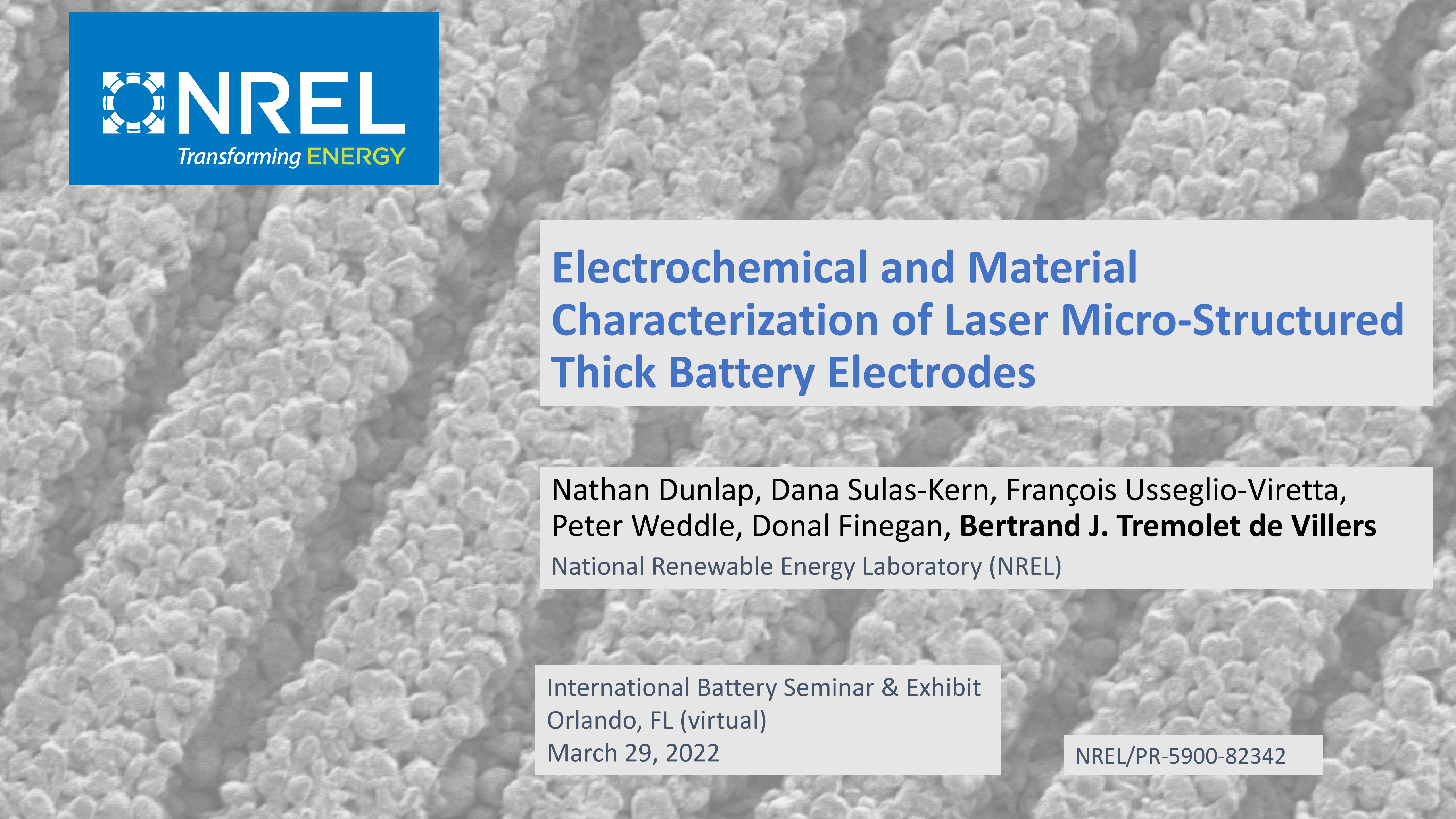


Electrochemical and Material Characterization of Laser Micro-Structured Thick Battery Electrodes

Nathan Dunlap, Dana Sulas-Kern, François Usseglio-Viretta, Peter Weddle, Donal Finegan, **Bertrand J. Tremolet de Villers**
National Renewable Energy Laboratory (NREL)

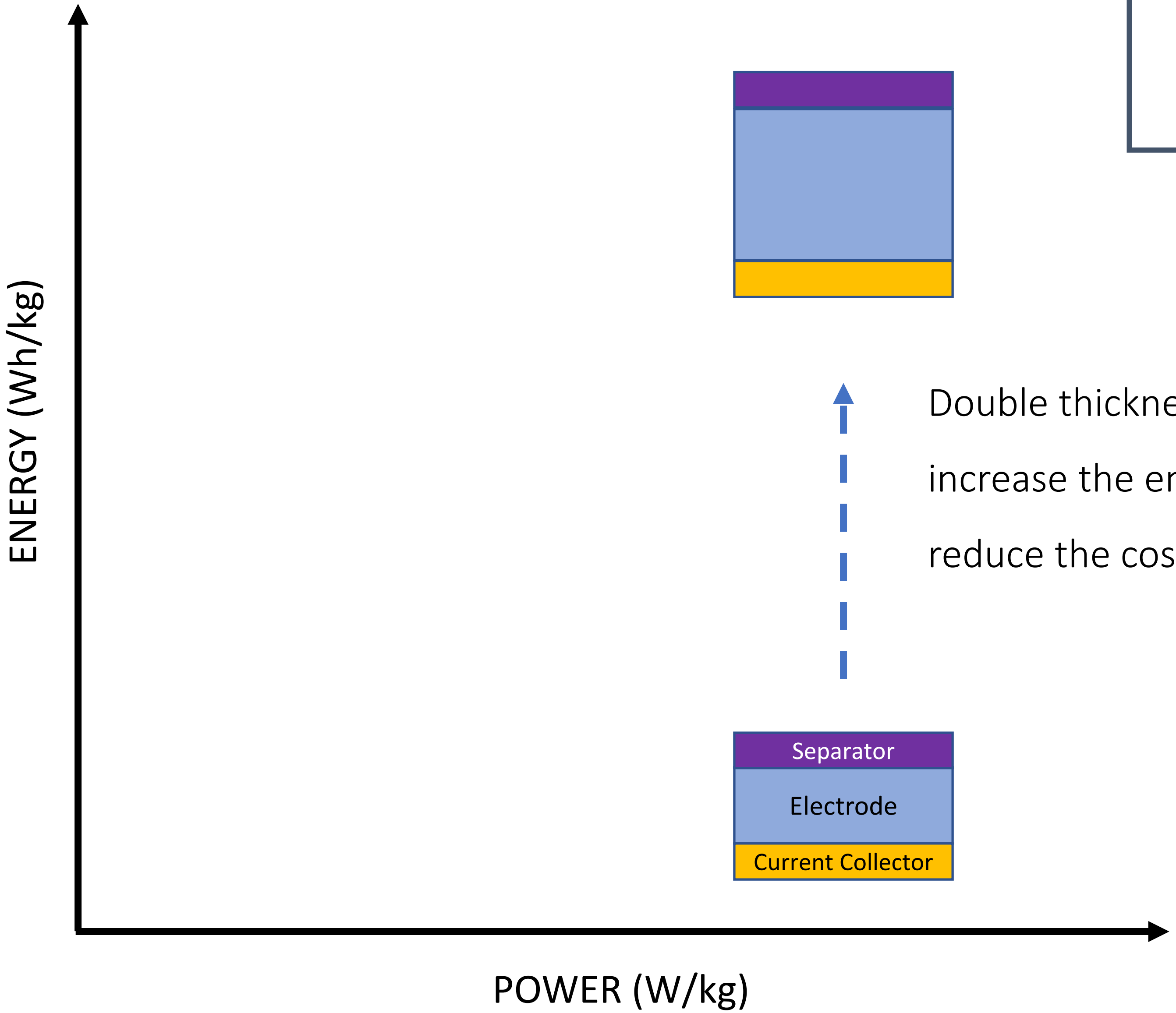
International Battery Seminar & Exhibit
Orlando, FL (virtual)
March 29, 2022

NREL/PR-5900-82342

Need Thicker Electrodes

Low-cost/Fast-charge EV cell-level goals (2023):

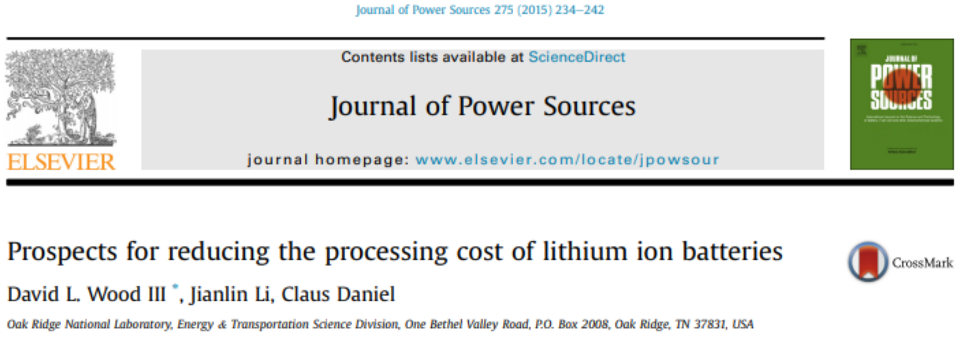
- Energy densities >275 Wh/kg,
- Cost less than $100/Wh
- 80% charge within 15 minutes.



Double thickness of electrodes in full cells from 50 µm to 100 µm

increase the energy density of the cell by about 16%

reduce the cost of the cell by 30% (from $249/kWh to $172/kWh)



Journal of Power Sources 275 (2015) 234–242

Contents lists available at ScienceDirect

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Prospects for reducing the processing cost of lithium ion batteries

David L. Wood III *, Jianlin Li, Claus Daniel

Oak Ridge National Laboratory, Energy & Transportation Science Division, One Bethel Valley Road, P.O. Box 2008, Oak Ridge, TN 37831, USA

Thick Planar Electrodes are Inadequate

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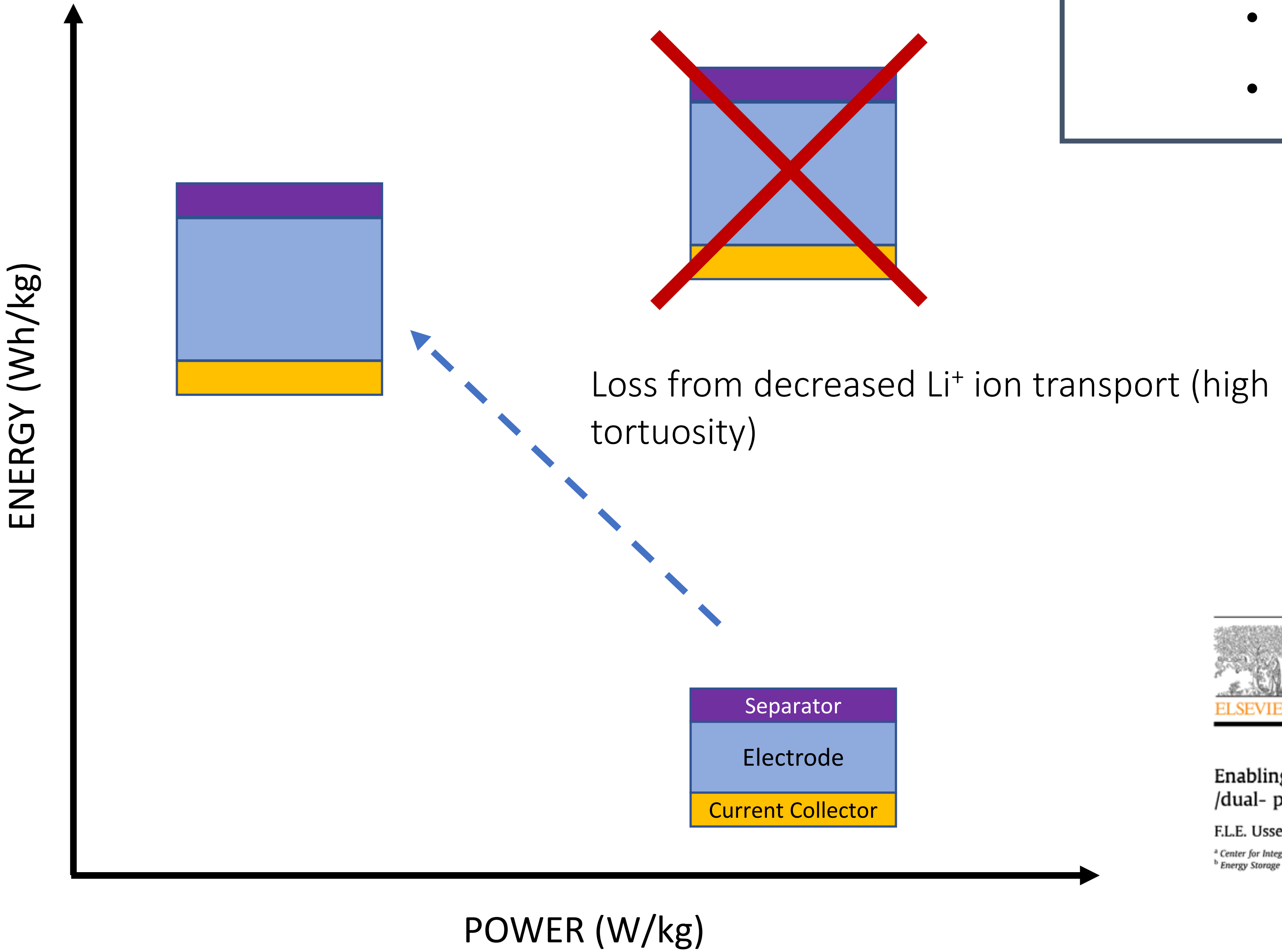
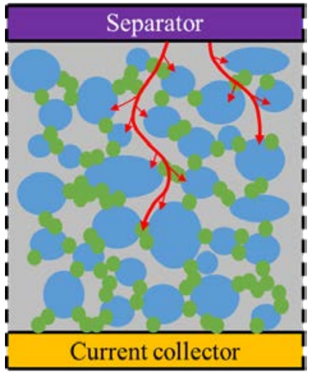
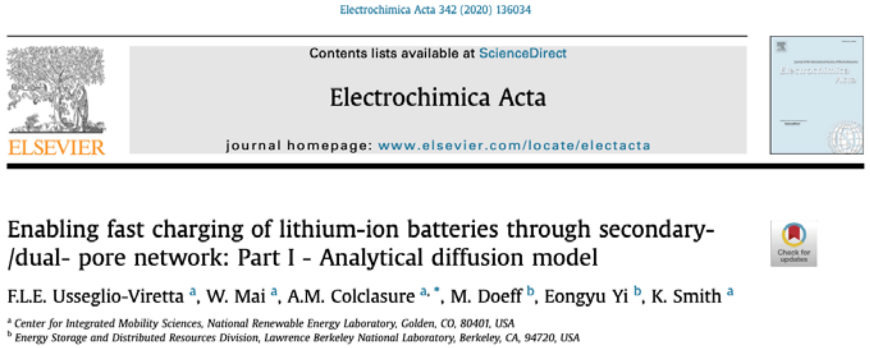


