VI.8 Optical Scatterfield Metrology for Online Catalyst Coating Inspection of PEM Soft Goods

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Objective

Evaluate the suitability of optical scatterfield metrology (OSM) as a viable measurement tool for in situ process control of catalyst coatings.

Technical Barriers

This project will address the following technical barrier from the Manufacturing R&D Fuel Cells 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 membrane electrode assembly (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 proton exchange membrane (PEM) fuel cells. (4Q, 2010)

Accomplishments

- Secured 3M as a provider of catalyst-coated membrane (CCM) samples necessary to evaluate the potential sensitivity of the OSM technique to the measurement of catalyst loading. (07/2008).
- Developed an initial 12-layer three-dimensional optical model of the 3M nano-structured thin-film (NSTF) CCM in an attempt to predict the optimal configuration of the OSM instrument parameters (i.e., wavelength of the light source, illumination angle, polarization) to guide the experimental investigation efficiently.
- Demonstrated sensitivity of the OSM technique to Pt loading to a level of 0.01 mg/cm^2 using 3M PtMnCo NSTF (01/2010) and 3M pure Pt NSTF CCMs (06/2010).
- Secured another major manufacturer as a supplier of conventional Pt on C CCM samples for our next round of testing to further define the range of applicability of the OSM technique.
- Developed a formal collaboration plan with the National Renewable Energy Laboratory (NREL) that provides both organizations the ability to leverage each others' capabilities in support of their own individual projects, share proprietary samples and information from industry partners using a special three-way non-disclosure agreement (NDA) executed with each interested industry partner (ongoing).
- Demonstrated our support of the NIST/NREL collaboration by providing NREL with defects fabricated using our dual beam gallium focused ion beam (FIB)/scanning electron microscope (SEM) in order to extend NREL's membrane hole defect performance study to hole diameter sizes smaller than 150 um (3/2010).

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Introduction

The need for high-speed, in situ process control measurement techniques for controlling the quality of the platinum-based catalyst layer has been identified during numerous DOE sponsored and non-DOE sponsored workshops. Current techniques for the various parameters of interest (e.g., SEM and X-ray fluorescence [XRF] to name a few) are extremely expensive and not easily amendable to in situ application in a manufacturing production line. The Precision Engineering Division within the Manufacturing Engineering 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. More precisely, this technique takes traditional optical metrology beyond the Rayleigh criteria and 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. Although quantitative in other applications, this technique is being used in a comparative form thus far in this application and must be correlated to measurements of the parameter of interest using the appropriate reference metrology. As such, the development for new applications requires research to optimize the OSM tool and establishing the appropriate reference metrology tool, along with the development of the appropriate analysis algorithms for both. Please refer to the stated reference for more technical details on the technique.

Prior to this project, this technique has only been applied to very discrete uniform structures, such as those typically encountered in the semiconductor industry. Because of this, the application of the OSM technique to random subwavelength structures has long been a goal but does present significant challenges. The underlying principle is that even random subwavelength structures exhibit some type of repeatable optical signature and that changes in these signatures can be correlated with the various manufacturing parameters of interest to control the quality of the product.

The overall objective of this project is to provide PEM, CCM and gas diffusion electrode manufacturers with an automated high-throughput approach for performing process control inspection of Pt loading with sensitivity equal to or better than that currently provided with XRF and other parameters of interest simultaneously. Simulations will give insight and enable manufacturers to tune their measurement equipment to the parameters of interest. For dual-side simultaneous catalyst-coating operations, this method will provide the ability to concurrently perform Pt loading measurements on both sides of a CCM independently versus XRF which is a “total” sample loading measurement.

Approach

To ensure accuracy of the technical details related to the fabrication and performance of catalyst layers, this project depends heavily on support from MEA manufacturers, as well as, other experts in the field. From the beginning, we have actively engaged MEA manufacturers and industry experts in an effort to identify the critical parameters of the catalyst layer and to solicit from them sample packages that vary these parameters to enable us to conduct a sensitivity study of the proposed technique.

