*2017 U.S. DOE HYDROGEN and FUEL CELLS PROGRAM and VEHICLE TECHNOLOGIES OFFICE ANNUAL MERIT REVIEW and PEER EVALUATION MEETING*

# Development of Corrosion Resistant Carbon (CRC) Support for Ultra-low PGM Catalysts (Phase I)

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FC 164

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# Overview

## Timeline

- Start date: February 21, 2017
- End date: November 20, 2017 (Phase I)

## Budget

- Total project funding $ 149,997

## Barriers

- Durability
- Performance
- Cost

## Partners

- GreenWay Energy, LLC (Project Lead)
- Savannah River National Laboratory (SRNL)
- Johnson Matthey Fuel Cell (JM) (In kind)

## DOE 2020 Technical Targets

| Electrocatalyst/MEA | 2020 Targets |
|---|---|
| PGM loading | 0.125 mg/cm$^2$ |
| Initial mass activity | ≥0.44 A/mg$_{PGM}$ |
| Mass activity and ECSA loss after 30k cycles **(0.6-1.0V)** **(Catalyst durability)** | ≤40% |
| Potential loss at 0.8 A/cm$^2$ after 30k cycles **(0.6-1.0V)** **(Catalyst durability)** | ≤30 mV |
| Mass activity and ECSA loss after 5k cycles **(1.0-1.5 V)** **(Support stability)** | ≤40% |
| Potential loss at 1.5 A/cm$^2$ after 5k cycles **(1.0-1.5 V)** **(Support stability)** | ≤30 mV |

# Relevance: Objectives

- This project addresses technical targets from DOE's FCTO Multi-Year R&D Plan to enable commercialization of fuel cell electric vehicles by improving the performance and durability, while reducing the cost, of catalyst supports within polymer electrolyte membrane fuel cells (PEMFC).
- Demonstration of **Corrosion Resistant Carbon (CRC) support stability** in the presence of Pt and Pt-alloy nanoparticles **under 1.0-1.5 V potential cycling** condition to **meet** the **2020 DOE technical targets** for catalyst support.
  - Optimize support physical properties
  - Enhance catalyst-support interaction
  - Synthesize Pt/CRC and Pt-alloy/CRC catalysts
  - Evaluate catalyst activity (at 0.9 $V_{iR\text{-}free}$)
  - Evaluate (i) support stability and (ii) high current density performance

# Approach

- Identification of carbon support
  - Ease of tailoring surface area, porosity, pore-size distribution, and hydrophilic/hydrophobic properties
- Optimization of metal/support interaction through surface functionalization
  - Stable Pt deposition with uniform particle distribution (3-6 nm)
- Combine transition metal (e.g. Ni and Co) with Pt
  - Enhance catalytic activity and catalyst stability
- Characterization studies
  - Physical characterization (BET, Raman spectroscopy, XRD, XPS, and HRTEM)
  - Electrochemical studies (RDE and fuel cell testing in 25 $cm^2$ MEAs)

