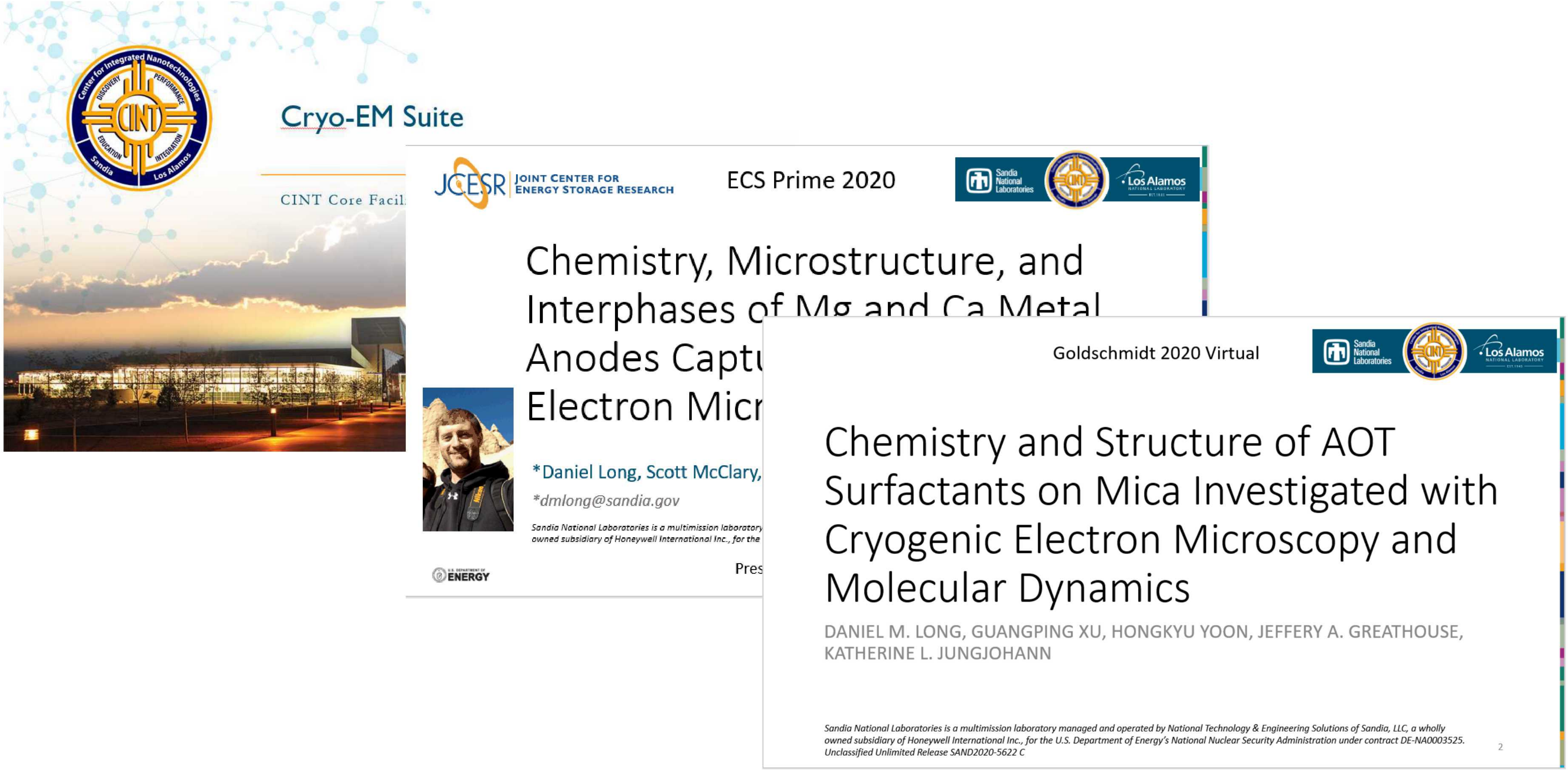
SAND2020-10154C

Cryo-FIB and cryo-TEM at CINT: Imaging solid/liquid interfaces, battery interphases and beam sensitive materials

Daniel Long, *email: dmlong@sandia.gov*

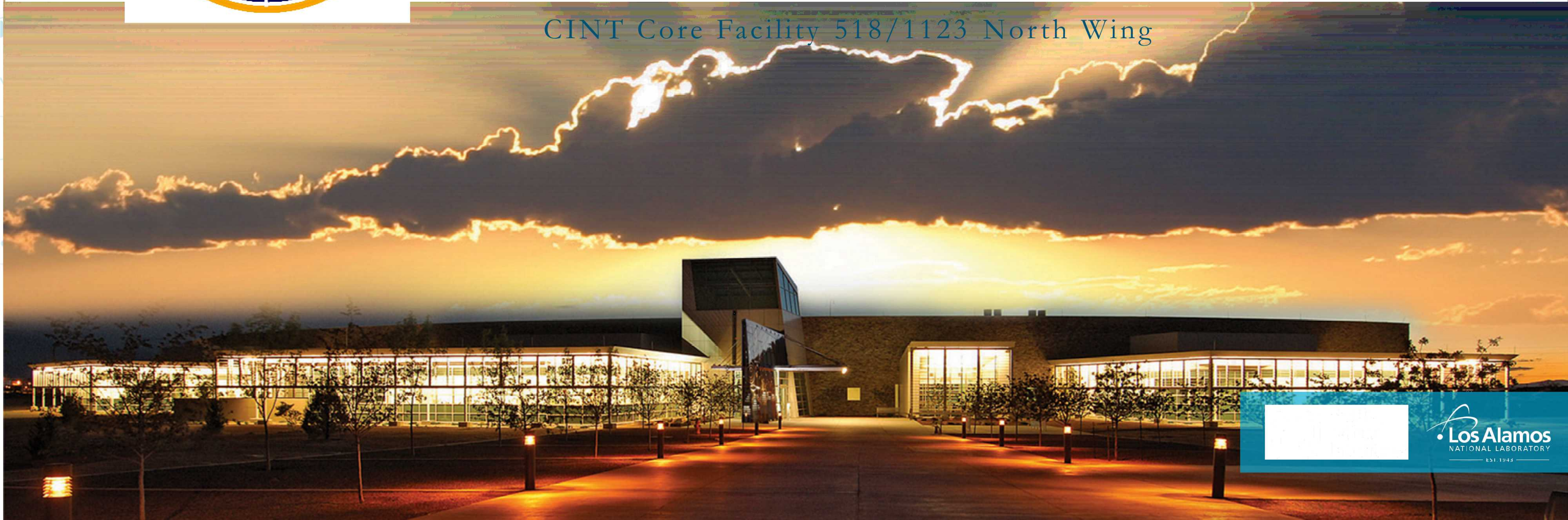
Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

Talk Outline



Cryo-EM Suite

CINT Core Facility 518/1123 North Wing



Cryo-EM Suite for Imaging of Soft Matter and Nanomaterials.

- A microscopy suite dedicated to minimizing electron dose for the imaging of materials and their interfaces in their native hydrated (or solvated state), providing our user community with optimized characterization of sensitive materials across multiple length scales.

Vitrobot

Scios FIB/SEM

Leica Cryo SEM Stage & Transfer Equipment

Talos L120C CryoTEM

- For imaging of biomimetic materials, polymers, nanocomposites and their interfaces, nanoparticles and solution dynamics, and low-Z systems and interfaces.

Cryo-Workflow Solution (Leica)

‘The most complete and robust cryo-workflow available….’

Vitrobot

Rapid, reproducible, vitrification.

EM VCM

Sample transfer station.

EM VCT500

Transfer shuttle ‘Thor’s Hammer’.

EM ACE600

Inert/Cryo Sample Coater & Freeze Fracture

Scios 2 Dual Beam SEM/FIB (Thermo Fisher Scientific)

For surface analysis, analysis of buried interfaces and 3D tomography of soft matter and nanomaterials in their native, hydrated state.

- LoVac system.
- 1.0 nm resolution at 30 kV.
- In-column T3 detector optimized for low-kV, low-energy SE detection.
- Auto Slice & View 4 – serial sectioning and imaging.
- AutoTEM 4 – lift-out sample preparation.
- Dedicated gas chemistries for milling carbon based materials.
- EDAX TEAM High Speed EBSD Camera.

- Cryo-cooled SEM stage and nanomanipulator….

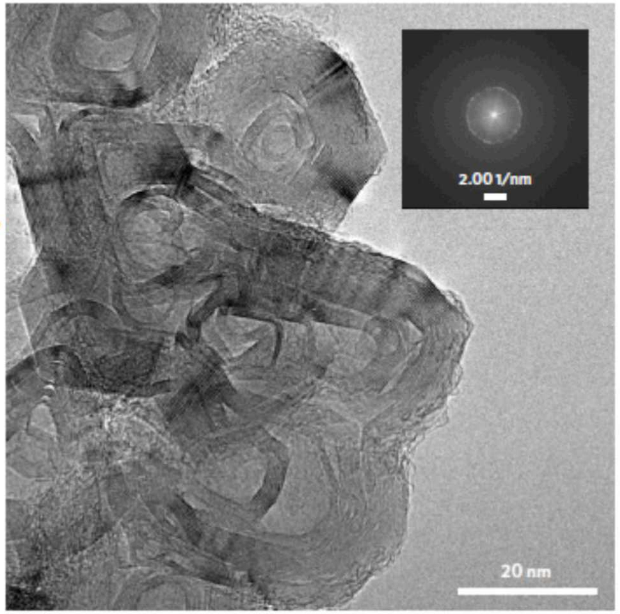
- Also available for room temperature work.

Talos L120C (Thermo Fisher Scientific)

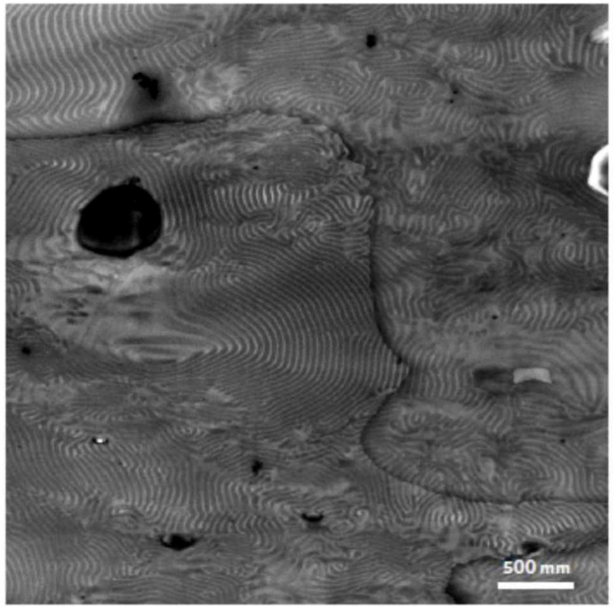
Dedicated low dose, low keV TEM for imaging of beam sensitive materials and analysis of buried sample features and interfaces

- High contrast, high resolution TEM.
- Low dose, low kV imaging.
- 20 – 120 kV *user switchable* accelerating voltage.
- < 0.204 nm resolution.
- Dedicated cryo box – improves imaging stability and user success in cryo experiments.
- Large pole piece gap increases angle for tomography (± 70^o). Acquisition and reconstruction software.
- High speed (40 fps) 4k x 4k CMOS camera optimized for low kV.
- Side entry – accommodates all 'FEI' type holders.

