



Access & Excellence



DOE Hydrogen Program

Montana Palladium Research Initiative

Detection of Trace Platinum Group Element Particulates with Laser Spectroscopy

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Montana State University-Billings
May 15, 2007

Project ID
#FCP2

Overview

Timeline

- Project start date 8/31/06
- Project end date 12/31/07
- Percent complete 5%

Budget

- Total project funding
 - DOE share \$339114
 - Contractor share\$113546
- Funding received in FY06 \$0
- Funding for FY07 \$452660

Barriers

- Barriers
 - Fuel Cell Durability and Performance
- Technical Targets
 - Fuel Cell Membrane Testing, Analysis, and Characterization to achieve a durability >40,000 hours

Partners

- PLUG Power, Montana Dakota Utilities, D. W. Hahn at Florida State University
- Project management: David McGinnis



Abstract

Laser-induced breakdown spectroscopy (LIBS) will be developed as a diagnostic technique to detect and characterize nanoparticles of the platinum group elements (PGEs) to support field trials to be conducted at Montana State University-Billings to assess the performance and survivability of proton exchange membrane fuel cells (PEMFC). The presence of nanoparticles of PGEs in filters and membranes is an indication of PEMFC degradation. The scope of this project is twofold. The first goal is to develop LIBS to detect and characterize PGE nanoparticles. The second goal is to apply this technique to monitor the performance of PEMFCs during the field trials by analyzing PEMFC filters and membranes for PGE nanoparticles. The membranes and filters will also be analyzed using well-established analytical chemistry techniques and the results compared.



Scope of Project

The first phase, or calibration phase, of the project involves correlating the LIBS signal with the distribution of particle size in a flow of PGE particulates. The PGE nanoparticles will be produced in a particle generator by atomizing an aqueous solution of platinum and palladium salts in a carrier gas of dry nitrogen. As the water undergoes desolvation, nanoparticles on the order of 10 nm and greater are formed. The laser beam is focused into the particle flow generating a LIBS signal. The LIBS signal depends on many factors. Most importantly, maximum sensitivity depends on finding strong PGE emission lines that are free from spectral interference from other species that are present. Other important factors are the laser pulse energy density and wavelength, and the time delay from the initiation of the microplasma to measurement of the LIBS signal. The LIBS signal will also depend strongly on the particle size distribution and on the number of particles actually in the microplasma. The particle size distribution can be determined from statistical analysis of shot-to-shot LIBS signals using techniques established by Prof. D. W. Hahn at Florida State University. Prof. Hahn will collaborate with us on this aspect of the research.



Scope of Project (continued)

The second phase of the project is applying the calibrated LIBS technique to detect and characterize Pt and Pd nanoparticles imbedded in PEMFC filters and membranes during field trials to be conducted at Montana State University-Billings (MSU-Billings) designed to assess the long term deterioration of the major components of PEMFCs using. Plug Power will also analyze the membranes and filters using well-established analytical chemistry techniques and the results will be compared.



Milestones

- Milestone 1: By early summer, complete the particle generator and setup the LIBS experimental arrangement. Calibrate the LIBS signal using known PGE standards.
- Milestone 2: By late summer, establish the relationship between PGE particle size and the intensity and frequency of occurrence of LIBS signals.
- Milestone 3: After installation on the MSU-Billings campus of the fuel cell units in early fall, begin LIBS experiments to analyze PGE particulates in membranes and filters from operating fuel cells. Characterize PGE particle-size distributions on PEMCFC membranes and filters in collaboration with the PEMFC field-study operational plan. These membranes and filters will then be sent to Plug Power scientists for analysis using well-established analytical chemistry techniques and the results compared. This work will continue for the duration of the PEMC field trials.



