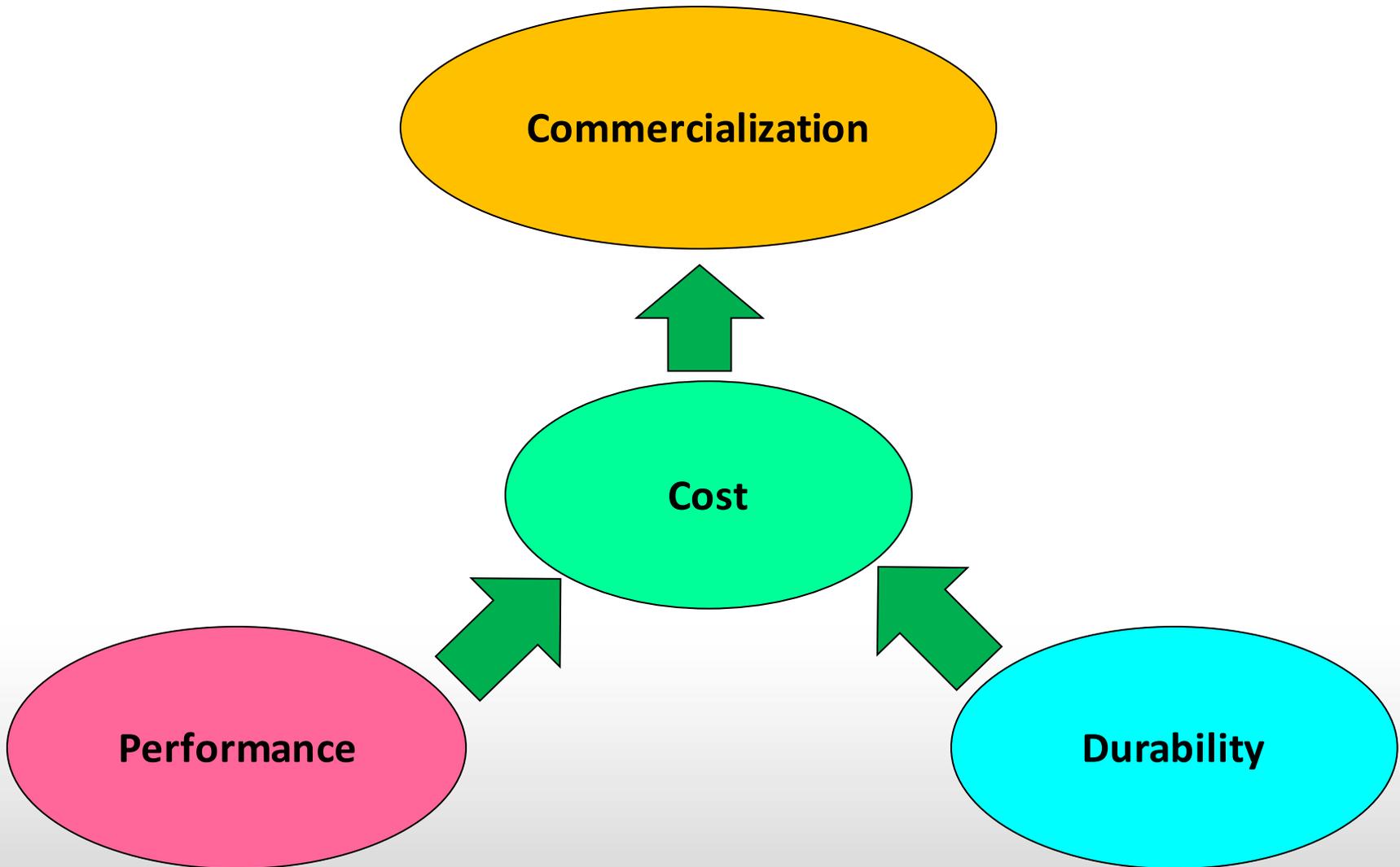


The challenges for PEMFC catalysts in automotive applications.

Stephen Campbell: 15th May 2013

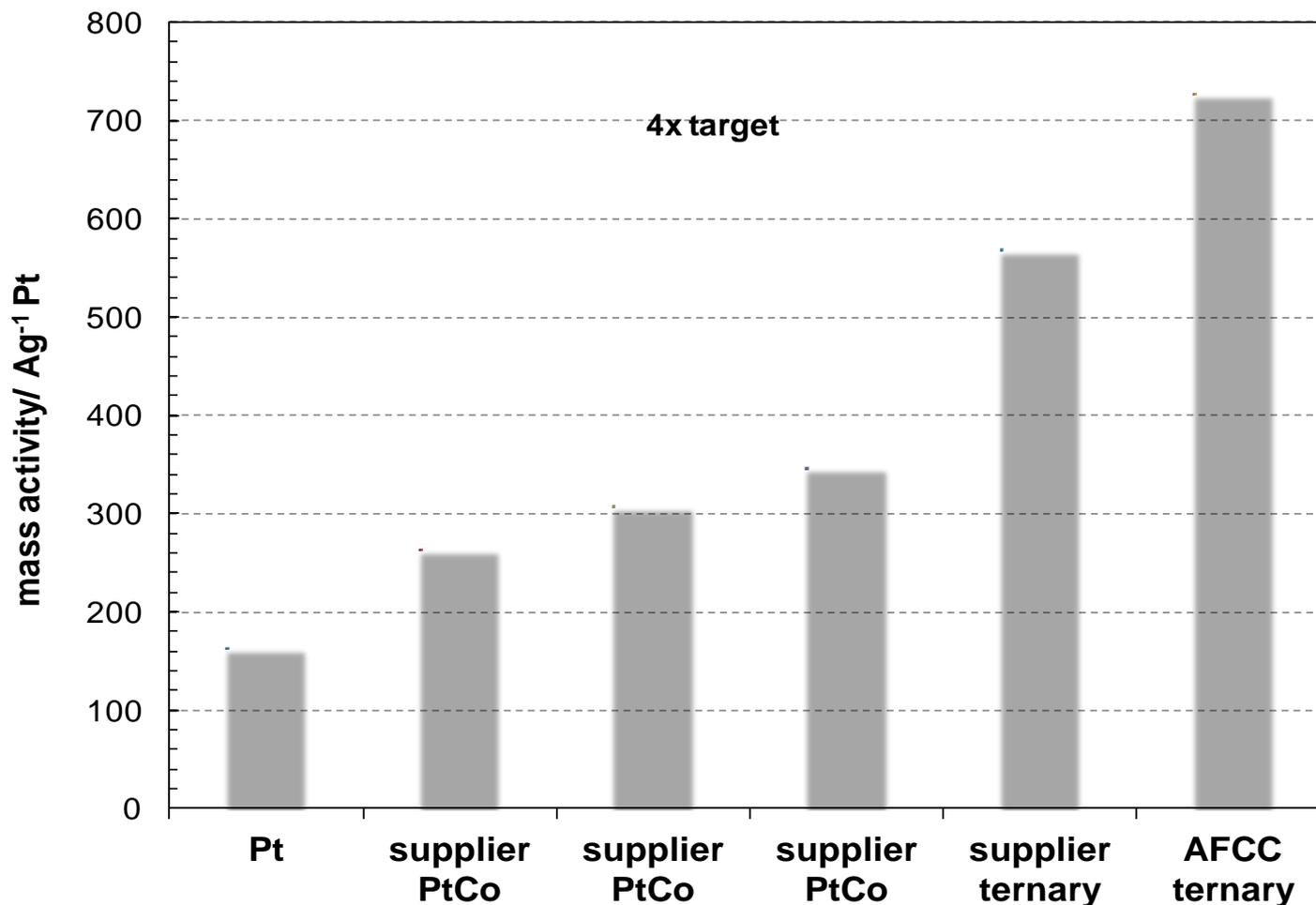


- Lower cost means less platinum group metals (PGM).
- Less PGM means
 - higher **performance** catalyst (in $\text{Ag}^{-1} \text{Pt}$)
 - reduced **durability** (especially SU/SD)
 - reduced tolerance to impurities.
- Optimization focussed upon: -
 - Fundamental materials properties
 - Component integration into MEA
 - **Catalyst layer structure/ performance relationship**
 - Stack/system trade-offs (for operational durability)

