Laser-Induced Breakdown Spectroscopy used to Detect Palladium metal Dispersed in Cellulose Membranes

Madhavi Martin  
Environmental Sciences Division, Oak Ridge National Laboratory, Oak Ridge TN, 37831-6038  
(865)-574-7828, (865)-576-8646, martinm1@ornl.gov

Barbara Evans, Hugh O’Neill, and Jonathan Woodward  
Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge TN, 37831-6194  
(865)-241-3185, (865)-574-1275, evansb@ornl.gov

Abstract: Metals dispersed in membranes have been used as active electrodes in fuel cell technology. Laser-induced breakdown spectroscopy (LIBS) was used to detect palladium in cellulose membranes. Different concentrations of palladium solution were used in the uptake of palladium into cellulose films. We have correlated the palladium concentration in various cellulose membranes to the standard laboratory technique of atomic absorption spectroscopy (AAS).

©2000 Optical Society of America  
OCIS codes: (140.3440) Lasers and laser optics

Introduction

The cellulose synthesized by bacteria of the genus *Gluconoacetobacter* is a gel-like skin or pellicule formed at the surface of the culture medium. Although chemically identical to plant cellulose, being composed of β-1,4-linked glucose chains, bacterial cellulose differs in its high hydration, up to two hundred fold its weight of water, and its netlike microstructure. The special properties of this cellulose enable it to catalyze deposition of palladium nanoparticles from solution inside the hydrated cellulose matrix (Evans et al., submitted). Such palladium-treated cellulose can be easily dried to thin membranes for application in membrane electrode assemblies and other electronic devices (Evans et al., patent pending).

The ability of LIBS to provide rapid multielemental microanalysis of bulk samples (solid, liquid, gas, aerosol) in the parts-per-million (ppm) range with little or no sample preparation has been widely demonstrated (Martin et. al.,). LIBS induces the vaporization of a small volume of sample material with sufficient energy for optical excitation of the elemental species in the resultant sample plume. The vaporized species then undergo de-excitation and optical emission on a microsecond time scale, and time-dependent ultraviolet-visible spectroscopy fingerprints the elements associated with the spectral peaks. LIBS is typically a surface analytical technique, with each laser pulse vaporizing microgram or submicrogram sample masses. However, the rapidity of sampling (typically 10 Hz laser repetition rate) and ability to scan a sample surface, ablate a hole into a solid sample with repeated laser pulses, for depth profiling or focus the laser spark below the surface of a liquid sample permits more versatile analyses and provides sufficient statistics for bulk sampling. Although calibration standards are required for quantitative analysis, the generation of a single calibration curve will suffice for analysis of samples in a similar matrix. We have previously demonstrated the technique of LIBS for sample vaporization and optical emission in the detection of RCRA metals (e.g., Hg, Cr, Pb, V, Ni, and Cu) present in aerosols for use in continuous emission monitoring from smoke stacks (Martin and Cheng).

Preparation of the metal doped cellulose membranes

The cellulose-producing bacterium *Gluconoacetobacter hansenii* (ATCC 10821, formerly classified as a strain of *Acetobacter xylinus*) was cultivated in rich medium for 7 to 10 days (Schramm and Hestrin, 1954). The gel-like cellulose pellicles that were produced were harvested and cleaned by soaking in boiling distilled water for 2 h, followed by 18 h in 1% sodium hydroxide. The hydroxide was neutralized with acetic acid. The cellulose samples were soaked in several changes of distilled water to removed salts from the neutralization, then stored in 20% ethanol. Palladium was deposited by incubation of purified cellulose with 0-10 mM ammonium hexachloropalladate solution in water for 2 h at 90°C. Black particles of palladium formed throughout the cellulose matrix. The samples were soaked in several changes of distilled water to remove residual hexachloropalladate. Dried samples of
palladium-treated and control cellulose were prepared by drying the cellulose pellicules to a thin membranes on a laboratory gel drier with application of vacuum.

**Experimental setup**

The experimental setup employs a Spectra Physics™ laser, model INDI-HG. This is a Q-switched Nd: YAG laser that has output wavelengths at the fundamental wavelength of 1064-nm, frequency doubled to 532-nm, and frequency quadrupled to 266-nm. For these experiments, we used the 266-nm laser wavelength with 20 mJ/pulse as the excitation energy. The laser pulselength is 6-8 ns and the repetition rate is 10 Hz. All the processes such as plasma formation, emission, gated detection, data collection, and analysis are completed within 100 milliseconds until the next pulse arrives in the sample volume. The light emitted by the resulting plasma is collected by an optical collection system situated at ~ 45° angle to the axis of the sample and the laser excitation beam and is delivered to an Acton Research Inc. spectrometer (SpectraPro-500) via a carbon-core fiber-optic cable bundle. The resolved spectrum is detected by an intensified charge coupled device (ICCD) built by Andor Technology with the ICCD delayed and gated by a Stanford Research Systems model SRS535 delay generator.

The typical spectrum for metallic palladium deposited on a cellulose membrane starting with a 10 mM solution of \([\text{(NH}_4\text{)}_2\text{PdCl}_6]\) is shown in figure 2. This shows that we can combine chemical analysis and imaging of the

![Figure 1. Schematic of the LIBS Experimental Setup](image)

![Figure 2. LIBS spectra obtained from Pd metal incorporated in a cellulose film.](image)
membranes to obtain complete information of the sample under test. Numerous cellulose membranes with varying concentrations of palladium were used to construct the calibration curve shown in figure 3. The concentrations of Pd in the cellulose membranes tested with the LIBS method were 2, 4, 6, 8 and 10 mM. There seems to be a decrease in the deposition of palladium metal by the bacteria when the concentration of $[(\text{NH}_4)_2\text{PdCl}_6]$ solution goes above 8 mM. It has been correlated to the calibration curve obtained for the same samples that were used to obtain the calibration curve using a well-established laboratory technique of atomic absorption spectroscopy (AAS).

**Conclusions**

We have demonstrated successfully that LIBS can be a viable technique in the determination of total Pd concentrations present in specially synthesized cellulose membranes. We have also tested this technique for the detection of silver metal-doped cellulose membranes. We have compared this to a standard technique of atomic absorption spectroscopy.

**References**


