Designing Electrode Architectures across Length Scales: Some Lessons Learned from Li-ion and “Beyond Li” Chemistries

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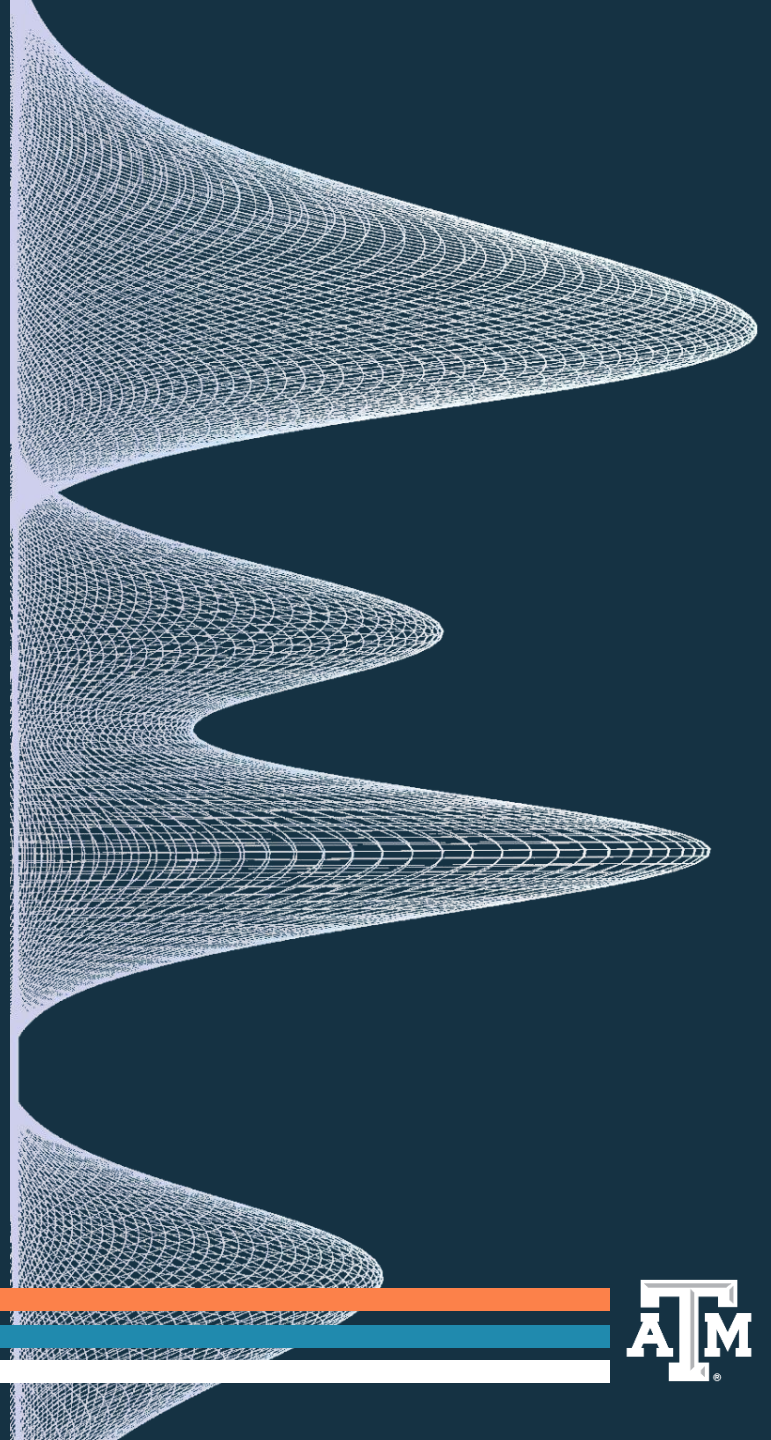

ACKNOWLEDGMENTS

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Identifying the orbital and atomistic basis for performance bottlenecks and degradation phenomena

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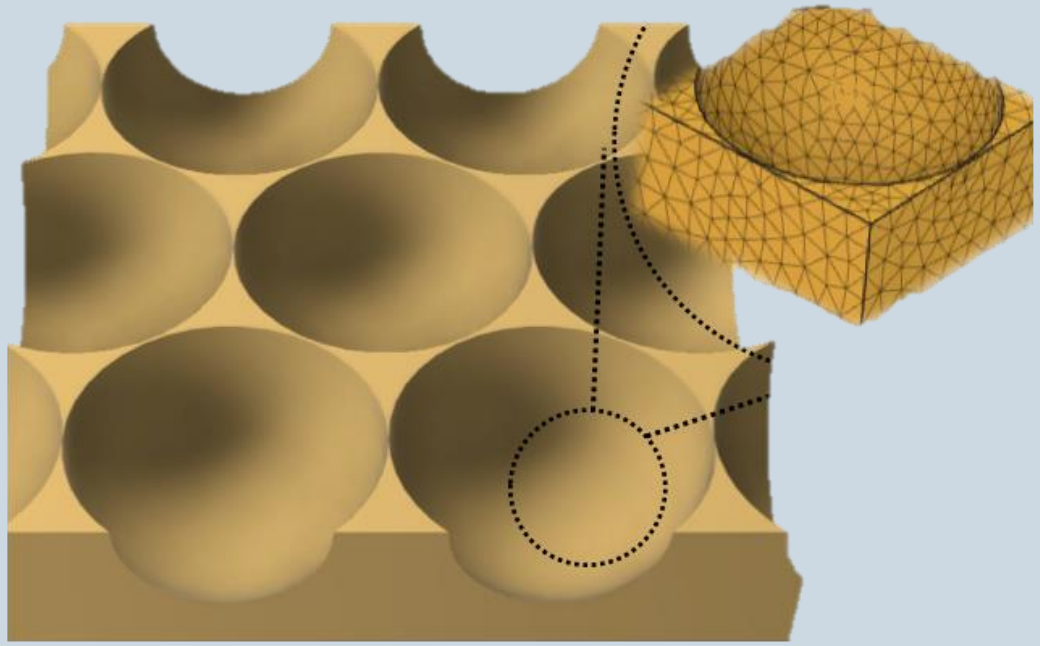
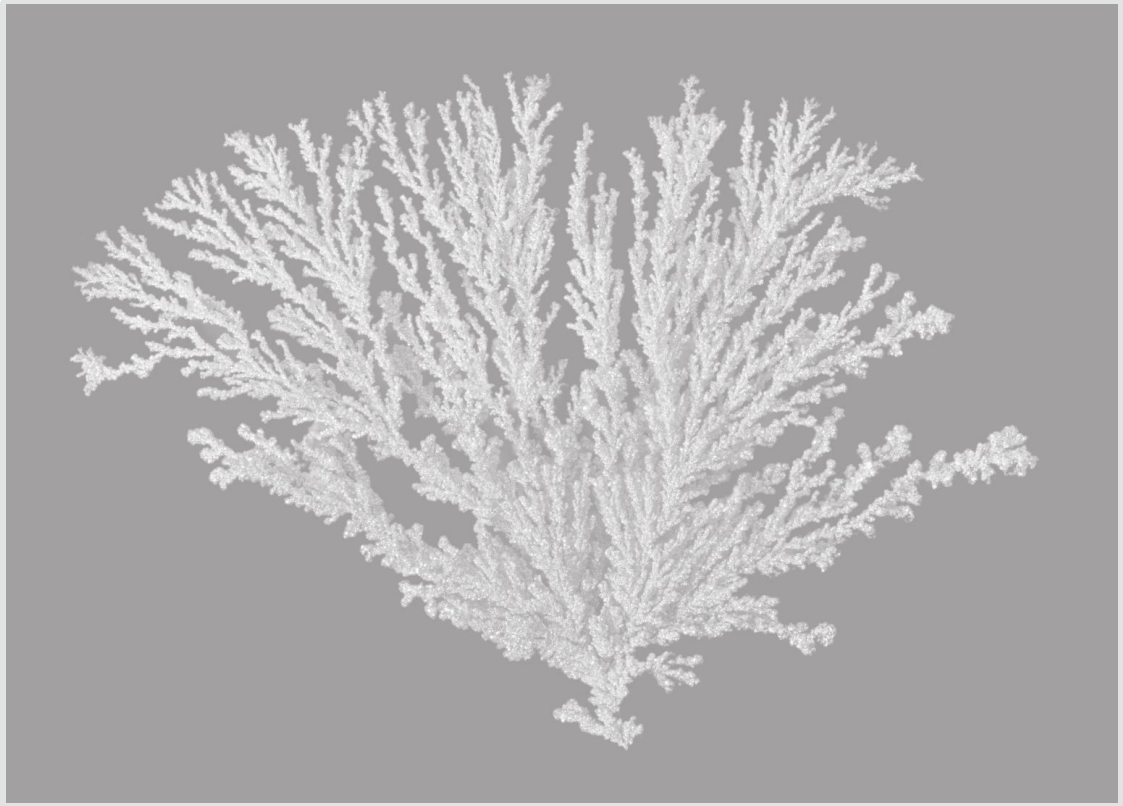


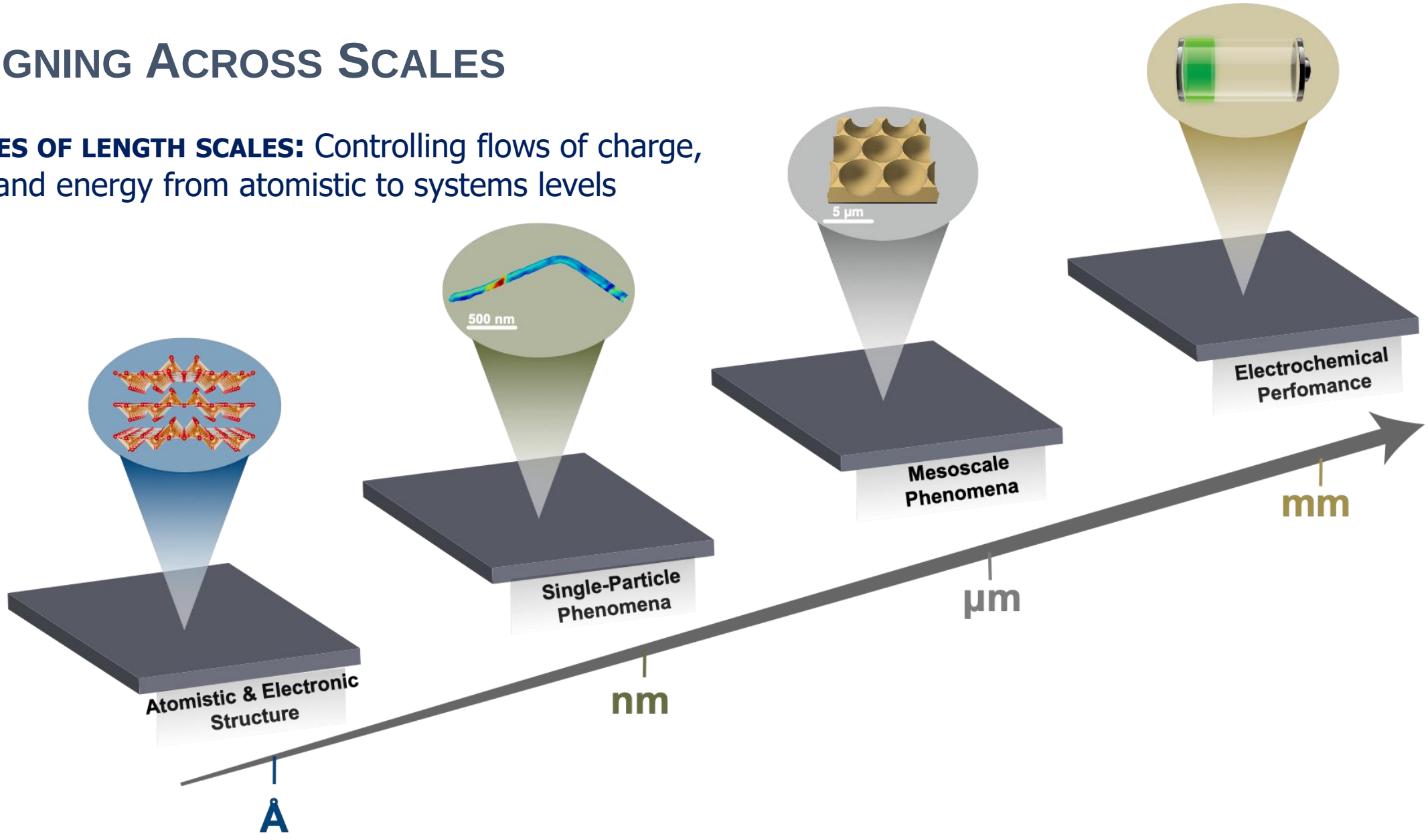
V_2O_5 Cathodes Across Scales



Mg Anodes

Designing Across Scales

Decades of length scales: Controlling flows of charge, mass, and energy from atomistic to systems levels



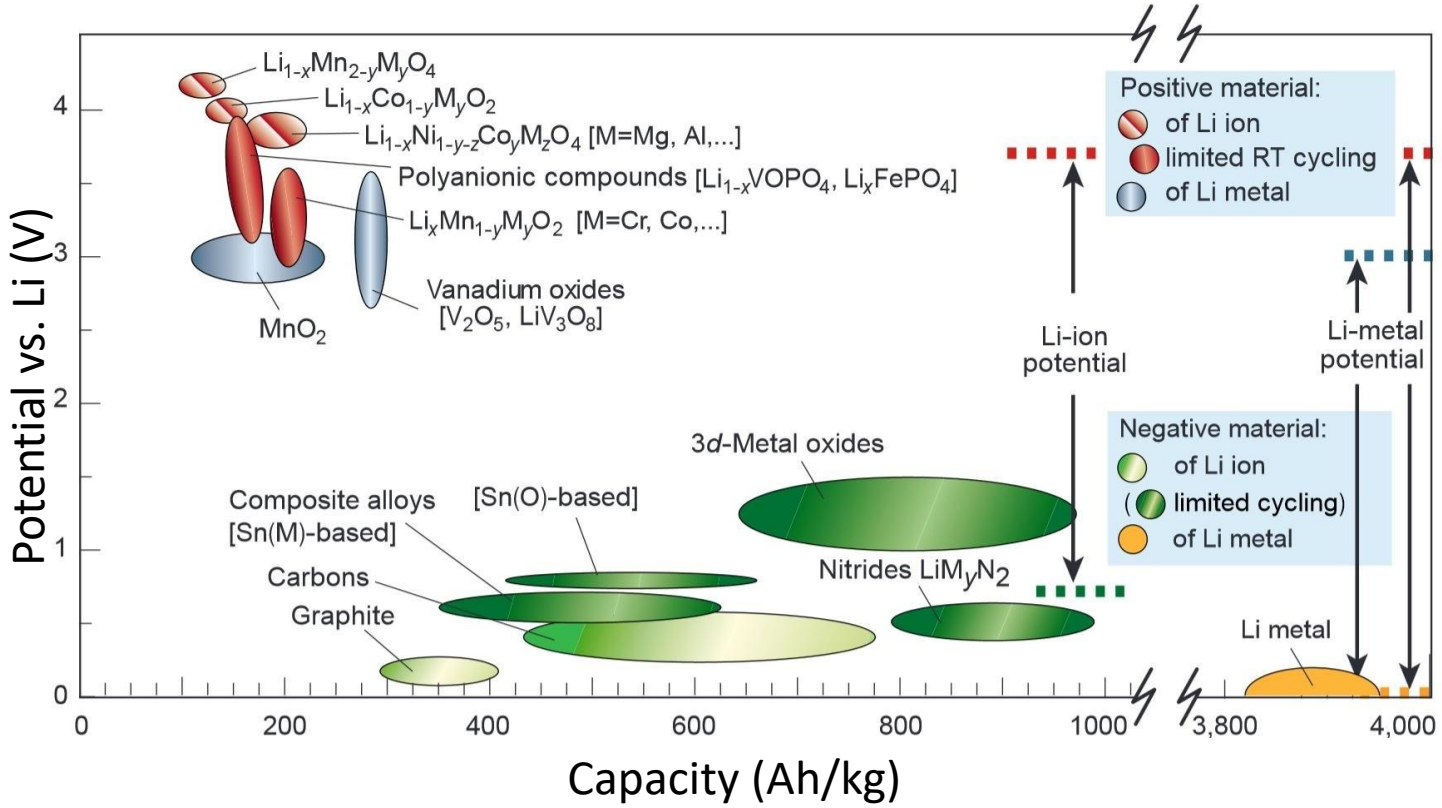
Decades of timescales: from femtoseconds (polarons) to seconds (mesoscale transport)

MATERIALS CONSIDERATIONS

standard cell reduction potential

$$E^o_{cell} = E^o_{cathode} - E^o_{anode}$$

standard electrode reduction potential



power density

cost

runtime

Coulombic efficiency

safety

cycle life

reversibility

propensity for dendrites

recyclability

number of transferred electrons

Faraday's constant

theoretical capacity

$$C_T = \frac{nF}{3.6M}$$

molecular weight

transferred electrons

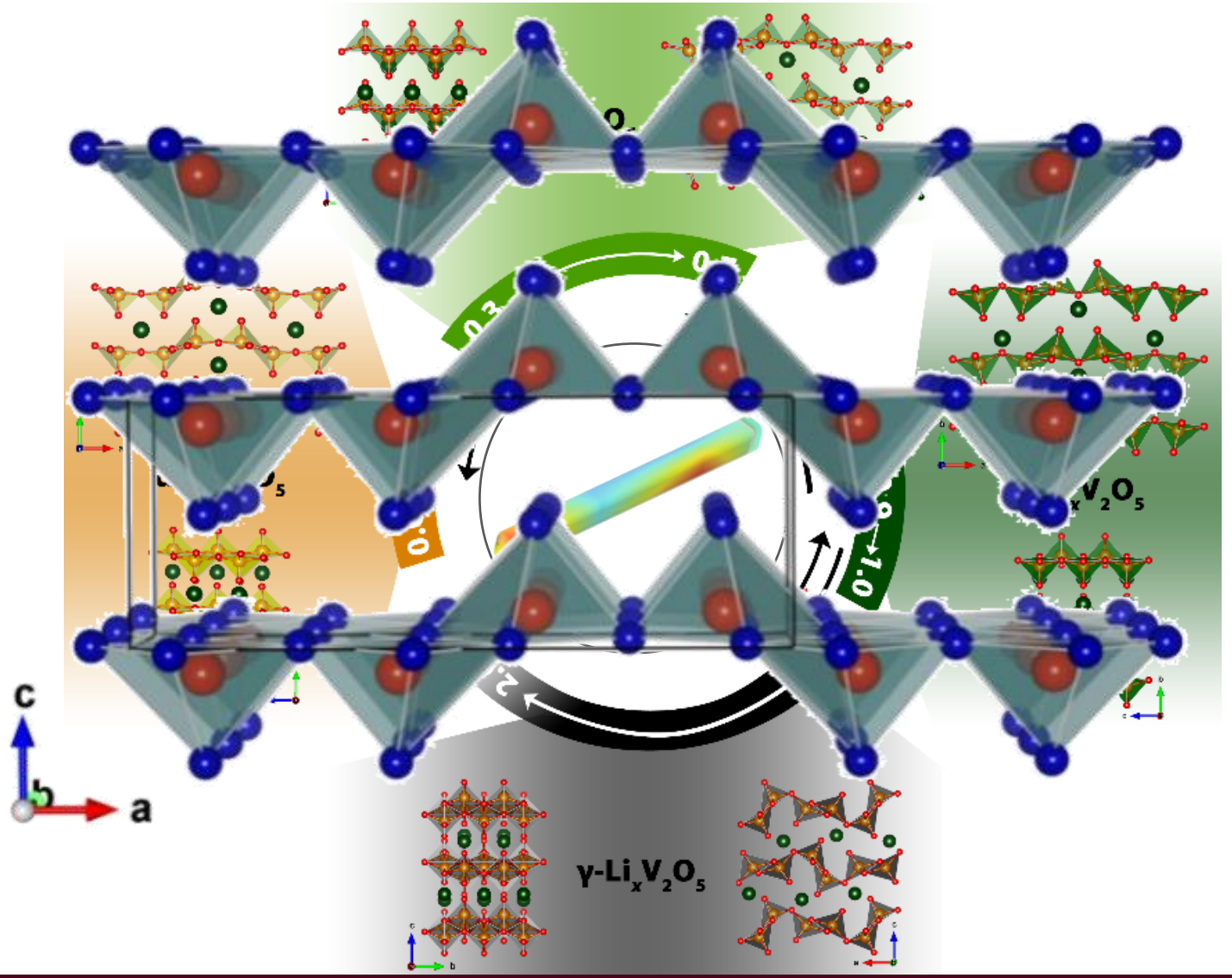
potential difference

$$\Delta G = -nFE$$

Gibbs free energy

Faraday's constant

V_2O_5 AS A MODEL CATHODE



Desirable

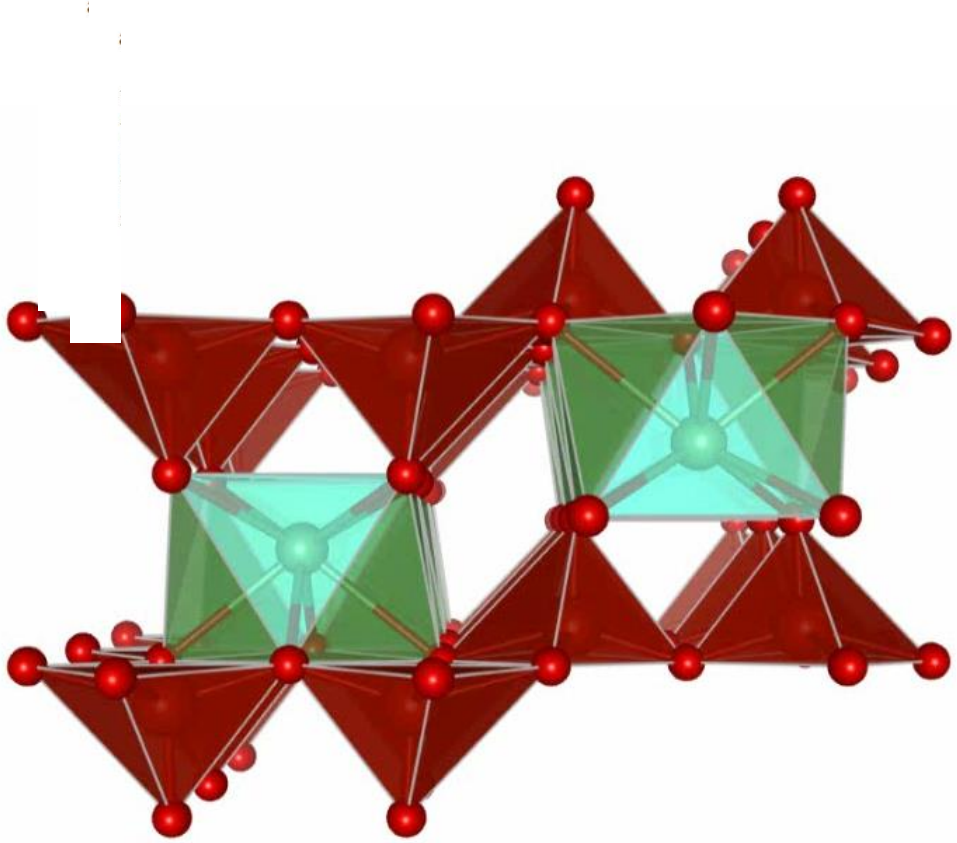
- High theoretical capacity
- Multiple accessible redox state
- Abundance of interstitial sites

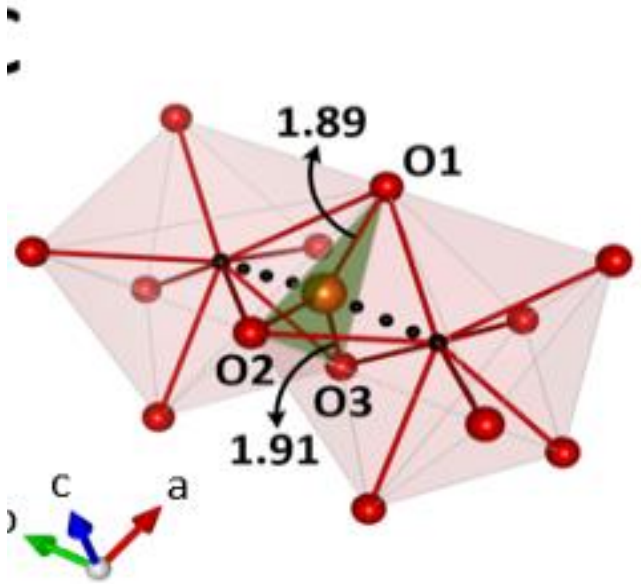
Undesirable

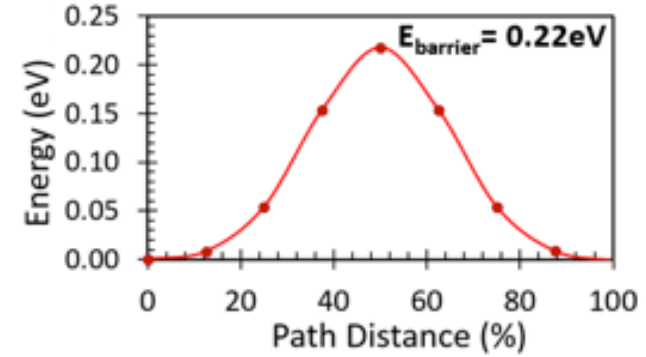
- Irreversible structural transitions
- Slow diffusion kinetics
- Poor electrical conductivity
- Cohesive delamination

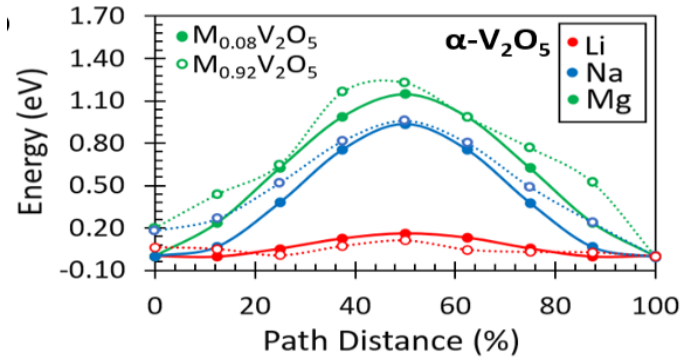
L. R. De Jesus, J. L. Andrews, A. Parija and S. Banerjee, *ACS Energy Lett.*, 2018, **3**, 915–931.
M. S. Whittingham, J. Electrochem. Soc., 1976, 123, 315–320.