Loss from decreased Li^+ ion transport (high tortuosity)





Electrochimica Acta 342 (2020) 136034

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ELSEVIER

Enabling fast charging of lithium-ion batteries through secondary-/dual- pore network: Part I - Analytical diffusion model

F.L.E. Usseglio-Viretta [a], W. Mai [a], A.M. Colclasure [a, *], M. Doeff [b], Eongyu Yi [b], K. Smith [a]

[a] Center for Integrated Mobility Sciences, National Renewable Energy Laboratory, Golden, CO, 80401, USA
[b] Energy Storage and Distributed Resources Division, Lawrence Berkeley National Laboratory, Berkeley, CA, 94720, USA

Micro-structures Reduce Li^+-ion Transport Tortuosity

USABC
UNITED STATES ADVANCED BATTERY CONSORTIUM

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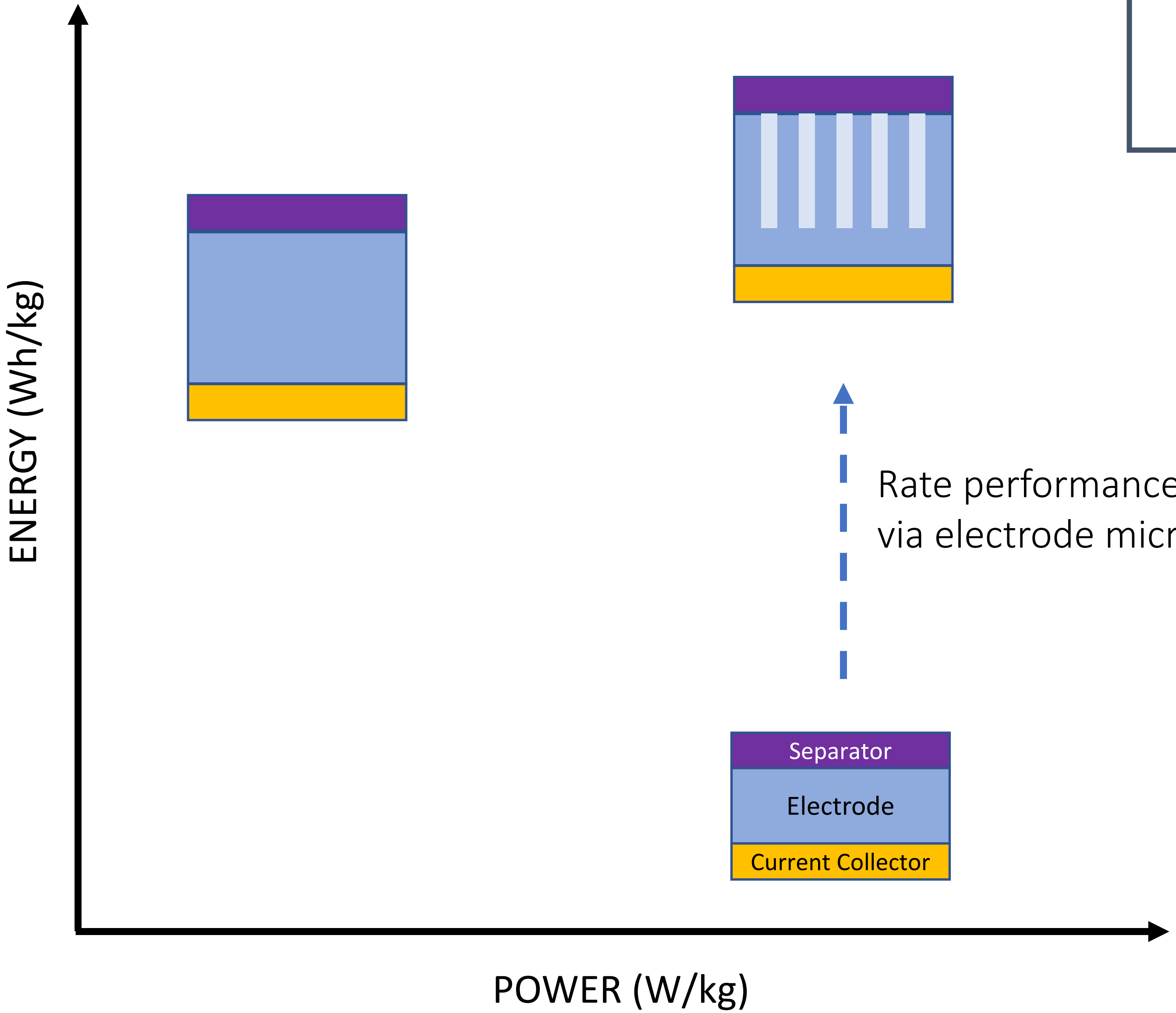
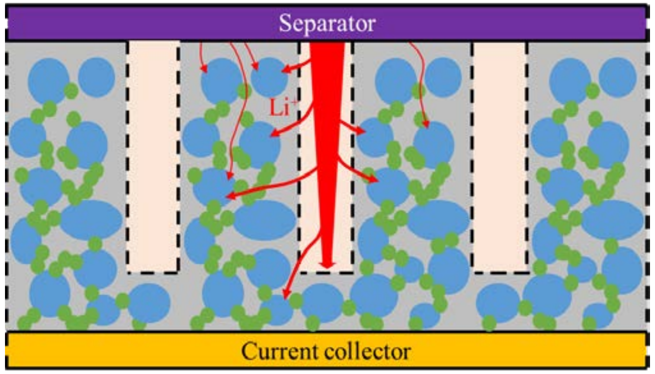
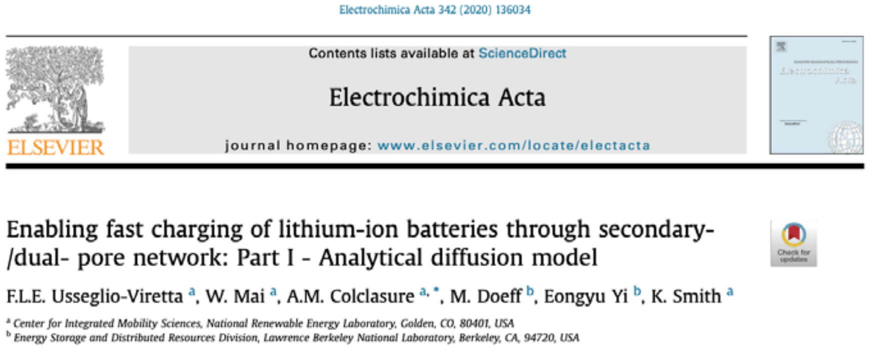


Rate performance improved via electrode micro-structuring

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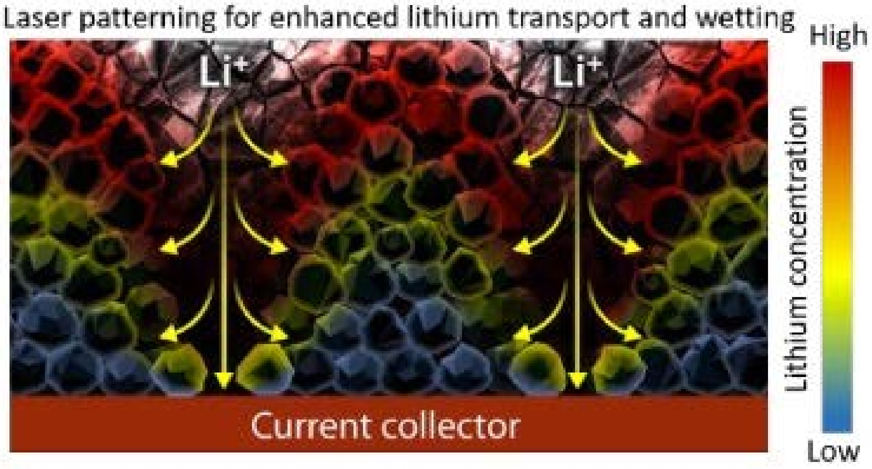
High-Throughput Laser Processing for Advanced Battery Electrode Performance and Manufacturing:

Project Motivation

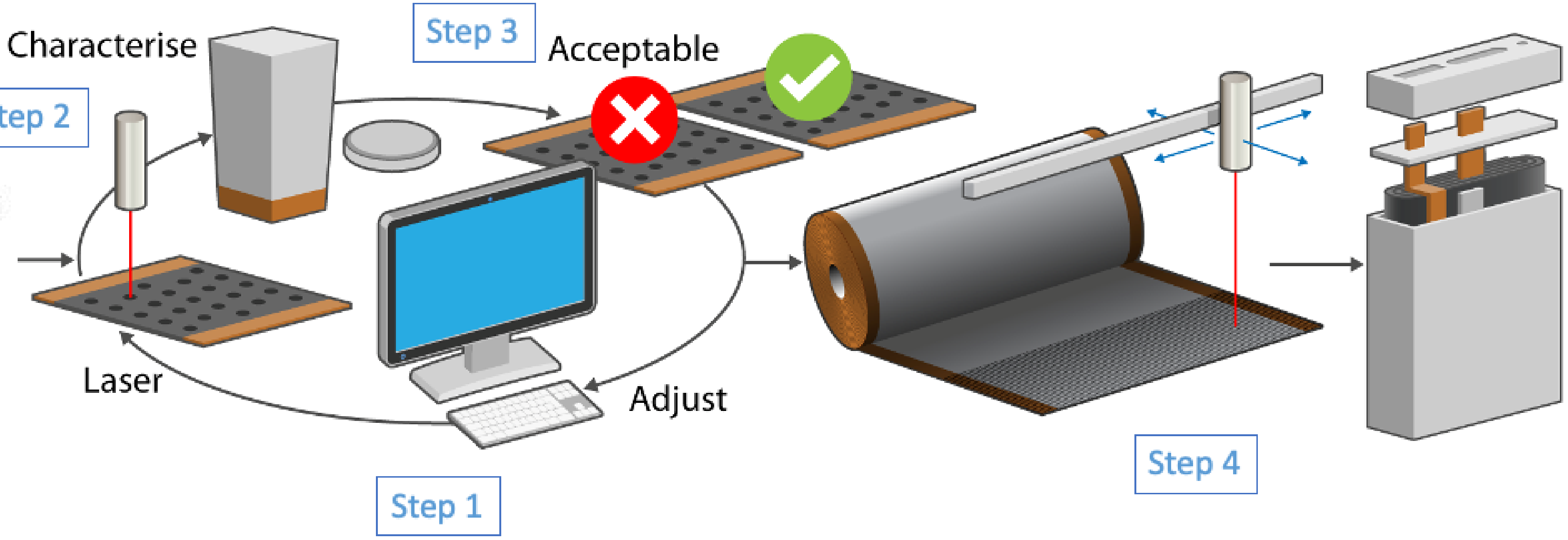
- Thicker electrodes ↑ energy densities and ↓ costs
  - Practical kinetic limitations
- Laser micro-patterned 3-D electrodes overcome trade-off between improving energy vs power densities
- Reduce costly time-consuming electrolyte wetting and cell formation processes during battery production

Project Goals

- Identify and manufacture laser-ablated 3-D electrode architectures for enhanced battery performance
  - Enable extreme fast charging rates >6C (<10min) at > 250 Wh/kg
    - Critical for widespread adoption of EV technology
  - Allow fast and uniform electrolyte wetting
- Scale laser patterns for high-throughput roll-to-roll processing
  - Reduce production costs



