V.E.2 Technical Assistance to Developers

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Project Start Date: October 2006
Project End Date: Project being discontinued at end of current funds

Overall Objectives

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

- Testing and validation of materials.
- Participation in the further development and validation of single cell test protocols.
- Assistance to Durability Working Groups, the U.S. Council for Automotive Research (USCAR), and the USCAR/DOE Driving Research and Innovation for Vehicle efficiency and Energy sustainability (U.S. DRIVE) Fuel Cell Technical Team.
- Providing technical experts available to DOE and the Fuel Cell Technical Team.

Fiscal Year (FY) 2017 Objectives

- Perform quantitative comparison of oxygen reduction reaction (ORR) activity and cyclic voltammogram redox peaks of different platinum group metal (PGM)-free catalysts defining what correlation exists from minimum two sets of externally provided PGM-free catalysts.
- Provide Ford a sufficient quantity (200 mg) of reactively sputter-deposited niobium oxide layers onto Ford-provided substrates for catalyst support synthesis for Ford electrochemical evaluation of NbO_x intermediate layer.
- Participate with Fuel Cell Tech Team with a minimum of six tech team meetings in person and reports on results of tech assistance to developers.
- Hold annual fuel cell training workshop for industrial and academic participants; give reports on results of tech assistance to developers.
- Test University of California, Los Angeles' (UCLA's) Mo-doped Pt_3Ni octahedra catalysts for performance and durability.
- Characterize and test industry catalyst for performance and durability and investigate the stability of a different support.

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) Electrode Performance

FY 2017 Accomplishments

- Ford Motor Co.
  - Provided eight catalyst samples
  - Performed approximately 134 depositions for multi-layering metal plates
- UCLA Catalysts
  - Performed initial testing of Mo-doped Pt_3Ni octahedra catalysts (10,000 cycles)
- Blue-O Technology, Inc.
  - Prepared catalyst inks and membrane electrode assemblies (MEAs)
  - Conducted initial performance tests in fuel cell: pressure and temperature dependence
  - Air vs oxygen polarization curves
  - X-ray diffraction showed well defined catalyst structures
- Savannah River National Laboratory (SRNL)
  - Independent tests results did correlate: redox potentials vs. ORR activity
- National Institute of Standards and Technology (NIST), University of Hawaii, University of Tennessee-Knoxville
  - Provided neutron imaging hardware and guidance on its usage

- Participate on the DOE/USCAR U.S. DRIVE Fuel Cell Tech Team
- Continue to support DOE working groups (WG)
  - Durability WG
  - Mass Transport WG
- Provide technical assistance to developers as requested by DOE and report on the results to DOE and the U.S. DRIVE Tech Team
- Provided input on refined fuel cell targets and multi-year program 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 the participation in the further development and validation of single cell test protocols, interacting with durability working groups, the USCAR and the U.S. DRIVE Fuel Cell Technical Team, and making technical experts available to DOE and the Fuel Cell Tech Team.

The work performed this fiscal year, approved by the DOE included customers and collaborators from industry, national laboratories, and various universities. In FY 2017, technical assistance included requests from Ford Motor Company, SRNL, Argonne National Laboratory, Lawrence Berkeley National Laboratory, NIST, National Physical Laboratory, Blue-O Technology, Inc., and several universities and colleges.

APPROACH

Our approach for this effort is governed by our customers' requests and the DOE's interest. Support is generally provided using available in-house equipment such as scanning electron microscopy or 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/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 are available for this project. In FY 2017, customers and their requests included:

- SRNL
  - Testing and validation of PGM-free
- NIST
  - Neutron imaging hardware
- University of Tennessee
  - Neutron imaging hardware
- University of Hawaii
  - Neutron imaging hardware
- Ford Motor Co.
  - Bipolar plate
  - Catalyst development
- Blue-O Technology
  - Catalyst testing of Pt, PtM, and Pt/TiO_2
  - Catalyst performance and durability
  - Investigate novel support materials
- UCLA
  - Catalyst testing of Mo-doped Pt_3Ni
  - MEA performance and durability using accelerated stress tests

RESULTS

In this section, we highlight some results from this year's accomplishments. These results and discussions are concise due to a length constraint of this document.

We continued working with Ford Motor Co. on novel catalyst support coating and metal bipolar plates. They were provided eight catalysts samples for their catalyst support request and 20 samples with approximately 134 depositions performed for multi-layering metal plates utilizing four different customizable sputtering systems to achieve desired thickness of titanium and gold, which acts as corrosion barrier on stainless steel substrates for metal bipolar plates. These materials were tested at their facilities and the results presented at the Electrochemical Society Meeting.

