Scale-up and Testing of Advanced Materials from the BATT Program

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es029

Objectives

An essential component of the OVT portfolio is the proper evaluation of promising materials from the exploratory research program (BATT).

We provide the means of testing materials developed by BATT PIs in half and full cells and compare their performance to a baseline chemistry.

- Fabricate electrodes and cells
- Test in well sealed cells
- Provide comparisons to baseline
- Identify sources of failure

Overview

Timeline

- Project start date: 10/2008
- Project end date: 9/2012
- Percent complete: 91 %

Barriers

- Barriers addressed
  - Cost: 300 $/kWh
  - Performance: 138 Wh/kg
  - Life: 10+ years, >3000 cycles

Budget

- Total project funding
  - DOE share: 100%
  - Contractor share: 0 %
- Funding received in FY11: $190 k
- Funding for FY12 $190 k

Partners/Collaborators

- NEI Corp.
- Daikin America, Inc.
- Daikin Industries, Inc.
- G. Ceder MIT
- A. Manthiram UT
- D. Scherson CWRU
- B. Lucht URI
- K. Zaghib HQ

Impact

Through the thorough evaluation of baseline materials of high voltage and capacity and the subsequent evaluation of competing materials is provided the necessary perspective for addressing the cost, energy density, and life challenges of chemistries targeted for PHEVs and EVs.

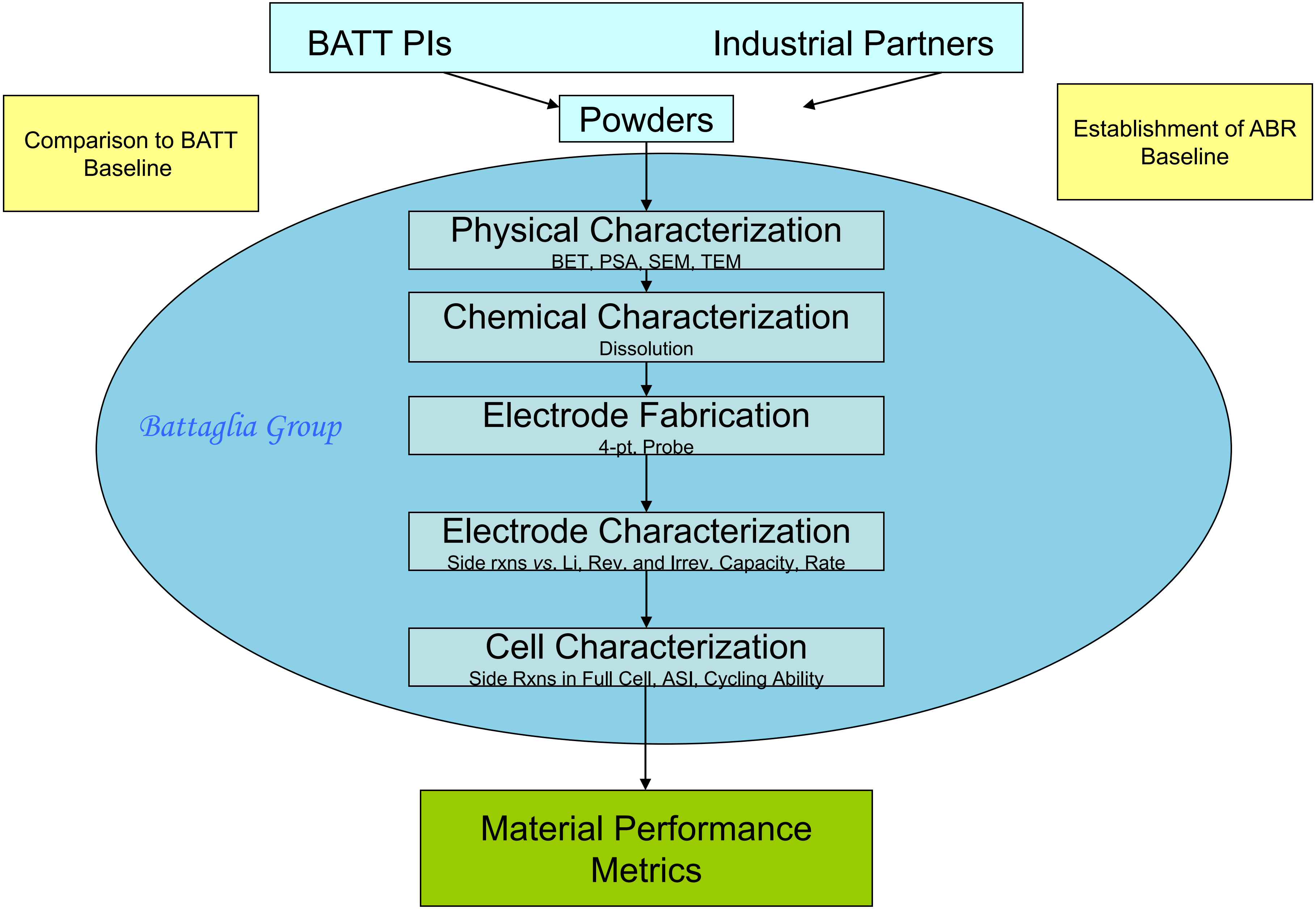
Approach

- Assess key physical, chemical, and electrochemical properties, including:
    - First cycle irreversible capacity loss
    - Reversible capacity
    - Rate capability (for electrodes with comparable loadings and porosities)
    - Cycleability *vs.* graphite

  as compared to BATT baseline materials.

- Acquire BATT materials
    - Discuss with PI the advantages of his/her material and appropriate testing
- Assess the advanced materials, with attention to key performance limitations of baseline.

Approach/Strategy



BATT PIs

Industrial Partners

Powders

Comparison to BATT Baseline

Establishment of ABR Baseline

Battaglia Group

Physical Characterization
BET, PSA, SEM, TEM

Chemical Characterization
Dissolution

Electrode Fabrication
4-pt. Probe

Electrode Characterization
Side rxns *vs.* Li, Rev. and Irrev. Capacity, Rate

Cell Characterization
Side Rxns in Full Cell, ASI, Cycling Ability

Material Performance Metrics

Milestones/Deliverables

Date	**Title**
October 2011	Contact BATT PIs and acquire samples of those materials demonstrating some promise over the baseline.
January 2012	Identify key performance limitations of baseline
May 2012	Report on the performance of BATT materials at the AMR.

Significance

- Several materials tested to address limitations of NCM and Ni-spinel:
  1. Three industry-based high-voltage electrolytes tested (for NCM)
  2. Three BATT and 3 industry cathode materials tested (for Ni-spinel)
  3. Three BATT salts/additives tested (for NCM and Ni-spinel)
- Side reactions are significant in both chemistries.
  - Presently, for NCM, there is a choice between first cycle loss and impedance rise
  - The side reaction with Ni-spinel *vs*. Li is so large that it must consist of a shuttle.
- Some of the additives are effective at passivating one of the electrode surfaces, which effectively stops the noisy side reaction for Ni-spinel
- The Ni-spinel full-cells show significant capacity loss with rate
  - The Ni-spinel appears to cause an increase in anode impedance
- A reference electrode cell that does not leak is needed to establish the source of cell impedance rise.

Improved life of these higher voltage materials will require methods to deal with electrolyte reactivity.

Establishing a baseline electrolyte for NCM

Full-Cell Cut-off Voltages: 3.0 and 4.5V

Four different electrolyte solutions:

1. Novolyte, 1M LiPF6 in 1:2 EC/DEC **for cell 8901, 8903**
2. Daikin BDK-03, 1.2M LiPF6 in FEC/EMC/D2(2/6/2)+PS1% **8904, 9603, 9602**
3. Daikin BDK-04, 1.2M LiPF6 in FEC/EMC/D2(2/5/3)+PS1% **8905**
4. Daikin BDK-05, 1.2M LiPF6 in FEC/A8/EMC/D2(1/1/6/2)+PS1% **8902**

D2, A8 – secret components
PS: 1,3-propane sultone

Cathode composition: NMC$_{333}$ 92.8%, PVDF 4.0%, AB 3.2%;

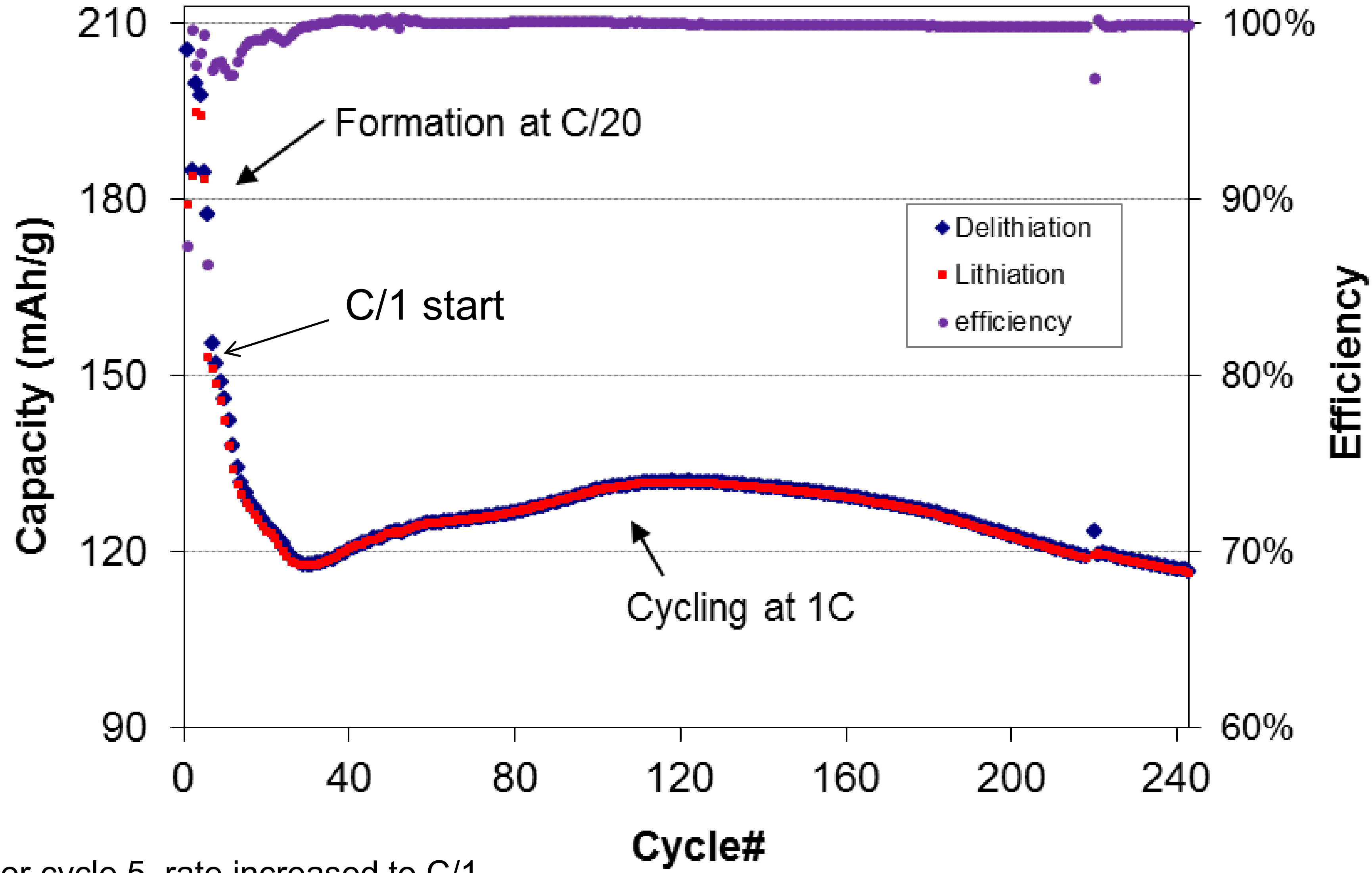
Anode composition: CGP-G8 89%, PVDF 8%, AB 3%.

Test procedures: Formation ~ C/20, to 4.5V 2cycles; C/20, to 4.6V 2cycles;
C/20, to 4.5V 1cycle; C/3 charge & 1C discharge, to 4.5V ~ cycling.
Or otherwise noted.

