

Metrology for Fuel Cell Manufacturing



Project

ID# MN006 2012 DOE Hydrogen and Fuel Cells Program Review

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This presentation does not contain any proprietary, confidential, or otherwise restricted information.

Overview

Timeline

October 1, 2009 September 30, 2012 80% Completed

Barriers

- B. Lack of High-Speed Bipolar Plate Manufacturing Processes
- F. Low Levels of Quality Control and Inflexible Processes

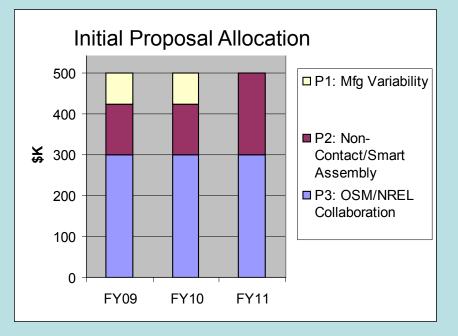
Partners

- Subproject #1 Only: LANL Tommy Rockward (Funded \$75K)
- Other Interactions & Collaborations addressed in each subproject section.

Overall Budget

Total Project Funding \$1.5 M Funding Received FY11 - \$200 K Funding for FY12 - \$175 K

[Cost share not required but NIST contribution to effort estimated at ~ 40% to 50% matching, Subproject P1 Manufacturing Variability Study – 100% NIST funding in FY11 & FY12]



Objectives:

- 1. Identify and evaluate the capability and uncertainty of commercially available non-contact, high-speed scanning technologies for applicability to bipolar plate manufacturing process control.
- 2. Original: Using capabilities identified in (1) demonstrate a "smart assembly" concept whereby plate parallelism data for each plate can be used to assemble the stack so that the cumulative parallelism of stack can be controlled tightly while simultaneously permitting greater parallelism variability for each individual plate.

Revised: Based on industry feedback, objective 2 has been revised to develop, demonstrate, and optimize the system's ability to measure thickness and variation-in-thickness, which can then be used to assess stack parallelism.

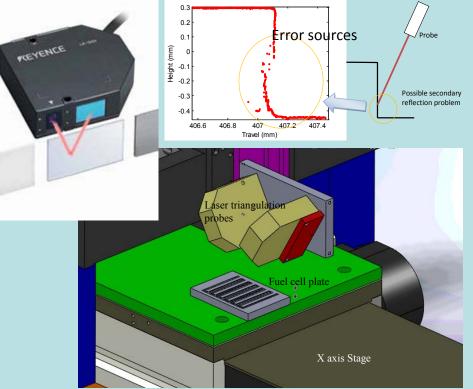
Approach:

•Identify suitable non-contact measurement technologies that can potentially be applied towards metrology of fuel cell plates

•Develop a stand alone system for fuel cell plate metrology

•Assess error sources in the measurement of parameters of interest such as channel width, thickness, sidewall profile, etc

•Demonstrate the ability to measure plate thickness (parallelism), an important parameter in assessing the overall stack parallelism



Benefits (Relevance):

•Provide bipolar plate manufacturers with a high-speed fully automated approach for process control dimensional inspection

•Enable rapid commercialization by indentifying, demonstrating, and characterizing QC inspection technologies suitable for high-volume bipolar plate production.

Background:

•Plate dimensional tolerances 50 μ m to12 μ m (some manufacturers have suggested even smaller tolerances)

•Target Measurement Solution Uncertainty $\sim 5 \ \mu m$.

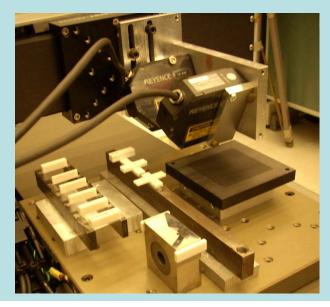
•Current State of the Industry

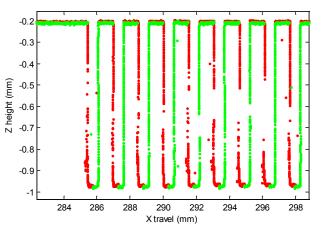
•Video Based Optical Inspection Predominantly Used - Semi-Automated, Very Subjective, Measurement Uncertainty versus higher end requirements questionable.
•Measurement Technology: No Packaged Systems Commercially Available....numerous structured light systems for depth and flatness measurements but feature (lateral) size and location questionable at required accuracy.

•Industry (Plate Mfgr) Perception: A solution is needed but the priority is low as they are nowhere near high-volume production rates.

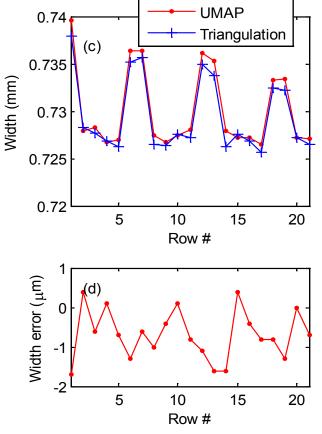
P2 Non-Contact Sensor Evaluation for Bipolar Plate Manufacturing Process Control and Smart Assembly of Fuel Cell Stacks 2010 and 2011 Accomplishments

The Solution - NIST designed measurement system using commercially available precision translation stages coupled with dual non-contact laser spot triangulation probes configured in a unique manner to enable sub-10 µm accuracy of vertical and lateral measurements for feature size and location.