**GWE Approach:**

**Precursor Carbon** → **Surface modification** → **Annealing** → **Corrosion Resistant Carbon (CRC)**

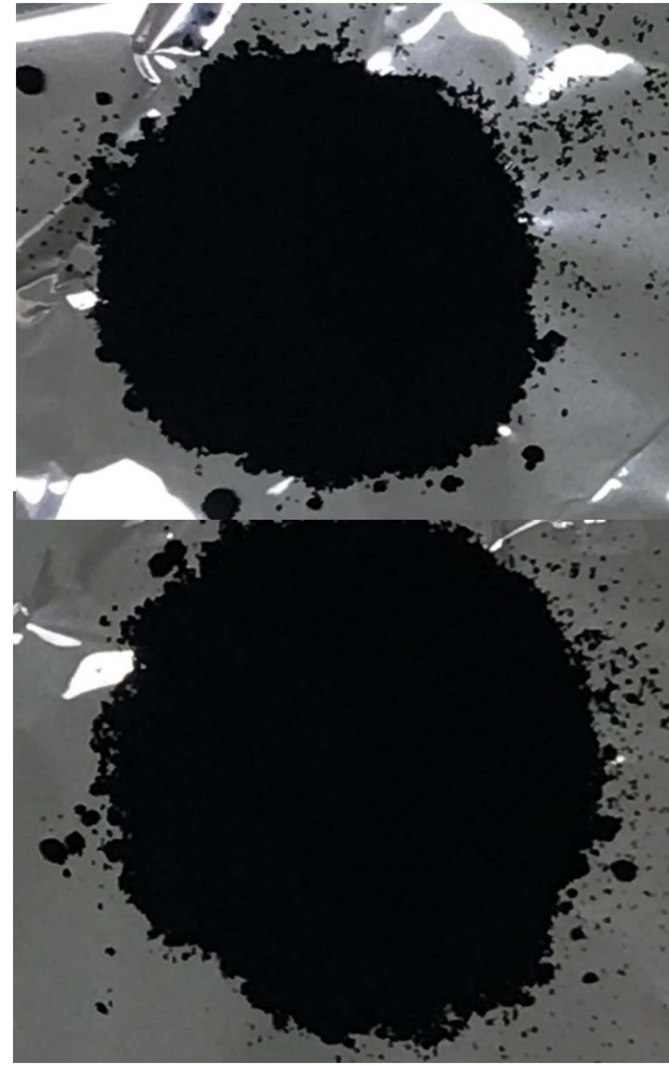
# Approach: Project Milestones

| Tasks | Milestones |
|---|---|
| *1.1 Corrosion resistant carbon support development* | ***(i)*** ***yields >90%*** <br> ***(ii)*** ***minimum ORR kinetics degradation*** *(at $E_{1/2}$) in the presence of Pt in RDE studies.* ***(M1)*** |
| *1.2 Support surface modification and functionalization* | *Demonstration of up to 10 wt.% bifunctional additive inclusion in the CRC support.* ***(M2)*** |
| *1.3 Platinum and Pt-alloy catalyst synthesis* | ***(i)*** ***Pt/CRC and Pt-alloy/CRC*** *catalysts having* ***3-6 nm particles*** <br> ***(ii)*** ***yields >90%****.* ***(M3)*** |
| *2.1 Characterization studies* | |
| *2.2 Rotating disk electrode (RDE) studies* | ***(i)*** ***≤40% ECSA loss*** *after 5k cycles (****Pt/CRC****)* <br> *(ii)* *(ii) initial* ***mass activity of 0.35-0.44 A/mg$_{PGM}$ at 0.9 V$_{iR-free}$*** *(****Pt-alloy/CRC)*** <br> ***(iii)*** ***≤40%*** *loss of mass activity and ECSA after 5k cycles (****Pt-alloy/CRC****).* ***(M4)*** |
| *2.3 Membrane electrode assembly (MEA) studies* | ***(i)*** ***≤30 mV loss*** *at 1.5 A/cm$^2$ and* ***<40% ECSA loss*** *(****Pt/CRC****)* <br> *(ii)* *(ii) initial mass activity of* ***0.35-0.44 A/mg$_{PGM}$*** *at 0.9 V$_{iR-free}$,* ***(Pt-alloy/CRC)*** <br> ***(iii)*** ***≤40% mass activity and ECSA*** *losses after 5k cycles* ***(Pt-alloy/CRC)*** <br> ***(iv)*** ***≤30 mV loss*** *at 1.5 A/cm$^2$ after 5k cycles.* ***(M5)*** |

# Accomplishments and Progress

## CRC Support Synthesis


## 2 g CRC support batches



**Highlight**

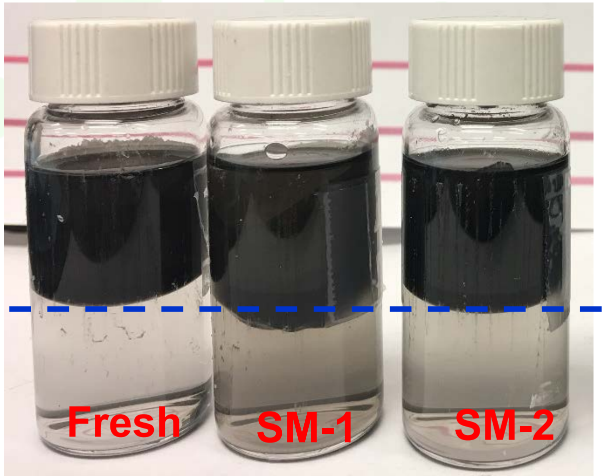
- 5X increase in batch size (400 mg to 2.0 g)
- Highly reproducible (yield, pore-size, pore volume, and surface area) multiple 2g batches are made.
- Optimization of 5 and 10g batches under progress.

