



STXM - in situ applications

Adam Hitchcock, Slava Berejnov, (BIMR, McMaster University)

PEM Fuel cells

Dmitri Bessarabov, Darija Susac (AFCC)



OUTLINE

- **Motivation**
- **Fuel cells**
- **Electrochromic devices**
 - with D. Guay (INRS)

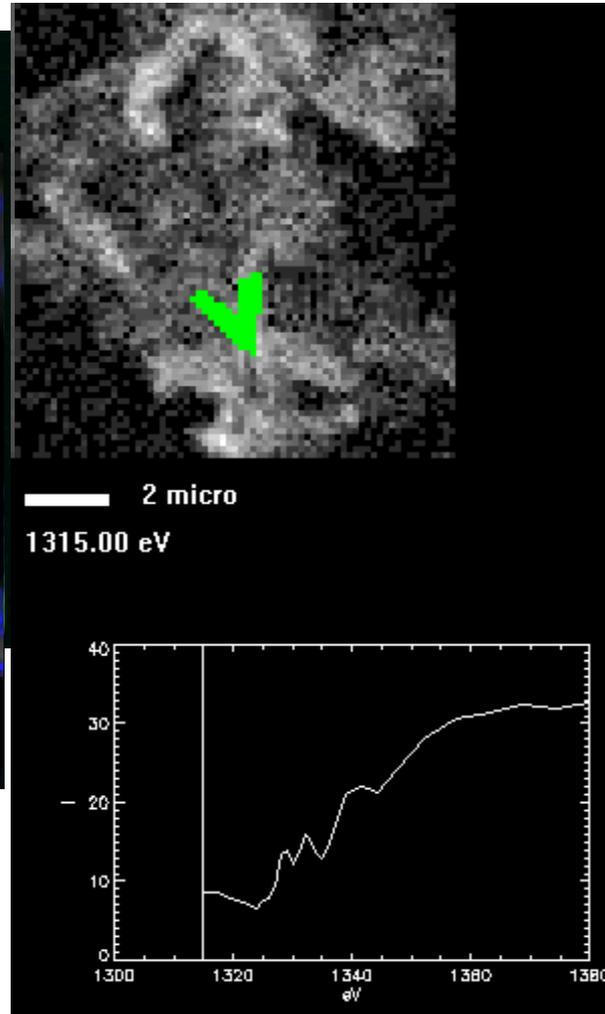
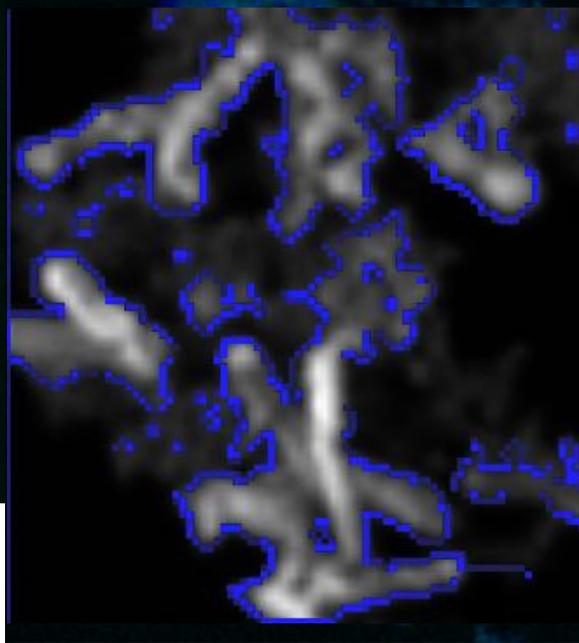




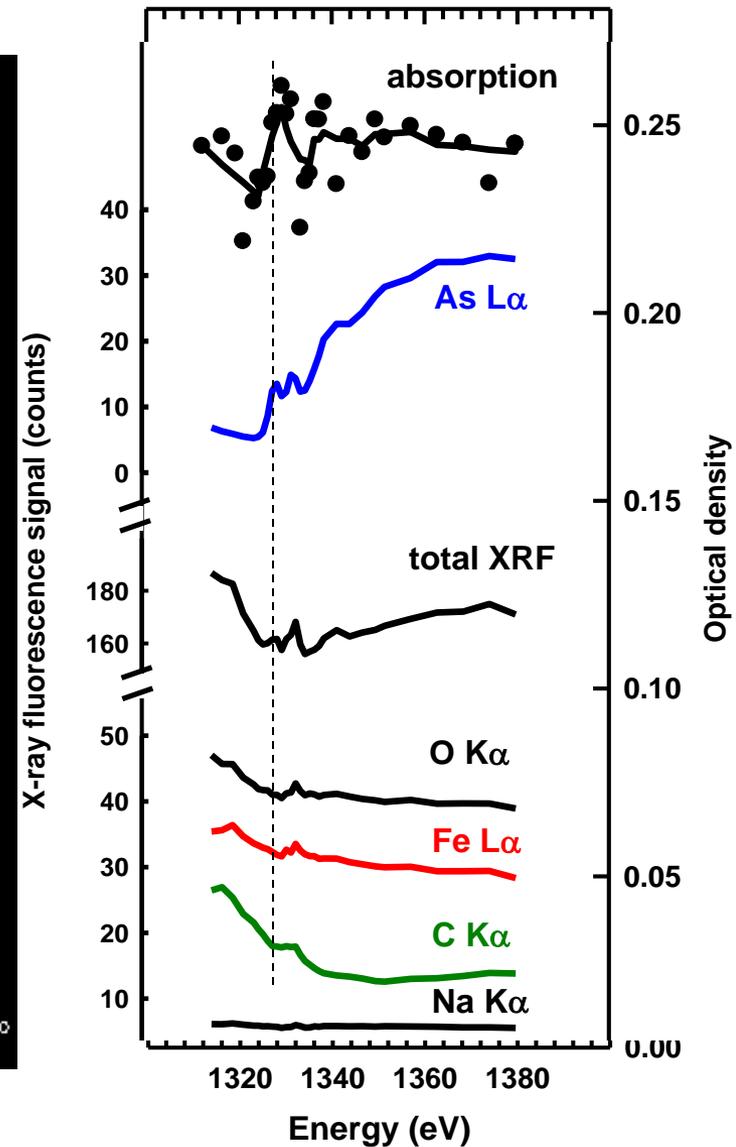
As 2p XRF-XAS stack

Stack of stacks

Fe map bio map (pre-Fe)



As L α XRF signal

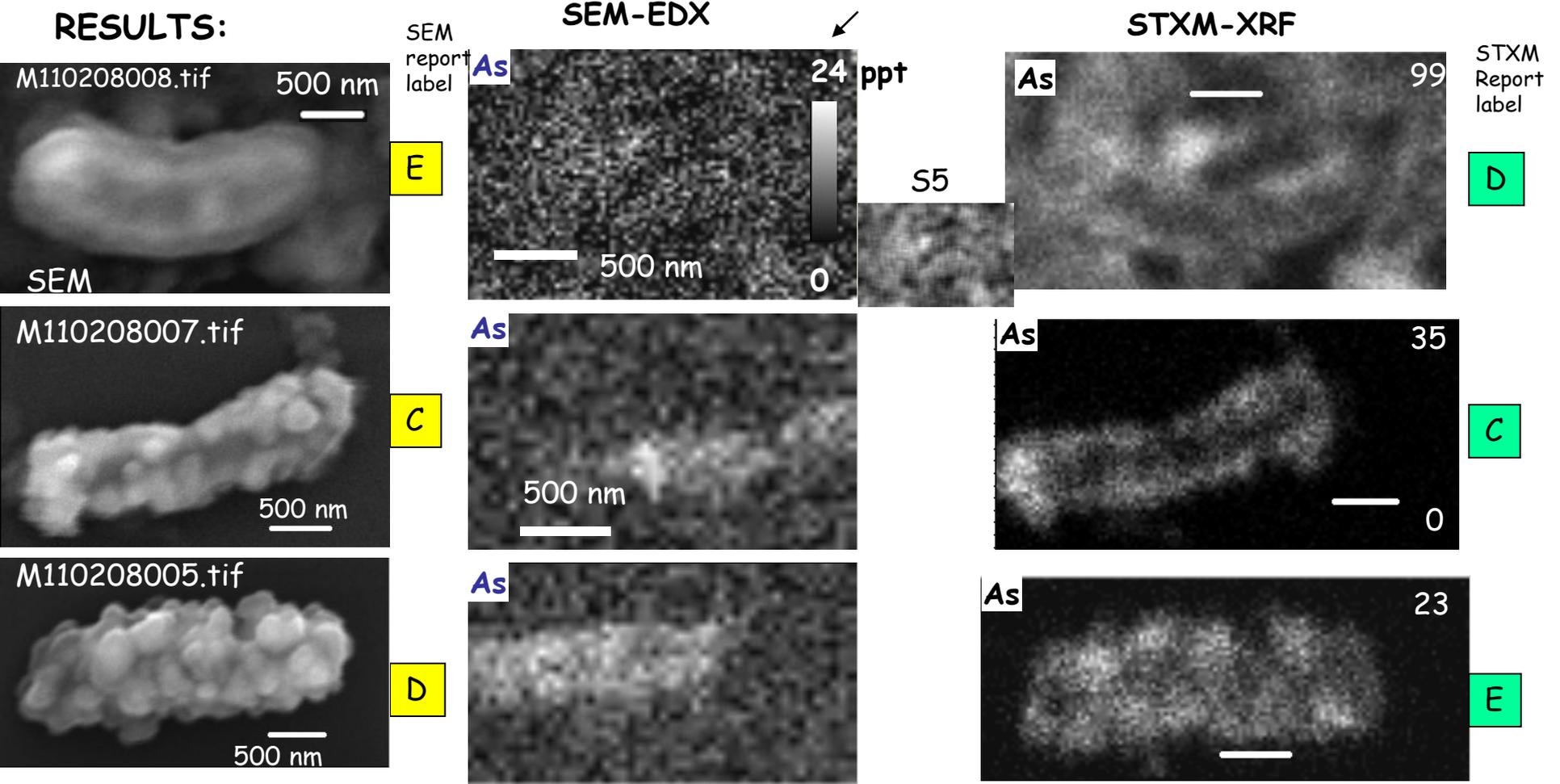


SEM-EDX of As:BoFeN

Adam Hitchcock, Marcia West (McMaster University), Tolek Tyliczszak (ALS), Martin Obst (Tuebingen)

GOALS: use Tescan Veag-3 Variable Pressure SEM and Oxford Xmax80 SDD to image and As map as in As:FeBoN bacterial sample - IDENTICAL individual cells examined by STXM

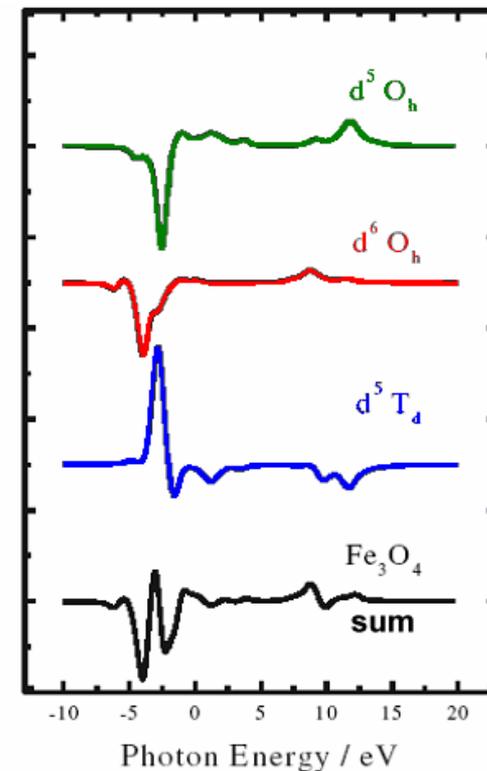
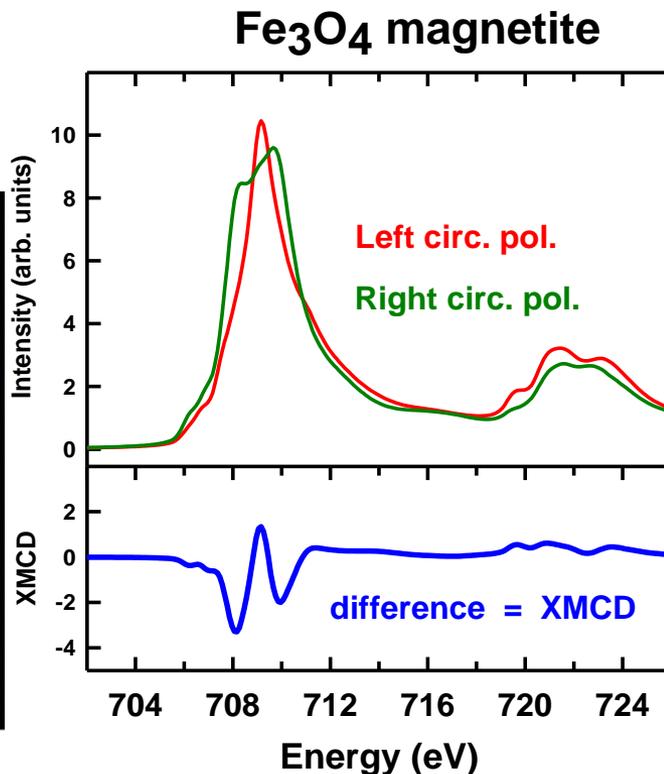
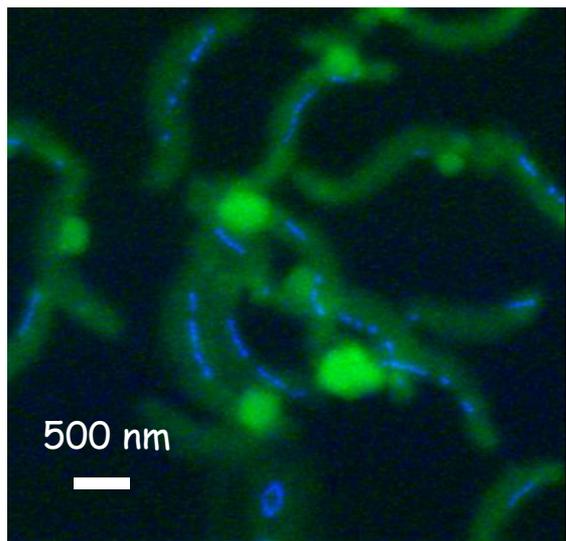
EXPERIMENTAL: sample returned from ALS; no additional Au coating; measured in SEM (continuously scanning beam) for ~7 hours
quantified from hot spot- see slide 20