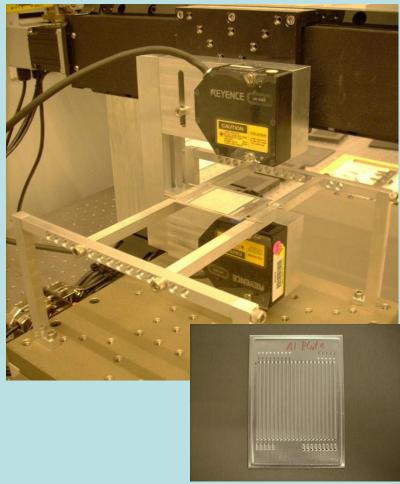
•Developed detailed uncertainty budget for height and width measurements •Measured Graphite and metallic plates, and plates made from different processes (machined, etched, etc) •Compared measurements from this system to those made on a contact probe CMM •Evaluated the performance of this system at different speeds and presented results •Worked with several plate manufacturers to provide dimensional data on plates so they could assess their process



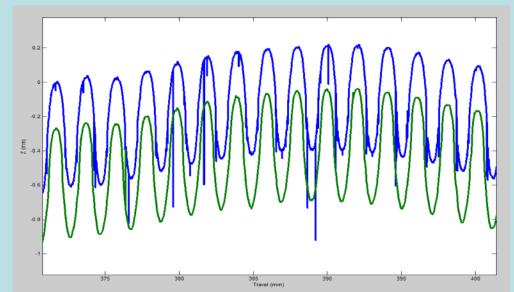
Width uncertainty = 6 μ m (k = 2) Height uncertainty = 3.8 μ m (k = 2)

2012 Accomplishments

Solution (Objective 2) We configured and demonstrated a dual opposed probe configuration using the existing laser spot triangulation probes to measure thickness and evaluate variation-in-thickness. [an ideal setup, given the availability of more probes, would be dual-probes on both sides of the plate to simultaneously evaluate all parameters of interest].

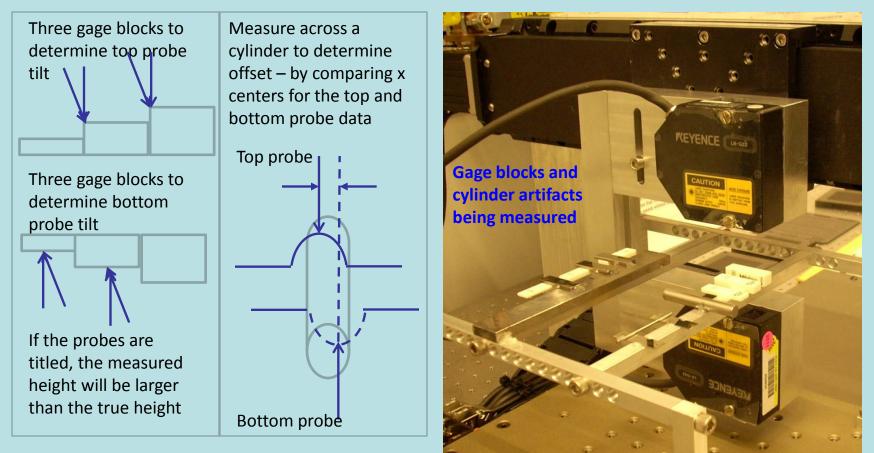


- Profiles (data from both probes) across a thin Al plate are shown.
- Point data from both probes can be used to calculate thickness and variation-in-thickness.
- This additional capability requires specific calibration protocols to determine system parameters, such as, probe offsets and probe tilt angles.



2012 Accomplishments

Current focus is on understanding error sources in measurement, and in developing an uncertainty budget for thickness measurements. We are currently developing methods to precisely calibrate probe offsets (along all three axes), and tilt angles as well, and also understand the influence of errors in these system parameters on the overall thickness error.



Collaborations and Interactions

-0.05

-0.1

-0.2 -0.25

-0.3

-0.35

-0.4

325

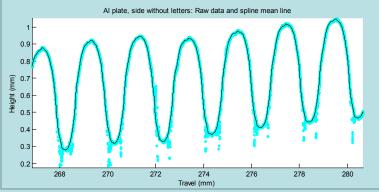
325.2 325.4 325.6 325.8 326

Travel (mm)

Height (mm) -0.15

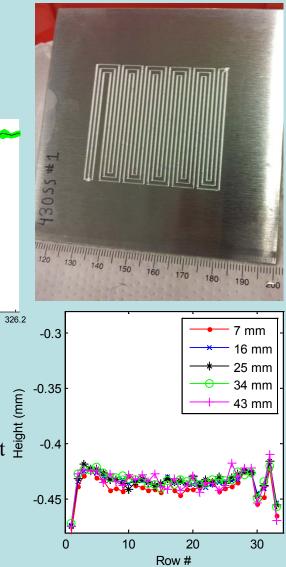
Faraday Technologies - SBIR to investigate application of their patented pulsing electric field technique to optimization of chemical etching SS plates. Provided first evaluation in 2011. Received second set of plates – performed measurements and submitted report in 2012.

