SCHOOL OF ENGINEERING
VANDERBILT UNIVERSITY

DOE Hydrogen Program

NanoCapillary Network Proton Conducting Membranes for High Temperature Hydrogen/Air Fuel Cells

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Project ID: FC038

Overview

Timeline

- Start date 3/1/2006
- End date 2/28/2012 (1-year no-cost extension)
- Percent complete 75%

Budget

- Total project funding
  - DOE $1,455,095
  - Contractor (CWRU and Vanderbilt) $406,479
- Funding received in FY10, $350,000
- Funding for FY11, $130,095

Barriers

- Barriers
  - Membrane performance (conductivity, mechanical properties, gas crossover)
  - Durability
  - Cost
- Targets
  - 0.10 S/cm proton conductivity at 120^{o}C and 50% RH
  - 0.02 Ohm-cm^2 area specific resistance
  - 2 mA/cm^2 crossover for oxygen and hydrogen

Interactions

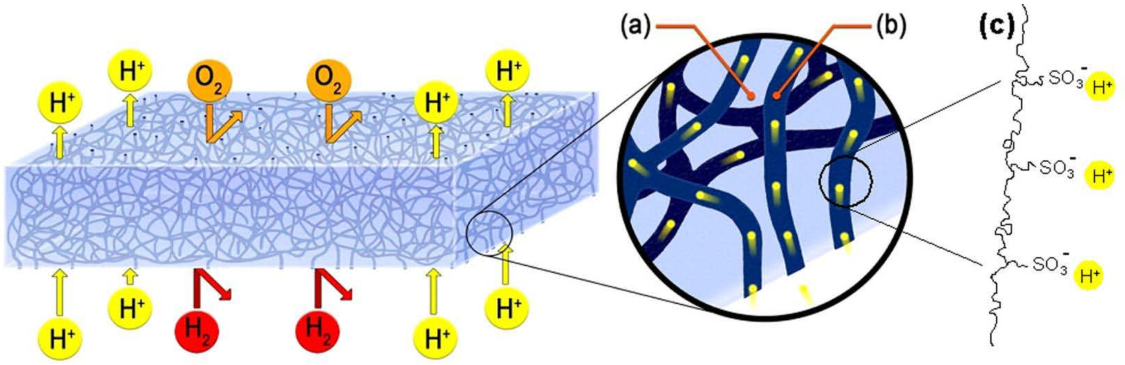
3M Corporation
Nissan Technical Center North America, Inc.
General Motors LLC

Objectives

Project Objective:

To fabricate and characterize nanofiber network proton conducting membranes for hydrogen/air fuel cells that operate under high temperature, low humidity conditions.

- High proton conductivity
- Low gas crossover
- Good mechanical properties



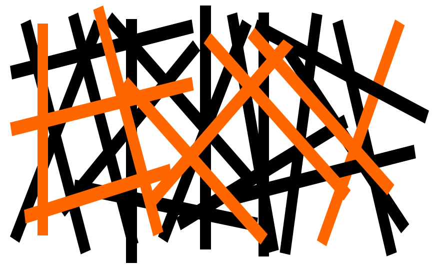
2010-2011 Project Goals:

1. Evaluate two different nanofiber composite membranes:
   a. Polyphenylsulfone (PPSU) nanofibers surrounded by perfluorosulfonic acid (PFSA)
   b. PFSA nanofibers surrounded by PPSU
2. Begin electrospinning low EW PFSA (660 EW from 3M Corp.)
3. Continue to investigate electrospun fuel cell electrodes

Milestones

Month/Year	Milestone or Go/No-Go Decision
March 2008	Milestone: Successfully electrospun sulfonated poly(arylene ether sulfone) (sPAES) and added varying amounts of sulfonated POSS (polyhedral oligomeric silsesquioxanes) to the ionomer nanofiber mats. Converted the mats into defect-free nanofiber network membranes.
April 2008	Milestone: Achieved a proton conductivity of 0.07 S/cm at 30^{o}C and 80% RH, for a nanofiber network membrane (nanofibers composed of sPAES + sulfonated POSS, with Norland Optical Adhesive 63 as the inert matrix).
December 2008	Go/No-Go Decision: Achieved a proton conductivity of 0.107 mS/cm at 120^{o}C and 50% RH for a nanofiber network membrane, where the fibers were composed of 825 EW PFSA polymer + SPOSS, with Norland Optical Adhesive 63 as the inert matrix.
March 2010	Milestone: Developed a new dual nanofiber electrospinning membrane fabrication scheme that eliminates the polymer impregnation step. NOA63 was replaced with polyphenylsulfone as the inert matrix polymer.
February 2011	Milestone: Prepared and assessed defect-free composite nanofiber membranes from low EW (660) PFSA and polyphenylsulfone (PPSU), using a dual fiber electrospinning approach. Prepared and tested high performance nanofiber fuel cell cathodes.

Dual Fiber Electrospinning

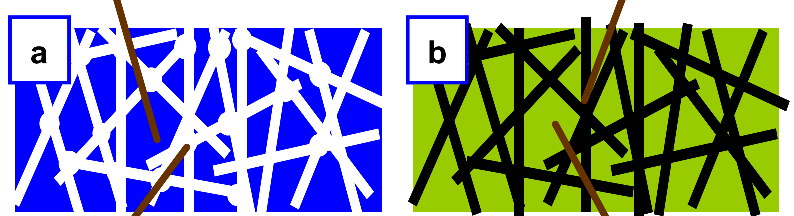


Simultaneously electrospin a dual nanofiber mat – one fiber is the ionomer and the second fiber is an uncharged/inert polymer (polyphenylsulfone)

Mat Processing

Interfiber voids are filled with the inert polymer matrix that provides mechanical strength and controls swelling

Interconnected 3-D network of inert polymer nanofibers that provides mechanical strength



Interconnected 3-D network of ionomer nanofibers

Inter-fiber voids are filled with ionomer

Method #1

“Melt” inert polymer around ionomer nanofibers

Year 5 work focused here

Method #2

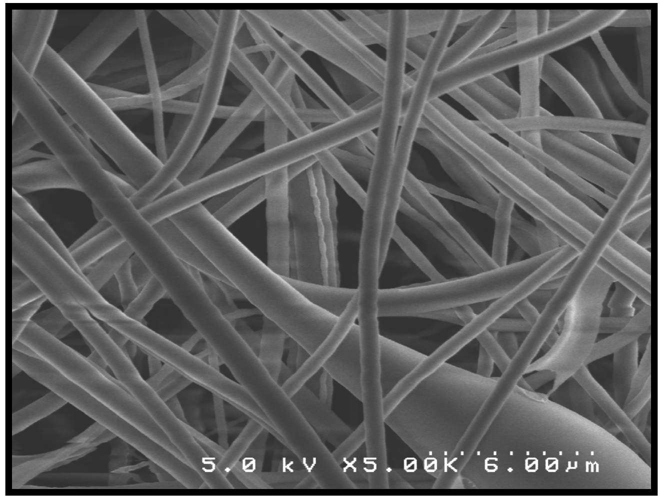
Melt ionomer around inert polymer nanofibers

Year 4 work focused here

Converting a Dual Nanofiber Mat into a Composite Membrane

Nafion® softens/flows to fill inter-fiber voids

1) **Hot Press (Compact) @ 6,000 psi at 127°C, 4x 10 sec. presses**
2) **Anneal (150°C for 2 hrs in vacuum)**
3) **Boil in 1M Sulfuric Acid**
4) **Boil in Water**



