VI.11 Optical Scatterfield Metrology for Online Catalyst Coating Inspection of PEM (Fuel Cell) Soft Goods

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Contract Number: DE-EE0001047

Subcontractor:
Los Alamos National Laboratory, Los Alamos, NM

Project Start Date: October 1, 2007 Revised Interagency Agreement (October 1, 2009)
Project End Date: October 1, 2009 Revised Interagency Agreement (October 1, 2011)

Fiscal Year (FY) 2011 Objective

Evaluate the suitability of optical scatterfield metrology (OSM) as a viable measurement tool for in situ manufacturing process control of dual-side simultaneous catalyst coating of membranes.

Technical Barriers

This project addresses the following technical barriers from the Manufacturing R&D section of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

(F) Low Levels of Quality Control and Inflexible Processes

Contribution to Achievement of DOE Manufacturing Milestones

This project will contribute to achievement of the following DOE milestones from the Manufacturing R&D section of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

- **Milestone 1.** Develop prototype sensors for quality control of MEA manufacturing. (4Q, 2011)
- **Milestone 2.** Develop continuous in-line measurement for MEA fabrication. (4Q, 2012)
- **Milestone 13.** Complete development of standards for metrology of PEM fuel cells. (4Q, 2010)

FY 2011 Accomplishments

- Demonstrated 0.03 to 0.05 mg/cm^2 sensitivity to loading differences using 3M pure Pt catalyst nano-structured thin-film (NSTF) samples that included four different loadings ranging from 0.05 mg/cm^2 to 0.20 mg/cm^2 (September 2010).
- Investigated transmission properties of the thin NSTF samples and eliminated interference from the substrate (sample holder) material reflection (October 2010).
- Using sample reversal along with atomic force microscopy (AFM), we discovered that the cause of a repeatable asymmetrical reflectivity response for the 0.20 mg/cm^2 pure Pt NSTF CCM was due to a large physical macroscopic sample asymmetry (November 2010).
- Demonstrated 0.03 to 0.04 mg/cm^2 sensitivity to loading differences using W.L. Gore & Associates Pt on carbon catalyst-coated membrane (CCM) (A510/M710.18/C510) samples that included four different loadings ranging from 0.10 mg/cm^2 to 0.40 mg/cm^2 (December 2010).
- Procured and took delivery of a spectroscopic ellipsometer which enables measurements of material optical properties n and k that are critical to the modeling effort (February 2011).
- Using the new ellipsometer, began spectroscopic measurements of constituent materials supplied by 3M that comprise their NSTF CCM and attempted bulk material measurements (using effective medium approximation) of the current Gore samples (March 2011).
- Continued refinement of our simulation models for both the 3M NSTF and the W.L. Gore & Associates Pt on carbon CCM (optical constants remain only limitation to having a useful working model) (March 2011).

Introduction

Industry has identified the need for high-speed, in situ process control measurement techniques for controlling the quantity of the platinum in the catalyst layer and for the rapid identification of critical defects. Online

X-ray fluorescence (XRF) is the current in situ technique for controlling the various parameters of interest, most commonly catalyst loading; however this technique provides the total through sample platinum loading thus must be implemented prior to the transfer of the anode and cathode catalyst layer to the membrane in the production of a CCM. The ideal solution would provide in-line process control of the finished product (CCM) by way of dual-side simultaneous but independent measurement of catalyst loading. The solution would eliminate concerns related to platinum lost and not accounted for during the decal transfer step and it would ultimately enable real-time loading process control when dual-side direct catalyst layer application becomes the standard approach.

The Mechanical Metrology Division within the Physical Measurement Laboratory has years of expertise with a technology identified as OSM [1], specifically its development as a process control tool for the semiconductor industry. This technique is a combination of the best attributes of traditional bright-field optical microscopy and scatterometry. This technique focuses on the complex optical signatures of subwavelength size features, where the response can be optimized by varying the illumination angle, varying the illumination source wavelength, and application of various image analysis algorithms. The overall objective of this project is to demonstrate the applicability of the OSM technique to this application with the hope that it will provide proton exchange membrane (PEM) CCM manufacturers with an automated high-throughput approach for process control inspection of Pt loading with sensitivity equal to or better than that currently provided by XRF and simultaneous identification/quantification of other parameters of interest, such as critical defects. Model-based simulations will be developed concurrently as they are critical to the study and optimization of this technique for this application and will ultimately give manufacturers insight that will enable them to tune their measurement equipment to the parameter(s) of interest as design changes are made.

