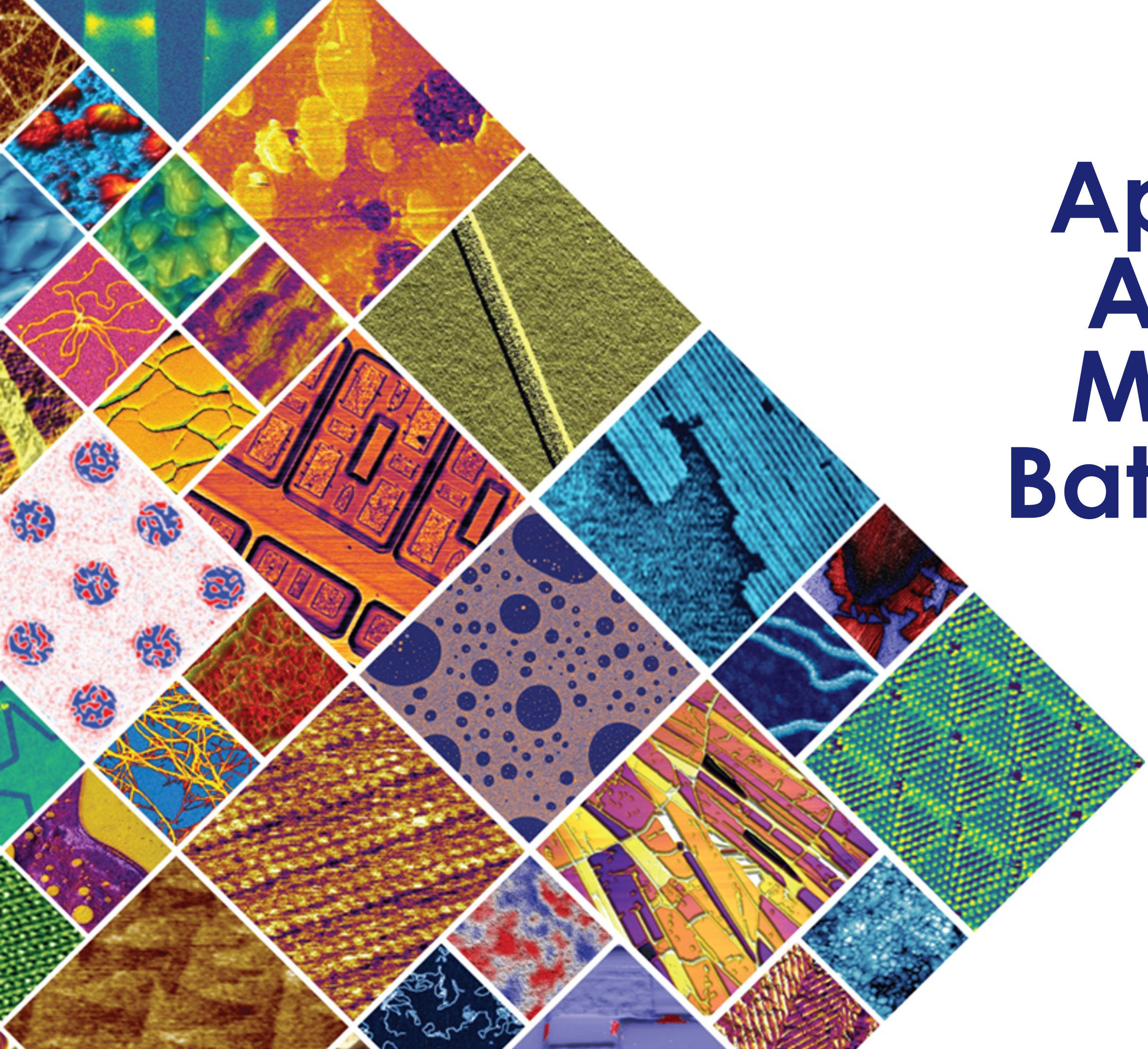


Applications of Atomic Force Microscopy in Battery Research

Will Linthicum, PhD
Oxford Instruments Asylum Research
Pleasanton, CA

What are AFMs?

AFMs are visualization tools

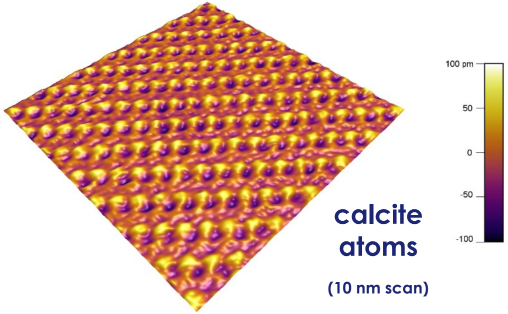
- 3D **surface topography**
- Very high resolution (atomic!)

AFMs use a mechanical probe

- Height resolution
  - Instrument Z-noise (**<15 pm**)
- Lateral Resolution
  - Tip radius (usu. **<10 nm**)

AFMs measure materials properties

- AFMs “touch” the surface
- AFMs can probe **local** material properties
  - Mechanical
  - Thermal
  - Electrical
  - Magnetic

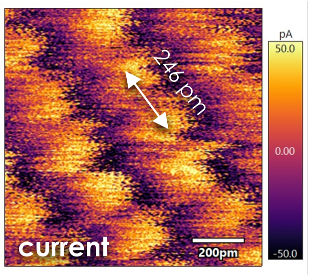


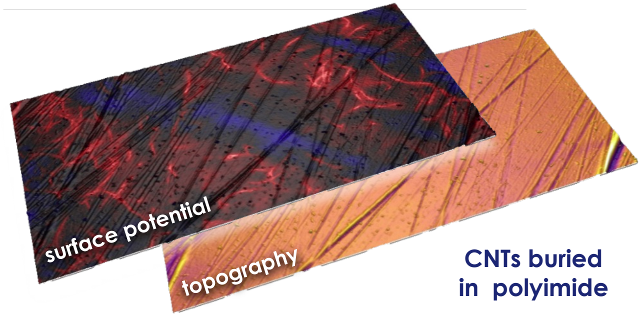
calcite atoms

(10 nm scan)

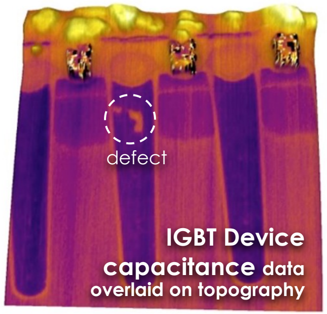
HOPG

(1 nm scan)



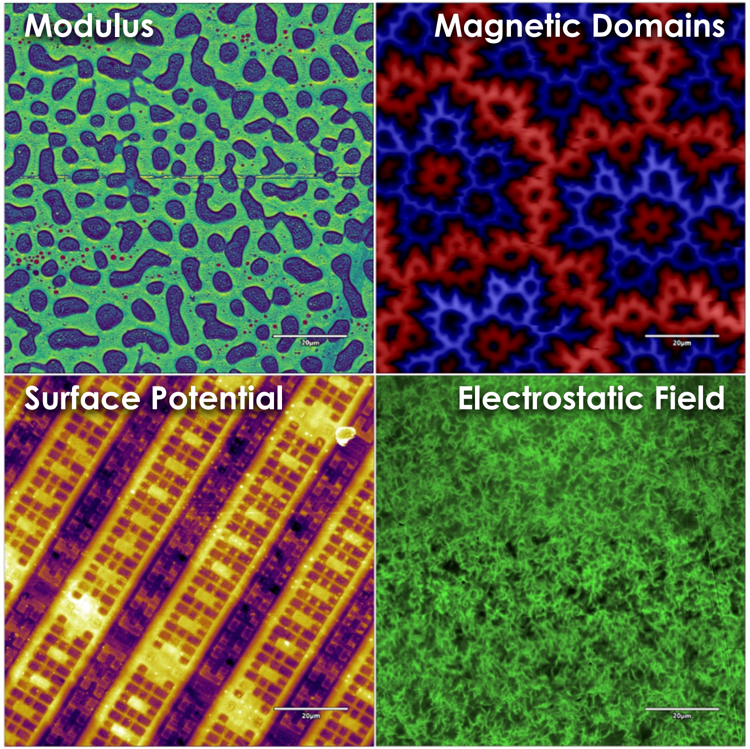


CNTs buried in polyimide



IGBT Device capacitance data overlaid on topography

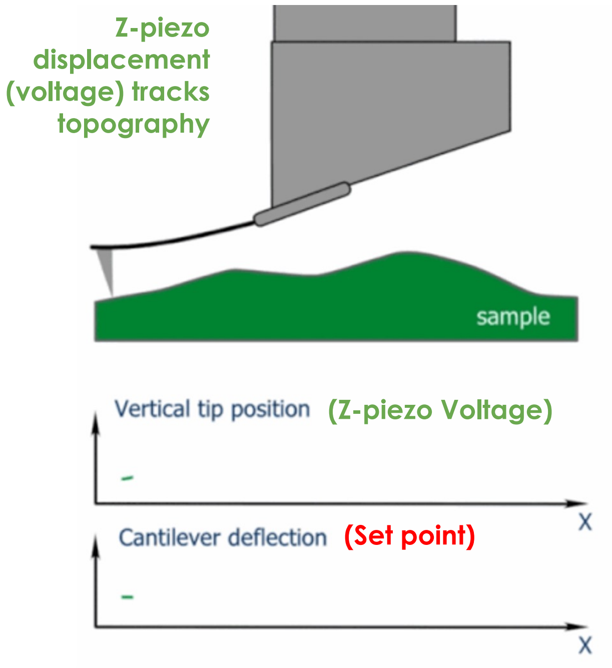
What can we measure with AFMs?



