Chicago Future Manufacturing Seminar Series – 2023
October 26, 2023

Nanomanufacturing: Size-Dependent Lithium Solubility in Alloy Anodes

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Contribution:

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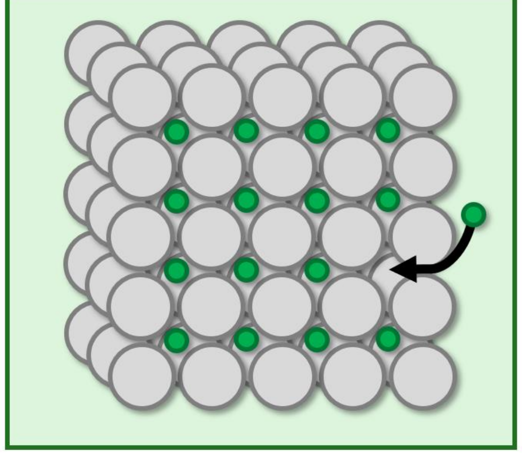
Dr. Sam Welborn (Detsi Group Alumnus)

Penn Engineering | MSE | 3D Advanced Functional & Structural Nanocomposites Lab

High-Capacity Alloy Anodes → Enhanced Energy Density

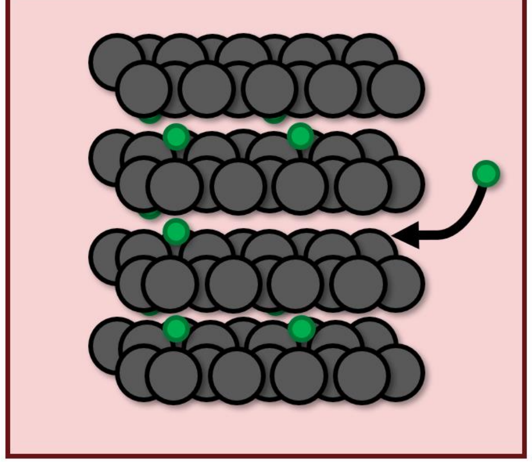
Alloying

3580 mAh/g for $Li_{15}Si_4$



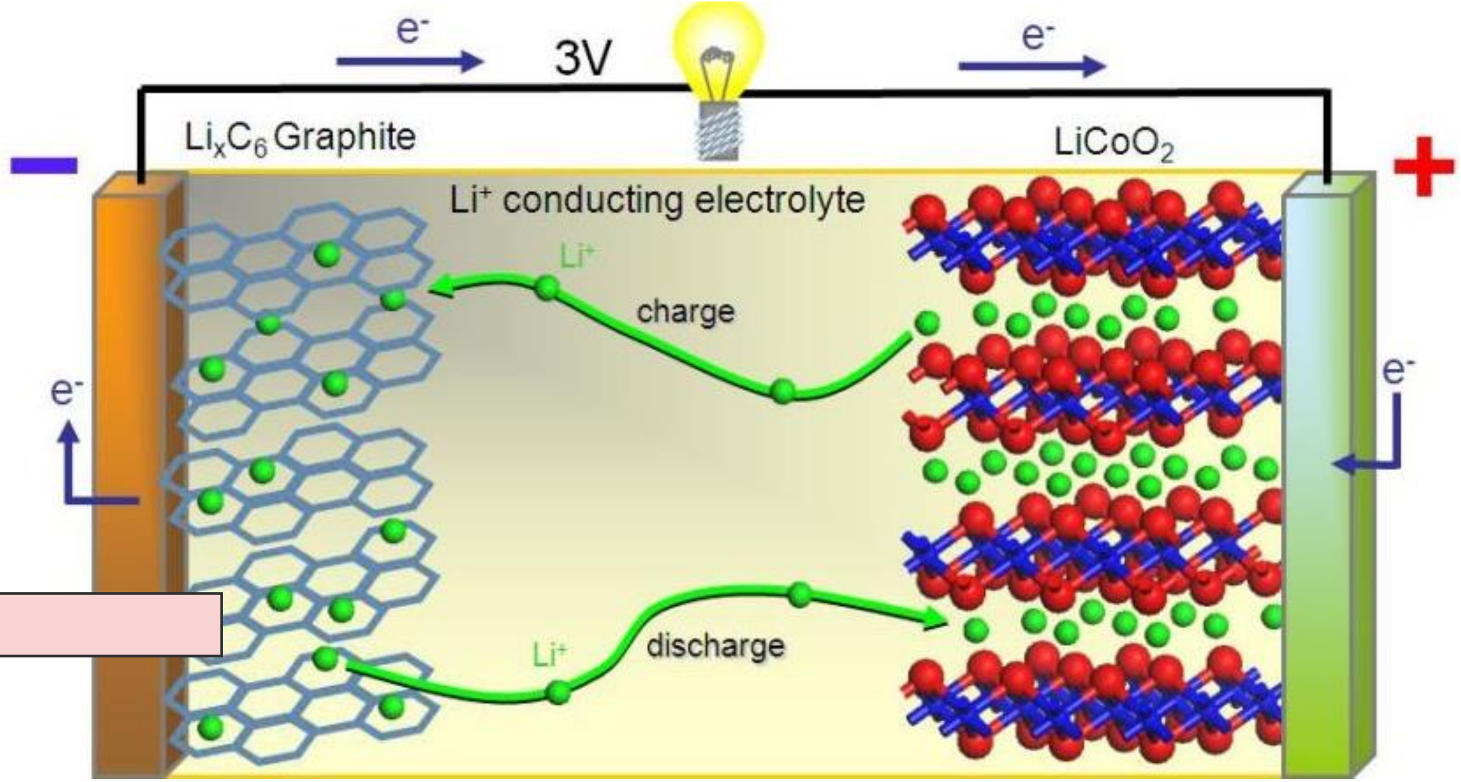
Intercalation

372 mAh/g for LiC_6



$$\Delta G = -q.\Delta V$$

$$(\Delta V = V_C - V_A)$$



Johnson Matthey Battery system (Axeon)

High-Capacity Alloy Anodes → Enhanced Energy Density

Candidates Alloy Anodes for Li Storage

											He
				mAhg^{-1} mAhcm^{-3}		B	372 756	N	O	F	Ne
						993 1383	3579 2190	2596 2266	S	Cl	Ar
Mn	**Fe**	**Co**	**Ni**	**Cu**	410 1511	769 1911	1384 2180	1073 2057	Se	Br	Kr
Tc	**Ru**	Rh	Pd	248 1368	238 1159	1012 1980	960 1991	660 1889	Te	I	Xe
Re	Os	Ir	Pt	510 2105	Hg	Tl	550 1906	385 1746	Po	At	Rn

N. Nitta & G. Yushin; **Part. Part. Syst. Charact.** 31 (2014)

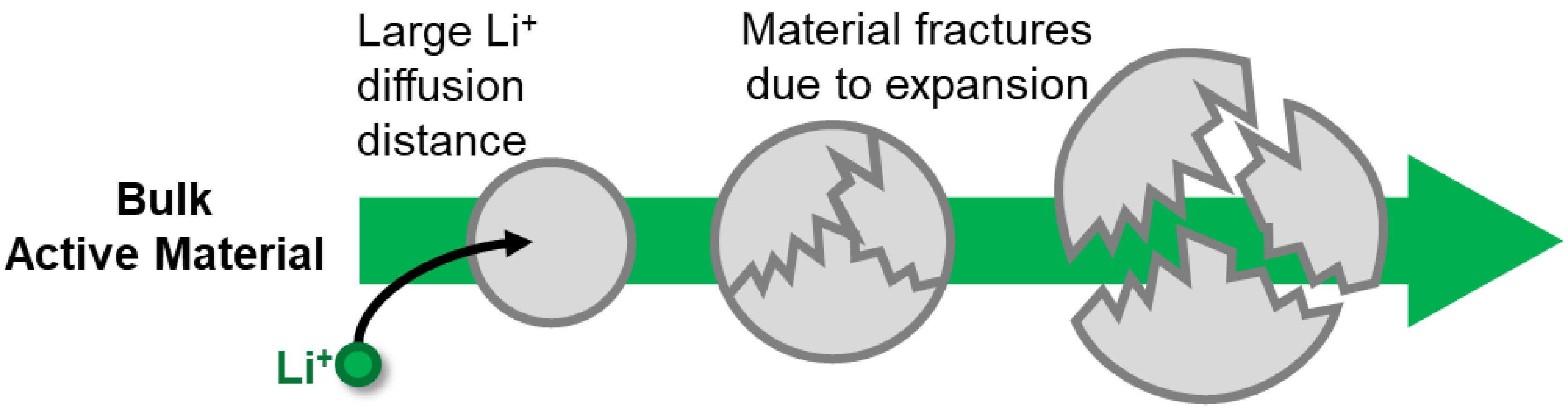
High-Capacity Alloy Anodes → Enhanced Energy Density

Problem: Macro-sized (Bulk) Alloy Anodes Fracture During Li Storage

Critical particle size to avoid fracture

$$\mathbf{d_{cr}} = \frac{\mathbf{\Gamma E}}{\mathbf{Z\sigma_y^2}}$$

d_{cr}: Critical size
Γ: Fracture energy
σ_y: Yield strength
E: Elastic modulus
Z: Material/crack param.



$\mathbf{d_{cr}^{Sn} \leq 22\ nm}$ $\mathbf{d_{cr}^{Al} \leq 345\ nm}$

H. Yaghoobnejad Asl, …, E. Detsi; **Chemistry of Materials** 30, 1815-1824 (2018)

High-Capacity Alloy Anodes → Enhanced Energy Density

Solution: Nano-Sized Alloy Anodes Should Not Fracture (?)

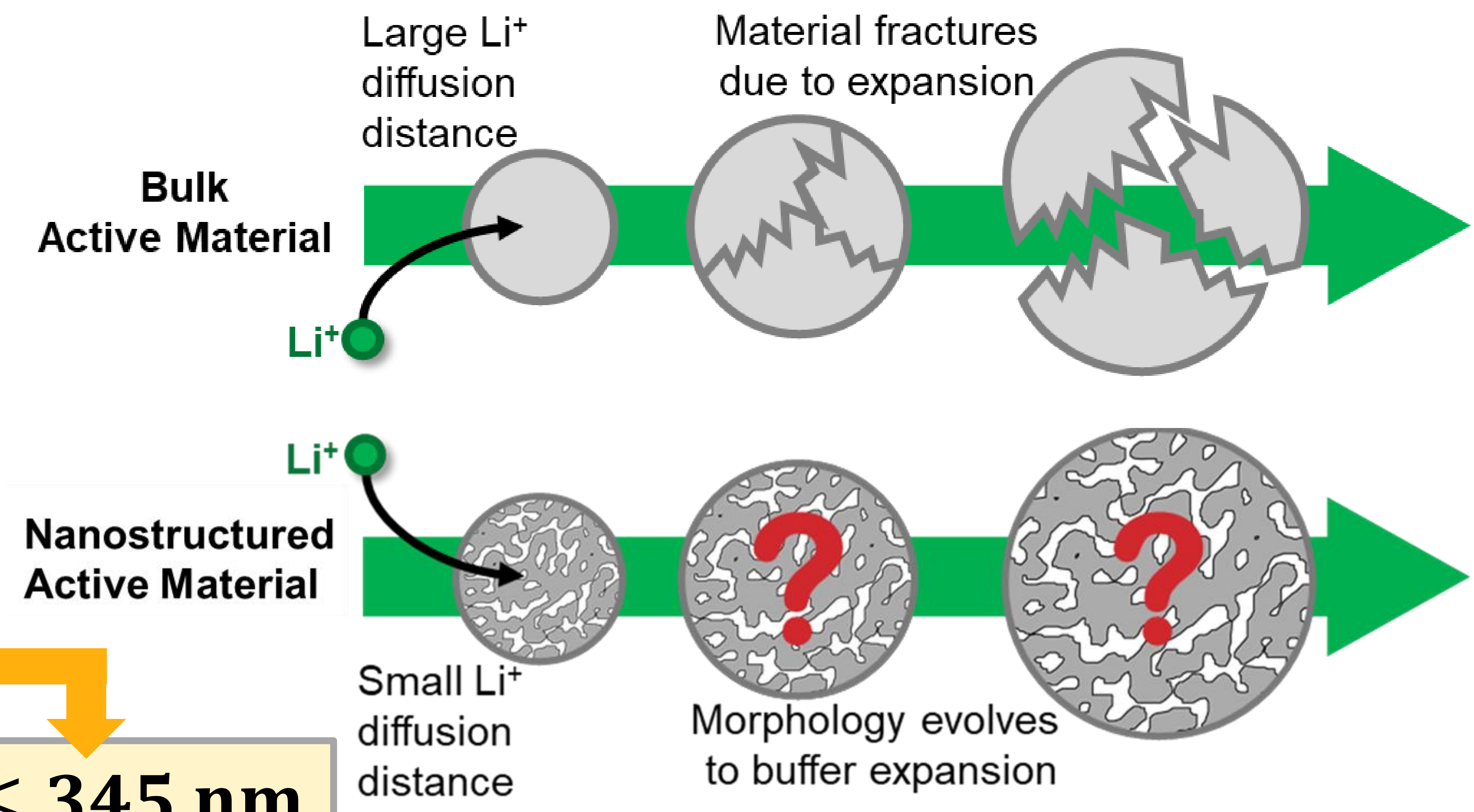
Critical particle size to avoid fracture

$$d_{cr} = \frac{\Gamma E}{Z\sigma_y^2}$$

d_{cr}: Critical size
Γ: Fracture energy
σ_y: Yield strength
E: Elastic modulus
Z: Material/crack param.

$d_{cr}^{Sn} \leq 22$ nm

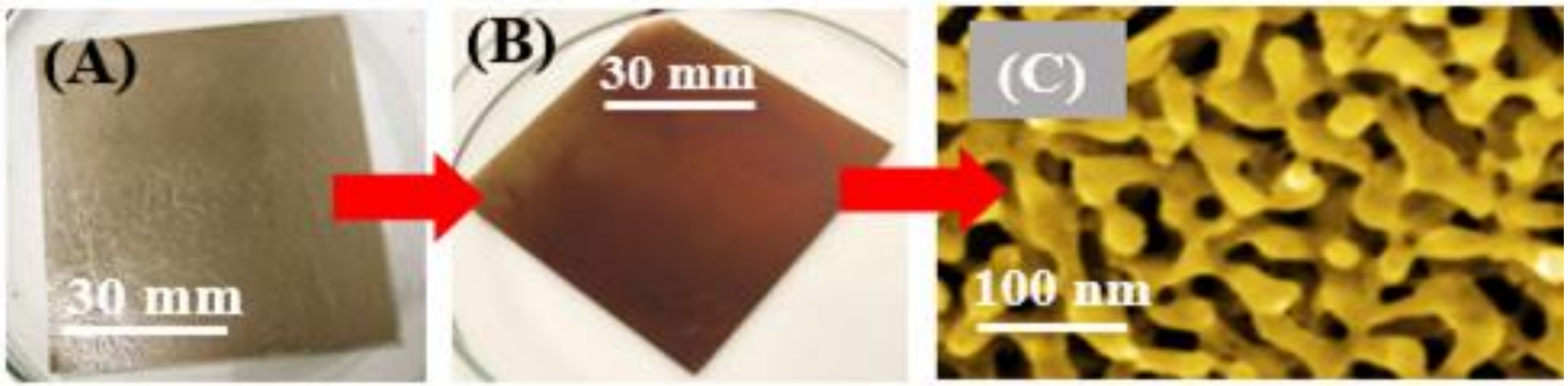
$d_{cr}^{Al} \leq 345$ nm



Creating Nano-Sized Alloy Anodes by Dealloying

Example 1: Nanoporous Gold (NP-Au)

$Au_{35}Ag_{65}$ at.% $\xrightarrow{15\text{ M } HNO_3}$ Nanoporous-Au



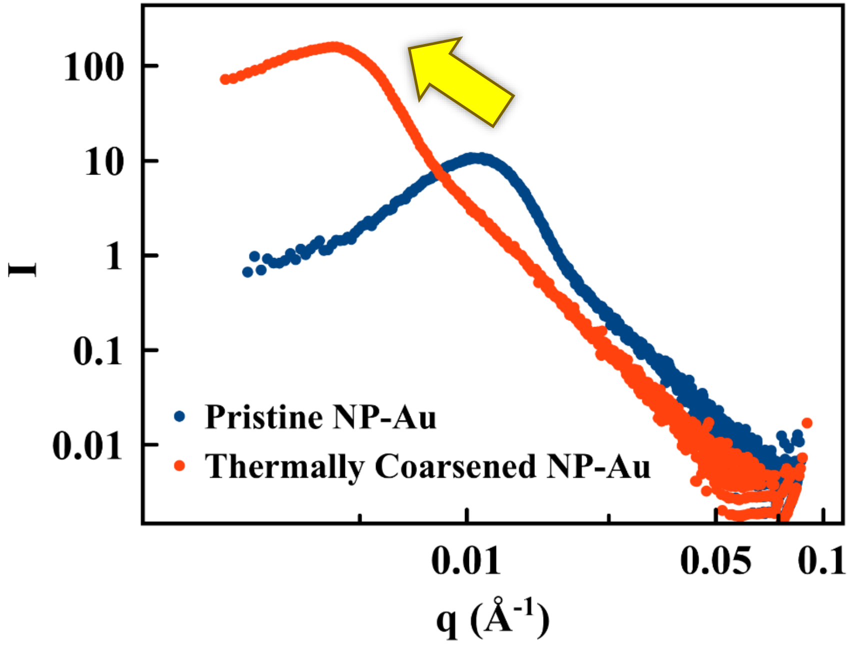
Precursor alloy film ($Au_{35}Ag_{65}$ at. %)

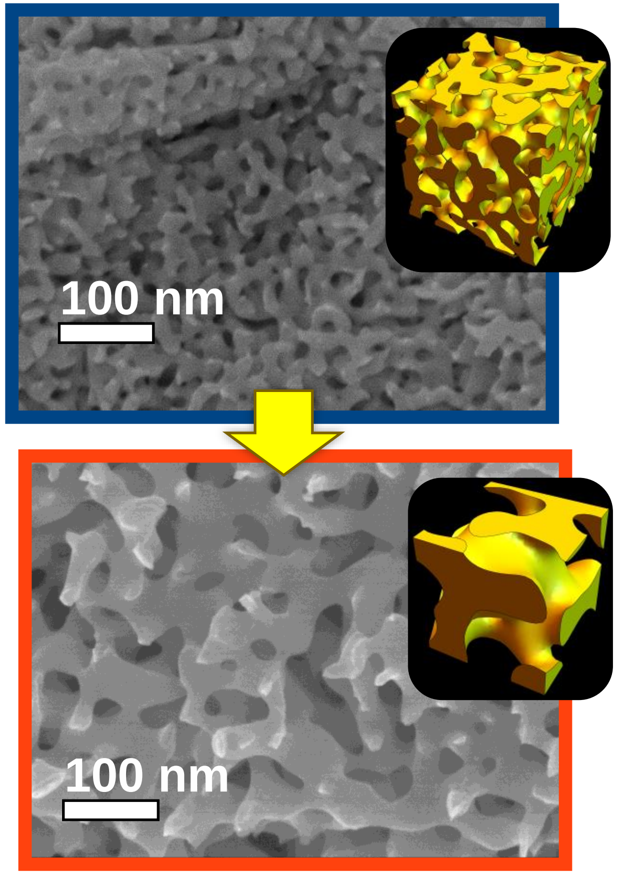
Nanoporous-Au film (naked eye)

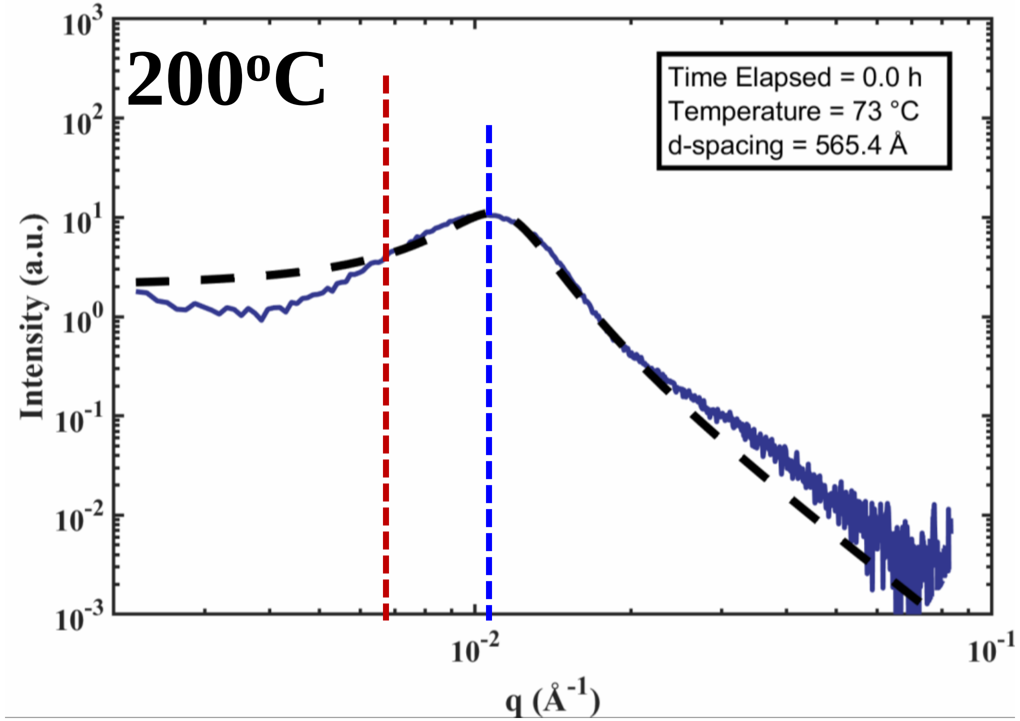
Nanoporous-Au (electron microscopy)

