Reliability & Durability of Materials & Components For Solid Oxide Fuel Cells

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SECA Core Technology Program

Pittsburgh, PA. June 19, 2002

Research sponsored by the U.S. Department of Energy, SECA Core Technology Program, under contract DE-AC05-00OR22725 with UT-Battelle, LLC

Thanks to Tim Armstrong (ORNL) and Scott Swartz and Matt Seabaugh (NexTech) for supplying test specimens.

Outline

- Objectives
- Approach
- Evaluation of Materials & Components
- Summary
- Future Work

Objectives

In collaboration with industrial teams and other Core Technology Program participants,

- **To develop/adapt/recommend test techniques to evaluate the properties and behavior of materials and components for SOFC.**

- **To identify and understand the mechanism responsible for the failure of materials and components for SOFCs.**

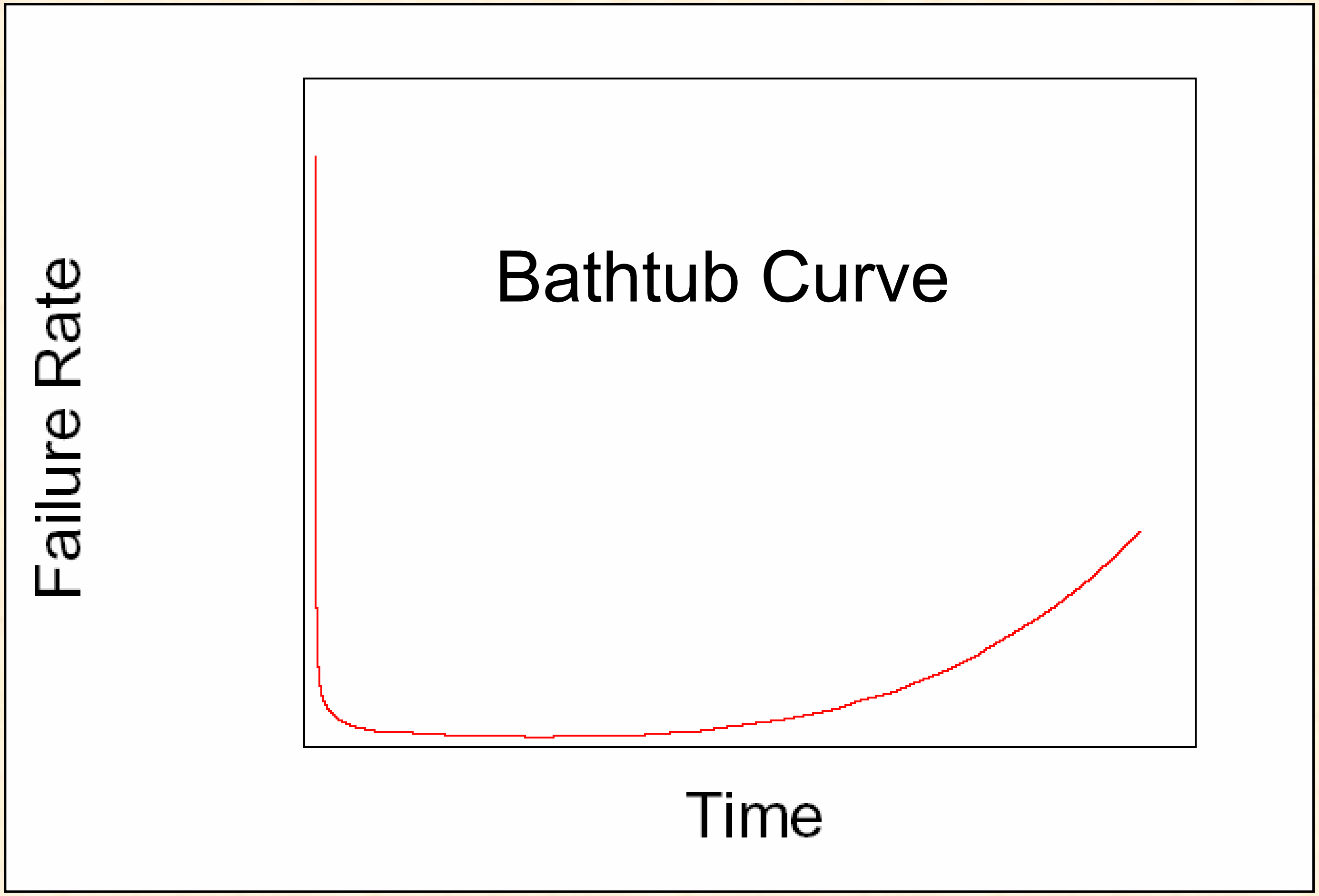
- **To develop methodologies for predicting the durability and reliability of materials and components for SOFCs.**

Background

The failure rate in complex systems usually follows three stages

- **a period with decreasing failure rate at the beginning of service life**

Approach: Background

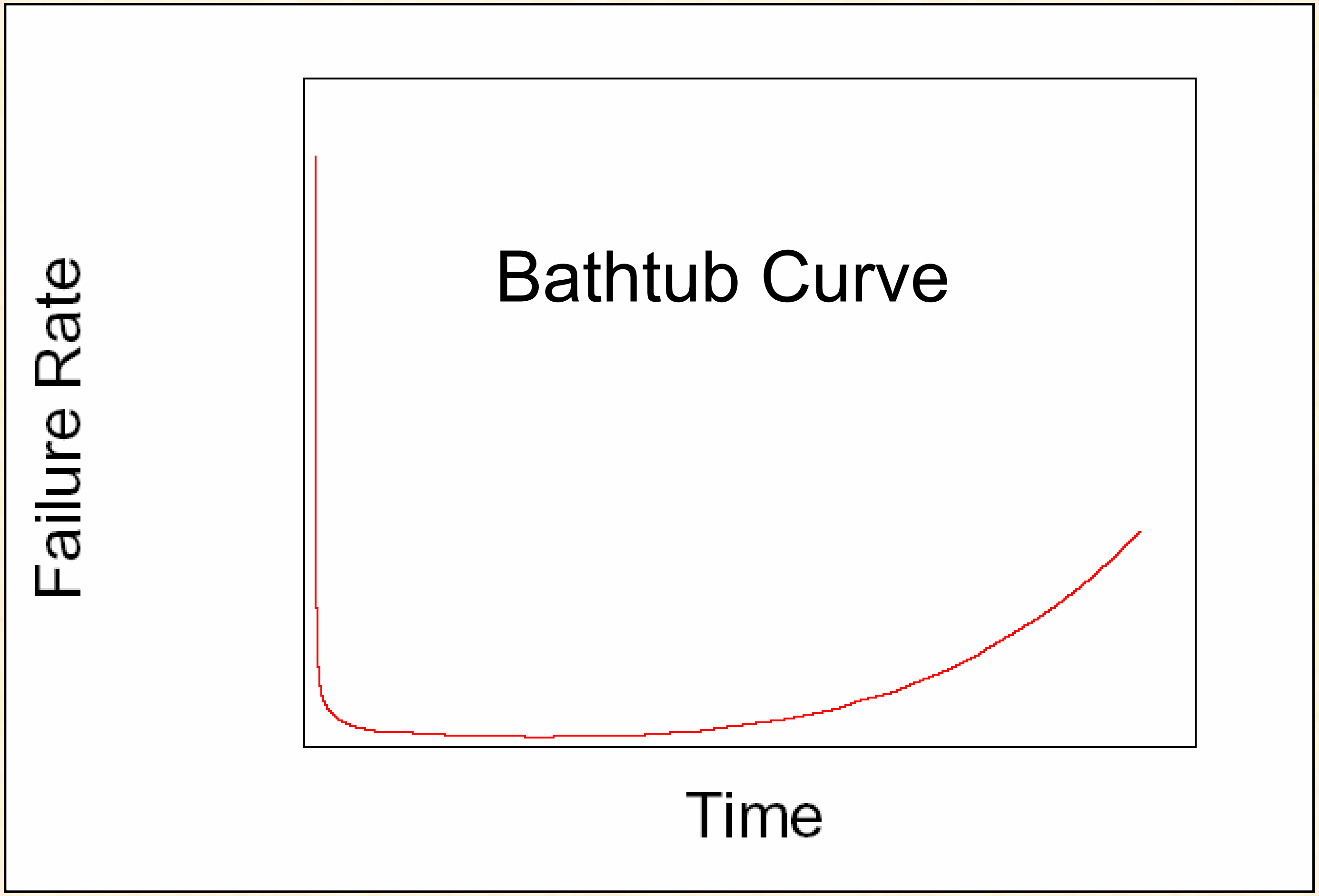


Background

The failure rate in complex systems usually follows three stages

- a period with decreasing failure rate at the beginning of service life
- **a period with a constant failure rate**

Approach: Background

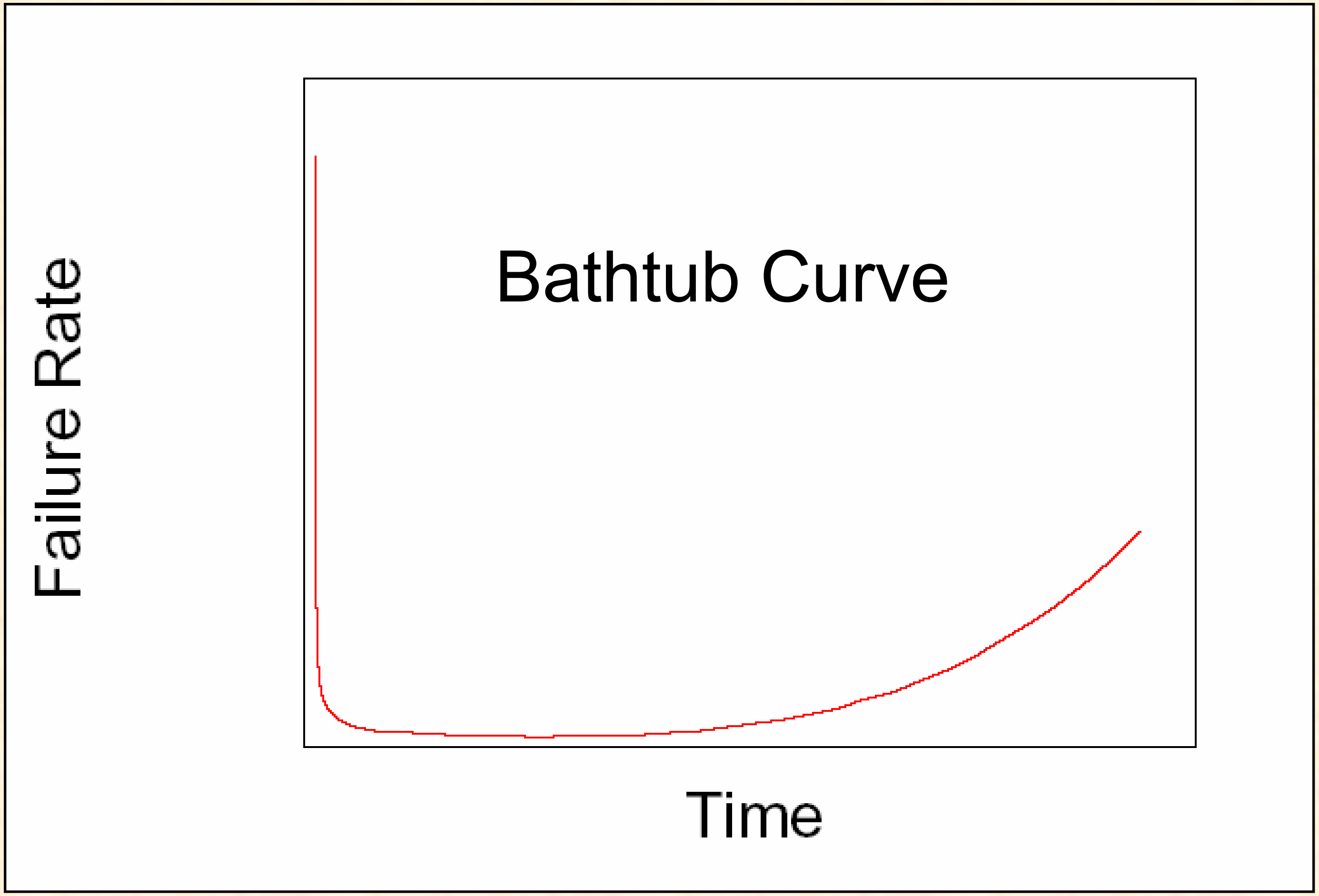


Background

The failure rate in complex systems usually follows three stages

- a period with decreasing failure rate at the beginning of service life
- a period with a constant failure rate
- **Increase of the failure rate at the later part of the life cycle.**

Approach: Background



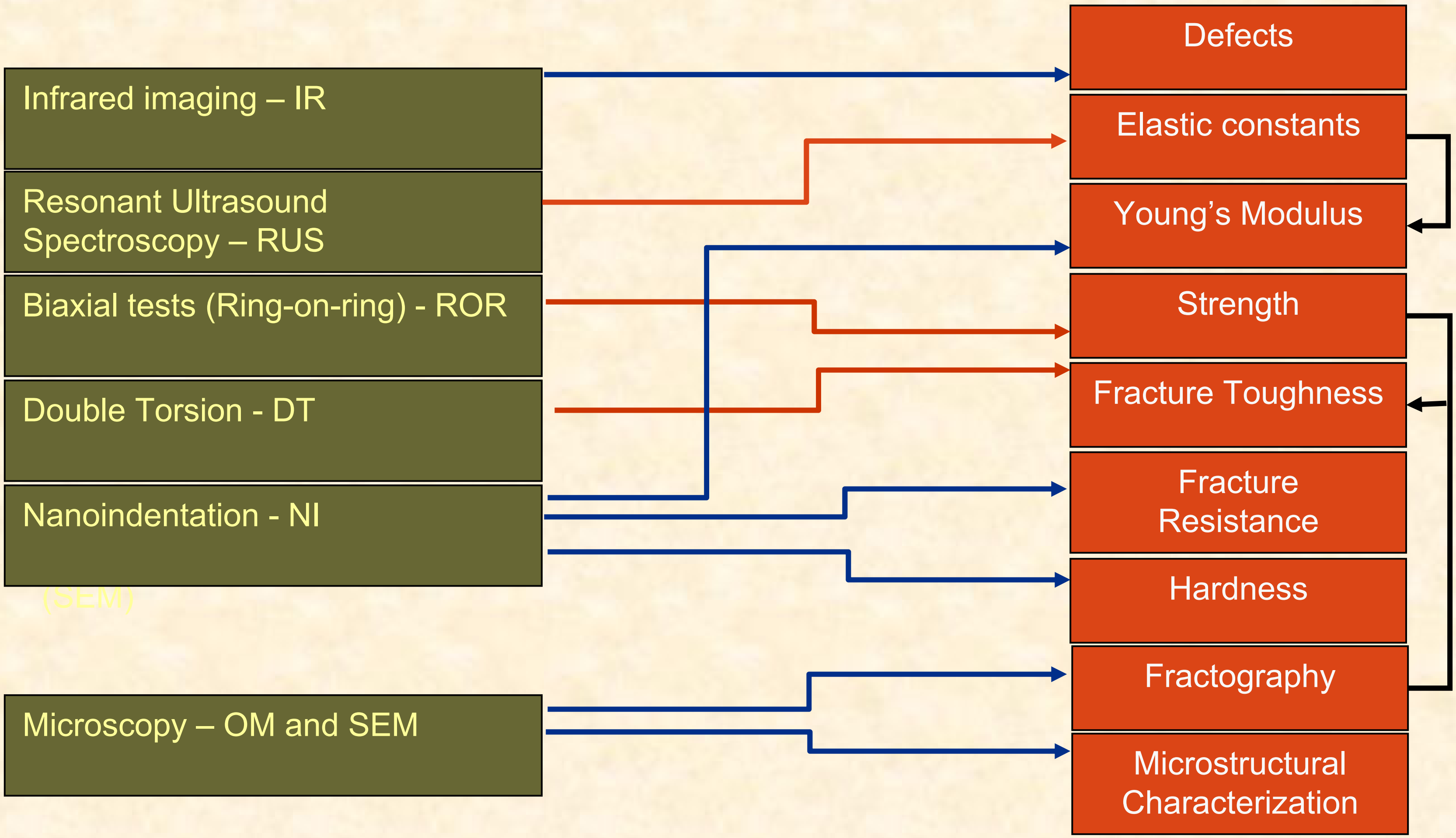
Approach

- Identification of mechanism that dominate the failure of SOFC materials and components at short times.
- Identification of mechanisms that dominate the failure of SOFC materials and components at long service times/cycles.
- Integrate information into life-prediction methodologies.

