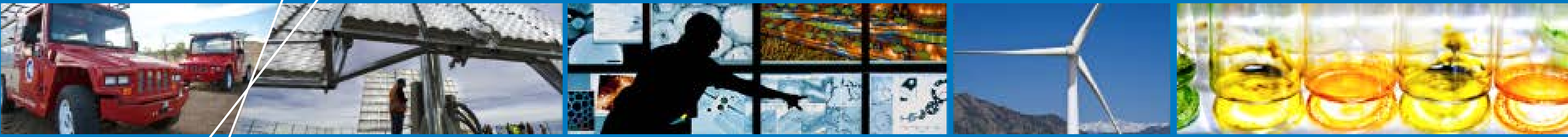
Fuel Cell MEA Manufacturing R&D



National Renewable Energy Laboratory

Michael Ulsh

June 18, 2014

MN001

Overview

Timeline

Start: July 2007

End: Project continuation and direction determined annually by DOE

% complete: N/A

Budget

Funding received in FY13

- $575,000 (includes $160,000 to partners)

Planned funding in FY14

- $850,000 (includes $310,000 to partners)

Barriers

Barriers	Target
E: Lack of Improved Methods of Final Inspection of MEAs	$21/kW (2017) at 500,000 stacks/yr
K: Low Levels of Quality Control	

Funded Partners

Lawrence Berkeley National Laboratory

Colorado School of Mines

New Jersey Institute of Technology

Relevance: Project addresses most MYPP milestones

From MYPP Section 3.5: Manufacturing R&D

Task 6: Quality Control and Modeling and Simulation	
6.1	Develop continuous in-line measurement for PEM MEA fabrication. (4Q, 2012)
6.2	Develop defect detection techniques in pilot scale applications for manufacturing MEAs and MEA components. (4Q, 2013)
6.3	Establish models to predict the effect of manufacturing variations on MEA performance. (4Q, 2014)
6.4	Demonstrate methods to inspect full MEAs and cells prior to assembly into stacks (4Q, 2014)
6.5	Validate and extend models to predict the effect of manufacturing variations on MEA performance. (4Q, 2014)
6.6	Demonstrate continuous in-line measurement for MEA and MEA component fabrication. (4Q, 2015)
6.7	Develop methods to mark identified defects for later removal (4Q, 2015)
6.8	Develop and demonstrate techniques and diagnostics for automated or continuous in-line measurement of high temperature cells and sub-assemblies during fabrication. (4Q, 2016)
6.9	Develop correlations between manufacturing parameters and manufacturing variability, and performance and durability of MEAs (4Q, 2017)

Task 1: Membrane Electrode Assemblies
Develop continuous in-line measurement for MEA fabrication. (4Q, 2012)
Reduce the cost of manufacturing MEAs by 25%, relative to 2008 baseline of $126/kW (at 1,000 units/year). (4Q, 2013)
Develop processes for direct coating of electrodes on membranes or gas diffusion media (4Q, 2014)
Develop processes for highly uniform continuous lamination of MEA components (4Q, 2014)
Develop cell manufacturing processes that increase throughput and efficiency and decrease complexity and waste (4Q, 2015)
Demonstrate processes for direct coating of electrodes on membranes or gas diffusion media (4Q, 2016)
Demonstrate processes for highly uniform continuous lamination of MEA components (4Q, 2016)
Develop fabrication and assembly processes for PEM fuel cell MEA components leading to an automotive fuel cell system that cost $30/kW. (4Q, 2017)
Develop fabrication and assembly processes for membranes that operate at T > 150°C with a projected durability of 60,000 hours. (2Q, 2019)

Relevance: Scale-up of Automotive Fuel Cells

…Auto experts say, however, that **defects frequently arise in the production of fuel cells.** Thus, the pending issue is how to improve the situation until the start of mass production.

January 29, 2014

Naoki Ogawa and Hajime Yamagishi / Yomiuri Shimbun Staff Writers Automakers are ready to begin full-fledged production of fuel-cell vehicles (FCVs), dubbed "the ultimate form of eco-friendly cars."

Collaborations

Industry Collaborators

- **GM, AFCC, W.L. Gore & Associates*, Ion Power, and other commercial MEA suppliers and membrane developers:** detailed input on manufacturing QC needs, prioritization of diagnostic development, feedback on technique capabilities, defect selection and sample fabrication

***** DOE Manufacturing project***

Funded Partners

- **NREL National Center for Photovoltaics/New Jersey Institute of Technology:** diagnostics development
- **Lawrence Berkeley National Lab:** model development and integration
- **Colorado School of Mines:** diagnostics development

Approach

- Understand quality control needs from industry partners and forums
- Develop diagnostics
  - Use modeling to guide development
  - Use in-situ testing to understand the effects of defects
- Validate diagnostics in-line
- Transfer technology

Date	Milestone/Deliverable	Complete
9/13	Demonstrate through-plane IR/DC on CCM sheet	100%
12/13	Demonstrate IR/DC on Ion Power production coating line	100%
3/14	Determine feasibility of capacitance measurement for bench-top roller (Go/No-Go)	100%
6/14	Preliminary demonstration of IR/RIF on web-line (as of 4/15/14)	40%
8/14	Demonstrate IR/RIF on web-line (as of 4/15/14)	20%

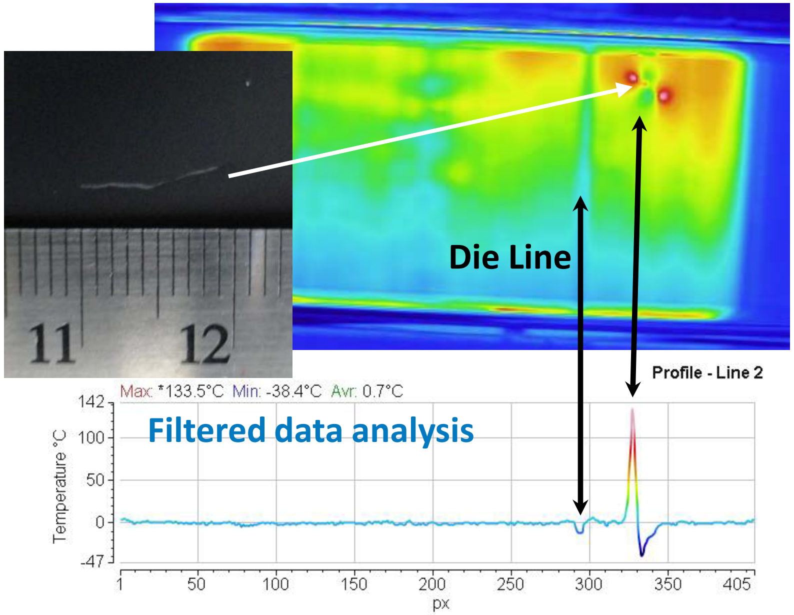
Technical Accomplishments: Implemented IR/DC on industrial coating line at Ion Power

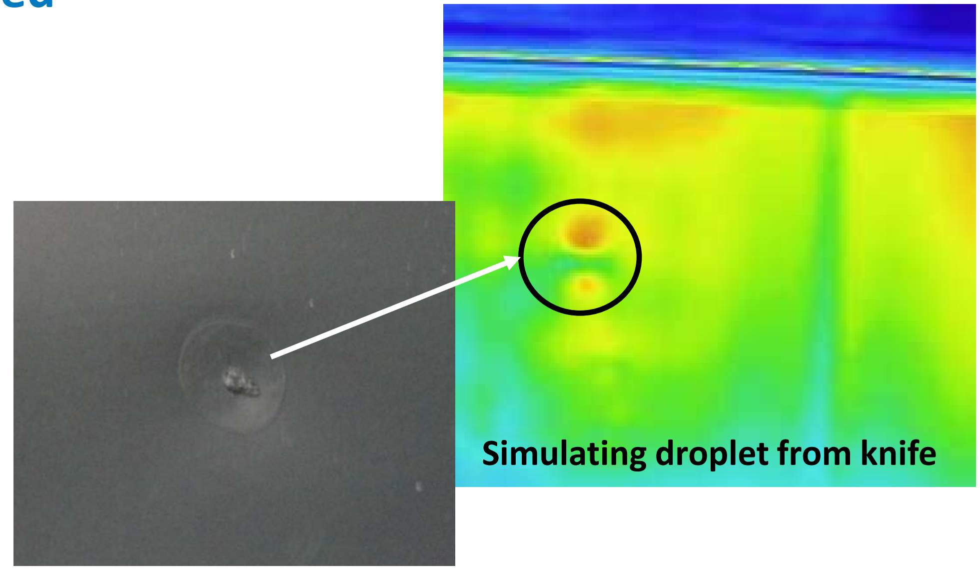
- **Previously reported:**
  - IR/DC of Ion Power electrode decal sheet on NREL web-line using small roller system
  - Agreement on coating line implementation with Ion Power
  - Design of larger roller system
- **New accomplishments:**
  - Fabrication and commissioning of new roller system
  - Verification of previous data on NREL web-line
  - Implementation at Ion Power
  - Additional testing of coated samples at NREL

