Control of Ionomer Distribution in Roll-to-Roll Coated Fuel Cell Catalyst Layers

Scott Mauger

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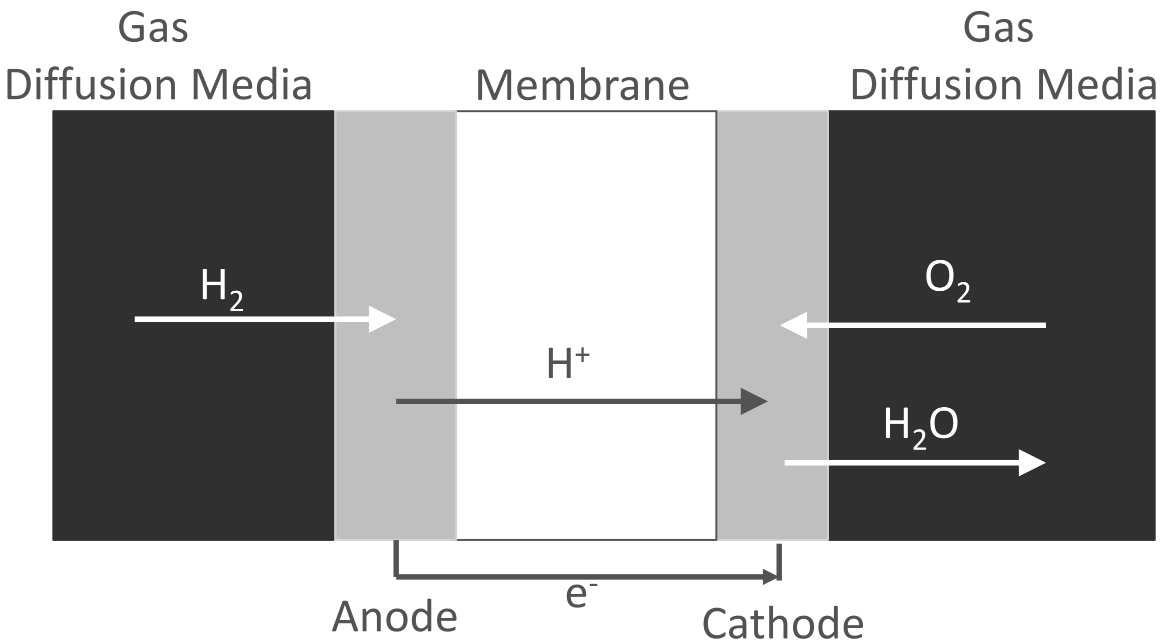
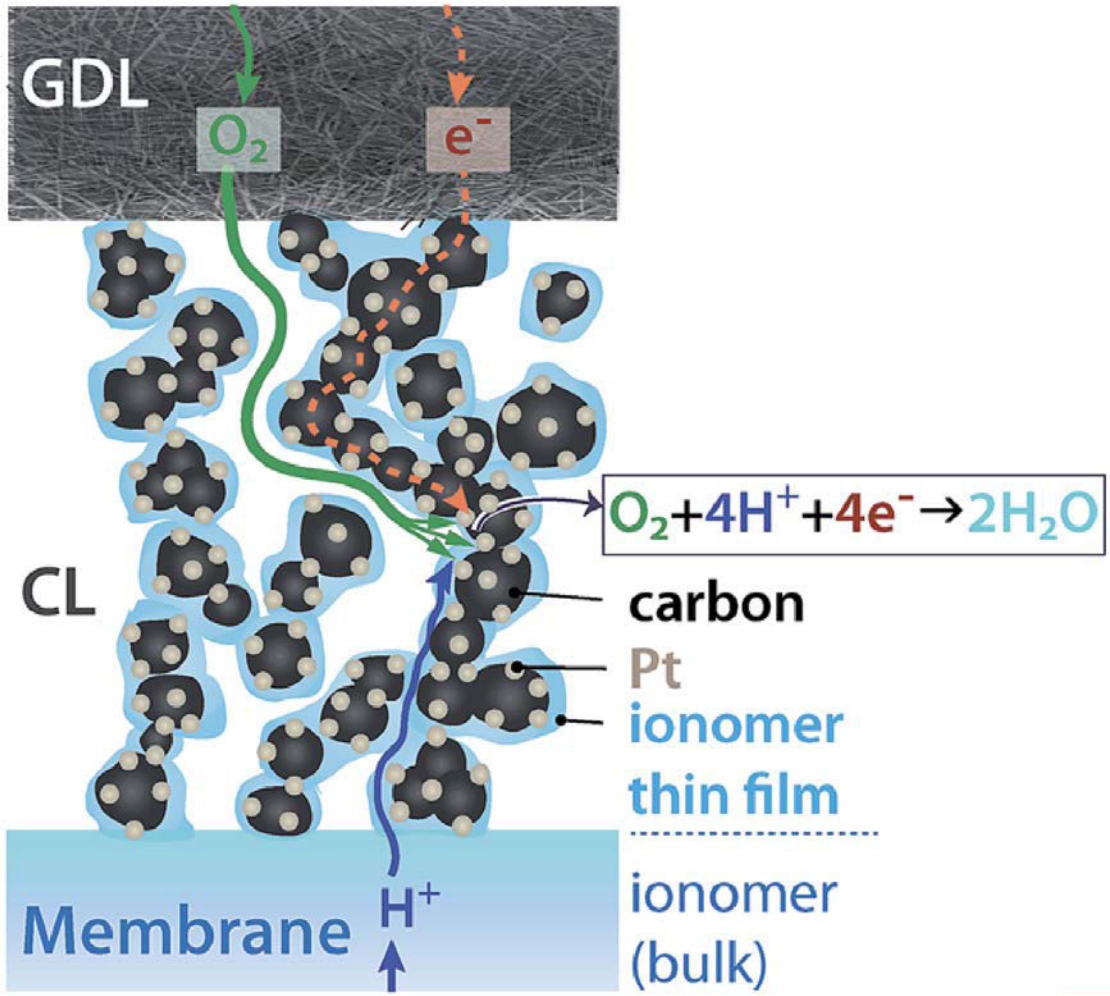
Proton Exchange Membrane Fuel Cells

