COVALENT METROLOGY

Welcome

COVALENT METROLOGY

ENERGIZING RESEARCH IN BATTERY PERFORMANCE WITH ADVANCED AFM

SPEAKER:

Dr. Nate Kirchhofer
Physical (Nano) Electrochemist and Applications Scientist, Asylum Research Oxford Instruments

Mar 25, 2021 | 11am PT

OXFORD INSTRUMENTS ASYLUM RESEARCH

COVALENT METROLOGY

COVALENT METROLOGY

Silicon Valley-based analytical labs and platform delivering quality data and expert analysis for advanced materials and device innovation

Comprehensive Solutions Stack

40+ cutting-edge instruments, offering 100+ Techniques

Analytical Services

Advanced Modeling

Method Development

Temp. Staffing Solutions

Affordable and Fast

Fast Turnaround Times, No Expedite Fees

Volume Savings

Instant Access to Data and Reports in Secure Portal

Flexible Business Model

Custom Consulting Solutions and Certified Onsite Support

Training and Certification on Instrumentation

Co-op and Tool-Share Opportunities

Laboratory Audits

Rich Network of Partnerships

Rigaku · J.A. Woollam · ThermoFisher Scientific · PVA TePla · Anton Paar · Asylum Research an Oxford Instruments company

Partner to World's Leading Instrument Manufacturers and Labs

Expanding Instrumentation, Lab Connections and Learning

Who We Are, Who We Serve

500 Clients + 40-60 New Clients/ Quarter

40 People, 12 PhDs

Cutting-edge Analytical Capabilities

Lab Location: Sunnyvale, CA

Covalent Technical Groups and Organization

COVALENT METROLOGY

PCBA, Semiconductor, and Electronic Device Metrology & Failure Analysis

- DPA / Mechanical Cross-section
- Dye & Pry Test
- Hot Spot Detection
- IR Imaging / Emission Microscopy
- Root-Cause Failure Analysis
- EBIC / OBIC failure analysis

+ many more advanced methods!

Electron / Scanning Probe Imaging & Microscopy

- SEM (+ EDS)
- FIB-SEM (+ EDS)
- S/TEM (+ EDS / + EELS)
- AFM & Advanced AFM Modes
- Scanning Acoustic Microscopy (SAM)

Optical Microscopy & Spectroscopy

- Laser Scanning Confocal
- White Light Interferometry
- Chromatic Aberration
- Digital Optical Microscopy
- Spectral Ellipsometry
- UV-Vis-NIR Spectroscopy

X-Ray Characterization

- X-Ray Diffraction
- X-Ray Reflectometry
- Micron-spot ED-XRF
- WDXRF
- Micro-CT
- 2D X-ray Inspection & X-ray Radiography

Chemical Analysis

- ICP-MS & LA-ICP-MS
- GC-MS
- FTIR
- Raman
- NMR (1D or 2D; solid-state and solution-state)
- EPMA

Nanoparticle Analysis

- Dynamic Light Scattering (DLS)
- Laser Diffraction Particle Size Analysis (PSA)
- Particle Zeta Potential

Material Property Characterization

- DSC
- TGA
- DMA & TMA
- Rheometry
- Surface Zeta Potential
- Nanomechanical Analysis
- Tensile-Test
- Taber Test

Surface Analysis

- X-ray Photoelectron Spectroscopy (XPS)
- Ion Scattering Spectroscopy (ISS)
- Ultraviolet Photoelectron Spectroscopy (UPS)
- ToF-SIMS (Static-SIMS)
- Dynamic-SIMS

Covalent Instrument Partners

OXFORD INSTRUMENTS
ASYLUM RESEARCH

COVALENT METROLOGY

- Partnership Announced May, 2020
- Collaboration aimed at further developing and promoting commercial applications for several advanced modes of atomic force microscopy (AFM)
  - Past Webinar: **Advanced AFM in Biological Applications** accessible in the Community Portal at www.covalentmetrology.com/portal

Other Partners

Rigaku

PVA TePla

J.A. Woollam

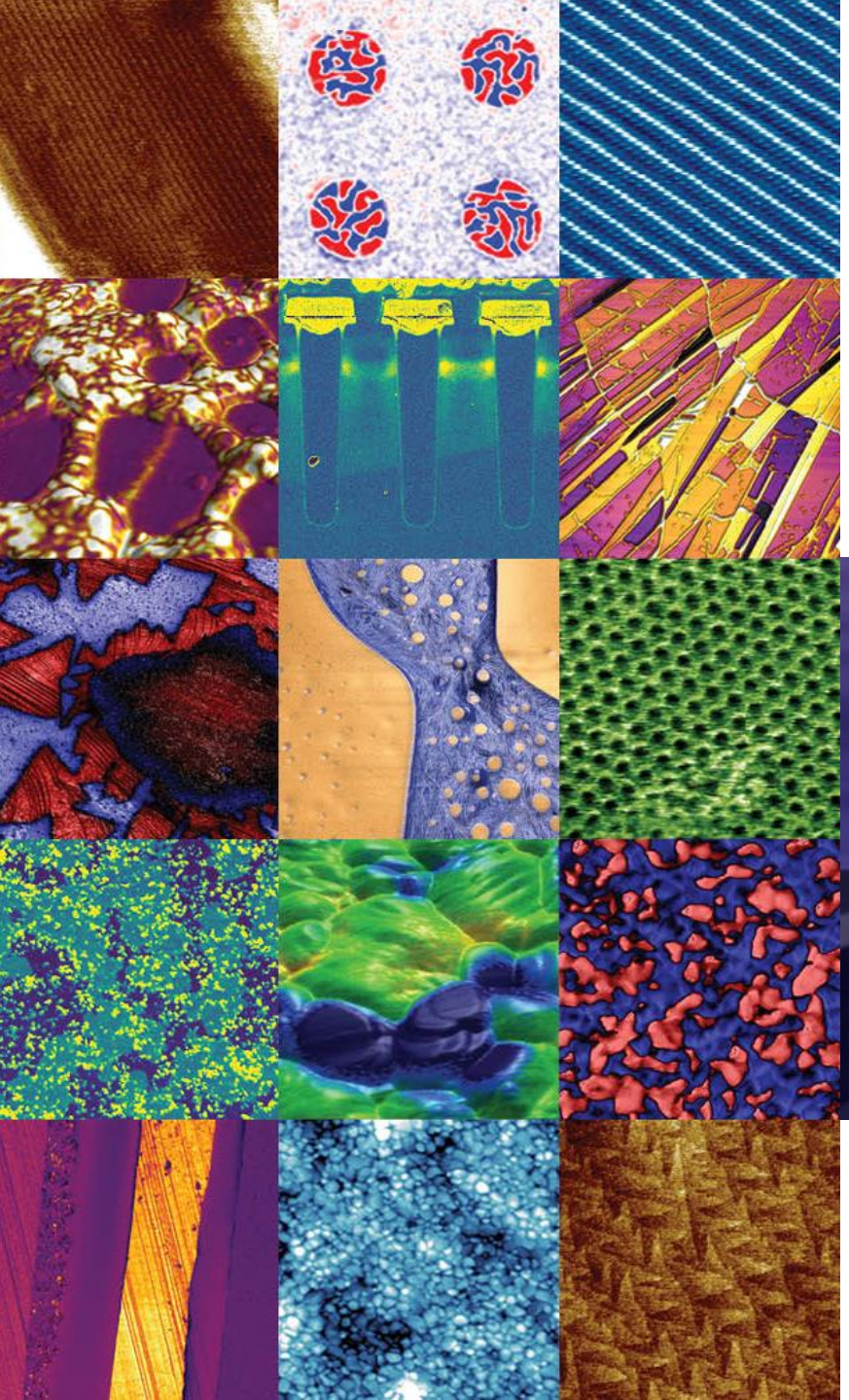
KEYENCE

ThermoFisher SCIENTIFIC

Nate Kirchhofer, PhD

Applications Scientist,
Asylum Research Oxford Instruments

- Dr. Nate Kirchhofer is a Physical (Nano-)Electrochemist and Applications Scientist at Oxford Instruments Asylum Research
- PhD in Materials from UC Santa Barbara
- More than ten years research experience and over ten peer reviewed publications
- One of his primary goals is to help researchers analyze cutting edge electrochemical systems—like batteries!



Energizing Research in Battery Performance with Advanced Atomic Force Microscopy (AFM)

Nate Kirchhofer, PhD

Applications Scientist, Oxford Instruments Asylum Research

Battery Components: Improved by Engineering

Targets of Engineering

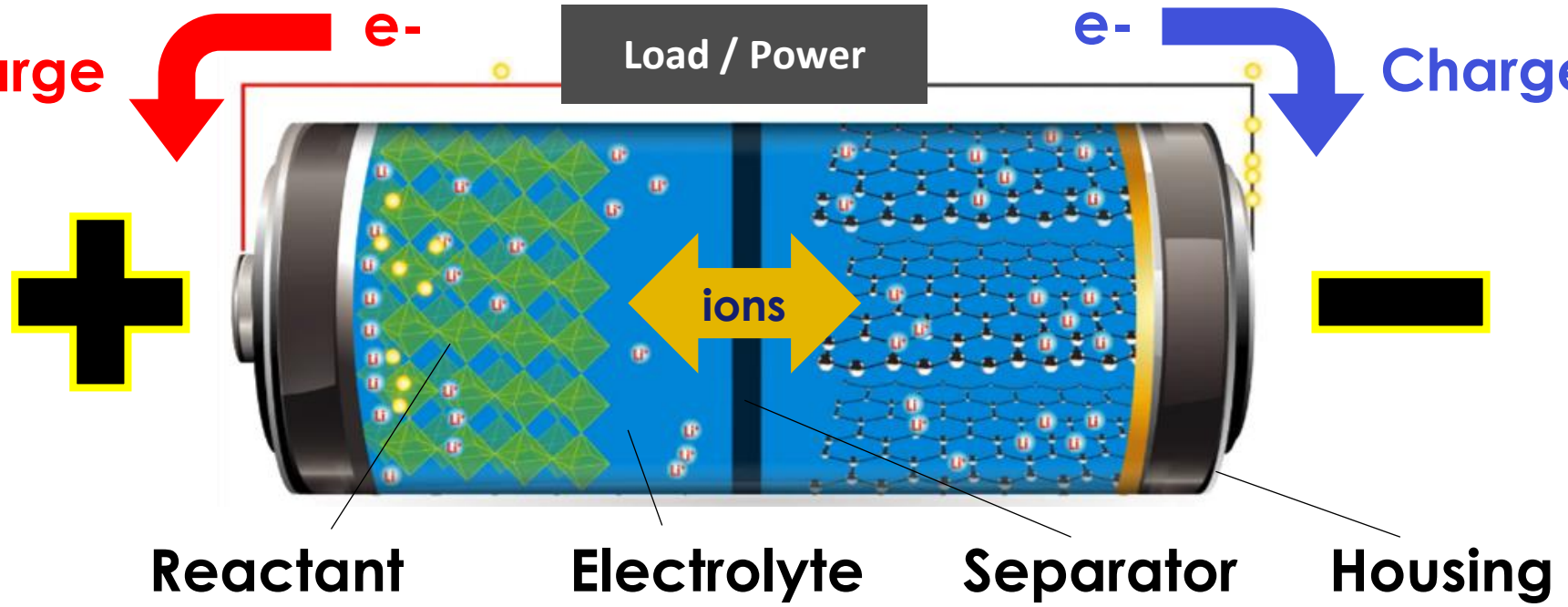
1. **Electrodes** (**–** Anode / **+** Cathode)
2. **Reactants** (chemistry / composition)
3. **Electrolyte** (ionically conductive solvent)
4. **Separator** (ion-permeable membrane)
5. **Housing** (device encapsulation)

Goals

1. **Increase Specific Energy Density** (Wh/g)
2. **Increase Specific Power Density** (W/g)
3. **Decrease Energy Storage Cost** ($/Wh)

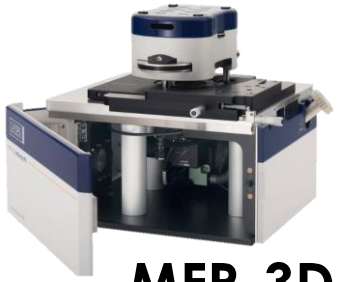
Key Question:

How can we "see" what happens inside a battery?