New roller system commissioning on NREL web-line

Technical Accomplishments: Implemented IR/DC on industrial coating line at Ion Power

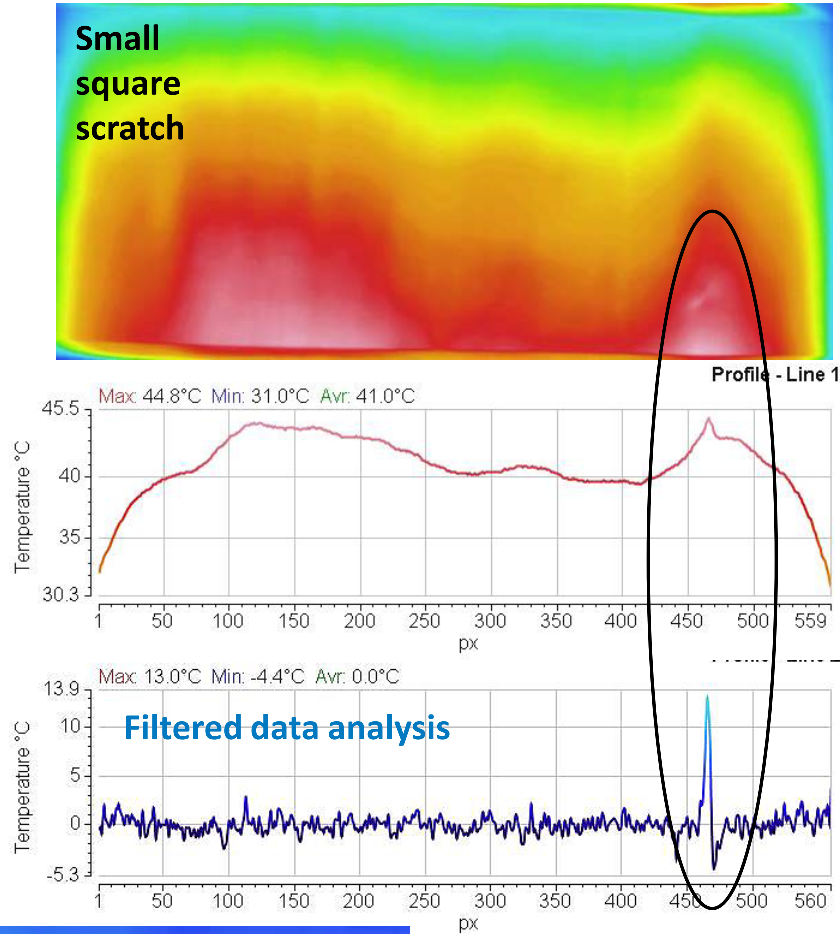
- **Ion Power Implementation:**
  - Set up IR/DC equipment on electrode coating line
  - Collected data on 3 coating runs
    - Defects created in wet coating
    - Defects created in semi-dry coating
    - Simulated process defects
  - Successfully detected defects at speed at the drying oven exit
    - Die line
    - Scratches: 10s of µm wide x few mm long
    - Added material (droplet/lump): 1 mm
    - Start/stop

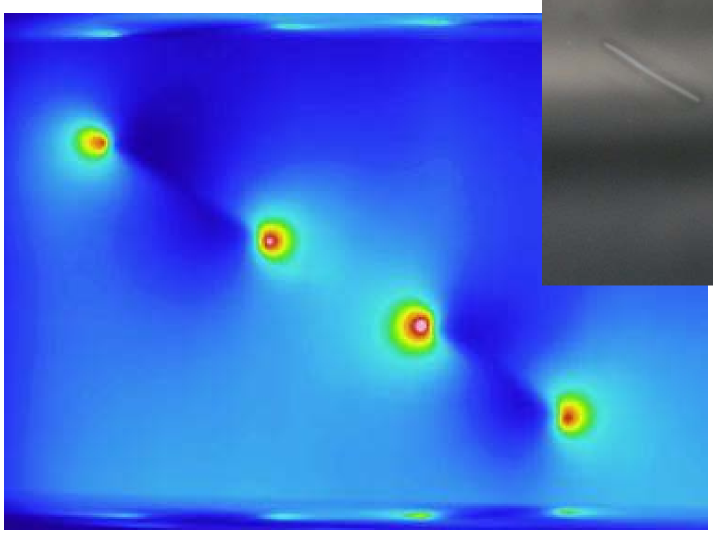


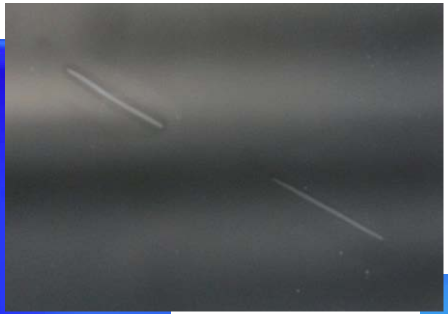


Technical Accomplishments: Implemented IR/DC on industrial coating line at Ion Power

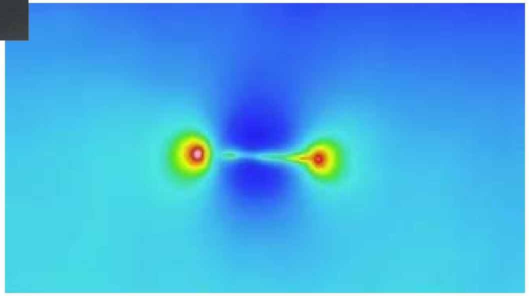
- **Additional Testing of Coated Samples at NREL:**
  - Replicated data taken on Ion Power line at same conditions
  - Determined excitation conditions required for higher line speeds
  - Successfully detected all defects at line speeds up to 60 ft/min





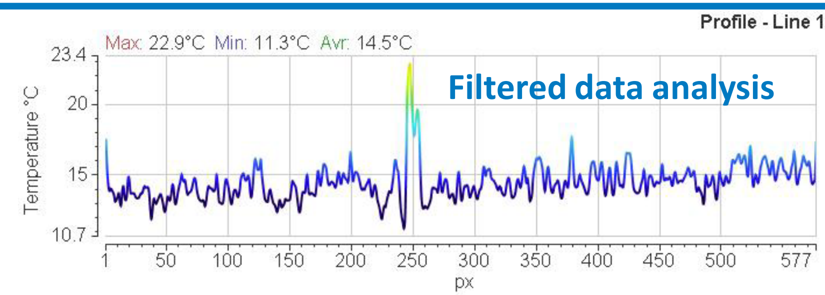


Diagonal and perpendicular scratches

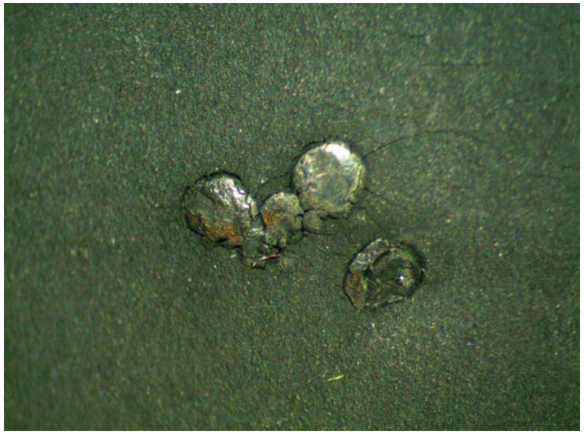


Technical Accomplishments: Demonstrated through-plane IR/DC on 2-sided CCM sheet

- Used sheet of two-side coated CCM from Ion Power on roller system
- Detected real shorting defect due to catalyst agglomerate
- Created and detected thru-plane defects including holes and conductive vias

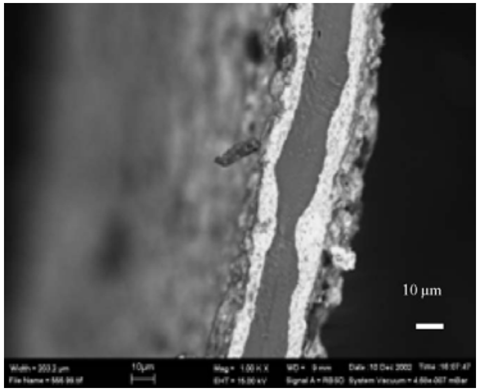


Agglomerates in catalyst layer and resulting thermal signature due to shorting

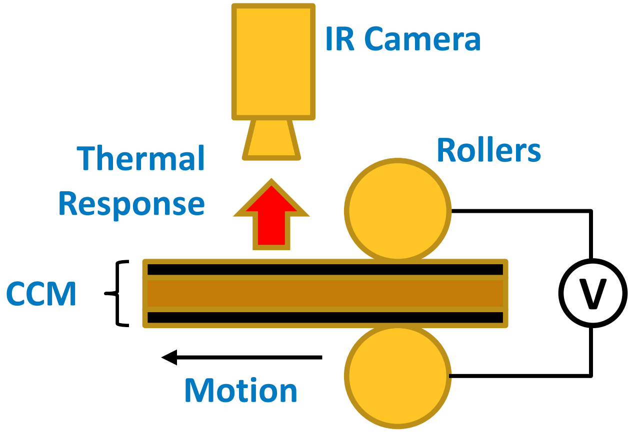


Reference Data

Gittleman et al., "Membrane Durability: Physical and Chemical Degradation", in *Modern Topics in Polymer Electrolyte Fuel Cell Degradation*, Elsevier, 2011, pp. 15-88.

