Mapping ionic currents and reactivity on the nanoscale: Electrochemical Strain Microscopy

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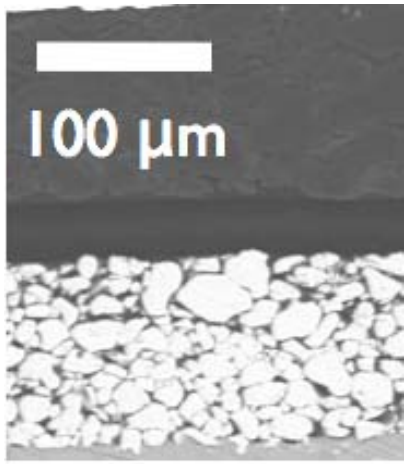
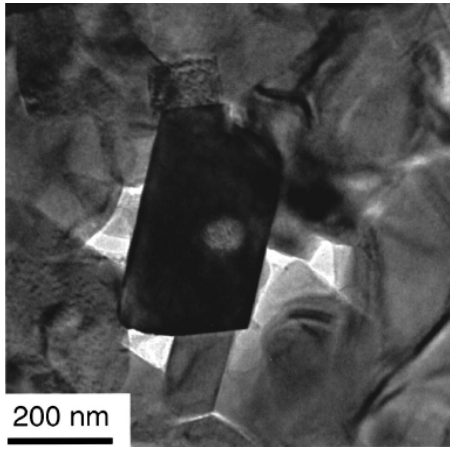
- Claus Daniels group (ORNL)
- Yang Shao-Horn group (MIT)
- Hans Christen group (ORNL)
- Anna Morozovska (NAS Ukraine)
- Edwin Garcia group (Purdue)

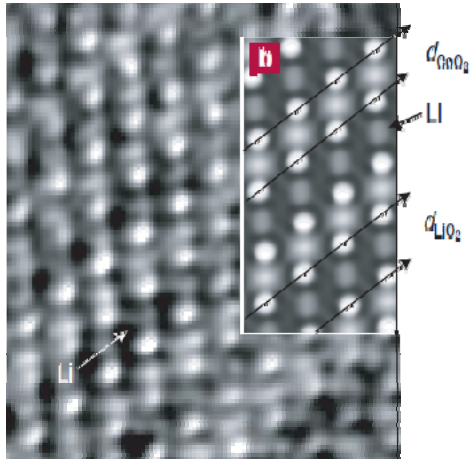
Structure and functionality in batteries on different length scales



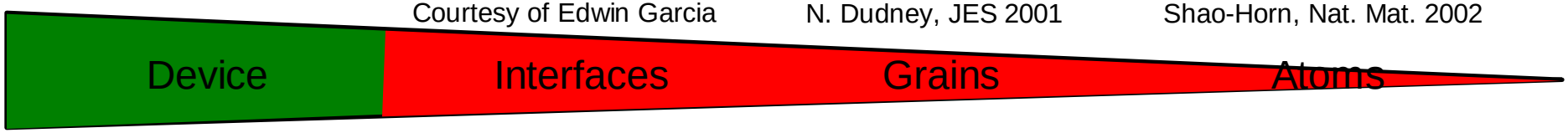
Courtesy of Edwin Garcia



N. Dudney, JES 2001



Shao-Horn, Nat. Mat. 2002



- interfacial reaction kinetics
- electronic and ionic transport

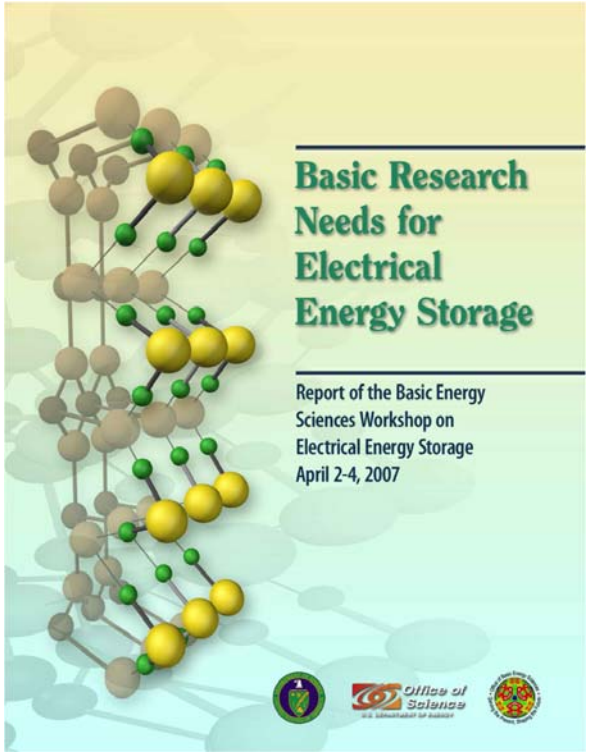
- grain boundaries
- grain orientation
- pores

- vacancies
- doping
- dislocations

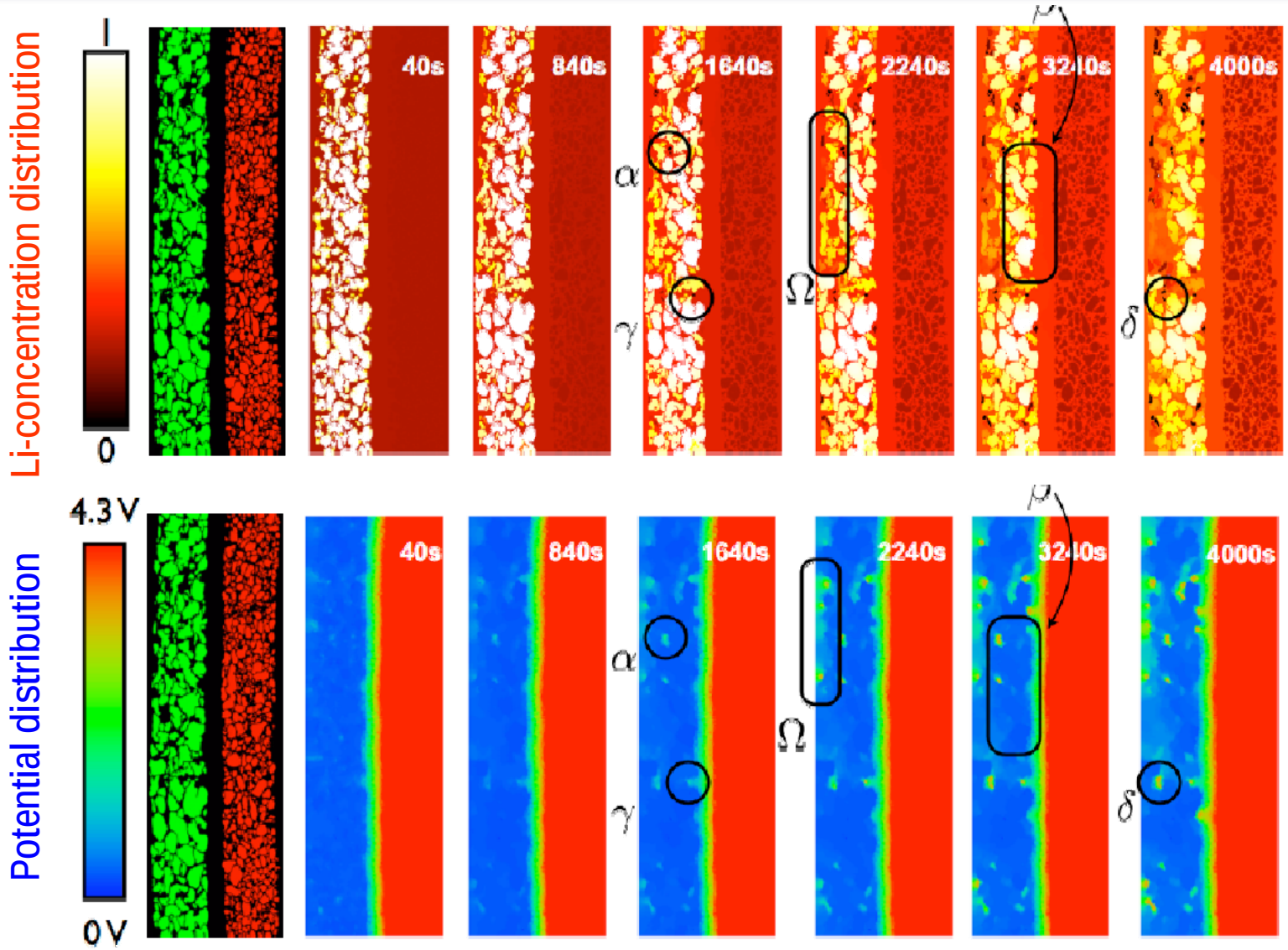
Material choice vs. Material engineering

Basic Research Needs for Electric Energy Storage

- New microscopic and spectroscopic techniques *spanning the atomic and mesoscopic scales*.
- "These measurements are critical to achieving the ability to design EES systems rationally, including materials and novel architectures that exhibit optimal performance".



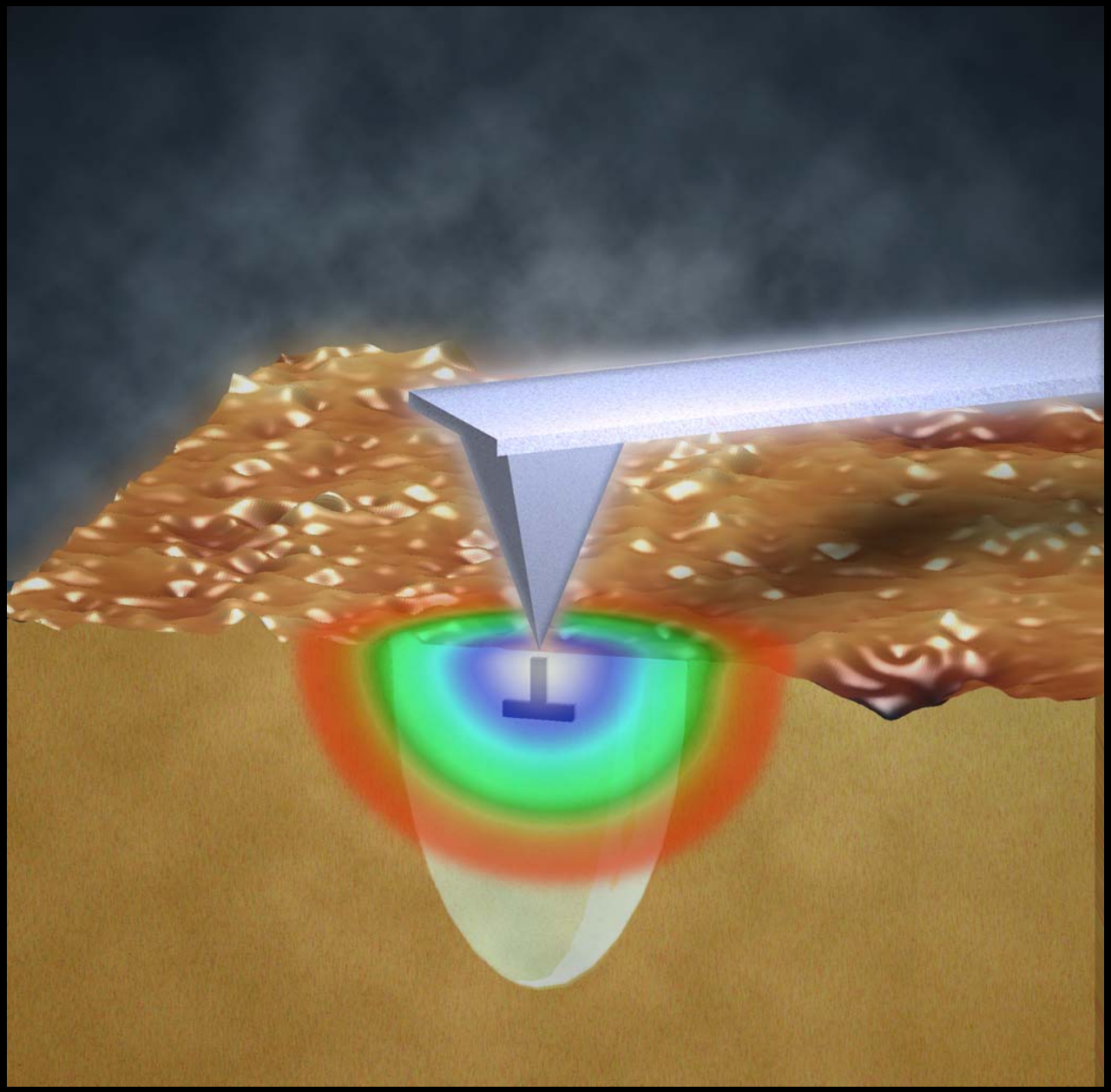
Real Battery Operation



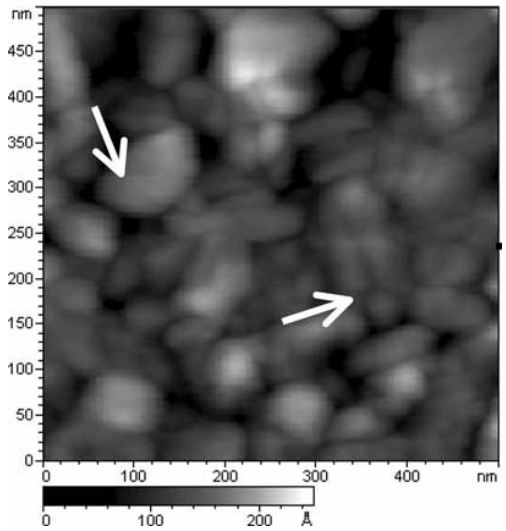
Realistic multiphase battery has complex micro-, meso- and macroscopic fields of potential and Li-ion concentrations.

E. Garcia, in print

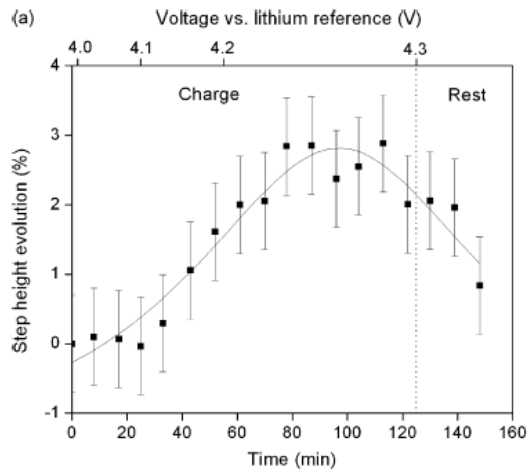
The Approach: Divide and Conquer



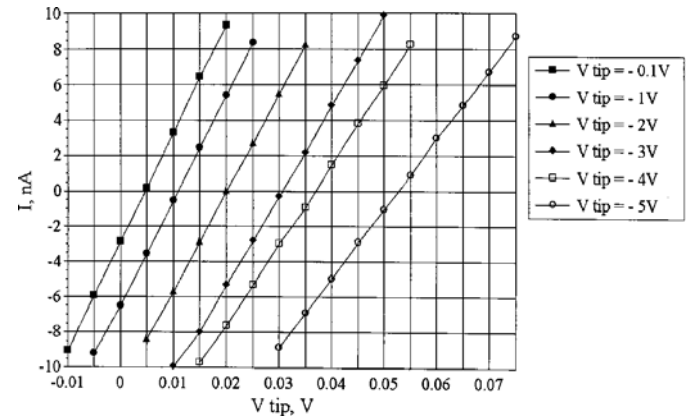
Previous SPM-based Studies



Electrochem. Comm. 6, 536 (2004).



Electrochim. Acta 52, 4572 (2007).



