

# The Detection of Palladium Particles in Proton Exchange Membrane Fuel-Cell Water by Laser-Induced Breakdown Spectroscopy (LIBS)

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Laser-induced breakdown spectroscopy (LIBS) using conditional data analysis was applied to aqueous suspensions of palladium particles in the reformate water of palladium-based proton exchange membrane fuel cells. A significant amount of palladium was found in the water, indicating degradation of the fuel-cell cathode catalytic layers. The palladium particle-size detection limit was found to be about 400 nm. Calibration procedures to quantify the palladium concentration are discussed.

Index Headings: Laser-induced breakdown spectroscopy; LIBS; Laser diagnostics; Particulate suspensions; Proton exchange membrane fuel cells; PEM fuel cells.

## INTRODUCTION

The catalytic properties of the platinum group elements (PGE) are well known. Platinum is extensively used as a catalyst in automobile catalytic converters and is currently the most common catalyst in proton exchange membrane (PEM) fuel cells (also referred to as polymer electrolyte membrane fuel cells). This type of fuel cell is considered to be the best option for use in vehicles and stationary applications because of their efficiency and relatively low operating temperatures.

A PEM fuel cell is composed of anode and cathode catalytic layers separated by the PEM. The catalyst layers are formed by depositing nanoparticles of platinum on to a carbon substrate. These combined layers are referred to as the membrane electrode assembly (MEA). Electrical current is produced in the MEA by generating electrons and protons from hydrogen at the anode layer in an oxidation reaction catalyzed by platinum. Protons pass through the PEM to the cathode layer while the electrons flow around the MEA to the cathode layer. At the cathode layer, the protons and electrons recombine and react with oxygen from the air to produce water. This reaction is also catalyzed by platinum. To produce the desired electrical power, multiple MEAs are assembled in series, forming what is known as a fuel-cell stack. A thorough review of PEM fuel cells can be found elsewhere.<sup>1,2</sup>

An important issue that must be addressed before PEM fuel cells can become a practical alternative energy source is the durability of the catalytic layers. The carbon substrate supporting the platinum nanoparticles is susceptible to chemical attack and mechanical failure.<sup>3-6</sup> The catalytic material is also subject to chemical attack. In the case of the cathode catalytic layer, the catalytic material is often an alloy

of platinum and chromium. Trace amounts of platinum and chromium have been found in the water formed at the cathode. This is an indication of the dissolution of the platinum/chromium alloy as a result of the oxidation reaction at the cathode.<sup>7</sup> These findings suggest that monitoring in real time the cathode water from a fuel-cell stack for the presence of catalyst nanoparticles would provide a continuous assessment of the status of the cathode catalytic layers during operation.

The cost of PEM fuel cells is another issue central to the development of this technology. Platinum is quite expensive. Research is being conducted on ways to reduce the platinum loads of the catalytic layers and at the same time improve performance.<sup>8</sup> At the present time, however, palladium is a promising alternative to platinum because of its excellent catalytic properties and lower price.

Field trials comparing the performance and durability of stationary palladium with stationary platinum PEM fuel-cell systems were conducted on the campus of Montana State University-Billings as part of the Montana Palladium Research Initiative (MPRI). To support the field trials, laser-induced breakdown spectroscopy (LIBS) was developed to detect the presence of trace amounts of palladium nanoparticles suspended in the cathode water to monitor degradation of the palladium fuel cells. The application of LIBS to study PGEs is limited. It has been used to detect palladium on bacterial cellulose membranes,<sup>9</sup> but to the authors' best knowledge, has not until now been applied to PGE aqueous suspensions.

