V.A.11 Non-Precious Metal Fuel Cell Cathodes: Catalyst Development and Electrode Structure Design

Piotr Zelenay (Primary Contact), H. Chung,
U. Martinez, G. Purdy, G. Wu
Materials Physics and Applications Division
Los Alamos National Laboratory (LANL)
Los Alamos, NM 87545
Phone: (505) 667-0197
Email: zelenay@lanl.gov

DOE Manager
Nancy Garland
Phone: (202) 586-5673
Email: Nancy.Garland@ee.doe.gov

Subcontractors
- J. Ziegelbauer, General Motors, Honeoye Falls, NY
- M. Odgaard and D. Schlueter, IRD Fuel Cells, Albuquerque, NM
- S. Litster and S.K. Babu, Carnegie Mellon University, Pittsburgh, PA
- M. Neidig and J. Kehl, J. Kneebone, University of Rochester, Rochester, NY
- Z. Chen, D. Higgins, and G. Jiang, M.-H. Seo, University of Waterloo, Waterloo, Canada
- K.L. More and D. Cullen, Oak Ridge National Laboratory, Oak Ridge, TN

Project Start Date: April 1, 2013
Project End Date: March 31, 2016

Overall Objectives

Advance non-precious-grade metal (non-PGM) cathode technology through the development and implementation of novel materials and concepts for oxygen reduction catalysts and electrode layers with:

- Oxygen reduction reaction (ORR) activity viable for practical fuel cell systems
- Much improved durability
- Sufficient ionic/electronic conductivity within the catalyst layer
- Adequate oxygen mass transport
- Effective removal of the product water

Fiscal Year (FY) 2014 Objectives

- Optimize the most active Fe-N-C catalysts by the heat-treatment approach for maximum hydrogen-air fuel cell performance
- Synthesize metal-free non-PGM catalysts
- Use surface probe approaches to identify the structure of active sites
- Optimize non-PGM cathodes using experimental and modeling tools
- Scale up membrane electrode assembly (MEA) to 50 cm^2

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section (3.4.5) of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan [1]:

(A) Durability (catalysts, electrode layers)

(B) Cost (catalyst, MEAs)

(C) Performance (catalysts, electrodes, MEAs)

Technical Targets

Non-PGM fuel cell catalyst research in this project focuses on the DOE technical targets outlined in Table 3.4.13 in section 3.4.4 (Technical Challenges) of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan [1]. The ultimate technical targets of the project are:

- Volumetric catalyst activity in an MEA at 0.80 V (iR-free[1]), 80°C: ≥ 300 A cm^{-3}
- Four-electron selectivity (rotating ring disc electrode): ≥ 99% (H_2O_2 ≤ 1%)
- MEA maximum power density at 80°C: ≥ 1.0 W cm^{-2}
- Performance loss at 0.80 A cm^{-2} after 30,000 cycles in N_2: ≤ 30 mV

[1] iR – internal resistance

FY 2014 Accomplishments

- A high-surface-area, graphene-rich polyaniline-iron-carbon catalyst was synthesized through a novel three-step heat-treatment strategy. It was tested in a fuel cell, reaching a current density of 0.19 A cm^{-2} at 0.80 V (iR-corrected) and a volumetric current density of 84 A cm^{-3} at 0.80 V (iR-corrected).
- A new “nanofoam” catalyst was developed using multiple nitrogen precursors, providing a microporous surface area of 1,585 $m^2 g^{-1}$ and significantly enhanced mass transport. In fuel cell testing, a power density of 0.87 W cm^{-2} was achieved at 1.0 bar O_2.

- A metal-free catalyst was developed, showing a $E_{1/2}$ of 0.32 V vs. the reference hydrogen electrode.
- Viability of the surface probe approach in combination with Mössbauer and nuclear resonance vibrational spectroscopy (NRVS) was demonstrated to identify the possible structure of active sites in Fe-based non-PGM catalysts.
- Computational simulation of transport process in a nano-X-ray tomography (nano-XRT) imaged non-PGM electrode was completed.