# Accomplishments and Progress

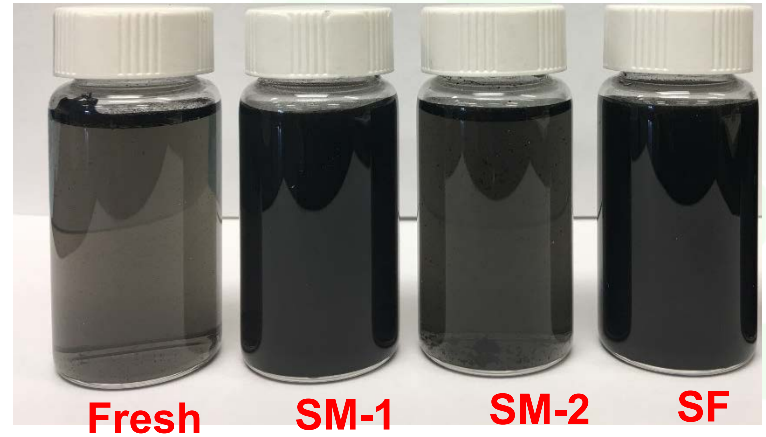
**Surface Modification (SM)** → **Surface Functionalization (SF)** → **Dispersion in DI water (After Sonication)**

n-Hexane

Water

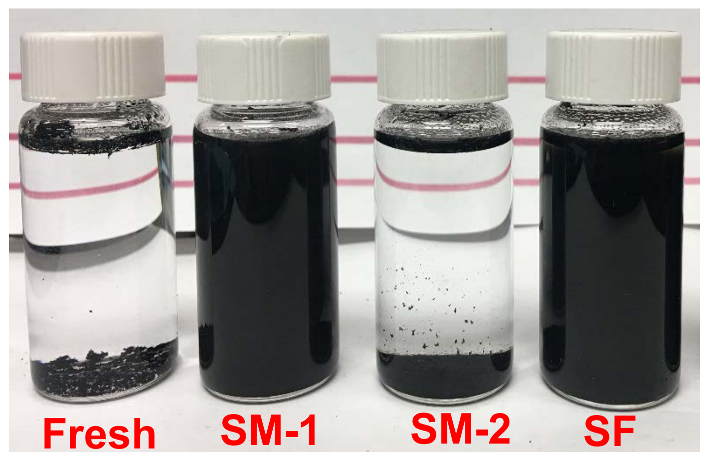







**Highlight**

- Simple surface modification procedure alters hydrophobicity of fresh carbon precursor.
- Surface modifications followed by surface functionalization produces stable dispersions in DI water to facilitate Pt deposition in aqueous medium.