LIBS is conceptually straightforward. Intense radiation from a pulsed-laser beam is focused to a small spot. A small amount of material present in the focal volume is vaporized, and a high-temperature microplasma is created. Analysis of the emission spectra from the microplasma determines the elemental composition of the ablated material. LIBS is essentially a noninvasive diagnostic tool that can provide real-time trace elemental analysis of solids, liquids, gases, and aerosols. It is a well-established technique that has been used extensively in the laboratory and has been developed for use in the field.<sup>10</sup>

Despite its apparent simplicity, using LIBS to analyze dilute aerosol or aqueous suspensions of nanoparticles can be challenging. If the particle size is too small, there is not enough vaporized material in the microplasma to give a spectral signal with an adequate signal-to-noise (SNR) ratio. Particle size detection limits also depend on the strengths of the emission lines of interest. For example, using prominent emission lines, a mass detection limit of about 3 fg of calcium and magnesium has been reported for aerosol dispersions of 175 nm diameter particles containing calcium and magnesium.<sup>11</sup> Obviously, a particle must be present when the

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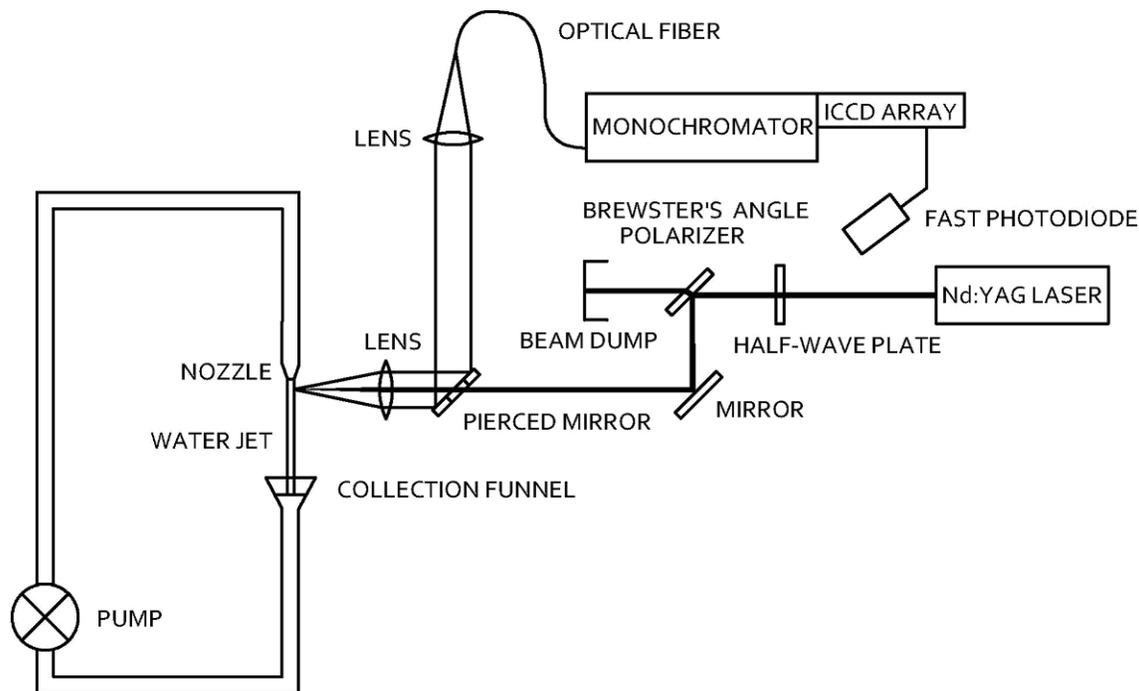


FIG. 1. Experimental schematic.

microplasma forms or there is no spectral signal. With conventional LIBS, data is typically acquired by accumulating signals 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. The accumulated data is essentially continuum radiation and the LIBS targeted atomic emission signal is overwhelmed. For LIBS to be successful with dilute particulate suspensions, a data acquisition and analysis technique called conditional analysis has been developed.<sup>12,13</sup> Conditional analysis evaluates the spectrum generated by each laser shot for the desired spectral information. If the intensity of the atomic 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. Conditional analysis greatly improves the signal-to-noise ratio (SNR) and detection limit. Hahn has demonstrated a detection limit on the order of 200 parts-per-trillion (ppt) for metallic nanoparticle aerosols using LIBS with conditional analysis.<sup>14</sup>

Using LIBS to analyze aqueous suspensions has additional problems. If the laser is focused into the bulk of the water, severe splashing occurs due to the shock wave created as the microplasma is formed. To minimize this effect, care must be taken to focus the laser on the surface of the water. A second problem that occurs is that water tends to quench the microplasma and the atomic emission lines.<sup>15</sup> A third problem is that molecular emission lines, most notably from the hydroxide ion, are excited and add structure to the background radiation. In-depth discussions of the application of LIBS to liquids can be found elsewhere.<sup>16–21</sup>

