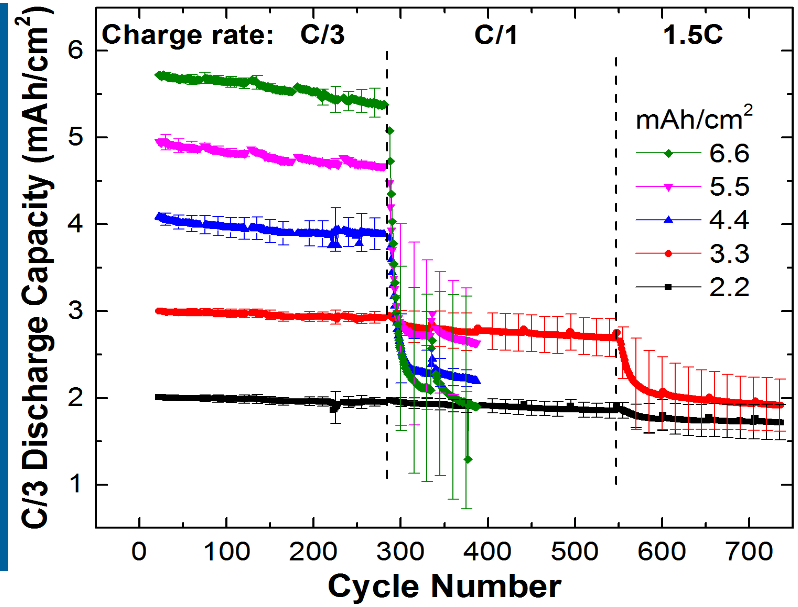
CAMP FACILITY ELECTRODE AND CELL DEVELOPMENT FOR FAST CHARGE APPLICATIONS



Cell Analysis, Modeling, and Prototyping Facility

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U.S. DEPARTMENT OF ENERGY
VEHICLE TECHNOLOGIES OFFICE
2018 ANNUAL MERIT REVIEW
June 19, 2018 - Washington, D.C.

Project ID BAT371

OVERVIEW

Timeline

- Start: October 1, 2017
- End: September 30, 2020
- Percent Complete: 25%

Barriers

- Need PHEV and EV batteries that meet or exceed DOE and USABC goals
  - Cost, Performance, and Safety
  - Enable Fast Charge Capability (recharge in <15 minutes)

Budget

- Funding for this Effort:
  - FY18 - $250K

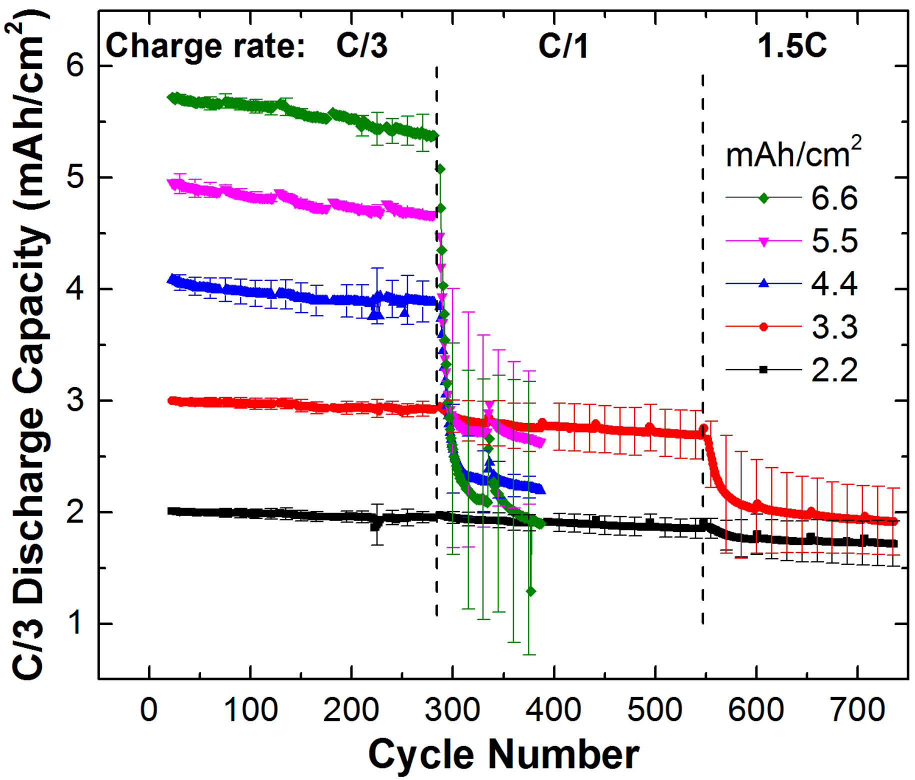
Partners

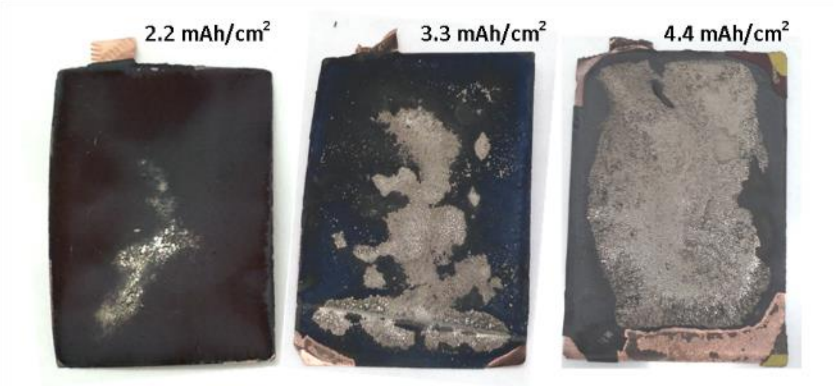
- National Renewable Energy Laboratory
- Idaho National Laboratory
- Argonne National Laboratory

RELEVANCE

Previous work by Argonne's CAMP Facility measured the rate capability of Graphite//NMC622 pouch cells as a function of electrode loading. These results indicated that:

- **Discharge capacity poorly utilized at higher C-rates (>C/2)**
- **Severe capacity loss for higher loadings near 1C charge rate**
- **Lithium plating proportional to loading**





Cycle # 812 Cycle # 812 Cycle # 548

Gallagher, *et al.*, *JES* 2016

OBJECTIVE

Use CAMP Facility resources to supply experimental electrodes and cells to XFC team with the aim in FY18 to identify causes of lithium plating at fast charges

APPROACH

- Chose at least four different graphite negatives for evaluation followed by a thickness study using the best performing graphite
  - natural vs. artificial graphite
  - coated/surface modified vs. virgin surface
  - surface areas
  - CMC-SBR binder vs. PVDF binder
- Vary electrode loading between 1 and 5 mAh/cm² with candidate graphite
- Use single-sided single-layer pouch cells in first year with NMC532

MILESTONE & DELIVERABLES

Select candidate materials for first cell builds	9/1/2017 - 11/15/2017
Deliver material information to NREL modeling team	11/1/2017 - 1/31/2018
Build & deliver first cell builds to ANL/INL/NREL test labs	1/1/2018 - 2/28/2018
Second cell builds(single-sided, single layer)	3/15/2018 - 4/27/2018