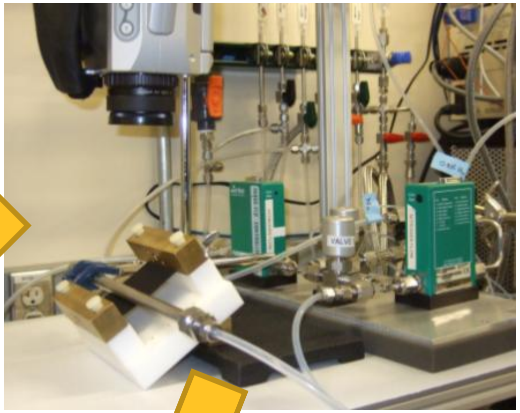


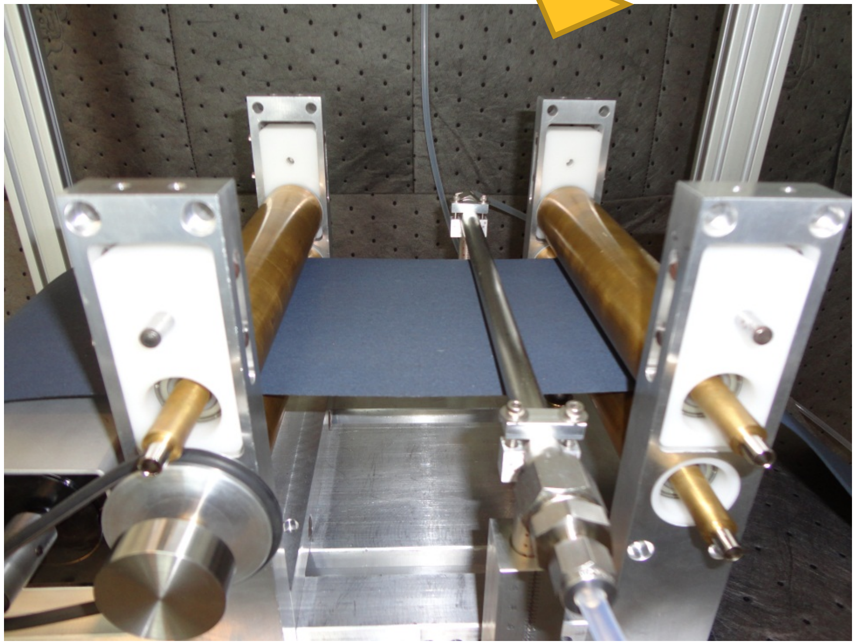
Kundu et al., *Journal of Power Sources*, **157** (2006) 650–656.



Technical Accomplishments: Demonstrated IR/RIF in open environment with moving GDE

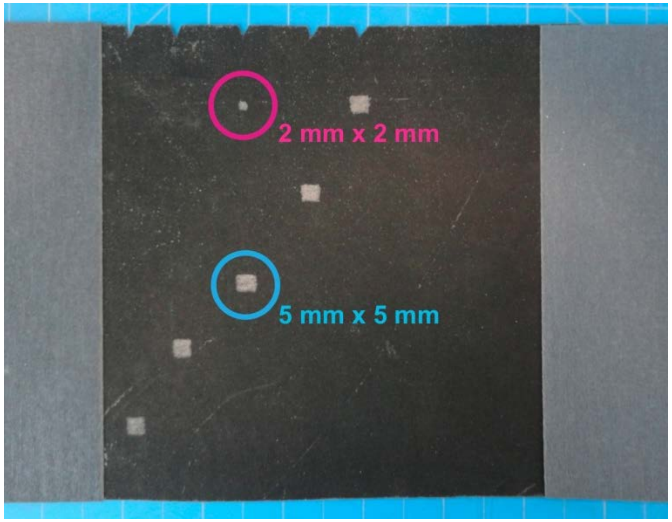
- **Previously reported:**
  - Development of IR/RFT for GDE defect detection in enclosed chamber
  - Feasibility test in open environment using gas knife but stationary GDE
- **New accomplishments:**
  - Demonstration of IR/Reactive Impinging Flow (RIF) technique with moving GDE sheet
  - Study of impinging flow dynamics
  - Modeling of impinging flow
  - Data and noise analysis

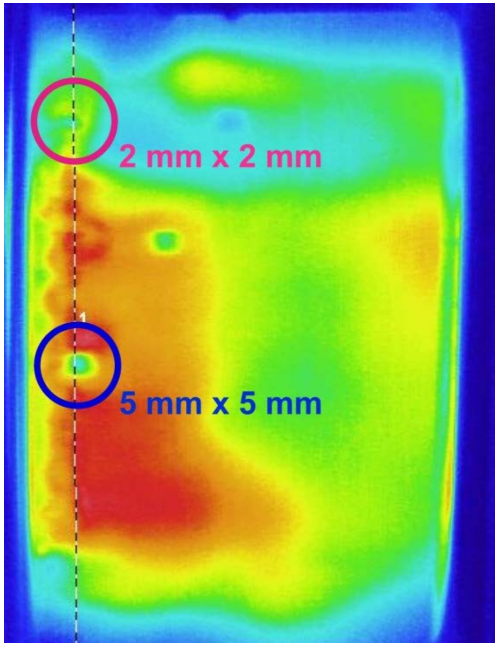


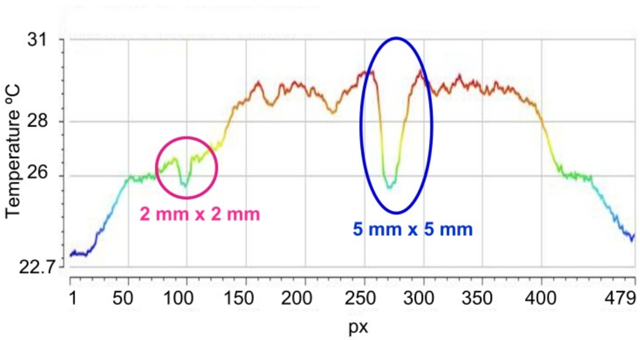


Technical Accomplishments: Demonstrated IR/RIF in open environment with moving GDE

- **IR/RIF Setup:**
  - Bench-top roller system
  - Gas knife
  - Non-flammable reactive gas with 2% H_2; flows up to 20 slpm
  - Commercially available GDE sheet with created defects
  - GDE sheet moving at 30 ft/min
- **Successfully detected bare spot defects as small as 2mm x 2mm**