Creating Nano-Sized Alloy Anodes by Dealloying

Example 1: Nanoporous Gold (NP-Au)





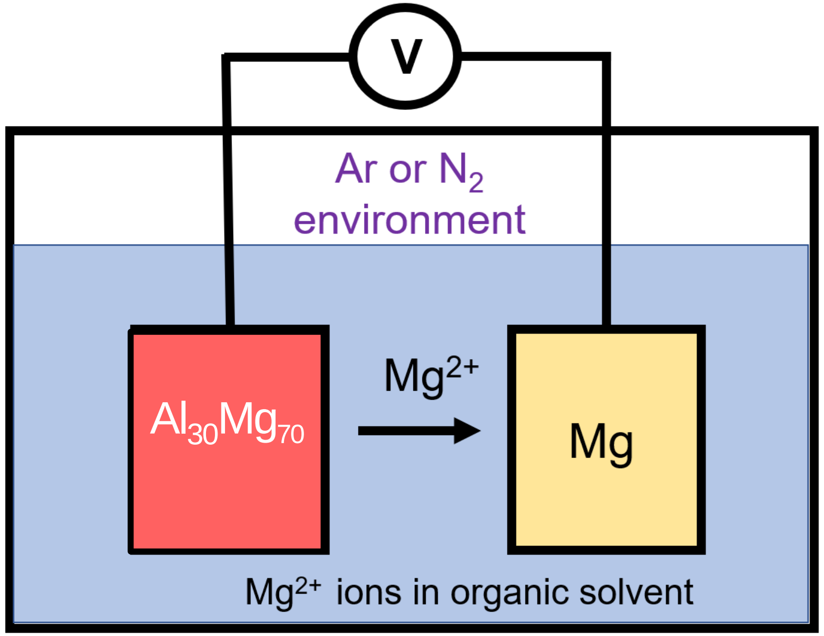


S. Welborn,…, E. Detsi **ACS Applied Materials & Interfaces** 13 (2021)

Creating Nano-Sized Alloy Anodes by Dealloying

Example 2: Ultrafine Nanoporous Aluminum (NP-Al)

$Al_{30}Mg_{70}$ at.% —Applied Voltage→ Nanoporous-Al



Working Electrode:
$Mg \rightarrow Mg^{2+} + 2e^-$

Counter Electrode:
$Mg^{2+} + 2e^- \rightarrow Mg$

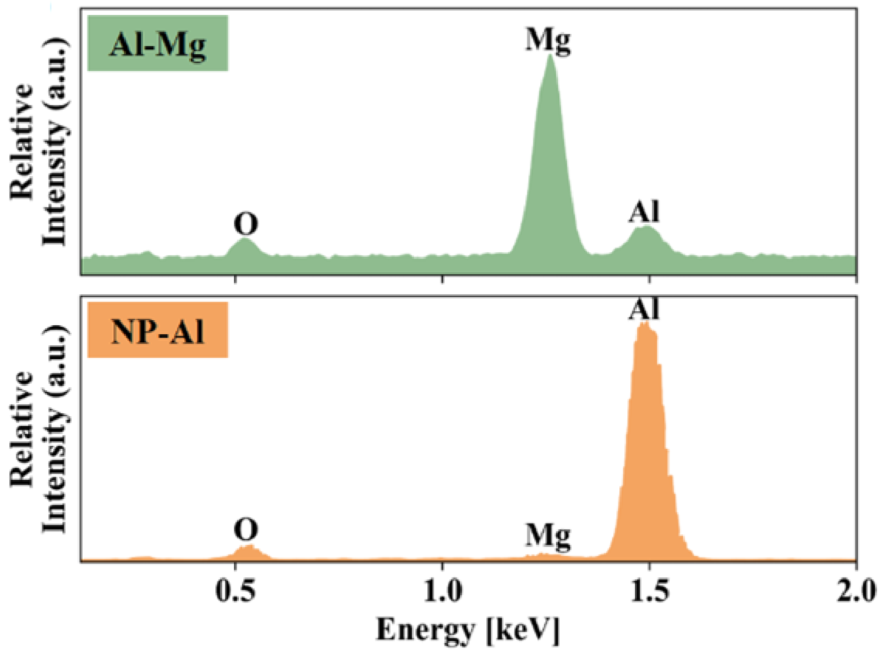
J.S. Corsi, …, E. Detsi; **ACS Sustainable Chem. Eng.** 7, 11194 (2019)

Creating Nano-Sized Alloy Anodes by Dealloying

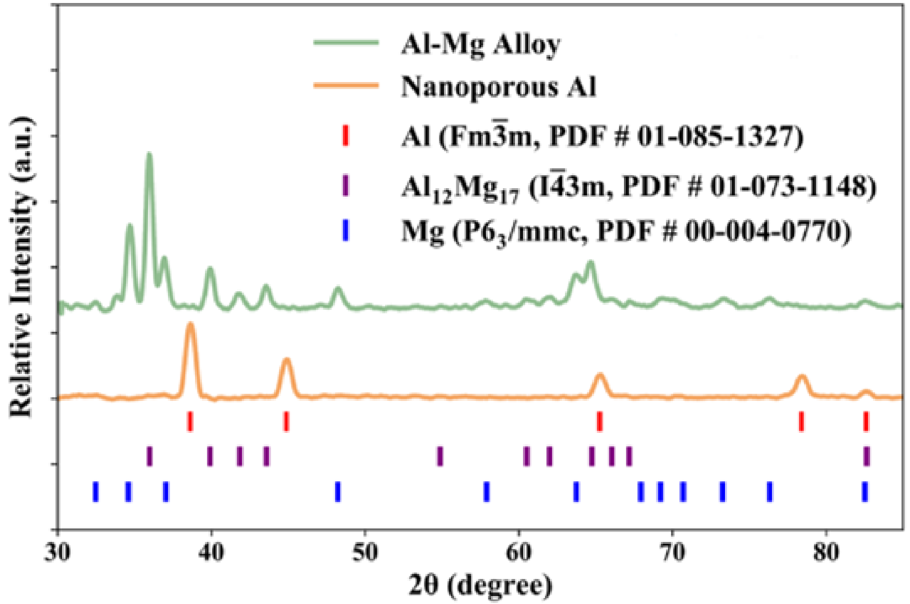
Example 2: Ultrafine Nanoporous Aluminum (NP-Al)

Before dealloying
After dealloying

EDX



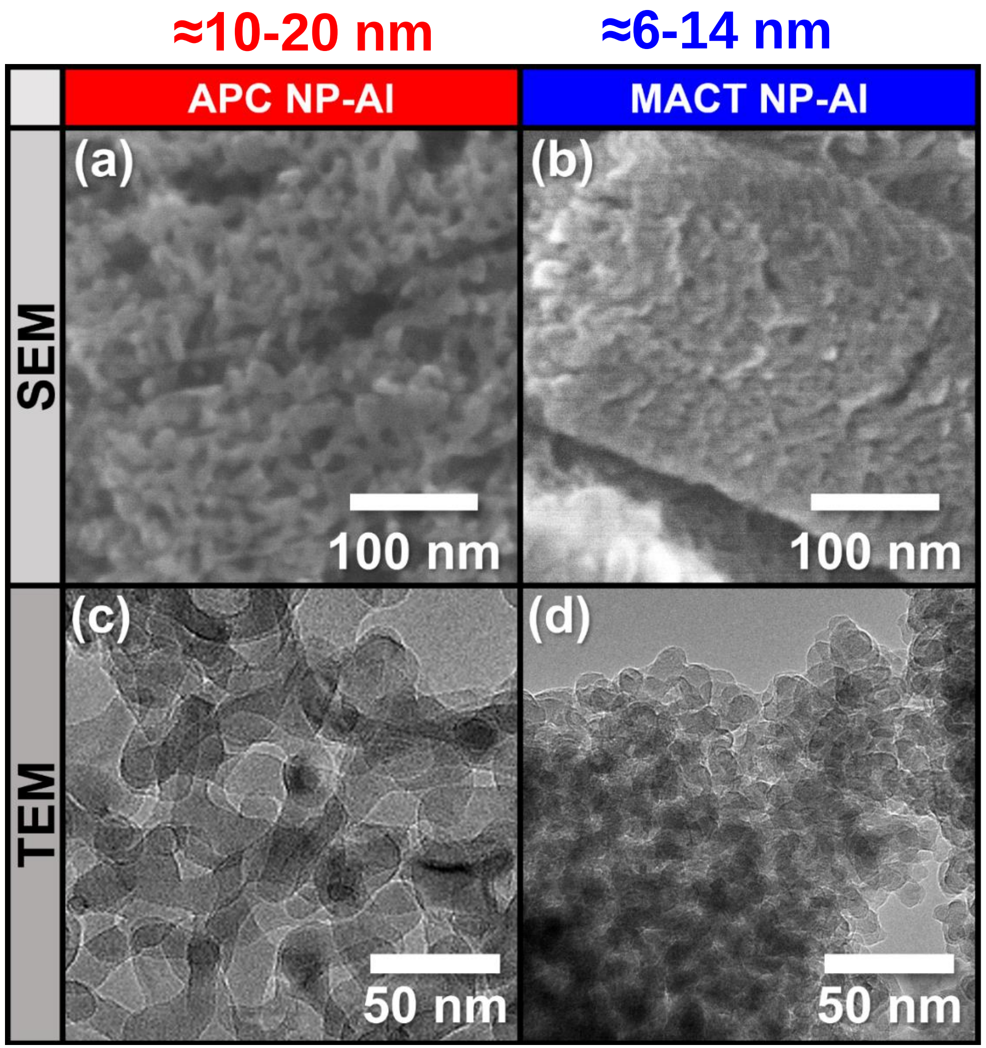
XRD

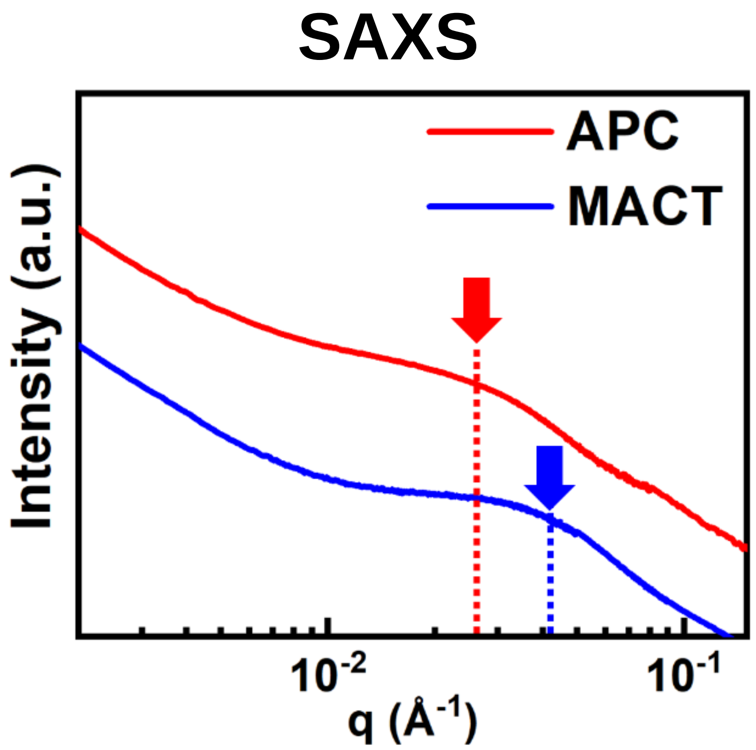


J.S. Corsi, …, E. Detsi; **ACS Sustainable Chem. Eng.** 7, 11194 (2019)

Creating Nano-Sized Alloy Anodes by Dealloying

Example 2: Ultrafine Nanoporous Aluminum (NP-Al)

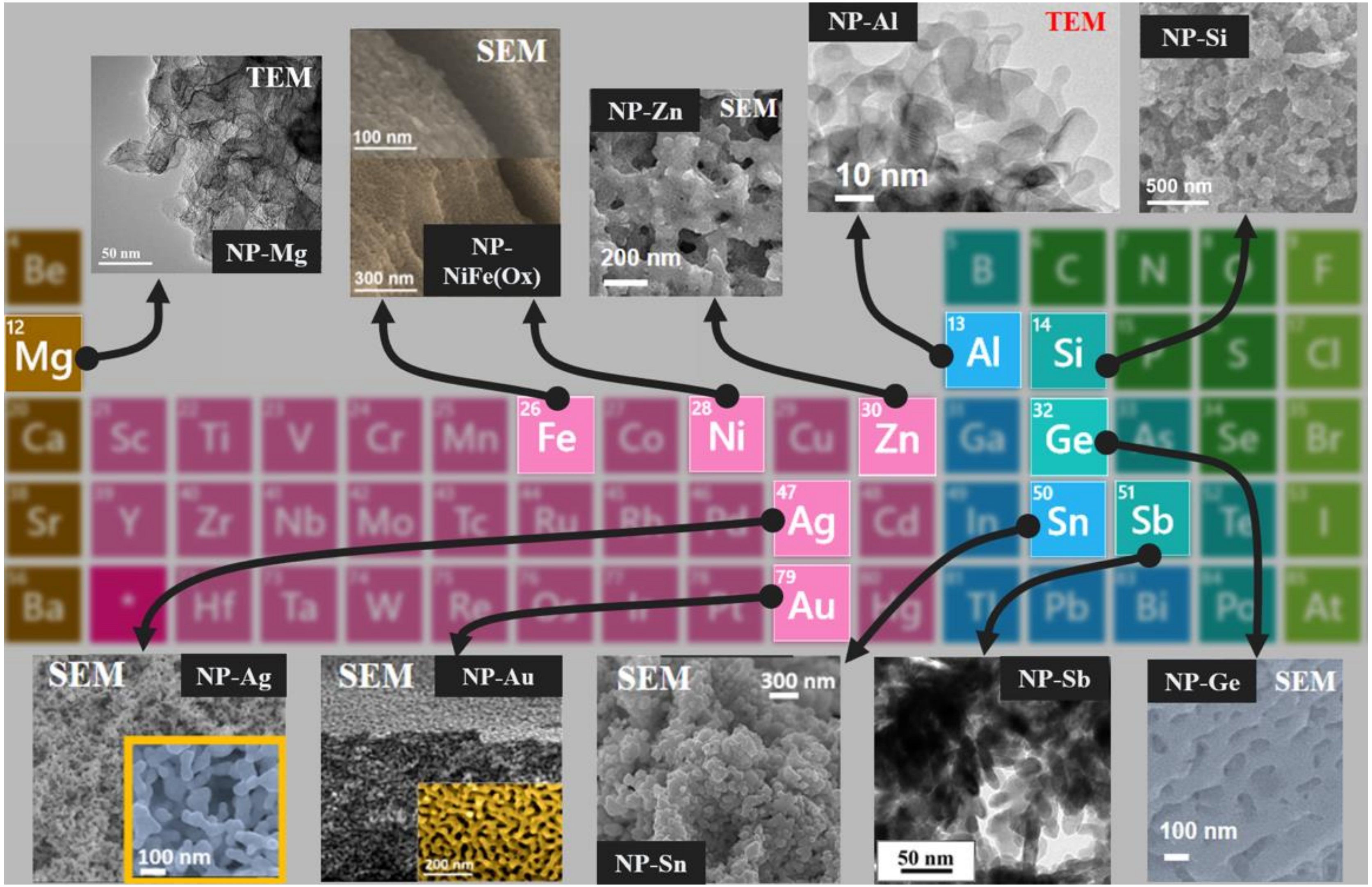




T. Lee,…, E. Detsi; **Scripta Materialia 221**, 114959 (2022)

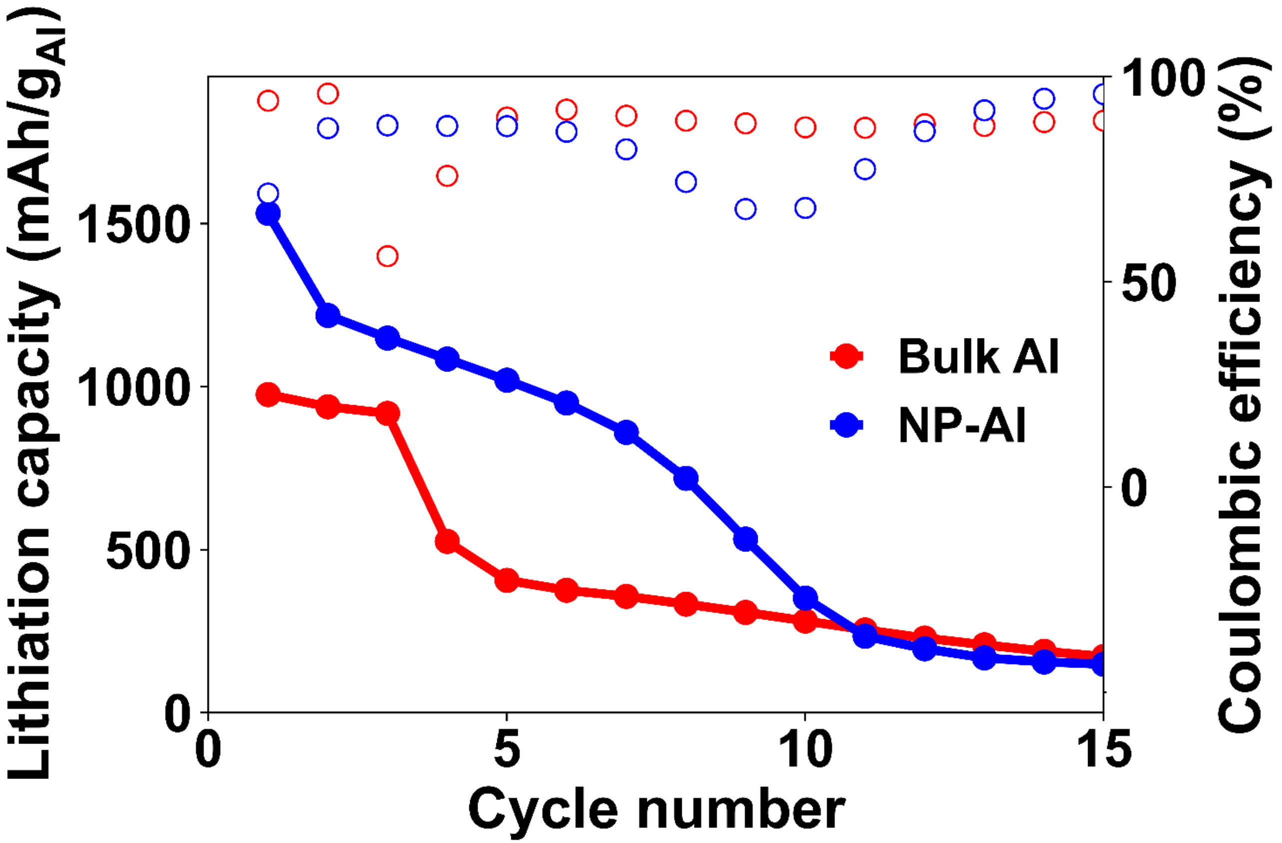
Creating Nano-Sized Alloy Anodes by Dealloying