TreadStone Technologies – has provided us with three different plates and we have measured them and provided results.



Numerous companies have expressed interest in working with us at the Fuel Cell Seminar in 2011: Dana Corporation Germany, 3M, EnerFuel in Florida, and FuelCell Energy in Connecticut

Both Ballard and UTC Power have engaged us to apply our capabilities in support of their plate manufacturing proposals.



Future Work

The primary focus now and in the next few months is to optimize the measuring accuracy of the new thickness measurement capability. Optimization is done by identifying and characterizing all error sources to aid in the development of an uncertainty budget*.

- Refine our methods for determining in system parameters, such as, probe offsets and tilt angles.
- Reduce most significant error contributions, where possible.
- Assess thickness measurement performance at different speeds to determine degradation in accuracy at higher speeds, if any.

Publications

Archival:

B. Muralikrishnan, W. Ren, D. Everett, E. Stanfield, T. Doiron, Performance evaluation experiments on a laser spot triangulation probe, Measurement: Journal of the IMEKO, 45(3) 2012, 333-343

B. Muralikrishnan, W. Ren, D. Everett, E. Stanfield, T. Doiron, Dimensional Metrology of Bipolar Fuel Cell Plates Using Laser Spot Triangulation Probes, Measurement Science and Technology, 22(7), July 2011

Conference:

B. Muralikrishnan, W. Ren, D. Everett, E. Stanfield, T. Doiron, Noncontact dimensional measurements of bipolar fuel cell plates, Proceedings of the annual meeting of the ASPE 2011, Denver, CO

Poster presentation:

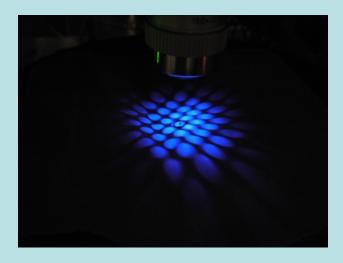
B. Muralikrishnan, W. Ren, D. Everett, E. Stanfield, T. Doiron, Dimensional metrology of fuel cell plates using laser spot triangulation probes, Fuel Cell Seminar 2011, Orlando, FL.

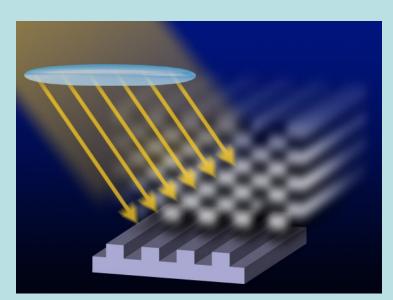
National Institue of Standards and Technology (NIST) Surface and Nanostructure Metrology Group

Optics Project Team

- Dr. Richard Silver Group leader / Physicist
- Mike Stocker Metrologist
- Dr. Bryan Barnes Physicist
- Dr. Hui Zhou Chemical Physicist
- Dr. Yeung-Joon Sohn Physicist
- Dr. Egon Marx Theoretical Physicist
- Francois Goasmat Computer Scientist
- Dr. Jing Qin Physicist

Expertise: optical based semiconductor metrology, microscope characterization, E & M simulation, scatterfield microscopy, tool design, target design, defect inspection, measurement uncertainty, etc.



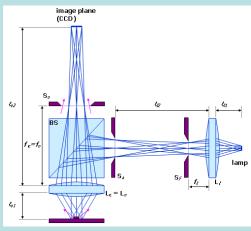


Subproject Overview P3 - Optical Scatterfield Metrology for Online Catalyst Coating Inspection of PEM (Fuel Cell) Soft Goods

Objective: Using catalyst coated samples provided by manufacturers with variations in critical parameters (i.e. Pt and Pt alloy catalyst loading) and inclusion of various types of defects characterized using standard methods (XRF, SEM), evaluate the Optical Scatterfield Metrology Tool's sensitivity to these parameters.

Approach: The Optical Scatterfield Microscopy technique employs both simulation and physical measurement of samples. Simulation is a key aspect of the approach as it allows one to develop accuracy when making optical measurements that require nanometer uncertainties. It provides a flexible and efficient platform to evaluate and optimize measurement parameters even before samples are measured. **Experimentally**, the approach involves acquiring angle and wavelength resolved data on one of three in-house custom designed and fabricated scatterfield capable microscopes or a commercial ellipsometer from Sopra.

