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Mesoporous Carbon-Based PGM-Free Catalyst Cathodes

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A Purdue University School

Indiana University Purdue University Indianapolis (IUPUI)

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Project ID: FC303

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Overview

Timeline and Budget

- Project Start Date: October 1, 2018
- Project End Date: December 31, 2020
- Percent complete:0
- Total Project Budget: $1,430K
  - Total Recipient Share:$428K
  - Total Federal Share: $1,002K
  - Total DOE Funds Spent*: $0

* As of 3/01/19

Barriers

B. Cost

- Reduce the cost of PEM fuel cells using Precious Group Metal (PGM)-Free catalysts to replace PGM catalysts

A. Performance

- Increase catalyst activity, improve the catalyst utilization, and facilitate the water dissipation to achieve the high power density operation

C. Durability

- Enhance the stability of PGM-free catalysts at relevant fuel cell operating conditions

Project lead

Indiana University Purdue University Indianapolis (IUPUI)

- PI: Jian Xie

Partners

University at Buffalo (UB) SUNY

- PI: Gang Wu

United Technologies Research Center (UTRC)

- PI: Zhiwei Yang

Electrocatalysis Consortium Members

Roles of TEAM Members

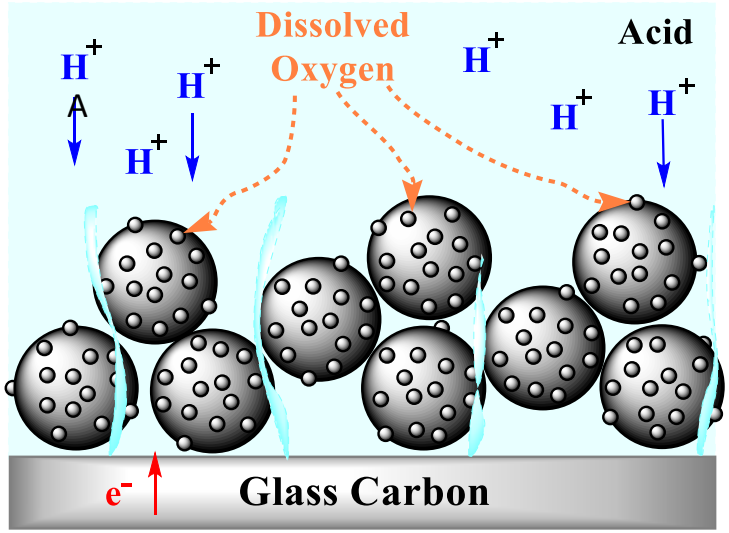
- IUPUI
  - Develop advanced MEAs using novel ionomer/catalyst interface via controlling the surface charges of ionomer and catalyst particles and ink formulations
- UB
  - Synthesize hierarchically porous carbon sphere (HPCS) PGM-free catalysts to improve the catalyst activity and utilization on intra-particle level
- UTRC
  - Test, diagnose sub-scale MEAs (25-50 cm^2) and carry out the economic analysis

