X-CELL: PERFORMANCE AND POST-TEST CHARACTERIZATION OF FAST-CHARGED BATTERIES

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PROJECT ID# BAT341

OVERVIEW

Timeline

- Project start date: October 2017
- Project end date: October 2020
- Percent complete: 25%

Budget

- Total project funding: $600K (ANL); $500K (INL)
- Funding received in 2018: $600K (ANL); $500K (INL)

Barriers

- Barriers addressed
  - Detecting/minimizing lithium plating in full pouch cells

Partners

- This was a collaborative effort between Argonne National Laboratory, Idaho National Laboratory, National Renewal Energy Laboratory
- The work in this presentation was divided into three parts, materials characterization, addressing different aspects of diffusion and lithium plating and post-test characterization
- Other aspects of the program will be discussed separately

RELEVANCE / OBJECTIVES

- Overall objectives
  - The rate of lithium diffusion into graphite directly impacts the performance and life of lithium-ion cells under extreme-fast-charging conditions. At high charge rates, if the rate of lithium production at the negative exceeds the diffusion of lithium into the solid, plating can occur (at ~0 V vs. Li/Li^+)
  - Investigate factors that can affect solid and liquid transport processes
    - Structure of the graphite – can we tell them apart easily?
    - Li^+ diffusion coefficient measurement
    - Effect of charging temperature using the 6-C charge rate
    - Effect of multi-stage charging to allow the transport process time to relax, possibly allowing lithium more time to diffuse into the solid
  - The present experiments will focus on the limitations and dynamics of the transport process during charge. They are not meant to optimize the charging algorithm

APPROACH

- Materials properties
  - Raman spectroscopy and X-ray diffraction on selected graphite powders
  - Galvanostatic, intermittent titration (GITT) using 15-min pulses at the C/20 rate followed by 90 min rest for both charge and discharge
- Cell testing
  - Small, 19-mAh cells containing NMC532/graphite chemistry were made by the CAMP Facility at Argonne
  - The cells were first characterized in terms of C/1 and C/20 capacities, HPPC, and EIS
  - Reference performance tests (RPTs) were conducted after every 25 cycles at the test temperature and consisted of a C/20 charge and discharge, HPPC (includes a profile at 0% DOD) and EIS at 3.8 V. The C/20 data were used to calculate $(1/Q_n)dQ/dV$ curves
  - Cells were cycled between 3.0 and 4.1 V
  - At Idaho, in addition to the above, the cells were characterized in terms of rate capability and charge acceptance using different protocols
  - At Argonne, the cells were cycled using four cycles of 6-C charge and 1-C discharge followed by 6-C charge and C/20 discharge at temperatures of 20, 30, 40 and 50°C

MILESTONES

- Milestones
  - Materials characterization
    - Raman spectroscopy of eight graphite powders and X-ray diffraction of six (Q1, complete)
    - Perform GITT experiment on selected graphites at 20, 30, 40 and 50°C (Q2, delayed to Q3; in progress)

  - Cell testing at Idaho
    - Acquire cells from CAMP and establish baseline procedures for initial evaluation (Go/No-go) (Q1, complete)
    - Assess variation in cells and provide initial understanding on variability and electrode balance. Start initial aging/characterization efforts (Q2, complete)
    - Perform initial proof-of-concept experiments to identify the impacts of fast charging at the cell level using non-destructive, *in operando* techniques including acoustics (Q3, in progress)
    - Report summarizing full cell, electrochemical evaluation methods that can be used for analysis of future XFC activities. This includes the ability to identify variability in cells and means to maintain safe operating conditions (SMART, Q4, in progress)

MILESTONES (CONTINUED)

- Cell testing at Argonne
  - Develop test plan (Q1, complete)
  - Obtain cells from CAMP and perform initial characterization (Q1, complete)
  - Determine effect of temperature on lithium plating and cell life (Q4, in progress)
  - Write report describing the results of cell testing and their implications regarding the temperature dependence of diffusion/lithium plating (Q4)

- Post-test Analysis
  - Complete characterization of anode materials from above experiments and develop hypothesis for electrochemical behavior (Q4)
  - Write report describing the finding from post-test analysis and their implications (Q4)

TECHNICAL ACCOMPLISHMENTS

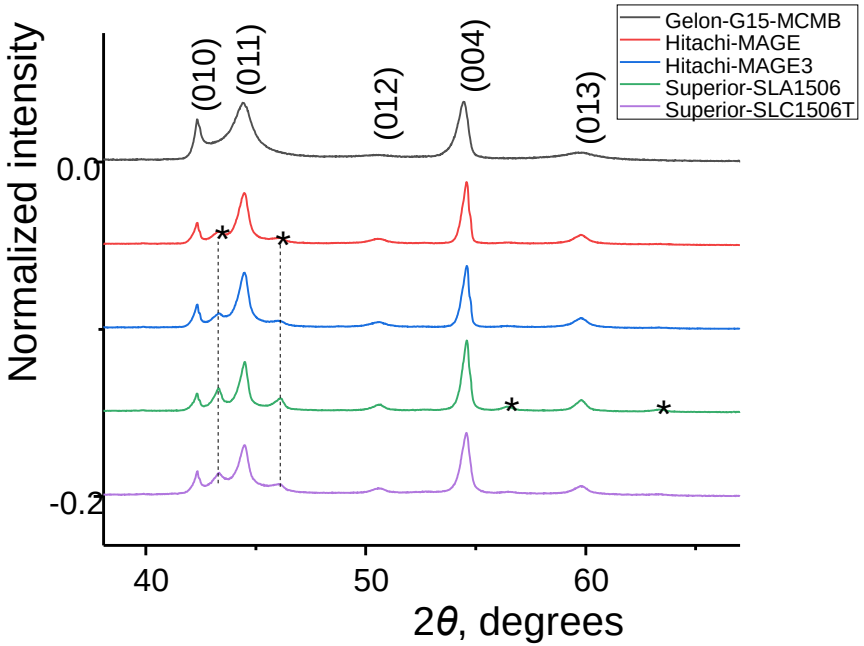
INTRODUCTION

- Typically, recharging lithium-ion batteries takes much longer than the average, liquid-fueled-internal-combustion-engine (ICE) car owner is used to. Consumer acceptance of electric vehicles (EVs) will be facilitated by a recharge ('refueling') experience similar to that of an ICE-powered car, roughly 8-10 min. Additionally, recharging does not have to be from a completely discharged battery (empty) to a completely charged one (full). As with an ICE car, partial recharging is possible and should not adversely affect the battery
- The increased charging rate necessary for fast charging can adversely affect the performance, safety and life of the battery, such as increased probability of lithium plating; increased rate(s) of side reaction(s); and increased battery temperature
- Experimentally characterize selected graphite materials to determine if there is a simple relationship between diffusion coefficient and structure
- Examine the effects of charging conditions (algorithm and temperature) to characterize limitations and dynamics of lithium transport under fast-charging conditions

ARE THERE STRUCTURAL FEATURES THAT MAY ENABLE SOME GRAPHITES TO PERFORM BETTER UNDER HIGH-CURRENT CHARGING CONDITIONS?

