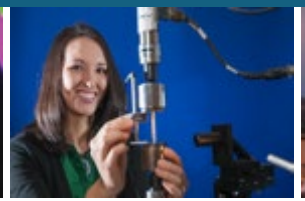
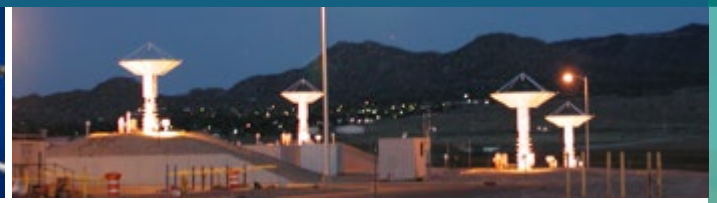
SAND2024-09509C

Sandia National Laboratories

Transport, interfaces and degradation in thin film solid state batteries





A. Alec Talin
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Livermore CA 94550
aatalin@sandia.gov

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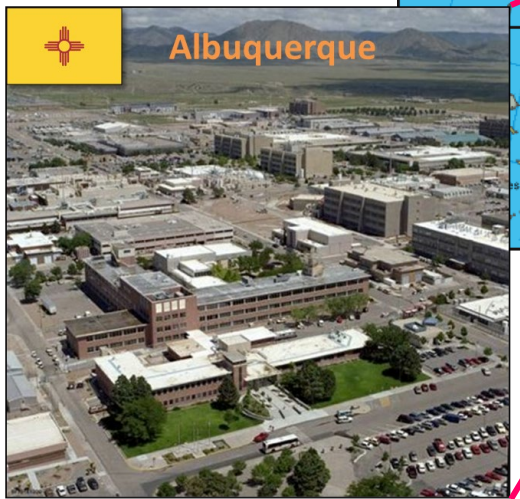
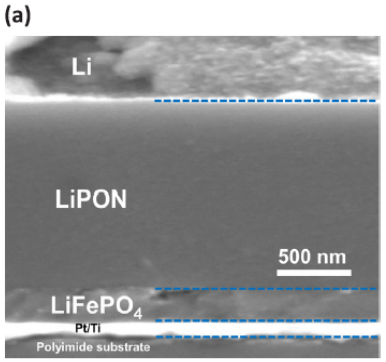
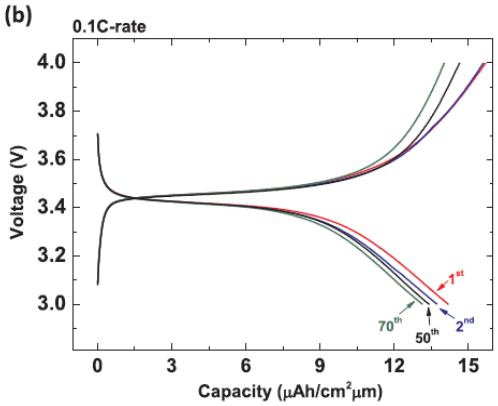
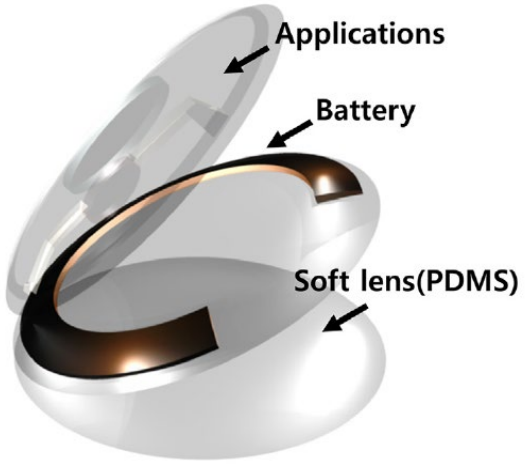


Part I: Thin film batteries with inorganic electrolytes

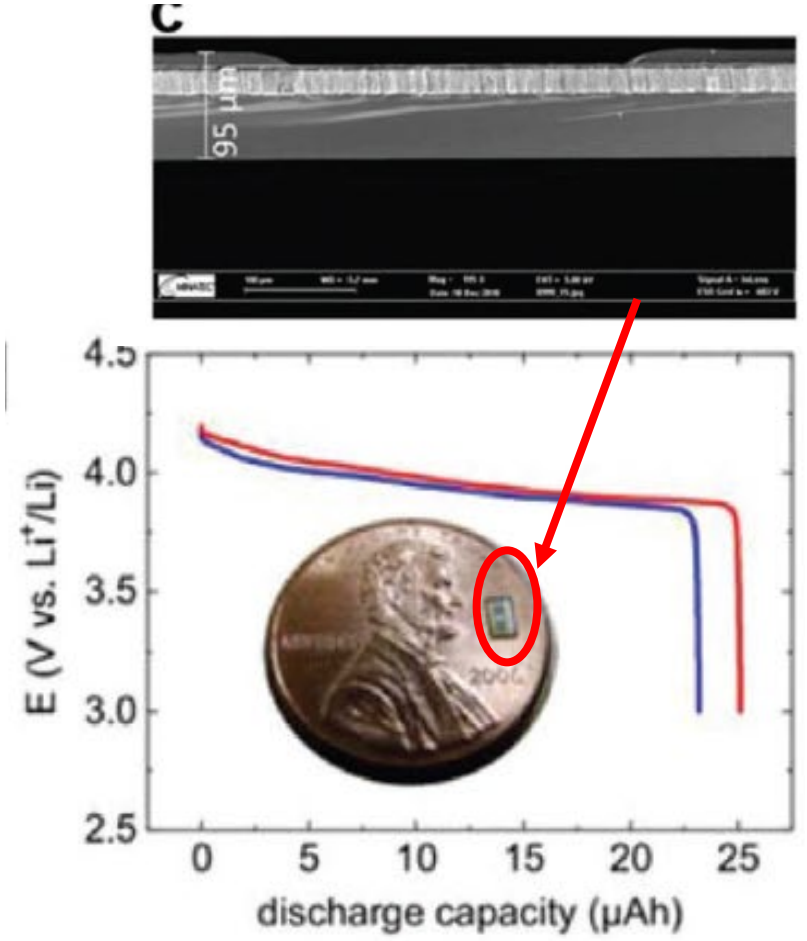
1. **Technology impact:** safe, long lasting power for consumer electronics, IoT, …
2. **Science Impact:** validate models through precision fabrication, characterization tools



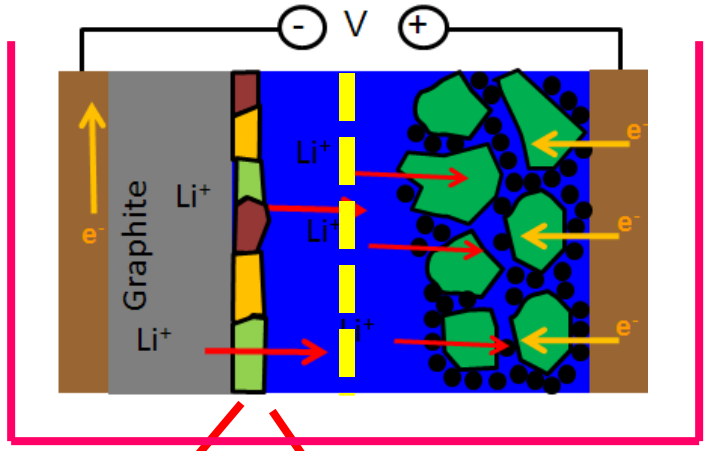


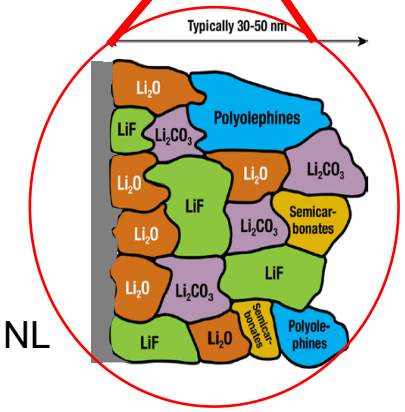


H. Lee, S. Kim, K. B. Kim, J. W. Choi, *Nano Energy* **2018**, *53*, 225



Liquid electrolytes degrade safety, lifetime





Argonne NL

$2e^-+2Li^++CH_3OCO_2CH_3 \rightarrow Li_2CO_3+C_2H_6$

Overcharge

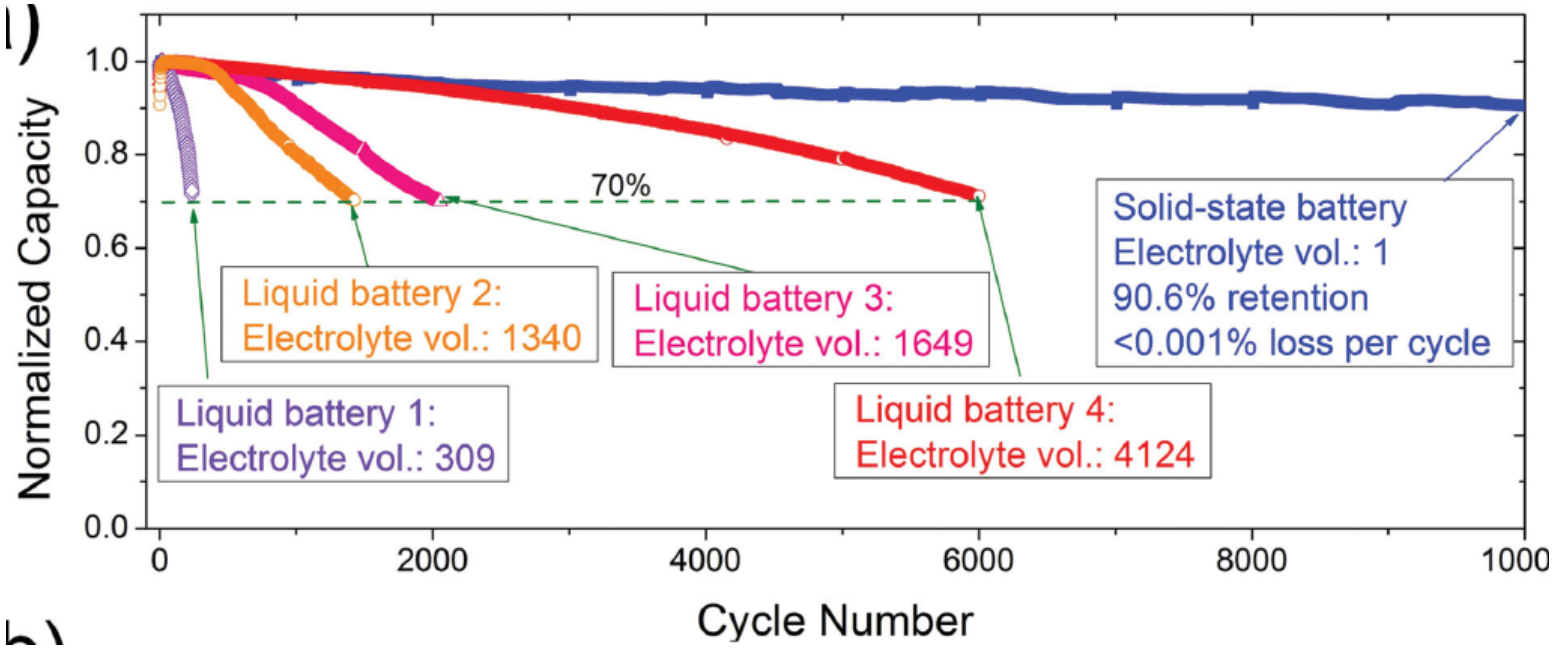
$LiCoO_2 \rightarrow Li^++e^-+CoO+1/2O_2(g)$

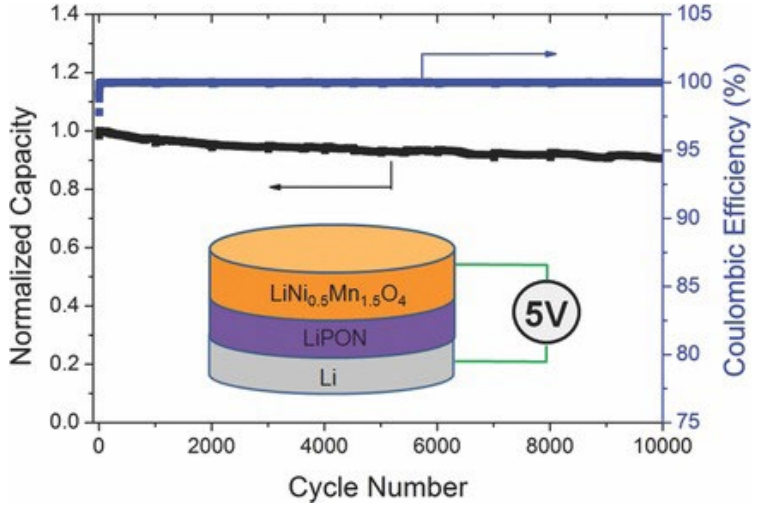
+organic +heat

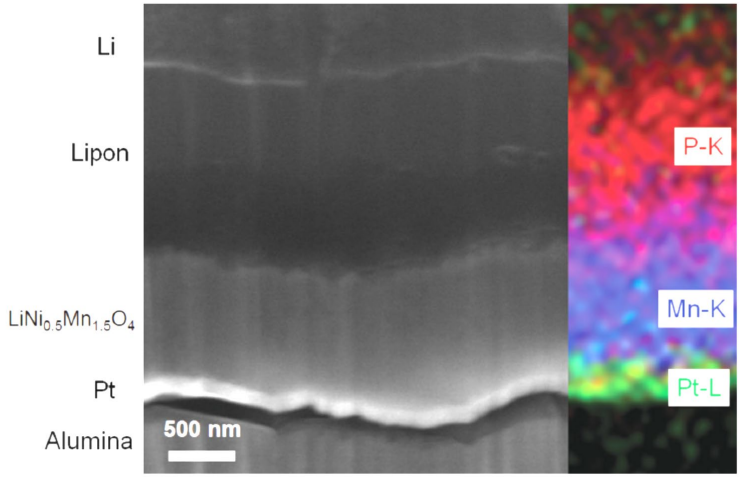
Solid Electrolyte: the Key for High-Voltage Lithium Batteries

Juchuan Li, Cheng Ma, Miaofang Chi, Chengdu Liang, and Nancy J. Dudney**

Adv. Energy Mater. **2015**, *5*, 1401408







Part I: Thin film batteries with inorganic electrolytes

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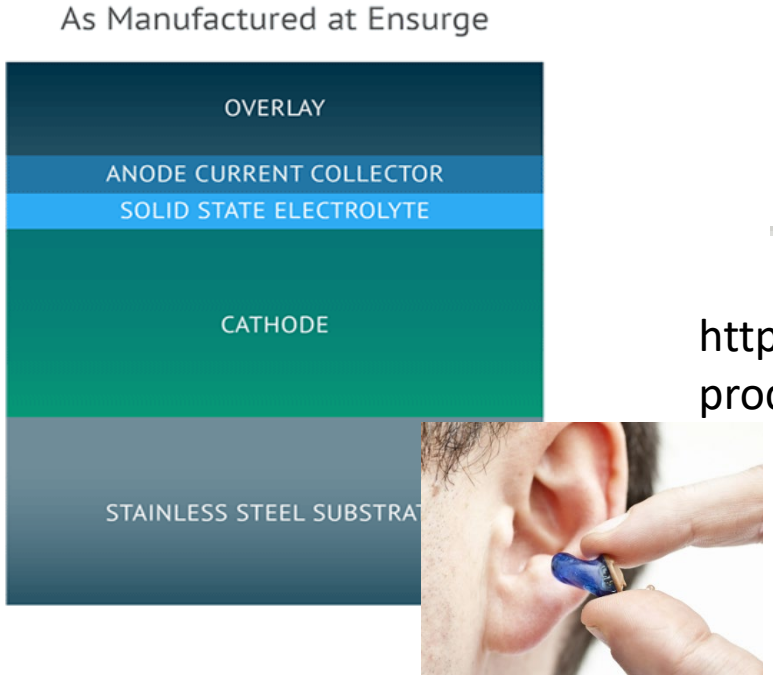
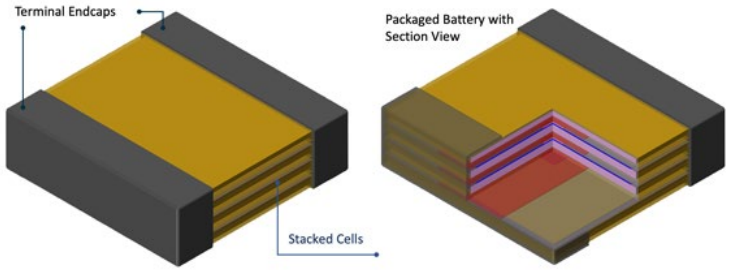
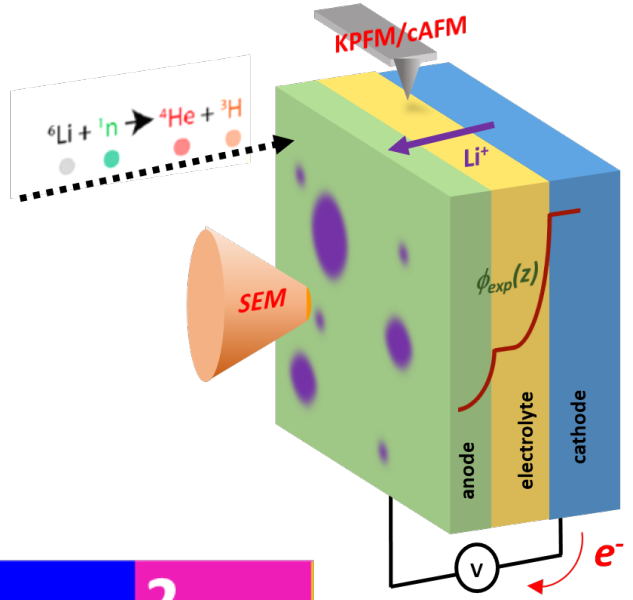
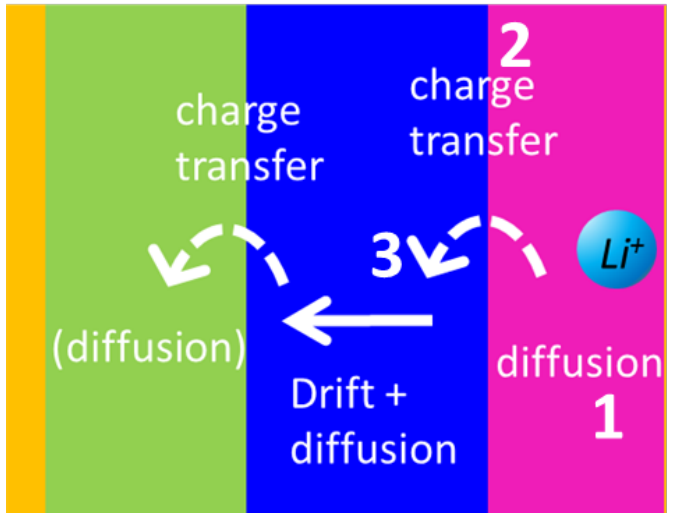


https://product.tdk.com/en/products/solid-state-batt/



https://www.ensurge.com/



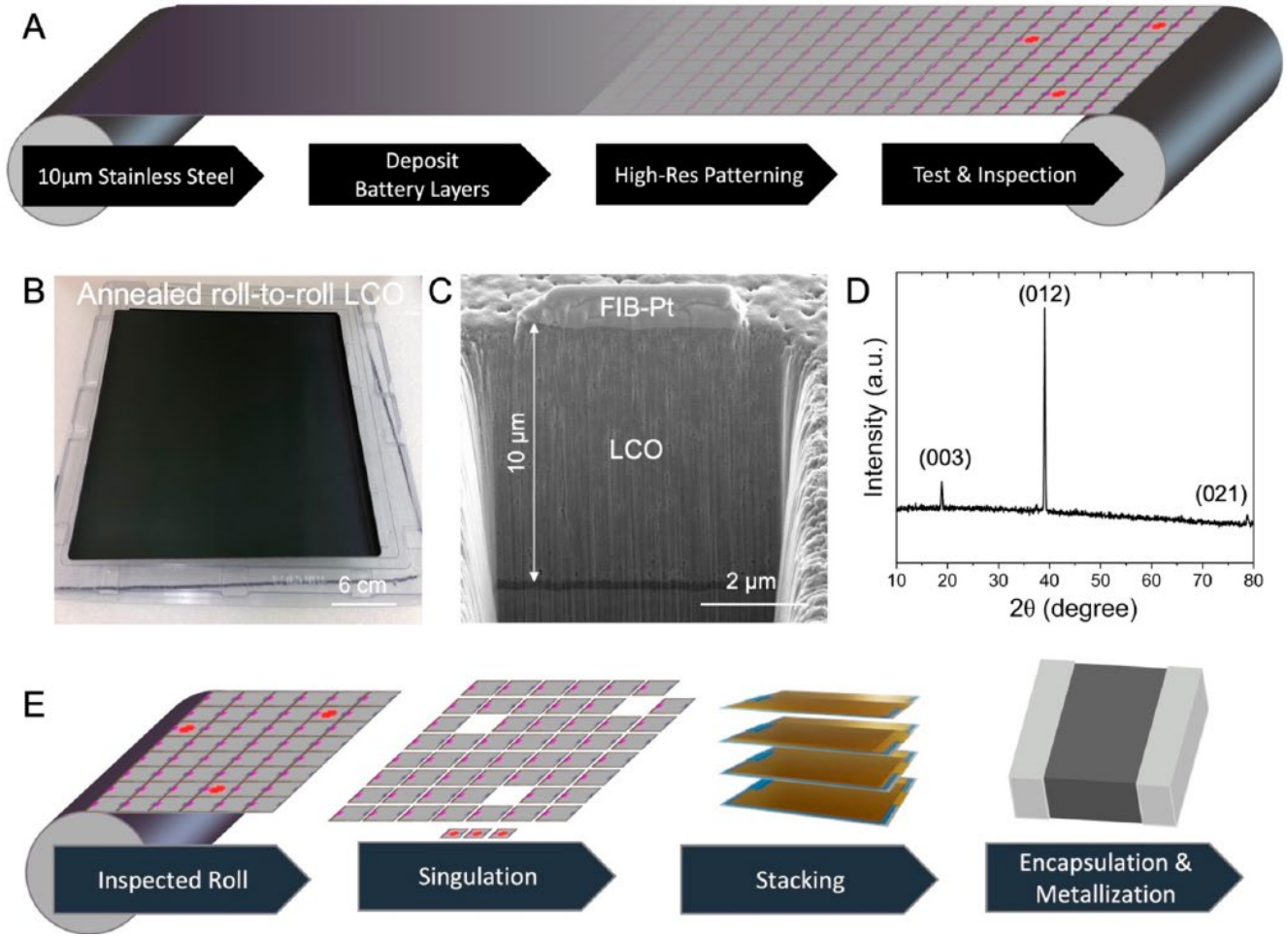


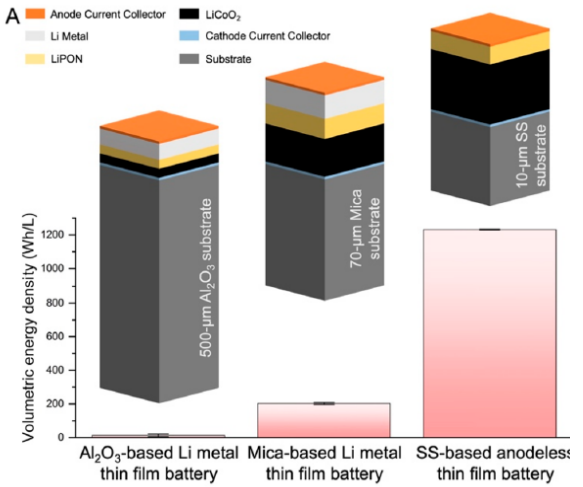
Manufacturing Scale-Up of Anodeless Solid-State Lithium Thin-Film Batteries for High Volumetric Energy Density Applications

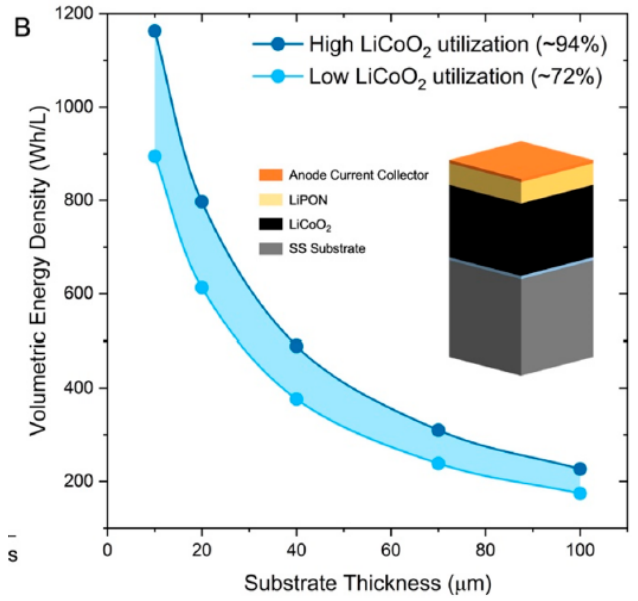
Diyi Cheng, Khanh Tran, Shoba Rao, Zhongchun Wang, Richard van der Linde, Shahid Pirzada, Hui Yang, Alex Yan, Arvind Kamath,* and Ying Shirley Meng*

Cite This: *ACS Energy Lett.* 2023, 8, 4768–4774 Read Online

ACS Energy Letters http://pubs.acs.org/journal/aelccp Perspective





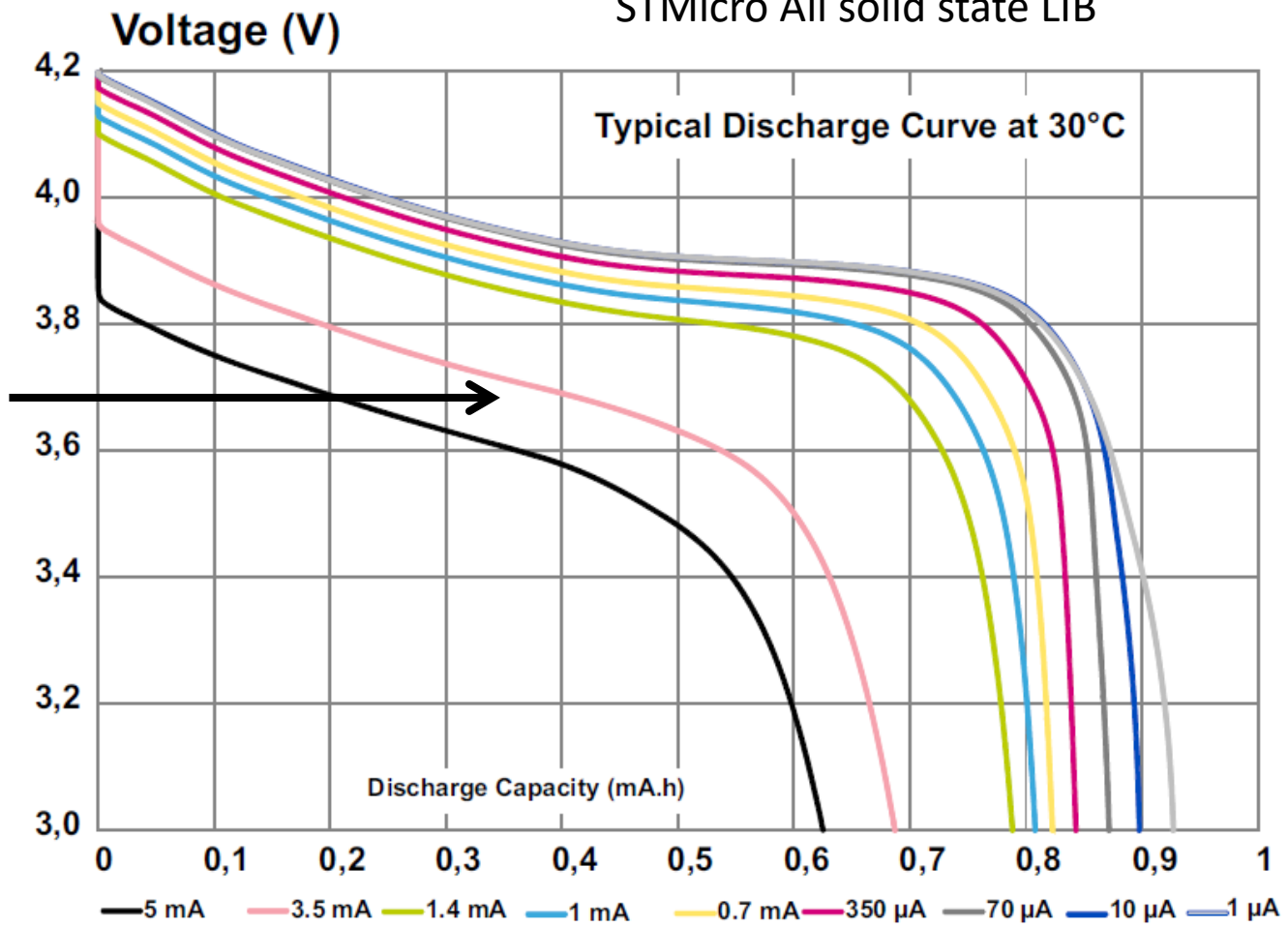


What limits power for thin film SSBs?

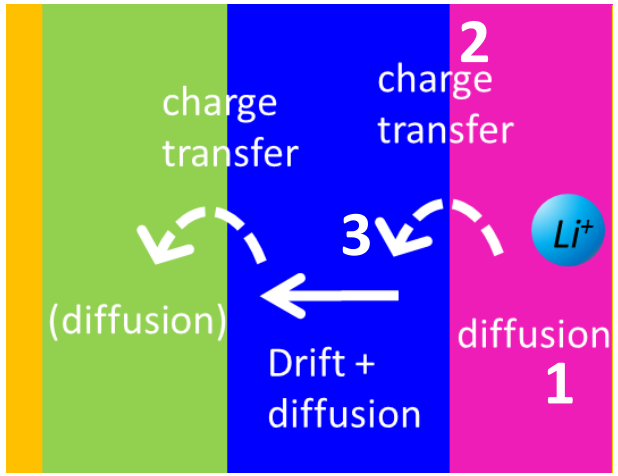
0.5 mA/cm²

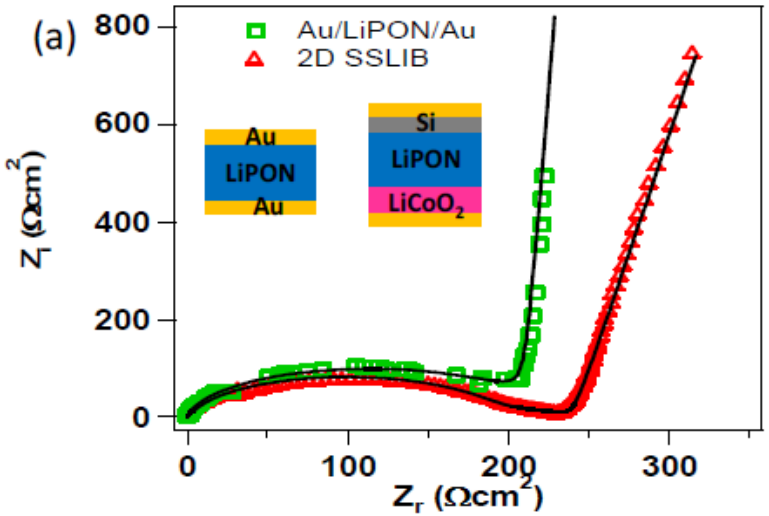
50 mA/cm²

STMicro All solid state LIB



Interfaces, electrolyte, Li diffusion can limit power



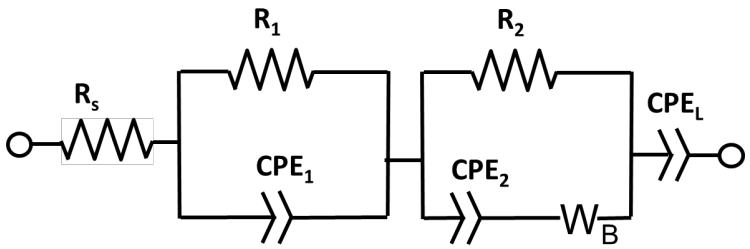


A. A Talin, D. Ruzmetov,⊥ A.Kolmakov, K. McKelvey, N. Ware, F. El Gabaly, B. Dunn, and H. S. White, ACS Appl. Mater. Interfaces 2016, 8, 32385

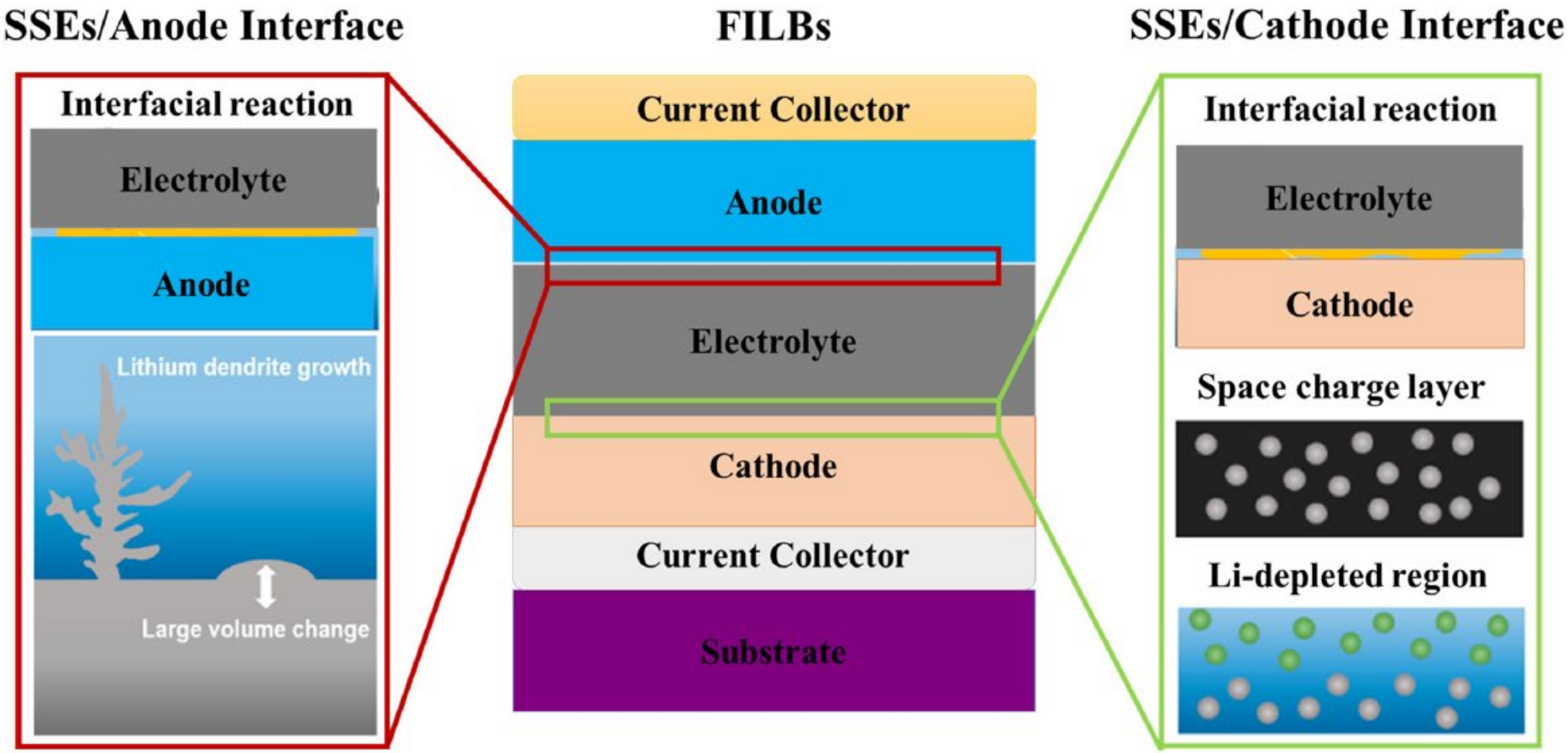
Table 1. Summary of the Conductivities (σ_{EL}) of Electrolytes (EL), and the Interface Resistances (R_i) and Activation Energies (E_a) of EL/$LiCoO_2$ Interfaces

sputtering position	EL	σ_{EL} [S cm^{-1}]	R_i [Ω cm^2]	E_a [eV]
on-axis	Li_3PO_4	2.3×10^{-8}	~200	0.38
	LiPON	1.8×10^{-6}	880	0.46
off-axis	LiPON	7.1×10^{-7}	8.6	0.38
references	Li_3PO_4[a]	4.6×10^{-7}	90	
	LiPON[b]		125	0.59
	PC[c,d]		25	0.64

Haruta et al., Nano Lett. 15, 1498 (2015)



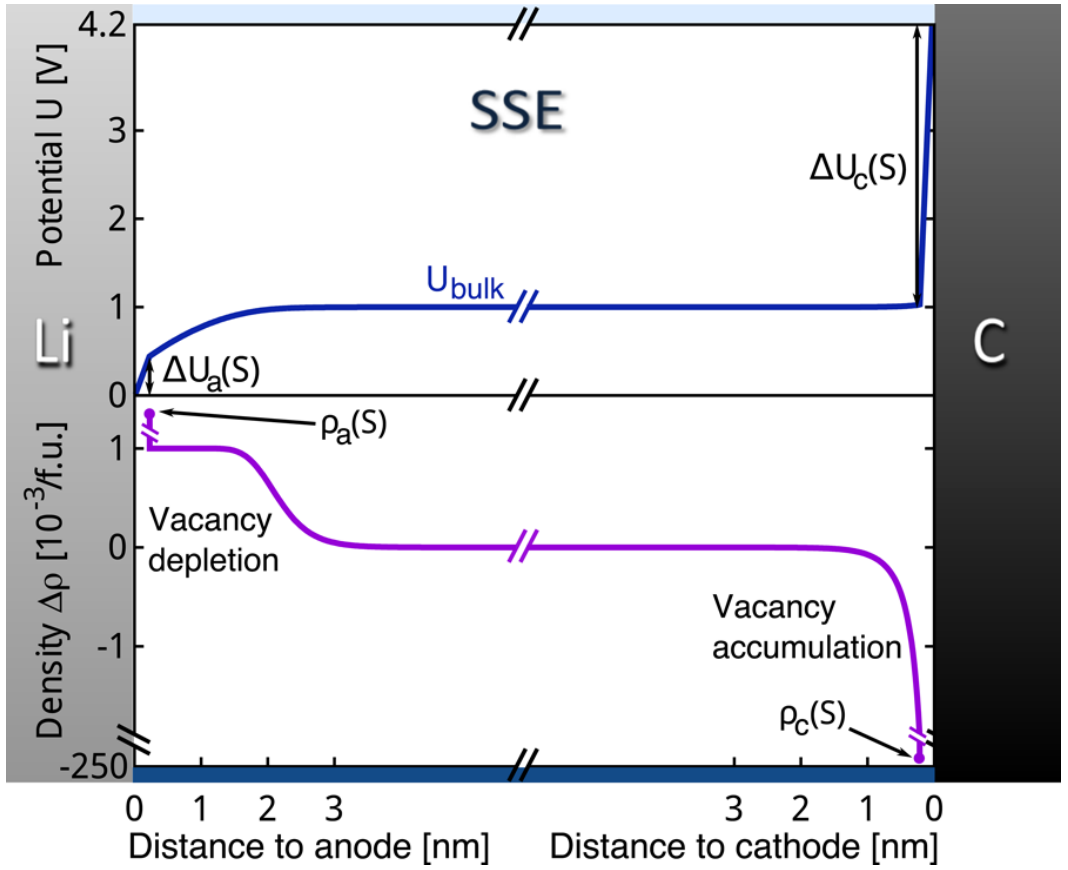
Space-charge layers, interface reactions, dendrides



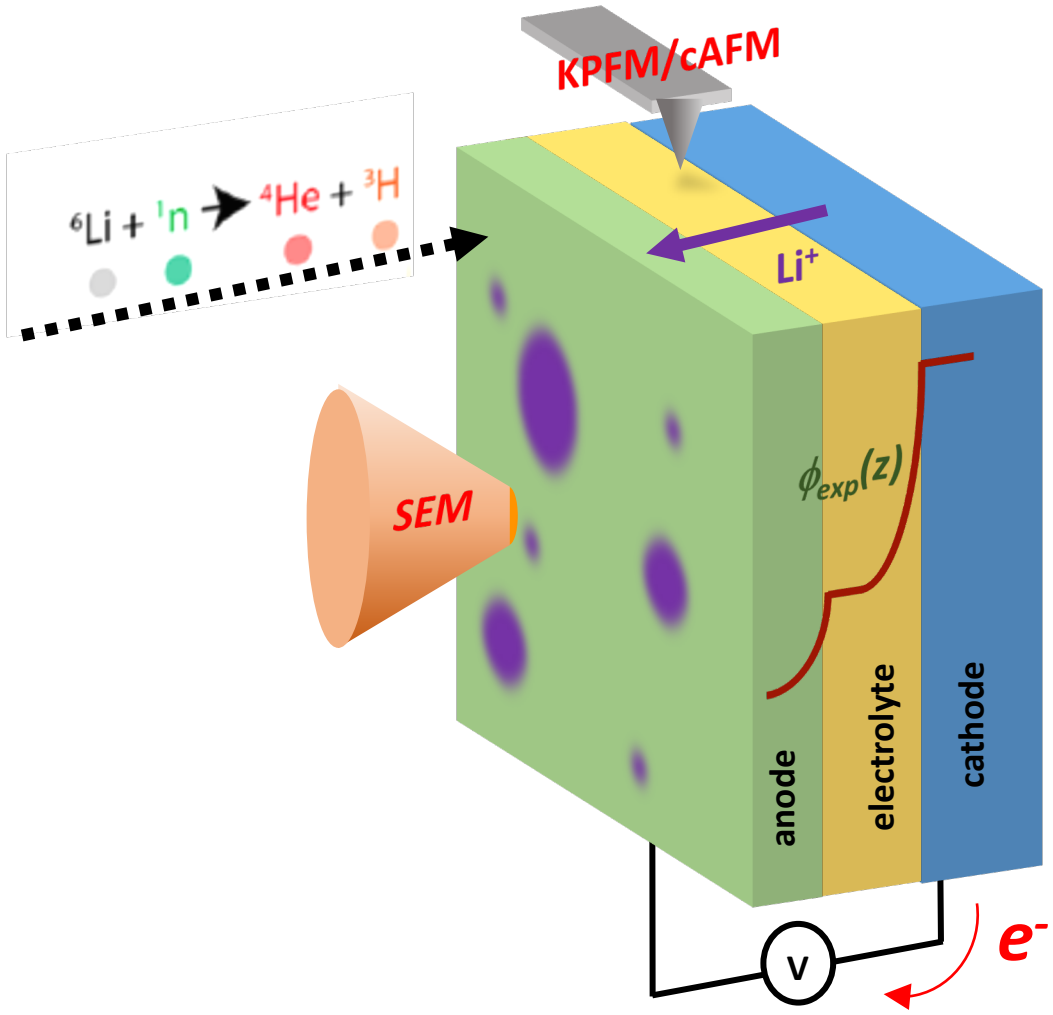
Yang, G.; Abraham, C.; Ma, Y.; Lee, M.; Helfrick, E.; Oh, D.; Lee, D. Appl. Sci. 2020, 10, 4727

Interface potentials determine performance & stability, but are generally unknown

