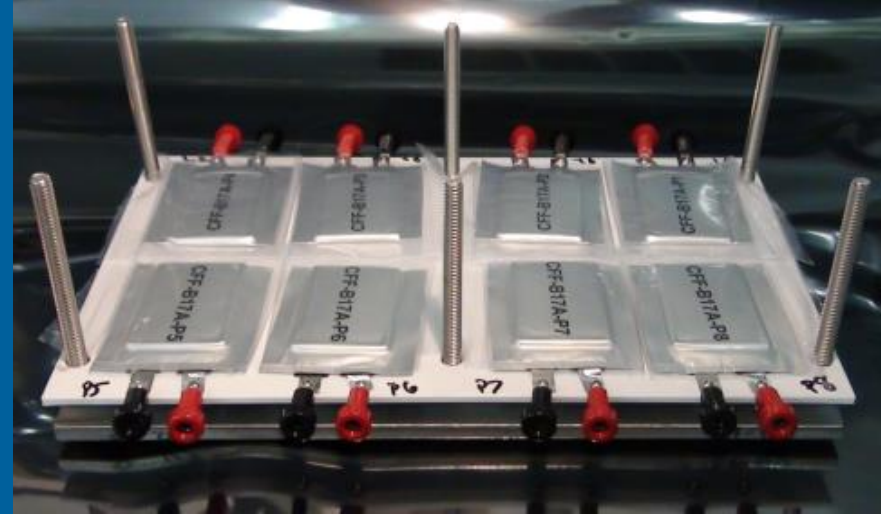


CELL ANALYSIS, MODELING, AND PROTOTYPING (CAMP) FACILITY RESEARCH ACTIVITIES



STEVE TRASK

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ARGONNE NATIONAL LABORATORY

2018 DOE VEHICLE TECHNOLOGIES
OFFICE ANNUAL MERIT REVIEW

Washington, D.C.

June 19, 2018

Project ID: BAT030

OVERVIEW

Timeline

- Start: October 1, 2014
- Finish: September 30, 2019

Budget

- \$1,600 K for FY18
 - 100% DOE-ABR

Barriers

- Need a high energy density battery for Electric Vehicle (EV) use that is safe, cost-effective, has long cycle life, and meets or exceeds DOE/USABC goals.
 - 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

- Coordinated effort with DOE-EERE-VTO Next Generation Anodes, HE-HV, and Fast Charge Projects (INL, LBNL, NREL, ORNL, PNNL, SNL)
- Argonne Facilities: MERF, EADL, CNM & PTF
- See Collaboration list at end

RELEVANCE/OBJECTIVES

- Transition new high energy battery chemistries invented in research laboratories to industrial production through independent validation and analysis in prototype cell formats (xx3450 & xx6395 pouch cells & 18650 cells) with 20 to 3,000 mAh capacity.



- Researchers are often not able to provide the quantities of novel materials needed to make a full size EV cell to demonstrate the merits of their discoveries. The CAMP Facility is specifically designed to explore new materials with quantities as small as 50 grams for active materials, and even less for electrode/electrolyte additives.

FY18 PROGRESS MEASURES & MILESTONES

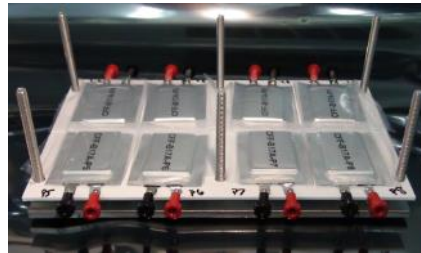
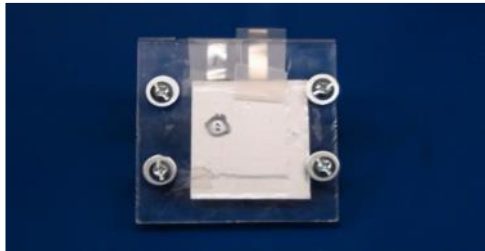
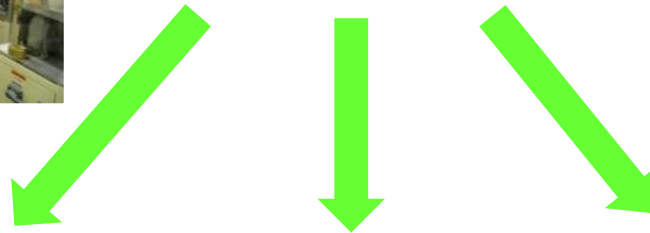
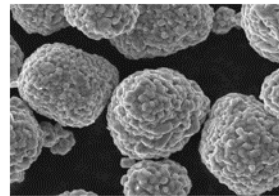
Milestone	Planned End Date	Type	Status
Determine effect of cycle life/calendar life/cell pressure on silicon-graphite vs. NMC532 pouch cells (FY17)	6/30/2017	Quarterly Progress	Completed
Fabricate 30 pouch cells with >400 mAh capacity using Si-Graphite anode and NMC cathode for NREL (FY17)	6/30/2017	Milestone	Completed
Fabricate pouch cells with at least 1 Ah capacity based on latest improvements to composite negative electrode developed in CAMP and high nickel NMC positive electrode (FY17)	9/29/2017	Milestone	Completed
Initiate development of methods to fabricate pre-lithiated high-energy electrode couples	12/21/2017	Quarterly Progress	Completed
Initiate development of methods to direct coat solid-state separators/electrolyte membranes onto electrodes	3/30/2018	Quarterly Progress	Completed
Submit final report summarizing approaches being developed to examine (in)homogeneity in pristine and cycled electrodes	6/30/2018	Quarterly Progress	On-schedule
Deliver needed experimental electrodes and cells to "Next Generation Anodes", "High-Energy High-Voltage" and "Fast Charge" programs, and other DOE-EERE-VTO projects	9/28/2018	Milestone	On-schedule

APPROACH/RESOURCES

- Researchers submit materials with promising energy density
- Small hand-coated electrodes are made
- Coin cells are made and tested
- Larger material samples are obtained (MERF, partnerships, etc.)
- Longer lengths of electrode are made from scaled materials
- Pouch cell or 18650s are made and tested
- Extensive diagnostics & electrochemical modeling on promising technologies

Glove box
Benchtop

Dry Room
Pilot scale



TECHNICAL ACCOMPLISHMENTS (NOT ALL PRESENTED AT AMR)

- Studied effects of applied pressure on silicon & graphite//NMC pouch cells
- Compared performance of small and big pouch cells
- Initiated development of electrode coating methods for prelithiation via the cathode electrode using Li_5FeO_4
- Initiated prelithiation of graphite powder & electrode electrochemically
- Initiated methods to coat ceramics on anode electrodes and tested in pouch cells
- Tested various Al_2O_3 coatings on NMC532 cathode particles (**see BAT254**)
- Fabricated pouch cells using MERF's gradient/core-shell cathode powders (**see BAT028 & BAT167**)
- Supported numerous DOE projects with prototype electrodes & cells
- Developed a reference electrode that provides reliable and reproducible data on electrode potentials during high-rate electrochemical cycling
- Devised a method to quantify the volume of gases generated during electrode slurry preparation, using the Archimedes principle
- Showed the presence of composition and impedance heterogeneity in the cross-sections of aged positive electrodes using Raman spectroscopy
- Designed a cell to image lithium-metal dendrites that form during cycling