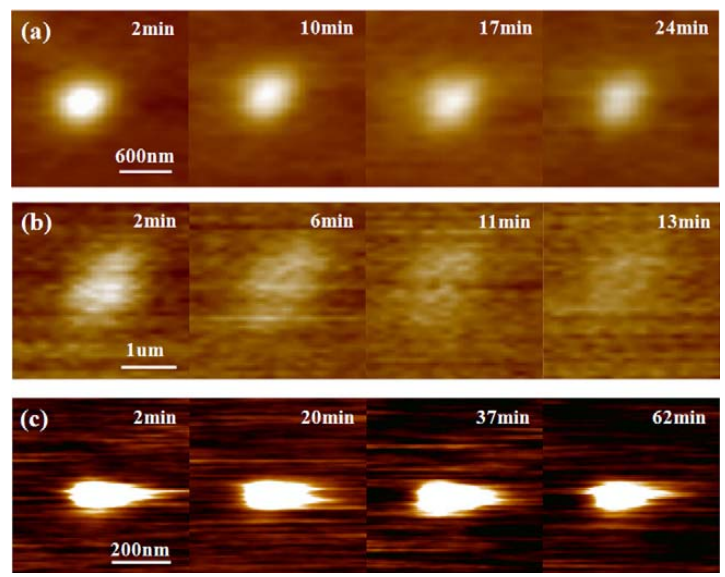
J. Electrochem. Soc. 148, A1239 (2001)

Topography measurements:
high resolution, but difficult to interpret

Step-height measurements:
time consuming, non-local

Current measurements:
cannot distinguish Li and electronic currents

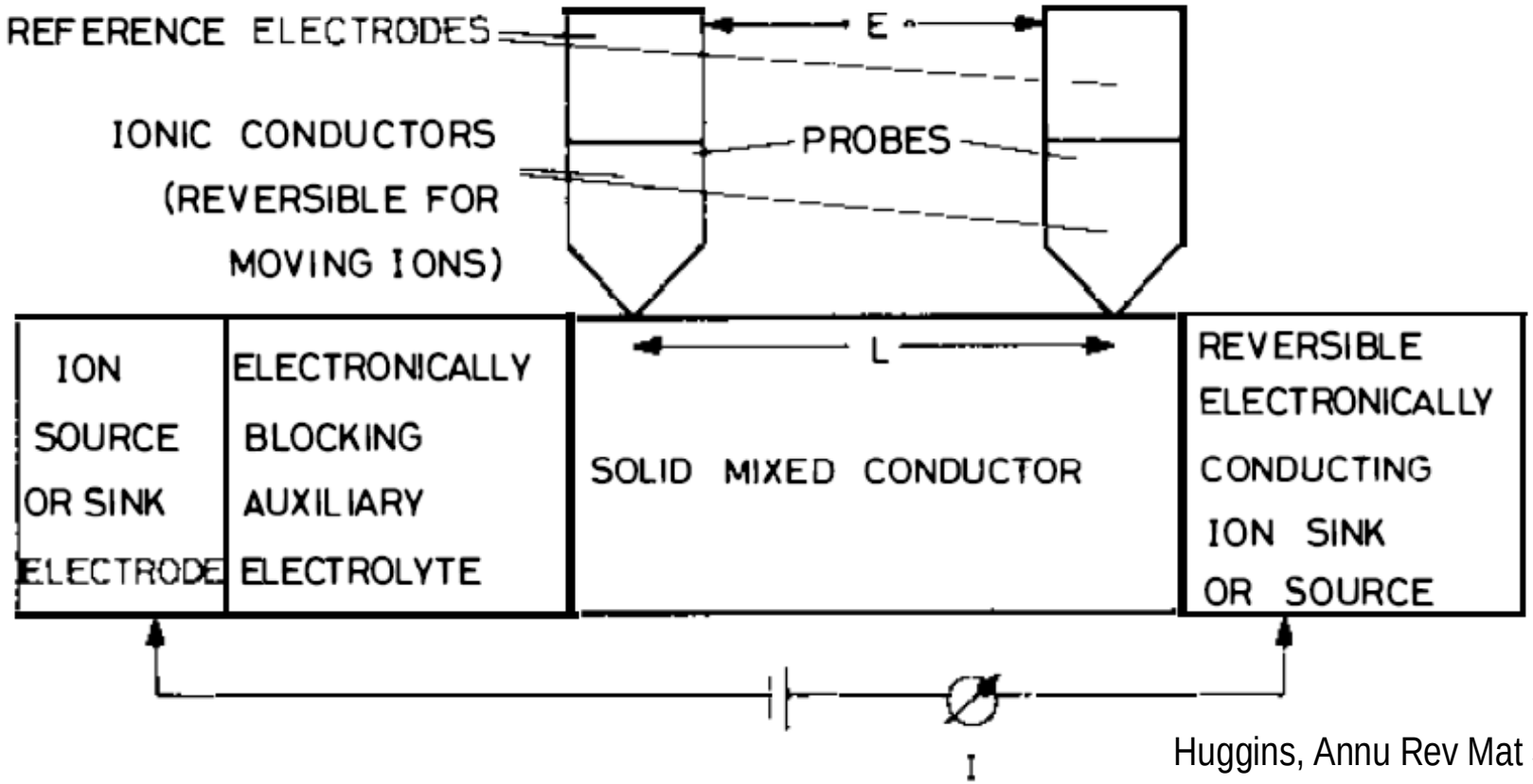
Potential measurements:
multiple mechnisms involved



Nanotechnology 20, 445706 (2009)

Challenge: Probing Li Diffusion on the Nanoscale

Revolution in nanoscale imaging has come with the STM and related scanning probe methods. Can we have STM for Li diffusion?



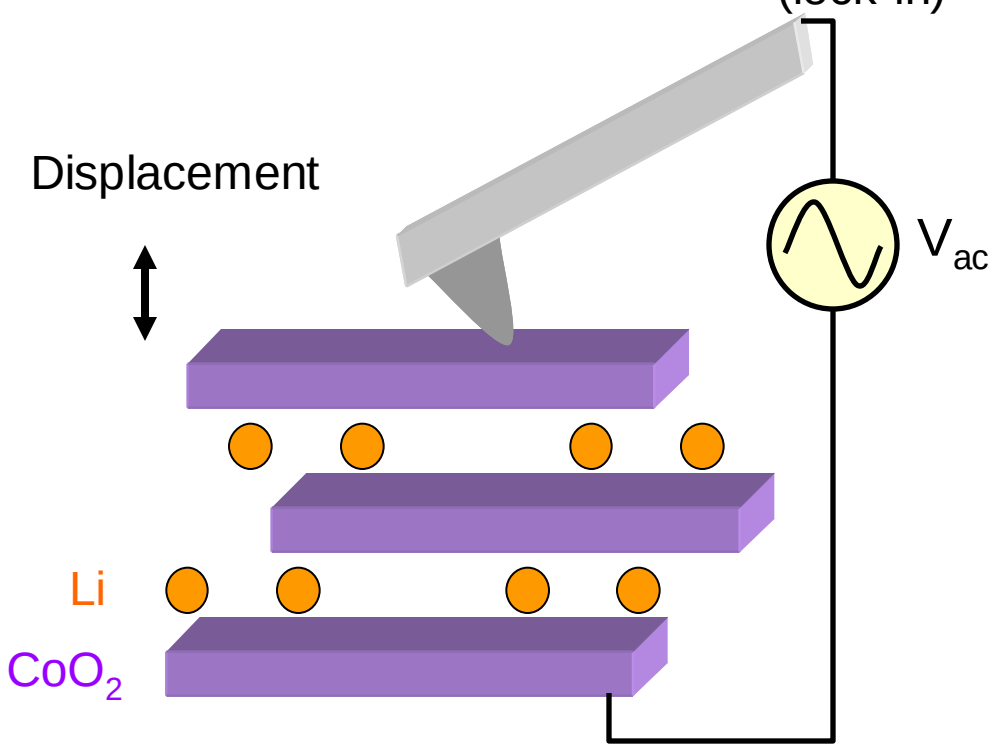
Huggins, Annu Rev Mat Sci. 1978

Due to extremely slow ion dynamics and high equivalent impedance, current detection on the nanoscale is impossible. Are there alternatives?

Electrochemical **S**train **M**icroscopy

Concept: Investigate local Li-ion dynamics based on $V = f(c_{Li})$ in **SPM time regimes**

SPM | ac fields (lock-in) | Electrochemical strain | <10 s per measurement

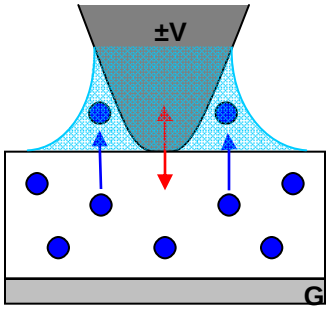


$$u = f(D_{Li}, c_{Li})$$

Local ac bias
↓
Change local c_{Li} profile
↓
Create local strain profile
↓
Surface displacement

Similar to Piezoresponse Force Microscopy

ESM signal: analytical



Analytical calculations to find frequency dependence of ESM signal

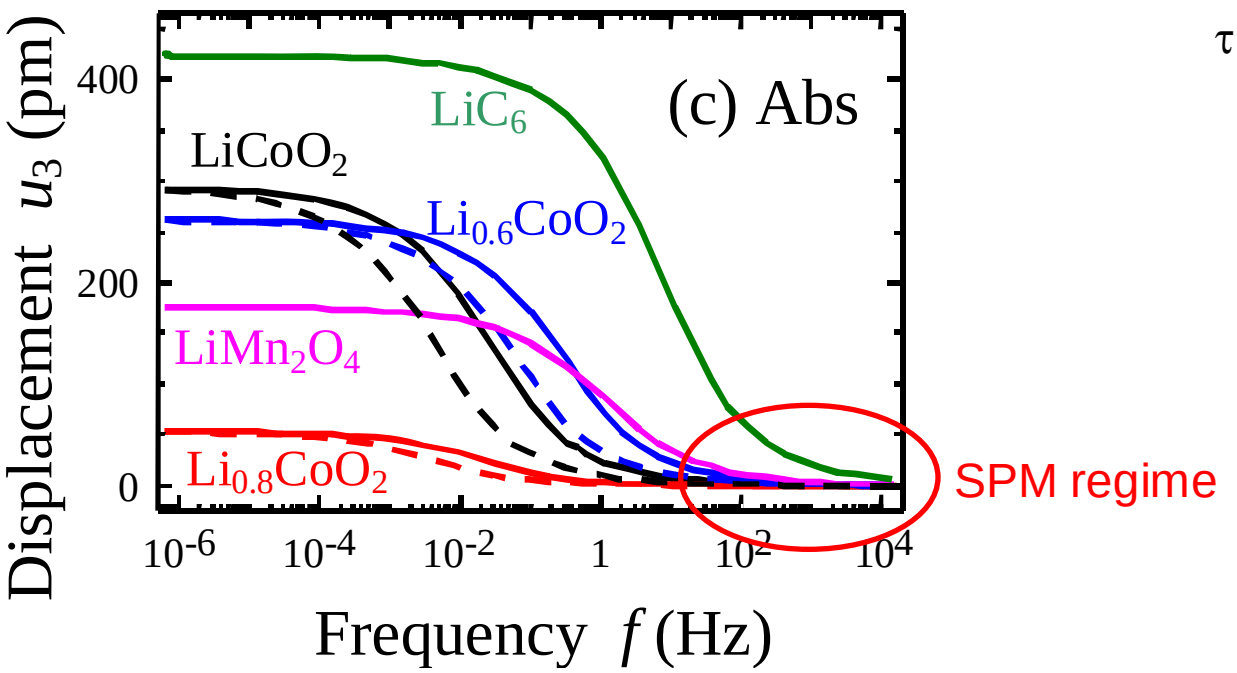
AC electrical probing fields

$$V_{tip}(x_1, x_2, t) \sim V_0(x_1, x_2, t) \sim V_0(x_1, x_2)\exp(i\omega t)$$

create surface oscillation (displacement)

$$u_3(0,\omega) = \frac{-(1+\nu)\beta V(\omega)}{\eta} \cdot \frac{R_0}{i\omega\tau}\left(\begin{array}{c}\exp\left(-(1+i)\sqrt{\omega\tau}\right) \\ -1+(1+i)\sqrt{\omega\tau}\end{array}\right)$$