- There is a need to reduce Pt loadings to $<300\text{mgcm}^{-2}$ in order to meet automotive cost targets **without any loss in performance**.
- A internal target was established to reach a 4x improvement in ORR activity for cathode catalysts
- There have been many studies of Pt-transition metal alloys that have enhanced activity but these have not been supplier-led.
- AFCC has compared the activity of the catalysts of several suppliers using ex-situ RDE screening in 0.1M HClO_4 at 30°C .
- So far none have met the 4x target but we have been able to make progress internally with a ternary alloy. Supplier scale-up requires more work.

Recent progress with Pt alloy/ carbon catalysts

Ex-situ RDE data for ORR (0.1M HClO₄) 30°C

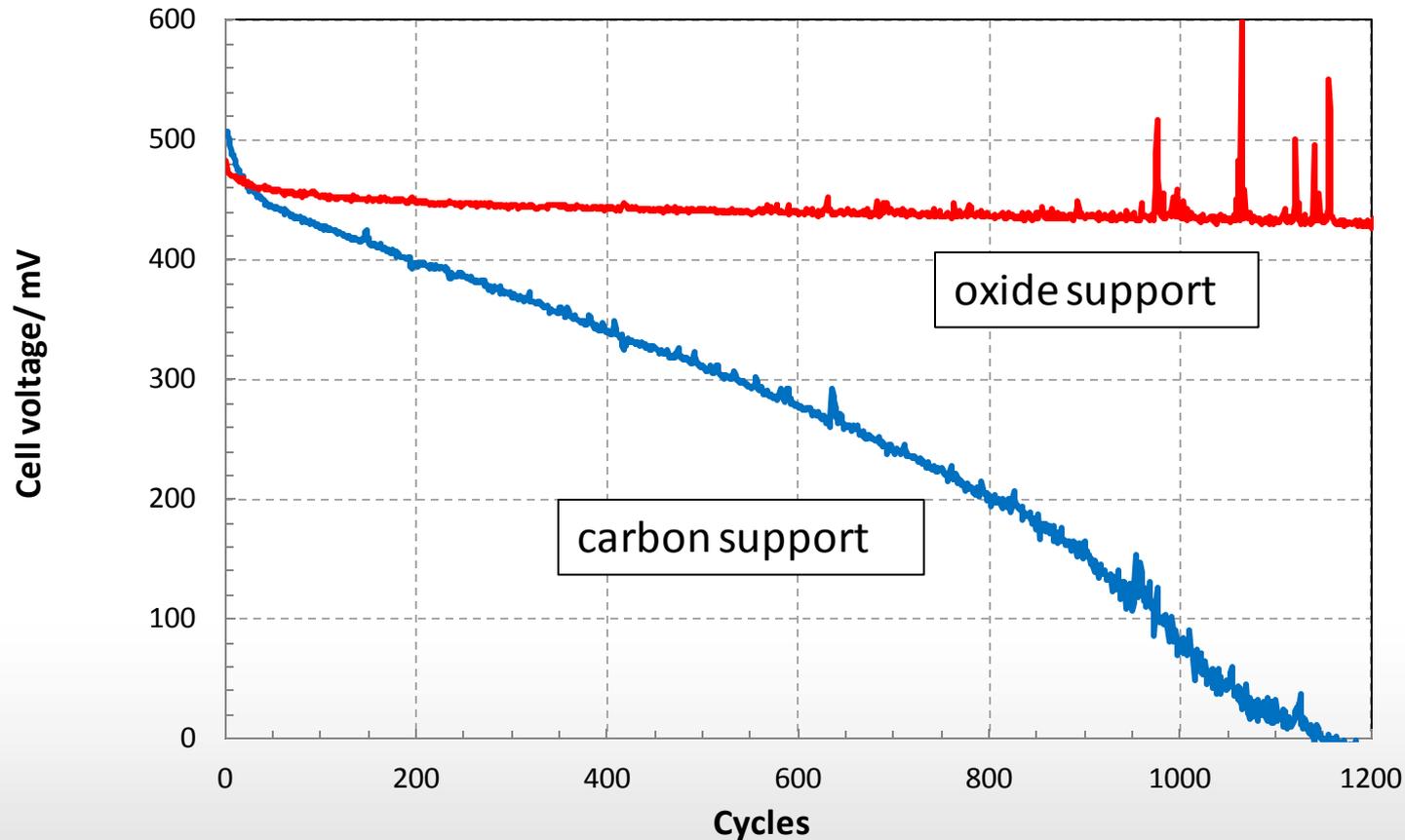


- Start-up causes high potentials due to hydrogen entering an air-filled fuel flow-field.
- Potentials can reach 1.8V which can damage the cathode catalyst.
- AFCC has pursued two materials approaches to mitigate this damage (independent of system mitigation).
 1. Alternative catalyst supports resistant to oxidation.
 2. Adding a selectively conducting component to the anode electrode structure to limit the potential transients.

- Oxide supports may be stable to oxidation but must also be:-
 - Electrically conductive
 - High surface area
 - Cost effective
 - Potentially interactive with the catalyst (SMSI)
- Common options are ITO, ATO but these have been found to have stability issues.
- AFCC has demonstrated baseline performance and enhanced SU/SD durability with an oxide supported Pt cathode catalyst.