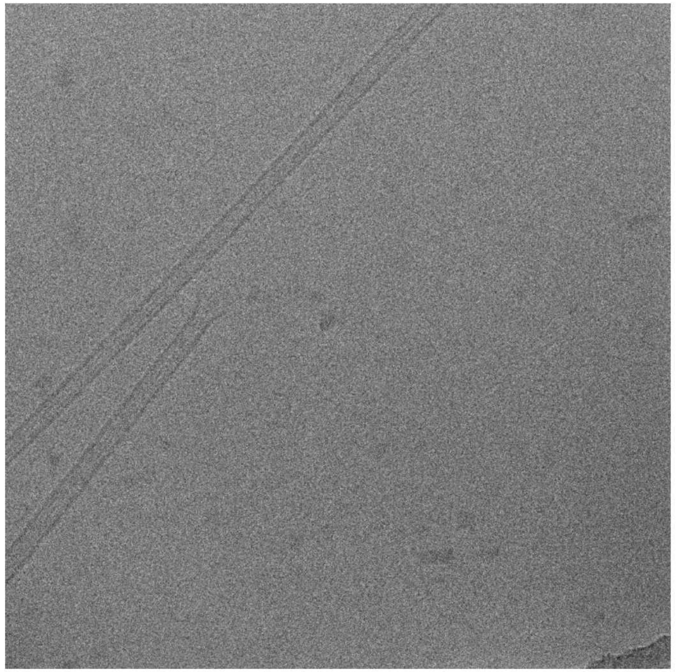
Talos L120C

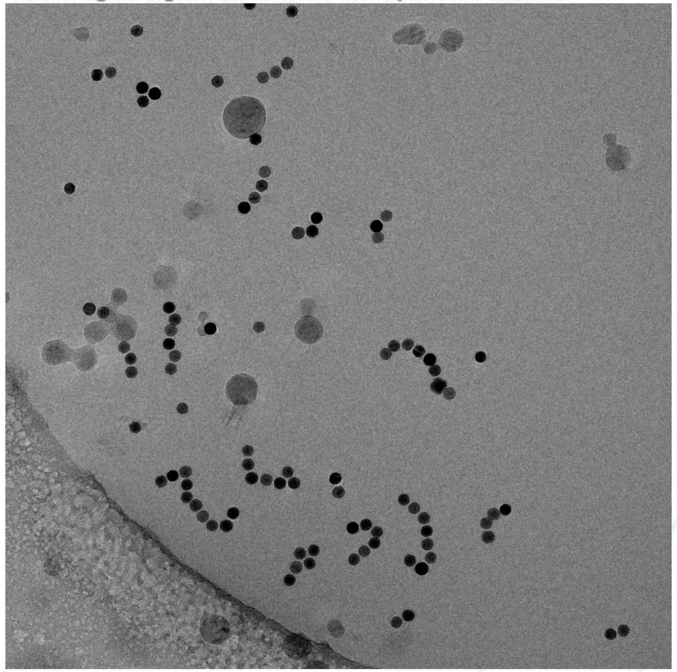


High-resolution TEM. Graphitized carbon and FFT.



TEM at 80kV. Block copolymer. Low-voltage TEM image showing morphology of an annealed polymer film made of the block copolymer Polystyrene-b-Poly(methyl methacrylate) showing a lamellar structure with PS regions (light contrast) and PMMA layers (dark contrast).





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ECS Prime 2020

Chemistry, Microstructure, and Interphases of Mg and Ca Metal Anodes Captured Via Cryogenic Electron Microscopy

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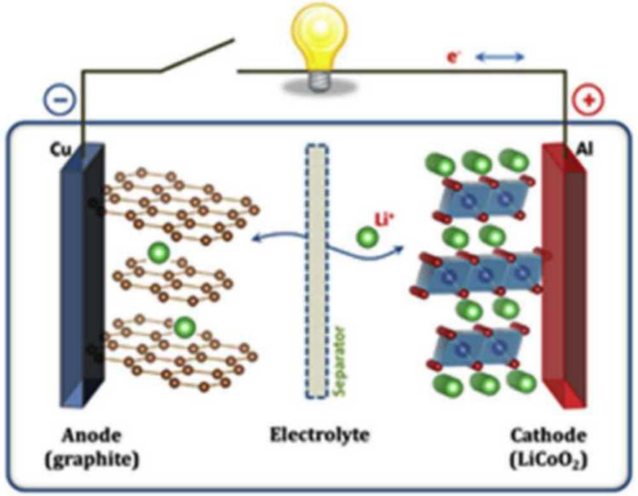
Presentation: A04-0776

Presentation Overview

1. Secondary batteries
    1. Lithium
    2. Multivalents
2. Cryo microscopy for interphases
3. Experiment details
4. Magnesium
    1. RT and cryo
5. Calcium
    1. RT and cryo
6. Summary

Secondary Batteries



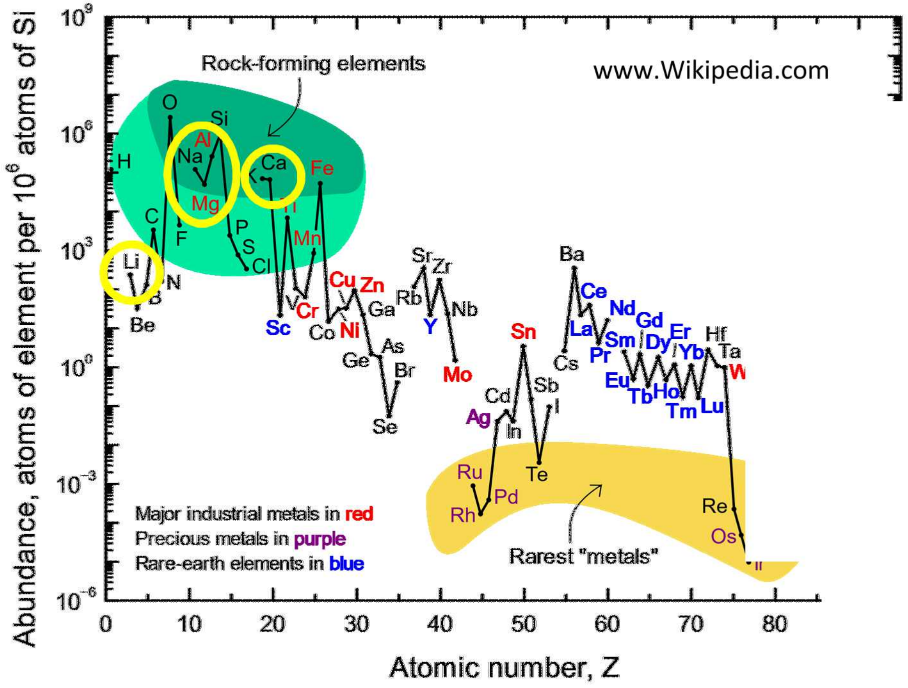
Ponrouch, A., Energy Storage Materials, 20 (2019) 253–262.

www.pngegg.com

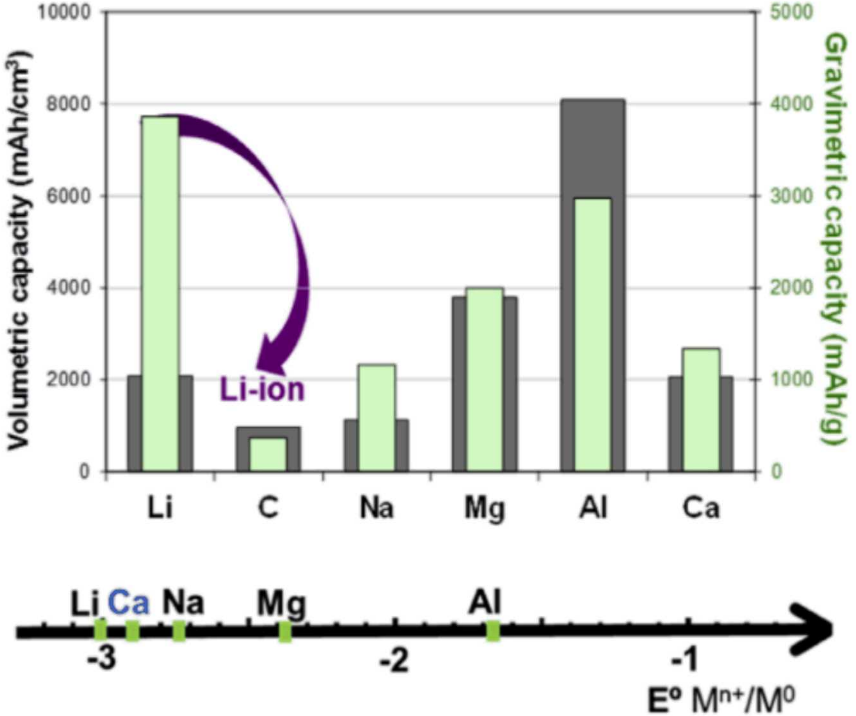
How Far **can we go with lithium?**

The Limits of Lithium

Natural Abundance of Elements



Other Options



Ponrouch, A., Energy Storage Materials, 20 (2019) 253–262.

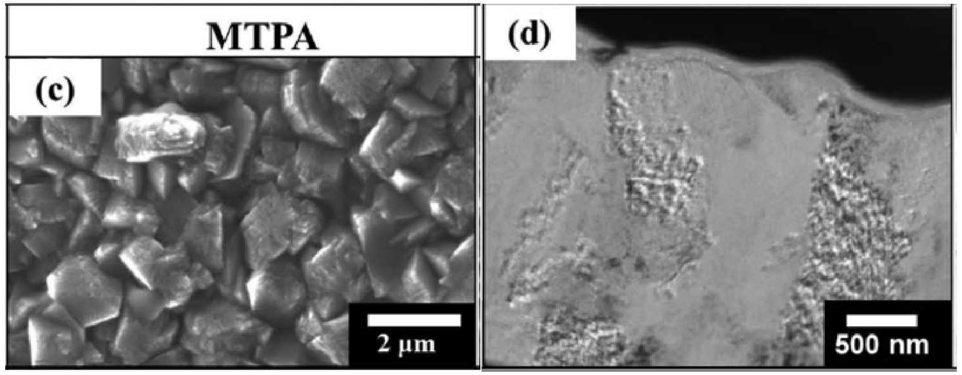
Systems Investigated Here

- ***Metal anode + high voltage cathode = transformative energy storage***
  - Viable electrolyte → stable and ionically conductive SEI
  - Viable electrolyte → dense deposit and high C.E.

Mg System

PhMgCl:$AlCl_3$ in THF deposited on Au

"The microstructure and chemistry of the Mg films, along with their overall cycling efficiency, showed a strong dependence on electrolyte chloride content."

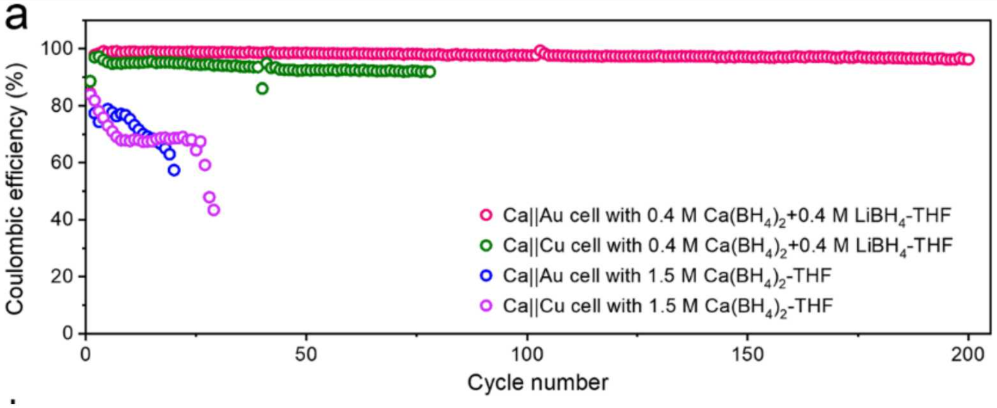


Bachhav et al., J. Electrochem. Soc., 163 (13) D645-D650 (2016).

