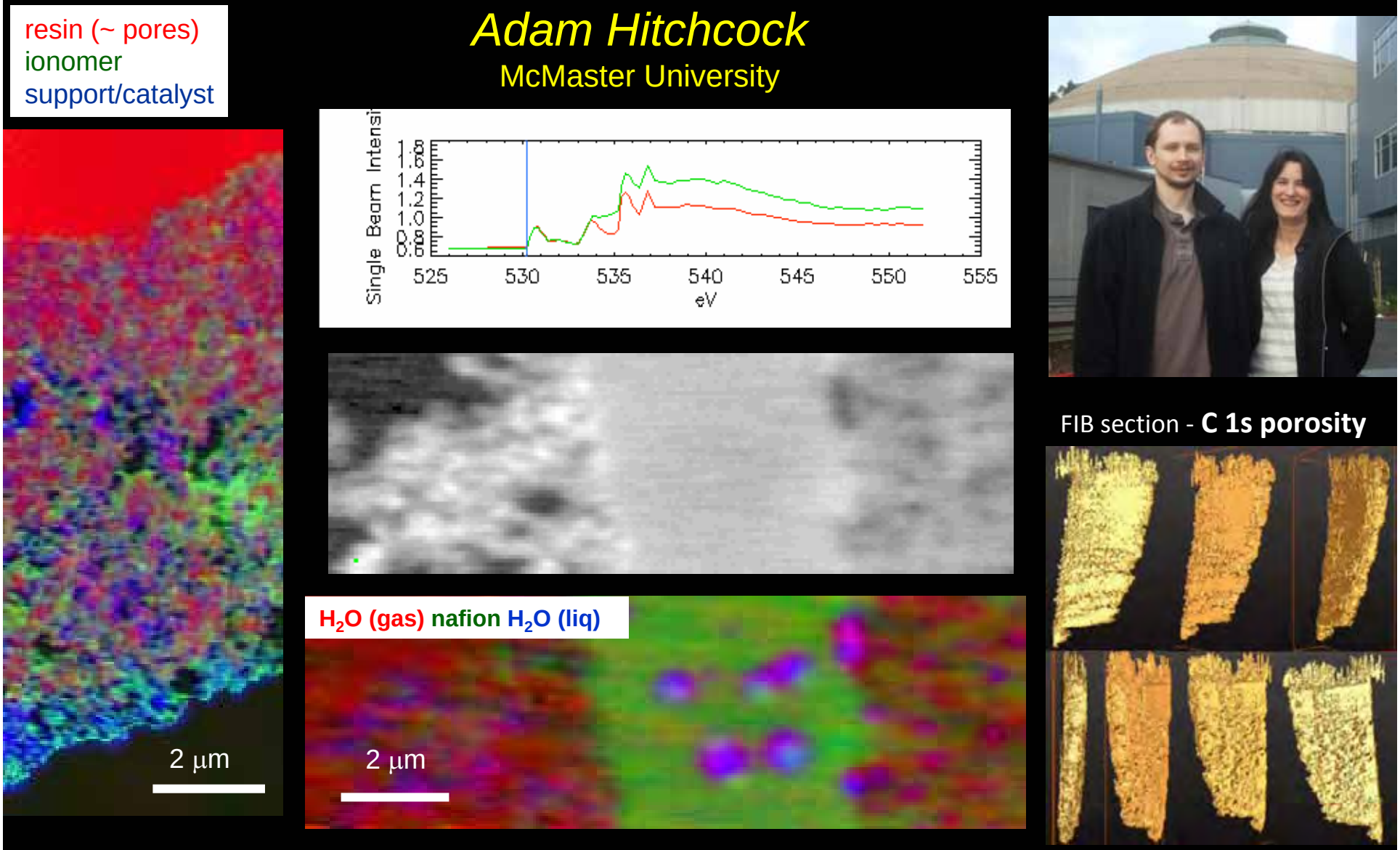
Chemical Anatomy of PEM-FC Fuel Cells

studied by Scanning transmission X-ray microscopy (STXM)

Adam Hitchcock
McMaster University



Chemical Anatomy of PEM-FC Fuel Cells

studied by Scanning transmission X-ray microscopy (STXM)

Adam Hitchcock, *Viatcheslav Berejnov*
Vincent Lee (BIMR, McMaster University)

Darija Susac, Jürgen Stumper (AFCC)
Silvia Wessel (Ballard)

OUTLINE

- Motivation
- STXM studies of PEM-FC
  - Ionomer mapping
  - degradation - carbon corrosion
  - Spectro-tomography
  - *in situ* (RH, T) studies
- Outlook & Summary

On September 13th 2012, a fleet of seven hydrogen fuel cell electric vehicles (FCEV) from Honda, Hyundai, Mercedes-Benz and Toyota embarked on the European Hydrogen Road Tour. The FCEV began their journey in Hamburg

http://www.fuelcelltoday.com/analysis/analyst-views/2012/12-09-26-european-hydrogen-road-tour-begins

Aug-2010 - Oct 2015: **NSERC Collaborative Research & Development**
Optimization of hydrogen fuel cells assisted by soft X-ray spectromicroscopy

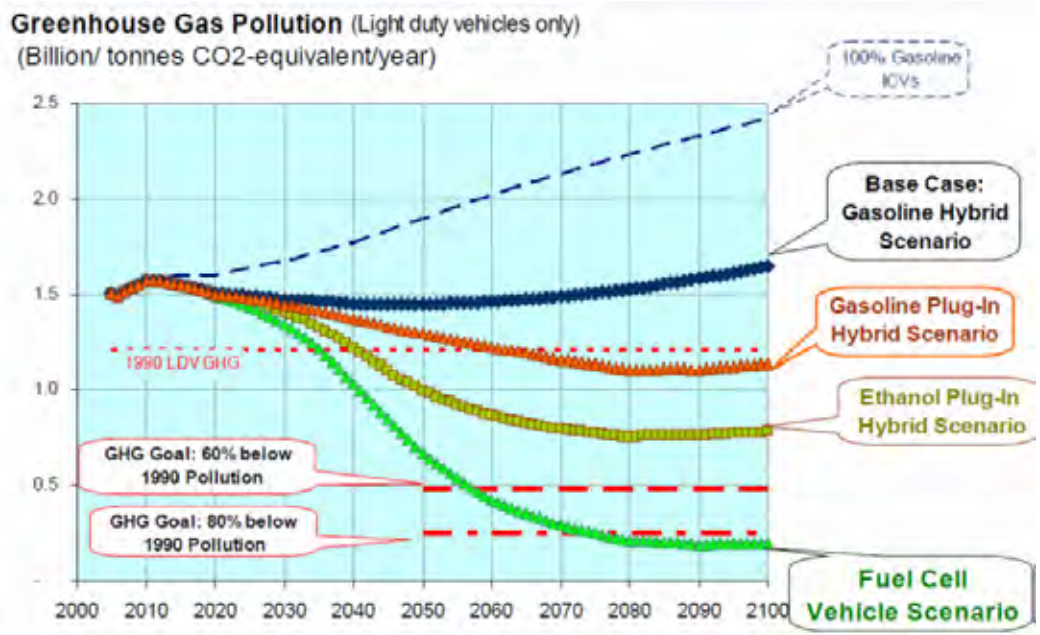
aph@mcmaster.ca

Automotive fuel cells

with Darija Susac, Juergen Stumper and Viatcheslav Berejnov (AFCC)

2008-now: collaboration with **Automotive Fuel Cell Co-operation** (**AFCC**)

AFCC is a partnership of Daimler (Mercedes-Benz) and Ford, evolved from Ballard



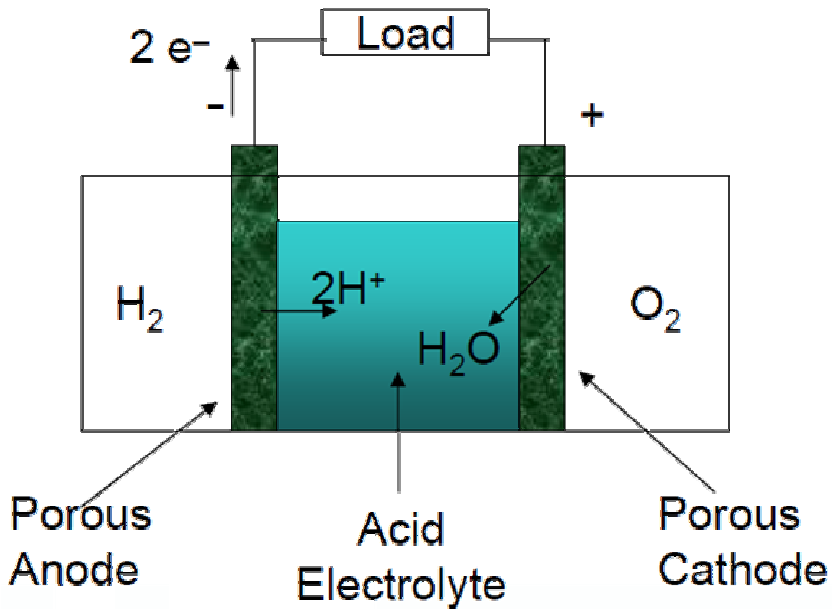
3 Daimler F-cell cars were driven around the world in May-July 2011

Daimler - $50 M fuel cell stack production plant in Vancouver

Fuel cell vehicles meet CO_2 reduction targets while retaining (or improving) range and performance

Hyundai will have 1,000 PEM-FC vehicles in Europe by 2015.

Hydrogen fuel cells - electrochemistry

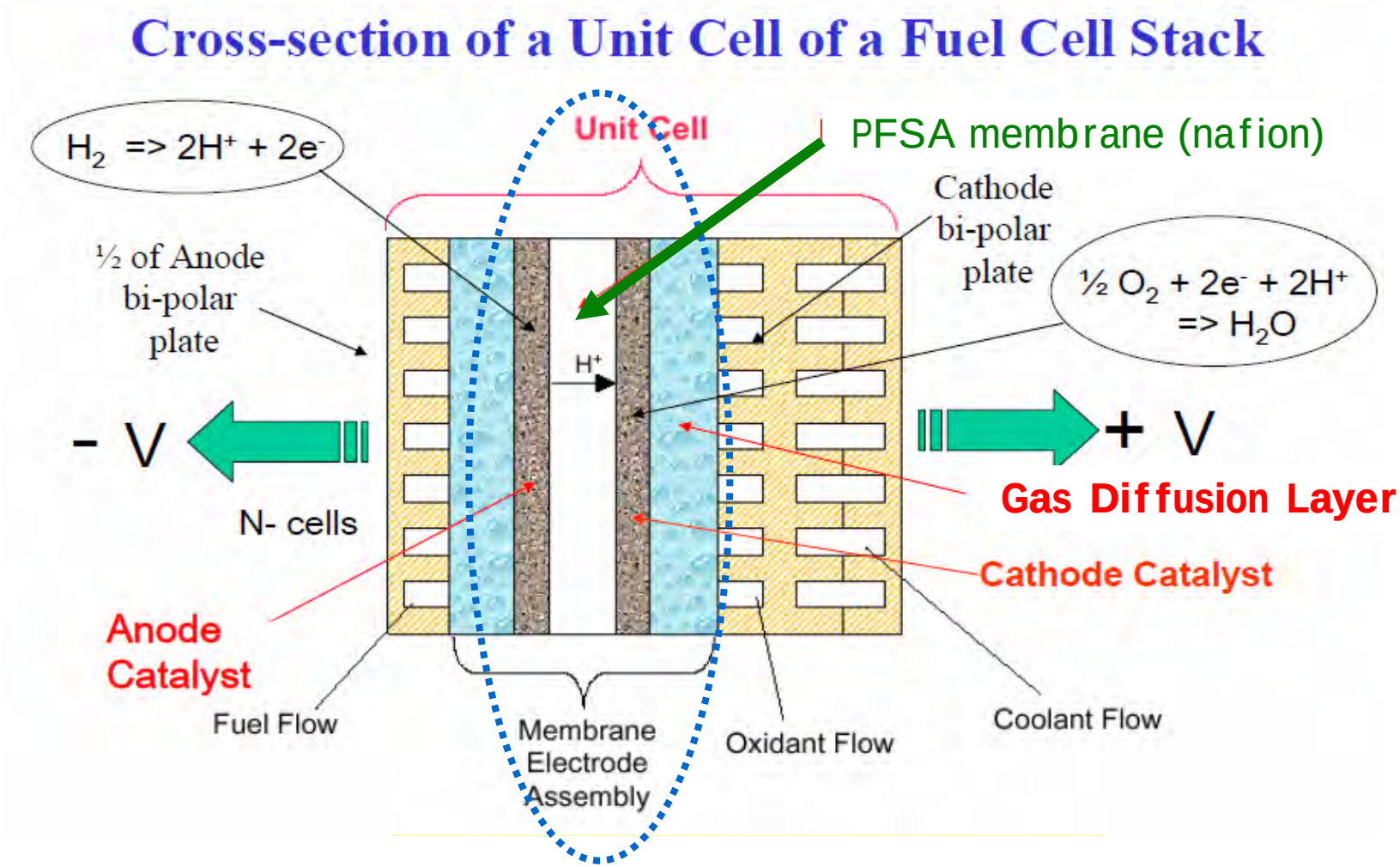


Anode: $H_2 \Rightarrow 2H^+ + 2e^-$

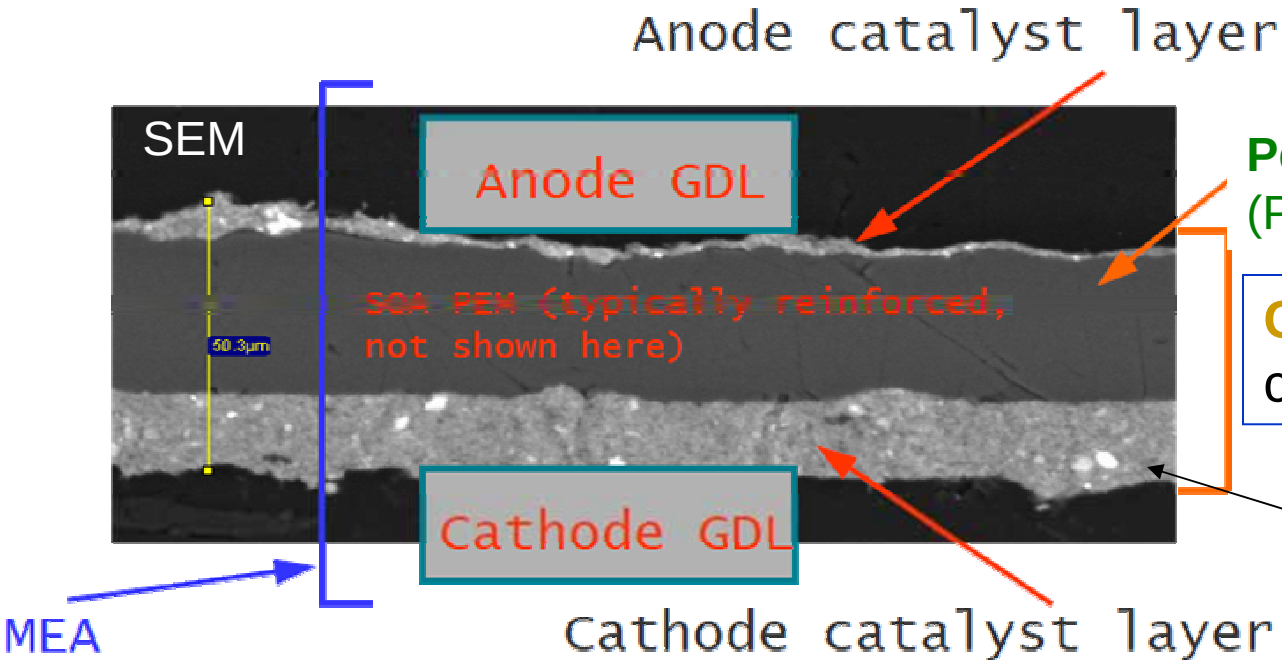
Cathode: $\frac{1}{2} O_2 + 2H^+ + 2e^- \Rightarrow H_2O$

