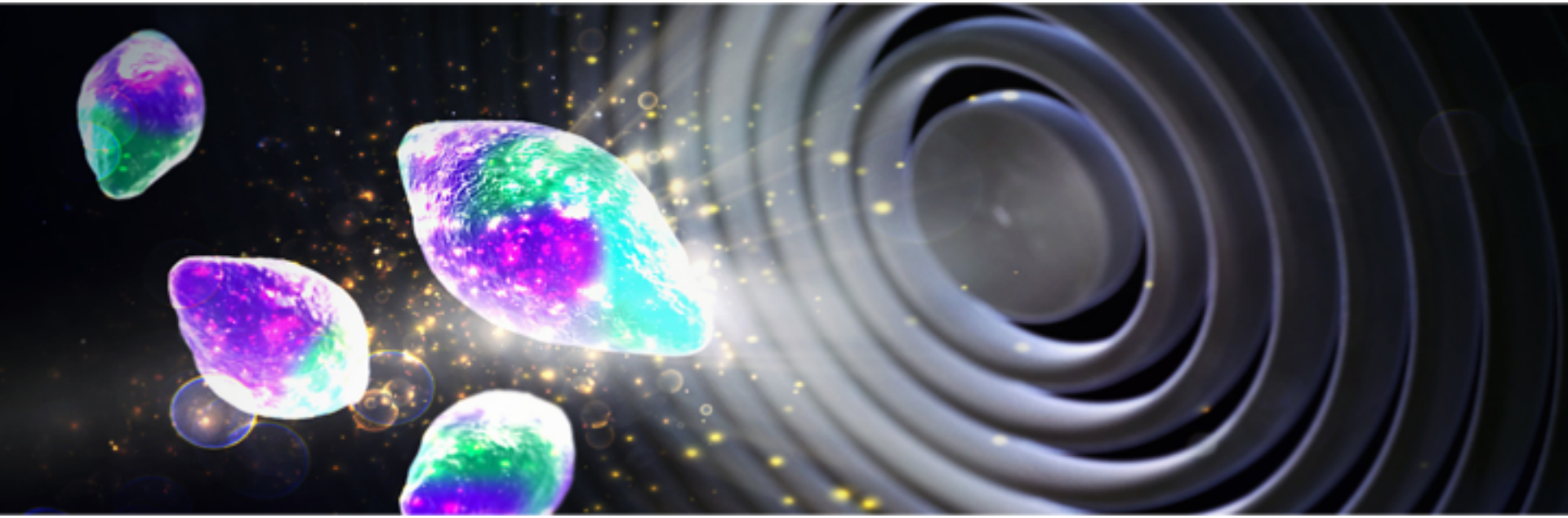
NANOSCALE ENERGY CARRIER TRANSPORT IN RENEWABLE APPLICATIONS

: THERMOELECTRICS and LITHIUM ION BATTERIES

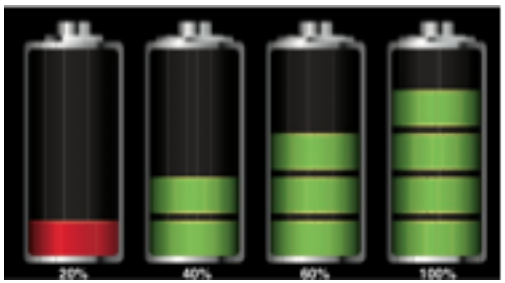


Jongwoo Lim

Assistant Professor
Department of Chemistry, SNU

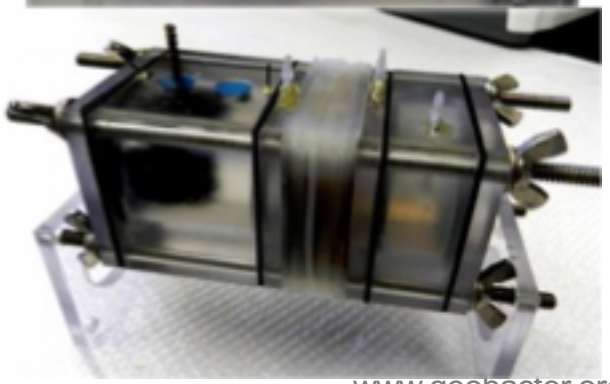
Introduction to renewable energy applications

Li-ion Battery
Energy Storage



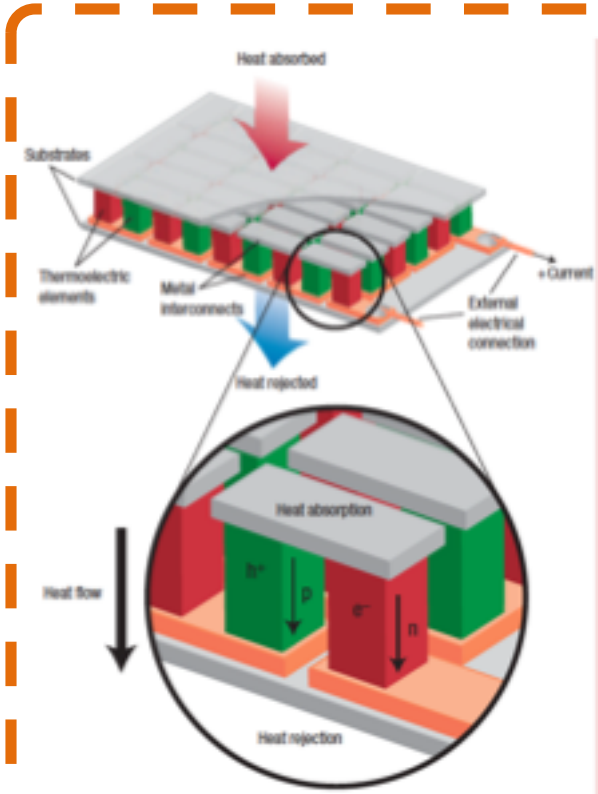
www.samsungsdi.com

Microbial Fuel Cell
Electricity from Waste water



www.geobacter.org

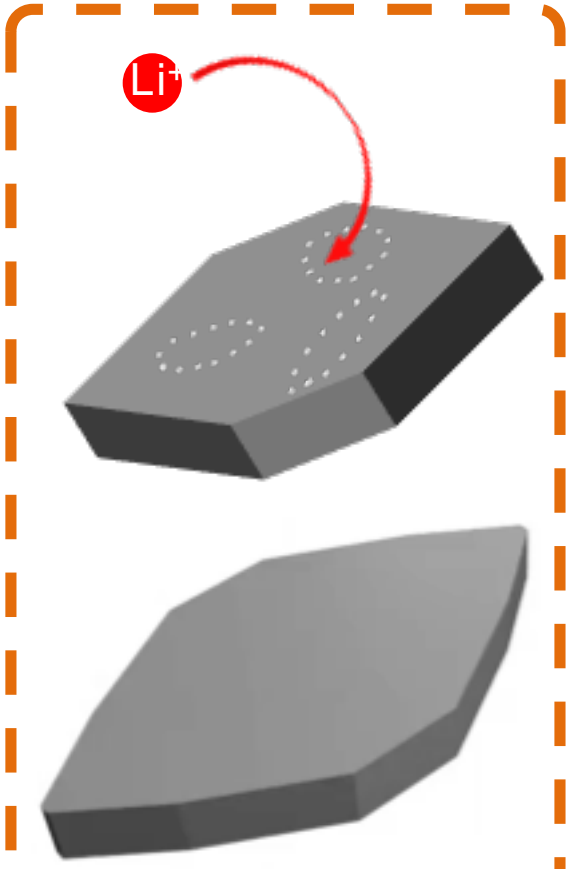
Thermoelectrics
Electricity from Waste heat



J. Snyder, Nat. Mat 2008

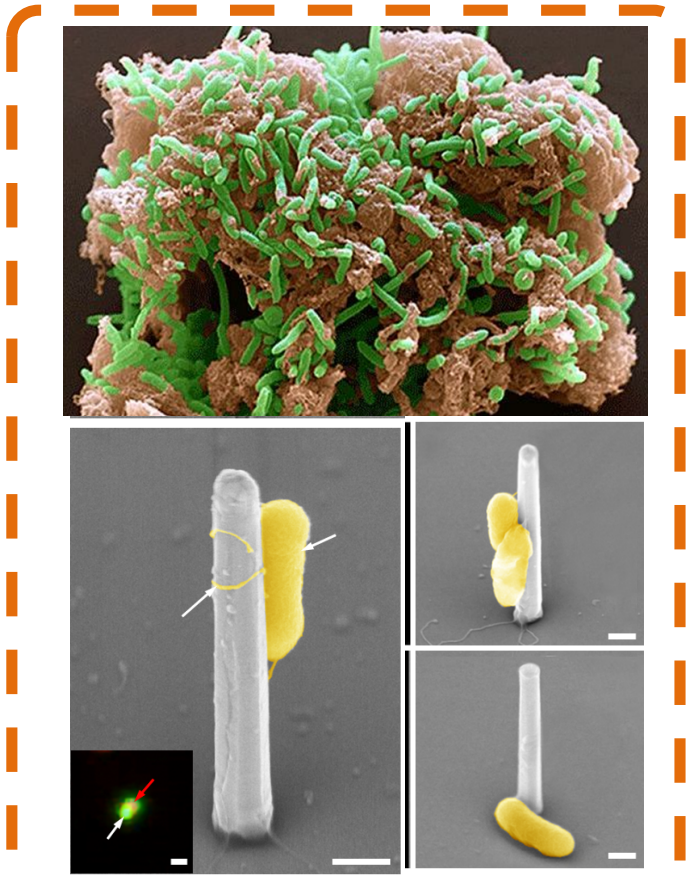
Energy carrier transport

Ion insertion kinetics
Li-ion battery



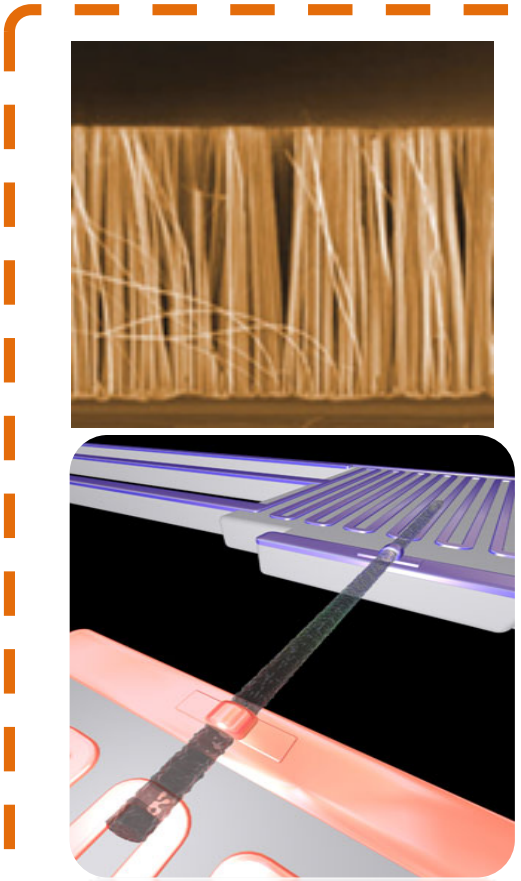
D. Cogswell et al., Nano Lett. 2014,11, 4890

Interfacial electron transfer
Microbial fuel cell



H. Jeong, et al., *Nano Lett*, **2013**, 13(6) 2864,

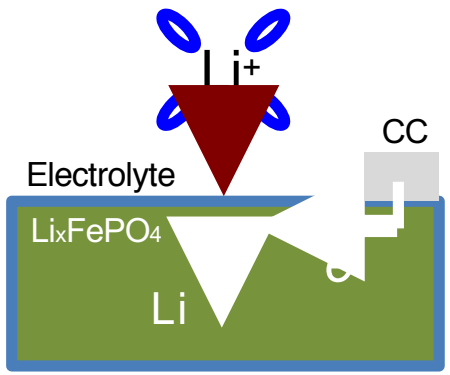
Electron-phonon transport
Thermoelectrics



Alphabetenergy.com

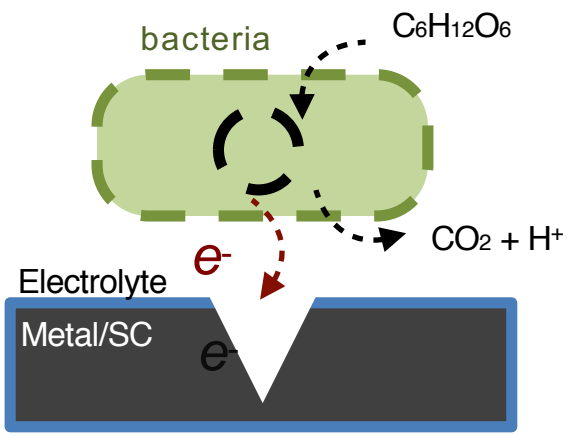
Energy carrier transport

Ion insertion kinetics
Li-ion battery



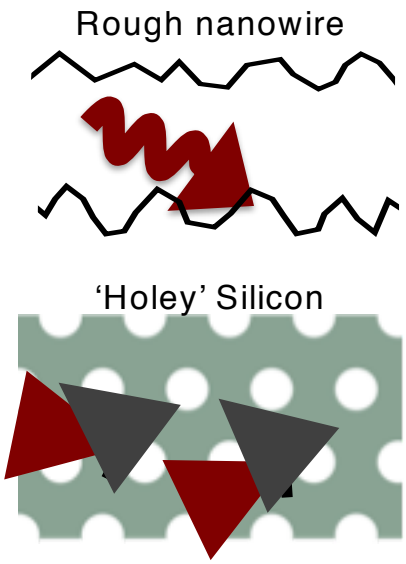
$Li_0FePO_4 + e^- + Li^+ \rightarrow LiFePO_4$

Interfacial electron transfer
Microbial fuel cell



$C_6H_{12}O_6 \rightarrow 12e^- + 12H^+ + CO_2$

Electron-phonon transport
Thermoelectrics

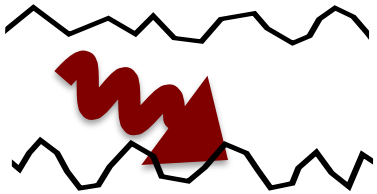


Energy carrier transport

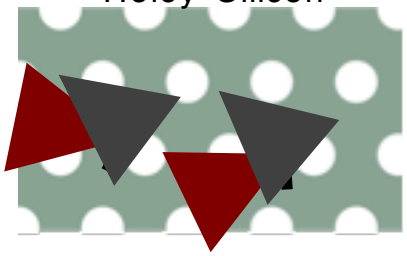
Electron-phonon transport

Thermoelectrics

Rough nanowire

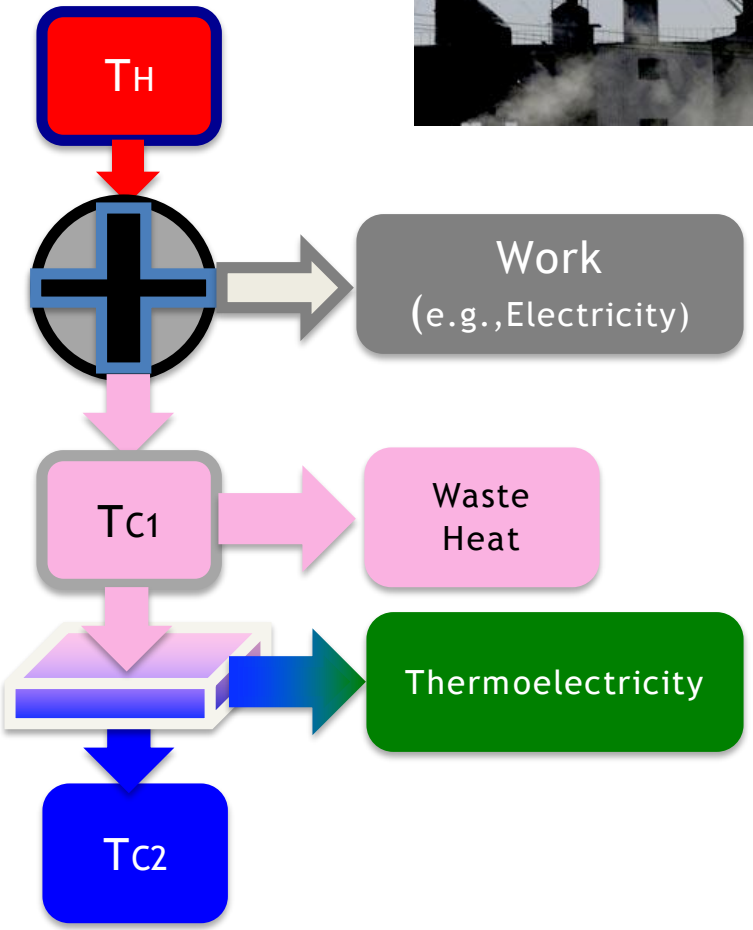


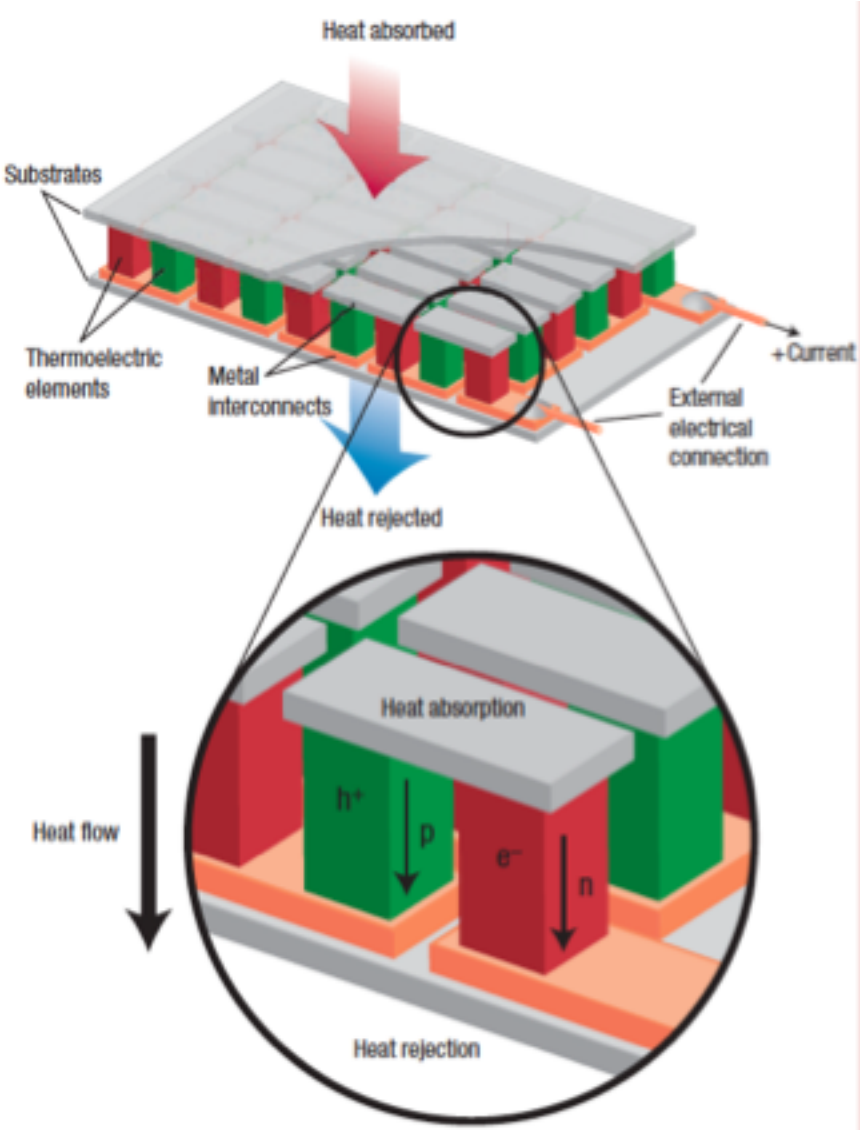
'Holey' Silicon



***Nano Letters*, 16, 4133 (2016)**
ACS Nano, 10, 124 (2016)
Nano Letters, 15, 3273 (2015)
Acta Materialia 64, 62 (2014)
Nano Letters, 12, 2475 (2012)