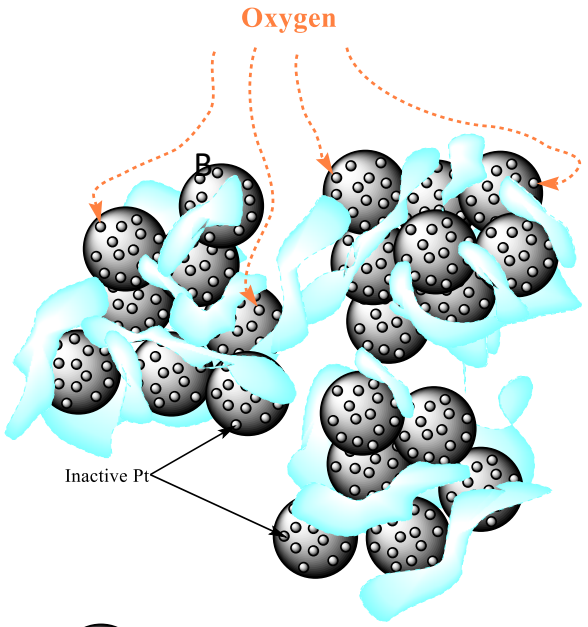
Relevance

- Objectives
  - The goal of this project is to (1) design and develop advanced HPCS@M-N-C catalysts for PGM-free cathodes in PEMFCs through controllable synthesis and (2) develop MEAs using the novel ionomer/catalyst interface via controlling the surface charges on catalyst particles to achieve improved catalyst activity, utilization and high current density performance by incorporating two approaches into MEA configuration.
- Impact
  - Meeting this objective will enable MEAs to achieve DOE Targets
    - Achieve intrinsic high activity ($E_{1/2}$ >0.85 V) and stability (potential loss of $E_{1/2}$ < 20 mV after 30K potential 0.6-1.0 V cycles in acidic media)
    - Demonstrate fuel cell MEAs (25-50 cm^2) with a mass activity of 0.044 A/cm^2 at 0.9 VIR-free (H_2-O_2) and 0.15 A/cm^2 at 0.8 V (H_2-air).
    - Achieve high power density of at least 0.5 W/cm^2 (*e.g.*, 0.50 V at 1.0 A/cm^2) following DOE catalyst performance metrics.
    - Achieve sufficient durability performance of MEAs following the DOE's catalyst durability testing protocols or any other protocols suggested from the ElectroCat Consortium such as voltage loss <30 mV after 30,000 potential cycles, 0.6-1.0 V in N_2.

Approach: Structures of Catalyst Layers on RDE and in MEA

Key for ORR in MEA, O_2 gas, H^+ and e^- come to the same site simultaneously. Plus, effective H_2O transfer.





RDE: 1. Well dispersed catalyst particles, ensuring good access for O_2, and 2. Good Catalyst/Liquid electrolyte interface: facile transport of H^+ to ORR sites.

MEA: 1. Agglomerated particles, reduced access for O_2, and 2. Poor Catalyst/Liquid electrolyte interface: transport of H^+ to ORR sites (coverage) and O_2 diffusion barrier (thickness of Ionomer film).

