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Curvature in SOFC's: New Tools, New Perspectives

LOW-COST FUEL CELL ALLIANCE

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Introduction

- DOE NETL/SECA "Low Cost Fuel Cell Alliance" began in 2000 and originally involved 11 organizations
- OSU: characterization as applied to NexTech tapes/laminates
- An avoidance of standard MSE techniques has driven us to examine 'pure' manufacturing issues
- Recently acquired optical profilometer
- Our "home-built" laser dilatometer

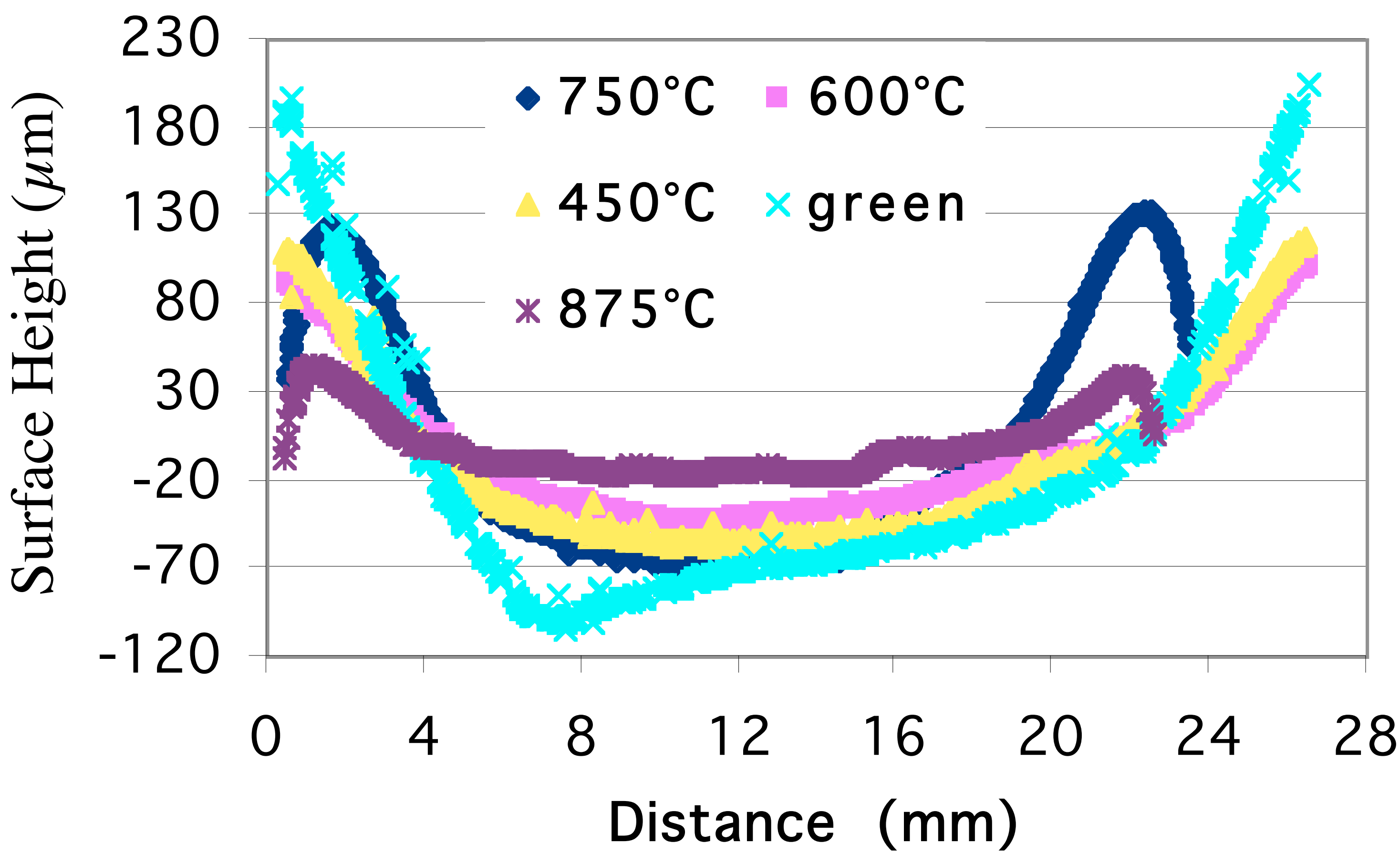
Introduction

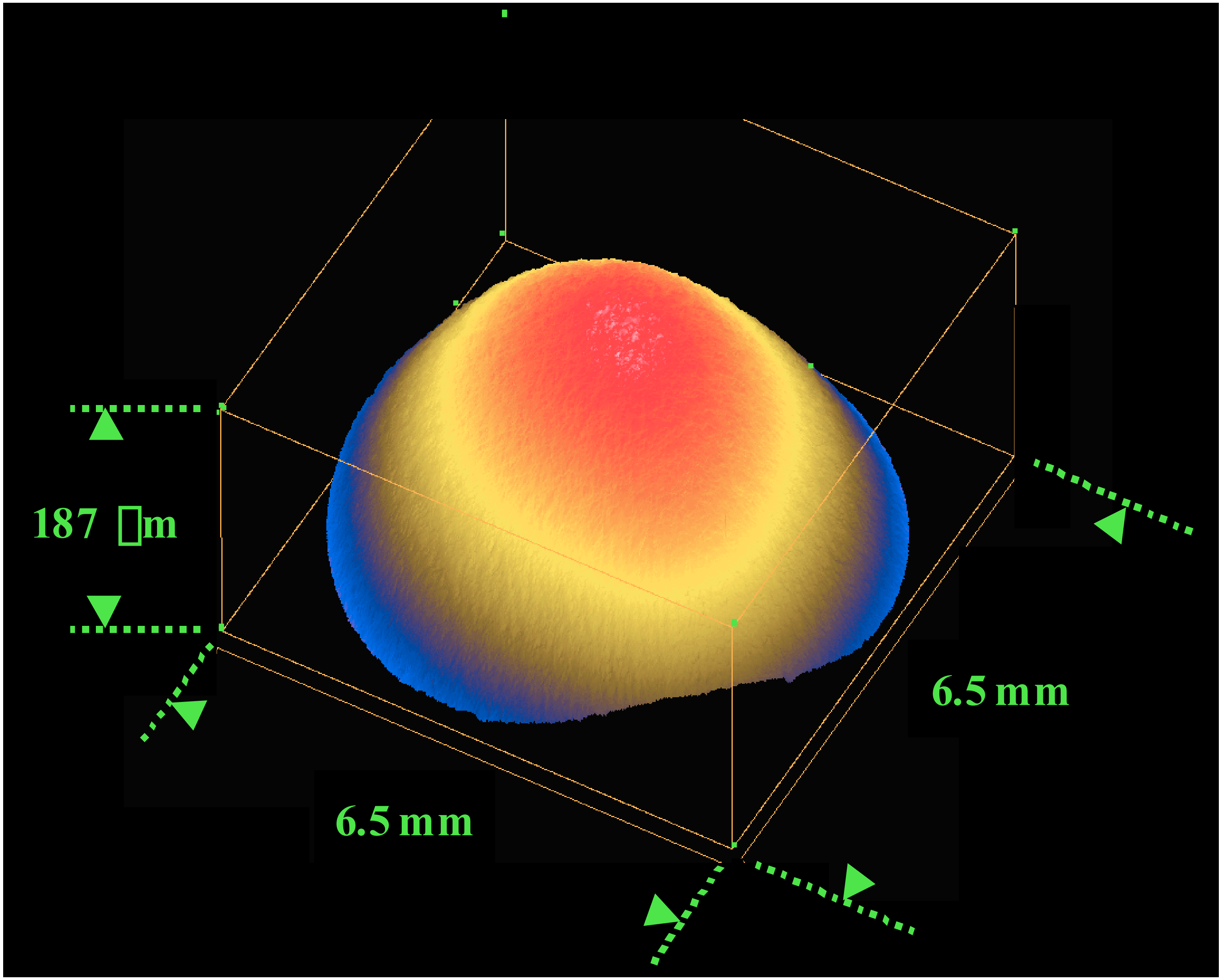
- Objective: demonstrate that these techniques can to serve as new tools to examine old problems
- Establish advanced characterization tools for process diagnostics during manufacture
- More knowledge about curvature allows reduction of the number of manufacturing steps
- Examples: manufacturing process development
- Examples: demonstrate value w/o revealing too much; not all samples are NexTech’s

Optical Profilometry

- Uses interference of filtered white light reflected from a surface as imaged by a CCD array
- <u>Not</u> contact-based (stylus)
- Provides information not visible to the naked eye
- Lower resolution than SEM; compatible with specific manufacturing problems
- Provides microstructural details <u>non-destructively</u>

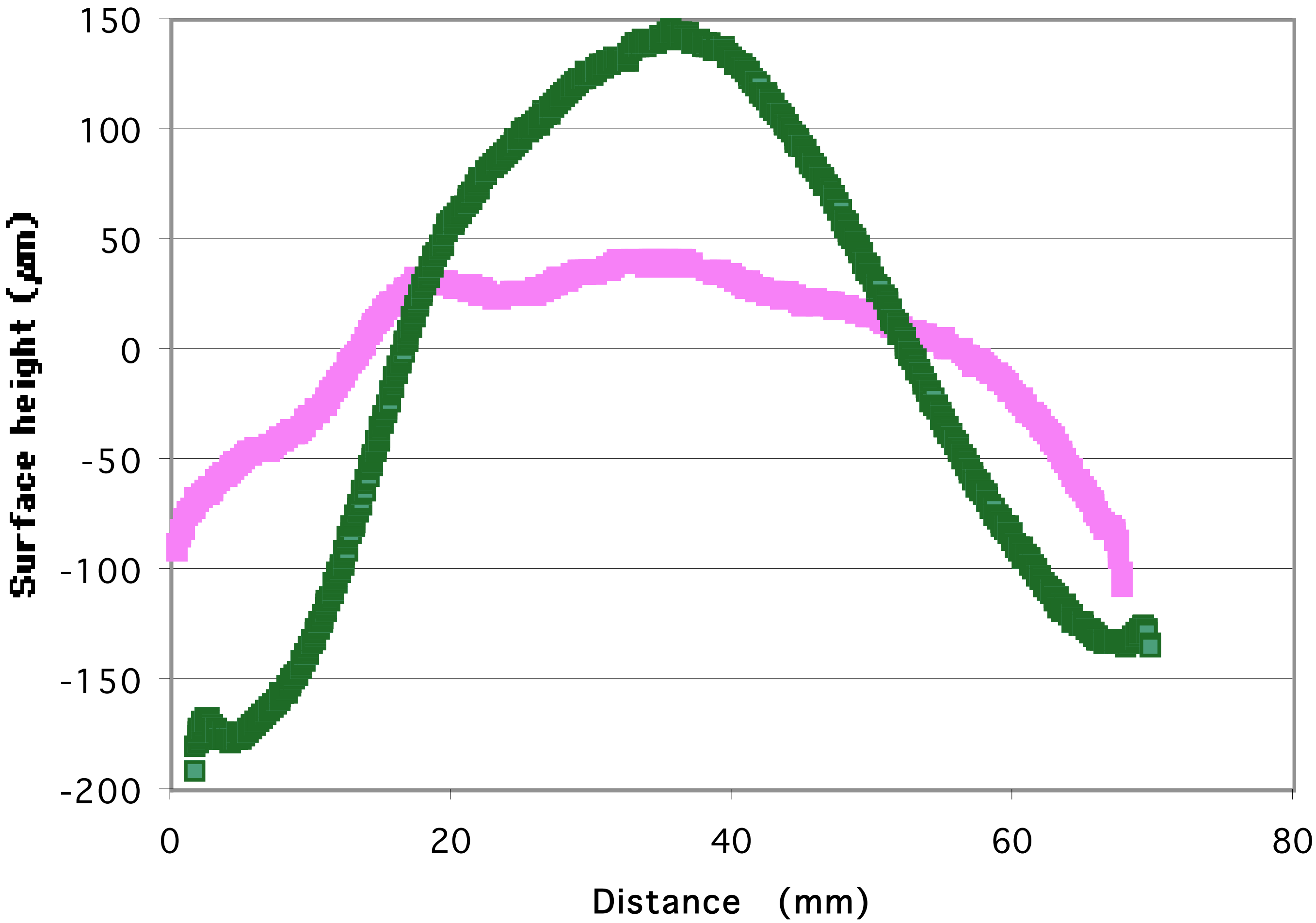
B&A Sintering: Standard Profilometry Data