100 x 100 µm scan on Jupiter XR

How is topography obtained?

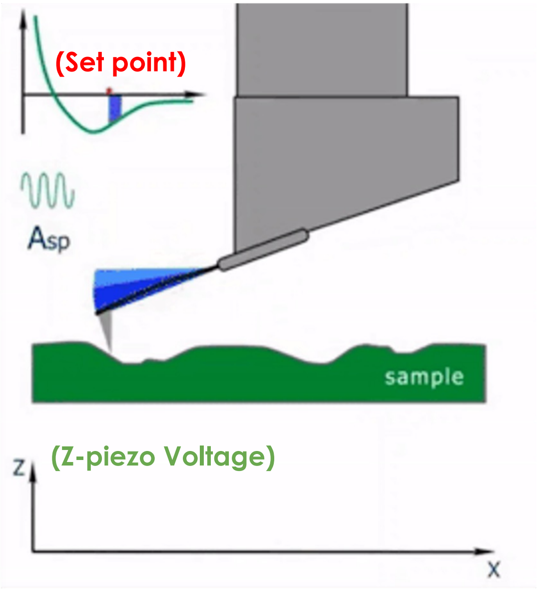
Contact Mode



How the AFM height feedback loop works:

- When an AFM tip is rastered across the surface, cantilever **deflection** (or **amplitude**) changes when the tip encounters variations in topographic slope.
- In **contact mode**, the height feedback loop looks at deflection; in **tapping mode**, it looks at amplitude.
- The height feedback loop **adjusts the tip z-position** to keep deflection (or amplitude) at setpoint, i.e., to maintain a constant loading **force** (or oscillation **damping**).
- The actuating voltage to adjust (extend/retract) the z-piezo therefore tracks topography.

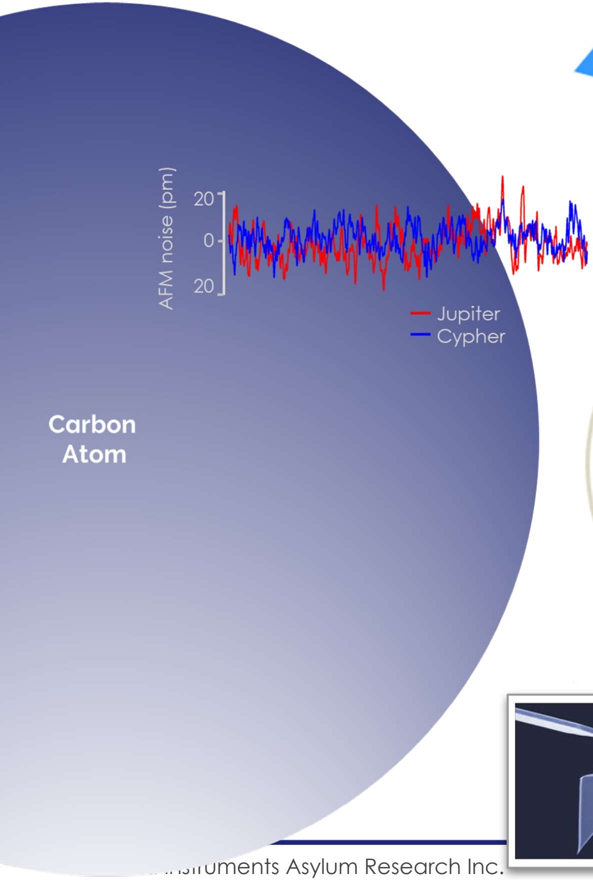
Tapping Mode

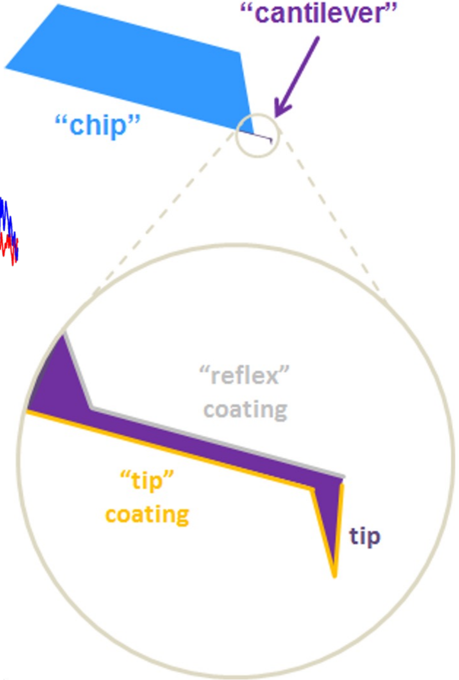


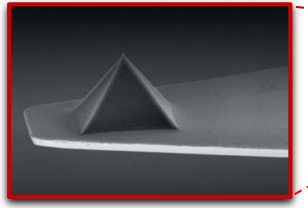
Z-piezo displacement (voltage) also tracks topography

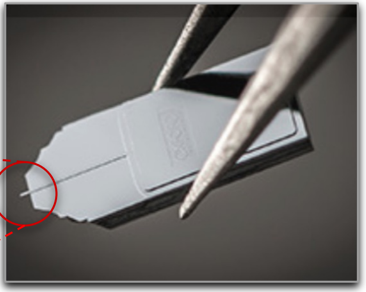
Image source: NTMDT Spectrum Instruments (www.ntmdt-si.com)