## EXPERIMENTAL METHOD

A schematic of the experimental layout is presented in Fig. 1. The laser used to create the microplasma was a Continuum Model Surelite III Q-switched neodymium-doped yttrium

aluminum garnet (Nd:YAG) laser operated at its fundamental wavelength of 1064 nm. The laser-pulse duration was about 8 ns, and the pulse rate was 5 Hz. The laser was operated at full power, but the pulse energy was adjusted to 300 mJ per pulse by rotating a half-wave plate in conjunction with a Precision Photonics part number PO1056-FY Brewster's angle polarizer. Following the work by Hahn and Lunden,<sup>11</sup> the laser beam with a diameter of about 10 mm passed through a pierced mirror and was focused to a spot size of about 100  $\mu\text{m}$  on the surface of the water jet using a 90 mm focal length fused silica lens. The resulting LIBS signal was collected by the same lens used to focus the laser beam and reflected by the pierced mirror to a second 90 mm,  $f/5.6$  lens. This lens focused the light on to a circular 1 mm diameter optical fiber bundle consisting of nineteen optical fibers with diameters of 200  $\mu\text{m}$  for transmission to an Acton Research Spectra Pro 2750 monochromator with a focal length of 0.75 m. At the entrance slit of the monochromator, the nineteen optical fibers are transformed to a vertical linear array. A 3600 grooves/mm holographic grating was used to disperse the light. The entrance slit width of the monochromator was 50  $\mu\text{m}$ . The spectrally resolved light was detected by a Princeton Research PI-MAX 512SB gated blue-intensified charge-coupled device (ICCD) array. The ICCD array size was  $512 \times 512$  pixels. The image of the ends of the optical fibers was confined vertically to the central 175 pixels. These pixels were binned together, and the remaining pixels were turned off to reduce noise. The horizontal pixels were not binned together. The ICCD array was thermoelectrically cooled to a temperature of  $-20^\circ\text{C}$  and operated at a relative gain of 150 for all experiments. The detector was triggered by a voltage pulse from a Thorlabs Model DET 10A fast photodiode that picked up laser light scattered by the half-wave plate. The LIBS spectrum was then sent to a computer for evaluation by the National Instruments LabView-based conditional analysis program for the presence

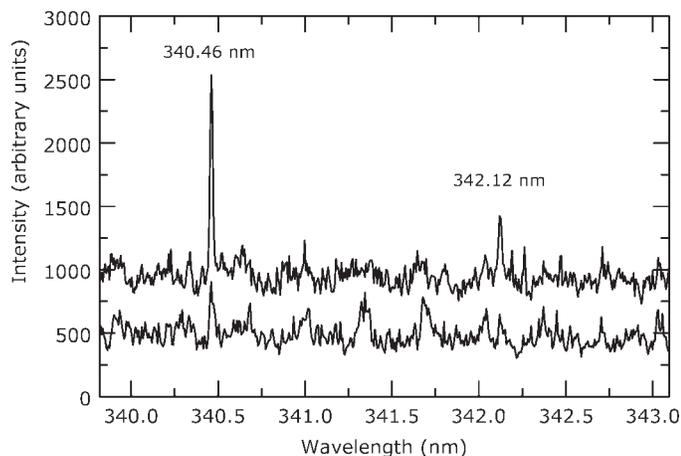


FIG. 2. The single-shot LIBS spectra from a large Pd particle in water (upper curve), and from a small Pd particle in water (lower curve). The principle Pd I emission lines used in this work are indicated. The baselines are shifted for clarity. The problem with OH<sup>-</sup> spectral interference is clearly evident in the periodic baseline structure in the spectrum from the small particle.

of a palladium spectral signature composed of two prominent neutral palladium emission lines at 340.46 nm and 342.12 nm (the transition of the  $^2[7/2]_4^0$  state at  $35928\text{ cm}^{-1}$  to the  $^2[5/2]_3$  state at  $6564\text{ cm}^{-1}$  and the transition of the  $^2[5/2]_2^0$  state at  $36976\text{ cm}^{-1}$  to the  $^2[5/2]_2$  state at  $7755\text{ cm}^{-1}$ , respectively).