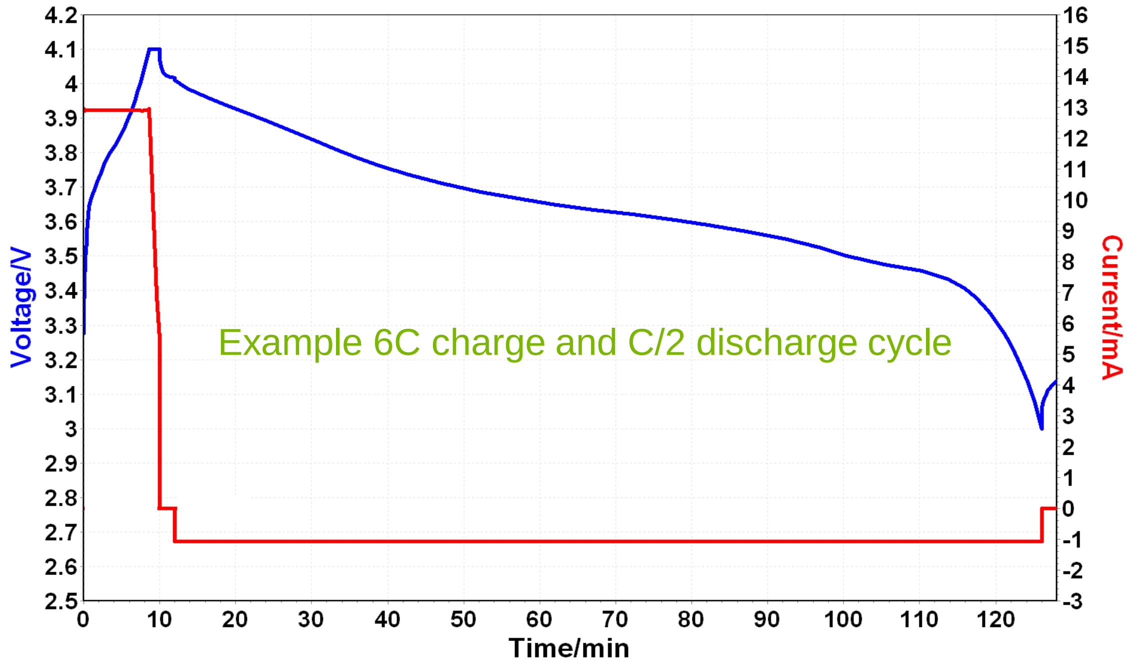
GRAPHITES SELECTED FOR SCREENING

Trade Name	Company	Type	Particle shape or morphology	Tap Density, [g/mL]	Surface Area, [m²/g]	Particle Size D10, [µm]	Particle Size D50, [µm]	Particle Size D90, [µm]
SLC1506T	Superior Graphite	Natural Graphite, coated	spherical graphite powder	1.03	1.936	5.37	8.06	13.15
SLC1520P	Superior Graphite	Natural Graphite, coated	spherical graphite powder	1.19	0.89	11.03	16.94	26.76
MagE3	Hitachi	Artificial Graphite, combines hard graphite additive	-	0.90	3.9	-	22.4	-
MCMB	Gelon	Artificial, Mesocarbon Microbeads, standard type-G15	MesoCarbon MicroBeads	1.324	2.022	-	17.649	-
CPG-A12	Phillips 66	Natural Graphite core coated with surface treatment	potato	-	2 to 4	-	9 to 12	-
BTR-BFC-10	BTR	Artificial Graphite, High Energy Fast Charge	-	0.770	2.487	6.539	11.196	18.891

COIN CELL SCREENING – TEST PROTOCOLS

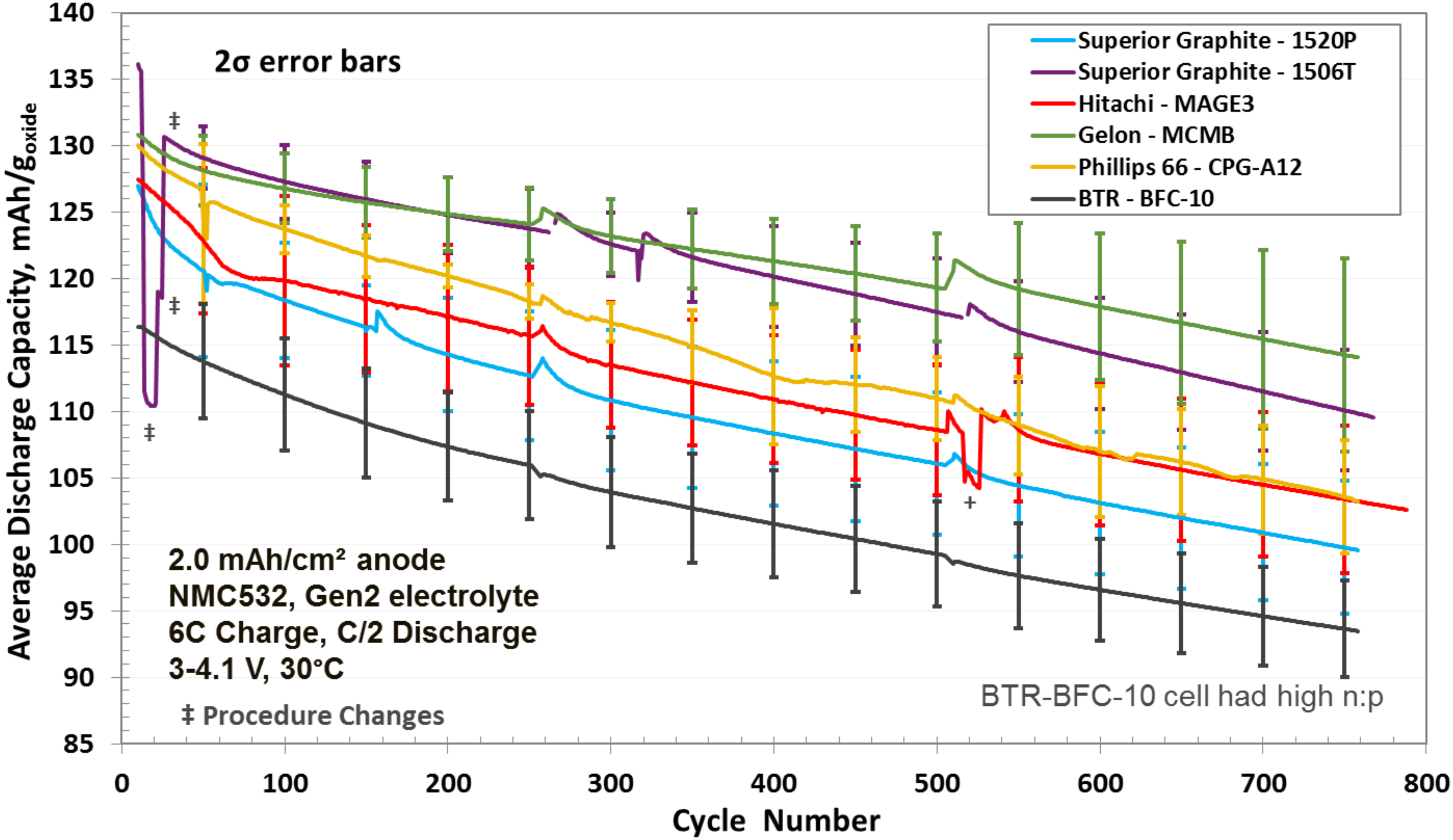
2.0 mAh/cm² graphite
1.7 mAh/cm² NMC532
(Electrode Library Loading)
1.2 M $LiPF_6$ in EC:EMC (3:7w)