U.S. DEPARTMENT OF ENERGY | Office of ENERGY EFFICIENCY & RENEWABLE ENERGY

AFMs are Nanoscale Surface Mapping Tools

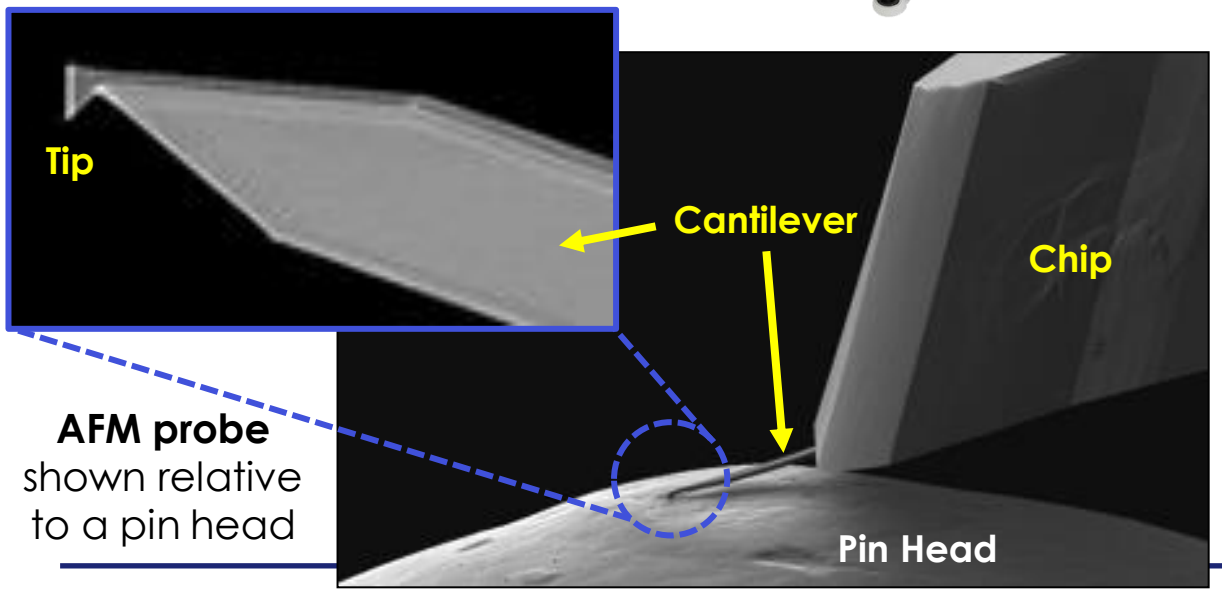


MFP-3D

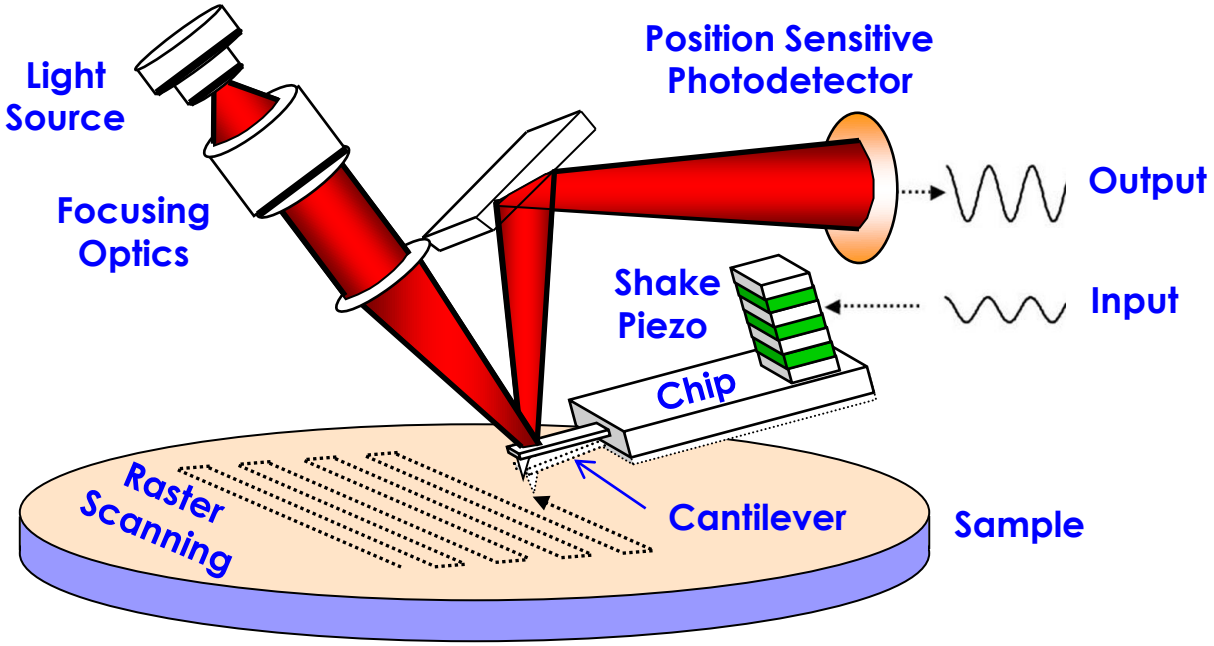
Cypher

Jupiter XR

- A **very tiny, very sharp mechanical probe** scans the surface, "feeling" the topography
- Images are **3D representations** of the surface
- Can achieve **sub-nm-scale resolution** (resolve molecules and atomic point defects)
- Operates in **ambient or controlled conditions**

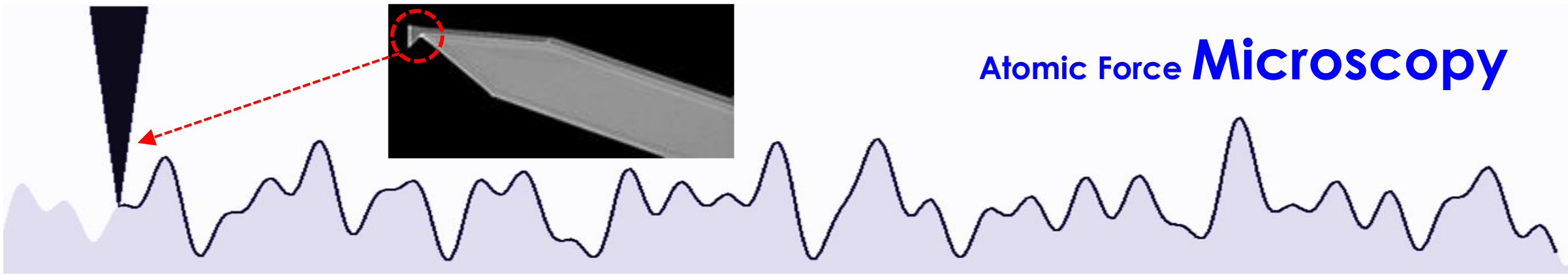


AFM probe shown relative to a pin head



The AFM raster scans a sample, building up the image **line by line.**

Mapping by “Touch” Reveals Local Properties



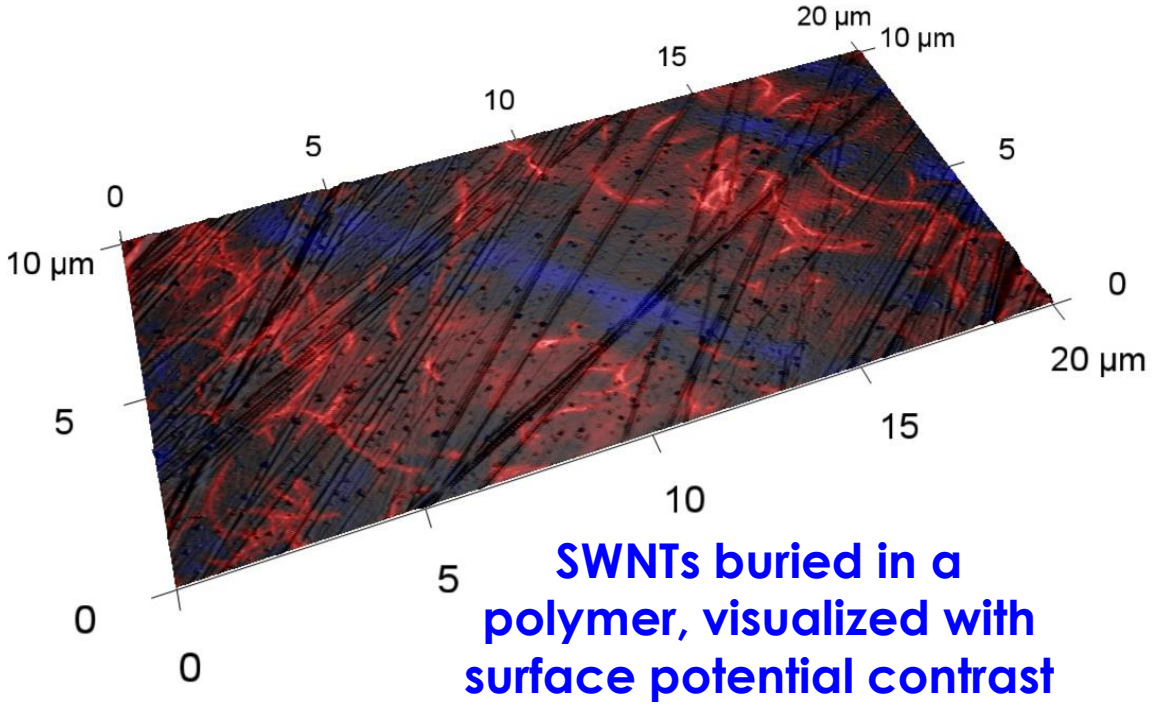
Atomic Force **Microscopy**

AFMs **“touch”** the surface

- Contact or proximity to the surface allows us to probe local material properties

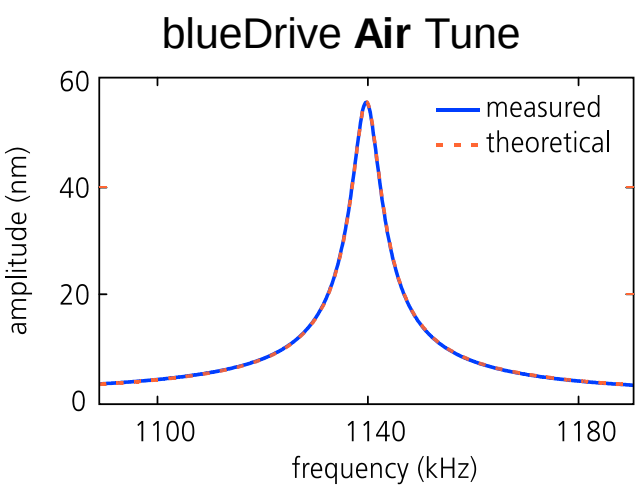
Main strength: **materials characterization**

