Electrode Fabrication and Performance Benchmarking

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LBNL

Wednesday, June 10, 2015

ES232

Overview

Timeline

- October 2011
- September 2015
- 80% complete

Budget

- Total project funding
  - $1800 k
- Funding received in FY14: $450 k
- Funding for FY15: $450 k

Barriers

- Barriers addressed
  - Performance: Specific energy – 350 Wh/kg cell level; 235 Wh/kg system level
  - Performance: Specific power – 700 W/kg cell level; 470 W/kg system level
  - Life: 15 years

Partners

- LBNL PIs
- Commercial material suppliers
  - *e.g*. NEI, Umicore, Daikin
- Several BMR PIs
- ANL, PNNL, HydroQuebec, BYU

Objectives, Relevance, and Impact

- Project Objectives (overall)
  - To be able to provide quality electrodes from **small amounts** of materials.
  - To test the materials to failure.
  - To assign the source of the failure.

- Specific Project Objectives (past year)
  1. Demonstrate quality electrodes of:
     - High voltage study: $LiCoO_2$, HV-$LiCoO_2$, $Ni_{1/3}Co_{1/3}Mn_{1/3}O_2$, and Mn-rich oxide
     - Si study: $LiFePO_4$ high-capacity counter electrode
  2. Determine failure mechanism of:
     - High voltage study: $LiNi_{1/2}Mn_{3/2}O_4$, $LiCoO_2$, HV-$LiCoO_2$, and $Ni_{1/3}Co_{1/3}Mn_{1/3}O_2$
     - Si study: Si particles

Objectives, Relevance, and Impact

- Relevance to VT Office
  - Researchers in the program have access to materials from the same experimental source.
  - The ability to make quality cells with small amounts of materials allows researchers to confidently assess "improved" materials.
  - With so many cathodes, anodes, and electrolytes being developed, it is difficult to gauge progress. This task allows for the standardization of electrode design and cell assembly and assess progress directly.

- Impact on Barriers
  - The specific energy and power capability targets are challenging. It will require advancements on all fronts. This task allows for the assessment of progress for all stakeholders.

Approach/Strategy

- Work with DOE BMR Program Manager to identify future direction in materials research
  - Higher Voltage Cathodes
  - Si
- Define a baseline material and willing supplier.
- Fabricate electrodes that demonstrate good cycleability at moderate cycling conditions using small amounts of material (~ 10 g of active material per electrode).
  - **Provide electrodes to interested colleagues**
- Push material to failure.
- Identify possible failure modes.
- Verify failure modes through additional techniques.

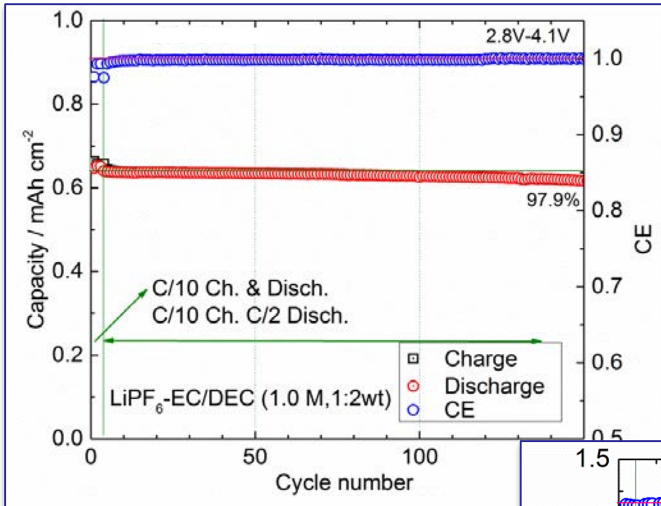
Approach/Strategy

- Milestones
  - HV – Identify the **baseline** materials for high voltage studies. (Mar. 14)
  - Si – Demonstrate a cycleable $LiFePO_4$ electrode for **Si** studies. (Jun. 14)
  - Si – Measure the difference in side reactions of graphite and **Si** when cycled against $LiFePO_4$. (Sep. 14)
  - HV – Measure and report the difference in capacity fade in mAh/h between LCO and HV-LCO at 4.3 V in mAh/h. (Dec. 14)
  - HV – Identify and report the electrochemical phenomena that is responsible for the capacity fade of the LCO and HV-LCO cells at 4.3 V. (Mar. 15)
  - HV – Measure and report the phenomena responsible for the capacity fade of higher loading cells in mAh/h (Jun. 15)
  - Li/S – Measure and report the self-discharge rate of the baseline Li/S cell in mA/(g of S) and decide if this is an appropriate baseline design. (Sep. 15)

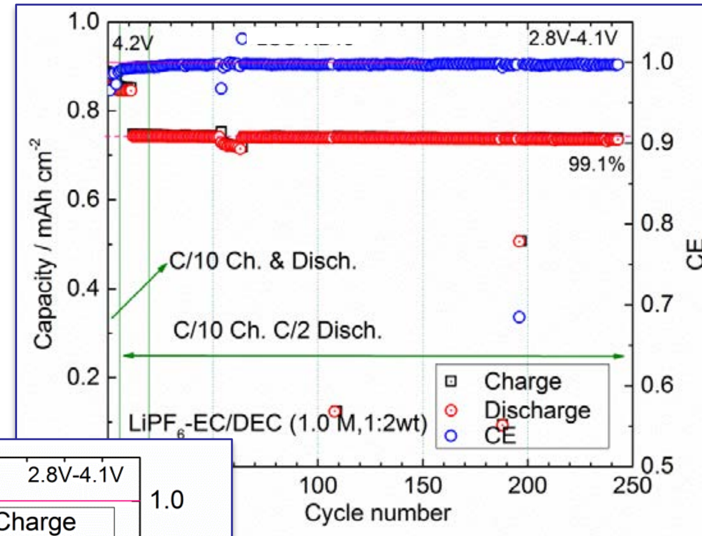
Tech. Accp. #1: Make "Good" Cells

vs. Li

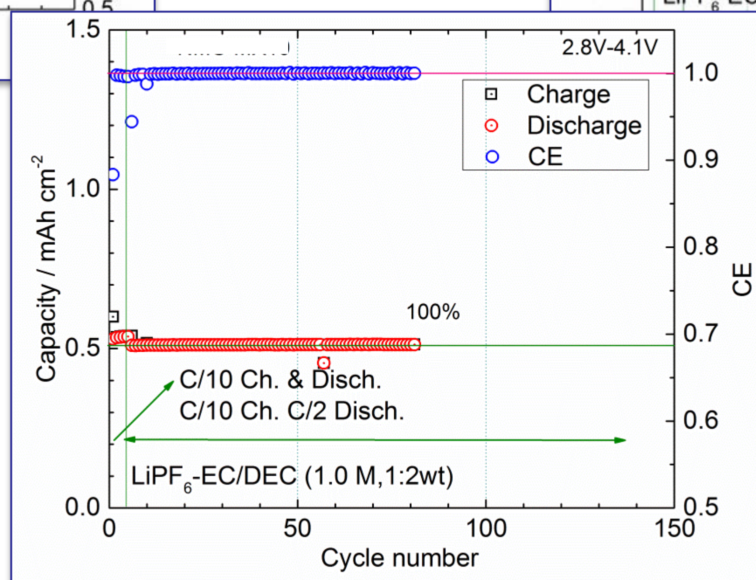
LCO



HV-LCO



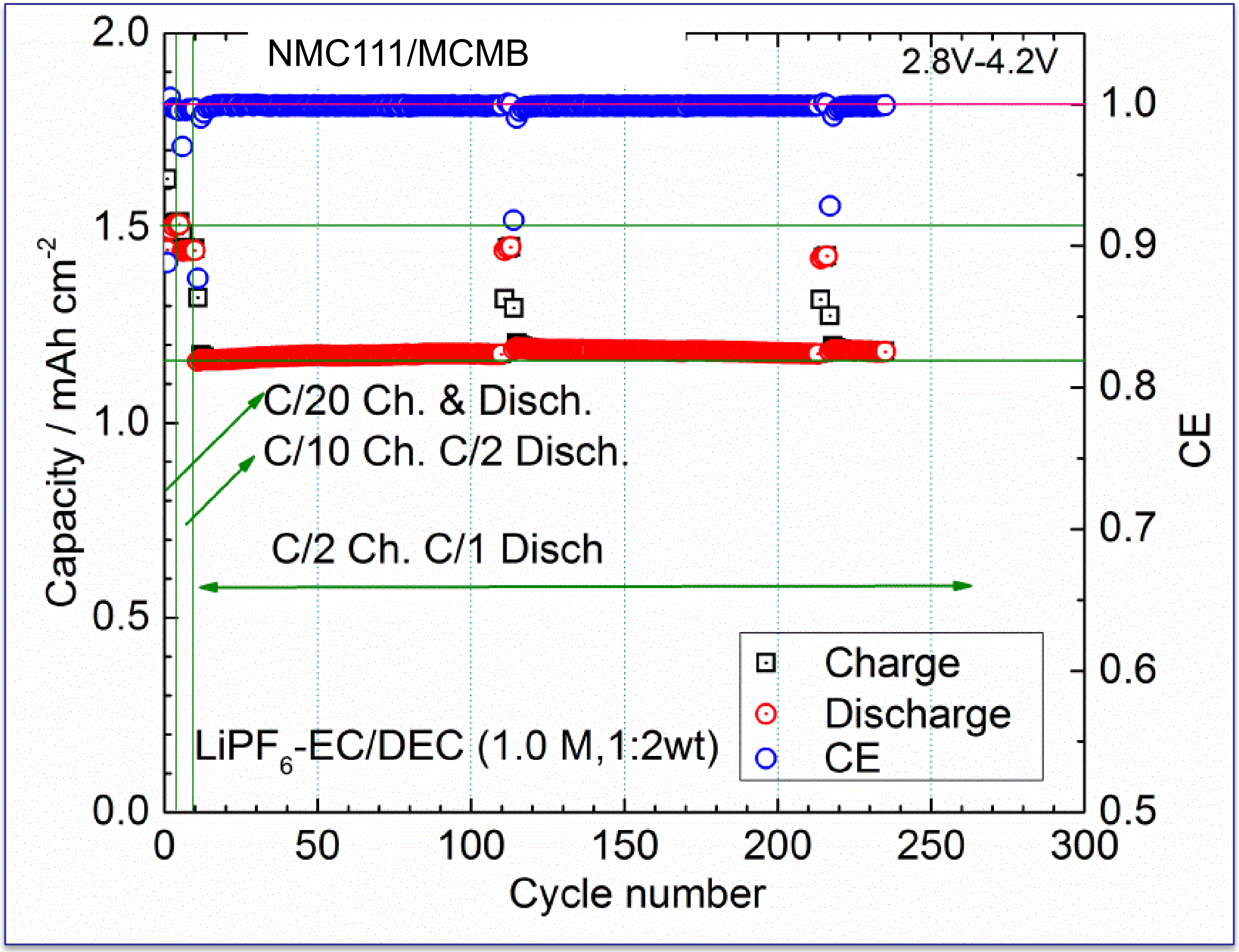
NCM



First time cells made; 10 g of powder.

Tech. Accp. #1: Make "Good" Cells

vs. Gr.

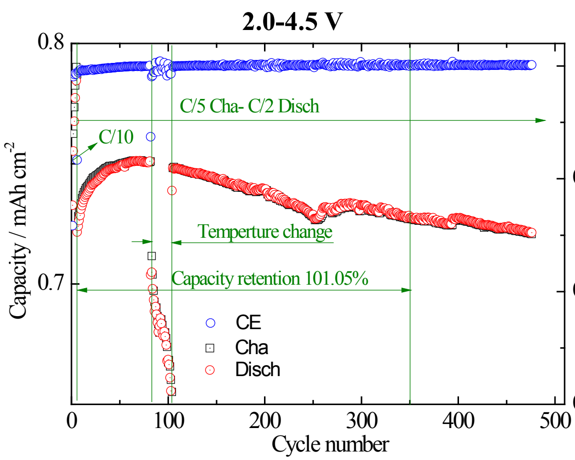


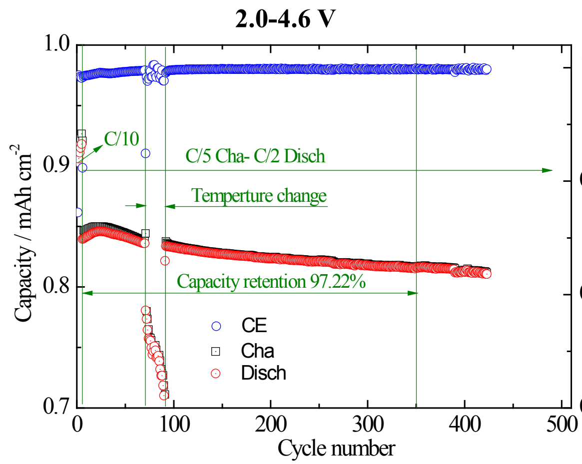
Full cells in a pouch (12 cm^2).