Used C-rate of <u>2.15 mAh</u> for all electrodes tested

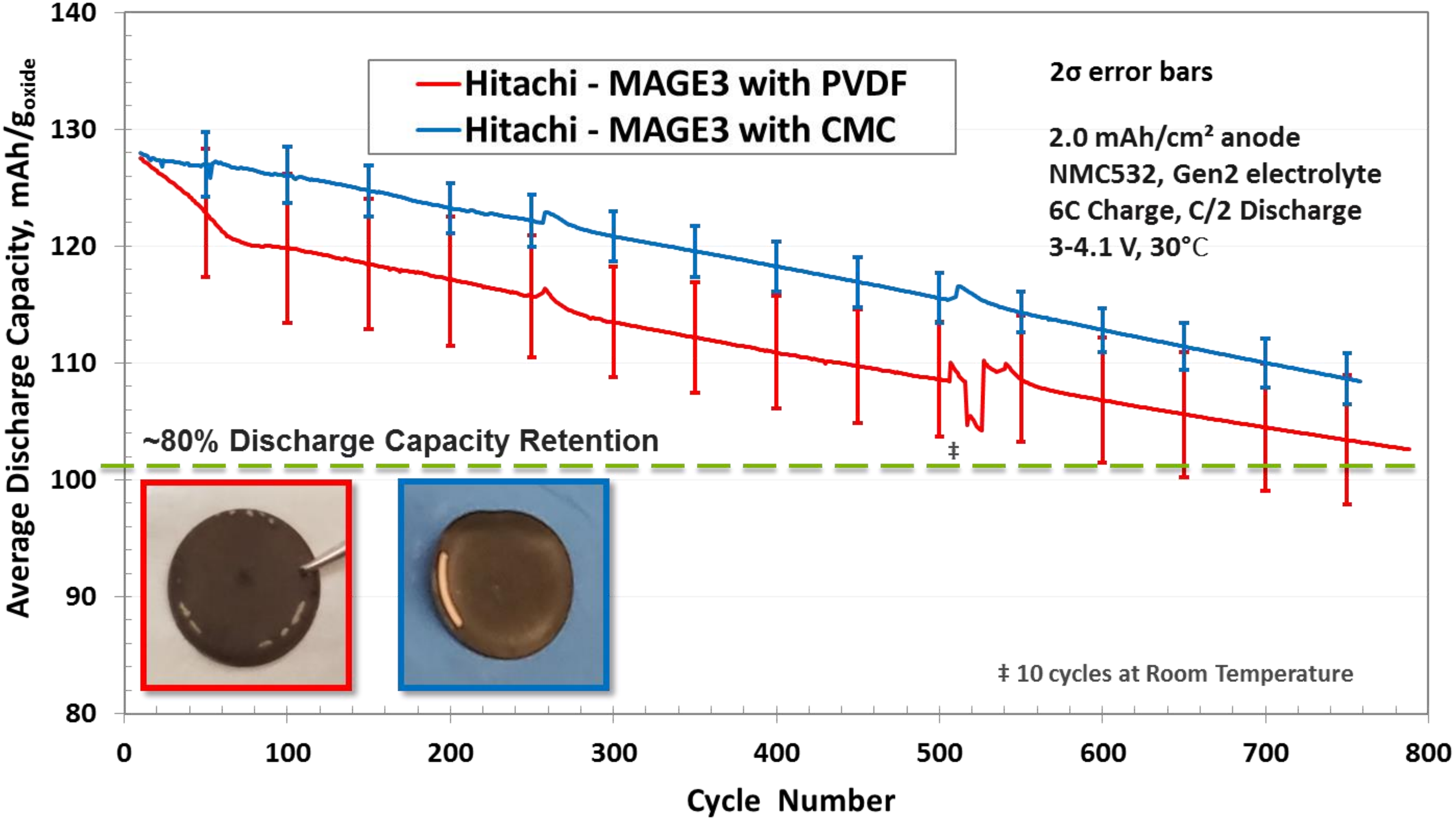


- C-rate value for 6C should be high enough to reach 4.1V within 10 minutes, but also low enough to not reach 4.1V too quickly (i.e. 5 minutes)
- Formation: 3 cycles of C/10 [w/ C/20 trickle charge]
- Cycling (3.0 to 4.1V, every 250 cycles perform 3 cycles at C/10)
  - 6C charge
    - Step limited to 10 minutes
    - Will trickle charge down to C/5 if total charge time has not reached 10 minutes
  - C/2 discharge
  - 2 minute rest open circuit between steps

SIMILAR FADE RATES OBSERVED FOR SELECTED GRAPHITES DURING 6C CHARGING



SIMILAR FADE RATES FOR PVDF & CMC-SBR BINDERS AT LOW LOADINGS



SELECTED GRAPHITES ARE STATISTICALLY SIMILAR AT LOW LOADINGS

All selected graphites can reach 750 cycles at 2 mAh/cm²

		Average Discharge Capacity Retention (%)		
Graphite Type	Coating Loading (mg/cm²)	At Cycle 750 (%)	# of Cells in Average	2σ [+/-] Standard Deviation at Cycle 750 (%)
Superior Graphite 1520P	6.3	78.5 %	4	3.22
Superior Graphite 1506T	6.4	80.9 %	3	2.12
Hitachi MAGE3 with PVDF	6.4	81.1 %	4	4.34
Hitachi MAGE3 with CMC-SBR	6.3	84.9 %	3	3.06
Gelon MCMB	6.4	87.3 %	5	5.61
CPG A12	6.1	79.7 %	3	4.77
BTR BFC-10	7.2	80.5 %	4	0.22

NMC532 (A-C013A) Loading = 11.3 mg/cm²

Discharge Capacity Retention is based on the 10^{th} cycle (6C Chg, C/2 Dchg)

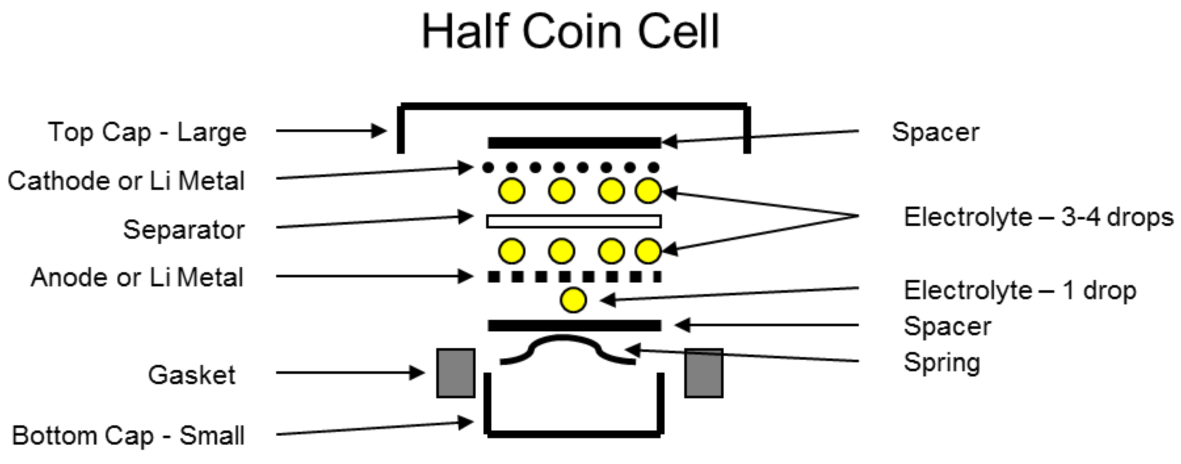
NREL NATIONAL RENEWABLE ENERGY LABORATORY INL Idaho National Laboratory Argonne NATIONAL LABORATORY

COIN CELL GITT STUDY – CELL BUILDS

Determine diffusion coefficients in selected graphites (BAT341)

- List of Graphite Cells for EADL
  - MCMB (A-A010)
    - Delivered 10/25/17
  - SLC1506T (A-A015)
    - Delivered 12/18/17
  - SLC1520P (A-A005A)
    - Delivered 12/19/17
  - MAGE3 (A-A016)
    - Delivered 2/22/18
  - BTR-BFC-10
    - Estimate 5/15/18
  - A12
    - TBD

- Half Cell Construction:
  - 15 mm Dia. Anode
  - 15.6 mm Li Metal Disk (MTI)
  - Gen 2 Electrolyte Flooded
  - Celgard 2325 Separator
- 15 Coin Cells Delivered per Graphite
- No Formation or Cycling



1ST POUCH CELL DELIVERABLE – CELL DESIGN

Anode: A-A015

91.83 wt% Superior Graphite SLC1506T
2 wt% Timcal C45 carbon
6 wt% Kureha 9300 PVDF Binder
0.17 wt% Oxalic Acid

Lot#:1506-01 received 02/04/2015
Electrode ID: LN3107-110-5
"SS = single-side, DS = double-side"