Approach

The initial focus, driven by industry input, is to demonstrate that the OSM tool is sensitive to differences in catalyst loading. To reach this Go/No-Go point this project has relied heavily on support from CCM manufacturers, specifically in the supply of samples by which sensitivity studies could be performed. CCM manufacturers were also helpful in establishing a benchmark catalyst loading sensitivity of 0.01 mg/cm^2 which is equivalent to that of the online XRF tool currently used. At this juncture, we now know that the tool is indeed sensitive to changes in catalyst loading at the benchmark level based on a sample set of 3M Pt alloy NSTF-type CCMs. With sensitivity successfully demonstrated, the remainder of the project is dedicated to developing accurate analytical models for each type of CCM tested then to use these models for simulations aimed at understanding and optimizing the tool's sensitivity to catalyst loading based on variation of the adjustable parameters of the tool and to further extend the study of the applicability of the tool to other critical catalyst layer parameters identified by the manufacturers. In the development of these models, we will again rely heavily on CCM manufacturers to supply specialized samples so that we can experimentally obtain optical constants for the constituent materials which are critical to ensuring accuracy. Lastly, to claim that a thorough investigation has been performed we aim to demonstrate the tool's capabilities on many of the common types of CCMs being manufactured, these include 3M's NSTF CCM with Pt and Pt alloy catalysts and the different conventional Pt on carbon-based CCMs made by several manufacturers.

Results

At the beginning of 2011, we determined that the Pt loading sensitivity was 0.03 to 0.05 mg/cm^2 for the 3M NSTF pure Pt CCM samples with loadings of 0.05, 0.10, 0.15, and 0.20 mg/cm^2 (Figure 1).

However, the reflectivity signature versus illumination angle for the 0.20 mg/cm^2, not shown in Figure 1, appeared non-symmetrical in comparison to the other three samples. Additionally, these pure Pt samples did not appear as opaque as the pure Pt alloy samples did thus we became concerned about transmission of the light through the sample and the effect of the reflection from the substrate or sample holder material. Both findings could be contributing to the

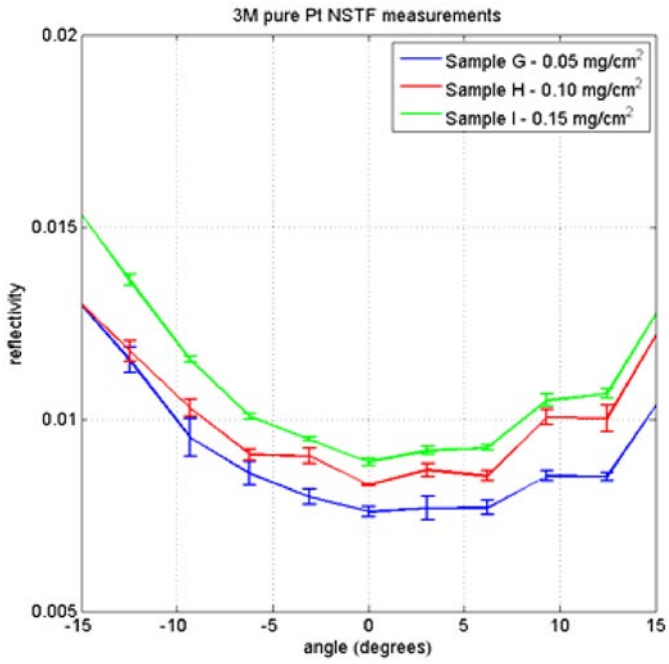

FIGURE 1. 3M NSTF pure Pt sample loading data. The separation between the curves relative to the error bars is a measure of the sensitivity.

increased variability as indicated in the calculated sensitivity level, which is short of the 0.01 mg/cm^2 target.

In order to determine if the asymmetry was associated with the optical tool or the sample, we performed a physical reversal of the sample. From this data seen in Figure 2, the asymmentry for the suspicious sample rotated with the reorientation of the sample but similar measurements using one of the other three samples did not change thus this was determined to be sample effect. To further understand the cause of the asymmetry our investigation focused on the sample. With the aid of an AFM we measured the profile of the samples macroscopic structure and compared the results from similar measurements performed on the other samples to find that there is a larger than normal asymmetry of the unique macrostructure geometry. The asymmetry is unimportant to the performance of the fuel cell, thus we were advised to find a way to make the measurement insensitive to this effect. This remains an ongoing effort. With regards to the transmission concern, experiments were performed where the intensity of the illumination source was significantly increased and where we changed the reflectivity characteristics of the substrate by introducing light absorbing material, both caused unexpected changes in the signature profile however the sensitivity and offsets between the samples remained. This too remains a work in progress and it is our hope that accurate simulation models will give us greater insight into these two effects.

