# Engineered Low-Pt Catalyst Layers

**Mahlon S. Wilson**
Los Alamos National Laboratory
June 8th, 2015

LA-UR-15-22924

Project ID FC125



Los Alamos NATIONAL LABORATORY EST. 1943

# Overview

## Timeline

1-year project

- Start date: 10/2014
- End date: 09/2015
- Percent complete: ~65%

## Barriers

- A. DURABILITY of low-Pt MEAs
- B. COST of current MEAs
- C. PERFORMANCE of low-Pt MEAs

## Budget

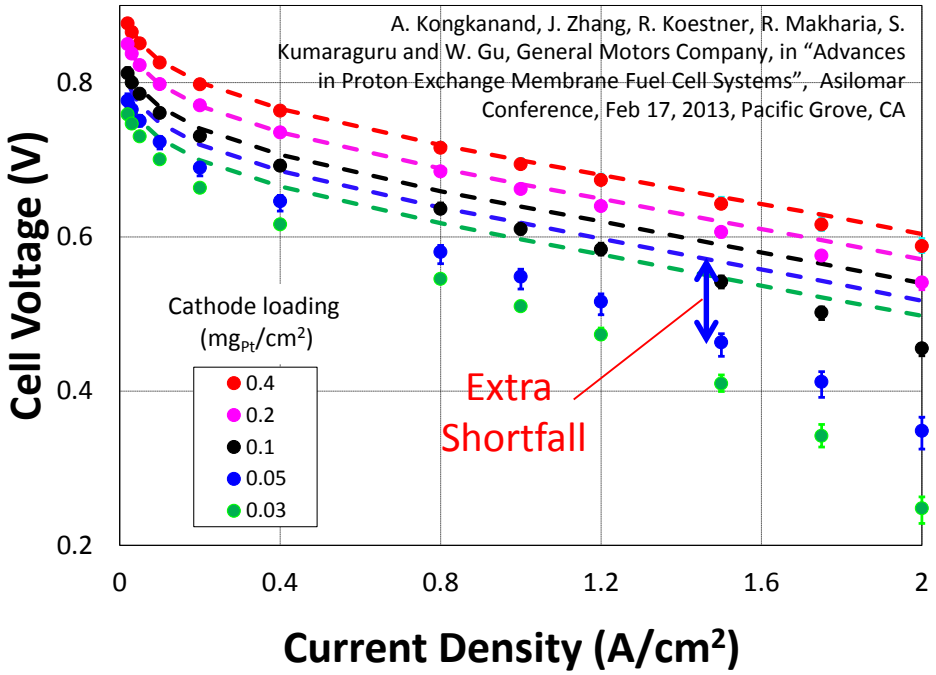
Total project funding: $500k

- LANL: $350k
- LBNL: $100k
- ORNL: $50k

## Partners

- Lawrence Berkeley National Laboratory
  PI: Adam Weber
- Oak Ridge National Laboratory
  PI: Karren More
- Los Alamos National Laboratory

# Relevance




A significant "extra" shortfall in FC performance is observed in standard MEAs when Pt loadings drop below ~ 0.1 mgPt/cm$^2$ that is manifested as an increased ionomer barrier to $O_2$ transport. Developing the means to correct this extra loss increases the performance and cost effectiveness of fuel cells.

- Objectives (over 1y project):
  - Introduce, model, and develop the materials and techniques for a new approach that focuses on an engineered ionomer topology (EIT) within the catalyst layer.
  - Attain 0.05 mgPt/cm$^2$ fuel cell performance that demonstrates the potential of the EIT approach

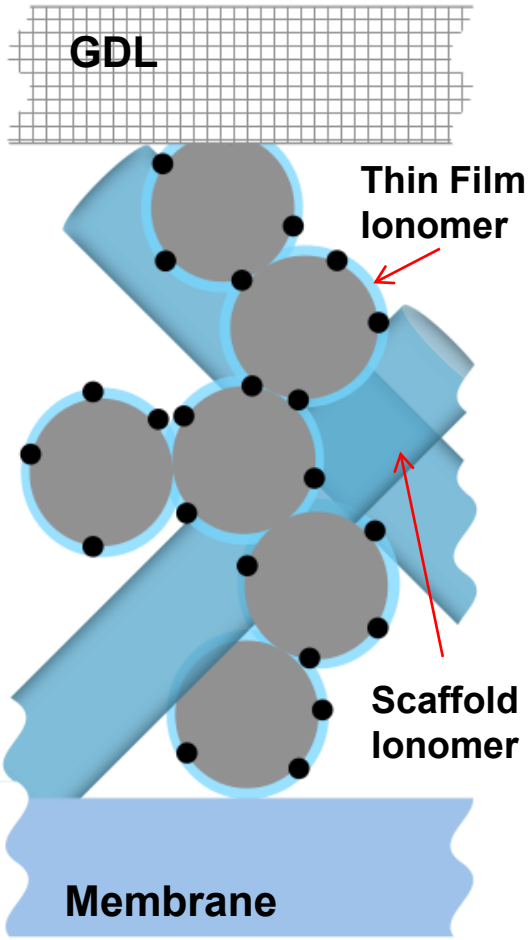
Los Alamos NATIONAL LABORATORY EST.1943

# Approach: Engineered Ionomer Topology (EIT)

- Optimize the ionomer topology of the catalyst layer to minimize the shortfall
  - Many past investigations on support structures (e.g., MWCNTs, NSTFs, etc.) but not on intentionally engineering ionomer structure and distribution, which can provide a greater payoff
- Use two "Phases" of ionomer:
  - 1st "thin-film" ionomer phase to coat the catalyst and provide local ionic continuity while minimizing the $O_2$ transport barrier.
    - The thinner the ionomer film the better
  - 2nd "nanofiber" ionomer scaffold phase to provide bulk conductivity/continuity and catalyst layer structural integrity.
    - High aspect ratio and durable ionomer component to provide ionic "highways"

Ideally, the EIT approach can be used directly in standard commercial MEA fabrication processes, wherein the catalyst layer is formulated and applied as an ink.

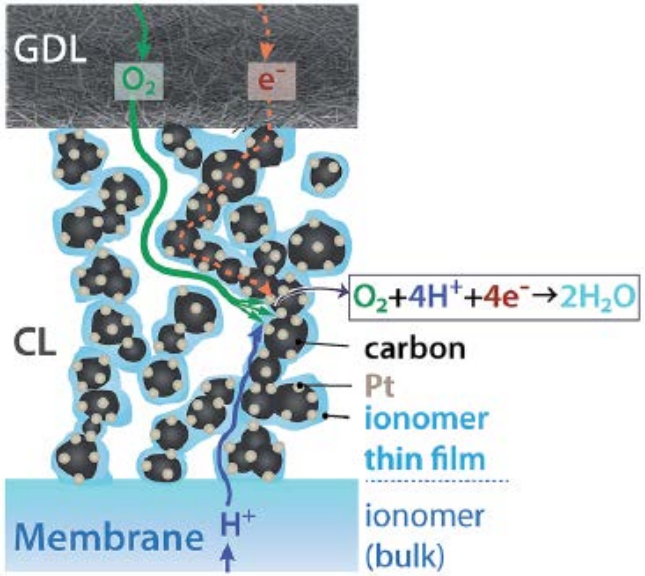
**Conceptual configuration for description & modeling**

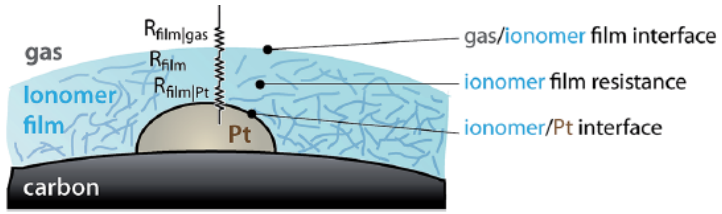


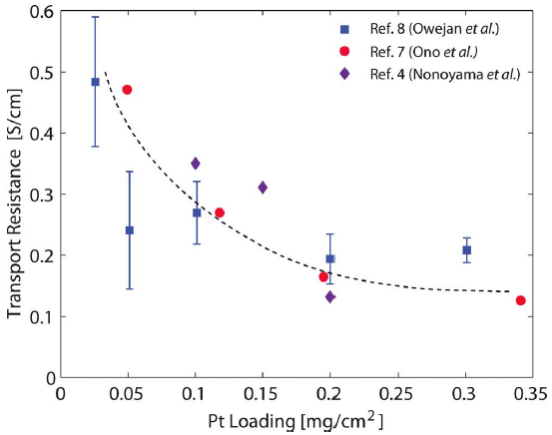

Los Alamos NATIONAL LABORATORY EST. 1943

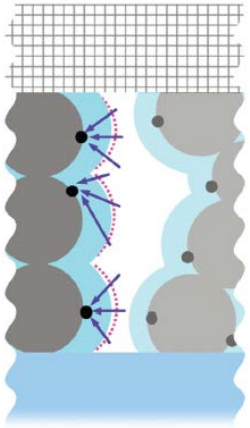
# Motivation for the ionomer nanofiber phase in the CCL

- The increased mass-transport resistance with lower Pt loading is attributed to the slow oxygen transport in the ionomer film (decrease in effective surface area for oxygen)**.