Laser patterning for enhanced lithium transport and wetting



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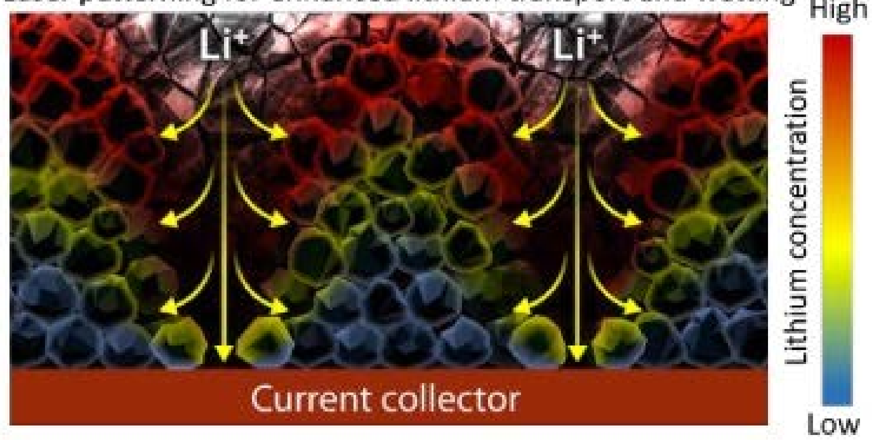
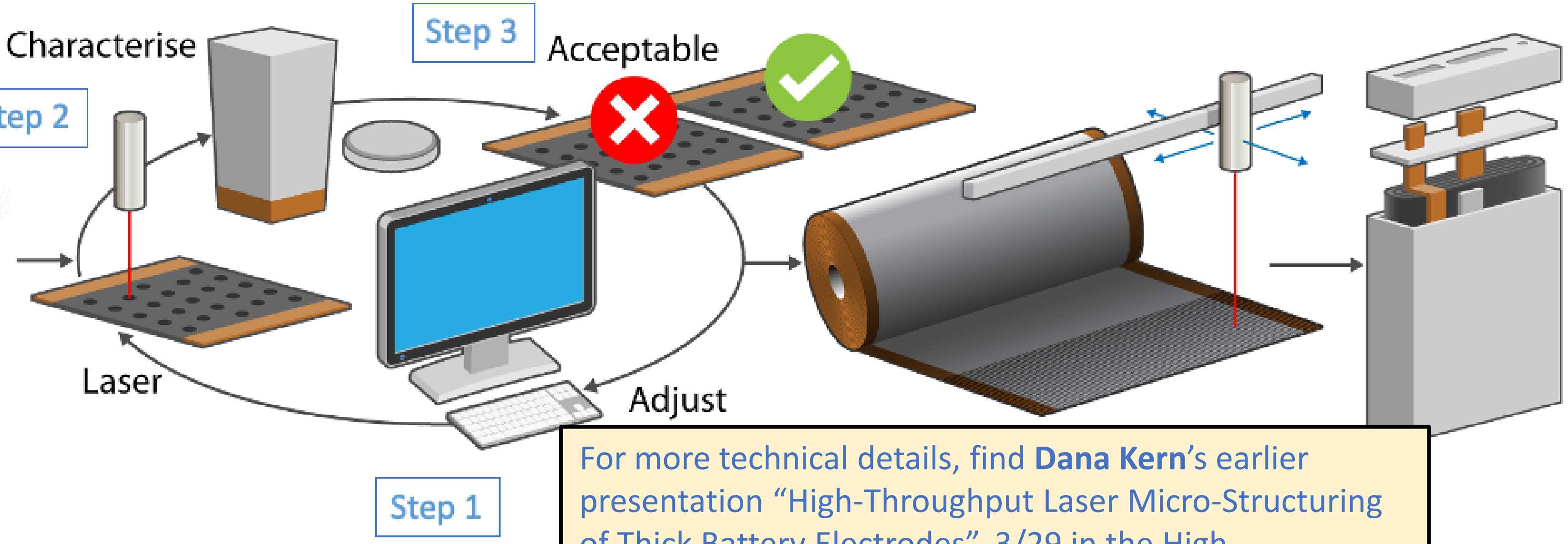
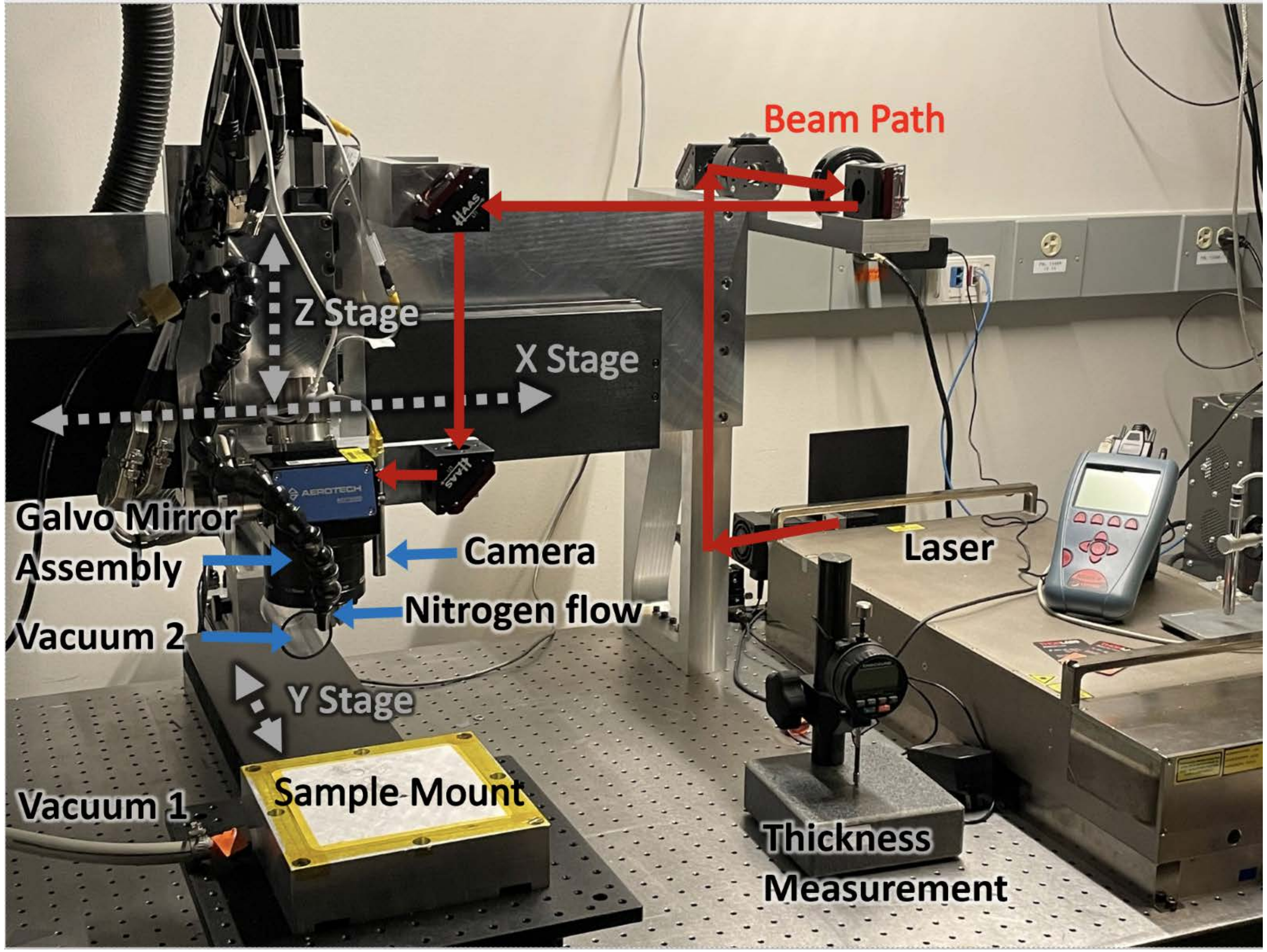


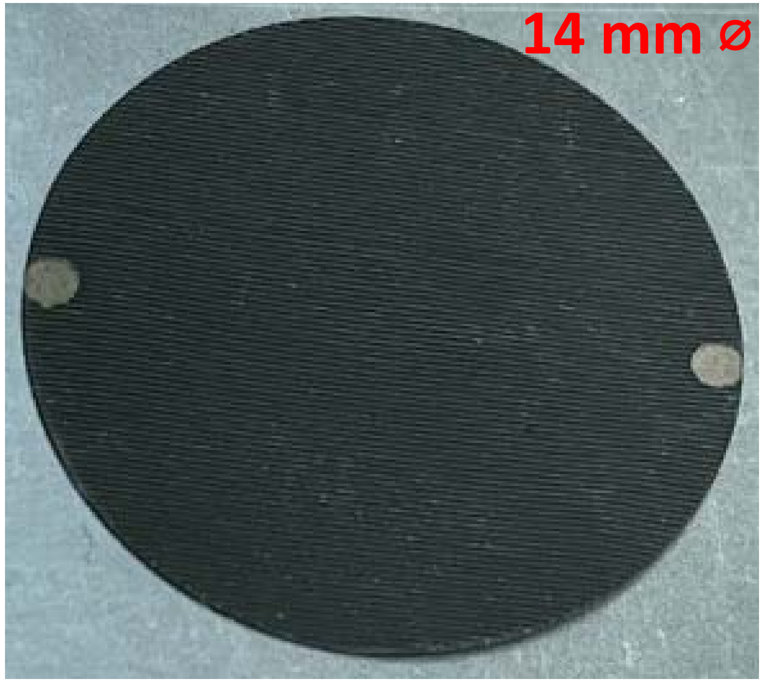


For more technical details, find **Dana Kern**'s earlier presentation "High-Throughput Laser Micro-Structuring of Thick Battery Electrodes", 3/29 in the High-Performance Battery Manufacturing session

Ultrafast laser patterning of Electrodes

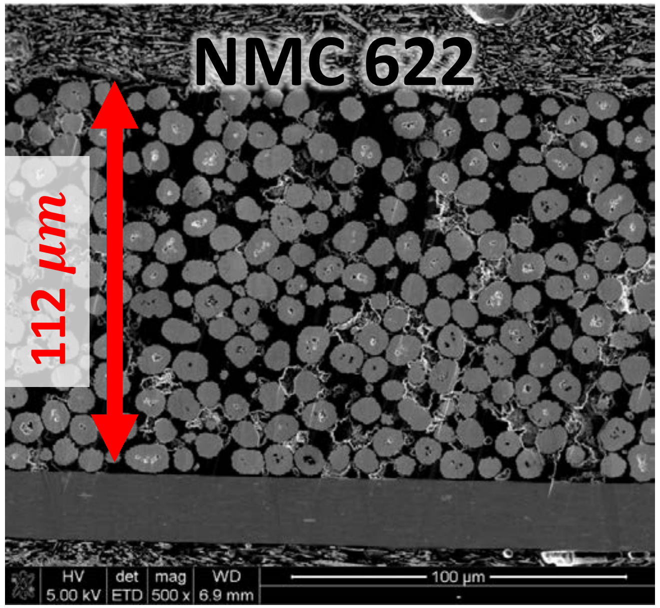


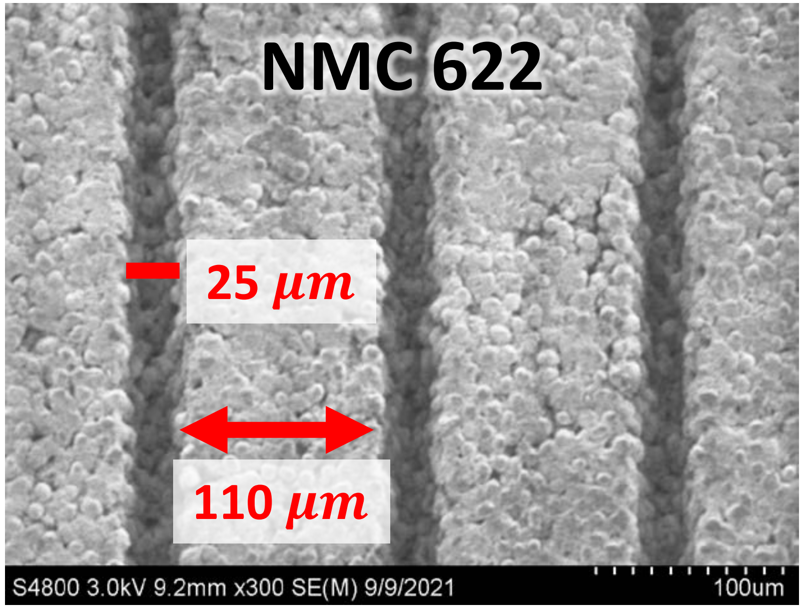
Laser Specs	
Product Model	AOFEMTO-IR-1030
Wavelength	1030 nm
Pulse Width	600 fs
Repetition Rate	100 kHz – 1 MHz
Max Average Power	10 W
Energy at 100 kHz	100 uJ
Spot Size from Laser	2.0 mm
Focused Spot Size	20 um

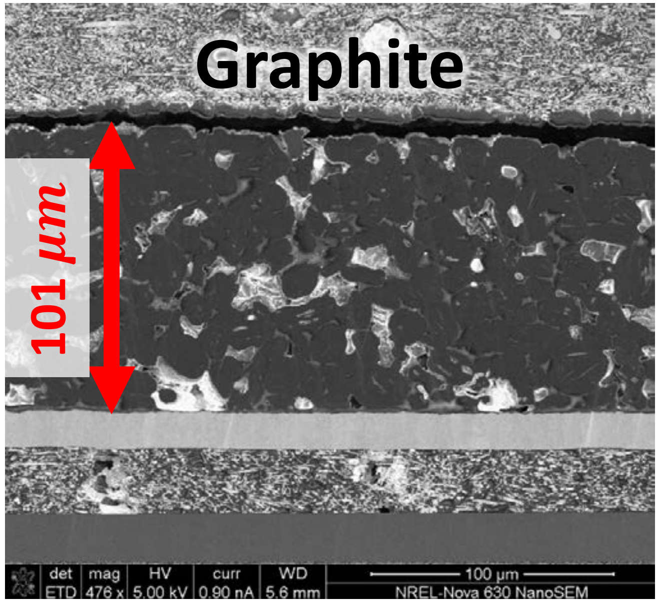


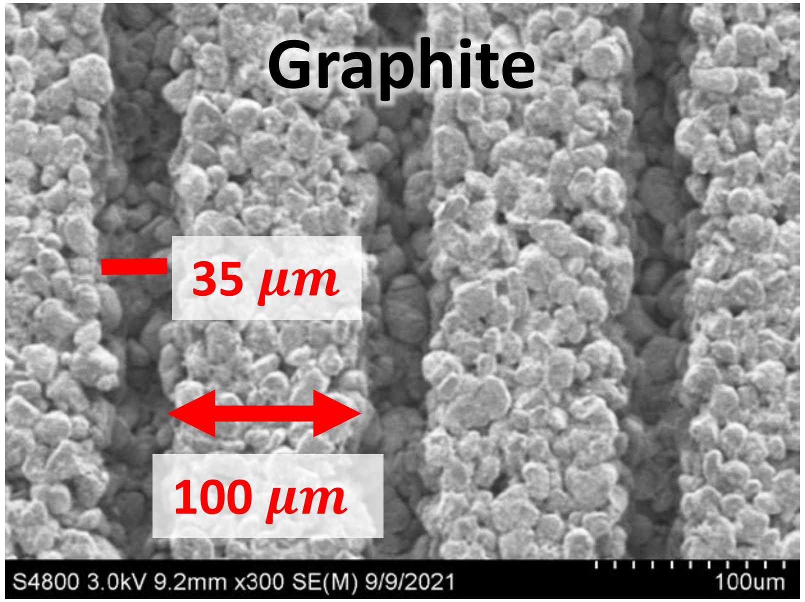
Article: Dunlap, N., et al., "Laser ablation of Li-ion electrodes for fast charging: Material properties, rate capability, Li plating, and wetting", 2022, Journal of Power Sources