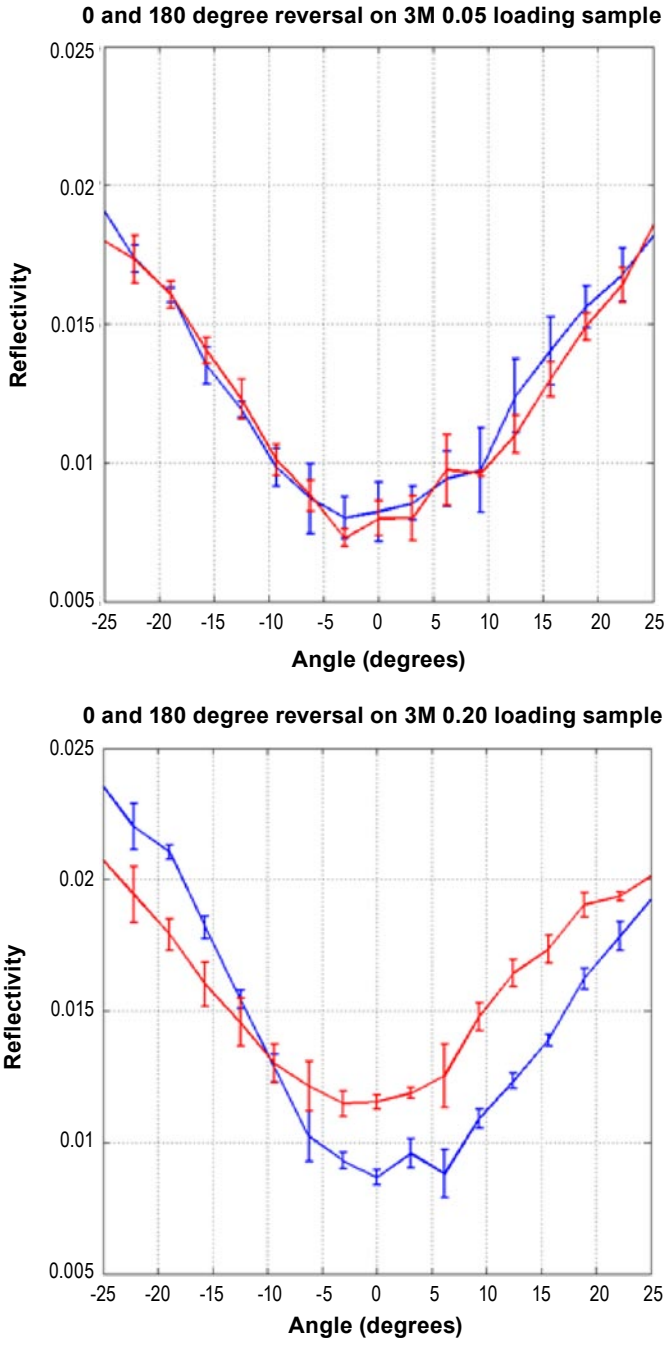

FIGURE 2. The plot on the top is the 0 and 180 degree reversal data for the 0.05 mg/cm^2 sample. The plot on the botttom is the 0 and 180 degree reversal data for the 0.20 mg/cm^2 sample, which displays the asymmetric behavior.

With sensitivity demonstrated on both catalyst compositions using the 3M NSTF samples, we investigated the applicability of the tool to catalyst loading sensitivity using W.L. Gore & Associates conventional Pt on carbon CCM samples of 0.10, 0.20, 0.30, and 0.40 mg/cm^2 loadings (A510/M710.18/C510). We performed experiments varying the angle of illumination and wavelength on two different tools. For the angle resolved measurements, sensitivity was demonstrated on the order of 0.03 to 0.04 mg/cm^2. Excellent static repeatability (multiple measurement scans same location) was shown for the wavelength resolved measurements. Performing wavelength resolved measurements at five locations on multiple days revealed variations in loading from one location to the next (on the scale of several millimeters apart), which makes the overall repeatability worse. However, this is not a limitation of the technique, it is a sample issue. This static repeatability and localized variation data are shown in Figure 3.