Gr./NCM

1st cycle ~
3.5 mAh/cm^2

Novolyte 1:2 EC/DEC

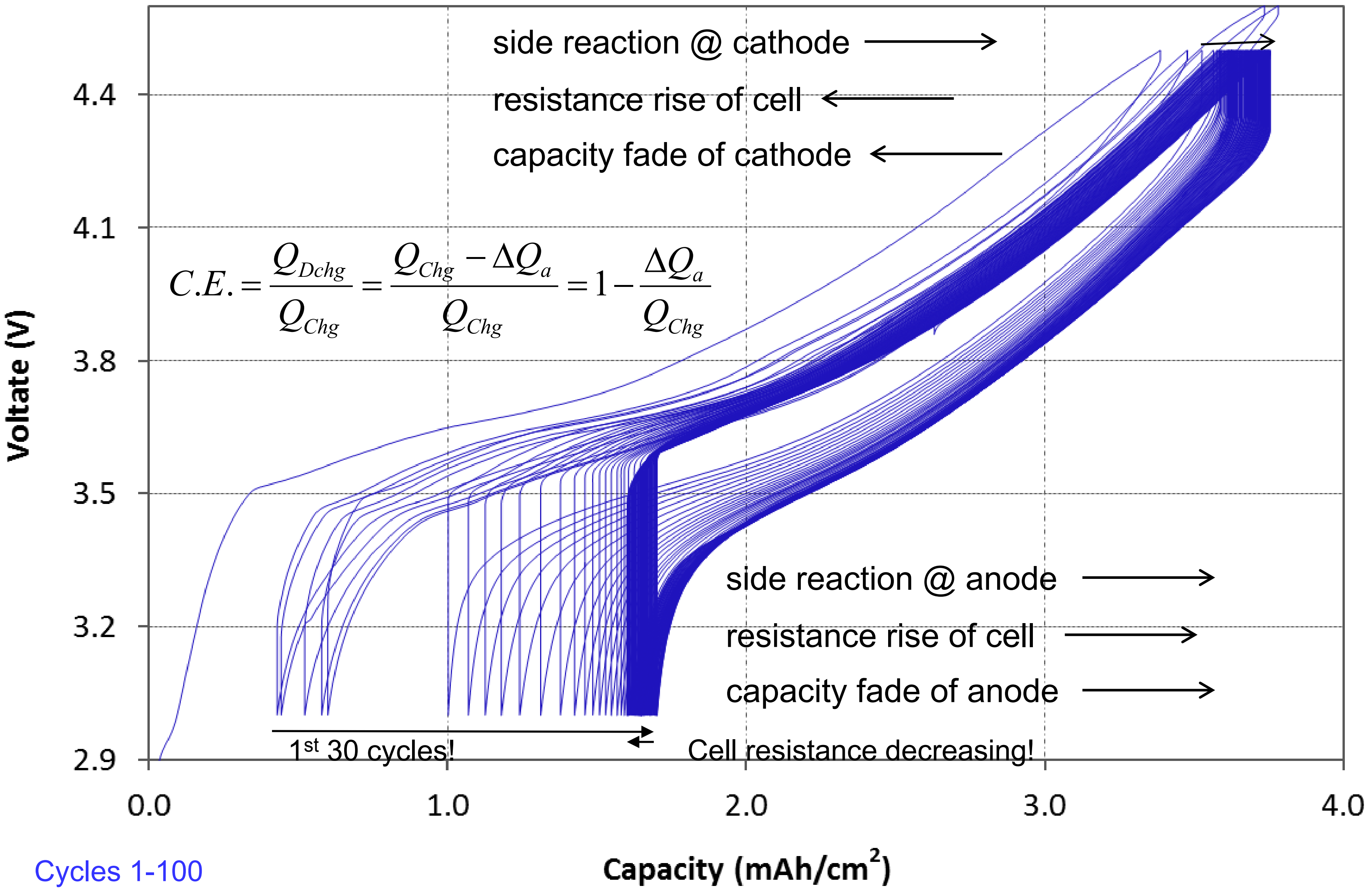


after cycle 5, rate increased to C/1

Gr./NCM

Novolyte 1:2 EC/DEC

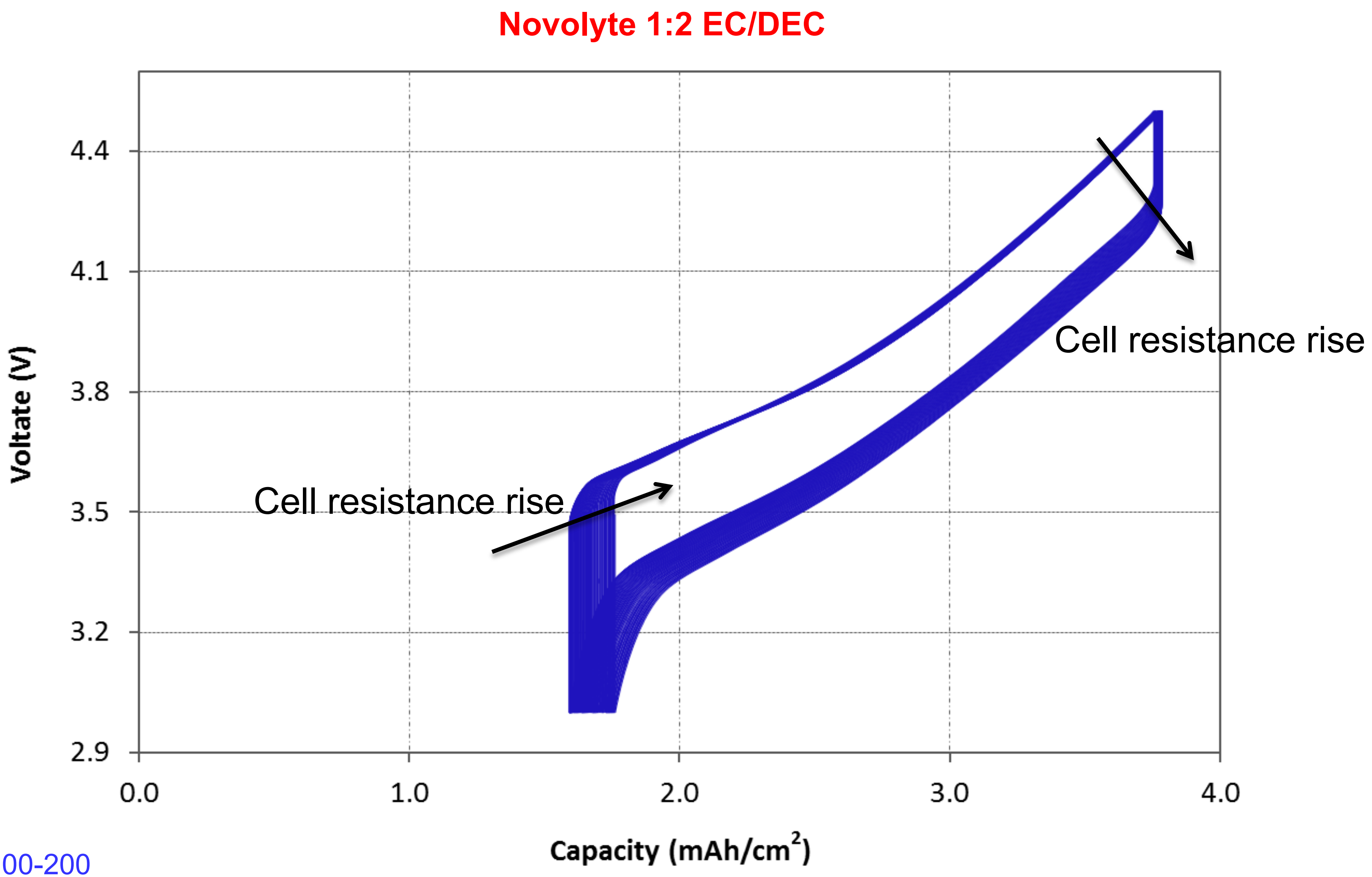
1st cycle ~ 3.5 mAh/cm^2



$$C.E. = \frac{Q_{Dchg}}{Q_{Chg}} = \frac{Q_{Chg} - \Delta Q_a}{Q_{Chg}} = 1 - \frac{\Delta Q_a}{Q_{Chg}}$$

Cycles 1-100

Cycles 100 to 200



Novolyte 1:2 EC/DEC

Cell resistance rise

Cell resistance rise

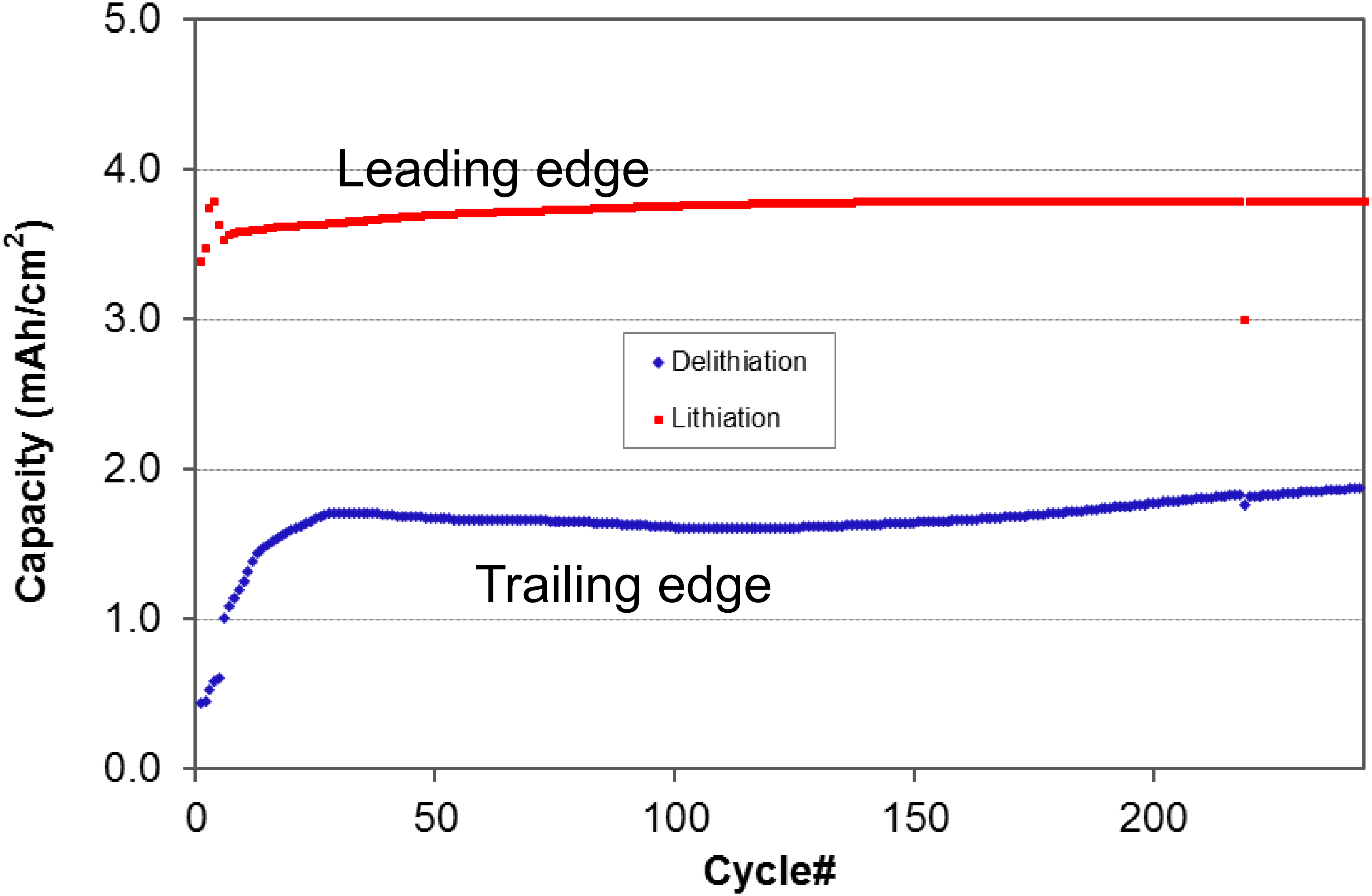
100-200

After the first 100 cycles, a steady resistance rise results in capacity fade.

Gr./NCM

Novolyte 1:2 EC/DEC

1st cycle ~ 3.5 mAh/cm^2



Of Special Note for Baseline Electrolyte

- Large side reaction at cathode on 1st cycle.

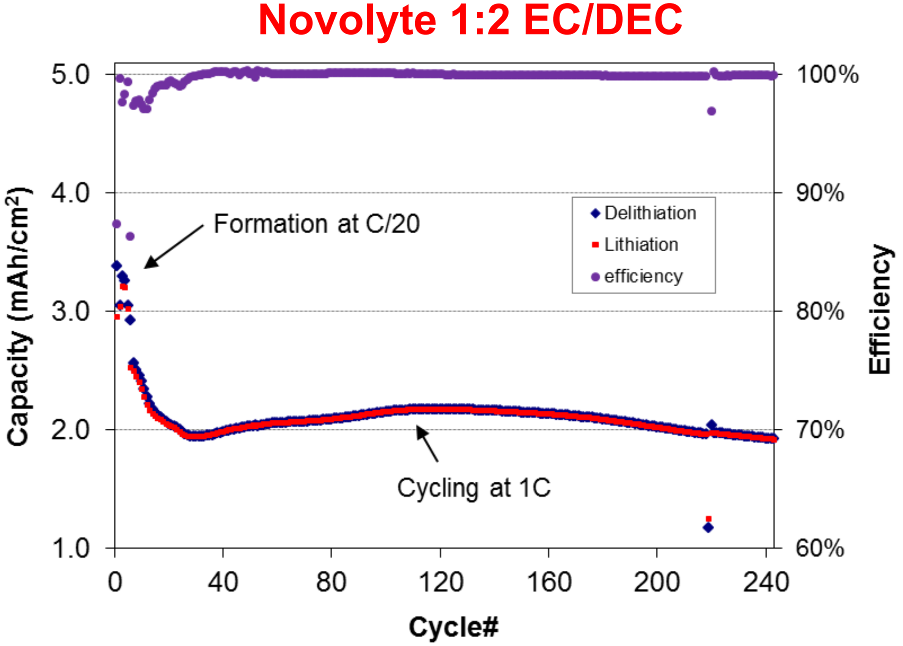
- Large impedance in cell near end of discharge results in a drop in capacity at cycle 6 where an increase in rate leads to a cell that is <u>cathode limited on discharge</u>.