TEST EFFECT OF PRESSURE ON PERFORMANCE

- Pouch cell using
 - Anodes (two sets):
 - Gr -> 91.8% Hitachi MagE3 graphite
 - 2.7 mAh/cm², 6% PVDF
 - Si-Gr -> 15% NA 70-130 nm silicon + 73% MagE3 graphite
 - 2.8 mAh/cm², 10% LiPAA
 - Cathode:
 - 90% Toda NMC532 (2.2 mAh/cm²)
- Electrode Architecture
 - Cathode Electrode Area: 14.1 cm² per side
 - **197 cm² and 2.78 grams of NMC532 per pouch cell**
 - Anode Electrode Area: 14.9 cm² per side
- Cell Assembly
 - Cathode Layers: 6 Double-Side + 2 Single-Side (outer) electrodes
 - Anode Layers: 7 Double-Side
 - Separator: Celgard 2325 - Trilayer PP/PE/PP, 48 mm wide
 - Electrolyte: 90 wt% [1.2M LiPF₆ in EC:EMC (3:7 w)] + 10 wt% FEC
 - 3.0 mL = 2.8 factor of calculated pore volume

CONTROL APPLIED PRESSURE WITH SPRINGS

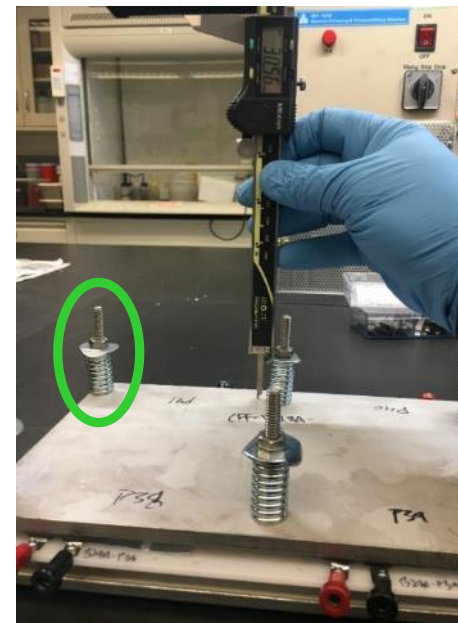
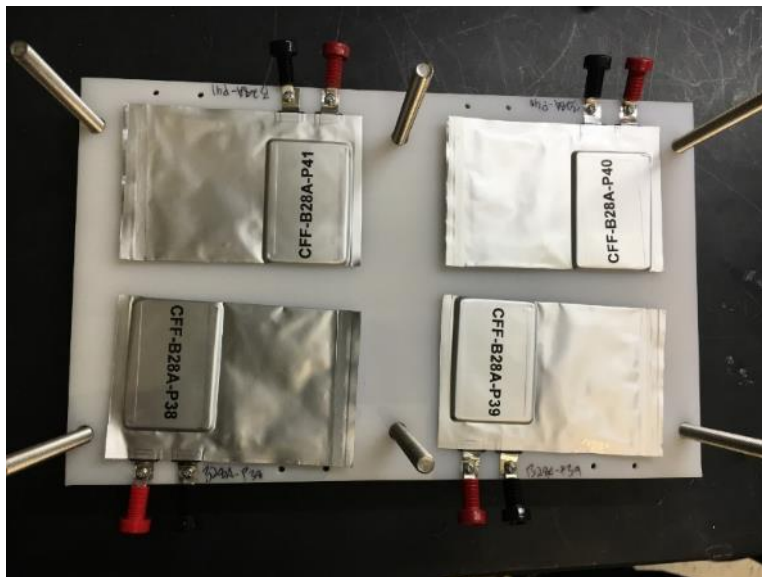
Extra pouch section left on cells to account for any gas generation, which is important for Si cells at low applied pressures

Cell Name	# of Cells	Cell Width (in)	Cell Length (in)	Spring Constant (k) (lbf/in)	Length when free (in)	Length when compressed (in)	# of Springs	Total Spring Force (lbf)	Steel Plate Force (lbf)	Total Force (lbf)	Cell Area (in ²)	Total Cell Area (in ²)	Cell Force Applied (lbf/in ²) (or psi)	Actual Force on Cell (lb)
~ 0.5 psi build	4	1.8	1.2	0	0	0	6	0.0	4.3	4.3	2.16	8.64	0.5	1.1
~ 2 psi build				13.04	1.5	1.33		13.3		17.6			2.0	4.4
~ 11 psi build				110.1	1.5	1.36		90.7		95.0			11.0	23.8
~ 76 psi build				311.7	1.5	1.15		654.6		658.9			76.3	164.7

