

# V.A.9 Montana Palladium Research Initiative: Detection of Trace Platinum Group Element Particulates with Laser Spectroscopy\*

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\*Congressionally directed project

(G) Startup and Shutdown Time and Energy/Transient Operation

## Technical Targets

The technology developed by this project will support the DOE 2011 Technical Target (Table 3.4.4):

- Increase durability of stationary PEMFCs to 40,000 hours.

## Accomplishments

- Developed and calibrated the LIBS experimental system including specialized data acquisition and analysis procedures to detect and quantify PGE nanoparticles in extremely dilute aqueous suspensions.
- Measured palladium nanoparticle concentration of 5 parts-per-billion (ppb) in water.
- Detected trace amounts of palladium in fuel cell water.
- Work to monitor fuel cell water for Pt and Pd nanoparticles has commenced and will continue for the duration of the project.

## Objectives

Develop instrumentation to study dilute nanoparticle suspensions of the platinum group elements (PGEs).

- Adapt laser-induced breakdown spectroscopy (LIBS) to characterize and quantify emissions of nanoparticles of PGEs from proton exchange membrane fuel cells (PEMFCs).
- Use LIBS to monitor PEMFC water for the presence of PGE nanoparticles in support field trials of PEMFCs underway at Montana State University-Billings (MSU-Billings).

## Technical Barriers

This project addresses the following technical barriers from the Fuel Cells Membrane Testing and Characterization Table 3.4.15, Task 3 of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-year Research, Development, and Demonstration Plan (revision 2007, updated 4/27/07), 3.0 Technical Plan, Section 3.4 Fuel Cells:

- (A) Durability
- (C) Performance



## Introduction

It is well known that proton exchange membranes are subject to chemical attack and mechanical breakdown. To support long-term field trials and degradation studies of PEMFC propane-fueled reformer/fuel cell systems and their critical components, a method for noninvasive, real time assessment of the state of the membrane is highly desirable. An indication of membrane electrode assembly (MEA) failure is the presence of PGE nanoparticles in the fuel cell water [1,2]. MEA degradation can therefore be studied by monitoring the fuel cell water for PGE nanoparticles. To accomplish this goal, LIBS is being developed to provide sensitive, on-site quantitative analysis of fuel cell water for palladium and platinum nanoparticles.

## Approach

Conventional LIBS is a straightforward laser spectroscopic technique capable of real time in situ material analysis of solids, liquids, and gases. With LIBS, a beam of pulsed laser light is focused on to the medium of interest. The intense laser light causes

dielectric breakdown of the medium and creates a microplasma with a peak temperature of around 15,000 K. The high plasma temperature reduces material ablated by the laser pulse to its elemental form, and excites atoms to higher energy states. As the excited atoms decay back to their ground states, they emit characteristic spectral light. The intensity of this light is proportional to the concentration of the emitting species. Due to the dynamics of the microplasma, peak emission intensities are delayed by 10 to 50  $\mu$ s from the initiation of the plasma.

The main problem with conventional LIBS is that realistic detection limits are only on the order of 0.1 to 1 part-per-million (ppm). For comparison, detection limits for inductively-coupled plasma spectroscopy are on the order of ppb or less. The reason for the comparatively poor detection limits of LIBS is that the continuum background radiation emitted by the microplasma is intense. In order for atomic emission lines to emerge above this background, there must be a relatively large amount of ablated analyte (on the order of 0.1 pg) in the microplasma. The difficulty with continuum radiation is particularly severe when LIBS is applied to dilute particulate suspension. In an effort to improve signal-to-noise ratios, LIBS signals are typically the average of data acquired from hundreds or even thousands of laser shots. With dilute particulate suspensions, it is often the case that less than 1% of the laser shots will generate a LIBS spectrum. Important spectral information is entirely lost in the continuum radiation.

For LIBS to be successful with dilute particulate suspensions, a data acquisition and analysis technique called conditional analysis [3] has been developed. Conditional analysis evaluates the individual LIBS spectrum for the desired spectral information. If the intensity of the emission line of interest is greater than a threshold value, typically 20-30% above the background radiation, the spectrum is recorded as a hit. Otherwise, the spectrum is not recorded. This technique ensures that the accumulated LIBS spectra are not overwhelmed by background radiation. Using conditional analysis, Hahn has demonstrated that the detection limit for metallic nanoparticle aerosols is on the order of 200 parts-per-trillion [4]. We are adapting the LIBS conditional analysis technique to aqueous suspensions of PGE nanoparticles.

The approach taken is to develop the established and proven technology of LIBS specifically to study PGE-particulate emission from fuel cells as a result of membrane degradation. This direct approach will result in a versatile, sensitive, real-time, and potentially in situ diagnostic technique to evaluate PEMFC particulate emissions. The first phase, or calibration phase, of the project involves correlating the LIBS signal with mass concentration in an aqueous flow of PGE particulates [3]. The second phase of the project

is applying the calibrated LIBS technique to detect and characterize Pt and Pd nanoparticles found in the fuel cell water as a result of the degradation of the MEAs in support of field trials that are being conducted at MSU-Billings to assess the long-term deterioration of the major components of PEMFCs.