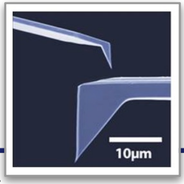
Stability, Resolution, Speed





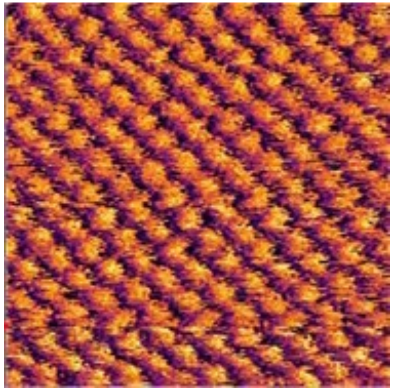




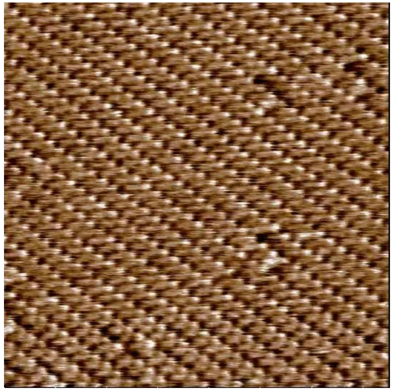


Smaller = quieter, faster

- ✓ Lengths as short as **10µm**
- ✓ f_{res} up to a few **MHz**

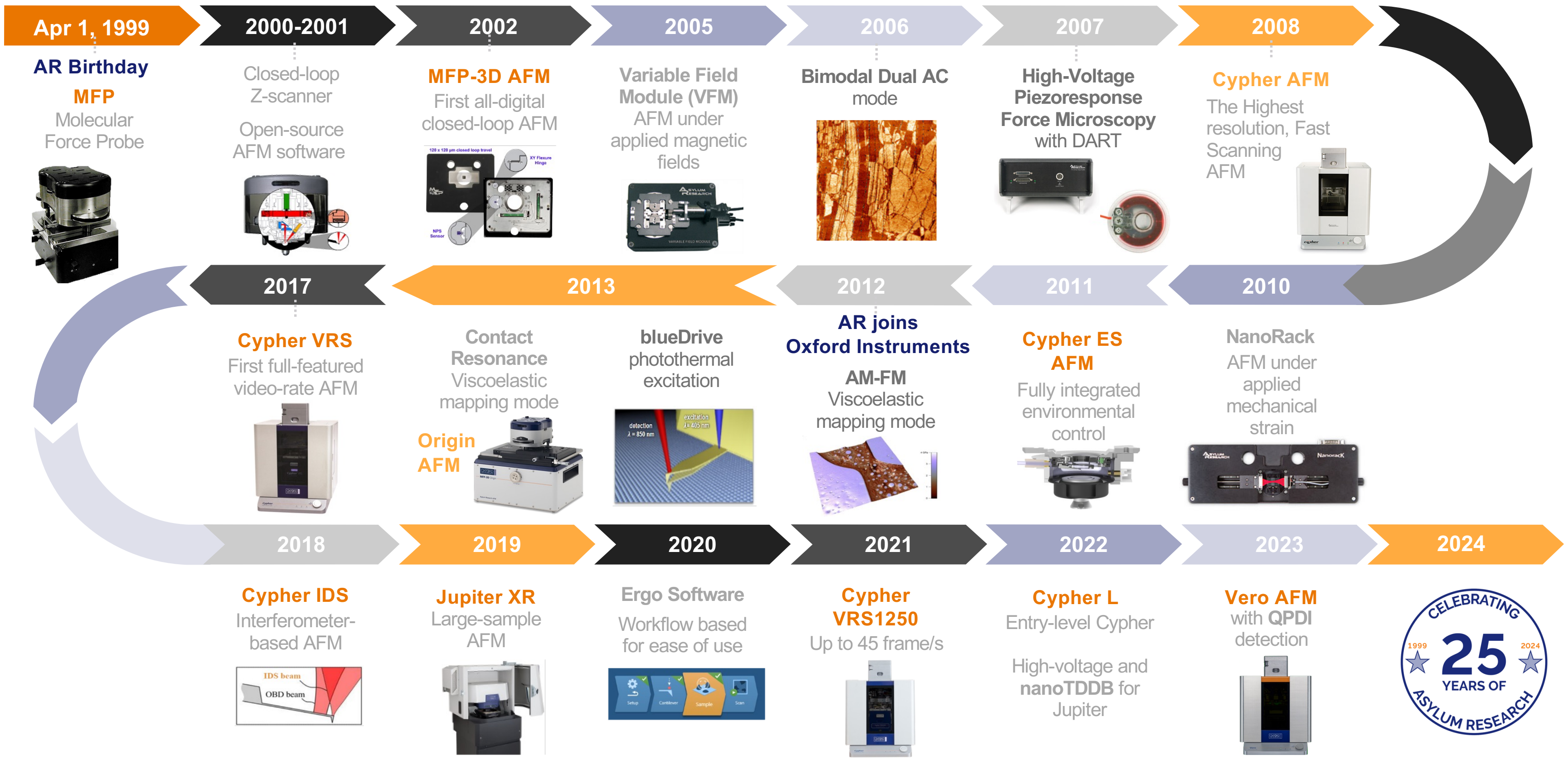


Graphite lattice
~~(contact mode – current image)~~

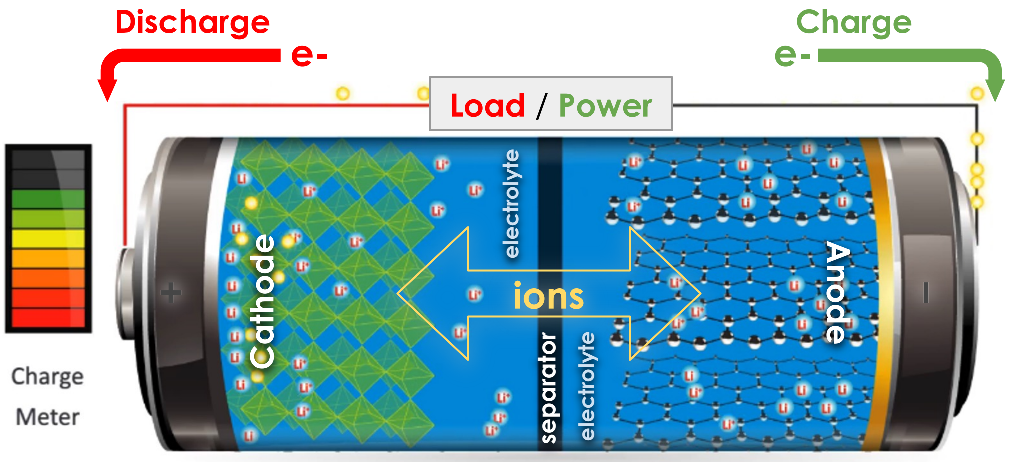


Calcite point defects
~~(tapping mode in liquid)~~

Innovation through NEW products



What are the goals of battery R&D?



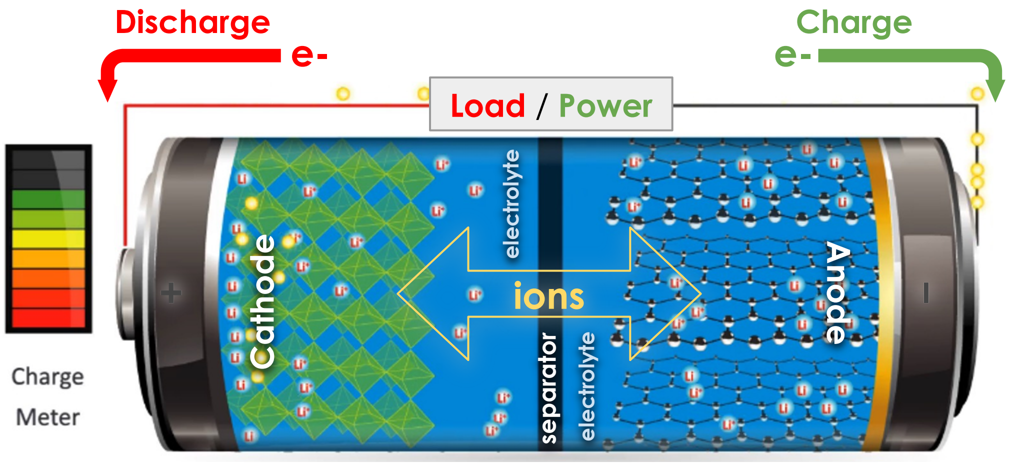
Targets of engineering:

- Electrodes (cathode, anode)
- Reactants (chemistry, composition)
- SEI: Solid Electrolyte Interphase
- Electrolyte (ion-conducting solvent)
- Separator (ion-permeable membrane)
- Housing (device encapsulation)

Performance criteria:

- **Energy Density** (Wh/g) - increase energy stored wrt mass
- **Power Density** (W/g) - increase power generation wrt mass
- Battery life - reduction of aging
- Storage Cost ($/Wh)

How can AFMs help battery R&D?



Targets of engineering:

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- Reactants (chemistry, composition)
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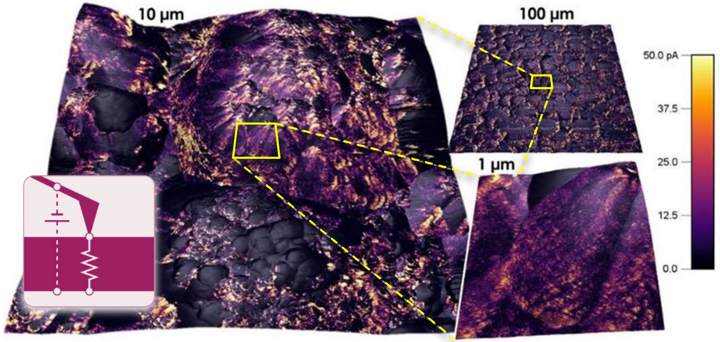
- Electrolyte (ion-conducting solvent)
- Separator (ion-permeable membrane)
- Housing (device encapsulation)

AFM can measure both topography <u>and</u> conductivity



NMC cathode material
$LiNi_xMn_yCo_zO_2$ on aluminum current collector plate

Engineering performance:

- Ex situ materials analysis of isolated components
- In situ observation of processes involving several components
- In operando measurement of whole battery cell

How can AFMs help battery R&D?