$\Delta \text{length} \times$
spring constant
 \times # of springs

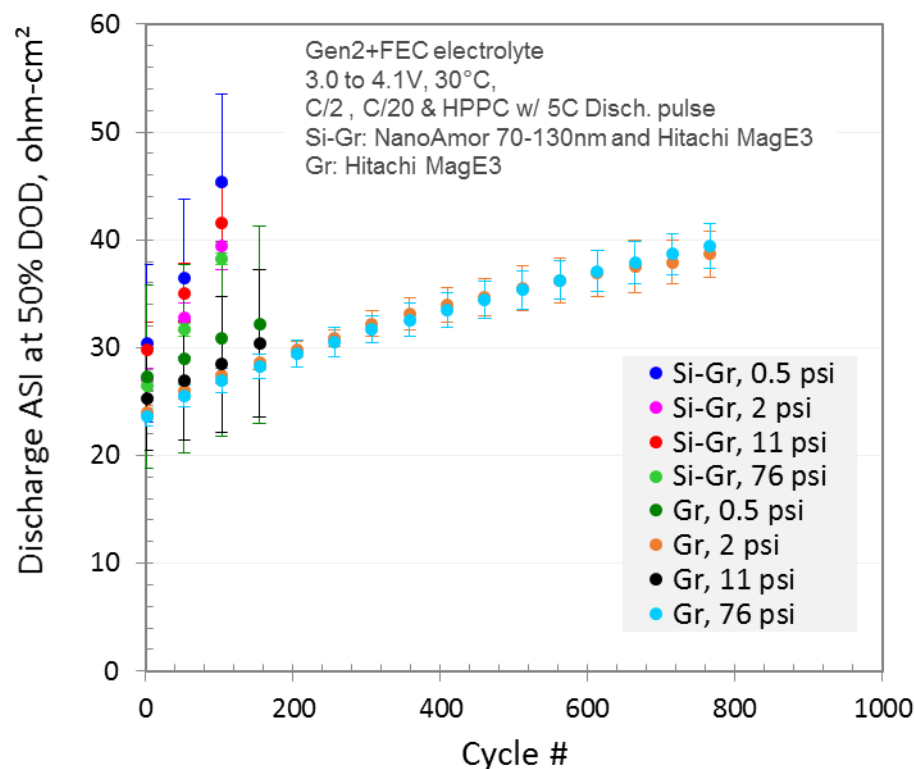
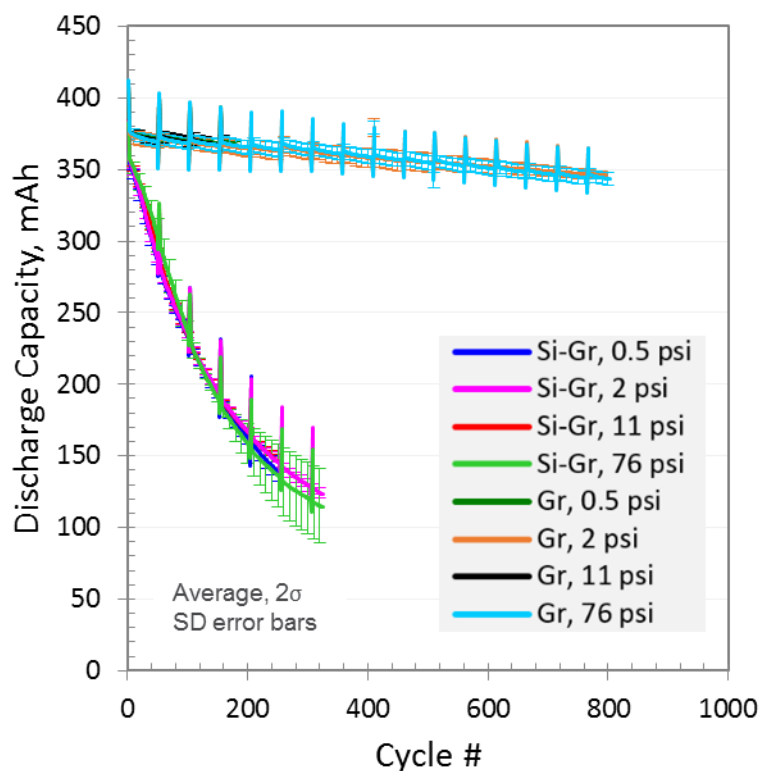
Spring force +
Steel plate force

Total force /
Total Cell Area



APPLIED PRESSURE HAS LITTLE IMPACT ON CYCLE LIFE AND IMPEDANCE

Gr//NMC532 and Si-Gr//NMC532 Cycling Performance

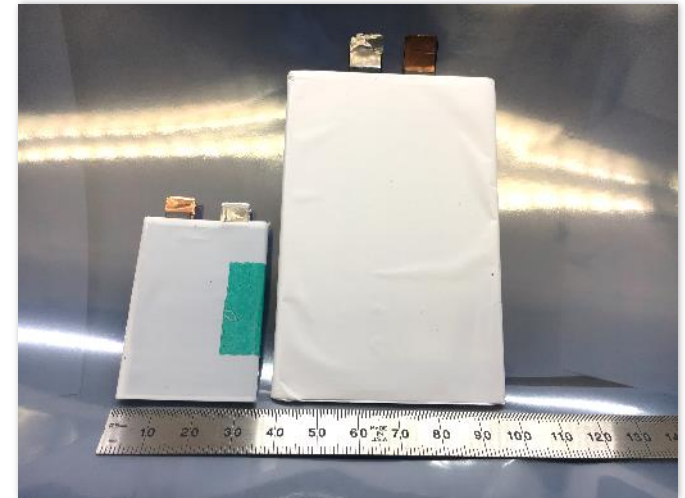


- All the silicon-containing cells show significant capacity fade and higher impedance values than the graphite only cells during cycling
- Each system appears to have minimal performance differences when applied with 2 psi to 76 psi, while the 0.5 psi ASI values are slightly higher

BIG VS LITTLE POUCH CELL

The CAMP Facility can now make xx6395 and xx3450 pouch cells, but is often limited by the amount of experimental materials available to make the larger xx6395 pouch cell. This study determines the impact of cell size on performance.

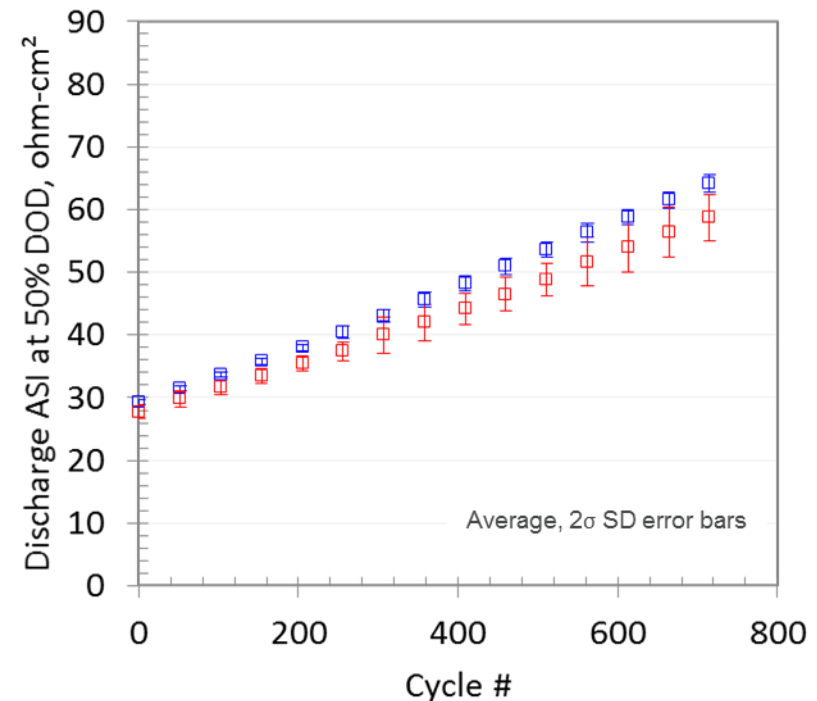
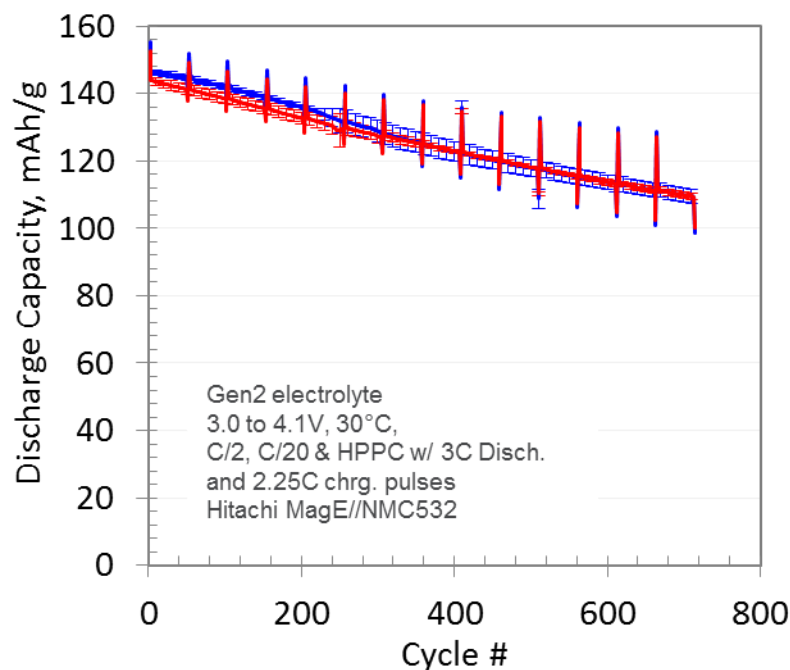
	xx3450	xx6395
cathode height, cm	4.5	8.35
cathode length, cm	3.13	5.55
cathode area, cm ²	14.1	46.3
cathode perimeter length, cm	15.26	27.79
# of interfaces in cell	12	12
Total Cell Cathode Area, cm ²	169	556
Total Cathode Perimeter Length, cm	183	334
Area : Perimeter	0.92	1.7



