Understanding Dry Electrode Processing

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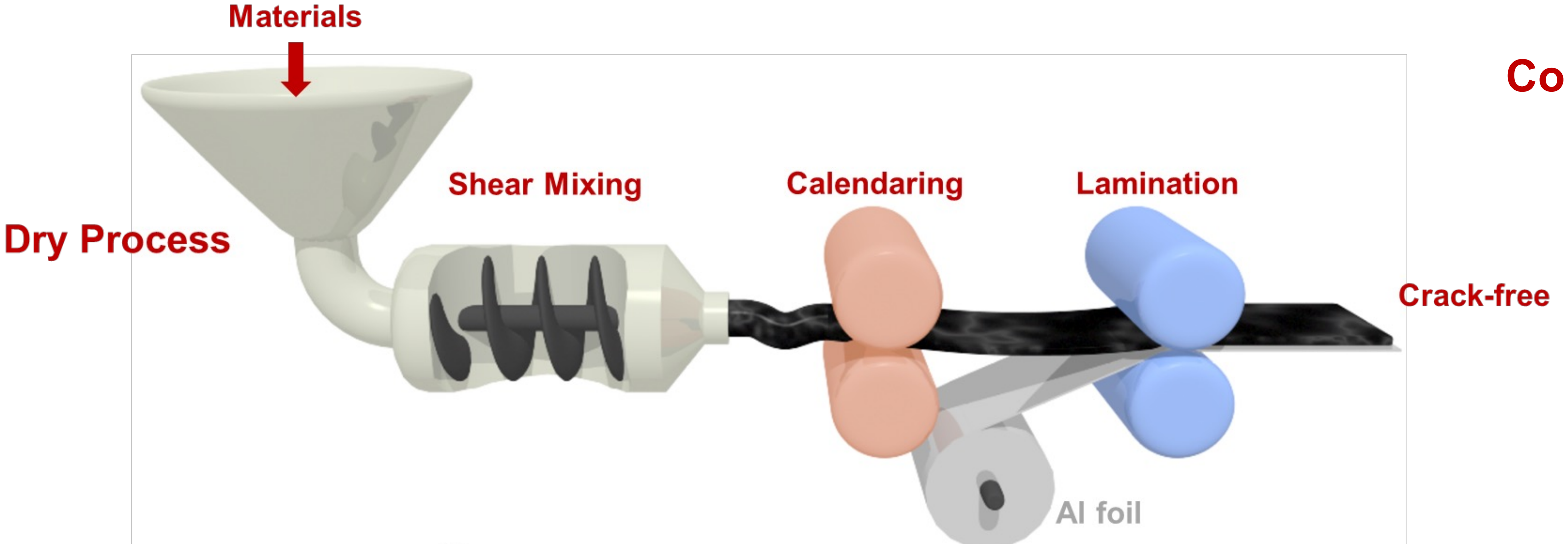
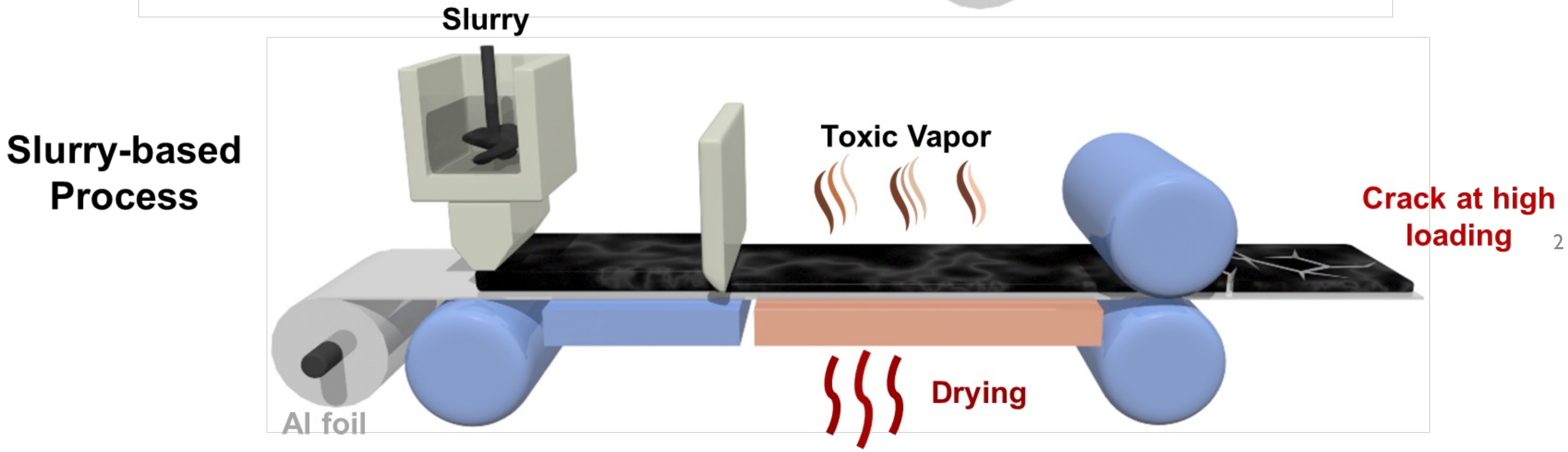
Slurry-based Method VS Dry Process





Conventional slurry-based method:

Use of toxic NMP solvent
Solvent drying process
Solvent recycling equipment
Cracks at high mass loading
High voltage degradation

Dry electrode method:

No solvent included
Easily achieve high mass loading without crack
More economical and simpler process
High voltage stability

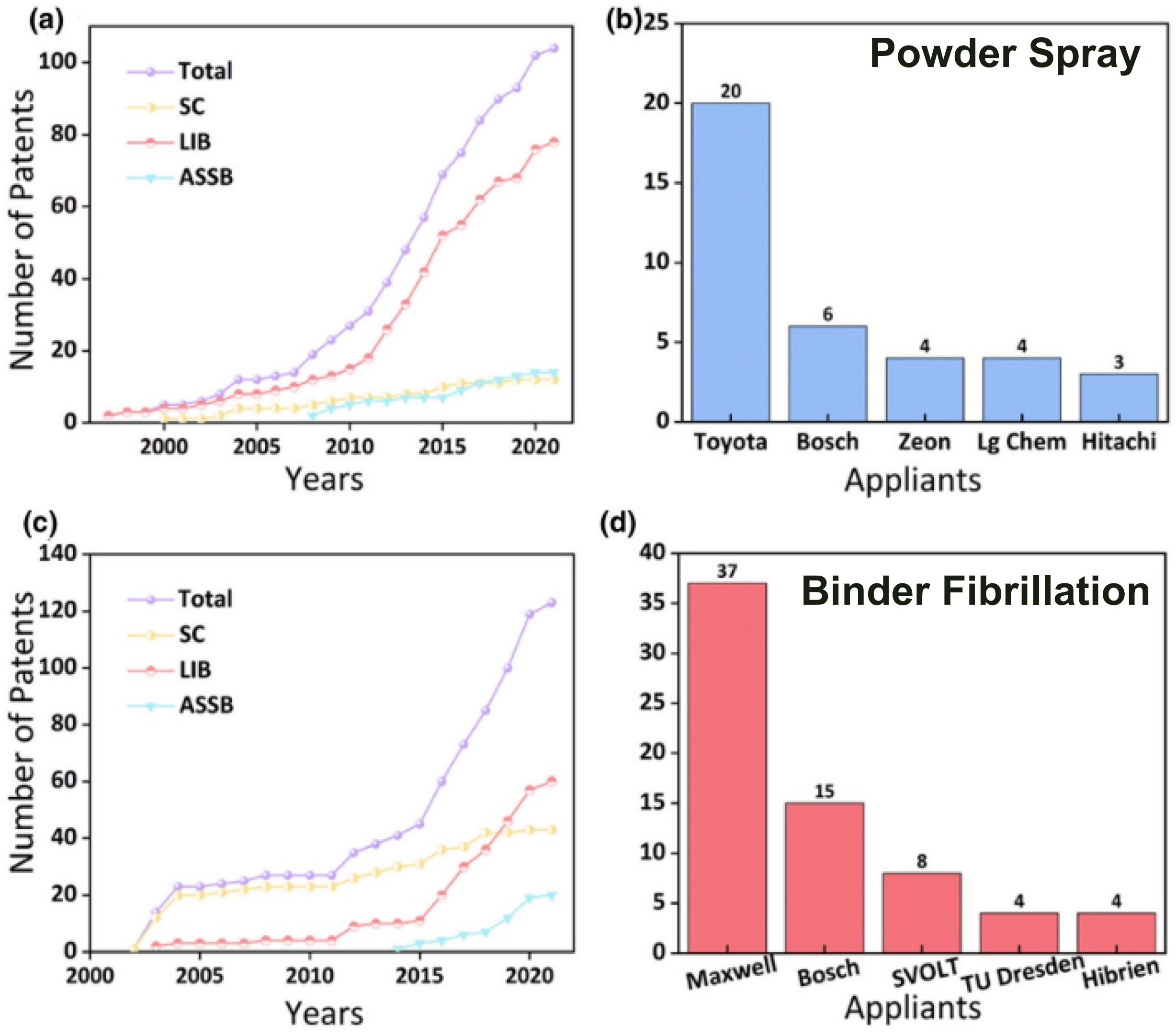
Yao, Weiliang, *et al*. "A 5V-class Cobalt-free Battery Cathode with High Loading Enabled by Dry Coating." Energy & Environmental Science (2023).

Literature Summary of Thick Electrode Work

Cathode Materials	AM : Binder: Carbon	Loading mg/cm^2	Capacity retention %	Novel Method	Leading author and year
LiFePO$_4$	LFP:CB:PVDF=**70:20:10**	168	LFP/LTO Full cell: 87% after 33 cycles, C rate not mentioned	LFP coated onto CNT textile	Liangbing Hu, 2011
NCM811	NCM811:CNT = **99.5:0.5**	155	Full cell: 70% after 37 cycles at **C/15**	NCM811-CNT slurry casting	Valeria Nicolosi, 2019
LiFePO$_4$	LFP:CB = **90:10**	150	LFP/LTO Full cell: 90% after 20 cycles at **C/20**	Plasma sintering	Vincent Seznec, 2018
LiFePO$_4$	LFP:CNT:CNF = **80:15:5**	90	LFP/LTO Full cell: 90% after 50 cycles at **C/5**	Composite film made by vacuum filtration	Sang-Young Lee, 2015
NCM111	NCM:PVDF:CB:Graphite = **84:9:3.5:3.5**	89	Only 3 cycles of C/50 shown	Slurry coating onto porous metal foam substrate	Harshad Tataria, 2011
LNMO	LNMO:PTFE:VGCF = **93:2:5**	67	22 mg/cm^2 Full cell: 68% after 1000 cycles at **C/3**	Dry electrode method	**Our work, 2023**
NCM111	NCM111:CB:graphite:PVDF = **90:3:4:3**	64.8	Rate test at **C/10, C/5 and C/2** for 20 cycles shown for rate test.	Slurry coating	Madhav Singh, 2015
LNMO	LNMO:MWCNT:PAN = **72:3.6:24.4**	57	Half cell: 78.5% after 30 cycles at **C/5**	Electro-spraying/spinning	Sang-Young Lee, 2016
LiFePO$_4$	LFP/C : CB: PVDF = **75:15:10**	56.3	Half cell: 90% after 50 cycles at **C/10**	Slurry-coating LFP onto porous metal foam substrate	Seung-Ki Joo, 2015
NCM622	NCM622:CB:PVDF = **91.5:4.4:4.1**	37.6	Full cell: 91% after 300 cycles at **C/3**	Slurry coating	Kevin G. Gallagher, 2015
NCM111	NCM111:CB:PVDF = **85:7:8**	24	Full cell: 90% after 500 cycles at **1C with 4.4V cutoff**	Slurry coating	Vincent S. Battaglia, 2012

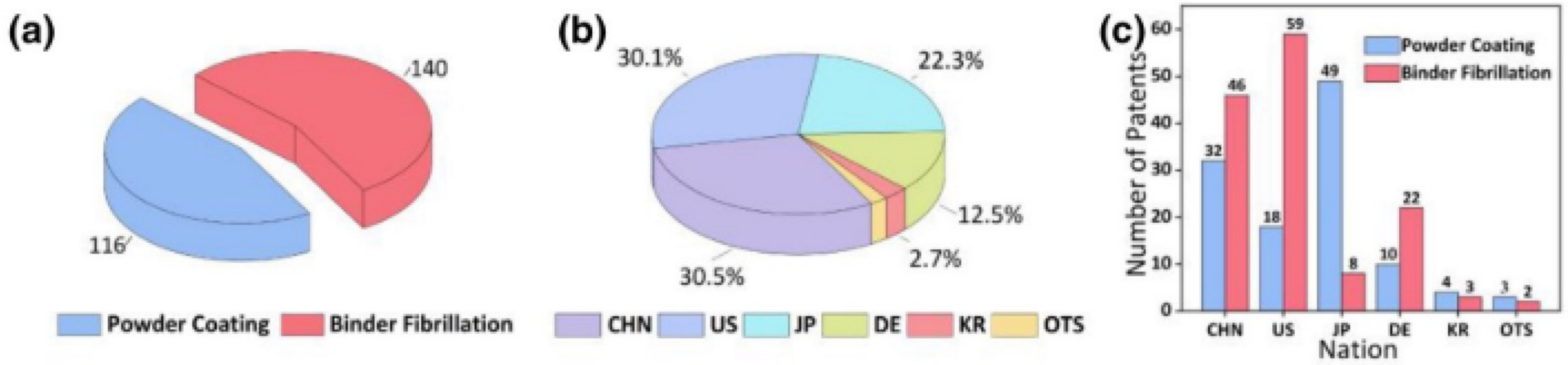
- Most of literature's work focus on slurry coating, other novel methods such as plasma sintering and Electro-spraying/spinning.
- Many novel methods are developed to achieve ultra-high loading, but the scalability, consistency and reliability are questionable.

Patents and Applications of Dry Electrode Technology



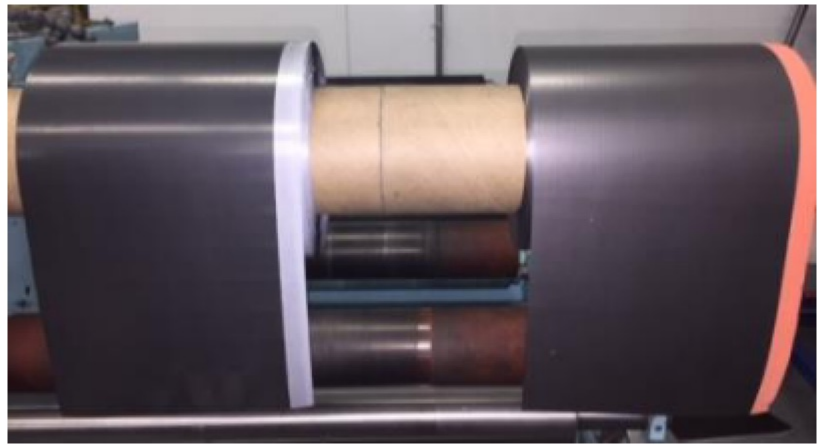
Li, Yongxing, *et al.* Materials Today (2022).

- Dry electrode is becoming increasingly popular in manufacturing supercapacitors (SC), lithium-ion batteries and (LIBs) and all-solid-state-batteries (ASSB).