Intro to Thermoelectrics

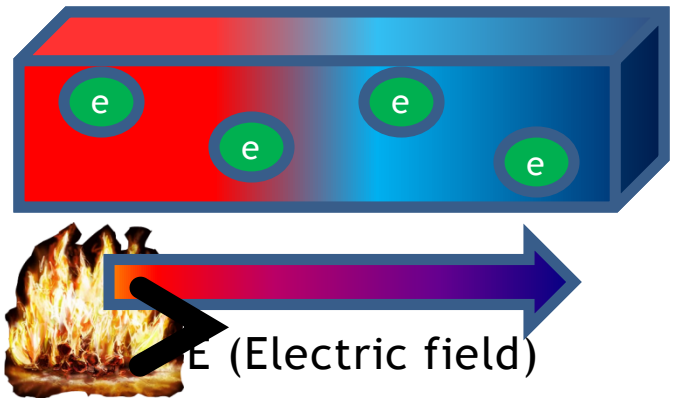




J. Snyder, *nature materials*, 7, 105 (2008)

Intro to Thermoelectrics

Seebeck effect



Seebeck Coefficient

$$S = \frac{\Delta V}{\Delta T} \quad (V/K)$$

Figure of Merit

$$zT = \frac{S^2\sigma}{\kappa}T$$

$\kappa = \kappa_{ph} + \kappa_{el}$ = Thermal conductivity
σ = Electric conductivity
S = Seebeck coefficient

Slow Phonon (Heat) Transport, Fast Electron (charge) Transport

$$\kappa_{ph} = \frac{1}{3}CvL$$

C = Heat capacity
v = Speed of sound
L = Phonon mean free path
κ = typical target 1~2W/mK

Silicon Thermoelectrics

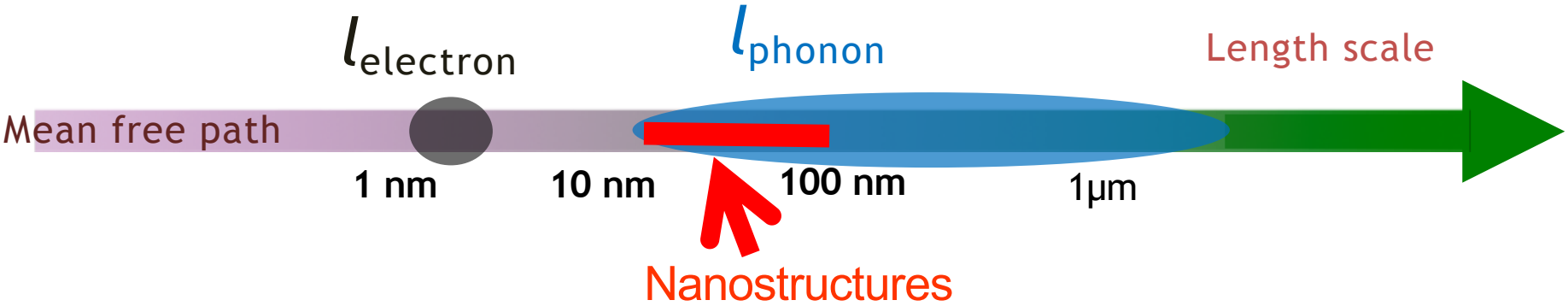
Advantage

- High power factor (High σ and S)
- inexpensive & abundant
- Relative Wide band gap
- Mass production infrastructure

Disadvantage

- Low ZT in Bulk
- High thermal conductivity in Bulk

Silicon Nanostructures



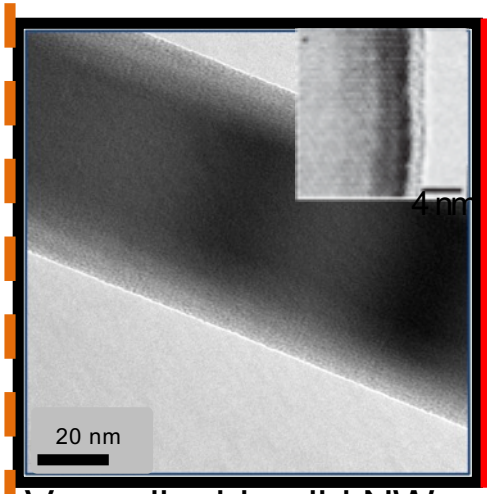
$$l_{electron} < d_{SiNW} < l_{phonon}$$

Enhanced phonon-boundary scattering

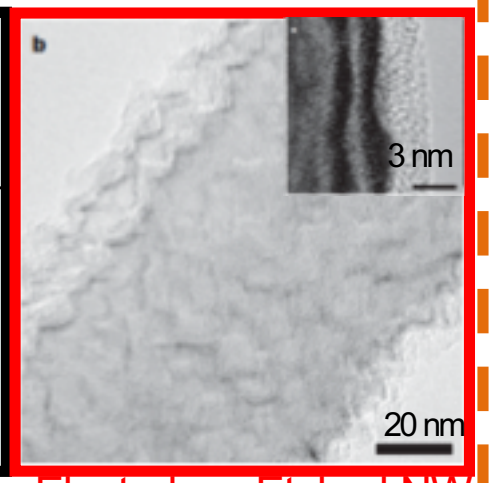
Chelikowski, *Silicon: evolution and future of a technology* , p.1, Springer, 2004