Bio-magnetism studied by X-ray magnetic circular dichroism (XMCD)
Magnetosomes = nano magnetite single crystals (20-80 nm diam)

Magnetite:
Fe 2p spectra & XMCD

Fe^{II} (O_h) and Fe^{III} (O_h & T_d)
Calculated XMCD components



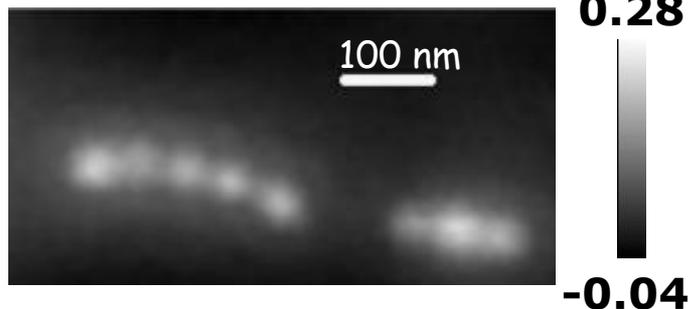
XMCD of magnetotactic MV-1

with U. Lins (Rio de Janeiro), D. Bazalinski (UNLV)

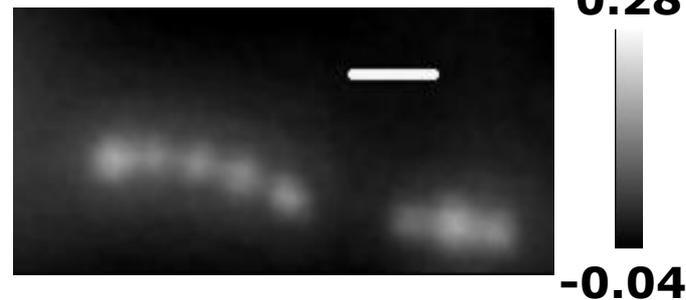
E = 708.1 eV - maximum XMCD signal

sample tilted 30° to project \underline{M} to \underline{S}

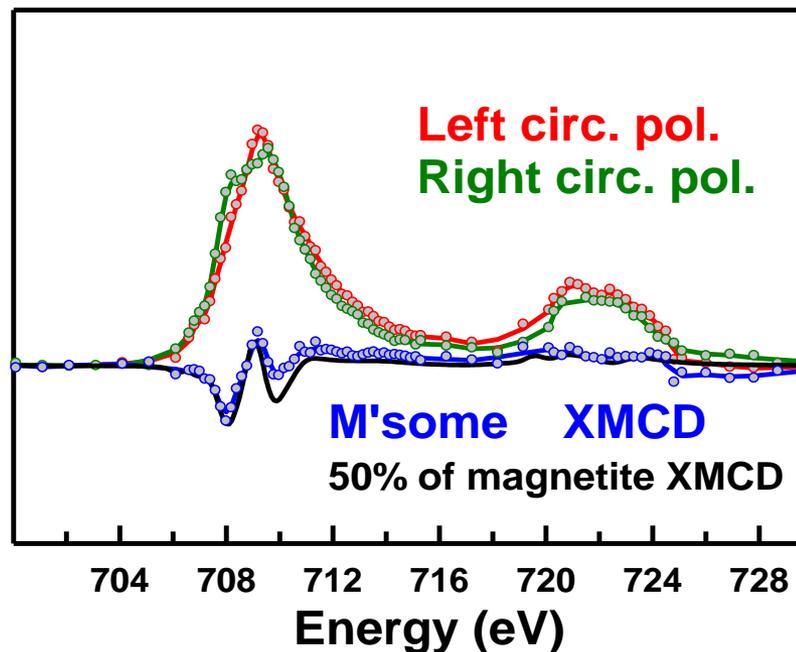
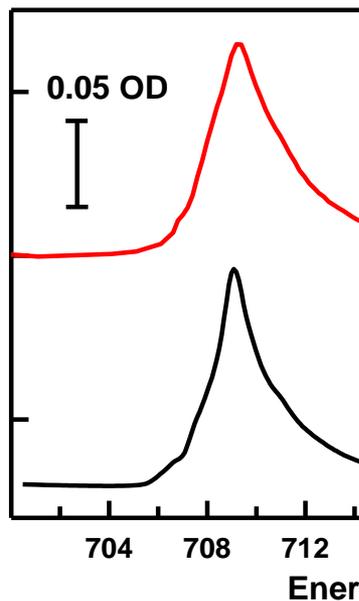
LCP



RCP



LCP = Left circular polarization

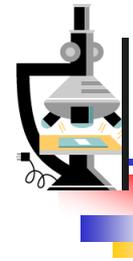


Linear polarization

magnetosome
average

Magnetite

Magnetite Fe 2p spectra courtesy E.J. Goering - see J. Mag. & Mag. Mats 310 (2007) e2493



Energy materials - motivation

Energy crisis exists & will get worse

Climate change - mankind's greatest challenge !

DoE initiatives

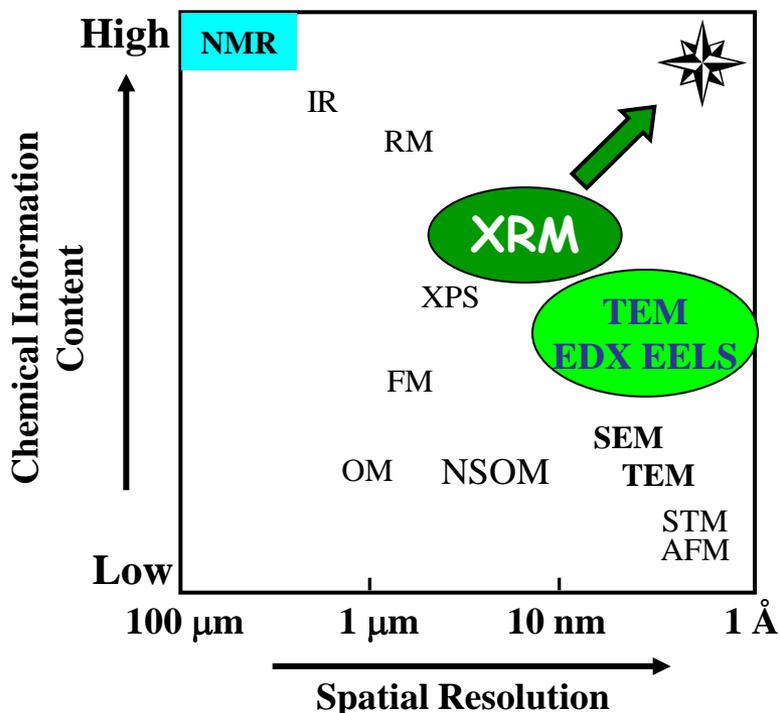
Synchrotron facilities

- microscopy
- spectroscopy
- *in situ* control

} powerful & versatile tools
for materials research

XRM & TEM vs. other techniques

GOAL: QUANTITATIVE CHEMICAL ANALYSIS at relevant spatial resolution

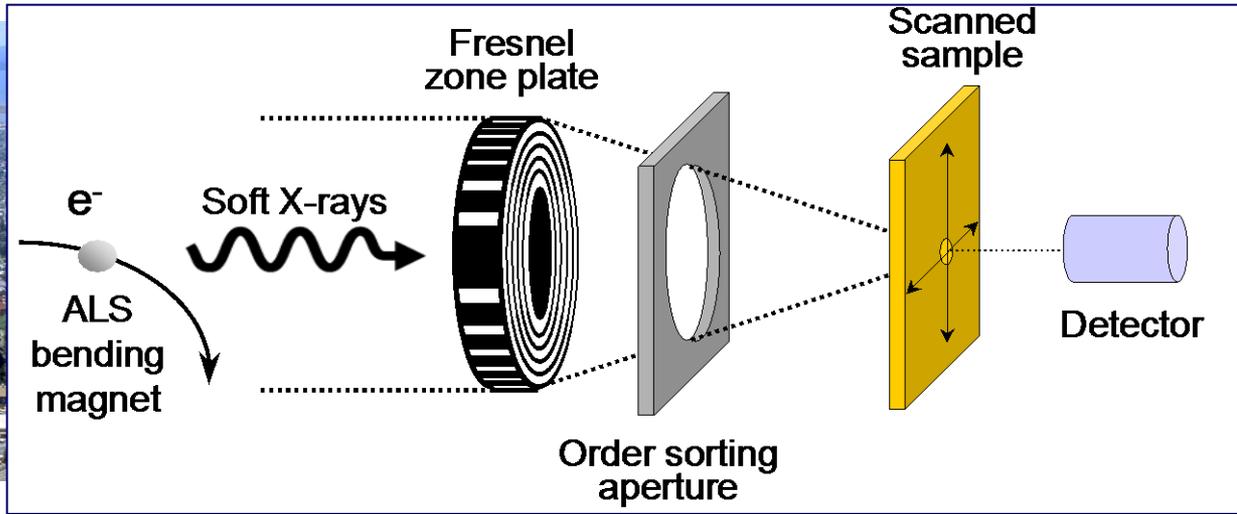


Technique	Spatial Resolution	Speciation Capability
nmr	> 1 μm	excellent
IR	> 1 μm	excellent
Raman	~0.3 μm	excellent
optical	~0.5 μm	needs chromophores
scanning probe	0.2-10 nm	variable
TOF-SIMS	~ 1 μm	excellent
EELS - (S)TEM	< 1 nm	good;

BUT . . . radiation damage !
wet samples & in situ are difficult

X-ray microscopy ~ 25 nm excellent
STXM radiation damage $10^3 <$ TEM-EELS (*)

* Direct comparisons of damage rates versus signal rates in STXM versus TEM-EELS
 J. Wang, G.A. Botton, M.M. West and A.P. Hitchcock, J. Phys. Chem B 113 (2009) 1869
 E.G. Rightor et al, J. Phys. Chem. B 101 (1997) 1950

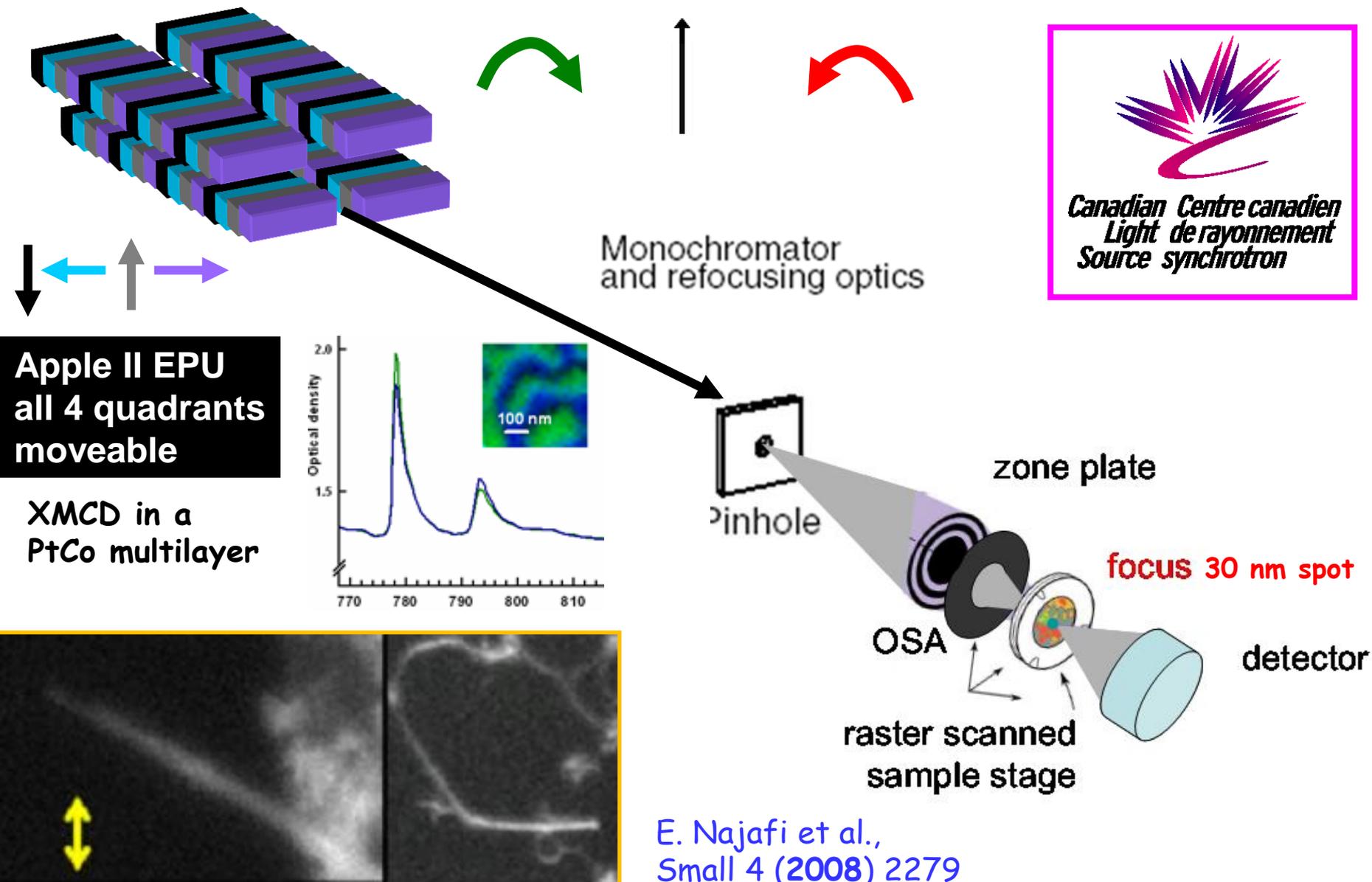


Chemical speciation through X-ray absorption spectra (NEXAFS)
 Spatial resolution ~30 nm; Energy resolution < 0.1 eV