Ex situ analysis of isolated components

Basic materials research on single isolated battery components

- Battery packaging
- Separator membranes
- Electrode materials

In situ observation of processes

Study of simplified, isolated processes involving two or more battery components

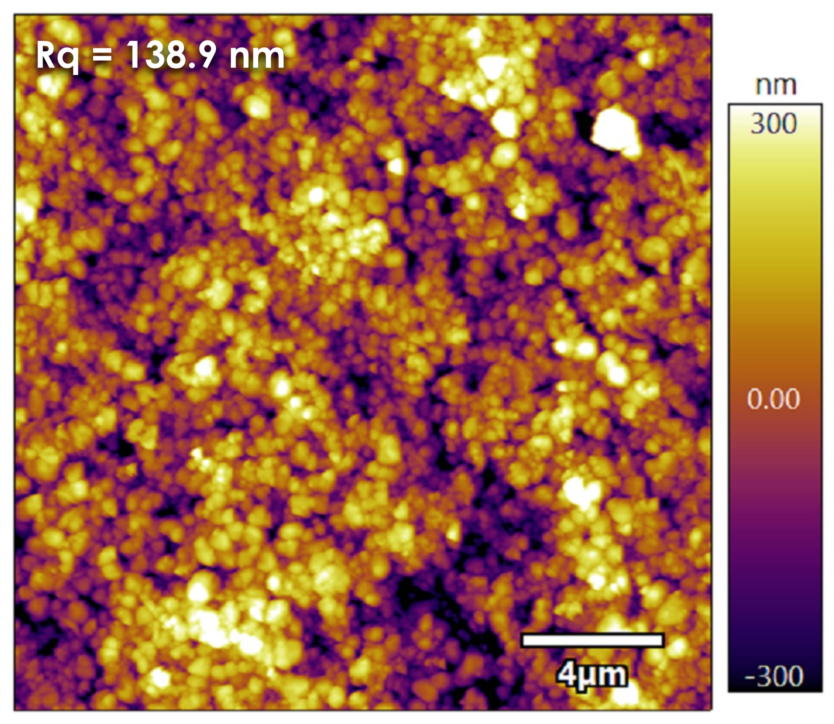
- Monitor electrochemical process at one electrode (i.e., half cell reactions)
- Characterize solid electrolyte interphase (SEI)
- Observe interaction of electrolyte with an electrode (e.g., Stern layer structure)

In operando measurement of whole battery

Observing electrode surfaces in fully functional cells during charge and discharge cycles

- Monitor electrochemical process at one electrode (working electrode) in a complete cell

Roughness Metrology



$LiFePO_4$ Cathode

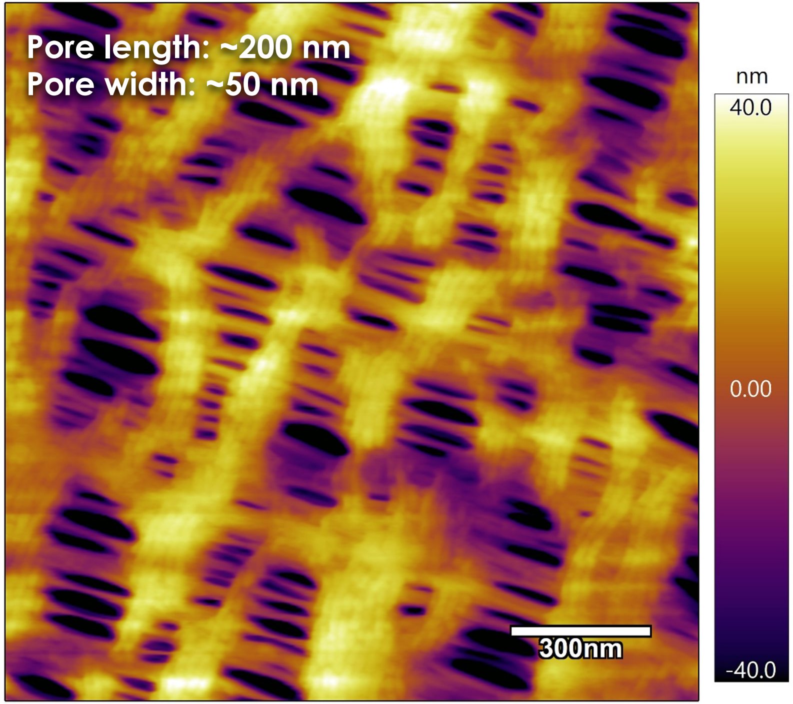
Electrode roughness affects:

- Surface area
- Ion diffusion
- Cycling stability

AFM measurement

- Topographic imaging (tapping mode)
- Glove box environment
    - Sub-ppm oxygen and water levels
    - Requires stable AFM

Morphology



Celgard™ separator membrane

- Uniaxially-oriented polypropylene membrane

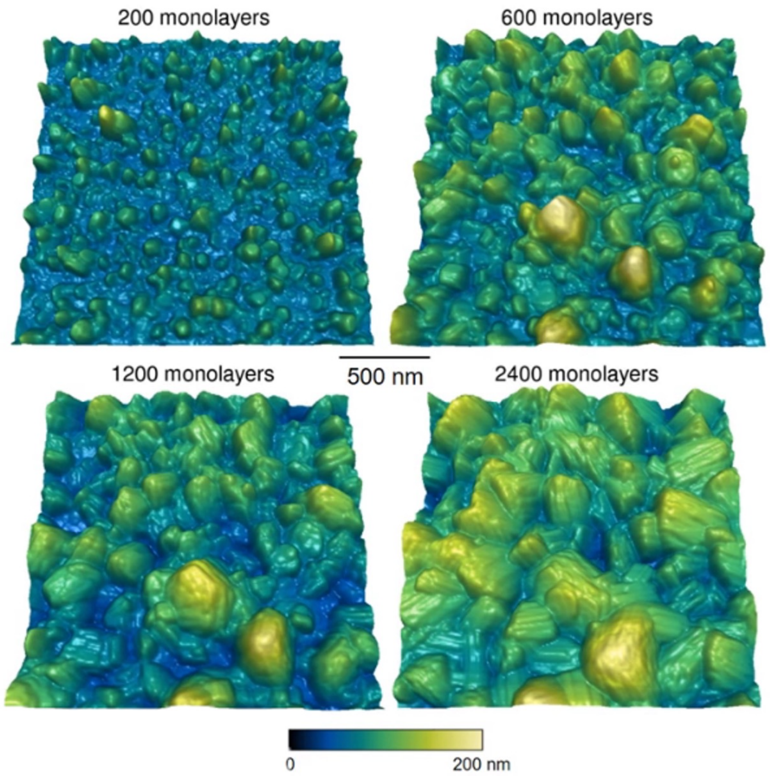
Membrane porosity and pore size

- Electrolyte saturation and ion transfer
- But risk membrane damage and shorting across the membrane

AFM measurement

- Topographic imaging (tapping mode)
- Minimal sample prep
- SEM: problem with charging; requires coating

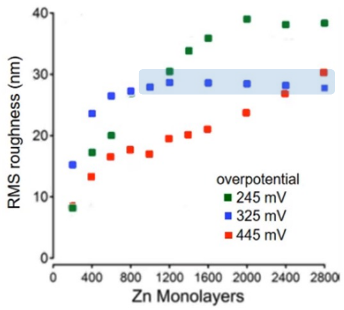
Process Control



Zinc electrodes in rechargeable batteries

Electrodeposition in ionic liquid electrolyte

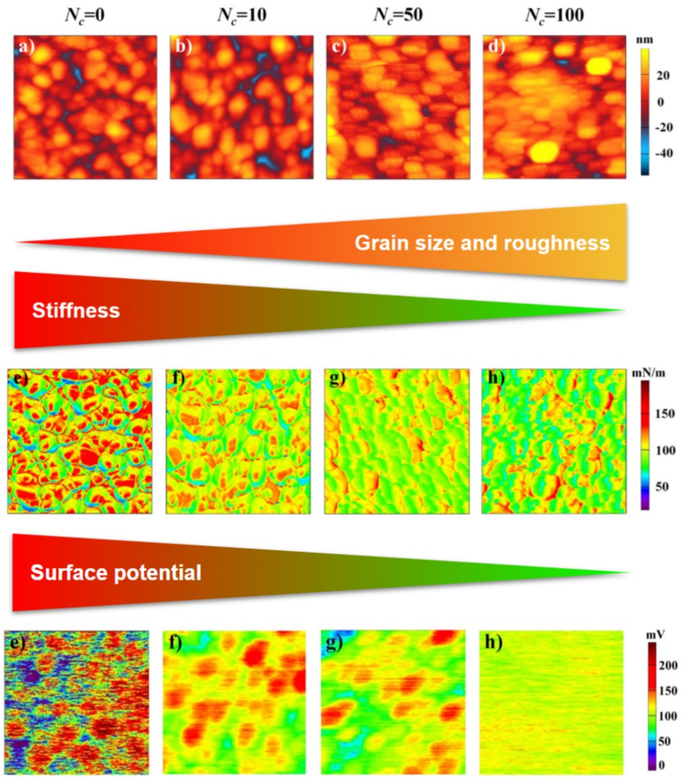
- Optimize electrodeposition process to improve long-term stability
- Monitor film growth in situ at different overpotentials