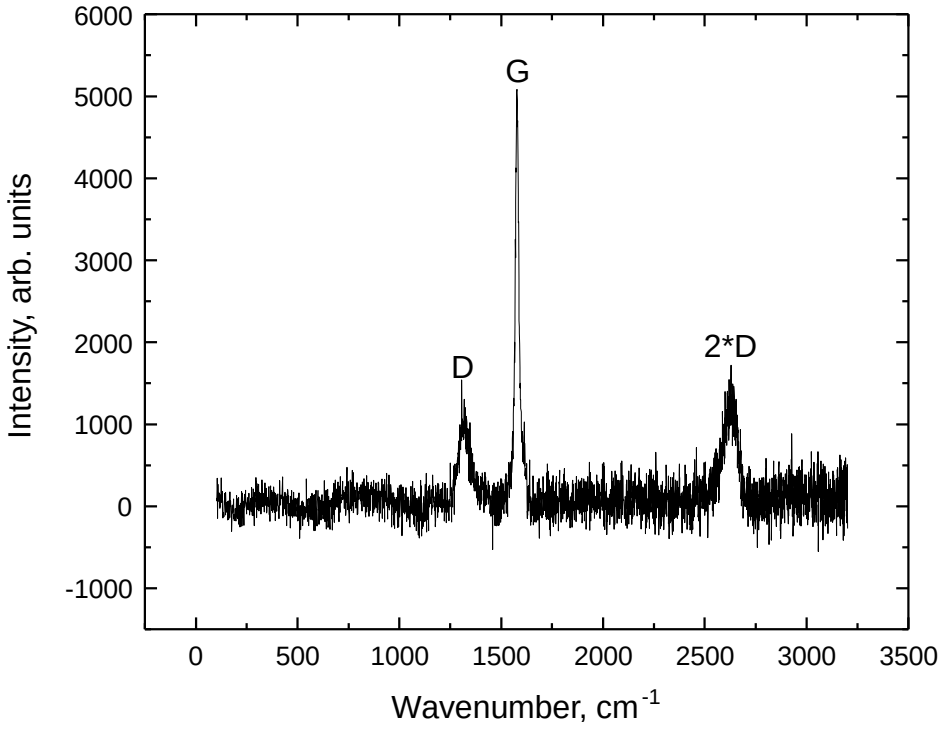
MATERIALS CHARACTERIZATION

- Perform X-ray diffraction on 5 graphites
- Perform Raman spectroscopy on 8 selected graphite materials
- XRD patterns were similar
- Most of the lines could be indexed in the space group *P*6/*mmc*.
- Some had additional reflections in the 2θ range of 40 to 60°
- All but MCMB contained extra reflections that could not be indexed; most likely due to coatings



THE AREA RATIO OF THE D AND G BANDS VARIED FROM MATERIAL TO MATERIAL

- Since all are graphitic materials, the Raman spectra were similar



	D:G area ratio
MAG E	1.00
MAG E3	1.08
MCMB	1.35
SLA1506	2.01
SLC1506T	1.89
A12	1.30
BTR	1.04
1520P	2.78

CELL MODELING NEEDS DIFFUSION COEFFICIENTS

- Coin, half-cells were constructed from CAMP laminates of anode materials. Galvanostatic intermittent titration (GITT) experiments were performed at 25, 35, 45 and 55°C. Here, cells were charged and discharged using C/20 currents. The current was on for 15 min and off for 90 min
- Because the graphites were not a single phase in most of the compositional range, the usual GITT equation could not be used to estimate the diffusion coefficient
- Instead, a depolarization analysis [1-3] was performed

$$\ln(|E(t) - E(t=\infty)|) = constant - \frac{t}{\tau^{\delta}}$$

$$\tau^{\delta} = \frac{L^2}{\pi^2 D_{Li^+}}$$

- Model is based on the relaxation of concentration gradients and should be less susceptible to phase changes/presence of multiple phases
- With all the pores in graphite, one cannot assume that each particle is spherical
- Calculate *L* from BET surface area and density: $1/L = 10^4 \times A_{BET} \times density$

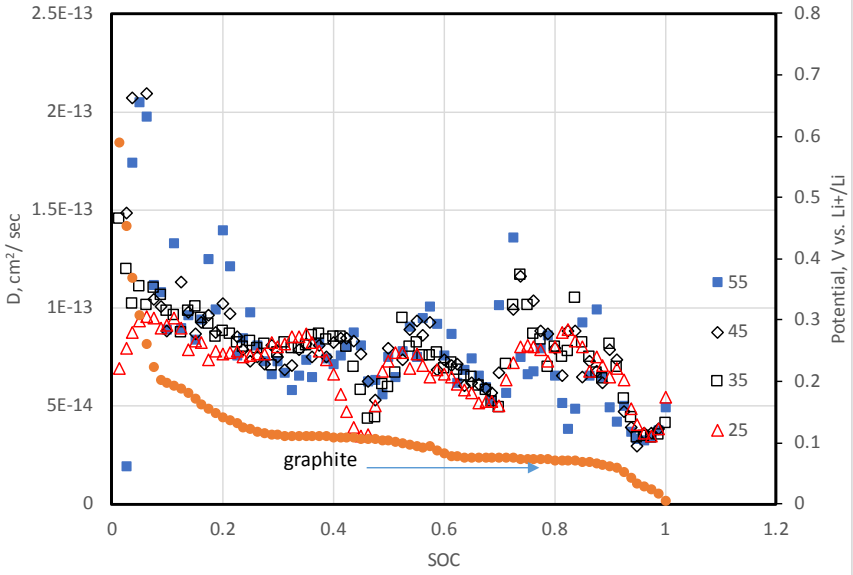
1. C. Wagner, *Proc. 7th Meeting Int. Comm. on Electrochem. Thermodynamics and Kinetics*, Lindau 1955, Butterworth, London, 1957.