More Examples of Dealloyed Nanoporous Materials



Performance: Macro-Sized vs. Nano-Sized Alloy Anode

Case Study: Bulk Aluminum vs. Nanoporous Aluminum



NP-Al anode performs better than bulk Al anode

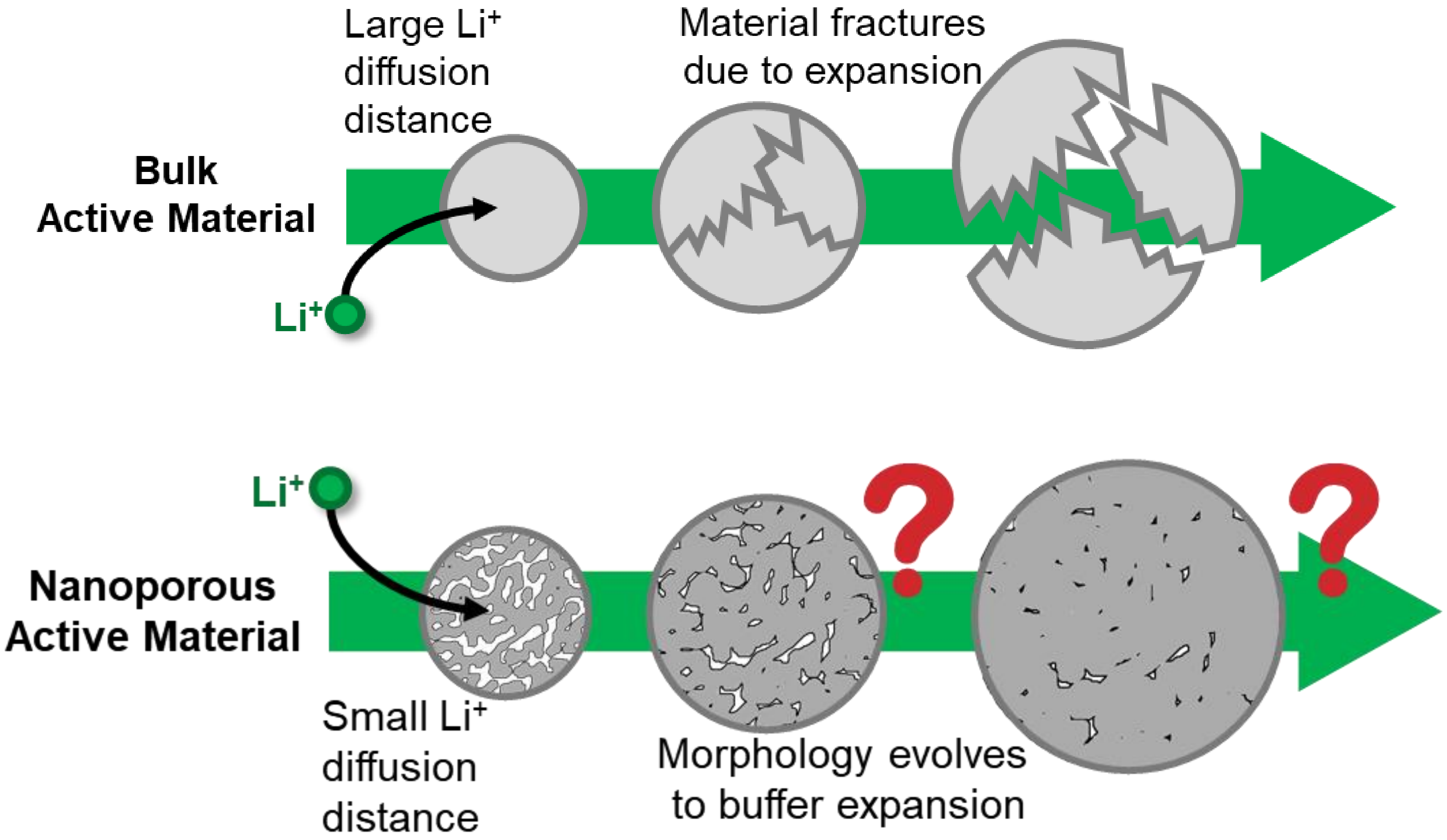
NP-Al anode still fails after only a few cycles

$$\mathrm{d}^{\mathrm{NP-Al}} < \mathrm{d}_{\mathrm{cr}}^{\mathrm{Al}}$$

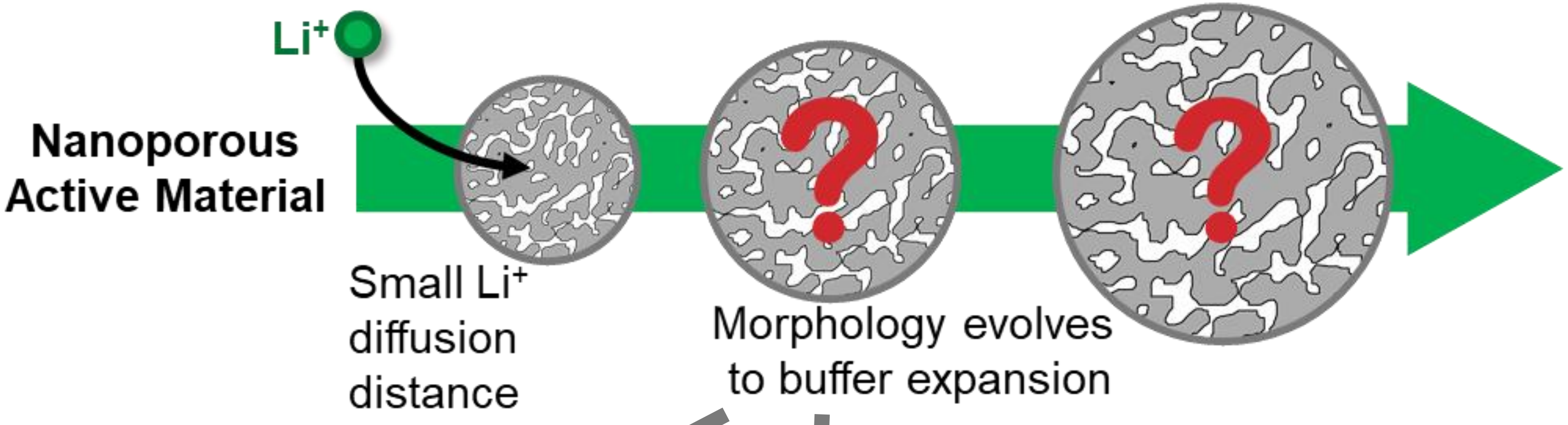
$$15\ \mathrm{nm} \ll 345\ \mathrm{nm}$$

Performance: Macro-Sized vs. Nano-Sized Alloy Anode

Why & How Do Nano-Sized Alloy Anodes Fail?



Morphology Evolution During Li Storage in Nanoporous Alloy Anodes



(1)
Phase Evolution

Ag & Al Model Anodes

(2)
Solid Electrolyte Interphase Evolution

Au Model Anode

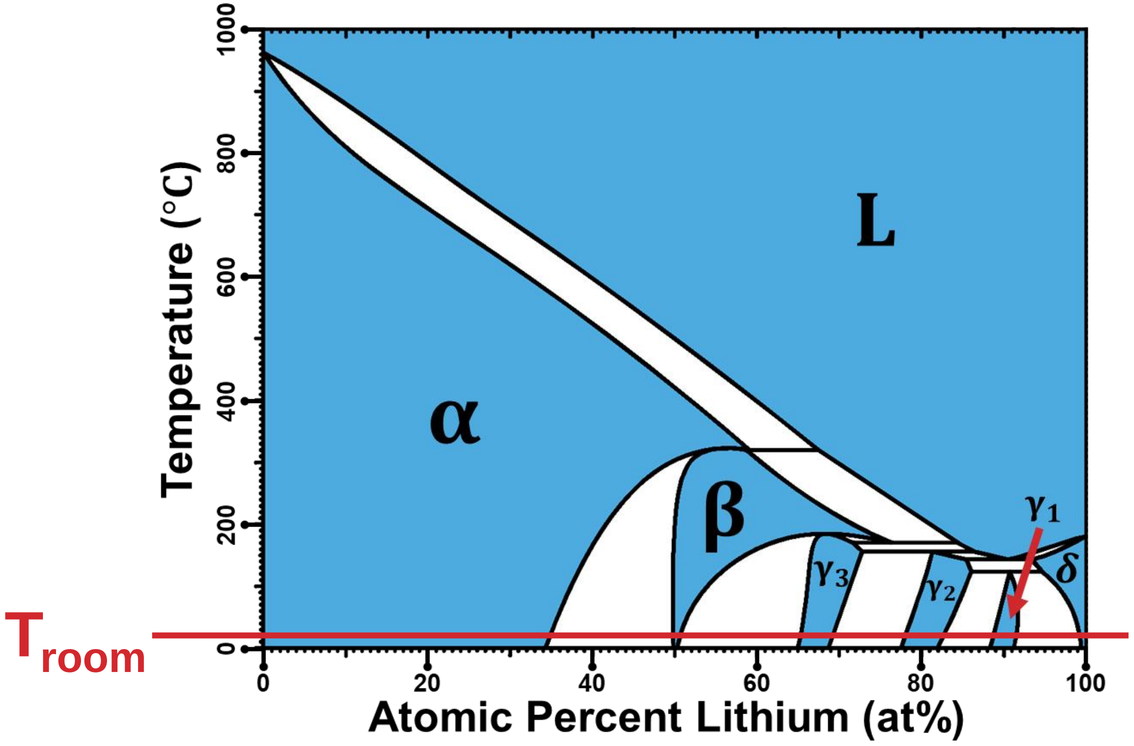
(3)
Microstructure Evolution

Au Model Anode

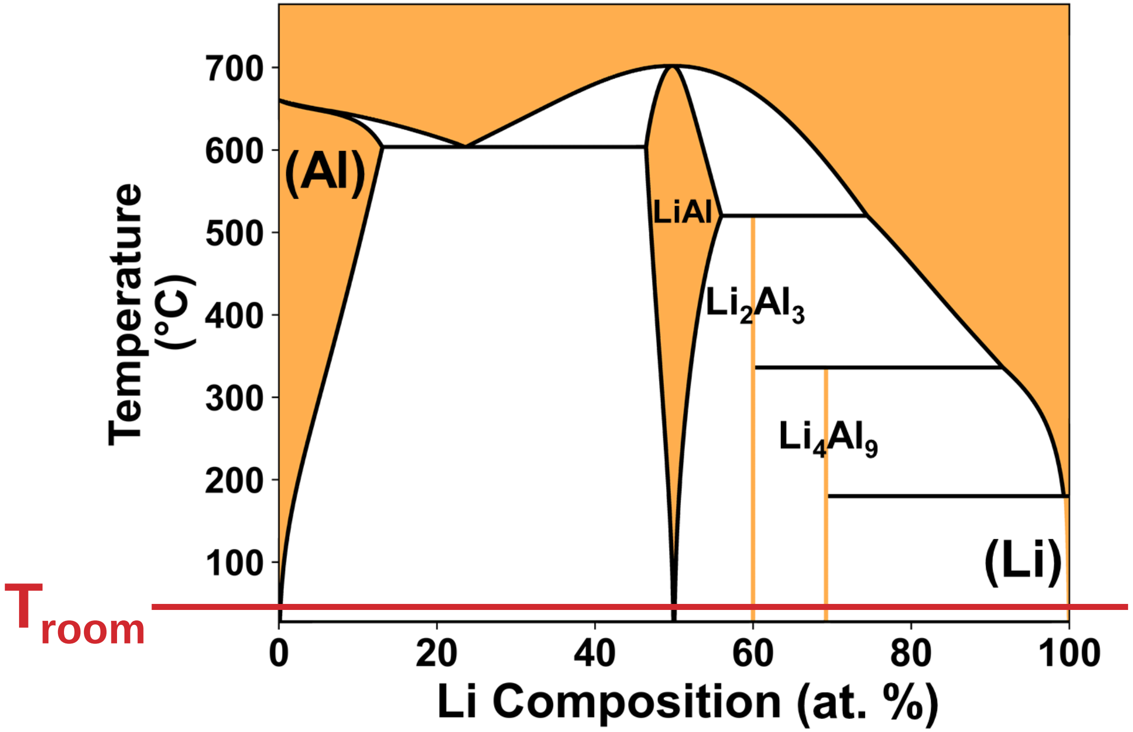
(1) Phase Evolution

Phase Diagrams for Ag and Al as Li-ion Battery Anodes

Ag – Li Phase Diagram



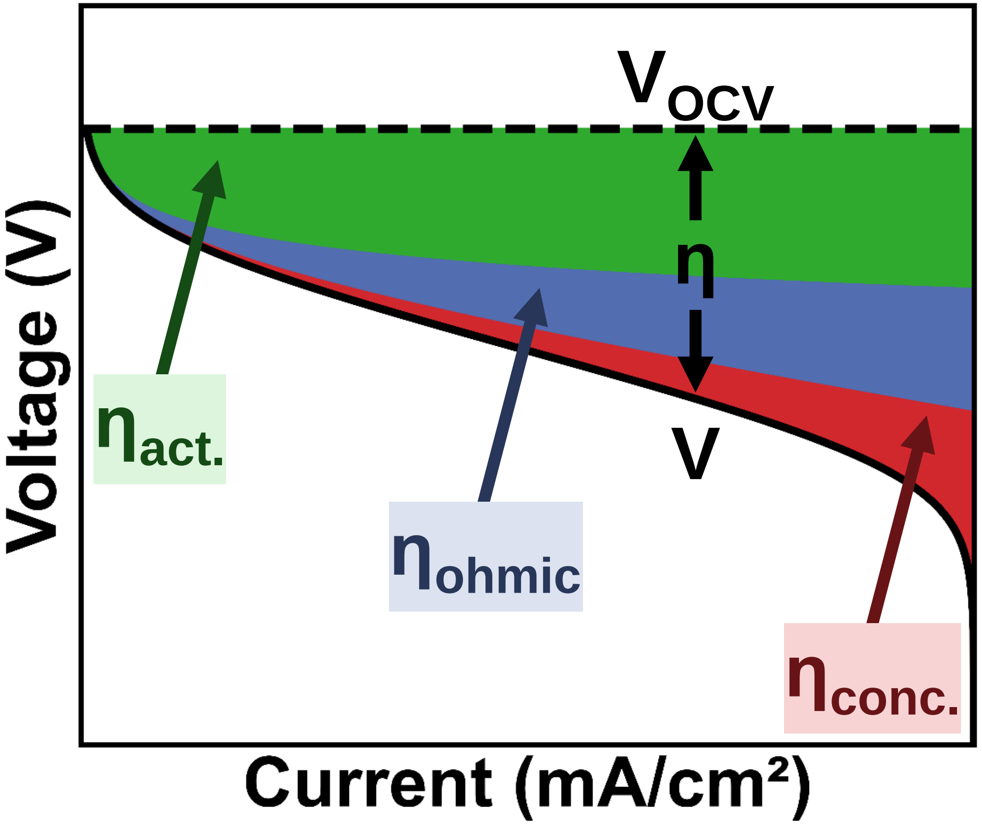
Al – Li Phase Diagram



J. Corsi, …, E. Detsi; **ACS Applied Energy Materials** 5, 4547 (2022)

(1) Phase Evolution

Background (1): Voltage Profile



$$V = V_{OCV} - \eta$$

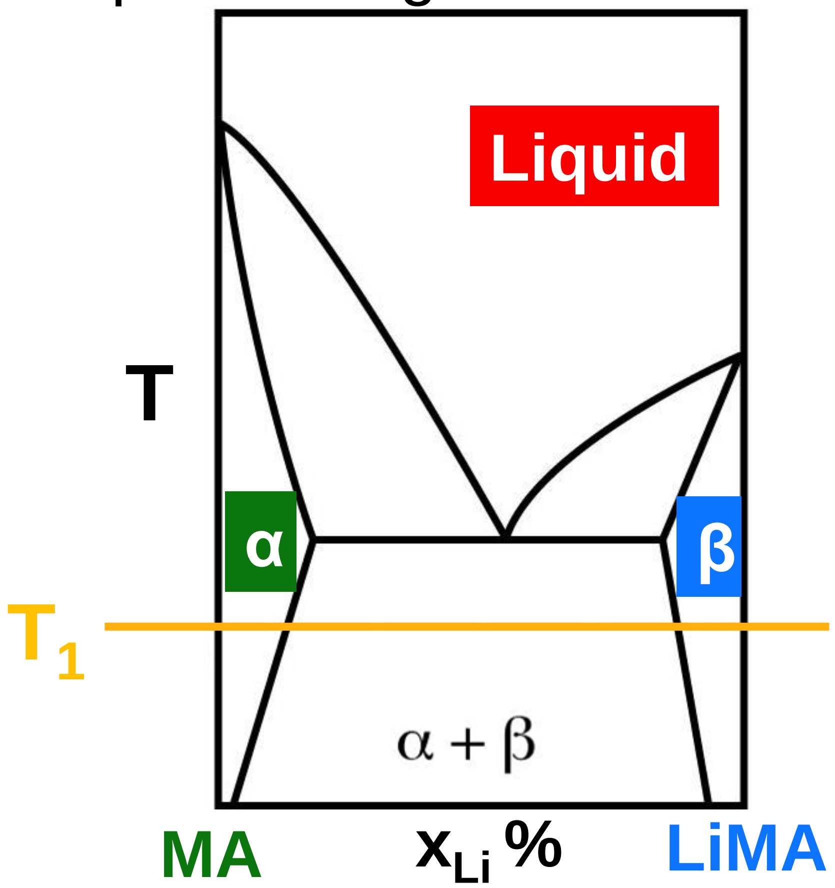
Equilibrium thermodynamic phase stability

Kinetic effects

(1) Phase Evolution

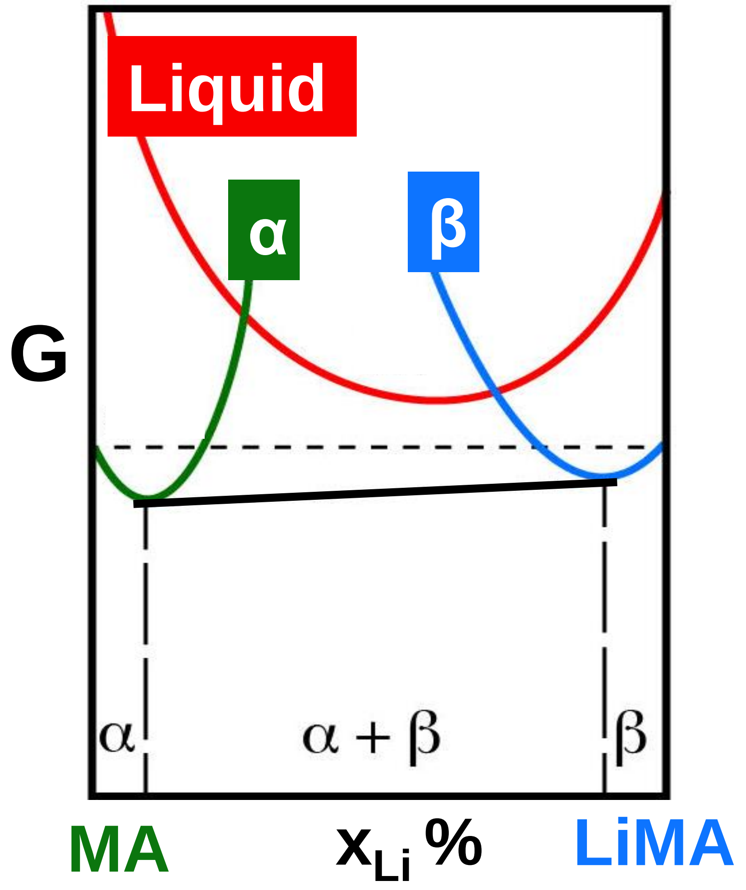
Background (2): From Phase Diagram to Gibbs Free Energy and Voltage Profile