Atomistic Diffusion Barriers







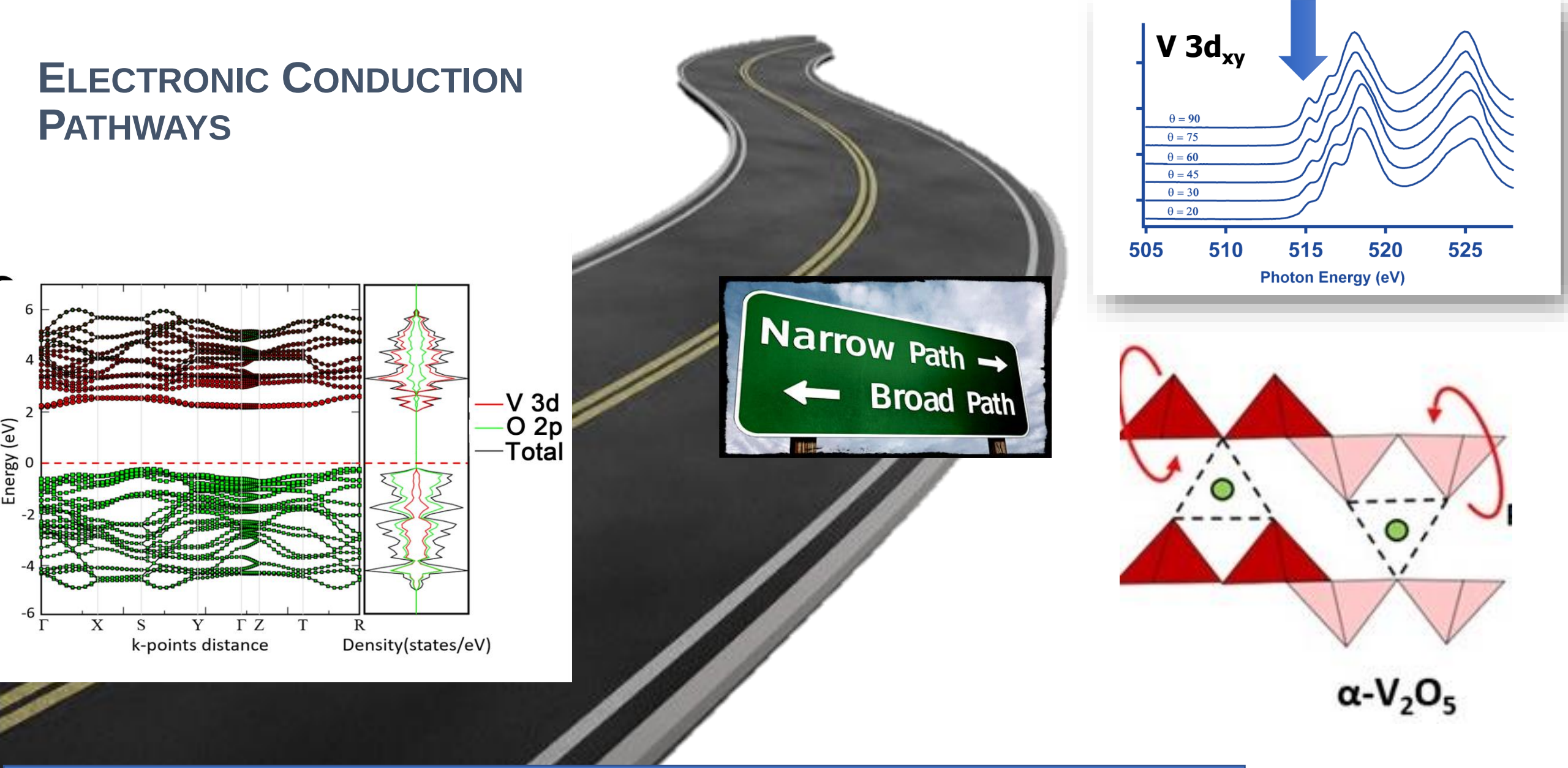


Large changes in local coordination environment result in substantial migration barrier

8→3→8

L. R. De Jesus, J. L. Andrews, A. Parija and S. Banerjee, *ACS Energy Lett.* **2018**, **3**, 915–931.

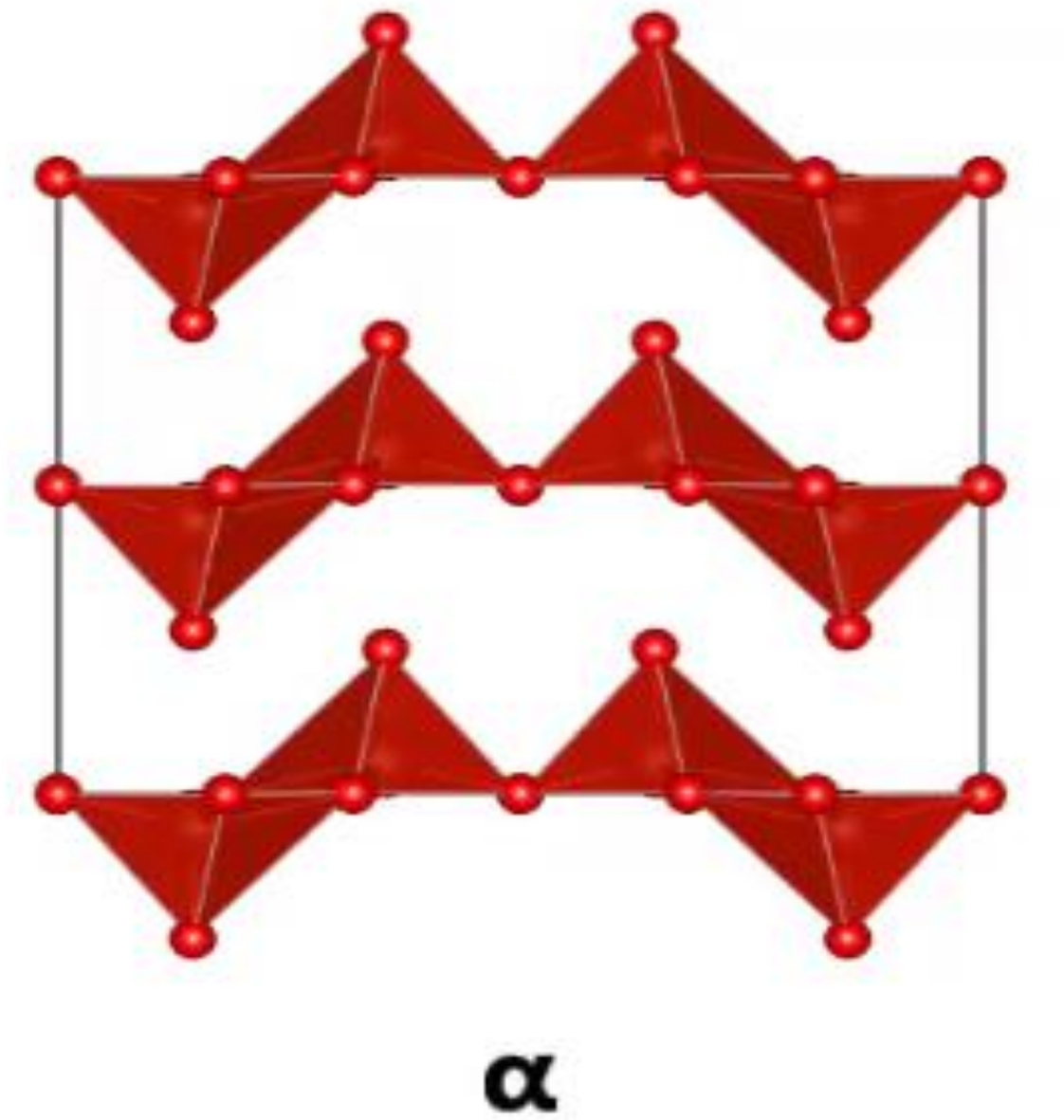
Electronic Conduction Pathways



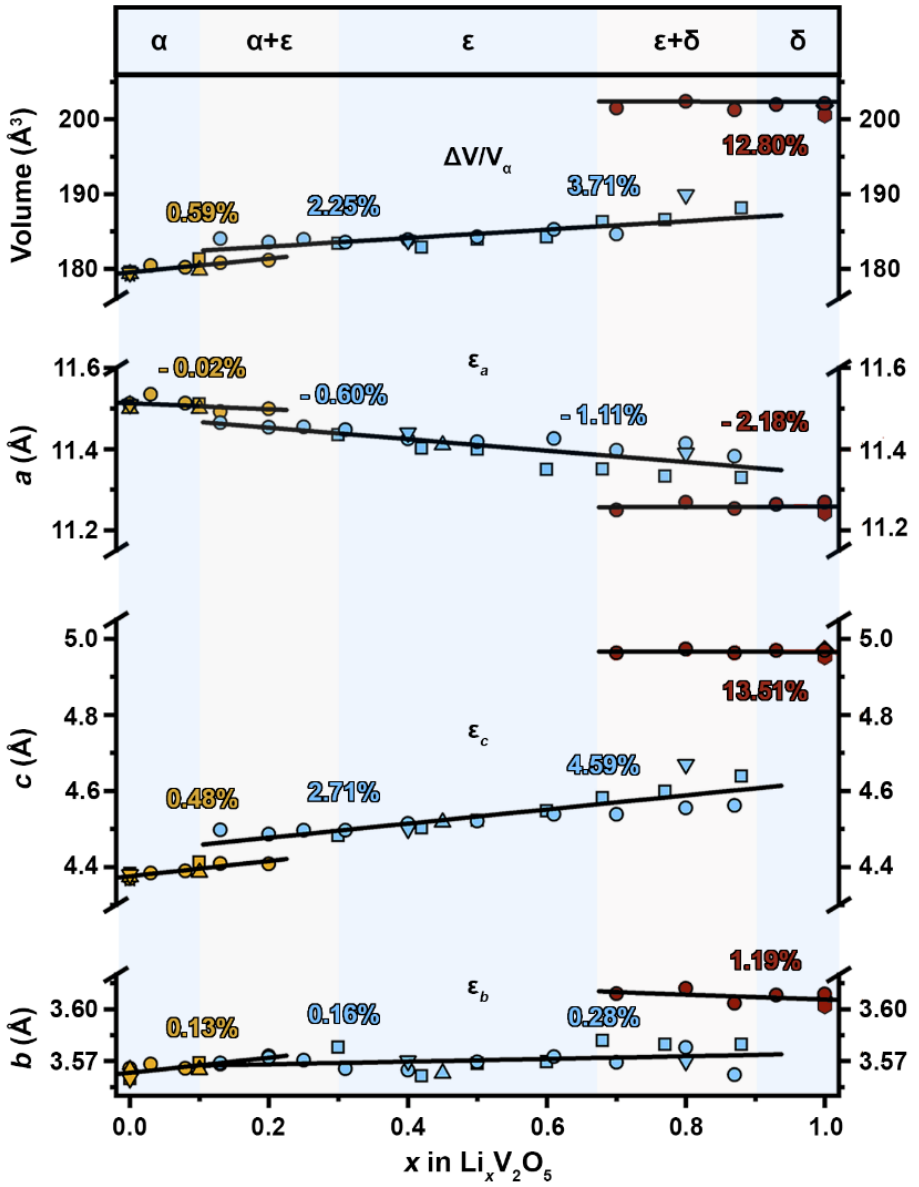
Narrow “split-off” conduction band leads to electron localization and poor electrical conductivity

L. R. De Jesus, J. L. Andrews, A. Parija and S. Banerjee, *ACS Energy Lett.*, 2018, **3**, 915–931.

Lithiation Phase Diagram in V_2O_5

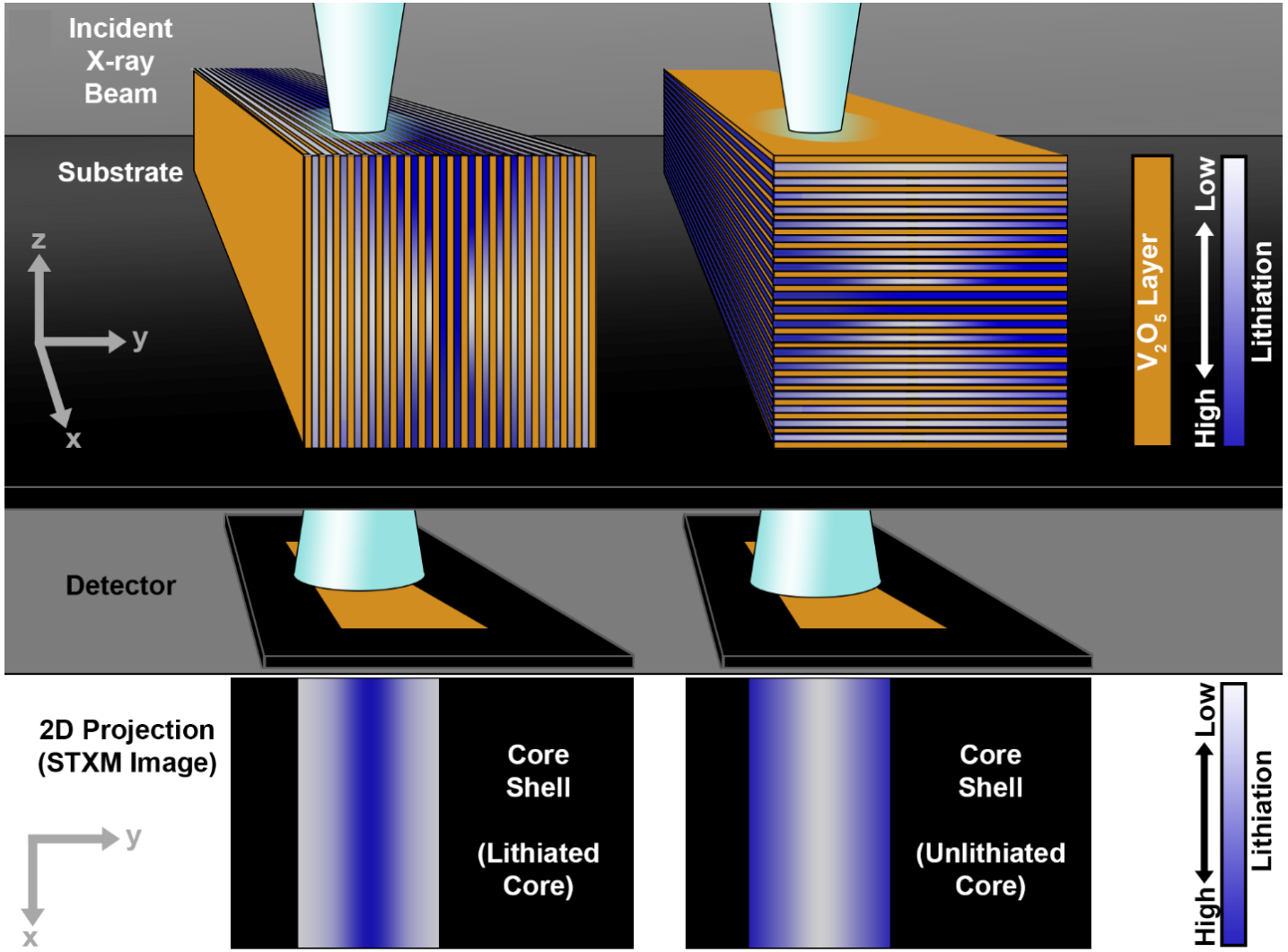


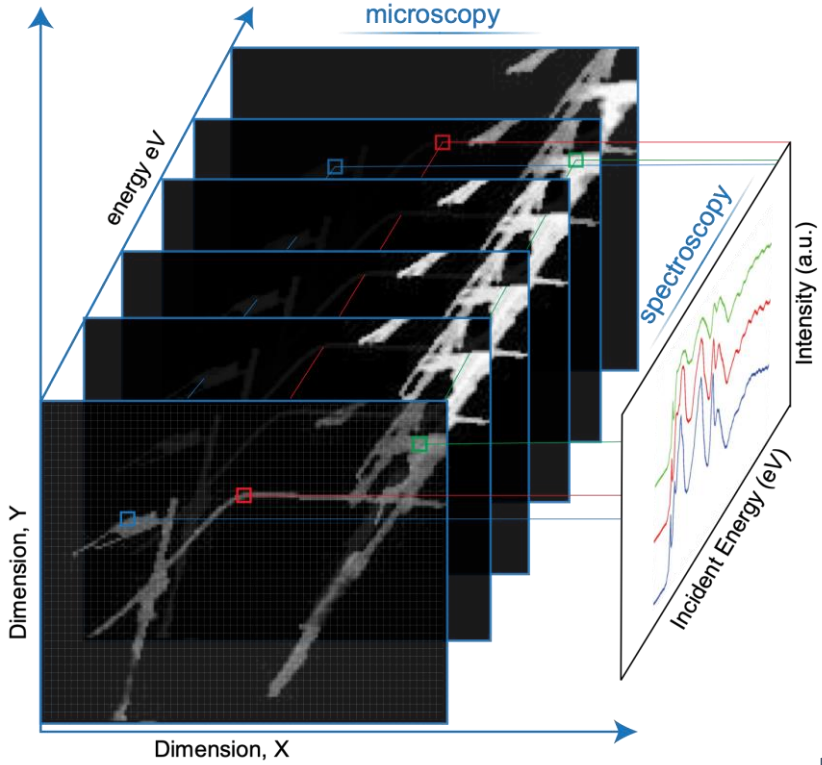
Series of phase transitions to accommodate increasing concentrations of intercalated ions



Horrocks, G. A.; Likely, M. F.; Velazquez, J. M.; Banerjee, S. *J. Mater. Chem. A*., **2013**, *1*, 15265. Santos,* Andrews,* Bai,* Stein, Luo, Zhang, Pharr, Xu, Banerjee. *Mater. Horiz. Just Accepted.* Andrews, , Stein, Santos, Chalker, De Jesus, Davidson, Gross, Pharr, Batteas, Xu, Banerjee. *Matter*, **2020**, *3* 1754.

Mapping Lithiation using X-ray Microscopy





Luis De Jesus

Justin L. Andrews

ALS

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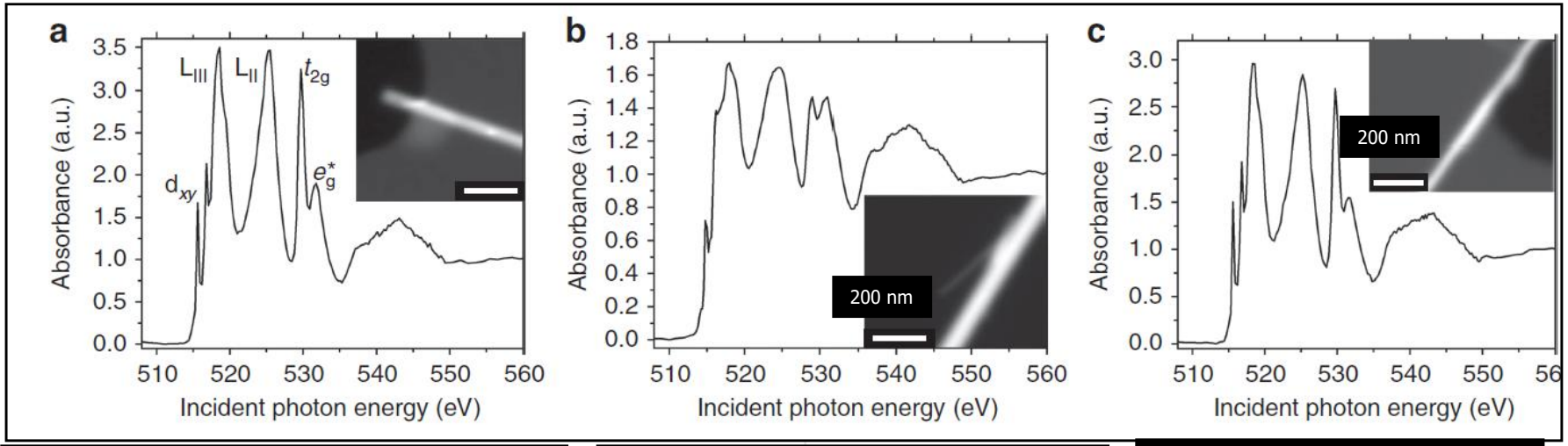
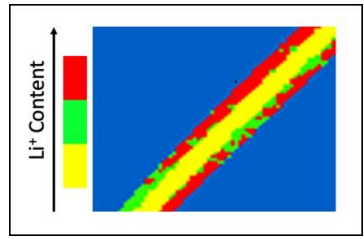
Mapping Heterogeneity across a Single Particle