Graphite ~3.50 mAh/cm²
 NMC532 ~2.98 mAh/cm²

LITTLE DIFFERENCE SEEN BETWEEN SIZES

- Capacity fade rate and initial cell impedances were nearly identical
- The xx6395 had a slightly higher impedance rise during cycle life
- Average voltages and energy densities were also similar (not shown)



xx6395 pouch cell, ~1600 mAh

•556 cm² and 10.6 g of NMC532 per cell

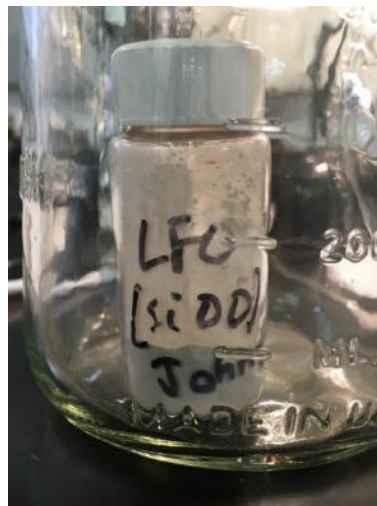
xx3450 pouch cell, ~500 mAh

•169 cm² and 3.21 g of NMC532 per cell

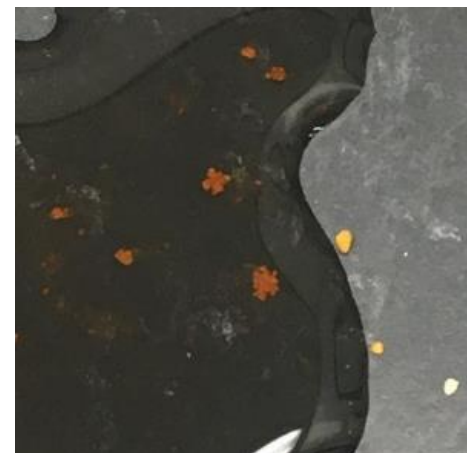
PRELITHIATION OF CELL VIA Li_5FeO_4 IN CATHODE

Investigating Material Preparation Steps using LFO

- Several LFO powders were provided by Chris Johnson in 10 g reproducible batches
- Simple tests performed to demonstrate material change with water
- All processing steps performed in dry room due to LFO's sensitivity to water (non-hazardous)
- Solvent and binder solution dried using molecular sieves



- Photo shows LFO is sensitive to water
- Not a safety concern – no signs of gas or heat evolution



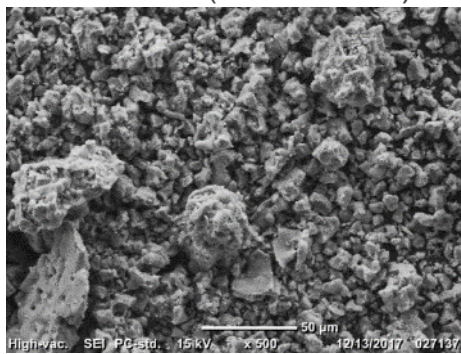
Pristine: light tan
 Humid: yellow
 Water: orange

PRELITHIATION OF CELL VIA Li_5FeO_4 IN CATHODE

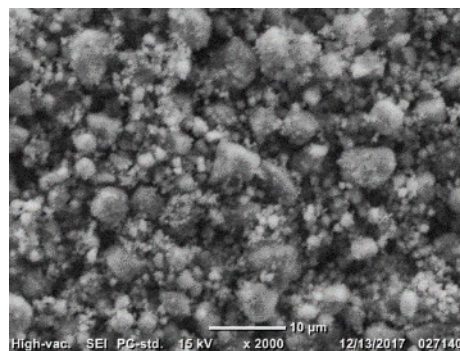
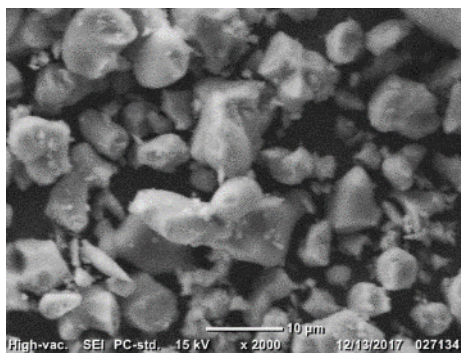
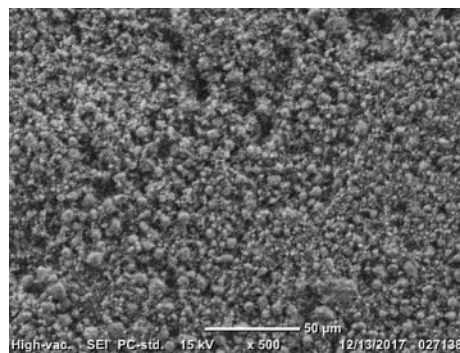
Investigating Material and Slurry Preparation Steps using LFO

Initial slurry coating had visible agglomerates, which was solved with ball milling

Pristine (as received)



Ball-milled (4 h.; planetary)



LFO powders - SEM

Provided by Chris Johnson

Slurry made with the ball-milled LFO gelled on early attempts

- Able to remake slurry with better control of mixing temperature
- Continuing to investigate effect of slurry pH



