Fuel Cell Membrane-Electrode-Assemblies with Ultra-Low Pt Nanofiber Electrodes

Peter N. Pintauro

Department of Chemical and Biomolecular Engineering
Vanderbilt University, Nashville, TN 37235

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Project ID: # FC158

This presentation does not contain any proprietary, confidential, or otherwise restricted information

Overview

Timeline and Budget

- Project Start Date: 11/1/2016
  - subcontracts and NDAs were not signed until early 2017
- Project End Date: 10/31/2019
- Percent complete: 7%

- Total Project Budget: $3,173,854
- Total Recipient Share: $640,291
- Total DOE Share: $2,533,563
- Total Funds Spent: $80,436

  = $56,374 (DOE) + $24,062 (Recipient)

Barriers and Targets

- Barrier Addressed:
  - High current density performance of MEAs is low for low cathode Pt-loading
- Targets: DOE 2020 performance targets for MEAs
  - Anode + Cathode Pt loading ≤ 0.125 mg_{Pt}/cm^2
  - 65% peak efficiency
  - 5,000 hour durability
  - > 1W/cm^2 at rated power

Partners

- Nissan Technical Center North America
- Georgia Institute of Technology
- 3M Company
- Project Lead: Peter N. Pintauro, Vanderbilt

Project Relevance and Objectives

Project Relevance:

- The VU/GaTech/NTCNA team seeks to better understand and further improve the performance and durability of low Pt loaded nanofiber mat fuel cell electrodes and MEAs.
- This project was selected to address the EERE/FCTO mission to advance PEMFC technology for automotive applications and is part of the FC-PAD consortium.

Project Objectives:

- Fabricate, characterize, and evaluate nanofiber mat electrode MEAs with highly active ORR catalysts for hydrogen/air fuel cells
- Focus on nanofiber cathodes with commercial Pt-alloy catalysts and Pt-Ni octahedra catalysts prepared at GaTech, with various ionomer and blended polymer binders.
- The nanofiber mat cathode/anode composition and morphology will be identified for MEAs that meet the DOE's 2020 performance and durability targets:

  Pt loading: ≤ 0.10 mg/cm^2 cathode and ≤ 0.025 mg/cm^2 anode; > 1 W/cm^2 at rated power for T = 80-95^{o}C; <40% drop in ORR mass activity after load cycling, <5% drop in voltage at 1.2 A/cm^2 after unmitigated start up-shut down and < 10% loss in rated power after drive cycle durability.

- Improved power output at low relative humidity (250 kPa and 40% RH), especially at high current density
- Generate useful correlations and insightful understandings regarding the structure and function of electrospun nanofiber electrodes to guide future nanofiber electrode R&D

Approach

1. Prepare nanofiber and sprayed electrode MEAs with commercial PtCo/C and PtNi/C cathodes with various binders (VU for nanofibers and painted cathodes; Nissan for sprayed cathodes).
2. Synthesize Pt-Ni octahedra catalysts with high ORR activity; Type-1 with no Pt coating and Type-2 with a Pt nanolayer coating (GaTech).
3. Incorporate the octahedra Pt-Ni catalysts into nanofiber and sprayed electrode MEAs with selected ionomer binders (VU and Nissan).
4. Evaluate MEA performance and durability. Optimize the nanofiber cathode mat composition and mat morphology to maximize fuel cell power output and durability at high and low relative humidity conditions (VU and Nissan).
5. Provide catalyst powder, electrospun cathode mats, MEAs, experimental skills, and electrospinning know-how to our FC-PAD collaborators.

Collaborations – Team Members

Vanderbilt University (Prime) led by Professor Peter Pintauro (project PI) and Dr. Ryszard Wycisk (technical contact)

- The VU team has extensive experience in nanofiber electrospinning of fuel cell membranes and electrodes.
- The VU team will perform the lab-scale electrospinning experiments, including MEA fabrication with electrospun electrodes and preliminary MEA fuel cell testing.

Georgia Institute of Technology (Sub) led by Professor Younan Xia (project co-PI) and Dr. D. Qin (technical contact)

- The GaTech team will use a batch reactor to prepare the Pt-Ni/C octahedra catalyst for initial screening and optimization and then switch to continuous-flow method to high-volume production.
- Prof. Xia has extensive expertise in facet-controlled synthesis of colloidal metal nanocrystals and the development of droplet reactors for the scalable production of these nanocrystals.

Nissan Technical Center North America (Sub) led by Dr. Nilesh Dale (project co-PI) and Dr. Amod Kumar (technical contact)

- Nissan will be responsible for fabrication of sprayed MEAs, evaluation of nanofiber and sprayed MEAs, and the final validation of the electrospun electrode performance (meeting DOE targets).
- Dr. Dale has extensive experience in fuel cell project management.

3M Company (Sub) led by Dr. Mike Yandrasits

- 3M Co. will provide low EW PFSA and PFIA ionomers for electrode binders, including 825 and 725 EW PFSA (two 300 g samples of each PFSA) and PFIA polymer with an EW in the 620-660 range (two 500 g samples).

Milestones and Go/No-Go Decision for 2017

Milestone Description	**Date**	**Status as of April 10, 2017**
Delivery of catalyst: 5 g to VU/NTCNA	April 1, 2017	1 g of catalyst received
Prepare/deliver nanofiber MEAs and nanofiber electrode mats: 20 MEAs for NTCNA and FC-PAD teams; 8 nanofiber anode and cathode mats delivered to NTCNA and FC-PAD.	July 1, 2107	On track
Prepare 8 sprayed MEAs	July 1, 2017	On track
Test/deliver nanofiber MEAs: 8 MEAs delivered to NTCNA	Oct. 1, 2017	On track
Test/deliver nanofiber and sprayed MEAs to FC-PAD: 6 nanofiber and sprayed MEAs delivered to FC-PAD	Dec. 31, 2017	On track
Go/No-Go Description		
• Nanofiber MEA with >240 mA/cm^2 at 0.8V • >800 mW/cm^2 at rated power • <50% drop in ORR mass activity after load cycling • <20% drop in voltage at 1.2 A/cm^2 after start up-shut down • <30% loss in rated power after drive cycle durability. Measurements at NTCNA and verification at FC-PAD	Dec. 31, 2017	On track

