## **Durable MEAs for Heavy-Duty Fuel Cell Electric Trucks**

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# **Project Goals**

- 1. Fabricate, characterize, and evaluate membrane electrode assemblies (MEAs) with novel catalyst layer structures to improve performance and durability.
- 2. Minimize Pt/Sulfonate interaction to unlock catalyst activity for identified <u>durable</u> catalysts (*e.g.* dissolution resistant shape-controlled alloys or another down-selected catalyst)
- **3.** Achieve high catalyst-layer oxygen diffusivity by engineering large homogeneous pores in the CL and reduce Knudsen O<sub>2</sub> transport resistance by decreasing ionomer clustering on Pt surfaces

### This will be accomplished using:

A "Nanocapsule" electrode structure: A repeating core/shell electrospun nanoparticle in the hundreds-of-nanometer diameter range which separates ionomer and Pt to maximize activity while allowing ionic transport

The outcomes of this project, if successful, will allow for better utilization of highly active and/or highly durable catalysts and the bridging of the activity gap between RDE and MEA.

# Overview

#### <u>Timeline</u>

Project Start: Q3 2020Project End: Q3 2023

#### <u>Budget</u>

•Total project budget: \$2,125,000

- Total Recipient Share: \$425,000
- Total Federal Share: \$1,700,000
- Total DOE funds spent\*: \$47,624 \*As of 12/31/2020

#### **Barriers**

#### Durability

- Improve stability of MEA for HD truck relevant operating conditions
- Performance
  - Increase catalyst while reducing ionomer poisoning effects to achieve high power density and higher efficiency
- Cost
  - Enable reduction in PGM catalyst loading and improve ionomer utilization

#### Partners

- Carnegie Mellon University
  - Modeling and characterization for MEA optimization
- Northeastern University
  - Durable IBAD catalysts
- Georgia Tech.
  - Durable alloy catalysts

#### M2FCT

 Conventional electrode fabrication, Ink Analysis, electrode analysis, MEA testing, MEA component ASTs, electronmicroscopy characterization

## **Collaboration and Coordination: Project Workflow**



## **Project Participants and Roles**

Institution; Personnel	Key Role(s)
Nikola Motor Company (Nikola); • Dr. Vivek Murthi (PI) • Dr. John Slack (Co-PI)	<ul> <li>Benchmarking MEA components</li> <li>Fundamental MEA architecture design, fabrication, optimization, testing and analysis</li> <li>MEA development and scale-up strategies and supplier collaboration</li> <li>Single-cell testing and MEA validation</li> <li>Program Management</li> </ul>
Georgia Institute of Tech. (Georgia Tech.); Prof. Younan Xia	<ul> <li>Durable supported catalyst development and sub-scale testing</li> <li>Catalyst physical and electrochemical characterization</li> </ul>
<b>Northeastern University (NEU);</b> Prof. Sanjeev Mukerjee	<ul> <li>Catalyst development based on Ion Beam Assisted Deposition (IBAD) on commercial and tailored carbon supports;</li> <li>Fundamental studies to elucidate electrocatalyst structure</li> </ul>
<b>Carnegie Mellon University (CMU);</b> Prof. Shawn Litster	<ul> <li>Catalyst layer nano-structure and MEA micro-structure 3D imaging and analysis</li> <li>Catalyst aggregate scale modelling</li> <li>O<sub>2</sub> and proton (H<sup>+</sup>) transport modelling to provide for MEA optimization</li> </ul>
M2FCT National Labs Consortium Members	<ul> <li>Advanced MEA fabrication, sub-scale performance testing and evaluation (NREL, LANL)</li> <li>Component Diagnostics and Characterization (ORNL)</li> <li>Operando Evaluation— Accelerated Stress Testing (AST) of MEA components and new AST protocol development for HD FCET (LANL)</li> </ul>

## **Targets and Status**

Characteristics	Target	Conditions
Operation hours		
Platinum Group metal Loading	0.3 mg/cm <sup>2</sup> (total)	DOE Advanced Truck Technologies: Technical Targets for Hydrogen-Fueled Long-Haul Tractor-Trailer Trucks (released 10/31/2019)
Performance @0.8V	> 350mA/cm <sup>2</sup> (interim)>500 mA/cm2 (end of project)	DOE Technical Target(2016) Table 3.4.5, Table P6
Performance @ rated power	> 700 mW/cm <sup>2</sup> at HD rated power at 80C <sup>[2]</sup> (Full-size MEA)	- DOE Technical Target(2016) Table P6
Loss in catalytic mass activity	< 25 % <sup>[3]</sup>	DOE Technical Target(2016) Table 3.4.7, Table P1
Loss in rated power	< 10 %	Heavy-duty Drive-Cycle
Hydrogen crossover (MEA chemical stability)		

**1.** Not relevant for HD; however used as initial target in the absence of HD specific ASTs.

2. Analysis of Fuel Cells for Trucks (TA024), R. Vijayagopal (ANL), 2019 DOE Hydrogen and vehicle technologies AMR

3. Not necessarily relevant for HD; however used as initial target in the absence of validated HD specific ASTs. Nikola HD truck durability targets are more aggressive.