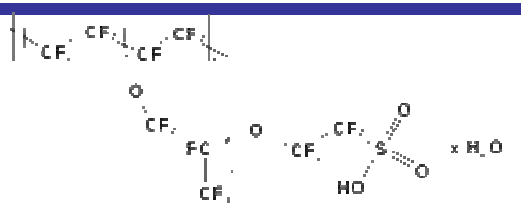
Overall Cell Reaction : $H_2 + \frac{1}{2} O_2 \Rightarrow H_2O$

Hydrogen fuel cells - electrochemistry



Membrane electrode assembly (MEA)





Perfluoro **s**ulfonic **a**cid (PFSA) membrane

CCM = catalyst coated membrane

Pt catalyst
Ionomer (nafion)
Carbon support

<u>Issues for automotive fuel cell optimization</u>

- Reducing cost: lower Pt by better ionomer distributions
- Making system more robust
  - Pt degradation, carbon corrosion
  - optimizing water management
  - cold start (reducing damage from residual water freezing)

- can Pt be replaced ?

CaRPE FC

Themes of our PEM-FC studies

Catalyst Coated Membranes (CCM)
& Membrane electrode assemblies (MEA)

ionomer mapping

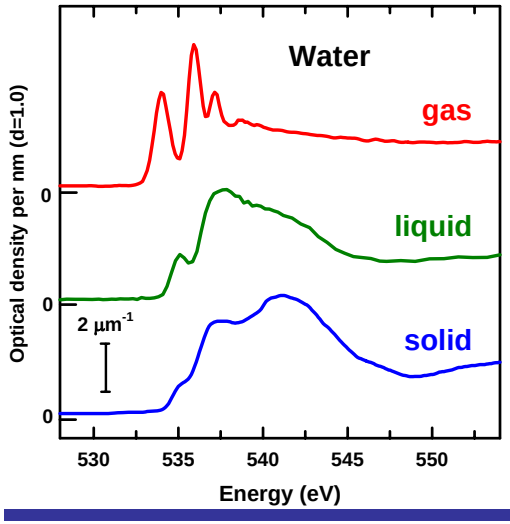
* 30 nm spatial resolution
* sensitivity to 1% ionomer in 100x100 nm
* 2d and **3d**

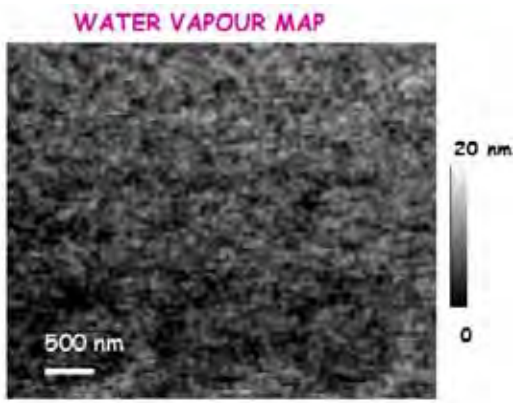
porosity mapping

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

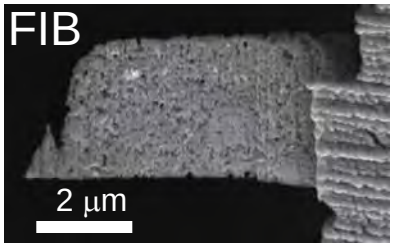
vapor / liquid water mapping

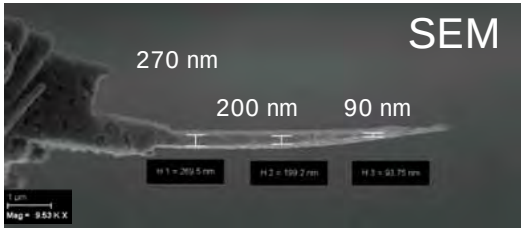
* environmental cell with controlled relative humidity (RH)
  - used to examine changes when the fuel cell CCM is hydrated.

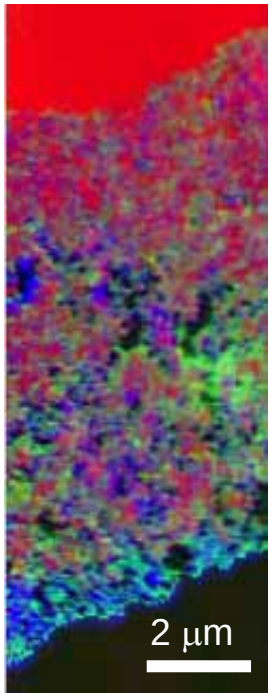




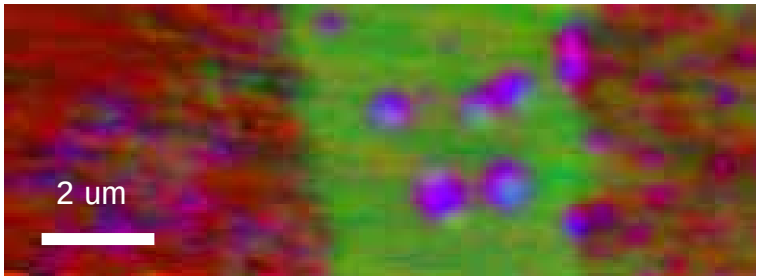
cathode
resin (= pores)
ionomer
support/catalyst







H_2O (gas) nafion H_2O (liq)



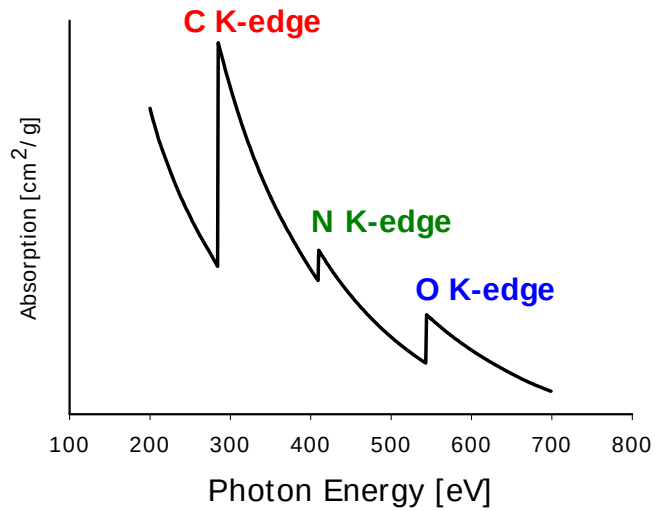
Susac et al, ECS Transactions 50 (2012) 405

Berejnov et al. ECS Transactions 50 (**2013**) 361

X-ray Absorption Spectroscopy

= inner shell electronic excitation and ionization

NEXAFS from each core level of the target - site specific



Elemental and chemical contrast

Elemental – from core level

Chemical speciation (functional group; pDOS ..)

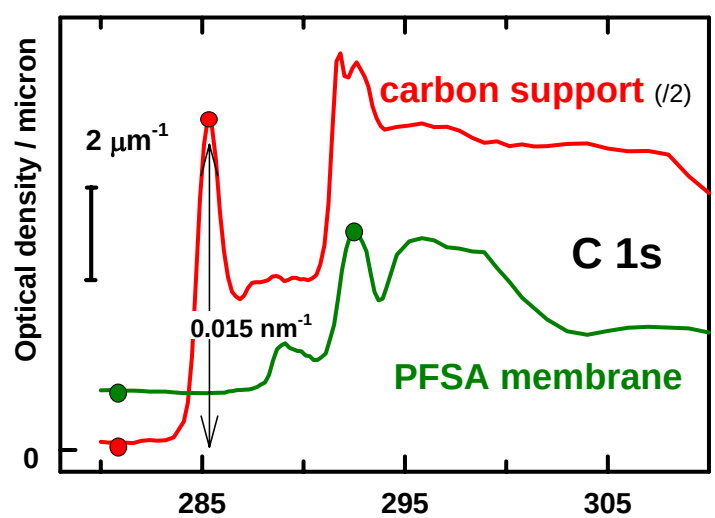
– via effects of local environment on upper level

Molecular approach:

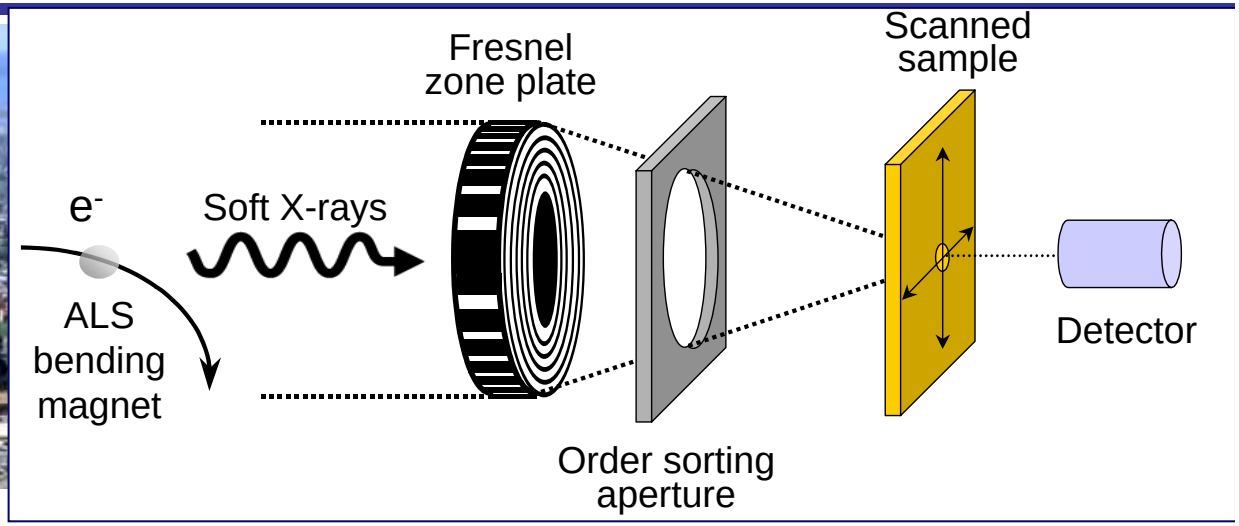
Electric dipole-allowed, localized core → unoccupied molecular orbital transitions

Solid state approach:

Dipole-selected unoccupied density of local states



Scanning Transmission X-ray Microscopy

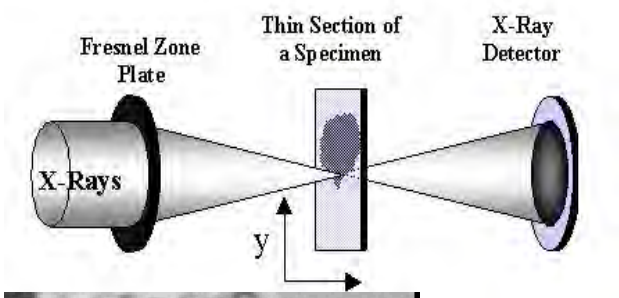


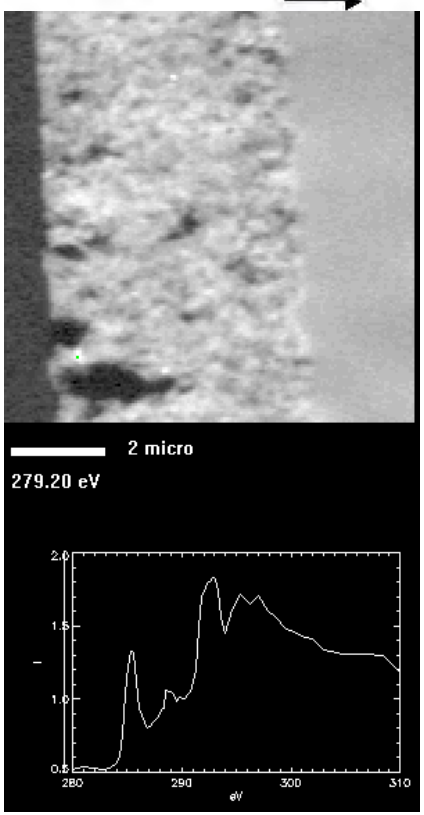
- **Chemical speciation through X-ray absorption spectra**
- **Spatial resolution : < 30 nm; Energy resolution < 0.1 eV**
  - Beamlines 5.3.2.(2,1) & 11.0.2 at the Advanced Light Source, Berkeley, USA
  - Beamline 10ID1 STXM at the Canadian Light Source, Saskatoon, Canada
- **Transmission requires thin samples - 0.1 to 2 OD**
  - polymers => microtomed sections ~100 nm thick for C 1s edge