**$O_2$ transport resistance through ionomer film**

$$R_{O_2\,film} = \frac{\delta_{film}}{\psi_{O_2}}$$

$$\psi_{O_2} = \frac{D_{film} H}{RT}$$

- By decreasing film thickness $\delta_{film}$ ,

Benefit: the high oxygen transport resistance $R_{O2,\,film}$ can be reduced.

Drawback: the proton transport in the ionomer film becomes rate-limiting.

→ 2nd ionomer phase with high $H^+$ conductivity (nanofiber) is needed to facilitate $H^+$ conduction.

*AZ Weber, A Kusoglu, J. Mater. Chem. A, 2014, 2, 17207–17211 **W Yoon, AZ Weber, JECS 158 (8) B1007-1018 (2011)

# Milestones

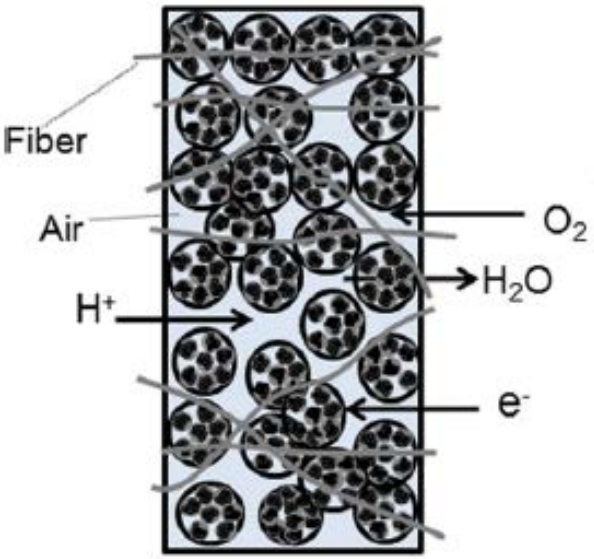
| Date | Milestone | Status | Comments |
|---|---|---|---|
| Dec 31, 2015 | *Functionalize supports to > 1 site/nm$^2$. | Re-Approach | Bulk doping not high enough – go to surface functionalization |
| Mar 31, 2015 | Synthesize high-aspect ratio ionomers with diameters < 500 nm.<br>Platinize the supports. | Ionomer Synthesis Achieved | Supports not yet ready for platinization |
| Jun 30, 2015<br><br>Annual Milestone | Demonstrate fabrication of engineered ionomer topology MEAs with ≤ 0.05 mg Pt/cm$^2$ with reproducible loading variations of ± 0.02 and performance of > 550 mV at 1 A/cm$^2$ and 100% RH, improving performance compared with 0.055 mg/cm$^2$ Pt/PPPy demonstrated in FC010 in FY14. | Exceeded Performance Target | FC performance aspect of milestone met – Pt distributions not yet mapped. |
| Aug 30, 2015 | Low-Pt EIT and GM baseline MEAs FC tested, characterized and compared. | Achieved | Two EIT cells already completed, compared with GM cells |

*The ability of the solubilized ionomer to wet the catalyst is key to forming a highly dispersed phase 1 ionomer thin film. Indeed, the ideal ionomer film is only 1.5 nm thick (Slide 8). Consequently, a portion of this project investigated the synthesis of heteroatom functionalized supports to improve ionomer attraction without sacrificing support durability.

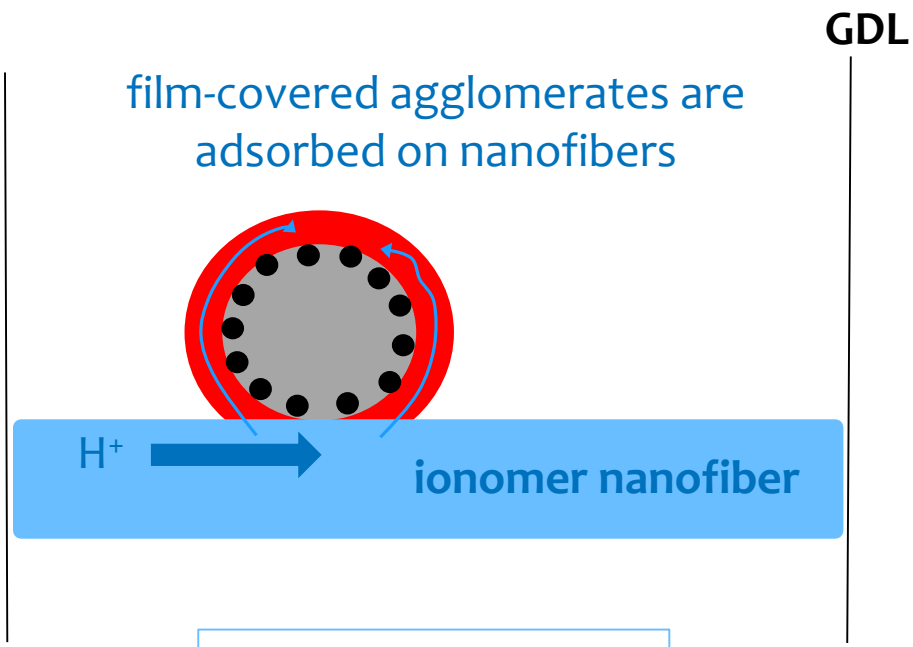
# Modeling: Nanofiber / Thin Film configuration

- Ionomers are in two phases, nanofibers and thin films.
- Protons transport from nanofibers (driving force) to thin films, ultimately arriving at the Pt sites around the agglomerate core.

