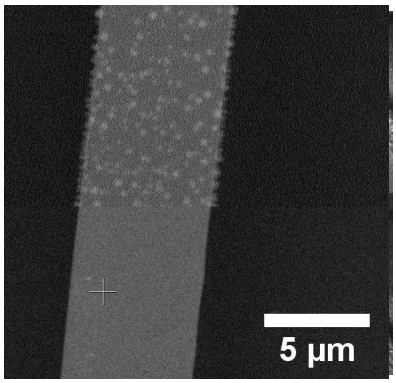
Challenges and Strategies for Microscopy and Microanalysis during In-situ Experiments in Modern Analytical TEM/STEM Instruments



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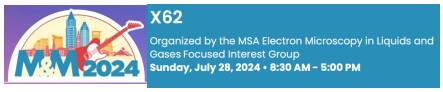
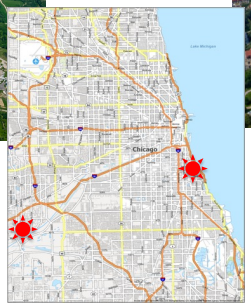
1

Acknowledgements





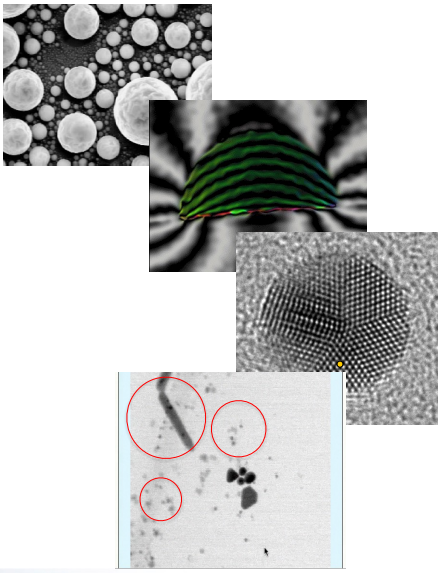
Permission Given to Photograph/Capture Slides or Just Request a PDF Copy by Email

2

"In-Situ" Microscopy & Microanalysis

Observation of the State of a material during Dynamic conditions

- **Dynamic Conditions**
  - Temporal
  - Temperature
  - Stress/Strain/Mechanical Deformation
  - Vacuum/Gaseous/Liquid Environment
  - EM Fields
  - Irradiation Environment
    - Charged Particles
    - Photons
- **State**
  - Morphology
  - Crystallography
  - Bonding/Electronic Structure
  - Elemental/Chemical Constituents



3

In-situ Characterization: The game has changed

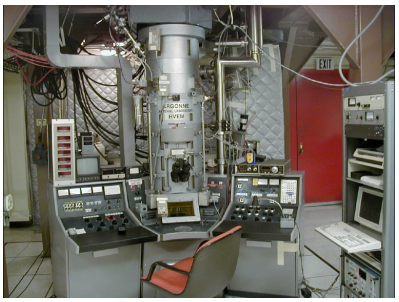
- *Improved Electron Optics*
  - *Improved Performance*
  - *Potentially Improved Experimental Space*
- *Improved Detector/Geometry*
  - *Higher Resolution*
  - *Higher Speed DAQ*
  - *Higher Efficiency*
- *Improved Experimental Geometry*
  - *In-Situ Holders/Environments*
- *Computationally Mediated Experiments*
  - *Exploit Electron Solid Interactions for State-of-the-Art Materials Characterization*

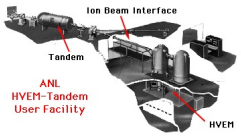
Challenges:

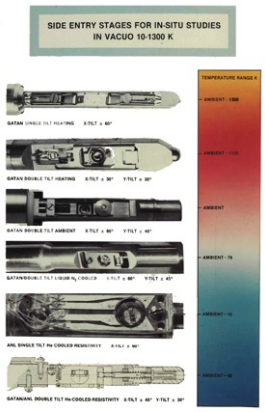
- *In-situ observation of growth processes - at atomic resolution in growth environment*
- *Simultaneous imaging of hard/soft components*
- *Dynamics - Fast detection schemes, detectors, and sources*
- *In-situ / high-spatial resolution elemental spectroscopy*

4

ANL there has a Long History in In-situ Experimentation in the TEM



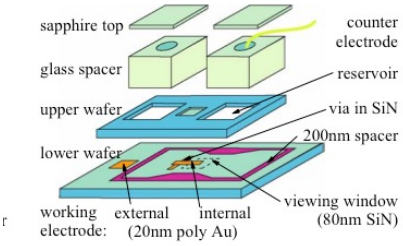


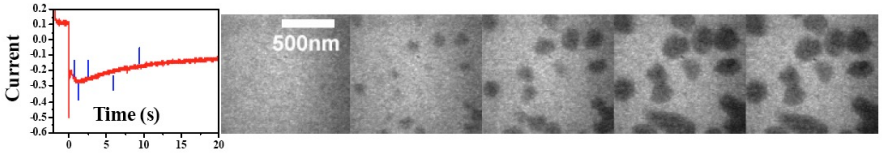


Decommissioned Fall 2001

5

In-Situ (SiNx) Cells and ETEM's have revolutionized L/G(TEM/STEM)





In situ Microscopy of Electrochemical Reactions

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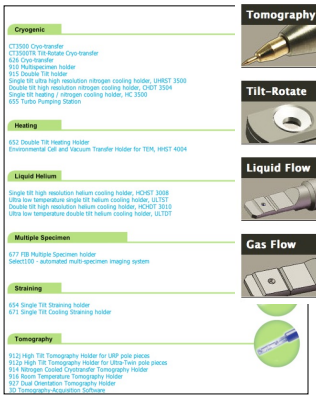
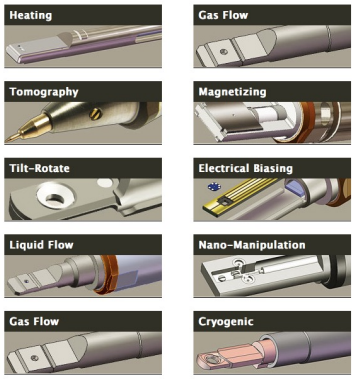
6

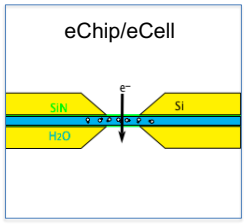
"In-Situ Holders" Today
Cover a wide range of Conditions

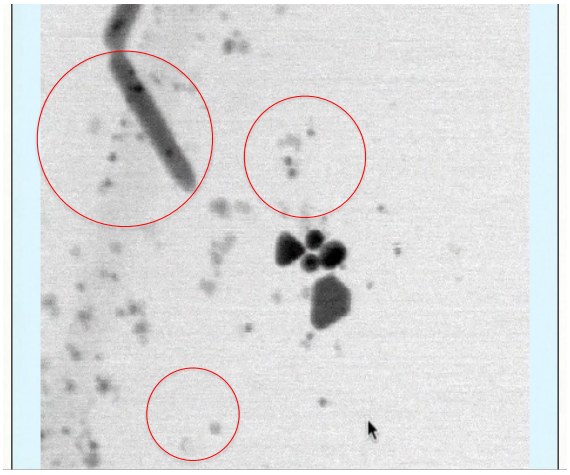




7

During dynamic in-situ experiments
spectroscopy can become essential to the interpretation



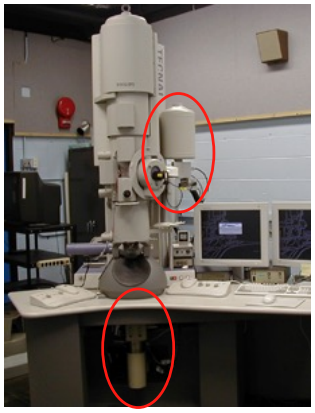


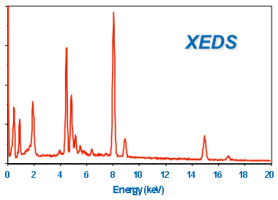
50 nm

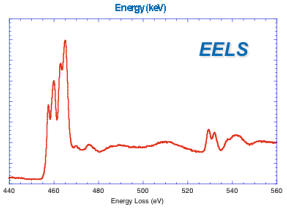
What is really happening?