The flow loop consisted of a peristaltic pump connected by tubing with a diameter of 0.5 cm to a vertical glass nozzle that was mounted on an x-y-z translation stage. The nozzle was simply a standard cylindrical glass medicine dropper with an inner diameter of 0.4 cm reduced to a 2.5 cm long small-diameter tip that produced a laminar water jet approximately 1 mm in diameter. The water jet was collected by a glass funnel and recirculated through the flow loop. The flow rate was 0.7 mL/s, and the total fluid volume in the flow loop was about 100 mL. The LIBS measurements were made about 0.5 cm below the tip of the nozzle.

Focusing the laser beam on to the water jet had to be done with care. The procedure adopted was to translate the nozzle so that the laser beam was focused well into the water jet and excited a strong LIBS signal. This, however, resulted in severe splattering of the focusing lens, which also served as the LIBS signal collection lens. The nozzle was then backed away until the splattering ceased but the LIBS signal remained. While this was a delicate adjustment, it was quite stable and repeatable. As a result, all LIBS data were collected from the surface of the jet or just within the jet.

Four palladium and four platinum GenSys model stationary fuel-cell systems, manufactured by Plug Power, were tested in the field trials. They were operated on liquefied petroleum gas. Each unit produced 5 kW of electrical power.

## EXPERIMENTAL RESULTS

Initial work with dilute particulate suspensions showed that the best SNR was obtained by recording spectra with a delay of 3  $\mu\text{s}$  after the initiation of the microplasma over a 10  $\mu\text{s}$  time interval. An example of a single-shot LIBS spectrum from a single palladium particle in water is presented in Fig. 2. The size of the particle is estimated to be about 1.2  $\mu\text{m}$ . The details of the estimation of particle size are discussed towards the end

of the paper. Also presented in Fig. 2 is the LIBS spectrum from a smaller particle for comparison.

The emission background shown in the spectra of Fig. 2 is a combination of continuum emission as well as a periodic feature presumably due to excitation of hydroxide-ion emission bands by the microplasma. The nature of this periodic structure was not studied in detail in this work, but its presence illustrates a potential problem with performing LIBS on water. Fortunately, the palladium lines fell in between the peaks of this background. Nevertheless, this spectral feature will obscure weak palladium signals, particularly the 342.12 nm line. This can be seen in the single-shot LIBS spectrum from the small particle in Fig. 2. The 340.46 nm line was used as the primary line for conditional analysis. Hahn and Lunden<sup>11</sup> recommend using the intensity of two lines to determine a hit, but because of the hydroxide-ion background, this was not practical. In order for the LIBS signal to be recorded as a hit, the intensity of the 340.46 nm peak had to be 28% greater than the average value of two 20-pixel-wide background windows centered at 340.1 nm and 340.8 nm. The hit threshold is slightly above the single-channel spectral background noise root mean square (rms) deviation of 25%. These conditional analysis settings resulted in a false-hit rate of less than 5%, which was deemed to be acceptable. Judging spectra for false hits was done manually and is somewhat subjective. If a shot is recorded as a hit, but there is no discernable palladium peak in the spectrum, then the shot is considered to be a false hit. A discernable palladium peak is one that is of course at the correct wavelength but also has an amplitude greater than the surrounding noise spikes and is broader than the surrounding noise spikes. The conditional analysis threshold criteria could be set so that no false hits were recorded, but this would prevent recording hits from small particles.

**Fuel-Cell Water Results.** Cathode water from two of the palladium fuel cells that had been operational for several months was tested for the presence of palladium. These fuel cells are referred to as number 501 and number 508. To avoid possible contamination of the flow loop by palladium particles from the early work with prepared particulate suspensions, the flow-loop tubes were replaced and the nozzle and collection funnel were thoroughly cleaned prior to any work with fuel-cell water. Initial LIBS measurements were then made on distilled water circulating through the flow loop. Out of 10 000 laser shots, 51 hits were recorded by conditional analysis as exceeding the threshold based on the 340.46 nm Pd emission line. The palladium spectral signature was only obvious in one of these hits, and the remaining 50 were deemed to be false hits. The resulting LIBS spectrum averaged over the 51 hits is presented in Fig. 3. The presence of the single palladium hit is not obvious, and the resulting spectrum is simply the characteristic background emission.