- High efficiency (>2x internal combustion)
- Zero GHG emissions
- Long-range EV (300+ miles/tank)
- Short refueling time (5 min)



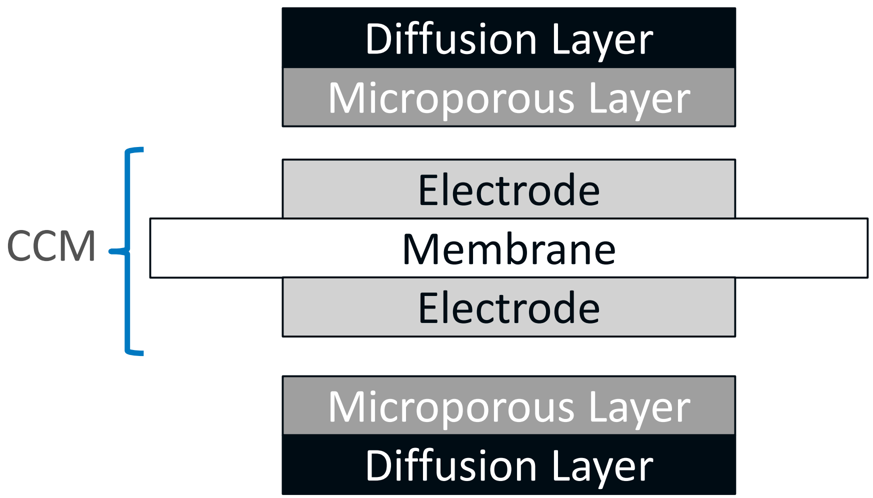
Fuel Cell Catalyst Layers



Weber and Kusoglu, *J. Mater. Chem. A* 2014, **2**, 17207–17211

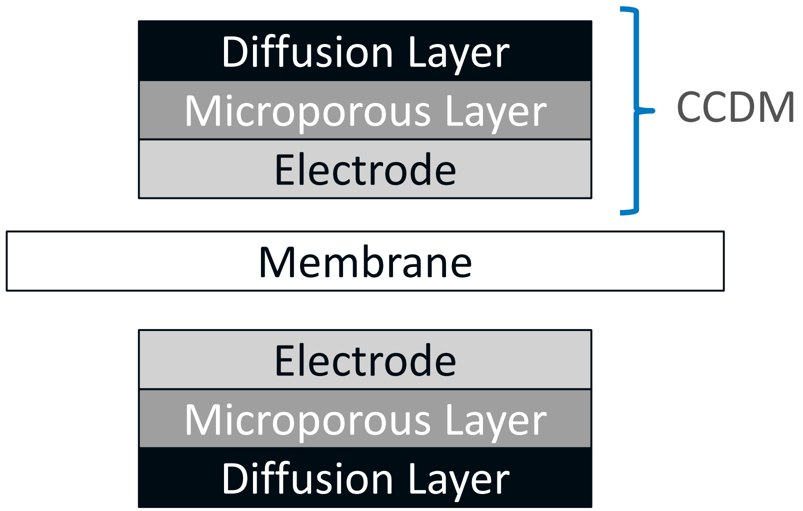
Fuel Cell Construction

Catalyst-Coated Membrane (CCM)



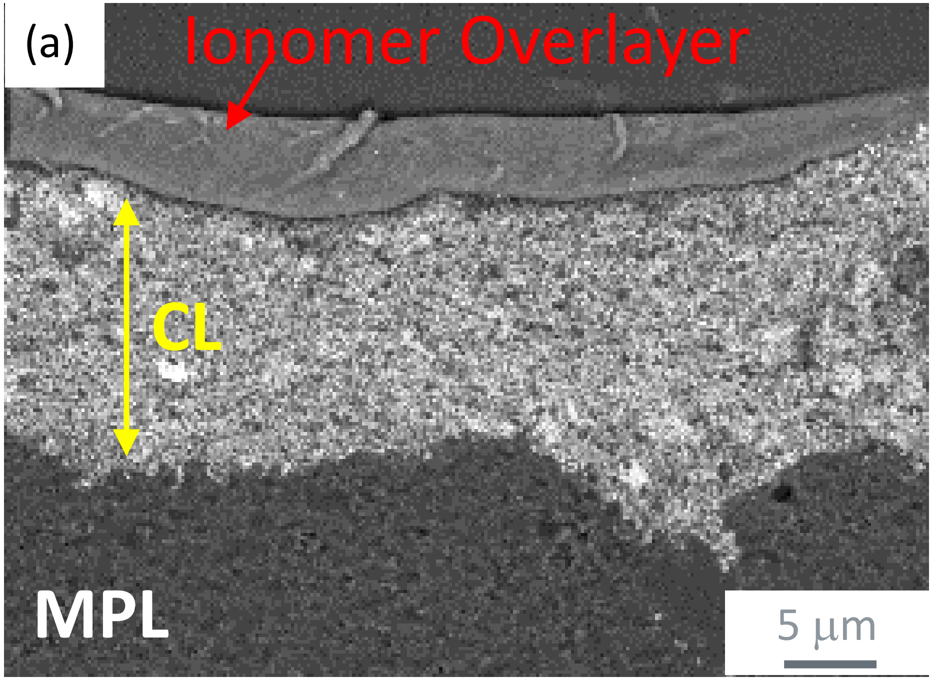
- Electrode applied to membrane
- Extensively used in laboratory experiments
- Challenging for manufacturing due to swelling of membrane