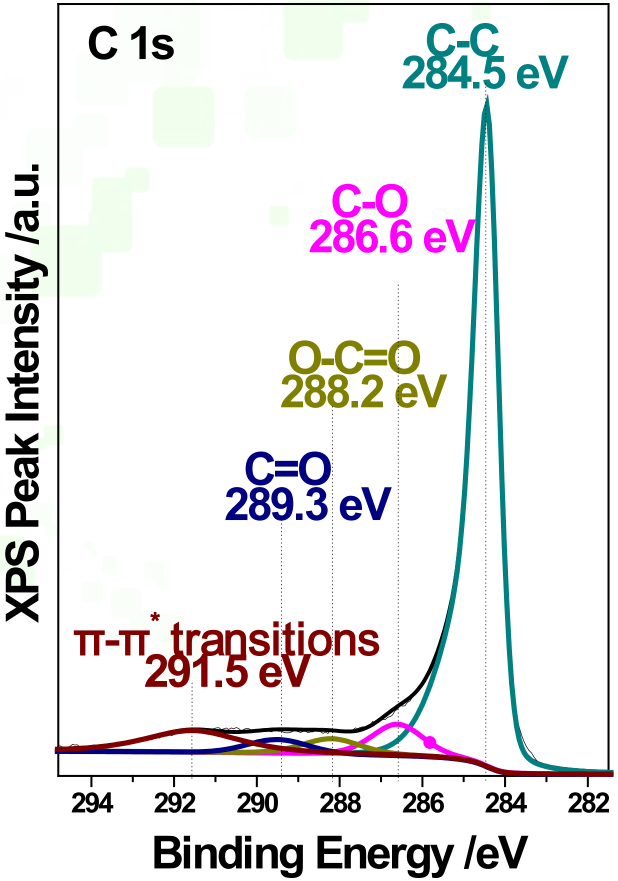


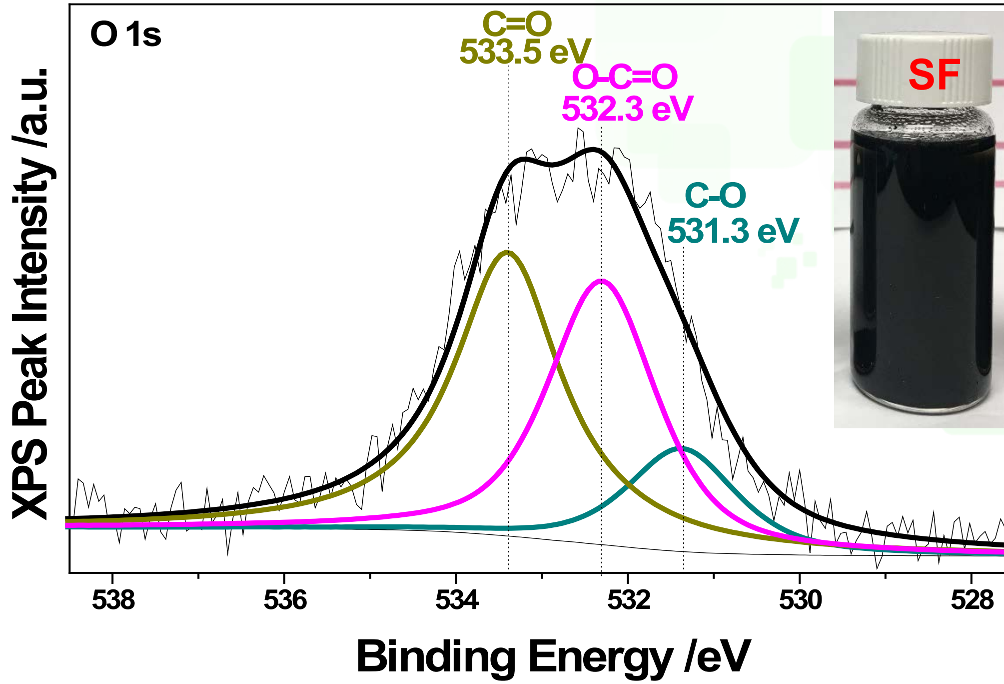

**Dispersion in DI Water (After 360 h)**

**SM = Surface Modification**
**SF = Surface Functionalization**

# Accomplishments and Progress

## XPS of optimized CRC support



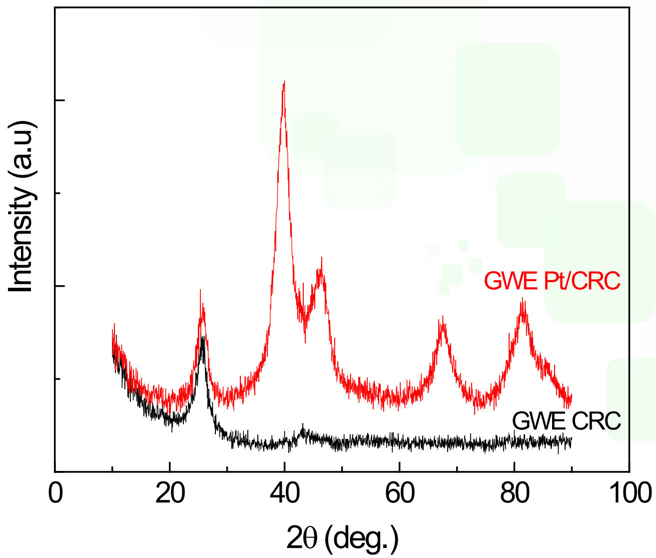

**Highlight**

- The main C1s line at 284.5 eV indicates that carbon is present in highly oriented pyrolitic graphitic form.
- Presence of 3 oxygen functional groups (C=O, C-O, and O-C=O) after surface modification and functionalization processes.
- Surface modification followed by functionalization significantly increase carboxylate functional group resulting in stable dispersion in DI water.

