Cell Fabrication Facility Team Production and Research Activities

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Argonne National Laboratory

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Washington, D.C.

Project ID: ES030

This presentation does not contain any proprietary, confidential, or otherwise restricted information.

Overview

Timeline

- Start: October 1, 2012
- Finish: September 30, 2014
- ~25% Complete

Budget

- $2500K FY13 (Effort Total)
  - 100% DOE-ABR
- Restructured as a DOE core-funded effort for FY13

Barriers

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

Partners

- Sandia and Oak Ridge National Labs
- Phillips 66
- Toda America
- Zeon Chemicals
- Solvay Solexis
- Kureha
- Illinois Institute of Technology
- University of Illinois
- Purdue University
- University of Rochester

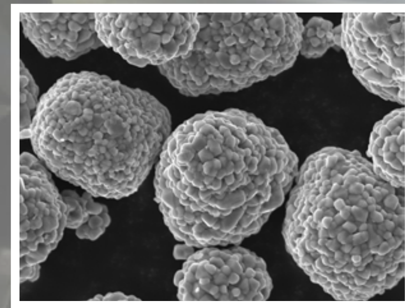
Relevance/Objectives

- Transition new advanced battery chemistries invented in research laboratories to industrial production through independent validation and analysis in prototype cell formats (xx3450 pouch & 18650 cells).

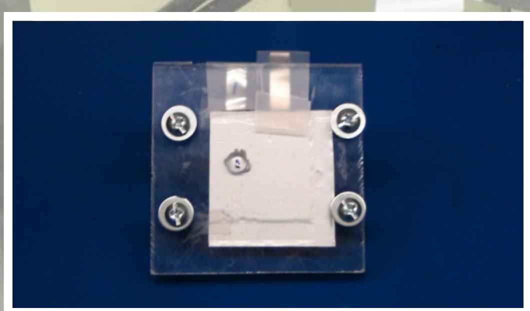
Milestones

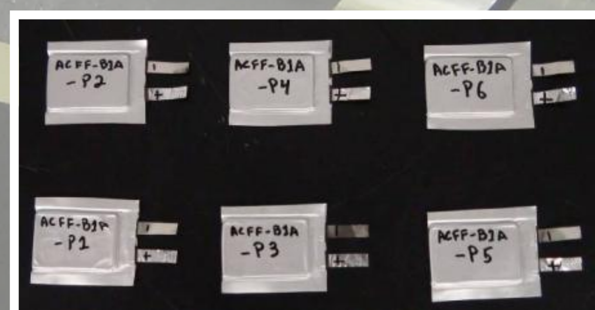
Restructured CFF activities into a core-funded team	**October, 2012**
Completed trial 18650 cell build	September, 2012
Released BatPac v2.1 to general public online	December, 2012
Evaluate second batch of scaled-up R&D cathode material from MERF	May, 2013
Examine impedance rise of LMR-NMC system	September, 2013
Evaluate silicon-carbon-binder systems	September, 2013

The CFF Team Turns Powder into Cells

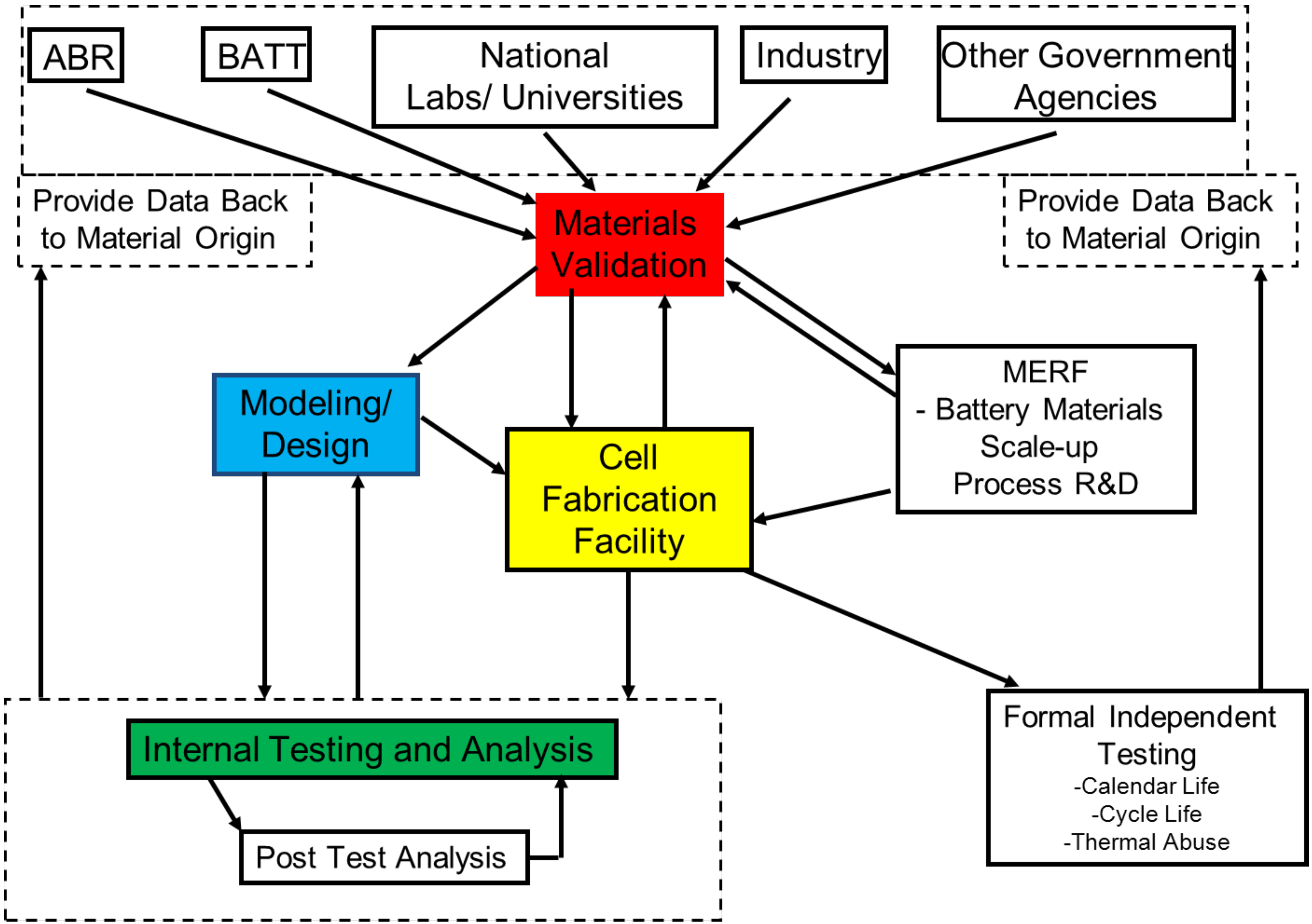


Today's talk will give a sampling of how





Cell Fabrication Facility Team Approach



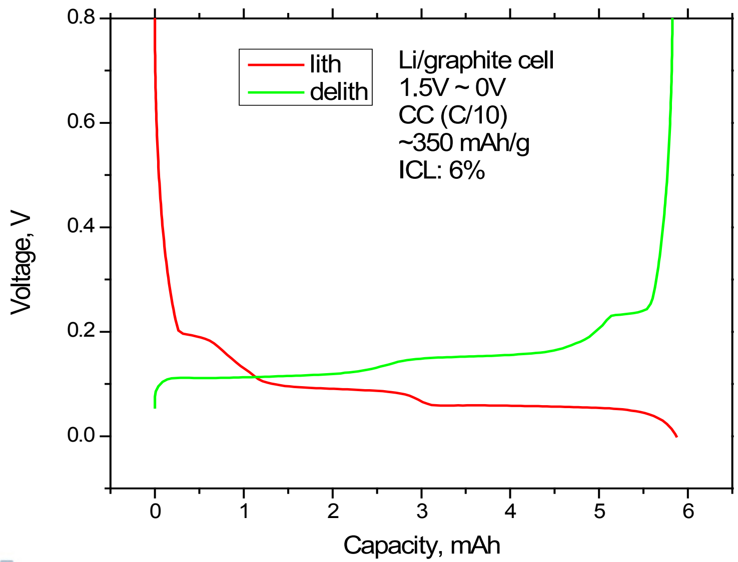
All Paths Begin with Materials Validation

which is usually done in a coin cell format

Coin Cell Data

Phillips 66 CPreme® A12 graphite was selected early in the ABR Program to be the high energy baseline anode.

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

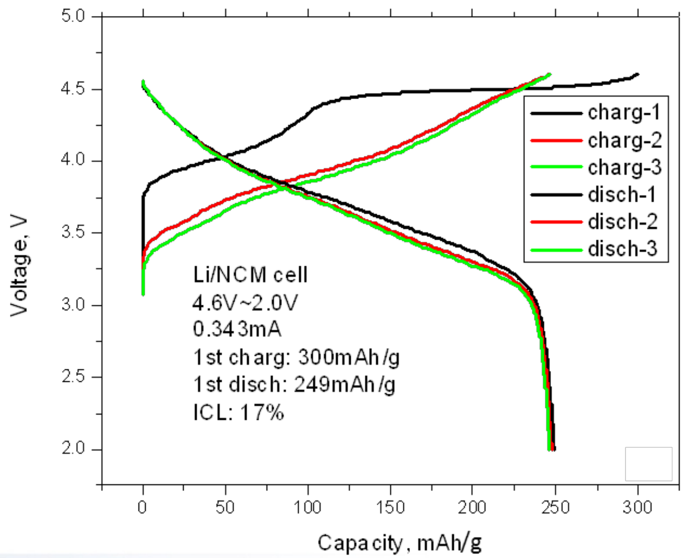


D50	4.9
Tap	1.05
BET	2.63
1st	
charge	320
discharge	270
ICL	13.7

Toda HE5050 was selected early in the ABR Program to be the high energy baseline cathode.