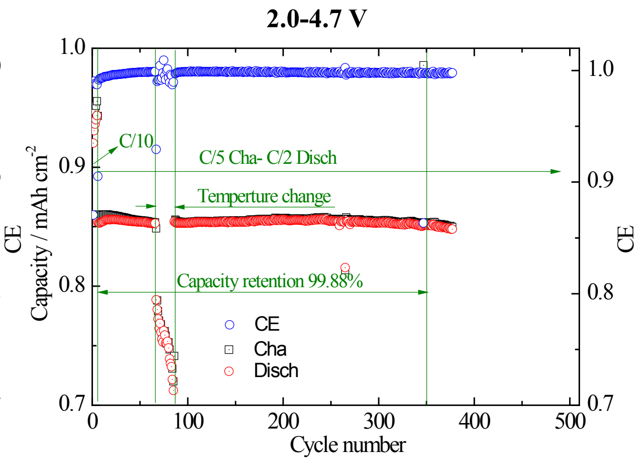
Tech. Accp. #1: Make "Good" Cells

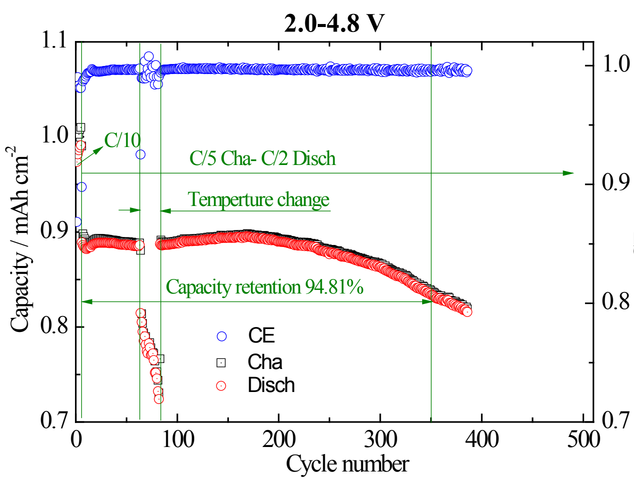
Li, Mn-rich Material

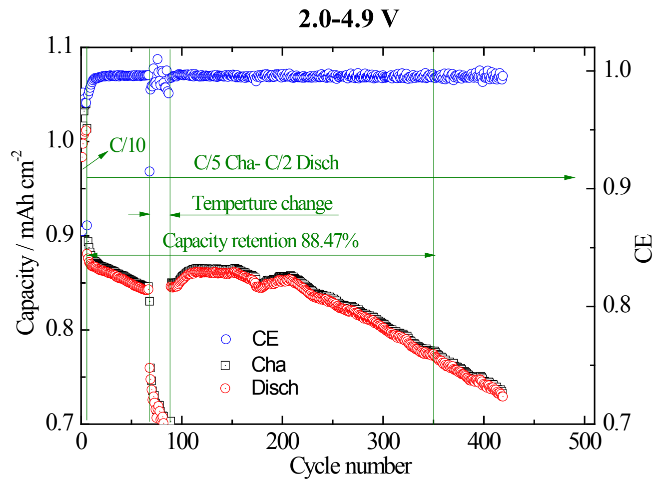
vs. Li











First attempt by a visiting researcher; 10 g per laminate.

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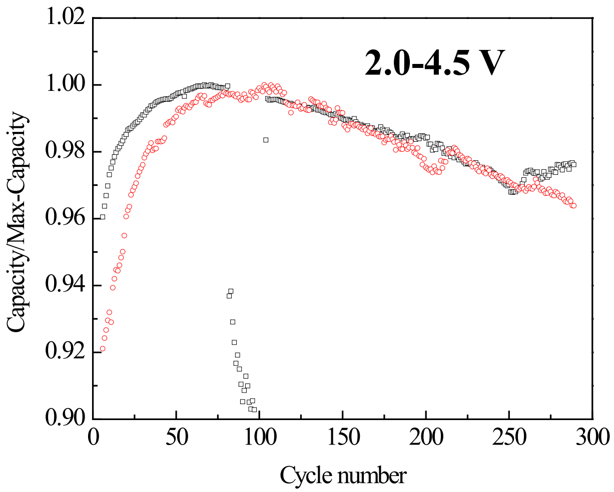
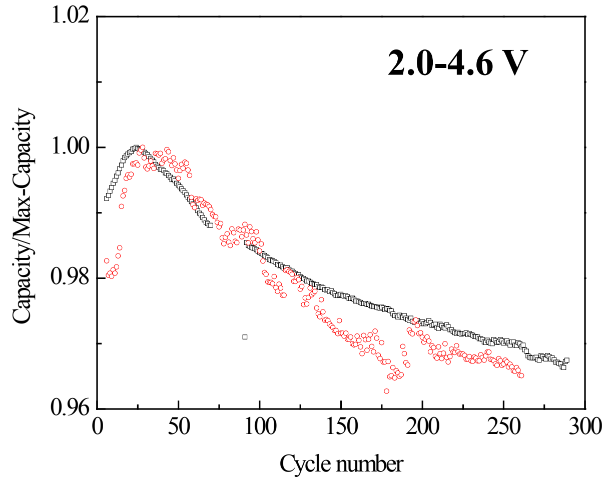
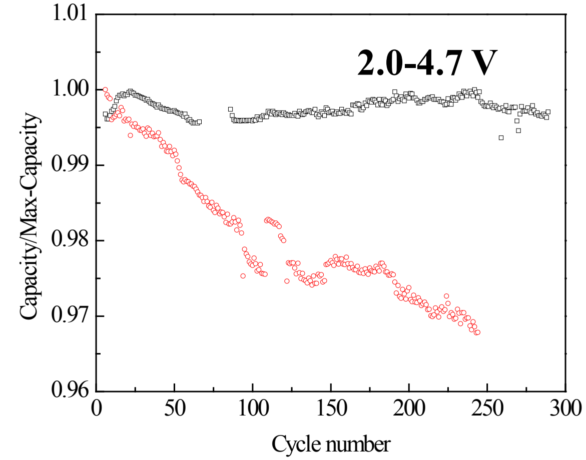
Tech. Accp. #1: Make "Good" Cells

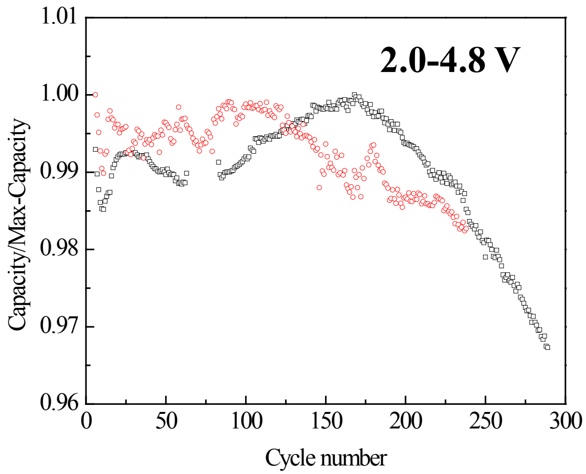
Direct comparison to industry electrodes

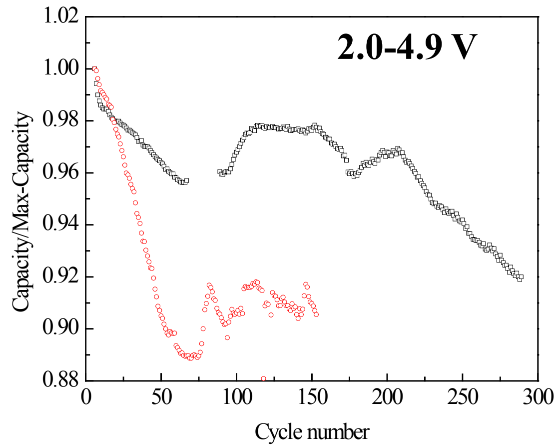
vs. Li











LBNL

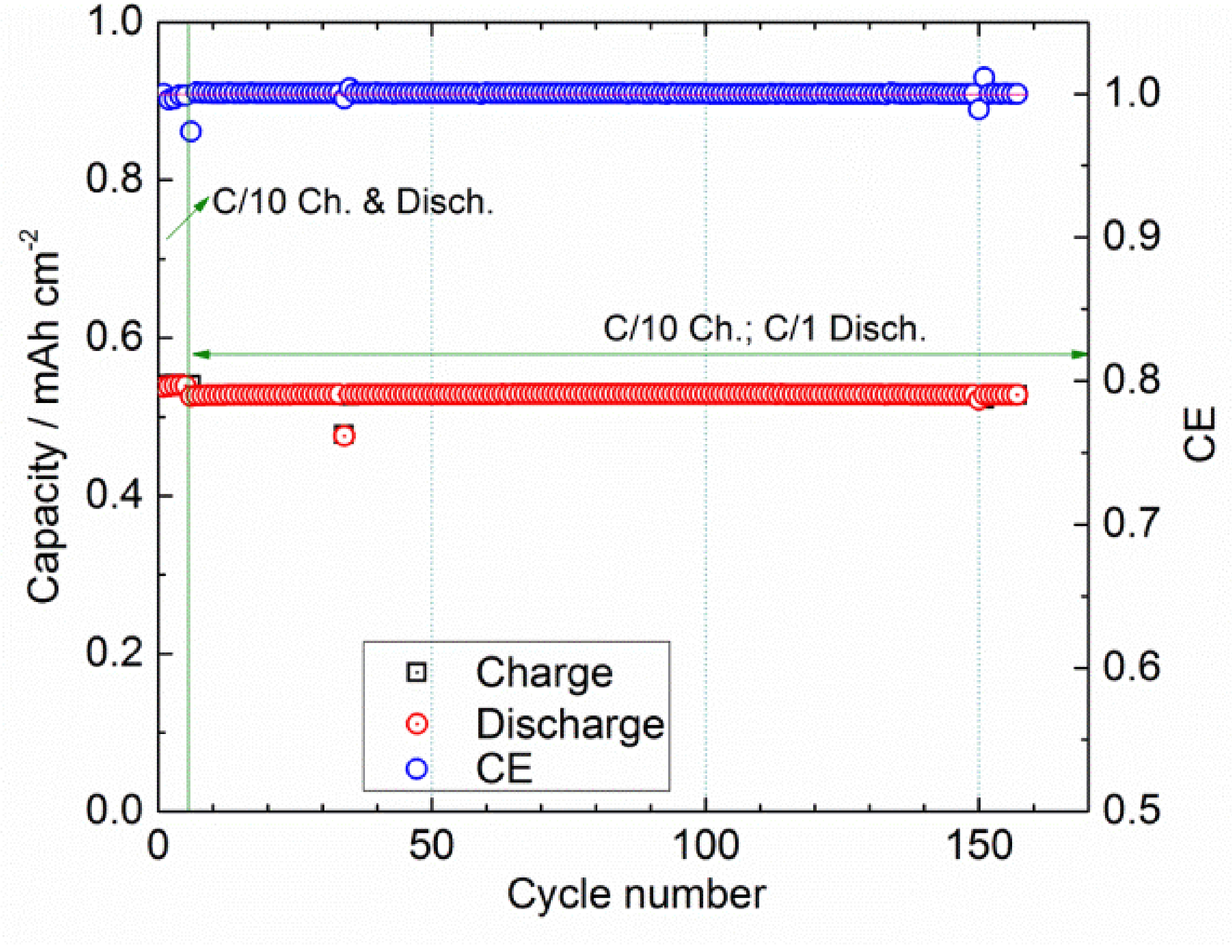
Ind. Partner

Ours stack up well.

Tech. Accp. #2: Higher Loading Electrodes

vs. Li

LFP

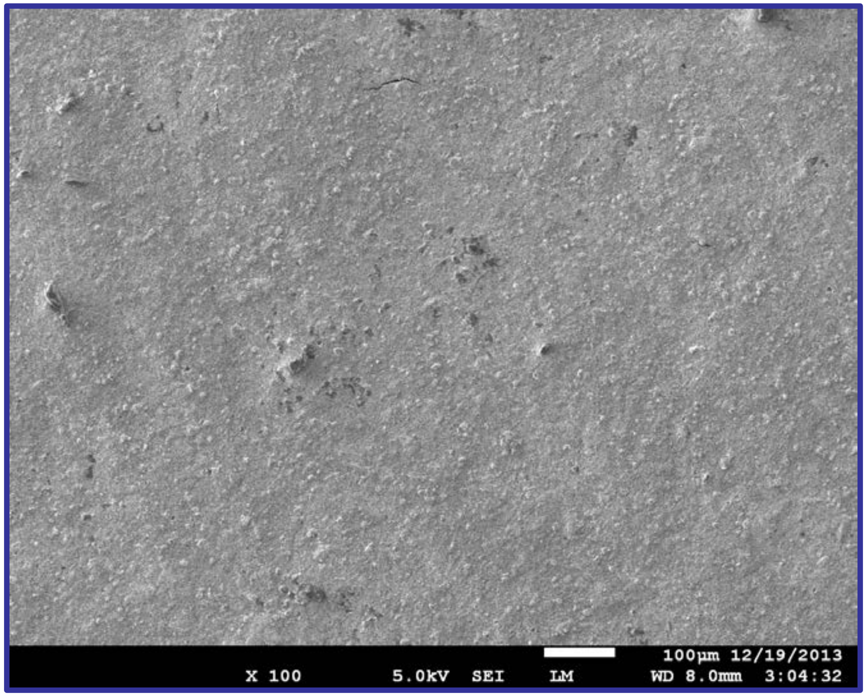


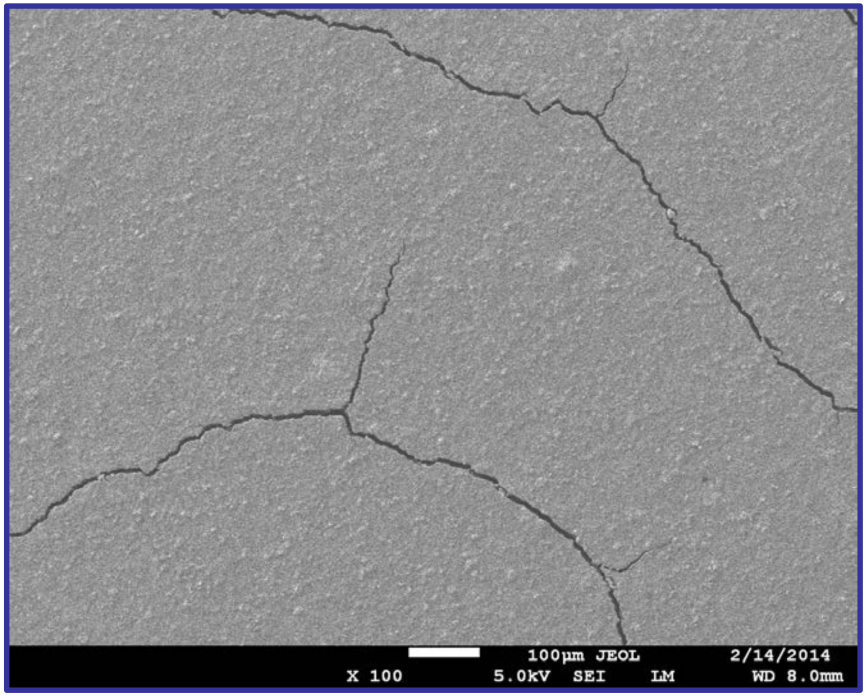
But these were mild loadings.

