Current Research Activities in Electrode and Cell Prototyping

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Argonne National Laboratory

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Project ID: ES185

Overview

Timeline

- Start: October 2012
- Finish: September 2014
- ~ 25% Complete

Barriers

- Need a high energy density battery for PHEV/EV use that is safe, cost-effective and has a long cycle life.
  - Validation tests of newly developed battery materials are needed in cell formats with at least 0.2 Ah capacity before larger scale industrial commitment

Budget

- 1,100K FY13
  - (as part of CFF Effort)
- 100% DOE-ABR

Partners

- Sandia National Laboratory
- Oak Ridge National Laboratory
- Army Research Laboratory
- Idaho National Laboratory
- Jet Propulsion Laboratory
- Lawrence Berkley National Laboratory
- National Renewable Energy Laboratory
- Materials Engineering Research Facility
- Post Test Facility
- Northwestern University
- University of Illinois at Urbana-Champaign
- Kureha
- Toda America
- Silatronix
- DuPont
- Electrochemical Materials
- Phillips 66
- Zeon Chemicals
- Solvay Solexis
- North Carolina State University
- Ohio State University

Relevance/Objectives

- Several new battery chemistries are being proposed for PHEV batteries that must be evaluated in cell formats that are larger then a few mAh in capacity.
- The Cell Fabrication Facility fabricates xx3450 pouch and 18650-sized cylindrical cells for direct comparison to industrially available cells.
- By controlling the entire cell building process, any variable can be quickly and easily changed to determine the effect on a cell's performance. Feedback is provided to the investigators to direct future research.
- Develop novel battery materials and electrodes for cell builds and research use.
- Provide standard and interchangeable anodes and cathodes to the battery research community to enable and speed up battery research.
- Provide specially designed cells for analysis of various battery materials to gain a better understanding of the material structural and electrochemical performance correlation.
- Support DOE-funded research programs such as ABR, BATT, SBIR, ARPA-E, etc.

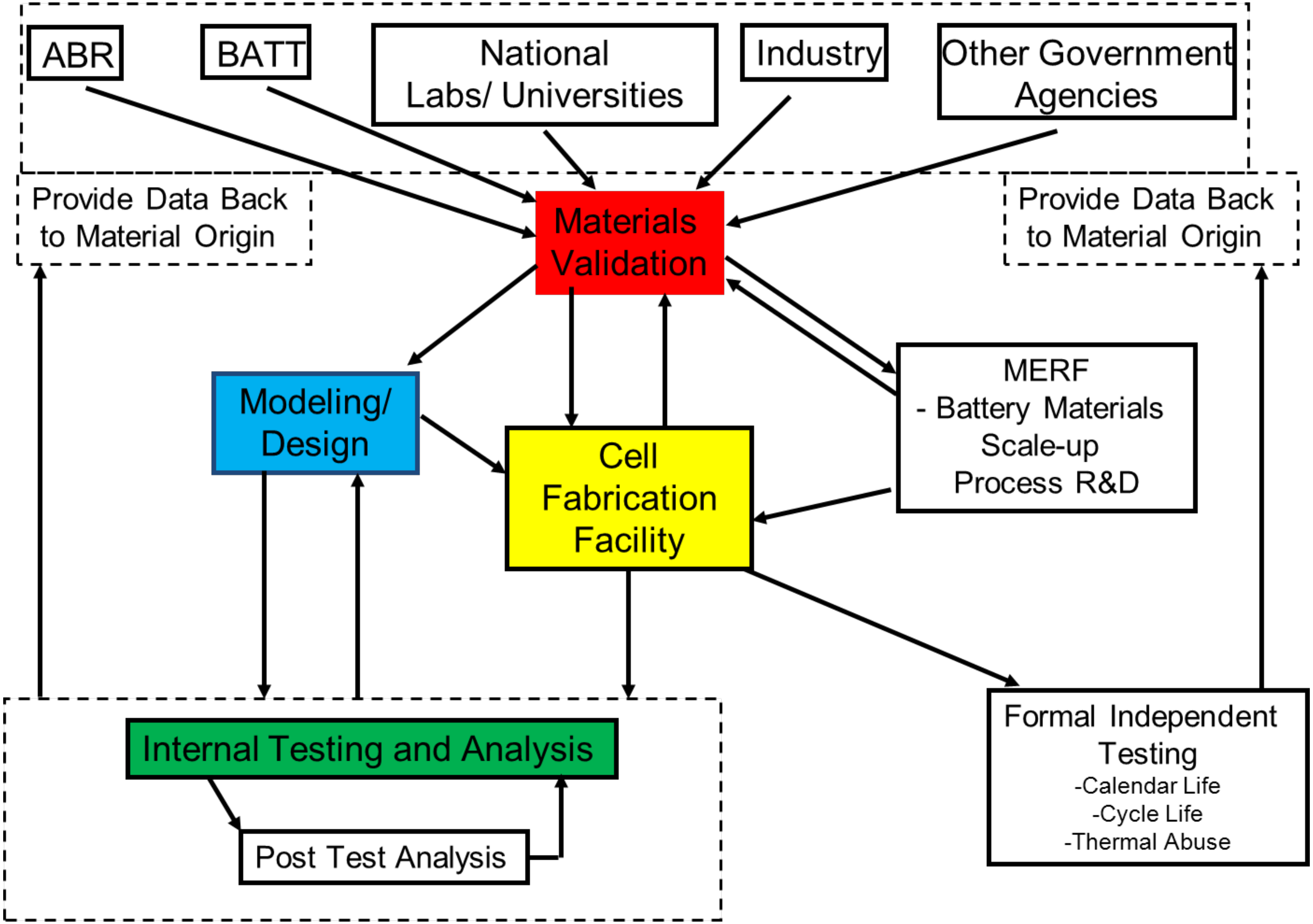
Milestones - Completed

▪ Started Evaluation of Si and Si/Graphite, and Binder Systems	June 2012
▪ Electrode Optimization of the A12 Graphite and Toda HE5050 (LMR-NMC) couple	July 2012
▪ 18650-sized Cell Build Complete	Sept. 2012
▪ MERF Cathode Evaluation of Multiple Batches	Oct. 2012
▪ High Temp Testing of Baseline xx3450 Cells	
– A12/5V Spinel	Nov. 2012
– A12/HE5050 (LMR-NMC)	Nov. 2012
– A12/523 (NCM)	Jan. 2013
▪ Evaluated Electrolyte Additives in xx3450 Cells	
– LiDFOB	Jan. 2013
– LiDFOB + LiBOB	Jan. 2013
– LiDFOB (made by MERF)	Jan. 2013

Approach/Strategy

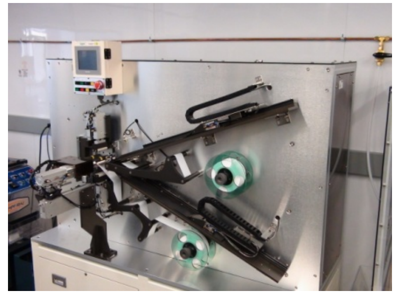
- Promising new exploratory materials are often developed in small coin cells, which may not scale up well in large PHEV battery designs. For this reason, industrially relevant cell formats such as pouch cells and 18650's are used for proofing of new materials in the capacity range of 0.2 to 2 Ah, which are produced by the Cell Fabrication Facility at Argonne.
- All new materials are evaluated in the materials validation effort within the CFF to obtain materials performance data for scaled-up cell design and to prioritize efforts on materials of value to DOE's energy storage programs.
- Partnerships with fellow battery research programs at other national laboratories are established to maximize the impact of collective efforts.
- Close working relationships are maintained with the diagnostics effort within the CFF and Post Test Facility during electrode fabrication and end-of-life analysis of cycled cells to elucidate failure mechanisms.
- Continued collaboration with Argonne's Materials Engineering Research Facility (MERF) to aid in scale up of R&D materials.
- SOP/QC/Traveler: Utilizing standard Travelers to record process and quality control (QC) data per safety and standard operating procedure (SOP) documentation.