Ca System

$Ca(BH_4)_2$ in THF, spiked with Na, deposited on Au

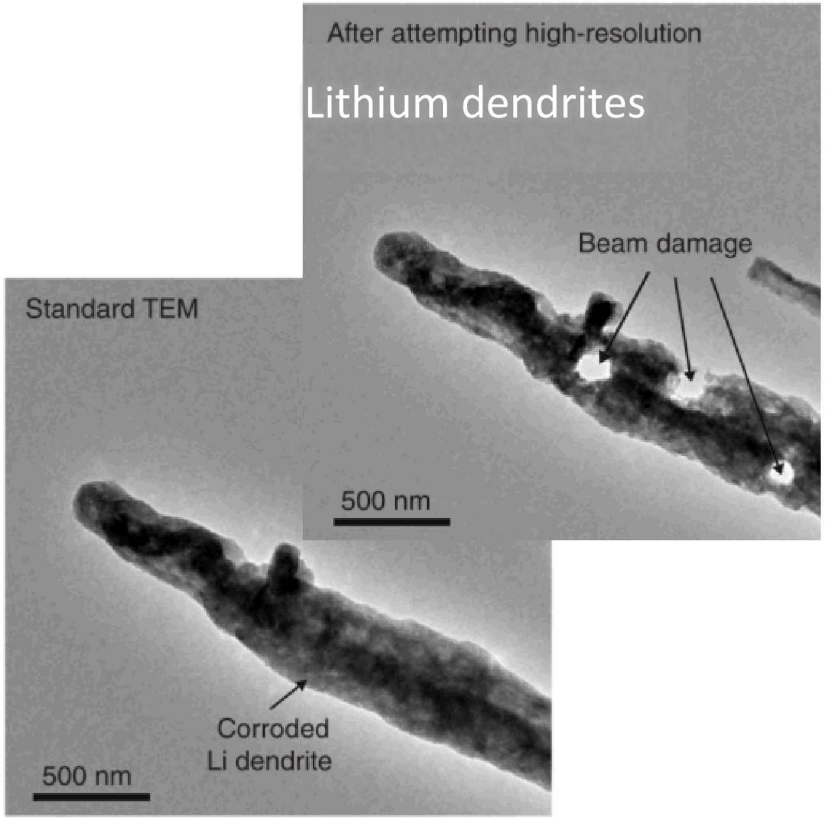
"…Coulombic efficiency of up to 99.1% is achieved for galvanostatic plating/stripping of the calcium-metal anode, accompanied by a very stable long-term cycling performance over 200 cycles at room temperature."



Jie et al., Angew. Chem. Int. Ed. 2020, 59, 12689– 12693

From Room Temperature to Cryogenic TEM

Room Temperature TEM

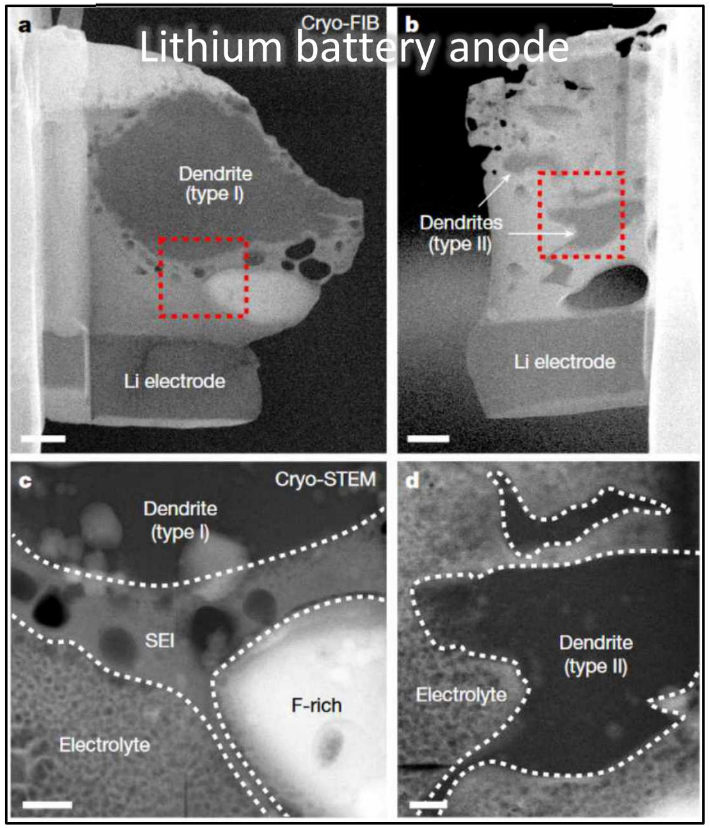


Li et al., Science 358, 506–510 (2017)

Easy to find literature
Available in more labs

Preserves native structures
Less damage
Less mass loss
Less reaction with atmosphere

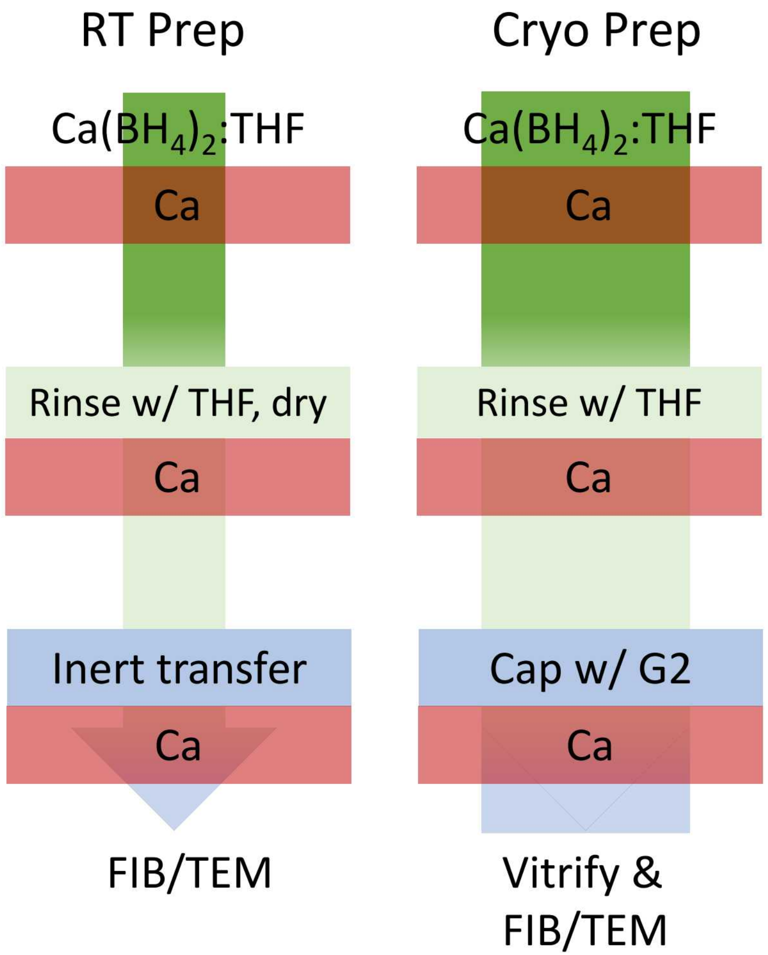
Cryo-STEM



Zachman, Nature, **560**, 345–349(2018)

Experimental approach

Half cells deposited on Au/Si substrate, no cycling

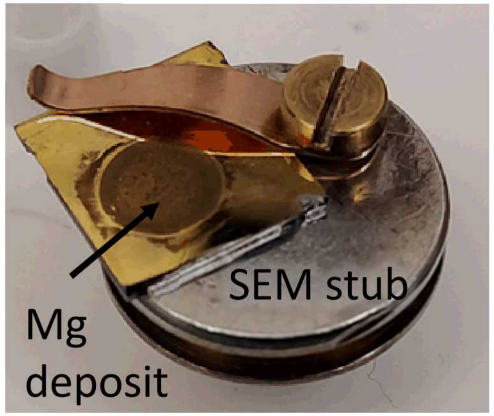


Microscopes	Room Temperature	Cryogenic
SEM/FIB	Helios G4	Scios 2 with Leica cryo-suite
(S)TEM EDS/EELS	JEOL 2100 F FEI Titan @200kV	FEI Titan @ 200kV

Cryo-EM Workflow For MIB/Electrolyte System

1 Vitrification

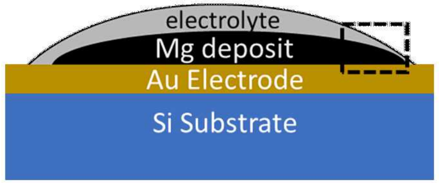
2 Sample Mounting



3 Load, Coat, Transfer

4 Scios FIB/SEM

5 Identify Region of Interest



6 Liftout and Thinning

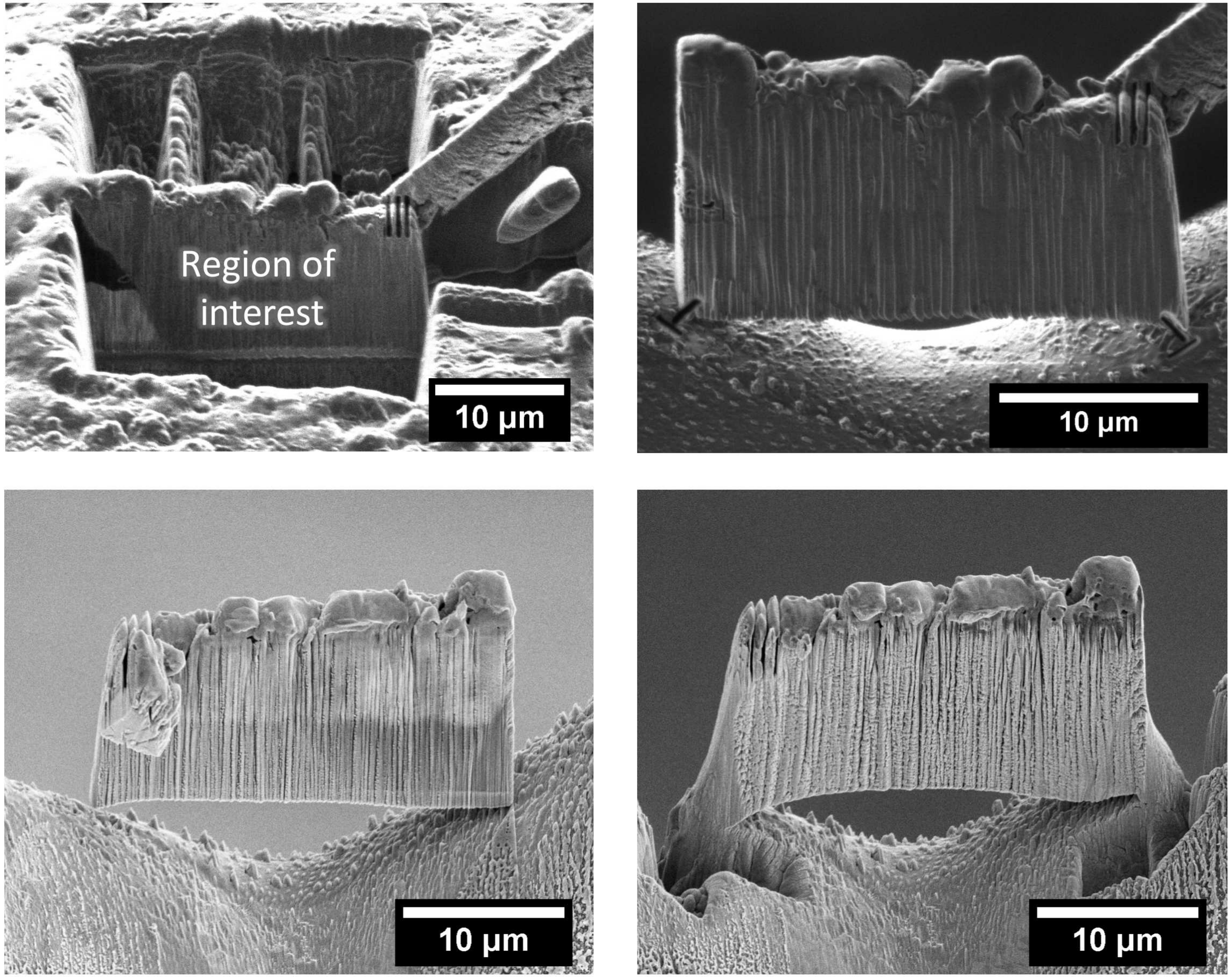
7 Storage & Transport

www.pngegg.com

8 FEI Titan 80-200

analyticalscience.wiley.com

Cryo-FIB Attachment



For more detail:

Zachman et al.,Microsc. Microanal. 22, 1338–1349, 2016.