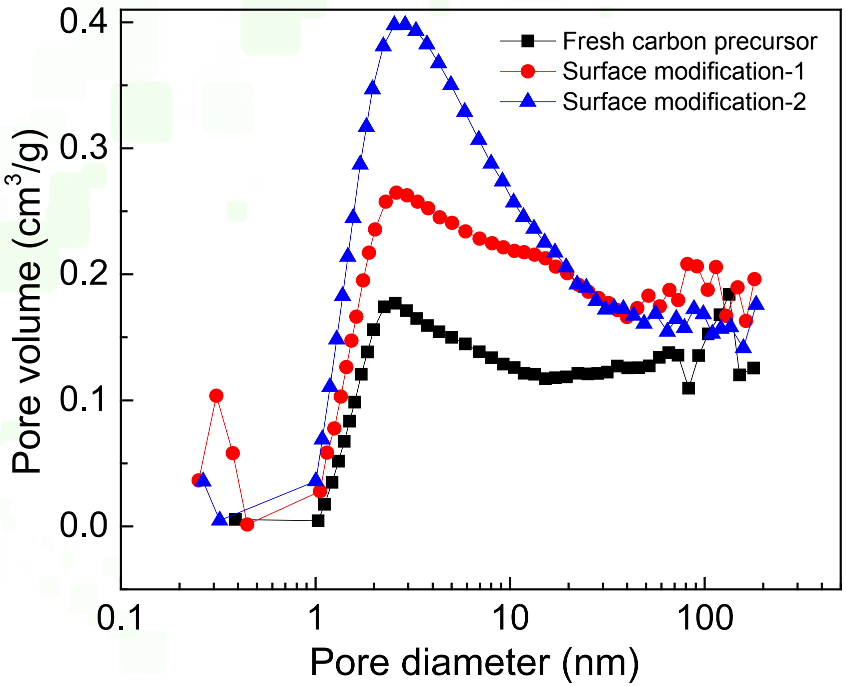
**SF = Surface Functionalization**

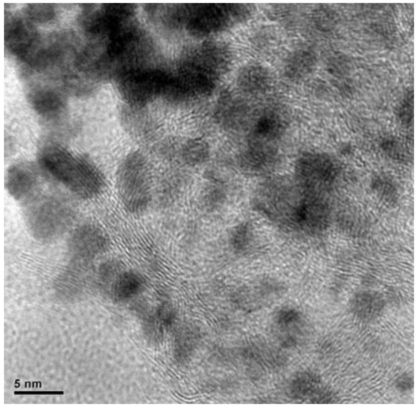
# Accomplishments and Progress

## Pt deposition on CRC support

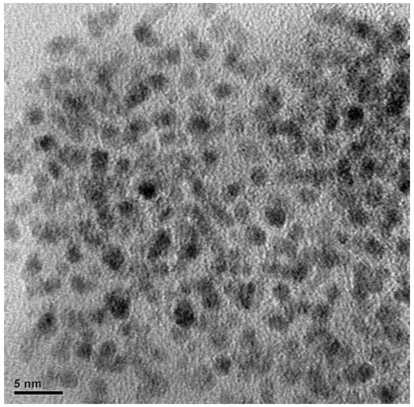



## Barrett-Joyner-Halenda (BJH) Pore volume analysis




**Traditional chemical reduction**




**GWE optimized chemical reduction**

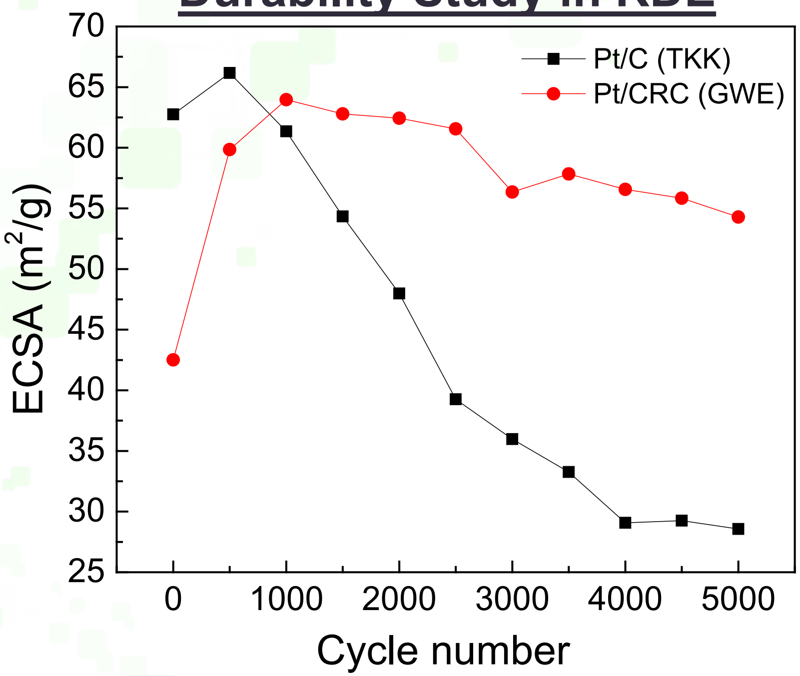
**Scale bar = 5 nm**

### Highlight

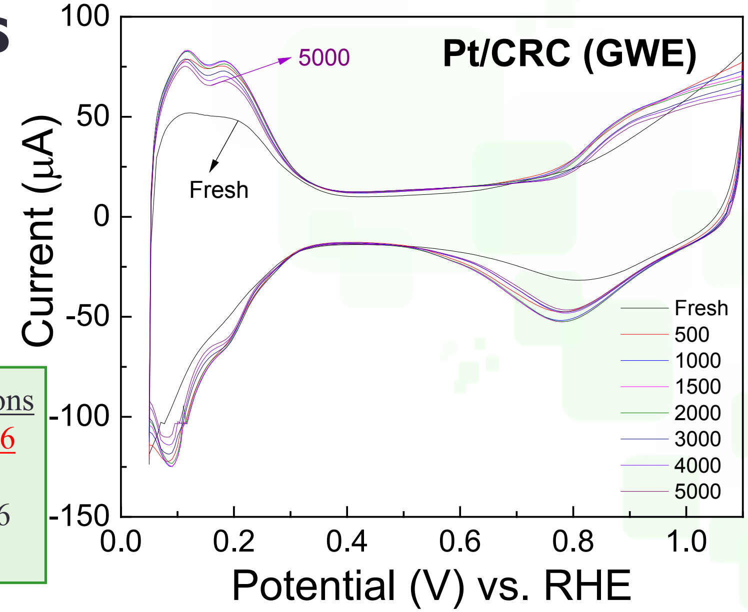
- It is possible to tailor the support pore volume, pore size distribution, and surface area using GWE surface modification process.