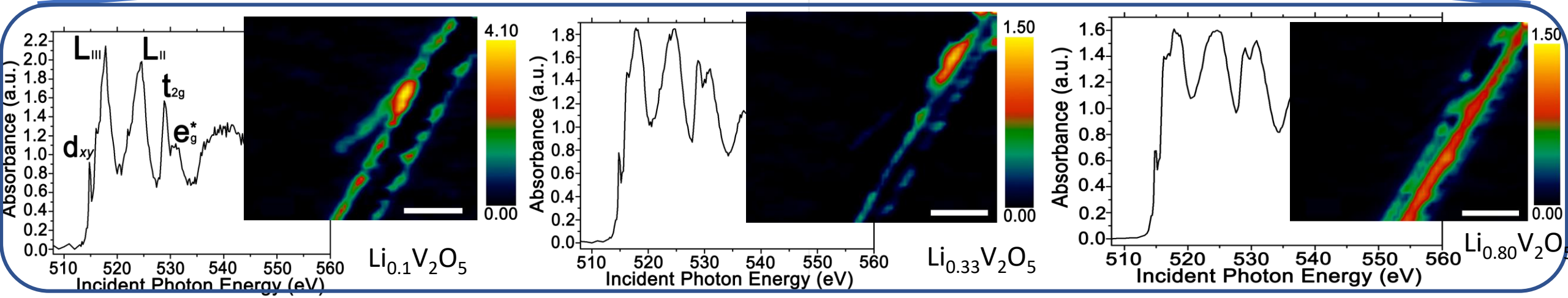


Nanowire before Li-ion Intercalation

Nanowire after Li-Ion Intercalation

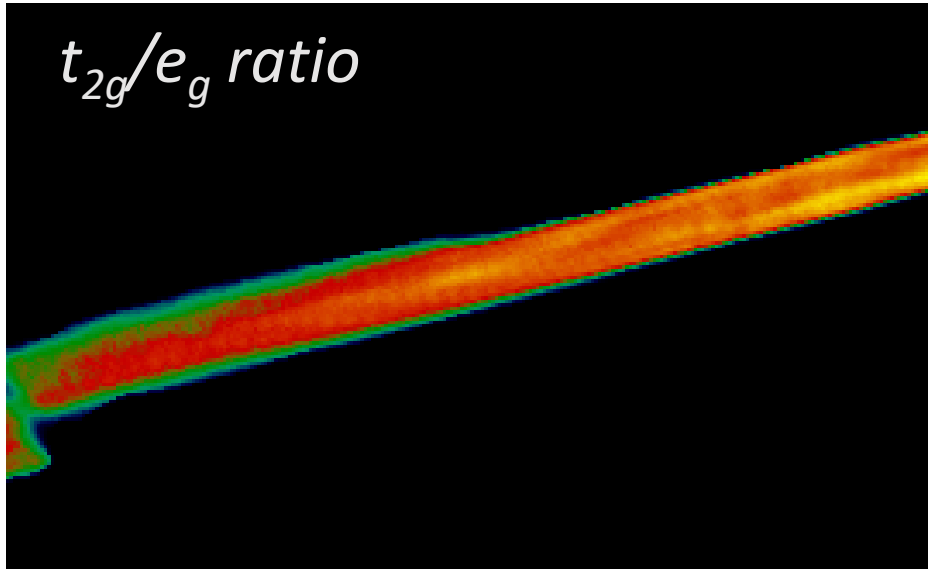
Nanowire after Delithiation

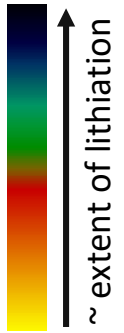


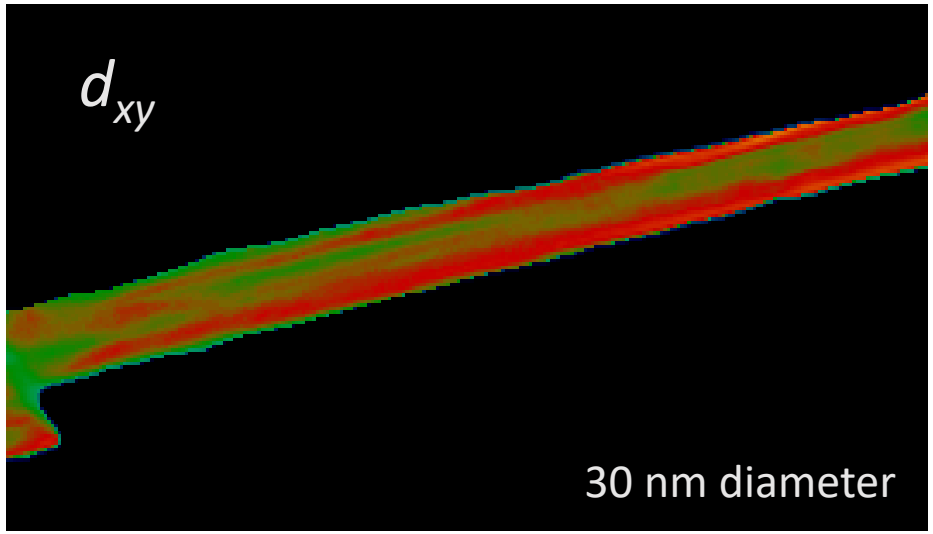


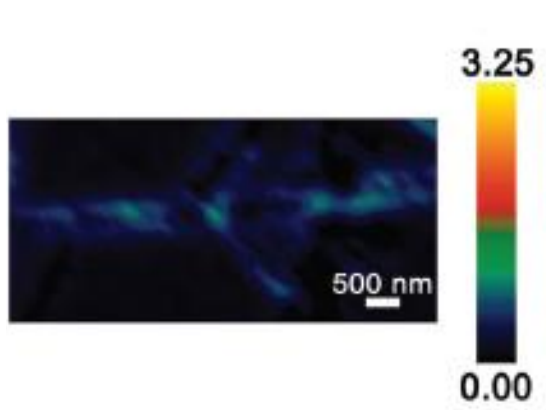
Closer Up through Ptychography

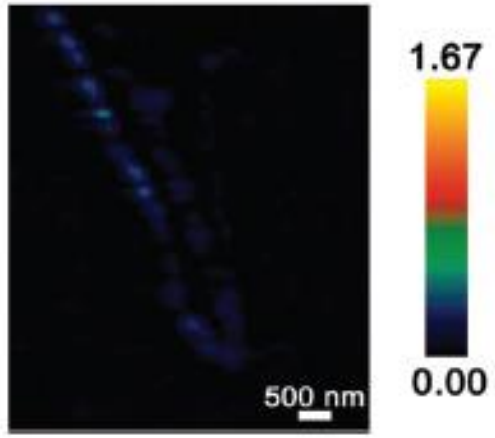
X-ray Ptychography Imaging





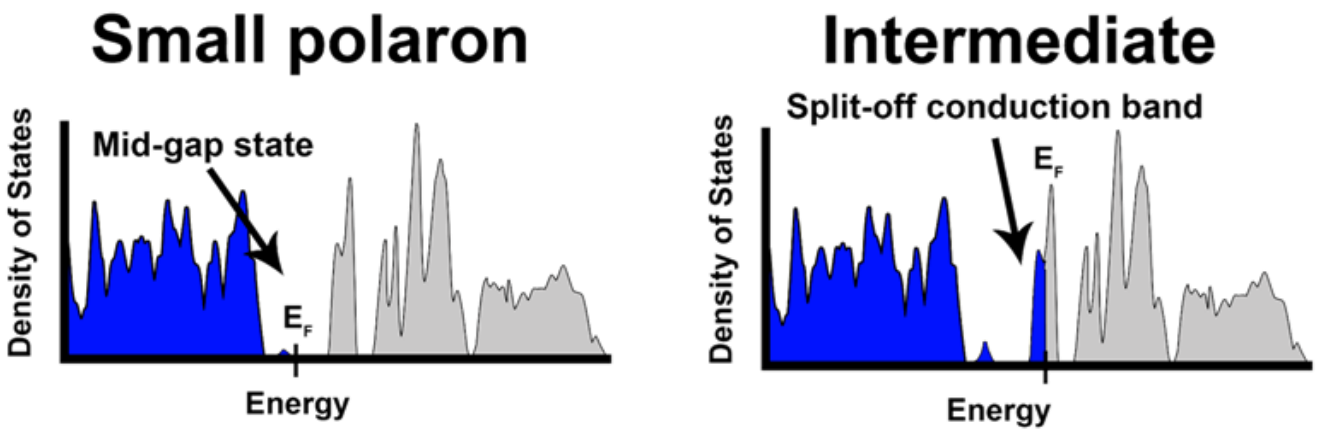


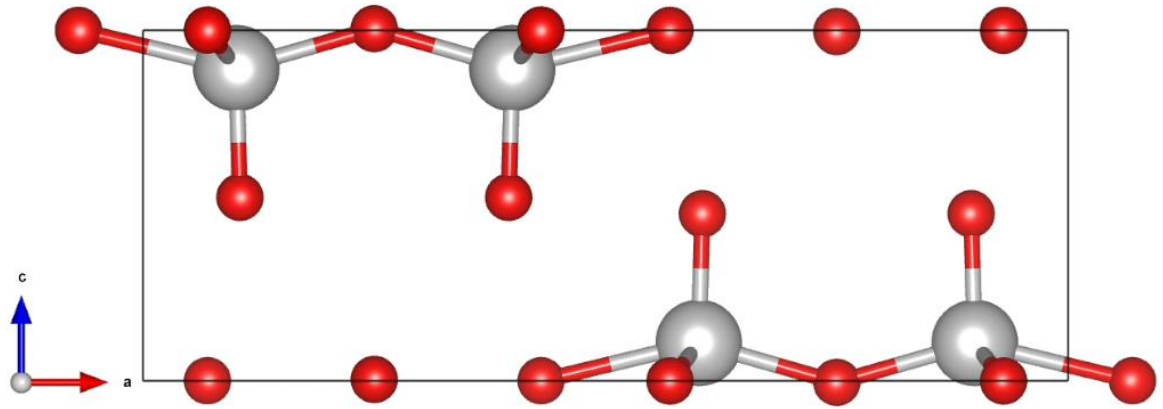




Core–shell and charge striping motifs observed across individual particles

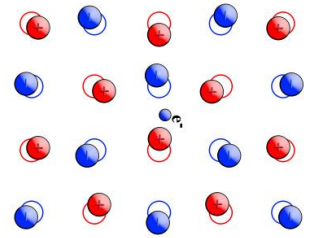
Atomistic and Electronic Structure Origins of Diffusion Impediments





Electronic and structural origins

- narrow 3*d* bands give rise to strong **electron correlation**
- upon lithiation electrons are **localized** on the $3d_{xy}$ orbital of V sites

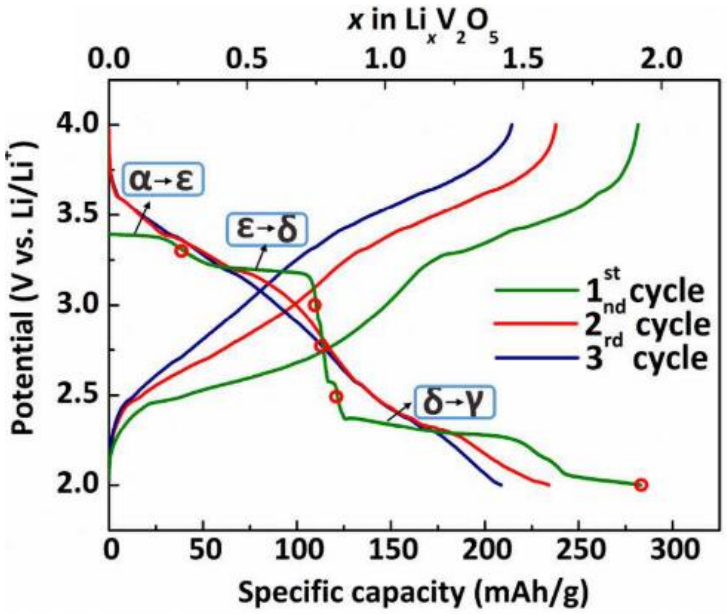


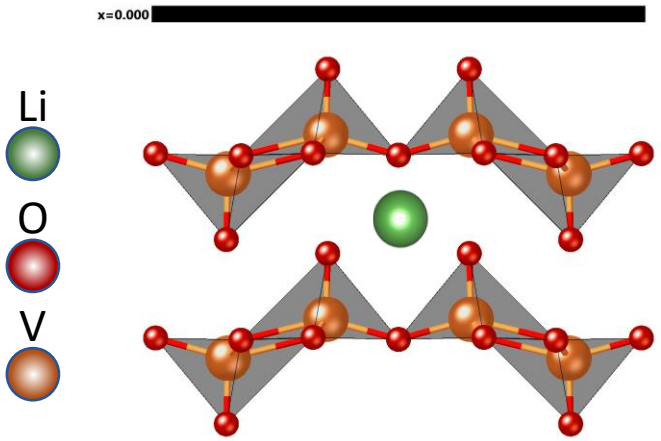
Polaron formation

- the combination of a localized electron and lattice distortion constitutes a **polaron**
- a polaron is further stabilized by a Li-ion yielding a **self-trapped polaron**

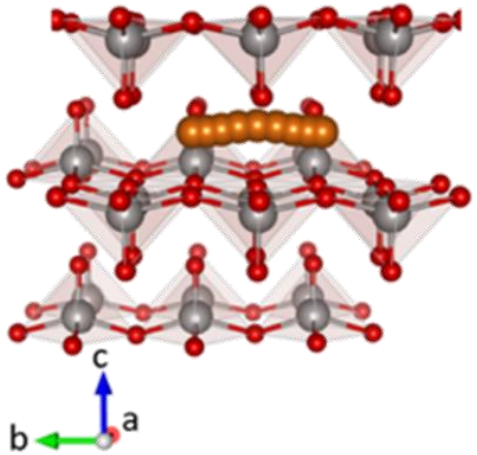
COUPLED POLARON/ION DIFFUSION IN OXIDE CATHODES

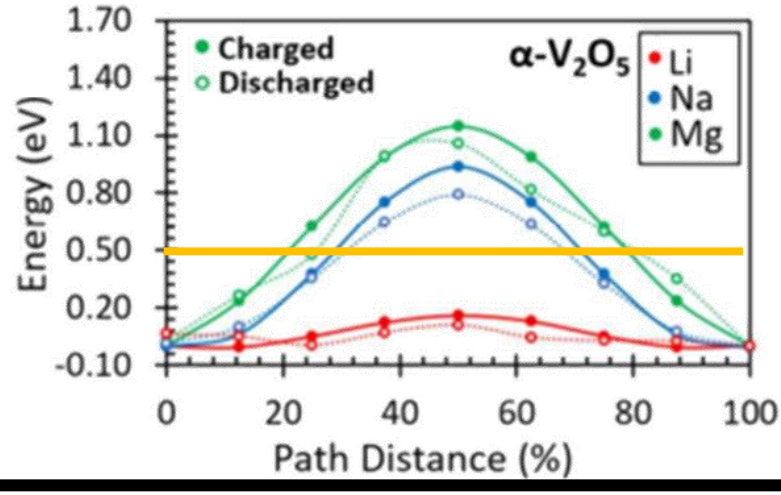
Formation of self-trapped polarons as the fundamental origin of diffusion limitations



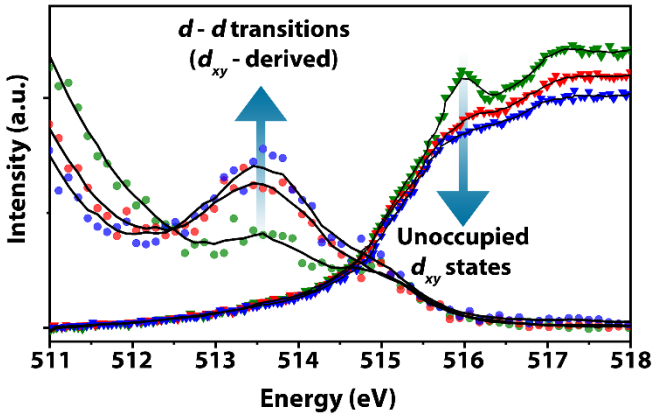


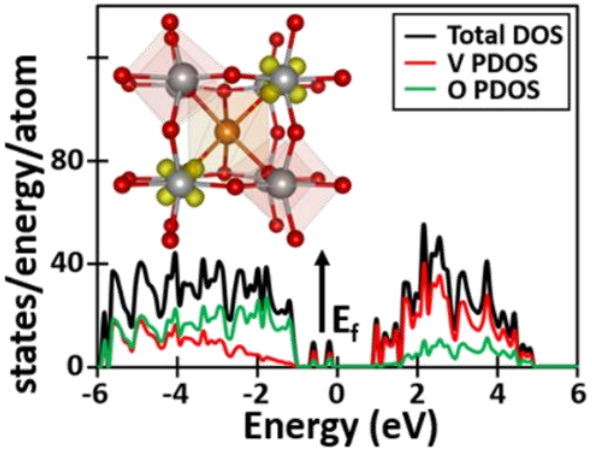
Ionic diffusion





Electronic Diffusion

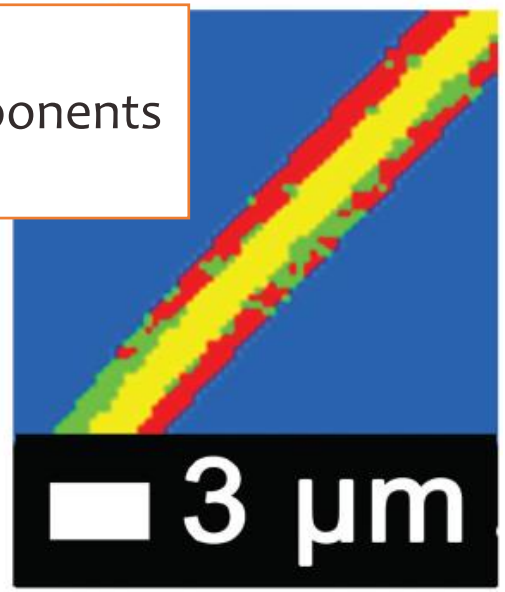




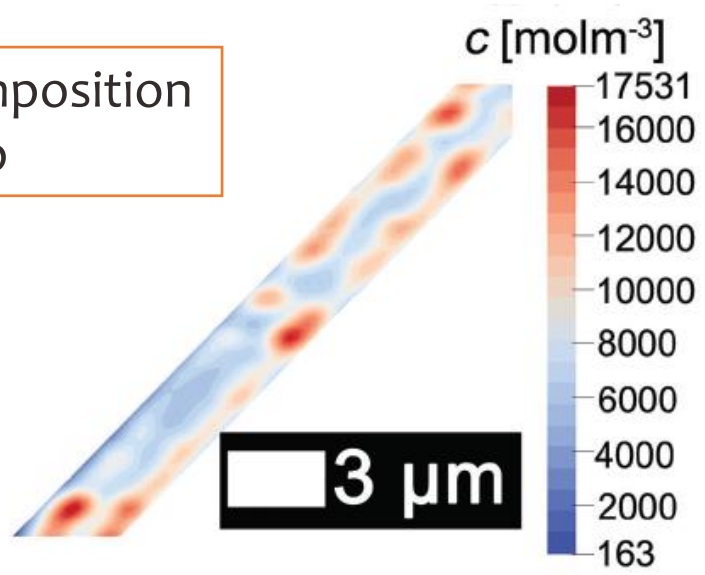
Andrews, , Stein, Santos, Chalker, De Jesus, Davidson, Gross, Pharr, Batteas, Xu, Banerjee. *Matter*, **2020**, *3*, 1754.
Tolhurst, Leedahl, Andrews, Marley, Banerjee, Moewes. *PCCP*, **2016**, *18*, 15798.
5611
De Jesus, et al. *Nat. Commun.* **2016**, 7, 12022.
Parija, Liang, Andrews, De Jesus, Prendergast, Banerjee. *Chem. Mater.* **2016**, *28* ,

Implications of Heterogeneities

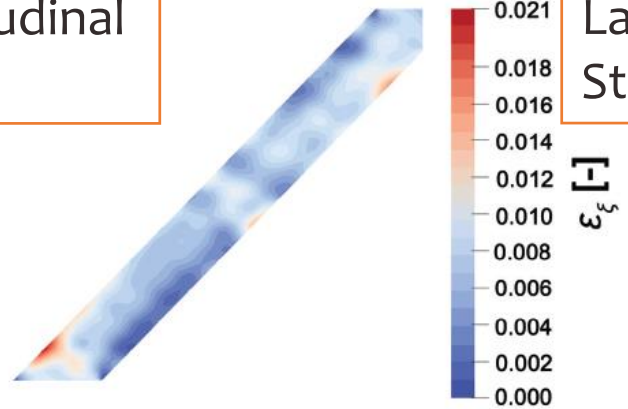
STXM Components Map



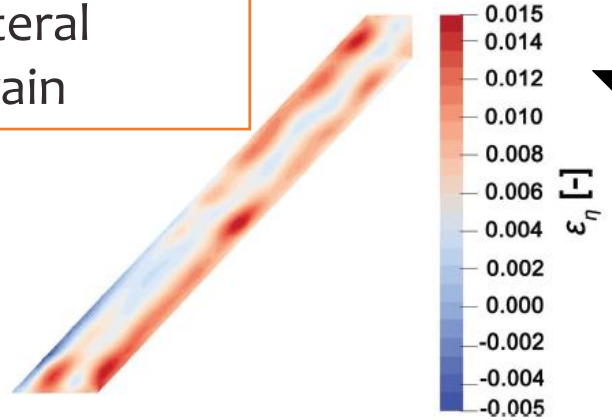
Composition Map



Longitudinal Strain



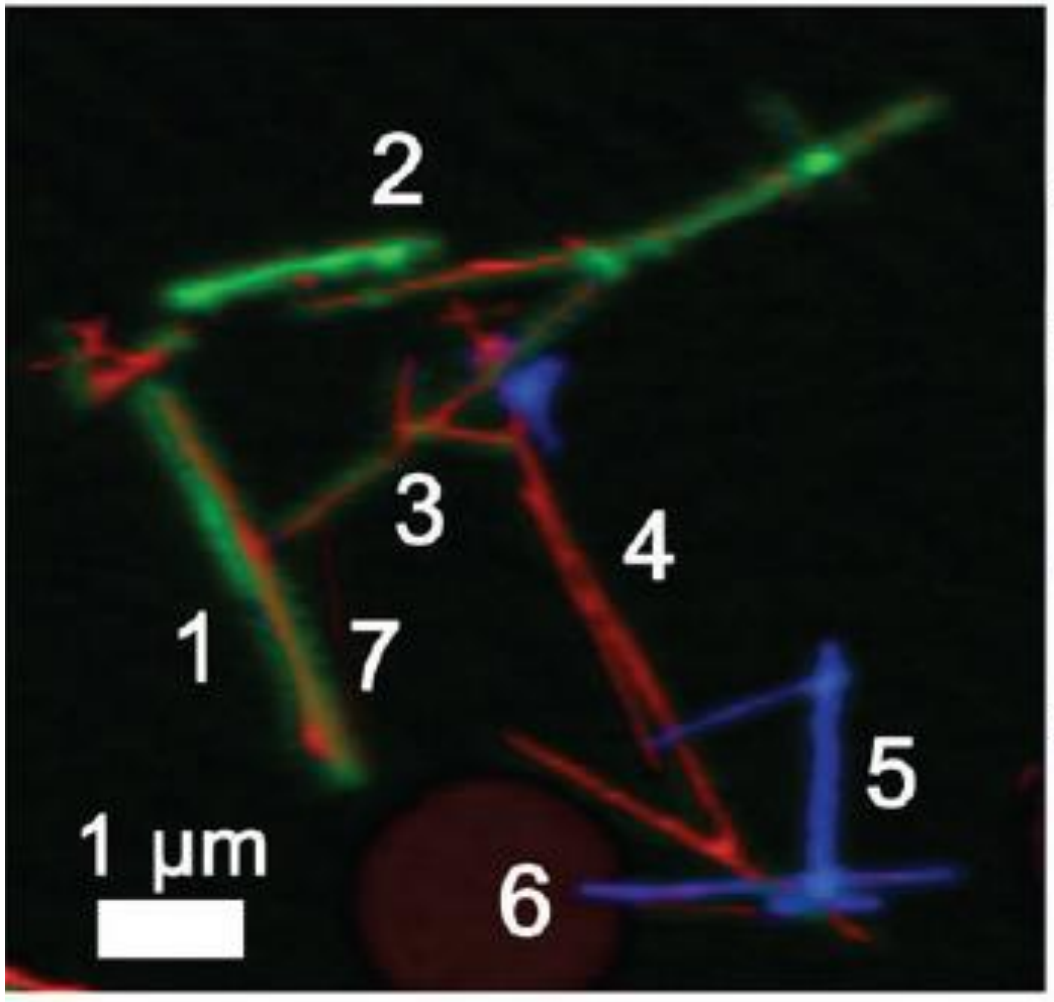
Lateral Strain

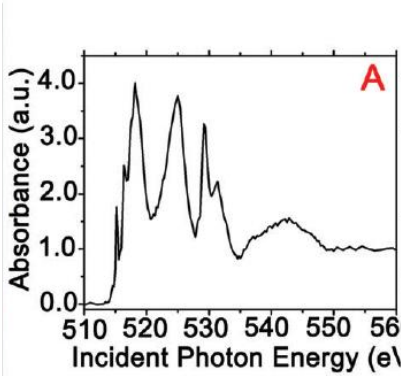


Dr. Peter Stein

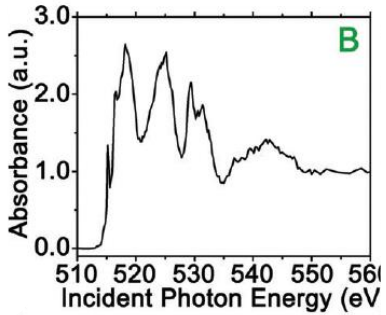
Prof. Bai-Xiang Xu

Heterogeneities Across Networks of Particles

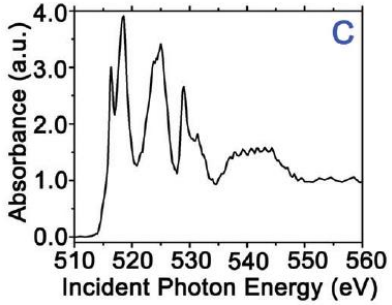




α-$Li_{0.1}V_2O_5$



ε-$Li_{0.40\text{-}0.50}V_2O_5$

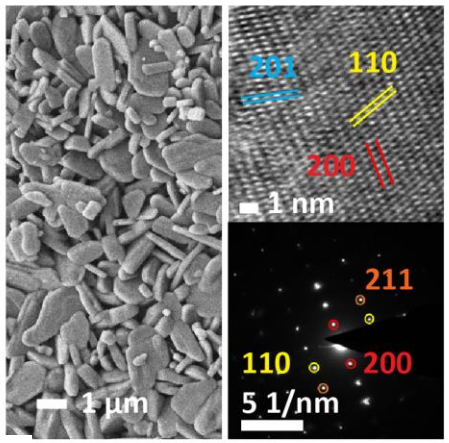


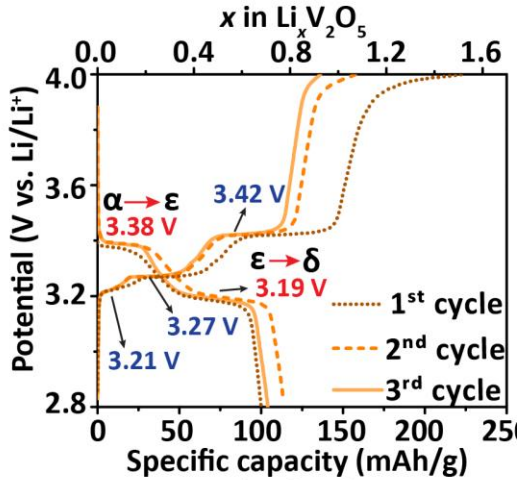
δ-$Li_{1.0}V_2O_5$

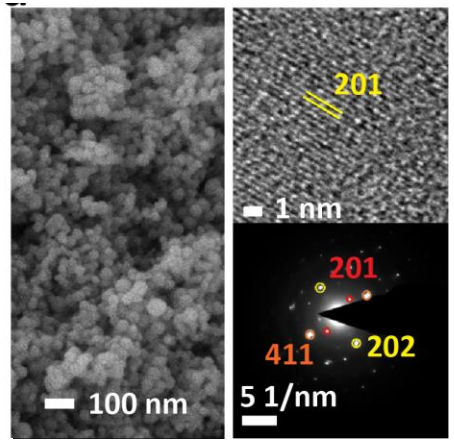
Luis De Jesus

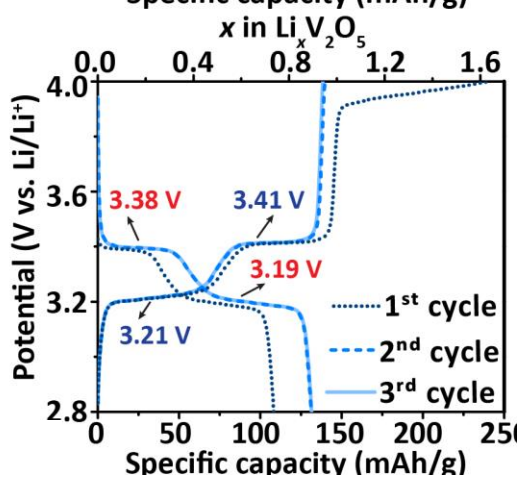
Justin L. Andrews

INTERCALATION-INDUCED PHASE TRANSFORMATIONS





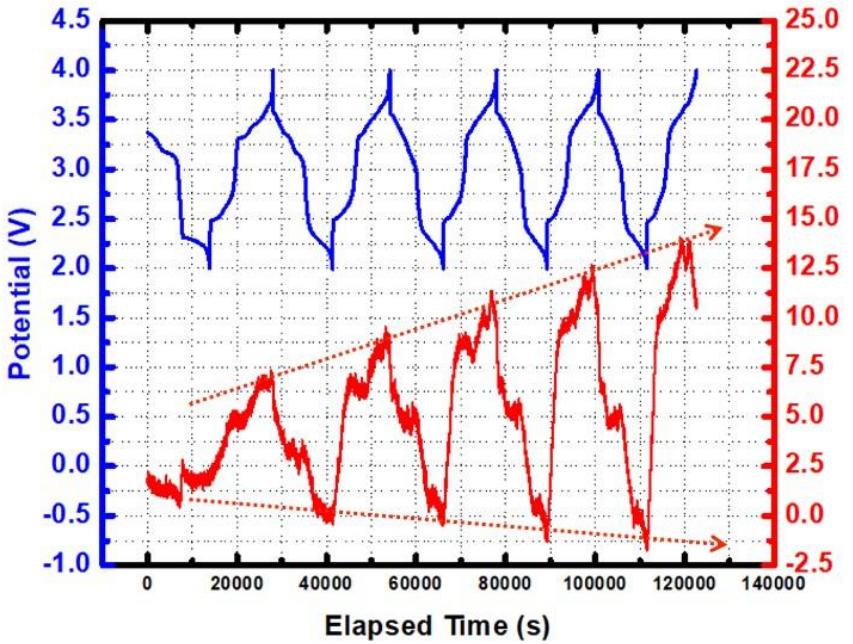




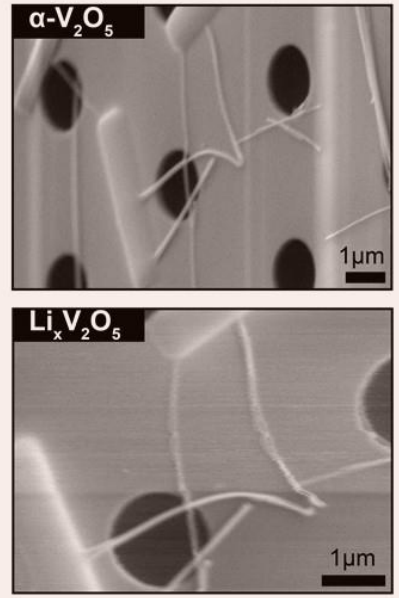
- Potential hysteresis between charge and discharge plateaus
- Substantial capacity loss and buildup of stress

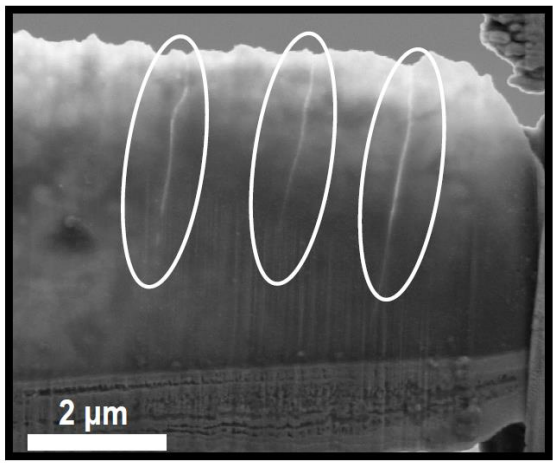
Y Luo et al. 2021. In revision.