Phonon Engineering in Nanostructures

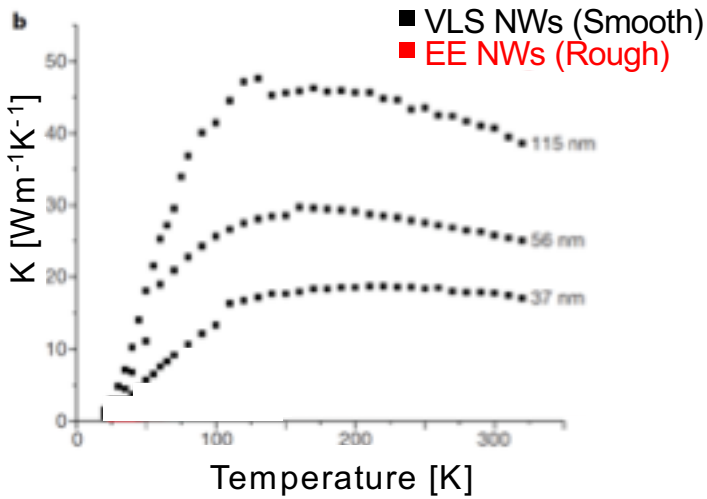
Silicon Nanowires



Vapor-liquid-solid NW

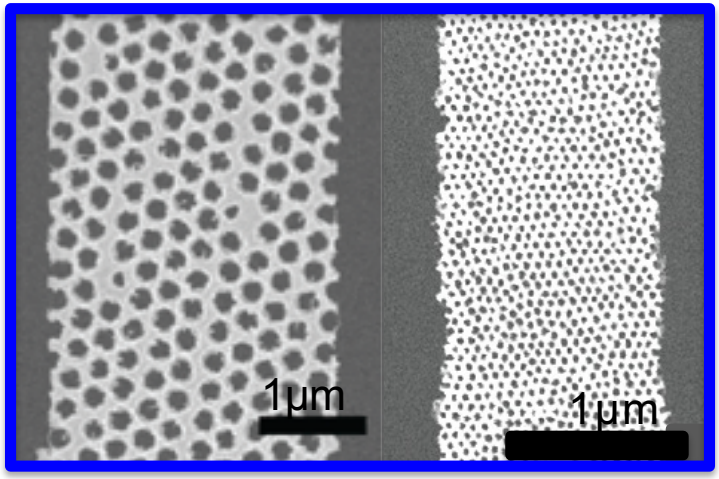


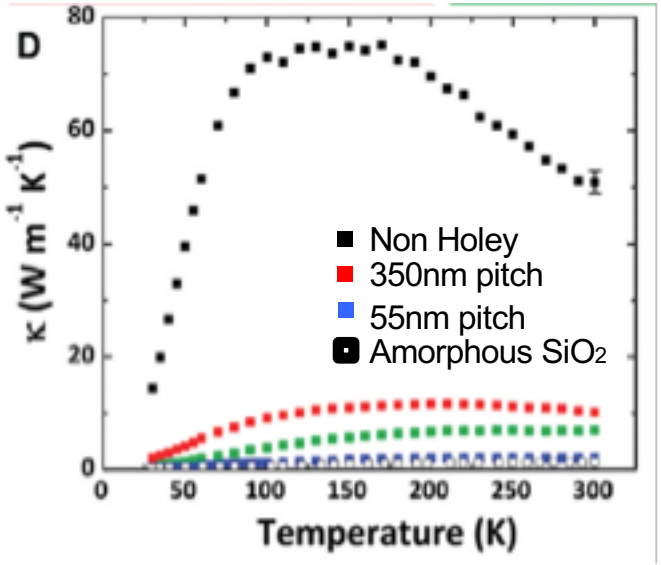
Electroless Etched NW



Hochbaum, A. el. Al., *Nature* **2008**

Holey Silicon Membrane

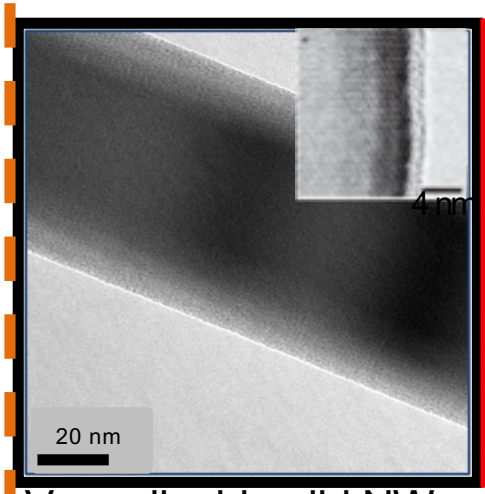




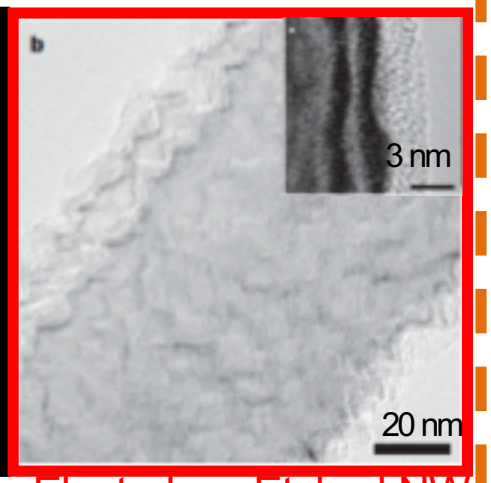
Tang, J. et. al., *Nano Lett* **2010**

Phonon Engineering in Nanostructures

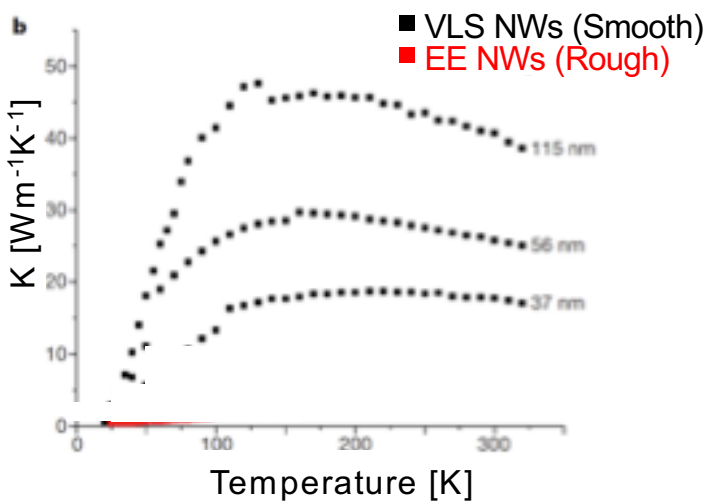
Silicon Nanowires



Vapor-liquid-solid NW

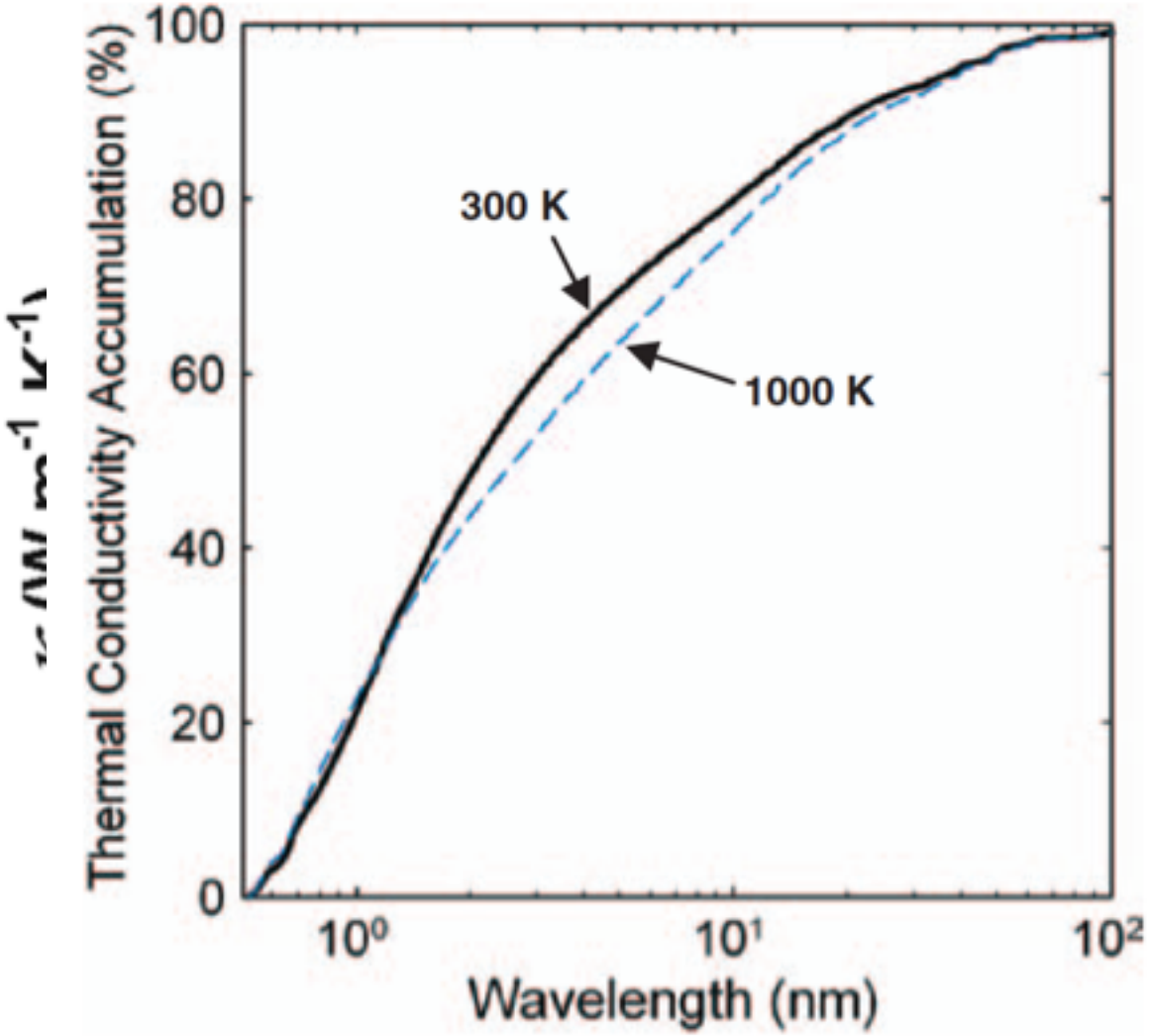


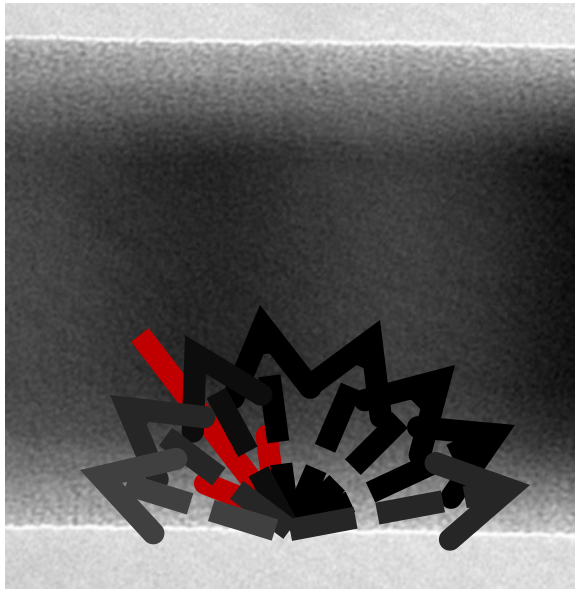
Electroless Etched NW

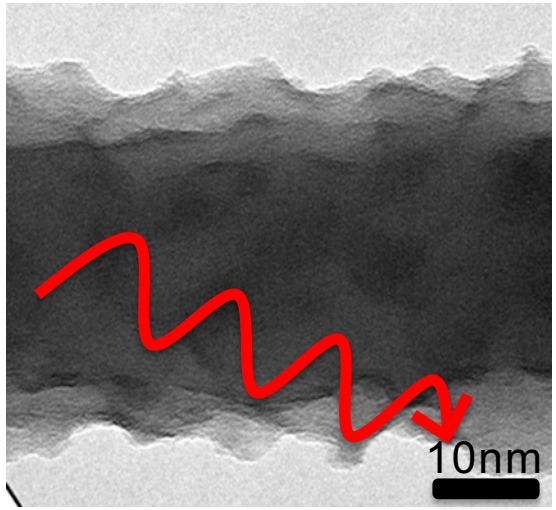


Hochbaum, A. el. Al., *Nature* **2008**

Breaking the Casimir Limit

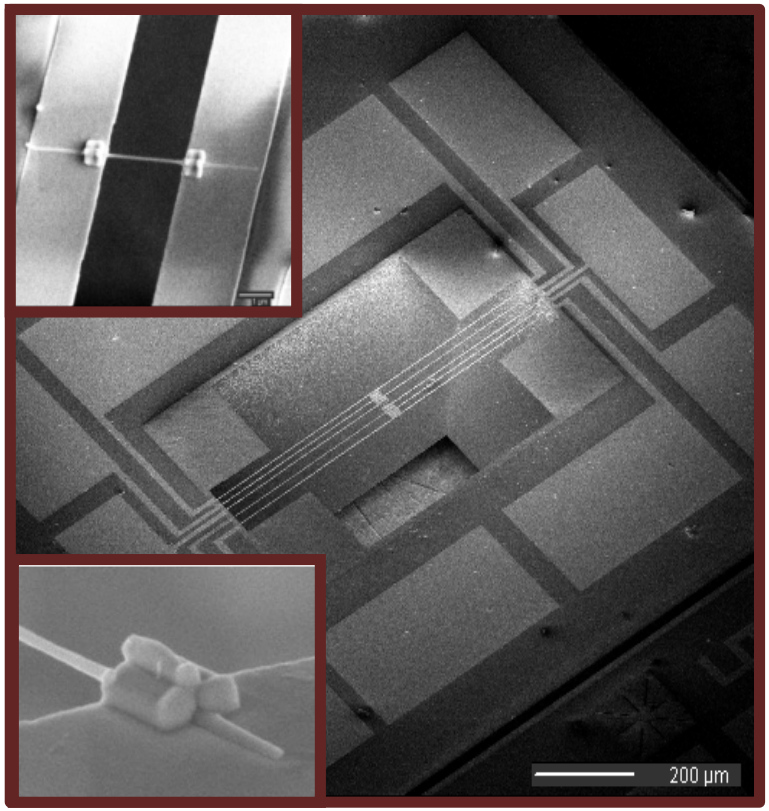


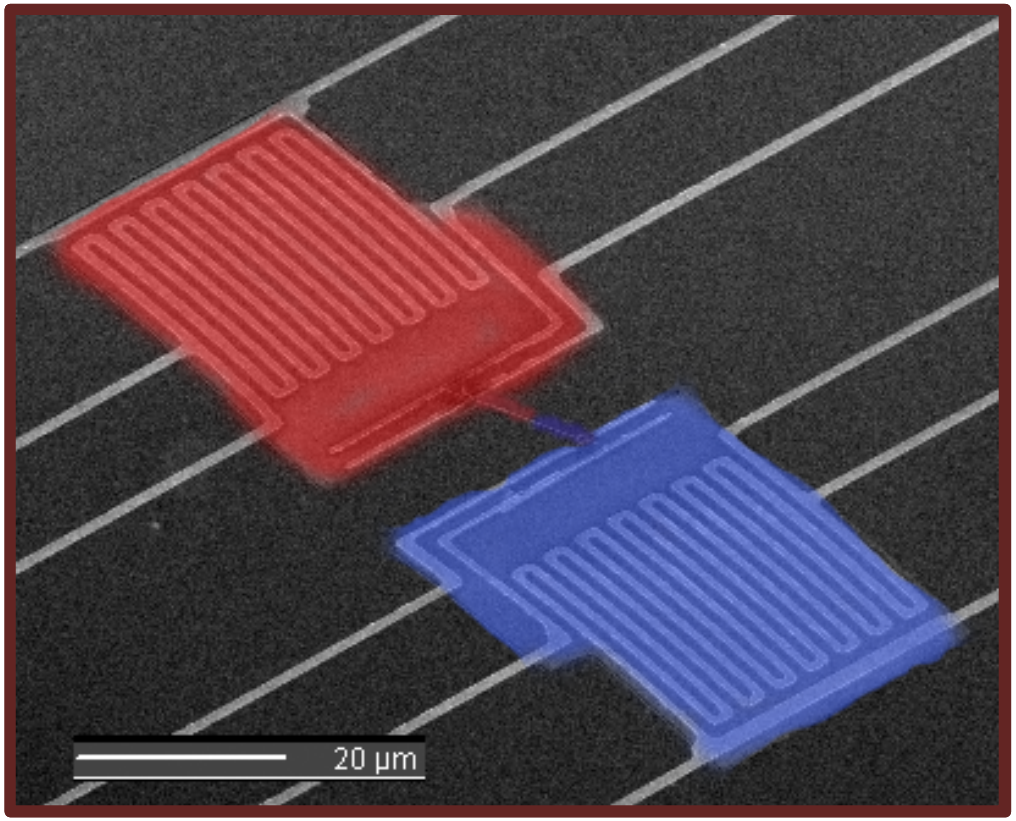




Li Shi. et al., **2012**

Probing Nanoscale Heat Transport



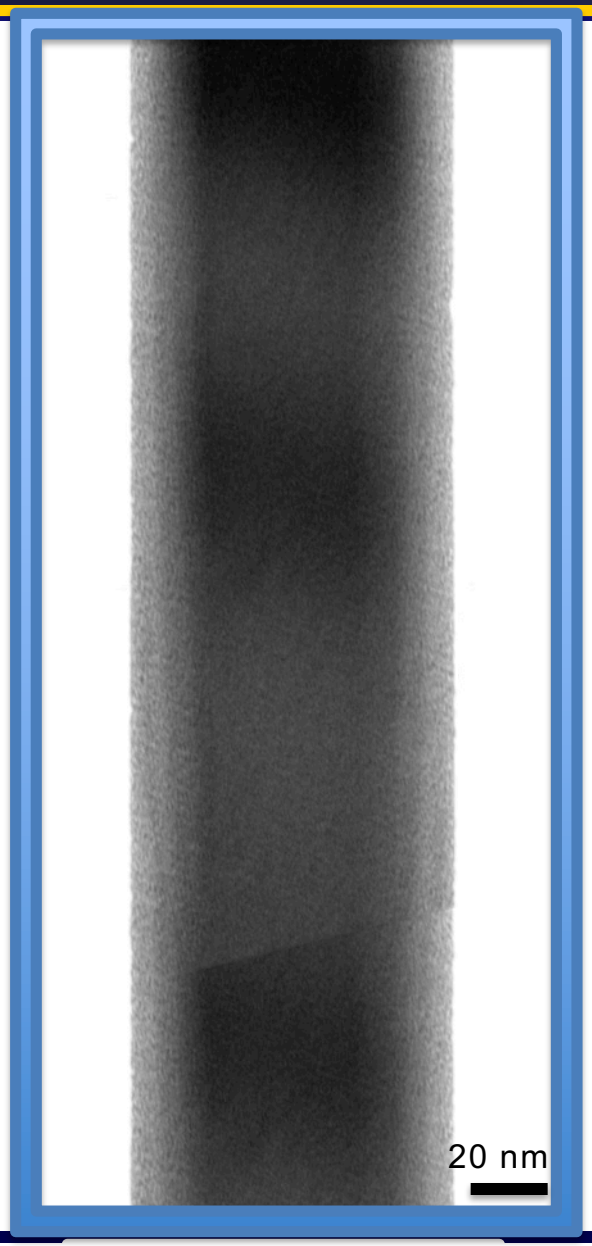


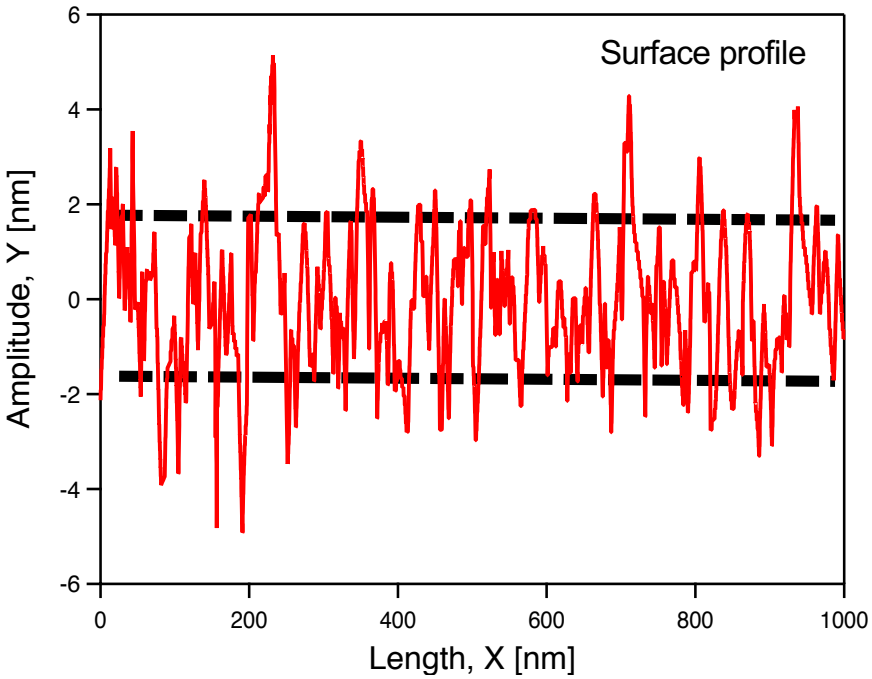
$$G_W = \frac{Q_s}{T_h - T_s}$$

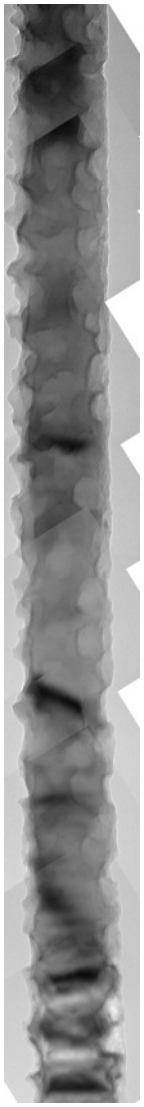
Q_s = Heat flux through the nanowire
G_W = Thermal Conductance of the nanowire
T_h = Temperature of the heating side
T_s = Temperature of the sensing side

J. Lim* and K. Hippalgaonkar,* *et. al*, Nano Lett. 2012
J. Lee and J. Lim* et al.,Nano Lett. 2015*
J. Lim and H. Wang* et al, ACS Nano. 2016*
J.Lee, W Lee*,and J Lim*, et al., Nano Lett, 2016*
K. Hippalgaonkar* and J. Lim.* *et al., in prep*

Experimental Methods : Probing Nanoscale Heat Transport

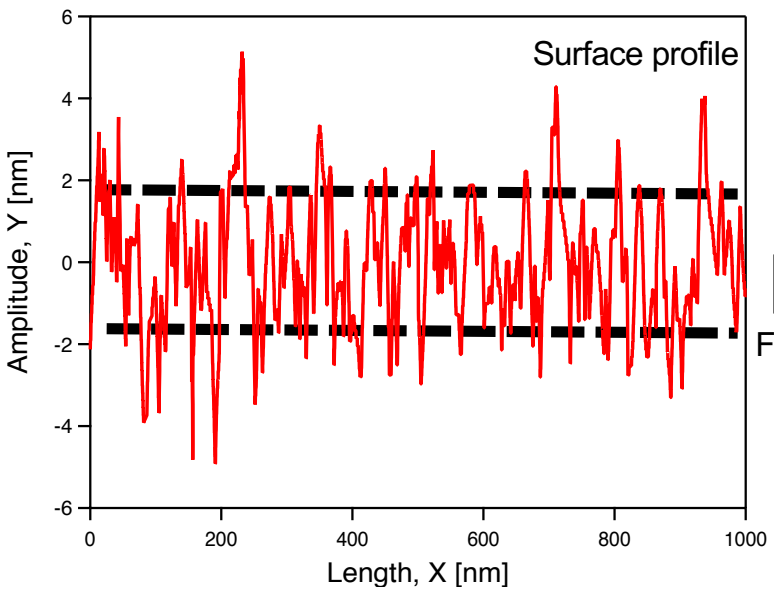




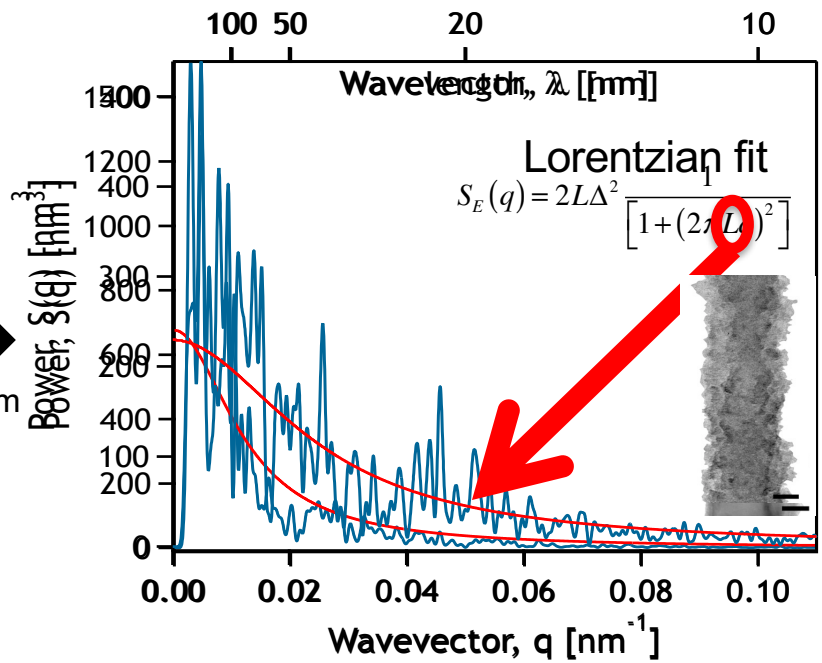


Roughness Parameters

- Roughness Parameters
  - rms (root-mean-square) : represents the amplitude of roughness
  - Correlation length (ξ) : related to mean distance between consecutive peaks. A statistical parameter that determines the decay of the autocovariance (exponential decay).

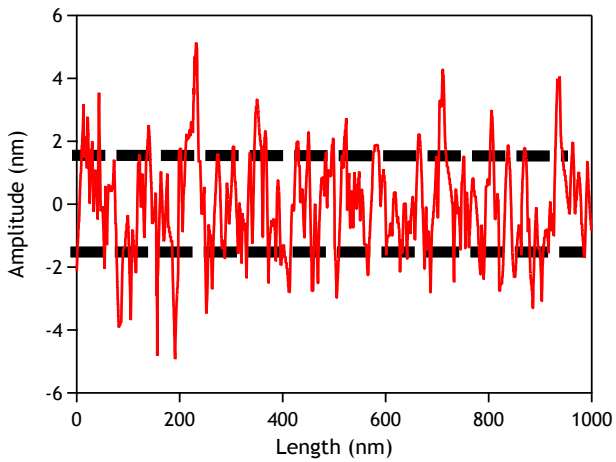


Fourier Transform

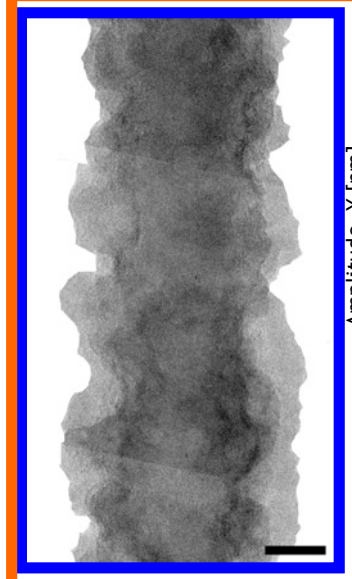


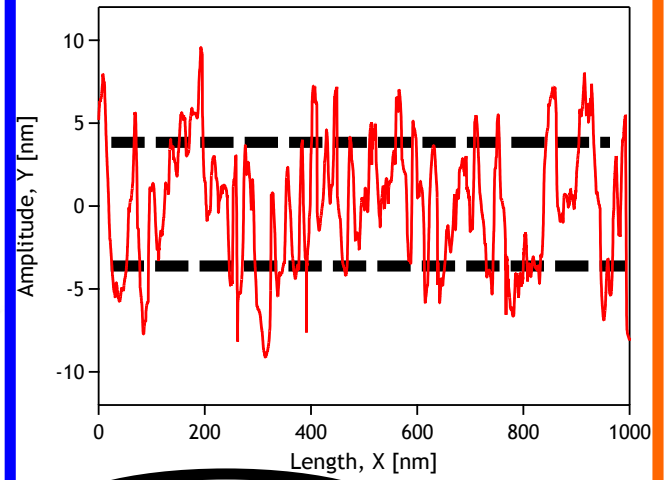
J. Lim, * and K. Hippalgaonkar,* *et. al*, Nano Lett. (2012), 12 2475