In 2015, UCLA reported high catalytic activity with rotating disk electrode activity with Mo-doped Pt_3Ni octahedral catalysts. In FY 2017, LANL received catalysts to test for performance and durability in a fuel cell for comparison against DOE targets. Catalyst inks and MEAs were prepared and tested. Polarization curves were measured as a function of voltage cycles to gauge both performance and durability. The voltage cycling followed a DOE accelerated stress test that cycled the voltage in a square wave pattern between 0.6 V to 0.95 V. We also measured the electrochemical surface area and mass activity of the catalyst. Polarization curves showed 20 mV in losses after 10,000 V-cycles measured at 0.8 A/cm^2. The electrochemical surface area lowered by 12% while the mass activity reduced by 18%. These losses are below the DOE targets, but testing is not complete considering the DOE protocols call for 30,000 cycles.

Blue-O Technology requested independent verification of performance and durability of their novel catalyst which utilizes a different support. LANL performed electrochemical characterization using rotating disk electrode to test the durability of the catalyst support, prepared catalyst inks, and made MEAs for fuel cell testing as well as performed X-ray diffraction on catalyst samples (Figure 1). Initial test results were performed on MEAs with un-optimized ionomer to catalyst ratios (total Pt loading <0.1 mg/cm^2). Performance at these ultra-low Pt loadings show promise and rotating disk electrode tests demonstrated a durable catalyst support.

LANL along with SRNL conducted independent experiments to investigate the electrochemistry of Fe-N-C catalyst. They focused on the redox couple in the cyclic voltammogram and whether or not it correlates to ORR performance. Both labs utilized different mixtures of H_2SO_4 and $HClO_4$ to perform their measurements. As a result, different redox potentials of the Fe-based catalyst were observed as the electrolyte ratios varied. The ORR of the catalyst was for each mixture and finding directly contradicts the literature. Both labs' results agreed and found no correlation between redox peaks and ORR performance (Figure 2).

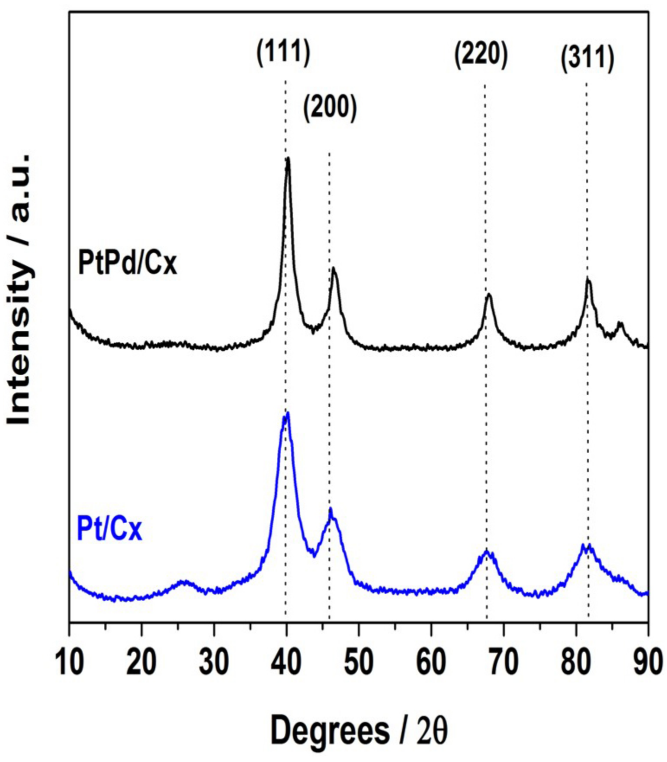
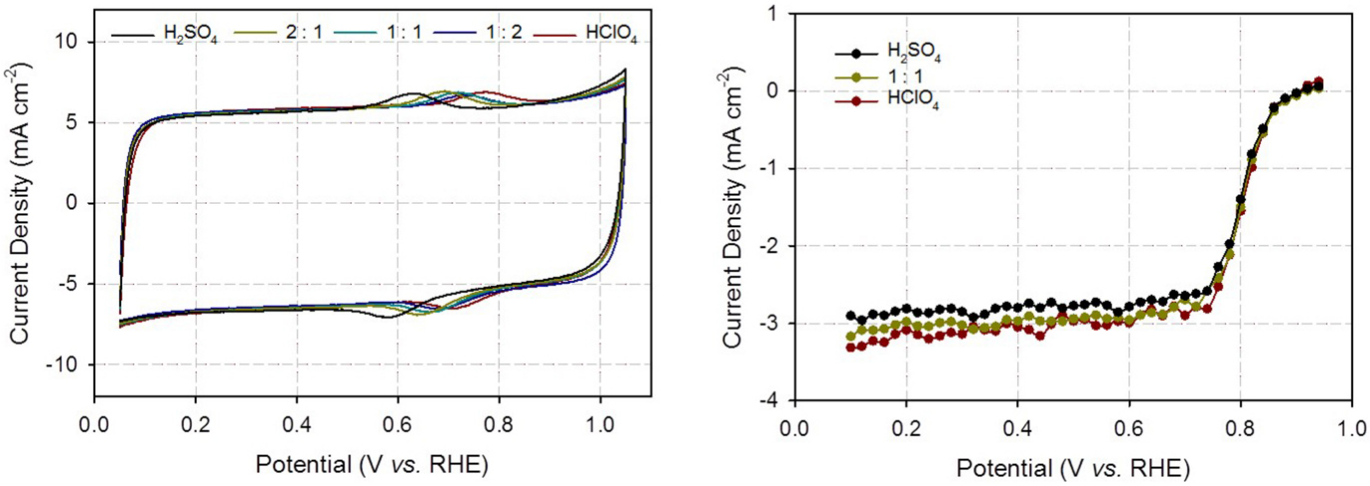