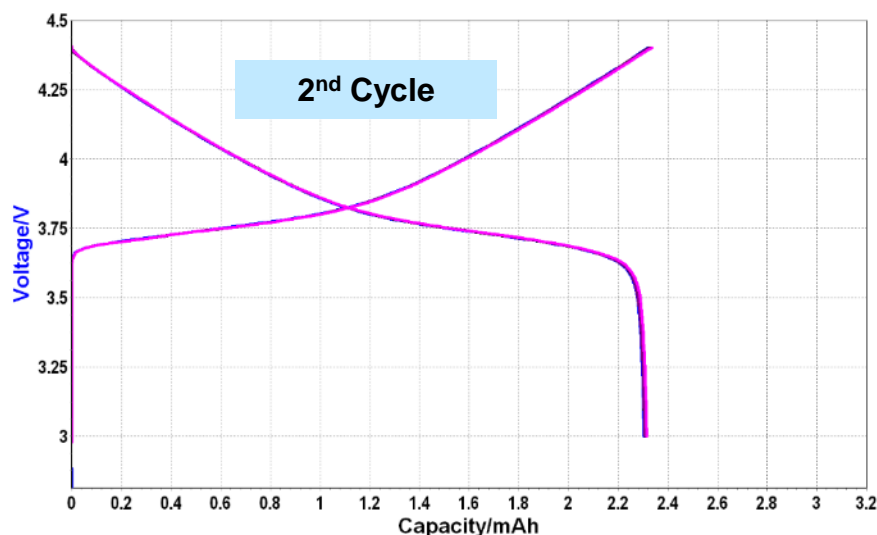
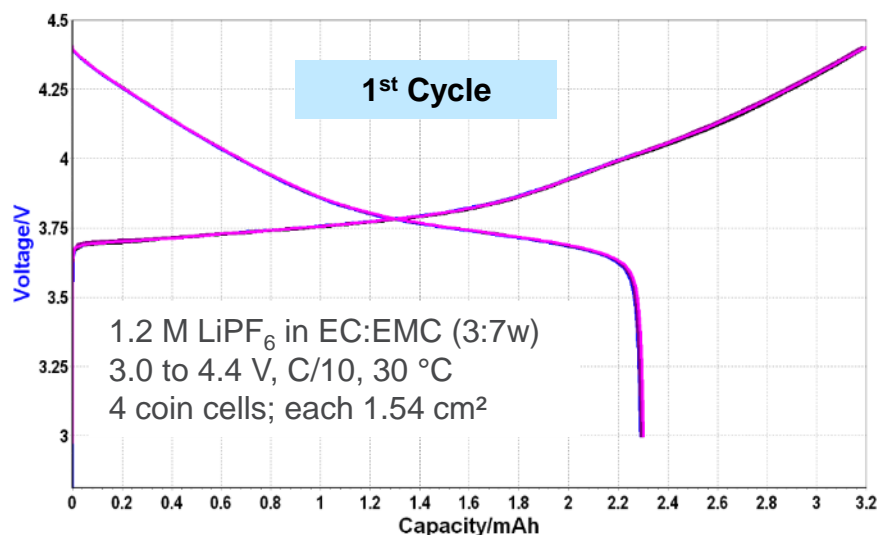
- 85 wt% Toda NMC 532
- 5 wt% Li_5FeO_4 (from C. Johnson)
- 5 wt% Timcal C45
- 5 wt% Solvay 5130 PVDF

Li₅FeO₄ (LFO) IN CATHODE PROVIDES EXTRA Li

Half-cell Formation Data Shows Capacity Provided by LFO on 1st Cycle

- NMC532 -> 206 mAh/g (4.4 V)
 - 2.6574 mAh
- **LFO -> 678 mAh/g (4.4 V)**
 - 0.5426 mAh

- NMC532 -> 187 mAh/g (3.0 to 4.4 V)
- NMC532+LFO -> 178 mAh/g (3.0 to 4.4 V)

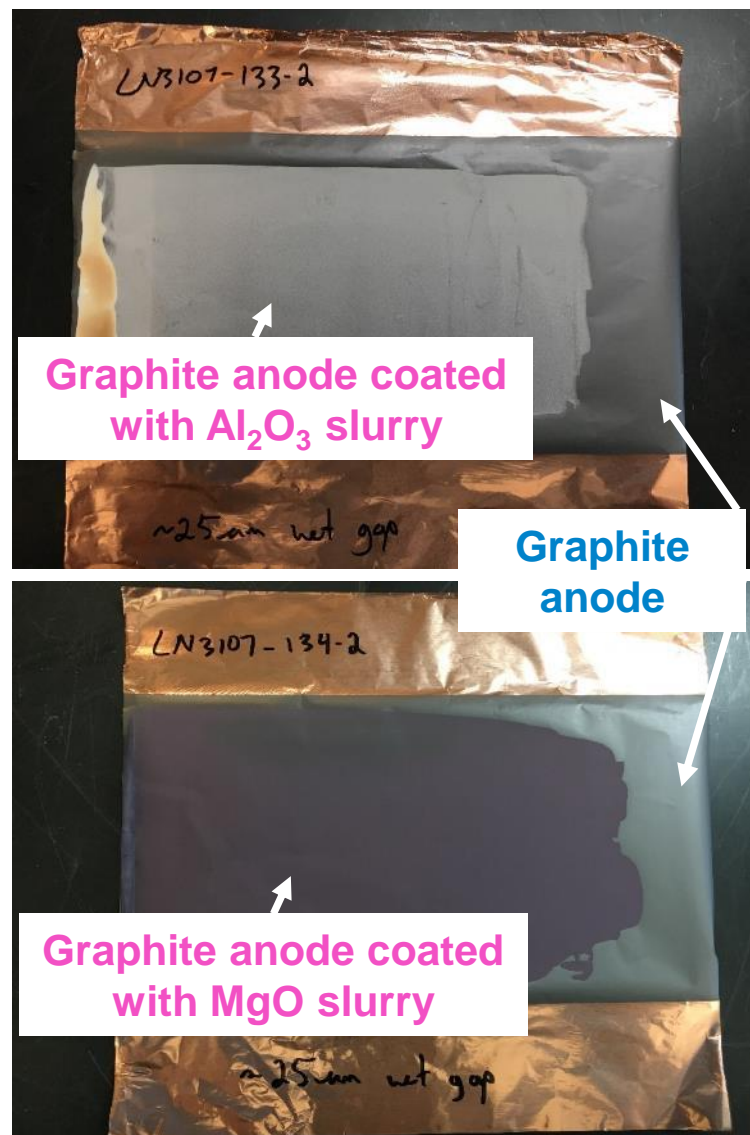
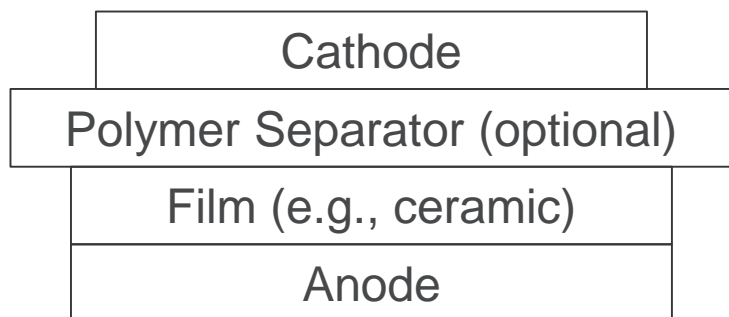


Once LFO is spent, weight of residual LiFeO species gives appearance of lower NMC capacity, but extra lithium now resides at anode (SEI formation, etc.). Adding more LFO beyond what is needed for SEI formation is probably not needed, and may lead to lithium plating on overcharge.