$\tau = r^2/2D$

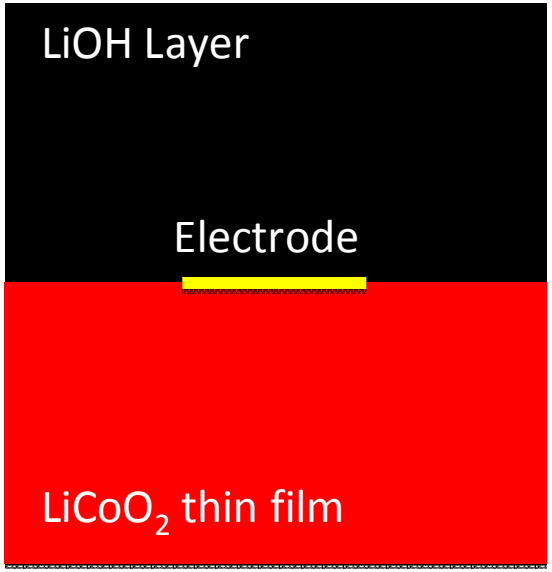


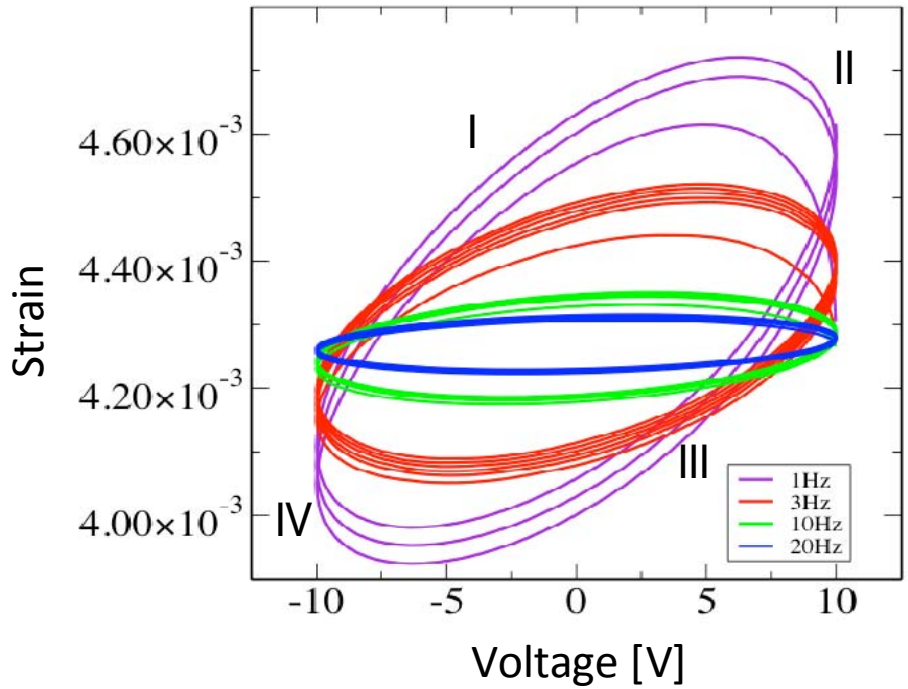
Anna Morozovska

Phase-Field Modeling of the PFM Dynamics

E. Garcia, Purdue University

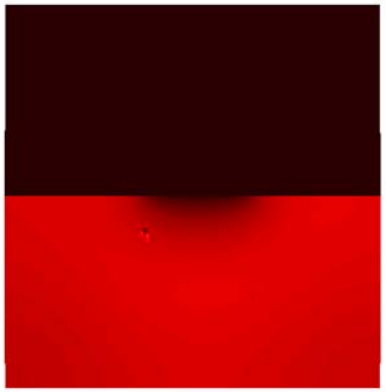
Phase-field model



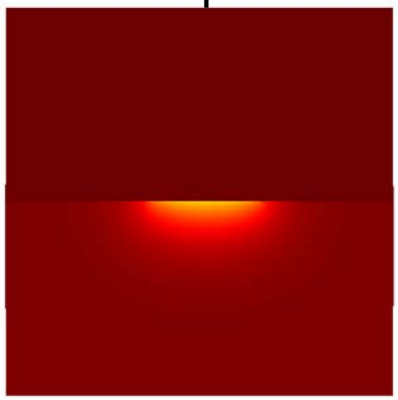


Potential

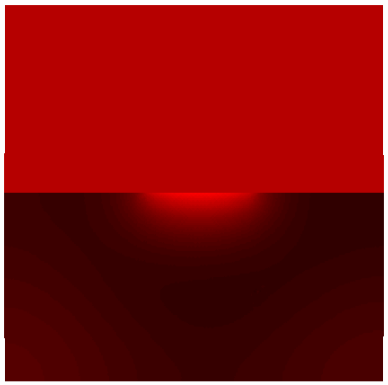
Step I



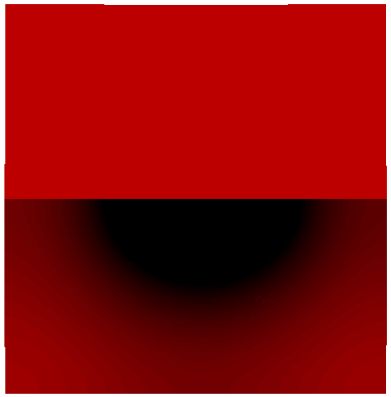
Step II



Step III



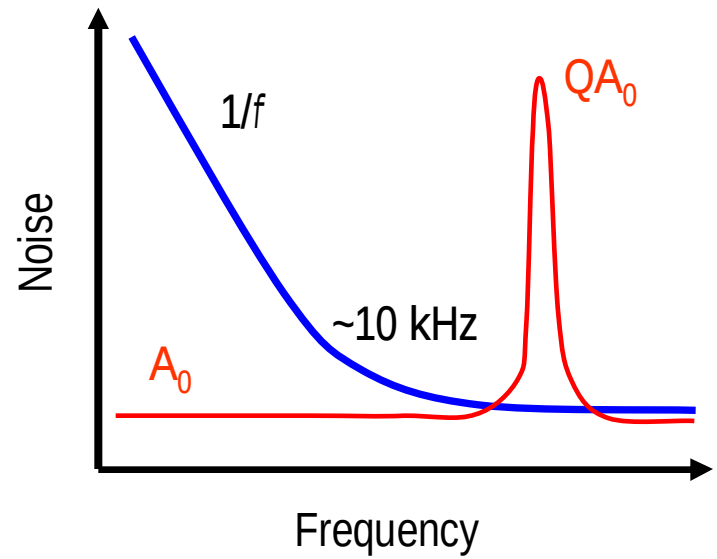
Step IV

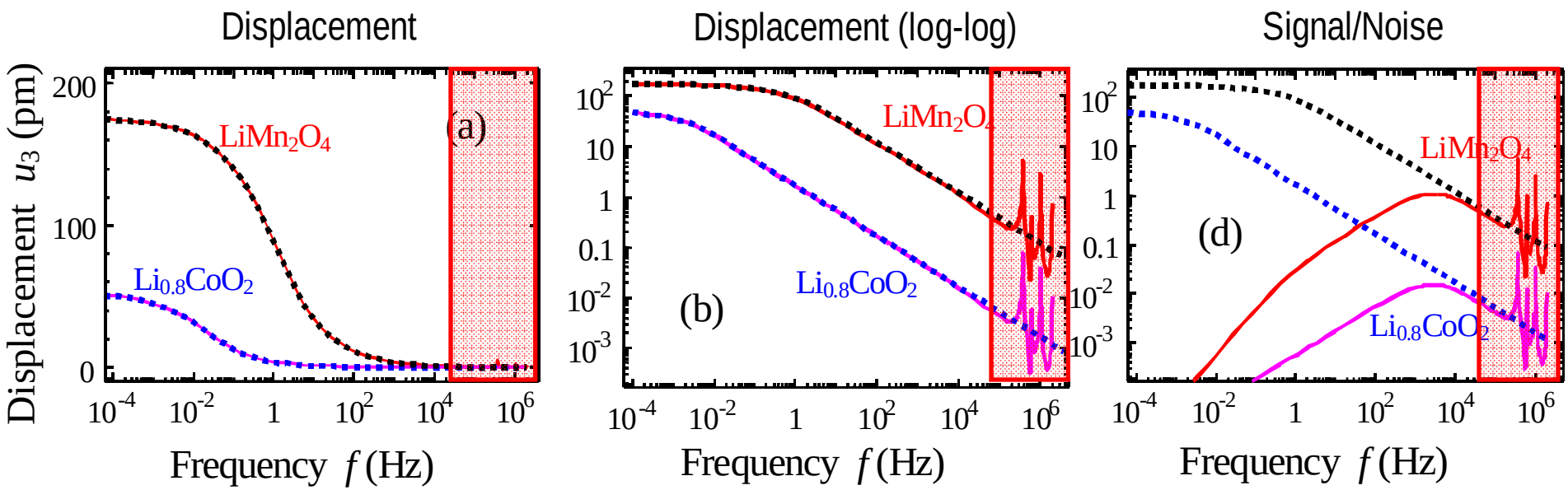


ESM signal: resonance enhancement

- stay away from 1/f noise
- mapping capabilities
- no sample decomposition
  (but also slowed down Li-ion dynamics)

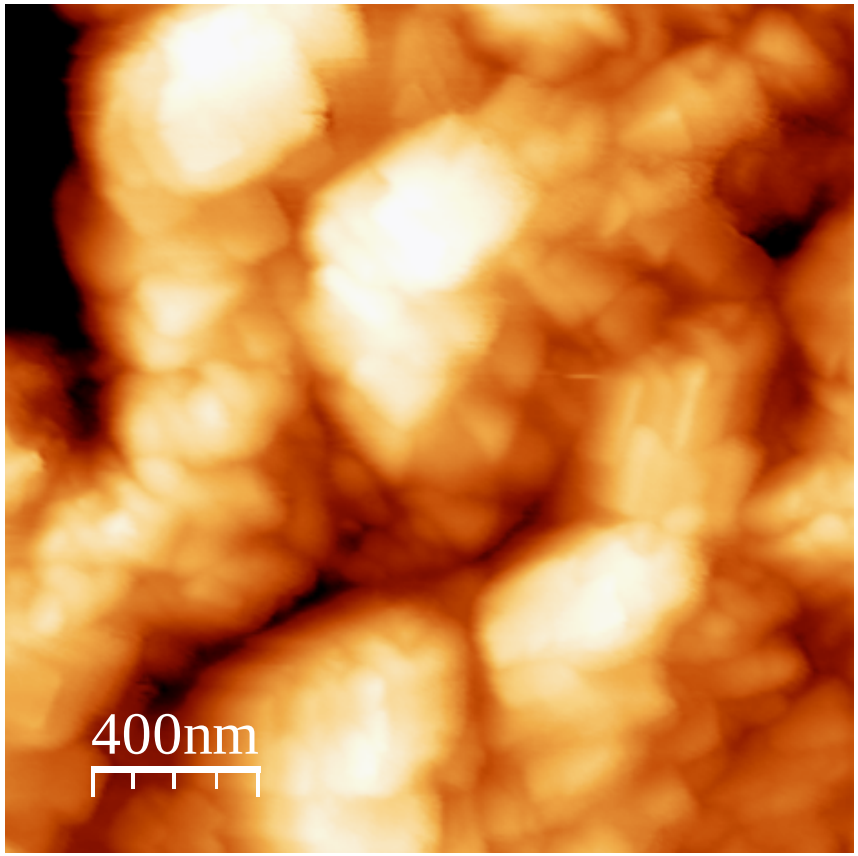
→ Contact resonance enhancement



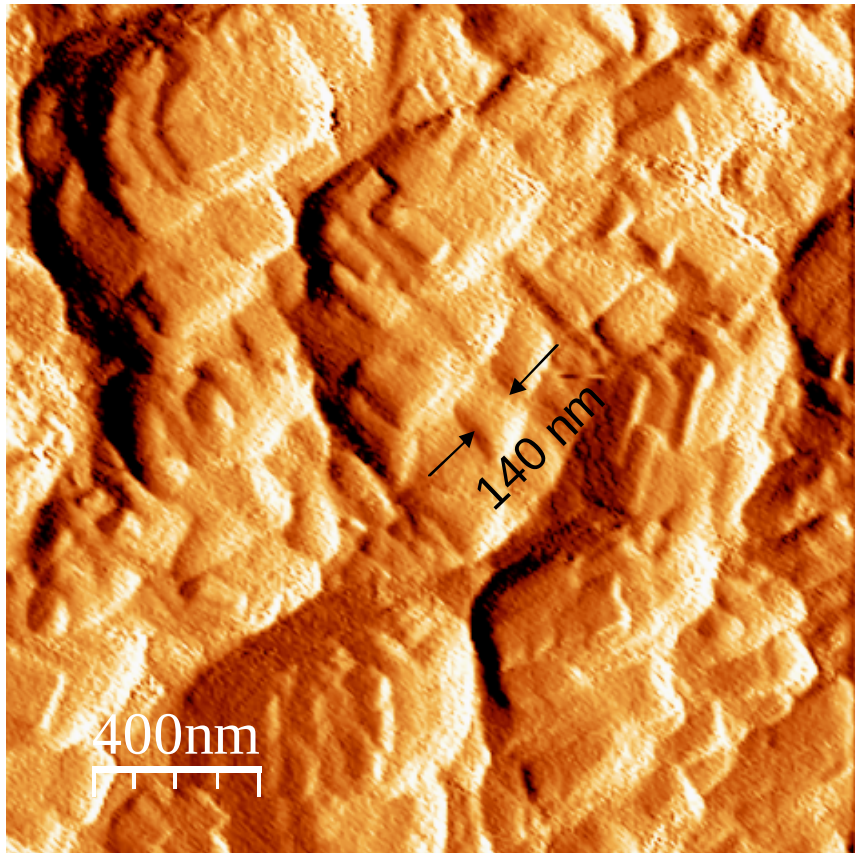


$LiCoO_2$: Topography

Topography

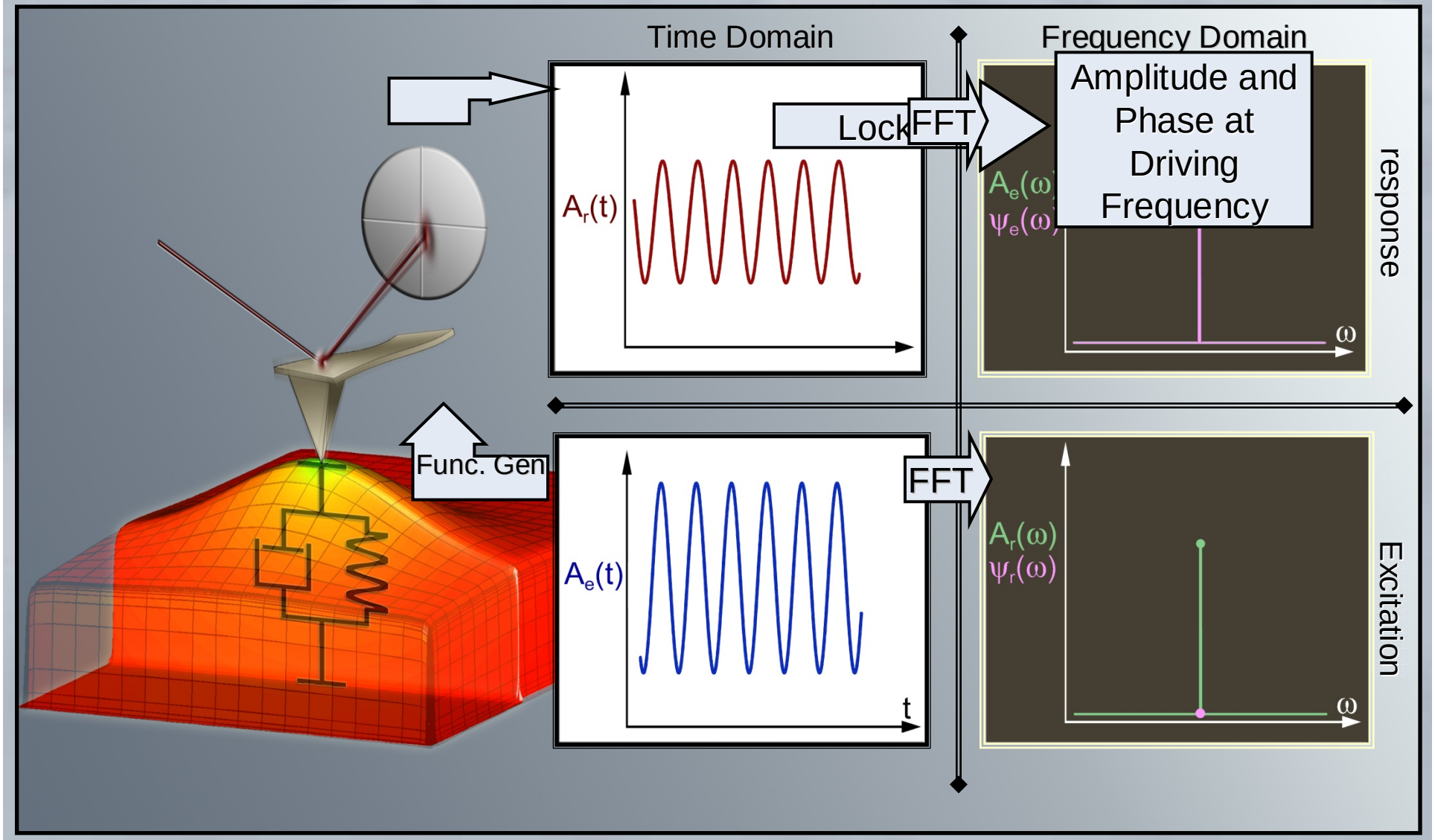


Deflection signal

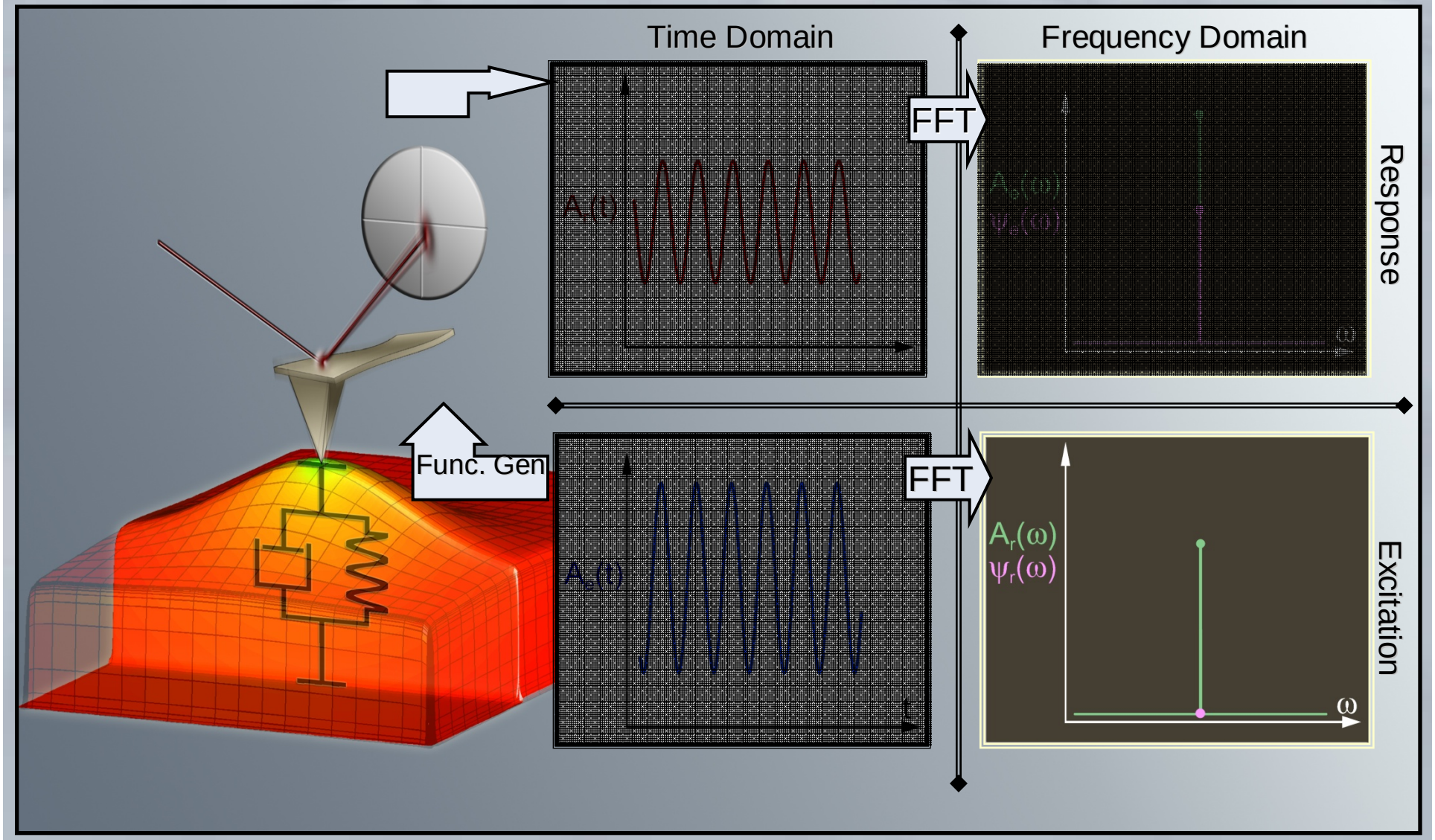


- $LiCoO_2$ thin film (500nm)
- Roughness around 100nm
- Grain size is hard to determine due to all the smaller substructures