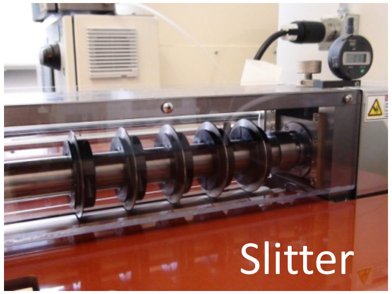
Approach/Strategy



Facility

Winder



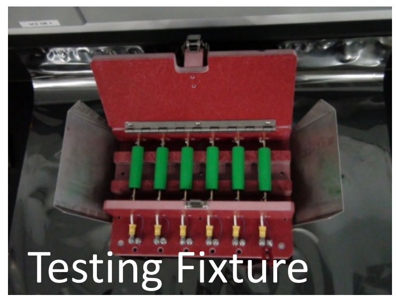


Slitter

Wound Cell

18650 equipment is operational and cells have been assembled and tested

Electrolyte Fill



Testing Fixture

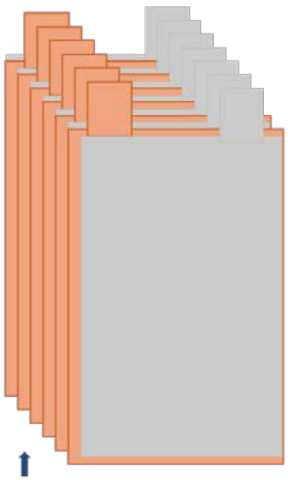
Crimper

Beader

*Cap assembly = Top electrode, gasket, PTC safety device & CID safety device

xx3450 Pouch Cell Format

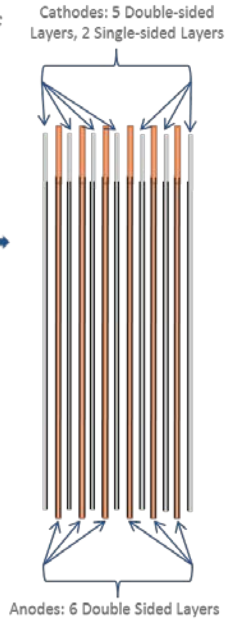
Stacking Illustration



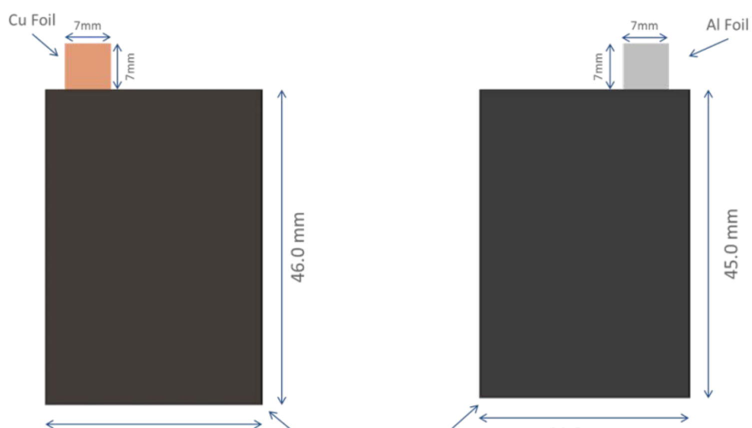
One separator layer "wound" between each anode and cathode interface (not shown in images)

Cross Section View of Stacked Electrodes

12 Anode/Cathode Interfaces per cell



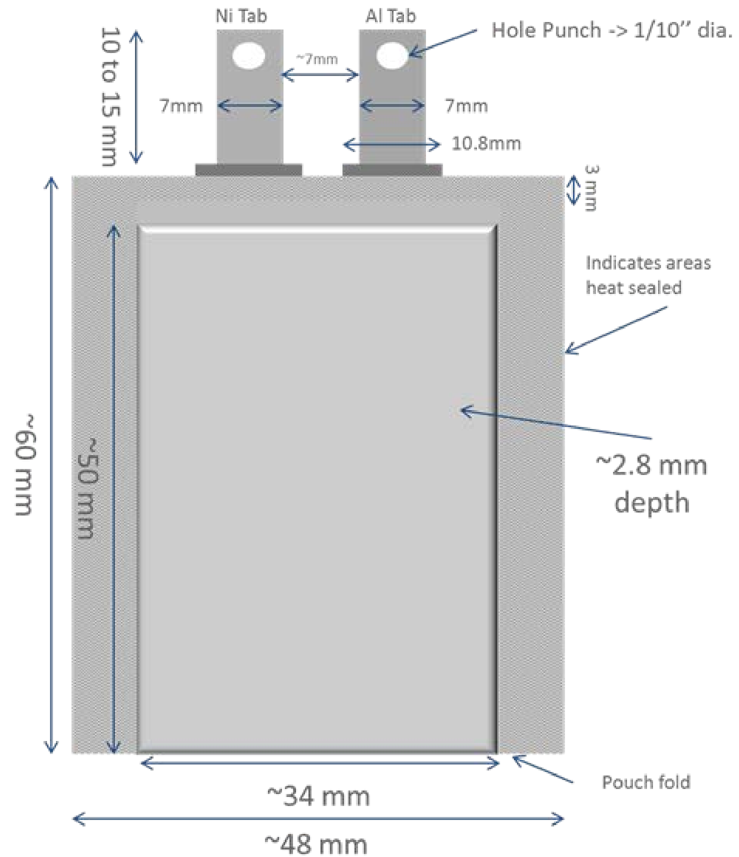
Punched Electrodes



Coating Area: 14.9 cm²

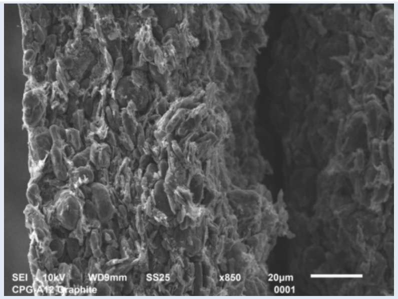
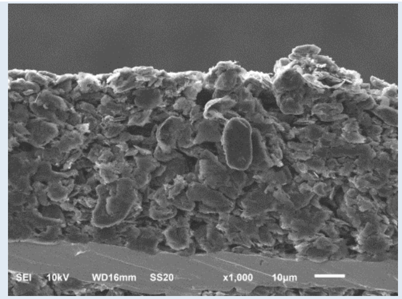
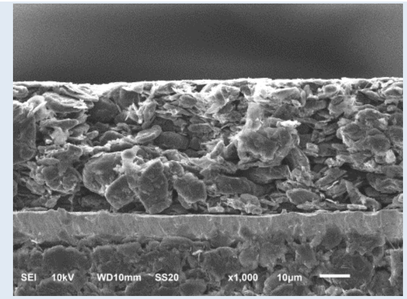
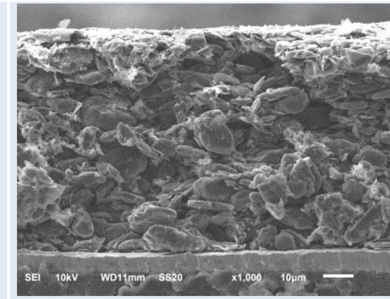
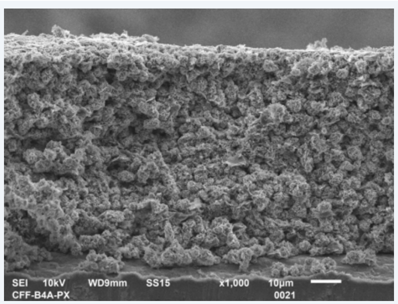
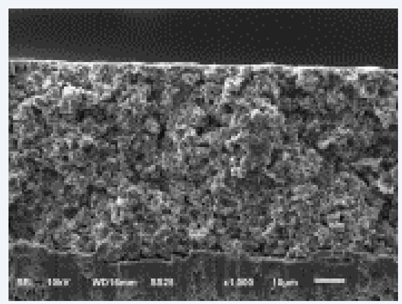
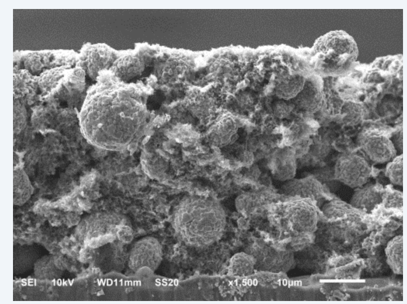
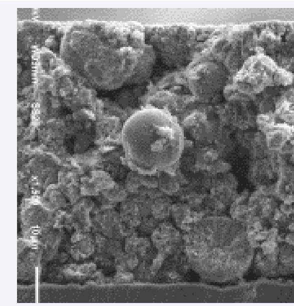
Coating Area: 14.1 cm²