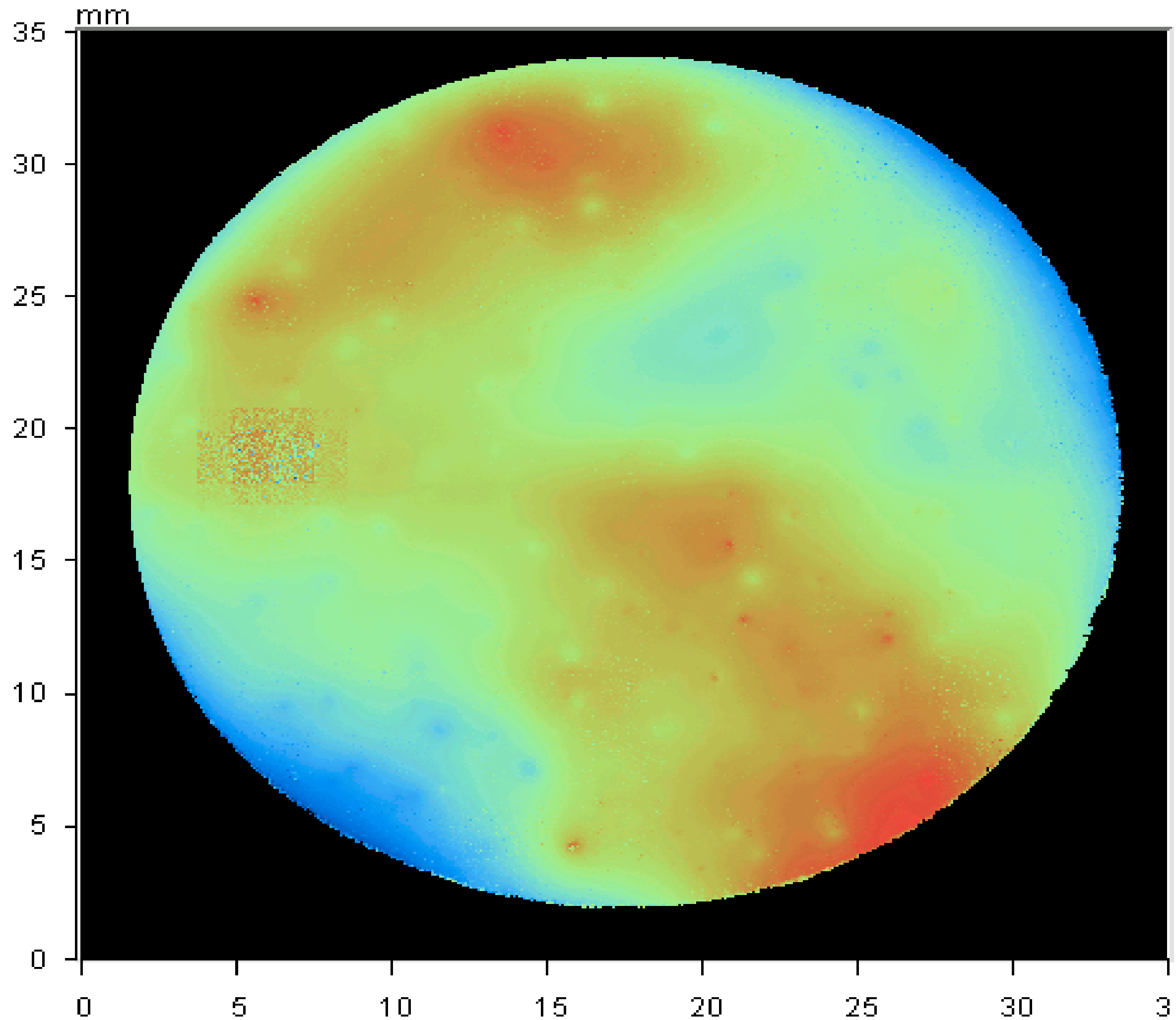


One-way curvature, convex/concave

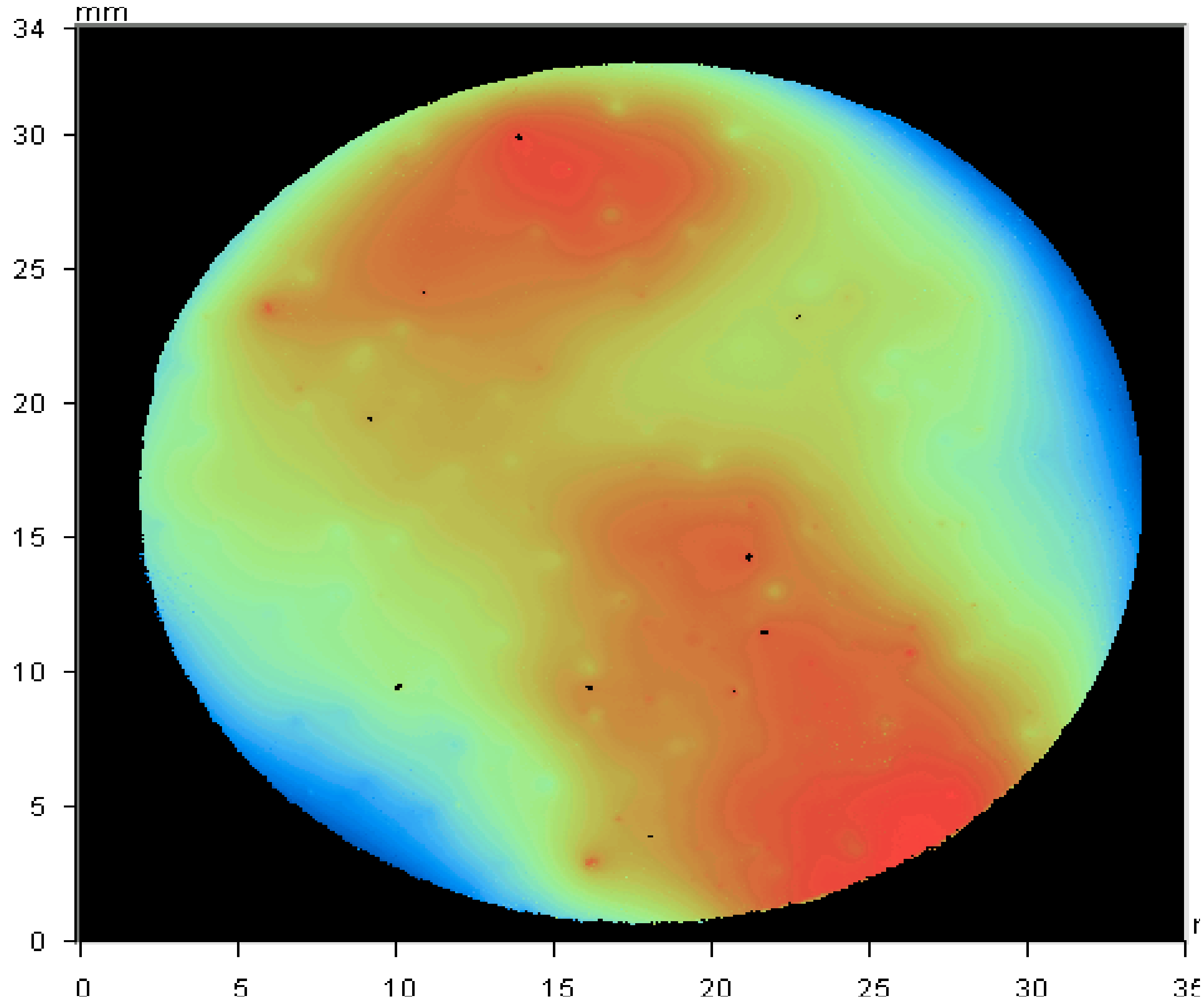
Permanent Curvature Reduction, Anode Support