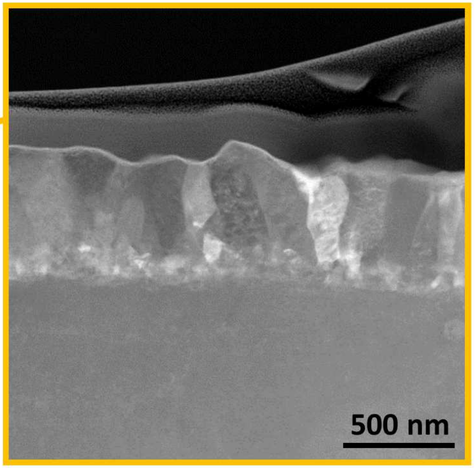
Schreiber et al., Ultramicroscopy 194 (2018) 89–99.

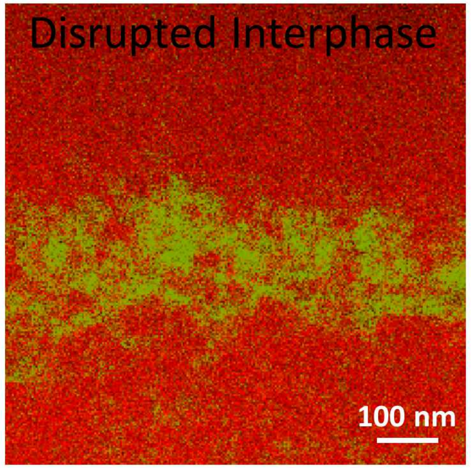
Magnesium Deposits @ RT

Coulombic Efficiency, %

Electrolyte	Structure	Control 1 cycle	50 cycles continuous
APC	faceted	99.7 ± 0.3	100.2 ± 0.3
	dense	99.4 ± 0.2	99.4 ± 0.1
	porous	99.4 ± 0.3	99.0 ± 0.5

Renucleation





EDS Red = Mg Green = Mg + C, O, Cl, Al

Zavadil et al., manuscript in preparation

Known: Surface Cl^- enables Mg deposition

Passivation during hold, low C.E. b/c reforming interphase

RT TEM/FIB prep does not trap this film in its native state

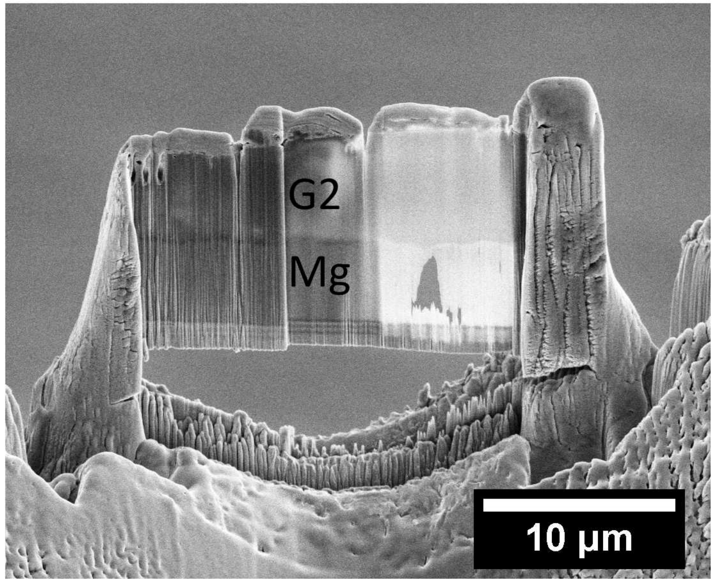
Goal: Nature of this temporary interphase

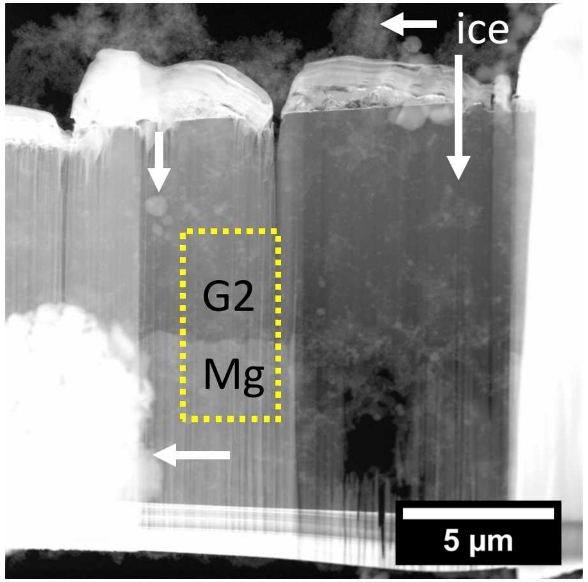
Mg-Cl(adsorbed) vs $MgCl_2$, Mg + (H, C, O)

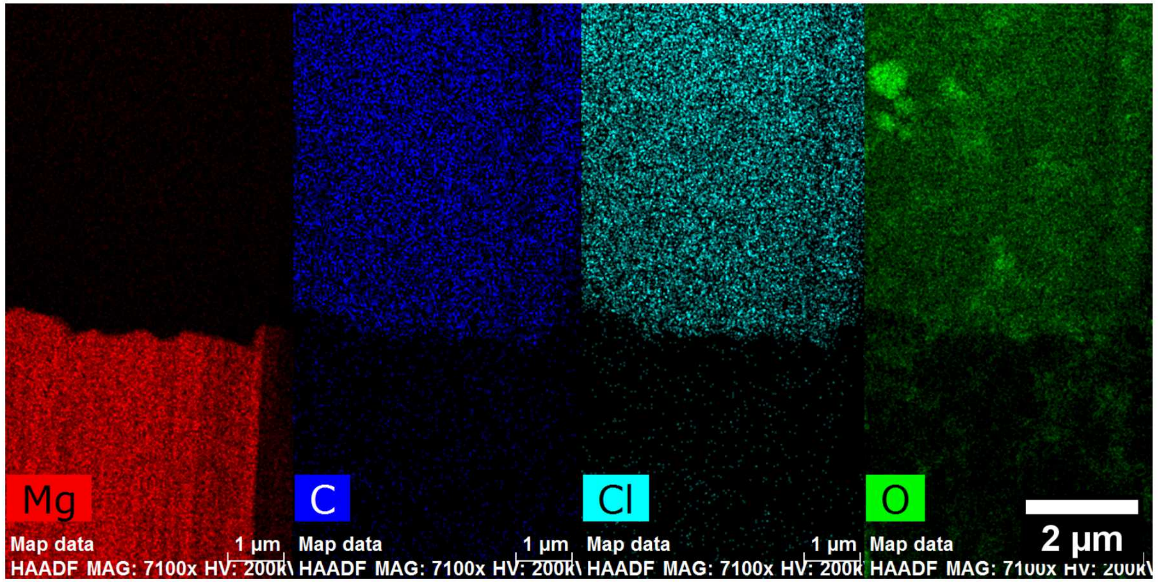
To cryo → stabilizes structure, discern adsorbed vs crystalline structure

Magnesium Deposits at Cryo

- Mg deposit
  - No cycling
  - Large grains
- Held 2 hours
- Capped with G2







- ✓ Amorphous electrolyte
- ✓ Solid/Liquid interface remains intact
- ❑ Minimal ice contamination

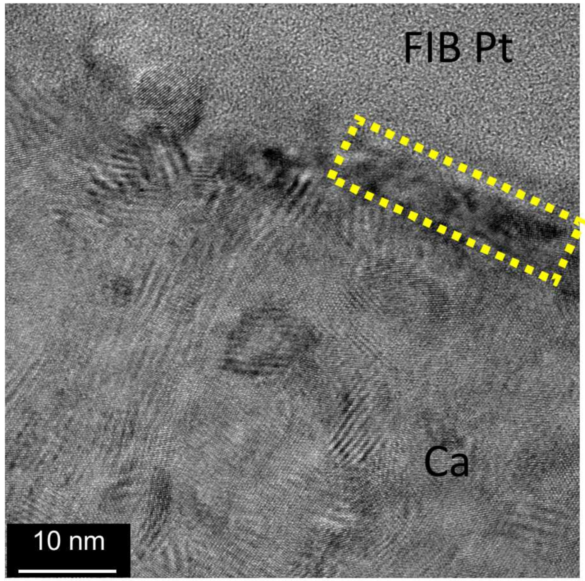
- ✓ Mg, C, Cl, O
- ✓ Cl in G2, gentle rinse
- ❑ Ice contamination causes high O signal everywhere
- ❑ No strong Cl signal at Mg/G2 interface

Old electrolyte did not achieve C.E. similar to previous work.
Purchased new, exp. soon

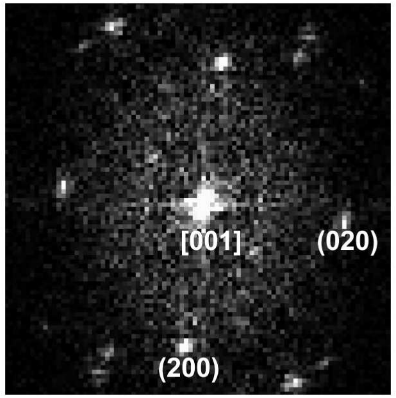
Calcium Deposits @RT

- Ca deposit
  - No cycling
  - Large grains
- Inert transfer

HR-TEM

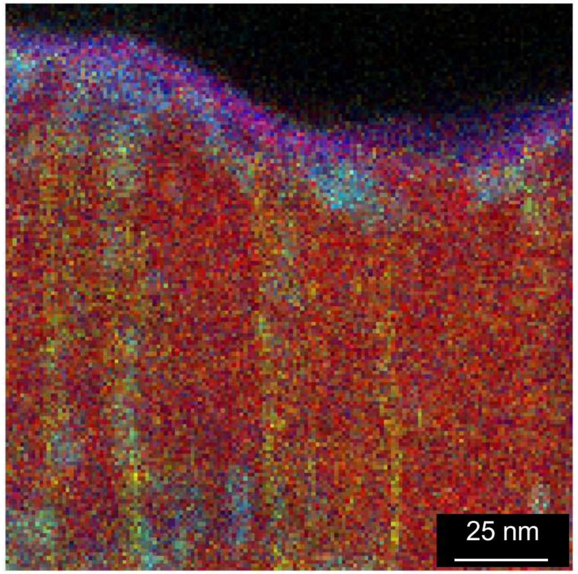


FFT of interface



CaO reflections

EDS



Red= Ca,Na, Yellow=Au, Cyan= Ca, O, F, Na, Magenta=Ca,O

Nanostructured interphase with structural and compositional heterogeneity

Open questions about CaO

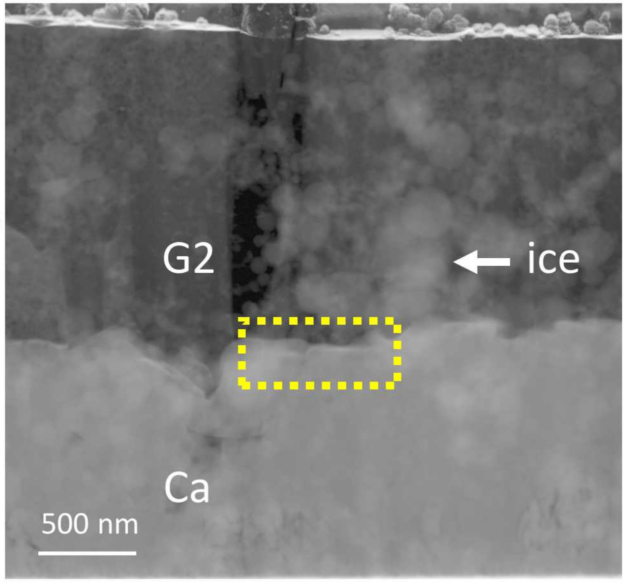
To cryo → Could CaO have formed during transfer or storage?
Is it from trace oxygen in electrolyte/processing?