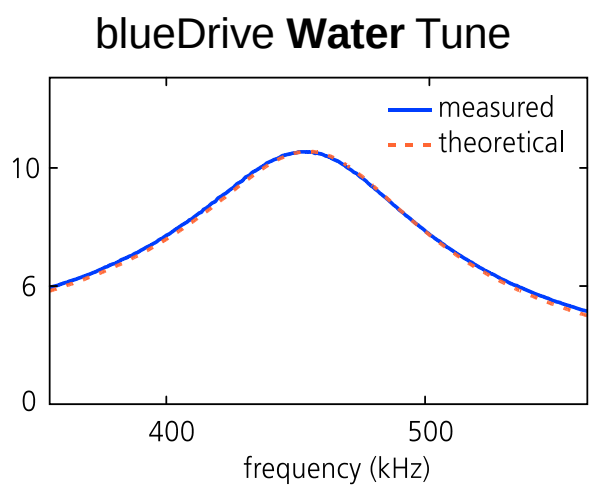
- Conformational, mechanical, thermal, electrical/magnetic properties
- Force sensor: pN to μN; kPa to GPa
- Mapped (located) on nanoscale topographic contours

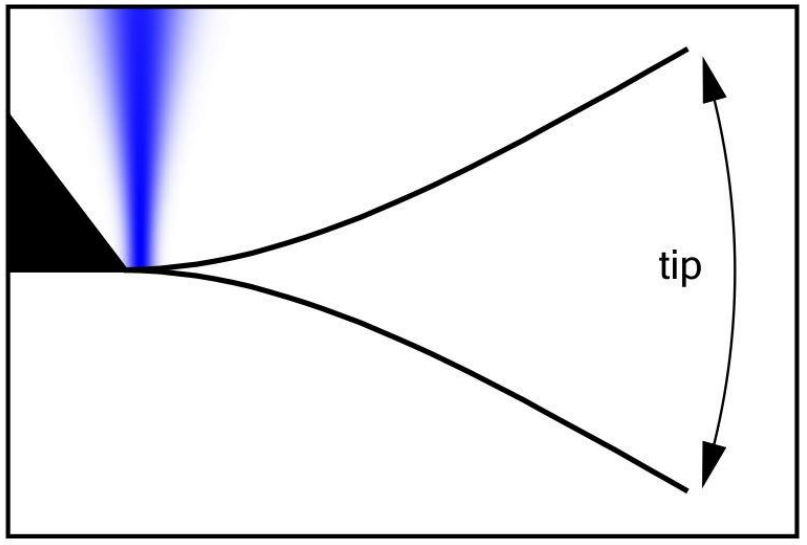


SWNTs buried in a polymer, visualized with surface potential contrast

blueDrive™ Photothermal Excitation for Fast, High-Res Tapping Mode

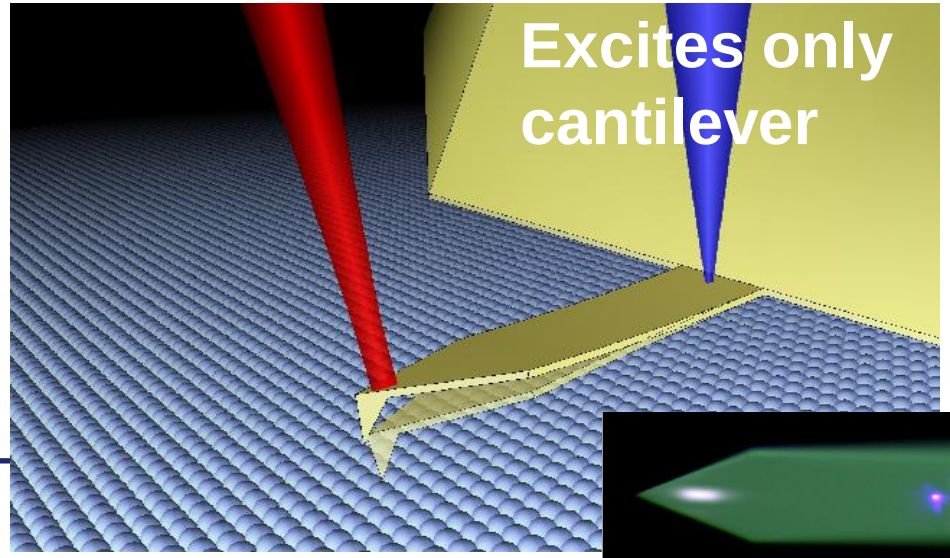




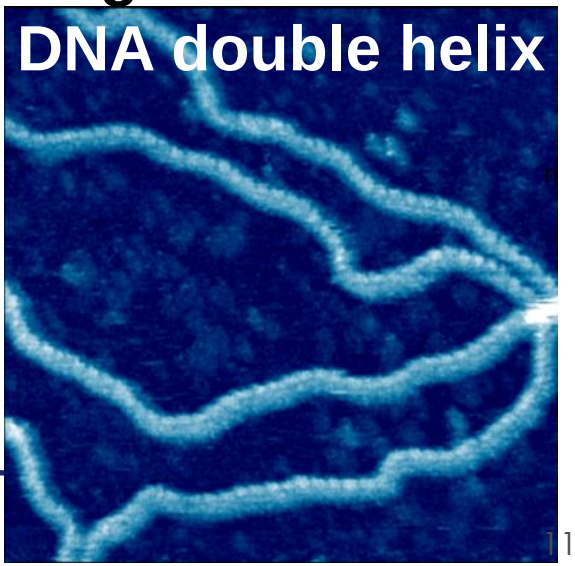


detection
$\lambda = 850$ nm

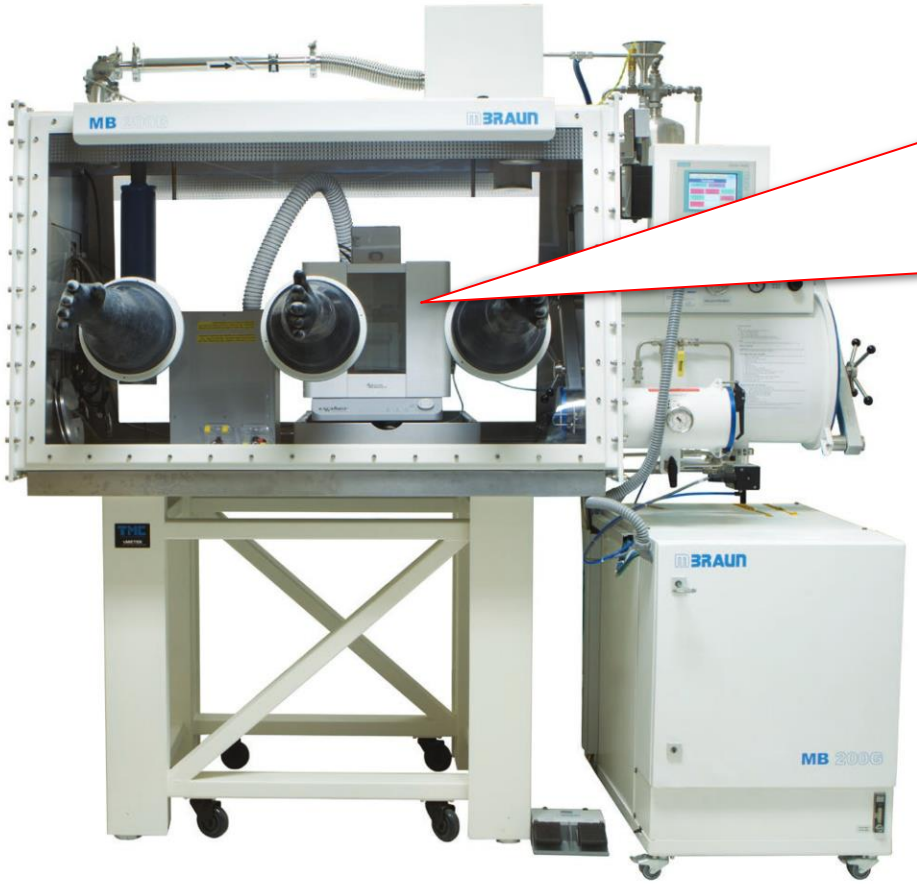
excitation
$\lambda = 405$ nm



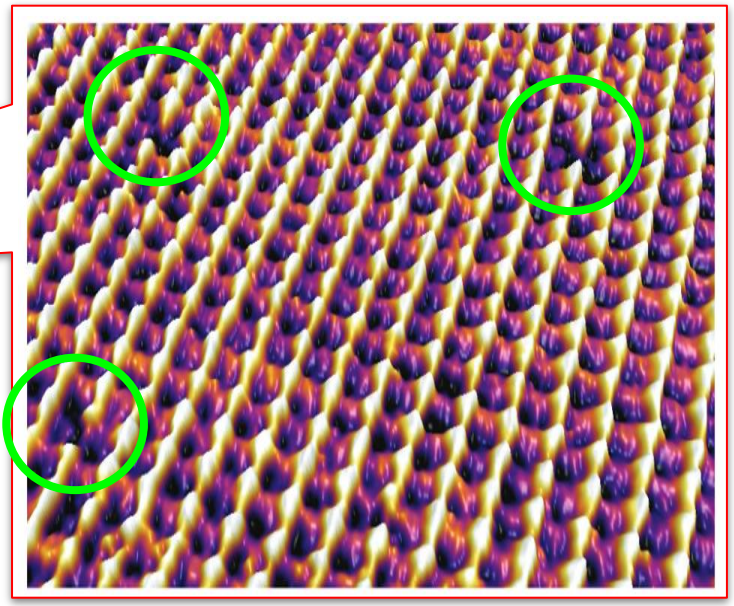
High Resolution



Environmental Control is Critical



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

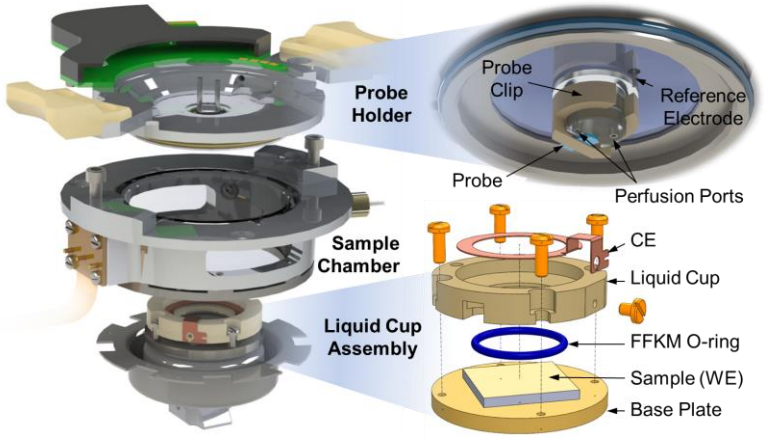


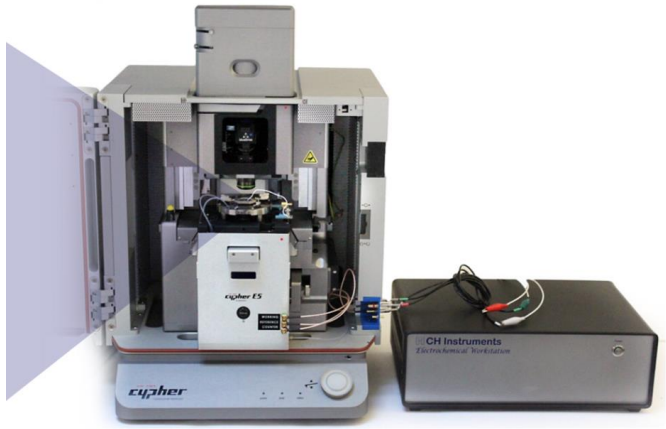
Atomic point-defect imaging during glovebox operation