Technical Accomplishments and Progress

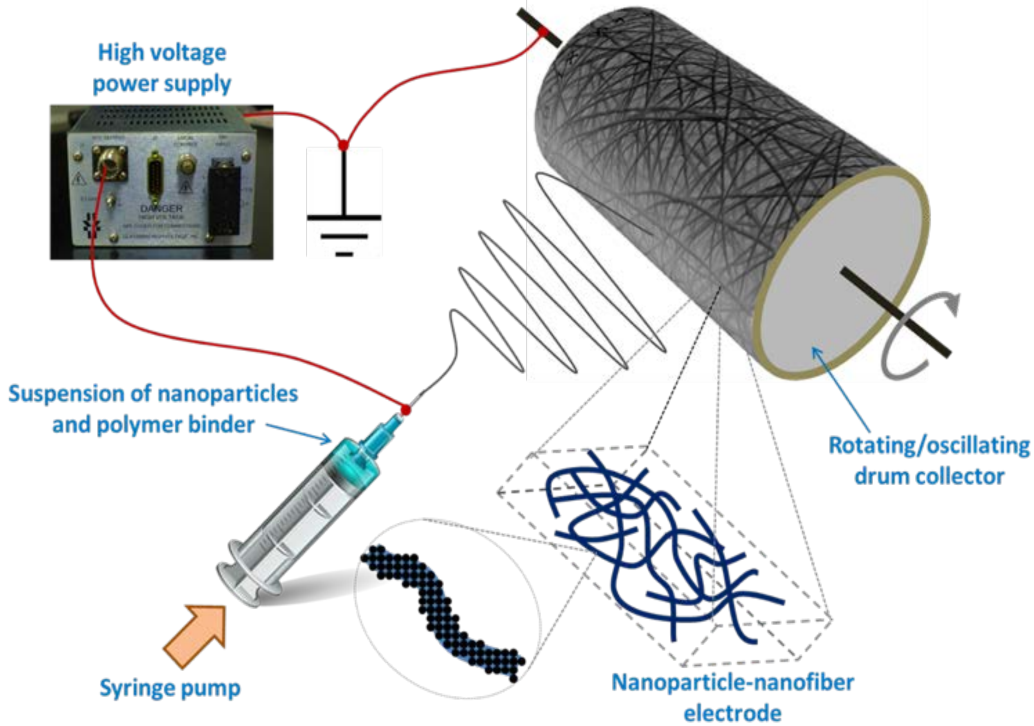
Ink: Catalyst+PFSA/PFIA +PAA

↓

Electrospinning on Aluminum Foil or GDE

↓

Hot Press with PEM and GDL to make MEA

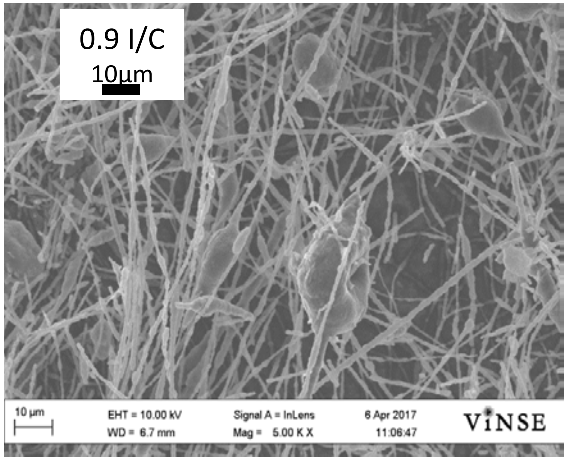


- Electrostatic forces overcome surface tension effects, resulting in the creation of a Taylor cone at the needle tip
- High molecular weight polymers with sufficient chain entanglements will form fiber structures that dry-deposit on a grounded collector
- High and low EW PFSA ionomers, including PFIA
- Carrier polymers: poly(acrylic acid) (PAA), PVDF, and polyvinylpyrrolidone (PVP).

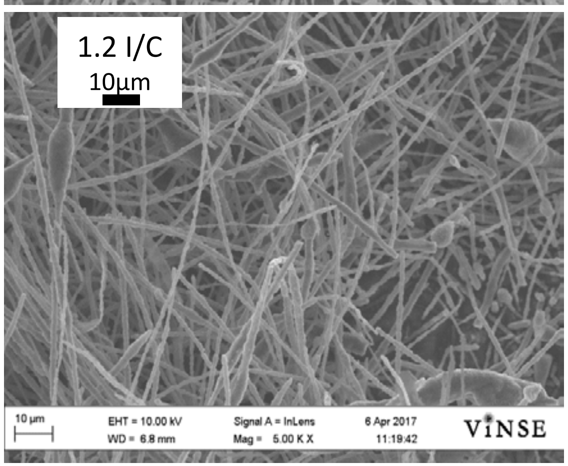
Accomplishment: Electrospun Nanofiber Cathode Mats with TKK PtCo/C and PtNi/C

TKK PtNi/C (20% metal on ketjen black)

Catalyst/Nafion/PAA mass ratio: 58/23/19

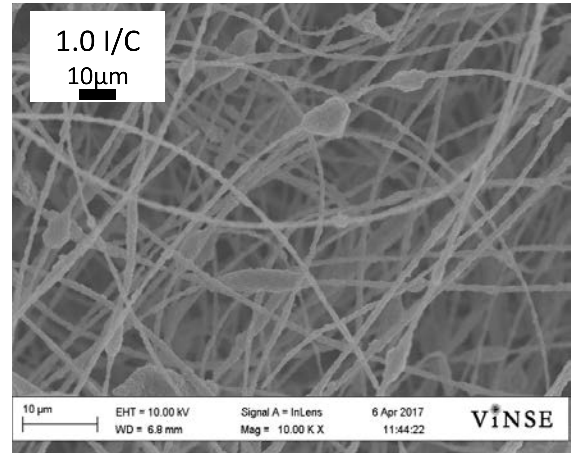


Catalyst/Nafion/PAA mass ratio: 51/27/22

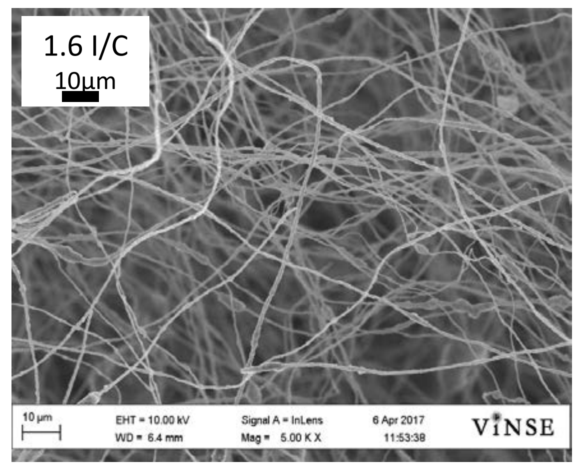


TKK PtCo/C (40% metal on ketjen black)

