V.F.3 Technical Assistance to Developers

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Project Start Date: October 2006
Project End Date: Project continuation and direction determined annually by DOE

Overall Objectives

This task supports LANL technical assistance to fuel cell component and system developers as directed by the DOE. This task includes:

- Testing and validation of materials and components.
- Participating in the further development and validation of single cell test protocols.
- Partaking in Durability Working Groups, the U.S. Council for Automotive Research (USCAR) and the USCAR U.S. Driving Research and Innovation for Vehicle efficiency and Energy sustainability (U.S. DRIVE) Fuel Cell Technology Team (FCTT) meetings and activities.
- Providing assistance includes making technical experts available to DOE and FCTT as questions arise.

Fiscal Year (FY) 2016 Objectives

- Perform fuel cell tests on different non-Pt anode catalyst materials provided by an outside developer; measure and verify performance and durability.
- Perform fuel cell tests on Pt/polybenzimidazole (PBI)-graphene, Pt-amine, Pt-SO_3-H, and a family of PtNi catalysts verifying performance and durability provided by an outside developer.
- Investigate the integrity and stability of the structure of novel membrane electrode assemblies (MEAs) using high resolution imaging (1–2 µ).
- Assist with ceramic coating of metal bipolar fuel cell components.
- Assist with novel supports for catalyst development by physical vapor deposition of noble metals on developer provide supports.
- Perform test on precious group metal (PGM)-free materials, testing for performance and durability using DOE accelerated stress tests (ASTs).
- Investigate high potential redox active species present in select PGM-free fuel cell electrocatalysts for the oxygen reduction reaction in acidic medium.
- Evaluate two-cell stack for hydrogen/air application. Provide feedback regarding any needed improvements that can be implemented to assist in its commercial development.
- Support DOE FCTT and working groups.

Technical Barriers

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

(A) Durability

(B) Cost

(C) Performance (Electrode)

FY 2016 Accomplishments

- Indiana University–Purdue University Indianapolis (IUPUI):
  – Performed fuel cell tests on the impact of spacers on nanographene vs. graphene.
    - Nanographene effectively shortens the length of pore and channels within typical graphene structures which inherently leads to improved mass transport.
  – Tested Pt/PBI-nanographene with and without spacers.
    - The addition of spacers between the graphene sheets shows significant improvements at the larger current densities, particularly in the mass transport region. Results performed at LANL were improved over IUPUI results.
    - AST results show larger losses in the mass transport region of the polarization as the number of voltage cycles increase.
    - Comparison of graphene vs. XC-72 carbon black supports proved graphene as a more durable support when subjected to AST.

  - Co-authored papers (two abstracts submitted and accepted to the Electrochemical Society).
- Nissan:
  - Characterized nanofiber MEAs to compare fresh vs. aged electrode using X-ray micro-tomography.
  - Provided high resolution images and movie of the samples.
  - Results revealed only minimal changes in the electrode structure after 1,000 voltage cycles.
- Ford Motor Company: Catalyst Support Development and Bipolar Plate Coatings
  - Built and tested sample tower for heating.
  - Added residual gas analyzer mass spectrometer for measuring surface contaminants.
  - Performed ~eight depositions and characterized each; sent Ford three samples. (X-ray diffraction, scanning electron microscopy, and energy dispersive X-ray analysis) for catalyst support development.
  - Performed over 100 depositions and delivered 42 samples with protective coatings for metal bipolar plates.
- Pajarito Powder, LLC:
  - Performed ASTs on three PGM-free samples.
  - Evaluated the samples' performance and durability as a function of pressure after ASTs.
  - Reported results to customer.
- DOE FCTT:
  - Provided a permanent member to the DOE U.S. DRIVE FCTT.
  - Provided input on new AST protocols.
  - Provided input on refined Fuel Cell targets and Multi-Year Research, Development, and Demonstration Plan.

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INTRODUCTION

This task provides technical support to fuel cell component and system developers, free of cost to the developer, by experts within the LANL fuel cell team. In addition, it also includes participation in the further development and validation of single cell test protocols; interacting with Durability Working Groups, USCAR, and the U.S. DRIVE FCTT; and making technical experts available to DOE and FCTT.

The work performed this fiscal year, approved by the DOE, included customers and collaborators from industry, national laboratories, and various universities. In FY 2016, technical assistance included requests from Ford Motor Company, Pajarito Powders, LLC (Albuquerque, NM), IUPUI, ElectroChem Inc., Nissan, Savannah River National Laboratory (SRNL), and Amalyst.