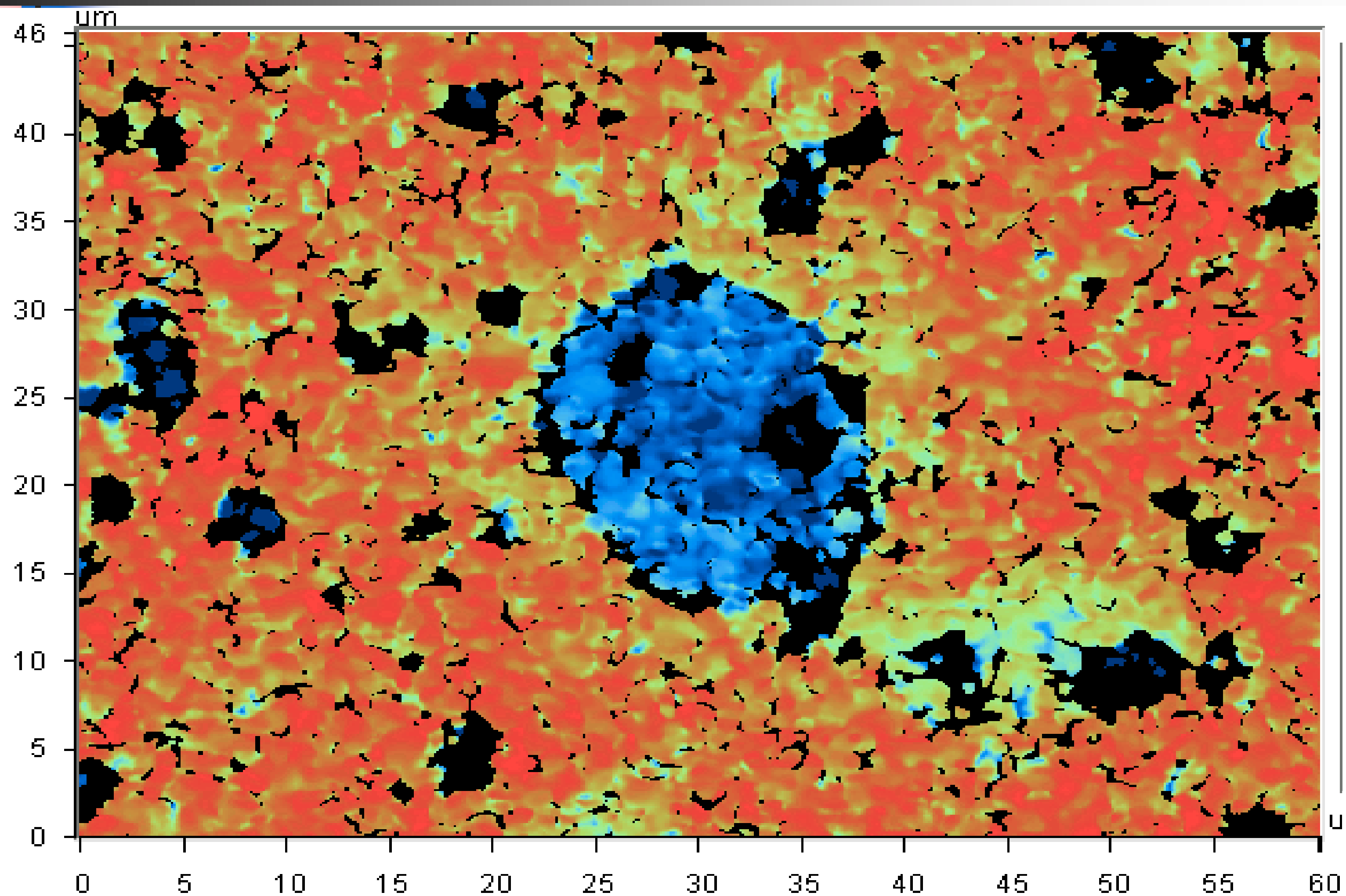
B&A: 1400°C Laminate Before Reduction (R_z = 292 µm)



B&A: After Reduction (R_z = 375 µm)



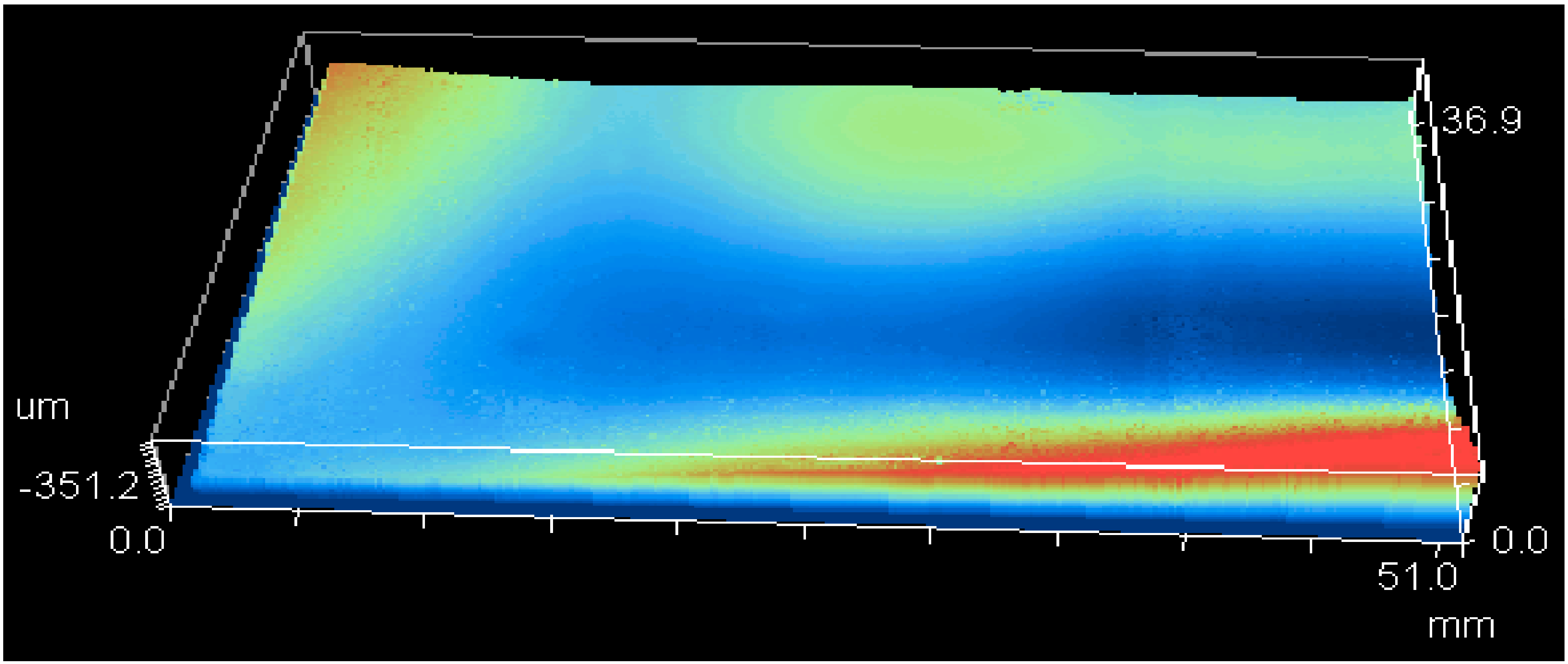
After Reduction: Ni in YSZ



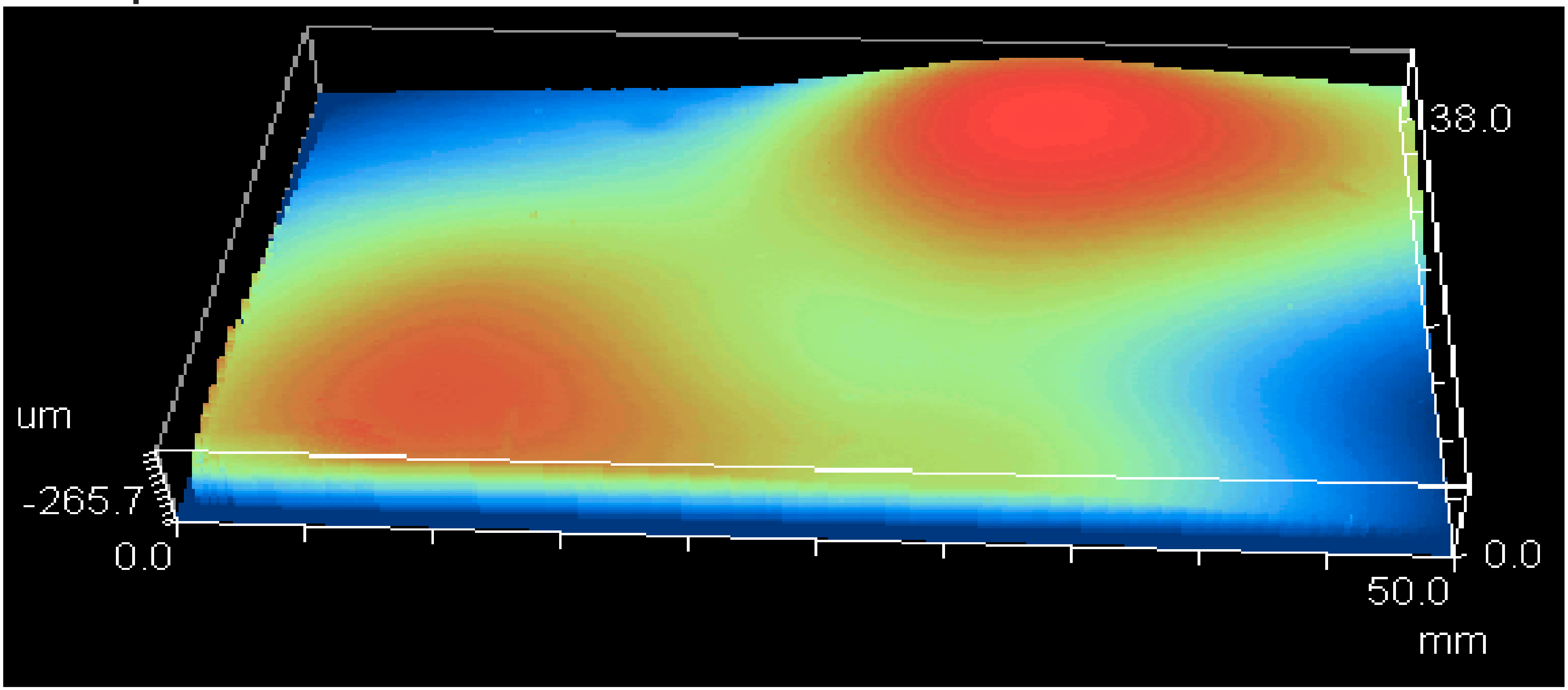
B&A Reduction: Significance

- How does NiO reduction affect residual stress in the electrolyte layer?
- <u>Gradients</u> in reduction-oxidation and the electrolyte layer?
- Effects of <u>repeated</u> redox on the electrolyte layer?
- Can degradation caused by redox cycling be minimized by optimizing cell fabrication?