Our initial focus over the last year or two, driven by industry input, has been to demonstrate the technique’s sensitivity to catalyst loading. Then if the technique is sensitive to catalyst loading, determine how broadly applicable it is. To satisfy the second task, sensitivity studies must be conducted over the entire range of catalyst types (Pt and Pt alloys), support structures (conventional carbon-based and novel non-carbon-based supports), and substrates (membrane and both paper and woven cloth gas diffusion layers [GDL]). The development and implementation of this technique integrates experimental work with simulation driven predictions to maximize efficiency.

Results

During the last year our efforts have been focused on simulation model development and experimental data collection based on 3M’s NSTF CCM, which was the first sample set we received from a major supplier. This first sample set included three NSTF CCMs with PtMnCo catalyst loadings of 0.10, 0.15, and 0.20 mg/cm^2. Experimentally we collected data which successfully demonstrated that the OSM technique is sensitive to catalyst loading and that the sensitivity of the technique for this specific CCM is on the order of 0.01 mg/cm^2. This is very comparable to the inline XRF systems available. Figure 1 shows the final reflectivity data for two different runs. The first run involves three repetitive measurements at the same location on each sample thus representing what we refer to as base repeatability. The second run involves three repetitive measurements on each sample but each measurement is at a different location. Figure 2 is additional data supporting sensitivity of the tool to catalyst loading; however in these measurements we are varying the wavelength of the illumination source. This data was collected varying different instrument parameters, illumination angle and wavelength, not only to show sensitivity to the parameter of interest but also in an attempt to determine the settings that optimize this sensitivity. These two instrument parameters are only a sampling of the variables that have been tested and that can be optimized based on the application.

To understand further the applicability of the technique we then acquired another sample set that included four 3M NSTF CCMs with pure Pt catalyst loadings of (0.05, 0.10, 0.15, and 0.20) mg/cm^2. Again the experimental results obtained in late May of 2010 showed sensitivity to the loading differences but more