AFM measurement

- Evolution of topography with thickness (deposition time)
- Roughness evaluated at different overpotentials
- Optimal at 325 mV

Cathode: Aging



Engineering Challenge:

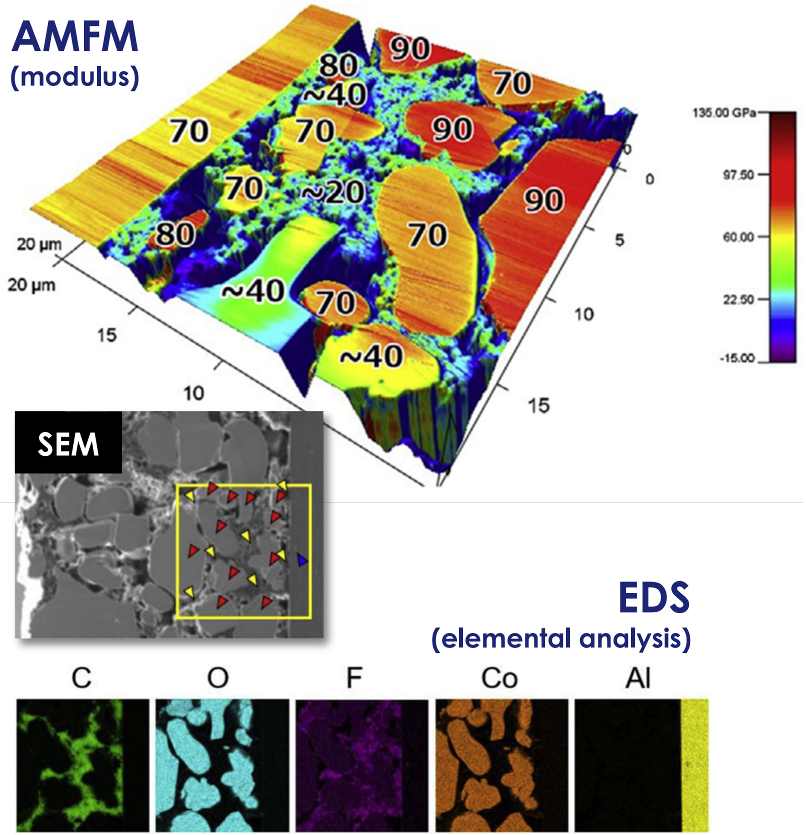
- Understanding **aging mechanisms** of lithium cobaltate cathode films, which is important to battery lifetime
- Goal: Evaluate surface **morphology**, **stiffness**, and **surface potential** over several charge/discharge cycles

AFM Solution:

- **Morphology**: increase in grain size and roughness
- **AMFM**: decrease in stiffness due to irreversible lithiation/de-lithiation during the discharge/charge
- **KPFM**: decrease in surface potential (and its variation) due to irreversible lithiation/de-lithiation
  - Coexistence of the two phases, offsetting each other's work functions

J. Wu, S. Yang, W. Cai, Z. Bi, G.i Shang, and J. Yao. Scientific reports 7, 1 (2017): 11164

Cathode: Aging



Engineering Challenge:

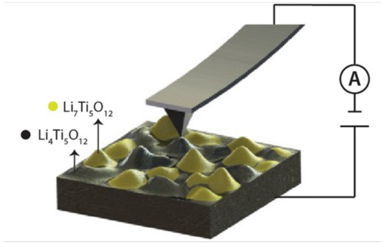
- Understanding **aging** of lithium cobaltate cathodes which is important to battery lifetime
- **Goal:** Understand **composition and structure** of these composite electrodes after cycling

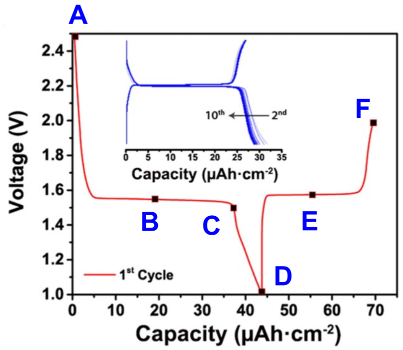
AFM & EM Solution:

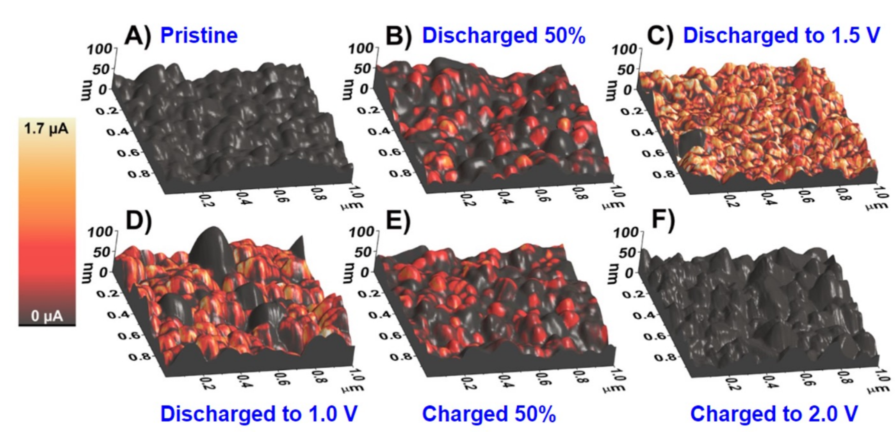
- **Correlative imaging**
- **SEM & EDS**: structure and composition
  - Aluminum: current collector plate
  - $LiCoO_2$: cathode material (particles)
  - Acetylene black: conductive additive
  - Polyvinylidene difluoride: binder
- **AMFM**: Several $LiCoO_2$ particles show much lower modulus after cycling, indicating possible damage due to over delithiation

Sakai, H., Taniguchi, Y., Uosaki, K., & Masuda, T. (2019) Journal of Power Sources, 413, 29-33.

Anode: Lithiation/Delithiation



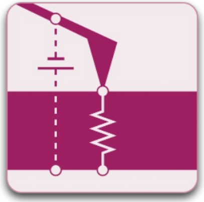




Engineering Challenge:

- Lithium titanate used as battery anode material
  - Lower capacity due to its high redox potential, but this also gives it better stability
  - Zero strain material—no volume (X-ray diffraction) change between lithiated and delithiated phases
- Goal: Understand lithiation/delithiation process during discharging/charging

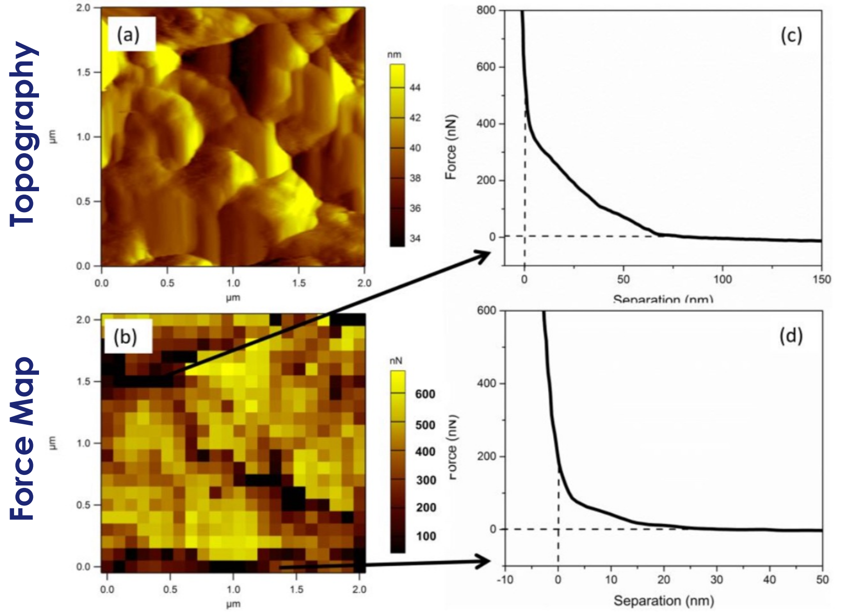
AFM Solution:



- Only lithiated phase is conducting
- CAFM can map lithiation/delithiation process during discharging/charging cycles
- No morphology change (as expected)
- Conductivity increased during discharge, indicating lithiation

M.G. Verde, L. Baggetto, N. Balke, G.M. Veith, J.K. Seo, Z. Wang, Y.S. Meng. ACS nano 10, 4 (2016): 4312-4321