Calculated potential and [Li] profile



A. C. Luntz, J. Voss, K. Reuter, J. Phys. Chem. Lett. 6, 4599 (2015)

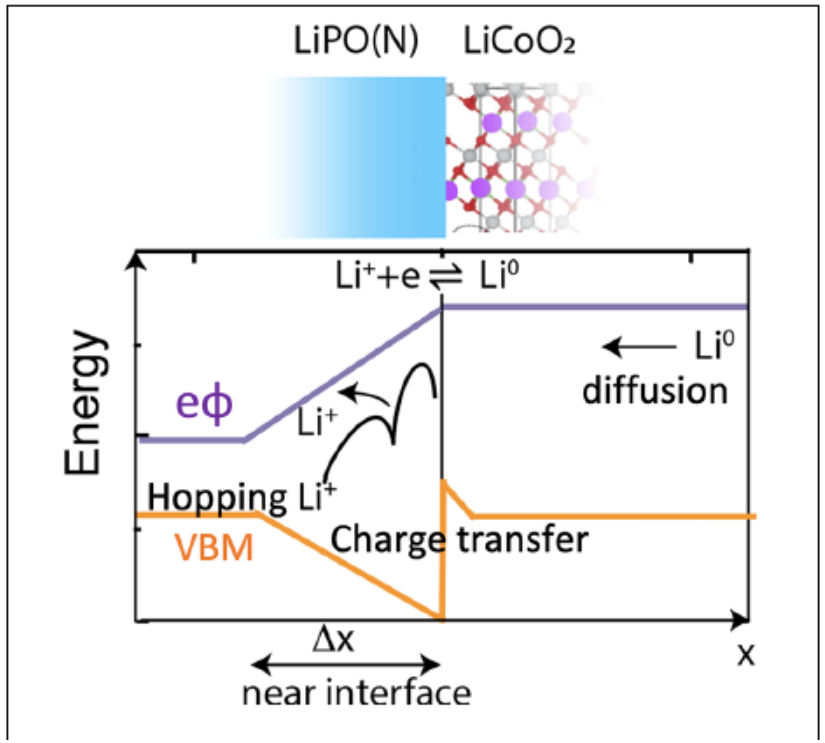


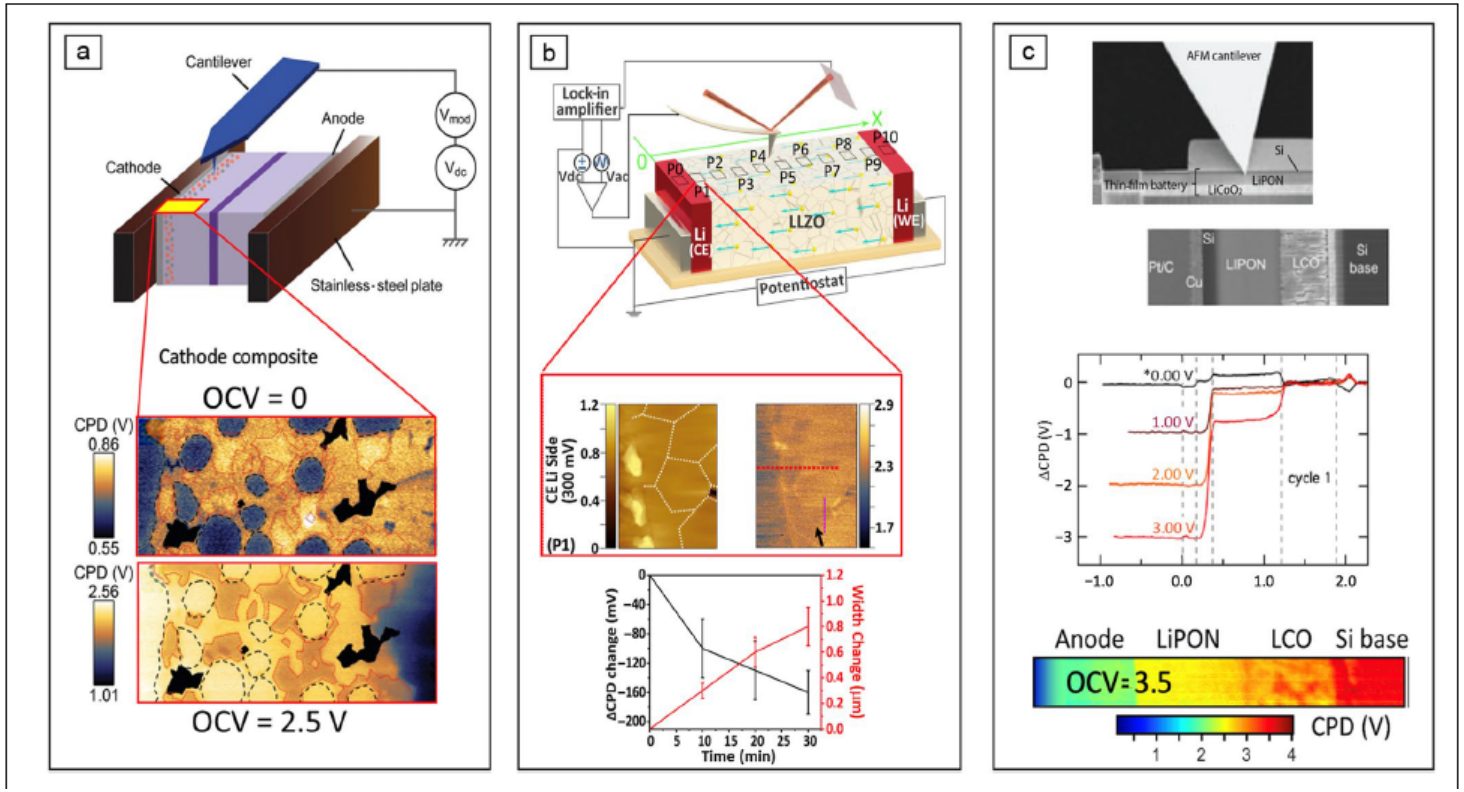
E. J. Fuller, E. Strelcov, J. L. Weaver, M. W. Swift, J. D. Sugar, A. Kolmakov, N. Zhitenev, J. J. McClelland, Y. Qi, J. A. Dura, A. . Talin, *ACS Energy Lett*. 6, 3944, 2021

Interface potentials inside solid-state batteries: Origins and implications

Yue Qi,* Michael W. Swift, Elliot J. Fuller, and A. Alec Talin

MRS BULLETIN • VOLUME 48 • DECEMBER 2023 • mrs.org/bulletin 1

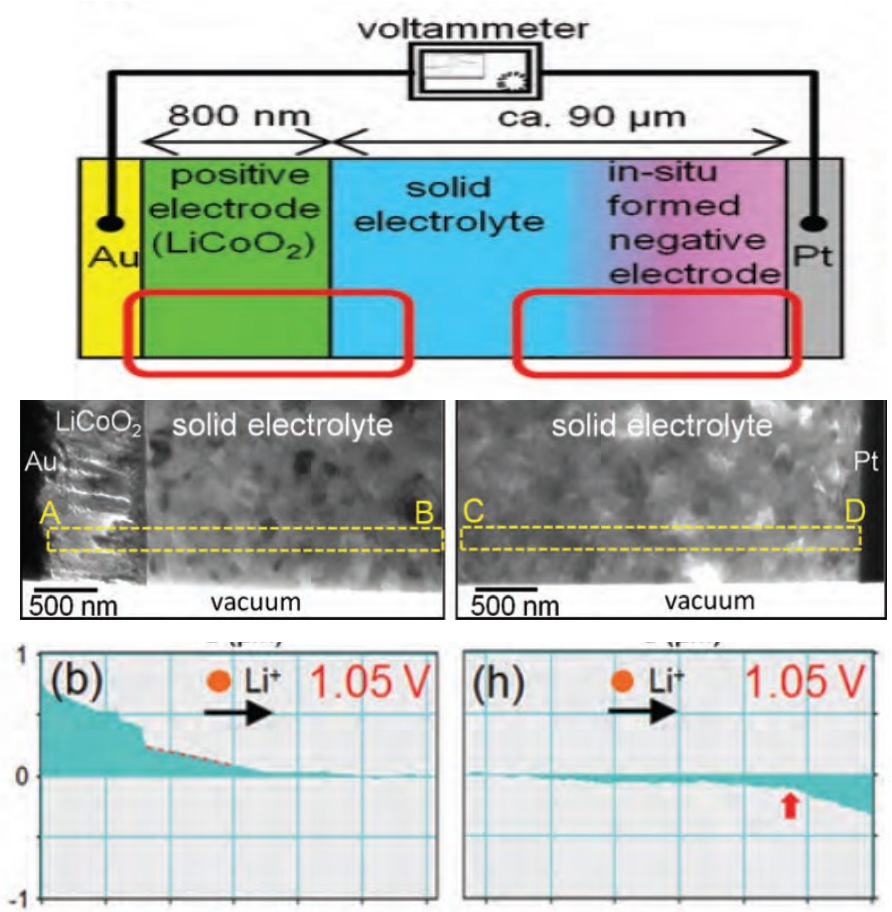




Few methods to measure local potential

Electron holography

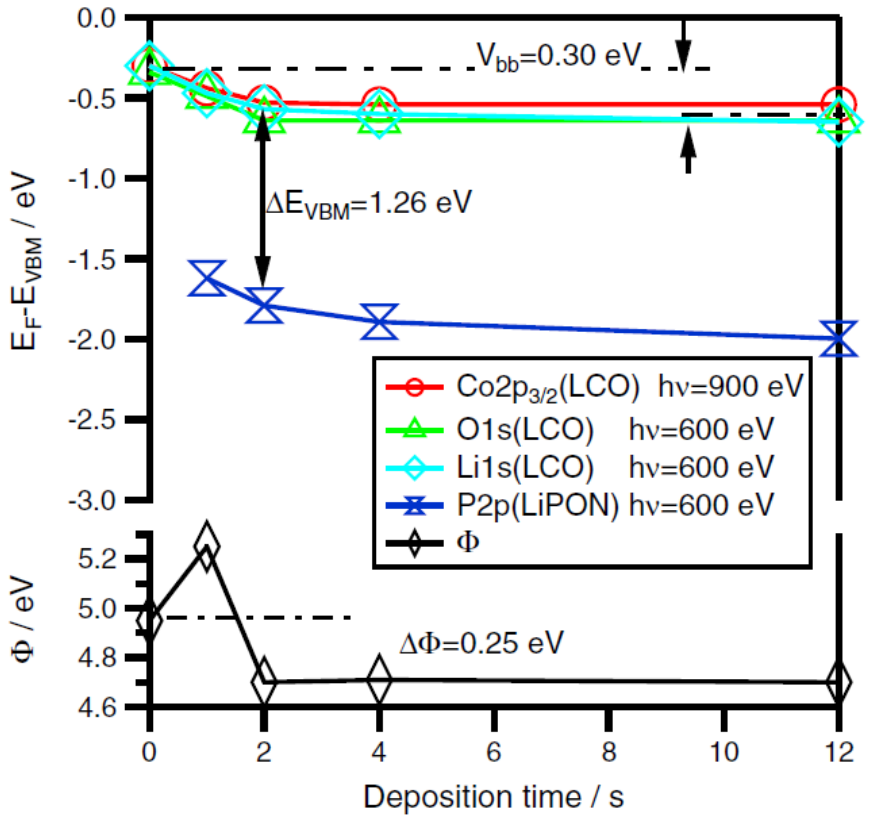
- Requires specimen thinning
- Complicated interpretation
- Beam effects
- Few results to date



K. Yamamoto, T. Hirayama, T. Tanji, Microscopy 62, S29, 2013

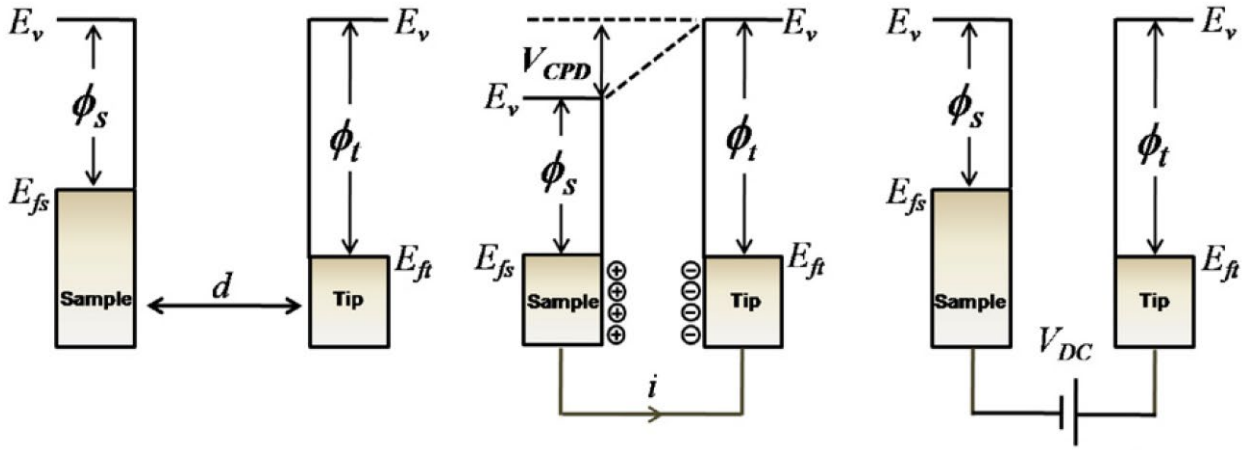
XPS

- Limited to very thin overlayers
- Need synchrotron for lateral resolution
- Operando studies very challenging



A. Schwöbel, W. Jaegermann, R. Hausbrand, Solid State Ionics 288, 244, 2016

Kelvin Probe Force Microscopy

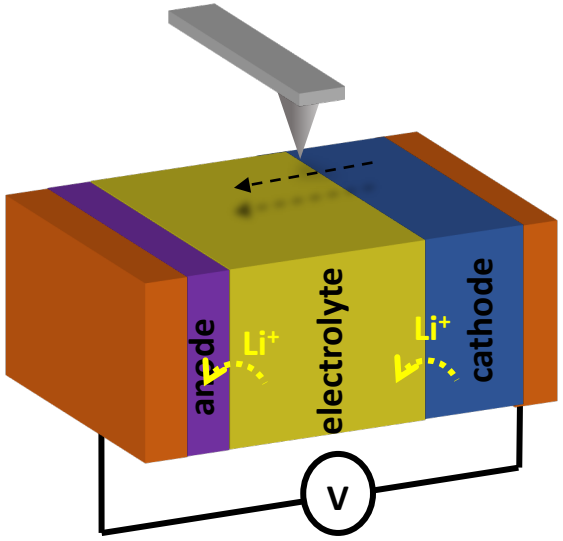


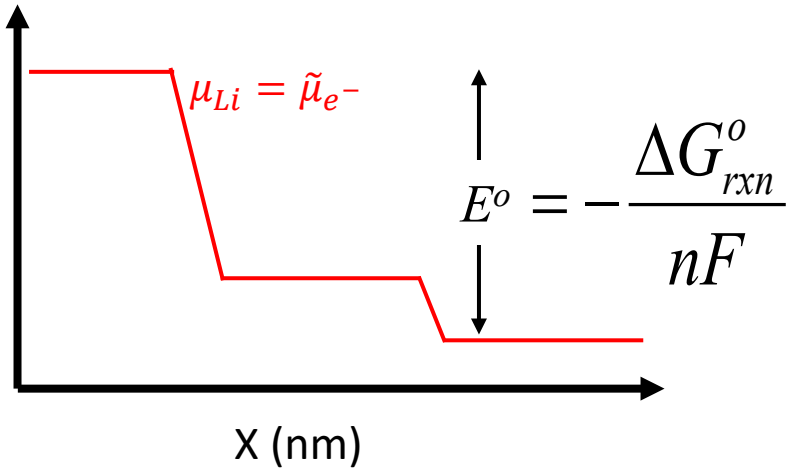
W. Melitz, J. Shena, A. C. Kummel, S. Lee Surf. Sci. Reports 66, 1, 2011

$$CPD = \frac{\Delta\Phi}{e}$$

$$\downarrow$$

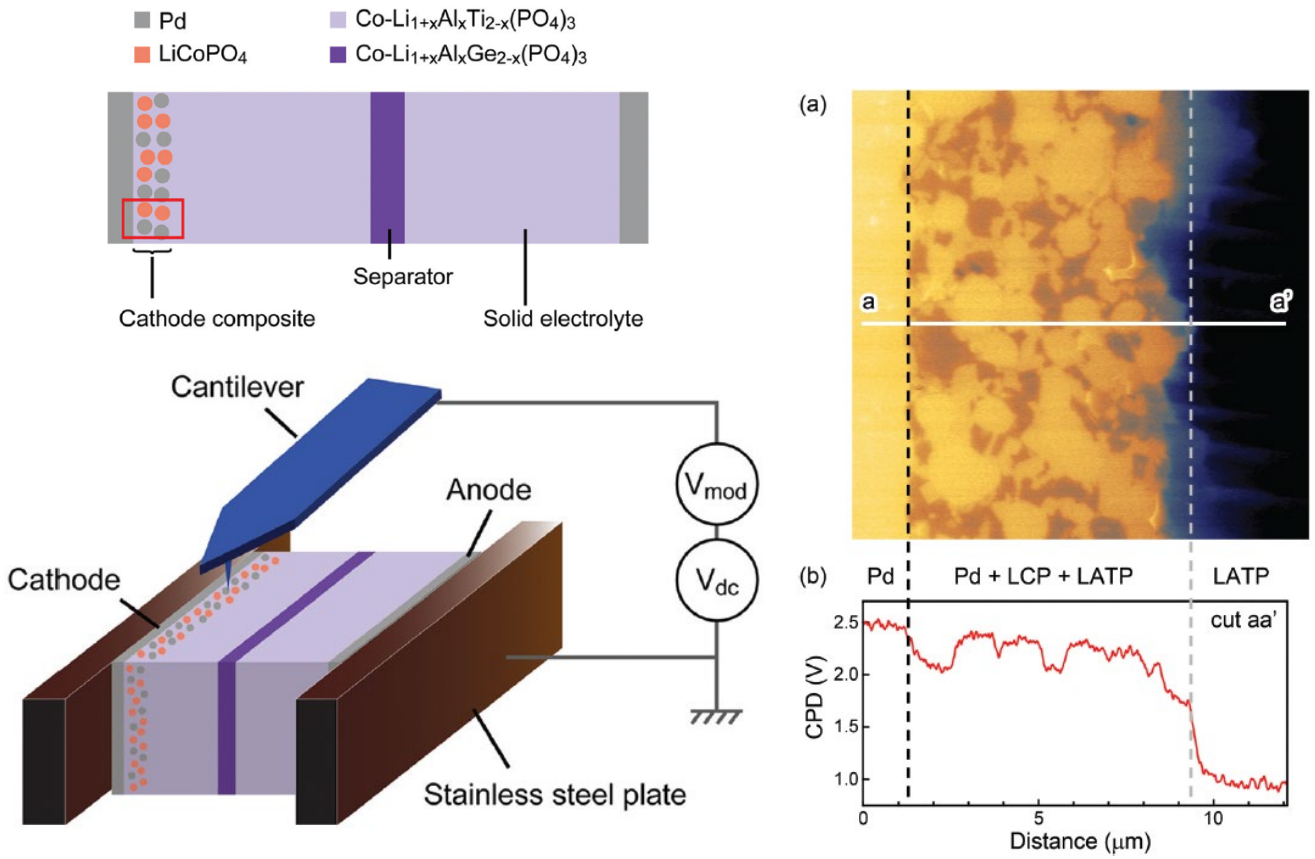
$$CPD = \frac{\Delta\Phi}{e} - \frac{\tilde{\mu}_{e^-}}{e}$$





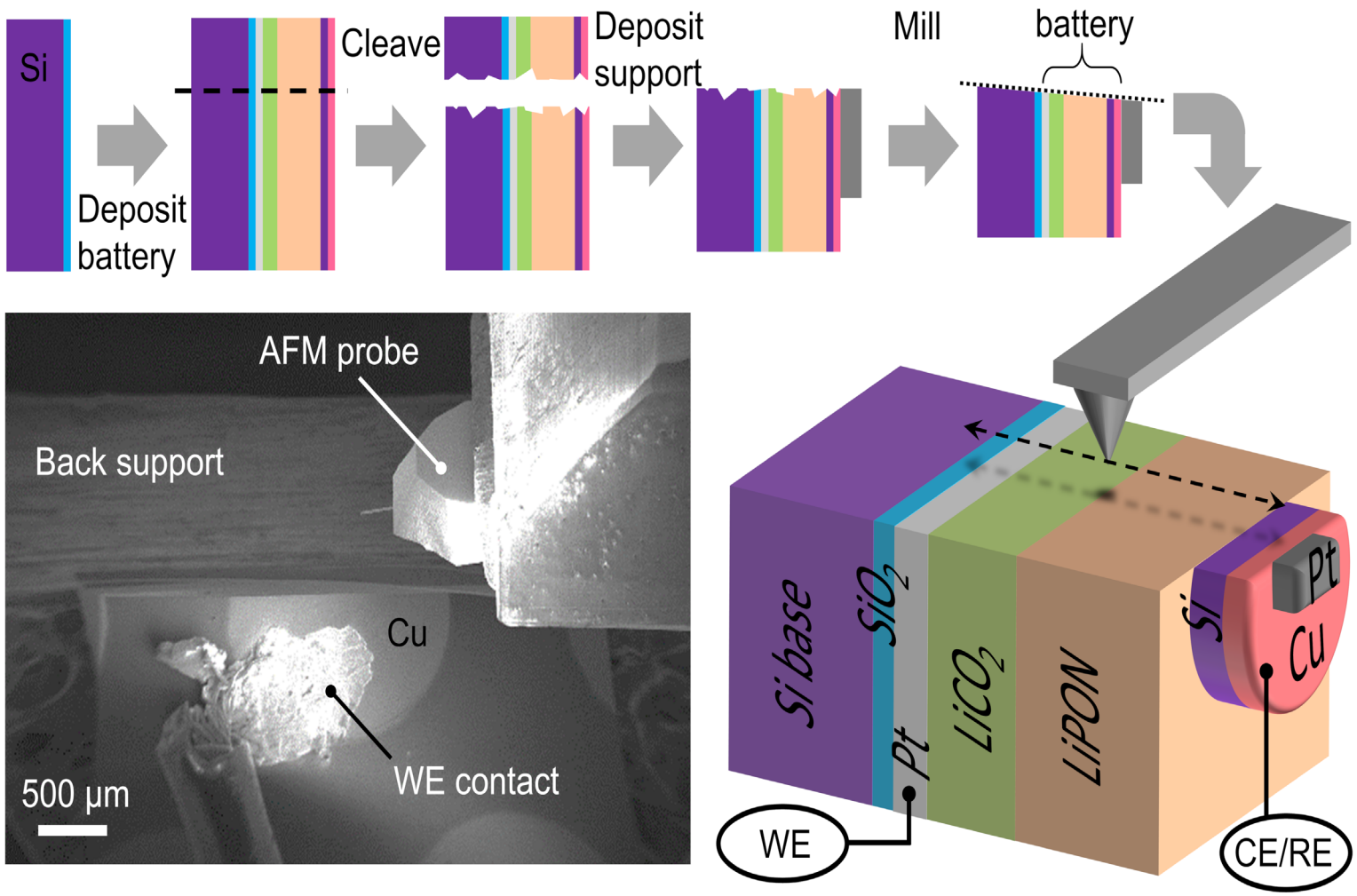
Previous KPFM potential profiling of SSBs

- Not done under inert ambient (~1000 ppm O_2, 250 ppm H_2O)
- Composite cathode (metal, cathode, SSE)
- Rough interface
- No profile of complete cell
- Challenging for model validation



H. Masuda, N. Ishida, Y. Ogata, D. Itoc, Daisuke Fujita, Nanoscale 9, 893, 2017

In situ cross section SSLIB to avoid contamination



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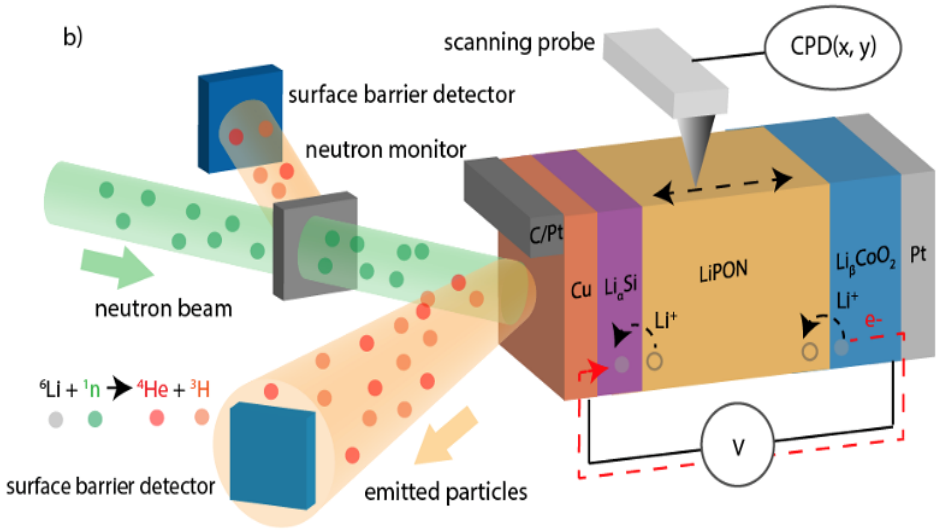
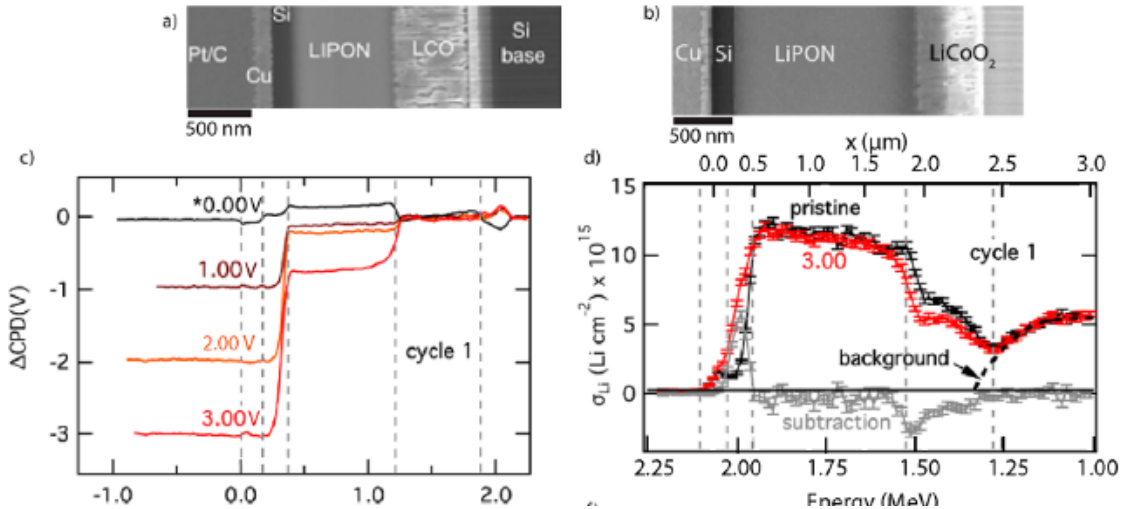
Operando measurement of potential, [Li] across SSB





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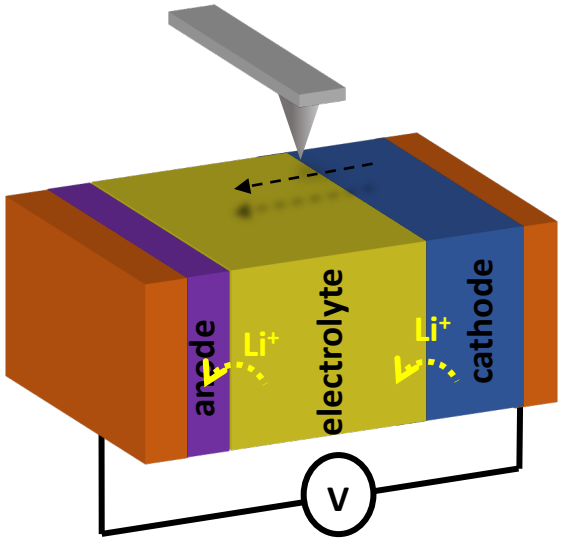
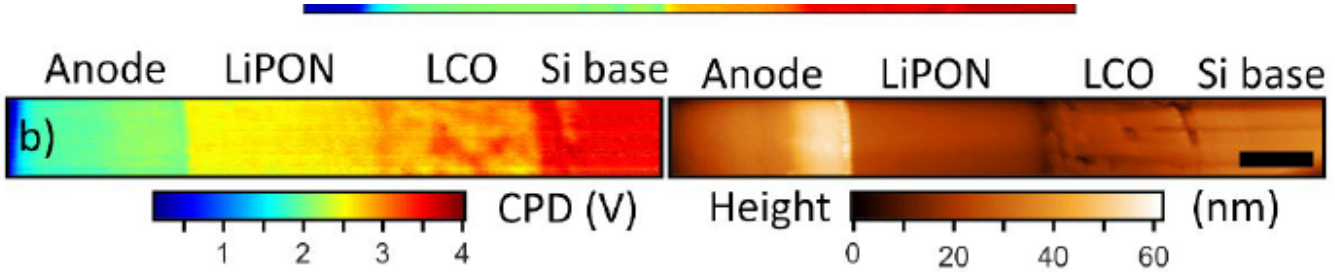
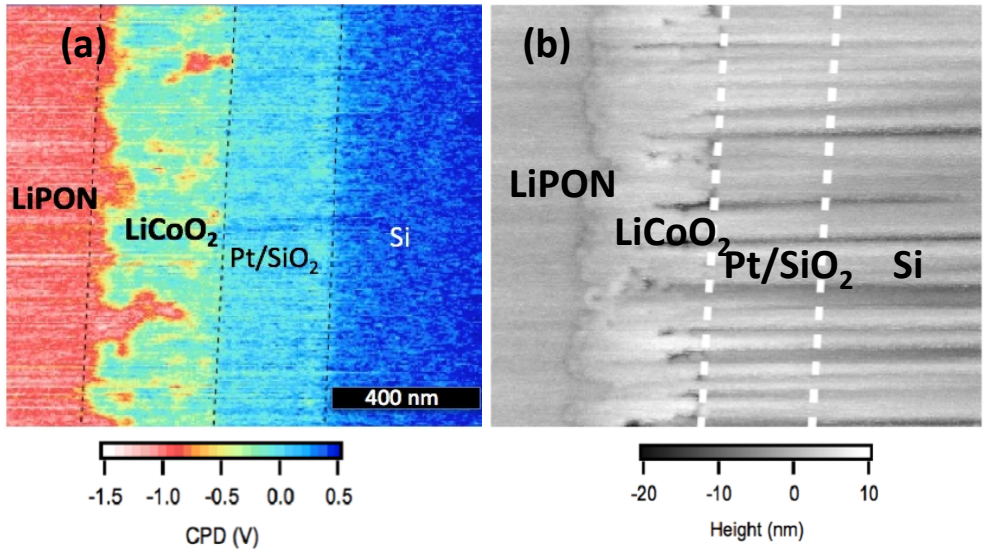
Local potential inhomogeneous at LiPON/LCO interface





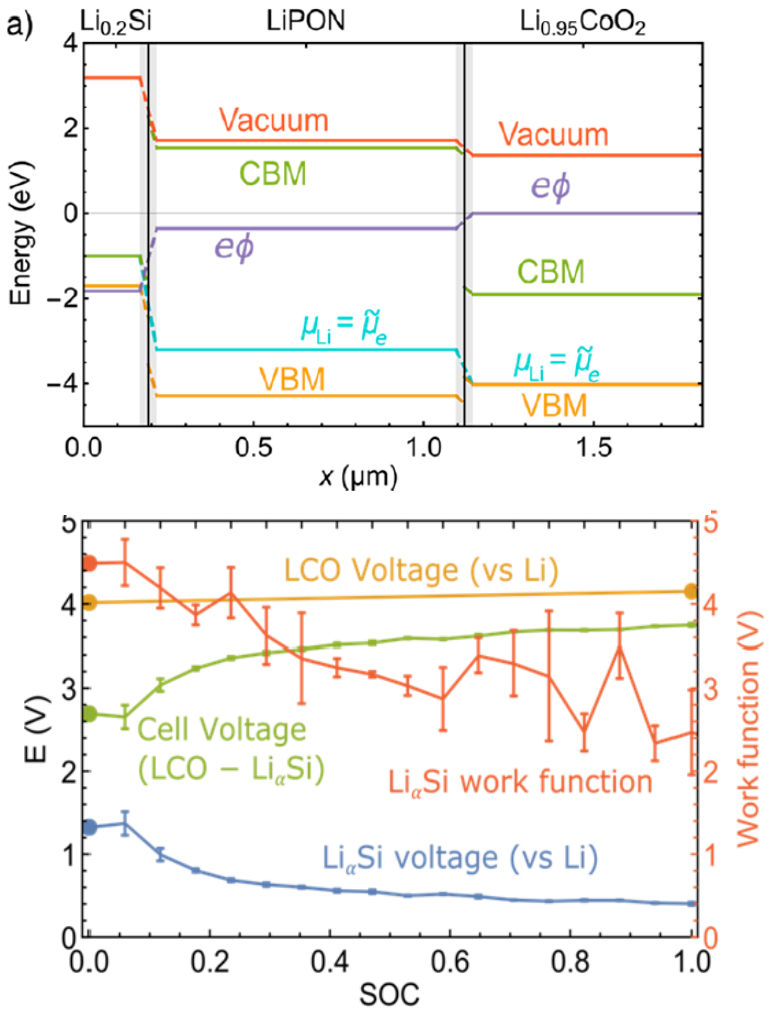


E. J. Fuller, E. Strelcov, J. L. Weaver, M. W. Swift, J. D. Sugar, A. Kolmakov, N. Zhitenev, J. J. McClelland, Y. Qi, J. A. Dura, A. . Talin, *ACS Energy Lett*. 6, 3944, 2021

A first-principles informed model of a Si/LiPON/LCO SSB

- *Ab initio* framework to calculate thermodynamic driving forces and interface potential drops at open circuit equilibrium
  - Model system Li / LiPON / Li_xCoO_2
- Open circuit voltage V from chemical potential energetics at equilibrium
  - Electronic and ionic components
  - Resulting V consistent with prior DFT and experiment
- Electronic E_F changes and drives battery operation
- Calculate defect formation energies, electronic band alignments, interface energy barriers

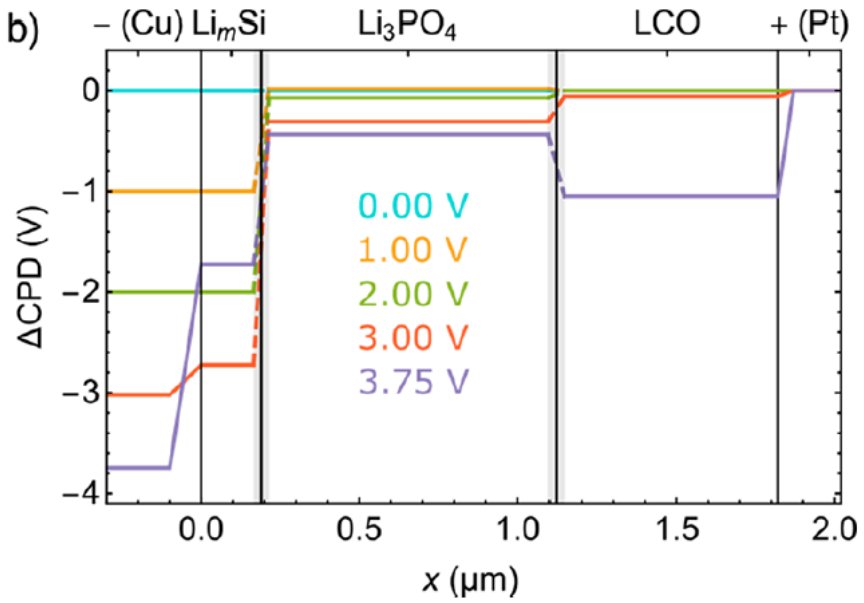
$$\tilde{\mu}_{\mathrm{Li}^+} = \mu_{\mathrm{Li}} - (E_F - IP + \psi^a - e\phi) = 0.$$

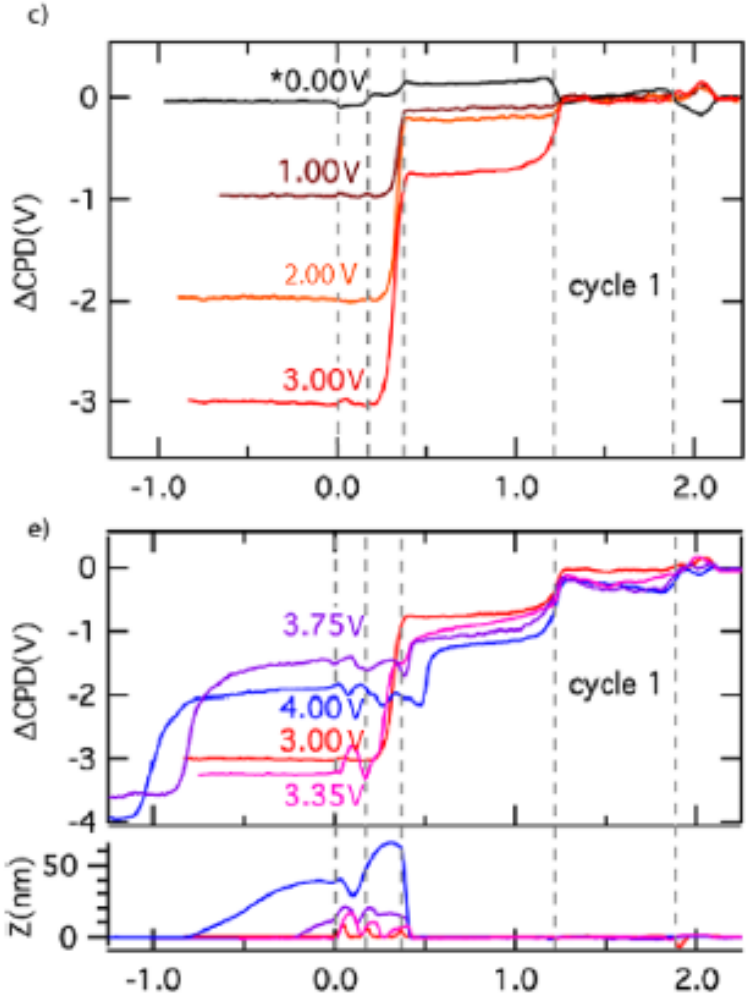


E. J. Fuller, E. Strelcov, J. L. Weaver, M. W. Swift, J. D. Sugar, A. Kolmakov, N. Zhitenev, J. J. McClelland, Y. Qi, J. A. Dura, A. . Talin, *ACS Energy Lett*. 6, 3944, 2021

Good agreement for calculated vs. measured ΔCPD

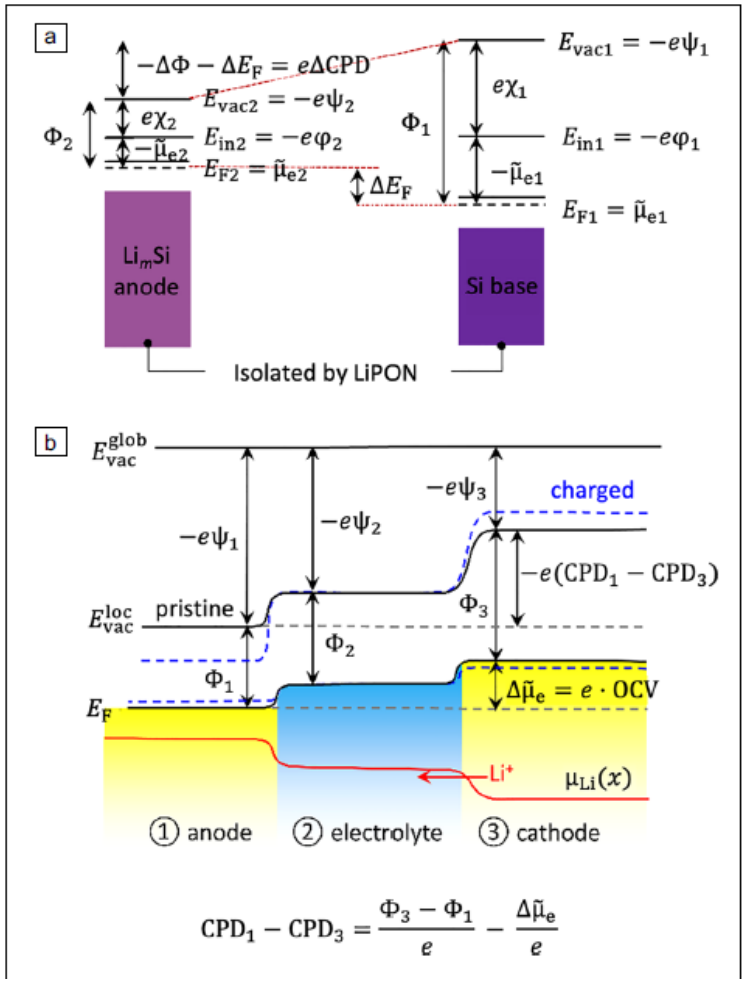
model ΔCPD

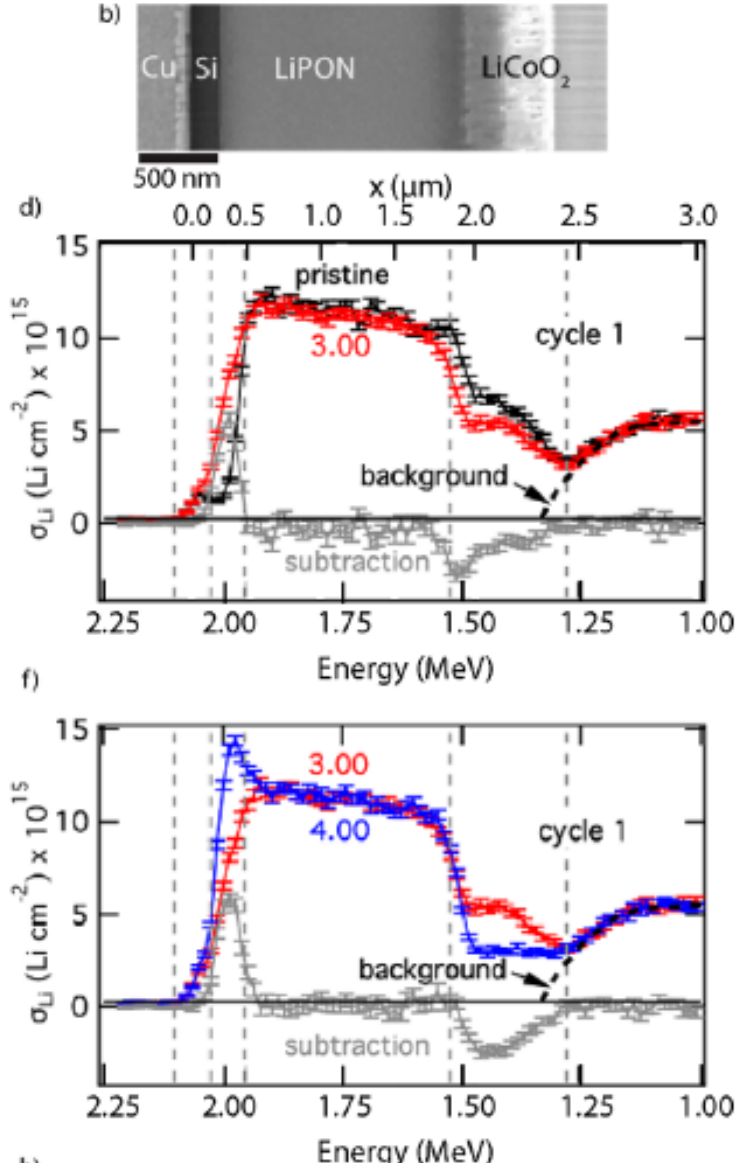


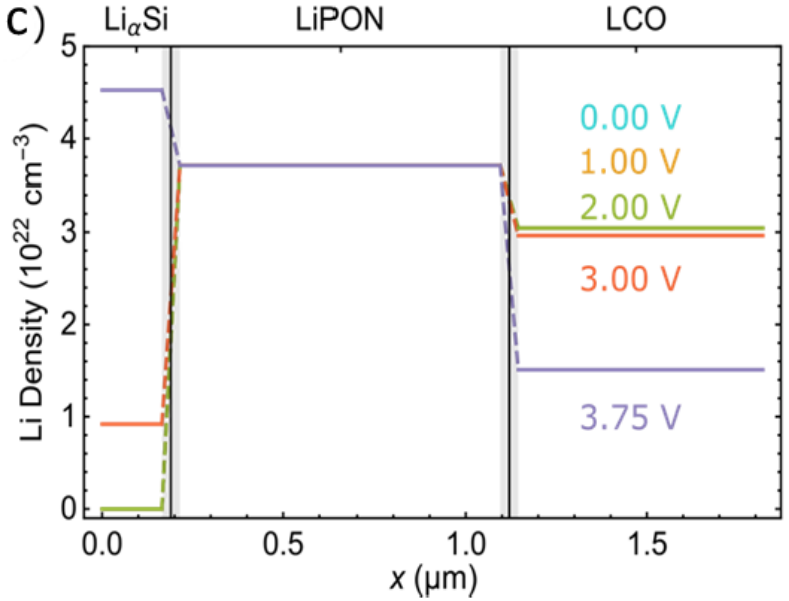


E. J. Fuller, E. Strelcov, J. L. Weaver, M. W. Swift, J. D. Sugar, A. Kolmakov, N. Zhitenev, J. J. McClelland, Y. Qi, J. A. Dura, A. . Talin, *ACS Energy Lett*. 6, 3944, 2021