8

In-Situ and Microanalysis
Information from Inelastic Scattering Events



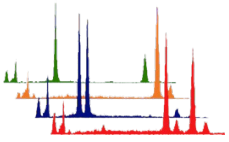




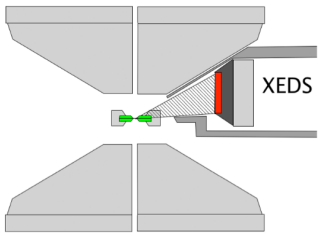
9

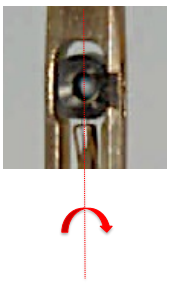
The Experimental Geometry & Holder
Is typically a limiting factor in many experiments
particularly for in-situ eCell configurations

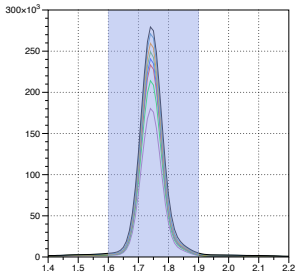
9

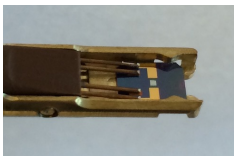


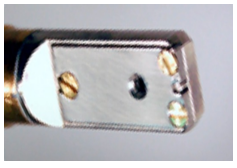
Penumbra of the specimen holder
is a limiting factor for XEDS in virtually all experiments
How do you determine it's real extent and minimize it or correct for it?

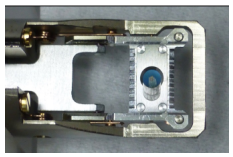


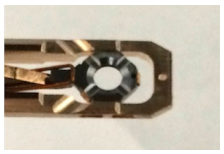






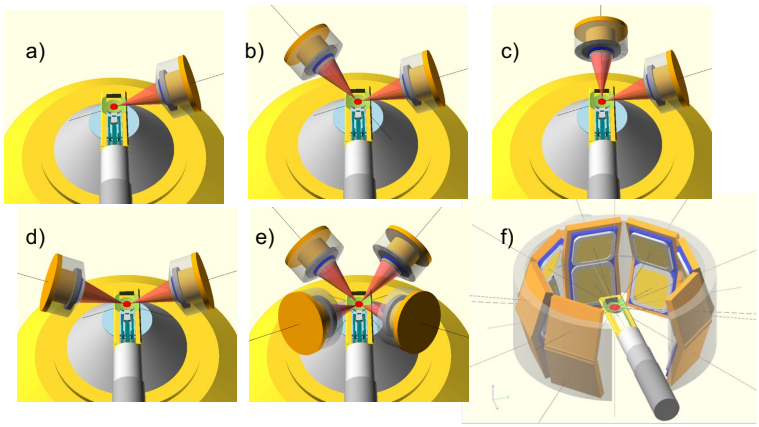






10

XEDS Geometries are extremely varied today



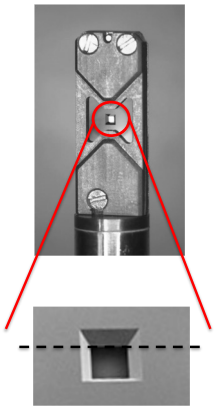
Using simple tilt series protocol, individual configurations can now be directly characterized and compared on equal and unbiased basis.

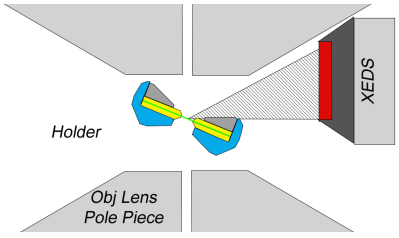
Microsc. Microanal. V 20, 1318–1326, 2014
Ultramicroscopy , V 151, 2015, Pages 240-249

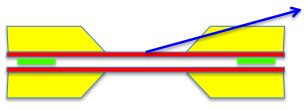
11

In-situ Cell (Liquid /Gaseous) Holders

Example: Protochips - Poseiden/Atmosphere Holder



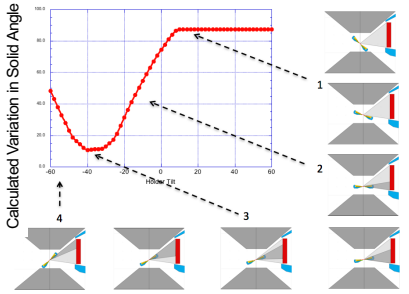


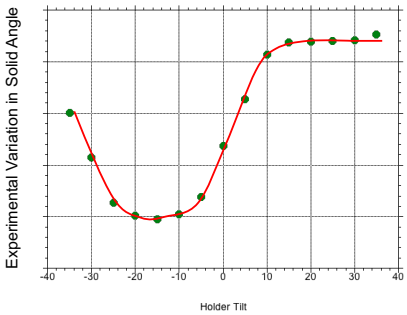


In-situ holders : FEI, JEOL, Hitachi, Gatan, Protochips, Hummingbird, DENsolutions,..

12

Penumbra/Geometry of the Specimen Holder is also Critical





Calculation of Holder Tilt to Minimize Holder and Detector Penumbra

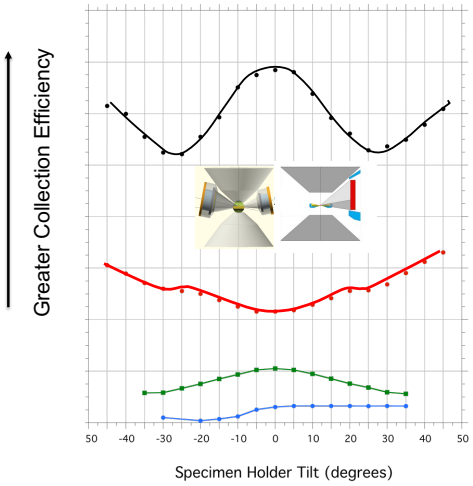
Parameter	Value	units
Holder Side Wall Half-Height (h_s)	0.5	mm
Holder Half-Width (w_s)	3.25	mm
Holder Penumbra Angle (θ_p)	8.75	degrees
Upper Detector Height (H_U)	6.3	mm
Lower Detector Height (H_L)	-1.7	mm
Radial Detector Distance (D)	11	mm
Detector Upper Elevation Angle (θ_E^U)	29.80	degrees
Detector Lower Elevation Angle (θ_E^L)	-8.78	degrees
Minimum Holder Tilt Angle ($\alpha = \theta_p - \theta_E^L$) to mitigate penumbra's of holder and/or detector	17.53	degrees

Calculate

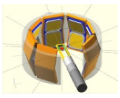
Note: some detector geometries can have H_L which is negative (i.e. below the specimen plane)

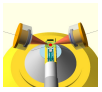
http://zaluzec.com/NJZTools/

Evolving Detectors & Geometries for XEDS
Collection Efficiencies have Significantly Increased this year

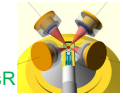


χ_{PAD} (~ 4.5 sR)



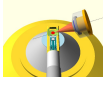


Dual SDD ~ 1-1.5 sR)