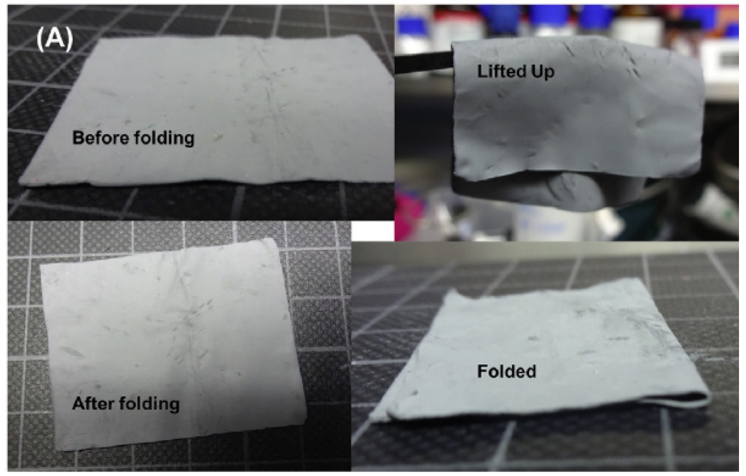
Li, Yongxing, *et al.* Materials Today (2022).

- Binder fibrillation and powder spray are most promising methods for large scale production.



Duong, Hieu, Joon Shin, and Yudi Yudi. "Dry electrode coating technology." 48th Power Sources Conference. Vol. 3. 2018.

- Dry-coated NCM cathode and graphite anode from Maxwell (now Tesla)



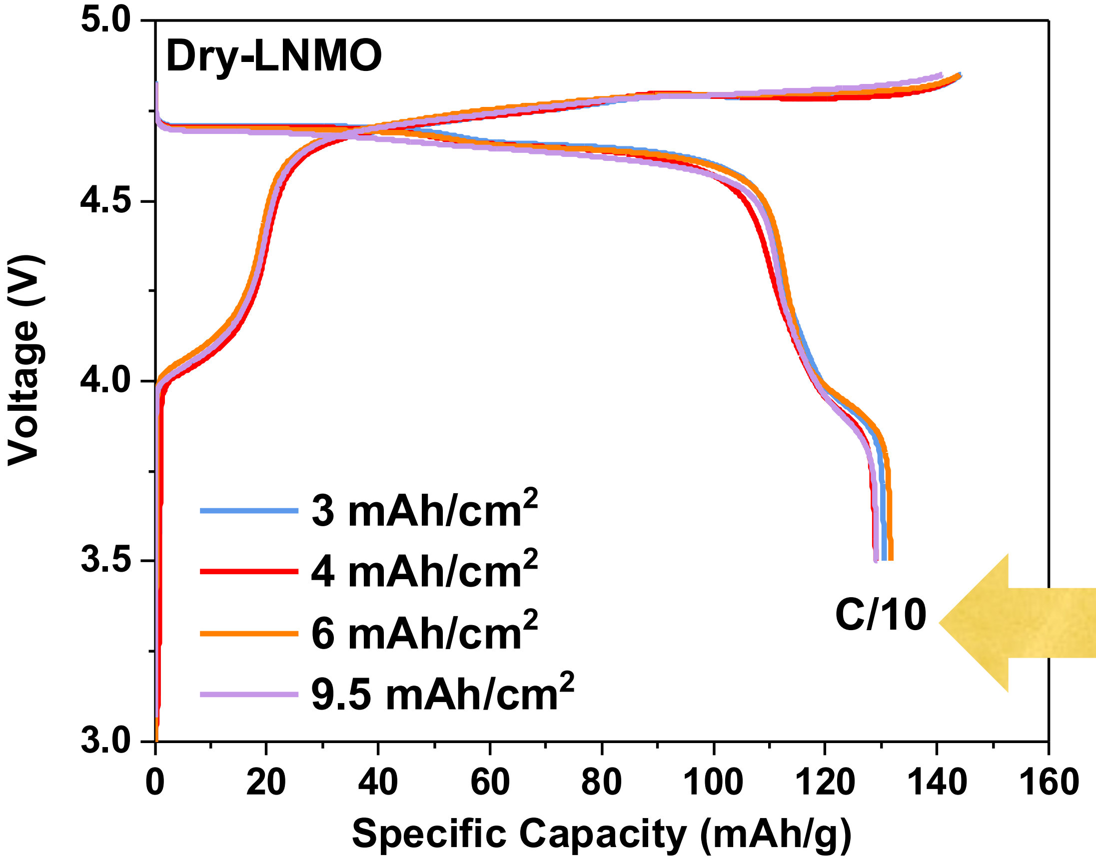
Hippauf, Felix, *et al.* Energy Storage Materials 21 (2019): 390-398.

- Lab-scale dry-coated all-solid-state battery (ASSB)) electrodes

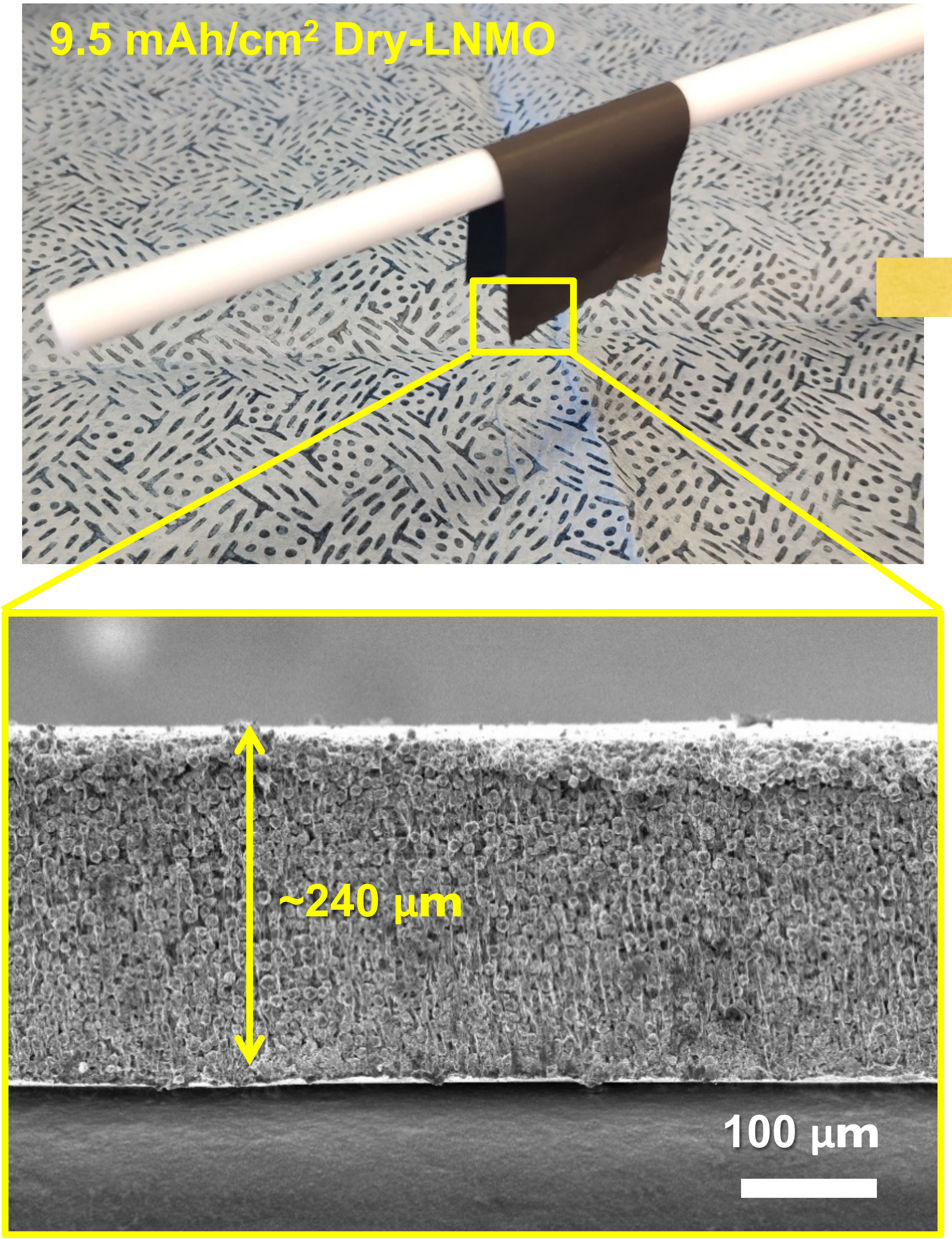
- In LIBs, usually low voltage cutoff is the focus for commercial products. High voltage application is yet to be explored.

Flexibility of Ultra-thick Dry-LNMO Electrodes

Yao, Weiliang, *et al*. Energy & Environmental Science (2023).



- Comparable performance with low loading electrodes

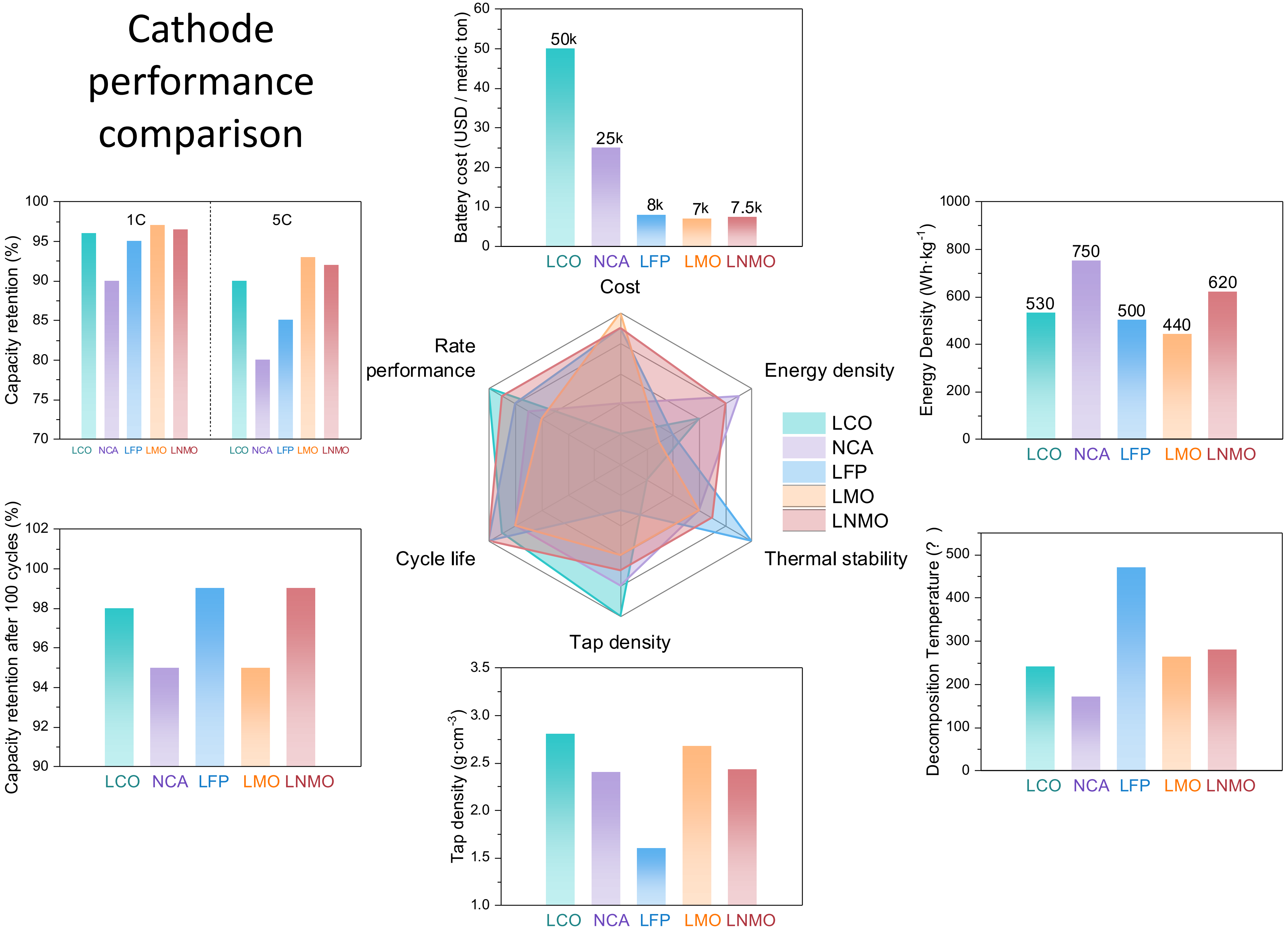


- Flexible and mechanically robust electrode film at ultra-high loading.

Co-free High Voltage LNMO Cathode

W. Li, M. Zhang, Y. S. Meng et al., Journal of Power Sources 2020, 473, 228579

Cathode performance comparison



Motivation for thick LNMO cathode

Average V = 4.7 V, Capacity = 140 mAh/g

Cathode areal capacity (mAh/cm^2)	Cell level energy density (Wh/kg)
4	282
10	308
20	315

With graphite as anode

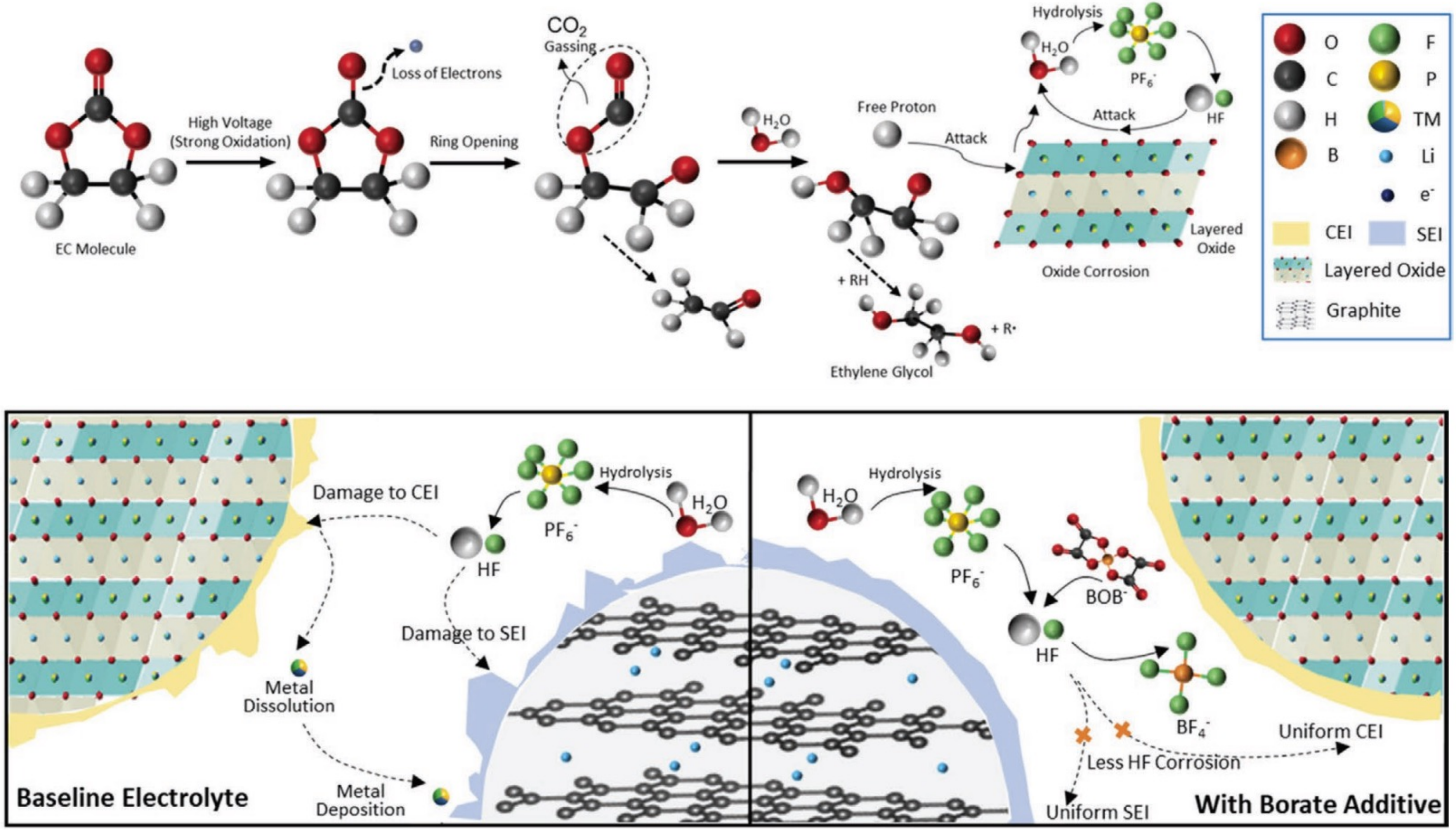
95% active mass ratio

Cathode areal capacity (mAh/cm^2)	Cell level energy density (Wh/kg)
4	356
10	386
20	398