- Beamlines 5.3.2 & 11.0.2 @ Advanced Light Source, Berkeley, USA
- Beamline 10ID1 @ Canadian Light Source, Saskatoon, Canada
- Transmission → **thin samples** (e.g. microtomed ~100 nm sections)

- Quantitative chemical mapping in 2d and 3d
- Quantitative molecular orientation mapping

STXM at CLS: orientation mapping



in situ STXM techniques

Tomography

Humid control / gas expose

Electrochemistry



Guay et al
Anal. Chem. 2005



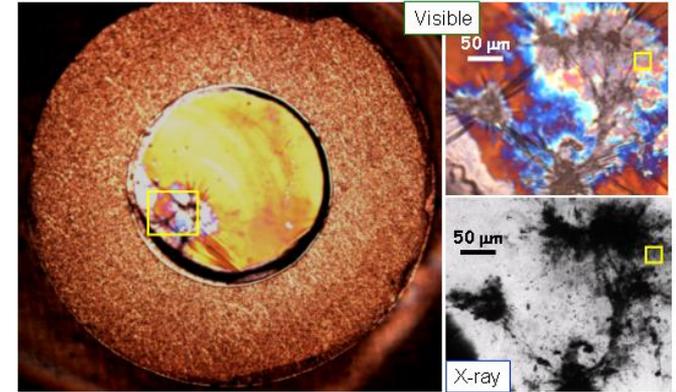
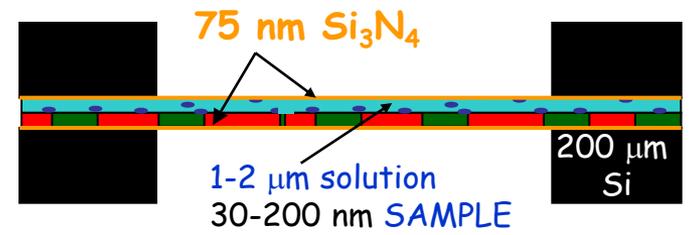
Johansson et al
JSR 2007



Lefevre et al
J Phys Conf 2008

Wet cells

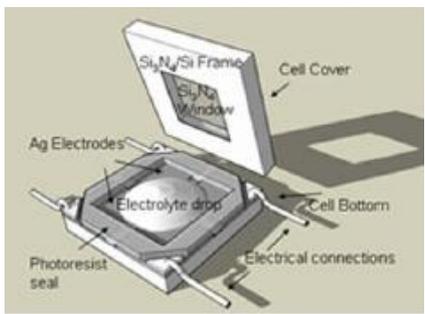
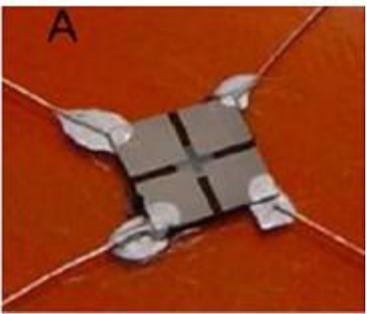
Gilbert SPIE 1992



30 nm polyimide Luxfilm™

Fluid flow / reaction cells

Gilles et al (2010)



in situ STXM techniques

Electrochemistry



Guay et al
Anal. Chem. 2005

Tomography



Johansson et al
JSR 2007

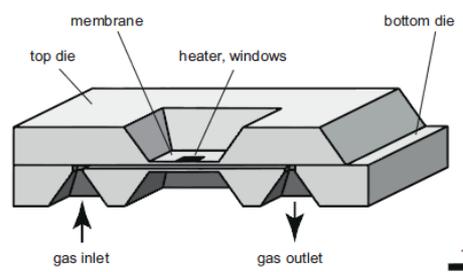
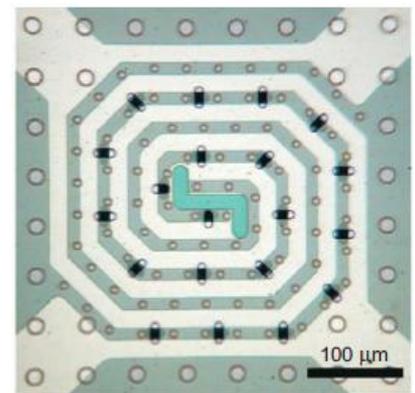
Humid control / gas expose



Lefevre et al
J Phys Conf 2008

In situ catalysis

High T (>500C), gas



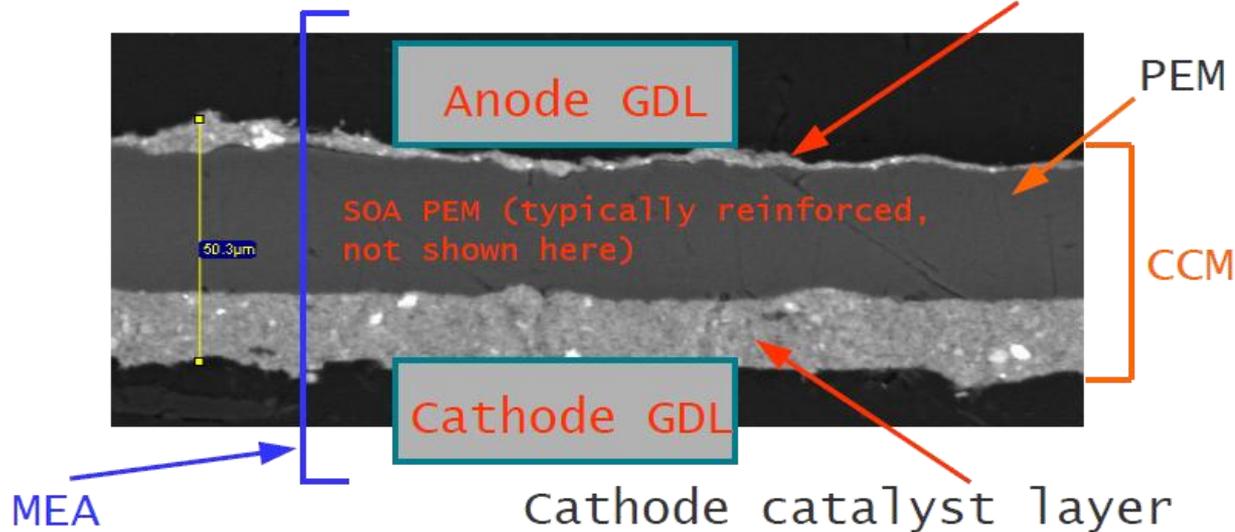
Creemer et al, Ultramic. 2008
de Smit Nature 2008



= Ford, Daimler consortium (formed 2008, in Vancouver)

- AFCC challenge - optimize performance, reliability, cost of hydrogen PEM fuel cells
- STXM mapping of critical components in membrane electrode assemblies (MEA)
- Catalyst migration - common failure mechanism

Anode catalyst layer



CCM = catalyst (e.g. PtCo) coated membrane

Bessarabov & APH Membrane Technology 6 (2009) 6
 Susac et al, ECS Transactions 33 (2010) 391

Thanks to
Slava Berejnov
 Marcia Reid - microtoming
 AFCC - funding & samples
 NSERC
 DoE - BES (ALS)

- A hydrogen-based fuel cell power train system must meet a number of demanding requirements to become commercially viable. Relative to existing systems, improvements in fuel economy, power efficiency, durability, and cost are needed.
- A typical automotive duty cycle consists of load transients and holds, periods of idling, and start-up/shutdowns, all at various relative humidity's and temperatures.
- Load/potential cycling in a FCV contributes to various operating conditions that may accelerate degradation of MEA components.
- Understanding the relationship between operating conditions and degradation mechanisms allows for the development of more robust fuel cells.
- Understanding the structure - performance relationship between the CL and FC

- ~~Fuel and oxidant purity are a concern - the FC catalysts are poisoned by CO, NO, etc. (*)~~
- Water transport and hydration levels in the membrane are critical

BOL = beginning of life

versus

EOL = end of life

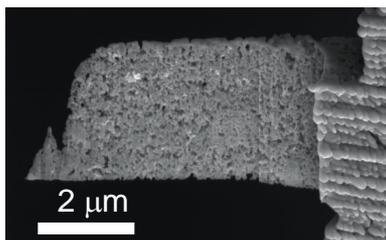
Slava Berejnov, Adam Hitchcock (McMaster); Darija Susac (AFCC); Silvia Wessel (Ballard)

ionomer mapping

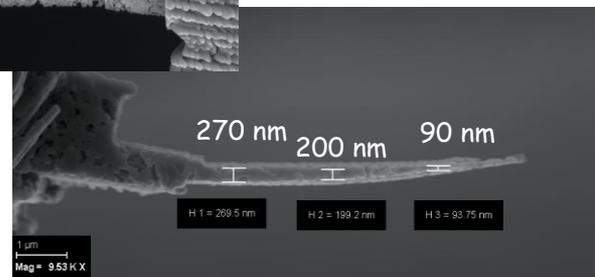
critical to performance. STXM is used to map with 30 nm spatial resolution the ~10-20% of ionomer in the catalyst layers (CL)

porosity mapping

* 2-d and **3d** pore mapping

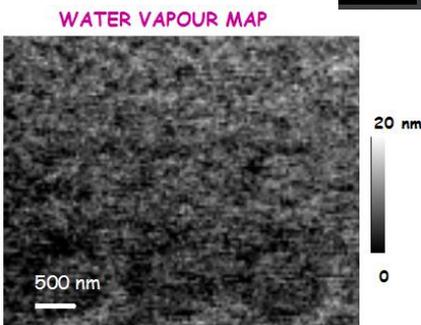
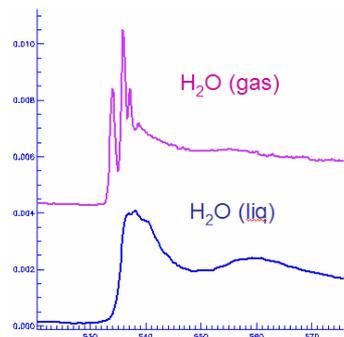
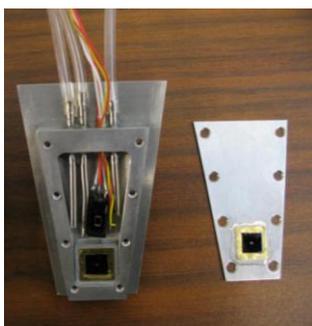


FIB, CCEM



vapor / liquid water mapping

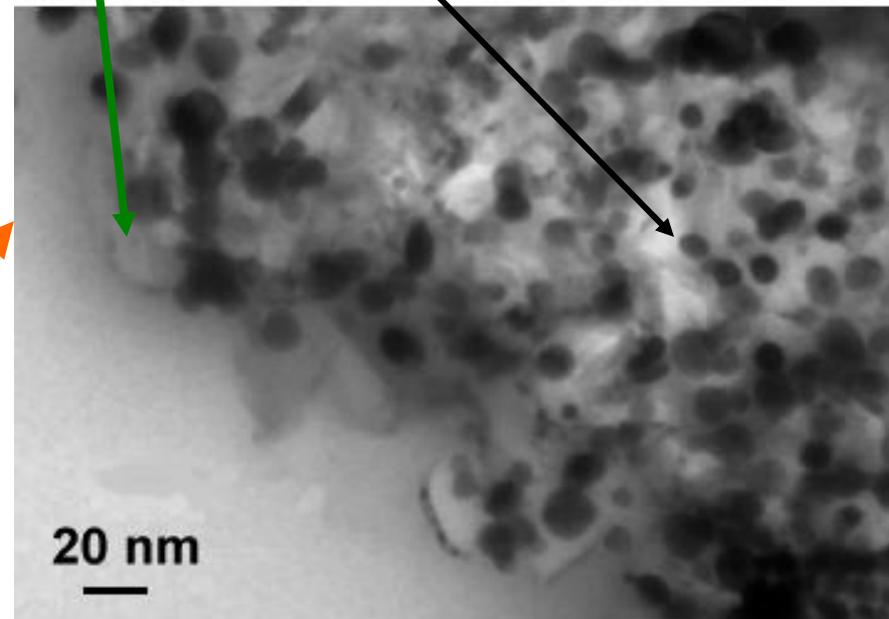
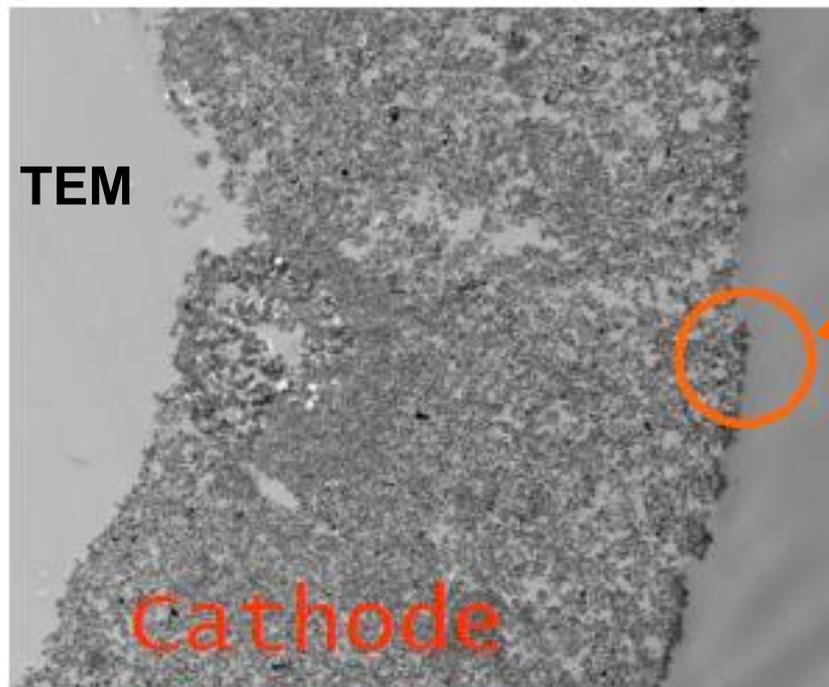
* environmental cell with controlled relative humidity (RH) is used to examine changes in MEAs (CL and membrane) when hydrated.