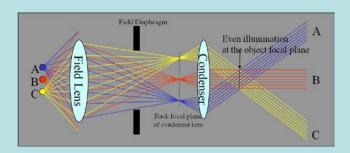
Benefits (Relevance): Provide PEM CCM and GDE manufacturers with an automated high-throughput approach for performing process control inspection of Pt loading with sensitivity equal to or better than that currently provided with XRF (and other parameters of interest simultaneously). Simulations will 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 "total" sample loading measurement.





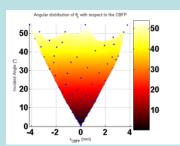
Outline of Presentation

- Review of significant past accomplishments
- 2011 2012 Accomplishments
 - Progress toward accurate electromagnetic (E&M) scattering models of CCMs
 - Perylene samples from 3M
 - Current CCM modeling results
 - Roughness measurements and simulations
 - Optical Design Large Aperture Scatterometry (LAS) measurement system for Pt Loading Measurements
 - Simulation Demonstrations
 - Pinhole defect detection
 - Independent one-sided measurement of double coated CCM
- Future Work
- Collaborations and Interactions









Significant Past Accomplishments: Experimental results from 3M NSTF PtCoMn and pure Pt sample packages

1st Sample Package: PtCoMn NSTF CCM

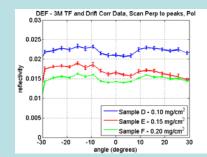
- Sample Loadings: 0.10, 0.15, and 0.20 mg/cm²
- 2010 AMR demonstrated successful application of approach to measurement of catalyst loading (sensitivity ~ 0.01 mg/cm²)
- GO decision for continued work

2nd Sample Package: Pure Pt NSTF CCM

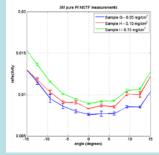
- Sample Loadings: 0.05, 0.10, 0.15 and 0.20 mg/cm²
- 2010 AMR demonstrated sensitivity
- Pt loading determination feasible for pure Pt samples, but not as good as the PtCoMn samples.

3rd Sample Package: W.L. Gore Pt nanoparticle on Carbon CCM (A510/M710.18/C510)

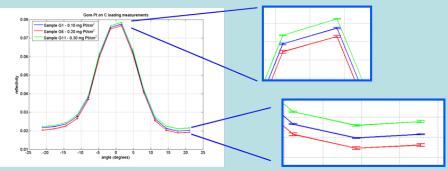
- Sample Loadings: 0.10, 0.20, 0.30, 0.40 mg/cm²
- Made angle-resolved measurements on SF tool, demonstrated sensitivity on the order of 0.03 to 0.05 mg/cm²
- Performed wavelength-resolved measurements on in-house ellipsometer, demonstrated sensitivity on the order of 0.03 to 0.05 mg/cm²
- Further experimental work and model simulation needed to achieve 0.01 mg/cm²



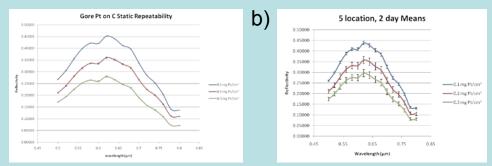
Angle-resolved scan of 3M PtCoMn samples, 150X, 3 location average



Angle-resolved scan of 3M pure Pt samples, 150X, 3 location average



Angle-resolved scan of W. L. Gore Pt nanoparticle on Carbon, 150X, 3 location average



Wavelength-resolved scan of W. L. Gore Pt nanoparticle on Carbon, 150X, a) static repeatability for 3 locations 5 times each, b) reproducibility for 5 locations over 2 day period

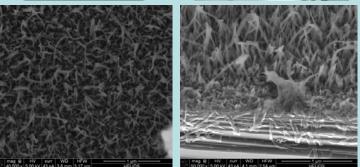
Accomplishments 2011→2012 Perylene Optical Properties

- Working Towards Accurate CCM E&M Scattering Models
 - Collaborating with 3M to generate samples that enable measurement of optical properties of CCM consituent materials. We need **accurate inputs** for the models.
- 2011 1st 3M Perylene/PR149 (Annealed) Sample Set
 - Made spectroscopic ellipsometry (SE) baseline measurements of six 4" Si wafers and provided to 3M for creating Perylene (PR149) samples
 - Sample set: 3 wafers with 1500 Å coating and 3 wafers with 1800 Å coating
 - Acquired SEM data on samples
 - Performed SE measurements on samples to obtain perylene n & k
 - Measurements difficult and limited by spatial dimensions of the surface texture
- 2012 2nd New 3M Perylene/PR149 (Unannealed) Sample Set
 - Provided another round of 4" Si wafers to 3M for new round of samples without annealing. These will give us information about the **bulk properties** of Perylene.
 - Acquired SEM data on samples
 - Performed SE measurements (see subsequent slide)