Catalyst/Nafion/PAA mass ratio: 65/20/15

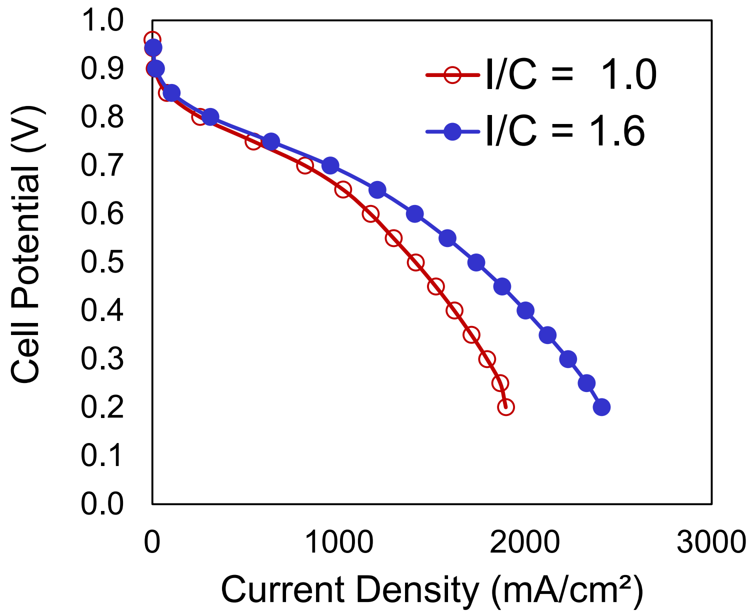


Catalyst/Nafion/PAA mass ratio: 55/30/15



No significant difference in the appearance of PtCo/C and PtNi/C nanofiber mats. The average fiber diameter is 250-400 nm. Some droplet defects are present at lower I/C ratios. The electrospinning conditions (e.g., applied voltage and humidity condition) change with I/C ratio, but not with catalyst composition.

Accomplishment: PtCo/C Nanofiber Cathode MEAs with Two Cathode Ionomer-to-Carbon (I/C) Ratios



MEA (5 cm^2) and Testing Conditions

Cathodes: PtCo/C/Nafion/PAA – 65/20/15 (I/C=1.0)
PtCo/C/Nafion/PAA – 55/30/15 (I/C=1.6)
(I=wt. of PFSA+PAA; C=wt. of carbon)

Anode: 65/35 JM Pt(Hispec)/Nafion

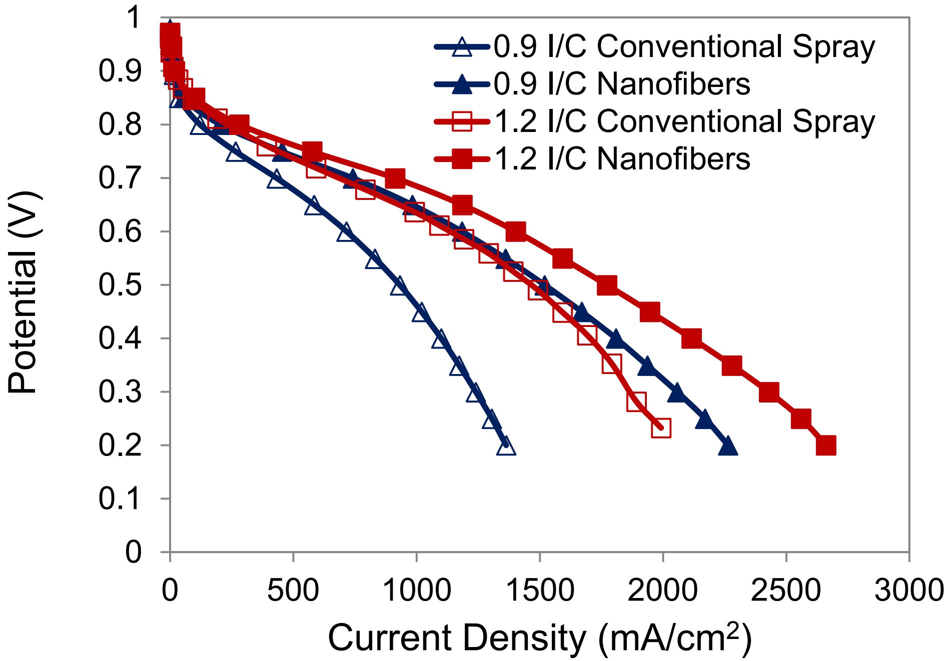
Cathode 0.1mg$_{Pt}$/cm^2 ; Anode 0.1mg$_{Pt}$/cm^2

Feed gas: H_2 (500 sccm); air (2000 sccm)
Membrane: Nafion 211
100% RH; 150 kPa$_{abs}$
Temperature: 80^{o}C

	Max Power (mW/cm^2)	Power at 0.65V (mW/cm^2)
I/C = 1.0	711	665
I/C = 1.6	868	783
Relative Performance increase	118%	122%

- Both PtCo/C and PtNi/C MEAs show improved performance when using an I/C ratio greater than 1.0
- PtCo/C improves by ~20% from I/C=1.0 to I/C=1.6

Accomplishment: Conventional Spray and Nanofiber Cathode MEAs with PtNi/C



MEA (5 cm^2) and Testing Conditions

Membrane: Nafion 211

Anode (0.1 mg_{Pt}/cm^2): Johnson Matthey Pt/C:Nafion Slurry

Nanofiber Cathodes (0.1 mg_{Pt}/cm^2):
58:23:19 PtNi/C:Nafion:PAA (0.9 I/C)
51:27:22 PtNi/C:Nafion:PAA (1.2 I/C)

Conventional Spray Cathodes (0.1 mg_{Pt}/cm^2):
58:42 PtNi/C:Nafion (0.9 I/C)
52:48 PtNi/C:Nafion (1.2 I/C)

Feed gas: H_2 (500 sccm); air (2,000 sccm)

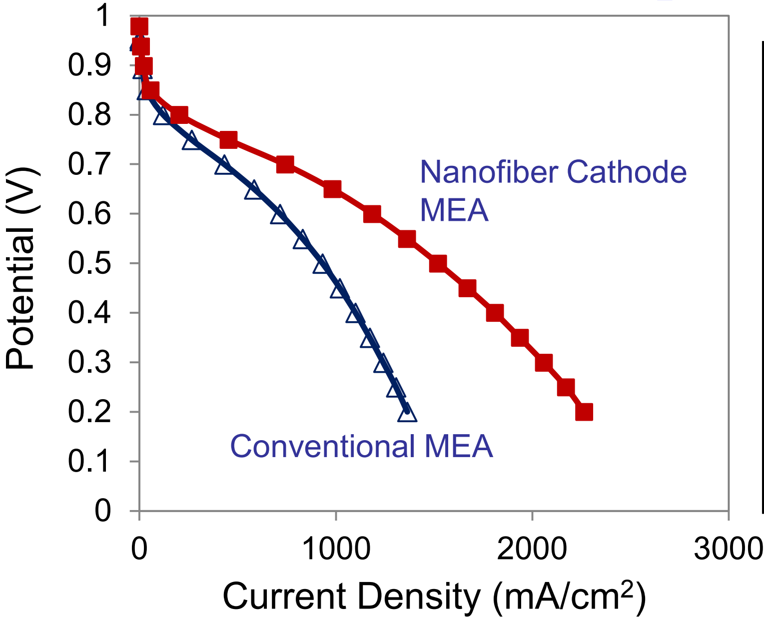
80^{o}C; 100% RH; 200 kPa_{abs}

At 0. 65 V:
Nanofiber cathode MEA produced 68% more power (0.9 I/C) and 33% more power (1.2 I/C).