Structure of catalyst coated membranes (CCM)

CCM/electro-catalyst is nanotechnology with hierarchical structure

- **Pt nano-particles** (2-4 nm) on C support particles
- Aggregates of C primary particles
- Branched structures to produce proper porosity
- Mixed with **perfluoro-sulfonic ionomer**

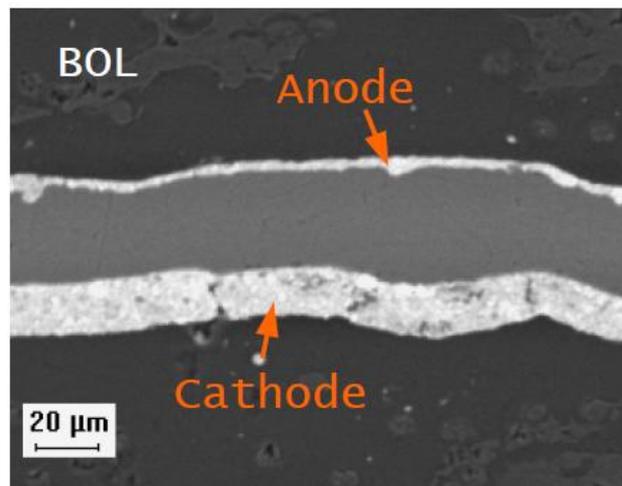


Components which may degrade during operation:

- Polymer electrolyte membrane (PEM)
- Catalyst layer ionomer
- pure Pt or PtX alloy catalyst
- Carbon support

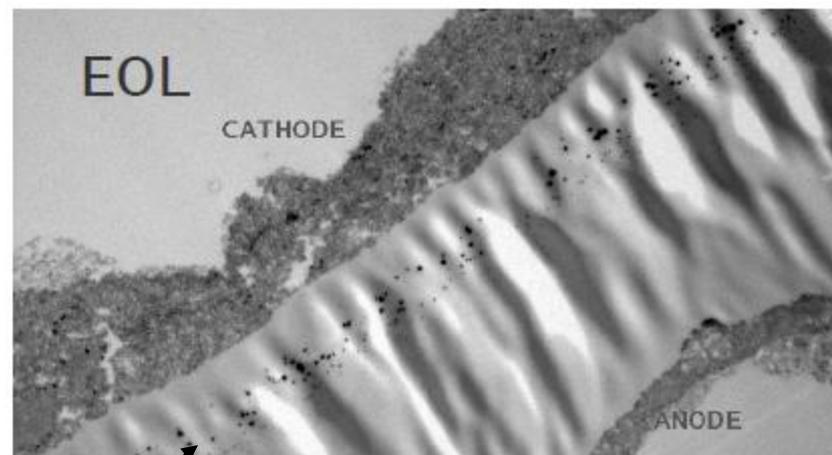
Degradation of CCM - most obvious is coarsening and migration of the catalyst into PEM

Beginning of life (**BOL**)



Accelerated
operation
under
simulated
automotive
conditions

End of life (**EOL**)

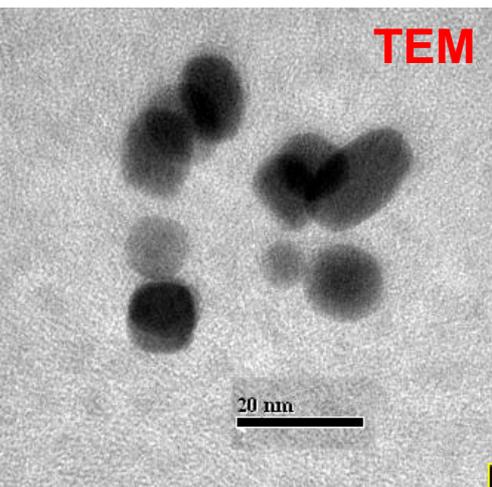


TEM

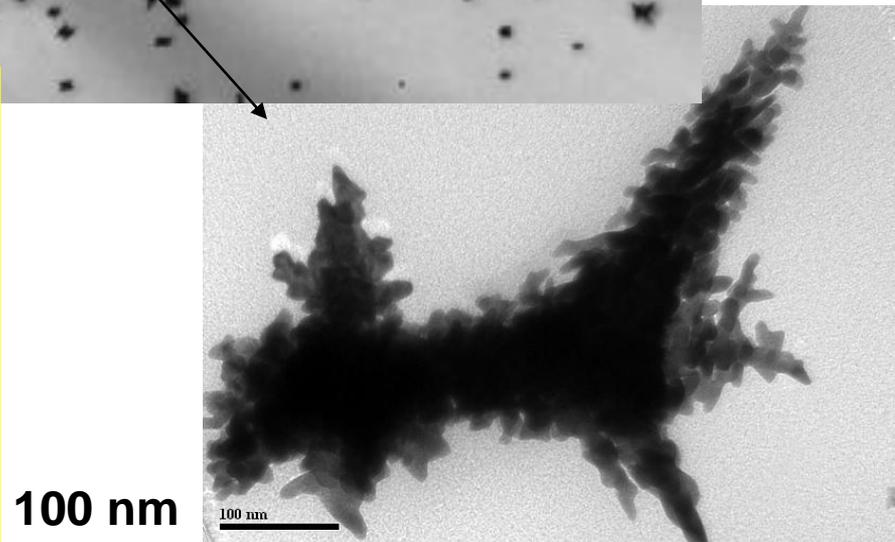
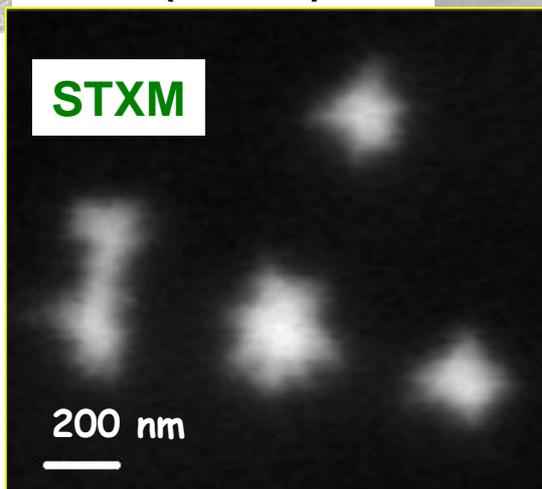
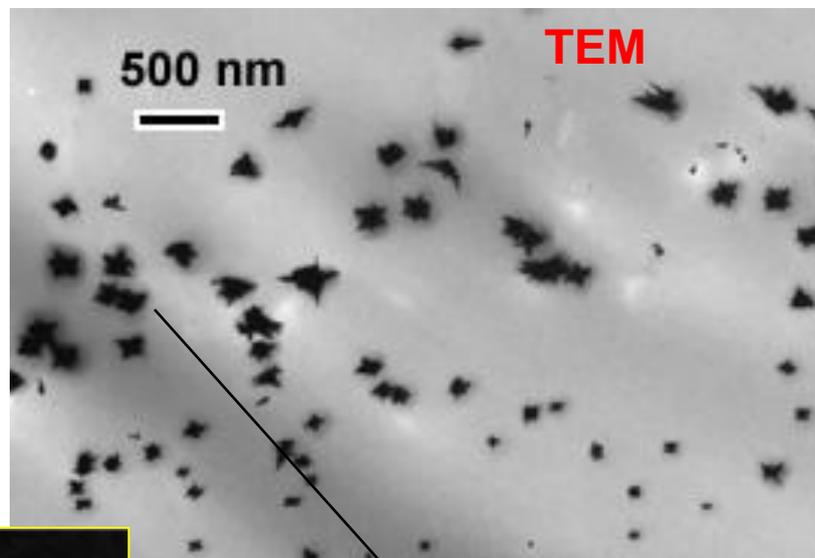
Pt band forms ~5-10 microns away from the cathode-PEM interface

Current model: Under certain operating conditions, Pt dissolves (as ion) and migrates into PEM where it is reduced to metallic Pt by hydrogen permeating from the anode

BOL - at edge of CCM

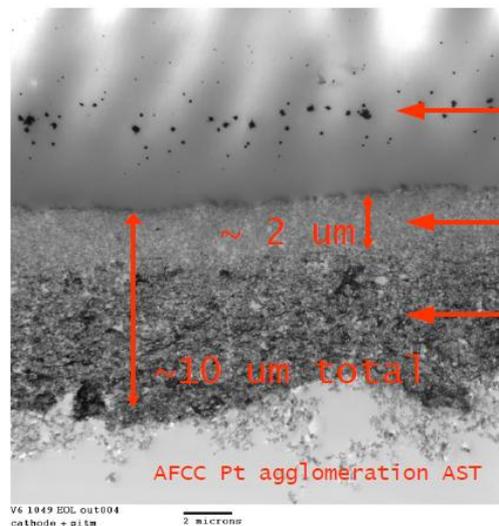


OD (282 eV)

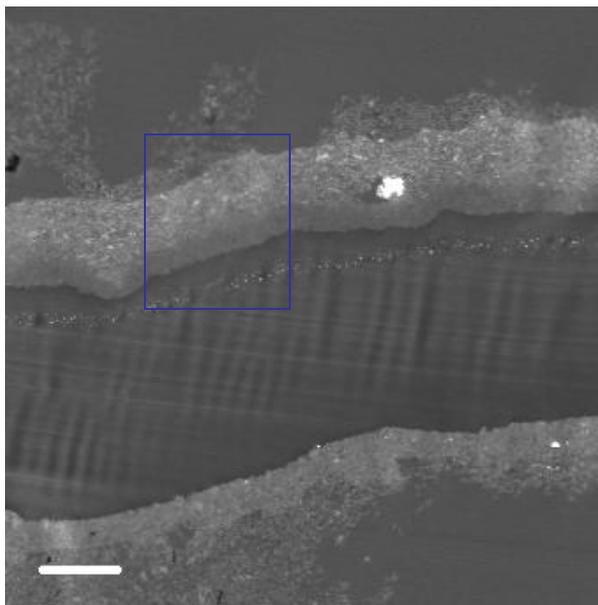


Change in density / structure in $\sim 2 \mu\text{m}$ band of cathode by membrane visualized by **SEM & TEM**

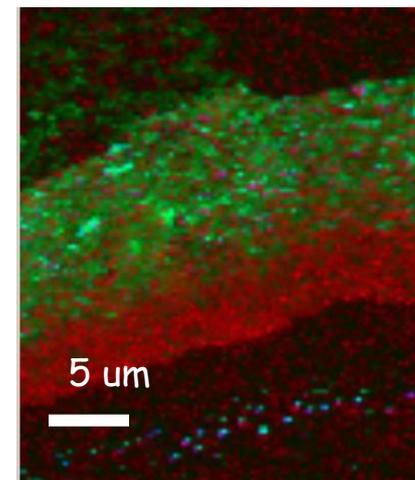
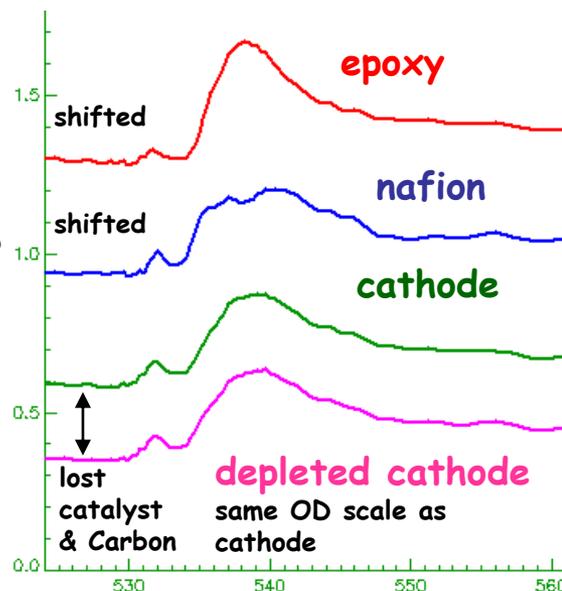
Also clear in **STXM** ... & can obtain chemical analysis