Cu Foil Thickness: 10 µm
Total Electrode Thickness: 57 µm
Total Coating Thickness: 44 µm
Porosity: 37.4 %
Total SS Coating Loading: 6.38 mg/cm^2
Total SS Coating Density: 1.36 g/cm^3

Made by CAMP Facility

Use SLC1506T from Superior Graphite

Cathode: A-C013B

90 wt% Toda NMC 532
5 wt% Timcal C45
5 wt% Solvay 5130 PVDF

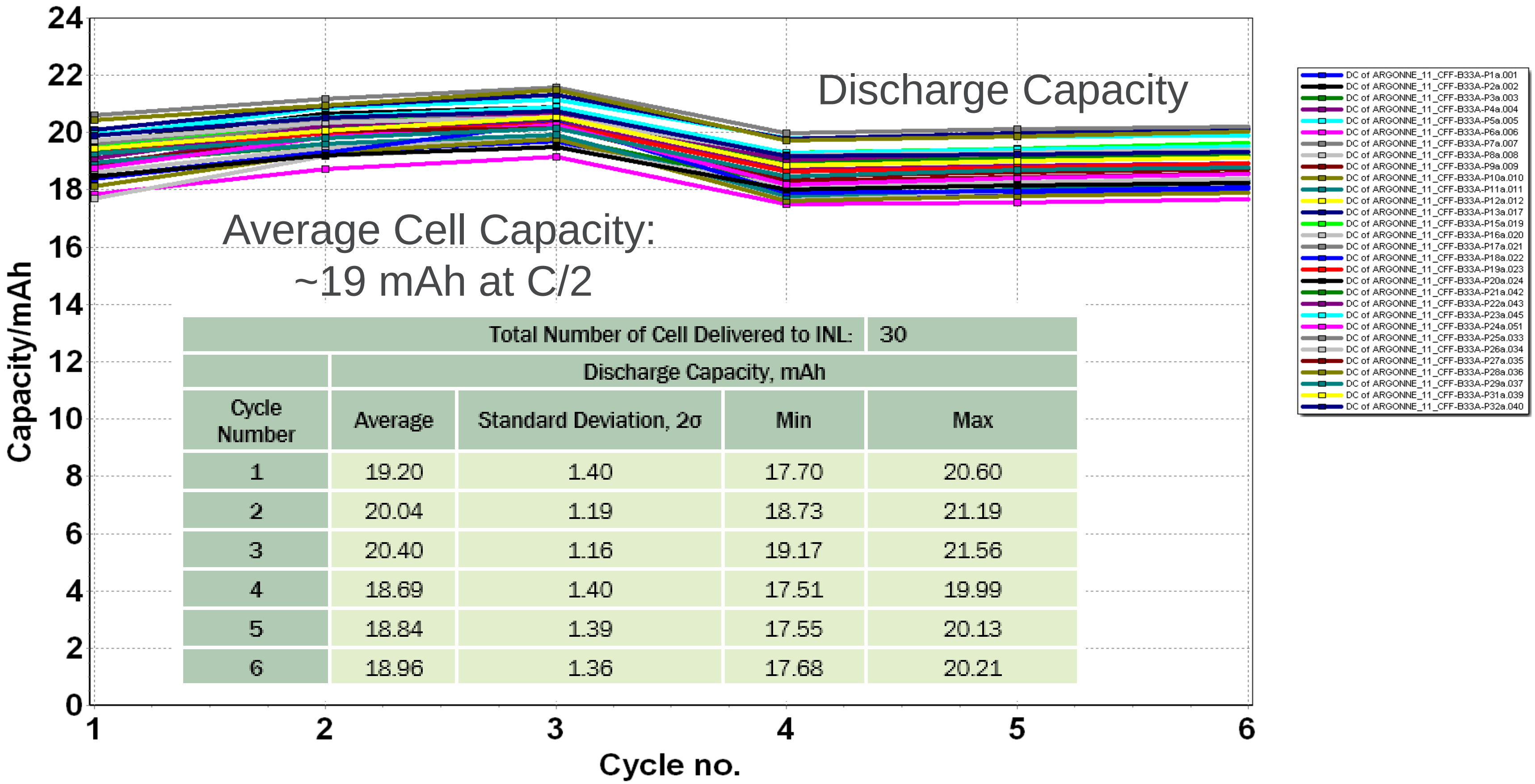
Matched for 4.2V full cell cycling
Prod:NCM-04ST, Lot#:7720301, Elect:LN3107-141-3

Al Foil Thickness: 20 µm
Al Foil Loading: 5.36 mg/cm^2
Total Electrode Thickness: 62 µm
Coating Thickness: 42 µm
Porosity: 33.1 %
Total Coating Loading: 11.40 mg/cm^2
Total Coating Density: 2.71 g/cm^3

Made by CAMP Facility

- Cathode Electrode Area: 14.1 cm² per side -> **0.145 grams of NMC532 per pouch cell**
- Cell Assembly
  - Cathode Layers: 1 Single-side Layer
  - Anode Layers: 1 Single-side Layer
  - Separator Used: Celgard 2320 - Trilayer PP/PE/PP
    - Single layer pouch cell z-fold winding -> 48 mm wide roll, 200 mm long per cell
  - Electrolyte Used: Tomiyama [A49] 1.2M $LiPF_6$ in EC:EMC (3:7 wt%) "Gen2"
    - CFF-B33A -> 0.5 mL = 4.2 factor of calculated pore volume
  - Applied cell pressure during formation: ~4 psi
  - n:p ratio: 1.12 to 1.22 (3.0 to 4.1V full cell)
- Cell Formation Protocol (shipped after Formation & Degassing)
  - 1.5V tap charge and hold 15 min, rest 12 hours, C/10 x 3, C/2 x 3, 3.0-4.1V, then safe SOC (3.5V hold for 6 hours) -> used 20 mAh as 1C-rate value for test

1ST POUCH CELL DELIVERED TO LABS



Total Number of Cell Delivered to INL:				30
	Discharge Capacity, mAh			
Cycle Number	Average	Standard Deviation, 2σ	Min	Max
1	19.20	1.40	17.70	20.60
2	20.04	1.19	18.73	21.19
3	20.40	1.16	19.17	21.56
4	18.69	1.40	17.51	19.99
5	18.84	1.39	17.55	20.13
6	18.96	1.36	17.68	20.21

30 Full Single-Layer Pouch (SLP) cells for testing; delivered ~2/13/18 to INL

16 Full SLP cells for testing; delivered 2/15/18 to ANL

16 Dry SLP cells ready for next round of testing; 2/15/18 at ANL

4 Full and 2 Dry SLP cells for testing; delivered ~2/27/18 to NREL

DESIGNING 2ND POUCH CELL BUILD

As in 1st pouch cell build, quick screening performed on options

- Since graphites fade similarly, continue to use SLC1506T
- Focus on higher electrode loading

Anodes available for screening:

91.83 wt% Conoco Phillips CGP-A12
2 wt% Timcal C45 carbon
6 wt% Kureha 9300 PVDF
0.17 wt% Oxalic Acid

Cathode:

90 wt% Toda NMC532
5 wt% Timcal C45 carbon
5 wt% Solvay 5130 PVDF

Targeted cell capacity, mAh/cm²	Anode Loading [mg/cm²]	Cathode Loading [mg/cm²]	Anode Capacity [mAh/cm²]	Cathode Capacity [mAh/cm²]	n:p ratio
1.5	6.0 (41µm)	11.3 (39 µm)	1.90	1.64	1.10 to 1.16
*3.0	14.0 (93 µm)	21.8 (80 µm)	4.45	3.16	1.32 to 1.44
4.5	17.4 (120 µm)	33.1 (125 µm)	5.51	4.79	1.08 to 1.15
5.5	21.7 (152 µm)	38.2 (152 µm)	6.88	5.54	1.16 to 1.26

*cathode from different slurry/coating due to lack of matching electrodes, but with the same composition