Cathode	Max Power (mW/cm^2)	Power at 0.65 V (mW/cm^2)	ECSA m^2/g_{Pt}	Mass Activity A/g_{Pt}
0.9 I/C Conventional Spray	466	380	53	176
1.2 I/C Conventional Spray	732	580	53	172
0.9 I/C Nanofibers	760	639	48	216
1.2 I/C Nanofibers	885	770	49	288

Accomplishment: Conventional Spray Cathode vs. Nanofiber Cathode with PtNi/C Catalyst

0.9 I/C for the cathode; H_2/air fuel cell test at 80°C, 100% RH, 200 kPa_{abs}



	Maximum Power (mW/cm^2)	Power at 0.65 V (mW/cm^2)	Mass Activity (A/g_{Pt})	ECSA (m^2/g_{Pt})
Conventional Spray MEA	466	380	176	53
Nanofiber Cathode MEA	760	639	216	48

MEA with a nanofiber cathode produced 75% more power (at max power) and 68% more power at 0.65 V vs. a conventional sprayed cathode MEA

MEA (5 cm^2) and Testing Conditions

Membrane: Nafion 211

Anode: 65:35 JM Pt/C(HiSPEC 4000):Nafion

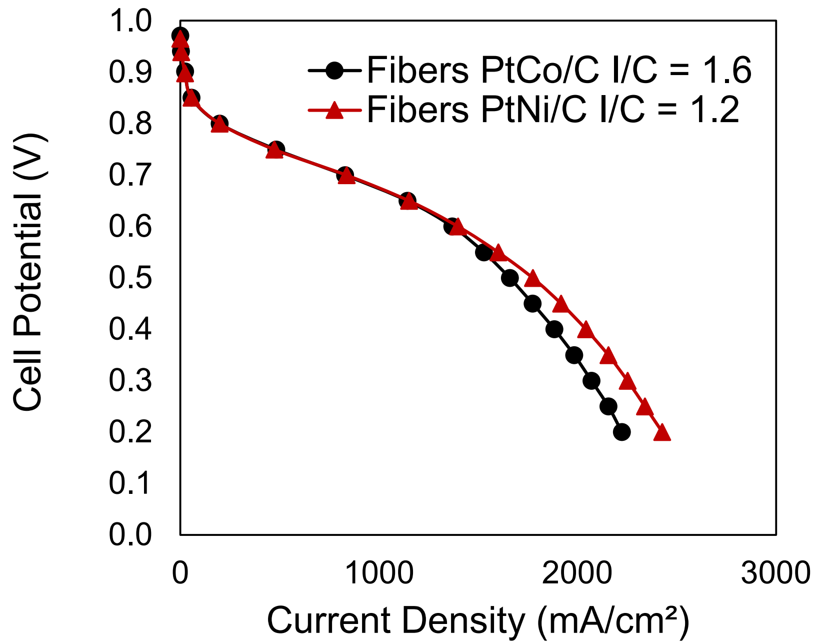
Fiber Cathode: 58:23:19 PtNi/C:Nafion:PAA (0.1 mg_{Pt}/cm^2)

Spray Cathode: 58:42 PtNi/C:Nafion (0.1 mg_{Pt}/cm^2)

0.1 mg_{Pt}/cm^2 Anode

Feed gas: H_2 (500 sccm); air (2000 sccm)

Accomplishment: Comparison of PtCo/C and PtNi/C Nanofiber Cathode MEAs at Rated Power and Best I/C



MEAs (5 cm²) and Testing Conditions

Cathode: PtCo/C/Nafion/PAA – 55/30/15
PtNi/C/Nafion/PAA – 51/27/22
Loading: 0.1mg_{Pt}/cm^2

Anode: 65/35 JM Pt(Hispec)/Nafion
Loading: 0.1mg_{Pt}/cm^2

Feed gas: H_2 (500 sccm); air (2000 sccm)
Membrane: Nafion 211
100% RH; 150 kPa_{abs}

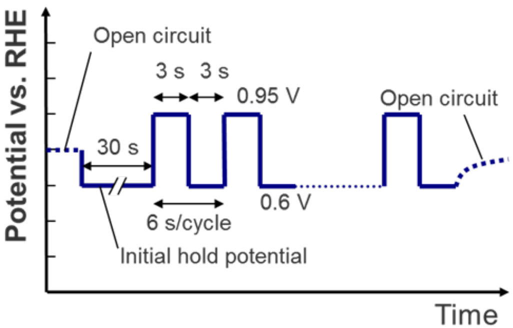
Temperature: 95°C

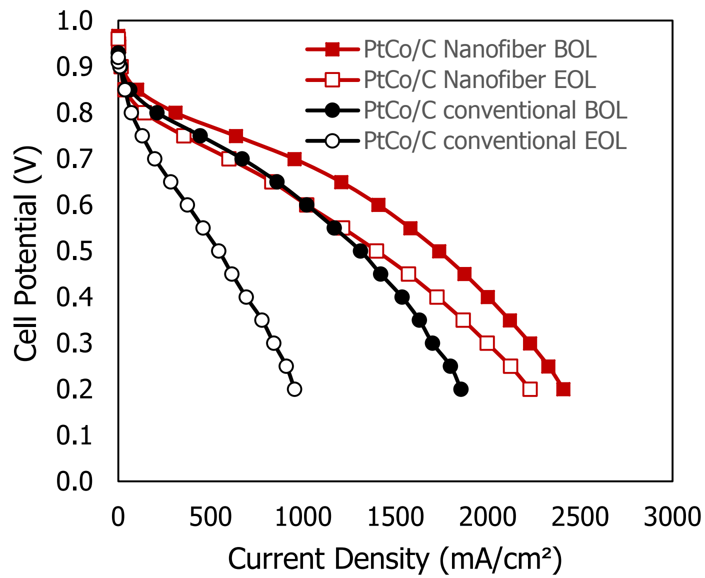
	Rated Power mW/cm² (at 0.674 V)	ECSA (m²/g)	Mass Activity (mA/mg)
PtCo/C	664	60	297
PtNi/C	670	49	288

- PtCo/C and PtNi/C perform equally well
- We are approaching the Year 1 Go/No-Go target of 800 mW/cm²