Tech. Accp. #2: Higher Loading Electrodes

LFP Electrode

Need higher loadings to test Si in full cells.





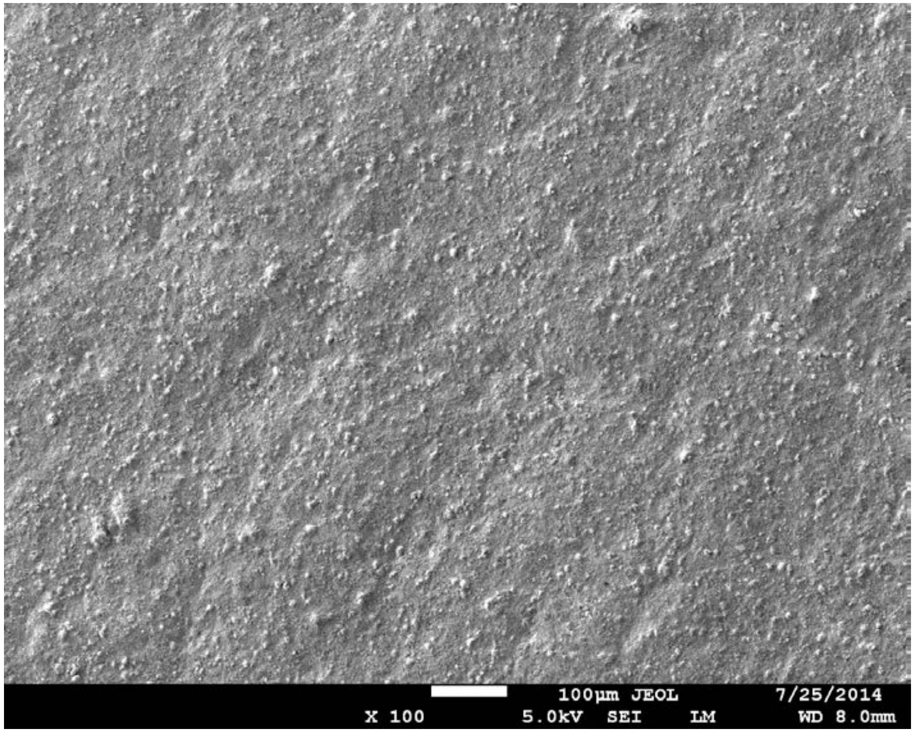
Loading: ~ 0.55 mAh cm^{-2}
Thickness: ~ 35 µm

Loading: ~ 0.8 mAh cm^{-2}
Thickness: ~ 50 µm

Couldn't make electrodes of 0.8 mAh/cm^2 without cracks.

Tech. Accp. #2: Higher Loading Electrodes

Modified Binder



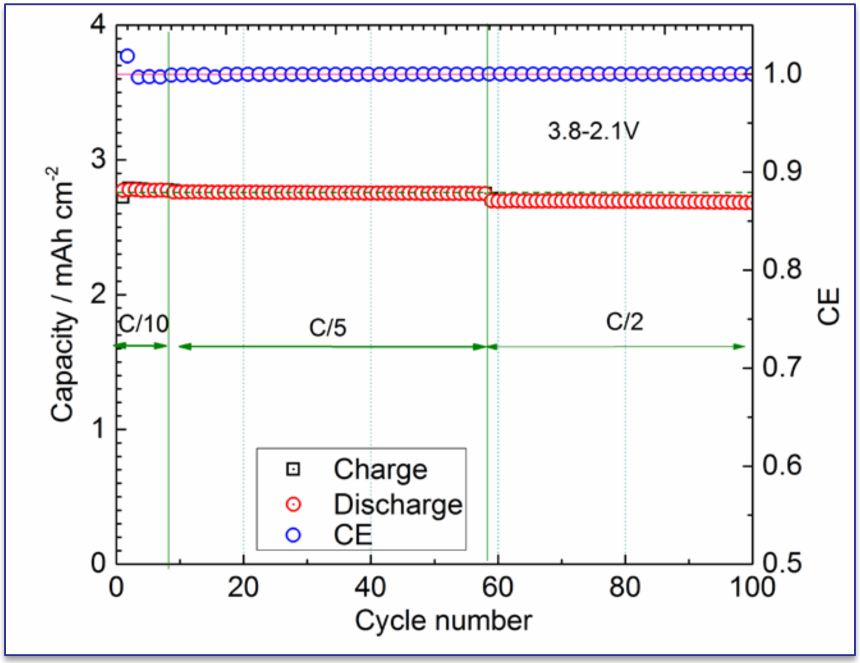
Loading: ~ 2.4 mAh cm^{-2}
Thickness: ~ 140 µm

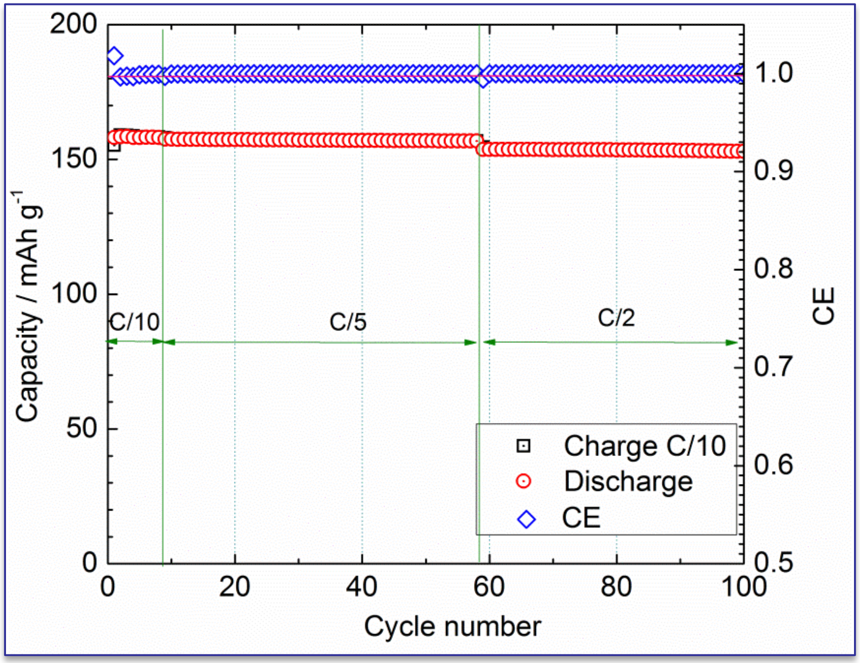
Cracks gone.

Tech. Accp. #2: Higher Loading Electrodes

vs. Li

Cycle Life Tested

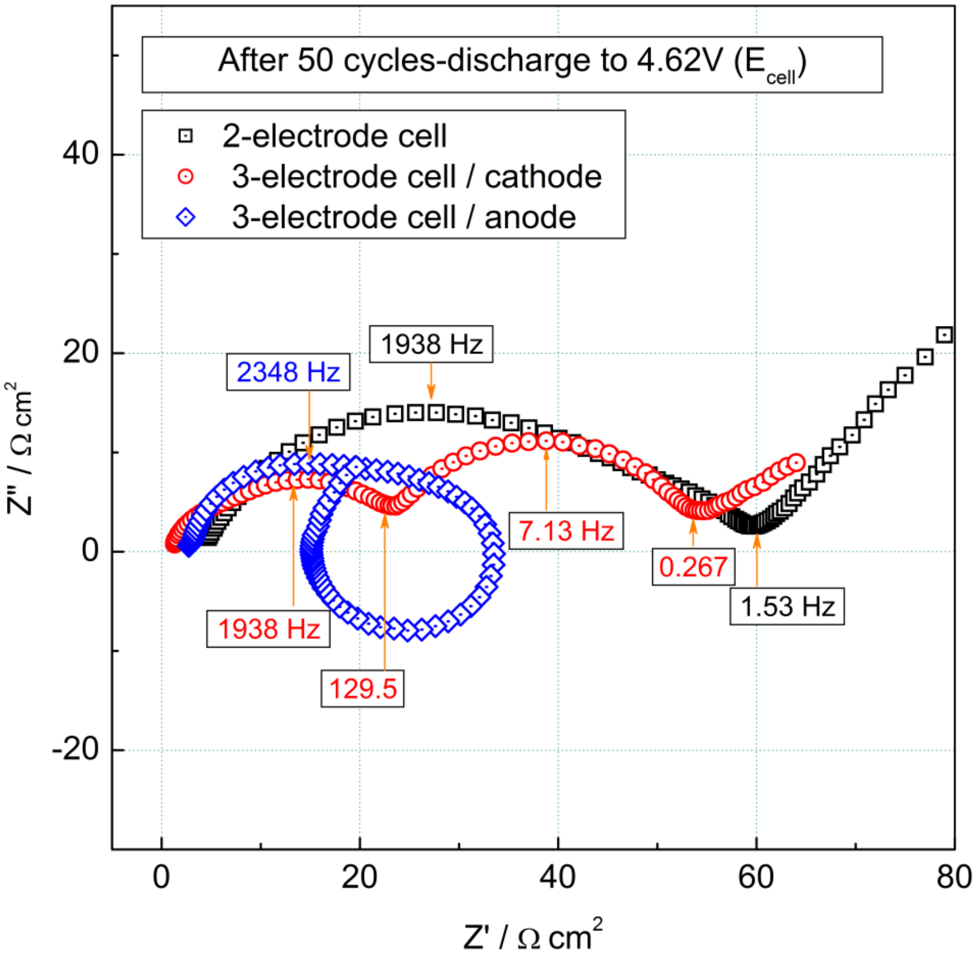




Cycles well and accesses full capacity.

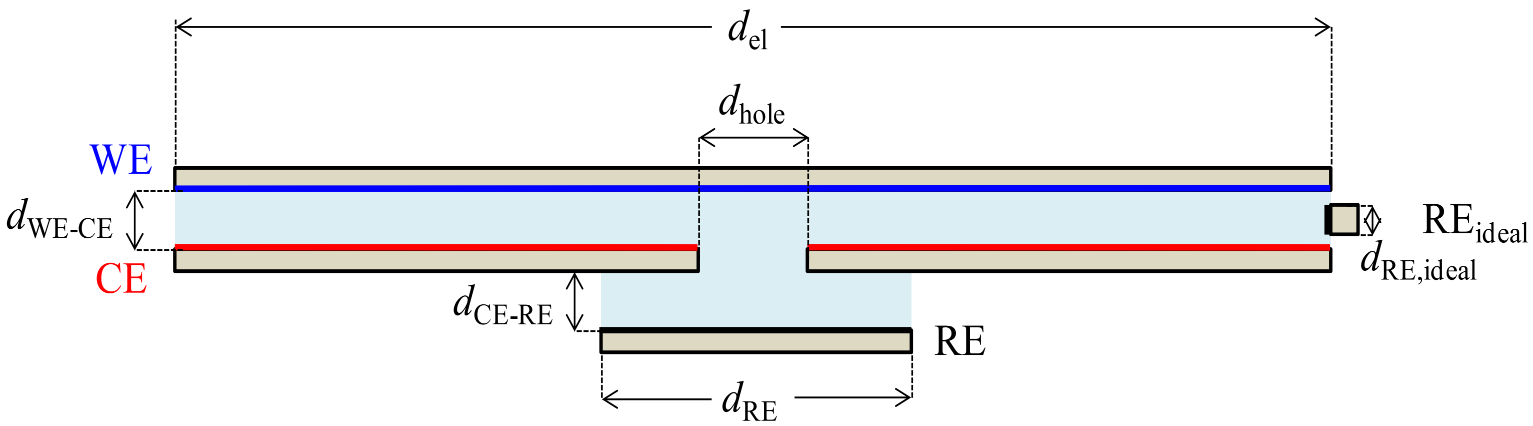
Tech. Accp. #3: EIS 3-electrode Cell

vs. Gr.



Not uncommon to see this.