APPROACH

LANL experts provide support to a broad customer base using available in-house equipment such as Scanning electron microscopy, energy dispersive X-ray analysis, X-ray fluorescence spectroscopy, differential scanning calorimetry, Fourier transform infrared spectroscopy, tapered element oscillating microbalance, thermogravimetric analysis, simultaneous thermogravimetric analysis and differential scanning calorimetry, differential thermal analysis, solid-phase and liquid-phase nuclear magnetic resonance, gas chromatography, mass spectroscopy, X-ray diffraction, solid-state diffuse reflectance infrared Fourier transform spectroscopy, Raman spectrometer, electron beam evaporation, radio frequency magnetron sputtering, alternating current impedance spectroscopy, and Brunauer-Emmett-Teller surface area measurements. LANL also has 38 test stands equipped with automated data acquisition and computer-controlling features that is available for this project. In FY 2016, requests included, but weren't limited to, perform fuel cell comparison tests on different non-Pt anode catalyst materials, PGM-free materials and Pt/PBI-graphene, Pt-amine, Pt-SO_3-H, and a family of PtNi catalysts by verifying performance and durability. In addition to using X-ray tomography to investigate the integrity and stability of a nanofiber electrode structure using high resolution imaging (1–2 μ), and deposition techniques to assist with ceramic coating of fuel cell components and catalyst development. Requests also included evaluation of high potential redox active species present in select PGM-free fuel cell electrocatalysts for the oxygen reduction reaction in acidic medium and a two-cell fuel cell stack for hydrogen–air application and provide feedback to assist in its commercialization.

RESULTS

We provided completed results and findings to our customers as detailed in the *FY 2016 Accomplishments* section of the 2016 DOE Hydrogen and Fuel Cells Program Annual Merit Review presentation. Due to the length constraint of this report, we will only discuss results from some of the objectives mentioned above.

For example, we worked closely with IUPUI to evaluate the performance and durability of their MEAs made with graphene-type supports. Several challenges exist when graphene is used as a support for Pt catalysts in fuel cell type applications. Because graphene is hydrophobic, it is often difficult to create a uniform dispersion of Pt on the substrate and hard to establish a bond between the two materials. Also, graphene substrates form layering sheets that can inhibit gas access to the catalyst which can reduce the electrochemical surface area and typically there are defects at the edges which can facilitate carbon corrosion due to its poor stability. By overcoming these challenges, the expectations are improvements in fuel cell performance and durability. IUPUI scientists functionalized the graphene to reduce hydrophobicity, introduced spacers to prevent layering of graphene sheets, and seal their edges to eliminate defects. Tests were conducted on these materials using, 5 cm^2 MEAs, made with Nafion® 212 membranes and 0.1 mg/cm^2 Pt at each electrode. The performance was measured using both H_2–air and H_2/O_2 at 80°C, 100% relative humidity, and 300 kPa of back pressure. Figure 1 shows the impact of adding spacers. The results show the significant improvements at the larger current densities, particularly in the mass transport region for the samples prepared with spacers. This may be due to the spacers producing a more open-type structure with pores and channels formed to allow better mass transport. We also tested their MEAs made with spacers using nanographene versus graphene as the support under the same operating conditions aforementioned as well as using the DOE AST protocol for supports (Triangle sweep: 500 mV/s from 1.0–1.5 V, H_2/N_2, 80°C, ambient pressure, and 100% relative humidity). The MEA made with nanographene and spacers performed much better at the beginning of life but suffered from larger losses in mass activity and electrochemical surface area after the 10,000 cycles using the AST (results not shown here).

In the analysis of samples provided by Nissan, LANL used high resolution imaging (X-ray tomography) to investigate the integrity and stability of their nanofiber structure used for MEAs. The MEA was aged using the above mentioned DOE AST protocol for 1,000 cycles. High resolution images comparing a "fresh" vs. "aged" MEA, showed only minimal changes in the electrode structure. This is captured in Figure 2.

The LANL-Ford cooperation began in FY 2015 and is ongoing. LANL is using a novel system for multi-layer deposition of materials to treat surfaces in order to