Laser-patterned Thick NMC622 and Thick Graphite



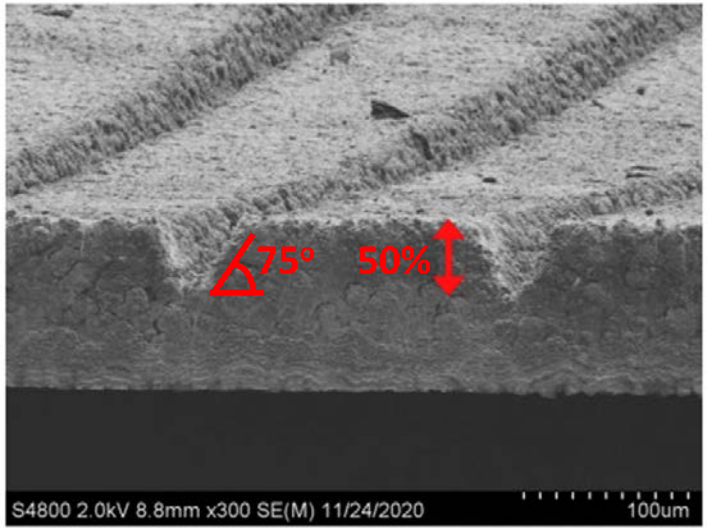






Electrodes from CAMP at Argonne National Lab

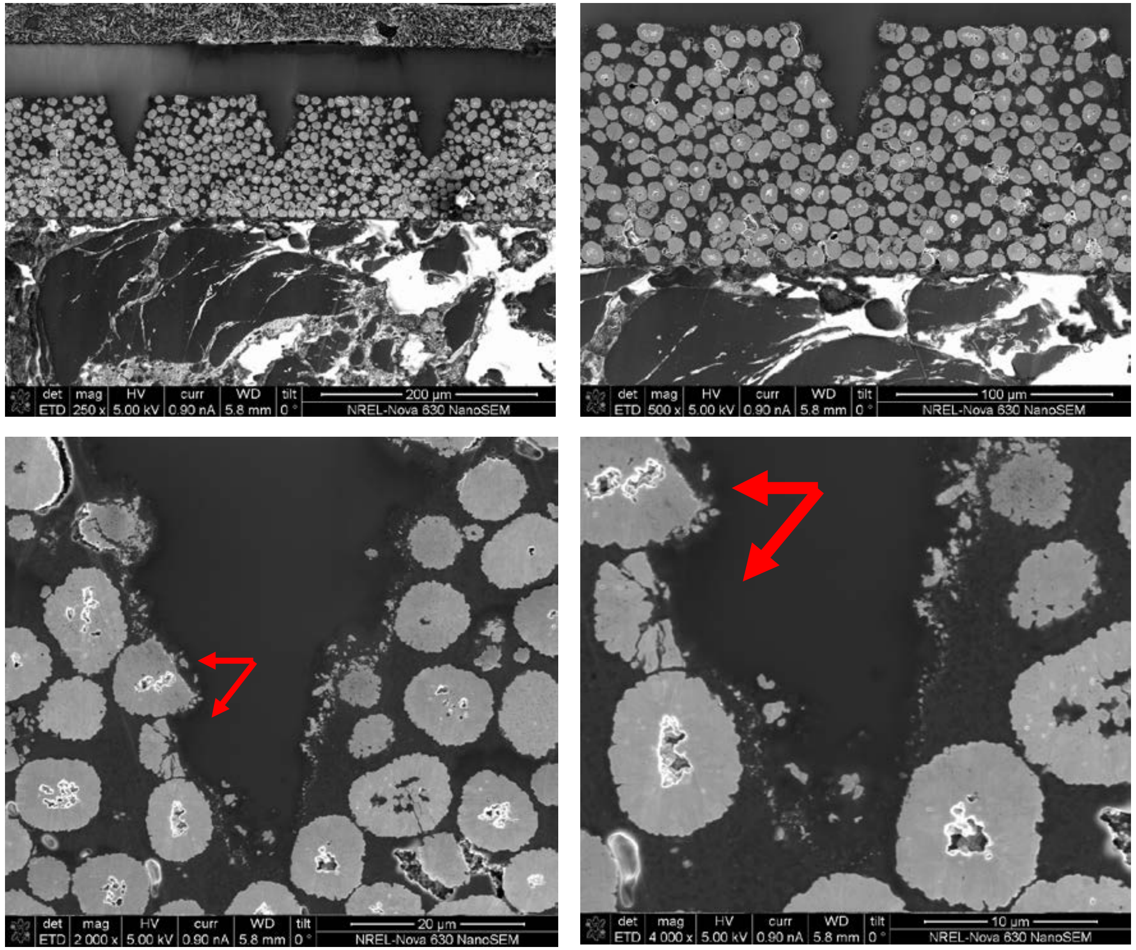
Anode	Cathode
91.83 wt% Graphite (Superior SLC1520P)	90 wt% NMC622 (ECOPRO)
2 wt% Carbon (Timcal C45)	5 wt% Carbon (Timcal C45)
6 wt% PVDF (Kureha 9300)	5 wt% PVDF (Solvay 5130)
0.17 wt% Oxalic Acid	N/A
15 um Cu Foil Thickness	20 um Al Foil Thickness
101 um Coating Thickness	112 um Coating Thickness
36.2% Porosity	34.0% Porosity
13.97 mg/cm^2 Coating Loading	30.24 mg/cm^2 Coating Loading
1.38 g/cm^3 coating density	2.70 g/cm^3 coating density
4.76 mAh/cm^2 Theoretical Areal Capacity	4.31 mAh/cm^2 Theoretical Areal Capacity



Pitch spacing and channel depth are based on our models and the constraint that ablated material wt% < 10%.

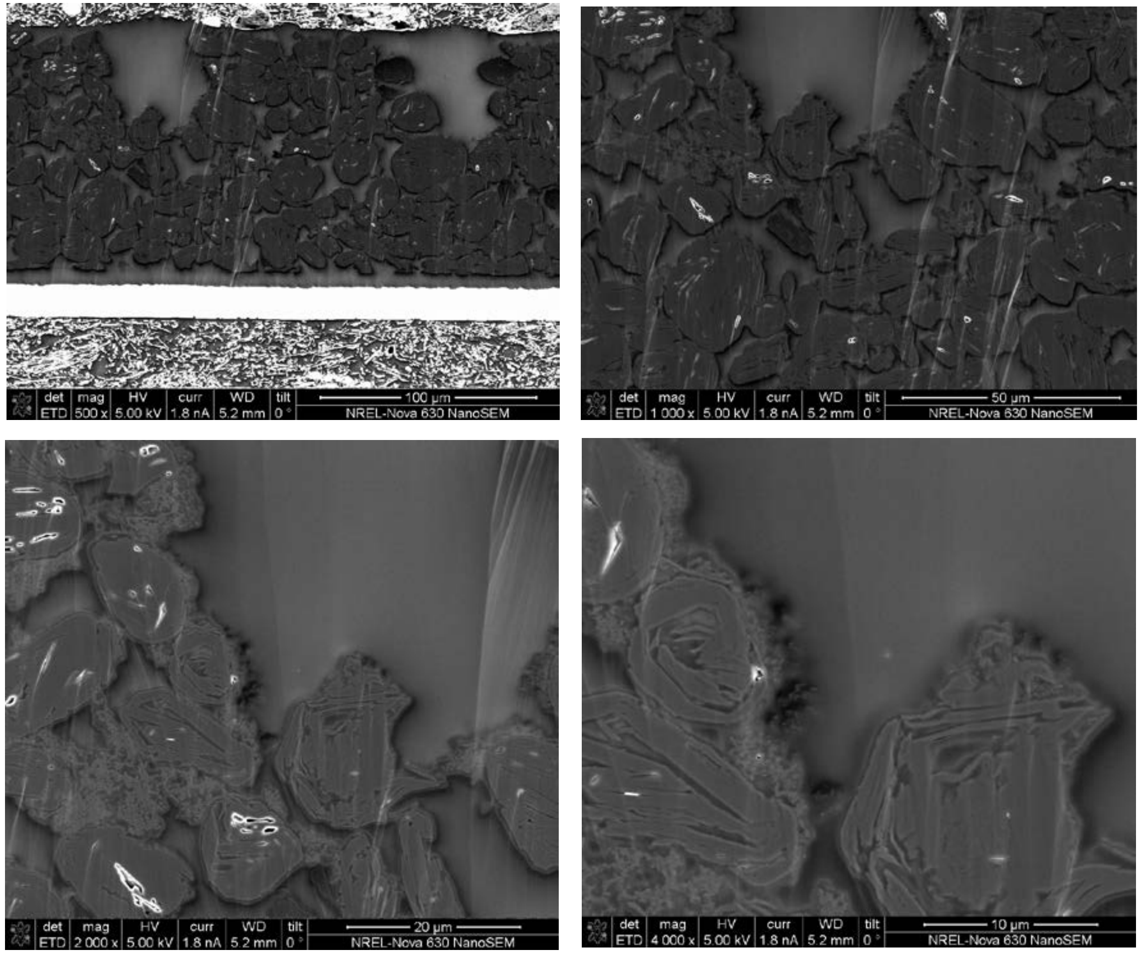
Material-dependent Laser Ablation

NMC 622



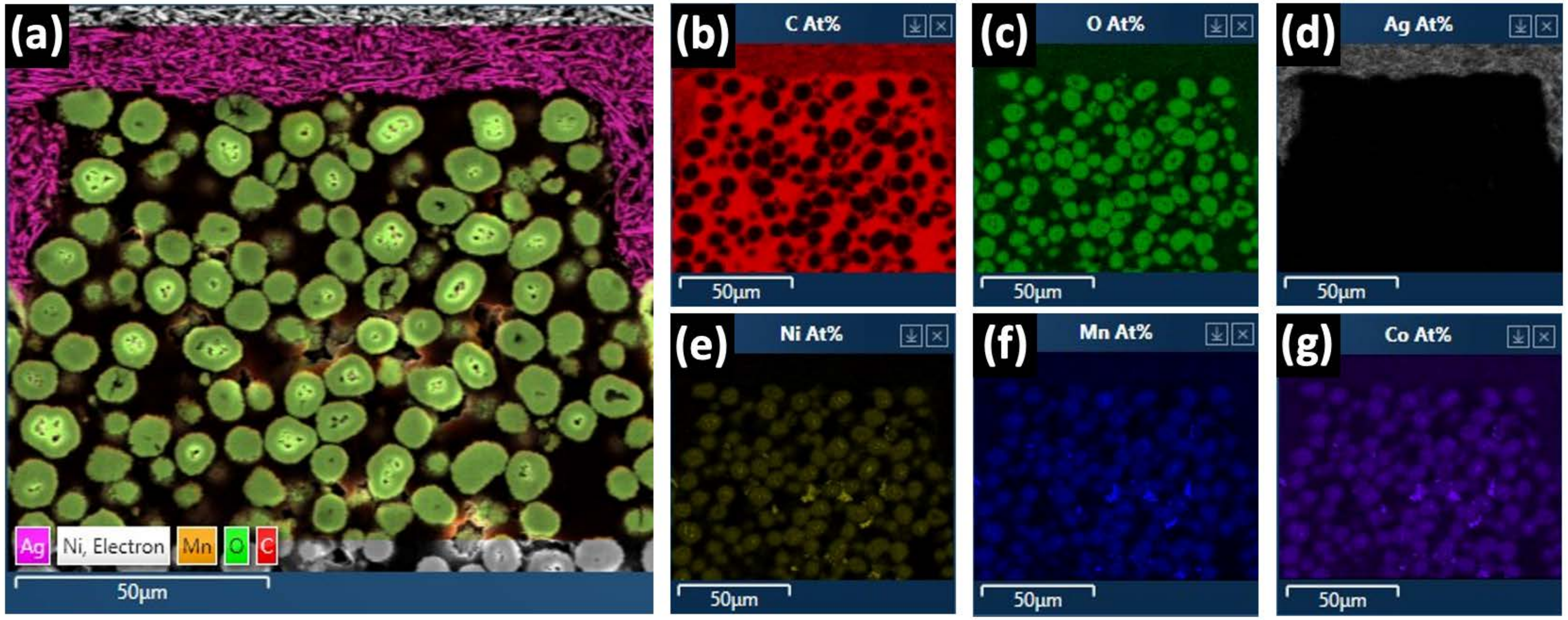
- Laser trench sidewall is relatively smooth and ~75˚ angle maintained
- Some NMC particles are cleaved and cracked

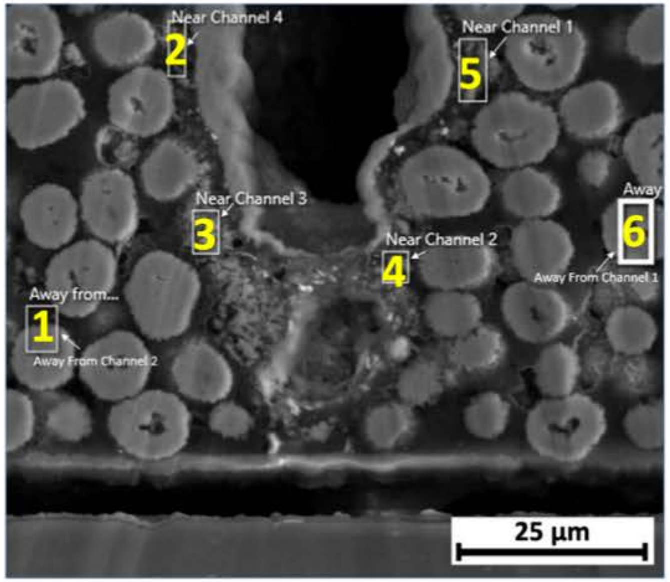
Graphite

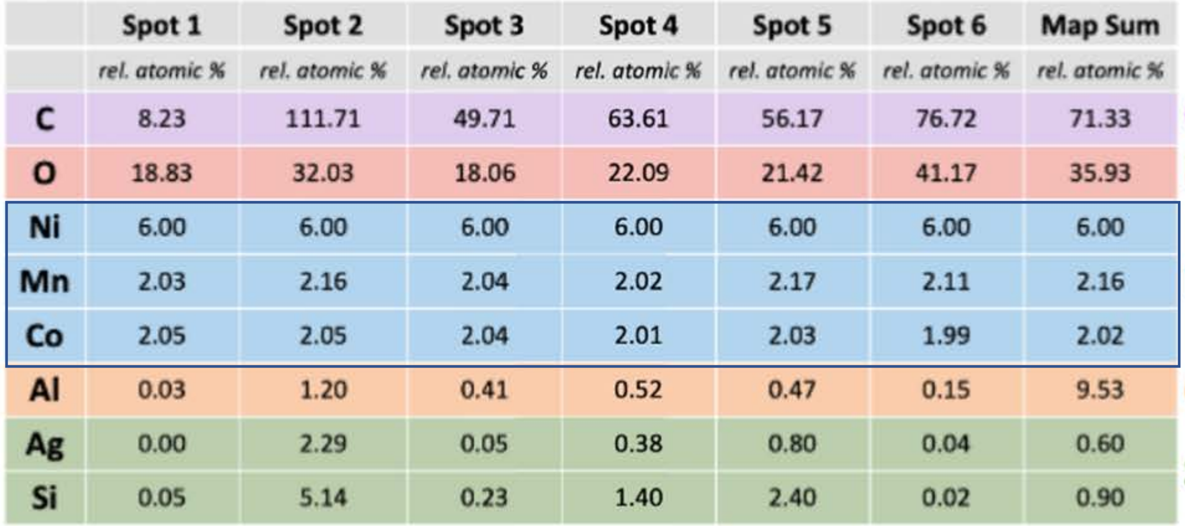


- Rough sidewalls
- No partial graphite particles b/c anisotropic heat conduction