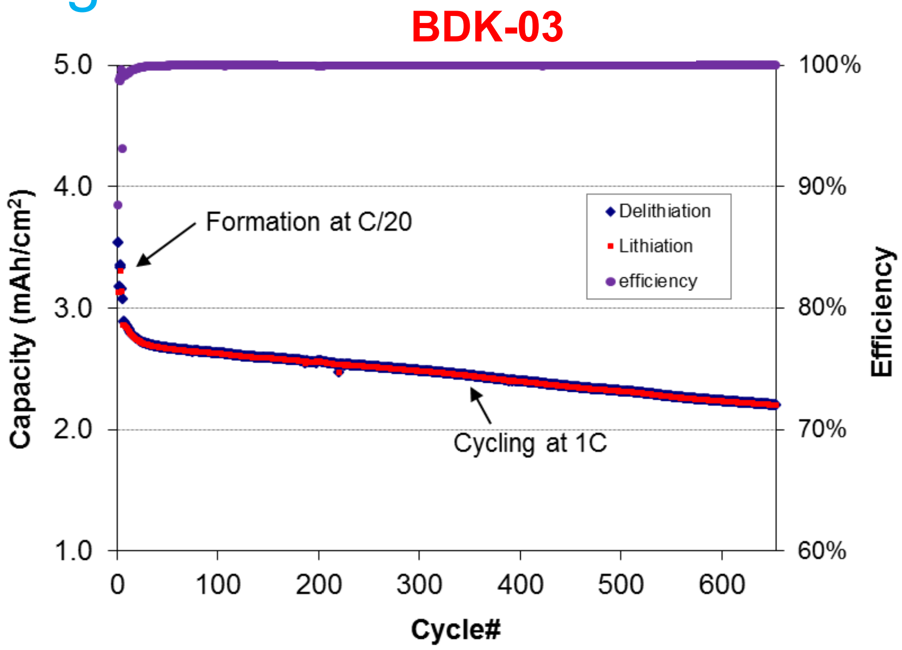
- Steady side reaction on both electrodes + cell impedance growth at end of discharge for first 15 cycles.

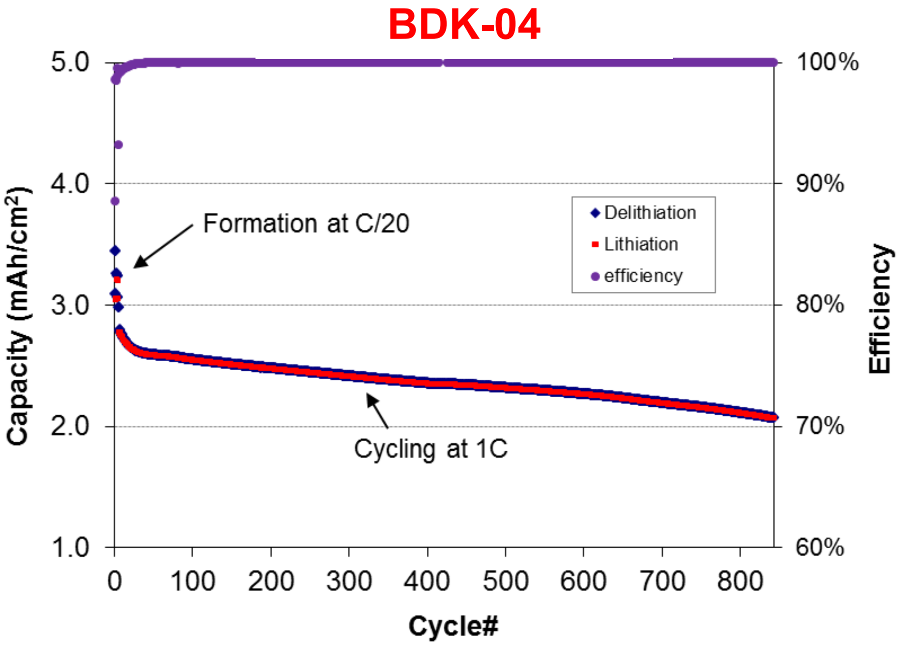
- The impedance near end of discharge after the first 30 cycles improves (*i.e.*, decreases) at a rate that faster than the rate of the side reaction
  - Increase in capacity on discharge
  - Coulombic efficiency > 1

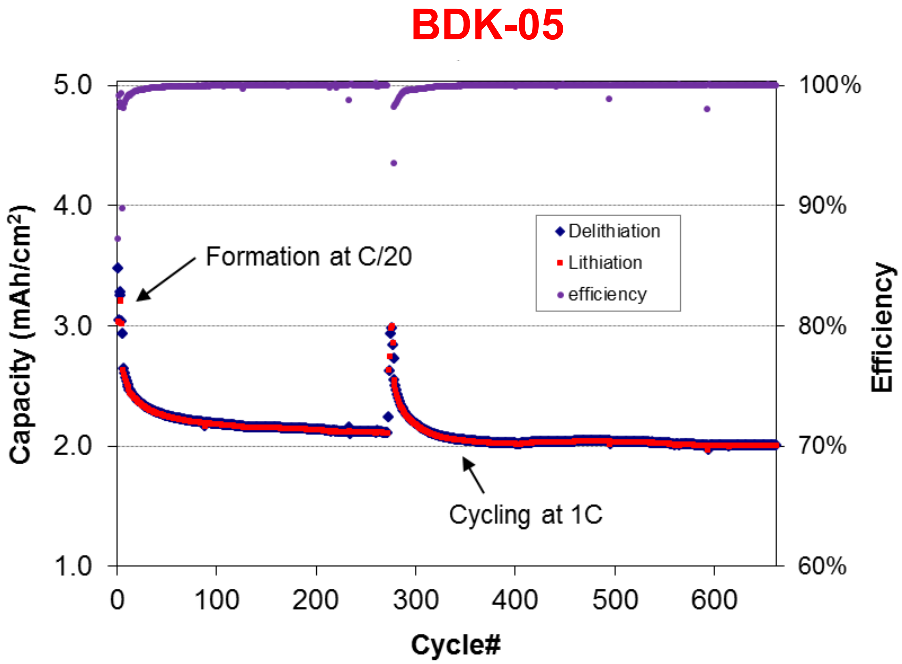
- After the first 100 cycles, the amount of impedance rise at top and bottom of charge are roughly equal, which leads to capacity decline with each cycle.