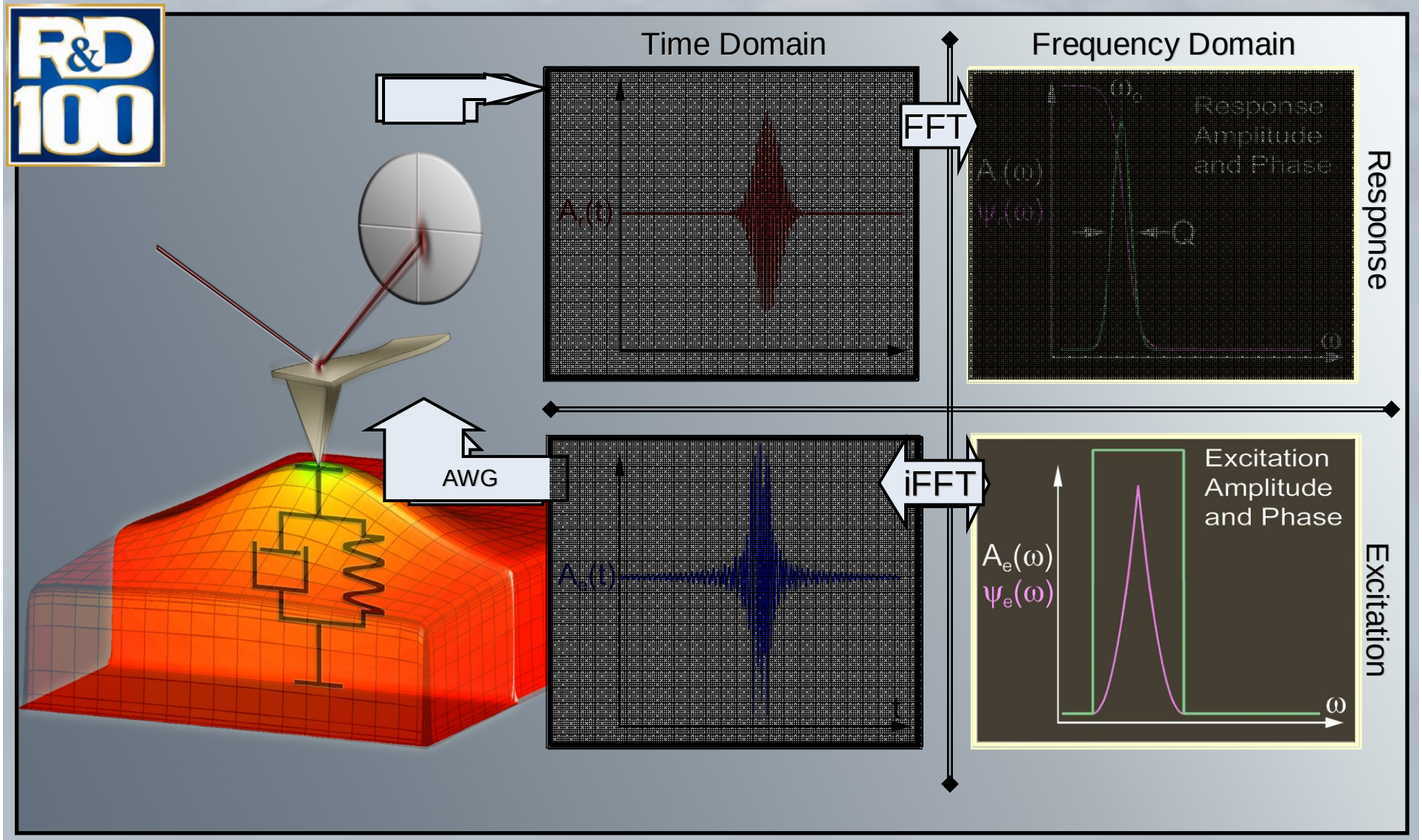
SPM Methods to Date



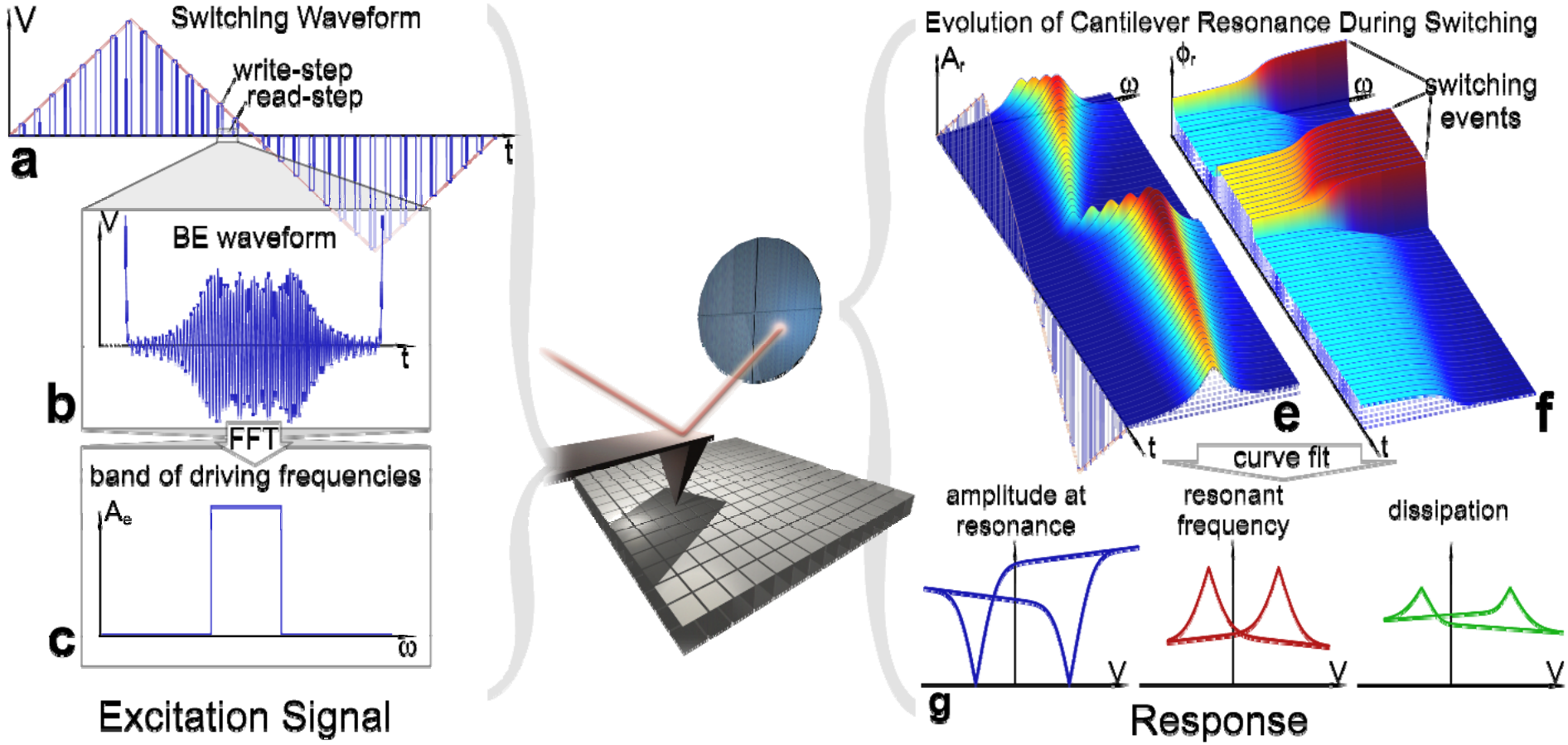
SPM Methods to Date



The Band Excitation Method: Dissipation Detection



Band Excitation Electrochemical Strain Microscopy



4D data array size: ~0.3-1 GB, Acquisition time: ~ 1 hour

5D data array size (FORC, kinetics): ~3-30 GB, Acquisition time: ~ 12 hours

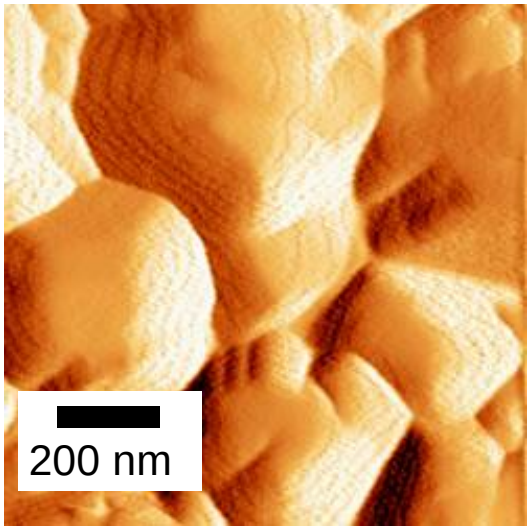
Fading or fatigue study: ~ 0.3 – 1 TB, Acquisition time: ~1-2 weeks

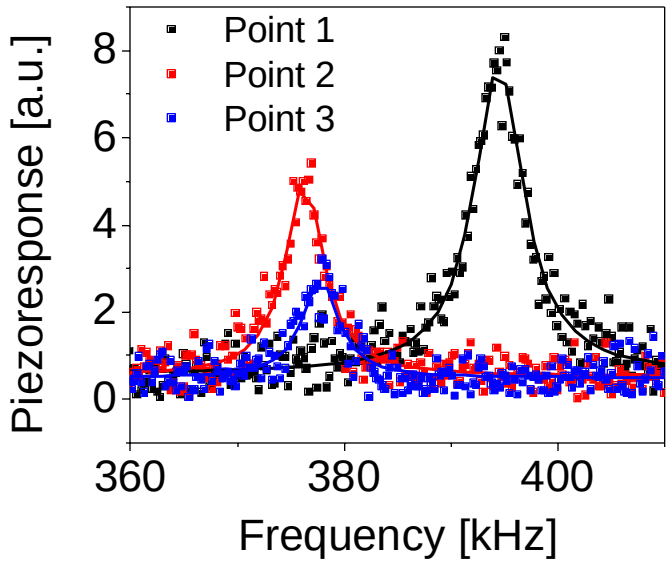
2008 winner

SPM Entering the Terabyte Age

Band Excitation PFM on $LiCoO_2$

Topography



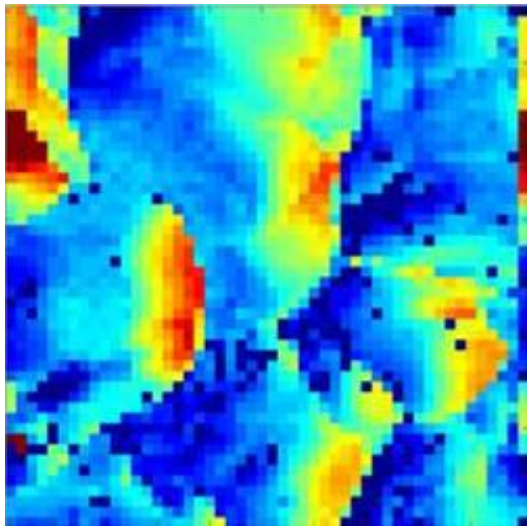


Electrochemical BE imaging with 2Vac on a 50x50 grid

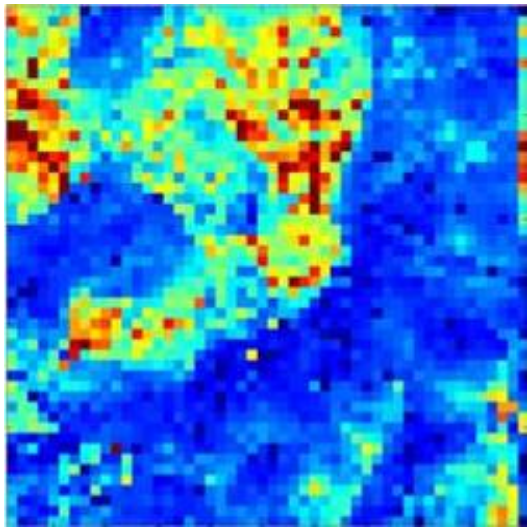
Resonance frequency shows crosstalk with topography

Amplitude image show grains/areas with different electromechanical response!

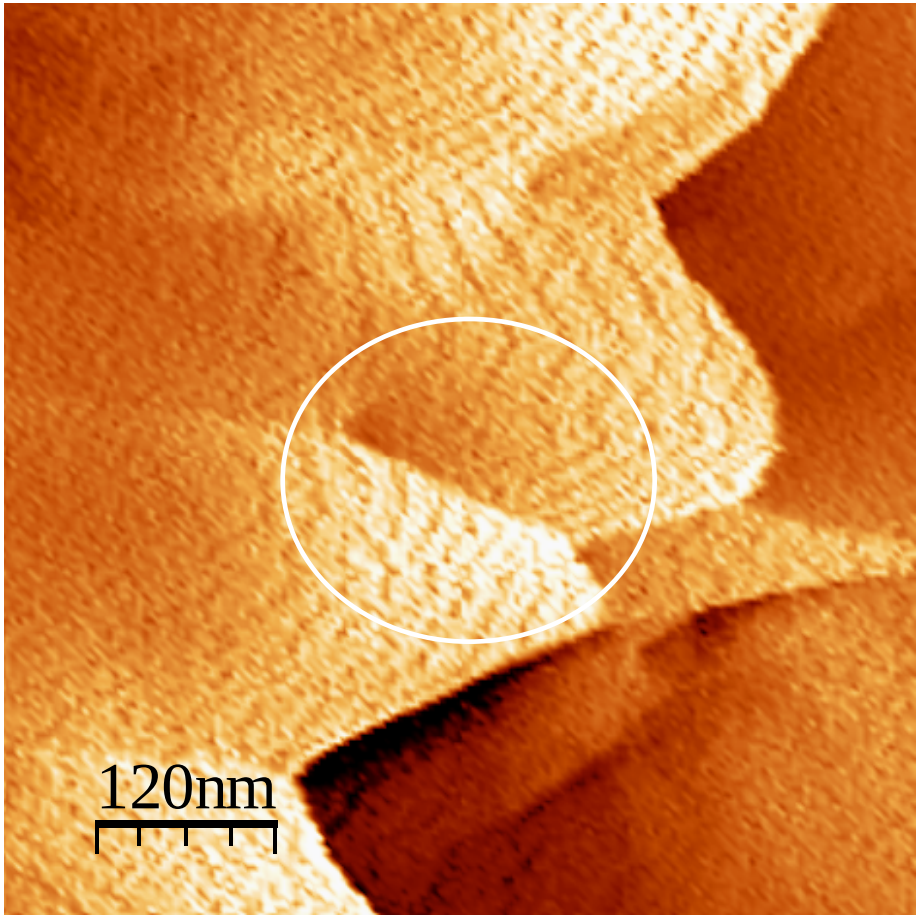
Resonance Frequency

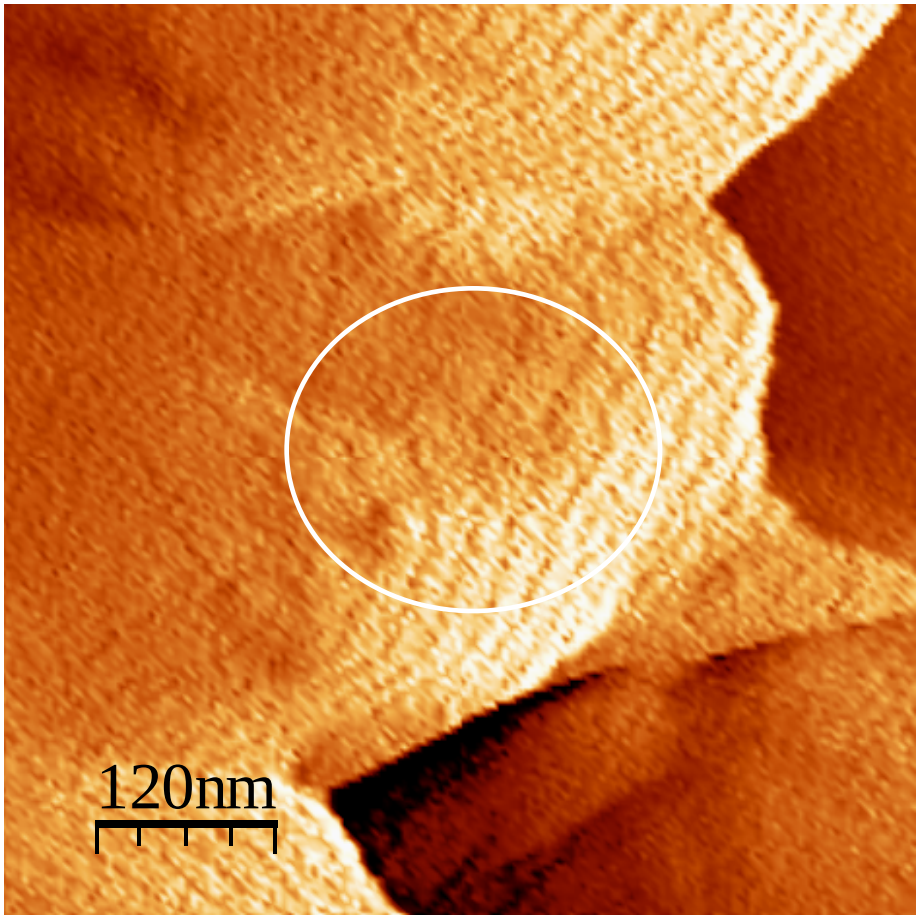


Response Amplitude



Can we manipulate Li concentration locally?