FIB-SEM with EDS: NMC622 Composition Unaffected by Laser Ablation







	Spot 1	Spot 2	Spot 3	Spot 4	Spot 5	Spot 6	Map Sum
	rel. atomic %	*rel. atomic %*	*rel. atomic %*	*rel. atomic %*	*rel. atomic %*	*rel. atomic %*	*rel. atomic %*
C	8.23	111.71	49.71	63.61	56.17	76.72	71.33
O	18.83	32.03	18.06	22.09	21.42	41.17	35.93
Ni	6.00	6.00	6.00	6.00	6.00	6.00	6.00
Mn	2.03	2.16	2.04	2.02	2.17	2.11	2.16
Co	2.05	2.05	2.04	2.01	2.03	1.99	2.02
Al	0.03	1.20	0.41	0.52	0.47	0.15	9.53
Ag	0.00	2.29	0.05	0.38	0.80	0.04	0.60
Si	0.05	5.14	0.23	1.40	2.40	0.02	0.90

Conductive Carbon

Polymer Binder

$LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$

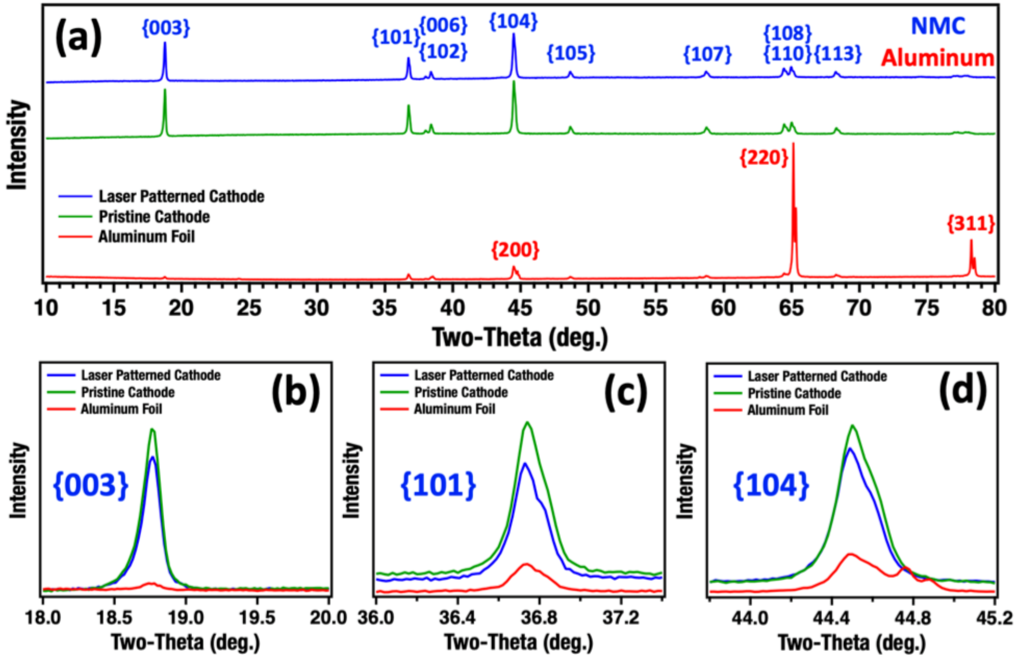
Current Collector

Sample Encasement

Cathode Composition: 90% NMC 622, 5% PVDF Binder, 5% C45 Carbon Additive

X-ray diffraction Structural Analysis Reveals Crystal Growth after Laser Ablation

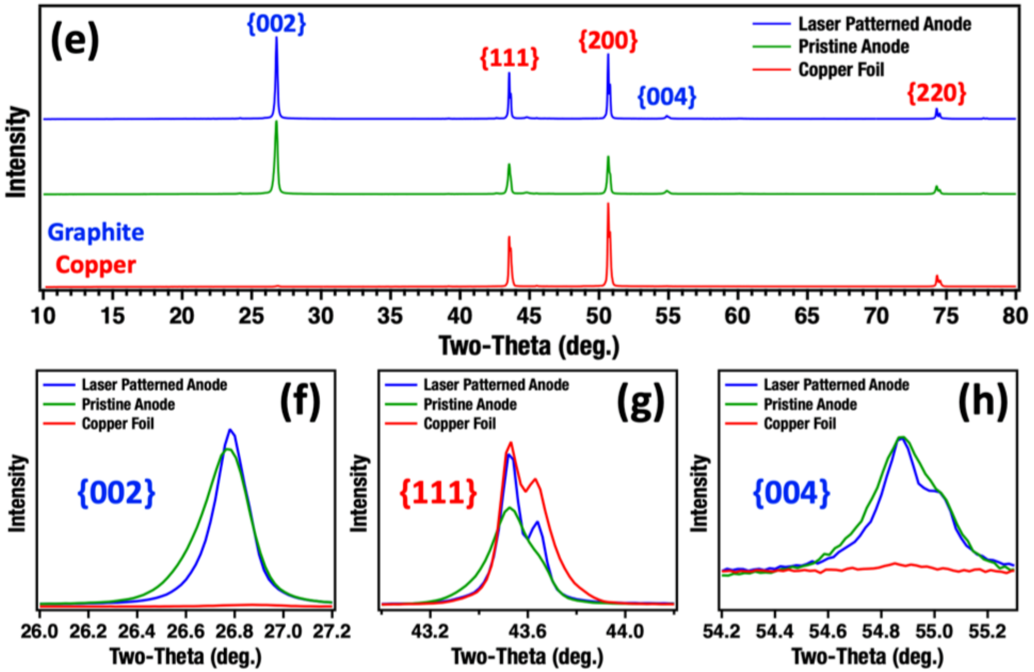
NMC622



Cathode	a (Å)	c (Å)	$c/(3a)$	Avg. Xtal Size FWHM (nm)	Avg. Xtal Size IB (nm)
Pristine	2.86965	14.2193	1.6517	122	132
Patterned	2.86971	14.2184	1.6515	163	228

Lattice parameters unchanged

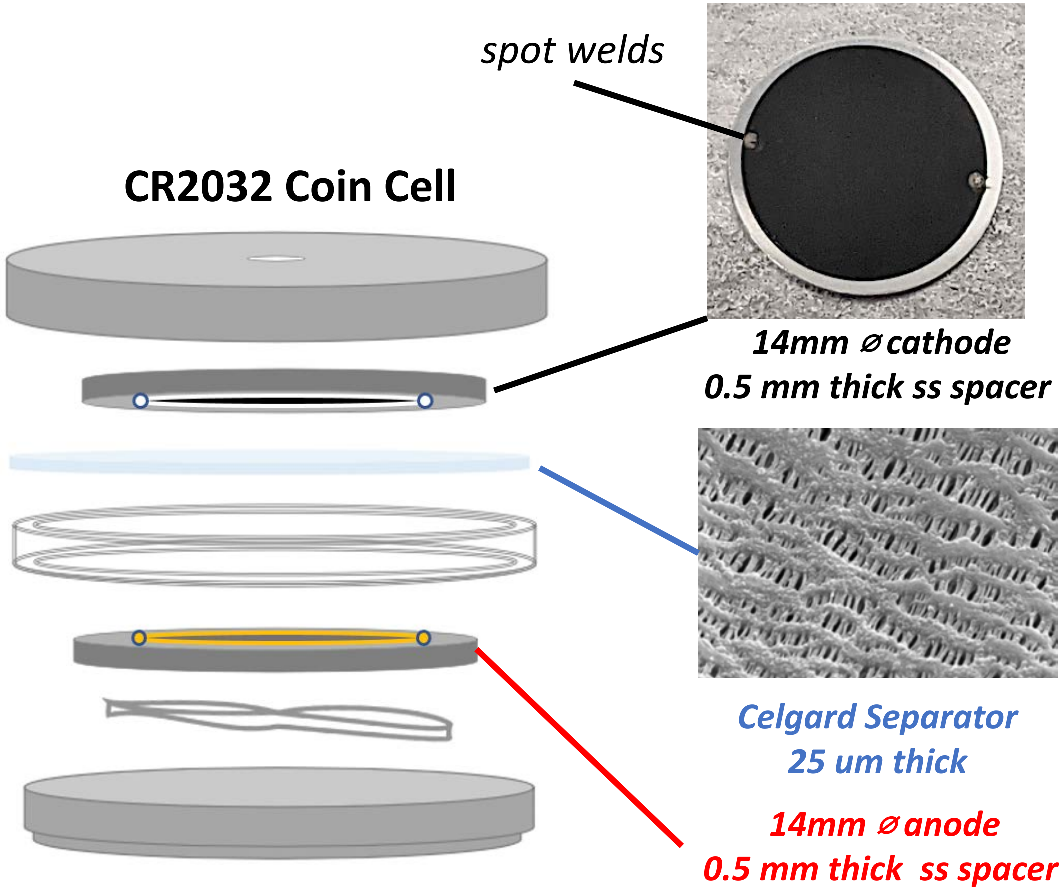
Graphite



Anode	a (Å)	c (Å)	Avg. Xtal Size FWHM (nm)	Avg. Xtal Size IB (nm)	Preferred Orientation
Pristine	2.462	6.712	48	68	(0 0 1)
Patterned	2.462	6.710	204	285	(0 0 1)

