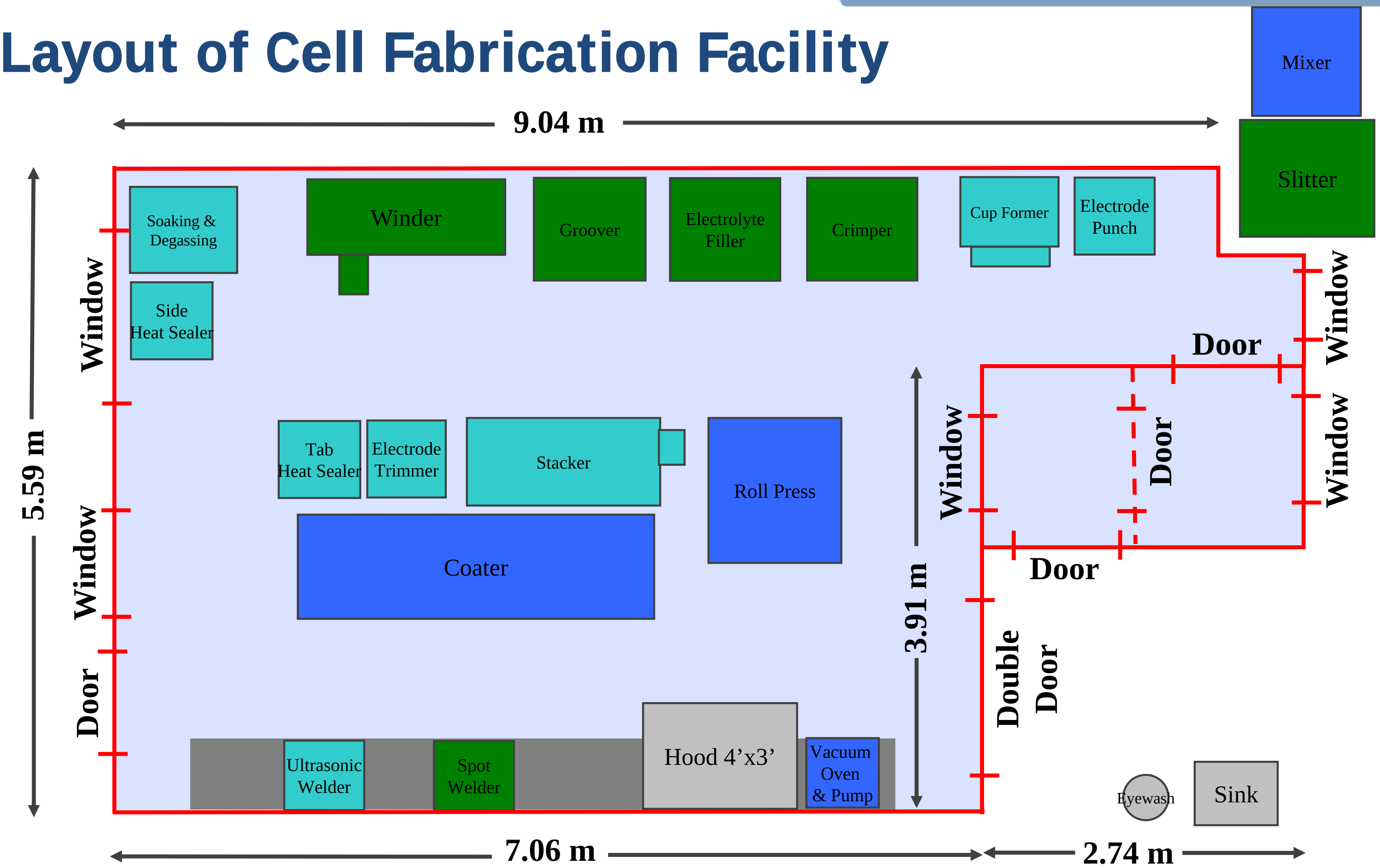




18650 Cell Making Equipment Installed in Dry Room



Layout of Cell Fabrication Facility



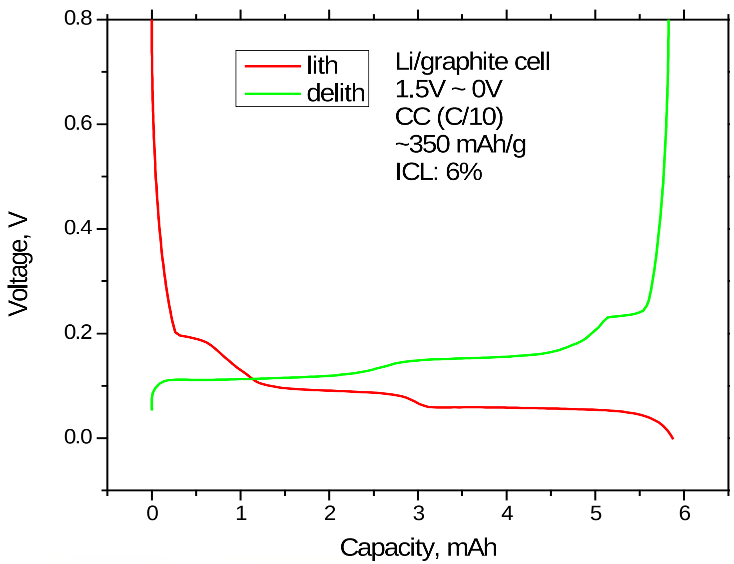
Argonne's Dry Room Cell Fabrication Facility

(Interior Dimensions)

ConocoPhillips CGP-A12 Graphite Selected as First Negative Electrode Build Based on Screening Results

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