- ➢ Wet & humidified samples ;in situ heat, cool, V, H
- ➢ Quantitative chemical (& magnetic) mapping
- ➢ Quantitative molecular orientation mapping

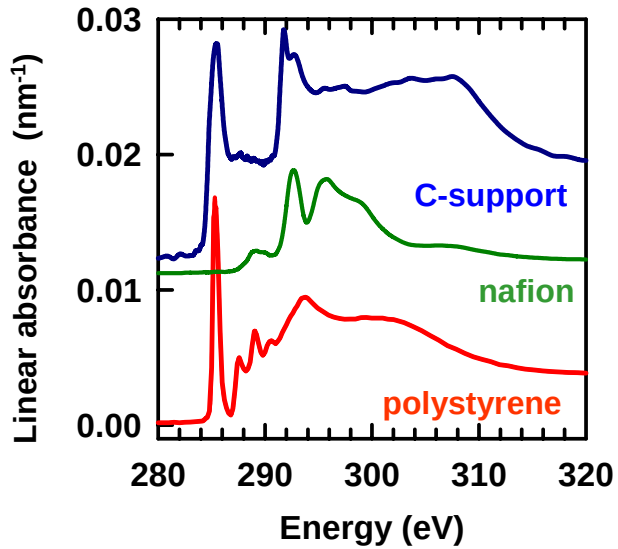
Generating chemical maps from stacks

1. Record stack

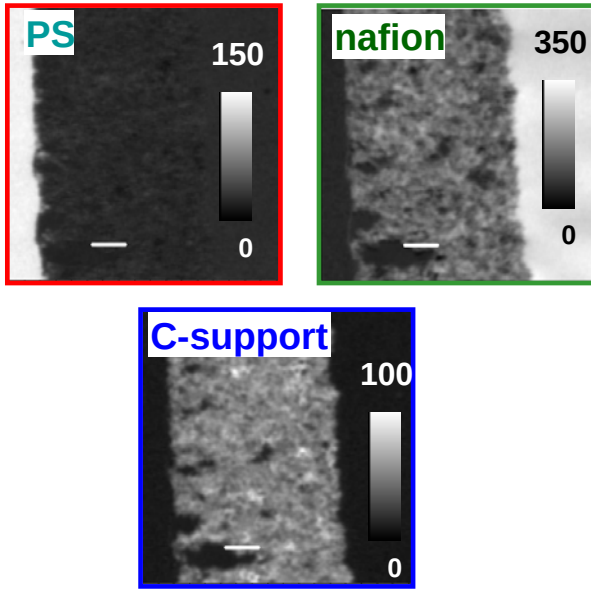




2. Generate reference spectra



Chemical component maps

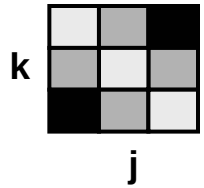


3. Generate component maps

$$OD(j,k) = \sum_i a_i(j,k) * (reference)_i$$

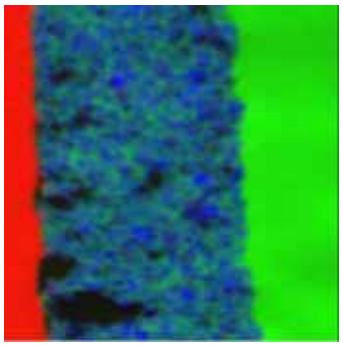
with a_i (j,k) = *THICKNESS* **(nm) at (jk) of species i**

a_j (j,k) map



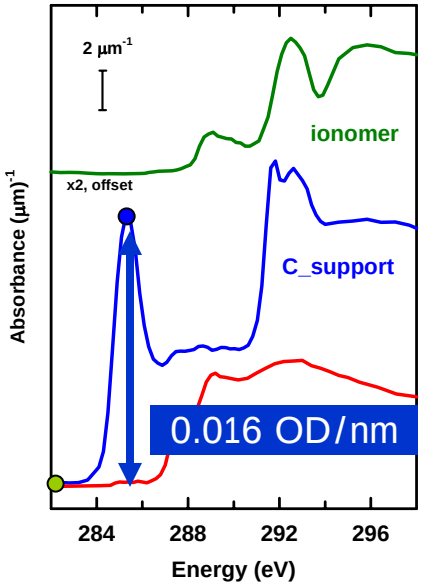
Fit using SVD in aXis2000

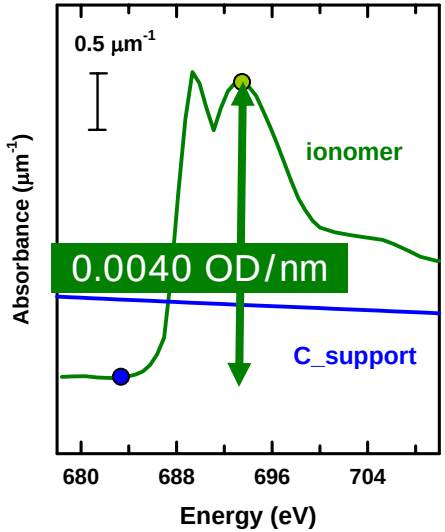
4. Generate RGB-composite

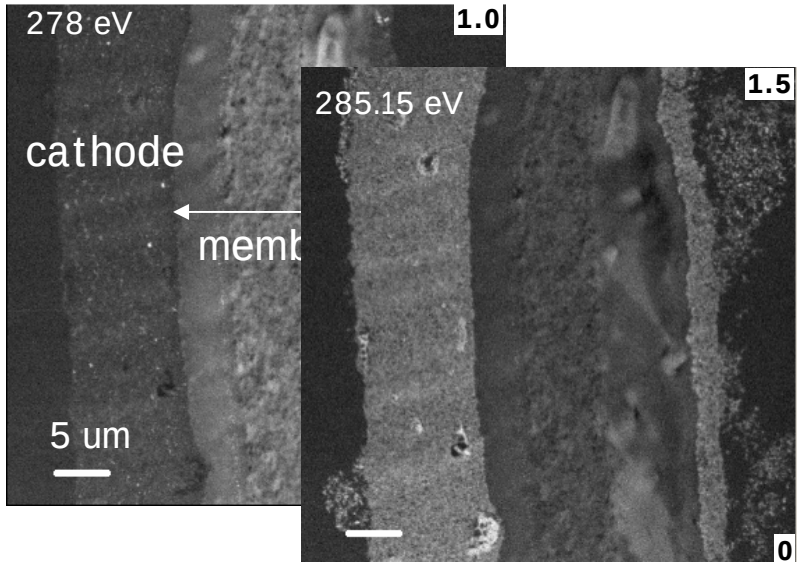


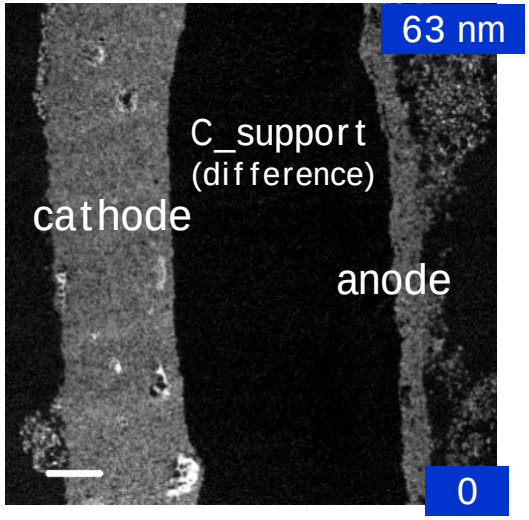
unicorn.mcmaster.ca\aXis2000.html

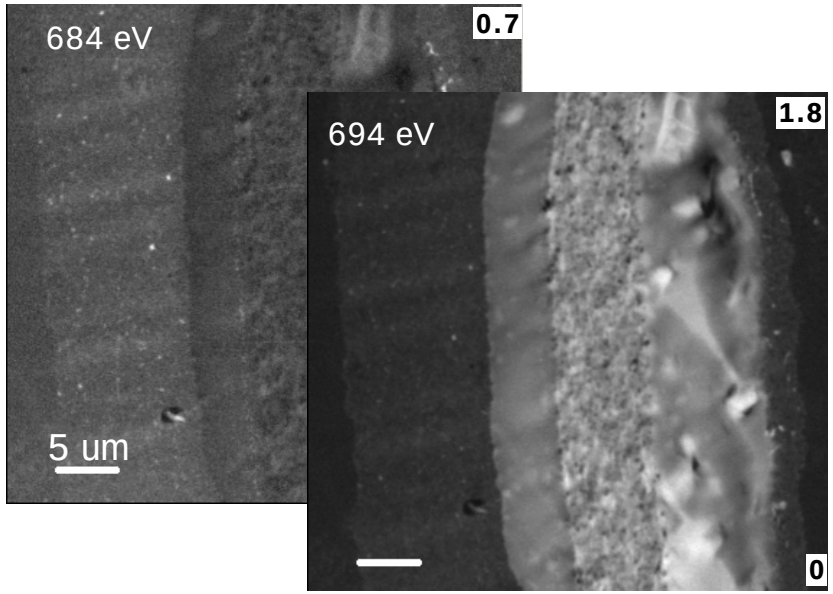
Mapping Ionomer in the cathode



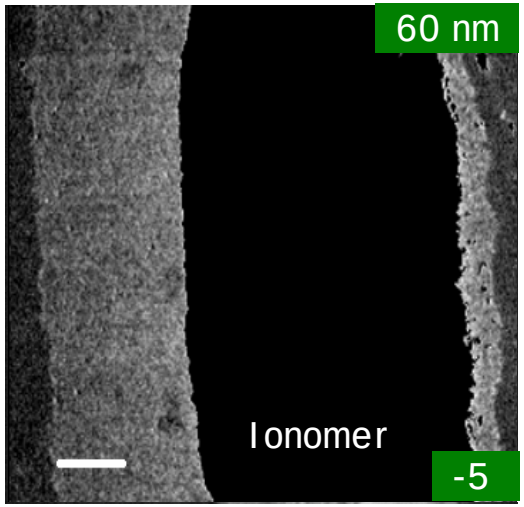








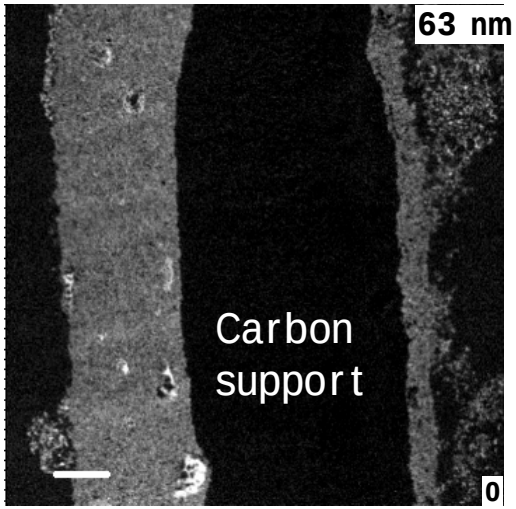
Fluorine

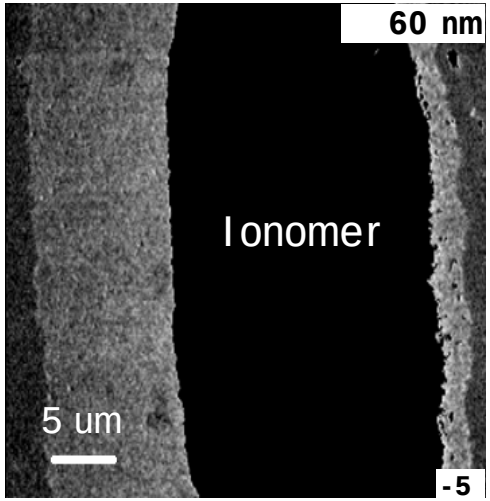


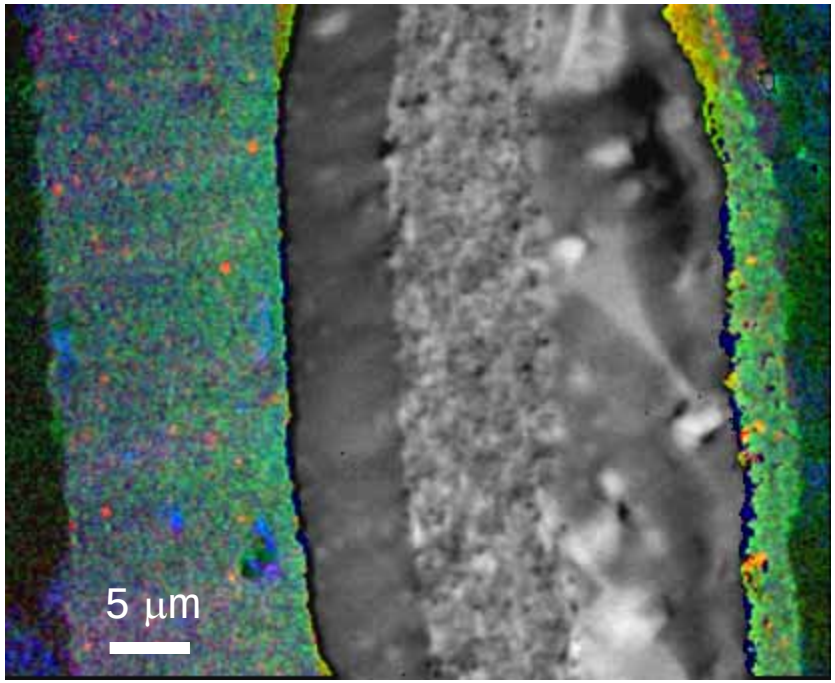
Susac et al, ECS Transactions **41** (2011) 629