Learn More

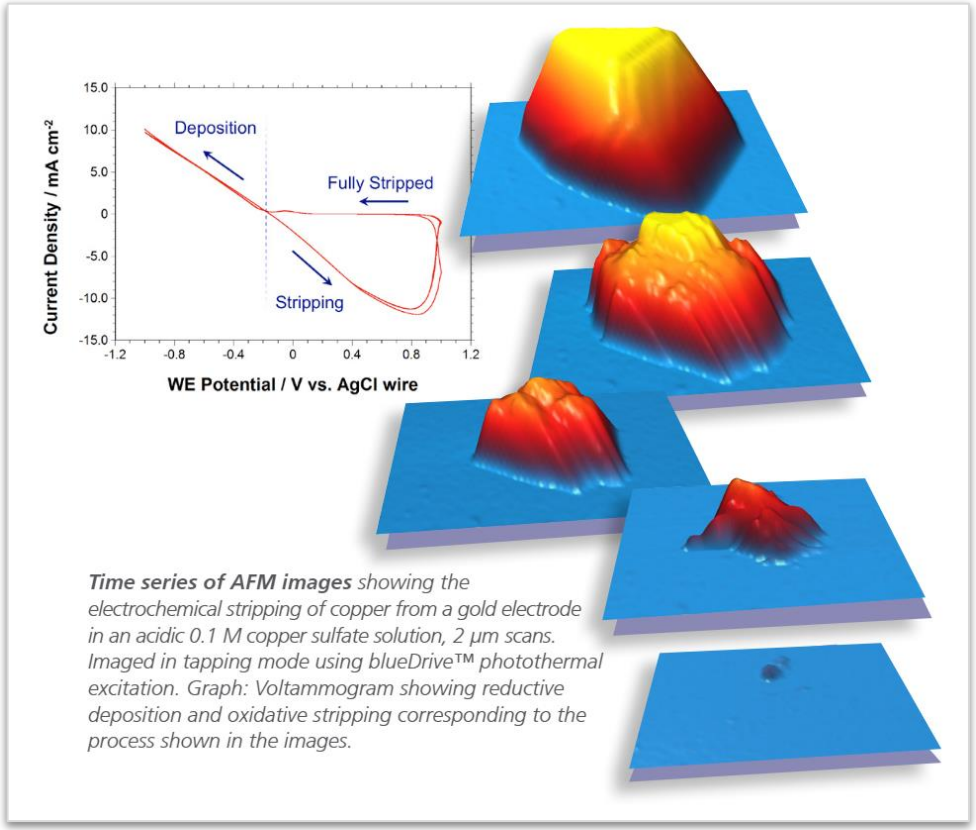
Electrochemical Control is also Critical

Electrochemistry Cell

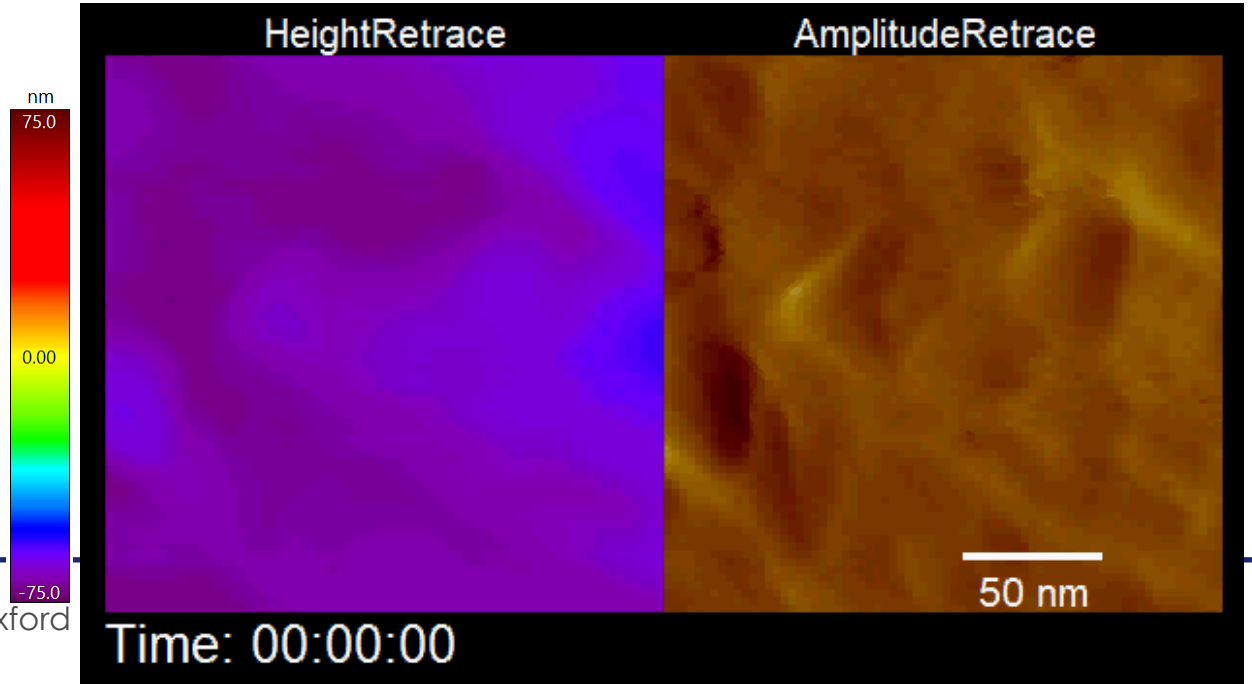




Copper Crystal EC-AFM



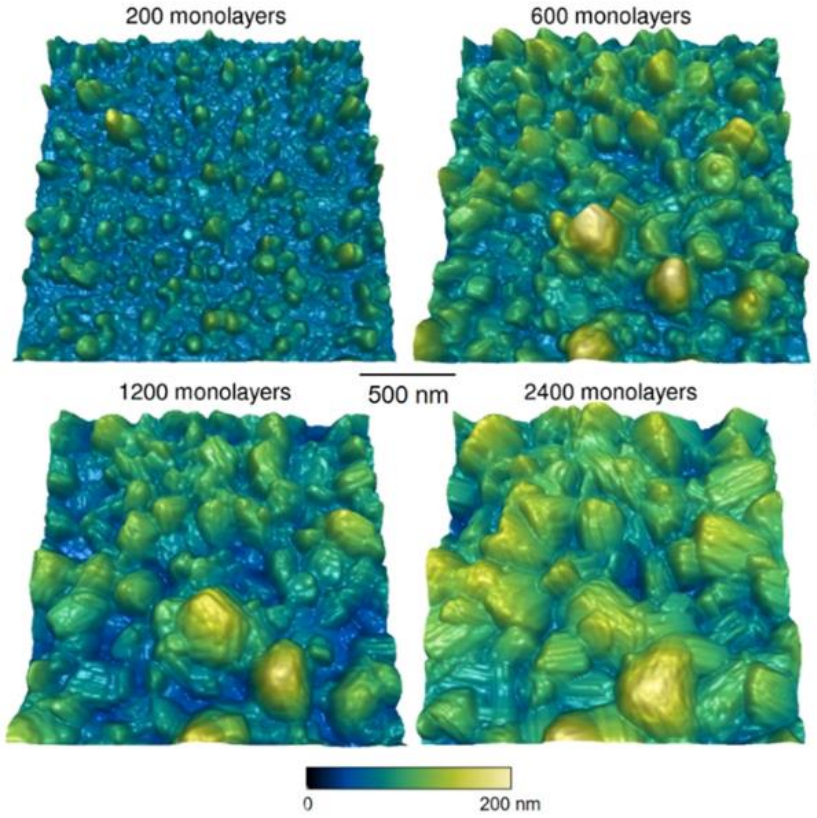
Time series of AFM images *showing the electrochemical stripping of copper from a gold electrode in an acidic 0.1 M copper sulfate solution, 2 µm scans. Imaged in tapping mode using blueDrive™ photothermal excitation. Graph: Voltammogram showing reductive deposition and oxidative stripping corresponding to the process shown in the images.*

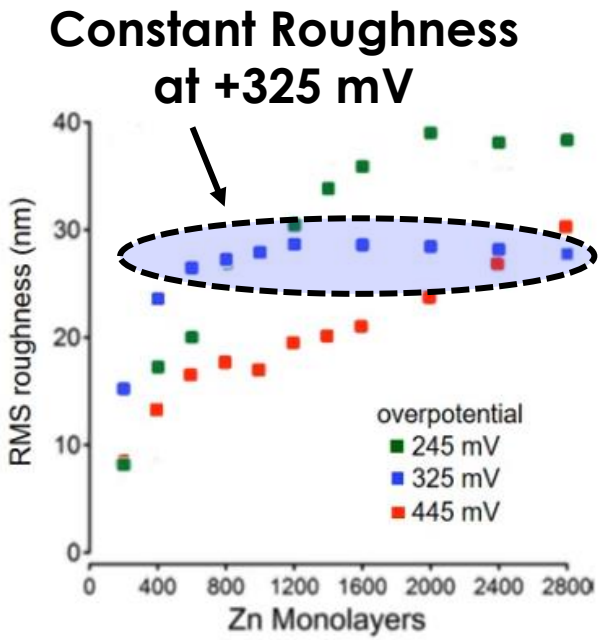


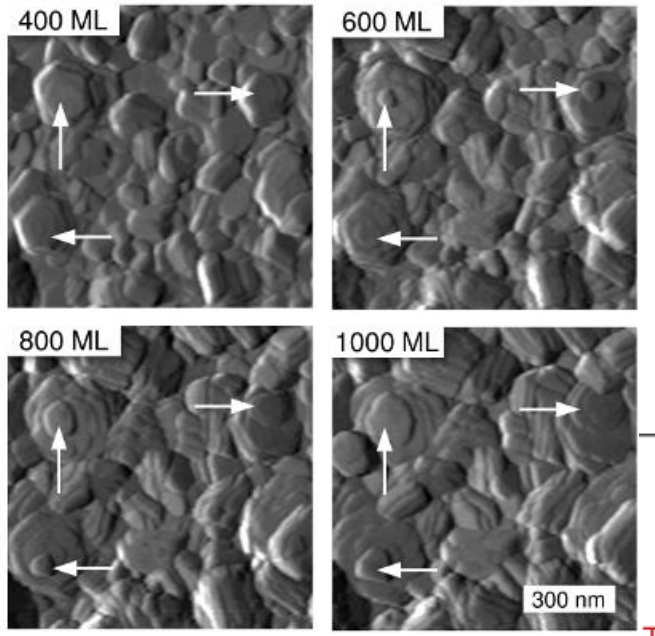
Anode: *in-situ* Zn electrodeposition (inert gas)