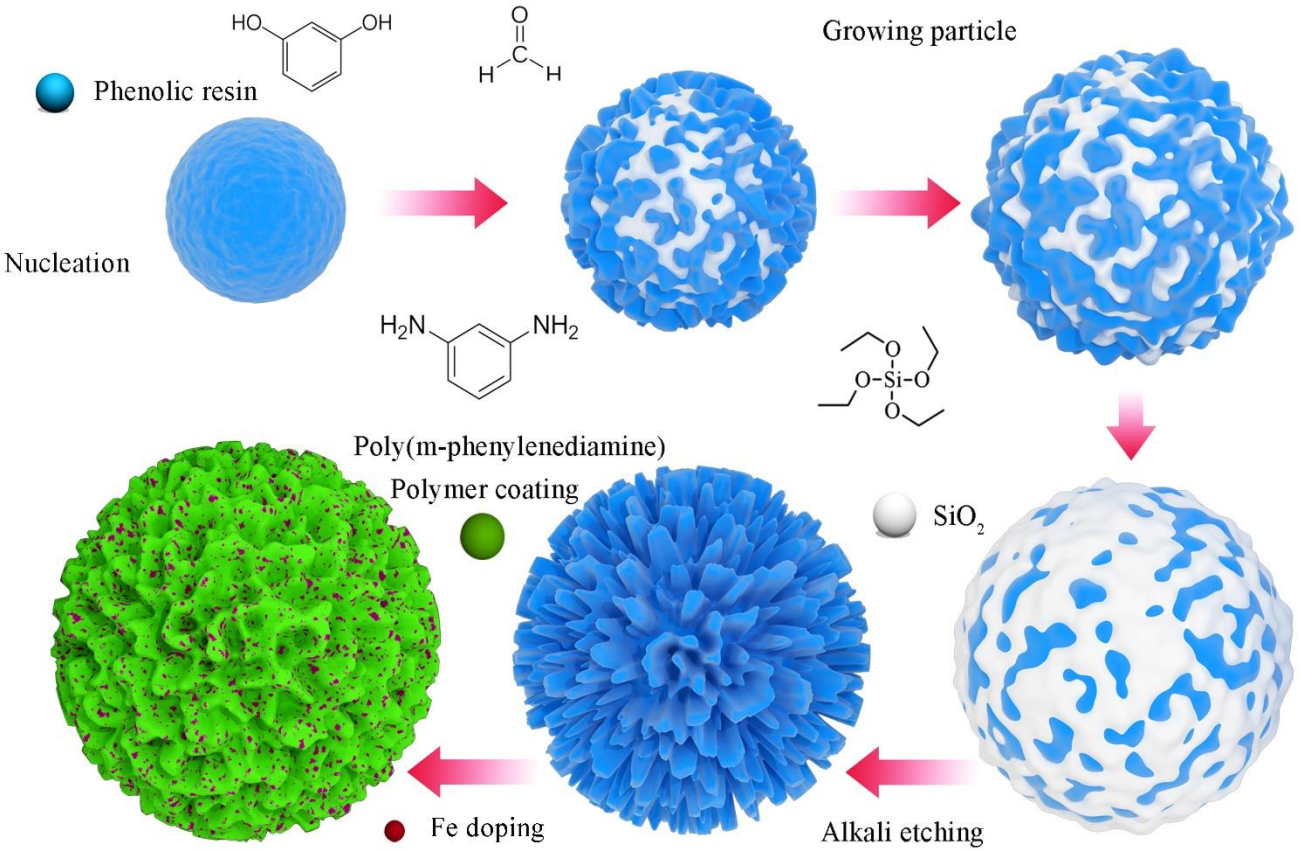
Approach: The Challenges for High Performance PGM-free Catalyst MEA

- PGM-free catalysts show the excellent ORR performance using RDE
- How to translate the RDE performance into MEA performance?
- DOE Targets
  - Mass activity of 0.044 A/cm^2 at 0.9 VIR-free (H_2-O_2)
  - 0.15 A/cm^2 at 0.8 V (H_2-air).
- Challenges for PGM-free Catalyst MEAs
  - High Performance PGM-free Catalysts (mass activity)
  - Catalyst utilization (mass activity)
  - Mass transport (high current density performance)