* * * * *

INTRODUCTION

Cost studies estimate that conventional Pt-based catalysts comprise almost half of the entire proton exchange fuel cell (PEFC) stack cost and as much as 20% of the overall system cost [2]. Since Pt is a precious metal resource, it will not benefit from economies of scale and is subject to volatile price fluctuations and monopolized global distributions. Reducing or ideally replacing expensive Pt catalysts in PEFC systems is highly desirable and has been a major focus of catalyst research and development efforts. Owing to the inherently slow ORR, the cathode requires much higher Pt content than the anode, at which the relatively fast anodic hydrogen oxidation reaction is taking place. Developing non-PGM catalysts for use at the cathode would provide the most significant economic advantage. However, hindering the successful elimination of Pt cathode catalysts in PEFC systems is the lack of non-PGM catalysts that can provide sufficiently high ORR activity and durability under fuel cell operative conditions.

APPROACH

In this multi-faceted research project we intend to accomplish major advancements in non-PGM cathode technology through the development and implementation of novel materials and concepts. Our catalyst development effort concentrates on novel synthesis methods, including heat-treated catalysts obtained using multiple nitrogen precursors, alternative supports for heat-treated catalysts, non-pyrolyzed phthalocyanine-derived catalysts and metal-free catalysts based on nitrogen-doped carbon nanostructures. Comprehensive testing of materials, including initial performance screening by in situ electrochemical techniques and ex situ characterization to assess catalyst activity and durability, identify catalytic sites and validate fuel cell performance of the most-promising materials, represents a substantial fraction of the efforts.

Since the use of non-PGM catalysts will almost certainly result in cathodes with greatly increased thickness compared to Pt-based cathodes, significant effort is required to address the resulting electrode design challenges. The key issues include oxygen mass transport, proton conductivity and the prevention of catalyst layer flooding. The research focuses initially on the validation of the General Motors electrode model for non-PGM electrodes and parameter estimation using in situ microstructured electrode scaffold diagnostics. Electrode optimization is based on insight obtained from the modeling, nano-XRT imaging, and advanced microscopy analysis. In parallel to the catalyst and electrode development components of this project, MEA fabrication, optimization and scale up will be performed to obtain a 50-cm^2 (or larger, if needed) MEA with the best-performing materials for independent testing and evaluation at a DOE-approved facility.

RESULTS

(a) Demonstrated $i_{0.8V}$ > 190 mA cm^{-2} and a volumetric activity of 84 A cm^{-3} at 0.80 V (iR-free) for non-PGM catalyst in single-cell MEA. High-surface-area polyaniline-iron-carbon (PANI-Fe-C) catalysts were prepared, optimized and tested for fuel cell performance. Using 30 wt% Fe in the catalyst and employing a three-step heating synthesis protocol, PANI-Fe-C allowed for an ORR current density of 190 mA cm^{-2} at a voltage of 0.80 V (iR-free) in fuel cell testing (Figure 1). This significantly surpasses the September 2014 ORR catalyst development milestone stating a specific activity of 150 mA cm^{-2}.

A new catalyst fabrication approach combining multiple nitrogen precursors was also applied to prepare a highly ORR-active non-PGM catalyst with a favorable micro- and meso-structure to facilitate mass transport through the catalyst layer. Improved mass transport is demonstrated by

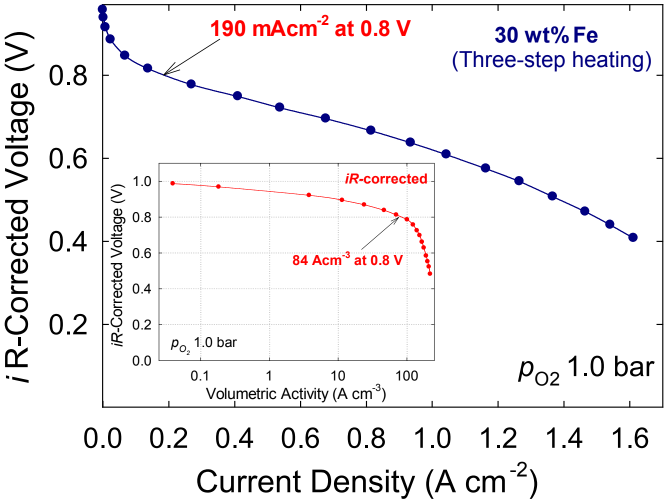

FIGURE 1. Fuel cell performance of a PANI-Fe-C non-PGM catalyst demonstrating ORR current density close to 190 mA cm^{-2} and volumetric current density of 84 A cm^{3} at 0.80 V.

a current density >3.0 A cm^{-2} at a cell voltage of 0.20 V (iR-free) and O_2 partial pressure (p_{O2}) of 1.0 bar, with minimal performance enhancement realized with a further increase in the partial pressure to 2.0 bar (Figure 2). A current density of 160 mA cm^{-2} was achieved through fuel cell testing at 0.80 V (iR-free), reaching the September 2014 ORR catalyst development milestone, with another catalyst developed in this project. At 0.40 V and 1.0 bar O_2 partial pressure, a very high current density and a power density of 0.87 W cm^{-2} was obtained, due to the high catalyst activity and facile mass transport.