SEI: Effect of Formulation

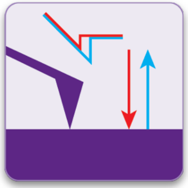


Polymer Electrolyte + 1M LiFSI

Engineering Challenge:

- **SEI**: **passivating layer** that dominates the interfacial performance of anodes, and impacts the battery's capacity and long term stability
- **Goal:** Evaluate different formulations of a hybrid polymer-gel electrolyte material with respect to **lithium salt** concentrations and **acetonitrile**, an organic solvent additive

AFM Solution:

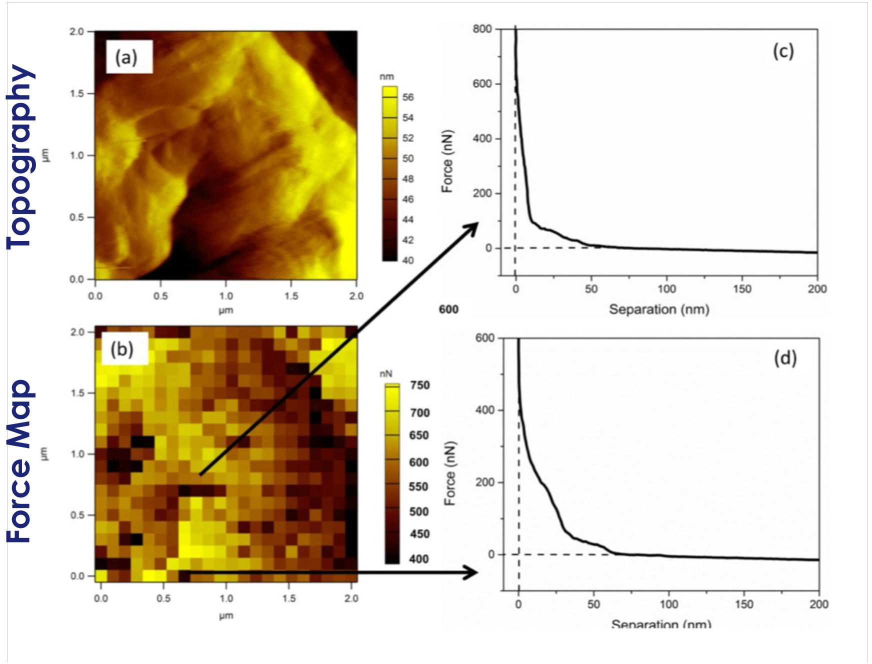


- **Topographic imaging** to assess the effect of different formulations on SEI morphology
- **Force maps** to determine thickness and mechanical property
  - Rupture force
  - Plasticity
- High concentration of lithium salt and addition of acetonitrile stabilizes SEI (thicker, more flexible)

A. Lahiri, G. Pulletikurthi, M.S. Ghazvini, O. Höfft, G. Li, F. Endres. J. Phys. Chem. C 122, 43 (2018): 24788-24800.

SEI: Effect of Formulation

OXFORD INSTRUMENTS

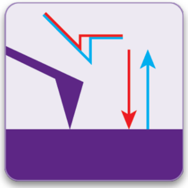


Polymer Electrolyte + 4M LiFSI + Acetonitrile

Engineering Challenge:

- **SEI**: **passivating layer** that dominates the interfacial performance of anodes, and impacts the battery's capacity and long term stability
- **Goal:** Evaluate different formulations of a hybrid polymer-gel electrolyte material with respect to **lithium salt** concentrations and **acetonitrile**, an organic solvent additive

AFM Solution:



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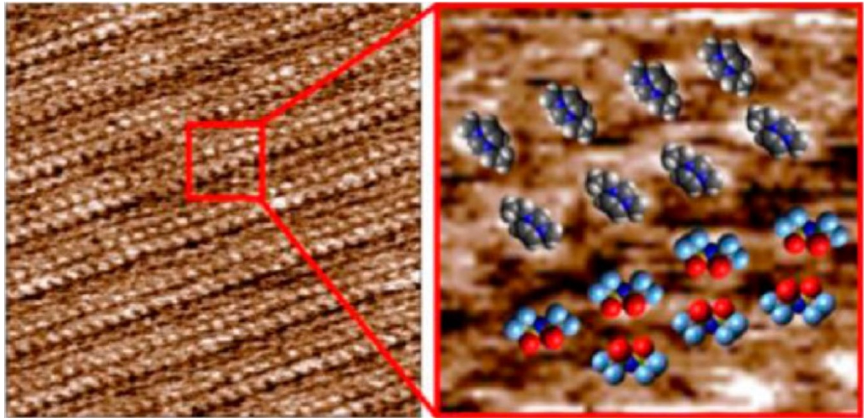
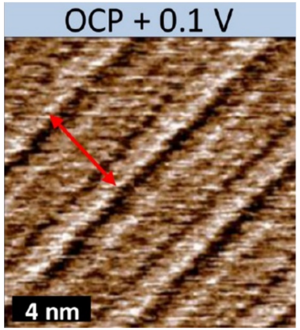
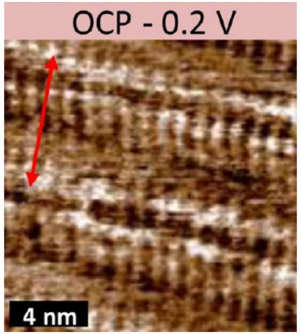
A. Lahiri, G. Pulletikurthi, M.S. Ghazvini, O. Höfft, G. Li, F. Endres. J. Phys. Chem. C 122, 43 (2018): 24788-24800.

Electrolyte Solvent: Stern Layers

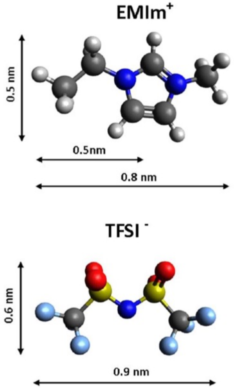




Positive Open Circuit Potential



Negative Open Circuit Potential



Engineering Challenge:

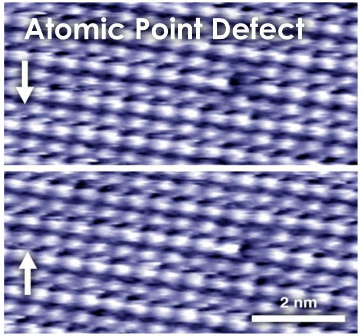
- **Ionic liquids** as LIB electrolyte material
  - Large electrochemical windows
  - Low volatility
  - High thermal stability
  - High conductivity
- Large molecules that do not behave like typical salt solutions; strongly interact with substrate, forming ordered **Stern layers**
- **Goal:** Visualize Stern layers on graphite

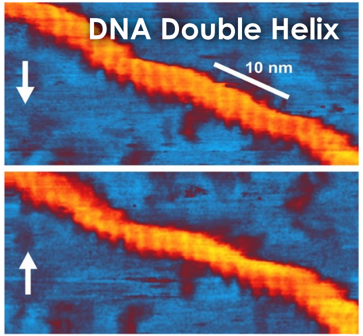
AFM Solution:

- **High-resolution imaging** directly visualizes molecular ordering of the Stern layers
- Applying potential to graphite surface changes the Stern layer structure to compensate for interfacial charge
- Adding Li and Cl ions also changes the Stern layer

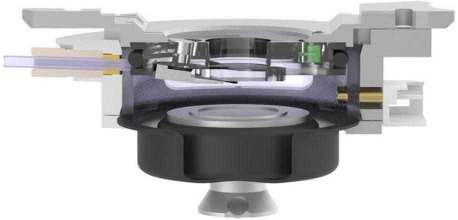
A. Elbourne, S. McDonald, K. Voïchovsky, F. Endres, G.G. Warr, R. Atkin. ACS nano 9, 7 (2015): 7608-7620.

