# Emerging Applications and Challenges
## in using
# Ceramics at General Electric

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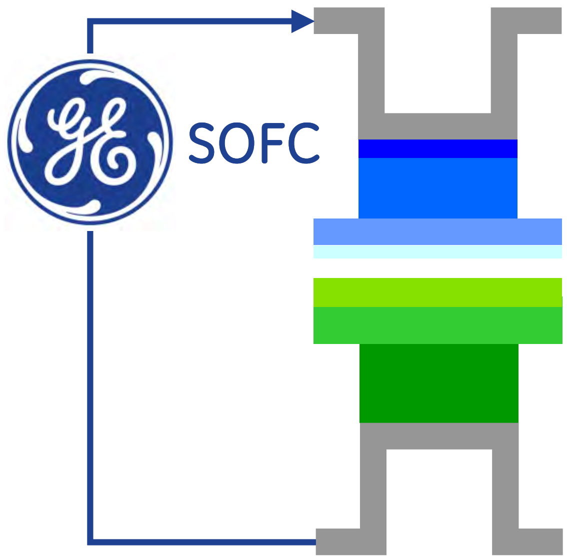
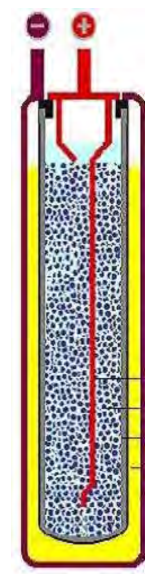
# Ceramics in Emerging Energy Systems

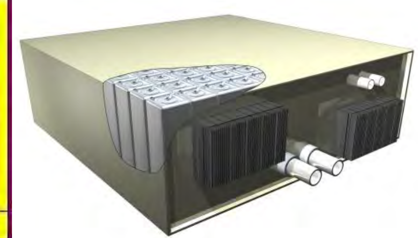
**Gas Turbine**

**SOFC**

**NaMx Battery**





**CMCs**
**Light weight, High Temperature**

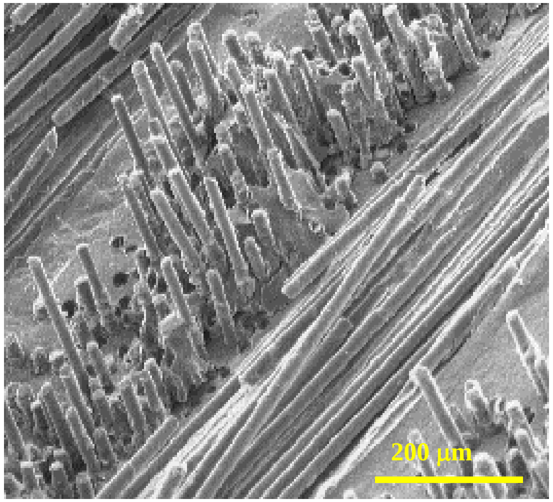
**Solid Electrolyte**
**Oxygen & Sodium Ion Transport**

# Outline

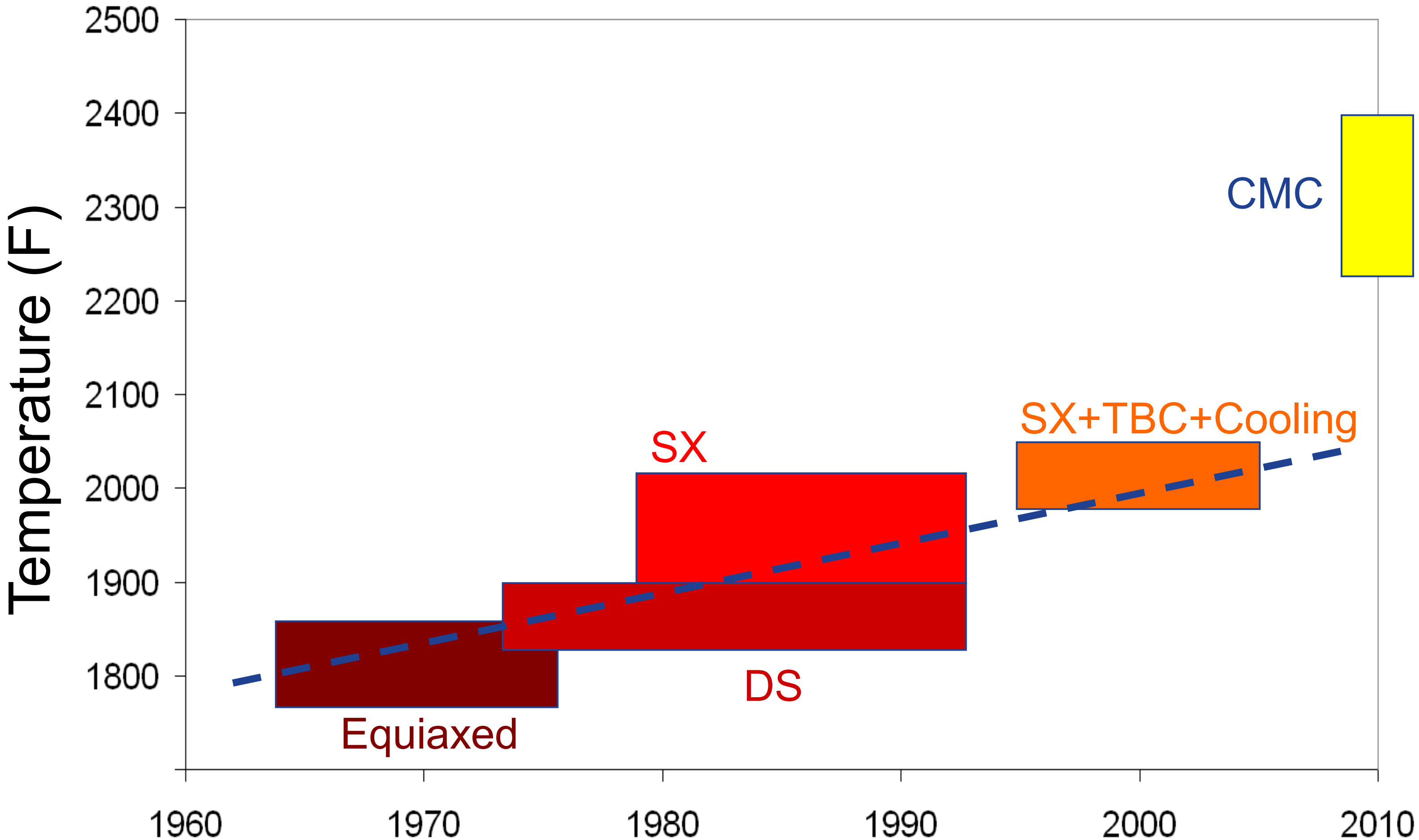
- **Introduction**
  - Ceramic Applications
- **Ceramic Matrix Composites (CMCs)**
- **Solid Oxide Fuel Cells**
- **NaMx Batteries**
- **Summary and Conclusions**

# Ceramic matrix Composites

- What is a CMC?
- SiC/SiC system by Melt Infiltration
- Properties of SiC/SiC composites
- Engine Test Experience
- Commercialization challenges/Barriers
- Summary