COATING SOLID FILMS ON ANODE

CAMP Facility is developing the capability to coat specialty films onto electrodes (preferably the anode). Initial focus is on ceramic-based films, but may later include active materials or polymer films, that could serve a variety of applications:

- Replace polymer separator with ceramic separator (added safety)
- Getter acids (HF) or other undesirable decomposition products with ceramic/functional film
- Suppress formation of lithium dendrites with novel electrode architecture



Graphite anode coated with Al₂O₃ slurry

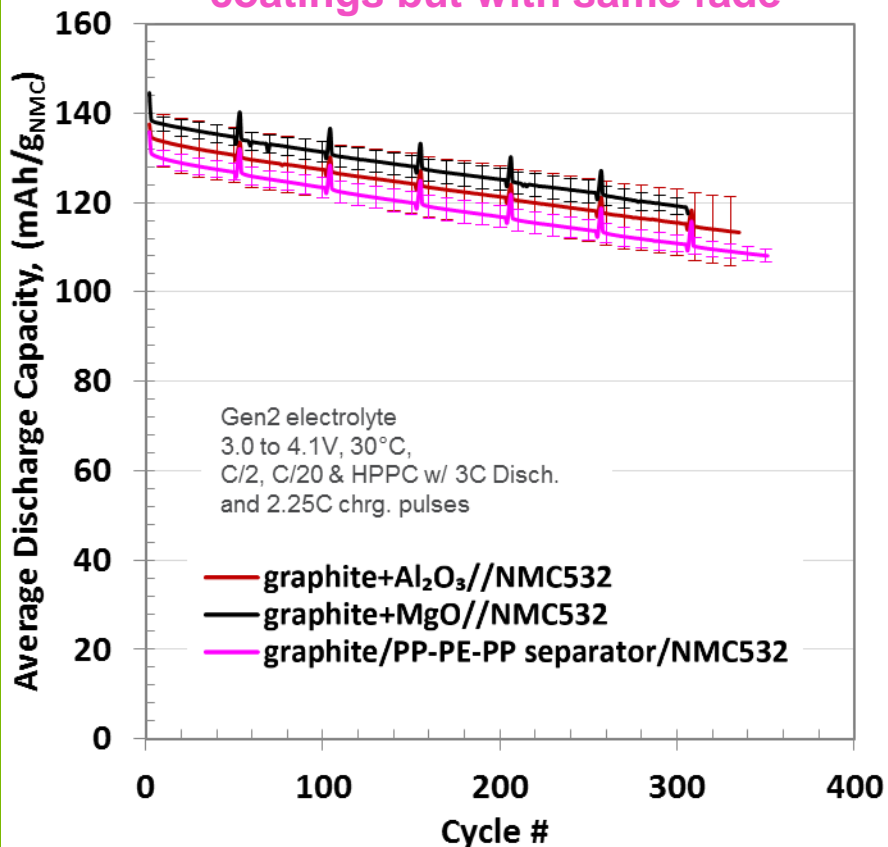
Graphite anode

Graphite anode coated with MgO slurry

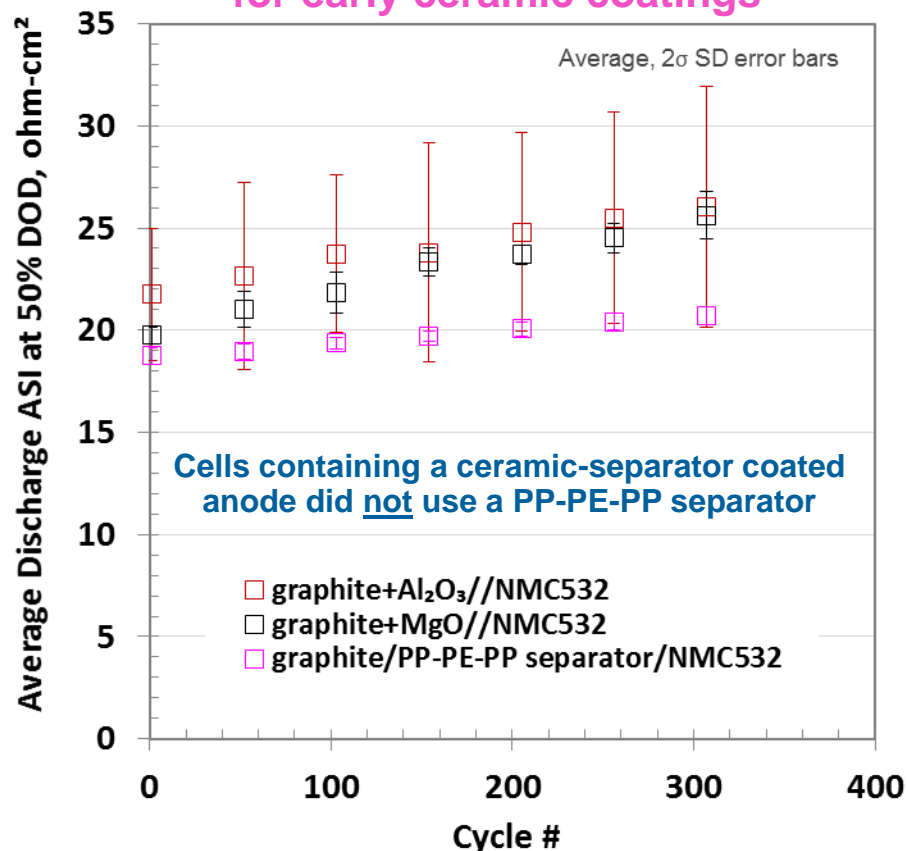
COATING CERAMIC-SEPARATORS ON ANODE

Full-cell Coin-cell Scoping with Al_2O_3 and MgO is Promising

Slightly higher mAh/g for coatings but with same fade



Impedance slightly higher for early ceramic coatings

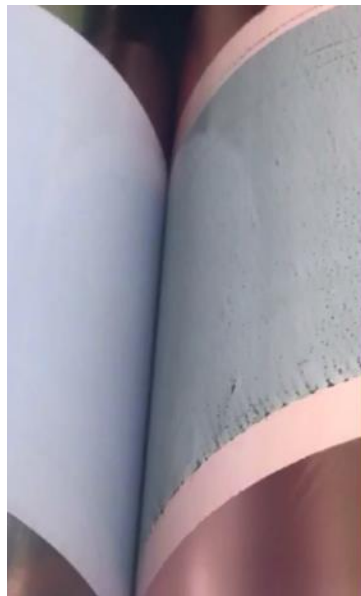


Ceramics coated directly onto a graphite electrode can provide electrical insulation for necessary separation from the positive electrode, while still achieving similar performance of a typical polymer separator containing cell.