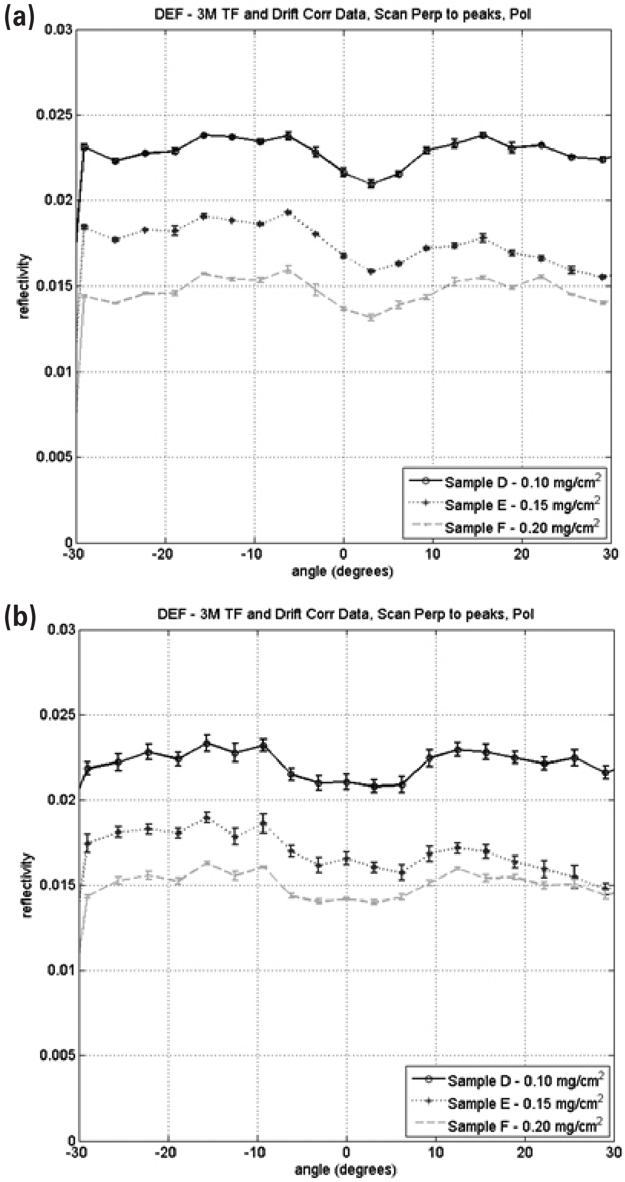

FIGURE 1. Final reflectivity results for variable illumination angle scans using 3M NSTF with PtCoMn catalyst samples were the difference in size of the error bars for each data point represents the difference between (a) repeated measurements at the same location and (b) repeated measurements at different locations on each of the three different loadings.

carefully collected data sets are needed to verify the exact level of this sensitivity. Concurrent with the experimental evaluation we have worked on simulation model development which supports the experimental data in that it predicts trends, but the accuracy of the models need improvement as we are lacking the true optical properties for the materials involved. Figure 3 shows our preliminary modeling efforts.

Over the last year we have also undertaken a parallel effort where we worked with NREL to develop a collaborative agreement between the two organizations.

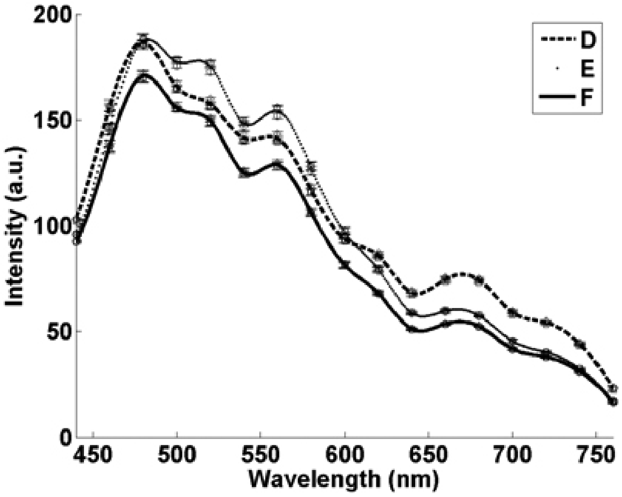

FIGURE 2. Variable illumination wavelength scan data using 3M NSTF with PtCoMn catalyst samples.