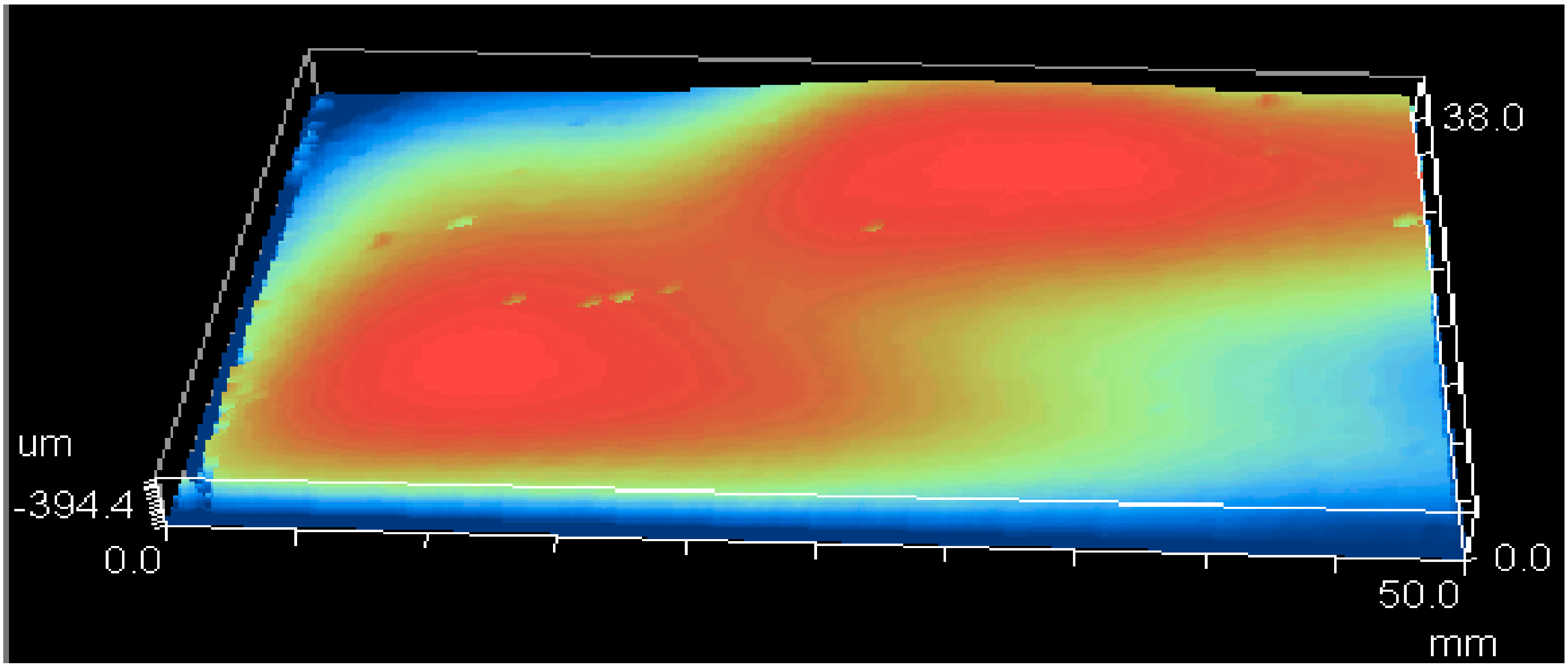
Edge Curvature Sample #1



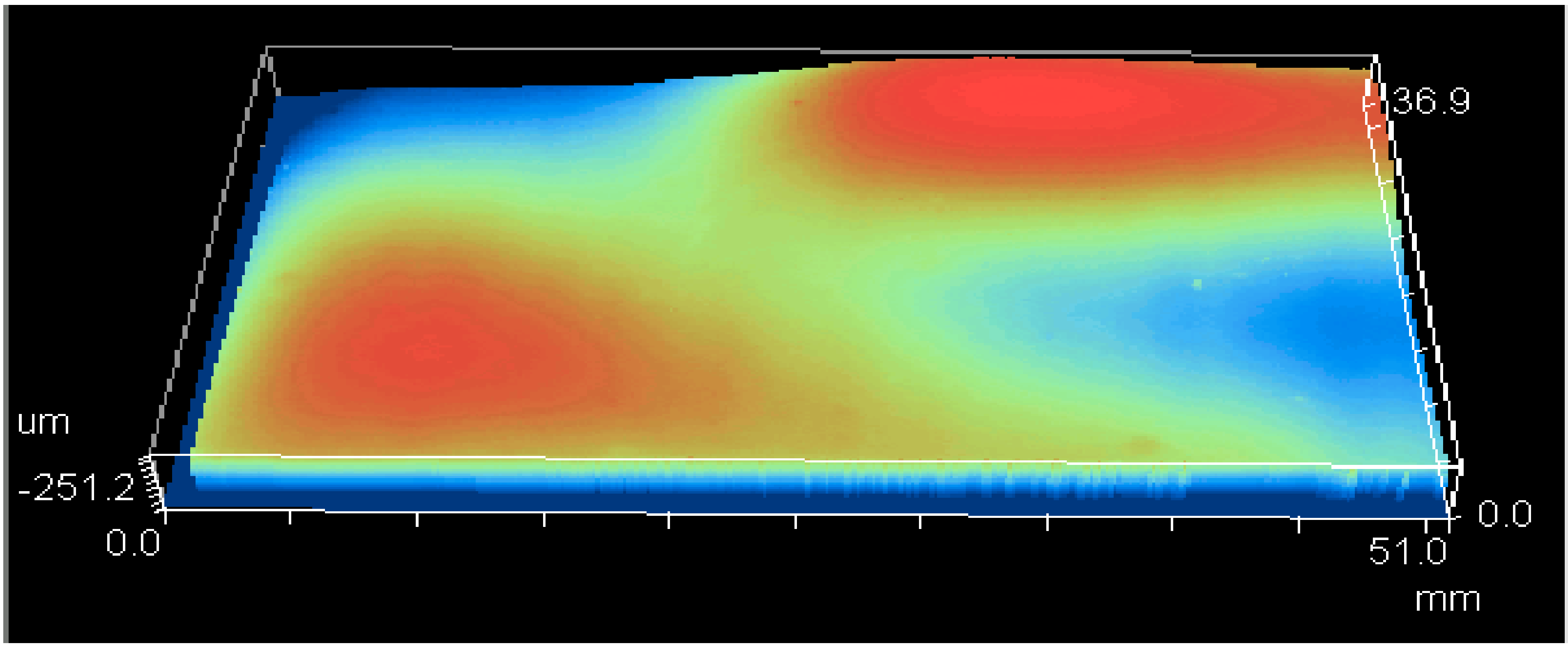
Edge Curvature #2



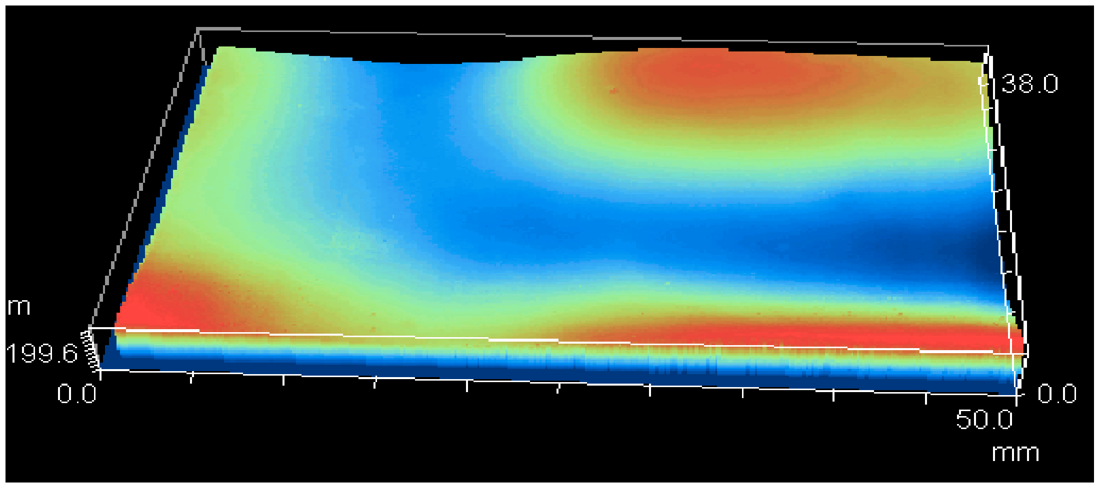
Edge Curvature #3



Edge Curvature #4

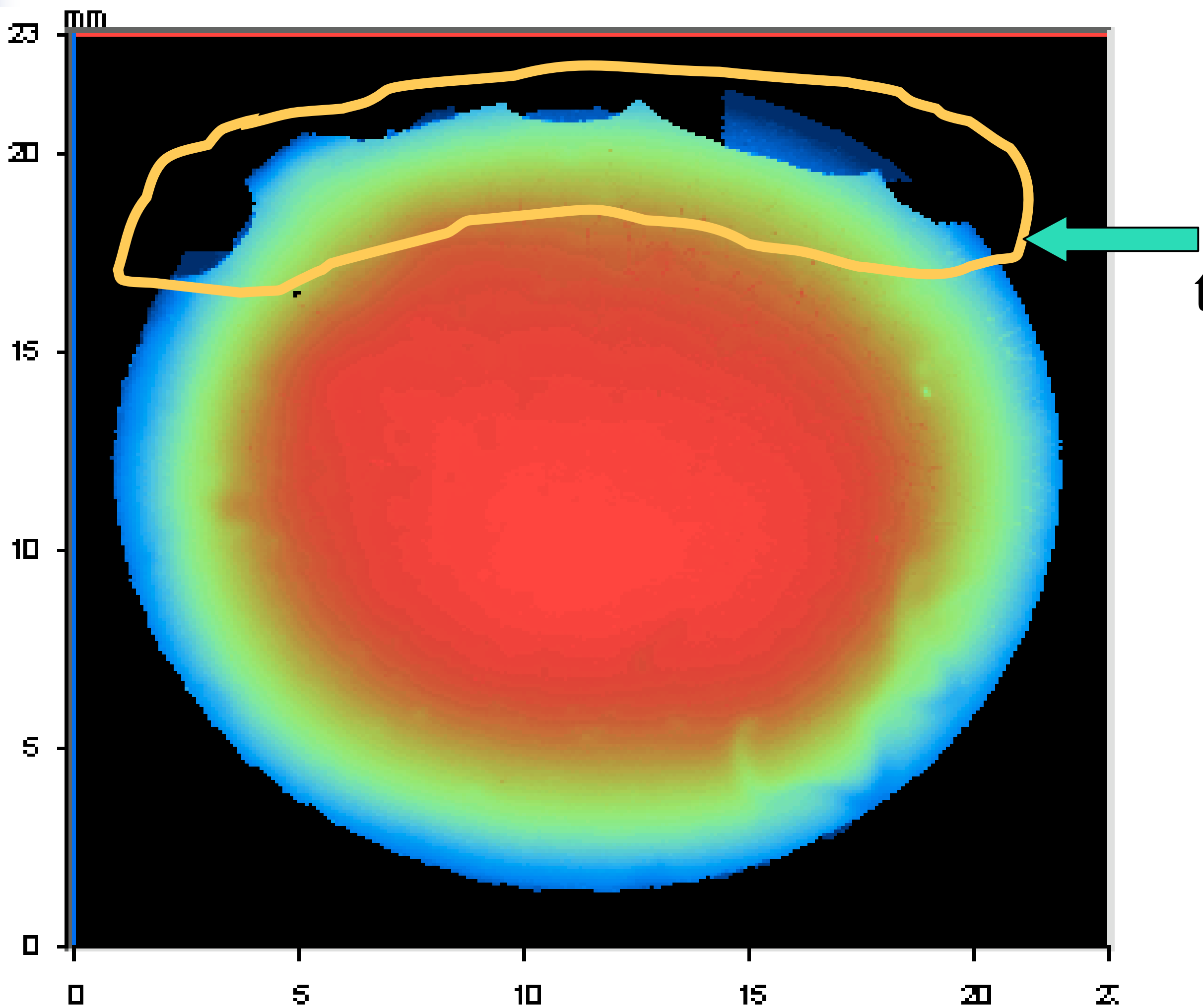


Edge Curvature #5



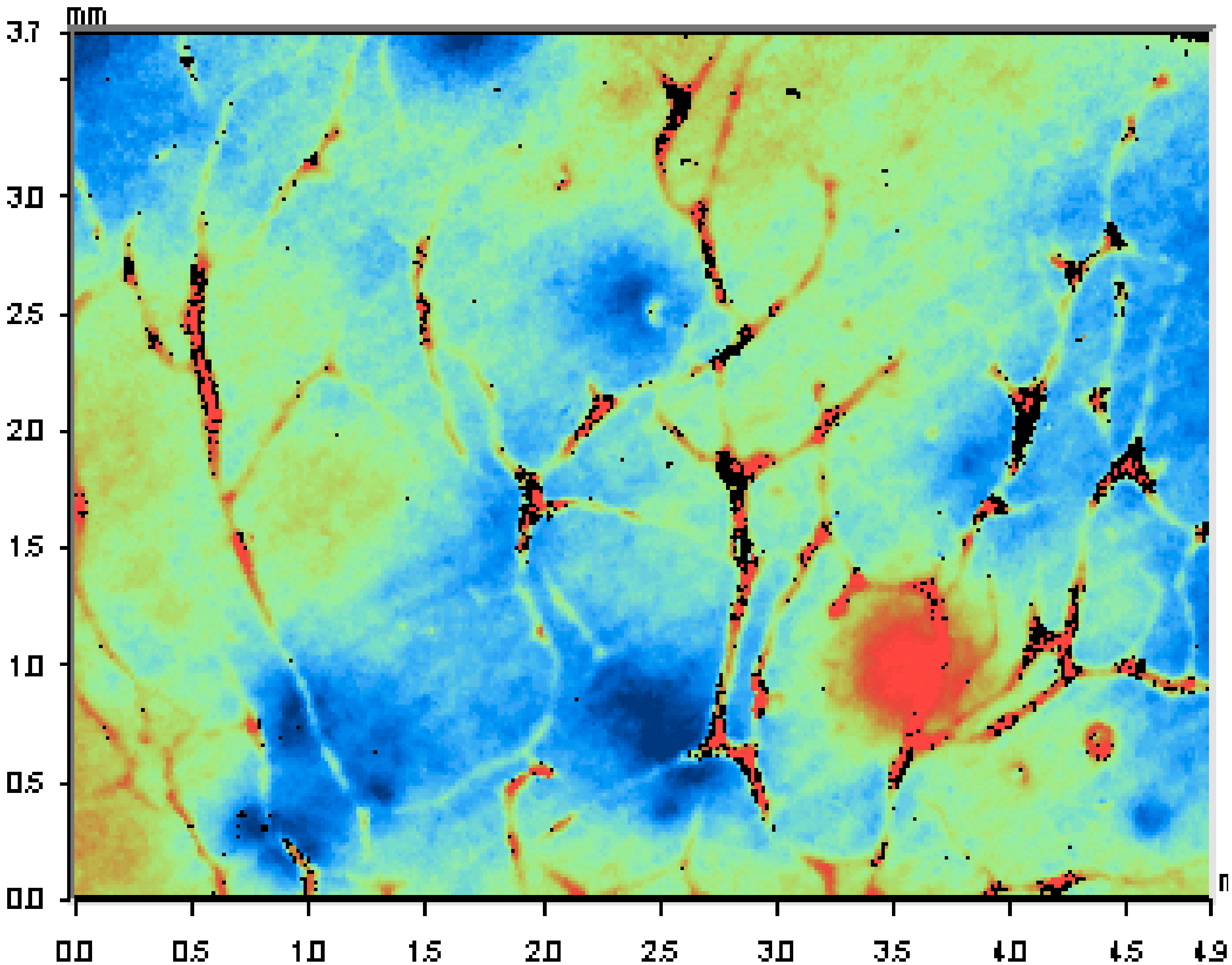
- Relevant to sealing (ceramic-ceramic, ceramic-metal) that must take place against these surfaces