Pt band in PEM
Pt depleted CL
Initial CL



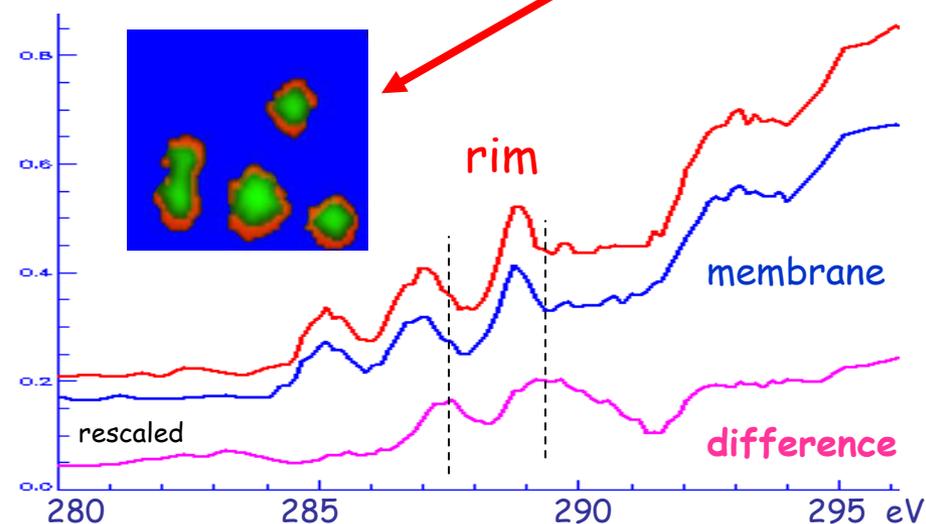
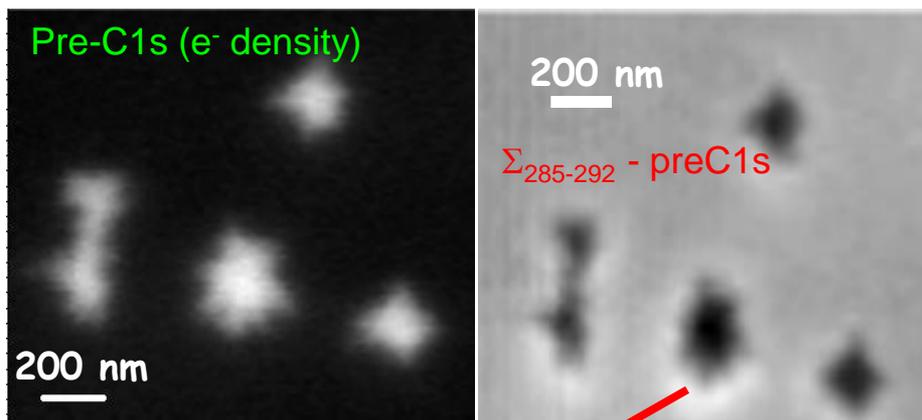
O 1s analysis



Depleted region
Regular cathode
Catalyst (high-Z)

10 μm

Chemical maps from C 1s stack



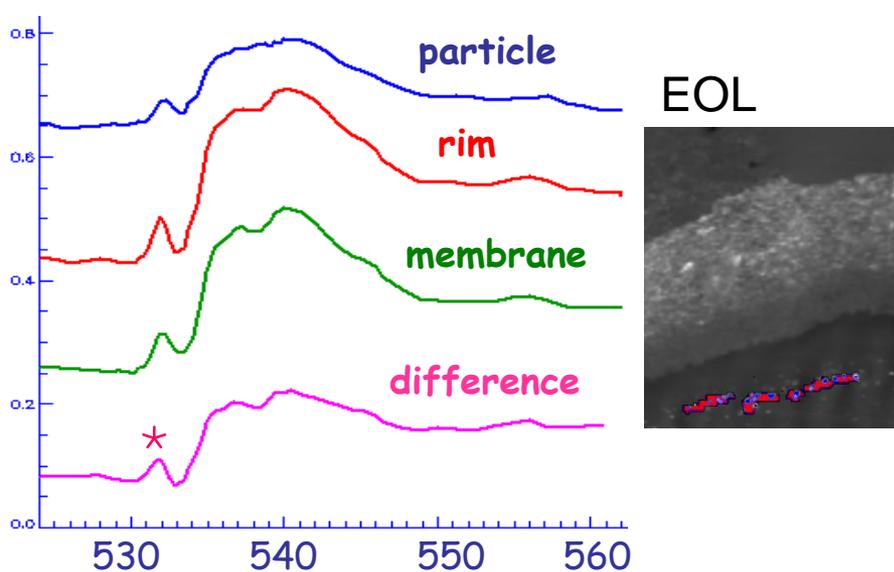
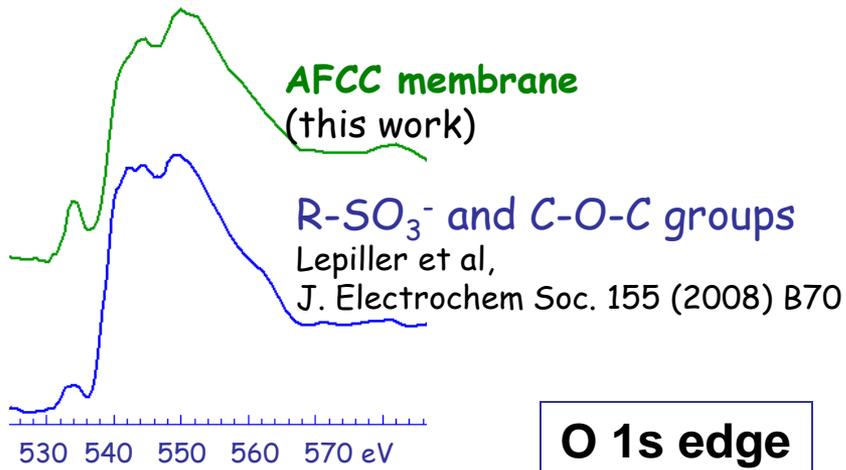
C 1s spectrum around Pt particles differs from that of the PEM membrane

Two additional spectral features at 287.5 eV and 289.4 eV - most likely C 1s $\rightarrow \pi^*_{C=O}$ transitions of ketone/aldehyde (287.5 eV) and carboxylic acid (289.4 eV) groups.

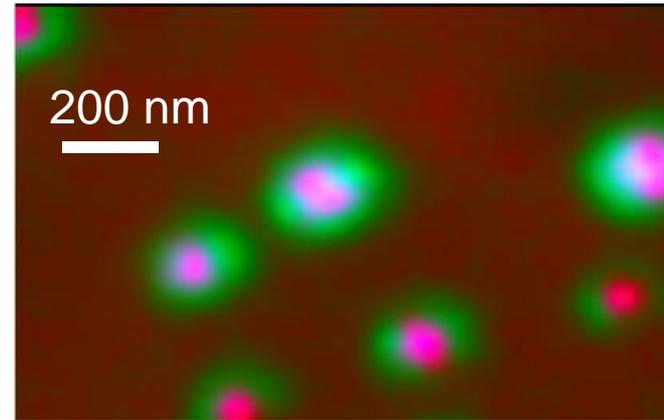
Possible origins of these additional organic components:

- * **indirect** - associated with radical damage to PEM, local to Pt particles
- * **intrinsic** - from 'ligands' of Pt ion that migrates from CCM into membrane

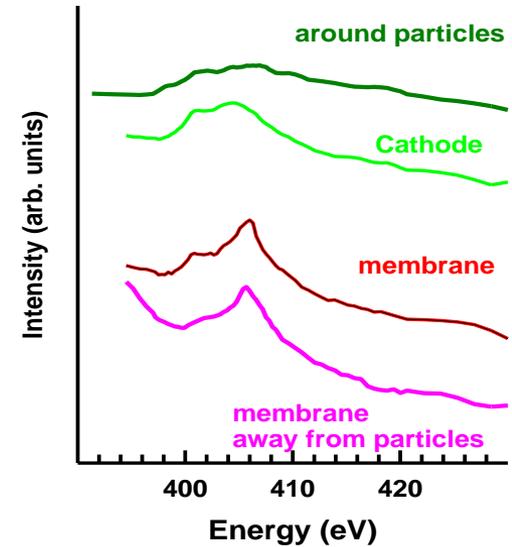
If 'intrinsic', similar spectral features similar to those around Pt particles in EOL MEA, should be found in the initial CCM



Nafion-like
"cathode"-like
Pt-particle



N 1s edge



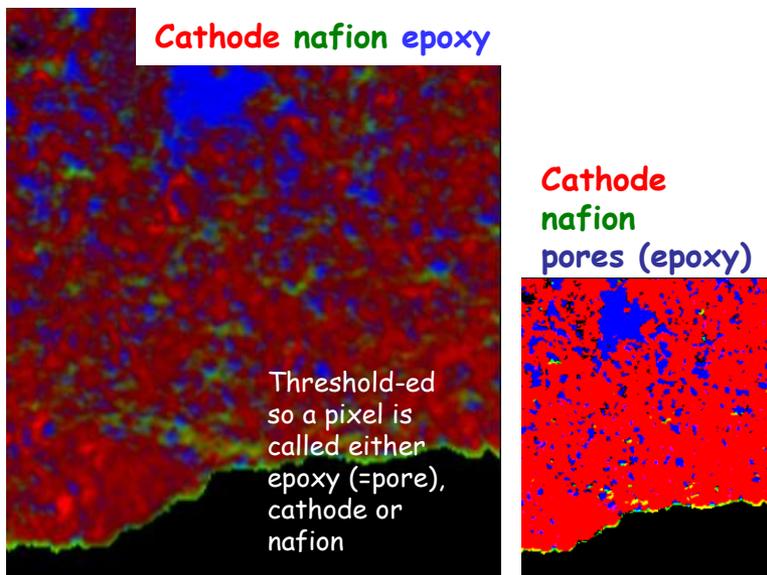
The same N-containing species that are in the cathode region are found in association with the Pt particles in the membrane

For cathode

- Embed MEA with non- or low penetrating medium; and map gaps (difficult to microtome)
- Infiltrate MEA with amine-epoxy; microtome; use STXM spectromicroscopy to map the resin = pores

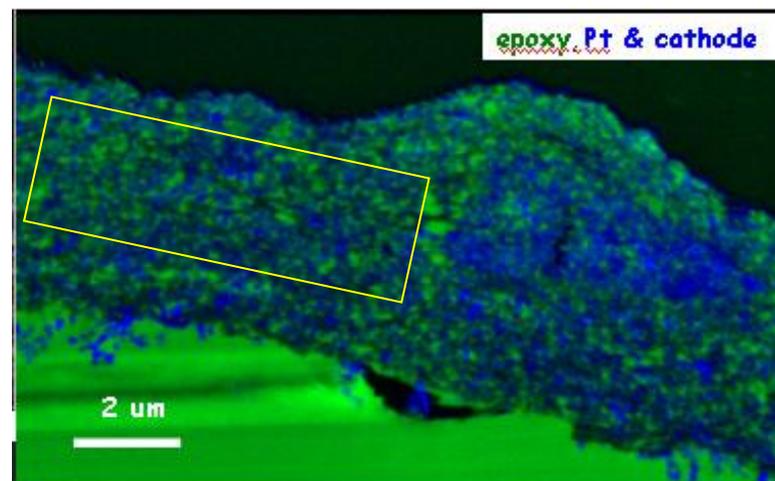
Done by careful control of embedding procedure and TEM (K.L. More and K.S. Reeves (ORNL) 2005)