Based on full cell, 3.0 to 4.1V design, ~35% porosity

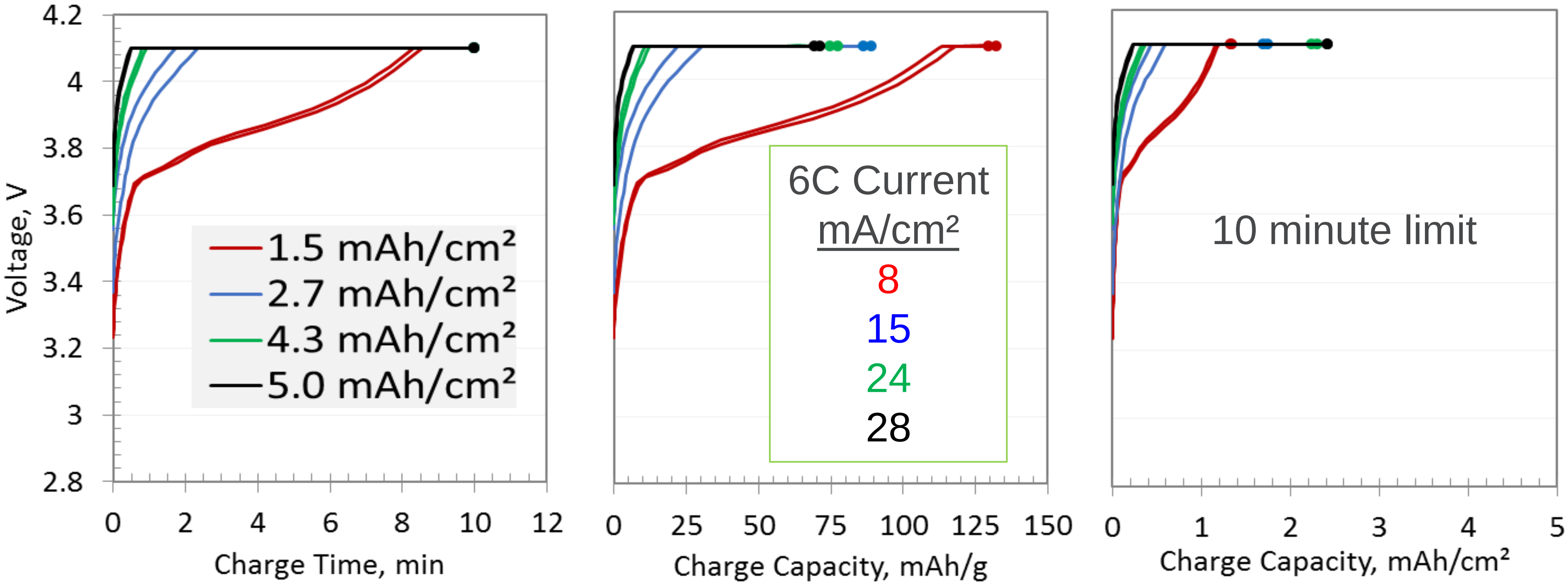
IMPACT OF ELECTRODE LOADING REVISITED

<u>1st 6C charge (after formation)</u>, full-cell coin-cells, scoping experiments

Higher loadings reach 4.1V within 2 minutes or faster while using same mA/g

Higher loadings acquire the majority of their capacity during the voltage hold

High loadings are able to achieve only a fraction of their C/10 capacity



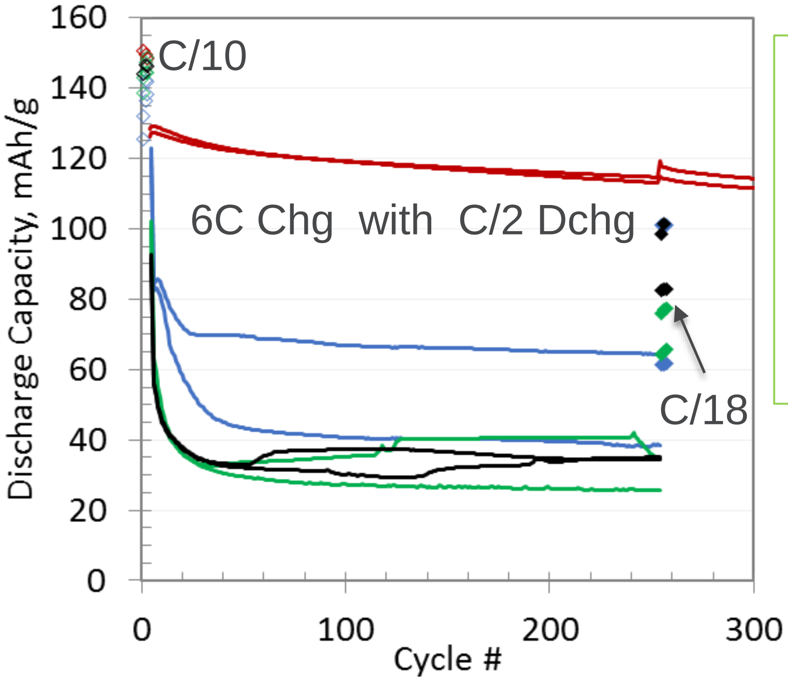
Legend of mAh/cm² is for initial cell capacity at ~C/10 (~140 mAh/g for all loadings)

Toda NMC532 vs. A12 graphite
Gen2 electrolyte, Celgard 2320
3.0 to 4.1V, 2 cells each, 30°C,

POOR UTILIZATION STILL SEEN AT FAST CHARGE FOR HIGHER LOADINGS

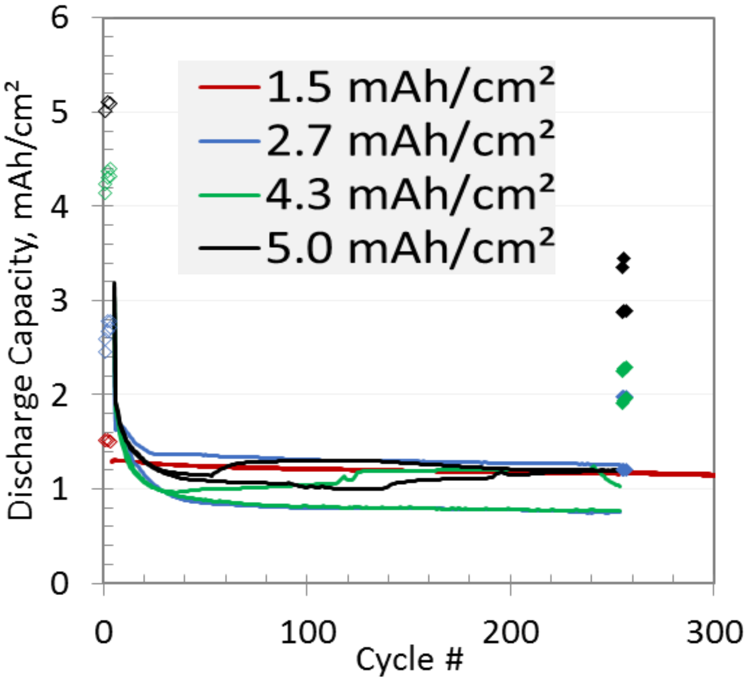
"6C" charge (reduced) and C/2 discharge cycling, full-cell coin-cells

Higher loadings have immediate capacity fade



"6C" Current
mA/cm²
8
11
14
15

High loadings fade quickly and level out at ~ 1.3 mAh/cm²



Legend of mAh/cm² is for initial cell capacity at ~C/10 (~140 mAh/g for all loadings)

Toda NMC532 vs. A12 graphite
Gen2 electrolyte, Celgard 2320
3.0 to 4.1V, 30°C
2 cells per loading

RESPONSES TO PREVIOUS YEAR REVIEWERS' COMMENTS

- This project was initiated after the last review and therefore has no previous year reviewers' comments.