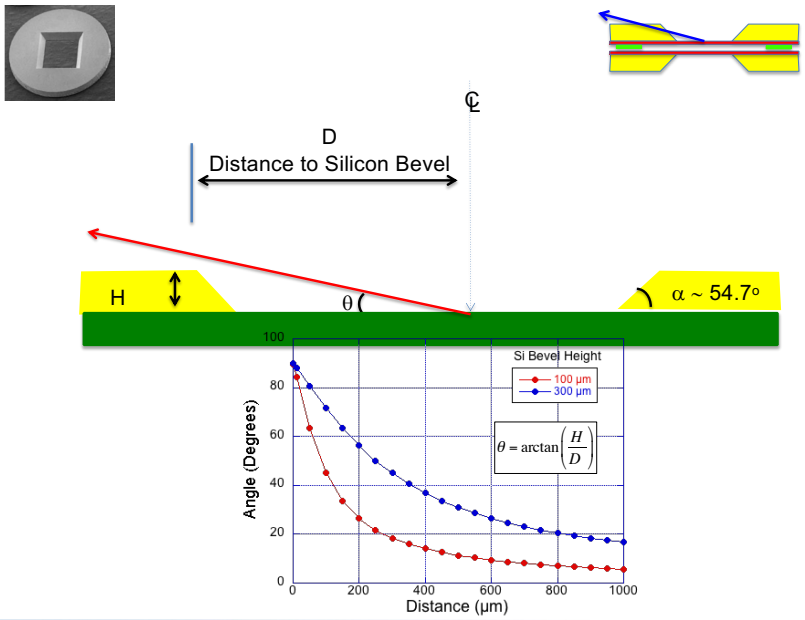
Quad SDD ~ 0.7-1 sR

Single SDD ~ 0.3 sR



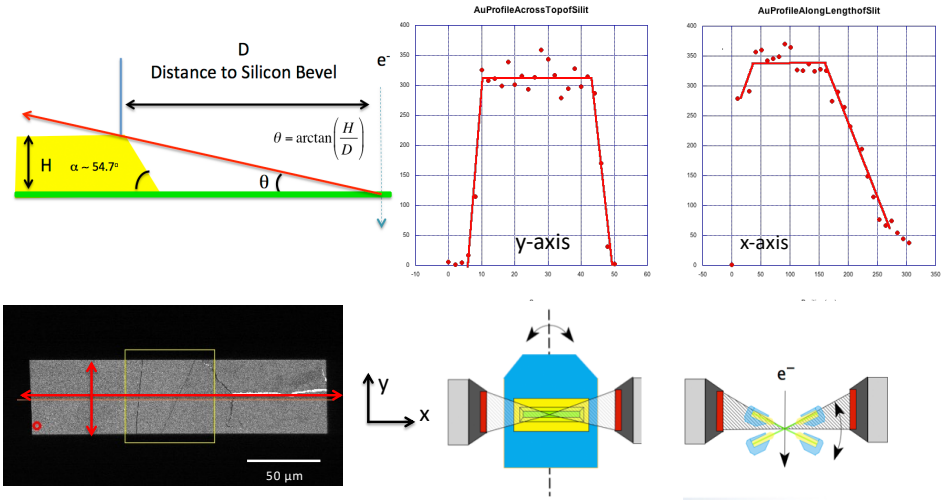
Protocol for XEDS System Penumbra Measurements:
Zaluzec etal Microsc. Microanal. 22 (Suppl 3), 2016, 278-279

During eCell ExperimentsPenumbra of Silicon Support Wafers must also be considered



15

The Penumbra of the eCell is also intimately related to the shape of the cell
Liquid Cells are more restrictive than Gaseous Cells.



16

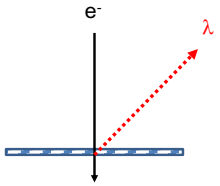
Quantitative Analysis Equations (minimalistic)

For an infinitely thin specimen

$$I_A^{Ka} = \sigma_A(E,Z) * \Gamma_A * \omega_A * C_A * \frac{N_o \rho t}{W_A} * \eta_o \tau * \varepsilon_A \frac{\Omega}{4\pi}$$

Probability X-ray/atom/electron * # Atoms * # Electrons * Probably of Detection

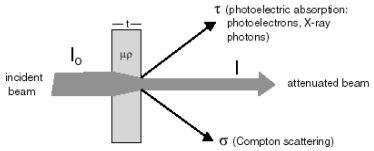
I_A = measured x-ray intensity (counts) per unit area,
σ_α (E_o, Z) = α^{th}-shell ionization cross section
E_o = electrons of incident energy (),
ω_α = α^{th}-shell fluorescence yield,
Γ_α = α^{th}-shell radiative partition function,
W_z and C_Z the atomic weight the composition
Z = atomic number
N_o = Avogadro's number,
ρ = local specimen density,
t = thickness of ROI
η_o = the incident electron beam current,
τ = acquisition (live) time
ε_α = the detector efficiency and
Ω_α = the detector collection solid angle.

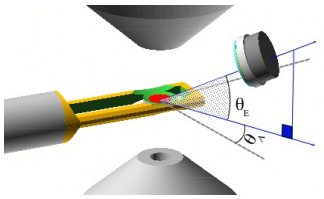


17

- No Electron Energy loss
- No X-ray absorption
- No X-ray fluorescence

$$I(\Omega,t) = \iint_{t,\Omega} I_0 \exp\left[-X\rho t(\Omega)\right] d\Omega$$



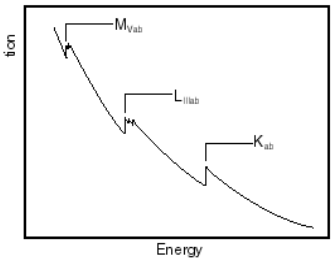


$\mu = \tau + \sigma$

where μ = bulk mass absorption coefficient,
τ = photoelectric absorption coefficient,
σ = Compton scattering coefficient.

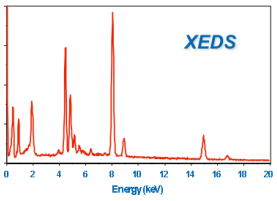
$I = I_O e^{-\mu\rho t}$

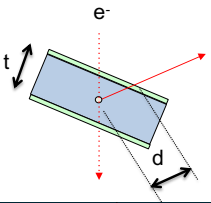
where I_O = initial intensity (cps),
I = final intensity (cps),
μ = bulk mass absorption coefficient of the material (cm^2/g),
ρ = density of the material (g/cm^3),
and t = thickness onf the material (cm).



18

Xray Attenuation by Various amounts of liquid cell media and an SiN_x window



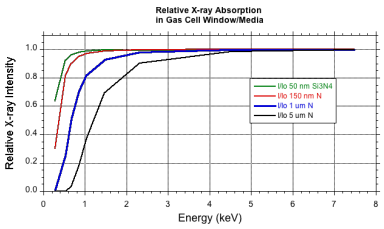


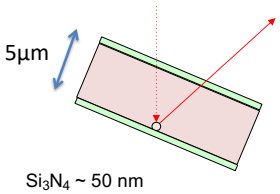
Line	Energy (keV)	μ/ρ @ Si_3N_4 ρ ~ 1.33	μ/ρ @ H_2O ρ ~ 1	I/Io in Si_3N_4 d ~ 50 nm	I/Io in H_2O d ~ 150 nm	I/Io in H_2O d ~ 500 nm	I/Io in H_2O d ~ 1 μm
Ni Kα	7.48	48.64	12.98	0.9997	0.9998	0.9994	0.9987
Ti Kα	4.51	197.3	56.22	0.9987	0.9992	0.9972	0.9944
S Kα	2.31	1267	390.6	0.9916	0.9942	0.9807	0.9617
Al Kα	1.48	655.2	1418	0.9957	0.9789	0.9315	0.8677
Na Kα	1.041	1767	3943	0.9883	0.9426	0.8211	0.6742
Ne Kα	0.851	3143	7050	0.9793	0.8997	0.7029	0.4941
F Kα	0.677	5878	13678	0.9617	0.8145	0.5046	0.2547
O Kα	0.52	12064	29376	0.9229	0.6436	0.2302	0.0530
C Kα	0.28	67557	176560	0.6381	0.0707	0.0001	0.00000001

Calculation of x-ray absorption as a function of pathlength for a range of characteristic x-ray lines in SiN_x window and various amounts of liquid H_2O. As I/Io approaches unity the effects of x-ray absorption can be ignored.

19

Modeling X-ray Absorption in eCell System Windows and Media





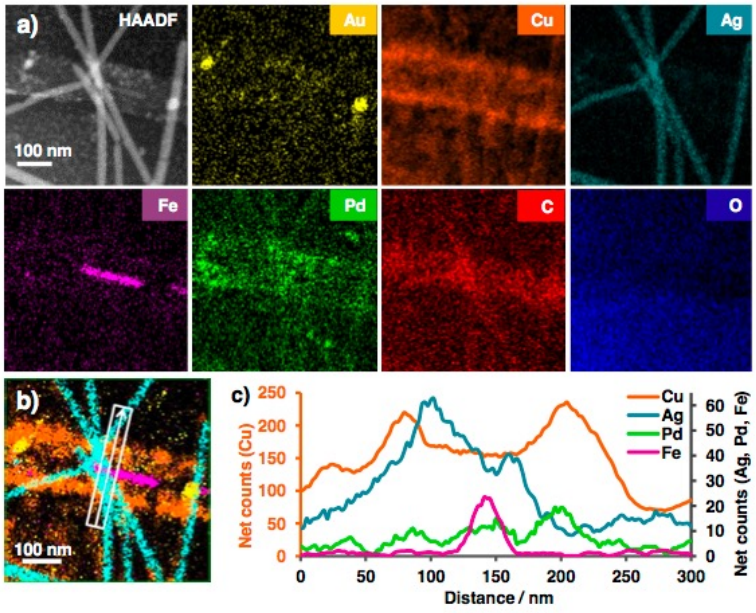
Si_3N_4 ~ 50 nm

N ~ 1000 nm (1 μm) @ 1 atm

Line	Energy (keV)	μ/ρ @ Si_3N_4 ρ ~ 1.33	μ/ρ @ N ρ ~ 0.81	I/Io in Si_3N_4 t ~ 50 nm	I/Io in N t ~ 150 nm	I/Io in N t ~ 1 μm	I/Io in N t ~ 5 μm
Ni Kα	7.48	48.64	9.25	0.9997	0.9999	0.9993	0.9963
Ti Kα	4.51	197.3	38.6	0.9987	0.9995	0.9969	0.9845
S Kα	2.31	1267.1	257.7	0.9916	0.9969	0.9793	0.9009
Al Kα	1.48	655.2	893.3	0.9957	0.9892	0.9302	0.6964
Na Kα	1.041	1767.5	2449.6	0.9883	0.9707	0.8200	0.3708
Ne Kα	0.851	3143.4	4372.7	0.9793	0.9483	0.7017	0.1702
F Kα	0.677	5878.2	8271.3	0.9617	0.9044	0.5117	0.0351
O Kα	0.52	12064.9	17191.5	0.9229	0.8115	0.2485	0.0009
C Kα	0.28	67557	98933	0.6381	0.3006	0.0042	0.0001