Capacity Cycling Curves

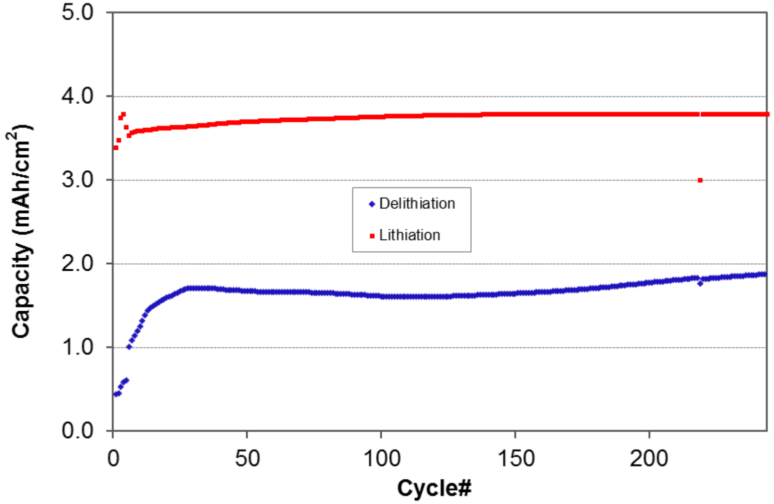




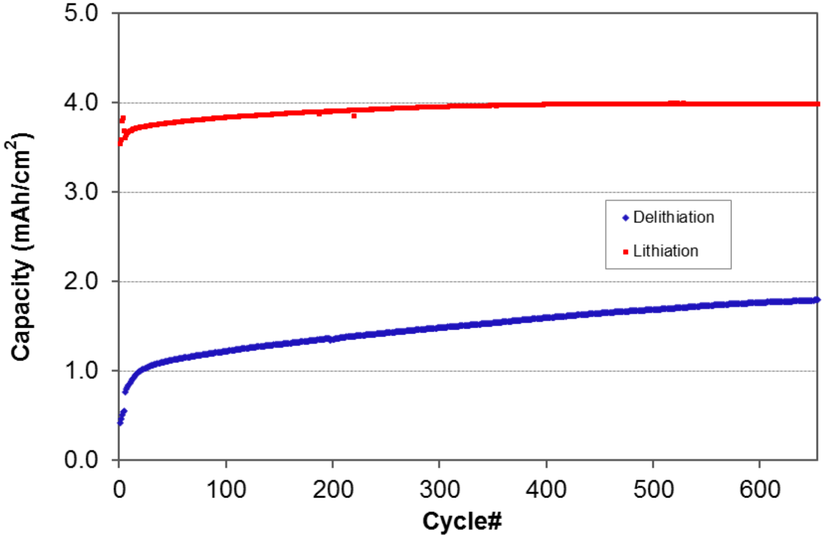




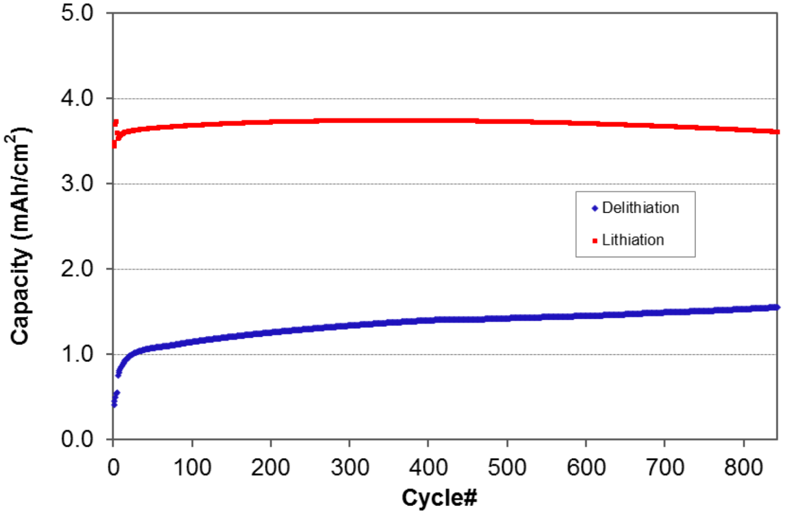
Capacity limits



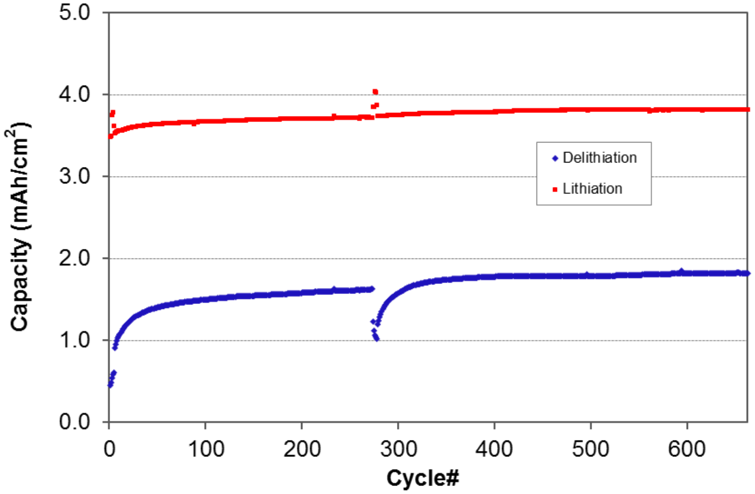
Novolyte 1:2 EC/DEC



BDK-03



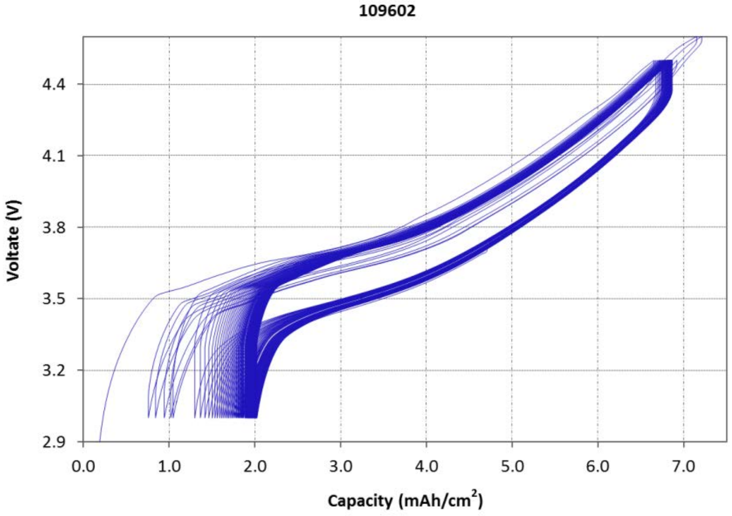
BDK-04

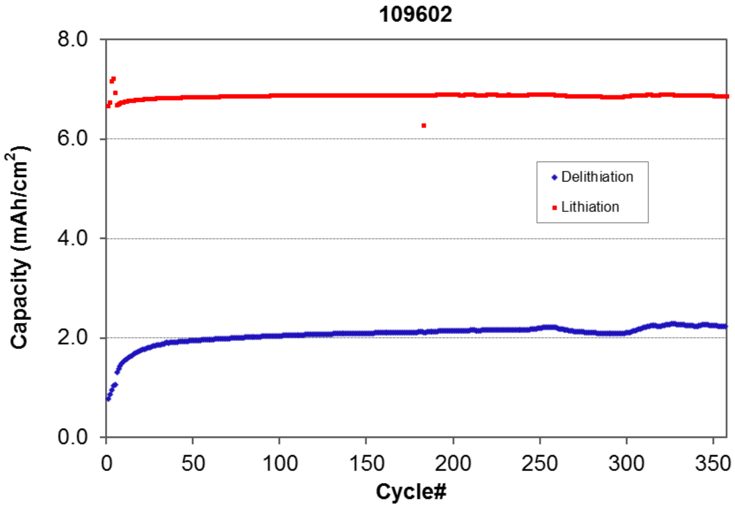


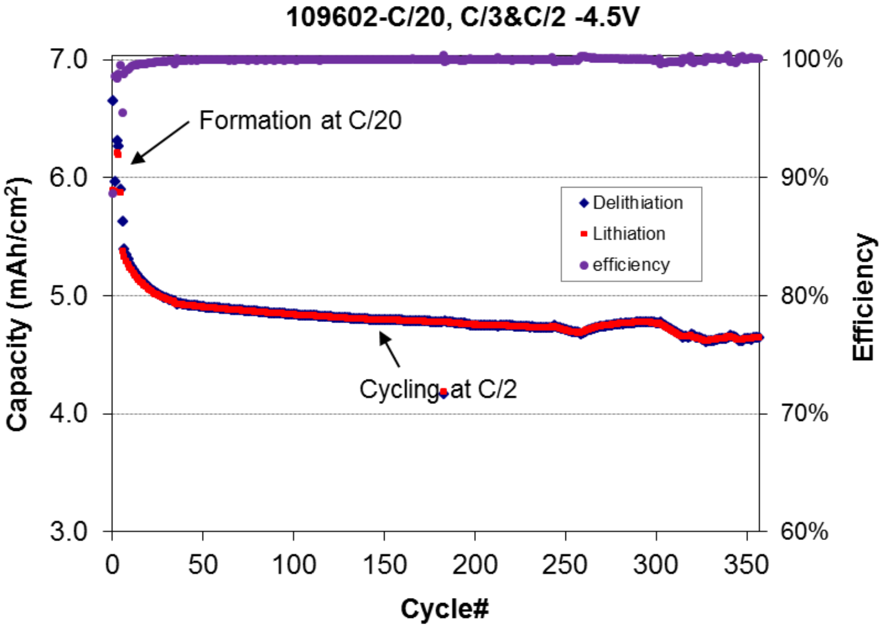
BDK-05

BDK-03 shows most of the capacity loss arises from a slight impedance rise

5 mAh/cm^2 and C/2 discharge





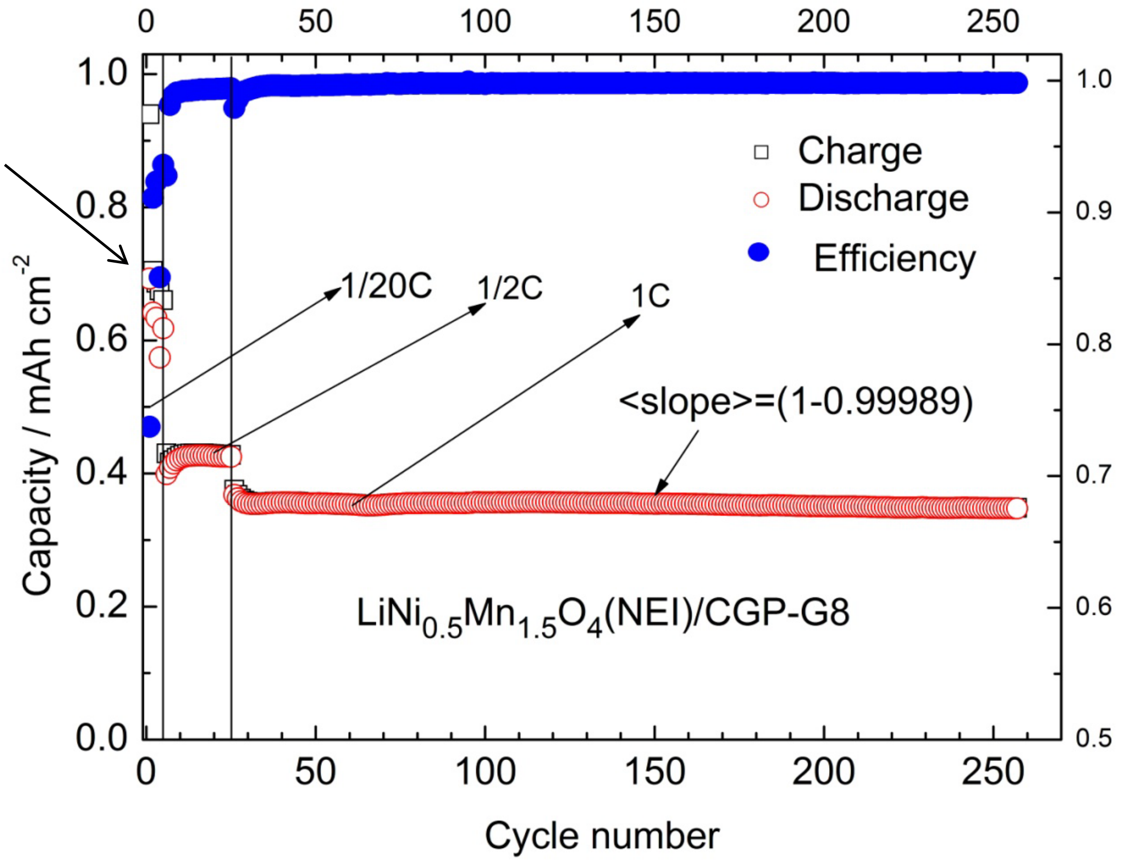


The **BDK-03** electrolyte led to:

- smaller first cycle loss
- smaller effects of impedance rise
- lower rate of side reactions
- good capacity retention

Full Cell Cycleability

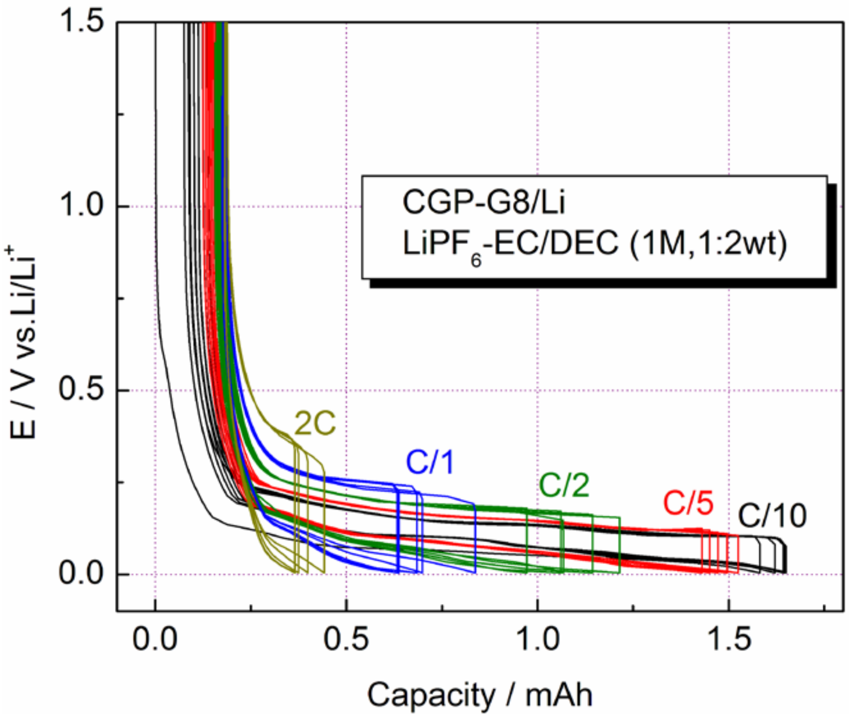
1st cycle dchg. cap.

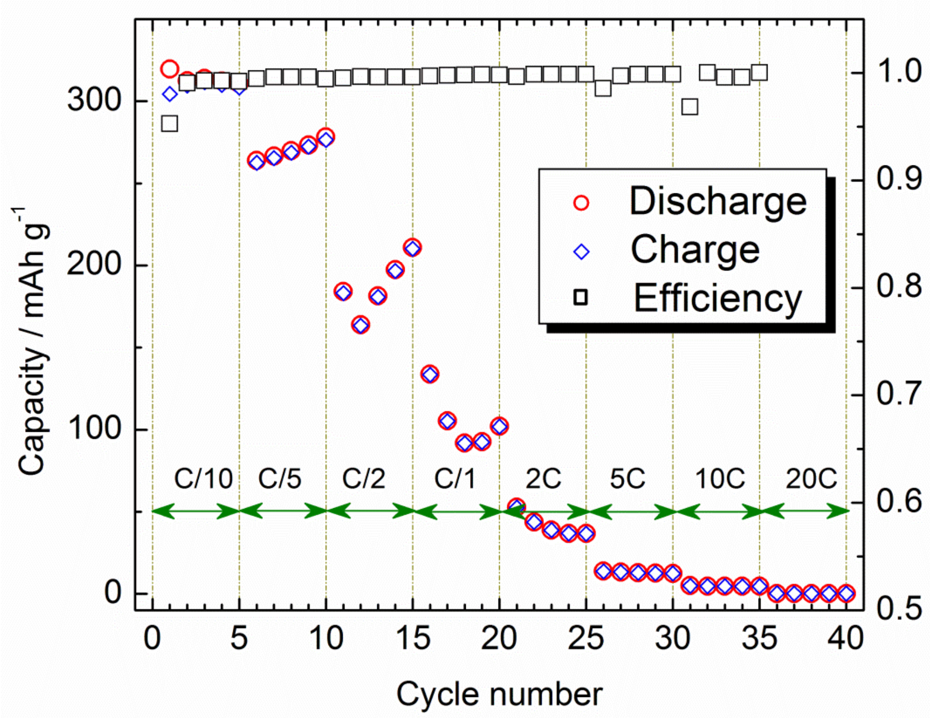


Charged & discharged at 1C

We showed this last year, so what is the problem?
The problem is that despite using thin, high-rate electrodes, there is a large capacity drop with rate from C/20 to C/2, why?