Crystal size growth from thermal annealing by laser energy

Cells Details and 6C Fast-Charge Protocol



14mm ⌀ cathode
0.5 mm thick ss spacer

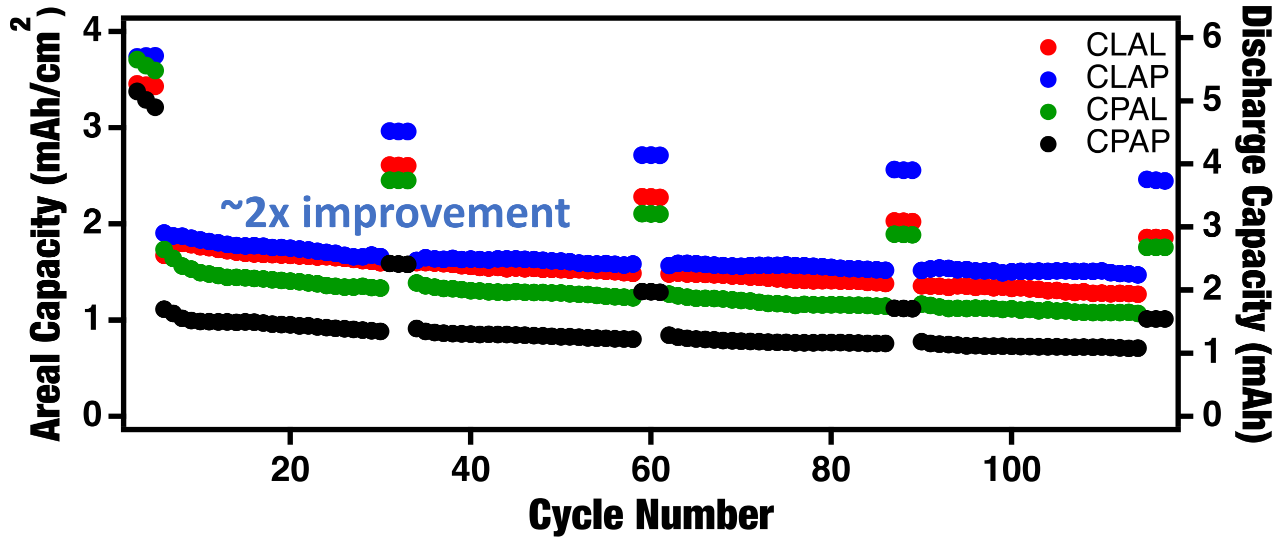
Celgard Separator
25 um thick

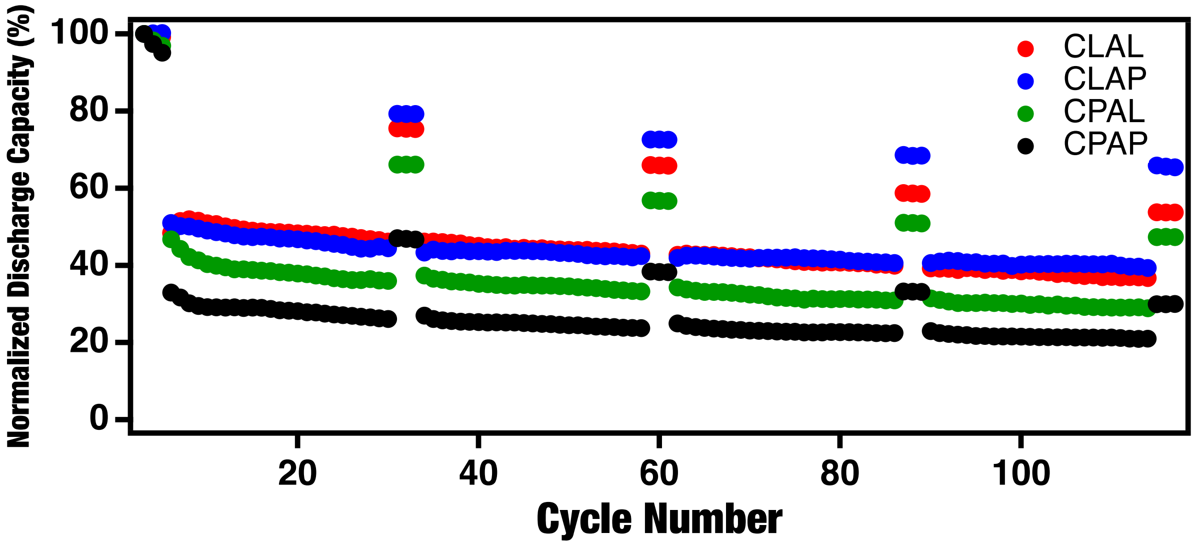
14mm ⌀ anode
0.5 mm thick ss spacer

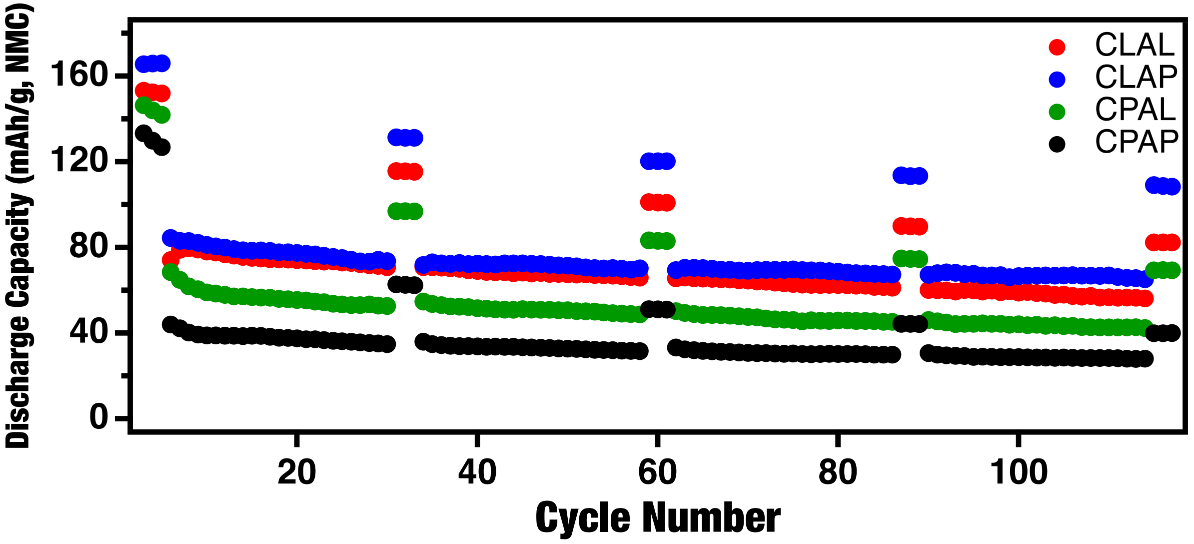
Electrolyte: EC:EMC (3:7 by wt.) + 1.2M $LiPF_6$
Voltage Window: 3– 4.2 V
Cycling Temperature: 24°C

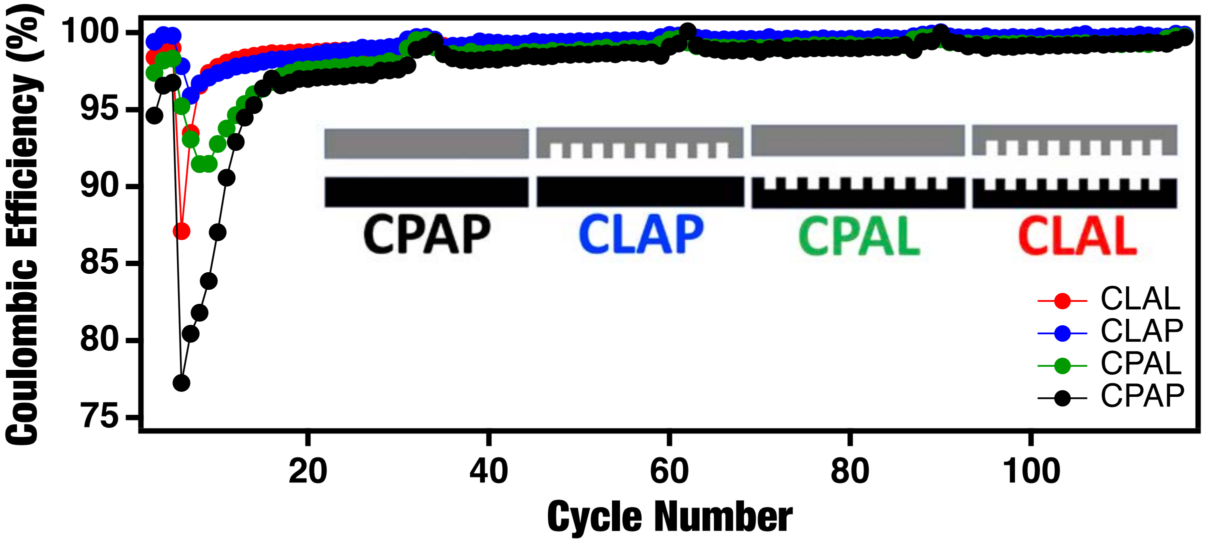
Step	End Conditions	Cycles	Repetitions
Charge – CC @ 0.1C Charge – CV @ 1.5 V Rest – OCP	V ≥ 1.5 V t = 15 min t = 6 hr	1	1
Charge – CC @ 0.1C Charge – CV @ 4.2 V Rest – OCP Discharge – CC @ 0.1C Discharge – CV @ 3.0 V Rest – OCP	V ≥ 4.2 V I ≤ 0.05C t = 15 min V ≤ 3.0 V I ≤ 0.05C t = 15 min	3	1
Charge – CC @ 0.5C Charge – CV @ 4.2 V Rest – OCP Discharge – CC @ 0.5C Discharge – CV @ 3.0 V Rest – OCP	V ≥ 4.2 V I ≤ 0.05C t = 15 min V ≤ 3.0 V I ≤ 0.05C t = 15 min	3	4
Charge – CC @ 6.0C Charge – CV @ 4.2 V Rest – OCP Discharge – CC @ 0.5C Discharge – CV @ 3.0 V Rest – OCP	V ≥ 4.2 V t + 6C CC = 10 min t = 15 min V ≤ 3.0 V I ≤ 0.05C t = 15 min	25	
Charge – CC @ 0.5C Charge – CV @ 4.2 V Rest – OCP Discharge – CC @ 0.5C Discharge – CV @ 3.0 V Rest – OCP	V ≥ 4.2 V I ≤ 0.05C t = 15 min V ≤ 3.0 V I ≤ 0.05C t = 15 min	3	1