An **in situ** AFM Study of the evolution of surface roughness for zinc electro-deposition within an imidazolium based ionic liquid electrolyte

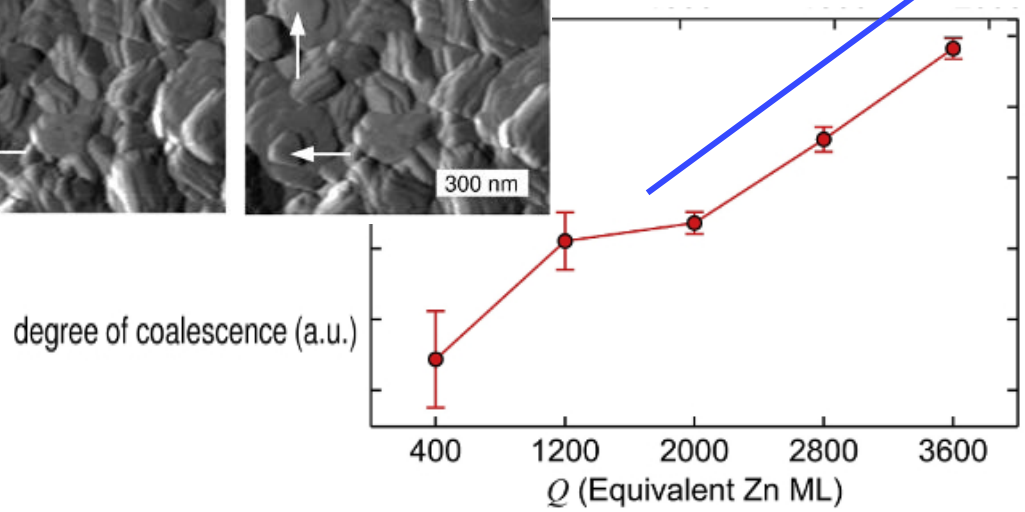
J.S. Keist, C.A. Orme, P.K. Wright, J.W. Evans. *Electrochimica Acta* 152 (**2015**): 161-171.
Lawrence Livermore National Lab







Increasing crystal coalescence with film thickness



Argon Atmosphere

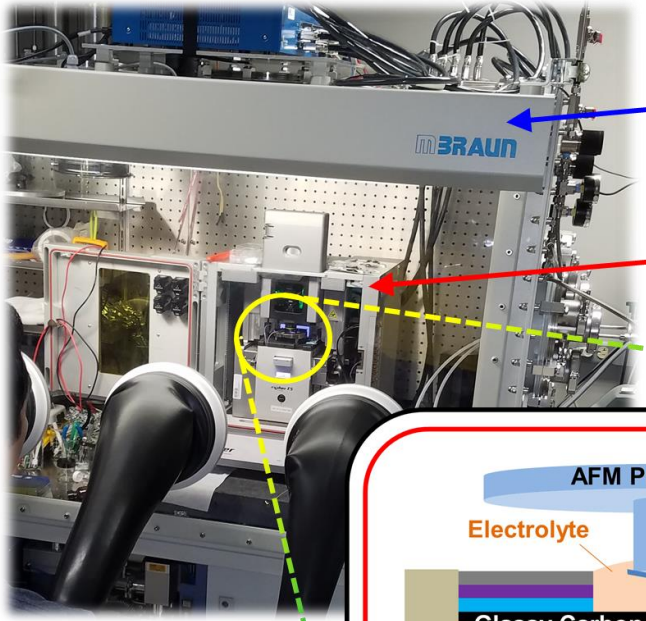
Coupling **in situ** atomic force microscopy (AFM) and ultra-small-angle X-ray scattering (USAXS) to study the evolution of zinc morphology during electrodeposition within an imidazolium based ionic liquid electrolyte.

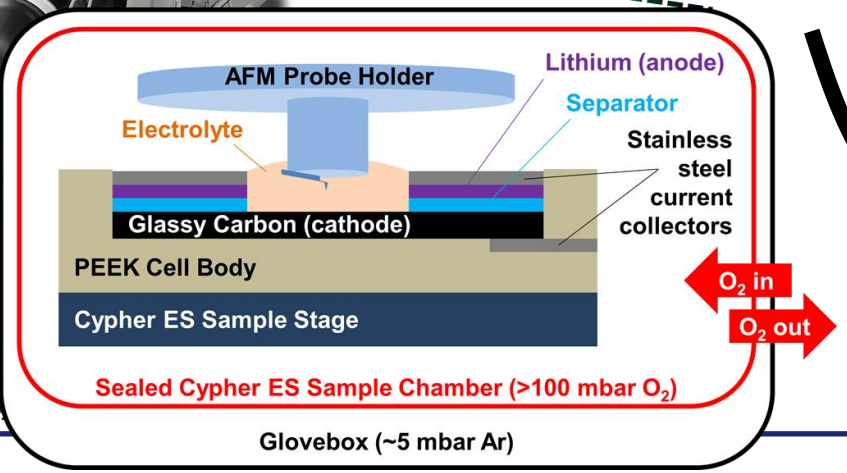
J. Keist, J. Hammons, P. Wright et al., *Electrochim. Acta* 342 (**2020**): 136073 (2020)

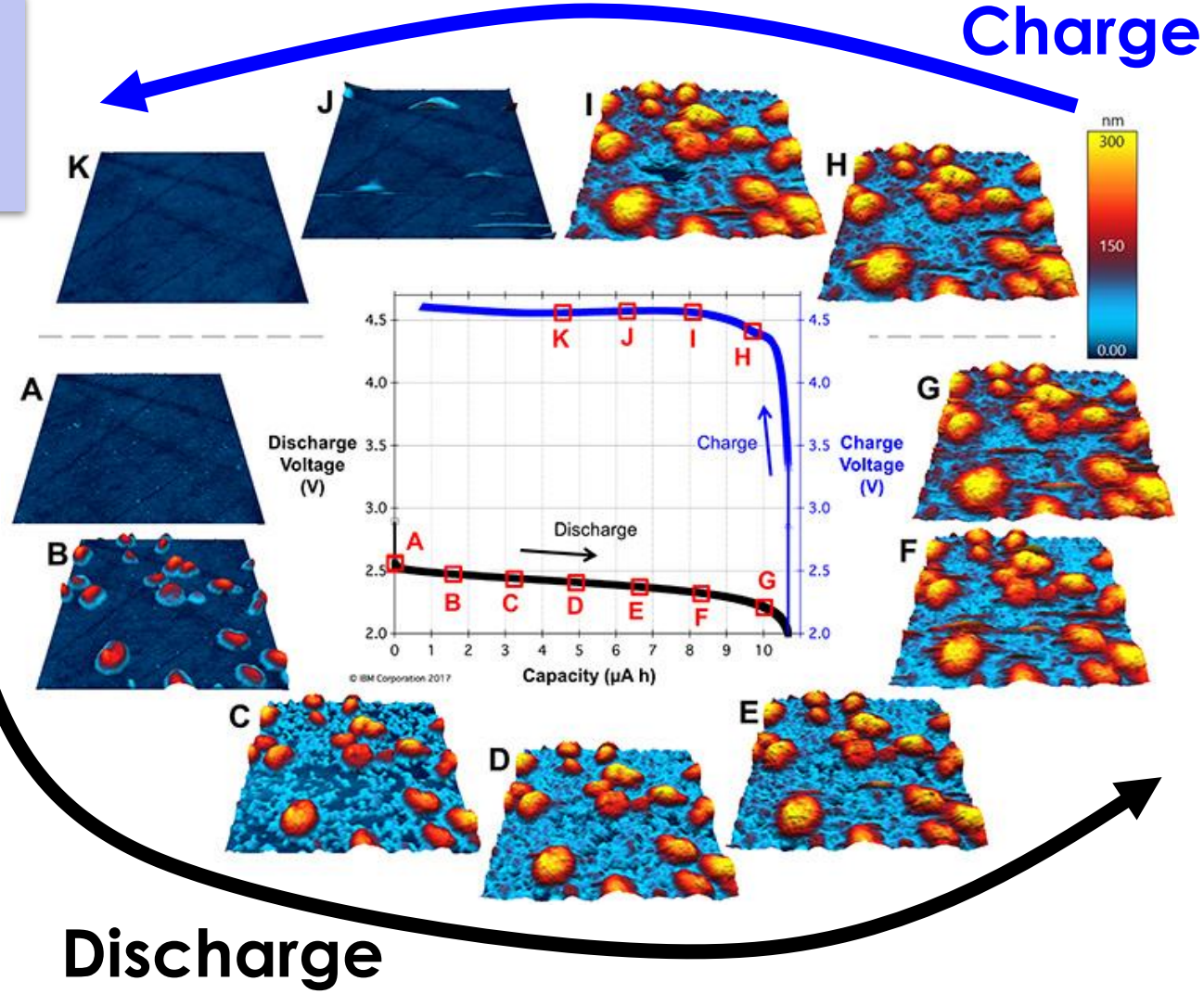
Cathode: *Operando* LiO_x images in a Li-O_2 Cell

In situ AFM visualization of Li–O_2 battery discharge products **during redox cycling** in an atmospherically controlled sample cell

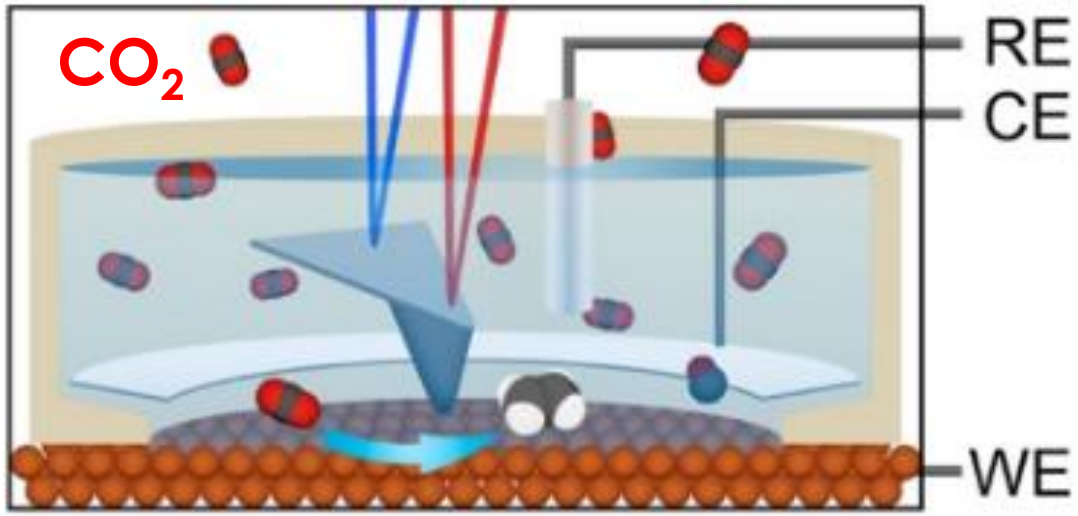
Virwani, K., et al. *Beilstein Journal of Nanotechnology* (**2019**): 930-940.
IBM Almaden