(b) Image three-dimensional structure of a state-of-the-art LANL electrode by nano-XRT and compute effective transport properties. Nano-XRT was used to image non-PGM electrodes (Figure 3a-c). The nano-XRT imaging provides the three-dimensional micro-scale and macro-scale structure of the electrode. Through image processing, computational reconstruction and numerical simulations, the nano-XRT data was used to extract the key morphological transport properties of the electrode (Figure 3d). The obtained information will be essential to

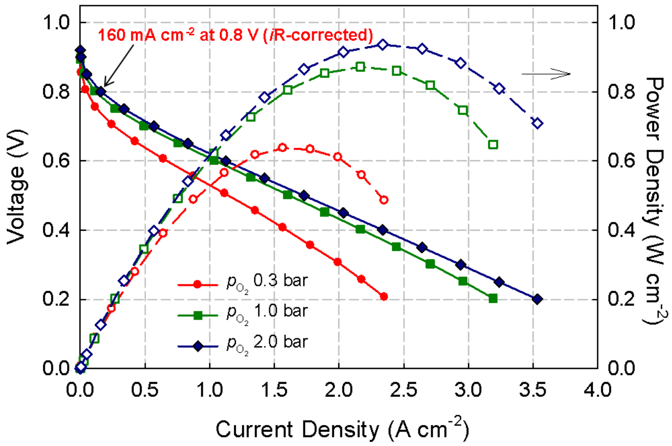

FIGURE 2. Fuel cell performance of the CM-PANI-Fe-C catalyst demonstrating (a) power density of 0.87 W cm^{-2} at 0.40 V and (b) ORR current density of 160 mA cm^{-2} at 0.80 V (iR-corrected). Anode: 0.5 mg cm^{-2} Pt (E-TEK) 1.0 bar (partial pressure), H_2 200 sccm; cathode: ~4.0 mg cm^2, 1.0 bar (partial pressure), O_2 200 sccm; membrane: Nafion® 211; cell: 80°C; 100% relative humidity.