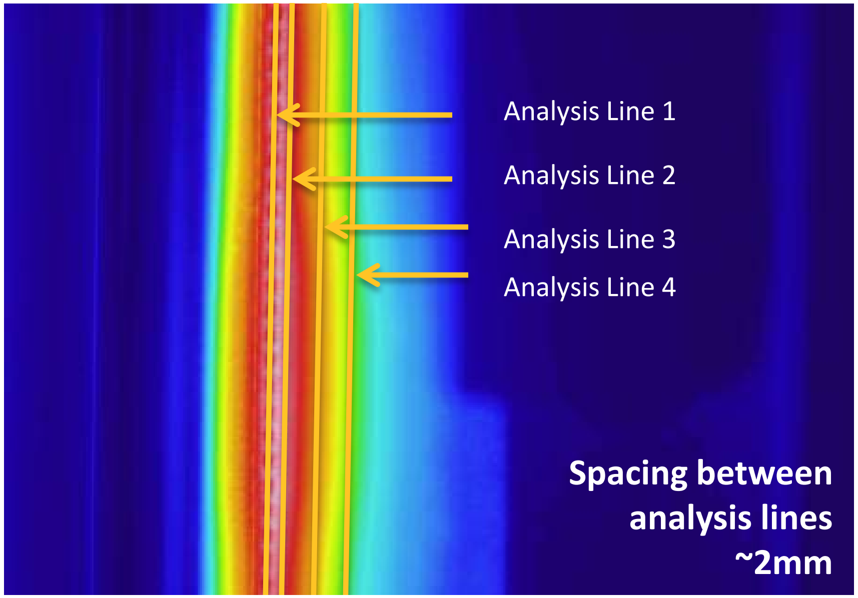


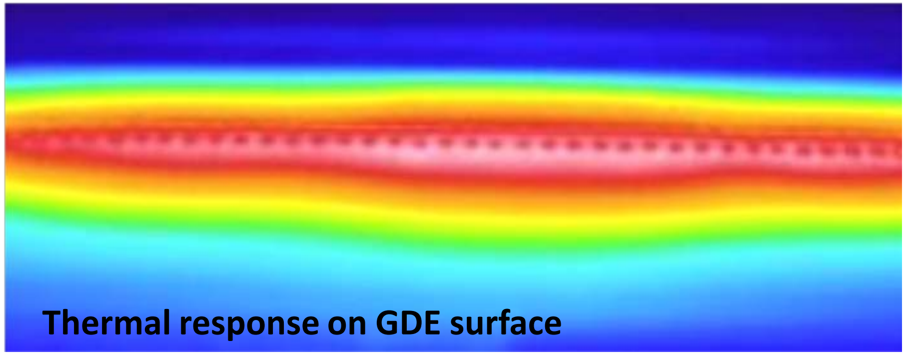
Reference Data

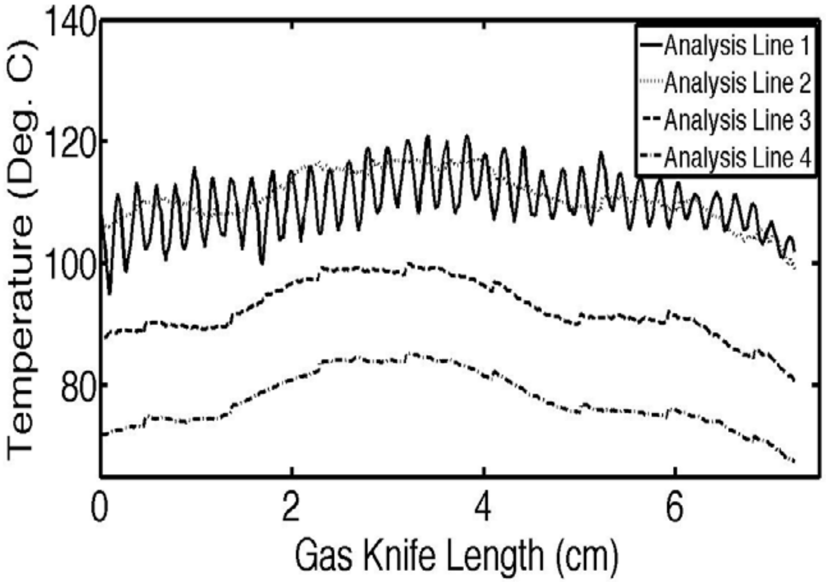
E De Castro, "High Speed, Low Cost Fabrication of Gas Diffusion Electrodes for Membrane Electrode Assemblies", 2010, Hydrogen Program Annual Merit Review

Technical Accomplishments: Studied IR/RIF impinging flow dynamics

- **Impinging flow dynamics study**
  - Camera angled to view underneath gas knife
  - Stationary GDE sample
  - Effects of knife holes observed
  - Thermal balance between convection and reaction
  - Thermal profile becomes uniform not far from holes

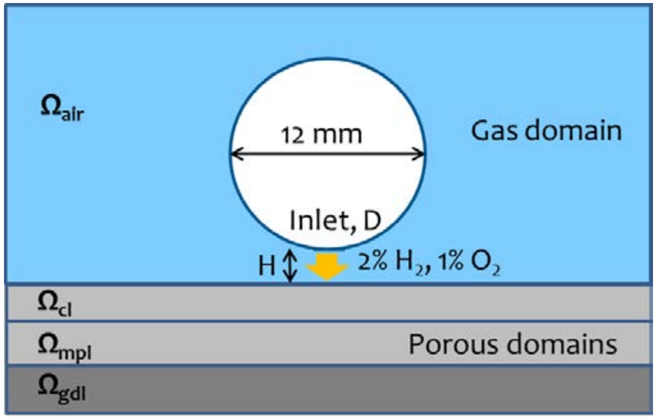


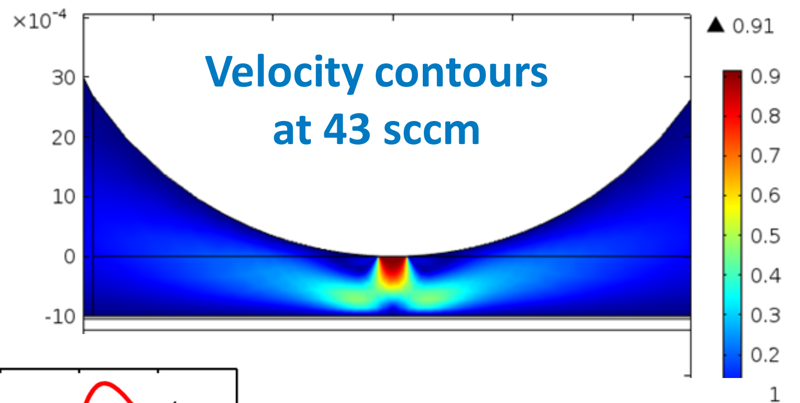


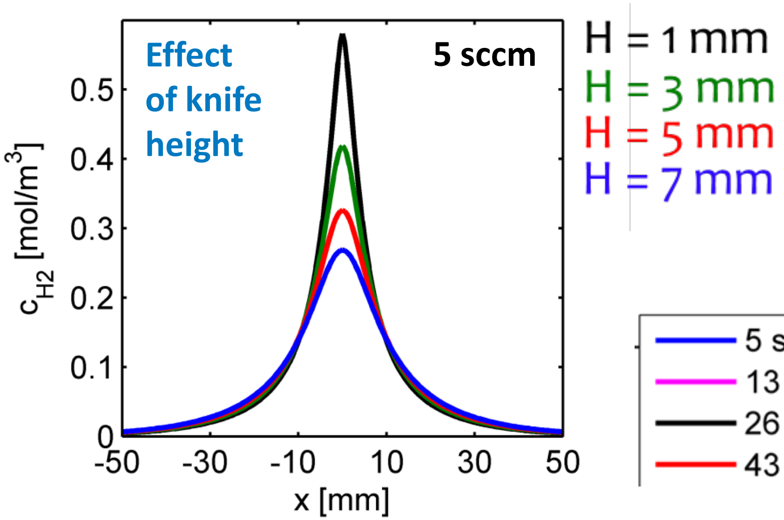


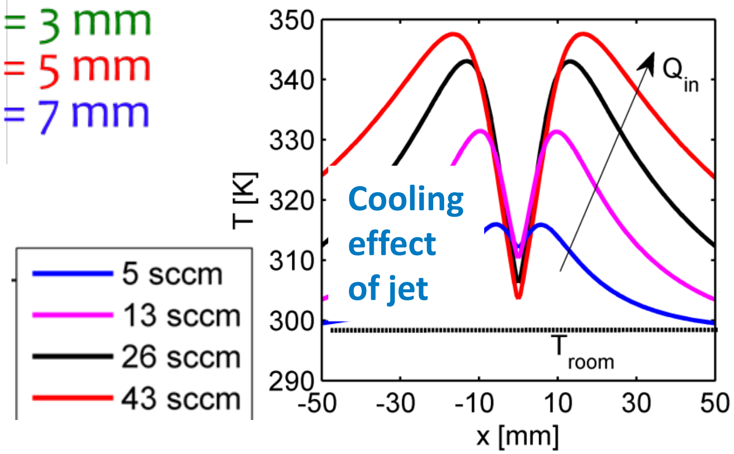
Technical Accomplishments: Developed impinging flow model to guide technique development

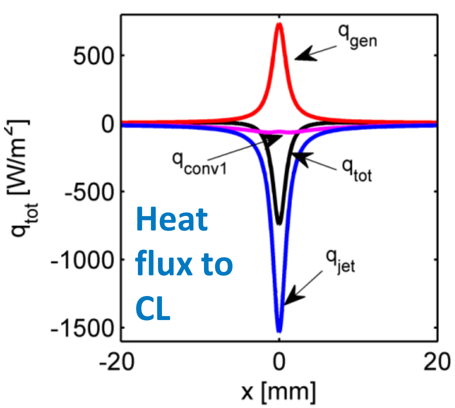
- **Impinging flow modeling (LBNL)**
  - Developed steady-state 2D model using Comsol Multiphysics®
  - Physics: fluid flow, diffusion of gas into GDE, surface reaction, heat transfer
  - Modeled: flowrate, flow angle, knife height, knife geometry
  - Very good qualitative agreement with experiment