…and for calculated vs. measured [Li] profile

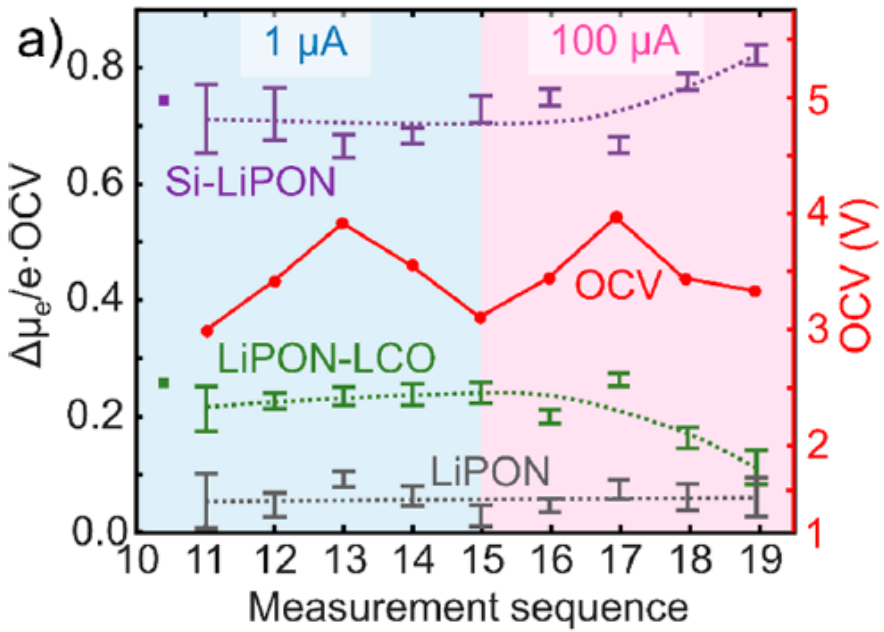


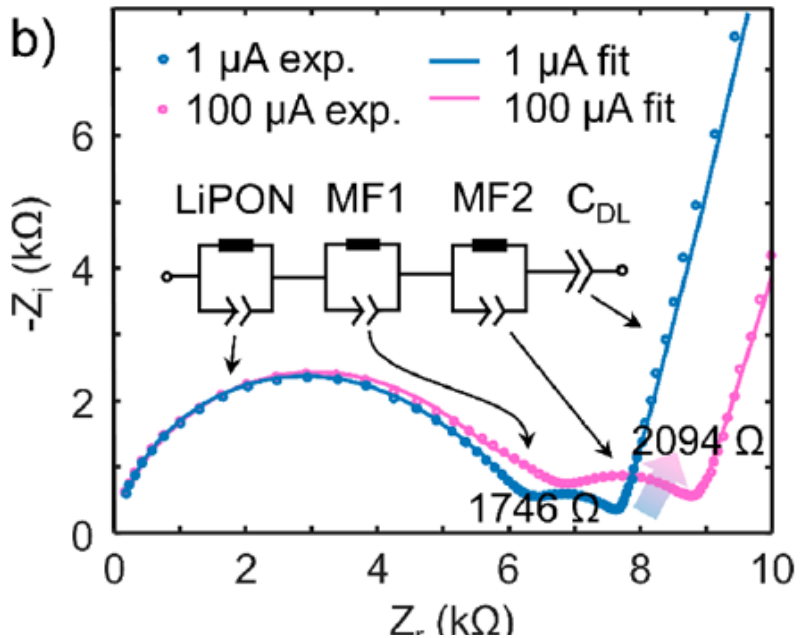


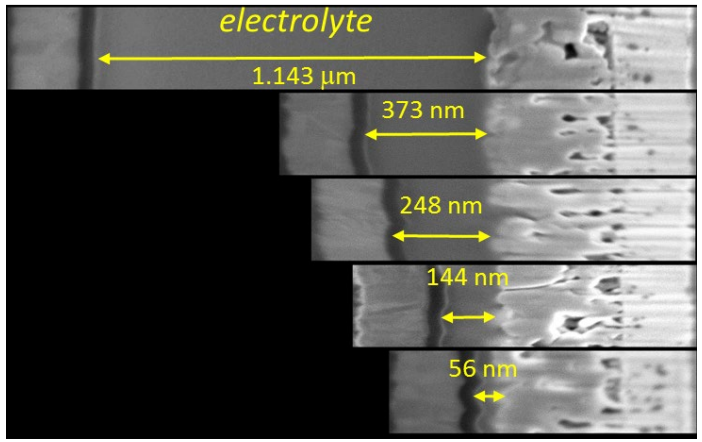


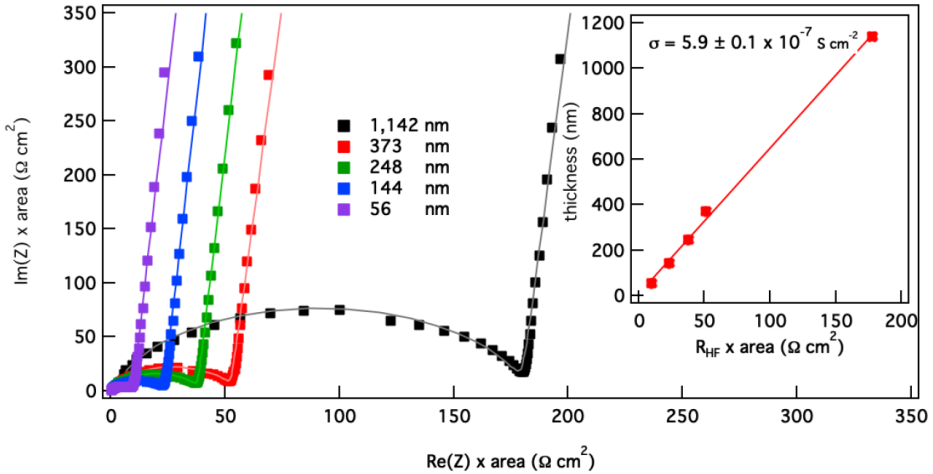
High current cycling leads to change in EIS

KPFM helps identify the interface responsible for change in EIS







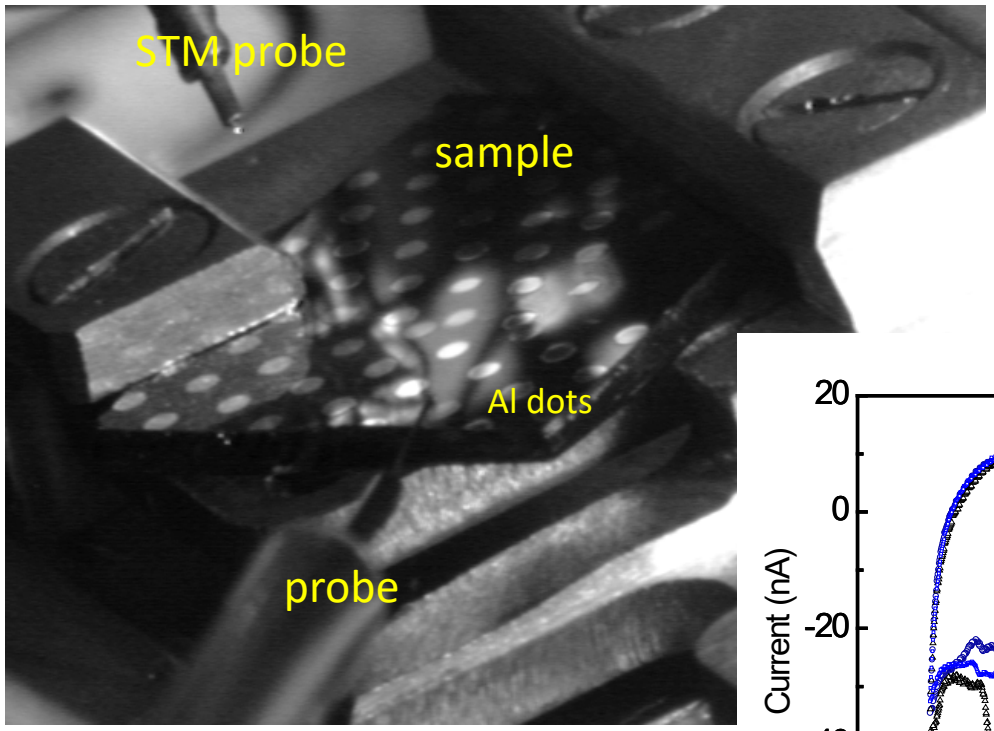


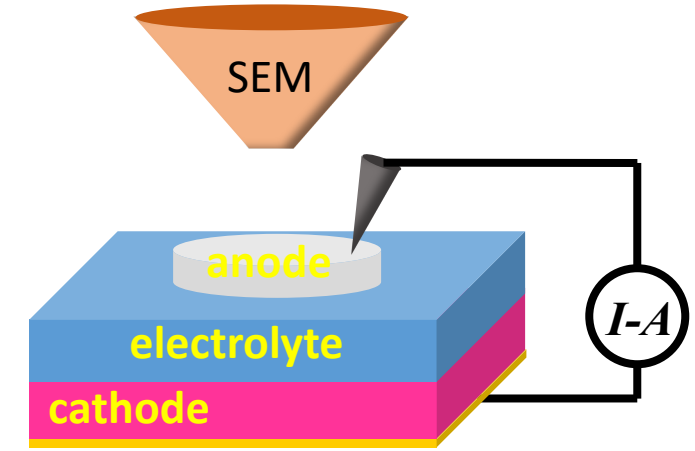
E. J. Fuller, E. Strelcov, J. L. Weaver, M. W. Swift, J. D. Sugar, A. Kolmakov, N. Zhitenev, J. J. McClelland, Y. Qi, J. A. Dura, A. . Talin, *ACS Energy Lett*. 6, 3944, 2021

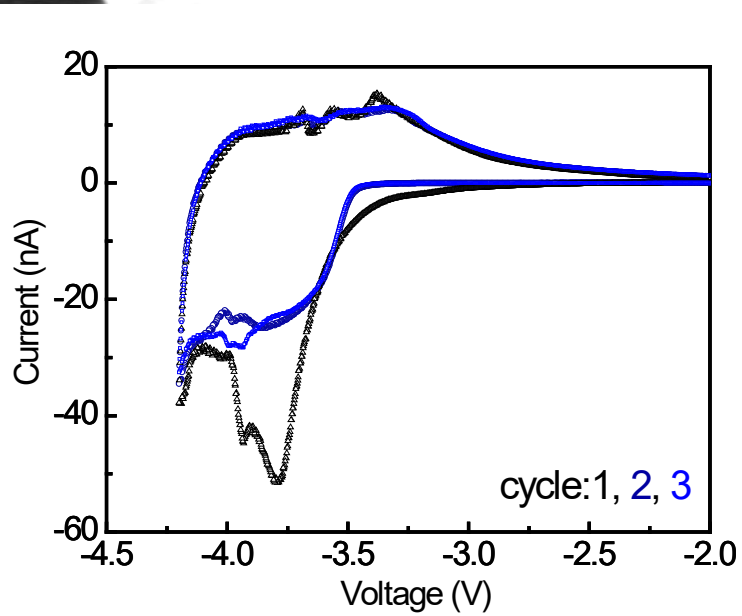
In situ characterization of Al anode thin film LIBs

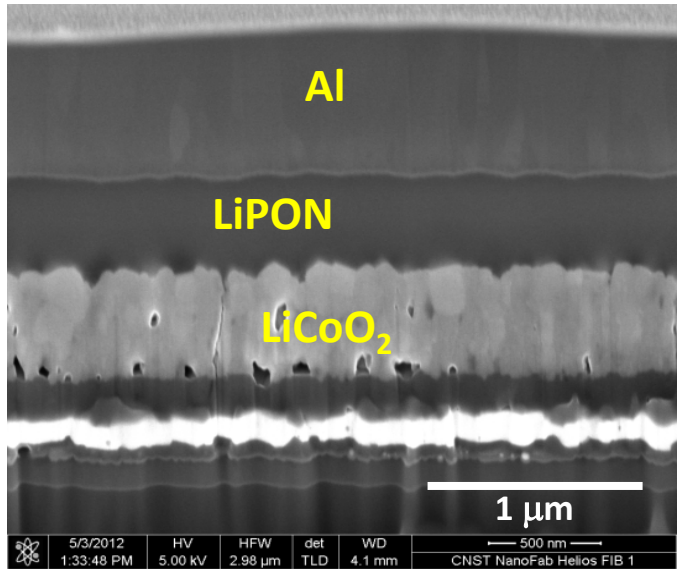
Al is conducting, high capacity, and cheap

$Li + Al \leftrightharpoons LiAl$, ~1000 mAh/g



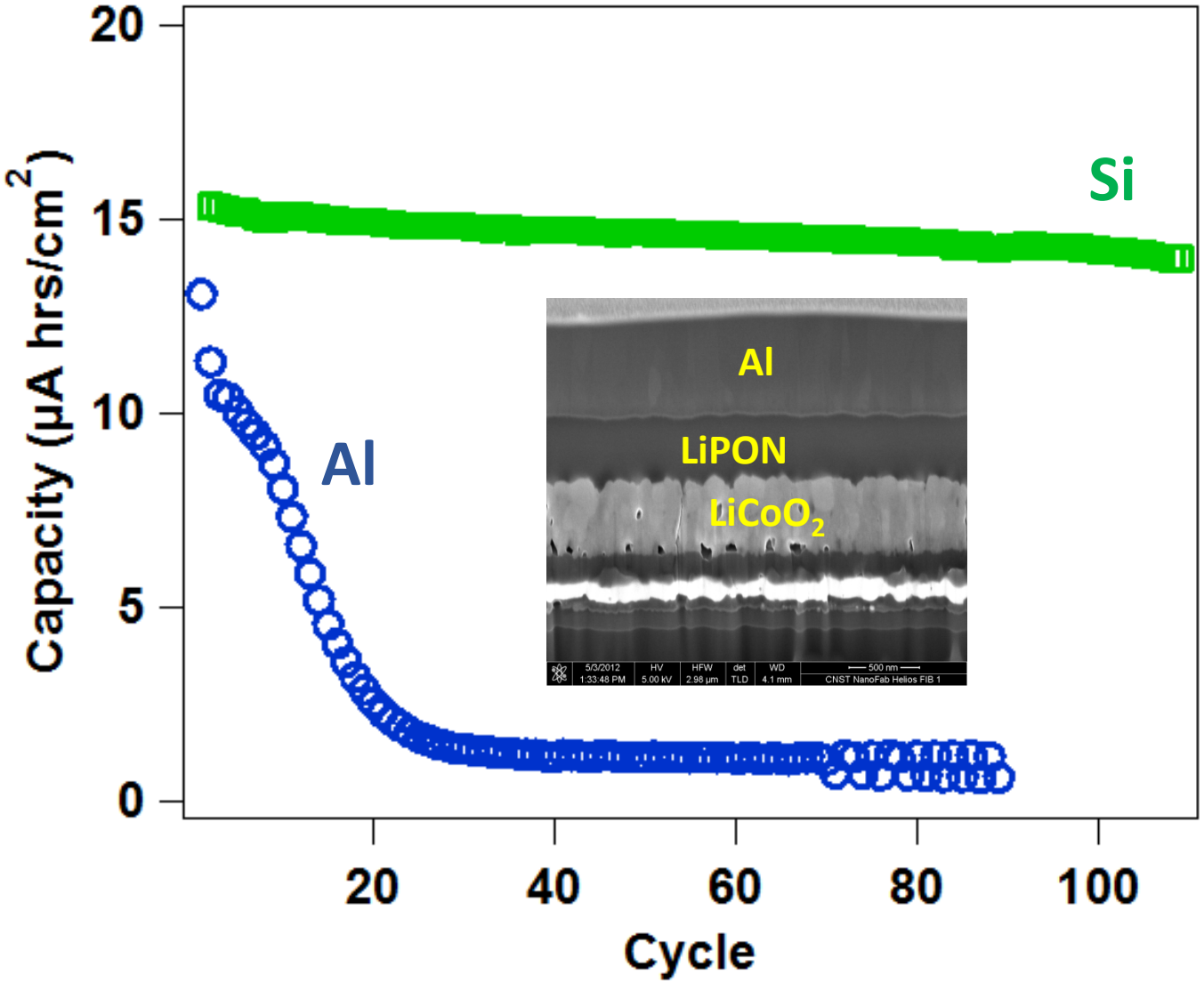


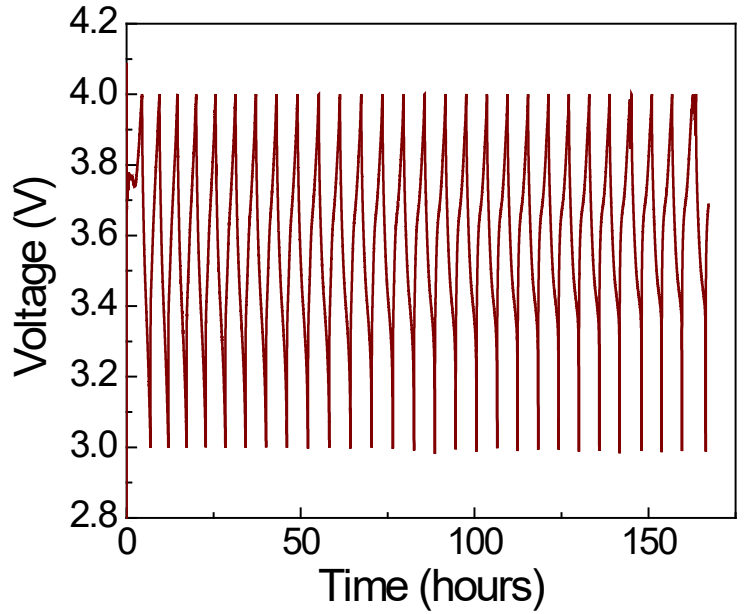


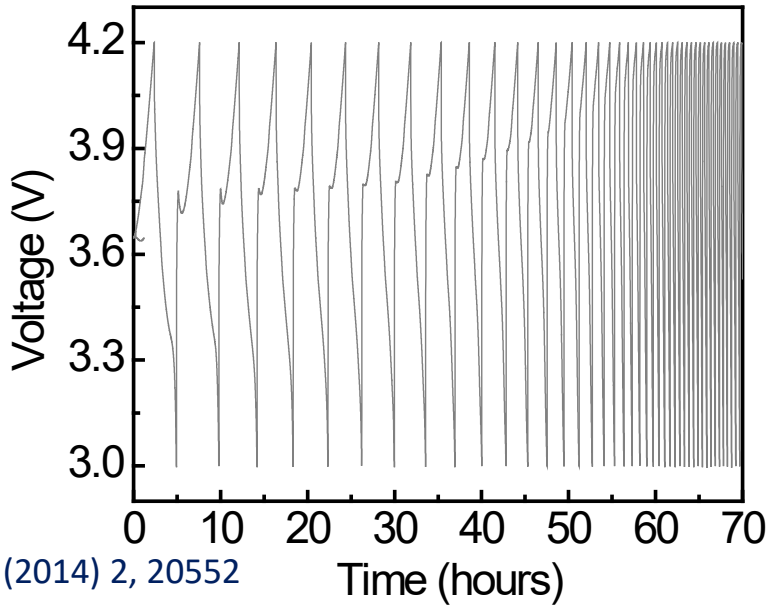


M.S. Leite, D. Ruzmetov, Z. Li, L.A. Bendersky, N..C. Bartelt, A. Kolmakov, A.A. Talin, J. Materials Chem A (2014) 2, 20552

What is the origin of rapid capacity loss for Al anodes?







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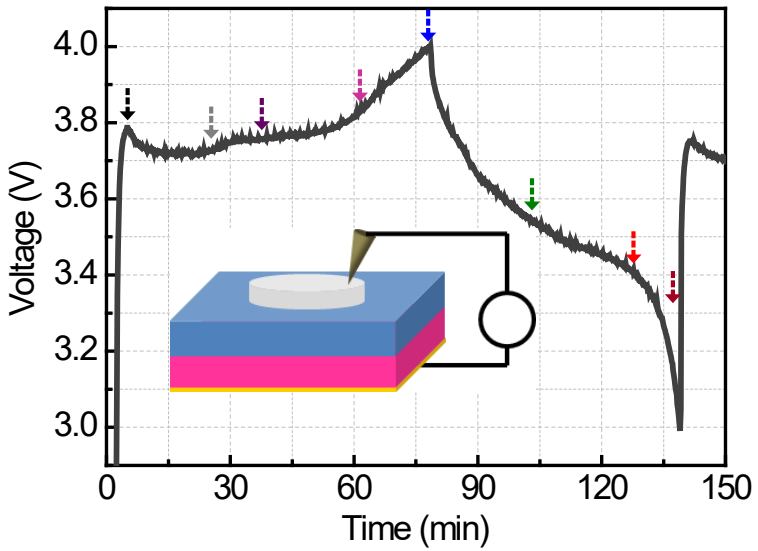
Morphology correlated with charge/discharge plot

I=30nA or 15.3 μA/cm^2

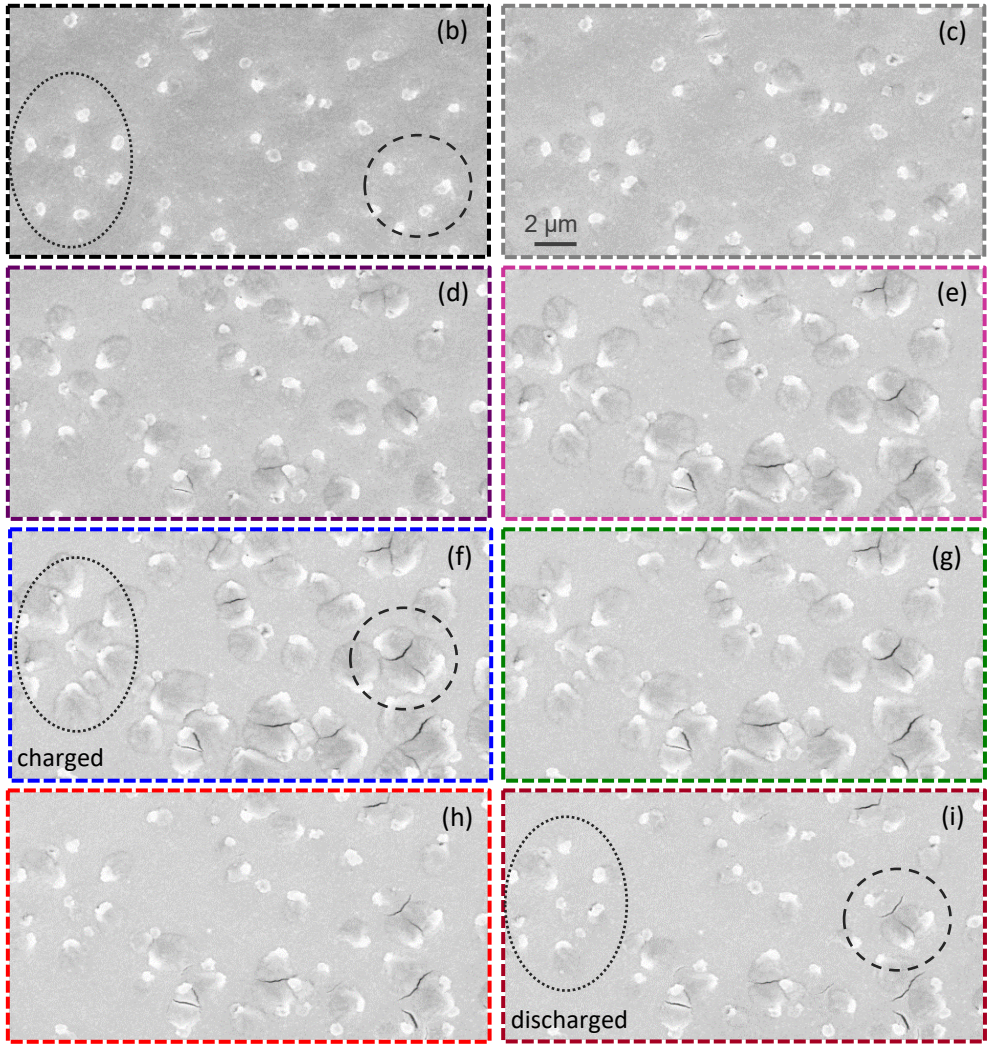


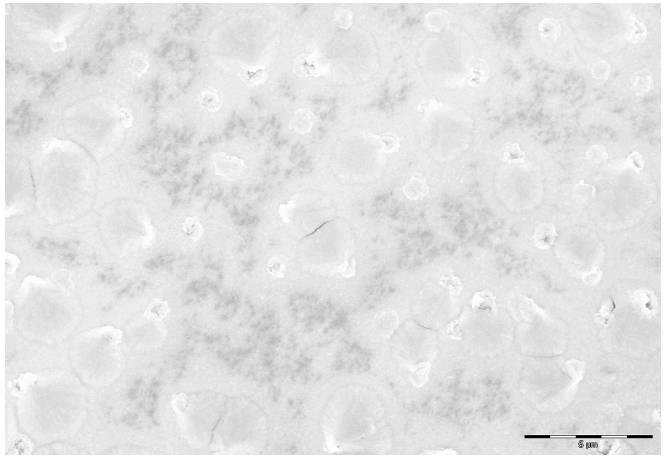
Al moles/dot: 1.09×10^{-8}

Li moles/hr: 1.19×10^{-9}

$$Li + Al \leftrightharpoons LiAl$$

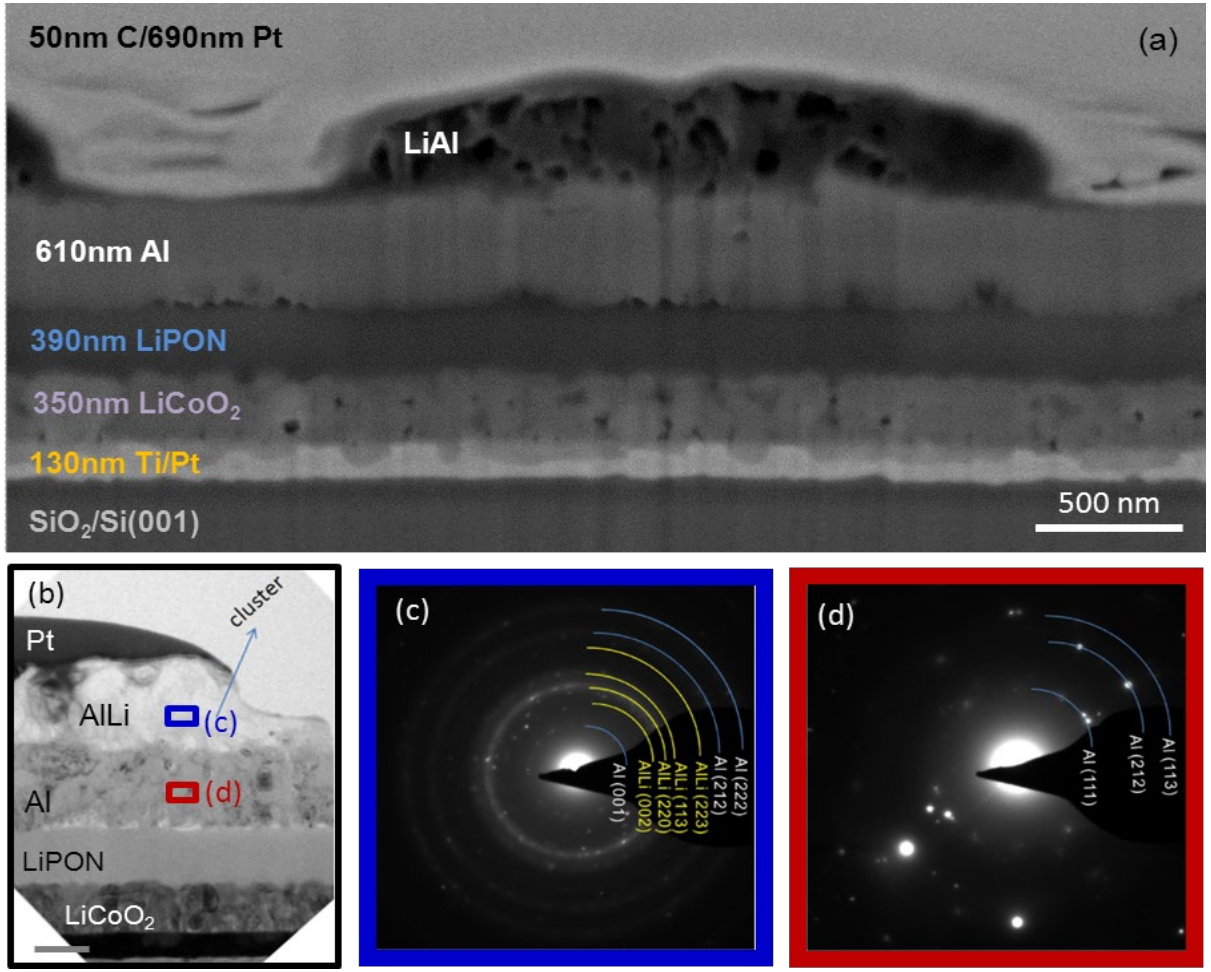
~11% lithiation w.r.t anode

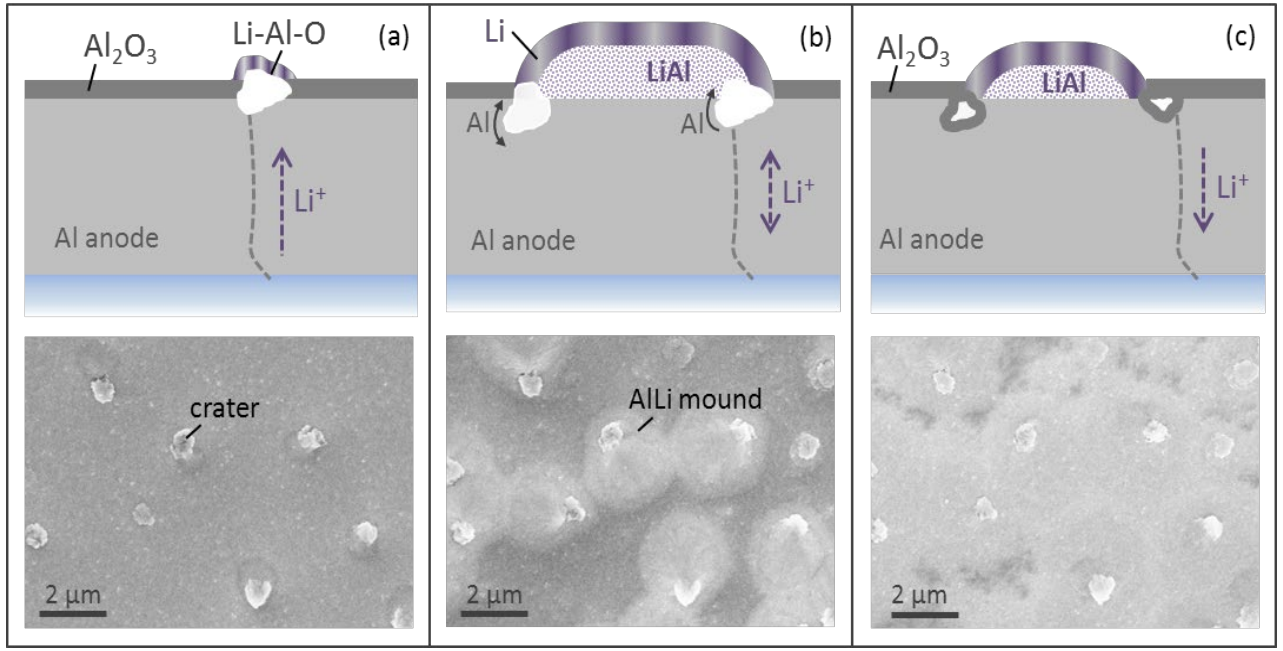




M.S. Leite, D. Ruzmetov, Z. Li, L.A. Bendersky, N..C. Bartelt, A. Kolmakov, A.A. Talin, J. Materials Chem A (2014) 2, 20552

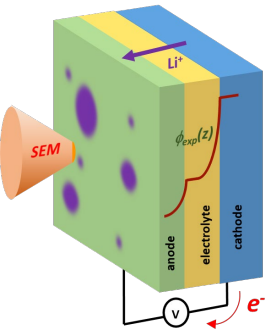
LiAl mounds appear on on the surface to accommodate volume increase

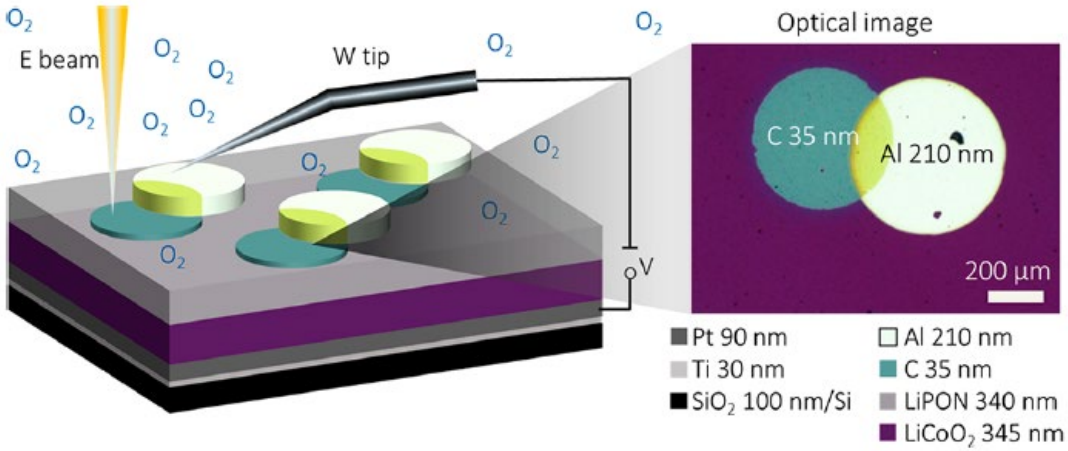


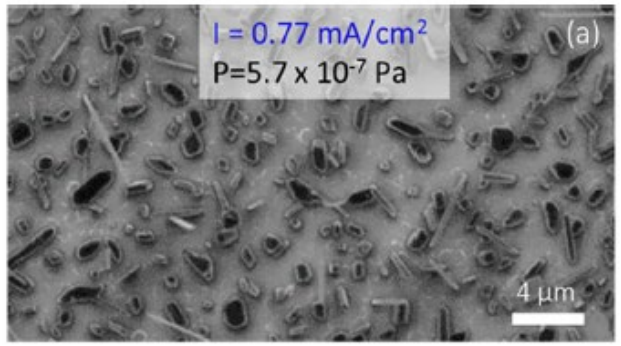


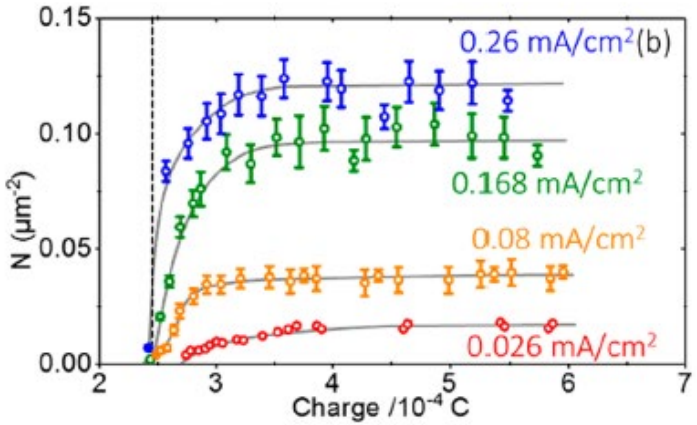
M.S. Leite, D. Ruzmetov, Z. Li, L.A. Bendersky, N..C. Bartelt, A. Kolmakov, A.A. Talin, J. Materials Chem A (2014) 2, 20552

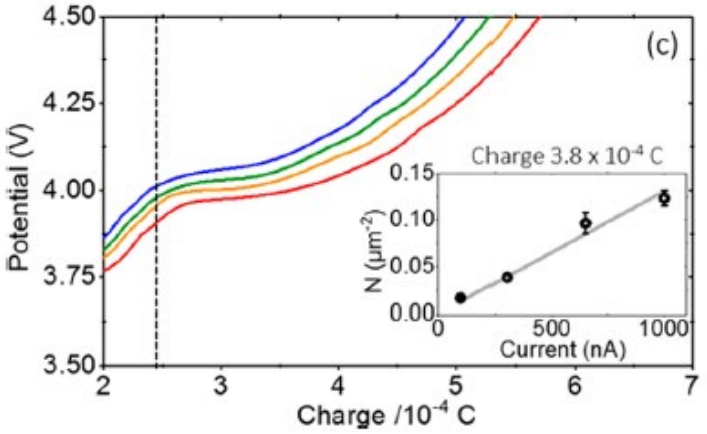
Graphene current collector enables imaging of Li plating











- Close analogy Li plating <--> film growth by PVD
- Model behavior implies uniform Li transport at J<0.3 mA/cm^2

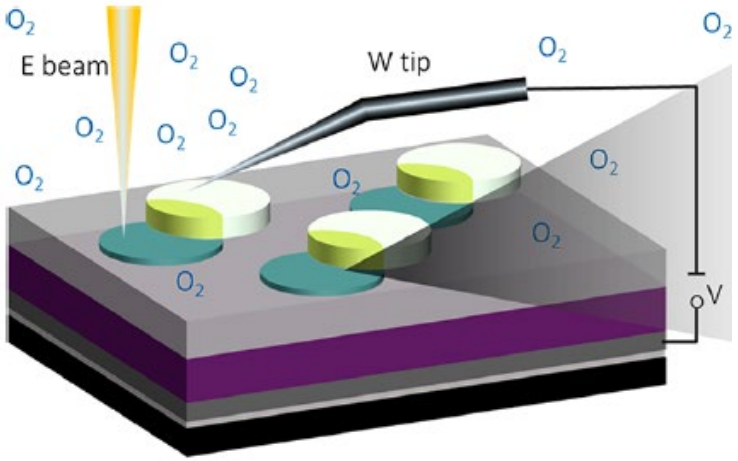
$$\#\text{ of Li clusters } \propto \left(\frac{J}{D}\right)^{z/z+2}$$

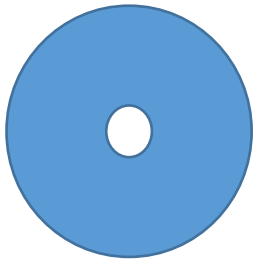
z-critical # of Li atoms in cluster
D-Li surface diffusion
J-current density

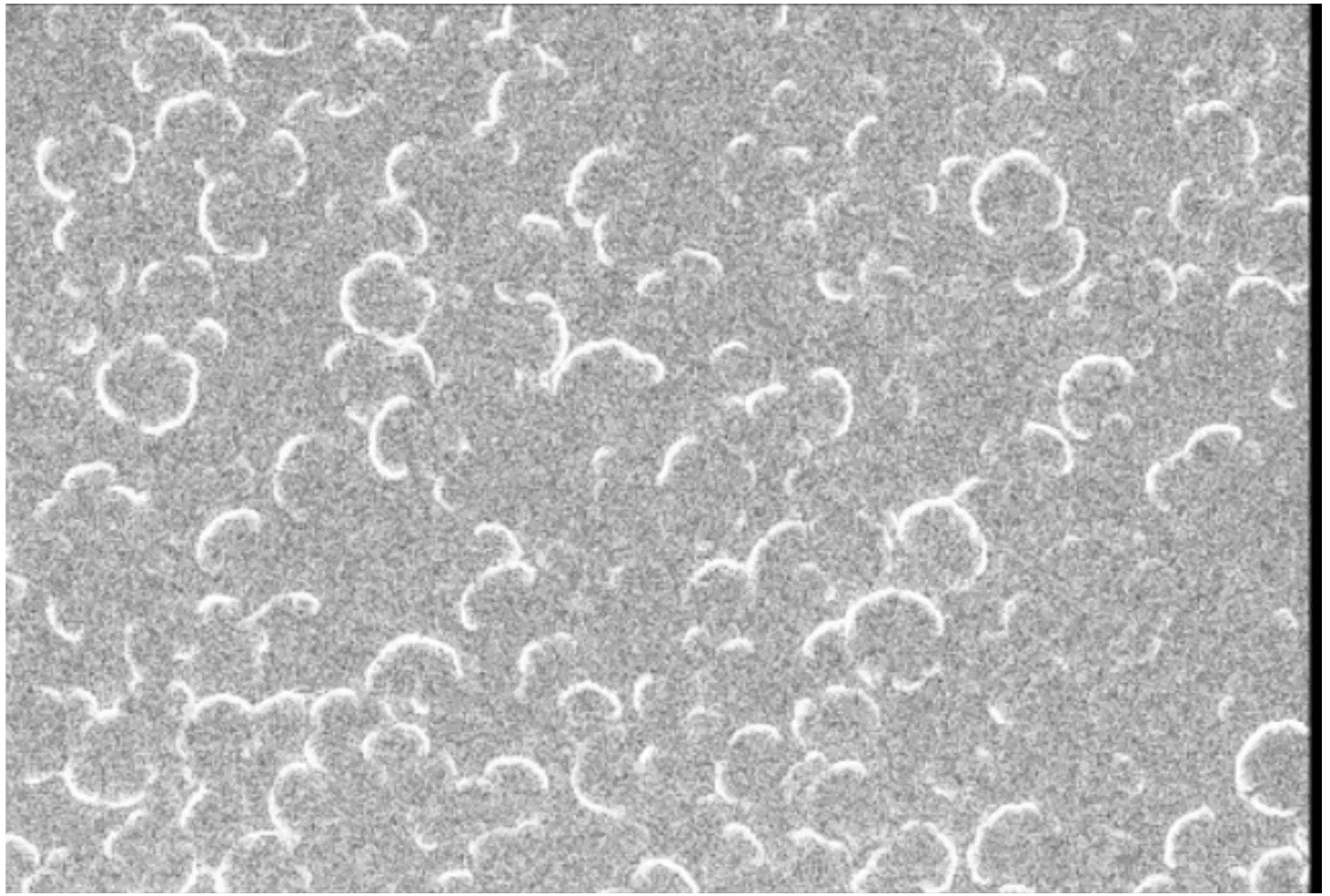
A. Yulaev, V. Oleshko, P. Haney, J. Liu, Y. Qi, A. A. Talin, M. S. Leite, A. Kolmakov, Nano Lett. 18, 1644, (2018).