cathode catalyst layer*

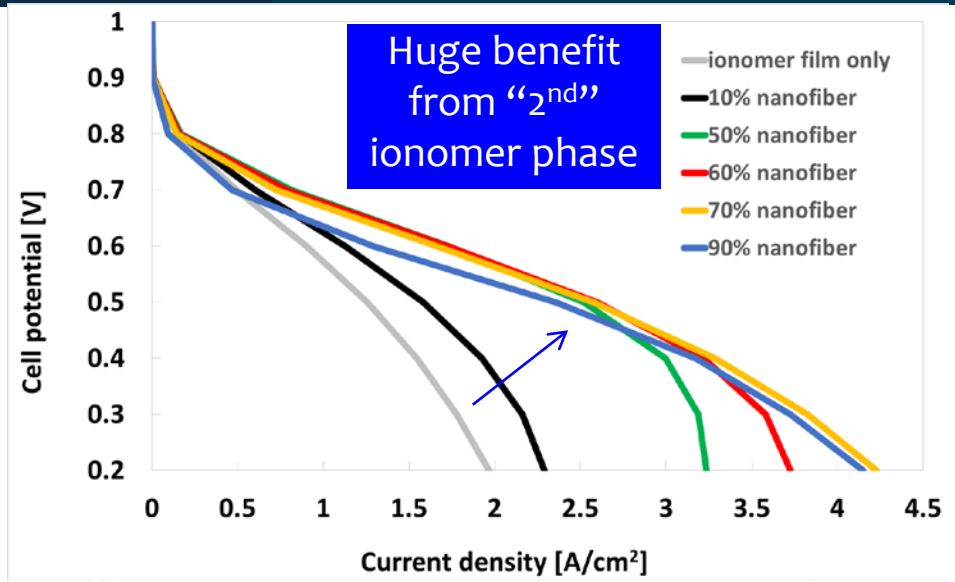


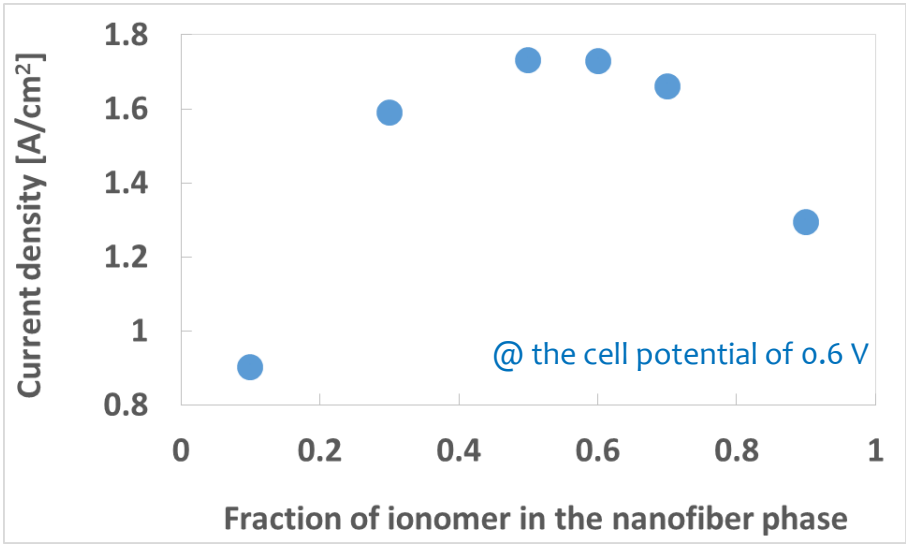

2D Model



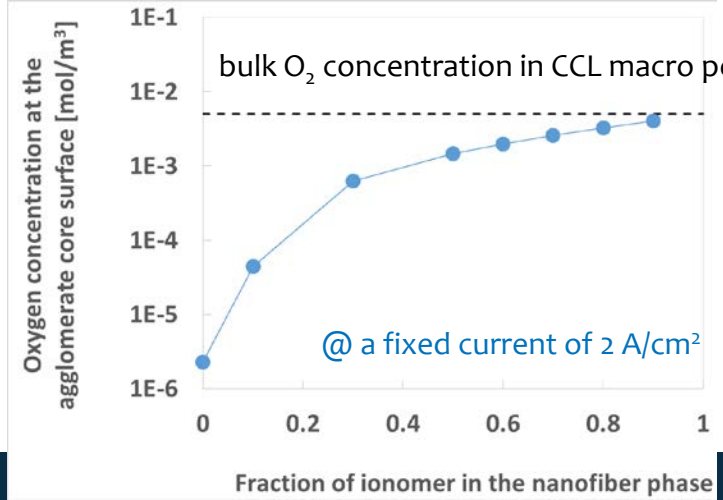

*D Denver et al, Journal of Fuel Cell Science and Technology, AUG 2014, Vol. 11 / 041007-3

# Compare agglomerate models with varying nanofiber fractions ($R_{agg}$ = 50 nm)




- The 70% nanofiber (30% film) case attains a maximum limiting current (with an optimal film thickness of 1.5 nm = 5 nm * 30%) by switching the rate-limiting step from oxygen permeation to proton conduction.
- At 0.6 V, a max current of 1.7 A/cm² is obtained from the case of 50% nanofiber (50% film).

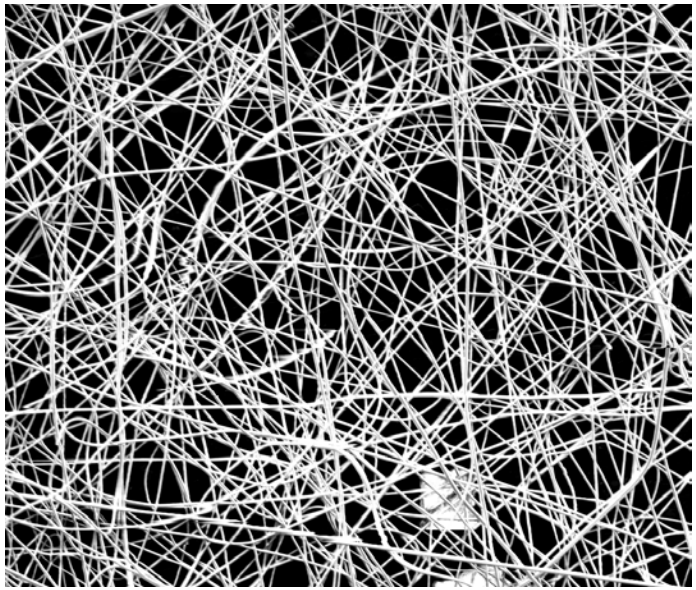



- Oxygen diffusion is slow for low nanofiber fractions due to low $O_2$ concentration at the agglomerate core surface.
- Surface $O_2$ concentration approaches its bulk value at high nanofiber fractions.

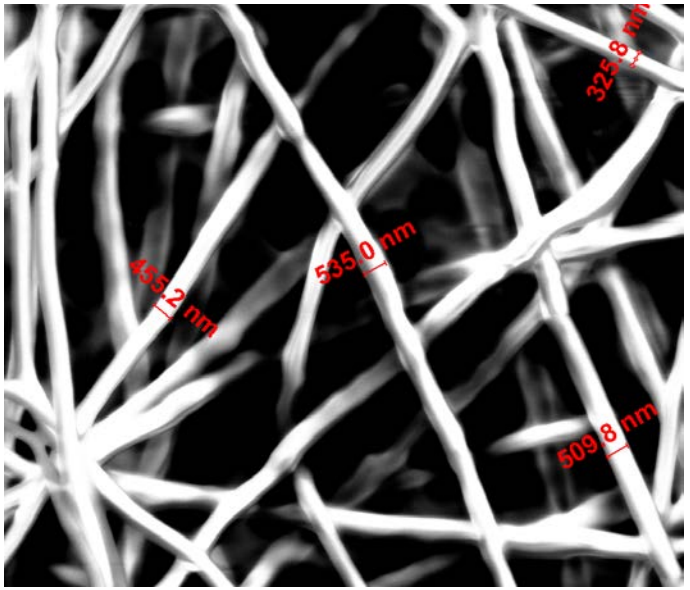
| Nanofiber fraction | Rate-liming transport |
|---|---|
| 0% (film only) | $O_2$ diffusion |
| 10% | $O_2$ diffusion |
| 50% | $O_2$ diffusion |
| 60% | $H^+$ conduction in film |
| 70% | $H^+$ conduction in film |
| 90% | $H^+$ conduction in film |

# Synthesis of Ionomer 2nd Scaffold Phase

- Nafion® nanofibers by electrospinning

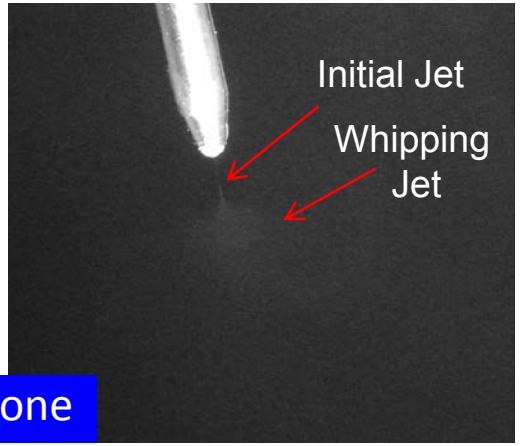


Micrographs of as-spun fibers fully dried at 60˚C




Typical Fiber Diameters (Fibers distorted by SEM electron beam under high magnification)

- Electrospun using commercial Nafion® solution
  - 1% PEO (polyethylene oxide) added (wrt ionomer) to facilitate spinning of ionomer suspension
  - Average fiber diameter slightly less than 500 μm*
  - Product mats have little physical integrity
    - Need to increase fiber toughness and durability




*Milestone

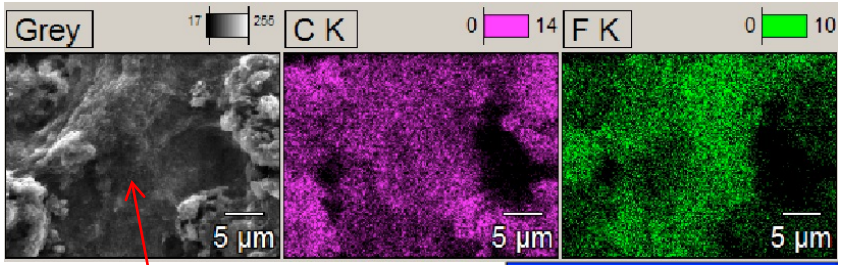
# Formation of Robust 2nd Scaffold Phase

- Ionomer-coated MWCNTs
  - Coated using anhydrous hi-temp casting solutions & process* for maximum ionomer strength and durability
  - MWCNTs provide electronic conductivity and rigidity (electrospun ionomers are too soft and malleable)
  - Scaffold is gravimetrically close to 2:1 Nafion®/MWCNT
    - High and uniform ionomer dispersion
    - Porosity remains open and high
    - Readily suspends in solution