20

Hyperspectral Imaging of Nanoparticle Soup in Liquids



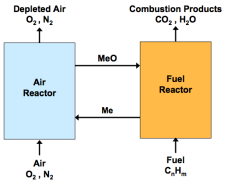
Lewis etal - Chem. Commun., 2014, 50, 10019

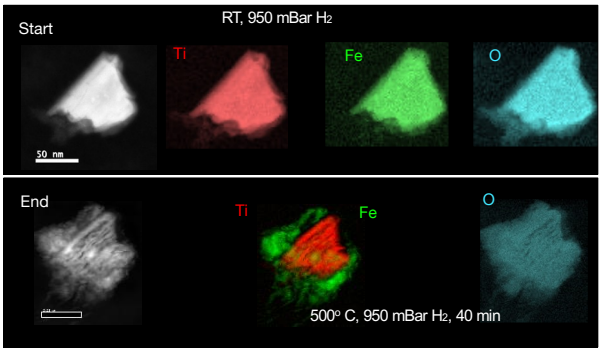
Spatial Resolution ~ 10-20 nm at present

21

In situ hyperspectral imaging of $FeTiO_3$ during H_2 reduction

In situ imaging and EDS of $FeTiO_3$ is during reduction reveled important aspects of the reduction process relevant to chemical looping combustion.





In situ hyperspectral imaging reveals:

- pseudomorphic reaction - shape of initial grains generally retained
- decomposition of $FeTiO_3$ to Ti-O and Fe-O

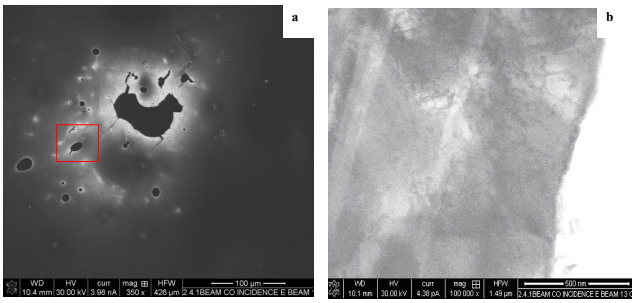
22

A.Janssen, et al.,
Microscopy & Microanalysis 2015 21 Sup 3 565-566

22

Hybrid Specimen Preparation Methods to Study Conventional Materials

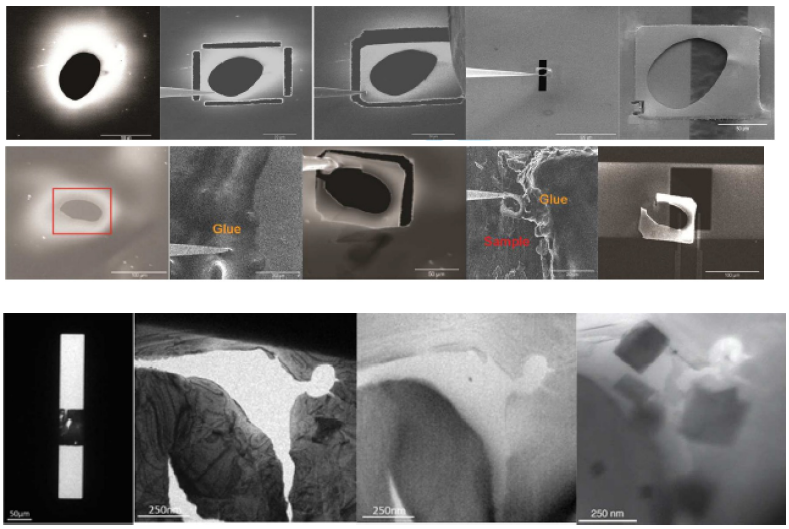
'Cut-and-Paste' approach using Dual Beam FIB



Quanta 3D DF-STEM image BF-STEM image

23

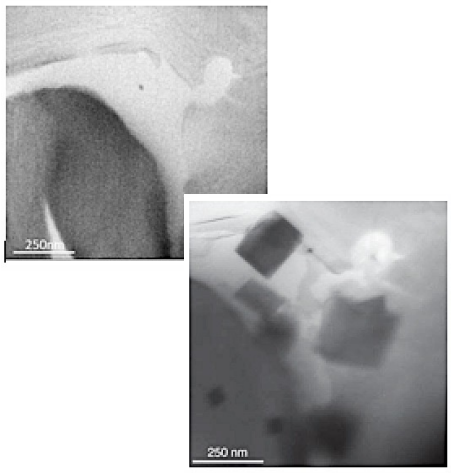
Spectrum Imaging
Type 304 Austenitic Stainless Steel in Water

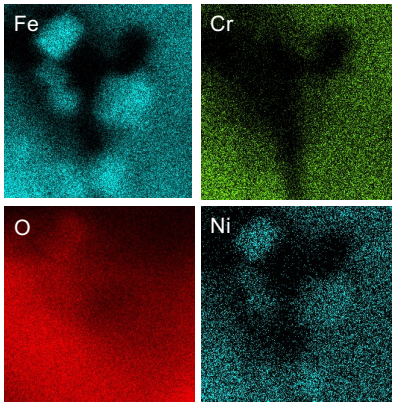


1 Atm Air 1 Atm H_2O 1 Atm H_2O + 24 hrs

24

Spectrum Imaging
Type 304 Austenitic Stainless Steel in Water





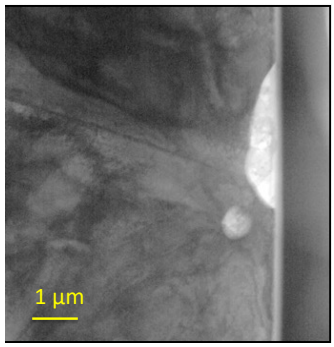
Microstructural Evolution in Liquid H_2O

Note absence of Cr in the Precipitates formed after emersion in H_2O ~ 24 hrs.

25

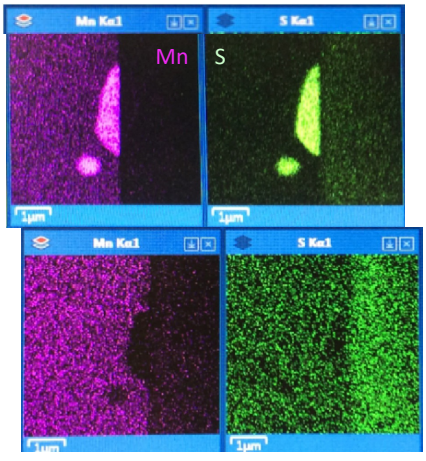
MnS Ppt in Steel

Dissolution in H_2O

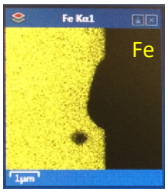


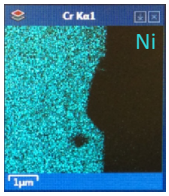
Dry

Dry



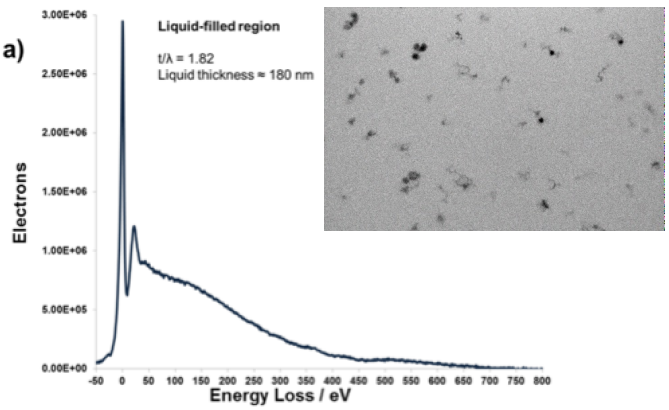
Wet





26

Why XEDS ? Just use EELS!

