VI.8 Optical Scatterfield Metrology for Online Catalyst Coating Inspection of PEM (Fuel Cell) Soft Goods

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Contract Number: DE-EE0001047

Project Start Date: October 1, 2009
Project End Date: October 1, 2012

Fiscal Year (FY) 2012 Objectives

- Collect crucial optical property data for catalyst-coated membrane (CCM) constituent materials.
- Improve theory to experiment agreement of CCM structures.
- Explore suitability of optical scatterfield microscopy (OSM) to CCM defect detection.
- Investigate other optics based measurement approaches as in situ process control fuel cell manufacturing metrology solutions.

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 R&D 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. Demonstrate sensors in pilot scale applications for manufacturing MEAs. (4Q, 2012)
- Milestone 2. Develop continuous in-line measurement for MEA fabrication (4Q, 2014)
- Milestone 3. Complete development of standards for metrology of production systems. (4Q, 2014)

FY 2012 Accomplishments

- Performed spectroscopic ellipsometry (SE) measurements on both the annealed and unannealed sample sets. Analyzed SE data and extracted meaningful numbers for the real (*n*) and imaginary (*k*) parts of the complex index of refraction for bulk perylene PR149.
- Demonstrated good qualitative agreement between a two-dimensional (2D) finite element model (FEM) and a 2D rigorous coupled waveguide analysis (RCWA) simulation of a 0.250-µm catalyst layer on top of a 20-µm finite ionomer substrate.
- Incorporating the new perylene PR149 *n* & *k* data, demonstrated good qualitative theory to experiment agreement for a 0.1 mg Pt/cm^2 3M nano-structured thin film (NSTF) CCM.
- Built and tested a varying height and cross-section pillar modeling structure to allow for the quantifying of surface roughness in CCM simulations.
- Devised a new scatterometry approach that has promising application to fuel cell process control metrology. This scatterometry approach is called large aperture scatterometry (LAS). Completed a design study of a LAS device.
- Completed initial computer simulations demonstrating: 1) sensitivity of OSM to detecting pinhole defects and 2) utility in identifying optimal measurement parameters for ensuring simultaneous independent single-sided measurements of a double-coated CCM.

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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 Semiconductor and Dimensional 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

Having demonstrated relevant sensitivities on industrial collaborator provided samples in the year before, the research direction this year focused largely on improving modeling accuracy and better theory to experiment agreement. The ability to perform accurate simulations facilitates developing accuracy when making optical measurements that require small uncertainties. It also provides a flexible and efficient platform to evaluate and optimize measurement parameters even before samples are available and measured.

In working towards accurate CCM electromagnetic scattering models, we collaborated with 3M to generate samples that would allow us to measure the optical properties of CCM constituent materials. The first sample set included six 4-inch perylene PR149-coated Si wafers. Three were coated with 1,500 Å and three with 1,800 Å of perylene and then annealed. The whiskers created a surface texture that made SE measurements extremely difficult. A second set of samples were made identical to the first, however, this time the wafers were coated, but not annealed. This created a smoother surface, relative to wavelengths of light we were using, allowing us to make useful SE measurements and extract an *n* & *k* for perylene PR149. We realize these optical constants are for bulk perylene, which is not the same crystal structure as the perylene whiskers, but these values provide valuable initial information in the modeling. The *n* & *k* data for bulk perylene PR149 are shown in Figure 1.