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. This material also offers one of the highest first-cycle efficiencies available with superior safety and cycle-life performance.



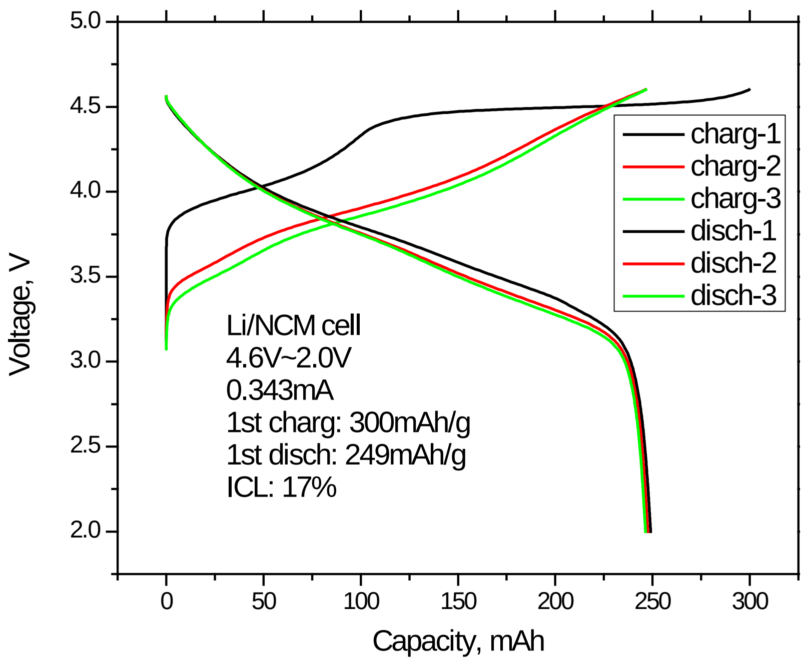
Toda HE5050 Selected as First Positive Electrode Build Based on Screening Results

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

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

	ICP, wt%	ICP, molar
Li	9.8	1.4119
Ni	10.4	0.177202
Co	6.9	0.117088
Mn	35.8	0.65162