## **Key Milestones**

Task Number	Milestone	Verification Process/Partner	Anticipated Date (Month)
1.1	Nikola CL design and fabrication	SEM and STEM-EDS / Oak Ridge National Lab	9
1.2	Development of cuboctahedral PtCo/C catalyst	RDE / Georgia Tech	9
1.3	Development of IBAD Pt/M-M/C catalyst	RDE / Northeastern University	9
1.4	Modeling and analysis of Nikola CL	Nano-XCT and more/ Carnegie Mellon University	12
2.1	Nikola CL MEA fabrication using new catalyst	Electrochemical + microscopy / NREL + ORNL	18
2.2	Synthesis of cuboctahedral PtCo catalyst on durable carbon supports	RDE / Georgia Tech	15
2.3	Synthesis of IBAD Pt/M-M/C catalyst on durable carbon supports	RDE / Northeastern University	15
2.4	Modeling and analysis of Nikola CL	Nano-XCT and more/ Carnegie Mellon University	24
3.1	Full-size Nikola CL MEA fabrication and evaluation with new catalyst	Electrochemical + microscopy / NREL + ORNL	30
3.2	Modeling and analysis of Nikola CL and MEA	Nano-XCT and more/ Carnegie Mellon University	36

## **Go/No-Go Decision Points**

#### Performance targets are set conservatively due to the low TRL nature of the proposed structure.

A learning curve in structure fabrication may be required before the expected advantage is achieved.

Budget Period	Go/No-Go	Anticipated Date (Month)
BP1	<ul> <li>Using Nanocapsule electrode 50cm<sup>2</sup> MEA:</li> <li>• 350 mA/cm<sup>2</sup> at 0.8V at 0.3 mg/cm<sup>2</sup> total.</li> </ul>	12
BP2	Using Nanocapsule electrode 50cm <sup>2</sup> MEA with experimental catalyst and durable carbon: • 350 mA/cm <sup>2</sup> at 0.8V • <25% drop in mass activity after load cycling (light-duty DOE catalyst ASTs)	24
End of Project Target	<ul> <li>Using Nanocapsule electrode full-size MEAs with experimental catalyst and durable carbon:</li> <li>500 mA/cm<sup>2</sup> at 0.8V</li> <li>Rated Power at 80 °C* = 700 mW/cm<sup>2</sup> at 0.69V</li> <li>10% power loss at 0.69V after heavy-duty drive cycle projected to 25,000 hours</li> </ul>	36

\*Rated Power is calculated using Argonne National Lab value of Q/ΔT for the limits for Diesel Trucks = 4.5 kW/°C for Hill climbing From: R.VIJAYAGOPAL, A.ROUSSEAU. Project ID # TA024. 2019 DOE Hydrogen Program and Vehicle Technologies Annual Merit Review

# **Relevance/Potential Impact**

### The impact of this project is to:

- Reduce the Pt-sulfonate interaction which can reduce ORR activity
- **Reduce O<sub>2</sub> transport resistance:** due to ionomer confinement effects
- Reduce CL flooding and therefore minimize catalyst metal dissolution
- Allow for better use of inherently durable materials which suffer from:
  - Significant sulfonate poisoning ( . shape controlled catalysts, etc.)
  - *Significant flooding/poor transport* ( . IBAD catalysts, crushed NSTF, etc.)

### The relevance of the results of this project is

- The enablement of Nikola, a US based company, to reach the DOE targets for long-haul, heavyduty trucks
- The unique value proposition is that we can unlock more of the full potential of other existing technologies
- Bridge the gap between RDE and MEA activity

### Purposefully heterogeneous lonomer & Catalyst within the catalyst layer

- Optimized local I/C: may reduce sulfonate poisoning while still providing conductivity
- Leverages non-zero conductivity: of protons across carbon and platinum surfaces<sup>[1,2]</sup>
- Tune I/C in the shell: minimum required for protonic transport from membrane to CL/MPL edge
- Tune I/C in the core: minimum required for protonic transport from shell to core to reduce confinement effects



[3] K. Takahashi et al. *Journal of The Electrochemical Society*, 163, F1182-F1188, **2016** 