Scale of surface spatial variations on the same order as the wavelengths





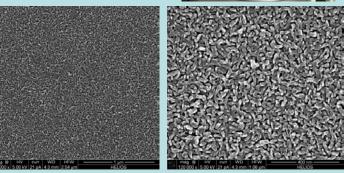


1st 3M Perylene (Annealed) Sample set

Scale of surface spatial variations less than the wavelengths



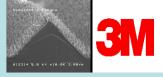




2nd 3M Perylene (Unannealed, No Whiskers) Sample set



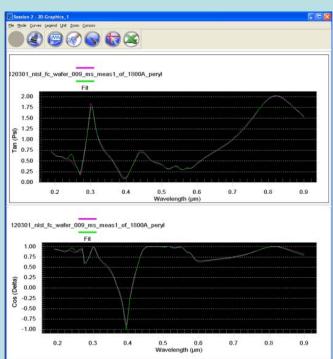
Accomplishments 2011→2012 Perylene Optical Properties



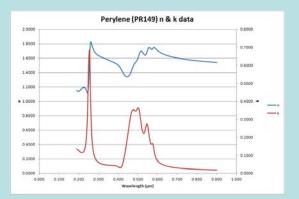
Making n & k Measurements on Bulk Perylene

- Acquired SE spectra for the unannealed 180 nm Perylene coating
- Consulted with ellipsometer manufacturer (Sopra) in fitting the complicated spectra.
- The fit (shown at right) was obtained by using a Modified Cauchy and 7 Lorentz Peaks.
- Obtaining the n & k for bulk Perylene allows us to get one step closer in creating a realistic E&M scattering model for the 3M NSTF CCM. The Perylene whiskers that are used in actual CCM fabrication have a different crystal structure than the bulk Perylene and hence, a different n & k. The effort to obtain n & k for the Perylene whiskers is ongoing.





SE spectra data and fit of 180 nm Perylene coating

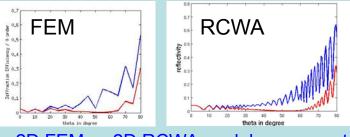


n & k for bulk Perylene/PR149

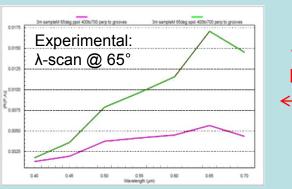
Accomplishments 2011→2012 – CCM E&M Scattering Modeling

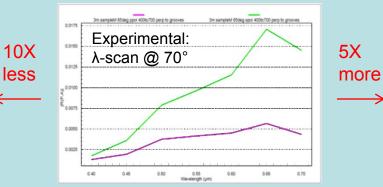
Comparing 2D RCWA and 2D FEM model outputs for 3M NSTF CCM

- Simulation: 0.250 µm EMA catalyst layer on top a 20 µm finite lonomer substrate, angleresolved at 450 nm wavelength
- Both polarizations (blue s pol, red p pol) trend the same direction with similar reflectivity values as a function of angle.
- The increased number of oscillations in the RCWA output is a result of the thin-film interferometric effect from the bilayer.
- The oscillations are part of the motivation for investigating the **effect of roughness**

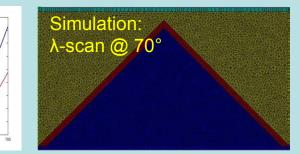


2D FEM vs 2D RCWA model agreement

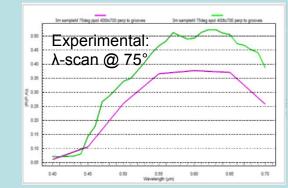




- Theory to Experiment Agreement for 3M NSTF CCM
 - Simulation data: 2D Wavelength scan of triangle structure with catalyst layer (in red) set to 0.1 mg Pt/cm², incorporating new Perylene n & k data
 - Experimental data: Wavelength scan of 3M NSTF CCM with 0.1 mg Pt/cm² loading using commercial spectroscopic ellipsometer
 - Promising agreement, data trends the same as function of λ at illumination angle of incidence of 70°, other angles of incidence give very different reflectivity values



Qualitative Agreement



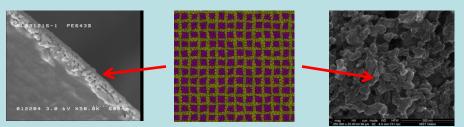
Accomplishments 2011→2012 Roughness Measurements and Simulation

2011 Experimental Roughness Measurements

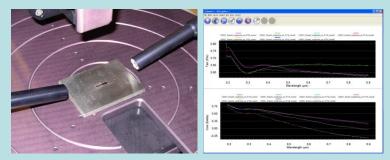
- Acquired 3 Rupert electroformed Nickel roughness samples with random roughness profiles. The samples have Ra values of 34.5 nm, 87.9 nm and 129.9 nm.
- Performed ellipsometric measurements on these samples. Fitting of the data is underway.
- Completion of this task will aid in quantifying the effect of roughness on SE and OSM type measurements of CCMs.