LCO morphology drives Li whisker formation at @ J>1mA/cm^2

- Li lateral diffusion too slow to match incoming flux

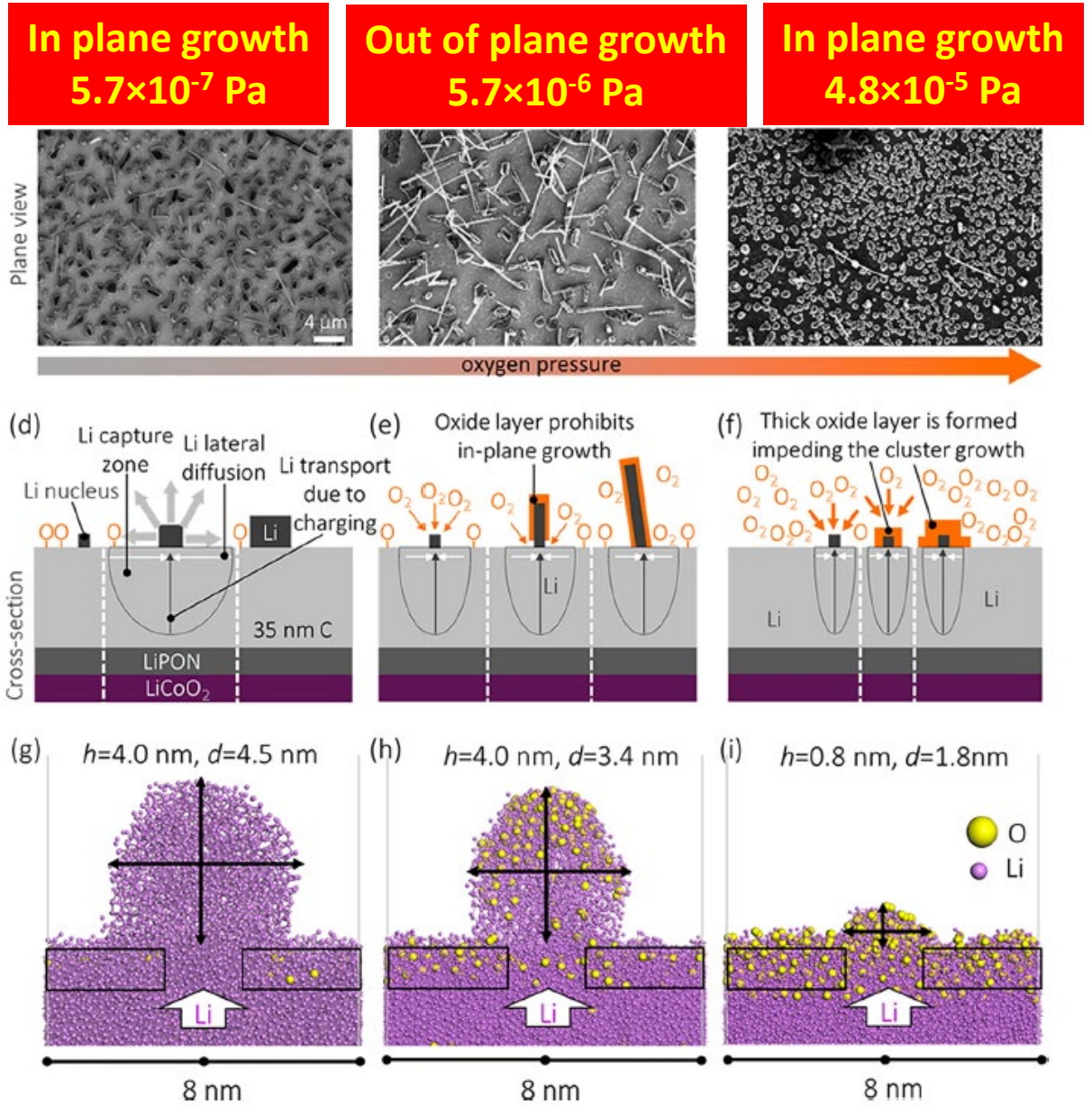






A. Yulaev, V. Oleshko, P. Haney, J. Liu, Y. Qi, A. A. Talin, M. S. Leite, A. Kolmakov, Nano Lett. 18, 1644, (2018).

Reaction with residual O_2 determines Li growth morphology



A. Yulaev, V. Oleshko, P. Haney, J. Liu, Y. Qi, A. A. Talin, M. S. Leite, A. Kolmakov, Nano Lett. 18, 1644, (2018).

Manufacturing Scale-Up of Anodeless Solid-State Lithium Thin-Film Batteries for High Volumetric Energy Density Applications

Diyi Cheng, Khanh Tran, Shoba Rao, Zhongchun Wang, Richard van der Linde, Shahid Pirzada, Hui Yang, Alex Yan, Arvind Kamath,* and Ying Shirley Meng*

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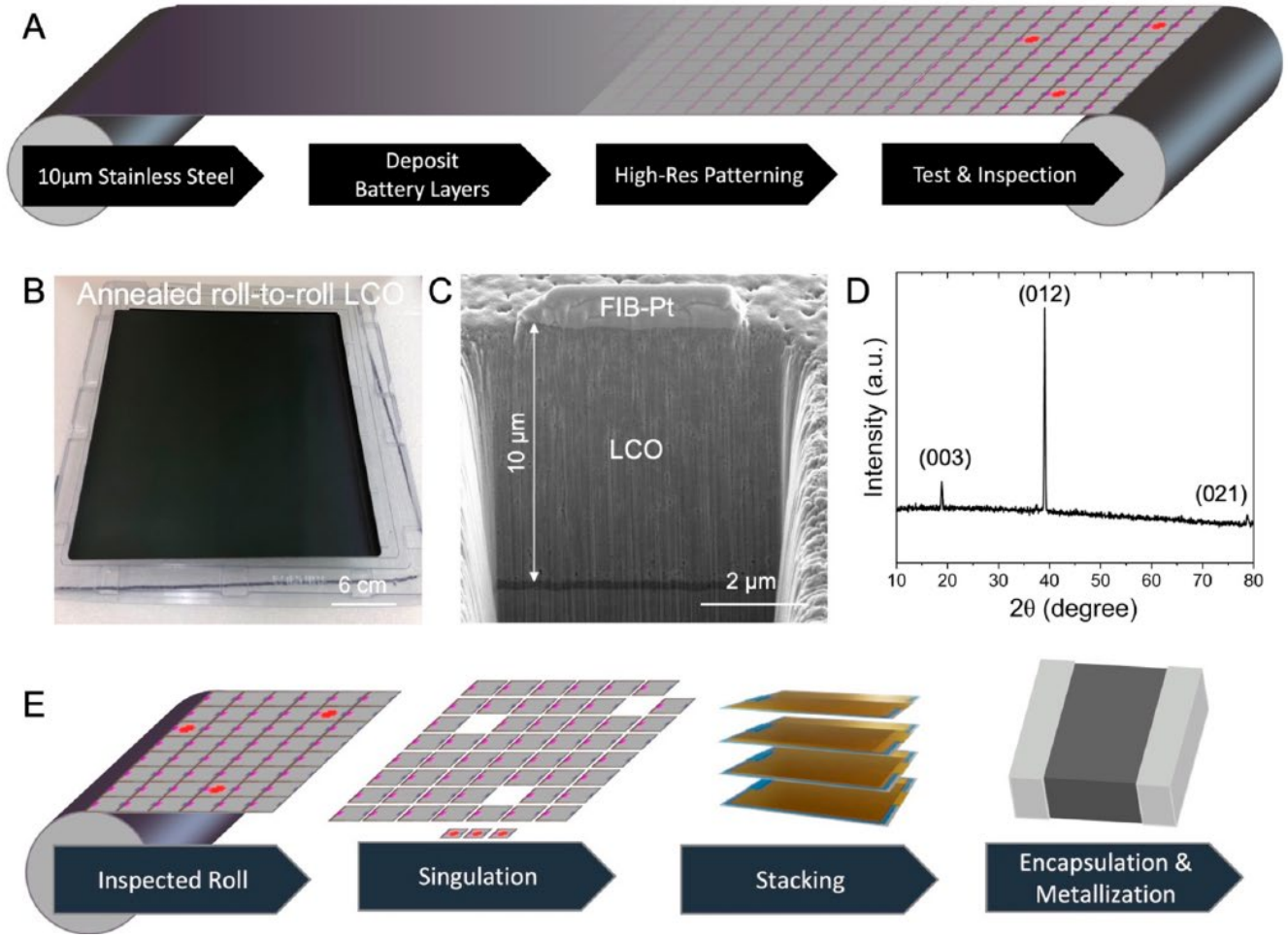
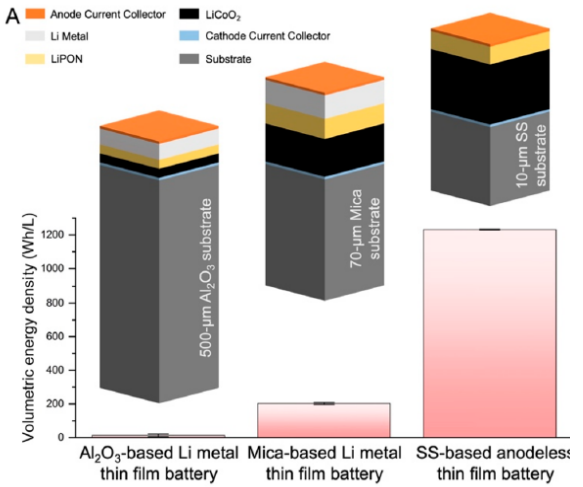
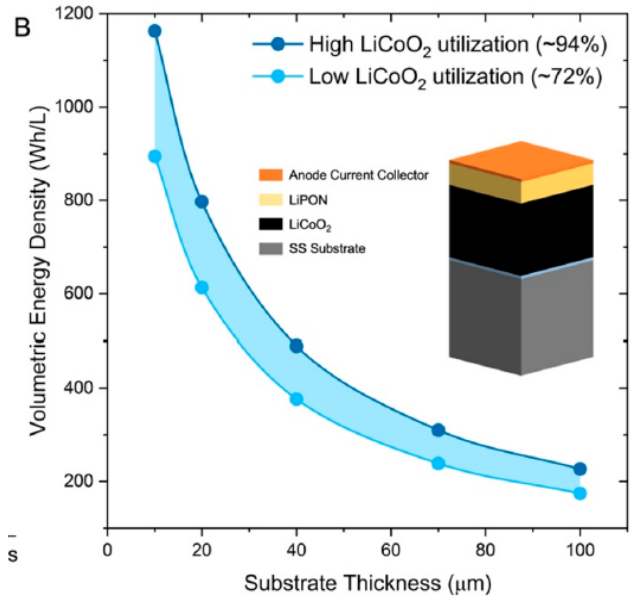
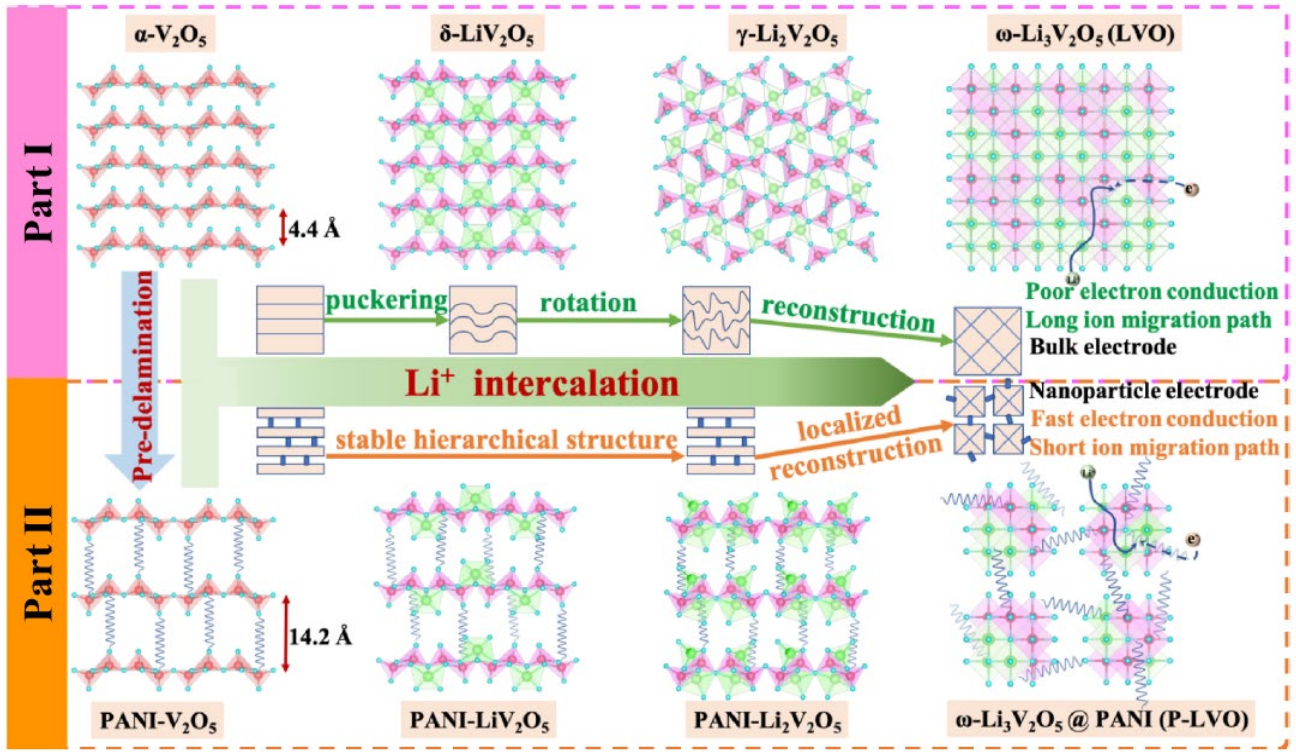
ACS Energy Letters http://pubs.acs.org/journal/aelccp Perspective



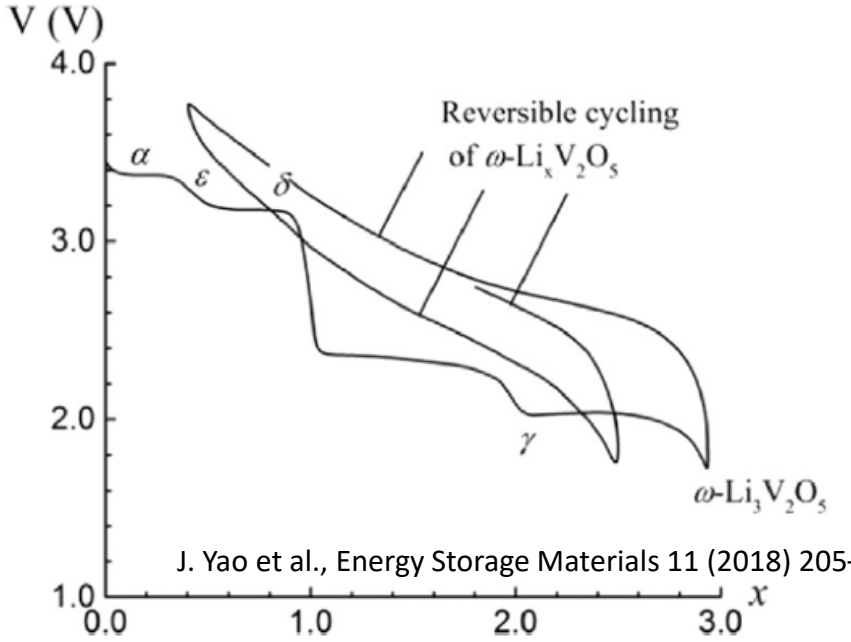




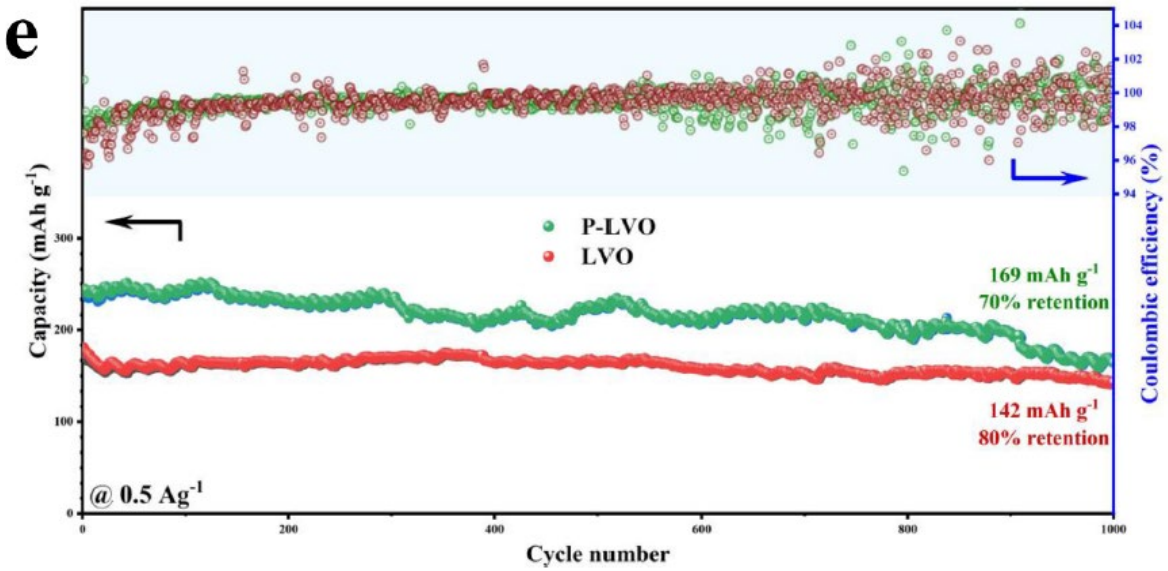
$Li_xV_2O_5$: abundant, non-toxic, and high capacity, but…



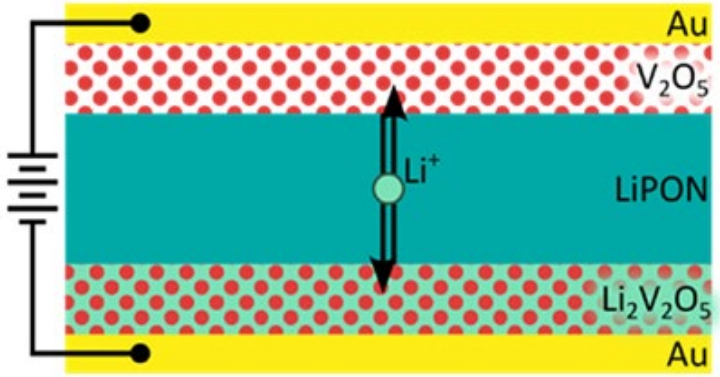
Z. Wang et al., Energy Storage Materials 54 (2023) 284–293

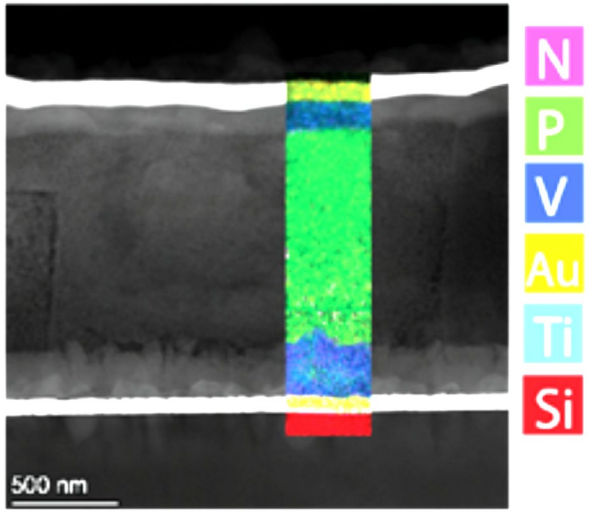


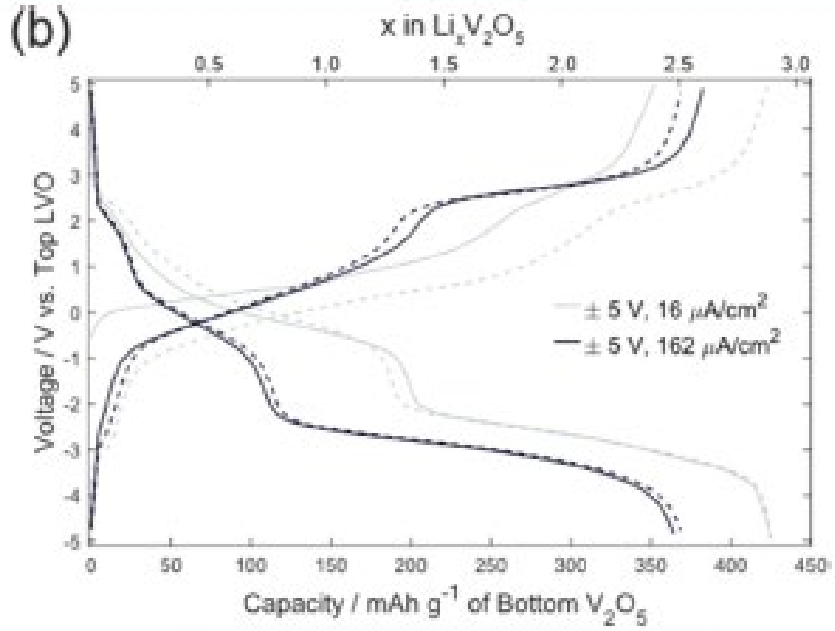
J. Yao et al., Energy Storage Materials 11 (2018) 205–259

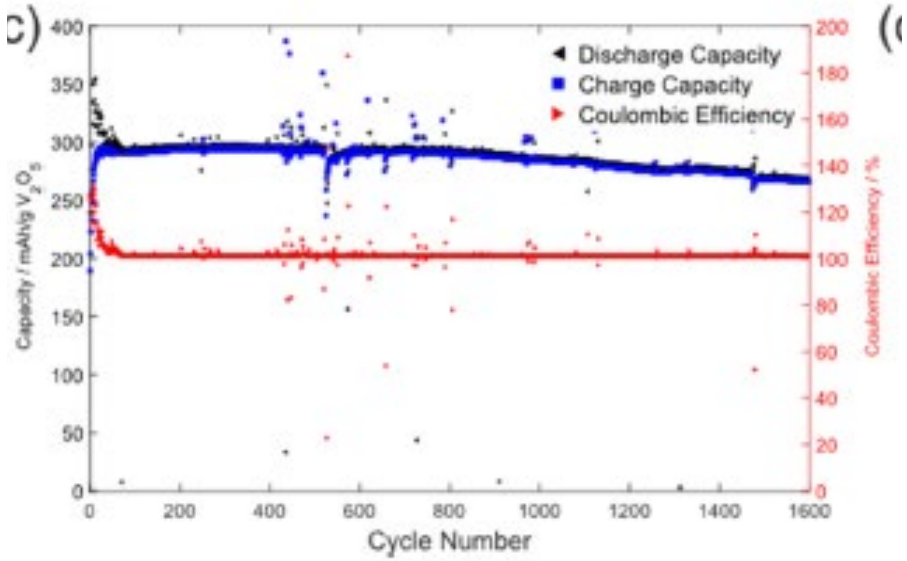


High capacity, endurance for symmetric TFSSB: $Li_xV_2O_5/LiPON/Li_xV_2O_5$









Simultaneous Solid Electrolyte Deposition and Cathode Lithiation for Thin Film Batteries and Lithium Iontronic Devices

Zoey Warecki, Victoria Castagna Ferrari, Donald A. Robinson, Joshua D. Sugar, Jonathan Lee, Anton V. Ievlev, Nam Soo Kim, David Murdock Stewart, Sang Bok Lee, Paul Albertus, Gary Rubloff, and A. Alec Talin*

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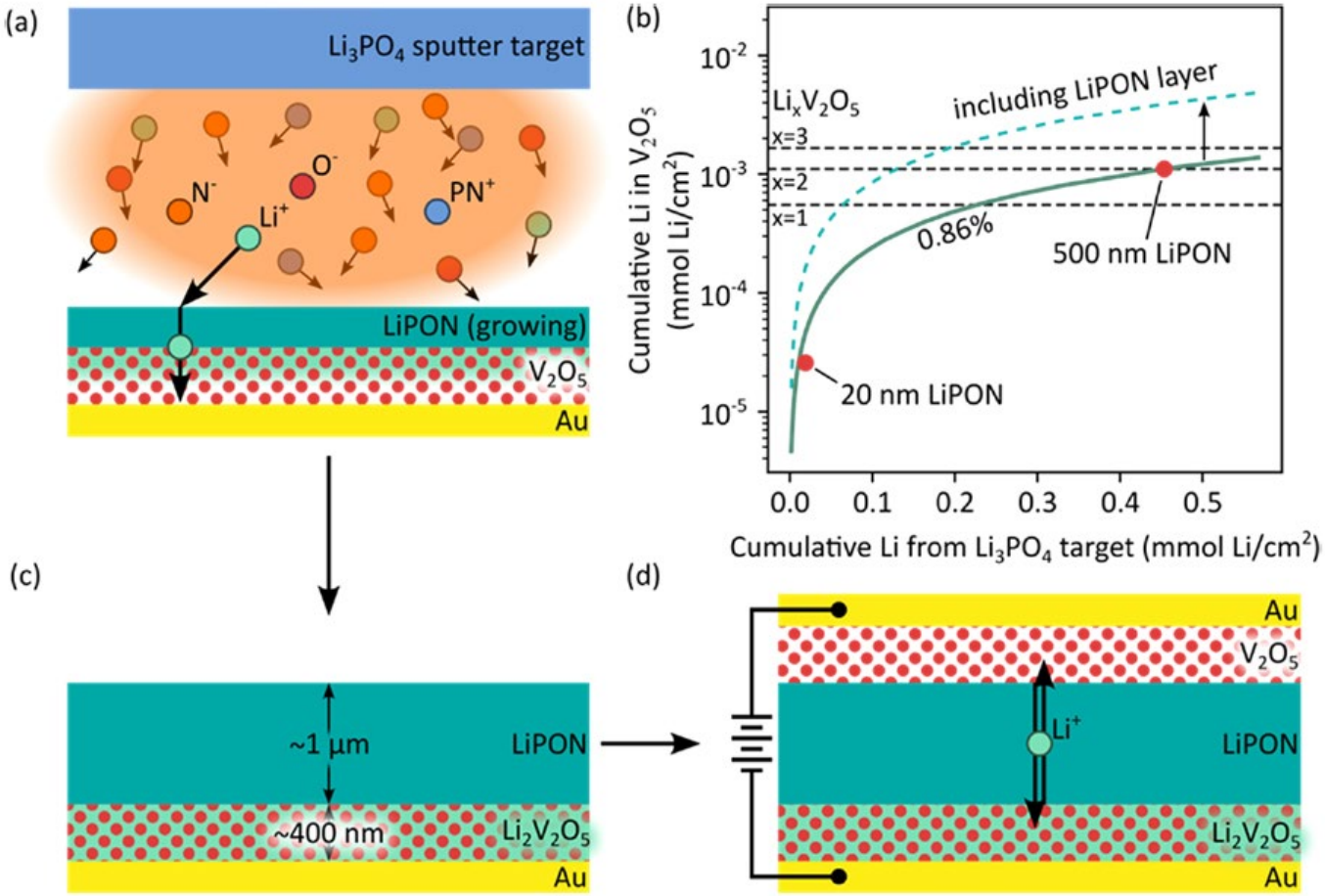
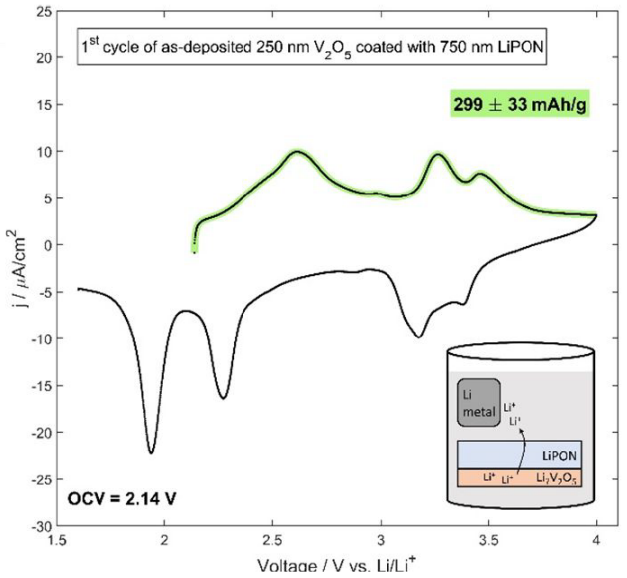
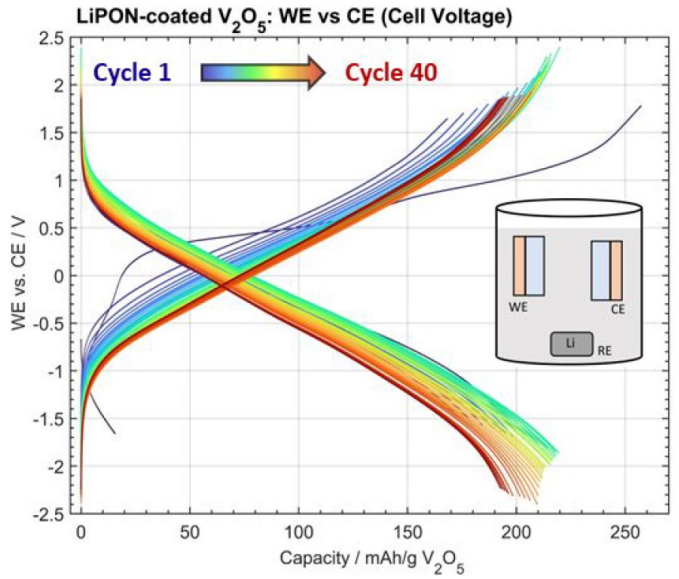
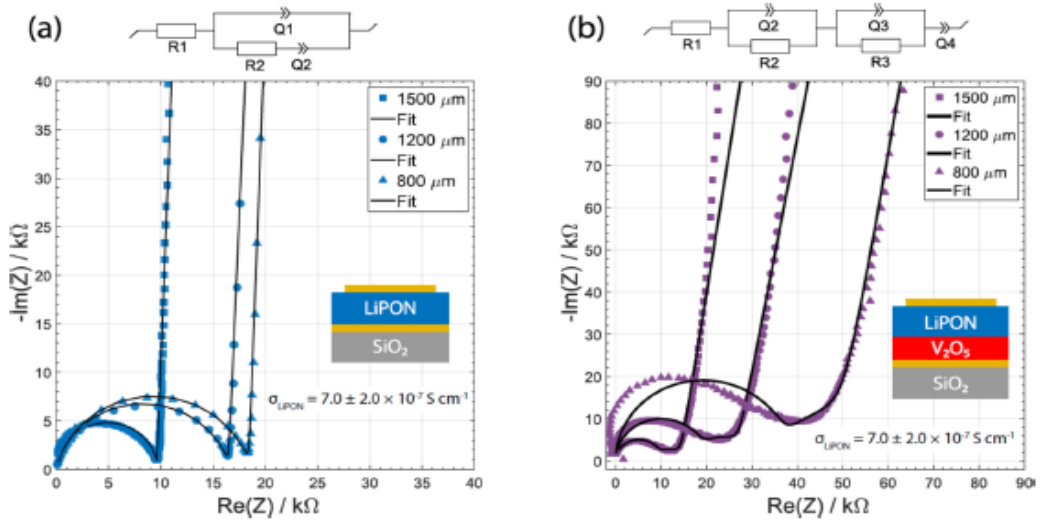




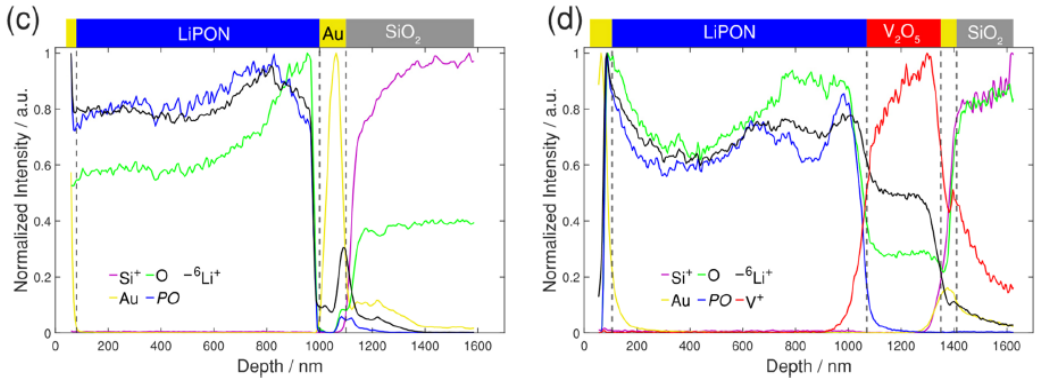


σ, [Li] ~same for LiPON/Au vs LiPON/V_2O_5→Li comes from plasma

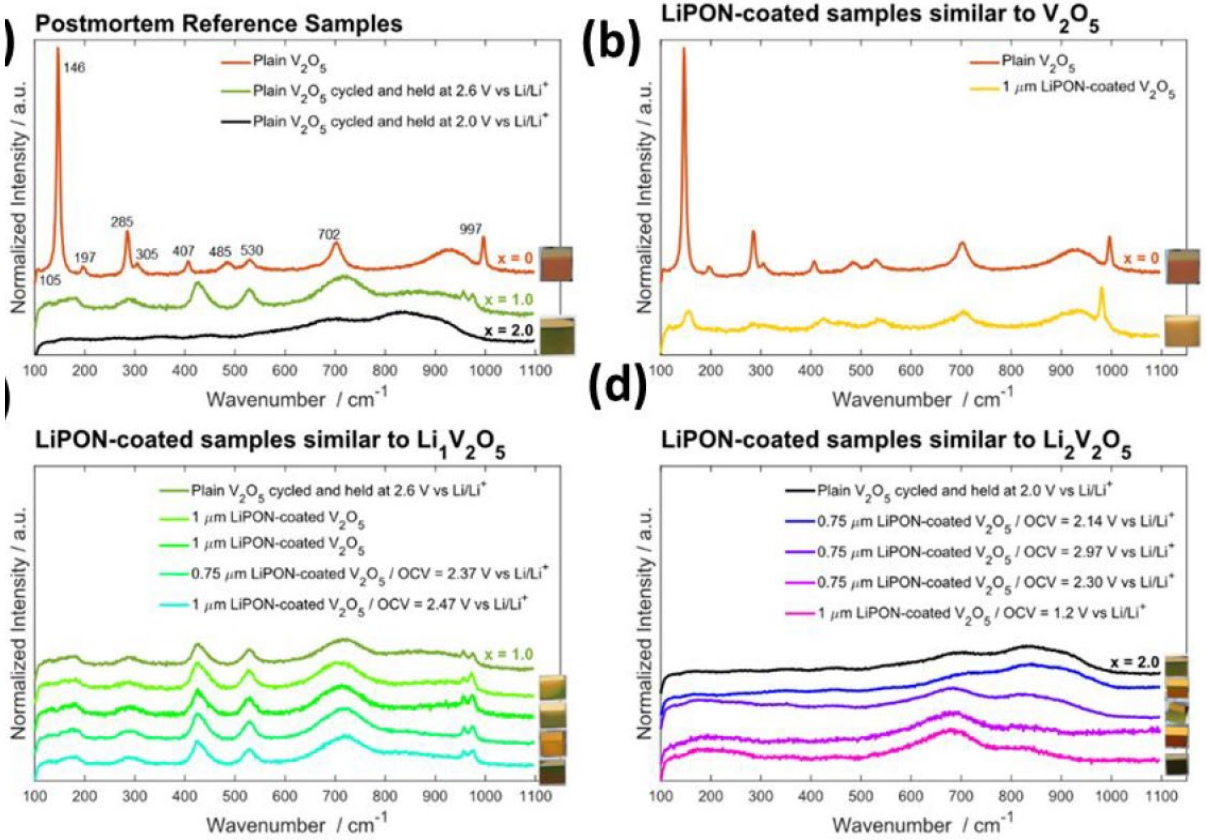
EIS



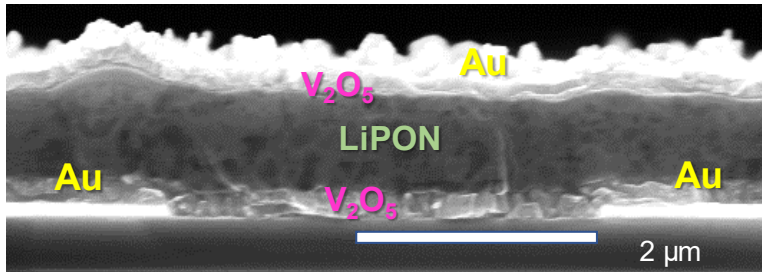
ToF-SIMS

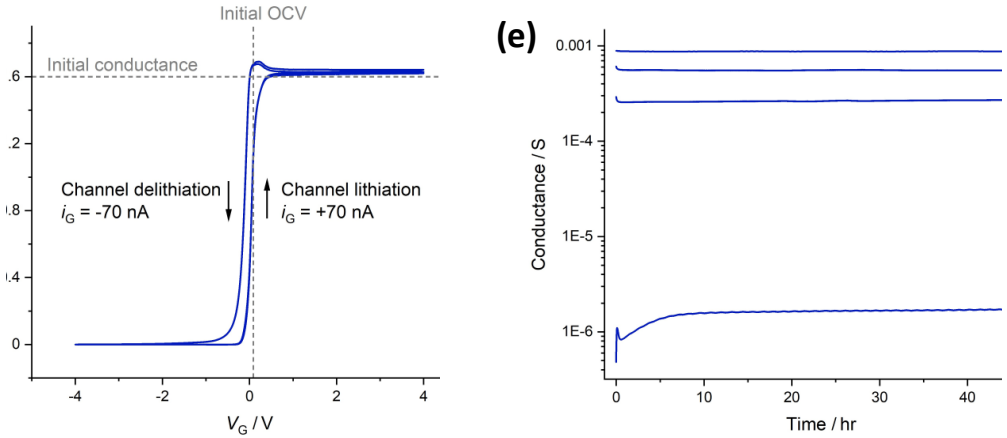


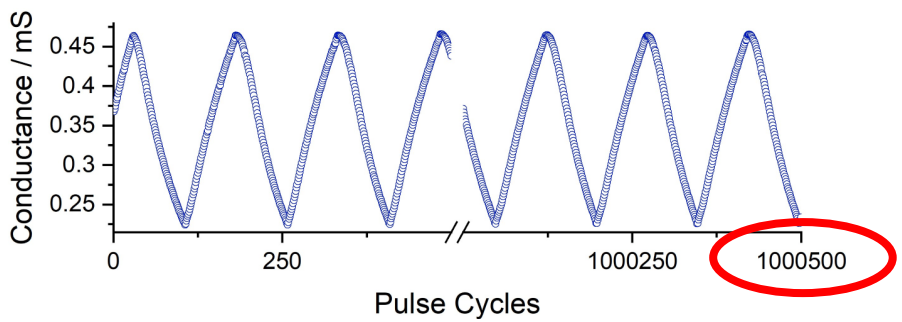
Raman



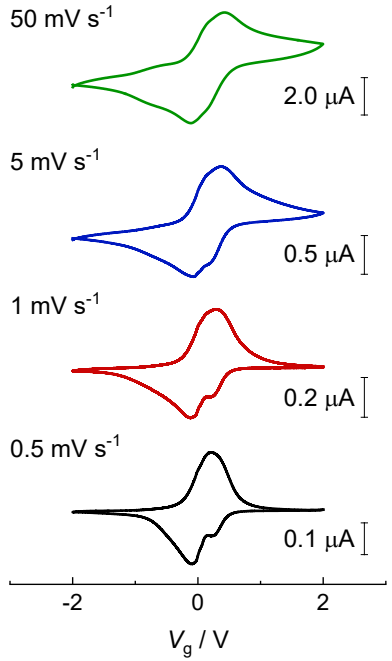
Autolithiation confirmed with ECRAM

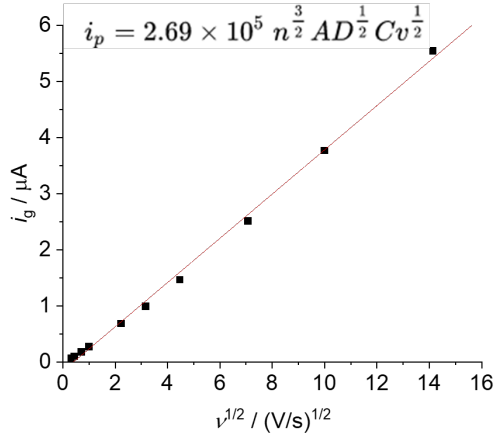






$$V_2O_5 + xLi^+ + xe^- \rightarrow Li_xV_2O_5$$





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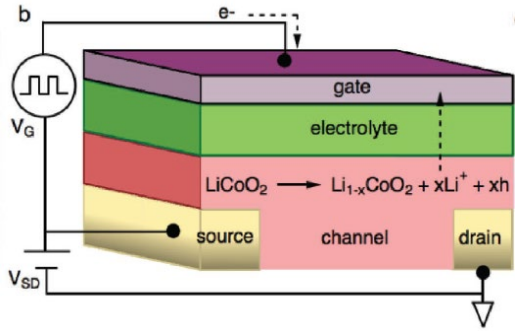
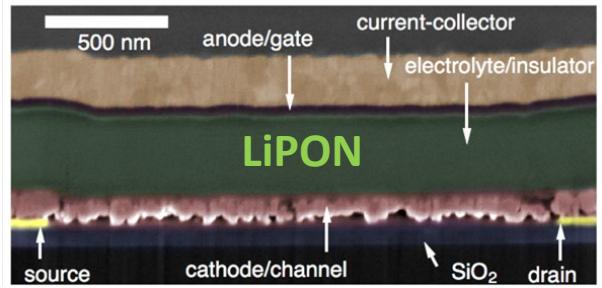
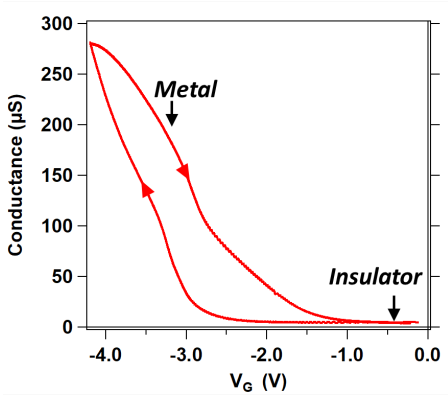
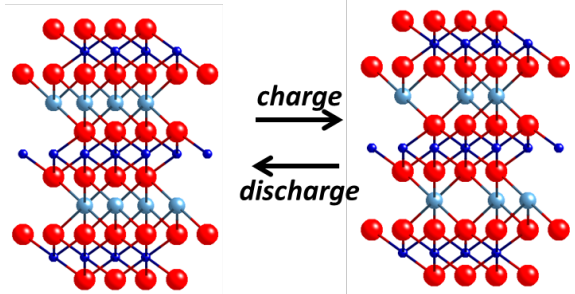
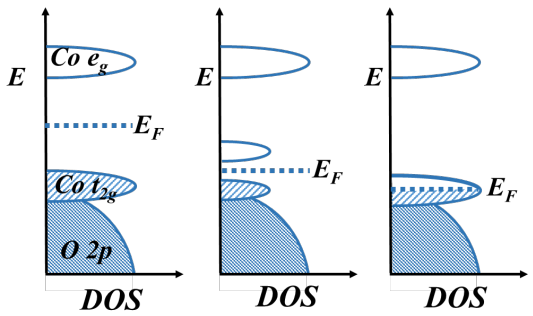
Autolithiation with $LiCoO_2$ previously not fully appreciated