Electrochemical Responses to 6C Fast Charge Testing

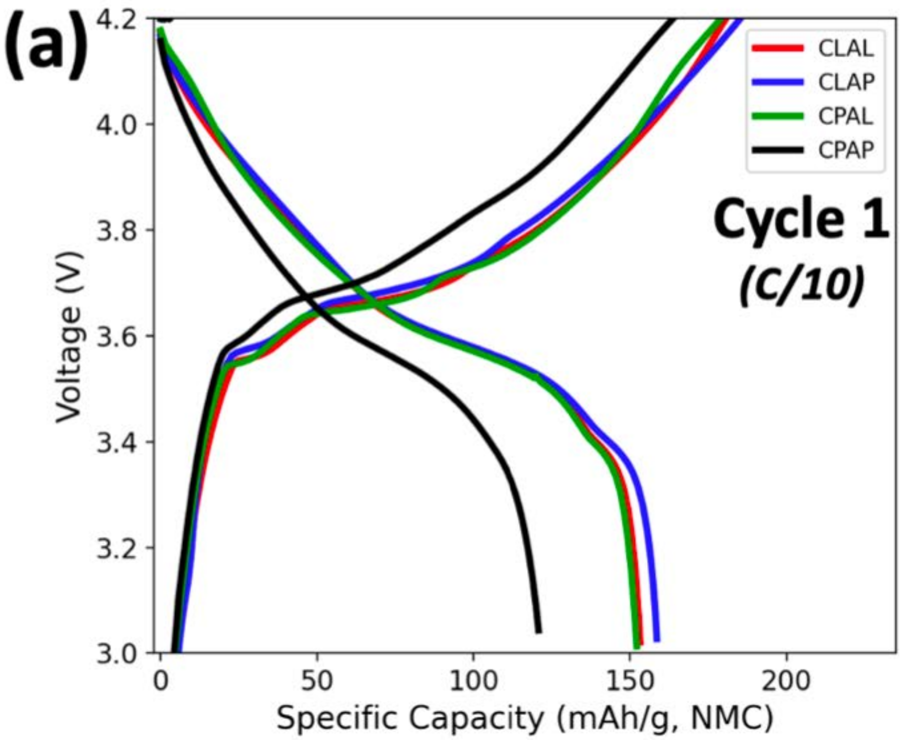

~2x improvement

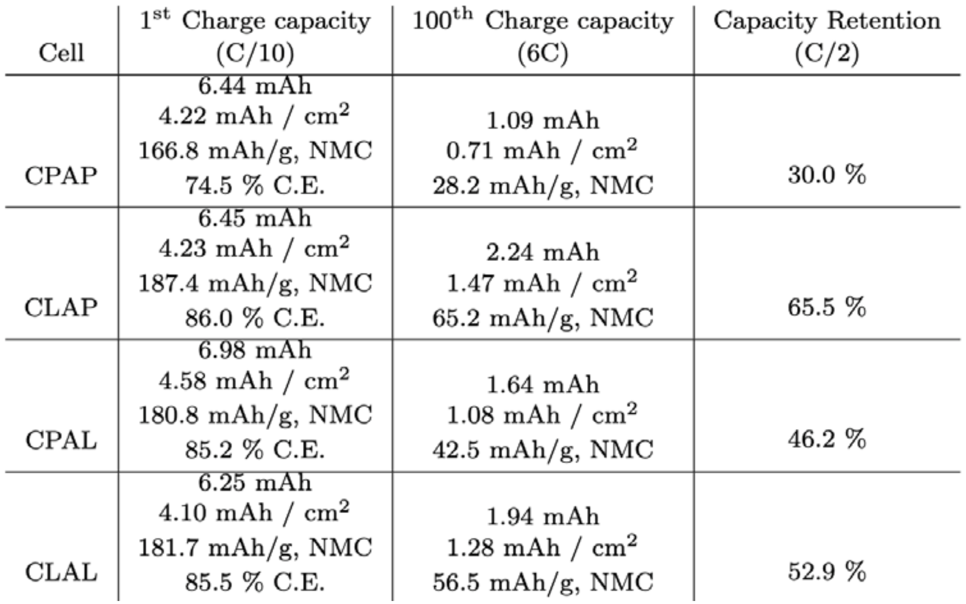






Cell Voltage Responses to 6C Fast Charge Testing

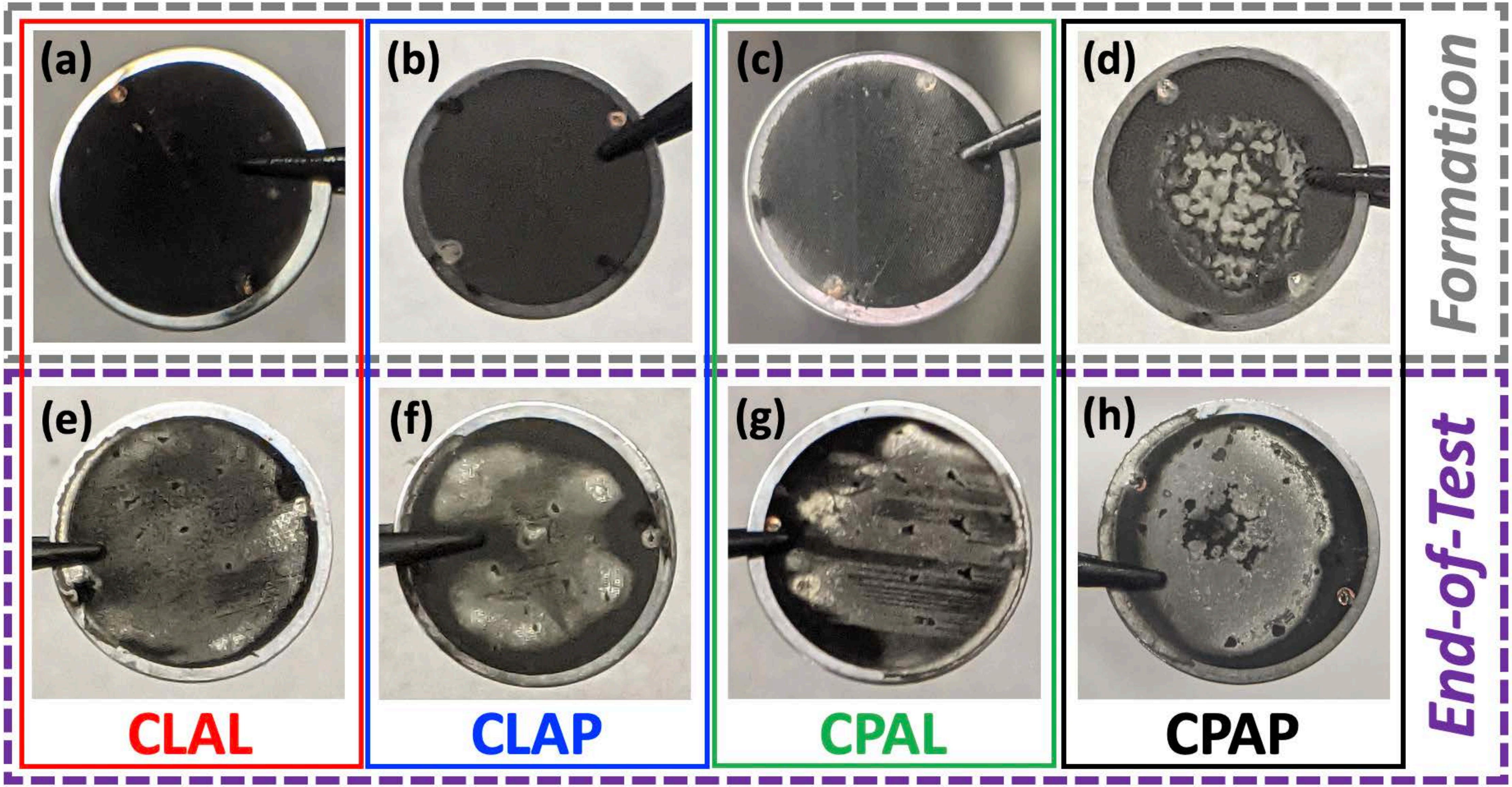




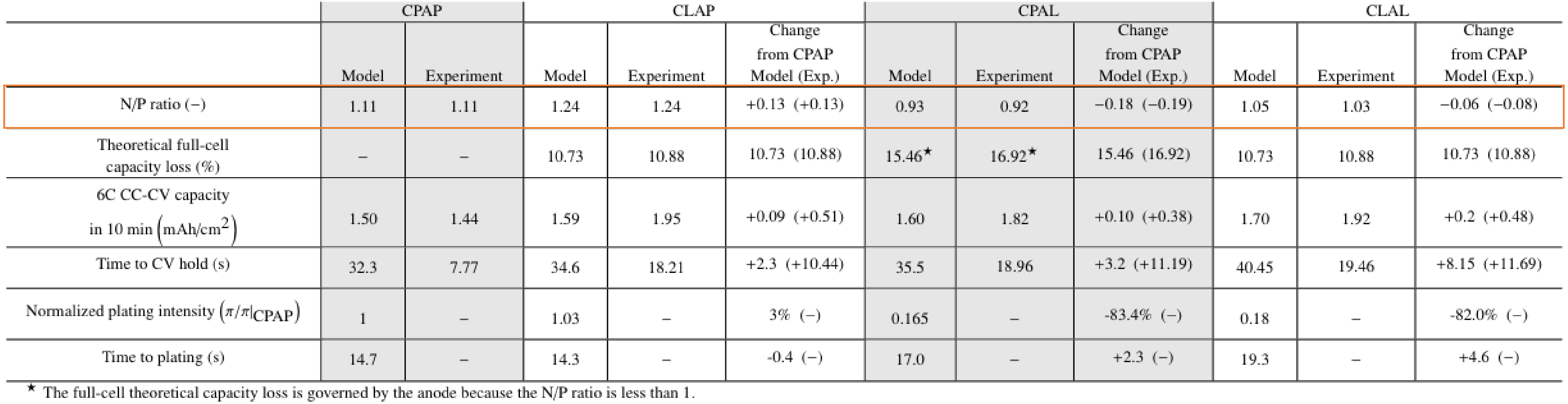
Cell	1st Charge capacity (C/10)	100th Charge capacity (6C)	Capacity Retention (C/2)
CPAP	6.44 mAh 4.22 mAh / cm^2 166.8 mAh/g, NMC 74.5 % C.E.	1.09 mAh 0.71 mAh / cm^2 28.2 mAh/g, NMC	30.0 %
CLAP	6.45 mAh 4.23 mAh / cm^2 187.4 mAh/g, NMC 86.0 % C.E.	2.24 mAh 1.47 mAh / cm^2 65.2 mAh/g, NMC	65.5 %
CPAL	6.98 mAh 4.58 mAh / cm^2 180.8 mAh/g, NMC 85.2 % C.E.	1.64 mAh 1.08 mAh / cm^2 42.5 mAh/g, NMC	46.2 %
CLAL	6.25 mAh 4.10 mAh / cm^2 181.7 mAh/g, NMC 85.5 % C.E.	1.94 mAh 1.28 mAh / cm^2 56.5 mAh/g, NMC	52.9 %

Even at the slow rate of C/10, the CPAP cell shows a significant overpotential on both charge and discharge → severe wetting problems

Severe Li Plating in Unpatterned Anodes



Li Plating Affected by n/p Ratio



	CPAP		CLAP			CPAL			CLAL		
	Model	Experiment	Model	Experiment	Change from CPAP Model (Exp.)	Model	Experiment	Change from CPAP Model (Exp.)	Model	Experiment	Change from CPAP Model (Exp.)
N/P ratio (–)	1.11	1.11	1.24	1.24	+0.13 (+0.13)	0.93	0.92	−0.18 (−0.19)	1.05	1.03	−0.06 (−0.08)
Theoretical full-cell capacity loss (%)	–	–	10.73	10.88	10.73 (10.88)	15.46★	16.92★	15.46 (16.92)	10.73	10.88	10.73 (10.88)
6C CC-CV capacity in 10 min $\left(\text{mAh/cm}^2\right)$	1.50	1.44	1.59	1.95	+0.09 (+0.51)	1.60	1.82	+0.10 (+0.38)	1.70	1.92	+0.2 (+0.48)
Time to CV hold (s)	32.3	7.77	34.6	18.21	+2.3 (+10.44)	35.5	18.96	+3.2 (+11.19)	40.45	19.46	+8.15 (+11.69)
Normalized plating intensity $\left(\pi/\pi\vert_{\text{CPAP}}\right)$	1	–	1.03	–	3% (–)	0.165	–	-83.4% (–)	0.18	–	-82.0% (–)
Time to plating (s)	14.7	–	14.3	–	-0.4 (–)	17.0	–	+2.3 (–)	19.3	–	+4.6 (–)

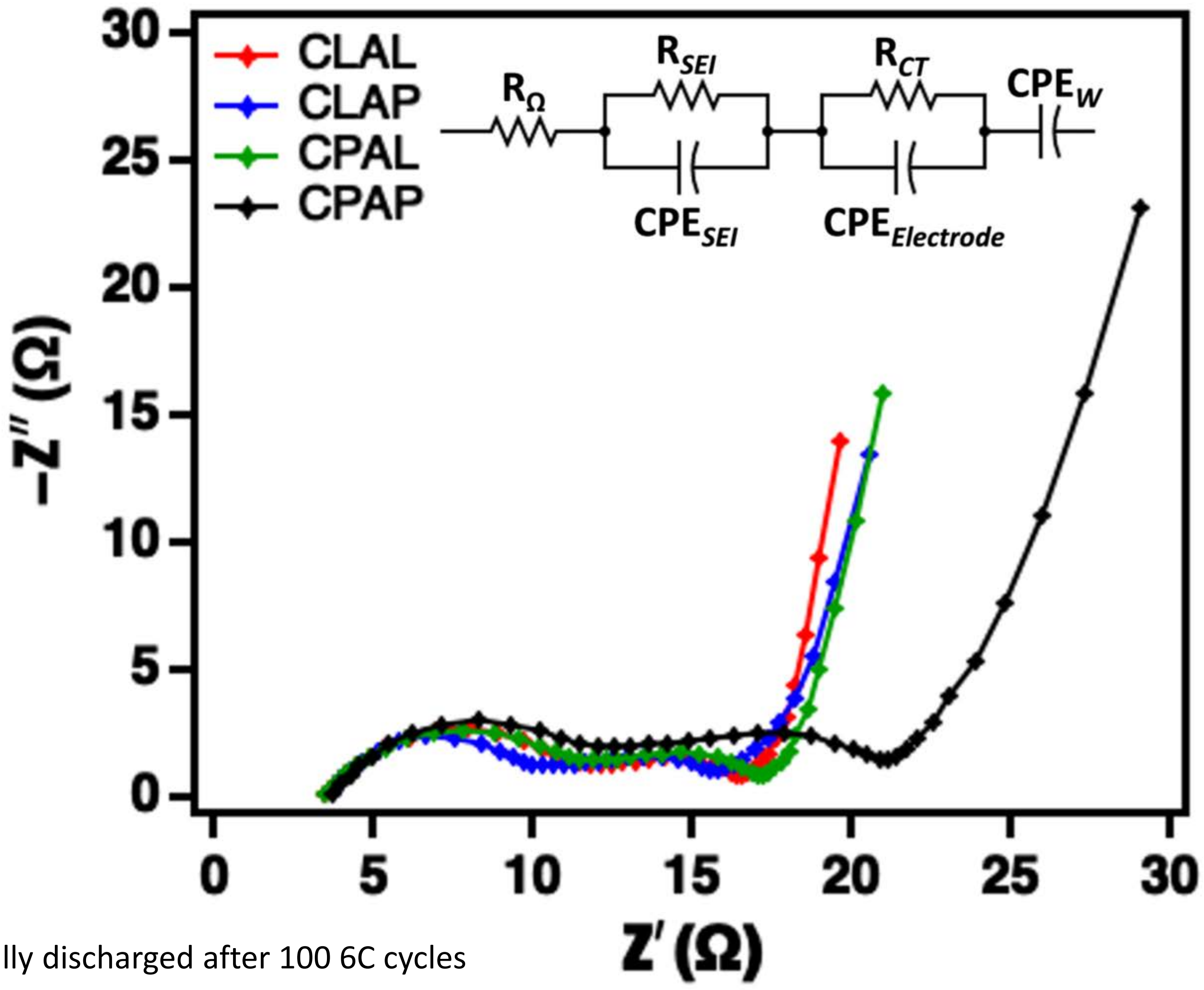
★ The full-cell theoretical capacity loss is governed by the anode because the N/P ratio is less than 1.

CLAP = Best performance

n/p < 1 explains Li plating
During formation

n/p = 1 could help explain why the CLAL cell under-performed in comparison to the CLAP cell

Electrode Patterning Significantly Improves Interfacial Charge-transfer Resistance

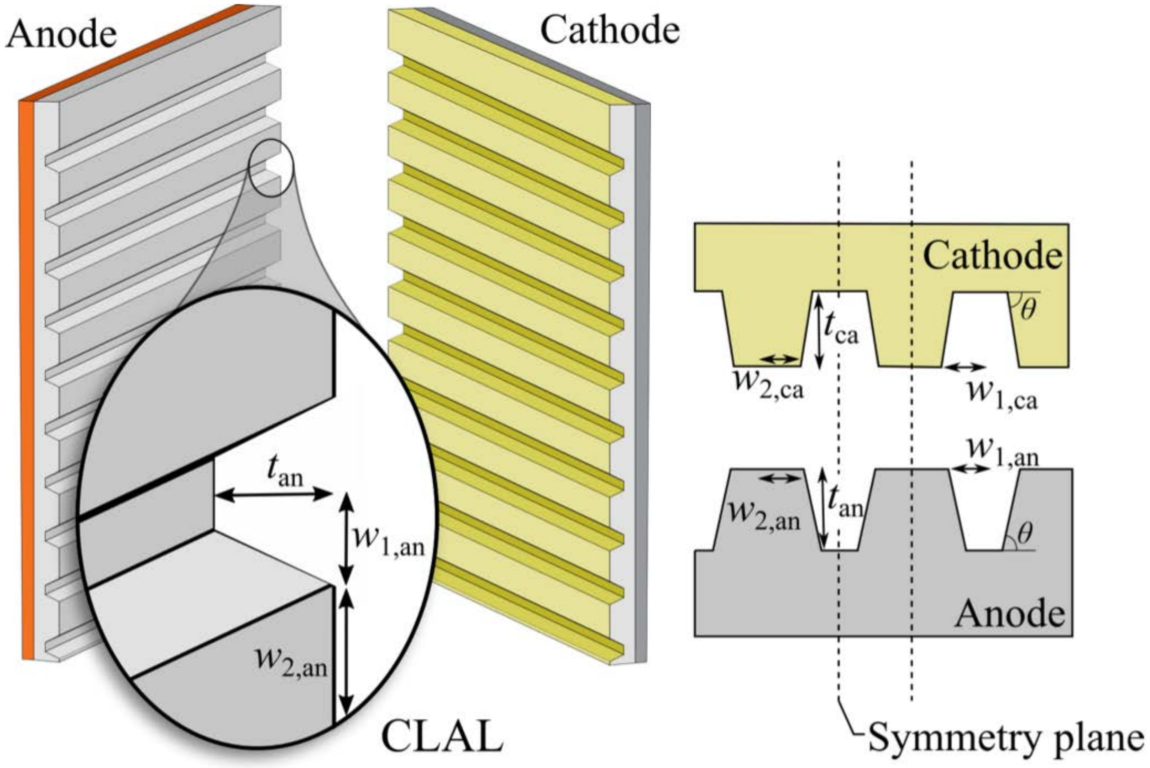


Cells are fully discharged after 100 6C cycles

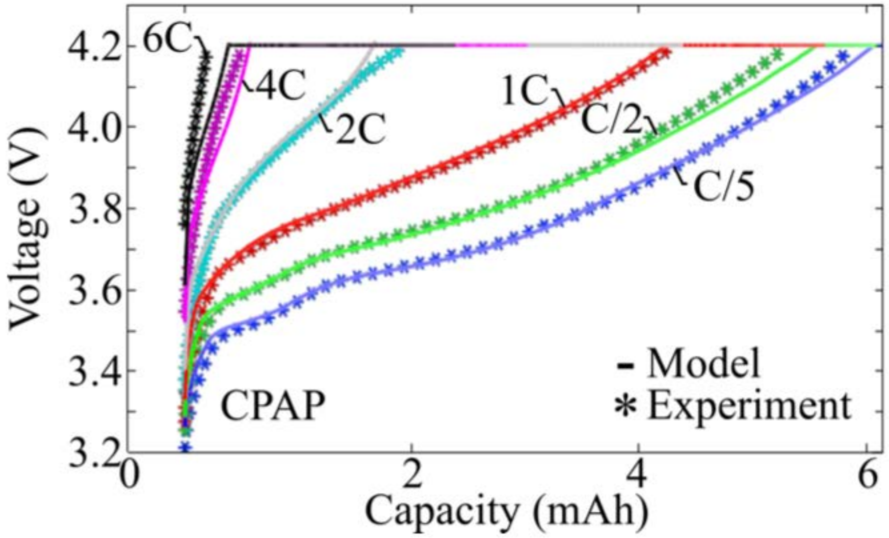
Cell	R_Ω (Ω)	R_{SEI} (Ω)	R_{CT} (Ω)
CPAP	3.74	9.81	11.4
CPAL	3.51	8.9	6.75
CLAP	3.7	7.04	6.87
CLAL	3.52	8.61	5.96

electrode patterning improves CT resistance: better ion-transport and reduced concentration gradients