Approach

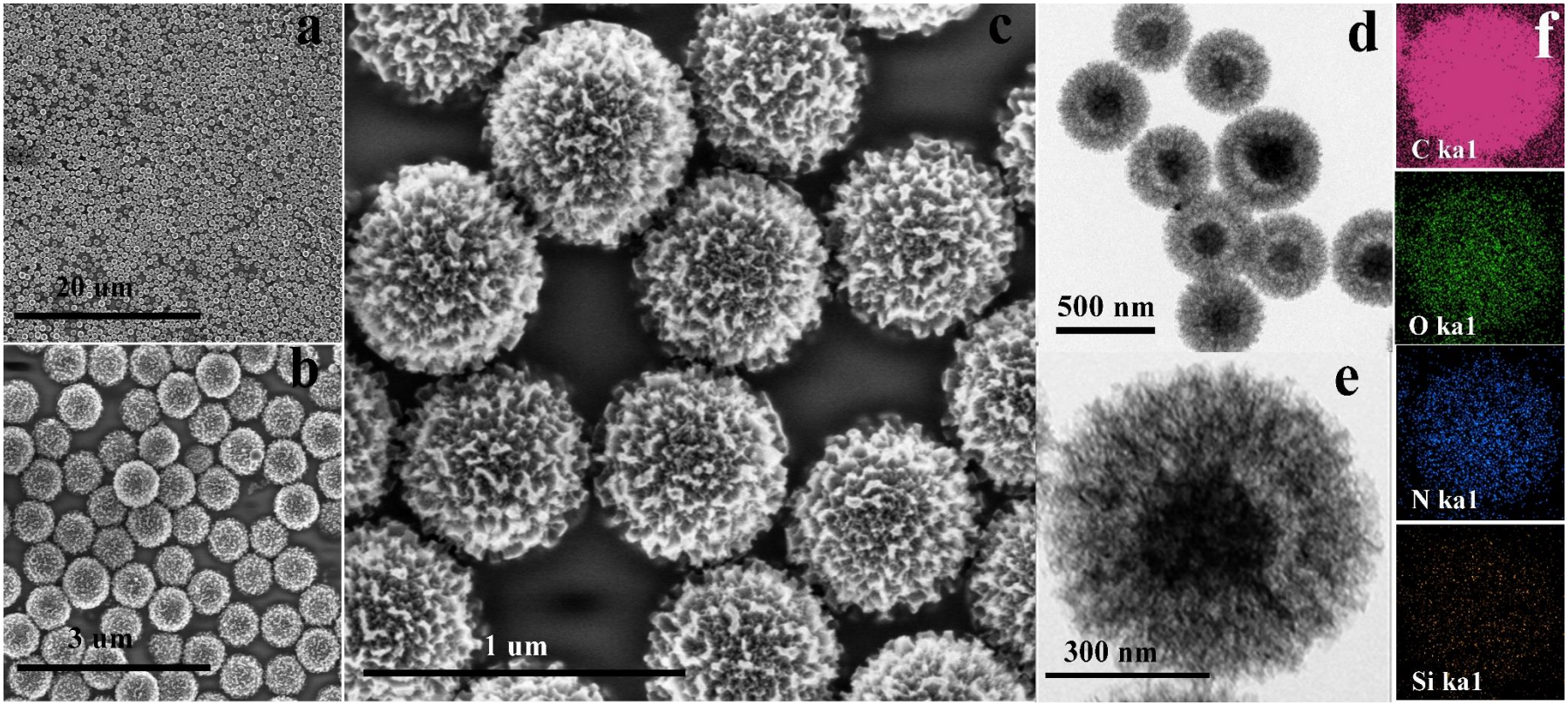
- Address the following two major challenges on both **intra-particle** and **inter-particle levels**:
  - Mass activity
  - High current density performance (mass transport)
- Approach 1: Develop high performance PGM-free catalysts with meso pore structure to achieve
  - Increased the mass activity (ionomer/catalyst interface within a catalyst particle)
  - Improved mass transport within the catalyst particles using hierarchical pore structure with high surface area
- Approach 2: Construct an ideal Nafion ionomer/catalyst interface within a catalyst layer of MEAs to achieve
  - Increased catalyst utilization (ionomer coverage)
  - Improved the high current density performance/mass transport (reducing the O_2 diffusion through ionomer film).

Approach 1: Develop hierarchically porous carbon sphere (HPCS) PGM Free Catalysts



Preparation schematic of HPCS@Fe-m-phenylenediamine (Fe-mPDA).