- Typical Cell Capacity: **200 to 500 mAh**



Pouch Cell Electrodes

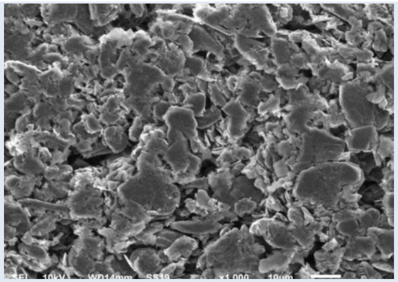
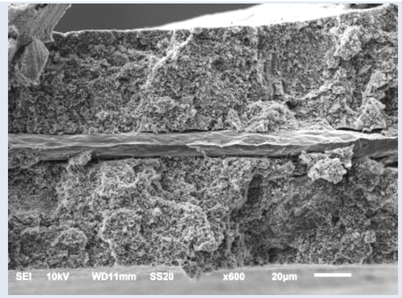
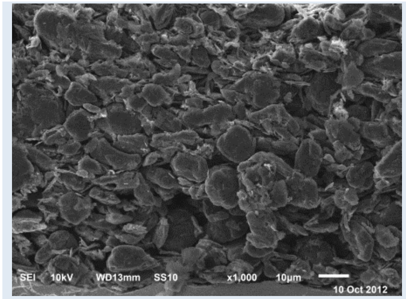
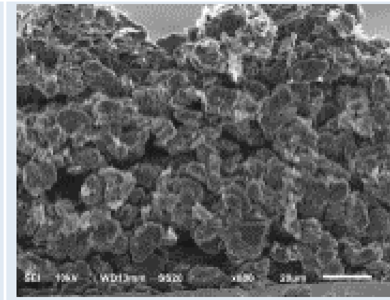
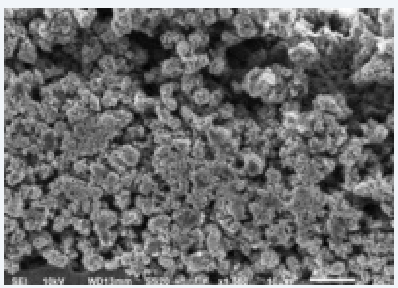
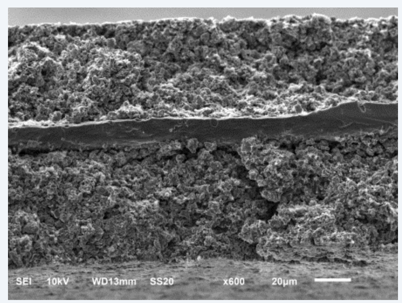
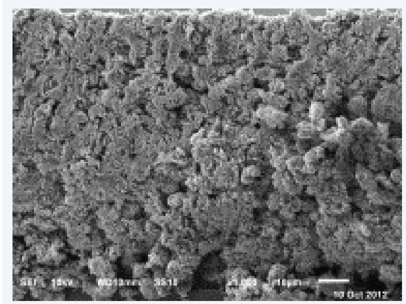
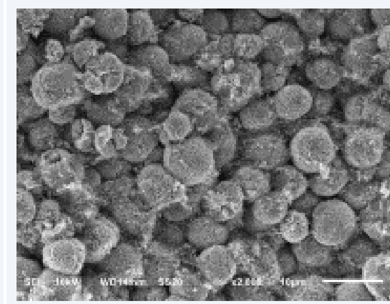
- Cross Section SEM Images of calendered electrodes

	CFF-B4A	CFF-B5A	CFF-B7A	CFF-B8A
Anode	 A12 Graphite (Mag: x850)	 A12 Graphite (Mag: x1,000)	 A12 Graphite (Mag: x1,000)	 A12 Graphite (Mag: x1,000)
Cathode	 HE5050 LMR-NMC (Mag: x1,000)	 5V Spinel (Mag: x1,000)	 NCM 523 (Mag: x1,500)	 MERF 1A LMR-NMC (Mag: x1,500)

Electrodes show well dispersed binder and carbon additives creating a high quality electrode.

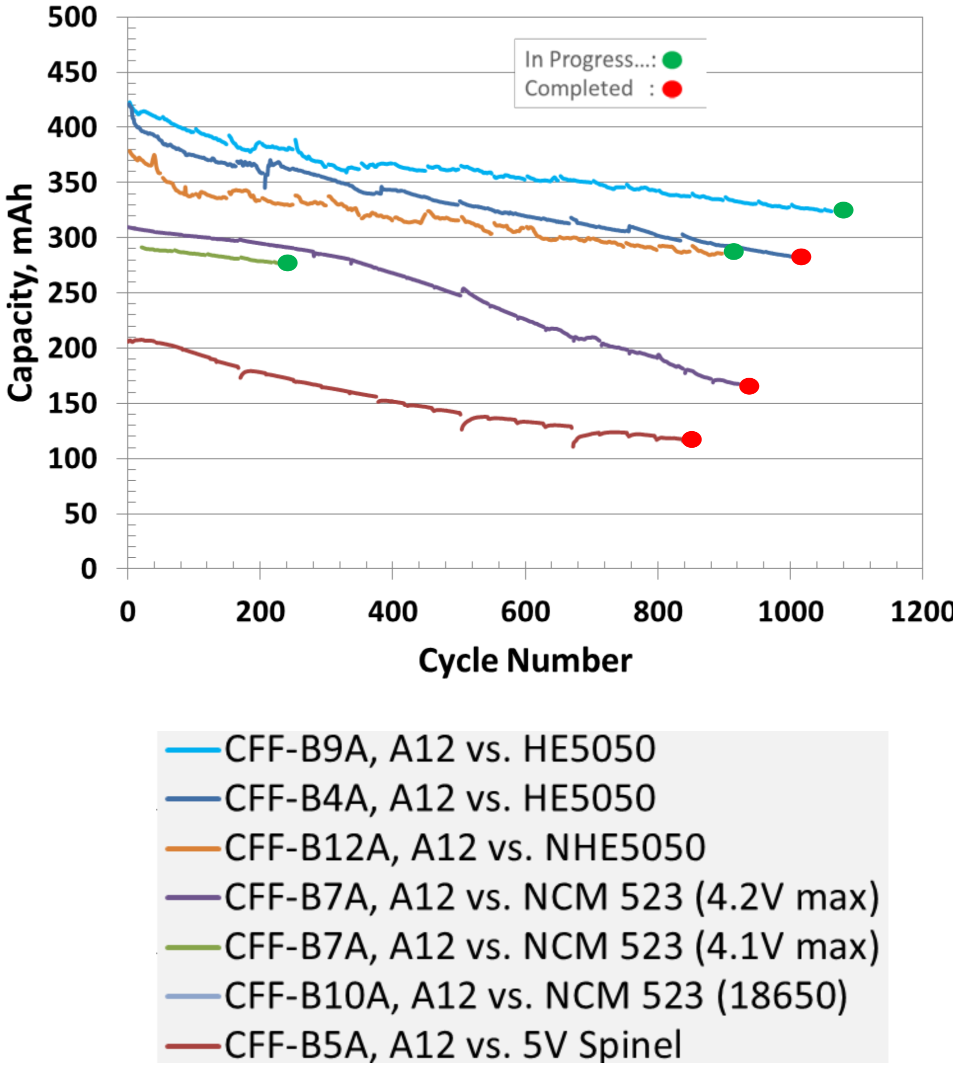
Pouch Cell Electrodes

- Cross Section SEM Images of calendered electrodes

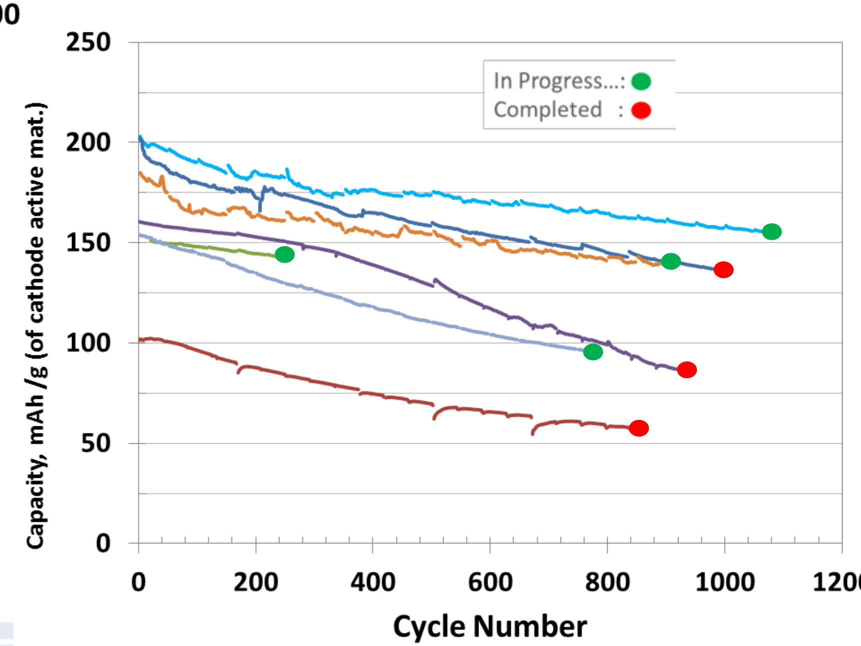
	CFF-B9A	CFF-B11A	CFF-B12A	CFF-B13A
Anode	 A12 Graphite (Mag: x1,000)	 LTO (Mag: x600)	 A12 Graphite (Mag: x1,000)	 A12 Graphite (Mag: x800)
Cathode	 HE5050 LMR-NMC (Mag: x1,500)	 5V Spinel (Mag: x600)	 NHE5050 LMR-NMC (Mag: x1,000)	 MERF 1B LMR-NMC (Mag: x2,000)

Electrodes show well dispersed binder and carbon additives creating a high quality electrode.