Hypothetical equilibrium phase diagram



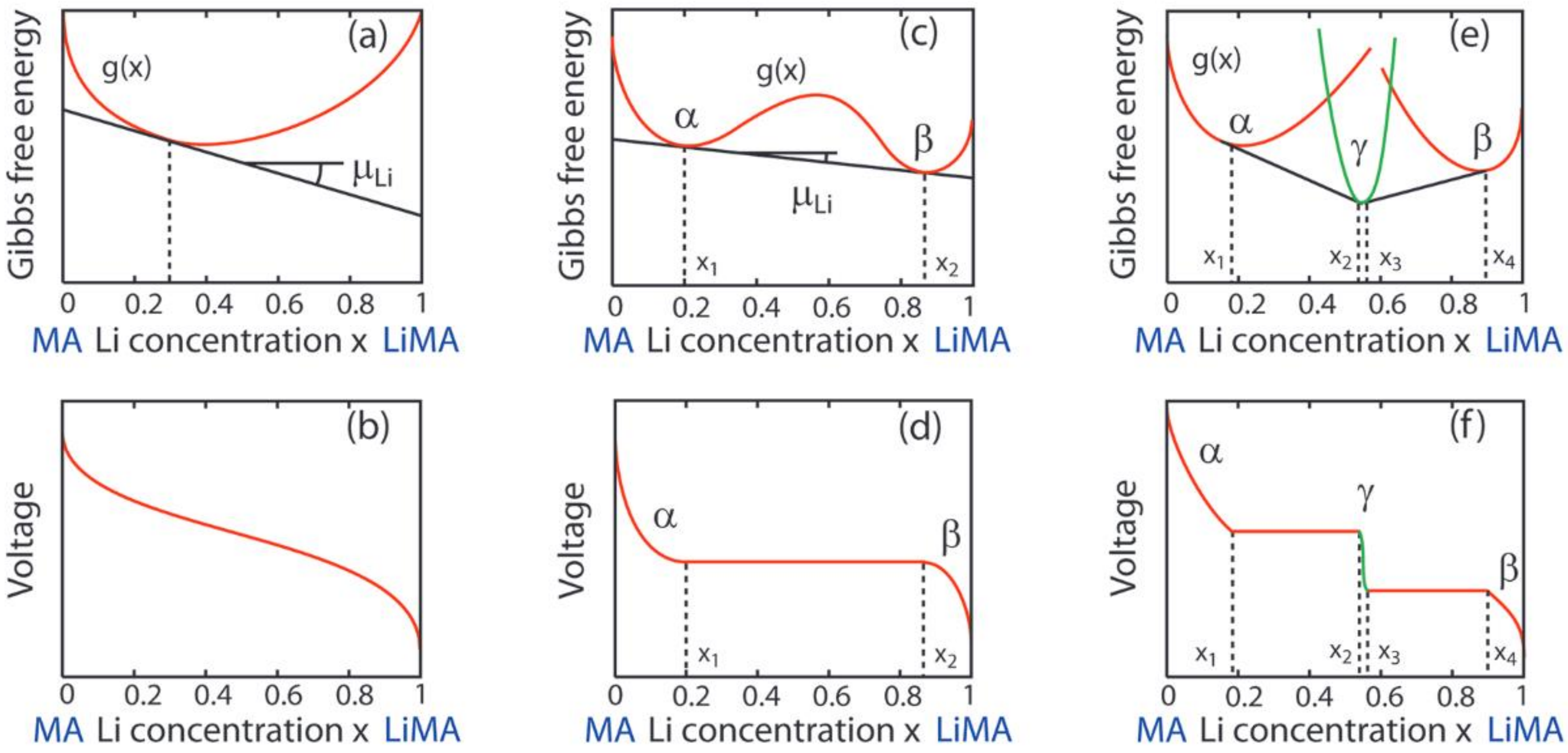
G(x) at T_1

Corresponding free energy curves at T_1



(1) Phase Evolution

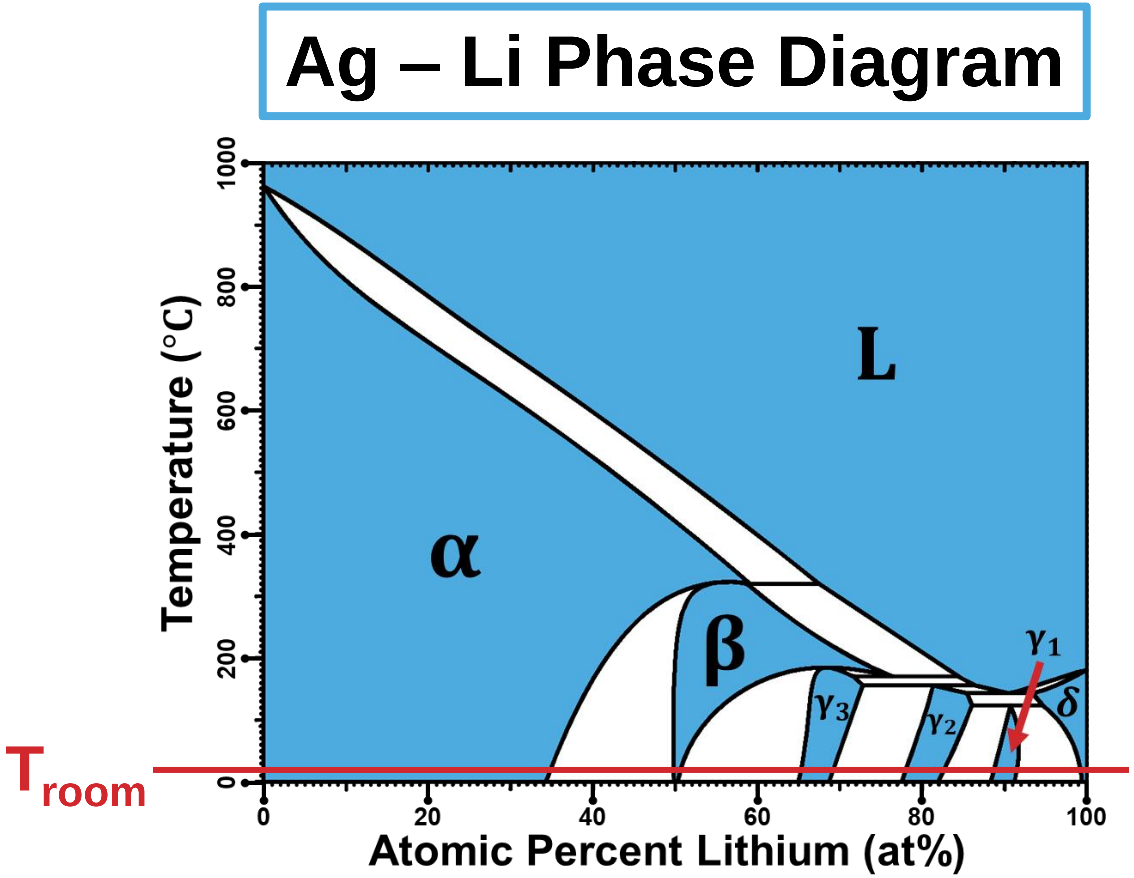
Background (2): From Phase Diagram to Gibbs Free Energy and Voltage Profile



Anton Van der Ven, Jishnu Bhattacharya, and Anna A. Belak: **Acc. Chem. Res.** 46, 1216–1225 (2013)

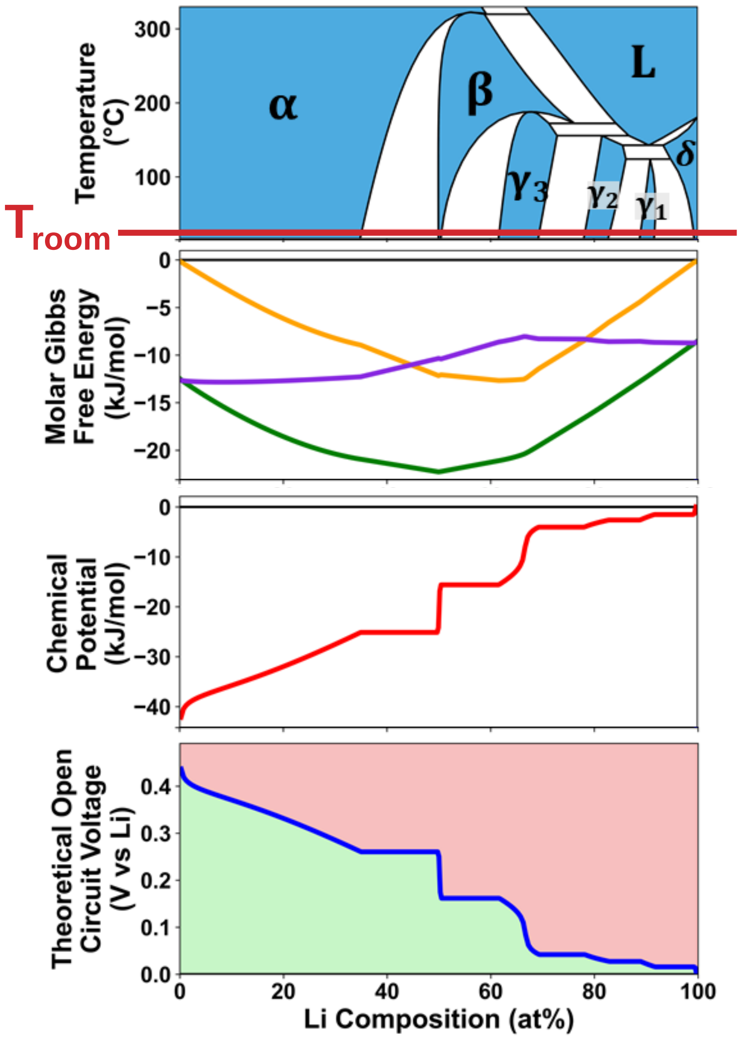
(1) Phase Evolution

Case 1: Ag-Li System



(1) Phase Evolution

Theoretical OCV Profile of Ag-Li System



(1) FactSage™

(2) $\mathbf{G(x) = H(x) - TS(x)}$

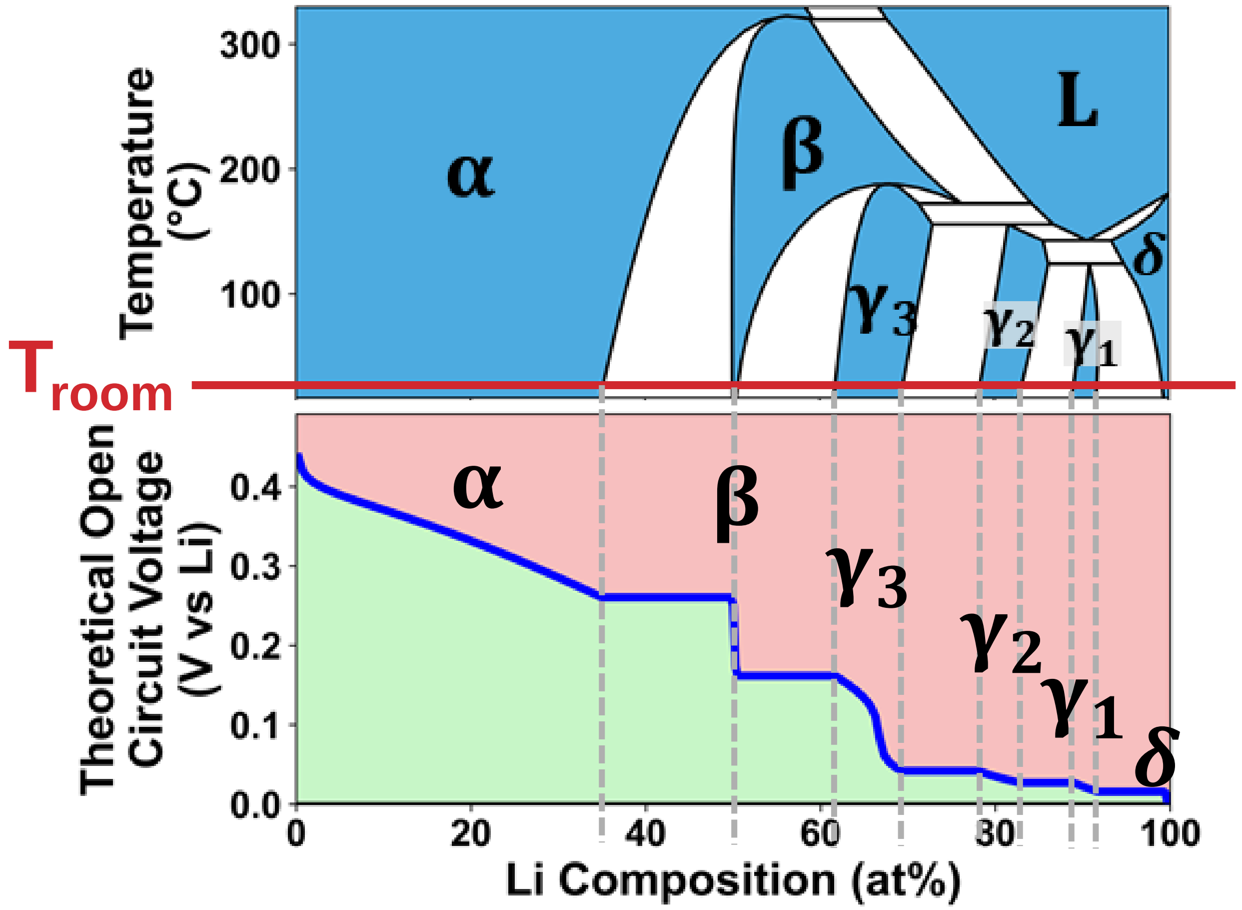
(3) $\mathbf{\Delta\mu_{Li} = \mu_{Li}(x) - \mu^{o}_{Li}}$

(4) $\mathbf{E_{OCV} = -\frac{\Delta\mu_{Li}}{zF}}$

J. Corsi, …, E. Detsi;
ACS Applied Energy Materials 5, 4547 (2022)

(1) Phase Evolution

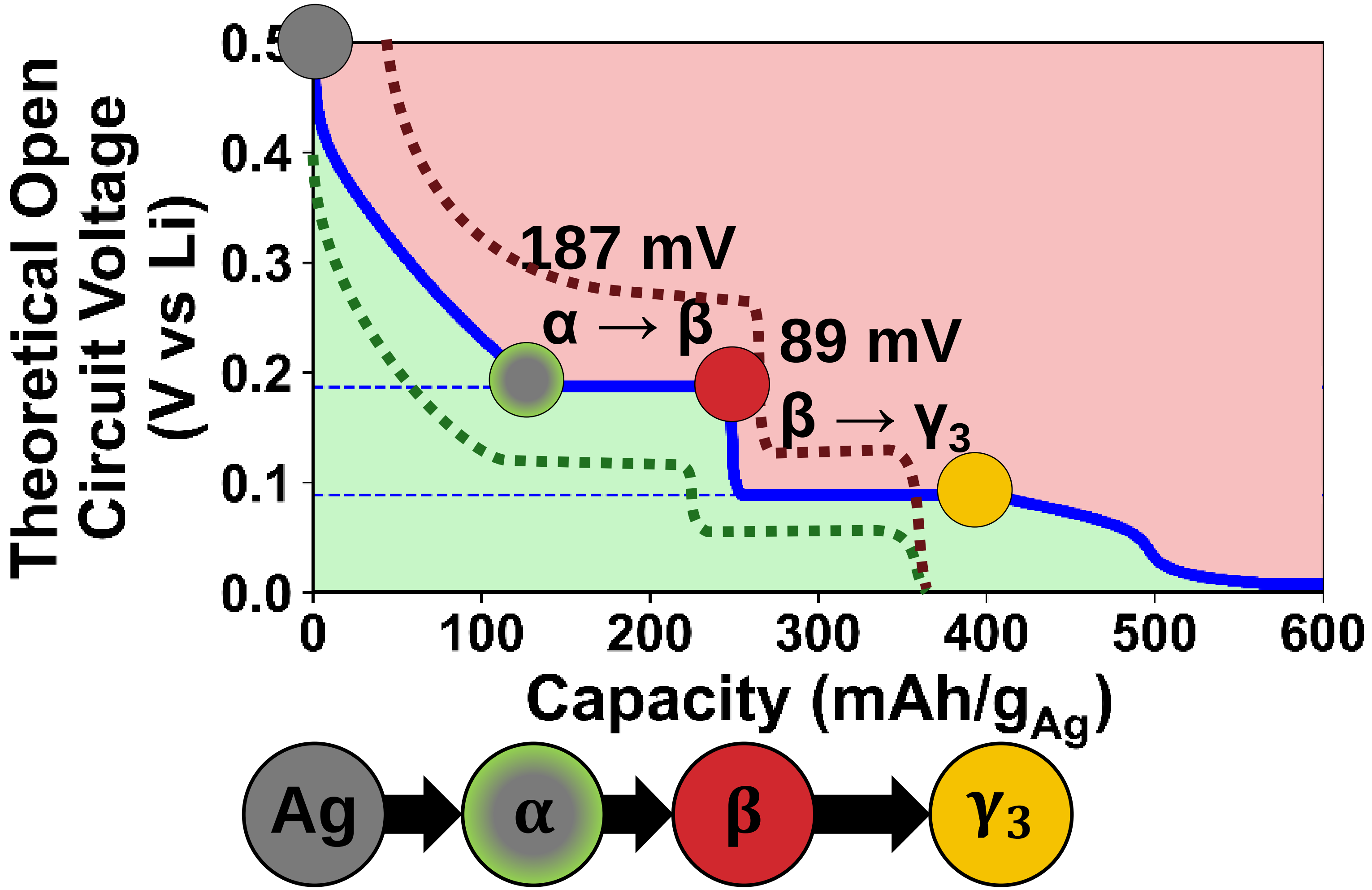
Theoretical OCV Profile of Ag-Li System



J. Corsi, …, E. Detsi; **ACS Applied Energy Materials** 5, 4547 (2022)

(1) Phase Evolution

Theoretical OCV Profile of Ag-Li System



J. Corsi, …, E. Detsi;
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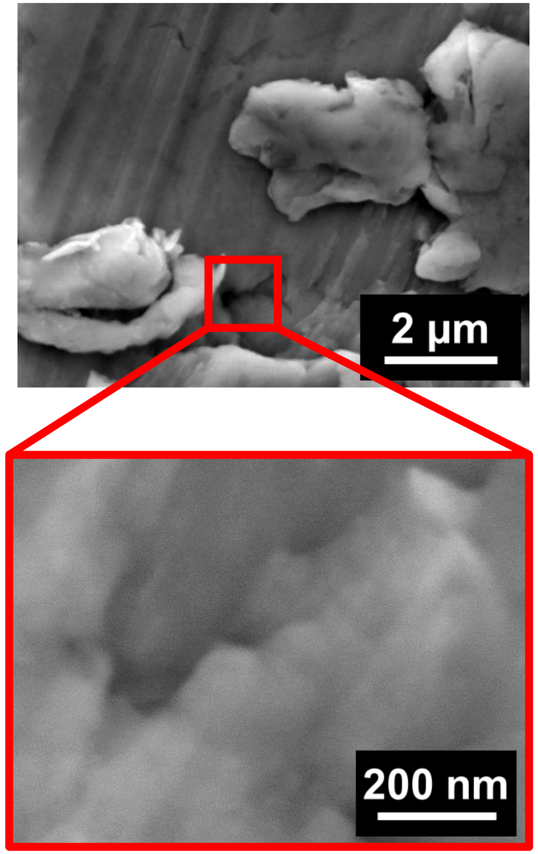
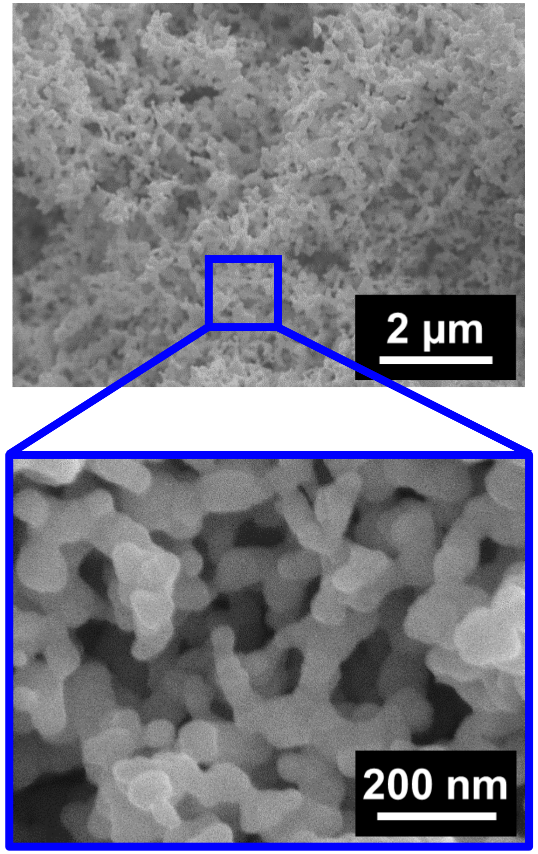
(1) Phase Evolution