Platinum on oxide support

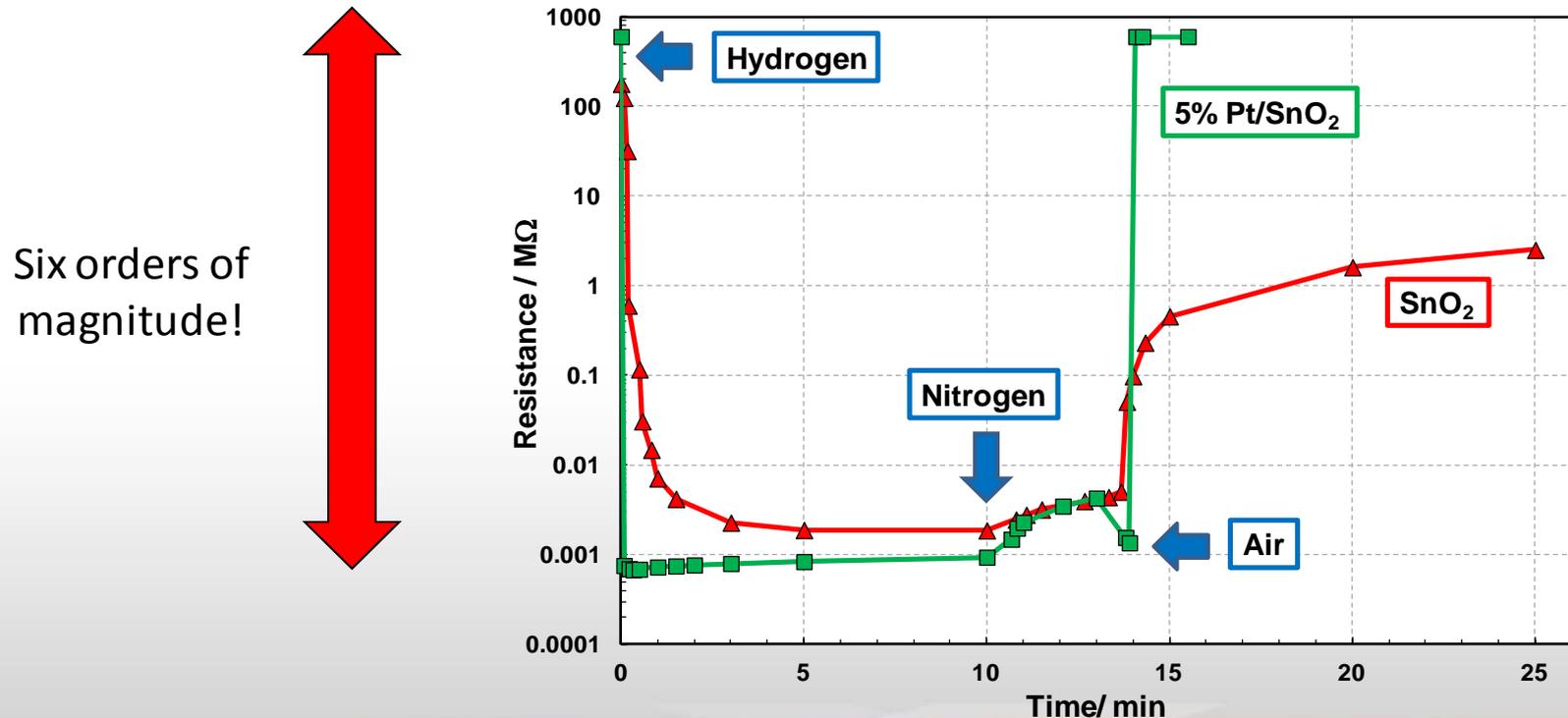
Subscale (50cm²) cell; startup/ shutdown AST cycles;
performance at 1.5Acm⁻²



Proof of concept only – not commercially viable

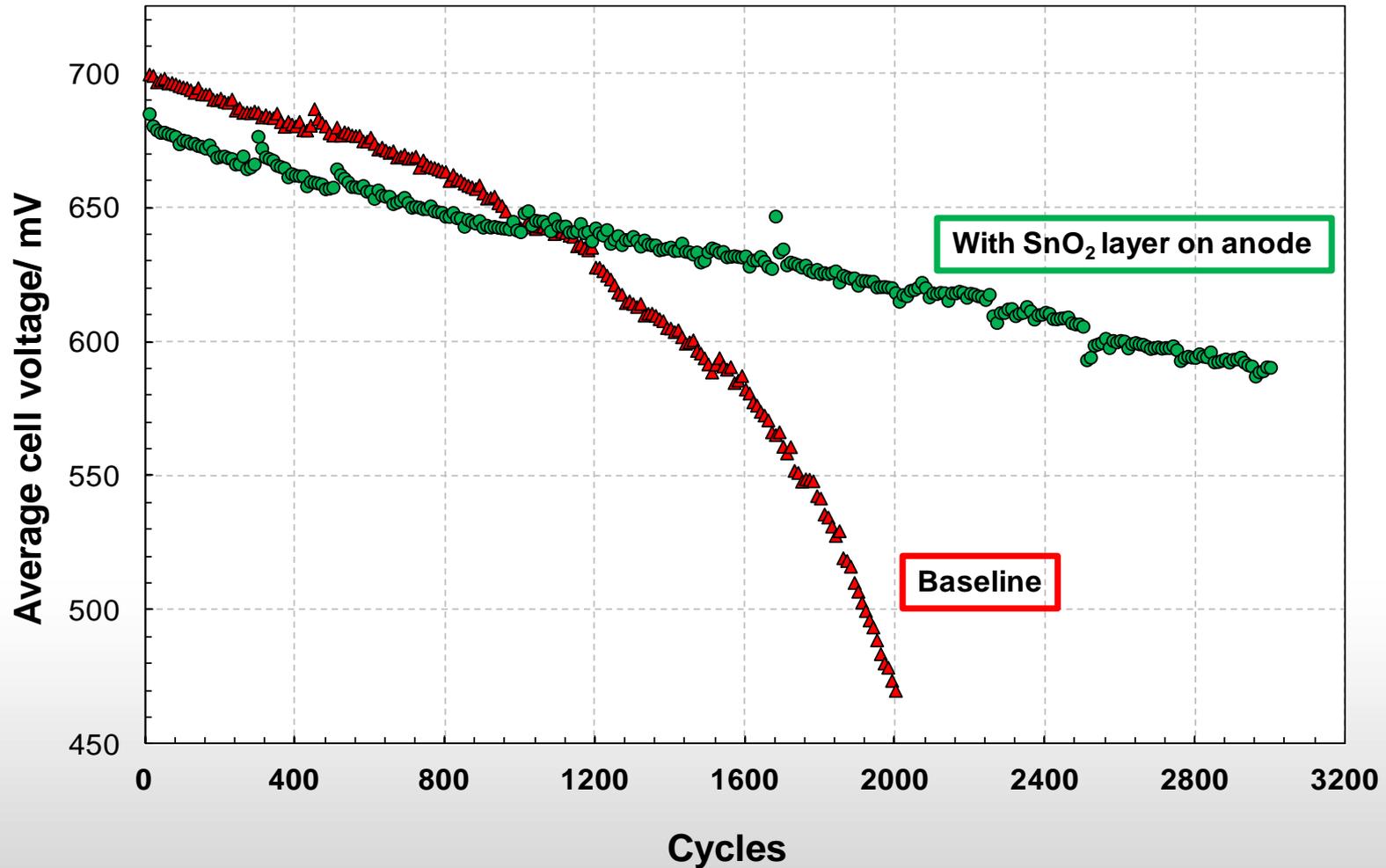
Selective oxide on the anode

- Tin oxide (SnO_2) may be switched from a conductive state in hydrogen, to a resistive state in air.
- The speed of switching may be enhanced by the addition of Pt onto the oxide surface.



- When an SnO₂ layer is placed between the anode catalyst layer and the GDL it is conductive during normal operation.
- When in an air state, however, it is resistive, limiting in-plane currents and holding the anode potential lower during the start-up transient.
- This keeps the cathode from going to damaging, high potentials and reduces cathode performance degradation.

Fuel cell start-up/shut down cycles



- In-house ternary alloys have demonstrated >4x ORR mass activity over Pt/C baselines using RDE (ex-situ).
- Durability of the catalyst during start-up transients may be enhanced by: -
 - an oxide layer in the anode that changes from conductive to resistive depending upon its environment, and/or
 - a conductive oxide catalyst support for the cathode that resists oxidation.

- In order to design the catalyst layer to provide the required transport properties for a high performing catalyst it is necessary to first be able to characterize the catalyst layer in terms of:-
 - Catalyst structure
 - Ionomer structure
 - Pore structure

- Then modeling may be used to design the optimum three phase structure.