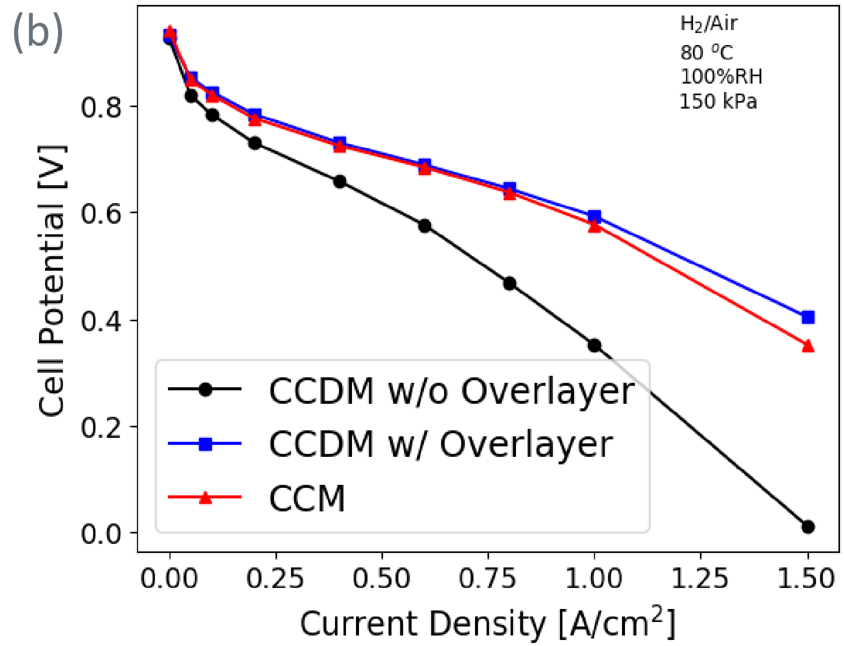
Catalyst Coated Diffusion Media (CCDM)



- Electrode applied to microporous layer
- Potentially simpler for manufacturing
- Some reports of improved fuel cell performance

CCDM Challenge





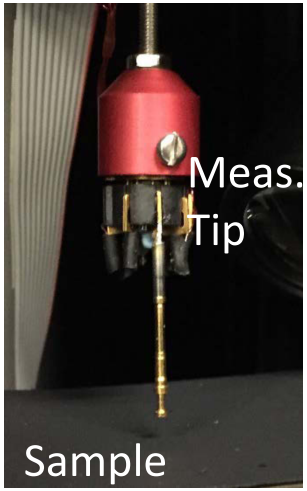
Can we control the distribution of ionomer to create a catalyst layer with an ionomer rich surface from a single coating step?

How can we control ionomer distribution?

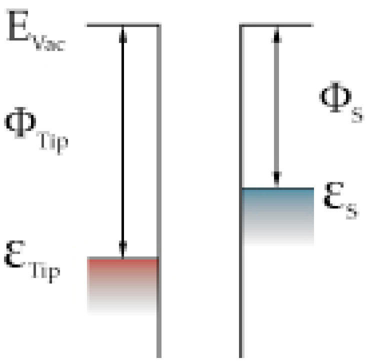
- Ink Formulation
  - Water to 1-propanol ratio
    - 25 and 75 wt% water
  - Ionomer-to-Carbon ratio (I:C)
    - 0.9
    - 1.2
    - 1.6
- Drying Temperature
  - 25 ˚C
  - 60 ˚C
  - 80 ˚C
- Initial samples prepared using Mayer rod coating