Baseline Pouch Cell Data



- The CFF focuses on a number of different materials because each one has some type of advantage in a cell. Baseline data is established on each of these materials so that any improvements in the cell configuration (materials, electrolyte, additives, separators, etc.) can be tested later and compared to the baseline data.
  - Baseline Cells include:
  - Separator: Celgard 2325 - Trilayer PP/PE/PP
  - Electrolyte: 1.2M $LiPF_6$ in EC:EMC (3:7 wt%) (Tomiyama)



Cycling @ C/2 Rate, 30°C

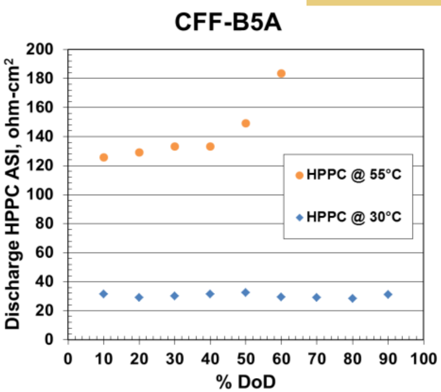
Elevated Temp Testing - Baseline xx3450 Pouch Cells

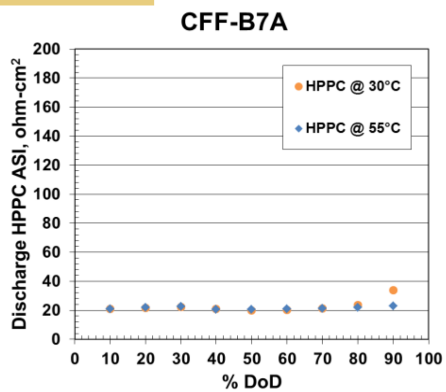
- In addition to room temperature testing (30°C), elevated temperature testing (55°C) is performed to speed up the aging process and to determine the temperature effects on cell performance.

- Rate Study

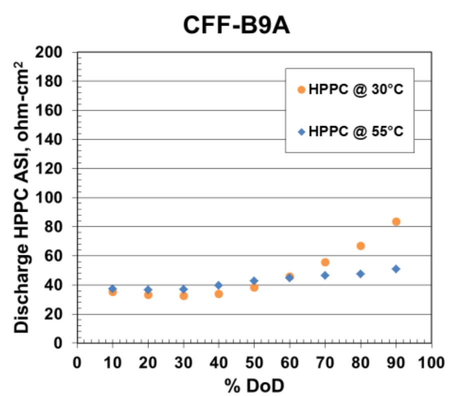
	CFF-B5A A12/5V Spinel		CFF-B7A A12/ NCM 523		CFF-B9A A12/ HE5050	
C-rate	mAh/g @ 30°C	mAh/g @ 55°C	mAh/g @ 30°C	mAh/g @ 55°C	mAh/g @ 30°C	mAh/g @ 55°C
2C	92	56	140	147	173	184
1C	95	64	143	149	191	201
C/2	98	72	147	150	208	218
C/3	100	76	149	151	218	228
C/5	102	82	152	152	231	240
C/10	105	90	156	153	248	257

- HPPC Study

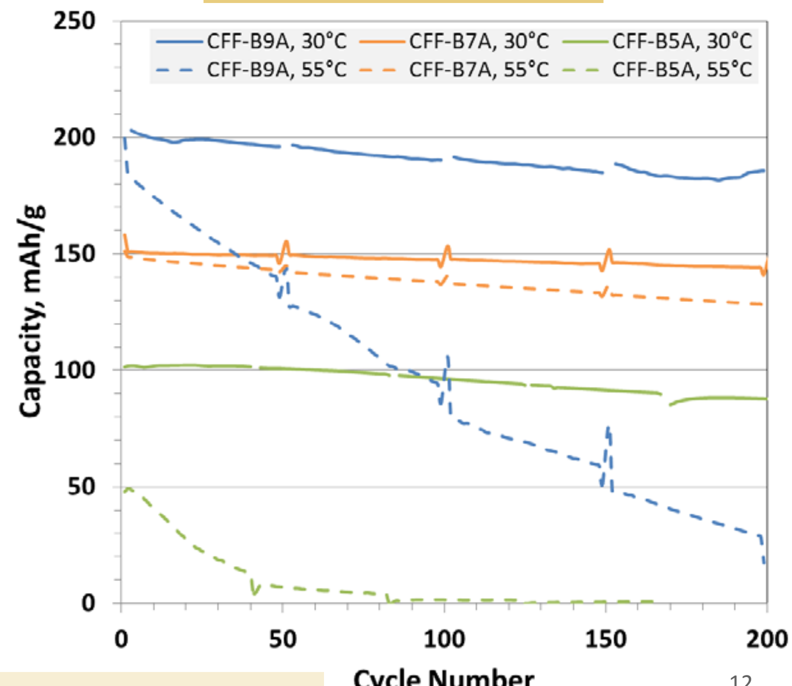




- Diagnostics group showed 5V spinel electrodes have significant impedance rise and coating delamination @ 55°C



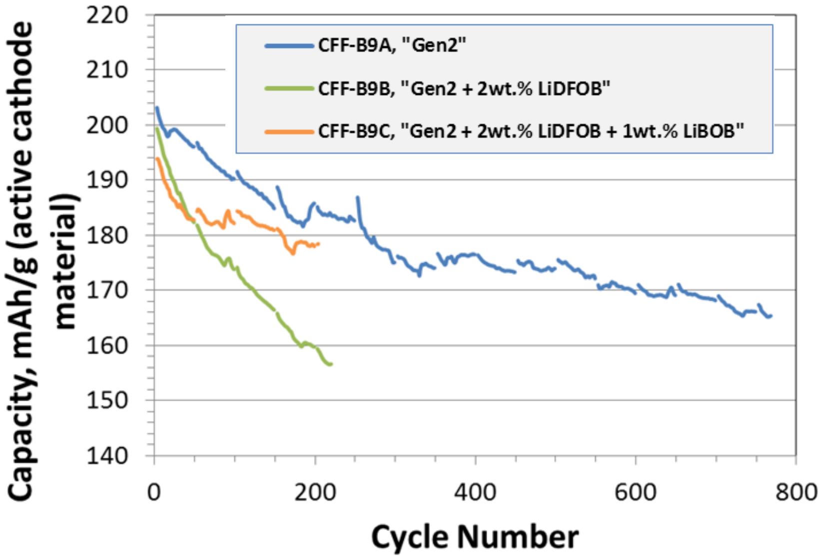
- Life Cycle Study



Cycling @ C/2 Rate

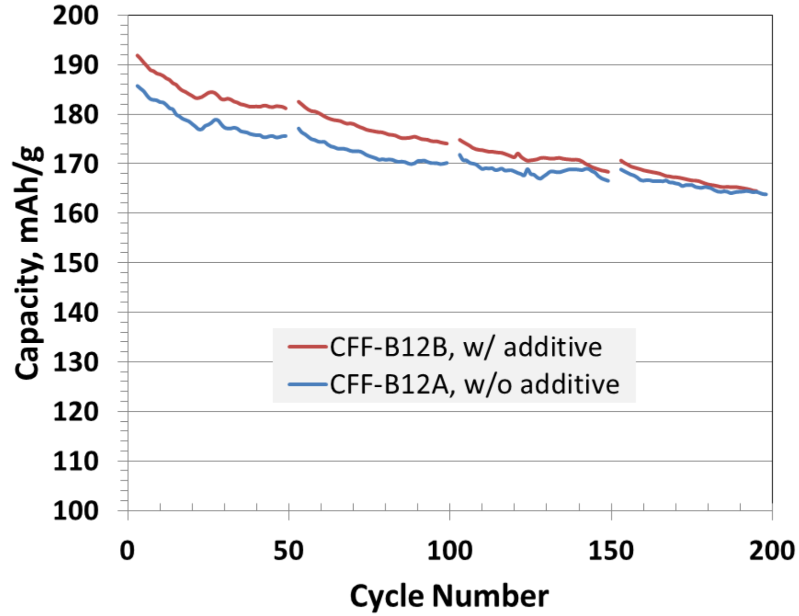
Electrolyte Additive Evaluation

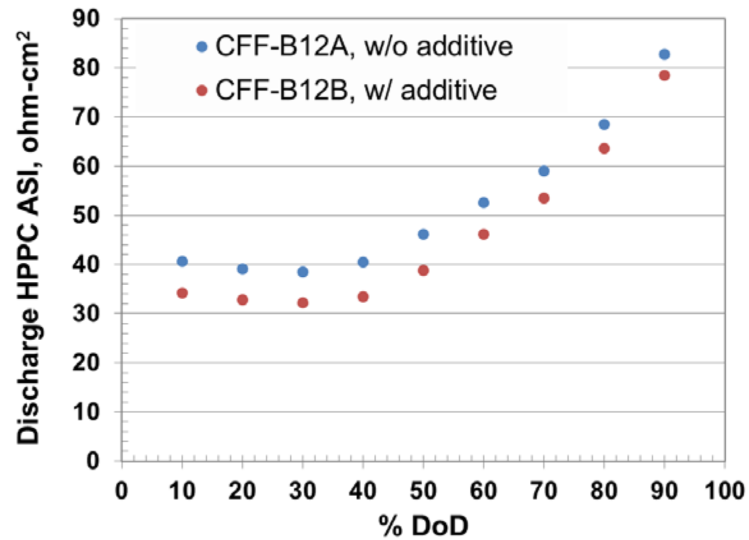
- Diagnostic Input for A12/HE5050 couple in xx3450 pouch cells
  - Gen2 (1.2M $LiPF_6$ in EC:EMC 3:7wt.%)
  - Gen2 + 2wt.% LiDFOB
  - Gen2 + 2wt.% LiDFOB + 1wt.% LiBOB



- The above pouch cells performance (B9A, B9B, B9C) did not replicate the improved coin cell performance with the additives. The formation process in the pouch cell, with additives, is being examined to see the effect on cell performance.