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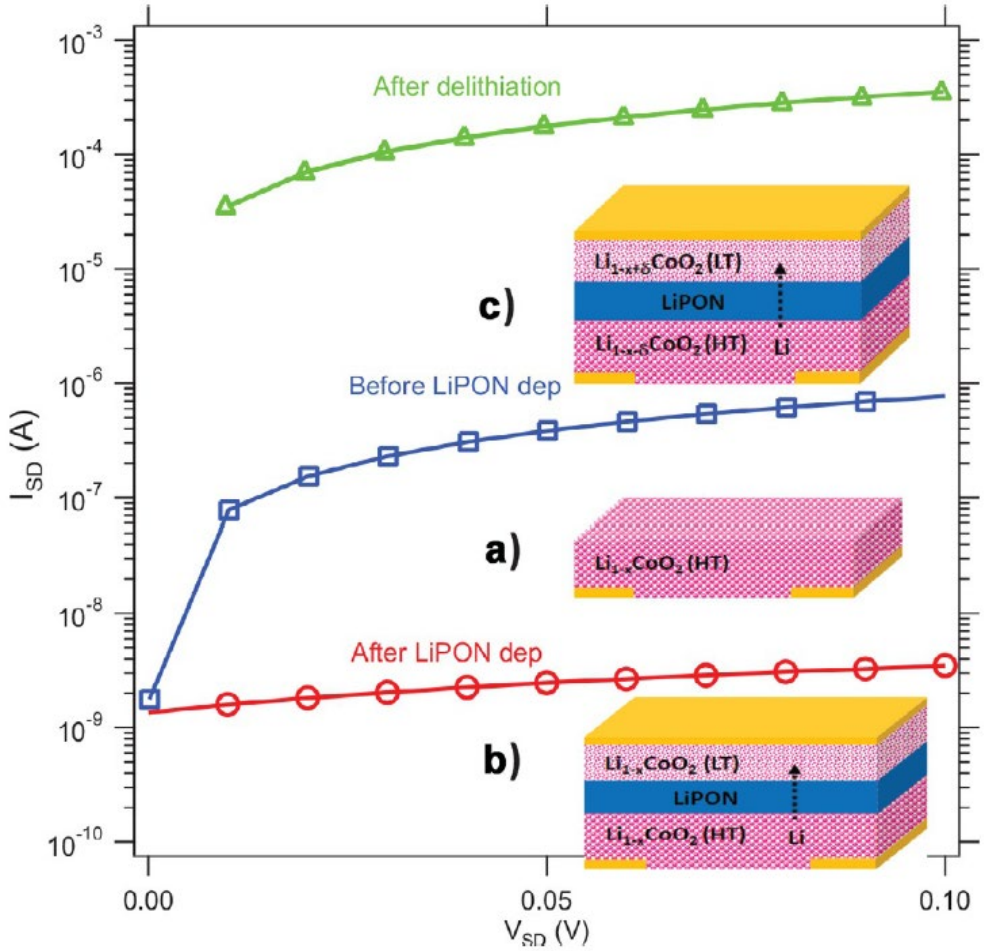

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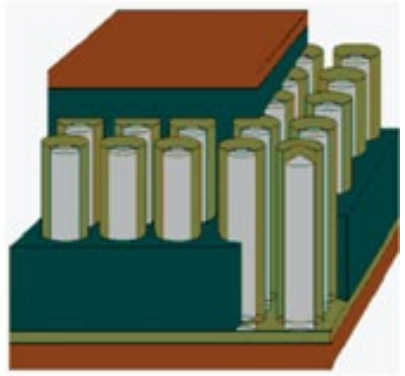
Summary Part I

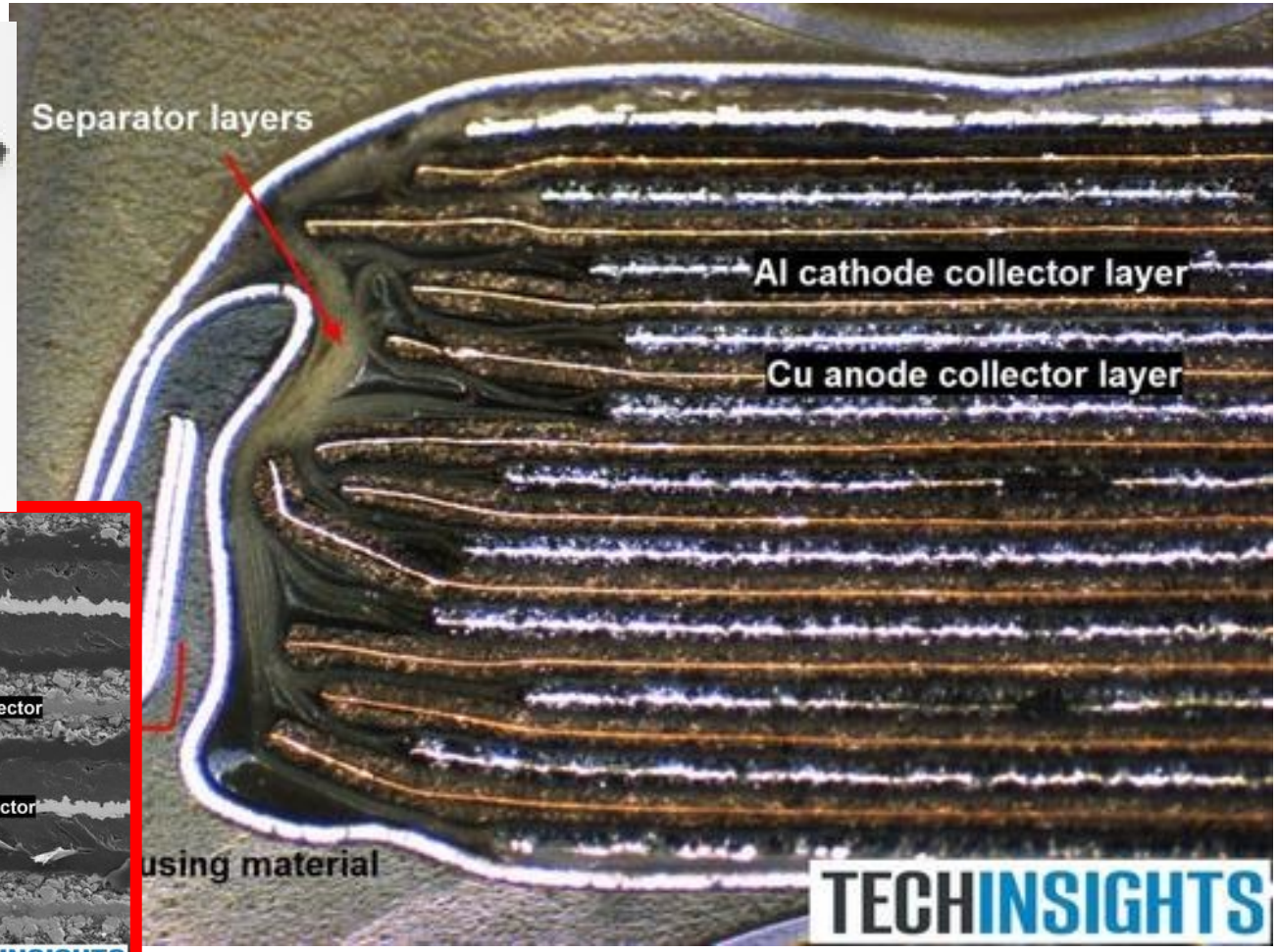
- Thin film batteries offer safe, high energy density, long-lasting energy storage solutions
- Stacked multilayer TFSSBs coming to markets, may widen applications space
- Excellent systems for fundamental studies
- Massive Li incorporation during deposition discovered, may simplify TFSSB fabrication
- Electronic conductivity is a sensitive in situ probe for Li incorporation

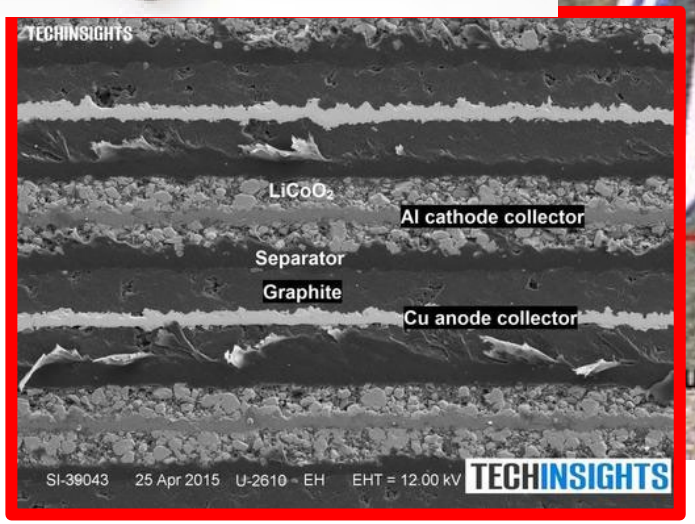
Part 2: ionogels, composites, and 3D-architectures



Arthur et al., MRS Bull. 2011

3D structure key for high power and energy density

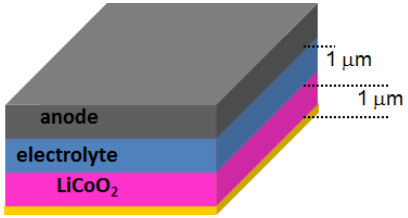


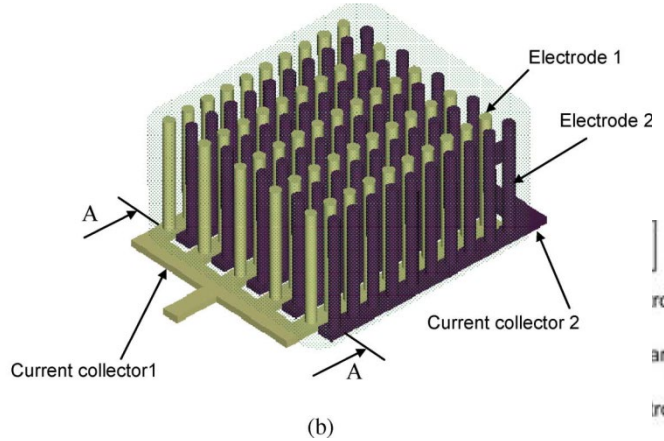


http://www.techinsights.com/Blog.aspx?id=27917288231&blogid=2147484418

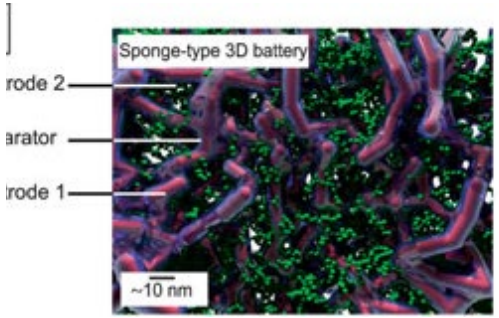
3D LIB designs for higher power, energy density

Planar (2D) battery

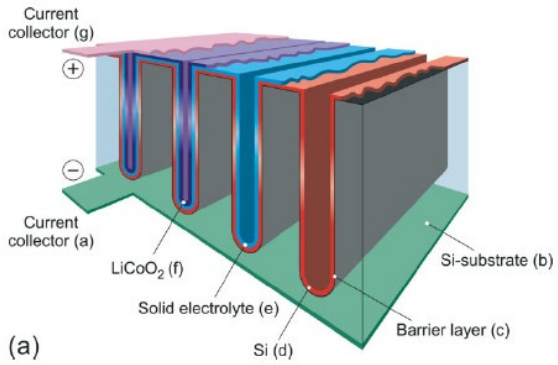




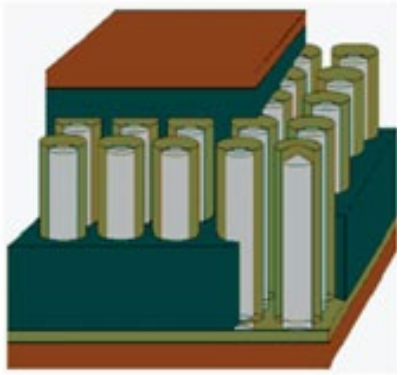
Fardad et al, J. MEMS 16, 2007



Long, Rolison , Acc. Chem. Res. 2007



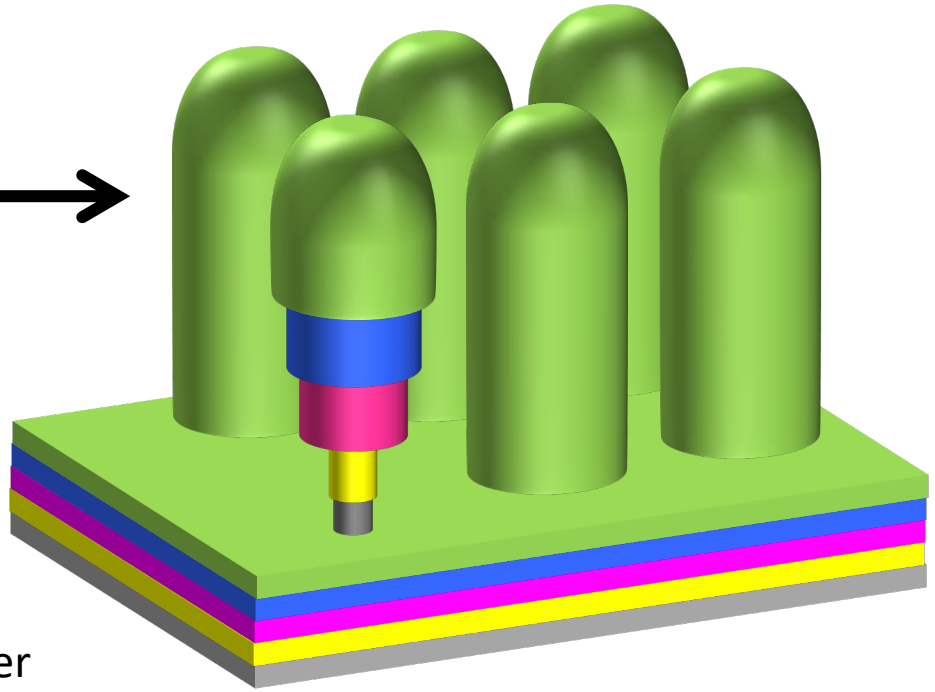
Notten et al., Adv. Mat. 2007

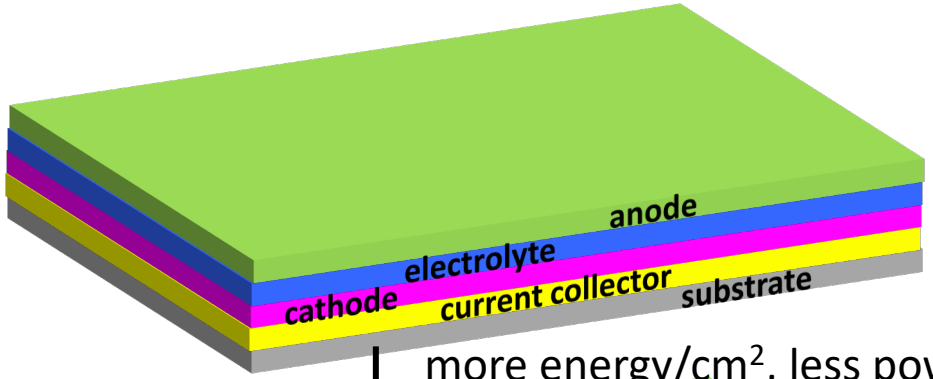


Arthur et al., MRS Bull. 2011

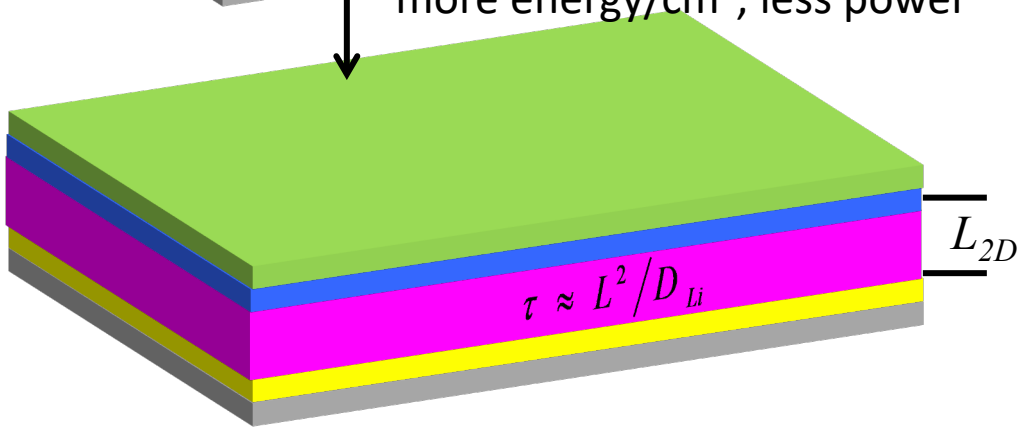
3D LIB designs for higher power, energy density

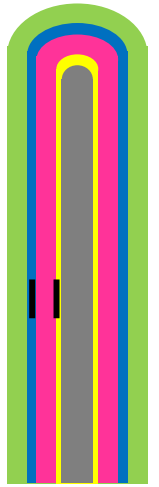
- *Decrease diffusion length*
- *Increase interface area*



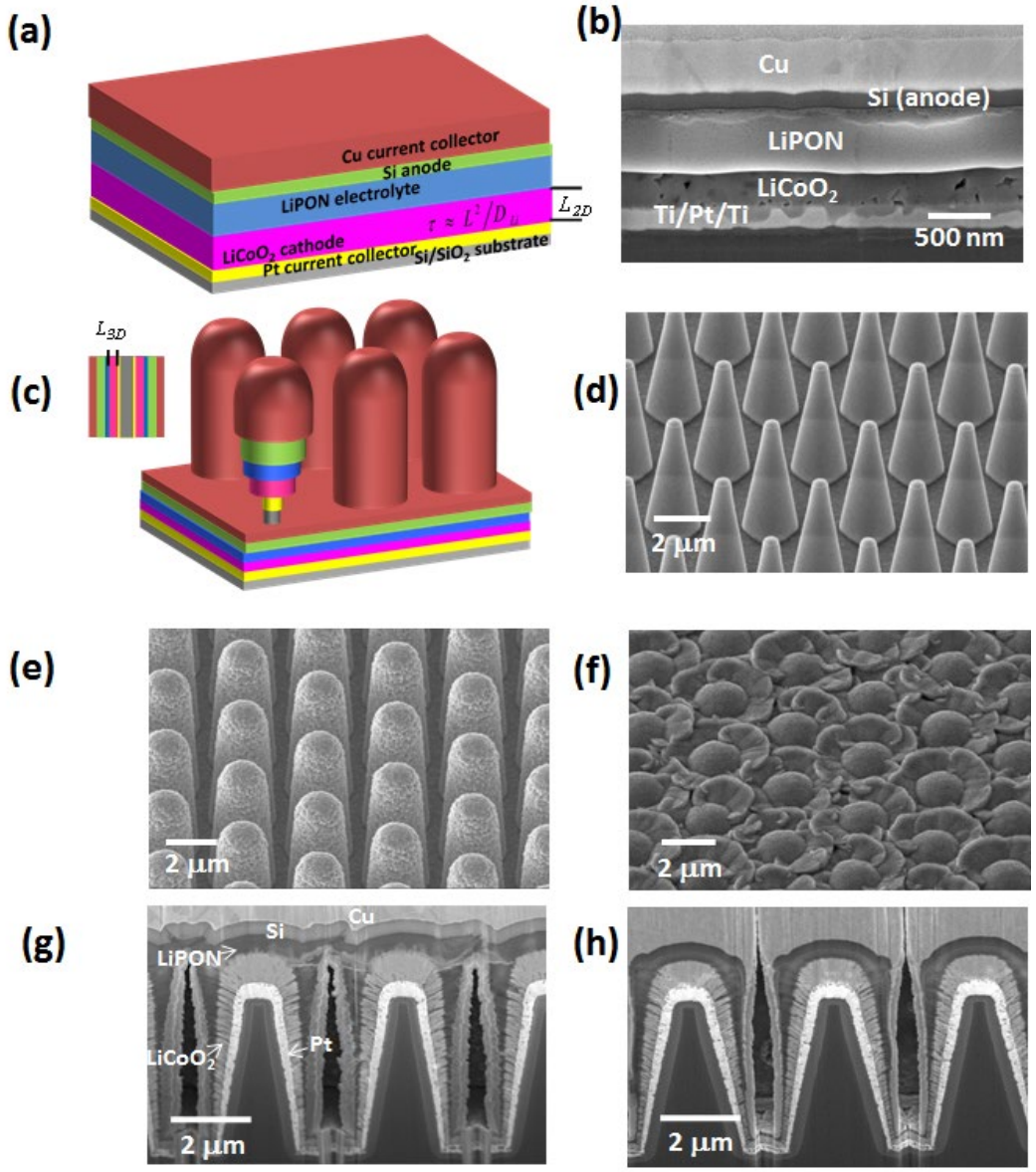


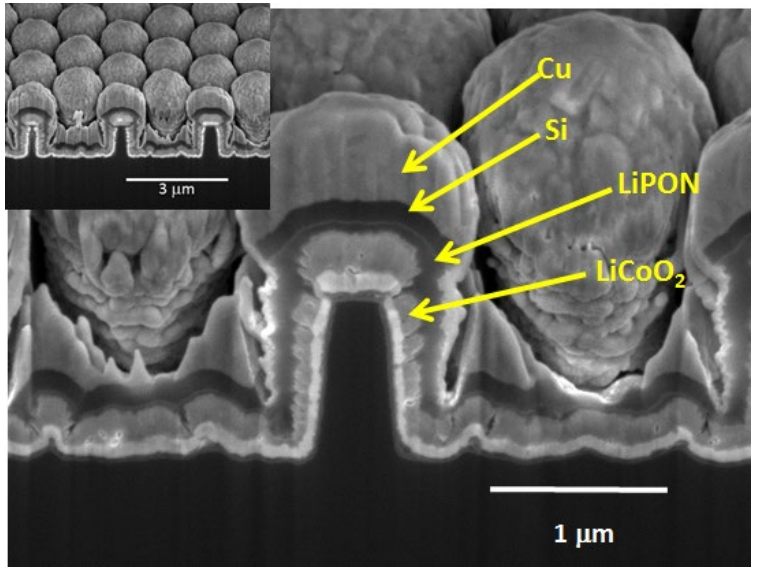
more energy/cm^2, less power





First all solid state 3D LIBs

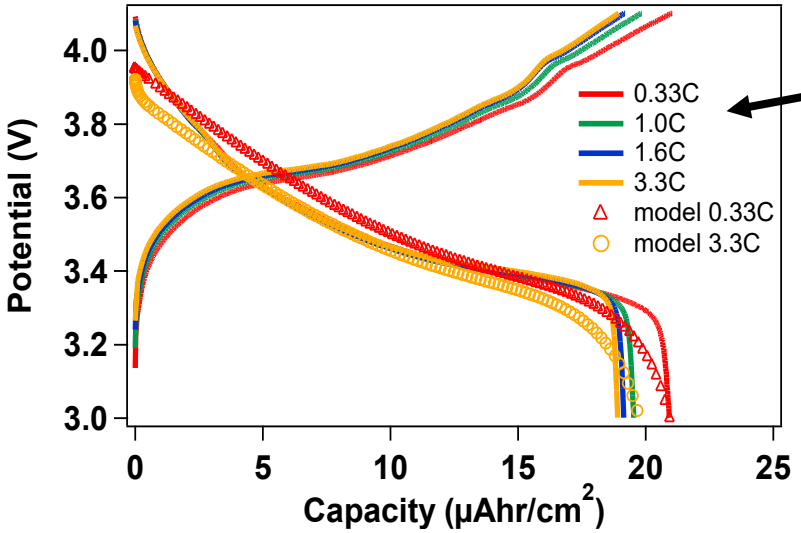


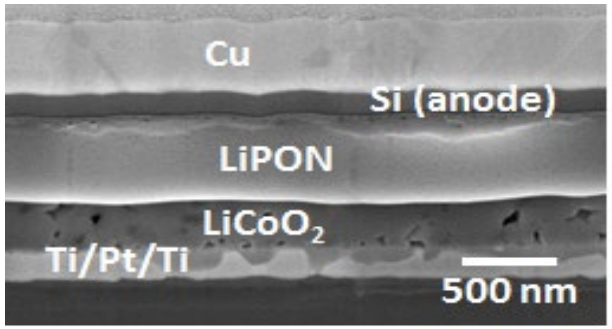


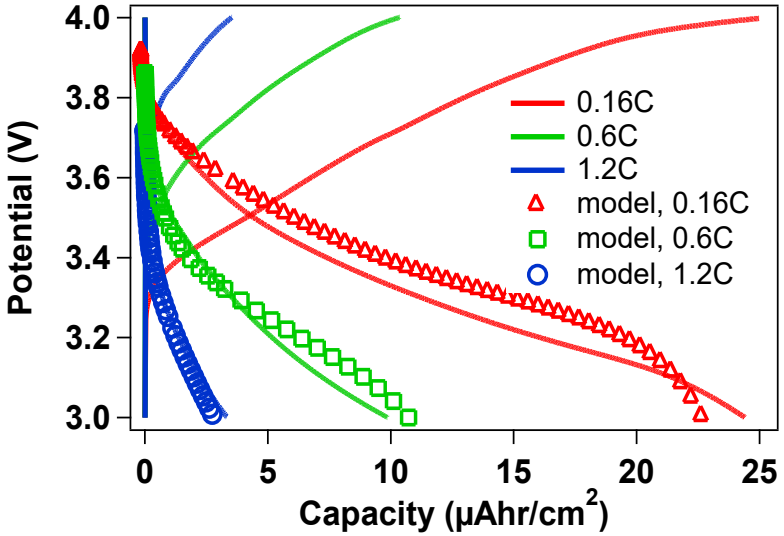
A. A Talin, D. Ruzmetov,⊥ A.Kolmakov, K. McKelvey, N. Ware, F. El Gabaly, B. Dunn, and H. S. White, ACS Appl. Mater. Interfaces 2016, 8, 32385

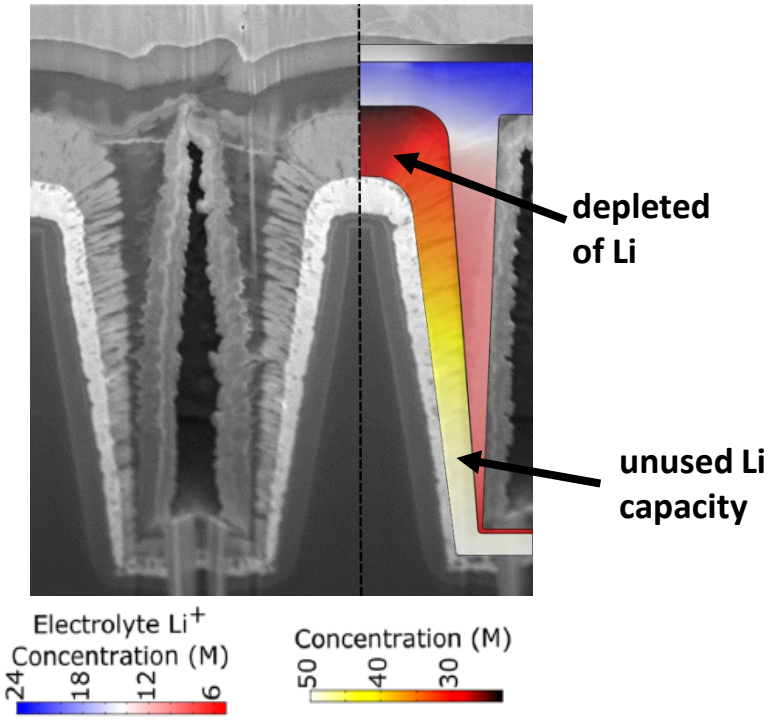
Planar battery works BETTER than 3D!

Non-uniformity causes Li depletion, poor performance

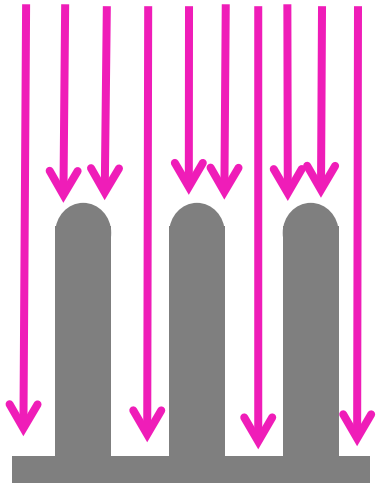


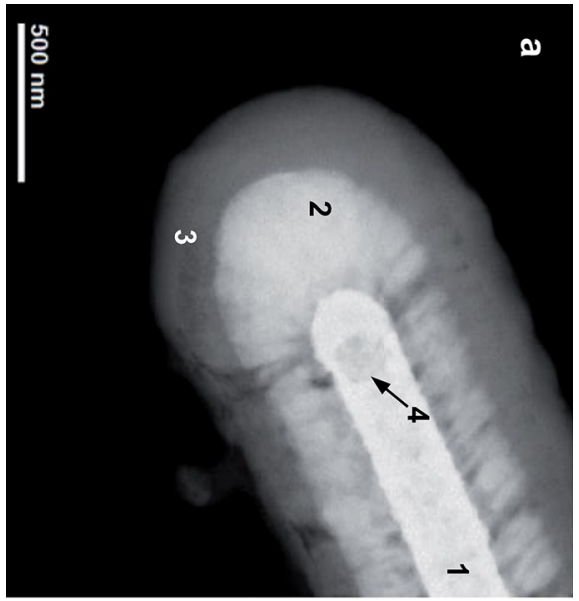


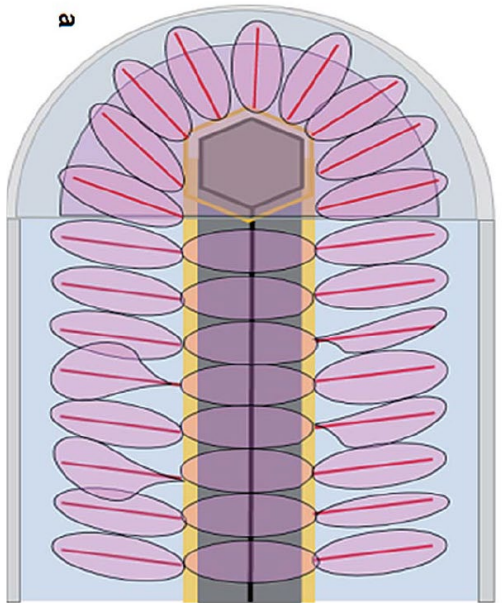


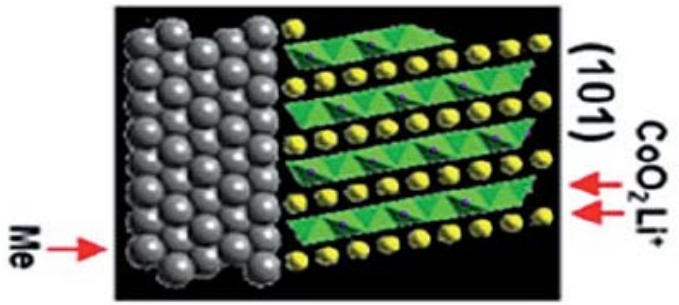


Glancing angle deposition affects $LiCoO_2$ microstructure



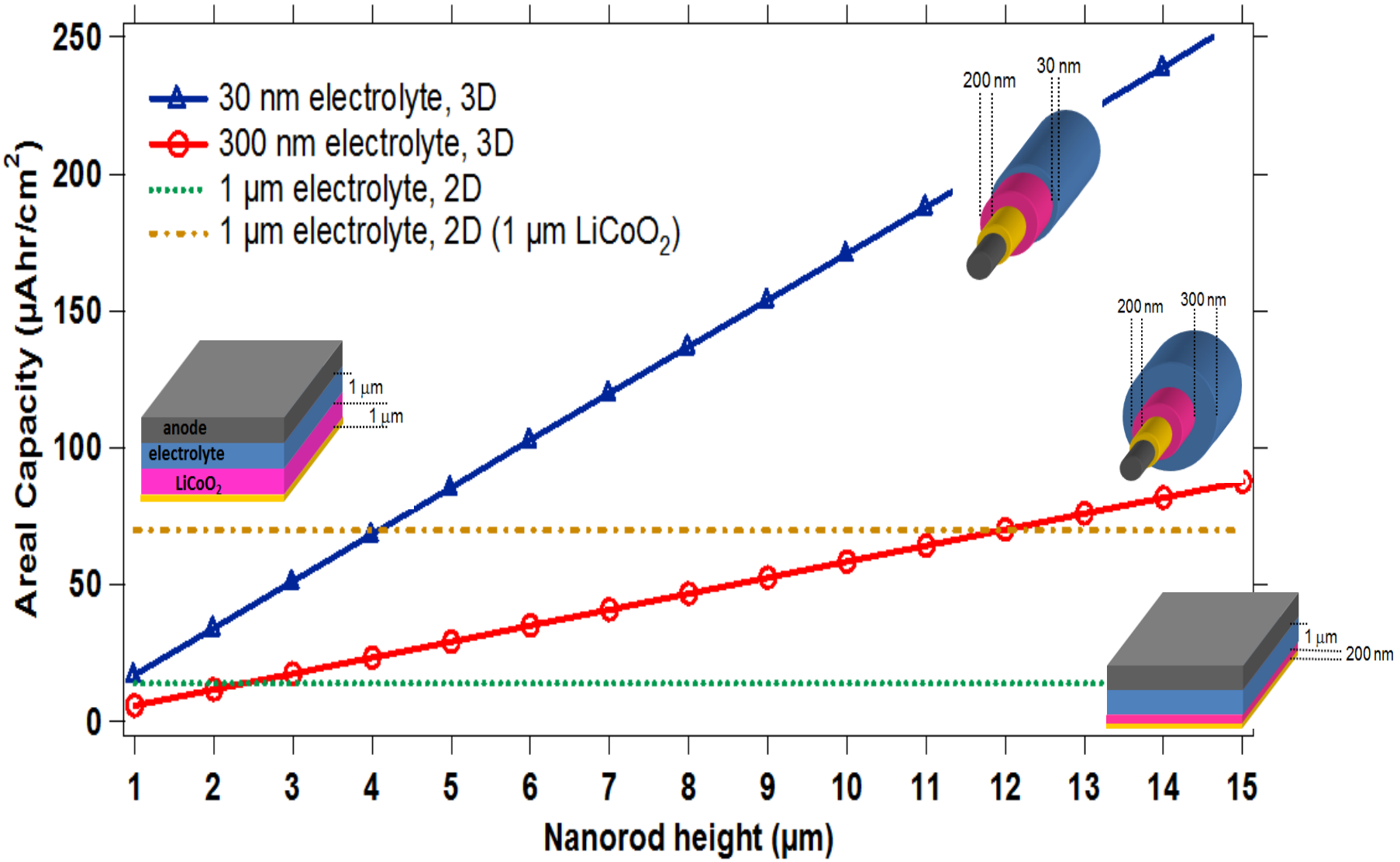




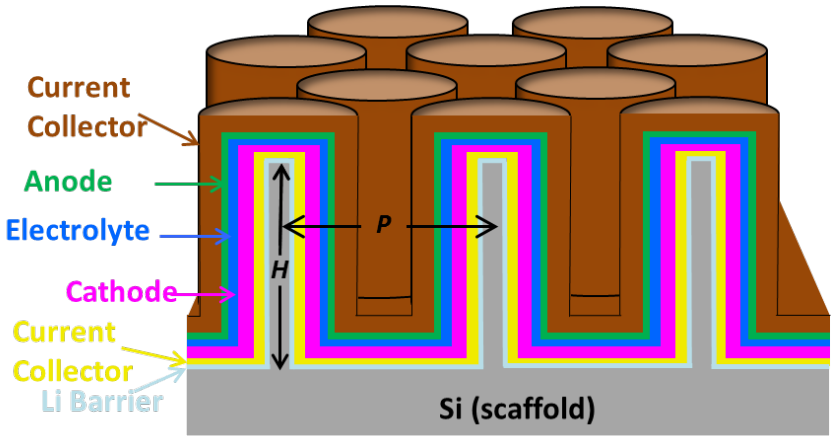


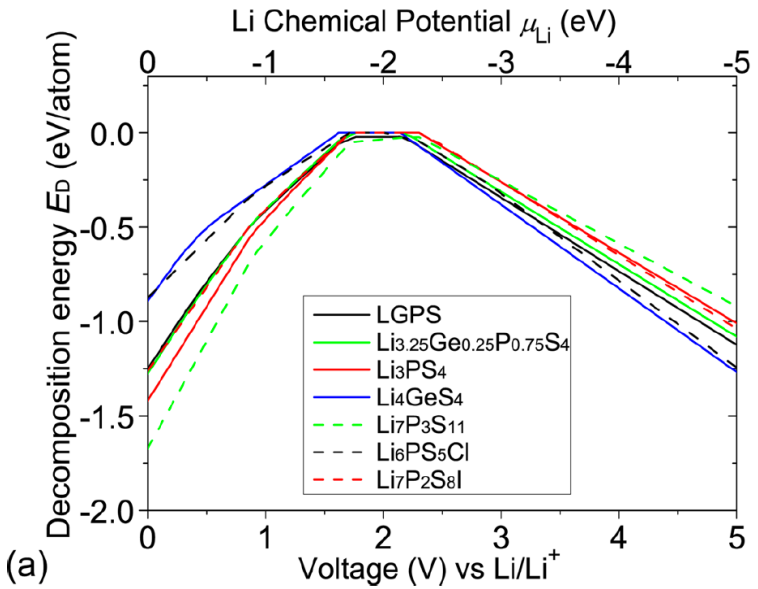
V. P. Oleshko, T. Lam, D. Ruzmetov, P. Haney, H. J. Lezec, A. V. Davydov, S. Krylyuk, J. Cumings and A. A. Talin, Nanoscale 6, 11756 (2014)

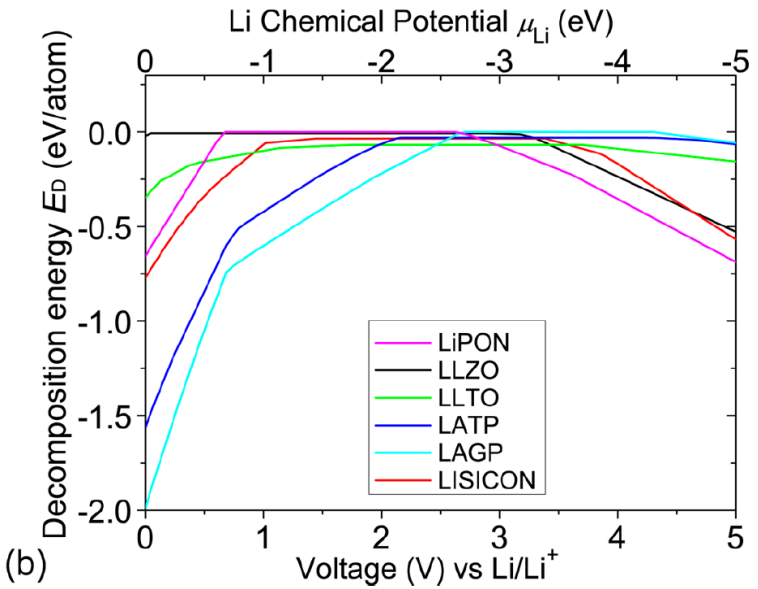
High energy density needs thin SSE, high aspect ratio