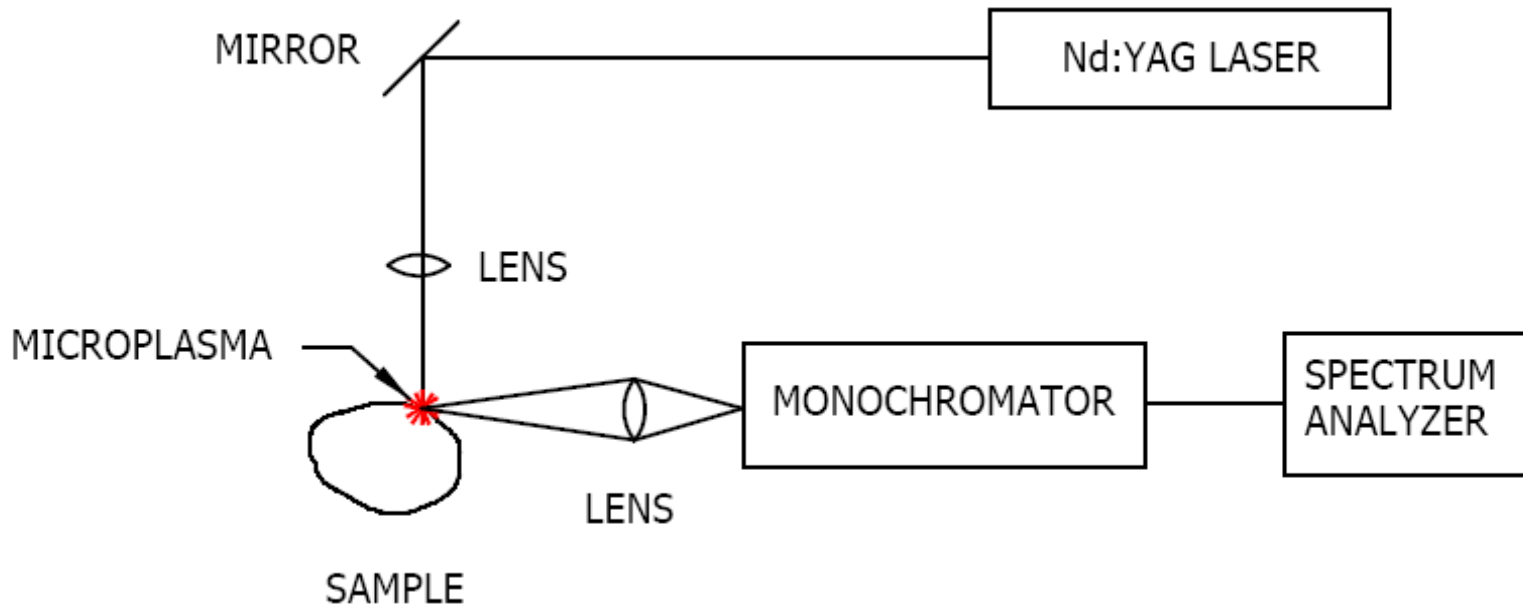
Laser-induced Breakdown Spectroscopy (LIBS)

- Laser beam is focused onto a substrate or into a liquid, gas, or aerosol.
- Intense radiation at the focal point creates a microplasma with a gas temperature ~ 15000 K.
- Microplasma vaporizes material and excites characteristic atomic spectral lines.
- Analysis of emission spectrum determines species type and concentration.