- GWE's surface functionalization and optimized deposition procedure produces 3-5 nm Pt particles and uniform deposition on CRC support.

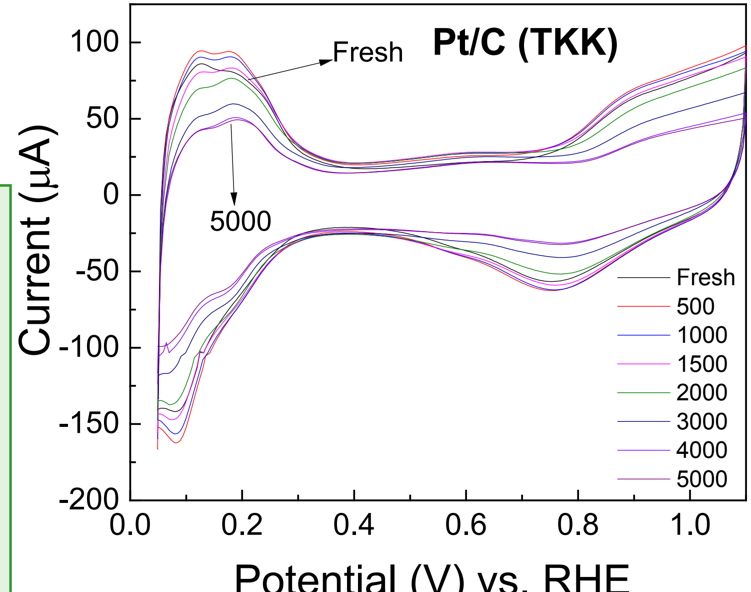
# Accomplishments and Progress

## Durability Study in RDE




RDE testing conditions
0.1 M $HClO_4$ (1.0-1.6 V, 100 mV/s)
Catalyst loading = 16 µg/cm$^2$




**Highlight**

- GWE Pt/CRC and TKK Pt/C showed maximum ECSA after 1000 and 500 cycles. The increase in ECSA after 1000 cycles for GWE Pt/CRC can be ascribed to the removal of impurities (from Pt deposition process) and surface Pt atom rearrangement.
- GWE Pt/CRC shows <10% ECSA loss after 5k cycles.
- TKK Pt/C shows ~56% ECSA loss after 5k cycles.