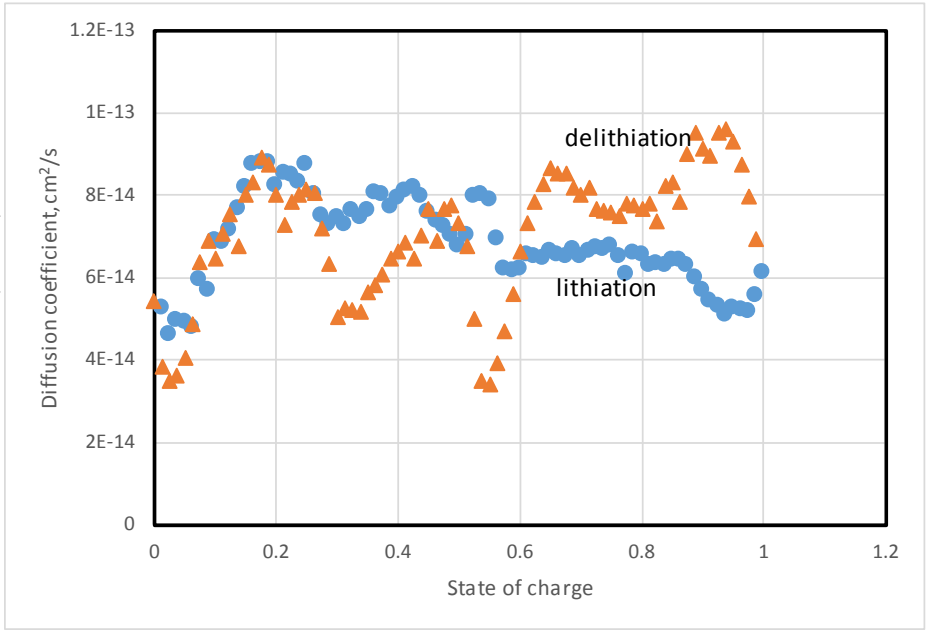
2. I. Yokota, J. Phys. Soc. Japan, 16 (1961) 2213.

3. J. Maier, Physical Chemistry of Ionic Materials: Ions and Electrons in Solids, Wiley, Chicester, England (2004).

VALUES OF *D* FOR DELITHIATION APPEAR TO BE SIMILAR TO THOSE FOR LITHIATION

- Changes in *D* appear at approximately the states of charge where phase changes would be expected
- Some sensitivity to state-of-charge was also seen
- There does not appear to be a temperature sensitivity in values of *D* among the graphites studied. They all seem to be in the range of 10^{-14} to 10^{-13} cm^2/s regardless of temperature for lithiation





Lithiation
1506T

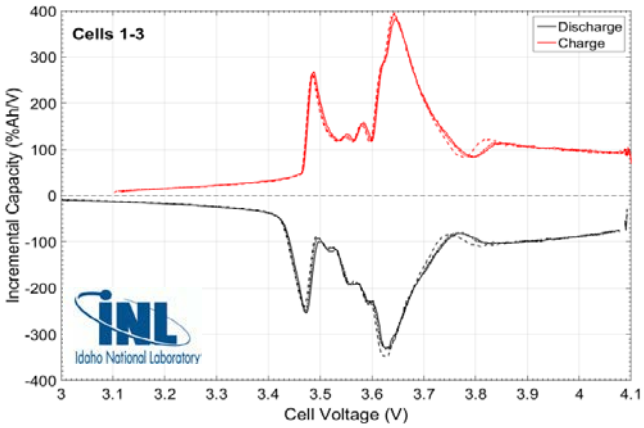
INVESTIGATE FACTORS AFFECTING SOLID AND LIQUID TRANSPORT PROCESSES (1)

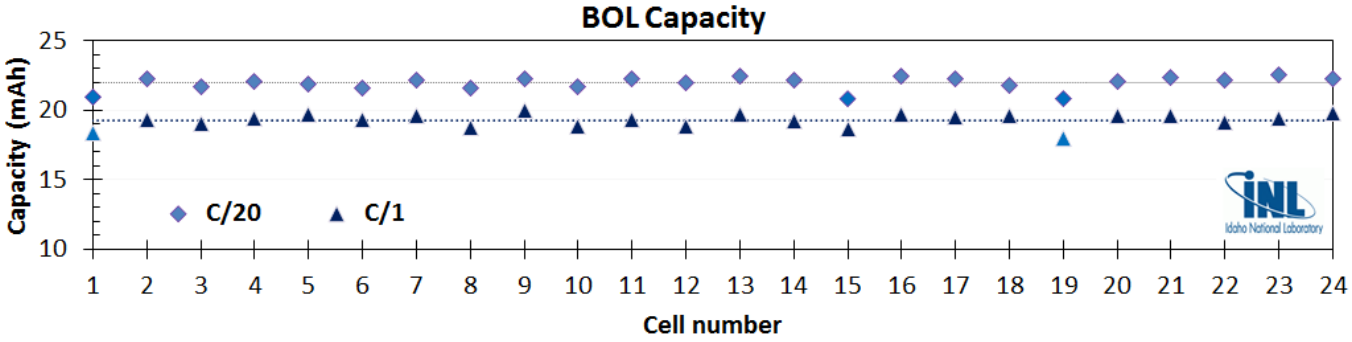
RELAXATION TIME: CELL TESTING AT IDAHO

Gr/ NMC523

V_{max}/V_{min}= 4.1V/3V

- Initial characterization: 24 cells
- Cells characterized at C/1, C/20, HPPC and EIS
- Capacity variability of 2.5%
- Uniform incremental capacity (dQ/dV) from C/20 data
- Cells split into groups of 3 for fast charge analysis