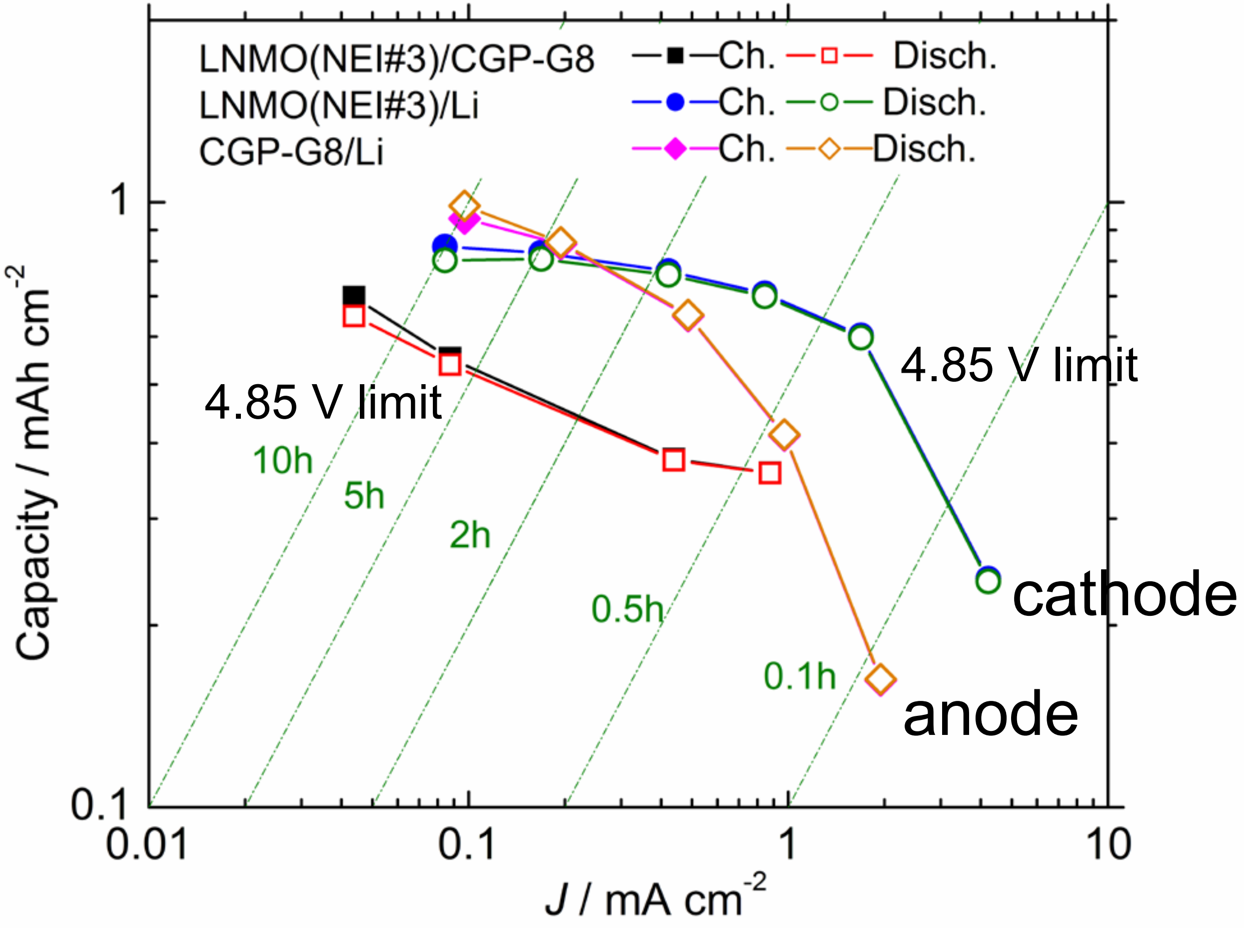
Symmetric Cycling of Anode





- These are low loading electrodes – expected to be high rate!
- Discharging to 1 V at 2C is not a problem.
- Charging limitations are seen at charging rates as low as C/5.
- Note: the cycle-to-cycle variability is attributed to variations of the Li impedance. It would be preferable to run these tests with a reference electrode.

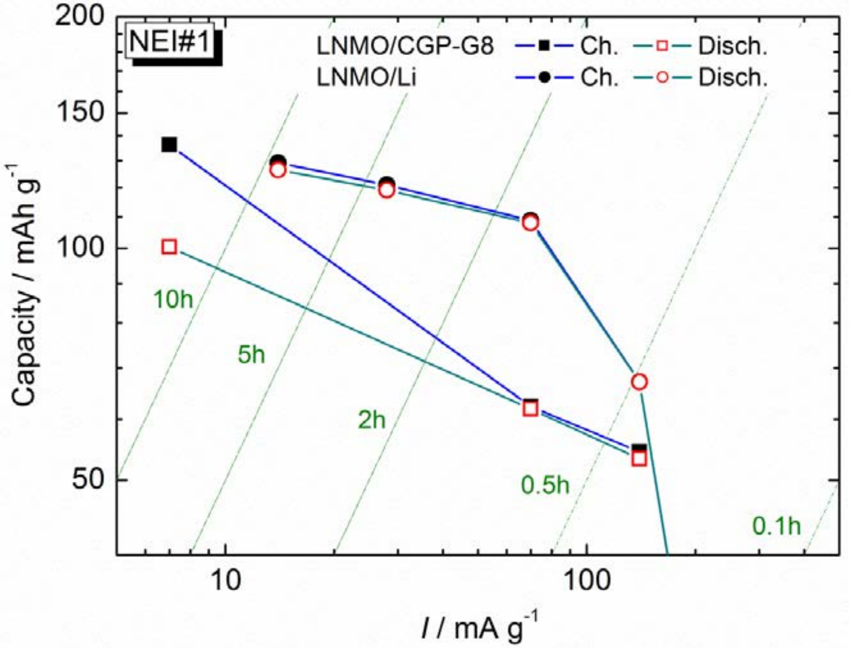
Charging Limits

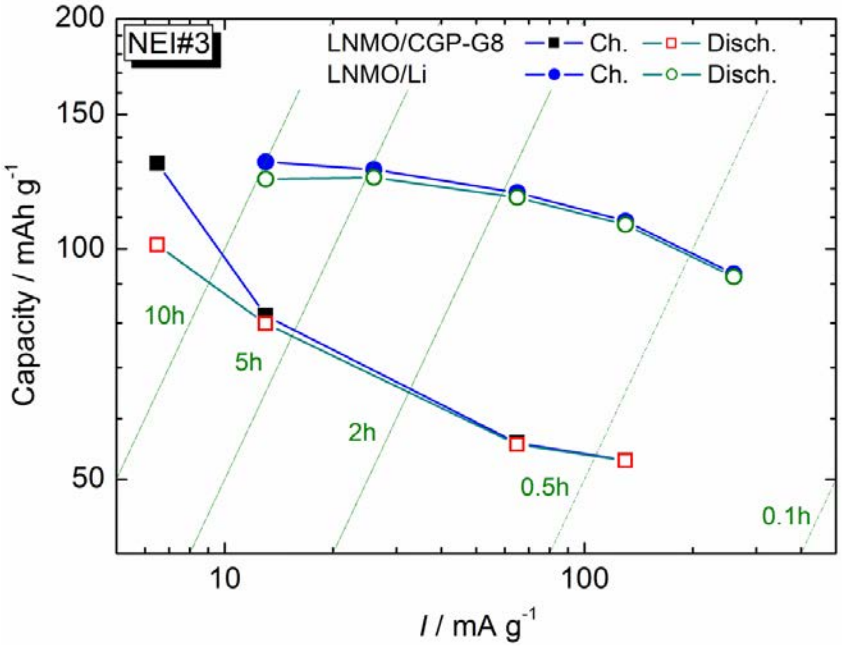


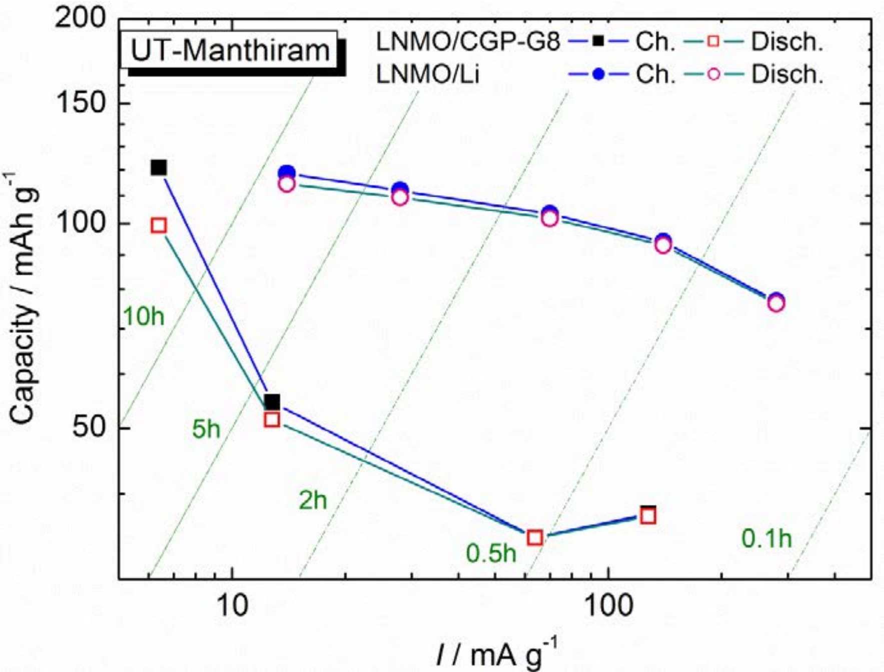
The rapid drop off in full cell capacity mirrors the capacity decline of the anode.

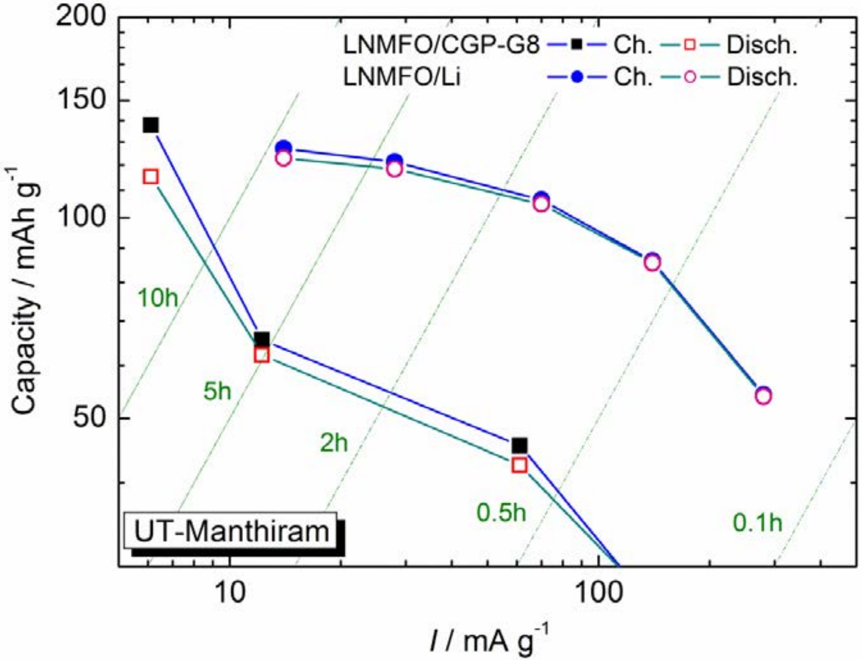
To safely avoid Li plating, these cells should <u>not</u> be charged faster than C/3.