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

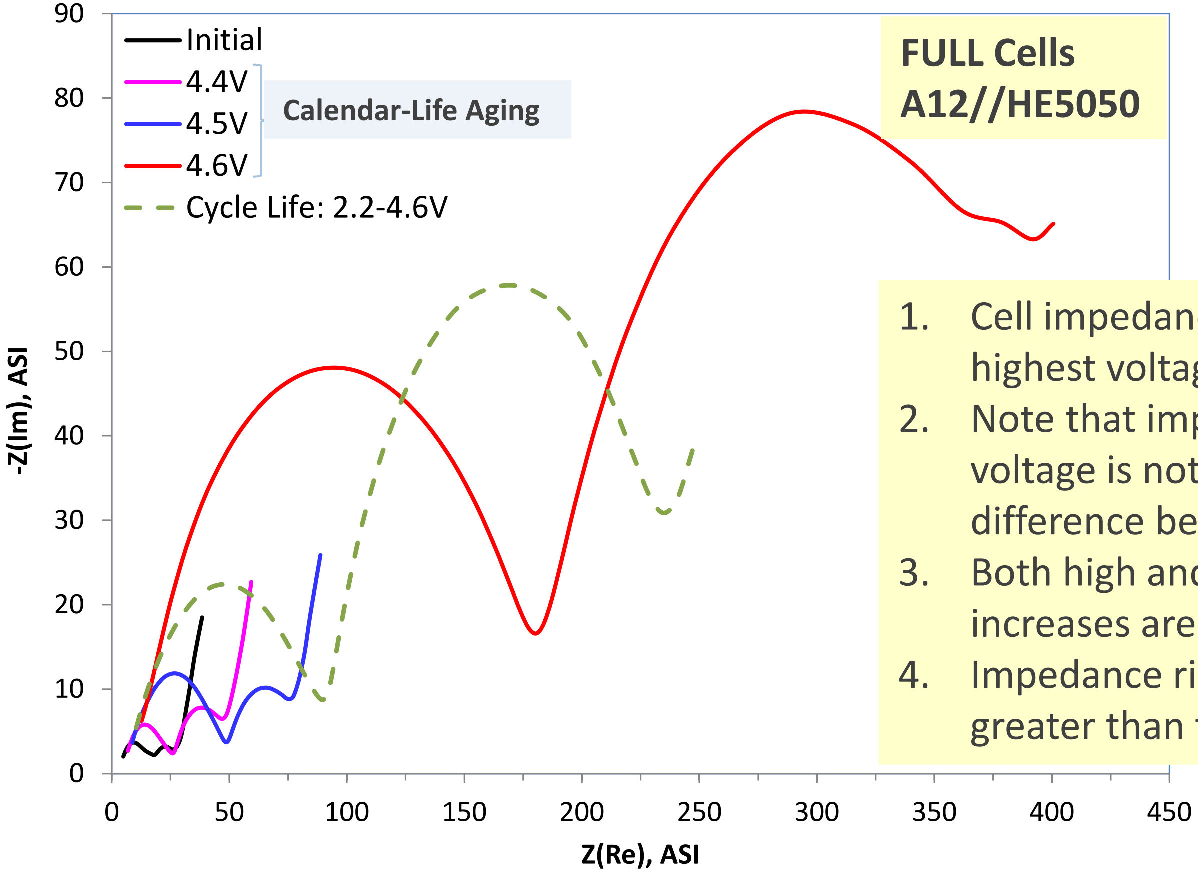
$(0.49Li_2MnO_3 \bullet 0.51LiNi_{0.37}Co_{0.24}Mn_{0.39}O_2)$



Selection of Upper Cutoff Voltage (UCV) for Cell Testing

Full Cells, EIS data, 3.75V, 30°C, 100 kHz-0.01Hz
Calendar Life Aging, 356h, 30°C, 4.4, 4.5, 4.6V. The 2.2 – 4.6V cycle life test took 356h

Coin Cell Data

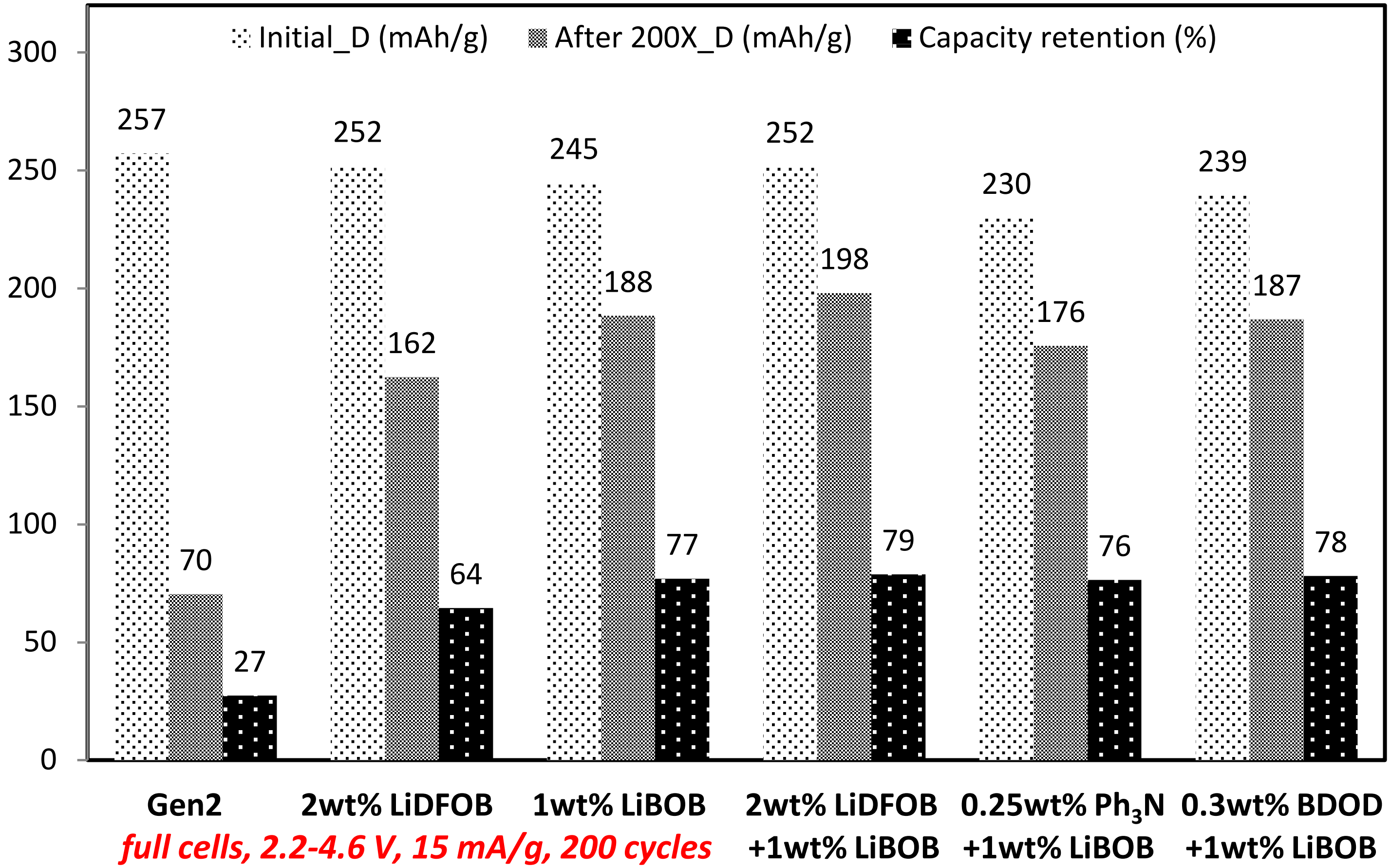


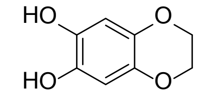
1. Cell impedance increase is greatest at the highest voltage.
2. Note that impedance increase vs. cell voltage is not linear – there is a significant difference between the 4.5 and 4.6V hold.
3. Both high and mid-frequency arc increases are affected by cell voltage
4. Impedance rise for cell held at 4.6V is greater than for 2–4.6V, 50-cycles, cell

The Upper Cutoff Voltage has a significant effect on cell performance degradation
Recommended an UCV of 4.4V to minimize cell impedance rise

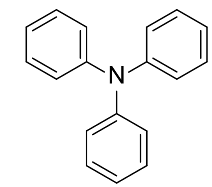
Electrolyte Additives Improve Capacity Retention of LMR-NMC (A12//HE5050)

Coin Cell Data

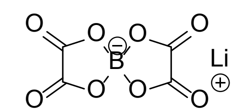




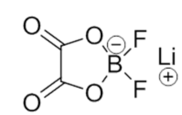
1,4-benzodiozane-6,7-diol
BDOD



triphenylamine
Ph_3N



LiBOB



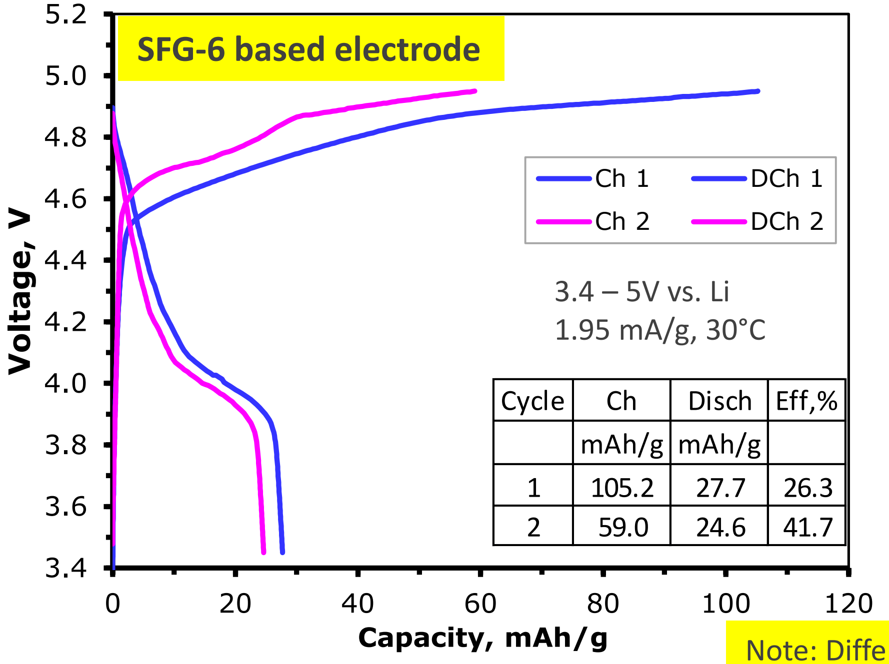
LiDFOB

Cells containing LiDFOB (half-BOB) or a LiDFOB+LiBOB mixture added to the Gen2 electrolyte show the best performance. Therefore, these additives were recommended for the CFF cell builds.