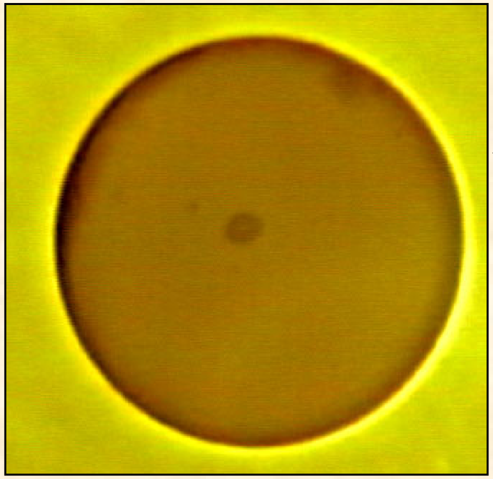
Evaluation of Materials and Components

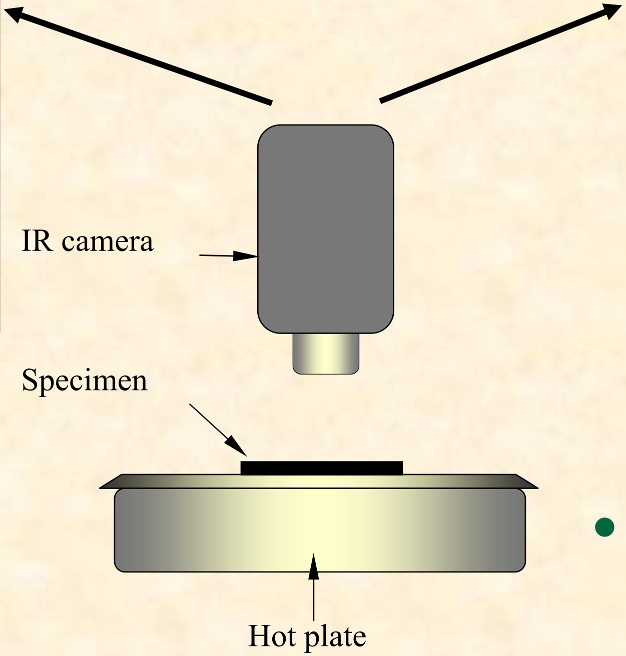
- **Experimental Techniques for Mechanical Characterization of SOFC Materials.**

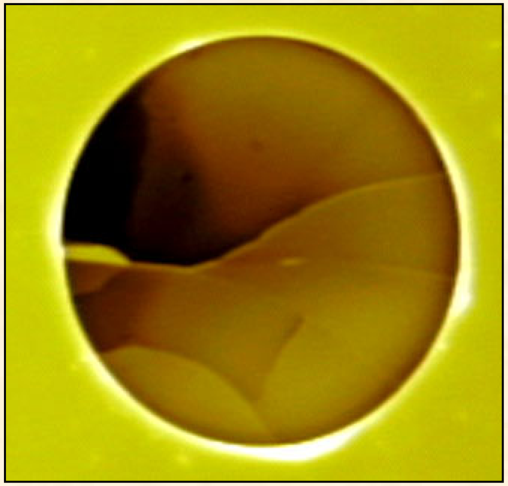
Experimental Techniques for Mechanical Characterization of Materials for SOFC



Infrared Imaging

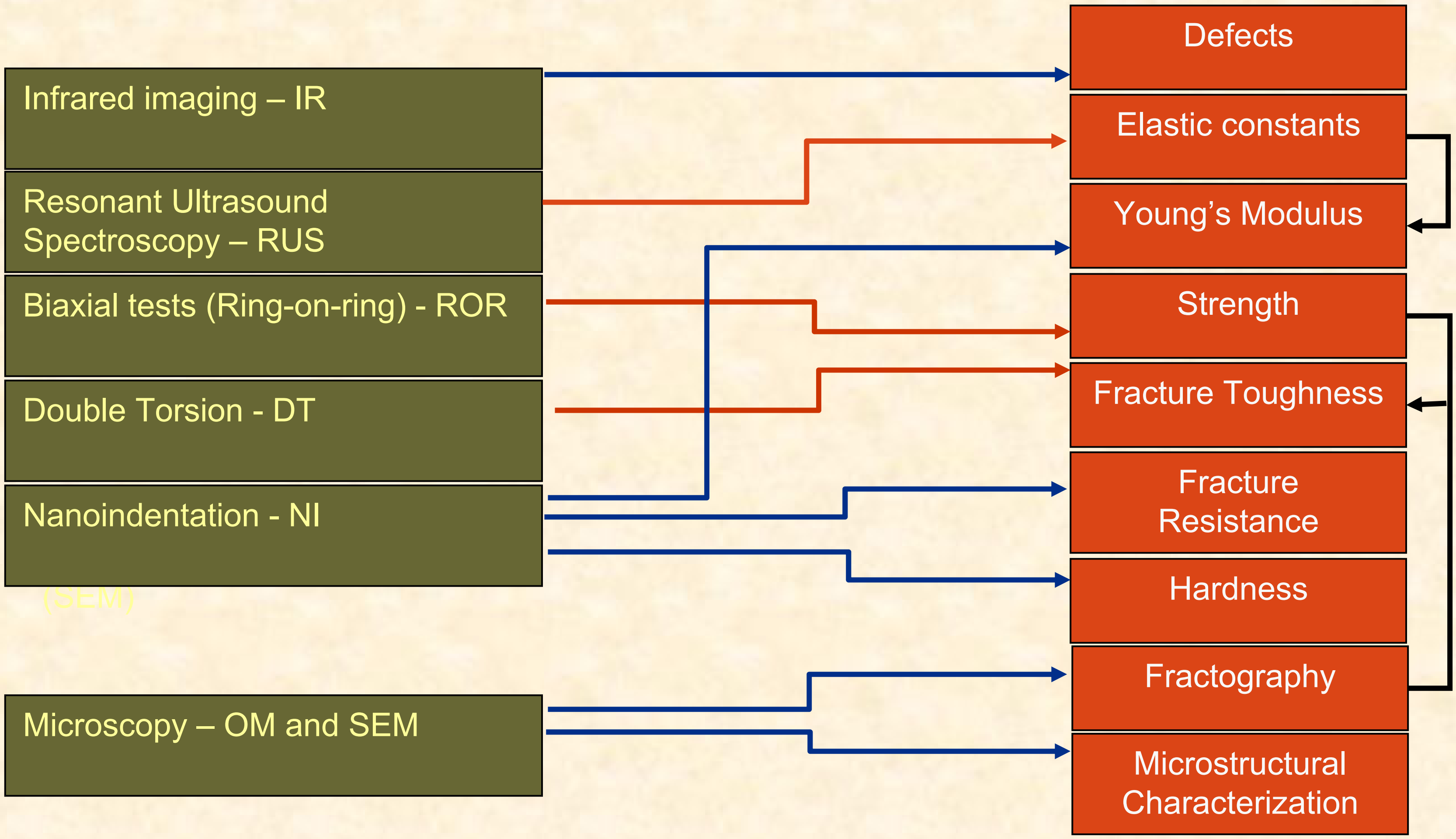




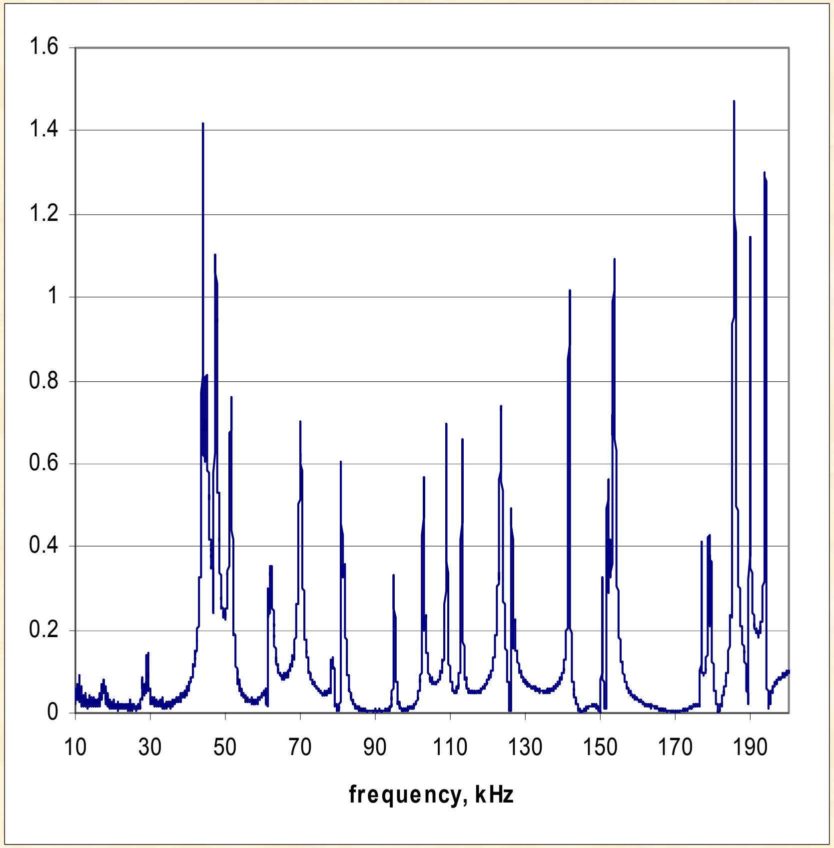


- **Characterization of Defects**
- **Crack propagation Study**

Experimental Techniques for Mechanical Characterization of Materials for SOFC



Resonant Ultrasound Spectroscopy



Resonant Ultrasound Spectrum

⇓

Unique "fingerprint" of each sample.

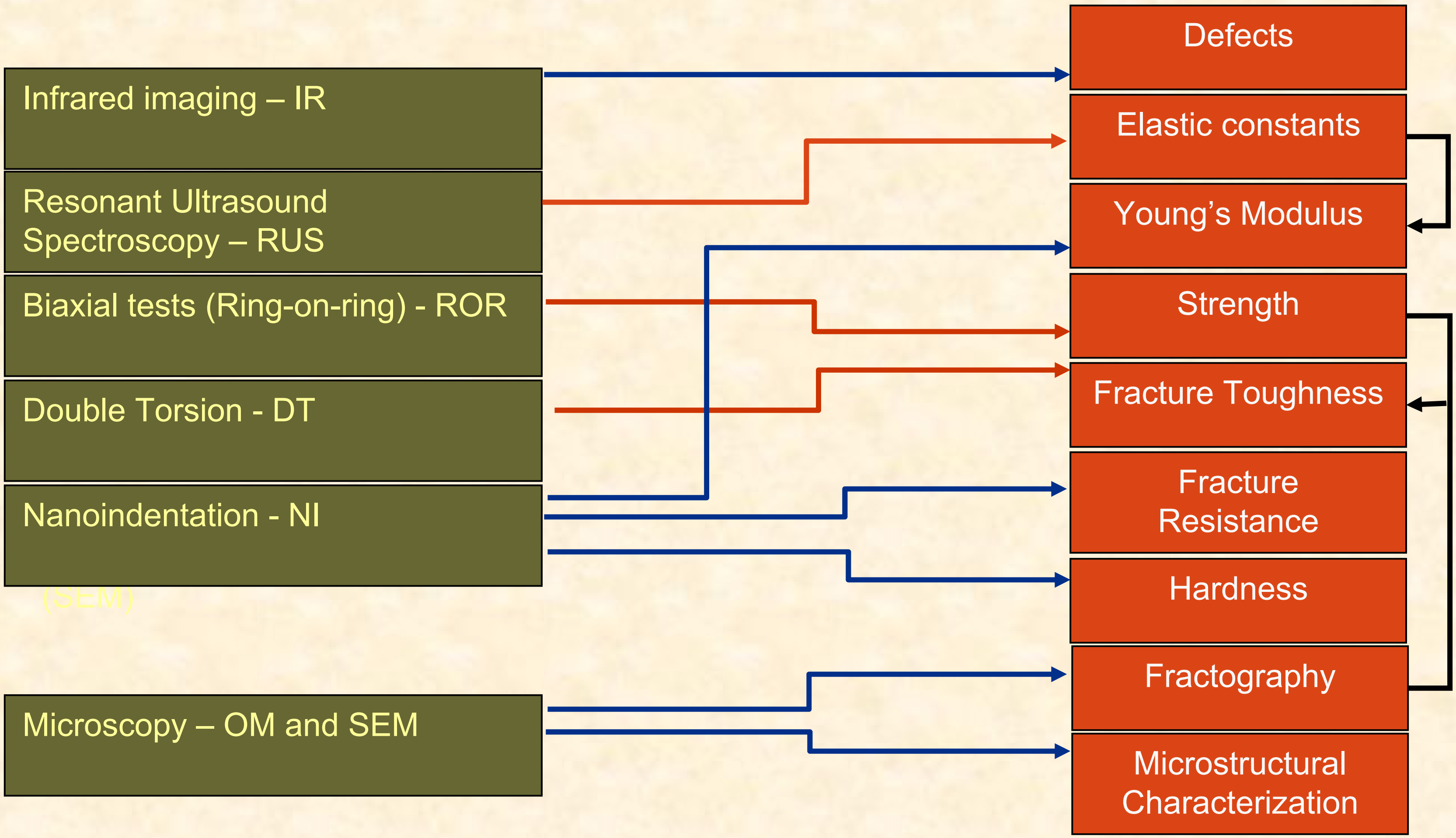
Depends on:

•Geometry (size and shape)

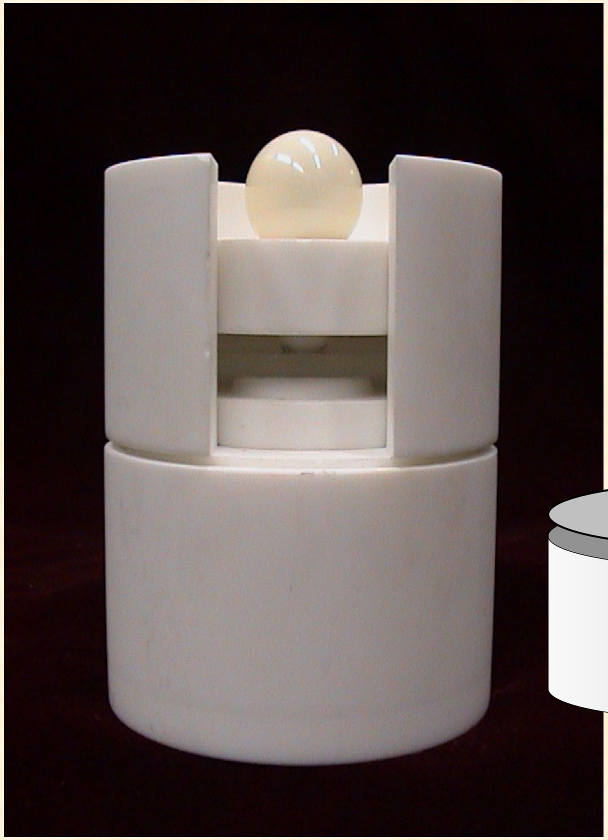
•Elastic properties of the material

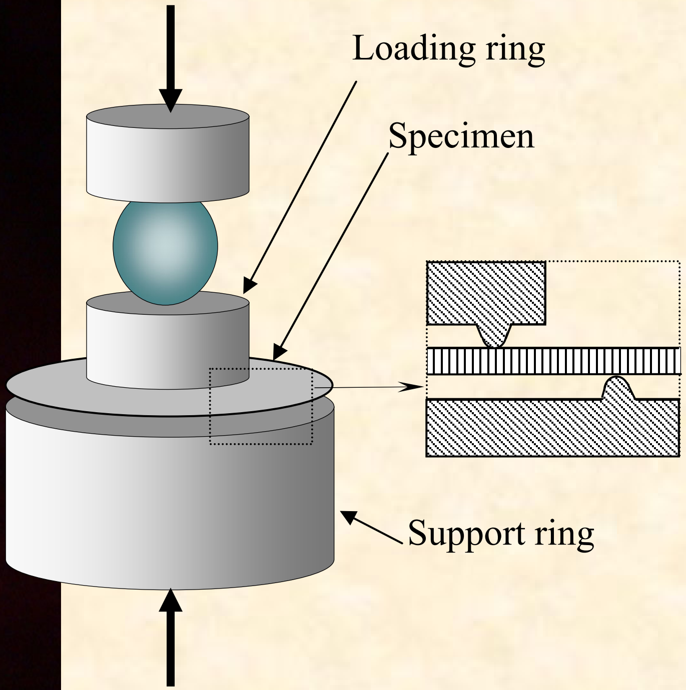
•Defects

Experimental Techniques for Mechanical Characterization of Materials for SOFC



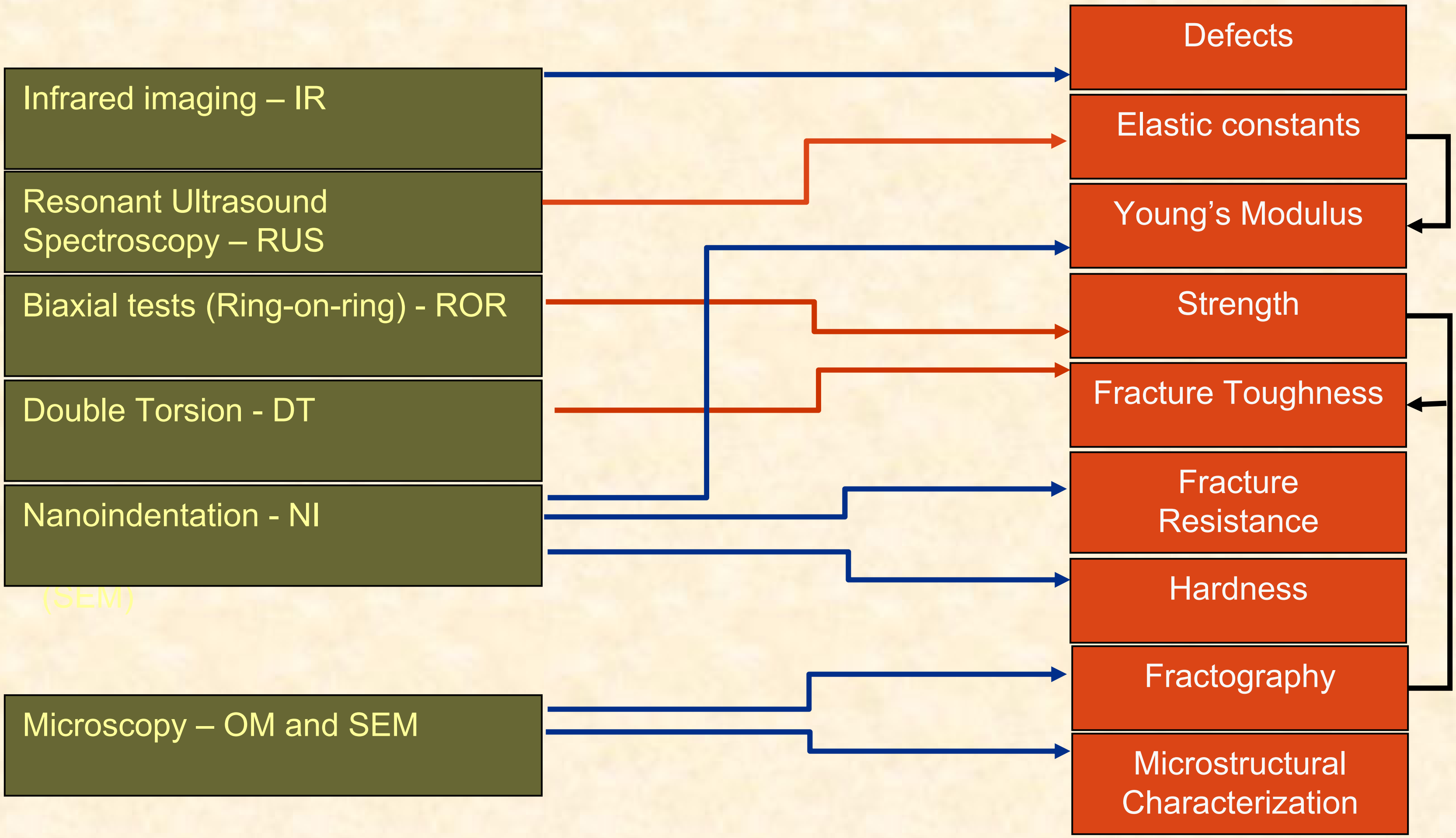
Biaxial Testing – Ring-on-Ring



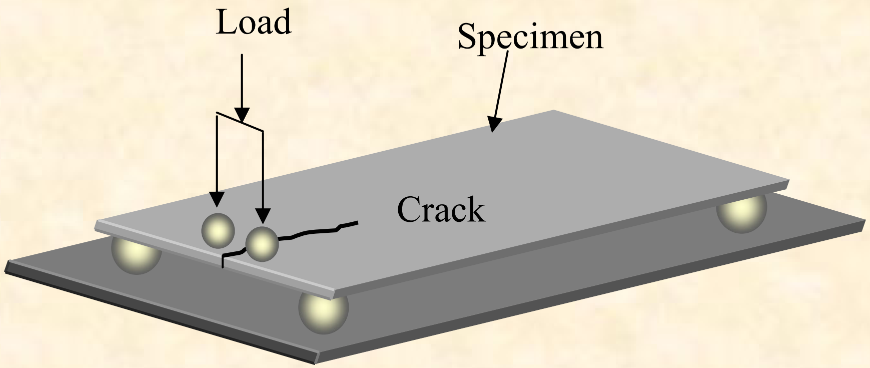


- Biaxial Strength
- Effect of defects, temperature and environment on strength.

Experimental Techniques for Mechanical Characterization of Materials for SOFC

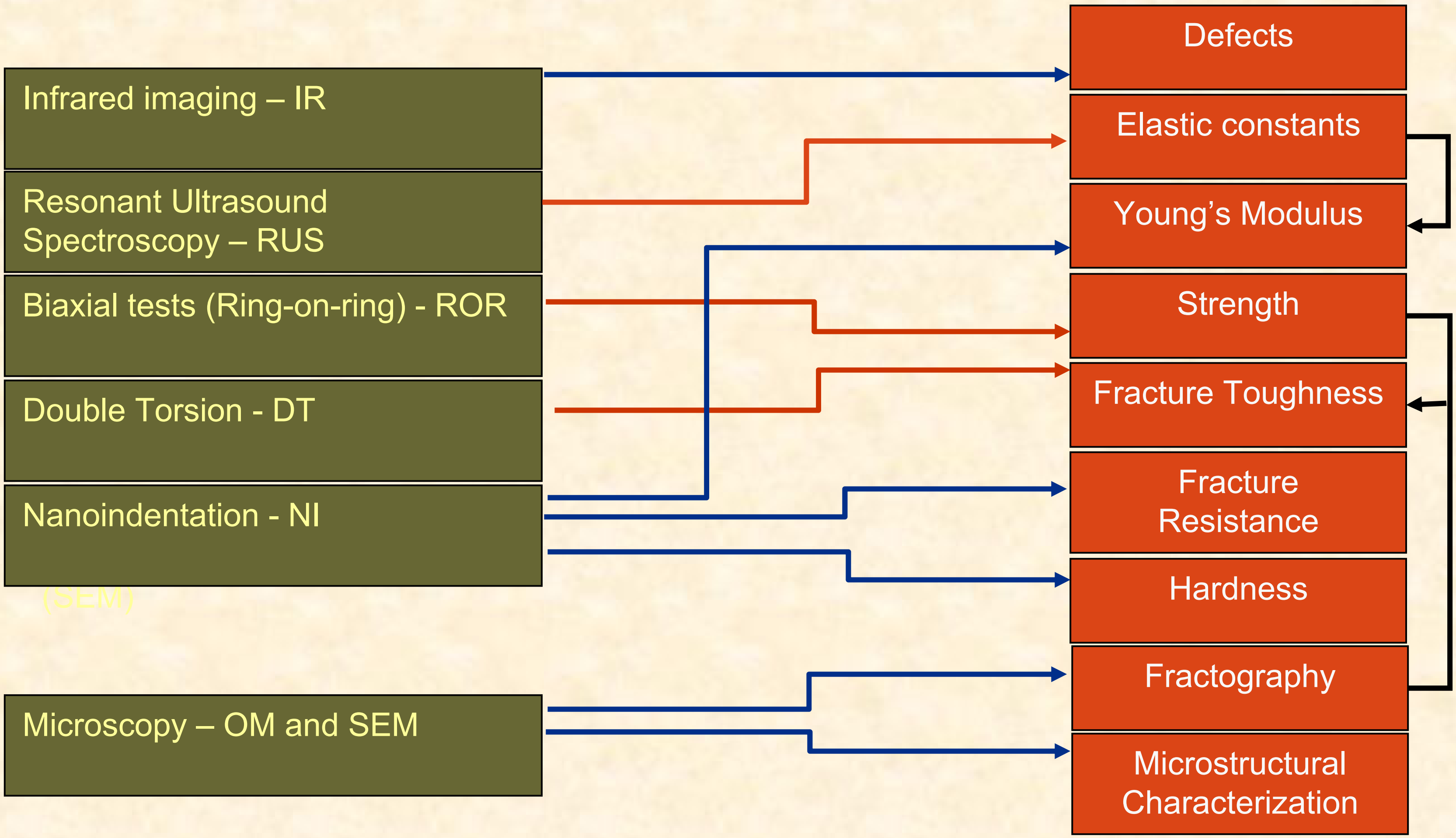


Double torsion test



- Fracture toughness, K_{IC}
- Crack Growth

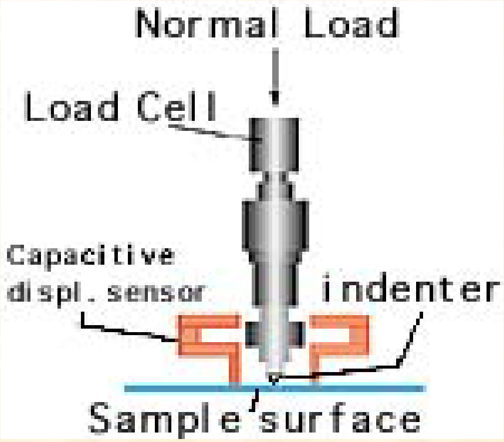
Experimental Techniques for Mechanical Characterization of Materials for SOFC

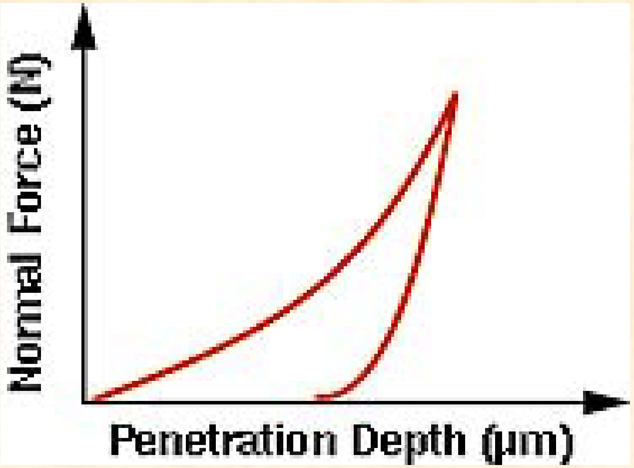


Indentation Method

Nano-indentation

- Nanohardness
- Young's Modulus
- Fracture Resistance





Characterized Materials

- **Electrolyte:**

  8mol% YSZ – ORNL (4 layers) ∅ 1”