## Results

Initial calibration experiments using conditional analysis to relate the LIBS signal to PGE mass concentration were adapted from a method developed by Hahn [3] for the calibration of LIBS signal from aerosol suspensions. An aerosol stream of PGE nanoparticles was generated using a nebulizer filled with a dilute aqueous suspension of PGE nanoparticles. The nebulized suspension was then entrained in a flow of carrier gas and transported to the microplasma. It was realized that this calibration method was not practical for dilute aqueous suspensions since the nebulization of PGE suspension decreases the particle concentration by a factor of about 1,000, and the LIBS signals were too infrequent. As a result of this work, the experimental procedure was redesigned to detect PGE nanoparticles directly in water. To our knowledge, this is the first time conditional analysis has been used with LIBS to study aqueous suspensions of nanoparticles.

Performing LIBS on aqueous suspension has some unique challenges. Most notably, water is very effective at quenching the microplasma. Peak atomic emissions occur from 1 to 10  $\mu$ s after the laser pulse. Also, spectral emission lines from molecular species such as the OH radical rapidly appear. The vibrational structure of these spectra can be a serious source of spectral interference. Another problem is that the shock wave produced by the microplasma can splatter water onto the collection optics. This was overcome by sampling a thin laminar flow with the microplasma instead of the surface of a bulk volume of water.

Work to date has concentrated on palladium and the PEMFCs that contain palladium. The partial emission spectrum of palladium is shown in Figure 1. This spectrum indicates the principal palladium emission lines. The LIBS signal used in this work is the background-corrected intensity of the 340.458 nm line. Calibration of the LIBS signal was accomplished by relating the average LIBS signal from prepared aqueous nanoparticle suspensions, collected using conditional analysis, to the mass concentration. The minimum palladium concentration measured during calibration experiments was 5 ppb. The palladium detection limit achievable with our system is estimated to be about 0.5 ppb. For comparison, the detection limit for palladium using inductively-coupled plasma spectroscopy is about 1 ppb. The calibration curve is shown in Figure 2.

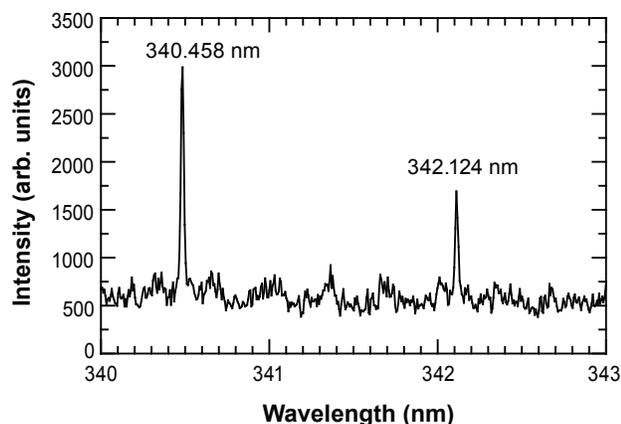


FIGURE 1. Partial Emission Spectrum of Palladium

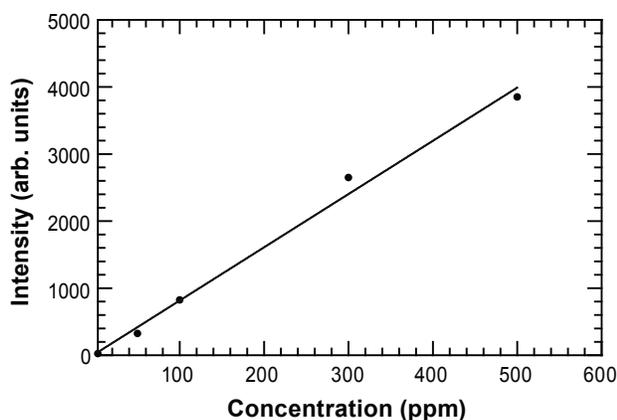


FIGURE 2. Calibration Curve of the LIBS Signal as a Function of Pd Concentration

The LIBS spectrum of a single particle of palladium in fuel cell water is shown in Figure 3. This spectrum was obtained using conditional analysis and was the only hit out of 10,000 laser shots. From the calibration curve, it was determined that the mass concentration of palladium in this sample of fuel cell water was about 10 ppb. Figure 4 shows LIBS data averaged over all of the 10,000 laser shots. In Figure 4, there is no suggestion of the palladium line. Figures 3 and 4 are convincing demonstration of the ability of conditional analysis to extract sporadic spectral data from otherwise overwhelming background radiation. The regular spectral structure in Figure 4 is the partial vibrational spectrum of the OH molecule.