With Si/C as anode

90% active mass ratio

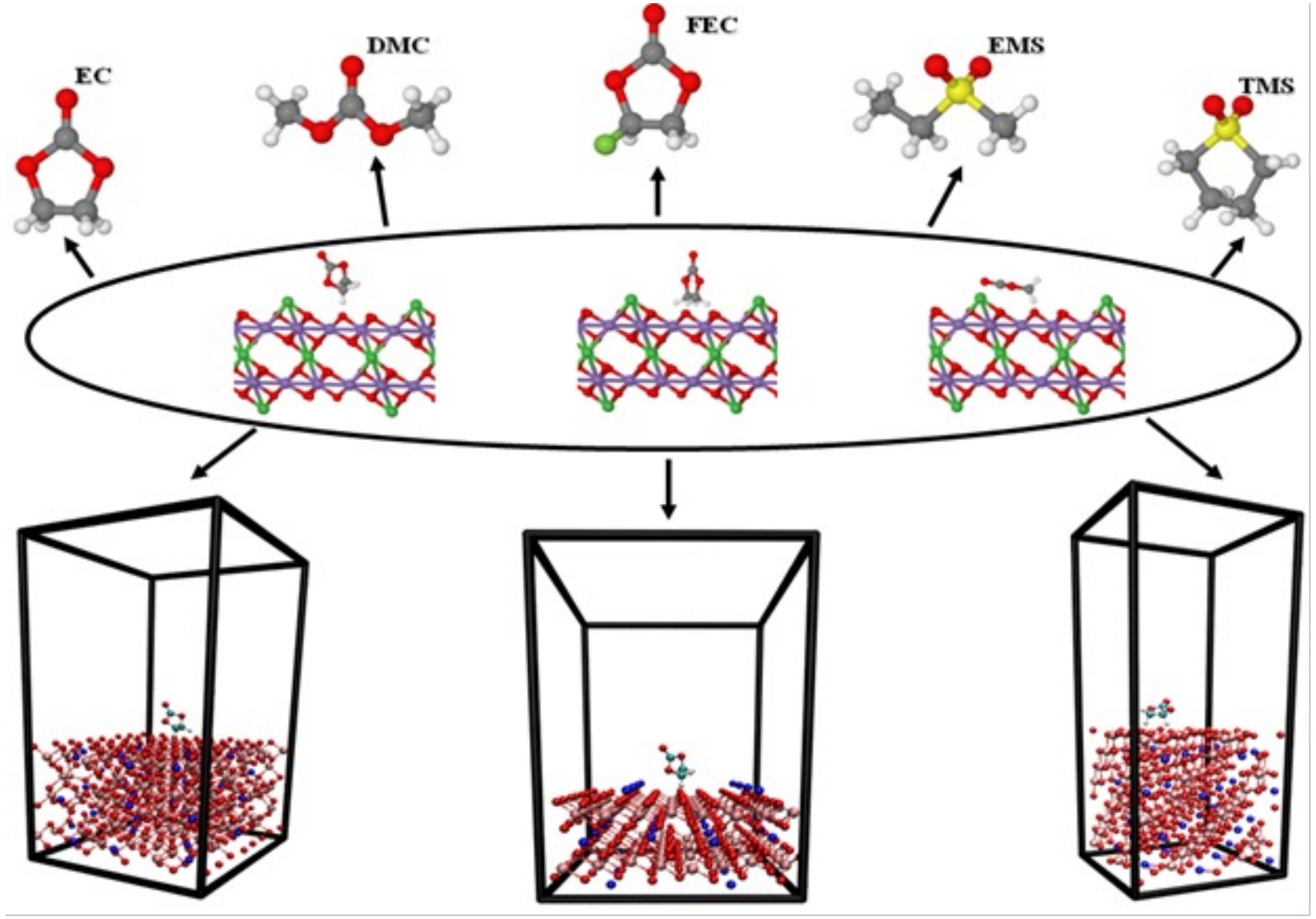
Carbonated-based Electrolyte Degradation Mechanism at High Voltage



- Electrons are extracted from EC molecules and lead to ring opening. Generation of free proton will occur with the participation of a trace amount of H_2O in the fresh electrolyte.
- The H_2O hydrolyze the $LiPF_6$ salt or PF_5 in the electrolyte and form HF, which would, in turn, corrode the CEI and the oxide cathode to generate even more H_2O.
- B based coatings or additives can serve as HF scavenger by preferentially reacting with HF.

Li, Yixuan, *et al*. "Elucidating the Effect of Borate Additive in High-Voltage Electrolyte for Li-Rich Layered Oxide Materials." Advanced Energy Materials 12.11 (2022): 2103033.

Electrolyte Decomposition Pathway and Fluorinated Electrolyte



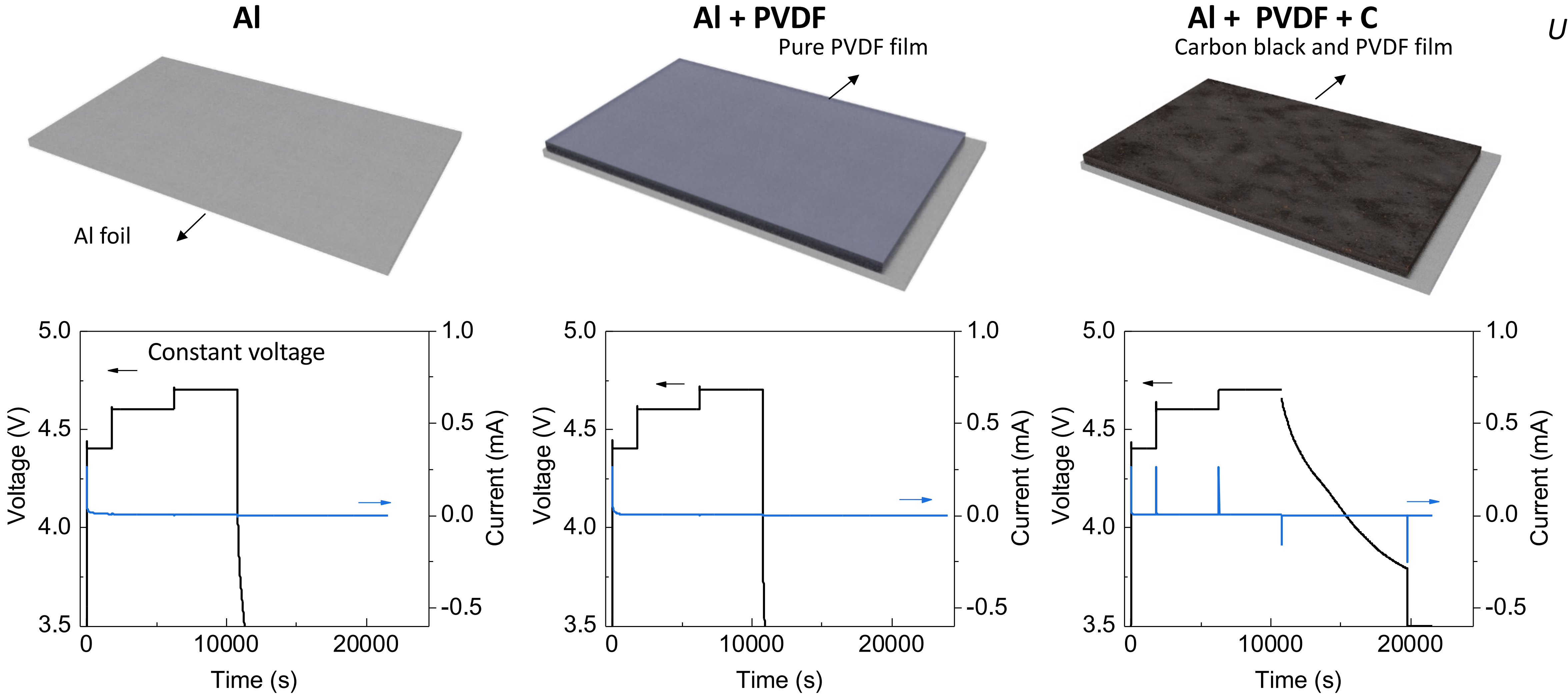
Unpublished Results from Meng's Group

- Deprotonation of electrolyte molecule energetically preferred to ring opening.
- FEC predicted to be most resistant to decomposition (highest reaction barrier).
- Reaction barrier generally higher for (111) facets.
- (100) promotes electrolyte decomposition, protonation of TM oxide surface.

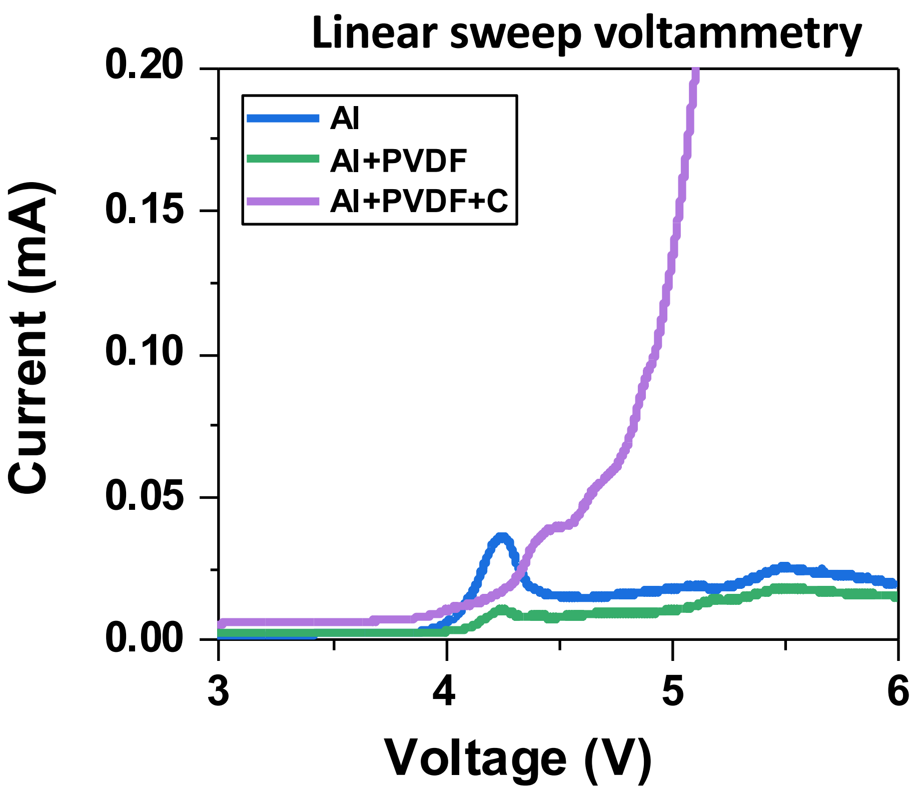
$Ni_{0.5}Mn_{1.5}O_4$(100) Fd3m	EC	DMC	FEC	TMS	EMS
Reaction Barrier (eV)	0.45	0.59	0.77	0.61	0.53
Reaction Energy (eV)	-1.53	-0.84	-1.30	-0.80	-1.00
$Ni_{0.5}Mn_{1.5}O_4$(111) Fd3m	EC	DMC	FEC	TMS	EMS
Reaction Barrier (eV)	0.54	0.80	0.90	0.51	0.87
Reaction Energy (eV)	-0.81	-0.20	-0.72	-0.37	-0.36

Parasitic Reactions Triggered by Carbon Additive

Unpublished results from Meng group



Simulated “charge and discharge” process for inactive components

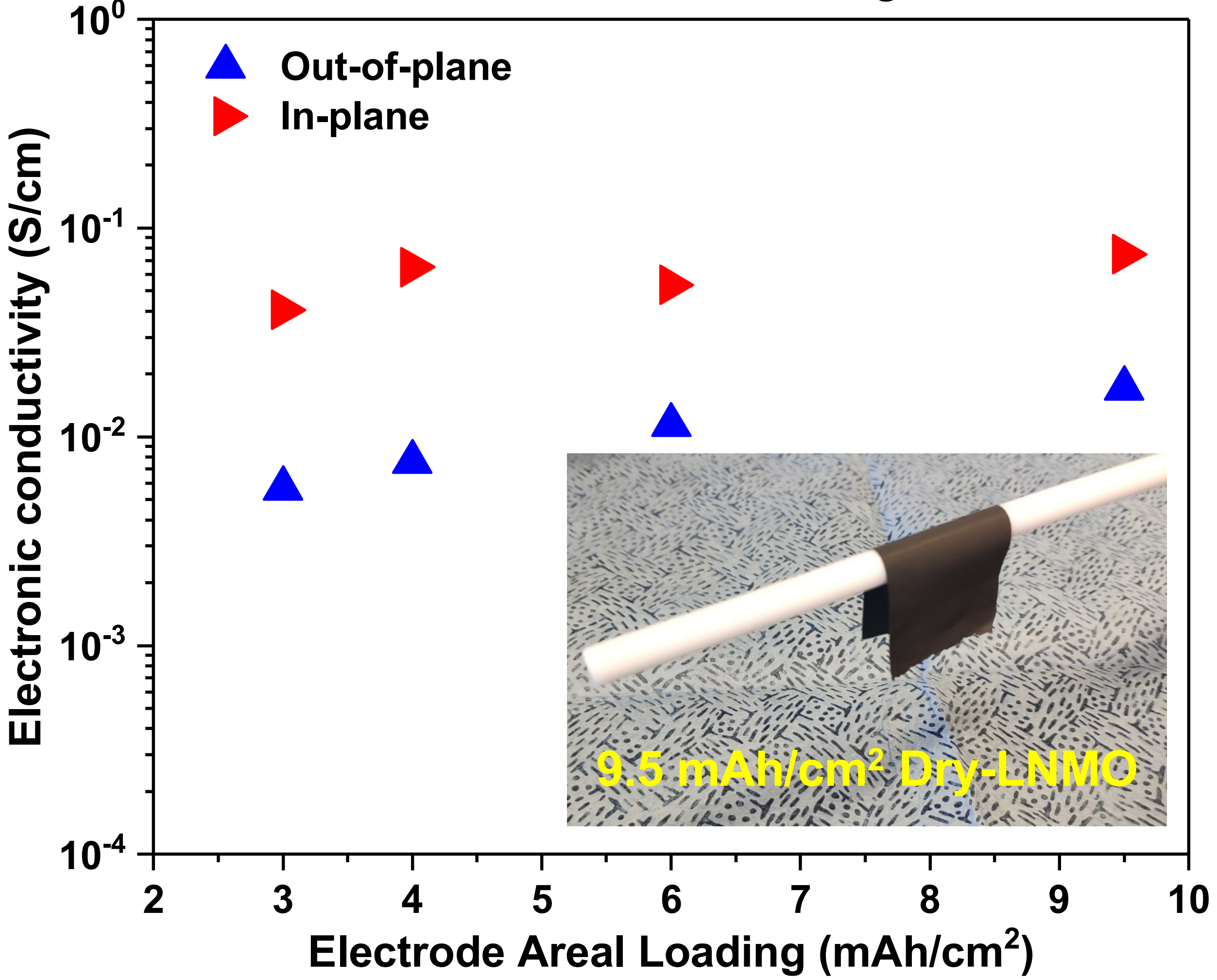


- All inactive components were evaluated via simulated charge-discharge process, and the presence of carbon resulted in obvious parasitic current.
- LSV also confirmed that the carbon would cause side reactions when charged to high voltage.