# High Temperature Structural Material Capability




CMCs are the only option for significant enhancement of material capability

Delivers significant fuel and pollution reductions

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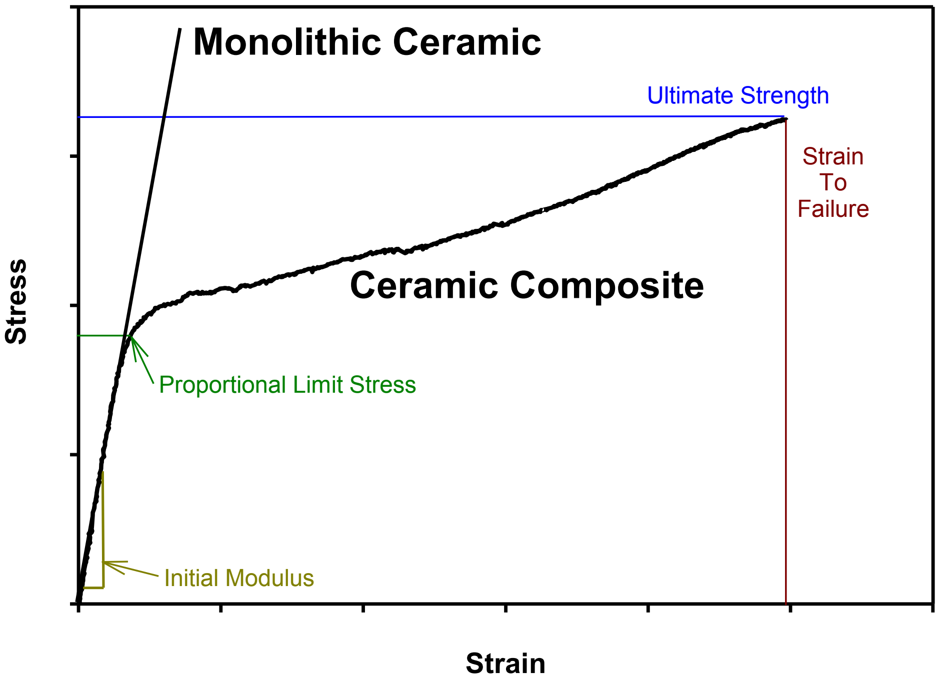
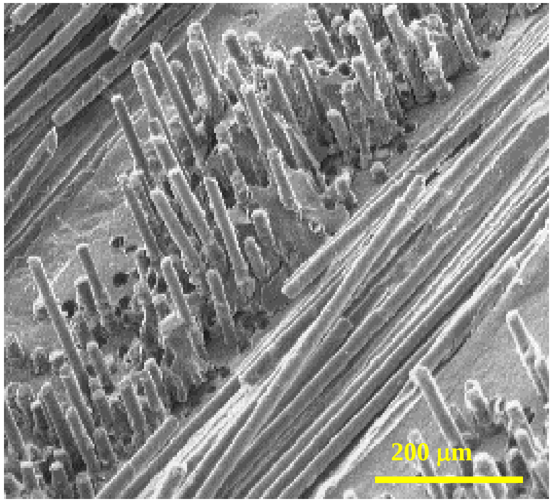
# Pseudo-Toughness from Continuous Fibers




- Toughness, or damage tolerance, is derived from energy dissipated by fiber-matrix debonding and fiber pull-out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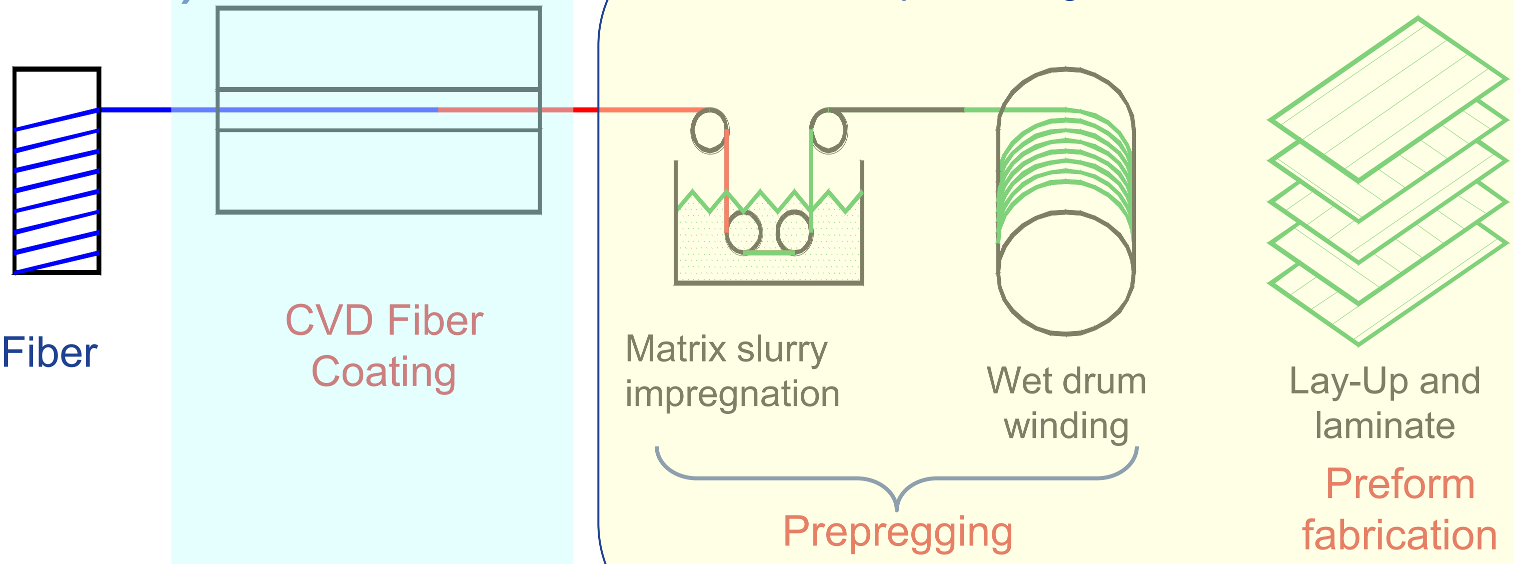
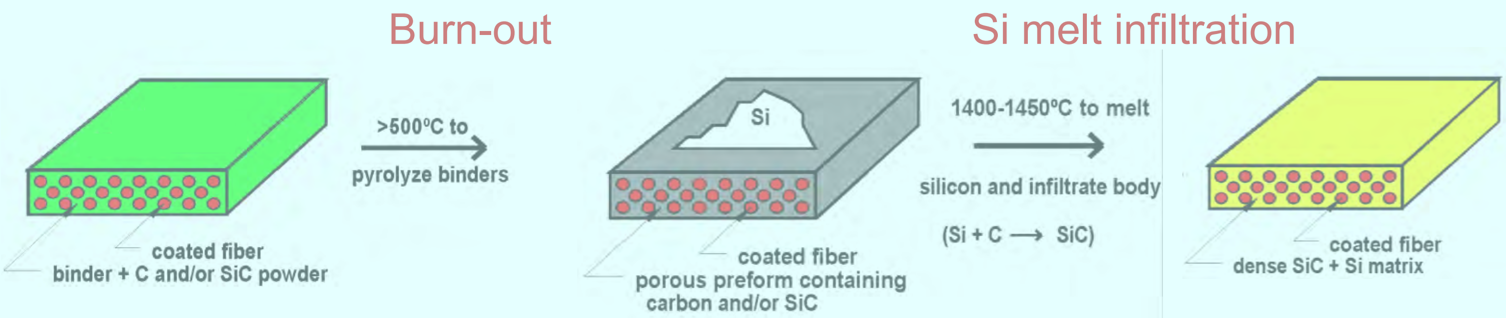
# GE's Melt Infiltrated, Prepreg CMC Process (1990's)