Impact of rms roughness

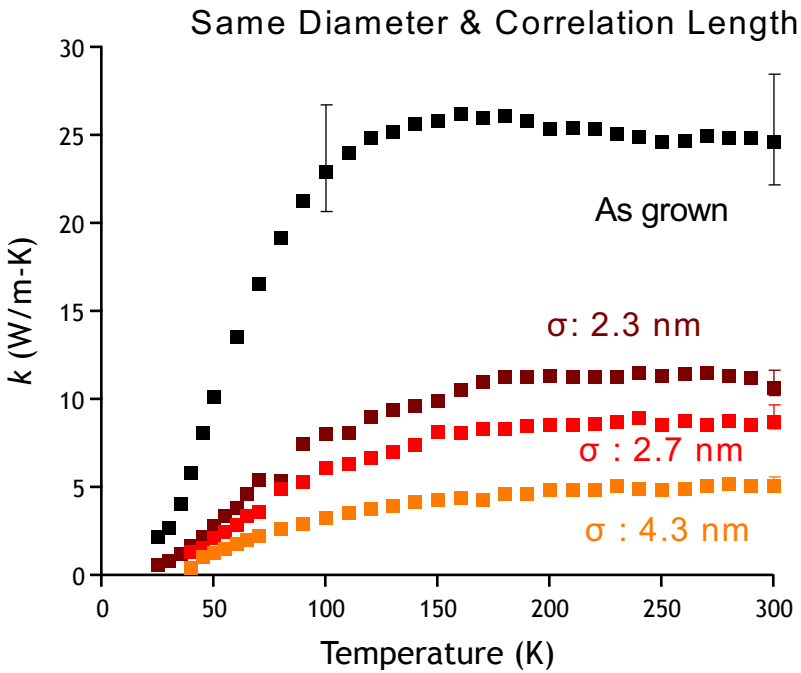


rms(σ): 2.3 nm ξ : 8.9 nm



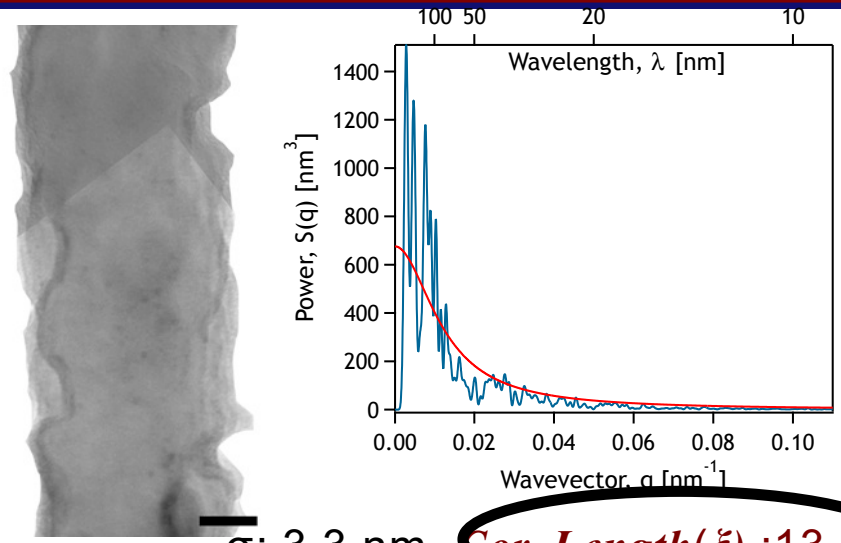


rms(σ) : 4.3 nm ξ : 8.4 nm

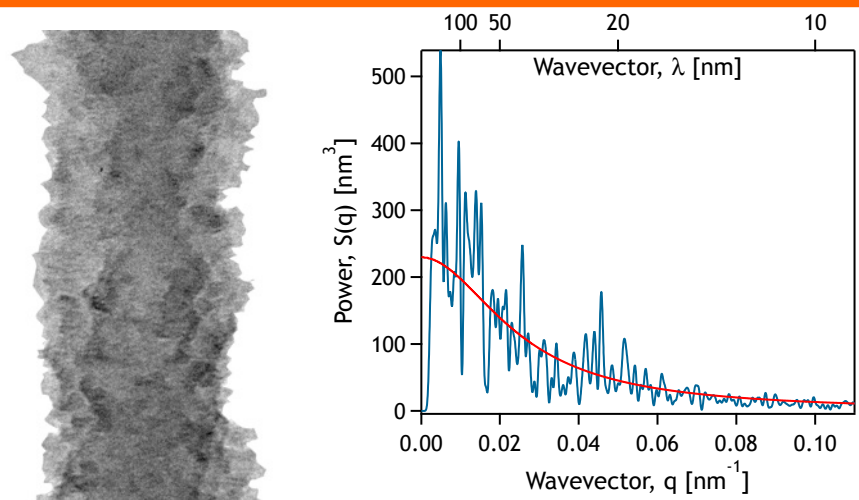


RMS (σ,nm)	Corr. Length (ξ,nm)	Diameter (D,nm)	Thermal Conductivity (W/mK) at 300K
As grown		72.8	24.7
2.3	8.9	77.5	10.68
2.7	8.4	79.8	8.39
4.3	8.4	69.7	5.09

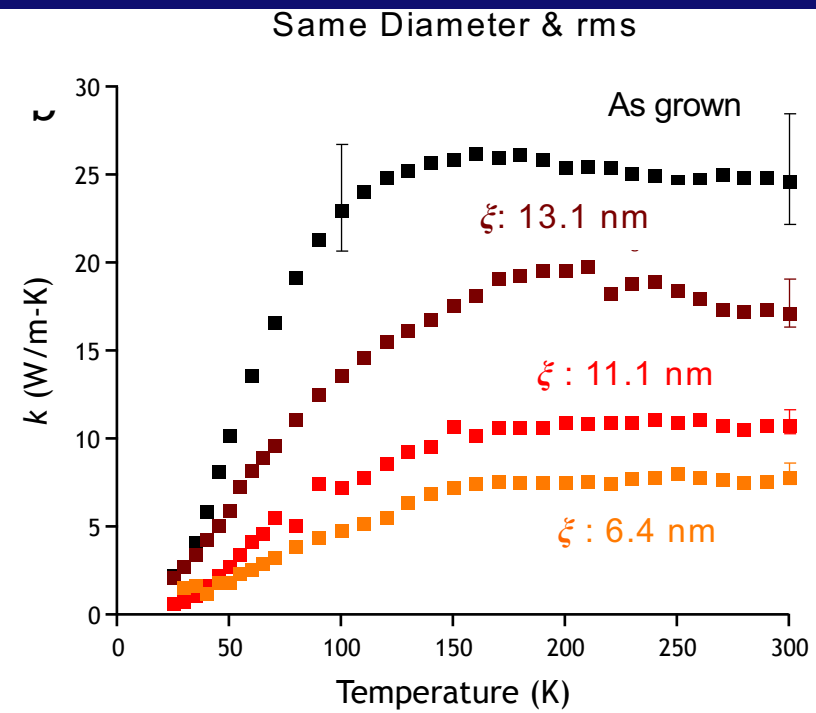
Impact of correlation length (ξ)



σ: 3.3 nm *Cor. Length*(ξ) :13.1nm

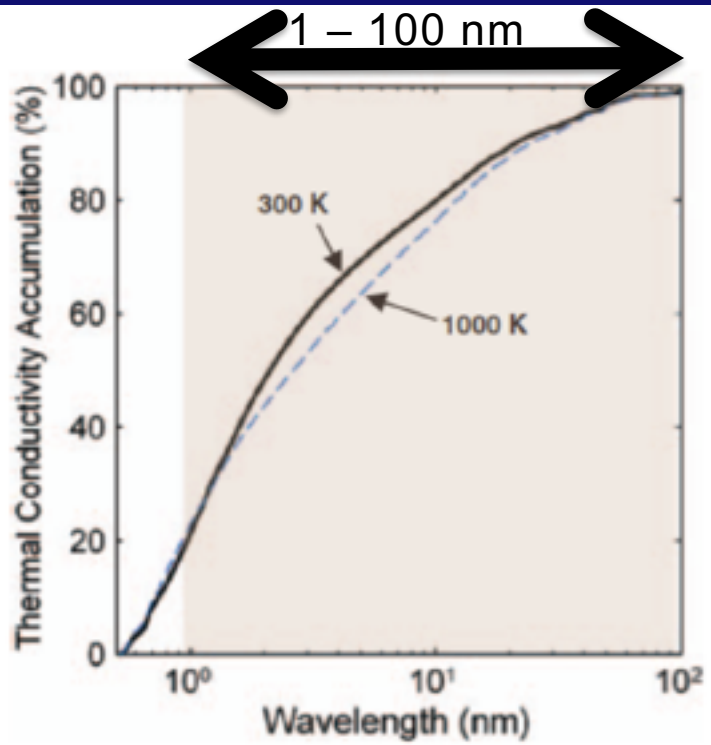


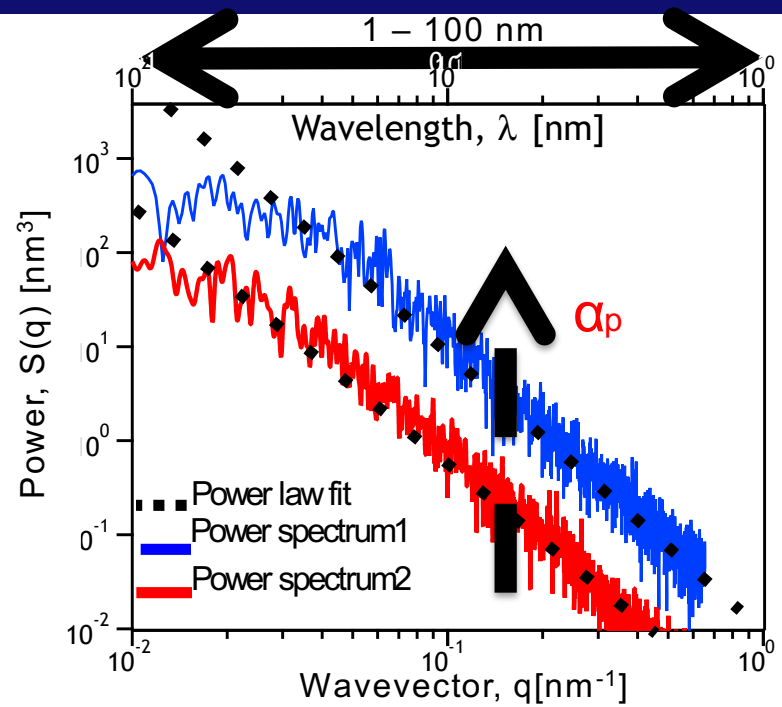
σ: 2.8 nm *Cor. Length*(ξ) : 6.4nm



RMS (σ,nm)	Corr. Length (ξ,nm)	Diameter (D,nm)	Thermal Conductivity (W/m-K) at 300K
As grown		72.8	24.7
3.3	13.1	77.9	17.16
3.1	11.1	71.0	11.19
2.8	6.4	70.0	7.78

Spectral Dependence of Phonon Transport





- 80% of heat conduction contributed from phonon wavelength ranging from 1nm to 100nm[1].
- Power law fits better in this characteristic length scale

Power Law

$$S(q)_{10^{-2}\to 10^{0}} = \alpha_p \left(\frac{q_0}{q}\right)^n$$

α_p= Roughness parameter

q = Surface wavevector

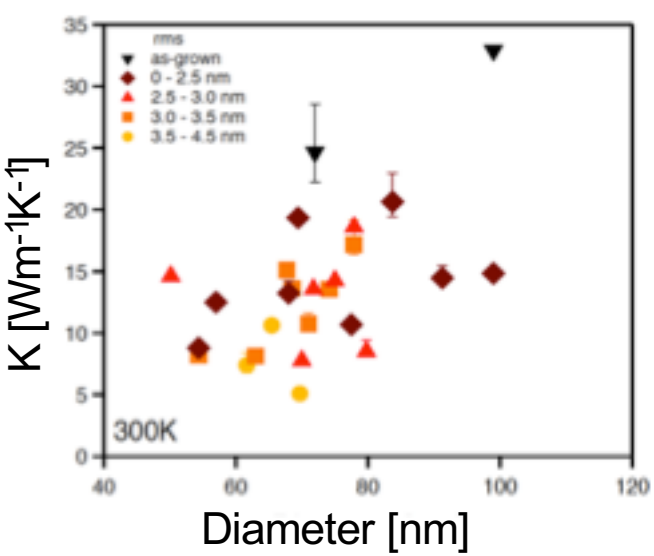
q_0= Lattice constant (0.31nm)

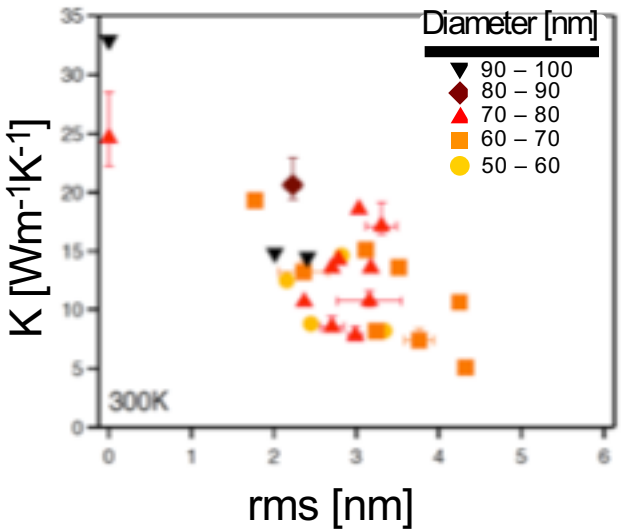
n = Power factor (~2.77)

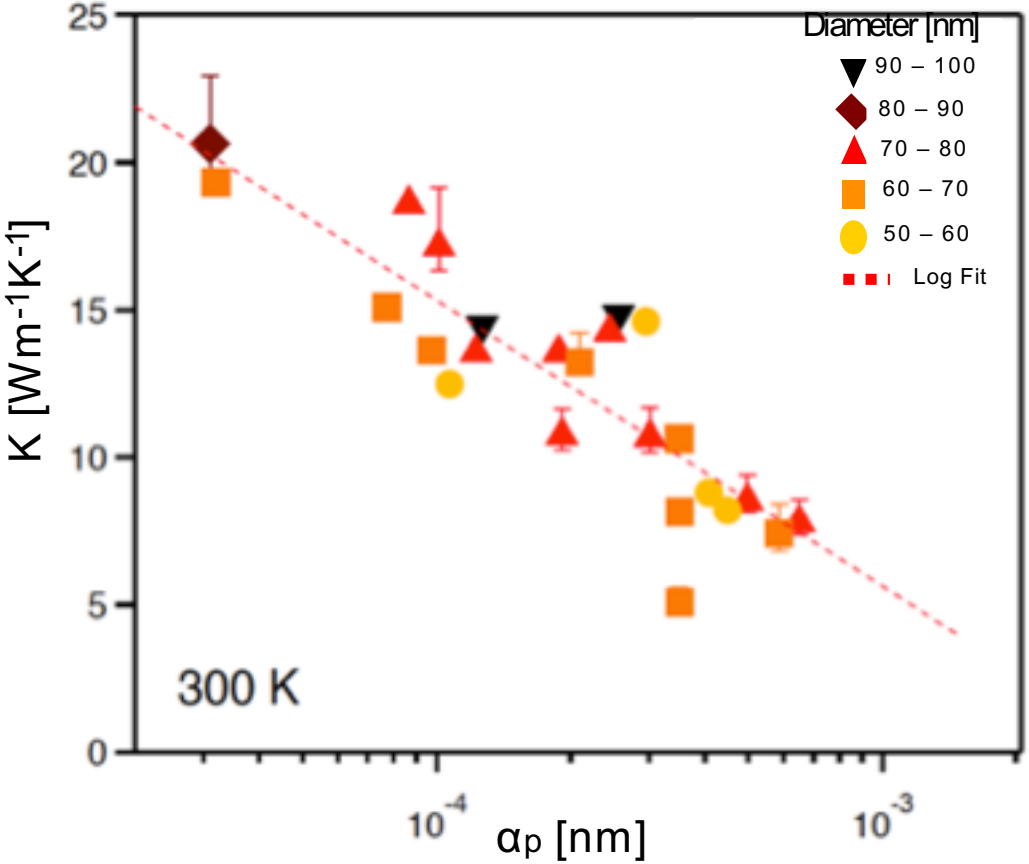
1.Henry, A. S. et. al., J. C. Th. N. 2008