Dual Fiber Mat Surface

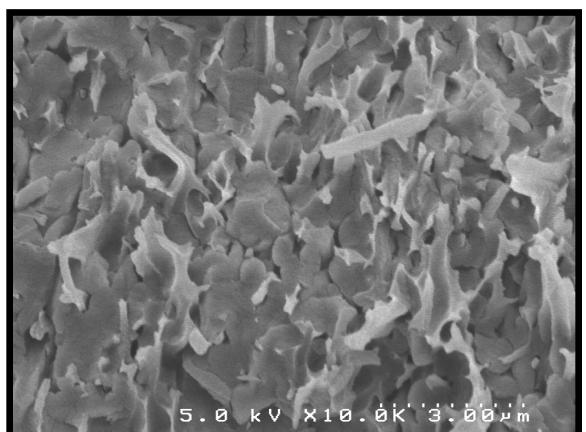
PPSU flows to fill inter-fiber voids

1) **Cold Press (Compact) @ 1500 psi at RT, 4x 5 sec. presses**
2) **Chloroform Vapor Exposure (16 min. at RT)**
3) **Anneal (150°C for 2 hrs in vacuum)**
4) **Boil in 1M Sulfuric Acid**
5) **Boil in Water**

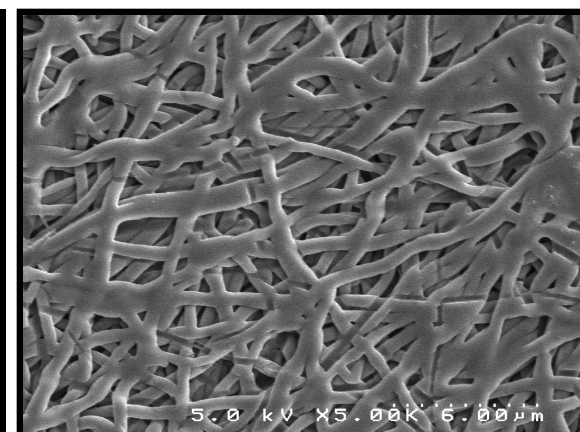
Nafion® with PPSU fibers

Cross-section

PPSU with Nafion® fibers



Cross-section



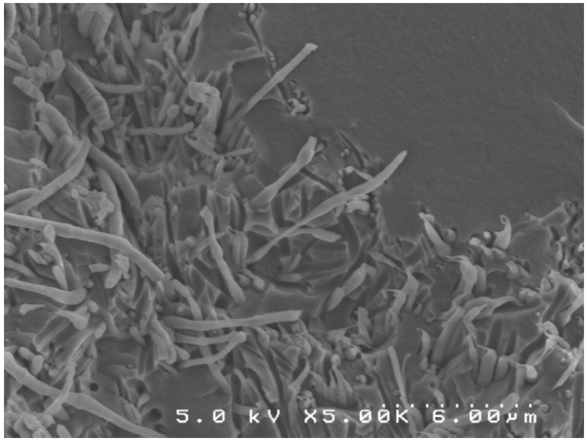
Surface after PPSU Removal

Summary of Inert Fiber Mat Reinforcement Membranes (with Nafion®)

	Nafion®	Nafion®/PPSU (70 vol% Nafion®)	Nafion®/PVDF (56 vol% Nafion®	Nafion®/PBI (75 vol% Nafion®)
Conductivity in water at 22°C [S/cm]	0.095	0.066	0.053	0.071
In-plane areal swelling in 100°C water [%]	**37**	**6**	**10**	**13**
Volumetric swelling in 100°C water [%]	75	42	62	52

Nafion®/PPSU

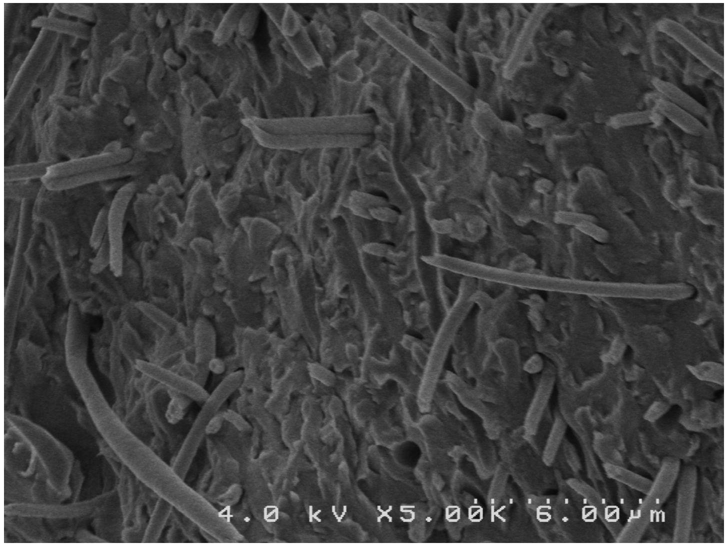
Nafion®/PVDF



Nafion®/PBI

Processing: Hot Press (127°C, 3500 psi) and Anneal (150°C, 2 hours)

3M 825 EW PFSA Surrounding PPSU Nanofibers

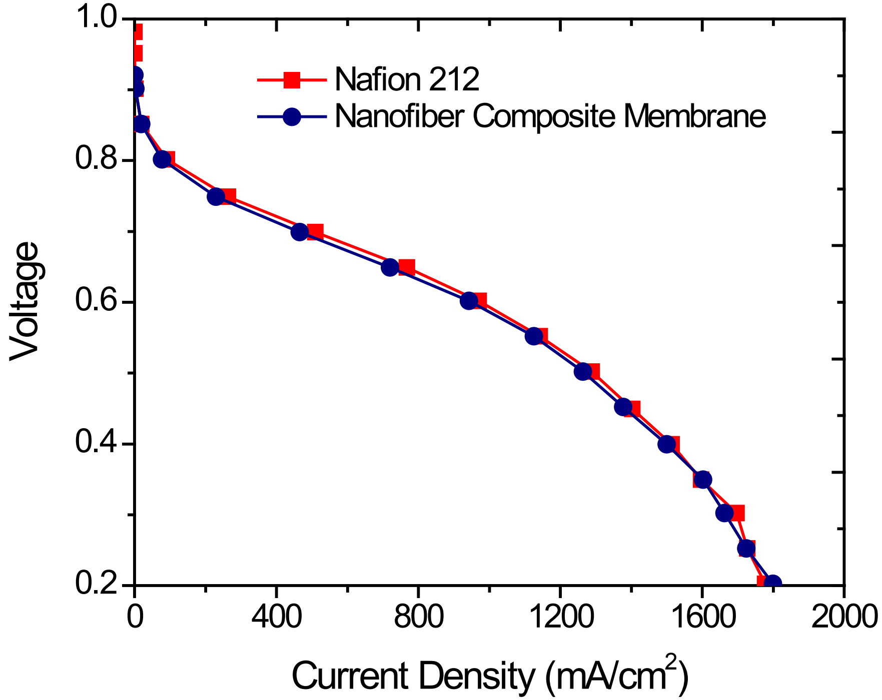


- Membrane was composed of ~80 wt% PFSA and 20 wt% PPSU
- PFSA was electrospun with 1 wt% PEO
- The nanofiber composite membrane has the same conductivity as Nafion® 212, but reduced in-plane swelling

Properties

Material	Conductivity in Water at 23°C [S/cm]	In-Plane Water Swelling at 23°C [%]	Volumetric Water Swelling at 23°C [%]
Nanofiber Composite (3M 825 EW:PPSU)	0.095	5	43
Cast 3M 825	0.115	25	85
Nafion® 212	0.095	19	35