Additional CMC process steps

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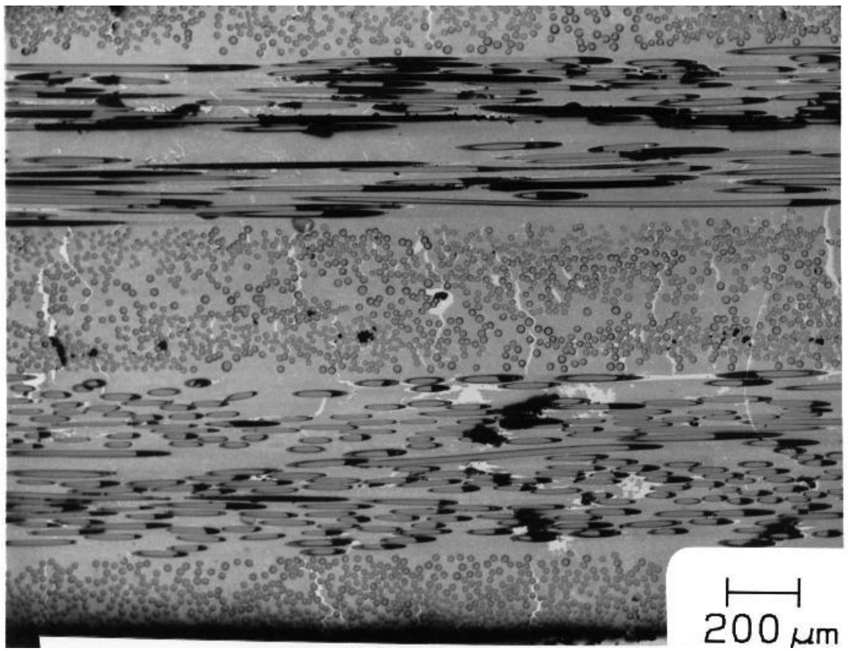
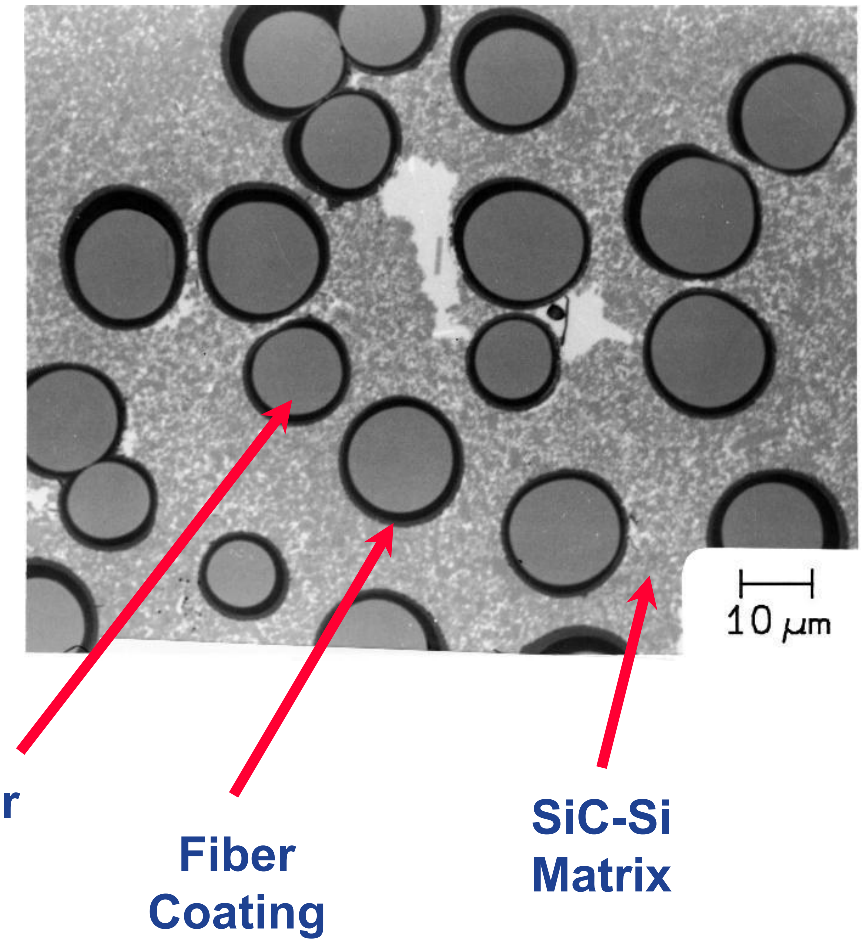
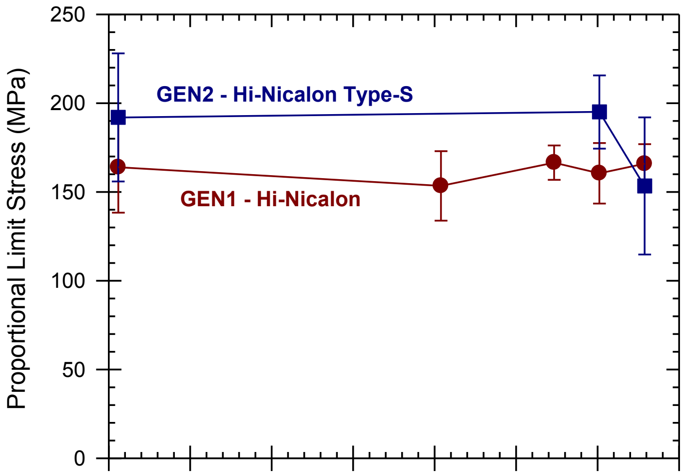
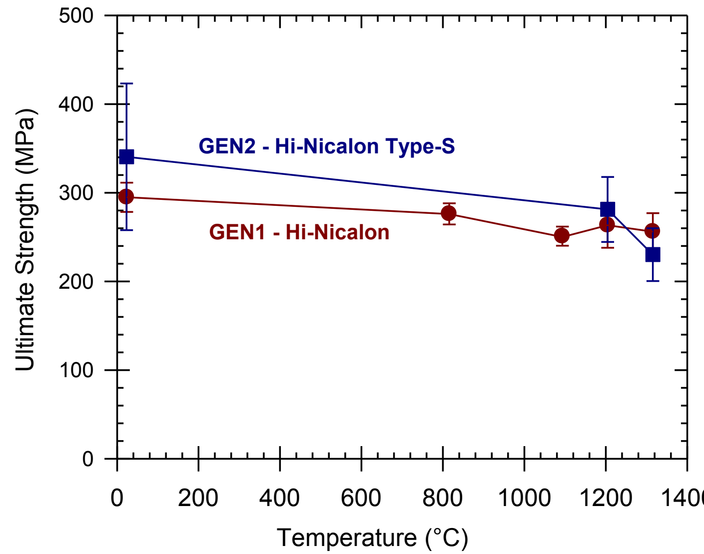
# Microstructure of Prepreg MI Composites