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



First Electrode Build Required Several Runs

ACFF Electrode Formulation Data Base

Date: **3/17/2011**

Electrode	Foil	Foil Thk (um)	Material	Material Wt%	Conductive Additive	Additive Wt%	Conductive Additive	Additive Wt%	Binder Solution	Binder Wt %	Other Additive	Additive Wt%	Doctor Blade Setting from Foil (um)	Coating Speed (m/min)	Drying Zone 1 Temp (C)	Drying Zone 2 Temp (C)	Total Dried Electrode Thickness (um)	Dried Electrode Porosity (%)	Calendering Speed (m/min)	Calendering Temperature (C)	Total Calendered Electrode Thickness (um)	Calendered Electrode Porosity (%)	Comments
Anode	Cu	10	CP-A12	94					K-9300	6				0.5			240		0.5	80	210		Bend Cracking
Anode	Cu	10	CP-A12	89.83	Super P	4			K-9300	6	Oxalic Acid	0.17		0.5			115						Test Batch
Anode	Cu	10	CP-A12	89.83	Super P	4			K-9300	6	Oxalic Acid	0.17		0.5			115						Test Batch
Anode	Cu	10	CP-A12	89.83	Super P	4			K-9300	6	Oxalic Acid	0.17		0.5	83	115	115	55	0.5	80	96	37	**Diagnostics Samples**
Cathode	Al	20	HE505	86	Super P	4	SFG 6	4	K-1700	6			200	0.5	83	115	120						Bend Cracking
Cathode	Al	20	HE505	86	Super P	4	SFG 6	4	K-1700	6			225	0.5	83	115	130						Bend Cracking
Cathode	Al	20	HE505	86	Super P	4	SFG 6	4	K-1700	6			250	0.5	83	115	150						Bend Cracking
Cathode	Al	20	HE505	86	Super P	4	SFG 6	4	K-1700	6			250	0.5	83	75	100						Coating wet; did not stick
Cathode	Al	20	HE505	84	Super P	4	SFG 6	4	K-1700	8			250	0.5	80	115	170						Coating not fully dry
Cathode	Al	20	HE505	84	Super P	4	SFG 6	4	K-1700	8			230	0.5	83	115	160						Coating dry; Bend Cracking
Cathode	Al	20	HE505	84	Super P	4	SFG 6	4	K-1700	8			215	0.5	80	115							Bend Cracking
Cathode	Al	20	HE505	84	Super P	2	SFG 6	4	K-1700	10			215	0.5	83	115	110						Small Bend Cracking
Cathode	Al	20	HE505	84	Super P	2	SFG 6	4	K-1700	10			267	0.5	83	115	135						Small Bend Cracking
Cathode	Al	20	HE505	84	Super P	2	SFG 6	4	K-1700	10			285	0.5	83	115	140						Small Bend Cracking
Cathode	Al	20	HE505	84	Super P	2	SFG 6	4	S-5130	10			285	0.5	83	115	110						All aspects good
Cathode	Al	20	HE505	84	Super P	2	SFG 6	4	S-5130	10			357	0.5	83	115	120						Coating wet; did not stick
Cathode	Al	20	HE505	84	Super P	2	SFG 6	4	S-5130	10			325	0.5	83	115	120						All aspects good
Cathode	Al	20	HE505	84	Super P	2	SFG 6	4	S-5130	10			335	0.5	83	115	125						Need More Data
Cathode	Al	20	HE505	88	Super P	2	SFG 6	4	S-5130	6			250	0.5	83	115	132						All aspects good
Cathode	Al	20	HE505	86	Super P	2	SFG 6	4	S-5130	8			250	0.4	83	105	150	60	0.5	80	94	46	**Cell Build 1 Double Side**
Cathode	Al	20	HE505	86	Super P	2	SFG 6	4	S-5130	8			250	0.4	83	115	132	60	0.5	80	94	46	**Diagnostics Samples/ Cell Bulid 1SS**
Anode	Cu	10	CP-A12	89.83	Super P	4			K-9300	6	Oxalic Acid	0.17	200	0.4	84	115	90	55					
Anode	Cu	10	CP-A12	89.83	Super P	4			K-9300	6	Oxalic Acid	0.17	282	0.4	84	115	125	55	0.5	80	98	38	**Cell Build 1 Double Side**

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/cm^2

    (Total Material wt; No Foil)
  - Capacity: 3.4 – 3.6 mAh/cm^2
  - 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