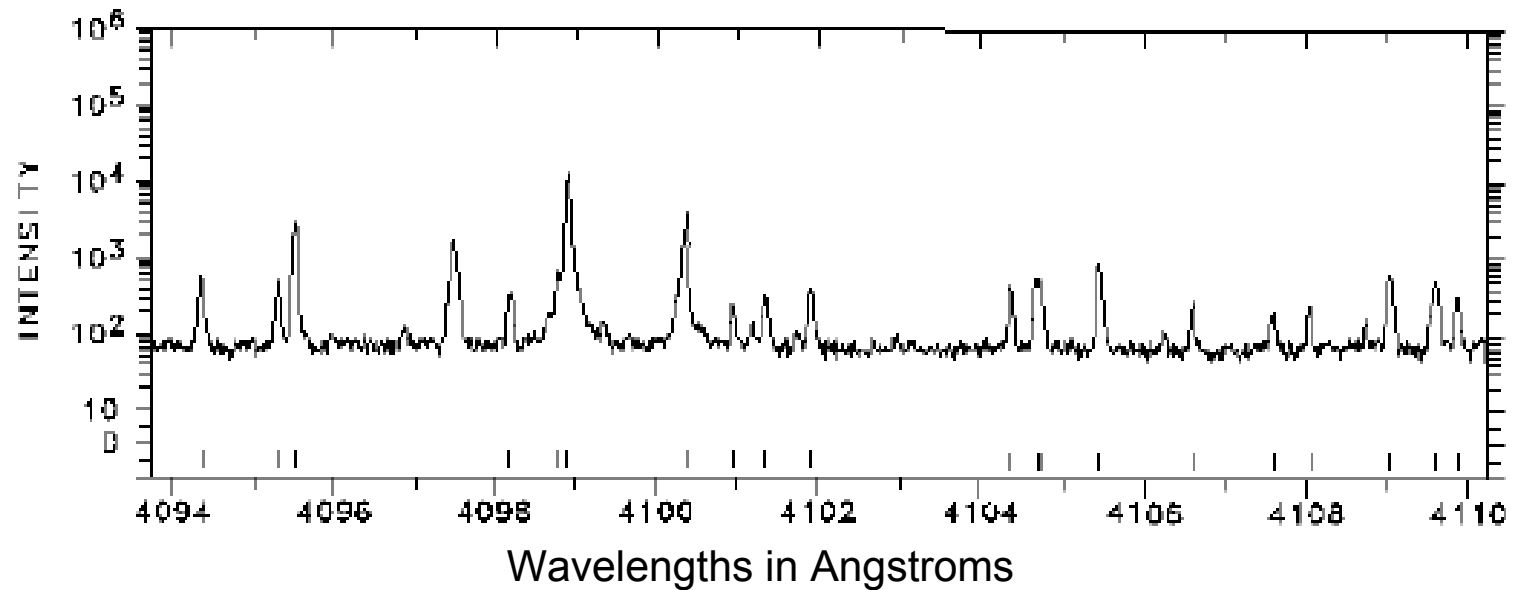
LIBS (continued)

- LIBS is a straightforward technique
- Requires:
 - high-powered pulsed laser
 - monochromator and spectral analyzer
- Can be portable and engineered for industrial applications

LIBS Experimental Schematic



Partial Emission Spectrum of Platinum



Progress to Data

- Laser system and spectrometer have been ordered.
- Nanoparticle generator for 10 nm and greater particle sizes is under construction. Particle generator is based on a design by D. W. Hahn at Florida State University and is vital for signal calibration.
- Prof. Hahn is internationally recognized for his work on LIBS in aerosols and has agreed to collaborate with us on data analysis.





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Permeable Membrane Fuel Cell Field Trials

Brian Gurney

Montana State University-Billings

May 15, 2007

Project ID

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Barriers

- Barriers
 - Reformer capital cost
 - Reformer Manufacturing
 - Operation and Maintenance
- Technical Targets
 - Cold startup time
 - Survivability at ambient temperatures
 - Durability and degradation

Partners

- PLUG Power, Montana Dakota Utilities
- Project management: David McGinnis



Abstract

Numerous small scale hydrogen reformers and fuel cell systems have been successfully demonstrated in laboratory and field settings. Most demonstrations have focused on proof of concept and/or system performance. Little if any data has been published on the long term deterioration of the major components within the reformer and the associated effects on system performance over time. This study will quantify the degradation of critical components utilizing a fleet of LPG fueled reformer/fuel cell systems. The systems will be installed in a field environment and operated over a range of usage patterns. The study will incorporate a two-level design of experiments to isolate the effect of usage patterns on component degradation. The proposed study will comprise a minimum of 12 months of system operation with an option to extend a subset of the fleet in order to explore longer term effects. The fleet will be managed by MSU-Billings in conjunction with Montana Dakota Utilities (MDU). Plug Power will be the equipment supplier and provide chemical and physical analysis for the study. The results of the study will be published in literature and will be available to academia and the industry.