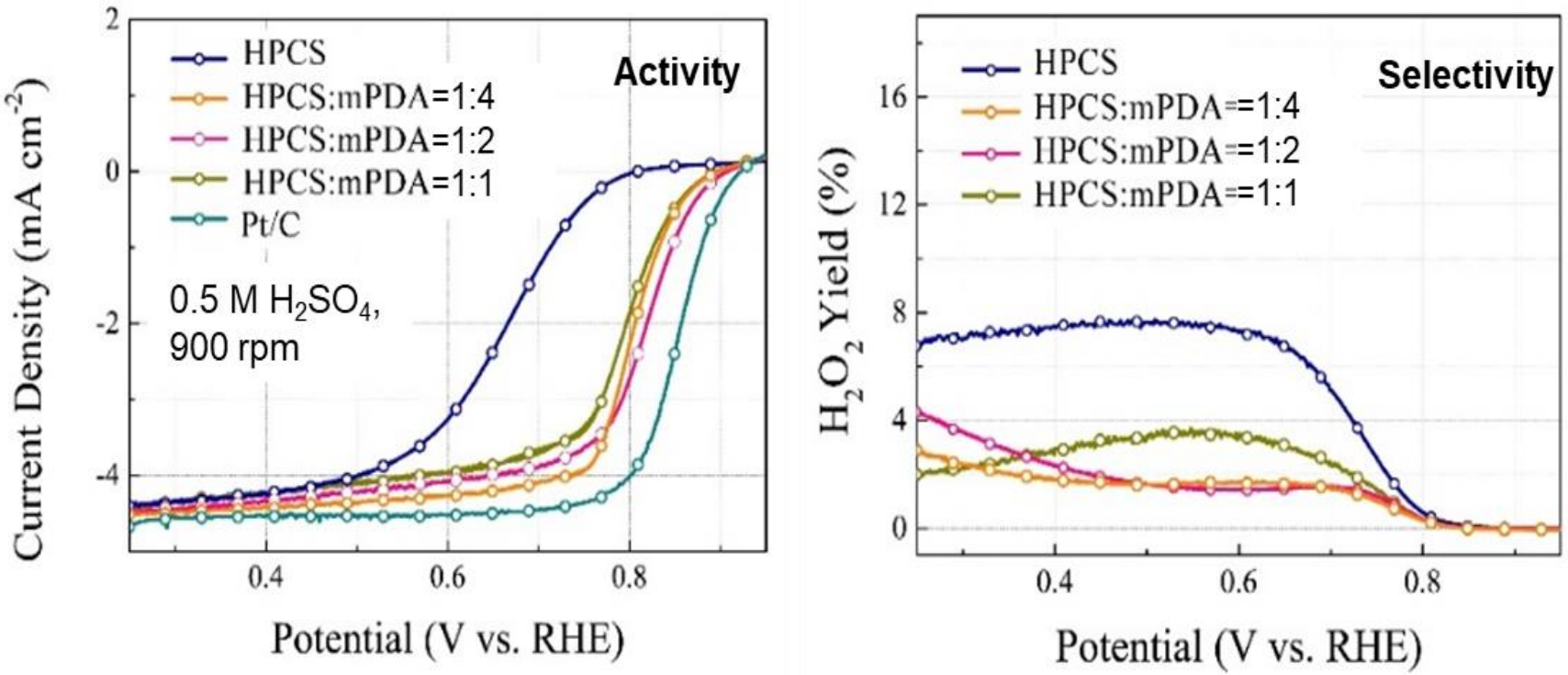
Approach 1: Morphology of HPCS and HPCS@Fe-mPDA



(a-c) SEM and (d, e) TEM images of the highly uniform and dispersible HPCS. (f) EDS elemental mapping of C, N, O and Si atoms.

Note: Kα1-the energy of X-ray used for EDS analysis

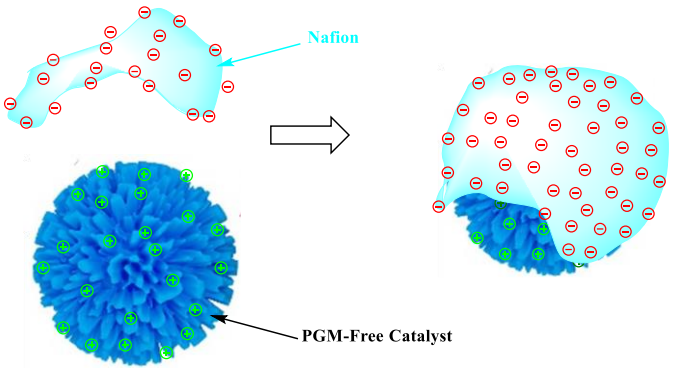
Approach 1: ORR Electrocatalytic Activity and Selectivity