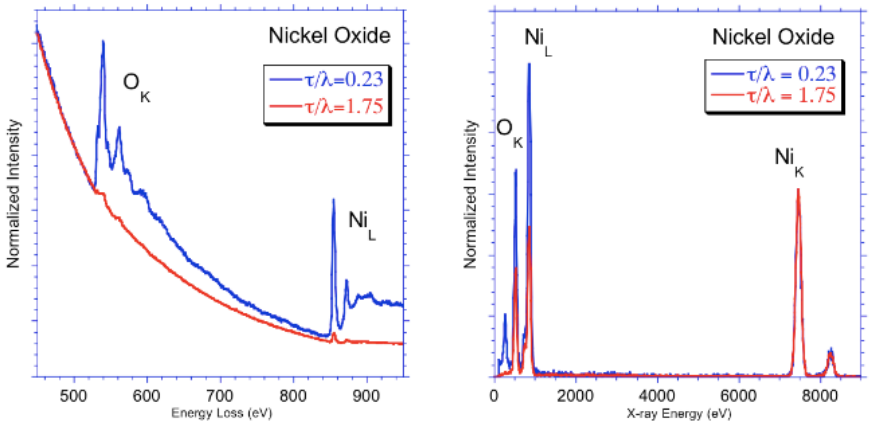


Gases are doable, but liquids are a real problem

27

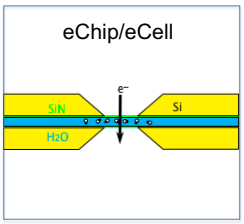
In-situ cells with SiNx windows, thick materials and media become problematic for spectroscopy. This can dictate the spectroscopic methodology

Simultaneous XEDS/EELS

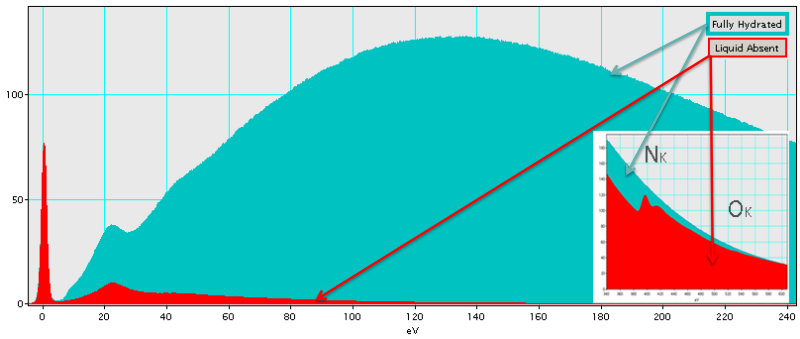


XEDS has a real advantage in thick "specimens"
Due to its improved performance wrt P/B
but there are geometrical collection solid angle issues

28



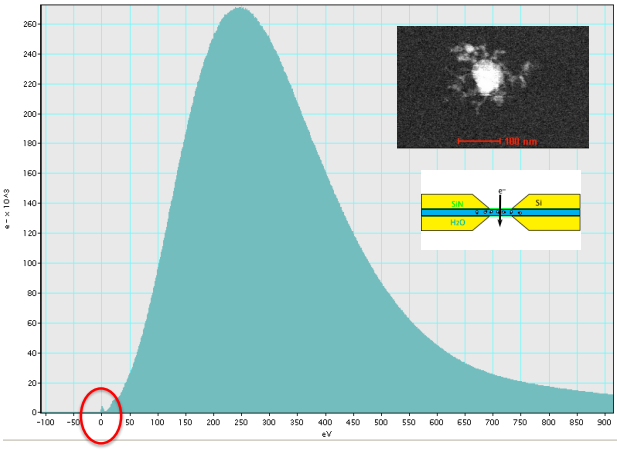
Spectroscopy in Liquid eCells

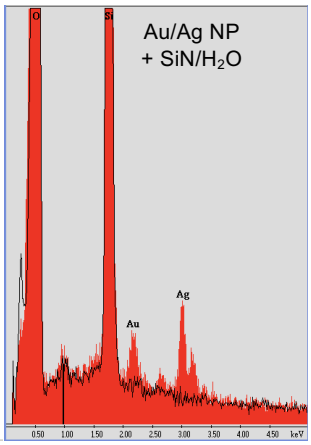


eCell Media Dominates EELS Signal

29

Compare Simultaneous EELS/XEDS
in eCell in H_2O



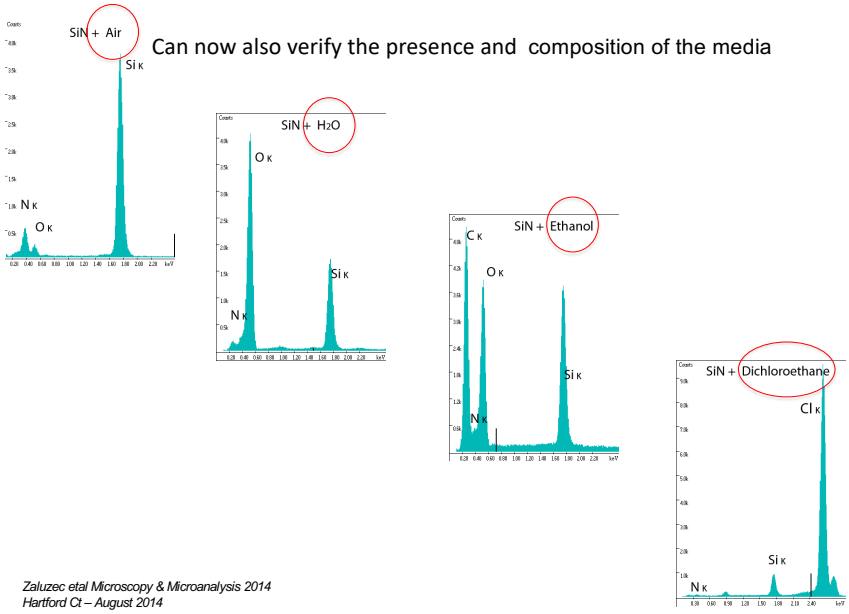


Simultaneous EELS/XEDS in Liquids
Multiple Scattering dominates EELS signal P/B is terrible
XEDS signal from the specimen not dominated by Bgnd
Si N, O are present from environmental media

30

XEDS of the "media" in the eCell

Can now also verify the presence and composition of the media

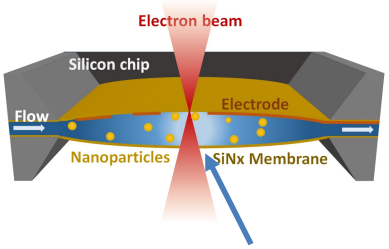


Zaluzec etal Microscopy & Microanalysis 2014
Hartford Ct – August 2014

31

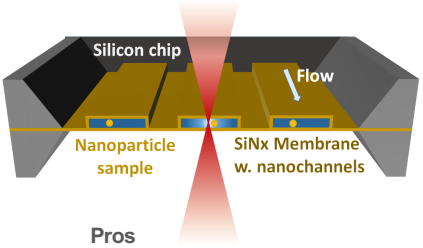
Traditional vs Nanochannel liquid TEM cells

'traditional' liquid cell with two clamped chips



Micrometer membrane bulging compromises the resolution in TEM experiments

Our nanochannel system

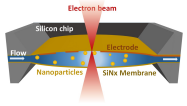


Pros
- Few nanometer membrane bulging - well defined liquid layer thickness
- Controlled Flow
+ mixing, electrophoresis, …

Yesibolati , Mølhave (DTU) & Zaluzec (ANL/AMEWS)

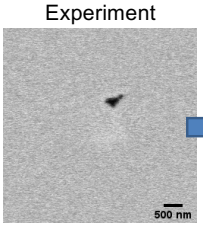
32

Rotational Diffusion – in clamped chip LPTEM



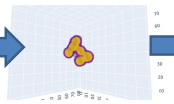
- *Tracking 3D motion, translation and rotation of complex structures*
- *Translational and rotational diffusion roughly as expected from simple continuum models on trimer*

Experiment



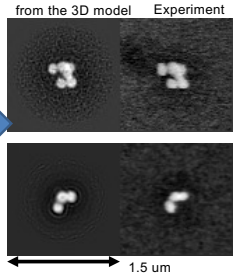
LPTEM with 150 nm citrate coated Au NPs in clamped liquid cell, 60% glycerol/water

Reconstructed 3D volume model using sphire.mpg.de



Projection from the 3D model

Experiment



1.5 um

Ongoing:
Perform 3D rotation analysis and get rotational diffusion tensor measurements