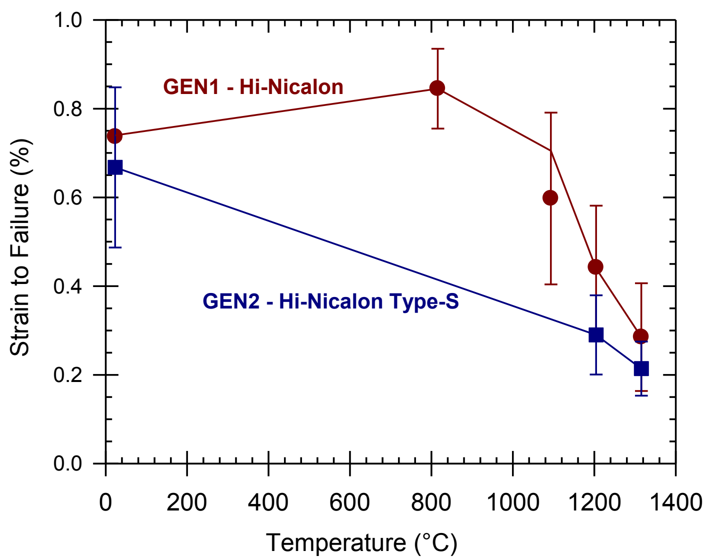



- **Fibers Homogeneously Distributed; Vf = ~25%**
- **Separated Fibers and Fiber Coatings**
- **~1-3% Matrix Porosity**

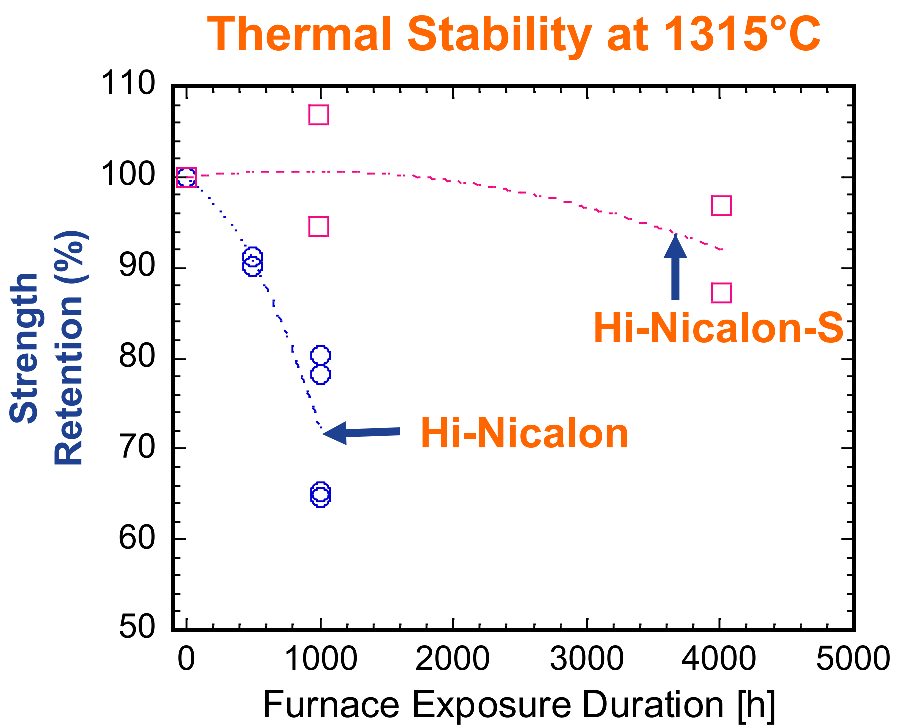


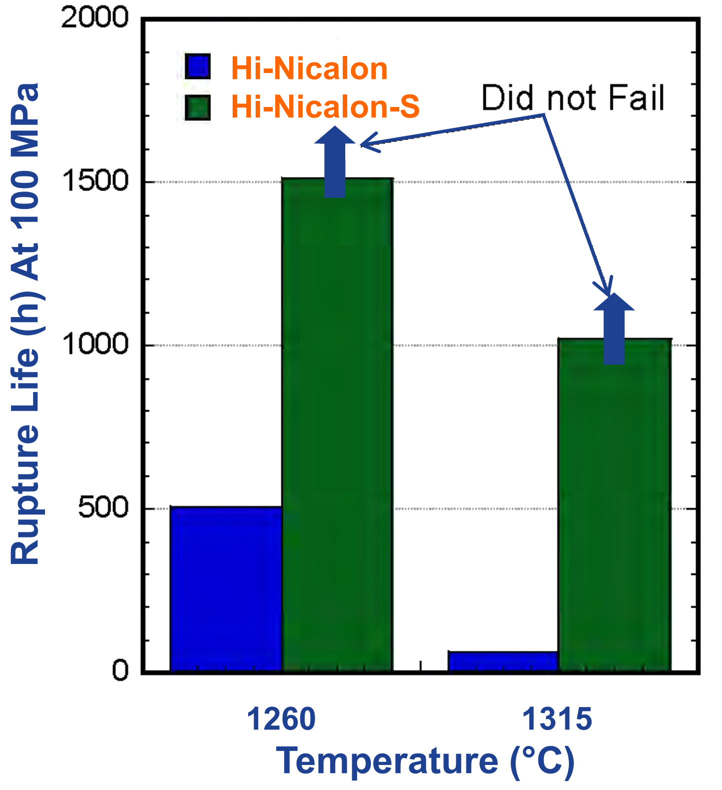




**Excellent Mechanical Properties up to ~1200 C**

# Prepreg MI Composites

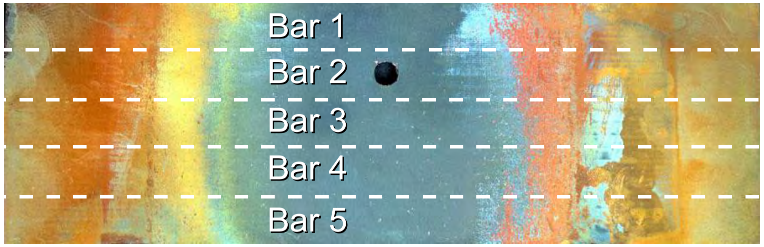


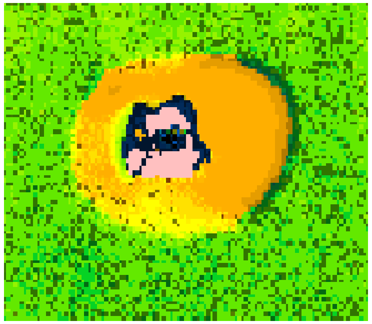



# Foreign Object Damage

- **Use ballistic impact to simulate foreign object damage**
  - 0.175” chrome steel ball bearing at 310m/s (18J)
  - damage localized to impact site
  - impacted sample exposed in shroud rig for 100 hours