- **Anode:**

  NiO/8mol% YSZ Cermet-ORNL (2, 4 and 6 layers) ∅ 1”

  ***Ni/8mol% YSZ Cermet-**ORNL (2, 4 and 6 layers) ∅ 1”

  NiO/8mol% YSZ Cermet-NexTech (multilayer) ∅ 1”

  ***Ni/8mol% YSZ Cermet-** NexTech (multilayer) ∅ 1”

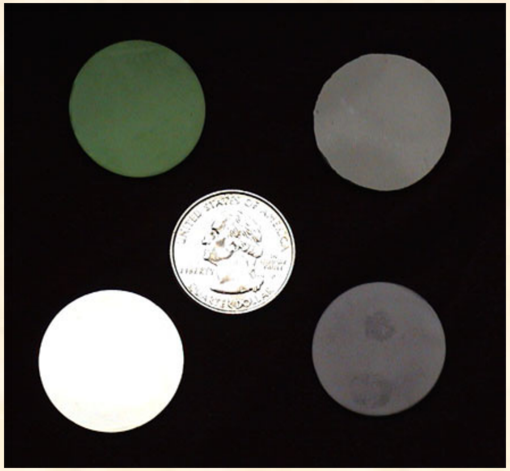
  *** reduced in hydrogen**

- **Cathode:**

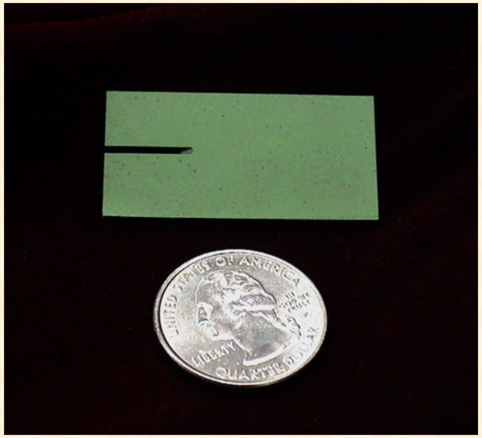
  LSM – NexTech (multilayer) ∅ 1”

Characterized Materials

- Disks 1” ∅
  Resonant Ultrasound Spectroscopiy
  Infrared Imaging
  Biaxial strength
  Nanoindentation



- Notched Plates
  Fracture toughness



Characterization of Electrolyte Materials

Characterization of Electrolyte Materials

8%mol YSZ - porosity: 8%

Elastic Properties at Room Temperature:

RUS: E =175±8 GPa

G = 67± 3 GPa

ν =0.32 ± 0.01

Nanoindentation: displacement ≈800 nm

surface	E =196±6 GPa	H =13±0.5 GPa
cross-section	E =176±4 GPa	H =12.6 ±0.5 GPa

A. Selcuk & A. Atkinson, J.Euro.Ceram.Soc. 17 (1997)

8% porosity E= 176 GPa, G=67 GPa

fully dense: E=220 GPa, G=83 GPa

Impulse excitation technique

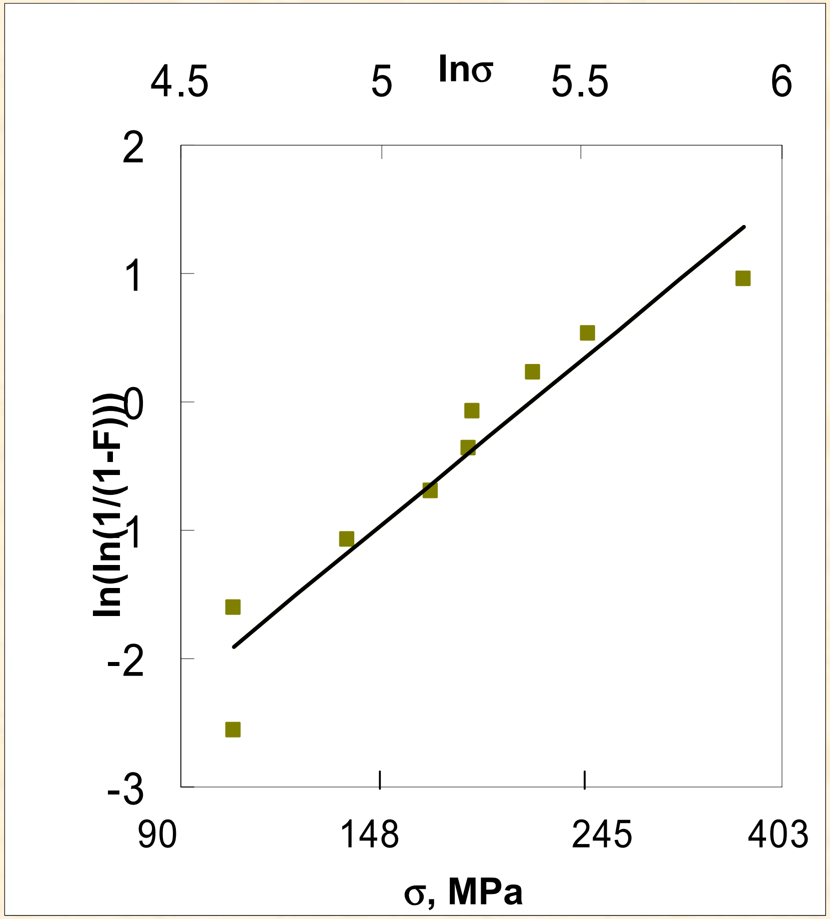
Characterization of Electrolyte Materials

Biaxial Strength at Room Temperature:

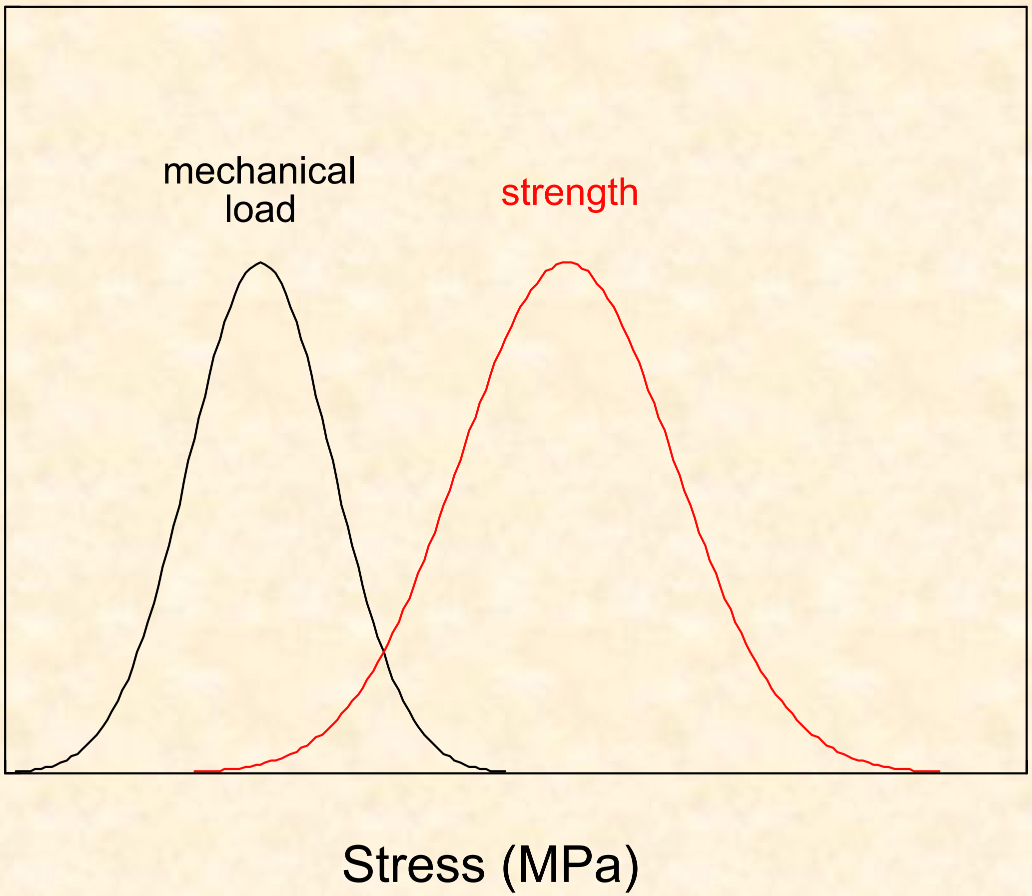
σ_{ave} =190±82 MPa

Weibull distribution analysis

Weibull strength: σ_o= 216 MPa
Weibull modulus: m=2.36



Distribution of Strengths

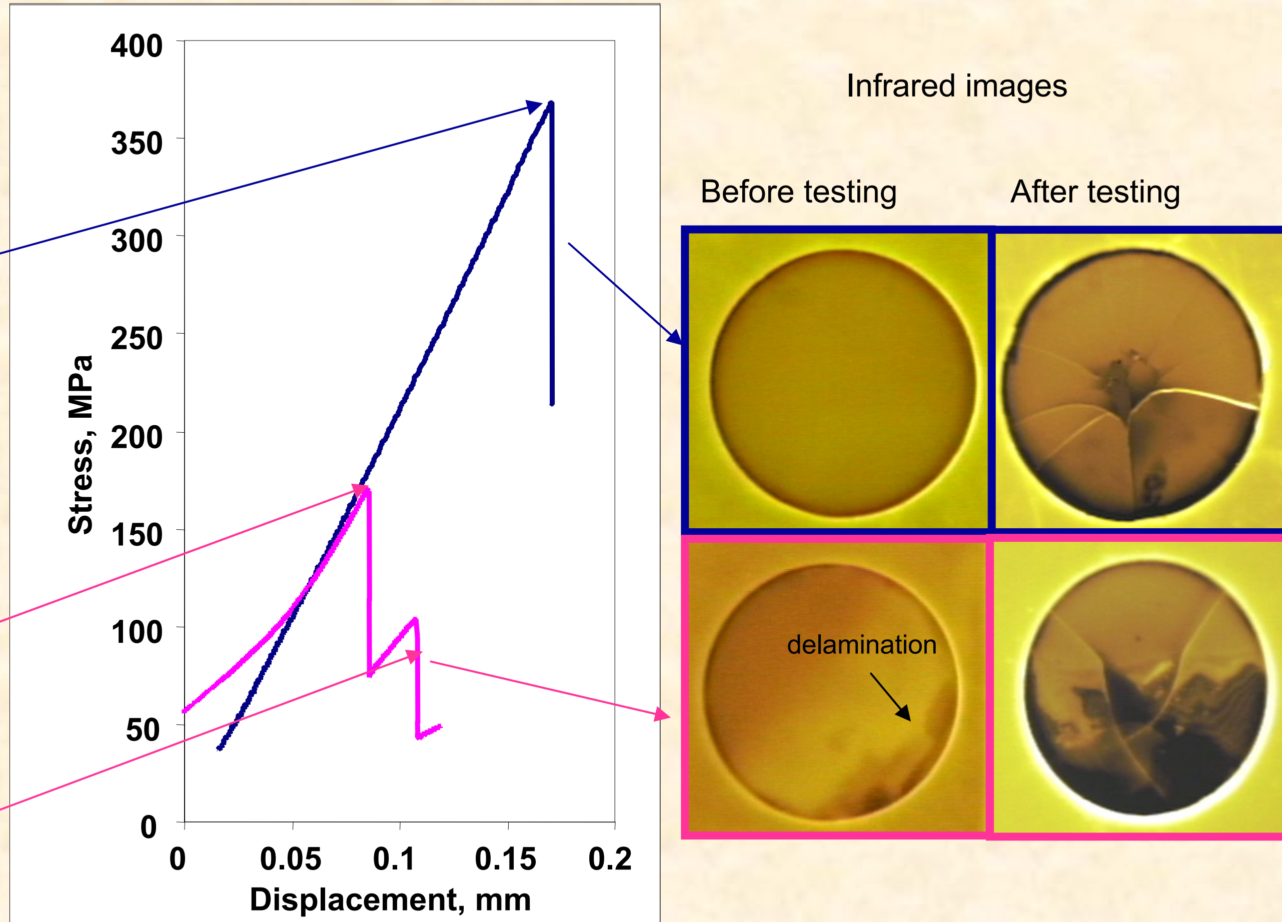


Characterization of Electrolyte Materials

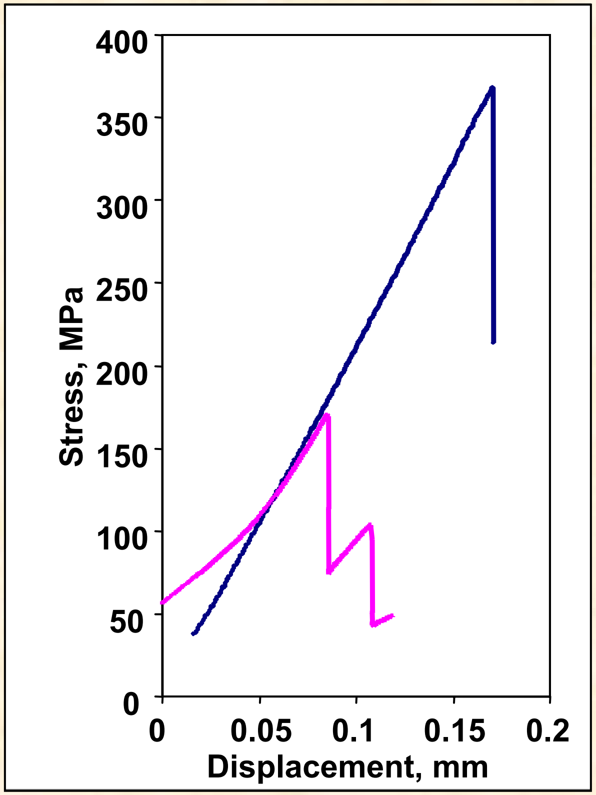
Failure with branched crack formation from the loading ring area