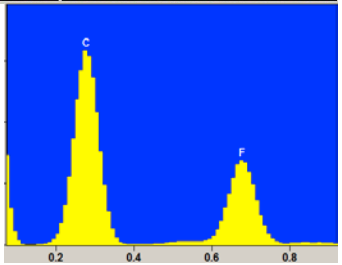
*Welch et al. (w/ Yu Seung Kim), *ACS Macro Lett*. **1**, 1403-1407 (2012)

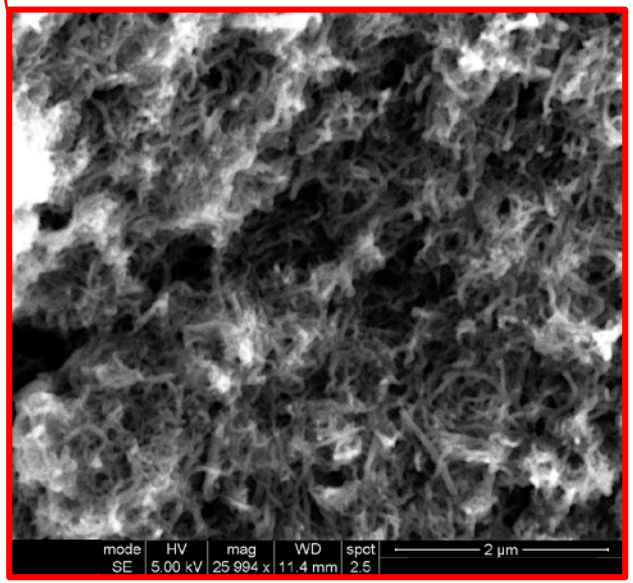
Protonated Nafion®/MWCNT scaffold phase in water

EDS indicates high and uniform ionomer content (F) within the MWCNTs




Apparently dense region is open and porous under higher magnification

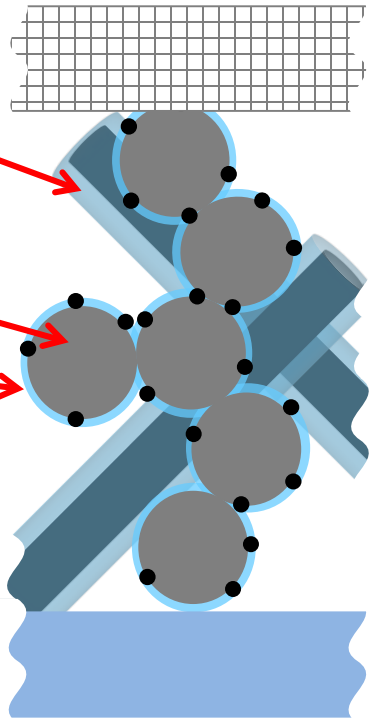





Los Alamos NATIONAL LABORATORY EST. 1943

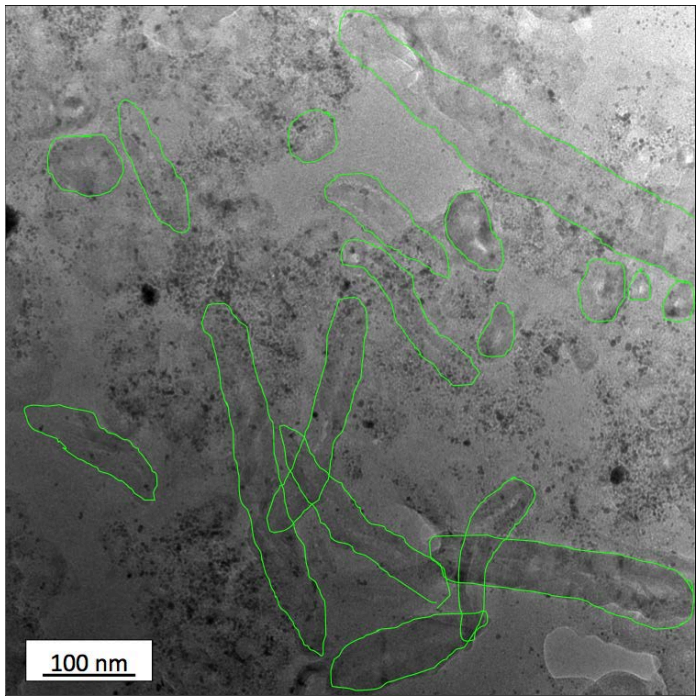
# Formulation of Initial EIT MEA Inks

- Ink components:
  - Scaffold 2nd Phase (~2:1 Nafion®/MWCNTs)
    - Specific surface area ~ 20 $m^2/g$
  - Pt/C catalyst (E-tech 20%Pt/XC72)
    - SSA ~ 220 $m^2/g$
  - Solubilized Nafion® thin film 1st Phase
    - Standard commercial 5 wt% $H^+$ Nafion® solution
- Ink compositions for initial 2 MEAs:
  - Equal amounts of catalyst and scaffold by weight
  - Amount of 1st Phase "thin-film" ionomer varied
    - 1st ink has a low Nafion® solubilized ionomer content (LowNaf)
    - 2nd ink has a high Nafion® solubilized ionomer content (HiNaf)

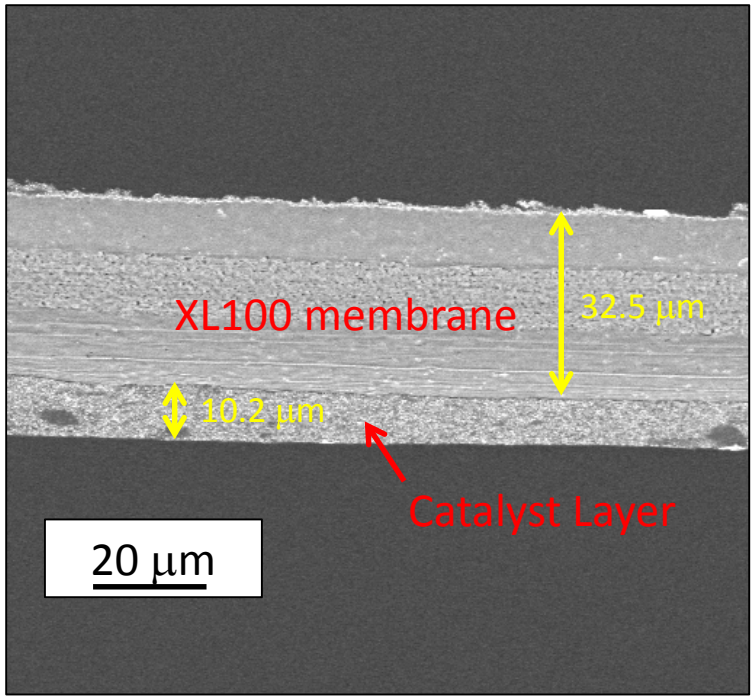


In typical catalyst layer ink formulations, the solubilized ionomer needs to simultaneously provide catalyst access, structural integrity, and bulk conductivity. Here, the EIT approach attempts to separate and optimize the effectiveness of the individual functions, with the solubilized ionomer providing local ionic access to the catalyst and the scaffold ionomer providing bulk conductivity and catalyst layer integrity.

# MEAs and FC Testing




TEM of catalyst layer. MWCNTs outlined in green.



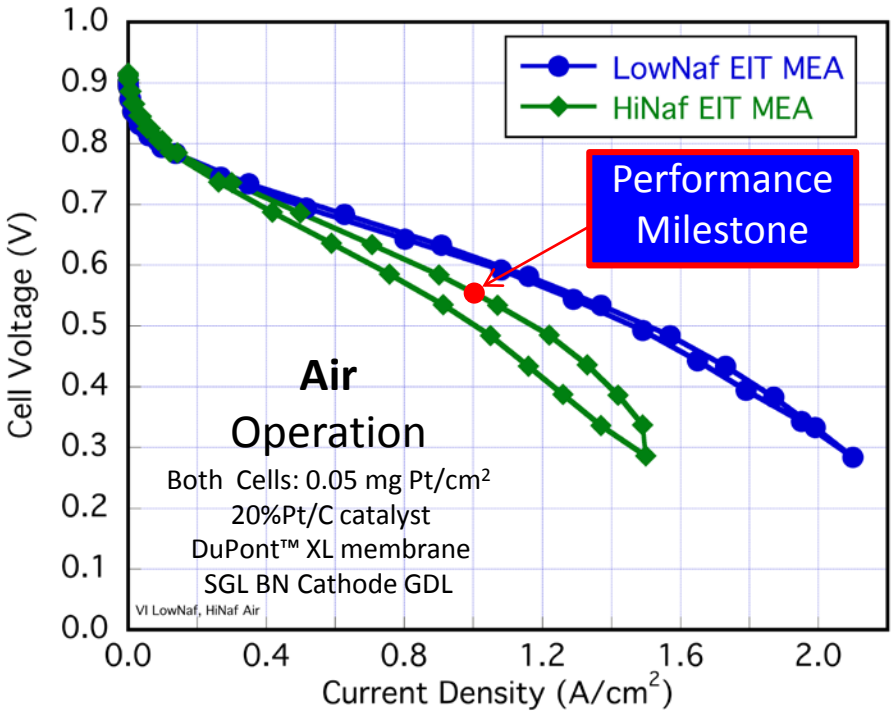

SEM cross-section of single-sided MEA.