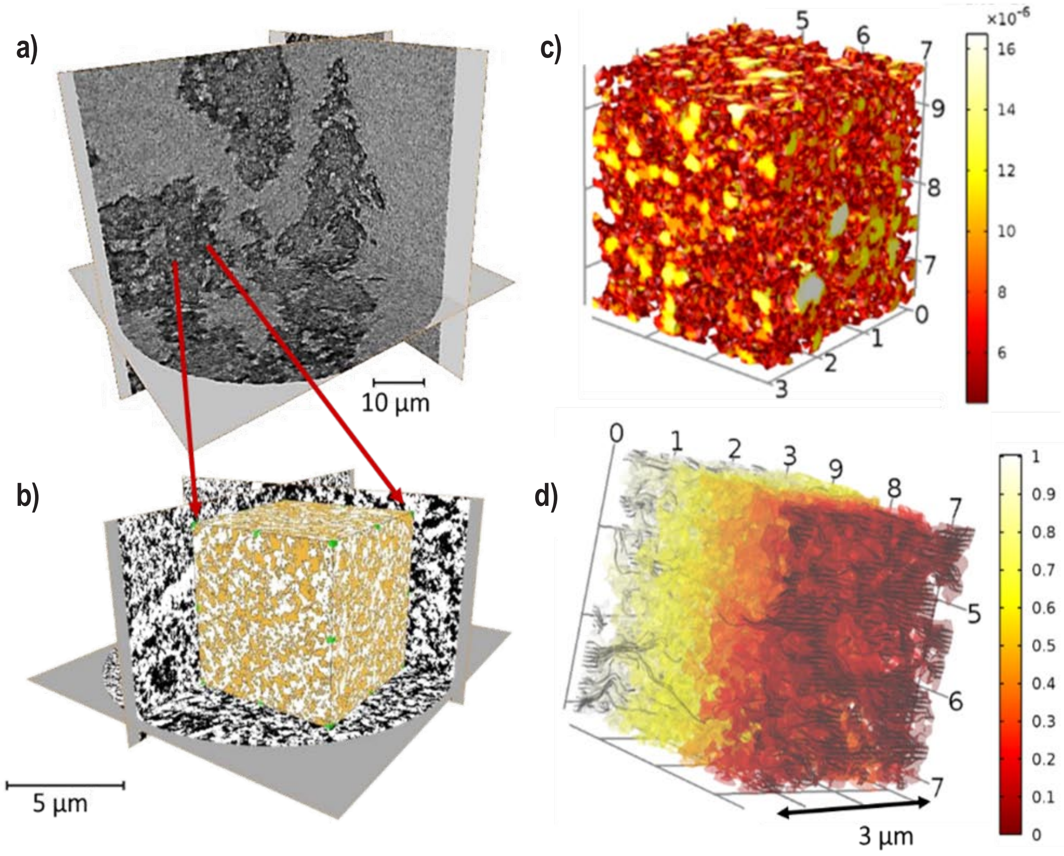

FIGURE 3. Ortho-slices from a large-field-of-view nano-XRT scan of the non-PGM electrode (a) and (b) the pore|solid phase segmented (pores white) data from a high resolution (50 nm) scan of the solid dense (dark) region in (a). (c) Three dimensionally reconstructed pore volume from the high resolution scan colored by the local oxygen diffusion coefficient calculated from local pore sizes. (d) Computational simulation of gas diffusion in the non-PGM electrode using pore geometry from nano-XRT imaging. Color is oxygen concentration.

future non-PGM electrode structure design and optimization. The March 2014 electrode design, integration and optimization milestone has been completed.

(c) Validate surface-probe approach for non-PGM catalysts using Mössbauer spectroscopy. Detection of surface iron based on perturbation by a gaseous probe provides a key advantage in that it allows for characterization of iron sites on the catalyst surface, accessible to gas phase reactants (i.e., oxygen). Mössbauer spectroscopy was used in combination with $NO_{(g)}$ probing to demonstrate the presence of Fe-species in PANI-Fe-C catalyst. Validation of the surface-probe approach with Mössbauer spectroscopy and previously with NRVS accomplishes the March 2014 characterization and active-site determination milestone. During the beam time at Advanced Photon Source (June, 2014), NRVS was used again to confirm the surface features of the same catalyst samples probed by Mössbauer spectroscopy. Reproducible data were obtained and relevant analysis is currently in progress.

(d) Electron microscopy analysis of state-of-the-art LANL catalysts and electrodes. Advanced scanning electron microscopy (SEM), transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM) were performed to study the new PANI-Fe-C materials in order to provide additional insight into the structure of high-performance catalysts with high surface area. As shown in Figure 4, the predominant morphology consisted of an intimate mixture of agglomerated Ketjenblack (KJ) particles and rumpled, multi-layered graphene sheets (Figure 4a). Fe particles, most likely FeS, were also occasionally identified (orange arrow, Figure 4a). An SEM image (Figure 4b) of the same region, shown in the TEM image in Figure 4a, also indicates that the rumpled, sheet-like morphology of the multi-layered graphene envelopes the KJ particles. An ADF-STEM image of a multi-layered graphene sheet and associated electron energy loss spectroscopy (EELS) analysis (Figure 4c) indicates that single Fe atoms are dispersed across the surface of the graphene. These Fe atoms were highly mobile under the electron beam, indicating that Fe is not incorporated within the carbon lattice. Additionally, EELS identified nitrogen in thicker areas of the layered graphene sheets.