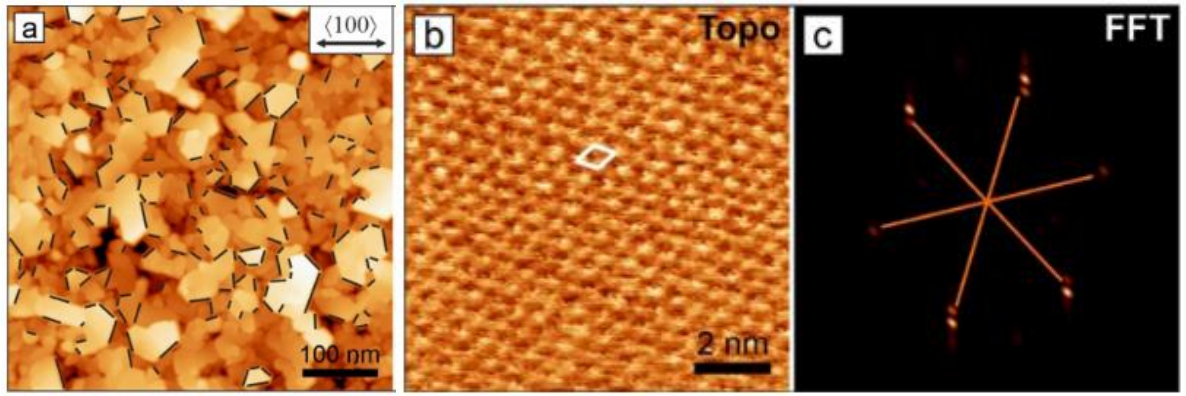




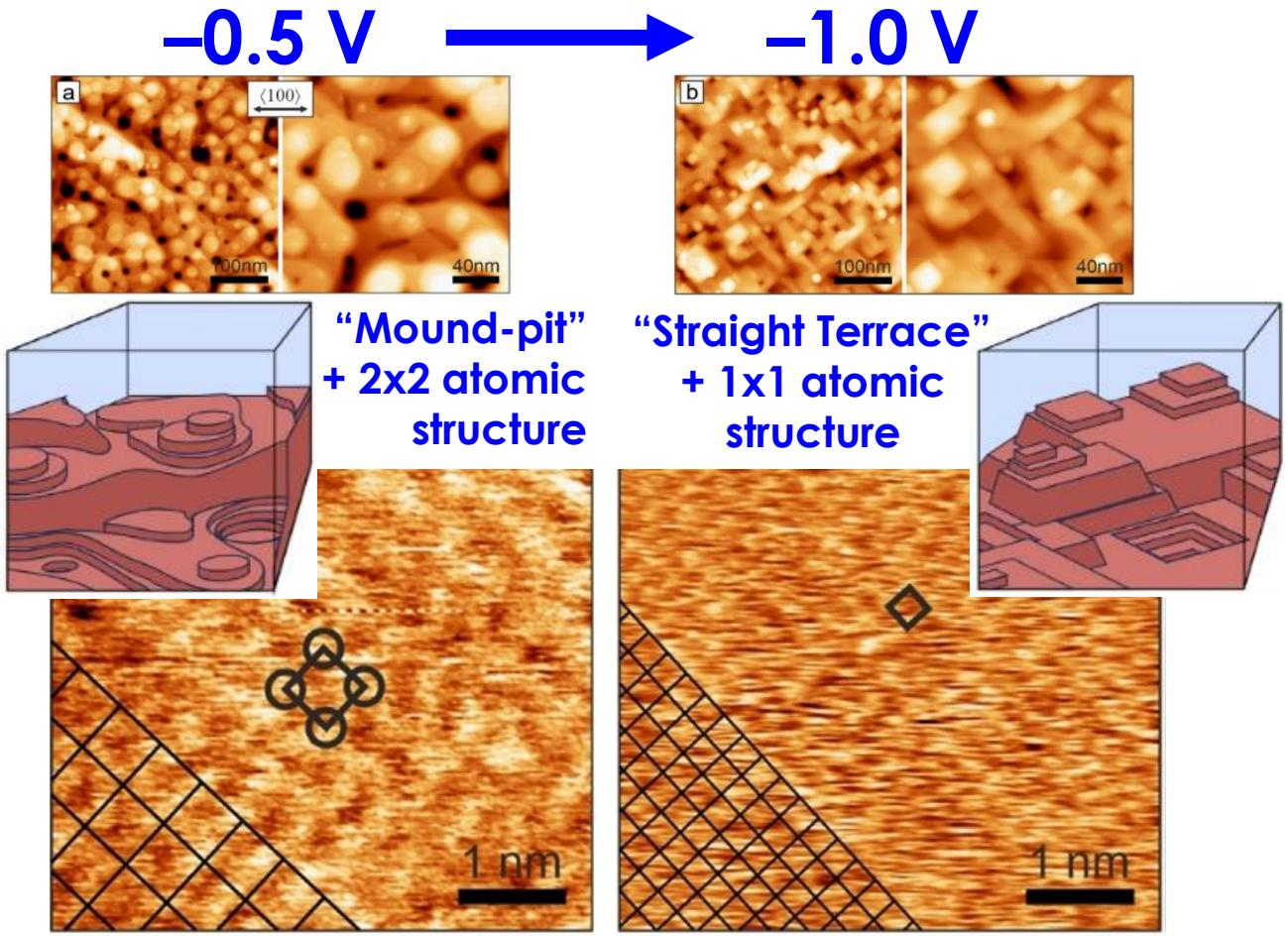
Electrode: *in situ* V-dependent nanotopography



AFM Electrochemical Cell



$Cu_2O(111)$ atomic resolution (V_{OC})



Potential-dependent Morphology of Copper Catalysts During CO_2 Electroreduction Revealed by **In Situ** Atomic Force Microscopy

Simon, G. H., Kley, C.S., Cuenya, B. R. Angewandte Chemie Int. Ed. (**2021**): 2561-2568
Fritz Haber Institute of the Max Planck Society

Separator: ion-exchange membrane morphology & conductivity in situ as a function of humidity

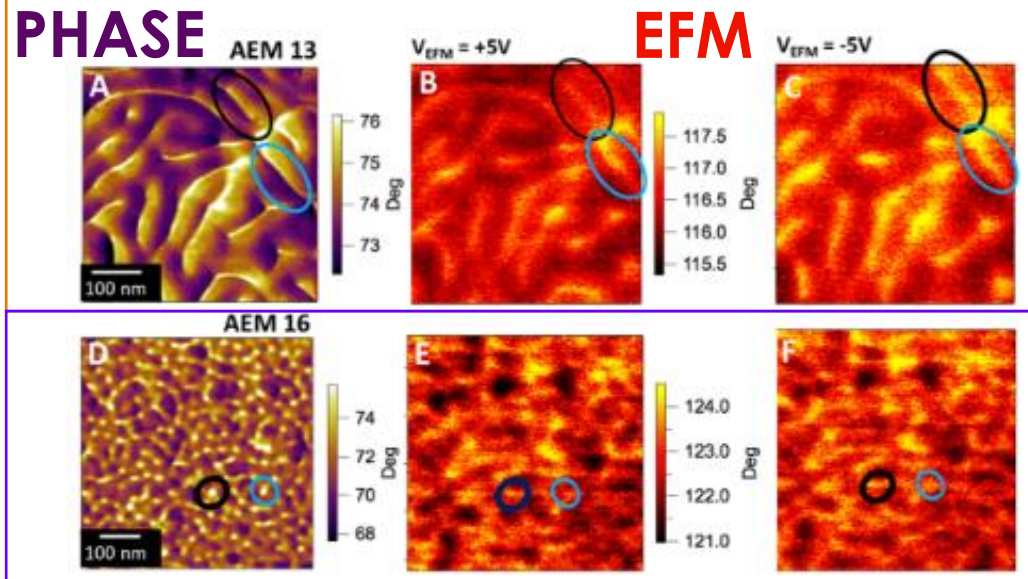
Effect of Surface Alignment on Connectivity in Phosphonium-Containing Diblock Copolymer Anion-Exchange Membranes

Barnes, A.M. et al. J. Phys Chem. C. (**2019**): 30819-30826
University of California Santa Barbara

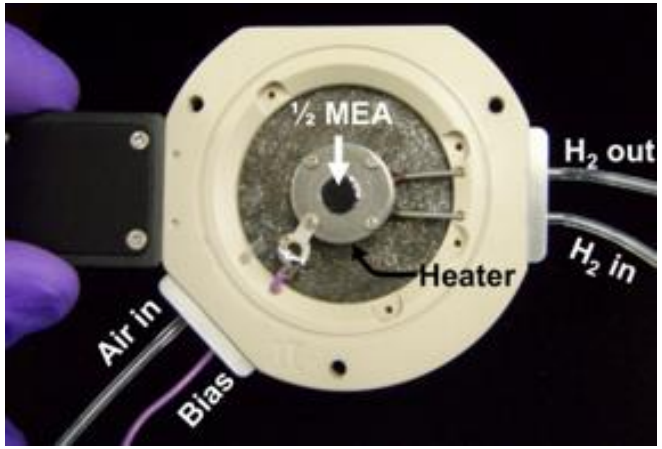
Humidity-Dependent Surface Structure and Hydroxide Conductance of a Model Quaternary Ammonium Anion Exchange Membrane

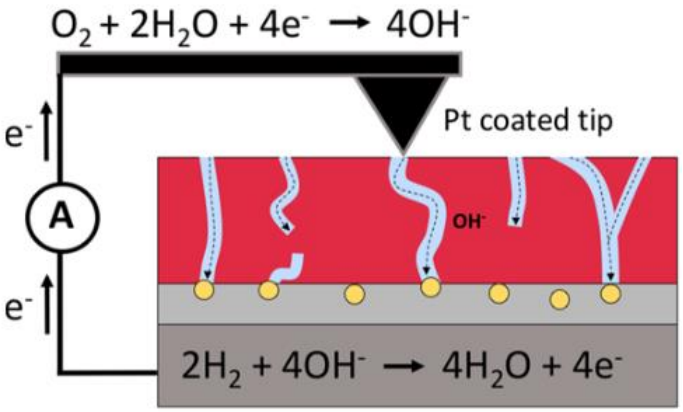
Barnes, A.M. et al. Langmuir (**2019**): 14188-14193
University of California Santa Barbara

Cylinders ∥ to membrane + Higher EFM response
LOWER ion conductivity/connectivity

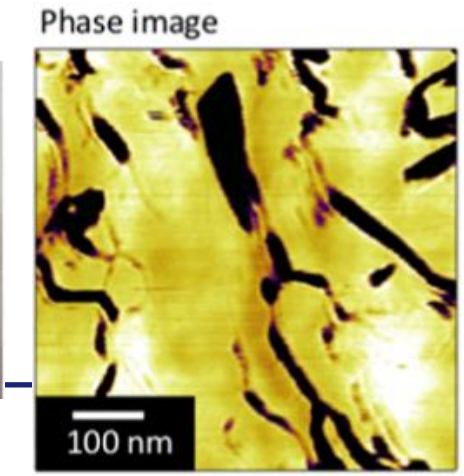


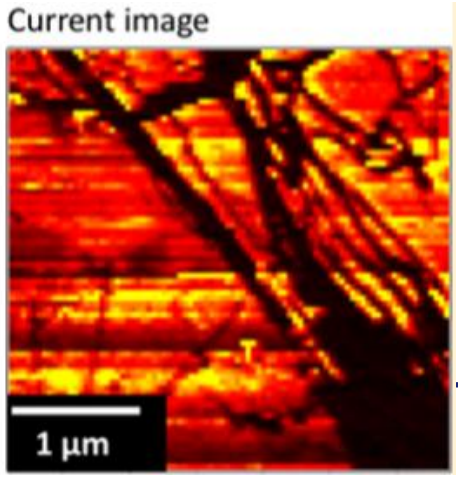
Cylinders ⊥ to membrane + Lower EFM response
HIGHER ion conductivity/connectivity