- Methods being developed through academic collaborations are:-
 - E-tomography (3D imaging with HRTEM)
 - FIB/ HRSEM (Focussed ion beam sectioning)
 - STXM (scanning transmission X-ray microscopy)

- These will be used as design tools for the next generation of fuel cell stacks.

Methods of catalyst layer characterization

E-tomography

Sample size: 0.5 x 0.2 x 0.1 μm

Voxel: nm x nm x nm

Speciation: Pt + Carbon

FIB tomography

Sample size: 5 x 3 x 2 μm

Voxel: 20x20x20 nm

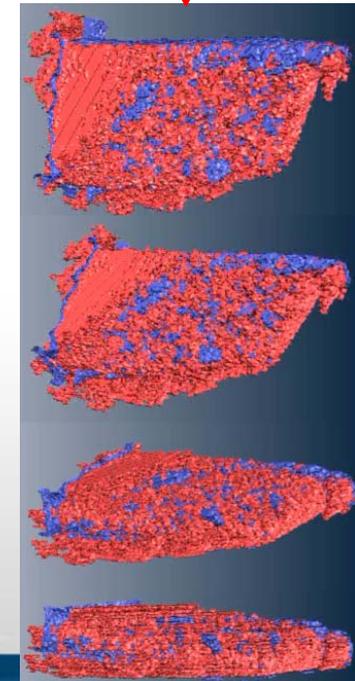
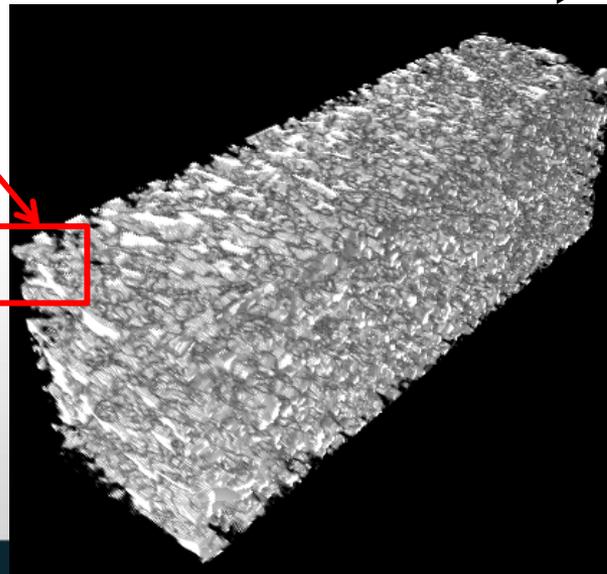
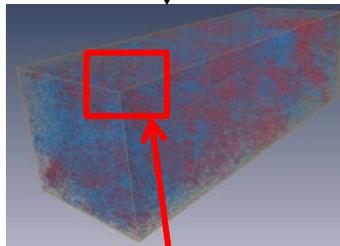
Speciation: no chemical info

STXM

Sample size: 5 x 3 x 0.2 μm

Voxel: 30x30x200 nm

Speciation: C + ionomer + Pt



E-tomography of catalyst

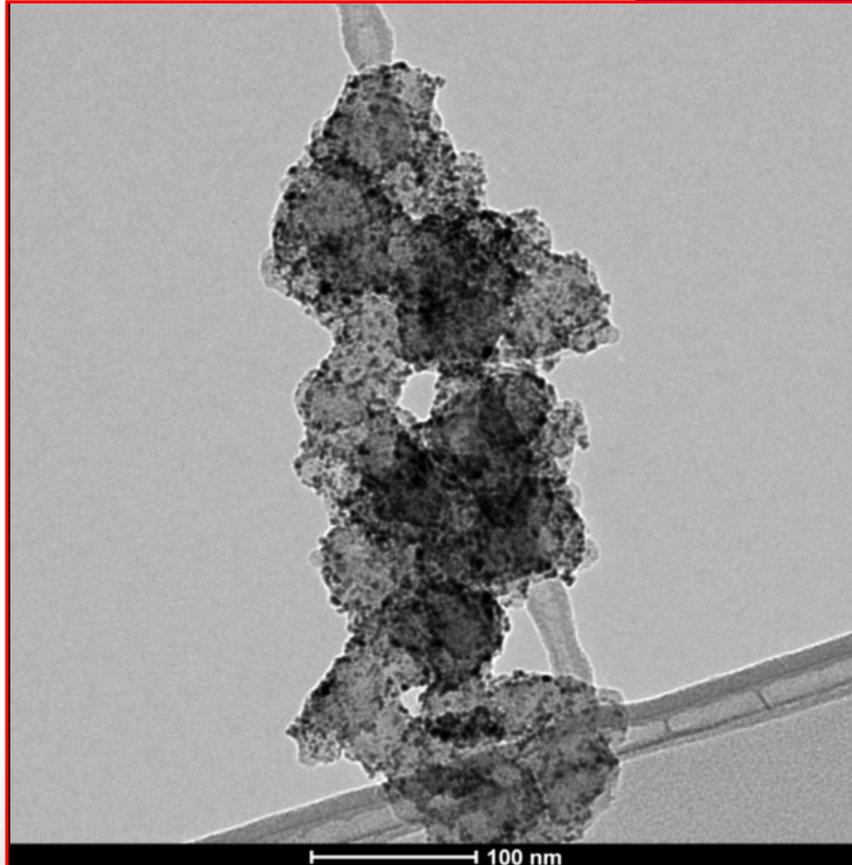
Sample size: 0.2x0.2 x 0.1 μm

Voxel: nm x nm x nm

Speciation: Pt + C



[TEC10-V50E-C+Pt- 80k-ali.av](#)