COATING CERAMIC-SEPARATORS ON ANODE

Initial Roll-to-Roll Coating Trials Identify Areas for Improvement

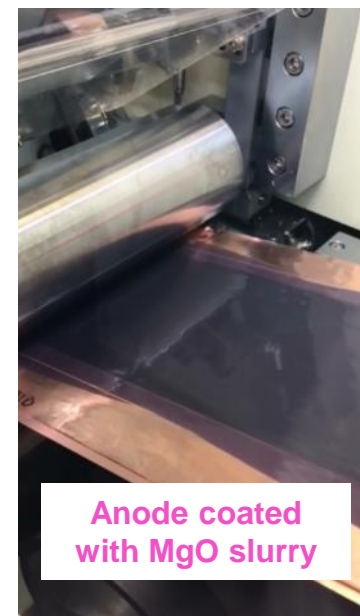
Slurry transfer challenges via reverse comma coating



Comma coating creates uniform coating



Anode coated with Al_2O_3 slurry



Anode coated with MgO slurry

While the comma coating method enables a uniform coating, other coating technologies are needed to enhance the process, namely need better control of film thickness

Argonne's Post-test Facility (PTF) examining samples now

POUCH CELL BUILDS WITH CERAMIC-COATINGS

Preliminary Testing to Determine Ceramic Compatibility with Cell System



Gen2 electrolyte
 Celgard 2320 separator
 NMC532 vs Coated-Graphite

Coated-graphite samples

POUCH CELL TESTS WITH CERAMIC-COATINGS

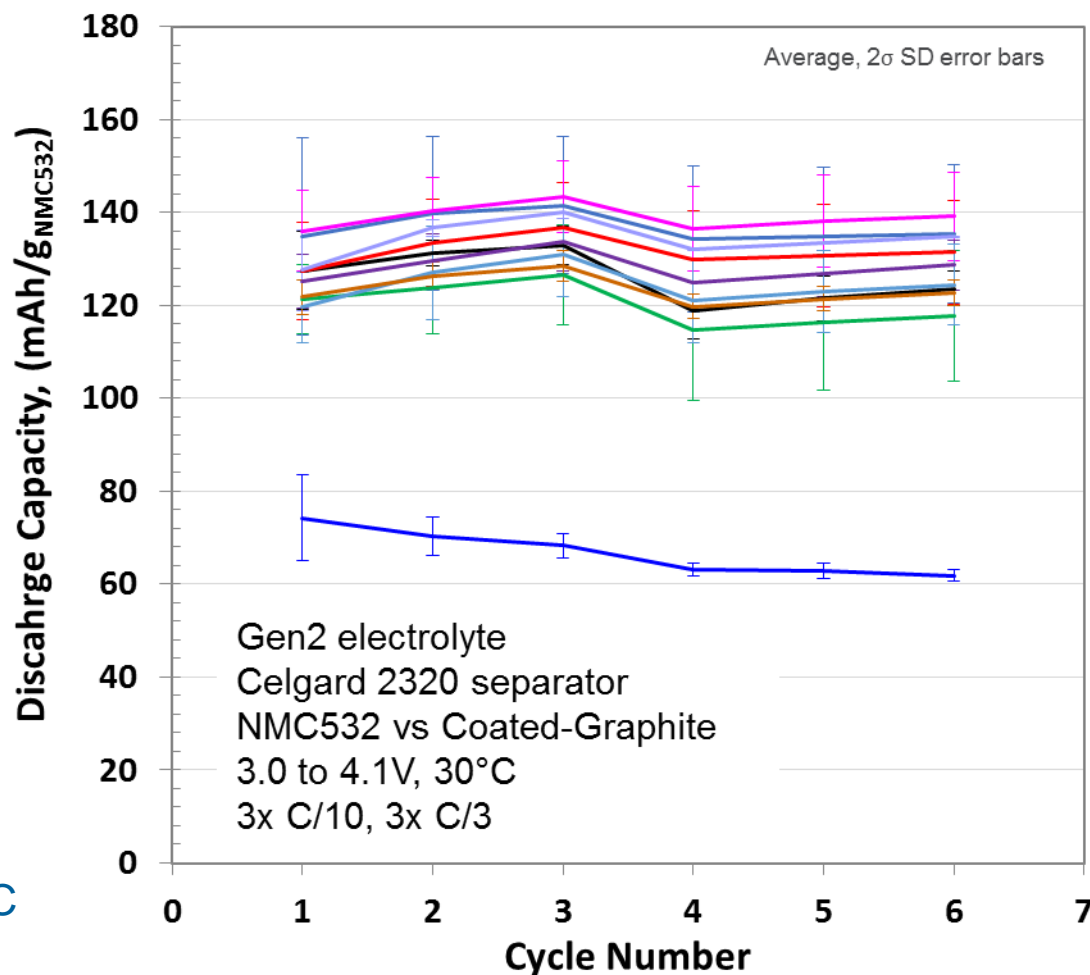
Preliminary Testing Indicates Good Ceramic Compatibility with Cell System

Initial results suggest most of the trial coatings have reasonable full cell performance.

- Baseline A12 graphite [S-A001]
- S-A001 hand coated with Zirconium(IV) oxide
- S-A001 hand coated with Aluminum silicate
- S-A001 hand coated with Zirconium(IV) silicate
- S-A001 hand coated with Boron nitride
- S-A001 hand coated with Aluminum oxide (10 μ m)
- S-A001 hand coated with Aluminum nitride
- S-A001 hand coated with Ohara glass LICG
- S-A001 APRO comma coated with Al₂O₃ (10 μ m)
- S-A001 APRO comma coated with MgO

A PP-PE-PP separator was included with these pouch cells to evaluate the stability of the ceramic coatings in the system

Cells finished formation, rate & HPPC tests, and are now on life cycle test



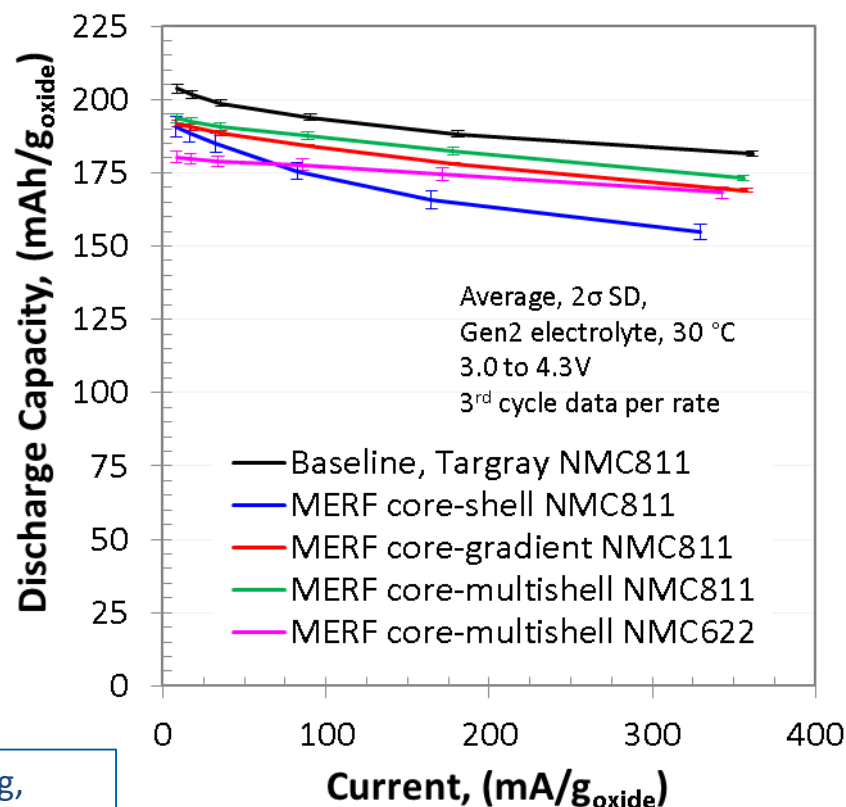
POUCH CELL PERFORMANCE OF MERF-MADE ADVANCED CATHODE POWDERS

Single layer pouch cells (~20 mAh) were made using core-shell (CS), core-gradient (CG), and core-multi-shell (CMS) cathodes from MERF - See BAT167 & BAT028