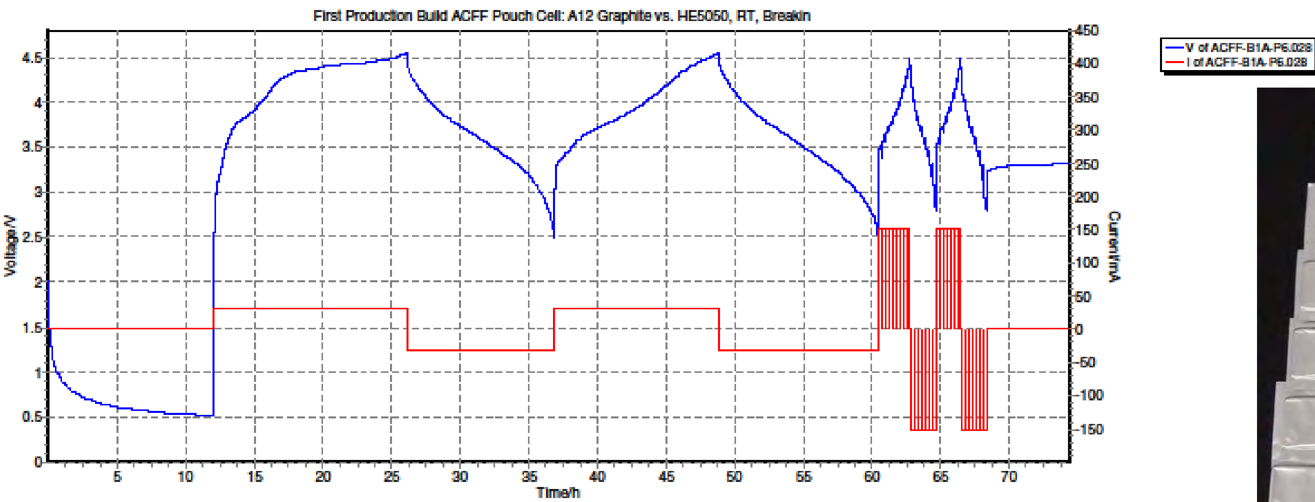
- Cathode Formulation (Dry Composition)
  - 86 wt% Toda HE-5050 NCM
  - 4 wt% Timcal SFG-6 Graphite
  - 2 wt% Timcal Super P
  - 8 wt% Solvay 5130 PVDF Binder

- Cathode Electrode Properties
  - Aluminum Foil Thickness: 20 microns
  - Total Electrode Thickness: ~88 microns
  - Cathode Coating Thickness: ~68 microns
  - Cathode Coating: 14.5 mg/cm^2 (Total Material wt; No Foil)
  - Capacity: 2.8 – 3.3 mAh/cm^2
  - Porosity Target: 40%-45%