Low variability and characterization at multiple rates

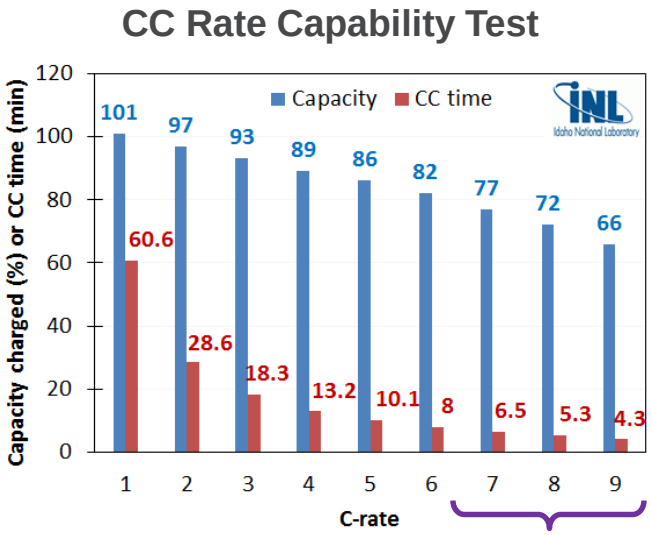
*Cell 7 failed after the BOL evaluation

RATE CAPABILITY TESTING: CELLS 1-3

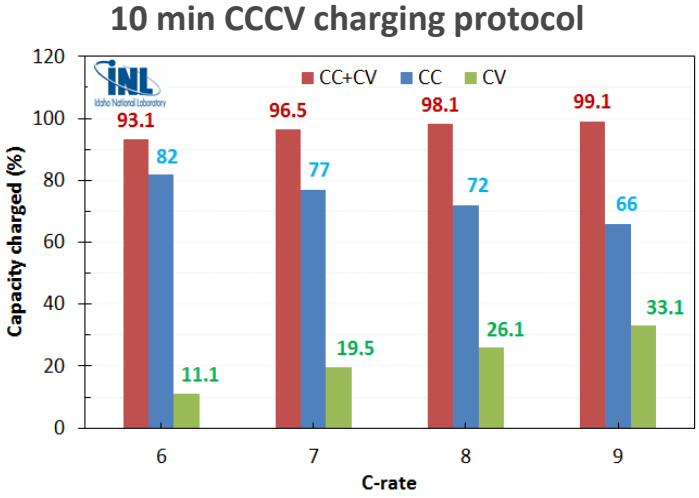
Gr/ NMC523

V_{max}/V_{min}= 4.1V/3V

- Rate capability evaluated using CC and CCCV protocols
- Percentage of capacity delivered during charge varies with rate
- Following charge 15 min rest used to study components of overvoltage



Charge completed <10 min



Quantification of charge acceptance

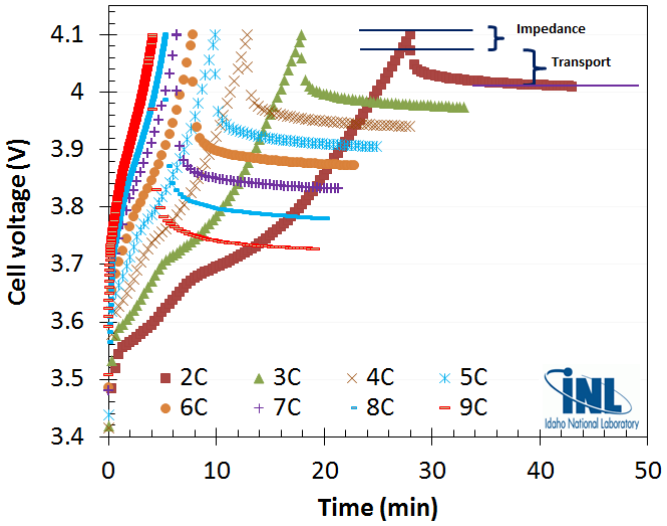
*CC: Constant Current, CV: Constant Voltage

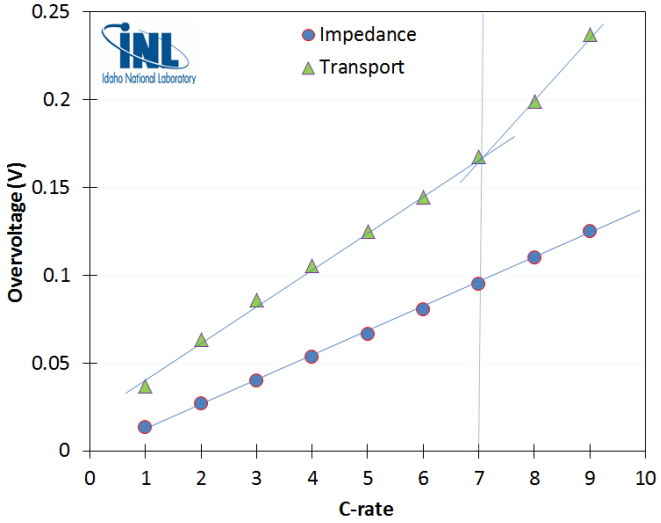
RATE CAPABILITY TESTING: CELLS 1-3 (CONT.)

- Overvoltage due to impedance (immediate relaxation) and transport (extended relaxation)
- Ohmic polarization varies linearly w/ C-rate
- Distinct transport limitation arises after 7C (for this electrode design)

Gr/ NMC523

V_{max}/V_{min}= 4.1V/3V





Clear distinction in transport at high rates

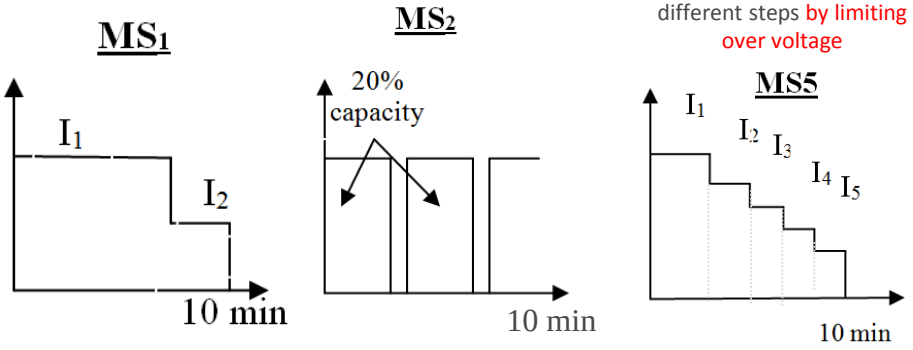
CHARGING PROTOCOLS

- **Charging protocols designed either by introducing rest time or modifying the current profiles, e.g. CV, multistage CC to minimize transport limitation.**
- **Rates defined based on transport change (slide 14)**