The data presented in Figure 3 is by no means compelling evidence for the presence of palladium in the fuel cell water. We estimate that palladium particles must be greater than about 500 nm in diameter in order to produce a LIBS signal that can be detected with conditional analysis. There is no reason to expect the palladium particles in the fuel cell water to be this large. To investigate this, a proprietary coagulant was

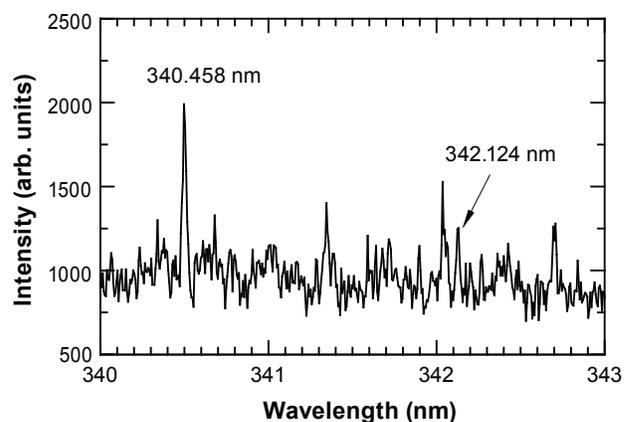


FIGURE 3. LIBS Spectrum from a Single Pd Particle in Fuel Cell Water (The spectrum is the result of one hit out of 10,000 laser shots.)

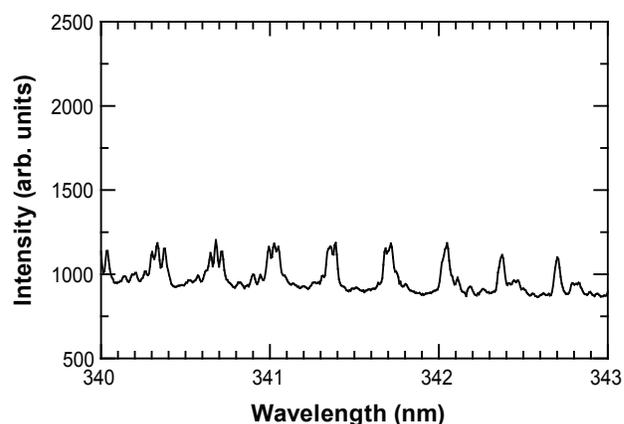


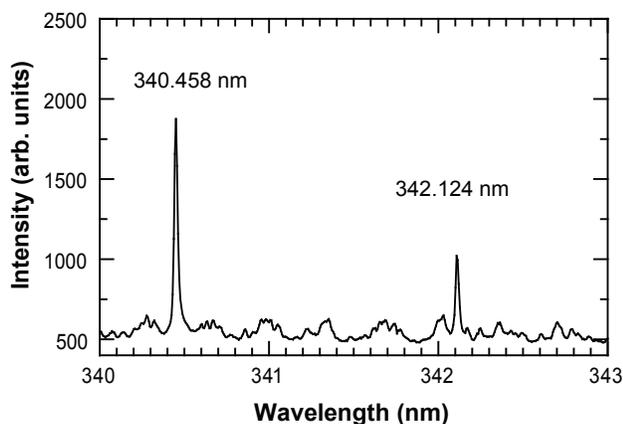
FIGURE 4. Average LIBS Spectrum of 10,000 Laser Shots from Fuel Cell Water (This is a conventional LIBS spectrum. The data from the single particle hit of Figure 3 is lost in the background.)

added to the fuel cell water in an attempt to coalesce the palladium nanoparticles. In this case, 1,553 palladium hits were recorded out of 10,000 laser shots, corresponding to a palladium mass concentration of about 15 ppm. The coagulant dramatically increased the LIBS signal and the presence of palladium in the fuel cell water was clearly confirmed. The average LIBS spectrum is presented in Figure 5.

## Conclusions and Future Directions

LIBS is a straightforward powerful laser-spectroscopic technique for elemental analysis:

- We have demonstrated that LIBS when combined with conditional data acquisition and analysis is capable of very sensitive trace analysis of aqueous palladium nanoparticle suspension.
- Palladium was detected in PEMFC water indicating MEA degradation.



**FIGURE 5.** Palladium LIBS spectrum from fuel cell water to which a coagulant was added. The LIBS signal is the average of 1,553 hits out of 10,000 laser shots.

- Since the fuel cell water can be analyzed within minutes of being collected, the technique is providing on-site support of PEMFC degradation studies.
- Calibration work with platinum will commence during the summer of 2008.
- The monitoring of fuel cell water for the presence of platinum and palladium nanoparticles will continue for the duration of the project.

## FY 2008 Publications/Presentations

1. S. C. Snyder and W. G. Wickun, "Detection of Trace Platinum Group Element Particulates with Laser Spectroscopy", 2008 Department of Energy Hydrogen Program Review, Washington D.C., June 9-13, 2008.
2. W. G. Wickun, "Detection of Trace Platinum Group Element Particulates with Laser Spectroscopy", Annual Meeting of the Montana Academy of Science, Montana Tech, Butte, MT, 12 April 2008.

## References

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2. F.A. deBruijn, V.A.T. Dam, and G.J.M. Janssen, *Fuel Cells* 08, pp. 3-22 (2008).
3. D.W. Hahn, J.E. Carranza, and G.R. Arsenault, *Review of Scientific Instruments* 72, pp. 3706-3713 (2001).
4. D.W. Hahn, *Applied Physics Letters* 72, pp. 2960-2962 (1998).