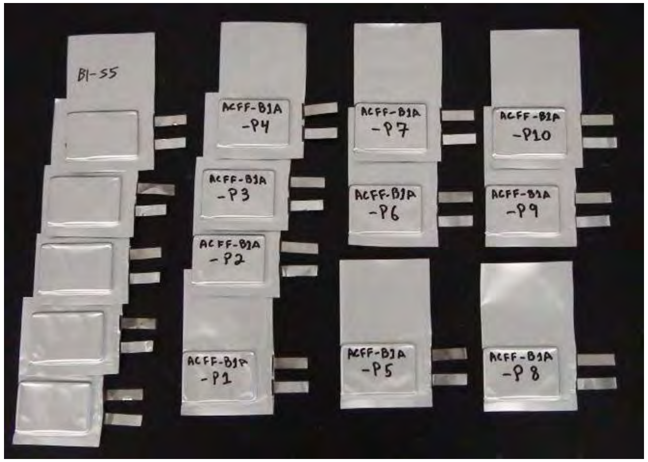
- n:p Ratio: 1.08-1.25

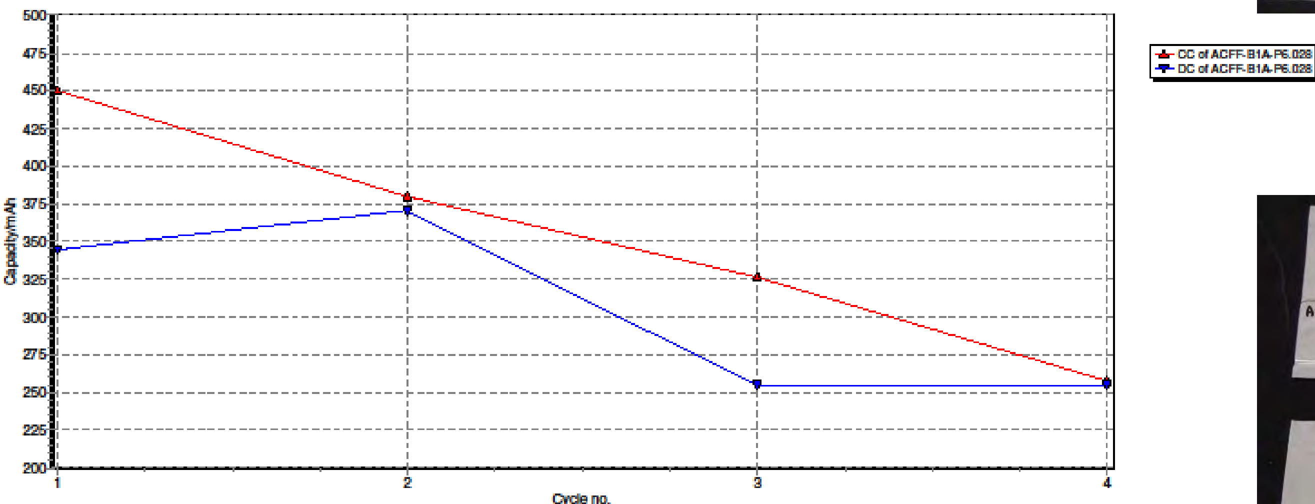
- Cathode Process
  - Mixing
    - 5130 + Extra NMP – Vibratory Mix 10 min
    - Add Super P and SFG-6 – Vibratory Mix 10 min
    - Add ½ HE-5050 – Vibratory Mix 10 min
    - Add ½ HE-5050 – Vibratory Mix 10 min
    - Ball Mill Mix for 1 hour
    - Thinky Mix for 3 min
  - De-Gassing
    - 3 mins in 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