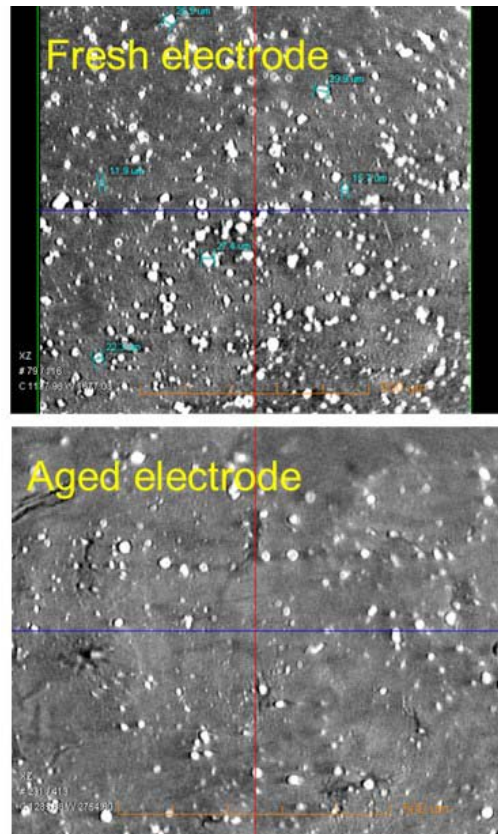

FIGURE 2. X-ray tomography results of nanofiber MEAs: fresh vs. aged

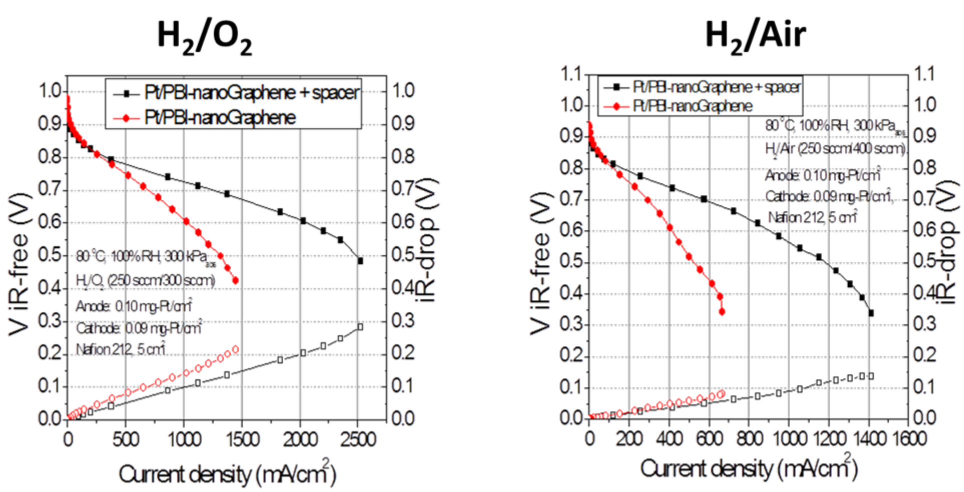

FIGURE 1. The impact of spacers on Pt/PBI-nanographene: H_2–air and H_2/O_2

prevent corrosion. LANL performed eight depositions and characterized each using X-ray diffraction, scanning electron microscopy, and energy dispersive X-ray analysis related to catalyst support materials, and over 100 depositions with 42 samples delivered for metal-ceramic coatings for bipolar plate materials.

In this fiscal year, LANL and SRNL started complementary work to investigate high potential redox active species present in select non-PGM fuel cell electrocatalysts for the oxygen reduction reaction in acidic medium. SRNL is currently conducting a study to investigate the electrochemistry of a catalyst prepared by SRNL from a metallic organic framework that displays high oxygen reduction reaction activity and a high potential redox couple measured during potential cycling. LANL will perform an electrochemical characterization similar to SRNL's study using catalysts synthesized from different materials and methodologies. Results produced will be compared to LANL's high activity catalysts.

FUTURE WORK

A large portion of work in this project is still ongoing and expected to continue into FY 2017. Below we list the collaborators along with the details of the anticipated work.

- Ford Motor Company:
  - Complete the test matrix of bi-polar plate multi-layer passivation samples.
  - Optimize coating catalyst supports with metals deposited using LANL acoustic agitation approach developed in FY 2015 and tested in FY 2016.
- Amalyst:
  - Non-Pt Anode catalyst (verify performance, durability)
- IUPUI:
  - Investigate novel catalyst–MEA architecture.
  - Continue testing PtNi MEAs.
- SRNL:
  - PGM-free testing of metal organic framework catalyst
- ElectroChem, Inc.:
  - Stack testing and validation
- Pajarito Powder, LLC:
  - Continue testing MEA samples with DOE ASTs.
- Participate on the DOE USCAR U.S. DRIVE Fuel Cell Tech Team.
- Continue to support DOE working groups.
  - Durability Working Group
  - Mass Transport Working Group
- Provide technical assistance to developers as requested by DOE and report on the results to DOE and the U.S. DRIVE Fuel Cell Tech Team.

FY 2016 PUBLICATIONS/PRESENTATIONS

A significant portion of this effort often goes unpublished at the customer's request.

1. *Polybenzimidazole (PBI) functionalized nanographene as highly stable catalyst support for polymer electrolyte membrane fuel cells (PEMFCs)*, Le Xin, Fan Yang, Yang Qiu, Aytekin Uzunoglu, Tommy Rockward, Rodney L. Borup, Lia A. Stanciu, Wenzhen Li and Jian Xie (submitted to Journal of the Electrochemical Society).

2. *Novel Catalyst-Layer Structures with Rationally Designed Catalyst/Ionomer Interfaces and Pore Structures Aided by Catalyst Functionalization,* Le Xin[1], Kang Yu[2], Fan Yang[1], Aytekin Uzunoglu[3], Tommy Rockward[5], Paulo Ferreira[2], Rod L. Borup[5], Jan Ilavsky[6], Lia A. Stanciu[3,4], Jian Xie[1*]