Advanced Electrolytes for Extreme Fast Charging

Principal Investigators: William Chueh, Mike Toney, Yi Cui, Johanna Nelson Weker, SLAC National Accelerator Laboratory

James Kaschmitter, SpectraPower LLC

Robert Kee, Colorado School of Mines

Project ID: bat401

Overview

Timeline

- Start: Oct 1, 2019
- End: Sep 30, 2021
- Percent complete: 60%

Barriers

Barriers addressed

- Enable extreme fast charging at 10 minutes
- Develop high conductivity electrolyte and additive package
- Develop advanced diagnostics to validate advanced electrolytes

Budget

- Total project funding
  $1.5M from DOE
- Funding for FY19
  $750k
- Funding for FY20
  $750k

Partners

- PIs: Chueh, Toney, Cui, Kaschmitter, Weker, Kee
- Collaborators:
- Victor Koch, Covalent Associates
- Konstatin Tikhonnov

Project Objective

Objectives: Develop an advanced electrolyte and four-step charging protocols that enable extreme fast charging on thick graphite-based anodes. Together with full-cell modeling, state-of-the-art X-ray and cryogenic electron microscopy (cryo-EM) characterization, we will:

(1) Tailor an advanced electrolyte paired with commercial graphite-based anodes to enable extreme fast charging in 10 minutes to 80% state-of-charge.

(2) Optimize the charging protocol to achieve 500 cycles with less than 20% capacity fade.

(3) Understand the impact of extreme fast charging on the battery components, and understand

and control Li plating/dead Li formation in full cells throughout extended cycling.

(4) Exhaustively validate results using not only through battery cycling but also in-situ X-ray and ex-situ cryo-EM characterizations of full cells.

Relevance

Relevance:

- Tomorrow's electric vehicles will require superior extreme fast-charging capability without compromising energy density and cost.
- With current state-of-the-art Li-ion battery technology, the general trend to reach energy densities >200 Wh/kg has been to design thicker, more dense electrodes. This poses a significant barrier to extreme fast charging since it is difficult to charge these thick electrodes at high rates without significant degradation. High rate charging on these anodes results in Li plating/dead Li, which can lead to graphite delamination, unacceptably high temperatures, and other irreversible side reactions such as the uncontrolled growth of solid electrolyte interphase.

Milestones

Tasks	MS #	Task or subtask	Quarters							
			1	2	3	4	5	6	7	8
1.0		**Electrolyte development and coin cell testing**								
1.1		Prepare baseline electrolyte	▬							
	1.1.1	Deliver baseline electrolyte	▲							
1.2		Adjust electrolyte composition		▬	▬	▬	▬	▬	▬	▬
	1.2.1	Report results of half cell testing and changes in electrolyte composition	▲	▲						
	1.2.2	Prepare modified electrolyte for use in nine 2Ah cells				▲				
	1.2.3	Report results of half cell testing and changes in electrolyte composition					▲	▲		
	1.2.4	Prepare optimized electrolyte for use in 18 2Ah cells								▲
2.0		**Physically based modeling**								
2.1		Quasi-1D submodels of cell assembly	▬	▬	▬	▬	▬	▬	▬	
	2.1.1	Update cell architecture and materials definition in submodels	▲		▲		▲		▲	
2.2		3D cell-scale models		▬	▬	▬	▬	▬	▬	
	2.2.1	Update 3D models with refined quasi-1D models	▲		▲		▲		▲	
2.3		Develop empirical Li-plating correlations Li plating predictions		▬	▬	▬	▬	▬	▬	▬
	2.3.1	Update correlations based on advanced characterization			▲			▲		
2.4		Predict cell performance using continuously updated models		▬	▬	▬	▬	▬	▬	▬
	2.4.1	Report results from performance predictions			▲			▲		
3.0		**Full cell optimization**								
	3.1	Identify promising electrode materials and formulations	▬	▬						
	3.1.1	Deliver 5 multi-layer cells with baseline electrolyte to SLAC	▲							
	3.1.2	Report results from fast charging in half cells with baseline electrolyte		▲						
	3.2	Finalized materials section for full cells		▬	▬	▬				
	3.2.1	Report fast charging in full single-layer cells with high-rate electrolyte			▲					
	3.2.2	Deliver 206 full single-layer cells with high-rate electrolyte to SLAC				▲				
	3.2.3	Deliver 200 full single-layer cells with high-rate electrolyte to SLAC				▲				
3.3		Optimize cell design in 2Ah cells				▬	▬	▬	▬	▬
	3.3.1	Fast charging in full multi-layer cells with high-rate electrolyte				▲				