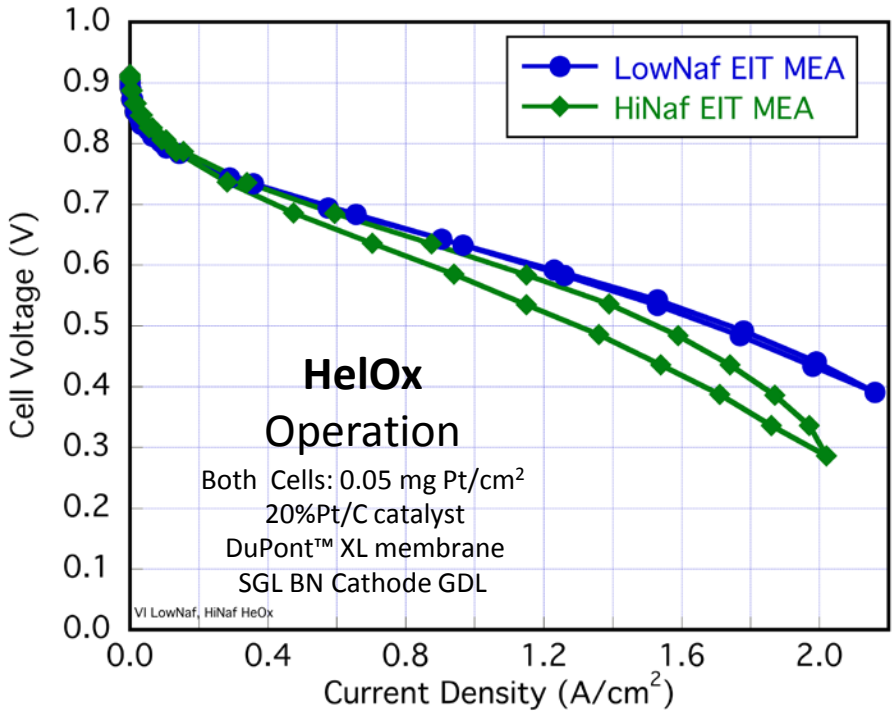
- MEAs fabricated by decal hot-press
  - Very nice decal wetting and coverage
  - Open, porous structure
  - Solids thoroughly intermingled
- FC Testing
  - Regimented side-by-side "3rd party" testing by the LANL durability team
  - In-house comparison to GM baseline MEA results using similar catalysts, Pt loadings, components & hardware

- FC Components
  - 50 $cm^2$ hardware
  - Catalyst: 20%Pt/XC72 (0.05 mg Pt/$cm^2$)
  - Membrane: DuPont® XL
  - Cathode GDL: SGL 25BN

Los Alamos NATIONAL LABORATORY EST.1943

# FC Testing of EIT MEAs



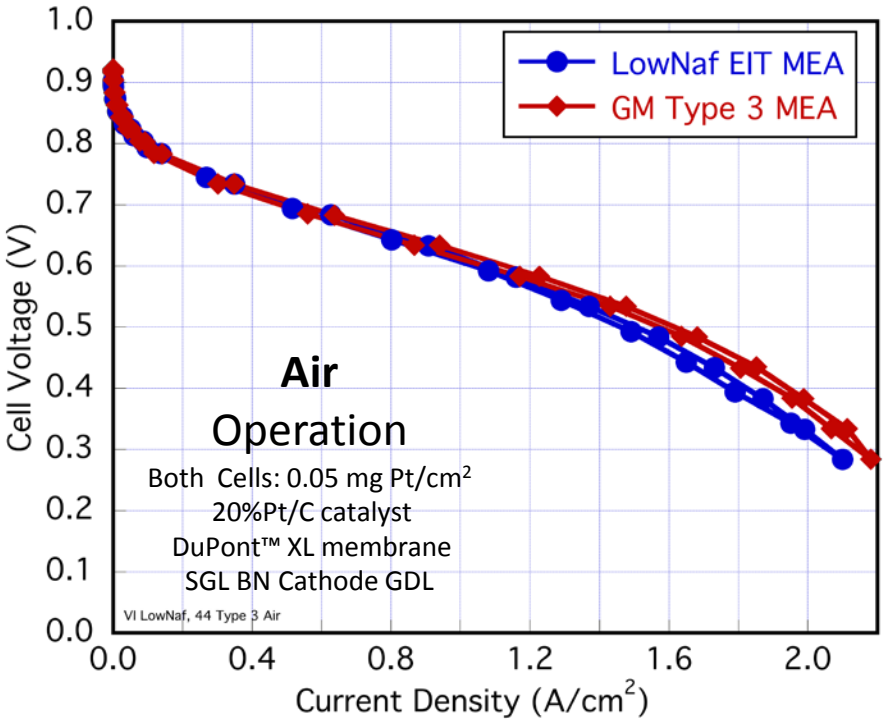



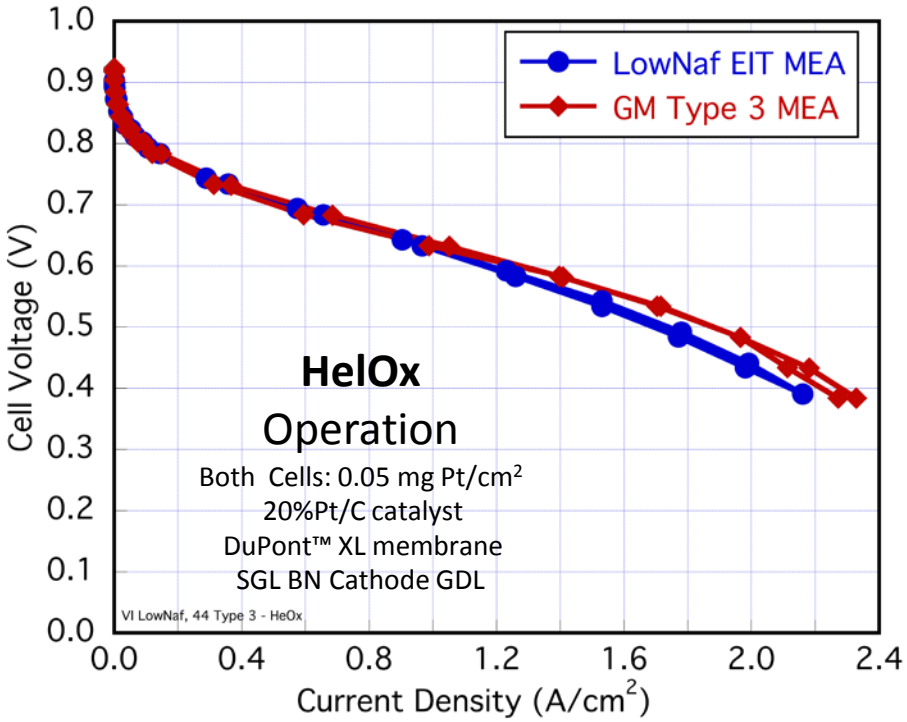

| MEA | ECSA ($m^2/g$) |
|---|---|
| Low-Naf | 31 |
| Hi-Naf | 61 |

Scan rate = 50 mV/s

- Comparison of low and high "thin-film" Nafion® loadings
  - Higher performance with low thin-film loading
    - LowNaf exceeds performance milestone ← Milestone
  - Higher ECSA with high 1st phase loading
    - More hysteresis with HiNaf
    - Additional Nafion® increases both ECSA and tortuosity
      - Extra ionomer appears to be adding to gas transport resistance more so than ionomer thin film resistance – possibly forming larger catalyst agglomerates?