Ionomer mapping

Gore Select membrane







membrane

Carbon support

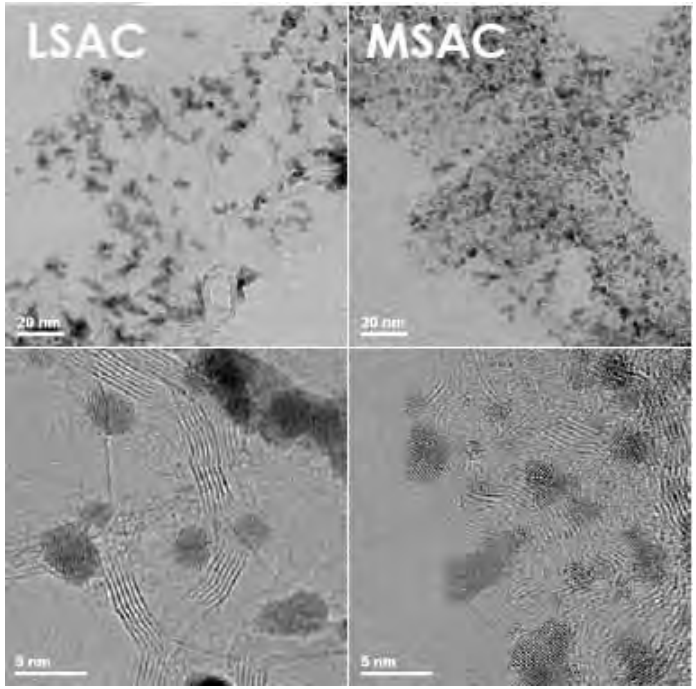
Catalyst (pre C1s)

Ionomer

Susac et al, ECS Transactions **41** (2011) 629

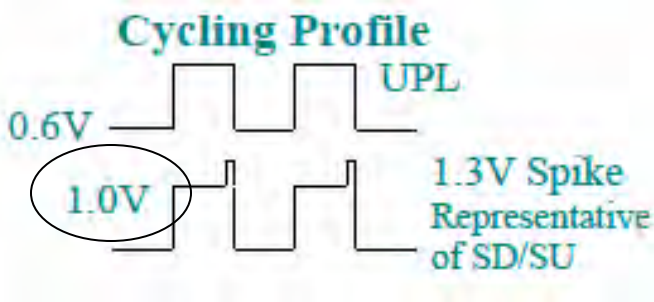
changes in cathodes caused by stress

S. Wessel et al., DoE funded study (2009-2012)

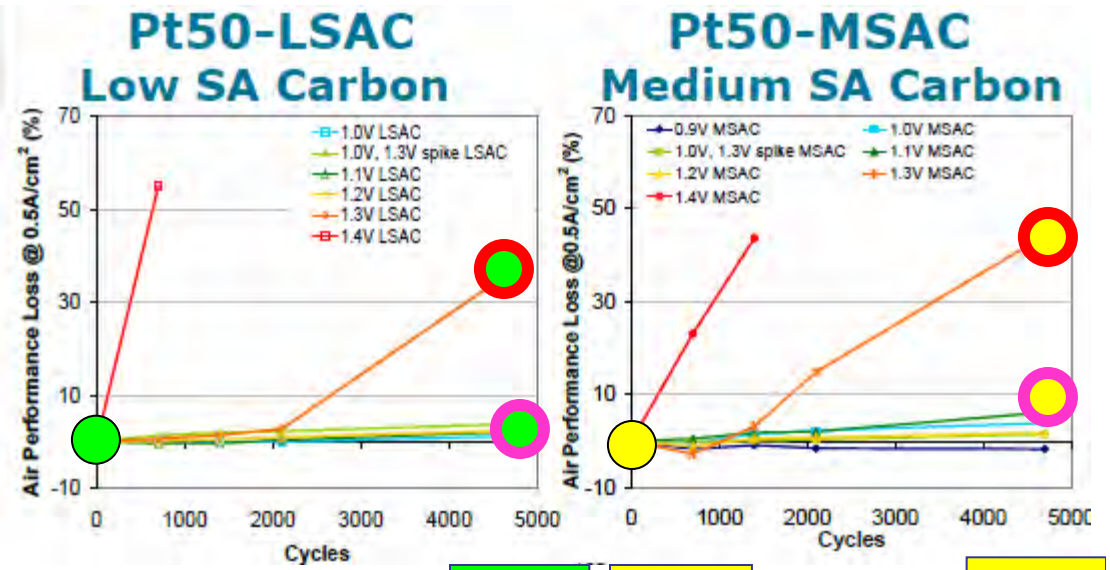


LSA = low surface area carbon

MSA = mid-range surface area carbon



Loos of performance



BOT **EOT** **BOT** **EOT**

<u>Effects seen by TEM/SEM</u>

Low-cycle # - Pt-dissolution

High cycle # - carbon corrosion

What is effect on ionomer ?

Compare **BOT** and **EOT** for **1.0, 1.2** and **1.3 V** 5000 cycle MEAs for each type of catalyst

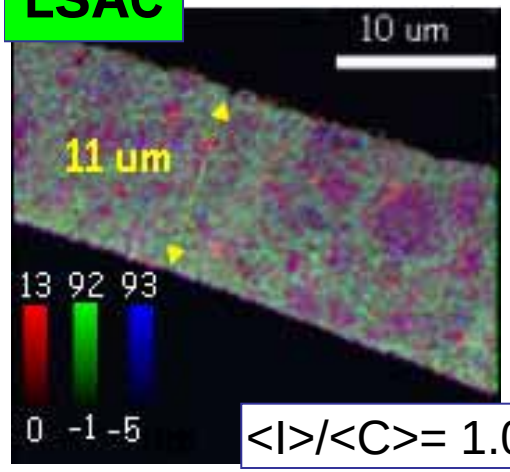
Hitchcock et al, J. Power Sources (2014)

changes in cathode caused by stress

S. Wessel et al., DoE funded study (2009-2012)

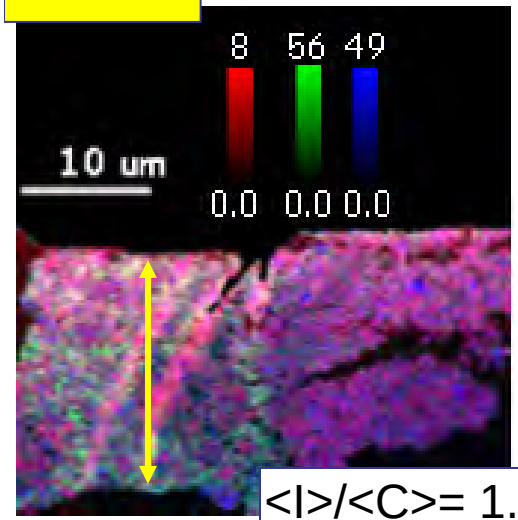
BOT Beginning Of Test

LSAC



<I>/<C>= 1.0

MSAC



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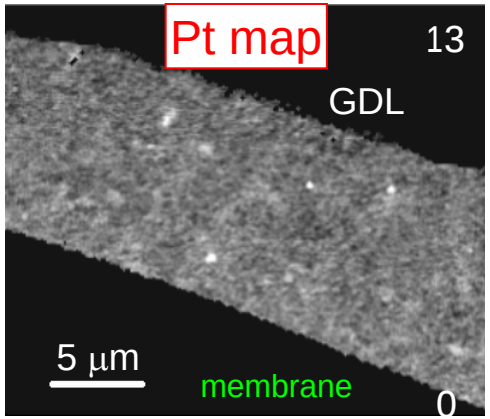
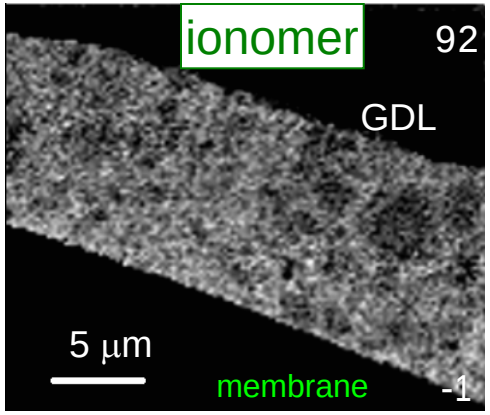
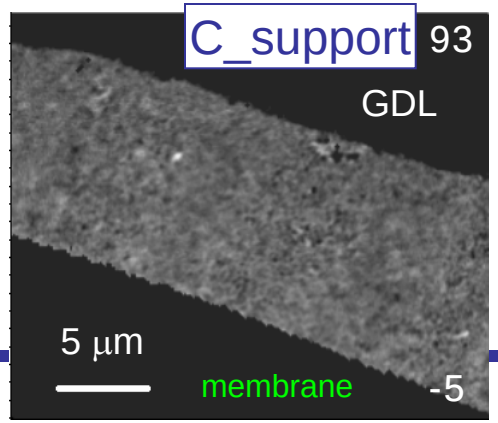
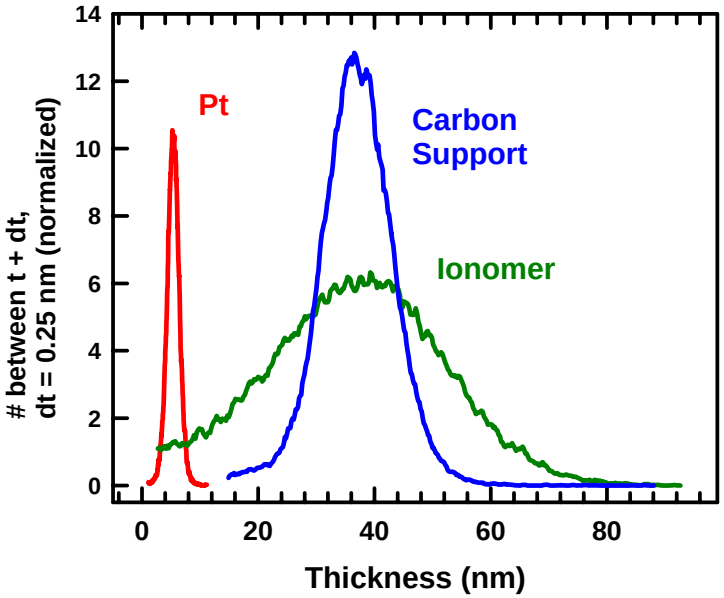






Pt, Ionomer, C-support

Histogram = thickness distributions



$$\langle I\rangle/\langle C\rangle = \langle t_{Ionomer}\rangle/\langle t_{C_support}\rangle$$

LSAC = low surface area C_support
MSAC = medium surface area "

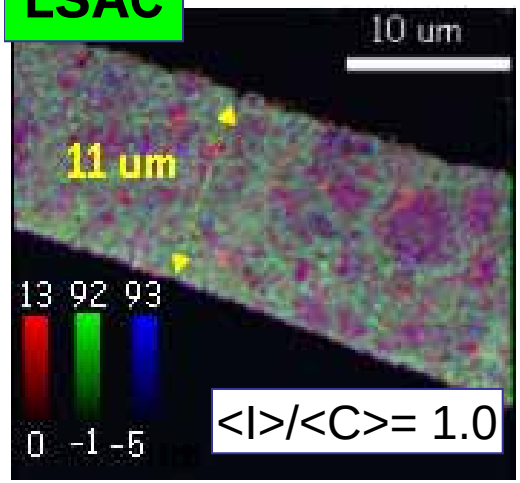
Hitchcock et al, J. Power Sources (2014)

changes in cathode caused by stress

<I>/<C>=<Ionomer>/<C_support>

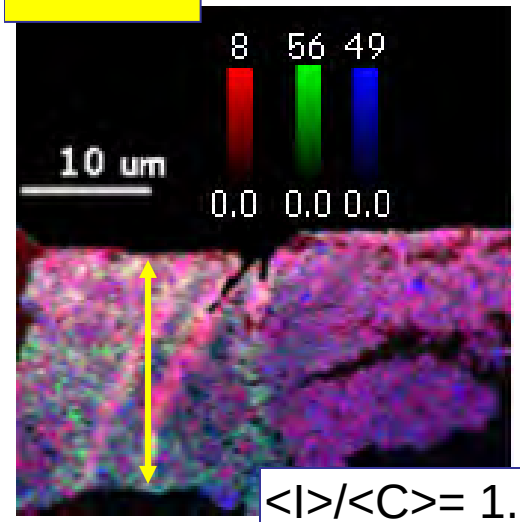
BOT

LSAC



<I>/<C>= 1.0

MSAC



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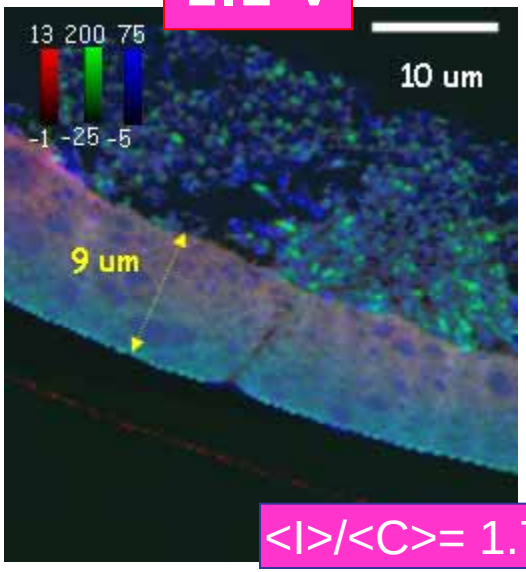
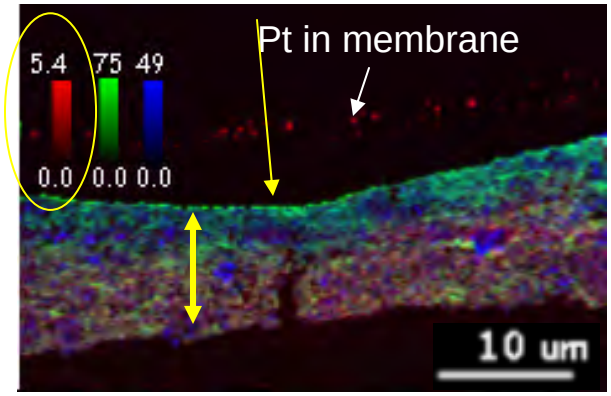
1.2 V