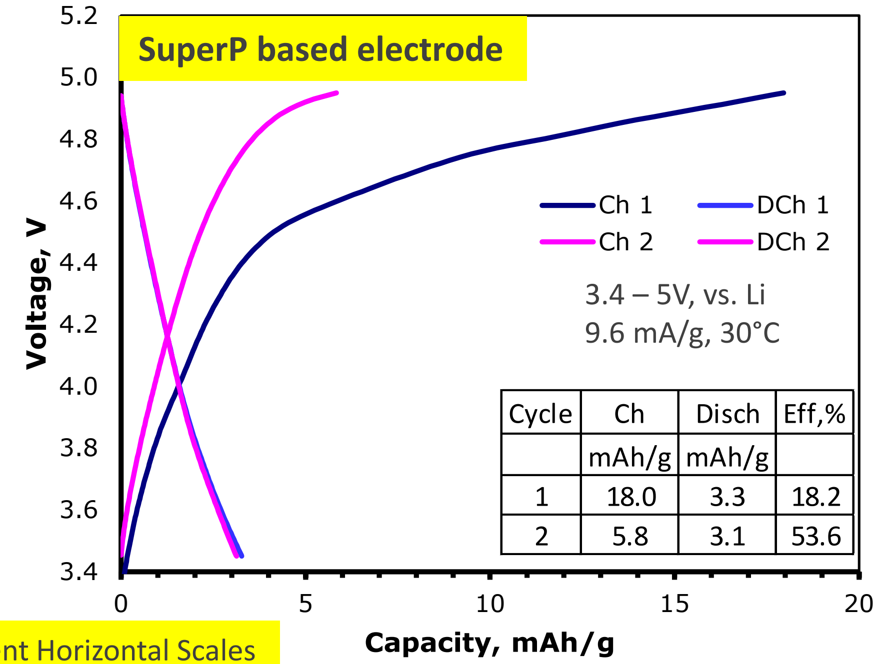
Ref: Zhu et al., Electrochim. Acta, accepted for publication

Positive Electrode Carbons Can be Electrochemically Active at High Cell Voltages

Coin Cell Data



Cycle	Ch	Disch	Eff,%
	mAh/g	mAh/g	
1	105.2	27.7	26.3
2	59.0	24.6	41.7



Cycle	Ch	Disch	Eff,%
	mAh/g	mAh/g	
1	18.0	3.3	18.2
2	5.8	3.1	53.6

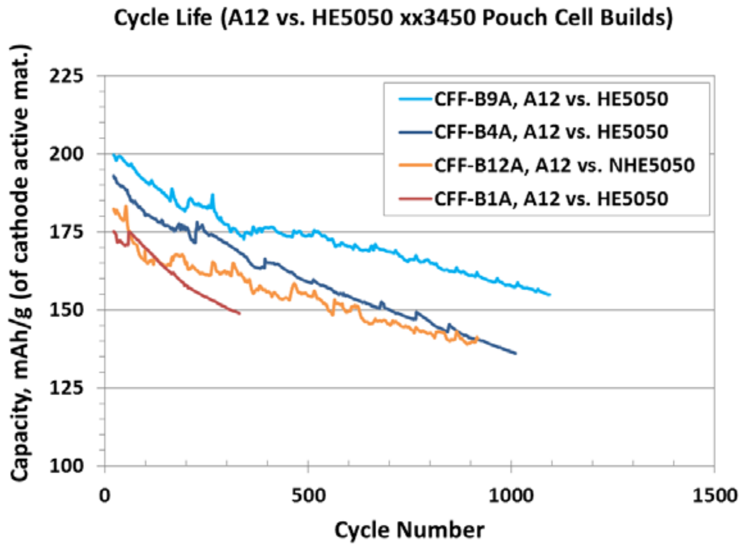
Note: Different Horizontal Scales

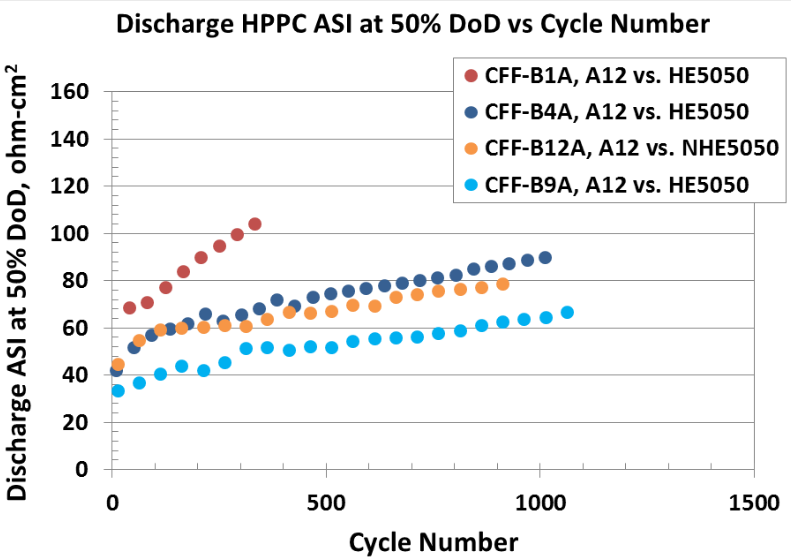
The reversible capacity is probably due to PF_6^- intercalation into the graphite; this capacity increases with the upper cut-off voltage limit. Note the coulombic inefficiency; which suggests significant electrolyte oxidation on the graphite surface. All capacities decrease on cycling, but do not go to zero.

PF_6^- intercalation is not expected to occur into the SuperP carbons; the reversible capacity is, therefore, small. The coulombic inefficiency is high, which again suggests significant electrolyte oxidation on the carbons. All capacities decrease on cycling but remain finite, especially the charge capacities.

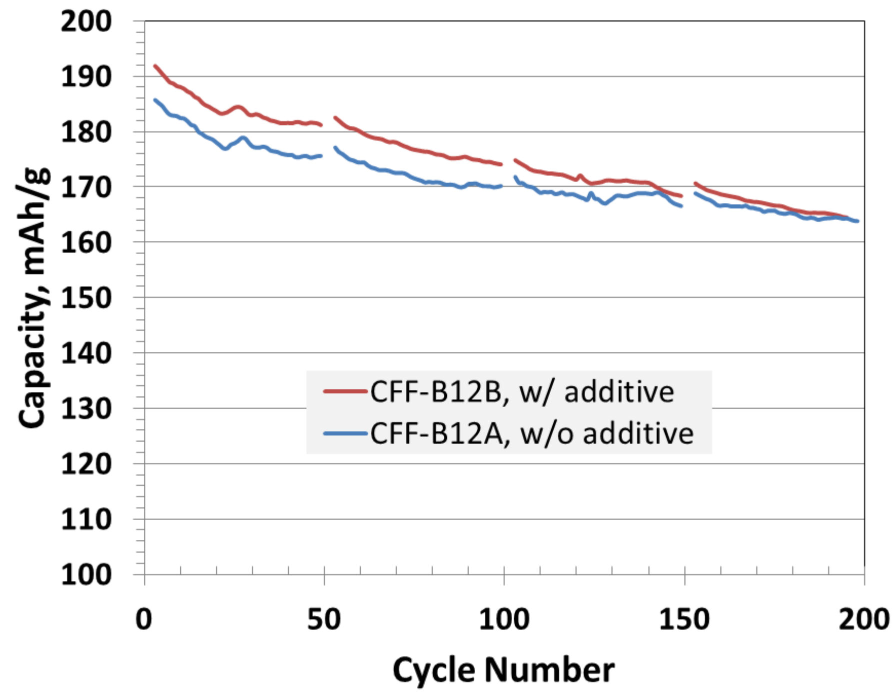
Optimizations Made in Electrodes and Cell System

Electrode Optimization





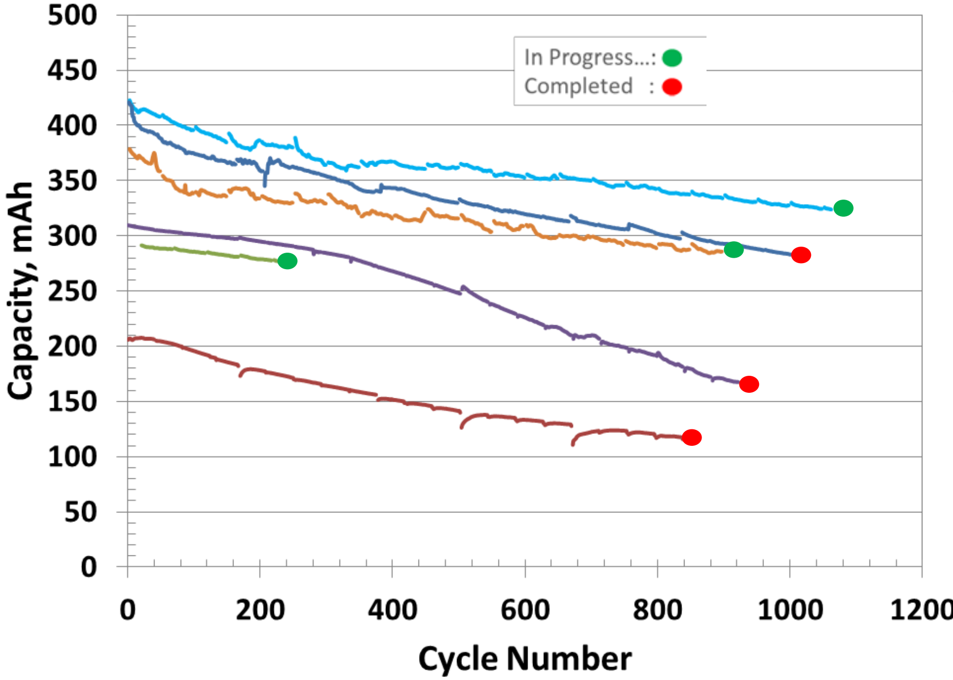
Cell Optimization



Build ID	Description	Electrolyte
CFF-B12A	**NHE-5050** "92/4/4" vs. **A12** "91.8/2/6/0.17"	Gen2 (1.2M $LiPF_6$ in EC:EMC (3:7 by wt.%))
CFF-B12B	**NHE-5050** "92/4/4" vs. **A12** "91.8/2/6/0.17"	Gen2 + 2wt.% LiDFOB (made by MERF)