High interface area requires stable interfaces

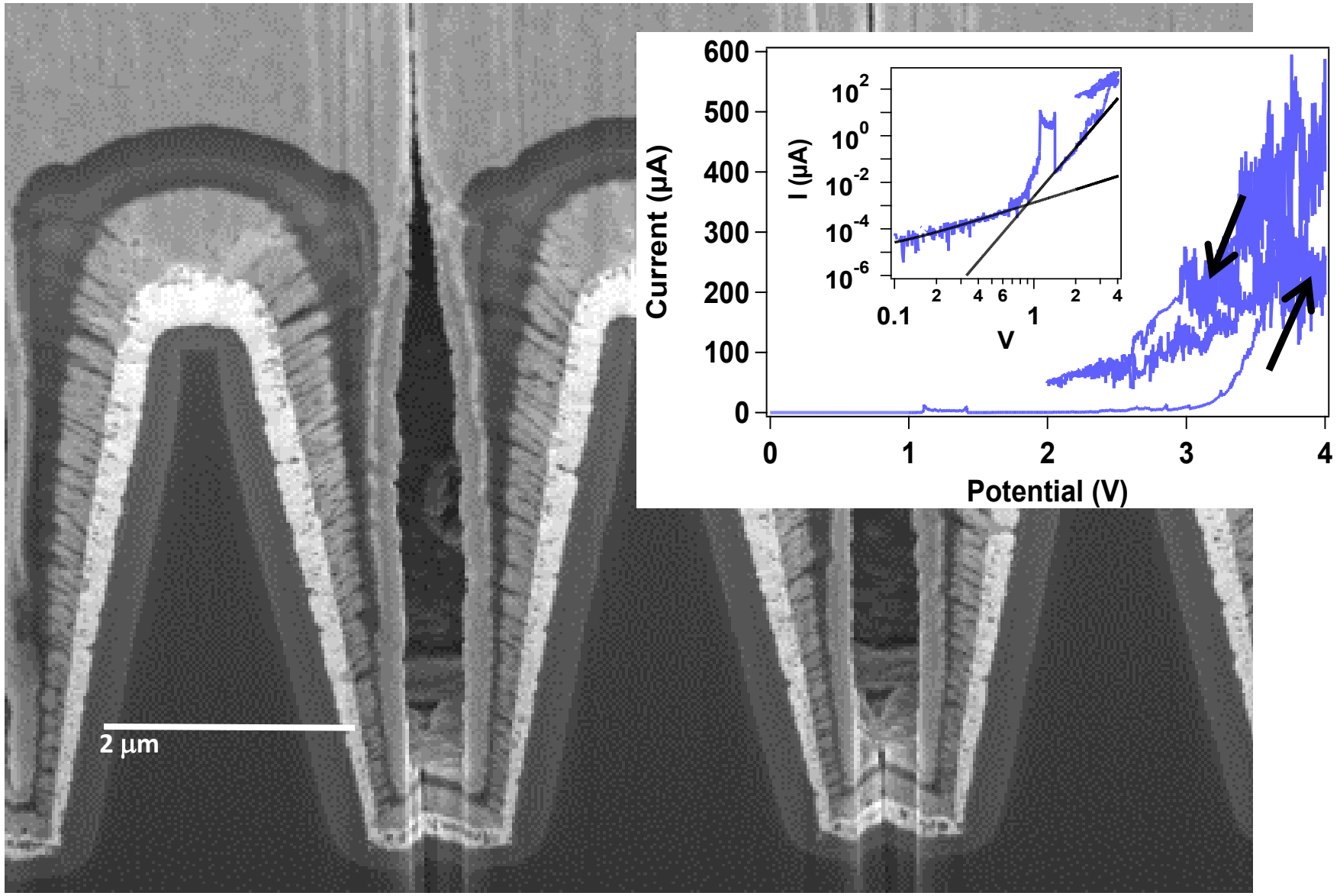




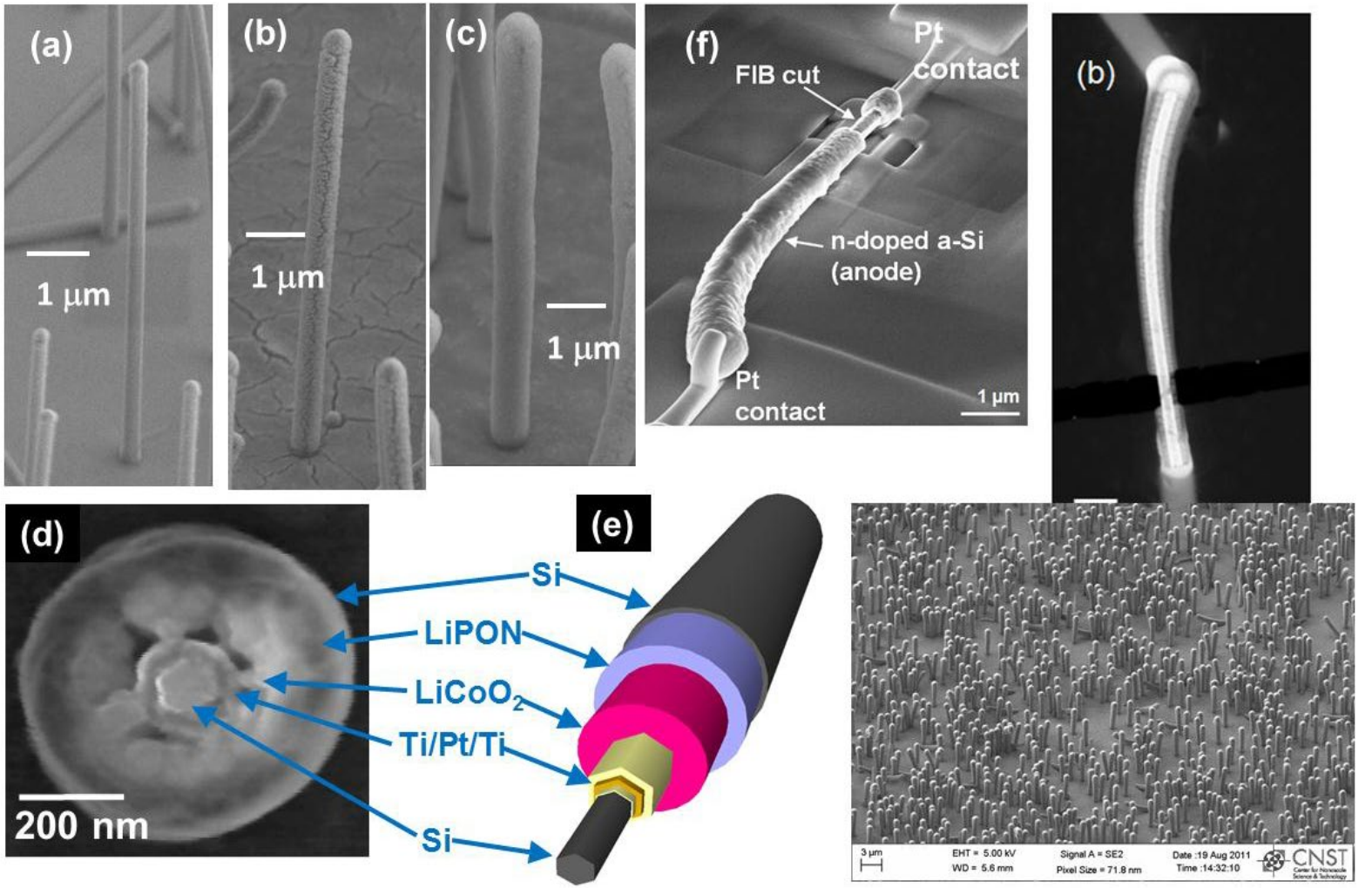


Y. Zhu, X. He, Y. Mo ACS Appl. Mater. Interfaces 2015, 7, 23685

Sputtered LiPON breakdown for thickness <100 nm

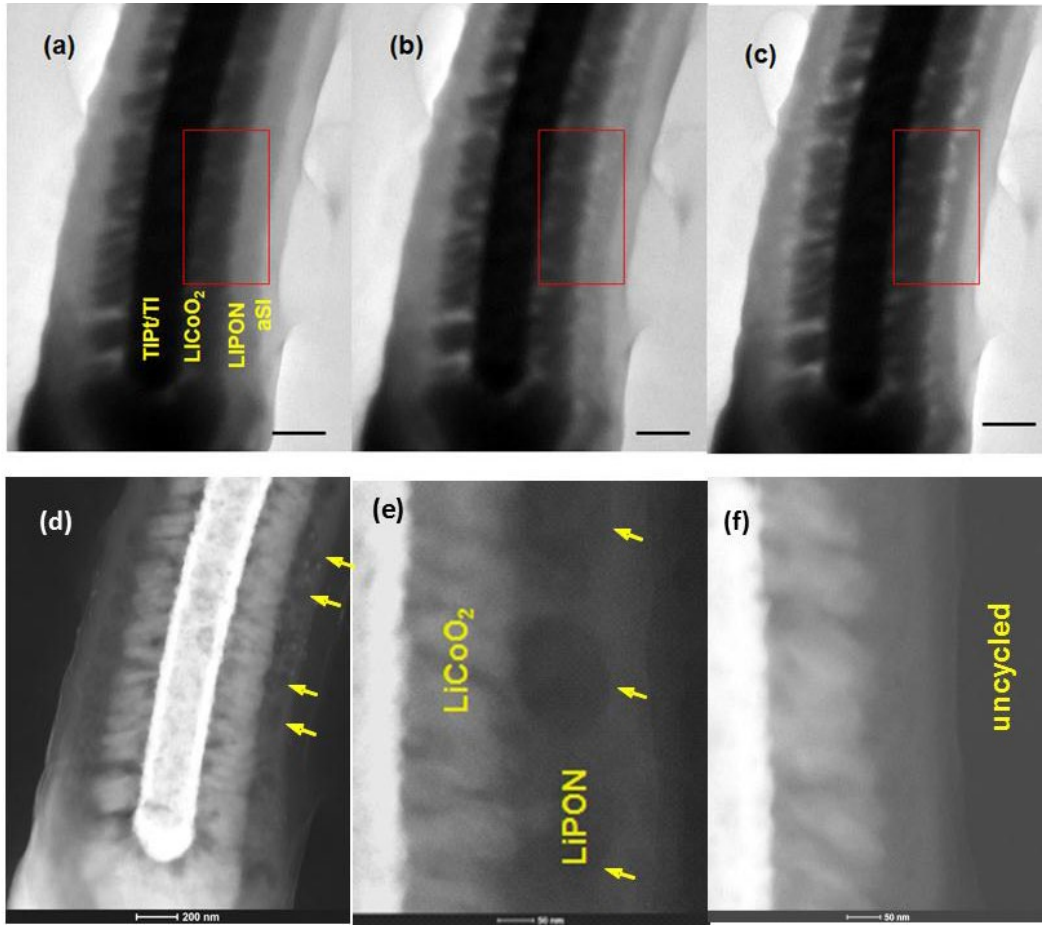


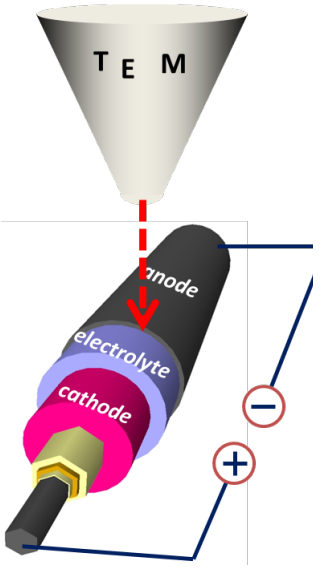
Nanowire LiBs excellent test-bed for 3D LiBs

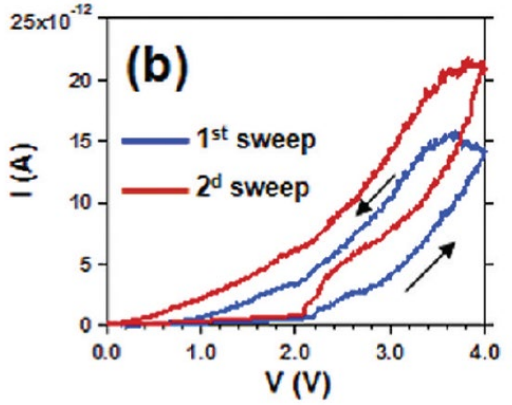


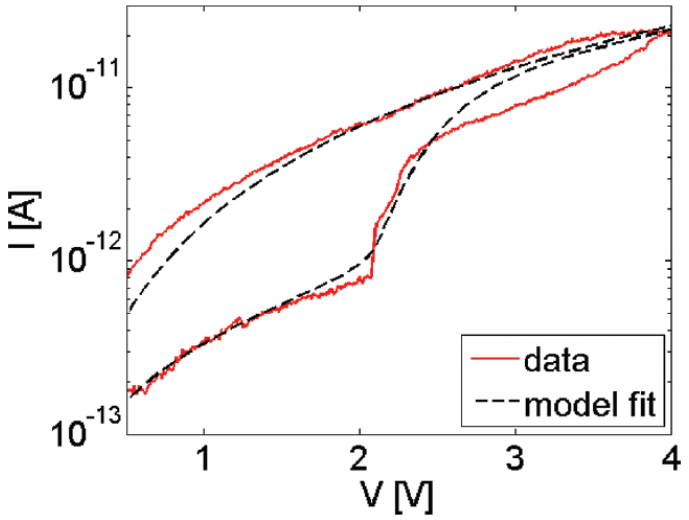
Ruzmetov et al. *Nano Letters* 12, 505, (2012)

Sputtered LiPON breakdown for thickness <100 nm



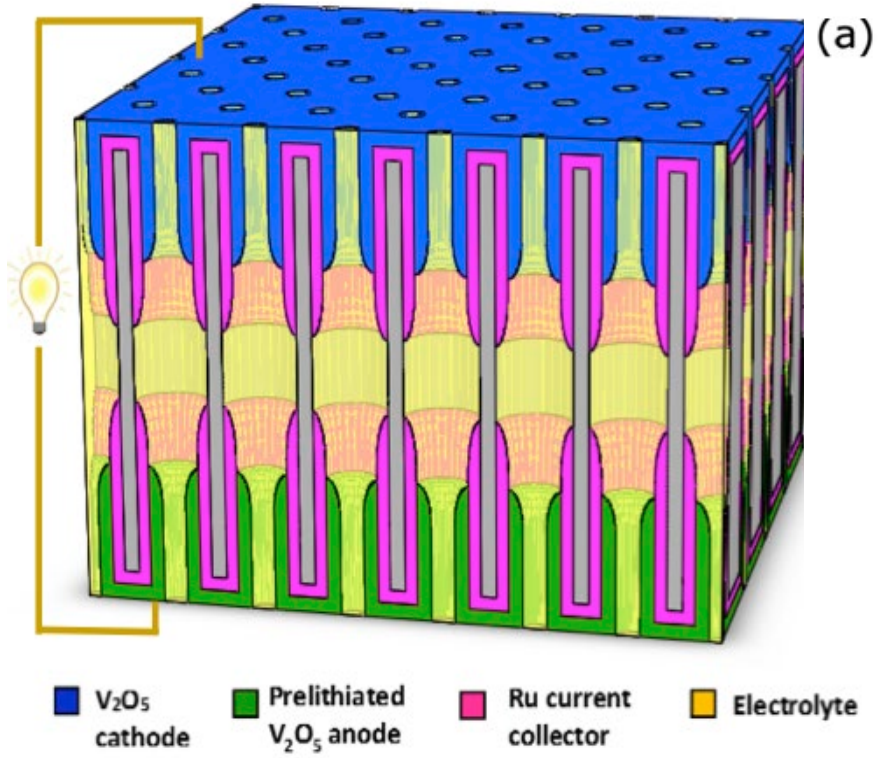






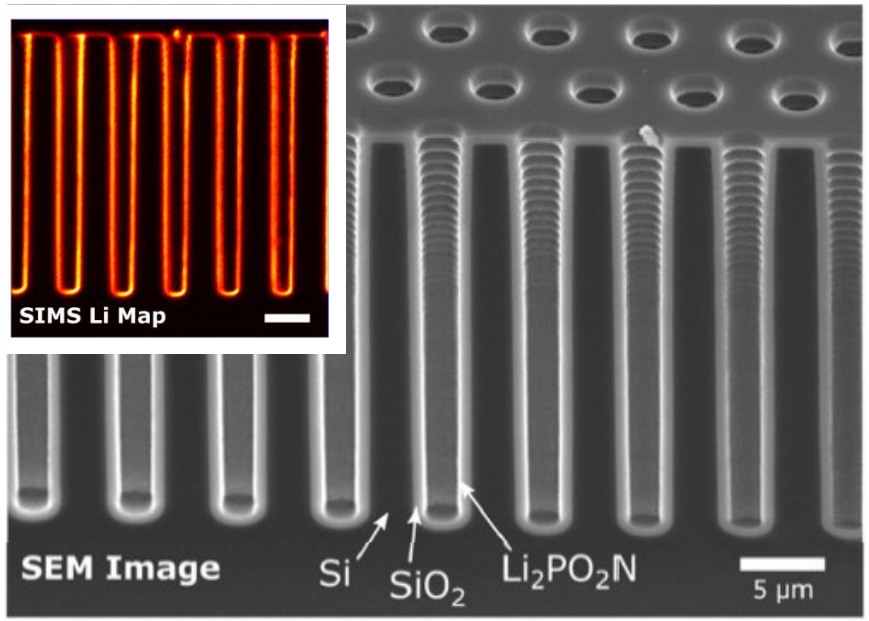
Ruzmetov et al. *Nano Letters* 12, 505, (2012)

Can a 3D SSLIB be fabricated by ALD?



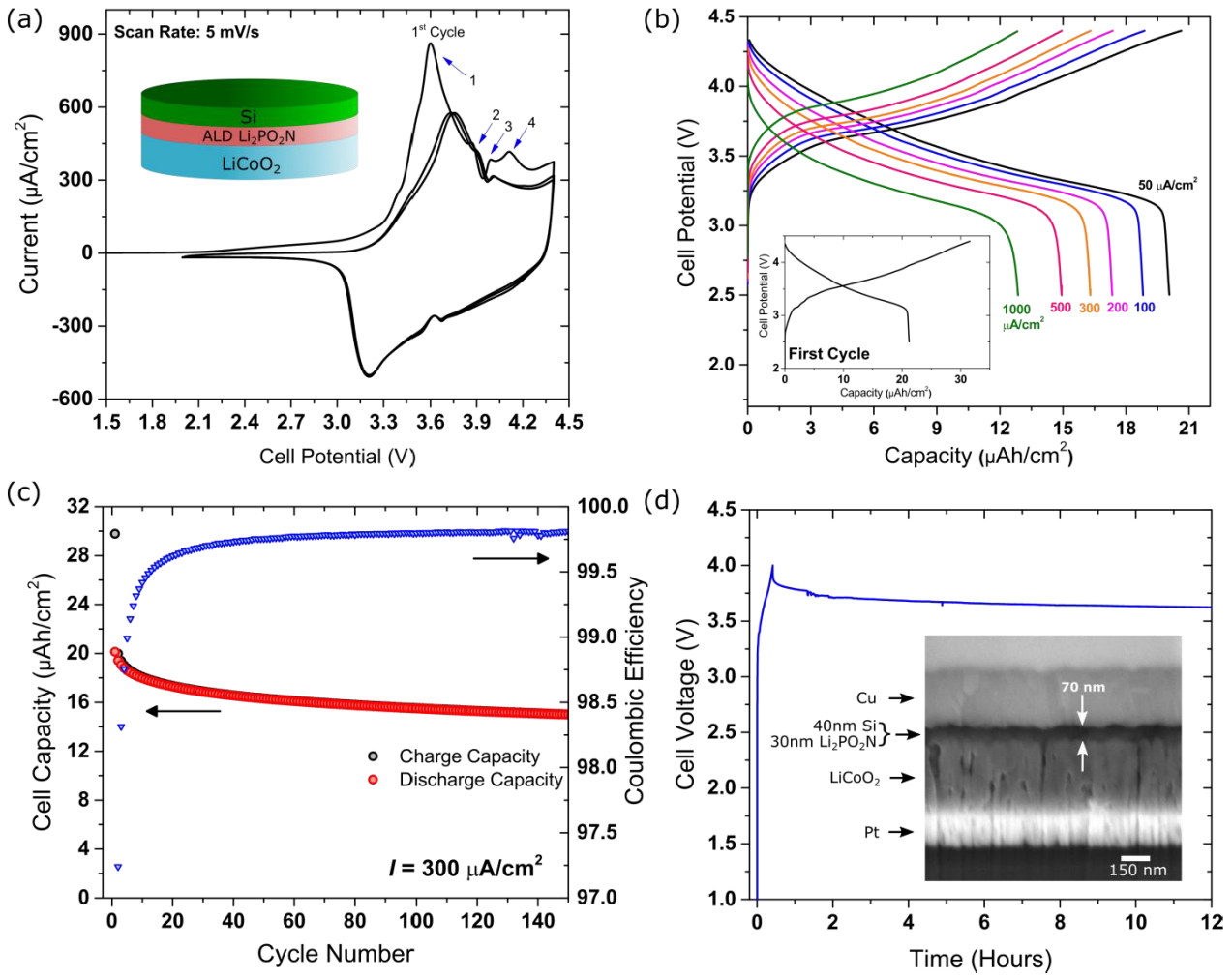
C. Liu, E.I. Gillette, X. Chen, A.J. Pearse, A.C. Kozen, M.A. Schroeder, K.E. Gregorczyk, S.B. Lee, G.W.Rubloff, Nature Nanotechnology doi: 10.1038/nnano.2014.247.

(LiOtBu) + diethyl phosphoramidate (DEPA)
@250 °C

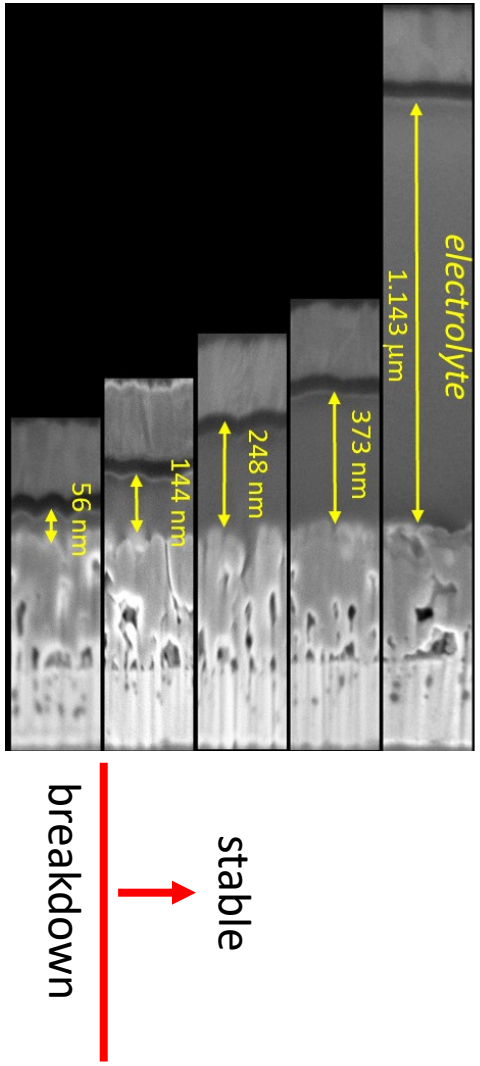


A. Pearse, T. Schmitt, E. Sahadeo, D. M. Stewart, A. Kozen, K. Gerasopoulos, A. A. Talin, S. B. Lee, G. W. Rubloff, and K. E. Gregorczyk, ACS Nano 12 (5), 4286 (2018)

ALD LiPON works great at 30 nm thickness!

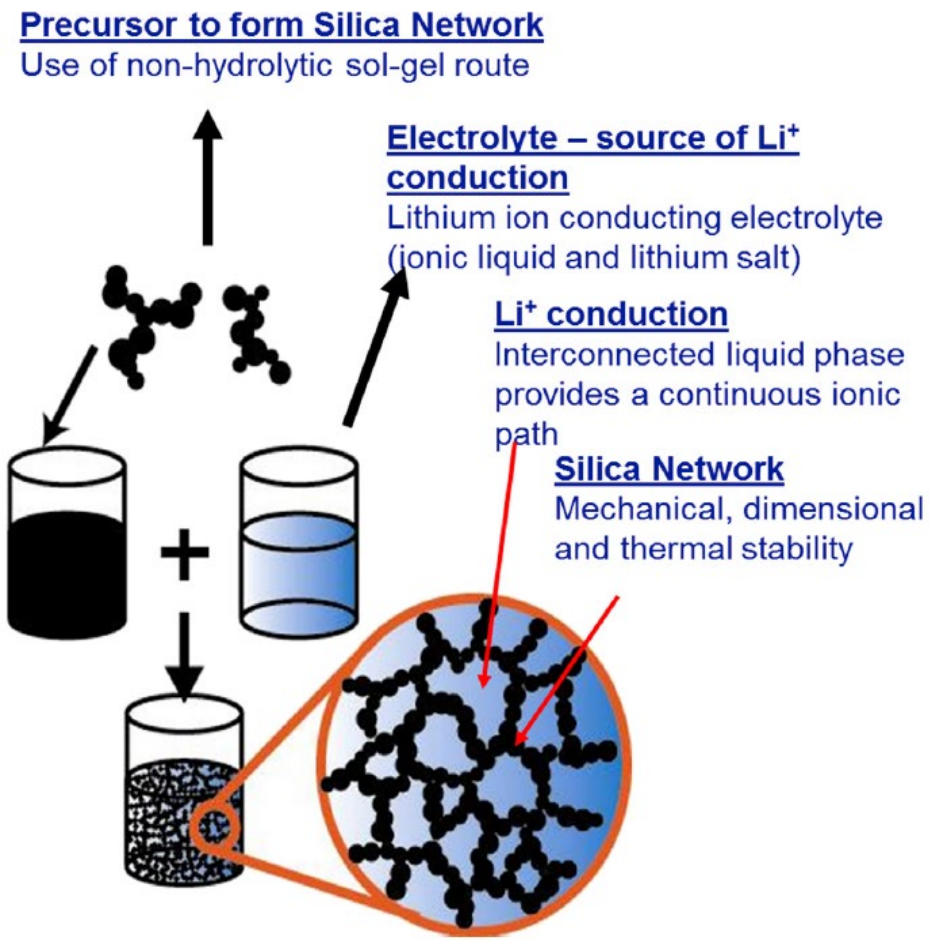


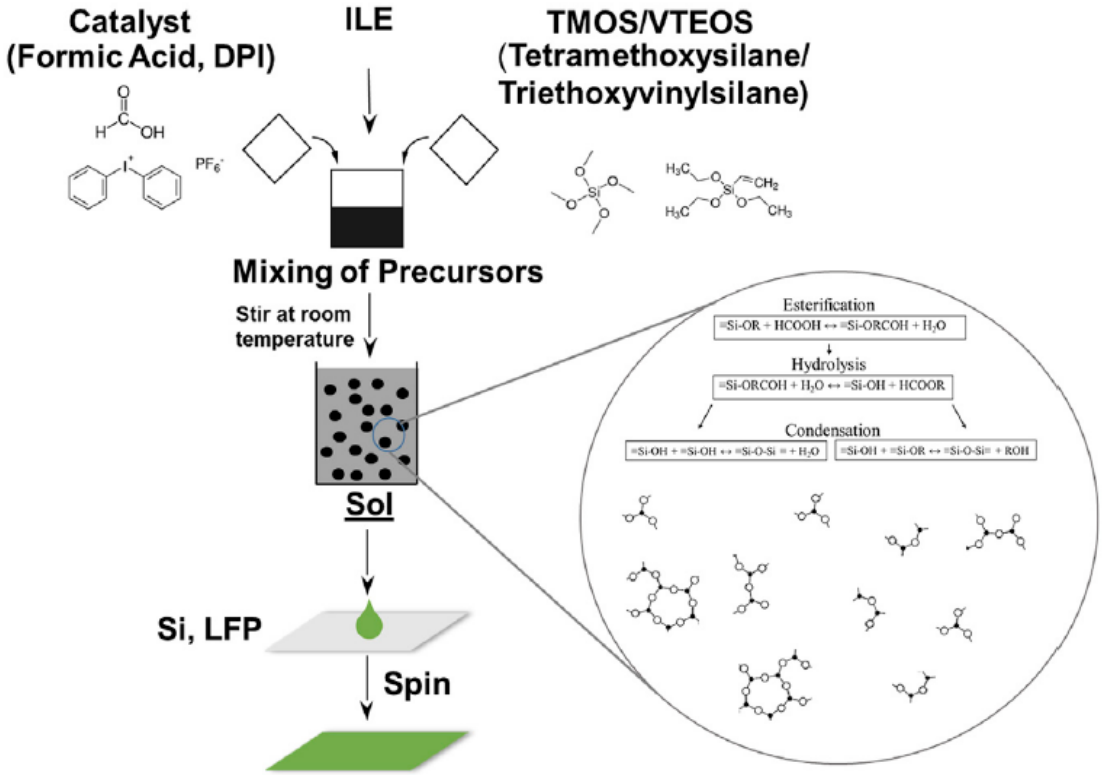
Sputtered LiPON



A. J. Pearse, T. E. Schmitt, E. J. Fuller, F. El-Gabaly, C-F Lin, K. Gerasopoulos, A. C. Kozen, A. A. Talin, G. Rubloff, K. E. Gregorcyzck, Chemistry of Materials, 29, 3740, 2017

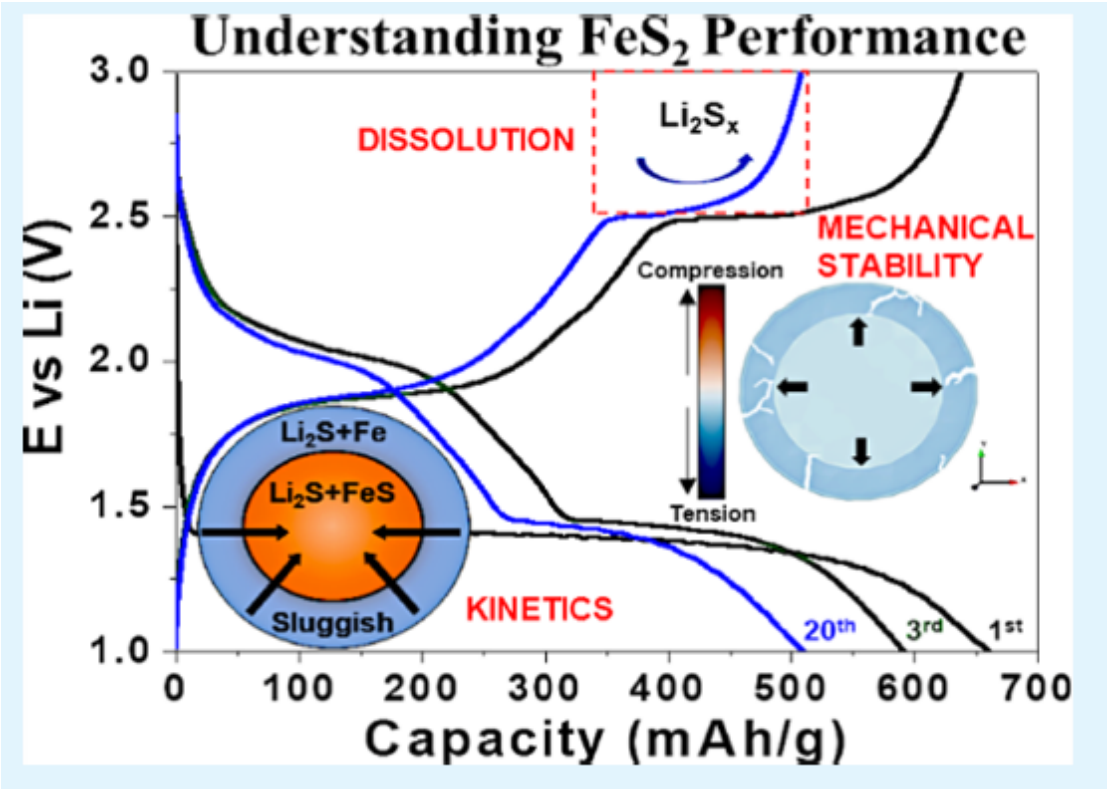
Ionogels: nanoporous matrix filled with ionic liquid electrolyte

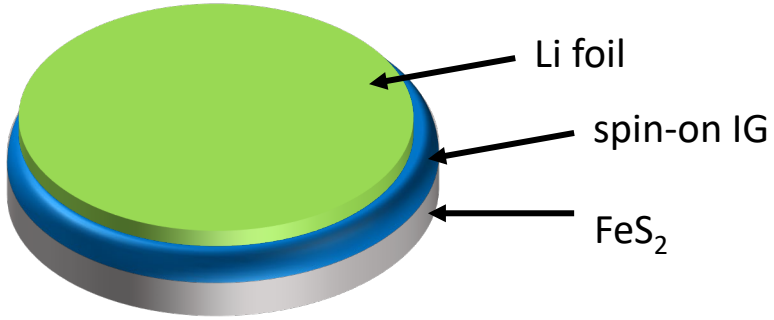


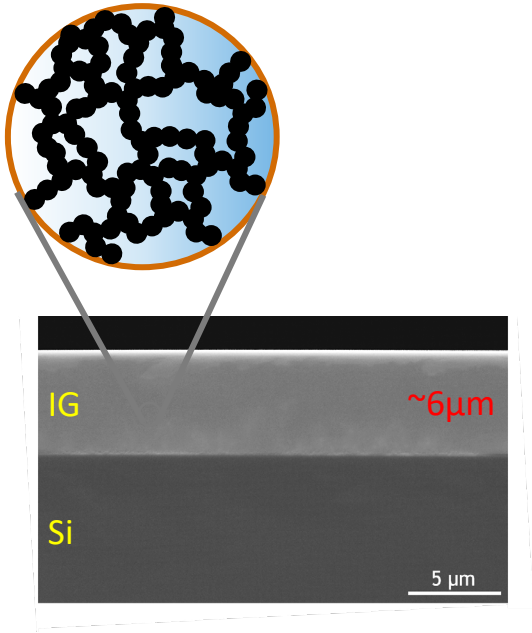


D. Ashby, B. Dunn et al., Joule 1, 344,, 2017

Ionogels: nanoporous matrix filled with ionic liquid electrolyte







High-Performance Solid-State Lithium-Ion Battery with Mixed 2D and 3D Electrodes

David S. Ashby,* Christopher S. Choi, Martin A. Edwards, A. Alec Talin, Henry S. White, and Bruce S. Dunn*

Cite This: https://dx.doi.org/10.1021/acsaem.0c01029

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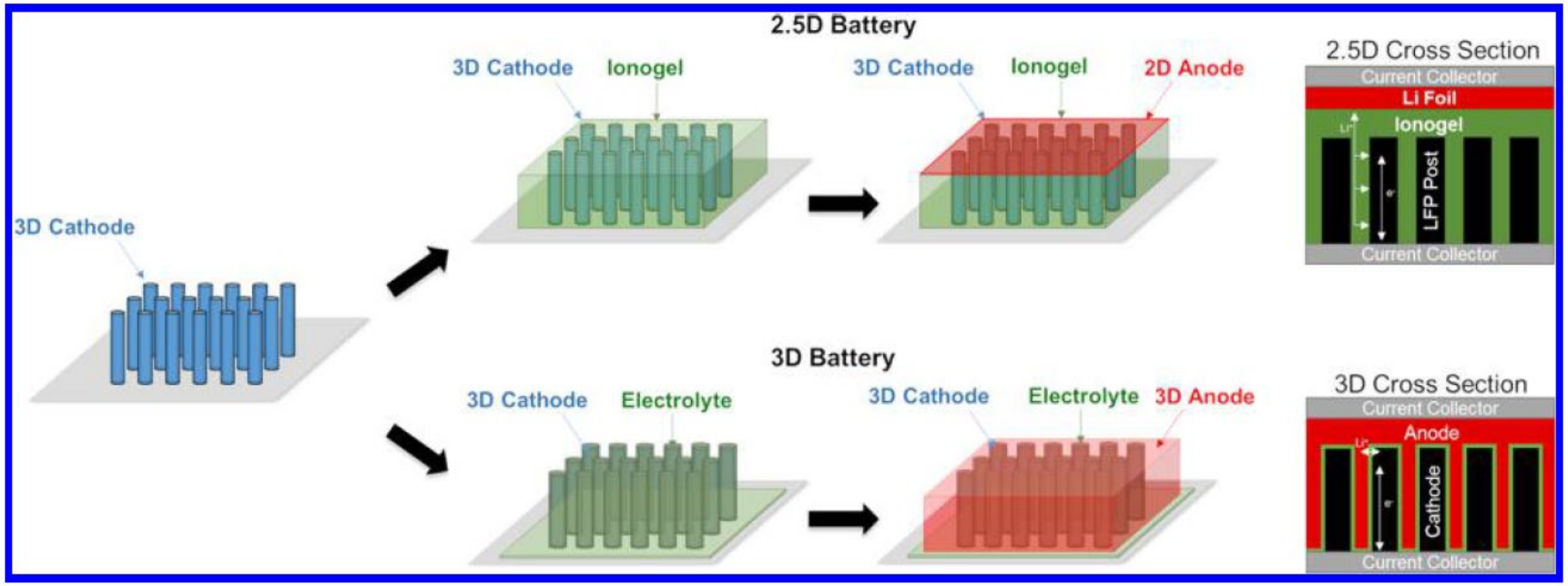
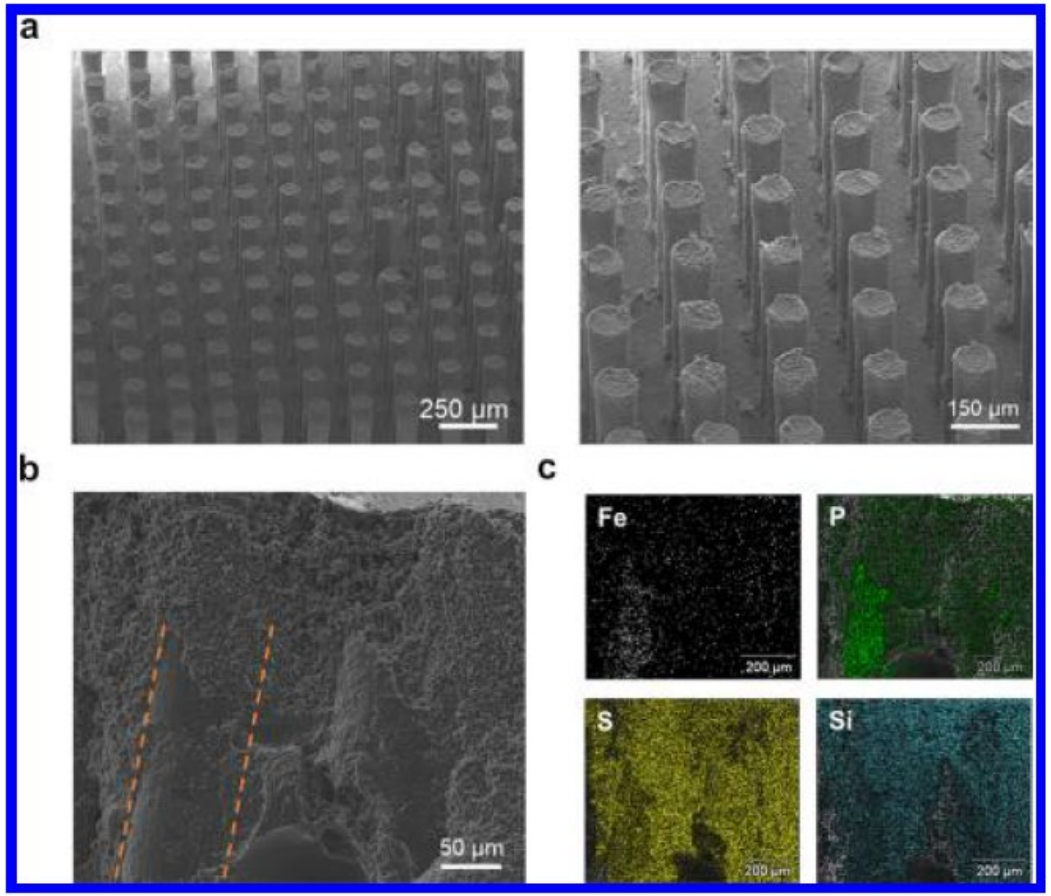
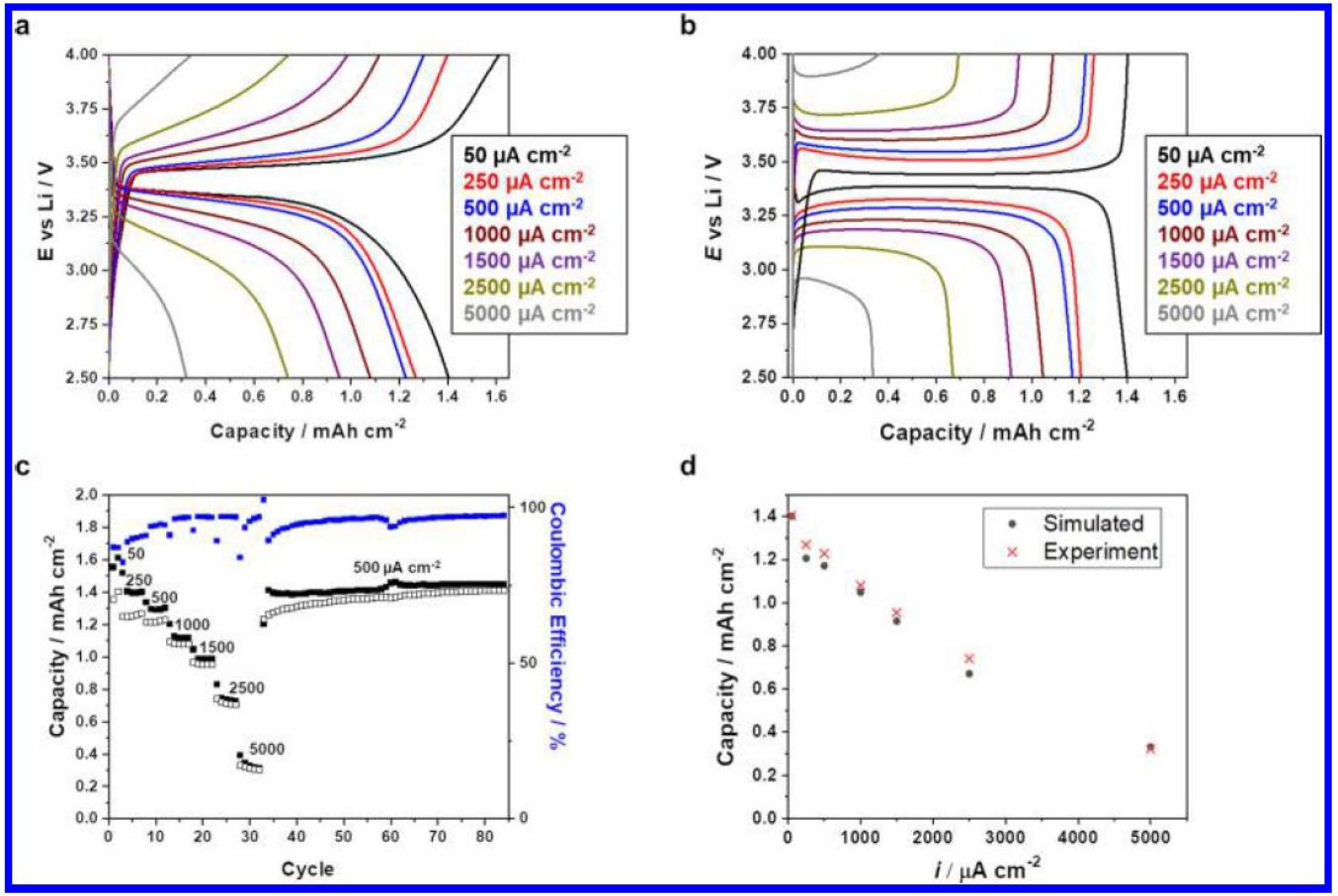
Table 1. Electrolytes for 3D Architectures[a]

electrolyte	σ_i (S cm^{-1})	fabrication method	electrolyte−electrode Interface
ionogel	2×10^{-3}	liquid casting	liquid-particle
LiPON	$\sim 10^{-7}$	ALD, sputtering	conformal
SU8	2×10^{-7}	UV lithography	conformal
SPE	10^{-5}–10^{-3}	liquid casting	conformal/particle-particle
LLZO	3.5×10^{-4}	powder pressing	particle−particle
LLT	1.1×10^{-3}	commercial	particle−particle
LAGP	3×10^{-5}	EPD	particle−particle



Mixed 2D/3D solid state battery





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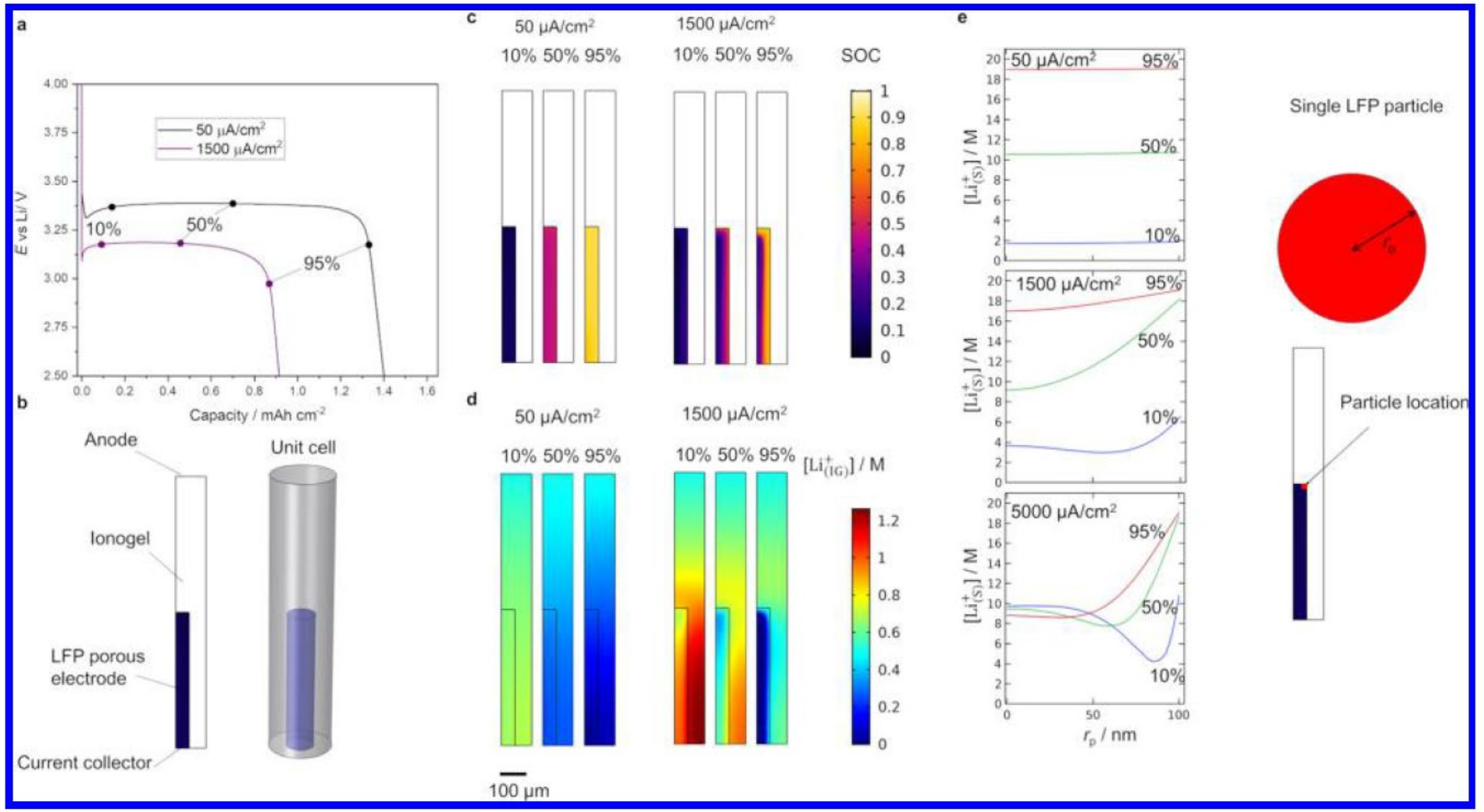