Milestones

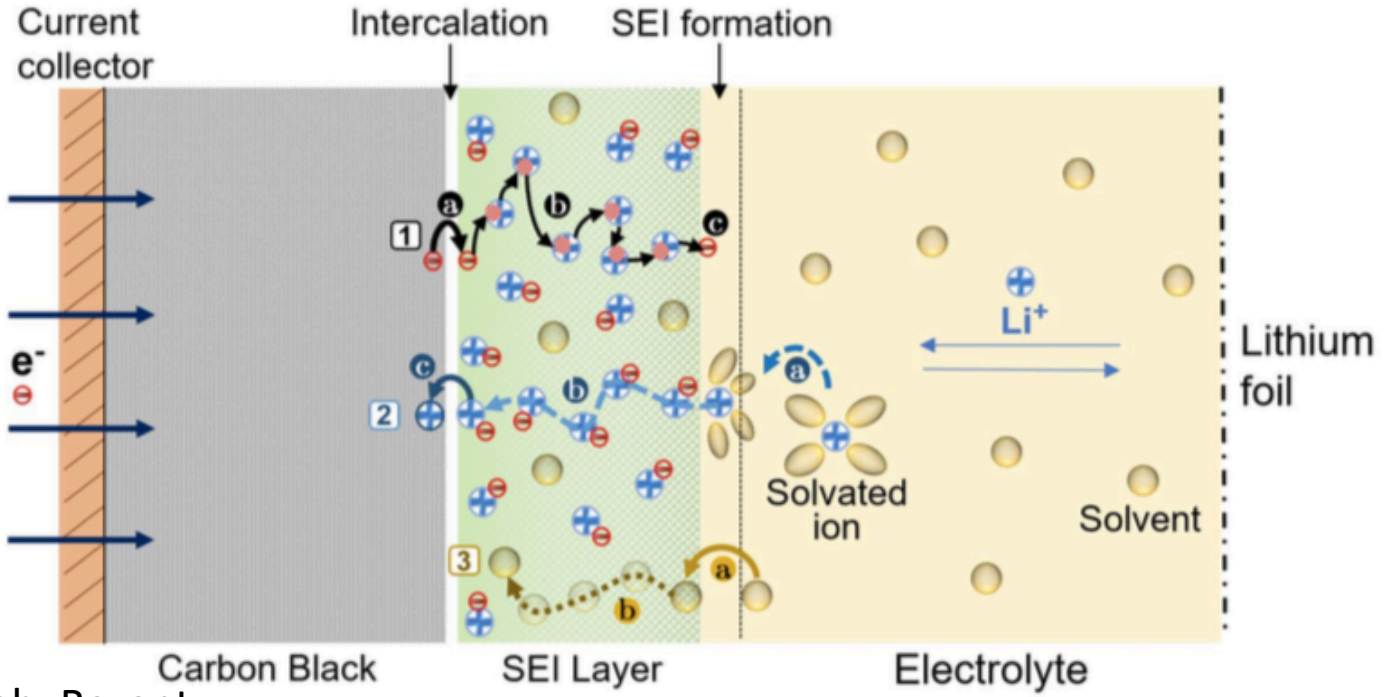
	3.3.2	Deliver 25 full multi-layer cells with high-rate electrolyte to SLAC					▲			
Go/No Go		Deliver 9 2Ah cells with high-rate electrolyte to DOE					■			
	3.3.3	Deliver 6 full multi-layer cells with high-rate electrolyte to SLAC						▲		
3.4		Build deliverable 2Ah cells with final extreme fast charging technology								▬
	3.4.1	Build 36 2Ah cells ready for test and ship								▲
Go/No Go		Deliver 18 2Ah cells with high-rate electrolyte to DOE								■
4.0		**Cryo-EM characterization**								
4.1		Optimize anode thin slice preparation	▬							
	4.1.1	Report optimized thin sectioning protocol	▲							
4.2		Characterize full cells with baseline electrolyte		▬	▬	▬				
	4.2.1	Report cryo-EM characterization on cycled anodes				▲				
4.3		Characterize full single-layer cells with high-rate electrolyte				▬	▬	▬		
	4.3.1	Report cryo-EM characterization on cycled anodes						▲		
4.4		Characterize full multi-layer cells with high-rate electrolyte						▬	▬	▬
	4.4.1	Report cryo-EM validation on cycled anodes								▲
5.0		**X-ray characterization**								
5.1		Characterize full cells with baseline electrolyte	▬	▬	▬	▬				
	5.1.1	Report X-ray characterization on cycled anodes				▲				
5.2		Characterize full single-layer cells with high-rate electrolyte				▬	▬	▬		
	5.2.1	Report X-ray characterization on cycled anodes						▲		
5.3		Characterize full multi-layer cells with high-rate electrolyte						▬	▬	▬
	5.3.1	Report X-ray validation on cycled anodes								▲
6.0		**Charging profile optimization**								
6.1		Develop early predications using full cells with baseline electrolyte	▬	▬						
	6.1.1	Report early estimations of failure methods		▲						
6.2		Identify promising charging policy candidates				▬	▬			
	6.2.1	Report preliminary fast charging protocol from full cell testing				▲				
	6.2.2	Report promising policies from full cell testing with high-rate electrolyte					▲			
6.3		Identify optimized charging profile					▬	▬	▬	
	6.3.1	Report optimized 3-step fast charging protocol for 2Ah cells							▲	

Approach

Low columbic & energy efficiency during XFC can be attributed to:

1) **Slow diffusion of Li+ in the electrolyte** (shift in Li plating potential)
2) **poor Li+ desolvation kinetics** (high overpotential)
3) **Poor transport kinetics of Li+ through the SEI** (limiting current)

Engineering an electrolyte that solves these issues is one key!



Das, Attia, Chueh, Bazant

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Approach: new electrolyte & additives

10-minute XFC on LFP/graphite cells already possible with an anode thickness of 35 microns **→ doubling thickness requires quadrupling in diffusivity → cannot be achieved solely by increasing electrolyte conductivity**

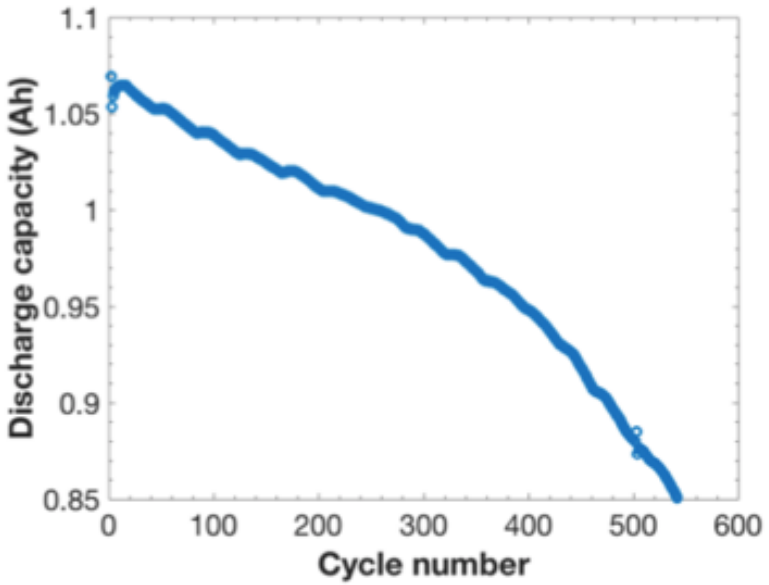


Figure 1. *Cycle lifetime for an A123 LFP/graphite (35-μm thick) 18650 cell under 6C CC-CV fast charging.*