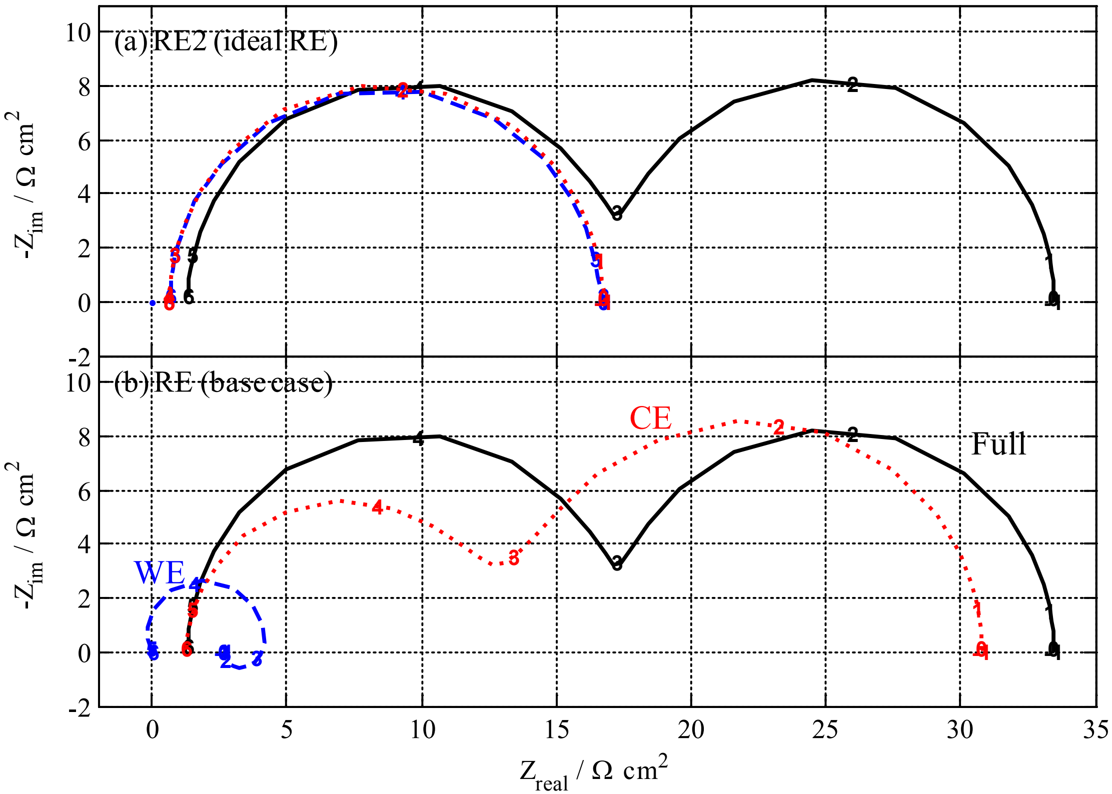
Tech. Accp. #3: EIS 3-electrode Cell



Assume resistance across interface was same for both electrodes but the capacitance was shifted by an order of magnitude to separate results.

Used Comsol to estimate impedance of secondary current distributions assuming two different reference electrode placements.

Tech Accp. #3. EIS 3-electrode Cell



Depending on the location of the reference, one gets entirely different impedance plots than expected.
As it turns out, one side of the cell appears to consist of more impedance than the other!
Placement of the 3rd electrode in a non-axial current distribution includes radial components that distort the signal.

This, however, allows for the assignment of impedance loops in the 2-electrode data!

Tech. Accp. #4: Failure of NMO

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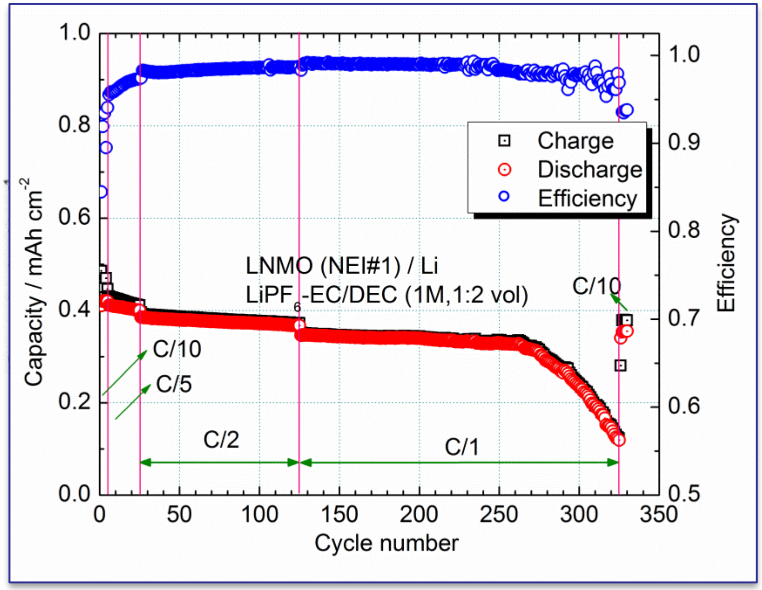
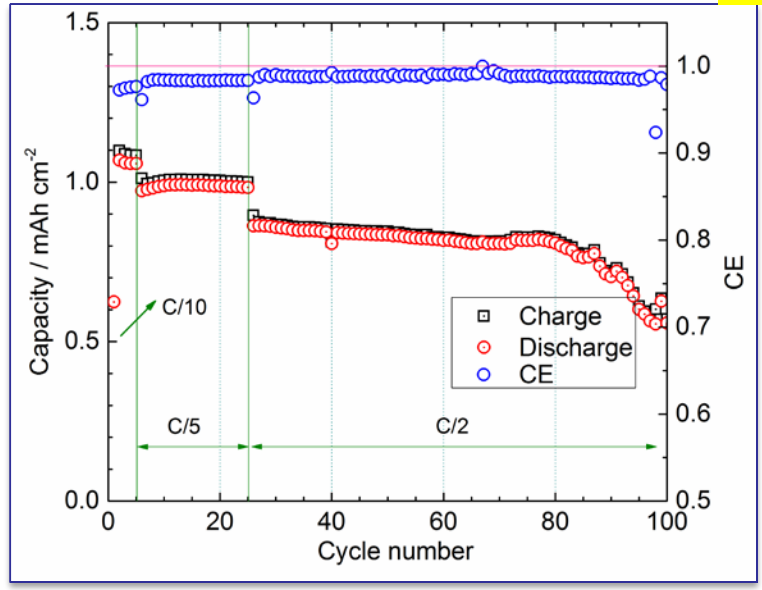
vs. Li

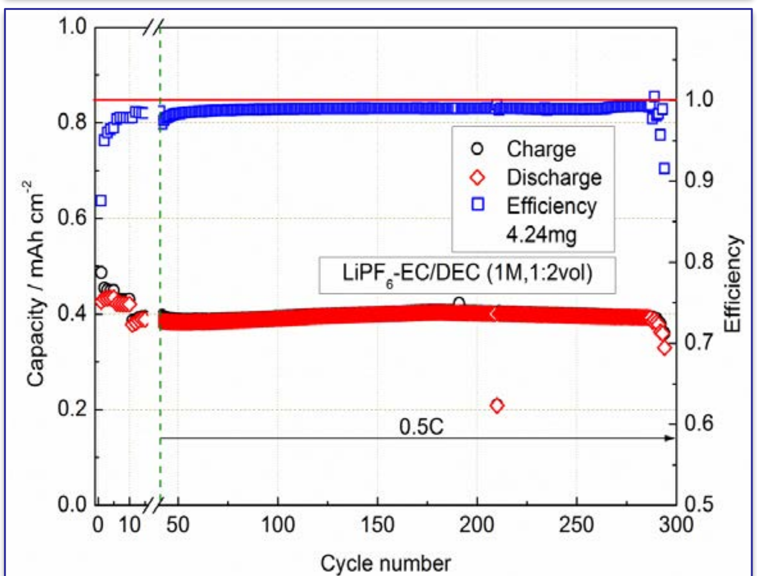
NEI#1



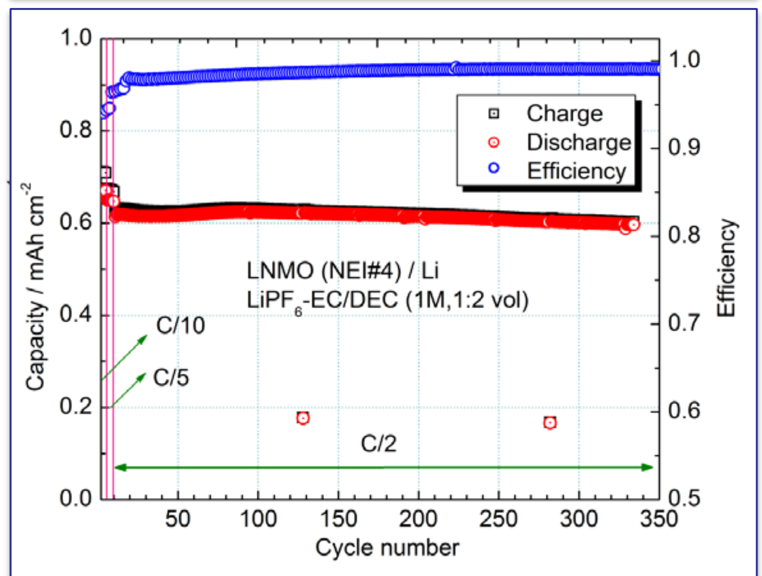
NEI#2



NEI#3



NEI#4

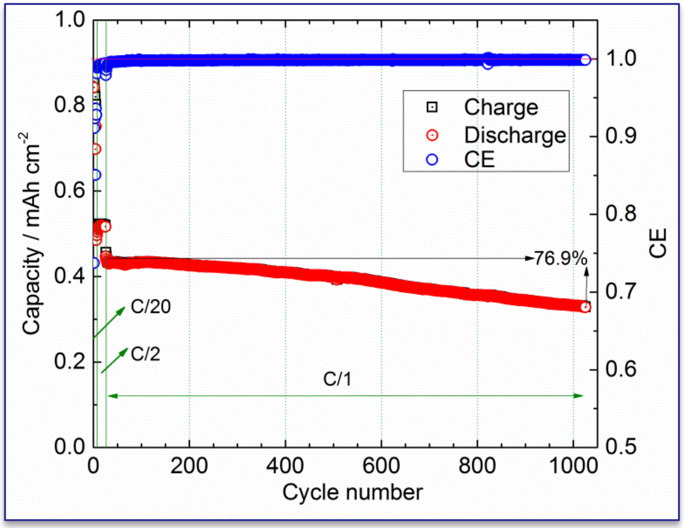


All electrodes cycle well in half-cells to a point (dry out? dendrites?).

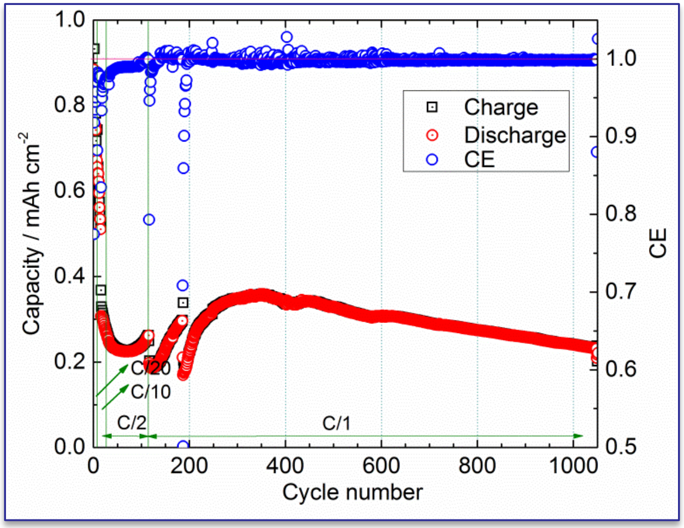
Tech. Accp. #4: Failure of NMO

vs. Gr.