Cycling @ C/2 Rate, 30°C



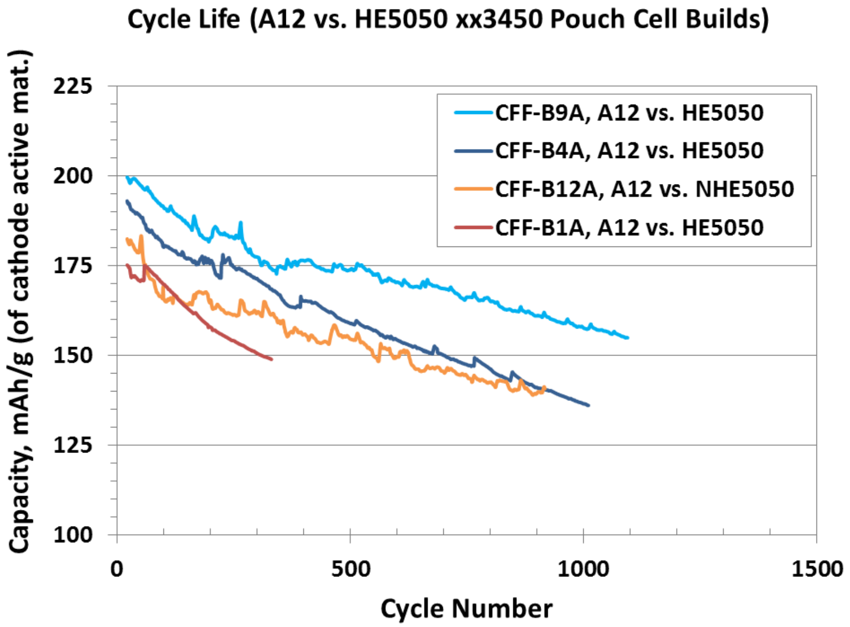


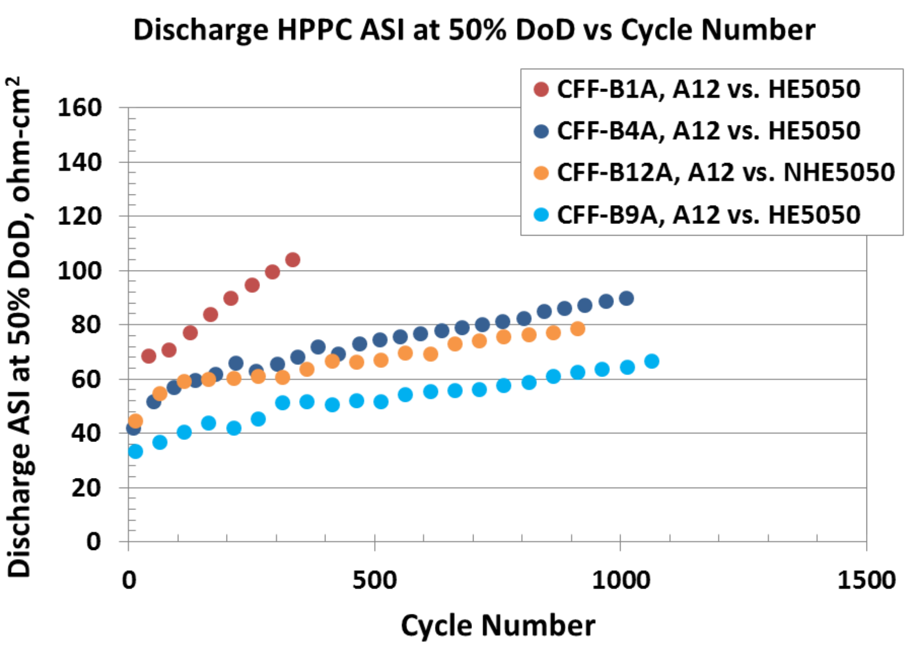
- *Improved performance in cycle life and initial HPPC using the MERF LiDFOB additive

Electrode Optimization

Cycling @ C/2 Rate, 30°C

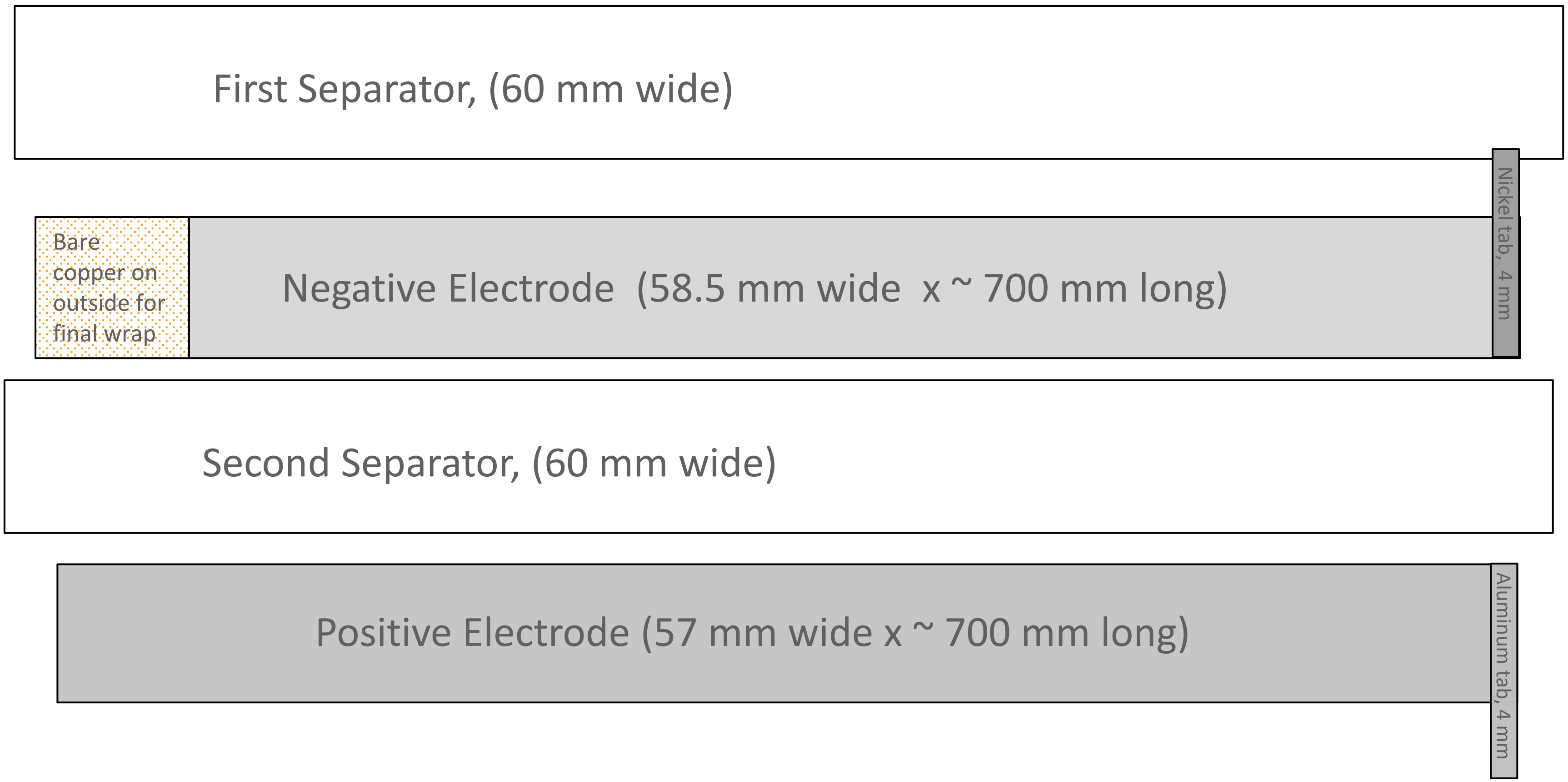
- Improved cell performance by implementing high shear mixing process for electrode making
  - Compare B1A (Ball Milling) to B4A (High Shear Mixing) performance
- Optimized A12 and HE5050 electrodes based on diagnostics studies:
  - Modified electrode composition by using reference electrode cell data to determine electrode impedance
  - Compare B4A (Initial) to B9A (Optimized) performance