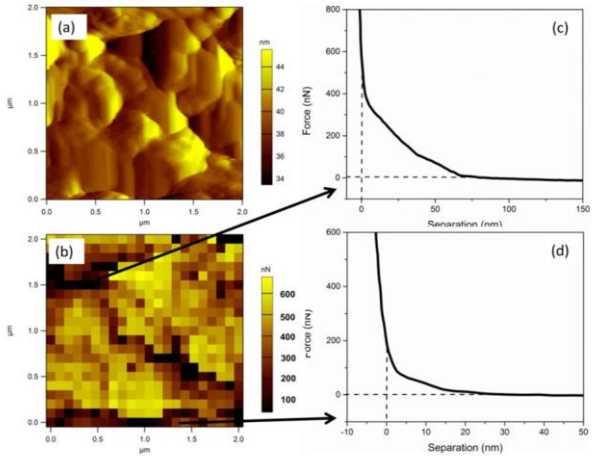
Closed Cell ↕



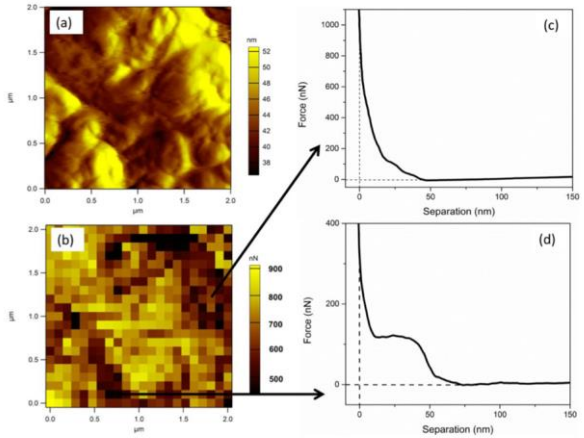


Electrolyte and SEI mechanical properties

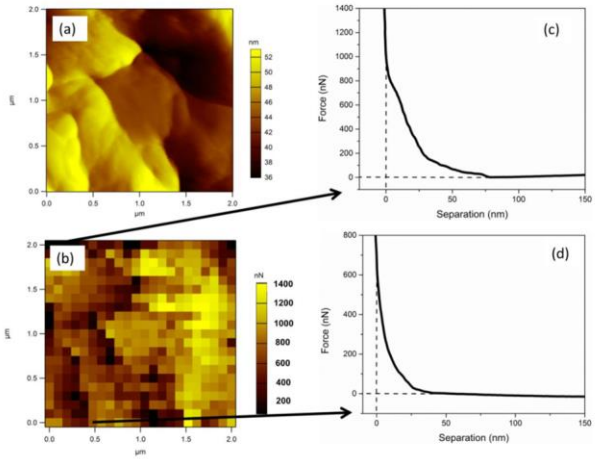
Polymer Electrolyte + 1M LiFSI



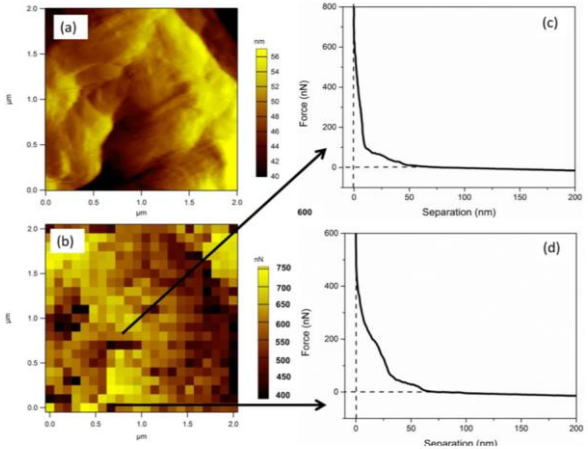
Polymer Electrolyte + 4M LiFSI



Polymer Electrolyte + 1M LiFSI + Acetonitrile



Polymer Electrolyte + 4M LiFSI + Acetonitrile



Ionic Liquid-Organic Solvent Mixture Based Polymer Gel Electrolyte with High Lithium Concentration for Li-Ion Batteries.

A. Lahiri et al. J. Phys. Chem. C 122, 43 (2018): 24788-24800.
Clausthal U of Tech (Germany)

Motivations

Performance of hybrid polymer-gel electrolyte material and SEI formation on a Germanium anode with varying chemical compositions

Measure

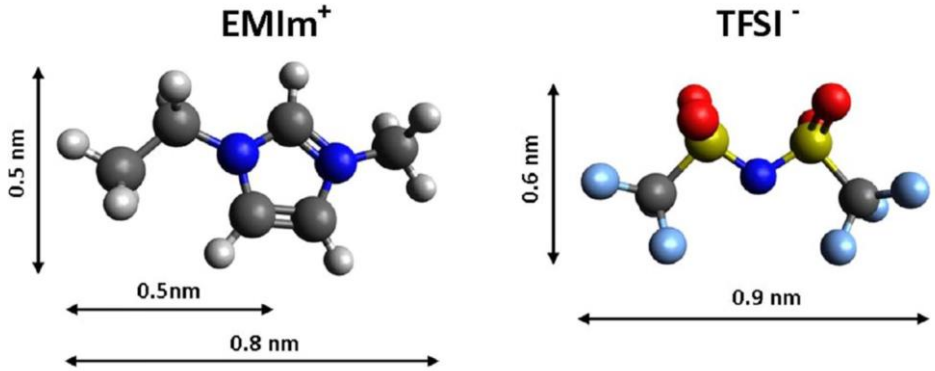
- Surface morphology
- Mechanical stability of the SEI

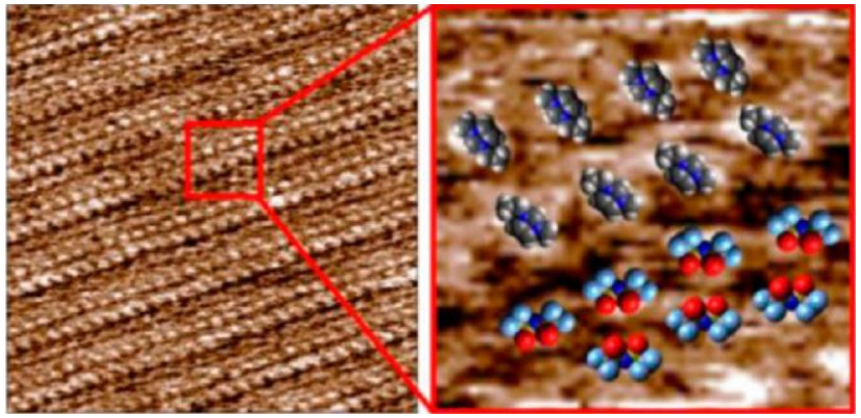
Conclusions

- Higher LiFSI concentrations result in higher Li storage capacity
- Addition of acetonitrile improves mechanical stability of SEI

✔ Stiffness
✔ Modulus
✔ Plasticity
✔ Adhesion

Electrolyte: Hi-Res, *in-situ*, biased Stern Layer



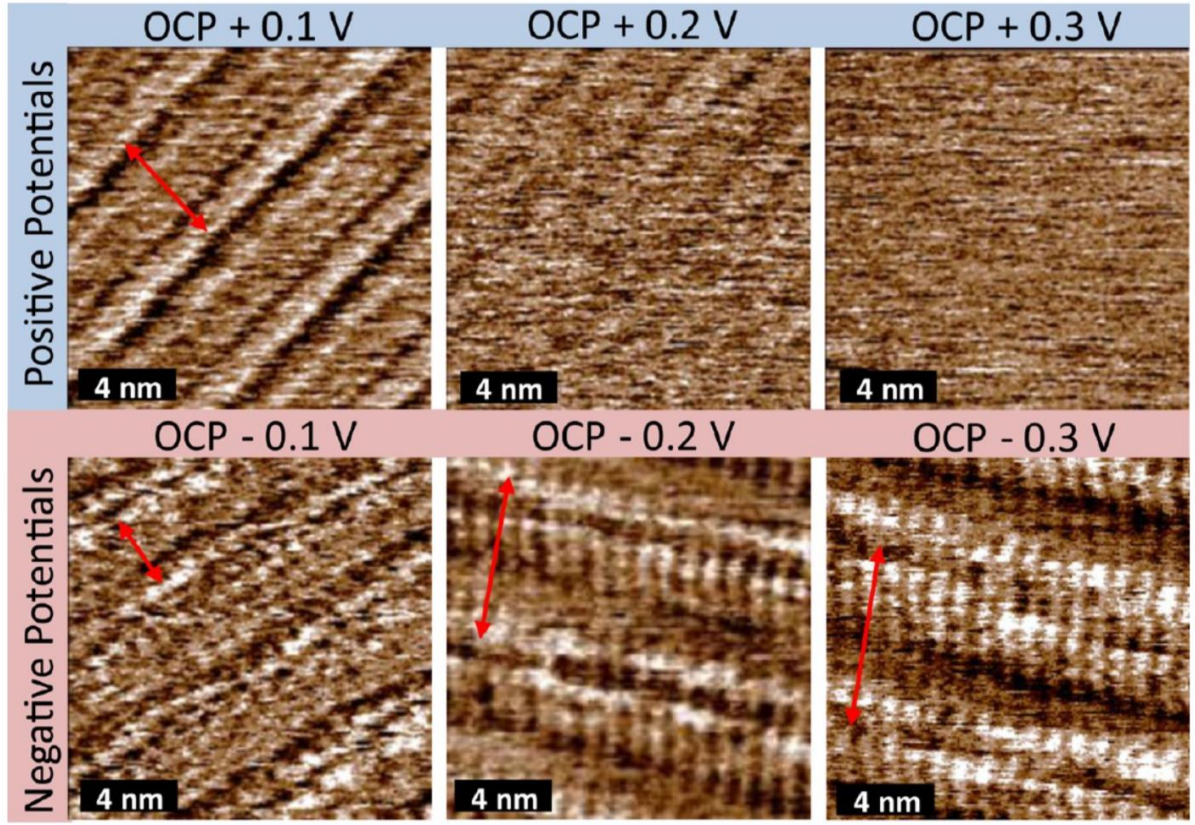


Ionic liquids as electrolyte material

- Large electrochemical windows
- Low volatility
- High thermal stability
- High conductivity

Nanostructure of the ionic liquid–graphite stern layer.