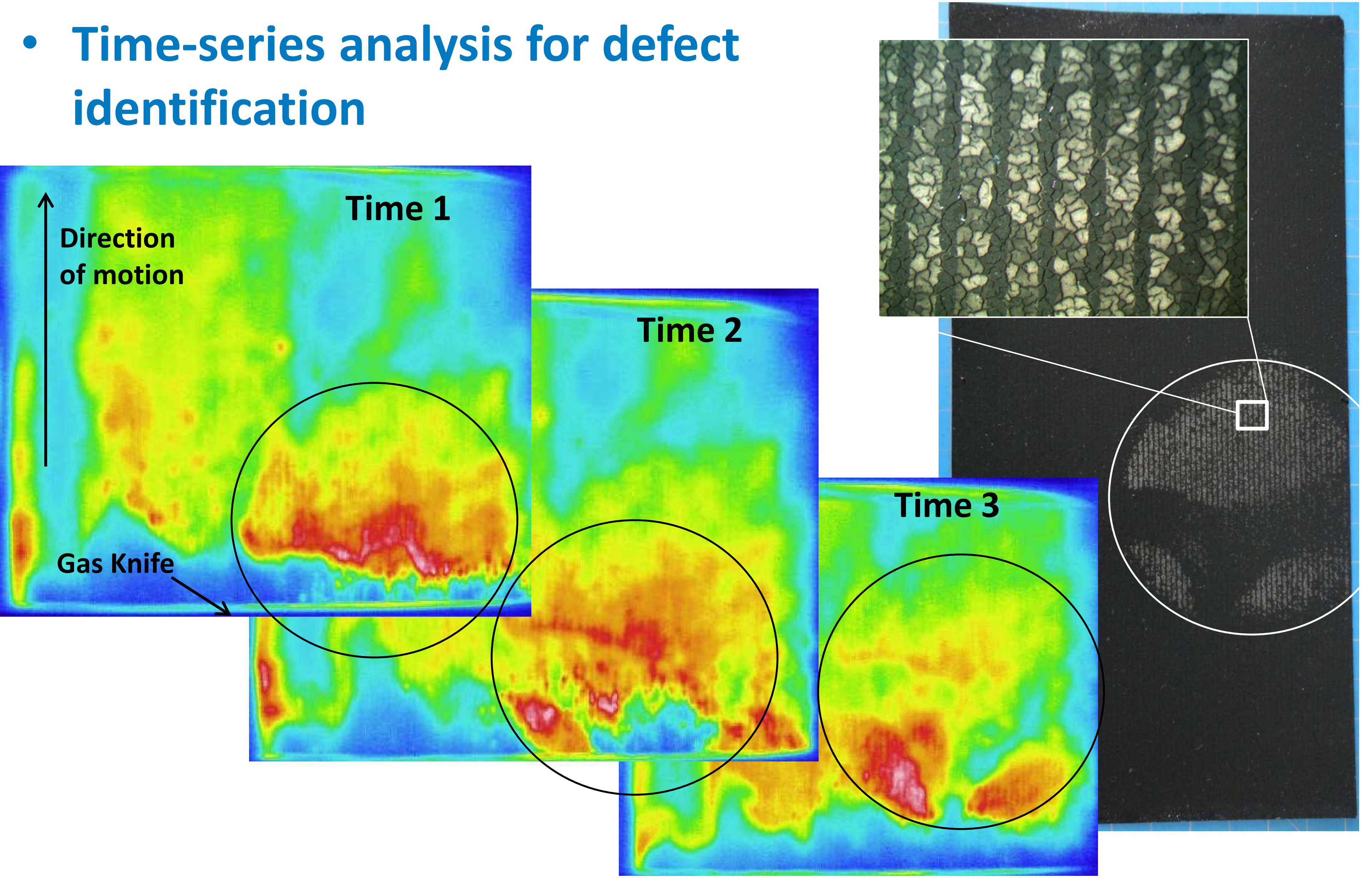




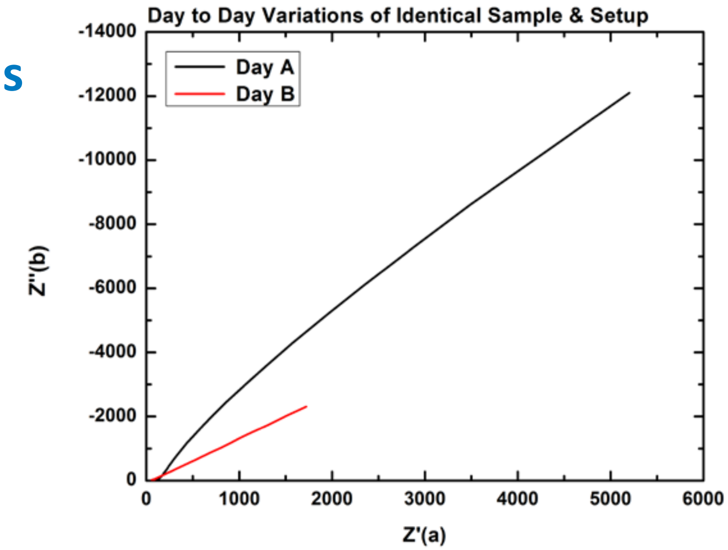


Technical Accomplishments: Demonstrated IR/RIF on commercial GDE sheet with coating defects

- Time-series analysis for defect identification



Technical Accomplishments: Recommended No-go decision for capacitance measurement of I:C



Day-to-Day Reproducibility

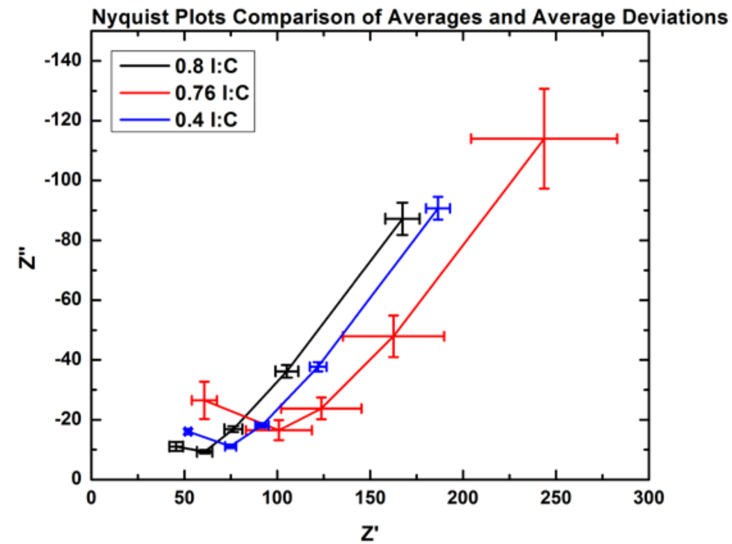
- Identical test sample, setup, and test conditions
- Results varied unacceptably

⇒ An unknown factor impacts the day-to-day reproducibility of the experiment

Variation in capacitance due to RH

- Water uptake of Nafion® strongly affects dielectric properties

⇒ Even with humidity control, potential variation of capacitance due to RH is unacceptable



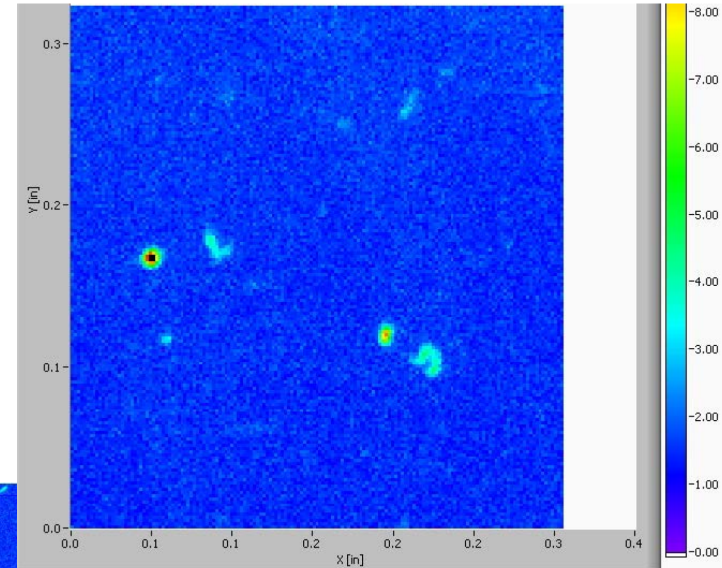
Exp-to-Exp Reproducibility & Dependence on I:C Ratio

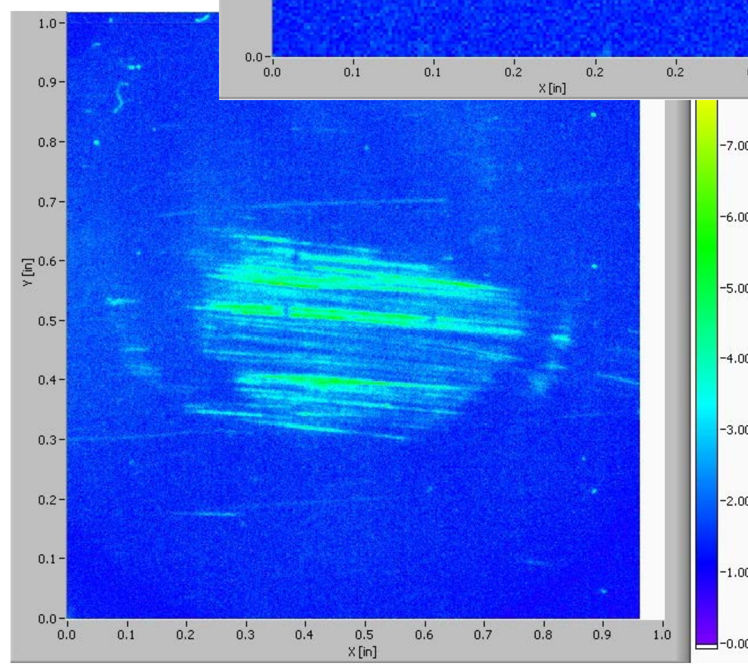
- Measurement variations ≥ 5% observed
- No conclusive trend observed with I:C ratio