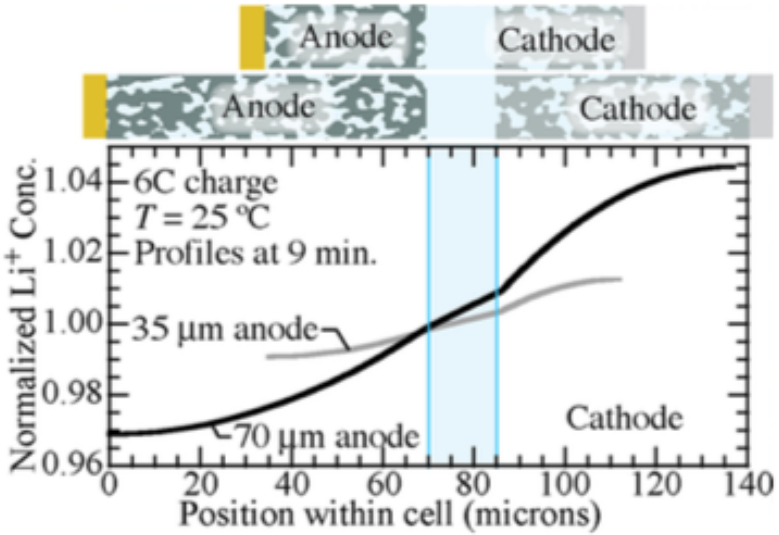
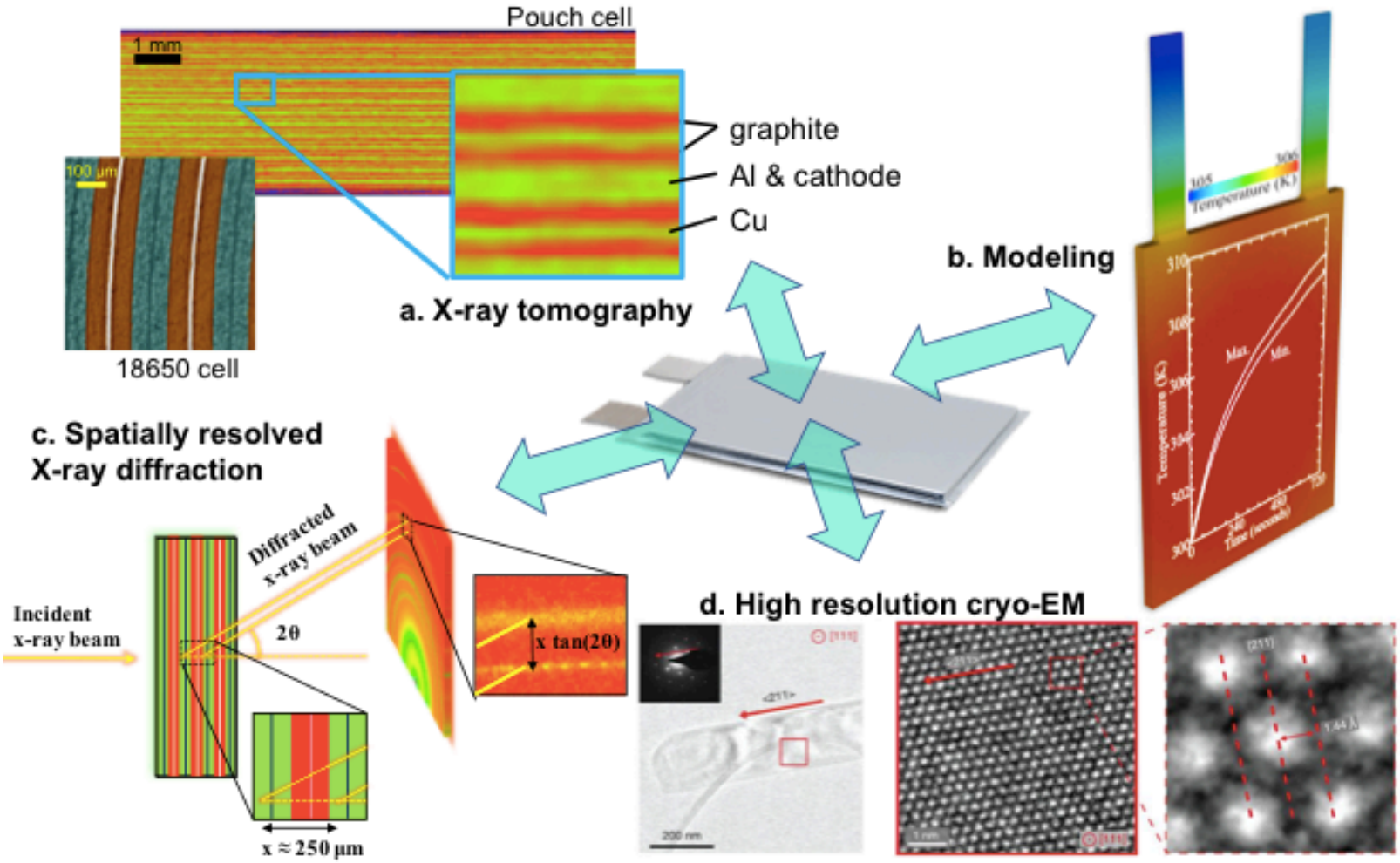


Figure 2. *Predicted effects of electrode thickness using a quasi-1D model.*

Need to (1) improve mass transport in electrolyte, (2) speed up desolvation kinetics, and (3) modify SEI to improve transport.

Approach: validate via advanced characterization

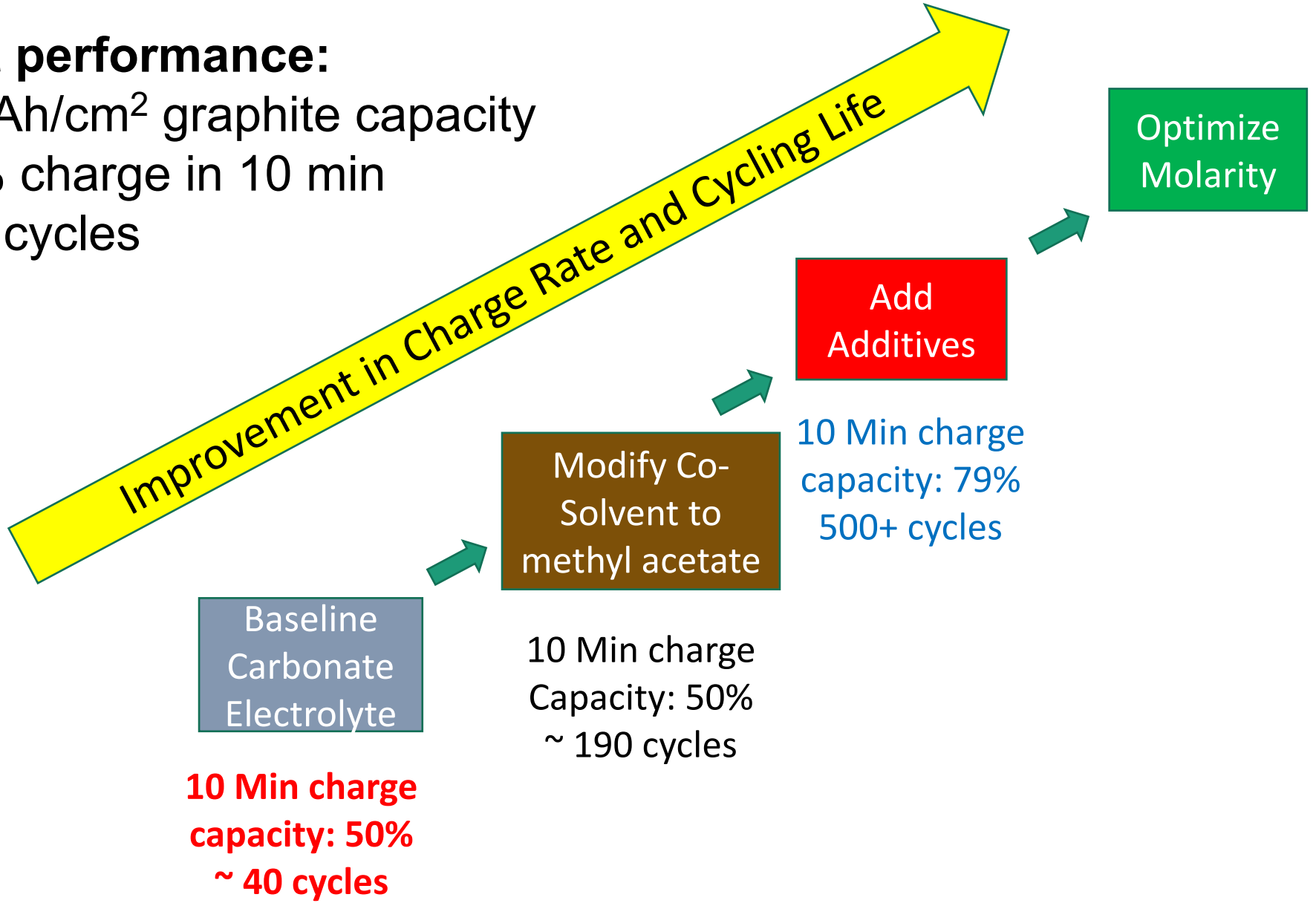
(1) **X-ray microscopy & diffraction**: detecting Li plating for full single-layer & multi-layer cells
(2) **Cryo-EM**: probe location of lithium plating and quantify SEI
(3) **Simulation**: resolve local rate of lithium plating