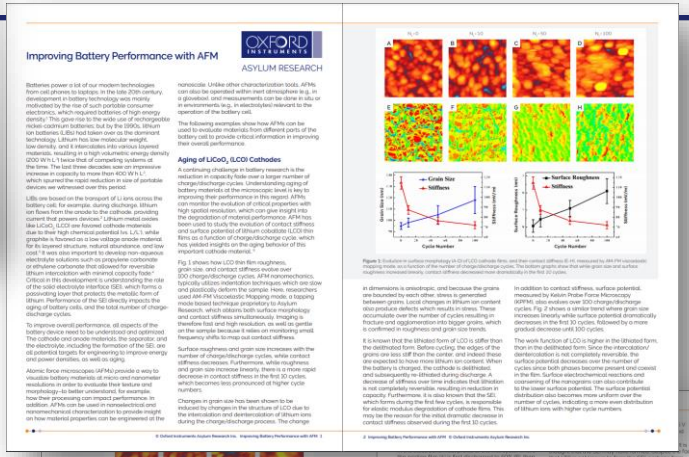
A. Elbourne, S. McDonald, K. Voïchovsky, F. Endres, G.G. Warr, R. Atkin. *ACS nano* 9, 7 (2015): 7608-7620.
U Newcastle and U Sydney (Australia), Clausthal U of Tech (Germany)

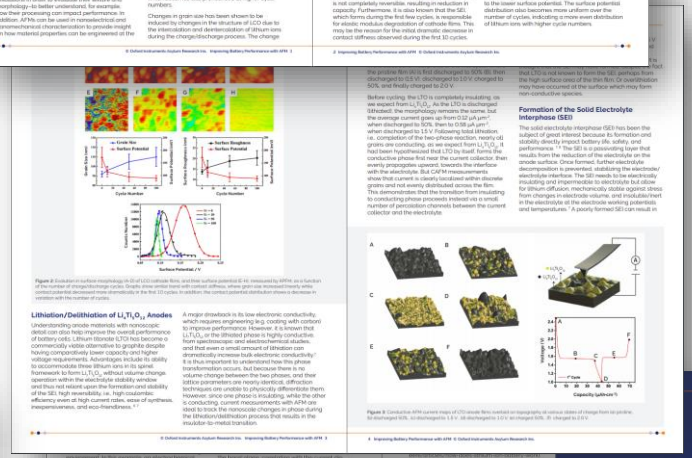


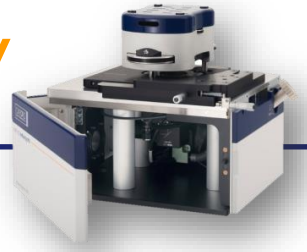
Applying a potential to the graphite surface significantly alters the Stern layer structure

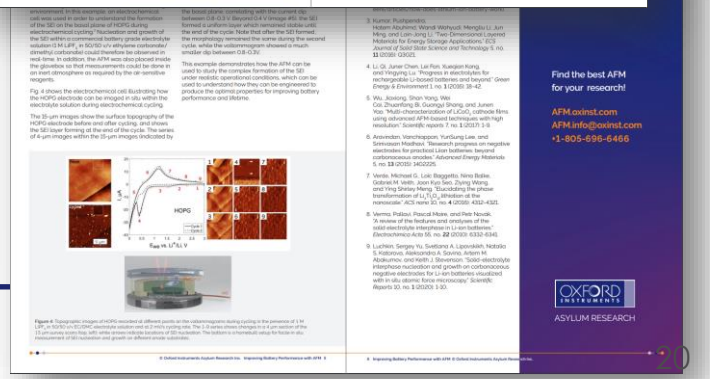
Final Comments

- AFMs are valuable for characterization of batteries, battery materials, and interfacial phenomena
- Experiments can be performed ***in situ*** and ***in operando*** to gain insight into true operational phenomena for batteries
- Voltage control achieved with an integrated electrochemical cell inside the AFM
- The AFM is compatible with glovebox environments for sensitive chemistries
- AFM helps obtain critical nanoscale insights into roughness, morphology, molecular ordering, and therefore charge transfer and battery operation
- **More at AFM.oxinst.com/battery**









Coming Up…

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COVALENT METROLOGY

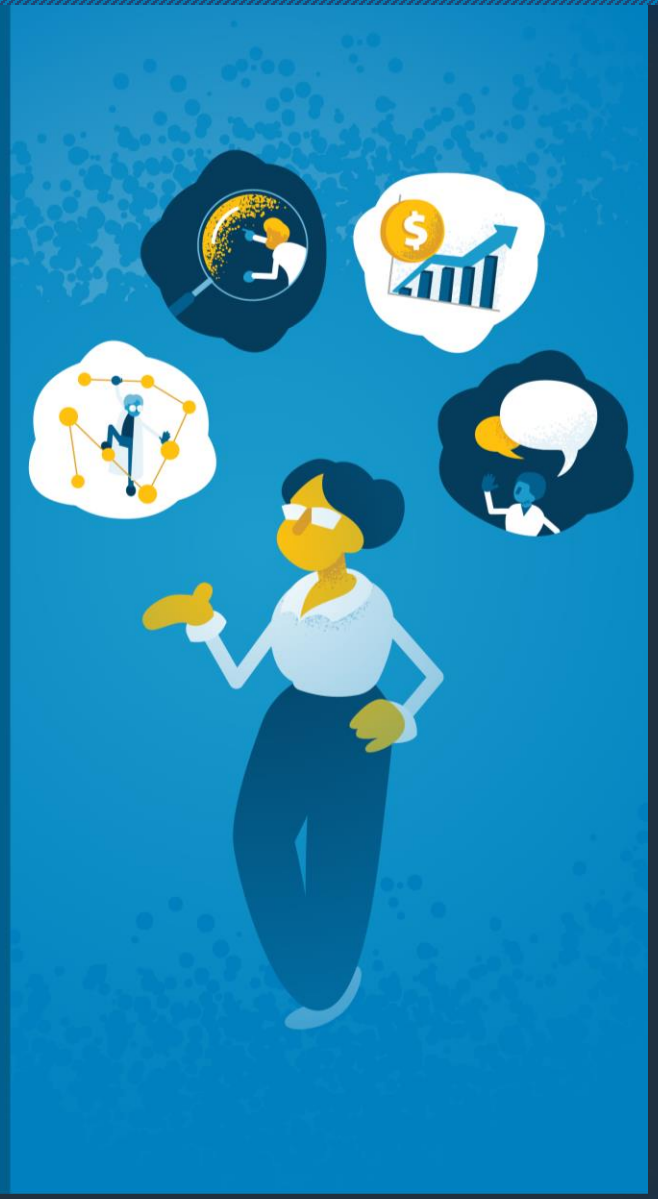
Solving Puzzles Using Metrology: Case Studies in Troubleshooting When (1+1) > 2

Speaker

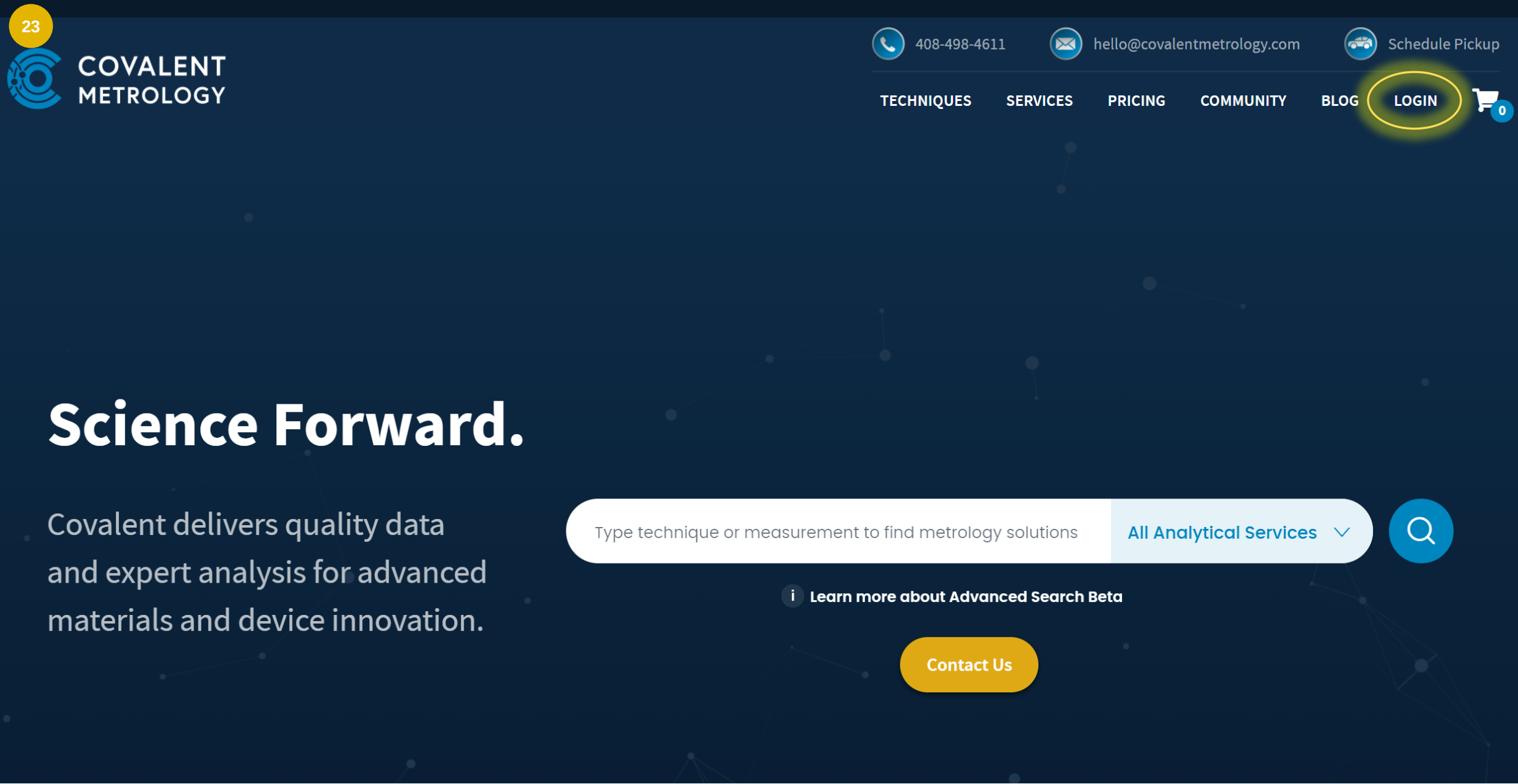
Dr. Chris Moore,
Vice President, Technology

April 22, 2021 | 11am PT

COVALENT ACADEMY
Episode 21



Covalent Community

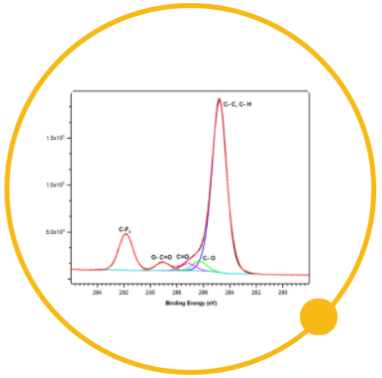


Covalent Community

COVALENT METROLOGY

Access Covalent Portals

Customer Access to Data & Community Content



The DATA PORTAL is used by Customers and Lab Partners for uploading and downloading data. It requires two-factor authentication and advanced password protection. Data Portal users have complete access through their home page on the portal to all Community content, and do not require a separate Community account.

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Community Content Access for All Other Users

The COVALENT COMMUNITY PORTAL requires password entry. It contains webinar and other metrology and characterization-related content that we believe would be useful and educational for the materials science innovation community. It does not provide access to any customer data and should only be used by individuals that are not Covalent customers or lab partners.

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Q & A Session

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Thank you