- IC connections also affected
- Sealing stresses will be unevenly applied
- Why are all five are unique?

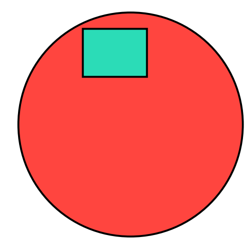
Curvature-stress interactions: examining compressive failure of the electrolyte layer



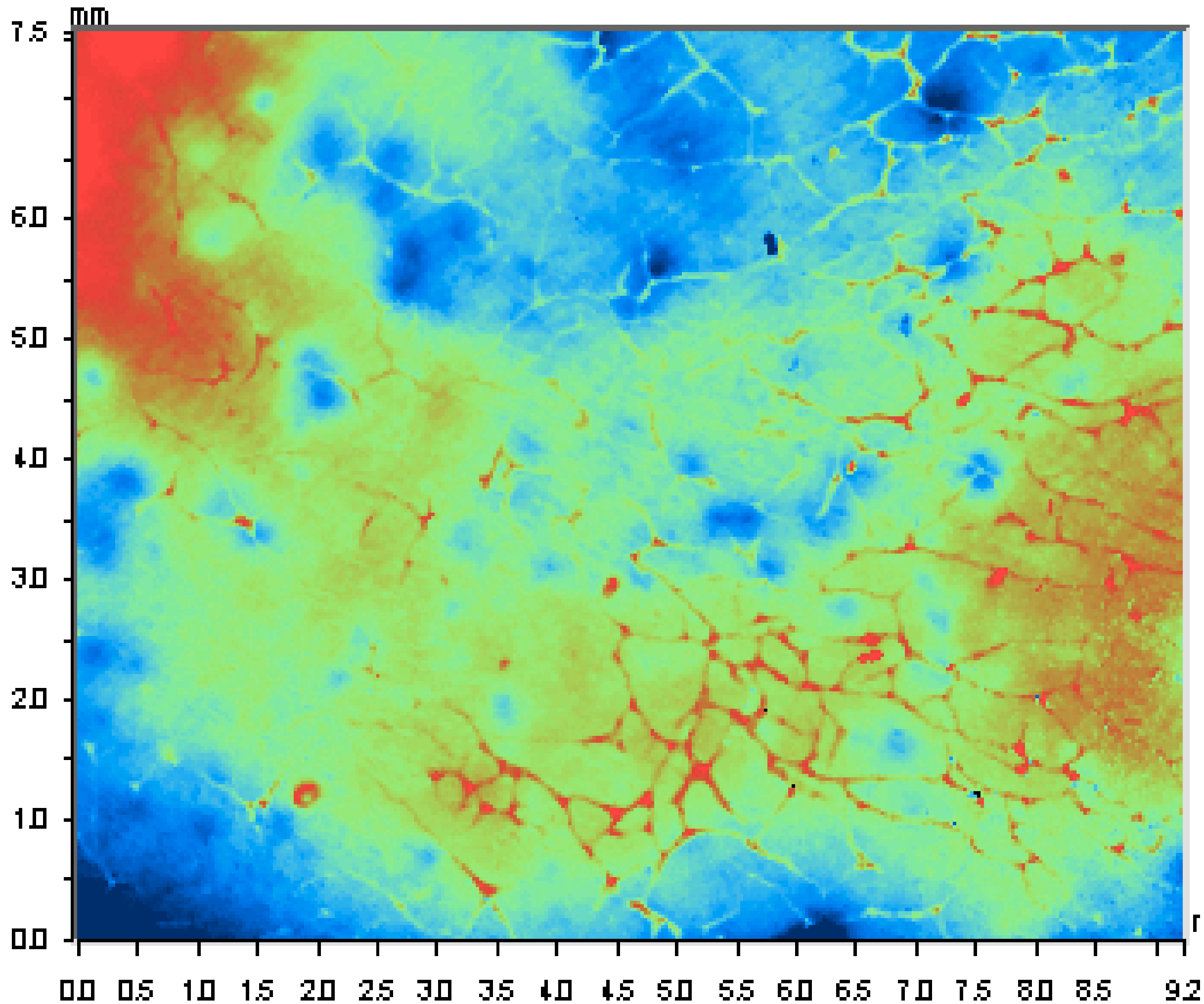
<u>Failure</u> of
the electrolyte
layer only
post-1400°C