*no evidence of CaH_2 from EELS, not shown

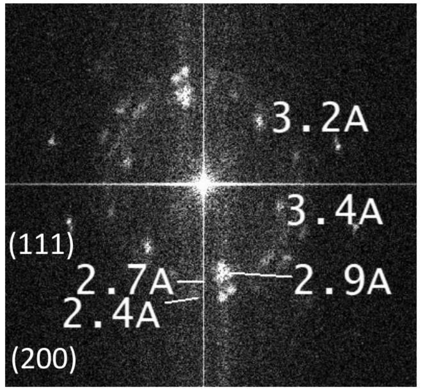
Calcium Deposits @ Cryo

- Ca deposit
  - No cycling
  - Large grains
- Capped with G2

Low Mag STEM

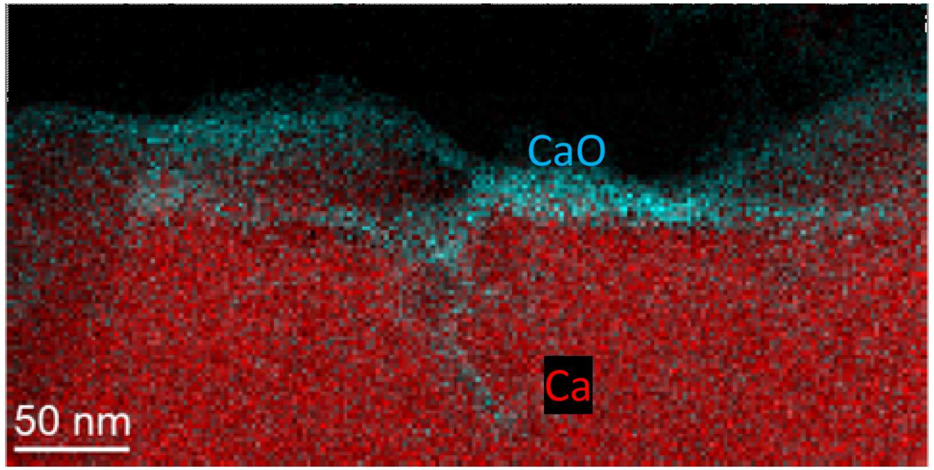


FFT of interface



CaO reflections

EDS



Red = Ca+Na, Cyan = Ca, O

*no evidence of a CaH_2 film in diffraction or EELS(not shown)

Nanoscale interphase composed of CaO

Oxide forms with Ca deposition, from impurities or THF decomposition

CaO is electrically insulating, partially ionically conductive

- critical thickness <10 nm allow Ca-ion conduction

Scott McClary, A04-0845 The Role of Sodium Electrolyte Impurities in Governing Interphase Formation and Impacting Calcium Anode Electrochemical Performance

U.S. DEPARTMENT OF ENERGY

Summary and Outlook

Summary

- Cryo-FIB locks in the native interphase
  - Will yield critical information about interphase and expedite battery development
  - Slow freezing retains solid/electrolyte interface
  - Lower kV eliminates electrolyte/SEI damage
  - Extensive redeposition required for transport
- Cl^- plays a critical role in stable Mg deposition
- CaO phase forms on Ca/electrolyte interface
  - parasitic vs. protective
- No evidence of CaH_2 found

And now for something completely different!

Acknowledgements

Funding provided by the Joint Center for Energy Storage Research (JCSER) and Sandia National Laboratories

JCESR Joint Center for Energy Storage Research

Center for Integrated Nanotechnologies CINT

Los Alamos National Laboratory EST. 1943

SNL MIB Research team

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Kevin Zavadil
Katherine Jungjohann
Paul Kotula (STEM, EDS)

Chemistry and Structure of AOT Surfactants on Mica Investigated with Cryogenic Electron Microscopy and Molecular Dynamics

DANIEL M. LONG, GUANGPING XU, HONGKYU YOON, JEFFERY A. GREATHOUSE, KATHERINE L. JUNGJOHANN

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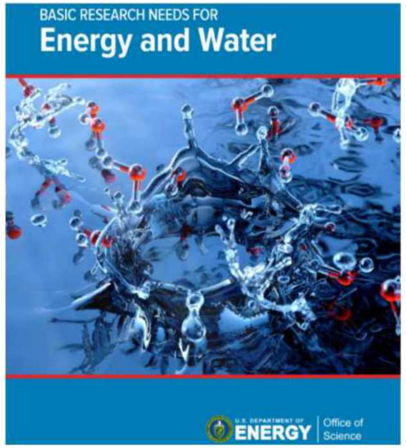
Surfactant-Mineral Interactions

Motivation

Understand the behavior of complex fluids in the subsurface.

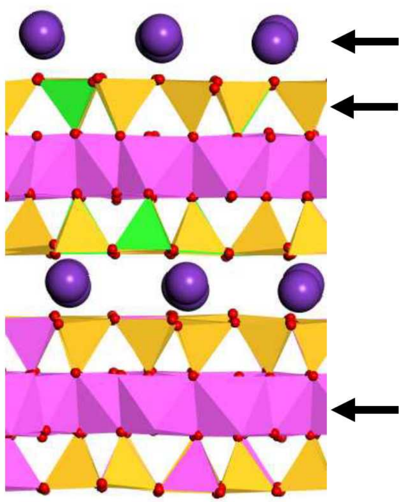
Energy extraction, water treatment (produced water, energy generation)

Workshop on Basic Research Needs for Energy and Water, 2017



Hypothesis

The partitioning of complex fluids with surfaces depends greatly on chemical and physical properties of fluids and surfaces.

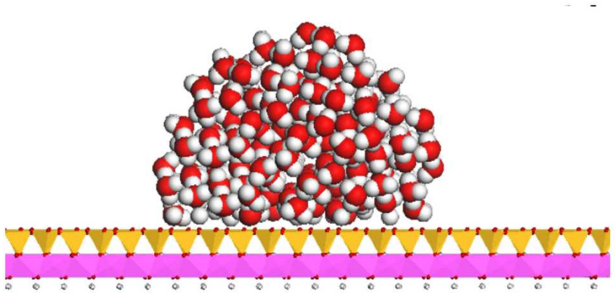


Project goal

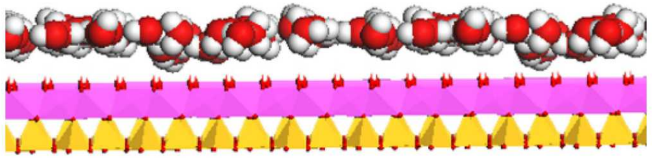
Quantify at the molecular scale the competing roles of fluid-fluid and fluid-surface interactions on fluid partitioning at a well-characterized mineral surface (**muscovite mica**).

Background on Surfactants

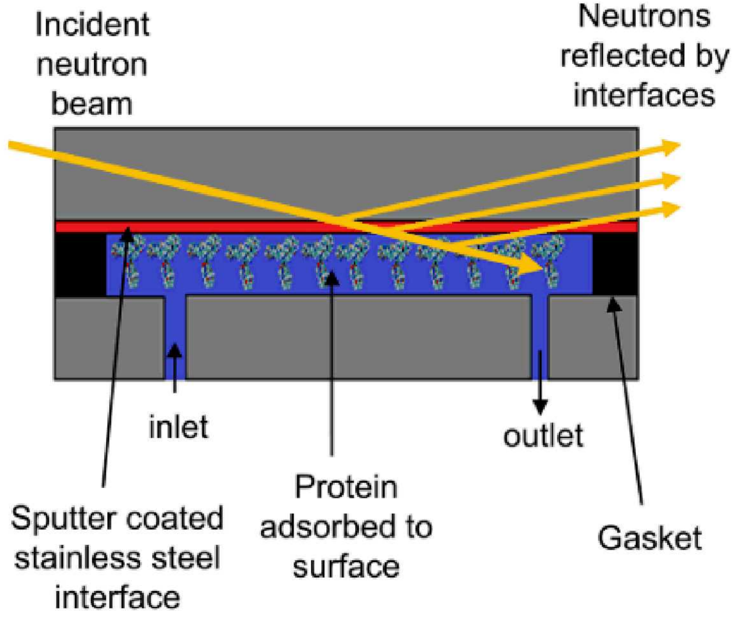
The partitioning of complex fluids at mineral interfaces depends greatly on chemical and physical properties of fluids and surfaces, particularly since intermolecular forces govern complex fluid interactions at interfaces.



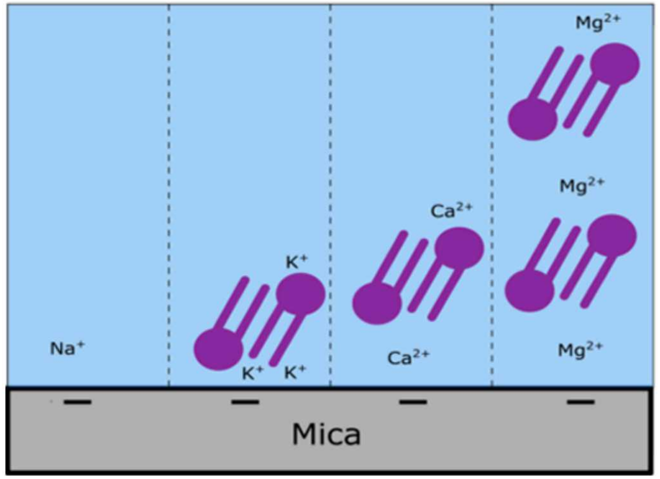
non-wetting



wetting



Kalonia, et al.,Mol. Pharmaceutics 2018, 15, 1319−1331



Recent neutron reflectometry data suggest that an anionic surfactant (AOT) can bind to a negatively charged mica surface through cation bridging.

Allen et al., *Langmuir* **2017**
Allen et al., *Langmuir* **2019**

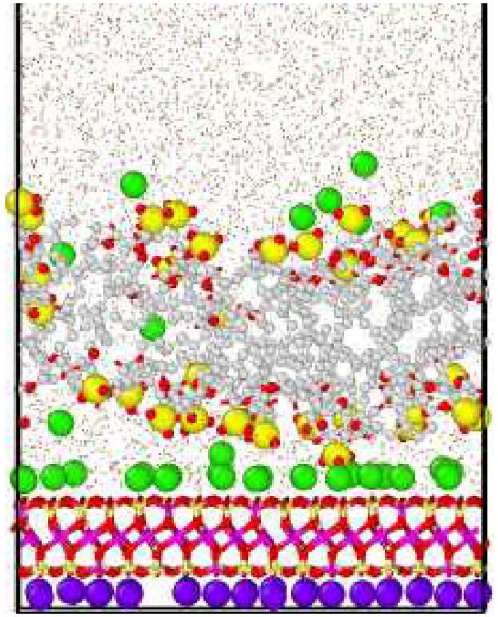
Research Plan

Experimental measurements + molecular modeling
→ Trends in wetting properties of a complex fluids on mineral surfaces.