H_2/Air Fuel Cell Performance - Nafion® Surrounding PPSU Nanofibers

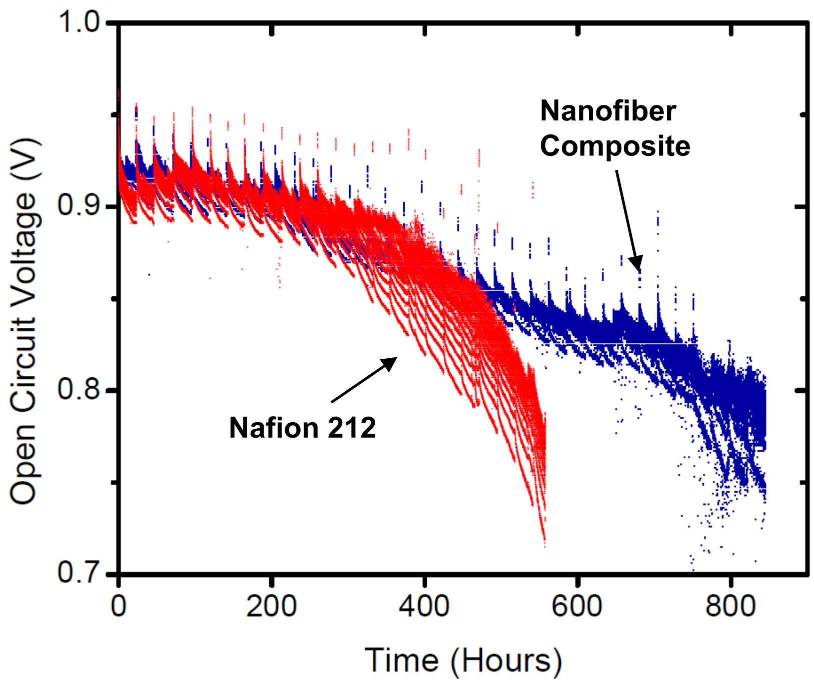


- 80°C, 100% RH
- 0.4 mg/cm² Pt loading (anode and cathode)
- 30% Nafion® binder content
- decal method for MEA preparation

Nafion® 212 (51 µm)

Nanofiber composite (30 µm dry thickness)

H_2/Air Fuel Cell OCV Durability Test



- 25 cm^2 MEA
- 80^{o}C, 100% RH
- Anode and Cathode: 0.4 mg/cm^2 Pt loading with 30% Nafion® binder content

Nafion® 212 (51 μm)

Nanofiber composite membrane – Nafion® polymer with a PPSU reinforcement mat (dry membrane thickness - 30 μm)

- Cycling: 2 minutes 100% RH H_2/Air, 2 minutes 0% RH H_2/Air. 25 cm^2 cell, 125 mL/min H_2, 500 mL/min air flow rates,

- **Nafion® 212 failed after 546 hours**
- **The Nanofiber Composite Membrane failed after 842 hour (a 54% increase in lifetime)**
- **Before failure, H_2 gas permeation was very low**

Technical Accomplishments and Progress for Year 5

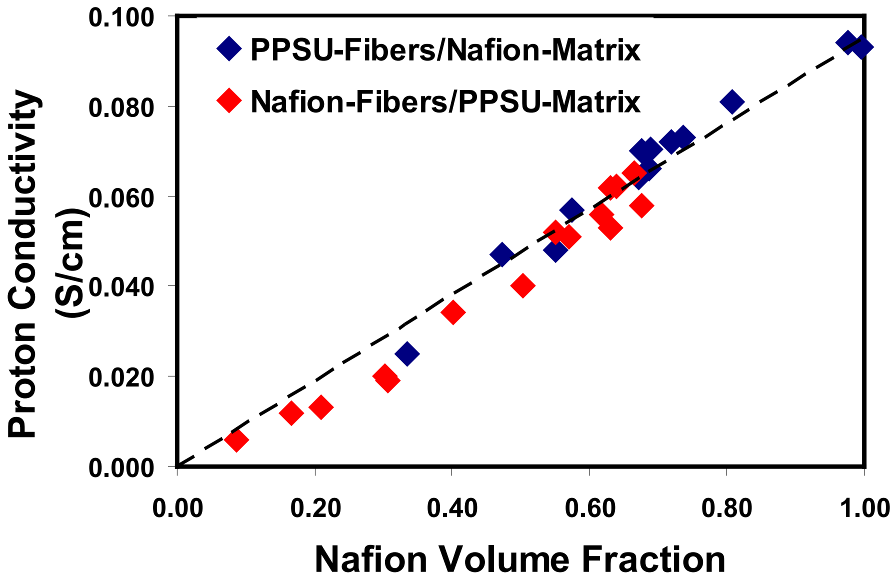
1. Fabricated nanofiber composite membranes with PFSA (Nafion®) nanofibers surrounded by uncharged polyphenylsulfone (the opposite morphology from the polysulfone fiber reinforced membranes studied in Year 4).
2. Electrospun low EW PFSA (660 EW polymer from 3M Corporation) and converted the mat into a membrane with a PPSU nanofiber reinforcement.
3. Continued to investigate electrospun nanofibers as fuel cell electrodes.

Conductivity and Volumetric Swelling

Membrane composed of Nafion® and polyphenylsulfone

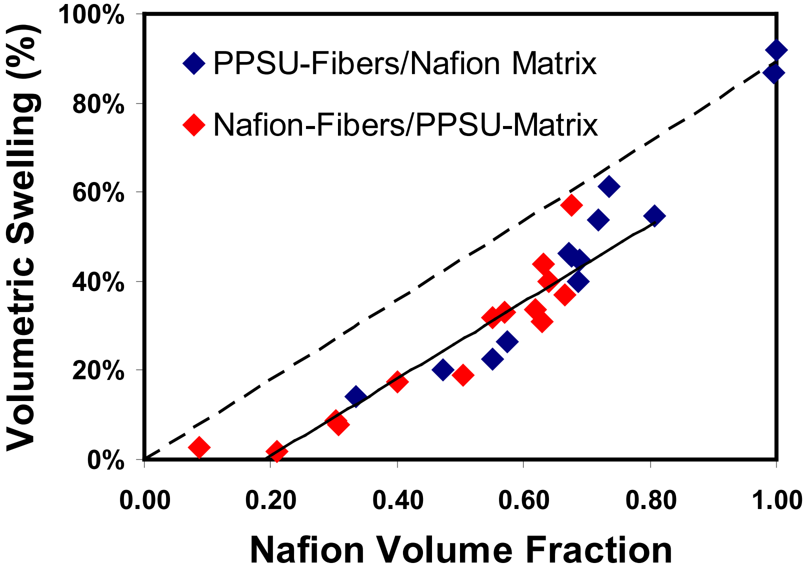
Conductivity

(measured in 25°C in water)



Volumetric Swelling

(measured at 100°C in water)

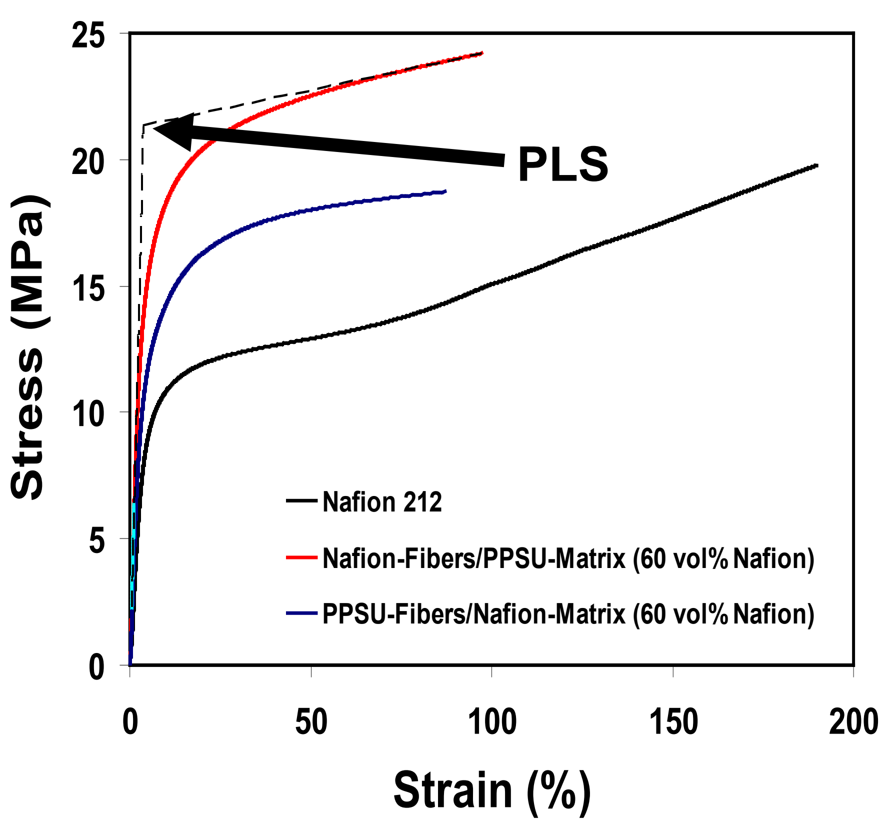


- Conductivity can be predicted by a volume fraction Mixing Rule (dashed line, above)
- Electrospun membranes have an exceptionally low percolation threshold (≤ 9 vol% Nafion)