Confident that the flow loop was clean, the distilled water was replaced by 100 mL of a sample of 500 mL of water collected from fuel cell 501, and LIBS data were taken. Twenty-six real palladium-particle hits were recorded out of 10 000 laser shots. The false hit rate for this data was roughly the same as that for the pure water. A plot of the LIBS signal averaged over these 26 hits is presented in Fig. 4. While this is clear evidence that there is palladium present in the fuel-cell water, it is doubtful that this data is an accurate assessment of the amount of palladium in the water for the following reasons.

Our initial work with prepared 300 nm palladium particles

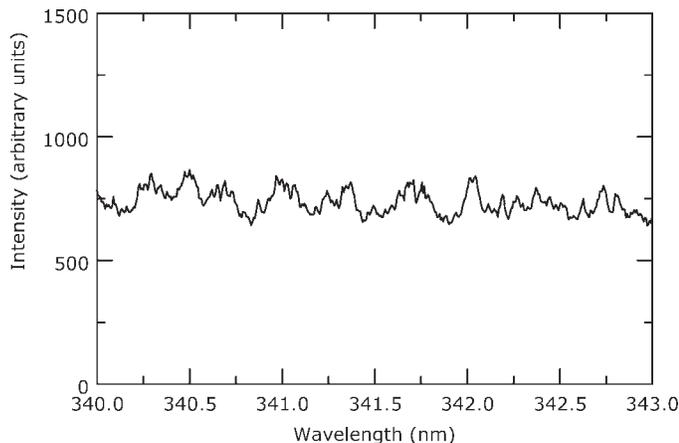


FIG. 3. The LIBS spectrum of pure water showing the average of 50 false hits and 1 real hit out of 10000 laser shots. There is no spectral evidence of Pd.

aqueous suspensions manufactured by Meliorum Technologies showed that particles on the order of 300 nm in diameter or less are too small to produce detectable LIBS signal. Research on cathode-layer degradation suggests that the palladium particles would be much smaller than this<sup>5</sup> and therefore would not generate hits. If this is indeed the case, the data in Fig. 4 is a serious underrepresentation of the amount of palladium in the fuel-cell water. A potential solution to this problem is to add a coagulant to the fuel-cell water to create particles large enough to detect. To investigate this, 20 mL of a 10% solution of the diallyl dimethyl ammonium chloride polymer coagulant known as coagulant 733, manufactured by Tramfloc, Inc., was added to 100 mL of the remaining 501 fuel-cell water in accordance with the manufacturer's recommendations. The LIBS measurements were then repeated. The increase in the LIBS signal was dramatic, with 1553 real hits recorded out of 10000 laser shots. The LIBS spectrum averaged over these hits is shown in Fig. 5. The coagulant had a similar but lesser effect on the 508 fuel-cell water. In this case, the real-hit frequency increased from 6 out of 2000 shots to 96 out of 2000 shots. It was verified by measurements on pure water to which the coagulant was added that the coagulant had no apparent matrix effects on the LIBS signals.

**Laser-Induced Breakdown Spectroscopy Signal Calibration.** Palladium suspensions with known mass concentrations were prepared to calibrate the LIBS signals. The procedure followed to make these standards was to mix a powder of 0.5 to 1.7  $\mu\text{m}$  diameter palladium particles manufactured by Alfa Aesar in about 1-1/4 liters of pure water. The certificate of analysis for the palladium powder states that 5% of the particles have diameters less than 600 nm. The exact mass of the palladium powder added to the water was not measured, but it was on the order of 0.5 g. The heavier particles immediately fell out of suspension. The mixture was allowed to rest undisturbed for about one week to ensure that only the smaller particles remained in suspension. About 1 liter of the palladium suspension was then carefully decanted. Of this, 500 mL was poured into a volumetric flask with a known mass and the water boiled off, leaving behind a deposit of palladium powder. Subtracting the mass of the empty flask from the mass of the flask now containing the powder gave the mass of the palladium in suspension with an uncertainty of about 2%. The mass concentration of the palladium suspension was