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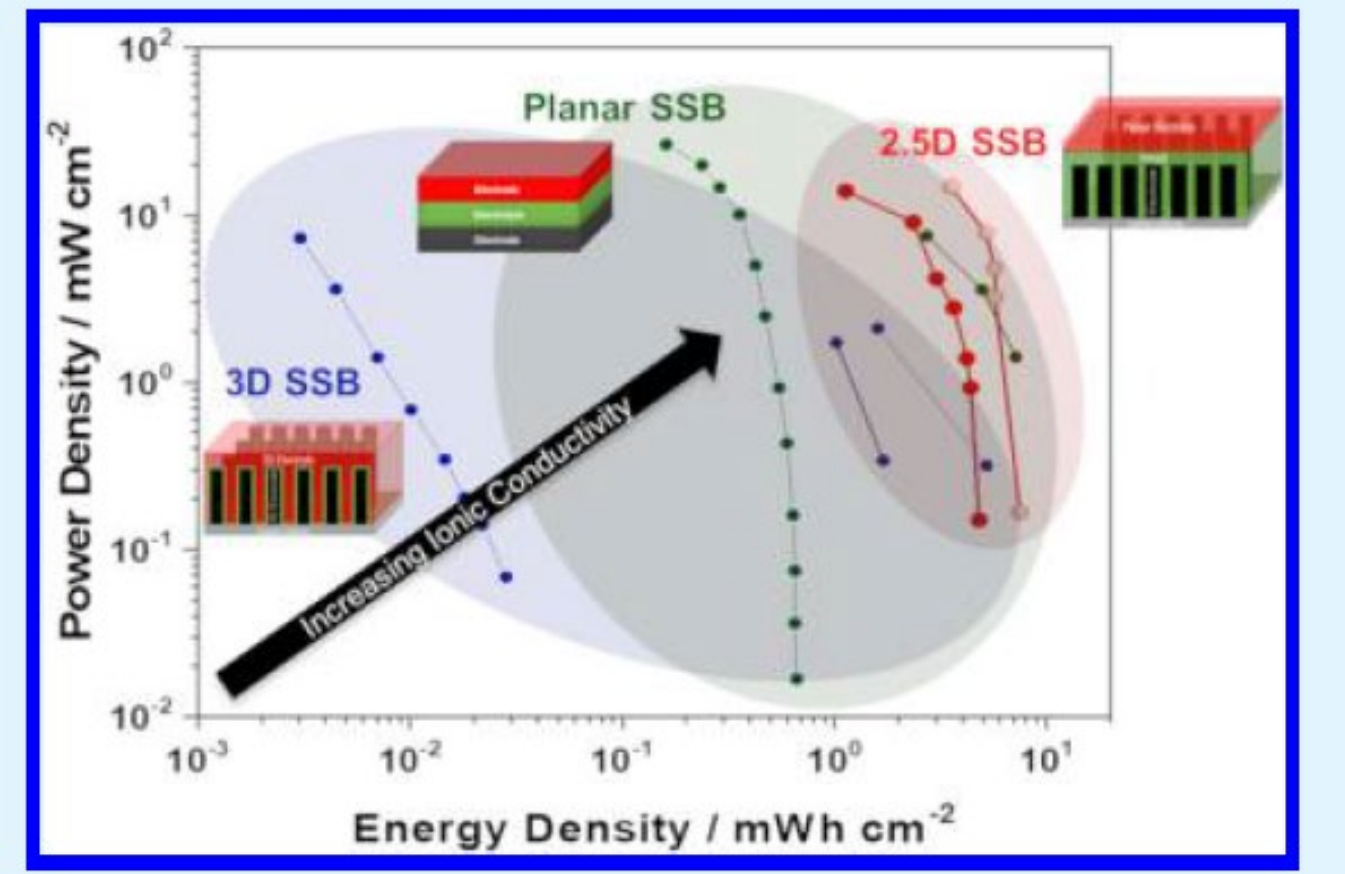
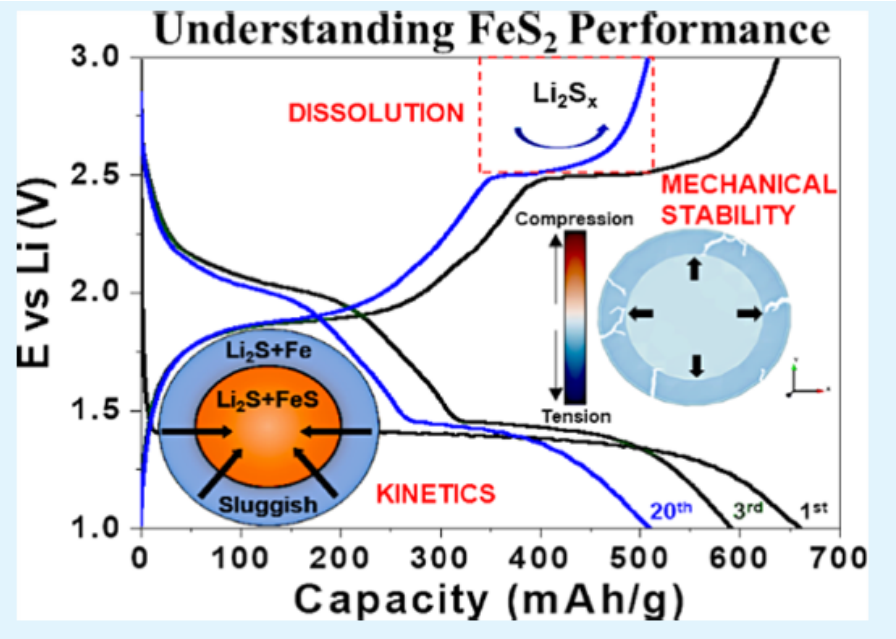


Understanding the Electrochemical Performance of FeS_2 Conversion Cathodes

David S. Ashby,* Jeffrey S. Horner, Grace Whang, Aliya S. Lapp, Scott A. Roberts, Bruce Dunn, Igor V. Kolesnichenko, Timothy N. Lambert, and A. Alec Talin*

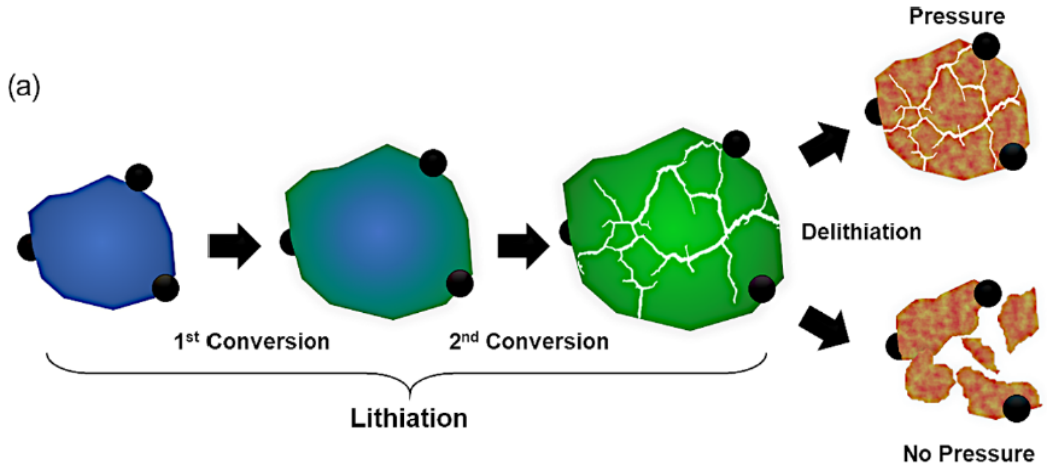


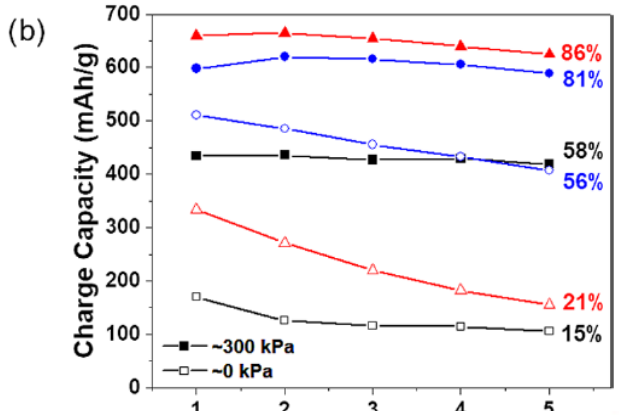
$$FeS + S + xLi^+ + xe^- \rightarrow FeS + xLi_2S \ (\sim 3\text{–}2\ V,\ \text{upperconversion}) \quad (1)$$

$$FeS + xLi_2S + yLi^+ + ye^- \rightarrow yLiFeS + xLi_2S \ (\sim 2\text{–}1.5\ V,\ \text{intercalation}) \quad (2)$$

$$yLiFeS + xLi_2S + zLi^+ + ze^- \rightarrow Fe + 2Li_2S \ (\sim 1.5\text{–}1\ V,\ \text{lowerconversion}) \quad (3)$$

FeS_2 conversion electrodes

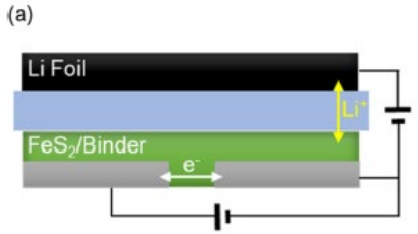


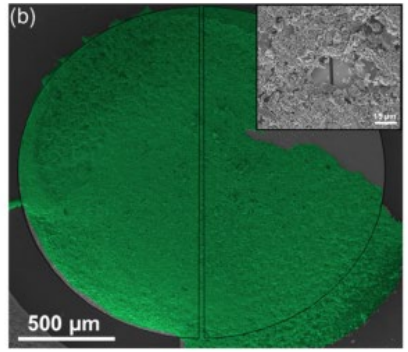


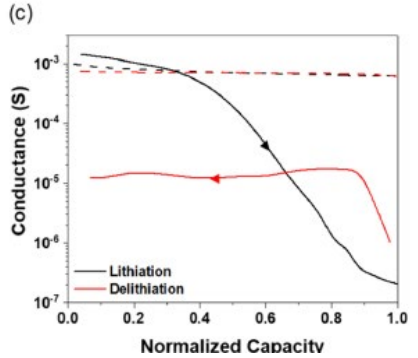
$$FeS + S + xLi^+ + xe^- \rightarrow FeS + xLi_2S\ (\sim 3-2\ V,\ \text{upperconversion}) \quad (1)$$

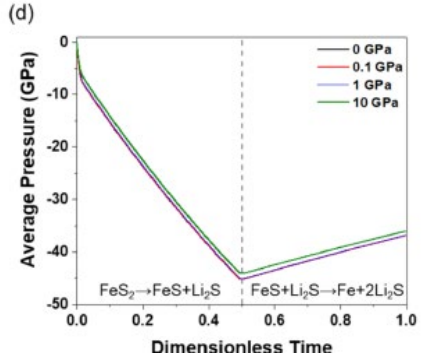
$$FeS + xLi_2S + yLi^+ + ye^- \rightarrow yLiFeS + xLi_2S\ (\sim 2-1.5\ V,\ \text{intercalation}) \quad (2)$$

$$yLiFeS + xLi_2S + zLi^+ + ze^- \rightarrow Fe + 2Li_2S\ (\sim 1.5-1\ V,\ \text{lowerconversion}) \quad (3)$$

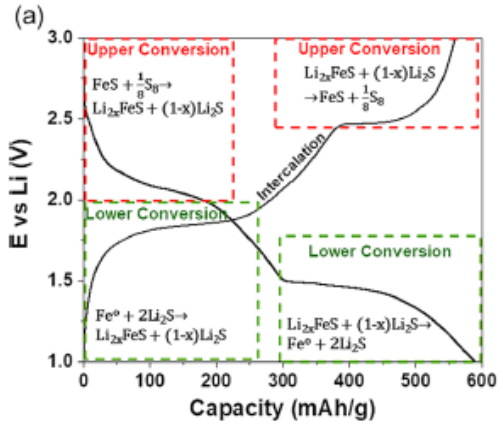


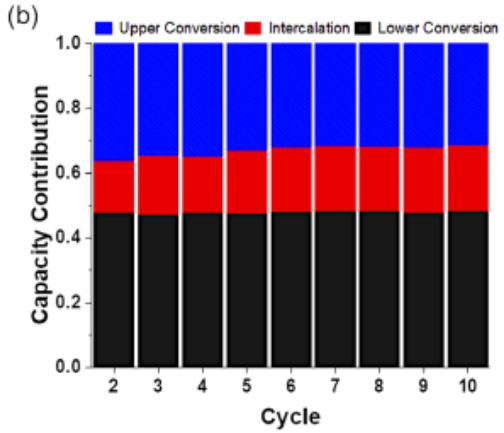


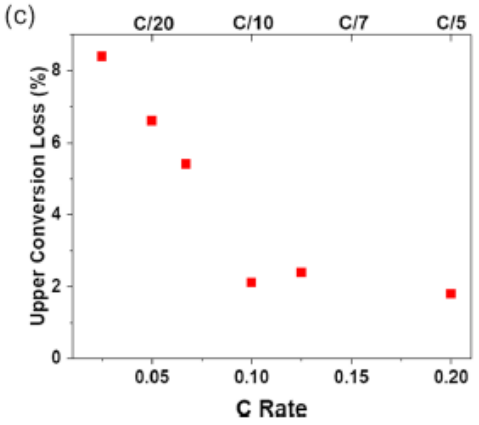


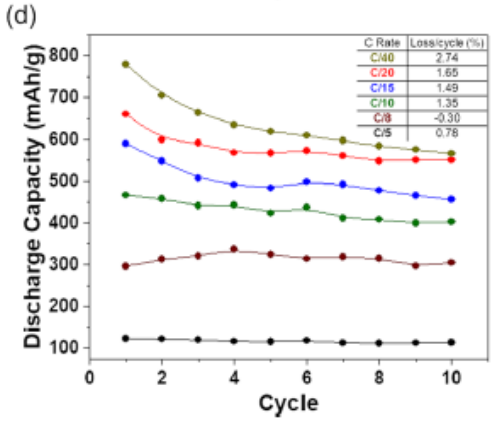


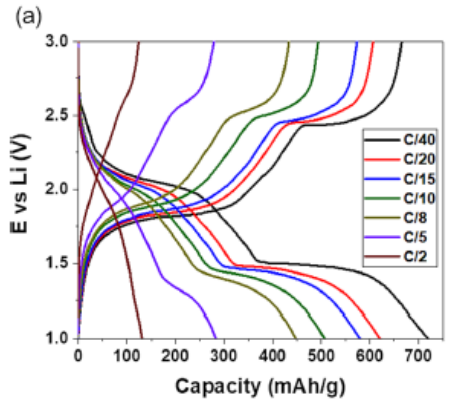
FeS_2 conversion electrodes

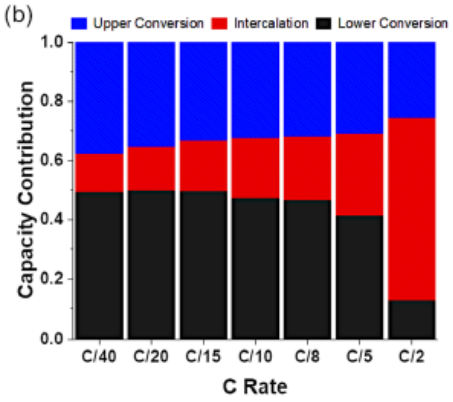


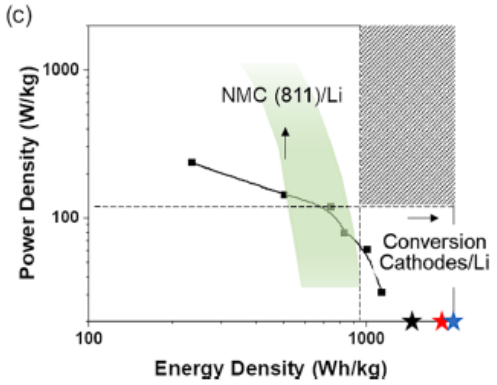












Joule

CellPress

Review

Electrochemical-mechanical coupling measurements

Yueming Song,[1,3] Bhuvsmita Bhargava,[1,3] David M. Stewart,[1] A. Alec Talin,[1,2] Gary W. Rubloff,[1] and Paul Albertus[1,*]

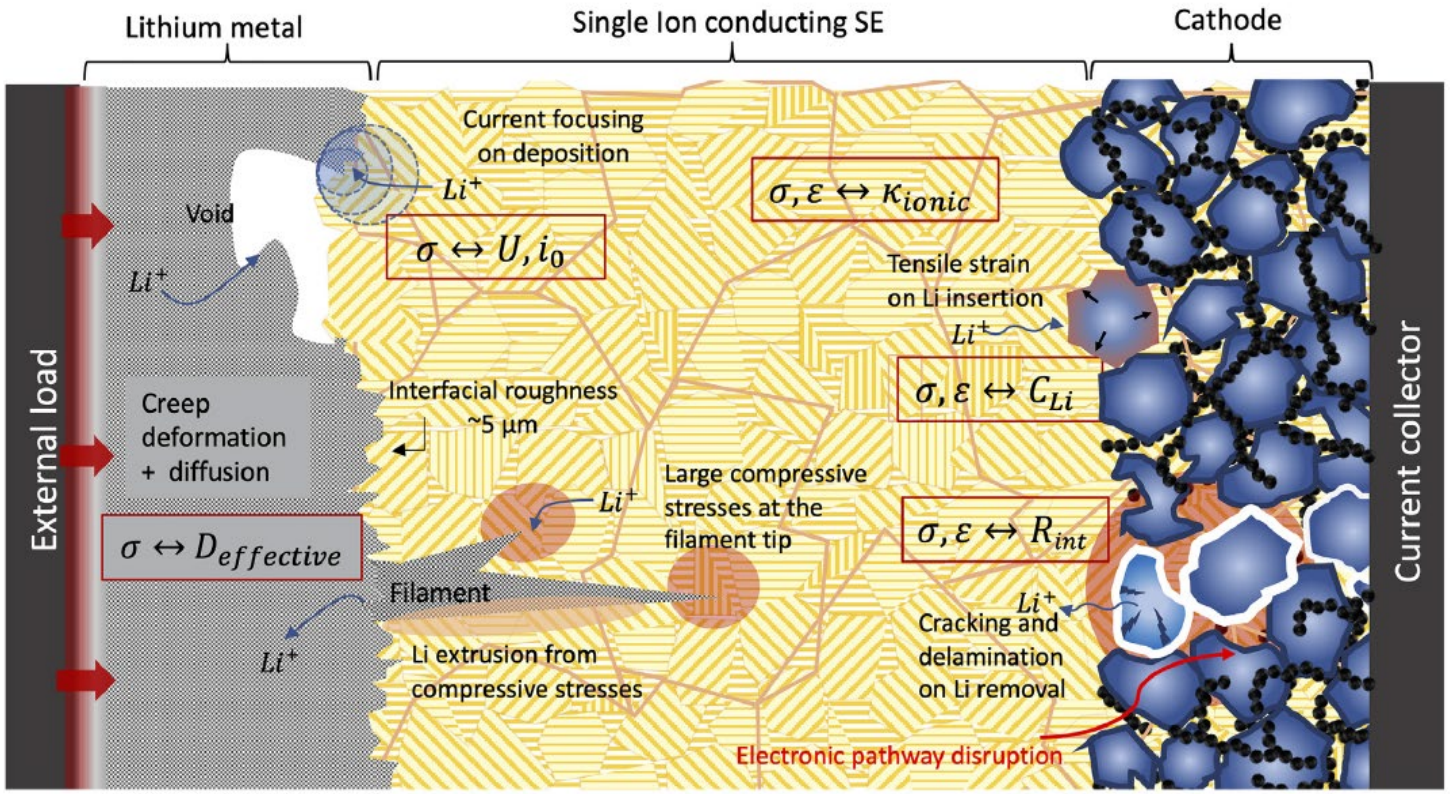
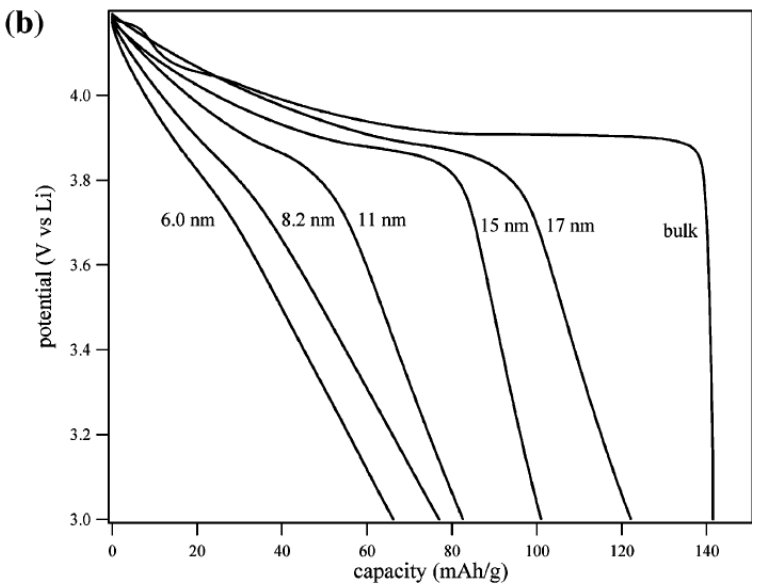
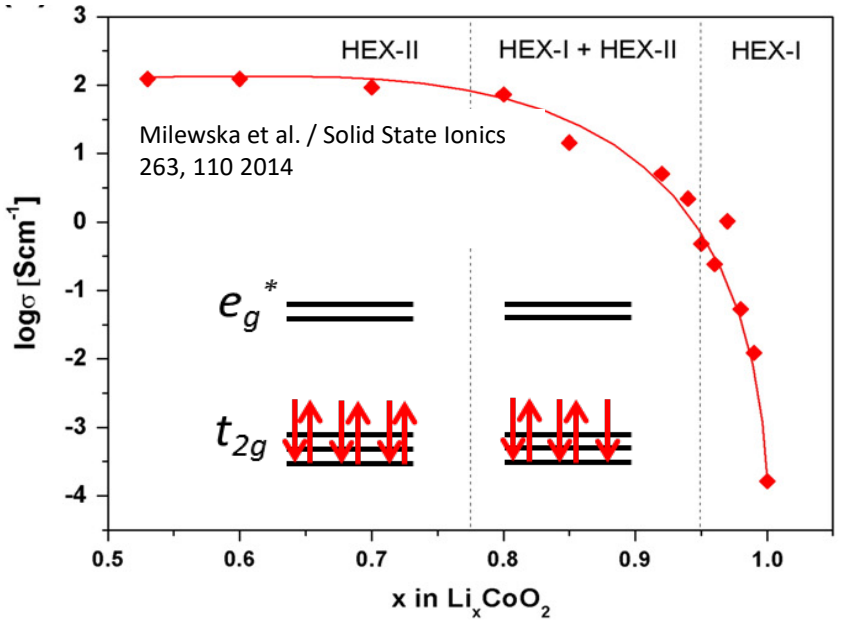
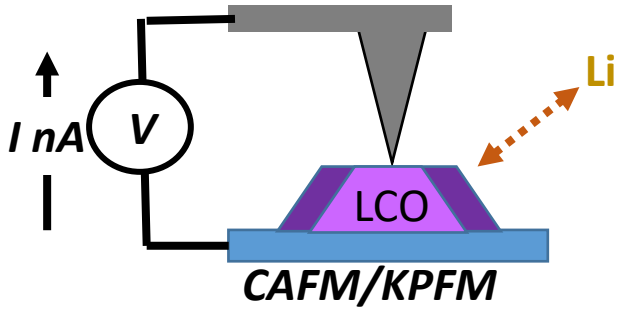


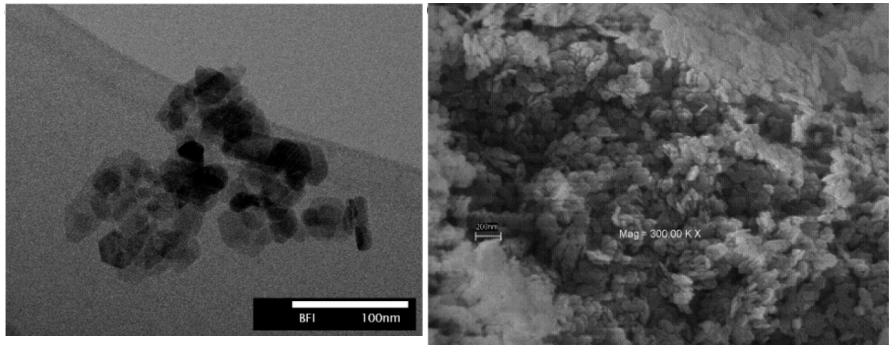
Figure 1. Effect of stresses on a range of processes in a full cell that consists of Li metal, a single ion conducting SE, and a porous cathode

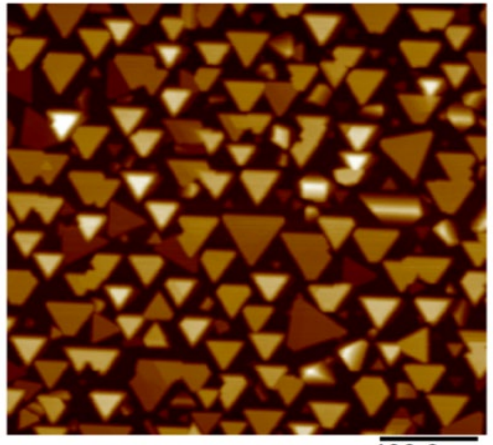
How can size, orientation effects be observed in thin film cathodes?

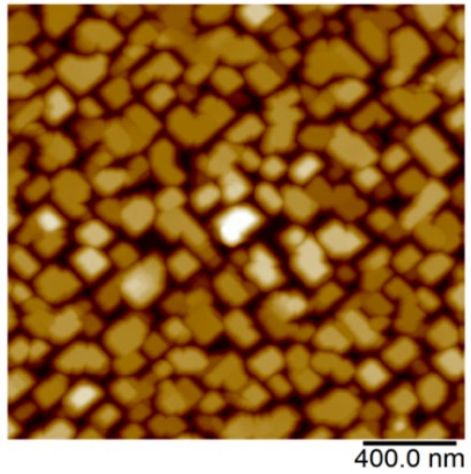






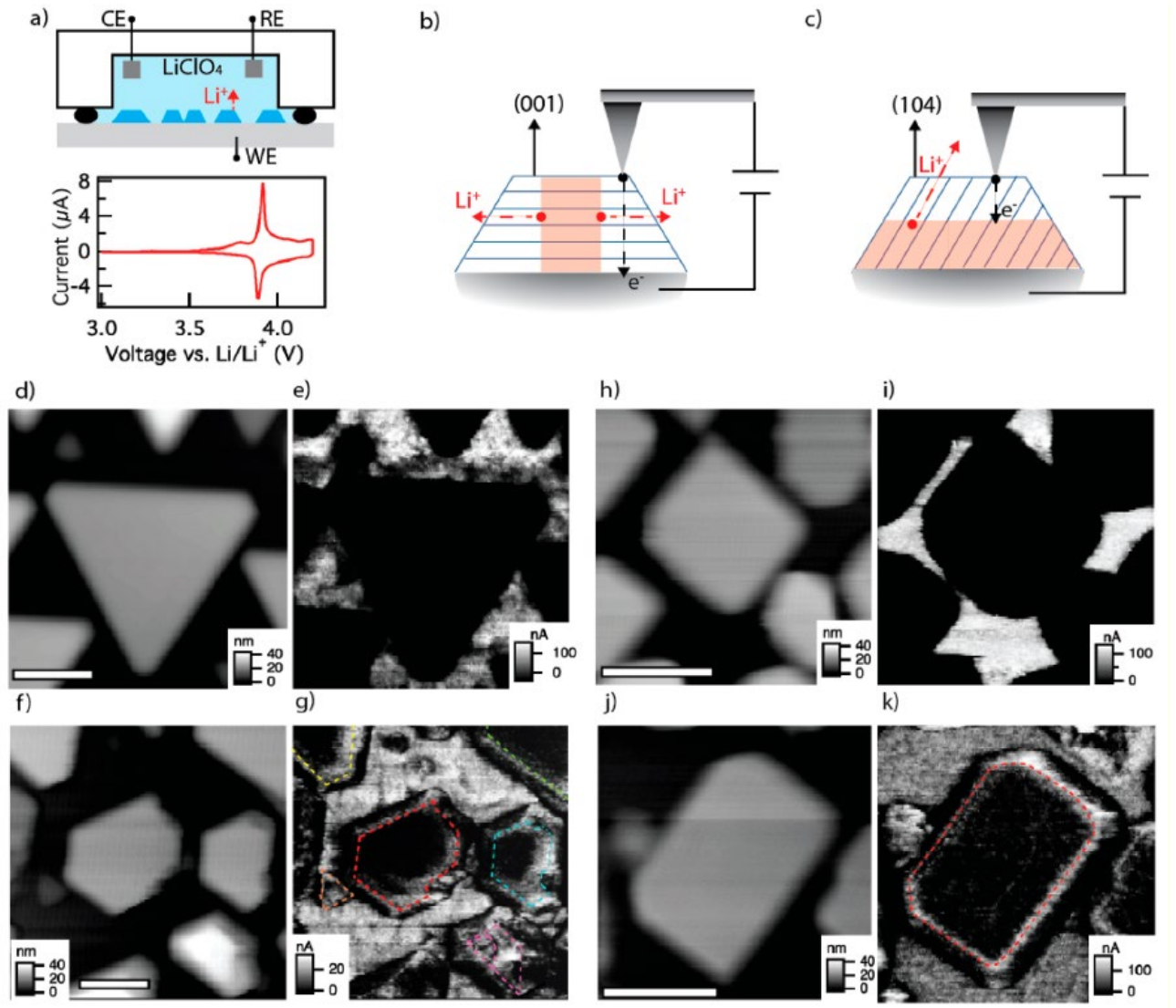




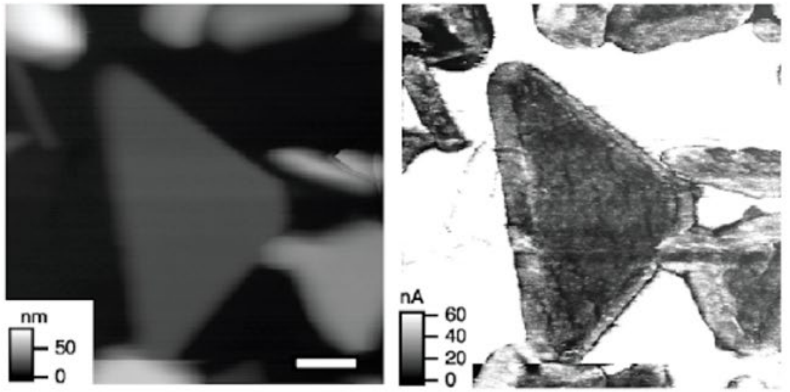


M. Okubo, E. Hosono, J. Kim, M, Enomoto, N. Kojima, T. Kudo, H. Zhou, I. Honma, JACS 129, 7444 (2007).

C-AFM reveals anisotropy in LCO delithiation, size and orientation effects

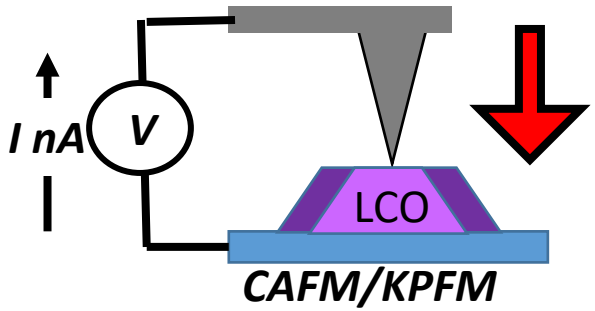


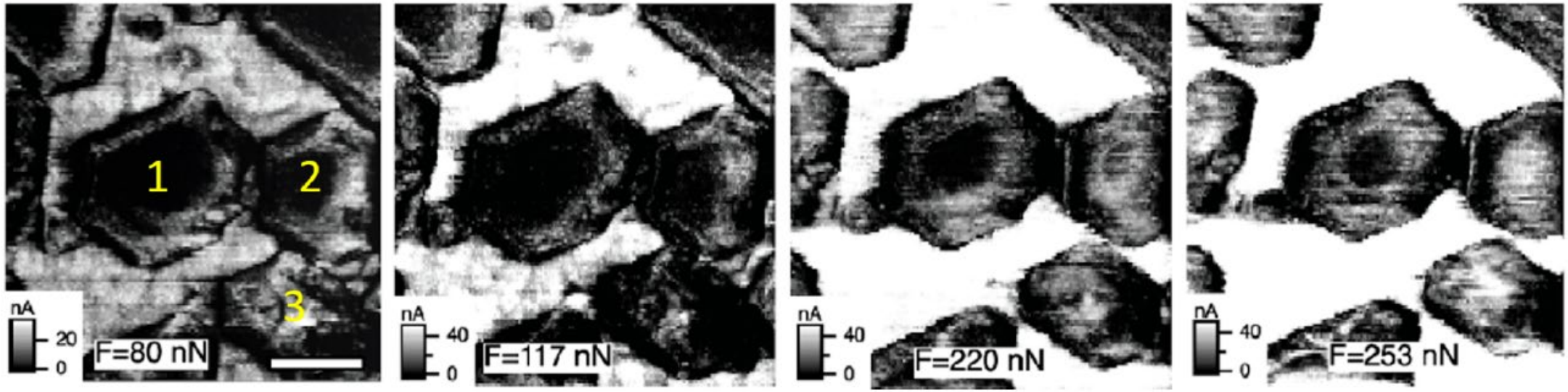
- Striping pattern for thickness < 20nm suggest surface coherent spinoidal decomposition



E. J. Fuller, D.avid S. Ashby, C. Polop, E. Salagre, B. Bhargava, Y. Song, E. Vasco, J. D. Sugar, P. Albertus, T. O. Menteş, A. Locatelli, P. Segovia, M. Á. Gonzalez-Barrio, A. Mascaraque, E. G. Michel, A. A. Talin, ACS Nano 2022
doi.org/10.1021/acsnano.2c05594

Application of force w/C-AFM reveals Li displacement





Modifying Ionogel Solid-Electrolytes for Complex Electrochemical Systems

David S. Ashby,* Jorge Cardenas, Austin Suhas Bhandarkar, Adam W. Cook, and A. Alec Talin*

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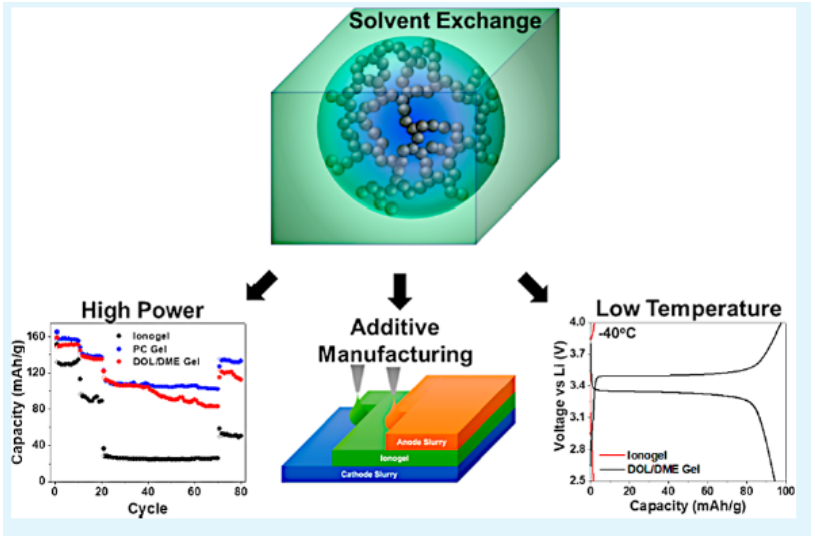

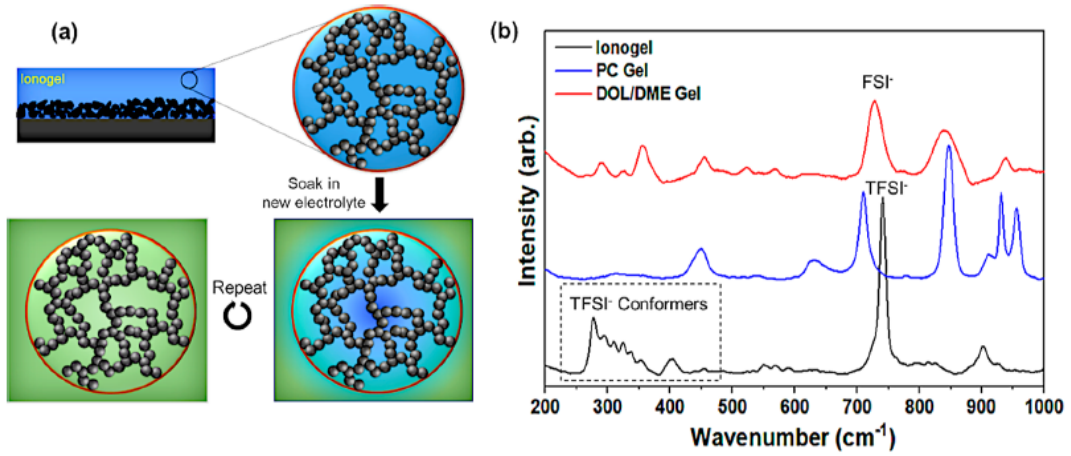

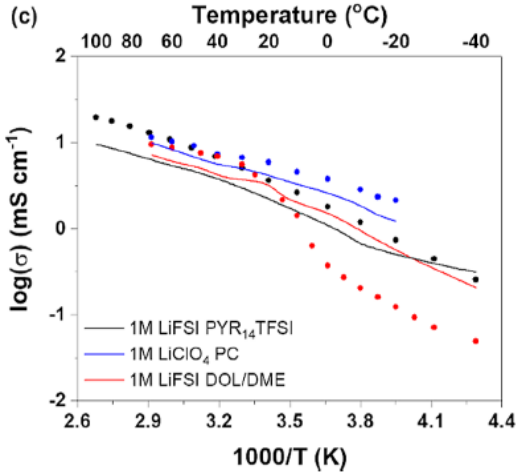

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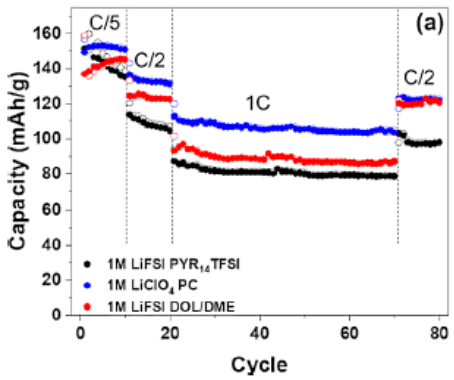

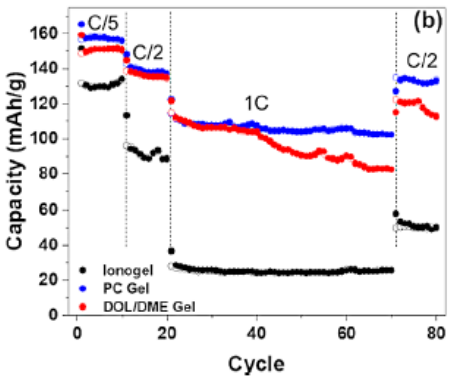

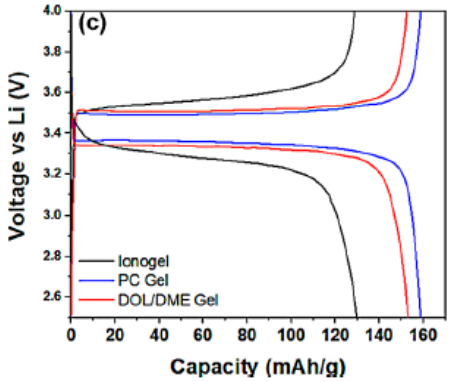

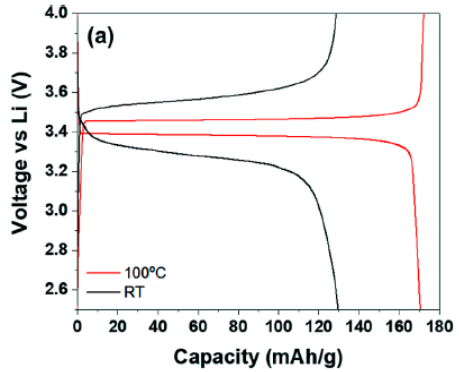

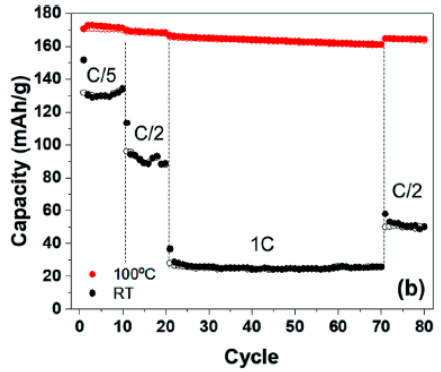

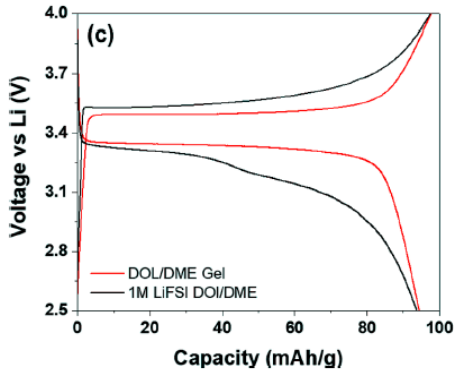

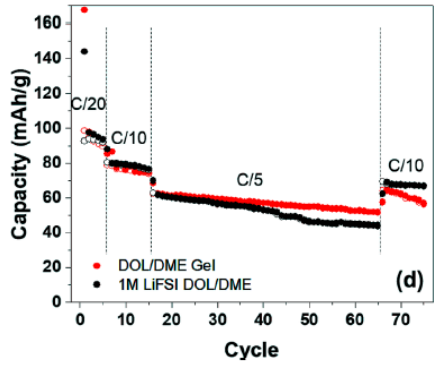

Room-Temperature Pseudo-Solid-State Iron Fluoride Conversion Battery with High Ionic Conductivity