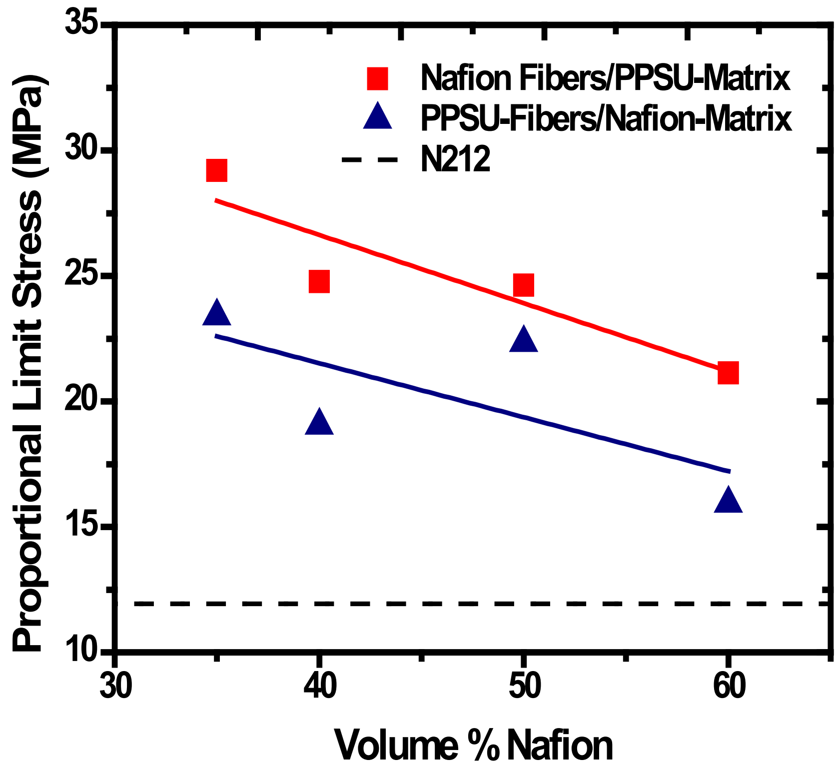
- Volumetric swelling is controlled by PPSU
- Volumetric swelling is lower than that predicted by a Mixing Rule.

Mechanical Properties

- **Stress-strain curves at 30°C, ~20% RH**

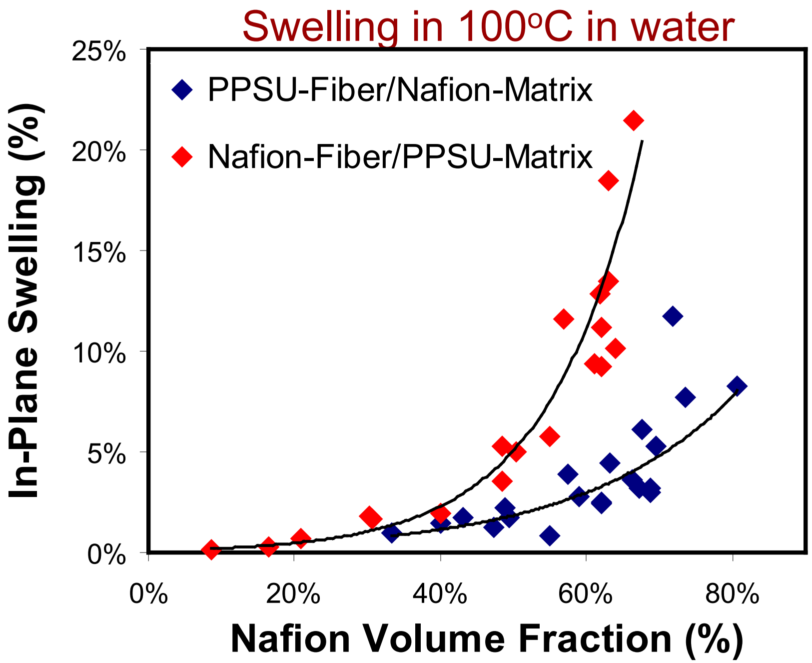


- **Data Points are average of 3 tests**



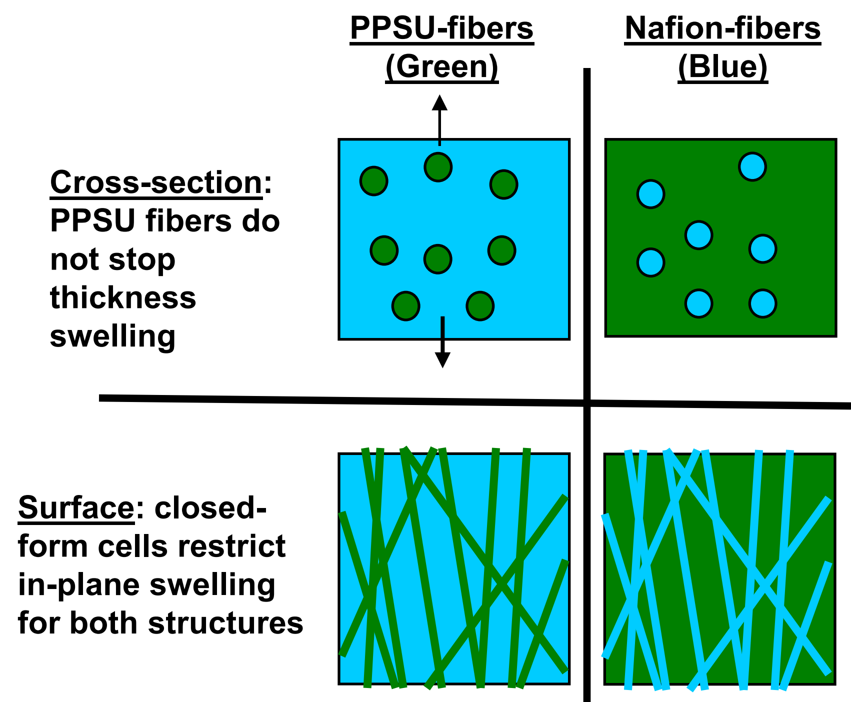
- **PPSU improves mechanical properties of composite membranes**
- **Nafion®-fiber/PPSU-matrix has best mechanical properties (3-D PPSU connectivity)**

In-Plane Swelling in 100°C Water



- PPSU-fiber/Nafion® -matrix has lower in-plane swelling
- PPSU-fibers/Nafion® -matrix can expand more easily in thickness direction (no 3-D connectivity of PPSU)
- Limited thickness swelling for Nafion® fiber/PPSU membrane (3-D PPSU connectivity)

- Both membrane structures have the same volumetric swelling for a given Nafion® volume fraction
- In-plane swelling is significantly lower than Nafion® for both composite membranes



Dual Fiber Electrospinning: 660 EW PFSA (from 3M Corp.) and Polyphenylsulfone

	3M 660 EW	**Polyphenylsulfone (PPSU)**
Polymer Comp.	99.7:0.3, 660EW:PEO (30 wt% total polymer)	25 wt%
Solvent	n-propanol:water in 2:1 wt. ratio	DMAc:acetone in 8:2 wt. ratio
Voltage	7.0 kV	7.5 kV
SCD	5.5 cm	8.5 cm
Flow Rate	0.40 mL/hr	0.10 mL/hr