With these new *n* & *k* data, we performed two modeling tests. The first was a model-to-model comparison. We compared a 2D RCWA model to a 2D FEM model. The simulation was of a 0.250 µm effective medium approximation (EMA) catalyst coating on a top of a 20 µm finite ionomer substrate. This set of simulations was run as angle-resolved scans. Both polarizations trended the same direction with similar reflectivity values as a function of angle. The second test was a theory to experiment comparison. The experimental data were acquired from a 3M 0.1 mg Pt/cm^2 NSTF CCM sample. For the simulation, a wavelength scan was performed on a 2D model of this structure built in the FEM code. There is promising

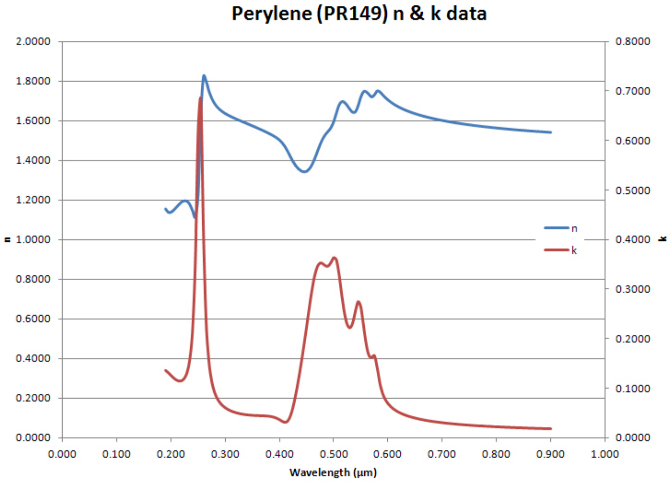

FIGURE 1. Perylene PR149 *n* & *k* data as function of wavelength

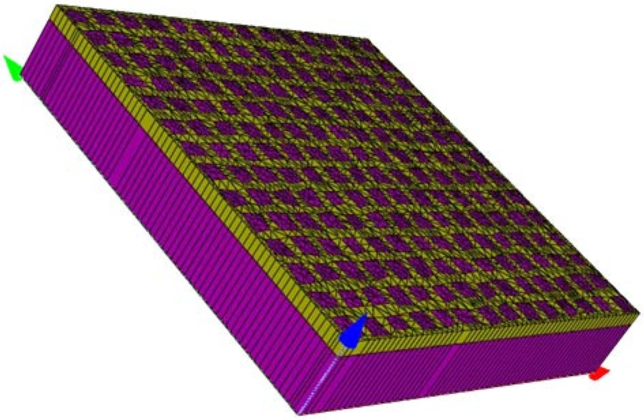

FIGURE 2. FEM-based roughness modeling structure

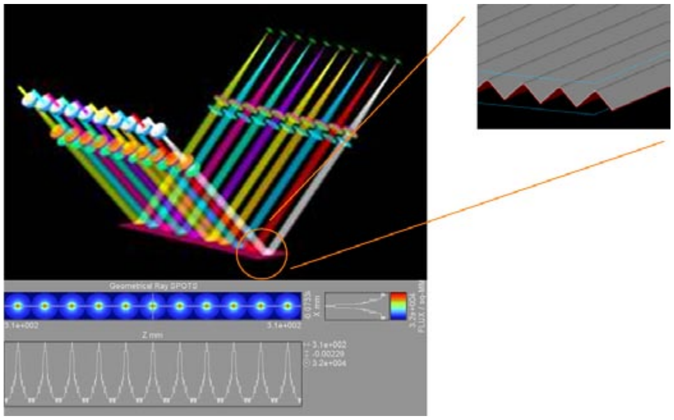

FIGURE 3. Multiple source, multiple detector LAS configuration design

qualitative agreement with both the theory and experiment trending the same as a function of wavelength at an illumination angle of 70 degrees. Other angles of incidence give very different values of reflectivity.

The modeling of CCMs presents a challenge for several different reasons, one of them being the randomness and magnitude of the surface roughness. To study this problem, we built a structure in the FEM model consisting of pillars with varying heights and cross-sections. This was designed to represent both: 1) the surface texture created from hot pressed Pt-coated perylene whiskers in the 3M NSTF CCM as well as 2) the surface texture from 50 nm to 100 nm carbon grains in a carbon-Pt nanoparticle CCM. Some initial simulations were run to see the effects of roughness on reflectivity as a function of grain size and illumination angle of incidence. This pillar modeling structure can be seen in Figure 2. The model consists of air (in gold) between pillars atop an EMA catalyst layer (in purple), which contains Pt, perylene, air, and ionomer.