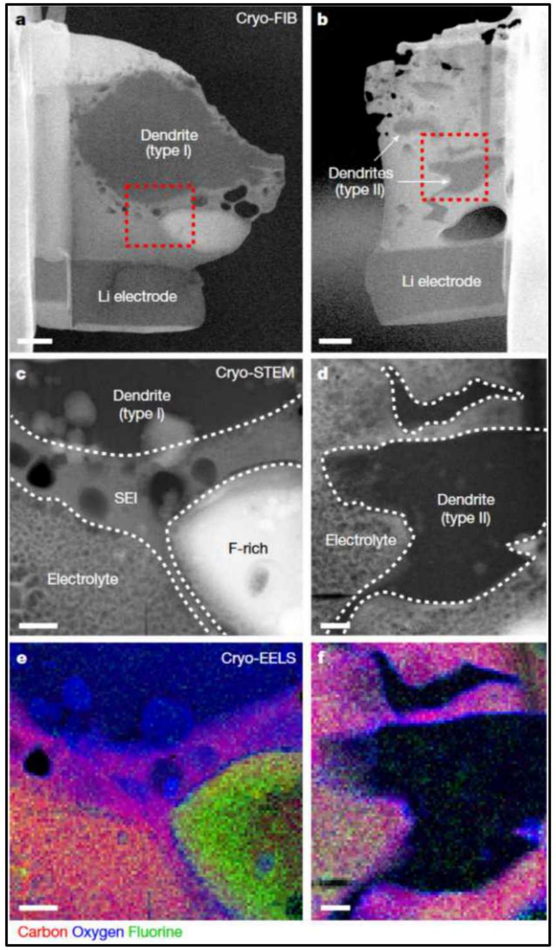
Complex fluid components: **water, aqueous cations**, nonpolar liquids, and **polar surfactant molecules**.

Control the distribution of complex fluids by changing fluid chemistry, and to control rheological properties of complex fluids.

Muscovite mica + NaAOT/H_2O



MD simulation

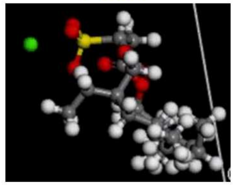


Cryo electron microscopy

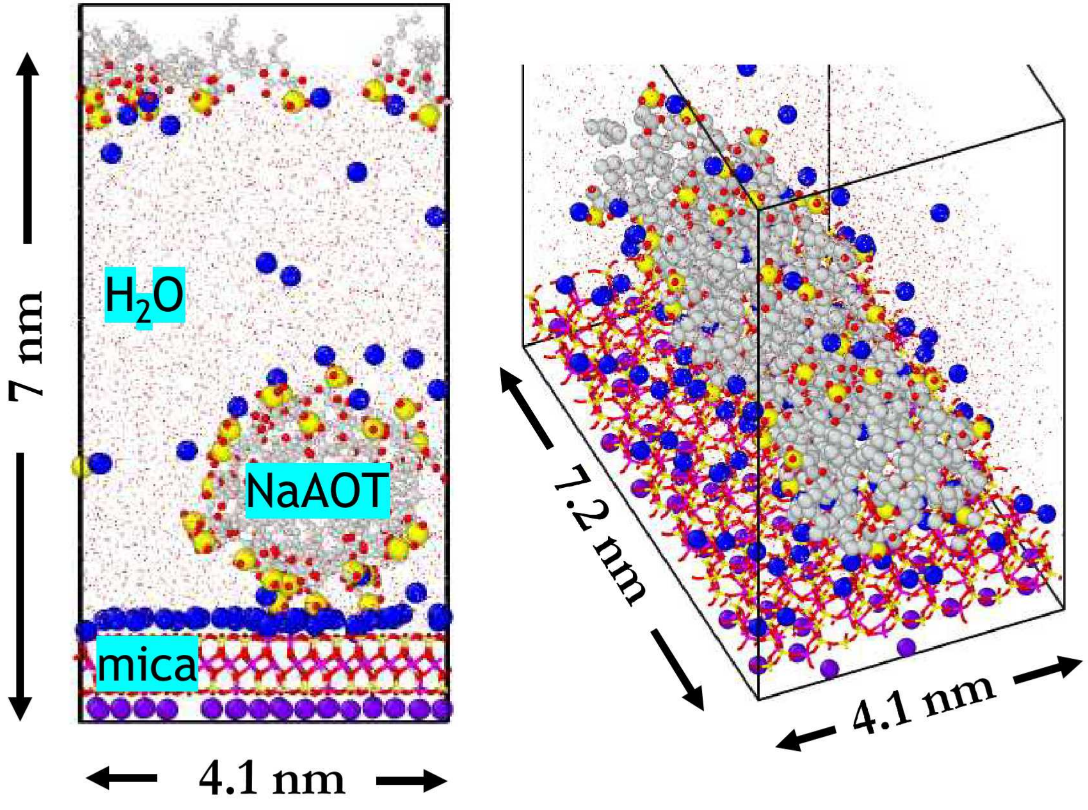
Zachman, Nature, **560**, 345–349(2018)

Effect of AOT Surface Loading on Interfacial Structure

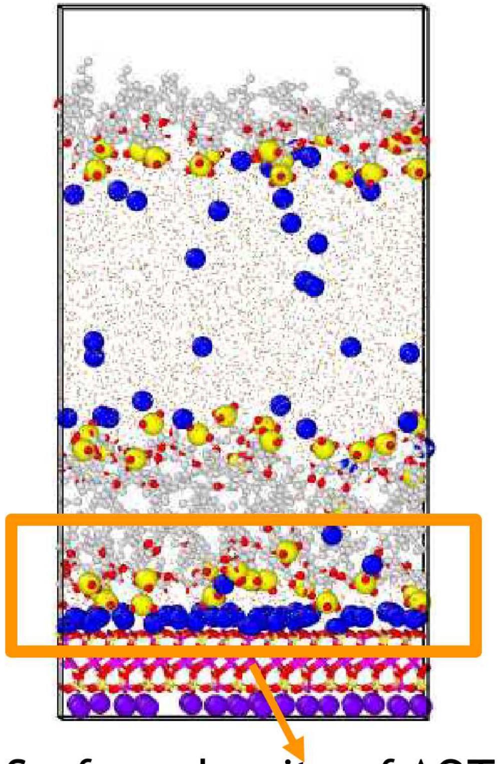
AOT



32 Na-AOT
1 AOT per binding site
Adsorbed micelle (cylinder)

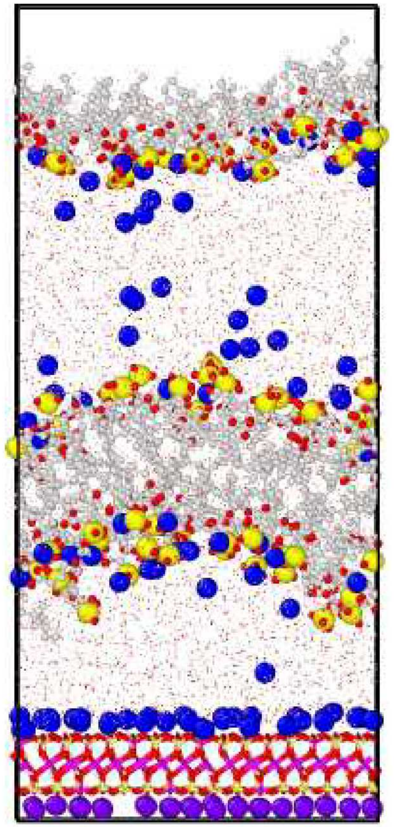


48 Na-AOT
1.5 AOT per binding site
Adsorbed bilayer



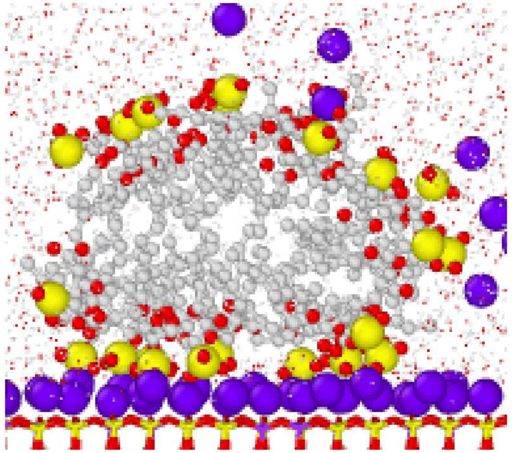
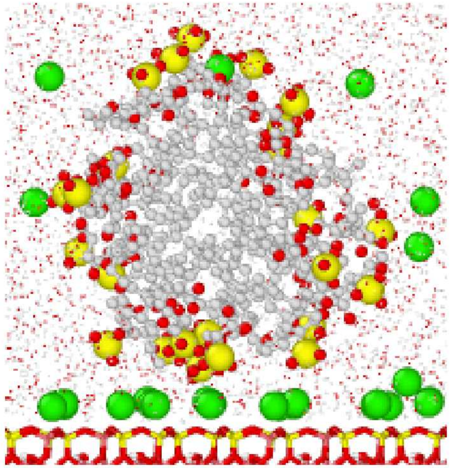
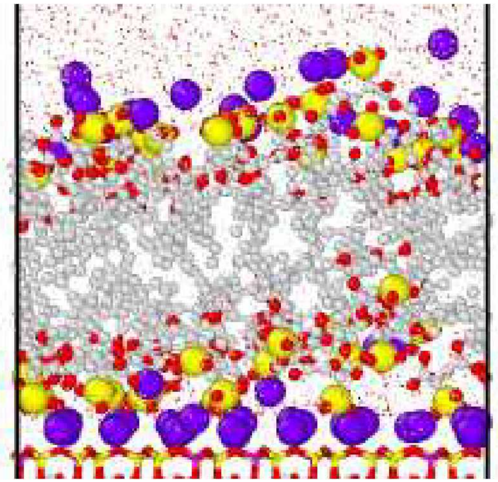
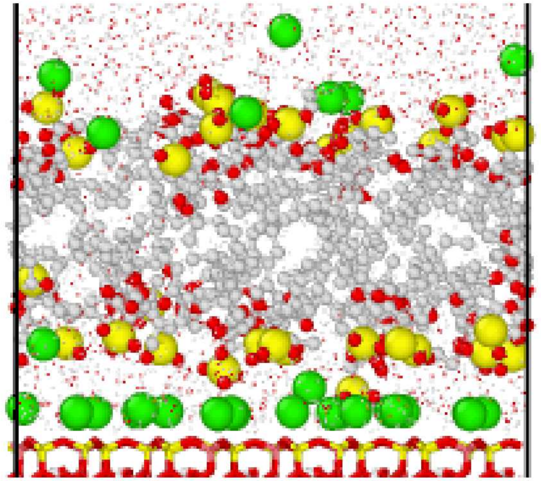
Surface density of AOT
0.9 AOT/nm^2 (Mg^{2+})
1.3 AOT/nm^2 (K^+)