First Cell Build Formation Cycles

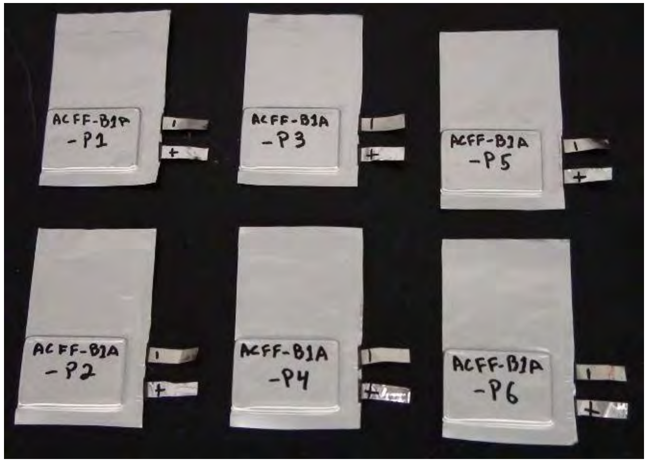


Before Formation Cycles

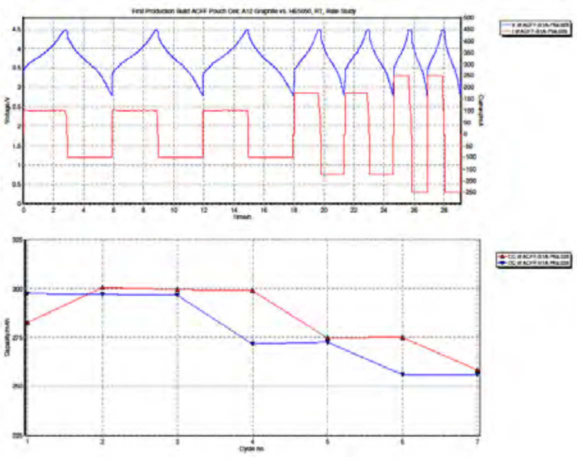


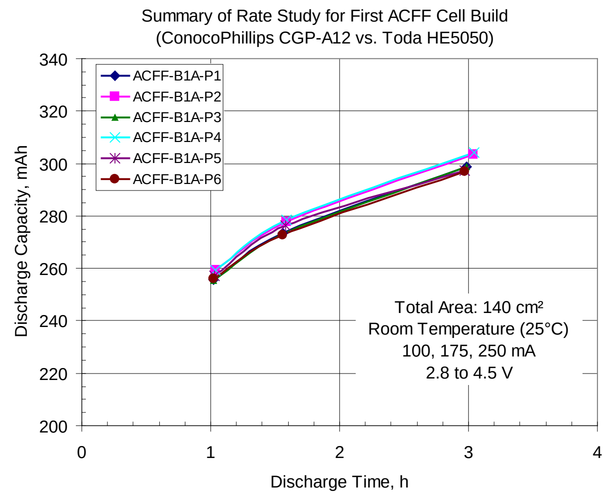


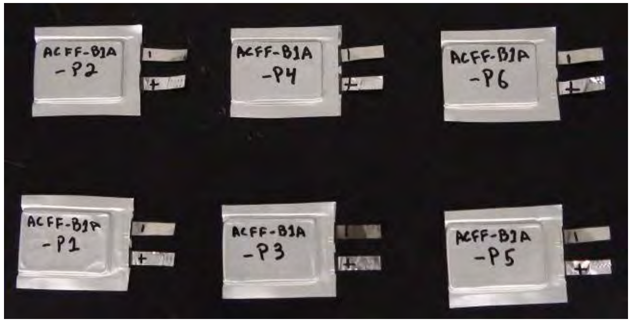
After Formation Cycles
(little gas generation!)



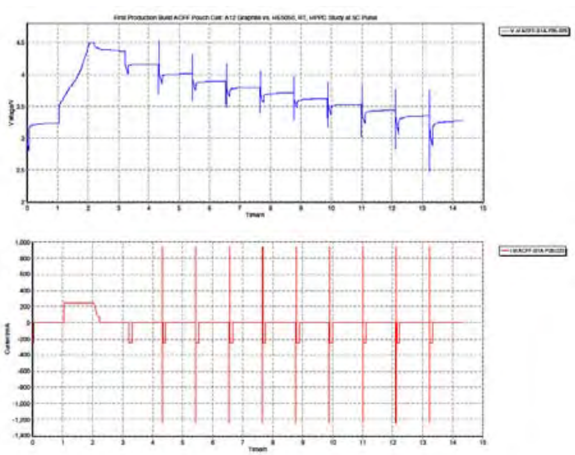
First Cell Build Characterization Cycles

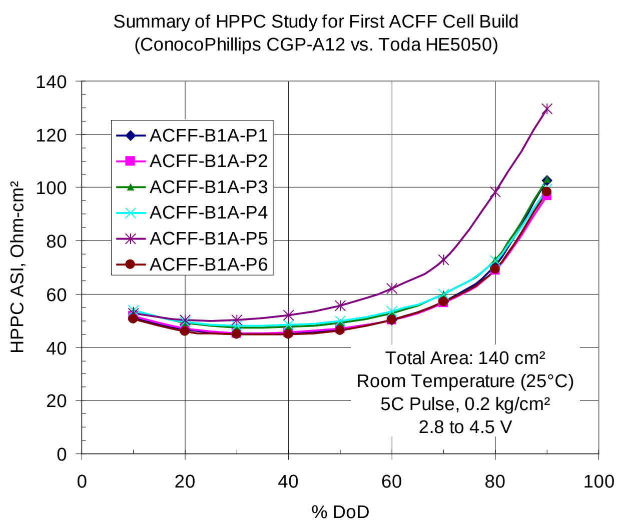


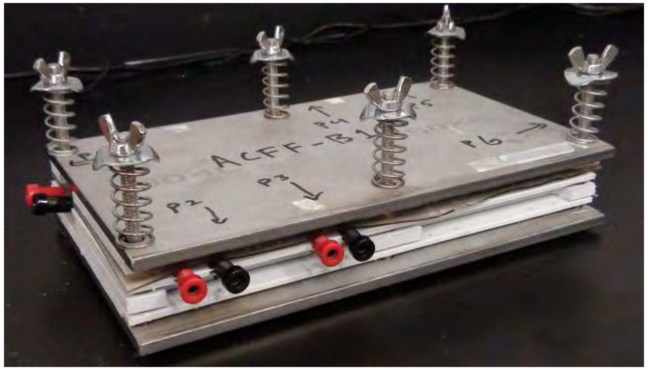




Cells Delivered for Independent Verification to EADL







One outlier (P5) was removed from further testing.