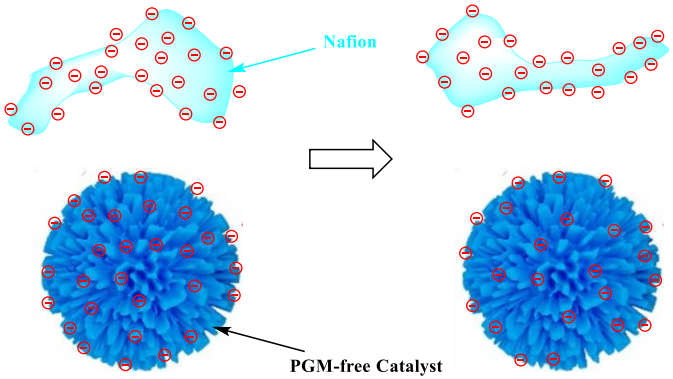
ORR activity and 4-e^- selectivity of new HPCS-based catalysts with various content of m-phenylenediamine (mPDA) nitrogen resources. Catalyst loading: 0.6 mg cm^{-2}, 0.5 M H_2SO_4 electrolyte, 900 rpm, 25°C

The optimal ratio of 1:2 for HPSC to mPDA yields the highest ORR activity and four-electron selectivity ($E_{1/2}$ of 0.82 V *vs* RHE and H_2O_2 yield < 2.0 %), likely due to the maximum atomic dispersion of FeN_4 sites on mesoporous carbon spheres

Approach 2: Construct an ideal ionomer/catalyst interface via electrostatic charge attraction



Spontaneous formation of ionomer/catalyst interface via charge attraction between catalyst and ionomer particles, resulting in **higher ionomer coverage** and **thinner ionomer film**

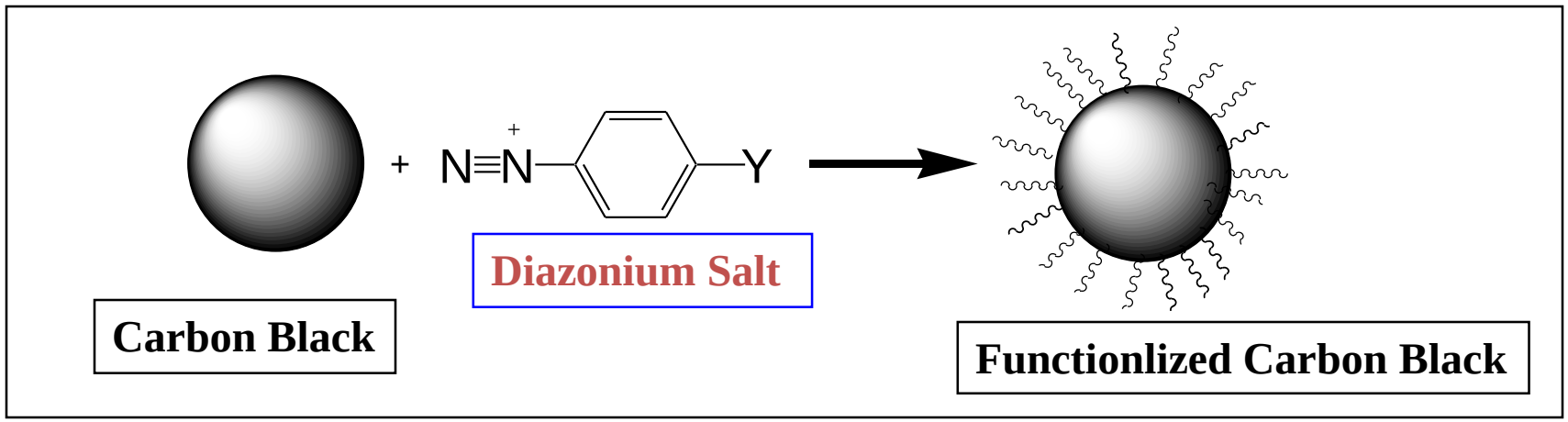


Non-Spontaneous formation of ionomer/catalyst interface via precipitation of ionomer (charge repelling between catalyst and ionomer particles), **less ionomer coverage** and **thick ionomer film**.

