V.A.11 Development of Corrosion Resistant Carbon (CRC) Support for Ultra-Low Platinum Group Metal (PGM) Catalysts (SBIR Phase I)

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Overall Objectives

- Demonstrate corrosion resistant carbon (CRC) support stability in the presence of Pt and Pt-alloy nanoparticles under 1.0–1.5 V potential cycling condition.
- Optimize support surface area, pore-size-distribution, and hydrophilic/hydrophobic properties.
- Enhance catalyst-support interaction through functionalization with an inexpensive additive.
- Synthesize Pt and Pt-alloy catalysts deposited on the CRC support.
- Evaluate catalyst activity (at 0.9 $V_{iR\text{-}free}$) through rotating disc electrode studies.
- Evaluate high power density performance under H-air in 25-cm^2 membrane electrode assemblies (MEAs).

Fiscal Year (FY) 2017 Objectives

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Technical Barriers

This project addresses the following technical barriers from Fuel Cells section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan.

(A) Durability

(B) Cost

(C) Performance

Technical Targets

The technical target for the Small Business Innovative Research (SBIR) Phase I project is the demonstration of CRC support stability in the presence of Pt and Pt-alloy nanoparticles under 1.0–1.5 V potential cycling conditions to meet the following 2020 DOE technical targets for catalyst support: (i) <40% loss of electrochemical surface area (ECSA) after 5,000 cycles for Pt/CRC catalysts and (ii) initial mass activity of 0.35–0.44 A/mg_{PGM} at 0.9 $V_{iR\text{-}free}$ and mass activity and ECSA losses of <40% after 5,000 cycles for Pt-alloy catalysts.

FY 2017 Accomplishments

- Optimized the parameters to prepare reproducible CRC support.
- Optimized a surface functionalization process.
- Deposited Pt uniformly on the CRC support.

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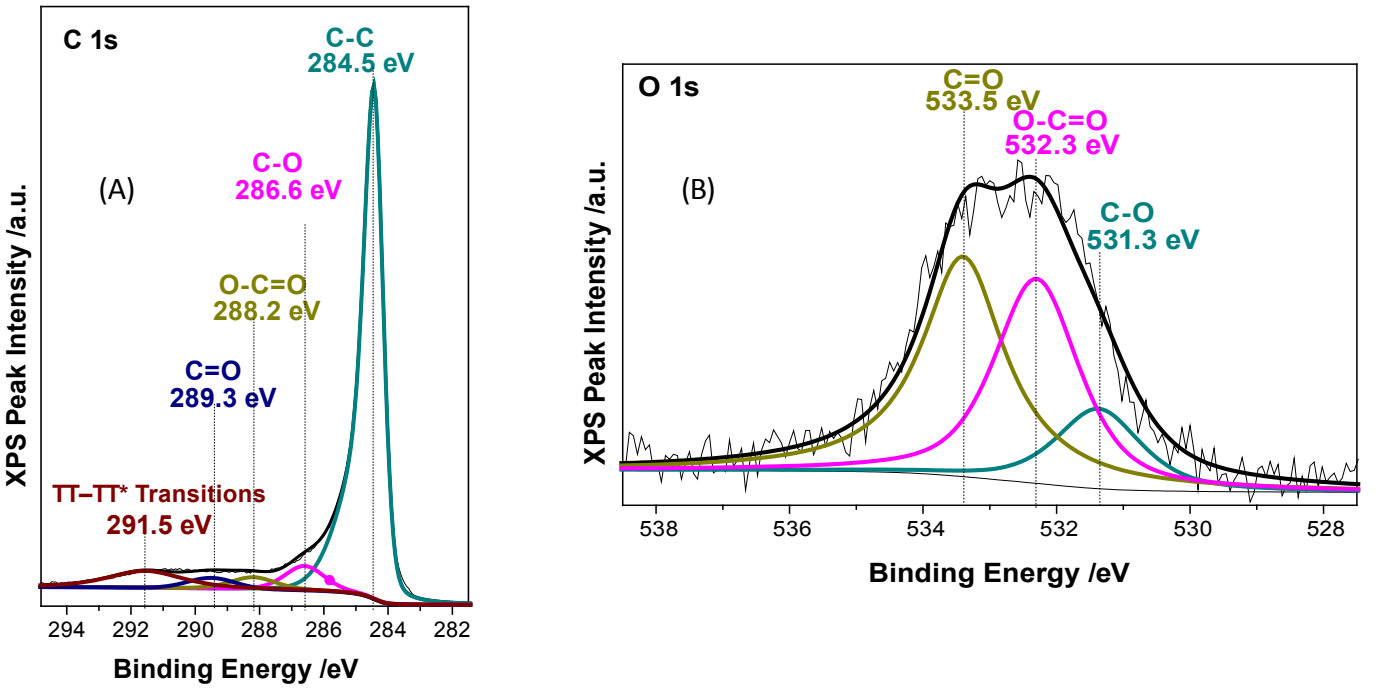
INTRODUCTION