2012 Modeling Roughness for CCMs

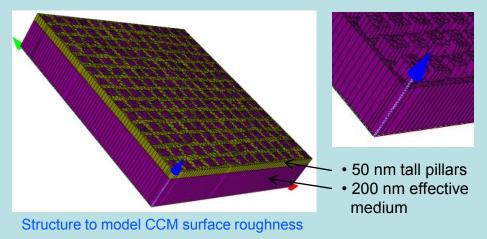
- Built structure to enable simulations for quantifying roughness effect on CCM Scatterfield measurements. Purple is an effective medium approximation (EMA) with Pt, Perylene, Air, and Ionomer. Gold is Air.
- Ran simulations varying the pillar crosssectional area and varying illumination angle of incidence. Change in specular reflection observed as a function of these variations.
- Results are **preliminary** and no quantitative conclusions have been drawn at this point.

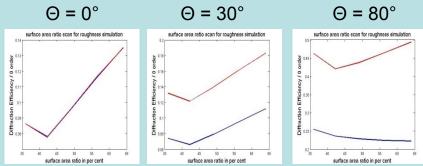


Varying pillar cross-section to simulate CCM roughness



Roughness measurements on Rupert samples



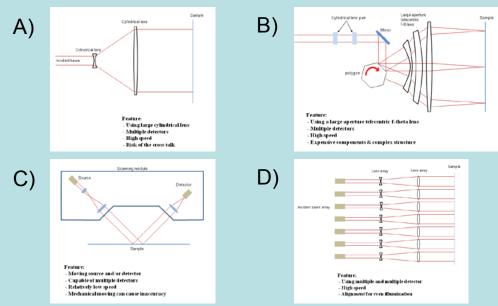


Roughness effect on reflectivity as function of grain size and illumination angle of incidence

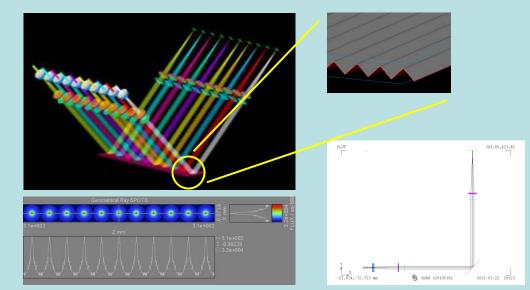
Optical Design of Large Aperture Scatterometry (LAS) system prototype for Fuel Cell CCM Pt Loading Measurements

LAS Optical Design

- For Pt loading measurement, we are investigating a scatterometric approach (No high-magnification)
- Still has advantages of acquiring data as function of wavelength, polarization, and angle of incidence
- Completed design study, arriving at four possible LAS configurations, factoring in field of view, web area of coverage, wavelength, sample reflectance, etc.
 - A) Wide Illumination Beam
 - B) Scanned Illumination Beam
 - C) Single Source and Detector
 - D) Multiple Source and Detector
- Performed a complete optical design of configuration D).
- Prototype Parts purchased
- Initial data expected by AMR 2012 meeting. Will perform dynamic Pt loading measurements as a function of web speed (simulating a real web by moving sample on a programmable stage)

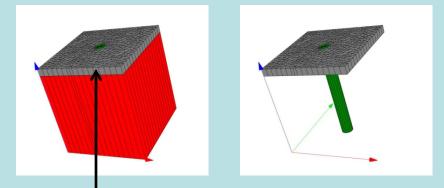


Four Possible LAS Design Configurations



Complete Optical Design of LAS configuration D)

Accomplishments 2011→2012 – Simulation Demonstration: Pinhole Defect



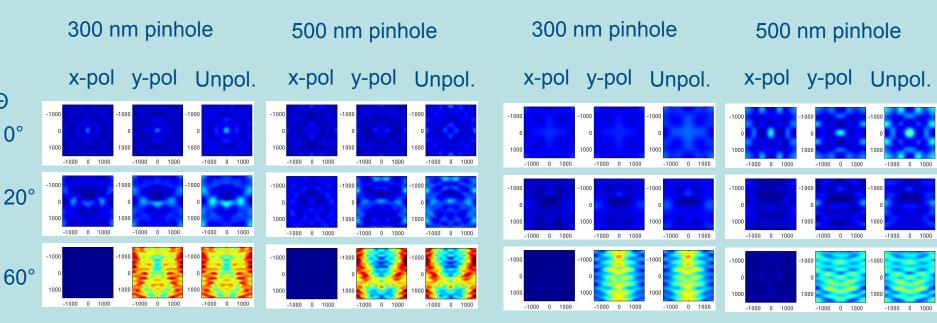
The domain size is 3 μ m by 3 μ m. The pinhole is created through the entire catalyst and PEM layer.

Θ

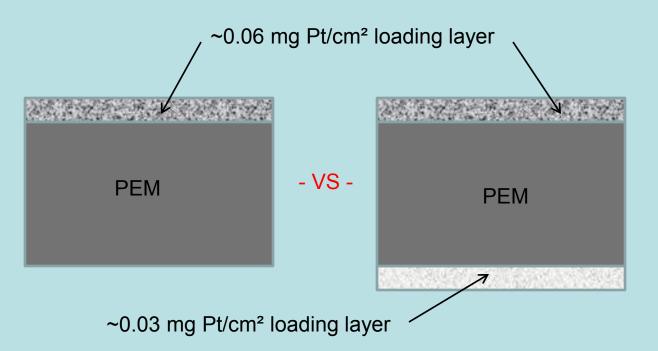
 $\lambda = 450 \text{ nm}$

Initial demonstration showing the change in intensity of a pinhole in a membrane measured as a function of polarization, wavelength, and illumination angle of incidence. Optical constants were used that are representative of the types of materials found in a modern CCM. No quantitative conclusions should be drawn at this point.