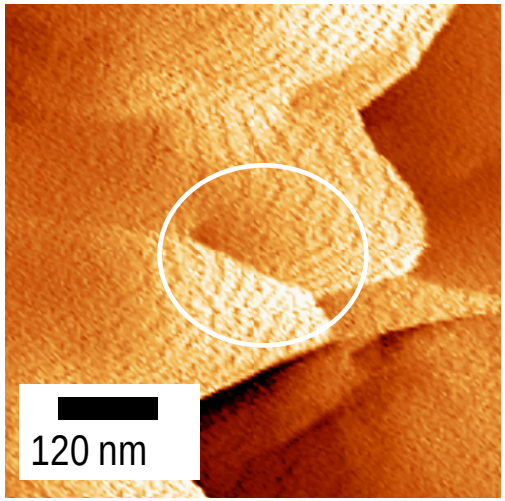


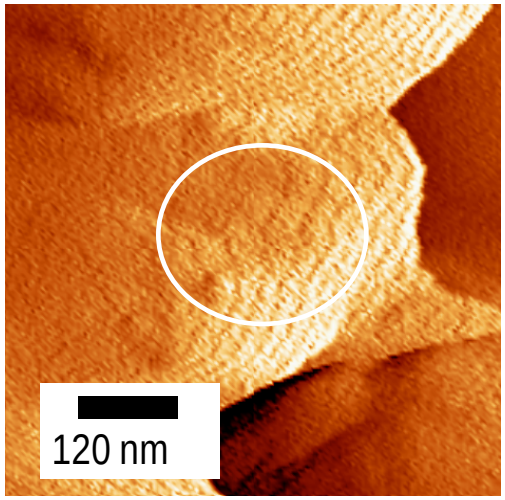


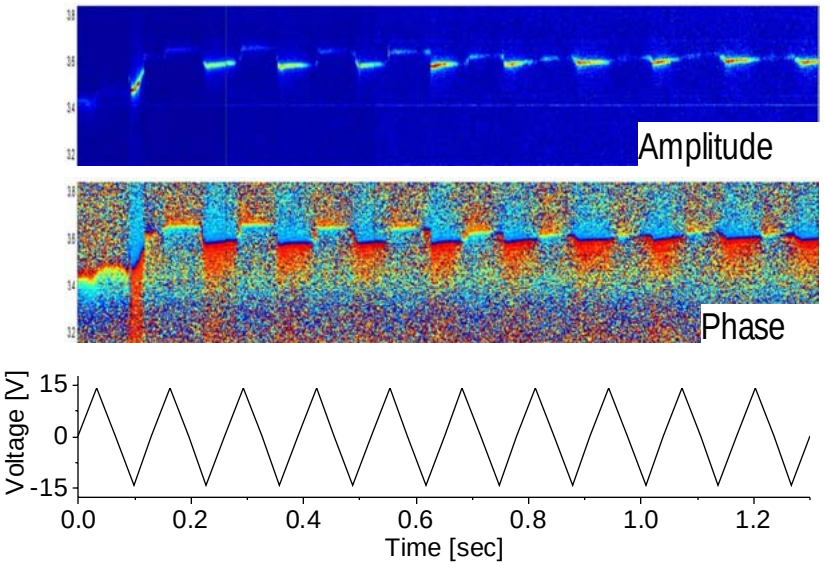
The bias pulse from an SPM tip can induce the redistribution of Li ions, while maintaining the step edges on the surface

Local Spectroscopy of Electrochemical Processes

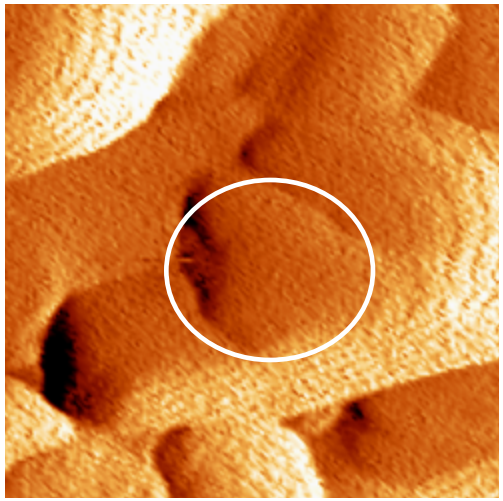
Single point (voltage pulse applied to topo minimum)

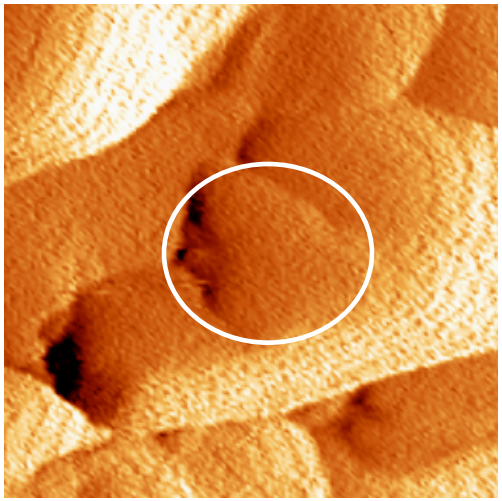


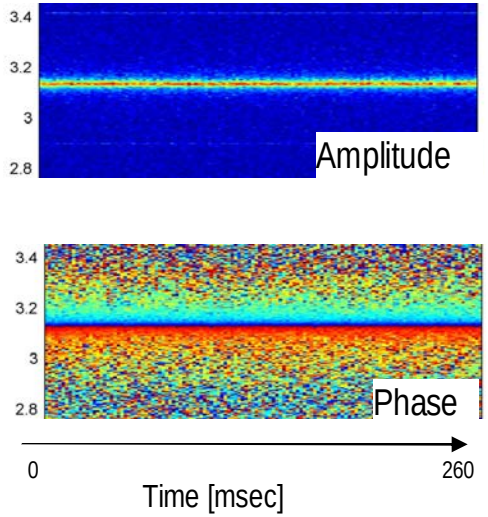




Single point (voltage pulse applied to plateau)

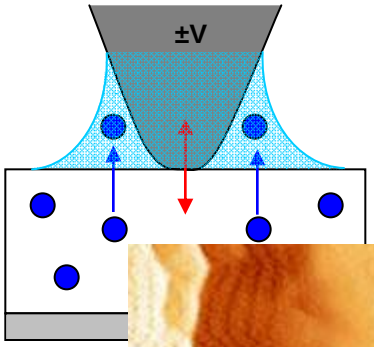






Li-ion Mapping in Layered Cathode Materials

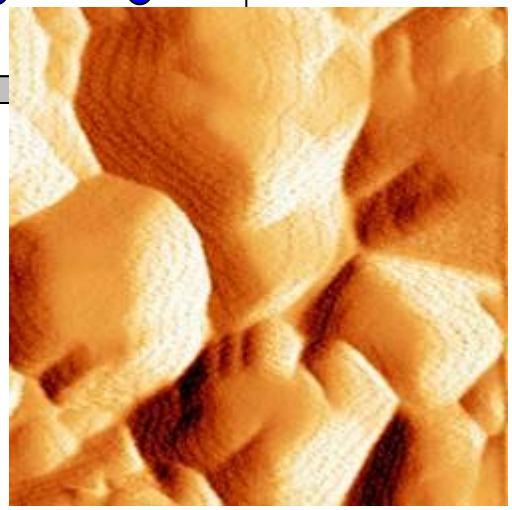
N. Balke et al, Nature Nano, AOP

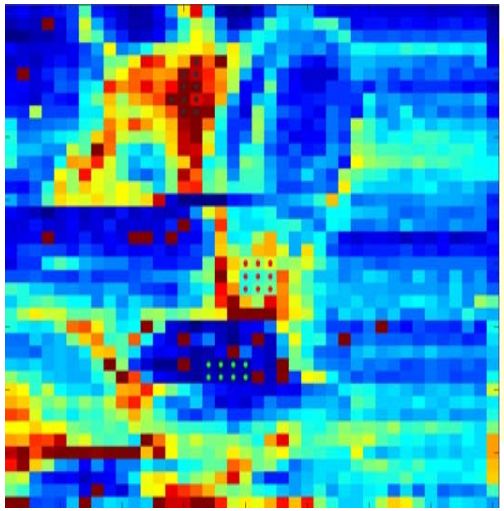


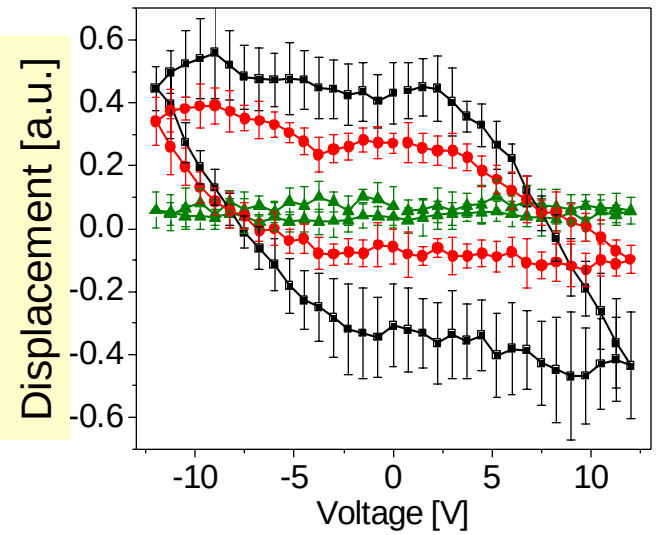
Water droplet around tip acts as electrolyte

Loop opening

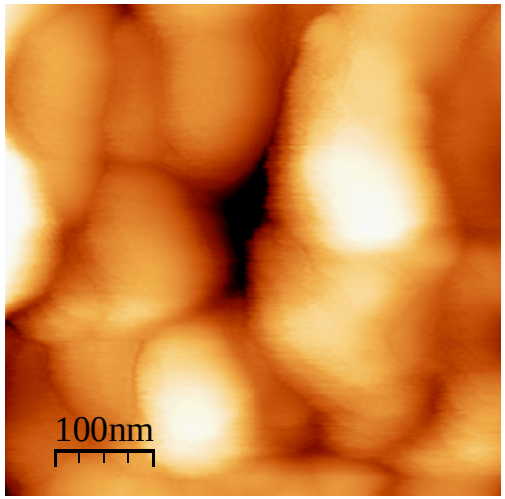
$LiCoO_2$

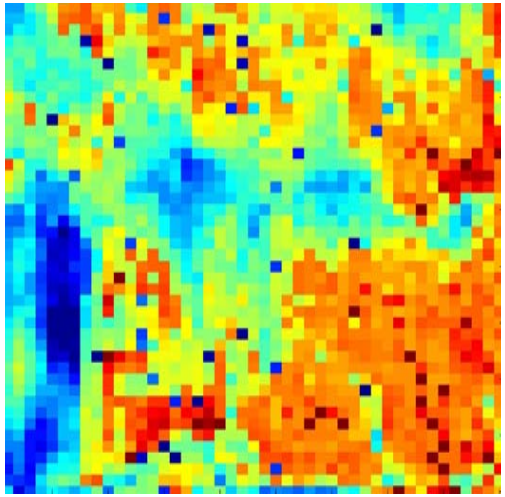


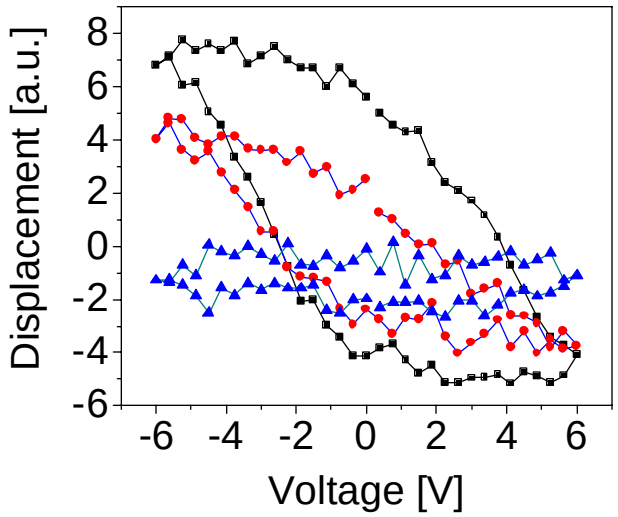




$LiMn_{1/3}Ni_{1/3}Co_{1/3}O_2$



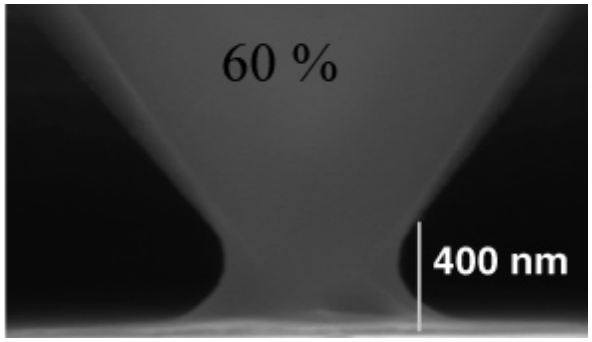




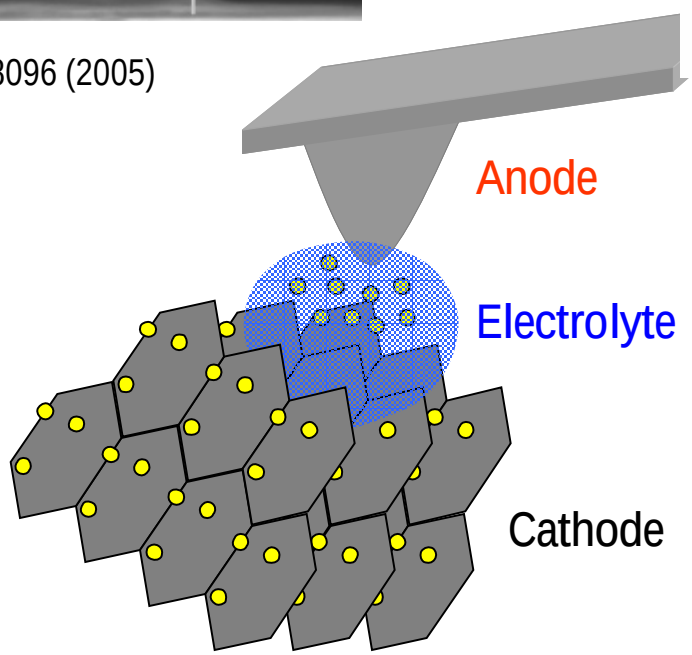
Imaging Electrochemical Reactions on The Nanoscale