An integral part of the OSM technique is electromagnetic scattering simulation of the samples being measured. Simulation provides a flexible and efficient method to evaluate the various parameters that have an effect on the actual physical measurement. Accurate simulation requires accurate inputs to the models, such as target dimensions, layer thicknesses, surface roughness, materials optical properties (complex index of refraction), etc. NIST procured and took delivery of a spectroscopic ellipsometer which enables measurements of material optical properties (n and k) that are critical to the modeling effort (February 2011). Using this new ellipsometer, NIST began spectroscopic measurements of constituent materials supplied by 3M that make up their NSTF CCM and attempted bulk material measurements of the current Gore samples (March 2011) as shown in Figure 4. In performing these measurements, it became apparent that surface roughness was limiting our ability to measure the n and k of the materials and began using an effective medium approximation for evaluating the materials optical

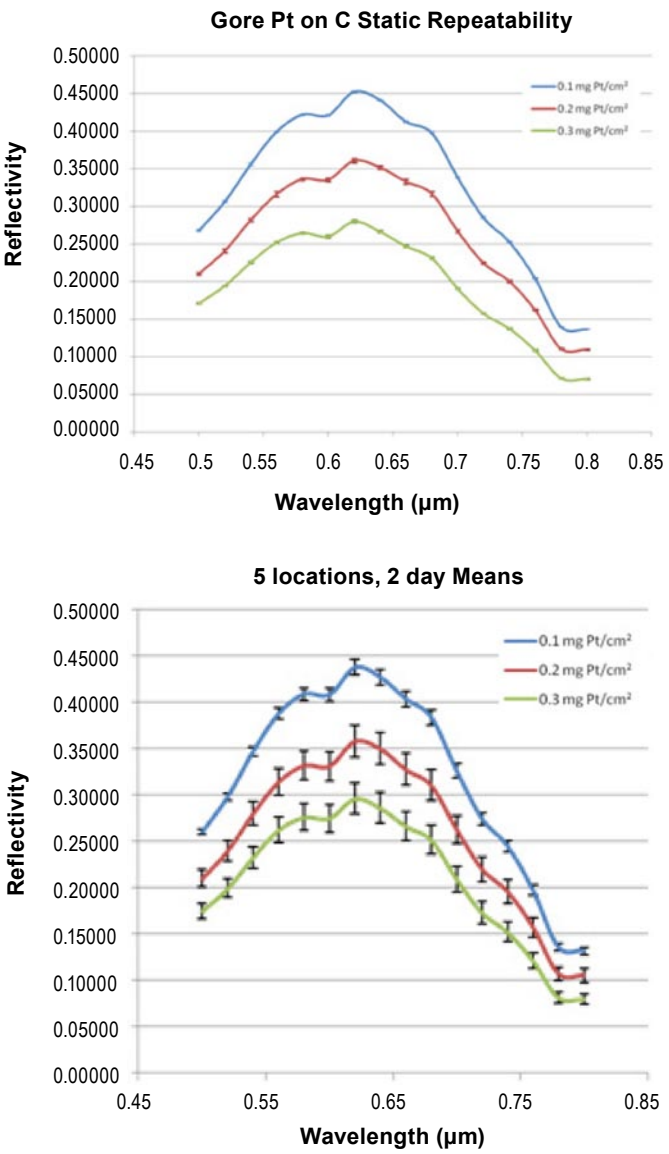

FIGURE 3. The plot on the top shows static repeatability data, looking at one location on each loading sample numerous times. The plot on the bottom is localized variation data, looking at five different locations on each loading sample over multiple days.