Follow-On Advanced Chemistry Cell Builds

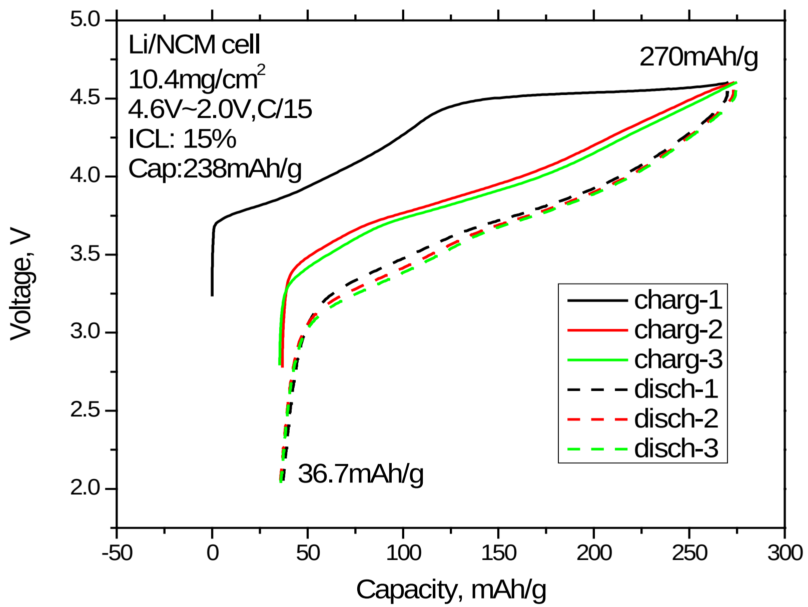
- Second cell build initiated in March
  - Positive: high-energy NMC $Li_{1.2}Ni_{0.3}Mn_{0.6}O_{2.1}$ (2kg Argonne material made by Huiming Wu)
  - Negative: graphite (ConocoPhillips: CGP-A12)

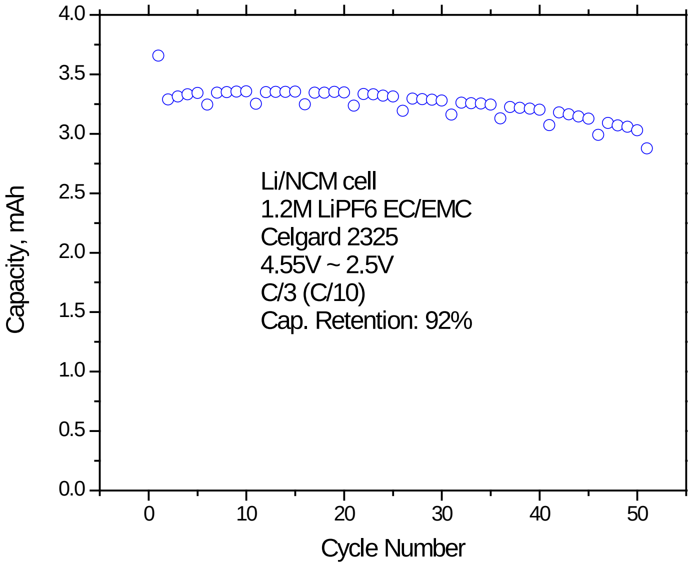
- Third cell build initiated in April
  - Positive: possible options for high-energy NMC materials
    - Ni-Mn material with compositional variation from Wu material used in second build (Argonne supplied material made by Ilias Belharouak)
    - $Li_{1.2}Mn_{0.525}Co_{0.10}Ni_{0.175}O_{1.95}F_{0.05}$ perhaps with surface coating (Argonne supplied material made by Sun-Ho Kang)
  - Negative: graphite (ConocoPhillips: CGP-A12)