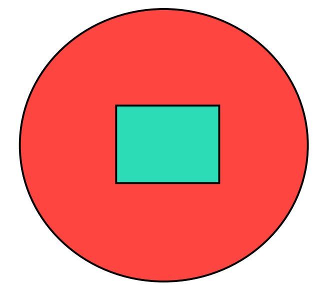
Adjacent to failure



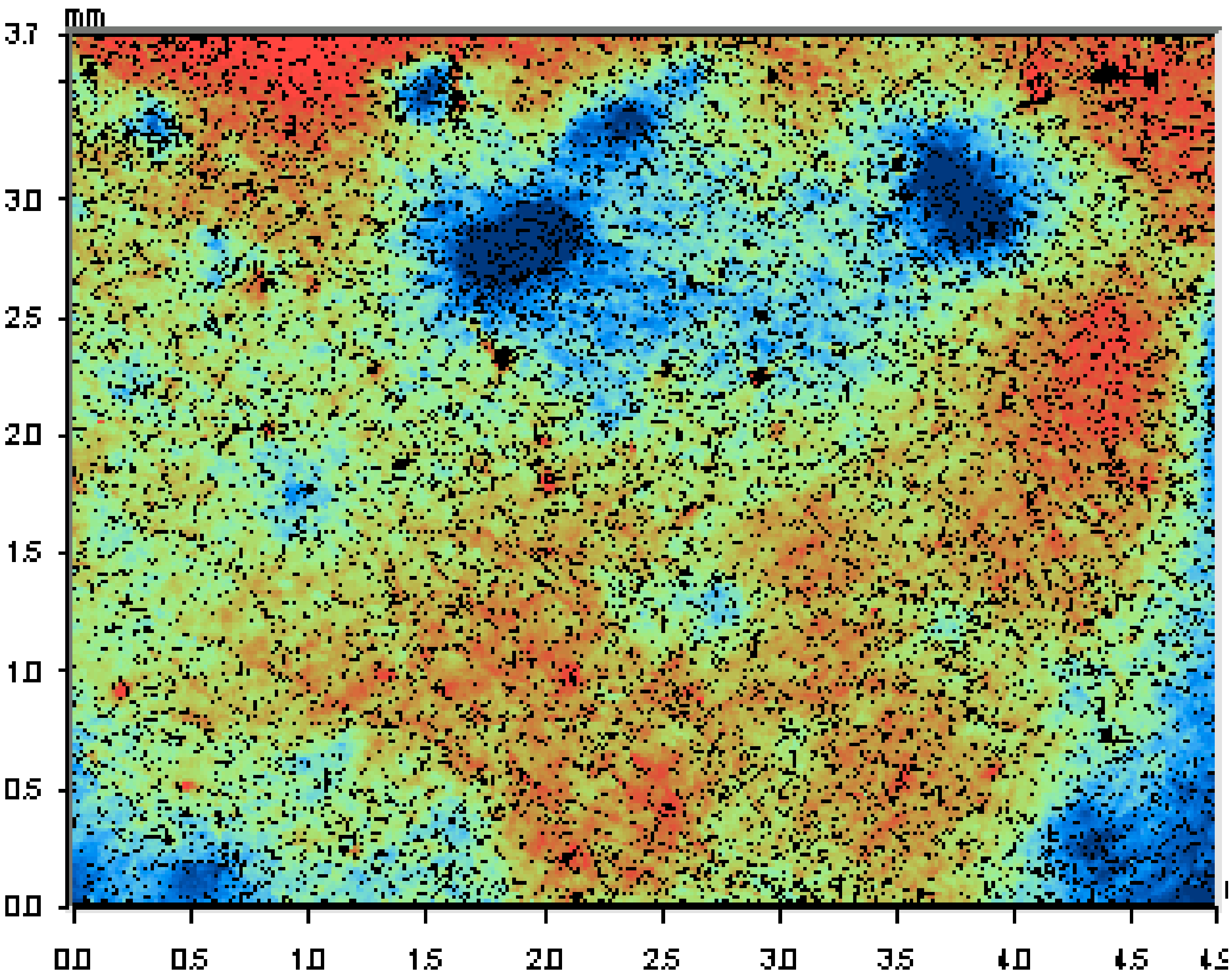


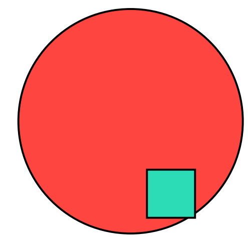
Middle of specimen





Far away from failure - no cracking





Curvature and Stress

- Stresses evolve <u>locally</u> as cells cool down
- Cracking of electrolyte layers controlled by localized high spots and low spots that deviate from perfectly flat geometries
- Out-of-plane stresses develop in real, as-fabricated cells
- Does sealing <u>increase</u> these stresses?
- Operating stresses can exacerbate pre-existing cracks; redox stresses are of concern as operational temperatures <u>decrease</u>
- NexTech solved this particular problem using data from our laser dilatometer

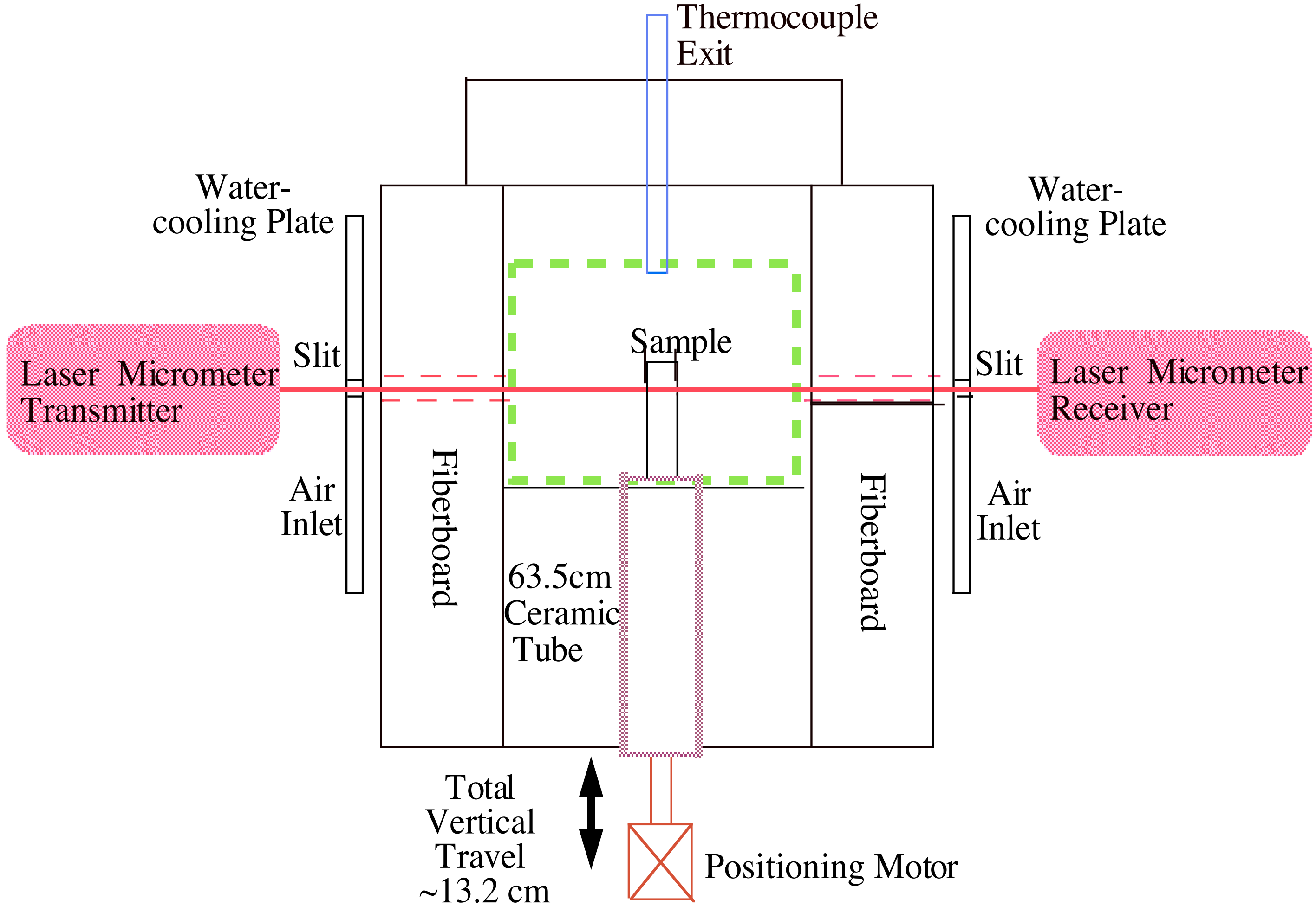
Summary: Using OP to Examine Curvature

- Large scale curvature; pass/fail criterion
- B&A various manufacturing operations - non-destructive
- B&A operation - non-destructive
- Defects/microcracking in the YSZ film can be identified for pass/fail or subsequent SEM
- Small vs. large scale curvature and failure mechanics
- Adaptive meshing of profilometry data for FEA approaches

Larger Questions

- How can the fabrication processes and/or thermal cycles be modified to reduce curvature?
- When exactly, does curvature evolve in anode-supported cells?
  - Green tape processing?
  - Precalcination?
  - Burnout?
  - Co-sintering?
  - Sealing?
- We have observed that each of these steps contributes to the final curvature (and thus the final localized stress state)