Gr/ NMC523

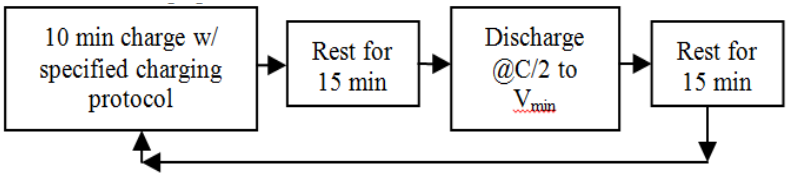
V_{max}/V_{min}= 4.1V/3V

Variable capacities in different steps by limiting over voltage

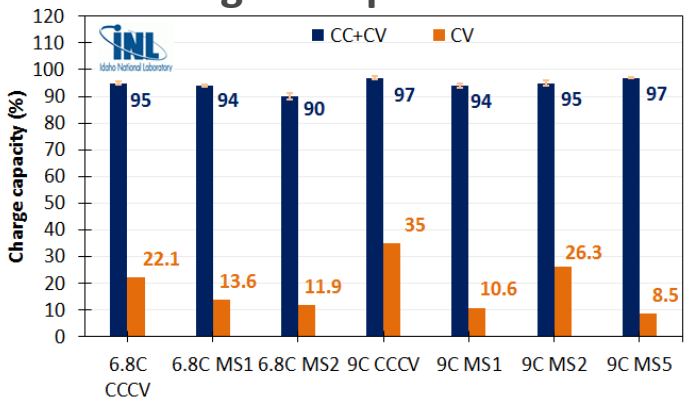


Gr.	Cell count	10 min charging protocol
B	4 to 6	6.8C CCCV
C	8 to 10	6.8C MS1 (2 step current)
D	11 to 13	6.8C MS2 (pulsed current)
E	14, 16 and 17	9C CCCV
F	18, 20, and 21	9C MS1 (2 step current)
G	22 to 24	9C MS2 (pulsed current)
H	15 and 19	9C MS5 (5 step current)

Cycling protocol



Charge acceptance at BOL



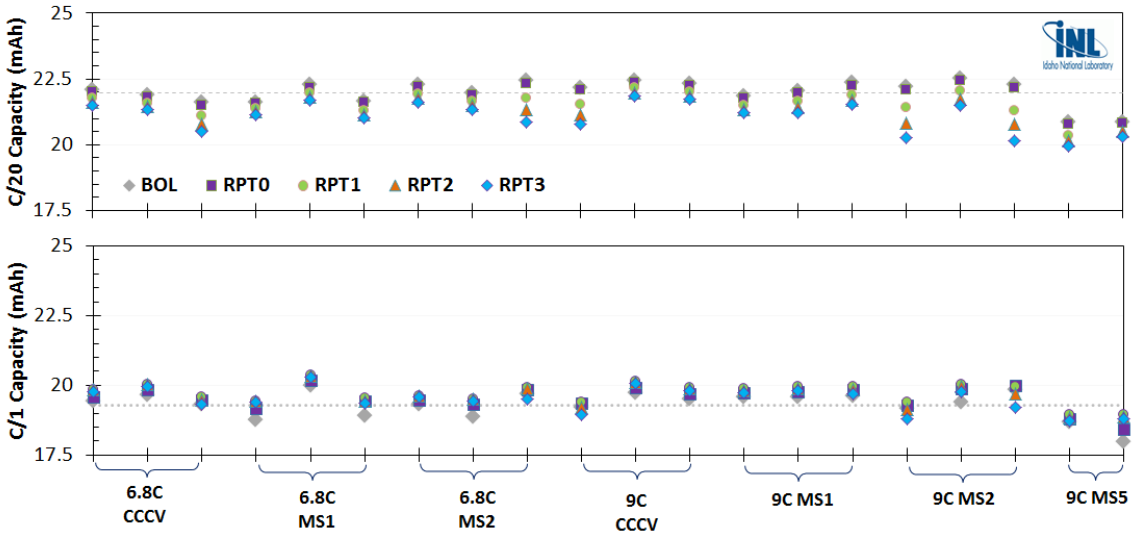
Recharge capacity is normalized by individual cells discharge capacity@C/1 at BOL and then averaged out

- **CCCV protocols needs longer CV recharge, i.e., more time spent in CV step. Ex. 57% time spent in CV step with 9C CCCV protocol.**
- **MS1 protocols show lower fraction of CV charging than CCCV, better than CCCV protocols**
- **9C MS5 has the lowest CV fraction and highest total recharge**

CYCLING RESULT

Gr/ NMC523
V_{max}/V_{min}= 4.1V/3V

- RPT after every 25 cycles
- 75 cycles (3 RPTs) completed as of April 10
- Rate of capacity fade started to diverge for different charging protocols (clearly visible at C/20)



Gr.	10 min charging protocol
B	6.8C CCCV
C	6.8C MS1 (2-step current)
D	6.8C MS2 (pulsed current)
E	9C CCCV
F	9C MS1 (2-step current)
G	9C MS2 (pulsed current)
H	9C MS5 (5-step current)

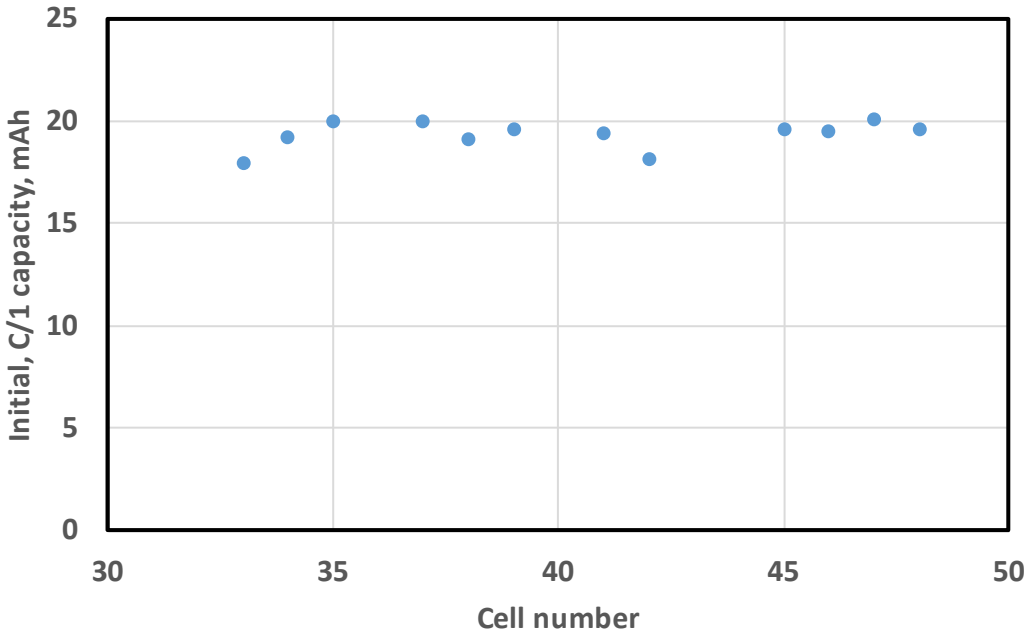
INVESTIGATE FACTORS AFFECTING SOLID AND LIQUID TRANSPORT PROCESSES (2)