⇒ Variations too large to observe small parameter changes

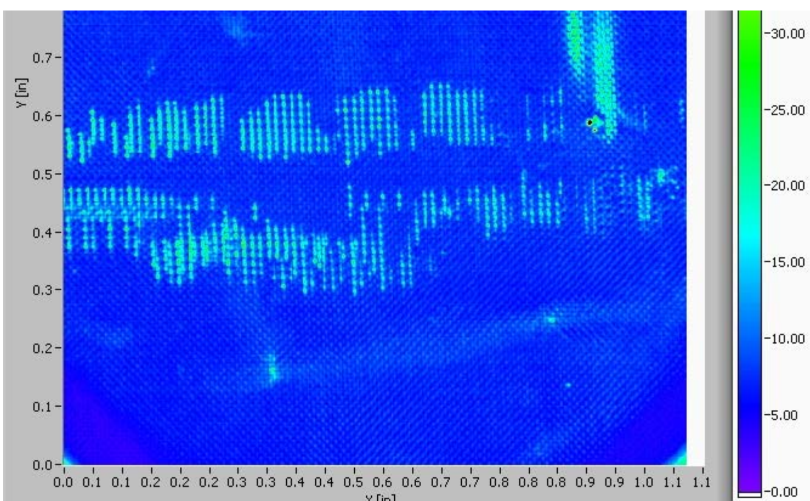
- Samples from commercial MEA supplier
- Detected known defects in PFSA and PFSA+reinforcing mesh membranes

Bubbles and scratches in PFSA membrane





Defects in mesh-containing membrane



Barriers, Needs and Future Work

Barriers and Needs

- General barriers and needs are documented in the MYPP (slide 3)
  - Developing and demonstrating QC methods
  - Understanding how defects affect performance and lifetime
- We actively engage with industry to understand their needs, based on their specific processes, materials and MEA constructions
  - QC for membranes, electrodes, various sub-assemblies and full MEAs
  - Increasing interest in applicability of techniques to in-process measurement

Future Work

- Demonstrate RIF on NREL web-line
- Apply optical and infrared techniques, with optimal excitations, to relevant industry MEA constructions
- Develop/modify techniques to address new needs
- Study the effects of relevant defects on cell performance and lifetime
- Develop and integrate models for optimizing diagnostics and for predicting performance effects of defects

Summary

- **Highlighted relevance of QC development for automotive fuel cell scale-up**
  - **Continued detailed information exchange with industry partners on QC development priorities**
- **IR/DC:**
  - **Implemented IR/DC on Ion Power production coating line**
  - **Studied excitation conditions as a function of web-speed**
  - **Demonstrated through-plane IR/DC for shorting defects on 2-sided CCM sheet**
- **IR/RIF:**
  - **Demonstrated RIF in open environment with moving GDE**
  - **Studied impinging flow dynamics experimentally**
  - **Developed multi-physics model for impinging flow**
  - ***Evaluated several data analysis techniques***
  - ***Initiated design and fabrication of equipment for web-line demonstration***
- **Optical Reflectometry:**
  - **Continued to expand application to additional materials**
- **Studied electrode capacitance vs. I:C ratio as a potential new diagnostic**
- ***Hosted EERE QC Workshop***
- ***Assisting HTAC Manufacturing subcommittee***

Response to Reviewer Comments

Comment: ***"Still to be resolved is the correlation between the prearranged defects that are used to develop the diagnostics and the defects encountered on high-speed lines."***

Response: We strive to use samples with actual defects as much as possible, for example slide 17 showing membranes with actual defects, slide 10 showing an actual agglomerate in an electrode layer, slide 15 showing a real surface defect on a GDE, and slide 8 showing a die line in a coated electrode layer.

Comment: ***"…It is not clear if these defects had a significant effect on performance."***

Response: Clearly there is strong interest in understanding how the sensitivity of the diagnostic techniques should be informed by how certain defects affect the performance and/or lifetime of the cell. There are clear benefits to a close coupling between these efforts, which includes the defects modeling effort at LBNL.

Comment: ***"Perception of relevance would be enhanced if there were clearer indications that the NREL project closely aligned with component suppliers' recommendations on diagnostic development needs."***

Response: We have, through the life of this project, always strived to gain as much industry input as possible to inform and direct our work. As companies' activities rise and fall, their interest in this topic changes, such that we typically have a mix of long-term partners and new or returning partners. Our strong interactions with several auto OEMs underlies this commitment. We continue to have very detailed discussions with these manufacturers with regards to the critical needs for manufacturing QC.

Acknowledgement

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- Michael Ulsh
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CSM

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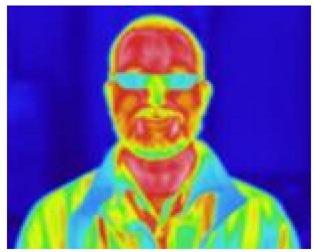
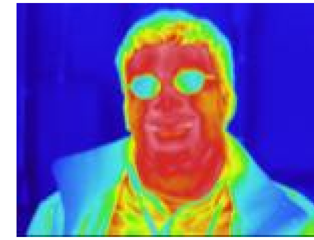
NJIT