Stress generation in bulk α-V_2O_5



Stress-induced cracking



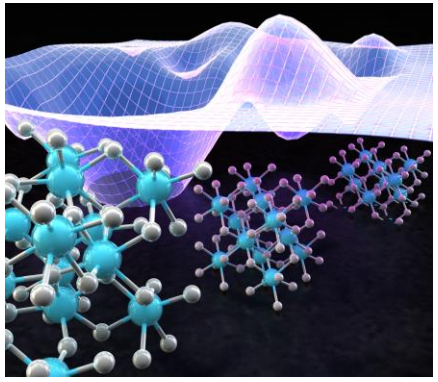


Multibeam optical stress sensor (MOS) measurements show an accumulation of stress with repeated cycling

Scanning electron micrographs provide evidence of fracture in pre-strained particles

- Small polarons are problematic and are stress/current concentrators!
- Charge striping along length of nanowires as a result of phase segregation
- Coupled ionic—electronic barriers profoundly alter phase evolution within individual particles and across ensembles of particles
- Li-ion diffusion and phase evolution strongly dependent on nature of interparticle contacts
- Substantial stresses develop across individual particles and ensembles because of phase heterogeneities

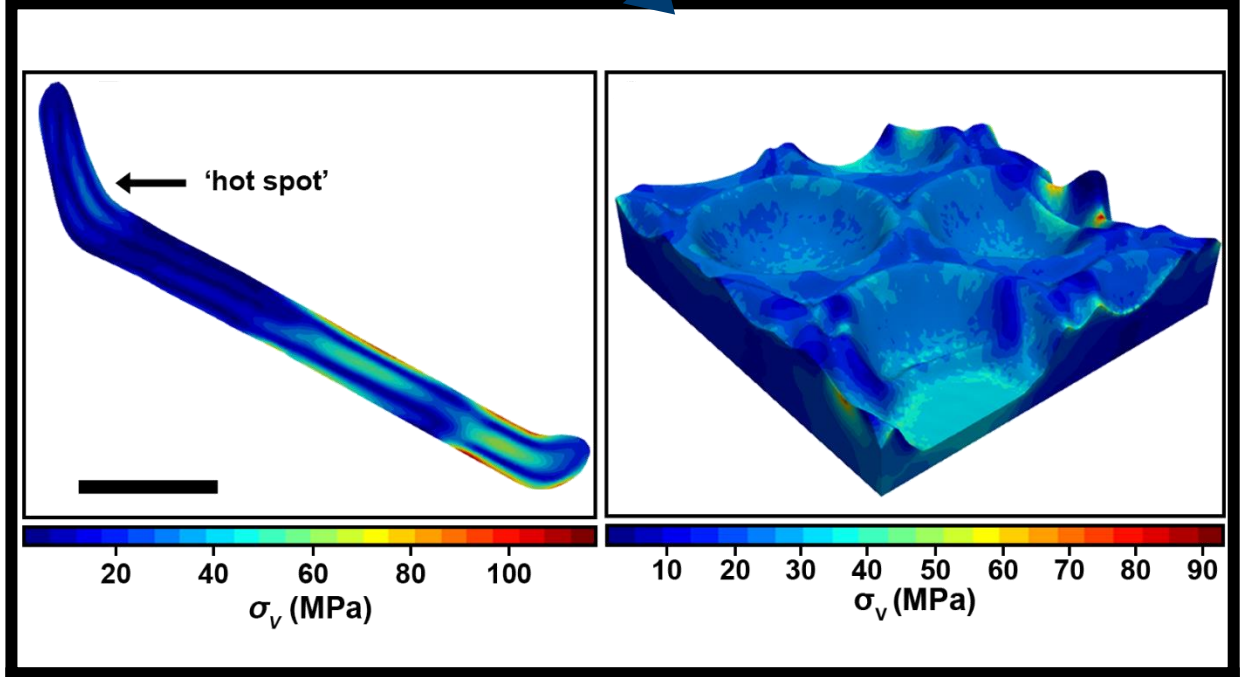
How do we resolve these problems?



Mitigating the consequences of coupled [Li^+-(polaron)$^-$] diffusion in V_2O_5

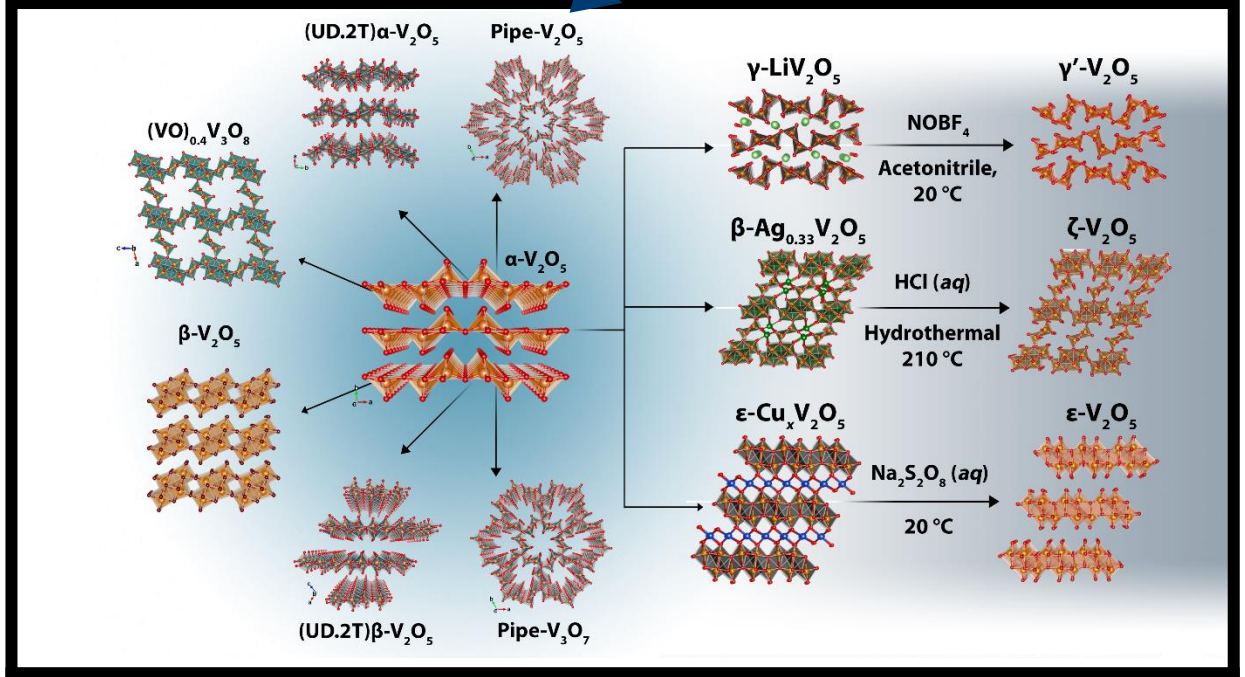
What approaches can we take to mitigate the mesoscale and atomistic consequences of polaron localization?

Geometric Modifications to Lithiation Phase Diagram



Phase separation, strain, battery failure

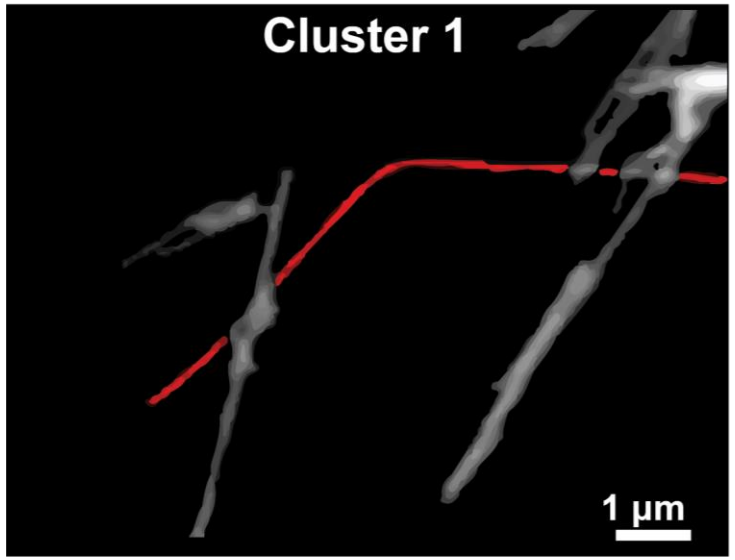
Atomistic Materials Design

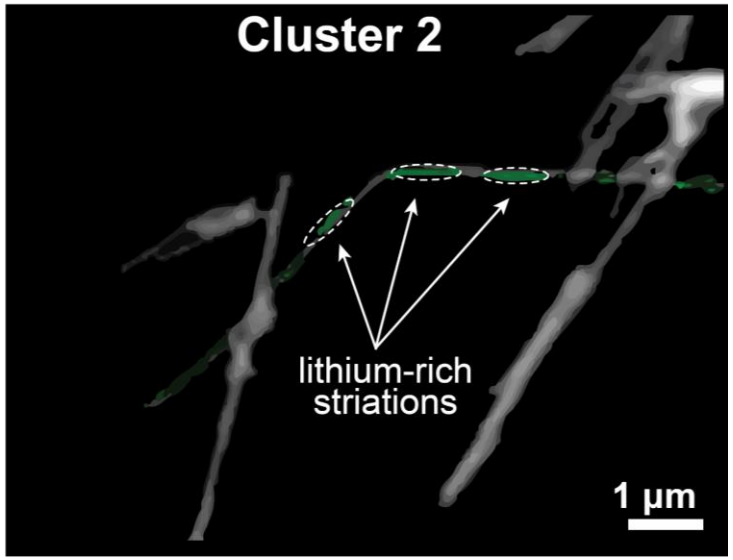


Sluggish diffusion kinetics, limited reversible capacity, chemo-mechanics

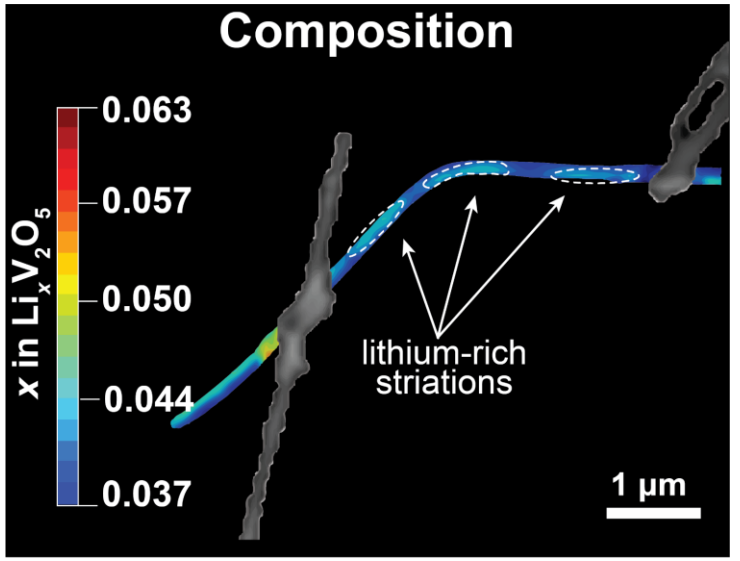
Andrews, , Stein, Santos, Chalker, De Jesus, Davidson, Gross, Pharr, Batteas, Xu, Banerjee. *Matter*, **2020**, *3*, 1754.
Parija, Waetzig, Andrews, Banerjee. *J. Phys. Chem. C.* ***2018,*** 122 (45), 25709.

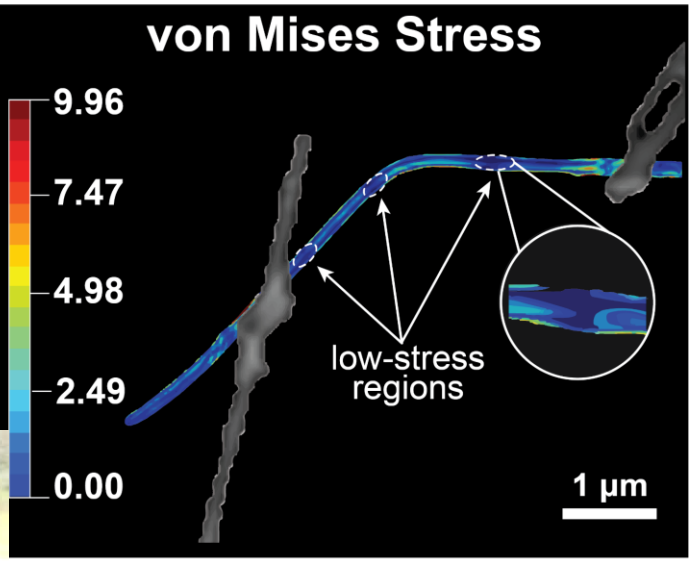
Elastic-Deformation-Driven Modification of Intercalation Phase Diagrams





- majority phase of the nanowire corresponds to a low-lithiated α-$Li_{0.1}V_2O_5$ phase
- clear striations (green) of the Li-rich $Li_{0.3}V_2O_5$ phase
- crystallographic incommensurability and volumetric expansion causes stress
- Elastic deformation drives morphogenesis that changes striation patterns

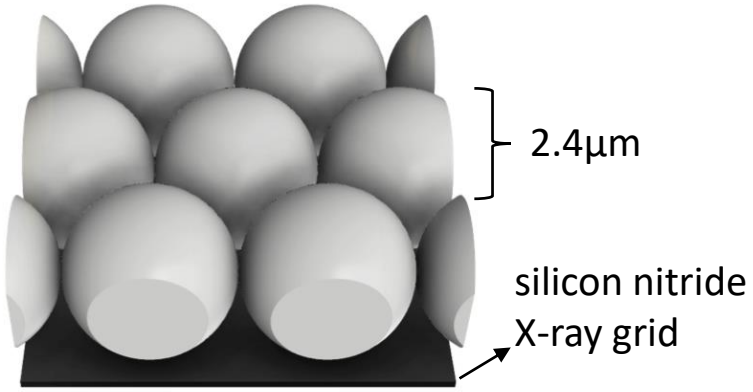


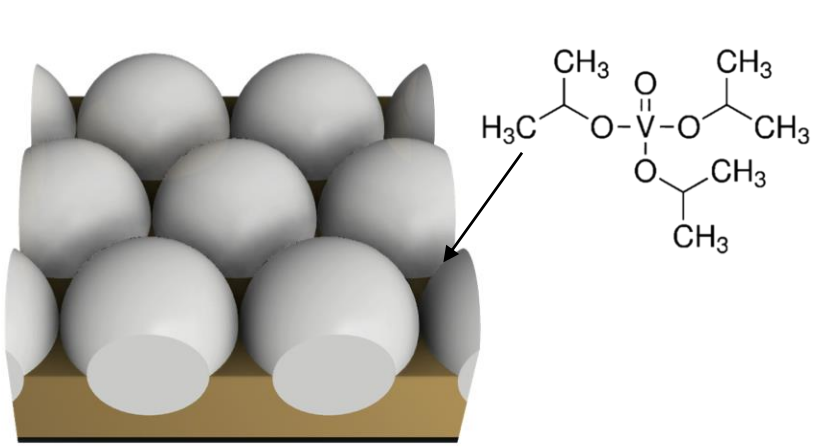


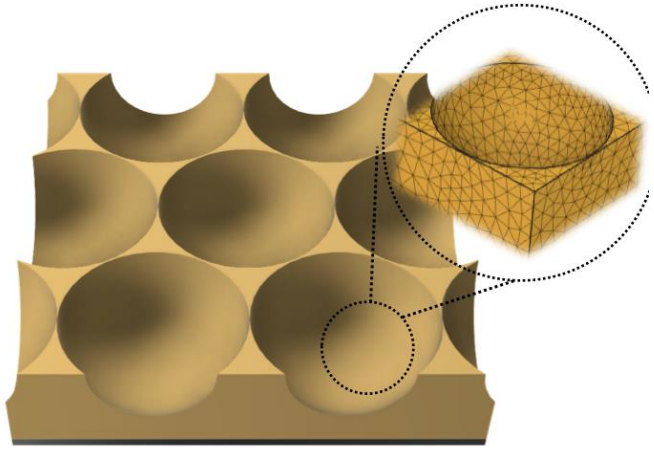
David A. Santos

Dr.-Ing Peter Stein

Incorporating Continuous Curvature



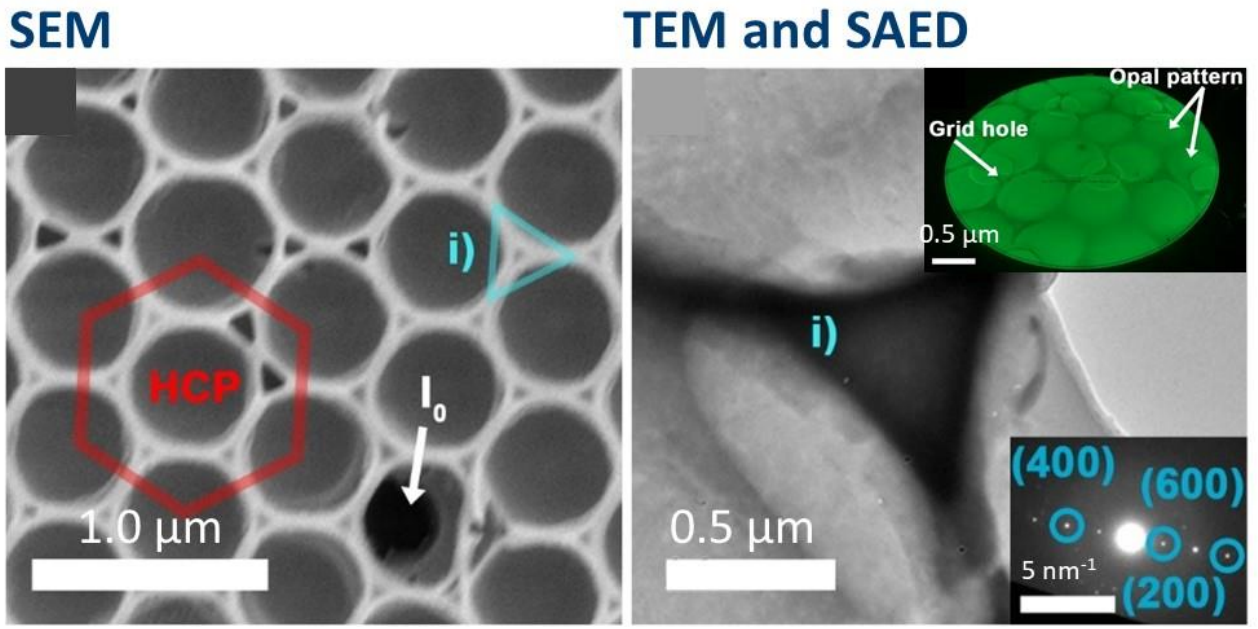




Monolayer Formation

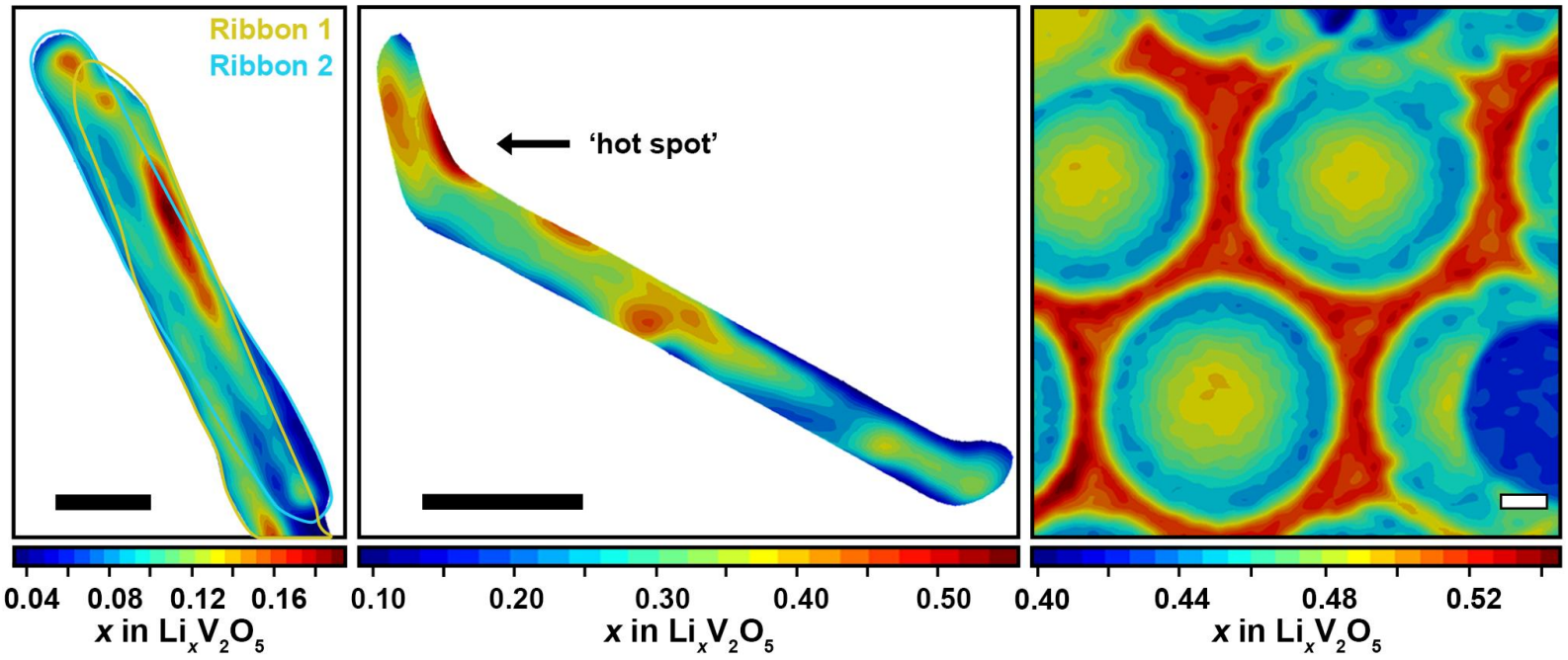
- monolayer of polystyrene spheres is formed on a water surface
- sodium dodecyl sulfate is added to increase the packing density
- monolayer of spheres is transferred to grid surface

V_2O_5 Infiltration and Calcination

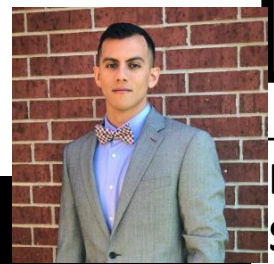


Leveraging chemo-mechanical coupling to improve Li-ion diffusion

Using STXM to image local lithiation inhomogeneities



Continuous curvature and porous framework lead to:
(1) Increased diffusion rates
(2) Increased homogeneity
Incorporating curvature represents a means of improving rate without sacrificing material stability since inhomogeneity leads to elastic misfit strain



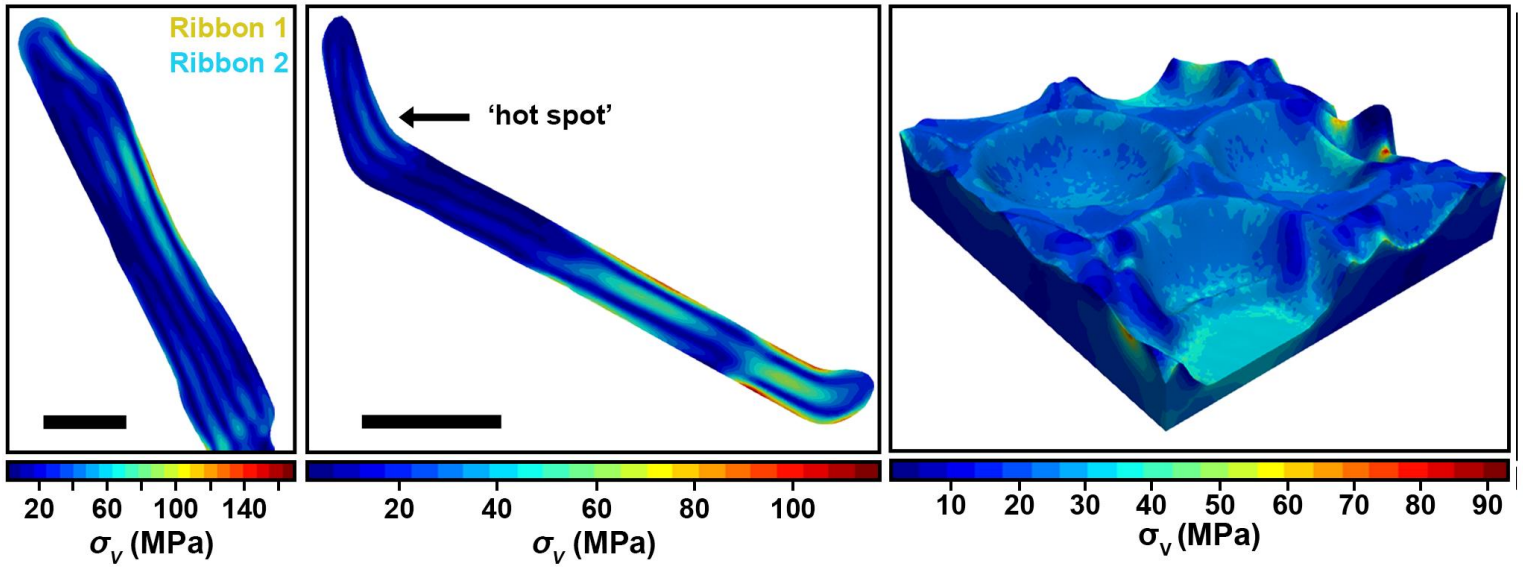
David A. Santos

Justin L. Andrews

Andrews, , Stein, Santos, Chalker, De Jesus, Davidson, Gross, Pharr, Batteas, Xu, Banerjee. *Matter*, **2020**, *3*, 1754.