**Entrance** **Exit**

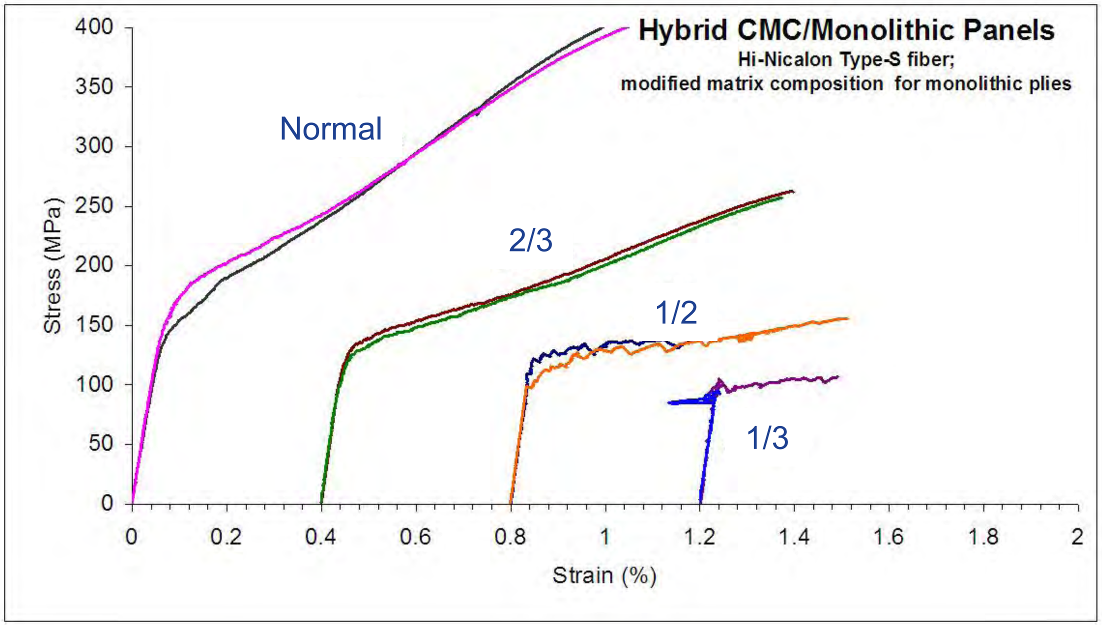


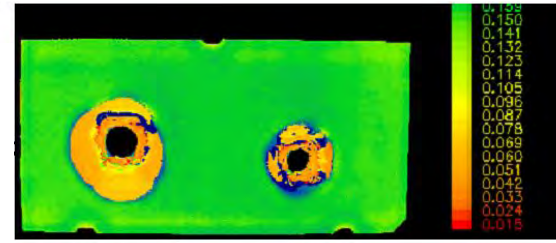
**NDE**

Little or no damage propagation on exposure to high temperatures

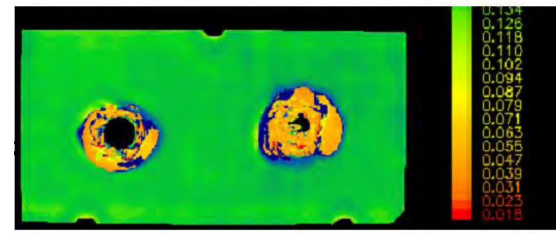
# Fiber Volume Fraction Effect on Damage Tolerance



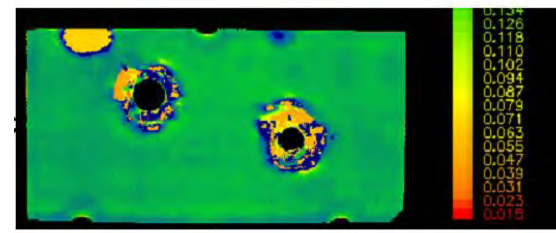

Normal fiber loading



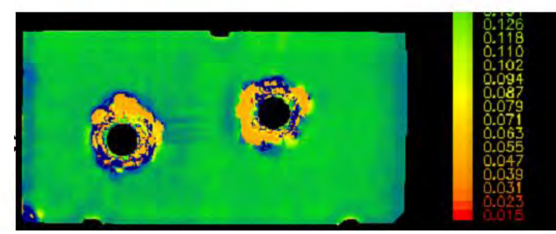
2/3 normal fiber loading



½ normal fiber loading



1/3 normal fiber loading

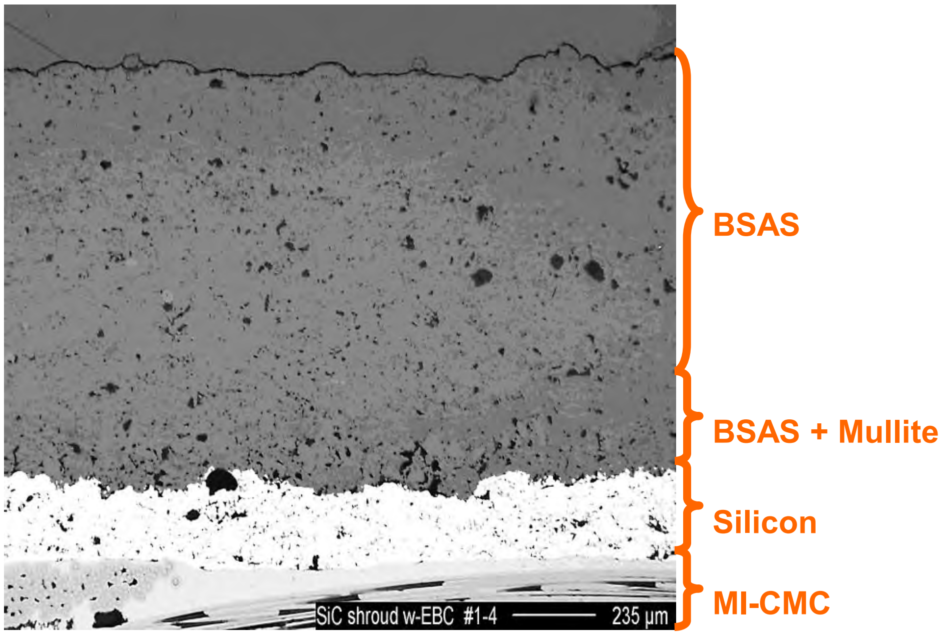


- **Detrimental effect on mechanical properties**
- **No effect on damage tolerance as measured by ballistic impact damage resistance**

# Material System

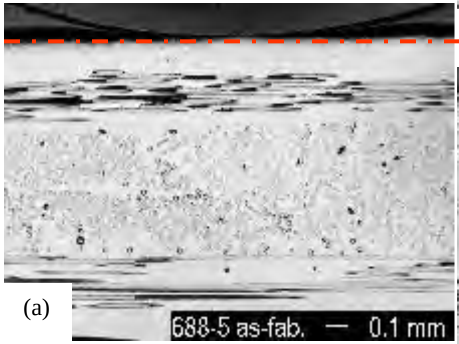
Environmental Barrier Coating (EBC) needed for turbine applications to prevent silica volatilization and surface recession from water vapor in combustion gas

$$SiO_2 + H_2O \rightarrow Si(OH)_x \text{ (gas)}$$

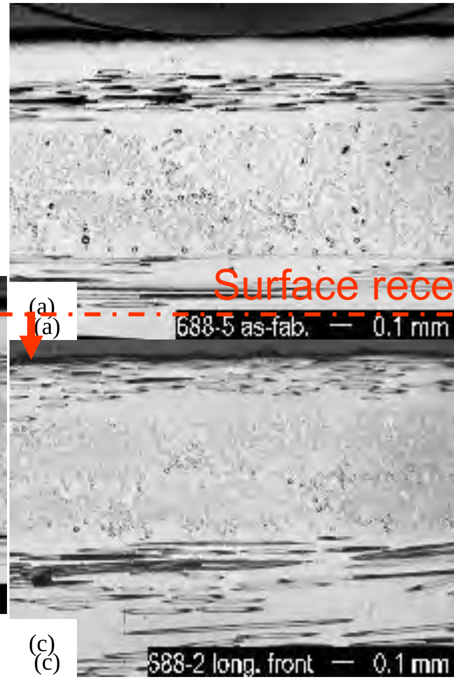



- 3-layer EBC system
- Application by thermal spray techniques
- BSAS – water vapor recession resistance
- BSAS + mullite – transition layer for CTE match
- Silicon – oxidation resistance