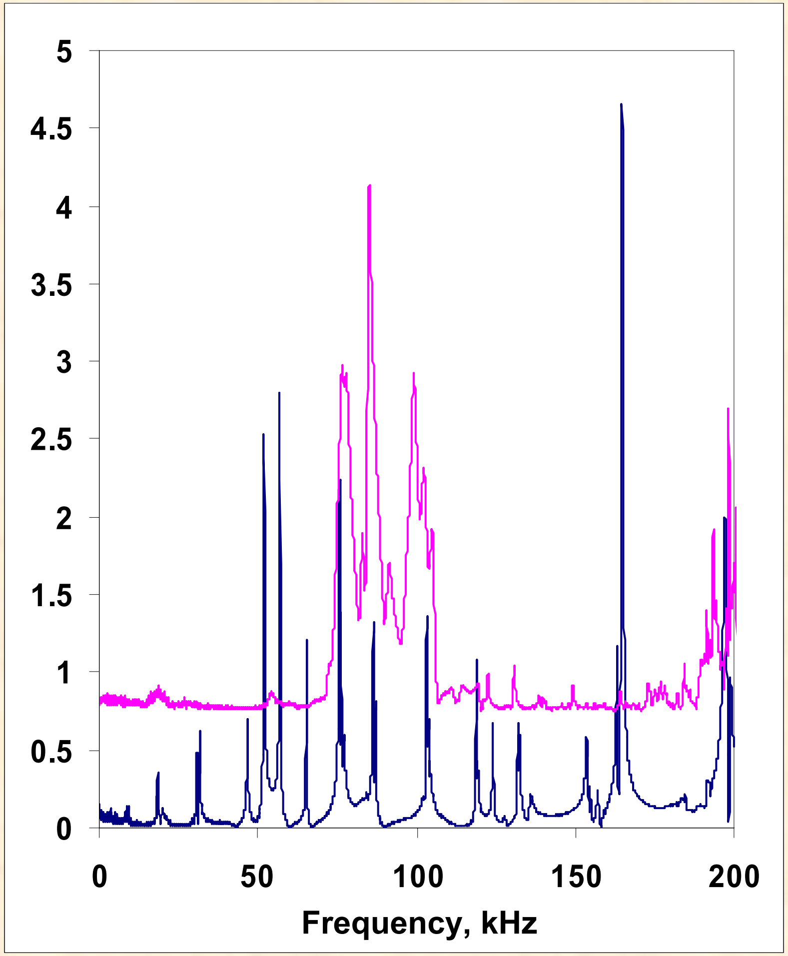
Primary crack formation

Secondary crack formation and delamination



Characterization of Electrolyte Materials

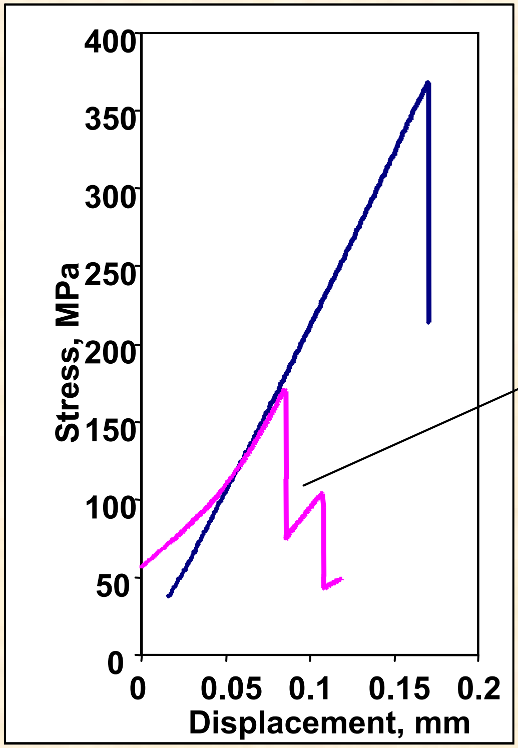




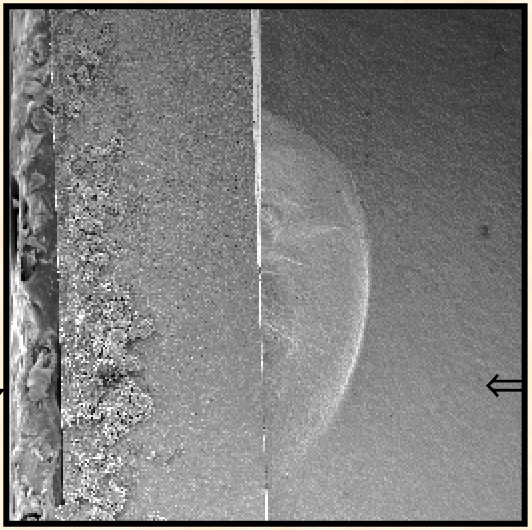
Blue: “good” spectra –sharp peaks

Pink: spectra with peak splitting and shifting associated with defects in sample

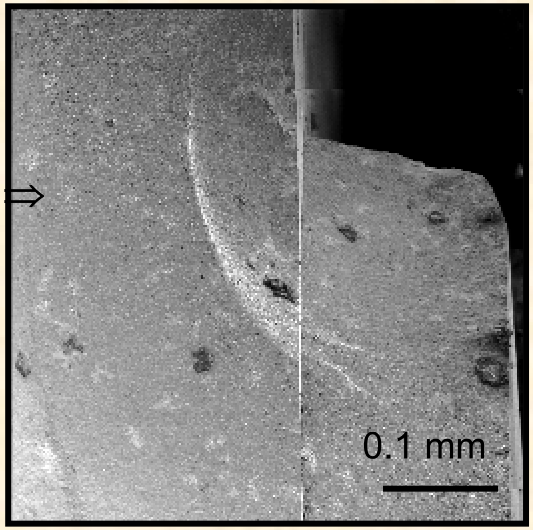
Characterization of Electrolyte Materials



Tensile surface



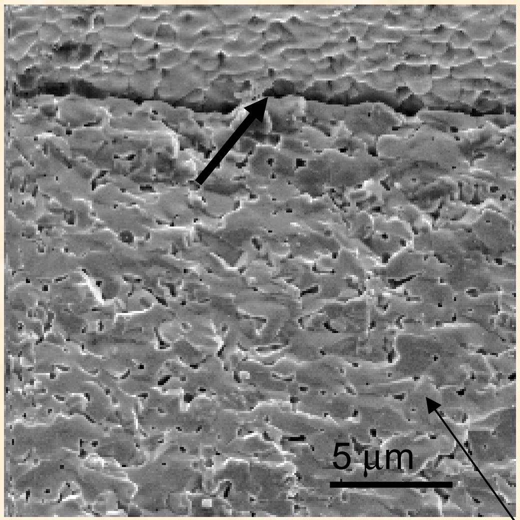
SEM - Fractography



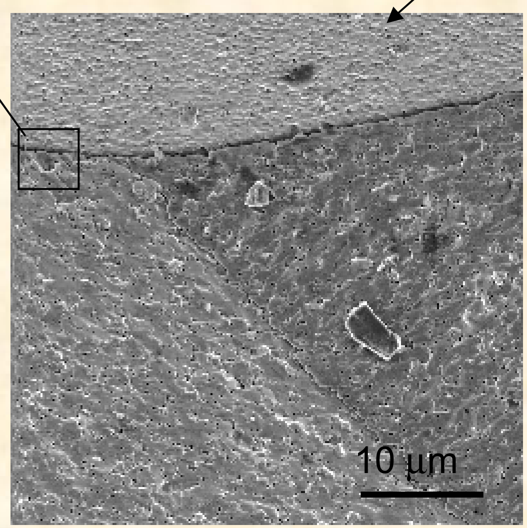
Tensile surface

Characterization of Electrolyte Materials

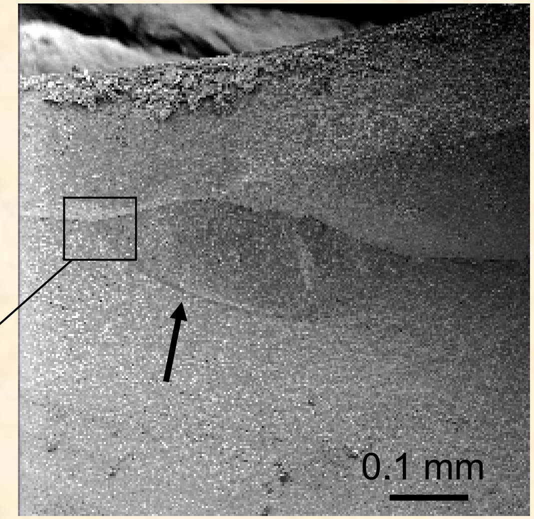
SEM - Fractography



Crack between two layers.



Tensile surface



Crack Initiation

Characterization of Anode Materials

Characterization of Anode Materials

NiO/YSZ Cermet– ORNL (2, 4 and 6 layers; 0.5, 1 and 1.5 mm thick) – 30% porosity
NiO/YSZ Cermet – NexTech (multilayer, 1mm thick)

Elastic Properties at Room Temperature:

RUS*:

ORNL:	E =103±6 GPa	G = 40± 2.5 GPa	ν =0.29 ± 0.03
NexTech:	E =106±6 GPa	G = 41± 2.4 GPa	ν =0.29 ± 0.01

A. Selcuk & A. Atkinson, J.Euro.Ceram.Soc. 17 (1997)

Impulse excitation technique – characterized anode 75mol%NiO/YSZ materials up to 14% porosity

Extrapolated data for 30 % porosity:

Exponential law $M=M_o exp(-bP)$: E= 99 GPa, G=38 GPa

Linear law $M=M_o(1-bP)$: E= 76 GPa, G=30 GPa

Non-linear law $M=M_o(1-(bP)/(1+(b-1)P)$: E= 99 GPa, G=38 GPa

Composite Sphere Method (CSM) $M=M_o(1-P^2)/(1+bP)$: E= 83 GPa, G=32 GPa

Characterization of Anode Materials

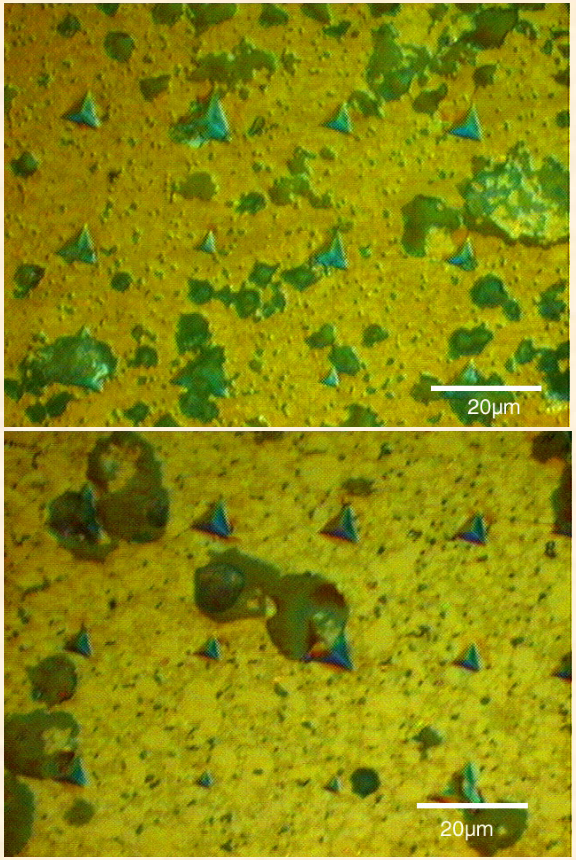
Elastic Properties at Room Temperature:

Nanoindentation:

NiO/8mol% YSZ Cermet– ORNL

NiO/8mol% YSZ Cermet – NexTech

		Displ., nm	Load, mN	E, GPa	H, GPa
Nex Tech	surface	1200	152	140±34	6.1±3.0
		1100	102	134±41	6.2±4.0
	Cross section	1000	103	132±16	5.2±1.4
		1500	155	112±31	3.4±2.2
ORNL	Surface	1400	158	124±29	4.6±3.0
		1000	104	144±26	5.9±2.9
	Cross section	1000	154	152±23	8.0±3.0
		800	51	147±65	4.0±3.0



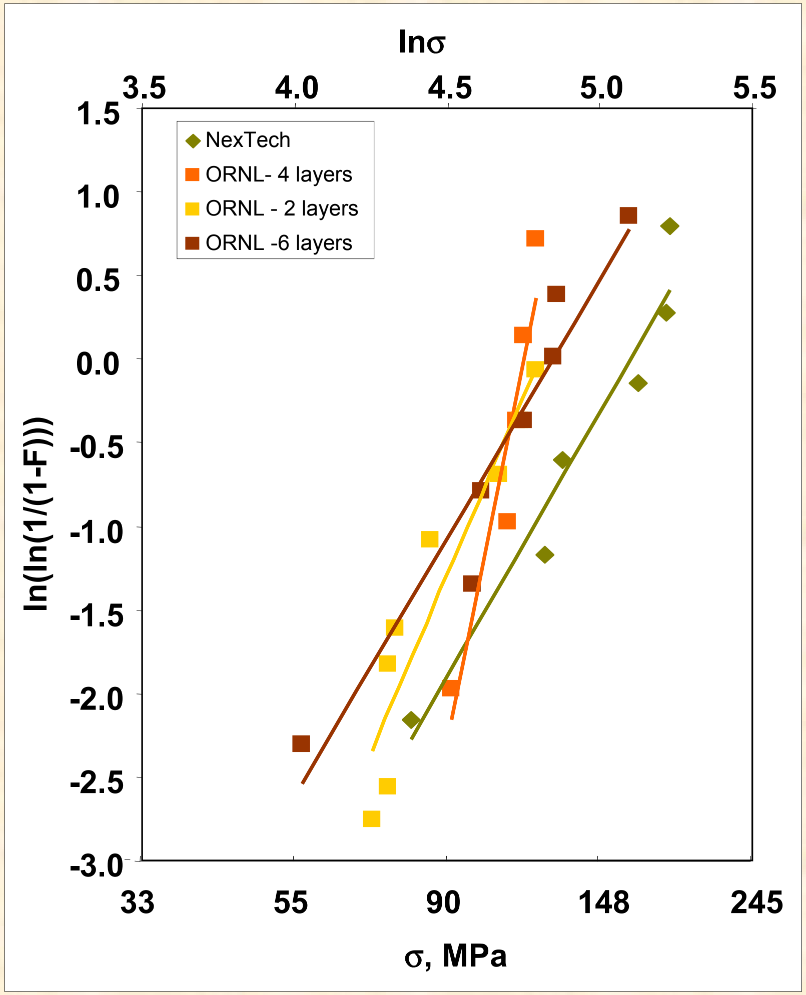
Characterization of Anode Materials

Biaxial Strength at Room Temperature:

NiO/8mol% YSZ Cermet– ORNL

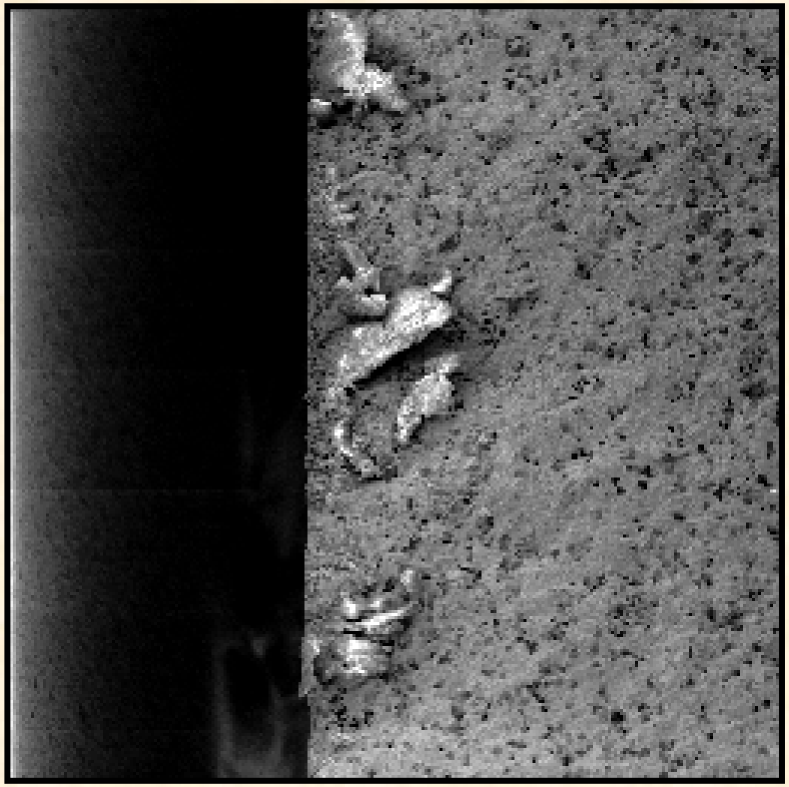
NiO/8mol% YSZ Cermet – NexTech

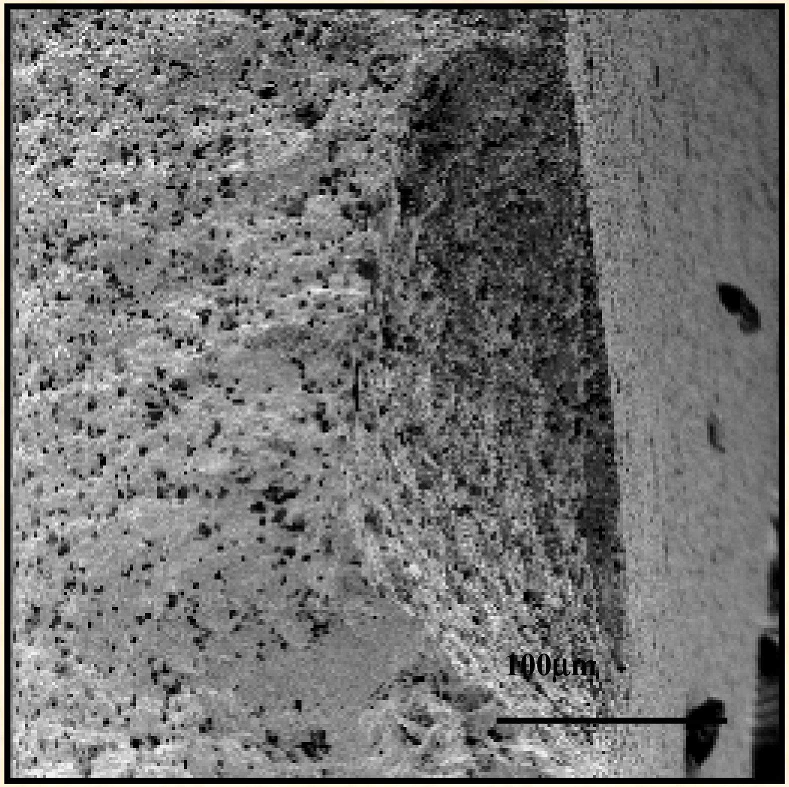
Sample	σ_{ave}, MPa	Weibull Distribution	
		σ_0, MPa	m
NexTech	145.8±41.8	163.9	3.17
ORNL 2 layers	107.1±18.0	121.8	4.26
ORNL 4 layers	110.6±11.0	115.5	9.29
ORNL 6 layers	112.0±33.0	127.36	3.08



Characterization of Anode Materials

NiO/YSZ Cermet– ORNL (4 layers; 1 mm thick) – 30% porosity





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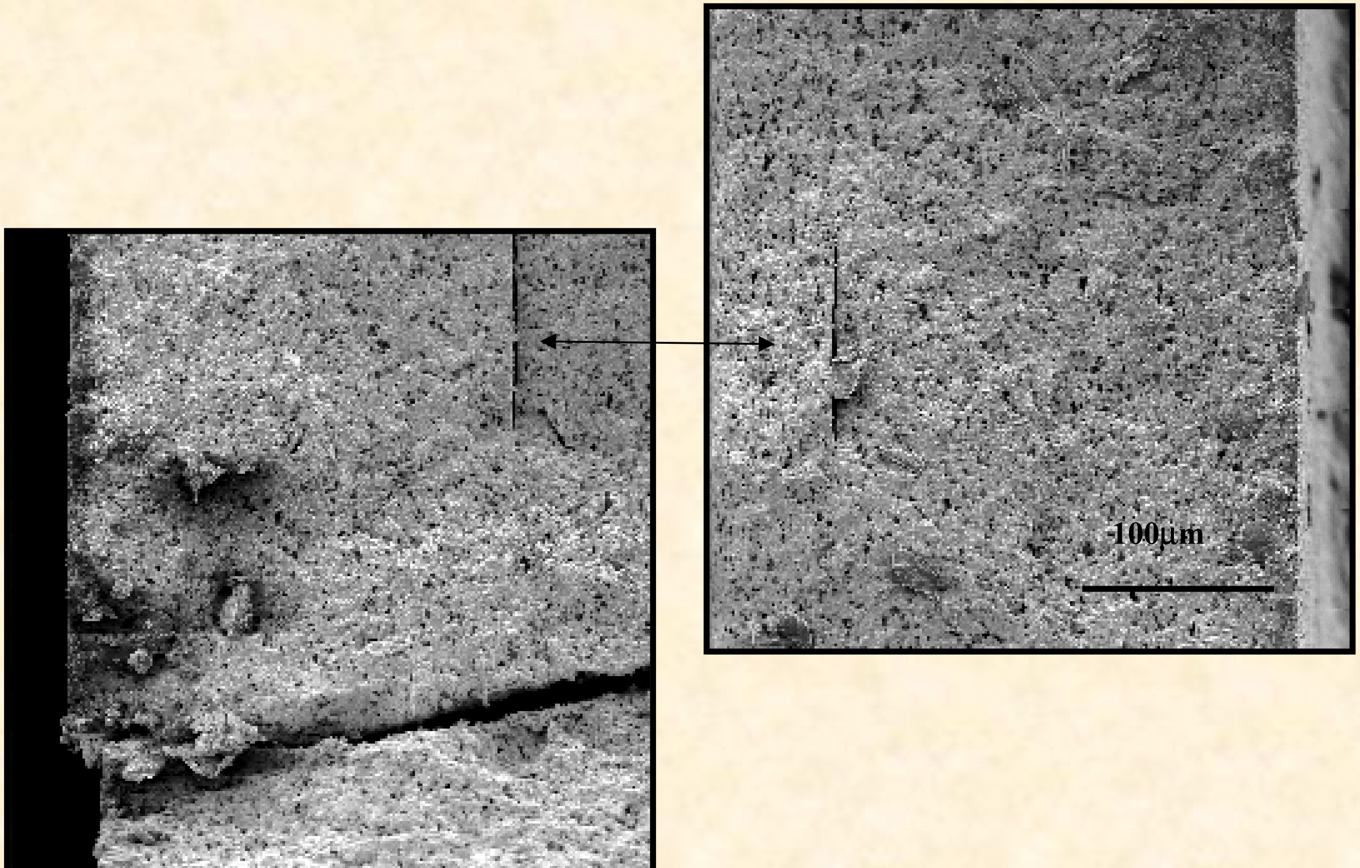
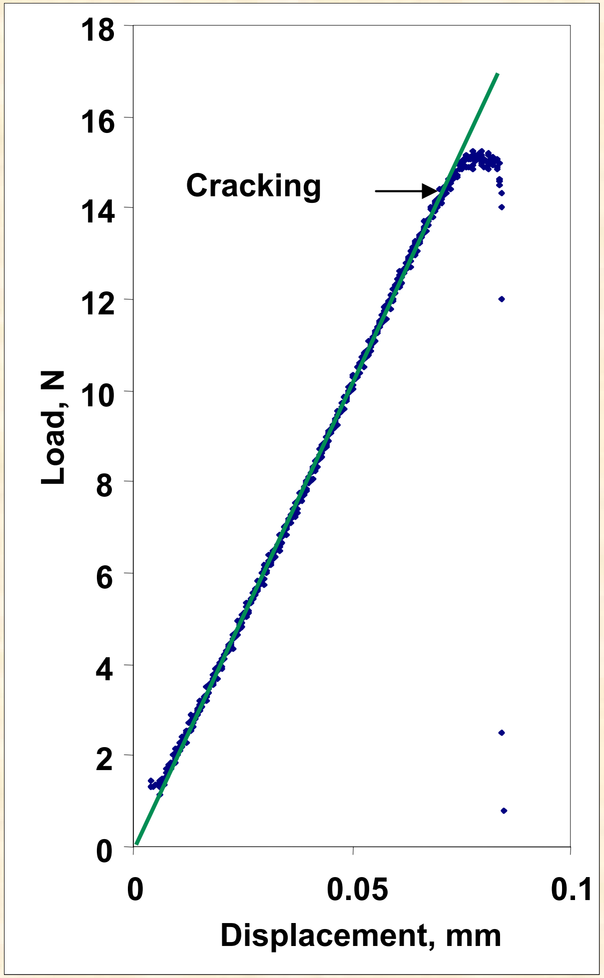
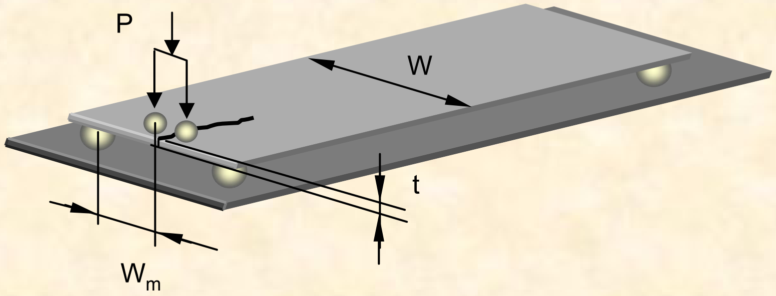


Characterization of Anode Materials



Double Torsion Testing at Room Temperature:

NiO/YSZ Cermet– ORNL



$$K_I = PW_m\left[\frac{3(1+\nu)}{Wt^4\xi}\right]^{1/2}, \xi = 1 - 1.26(t/W) + 2.4(t/W)\exp[-\pi W/(2t)]$$

Precracked @ 0.02 mm/min and tested @ 1 mm/min

K_{IC}= 1.05±0.14 MPam$^{1/2}$

Characterization of Anode Materials

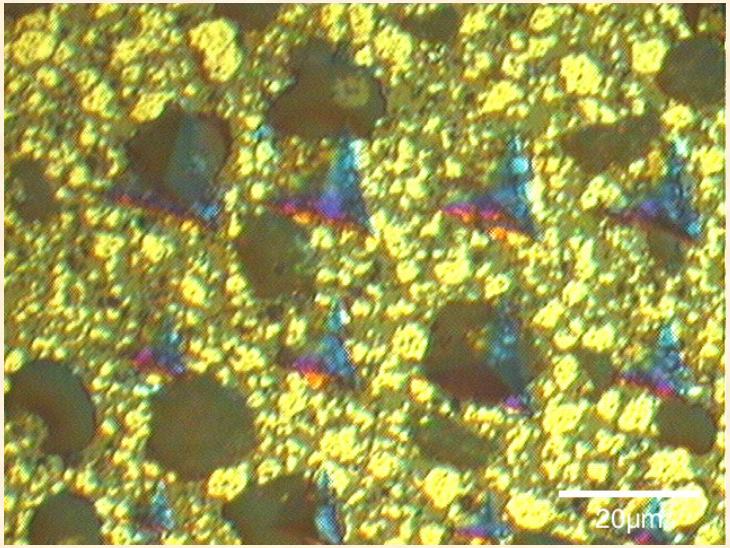
NiO/8mol% YSZ Cermet– ORNL (2, 4 and 6 layers; 0.5, 1 and 1.5 mm thick) reduced in 4% H_2 at 600°C for 4 h

NiO/8mol% YSZ Cermet – NexTech (multilayer, 1mm thick), reduced in hydrogen

Elastic Properties at Room Temperature:

Nanoindentation

NexTech	Displ., nm	Load, mN	E, GPa	H, GPa
surface	2300	155	47±16	1.31±0.4
	1700	103	53±5	1.6±0.4
Cross section	2200	153	54±4	1.4±0.2
	1600	103	47±16	0.9±0.2



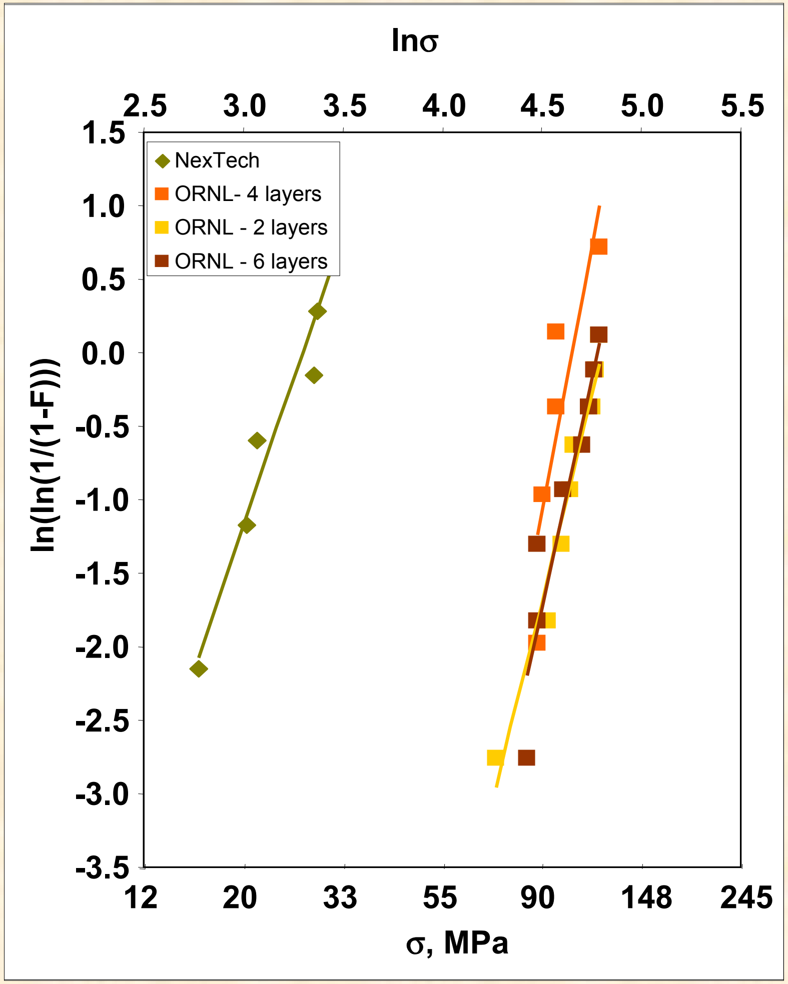
Characterization of Anode Materials

Biaxial Strength at Room Temperature:

NiO/8mol% YSZ Cermet– ORNL reduced in 4% H_2 at 600°C for 4 h

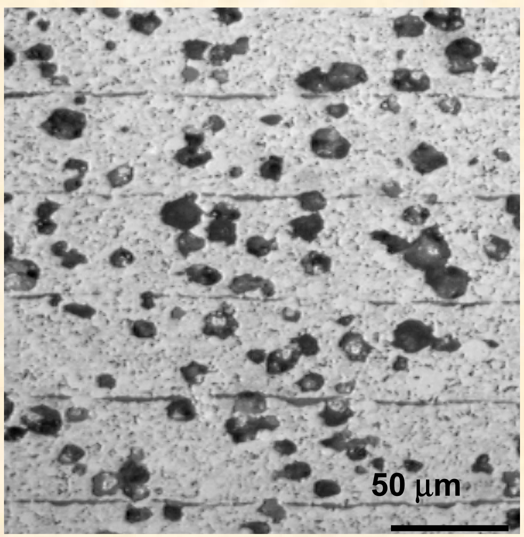
NiO/8mol% YSZ Cermet – NexTech reduced in hydrogen

Sample	σ_{ave}, MPa	Weibull Distribution	
		σ_0, MPa	m
NexTech	24.5±5.9	27.03	3.96
ORNL 2 layers	109.9±14.0	122.3	5.51
ORNL 4 layers	98.5±12.7	104.7	7.25
ORNL 6 layers	102.9±12	119.9	6.16

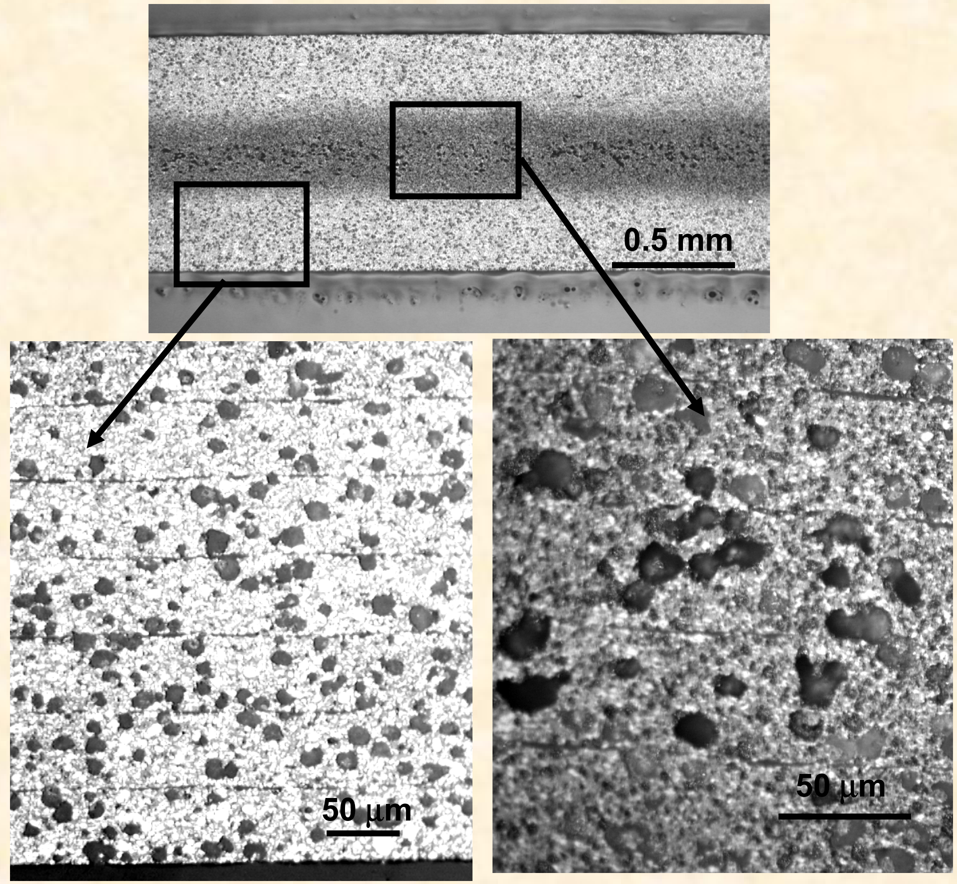


Characterization of Anode Materials

Optical Microscopy

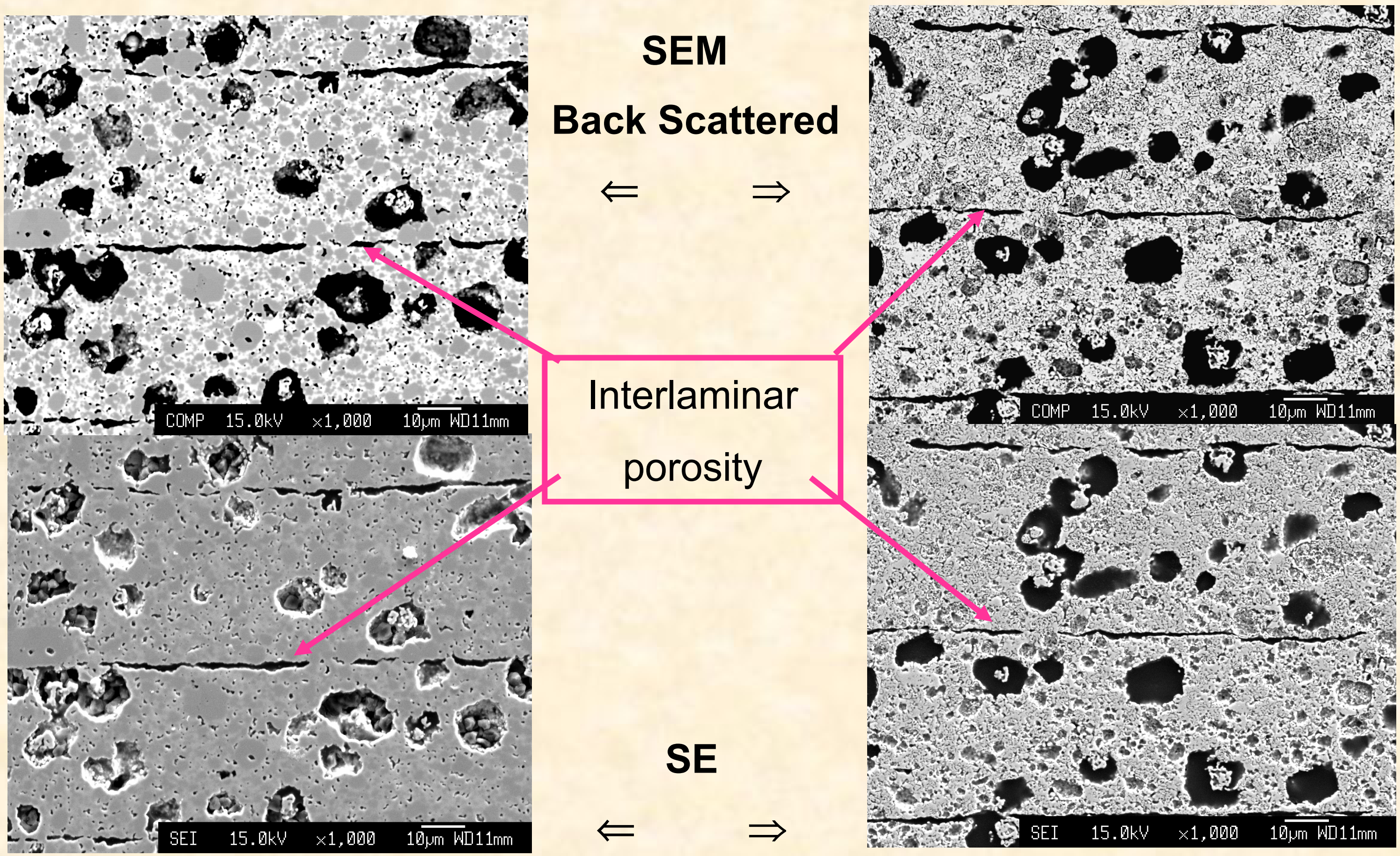


NiO/8mol% YSZ Cermet – NexTech



NiO/8mol% YSZ Cermet– NexTech
reduced in hydrogen

Characterization of Anode Materials

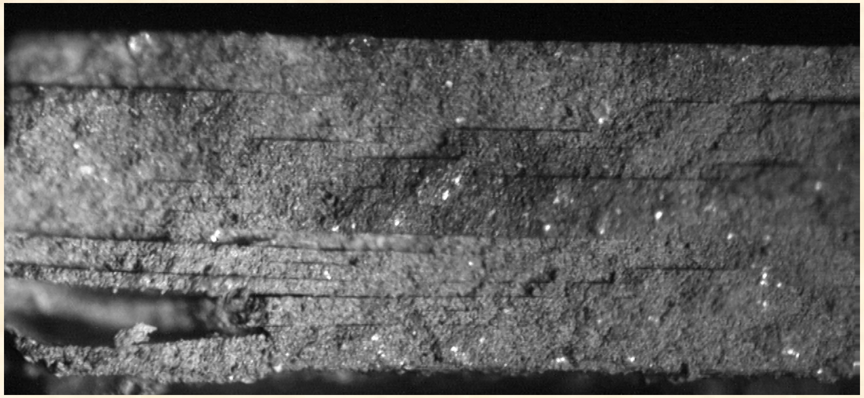


NiO/8mol% YSZ Cermet – NexTech

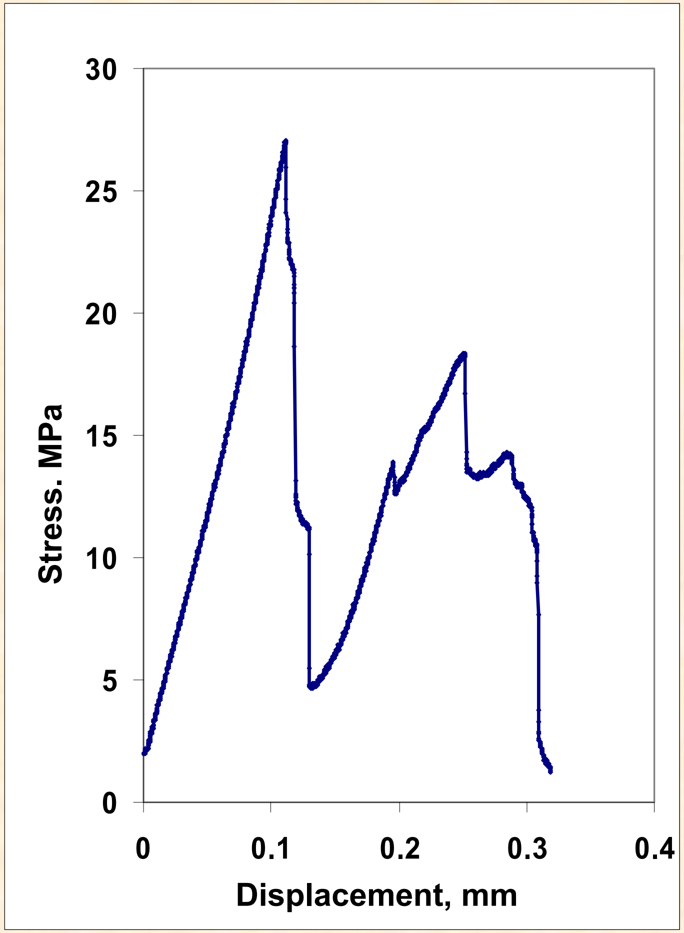
NiO/8mol% YSZ Cermet– NexTech **<u>reduced in hydrogen</u>**