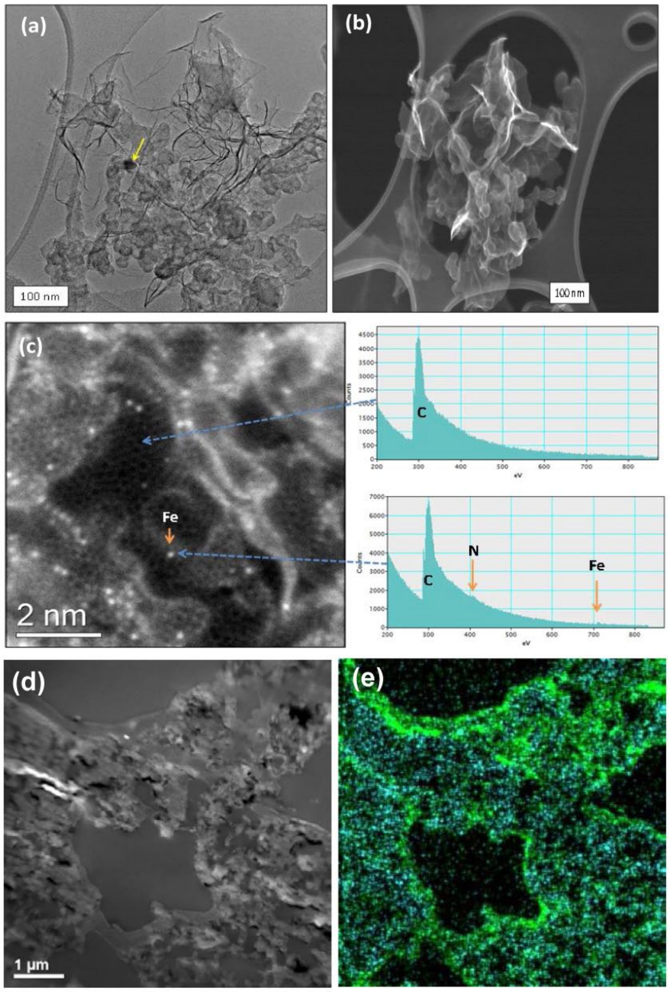

FIGURE 4. Microscopy studies for newly developed non-PGM catalysts and cathodes. (a) TEM image for PANI-Fe-C (30 wt% Fe) catalyst and (b) SEM image of the same agglomerated area showing KJ particles mixed with multi-layered graphene sheets. The yellow arrow indicates a large FeS particle. (c) Annular dark-field imaging-STEM of graphene sheet and associated electron energy loss spectra showing presence of single Fe atoms on surface of graphene. (d, e) Microstructure and chemistry of PANICM-Fe-KB + 35% Nafion® cathode in MEA: fluorine, associated with ionomer, is shown as green; and sulfur, predominantly associated with all carbon phases in catalysts, shown in blue.

The non-PGM catalysts, prepared by mixing nitrogen precursors, were integrated into electrodes containing Nafion® ionomer and studied using microscopy. A relatively thick (0.1-0.5 μm) ionomer film was found to surround CM-PANI-Fe-KJ catalyst agglomerates (Figure 4d), but very little ionomer penetrated inside the agglomerates. Elemental mapping (Figure 4e) shows fluorine (green, associated with ionomer) and sulfur (blue, associated with all carbon phases and ionomer). Areas where the imaged sulfur does not overlap with the fluorine can be attributed to ionomer-free carbon. These results suggest that the optimal dispersion of ionomer within carbon-based catalysts in the cathode is a key strategy to increasing catalyst utilization, thereby significantly improving catalyst performance.

CONCLUSIONS

- A high-surface-area, graphene-rich, polyaniline-derived catalyst was synthesized and tested in a fuel cell reaching a current density of 0.19 A cm^{-2} at 0.8 V (iR-free), exceeding the September 2014 current density milestone (150 mA cm^{-2}).
- A volumetric activity of 84 A cm^{-3} was achieved at 0.8 V (iR-free), an over 30% enhancement in the

volumetric current density compared to the 2011 baseline (60 A cm^{-3}), approaching the June 2014 catalyst activity milestone (100 A cm^{-3}).

- Computational simulation of transport processes in the nano-XRT imaged non-PGM electrode was completed, achieving the December 2013 electrode imaging milestone.
- Advanced electron microscopy provided insightful information about the catalyst structure at the atomic level, as well as about the ionomer dispersion in non-PGM cathodes.