Sample A - low porosity

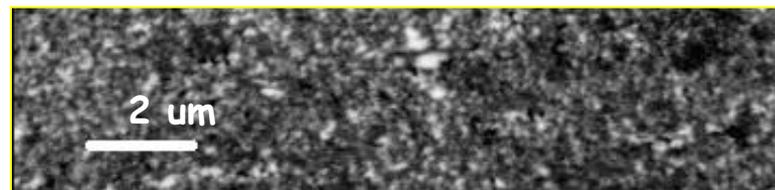


→ 27% pores

Sample B - high porosity



Epoxy map rotated - epoxy = pores



→ 63% pores

May be too high if epoxy swells the pores in the cathode

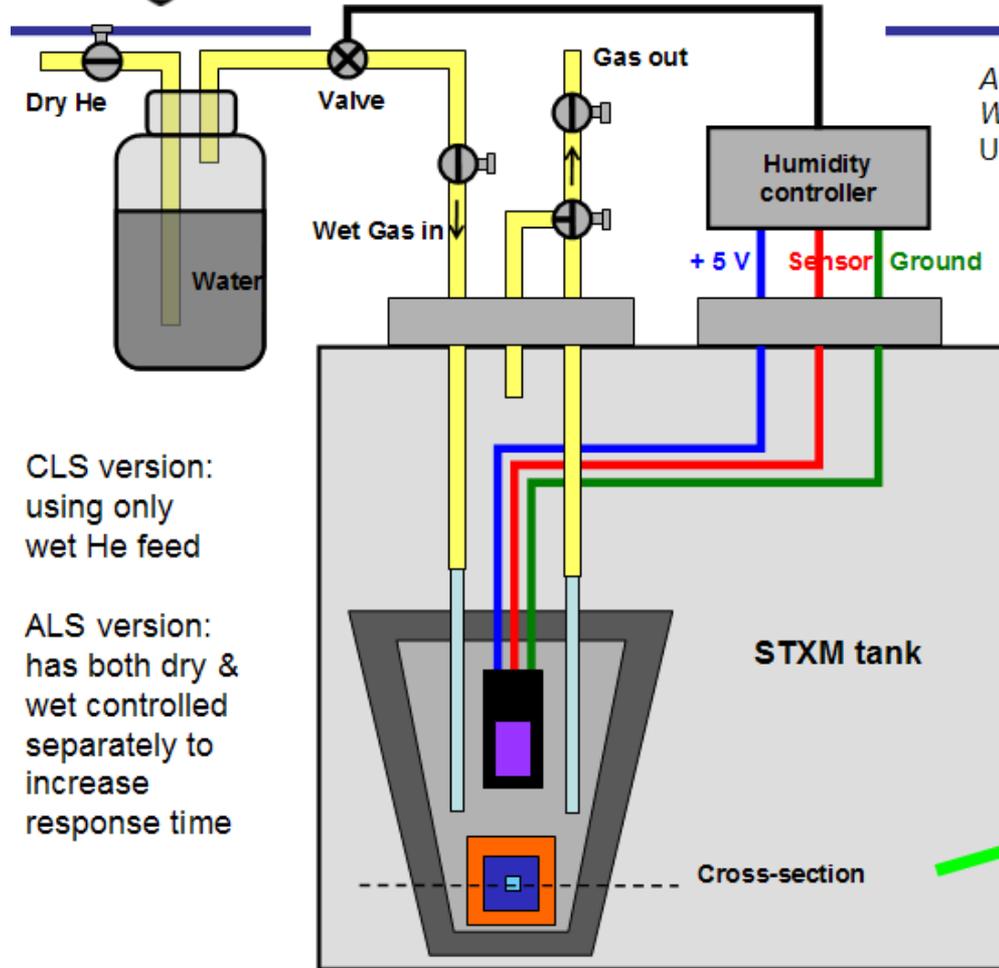


STX: Fuel cell MEA under controlled humidity

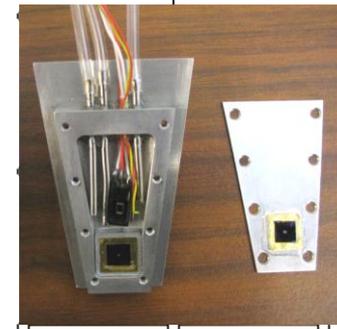
Slava Berejnov, Adam Hitchcock (McMaster); Darija Susac (AFCC)



Humid cell



Adam Hitchcock, Martin Obst, Jian Wang, Glyn Cooper (McMaster University)



X-ray

Sample

Teflon gasket

CLS version:
using only
wet He feed

ALS version:
has both dry &
wet controlled
separately to
increase
response time

GOAL: set up a fully operational fuel cell inside STXM & investigate:

- * transient species formed under certain potential / power regimes (e.g. H_2O_2)
- * failure mechanisms (carbon corrosion, Pt migration)
- * gradients of reagents, liquid and vapor water under various conditions including potential, "RH", and temperature

CHALLENGES

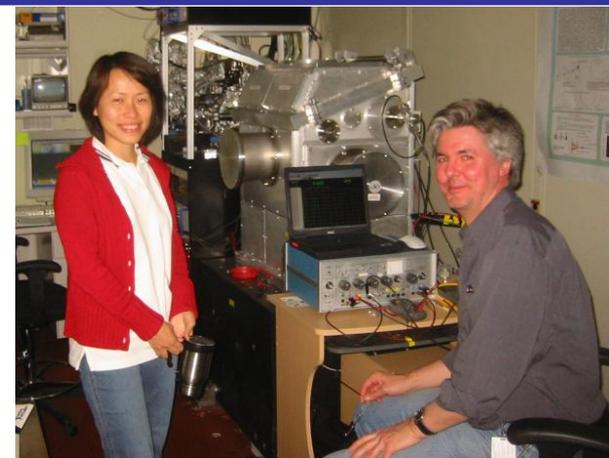
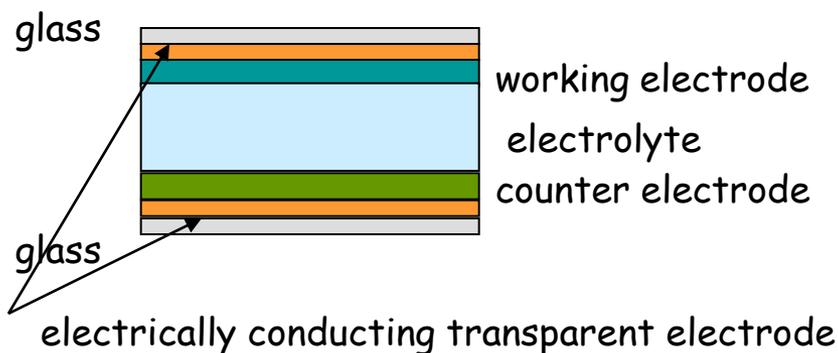
- * sample preparation - preserving structure and chemistry
- * contacting electrodes (positioning microtomed section)
- * separating H_2 from direct contact with oxidant

WHAT IS FEASIBLE NOW ?

- * controlled humidity
- * potential control
- * variable temperature (-40 C to + 100 C)

* **SMART WINDOWS:** conducting polymer films that change their optical properties as a function of potential

Typical electrochromic device



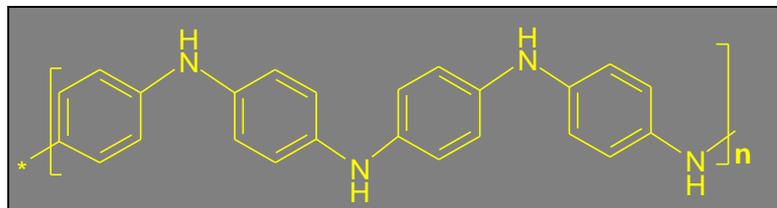
ALS polymer STXM on beamline 5.3.2 at the Advanced Light Source. **Sherry Zhang** and **Daniel Guay** after first successful in situ Echem-STXM (April 2004)

While many systems are known, development of practical devices is dependent on solving problems of switching speed, power consumption, chemical stability, thermal stability, etc

- * **Can *in situ* Echem-STXM measurements through multiple electro-chemical cycles investigate the relationship of performance to morphology . . .**
- on the sub-100 nm scale?**
- on the msec time scale?**

Polyaniline - NEXAFS

leucoemeraldine (yellow)



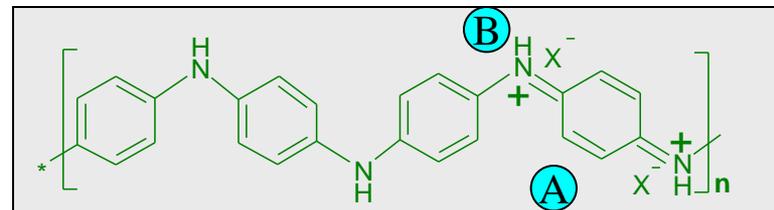
oxidation



reduction



emeraldine salt (green)



Large spectral changes when converted from reduced to oxidized state

C 1s

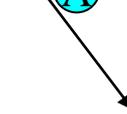
OXIDIZED (green)

REDUCED (yellow)

quinone ring

$\pi^*_{C=C}$

(A)



280 285 290 295

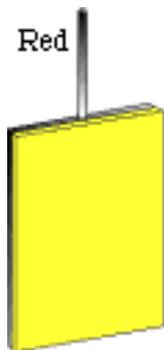
N 1s

OXIDIZED (green)

REDUCED (yellow)

$\pi^*_{C=N}$

(B)



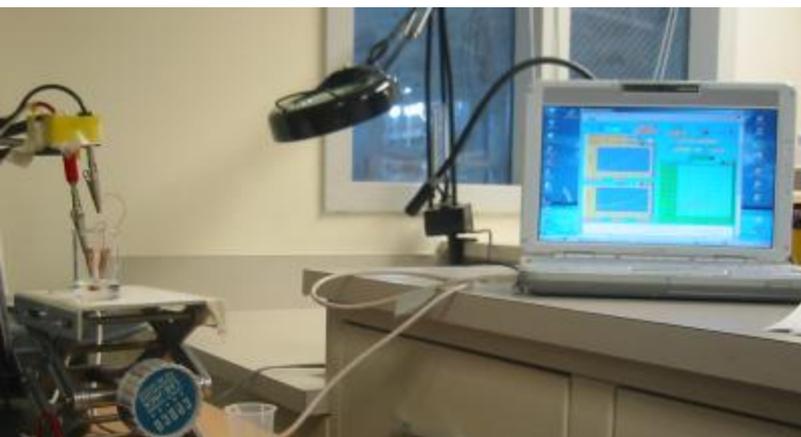
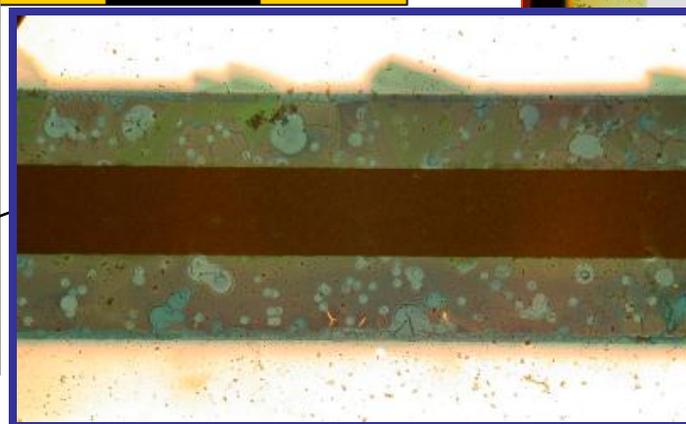
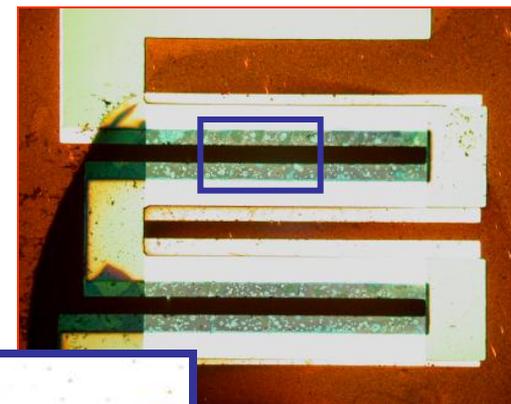
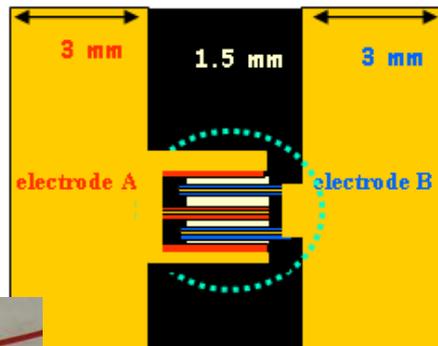
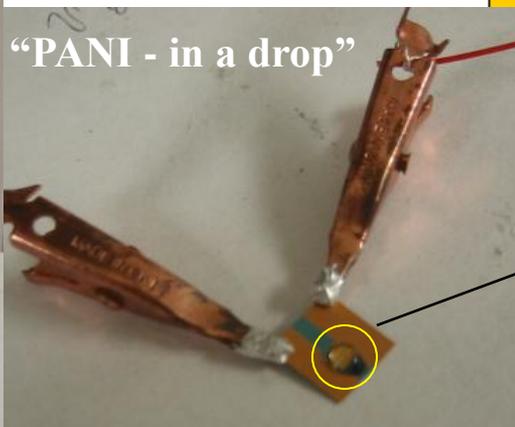
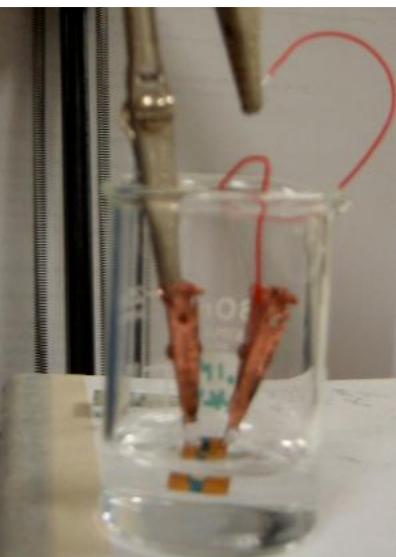
390 400 410 420 430

see also Magnuson et al, J. Chem. Phys. 111 (1999) 4756 *X-ray absorption and emission of polyaniline*

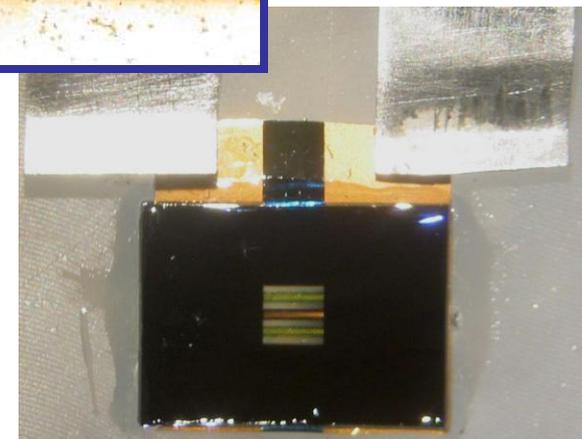
Guay et al., Analytical Chemistry 77 (2005) 3479