Technical Accomplishment 2

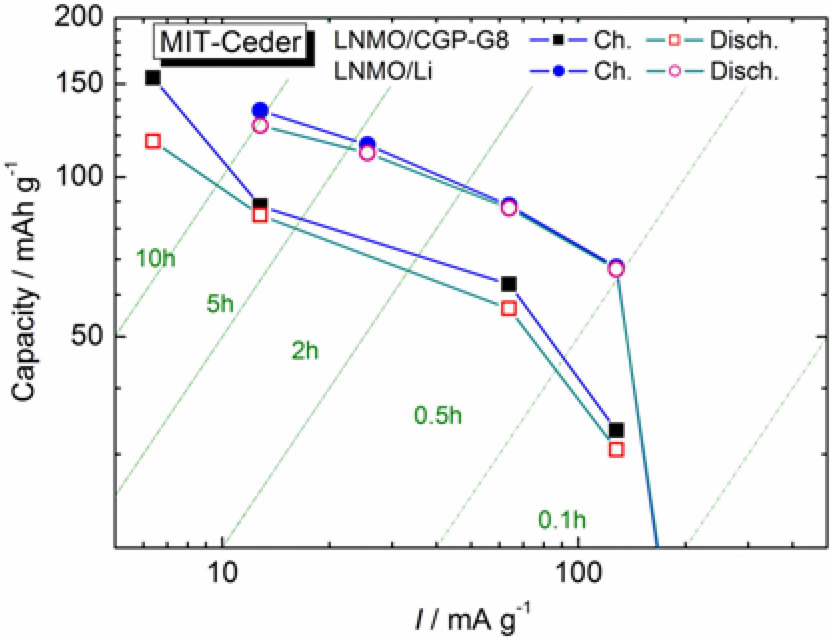


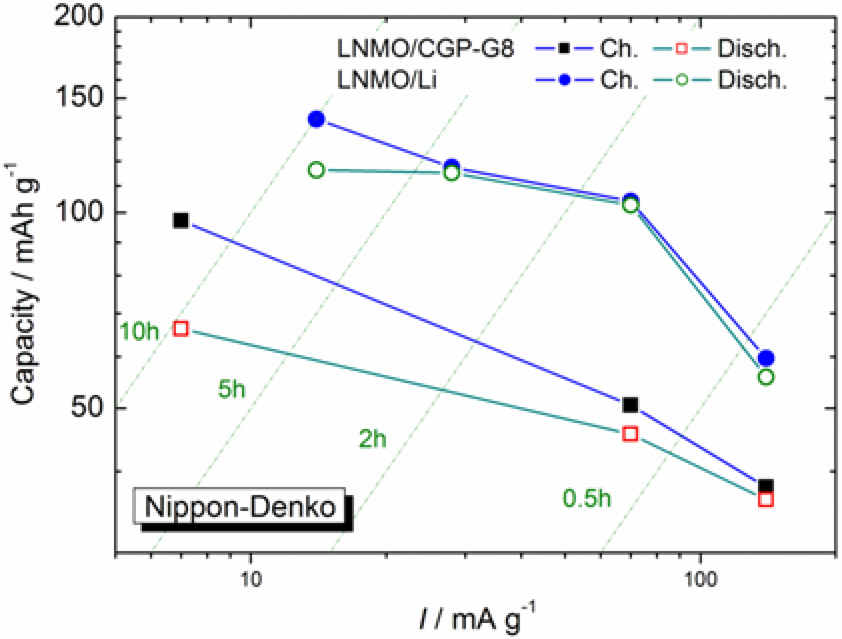


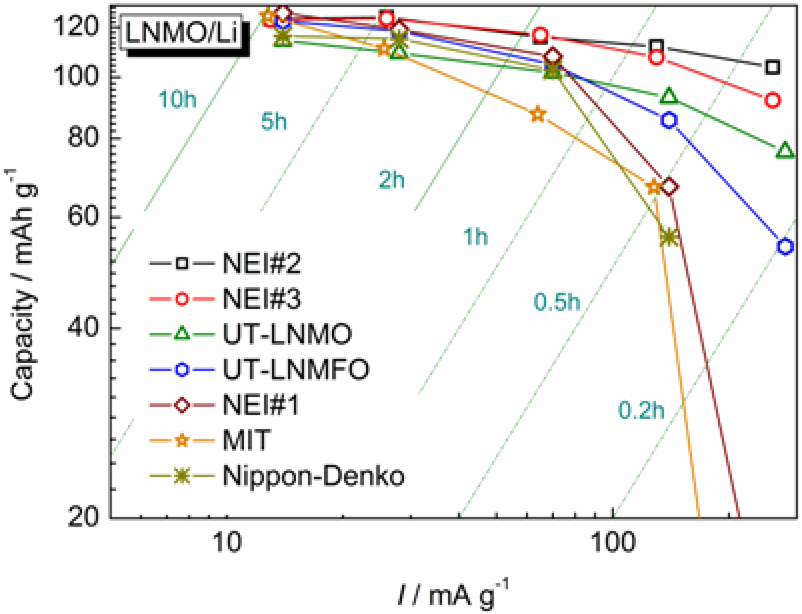


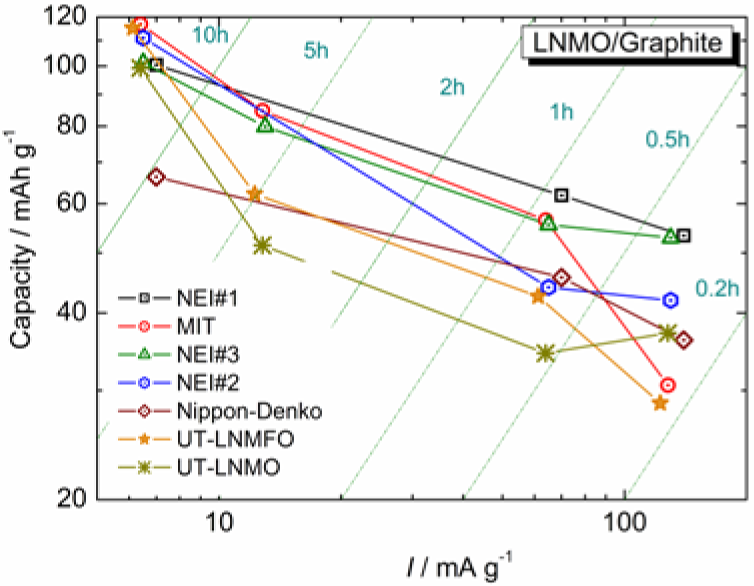


Technical Accomplishment 2



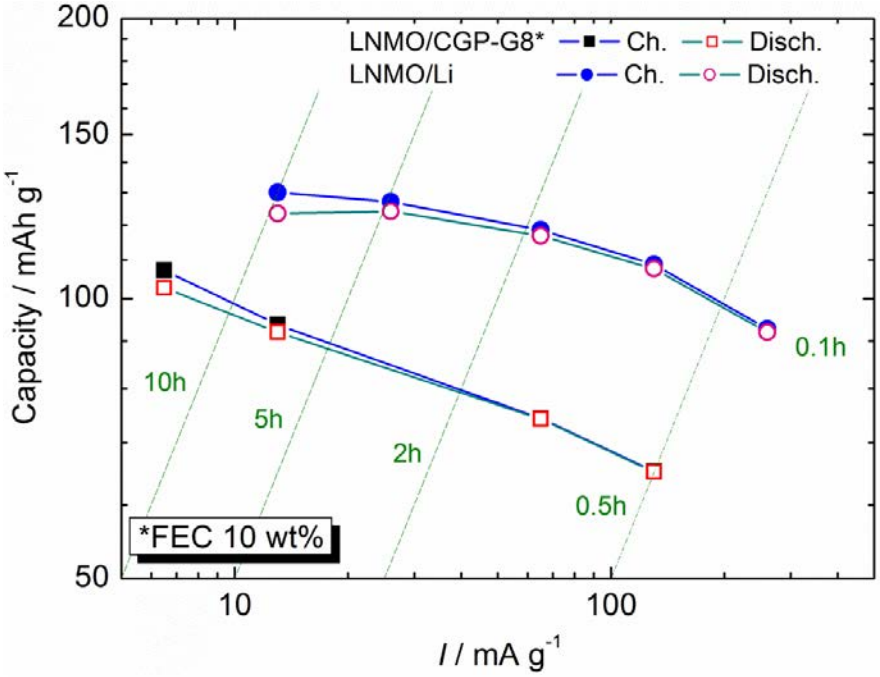


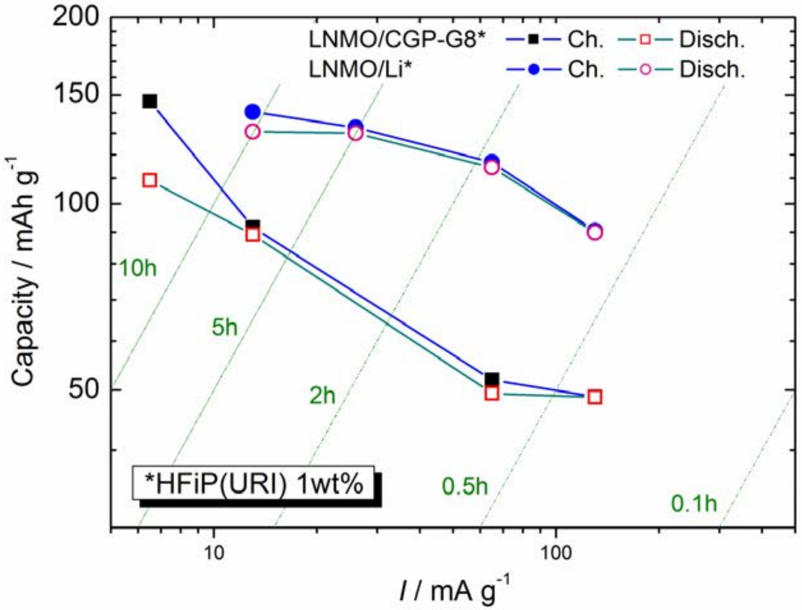


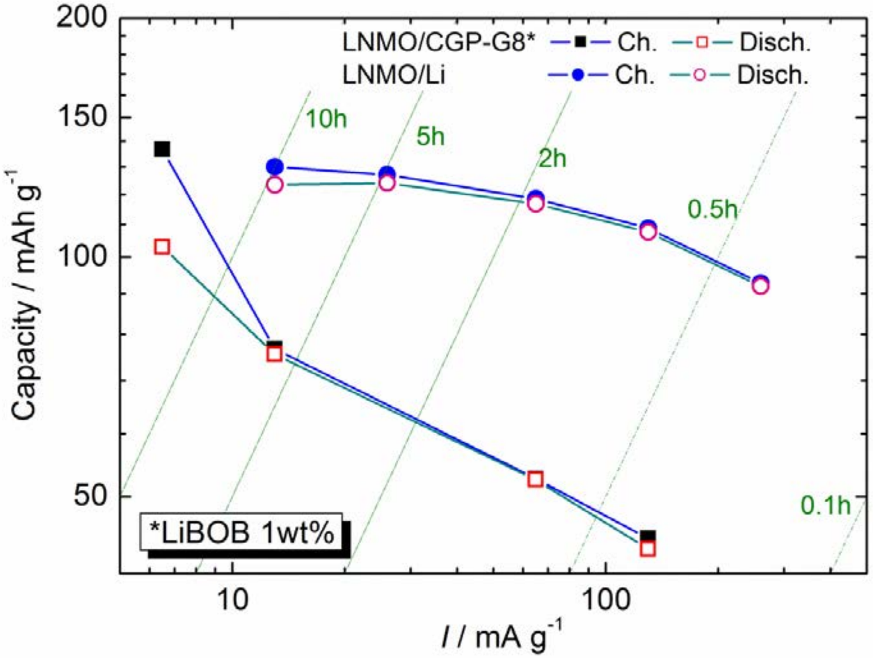


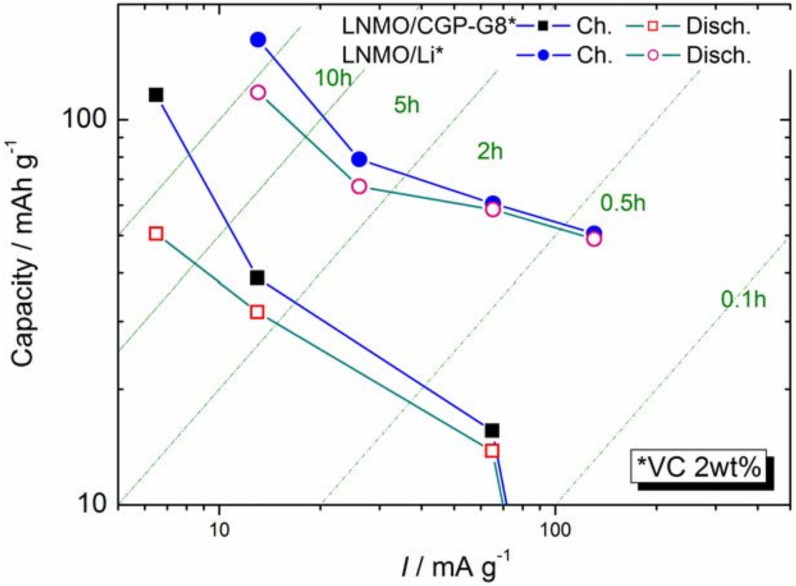
The **NEI #1** and **MIT** materials show the least negative impact in full cells.

Effect of electrolyte additives

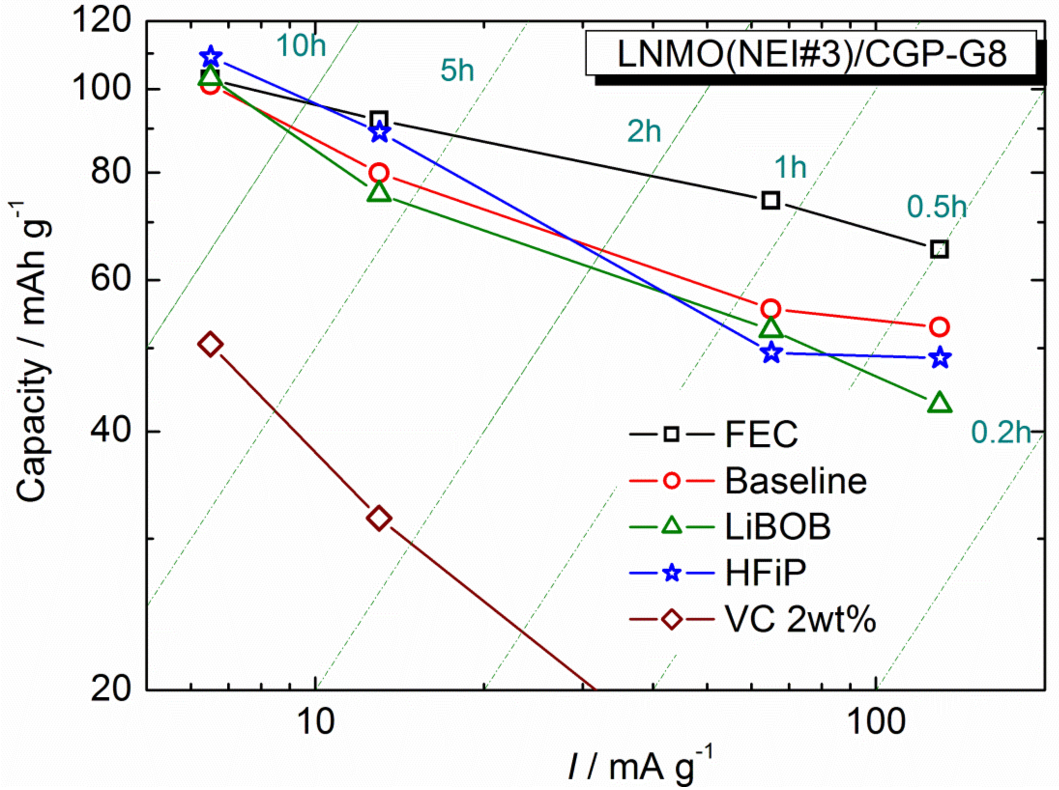








Effect of electrolyte additives



FEC appears to be the best additive at limiting the capacity loss at high charge rates in full cells.