Critical Electronic Conductivity Testing

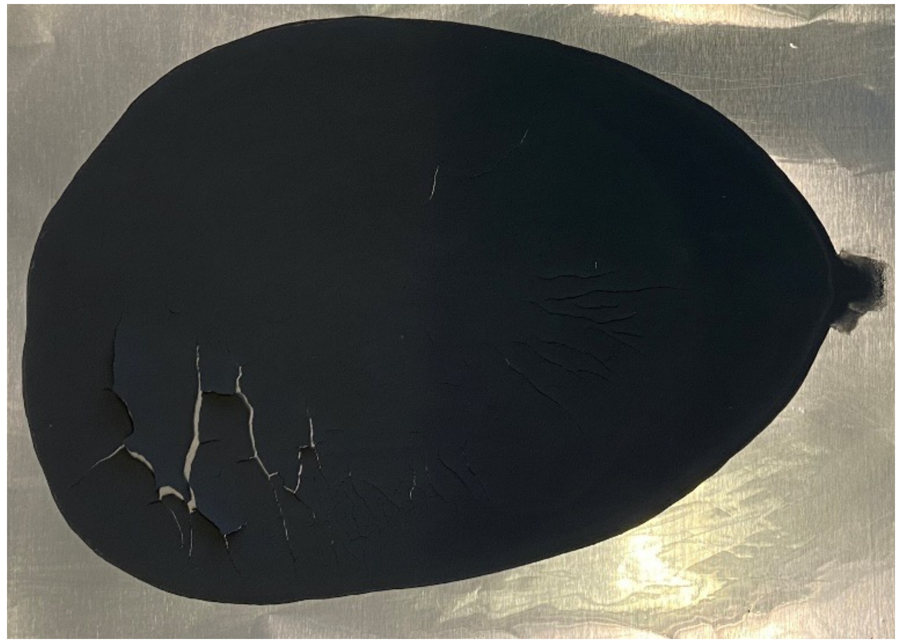
Yao, Weiliang, *et al.* Energy & Environmental Science (2023).

Conductivity testing results for dry electrodes with various areal loadings.

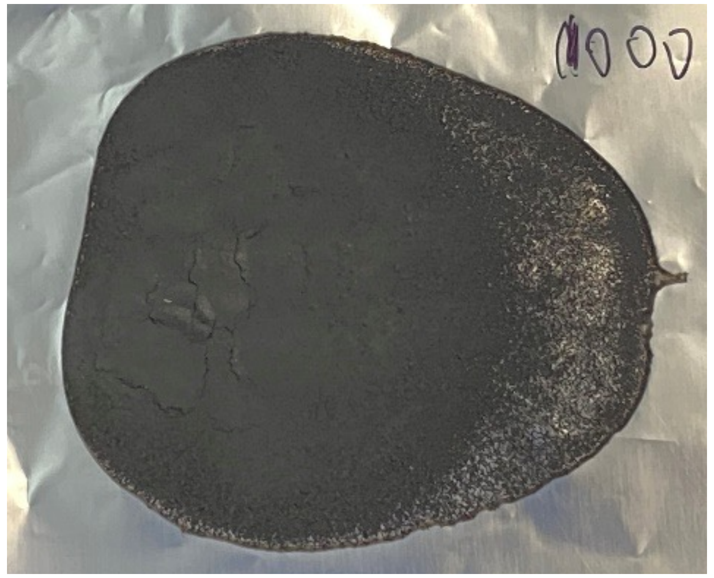


Mass ratio of LNMO: Binder: carbon = 93:2:5

6 mAh/cm^2 level slurry-based LNMO (with SC65)

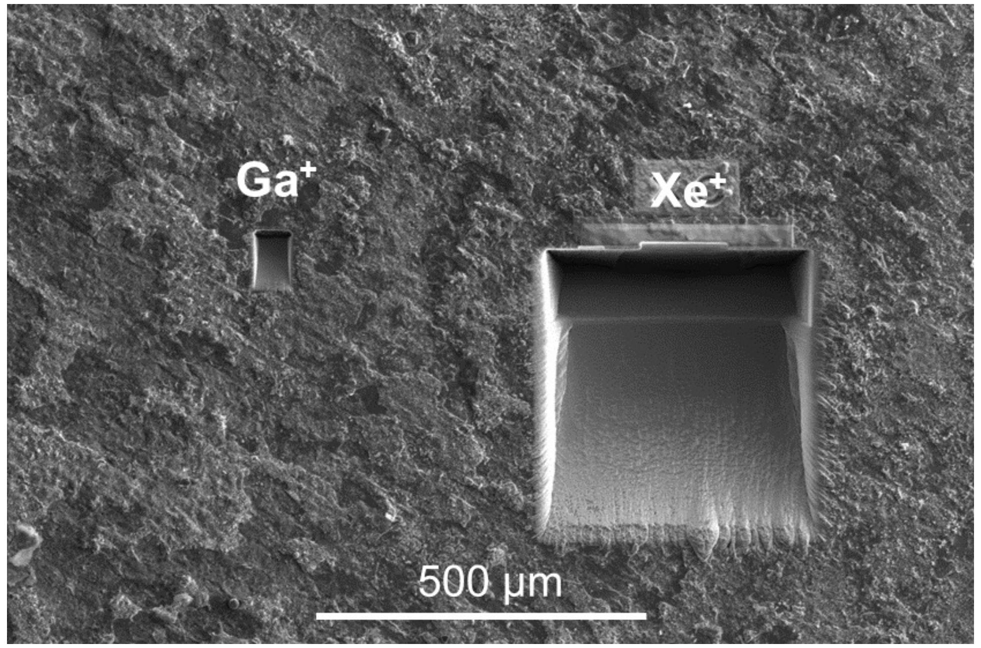


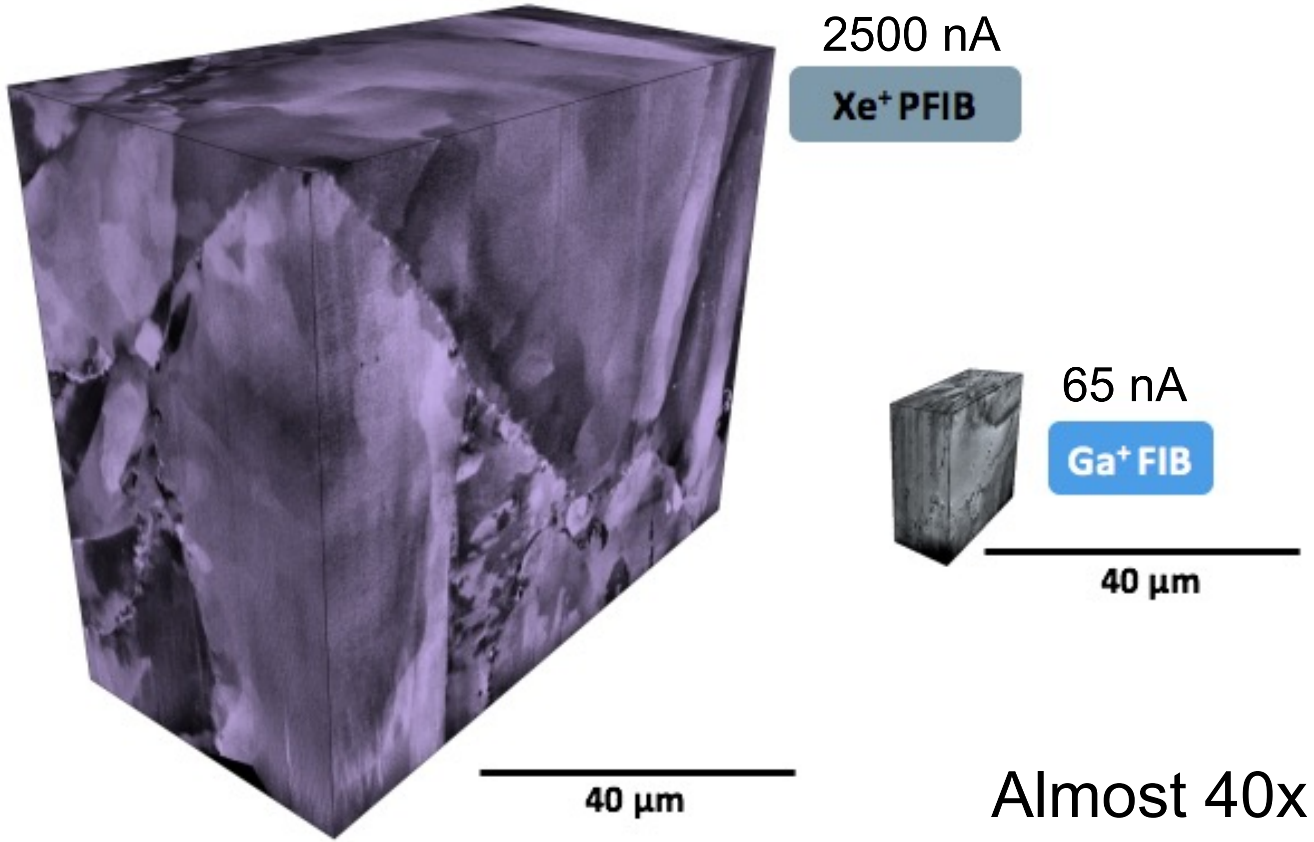
6 mAh/cm^2 level slurry-based LNMO (with VGCF)

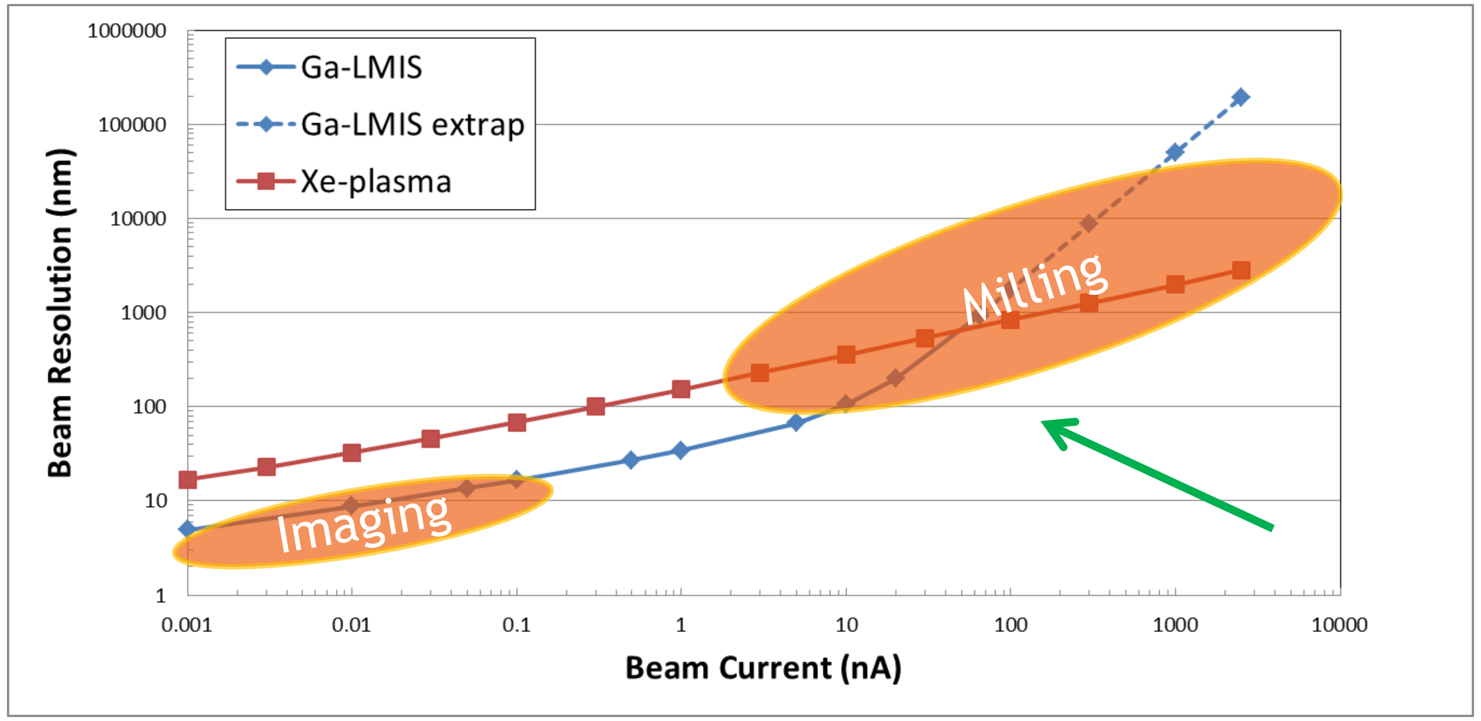


Unlike slurry-based LNMO showing cracks at 6 mAh/cm^2 level, dry-LNMO is still robust with constant electronic conductivity values in both directions.

Quantitative Analysis of Large Volume Thick Electrode







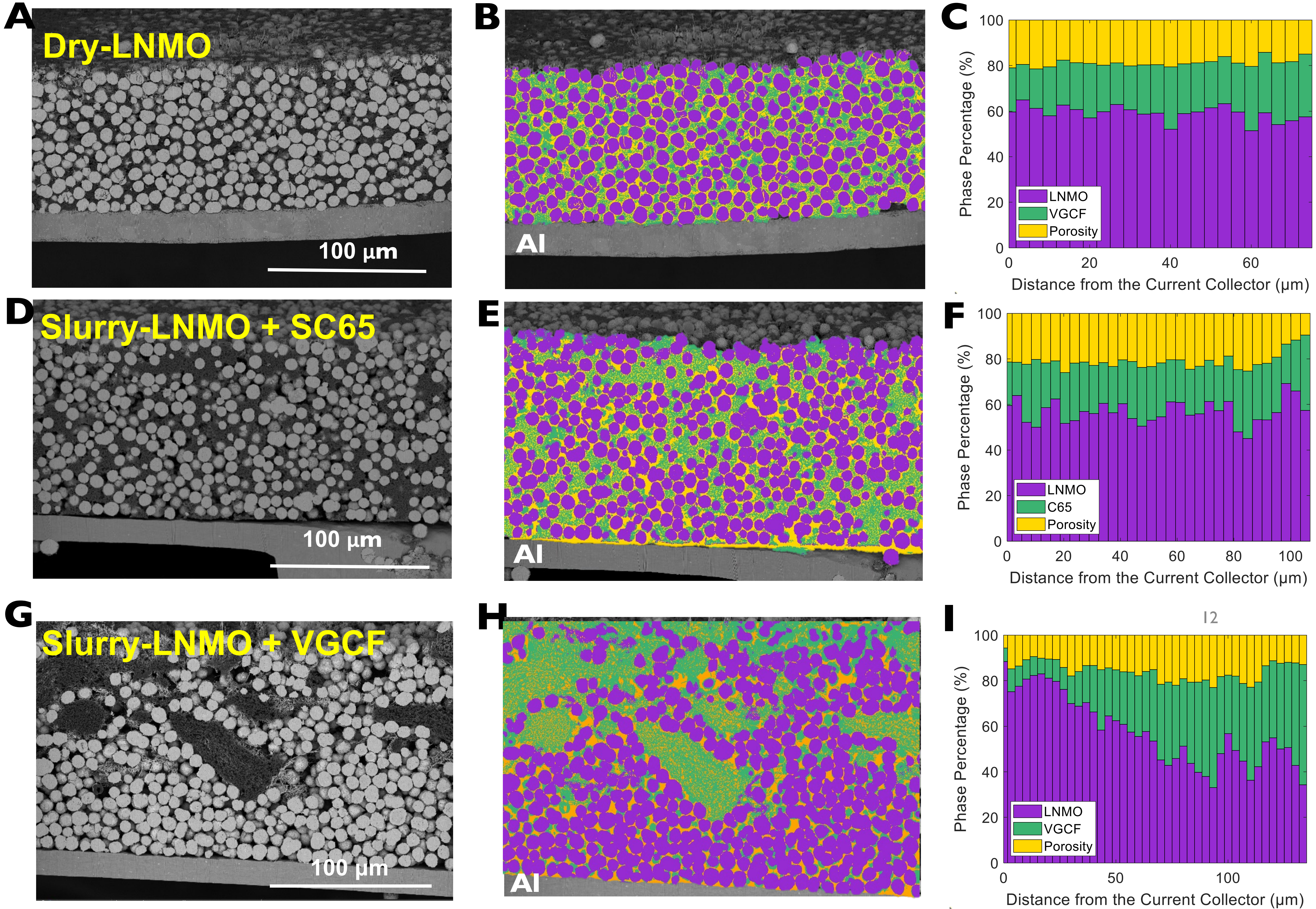
- Both systems offer excellent ion beam performance;
- Gallium offers the lowest accelerating voltages (down to 500 V);
- Plasma offers the highest beam current (2.5 µA) and Ga-free milling.