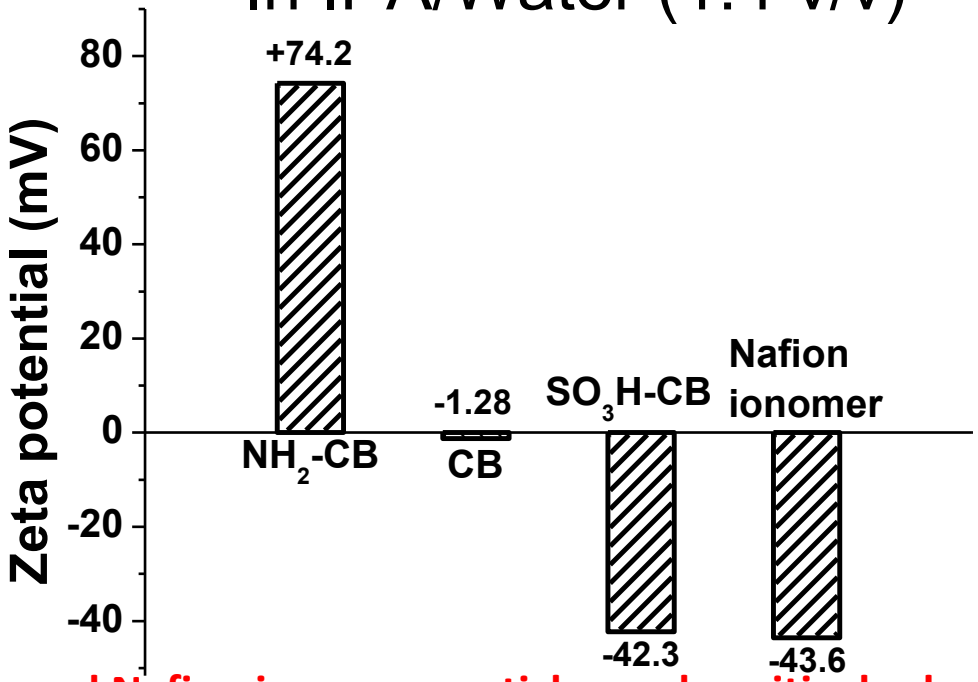
Approach 2: Surface Charge Modification—Covalently Bond Functional Groups

General Approach: functionalizing agent **X-R-Y**

X - reacts with CB surface
R - linking group
Y - functional group



Approach 2: Driven Force for Spontaneous Formation of Ionomer/Catalyst Interface-Zeta Potential In IPA/Water (1:4 v/v)



The negatively charged Nafion ionomer particles and positively charged NH_2-CB particles attract each other driven by the zeta potential difference, which serves as the driven force for the spontaneous formation of ionomer/catalyst Interface. The large the zeta potential difference is for the two different particles in the same liquid, the larger the driven force for the formation of the interface.

Zeta potential is the potential difference between the dispersion medium and the stationary layer of fluid attached to the dispersed particle. The zeta potential is caused by the net electrical charge contained within the region bounded by the slipping plane, and also depends on the location of that plane. Thus it is widely used for quantification of the magnitude of the charge.

Approach

Project Timeline

April 1, 2019

Task	Sub-task	Year 1				Year 2			
		Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4
Task 1 - HPCS-based M-N-C catalyst development for high mass activity and durability enhancement	1.1 Optimize morphology, diameter, and pore structure of MCSs (UB)								
	1.2 Optimize Nitrogen doping, M-Nx active sites on MCS@M-N-C (UB)								
	1.3 Enhance the stability of MCS@M-N-C (UB)								
Task 2 - Development of the PGM-free cathode layer using novel ionomer/catalyst interface	2.1 Functionalize PGM-free catalysts (IUPUI)								
	2.2 Adjust the surface hydrophobicity of the PGM-free catalysts (IUPUI)								
	2.3 PGM-free cathode layer design and MEA fabrication (IUPUI)								
Task 3 - Fabricate PGM-free catalyst MEA	3.1 PGM-free MEA fabrication (IUPUI)								
	3.2 Characterize CL/CCM structure and performance(IUPUI/UTRC)								
Task 4 - Evaluate Catalyst and System Economics	(UTRC)								