LEVERAGING CHEMO-MECHANICAL COUPLING TO IMPROVE LI-ION DIFFUSION

Mapping phase separation and battery failure to orbital considerations

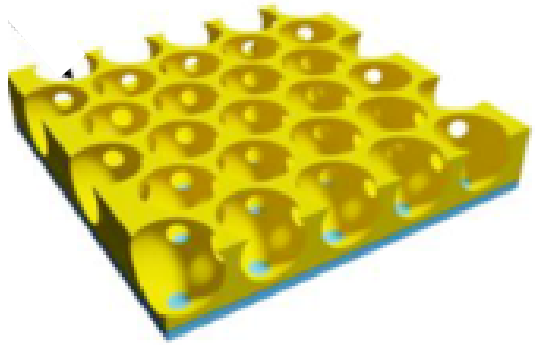


Electronic structure mapping can be used to related orbital considerations to battery failure mechanisms

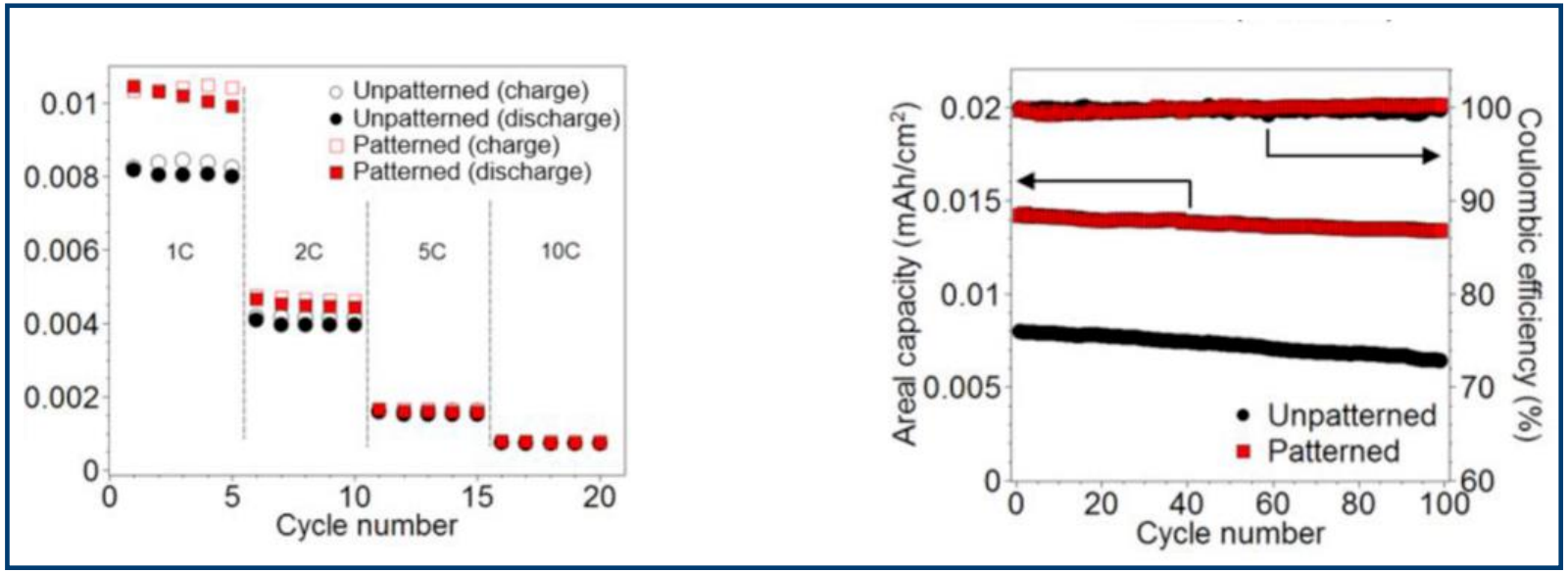
Geometric and deformation effects can mitigate strain evolution due to polaron-induced phase separation and improve battery lifetimes

Architected Electrodes: Inverse Opal

patterned V_2O_5 electrode



capacity retention upon electrochemical cycling

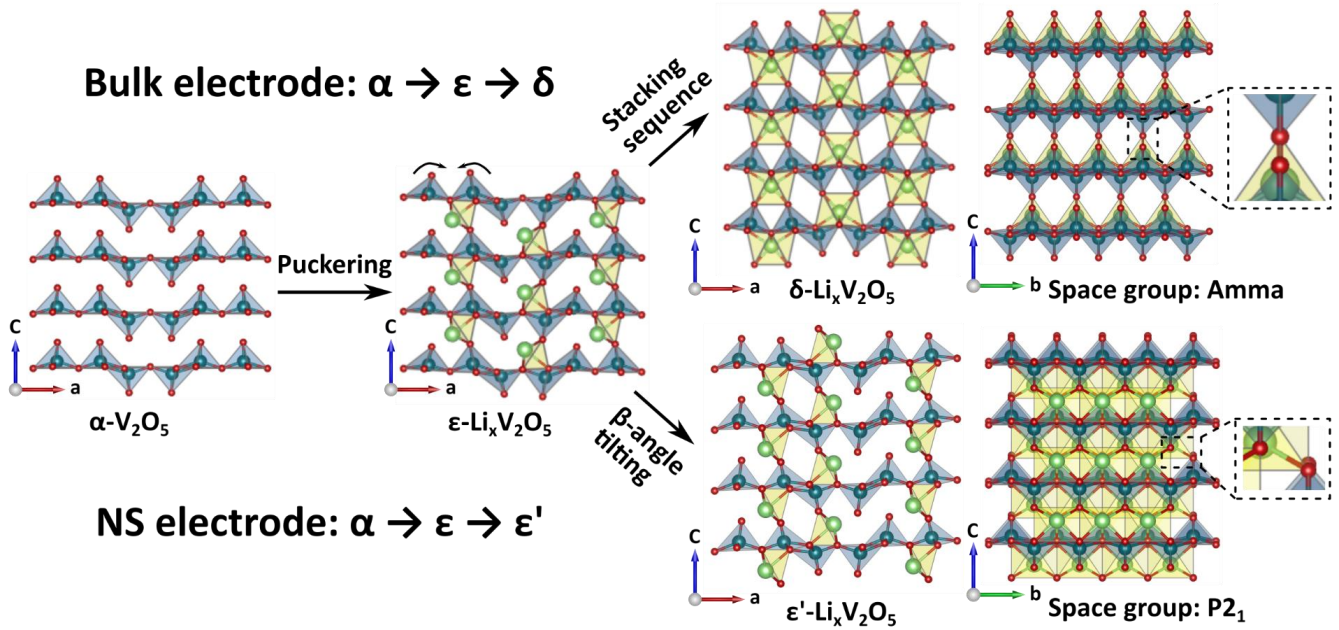


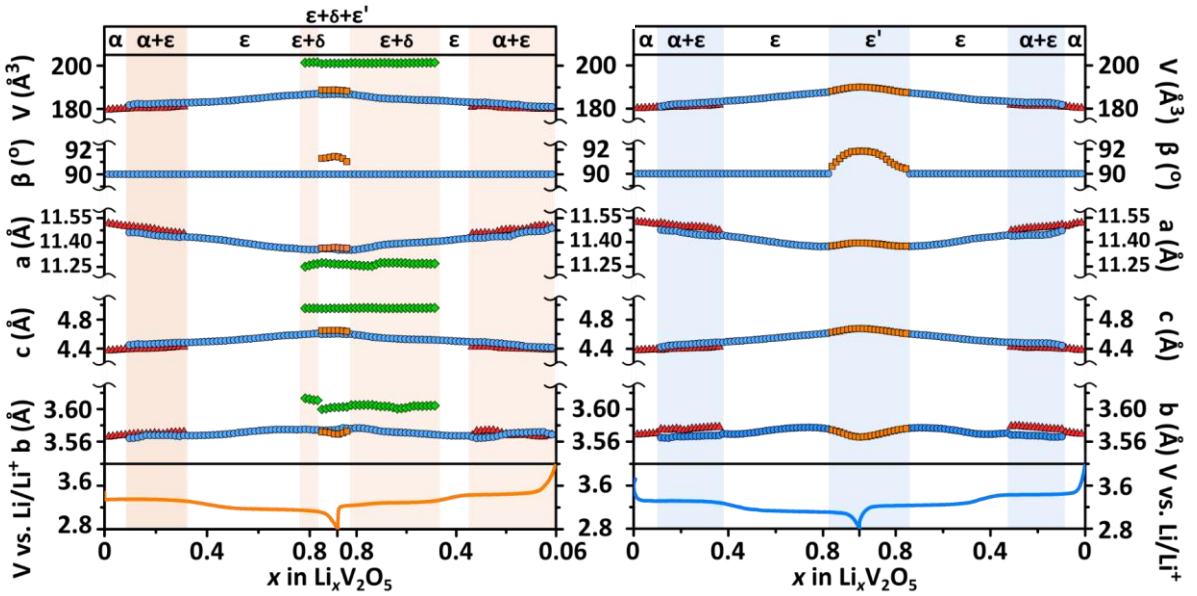
- patterned films show accelerated kinetics compared to unpatterned counterparts
- patterned films perform better with respect to capacity retention at lower C-rates
- 94% retention of discharge capacity after 100 cycles

Abhishek Parija

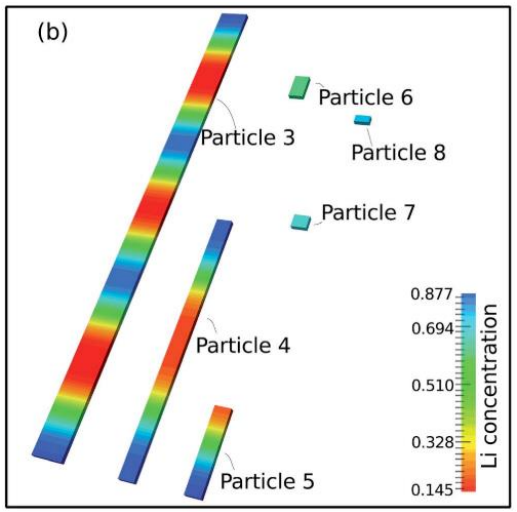
Cody Chalker

Effects of Particle Geometry on Intercalation Phase Diagrams



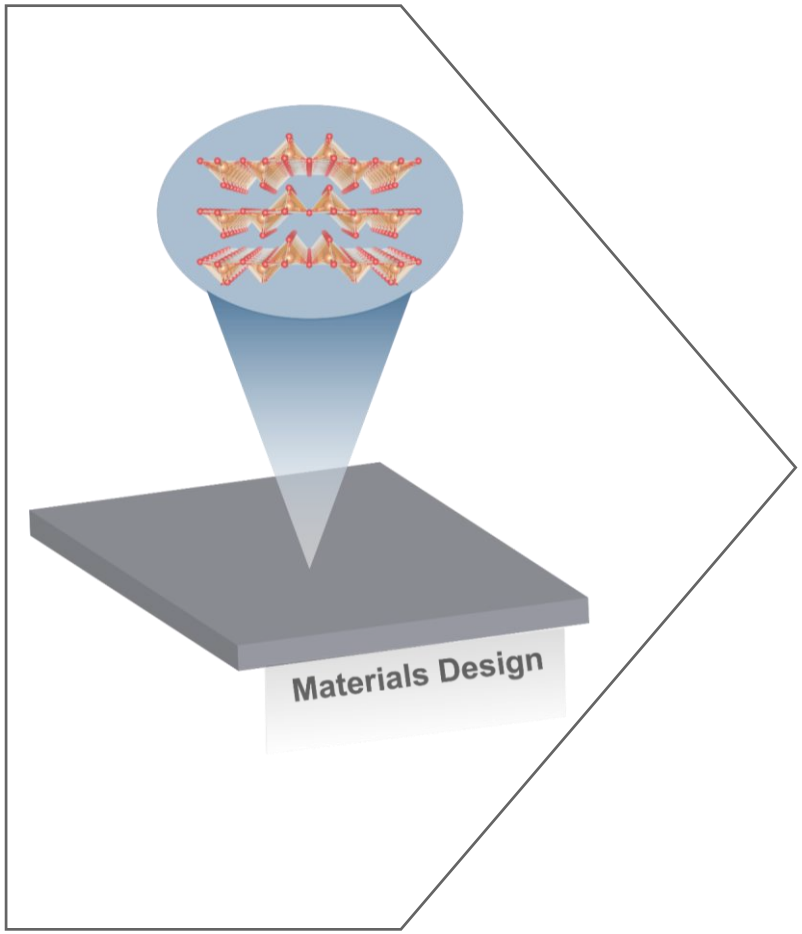


- Particle geometry effects, strongly modify the progression of intercalation-induced transformations in $Li_xV_2O_5$



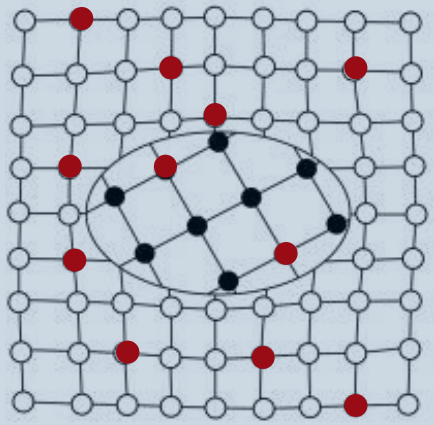
Y Luo et al. **2021**. In revision.

Mitigating Diffusion Impediments Through Chemical Modification



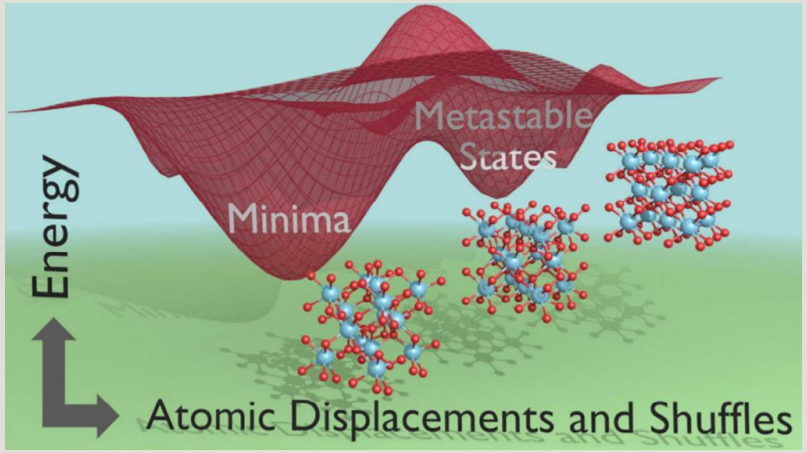
Doping

modulating the magnitude of lattice incommensurability



Topochemical Modification

metastable phases with alternative atomic frameworks and electronic structure

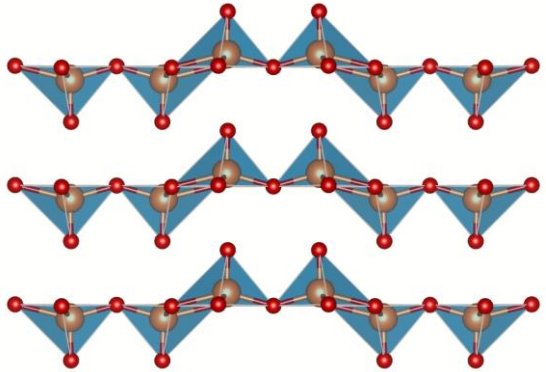


G. A. Rance, D. H. Marsh, S. J. Bourne, T. J. Reade, A. N. Khlobystov, *ACS Nano* **2010**, DOI 10.1021/nn101287u.

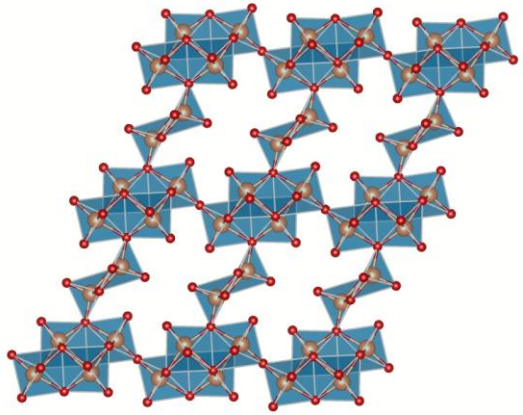
Mitigating coupled ionic/polaronic diffusion through materials design

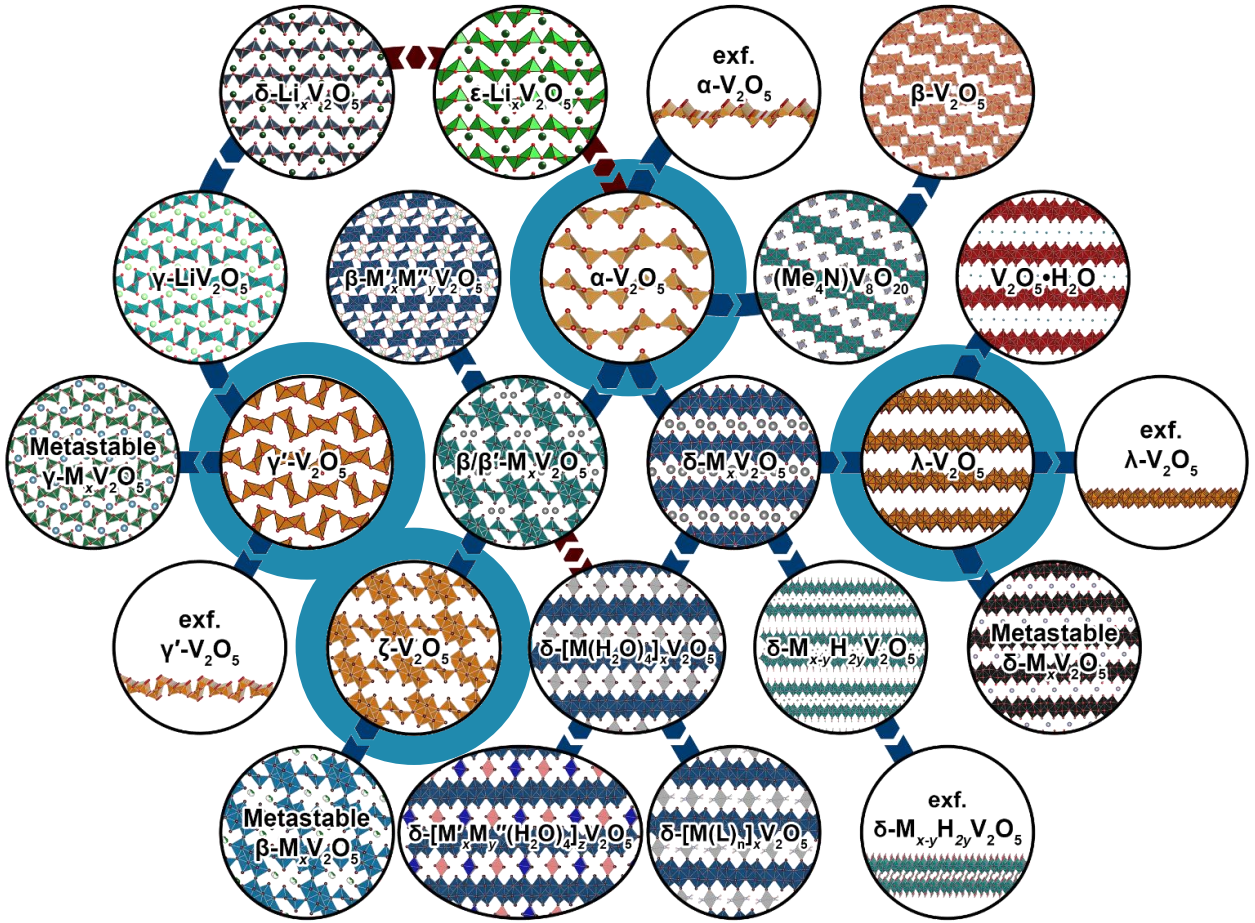
Composition is not structural destiny!

α-V_2O_5

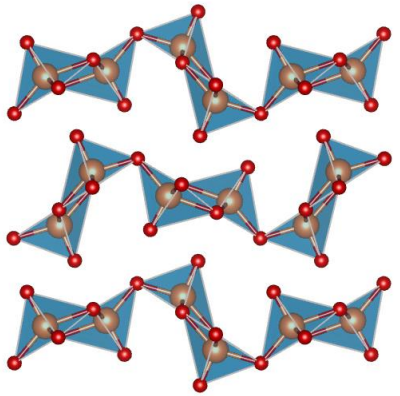


ζ-V_2O_5

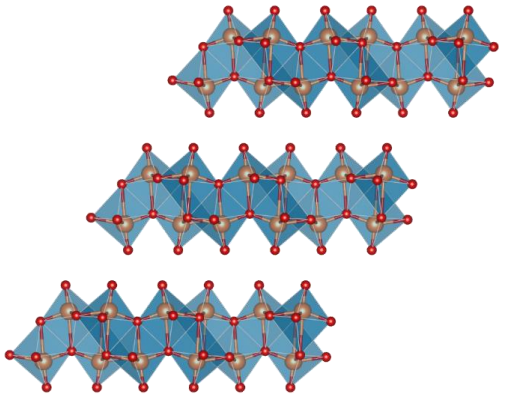




γ′-V_2O_5



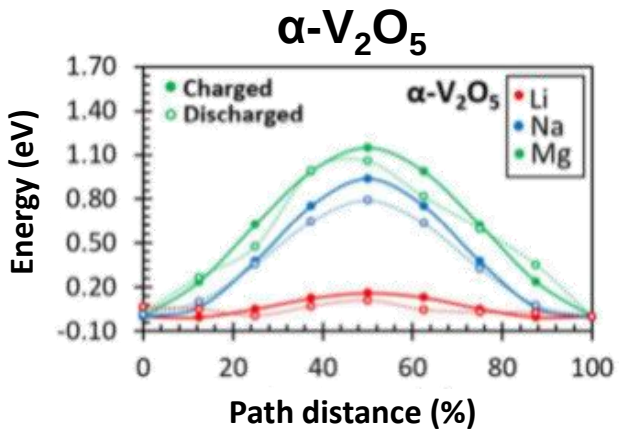
λ-V_2O_5

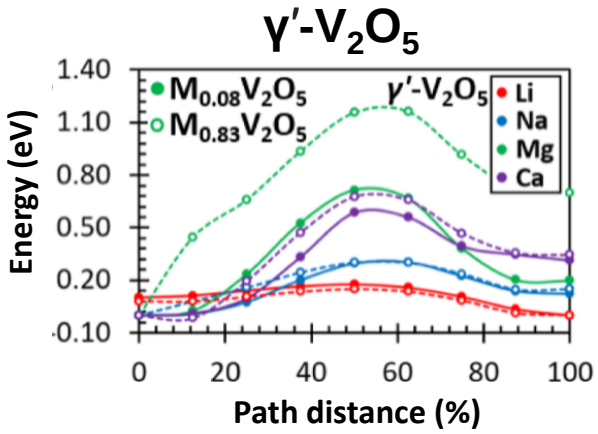


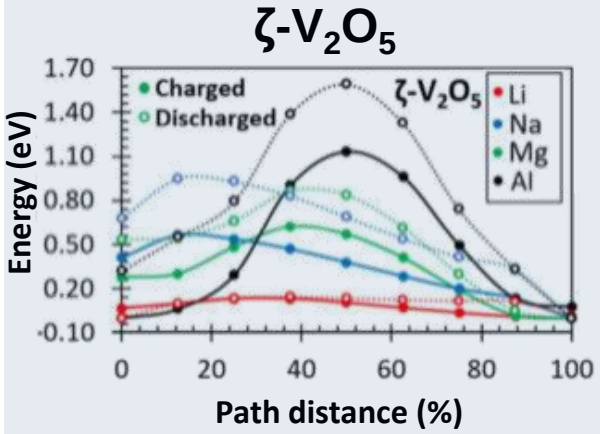
Parija, Waetzig, Andrews, Banerjee. *J. Phys. Chem. C.* ***2018,*** 122, 25709.
Parija, Liang, Andrews, De Jesus, Prendergast, Banerjee. *Chemistry of Materials*, **2016,** *28*, 5611.