EFFECT OF TEMPERATURE: CELL TESTING AT ARGONNE

Gr/ NMC523

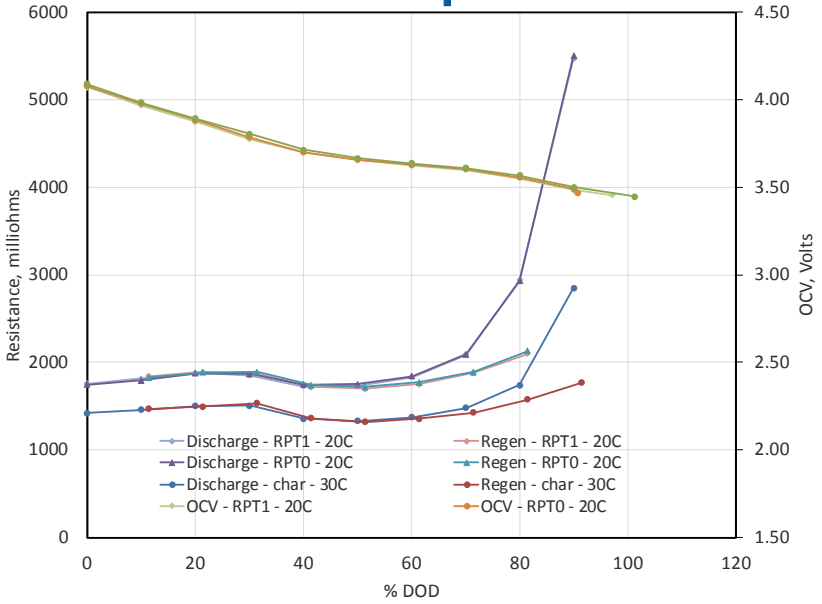
V_{max}/V_{min}= 4.1V/3V

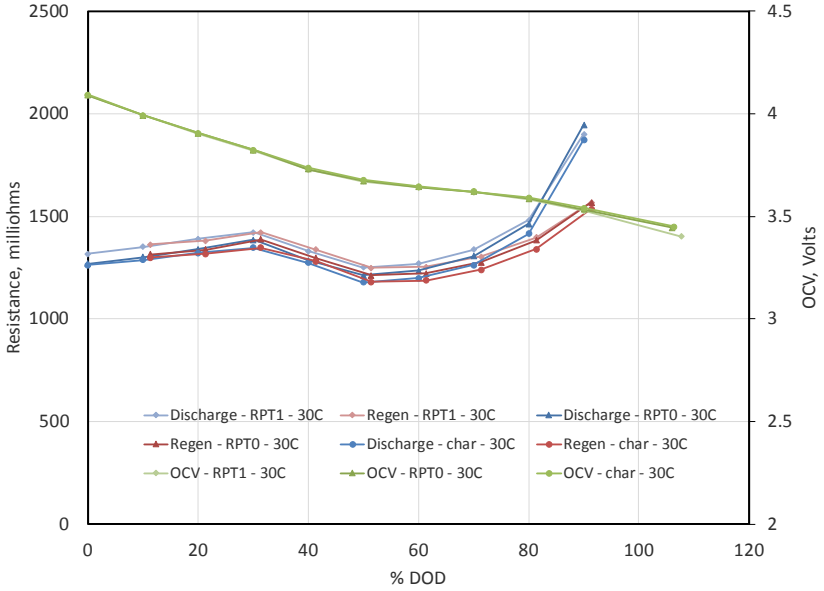
- Twelve cells were delivered and characterized
  - Average, initial C/1 capacity: 19.34±0.67 mAh at 30°C
- They were divided into four temperature groups
- The cells were cycled using four cycles of 6-C charge and 1-C discharge followed by 6-C charge and C/20 discharge at temperatures of 20, 30, 40 and 50°C
- RPTs were performed at test temperature