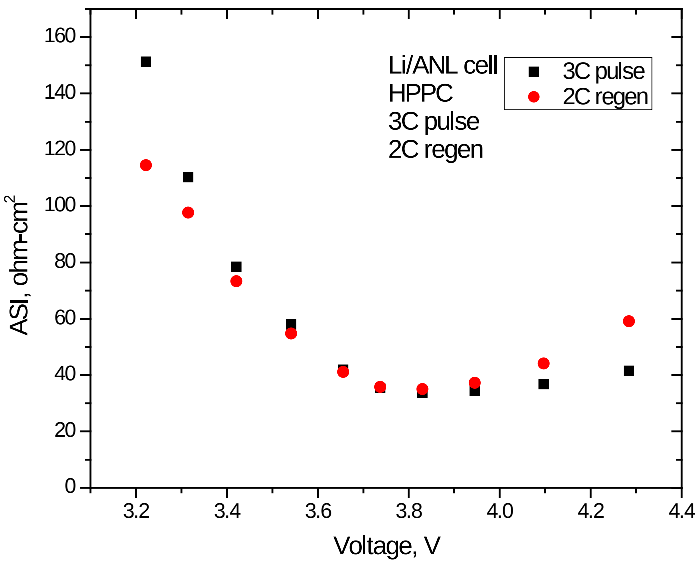
Advanced Cathode for Second Cell Build

$Li_{1.2}Ni_{0.3}Mn_{0.6}O_{2.1}$ (H. Wu)

Half cell results of Wu's material batch submitted to Screening Task (W. Lu) for validation before cell build







Electrode Builds for High Voltage Electrolyte Study

Anode	Cathode
89.8 wt% ConocoPhillips: CGP-A12 4 wt% Timcal Super P 0.17 wt% Oxalic Acid 6 wt% KF-9300 Kureha PVDF binder 6.0 mg/cm^2 (graphite , carbon, & binder) Single-sided electrodes made by Saft	**86 wt% High-Energy NMC (Toda HE-5050)** 4 wt% Timcal SFG-6 graphite 2 wt% Timcal Super P 8 wt% Solvay 5130 PVDF binder 7.3 mg/cm^2 (oxide, carbon/graphite, & binder) Single-sided electrodes made by Saft
84 wt% $Li_4Ti_5O_{12}$ 6 wt% Carbon black 10 wt% PVDF binder 9.6 mg/cm^2 (oxide, carbon, & binder) Single-sided electrodes made by EnerDel	**84 wt% $LiNi_{0.5}Mn_{1.5}O_4$** 8 wt% Carbon black 8 wt% PVDF binder 15.7 mg/cm^2 (oxide, carbon, & binder) Single-sided electrodes made by EnerDel
	86 wt% NCA (Toda) 4 wt% Timcal SFG-6 graphite 2 wt% Timcal Super P 8 wt% Solvay 5130 PVDF binder 11.2 mg/cm^2 (oxide, carbon/graphite, & binder) Single-sided electrodes made by Saft

Collaborations with Industry

- While Argonne's Cell Fabrication Facility was being installed, outside companies experienced at making lithium-ion batteries 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 many 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

- All electrode and cell making equipment was 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
- First electrodes and cells using advanced materials were built in Argonne's Cell Fabrication Facility in March, 2011
- Electrodes were made by vendor per Argonne's instructions to be used in high voltage electrolyte study

Future Plans

- Continue to make xx3450 pouch cells using electrodes from first three builds with variations in electrolyte additives and breakin/test conditions
- Fabricate 18650 and pouch cells in-house with exploratory materials

Contributors and Acknowledgments

- Sun-Ho Kang (Argonne)
- Dennis Dees (Argonne)
- Ira Bloom (Argonne)
- Wenquan Lu (Argonne)
- Kevin Gering (INL)
- Jon Christophersen (INL)
- Huiming Wu (Argonne)
- Jeff Chamberlain (Argonne)
- Pete Roth (SNL)
- Chris Orendorff (SNL)
- Khalil Amine (Argonne)
- Paul Nelson (Argonne)
- Gary Henriksen (Argonne)
- Dan Preuss (Argonne)

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- A-Pro
- EnerDel
- Howard Battery Consulting
- ConocoPhillips
- Toda America
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Support from David Howell and Peter Faguy of the U.S. Department of Energy's Office of Vehicle Technologies is gratefully acknowledged.