[1] K. Takahashi et al. Journal of The Electrochemical Society, 163, F1182-F1188, 2016

The electrospray technique is a tried-and-true method for nanoencapsulation used in other fields and can be applied to electrode fabrication



Core-shell electrospray technique used in food & drug industry<sup>[1]</sup>

#### **Quality Control**

- **Dry before deposition:** minimizing cracks arising from solvent evaporation.
- High through-plane precision: Thickness and Pt loading of the CL are easily controlled
- Ease of adjustment: Deposition parameters are easily controlled

Property:	Controlled by:
Core/Shell Thickness	Pump rate ratio Solids content ratio
Total Sphere Radius	Solids %, Total Pump Rate, Electric Field
Loading/CL Thickness	Deposition Time

### Critical path barriers for Nanocapsule Design & Plans to address them

Questions to Answer	Primary Affecting Variables	<b>Relevant Analyses</b>
Nanocapsule design? (Relation to performance & Durability)	<ul> <li>Core/shell thickness ratio</li> <li>Overall effective I/C ratio</li> <li>Overall diameter</li> <li>Fabrication Parameters</li> </ul>	Physical Analysis Beginning of life (BOL) and End of Test (EOT) • SEM/TEM
<b>Core/Shell compositions?</b> (Relation to performance & Durability)	<ul> <li>I/C ratio of core &amp; shell (including 0 &amp; ∞)</li> <li>Type of shell ionomer</li> <li>Type of core catalyst (metal + support)</li> <li>Pt loading % on C</li> </ul>	<ul> <li>STEM/EDS</li> <li>pFIB</li> <li>Micro/Nano-XCT</li> <li><u>Electrochemical Analysis</u></li> </ul>
Additive package(s)? (Relation to performance & Durability)	<ul> <li>Is a "stabilizing" polymer required?</li> <li>Poly(amide-imide) / polyvinylidene fluoride scaffolding</li> <li>Carbon nanotube structural/e- conductivity enhancement</li> <li>Core/Shell Pore-formers</li> </ul>	<ul> <li>Beginning of life (BOL) and End of Test (EOT)</li> <li>Polarization data BOL/EOT</li> <li>Mass activity BOL/EOT</li> <li>CV: ECSA BOL/EOT</li> <li>H<sub>2</sub> crossover/FER EOT</li> </ul>
Structure Effect on Catalyst Poisoning & Oxygen Diffusion?	<ul> <li>Above mentioned structural &amp; compositional matrices</li> </ul>	<ul> <li>CO stripping chronoamperometry</li> <li>Limiting current GTR</li> <li>H<sub>2</sub>/D<sub>2</sub> limiting current</li> <li>Polarization modeling</li> <li>EIS: LFR H<sub>2</sub>/air – H<sub>2</sub>/HelOx</li> </ul>

Goal: understand the effect of the following catalyst properties in combination with the proposed ionomer distribution:

- Distance between Pt particles (e.g. %loading, IBAD method, carbon type, etc.)
- Crystal face composition (e.g. shape controlled nanoparticles)
- Location of Pt nanoparticles: Percentage on support surfaces vs. in support primary pores
- RDE Activity with perchloric acid

#### **Commercial catalysts**

- Varying loading %
- Varying carbon support



#### Georgia Tech (durable shape controlled)

• Truncated Octahedral Pt-Co



#### Northeastern University (Dual IBAD onto support)

continuous Pt surfaces on C



#### **Truncated octahedral nanocrystals**

**Original Synthesis of Pt-Co** 

Scalable One-Pot Synthesis of Pt-Co/C



- **4.5 nm Pt-Co truncated octahedral nanocrystals** (TON) supported on carbon black.
- **One pot synthesis:** directly onto/into the support.

#### Initial durability evidence<sup>[1]</sup>:

Georgia



87% retention vs. 42% retention of activity after catalyst AST + recovery protocol.

- **Potential** for good durability in MEA (data from unoptimized, painted electrodes)
- Synthesized nanoparticles first, then loaded onto carbon

[1] M. Shen et al. Nanoscale, 12, 11718, 2020

### Northeastern University

#### Pt covers surface of carbon

### **IBAD Pt Catalysts from Northeastern University**

• Dual Ion Beam-Assisted Deposition (IBAD)

#### **Questions to Answer**

- Minimum Pt surface thickness on carbon black?
- **Uniformity** of thickness?
- Pt surface strain differences?

#### **Relation to Nanocapsule:**

- Sulfonate interaction with this structure?
- Mass transport issues of previously prepared IBAD CL MEAs
- **Proton transport within the nanocapsule core** may be enhanced with more Pt-surface dominated structure.