J. Lim, * and K. Hippalgaonkar,* *et. al*, Nano Lett. (2012), 12 2475

Roughness Impact on Thermal Conductivity



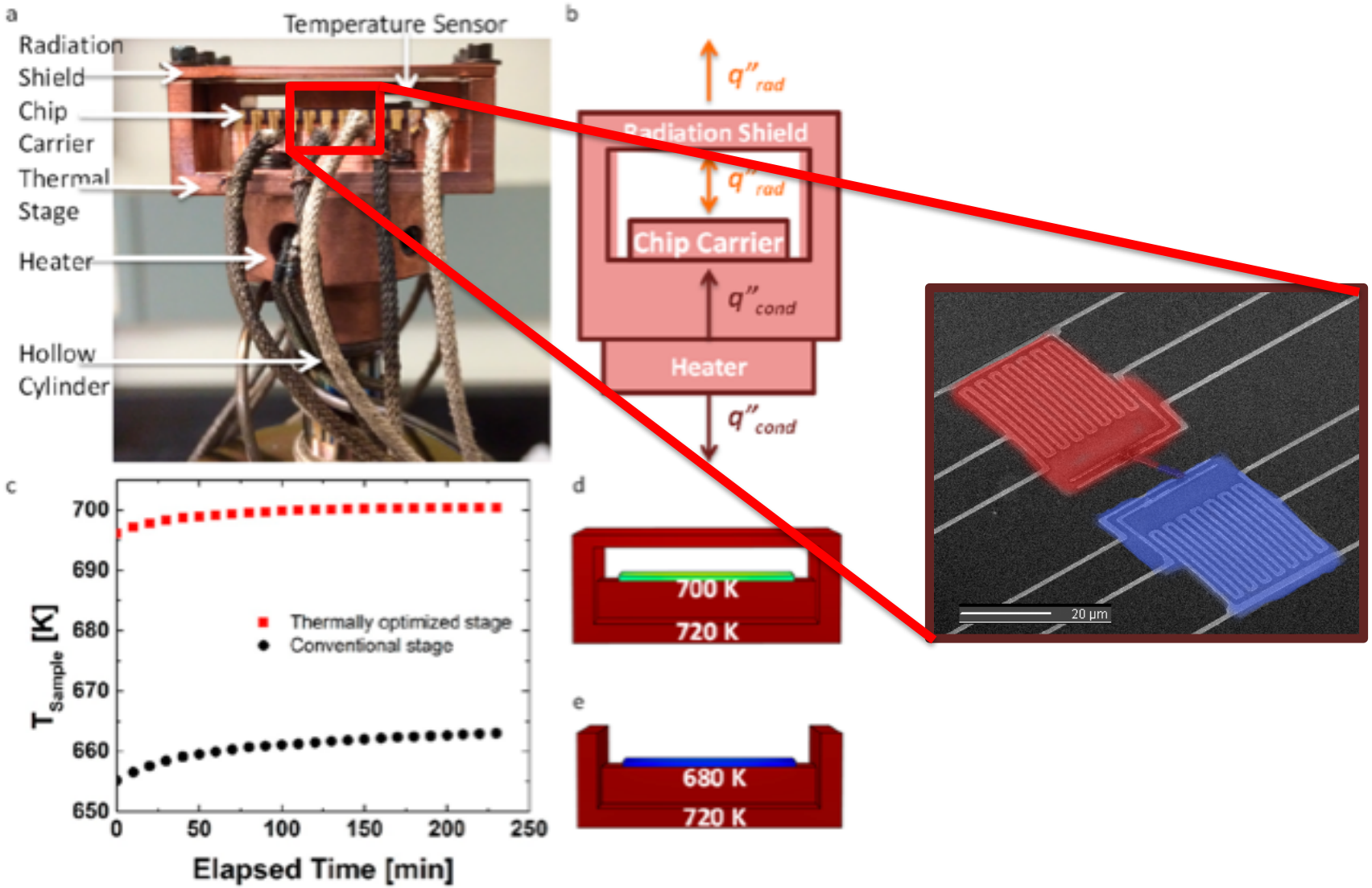




Spectral roughness factor, α_p shows tighter trend than rms

J. Lim, * and K. Hippalgaonkar,* *et. al*, Nano Lett. (2012), 12 2475

High temperature measurement

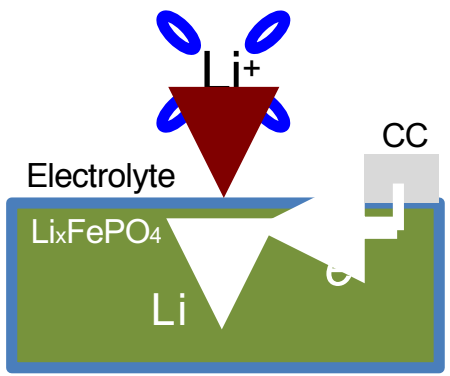


J. Lee*, W. Lee* and J. Lim, * *et. al, Nano Lett (2016), 16, 4133*

Energy carrier transport

Ion insertion kinetics

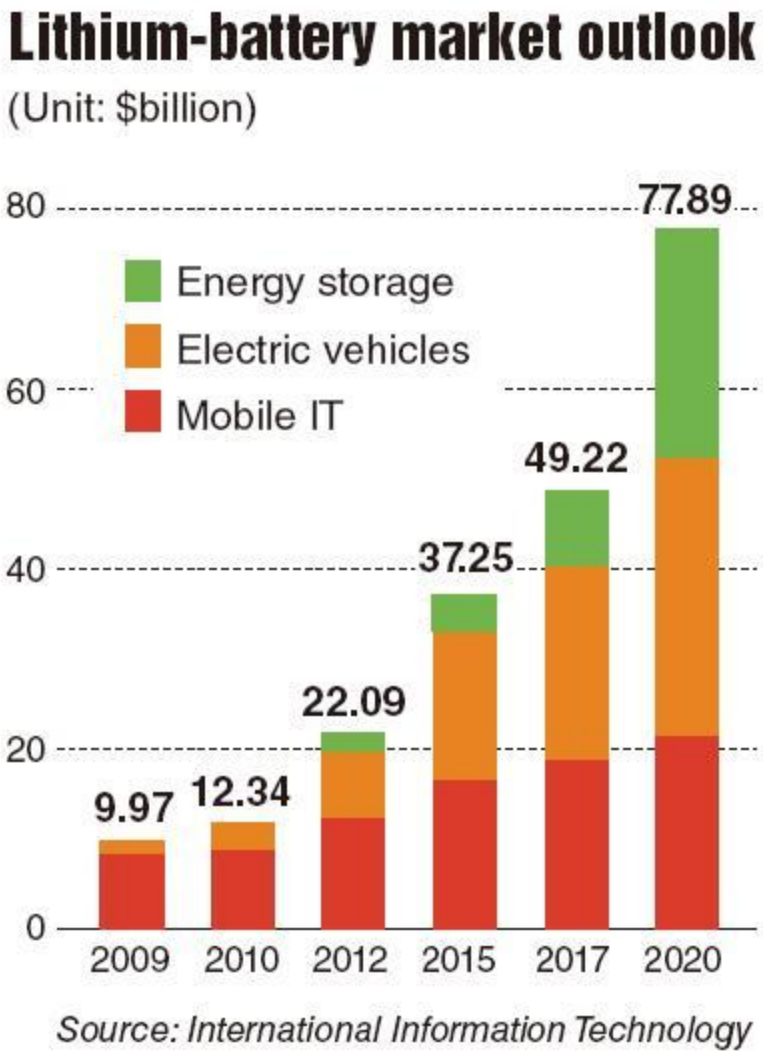
Li-ion battery



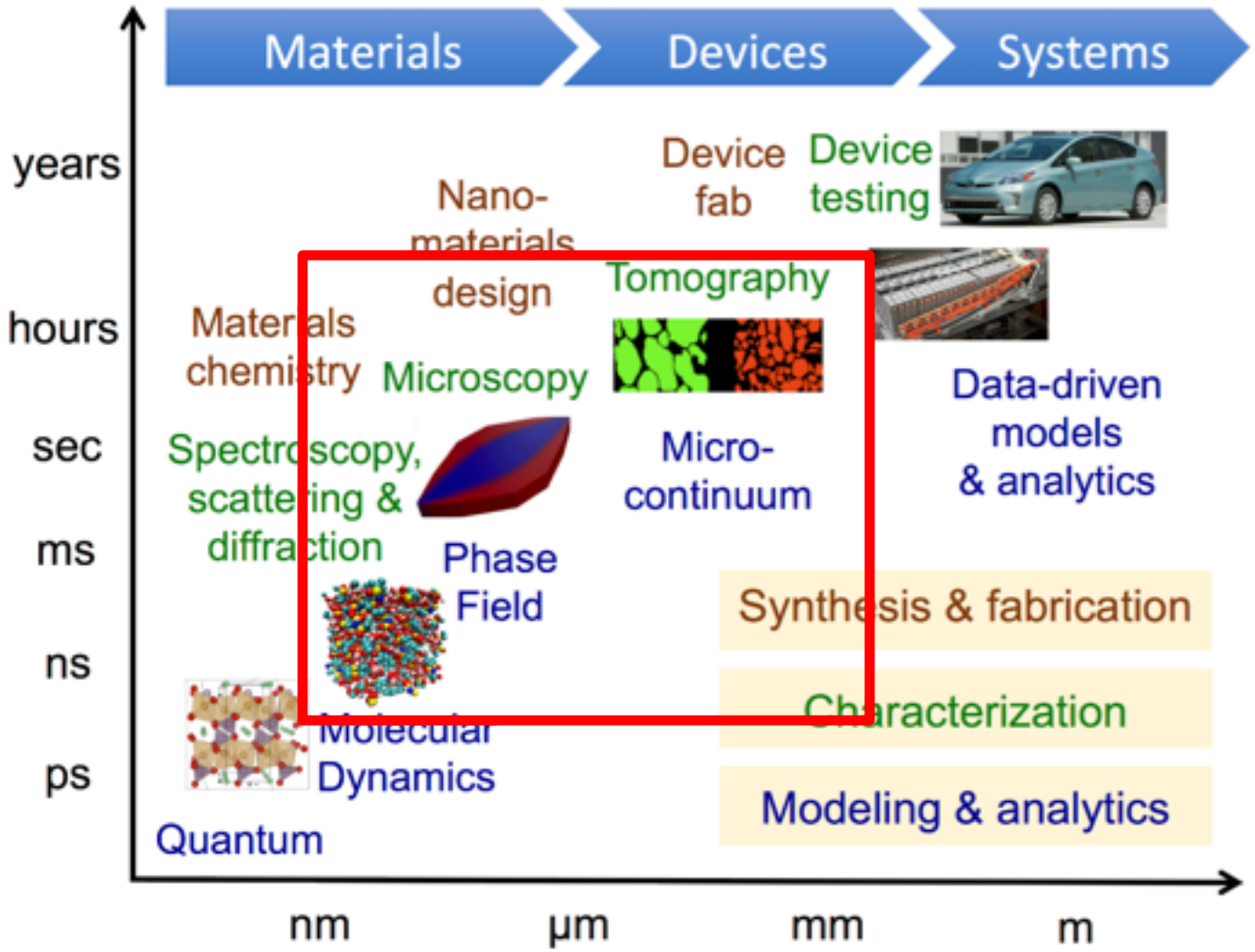
$Li_0FePO_4 + e^- + Li^+ \rightarrow LiFePO_4$

Nature Materials. (2018) *in press*
Science 353, 566 (2016)
Adv. Mat. 28, 6631 (2016)
Adv. Mat. 27, 6591(2015)
Adv. Func. Mat 25, 3677 (2015),

Market outlook of Li-battery

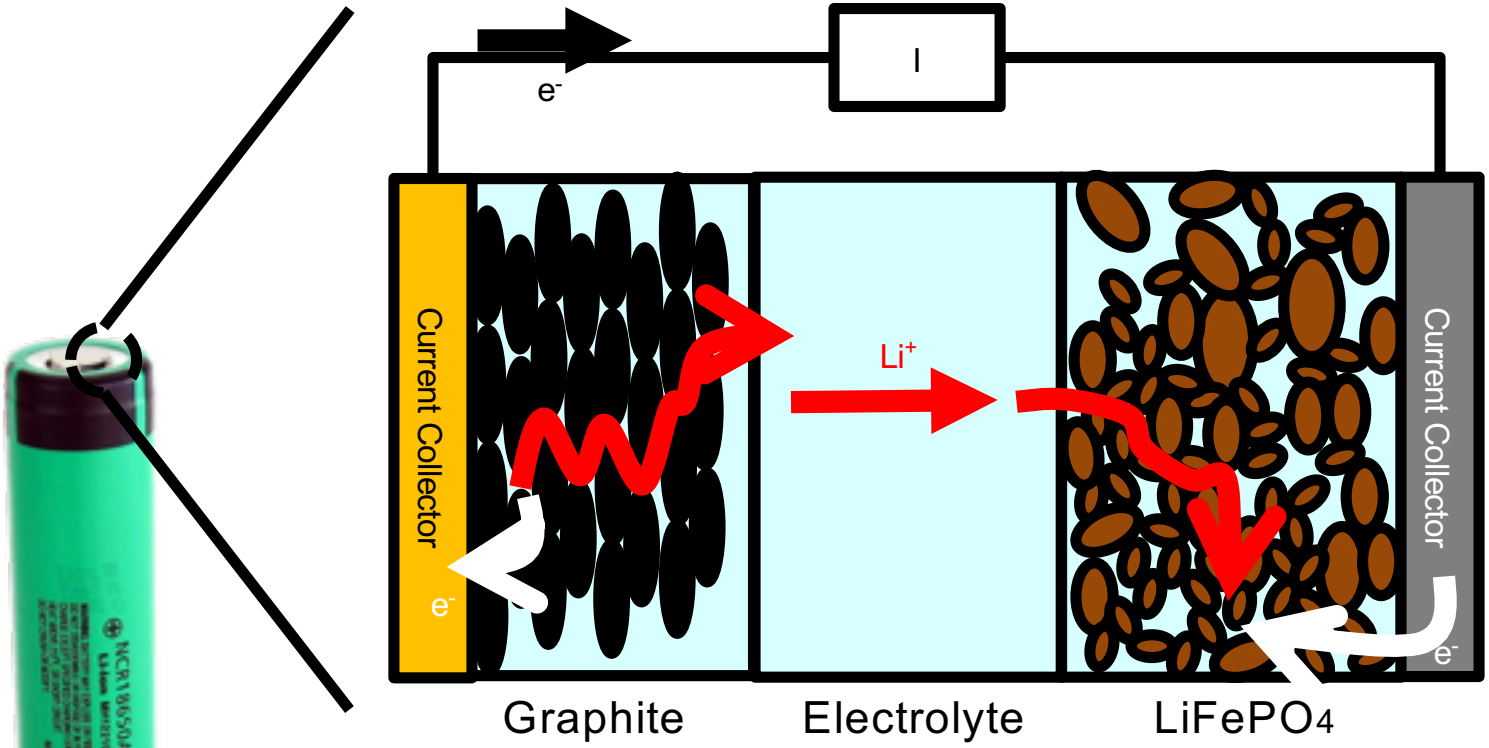


Multi length-time scale



Source: D3BATT Center MIT/Stanford/Purdue

Battery electrochemistry



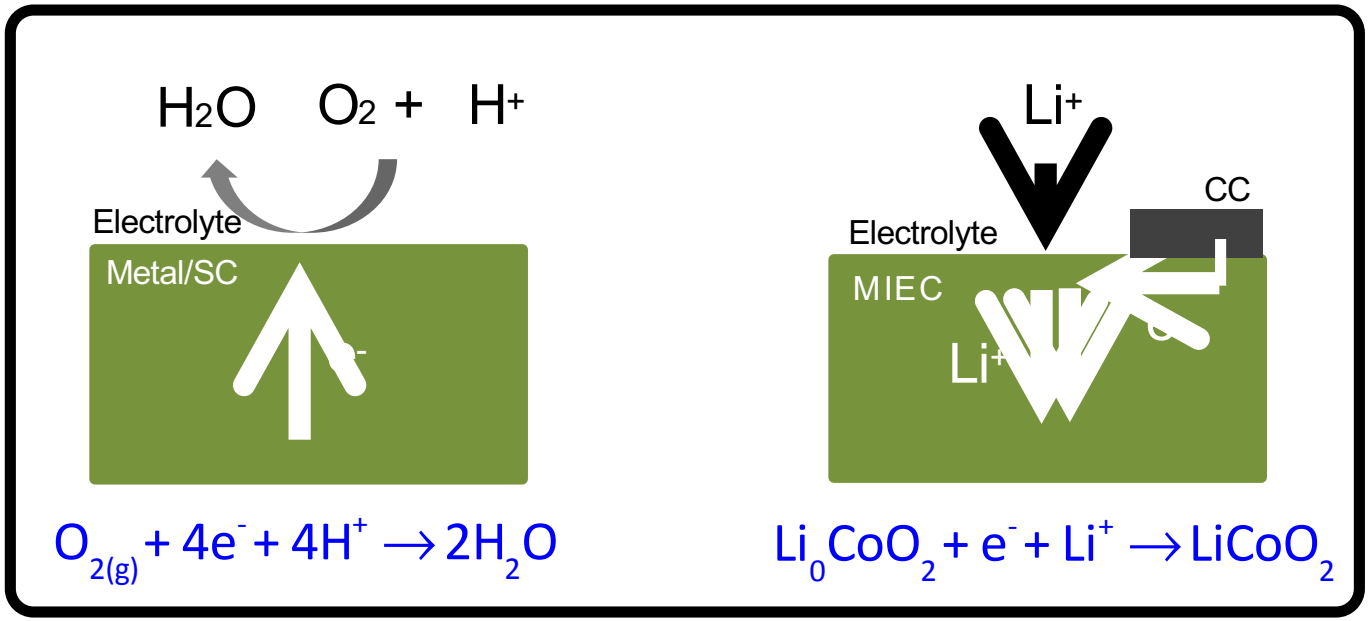
$LiC_6 \rightarrow Li^+ + e^- + C_6$ | $Li^+ + e^- + Fe^{3+}PO_4 \rightarrow LiFe^{2+}PO_4$

Net Reaction : $LiC_6 + FePO_4 \rightarrow C_6 + LiFePO_4$

$\Delta G = -320 kJ/mol$

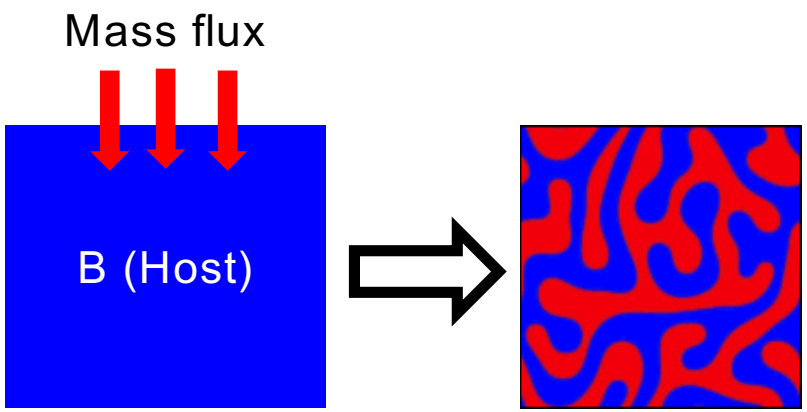
$V = -\Delta G/nFe = 3.4V$

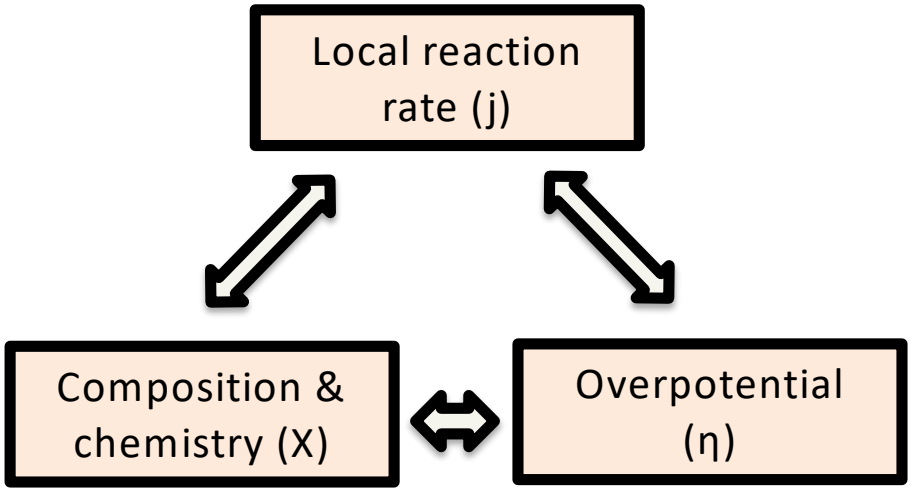
Electrochemical insertion reaction



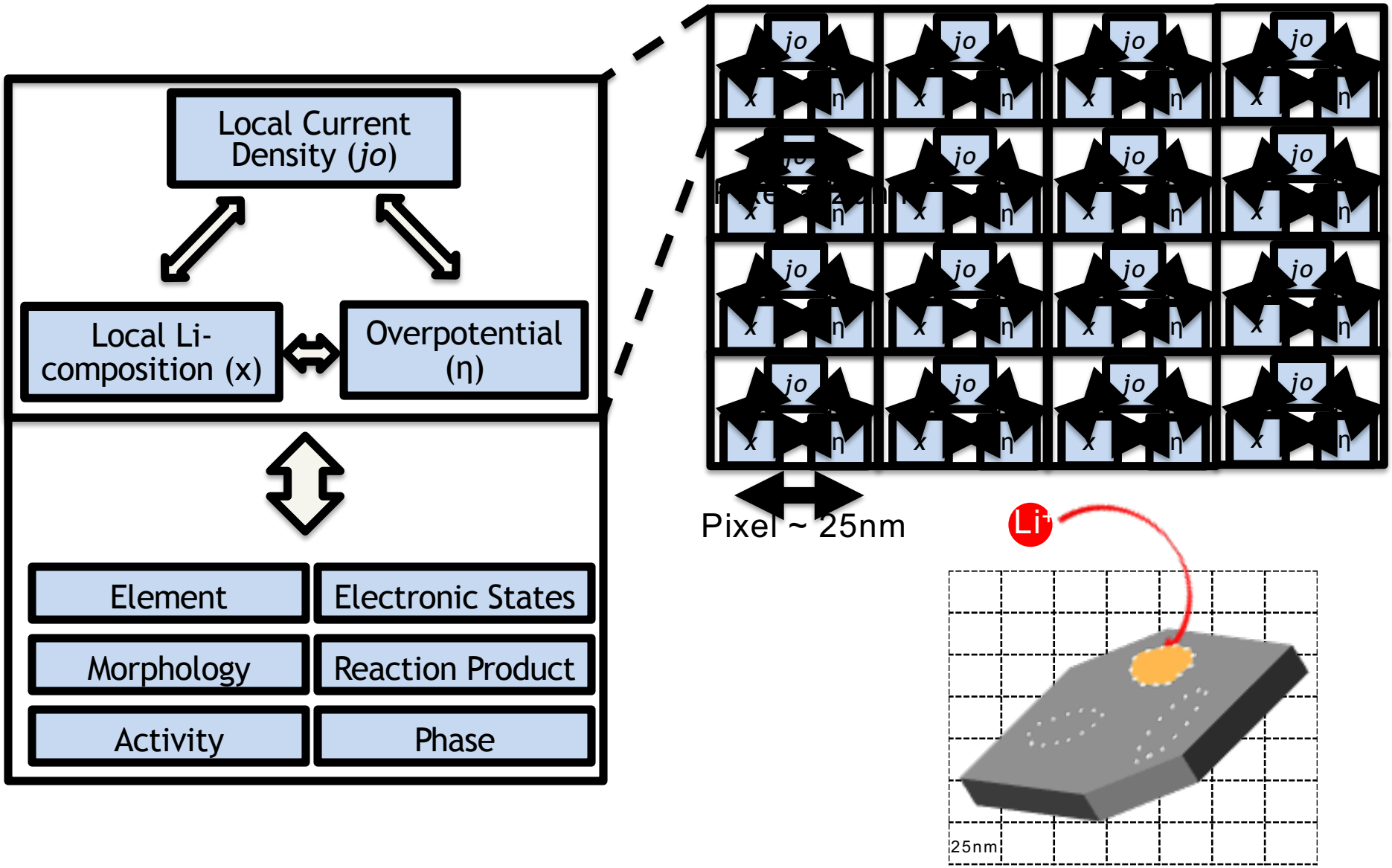
$O_{2(g)} + 4e^- + 4H^+ \rightarrow 2H_2O$