Almost 40x more beam current

Credits to Thermo Fisher Scientific

PFIB and Phase Segmentation of Electrodes

Yao, Weiliang, *et al.* Energy & Environmental Science (2023).

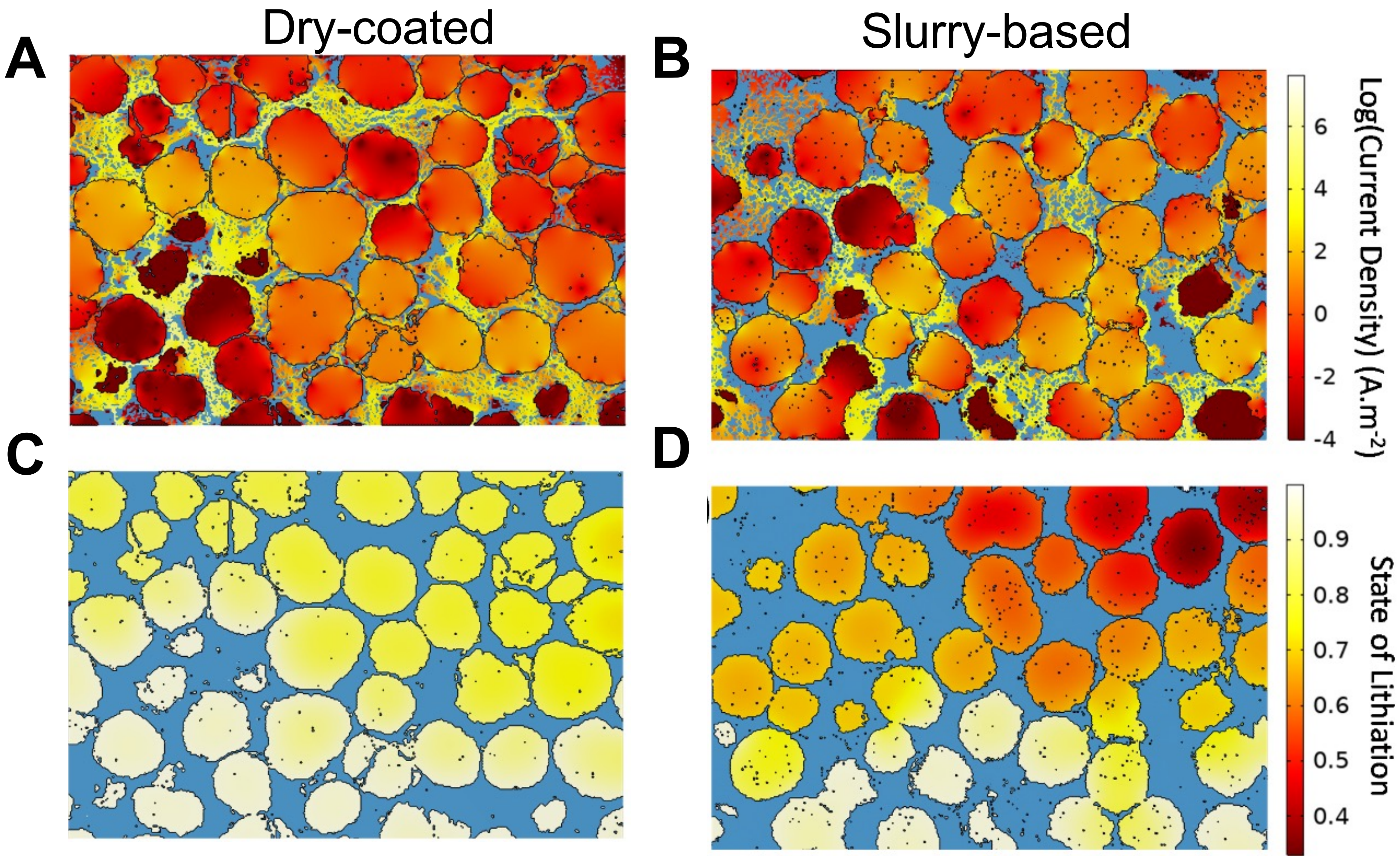


Mass ratio of LNMO: Binder: carbon = 93:2:5

More uniform carbon distribution in dry electrodes compared to slurry-based. Slurry-based method (lab scale) cannot disperse the VGCF well compared to SC65 (nano-agglomerate type carbon). Unlike PTFE, PVDF is difficult to identify in SEM-EDS due to peak overlap with Mn.

2D Modeling of Thick Electrode

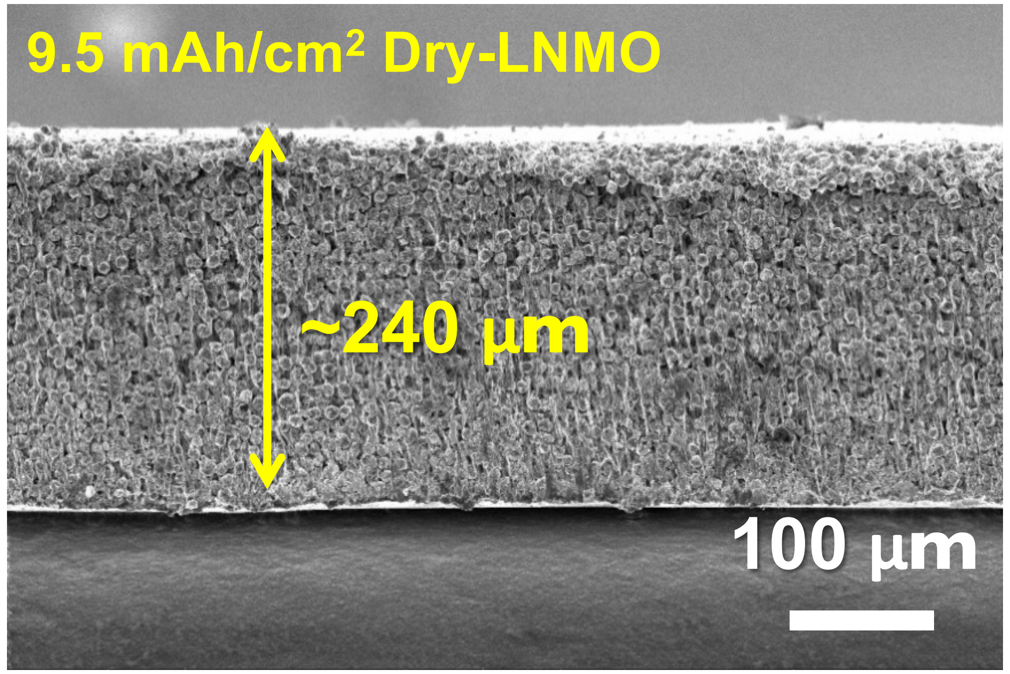
Yao, Weiliang, *et al.* Energy & Environmental Science (2023).

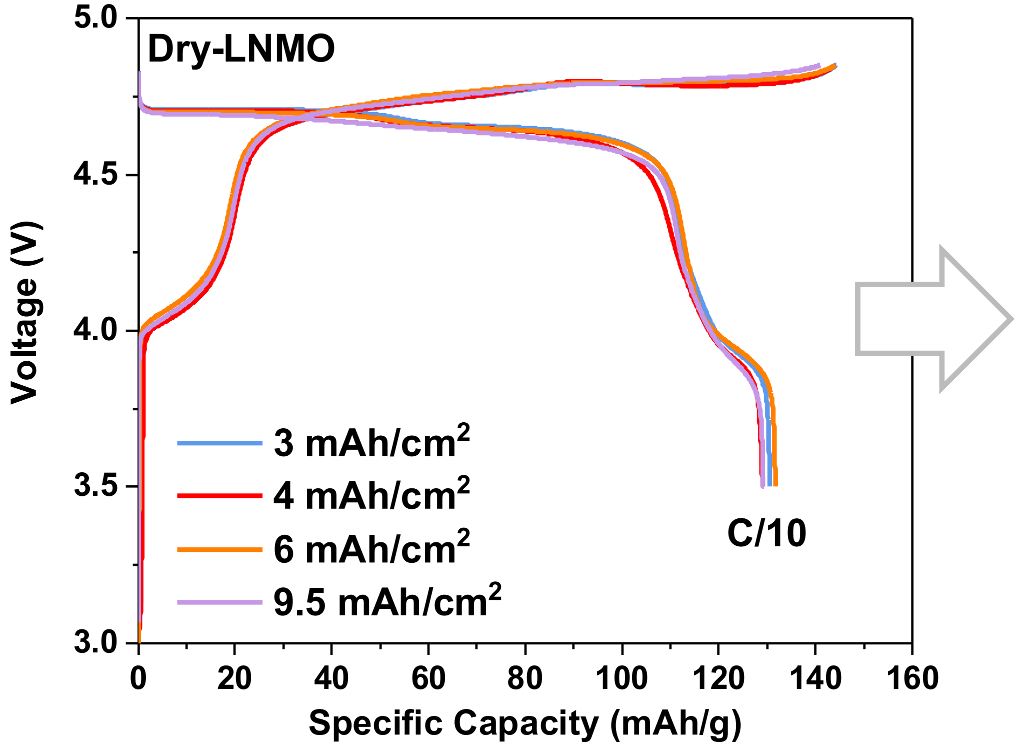


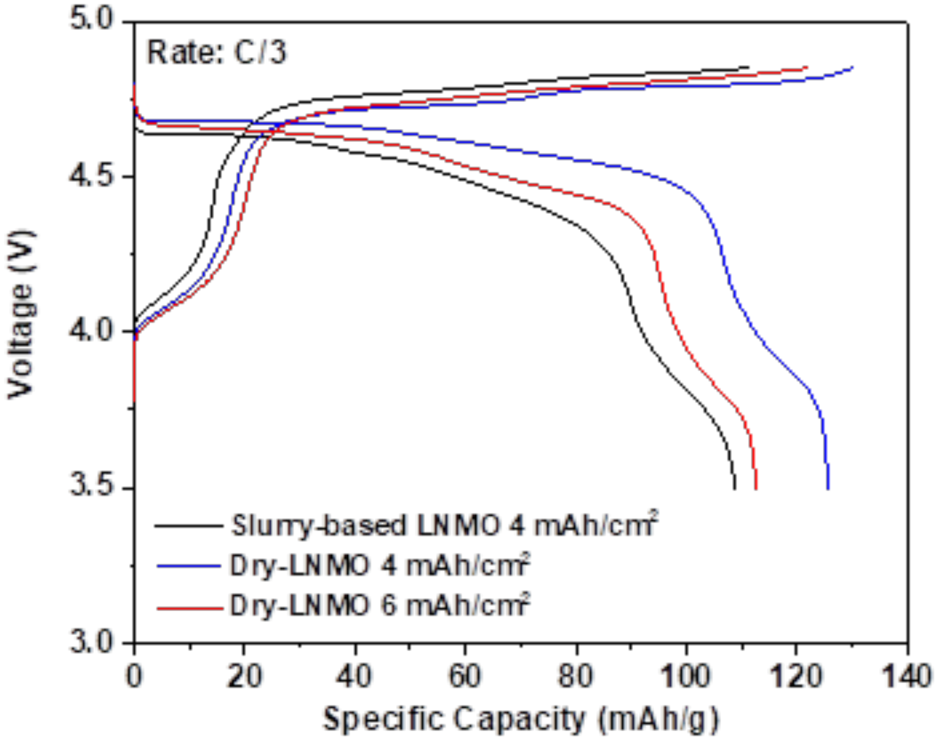
The current density in the solid phase and the state of lithiation reported for the dry-LNMO respectively in (A, C), and for the slurry-based LNMO respectively in (B,D).

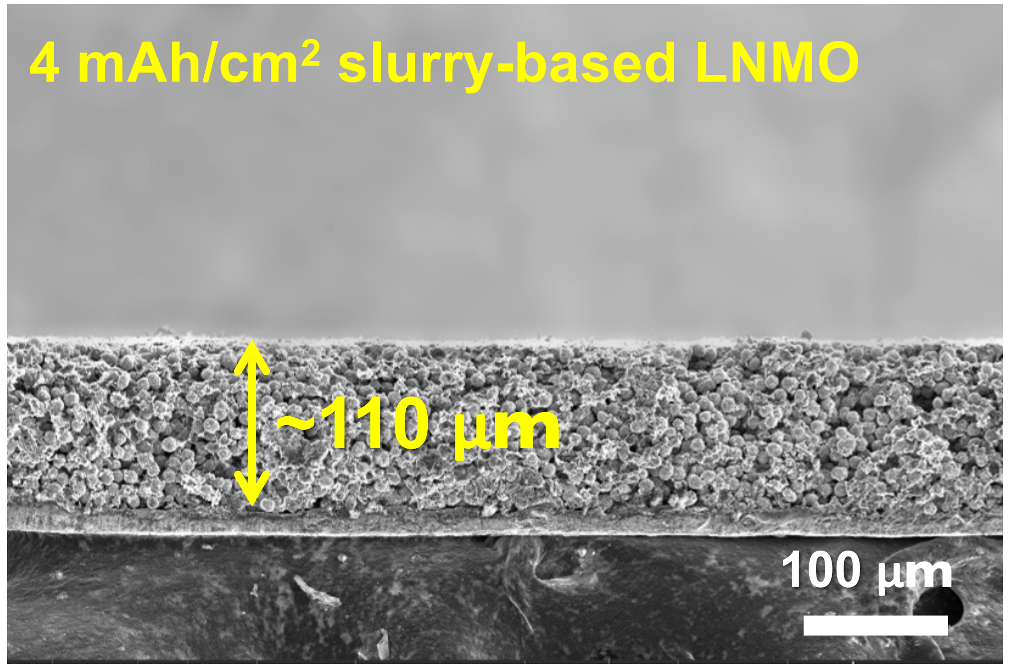
- 2D simulation based on discharge.
- More efficient electron transport in the dry electrodes compared to slurry-based LNMO.
- More homogenous lithiation process during cycling, leading to longer cycle life.