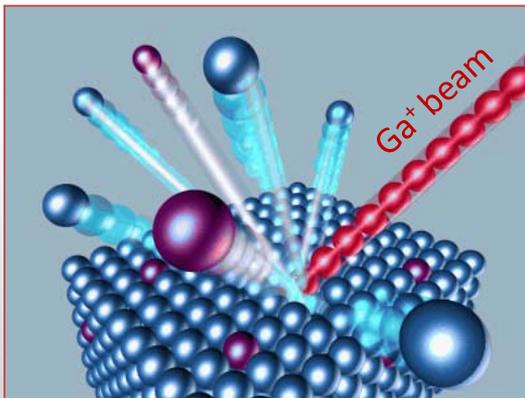
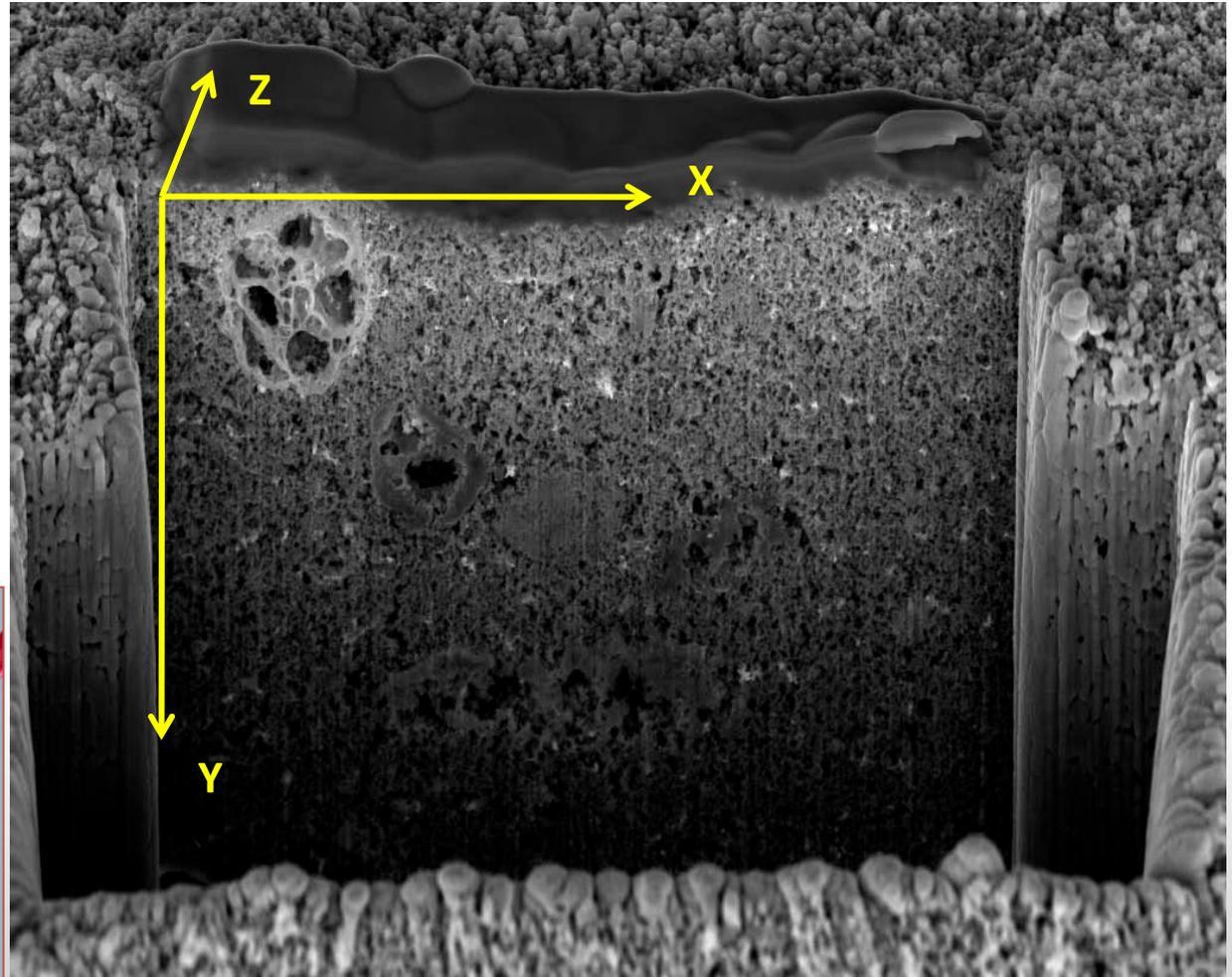
- Individual catalyst agglomerates on TEM grid.
- Sample rotated and multiple images taken.
- Composite of images produces 3D representation of Pt particles on carbon support.
- Advantage over 2D image is that position of individual Pt particles on support surface can be determined.
- No ionomer in sample.

Visualization of the catalyst layer structure by FIB tomography

Catalyst layer cross-sections are made by application of focused ion beam (FIB) and imaged by high resolution secondary electron microscope (HRSEM).

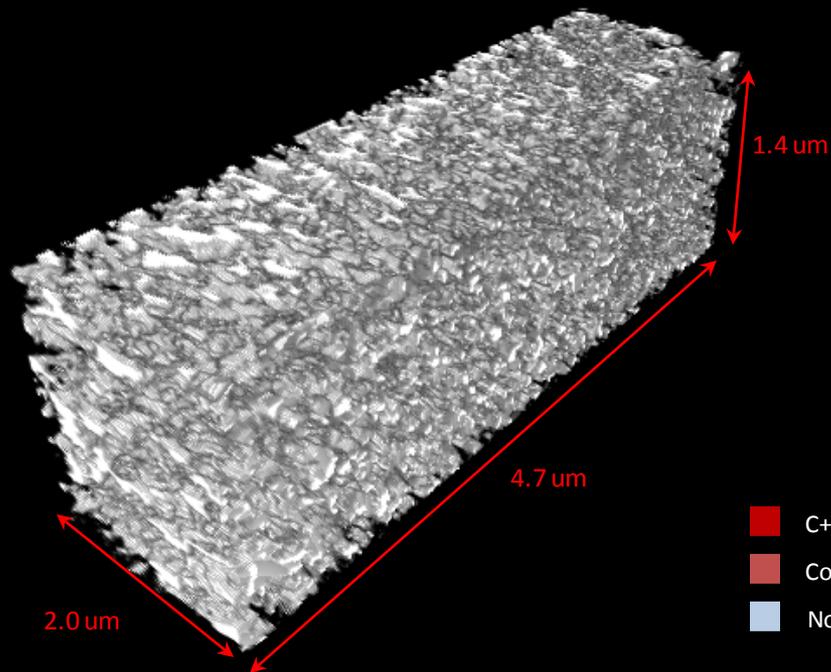
Sectioning of the CL is done by application of the focused ion beam (FIB). CL is bombarded with accelerated Ga ions.

FIB tomography: FIB slicing and subsequent HRSEM imaging to get the 3D CL model.