Characterization of Anode Materials

NiO/8mol% YSZ Cermet– NexTech
reduced in hydrogen



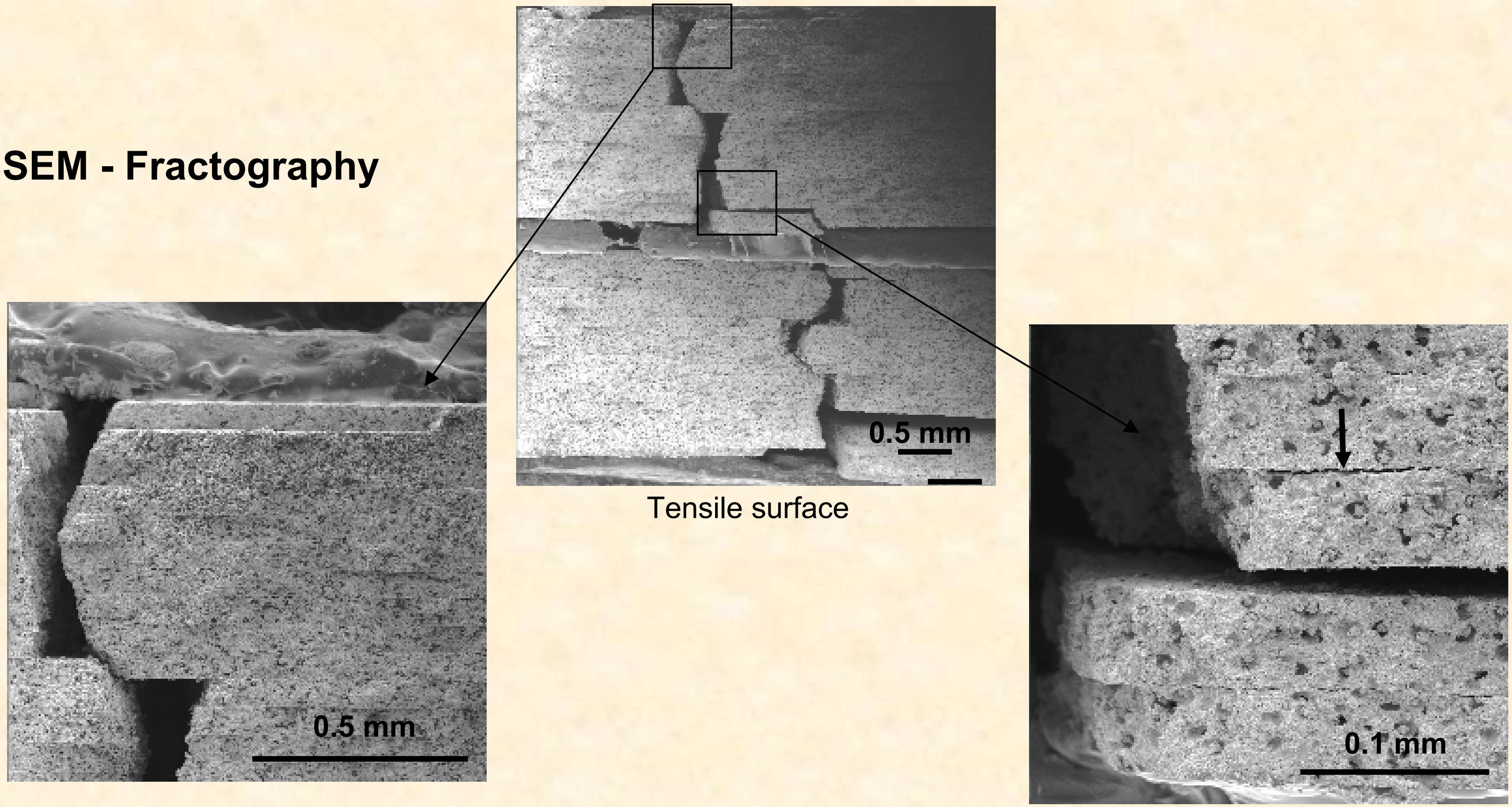
Fracture Surface



Characterization of Anode Materials

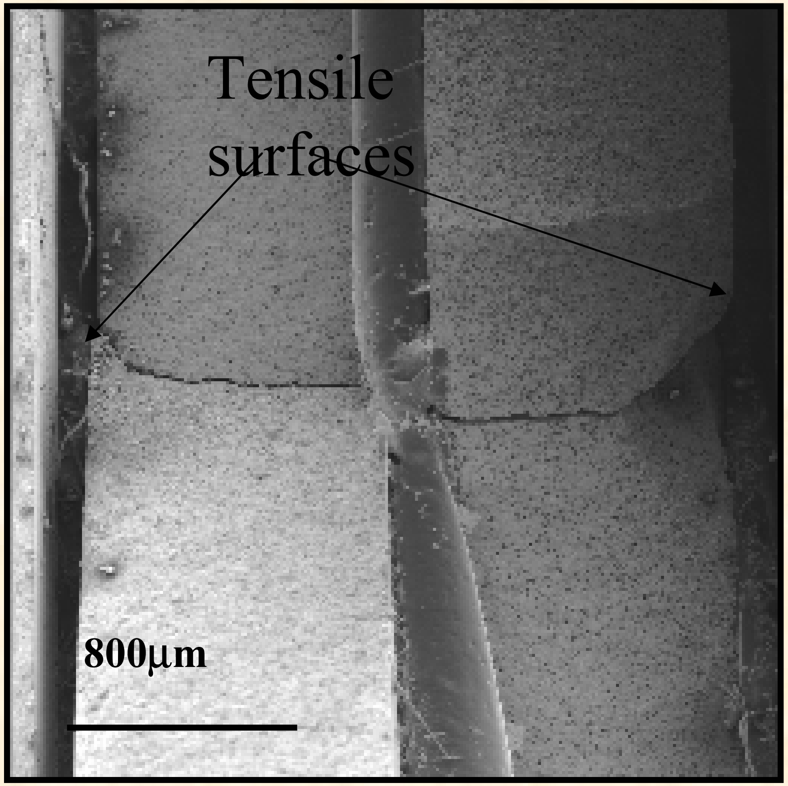
NiO/8mol% YSZ Cermet– NexTech
reduced in hydrogen

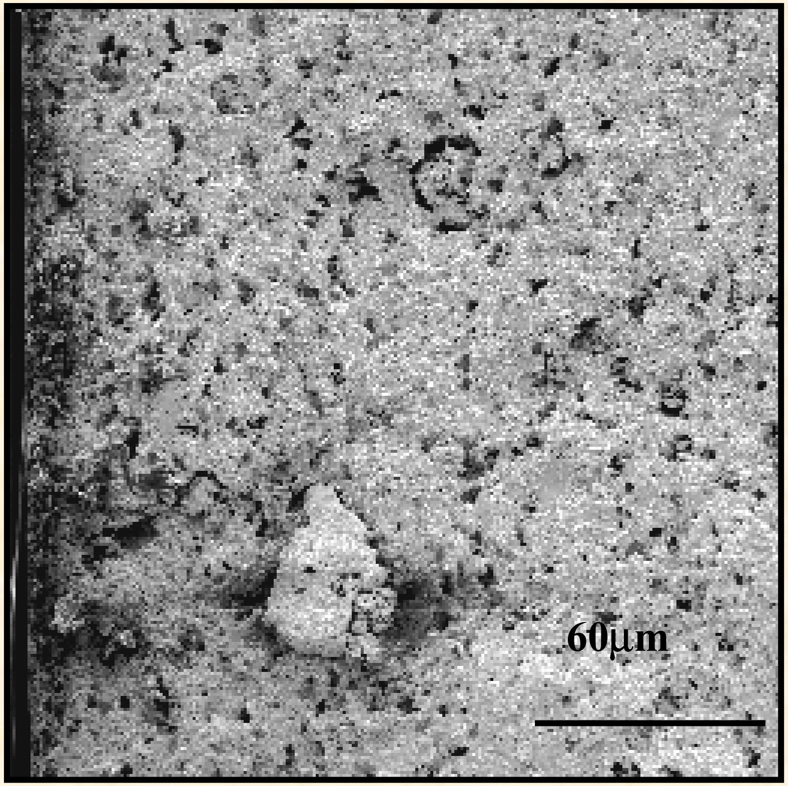
SEM - Fractography



Characterization of Anode Materials

reduced NiO/YSZ Cermet– ORNL (4 layers; 1 mm thick) – 30% porosity





Characterization of Cathode Materials

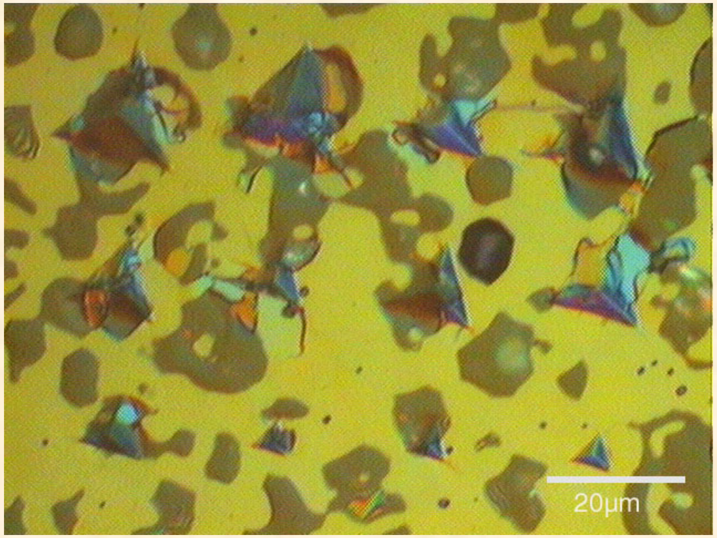
Characterization of Cathode Materials

LSM – NexTech (multilayer, 1mm thick), reduced in hydrogen

Elastic properties at Room Temperature:

Nanoindentation

NexTech	Displ., nm	Load, mN	E, GPa	H, GPa
surface	2300	155	47±5	1.31±0.4
	1700	103	52±8	1.5±0.3
Cross section	2800	156	48±19	1.4±1.6
	1600	103	59±14	2.3±1.4



Characterization of Cathode Materials

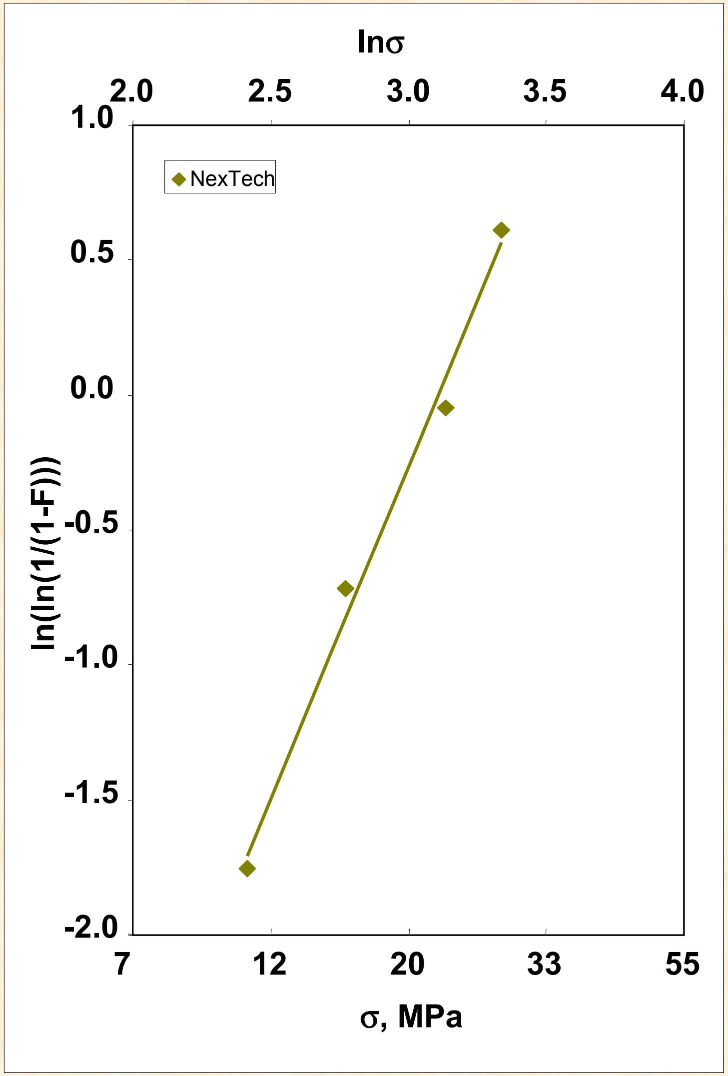
Biaxial Strength at Room Temperature:

σ_{ave} =19.6±5.7 MPa

Weibull distribution analysis

Weibull strength: σ_o= 22.4 MPa

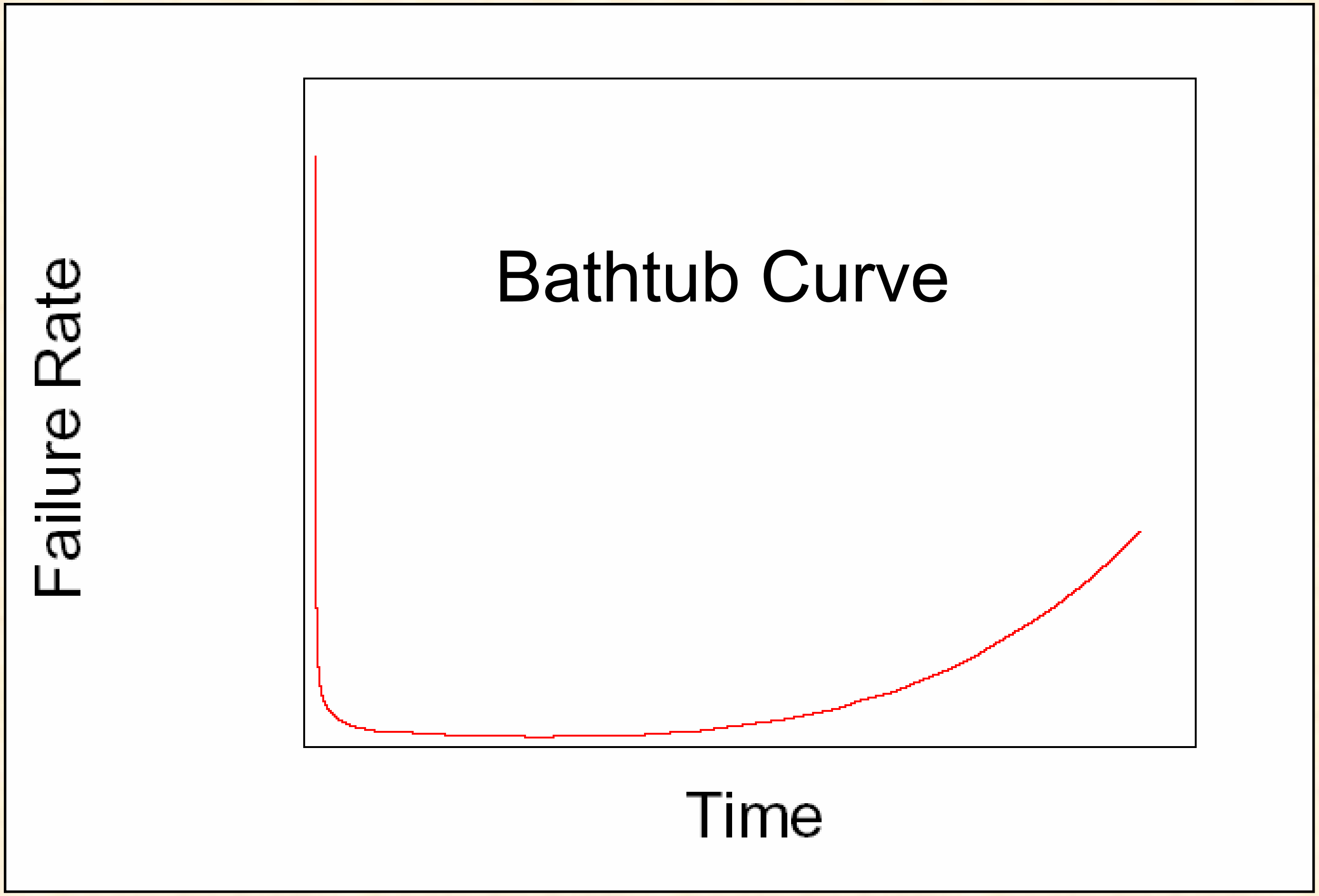
Weibull modulus: m=2.46



Summary

- NDE techniques (infrared imaging, RUS) have been adapted/used to detect defects (e.g. delamination, voids…) in SOFC materials. Powerful tools for quality control.
- Test methods have been adapted to determine elastic properties, in-plane biaxial strength and fracture toughness of SOFC at RT and elevated temperatures, in air or controlled environments.
- Fractographic analysis were used to identify defects and mechanisms responsible for failure of SOFC materials.
- Methodology can help industrial teams address short term failures to increase reliability of SOFCs. It also constitutes the basis for the evaluation of long-term behavior of these materials.

Summary



Current and Future Work

- Characterization of SOFC materials at high temperatures (strength, fracture toughness, elastic properties) in air/controlled environments.
- Effect of porosity and pore size on elastic properties, strength and fracture toughness.
- Identification of defects and microstructural features responsible for failure.
- Long term reliability, transient, time-dependent phenomena.