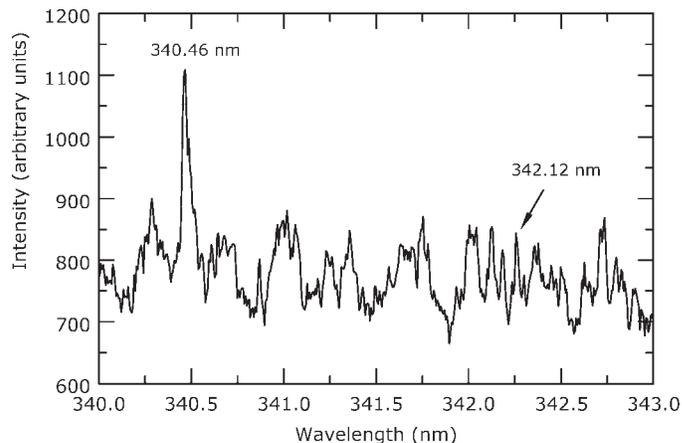


FIG. 4. The LIBS spectrum from fuel-cell 501 water. Twenty-six palladium hits were recorded out of 10000 laser shots. There is some evidence of a contribution to the main peak from a random noise spike.

therefore determined. The remaining suspension was the stock solution from which calibration standards were prepared by dilution with water mixed with the coagulant 733 in the same concentration that was used in the fuel-cell water experiments. The palladium concentration of the 100% stock solution with the coagulant was 71 ppm. The uncertainties of the mass concentrations of the calibration standards were estimated to be 3%.

Calibration data was collected beginning with pure water and then progressing to higher concentrations. For this work, the number of hits out of 1000 laser shots was recorded. The palladium LIBS signal was calculated from the hit-averaged LIBS spectrum by integrating the intensity of the background-corrected 340.46 nm Pd I peak from baseline to baseline and then multiplying this result by the hit frequency. The hit frequency is defined as the ratio of the number of recorded hits to the total number of laser shots. A graph of the LIBS signal versus palladium mass concentration is shown in Fig. 6. The calibration curve is linear with a linear regression coefficient of  $r^2 = 0.99$ . In addition, the y-intercept value is essentially zero, noting that the curve was not forced through zero. Overall, the

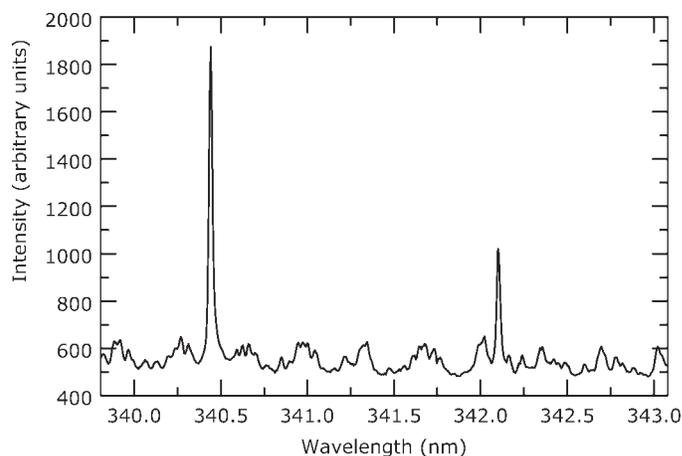


FIG. 5. The hit-averaged LIBS spectrum from fuel-cell 501 water with the Tramfloc 733 coagulant added. The coagulant was very effective and increased the particle hit rate to 1553 hits out of 10000 laser shots.

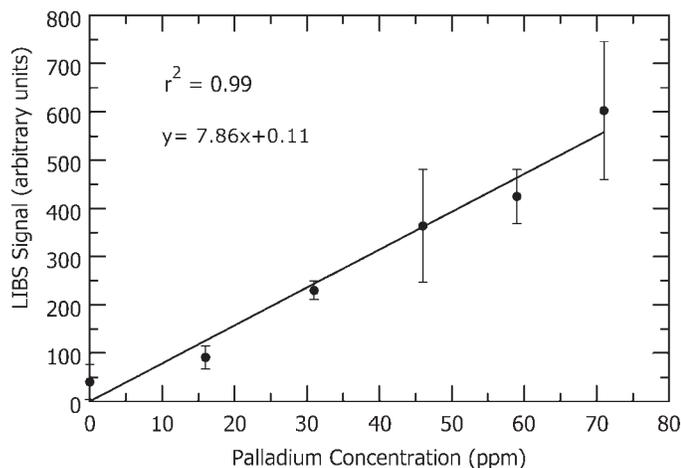


FIG. 6. The LIBS signal as a function of palladium-particle mass concentration.

calibration curve displays the desired traits for quantitative analysis.