$Li_0CoO_2 + e^- + Li^+ \rightarrow LiCoO_2$





Spatio-electrochemistry of battery

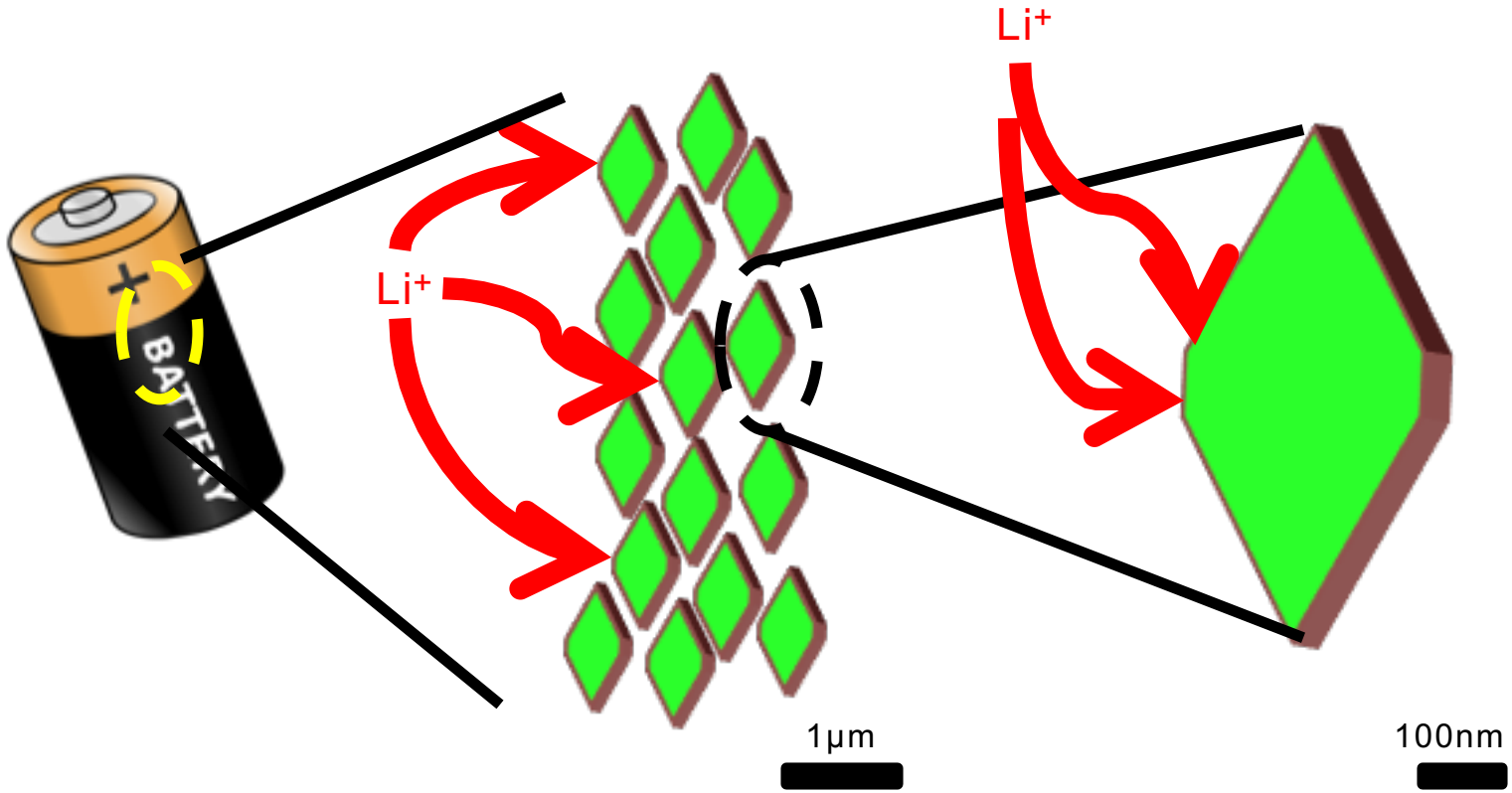


Spatio-dynamics at varying lengthscale

Conventional electrochemistry

Inter-particle dynamics 1~100μm

Sub-particle dynamics 10nm ~ 1μm

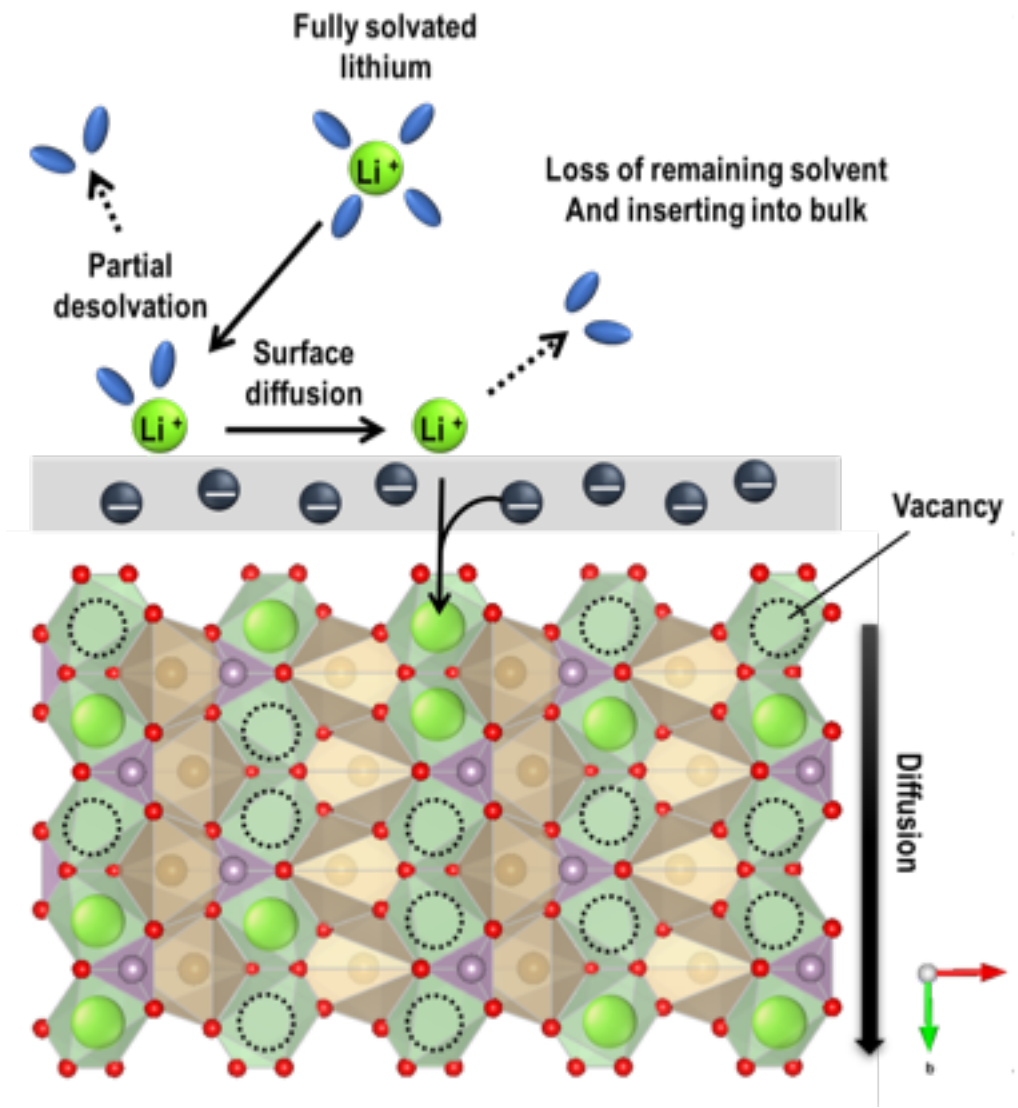


Capacity : 100~ 1000mAh

Capacity : 100fAh

Zhang, *et al. Nat. Comm.* **7** (2015) 8333
Wang, *et al. Nat. Comm.* **6** (2014) 4570
Li, *et al. Nat. Mater.* **13** (2014) 1149

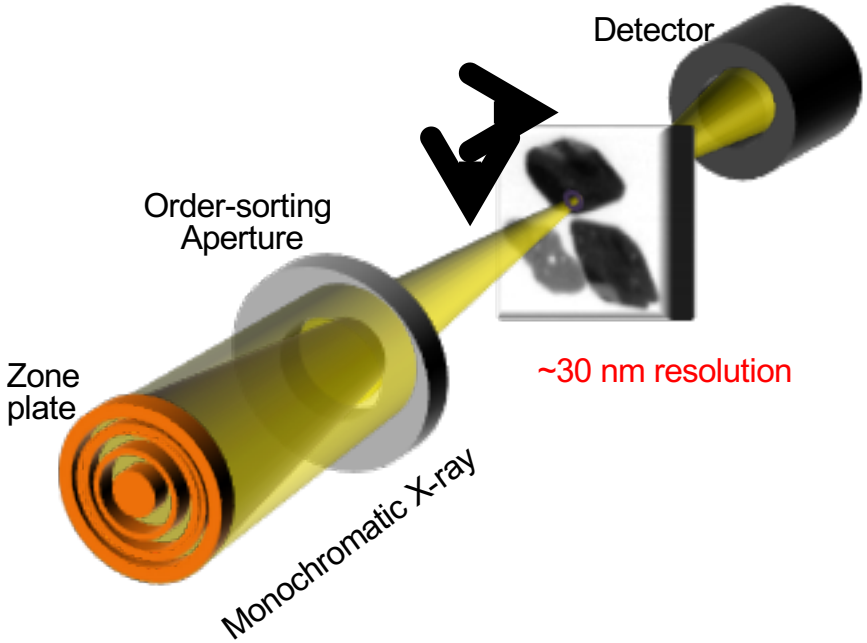
Role of surface dynamics for ion insertion

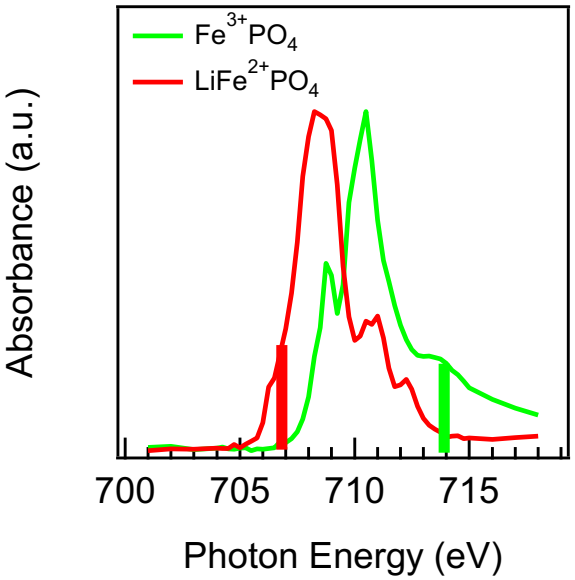


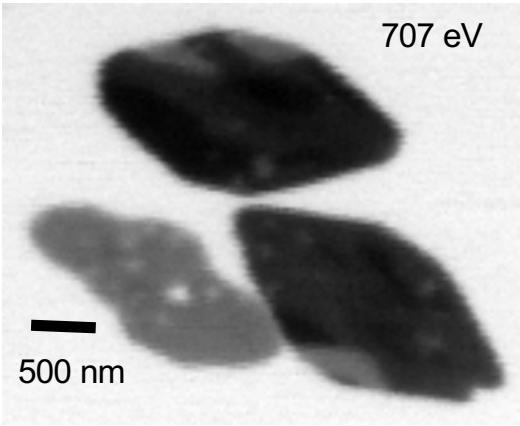
Charge transfer

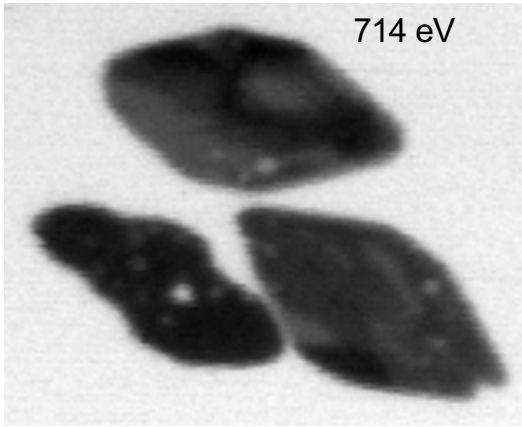
Ion diffusion

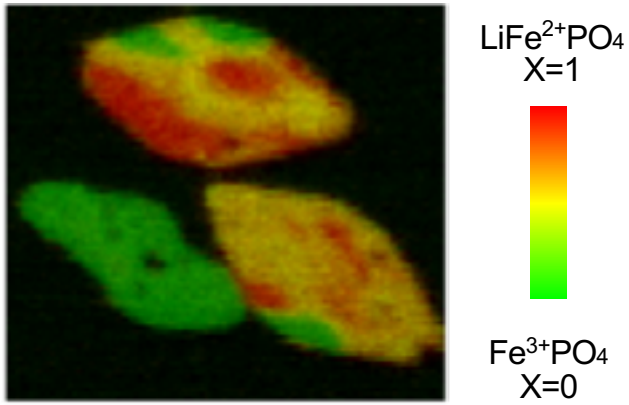
X-ray spectro-microscopy





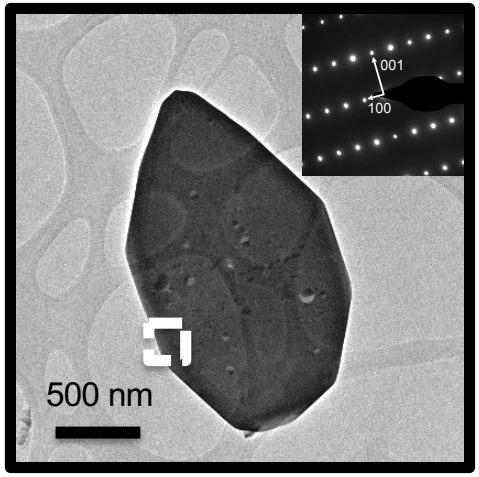


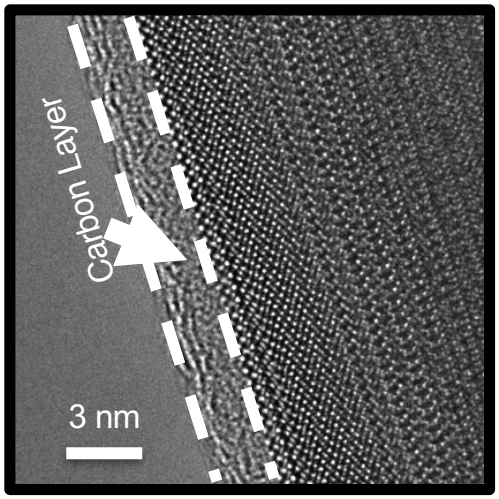


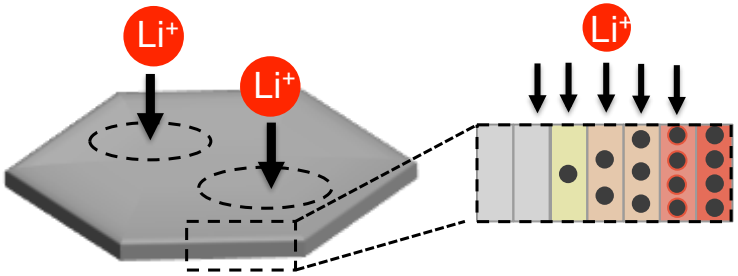


Spatially-resolved map of Li composition

$LiFePO_4$ battery particle synthesis







Particle Synthesis

$$H_3PO_4 + 3LiOH_{(aq)} \longrightarrow Li_3PO_{4\,(s)} + 3H_2O_{(l)}$$

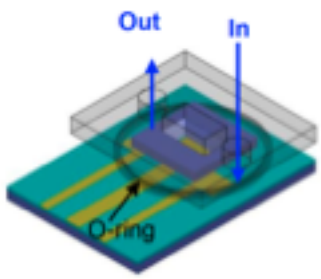
$$Li_3PO_{4\,(s)} + FeSO_{4\,(aq)} \xrightarrow[\text{PEG+Water}]{\text{140C 1h + 210C 17h}} LiFePO_{4\,(s)} + Li_2SO_{4\,(aq)}$$