λ = 700 nm



Accomplishments 2011→2012 – Simulation Demonstration: Independent One-sided Measurement of a Double Coated CCM

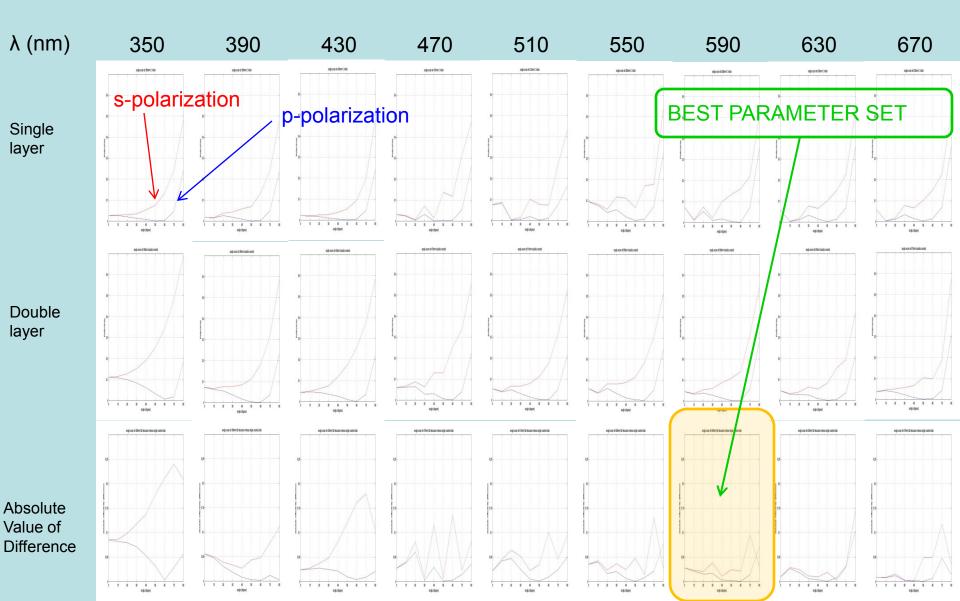


Simluation Description:

Angle scans ranging from 0° to 80° were performed at multiple wavelengths ranging from 350 nm to 700 nm of the single coated CCM and the double coated CCM.

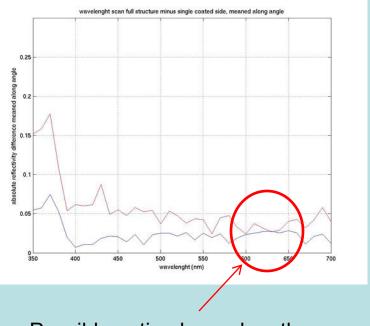
Initial simulation of a one and dual sided CCM as a function of polarization, wavelength, and angle of incidence. The difference between the two simulations was calculated. From looking at the difference plots, one can observe the **optimal measurement configuration** for the microscope with respect to polarization, wavelength, and angle of incidence. This is where you would perform a measurement of the top loading layer with **minimal influence** from the bottom loading layer. This set of simulations is intended to demonstrate the flexibility in the optical technique to optimize or tune the microscope to perform a given measurement task.

Accomplishments 2011→2012 – Simulation Demonstration: Independent One-sided Measurement (Simulation) of a Double Coated CCM – Raw Simulation Data



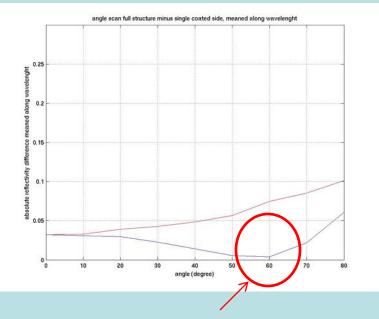
Accomplishments 2011→2012 – Simulation Demonstration: Independent One-sided Measurement (Simulation) of a Double Coated CCM – Simulation Data Summary

Mean absolute difference of every angle at each wavelength



Possible optimal wavelength range

Mean absolute difference of every wavelength at each angle



Possible optimal polarization and angle of incidence.

- Averaging the simulation data for every angle, a possible optimal wavelength range is observed.
- Averaging the simulation data for every wavelength, a possible optimal polarization and angle of incidence is observed.