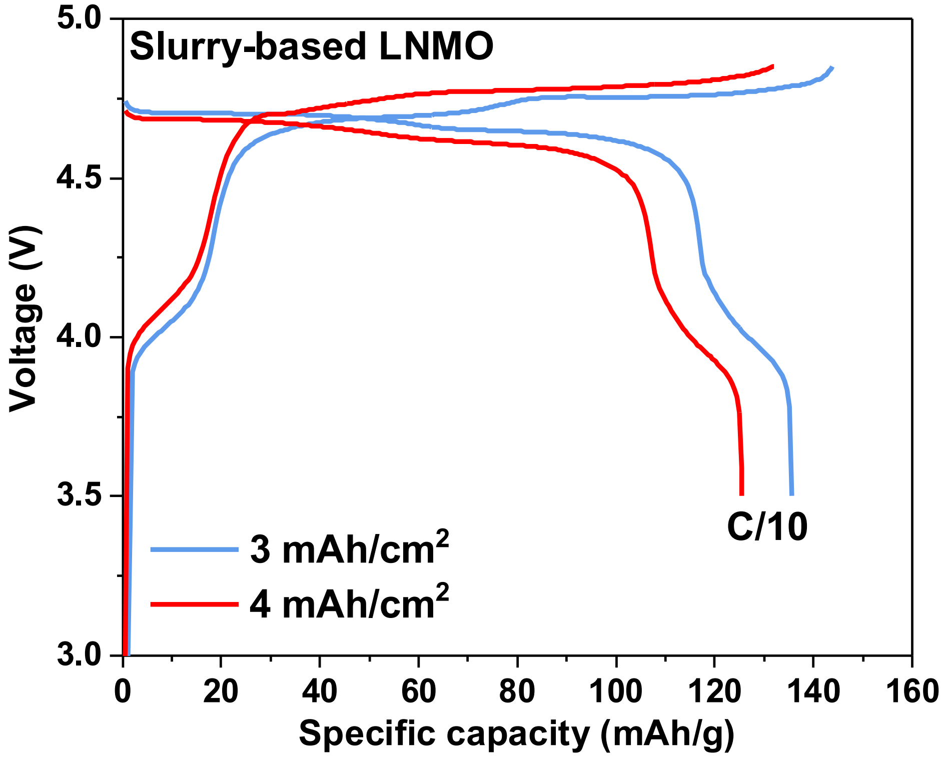
Half Cell Electrochemical Performance











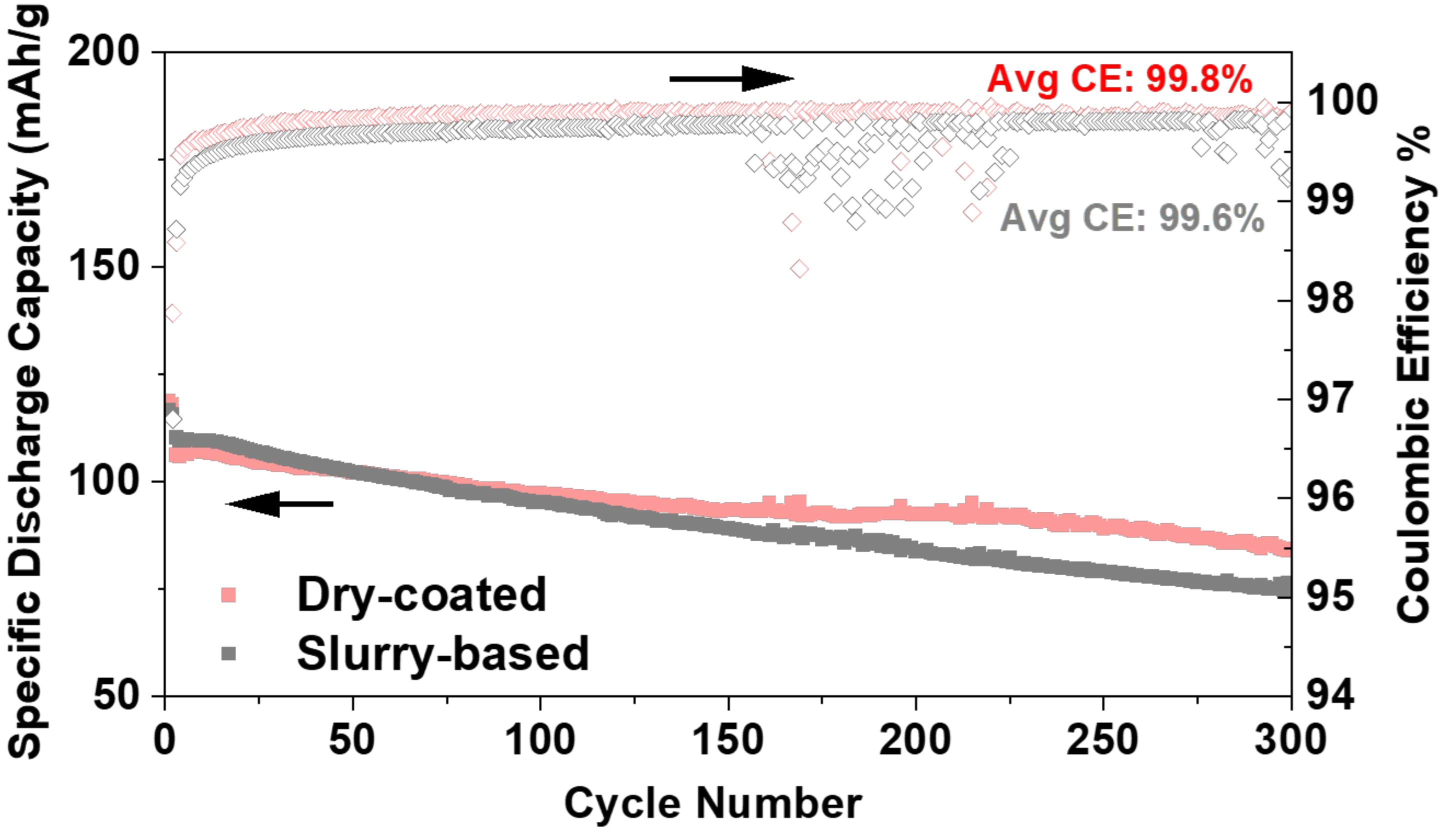
Testing conditions:

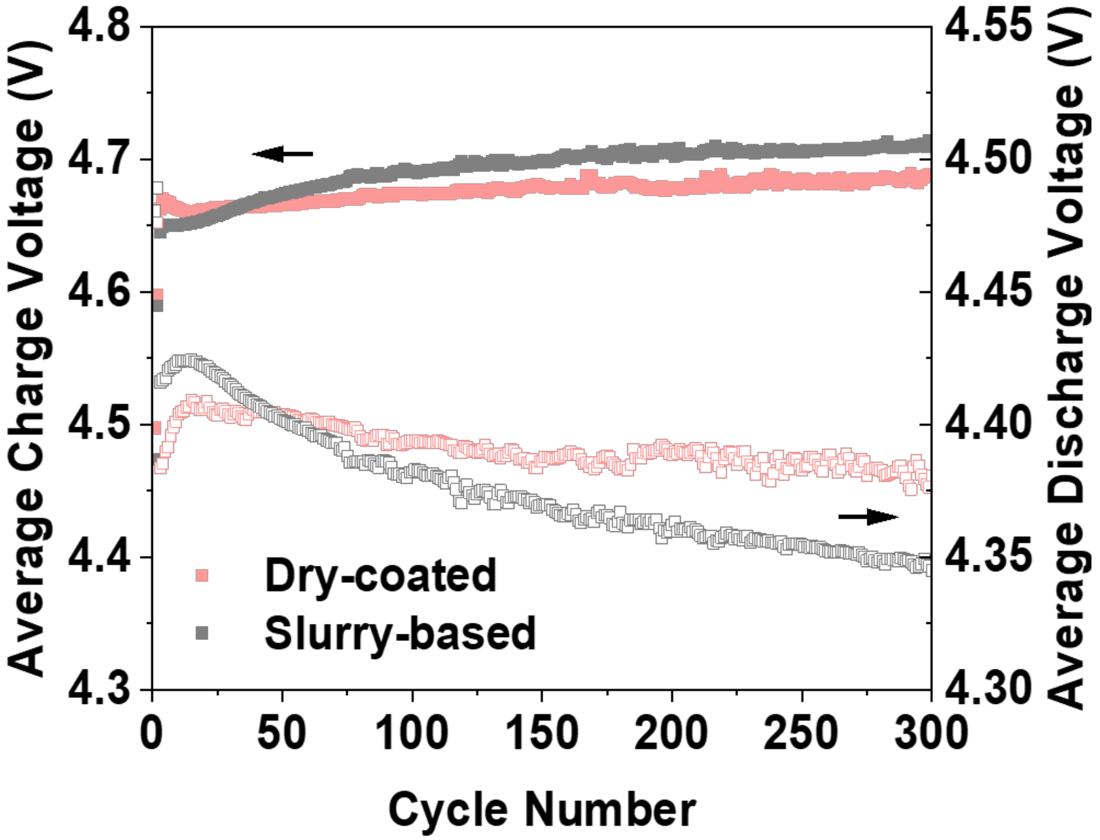
- LNMO:PTFE:VGCF = 93:2:5; LNMO:PVDF:SC65 = 93:2:5
- Gen2 electrolyte (1M $LiPF_6$ in EC:EMC = 3:7 wt%)
- 1-mm Li metal in coin cells.

With robust mechanical strength and well distributed carbon and binder, the dry-LNMO unsurprisingly outperform slurry-based electrodes with ultra-high loading.

1. Yao, Weiliang, *et al*. "A 5V-class Cobalt-free Battery Cathode with High Loading Enabled by Dry Coating." Energy & Environmental Science (2023).
2. CATHODES FOR HIGH VOLTAGE LITHIUM-ION SECONDARY BATTERY AND DRY METHOD FOR MANUFACTURE OF SAME. FL0670-US02-PRV

Full Cell Electrochemical Performance with Gen2 Elyt





Testing conditions:

- LNMO:PTFE:VGCF = 93:2:5; LNMO:PVDF:SC65 = 93:2:5
- Gen2 electrolyte (1M $LiPF_6$ in EC:EMC = 3:7 wt%)
- 3 mAh/cm^2 level cathode and graphite in coin cells.

- Dry-LNMO full cells at 3 mAh/cm^2 level with commercial Gen2 electrolyte can achieve 80% capacity retention after 300 cycles. In contrast, slurry-based LNMO full cells can only achieve 67%.
- Faster CE% in dry-LNMO full cell and stable voltage hysteresis show faster interphase passivation which can be attributed to the use of low surface area carbon.

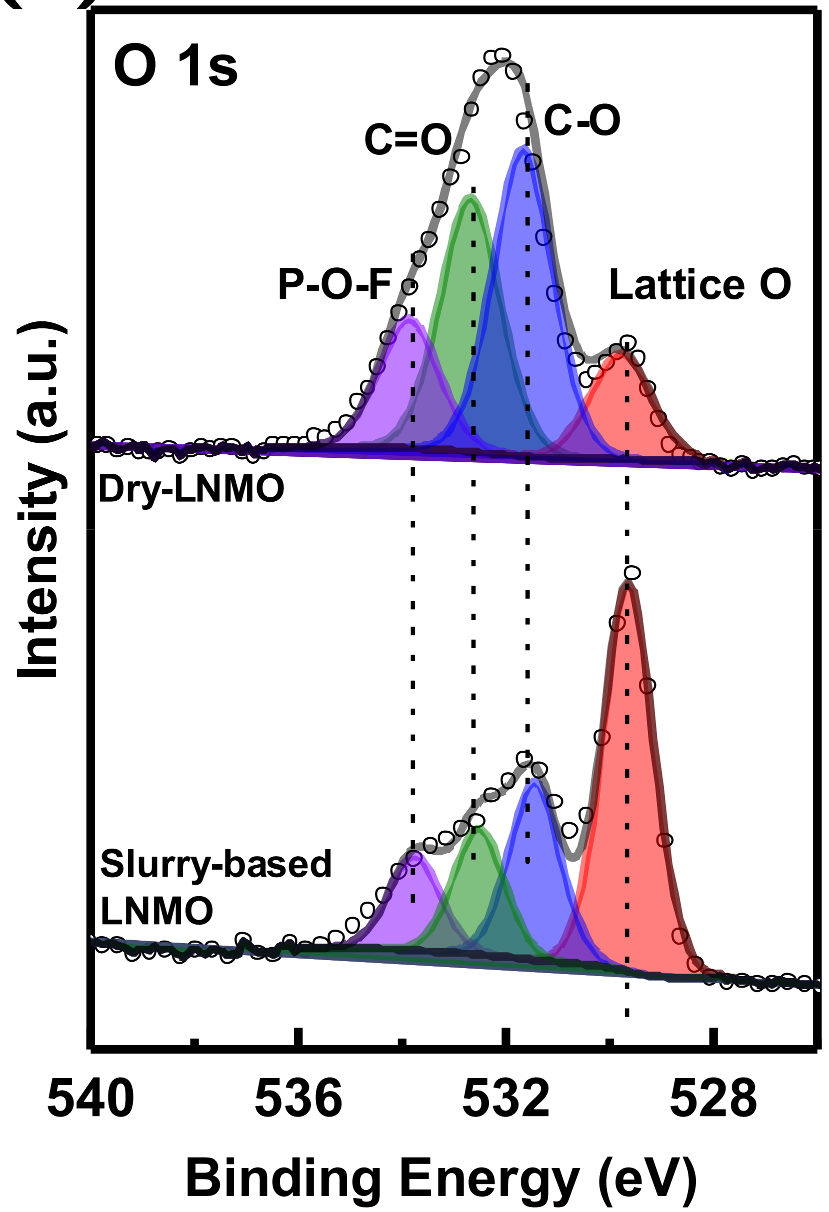
Yao, Weiliang, *et al*. "A 5V-class Cobalt-free Battery Cathode with High Loading Enabled by Dry Coating." Energy & Environmental Science (2023).

Post-mortem Analysis Using XPS and HRTEM

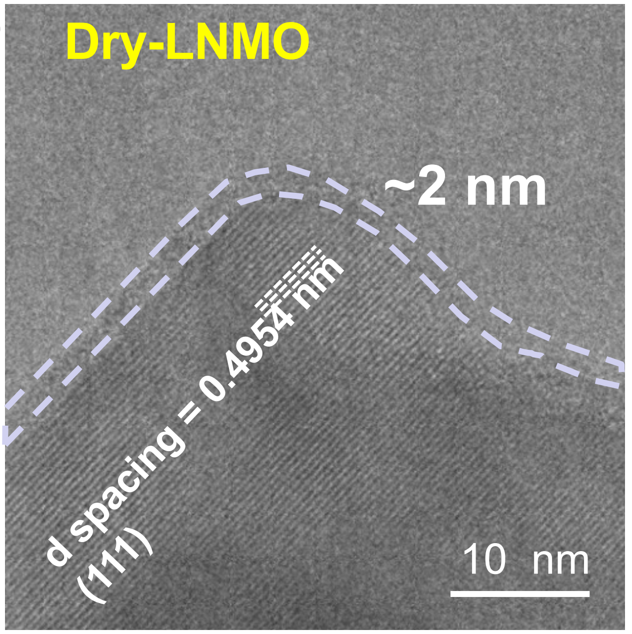
Yao, Weiliang, *et al.* Energy & Environmental Science (2023).