Accomplishment: PtCo/C Nanofiber Cathode MEA After Metal Dissolution AST

Load cycling Protocol





MEA (5 cm^2) and Testing Conditions

Nanofiber Cathode:
PtCo/C/Nafion/PAA – 55/30/15
Loading: 0.1mg$_{Pt}$/cm^2

Slurry cathode: PtCo/C/Nafion – 55/45
Loading: 0.1mg$_{Pt}$/cm^2

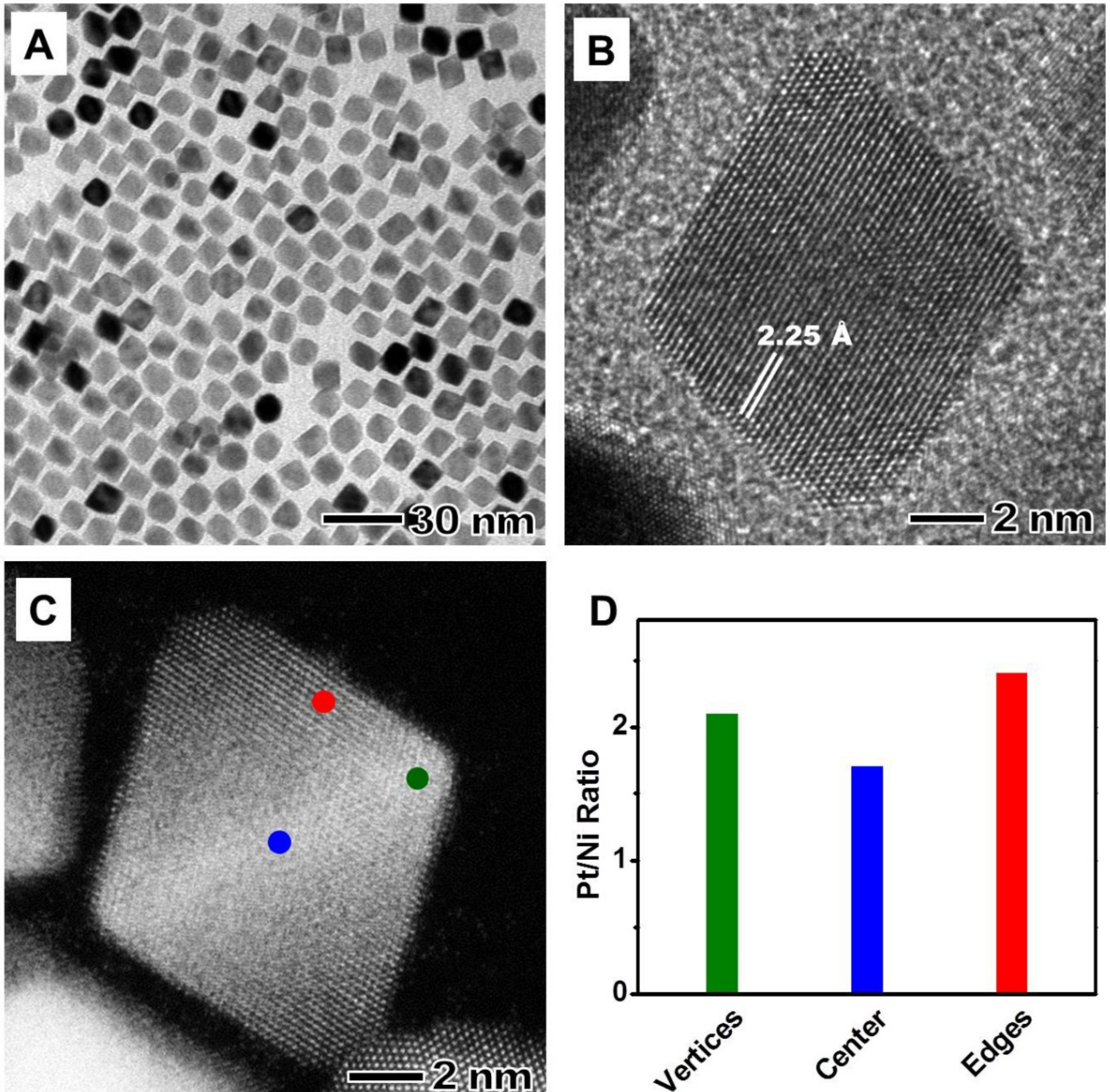
Anode: 65/35 JM Pt(Hispec)/Nafion
Loading: 0.1mg$_{Pt}$/cm^2

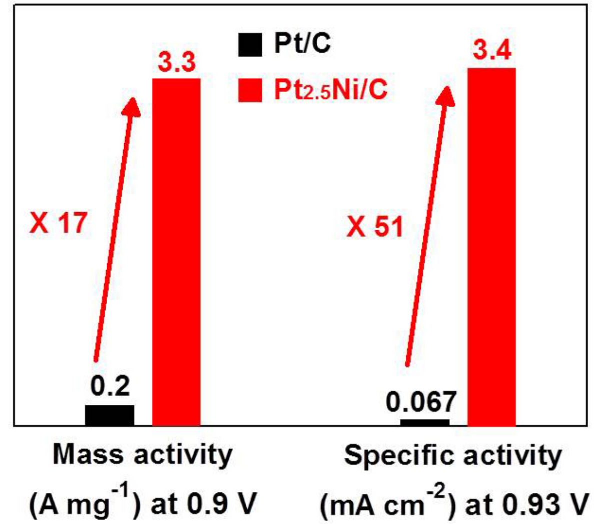
Feed gas: H_2 (500 sccm); air (2000 sccm)
Membrane: Nafion 211
100% RH; 200 kPa$_{abs}$
Temperature: 80^{o}C

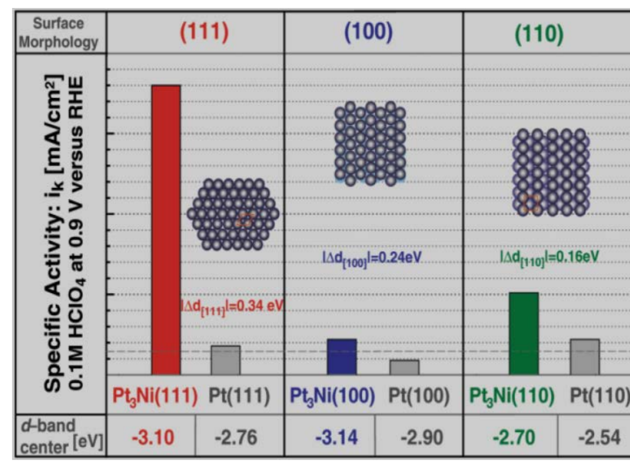
	Nanofiber Cathode MEA		Conventional MEA	
	mW/cm^2 at 0.65 V	mW/cm^2 at Max Power	mW/cm^2 at 0.65 V	mW/cm^2 at Max Power
At BoL	783	868	559	655
At EoL (30,000 cycles)	541	707	185	277
EoL/BoL 100%	69%	81%	33%	42%

Nanofibers offer greater protection from load cycling degradation at 30,000 cycles.