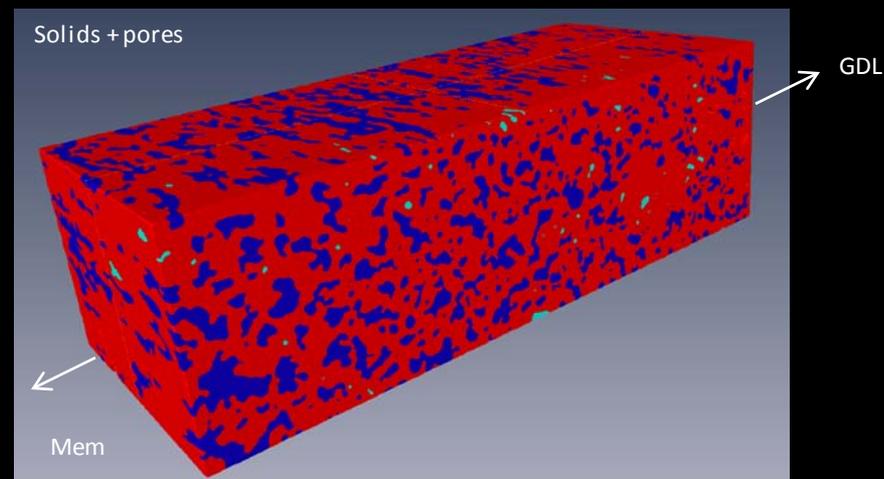


3D representation of the catalyst layer

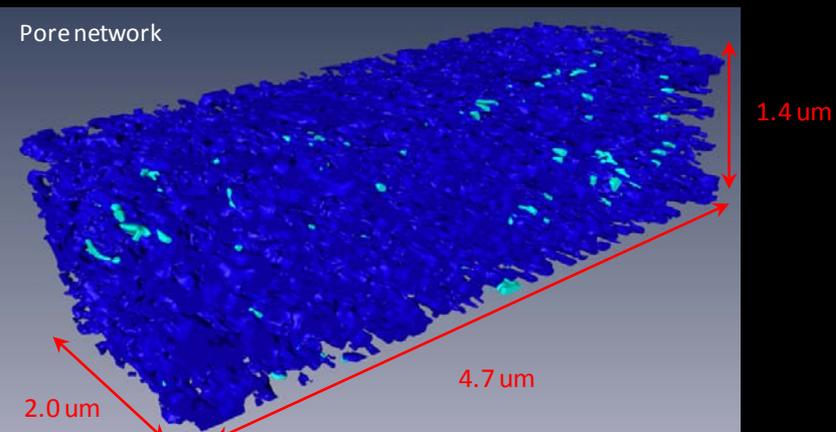
Image J



Amira

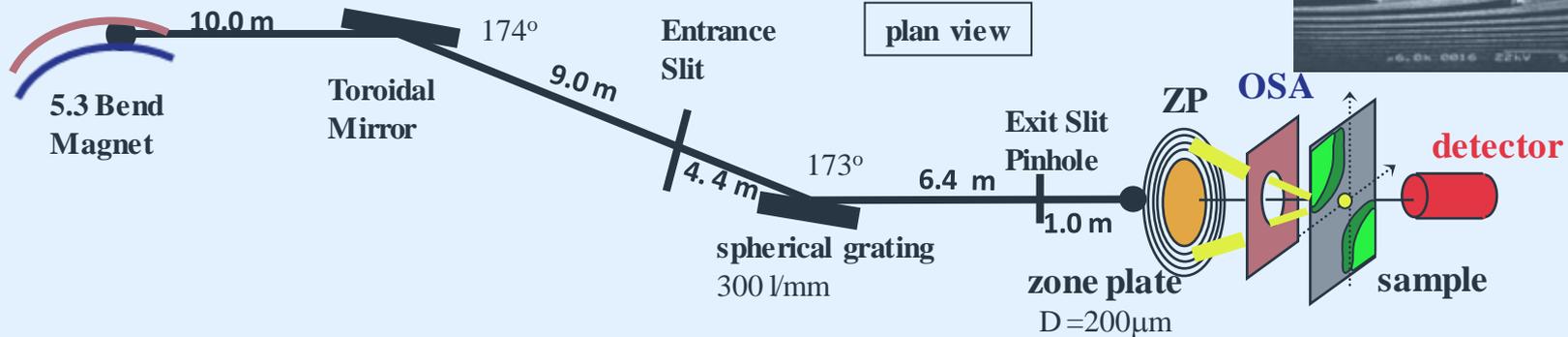


-  C+Pt+Nafion
-  Connected pores
-  Non-connected pores



- HRTEM tomography can be used to show 3D structure of the Pt/carbon structure of the catalyst agglomerates.
- It can also be used to generate 3D representations of the catalyst layer structure showing the Pt and pore distribution.
- No chemical speciation can be done so cannot distinguish between carbon support and ionomer.
- FIB tomography can be used to generate larger scale representations of the pore structure within the catalyst layer.
- Can only separate solids and pores.
- A method to distinguish between Pt, carbon, ionomer and pores is needed.

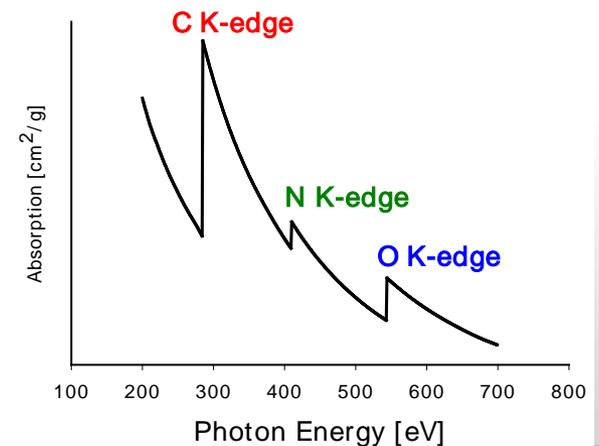
ALS Bend Magnet beamline 5.3.2



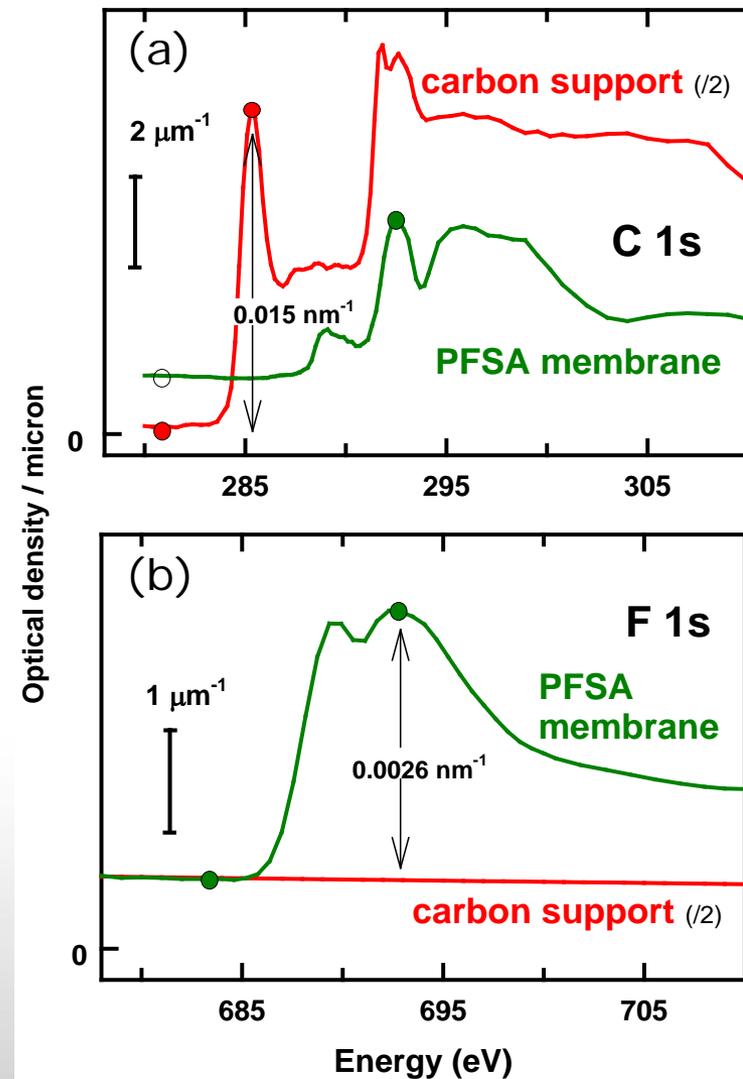
- Chemical speciation through X-ray absorption spectra (NEXAFS)
- Spatial resolution ~ 30 nm; Energy resolution < 0.1 eV
- Quantitative chemical mapping (Beer's law)
- All elements (100-2500 eV)
- Transmission requires thin samples \Rightarrow microtomed sections (~ 100 nm thick)

Beamlines 5.3.2 & 11.0.2 at the Advanced Light Source, USA
Beamline 10ID1 at the Canadian Light Source, Canada