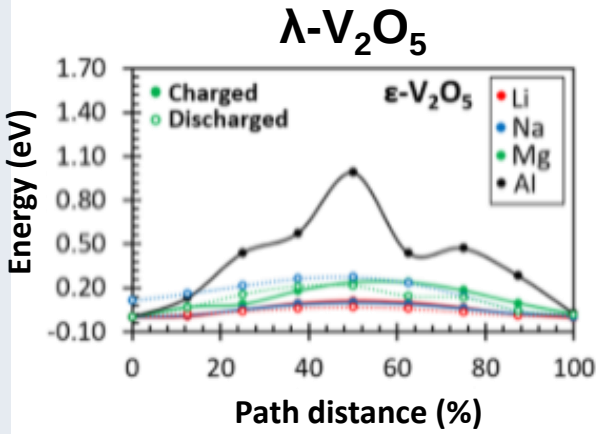
MITIGATING COUPLED IONIC/POLARONIC DIFFUSION THROUGH ATOMIC DESIGN

Using metastable polymorphs to tune ionic diffusion pathways

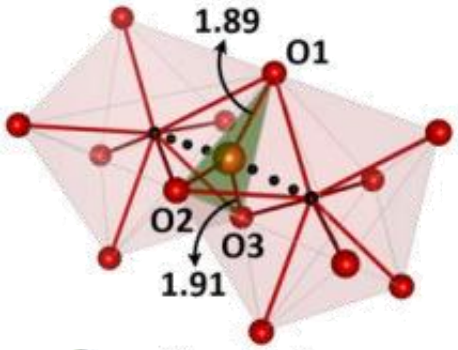




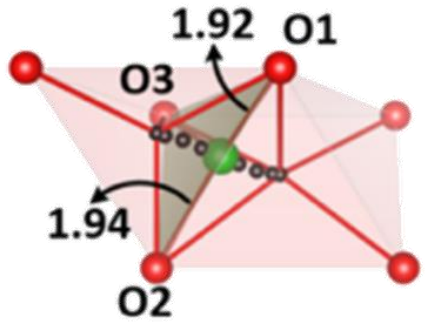




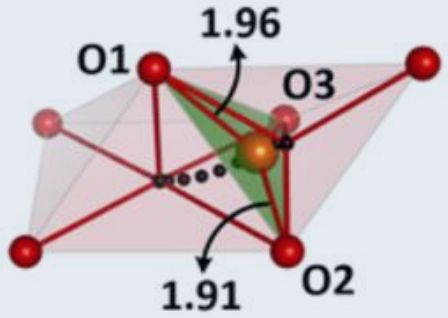
Change in coordination



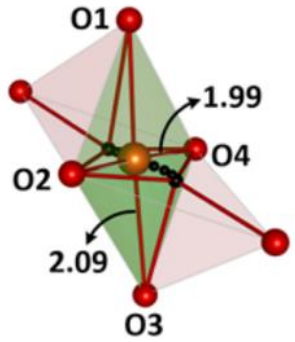
8→3→8



5→3→4→3→5



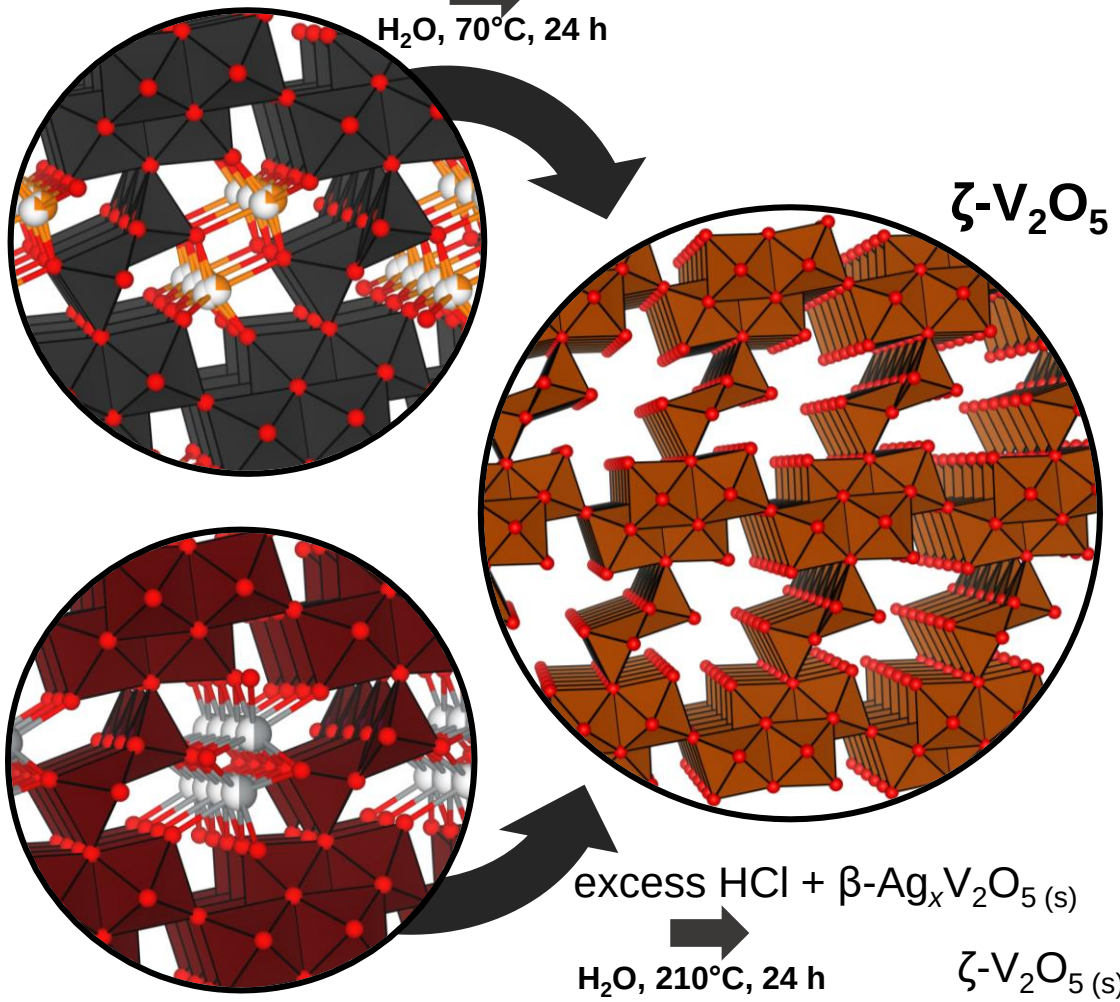
4→3→5→3→4

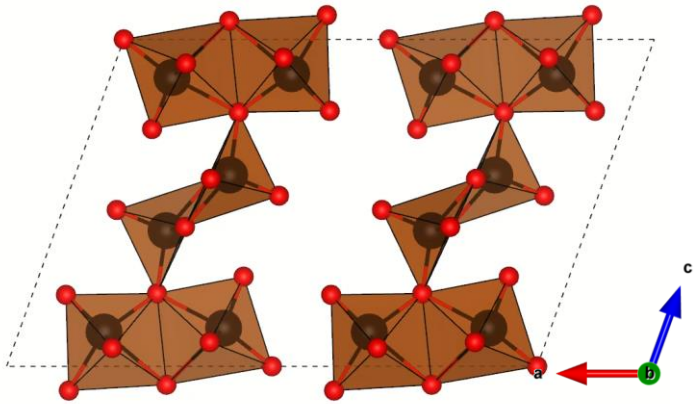


6→4→6→4→6

Parija, Liang, Andrews, De Jesus, Prendergast, Banerjee. *Chemistry of Materials*, **2016,** *28*, 5611.
Parija, Prendergast, Banerjee. *ACS Appl. Mater. Interf.* **2017,** *9,* 23756.

ζ-V_2O_5: A ROBUST METASTABLE POLYMORPH





- Only accessible **topochemically**
- Stable up to 600 °C
- Monoclinic β-angle correlates to occupancy of tunnel sites

JUSTIN L. ANDREWS

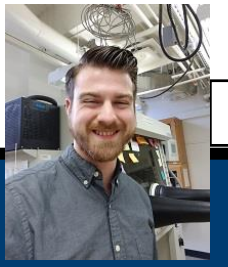
PETER MARLEY

Structure	β (°)
β'-$Cu_{0.65}V_2O_5$	105.5
β'-$Cu_{0.35}V_2O_5$	106.6
β-$Ag_{0.25}V_2O_5$	109.7
ζ-V_2O_5	110.0

AN ATOMIC VIEW OF DIFFUSION PATHWAYS IN INTERCALATION BATTERIES

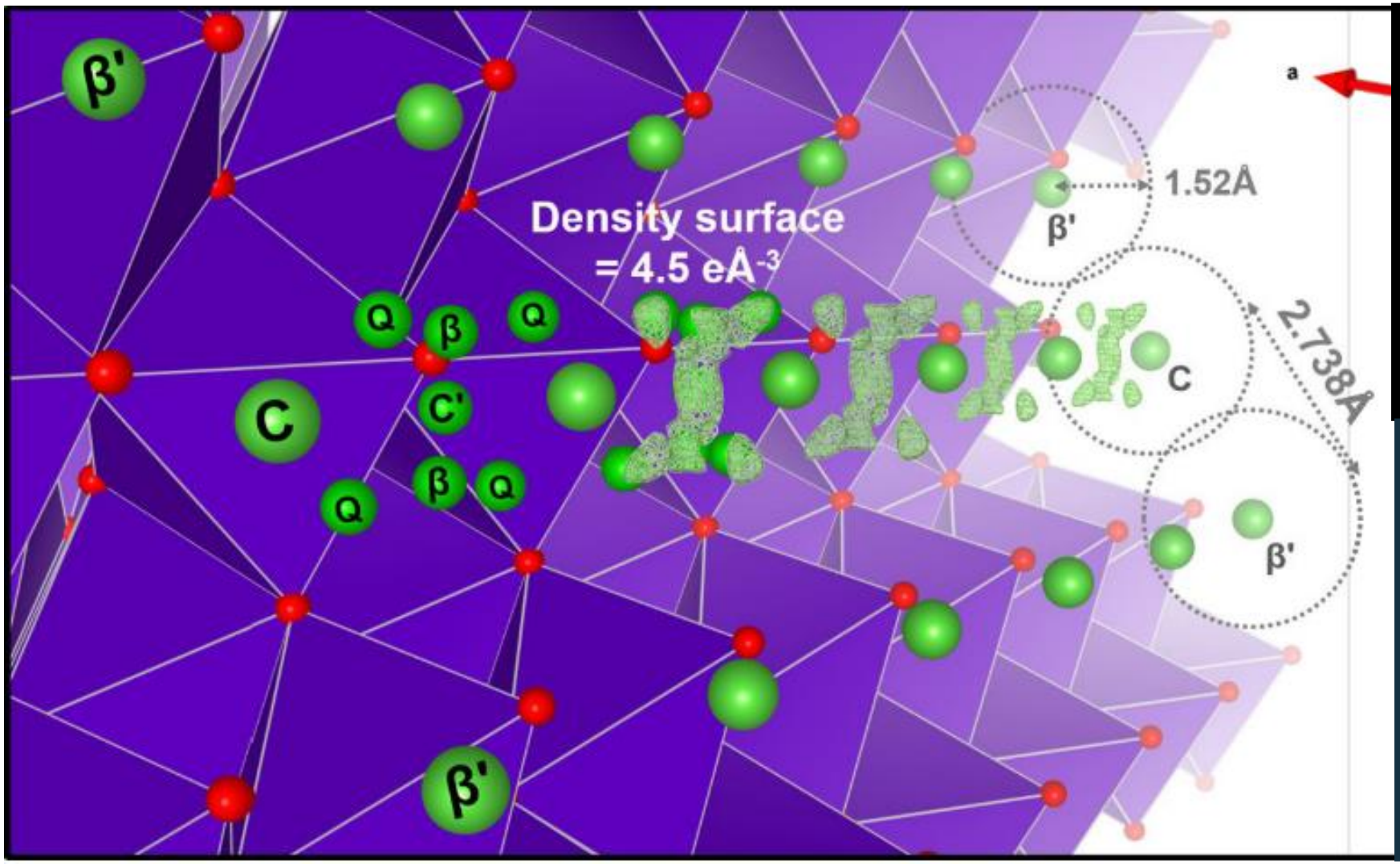
Imaging Li-ion diffusion pathways in single crystals of ζ-V_2O_5

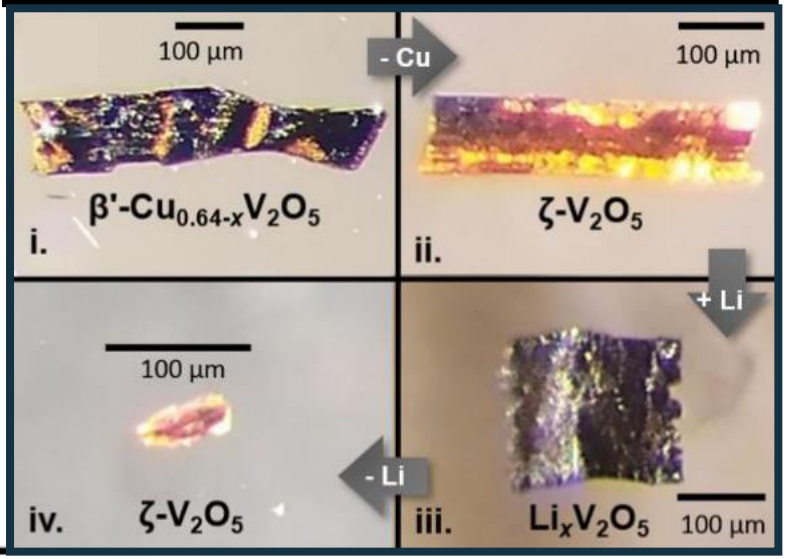
JUSTIN L. ANDREWS



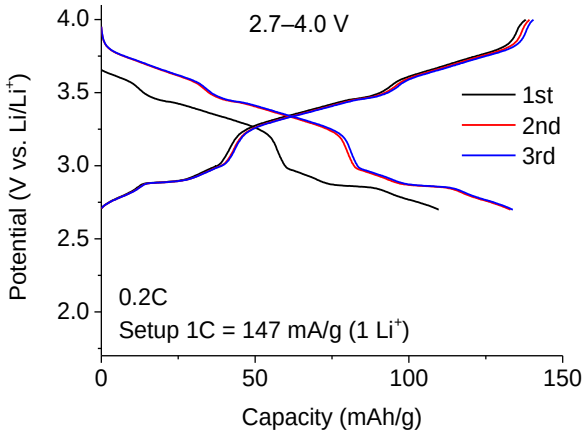
JOSEPH V. HANDY

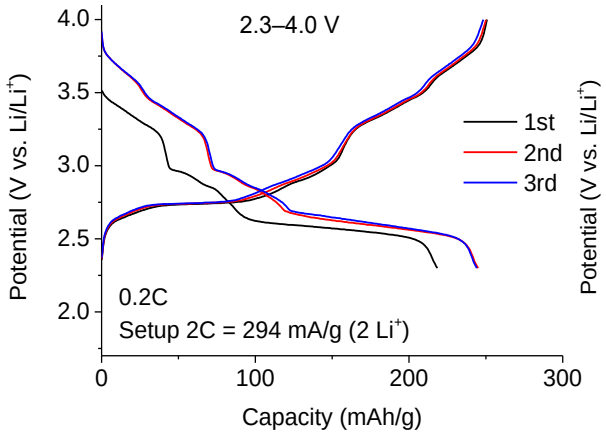
Single-crystal diffraction enables the imaging of Li-ion diffusion pathways at the atomistic level

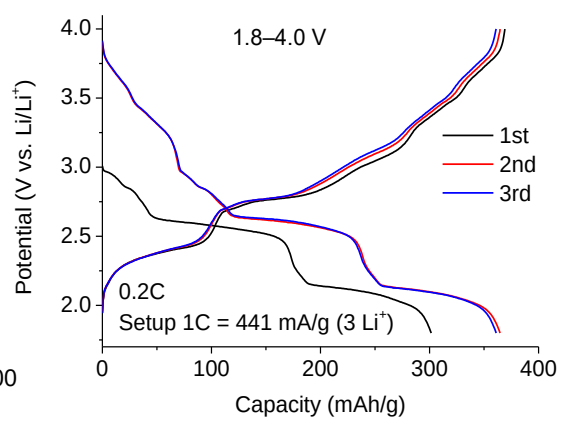


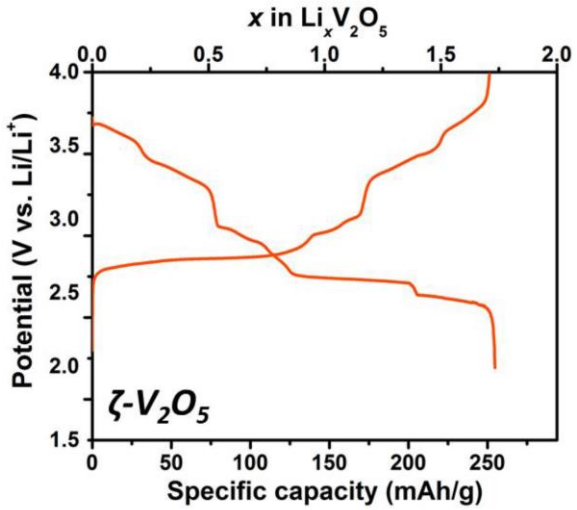


Up to 3 Li per V_2O_5



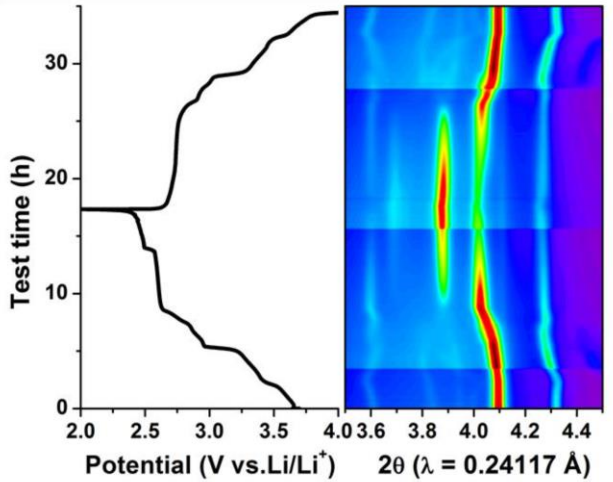






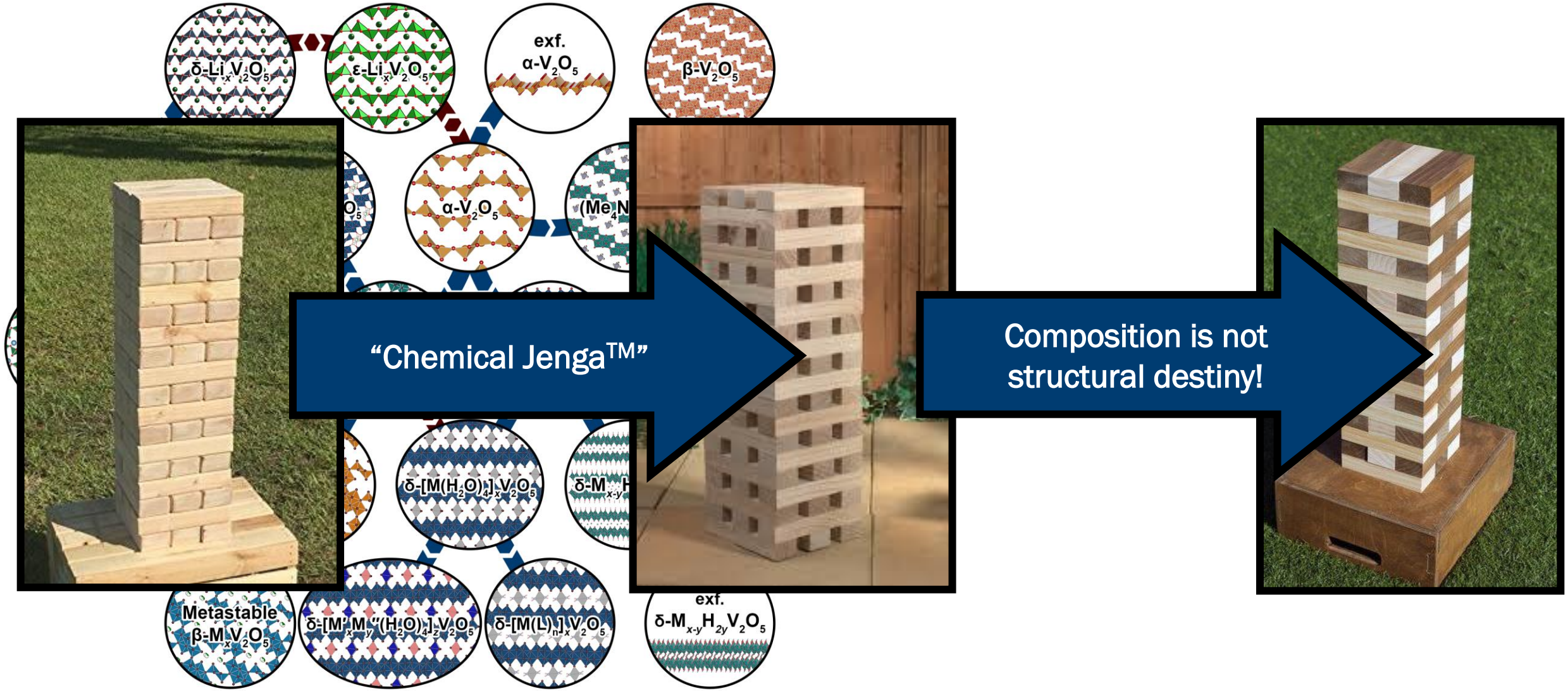
- Three Li^+ insertion window in polymer electrolyte?
  2.7–4.0 V (1 Li^+ insertion)
  2.3–4.0 V (2 Li^+ insertion)
  1.8–4.0 V (3 Li^+ insertion).

- Reversible capacity of 240 mAh/g in 2.3–4.0 V using polymer electrolyte.



ACCESSING METASTABLE PHASE SPACE THROUGH TOPOCHEMISTRY

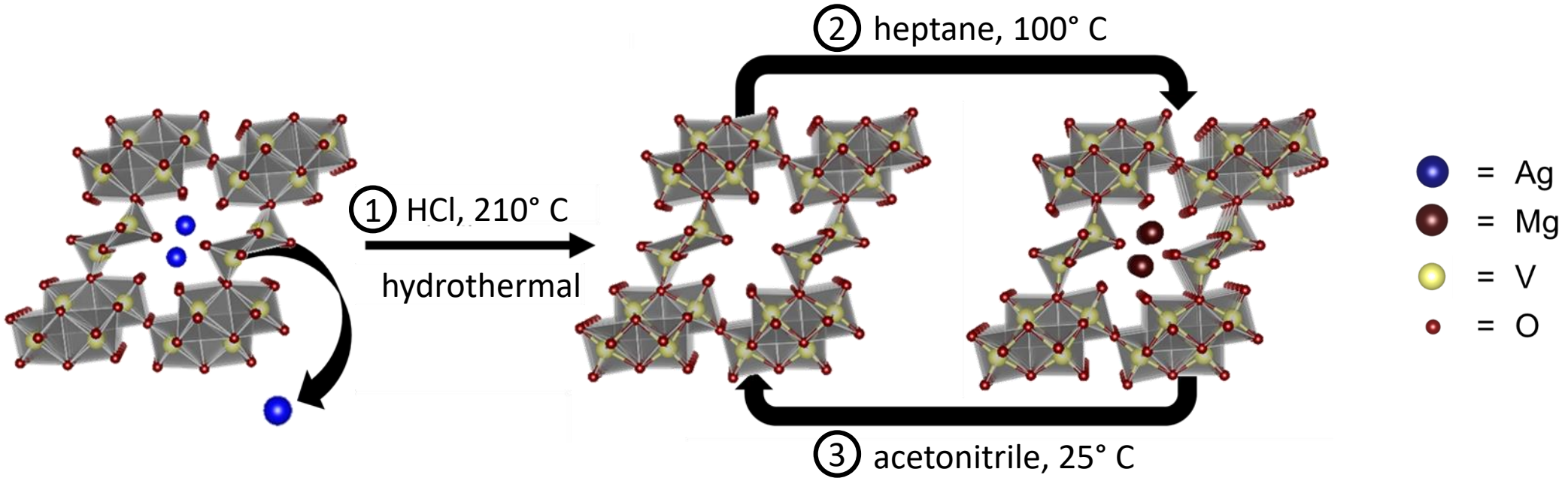
Synthesis of low-dimensional binary V_2O_5 and ternary $M_xV_2O_5$ phases



Images taken from: https://www.google.com/search?q=lawn+jenga&rlz=1C1CHBF_enUS769US769&source=lnms&tbm=isch&sa=X&ved=2ahUKEwjzi4v82YXtAhVHpFkKHTMwDxEQ_AUoAnoECAYQBA&biw=1280&bih=578#imgrc=-wH2wJRAc2Lr4M
And

ζ-V_2O_5: A HIGH-CAPACITY MG-ION CATHODE MATERIAL

Playing "chemical Jenga™" with ζ-V_2O_5



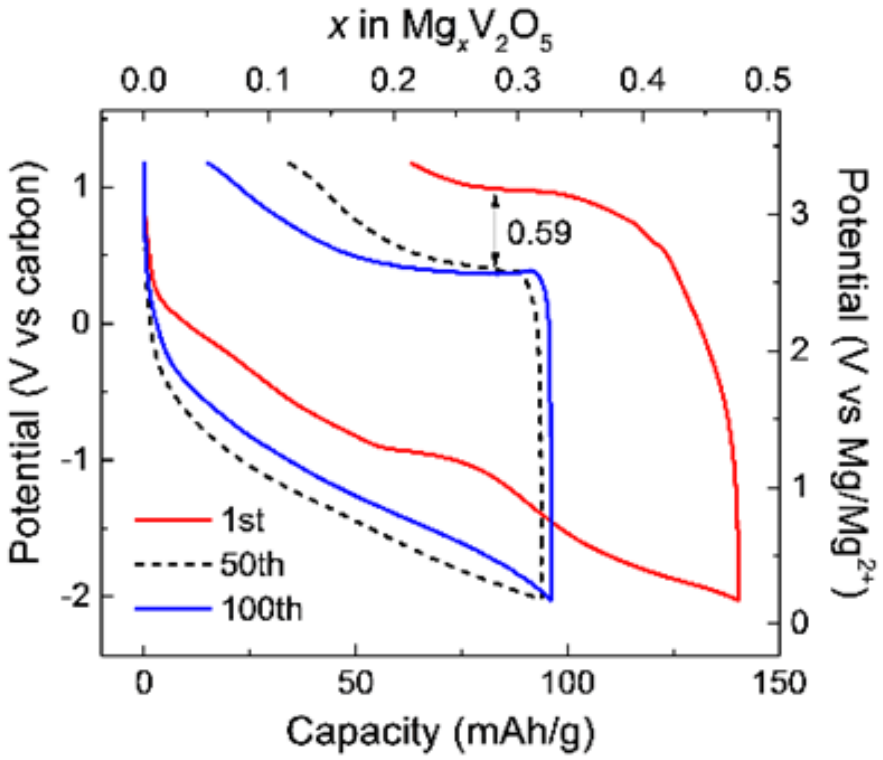
① $\beta-Ag_{0.33}V_2O_5(s) + 0.29\ HCl(aq.) + 0.145\ O_2(g) \rightarrow \zeta-(Ag_{0.04})V_2\ O_5(s) + 0.29\ AgCl(s) + 0.145\ H_2O(l)$

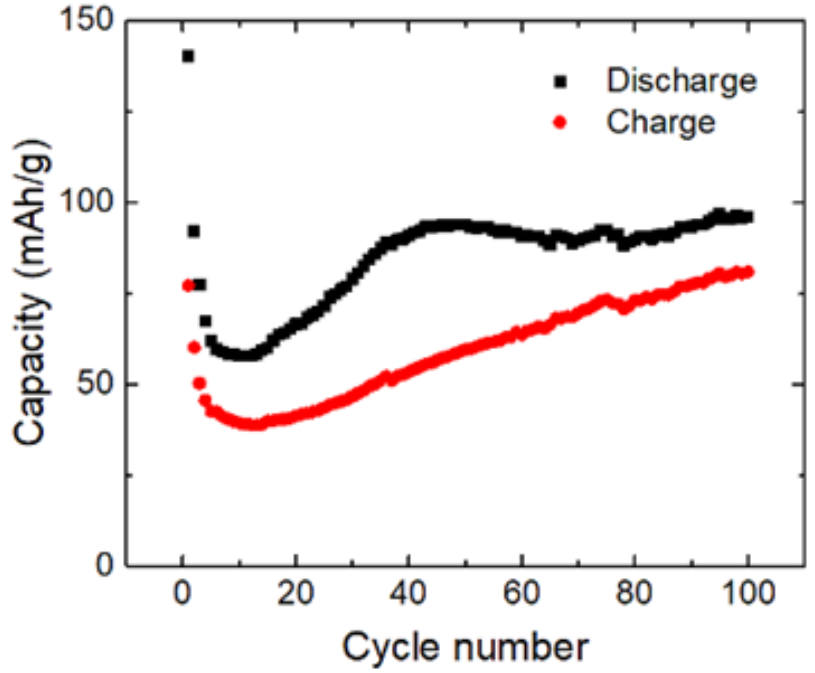
② $\zeta-V_2\ O_5(s) + 0.33\ Mg(C_4H_9)_2(n-heptane) \rightarrow\ \beta-Mg_{0.33}V_2O_5(s) + 0.33\ C_8H_{18}(g)$

③ $\beta-Mg_{0.33}V_2O_5(s) + 0.66\ NOBF_4(MeCN) \rightarrow\ \zeta-V_2\ O_5(s) + 0.33\ Mg(BF_4)_2(MeCN) + 0.66\ NO(g)$

ζ-V_2O_5: A HIGH-CAPACITY MG-ION CATHODE MATERIAL

Improved Mg-ion diffusion in ζ-V_2O_5 compared to α-V_2O_5



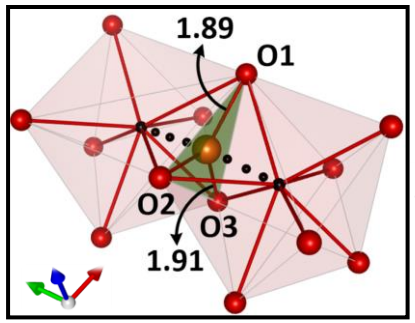


Reversible Mg-ion insertion in ζ-V_2O_5 makes it the first high-capacity, high-voltage oxide for Mg-ion storage

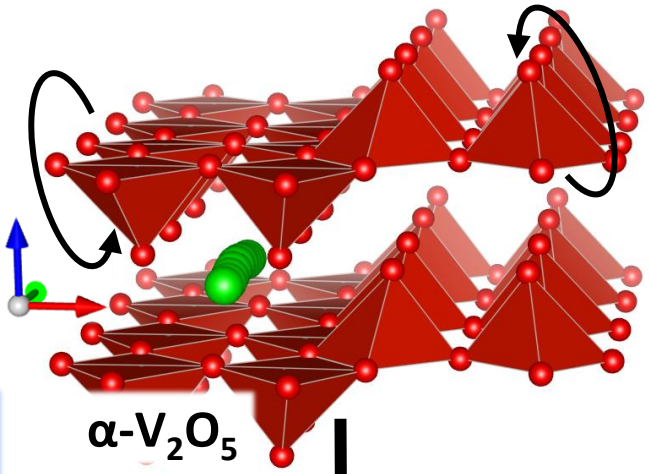
130 mAh g^{-1} at 2.5 V vs. Mg/Mg^{2+}

Andrews , Mukherjee, Yoo, Parija, Marley, Fakra, Prendergast, Cabana, Klie, Banerjee. *Chem*, **2018**, *4*, 564.
Johnson, Nolis, Yin, Yoo, Parajuli, Mukherjee, Andrews, Lopez, Klie, Banerjee, Ingram, Lapidus, Cabana, Darr. *Nanoscale*. **2020**, *12*, 22150.