CRC support with excellent support stability was developed at Greenway Energy, LLC. The CRC support showed ~10% ECSA loss in the presence of platinum when tested under 1.0–1.6 V potential cycling condition in a rotating disk electrode study when compared to the commercial Pt/C catalyst (56% ECSA loss) (Figure 1).

APPROACH

A commercial carbon was selected and its properties such as pore size, pore volume, and Brunauer–Emmett–Teller surface area were modified by optimizing the heat treatment temperature, time, and atmosphere to prepare the CRC support. A surface functionalization procedure was used to achieve an optimum hydrophilic/hydrophobic property to



a.u. – arbitrary units

FIGURE 1. XPS analysis of CRC support. (A) C1s peak and (B) O1s peak.

enable uniform platinum deposition and distribution on the CRC support.

RESULTS

During the reporting period, parameters were optimized to prepare CRC supports in 5 g batches and surface functionalization of CRC supports in 1.5 g batch sizes. X-ray photoelectron spectroscopy (XPS) analysis showed the presence of highly oriented pyrolytic graphite having carbonyl (C = O) and carboxylate (O – C = O) functional groups on the surface (Figure 1A and Figure 1B).

Barrett-Joyner-Halenda pore volume analysis of CRC support indicated a significant increase in pore volume when the fresh carbon precursor was subjected to surface modification Processes 1 and 2 (Figure 2).

The surface functionalization of CRC support resulted in an average Pt particle size of 3–4 nm as measured by the high-resolution transmission electron microscopy (Figure 3).

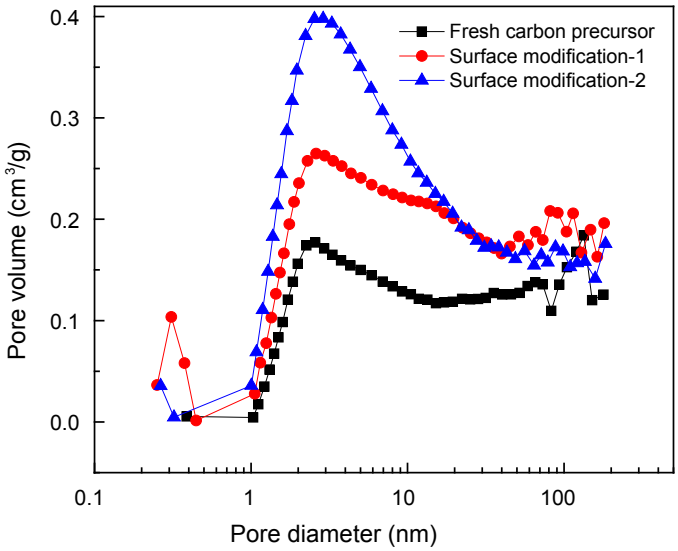


FIGURE 2. Barrett-Joyner-Halenda pore volume analysis of CRC support

CONCLUSIONS AND UPCOMING ACTIVITIES

Conclusions

- Optimized the parameters to prepare reproducible 5 g batches of CRC support (10X increase since project start).
- Optimized a surface functionalization process to prepare 1.5 g batches (15X increase since project start).
- Deposited 3–5 nm Pt particles uniformly on the CRC support.