# LowNaf EIT MEA vs. Baseline GM MEA




| MEA | ECSA ($m^2/g$) | CL thicknes s (μm) |
|---|---|---|
| Low-Naf | 31 | 10 |
| Type 3 | 47 | 7 |

Scan rate = 50 mV/s

- Comparison between EIT and Commercial MEAs
  - Nearly equivalent performance

↑ Milestone

    - But only ⅔ the ECSA of the Type 3 MEA
      - Little or no kinetic hit
    - No optimization of the EIT MEA or process
    - Transport region losses, but thicker CL (catalyst layer)

Los Alamos NATIONAL LABORATORY EST.1943

# Collaborators and Contributions

- Lawrence Berkeley National Laboratory
  - Adam Z. Weber (PI) - modeling
    - Huai-Suen Shiau - modeling
- Los Alamos National Laboratory
  - Mahlon S. Wilson (PI) - EIT MEA development
    - Yu Seung Kim - anhydrous ionomer solutions
    - David Langlois - FC testing
    - Kwan Soo Lee - anhydrous ionomer solutions
    - Rangachary Mukundan - testing logistics
- Oak Ridge National Laboratory
  - Karren More (PI) - imaging and characterization

# Remaining Challenges and Barriers

- Modeling
  - The primary challenge is accurately capturing the true distribution and properties of the ionomer within the catalyst layer (e.g., conductivity & water uptake are thickness dependent).
- EIT Catalyst layer development
  - The modeling indicates that the optimal 1st phase thin film ionomer thickness is only 1.5 nm (about a monolayer), thus an enormous challenge is approaching this high degree of ionomer dispersion* while simultaneously minimizing agglomerate particle size
  - The conventionally electrospun ionomers are not suitable for the fabrication of open, porous catalyst layers (too soft and malleable). Obtaining robust and durable unsupported ionomer nanofibers will be necessary to effectively achieve this particular EIT structure

*For example, if the entire 20wt% Pt/XC72 catalyst (220 $m^2/g$) is coated with a monolayer of Nafion® that is 1.3 nm thick (per Bertoncello et al., *Phys. Chem. Chem. Phys.*, **4** 4036-4043 (2002)), the coated catalyst will be at least 37 wt% Nafion® (depending upon geometry).

# Proposed Future Work

- Modeling
  - Study the effect of relative humidity on the performance curve
  - Investigate the influence of connections between multiple nanofiber tubes, which becomes significant at high nanofiber fractions (crowded effect)
  - Validate the model by experimental data, with tested empirical relationships that relate the oxygen permeability and proton conductivity to the film thickness
- EIT Catalyst Layer Development
  - Improve the distribution of the 1st phase ionomer
    - Via functionalized supports
      - Directly functionalize nanofiber support surfaces (rather than bulk-doping)
    - Via directly enhancing the ionomer distribution (by ink formulation or processing)
  - Improve properties of electrospun ionomers
    - Investigate spinning / curing process akin to “high-temp” casting to attain nanofibers with “bulk-like” ionomer properties
  - Explore further generations of EIT catalyst layer configurations and thicknesses to understand the degree and significance of the individual component contributions (not an optimization effort)
- FC Testing
  - Further generations of EIT MEAs
    - Low RH operation
    - Preliminary durability testing

Los Alamos NATIONAL LABORATORY EST. 1943

# Technology Transfer Activities

- Project contributors have participated in various Tech2Market activities (e.g., the National Lab Showcase at the 2014 Fuel Cell Seminar), but thus far there have not been any tech transfer activities specific to this project.
- In the longer term, once clearly superior EIT catalyst layer formulations have been developed, the EIT components (or possibly actual inks), will be supplied to at least one commercial MEA supplier (per agreement) and offered to all interested domestic suppliers.
  - If results are obtained by the suppliers that suffice to stimulate their interest in acquiring the technology, our tech transfer organization (LANL Feynman Center of Innovation) oversees the process.

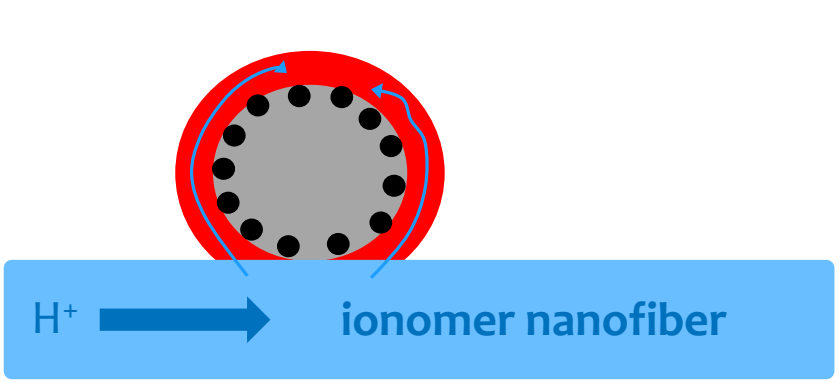
# Summary

- Developed a catalyst layer nanofiber / thin-film model
  - Illustrates that adding the 2nd ionomer phase (nanofibers) dramatically increases performance
    - High ionic potential of the "bulk" nanofibers facilitates activity of the catalyst agglomerates
  - the 70% nanofiber (30% film) case achieves a maximum limiting current
  - $O_2$ concentration at the surface of the agglomerate core approaches its bulk value at high nanofiber fractions.
  - The optimal film thickness = 5 nm • 30% = 1.5 nm (about a monolayer)
- Developed approach, materials, and processes for EIT catalyst layers
- Observed that the thin-film ionomer content in the EIT catalyst layer has a significant effect on transport and performance
  - Higher 1st phase ionomer loadings increase ECSA, but also catalyst layer tortuosity
- Using similar 20%Pt/C catalysts, an EIT MEA with low thin-film ionomer content approaches baseline commercial MEA performance
  - Un-optimized EIT cell close to commercial MEA despite only ~⅔ the ECSA

Conclusion: the modeling and initial results demonstrate the substantial promise of the EIT catalyst layer approach to overcome the low-Pt performance shortfall

# Technical Back-Up Slides

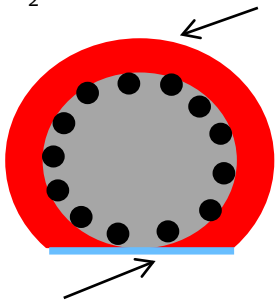
# Boundary conditions and constants used in the modeling simulation




**At the gas/film interface:**

(1) *No proton flux*

(2) Bulk $O_2$ concentration is given as 0.005 mol/m$^3$ (assume uniform $O_2$ distribution in CCL macro pores)



**At the film/nanofiber interface:**

(1) *No oxygen flux* (possibly limiting $O_2$ transport)

(2) The ionic potential is determined by the film and nanofiber conductivities.

**Properties:**

(1) The electronic potential is assumed to be 0.6 V uniformly throughout the CCL.

(2) The agglomerate core radius ($R_{agg}$) is 50 nm, assumed to be constant while varying nanofiber fractions. The intrinsic $H^+$ conductivity of the film phase is 0.001 S/cm at RH of 30%* and the intrinsic $H^+$ conductivity of the nanofiber phase is 0.1 S/cm. The extensive $H^+$ conductivities in two phases depend on the volume fraction of ionomer in each phase.

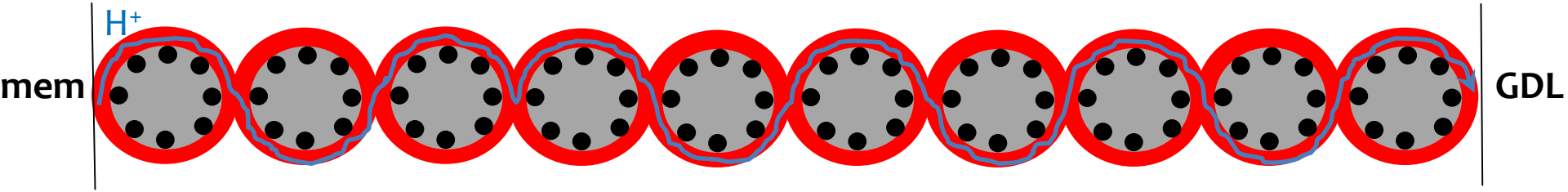
(3) The oxygen diffusion coefficient in the film is 9.7E-6 cm$^2$/s. *The $O_2$ transport resistance through film is assumed to be proportional to the film thickness.*

(4) When no nanofiber is present, the film is 5 nm in thickness, covering agglomerates of $R_{agg}$ = 50 nm. With increasing nanofiber fraction (0 to 100%), the film will get thinner, favorable for $O_2$ transport but unfavorable for $H^+$ conduction.