Accomplishment: GaTech Shape-Controlled Pt-Ni Octahedral Catalysts





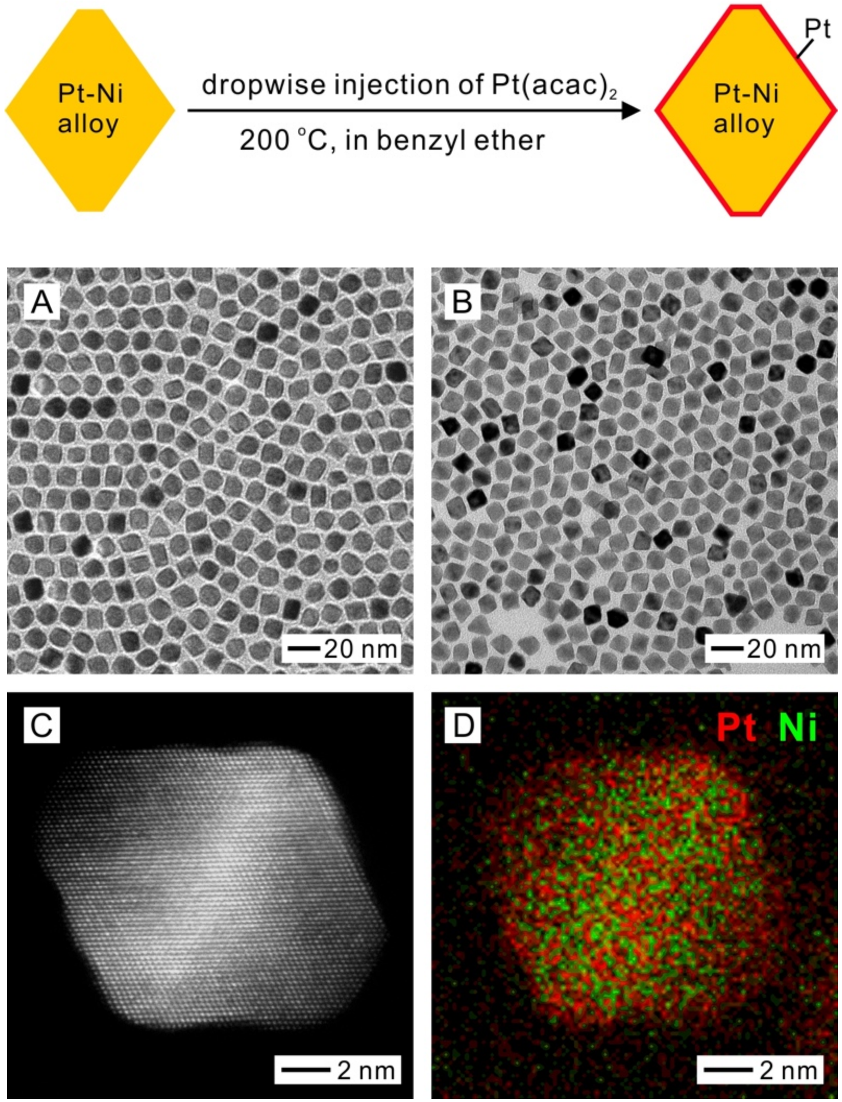


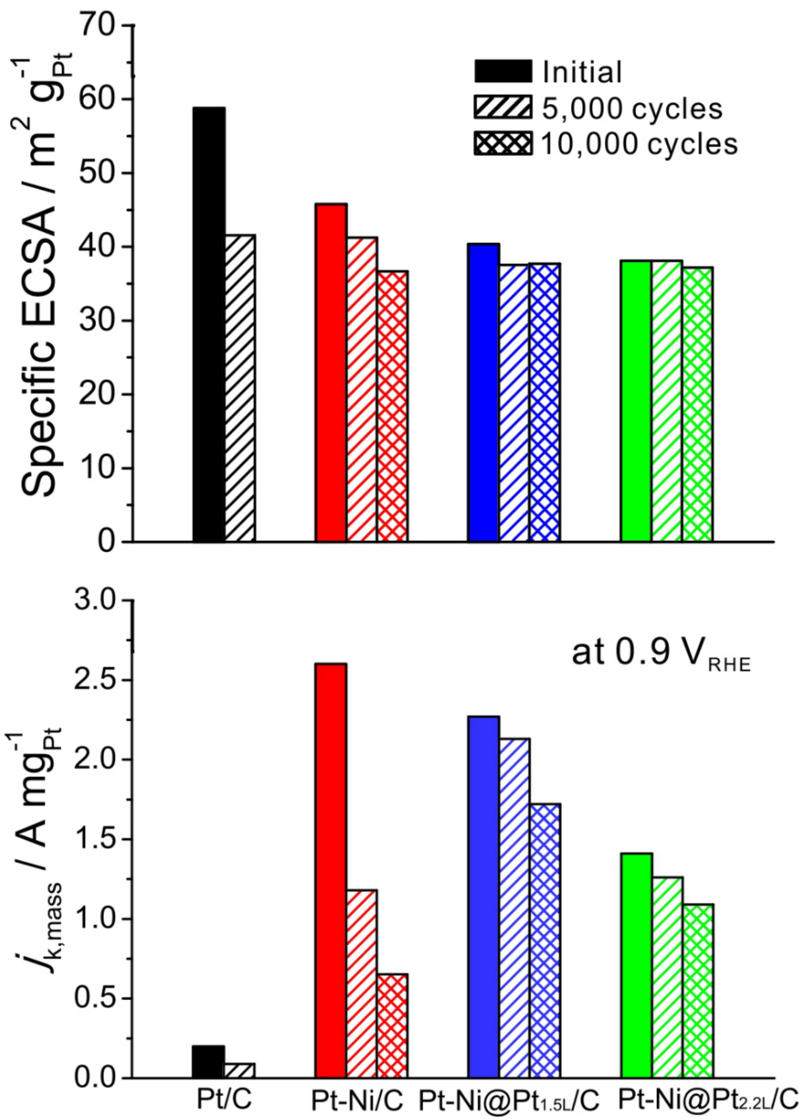
Stamenkovic *et al. Science* 2007, 315, 493

Choi, Xie, Shao, Lu, Guerrero, Odell, Park, Wang, Kim, Xia, *ChemSusChem* 2014, 7, 1476

Choi, Xie, Shao, Odell, Lu, Peng, Protsailo, Guererro, Park, Xia, Wang, Kim & Xia, *Nano Lett.* 2013, 13, 3420

Accomplishment: Enhance the Catalytic Durability with Conformal Pt Coating





Park, Liu, Peng, Figueroa-Cosme, Miao, Choi, Bao, Yang & Xia, *ChemSusChem* 2016, 9, 2209

NTCNA Role: Experimental Overview

- All experimental data will be shared with project partners and relevant FC PAD partners to support modeling efforts.
- **ORNL** will be provided BoL and EoL MEAs for HR TEM imaging and ionomer mapping.