Cypher: Stability, Resolution, Speed



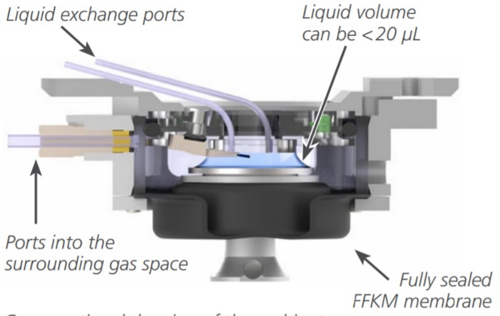


Unmatched Resolution



Environmental Control

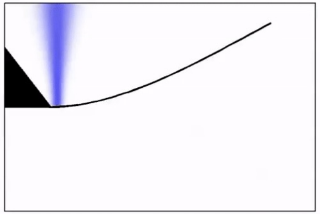
✓ Heating ✓ Cooling ✓ Humidity

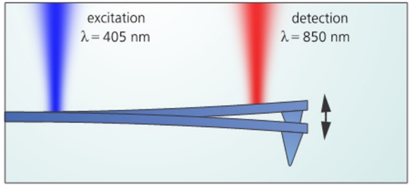


Cross-sectional drawing of the ambient stage and fluid perfusion probe holder

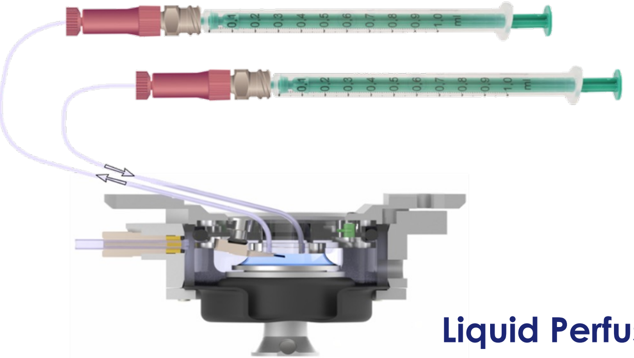
Hermetic Chamber

✓ Gas ✓ Liquid





Photothermal Excitation (blueDrive™)

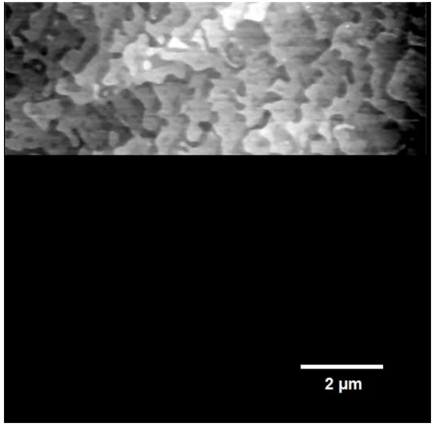


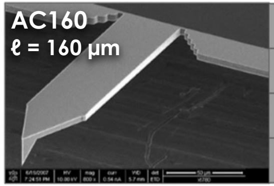
✓ High Voltage
✓ Electrochemistry
✓ Glove Box

Liquid Perfusion

How fast can we image?

Conventional AFM



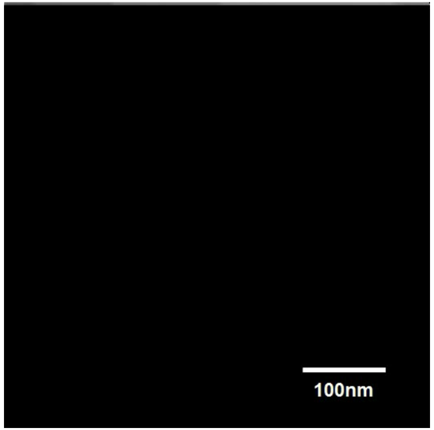


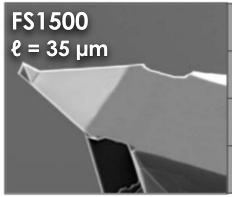
k	26 N/m
r	7 nm
f	300 kHz
Q	466

0.0024 fps (1Hz line rate)

Sapphire **in ambient air**

Fast-Scanning AFM



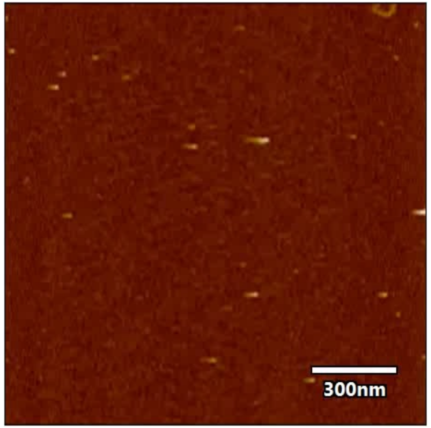


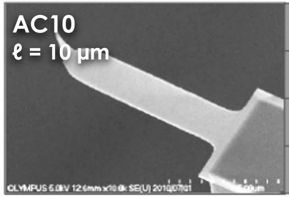
k	6 N/m
r	10 nm
f	1.5 MHz
Q	183

0.15 fps (20Hz line rate)

Calcite **in water**

Video-Rate AFM



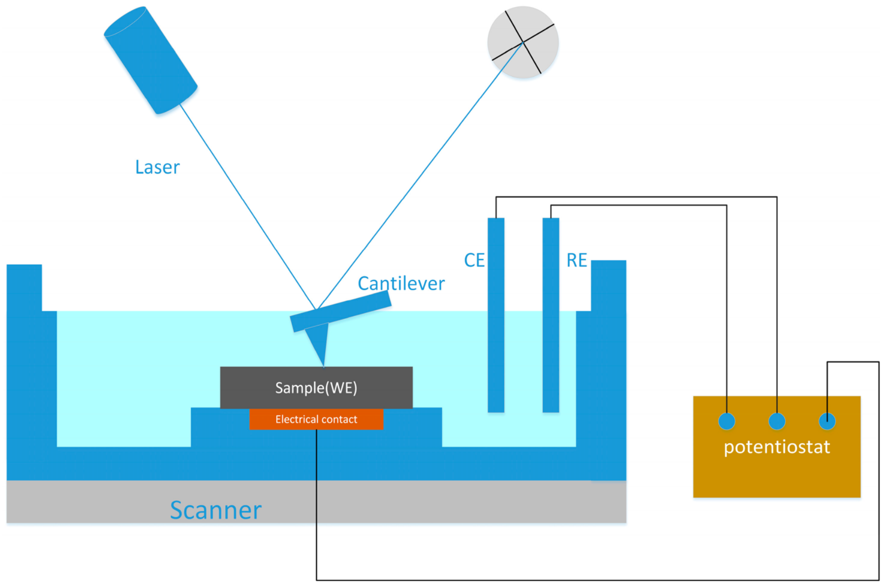


k	0.1 N/m
r	27 nm
f	1.5 MHz
Q	1.8

3 fps (396 Hz line rate)

Lambda digest DNA **in buffer**

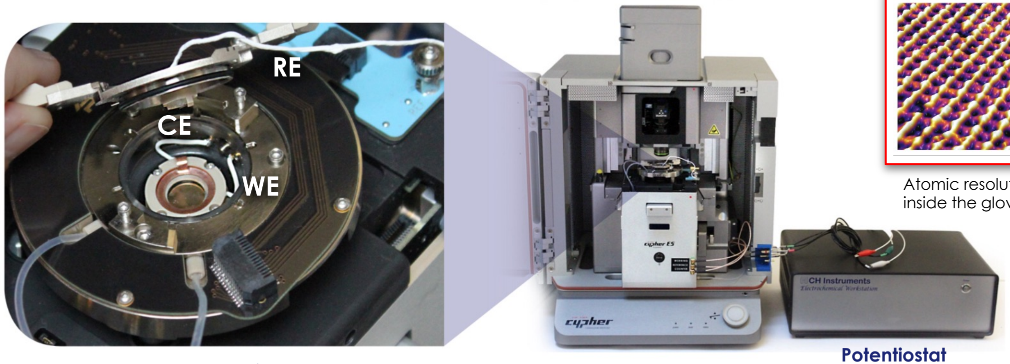
Electrochemical AFM (EC-AFM)



- Electrochemical AFM (EC-AFM) is when AFM used with a special EC cell to observe an electrochemical reaction at an electrode.
  - AFM probe is a passive observer, not an electrode
- The EC cell holds three electrodes:
  - **Working**: The sample where the reaction occurs. Immersed in the electrolyte solution.
  - **Reference**: Working electrode potential is measured relative to reference electrode.
  - **Counter**: Allows current to pass to maintain the desired working electrode potential.
- Used together with a potentiostat
  - Controls the potential at the working electrode while measuring the current that passes through the counter electrode.