Future Work

- 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. Solicity industry input as to the types/sizes/distributions of defects that cause real performance losses
- Publish OSM fuel cell results in refereed journal

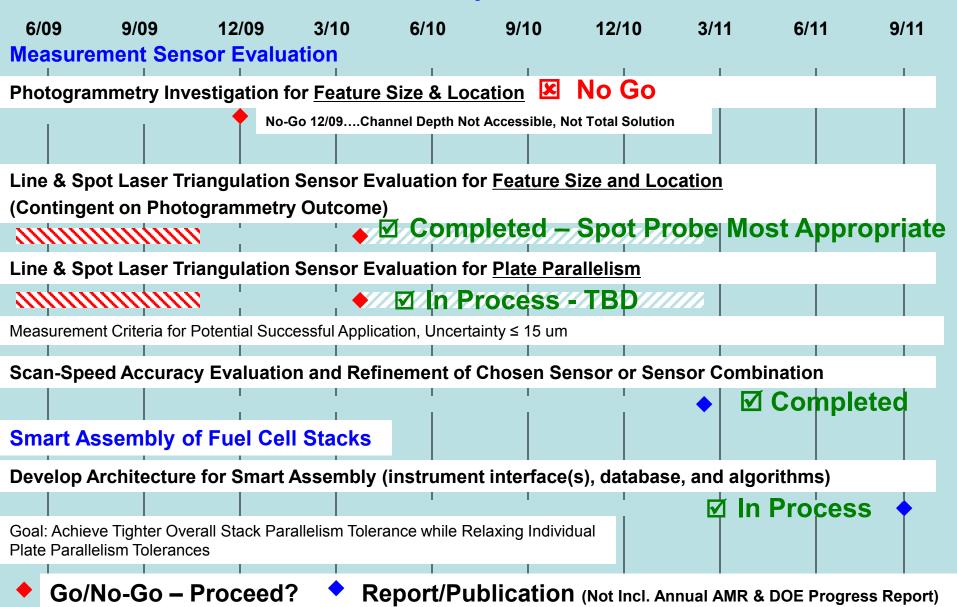
Collaborations and Interactions

- Continued collaborations with 3M Company and W. L. Gore to further develop and advance OSM as a viable manufacturing metrology solution for performing Pt loading measurements as well as defect detection measurements.
- Engaging in R&D discussions with leading semiconductor toolmaker for future collaborations to develop real OSM or LAS process control prototype measurement system.
- NIST included in DOE IMI proposal (DE-FOA-0000560) with Los Alamos National Laboratory and Electro-Chemical Devices (Concept Paper Control Number: 0560-2984) to provide a unique high-throughput optical metrology technique capable of nanometer-scale materials characterization and defect detection based on the highly successful Scatterfield Microscopy platform.

Technical Backup Slides

(Revised 11/25/2009) Deliverables 3rd Quarter FY2009 – End of FY2011

Non-Contact Sensor Evaluation for Bipolar Plate Manufacturing Process Control and Smart Assembly of Fuel Cell Stacks



(Revised 11/25/2009) Deliverables 3rd Quarter FY2009 – End of FY2011 **Optical Scatterfield Microscopy (OSM) for Online Catalyst Coating Inspection of** Proton Exchange Membrane (PEM) Fuel Cell Soft Goods 12/09 12/109/11 6/09 9/09 3/10 6/10 9/10 3/11 6/11 **NIST/NREL** Cooperative Effort ✓ Ongoing **Develop NIST/NREL Cooperative Plan** NDA Establishment with Industry Mfgrs & Execution of Deliverables Define scope of support with deliverables, cross-link manufacturer agreements, information sharing NIST OSM Catalyst Coating Sensitivity Study Preliminary Catalyst Loading Measurements of Novel CCM Samples MSTF Pt Alloy & Pt Completed Validate Sensitivity OSM sensitivity using other conventional Ongoing \square Pt/C CCM \rightarrow GDE catalyst coated components (other CCMs, GDEs (cloth and paper). 2nd Package consists of samples with various Pt loadings from various Pt/C weight percentage mixtures **OSM Parameter Investigation for Catalyst Loading Measurements** ✓ GO! Success Investigate Obvious Technique Modifications to Enhance Sensitivity to Loading [Instrument Illumination: angle, wavelength, (1) polarization, and spatial filters.....Instrument Collection: spatial (wavelength) filters.....Algorithm Studies: intensity, thresholding, spatial (pixel size) filters, pixel histograms] Investigate New Approaches to Enhancing and Understanding OSM's Potential Sensitivity to Pt Loading: (a) incorporation (2) of time-dependent illumination and CO tagging into current OSM technique and (b) perform finite domain time difference (FDTD) parametric modeling of one or both types of CCMs.

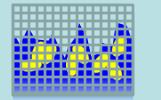
OSM Parameter Investigation for <u>Other</u> Critical Catalyst Coating Parameters

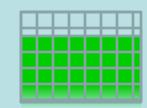
Specific parameters to be identified as a result of NIST/NREL cooperative plan

Go/No-Go – Go to Proceed! **Report/Publication** (Not Incl. Annual AMR & DOE Progress Report)

Motivations for using an Effective Medium Approximation

- We have a lack of blanket constituent films.
- Surface roughness drives need for EMA.
 - Rigorous modeling of roughness requires 3-D models
- Computational requirements necessitate approximation.
 - Memory constraints
 - CPU constraints





and

VS.