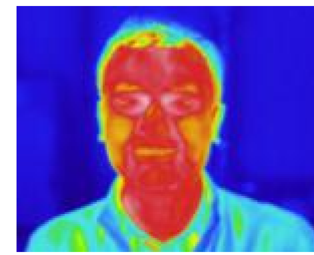
- Srinivas Devayajanam

DOE

- Nancy Garland



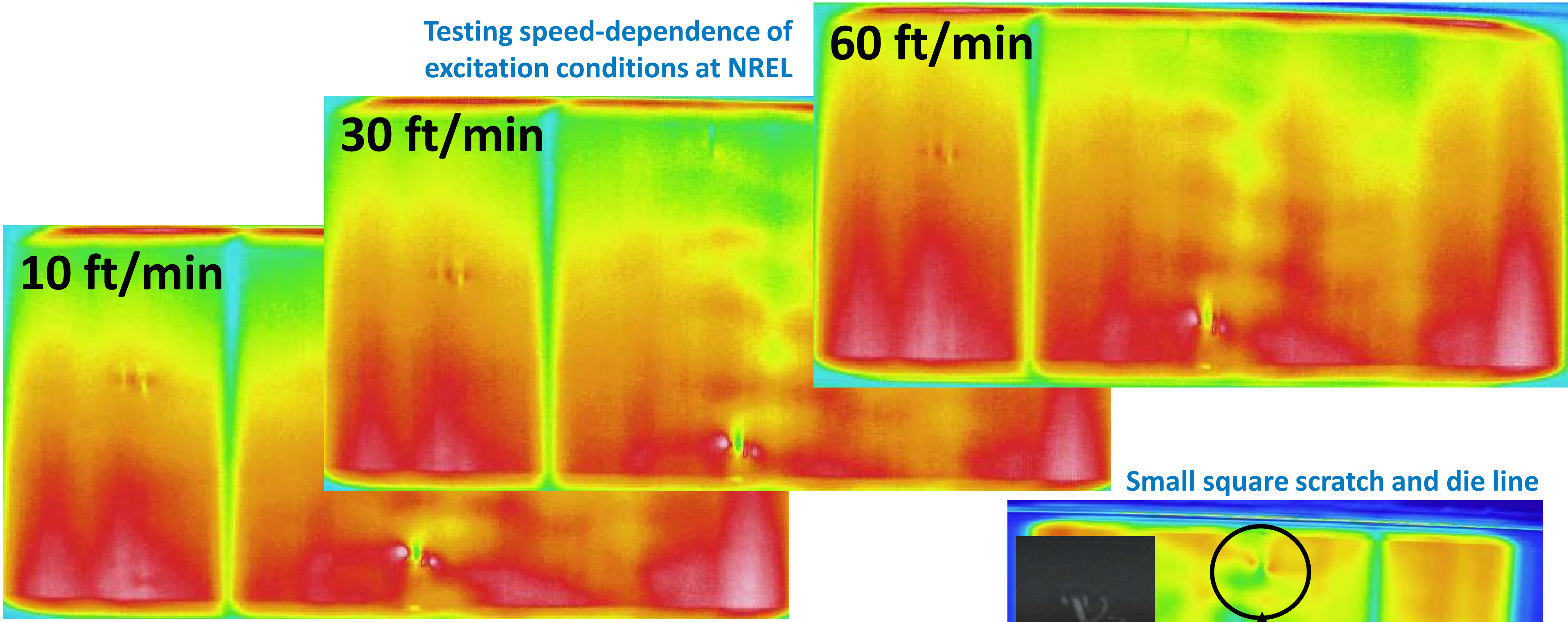




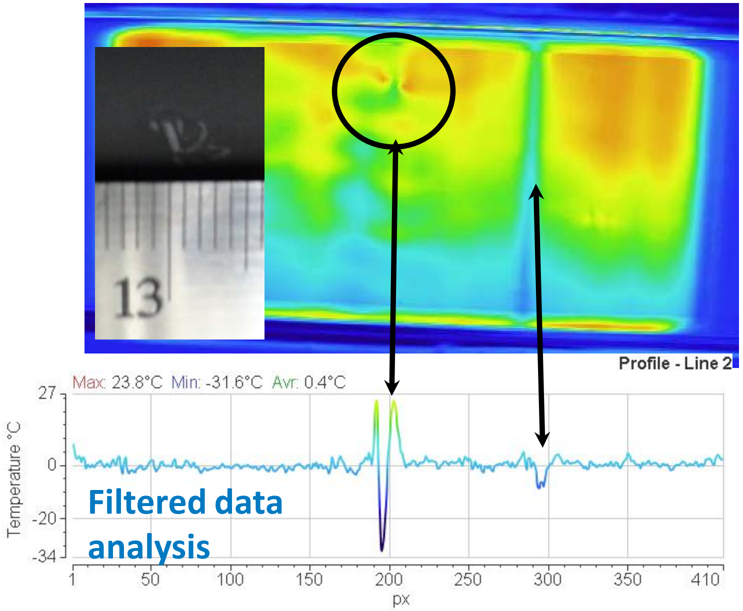
TECHNICAL BACK-UP SLIDES

Technical Accomplishments: Implemented IR/DC on industrial coating line at Ion Power

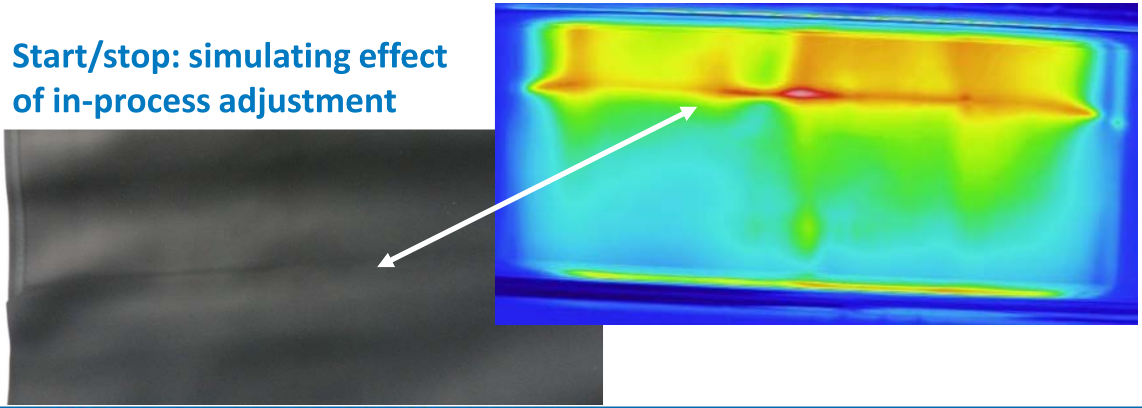
Testing speed-dependence of excitation conditions at NREL



Small square scratch and die line

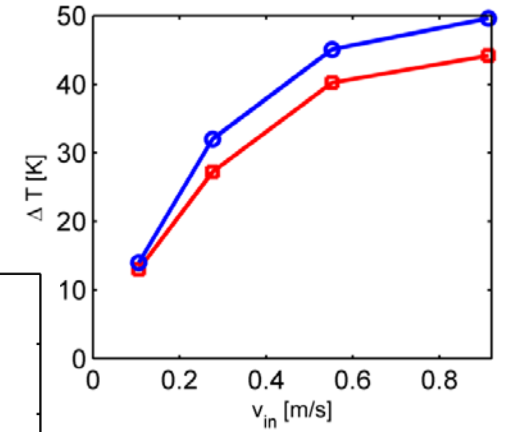


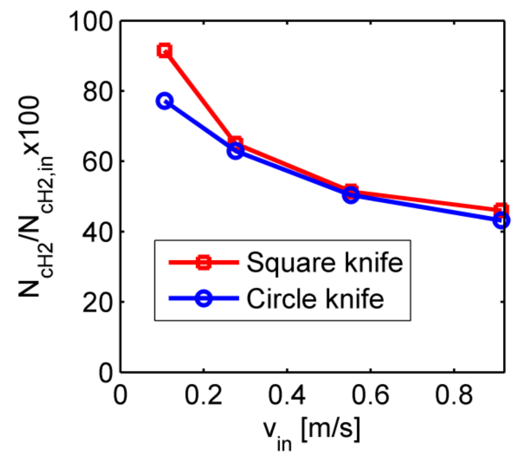
Start/stop: simulating effect of in-process adjustment



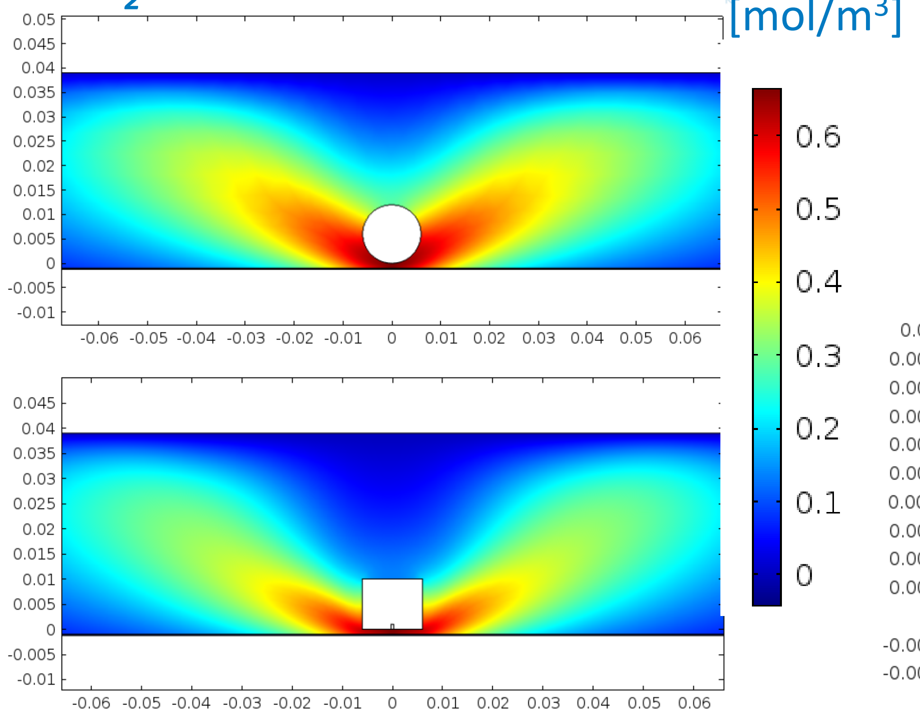
Technical Accomplishments: LBNL model used to compare different knife geometries

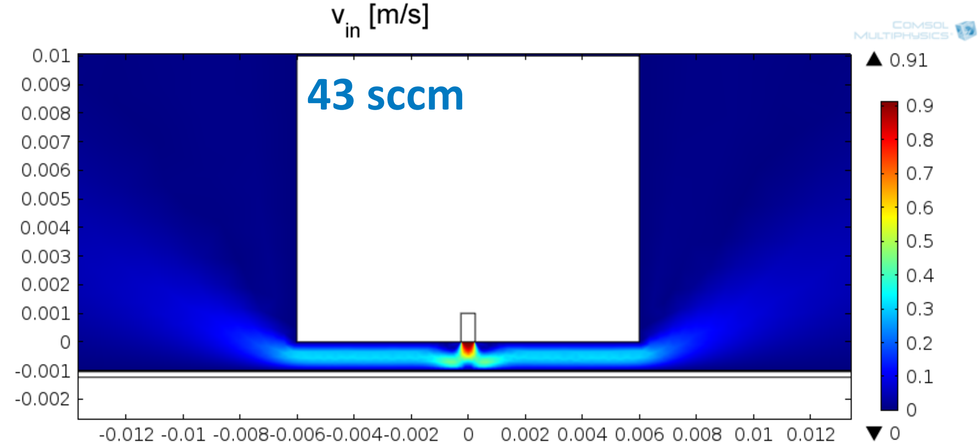
- **Rectangular vs. circular knife**
  - Square: Flow is 'trapped' against GDE surface
  - Square: Less H_2 is lost to the environment
  - Circular: Increased temperature rise