Psuedo-2D Electrochemical Model Used to Simulate Cell Performance

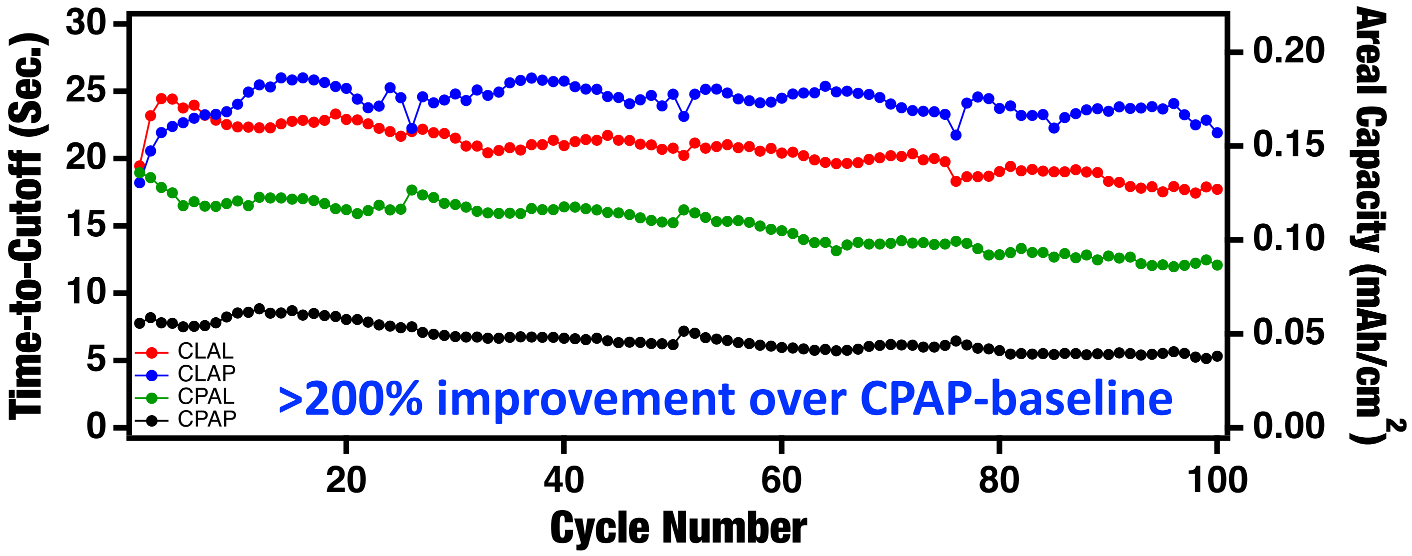


CPAP

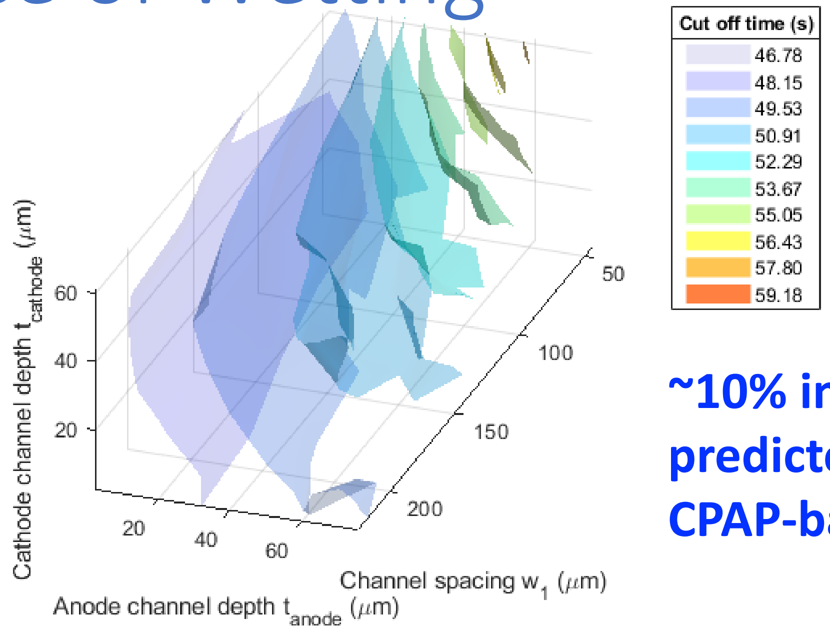


At high charging rates (>4C), the model underpredicts cell resistances due to assumption of perfect electrode wetting

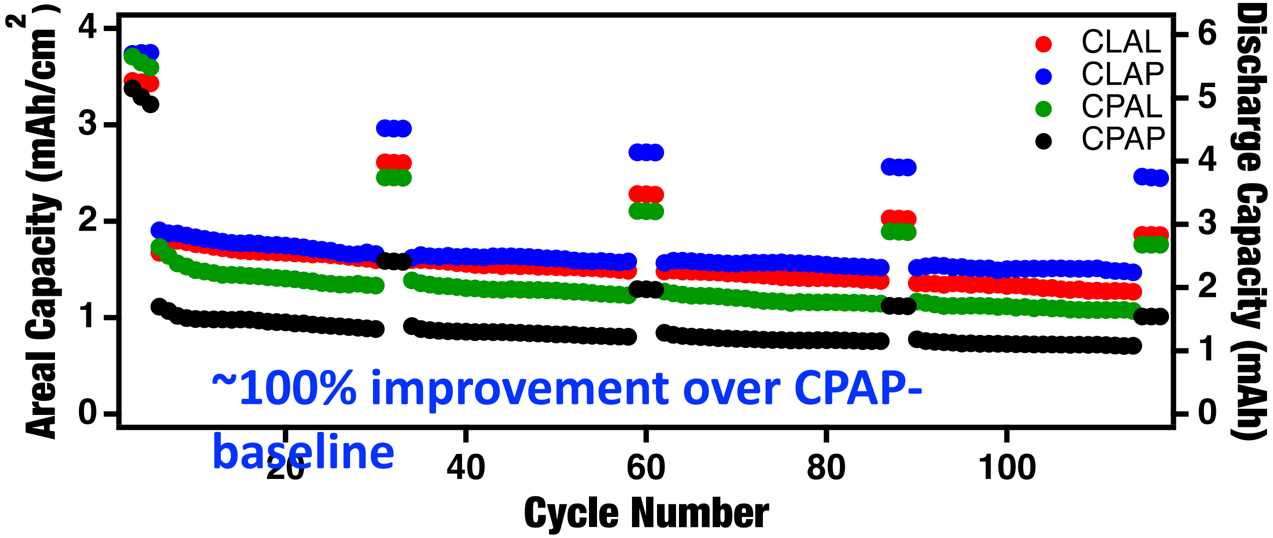
Discrepancy between experiment and Psuedo-2D Model Highlights Importance of Wetting



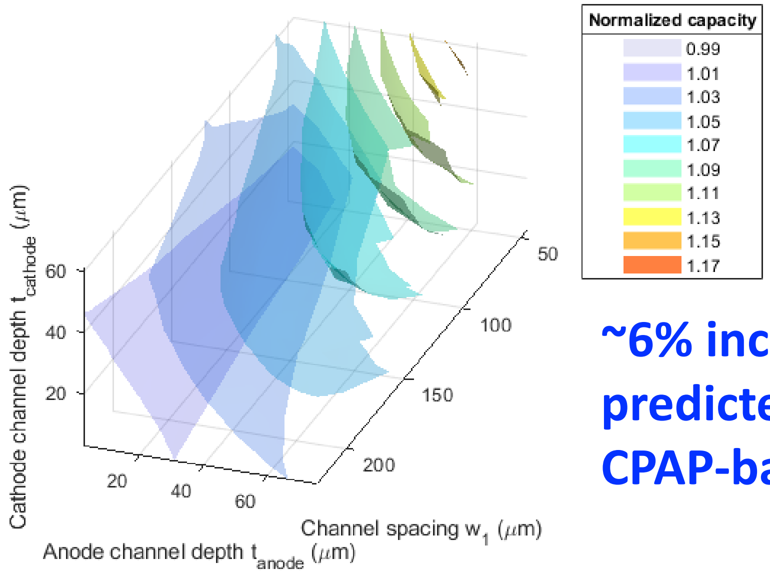
>200% improvement over CPAP-baseline



~10% increase predicted over CPAP-baseline

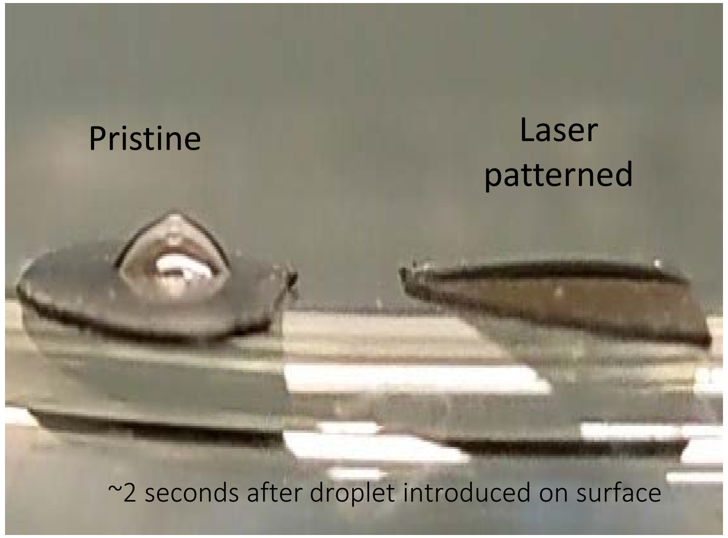


~100% improvement over CPAP-baseline

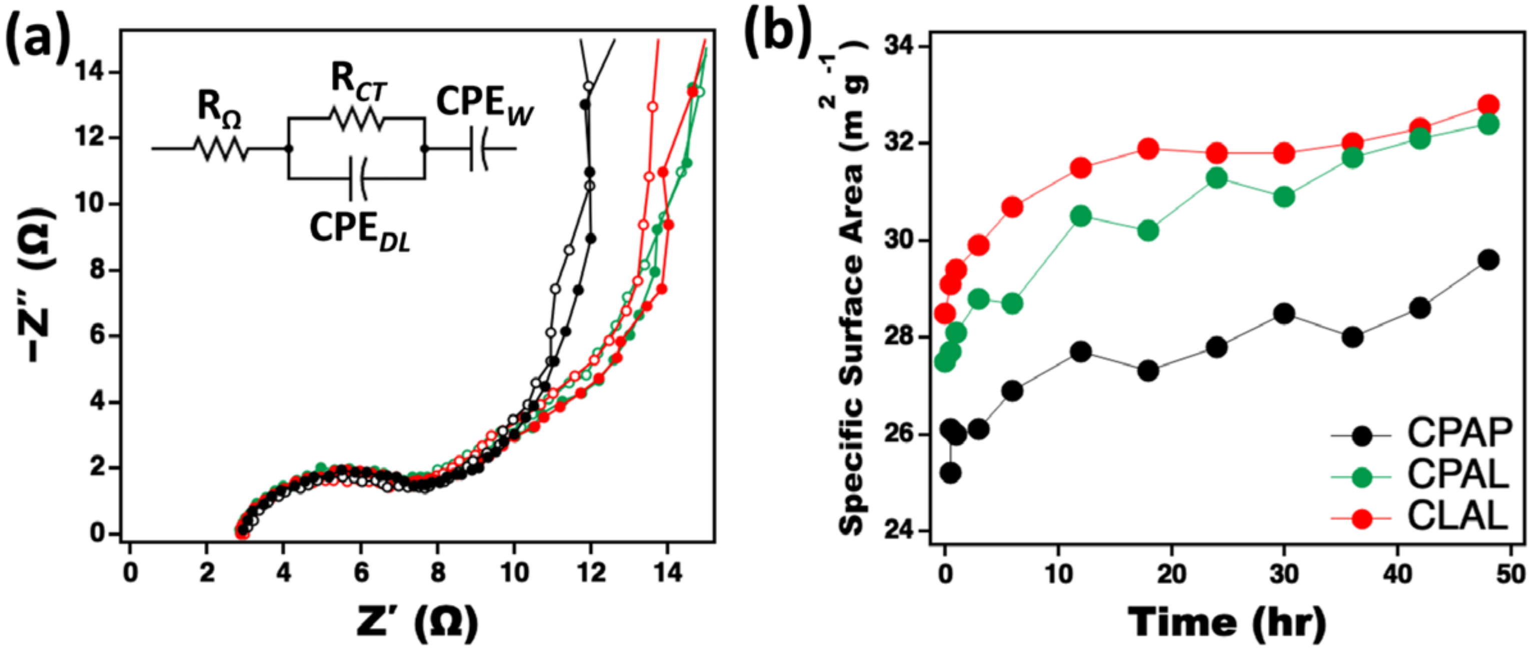


~6% increase predicted over CPAP-baseline

Micro-structures Improve Electrode-Electrolyte Wetting



~2 seconds after droplet introduced on surface



Summary

- Fast charging of high-energy density thick electrodes is hampered by transport limitations and lithium concentration gradients
- Severe polarization in electrodes at high charging rates leads to high-current densities near the separator and favorable conditions for Li-plating
- Strategically laser-ablating channels into electrodes can reduce tortuosity, improve electrolyte wetting and increase rate capability
- Ongoing work to demonstrate feasibility of scaling up laser-ablation pilot lines

Patent: NREL 21-48 LASER ABLATION FOR LITHIUM-ION BATTERIES (non-provisional application)

Patent: NREL 22-19 SENSOR-GUIDED ADAPTIVE LASER ABLATION OF BATTERY ELECTRODES (provisional application)

Dunlap, N. et al., Laser ablation of Li-ion electrodes for fast charging: Material properties, rate capability, Li plating, and wetting, 2022 Journal of Power Sources

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Nathan Dunlap, Dana Sulas-Kern, François Usseglio-Viretta, Peter Weddle, Donal Finegan, **Bertrand J. Tremolet de Villers**

National Renewable Energy Laboratory (NREL)

Bertrand.Tremolet@nrel.gov

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