Two Different Ag Morphologies Considered

Bulk



Nano

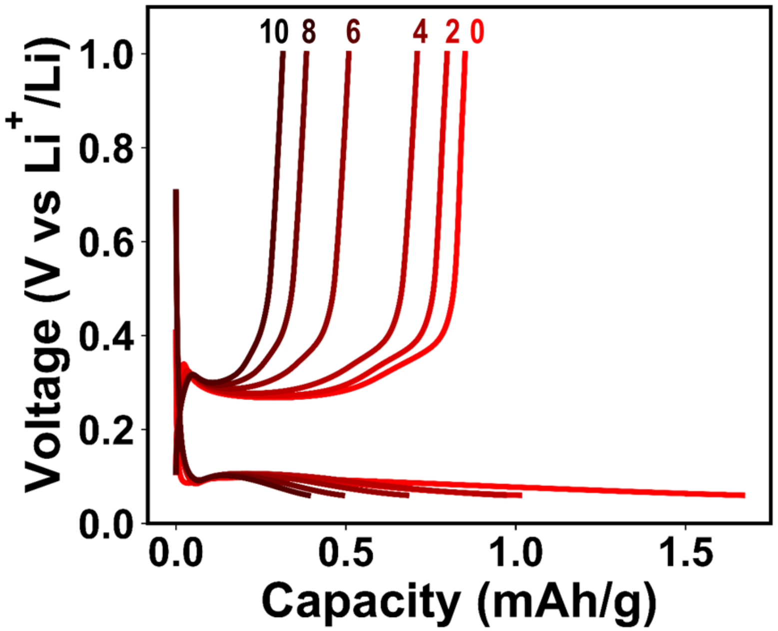


J. Corsi, …, E. Detsi;
ACS Applied Energy Materials 5, 4547 (2022)

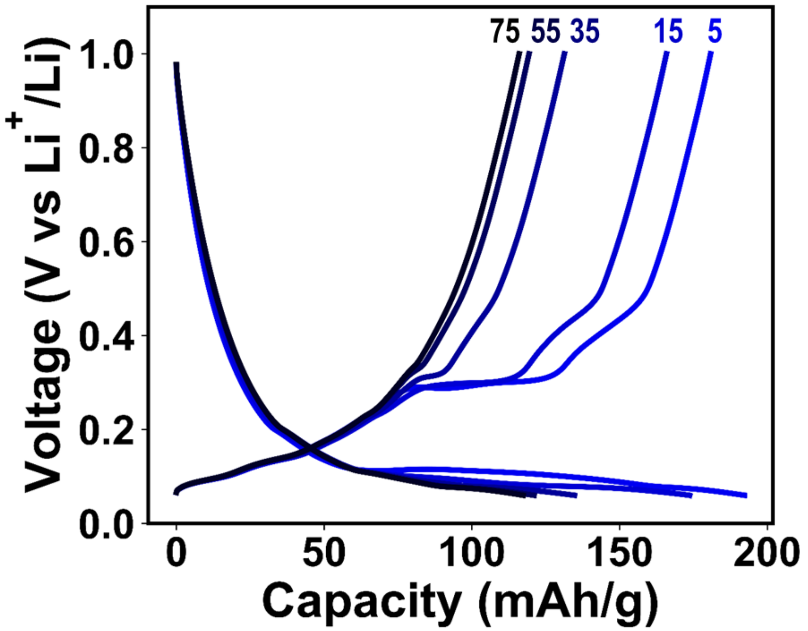
(1) Phase Evolution

Bulk vs Nanoporous Ag Cycling Performance

Bulk



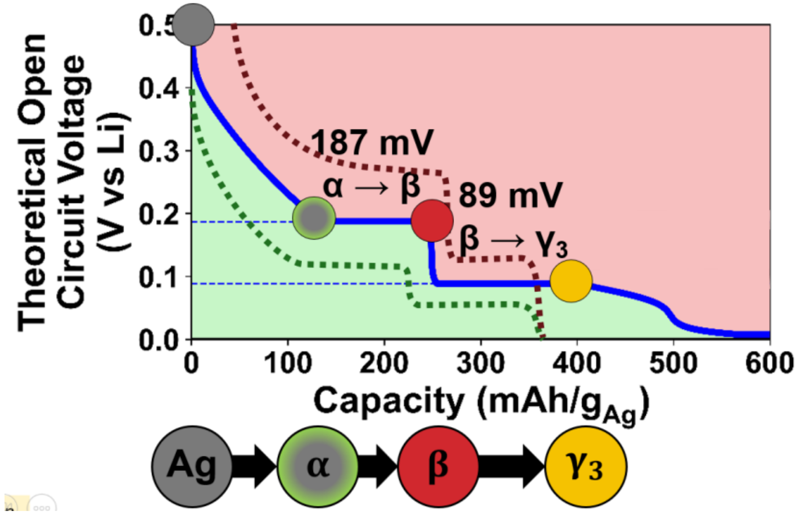
Nano



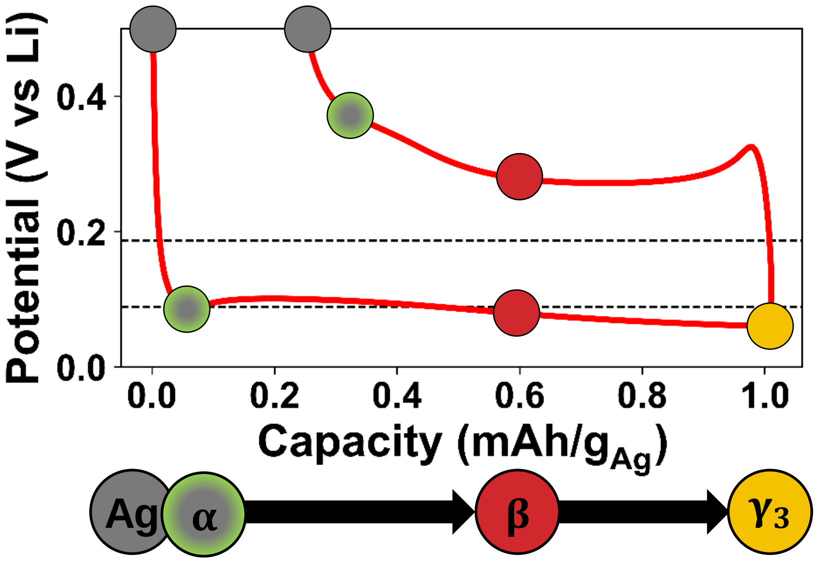
J. Corsi, …, E. Detsi; **ACS Applied Energy Materials** 5, 4547 (2022)

(1) Phase Evolution

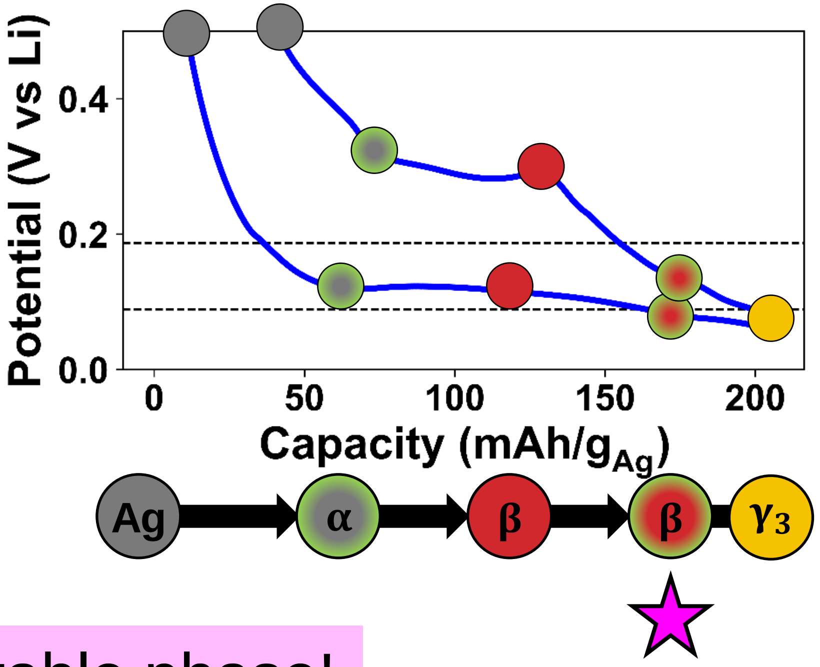
Experimental Voltage Profile of Ag-Li System



Bulk Ag

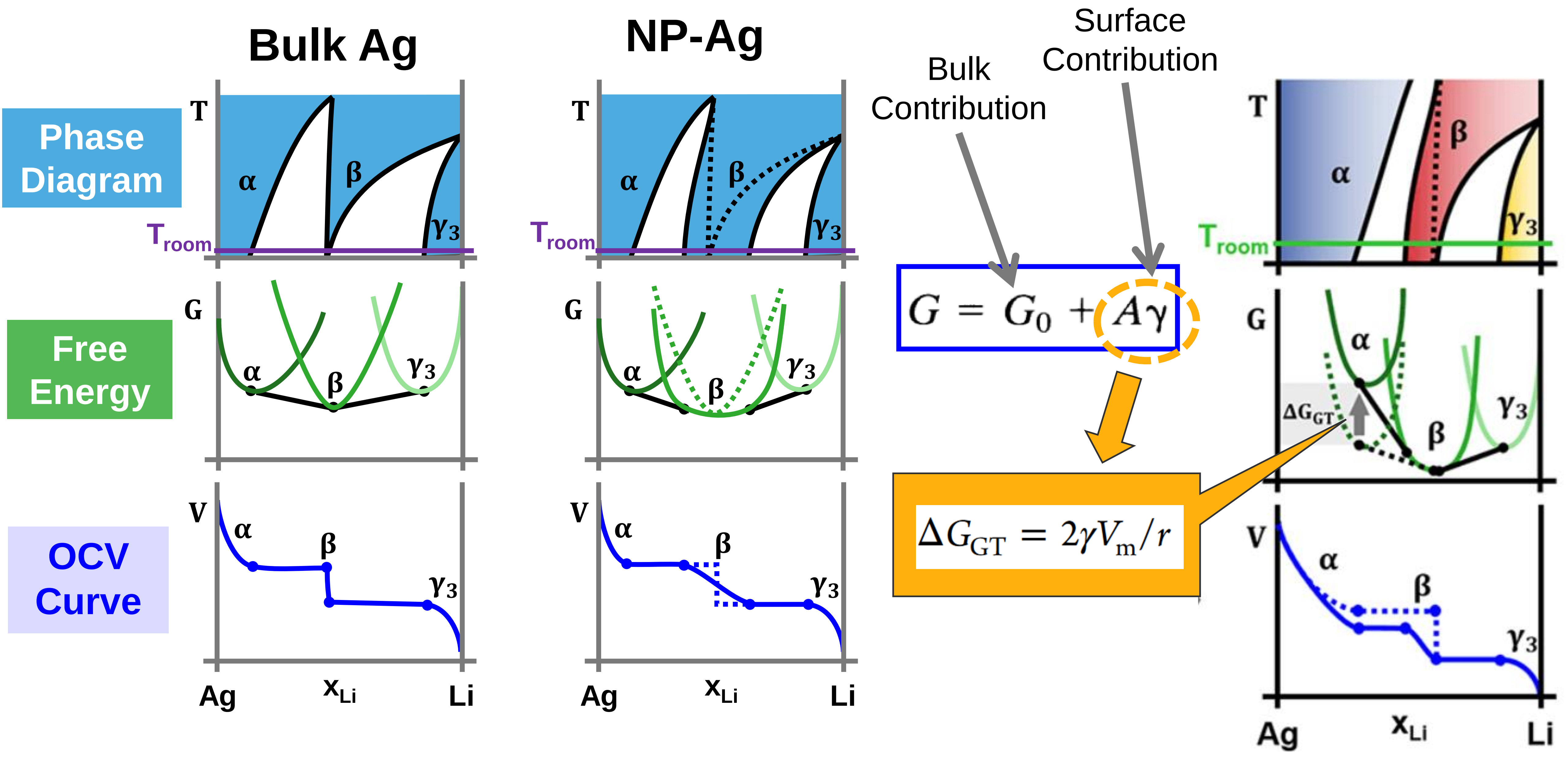


Nano Ag



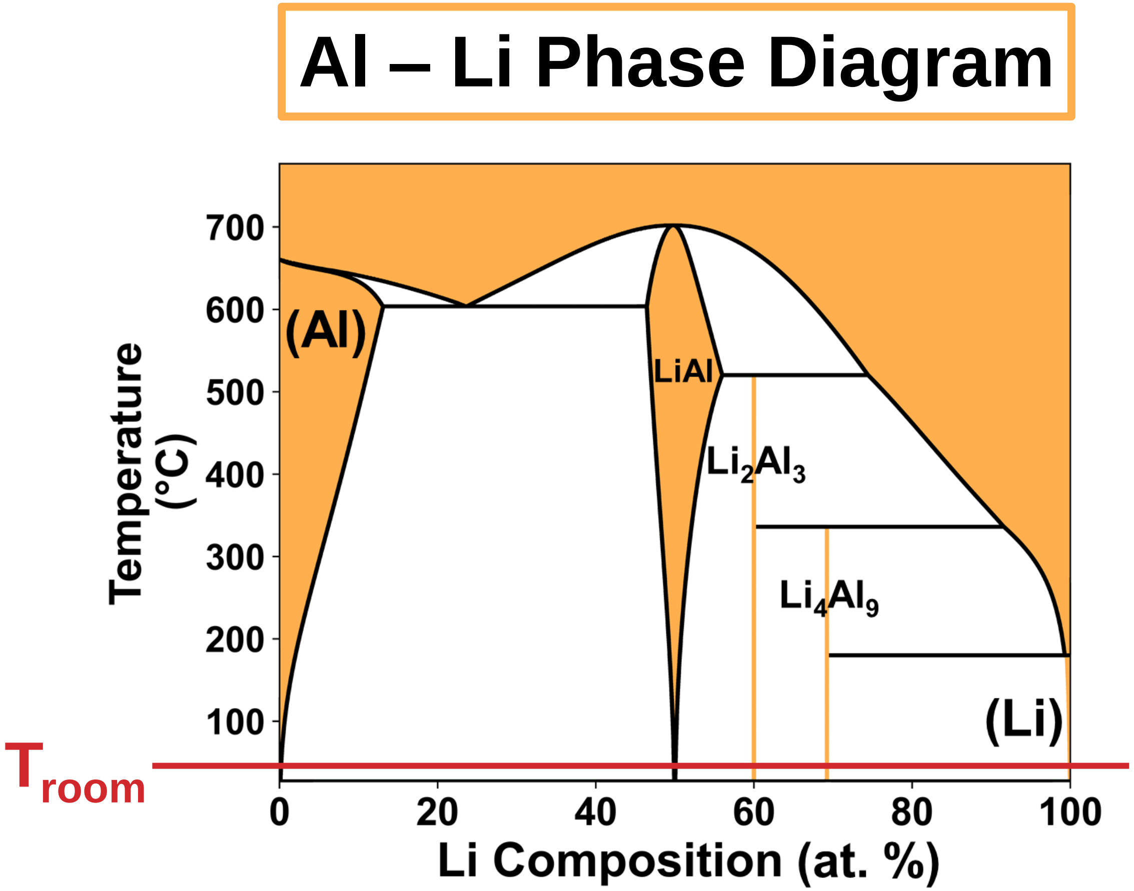
Nanostructure causes formation of metastable phase!