PEO= Poly(ethylene oxide) – 1,000 kDa

PPSU: Radel® R-5500NT polyphenylsulfone from Solvay Advanced Polymers LLC

Relative Humidity = 35 %

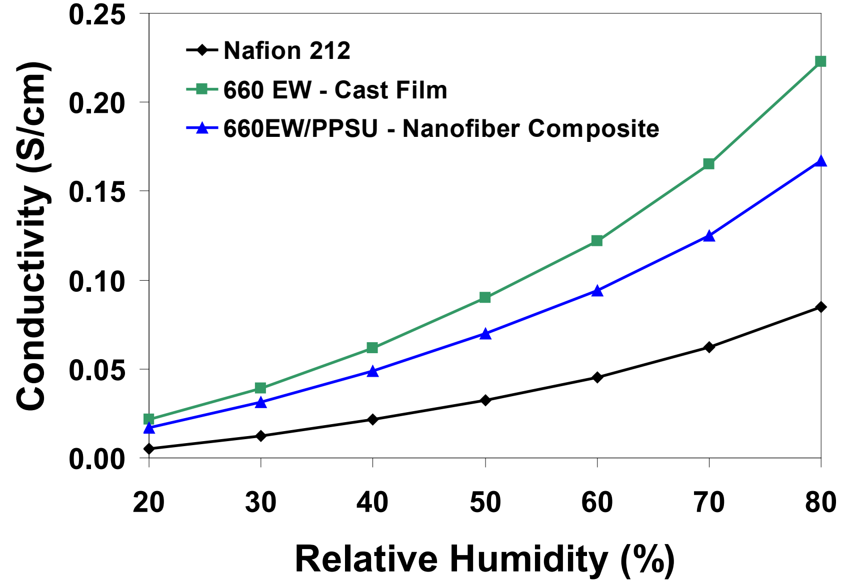
3M 660 EW/PPSU Nanofiber Composites

Membrane Processing (PPSU-fibers/660 EW-matrix)

1) Compress to 6000 psi at 127°C for a few seconds
2) Anneal 2 hours at 150°C in vacuum
3) Soak in 1M H_2SO_4 for 16 hours at 23°C
4) Soak in water for 6 hours at 23°C (replacing with fresh water periodically)
5) Dry membrane thickness: 49μm.

Conductivity vs. RH at 80°C

(based on dry dimensions)



Swelling and Conductivity Data

(Swelling in 23°C liquid water; conductivity at 80°C, 50%RH)

Membrane	Mass Swelling [%]	Volumetric Swelling [%]	In-Plane Swelling [%]	Conductivity 80°C, 50% RH [S/cm]
660EW-Matrix/PPSU Fibers	53	87	5	.070
Cast 660 EW film*	71	137	34	.090
Nafion® 212	16	35	25	.028

*Cast 660 EW Film was annealed 1 hour at 150°C

Preliminary Membrane Cost Analysis

Nanofiber Composite Membrane:

70 vol% PFSA (@ $200/kg, from September 2010 DTI Report[a], for 100,000 kg polymer purchase per year)

30 vol% polyphenylsulfone, PPSU (Radel® R-5500NT from Solvay Advanced Polymers LLC @ $15.86/lb)

20 μm thick

Electrospinning costs:

0.19 cents per cm^2 (for a 200 inch wide electrospinning line; further savings are possible for larger production lines); cost estimate from eSpin Technologies, Inc., Chattanooga, TN

Costs:

PFSA - $7.96/$m^2$
PPSU - $0.39/$m^2$
Electrospinning - $19/$m^2$
TOTAL - $27.35/$m^2$

[a] Mass Production cost Estimation for Direct H_2 PEM Fuel Cell Systems for Automotive Applications: *2010 Update,* Directed Technologies, Inc., September 30, 2010

Electrospinning Fuel Cell Catalyst Into a Nanofiber Cathode

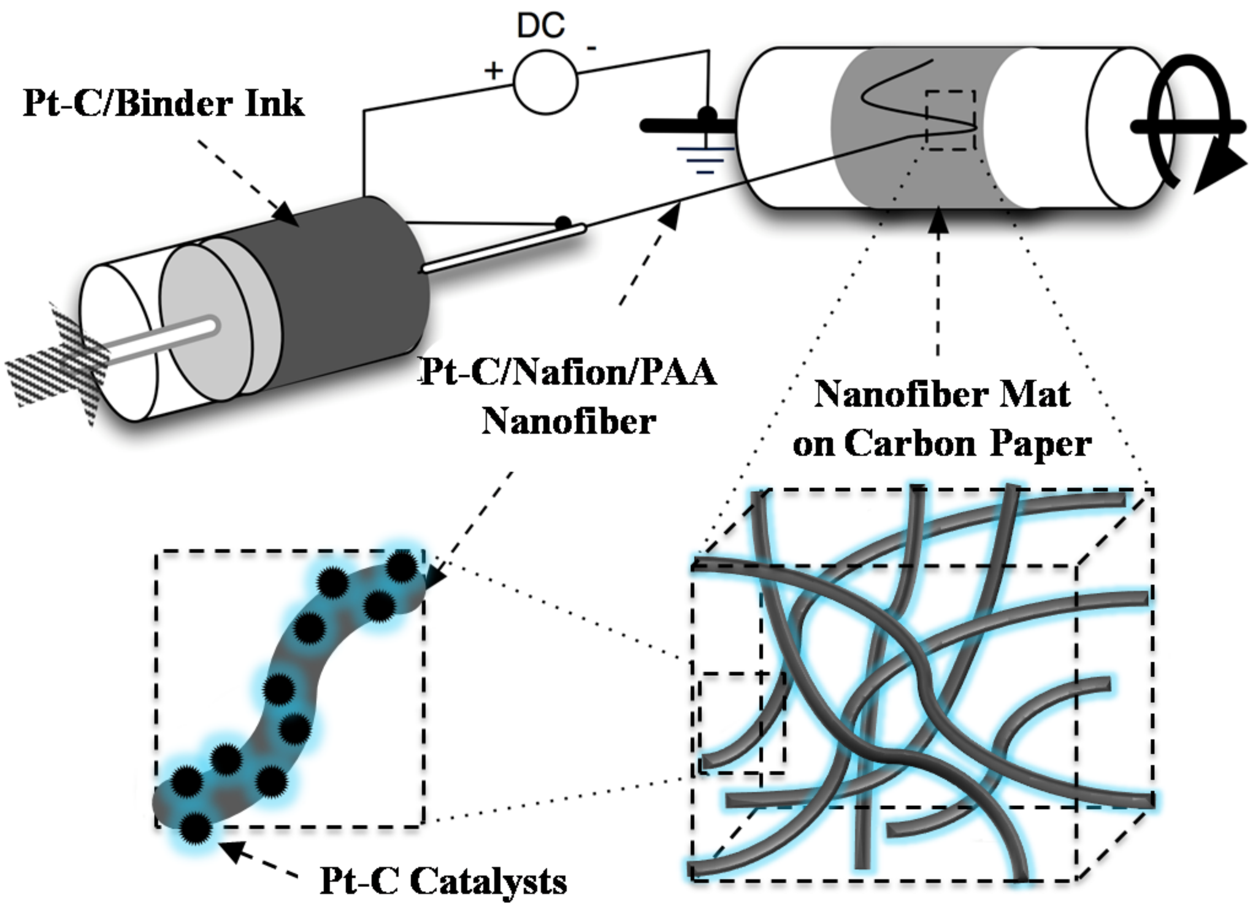
Ink (Pt/C+Nafion®+PAA)