18650 Cells

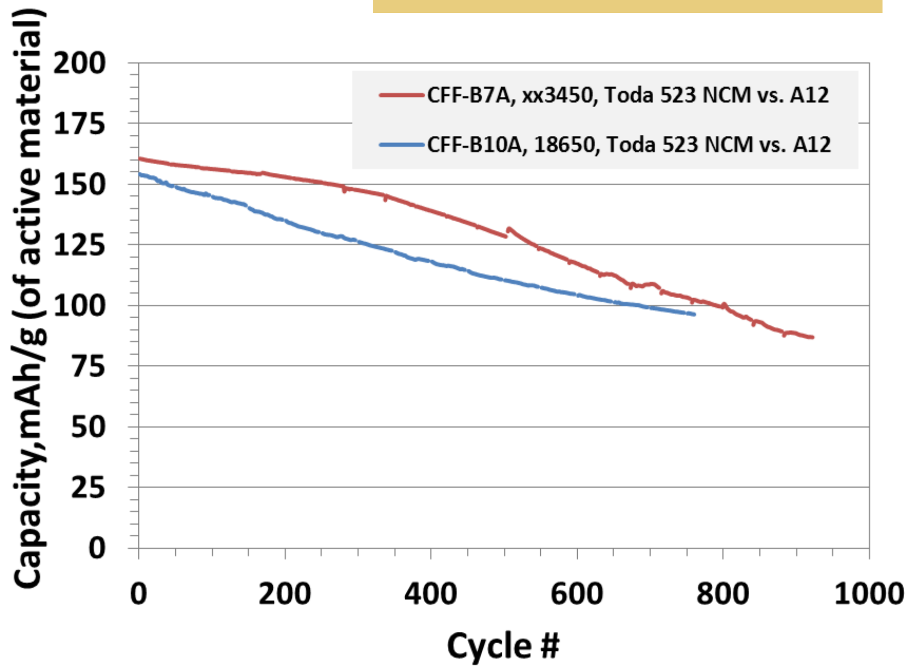
- 18650 Cell
  - Cathode Electrode Dimensions : 56.0 mm W x ~701 mm L
    - Cathode Electrode Area : 393 cm^2 per side
  - Anode Electrode Dimension : 58.0 mm W x ~701 mm L
    - Anode Electrode Area : 407 cm^2 per side

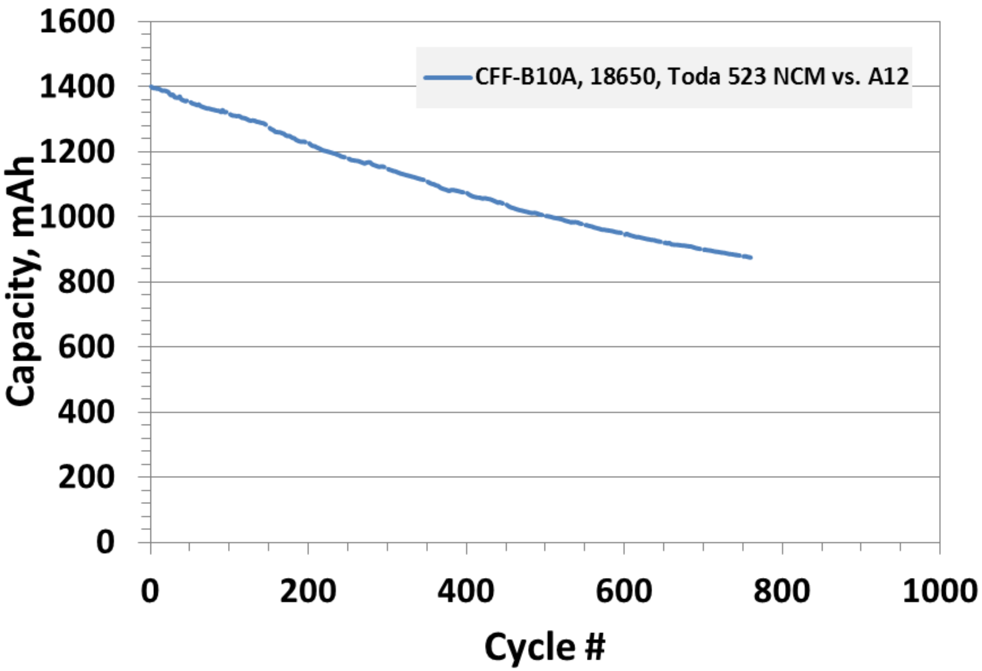


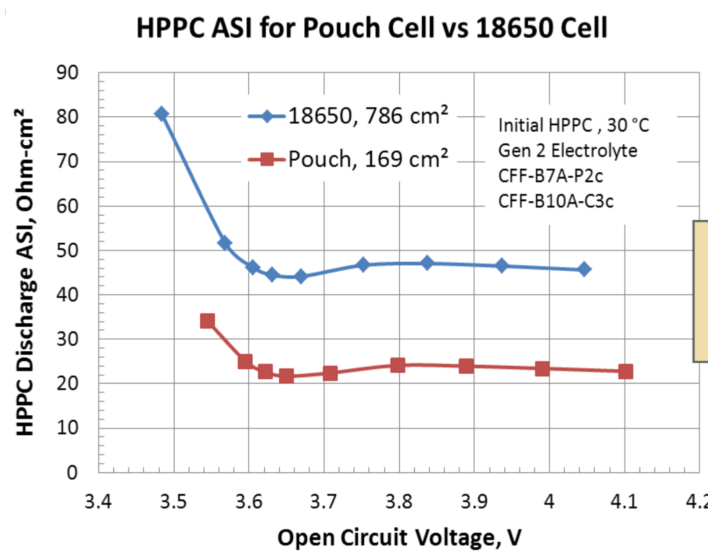
18650 Cell Performance and Pouch Cell Comparison

- 18650 cells and xx3450 pouch cells were made with identical anodes and cathodes. The graph below shows the performance of the 18650 cell. The graphs on the right show the performance difference between the two different cell types.