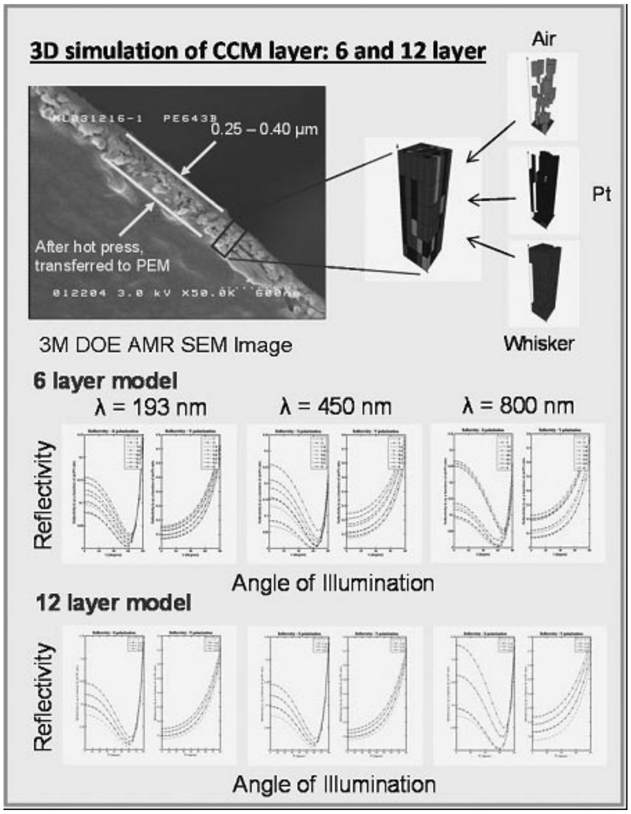

FIGURE 3. Preliminary Simulation Model for 3M NSTF CCM

This agreement was described in a one-page summary that we sent to all of our industry partners in the fall of 2009. This summary explained a coordinated effort for achieving each of our project's goals and that this is justified by the fact that the individual projects of both organizations were related but complimentary, and such a relationship would enable us to leverage our relationship with our industry partners together to maximize efficiency through the sharing of samples and information. Finally, the summary recommended that this agreement would be facilitated by three-way NDAs among NREL, NIST, and each industry partner. Without this, both organizations would negotiate individual NDAs with each industry partner and in some instances for the same sample and information requests, in essence doubling the number to NDAs needed. Furthermore, this agreement formalizes the commitment of both organizations in leveraging each other's capabilities in support of each organization's individual projects without the need for funding transfers. Because of the relationship between the NIST/NREL Collaborative Agreement, NIST reference metrology, and the OSM project we have combined this arrangement with the OSM project. To date all our industry technical partners have concurred with the proposed benefits. Several NDAs have been completed but others still remain outstanding. The following figures represent our recent efforts to demonstrate our commitment to the collaboration, in that, we provided defects fabricated using dual-beam SEM/gallium FIB in support of NREL's desire to expand their membrane defect study to sub 150 um features (Figure 4) [2].

Conclusions

- Demonstrated OSM technique sensitivity to catalyst loading using two 3M NSTF CCM sample packages, one with pure Pt and the other with a PtMnCo alloy catalysts.
- Developed preliminary simulation model of 3M NSTF CCM to ultimately guide efficient experimental measurement efforts and manufacturer tool customization.
- Procured (awaiting delivery) an ellipsometer with a integrated variable environmental chamber for experimental determination of optical properties "n" and "k" for materials comprising each CCM design used for OSM sensitivity testing to support a more accurate simulation model.
- Secured a manufacturer/supplier of conventional Pt on C CCMs and a sample package for further OSM catalyst loading sensitivity testing, in an effort to more precisely define the range of applicability.
- Developed a collaborative agreement with NREL to leverage resources between organizations and industry partnerships.
- Demonstrated support of this collaborative effort by fabricating membrane defects in support of NREL defect studies.

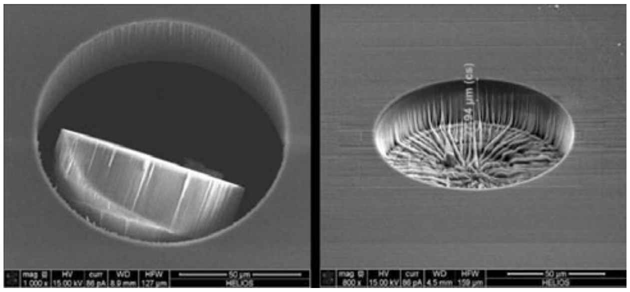

FIGURE 4. 100 um Diameter Through Hole and 100 um Diameter Cavity/Blind Hole 12 um Depth Membrane

Future Directions

- Use ellipsometer and additional special material sample packages to determine optical properties for 3M's NSTF CCM.
- Refine simulation model using these optical properties and demonstrate correlation between the model and experimental results.
- Determine the level of sensitivity of the OSM technique to catalyst loading using pure Pt NSTF CCM.
- Continue experimental catalyst loading sensitivity testing using conventional Pt CCMs.
- Secure supplier(s) of catalyst-coated, paper and cloth, GDL samples.
- Develop a conceptual compact tool design suitable for manufacturing lines.
- Work with NREL and industry partners to determine the next most sensible catalyst loading parameter to study with the OSM technique.

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 NIST, nor is it intended to imply that the materials or equipment identified are necessarily the best available for the purpose.

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FY 2010 Publications/Presentations

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