<I>/<C>= 1.7

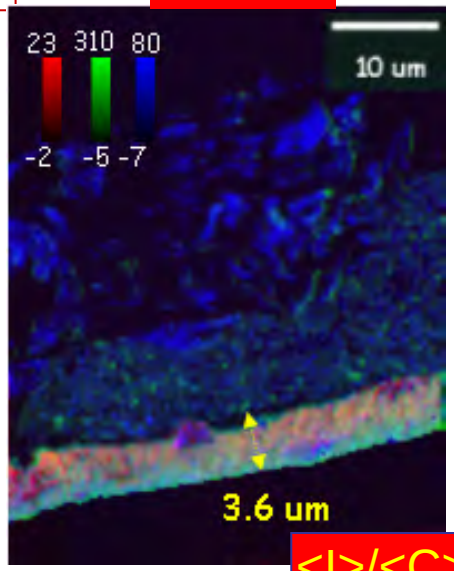
Depletion layer easily visible



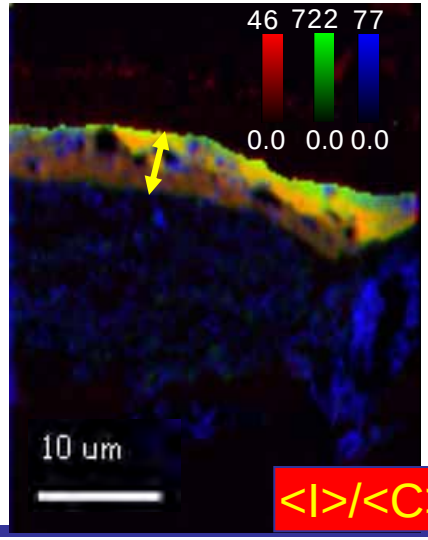
<I>/<C>= 1.5

EOT

1.3 V



<I>/<C>= 3.9

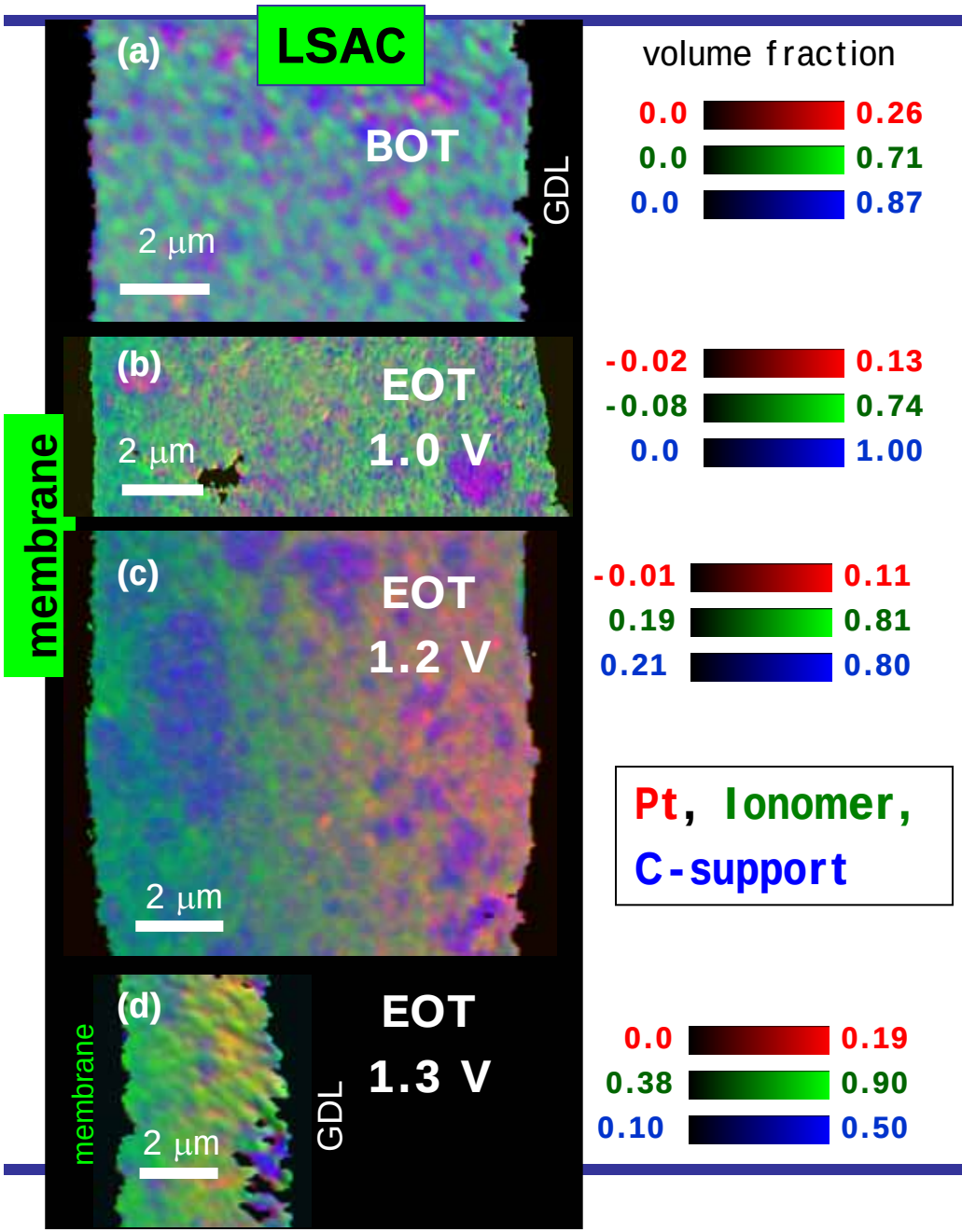


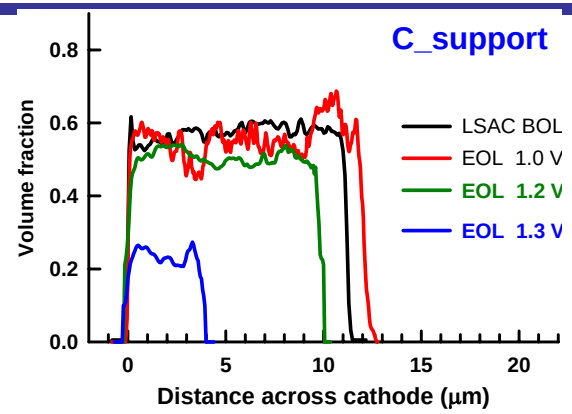
<I>/<C>= 9.4

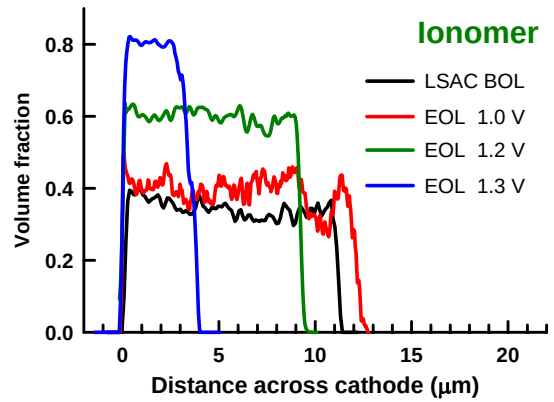
Pt, Ionomer, C-black

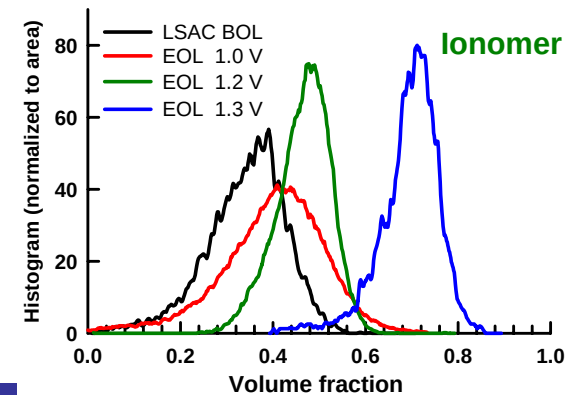
Hitchcock et al, J. Power Sources (2014)

Quantitative evaluation – vol. fr.





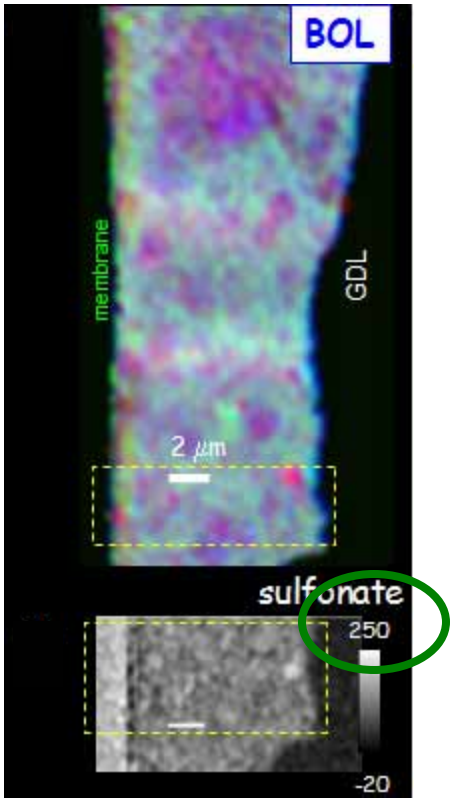


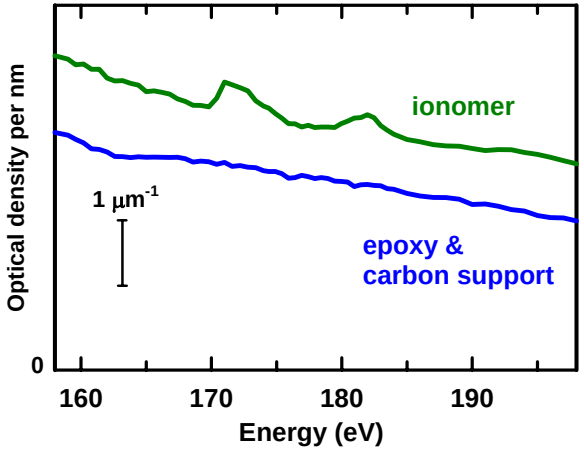


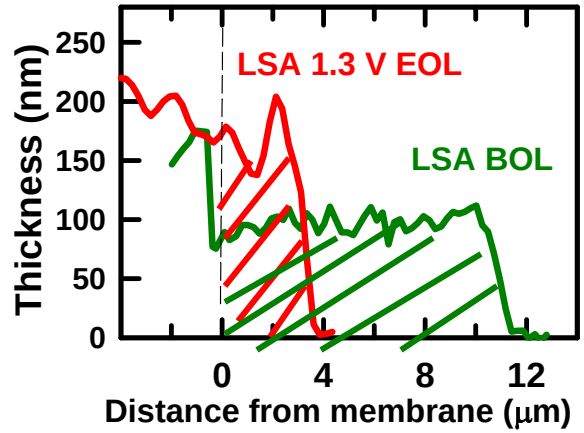
Hitchcock et al, J. Power Sources (2014)

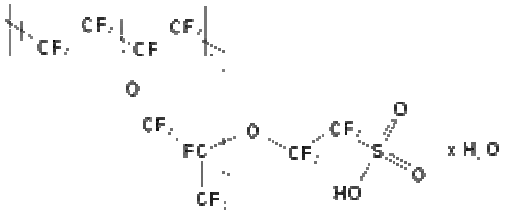
Is the ionomer still functional ?

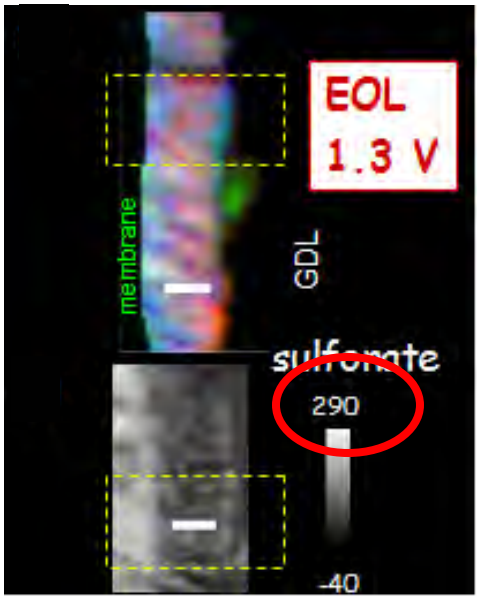
F 1s analysis of ionomer only says the CF_2 backbone is present . But …are the critical sulfonate side groups still present ? ➔ use S 2p STXM to determine









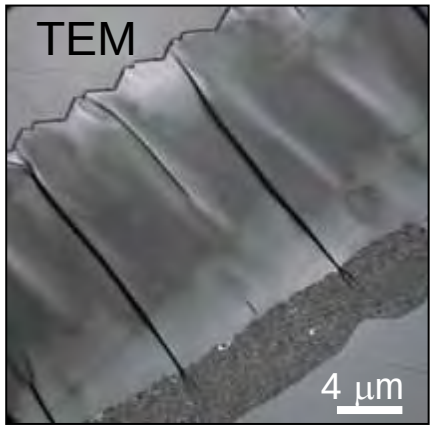


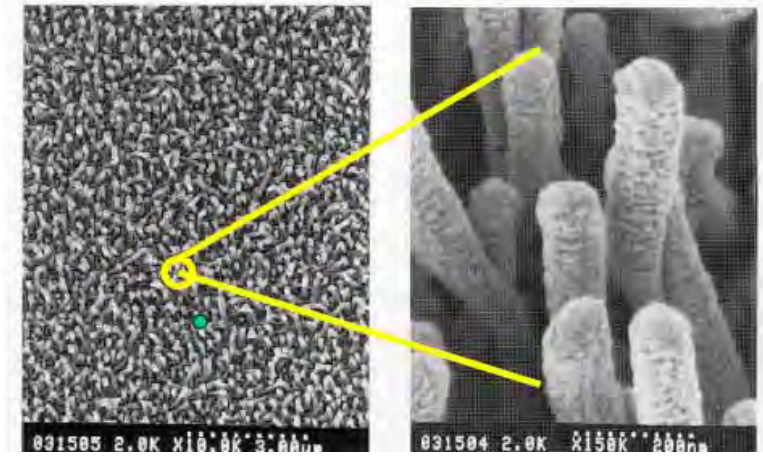
S 2p STXM ➔ sulfonates are still present, but at ~50% less than in 1.3 V EOT than on the BOT sample, based on signal integrated over cathode