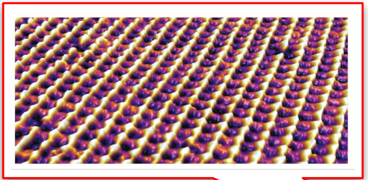
Figure taken from: Chen, H.; Qin, Z.; He, M.; Liu, Y.; Wu, Z. Application of Electrochemical Atomic Force Microscopy (EC-AFM) in the Corrosion Study of Metallic Materials. Materials 2020, 13, 668. https://doi.org/10.3390/ma13030668

Cypher ES Battery Edition



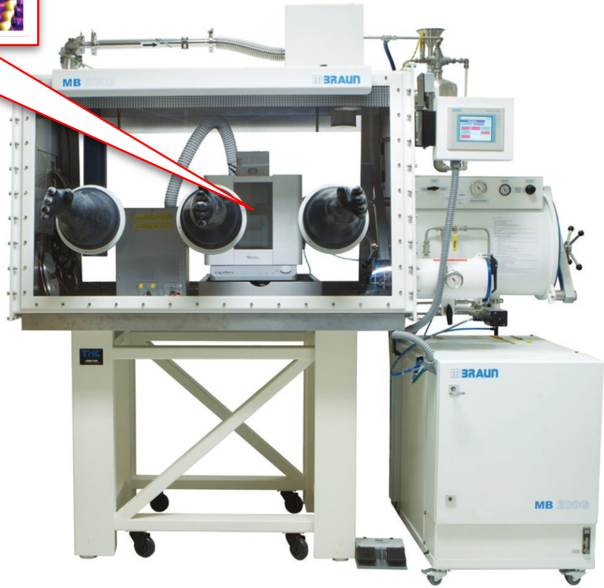
Potentiostat

Electrochemical Cell

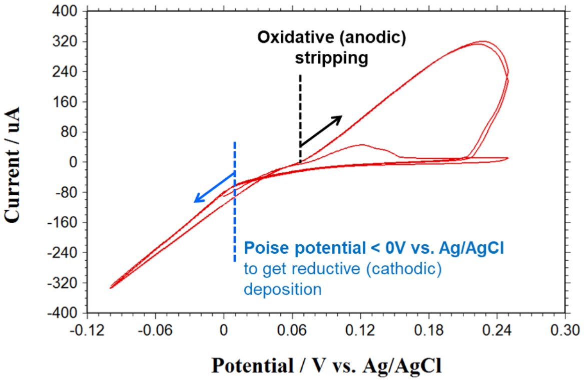


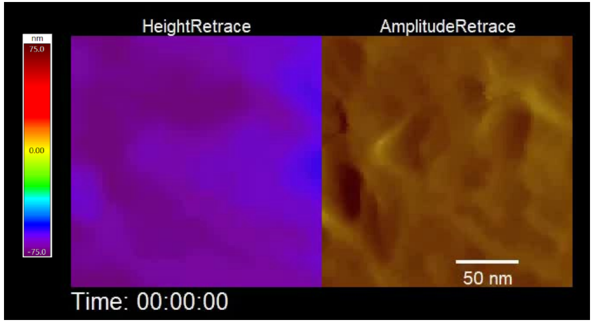
Atomic resolution even inside the glove box

AFM in the Glove Box: Inert Atmosphere



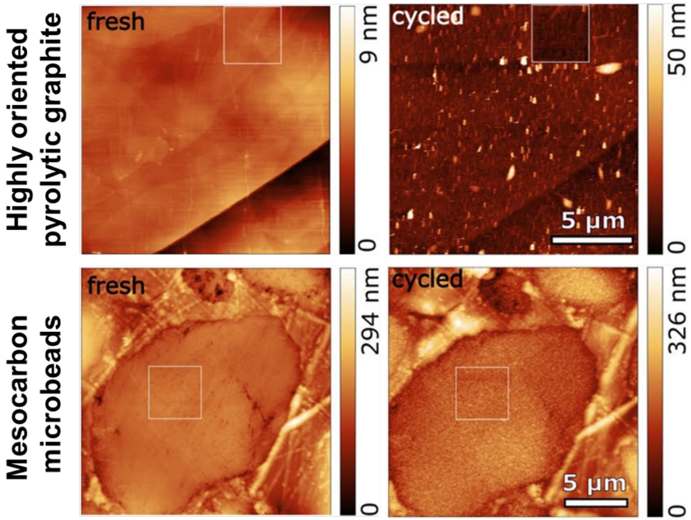
Cypher AFM in MB200 customized glovebox shown with full instrument translation stage, air temperature control, and humidity control option.

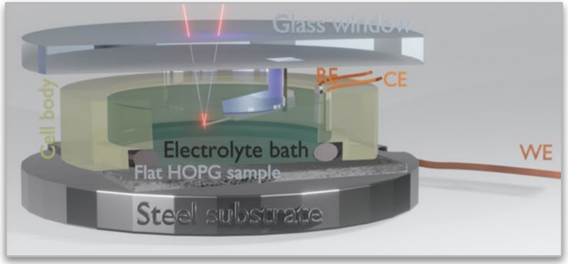




Copper Deposition

In situ formation of SEI on Anode

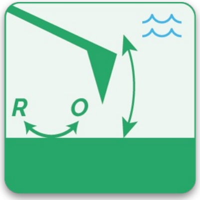




Engineering Challenge:

- SEI: passivating layer that dominates the interfacial performance of anodes, and impacts the battery's capacity and long term stability
- Poorly formed SEI can result in capacity fade and reduction in power density
- Goal: Understand SEI formation after initial cycling

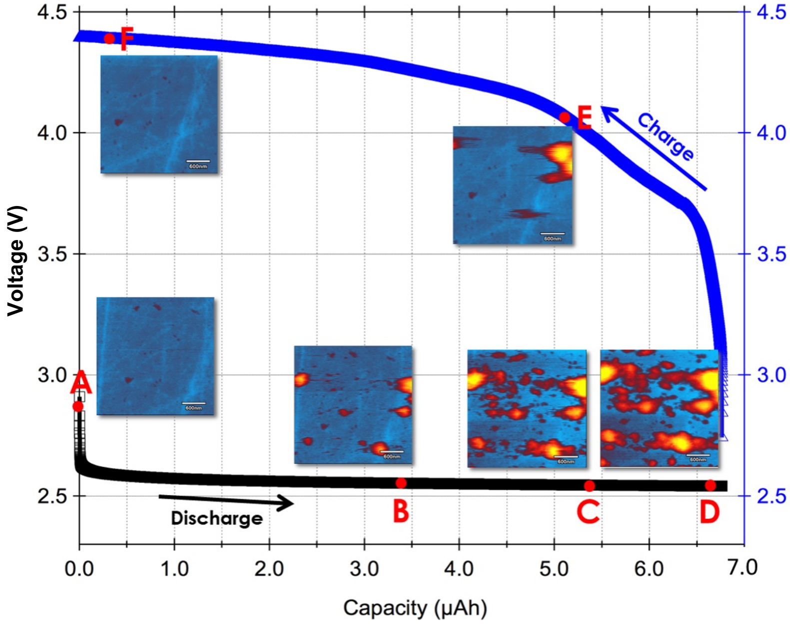
AFM Solution:

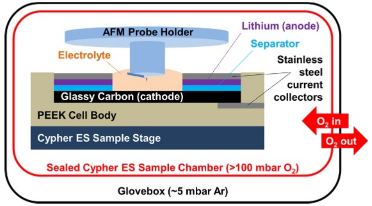


- EC-AFM: in situ electrochemical AFM used to monitor SEI formation on anode surface during cycling in Ar-filled glove box
- Nucleation and growth observed along step edges and and basal planes, correlating with current dips in the voltammogram.
- Forms more uniform layer on MCMB vs. HOPG; also more stable based on AFM-based mechanical testing

Luchkin, S. Y., Lipovskikh, S. A., Katorova, N. S., Savina, A. A., Abakumov, A. M., & Stevenson, K. J. (2020) Scientific reports, 10(1), 8550.

In operando EC reactions on Cathode

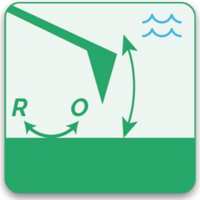




Engineering Challenge:

- Electrochemical reactions between Li and O_2 offer the highest theoretical potential of any battery technology
  - Need to investigate morphological changes on glassy carbon cathode during Li/O_2 electrochemical reactions
  - Challenging to do in situ because the materials are air and water sensitive
- **Goal:** Monitor in situ **changes in morphology** during the discharge/recharge of Li-O battery electrode

AFM Solution:



- **EC-AFM**: sealed electrochemical cell; AFM in a glove box
- Discharge resulted in the **formation of electrochemical products** on the surface
- Dependent on the amount of water present, which increases discharge capacity
- Deposits disappear during the recharge cycle

Virwani, Kumar, et al., Beilstein journal of nanotechnology 10.1 (2019): 930-940.

Summary

OXFORD INSTRUMENTS

Find out more:

How can AFMs help battery R&D to deliver performance?

1. Ex situ materials analysis of isolated components
2. In situ observation of processes involving several components
3. In operando measurement of whole battery cell

AFMs can provide critical information to improve all aspects of the battery device.