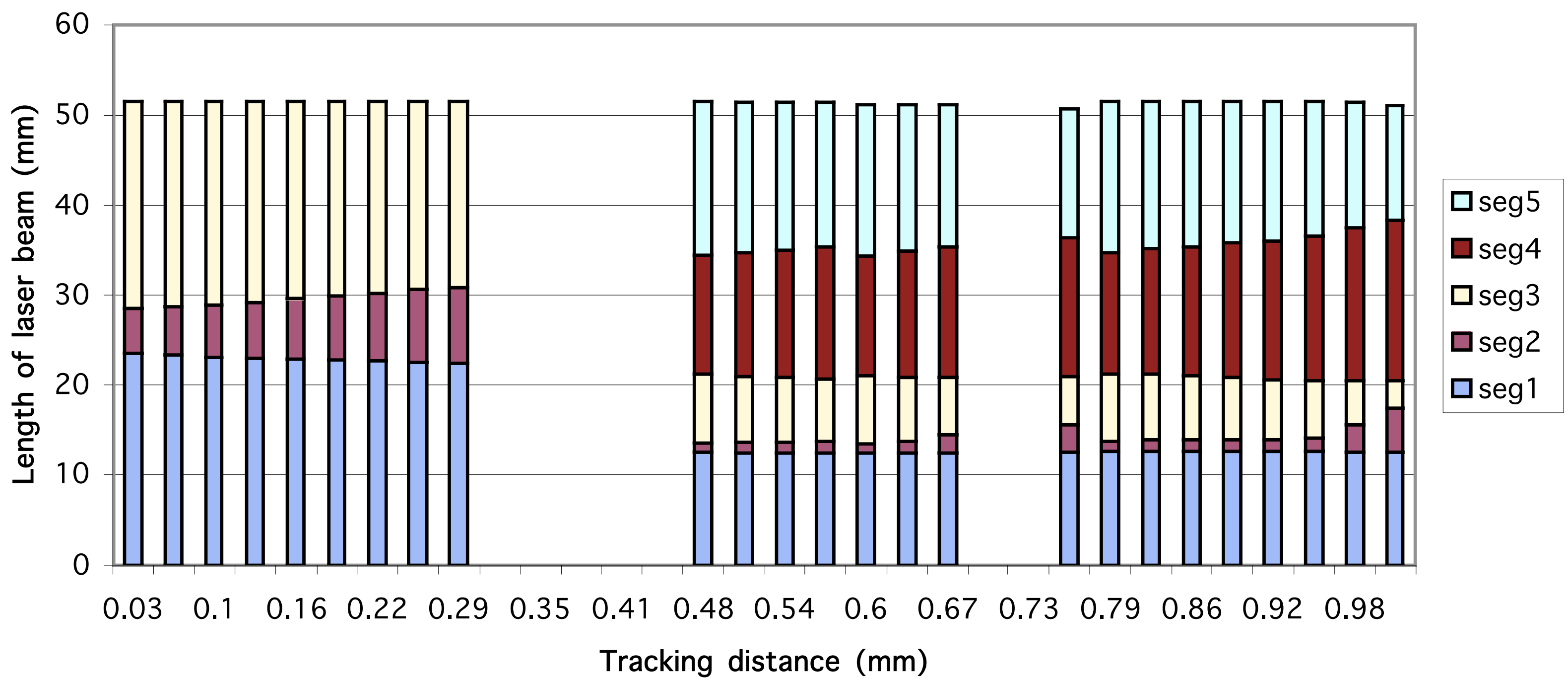
Laser Dilatometry



Unlocking the “Black Box” of Thermal Processing

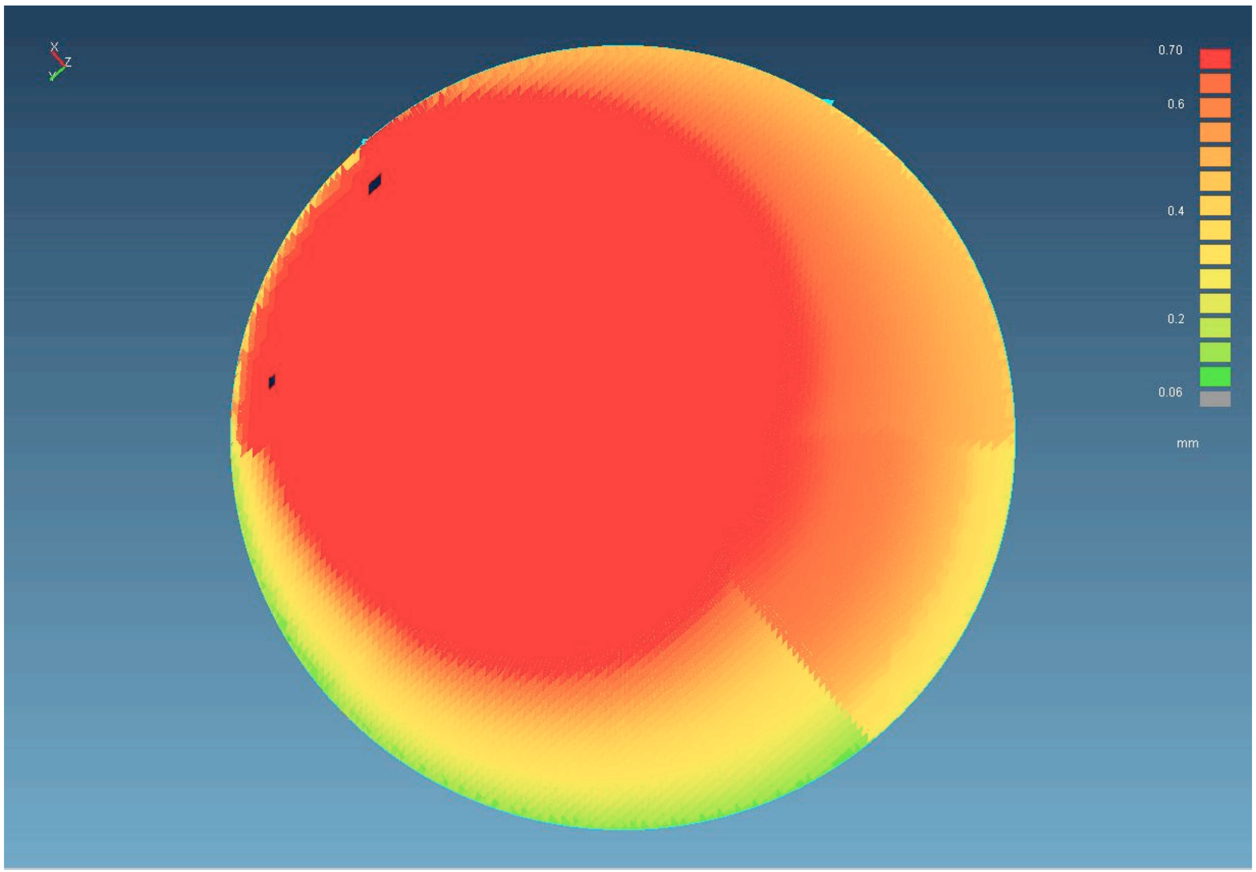
- Once the furnace door is closed all dimensional information about the sample ceases; makes problem solving difficult/impossible?
- LD Non-contact - can monitor tape through all stages of heating and when liquid phases are present
- Non-contact - can monitor <u>seal</u> materials when liquid phases are present
- Accuracy - +/-0.5 μm; about the same as standard LVDT-based dilatometry
- Accuracy - does <u>not</u> average data (i.e., standard dilatometry) and is standardless

Vertical traverse of a 1.5” wide, 6-layer laminate@898°C



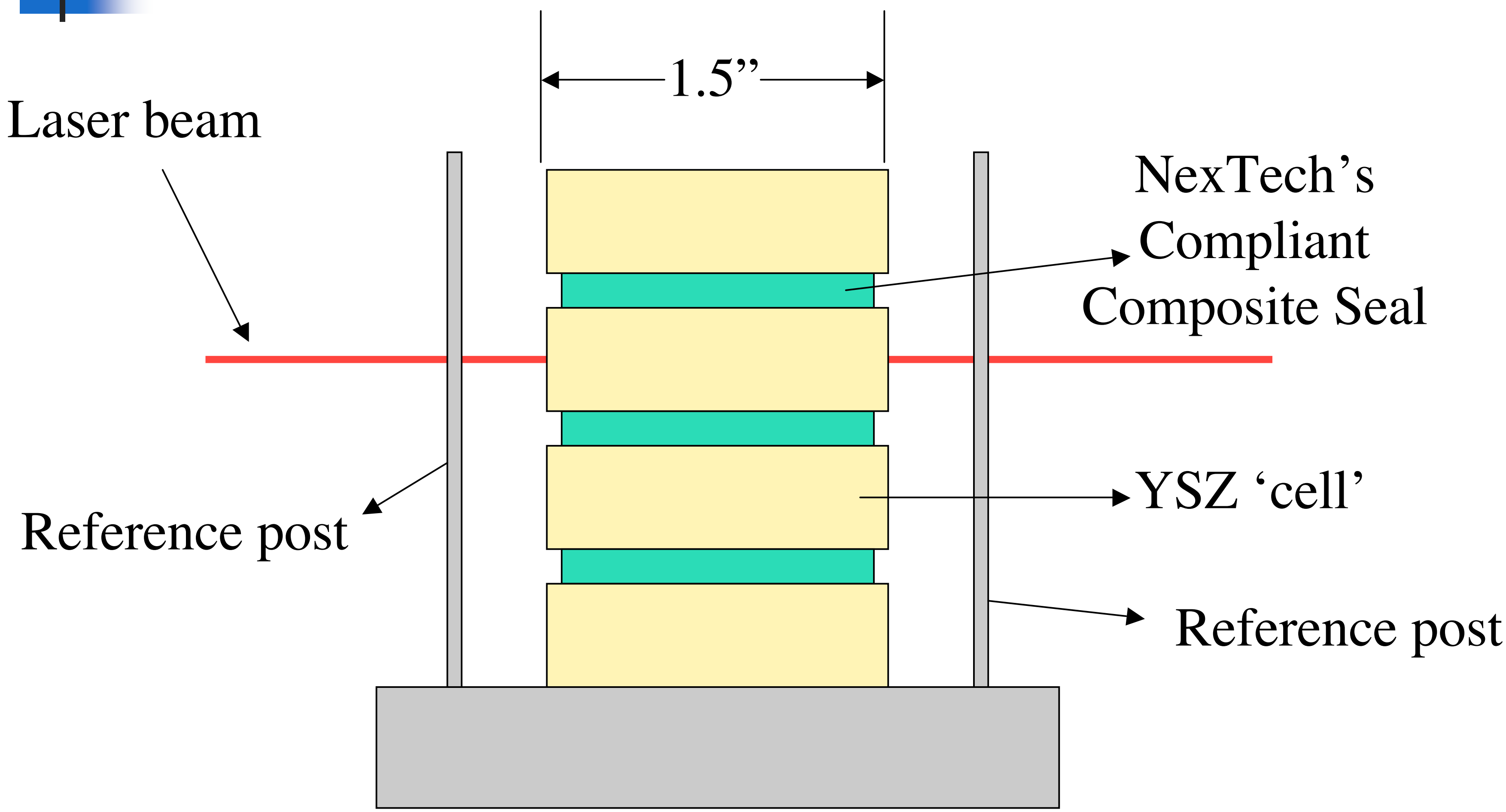
Segments 2 & 4 are due to curved “peaks” within the sample