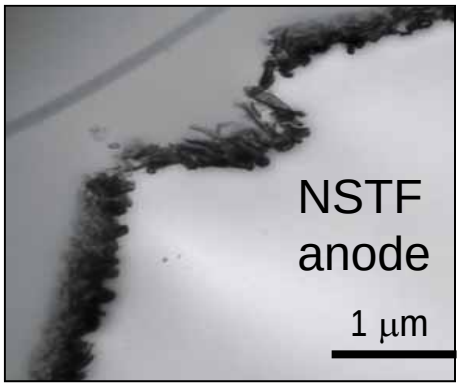
Hitchcock et al, J. Power Sources (2014)

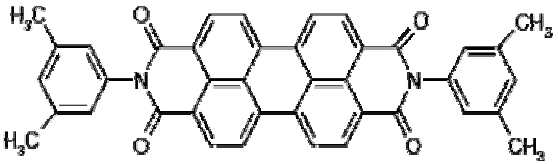
Alternate catalysts – 3M NSTF

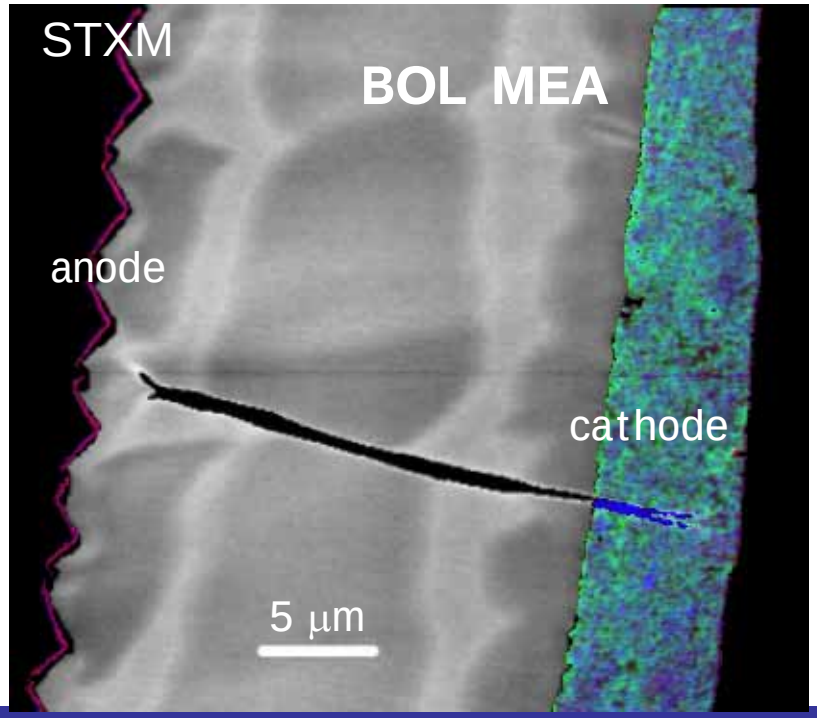
Nanostructured thin film catalyst (NSTF)

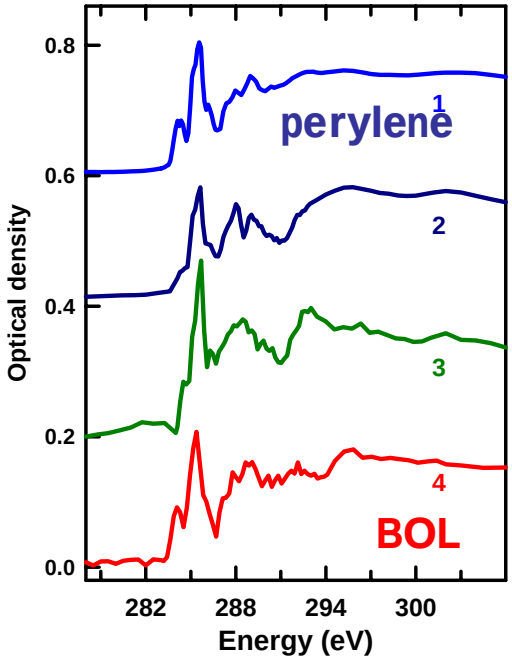












M.K. Debe, Nature 486 (2012) 43

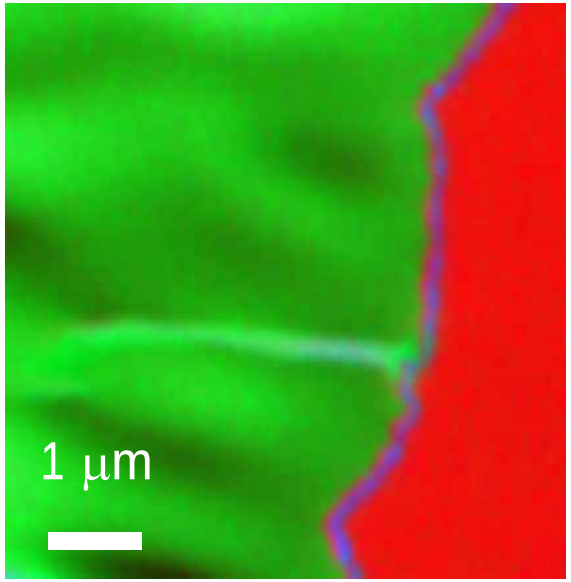
Lee et al, J. Power Sources (2014)

3M NSTF– do they degrade ?

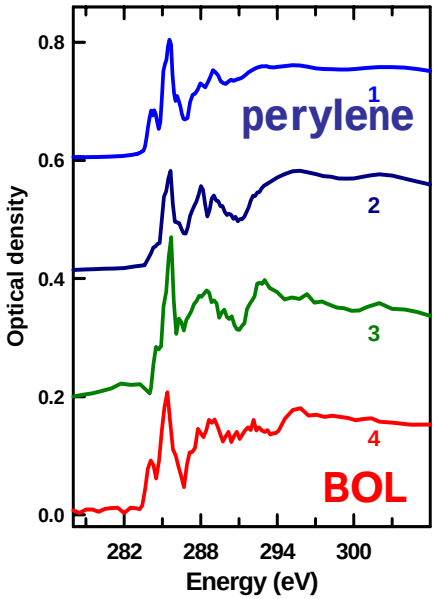
Nanostructured thin film catalyst (NSTF)
- is the perylene corroded during operation ?

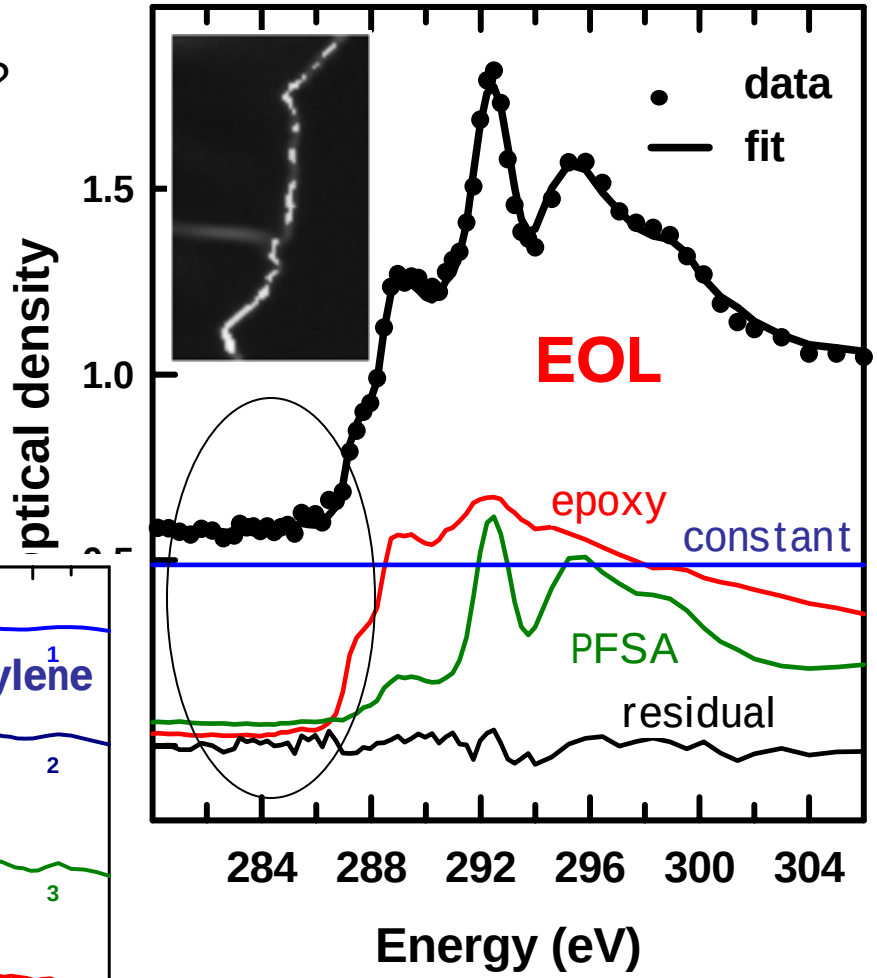
After reversal
& **start-up, shut-down testing**

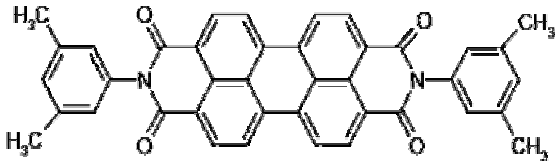
epoxy **PFSA** **constant** (=metal catalysts)



ANODE







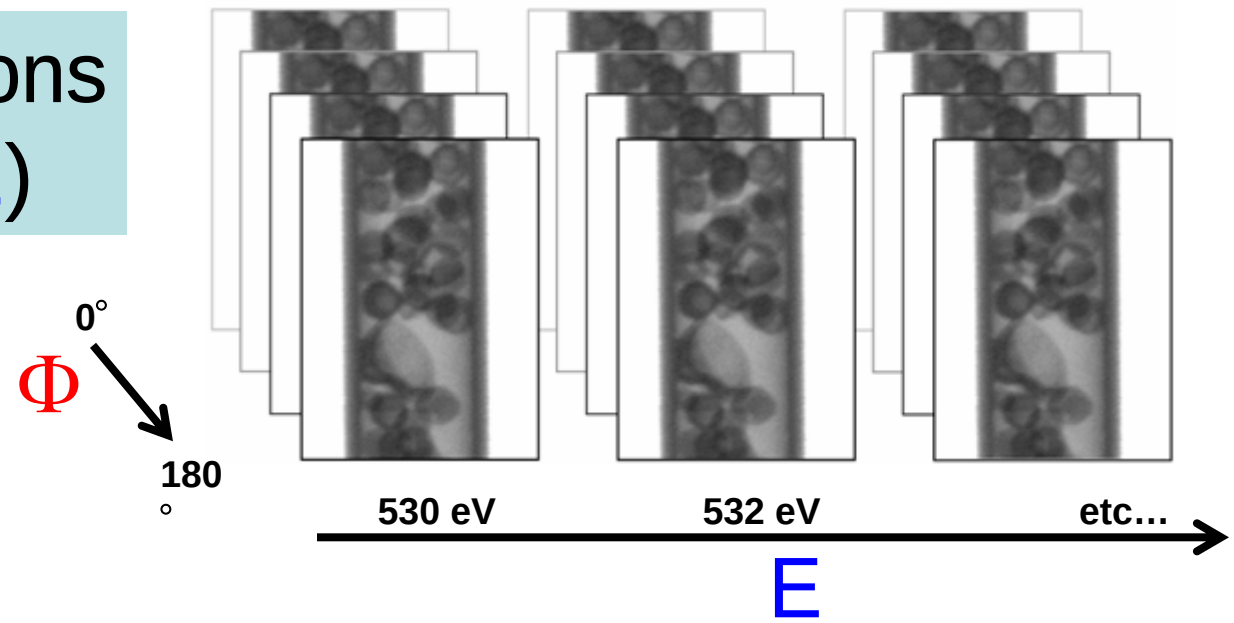
Lee et al, J. Power Sources (2014)

Spectro-tomography: 3-d chemical mapping

To produce a three-dimensional map of a chemical species in a sample…

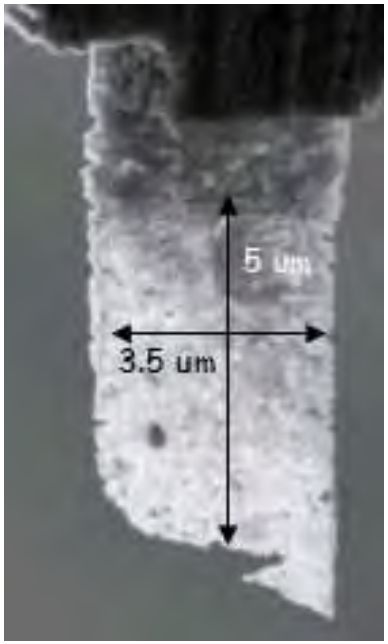
- we need stacks of images made at different energies.
- we need images made at different angles.