64 Na-AOT
2 AOT per binding site
Desorbed bilayer



Mica surface charge
2.2 e/nm^2

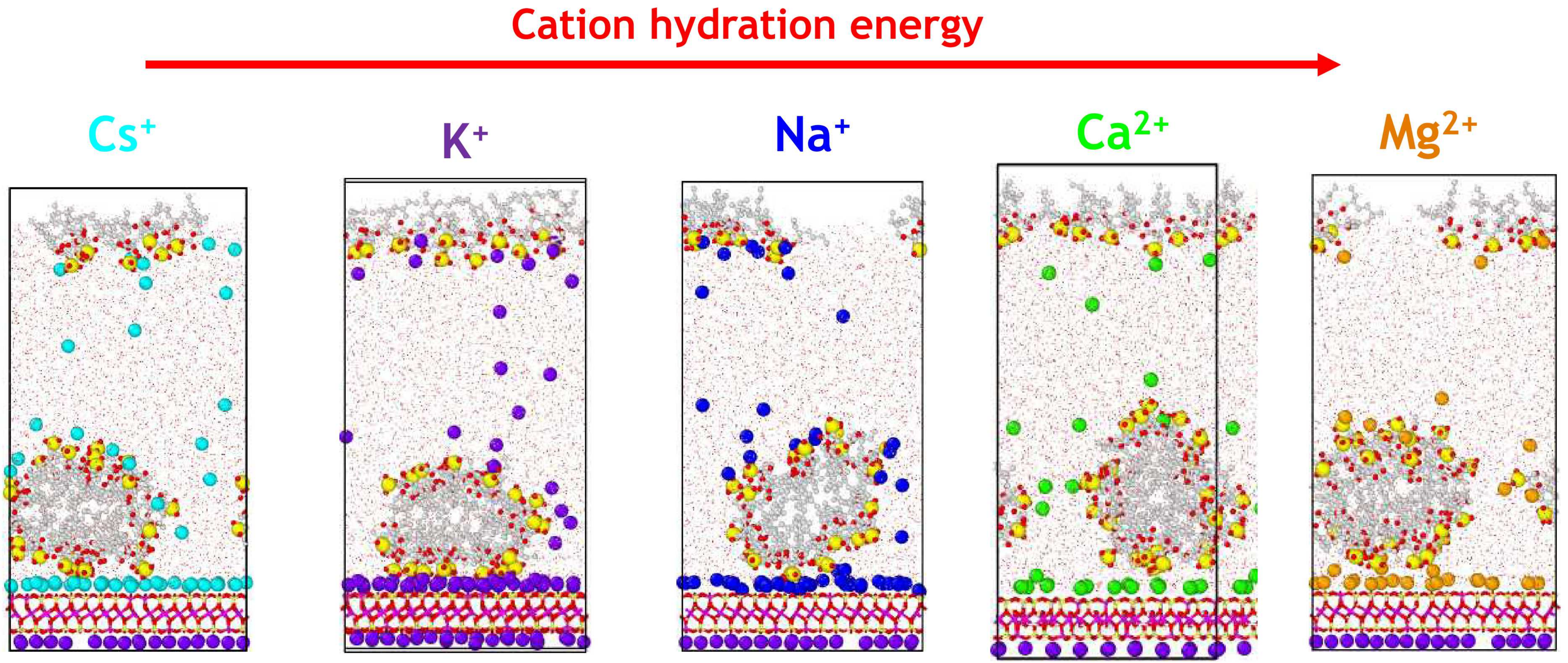
Surfactant Structure – Layer Thickness

	K^+		Ca^{2+}	
Micelle	2.3 nm		3.0 nm	
Bilayer	2.0 nm		2.3 nm	

Ideal thickness of a single AOT chain 1.8 nm

Bilayer thickness from neutron reflectometry 2.2 nm

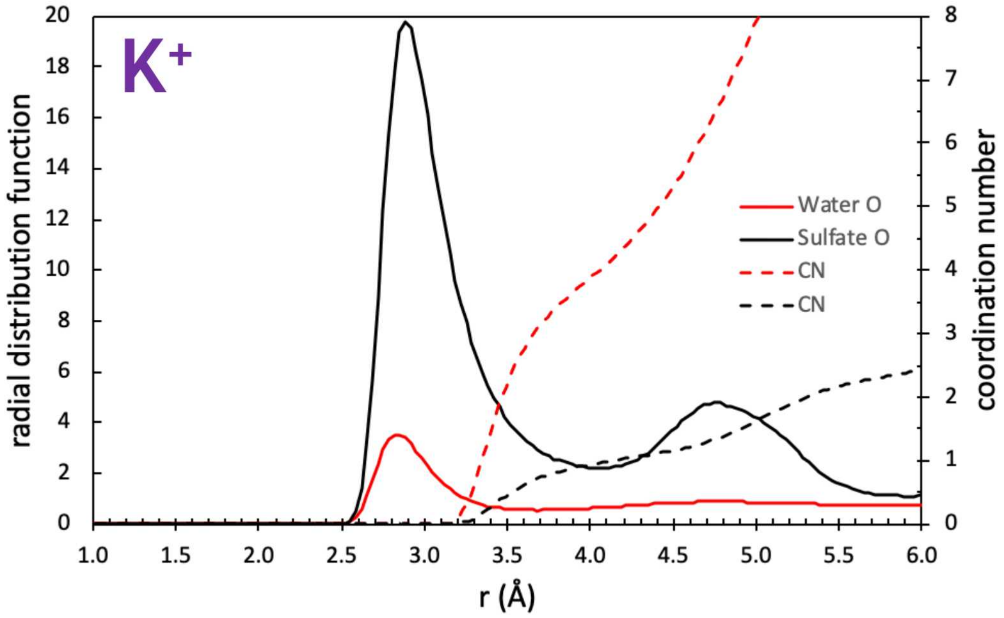
Cation Dependence on Interfacial Structure

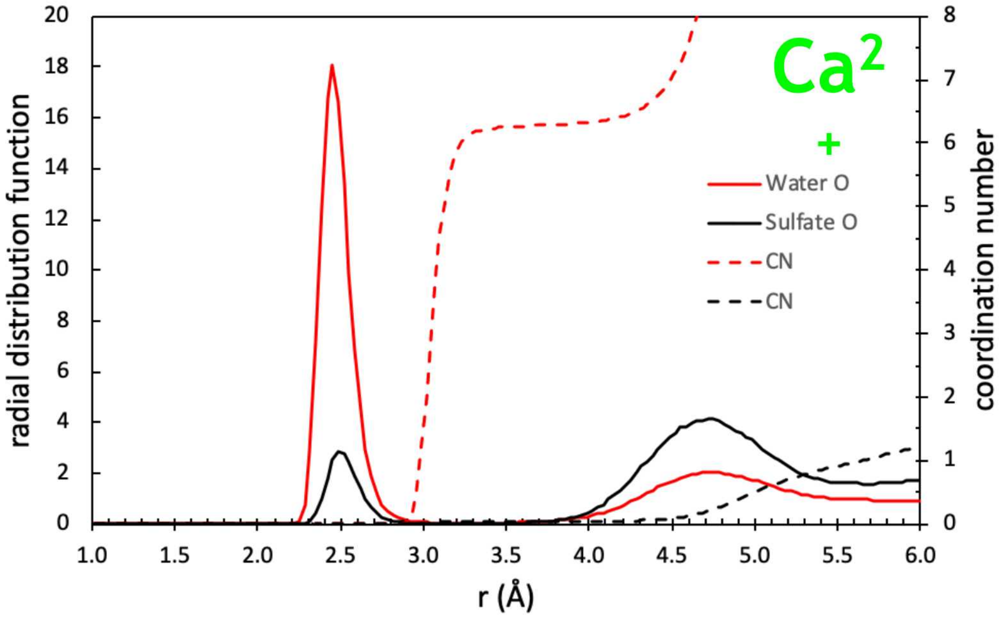


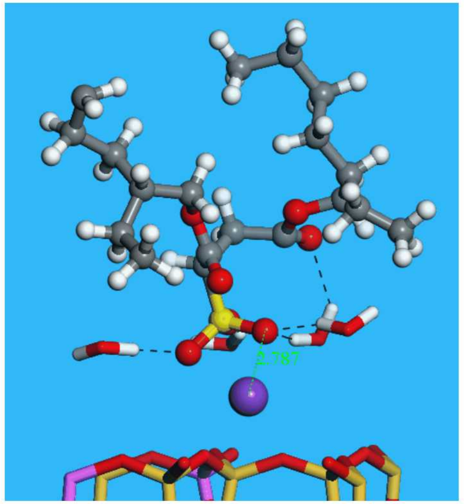
Equilibrium structures with 32 AOT after ~100 ns of MD simulation

Surfactant Binding Mechanisms

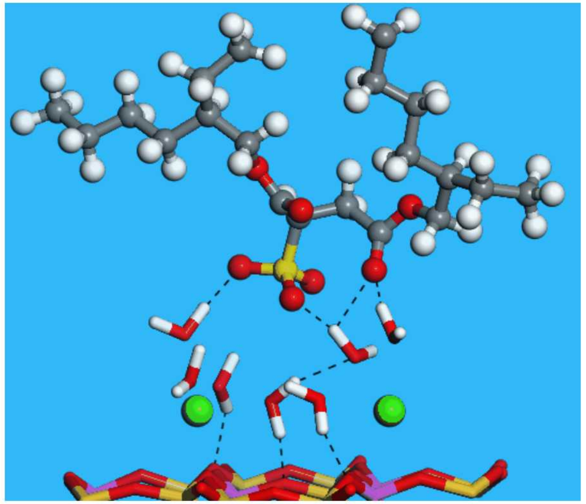
Cation-oxygen distances from radial distribution functions (RDFs)







- Weakly hydrating cations (K^+) bind sulfate O atoms directly (inner-sphere coordination).
- Strongly hydrating cations (Ca^{2+}) retain water hydration shells, which in turn form H-bonds with sulfate O atoms (outer-sphere coordination).



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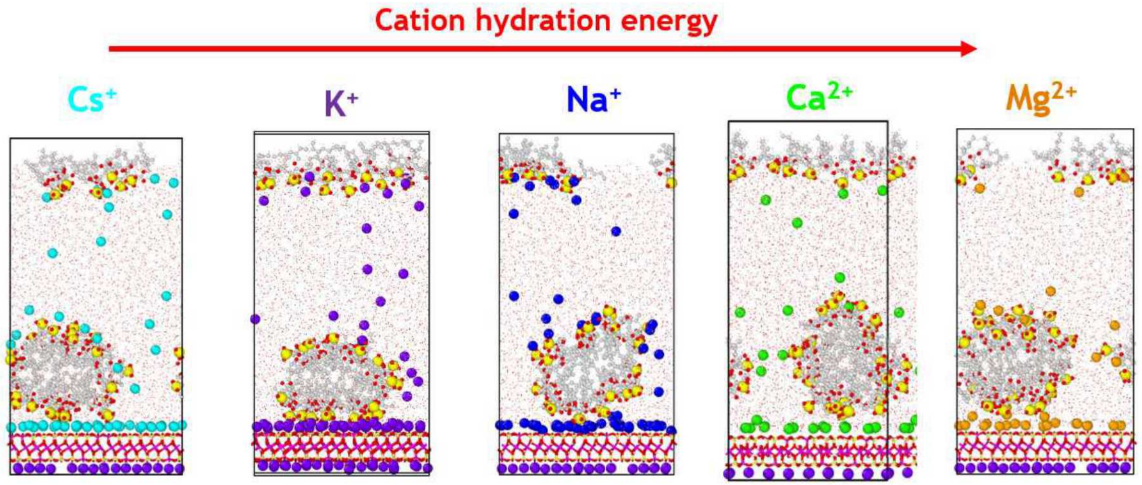
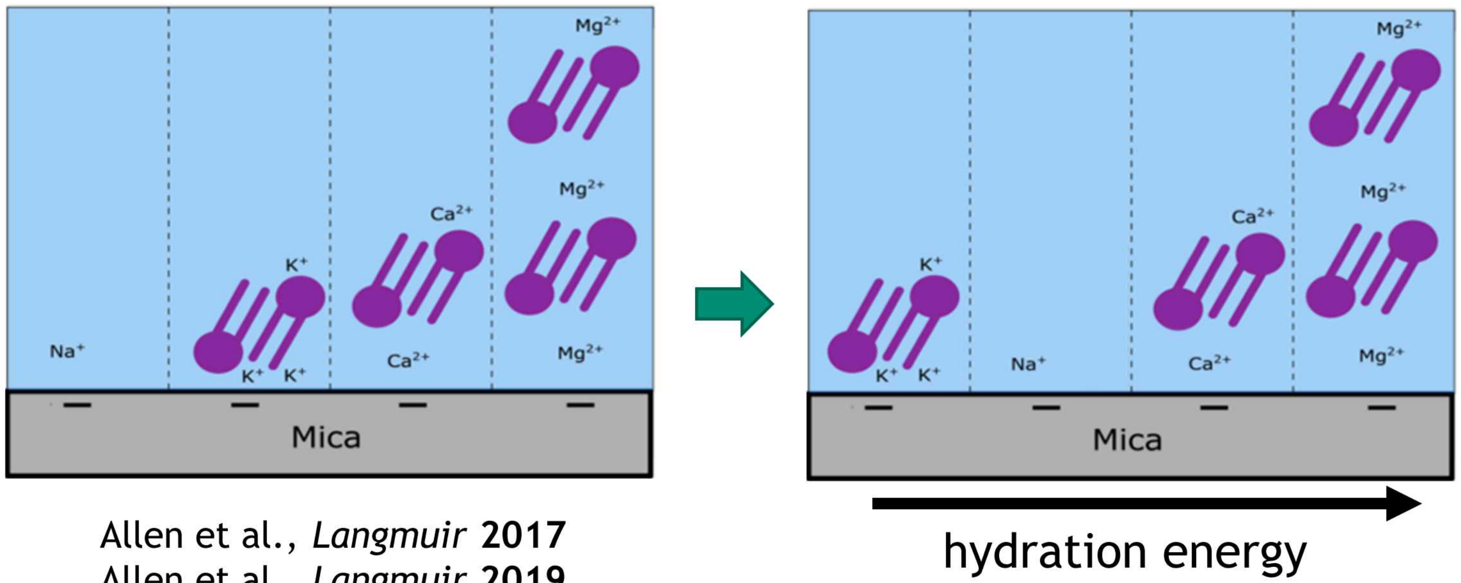