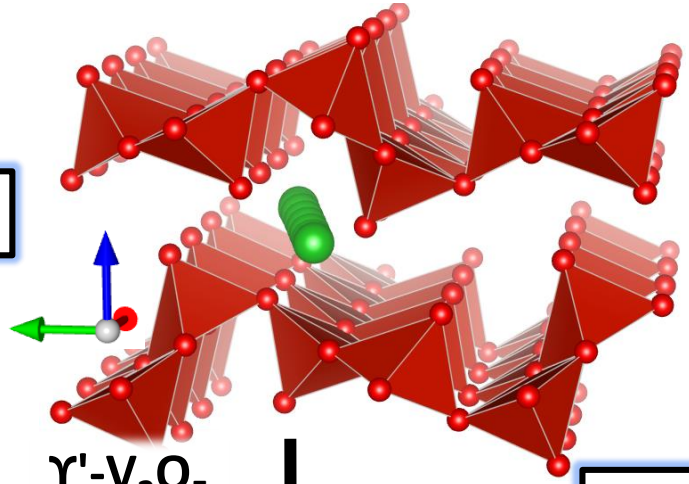
Other Metastable V_2O_5 phases

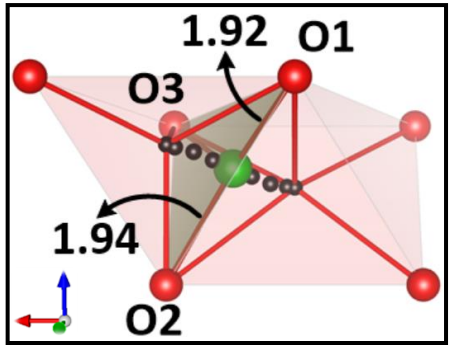


Single Layer vs Double Layer

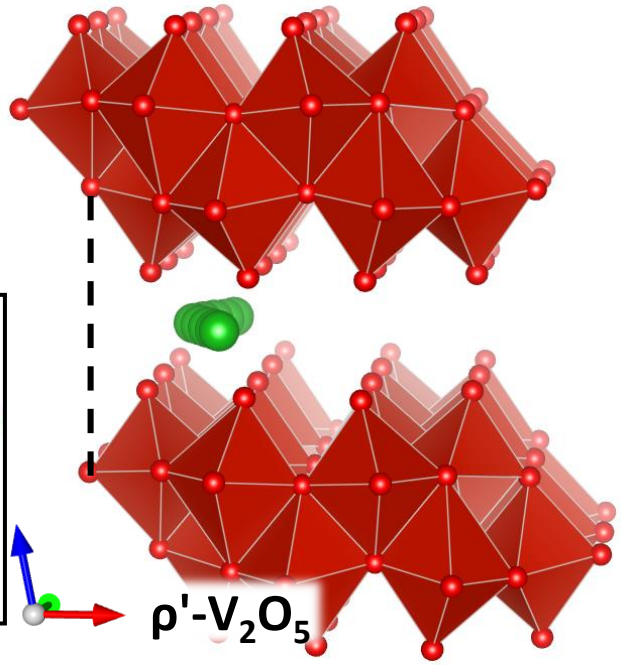


Puckering

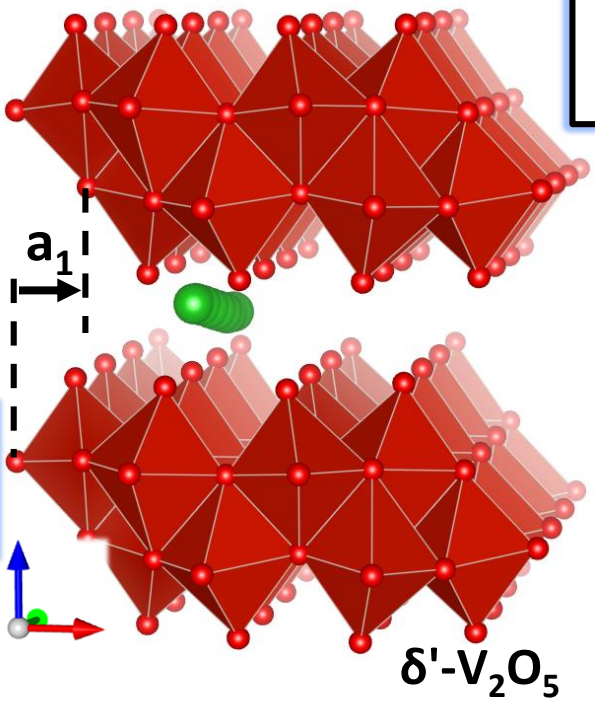


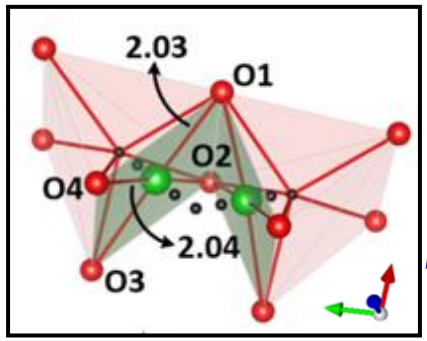


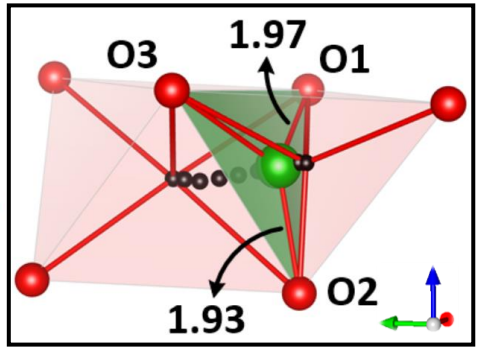
Single Layer vs Double Layer



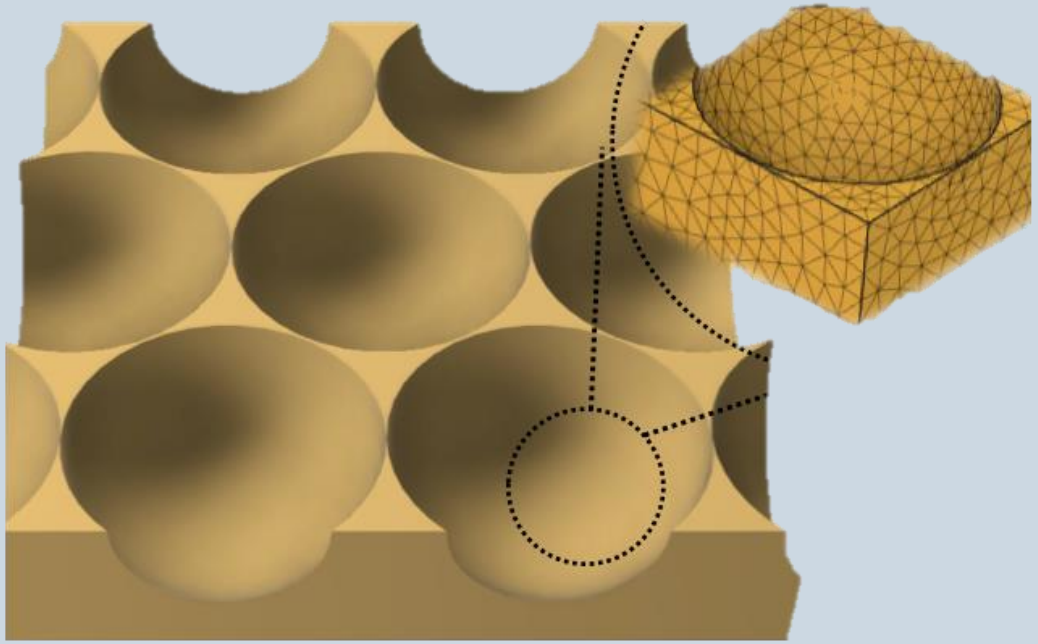
Stacking Sequence



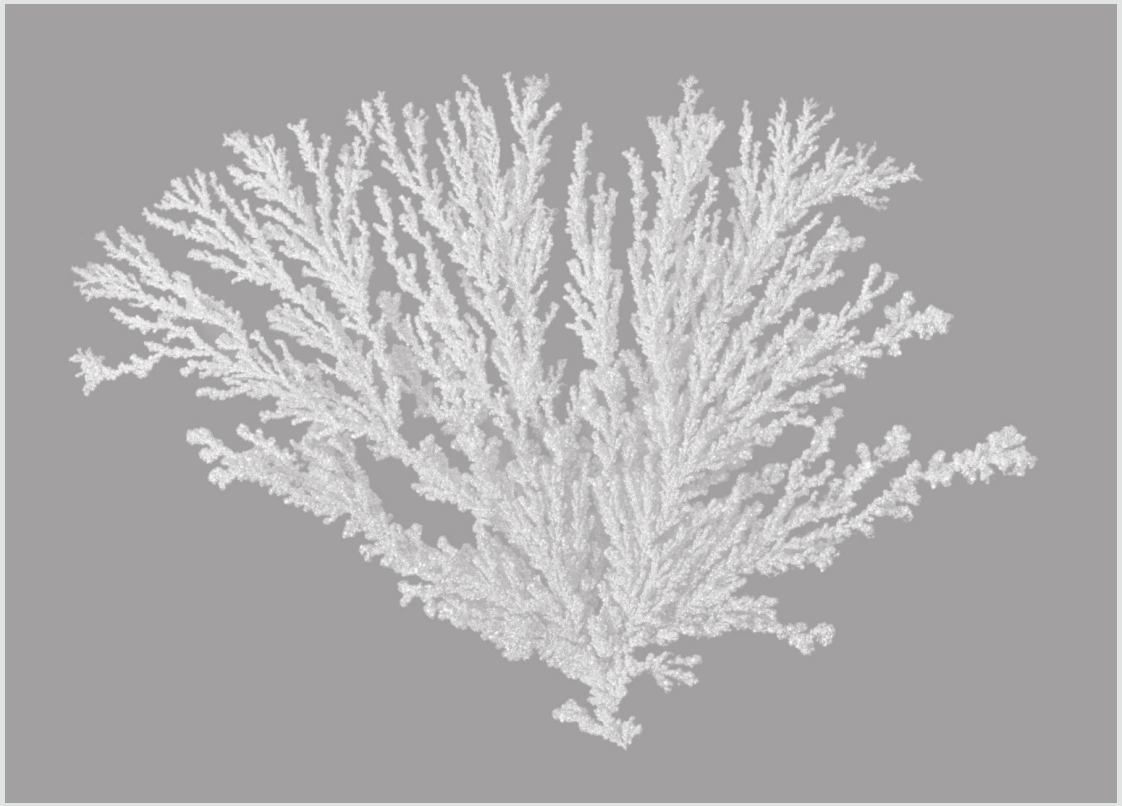




Parija, A.; Prendergast, D.; Banerjee, S. *ACS Appl. Mater. Interfaces* **2017,** *9*, 23756-23765.

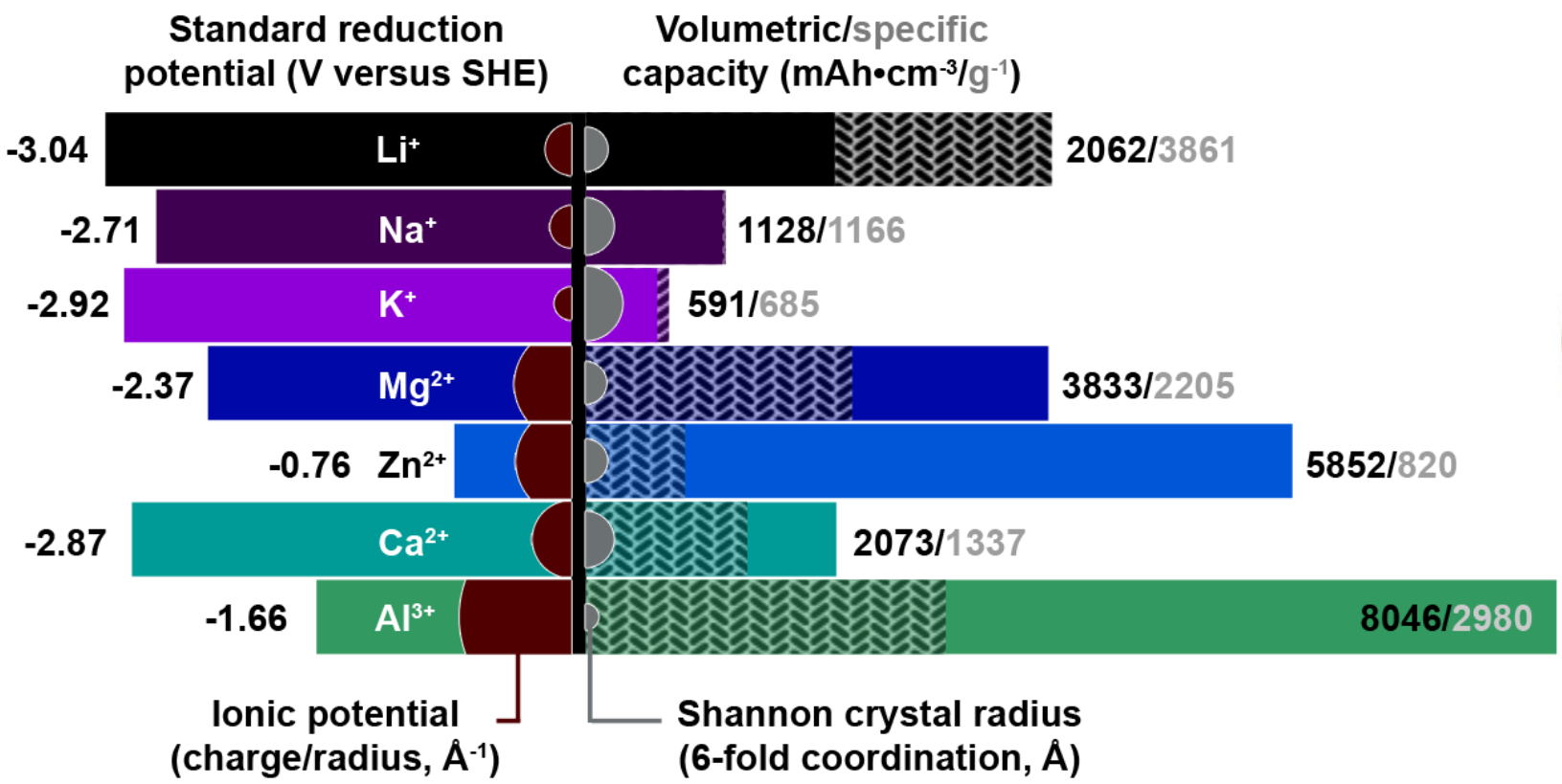


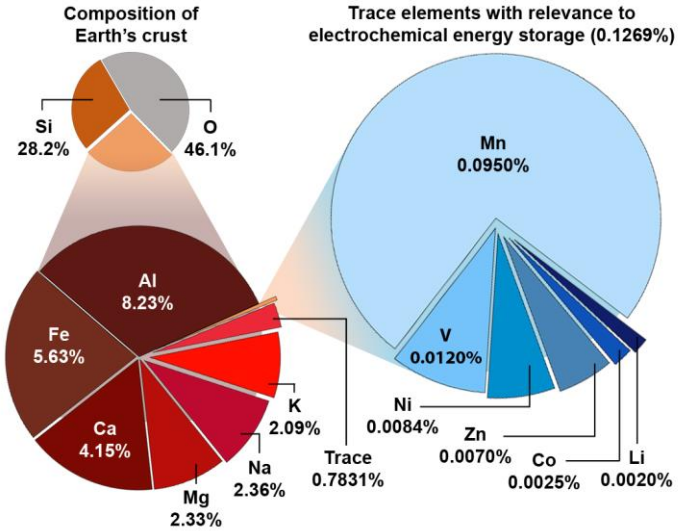
V_2O_5 Cathodes Across Scales



Mg Anodes

Thinking beyond Li…





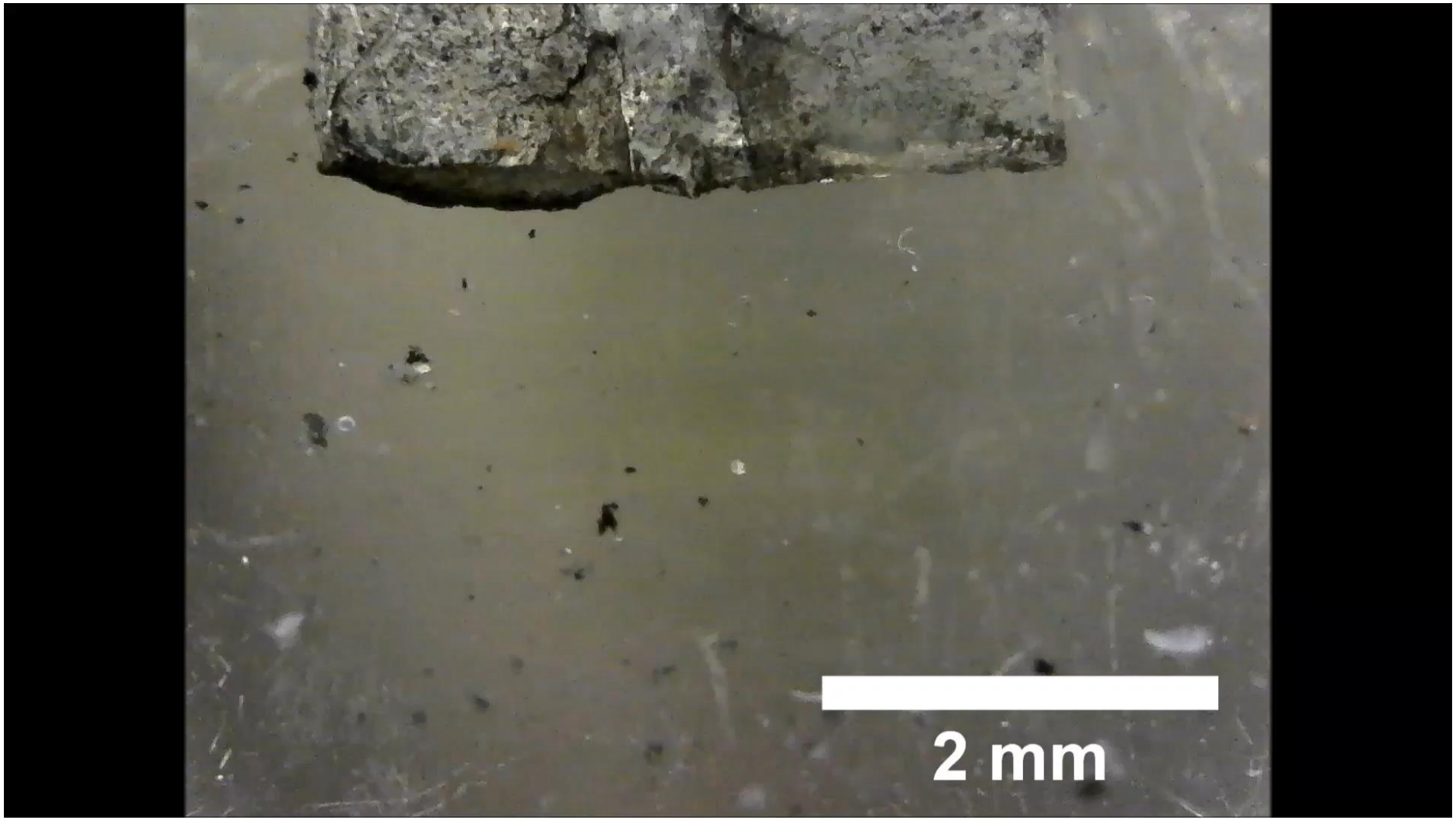
Metal anodes…
Earth abundance and criticality…
Safety

Graphite
372 mAh/g

Sluggish diffusion
Desolvation
Sparse palette of electrolytes

A Case for Magnesium?