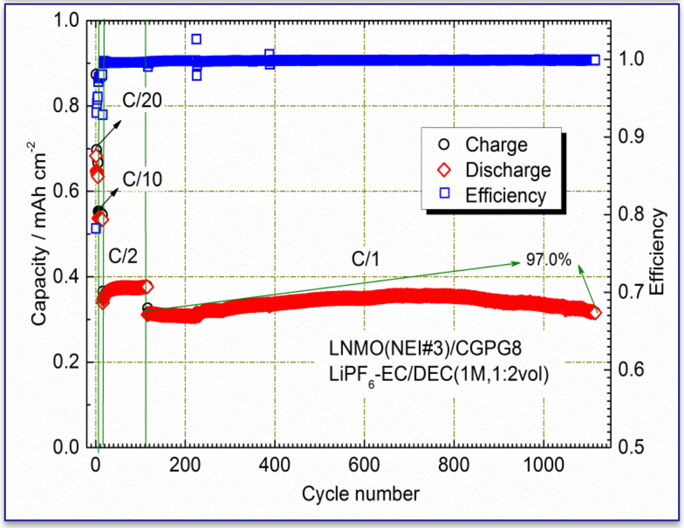
NEI#1



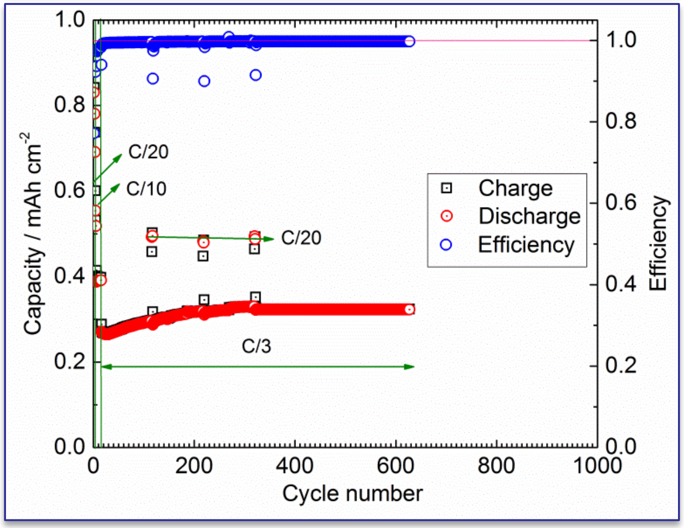
NEI#2



NEI#3

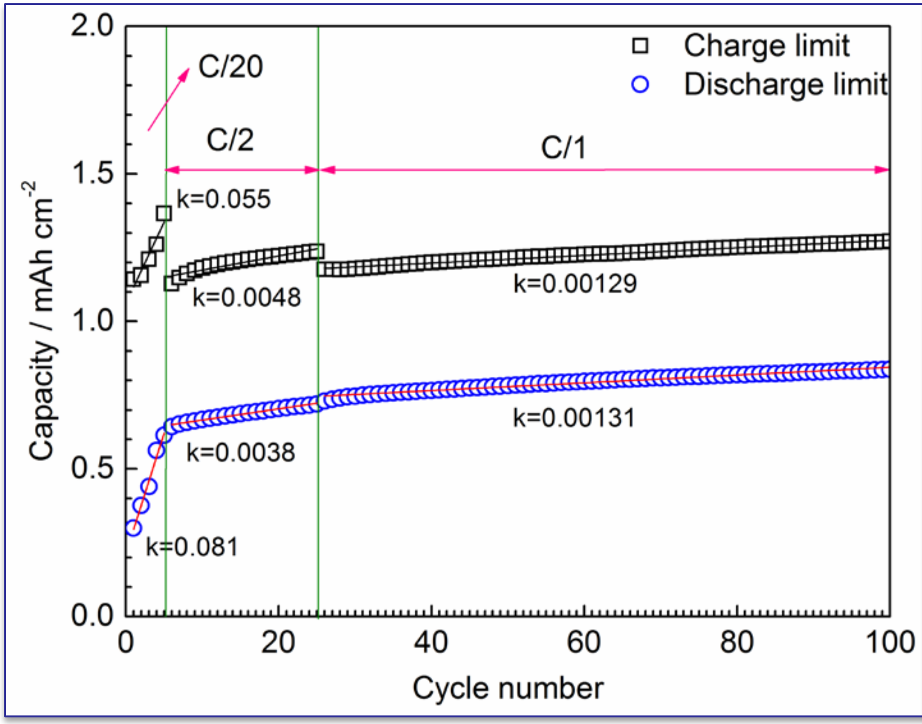


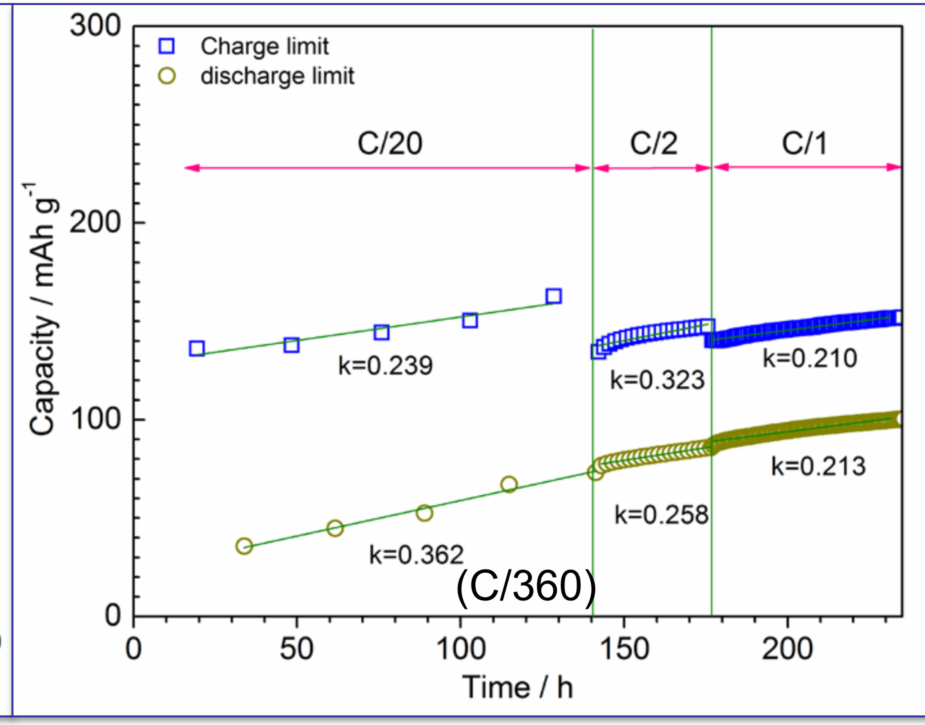
NEI#4



They all cycle well against graphite, **except** they lose half of their capacity in the first **5** cycles.

Tech. Accp. #4: Failure of NMO





Cycle	Q loss mAh/cm^2	Q loss %	Total loss %
1st	0.299	27.9%	**27.9%**
2-5	0.026	1.9%	7.6%
6-25	-0.001	-0.09%	-1.87%
26-100	2-E5	0.0019%	0.14%

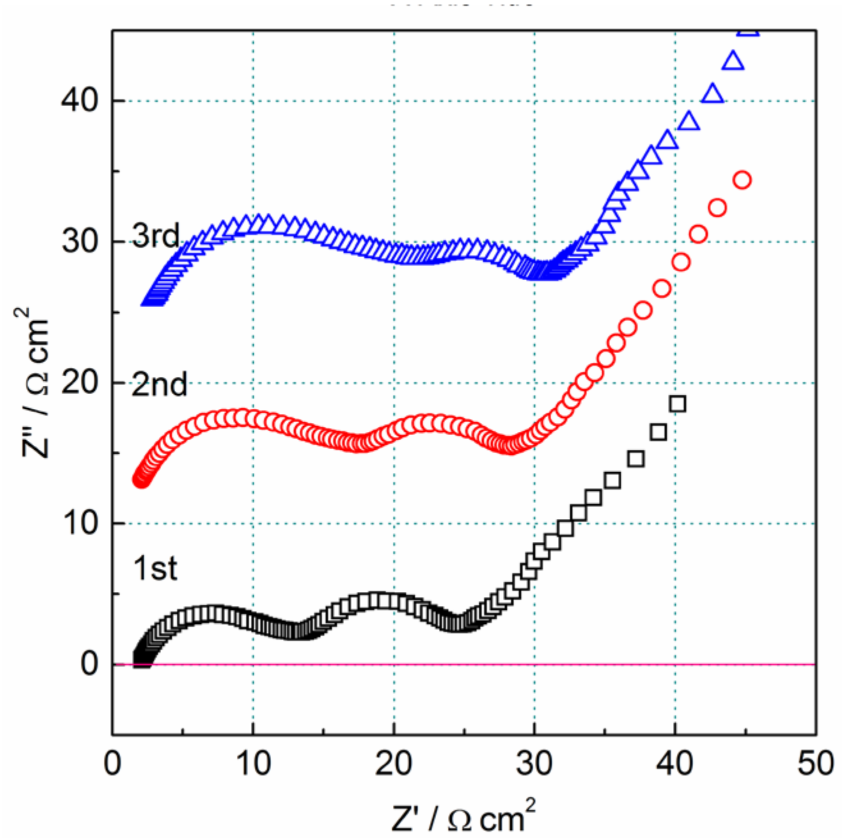
C-rate change	Q loss mAh/cm^2	Q Loss %
C/20-C/2	0.2375	**22.1%**
C/2-C/1	0.0603	5.62%

1st-26th total Q loss ≈ 60%

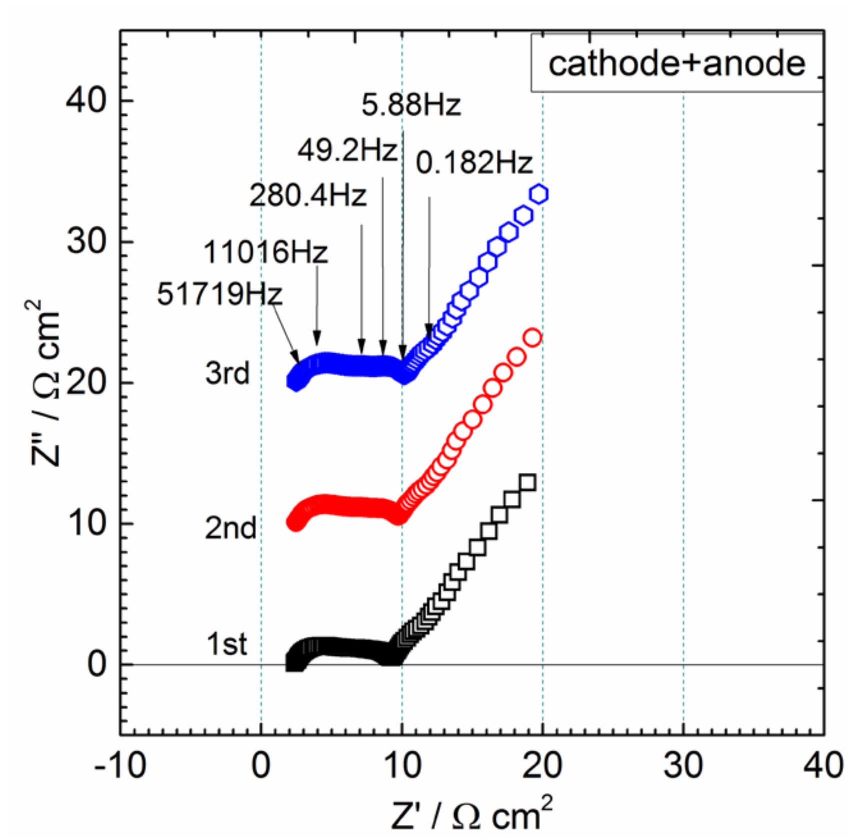
Tech. Accp. #4: Failure of NMO

vs. Gr.

NEI#4



NCM

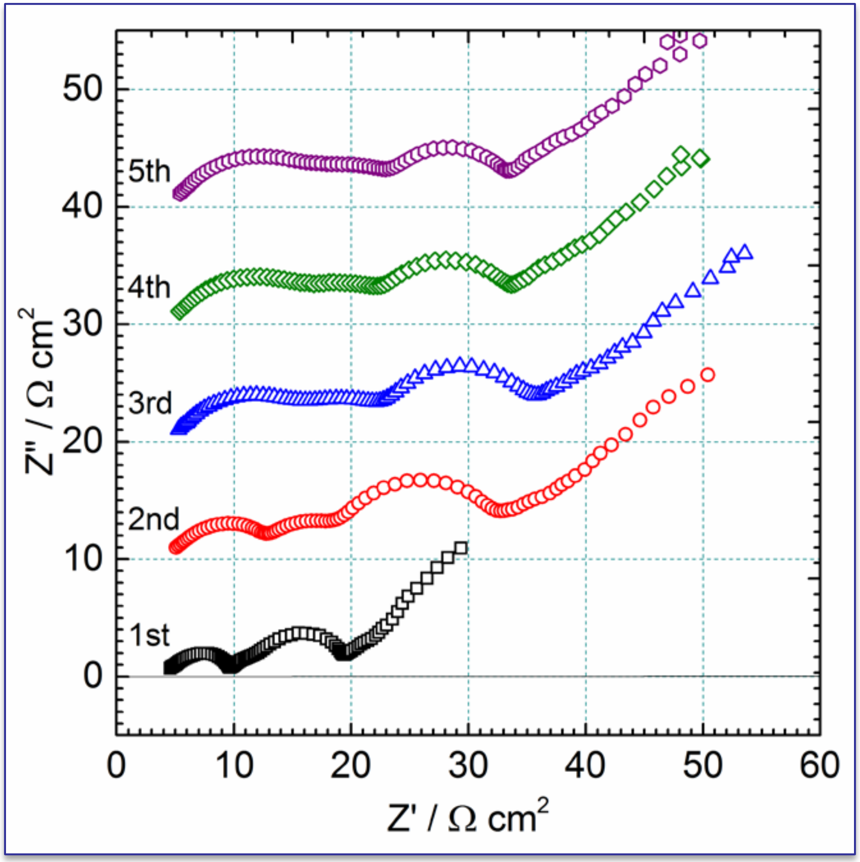


Within the first charge, NMO cells have a lot of impedance.

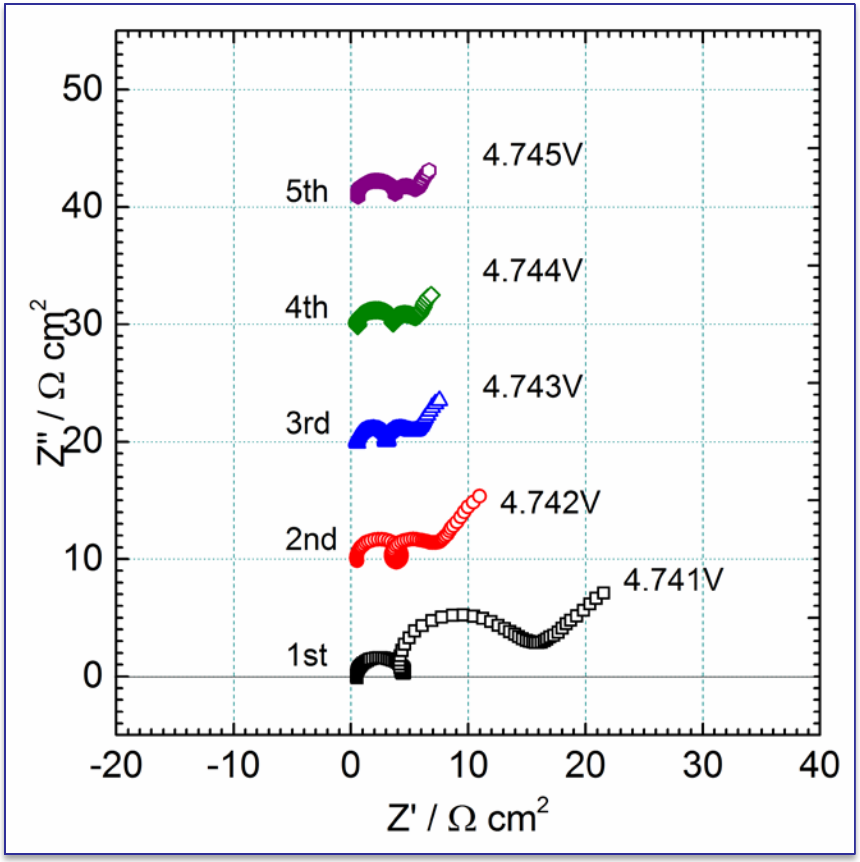
Tech. Accp. #4: Failure of NMO

vs. Gr.