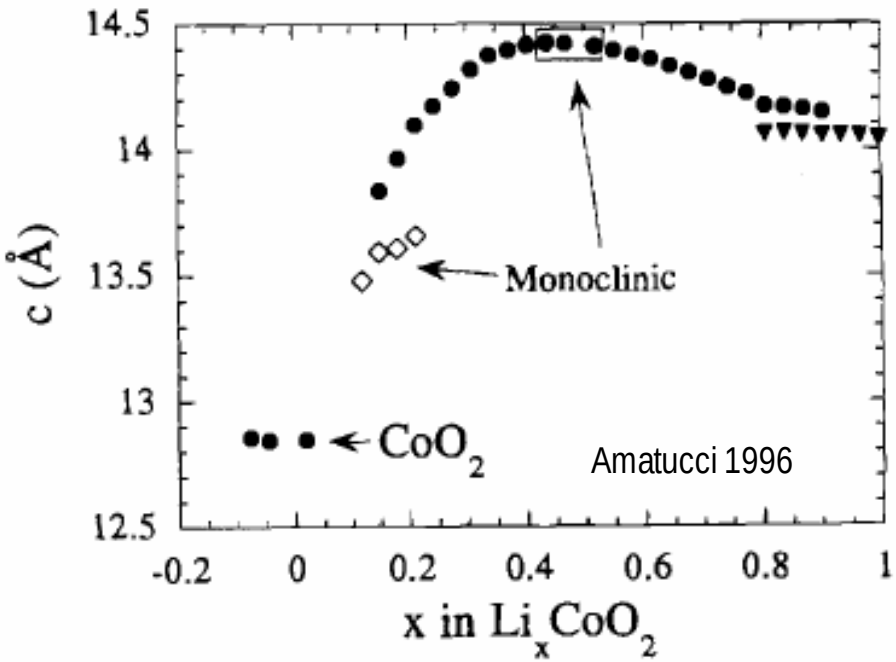
Key: Lattice parameters of $LiCoO_2$ are a function of Li-concentration

Method: Using a biased tip to locally change $c(Li^+)$ and detecting the strain response



Langmuir 21, 8096 (2005)

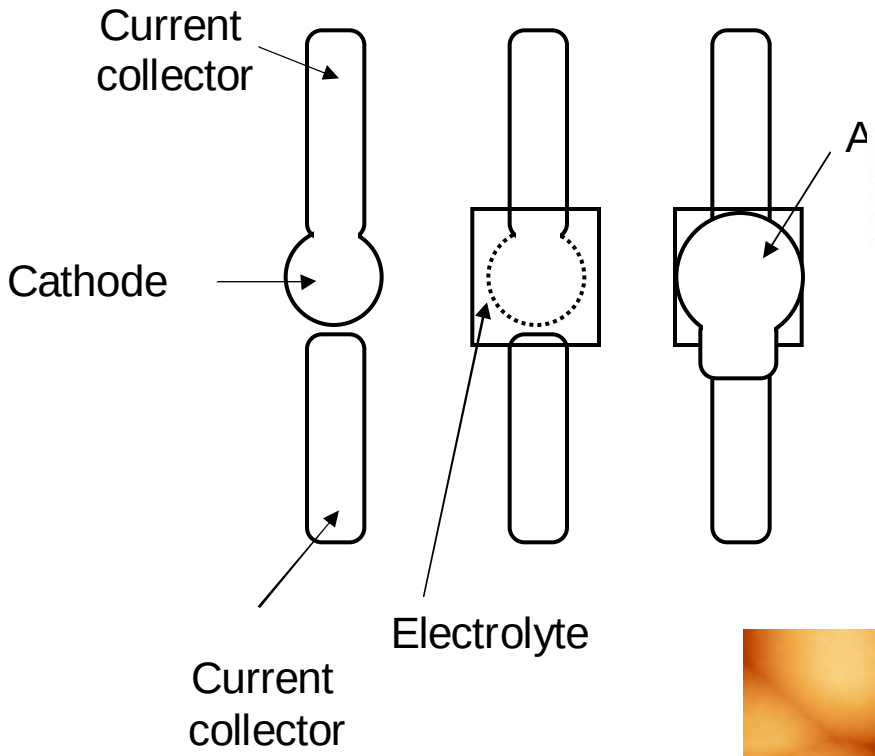




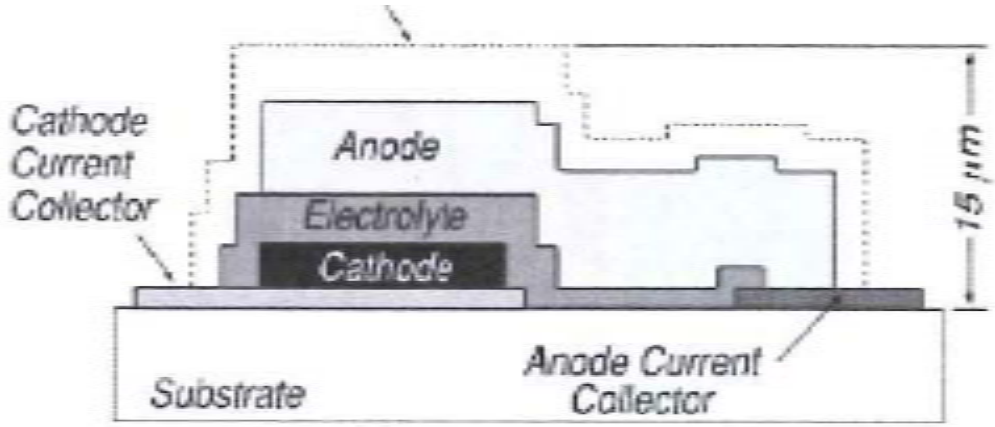
- Formation of a nanoscale battery with the biased tip and the water droplet on the cathode surface
- $LiCoO_2$-LiOH system is (almost) reversible
- CoO_2 layers are stable up to high degrees of delithiation

Battery Heterostructure

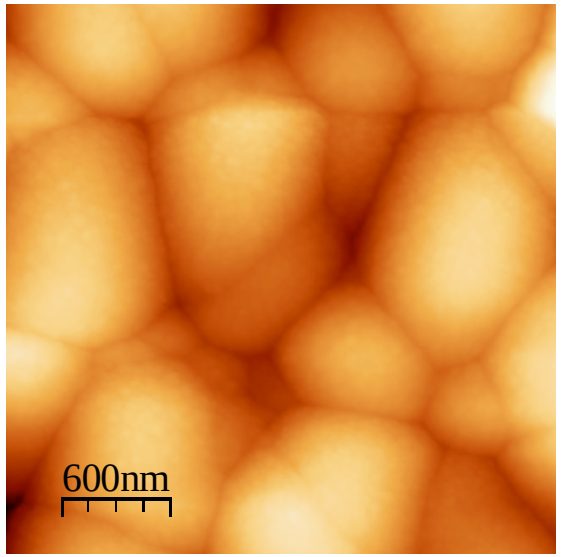
Top view



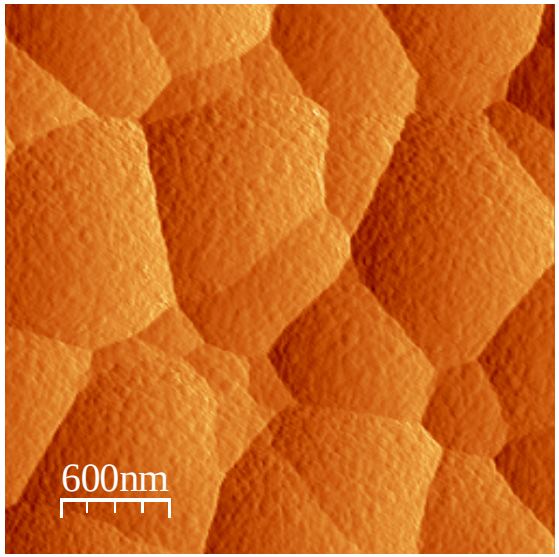
Cross section



Topography

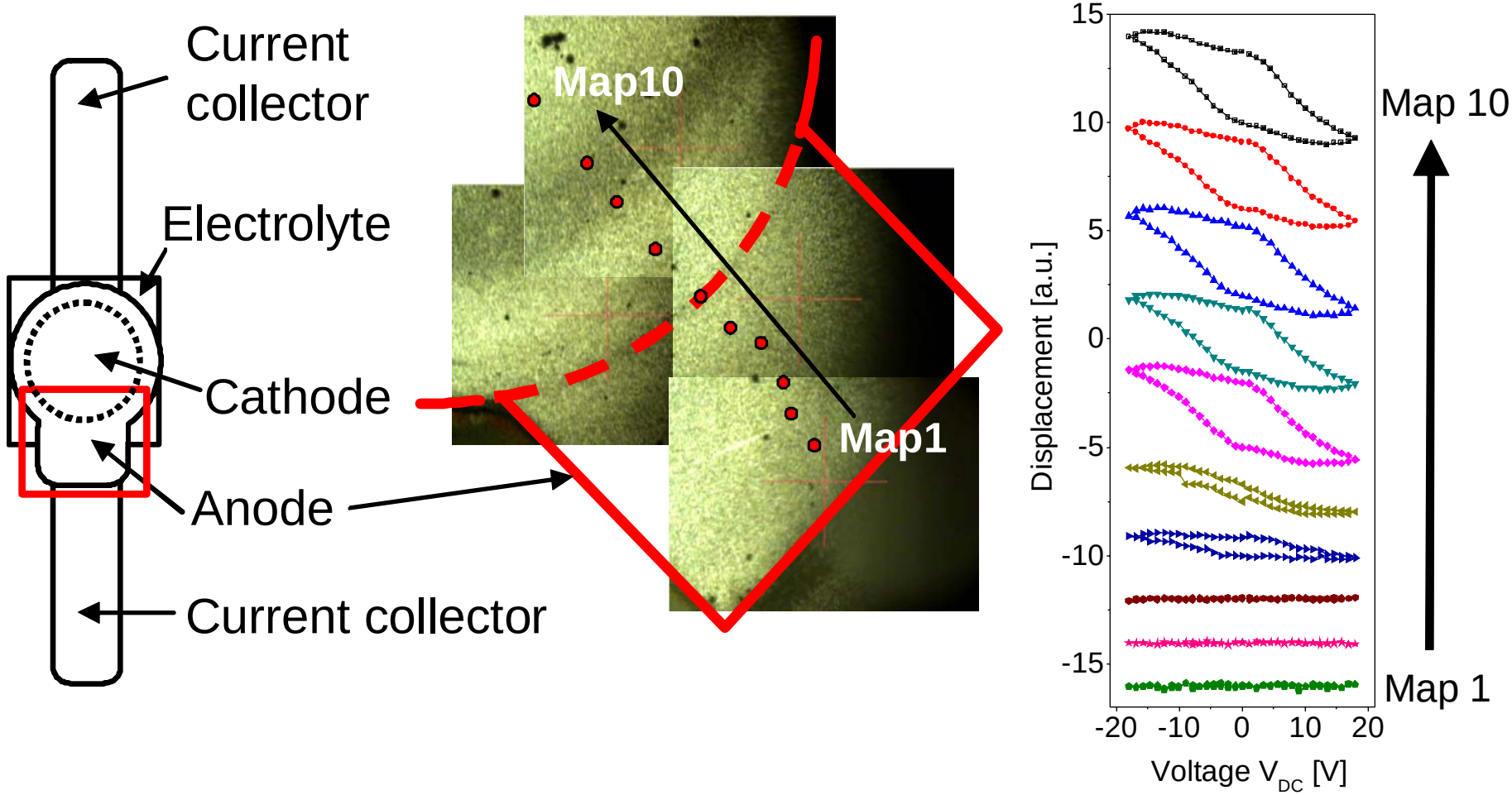


Deflection



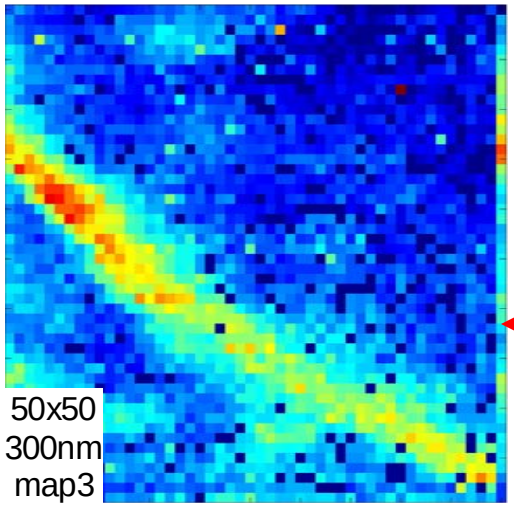
Cathode: $LiCoO_2$
Electrolyte: Lipon
Anode: Cu, Sn, C, Si

ESM: Voltage spectroscopy

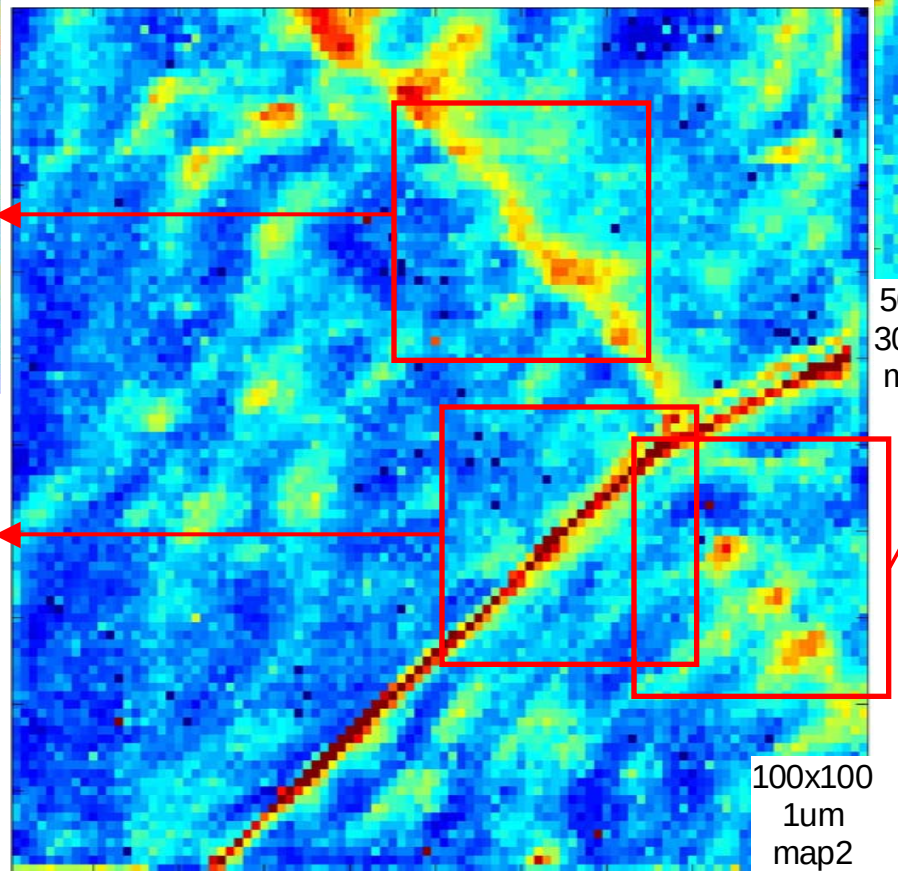


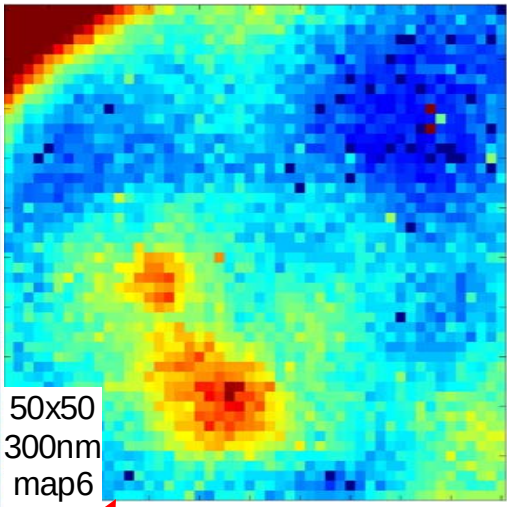
Loops can only be measured on the complete battery stack.