Cycling @ C/2 Rate, 30°C

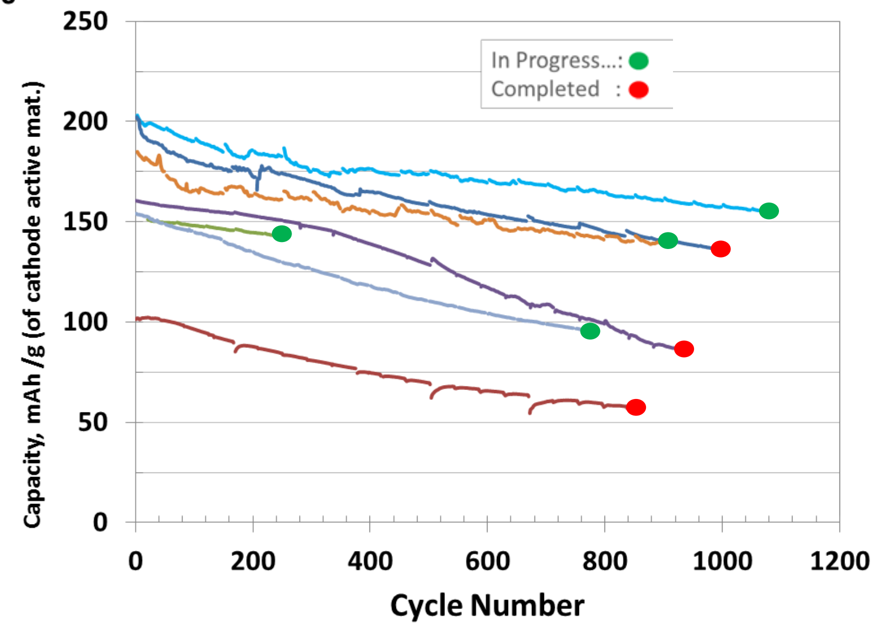
CFF Baseline Cell Build Life Cycle Summary



Cell Assembly

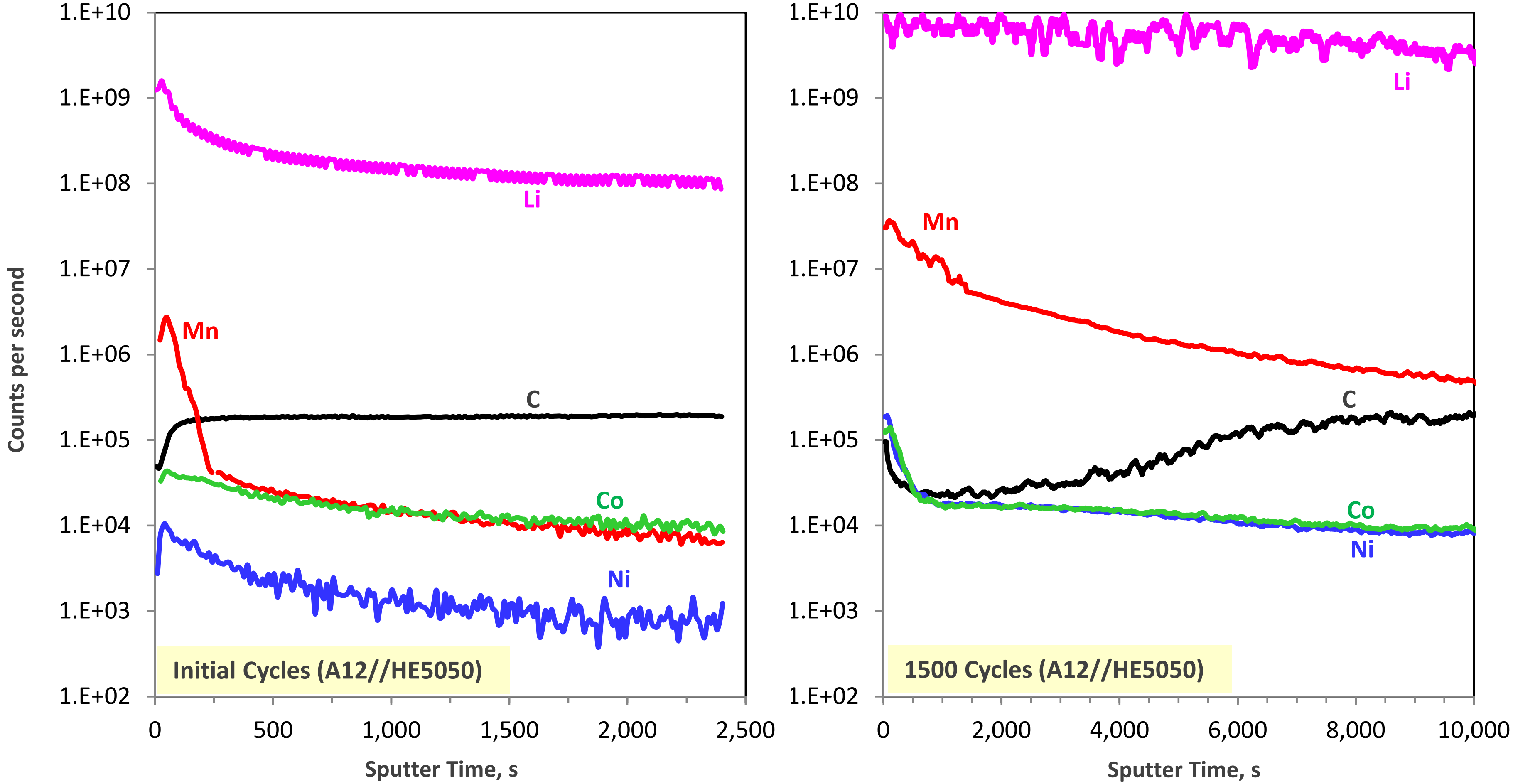
– Total Number of Layers : 13
  - Cathode : 5 Double Side Layers
    + 2 Single Side Layers (outer 2 electrodes)
  - Anode : 6 Double Side Layers
– Separator: Celgard 2325 - Trilayer PP/PE/PP
– Electrolyte: 1.2M $LiPF_6$ in EC:EMC (3:7 wt%) (Tomiyama)

- CFF-B9A, A12 vs. HE5050
- CFF-B4A, A12 vs. HE5050
- CFF-B12A, A12 vs. NHE5050
- CFF-B7A, A12 vs. NCM 523 (4.2V max)
- CFF-B7A, A12 vs. NCM 523 (4.1V max)
- CFF-B10A, A12 vs. NCM 523 (18650)
- CFF-B5A, A12 vs. 5V Spinel



Cycling @ C/2 Rate, 30°C

SIMS Sputter Depth Profiles Show Li, Mn, Ni, Co Accumulation at the Graphite Negative Electrode

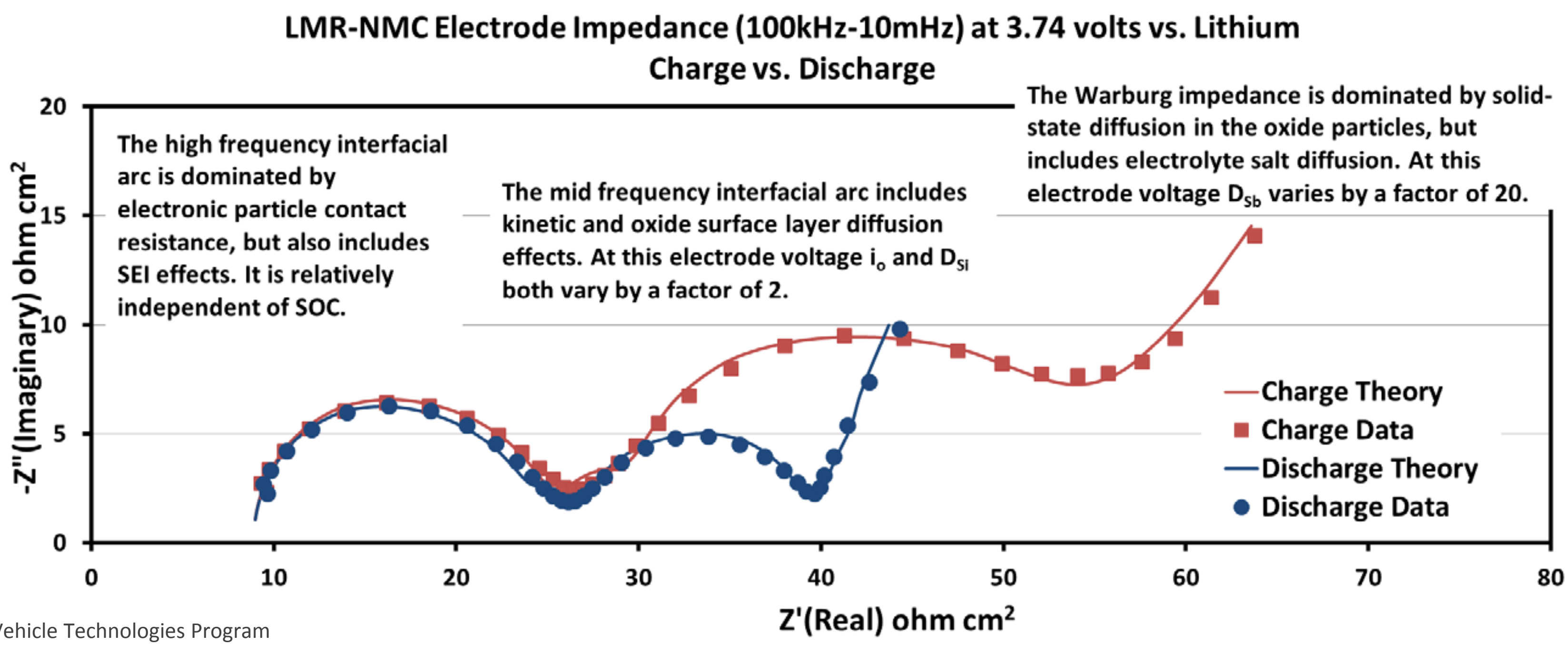


SEI is thicker after cycling/aging. This is seen from the C profiles; longer sputter times are needed to obtain steady state values for the 1500 cycle sample