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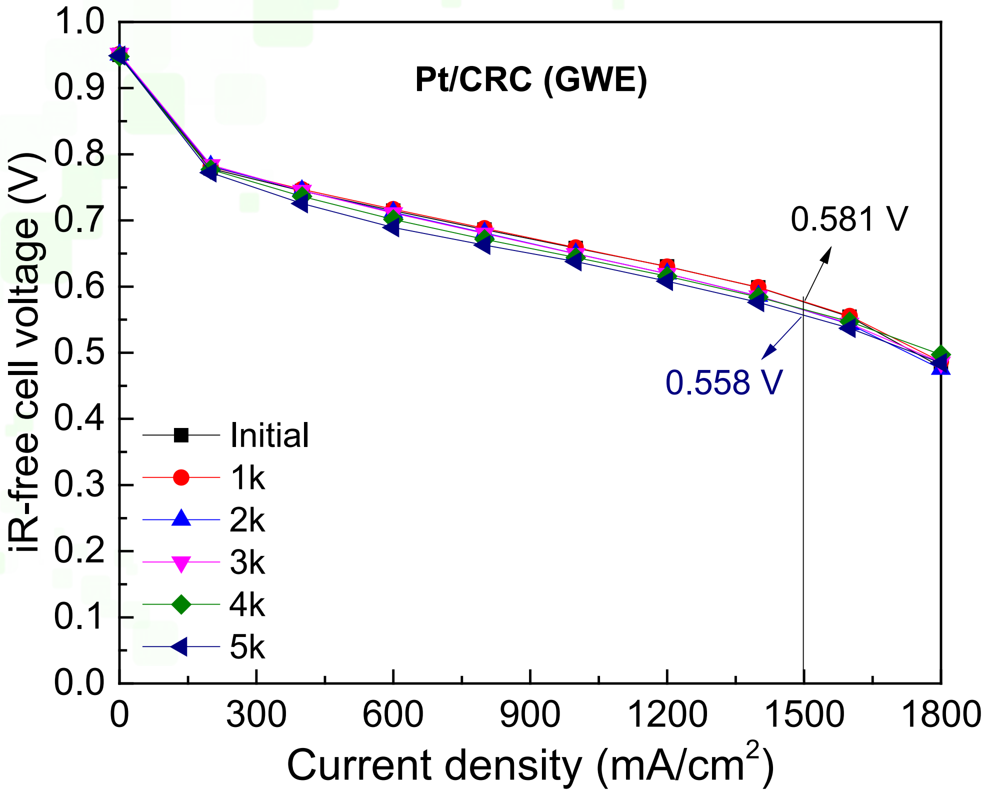
# Accomplishments and Progress

## Support stability (25 cm² MEA)




**Fuel cell testing conditions**:

- $H_2$-air (2/2 stoic.), 80°C, 50% RH, and 170 kPa back pressure.
- Pt loading: 0.055 mg/cm² (anode)
  0.13 mg/cm² (cathode)

**Highlight**

- $H_2$-air fuel cell shows ~1.4 A/cm² at 0.6 $V_{iR\text{-}free}$(170 Kpa was used to achieve maximum $H_2$-air fuel cell performance)
- 23 mV loss at 1.5 A/cm² after 5k cycles (1.0-1.5 V)

# Collaborations

## Savannah River National Laboratory (SRNL)

- Pt-alloy catalyst deposition on CRC support
- Physical characterization
- RRDE and MEA studies

**Cooperative Research and Development Agreement (CRADA) completed**

## Johnson Matthey Fuel Cells (JM) (In kind)

- Pt and Pt-alloy catalyst deposition on CRC support

**Material Transfer Agreement (MTA) completed**

# Remaining Challenges and Barriers

**<u>Scale-up (CRC Support and Pt/CRC and Pt-alloy/CRC Catalysts)</u>**

- Production of CRC support and Pt/CRC and Pt-alloy/CRC catalysts in quantities >100g/batch is necessary to validate: (i) support stability in the presence of Pt and Pt-alloy under start-up/shut-down conditions and (ii) catalyst durability under load cycling conditions by OEMs.

**<u>Durability</u>**

- Development of a catalyst with mass activity of at least 0.44 $A/mg_{PGM}$ that meets DOE 2020 technical targets for both support and catalyst.
  - ✓ **<u>Support</u>** (<30 mV loss at 1.5 $A/cm^2$, <40% mass activity loss at 0.9 $V_{iR\text{-}free}$, and 40% ECSA loss after 5k cycles between 1.0 and 1.5V).
  - ✓ **<u>Catalyst</u>** (<30 mV loss at 0.8 $A/cm^2$, <40% mass activity loss at 0.9 $V_{iR\text{-}free}$, and 40% ECSA loss after 30k cycles between 0.6 and 1.0V).