Quantification of Ionomer Distribution

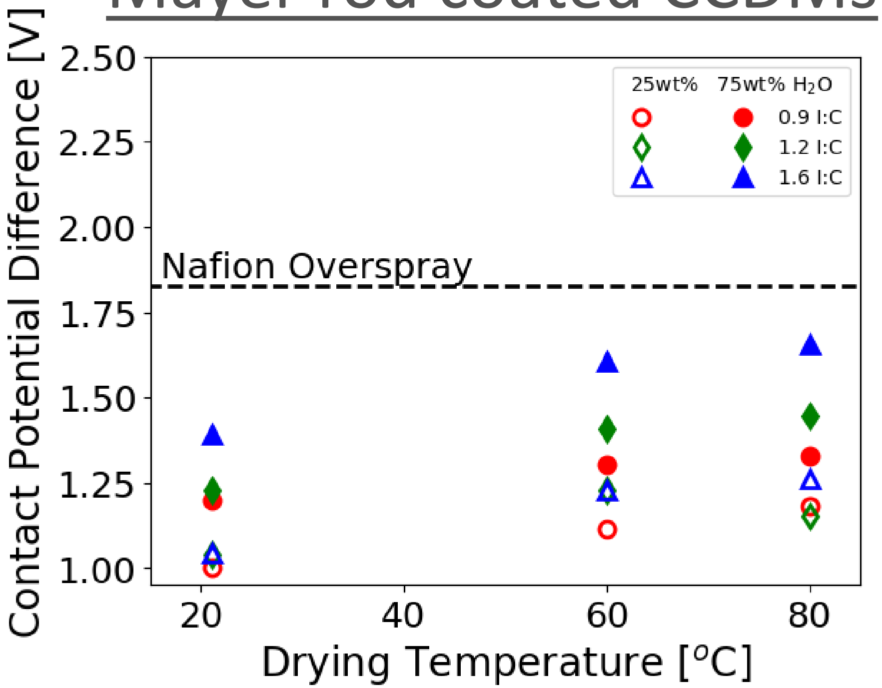
Kelvin Probe



$$CPD = \phi_S - \phi_{Tip}$$

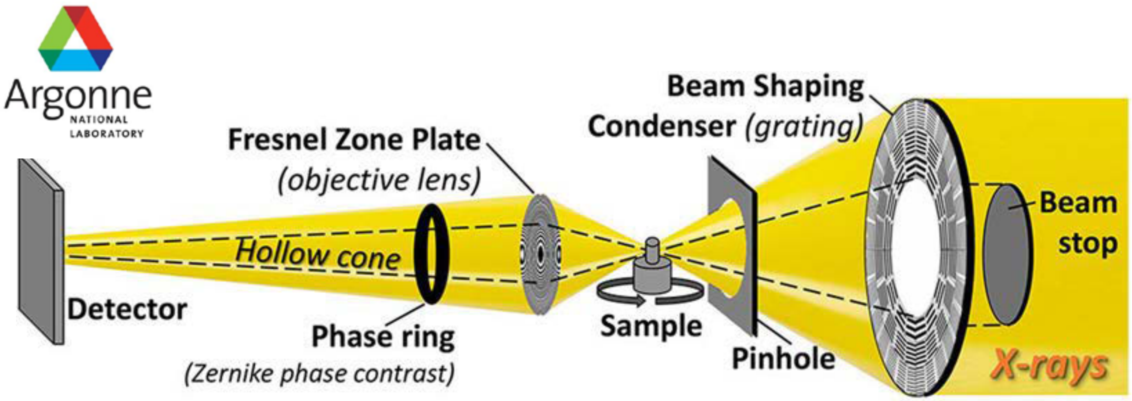


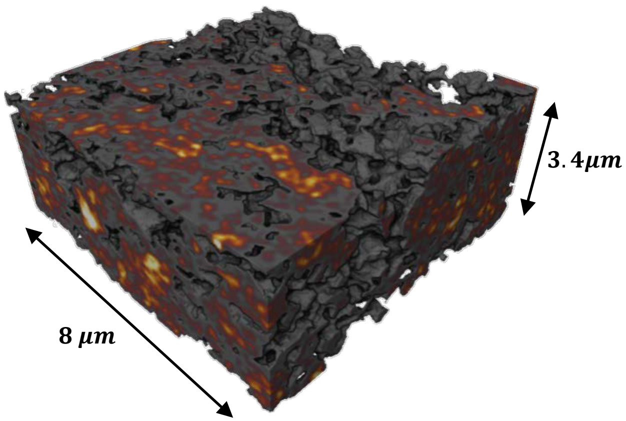
Mayer rod coated CCDMs

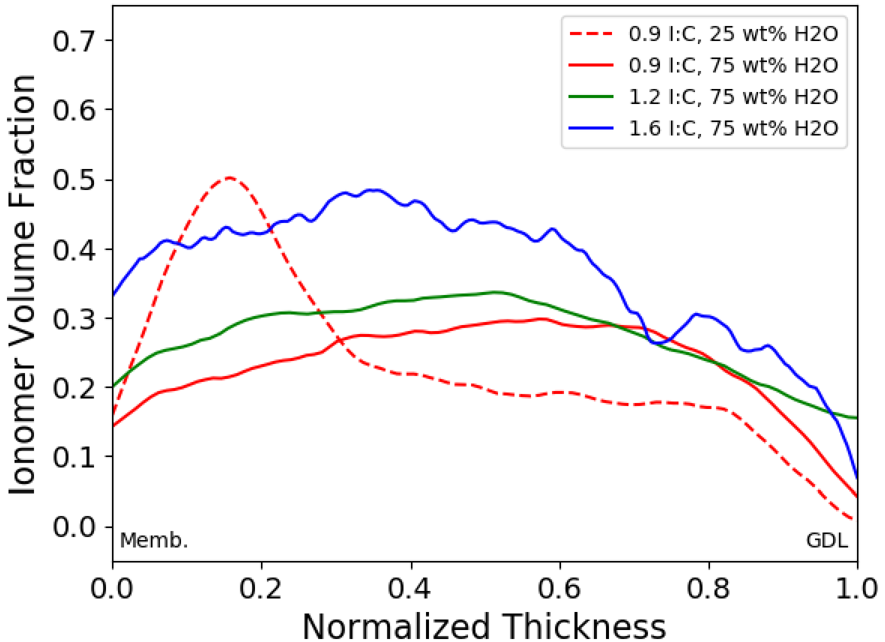


Kelvin probe provides a simple, non-destructive method for screening of surface ionomer content

X-ray Computed Tomography

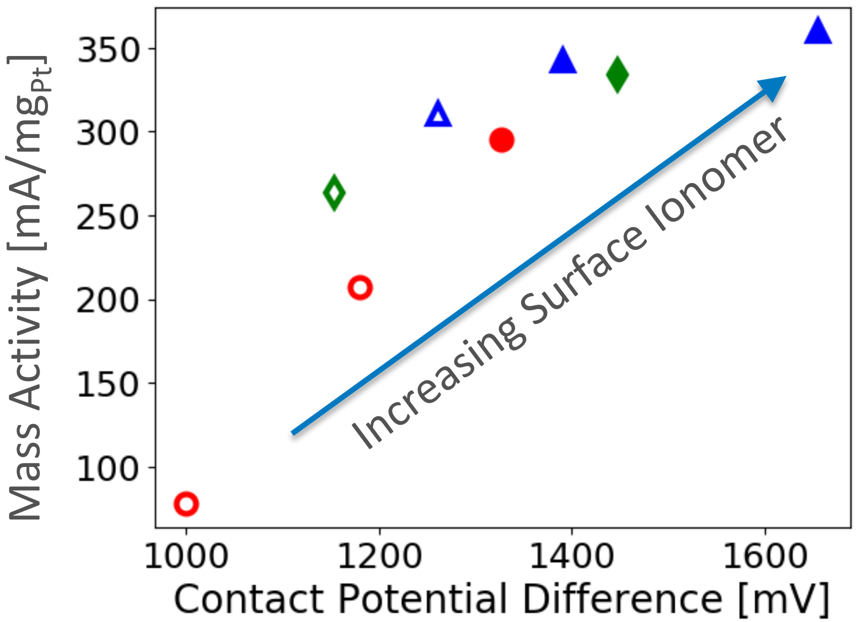


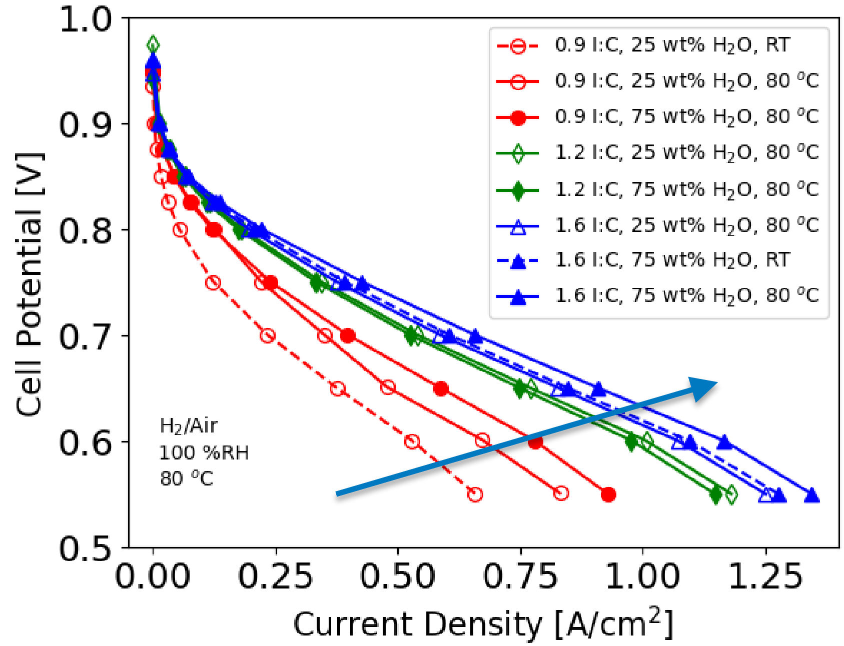




- XCT verifies Kelvin probe results
- Water/1-propanol ratio influences ionomer distribution