Ref: Li et al., J. Electrochem. Soc. 160 (2013) A3006

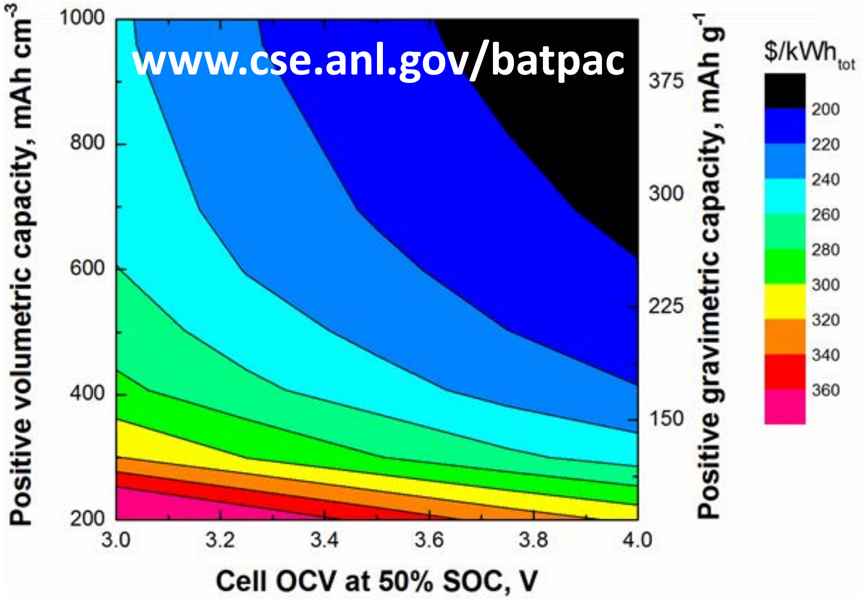
Electrochemical Modeling of LMR-NMC Electrode

- Differential and algebraic equations describing transport, thermodynamic, and kinetic phenomena are solved to determine current, potential, and concentration distributions
  - Volume-averaged continuum transport equations, also possible phase change in active particles
  - Complex active material / electrolyte interfacial structure included
  - Conducted multi-dimensional, multi-scale, and transient simulations
- Activities integrated with other CFF efforts
  - Focus this year on LMR-NMC electrode impedance effects (e.g. voltage, SOC, charge vs. discharge)
  - Additional simulations on active material individual particle performance
  - Continue study of electrode electronic conductivity effects

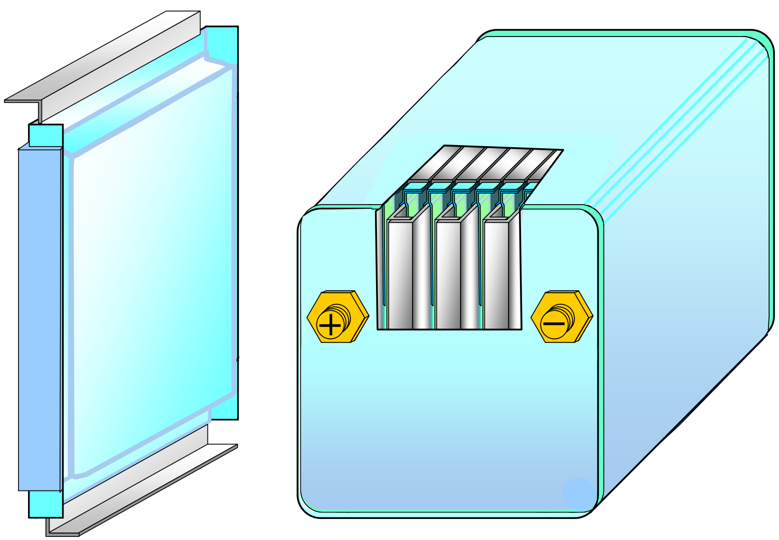


Battery Performance and Cost Modeling: BatPaC

- Efficient simulation and design tool for Li-ion batteries
  - Design and predict performance, including thermal management
  - Precise overall (and component) mass and dimensions
  - Battery pack (and component) costs
- Modeling real-world battery packs from bench-scale data

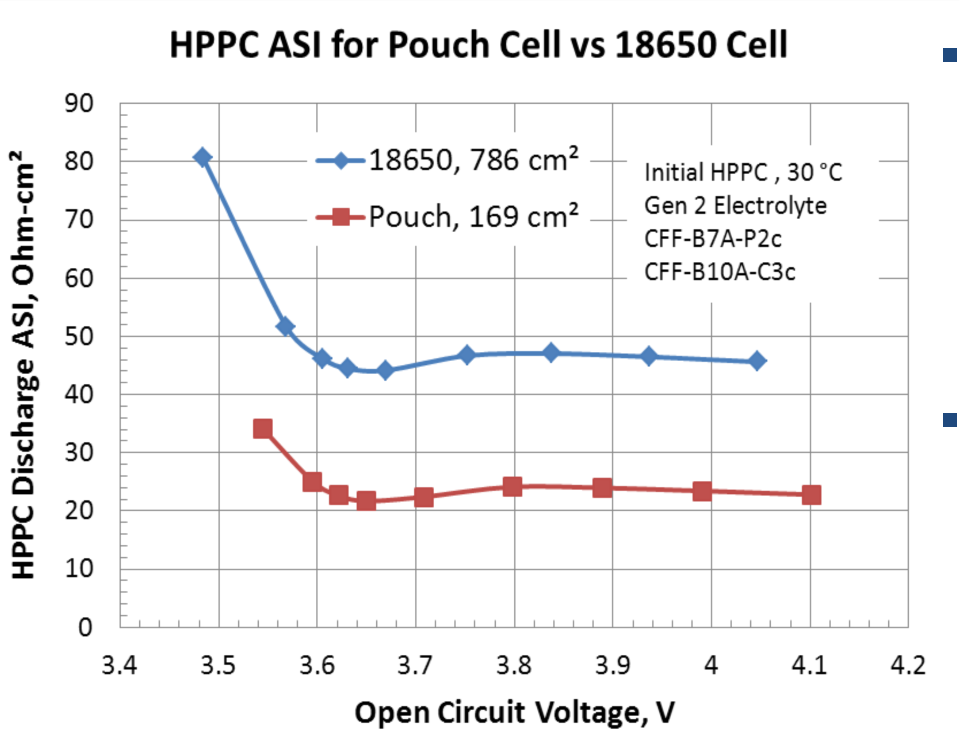


Cell and Module Design



- Examined trade-offs between voltage and capacity
  - Shown above, impact of positive electrode volumetric capacity and OCV on the price per unit energy for a PHEV40 60 kW and 17 kWh (graphite negative)
- BatPaC first openly distributed to the public in FY2012 (450 unique downloads during first year)
- Completed public release of BatPaC v2.1 with considerable improvements in thermal management , uncertainty estimates, material costs, pack configuration, and output formats

Pouch Cell Preferred over 18650 Cell due to Tabbing
(Toda NCM523 vs. Phillips 66 A12 Graphite)



- A large fraction of the cell ASI increase from the pouch to the 18650 configuration can be attributed to the current collector resistance
  - One 4 mm wide tab for 786 cm² in 18650 cell
  - Six 7 mm wide tab for 169 cm² in pouch cell
- Finite element simulations indicate that the current collector impedance in the 18650 cell configuration raises the ASI from 24 ohm cm² to 36.2 ohm cm²
  - 39.5 ohm cm² if the impedance of the tabs, from the foils to the cell housing, is included

- Fully utilize pouch cell format before attempting 18650 fabrication
  - -Conserve use of limited experimental materials
  - -Maximize utilization of dedicated MACCOR channels and chamber space
  - -Reduce capacity (thermal runaway) hazard by over 80% (2.5 Ah vs. <0.5 Ah)