COLLABORATION AND COORDINATION WITH OTHER INSTITUTIONS

- Three National Laboratories have teamed to form this integrated effort focused on enabling fast charge capability.
- This effort is part of a broad range of unified studies (BAT338, BAT339, BAT340, BAT341, and BAT371).

REMAINING CHALLENGES AND BARRIERS

- Develop methods of altering the electrode microstructure to improve tortuosity during slurry making/coating process
- Develop thinner anode electrodes with higher loading and low porosity (<20%) without distorting electrode
  – May require multi-modal distribution of particle sizes and morphologies

PROPOSED FUTURE RESEARCH

- Complete remaining coin cell builds for GITT study
- Fabricate and delivery specialty pouch cells (4 anode and 4 cathode half-cells) and punched pristine electrodes to NREL
- Finish second cell build and deliver to INL, ANL, and NREL
  – Single-layer pouch cells
  – Use Superior Graphite SLC1506T
  – Use graphite loading of 3.0 mAh/cm^2
- Test effect of porosity (thickness) and tortuosity
- Develop more robust high-loading CMC-SBR based anodes
- Explore need for alternative tabbing designs in larger cells

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

SUMMARY

- Six different graphite negatives were chosen from the CAMP Facility's Electrode Library for fast-charge prescreening and GITT study in coin-cells
- Surprisingly similar fade rate observed at 6C charge for many graphites
- Selected SLC1506T graphite from Superior Graphite for first cell build
  - 2.0 mAh/cm^2 graphite loading
- CMC-SBR vs. PVDF binder showed little difference (at 2.0 mAh/cm^2)
- Over 70 single-sided single-layer pouch cells were fabricated and delivered to lab partners (INL, ANL, and NREL) for fast charge study
  - Recommend 19 mAh as the 1C rate nominal capacity
- Provided technical data and electrochemical results to modeling teams
- Initial screening results at higher electrode loadings confirm that fast charging will have negative effect on cycle life with present cell designs

CONTRIBUTORS AND ACKNOWLEDGMENT

Argonne

- Daniel Abraham
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- Venkat Srinivasan
- Steve Trask
- Pierre Yao
- Linghong Zhang

- INL
- NREL

Research Facilities

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

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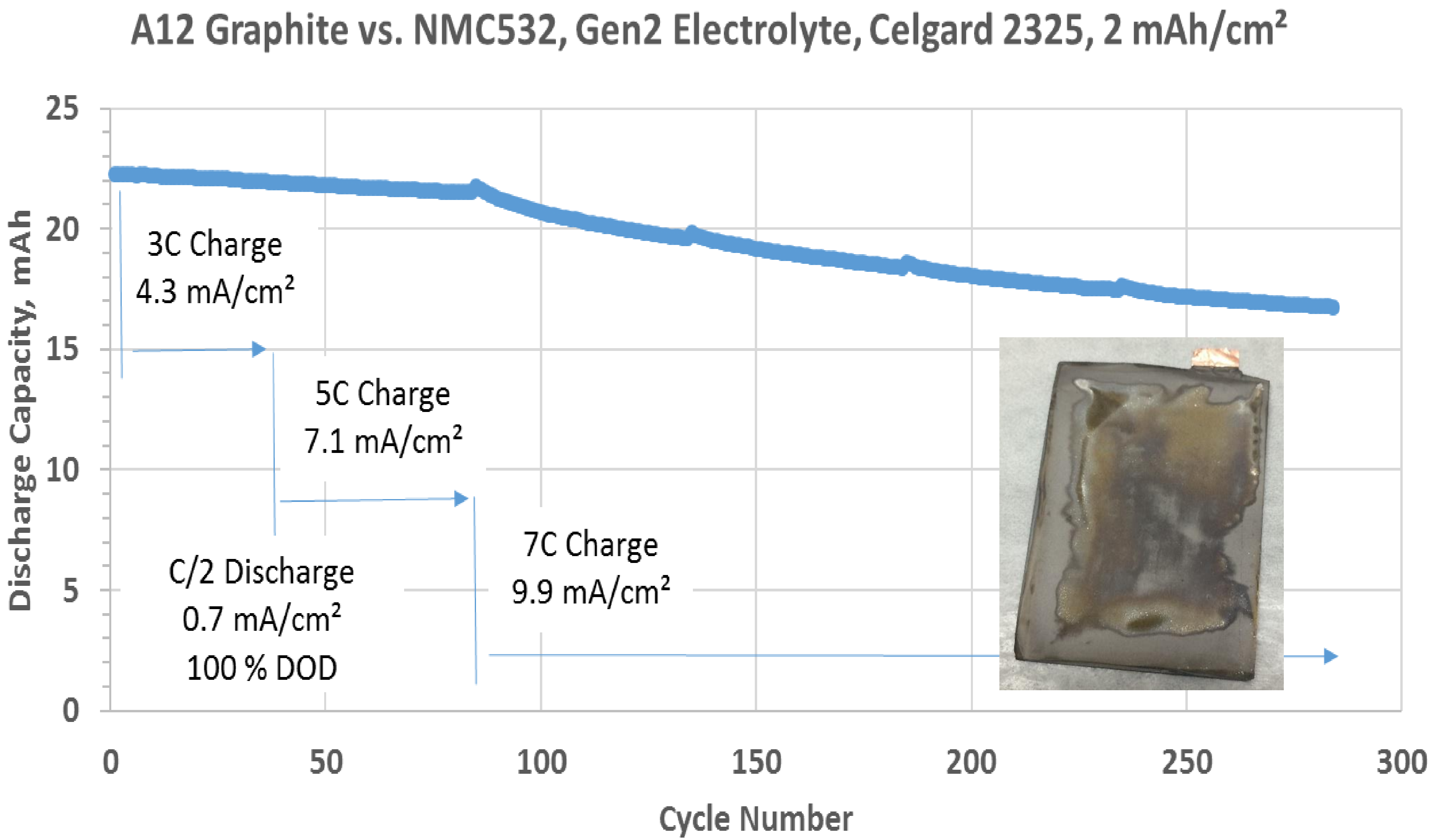
Technical Back-Up Slides

INITIAL TESTING OF A12 GRAPHITE AT 7C RATE



COIN CELL SCREENING – CELL DESIGN

Anode: A-A010
91.83 wt% Gelon G15 MCMB graphite
2 wt% Timcal C-45
6 wt% Kureha 9300 PVDF Binder
0.17wt% Oxalic Acid
Lot#: 1506-1, LN3024-159-3
"SS = single-side, DS = double-side"
Cu Foil: 10 microns
Total Electrode Thickness: 58 µm (SS)
Coating Thickness: 48 µm (SS)
Porosity: 38.1 %
Total SS Coating Loading: 6.44 mg/cm²
Total SS Coating Density: 1.34 g/cm³
Made by CAMP Facility

Cathode: A-C013A
90 wt% Toda NMC 532
5 wt% Timcal C45
5 wt% Solvay 5130 PVDF
LN3012-180-7
Al Foil Thickness: 20 µm
Total Electrode Thickness: 62 µm
Coating Thickness: 42 µm
Porosity: 33.6%
TTL Coating Loading: 11.32 mg/cm²
TTL Coating Density: 2.70 g/cm³
Made by CAMP Facility

Anode: A-A002B
91.83 wt% Phillips 66 CPreme A12
2 wt% Timcal C45 carbon
6 wt% Kureha 9300 PVDF Binder
0.17 wt% Oxalic Acid
LN3024-177-4 (SS)
"SS = single-side, DS = double-side"
Cu Foil Thickness: 10 µm
Total Electrode Thickness: 53 µm
Total Coating Thickness: 43 µm
Porosity: 34.9%
Total SS Coating Loading: 6.07 mg/cm²
Total SS Coating Density: 1.41 g/cm³
Made by CAMP Facility

VS.