Partners

Partner	Type	Within or outside of OVT	Extent	Outcome
NEI	Industry	outside	Ni-spinel (2)	Baseline identified
Daikin, America	Industry	outside	Electrolyte (1)	Baseline identified
Daikin Industries	Industry	outside	Electrolyte (3)	High voltage electrolyte
HQ	Industry	inside	Electrodes (2)	One delivered
MIT	University	inside	Ni-spinel (1)	Low Mn^{2+}
UT	University	inside	Ni-spinel (2)	High Mn^{2+}
URI	University	Inside	Salts (1) and additives (2)	Modest effect
CWRU	University	Inside	Additive (1)	Still testing

Plans

- Shared results at a meeting w/Daikin; we are expecting to receive their next generation of materials.

- Evaluate electrodes fabricated by HQ of **NEI #3** and distribute to other PIs.

- Seek correlations between material characteristics and cell performance; especially, in regards to why **MIT** and **FEC** materials do so well to limit capacity loss with rate.

- Within the Ni-spinel Focus Group, we hope to identify key material metrics and specify the synthesis requirements for scale-up
  - NEI
  - UT (Manthiram)
  - HQ
  - ANL

- Early three electrode cell data indicate that the resistance rise is in the anode for Gr./$LiNi_{1/2}Mn_{3/2}O_4$ cells; however, our two electrode and three electrode cell data are not identical (3 better than 2). We seek to resolve this discrepancy.

Proposal

- We hope to carry out a similar task in future years
  - An important part of the DOE/OVT research portfolio
- Will work with other Labs and industry to develop a proposal for the next phase of the ABR Program.

Key Points

- Superimposed voltage curves reveal the effect of side reaction rates (one's equipment needs to be accurate to ~ 1 μA.)
  - Require a reference electrode to identify source of impedance growth
  - Presently, our three electrode cells perform different (better) than our two.
- NCM reacts with the electrolyte which results in capacity fade; thus, cycling approached acceptable levels only at modest C/rates
- Ni-spinel cycles 100's of times against Li and Graphite at room temperature with little capacity fade
- Ni-spinel causes impedance rise and side reactions on the anode, which drastically reduces the available capacity starting with the initial cycles.
- **MIT** and **FEC** resulted in best capacity retention *versus* CGP-G8.

Advances relative to 2011

Advances
More in-depth explanation of voltage cycling curves provided
Effects of different electrolytes on NCM cycleability identified
Several Ni-spinel cathode materials characterized for half- and full-cell performance.
Several electrolyte additives characterized for full cell performance
Ni-spinel cells appear capacity limited by an initial impedance rise and/or side reaction on the anode as the electrode is cycled to higher rates.

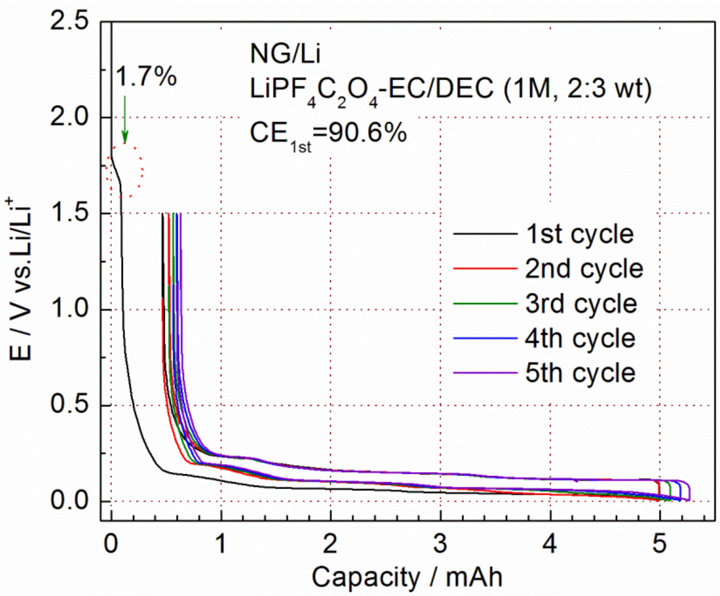
Technical Back-Up Slides

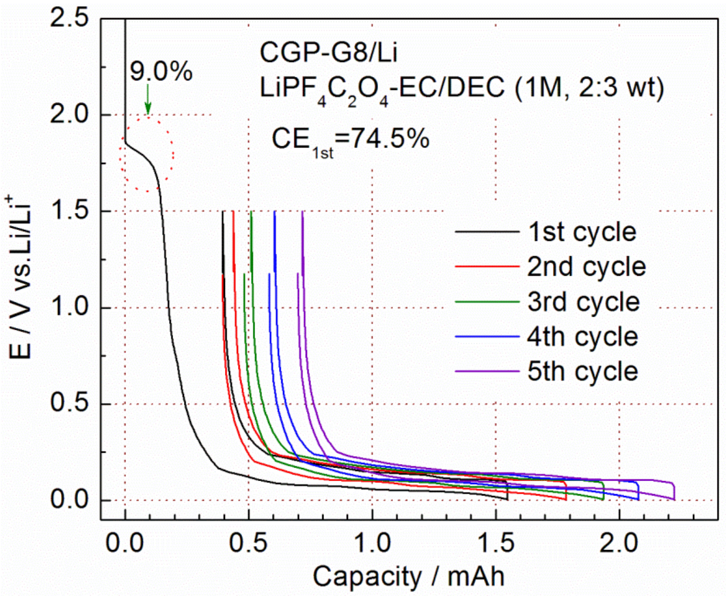
(Note: please include this “separator” slide if you are including back-up technical slides (maximum of five). These back-up technical slides will be available for your presentation and will be included in the DVD and Web PDF files released to the public.)

$LiPF_4C_2O_4$ from URI

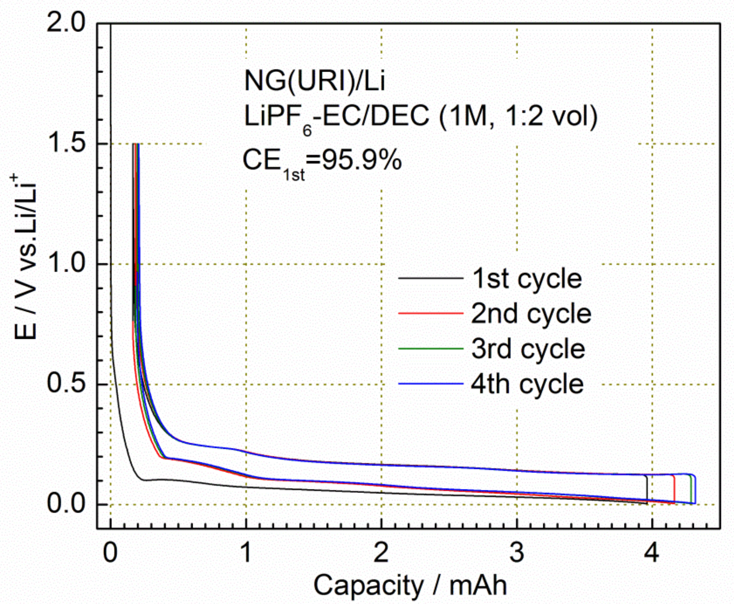
Natural graphite

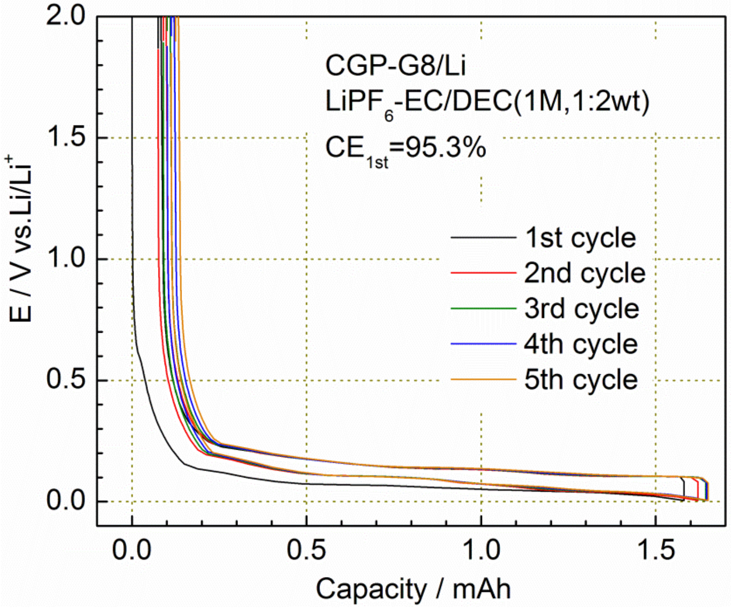
CPG-G8





$LiPF_4C_2O_4$





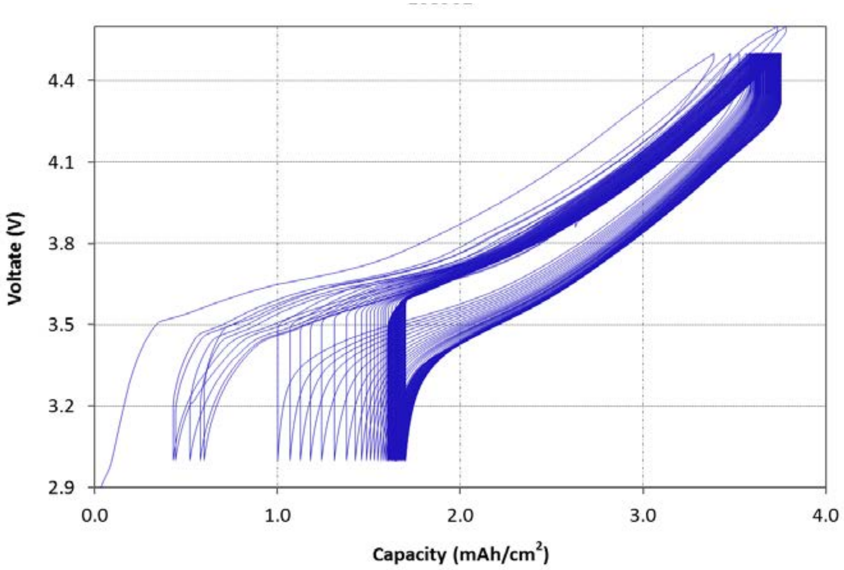
$LiPF_6$

$LiPF_4C_2O_4$

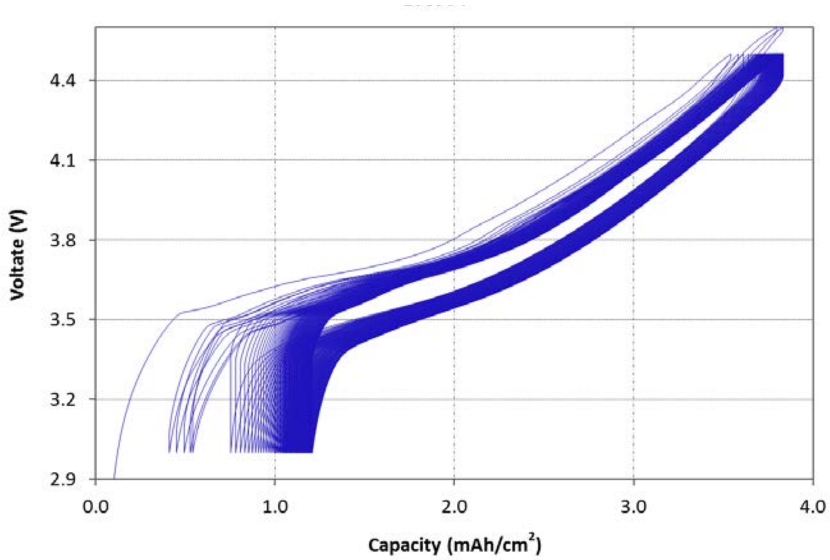
- Both cells assembled with the same amount of electrolyte (50 ml) with a positive electrode at 3 V and Li counter electrode
- Approximately 10 % of the salt is lost in the first cycle:
  - $C_2O_4^{2-}$ -> $2e^-$ + $2CO_2$ oxidation of an impurity? But this is a reduction current
  - Possible the component is reduced on the Li to form CO_2 during cell assembly and it’s the CO_2 being reduced on the first discharge back to $C_2O_4^{2-}$
  - We plan to perform mass spectroscopy on the gas in the cell to test this theory.