(1) Phase Evolution



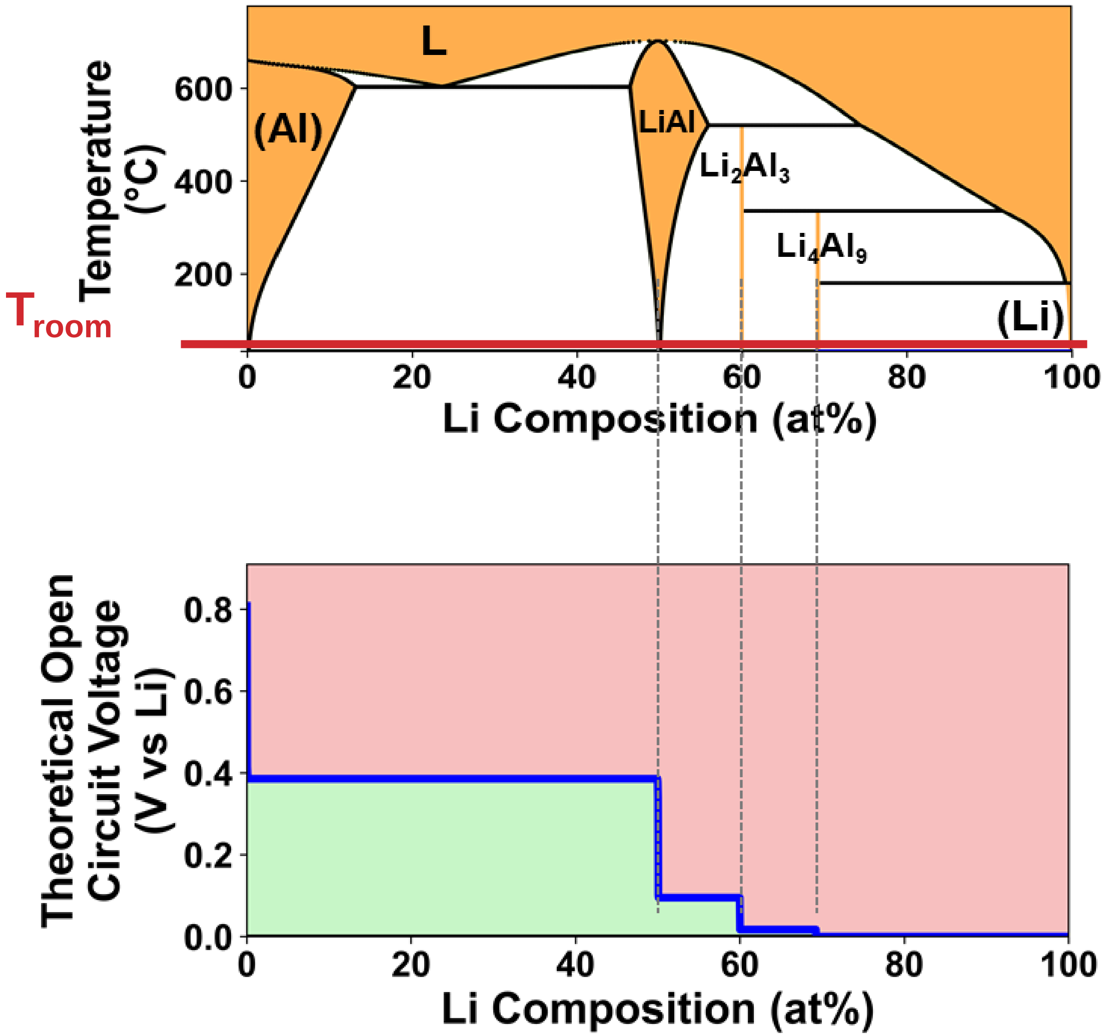
(1) Phase Evolution

Case 2: Al-Li System



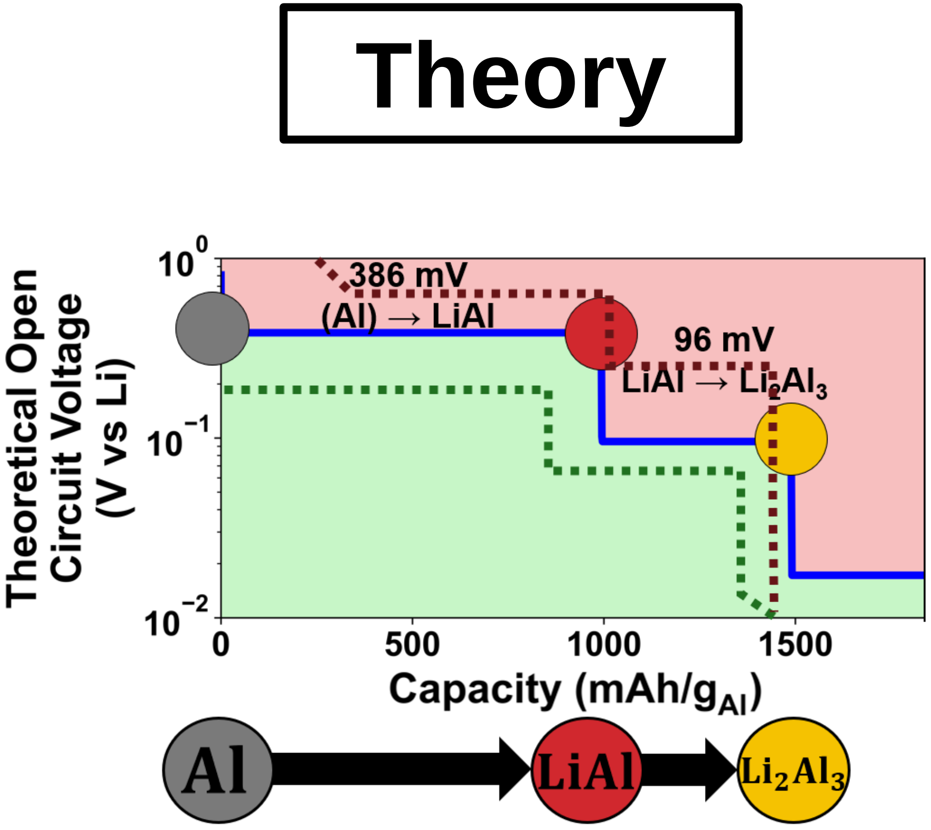
(1) Phase Evolution

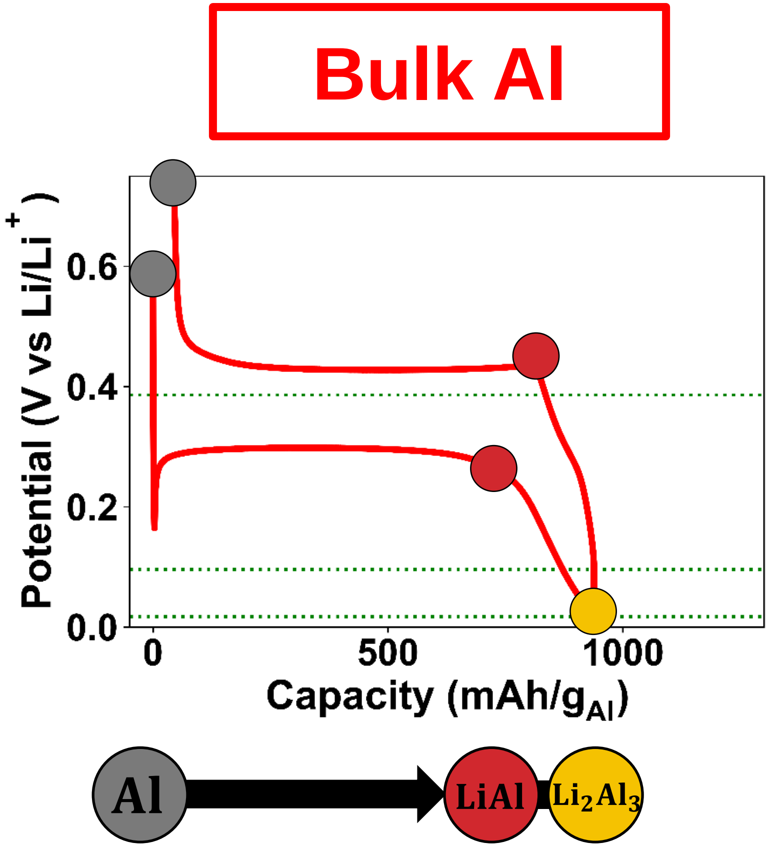
Theoretical OCV Profile of Al-Li System

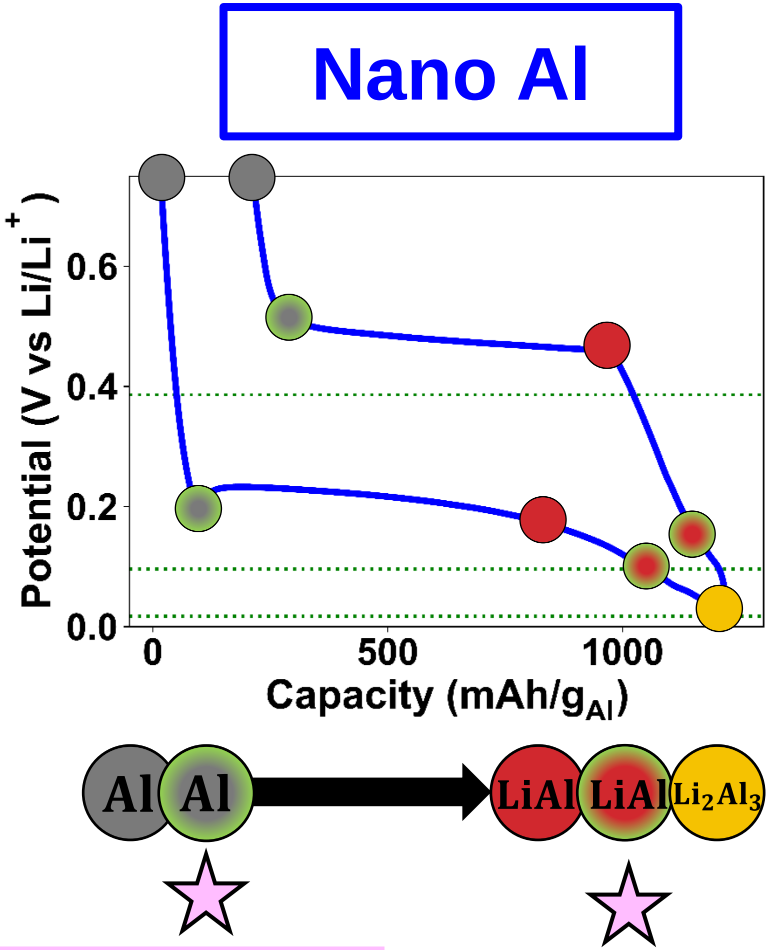


(1) Phase Evolution

Experimental Voltage Profile of Al-Li System







Nanostructure causes formation of metastable phase!

(1) Phase Evolution

Summary

Structure

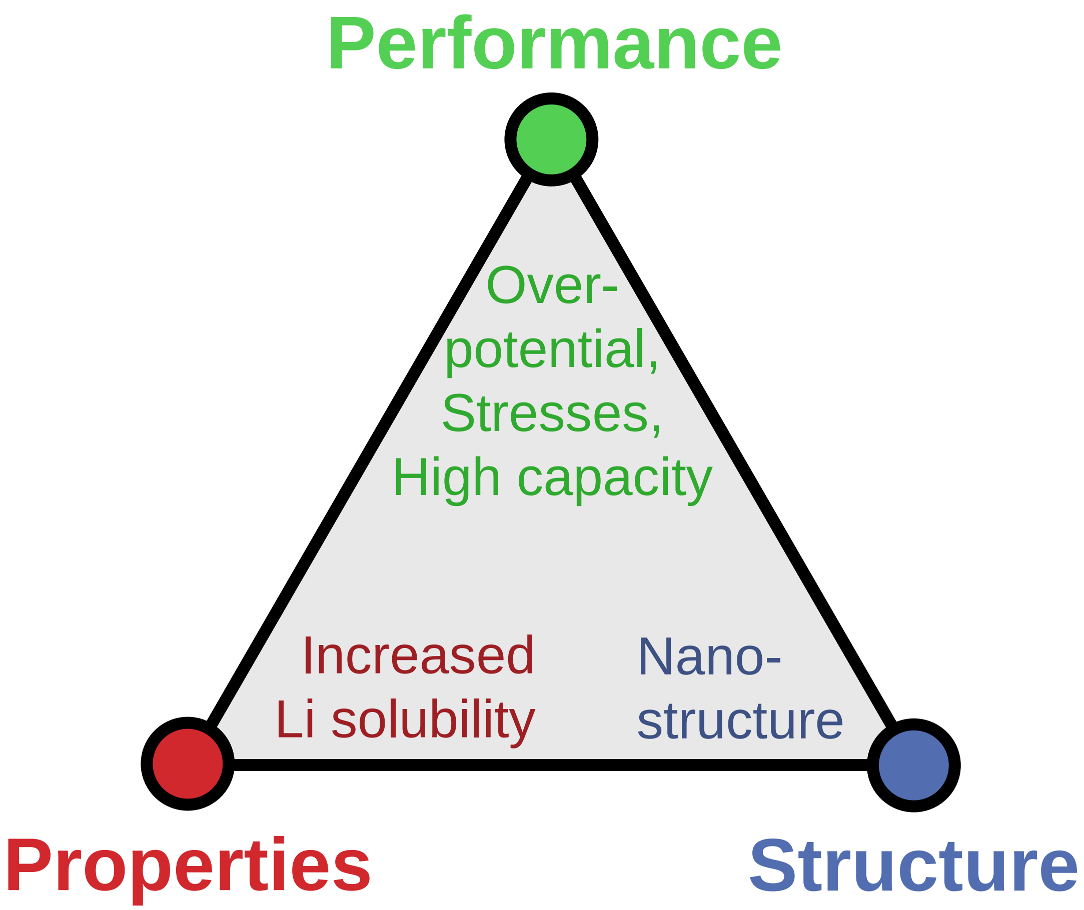
- Bulk vs. nanoporous anodes

Properties

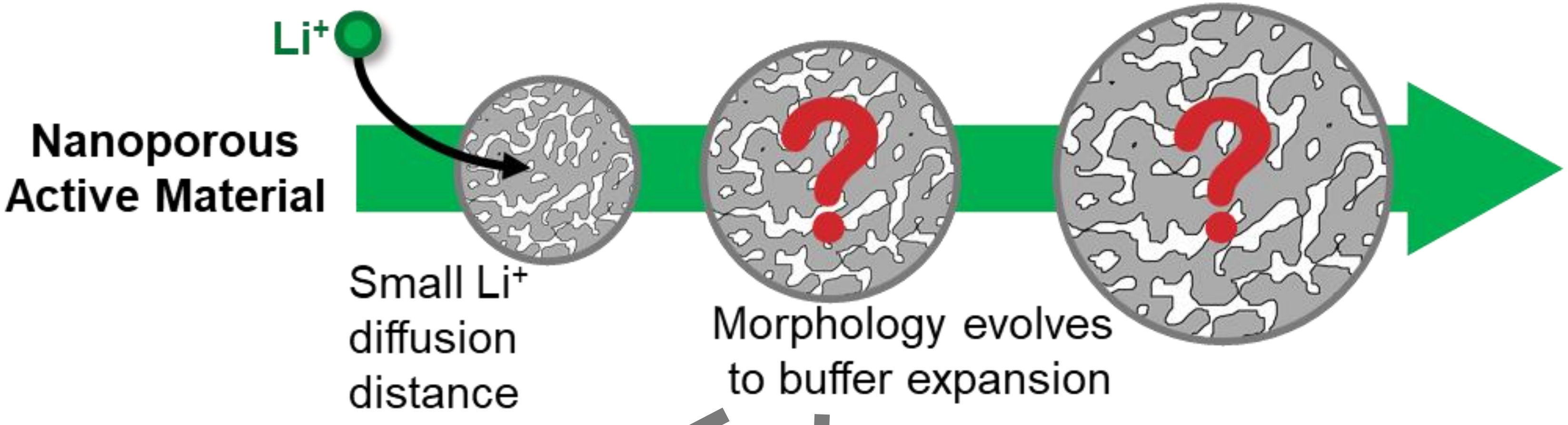
- Bulk anodes follow OCV simulation
- Nanoporous anodes have metastable phases

Performance

- Nanoporous anodes have enhanced capacity
- Metastable phases cause overpotential, stresses



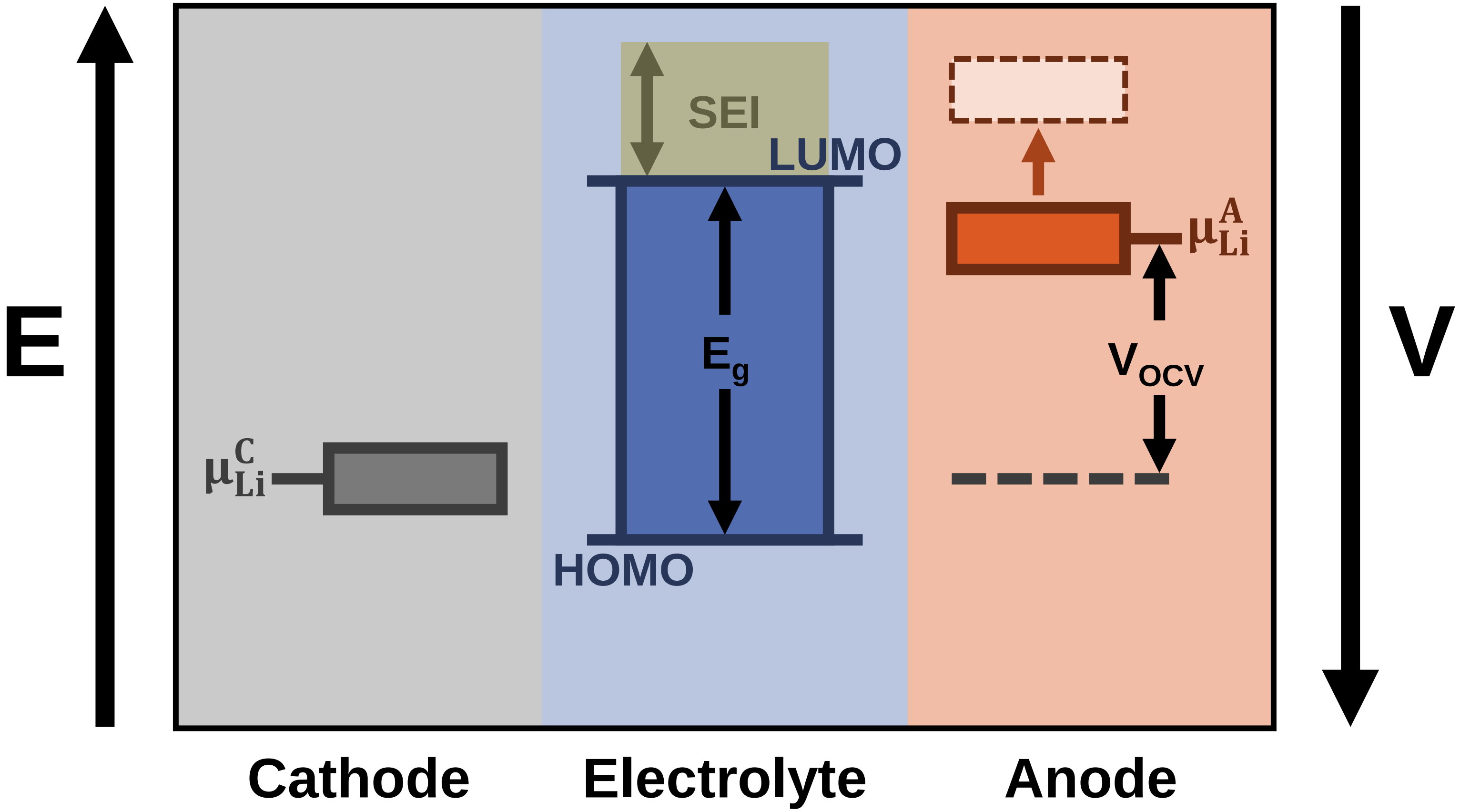
Morphology Evolution During Reversible Li Storage



(1) Phase Evolution	(2) Solid Electrolyte Interphase Evolution	(3) Microstructure Evolution
Ag & Al Model Anodes	Au Model Anode	Au Model Anode

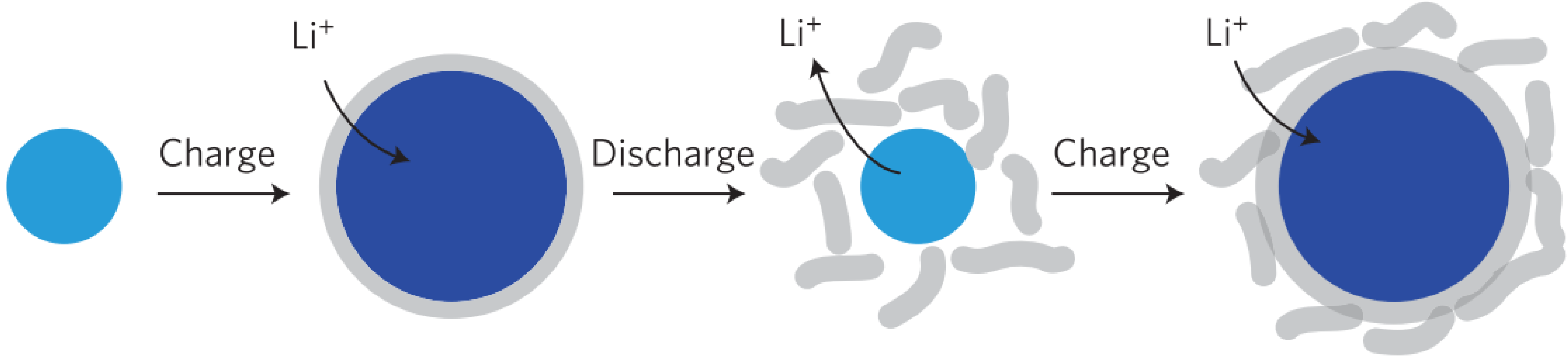
(2) SEI Evolution

Formation of solid electrolyte interphase (SEI)



(2) SEI Evolution

Alloy anode SEI model for dense materials



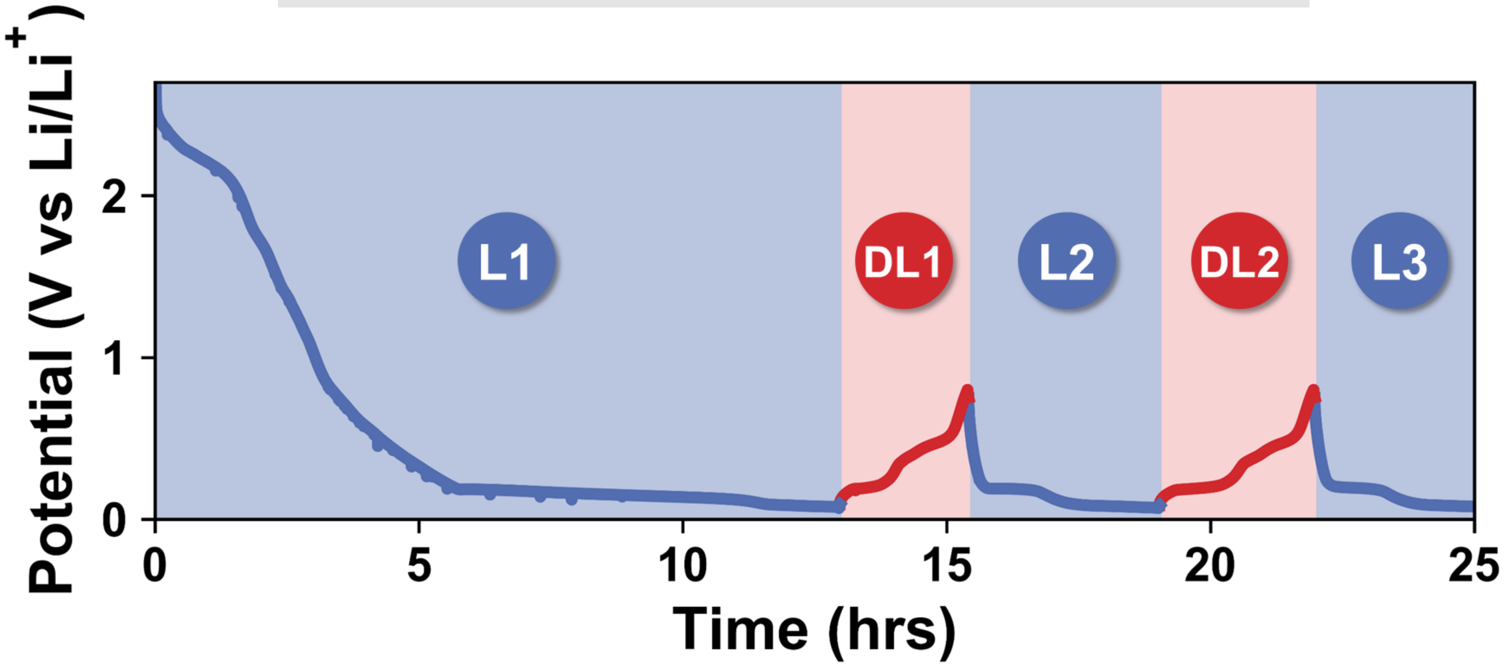
<u>Key question:</u> Does this model apply to **nanoporous** anode materials?