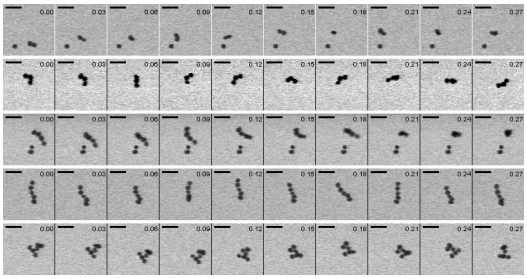
Combine with Nanochannel chips for higher resolution and smaller particles + can be quasi 2D

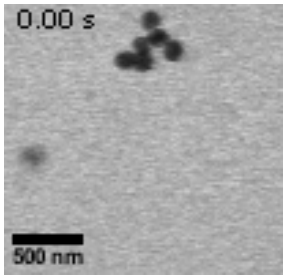
Aim to validate and improve **hydrodynamic models of complex nanostructure translation & rotation** in liquids under fields and flow – and in nanochannels

33

Complex shape dynamics

Quantify rotational and translational dynamics of complex nanostructure
Experiment → modeling and simulation (need discussion and help)

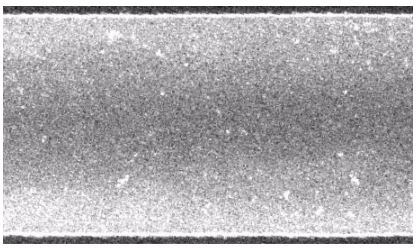




Scale bar 500 nm

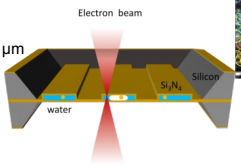
34

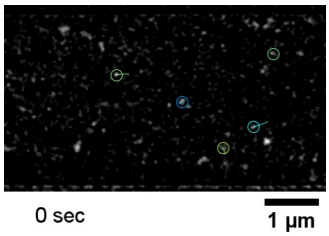
NPs flow/diffusion dynamics in nanochannel



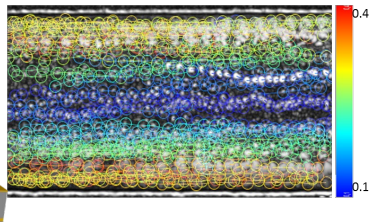
STEM imaging

- 5 µs pixel dwell time, 2s per frame
- Beam current 1.6 pA, FOV 8 *8 µm^2
- 20 mM HAuCl4 solution
- Beam induced Au NPs
- Beam induced Bubble
- Bubble induced flow
- Channel height 200 nm, width 3 µm





Color represents mean velocity

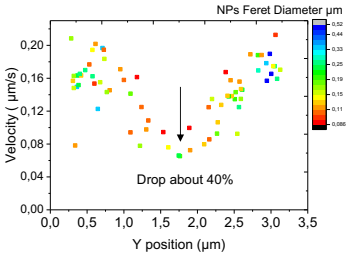


35

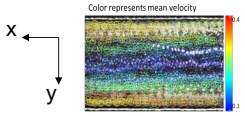
35

NPs flow/diffusion dynamics in nanochannel

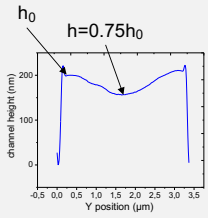
X-direction, flow direction velocity profile



✓ **Experimental flow profile matches theory prediction**



$$Q = -\frac{\nabla P}{12\eta}\rho\omega h^3\left(1-\frac{186}{\pi^5}\zeta(5)\frac{\omega}{h}\right)$$



In theory

$Q_h = 0.75^3\ Q_0 = 0.42Q_0$

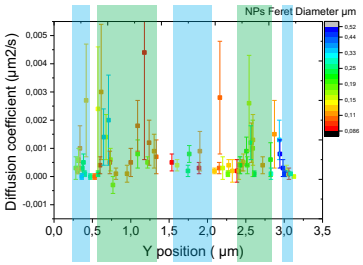
$$Q \simeq -\frac{\nabla P}{12\eta}\rho w h^3\left(1-\frac{186}{\pi^5}\zeta(5)\frac{w}{h}\right).$$

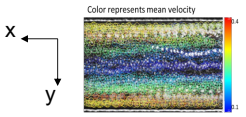
36

36

NPs flow/diffusion dynamics in nanochannel

Y-direction, vertical to flow direction diffusion coefficient





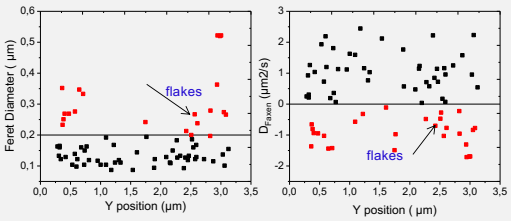
- $2*10^3$ less diffusion coefficient
- Near the edge and middle of the nanochannel (light blue regions), diffusion is diminished as the flow is ;
- Between middle and edge (green regions), there are spaces that allows slightly higher diffusion and flow rate
- But how would it be for flakes rather than spheres?? Likely much lower
- ……..

37

In theory

Faxen corrected diffusion coefficient

Particle size



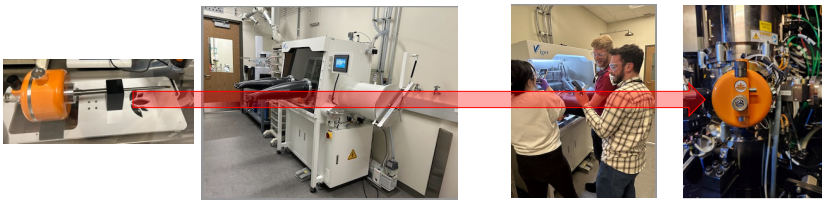
$$D_{//} \cong D_0\left[1-\frac{9}{8}\frac{a}{H}+O\left(\frac{a}{H}\right)^2\right]$$

Theoretical values for each particle between two rigid walls, first order approximation

37

Energy Materials Challenges - Inert Atmosphere Transfer

Successful acquisition and modifications of mulitple resources as well as implementation of workflow in Vacuum / Argon Glove Box with Inert Transfer between resources

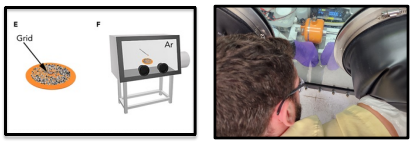


New Inert Cryo Transfer Holder

Transfer to Argon Glove Box

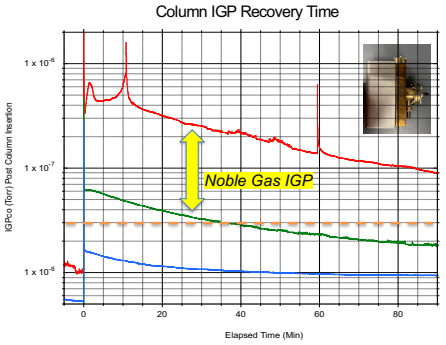
Inert Loading

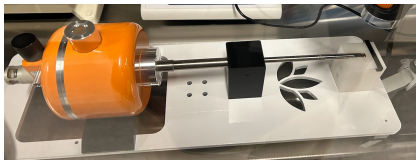
Transfer to PicoProbe



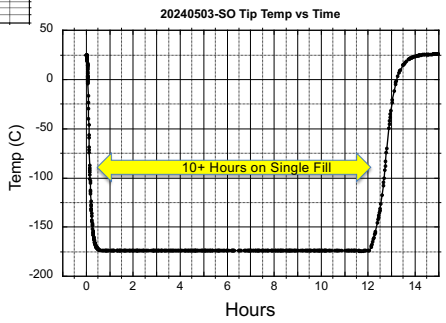
38

Validation Tests





Standard Ion Pump – Argon Loading
Noble Gas Ion Pump – Argon Loading
Standard Holder – Air Loading

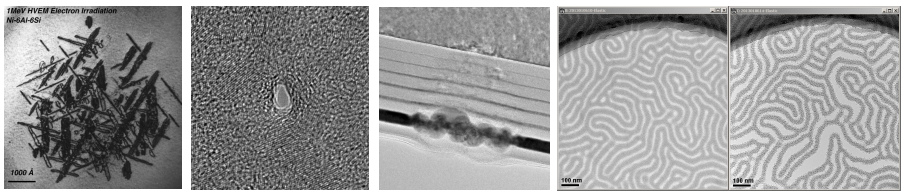


Summary:

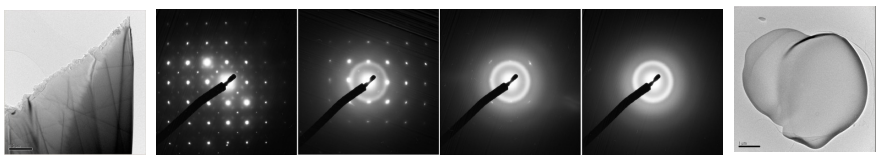
Upgraded Noble Gas Ion Pump was essential
Simple Origin Performs to updated specifications