↓

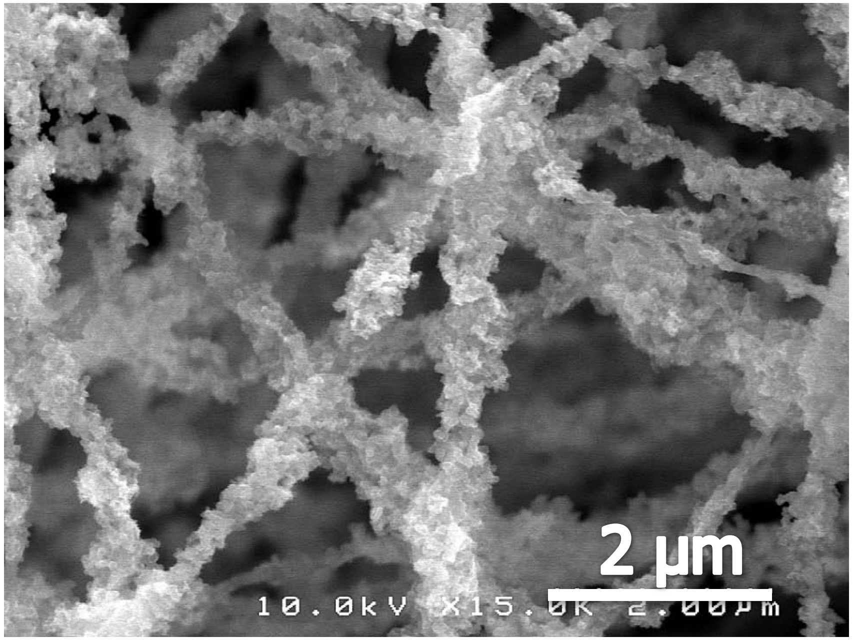
Electrospinning on Carbon Paper

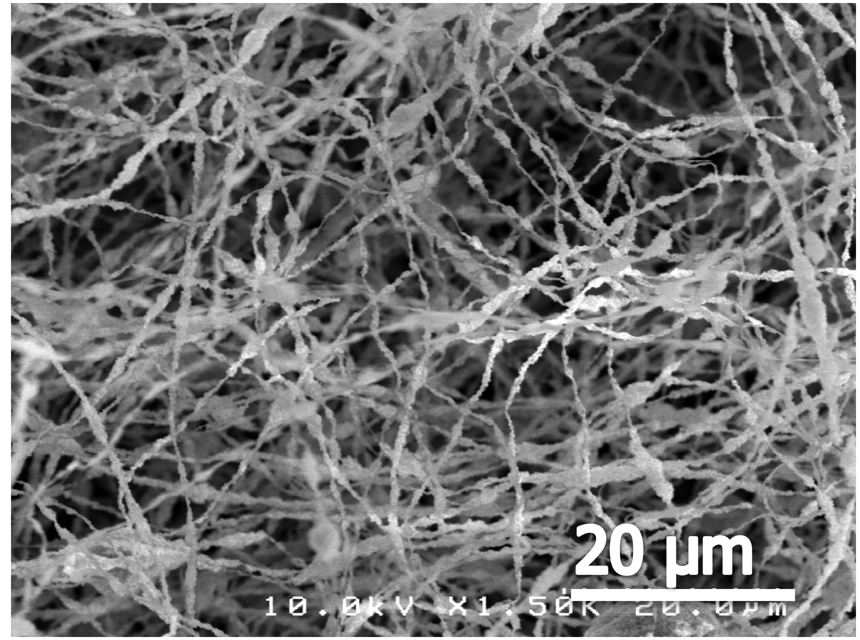
↓

Hot Press on PEM



Nanofiber Electrode Mat

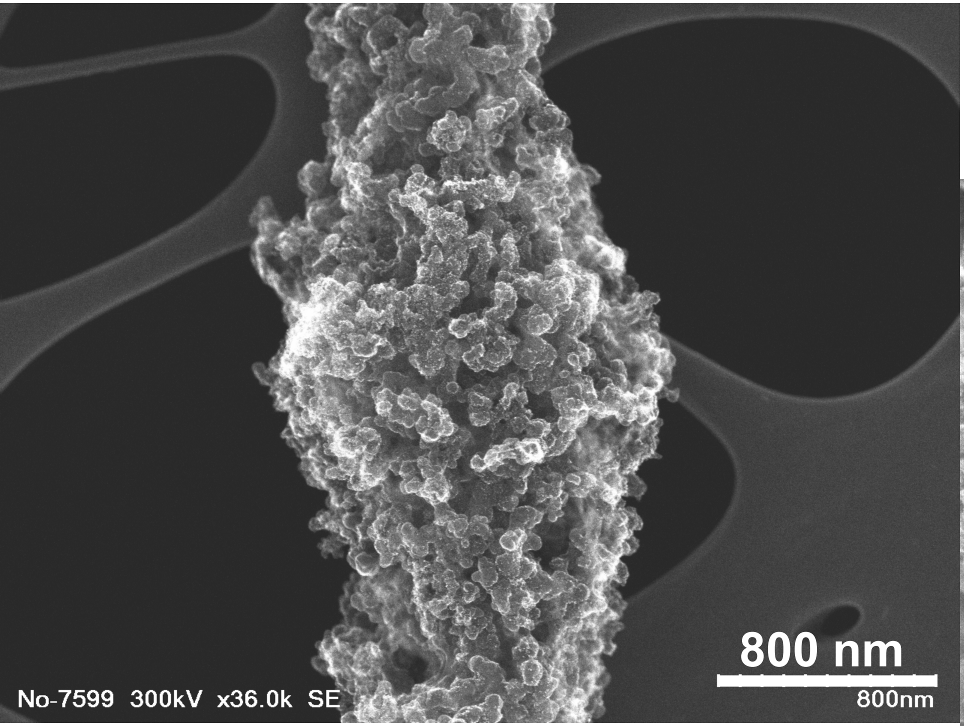


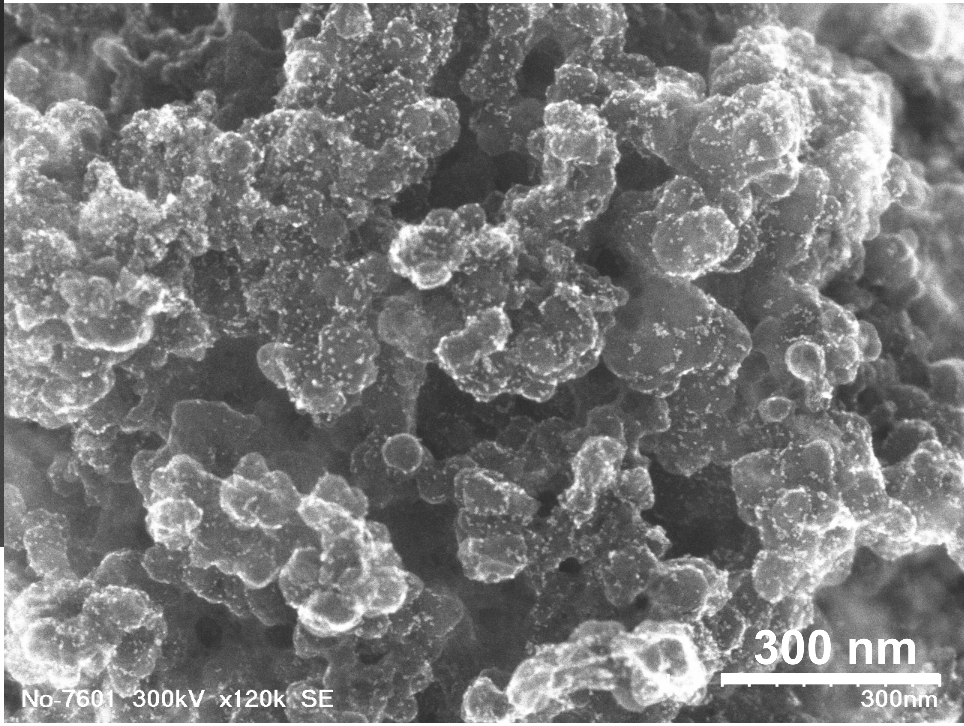


SEM picture of electrospun catalyst (75 Pt-C/15 Nafion®/10 PAA)

- Nanofiber architecture for improving accessibility of gas to Pt reaction sites
- 470 nm average fiber diameter
- High concentration of Pt/C particles insures high electronic conductivity in the fibers
- Sufficient Nafion® content in the fibers for proton conductivity

Nanofiber Electrode Mat (High Magnification SEMs)