Accomplishments and Progress for Current Reporting Period: Modeling of Nanocapsule MEA

Carnegie Mellon University

- Nanocapsule implemented in CMU's multi-phase, non-isothermal MEA model
- Agglomerate model with ionomer film
- Nanocapsule interior modeled with conventional catalyst layer microstructure but no ionomer
- Film thickness estimated from material loading and nanocapsule catalyst agglomerate diameter (excludes film)
- Ionomer film occupies tertiary pores as a function of I/C





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## Modeling: Nanocapsule vs. Conventional

- Compared to conventional 0.2 mg<sub>Pt</sub>/cm<sup>2</sup> Pt/Vu cathode
- Experimental conventional cell was fabricated and tested at CMU with HiSPEC 4000, D2020
- Increased mass activity due to ionomer-free catalyst surface
- Increased limiting current density with reduced R<sub>02,Pt</sub> due to ionomer-free catalyst
- More vertical limiting current due to greater common diffusion barrier due to thick ionomer film









# **Preliminary modeling Conclusions**

- Significantly increased mass activity and 0.7 V current density if ionomer-free catalyst performance can be achieved in practice
- The most robust design is likely a 500 nm nanocapsule made with an I/C of 0.6 for the outer film ionomer
- Larger diameters result in a very thick ionomer film for a given total I/C ratio
- Increased efficiency with I/C of 0.6 versus 0.4 without significant compromise in maximum power density
- Higher film I/C will likely result in the most robust nanocapsule with better binding



## **Accomplishments and Progress for Current Reporting Period**

Experimentation with electrospraying PFSA dispersions alone is necessary due to their critical role in encapsulation as the primary polymeric component in the system.

980EW PFSA Solutions:



### **Using optimized solvent system and PFSA concentration**

- Solvents were chosen by minimizing the covariance of the Hansen Solubility Parameters for Nafion<sup>®[1]</sup>
- And keeping the boiling point above 100°C

## **Accomplishments and Progress for Current Reporting Period**



### Successful bi-axial electrospray

• Optical Taylor Cone analysis

shows clearly that separate core and shell streams have been achieved

- Visible dark region indicates catalyst "core" dispersion Comprised of Pt/C suspended in solvent
- Visible light region indicated ionomer "shell" dispersion Comprised of PFSA suspended in solvent
- This was achieved using an annular arrangement of: 22-gauge (inner) and 18-gauge (outer) needle in which the inner needle protrudes ~1mm from the outer needle

Resultant nanoparticle must be analyzed via STEM/EDS at Oak Ridge National Lab to determine core/shell parameters

## **Progress: Response to 2020 Peer Evaluation**

This project was not reviewed last year due to concerns about the COVID-19 pandemic.

# Remaining Challenges and Proposed Future Work

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

- Remaining questions to answer are listed in the table on slide 18.
- In addition, specifically, the next nanocapsule-specific work is:
  - What deposition parameters and ink compositions are required for stable electrospray deposition to achieve 50+ cm<sup>2</sup> electrodes that meet the Go-No/Go target for BP1?
  - What are the physical characteristics of the resultant nanocapsule electrodes (*e.g.* particle size distribution, core/shell diameter ratio, effective I/C)
  - What is the electrochemical performance of the first iteration of nanocapsule? Using this information, structural parameters will be changed accordingly.
- Synthesis and incorporation of experimental/durable catalysts by the sub-prime collaborators

## Summary

#### **Project Goals**

- Utilize highly durable catalysts and minimize sulfonate/Pt interaction
- Obtain high CL oxygen diffusivity through engineered "tertiary" porosity between spheres & less Knudsen O<sub>2</sub> transport resistance due to less ionomer clustering on Pt surfaces

### **Initial Results**

- Modeling suggests encouraging results
   4.5x catalyst activity
   Significantly higher current at 0.7 V if ionomer-free catalyst performance can be achieved
- First successful Taylor cone using bi-axial annunar electrospray setup was achieved

### **Expected Key Challenges**

- Compositional and Structural Parameters must be determined
- Physical and Electrochemical Analysis must be performed
- New experimental catalysts must be incorporated into the structure

# Technical Backup and Additional Information

# **Technology Transfer Activities**

### **Prior Patent Application Associated with this Project**

CATALYST LAYERS OF MEMBRANE-ELECTRODE ASSEMBLIES AND METHODS OF MAKING SAME

- United States Patent Application
   Publication No. 20200365910
- Application Number: 16/891506
- Inventors: Slack, John (Phoenix, AZ, US)
- **Publication Date:** 11/19/2020
- Filing Date: 06/03/2020

- Technology-to-market strategies are currently unfinalized and under development
- At this time there are no plans for future funding from alternative sources