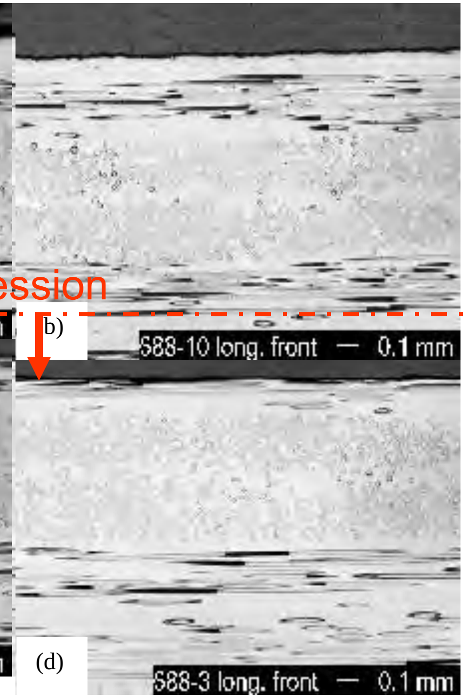
# Long-Term



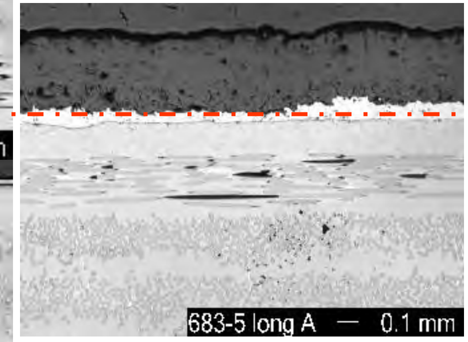

as fabricated




500 hr rig exposure




1000 hr rig exposure



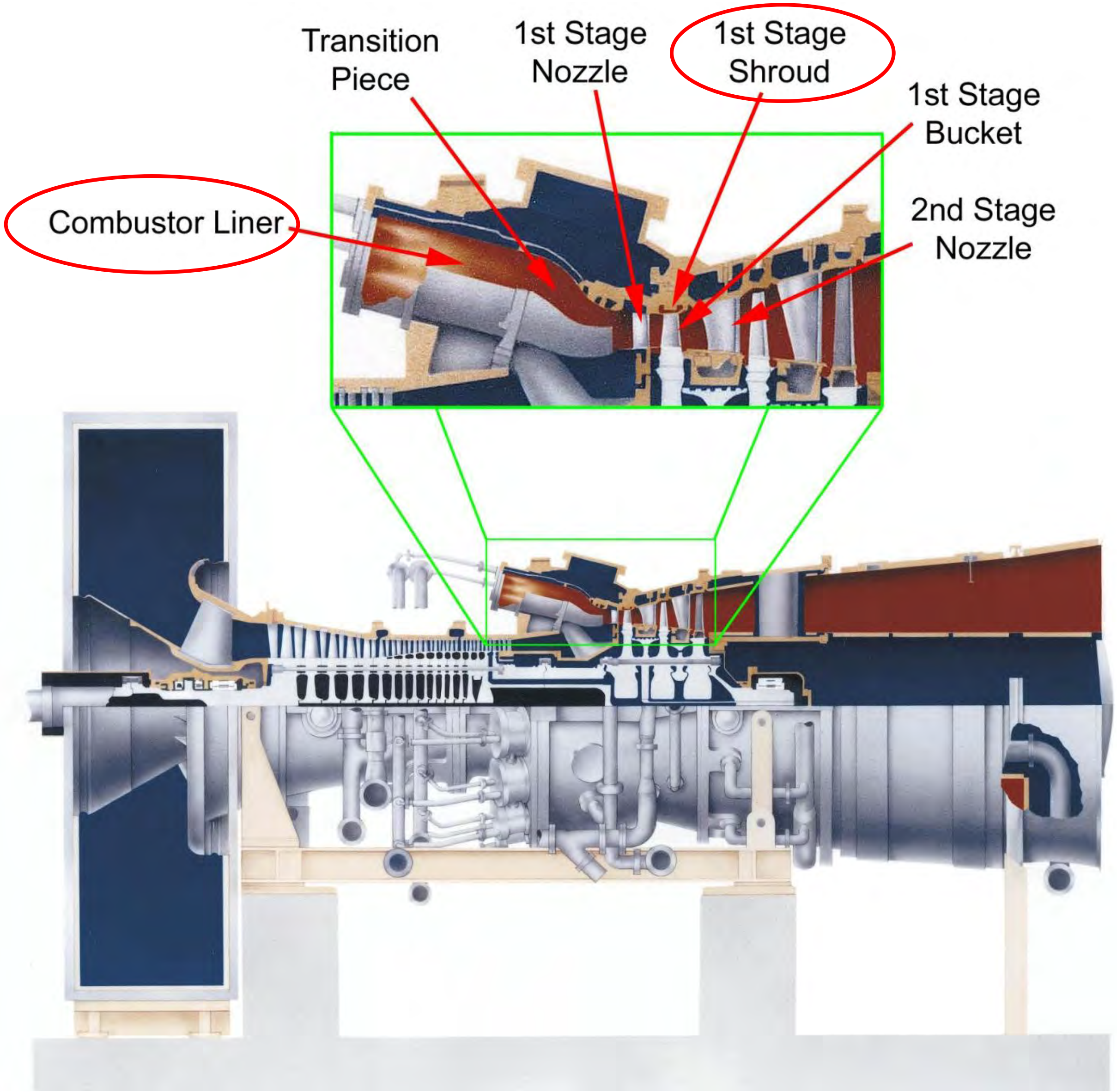

1000 hr rig exposure with EBC

(c) (d)