4 Dimensions
(X, Y, Φ, E)

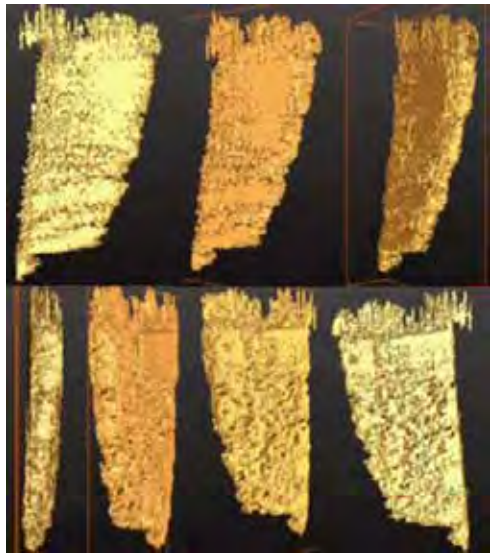


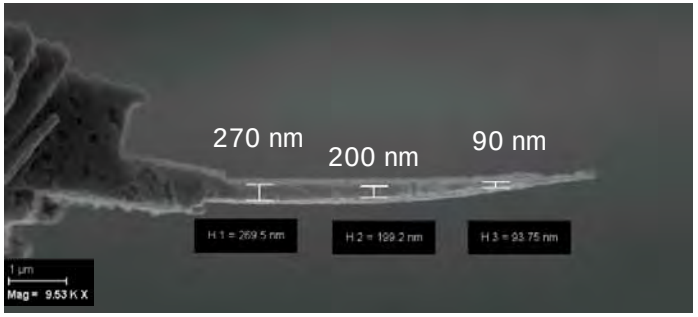
STXM spectro-tomography

FIB sample preparation (CCEM, McMaster)

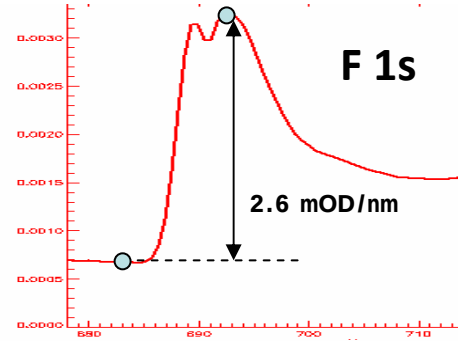


FIB section - **C 1s porosity**

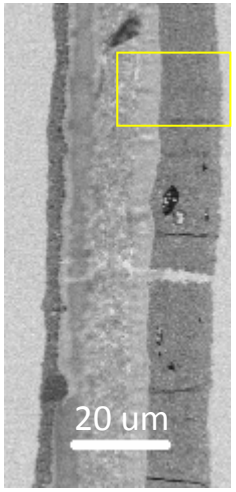


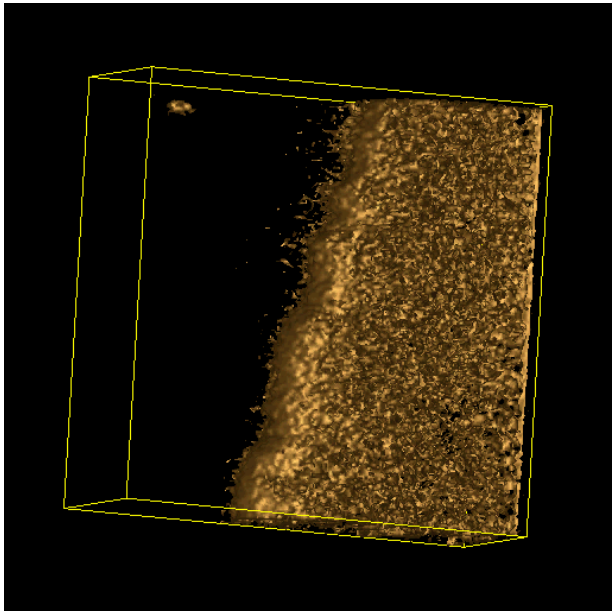


Grid strip - **ionomer - in -cathode**



Ionomer in cathode



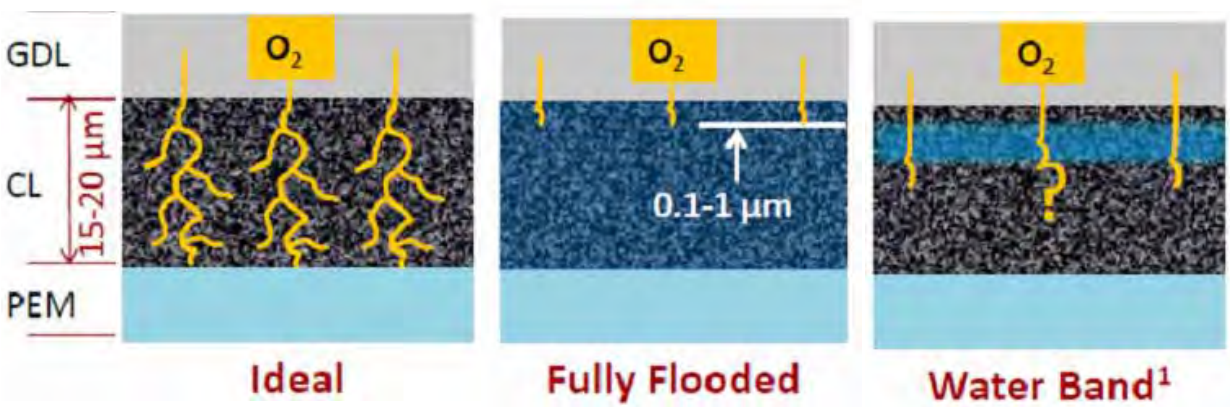


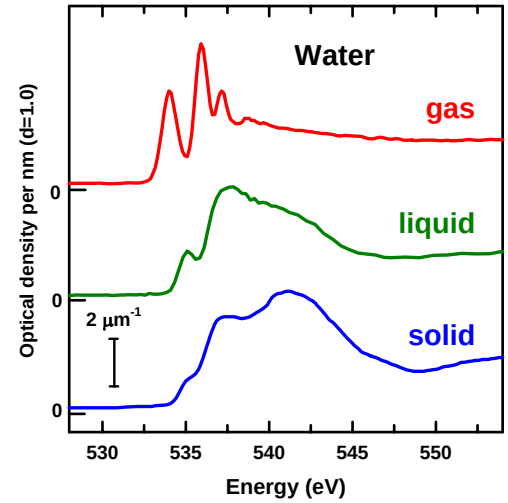
Berejnov et al. ECS Transactions 50 (**2012**) 361

Mapping water in PEM-FC - motivation

Water management in cathode is a current challenge

courtesy: Shawn Litster (CM, Pittsburgh)





- Ionomer must be hydrated
- Too much water blocks O_2 transport

Theoretical model (Eickerling) of excess water
- initial flooding of small primary pores
- subsequent flooding of larger pores - **water band**

- How does water (gas, liquid) transport relate to porosity ?

water in the cathode
- how much ?
- where ?
- what phase ?

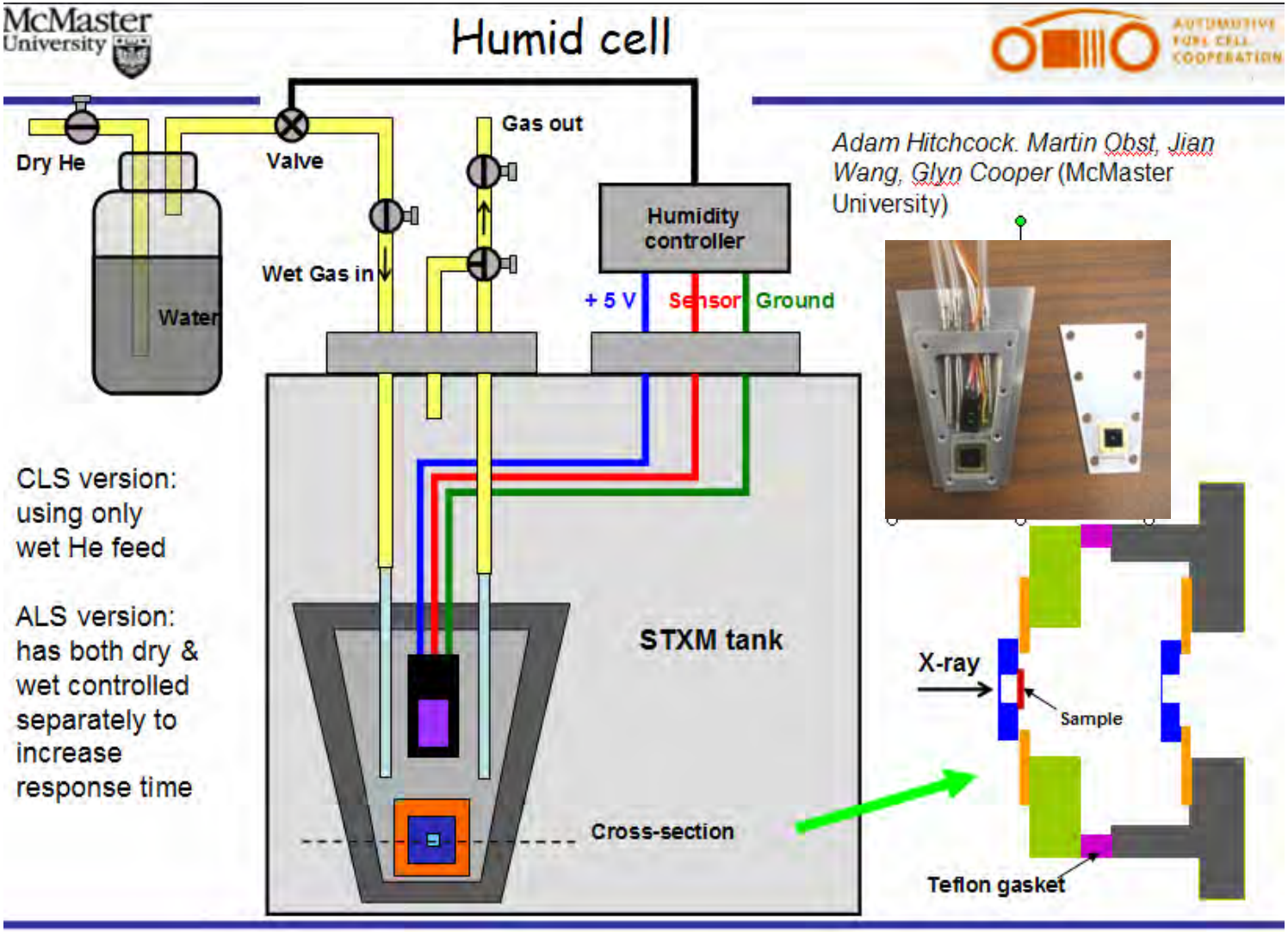
➢ Optimization of MEA structure for **cold start**

– supercooled water vs ice

[1] M. Eikerling, J. ElectroChem Soc.153 (2006) E58

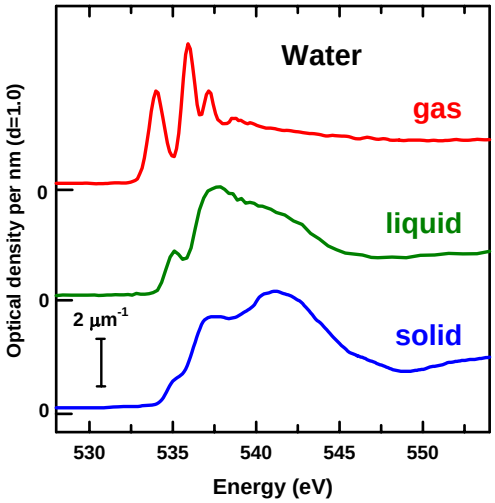
STXM: Fuel cell MEA under controlled humidity

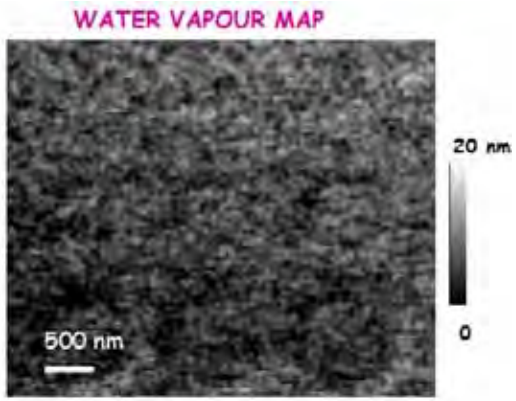
Slava Berejnov, Adam Hitchcock (McMaster); *Darija Susac* (AFCC)



Humidity induced changes in MEA

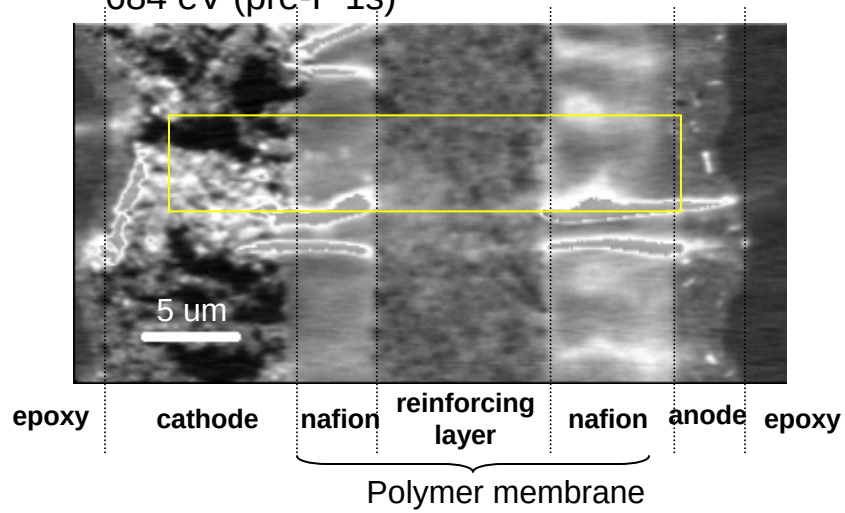
STXM mapping of location of water vapor in membrane of a MEA (in humid cell) - 2010





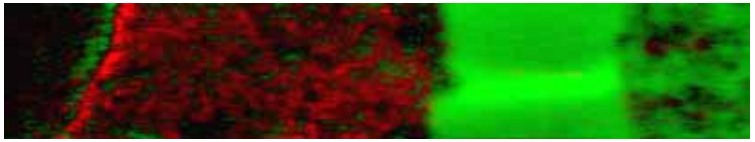
Gore-SELECT® ePTFE micro-reinforced membrane

684 eV (pre-F 1s)



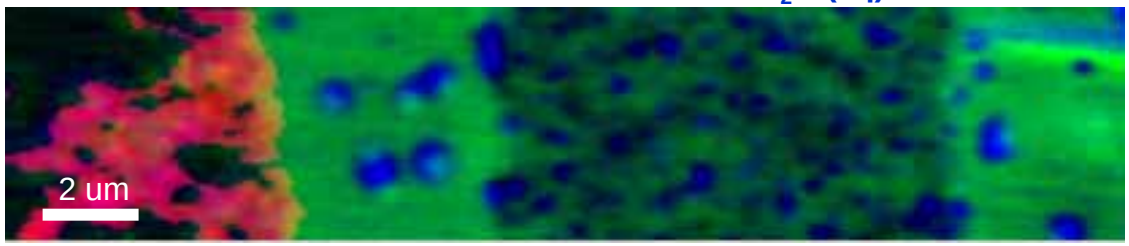
O 1s stack (524-564 eV) measured at RH = 0.0 (He atm)

cathode nafion

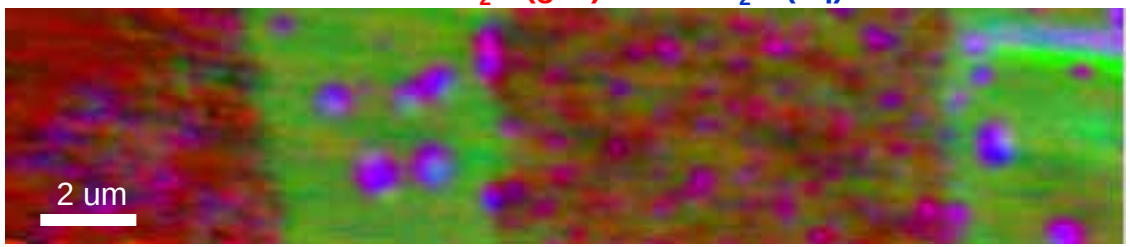


O 1s stack (524-564 eV) measured ~1 hour after setting RH = 0.85

cathode nafion H_2O (liq)