For Pt loading measurement, we devised a new scatterometric approach (no high magnification) we call LAS, allowing for averaging over a large sample area. A design study was completed in which four LAS configurations were considered. We decided a multiple source and multiple detector configuration showed the most promise, factoring in cost, simplicity of design, and failure modes. A schematic of this design can be seen in Figure 3. We have completed an optical design for this configuration and have ordered prototype parts. Assembly and testing of this LAS is currently underway.

Lastly, some initial simulation demonstrations were performed. The first was a pinhole defect simulation. We ran simulations of a 300 nm and a 500 nm pinhole as a function of wavelength, polarization, and illumination angle of incidence. Sensitivity to the change in diameter of the pinhole was observed. We are working with collaborators to obtain actual samples with intentional defects (pinholes, hotspots, etc.) created in the CCM. The second simulation was a demonstration of the capability of OSM to perform simultaneous independent single-sided measurements of a double-coated CCM. In this simulation, we compared results from: 1) a 20-µm PEM layer coated with 0.06 mg Pt/cm^2 on one side and nothing on the other side to 2) a 20-µm PEM layer coated with 0.06 mg Pt/cm^2 on one side and 0.03 mg Pt/cm^2 on the other. We were able to observe that an optimal set of simulation measurement parameters (wavelength, polarization, illumination angle of incidence, etc.) existed that minimized the influence of the 0.03 mg Pt/cm^2 side on the measurement of the 0.06 mg Pt/cm^2 side. This observation shows the flexibility to tune an optical system to a given measurement task.

Conclusions

We turned our attention to the time consuming task of developing accuracy and achieving quantitative theory to experiment agreement. We successfully obtained index of refraction data for bulk perylene PR149 and subsequently used them in performing various simulations that indicate improvement in accuracy and progress towards theory to experiment quantitative agreement. Surface roughness remains a difficult issue to address in our CCM modeling although measurable progress was made in our ability to quantify the effect. There is still much work to be done in these areas. We investigated the applicability of LAS as a process control solution for fuel cell manufacturing metrology. It is our belief that OSM, LAS, or the combination of the two remains a viable in situ process control solution for Pt loading and defect detection.

Future Directions

- Continue working with industrial collaborators to create samples that allow optical property measurements of CCM constituent materials. The next materials to characterize are the actual proton exchange membrane (Nafion® and 3M membrane) and amorphous carbon. Continue optical index of refraction measurements of CCM constituent materials.
- Demonstrate quantitative theory-to-experiment agreement on traditional carbon/Pt nanoparticle and 3M NSTF CCMs.
- Finish design and optimization of LAS sensor. Collect data on various CCMs as a function of web speed, illumination angle of incidence, wavelength, and polarization.
- Continue to investigate applicability of OSM to fuel cell defect detection. Solicit industry input as to the types of defects that cause real performance losses.
- Pursue testing of OSM and LAS approaches on the NREL webline after completion of feasibility studies at NIST.
- Publish OSM fuel cell results in refereed journal.

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 Colin Busby (W.L. Gore), Mike Ulsh (National Renewable Energy Laboratory, NREL), Richard Silver, Francois Goasmat, Jing Qin, Bryan Barnes, John Kramar, Bin Ming, Brad Damazo, Hui Zhou, Prem Kavuri, Yeung-Joon Sohn.

FY 2012 Publications/Presentations

1. Stocker M, Goasmat F, Qin J, Silver R, Barnes B, Stanfield E. Optical Scatterfield Microscopy for PEMFC Catalyst Coating Manufacturing Process Control. Poster session presented at: Fuel Cell Seminar and Exposition 2011; 2011 Oct 31 – Nov 3; Orlando, FL.

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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.