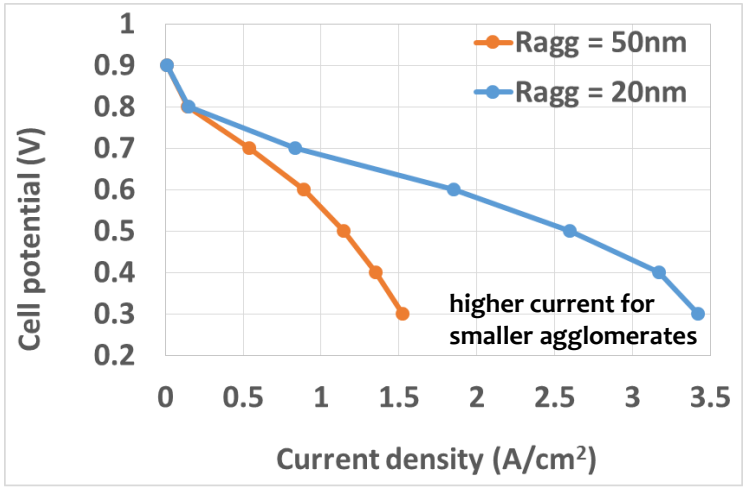
(5) The volume fractions of carbon and ionomer in the CCL are 0.363 and 0.334, respectively. The specific Pt surface area per unit CL volume is $10^5$ cm$^{-1}$.

*Self-Assembly and Transport Limitations in Confined Nafion Films, *Macromolecules* 46, no. 3 (2013): 867-873

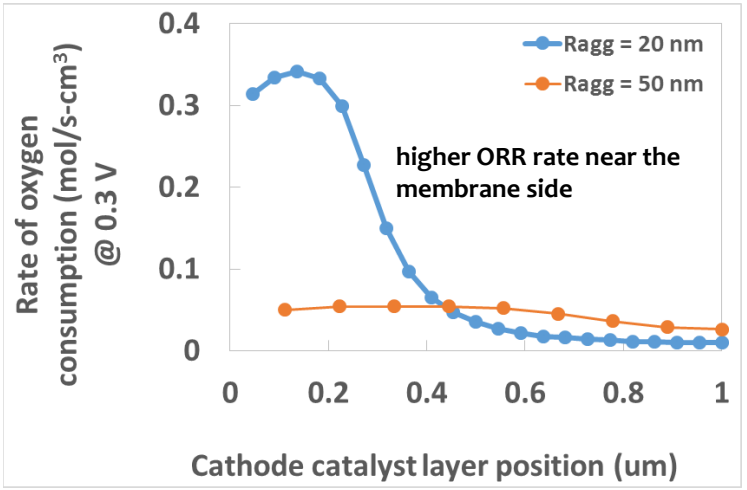
# Base case (ionomer film only): agglomerate model w/o nanofiber in the CCL




## Cell potential vs. current density




## Rate of ORR across the CCL

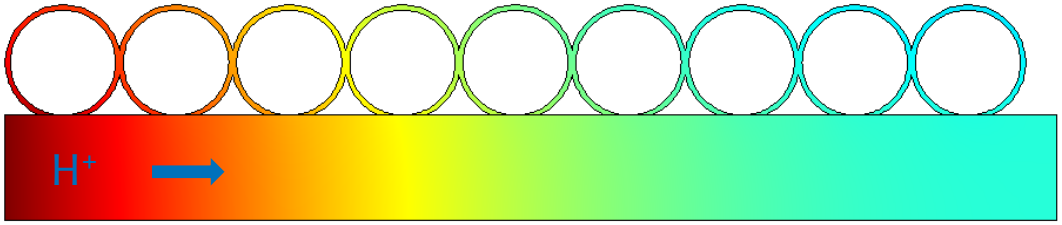



## Ionic potential profile across the CCL: consistent with higher ORR rate near the membrane side

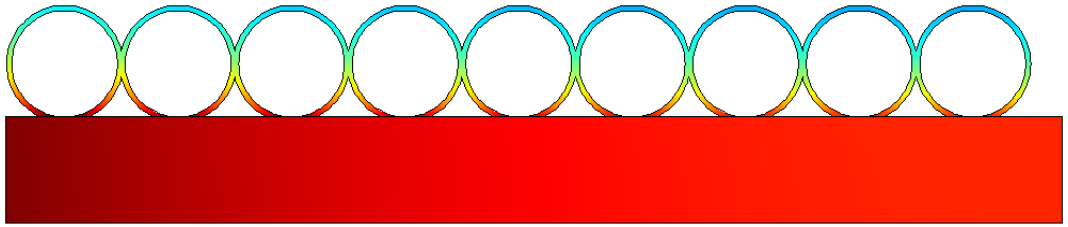
# Thin-film proton conduction is sluggish for 70% and 90% nanofiber: significant decrease in the film potential

## Distribution of ionic potential (V) in the film and nanofiber

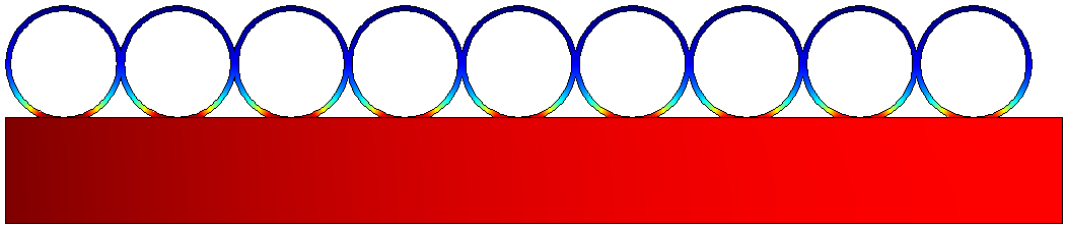

- 10% nanofiber

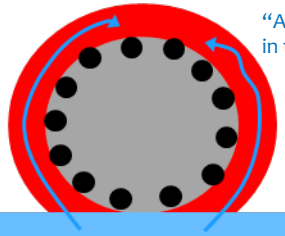



- 70% nanofiber

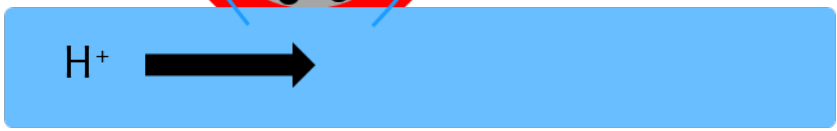


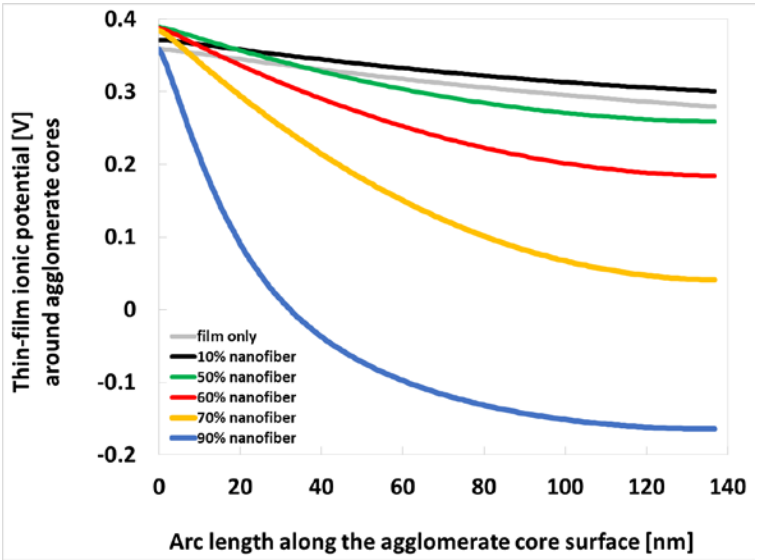
- 90% nanofiber





"Arc length along agglomerate core surface" in the plot below follows the blue arrow.