Aliya S. Lapp, Laura C. Merrill, Bryan R. Wygant, David S. Ashby, Austin S. Bhandarkar, Alan C. Zhang, Elliot J. Fuller, Katharine L. Harrison, Timothy N. Lambert, and A. Alec Talin*

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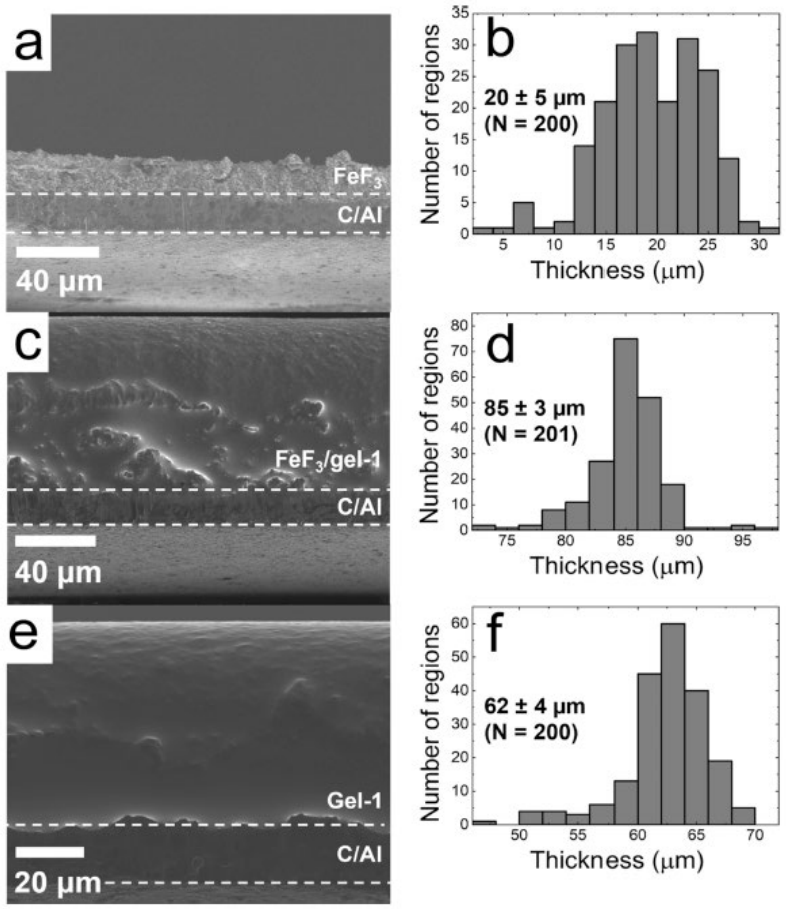
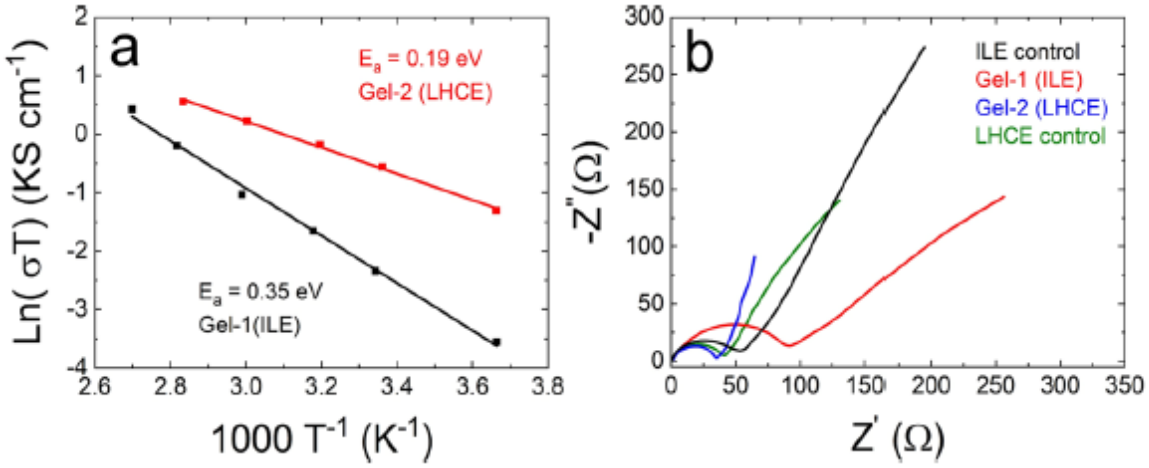


Table 1. Ionic Conductivity (σ) of the PVDF-HFP Gels before and after Electrolyte Exchange

Temperature (°C)	$\sigma_{Gel\text{-}1}{}^{a}$ (mS cm^{-1})	$\sigma_{Gel\text{-}2}{}^{b}$ (mS cm^{-1})
0	0.11	0.99
25	0.33	1.92
40	0.67	2.67
60	1.18	3.74
80	2.85	4.94



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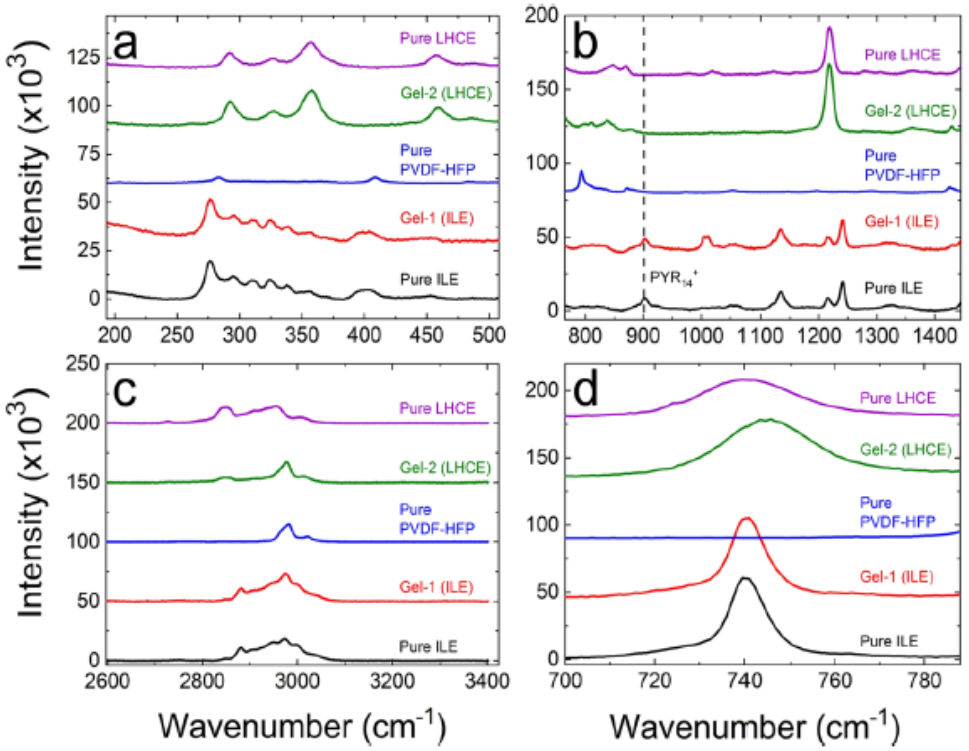

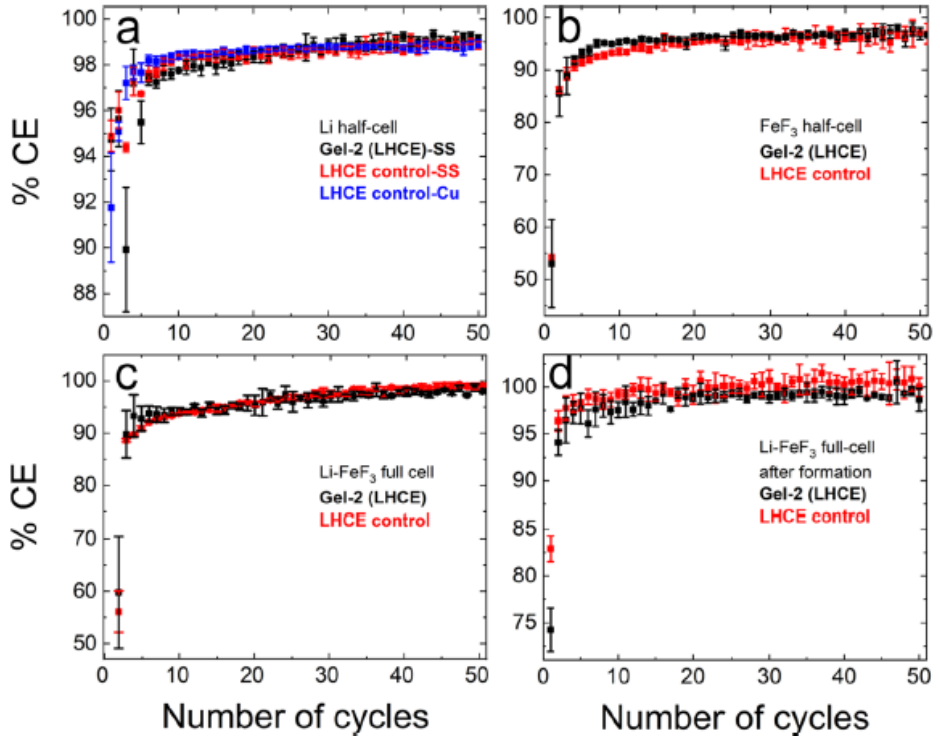

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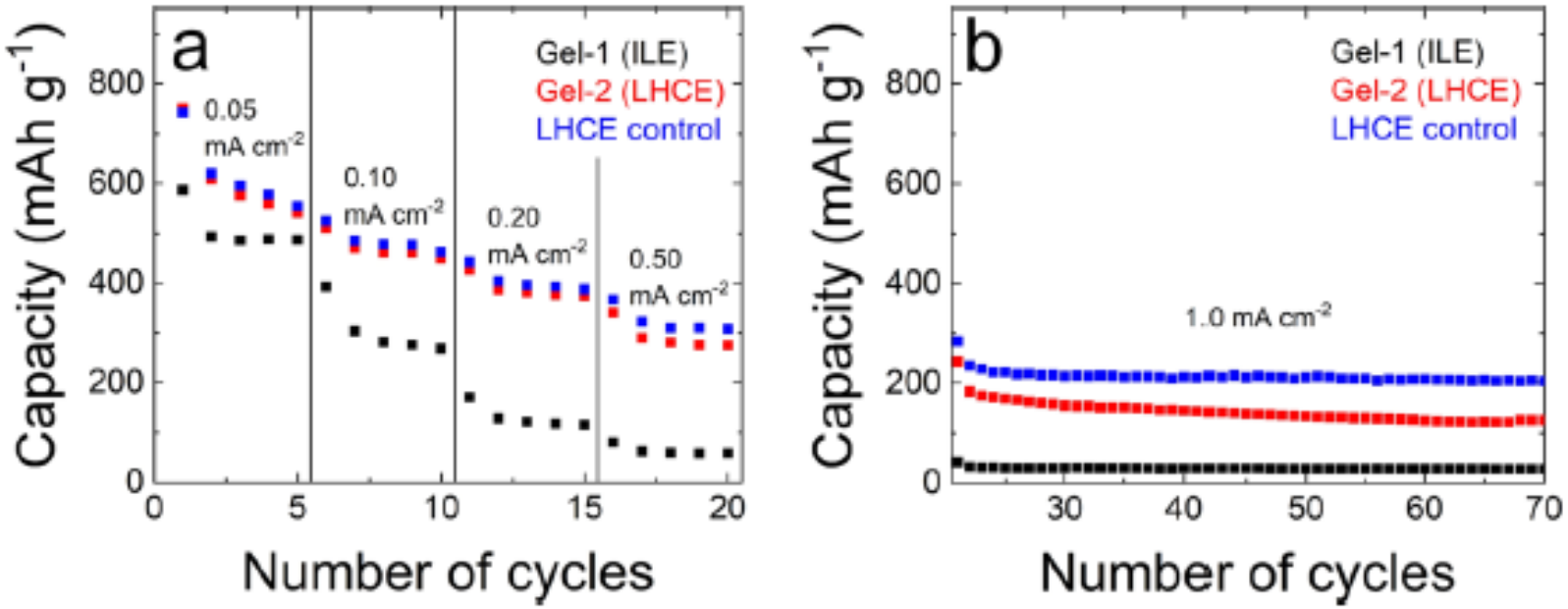
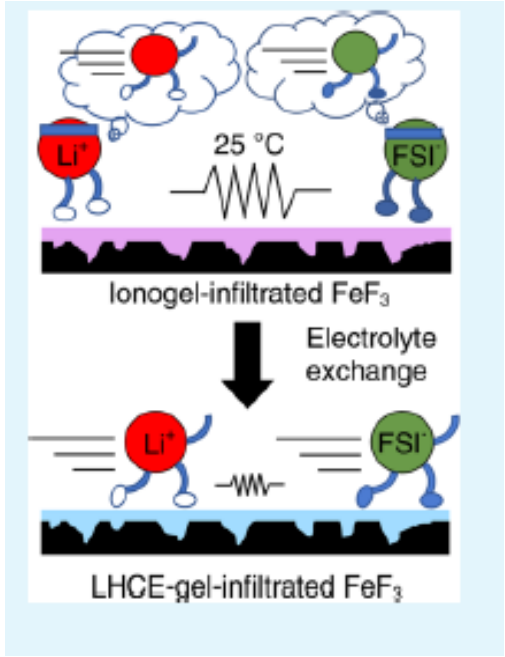
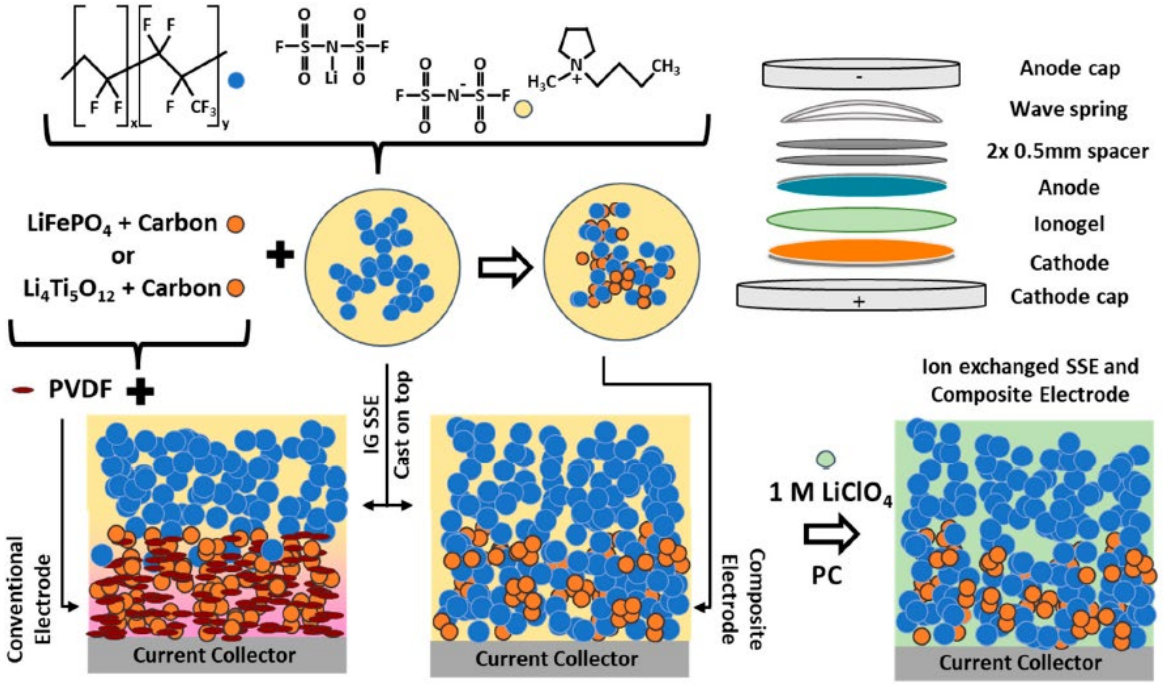


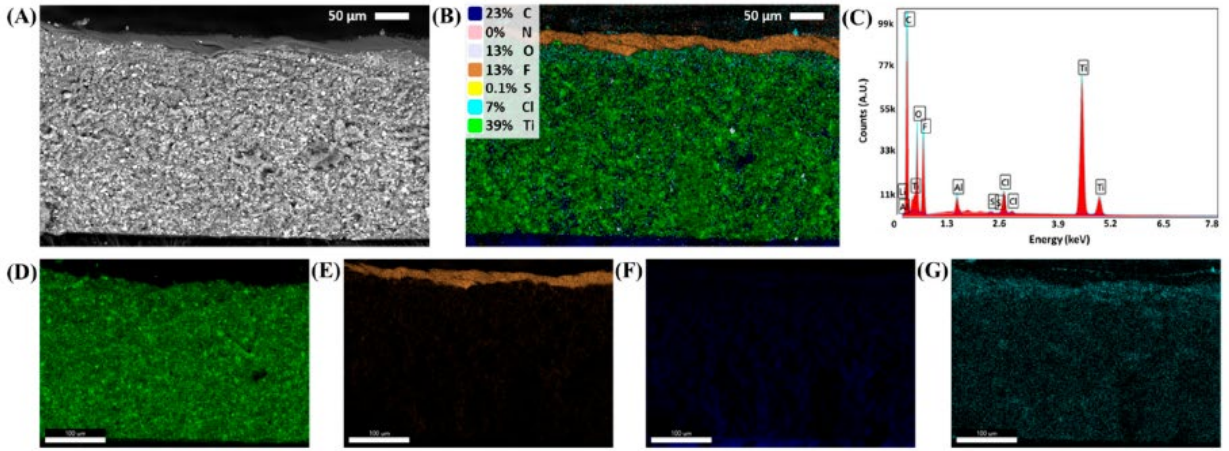


Composite Ionogel Electrodes for Polymeric Solid-State Li-Ion Batteries

Noah B. Schorr [1,*], Austin Bhandarkar [2], Josefine D. McBrayer [1] and A. Alec Talin [2,*]

Polymers **2024**, *16*, 1763. https://doi.org/10.3390/polym16131763

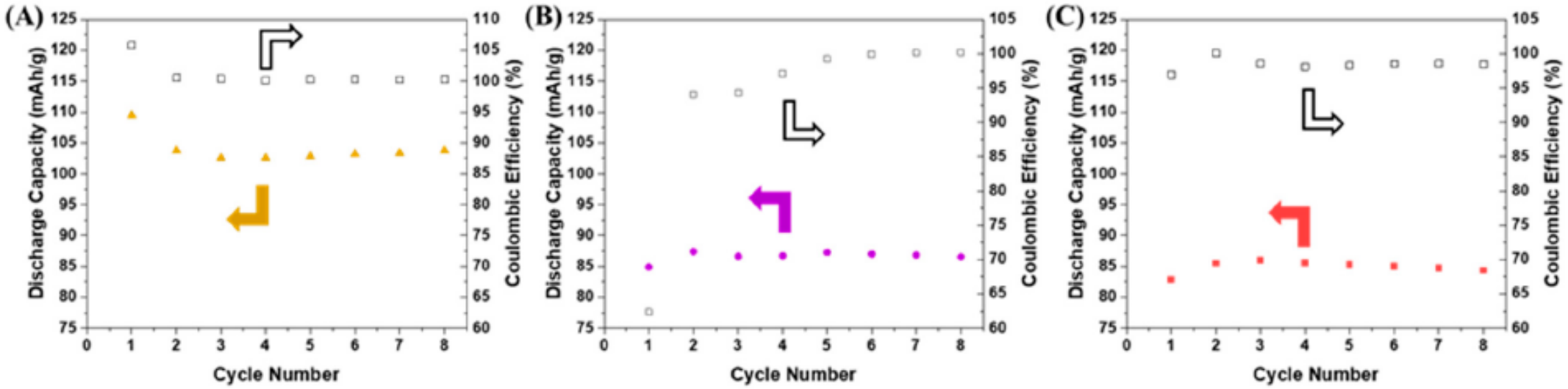




Composite Ionogel Electrodes for Polymeric Solid-State Li-Ion Batteries

Noah B. Schorr [1,*], Austin Bhandarkar [2], Josefine D. McBrayer [1] and A. Alec Talin [2,*]

Composition	Mass Percent Loading			Mass Ratio	
	Active Material	Carbon	PVDF-HFP	Active/Carbon	Active/PVDF-HFP
1	45.29%	19.41%	35.29%	2.33	1.28
2	55.00%	23.57%	21.43%	2.33	2.57
3	62.35%	13.36%	24.29%	4.67	2.57
4	71.30%	10.19%	18.52%	7.00	3.85



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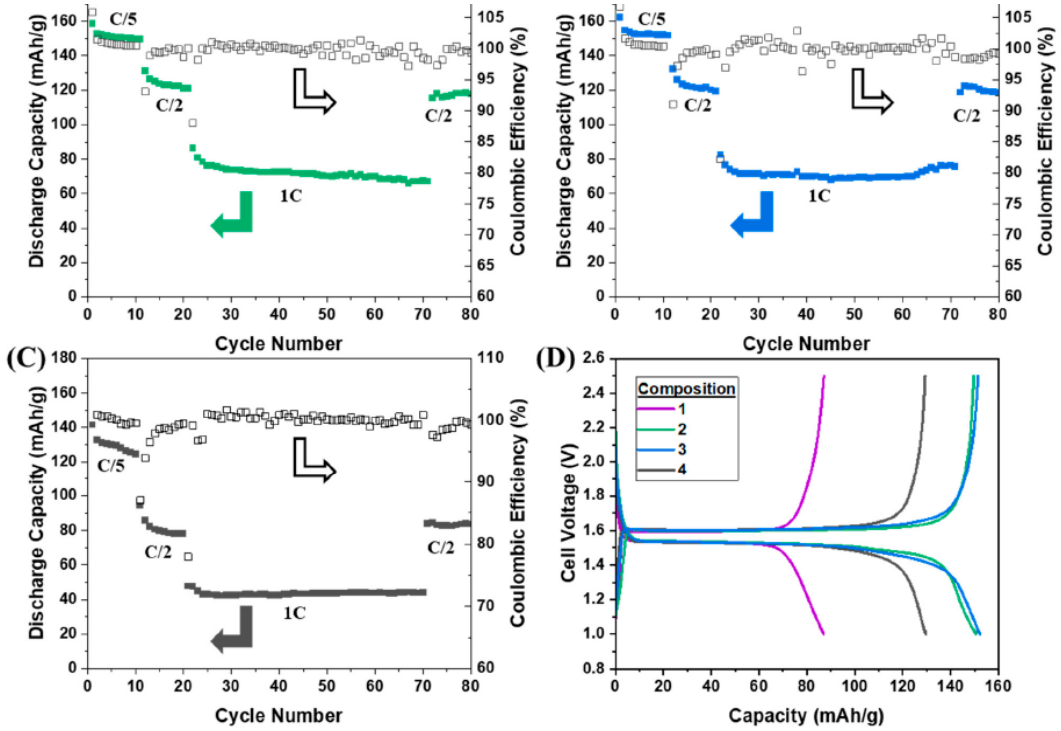
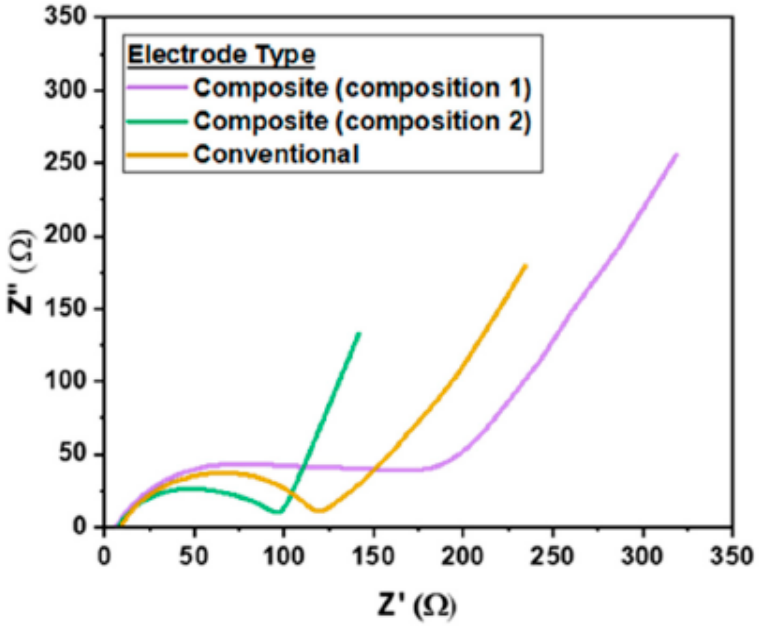


Composition	Active Material (mg/cm^2)	Capacity (mAh)	Rate (mA) C/5	Rate (mA) C/2	Rate (mA) C/1	Rate (mA/cm^2) C/5	Rate (mA/cm^2) C/2	Rate (mA/cm^2) C/1	Rate (A/g) C/5	Rate (A/g) C/2	Rate (A/g) C/1
1	7.76	2.49	0.50	1.24	2.49	1.32	3.30	6.60	0.034	0.085	0.17
2	10.52	3.37	0.67	1.69	3.37	1.79	4.47	8.94	0.034	0.085	0.17
3	10.55	3.38	0.68	1.69	3.38	1.79	4.48	8.97	0.034	0.085	0.17
4	13.76	4.41	0.88	2.21	4.41	2.34	5.85	11.70	0.034	0.085	0.17

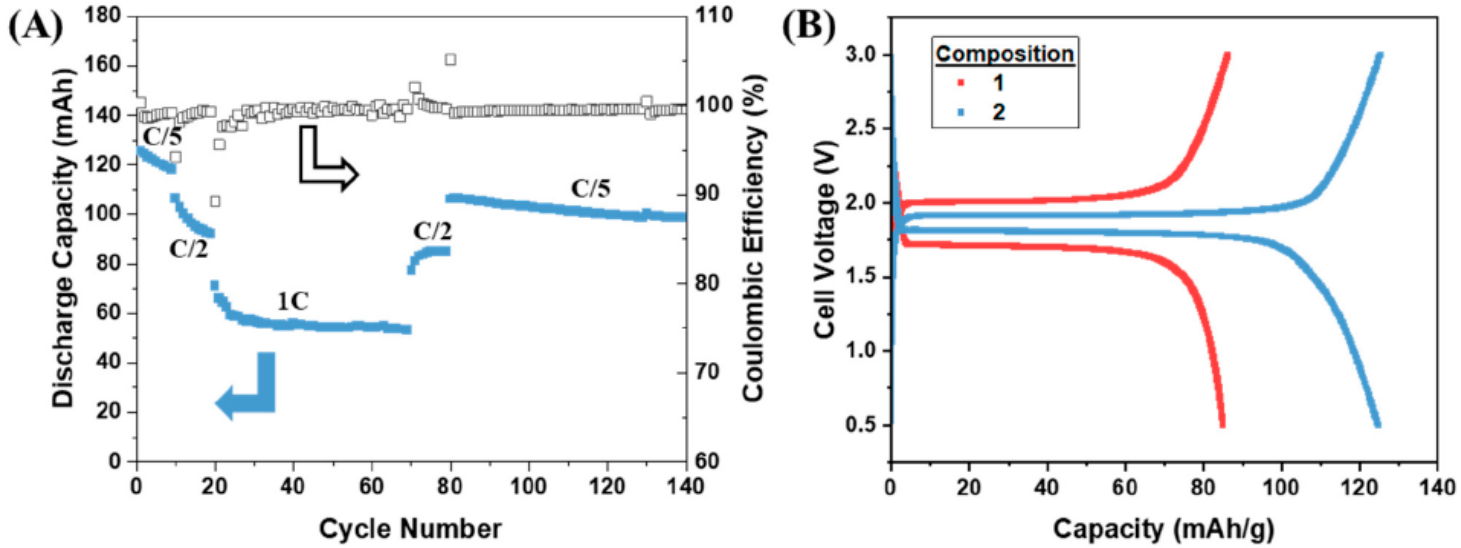
Composite Ionogel Electrodes for Polymeric Solid-State Li-Ion Batteries

Noah B. Schorr [1,*], Austin Bhandarkar [2], Josefine D. McBrayer [1] and A. Alec Talin [2,*]

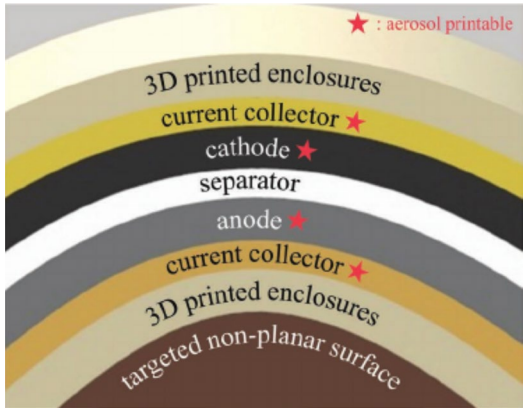


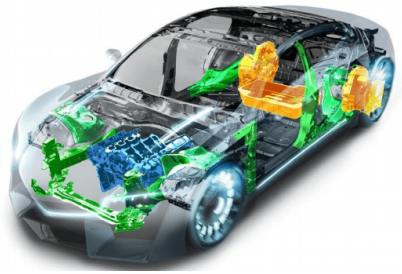
Electrolyte	Active Material	Loading mg/cm^2	Reference
PU-SN-LiTFSI	LFP||Li	1	[26]
PVDF-HFP-LiTFSI-NMP	LFP||Li	1.5	[19]
PVDF-HFP-LiMNT-PEG	LFP||Li	1.2	[30]
LLZO-polymerized DOL gel bilayer	SPAN||Li	5.2	[20]
LLZO-plastic crystal electrolyte (LiTFSI-SN)	LFP||Li	4.88	[28]
GO-PEO	LFP||Li	2.5	[29]
PEO-LiTFSI	LTO||Li	3	[31]
Solvent Exchanged PVDF-HFP	LFP||LTO	10.5	This Work

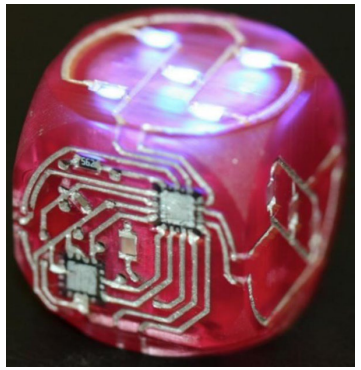
Polyurethane (PU), lithium lanthanum zirconium oxide (LLZO), sulfurized polyacrylonitrile (SPAN), Dioxolane (DOL), graphene oxide (GO), polyethyleneoxide (PEO), lithium montmorillonite (LiMNT), polyehtlyne glycol (PEG), succinonitrile (SN).



- **Batteries of custom-form can enable higher practical energy density**
  - **In practical applications, custom-form batteries can be packed more efficiently into a given space**





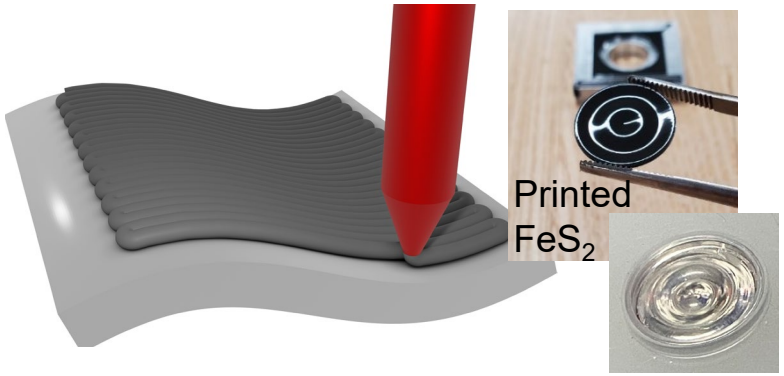


X. Yu, *et al*. "Customizable Nonplanar Printing of Lithium-Ion Batteries." *Advanced Materials Technologies* 4, 2019.

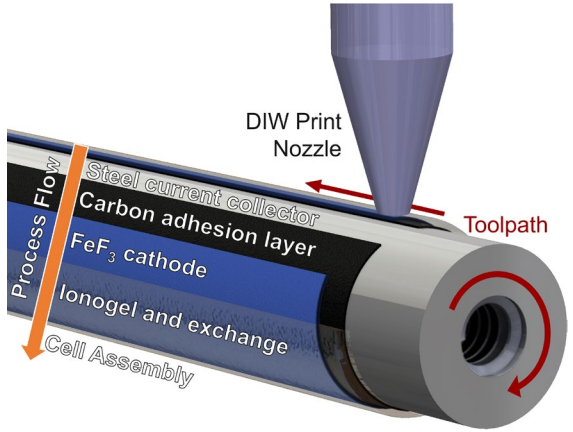
E. Macdonald, *et al*. "3D Printing for the Rapid Prototyping of Structural Electronics." *IEEE Access* 2, 2014.

- **3-5 axis direct-write printing is a straight forward way to produce custom-form cells**

Non-planar geometries



Direct-write printing onto cylindrical mandrels



J. Cardenas, *et al*. *ACS Appl. Mater. Interfaces* 14, 45342, 2022.

Modifying Ionogel Solid-Electrolytes for Complex Electrochemical Systems

David S. Ashby,* Jorge Cardenas, Austin Suhas Bhandarkar, Adam W. Cook, and A. Alec Talin*

Cite This: *ACS Appl. Energy Mater.* 2022, 5, 12467−12474

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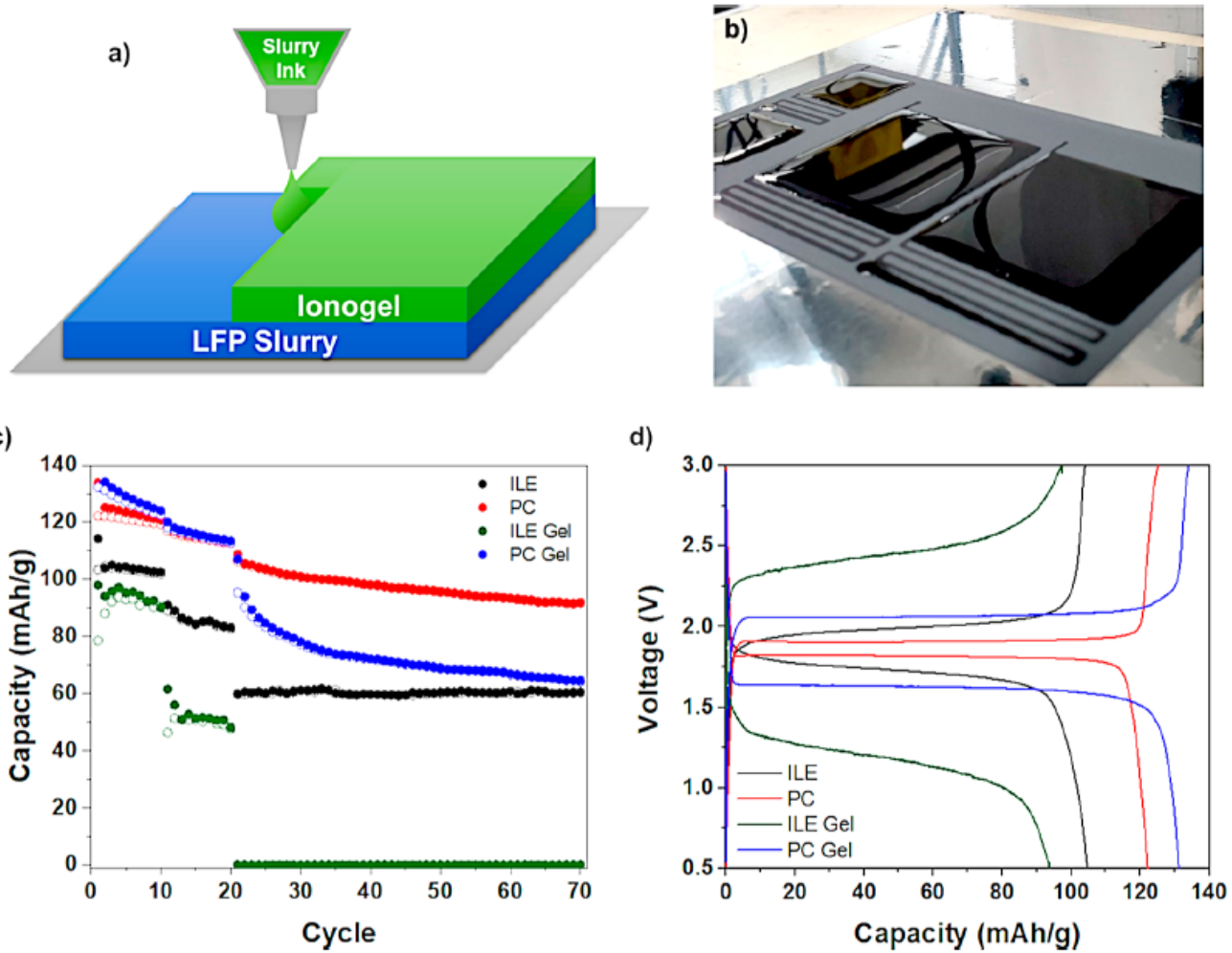
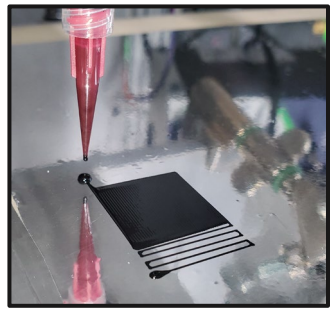
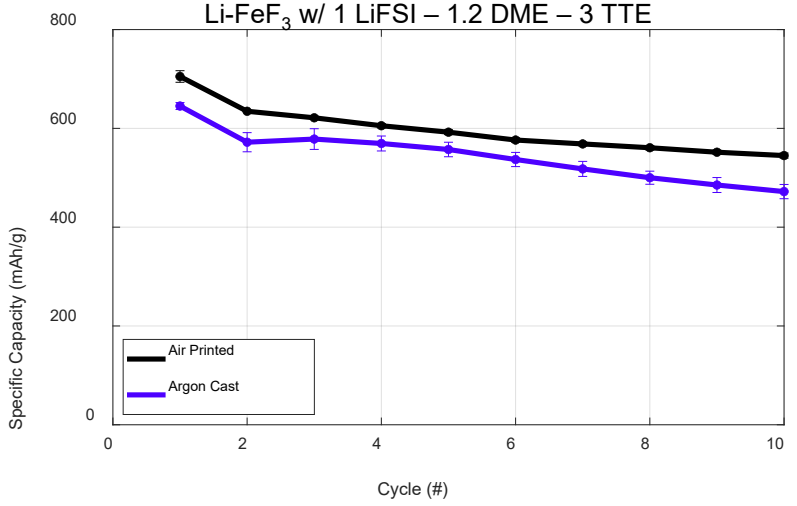


Enabling custom-form FeF_3 cells with exchanged ionogels

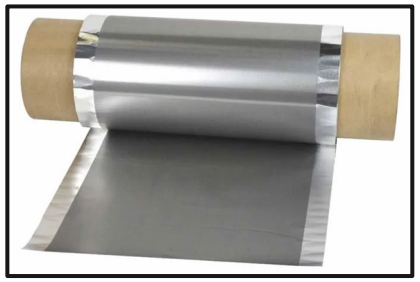
Glovebox blade coating
vs.
printing in air

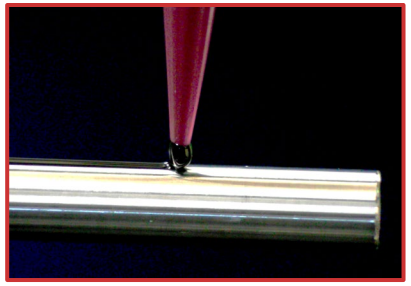


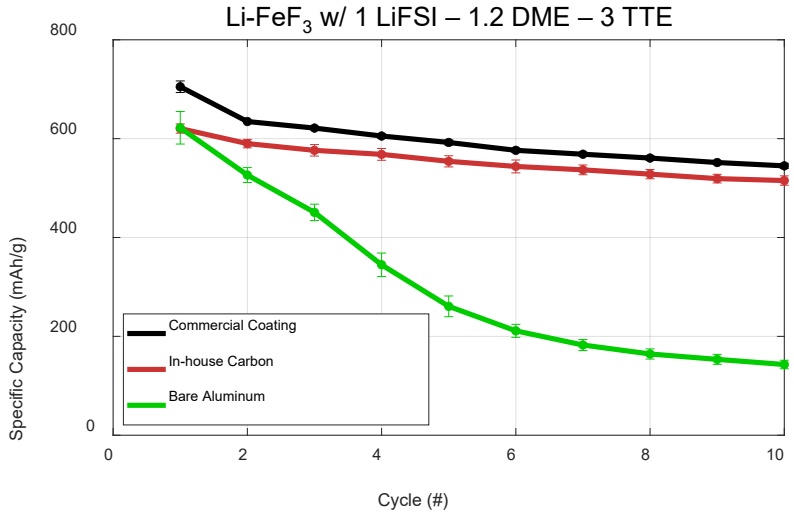


- FeF_3 compatible with air printing

Carbon coated Al foil
vs.
Custom carbon ink

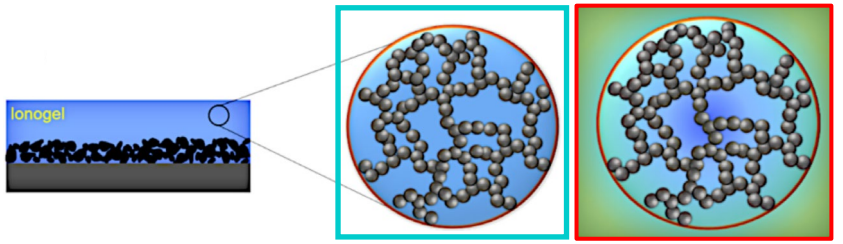


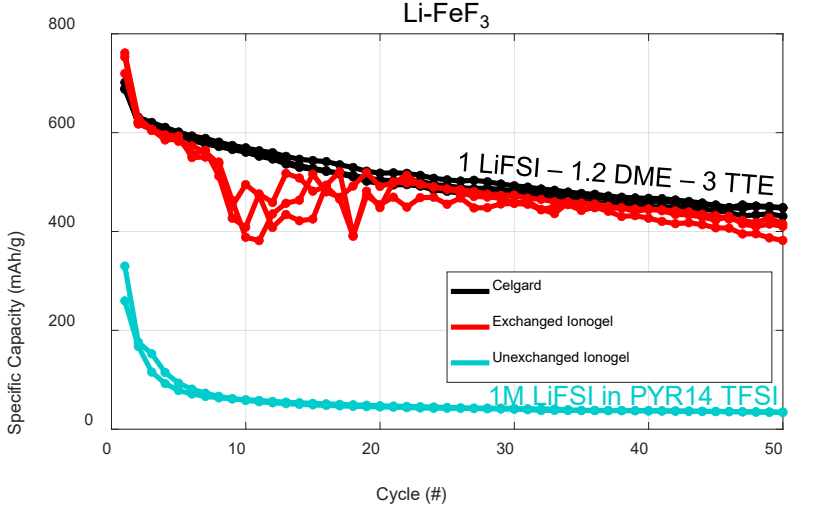




- Carbon ink developed for custom-form adhesion layers

As-printed ionogels
vs.
Exchanged ionogels





- Electrolyte exchange needed
- Soft shorts in cycle 8-20 range

J. Cardenas, *et al*. Custom-Form Iron Trifluoride Li-Batteries using 3D Printing and Electrolyte Exchanged Ionogels. In preparation…

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Thank You!