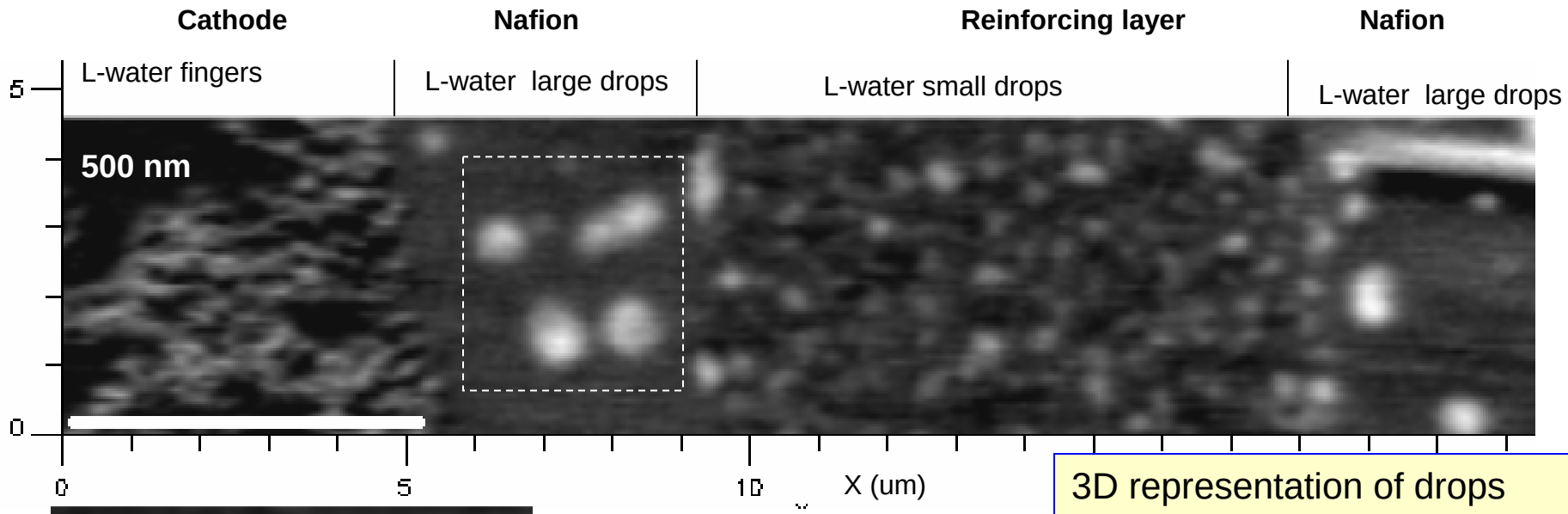


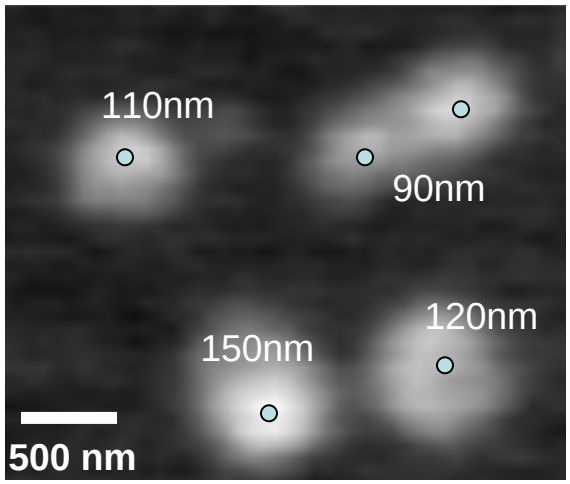
H_2O (gas) nafion H_2O (liq)



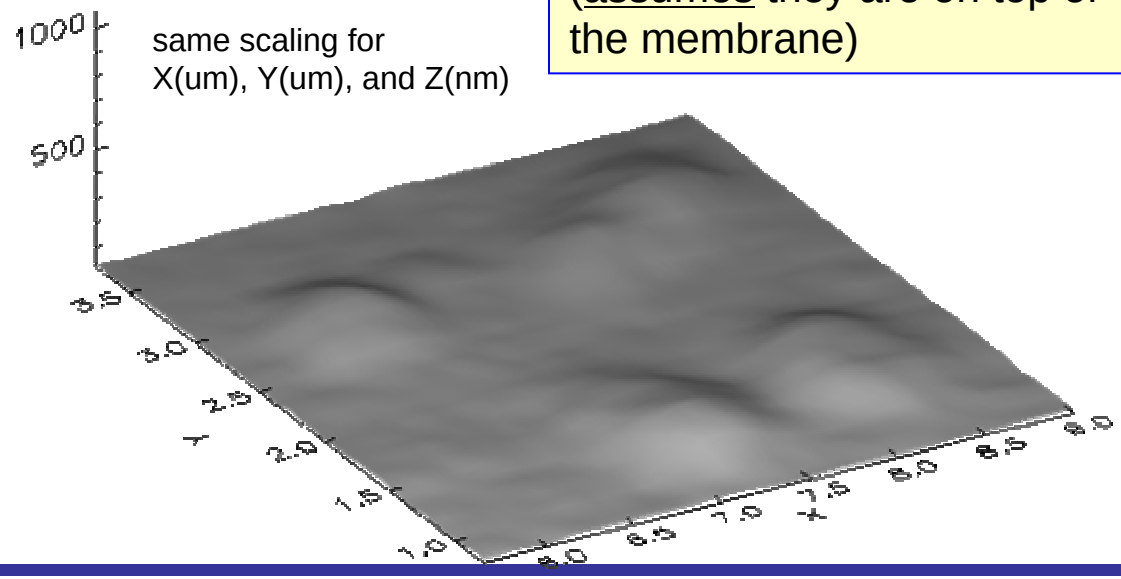
Berejnov et al. ECS Transactions 41 (**2011**) 395

Liquid drops in/on PFSA membrane





<contact angle> ~ 15.3^{o}



3D representation of drops (assumes they are on top of the membrane)

Berejnov et al. ECS Transactions 41 (**2011**) 395

Outlook

AFCC finds STXM analysis of fuel cell materials sufficiently useful
* to hire a dedicated STXM researcher (V. Berejnov) and
* to purchase proprietary access on a monthly basis

Reliable performance with verified methodologies is critical

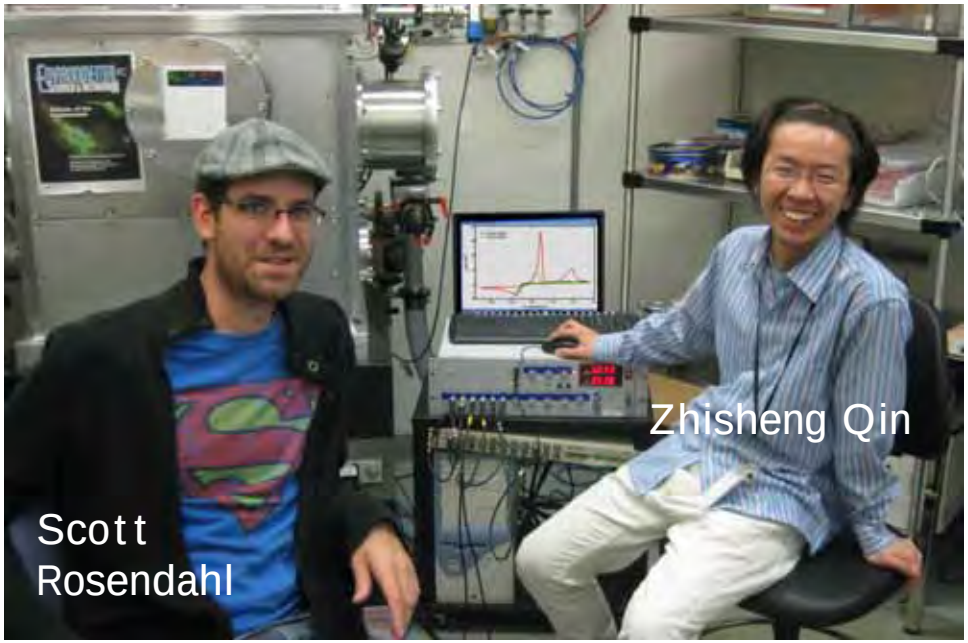
Further technique development -

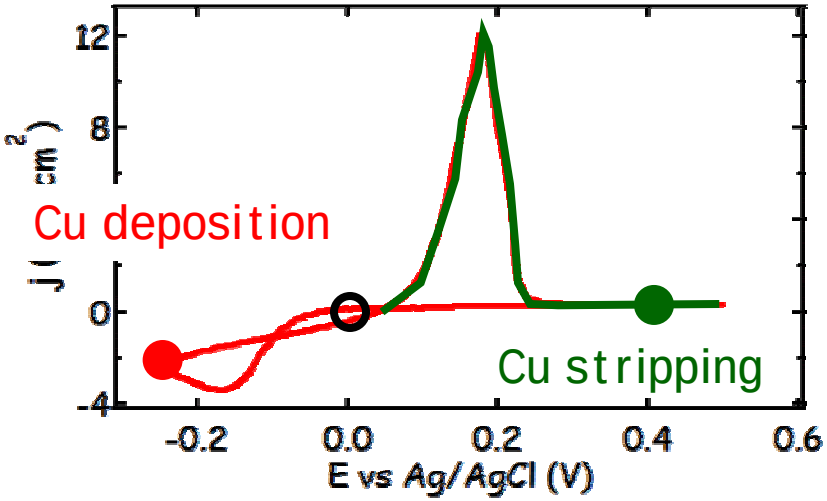
Cryo-spectro-tomography ➔ quantitative 3D distributions of ionomer in cathodes

Environmental cell - improve performance at lower T; (high T & high RH)

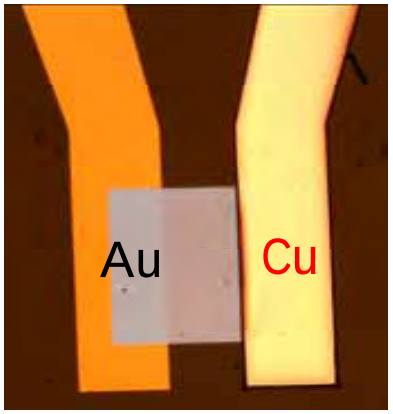
***in situ* electrochemistry** – biasing fuel cell MEA to study proton transport

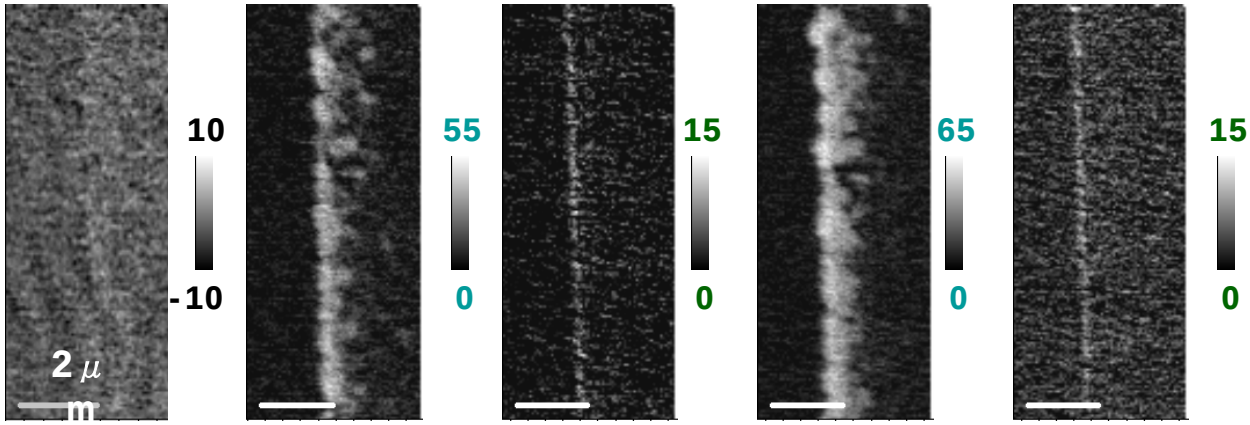
in situ electrochemistry





Cu map (OD_{940} - OD_{928})





Qin et al, J. Phys. Chem B (in prep)

Summary

- STXM - powerful analytical technique for PEM-FC materials and processes
  - multi-element speciation
  - quantitative mapping of chemical species
  - porosity
  - *in situ* capabilities
  - spectro-tomography at R.T.

    - soon cryo-spectro-tomography @ CLS

- Our STXM papers on PEM-FC

Methods

- ionomer mapping — Susac et al. ECS Transactions 41 (**2011**) 629; ibid 50 (**2012**) 405
- spectro-tomography — Berejnov et al. ECS Transactions 50 (**2012**) 361
- *in situ* humidity studies — Berejnov et al. ECS Transactions 41 (**2011**) 395

Alternate catalyst systems

- 3M Nanostructured Thin Films — V. Lee et al, ECS Transactions, 58 (**2013**) 473; V. Lee et al. J. Power Sources (**2014**)
- Ink-jet print cathodes — M. Saha et al., ECS Transactions, 58 (**2013**) 797

Degradation effects and mechamisms

- Pt degradation — Berejnov et al. Phys. Chem. Chem. Phys. 14 (**2012**) 4835
- Carbon corrosion — Hitchcock et al. J. Power Sources (**2014**)

Acknowledgements

Synchrotron Facilities

Collaboration

Funding