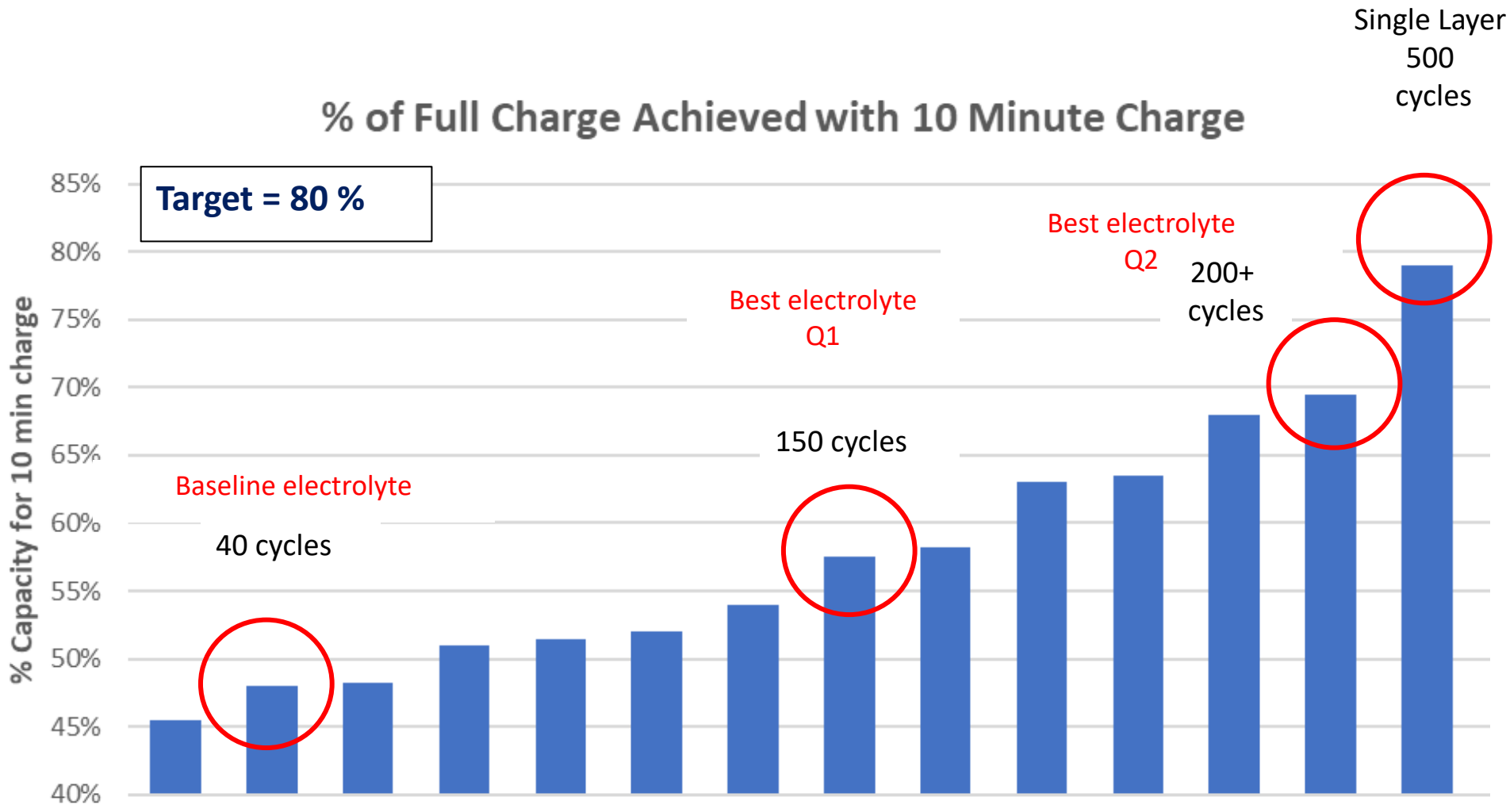
Technical Accomplishments and Progress

Target performance:

- 3 mAh/cm^2 graphite capacity
- 80% charge in 10 min
- 500 cycles

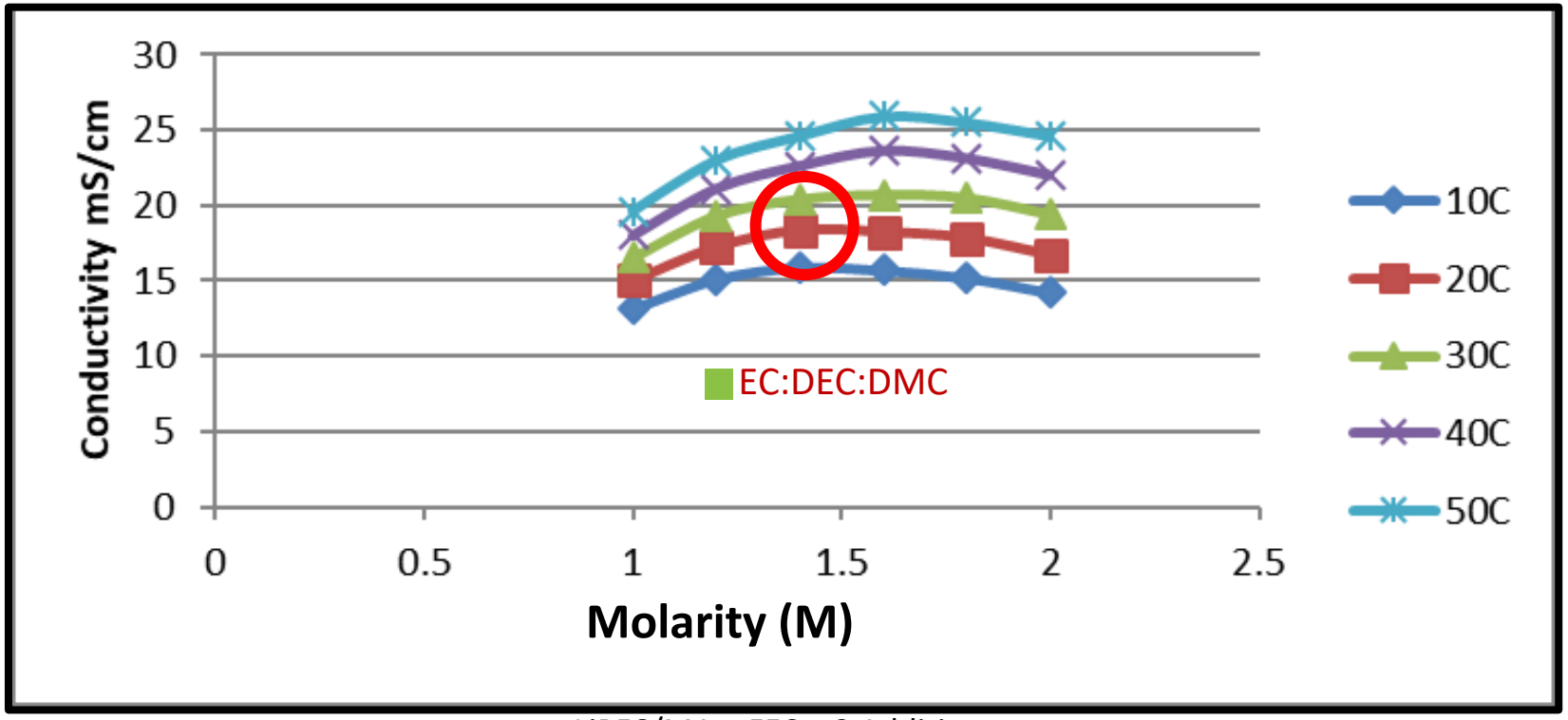


Technical Progress: extreme fast charge acceptance



2.8-3.1 mAh/cm^2 ShanShan graphite, LCO

Technical Progress: approaching 20 mS/cm @ RT

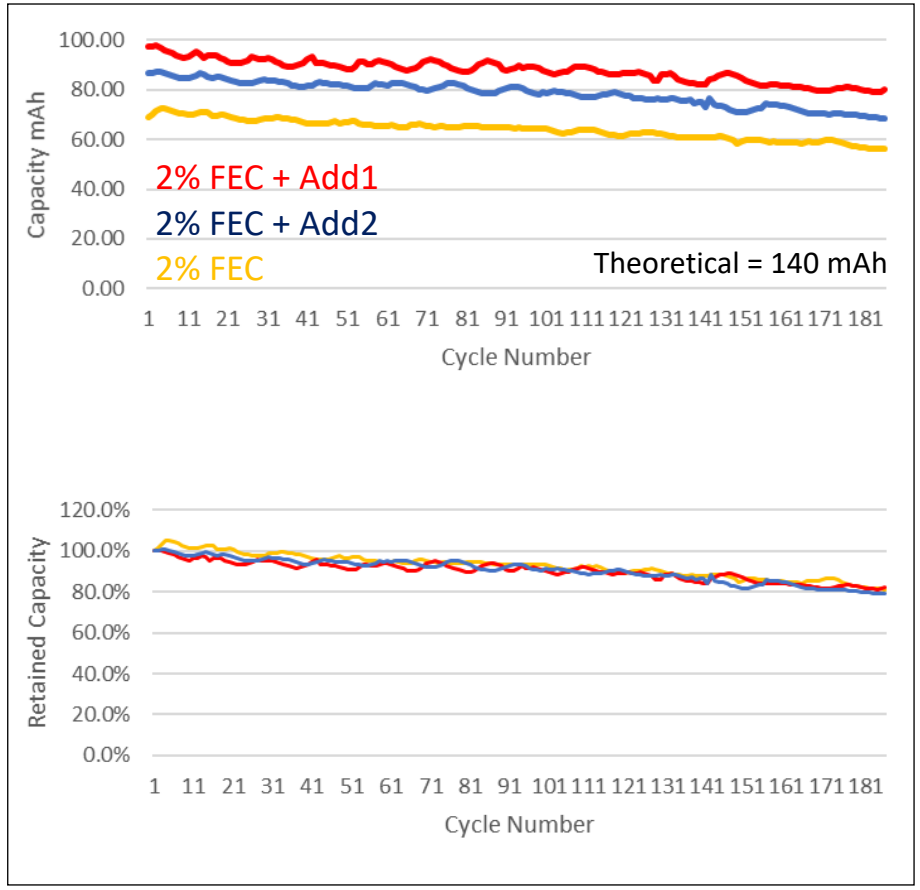


LiPF6/MA + FEC + 2 Additives

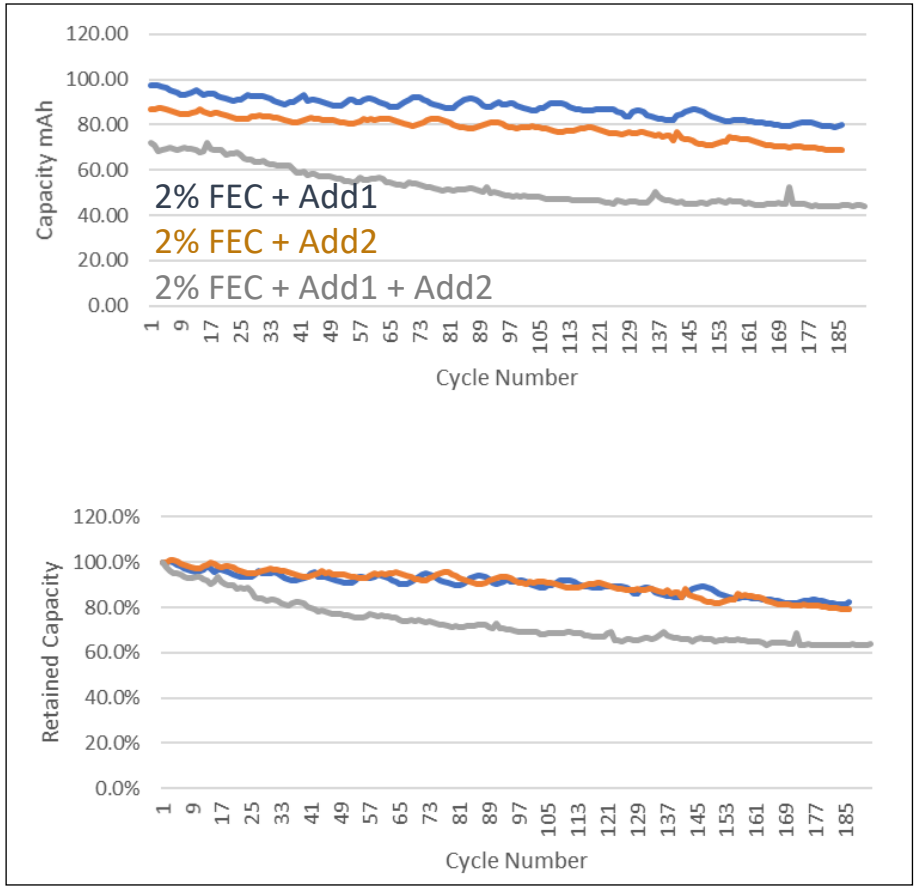
- **<u>Change Solvent to methyl acetate (MA)</u>**
  - *MA reduces electrolyte viscosity and increases ionic conductivity thus providing high rate capability on charge*
- **<u>Add Additive</u>**
  - *Additive package provides thin, conformal SEIs thus reducing charge transfer resistance*
- **<u>Increase Molarity</u>**
  - *High [LiPF6] maintains anode Li inventory insuring long cycle life*