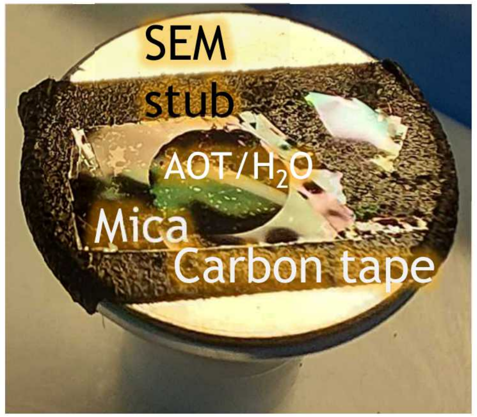
Allen et al., *Langmuir* **2017**
Allen et al., *Langmuir* **2019**

M.D.→ Hydration energy determines bonding
N.R. → Charge density determines bonding

Does Na create any bonding?

Cryo-EM Workflow For Mica/AOT System

1 Sample Setup



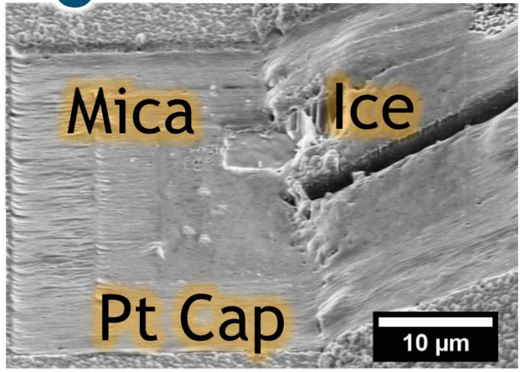
2 Vitrification

3 Load, Coat, Transfer

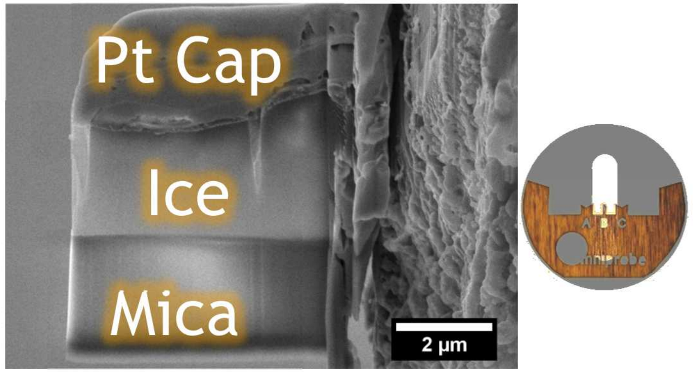
4 Scios FIB/SEM

5 Identify Region of Interest

6 Pt deposition, FIB Milling



7 Liftout, Thinning and Transfer

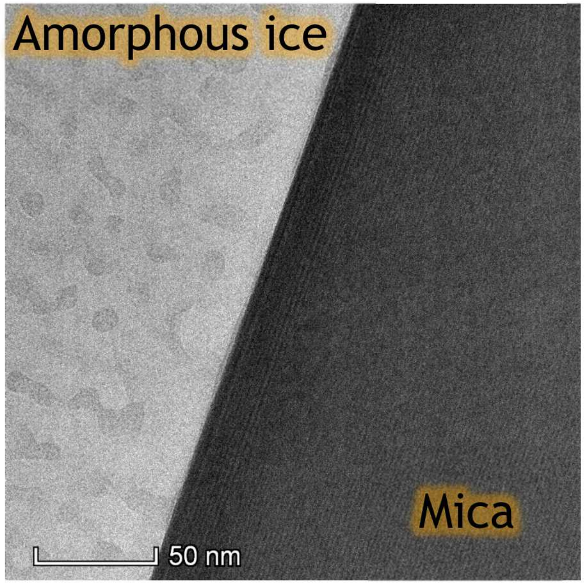


8 Talos L120C Cryo-TEM

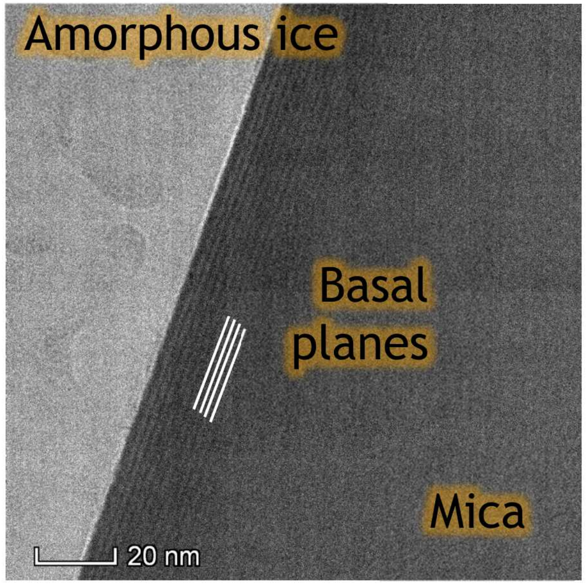
Cryo-TEM Results

Control Sample – Deionized H_2O on Mica
Imaging – Talos 120 kV

Region 1



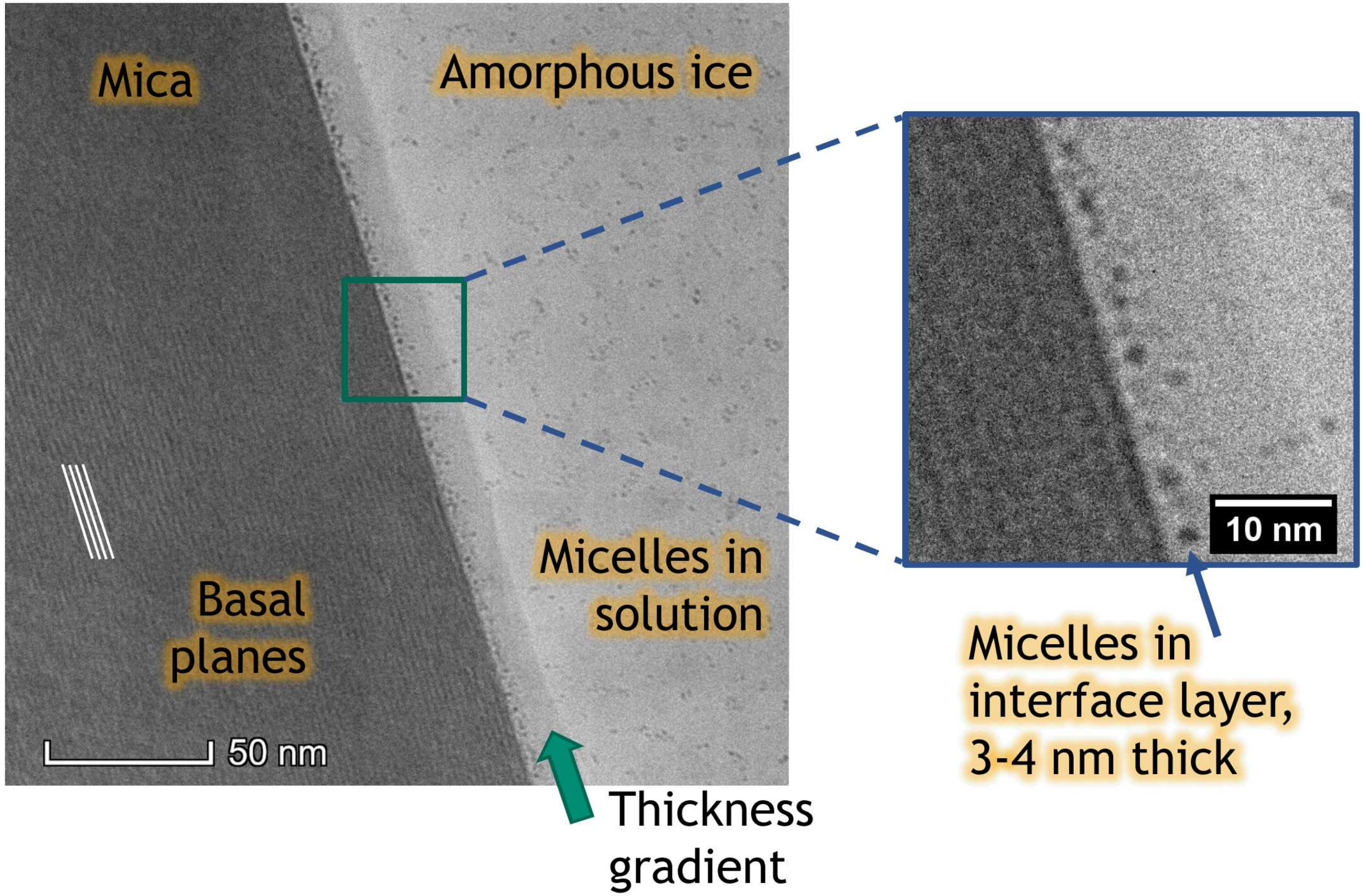
Region 2



- Sample successfully thinned to electron transparency, difficult given large difference in material density and milling rates
- Sample prepared with mica/H_2O interface normal to incident beam
  - Mechanical exfoliation of mica yields atomically flat surface
  - Preparation allows for easy visibility of the interface
- Features in ice layer due to surface damage, difficult to avoid

Cryo-EM Results

2.3 mM (0.92 CMC) Na-AOT on Mica
Imaging – Talos 120 kV



- Organized interfacial layer, AOT micelles ~2 nm diameter
- Thin ice layer between mica and micelles
- Surface damage caused the micelles in the amorphous-ice bulk to cluster
- Micelles in bulk indicate >1 CMC
- Good agreement with MD: Interfacial micelle formation predicted at low surface concentration.

Summary of Surfactant Interactions with Mica Surfaces

- MD simulations of an anionic surfactant (AOT) are consistent with observations from published neutron reflectometry:
  - AOT binds to the negatively-charged mica surface via cation bridging.
  - Surfactant thickness is consistent with a bilayer (or micelle).
- Cation hydration properties govern the presence of water layers at the mineral-surfactant interface.
- AOT bilayers form at the mica surface at surface concentration of ~ 1 AOT/nm^2. In experiments, the critical micelle concentration (CMC) of the cation-AOT pair must also be considered.
- The combination of nano-scale characterization (spectroscopy, cryo-EM) and molecular modeling will provide the molecular-level insight to drive innovation to control complex fluid behavior in the subsurface.

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LABORATORY DIRECTED RESEARCH & DEVELOPMENT

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Thank you for listening!

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