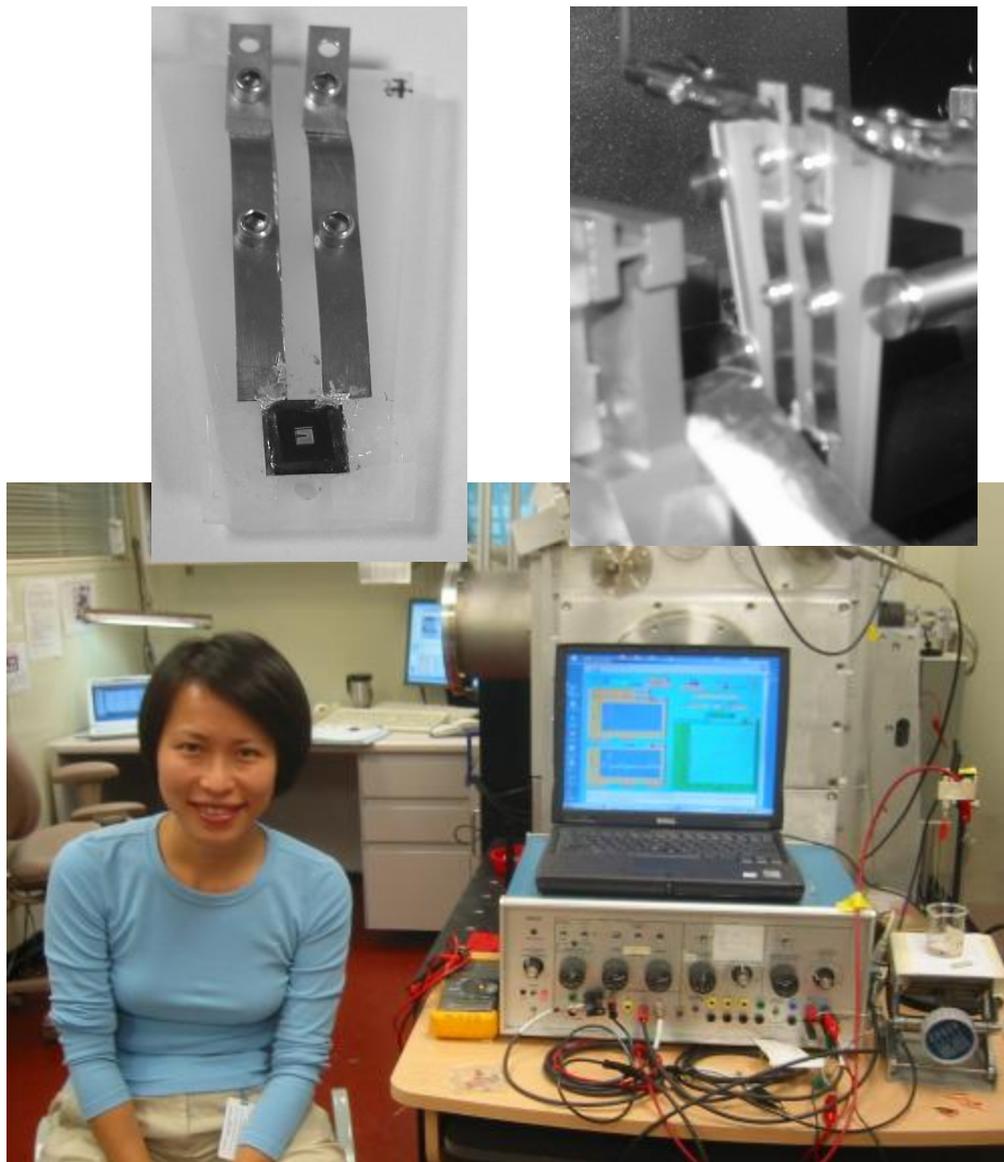
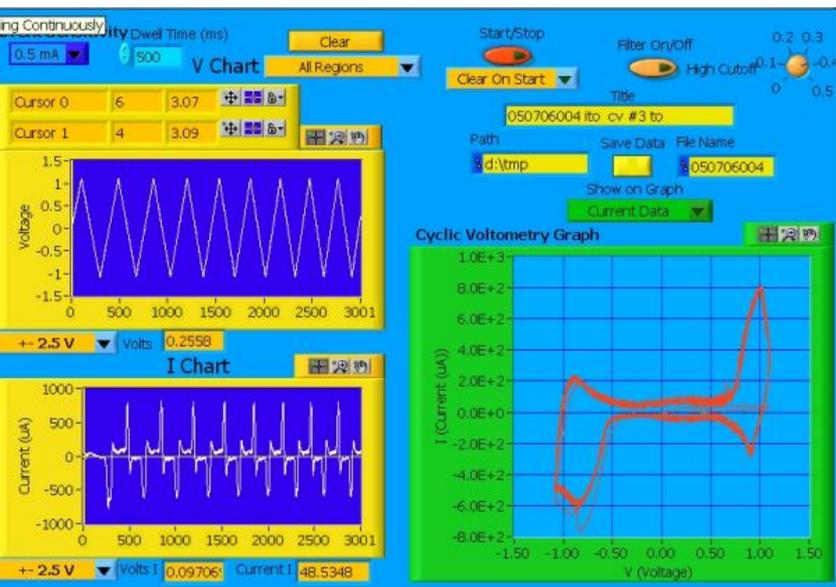
NLS2 Workshop, BNL, 20 May 2011

Polymerizing aniline on STXM
ECHEM window



1. prepare PANI layer ex situ
2. confirm suitable thickness
3. mount, add $\sim 1 \mu\text{l}$ 0.1 M HCl
4. position top window
5. seal with epoxy
6. check contacts
7. confirm non-ohmic + electrochemically active



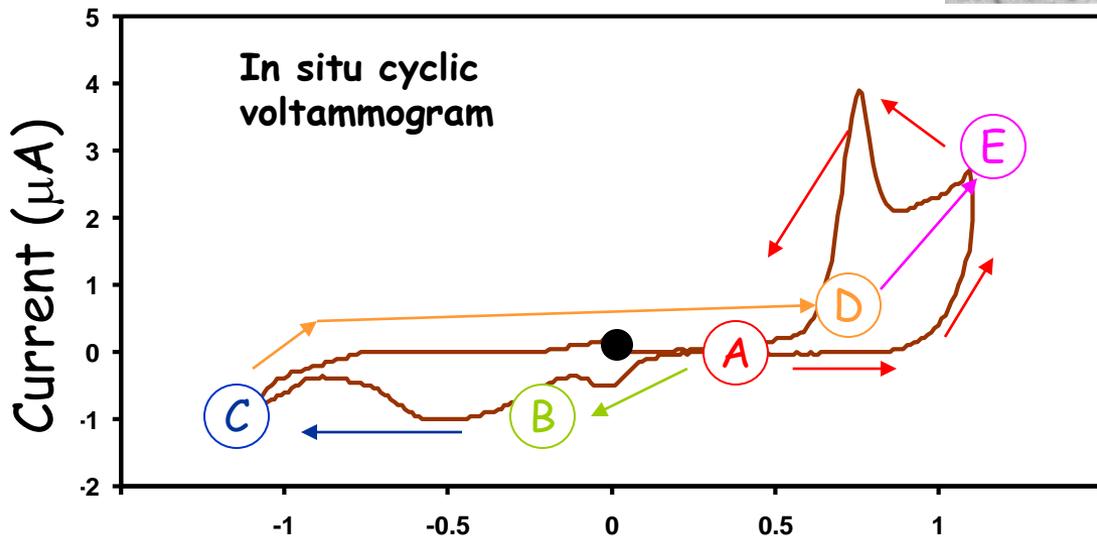
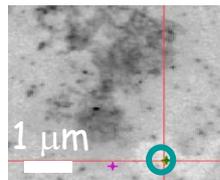
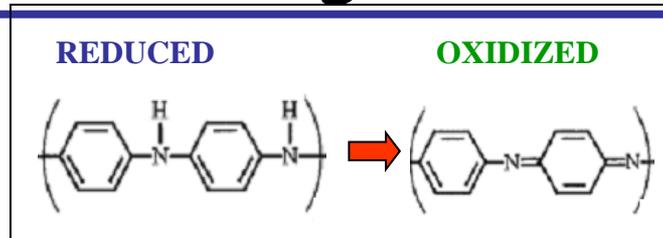


Potentiostat + Labview acquisition program

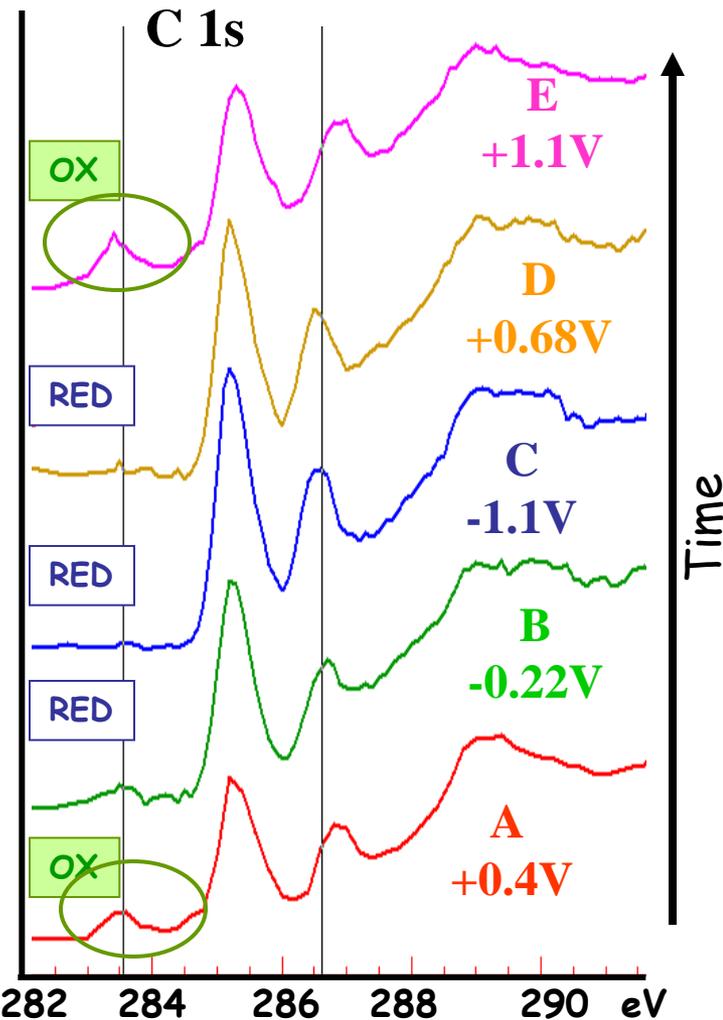
STXM_control reads potential for time synchronization

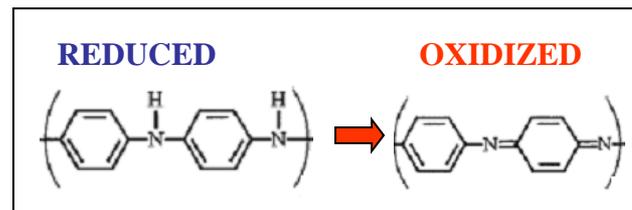
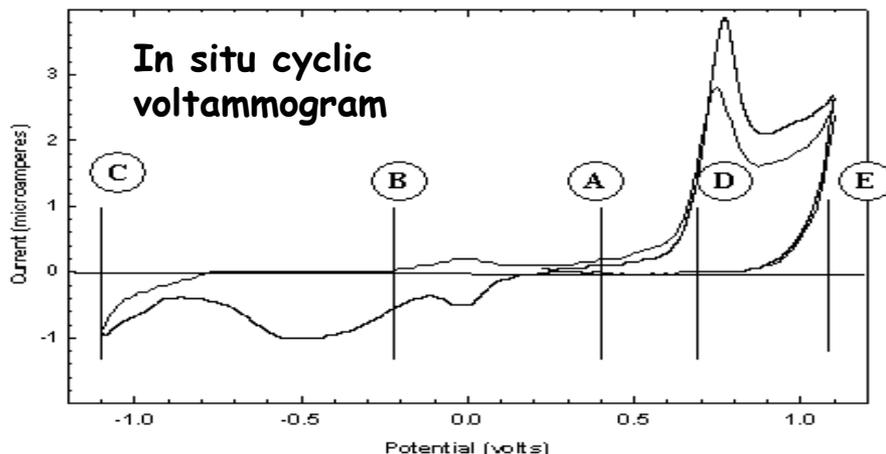
Tracking electrochemical changes

- Scanning Transmission X-ray Microscopy (STXM) used to track *in situ* electrochemical changes - **reduced** \longleftrightarrow **oxidized polyaniline**
- sample electropolymerized *ex situ*
- wet cell with $\sim 1 \mu\text{m}$ of 1 M HCl electrolyte
- spectra at a single point as f(potential)