Cycled Cathode

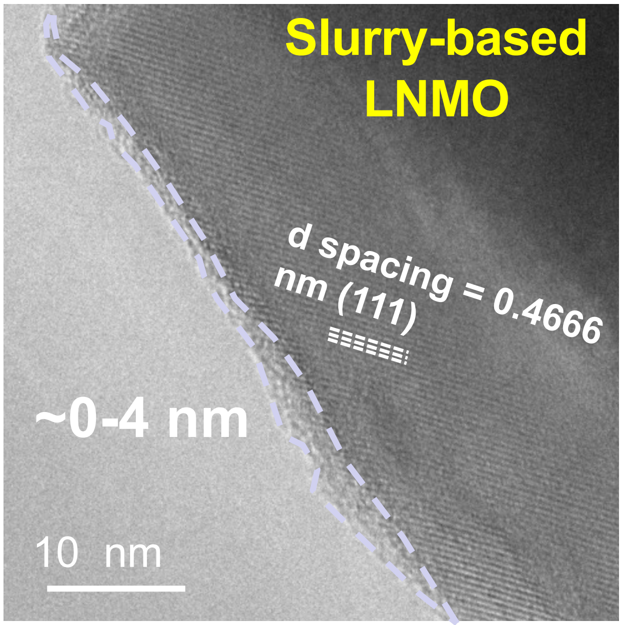
(A)



(B)

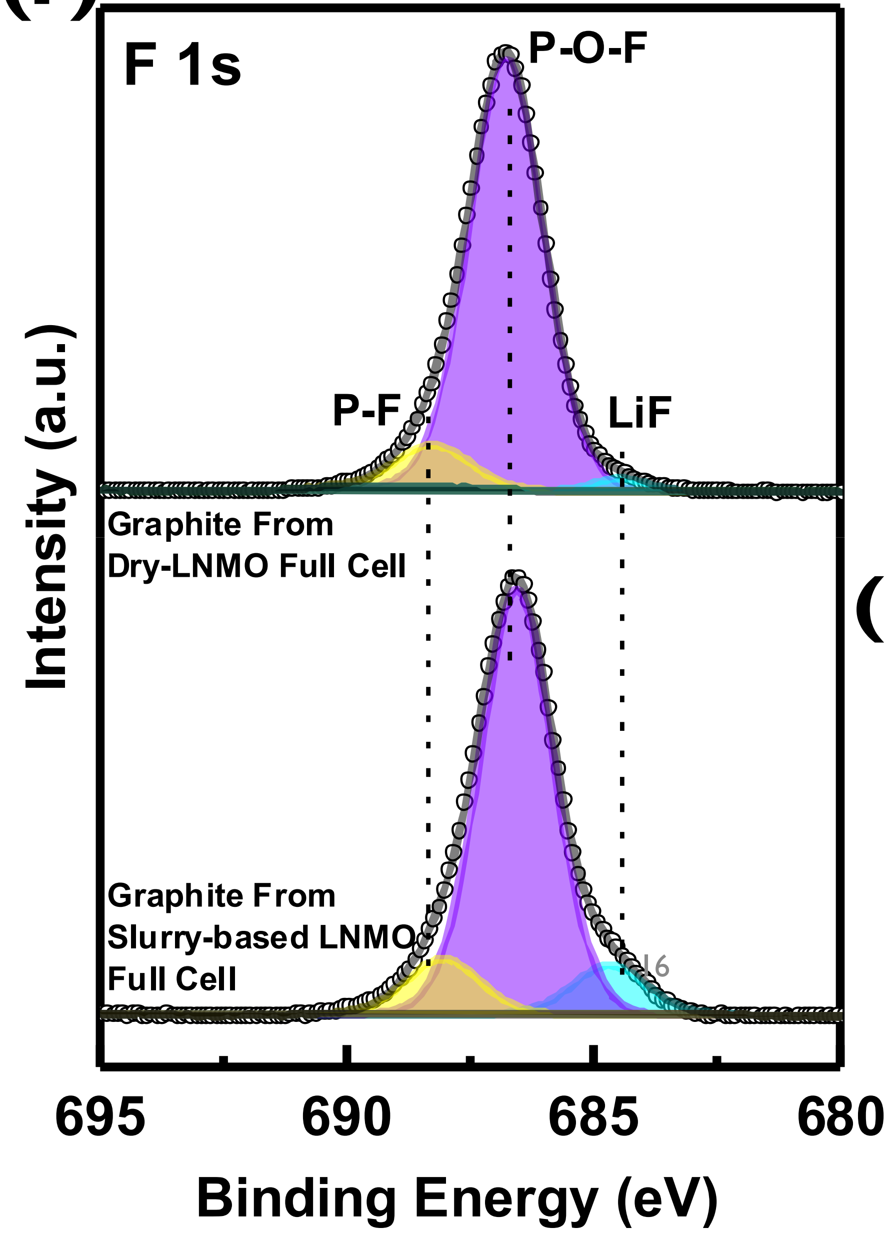


(C)

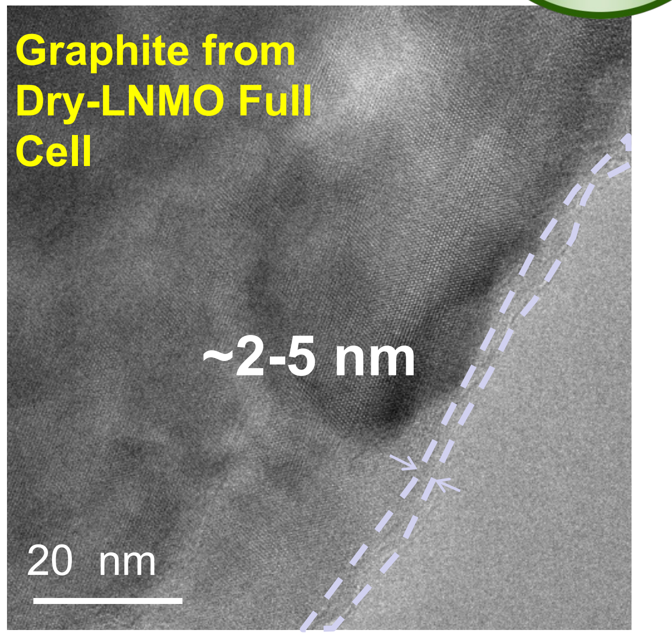


Cycled Graphite

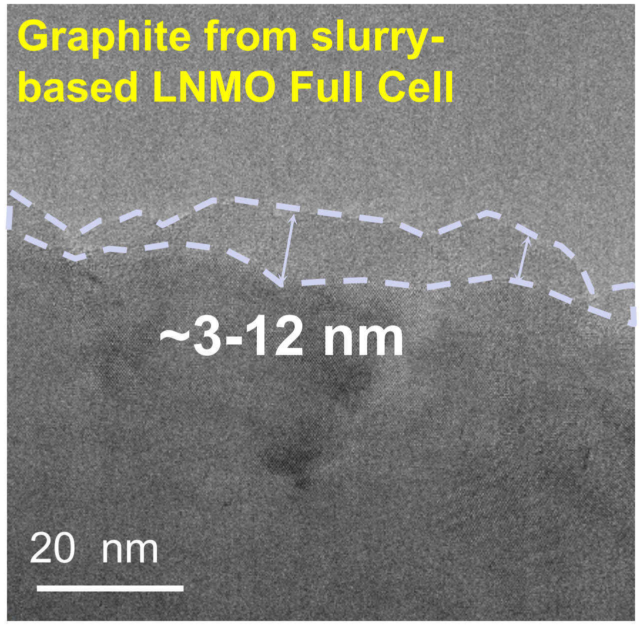
(F)



(G)

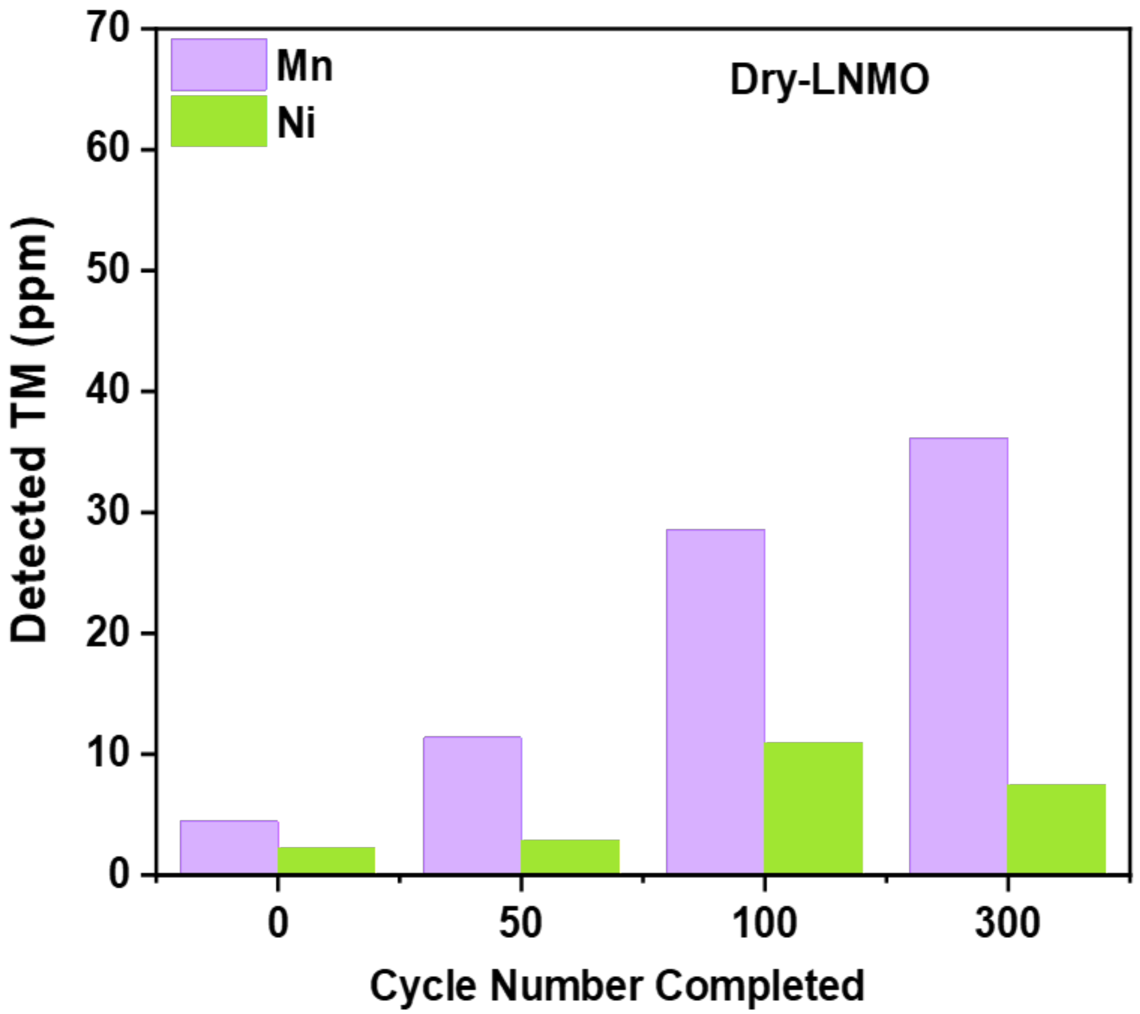


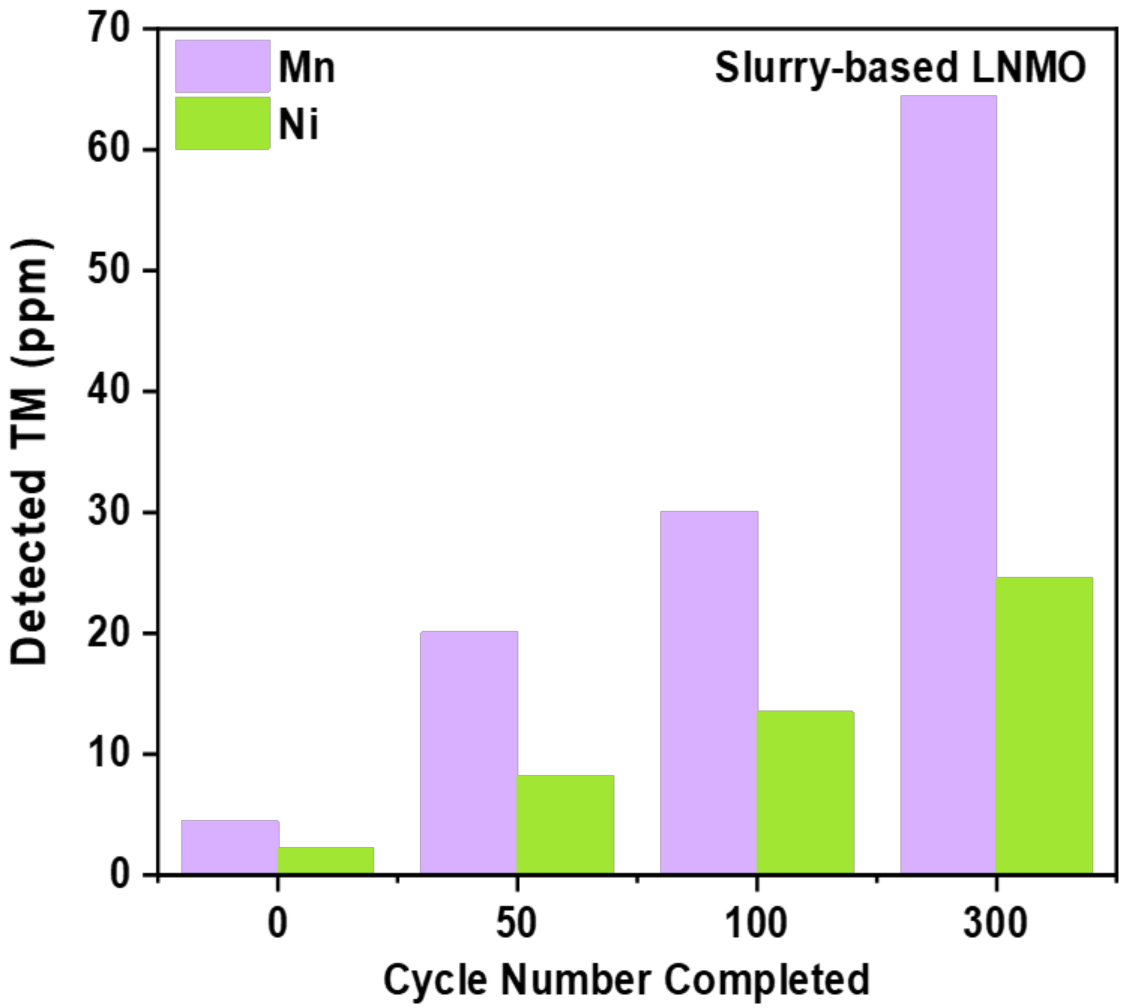
(H)



- Lattice O peak of dry-coated is smaller than the slurry-base LNMO. The dry-coated LNMO could have a thicker CEI. It is also possible that the CEI in the slurry-base is not as uniform as dry-coated. This has been verified by TEM.
- Thicker SEI and more LiF in slurry-base graphite also implies more Li inventory loss and more salt decomposition.

Post-mortem Analysis: ICP of Cycled Graphite





The continuous generation of HF from slurry-based LNMO full cells will keep attacking the LNMO surface and trigger more TM dissolution.