Addition of FEC and Limiting the Extent of Lithiation Enhances Cycle Life

Coin Cell Data

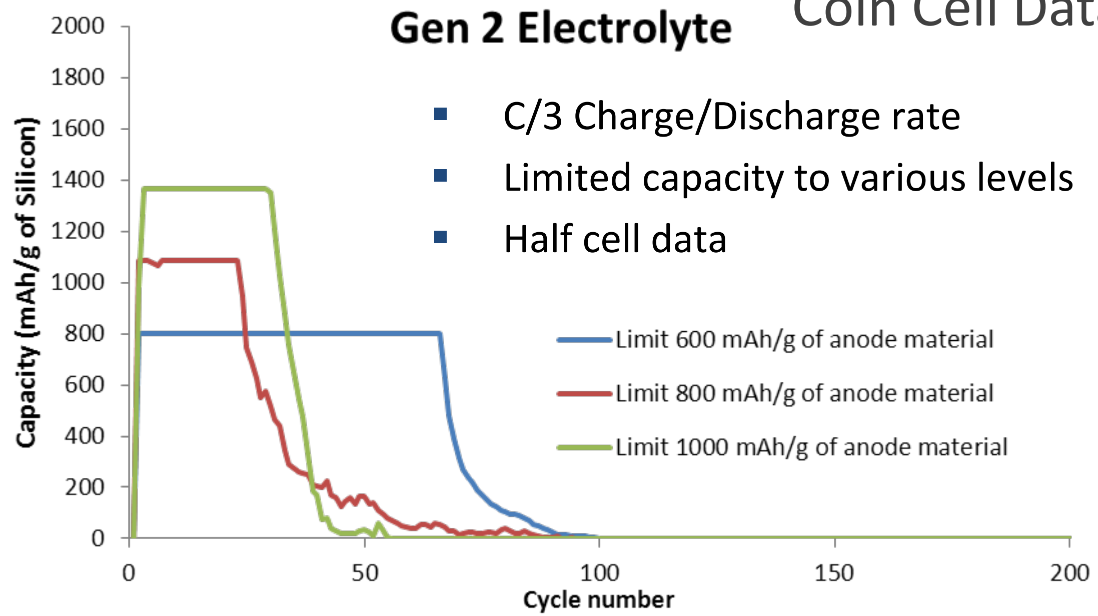
Current work being done

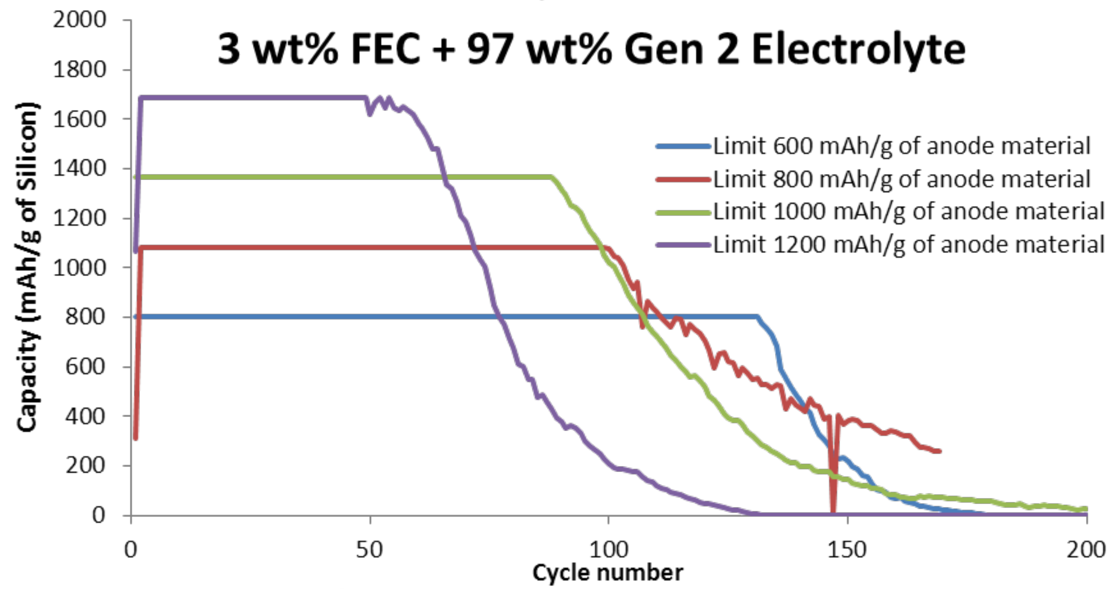
- Si and Si/graphite composites
- Electrolyte additives (FEC)
- Different Binders
- Limiting Capacities/Voltage
- Range of Silicon morphologies
  - 100 nm to 10 µm range
- Slurry additives
  - (Acids, bases, thickening agents)

Electrode Composition

- 76% Silicon
- 14% Sodium Alginate
- 10% Super P Carbon
- Citric acid buffer

- C/3 Charge/Discharge rate
- Limited capacity to various levels
- Half cell data





Silicon Electrodes Require New Binder Systems

In order to create a working Si or 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

Binder	Pros	Cons
Na-Alginate + Buffer	• Higher 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 • Higher degree of cyclability	• Laminates are brittle • Binder traps air bubbles
CMC	• Higher 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

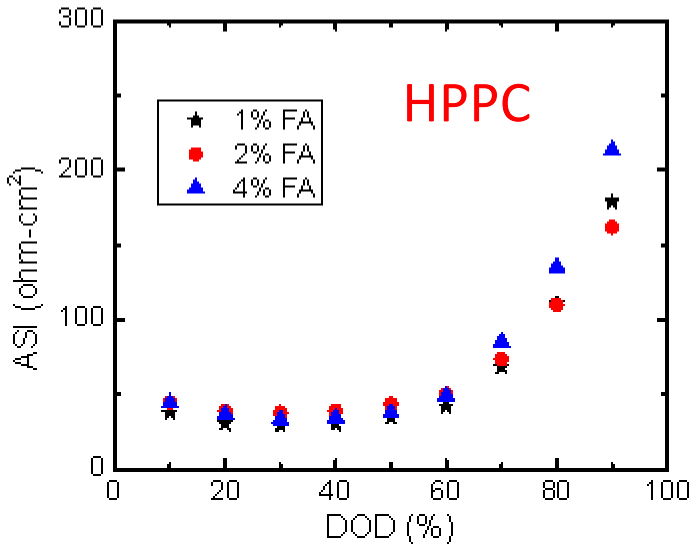
Total Aqueous Binder Lithium-ion Battery is Possible

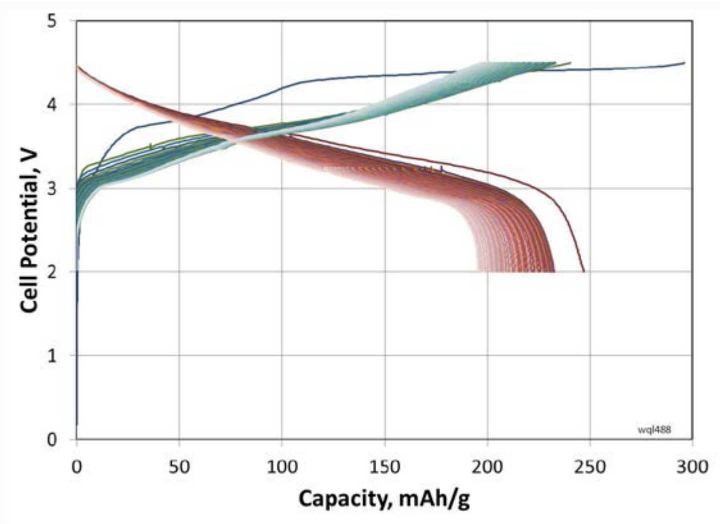
<u>Cathode</u>
LMR-NMC (HE5050, Toda)
FA (TRD202A, JSR)
CMC (MAC350HC, Nippon Paper)
Carbon black (C45, Timcal)

<u>Anode</u>
Graphite (A12, Phillips66)
SBR (TRD2001, JSR)
CMC (MAC350HC, Nippon Paper)
Carbon black (C45, Timcal)

Styrene-Butadiene Rubber (SBR)
Fluorine acrylic latex (FA)

Coin Cell Data





- Lithium ion battery with all aqueous binders for both anode and cathode were demonstrated.
- For graphite/LMR-NMC system, no obvious negative effect on electrochemical performance was observed.

Collaborations with Other Institutions

- In the past year the CFF has supplied the following items to various Universities, National Laboratories, Research Institutions, and Industry:
  - ~7 kg of Anode, Cathode, Carbon Additives and Binder
  - ~280 Sheets of Anode and Cathode Single Side Electrodes from the Electrode Library (1 Sheet = 100mm wide x 220mm long coating strip)
  - ~40 Single Layer Pouch Cells for analytical work (For use at the Advanced Photon Source at Argonne)
  - ~35 xx3450 pouch cells for Safety Testing (SNL), Neutron Studies (ORNL) and baseline testing (ANL and INL)
- Research collaborations are on-going with University of Illinois, University of Rhode Island, Purdue University, Army Research Laboratory, and Illinois Institute of Technology
- Argonne's CFF personnel coordinate their efforts with fellow electrode and cell making national labs (Sandia and Oak Ridge), and with Argonne's Post Test Facility (PTF) and Materials Engineering Research Facility (MERF)
- Numerous discussions were held with battery developers, auto industry, and the EPA in developing the BatPac battery performance and cost model
- Working relationships were established with materials suppliers regarding their material properties and applications. Relevant companies in this work shown include Phillips 66, Toda America, Zeon Chemical, JSR Micro, Solvay Solexis, and Kureha

Work in Progress/Future Work

- Continue to explore high energy cathode materials (LMR-NMC, 5V Spinel) and high energy anode materials (silicon/carbon composite) as they become available
- Investigate mechanisms in cells with silicon-based negative electrodes
  - Influence of binder-type, carbon, cycling protocols, electrode coating, and electrolyte additives
  - Still no definitive open source of battery grade silicon
- Continue development of various LMR-NMC//Graphite couples
  - Examine effect of alternative formation cycling protocols
  - Show effect of Negative to Positive capacity ratio
  - Identify electrode additives that eliminate capacity fade
  - Complete LMR-NMC impedance SEI electrochemical model and integrate into bulk material transport model
  - Determine effect of transition metal content (such as Mn) at the negative electrode
- Utilize BatPaC to further examine advanced electrode couples (improve as needed)
- Initiate development of Gr-Si electrode electrochemical model
- Continue work with MERF on scaling-up electrolyte additives and LMR-NMC $Li_{1.25}Ni_{0.3}Mn_{0.62}O_2$ (hydroxide vs. carbonate precursor)