FUTURE DIRECTIONS

- Synthesis of non-PGM catalysts supported on highly-graphitic carbon(s) as a way of enhancing active-site density and improving performance durability.
- Use of developed surface-probe approach to identify the non-PGM ORR active-site structures.
- Full implementation of advanced catalyst characterization methods (NRVS, magnetic circular dichroism, Mössbauer spectroscopy, microstructured electrode scaffold, low-voltage aberration-corrected STEM, nano-XCT, X-ray absorption, thermogravimetric analysis, porosimetry, etc.) in non-PGM catalysis studies.
- Initiation of the predictive model for non-PGM catalyst layers (ORR activity, conductivity, and O_2 transport); validation of the preliminary model.
- Fabrication of MEAs with optimized microstructure and morphology.
- Demonstration of Generation-1 spray-coated MEA with non-PGM cathode.

SPECIAL RECOGNITIONS & AWARDS/ PATENTS ISSUED

1. Piotr Zelenay has been named a Fellow of The Electrochemical Society, 2014.

FY 2014 PUBLICATIONS/PRESENTATIONS

(a) Peer-Reviewed Publications

1. W. Gao, G. Wu, M. Janicke, D. Cullen, R. Mukundan, J. Baldwin, E. Brosha, C. Galande, P. Ajayan, K. More, A. Dattelbaum, P. Zelenay, "Ozonated Graphene Oxide Film as a Proton Exchange Membrane", *Angew. Chemie Int. Ed.*, **53** (14), 3588-3593 (2014).

2. S. Litster, W. Epting, E. Wargo, S. Kalidindi, E. Kumbur, "Morphological Analyses of Polymer Electrolyte Fuel Cell Electrodes with Nano-Scale Computed Tomography Imaging", *Fuel Cells*, **13** (5), 935-945 (2013).

3. M. Seo, D. Higgins, G. Jiang, S. Choi, B. Han, Z. Chen, "Theoretical and experimental study of highly durable iron phthalocyanine derived non-precious catalyst for oxygen reduction reaction", *J. Mater. Chem. A.*, submitted (2014).

4. P. Zamani, D. Higgins, F. Hassan, J. Wu, S. Abureden, Z. Chen, "Electrospun Iron–Polyaniline–Polyacrylonitrile Derived Nanofibers as Non-Precious Oxygen Reduction Reaction Catalysts for PEM Fuel Cells", *Electrochim. Acta*, accepted, (2014).

5. D. Higgins, M.A. Hoque, F, Hassan, J.Y. Choi, B. Kim, Z. Chen, "Oxygen Reduction on Graphene-Carbon Nanotube Composites Doped Sequentially with Nitrogen and Sulfur" *ACS Catalysis*, accepted 2014.

6. Q. Li, G. Wu, D.A. Cullen, K.L. More, N.H. Mack, H.T. Chung, P. Zelenay "Phosphate-Tolerant Oxygen Reduction Catalysts" *ACS Catalysis*, accepted 2014.

(B) Conference Presentations

1. G. Wu, P. Zelenay, "Mn-Based Non-Precious Catalyst for the Polymer Electrolyte Fuel Cell Cathode", *225th Electrochemical Society Meeting*, Orlando, Florida, May 11-16 (2014).

2. U. Martinez, G. Purdy, M. Misra, N. Mack, D. Cullen, H. Chung, K. More, A. Dattelbaum, A. Mohite, P. Zelenay, G. Gupta, "Graphene-Oxide-Based Electrocatalysts for Oxygen Reduction Reaction", *225th Electrochemical Society Meeting*, Orlando, Florida, May 11-16 (2014).

3. H. Chung, G. Wu, U. Martinez, P. Zelenay, "Carbon-based catalysts for oxygen reduction in polymer electrolyte fuel cells", *247th American Chemical Society Meeting and Exposition*, Dallas, Texas, March 16-20 (2014) Invited lecture.

4. D. Kim, N. Zussblatt, P. Minoofar, R. Ganguli, P. Zelenay, B. Chmelka, "Effects of transition metals on oxygen reduction and oxygen evolution electrocatalytic activities of N-doped mesoporous carbon catalysts", *247th American Chemical Society Meeting and Exposition*, Dallas, Texas, March 16-20 (2014).

REFERENCES

1. *Multi-Year Research, Development and Demonstration Plan: Section 3.4 Fuel Cells*, Fuel Cell Technologies Program, 2011. http://www1.eere.energy.gov/hydrogenandfuelcells/mypp/pdfs/fuel_cells.pdf

2. James et al., DTI, Inc., 2010 DOE Hydrogen Program Review, Washington, DC, June 9, 2010