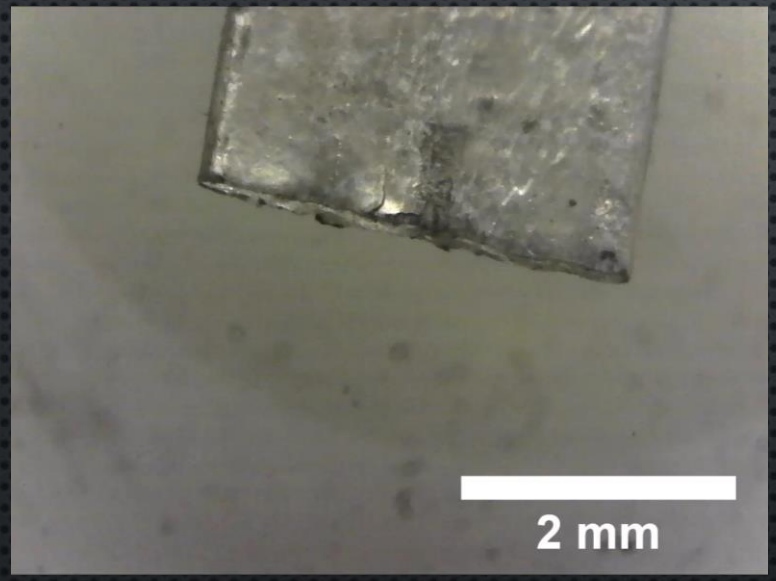
CHEMISTRY
TEXAS A&M UNIVERSITY



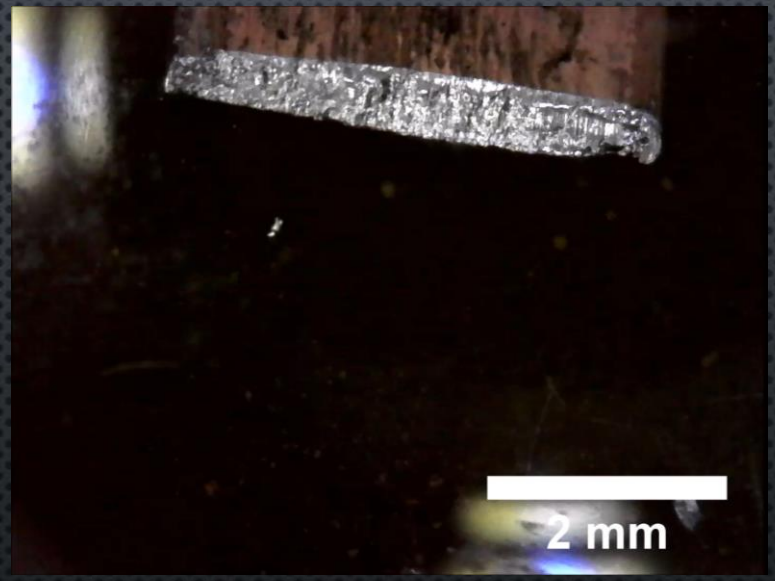
RACHEL DAVIDSON

Effects of Concentration on Magnesium Dendrite Growth

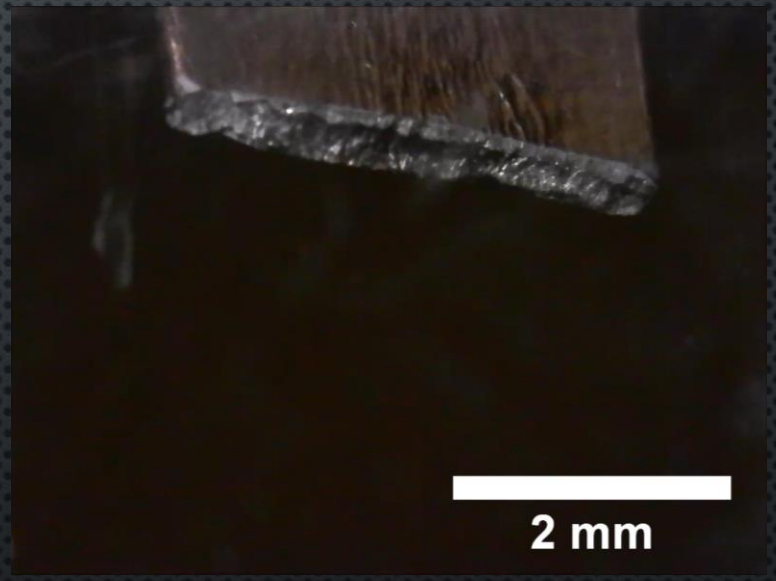
0.5 M 3 mA 24 h



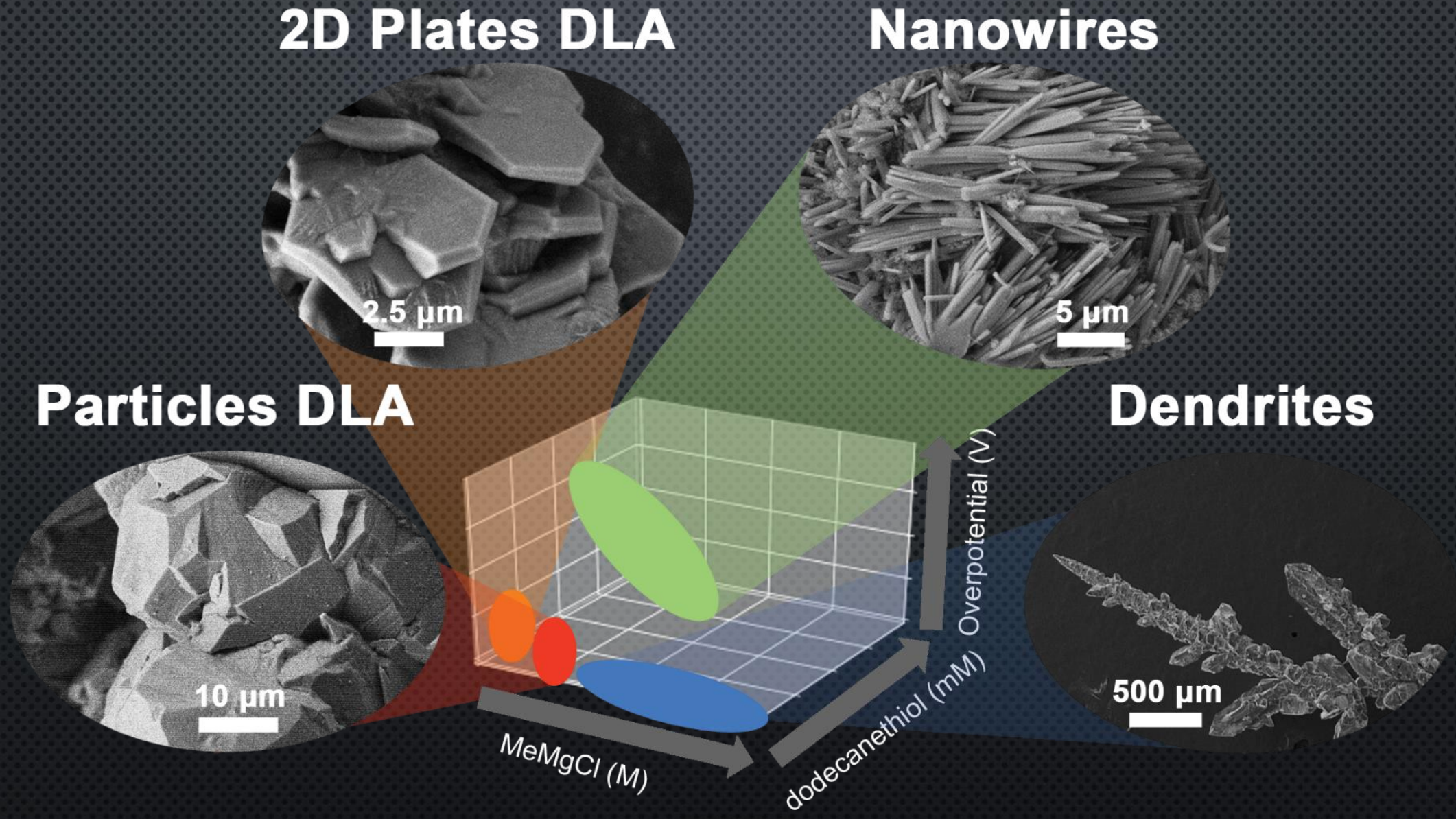
1 M 3 mA 24 h



1.5 M 3 mA 24 h



R. Davidson, A. Verma, D. Santos, F. Hao, C. Fincher, D. Zhao, V. Attari, P. Schofield, J. Van Buskirk, A. Fraticelli-Cartagena, T. Alivio, R. Arroyave, K. Xie, M. Pharr, P. Mukherjee and S. Banerjee, *Mater. Horizons*, , DOI:10.1039/C9MH01367A.



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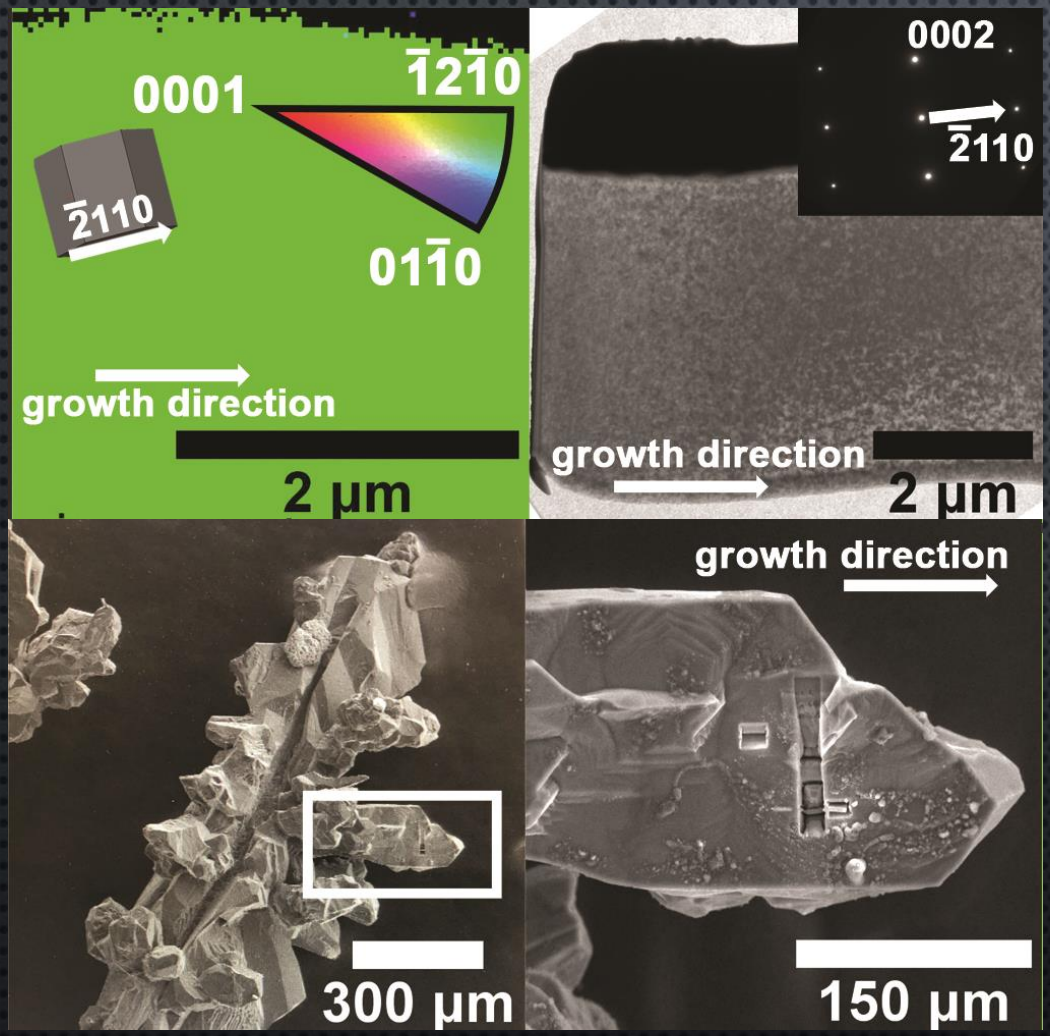
Single Crystal Electrocrystallization

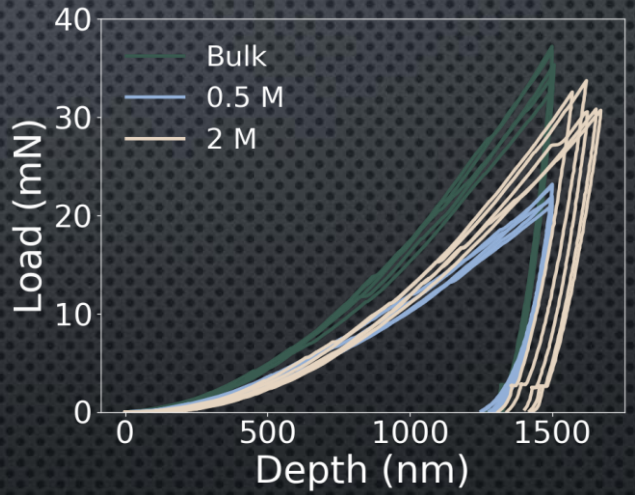
Prof. Matt Pharr

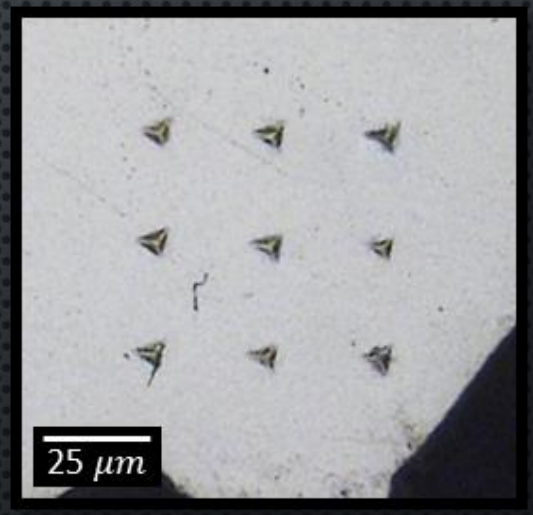
Cole Fincher

Prof. Kelvin Xie

Dexin Zhao







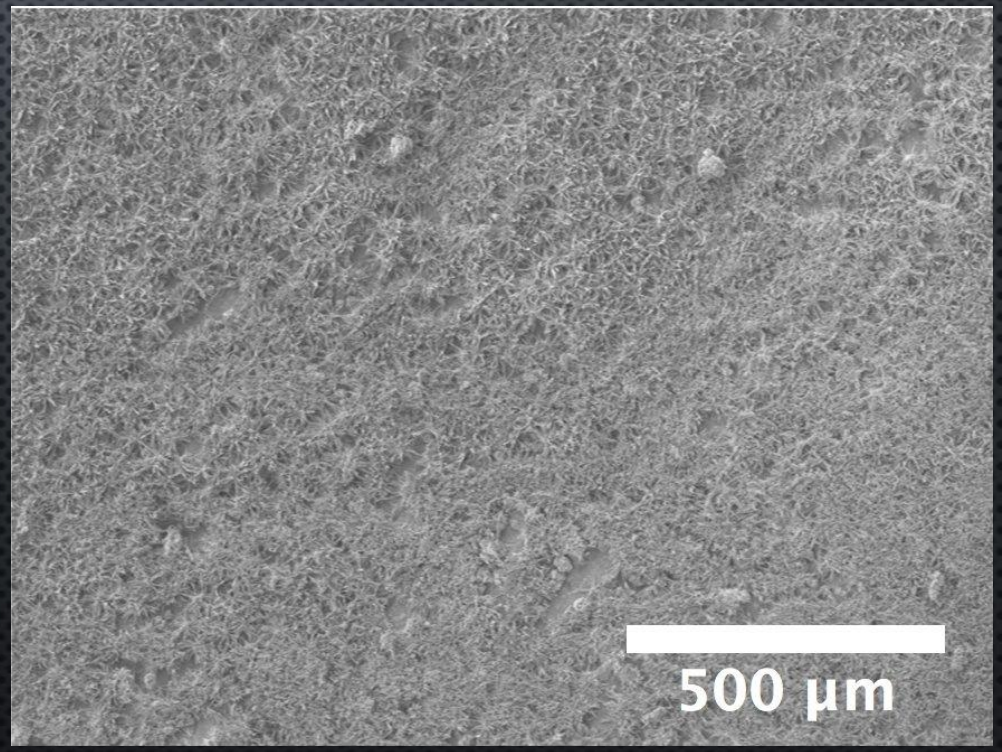
Approximate Shear Modulus	
Mg	10 GPa
Polymer Separators	0.34 GPa
Li	4 GPa

R. Davidson, A. Verma, D. Santos, F. Hao, C. Fincher, D. Zhao, V. Attari, P. Schofield, J. Van Buskirk, A. Fraticelli-Cartagena, T. Alivio, R. Arroyave, K. Xie, M. Pharr, P. Mukherjee and S. Banerjee, *Mater. Horizons*, , DOI:10.1039/C9MH01367A.

Ligand-Directed Growth of Magnesium Nanowire Arrays

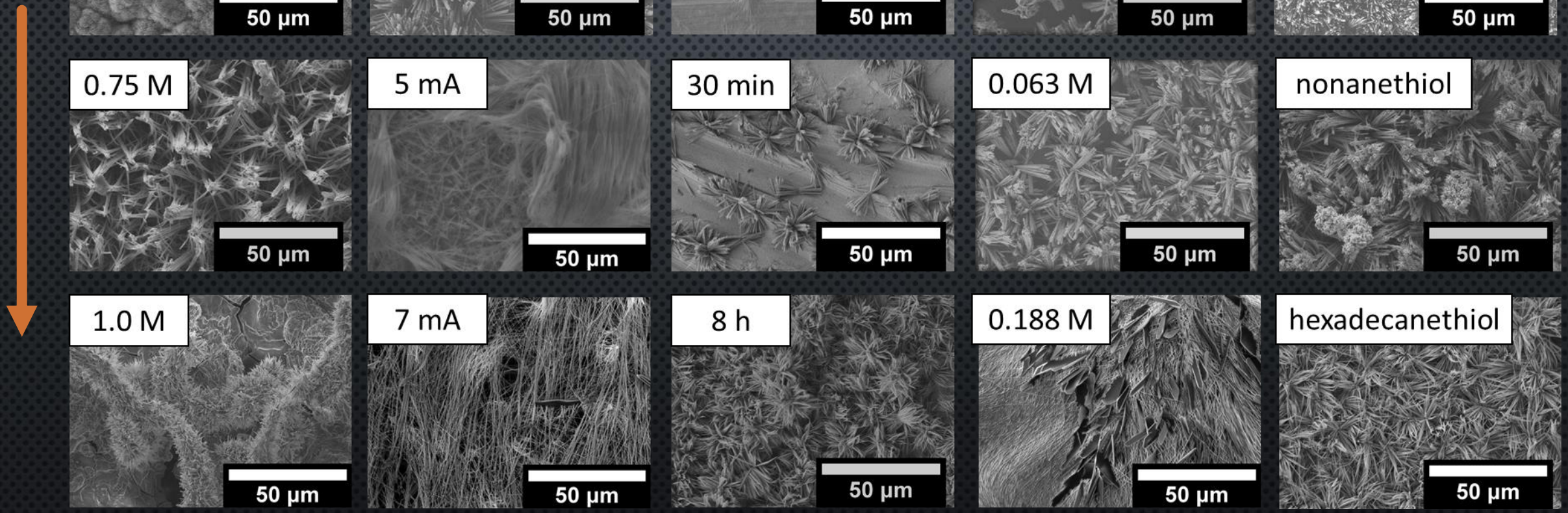
- Addition of alkyl thiol results in consistent deposition of only wires
- Gas evolution
  - Production of methane
  - $MeMgCl + CH_3(CH_2)_{10}CH_2S\text{-}H \rightarrow MgCl^+ + CH_3(CH_2)_{10}CH_2S^- + CH_{4(g)}$

Typically, reactions run at 3 mA (0.921 mA/cm^2) in 0.5 M MeMgCl for 4 hours with addition of 0.125 M dodecanethiol



GROWTH ALONG $(\bar{2}11\bar{1})$

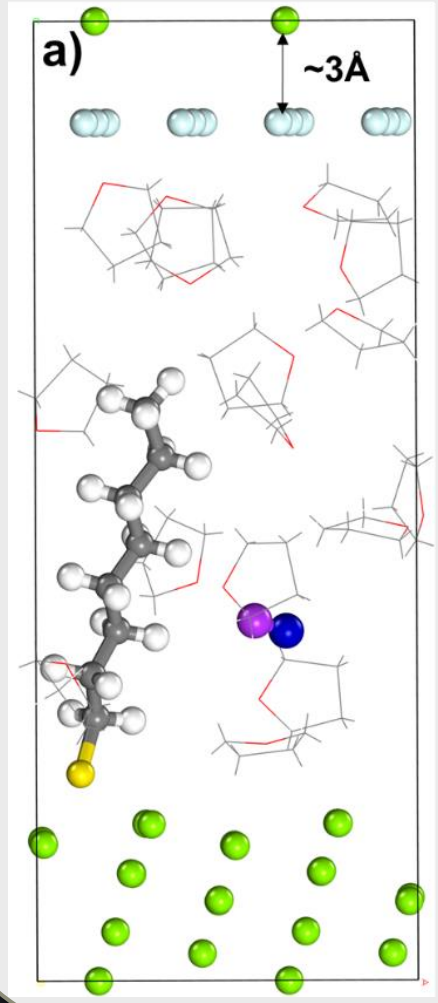
Concentration of MeMgCl	Current	Time	Concentration of Dodecanethiol	Identity of Thiol
0.25 M	1 mA	10 min	0.031 M	octanethiol
0.75 M	5 mA	30 min	0.063 M	nonanethiol
1.0 M	7 mA	8 h	0.188 M	hexadecanethiol
Increase diameter	Increase length	Increase length	Decrease diameter	No major effect

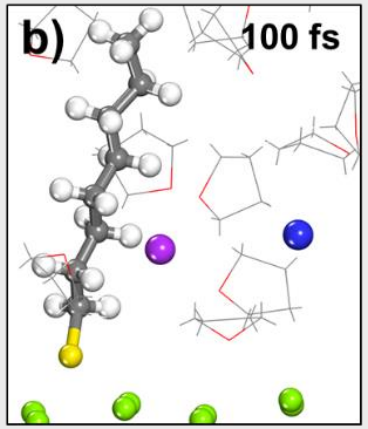


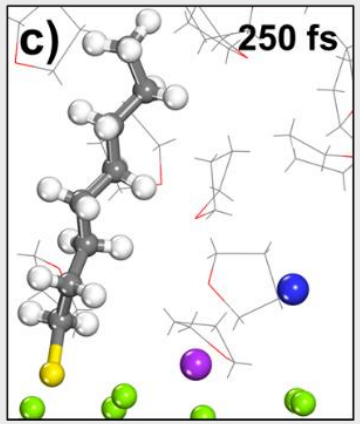
PREFERENTIAL DEPOSITION ON $(\bar{2}11\bar{1})$

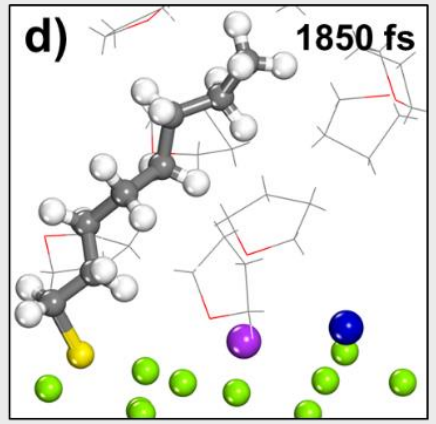
- 3 layers Mg slab
- $MgCl^+$ at 0.5 M
  - Placed at ~5.6 Å from surface
- $CH_3(CH_2)_{10}CH_2S^-$ at 0.5 M – initially adsorbed

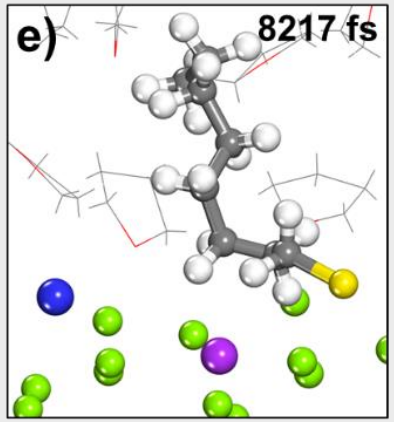
- Within 250 fs $MgCl^+$ splits
- and deposits
- Cl^- also near surface
- Thiolate undergoes reconfiguration at various stages of deposition











f)

Component \ time	100 fs	250 fs	1850 fs	8217 fs
Mg Slab	1.77	2.49	2.25	2.63
$MgCl^+$	-0.06	-0.54	-0.46	-1.06
Thiolate	-0.87	-0.91	-1.04	-0.99
THF Solvent molecules	-0.58	-0.78	-0.41	-0.23
He layer	-0.26	-0.25	-0.35	-0.35
Total	0.00	0.00	0.00	0.00
Net Bader charge breakdown for $MgCl^+$				
Mg	0.76	0.26	0.46	-0.07
Cl	-0.82	-0.81	-0.91	-1.00

Mg S He H O C Mg^{2+} Cl^-

Summary

Batteries are a major bottleneck to the renewable energy transition

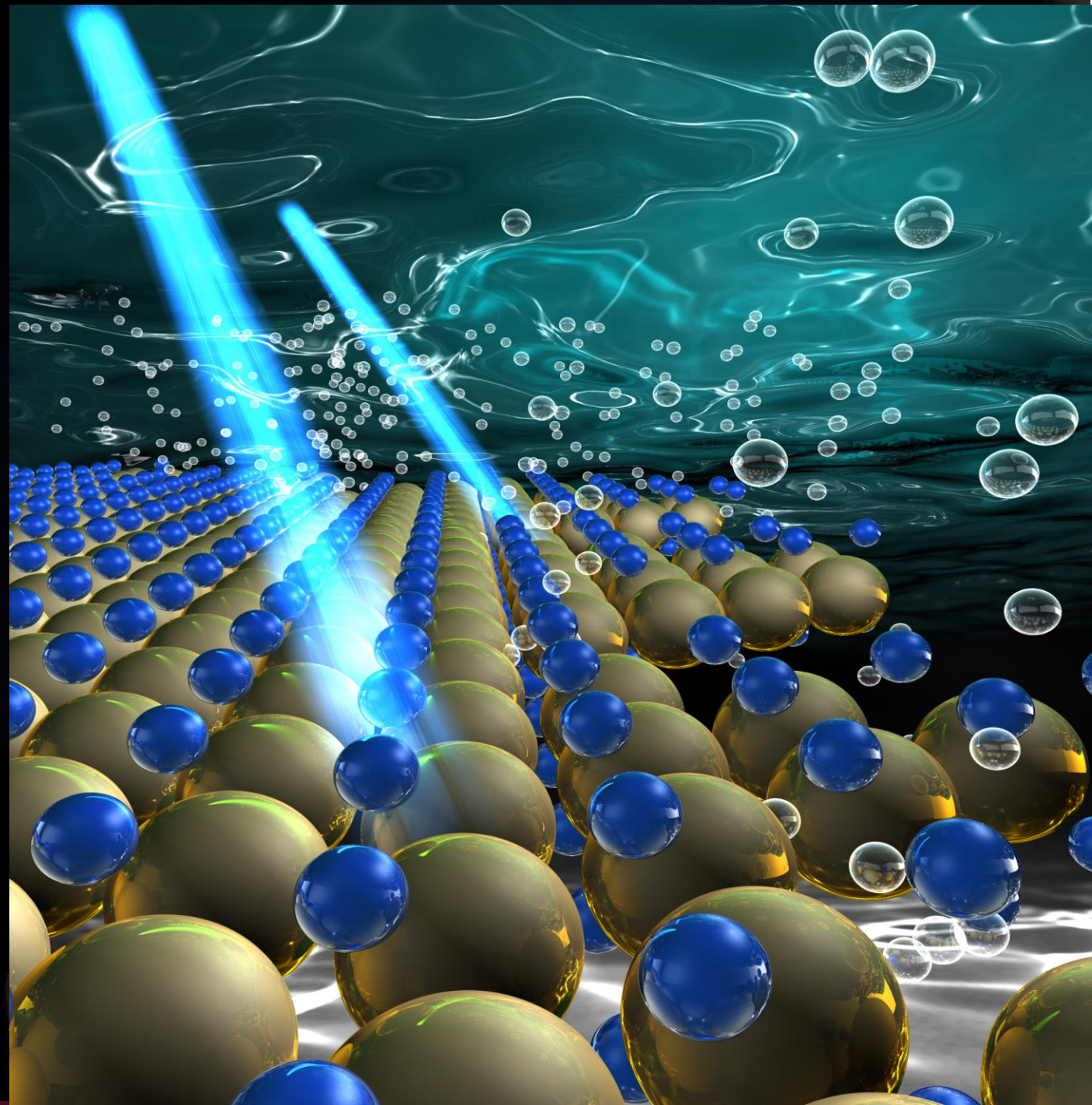
Broad diversity of battery chemistries are urgently needed—no one size fits all

Consideration of materials criticality and earth abundance is urgently required

Considerable nuance (and need to go beyond hype) when considering ‘beyond Li’ chemistries

Design considerations must extend across scales

Materials design choices have profound implications on systems performance

Thank You!

@SarbajitBanerj1