Anode vs. Ref.



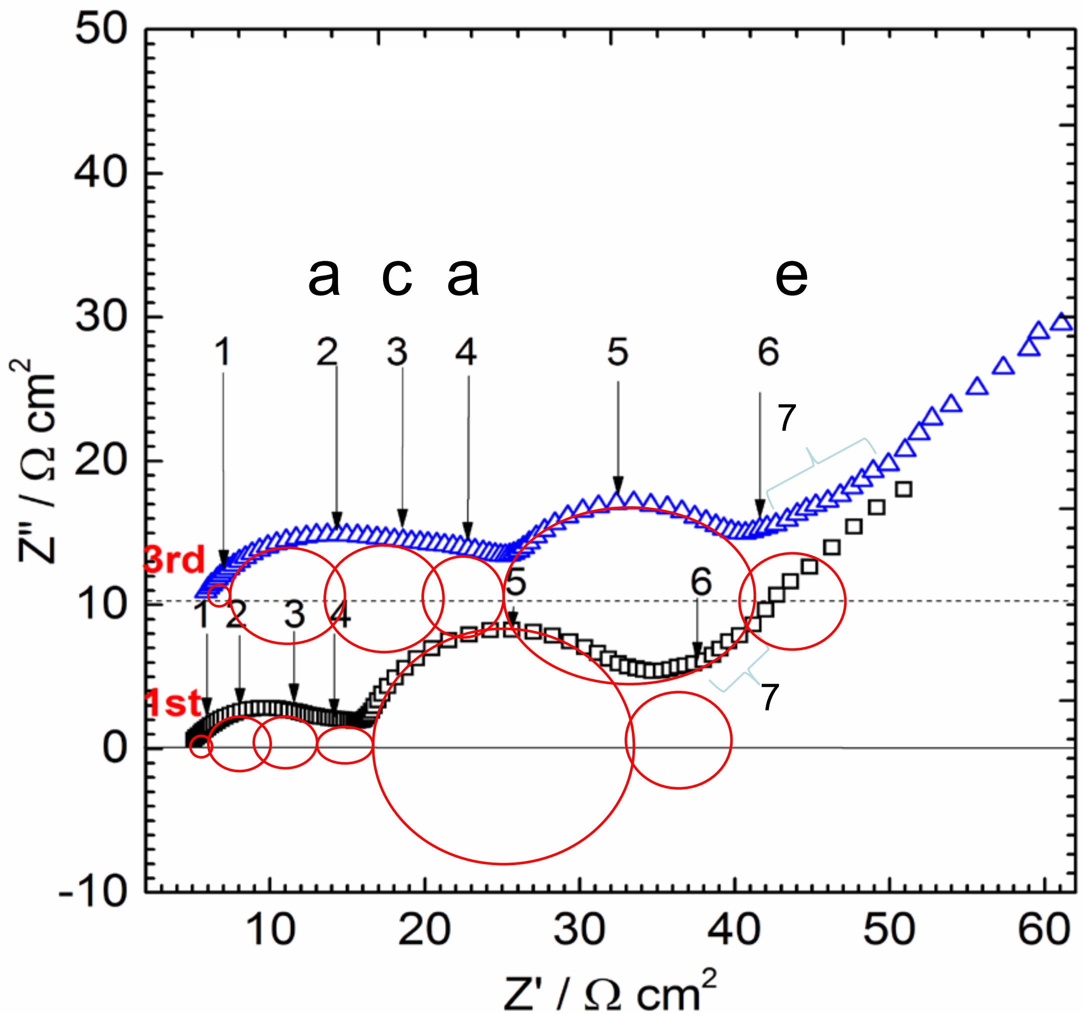
Cathode vs. Ref.



Clearly, all of the impedance is in the anode, or is it?

Tech. Accp. #4: Failure of NMO

vs. Gr.



Majority of impedance at the cathode interface; growth in the anode.

Tech. Accp. #4: Failure of NMO

1st Cycle	1	2	3	4	5	6	7
frequency	51719	11015	2347	190.3	5.883	0.182	
Anode (side)	2	4	0.5	3.5	6	4	1.5
frequency	51719	11015	1938	190.3	2.24	0.057	
Cathode (side)	-0.5		3.5	-0.5	11	3	1
frequency	51719	6199	1938	280.4	3.30	0.123	
sum	1.5 (a)	**4(a)**	**4 (c)**	**3 (a)**	17 (c)	7 (c)	**2.5**

3rd Cycle	1	2	3	4	5	6	7
Frequency	51719	6199	1317	280.4	7.13	0.477	
anode	1.5	7.5	4.5	5.5	14	4	6.5
frequency	51719	6199	2348	280.4	1.53	0.069	
cathode			2.5	-0.5	3	3	0.5
frequency	51719	5086	1084	280.4	5.883	0.477	
sum	1.5 (a)	**7.5 (a)**	**7 (c)**	**5 (a)**	17 (c)	7 (c)	**7 (?)**

Anode impedance from **8.5 to 14 ohm-cm²** ; **Cathode** impedance from **28 to 31 ohm-cm²**

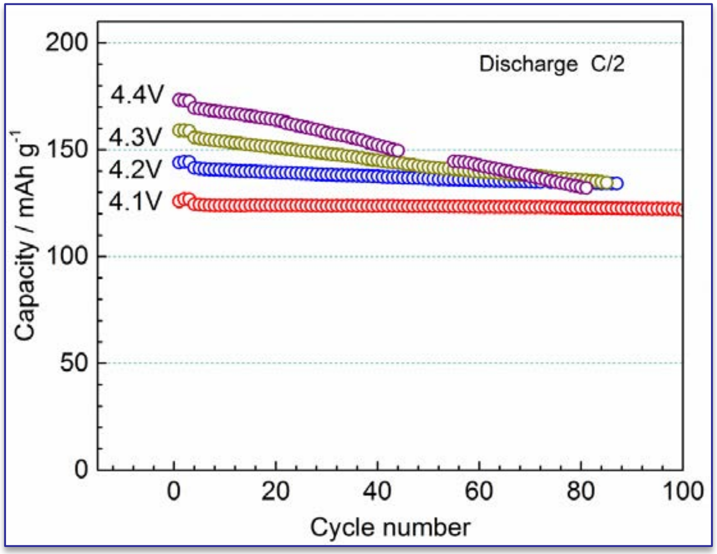
Tech. Accp. #4: Failure of NMO

- Summary
  - NMO: Consists of large, single crystals – no secondary particles)
  - Large first cycle loss as a result of large side reaction on the anode
  - Large impedance seen on first charge attributed to the cathode
  - Little impedance rise after first three cycles - rise in first 3 cycles attributed to anode and clogging of pores.

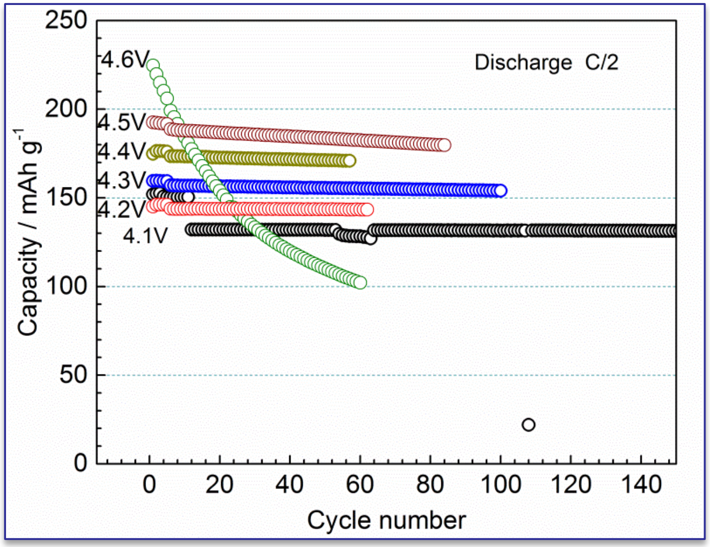
Tech Accp. #5: Initial Analysis of H.V.

vs. Li

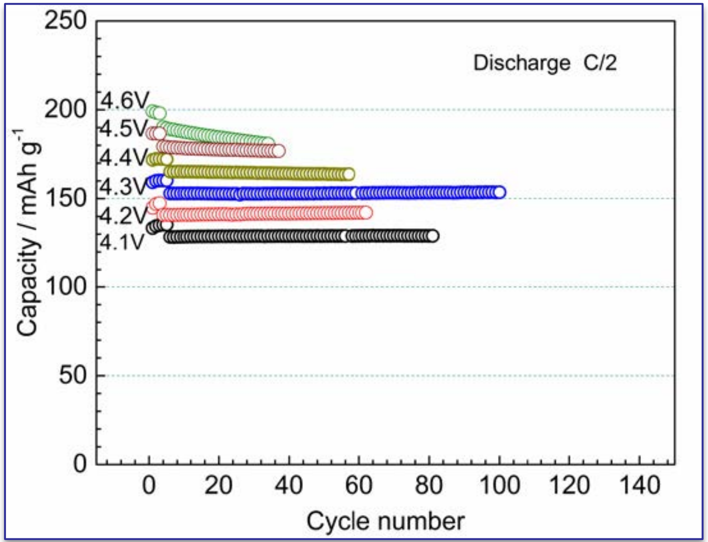
LCO



HV-LCO



NCM

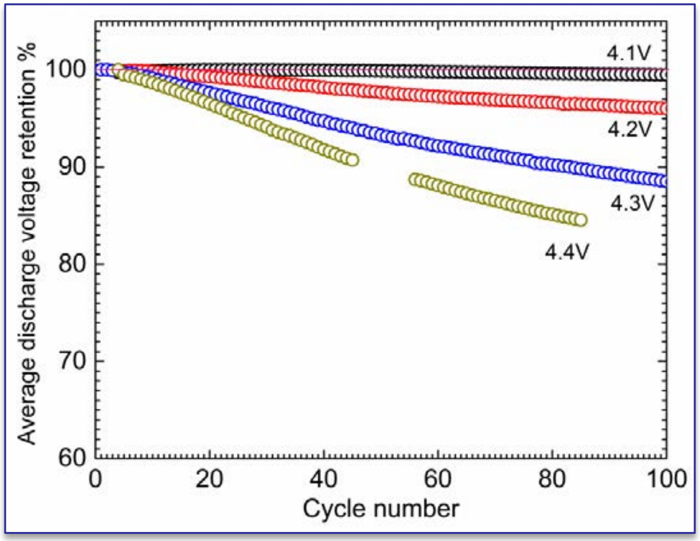


LCO: Capacity fade begins at 4.3 V.
HV-LCO: Capacity fade begins at 4.6 V.
NCM: Capacity fade begins at 4.6 V

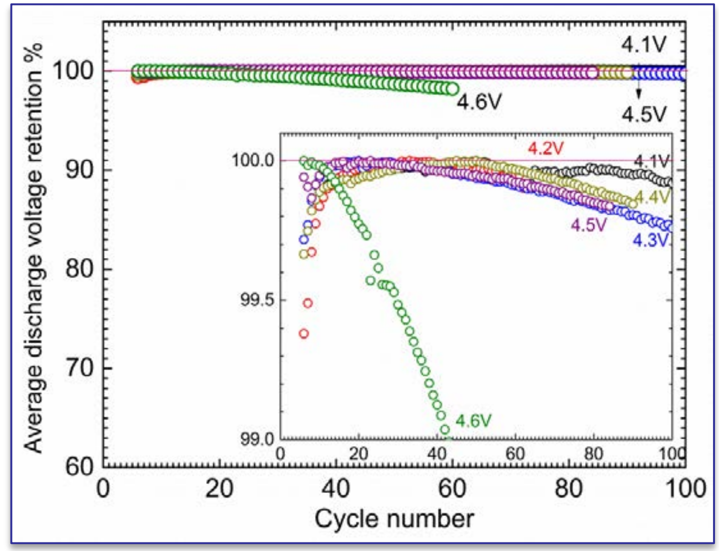
Tech Accp. #5: Initial Analysis of H.V.