Beginning of Life Diagnostics → Beginning of Life Polarization → AST → End of Life Diagnostics → End of Life Polarization

Beginning of Life Diagnostics

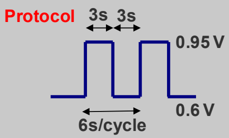
- Cyclic Voltammetry (Hupd and CO stripping)
  - Electrochemical Area
  - Pseudo-capacitance
- LSV
  - H_2 Crossover
  - Shorting Resistance
- H_2/N_2 EIS
  - Electrode & Membrane Resistance
- Limiting current
  - O_2 Gas transport resistance

Beginning of Life Polarization

- All Tests: 100%, 90% and 40% RH and 80°C
- Pressure: 0 and 100 kPa_g
- Performance tests:
  - H_2/O_2
  - H_2/Air
  - H_2/Helox (21%O_2 / He)
  - H_2/4% O_2 in He

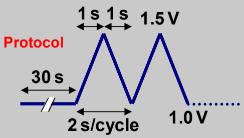
AST

Load Cycling



- CV @ 0, 100, 200, 500, 1k, 2k, 5k, 10k cycles

Start-Stop Cycling



- CV @ 0, 10, 20, 50, 100, 200, 500, 1k cycles
- CO_2 detection from Cathode Exhaust

End of Life Diagnostics

- Cyclic Voltammetry (Hupd and CO stripping)
  - Electrochemical Area
  - Pseudo-capacitance
- LSV
  - H_2 Crossover
  - Shorting Resistance
- H_2/N_2 EIS
  - Electrode & Membrane Resistance
- Limiting current
  - O_2 Gas transport resistance

End of Life Polarization

- All Tests: 100%, 90% and 40% RH and 80°C
- Pressure: 0 and 100 kPa_g
- Performance tests:
  - H_2/O_2
  - H_2/Air
  - H_2/Helox (21%O_2 / He)
  - H_2/4% O_2 in He

- Drive cycle durability protocol and unmitigated start-stop durability protocol can also be included in the AST task. **LANL** can help perform these durability tests.

Response to Previous Year Reviewers' Comments

This project is a new start with no reviewer comments from the previous year.

FC-PAD National Lab Collaborations

Oak Ridge National Laboratory

- Analysis of nanofiber electrode MEAs by high resolution TEM imaging
- Mapping of ionomer and Pt catalyst in nanofiber mat cathode MEAs at beginning of life (BoL) and end of life (EoL).

Los Alamos National Laboratory

- Drive cycle testing of nanofiber and sprayed electrode MEAs with TKK PtCo and PtNi catalysts and various PFSA/PAA and PFSA/PVDF binders.

National Renewable Energy Laboratory

- O_2 limiting current measurements in nanofiber and sprayed electrode MEAs, with PtCo and PtNi catalysts with PFSA/PAA and various PFSA/PVDF binders.

Argonne National Laboratory

- The effect of Nafion and other PFSA binders on the performance of shape controlled PtNi catalyst using a rotating disk electrode experiment, to provide guidance in formulating MEA ink recipes.
- Nano level X-ray computed tomography, to better understand nanofiber electrode structures at BoL (i.e., the nanofiber mat after hot-pressing into MEA) and at EoL.

The Vanderbilt/GaTech/NTCNA team will supply the necessary catalyst inks, electrodes, and MEAs for the FC-PAD experiments.

Vanderbilt will also provide assistance to any group that would like to begin electrospinning particle/polymer electrodes.

Remaining Challenges and Barriers

Understand and improve the high current density performance of low Pt loadings nanofiber MEAs ($\leq$0.125 mg_{Pt}/cm^2)

1. Identify the best Pt-alloy catalyst and the optimum I/C ratio for various fuel cell operating conditions (gas flow rates, humidities, temperatures, and backpressures) for a nanofiber cathode MEA.
   - Cathode that gives highest power at BoL
   - Cathode that exhibits minimum power loss after carbon corrosion and Pt dissolution ASTs.

2. Better understand:
   - Why nanofiber cathodes produce higher power than conventional cathode MEAs
   - Why nanofiber cathodes show less power loss after ASTs

3. Achieve:
   - 1000 mW/cm^2 at rated power while meeting the $Q/\Delta T$ target requirement
   - <40% drop in ORR mass activity after load cycling
   - <5% drop in voltage at 1.2 A/cm^2 after unmitigated start up-shut down
   - < 10% loss in rated power after drive cycle durability

Proposed Future Work for April 2017 – April 2018

Demonstrate Feasibility and Assess Performance of Commercial Pt-alloy Catalysts and Shape-Controlled Pt-Ni Catalysts in Nanofiber Cathode MEAs:

1. Synthesize Type-1 GaTech Pt-Ni/C catalyst;
2. Identify and optimize conditions for electrospinning nanofiber mats with Type-1 catalyst and with commercial TKK PtCo/C and PtNi/C catalysts with different PFSA and PFIA binders;
3. Fabricate and evaluate performance and durability of nanofiber and sprayed MEAs, 0.1 mg/cm^2 (cathode) and 0.025 mg/cm^2 (anode);
4. Measure O_2 limiting current in nanofiber cathodes and modify the binder to improve oxygen transport to catalyst sites.

Milestones

1. Prepare nanofiber cathode MEAs (5 cm^2 and 25 cm^2) with different PFSA and PFIA binders and different catalysts.
2. Vanderbilt delivers at least 8 nanofiber electrode MEAs (10 and 25 cm^2) to NTCNA with 3 catalysts (TKK PtCo/C and PtNi/C and Type-1 Pt-Ni/C).
3. Vanderbilt/NTCNA delivers at least 6 nanofiber and 6 sprayed electrode MEAs to FC-PAD members for SEM/TEM analyses (ORNL) and durability and XCT analyses (LANL).