Wu et al: **Nat. Nanotechnol.** 7, (2012)

(2) SEI Evolution

Sequential Lithiation-Delithiation Cycling

Sequential charge states explored



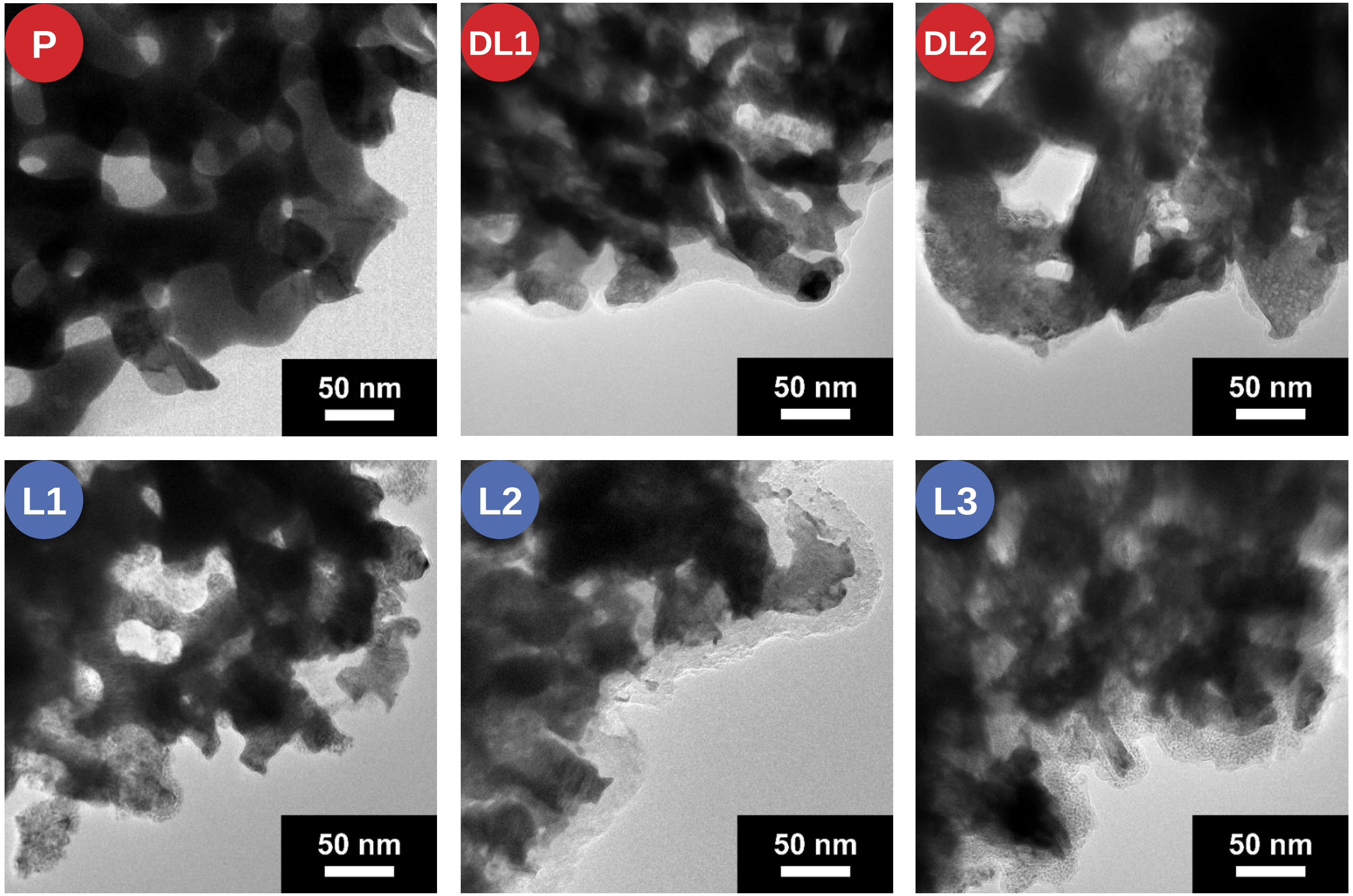
J.S. Corsi, S.S. Welborn, E. Stach, E. Detsi; **ACS Energy Letters**. 6, (2021)

(2) SEI Evolution

TEM Characterization of SEI Evolution

Delithiation:
SEI fractures

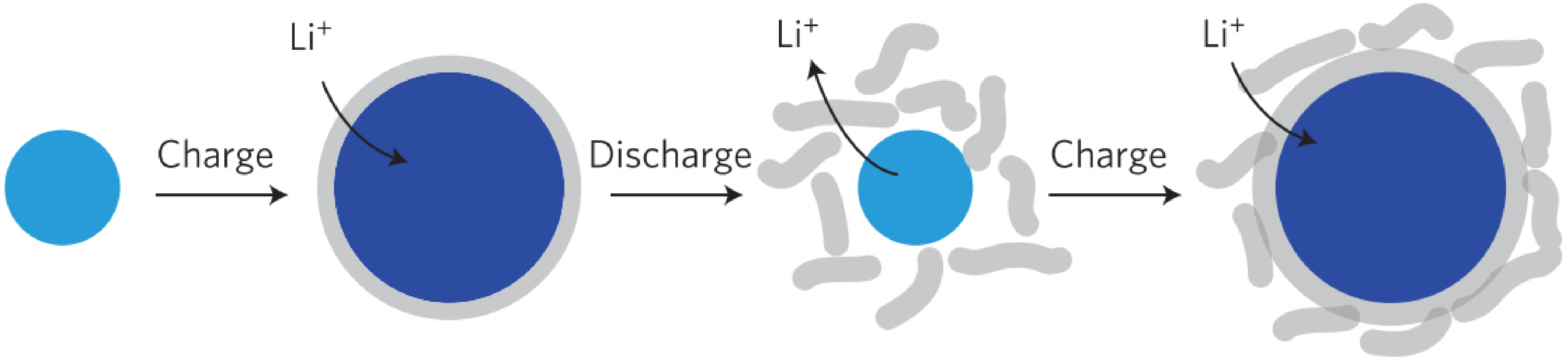
Lithiation:
Thick SEI grows



J.S. Corsi, S.S. Welborn, E. Stach, E. Detsi; **ACS Energy Letters**. 6, (2021)

(2) SEI Evolution

Conclusion

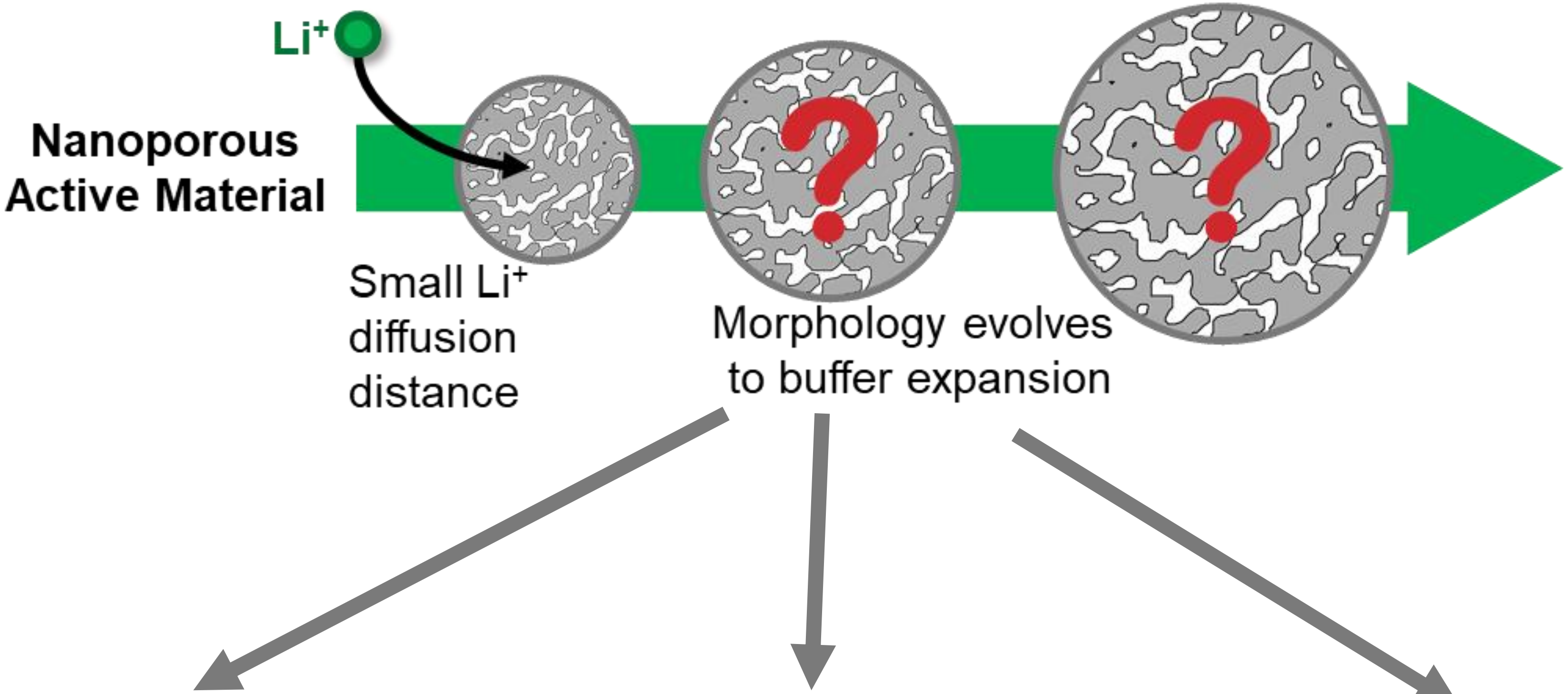


<u>Model confirmed for nanoporous materials:</u>

- Thick SEI which grows in thickness with cycling
- SEI delamination during delithiation

Dramatic SEI growth/fracture likely to impart stress on active material

Morphology Evolution During Reversible Li Storage



(1)
Phase Evolution

Ag & Al Model Anodes

(2)
Solid Electrolyte Interphase Evolution

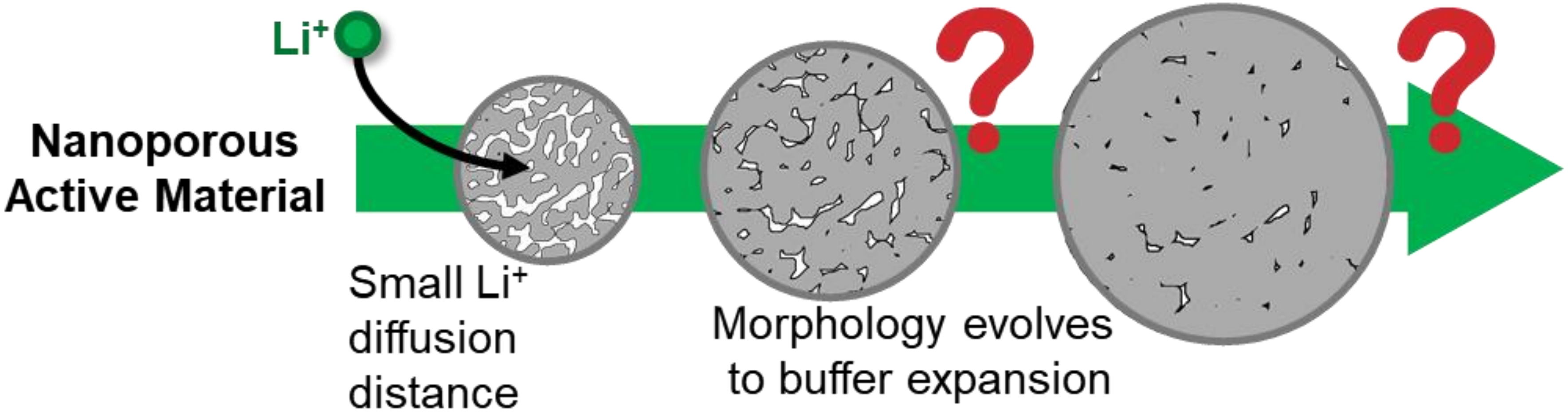
Au Model Anode

(3)
Microstructure Evolution

Au Model Anode

(3) Microstructure Evolution

NP-Au as Model Anode for Investigation



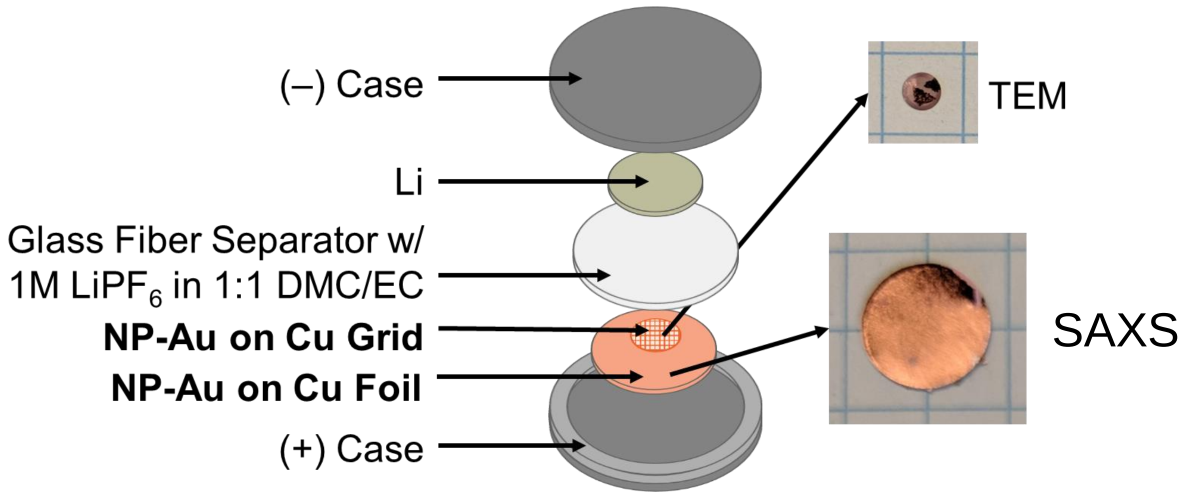
NP-Au is used as a model anode for this investigation:

- Model nanoporous metal
- Au has high contrast TEM images
- NP-Au has strong SAXS peak signature

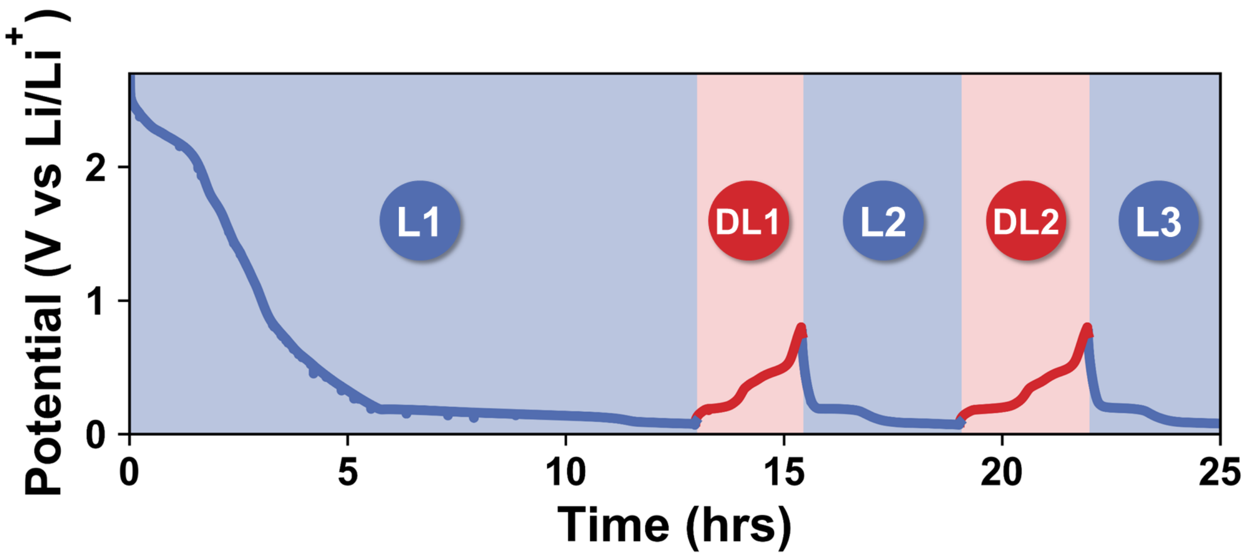
(3) Microstructure Evolution

Sequential Charge States Explored

Grid-in-a-coin cell configuration



Sequential charge states explored



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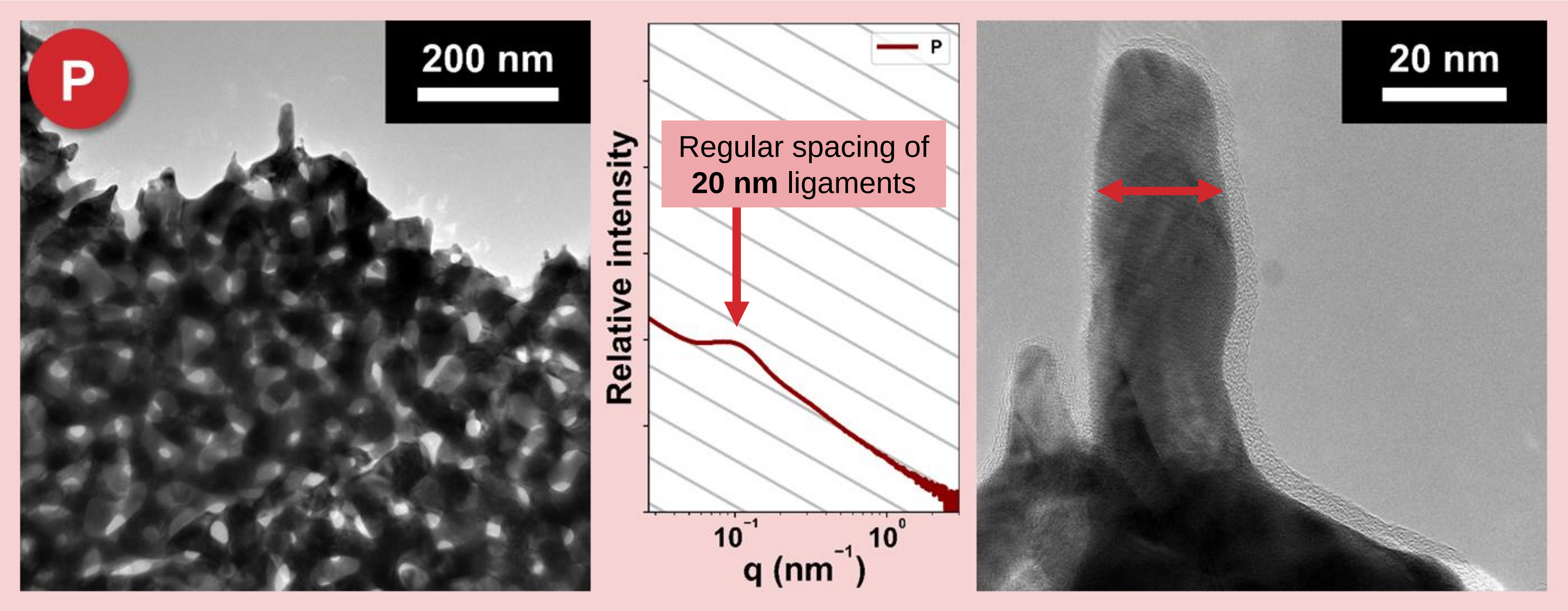
(3) Microstructure Evolution

Pristine (P)



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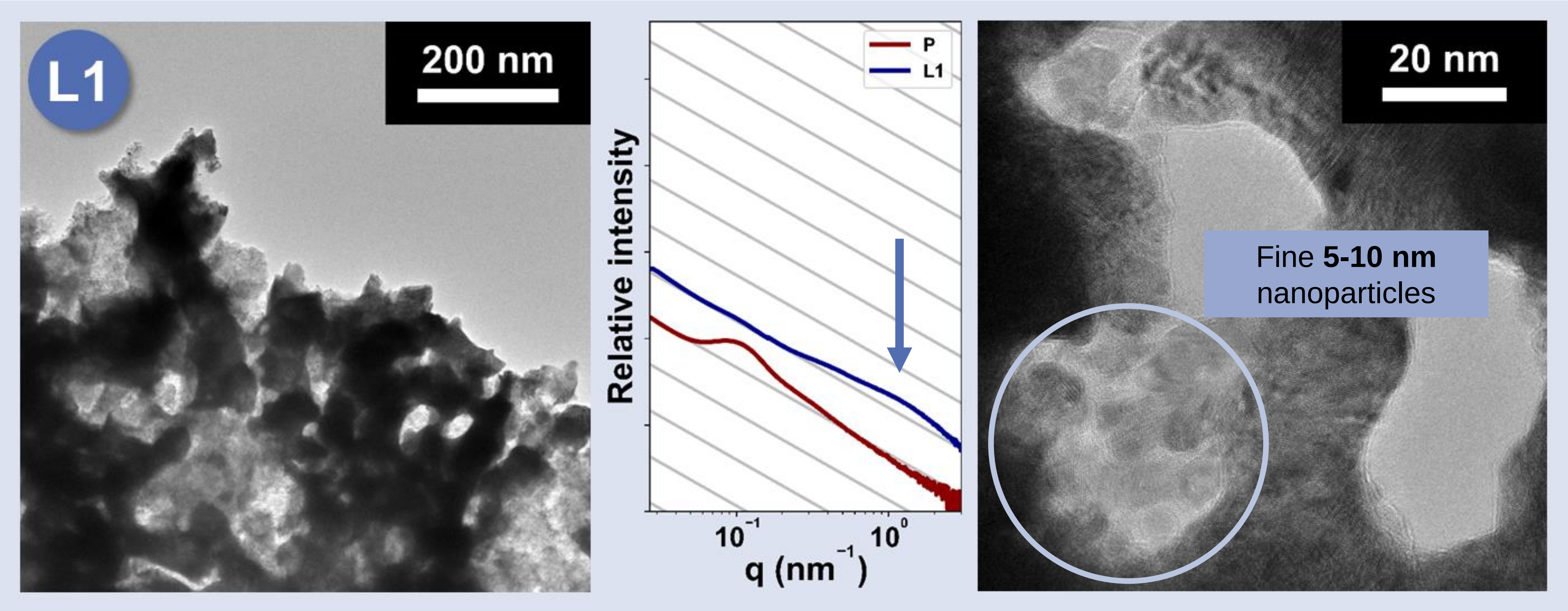
(3) Microstructure Evolution