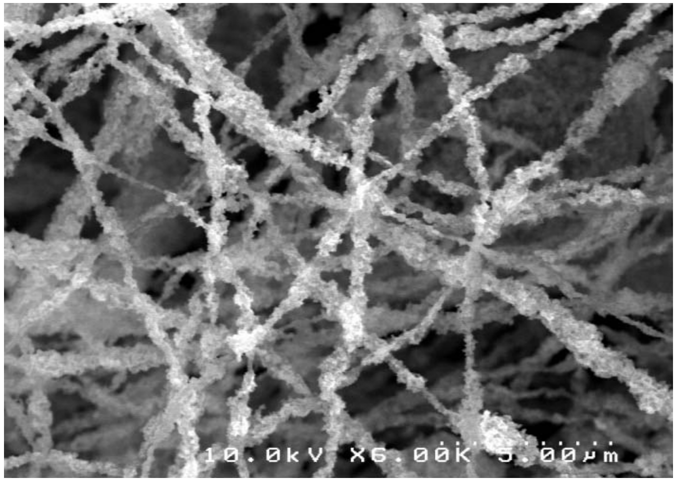




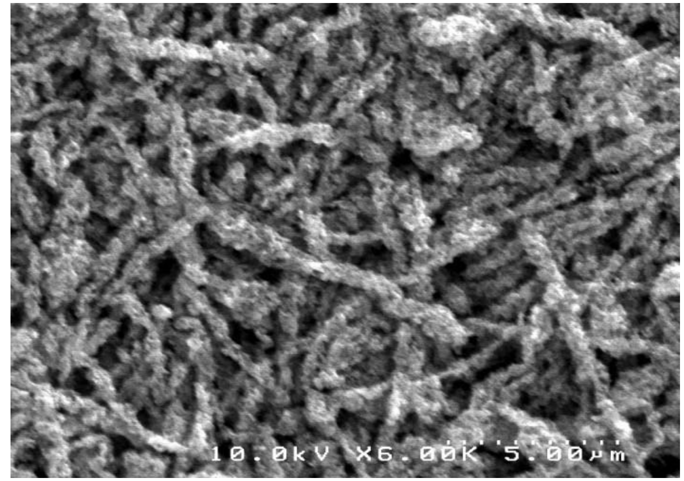
SEMs courtesy of Karren Moore at ORNL.

Nanofiber Structures are Intact After Hot-Pressing

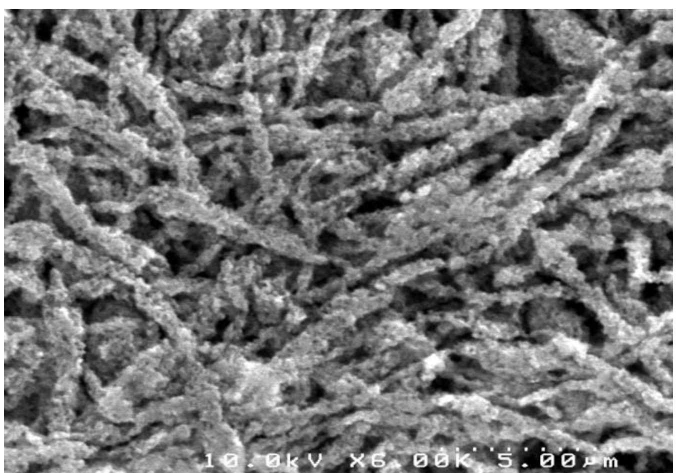
(140^{o}C for 10 minutes)