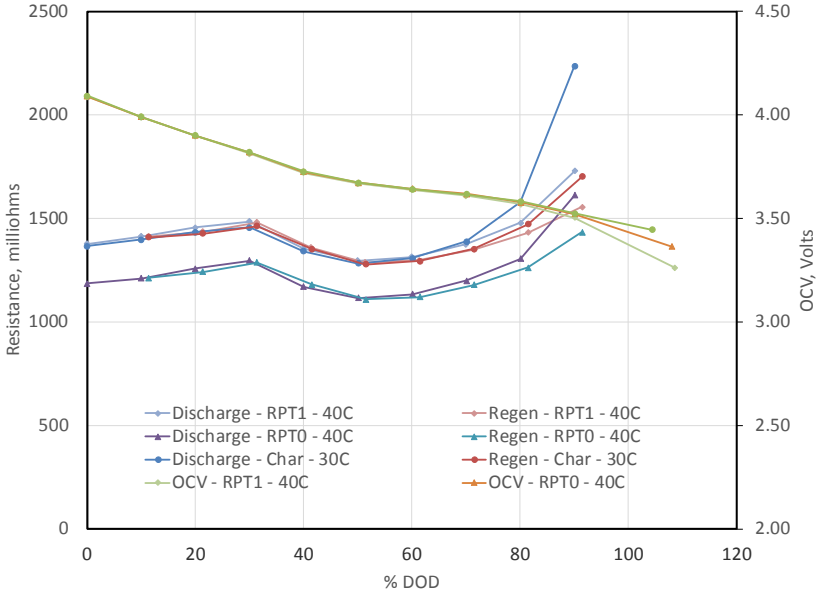


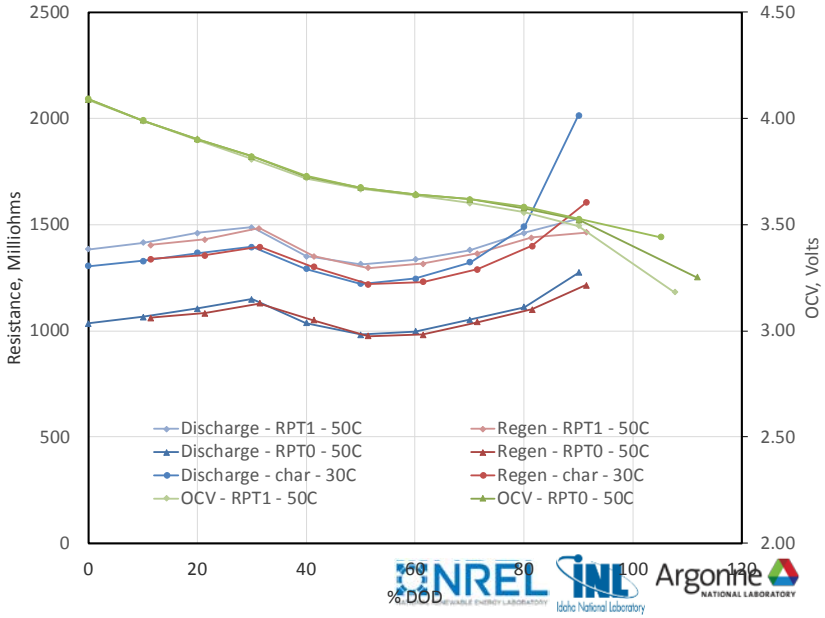
CHANGES IN CELL RESISTANCE FROM CELL AGING WERE SEEN

HPPC at test temperature



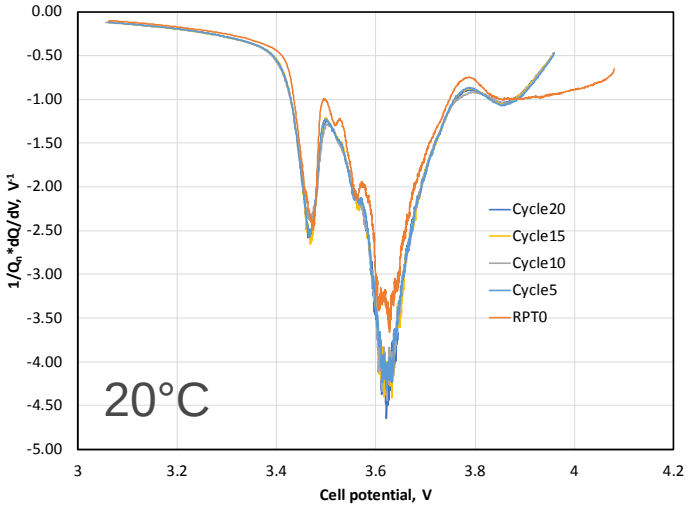


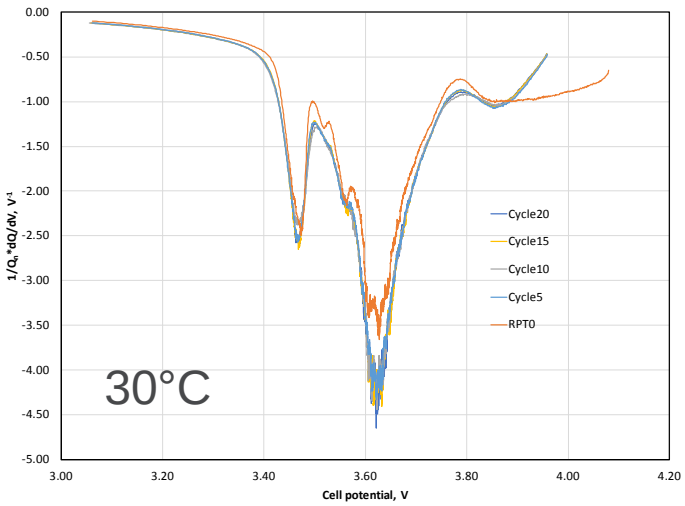


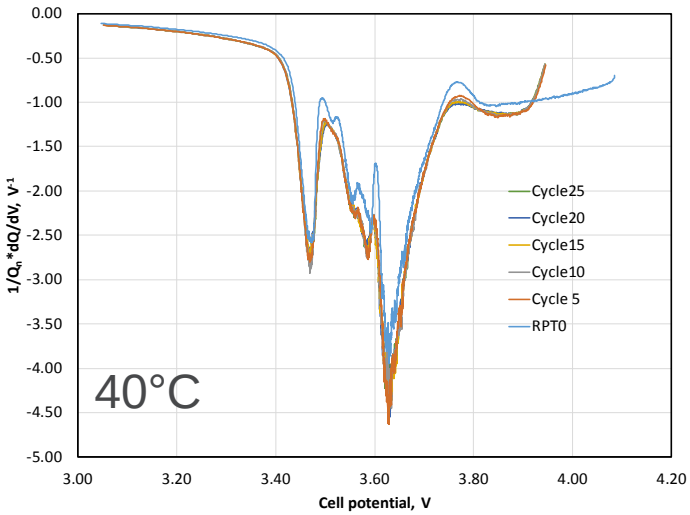


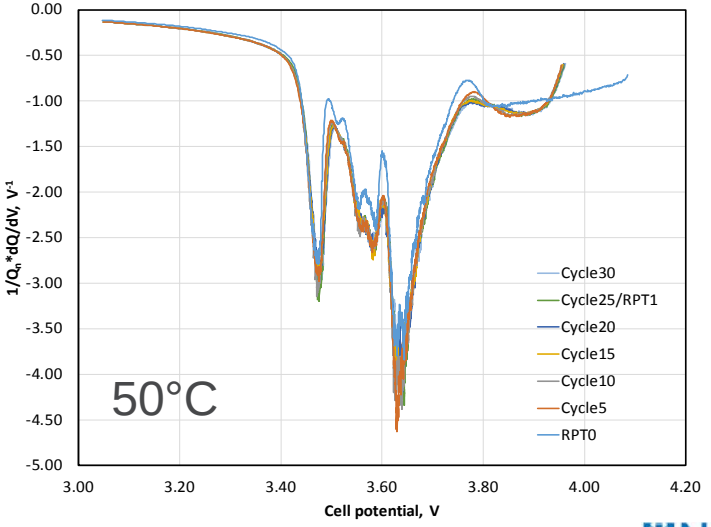
NO PEAKS INDICATIVE OF LI PLATING WERE SEEN AT HIGH POTENTIAL

dQ/dV







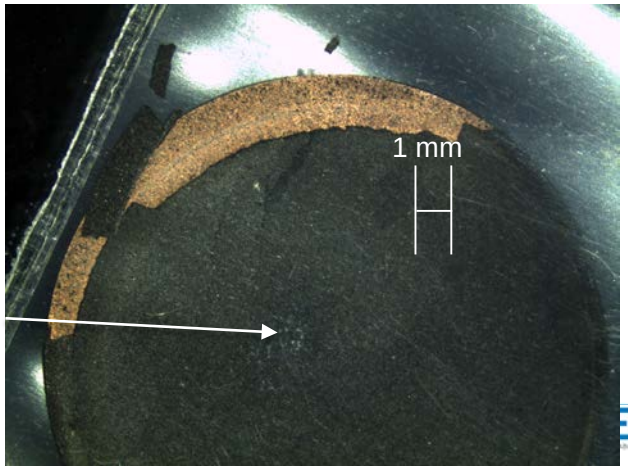


WHAT IS THE SMALLEST LITHIUM METAL DEPOSIT THAT CAN BE SEEN?