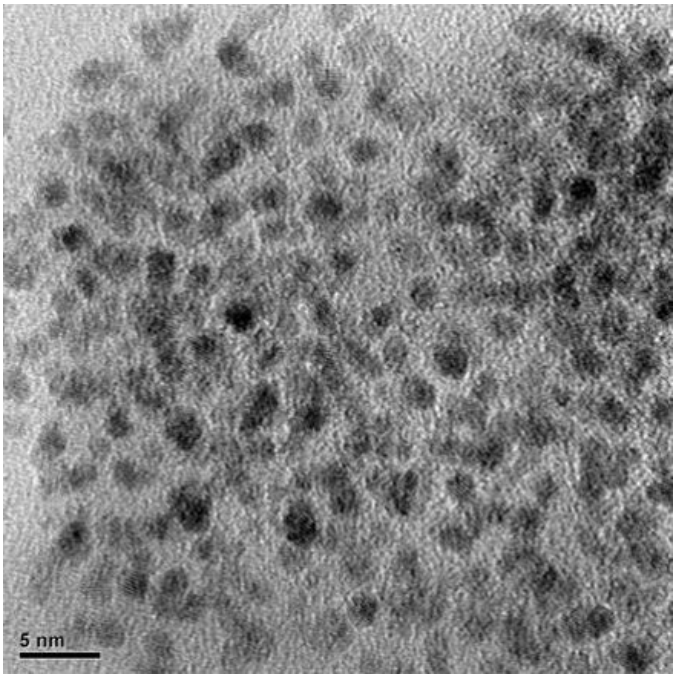


FIGURE 3. High-resolution transmission electron microscopy image of Pt/CRC catalyst

Upcoming Activities

Phase I

- Scale-up synthesis of CRC support; process optimization for 10g batch size.
- Synthesis and performance evaluation of Pt-alloy/CRC catalysts.
  - Evaluation of initial mass activities of PtCo/CRC catalyst in rotating ring disk electrode and fuel cell MEAs.
  - Support stability studies under accelerated stress test conditions in rotating ring disk electrode (1.0–1.6 V) and MEAs (1.0–1.5 V).
- Support preparation for industrial partner for Pt and Pt-alloy catalyst synthesis.
  - Agreed to provide 100 g CRC support and 10 g functionalized CRC support (25 g support shipped to Johnson Matthey Fuel Cell; 75 g CRC support and 10 g functionalized CRC support preparation is in progress).

Phase II

- Scale-up synthesis of CRC support; process optimization for 10–100 g batch size.
- Negotiation for trial runs using a rotary tube furnace at a leading furnace manufacturer's facility has been initiated. 50 g 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 Johnson Matthey Fuel Cell).
- Uniform Pt deposition process (3–5 nm particles) optimization for 1 g, 5 g, 10 g, 50 g, and 100 g batches.
- Process optimization for Pt-alloy/CRC with enhanced activity and catalyst-support interaction.
- Support stability studies using 25/50 cm^2 MEAs (1.0–1.5 V cycling).
  - Initial mass activity ≥0.44 A/mg_{PGM}.
  - Mass activity and ECSA losses ≤40% after 5,000 cycles.
  - 30 mV loss at 1.5 A/cm^2 after 5,000 cycles.
- Catalyst stability studies using 25/50 cm^2MEAs (0.6-1.0 V cycling).
  - Initial mass activity ≥0.44 A/mg_{PGM}.
  - Mass activity and ECSA losses ≤40% after 30,000 cycles.
  - 30 mV loss at 0.8 A/cm^2 after 30,000 cycles.
- MEA optimization studies (in collaboration with General Motors).
  - Performance evaluation of optimized catalyst in single cells (50 cm^2) and short stacks.
- Commercialization strategy.
- Intellectual property.
- Technology transfer.

FY 2017 PUBLICATIONS/PRESENTATIONS

1. Development of Corrosion Resistant Carbon (CRC) Support for Ultra-low PGM Catalysts (Phase I). Poster presented at 2017 U.S. DOE Hydrogen and Fuel Cells Program and Vehicle Technologies Office Annual Merit Review and Peer Evaluation Meeting, June 5–9, 2017, Washington, DC.