First Lithiation (L1)



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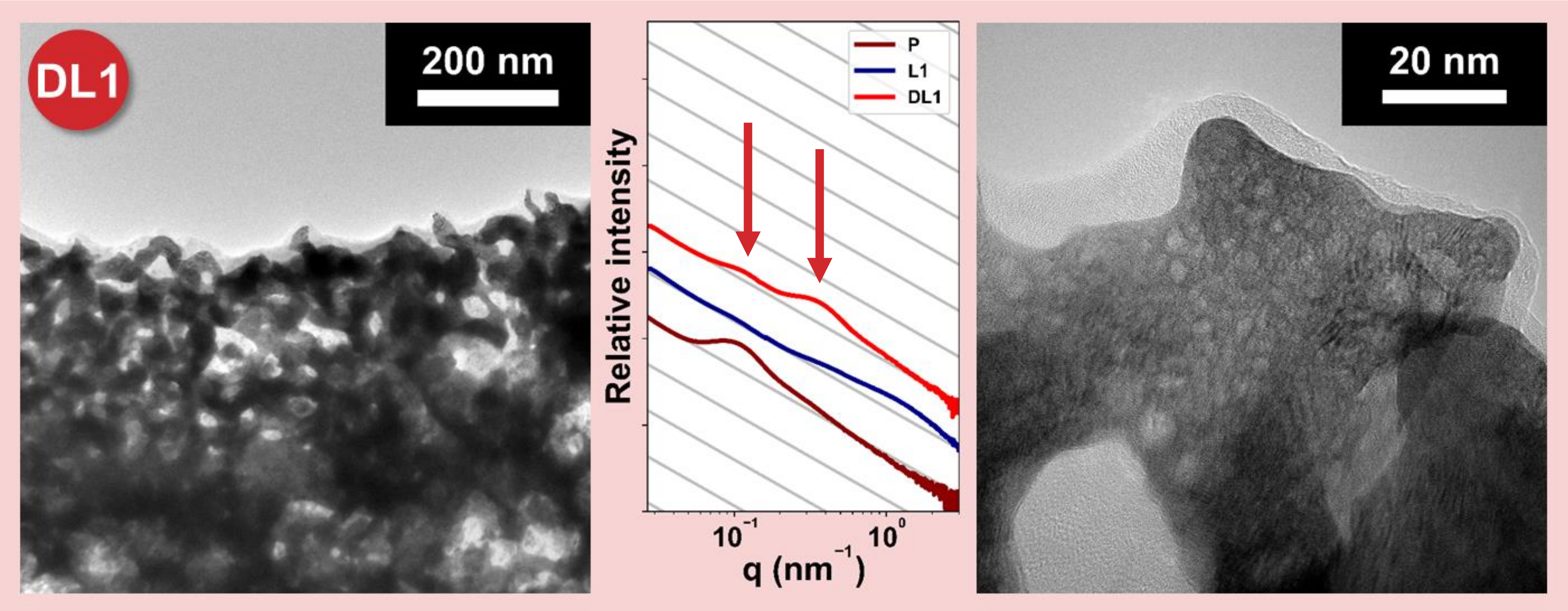
(3) Microstructure Evolution

First Delithiation (DL1)



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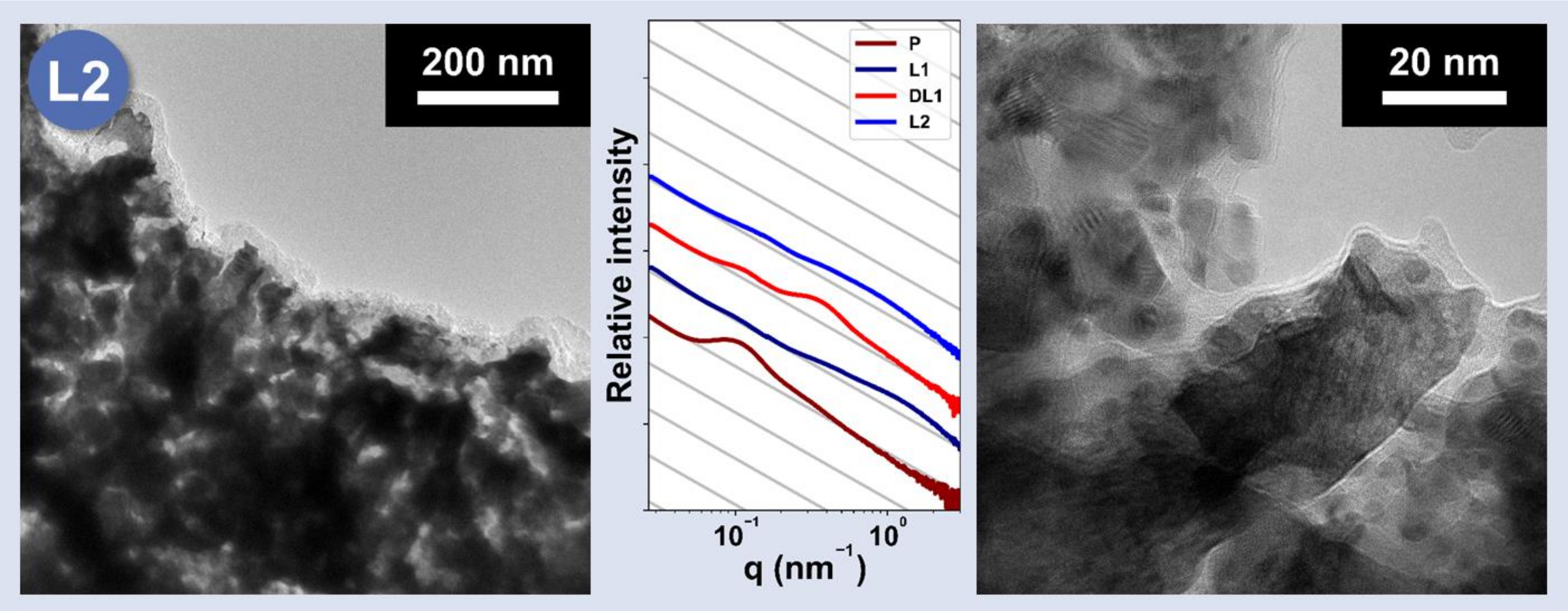
(3) Microstructure Evolution

Second Lithiation (L2)



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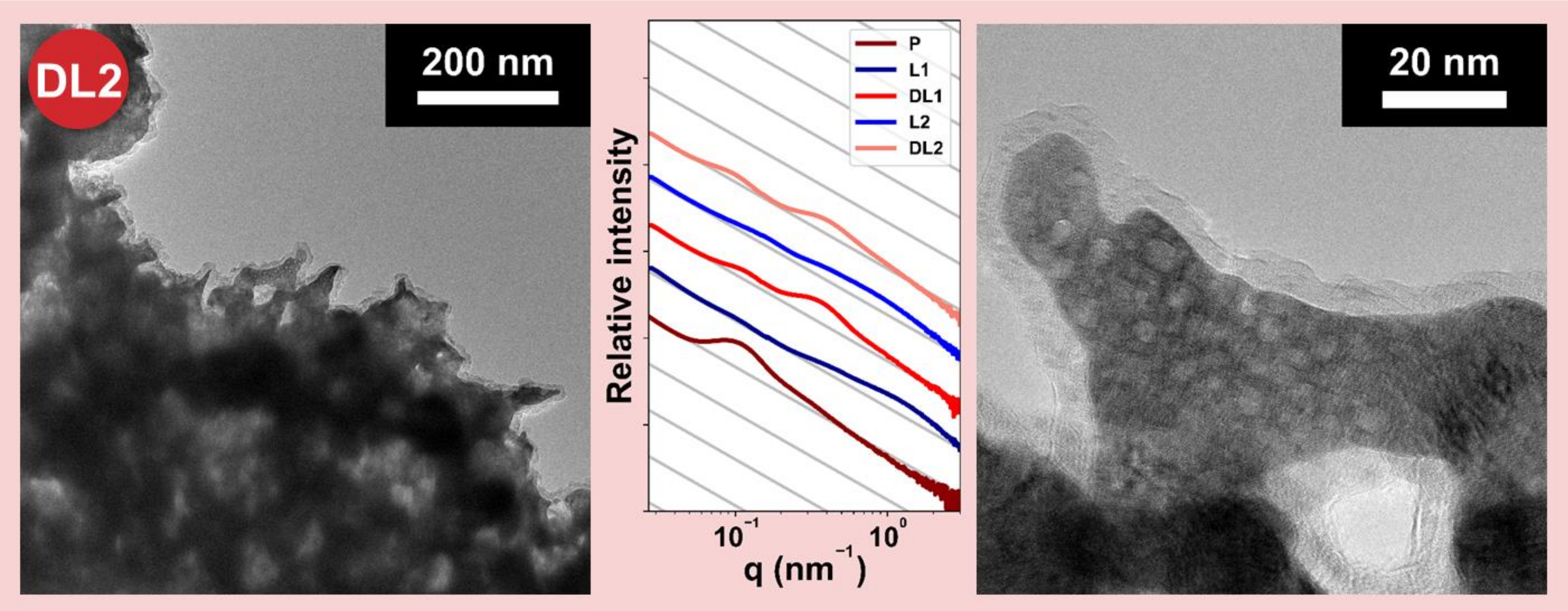
(3) Microstructure Evolution

Second Delithiation (DL2)



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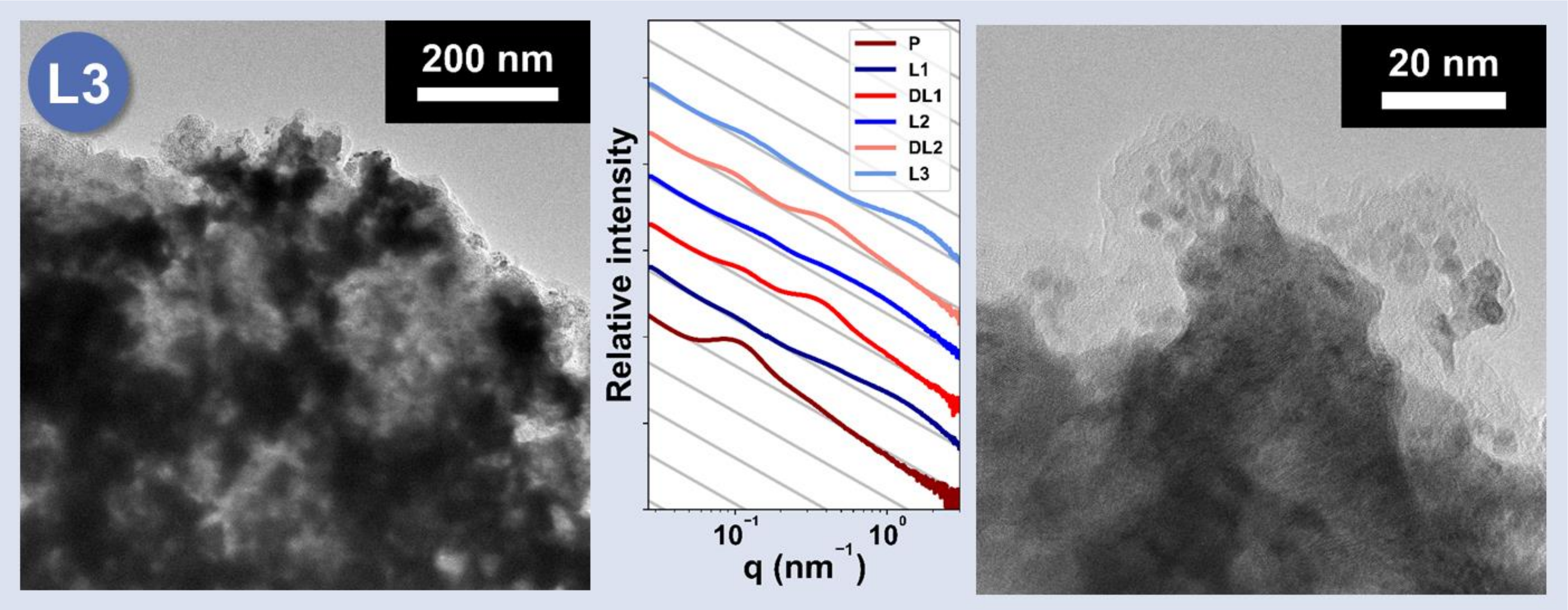
(3) Microstructure Evolution

Third Lithiation (L3)



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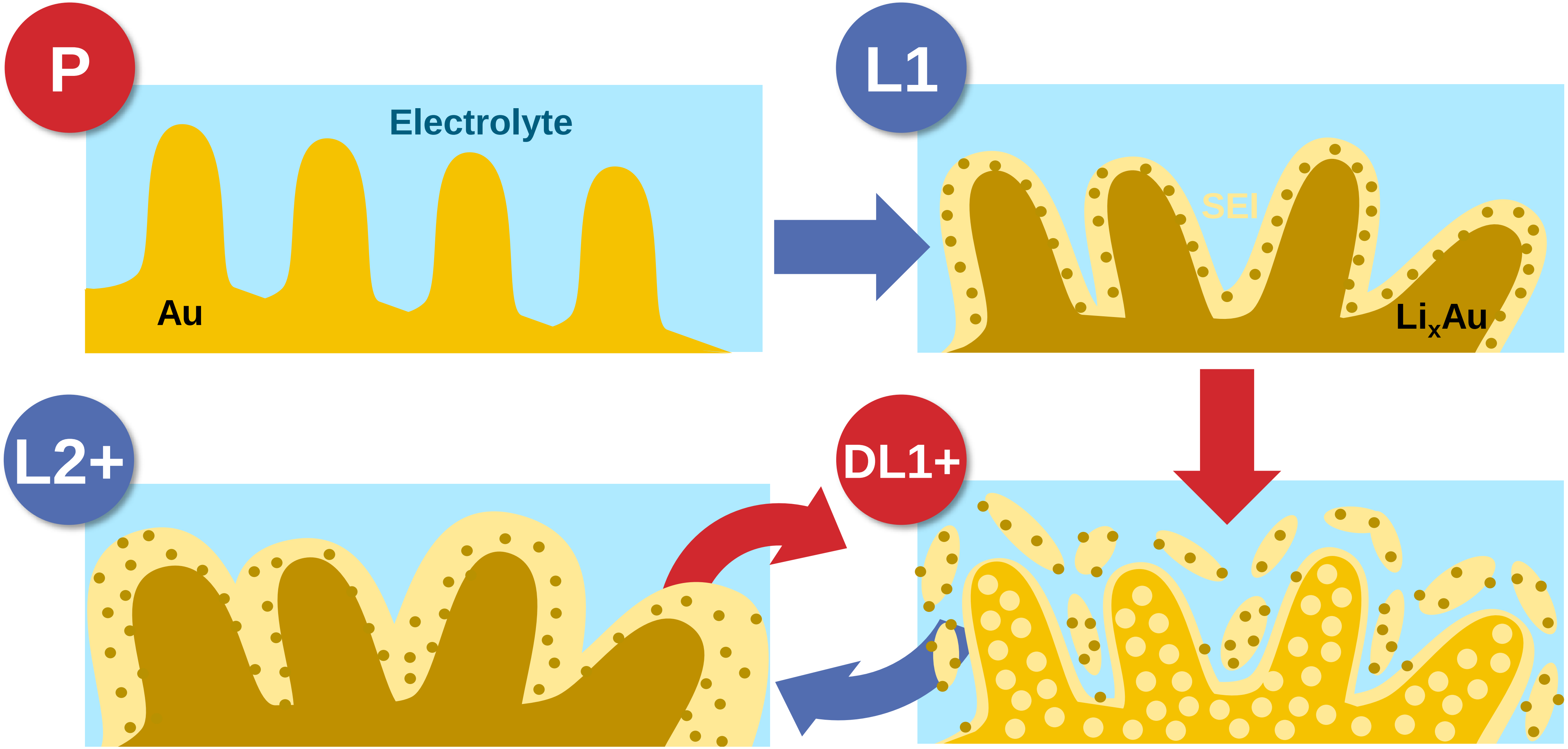
(3) Microstructure Evolution

Model: NP-Au Microstructural Evolution



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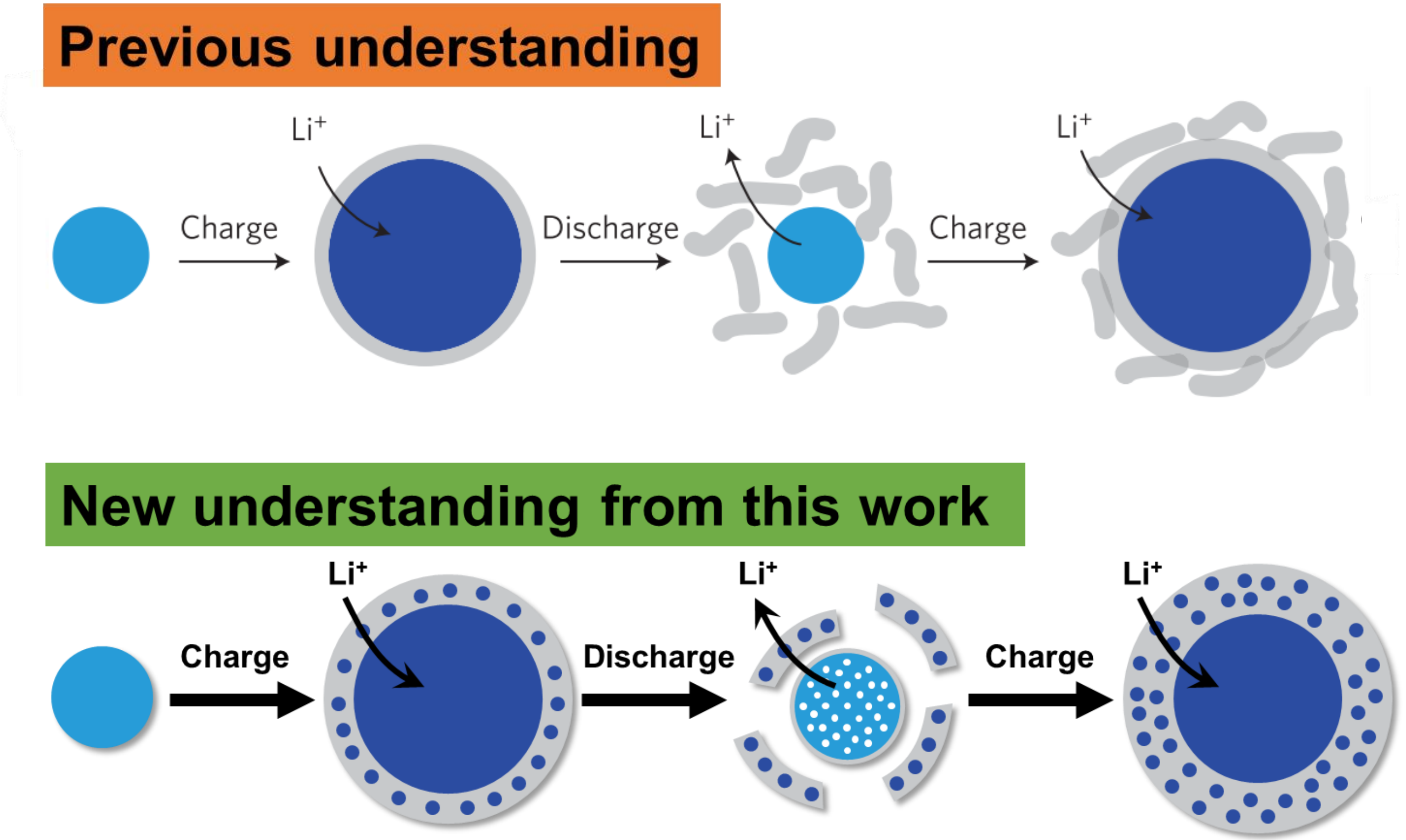
(3) Microstructure Evolution

Model: Updated Understanding of Alloy Anode Cycling



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Conclusion

What causes poor performance of nanoporous Al?

(1) Phase Evolution	(2) Solid Electrolyte Interphase Evolution	(3) Microstructure Evolution
Stresses from metastable phases	Stresses from dramatic SEI growth and removal processes	Ligament degradation due to complex pulverization - dealloying mechanism

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Thank you for your attention