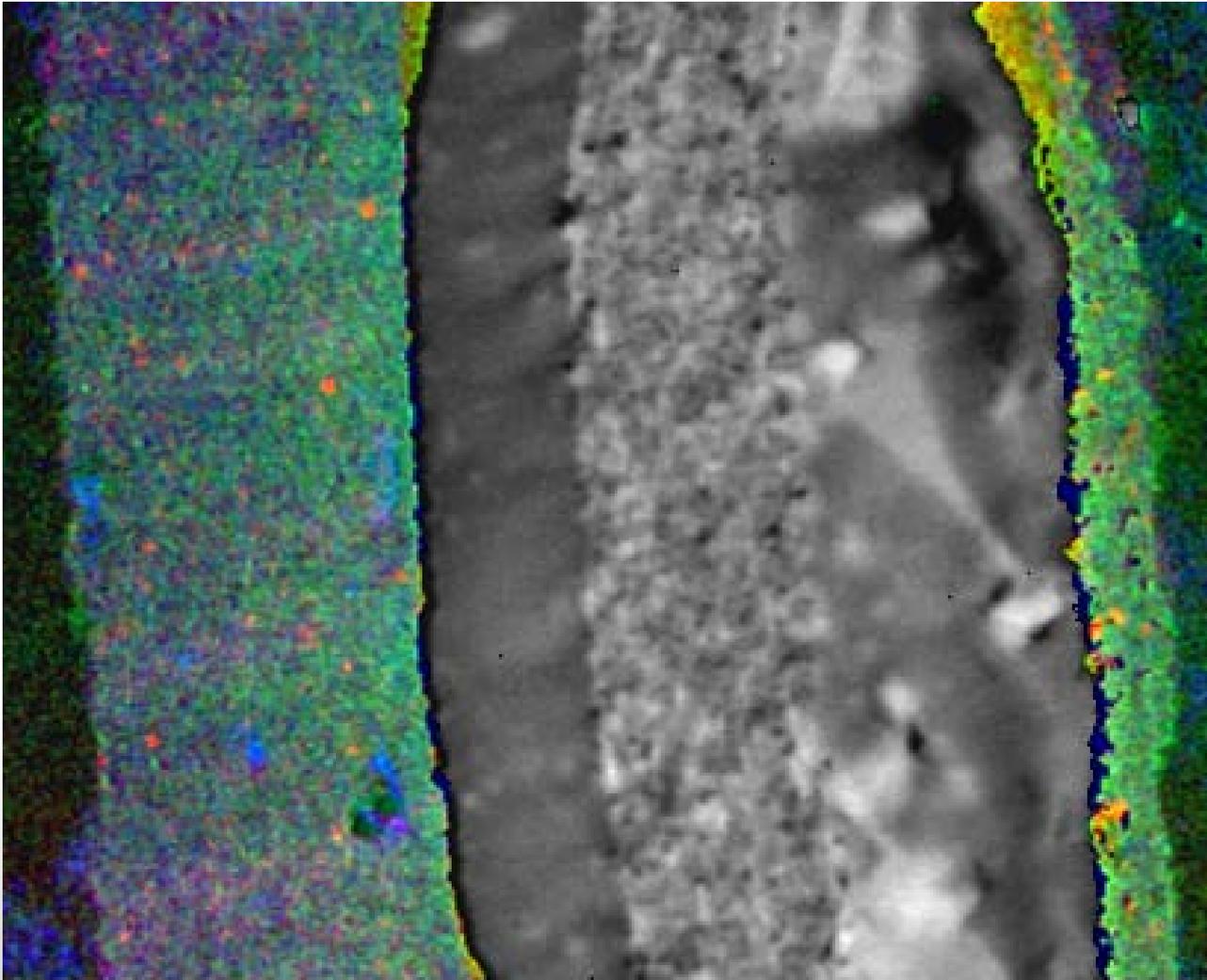
NEXAFS from each core level of the target - site specific



- ❑ For mapping of the ionomer in the catalyst layer must record X-ray transmission images at two different X-ray absorption energies for carbon (C) and fluorine (F).
- ❑ C 1s map provides information on the carbon support
- ❑ F map provides info on fluoride-containing species in the catalyst layer (ionomer, PTFE)



2D Reconstruction of the catalyst layer



membrane

carbon support

platinum

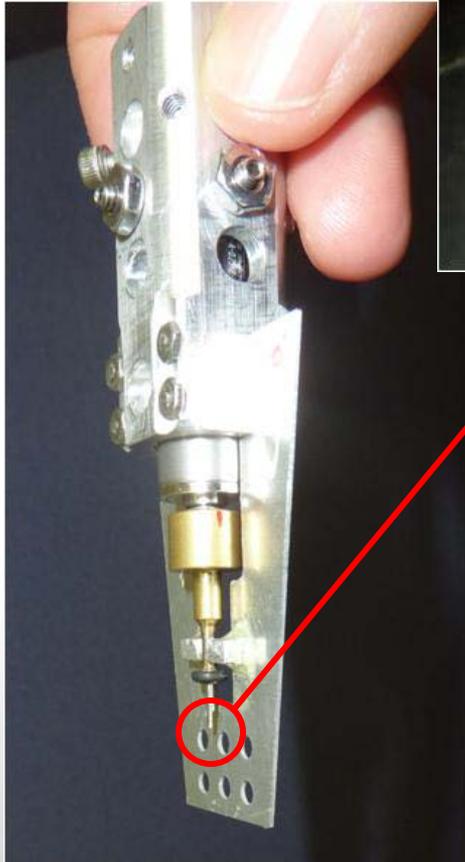
ionomer

Note: each pixel contains a complete NEXAFS spectrum of the species present.

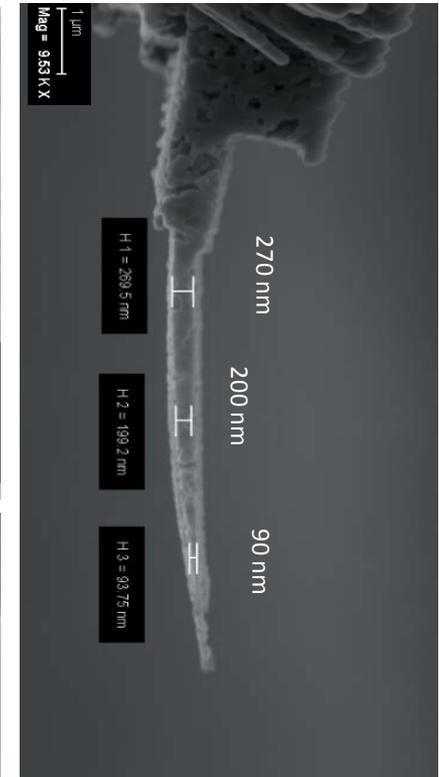
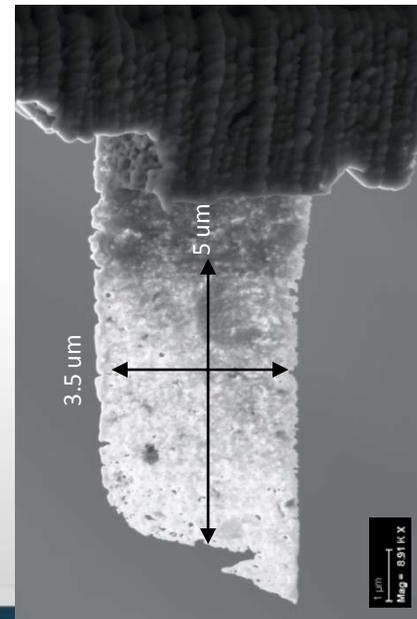
- STXM allows for chemical speciation within the catalyst later thin section.
- Can differentiate between carbon, platinum, ionomer, pores.
- This 2D capability can be used tomographically to generate a 3D representation of all these species by rotating a FIB section of the catalyst layer and recording multiple images.

CCM sample preparation for the 3D STXM tomography (FIB sample prep.)