Summary

- The Cell Fabrication Facility Team was successfully organized into a streamlined core-funded effort with the task of assessing new battery materials in industrially relevant prototype formats
- Over 14 cell builds were performed with combinations of baseline NCM523, 5V spinel, and high energy composite structure cathode materials (LMR-NMC) from Toda Kogyo, ABR researchers, and the Materials Engineering Research Facility (MERF). Over a thousand deep discharge cycles were achieved with many of these cells
- The second version of BatPac was released for the general public
- An upper voltage cutoff was determined for LMR-NMC, as well as for graphite
- Electrolyte additive study for LMR-NMC suggest the effect of additives is dependent on formation protocol and/or cell format
- The effective utilization of silicon in the anode will require a tailored silicon-carbon-binder system with limits on the silicon lithiation and use of electrolyte additives (FEC)

See Related Posters for More Information

ES028, ES032, ES185

Contributors and Acknowledgments

Argonne CFF Team

- Andrew Jansen
- Dennis Dees
- Bryant Polzin
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- Nancy Dietz-Rago
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- Khalil Amine
- Paul Nelson
- Gary Henriksen
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Outside Argonne

- Robert Kostecki (LBNL)
- Chris Orendorff (SNL)
- Kyle Fenton (SNL)
- David Wood III (ORNL)
- Claus Daniel (ORNL)
- Jai Prakash (Illinois Institute of Technology)
- Ivan Petrov (University of Illinois)
- Alex Wei (Purdue University)
- Yan Li (University of Rochester)

Research Facilities

- Materials Engineering Research Facility (MERF)
- Post-Test Facility (PTF)
- Electrochemical Analysis and Diagnostic Laboratory (EADL)
- Center for Nanoscale Materials (CNM)
- Advanced Photon Source (APS)

Industry

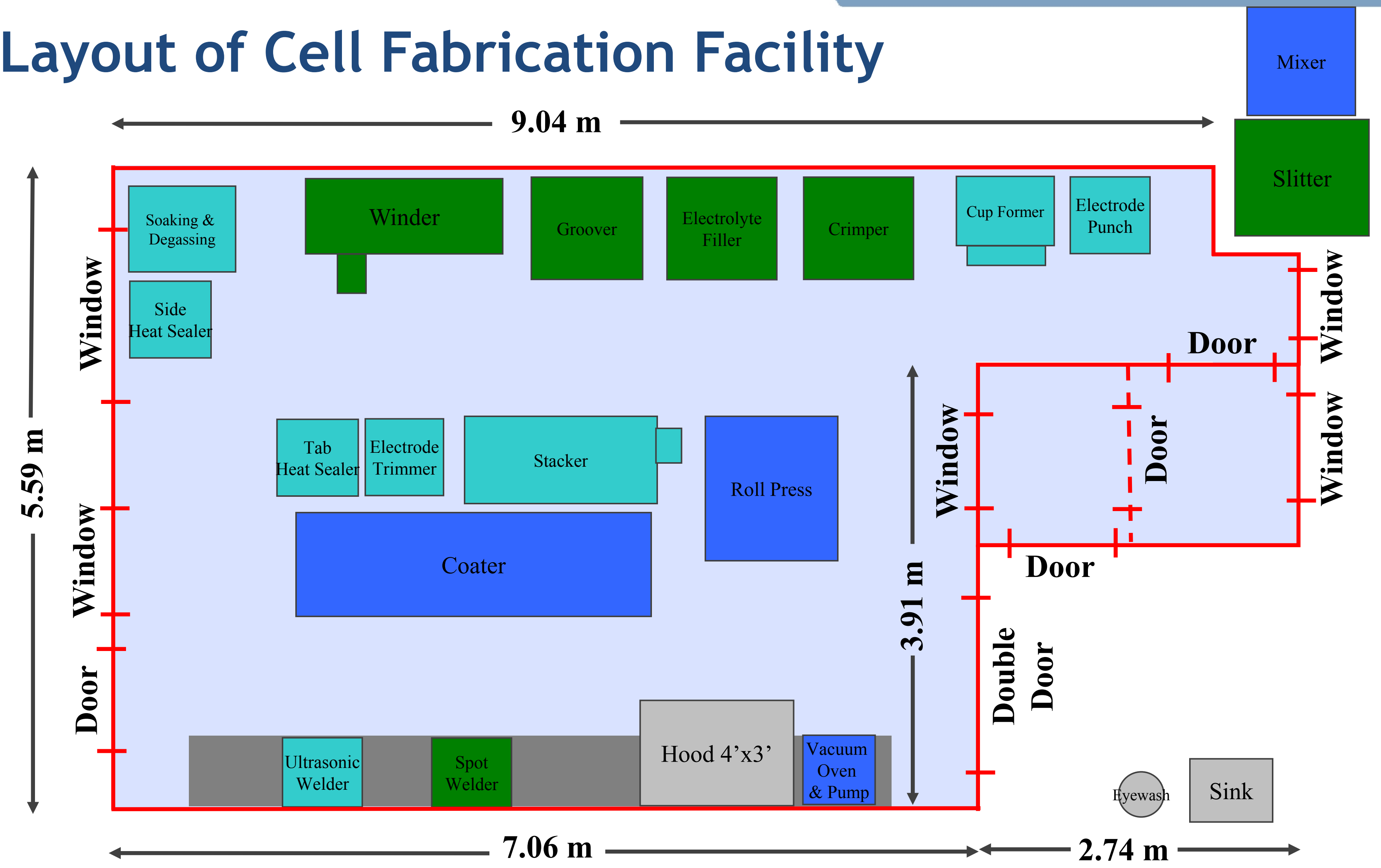
- Toda America/Kogyo
- Phillips 66
- JSR Micro
- Zeon Chemicals

Support from Peter Faguy and David Howell 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

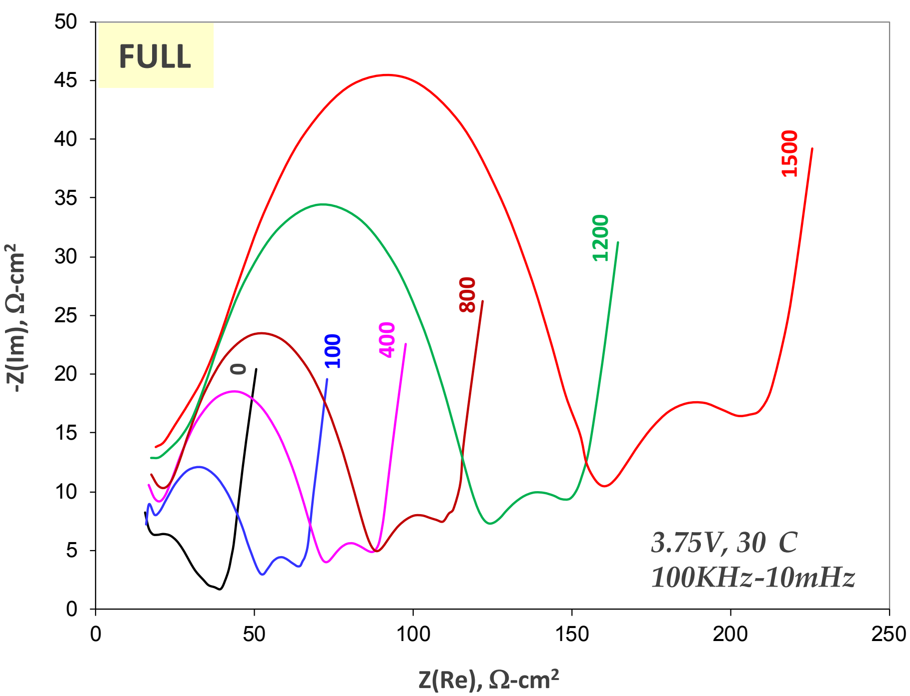
(Interior Dimensions)

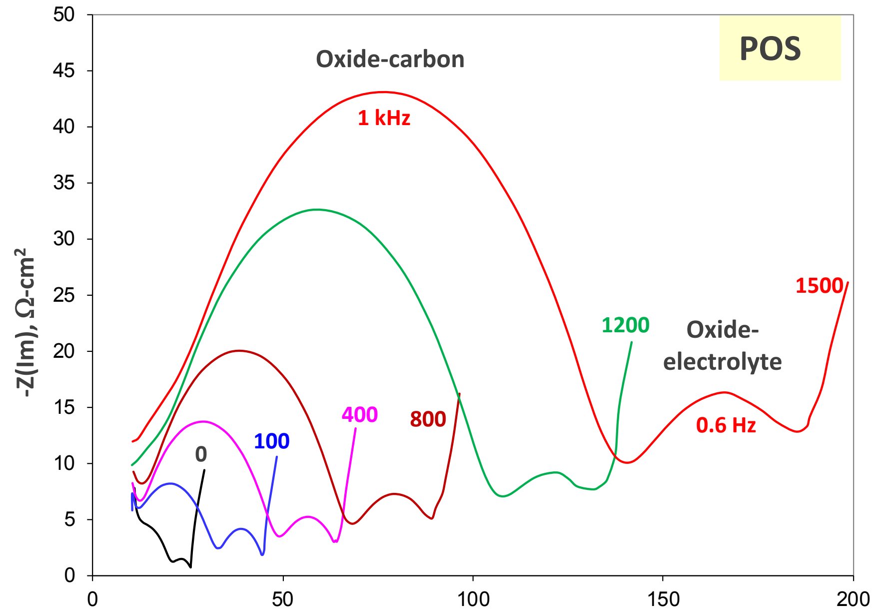
Argonne's Cell Fabrication Facility Consists of:

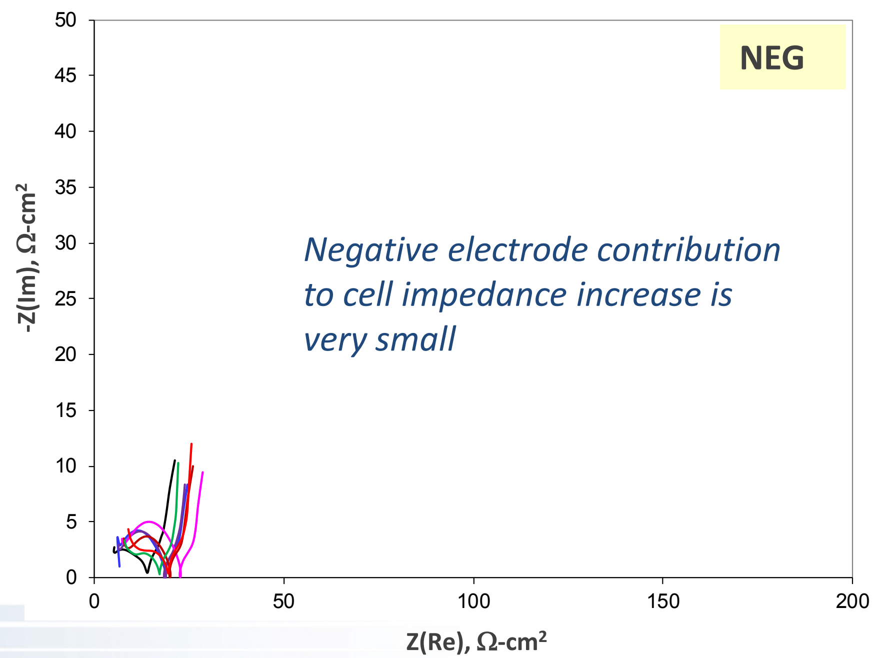
- A Ross planetary with high speed disperser Power Mixer; a high precision electrode coater with two drying ovens; and a hot roll press, which enables the fabrication of high quality electrodes in the range of 5 to 50 m.
- Semi-automated equipment to make xx3450 lithium-ion pouch cells with a typical capacity of 200 to 500 mAh.
- Semi-automated equipment to make 18650 lithium-ion cells with a typical capacity of 1 to 3 Ah.
- Most equipment located in a dry room with an area of ~45 m^2 that is capable of maintaining <100 PPMv (-42°C dew point) with 6 people working and 750 SCFM of exhaust ventilation.

Cells show impedance rise on aging

After 30°cycling in the 2.5-4.4V voltage window – up to 1500 cycles





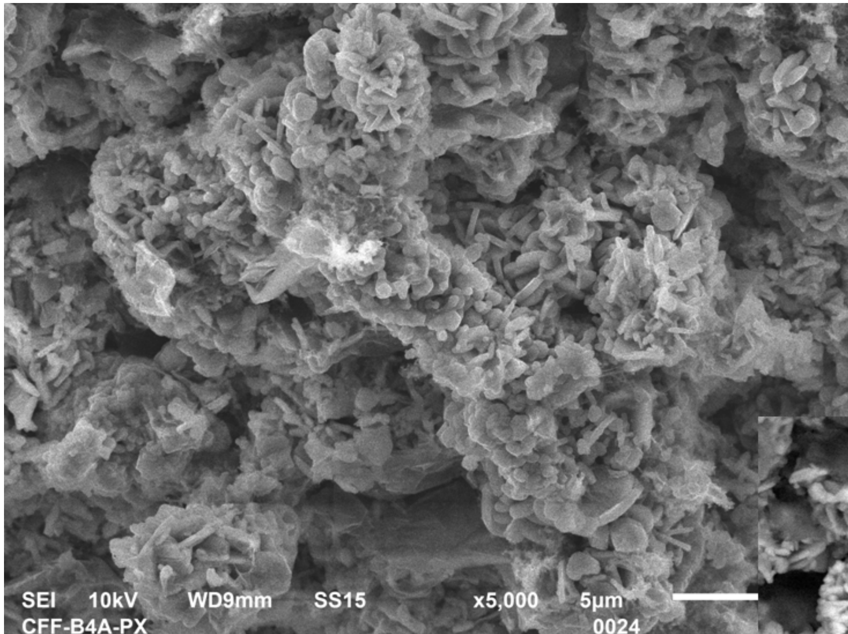


Reference Electrode Cell Data

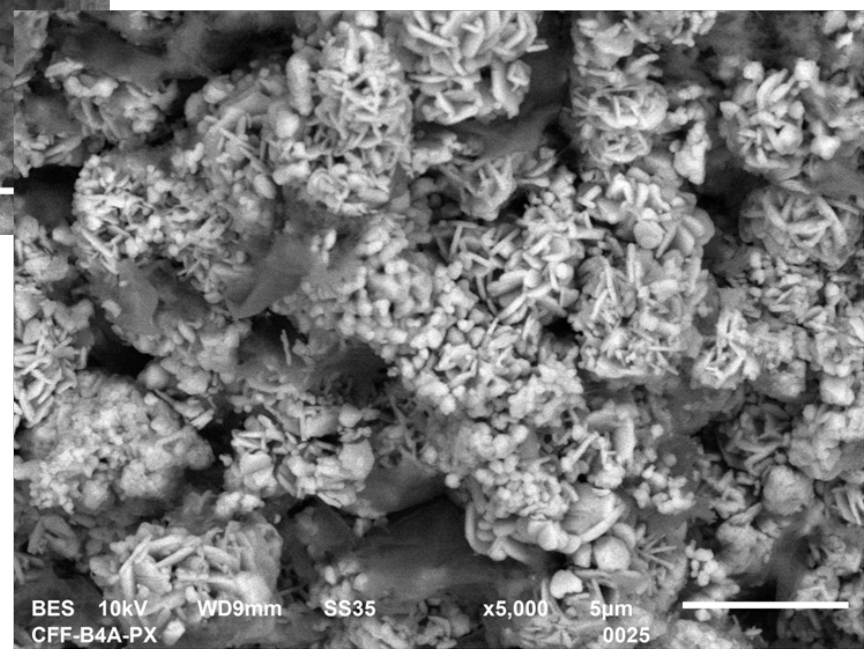
The Full Cell impedance increase is mainly from the Positive Electrode, at the oxide-carbon (high-frequency arc) and oxide-electrolyte (mid-frequency arc) interfaces.

Ref: Li et al. J. Electrochem. Soc. 160 (2013) A3006

Quality Check of CFF Electrodes Using SEM Analysis



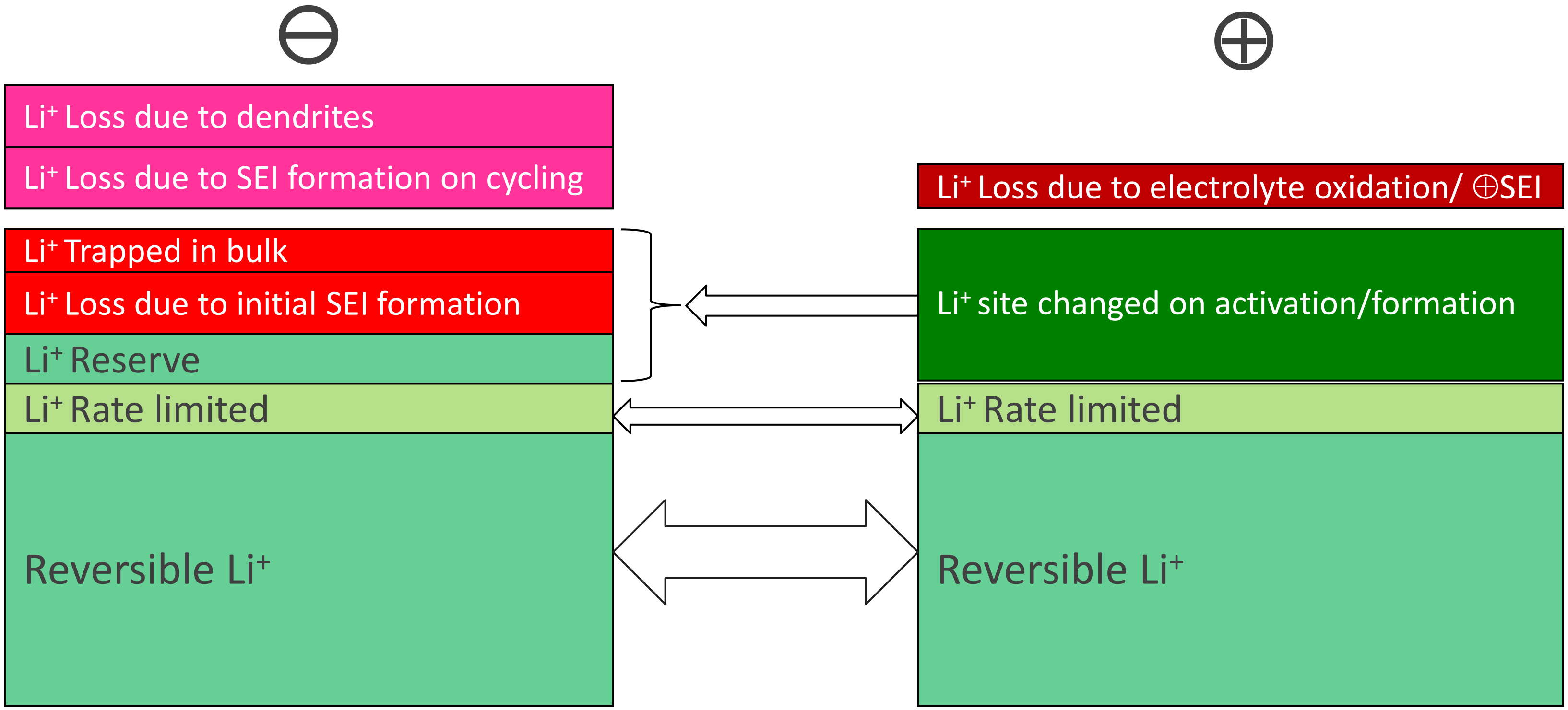
The Toda HE5050 is made by a process that yields rosettes instead of spheres.



No signs of particle cracking during calendering.

Photos from Post Test Facility.

Electrode Capacity Balancing done on mAh/cm² Basis



- Adjust n:p ratio to range between 1.03 to 1.2 in five calculated methods:
  - C/1 rate with & without differences in irreversible capacity of ⊖ and ⊕
  - C/10 rate with & without differences in irreversible capacity of ⊖ and ⊕
  - C/10 rate based on first cycle capacity of ⊖ and ⊕ only.
- Error on side of caution due to uncertainty of capacity dependence on temperature, rate, and half cell anomalies, in order to prevent dendrite formation.