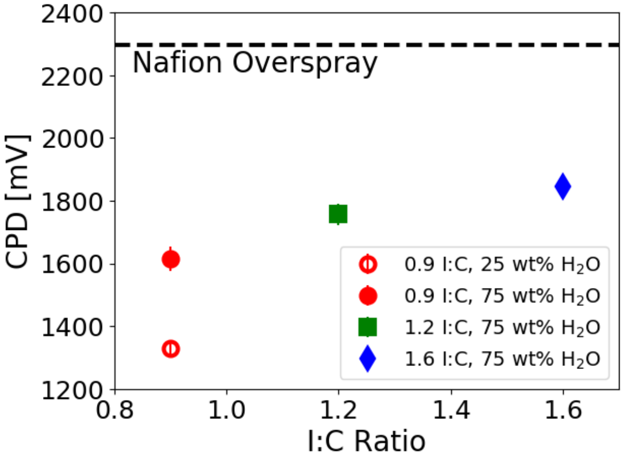
Influence of Surface Ionomer Content

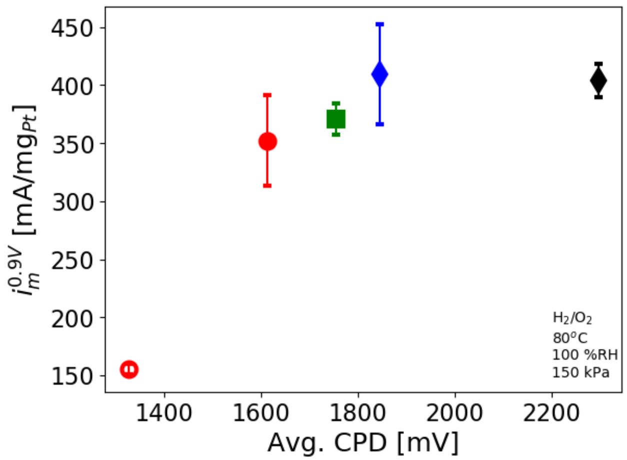


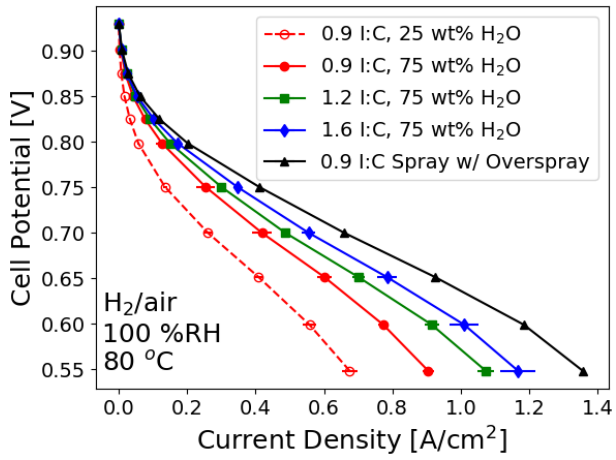


- Increasing surface ionomer content increases:
  - Catalyst activity
  - Fuel cell perormance