Cycling @ C/2 Rate, 4.2V max, 30°C

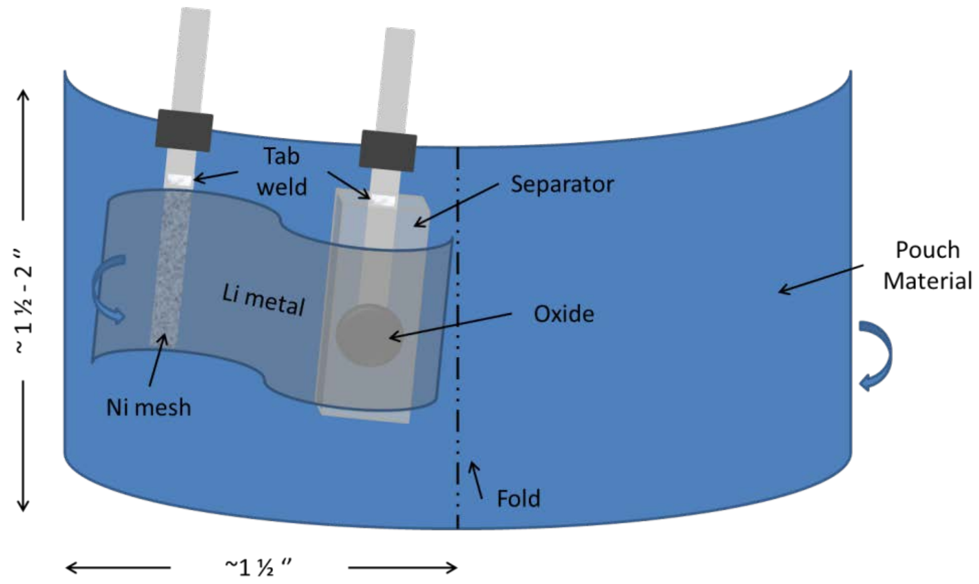






Difference in ASI due to tabbing

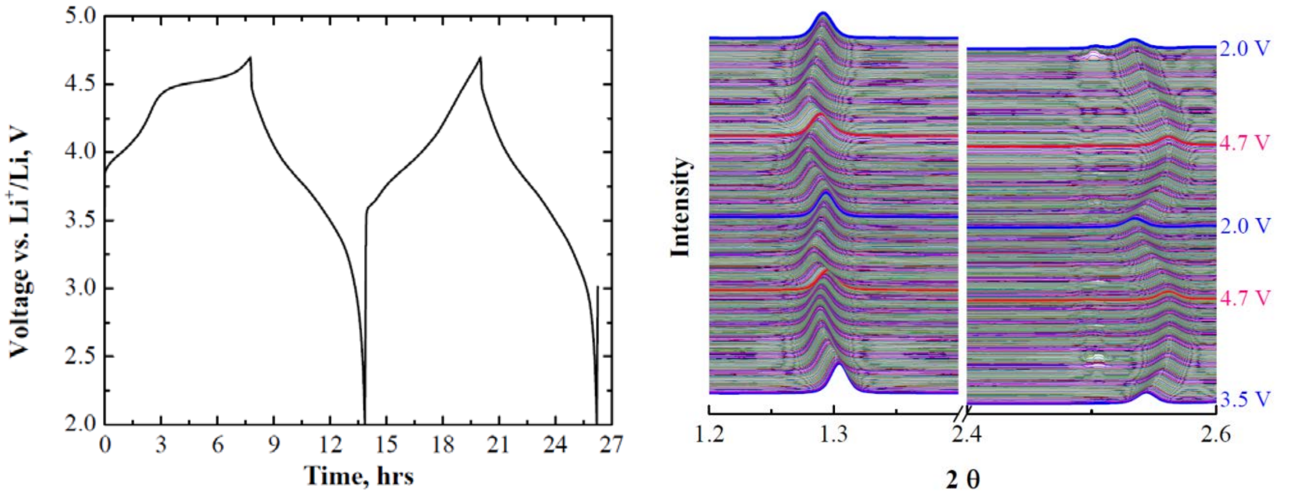
Advanced Analytical Cells



Chemistries Tested	
ANODE	CATHODE
Li	Li1.2Ti0.4Cr0.4O2
Li	Se/SeS
LTO	5V Spinel
A12	HE5050
Li	LiVPO4F
Li	Li2MnO3
Li	Li1.2Mn0.6Ni0.2O2

- Cells have been made for use at the Advanced Photon Source located at Argonne National Laboratory
- Thus far, APS Cell studies include in situ XAFS, XANES, HRXRD, and HEXRD

HEXRD of HE5050 vs. Li, Gen2 electrolyte

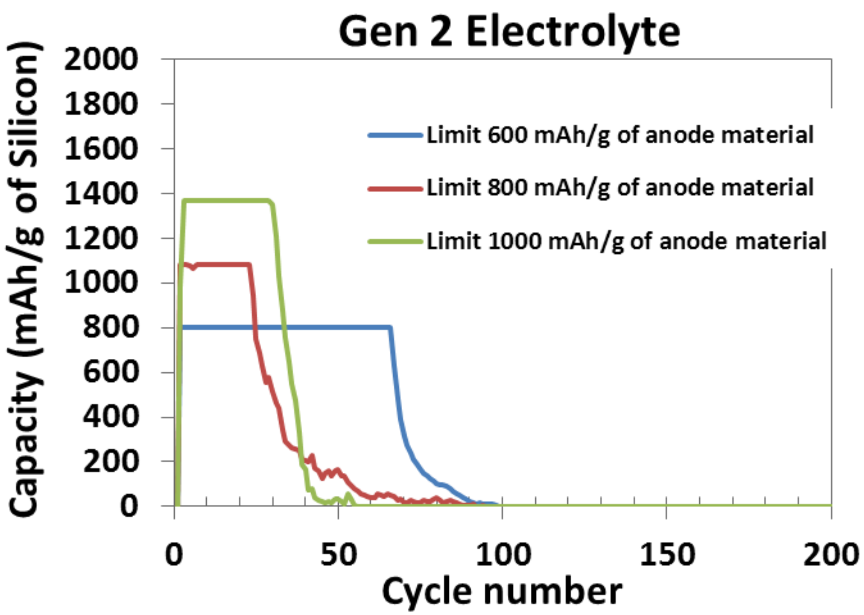


Silicon Anodes

- In order to create a working Si and Si/Graphite composite electrode, much of the work done with silicon has been optimizing a binder system that is able to accommodate the large volume changes of the silicon during cycling
- Initial efforts have taken place for coating Si and Si/Graphite slurries in the CFF

Binder	Pros	Cons
Na-Alginate + Buffer	▪ High degree of cyclability ▪ Relatively inexpensive ▪ Easy to mix ▪ Non-hazardous ▪ Generally works well with 1 pot mixing	▪ Binder solutions can not be stored for long periods of time (< 1 week) ▪ Laminates can be brittle if the binder concentration is too high ▪ Sodium ions add extra inactive material, increases amount of binder required
Li-PAA	▪ Doesn't hydrolyze in water ▪ High degree of cyclability	▪ Laminates are brittle ▪ Binder traps air bubbles
CMC	▪ High degree of cyclability ▪ Relatively inexpensive ▪ Non-hazardous ▪ Coats relatively well	▪ Because the concentration of a usable CMC binder solution is ~1%, it becomes hard to create a laminate with high concentrations of binder
CMC + SBR	▪ Relatively inexpensive ▪ Non-hazardous ▪ Coats relatively well	▪ Special drying scheme required to prevent migration of SBR ▪ Low shear mixing ▪ Laminates can be brittle
PVDF	▪ Makes the best electrode coating	▪ Does not cycle in uncoated silicon systems – organic-coated silicon shows promise

Silicon Anodes

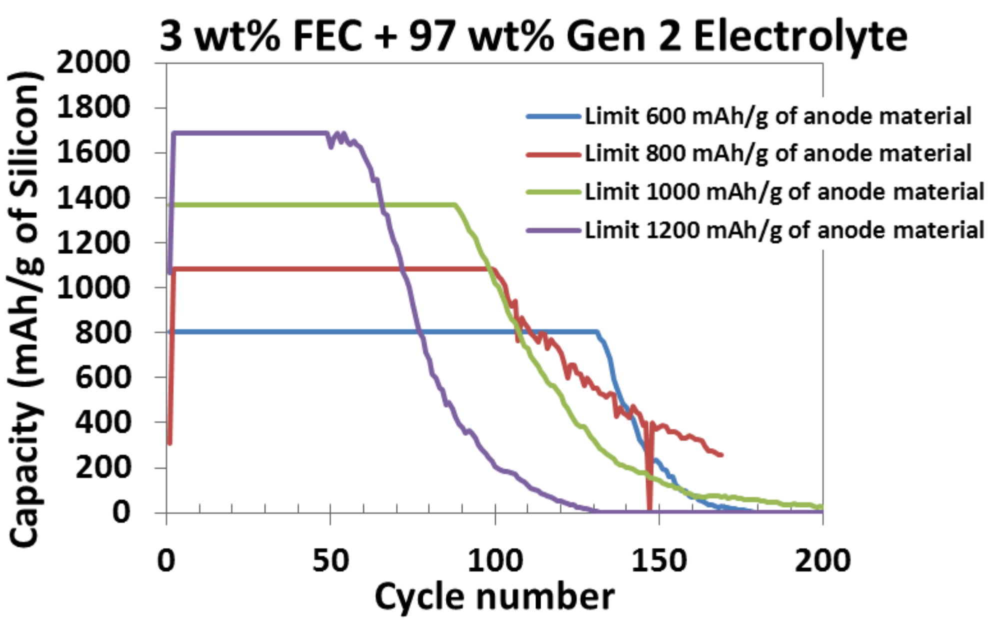


Current work being done

- Si and Si/graphite composites
- Electrolyte additives (FEC)
- Different Binders
- Limiting Capacities \ Voltage Cutoffs
- Range of Silicon morphologies
  - 100 nm to 10 µm range
- Slurry additives
  - (Acids, bases, thickening agents)

Electrode Composition (applies to plots shown)
- 76% Silicon
- 14% Sodium Salt of Alginic Acid
- 10% Super P Carbon
- Citric acid buffer

Tested in CR2032 Coin Cell (Half Cell)



Electrode Library

- **The Electrode Library serves as a supply of standard electrodes that are designed to be interchangeable with one another (capacity matched)**