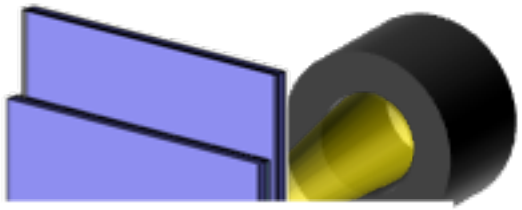
Solvothermal synthesis

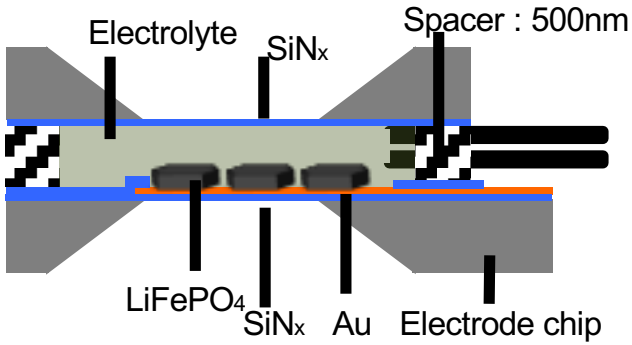
Carbon-coating

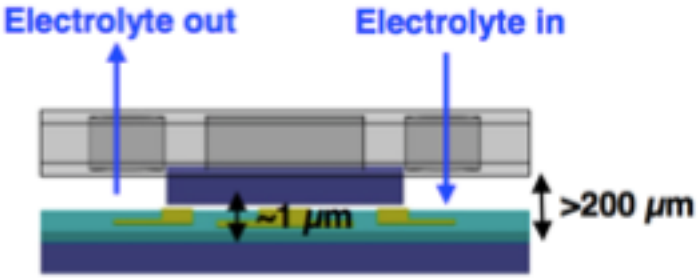
$$LiFePO_{4\,(s)} + n\text{Sucrose}(C_{12}H_{22}O_{11}) \xrightarrow[\text{Ar}]{\text{600C}} LiFePO_{4\,(s)}/C + nH_2O$$

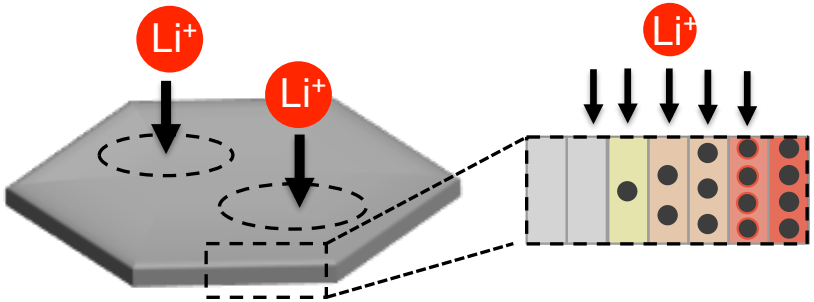
Microfluidic transmission battery

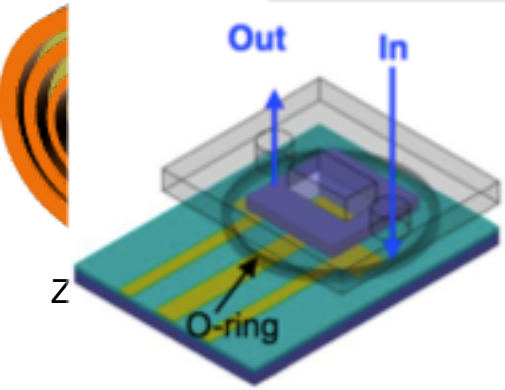


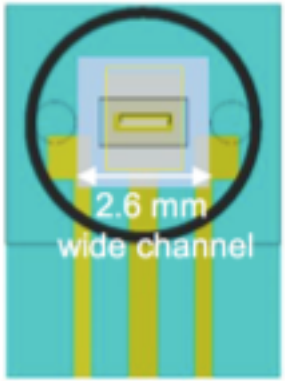


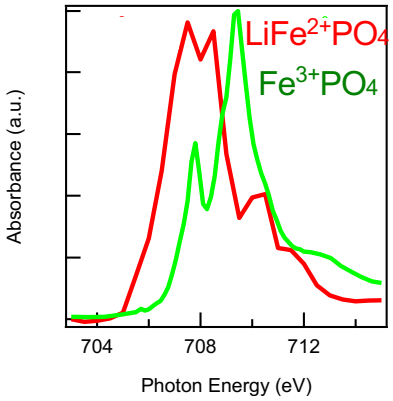


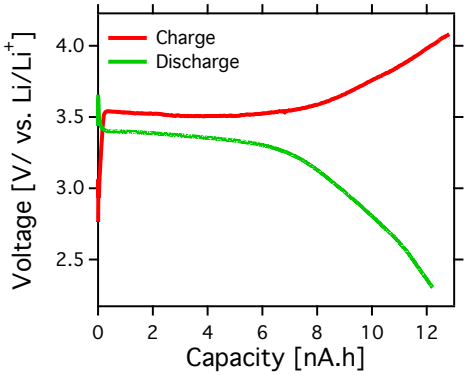












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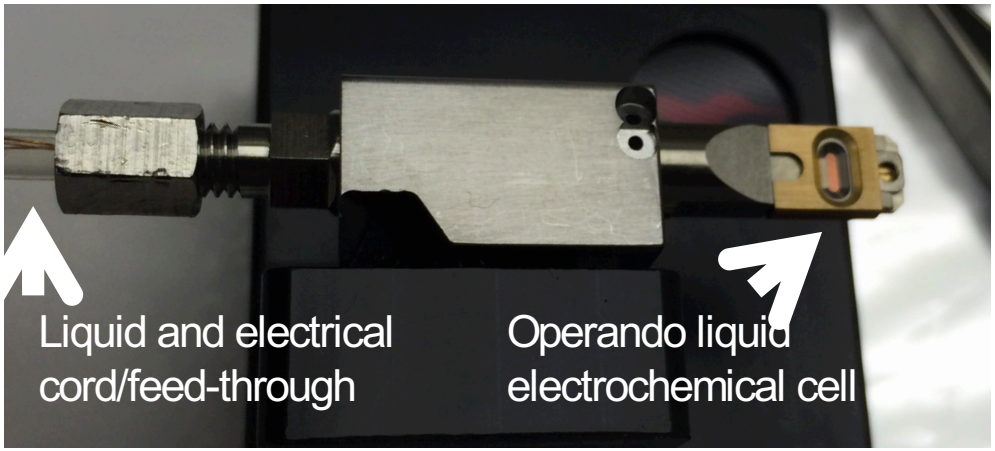
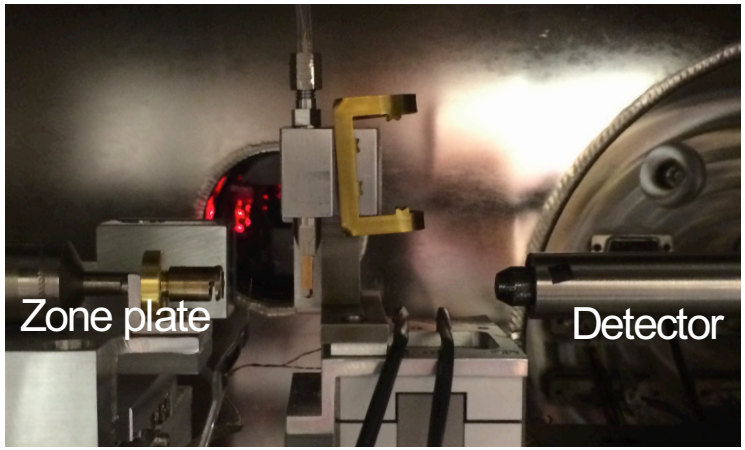
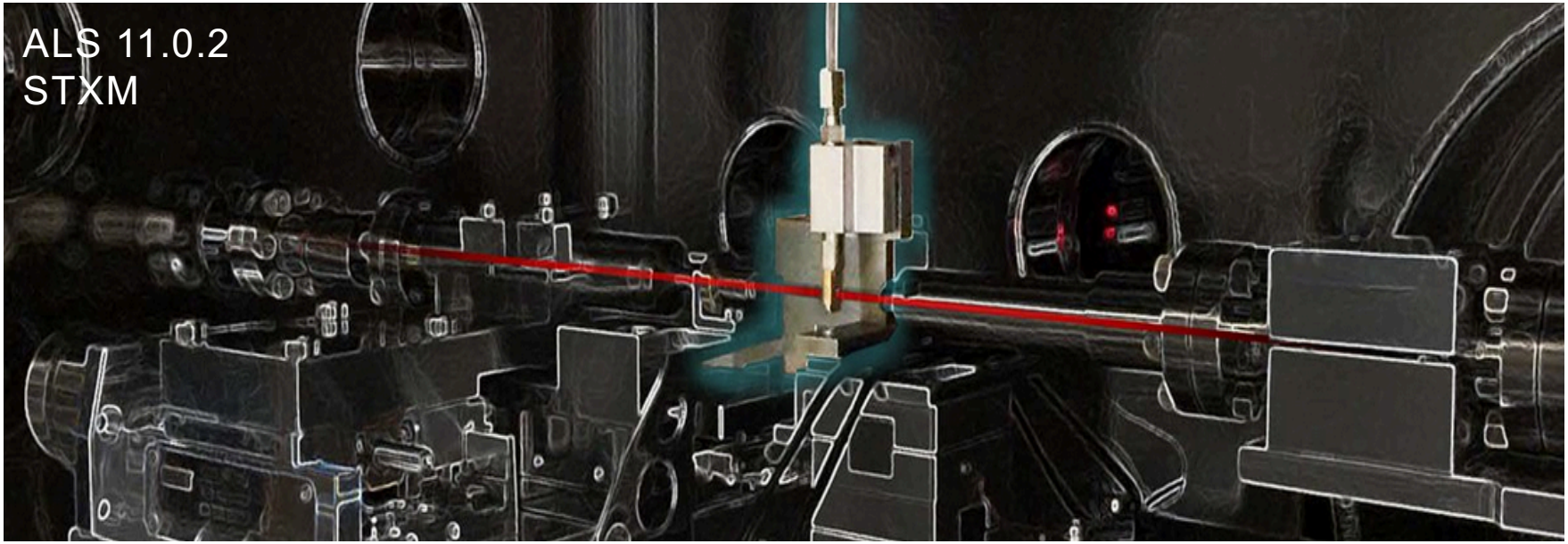
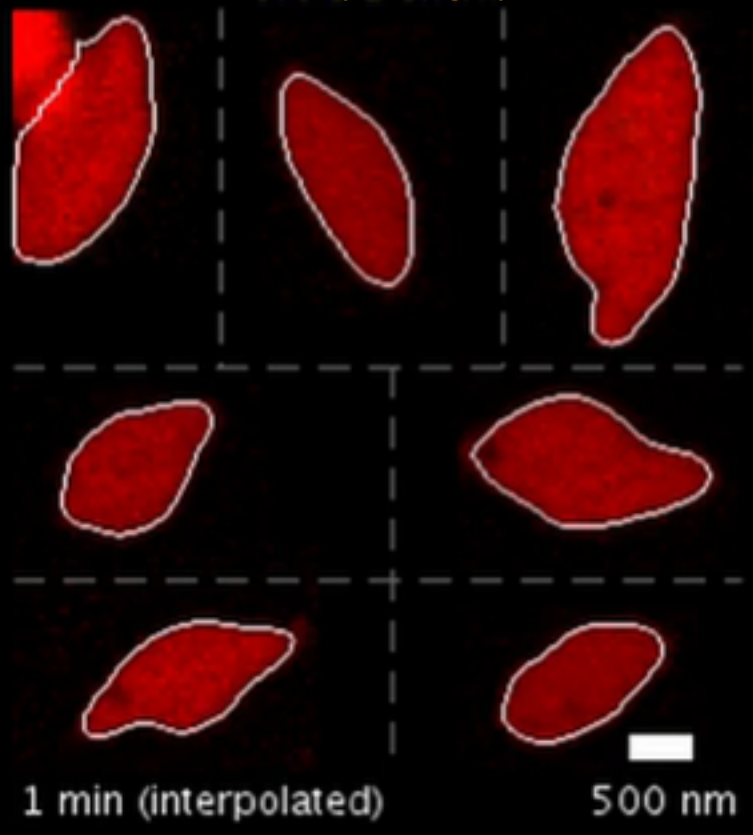

Liquid and electrical cord/feed-through
Operando liquid electrochemical cell


Zone plate
Detector

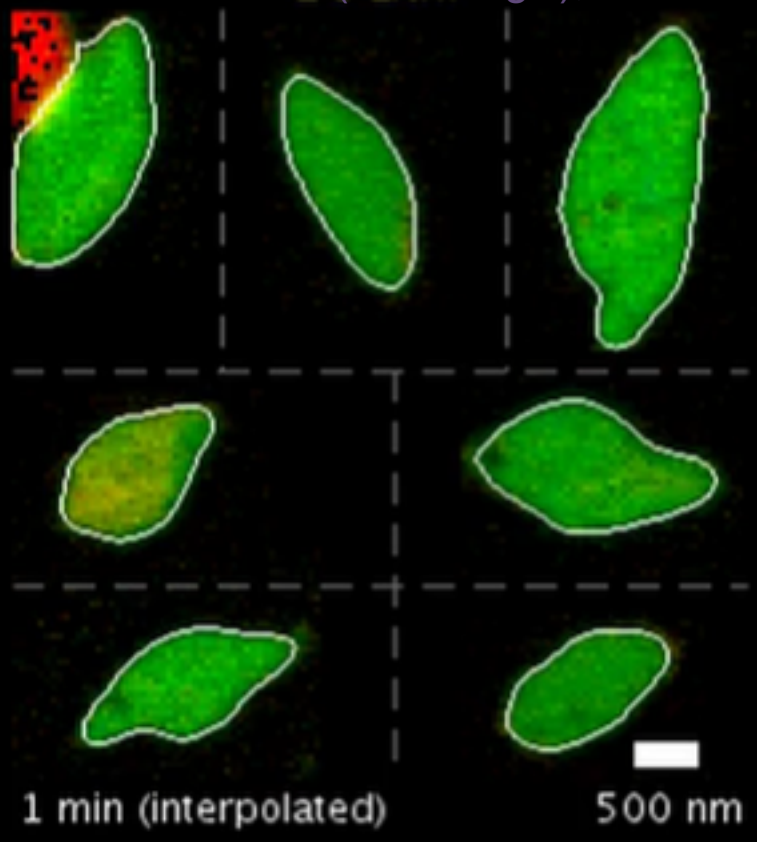

ALS 11.0.2
STXM

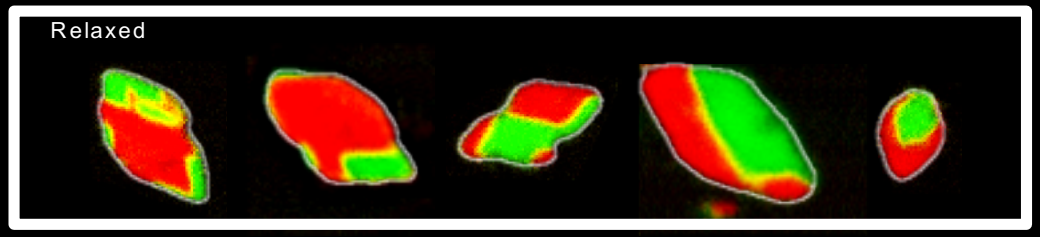
In situ movies of (de)lithiation

Delithiation(charge), 0.6C



Lithiation(discharge), 2C





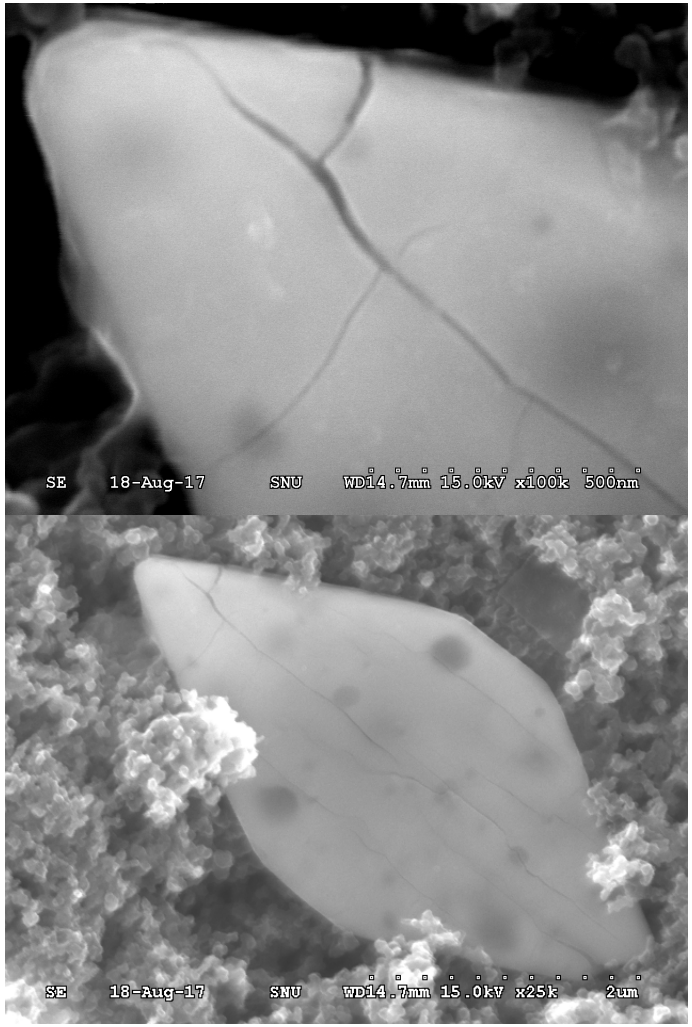
$Fe^{3+}PO_4$
X=0

$LiFe^{2+}PO_4$
X=1

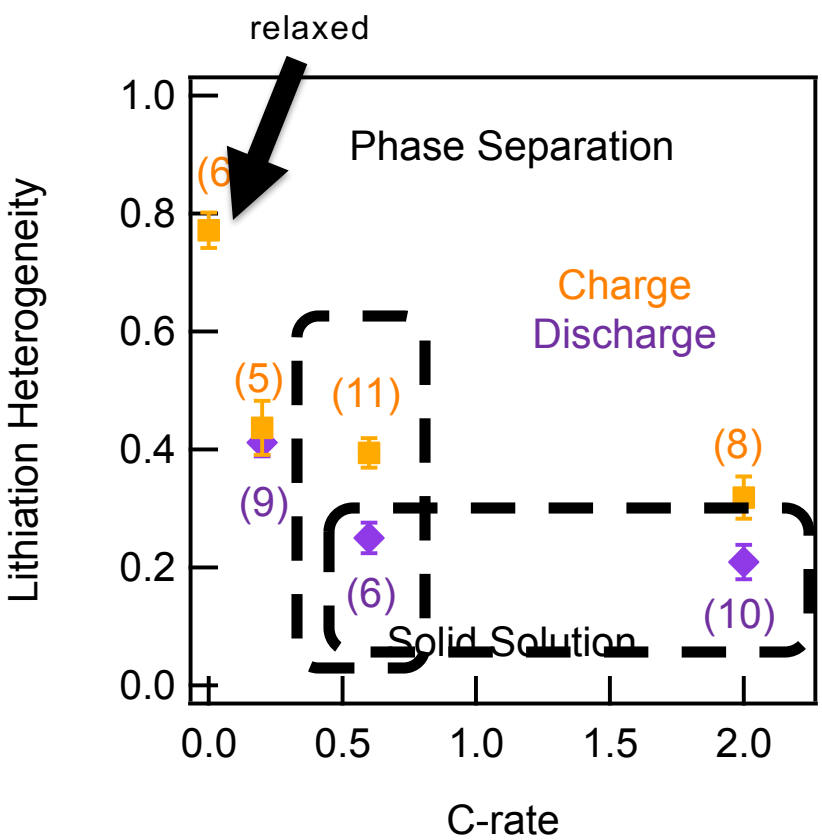
Spatial resolution – 50nm
Temporal resolution – 30s