39

Radiation Damage in Hard vs Soft Materials
Displacement versus Ionization/Radiolysis



Atomic Displacement | Sputtering | Melting | Radiolysis

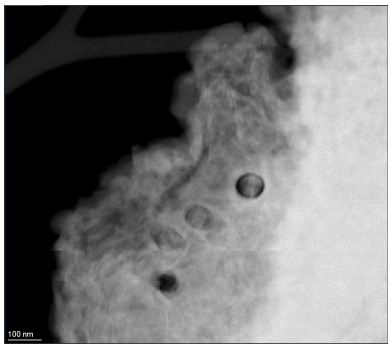


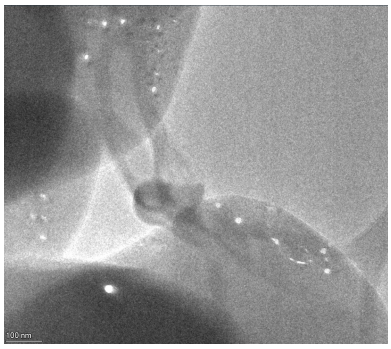
0.0 D_c | 0.4 D_c | 0.8 D_c | 1.0 D_c

Amorphization

40

Beam Damage Challenge
Both Lithium Hydroxide and Carbonate Damage
in STEM @ 300 kV @ 6 pA



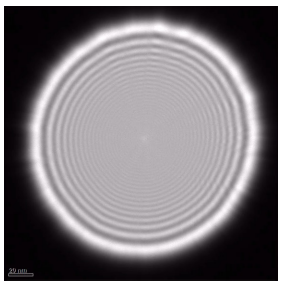


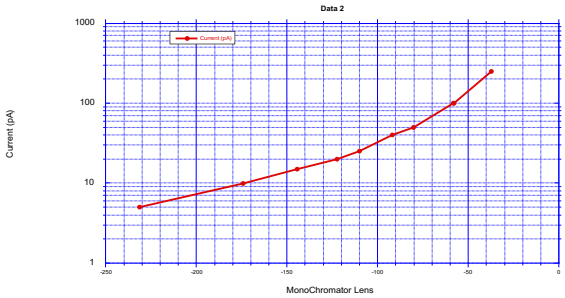
2023111412 - LiHxOy

2023111542 -LiCxOy

41

Accurate and Dose Control via MonoChromator
No need to change Electron Optical Conditions



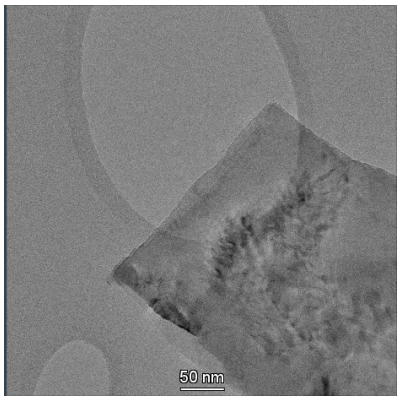


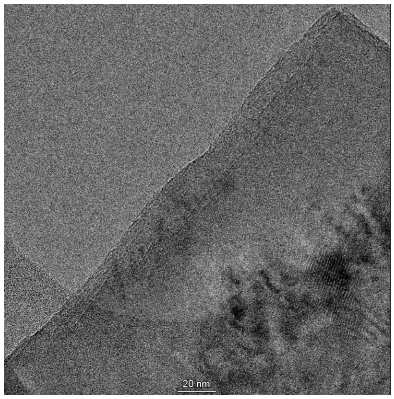
Mag	Probe (nm)	Beam Current (pA)	Dose Rate ($e^-/Å^2/s$)
1.9 kx	20000	75	0.01
10 kx	4000	75	0.4
55 kx	4000	75	0.4
115kx	2000	75	1.5
290kx	1000	200	16
290kx	200	50	100
STEM	100	10	$8x10^1$
STEM	10	10	$8x10^3$
STEM	1	10	$8x10^5$
STEM	0.1	10	$8x10^7$
STEM	0.1	1	$8x10^6$

42

42

Irradiation Damage CTEM
LiF @ ~ 16e⁻/A²/s @ 200 kV @ RT





43

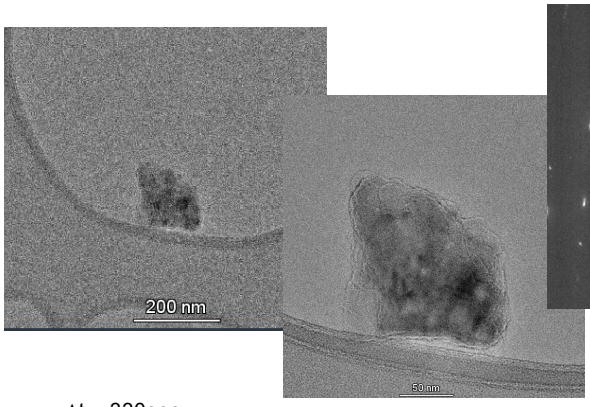
Δt ~ 3500sec
D_R ~ 16 e-/A²/s D_{Onset} ~ 1.3x10³ e⁻/A²
D_T ~ 5.7x10⁴ e-/A²

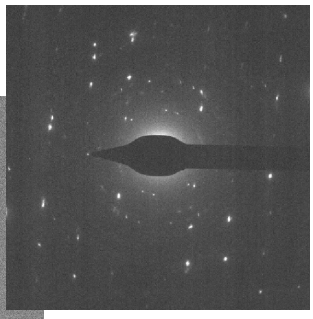
Spec Pure LiF Powder
Drop Cast Dry on
Formvar Less Holey Carbon

2024040501

43

Irradiation Damage CTEM
Li_2CO_3 @ ~ 16 e⁻/A²/s @ 200 kV





D_T ~ 5. x10³ e-/A²

Δt ~ 330sec
D_R ~ 16 e-/A²/s

D_T ~ 5.3 x10³ e-/A²

Spec Pure Li_2CO_3 Powder
Drop Cast Dry on
Formvar Less Holey Carbon

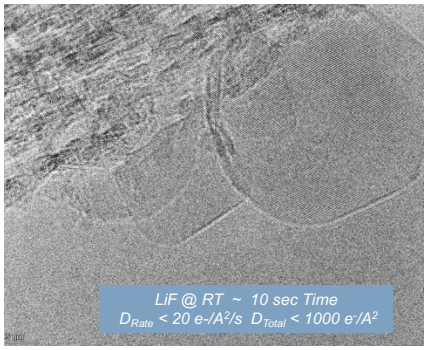
2024040322

44

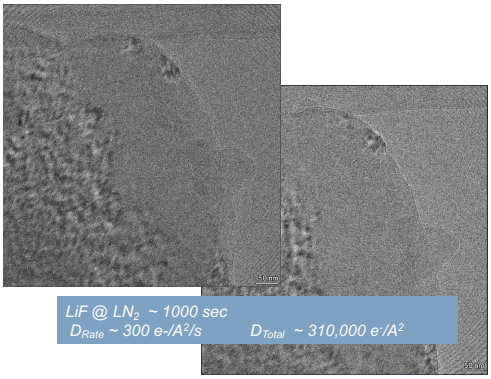
44

Damage Onset Values - RT vs LN_2

LiF @ RT



LiF @ LN_2



2024050622

D_{onset}^{LiF} ~ 700-750 e-/A² @ 18 e-/A²/s @ 200 kV @ RT

$D_{onset}^{Li_2CO_3}$ < 75 e-/A² @ 16 e-/A²/s @ 200 kV @ RT

45

LiF Irradiation Damage Comparisons RT vs LN_2

Condition	Observation Time (s)	Dose Rate [e/A²/s]	Total Dose [e/A²]
LN_2 - 300 kV RT - 300 kV	1000 < 10	~ 300 ~ 20	3.1 x 10^5 < 2 x 10^2
LN_2 - 200 kV RT - 200 kV	100 < 10	~ 400 ~18	4.1 x 10^4 < 2 x10^2
LN_2 - 60 kV RT - 60 kV	76 < 10	~800 ~ 90	6 x 10^4 <1 x10^2