# Future Work (Phase I)

- **Scale-up synthesis of CRC support**
  - Process optimization for 5 and 10g batch size
- **Synthesis and performance evaluation of Pt-alloy/CRC catalysts**
  - Evaluation of initial mass activities of PtCo/CRC catalyst in RRDE and fuel cell MEAs.
  - Support stability studies under accelerated stress test conditions in RRDE (1.0-1.6 V) and MEAs (1.0-1.5 V)
- **Support preparation for industrial partner**
  - Agreed to send 100 g CRC support: 25 g support is ready for shipment; 75 g CRC support to be prepared and shipped to JM for Pt and Pt-alloy catalyst synthesis.

# Proposed Future Work (Phase II)

- ❖ **Scale-up synthesis of CRC support**
  - ➢ Process optimization for 5-100 g batch size
  - ➢ Maintain the desired physical properties (surface area, porosity, and pore-size distribution) as of 0.5-2.0 g current batch size.
  - ➢ Optimize hydrophilic/hydrophobic properties in large batch sizes
- ❖ **Negotiation for trial runs using a rotary tube furnace at a leading furnace manufacturer's facility has been initiated. 50 and 100 g batch sizes are planned to optimize the process parameters.**
- ❖ **Continuous process to produce CRC support has also been planned after acquiring the rotary tube furnace.**
- ❖ **Scale-up surface functionalization process for CRC support**
- ❖ **Scale-up synthesis of Pt/CRC and Pt-alloy/CRC catalysts (in collaboration with JM)**
  - ➢ Pt deposition process optimization for 1, 5, 10, 50, and 100 g batches
    - ✓ Uniform Pt deposition with 3-5 nm particle size.
  - ➢ Process optimization for Pt-alloy/CRC with enhanced activity and catalyst-support interaction.

# Proposed Future Work (Phase II)

- **Stability studies (25/50 $cm^2$ MEAs)**

  **Support (1.0-1.5 V cycling)**
  - Initial mass activity ≥0.44 $A/mg_{PGM}$
  - Mass activity and ECSA losses ≤40% after 5k cycles
  - 30 mV loss at 1.5 $A/cm^2$ after 5k cycles
- **Stability studies (25/50 $cm^2$ MEAs)**

  **Catalyst (0.6-1.0 V cycling)**
  - Initial mass activity ≥0.44 $A/mg_{PGM}$
  - Mass activity and ECSA losses ≤40% after 30k cycles
  - 30 mV loss at 0.8 $A/cm^2$ after 30k cycles
- **MEA optimization studies (in collaboration with GM)**
  - Performance evaluation of optimized catalyst in single cells (50 $cm^2$) and short stacks
- **Commercialization strategy**
  - Intellectual property
  - Technology transfer

# Summary

- Optimized the surface modification process to synthesize CRC supports with controlled surface area, pore size, and pore size distribution. (**M1 partially met for CRC support synthesis**)
- 5x increase in CRC support synthesis; process optimization of 5 and 10g batches under progress.
- Optimized the procedure for surface functionalization of CRC support to tailor hydrophilic/hydrophobic properties.
- Pt nanoparticles with controlled particle size (3-6 nm) and uniform distribution were deposited on optimized CRC support. (**M3 partially met for Pt deposition**)
- Potential cycling between 1.0-1.6V (5k cycles in 0.1M $HClO_4$) in RDE showed <10% ECSA loss for Pt/CRC and ~56% ECSA loss for commercial Pt/C catalysts. (**M4 partially met for ECSA loss**)
- Pt/CRC showed 23 mV loss at 1.5 A/cm$^2$ after 5k cycles (1.0-1.5 V) in 25 cm$^2$ MEA. (**M5 partially met for Pt/CRC catalyst**)
- MTA has been signed with JM to send CRC support for Pt and Pt-alloy catalyst synthesis. A total of 100 g CRC support to be shipped to JM and 25 g CRC support has been made and is available for shipment.

# Acknowledgements

DOE SBIR Program

Manager: Ms. Donna Ho

Team Members

Dr. Scott Greenway (GWE)

Dr. Hector Colon-Mercado (SRNL)

Dr. Jonathan Sharman (JM)