Anode: A-A015
91.83 wt% Superior Graphite SLC1506T
2 wt% Timcal C45 carbon
6 wt% Kureha 9300 PVDF Binder
0.17 wt% Oxalic Acid
Lot#:1506-01 received 02/04/2015
Electrode ID: LN3107-110-5
"SS = single-side, DS = double-side"
Cu Foil Thickness: 10 µm
Total Electrode Thickness: 57 µm
Total Coating Thickness: 44 µm
Porosity: 37.4 %
Total SS Coating Loading: 6.38 mg/cm²
Total SS Coating Density: 1.36 g/cm³
Made by CAMP Facility

Anode: A-A005A
91.83 wt% Superior Graphite SLC1520P
2 wt% Timcal C45 carbon
6 wt% Kureha 9300 PVDF Binder
0.17 wt% Oxalic Acid
Cu Foil Thickness: 10 µm
Total Electrode Thickness: 55 µm
Coating Thickness: 45 µm
Porosity: ~35.1%
TTL Coating Loading: 6.33 mg/cm²
TTL Coating Density: 1.41 g/cm³
Made By CAMP Facility

Anode: LN3107-115-1 (SS)
95 wt% Hitachi MagE3
2 wt% Timcal C-45
1 wt% Nippon MAC350HC CMC
2 wt% JSR TDR104A SBR
Prod: MagE3, Lot#: 160523, initial CMC+SBR mix using Primix/Buhler mixer
"SS = single-side, DS = double-side"
Cu Foil Thickness: 10 µm
Total Electrode Thickness: 57 µm (SS)
Coating Thickness: 47 µm (SS)
Porosity: 38.7 %
Total SS Coating Loading: 6.41 mg/cm²
Total SS Coating Density: 1.36 g/cm³
Made by CAMP Facility

Anode: A-A016
91.83 wt% Hitachi MagE3
2 wt% Timcal C45 carbon
6 wt% Kureha 9300 PVDF Binder
0.17 wt% Oxalic Acid
Lot#: 160523, Electrode ID: LN3107-124-2
"SS = single-side, DS = double-side"
Cu Foil Thickness: 10 µm
Total Electrode Thickness: 52 µm
Total Coating Thickness: 42 µm
Porosity: 30.3 %
Total SS Coating Loading: 6.35 mg/cm²
Total SS Coating Density: 1.51 g/cm³
Made by CAMP Facility

Anode: LN3107-116-1 (SS)
91.83 wt% BTR BFC-10 graphite
2 wt% Timcal C-45
6 wt% Kureha 9300 PVDF Binder
0.17wt% Oxalic Acid
Prod: Targray graphite, SPGPT805, Artificial Graphite High Energy Fast Charge, **BTR BFC-10**, Lot#: 161541202-3
"SS = single-side, DS = double-side"
Cu Foil Thickness: 10 µm
Total Electrode Thickness: 59 µm (SS)
Coating Thickness: 49 µm (SS)
Porosity: 32.1 %
Total SS Coating Loading: 7.21 mg/cm²
Total SS Coating Density: 1.47 g/cm³
Made by CAMP Facility

Graphite Selected:	Corresponding Electrode Tested
MCMB Graphite	A-A010
Superior Graphite 1506T	A-A015
Superior Graphite 1520P	A-A005A
MAGE3 w/CMC+SBR	LN3107-115-1
MAGE3 w/PVDF	A-A016
BTR-BFC-10	LN3107-116-1
A12 Graphite	A-A002B

- Cathode Electrode Area: 1.54 cm² [14 mm dia.]
- Anode Electrode Area: 1.77 cm² [15 mm dia.]
- Cell Assembly
  - Separator Used: Celgard 2320 - Trilayer PP/PE/PP
    - 5/8'' dia.
  - Electrolyte Used: Tomiyama [A49] 1.2 M $LiPF_6$ in EC:EMC (3:7 wt%) "Gen2"
    - Flooded
- n:p ratios are: ~1.1 to 1.2 (BTR slightly higher)

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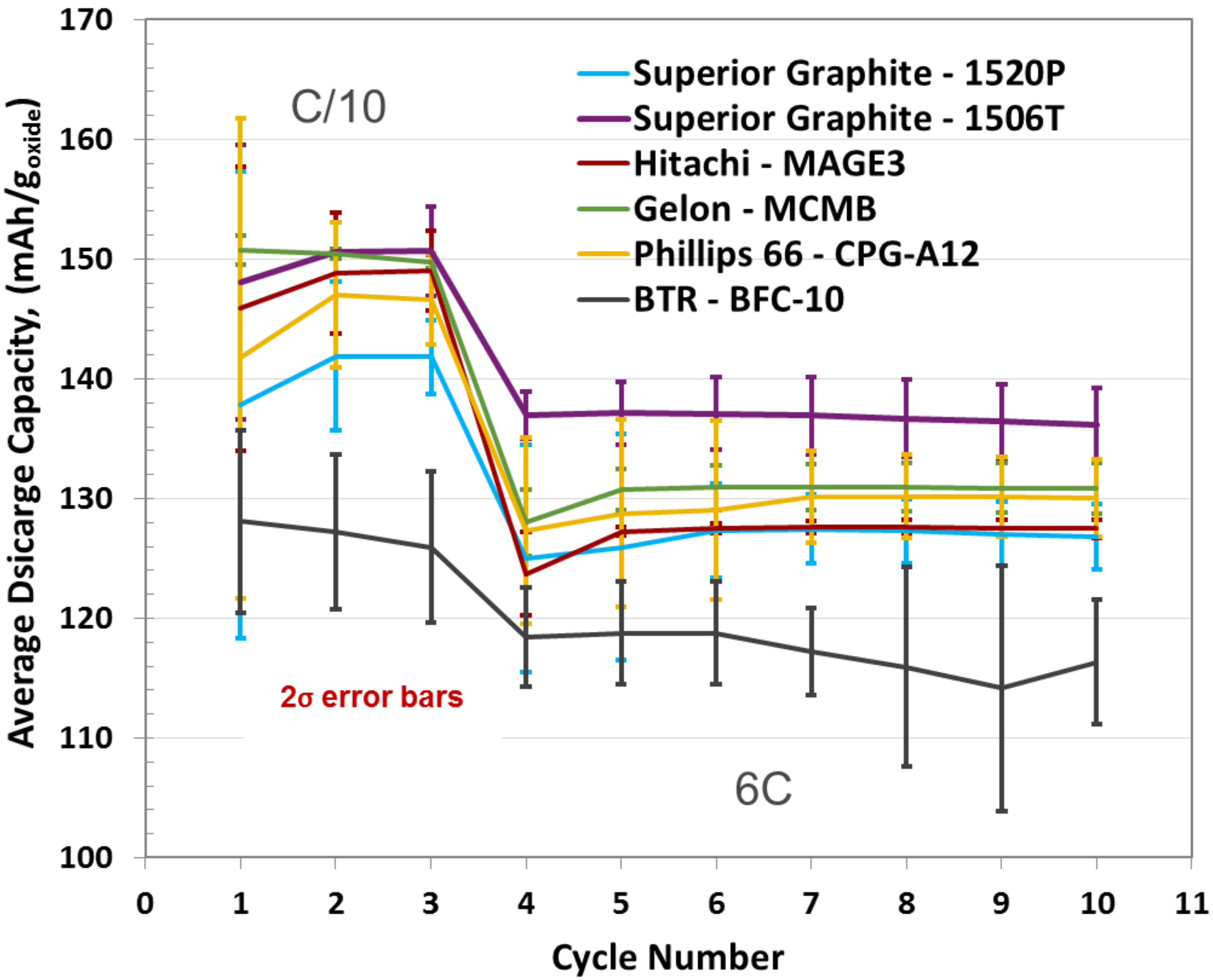
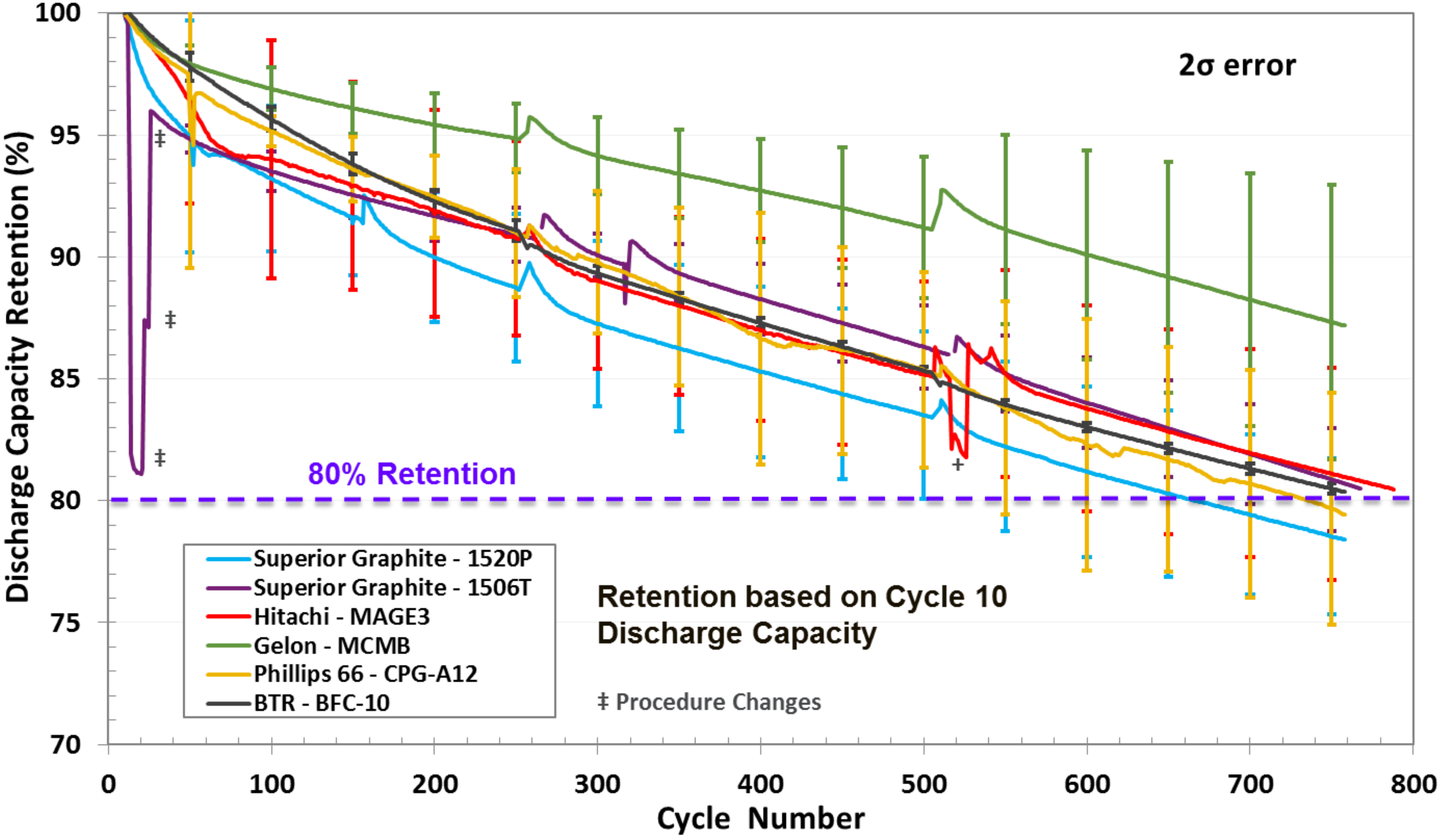
XFC SCREENING - FIRST 10 CYCLES:
Formation and Stabilization