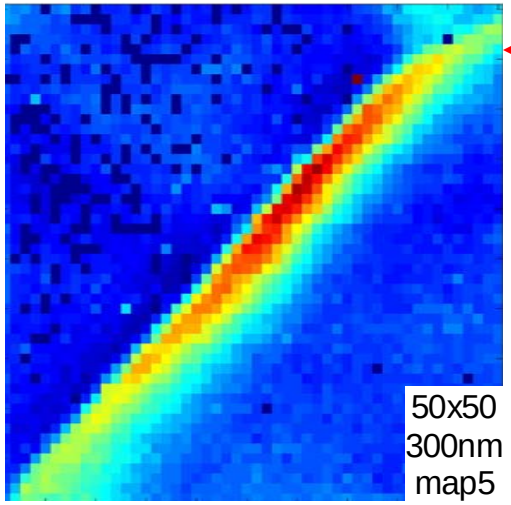
High-resolution BEPS Maps at 15 V Bias Window



Loop opening (2Pr)

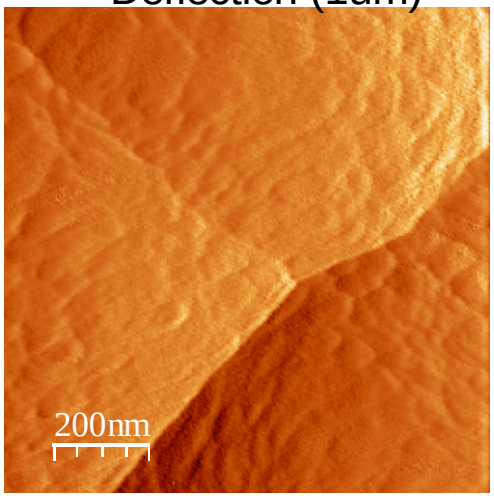






- GB are more active
- hot spots within grains

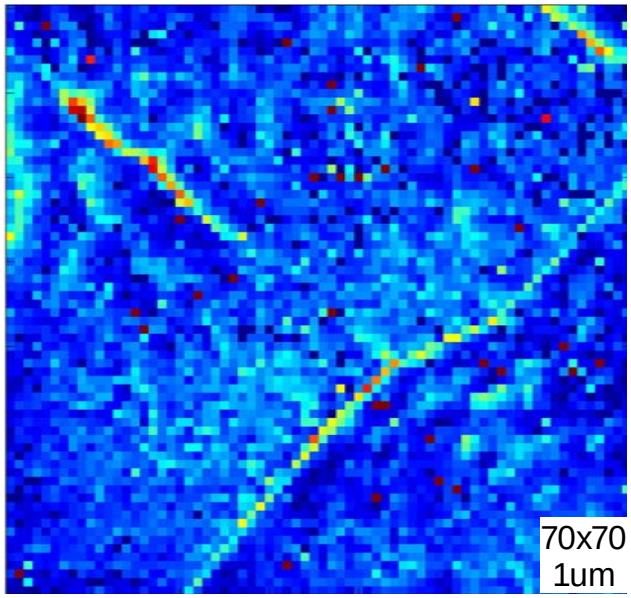
Deflection (1um)



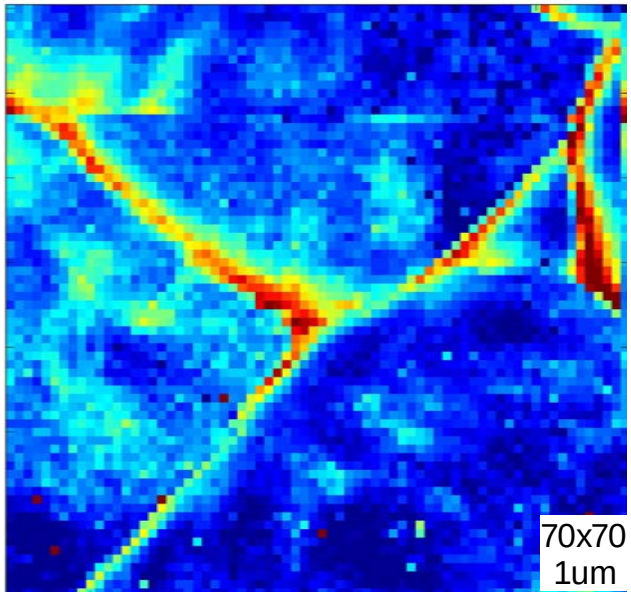
N. Balke et al, Nano Lett., AOP

Evolution of Response with Bias Window

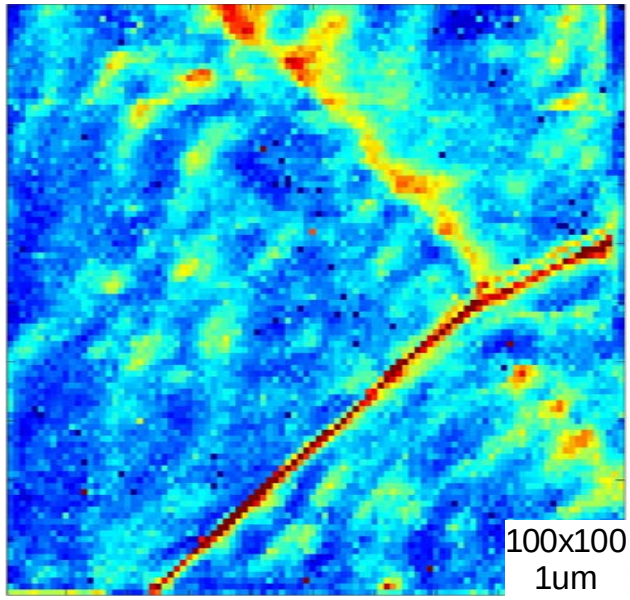
10Vdc



12Vdc



15Vdc

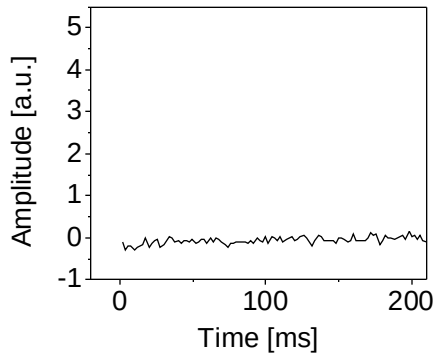


Different regions are activated at different biases!

Role of Electrochemical Reactivity

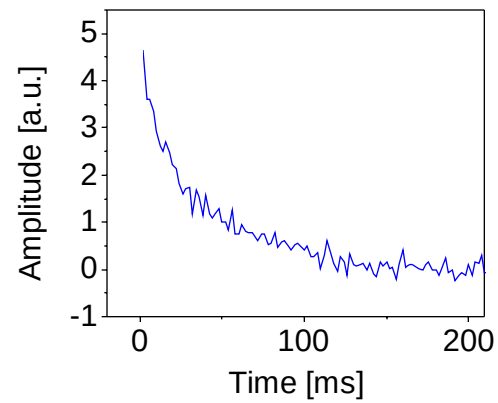
Transport is linear in driving force (potential)
Reaction is exponential in overpotential (Volmer-Bultler)

Time relaxation

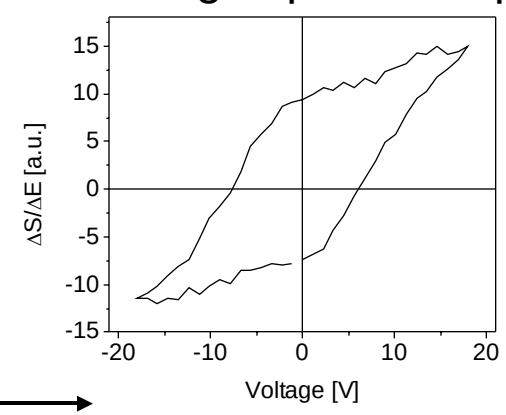


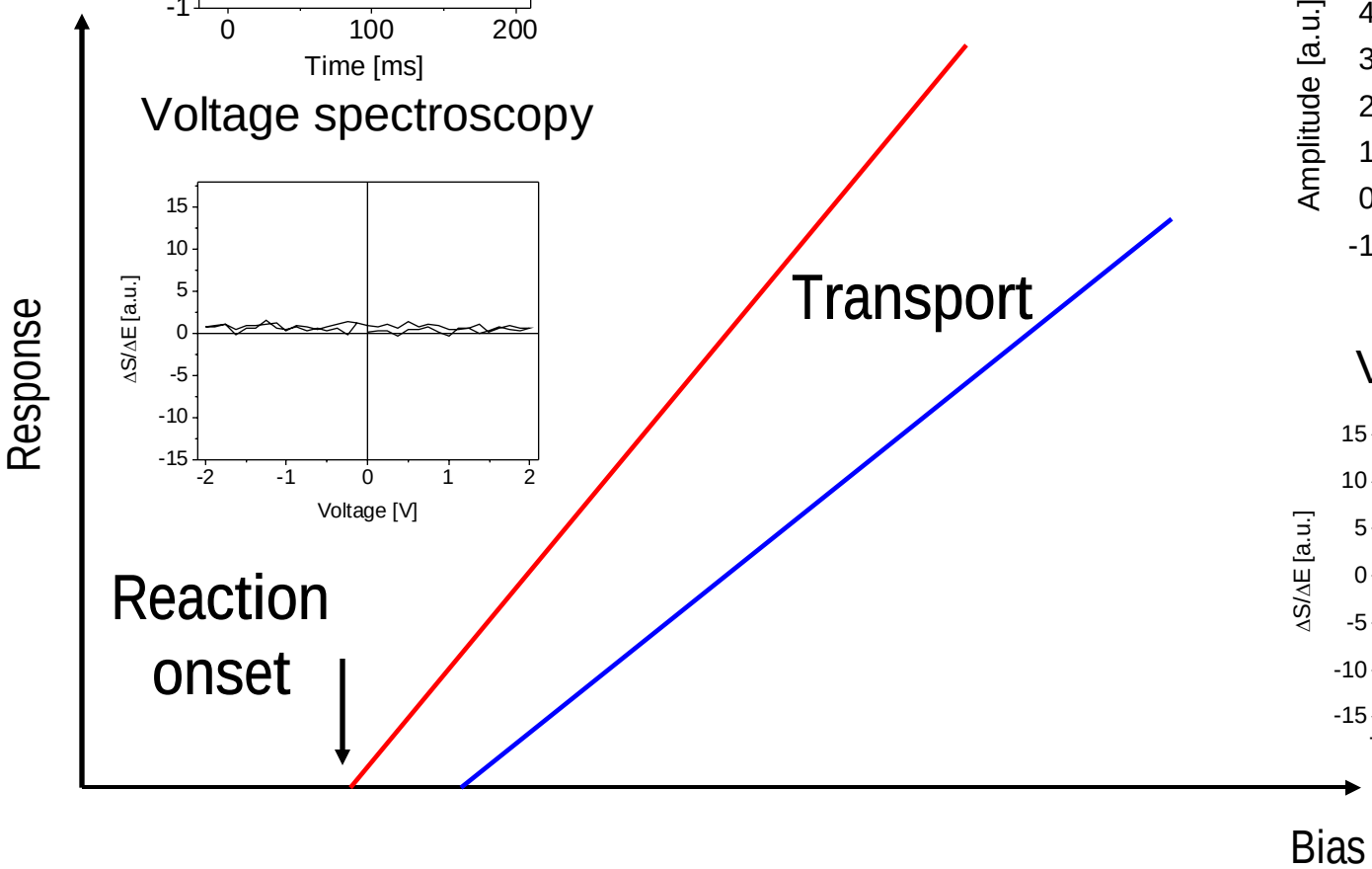
Voltage spectroscopy

Time relaxation



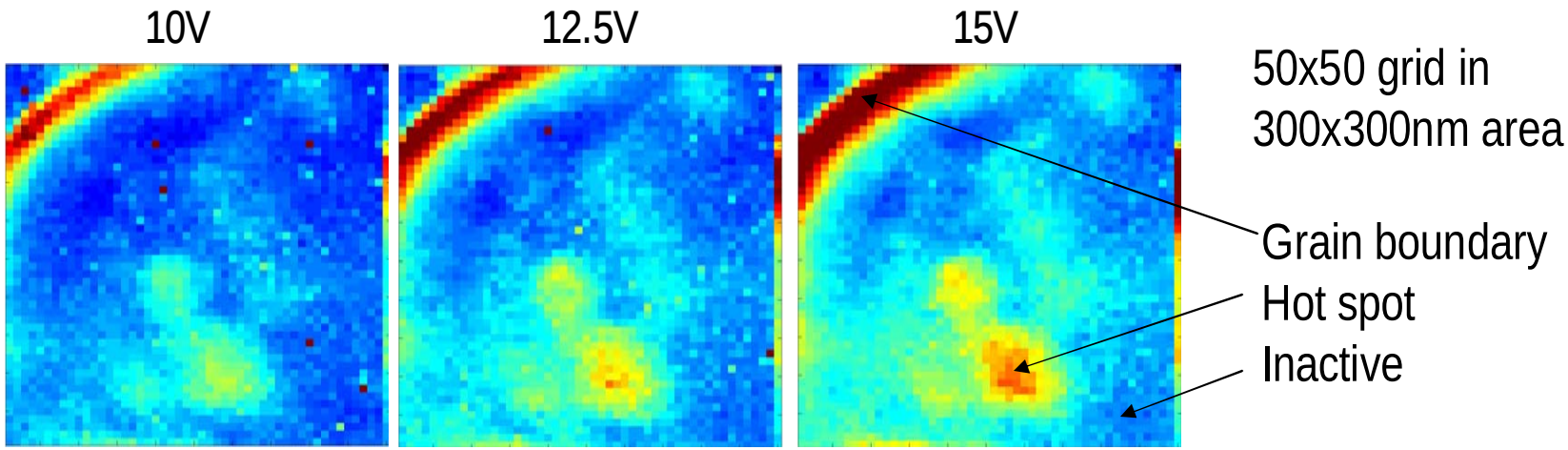
Voltage spectroscopy



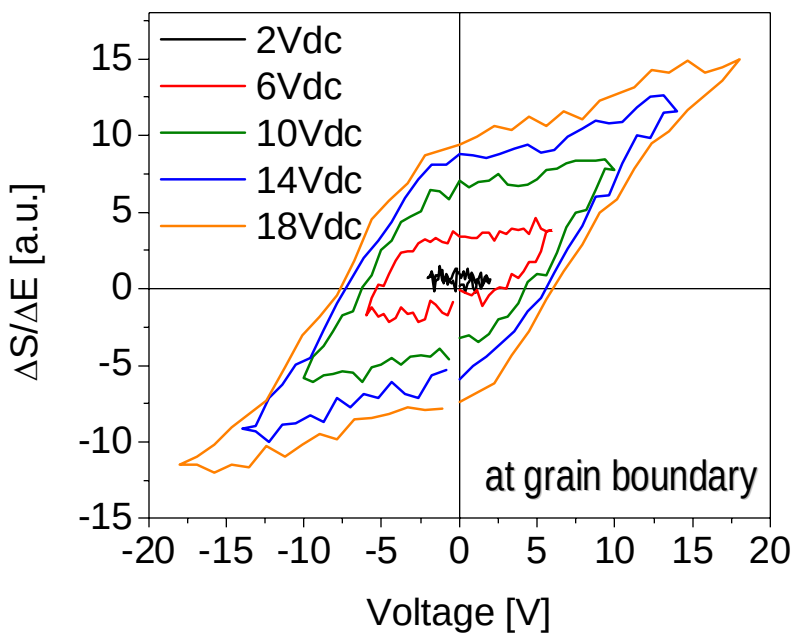


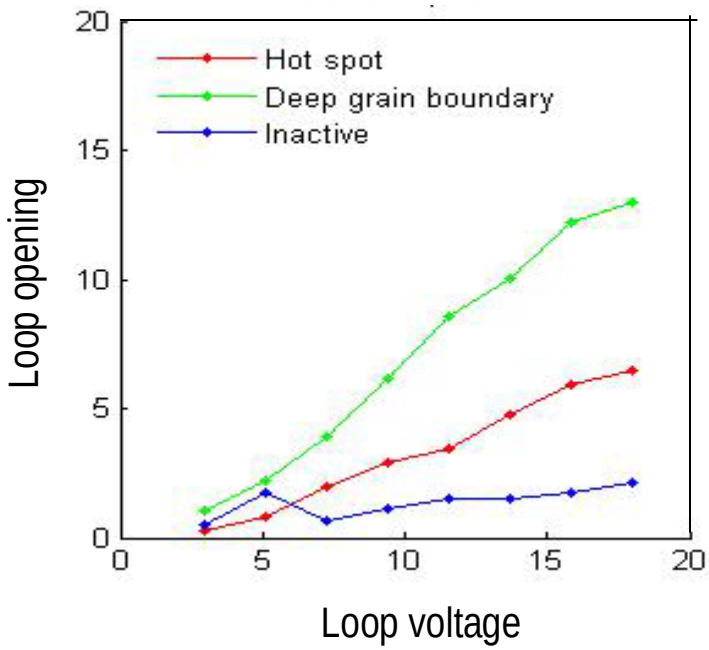
Can we distinguish onset of reaction and activation energy for transport locally?