Post-test examination of aged* X-CELL, CAMP cells

- The answer to this question may impact the further characterization of X-CELL cells in the program
- Coin cells containing 1506T, 1520P, MAG E (PvDF binder), MAG E (CMC binder), A12, MCMB, or BTR BFC-10 negative electrodes were opened in an Ar-filled glove box. After drying, cells were placed in small plastic bags and taken out of the glove box for optical microscopy
- Evidence of possible Li plating was seen on 1520P-, A12- and MAG E (PvDF)-containing electrodes. No obvious evidence of plating was seen on MAG E (CMC), though electrode delamination was seen

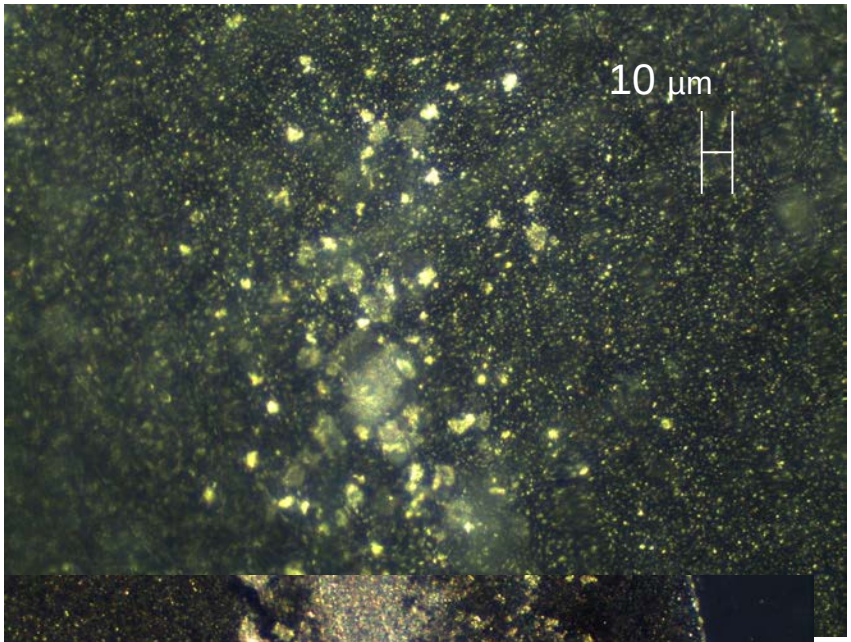
*3 x {3 C/10 cycles; 250 6-C charge/C/2 discharge}; 3 C/10 cycles; 10-h rest; T=30ºC; 762 total cycles



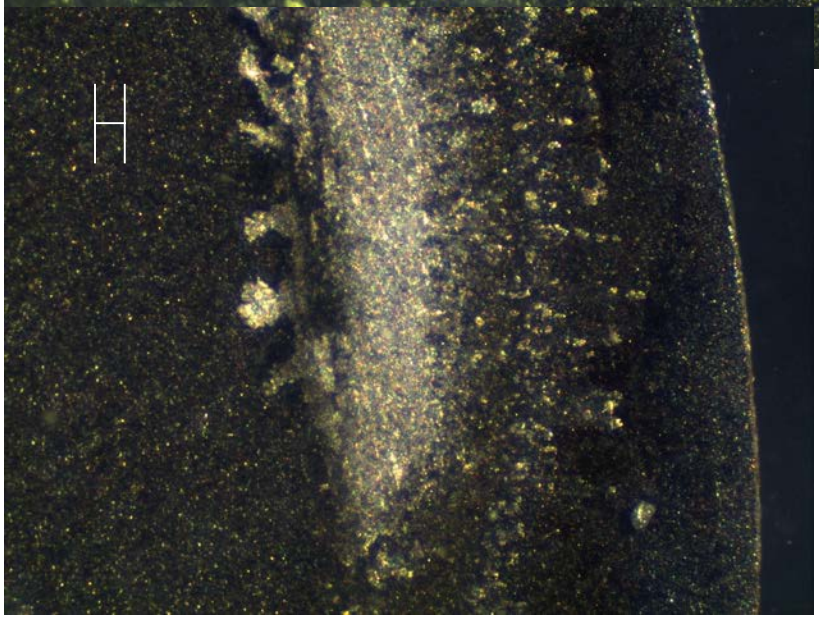
MAG E (CMC)

EVIDENCE OF POSSIBLE LITHIUM PLATING OBSERVED

- Possible lithium plating seen on 1520P-containing electrode
- Minimum size: ~2-3 µm



- Location and morphology seem to be dependent on graphite
  - A12 : large region near edge of electrode
- Also, observe sensitivity to binder
  - Possible lithium plating was seen on MAG E (PvDF)-containing electrode, but not on that made with CMC binder



SUMMARY

Materials Characterization

- Graphites are too similar by XRD for identification. The D:G ratio in the Raman can be used that purpose
- The estimated diffusion coefficients of some graphites are in the range of 10^{-14} to 10^{-13} cm^2/s

Cell testing at Idaho

- Distinct change in transport can be clearly identified through overvoltage analysis.
- Despite transport limitations at high rates, the use of defined multi-stage profiles can improve performance
  - Charge acceptance
  - Lower fade

SUMMARY

Cell testing at Argonne

- Cells are beginning to display age-related declines in performance
- No obvious changes in the dQ/dV plot indicating Li plating were seen

Post-test characterization

- Evidence of lithium plating were seen on anodes containing 1520P, MAG E (PvDF) and A12 graphites, but not in the others
- The minimum size of a detectable lithium deposit was ~2-3 µm; smaller may be possible, but has not been demonstrated
- The nature of the binder may play an important part in lithium plating and morphology

FUTURE WORK

Argonne

- Extend diffusion coefficient measurements to other electrode materials, including lack of temperature sensitivity using a model system
- Determine effects of cell chemistry on lithium plating location and morphology
- Explore binder effects on lithium plating / morphology further
- Continue cell testing. Determine effect of thicker (EV-type) electrodes on lithium plating and morphology
- Explore effects of electrode cross-talk on the aging behavior of selected cells under extreme fast charging conditions

Idaho

- Extend dQ/dV analysis as aging continues
- Look at the impact of electrolyte properties (transference number, diffusivity and conductivity)
- Refine overvoltage analysis to better identify limitations
  - Extend characterization on cells with high electrode loadings
  - Extend link between aged electrodes, electrolytes and electrolyte transport

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

ACKNOWLEDGMENT

We gratefully acknowledge the support from the US Department of Energy, Office of Vehicle Technologies– Samm Gillard, Peter Faguy and Dave Howell. We also thank the CAMP Facility at Argonne for providing the pouch and coin cells used in these experiments

QUESTIONS?