- Different Graphites Stabilized at Different Cycles
- Amongst All the Graphites, Stabilization Occured Between Cycle 5 and 10
- Cycle 10 was Used as the Common Stabilized Cycle (Defined as 100% Capacity)

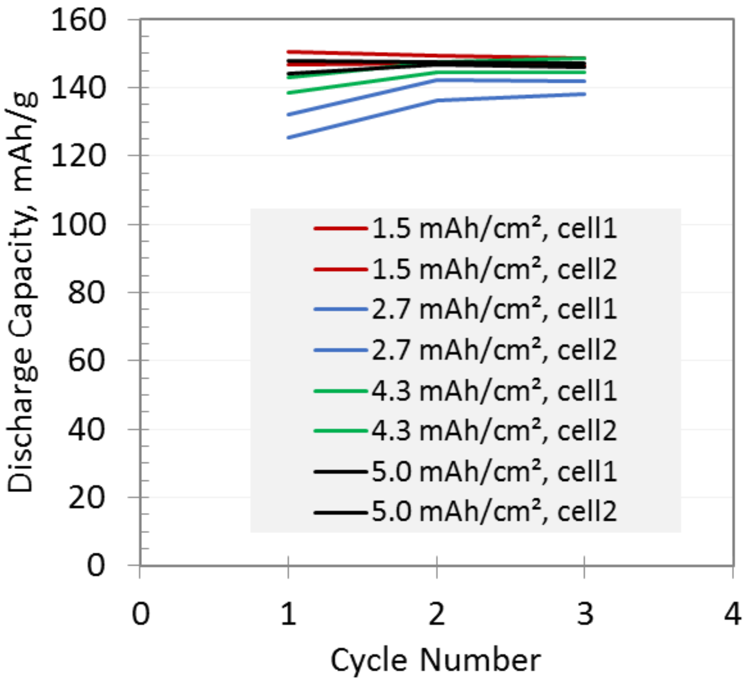
SELECTED GRAPHITES CAN EXCEED 750 CYCLES OF 6C CHARGING AT LOW LOADINGS



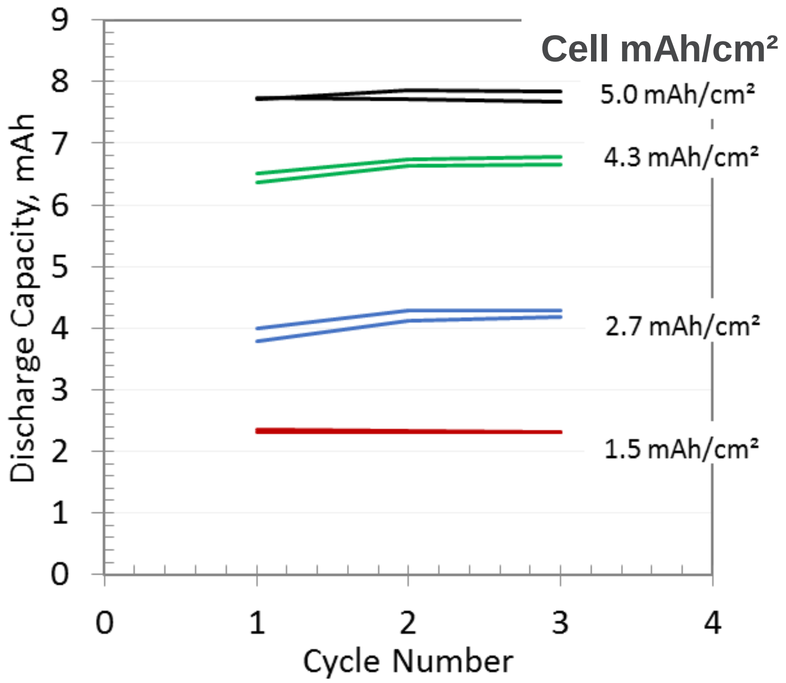
IMPACT OF mAh/cm² ON PERFORMANCE

Formation, full cell coin cells, scoping experiments

After break in, the capacities of the cells are roughly 140 mAh/g



The different cell areal capacities of the cells range from 1.5 to 5.0 mAh/cm²



Reported mAh/cm² is in terms of the initial cell capacity at ~C/10

Gen2 electrolyte
3.0 to 4.1V, ~C/10
30°C, Celgard 2320
Pos: Toda NMC532
Neg: A12 graphite