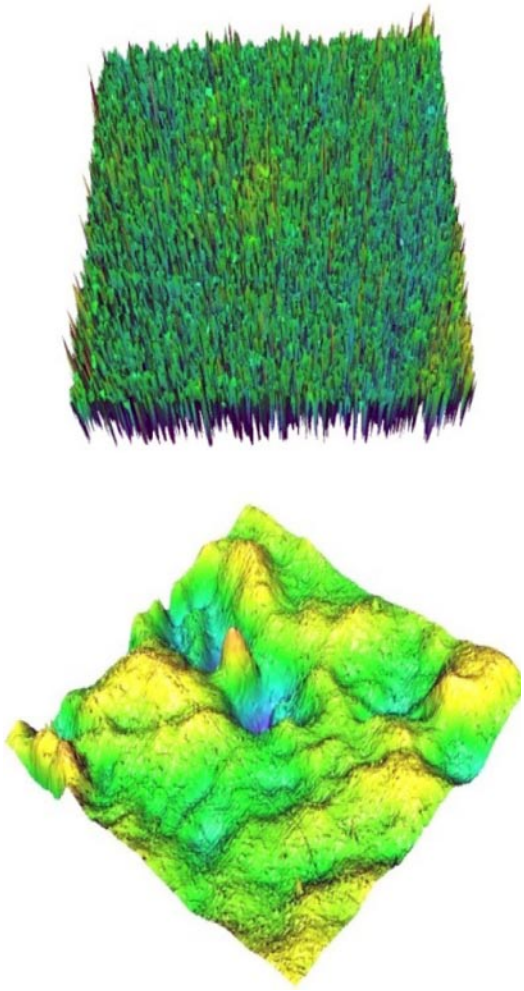

FIGURE 4. The plot on the top is a measure of the surface roughness of the Gore PEM layer. The plot on the bottom is a measure of the surface roughness of the 3M PEM layer.

properties. We continued refinement of our simulation models for both the 3M NSTF and the W.L. Gore & Associates Pt on carbon (optical constants remain only limitation to having a useful working model) (March 2011).

Conclusions

The work presented for this project, to date, undeniably shows that OSM has sensitivity to catalyst loading regardless if the loading is pure Pt or a Pt alloy. The ability to achieve sensitivity levels equivalent to the 0.01 mg/cm^2 benchmark has been shown for the sample types investigated. From the conventional Pt on C catalyst CCM samples we clearly see that this sensitivity level is achievable, however local variations in catalyst loading increase the uncertainty of assigning a definitive loading figure to a sample. Also from the work to date we see that this technique is clearly sensitive to other variables whether they are other sample specific parameters (i.e., macro geometry) or external (i.e., through sample transmission/background interference). These issues alone solidify the need for determination of material optical properties in support of the development of accurate models, which has eluded us to this point. Furthermore, optical property determination is not a simple task and in itself requires a significant effort. Support from major manufactures has been excellent but sensitivity regarding intellectual property rights always impacts the rate of progress. At this juncture, we clearly have all the elements in place to make commendable strides towards true optimization of the OSM tool for this specific application. It is our belief that manufacturers like 3M and W.L. Gore & Associates see the potential for this measurement technique thus are eagerly

awaiting completion of the development work and subsequent availability of a commercialized product.

Future Directions

Our focus for the remainder of this project will be acquiring much needed material optical constants using our new spectroscopic ellipsometer and with these constants we intend to refine our models to a level that predictive simulations can be performed to study sensitivity to different variables ultimately leading us to an optimized tool configuration that may be unique to the samples of interest. An accurate model will be achieved when predictions can be made using the model and those predictions verified experimentally. Concurrently, we hope to explore the sensitivity of the technique to different defects identified by the manufacturers as being critical through the measurement of samples with know defects and investigated further through simulation efforts.

Disclaimer

Certain commercial equipment, instruments, or materials are identified in this paper in order to specify the experimental procedure adequately. Such identification is not intended to imply recommendation or endorsement by the National Institute of Standards and Technology, nor is it intended to imply that the materials or equipment identified are necessarily the best available for the purpose.

Acknowledgements

The work detailed in this report would not have been possible without the contributions of the following, all are NIST personnel and guest researchers unless otherwise noted: Mark Debe (3M), Judy Rudolf and Collin Busby (W.L. Gore), Mike Ulsh (National Renewable Energy Laboratory, NREL), Guido Bender (NREL), Michael Stocker, Richard Silver, Andras Vladar, John Kramar, Bin Ming, Brad Damazo, Bryan Barnes, Richard Quintanilha, Hui Zhou, Yeung-Joon Sohn, Francois Goasmat, Jing Qin.

FY 2011 Publications/Presentations

1. E. Stanfield and M. Stocker, "Metrology for Fuel Cell Manufacturing," DOE Annual Merit Review Proceedings, MN006, May 12, 2011, http://www.hydrogen.energy.gov/pdfs/review11/mn006_stanfield_2011_o.pdf.

2. E.Stanfield, M. Stocker, and B. Muralikrishnan, "Metrology for Fuel Cell Manufacturing," Invited Presentation Given to the FreedomCAR Tech Team, USCAR, Southfield, MI, March 16, 2011.

3. E. Stanfield, "Optical Scatterfield Metrology for Online Catalyst Coating Inspection of PEM Soft Goods," FY 2010 Annual Progress Report, DOE Hydrogen and Fuel Cells Program, February 2011, http://www.hydrogen.energy.gov/pdfs/progress10/vi_8_stanfield.pdf

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