Gravure-Coated Catalyst Layers

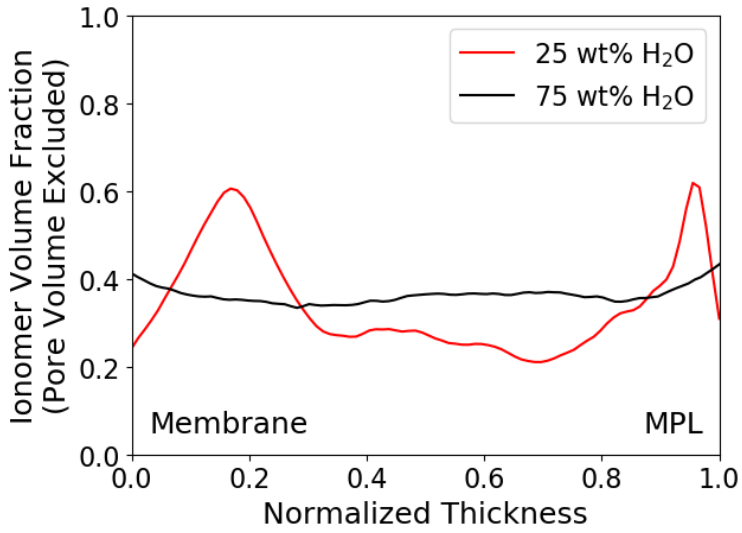


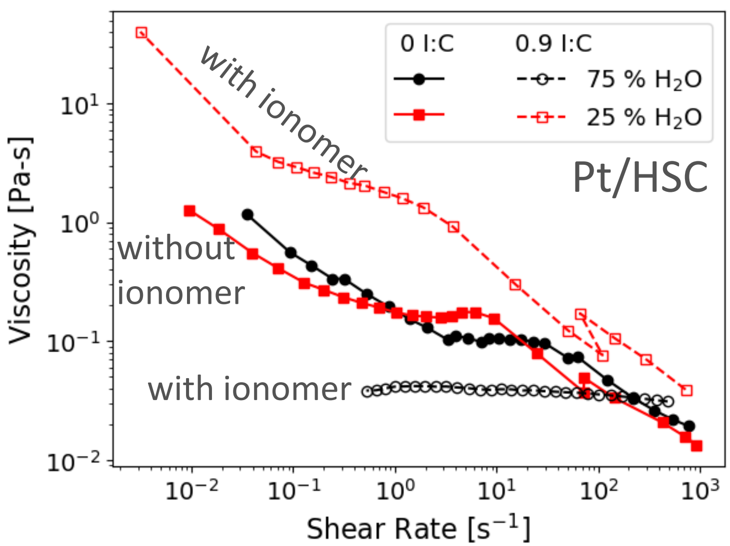


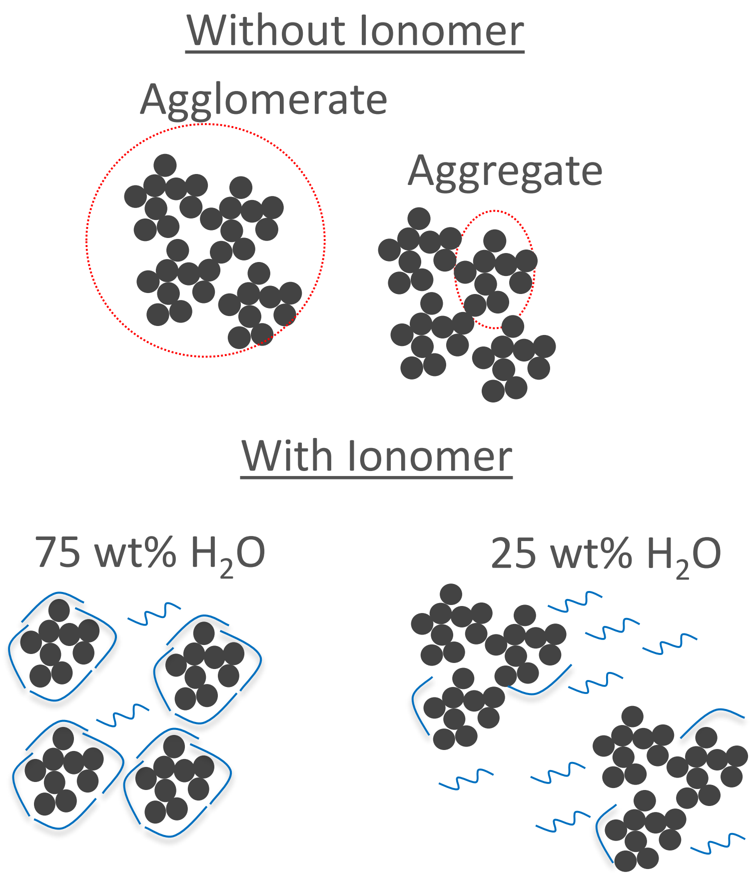


- Coated selected inks based on Mayer rod results
- 1-2 m coated for each condition
- Compared to spray-coated CCDM with ionomer overcoat, R2R-coated CCDMs achive
  - Same catalytic mass activity
  - 85% of high current density performance

Influence of Solvent on Ionomer Distribution



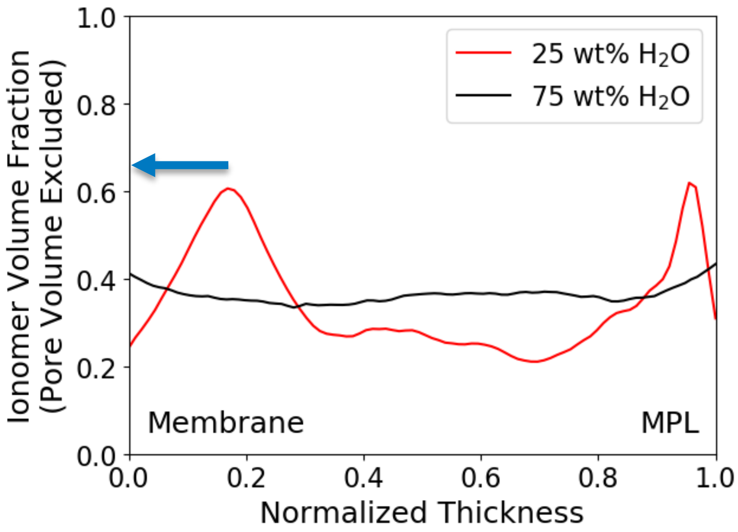




Sunilkumar Khandavalli, Today at 3:00 in International III

Conclusion and Future Work

- Increasing surface ionomer content increases catalytic activity and fuel cell performance of R2R-coated CCDMs
- Adjusting the ratio of water and 1-propanol in catalyst ink modifies the distribution of ionomer
- Ongoing work: exploring alcohols with higher boiling points to further control ionomer distribution



Want to work at NREL?

- R3643: Postdoctoral Researcher – Coating Process Science-Fuel Cells and Electrolysis
- http://www.nrel.gov/careers
- Come talk to Scott Mauger or Mike Ulsh