The mass concentration of palladium in the fuel-cell 501 water was extrapolated from the calibration curve to be  $165 \pm 30$  parts-per-million (ppm) where the uncertainty was calculated using standard techniques of error analysis of predicted values from linear calibration equations.<sup>22</sup> We feel that such a modest extrapolation (i.e., factor of 2.4 beyond the upper limit) is justified because of the linearity of the calibration curve. Nonlinear effects in LIBS calibration curves have been studied, but they do not generally occur at low analyte concentrations.

For example, it has been shown that nonlinear effects in LIBS calibration curves for chromium in steel are not important at chromium concentrations less than 1000 ppm.<sup>23</sup> The mass concentration of palladium in the fuel-cell 508 water was determined to be about  $20 \pm 7$  ppm. Because of the different operating conditions of the two fuel cells, it is not possible to correlate the palladium concentrations in the fuel-cell water other than to say that the cathode layer is degrading in both units.

**Particle Size Distribution.** It is interesting to compare histograms of the hit frequency versus the background-corrected LIBS signal intensity for the fuel-cell and calibration data. These plots for fuel-cell 501 water with and without the coagulant and the results for the 100% calibration stock suspension with and without the coagulant are presented in Figs. 7a through 7d as typical results. It is assumed that the LIBS signal intensity is proportional to the mass of the ablated palladium particle and hence proportional to the particle diameter to the third power. It is evident in Figs. 7b and 7d that the coagulant increased particle sizes in the calibration suspension. The greatest effect of the coagulant on particle size can clearly be seen in the fuel-cell water histograms of Figs. 7c and 7d.

While we cannot make any definitive statements about the size distribution of the palladium particles in the fuel-cell water, we can at least estimate it. Because of the manner in which the calibration samples were prepared, the smallest particle size possible in the calibration stock solution without the coagulant is assumed to be about 500 nm in diameter. The weakest LIBS signal intensity for this suspension (see Fig. 7a) is in the 50 to 100 unit intensity interval. Figures 7c and 7d