CAMP Facility:

- Received 4 powders from MERF (YoungHo Shin) (100g each)
 - YS811CS-2I (3/16/2018)
 - YS811CG-2I (3/16/2018)
 - YS811CMS-2I (3/23/2018)
 - YS622CMS-2I (3/30/2018)
- Made electrodes to match a graphite anode (A-A002B)
- Made 4 single-layer pouch cells for each cathode
- Placed on test (completed Formation, Rate Study, and HPPC -> now on life cycle)

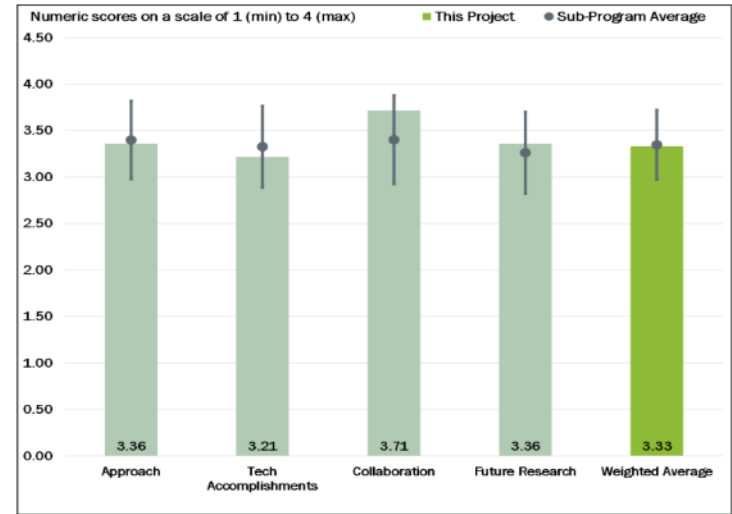
A gelling problem occurred during the slurry making, which is probably due to a high pH for these cathodes -> MERF is currently making improvements



REVIEWER COMMENTS FROM 2017 ANNUAL MERIT REVIEW

- *One reviewer said it appears that work is most all “experimental with no up-front computational work... being first accomplished. As a result, it seems that the experimental approach wanders year to year without a formal go/no-go established to determine when the team should instead prioritize other efforts and move away from Si-Li-ion materials, etc.”*

- Initial approaches in developing Si-based electrodes were based on the idea that traditional coating processes could solve the cycle life problem. It became clear that new tactics were needed. The Si Deep Dive and SEISta programs are now taking the lead in understanding the complex interface conditions on Si – the CAMP Facility will follow their suggestions. CAMP has refocused its effort on other supporting topics such ceramic coatings on the anode and developing prelithiation methods.



- *One reviewer “suggested that the team should select narrowly defined tasks so as to enable focus on the ultimate DOE objective and not be distracted by lower priority issues.”*
- CAMP is faced with numerous requests for help. We limit these lower priorities to organizations that have DOE awards, which is one of our core functions, but can appear disjointed from our larger objectives. We strive to maintain a balance.

CAMP FACILITY'S ELECTRODE LIBRARY SERVES THE BATTERY COMMUNITY

- The Electrode Library serves as a supply of standard electrode samples that are designed to be interchangeable with one another (capacity matched).
- Electrodes can be made with as little as 50g of experimental material, and can be made to match an existing counter electrode.

Currently Available:

- 16 anodes

- 23 cathodes

- Neg:Pos balanced

- 2 mAh/cm²

- 220 mm x 110 mm

- of coating per sheet

Electrodes Delivered	FY14		FY15		FY16		FY17	
Argonne	116	13 %	206	12 %	174	8 %	142	9 %
Other National Labs	213	24 %	373	22 %	726	36 %	172	11 %
Universities	119	14 %	83	5 %	117	6 %	151	10 %
Industry	423	49 %	1028	61 %	1004	50 %	1083	70 %
Total:	871		1690		2021		1548	

CAMP FACILITY COLLABORATIONS

Majority of these collaborations over the past several years are centered on the CAMP Facility providing its advice and electrodes from the Electrode Library

Universities



Industry



National Laboratories



REMAINING CHALLENGES/FUTURE WORK

- Develop method to prelithiate anode active material and/or electrode that is capable of being scaled up in industry
 - Lithiate graphite (or silicon) powder by ~6%
 - Lithiate graphite (or silicon) electrode powder by ~6%
 - May require solvent rinsing of powder or electrode before further assembly
- Determine ideal coating method to apply ceramic coatings onto electrodes
 - Apply processing knowledge gained of specialty coatings to other materials such as active materials or polymer films
- Continue testing of ceramic-coated anodes to determine long-term impact on cycle life performance
 - Work with Post-Test Facility on inspecting the interface between anode and ceramic layer and determine possible failure mechanisms in cells
- Design and build pouch cells using Li_5FeO_4 (LFO) to find optimum concentration
 - Evaluate impact of residual iron species on energy density and cycle life
- Continue work with MERF on demonstrating performance of new cathode materials, esp., core-shell, core-gradient, and core-multi-shell

- Any proposed future work is subject to change based on funding levels

SUMMARY

- Determined that applied pressure (> 0.5 psi) on Li-ion cells had little influence on performance
 - High pressure (76 psi) on Si-based cells did not improve cycle life
- Demonstrated that electrochemical performance of small (xx3450) and big (xx6395) pouch cells are very similar, which means results from smaller pouch cells made with limited material quantities are still valid
- Identified and remedied problems with coating Li_5FeO_4 (LFO) in cathode slurries
 - LFO remains a viable method of prelithiating cell systems
- Coated a variety of ceramic powders on graphite anodes and assembled in coin-cells and single-layer pouch cells
 - Demonstrated that full cells can operate without polymer-based separators
 - Identified problems using reverse-comma coater for coating ceramics due to hardness of ceramic powders and wetting of the porous graphite electrode
- Successfully made electrodes and pouch cells with core-shell, core-gradient, and core-multi-shell cathode powders from MERF
- Provided numerous experimental electrodes and cells to DOE programs

CONTRIBUTORS AND ACKNOWLEDGMENTS

Argonne

- Daniel Abraham
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Outside Argonne

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- Chris Orendorff (SNL)

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

- Paraclete Energy
- Celgard
- Superior Graphite
- Targray

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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.

No Technical Back-up Slides