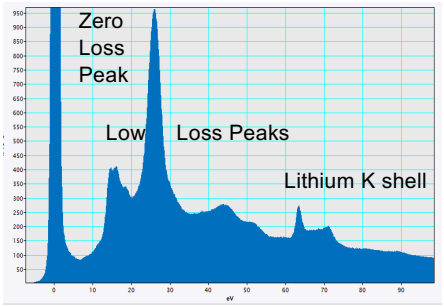
} ΔD ~ 200+

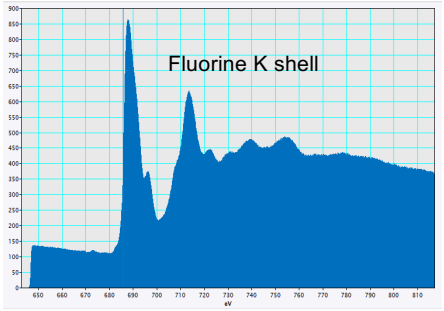
But… there is also a Dose Rate Effect

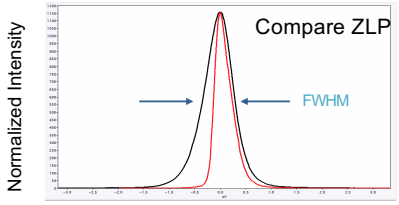
46

Electron Energy Loss Spectroscopy of Lithium Compounds

Conventional Core Loss Spectroscopy
Generally Requires ~ 1-2 eV Resolution







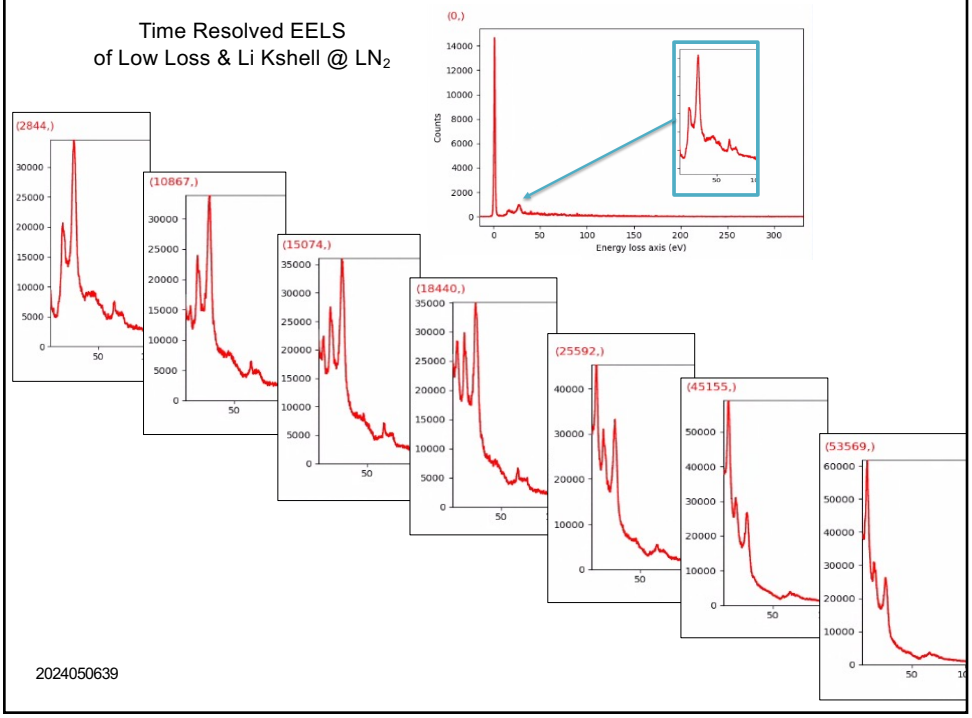
Both XFEG & CFEG System are Suitable
for Core Loss Spectroscopy

XFEG ~ 650 meV @ 300 kV
CFEG ~ 300 meV @ 300 kV

20231113-15

47

Time Resolved EELS of Low Loss & Li Kshell @ LN_2



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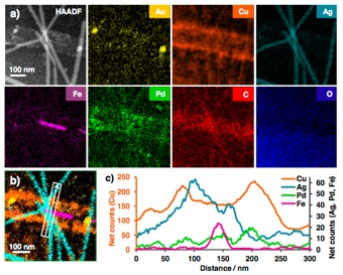
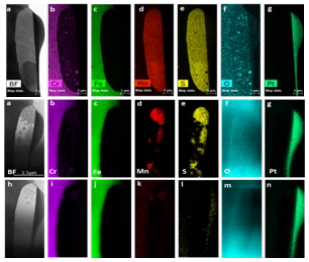
48

Hyperspectral Imaging in Liquids & Gases @ 1 ATM @ Temperature

Characterization of nanoparticles in liquids



In Situ Metallurgical Studies
MnS Inclusion Dissolution in Water



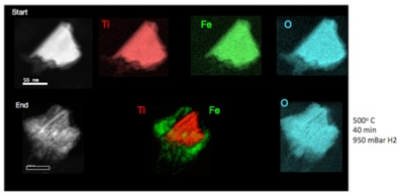
In Air, 1 atm

2 hr. in H_2O

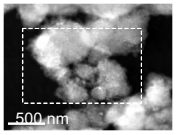
24 hr. in H_2O

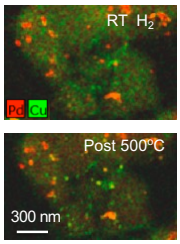
Ilmenite reduction by hydrogen

$FeTiO_{3(solid)} + H_{2(gas)} \rightarrow Fe_{(solid\ metal)} + TiO_{2(solid)} + H_2O_{(vapor)}$



Pd/Cu NP Catalysts on TiO_2
Calcined vs Reduced
0.7 atm H_2





With M.G. Burke etal U of Manchester

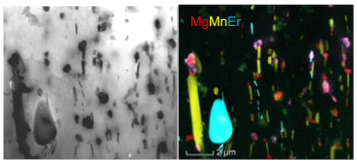
49

The Characterization Wish List

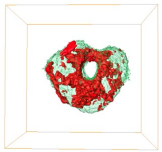
- Imaging resource with mm to sub-nm resolution ✓
- Imaging resource with spectrographic (elemental/ chemical/electronic) contrast ✓
- Capable of dynamic processes (time scales) ✓
- Capable of environmental conditions (in-operando) ✓
- Quantitative in all modes ✓
- Applicable to Hard & Soft materials ✓
- In multi-dimensions (x,y,z,t,…..) ✓
- Multi-modal platform which integrates other complementary resources (probes/signals) ✓
- Non intrusive → Non destructive ✓

50

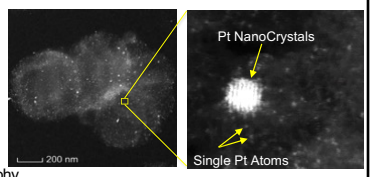
Dynamic In-situ, Multi-Modal Multi-Dimensional, Correlative High Spatial Resolution HyperSpectral Characterization



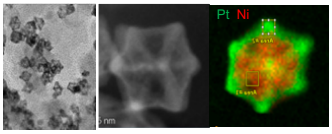
Materials Engineeering at the Meso->Nanoscale



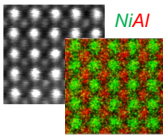
Ptychography/Tomography



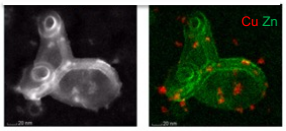
Nano Particle Enhancement of PS 1 Photocatalysts



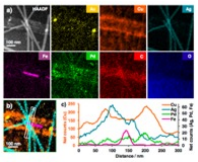
Molecular & Oxide Frameworks



Sub-nm HyperSpectral Channeling

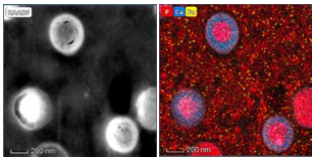


Heavy Metal Segregation - Polyamide Nanomembranes



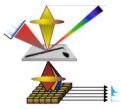
NP Evolution In-situ Gaseous/Liquid Media

Sub-Angstrom Resolution of 2D & Quantum Materials

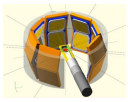


Role of Nanostructures in Bio-System Organelles

51



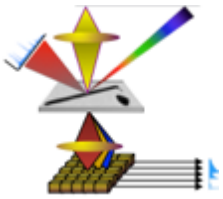
Answering Today's Science Questions: It all starts with getting the data



- New Hard and Soft Materials opportunities require advances in our ability to observe, characterize, simulate and control matter.
- The inherent complexity of materials requires measurements that are dynamic, in-situ and multi-modal to capture and understand phenomena.
- Current off-the-shelf resources are based upon both established technology and existing understanding of what can be done using mainly commerical instrumentation.
- Anticipation of future needs of the scientific community compels us to explore new areas of innovative methodologies/instruments to enable analysis and discovery.

52

If you can't detect it, then you can't measure it.



Thanks !

Questions ?

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Zaluzec@Microscopy.com

53