W-FORC-BEPS Measurements



Piezoresponse loop and loop opening as f(V)

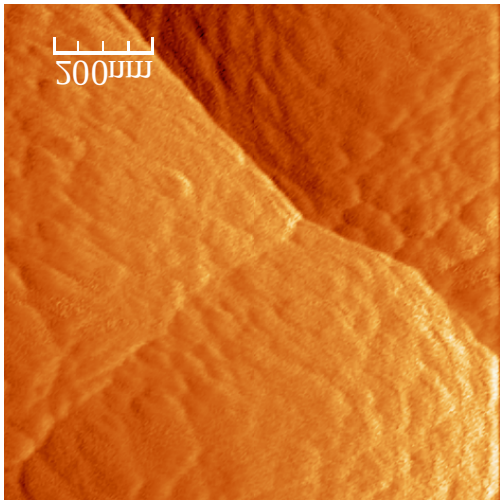




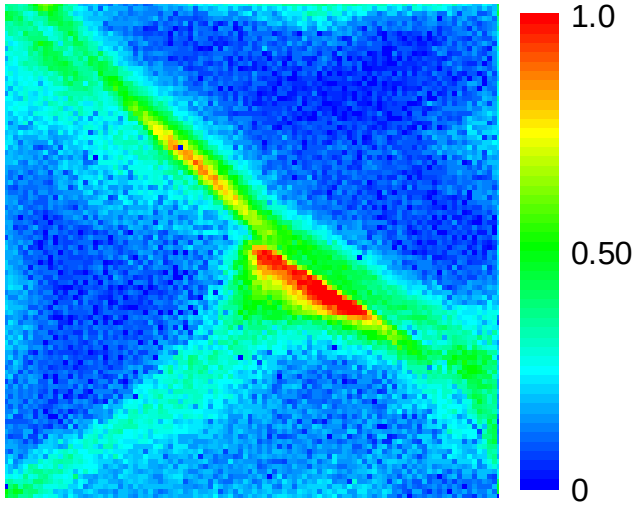
Decoupling Transport and Interfacial Reaction

Linear fit of loop opening as function of voltage to y = a + bx

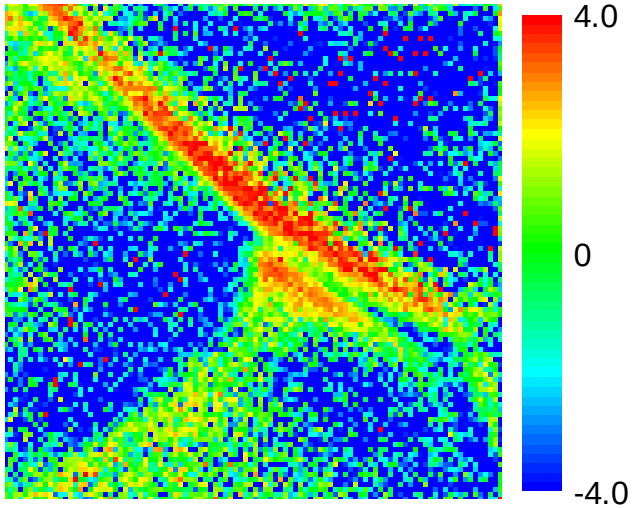
Deflection

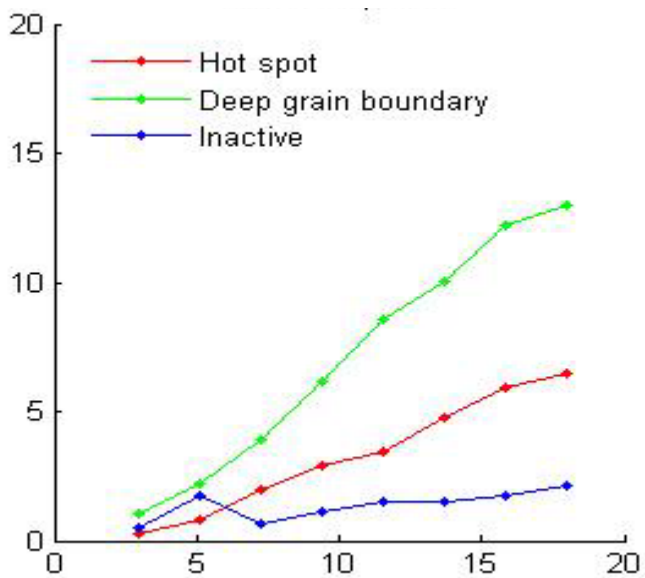


Transport



Activation voltage



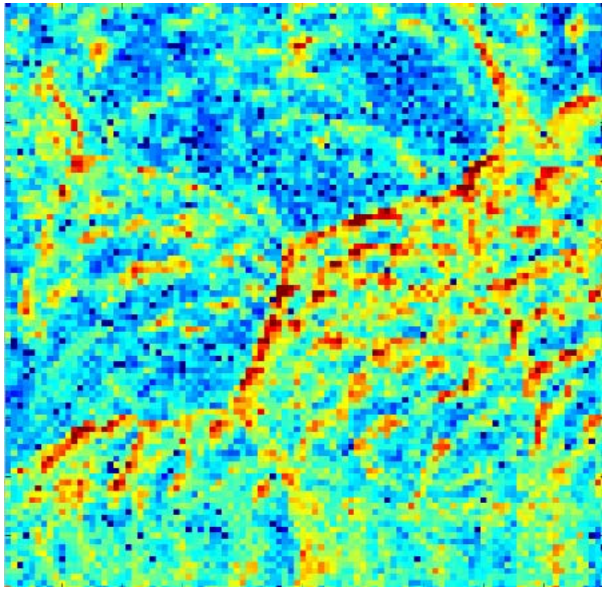


- The Li -activity can be mapped on the sub-10 nm scale in cathode and anode materials
- It may be feasible to distinguish transport and electrochemical reaction using multidimensional SPM
- Opens the road to probe these behaviors on a single-defect level (link to theory and materials engineering)

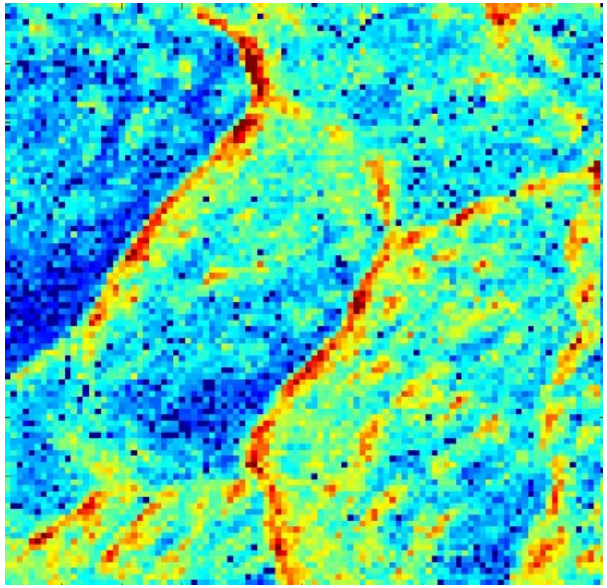
N. Balke et al, ACS Nano, AOP

Response Evolution with Charging

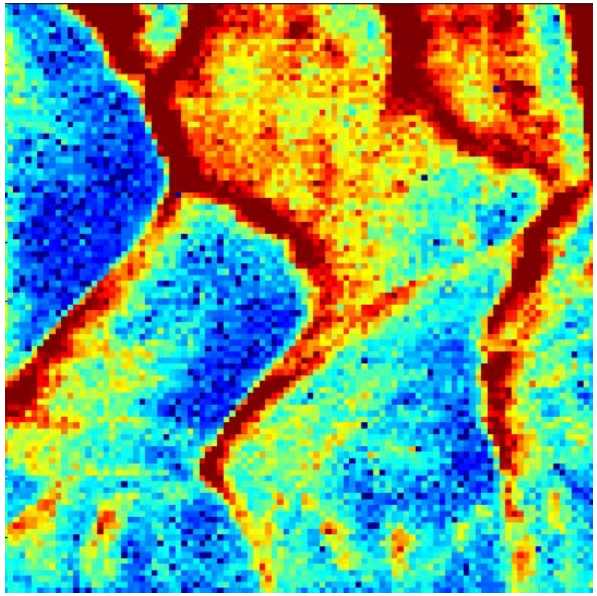
X cycles



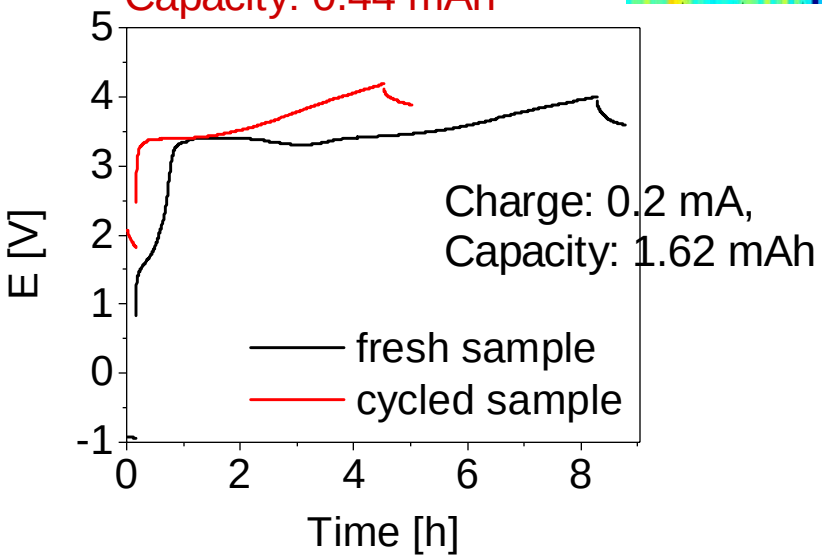
X+3*10^4 cycles



X+10^5 cycles



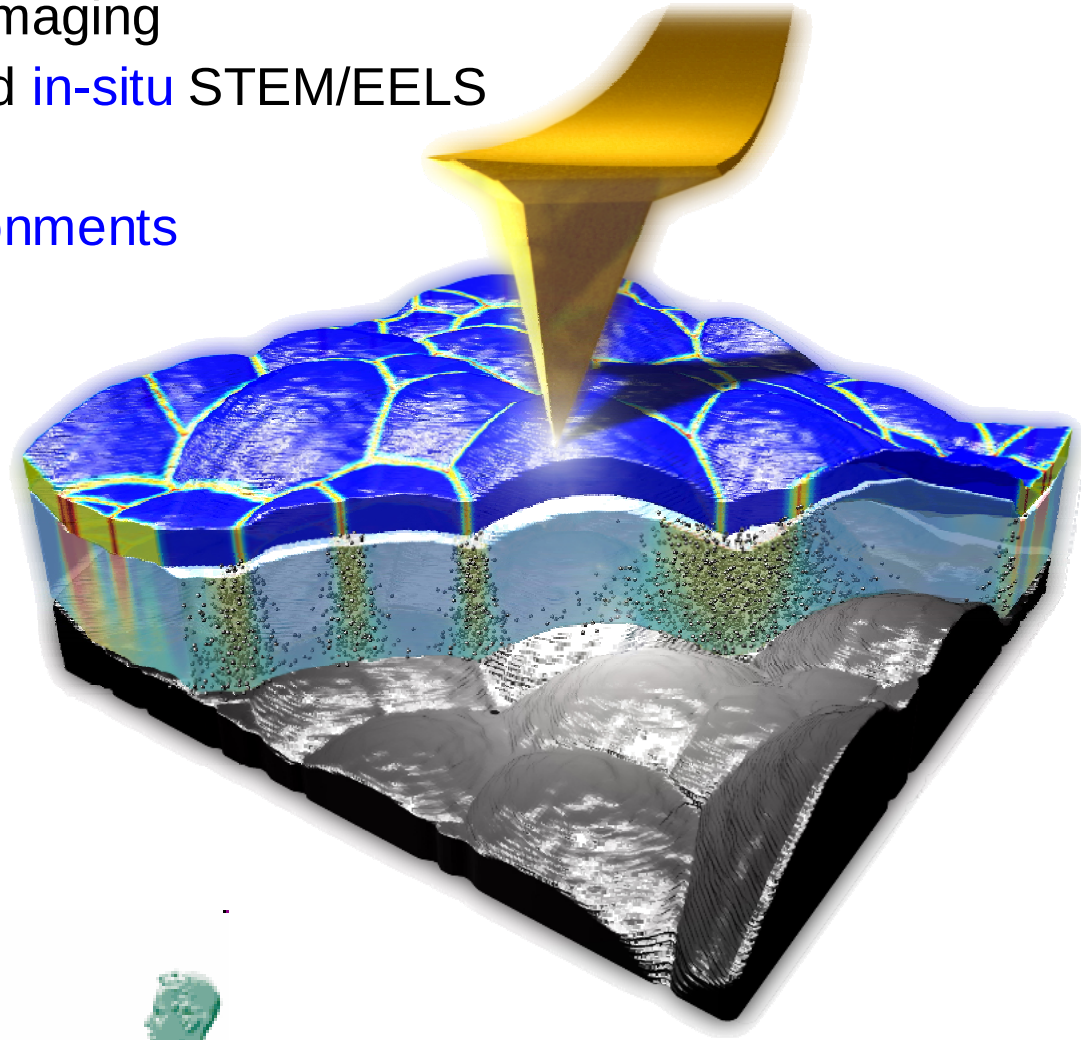
Charge: 0.1 mA,
Capacity: 0.44 mAh



- Response evolution with cycling (32V_{pp} at 7Hz)
- With increasing cycle number hot spots disappear and the grain boundaries become more active
- Charge state can be ascertained by macroscopic measurements

Electrochemical Strain Microscopy

- Measure local reversible ion dynamics - correlate dynamics to microstructure
- Separate transport and interfacial reaction
- Works for Li-ion and O-vacancy imaging
- Can be combined with ex-situ and in-situ STEM/EELS
- Need more theory
- Controlled electrochemical environments



What will it lead to:

- Understand and identify battery processes on the nanoscale
- Role of defects in functionality
- Origins of battery failure
- Mechanisms of electrocatalysis
- … and much more

Alexander von Humboldt
Stiftung/Foundation

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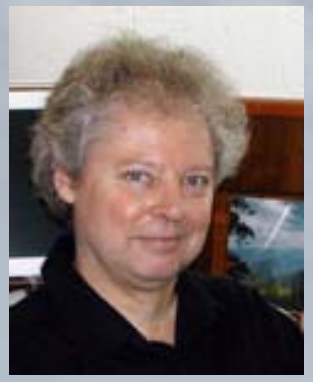

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Donovan Leonard
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Support:
Li – ion: FIRST EFRC, AvH
SOFC: DOE SISGR
ESM: DOE BES Scientific User Facilities

Collaborative opportunities at ORNL

Center for Nanophase Materials Sciences at ORNL

http:\\imaging.ornl.gov

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