FIGURE 1. X-ray diffraction results of Blue-O Technology catalyst samples

UPCOMING ACTIVITIES

The Fuel Cell Technologies Office has decided to discontinue this project; as a result, the completion of any ongoing and or future work is uncertain. Below we still list the details of the anticipated work:

- UCLA catalysts
  - Continue to perform testing of Mo-doped Pt_3Ni octahedra catalysts
- Blue-O Technology
  - Complete catalyst testing of Pt, Pt, and Pt TiO_2
  - Catalyst performance and durability
  - Investigate novel support materials
  - ElectroChem, Inc.
  - Stack testing and validation (awaiting stack)
- SRNL
  - Compete results with PGM-free testing to solidify finding: redox potentials vs. ORR activity
- NIST, University of Hawaii, University of Tennessee-Knoxville
  - Provide neutron imaging hardware and guidance on its usage
- Participate on the DOE/USCAR U.S. DRIVE Fuel Cell Tech Team
- Continue to support DOE working groups
  - Durability WG
  - Mass Transport WG
- Provide technical assistance to developers as requested by DOE and report on the results to DOE and the U.S. DRIVE Tech Team



RHE – reference hydrogen electrode

FIGURE 2. Left graph shows cyclic voltammograms for different mixtures of H_2SO_4 and $HClO_4$; right graph compares ORR for H_2SO_4, $HClO_4$, and a 50% mixture of the two

FY 2017 PUBLICATIONS/PRESENTATIONS

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

1. Le Xin, Yu Kang, Fan Yang, Aytekin Uzunoglu, Tommy Rockward, Paulo Jorge Ferreira, Rod L. Borup, Jan Ilavsky, Lia Stanciu, Jian Xie, Novel Catalyst-Layer Structures with Rationally Designed Catalyst/Ionomer Interfaces and Pore Structures Aided By Catalyst Functionalization, 2016/9/1, Meeting Abstracts, The Electrochemical Society.

2. Le Xin, Fan Yang, Aytekin Uzunoglu, Tommy Rockward, Rod L. Borup, Lia Stanciu, Jian Xie, Highly Stable Hierarchical Polybenzimidazole (PBI) Grafted Graphene/Nanographene Hybrids As Catalyst Supports for Polymer Electrolyte Membrane Fuel Cells, 2016/9/1, Meeting Abstracts, The Electrochemical Society.

3. Jacob S. Spendelow, Luis Castanheira, Gareth Hinds, Tommy Rockward, David A. Langlois, Rangachary Mukundan, Rod L. Borup, Measurement of Local Electrode Potentials in an Operating PEMFC Exposed to Contaminants, 2016/9/1, Meeting Abstracts, The Electrochemical Society.

4. Xin, Le; Yang, Fan; Qiu, Yang; Uzunoglu, Aytekin; Rockward, Tommy; Borup, Rodney L.; Stanciu, Lia A.; Li, Wenzhen; Xie, Jian, Polybenzimidazole (PBI) Functionalized Nanographene as Highly Stable Catalyst Support for Polymer Electrolyte Membrane Fuel Cells (PEMFCs), Journal of the Electrochemical Society (2016), 163(10), F1228–F1236.

5. Kerrie K. Gath, Mark Ricketts, Jun Yang, Chunchuan Xu, and Shinichi Hirano, Multi-Layer Thin Film Coatings on Bipolar Metal Plates for PEMFC, 2016/9/1, Meeting Abstracts, The Electrochemical Society.