Thank you

www.nrel.gov

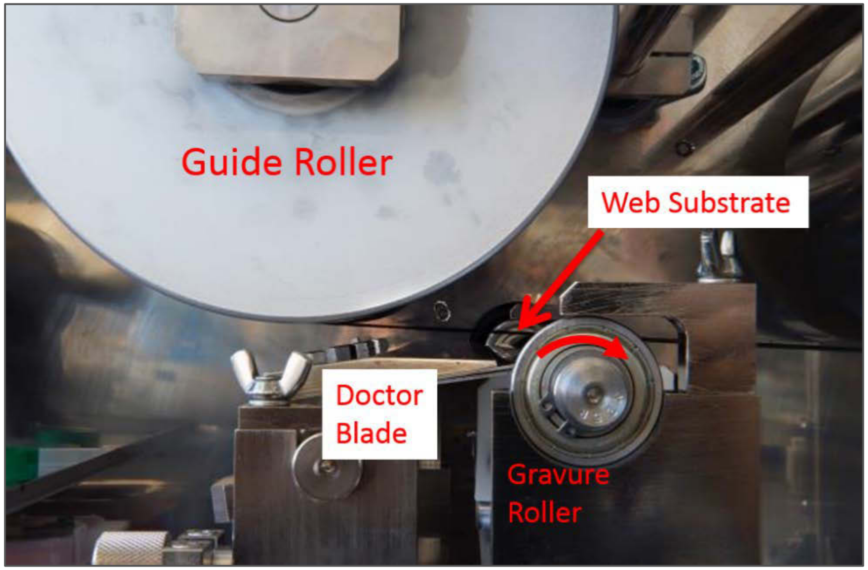
Materials and Methods

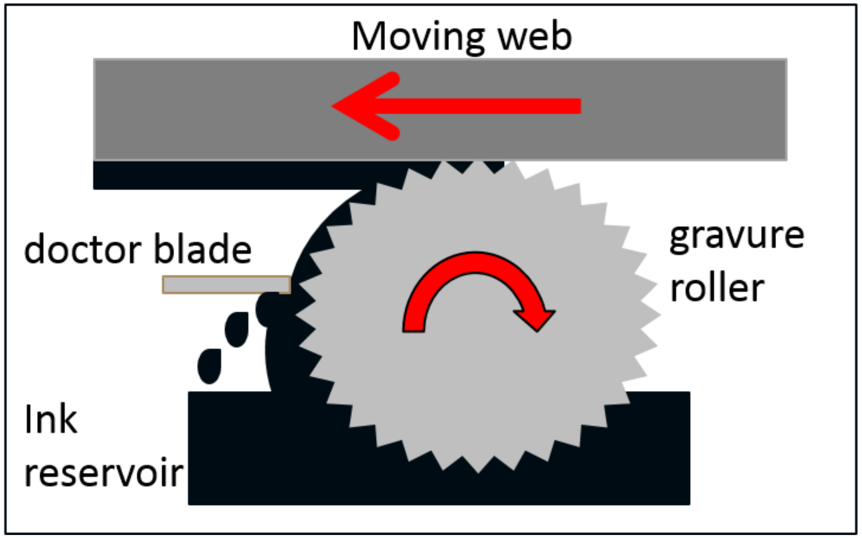
- Catalyst: Pt on high surface area carbon (TKK TEC10E50E)
- Ionomer: Nafion, 1000 EW (Ion Power D2020)
- Membrane: Nafion, 1000 EW, 25 µm (Nafion NR211)
- Diffusion Media: SGL Sigracet 29BC
- Catalyst ink – 3.2 wt% PtHSC
- Ink Dispersion: High shear mixer (Ika Ultra Turrax)
- Gravure Coating
  - 1 m/min
  - Air floatation oven: 80 ˚C

R2R Coating of Ionomer Gradient Electrodes

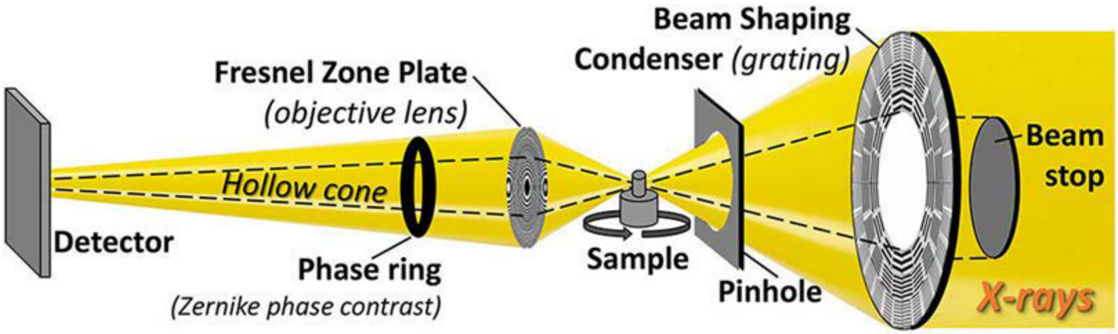
Down-selection from rod-coating screening experiment to demonstrate successful R2R coating

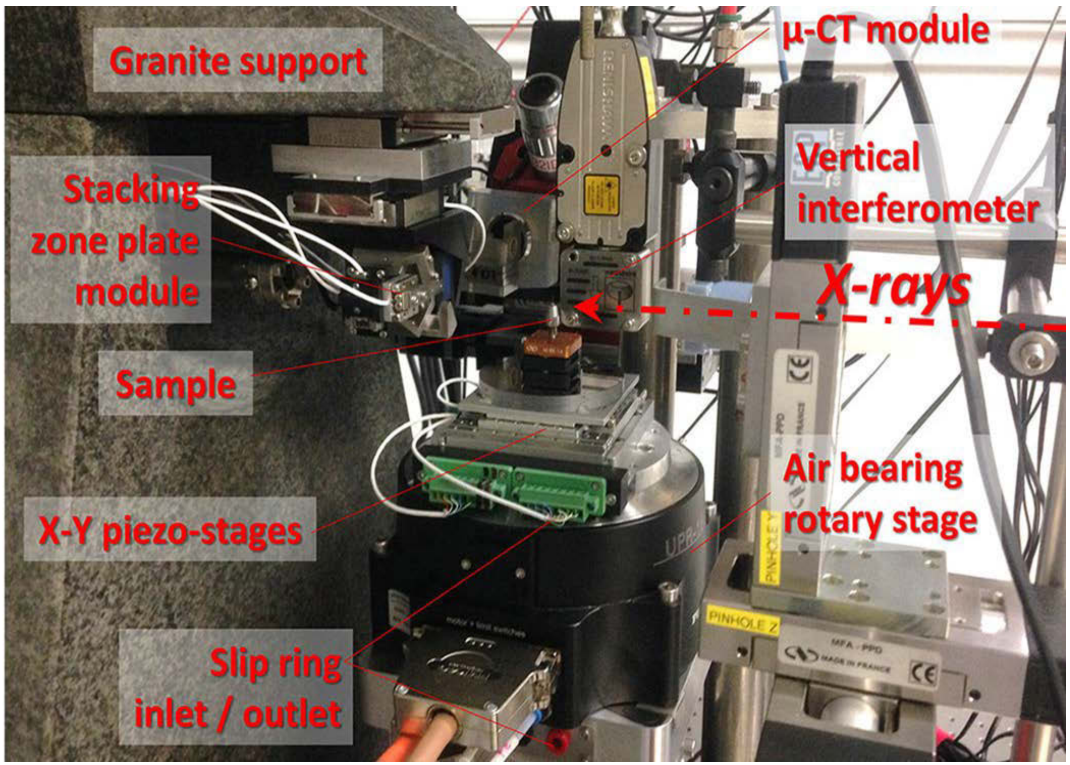
- Inks – Coated 2 m each
  - 0.9 I:C, 25 wt% H_2O
  - 0.9 I:C, 75 wt% H_2O
  - 1.2 I:C, 75 wt% H_2O
  - 1.6 I:C, 75 wt% H_2O
- Solvents: water and 1-propanol
- Catalyst: 50 wt% Pt/HSC
  - Loading: 0.1 ± 0.01 for all coatings
- Ionomer: Nafion 1000 EW
- Substrate: SGL 29BC
- Oven Temp: 80 ˚C
- Web Speed: 1 m/min