Electrode ID	Foil	Foil Thk (um)	Material	Batch ID	Material Wt%	Conductive Additive	Additive Wt%	Conductive Additive	Additive Wt%	Binder Solution	Binder Wt %	Other Additive	Additive Wt%	Total Calendered Electrode Thickness (um)	Calendered Electrode Porosity (%)	Coating Loading – No Foil (mg/cm²)	Specific Reversible Capacity @ ~1C (RT) (mAh/g)	Reversible Capacity @ ~1C (RT) (mAh/cm2)
A-A001	Cu	10	CPG-A12		89.8	Super P Li	4			Kureha 9300	6	Oxalic Acid	0.17	96.2	37	15.5	330	4.59
A-C001	Al	20	Toda HE5050		86	SFG-6	4	Super P Li	2	Solvey 5130	8			94	46	14	210	2.53
S-A001	Cu	10	CPG-A12		89.8	Super P Li	4			Kureha 9300	6	Oxalic Acid	0.17	50	26	6.06	330	1.80
S-C001	Al	15	Toda HE5050		86	SFG-6	4	Super P Li	2	Solvey 5130	8			50	37.1	7.44	210	1.34
S-C002	Al	20	Toda NCA		86	SFG-6	4	Super P Li	2	Solvey 5130	8			65	30.8	11.59	150	1.50
E-A001	Cu	10	LTO		84	Carbon Black	6			Unknown	10			60		9.6	140	1.13
A-C002	Al	20	$Li_{1.2}Ni_{0.3}Mn_{0.6}O_{2.1}$	101217 Blend	84	SFG-6	4	Super P Li	4	Solvey 5130	8			60	45	7.73	217	1.41
A-C003	Al	20	$Li_1Mn_{1.5}Ni_{0.5}O_4$	NEI SP-10 5V Spinel	84	Super P Li	8			Solvey 5130	8			92	38.5	14.36	125	1.51
A-C003A	Al	20	$Li_1Mn_{1.5}Ni_{0.5}O_4$	NEI SP-10 5V Spinel	84	Super P Li	8			Solvey 5130	8			82	33.1	15.05	125	1.58
A-A002	Cu	10	CPG-A12		91.8	C45	2			Kureha 9300	6	Oxalic Acid	0.17	53	38.8	5.71	330	1.73
A-A003	Cu	10	CPG-A12		92	Super P Li	2			Kureha 9300	6			60	37.7	6.74	330	2.05
A-C004	Al	20	Toda 523	NCM-04ST, Lot# 240202	90	Denka Carbon	5			Solvey 5130	5			70	37.7	12.63	145	1.65
A-C005	Al	20	Toda 523	NCM-04ST, Lot# 240202	90	Denka Carbon	5			Solvey 5130	5			58	30	10.89	145	1.42
A-C006	Al	20	Toda HE5050	Lot# 5-P767	92	C45	4			Solvey 5130	4			46	36.1	6.4	210	1.24
A-A004	Al	20	LTO	NEI Corp - BE-10	87	C45	5			Kureha 9300	8			84	33.9	13.14	165.9	1.90

- **Electrodes are available upon request (1 sheet = 110 mm by 220 mm coating area)**
- **Special request electrodes can be made with a minimum of 50 g of active material**
- **Materials coming soon: LFP, LCO, 4V Spinel, Hard Carbon**

Collaboration and Coordination with Other Institutions

- MERF
  - Providing feedback on Electrolyte, Additive and Cathode Material performance for process optimization
- Post Test Facility
  - Provide raw materials and cycled cells for baseline data collection
- Sandia National Laboratory
  - Working jointly on performing safety testing on xx3450 and 18650 cells produced by CFF
- Zeon Chemical
  - Collaborating on Si/Si-Graphite anode electrode fabrication and electrochemical testing
  - Evaluation of water based SBR/CMC binder system
- Toda America
  - Providing standard and experimental cathode materials for evaluation and distribution
- Army Research Laboratory
  - Providing standard electrodes for electrolyte development work
  - ARL providing electrolyte additives for future cell builds

Proposed Future Work

- Continue to make advanced cell chemistry batteries and perform electrochemical testing
- Continue the electrode optimization process on all materials / electrodes
- Continue Si and Si/Graphite development work to advance the state of Si anodes and to make standard cells and electrodes available to the battery research community
- Continue electrolyte and additive evaluation work
  - Examine how the formation process effects the performance of the electrolyte/additive in larger format cells (xx3450 and 18650)
- Continue to work with the MERF to evaluate current and future electrolytes, additives, and cathode materials in large format cells
- Continue to increase the number of available materials in the Electrode Library
- Continue support of all DOE-funded programs (ABR, BATT, SBIR, ARPA-E, etc.) by providing electrodes and cells for testing

Summary

- Completed 9 Cell builds in the past year:

CFF-B4	A12 vs. HE5050	CFF-B8	A12 vs. MERF LMR-NMC	CFF-B11	LTO vs. 5V Spinel
CFF-B5	A12 vs. 5V Spinel	CFF-B9	A12 vs. HE5050	CFF-B12	A12 vs. NHE5050
CFF-B7	A12 vs. NCM 523	CFF-B10	A12 vs. NCM 523 (18650)	CFF-B13	A12 vs. MERF LMR-NMC

- Completed 18650 cell build successfully
  - Compared performance of xx3450 pouch cells to 18650-sized cells
- Supported various battery research partners and collaborators by providing support in the form of:
  - Powders – Anode, Cathode, Binders, Carbon Additives (2012 total amount ~7kg)
  - Single Side Electrode Sheets – Anode and Cathodes (2012 total amount ~280 sheets)
  - Single Layer Pouch Cells – (2012 total amount ~40 cells)
  - xx3450 Pouch Cells – (2012 total amount ~35 cells)
- Started development of silicon based anodes for future high energy cell builds

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- Post-Test Facility (PTF)
- Electrochemical Analysis and Diagnostic Laboratory (EADL)

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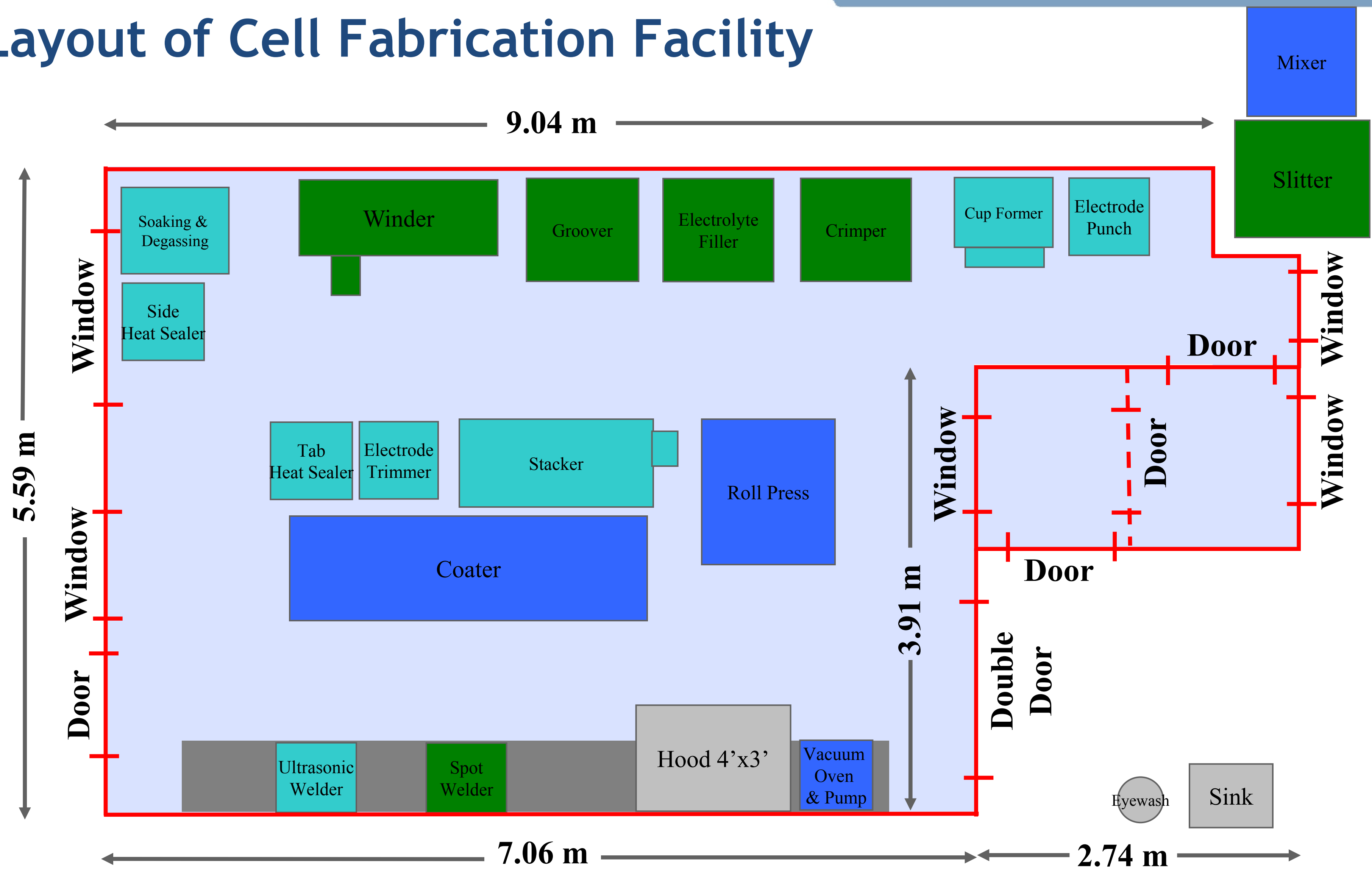
Technical Back Up Slides

Layout of Cell Fabrication Facility



Argonne's Dry Room Cell Fabrication Facility

(Interior Dimensions)

Pouch Cell Making Equipment Installed in Dry Room