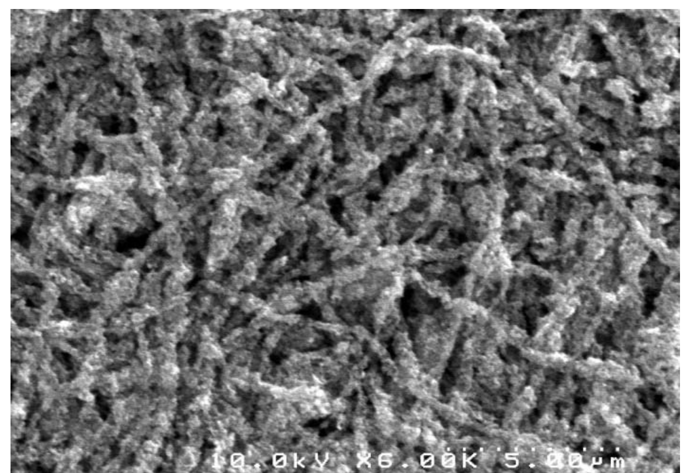
Hot –pressed @ 0MPa



Hot –pressed @ 10MPa



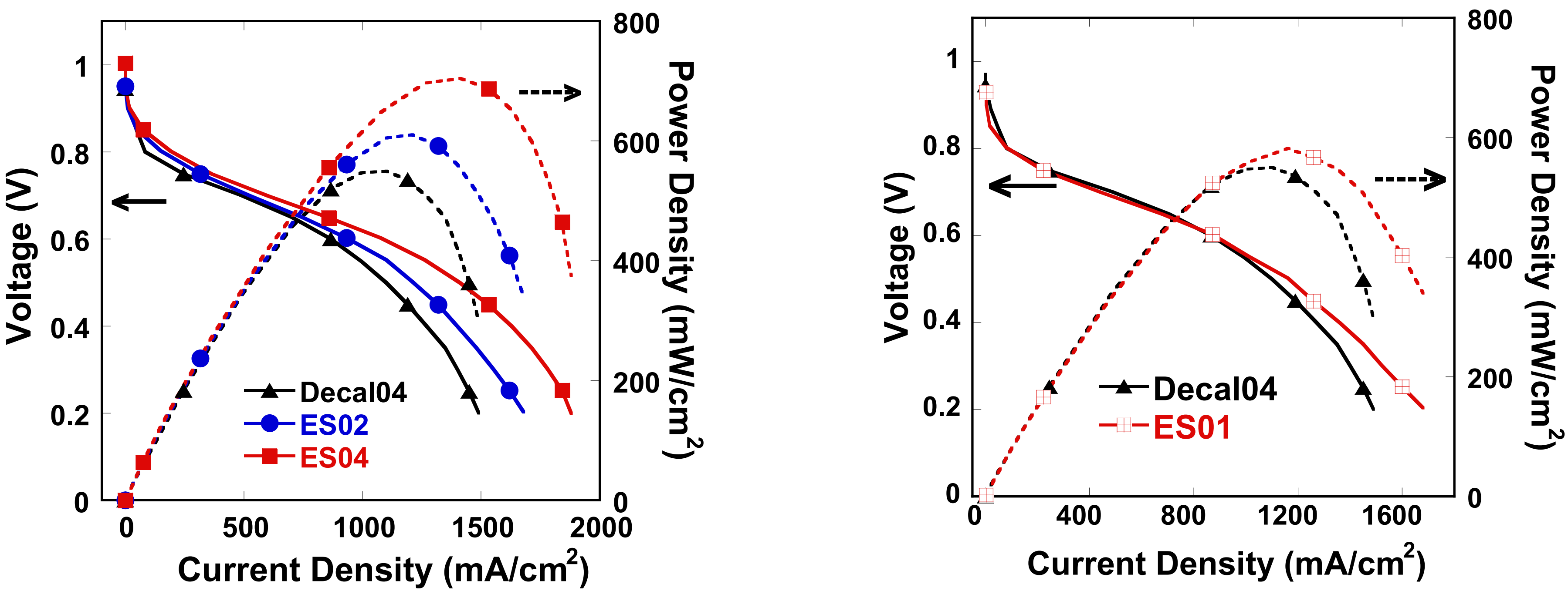
Hot –pressed @ 16MPa



Hot –pressed @ 80MPa

4-fold Reduction in Pt-loading With No Loss in Performance

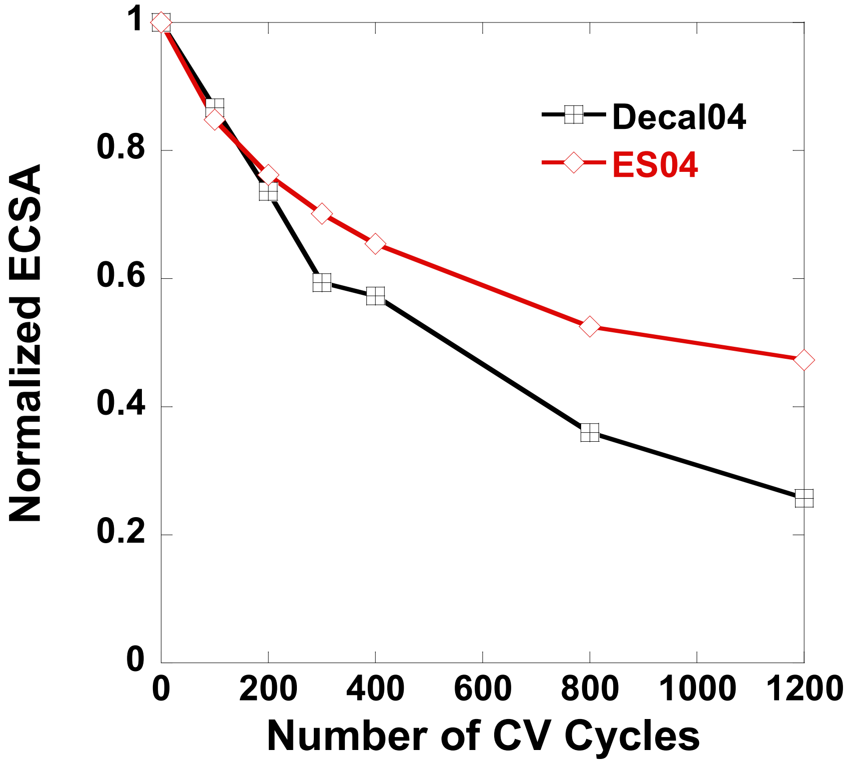
(5 cm^2 MEA; 80°C; fully humidified H_2/air; no backpressure)

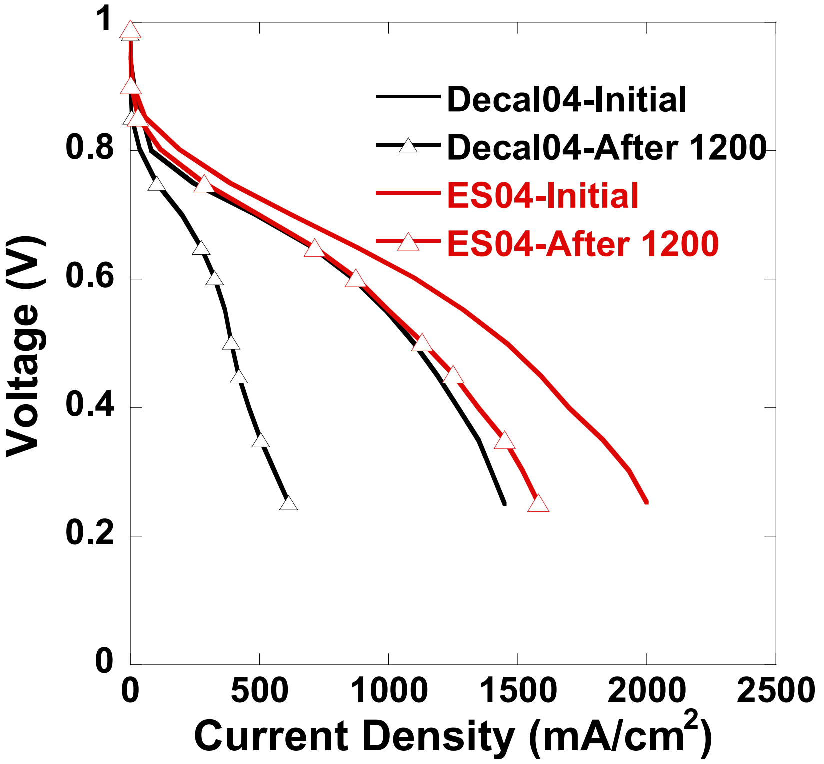


Cathode	Pt-loading (mg/cm^2)	Power Density @ 0.6V (mW/cm^2)	Mass Activity @0.9V (A/mg_{Pt})
Decal04	0.4	519	0.11
ES04	0.4	647	
ES02	0.2	561	
ES01	0.1	524	0.23

Nanofiber Cathode Exhibits Excellent Durability

- **Cathode voltage was continuously raised and lowered between 0.6 V and 1.2 V at 20 mV/s.**
- **Humidified H_2 (anode) and N_2 (cathode) were supplied at 80°C**





Collaborations

Partners

- **3M Corporation:** Provided samples of short side-chain low EW PFSA polymer (in solution) for electrospinning studies and membrane development; provided background information on casting membranes from solutions of low EW PFSA (e.g., polymer annealing conditions).
- **Nissan Technical Center North America, Inc.:** Collaborations with Nissan Technical Center NA involve sharing of MEA testing protocols.
- **General Motors LLC:** Began testing properties and durability of nanofiber composite fuel cell membranes (Nafion® with a reinforcing mat of polyphenylsulfone; membranes fabricated at Vanderbilt).
- **ORNL (Karren More):** SEM and TEM analyses of electrospun nanofiber electrodes

Proposed Future Work

1. **Prepare and test nanofiber composite membranes with 660 EW PFSA from 3M Corporation. Use the dual fiber electrospinning approach.**
   - Prepare and compare composite membranes where the nanofibers are either the inert polymer (fro reinforcement) or ionomer (where the inert polymer surrounds the nanofibers)
   - Characterize the membranes in terms of conductivity, in-plane and volumetric swelling, and mechanical properties.
2. **Prepare and test MEAs with nanofiber network composite membranes composed of low (660) EW PFSA.**
   - Collect V-I polarization data at high and low RH operating conditions
   - Perform a RH cycling experiment
3. **Continue to investigate and improve on the performance/properties of electrospun nanofiber fuel cell electrodes.**
   - Decrease the electrode fiber diameter
   - Optimize the PFSA and carrier polymer concentrations
4. **Prepare and test a nanofiber MEA (hot-press a nanofiber anode and a nanofiber cathode to a nanofiber composite membrane).**

Summary

- Two different membranes were prepared from the same dual fiber electrospun mat, where the ionomer was PFSA and the inert polymer was polyphenylsulfone.
  - Inert/uncharged polymer nanofibers are surrounded by ionomer
  - Ionomer nanofibers are surrounded by inert/uncharged polymer
- 660 EW PFSA from 3M Corporation was successfully electrospun and a dual fiber mat (with electrospun nanofibers of polyphenylsulfone) was converted into a functional proton conducting membrane.
  - In-plane water swelling was very low (5% in RT water) and the conductivity was high (0.70 S/cm at 80^{o}C and 50% RH)
- Electrospun nanofiber electrode structures have been fabricated and preliminary tests were performed in a H_2/air fuel cell. A nanofiber cathode at 0.1 mgPt/cm^2 generated the same power in a H_2/air fuel cell as a decal cathode at 0.4 mgPt/cm^2. The nanofiber cathode also exhibited improved durability during voltage cycling.

Summary of 2010-11 Work

Relevance: Seeking novel high performance membranes for high temperature and low relative humidity PEM fuel cell operation.

Approach: Fabricate nanofiber network composite membranes from high IEC (low EW) ionomers, using a dual fiber electrospinning approach (which circumvents the need for a polymer impregnation step).

Technical Accomplishments and Progress: Two different fuel cell membranes were fabricated from the same dual fiber electrospun mat; polyphenylsulfone nanofibers surrounded by PFSA and PFSA nanofibers surrounded by polyphenylsulfone. A composite membrane with 660 EW PFSA and a polyphenylsulfone reinforcing fiber mat was fabricated and characterized (swelling and conductivity). High performance nanofiber fuel cell cathodes were prepared and tested.

Technology Transfer/Collaborations: Continued collaborations with 3M Corporation and Nissan Technical Center North America. GM was given membranes for testing. Continue to work with Karren More at ORNL. The PI gave numerous presentations, wrote papers, and submitted a patent application (on nanofiber fuel cell electrodes).

Proposed Future Research: Prepare more samples of fuel cell membranes using low EW PFSA and polyphenylsulfone. Determine membrane properties and test new membranes in a H_2/air fuel cell. Continue to develop electrospun nanofiber electrodes.

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