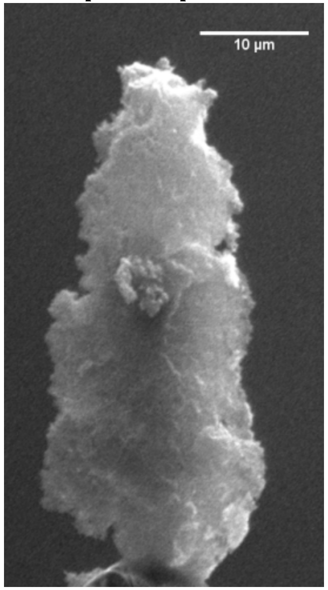


Hard X-ray Nanoprobe Beamline at APS

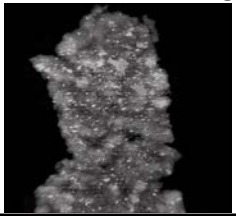




Sample Preparation



Reconstructed Images



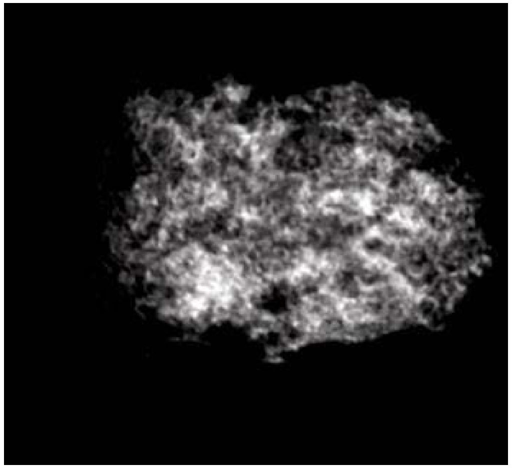
Optical Enclosure for X-ray Nanotomography at APS

- Images were taken at 32-ID
- X-ray energies from 3 to 30 keV
- ~20 nm pixel size was obtained
- Air bearing stage dampens most of the jittering and helps in aligning projection images at 32-ID
- Large field of view and flexible sample environment for in situ experiments
- Beamline is capable of absorption contrast and Zernike phase contrast imaging

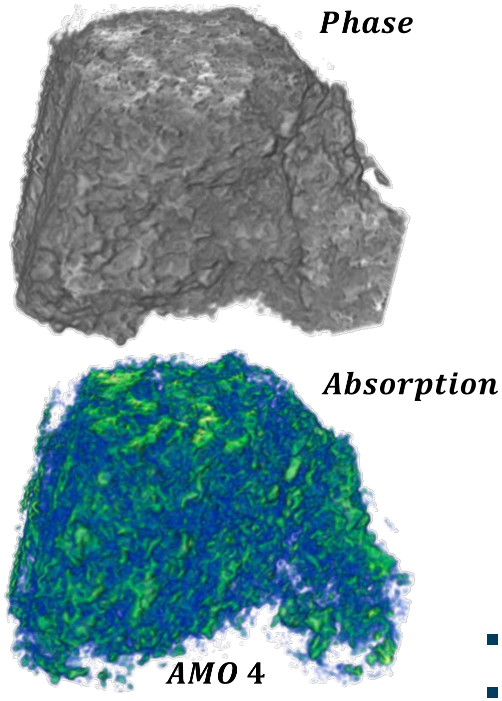
Phase and Absorption Contrast Images

- The samples were Cs^+ stained to visualize ionomer along with pore morphology

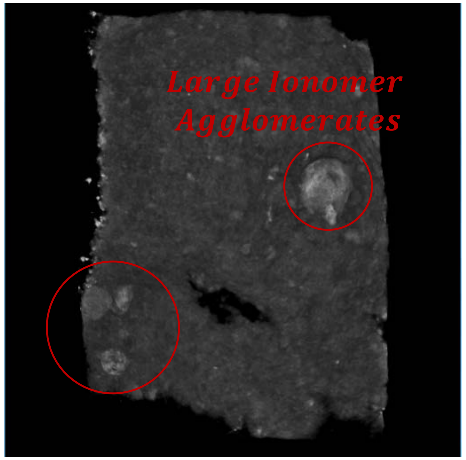
Phase Contrast AMO 1



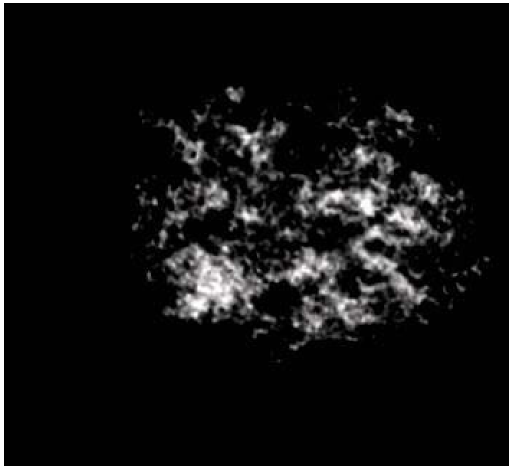
- Relies on determination of phase shift of the transmitted X-ray
- It helps for imaging low atomic number materials
- Phase contrast mode shows all the materials above resolution (including Cs+, C)
- All the dark regions correspond to the pores (above 20 nm)
- Raw data shows tiny pores and dense electrode



AMO 4



Absorption Contrast AMO1



- Resolves based on e- density
- Absorption contrast mode provides contrast of the high atomic number materials
- Absorption intensity is related to Cs+ and indicates the presence of ionomer
- Ionomer with sizes below nano-CT resolution can't be visualized
- Bright regions correspond to ionomer agglomerates