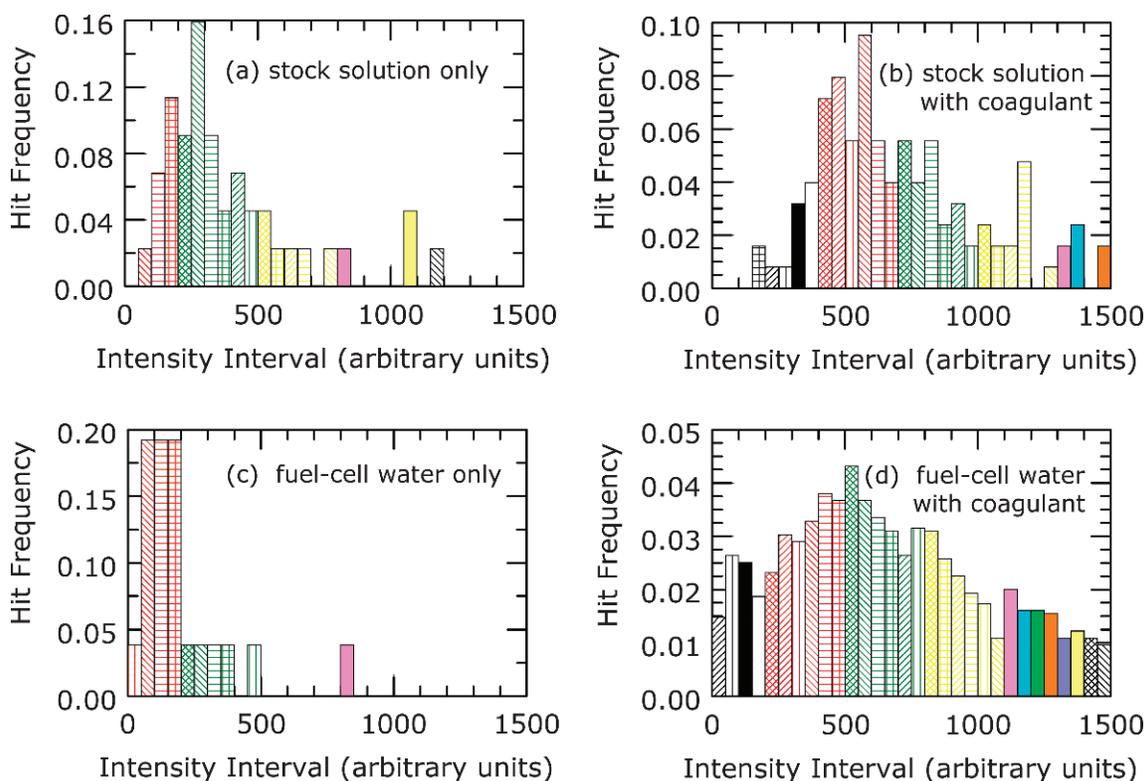


FIG. 7. Histograms comparing the particle hit frequency versus signal intensity for the undiluted stock calibration solution and the fuel-cell 501 water. (a, c) Water suspensions only. (b, d) Water suspensions to which the 733 coagulant was added. For clarity, intensity intervals greater than 1500 are not presented.

show that the smallest particles in the fuel-cell water produced signals in the 0 to 50 unit intensity interval. Because LIBS signals scale with particle mass, one can extrapolate that these particles are about 400 nm in diameter. This is effectively the smallest particle detectable with our technique. The maximum intensity recorded for the fuel-cell water with the coagulant was 5700 units (not shown in Fig. 7d). This corresponds to a particle size of about 2  $\mu\text{m}$ . If particles are too large, complete vaporization does not occur and the LIBS signal is no longer linear with increasing mass. The effect of particle size on the analytical LIBS signal has recently been studied with regard to particle composition and delay time after initiation of the microplasma.<sup>24,25</sup> It was reported that particle-size effects and increasing delay times are not an issue for single-component particles less than about 2.5  $\mu\text{m}$  in diameter in an aerosol. The palladium particles of the current study fall within this range, and particle-size limitations are not considered to be an issue.

The particle-size detection limit estimate of 400 nm is consistent with the reported 3 fg detection limit for calcium.<sup>11</sup> Hahn has observed that relative LIBS detection limits for different elements are similar to relative detection limits for the same elements obtained from inductively coupled atomic emission spectroscopy (ICP-AES).<sup>26</sup> For the Ca II line at 343.4 nm, the ICP-AES detection limit is 0.02 ppm, and the detection limit for palladium using the 340.46 nm line is 5 ppm.<sup>27</sup> The LIBS mass-detection limit for palladium therefore scales to 750 fg. This corresponds to a particle diameter of about 500 nm, which is in reasonable agreement with our detection limit of 400 nm. Particle-size detection limits could probably be improved using a dual-beam technique that combines LIBS with laser-induced fluorescence (LIF).<sup>18,23,28,29</sup> With this approach, the dominant spectral line of the ablated material excited in the microplasma by the LIBS process is enhanced by laser excitation from a second probe laser beam tuned to the wavelength of an appropriate atomic transition.

## CONCLUSION

Laser-induced breakdown spectroscopy was successfully developed to detect and quantify palladium particles in aqueous suspension. The LIBS signal-to-noise ratio was greatly increased by using conditional analysis of the single-shot LIBS spectra to reject data that did not contain spectral information from a palladium particle. The technique was used to evaluate the reformate water of operational palladium-based PEM fuel cells for the presence of palladium. A significant concentration of palladium was found after a polymer coagulant was added to the water to increase the palladium-particle size. The particle size detection limit for this technique is estimated to be 400 to 500 nm. The fact that palladium was found in the reformate water is strong evidence that the cathode catalytic layers in the fuel cell are degrading.

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