H_2 concentration at 43 sccm

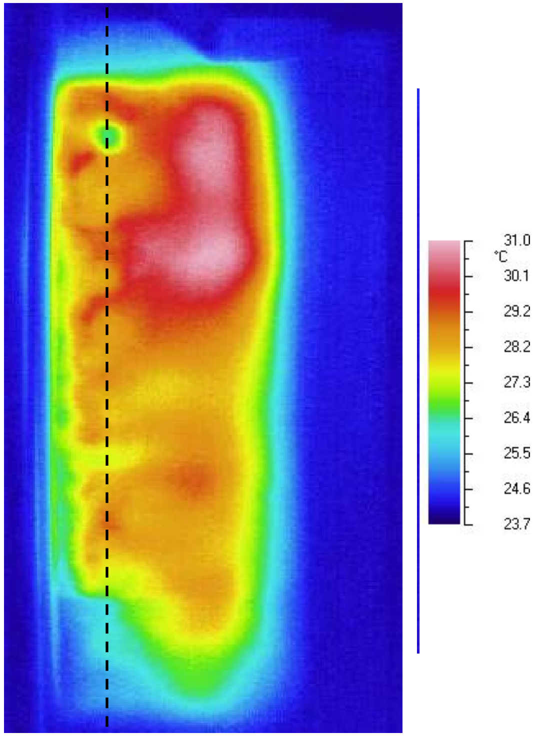




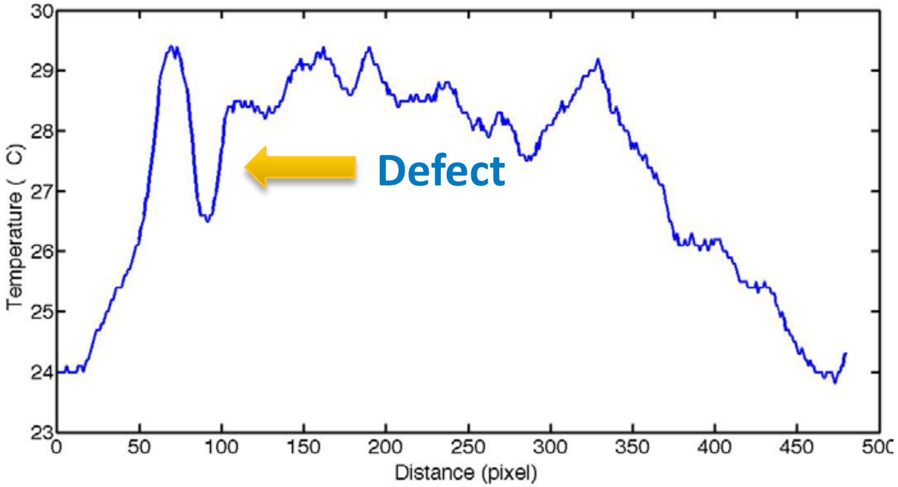
12 mm diameter circle and 12 mm rectangular knife

Technical Accomplishments: Evaluated data analysis techniques for IR/RIF to reduce noise

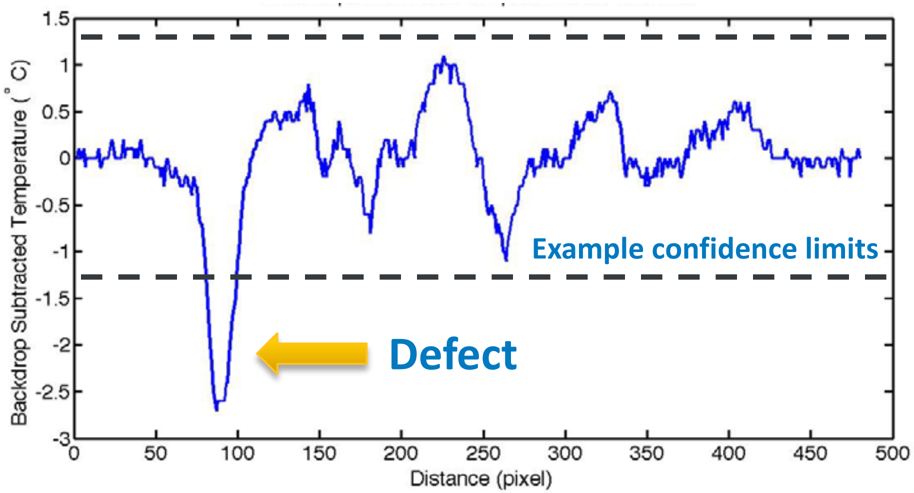
- **Subtraction data analysis for noise reduction:**
  - Standard technique in infrared thermography
  - Subtract time t_i profile from baseline time t_0 profile



Absolute Temperature Profile



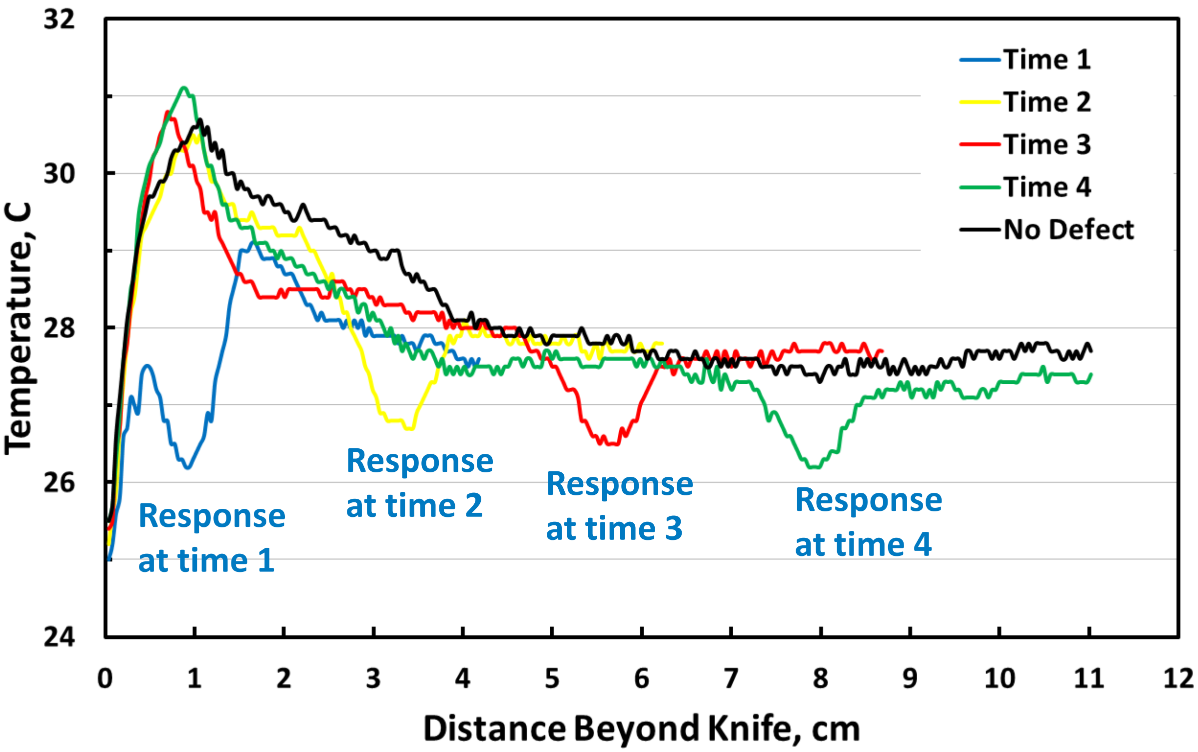
Subtracted Temperature Profile



Technical Accomplishments: Evaluated data analysis techniques for IR/RIF to optimize detection

- **Parallel line analysis:**
  - Evaluate the dynamic thermal response of a defect as a function of distance from the knife to identify an optimal data collection location (line)

- Response at time 1 is large, but initial peak is truncated due to reflection from knife
- Response at time 2 is still large, and fully formed
- Responses at times 3 and 4 are smaller



Technical Accomplishments: Analysis of RH dependence of capacitor with Nafion®

Plate Capacitor Estimation with NRE212 as dielectric at various RH:

	RH [%]			λ [n_{H2O}/n_{-SO3H}]		ε_r		Capacitance [nF]		
	Min	Max	ΔRH	Min	Max	Min	Max	Min	Max	Δ[%]
Golden, CO	29	75	46	2.4	5.5	14	40	6.1	17.5	187
Miami, FL	49	84	35	3.3	6.8	27	46	11.8	20.1	70
Low	30	40	10	2.4	2.9	14	23	6.1	10.1	66
High	85	95	10	8	12.5	50	61	21.9	26.7	22

- **The ambient relative humidity can vary up to 40% throughout a day, and additionally varies throughout the year**
- **The water content in Nafion® is strongly dependent on ambient conditions**
  (Zawodzinski et al., J. Electrochemical Society, 140, Vol.4, (1993) 1041 - 1047)
- **The water content in Nafion® strongly impacts its dielectric constant**
  (Paddison et al., J.Electroanalytical Chemistry 459 (1998) 91-97)

⇒ **The potential impact of ambient and controlled RH changes on results with NREL's experimental setup was estimated**

⇒ **Results indicated that the potential variability of the method is likely unacceptable, even with tightly controlled relative humidity**