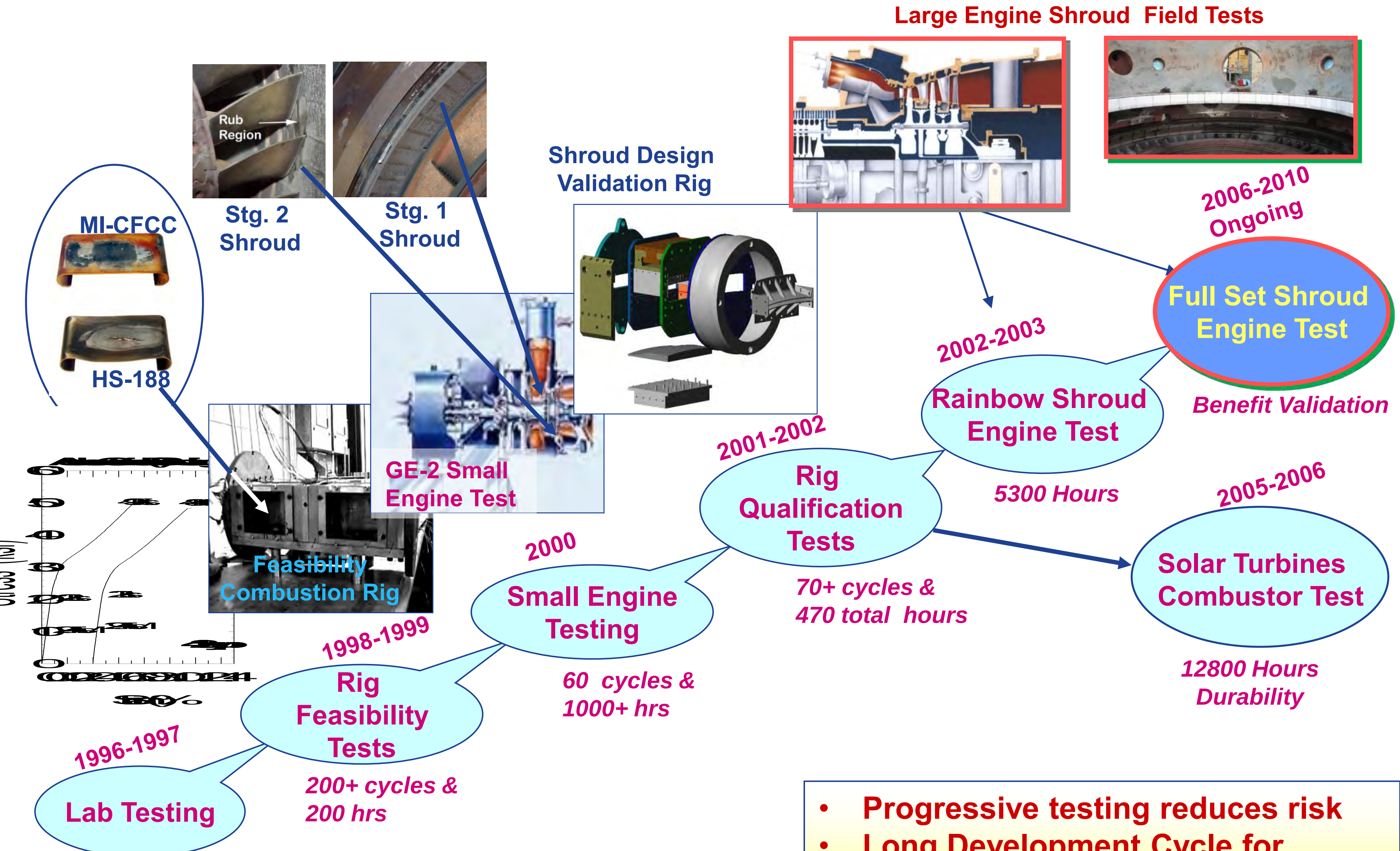
**Prepreg MI composite w/o EBC**
- **damage limited to surface recession**

**Prepreg MI composite with EBC**
- **no surface recession or internal oxidation**

# Industrial Turbine Applications



# CMC Development Path for Gas Turbines*




- Progressive testing reduces risk
- Long Development Cycle for Revolutionary Materials

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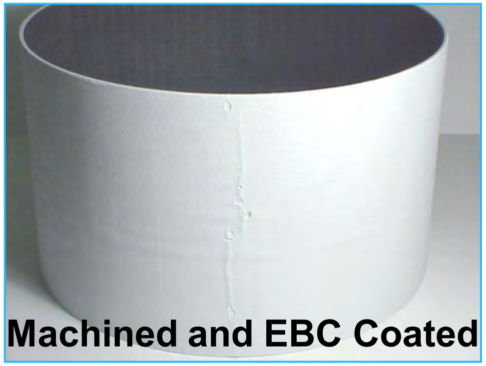
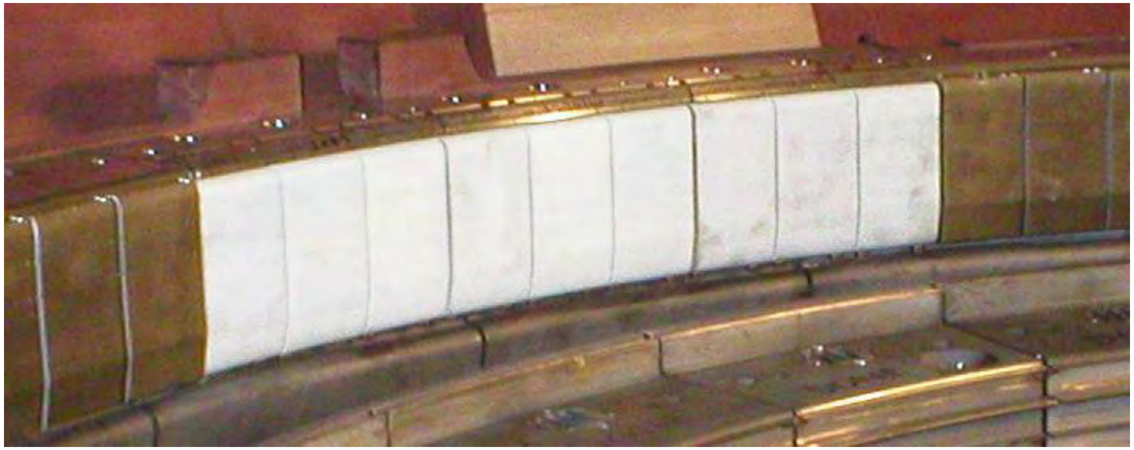
* Work partly funded by U.S. DOE

# Prepreg CMC Combustor Liner in Solar CSGT Engine

- Combustor liner fabricated in late 2004, tested in CSGT engine (modified Solar Centaur 50s, 4MW) at Chevron/Texaco site in Bakersfield, CA from Jan 2005-Nov 2006
  - 12822 hours including 46 start/stop cycles
- CMC survived relatively unharmed despite presence of pre-existing processing defects
- EBC retained over >99% of surface


# 7FA Field Engine Rainbow Test

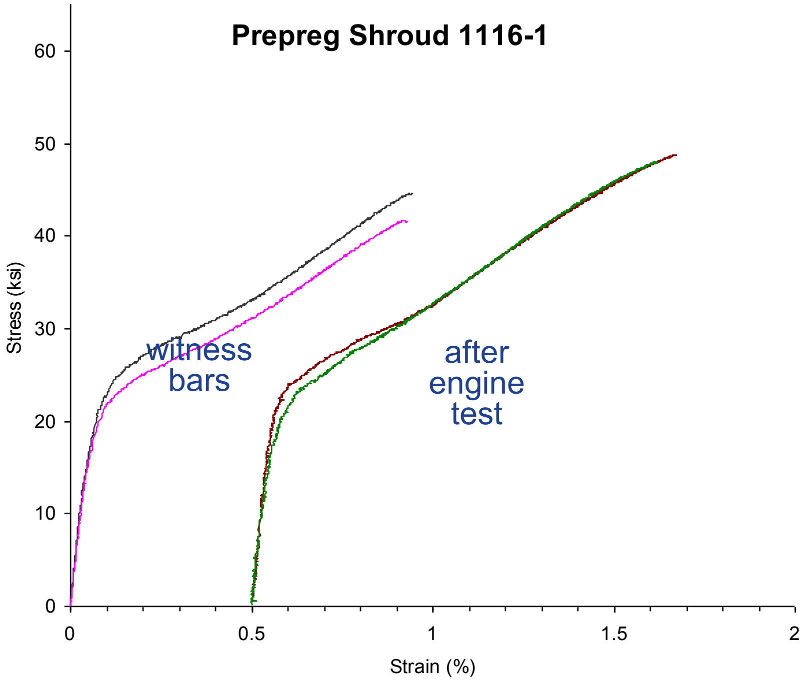



- **Shrouds exposed for 5000+ fired hours and 15+ start/stop cycles with no shroud failures, engine operation issues or instrumentation anomalies**
- **Engine firing temperature range 1232-1288°C on daily cycle**
- **CMC inner shroud maximum surface temperature ran 1200° to 1260°C**