Approach: Milestones, Go/No-Go Decision Point, Project Deliverable

- FY19 Milestone (Y1-Q4)
  - Synthesize HSPC PGM-free catalysts achieving E½ > 0.82 V and generate 0.25 mA/cm^2 at 0.90 V
  - Demonstrate MEA performance: 20 mA/cm^2 at 0.9 $V_{IR\text{-}free}$, 100 mA/cm^2 at 0.80 $V_{IR\text{-}free}$
    - Work in progress
- Go/No-Go Decision Point
  - Go/No-Go Decision Point (Y1-Q4): Demonstrate MEA using the developed catalyst and ionomer/catalyst interface to achieve: mass activity (100 mA/cm^2 at 0.80 V) and power density (0.150 W/cm^2 at 0.70V) (both for H_2/Air, 150 KPa_{abs})
- Project Deliverable
  - MEAs with a mass activity of 0.044 A/cm^2 at 0.9 VIR-free (H_2-O_2) and 0.15 A/cm^2 at 0.8 V (H_2-air) by month 12.
  - MEAs with high power density of at least 0.5 W/cm^2 (*e.g.*, 0.50 V at 1.0 A/cm^2) following DOE catalyst performance metrics by month 24.

Proposed Future Work for FY19

- **Develop HPCS-based M-N-C catalysts (UB)**
  - Optimize the morphology, diameter, and pore structure of MCSs through tuning the dosage of surfactant, initiator, and reaction time.
  - Optimize the Nitrogen doping, M-Nx active sites on the surface of MCS@M-N-C catalysts through tuning the carbon/nitrogen precursors and attempting various coating methods
- **Develop the PGM-free cathode layer using novel ionomer/catalyst interface (IUPUI)**
  - Functionalize PGM-free catalysts to attach charge groups onto the surface
- **Design PGM-free cathode layer and fabricate MEA (IUPUI and UB)**
  - Construct the ionomer/catalyst interface via appropriate charge attraction
  - Formulate the inks
- **Evaluate Catalyst and System Economics (UTRC)**
  - The cost of all catalysts will be analyzed by UTRC in collaboration with UB and IUPUI in the context of a small-scale, short production as well as a commercial mass production.
- **Future activities are subject to appropriations**

Summary

- **Objective**: To achieve the high mass activity and high current density in MEAs by improving the catalyst utilization and mass transport on both intra-particle and inter-particles levels.
- **Relevance**: To realize the ORR mass activity benefits of advanced PGM-free catalyst observed at low current densities and on oxygen and in rotating-disk electrode measurement in MEAs operating at high current densities and on air to enable MEAs to achieve the DOE PGM-free catalyst targets.
- **Approach**: (1) Develop high performance PGM-free catalysts with meso pore structure; and (2) construct an ideal Nafion ionomer/catalyst interface within a catalyst particle and a catalyst layer of MEAs respectively to achieve the increased catalyst utilization and enhanced high current density performance.
- **Accomplishments**: Project anticipated start date of April 1, 2019. The synthesis of the PGM-free catalysts, functionalization of PGM-free catalysts and ink formulation have been started. MEA fabrication and characterization also have been started.
- **Collaboration:** Project team of UB and UTRC.
- **Future work**: (1) Develop HPCS-based M-N-C catalysts (UB) through optimizing the morphology, diameter, and pore structure of MCSs; (2) develop the PGM-free cathode layer using novel ionomer/catalyst interface (IUPUI); (3)design PGM-free cathode layer and fabricate MEA by constructing the ionomer/catalyst interface and (4) evaluate catalyst and system Economics (UTRC).

Collaboration and Acknowledgements

- Project teams
  - University at Buffalo (UB)
  - United Technologies Research Center (UTRC)

Thanks!

- DOE, Office of Energy Efficiency and Renewable Energy, Fuel Cell Technologies Office – Nancy Garland (Technology Development Manager)