Any proposed future work is subject to change based on funding levels

Summary

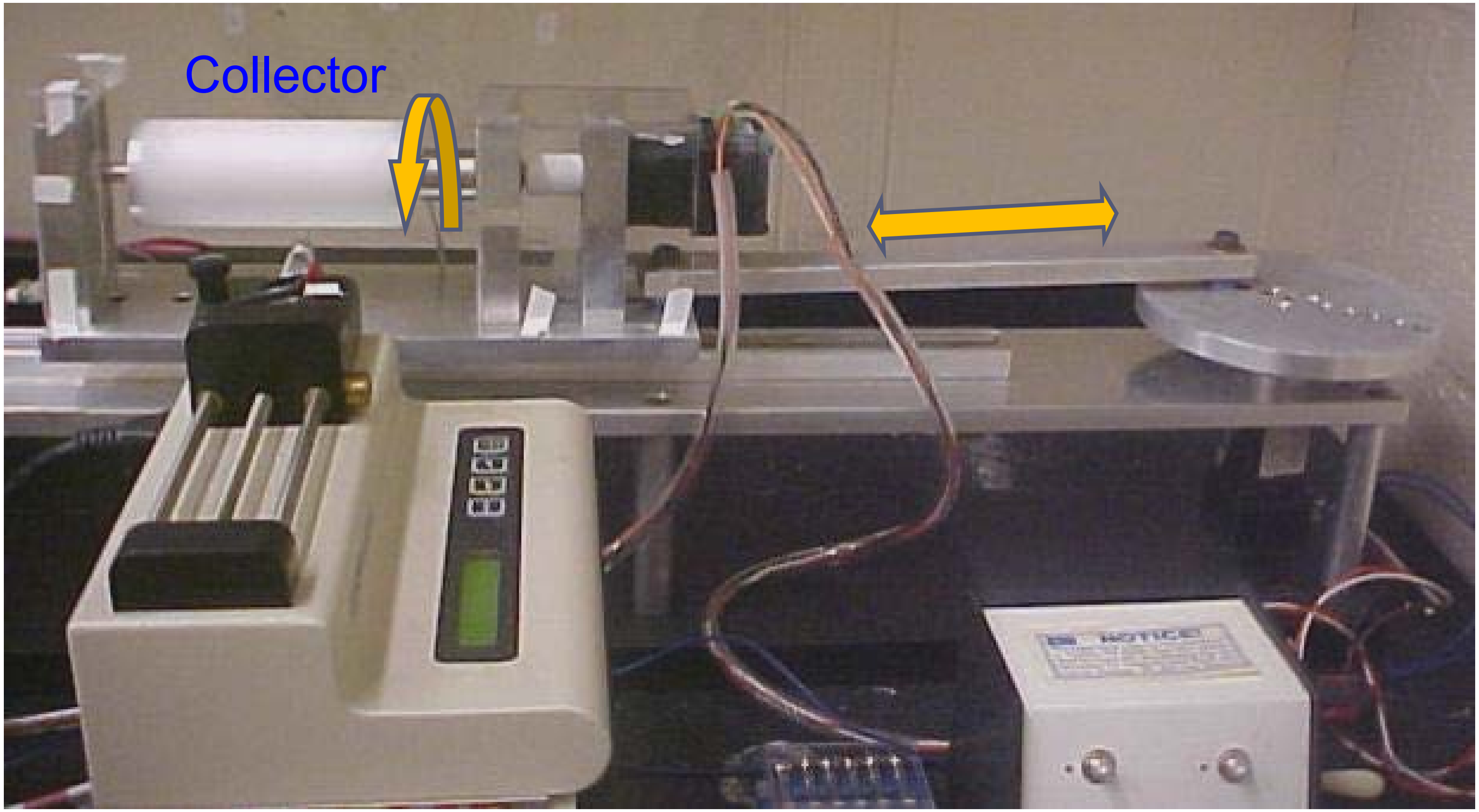
- New fuel cell electrode fabrication techniques are needed for next-generation MEAs which accommodate and control the multi-scale organization of nanoparticles into macroscopic electrode constructs with improved power output and durability.
  - Electrode macroporosity, microporosity, and particle and binder interconnectivity become more critical when high-performance nanomaterial catalysts are used in fuel cell electrodes

- Particle/polymer nanofiber mat electrodes are a promising alternative to conventional fuel cell electrode structures
  - Electrospinning is a versatile and scalable nano/micro-fabrication method for preparing MEAs
  - The method can exploit new catalysts and binders, as they are developed/discovered, such as GaTech's shape controlled PtNi catalyst

- Initial experiments were performed with a TKK PtCo/C and PtNi/C cathode catalysts and Nafion/PAA binder
  - Fuel cell results are encouraging for a cathode catalyst loading of 0.10 mg/cm^2
  - 562 mW/cm^2 at rated power, 80^{o}C and 200 kPa_{abs};
    664 mW/cm^2 at rated power, 95^{o}C and 150 kPa_{abs} (PtCo/C catalyst)
  - 20-30% loss in power after a load cycling durability test (30,000 voltage cycles)

Technical Back-Up Slides

Electrospinning – Rotating Drum Apparatus



Ink Preparation and Electrospinning Conditions for PtNi/C and PtCo/C Nanofiber Electrodes

Preparation of PtNi/C inks

- Add water and 21 wt% Nafion solution (water/alcohol)
- 30 minute sonication bath
- Add catalyst
- 30 minute sonication bath
- Add alcohol
- Homogenize 4 hours at 10,000 RPM in ice bath
- Add carrier polymer (PAA)
- Mechanical mixing for 48 hours

Preparation of PtCo/C inks

- Add water and 21 wt% Nafion solution (water/alcohol)
- 30 minute sonication bath
- Add catalyst
- 30 minute sonication bath
- Add alcohol
- Homogenize 4 hours at 10,000 RPM in ice bath
- Add carrier polymer (PAA)
- Mechanical mixing for 48 hours

Electrospinning Conditions of PtNi/C inks				
	0.9 I/C	1.2 I/C	1.6 I/C	2.32 I/C
Potential (kV)	7.2	9	10.5	9
Relative Humidity (%)	20	21	50	30
Flow Rate (ml/hr)	1	1	1	1
Needle to Collector Distance (cm)	9	9	9	9

Electrospinning Conditions of PtCo/C inks				
	0.9 I/C	1.2 I/C	1.6 I/C	2.32 I/C
Potential (kV)	7.2	9	10.5	9
Relative Humidity (%)	20	21	50	30
Flow Rate (ml/hr)	1	1	1	1
Needle to Collector Distance (cm)	9	9	9	9

Rated Power and Q/ΔT Constraint

- **Q/ΔT is a measure of radiator size**
- **Rated Power is Power at which Q/ ΔT is met**
- **Target Q/ΔT<1.4 kW/°C heat loss constraint based on car radiator's Q/ΔT**

$$Q/\Delta T = \frac{\left[Stack\ Power(90kW) \times {}^{(1.25 - V\ @\ rated\ power)}\!\big/_{V\ @\ rated\ power} \right]}{Stack\ coolant\ outlet\ temperature - ambient\ temperature(40°C)}$$

- **To meet this constraint**
  - **$T_{coolant\ stack}$ need higher → Operate FC stack at higher Temp (limited by current membrane technologies)**
  - **V@ rated power need higher → Operate FC stack at higher Pressure and/or high ORR activity catalyst**