vs. Li

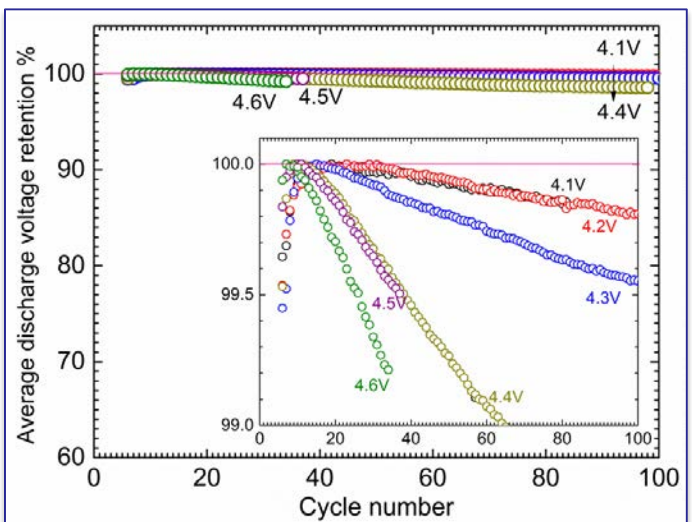
LCO



HV-LCO



NCM

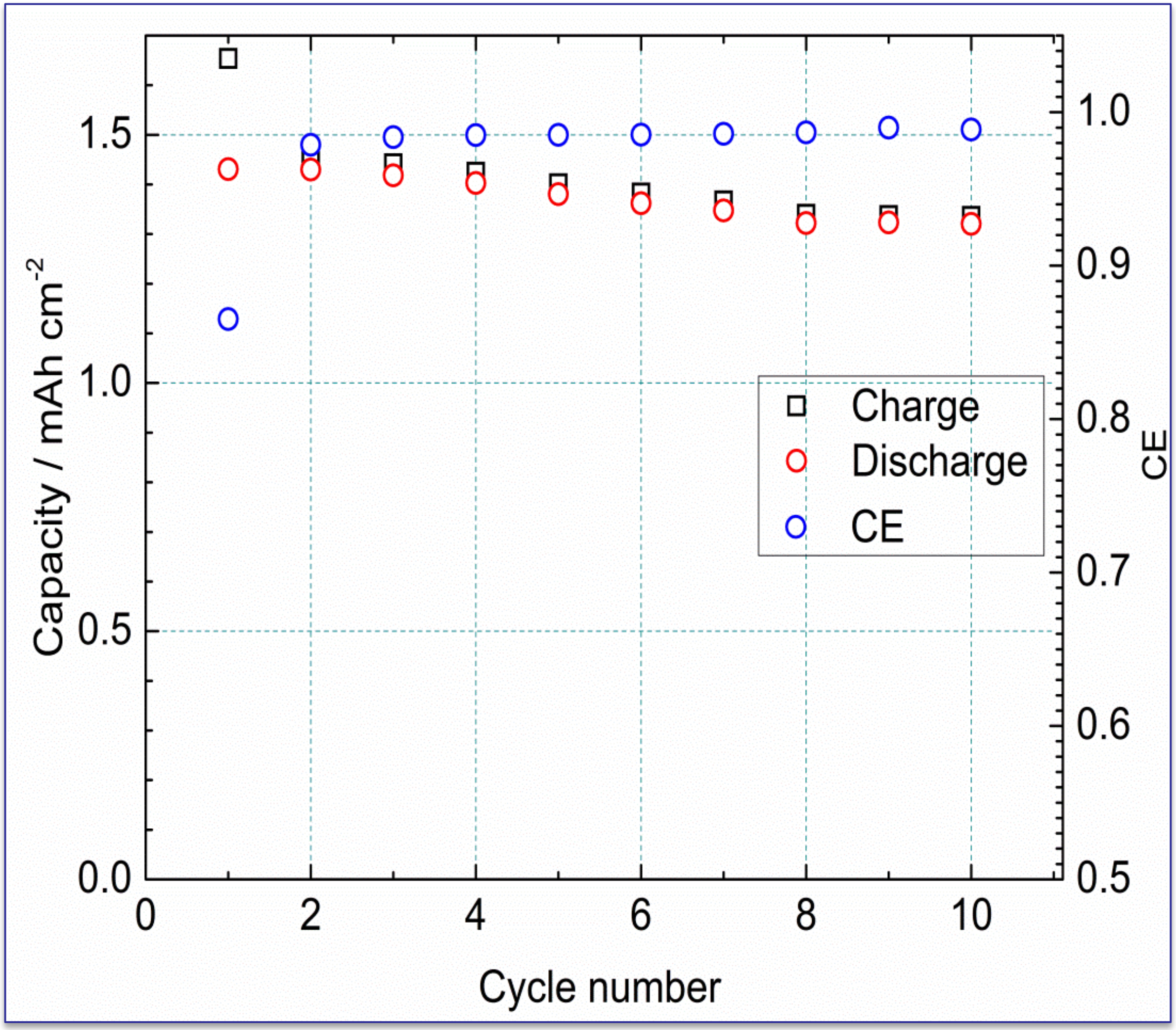


LCO: Resistance rise at 4.2 V.
HV-LCO: Resistance rise at <u>**4.6 V**</u>.
NCM: Resistance rise begins at 4.3 V.

Need more research into the stability of these materials.

Tech. Accp. #6: Failure of NCM Full Cell at 4.2V

vs. Gr.



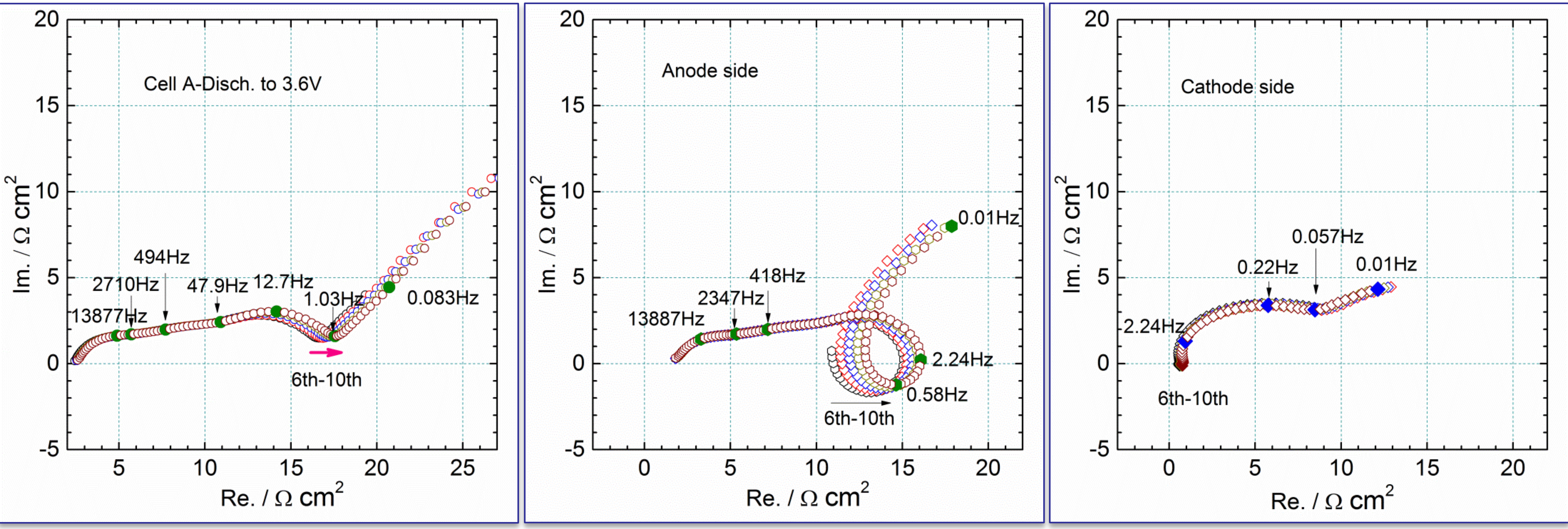
Related to large anodes in a coin cell.

Tech. Accp. #6: Failure of NCM Full Cell at 4.2V

vs. Gr.

EIS of Cycles 6 to 10

Cells discharge to 3.6V, rest 1 hour, then EIS.



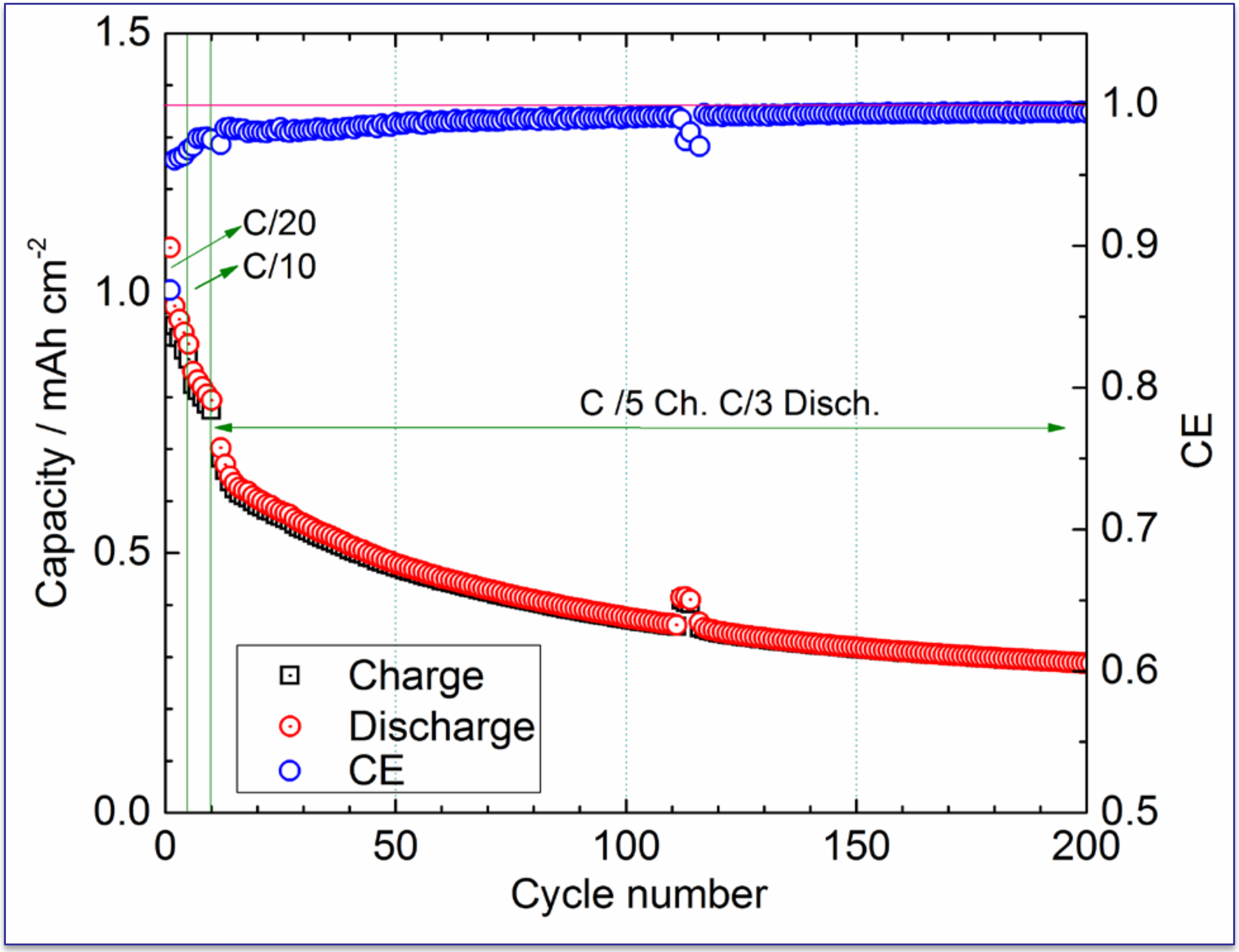
Slow, steady impedance raise of the anode.

May have some thing to do with coin cell configuration.

Tech. Accp. #7: Si failure

vs. Li

Pure Si particles with PVA binder.

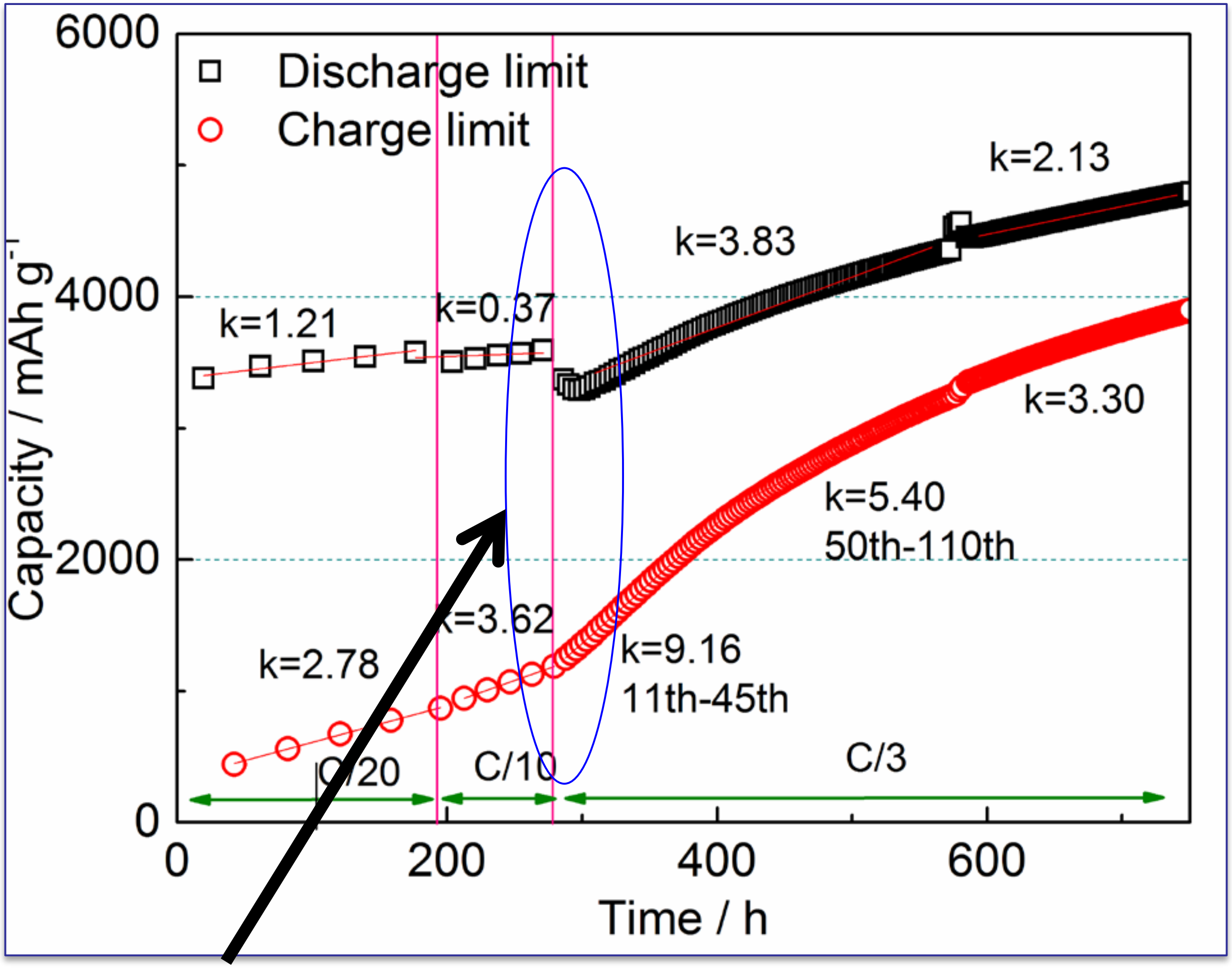


Anything remarkable?