Technical Progress: optimizing additive packages

Two vs. one component



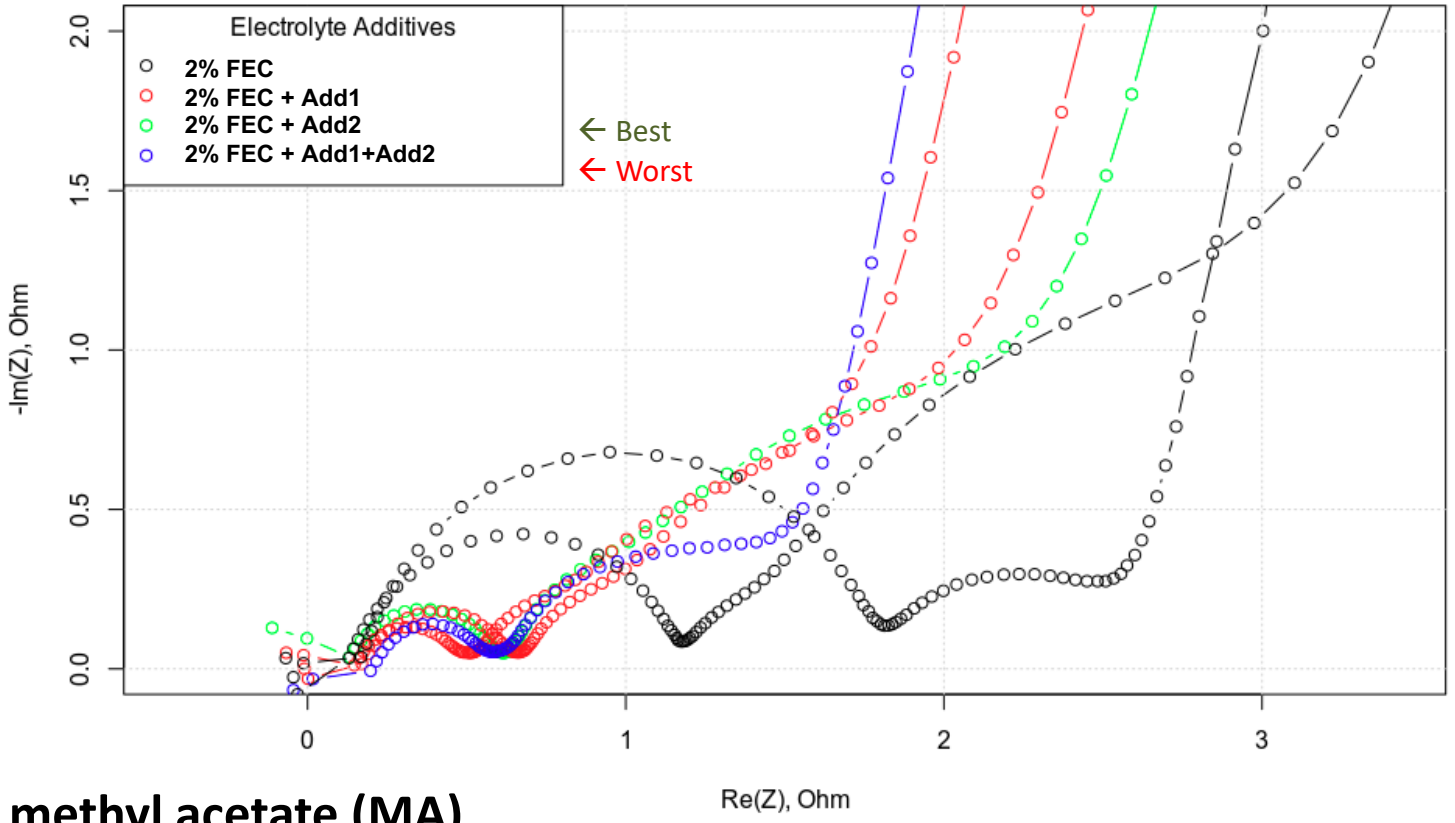
Three vs. two component



- All Loadings at 3 mAh/cm2 (Shan Shan)
- Charge cycle at 6C (900 mA for 10 min, 18.75 mA/cm2)
- Discharge Rate at C/3
- 10 minute rest between cycles
- Single Layer Pouch Cells

Two component additive package gave ~ 70% charge acceptance in 10 min & 200+ cycles for 3 mAh/cm^2 graphite