3D laminate surface data collected at 1304°C

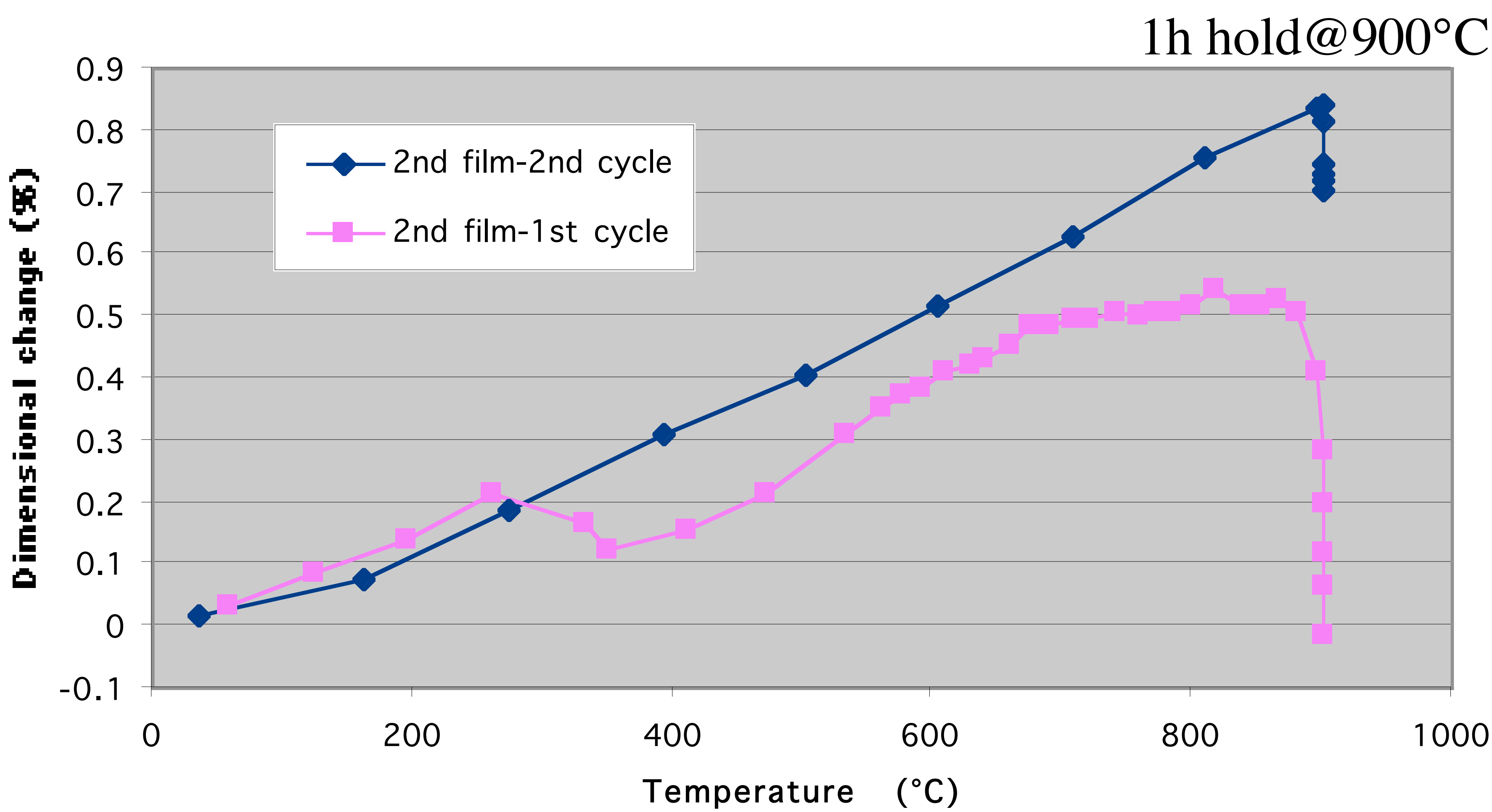


Color coded to match optical profilometry scale

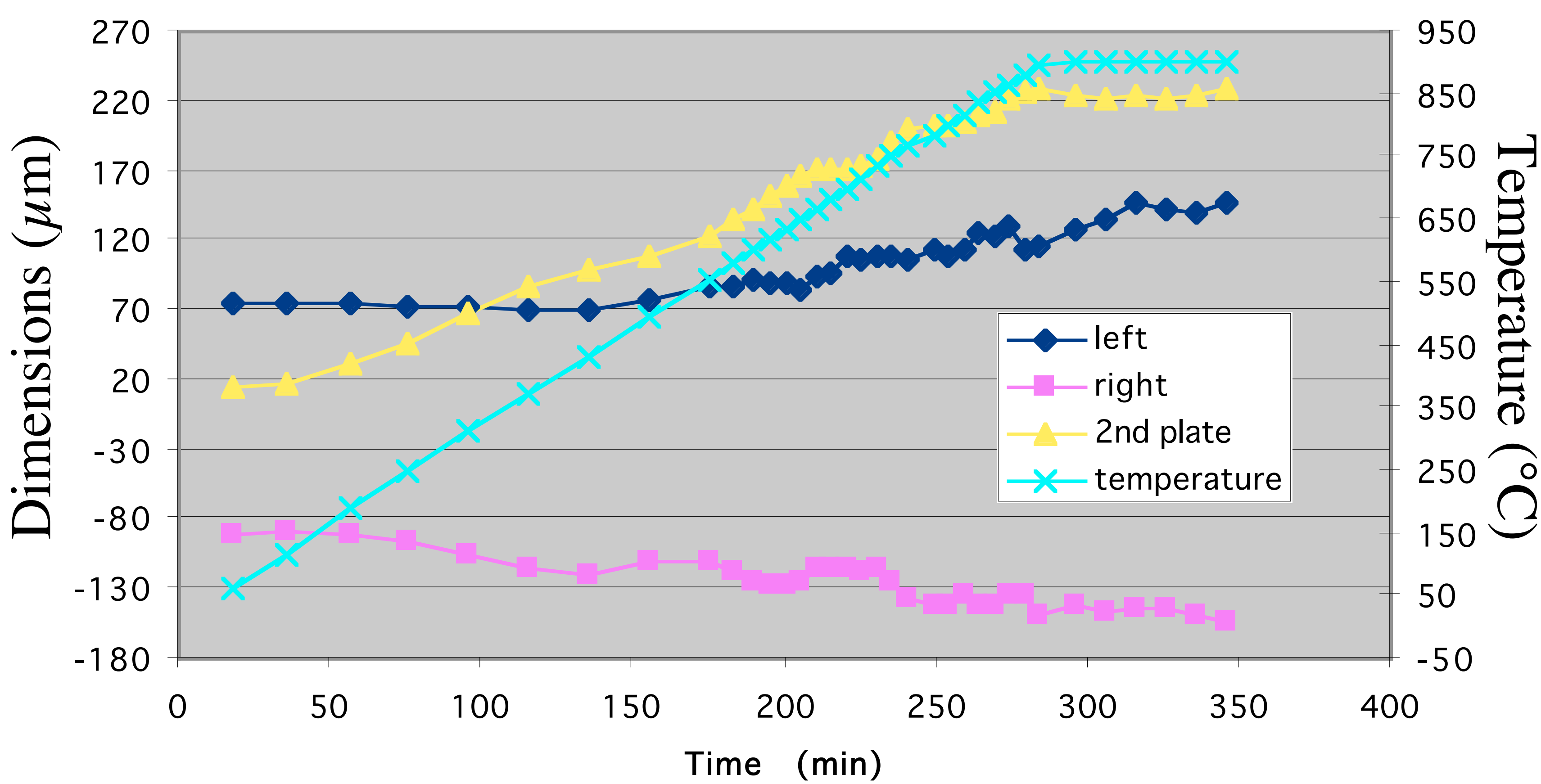
From Cells to Stacks? - Experimental Setup



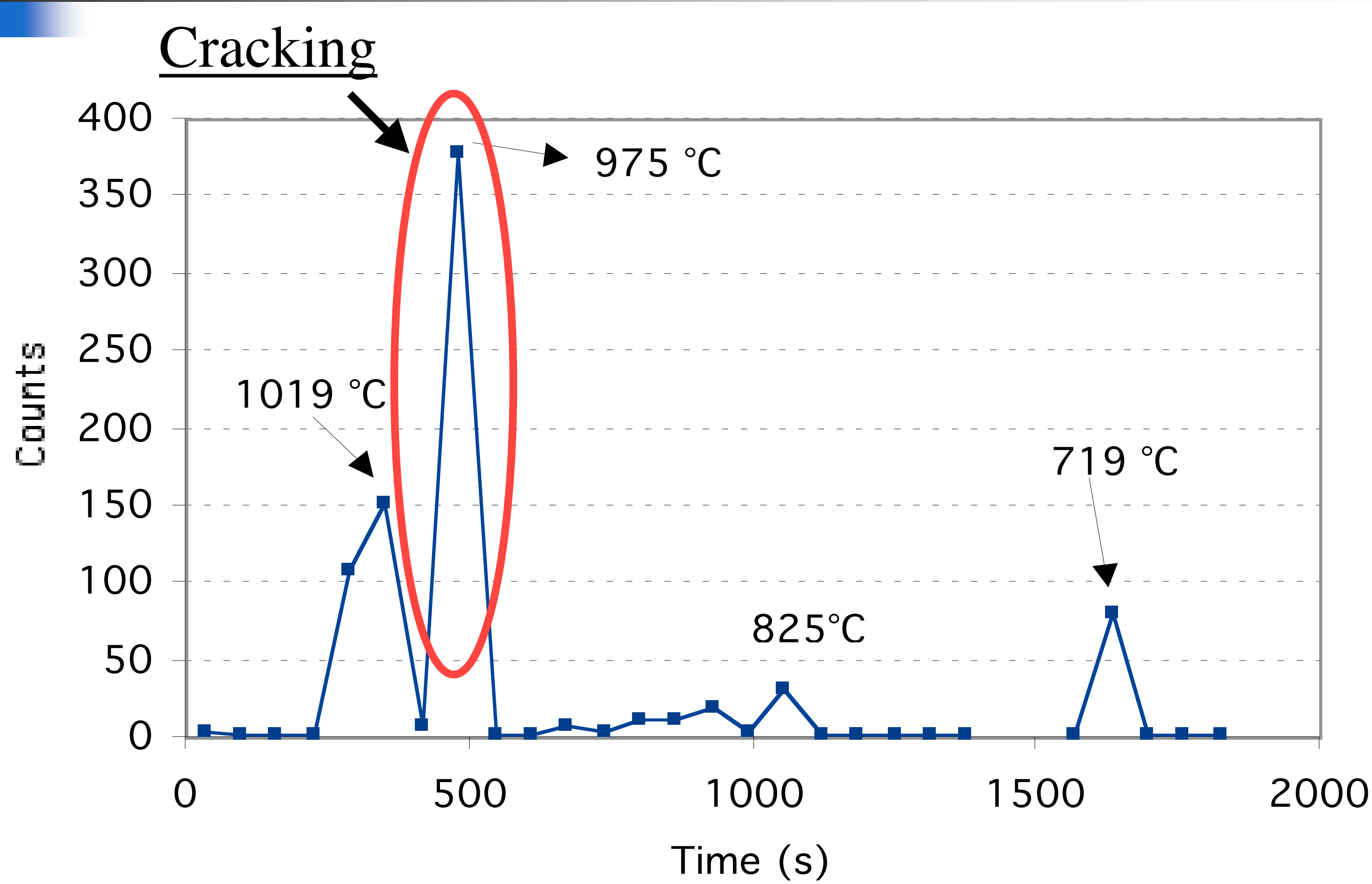
Dimensional Behavior of Seal vs. T and Cycle



Dimensional Behavior of ‘Cell’ vs. T



Acoustic Emission - Cracking Under Constraint



Conclusions

- The field needs additional experimental techniques
- <u>Non-contact</u> profilometry: accept/reject criterion for fuel cell manufacturing?
- B&A testing of manufacturing processes
- Laser dilatometry can be used to open up the "black box" and demystify thermal treatment processes; possible NexTech business interest
- Laser dilatometry can render both single cells and <u>stacks</u> in three dimensions *in situ*

Applicability

- Curvature: everyone's got it; what are the contributing factors?
- How does curvature influence durability and response to *operational* stresses?
- Laser dilatometry can be used to provide new information regarding not only cells but also <u>stacks</u> - cells, ceramic-ceramic seals, ceramic-metal seals

Future work

- Continue to demonstrate that optical profilometry and laser dilatometry are valuable tools for manufacturing
- Evaluate curvature evolution in various steps during the fabrication of anode-supported cells (B&A)
- Determine effects of anode reduction and redox cycling on planar cells/the electrolyte layer (B&A); responsible for slow degradation in performance?
- Investigate Raman spectroscopy as a useful tool for characterizing variations in stress within the electrolyte layer and connections to curvature

Ohio's Wright Center Power Partnership for Ohio