Tech. Accp. #7: Si failure

vs. Li

Charge and discharge endpoints *vs* time

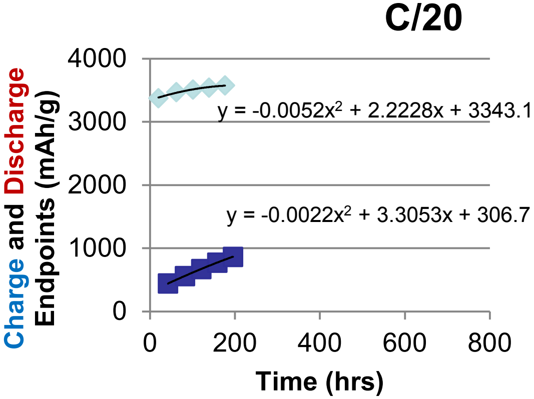


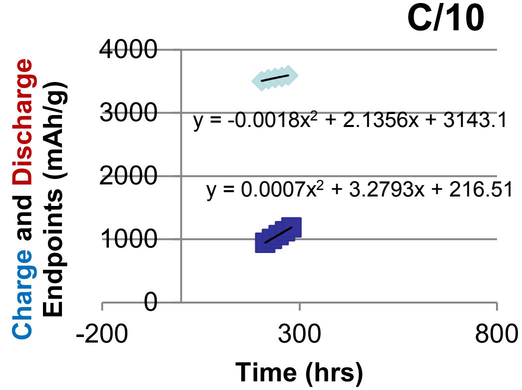
What is this?

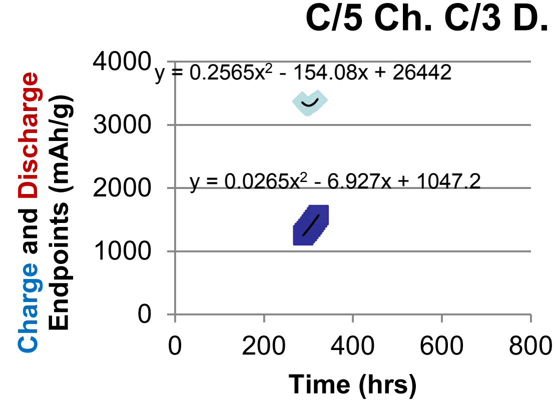
Tech. Accp. #7: Si failure

vs. Li

Transitions to new C-rates







SR = 2.8 – 0.0074t [mA/g] = 2.8 to 1.3 [mA/g]

PI = 0.54 + 0.003t [mA/g] = 0.54 to 1.1 [mA/g]

t = 0 to 195 [hrs]

SR = 2.7 – 0.0011t [mA/g] = 2.5 to 2.4 [mA/g]

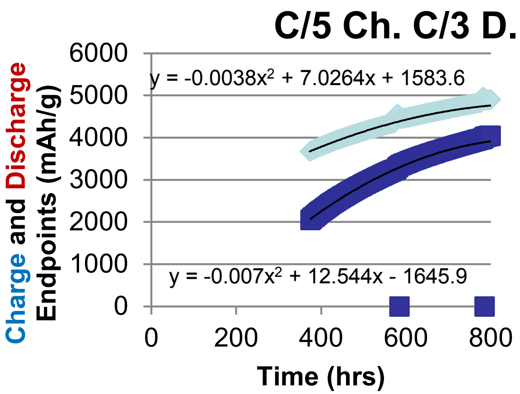
PI = 0.57 + 0.0025t [mA/g] = 1.1 to 1.3 [mA/g]

t = 195 to 279 [hrs]

SR = -81 + 0.28t [mA/g] = 0.72 to 11 [mA/g]

PI = 74 – 0.23t [mA/g] = 7.6 to -0.45 [mA/g]

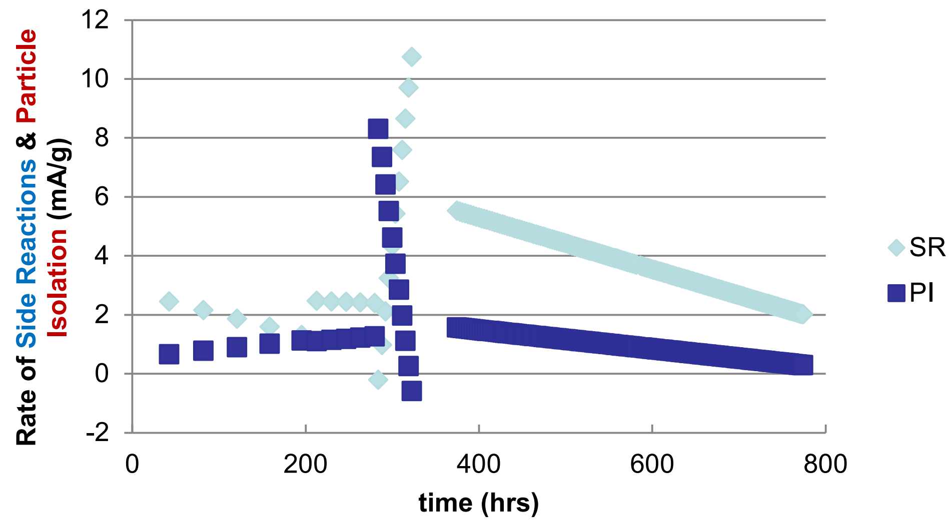
t = 287 to 322 [hrs]



SR = 9.8 – 0.011t [mA/g] = 5.5 to 1.8 [mA/g]

PI = 2.8 – 0.0032 t [mA/g] = 1.6 to 0.21 [mA/g]

t = 375 to 800 [hrs]



Collaboration and Coordination

- Umicore: Project Partner
  - Outside of VT Program
  - Cathode and Anode material supplier
- NEI Corp.: Project Partner
  - Outside of VT Program
  - Cathode material supplier
- HydroQuebec: Program Subcontractor
  - Inside VT Program
  - Cathode and Anode material supplier
- Daikin, America: Program Partner
  - Inside VT Program
  - Cathode and Anode material supplier
- BYU: Program Partner
  - Inside VT Program
  - Separator supplier
- ANL: Program Partner
  - Inside VT Program
  - Anode supplier
  - Provide electrodes to
- PNNL: Program Partner
  - Inside VT Program
  - Provide electrodes to

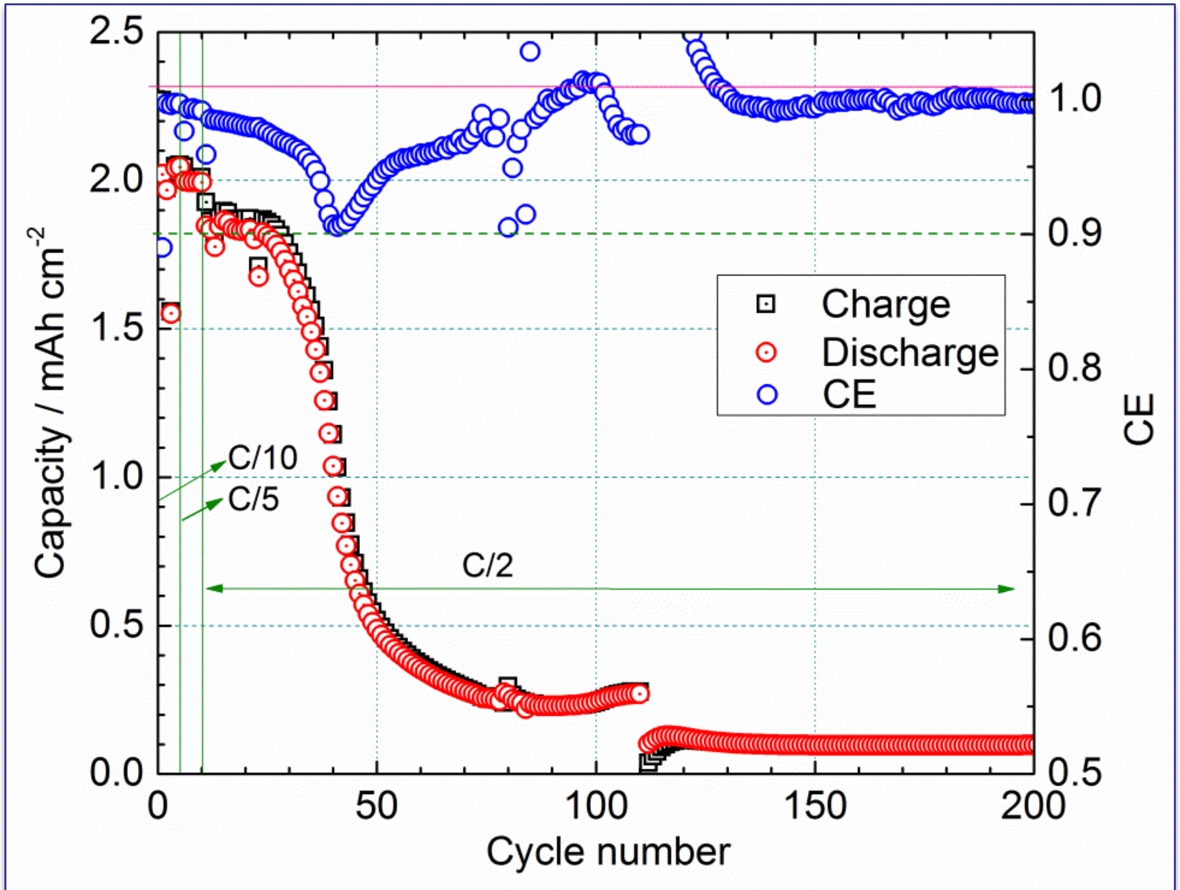
Remaining Challenges and Barriers

- For the Present Project (which ends in September):
  - Is there an electrolyte being developed in the program that improves the NMO couple by either resulting in higher charge transfer kinetics at the cathode or less first cycle irreversible capacity loss at the anode?
  - Why is there a significant change in resistance rise in the HV-LCO material at 4.6 V but a continuous increase in resistance for LCO and NCM?
  - Why is it that the graphitic anode in full cells show much more irreversible side reactions than the graphitic anode in pouch cells?
  - Can we create an all-purpose cell design that allows for the accurate determination of the energy density of the many-proposed/investigated Li/S systems?

Remaining Challenges and Barriers

vs. Li

High loading NCM Electrode



Laminate shows cracks and easily delaminates.

Remaining Challenges and Barriers

- For a Follow-on Project:
  - How thick of an electrode can we make and still meet the power to energy targets of an EV.
  - Will a higher molecular weight binder eliminate the cracking?
  - Will a higher molecular weight binder improve the adhesion to the current collector?
  - To what extent does a higher molecular weight binder affect the electrochemical performance and cycling characteristics?
  - Can a thicker electrode be cast at the same speed as today's laminates (~50 m/min).
  - Can a thicker electrode be cast at the same speed and with the same drying times as today's laminates?
  - To what extend can we use temperature in the processes prior to casting to meet the casting speed and drying time.

Proposed Future Work

- The project is scheduled to end in September, in the mean time…
  - Assess high voltage electrolytes in the program against NMO and NCM.
  - Complete analysis of LCO, HV-LCO, and NCM.
  - Complete analysis between Gr./NCM in coin cells *vs*. pouch cells.
  - Complete a cell design for Li/S.

- In a follow-on project
  - We hope to extend our work into high electrode loadings using high molecular weight polymers and advanced diagnostic techniques to determine polymer distribution as a function of processing conditions.

Summary

- Key take-away points:
  - We have a sound methodology for making quality electrodes and cells of 1 mAh/cm^2 or less in the first attempt, with just 10 g of active material powder.
  - There may be an avenue for making thicker electrodes with higher molecular weight binders and modifications to the processing steps.
  - Cells with NMO cycle really well even though the upper cut-off voltage is close to 5 V. The biggest challenge is the resistance in the cell and the loss of capacity at the anode on the first cycle.
  - The resistance rise as a function of voltage in HV-LCO is abrupt at 4.6 V, unlike what occurs in LCO and NCM.
  - There is significant capacity fade in full, coin cells that is not apparent in full, pouch cells.
  - Increasing the cycling rate in a Si material can result in cracking of the particles at rates as low as C/3.

- END pres.