Technical Progress: optimizing additive packages



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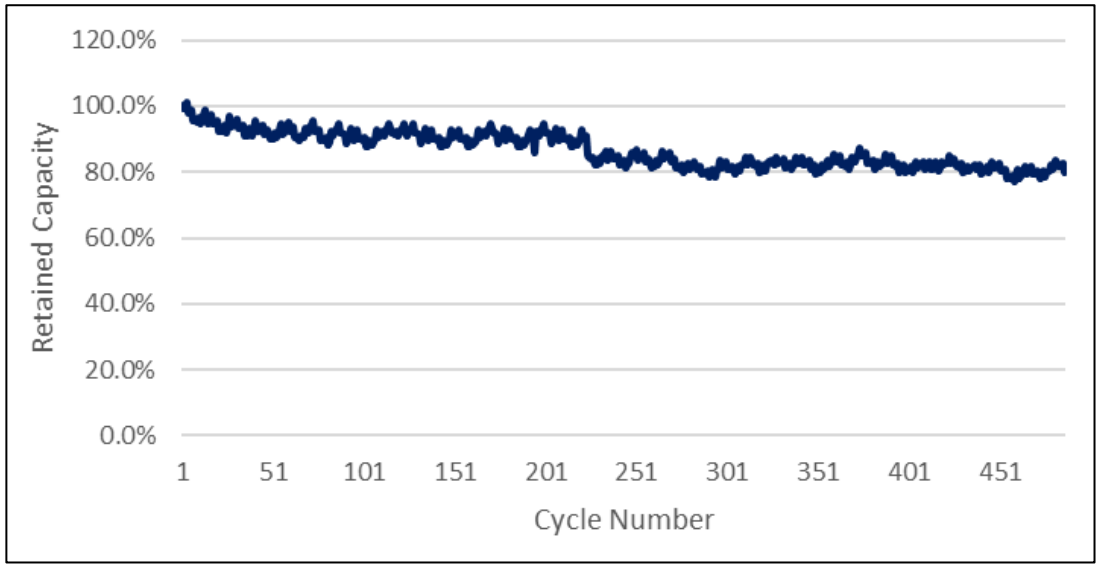
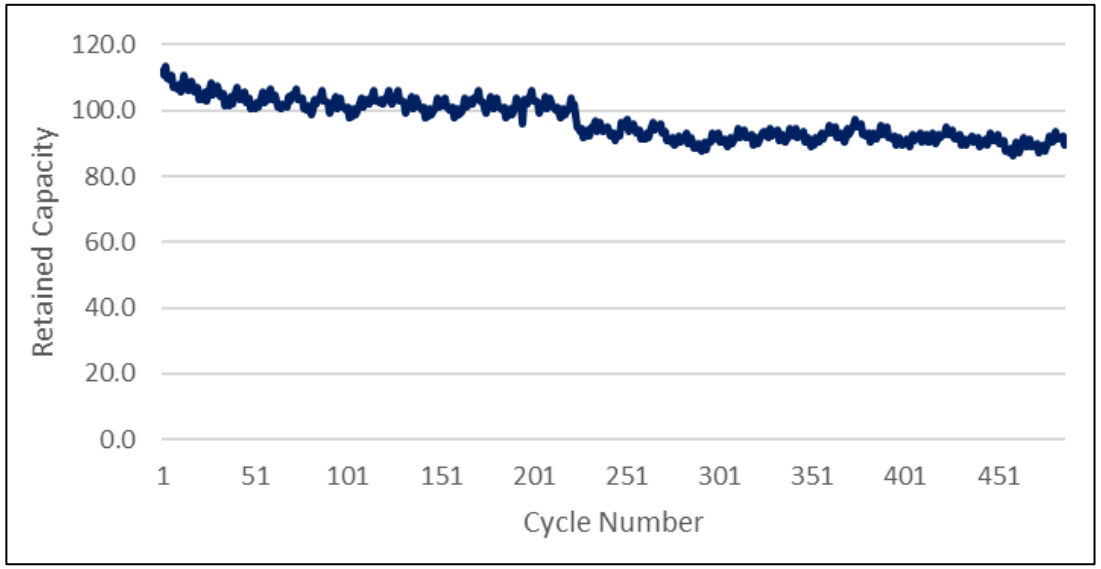
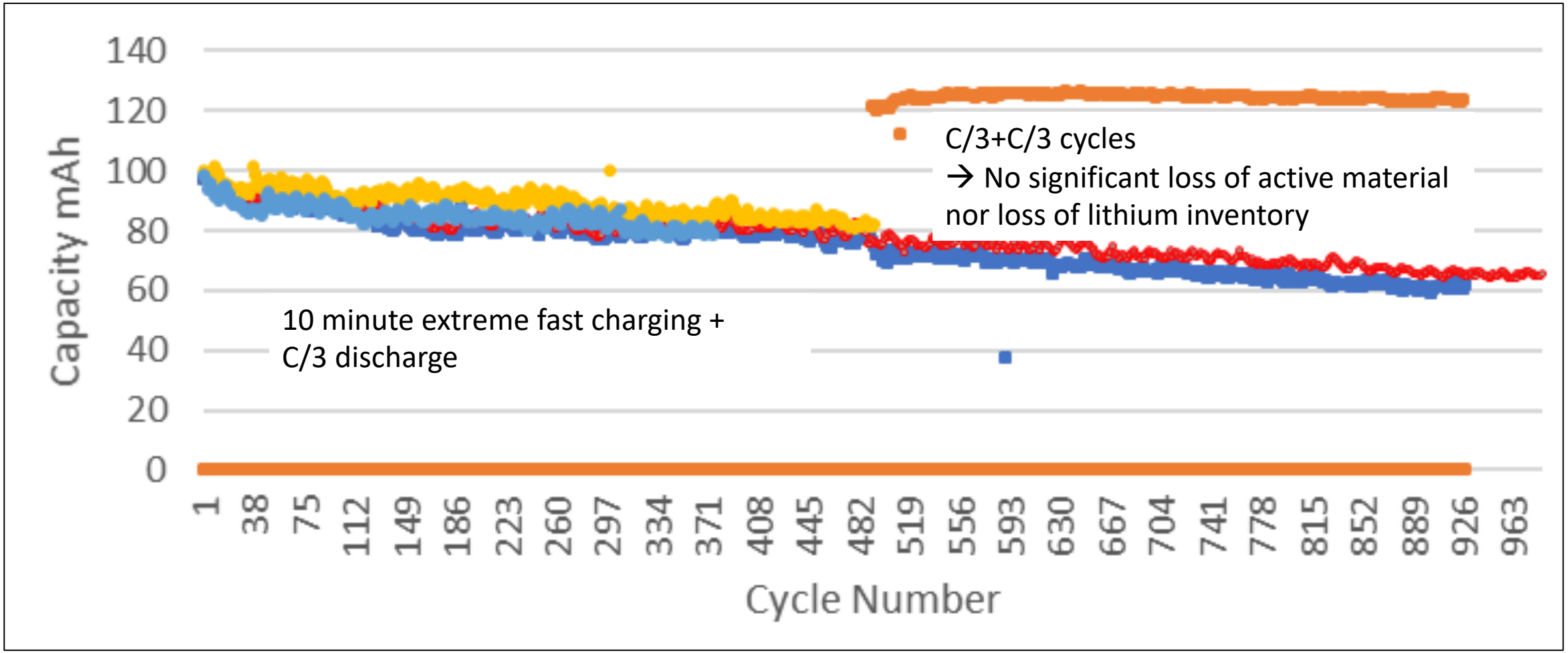
Technical Progress: 500 cycles achieved in single-layer cells





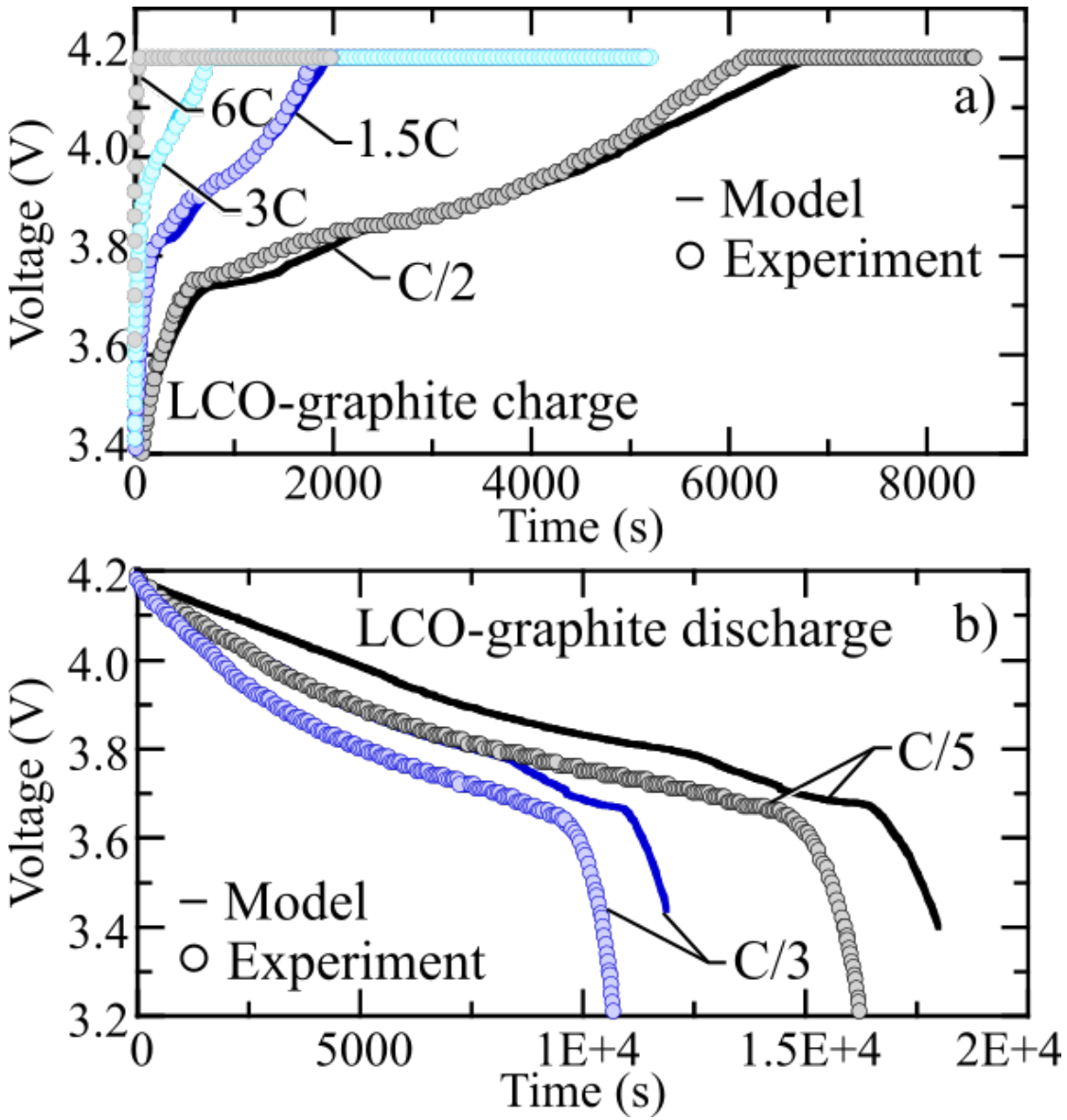
- 79% Capacity @ 10 minutes
- Optimized two component additive package
- Loading 3mAh/cm^2
- Able to Achieve 500 Cycles