$LiPF_6 \leftrightarrow LiF + PF_5$ Equation 1

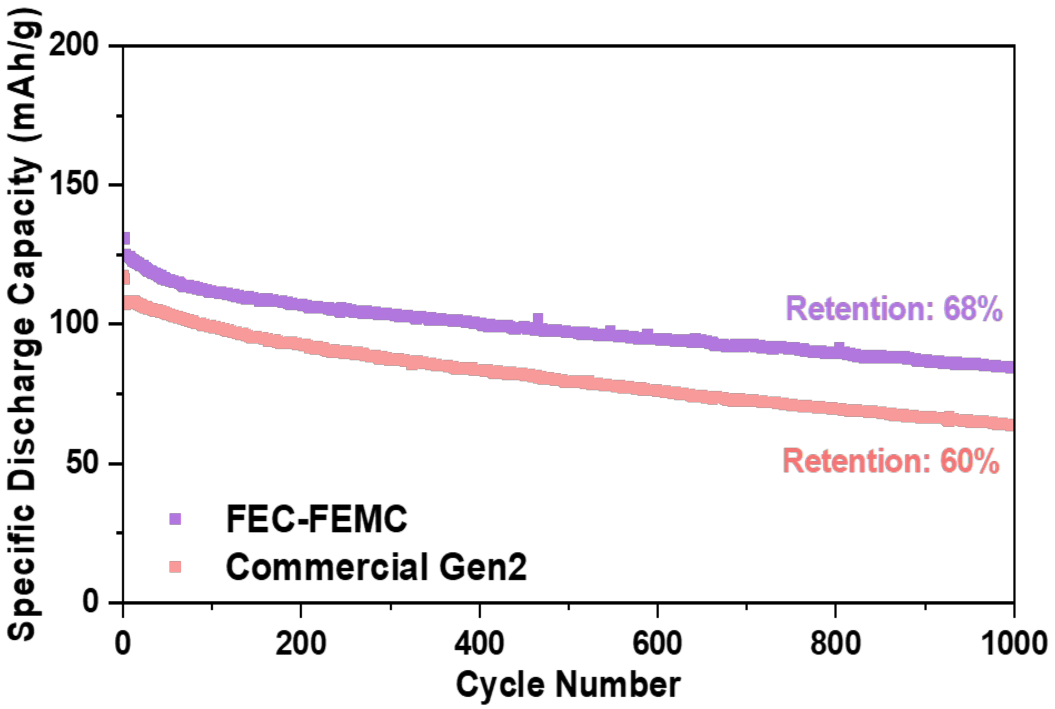
$PF_5 + H_2O \rightarrow OPF_3 + 2\mathbf{HF}$ Equation 2

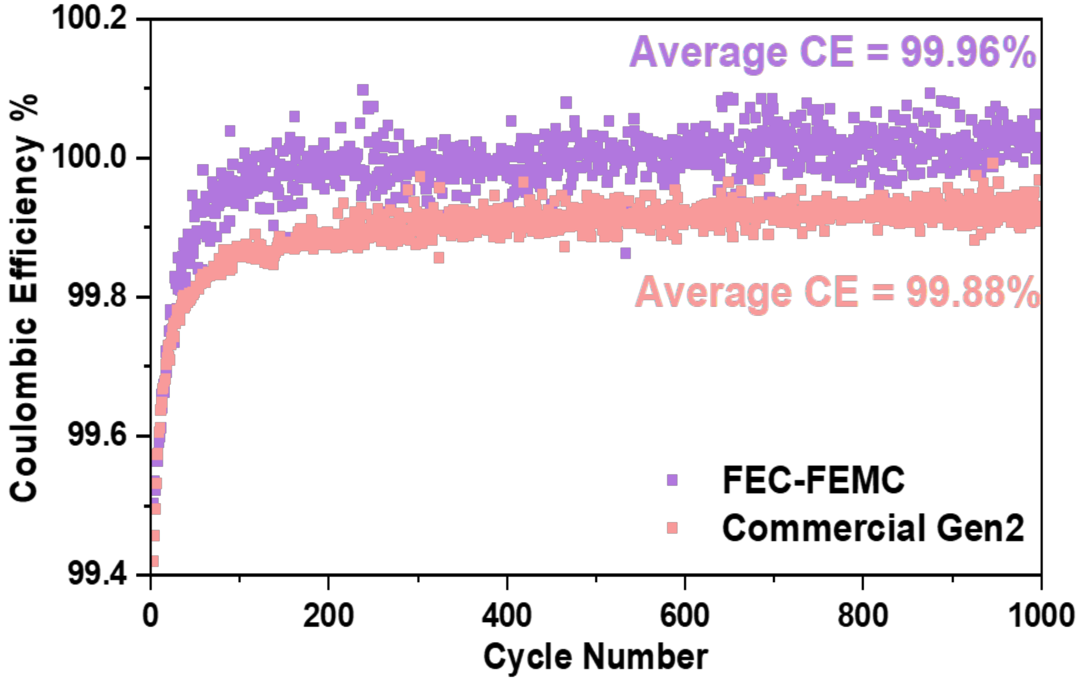
$OPF_3 + 2xLi^+ + 2xe^- \rightarrow Li_xPF_{3-x}O + xLiF$ Equation 3

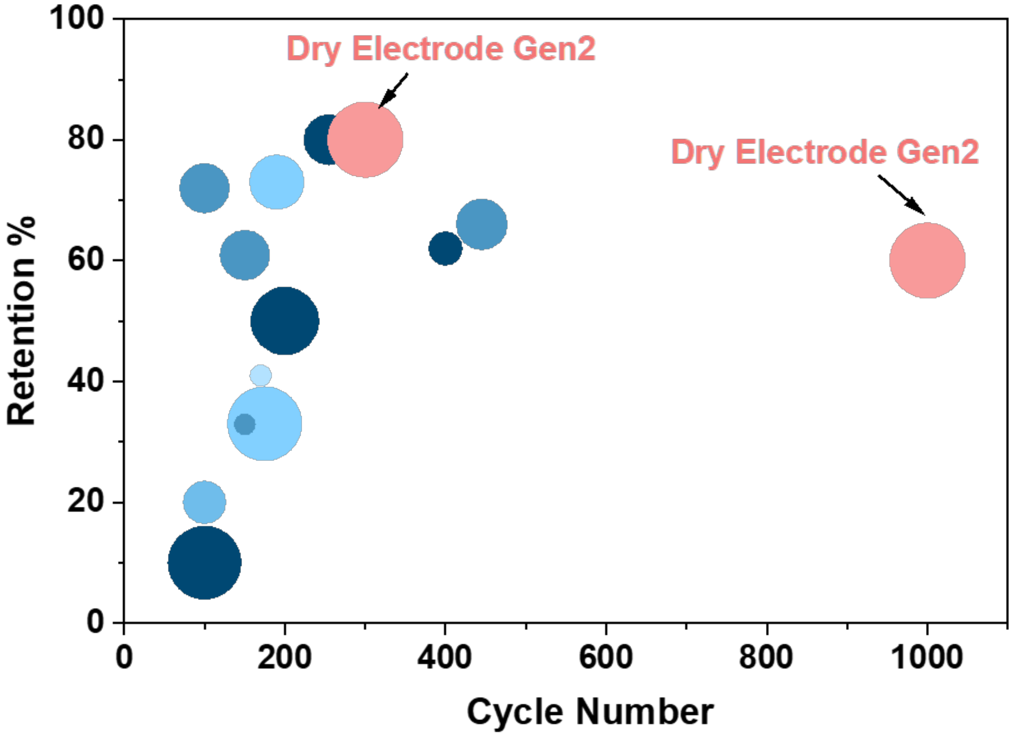
$OPF_3 + 3H_2O \rightarrow PO_4H_3 + 3\mathbf{HF}$ Equation 4

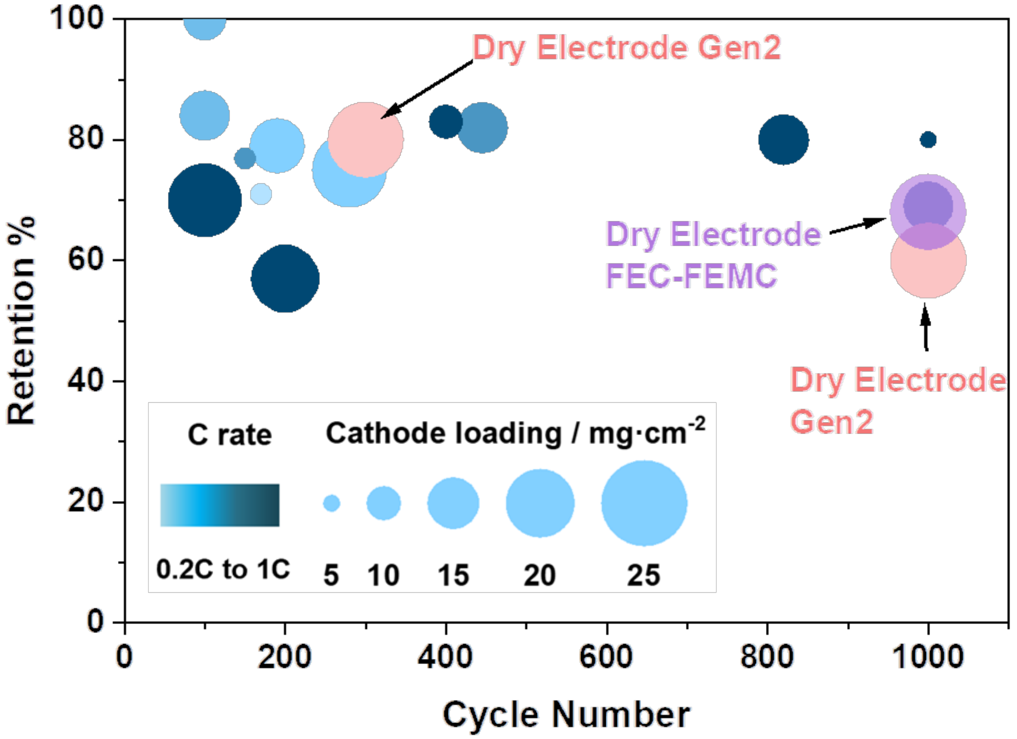
Yao, Weiliang, *et al*. "A 5V-class Cobalt-free Battery Cathode with High Loading Enabled by Dry Coating." Energy & Environmental Science (2023).

Cycling Performance Comparison with Literature





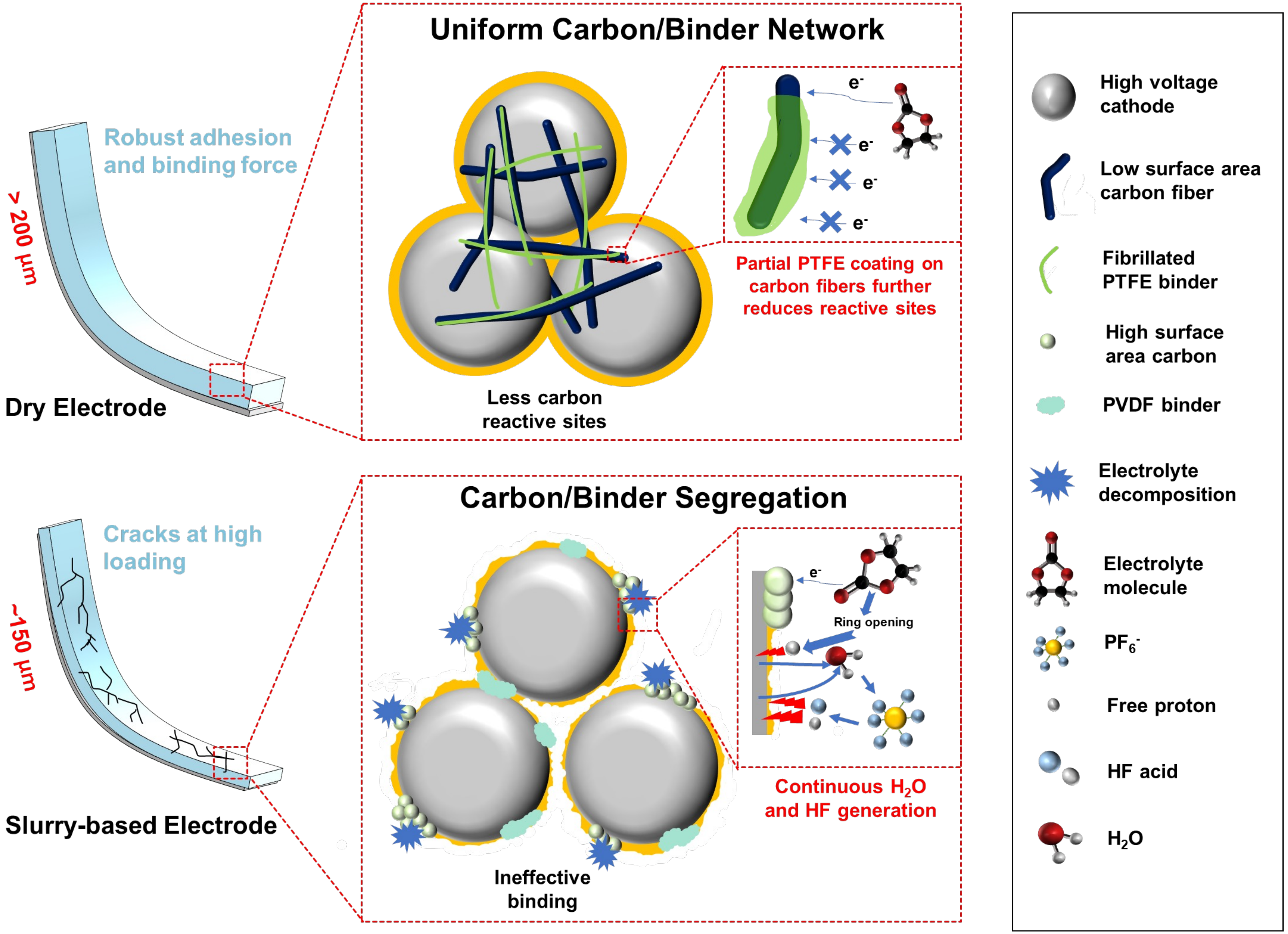




- Both Gen2 (1M $LiPF_6$ in EC:EMC = 3:7 wt%) and FEC-FEMC (1M $LiPF_6$ in FEC:FEMC = 3:7 wt%) were used for long term cycling testing.
- C/3 rate is used and the loading of dry electrode is 3 mAh/cm^2 (~21 mg/cm^2).
- Long-term cycling performance using both Gen2 and FEC-FEMC chemistries outperform literature values in terms of both mass loading and capacity retention.
- Faster passivation is the key of stable high voltage LIBs cycling, as seen from the faster CE% rise from the beginning.

Yao, Weiliang, *et al*. "A 5V-class Cobalt-free Battery Cathode with High Loading Enabled by Dry Coating." Energy & Environmental Science (2023).

Advantages of High Voltage Dry Electrodes



- Dry electrode can easily achieve electrode thickness > 200 µm with robust mechanical strength.
- Using carbon fibers can not only build a good electronic conductive network, but can also reduce side reactions impact at high voltage.
- Same approach can be deployed to LFP, NMC, LNMO, Solid State Batteries and chemistries beyond Lithium

Yao, Weiliang, *et al*. "A 5V-class Cobalt-free Battery Cathode with High Loading Enabled by Dry Coating." Energy & Environmental Science (2023).

Collaborators and Funding

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Dr. Jihyun Jang, Dr. Mehdi Chouchane,

Dr. Yixuan Li, **Weiliang Yao**

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Dr. Ziying Wang, Dr. Hieu Duong (Tesla, Inc.)

Dr. Marshall Schroeder, Dr. Kang Xu (ARL)

PFIB Microscopy

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Office of Science

ThermoFisher SCIENTIFIC

LNMO 5V

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy
VEHICLE TECHNOLOGIES OFFICE

Binder development

Chemours™

electrolytes

ARL

TEXAS
The University of Texas at Austin

BERKELEY LAB

Maxwell

TESLA

SC LNMO

umicore

All Solid State Battery Dry Processing

LG Energy Solution