Battery Failure with Crack

After cycling

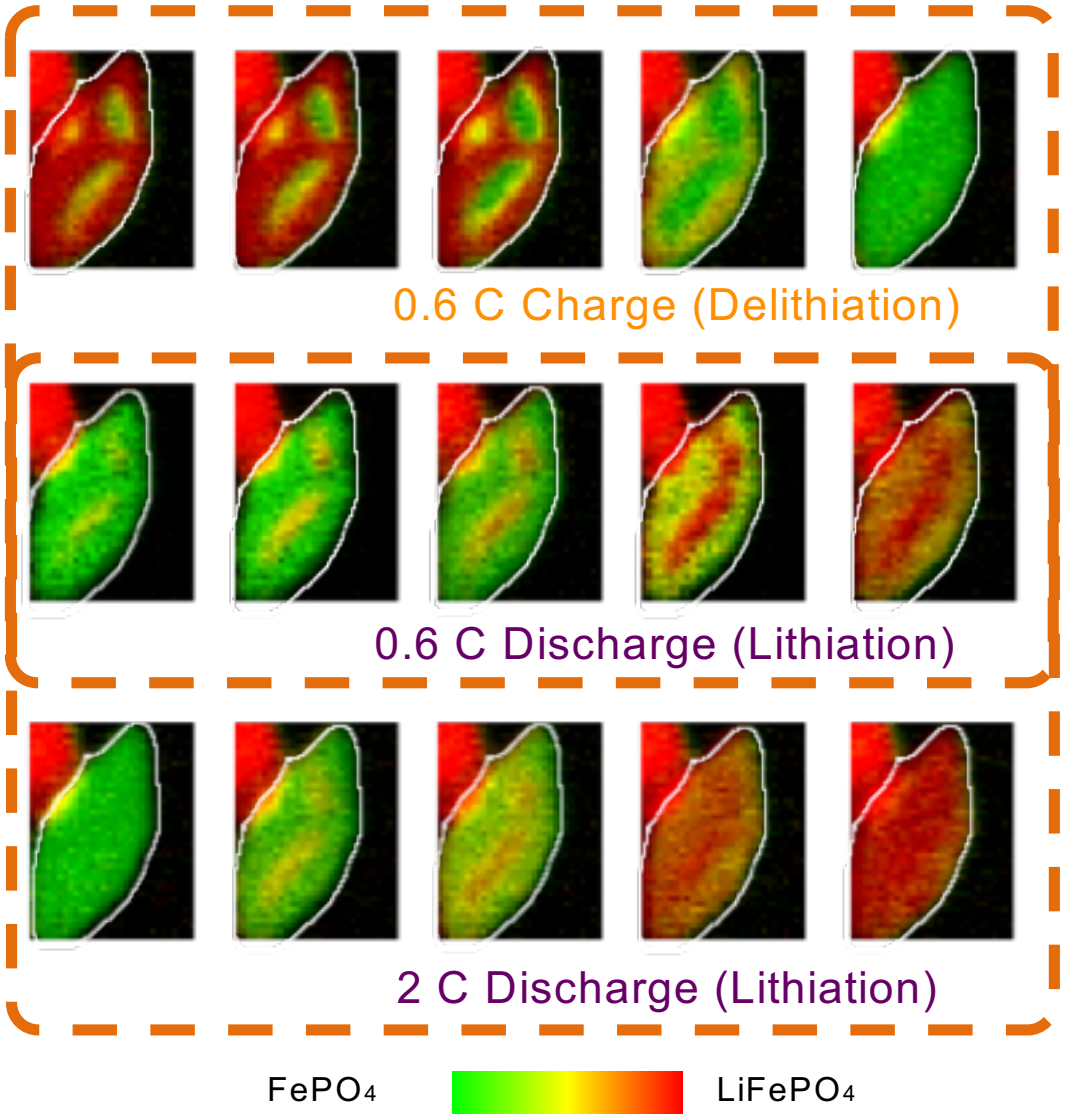


Rate Dependent (de)Lithiation Heterogeneity



Heterogeneity = 1

Heterogeneity = 0



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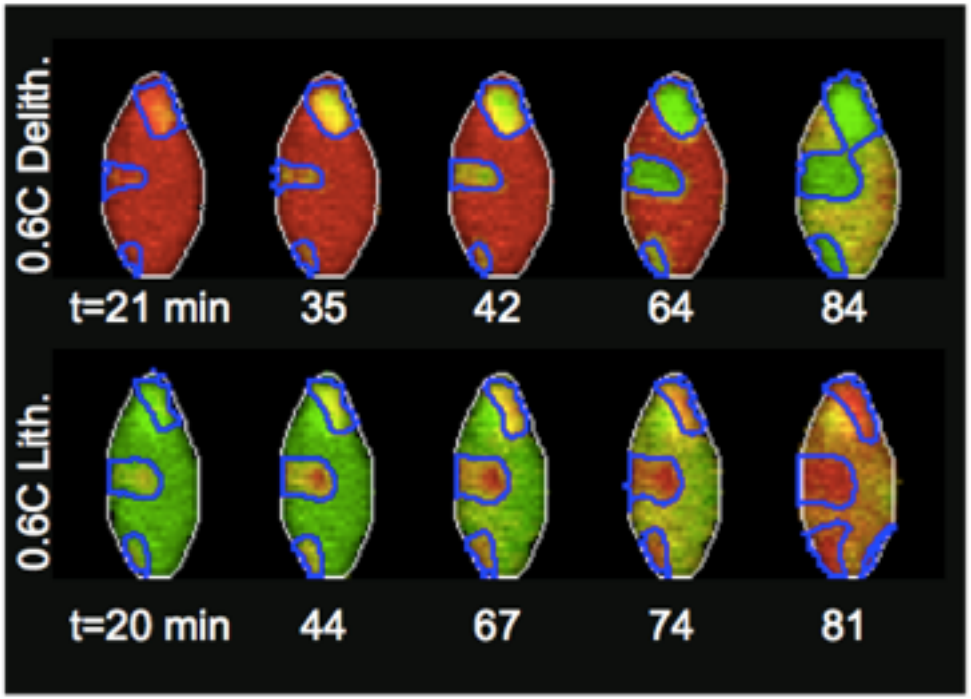
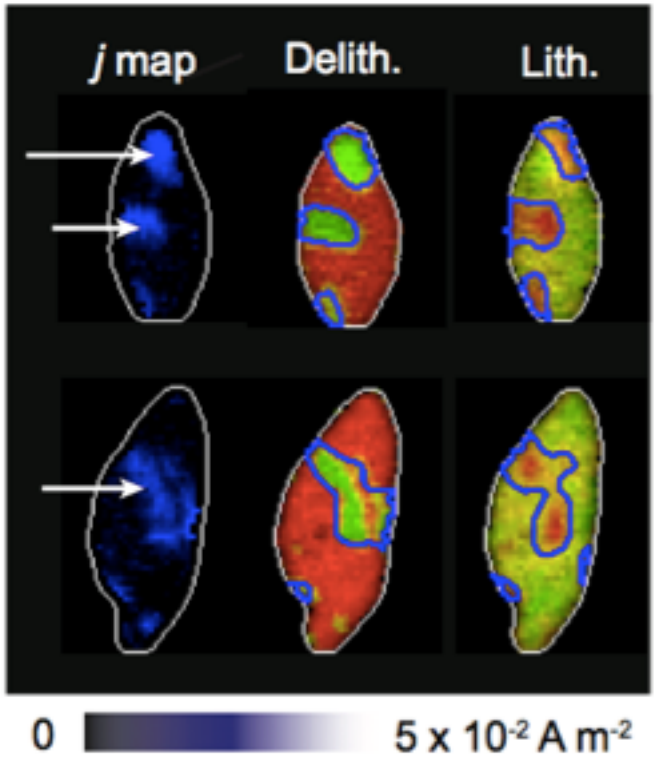
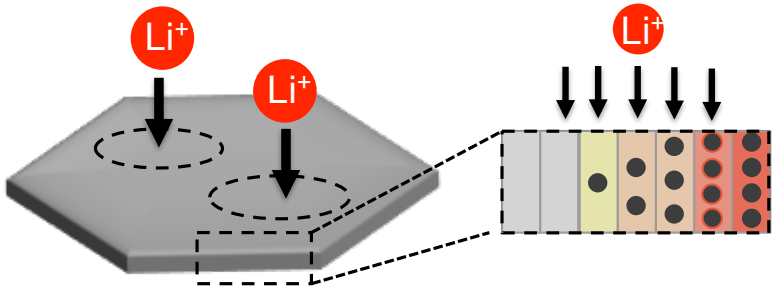
Current density (insertion rate) quantification







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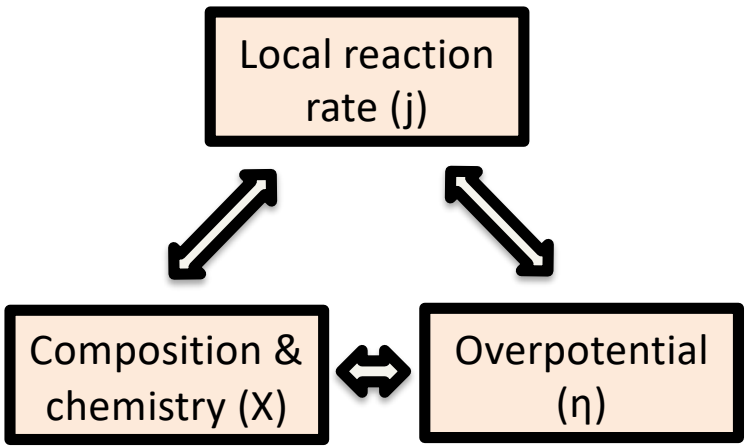
Exchange current density vs. Li composition

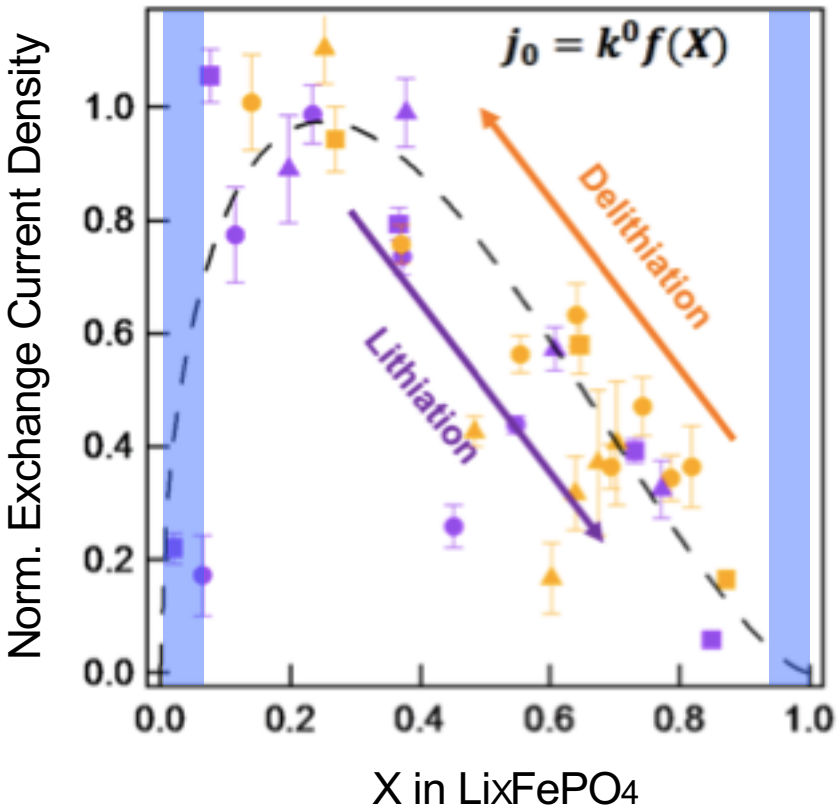
$$J_0 = J / f(\eta)$$

J_0 = Exchange current density
= *intrinsic rate property*

J = Local current density
= current /active area

η = *Overpotential*





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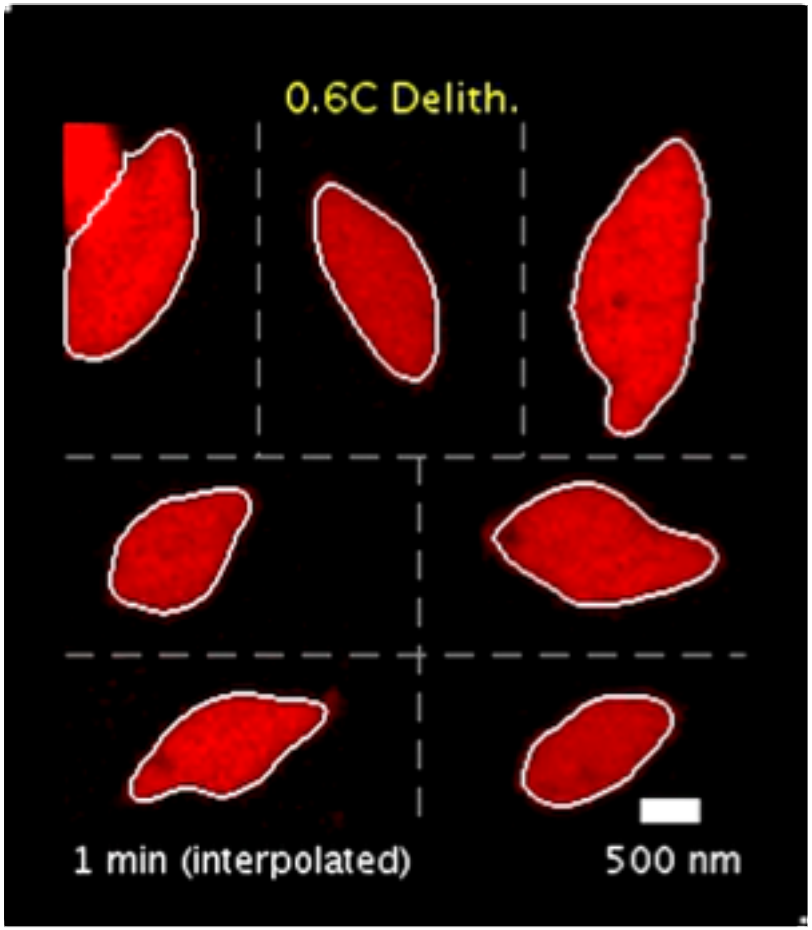
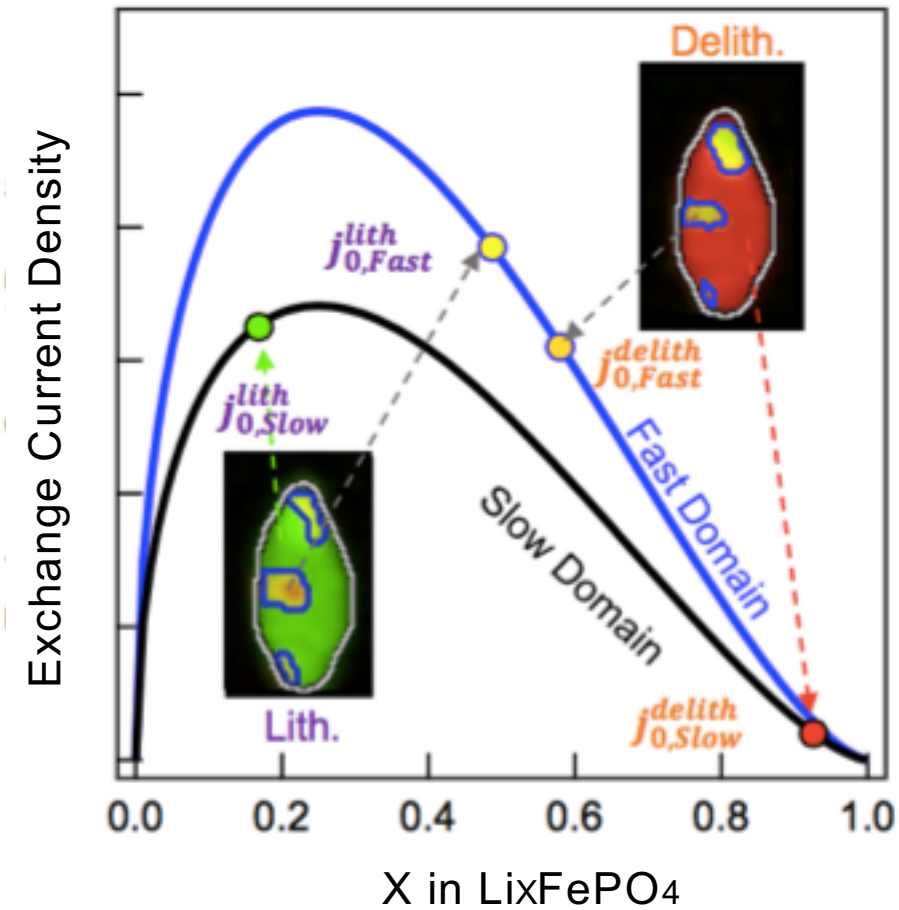
Origin of heterogeneity





Spatial and compositional dependence of kinetics determine the uniformity of lithiation

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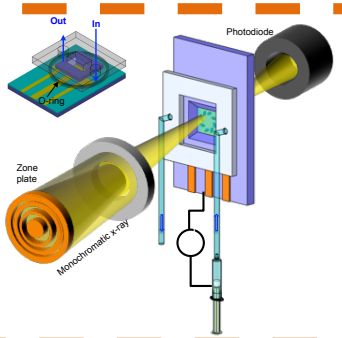
Research summary

In-situ/Single level Platform enigneering

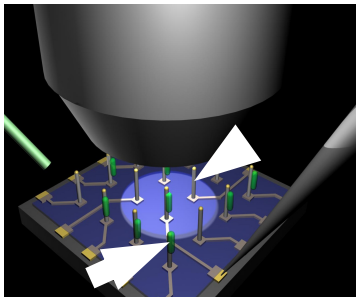
Spectro-microscopy

Science Understanding!

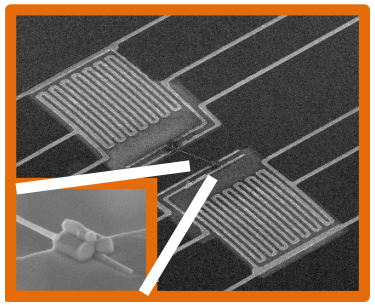
Battery



Bio-Echem



Thermoelectrics



Q&A

감사합니다