Technical Progress: optimizing additive packages



Capacity fade can be recovered when charging at a lower rate, indicating that increased impedance, rather than loss of active material or loss of lithium inventory is responsible for fade at extreme fast charging.

Technical Progress: cell modeling



Constant-current charging

- Excellent model agreement
- Significant time at 4.2 V cut-off
- Ohmic resistance dominates impedance → electrolyte mass transport is not rate limiting neither is charge-transfer

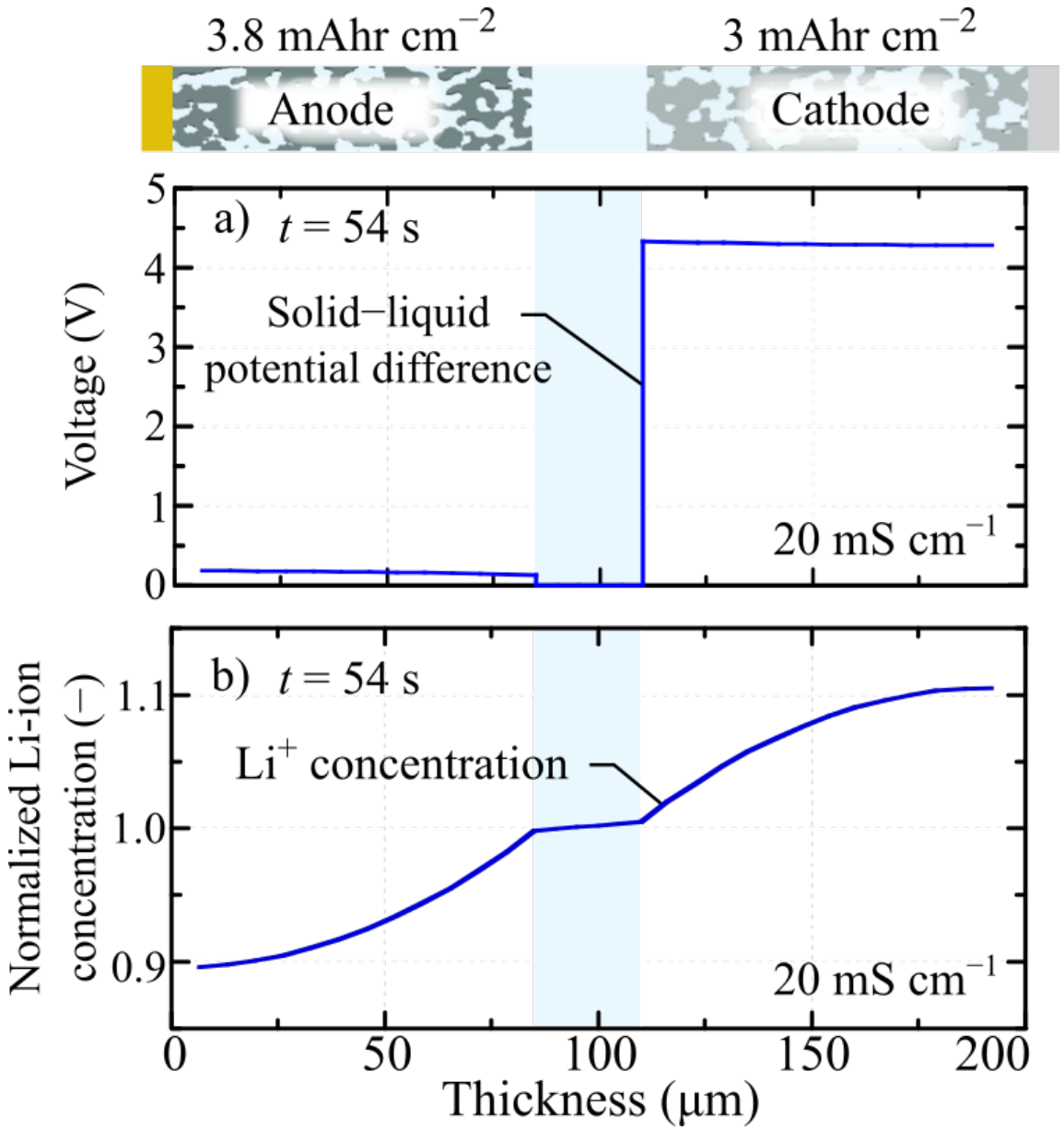
Constant-current discharge

- Reasonable model agreement
- Underpredicted model resistance

Good news, bad news

- Exceptional CC-CV agreement
- Still many unknown parameters

Technical Progress: cell modeling



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- Still many unknown parameters

Responses to Previous Year Reviewers' Comments

None

Collaboration and Coordination

Stanford Synchrotron Radiation Lightsource
Advanced Photon Source
Covalent Associates

Remaining Challenges and Barriers

- Translate single layer performance (80% charge acceptance within 10 minutes) to multi-layer cells.
- Translate single layer cycle life (500 cycles) to multi-layer cells.

Proposed Future Work

- Optimize charging protocol to increase charging capacity at 10 minutes to 80%.
- Perform X-ray and electron characterizations to assess the effect of electrolyte on SEI thickness and lithium plating during extreme fast charging.
- Optimization of rate capability and cycle life in multi-layer cells.

Summary

- A low viscosity, high conductivity (20 mS/cm) electrolyte has been developed.
- X-ray diffraction microscopy & cryogenic electron microscopy reveal Li plating and SEI formation.
- Excellent charge acceptance (80% in 10 minutes) and cycle life (500+) have been demonstrated in single-layer pouch cells.
- Electrolyte mass transport is no longer limiting cell performance.