Voltage Cycling Curves (first 100 cycles)

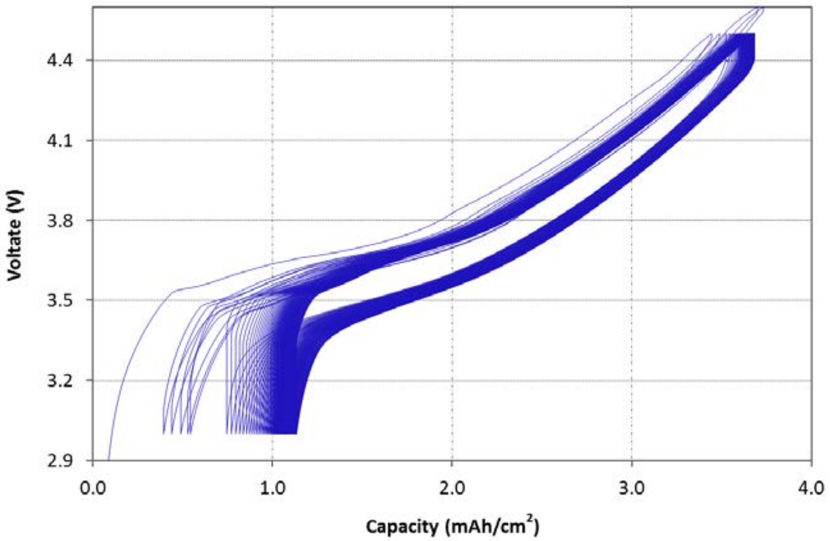
Novolyte 1:2 EC/DEC



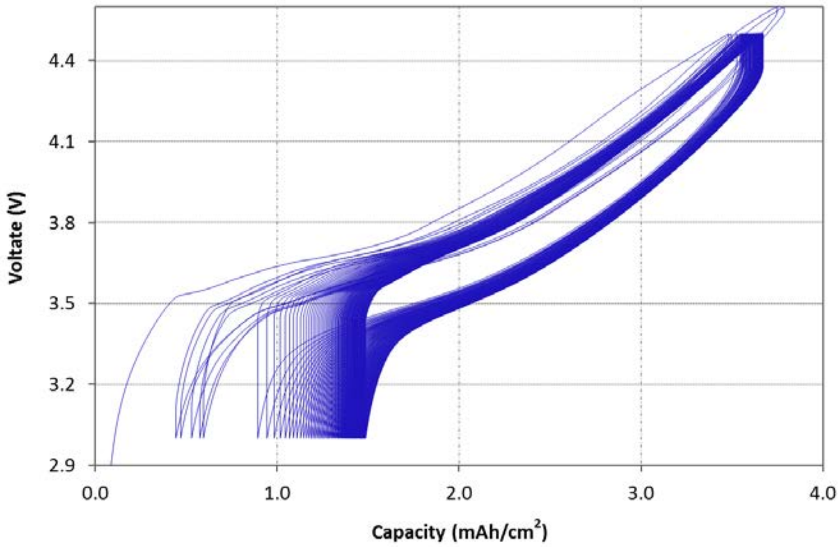
BDK-03



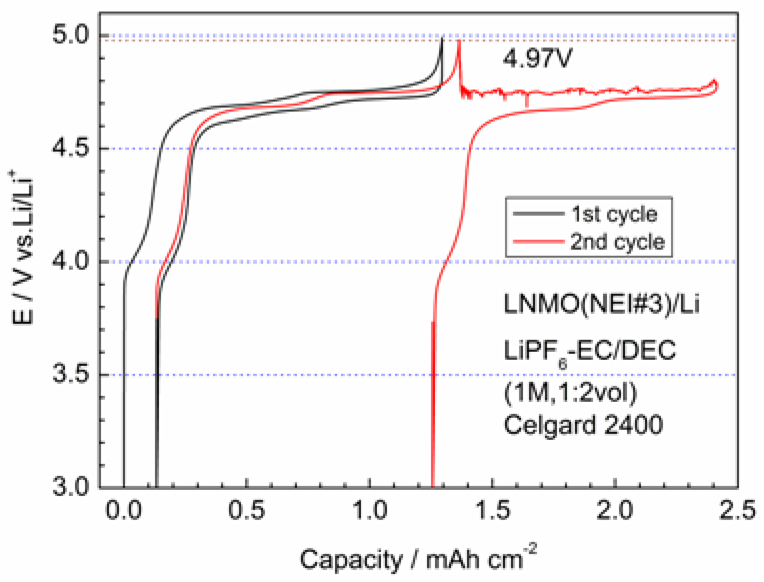
BDK-04

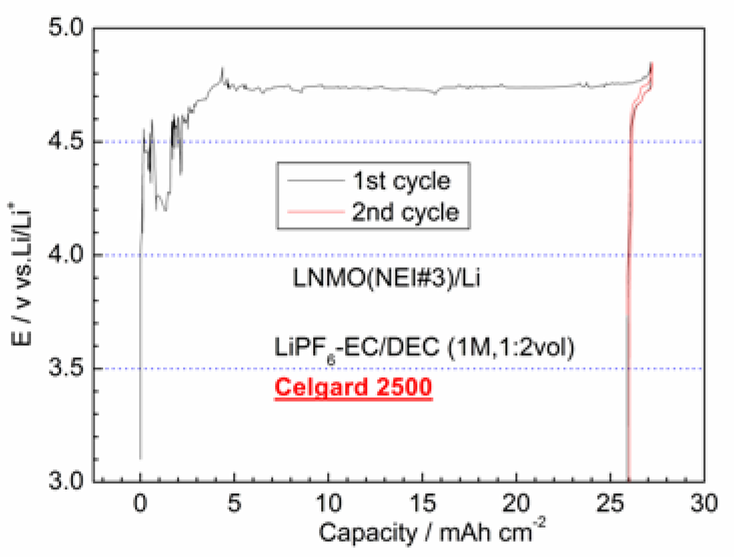


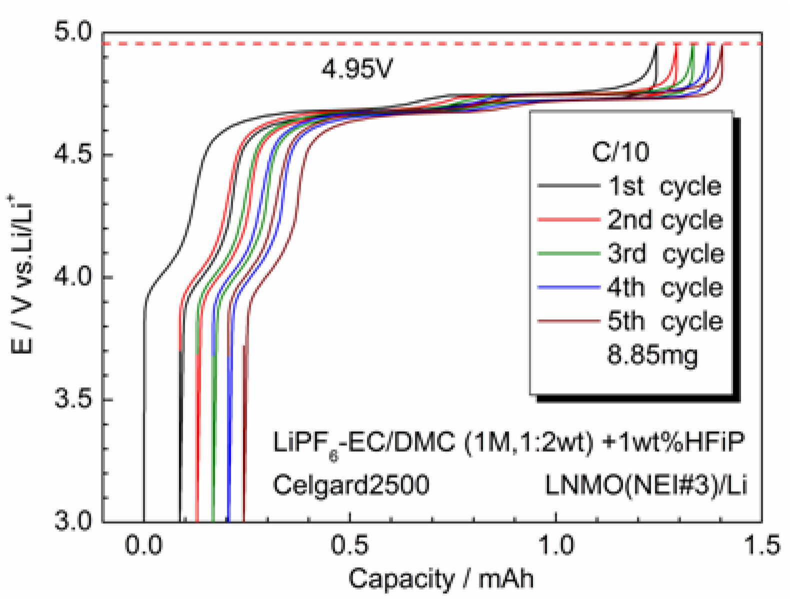
BDK-05



Electrochemical stability window





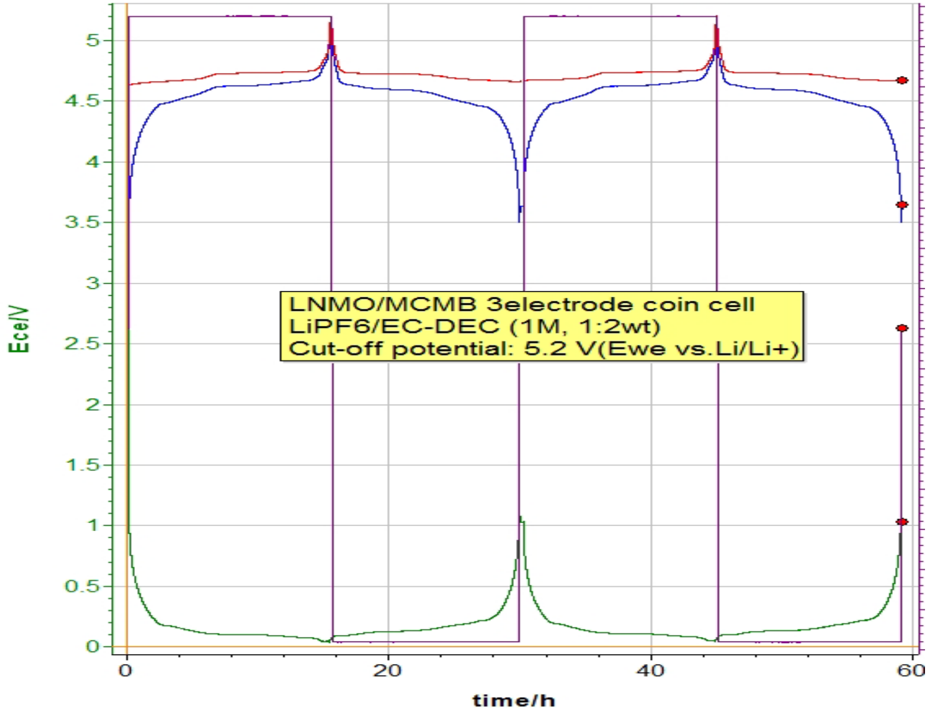


- The side reaction is increased when a separator of higher porosity is used.
- This can be corrected with the introduction of HFiP as recommended by URI.

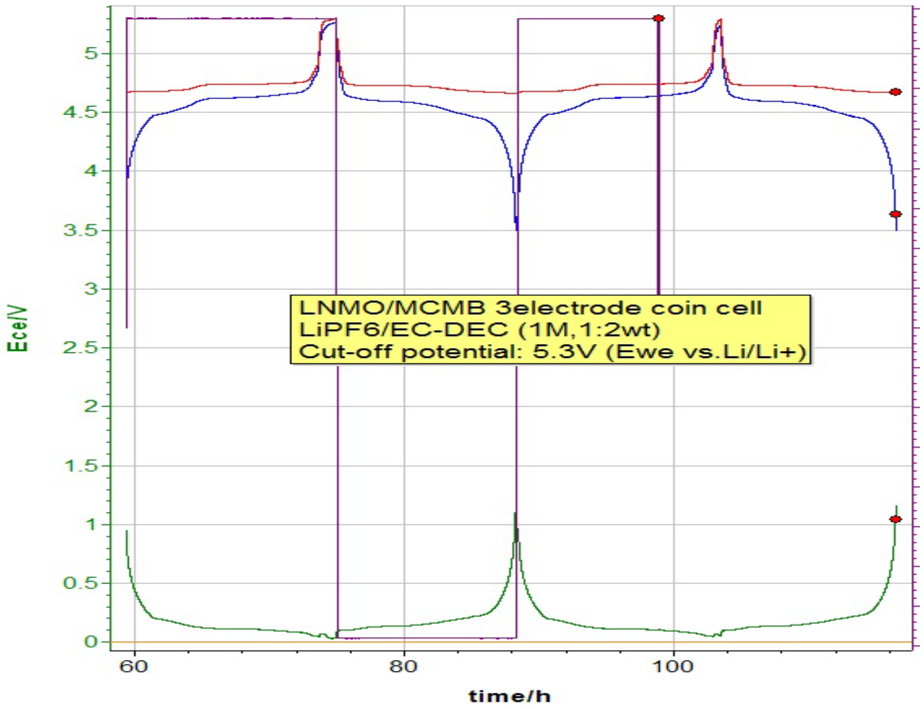
Electrochemical Stability of Full Cells

MCMB/NEI #3

5.2 V upper cut-off voltage


LNMO/MCMB 3electrode coin cell
LiPF6/EC-DEC (1M, 1:2wt)
Cut-off potential: 5.2 V(Ewe vs.Li/Li+)

5.3 V upper cut-off voltage


LNMO/MCMB 3electrode coin cell
LiPF6/EC-DEC (1M,1:2wt)
Cut-off potential: 5.3V (Ewe vs.Li/Li+)

We see this with all of the cathodes *versus* a graphitic anode: stability to 5.3 V and not noisy.