Need to have a rotator for +/- 60° sample rotation

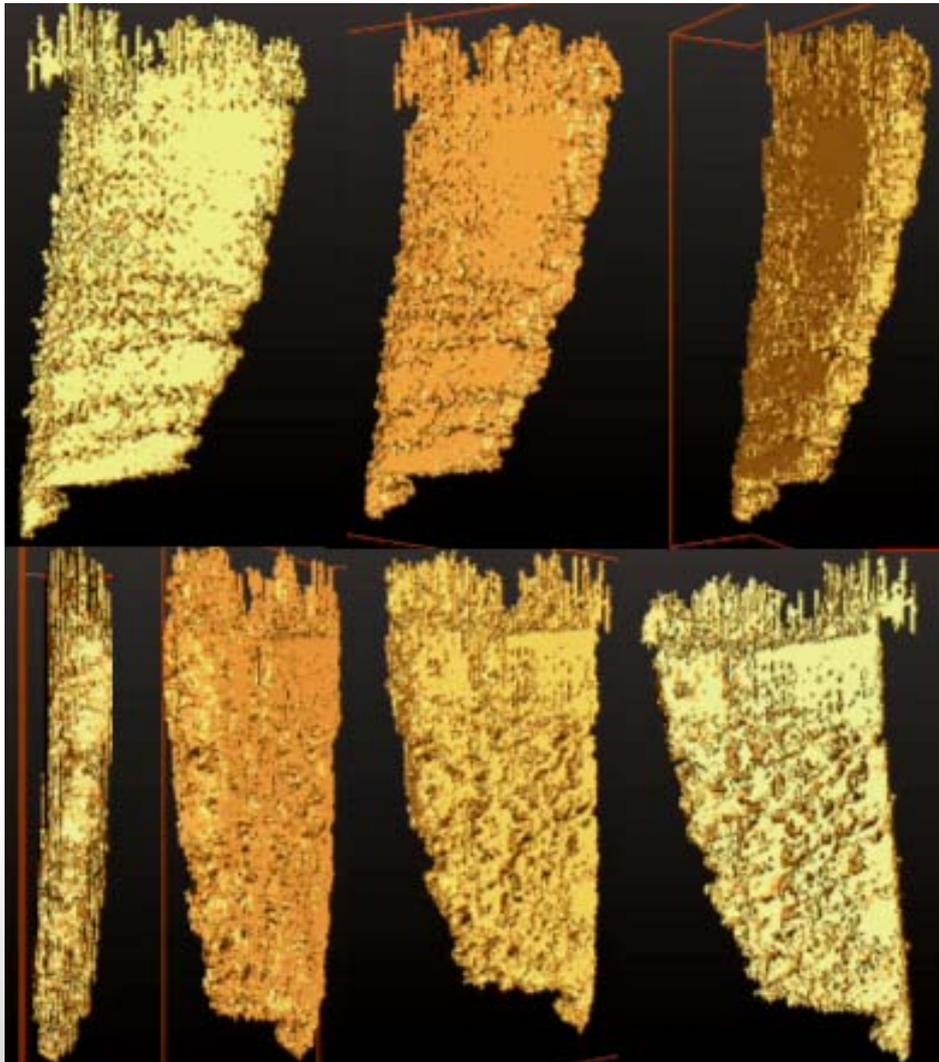


Sample is prepared using FIB.

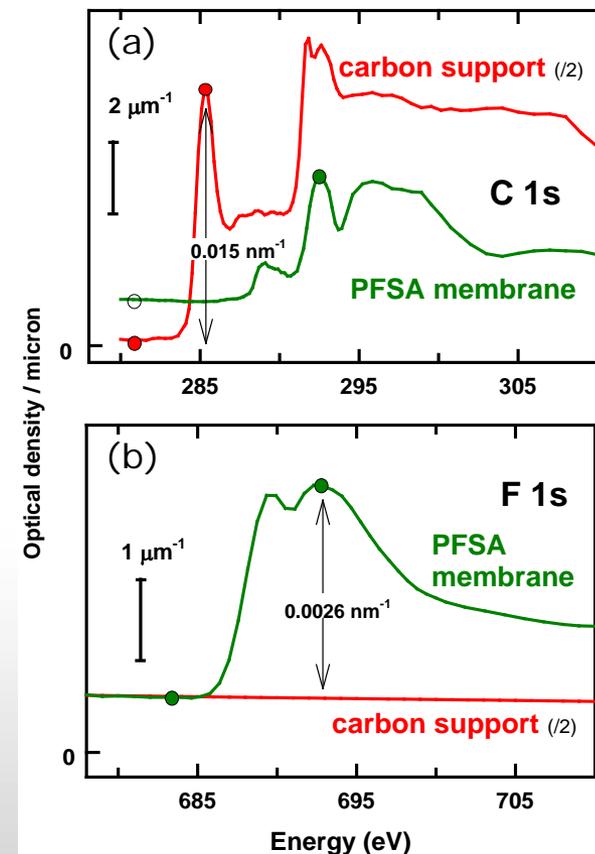


FIB sample prep. done by Julia Huang, McMaster

Now Rotate the CL Sample for $\pm 60^\circ$ and Record the C and F maps every 2 Degrees.



Every pixel in these images contains a spectrum characteristic for the chemical species.

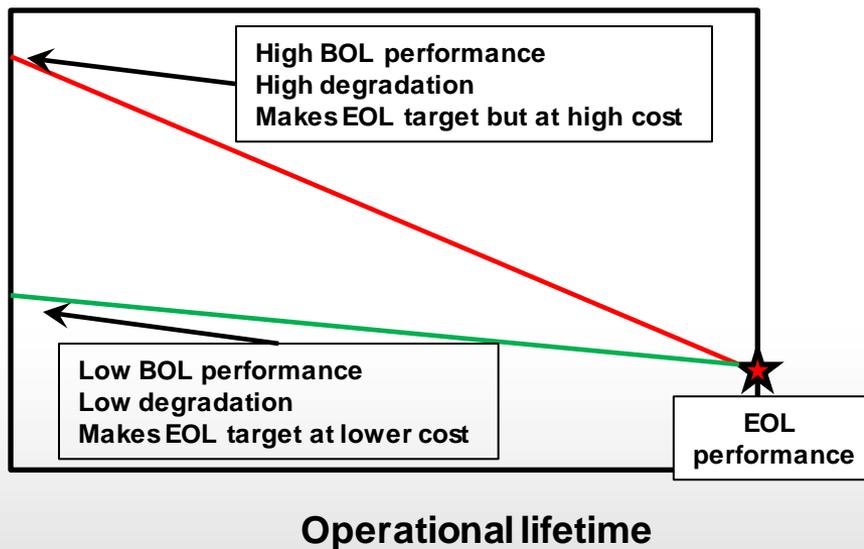


FIB-1 sample: 2071 TPM BOL cathode, height~8 μm , width~4 μm , thickness~200 nm

- Thin sections may be analyzed to differentiate between platinum, carbon support, ionomer and pores.
- By rotating the thin section 3D tomographic representation may be constructed from multiple images.
- Carbon and ionomer 3D structures have been demonstrated.
- Work continues.

- Significant progress has been made in the development of MEA components (catalyst, membrane, etc.) that address the challenges that must be overcome for commercialization of PEMFCs for automotive applications.
- Tools are being developed to understand the structure of the catalyst layer and these will be critical in the design of the next generation of MEAs.
- The fundamental materials and the means to put them together in an optimized way are at hand and the path forward is exciting!

- Will it ever be possible to eliminate PGMs from the cathode of a PEMFC?
- DOE targets: -
 - Does an EOL performance and a BOL cost target define the target sufficiently?



This approach tends to focus upon the **durability** of the catalyst layer and its degradation rate at cost.