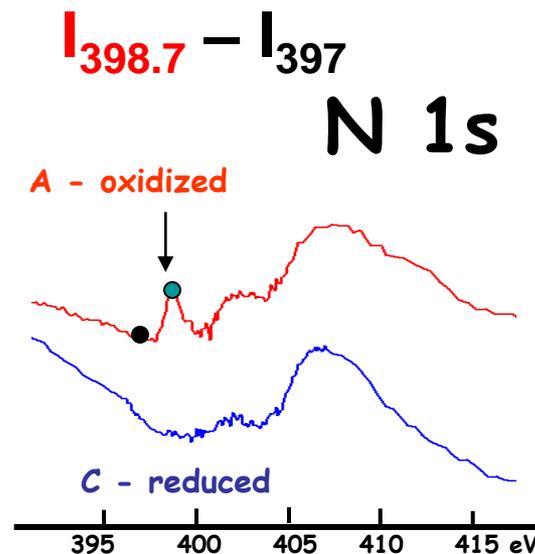
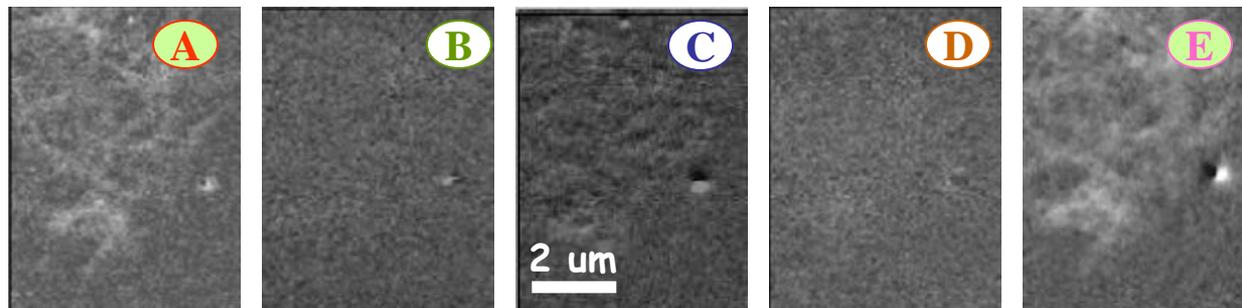
Visible light microscopy (ex situ)

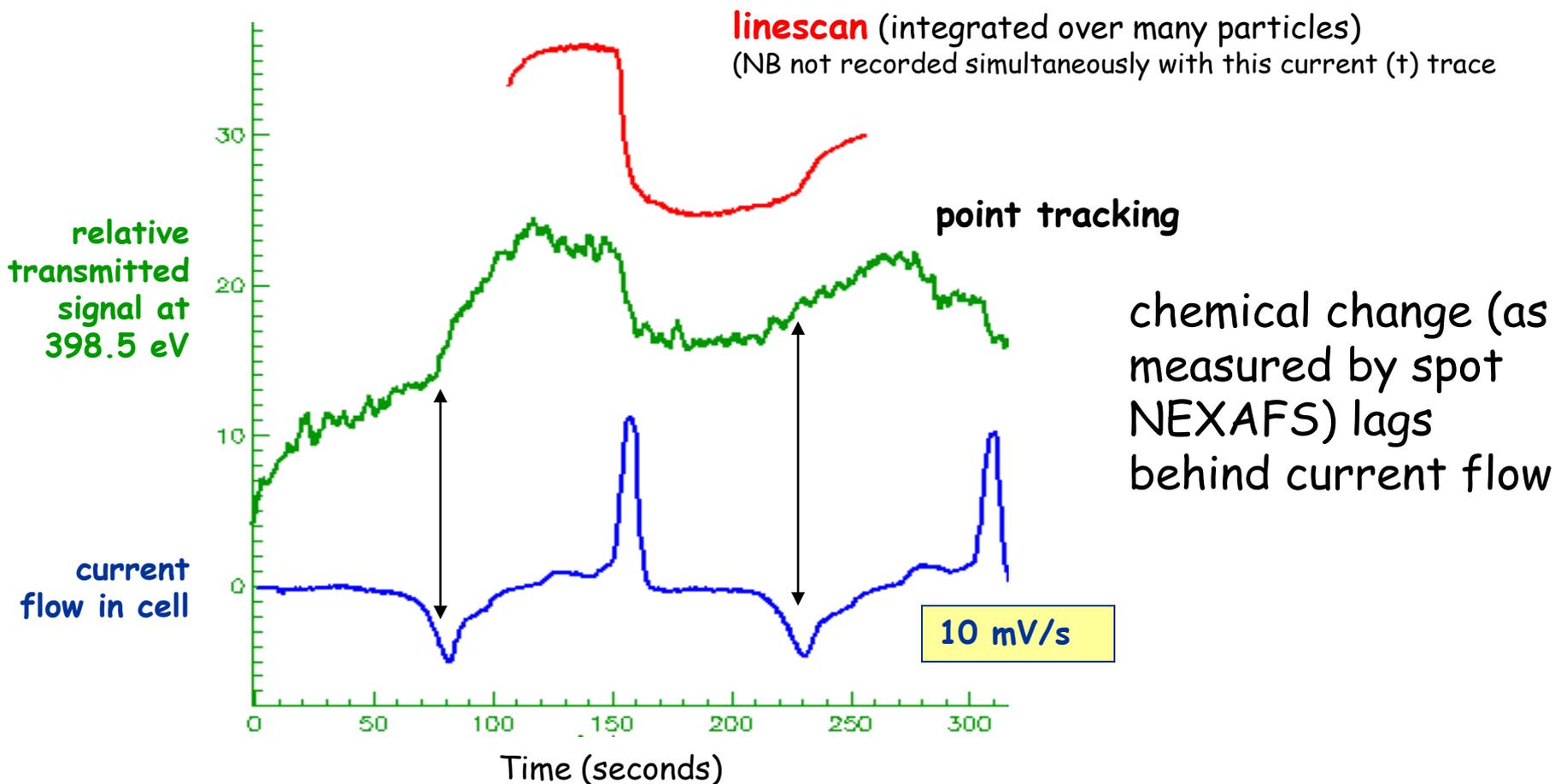




Electrochemical Contrast

= difference in N 1s region images:



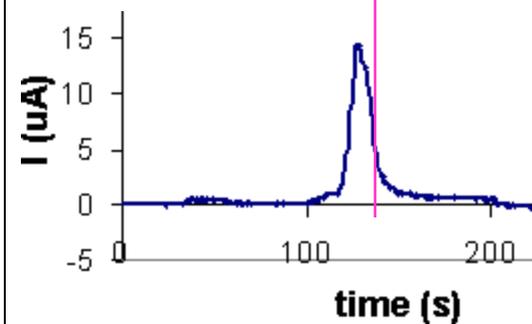
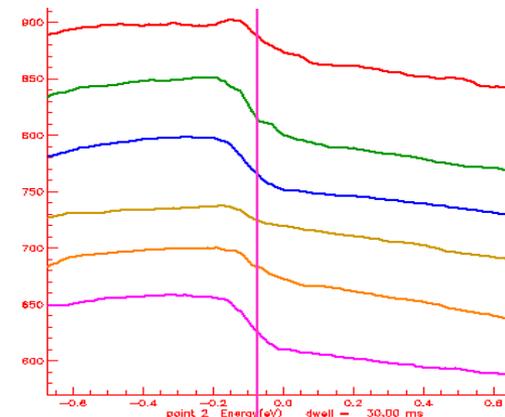
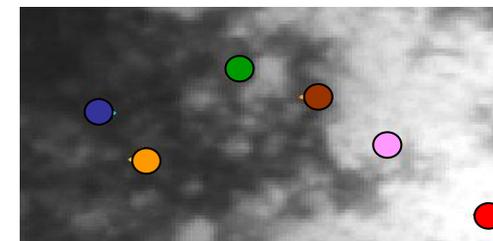
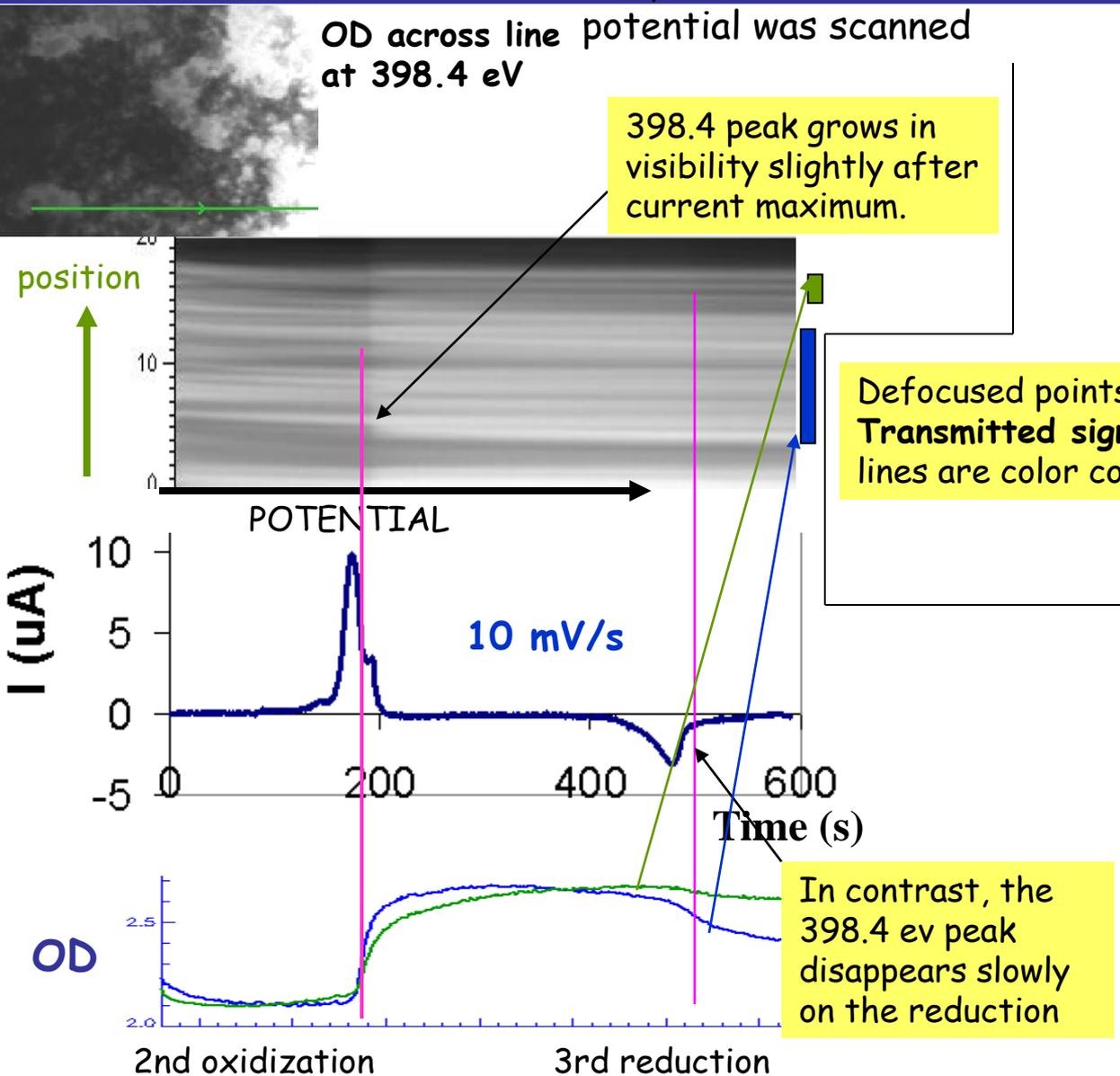


Electrochemical kinetics in the sub-second regime - **limited by SAMPLE response** not by - STXM spectroscopy (1 msec) or
- ability to change potential (microseconds)

Spectral response in sub-second scale

0.2 μm defocus line recorded successively as the

OD across line potential was scanned at 398.4 eV



- potential scanned
- measure at 398.4 eV

Scanning Transmission X-ray Microscopy has been applied to track *in situ* electrochemical changes

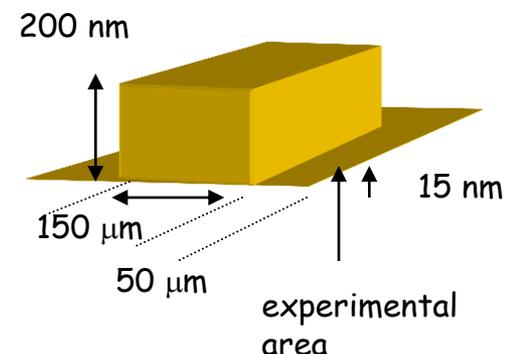
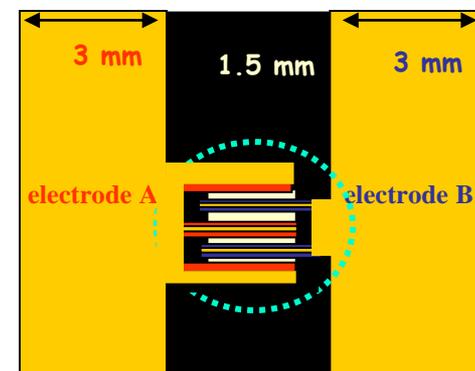
Multiple electrochemical cycles achieved to investigate morphology, chemical specificity on the sub-100 nm scale, and sub-second time scale.

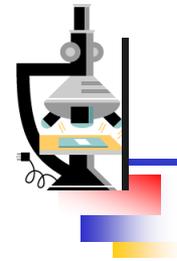
- Further improvements planned
 - more robust electrodes
 - **patterned electrodes**
 - cell systems optimal for transverse fields

This system can be adapted to study:

- batteries and fuel cell chemistry
- Electroluminescent displays
- Organic light emitting diodes
- Biosensors, etc

* Transverse fields can be achieved by using a conducting electrode above and below the sample.





Perspectives

- Soft X-ray spectromicroscopy at a bright source like NSLS II has incredible potential in helping optimize materials and processes for energy conversion
- Both full field and scanning modes have useful roles to play.
- Complementary instrumentation (e.g. state-of-art analytical TEM) would be invaluable, especially if also capable of *in situ* studies