This research addresses DOE Technical Targets 3.4.7 related to:

1. Cold startup time
2. Survivability at ambient temperatures
3. Durability and degradation



Task 1: Install and run 8 fuel cell / reformer units

- 8 fuel cell/reformer units will be installed and operated on LPG fuel for 12 months.
- Units will be subjected to different usage patterns, and the impacts of differences in usage characteristics on durability of the units will be studied.
- Durability metrics to be studied are number of cold start/stop cycles (1 per month or 1 per week) and load profile (dynamic building load or continuous equipment loads).
- Condensate formation on shutdown is hypothesized to accelerate the buildup of contaminants in the deionized (DI) water circuit. Samples of DI water and stack coolant will be collected monthly from each unit and analyzed to quantitatively determine rates of contaminant buildup. Steam generator heat exchanger fouling is presumed to correlate with buildup of contaminants in the DI water circuit.
- Contaminant analysis will be performed at MSU-Billings. DI water samples will be analyzed to measure changes in conductance, pH, total dissolved solids, hardness, and dissolved concentrations of the following elements (as ions, of course): F, Na, Mg, Ca, Al, Cr, Sb, Si, Fe, Cu, Ni, and Zn.



Task 2: Measurement of heat exchanger fouling rates

- Fouling rates for heat exchangers in small scale hydrogen reformers are not well known. In this task, three key heat exchangers will be removed from each reformer and analyzed after the exposure test is completed.
- The overall heat transfer coefficient in each heat exchanger will be measured in a laboratory test stand, and compared to the as-built heat transfer coefficient, to determine a mean fouling factor.
- Start/stop cycling is hypothesized to accelerate fouling in the autothermal reformer (ATR) heat exchanger, due to the introduction of air on shutdown. The ATR heat exchangers will be characterized on a test stand located at Plug Power. overall heat transfer coefficients in these heat exchangers will be measured in a laboratory test stand located at the supplier. This data will benefit the entire fuel cell industry.

Task 3: Measurement of reformer material corrosion and scale buildup rates.

- Hydrogen corrodes and embrittles most metals. Although these phenomena are well known, remarkably little data is available on corrosion rates of metal alloys at the conditions typical of distributed PEM fuel cell systems.
- The reducing environment can also lead to carburization of metal alloys. These phenomena combine to cause heat exchanger fouling and eventually can lead to loss of integrity of the reactor wall. In this task, the ATR reactor walls and ATR heat exchanger will be sectioned and subjected to metallographic analysis. Sectioned samples will be examined for precipitation at grain boundaries and will be characterized by the depth of the penetrated layer. In this manner, corrosion rates for typical alloys used in fuel processor reactor and heat exchanger construction may be correlated to start/stop cycling and load profile.
- The steam generator vessels will also be sectioned and metallographically analysed. The thickness of the scale buildup will be characterized, and samples of the scale will be collected and subjected to elemental analysis. We will attempt to correlate thickness of scale buildup with water contaminant measurements (from Task 1) and start I stop cycling.

Task 4: Measurement of reformer catalyst degradation rates

- After completion of the tests, the reformer reactors, consisting of the ATR, the water-gas-shift reactor (WGS), the preferential CO oxidation reactor (PROX), and the anode tailgas oxidizer (ATO) will be removed from each unit and returned to Plug Power for catalyst activity measurements.
- Start /stop cycling is known to cause WGS shift catalyst deactivation; load fluctuations are hypothesized to cause catalyst temperature variations which can accelerate ATR, PROX, and ATO catalyst deactivation.
- The activity of the aged samples will be compared to the fresh catalyst samples to determine the extent of catalyst deactivation. ATR catalyst deactivation is typically characterized by an increase in methane slip; WGS and PROX catalyst deactivation are typically characterized by a decrease in CO oxidation; ATO catalyst deactivation is typically characterized by a decrease in methane destruction activity.

Milestones

- **Complete schedules, purchase orders and subcontracts**
 - July 2007
- **Site Engineering, Approval of Plans (city) and Interconnection with campus power grid plan**
 - July 2007
- **Site Prep, Fuel Cell Installation**
 - October 2007
- **Startup, System Verification and Commissioning**
 - November 2007
- **Implement Research Plan**
 - Start November 2007
- **Decommissioning and Site Restoration**
 - Summer 2009



Fuel Cell Unit



The latest generation 5kW stationary fuel cell from Plug Power will be used in these experiments.