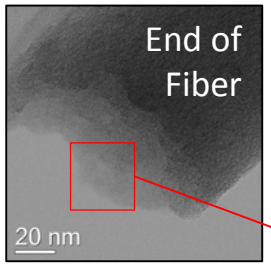


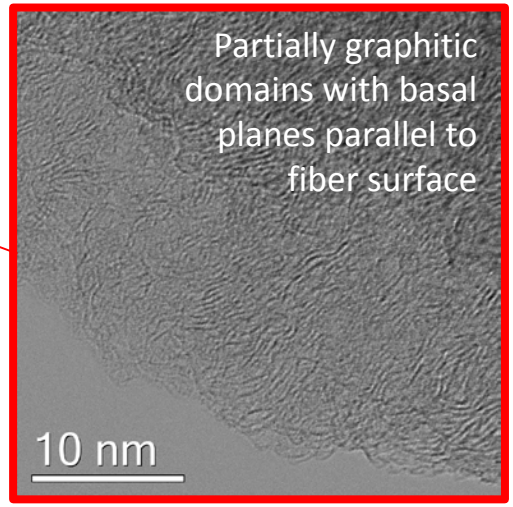



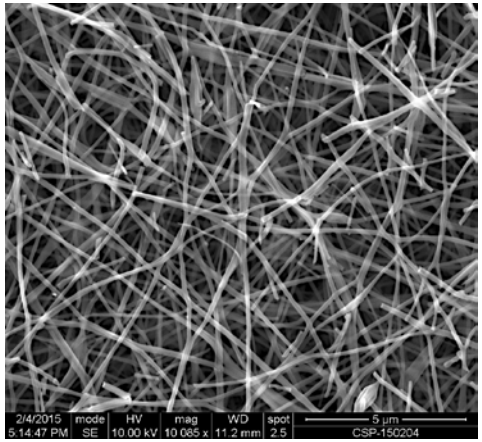

- The decrease in the film potential is more significant with higher nanofiber fraction (film getting thinner), meaning that the thinner film has a rate-limiting $H^+$ conduction.

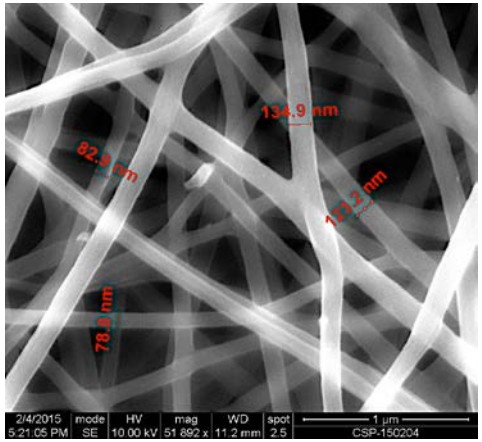
# Bulk Heteroatom Functionalized Supports

- Intent is to form bulk functionalized carbon supports adding heteroatoms (e.g., B, P) to improve durability & wettability over N doped alone.
- Pyrolyzed PAN/Phos-Acid Nanofibers
  - Fibers formed by electrospinning
  - Oxidatively stabilized & cross-linked
  - Pyrolyzed in various gas atmospheres
- Results:
  - Low graphitization (retarded by phos-acid?)
  - Low heteroatom surface compositions (but bulk P up to 4% by EDS)
  - Appreciable surface contamination by Si, K, Na.



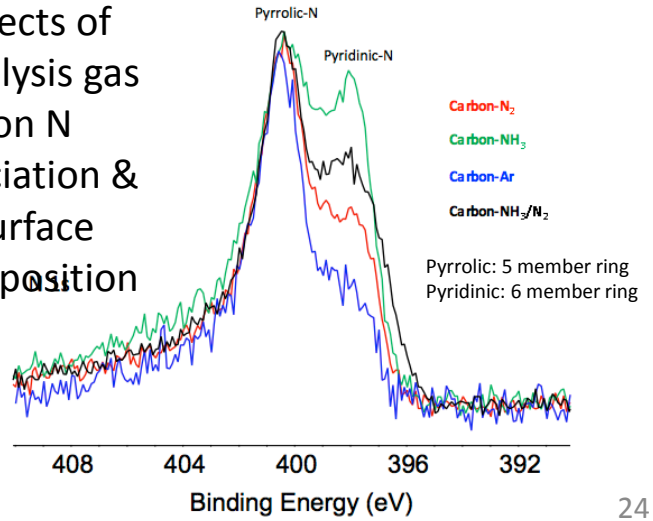






SEMs

Effects of pyrolysis gas on N speciation & surface composition

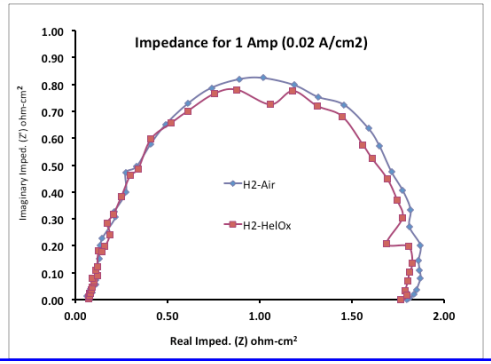
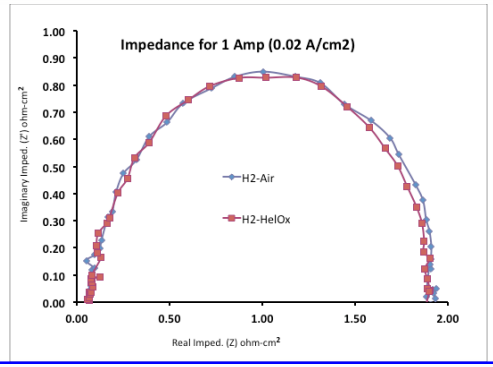
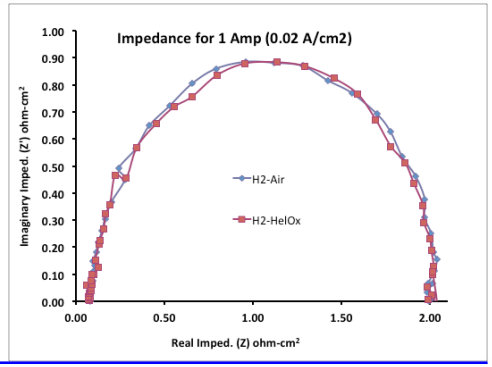
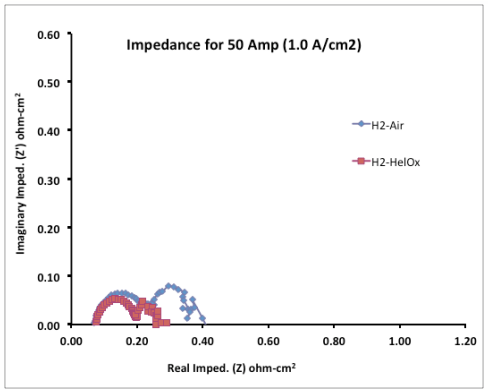
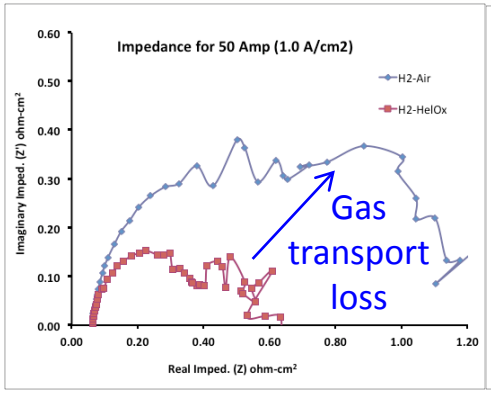
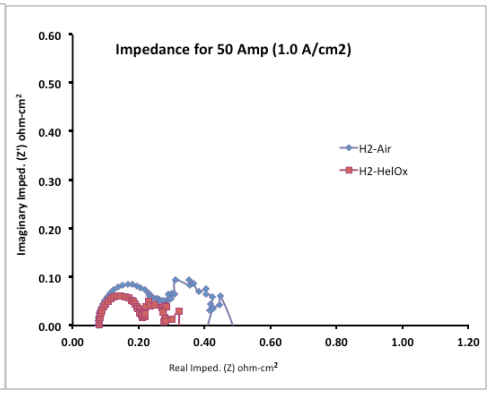



**Surface Composition (at.%)**

| | C | O | N | P | Si | K | Na |
|---|---|---|---|---|---|---|---|
| C-$N_2$ | 84.1 | 8.9 | 3.4 | 1.5 | 0.8 | 1.1 | 0.1 |
| C-$NH_3$ | 83.8 | 9.5 | 3.6 | 0.4 | 2.7 | 0.0 | 0.1 |
| C-Argon | 82.2 | 11.9 | 1.7 | 1.5 | 1.9 | 0.6 | 0.1 |
| C-$NH_3/N_2$ | 89.9 | 3.7 | 3.9 | 1.8 | 0.5 | 0.0 | 0.2 |

Los Alamos NATIONAL LABORATORY EST.1943

# MEA Impedance Spectra

| | Low Solubilized Nafion® EIT MEA | High Solubilized Nafion® EIT MEA | GM Type 3 MEA |
|---|---|---|---|
| 20 mA/cm² |  |  |  |
| 1A/cm² |  |  |  |





- The cells are very similar in the kinetic region, but at high current densities substantial gas transport losses are incurred in the HiNaf cell

Los Alamos NATIONAL LABORATORY EST. 1943