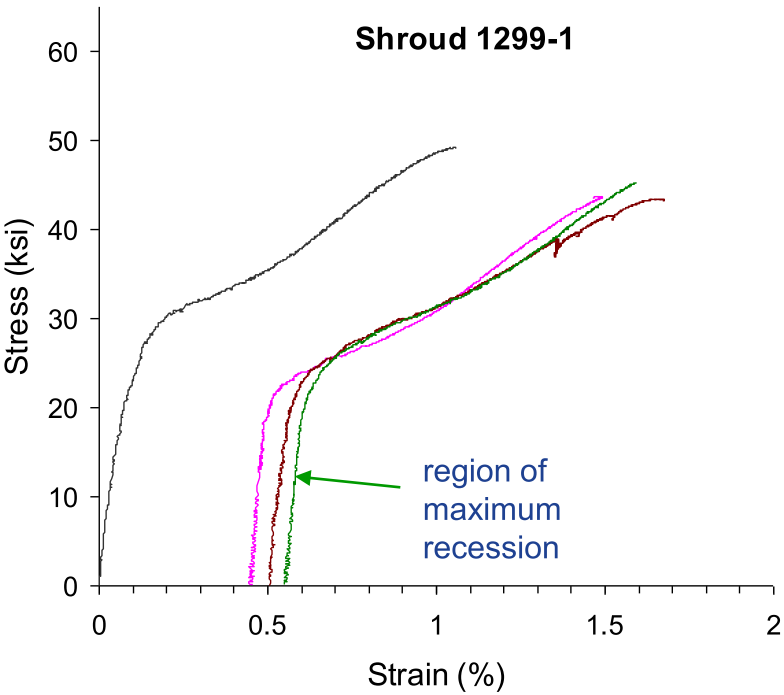
**No shroud failures or performance anomalies**

# Prepreg CMC Shroud Residual Strength

**Prepreg Shroud**
without EBC spallation



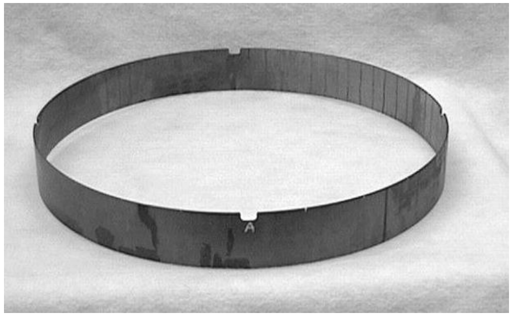

**Prepreg Shroud**
with EBC spallation



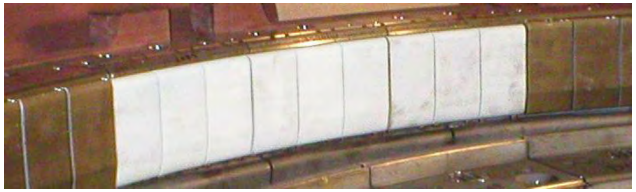

**No degradation in mechanical properties**

# Nearly 20,000 hours of Field Experience with Shrouds & Combustor Liners

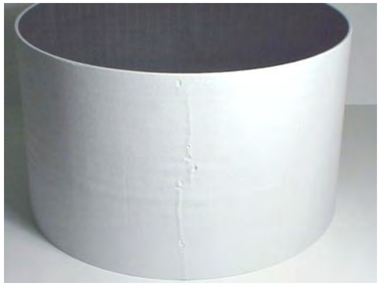
**47cm CMC Second Stage Shroud Ring**
**1000 hrs**
**2 MW Machine (2000)**



**~8 cm x 15 cm first stage shrouds**
**160 MW machine**
**5366hrs, 14 cycles**
**2002-2003**



**~30 cm dia x 27 cm length**
**Combustor liner**
**12,855hrs, 45 cycles**
**Solar 10 MW gas turbine**
**2005-2006**

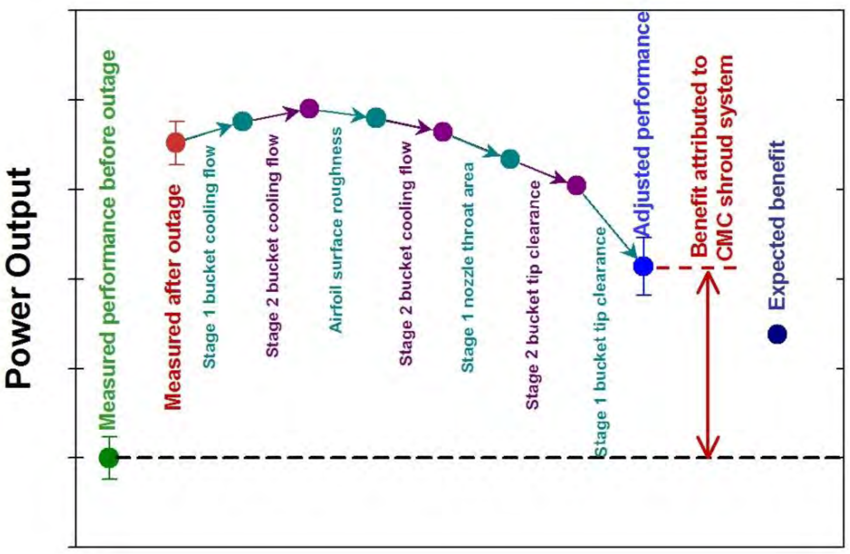


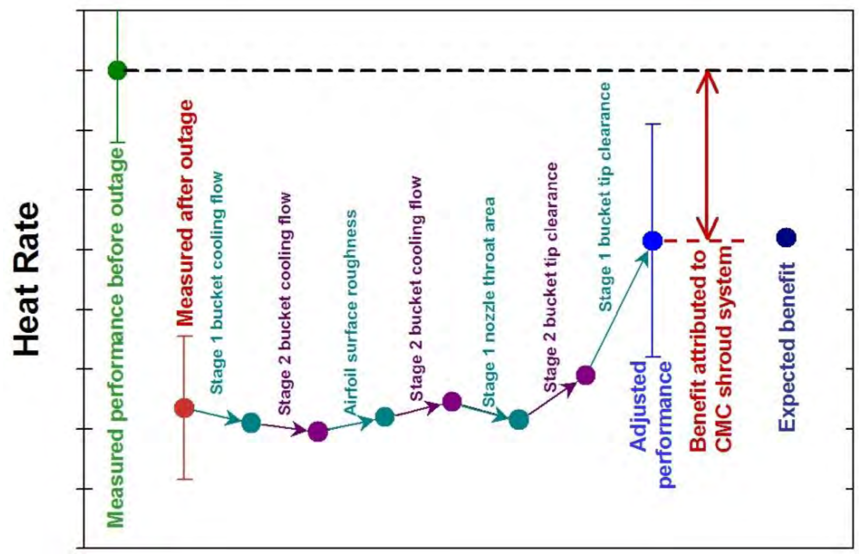
**~8 cm x 15 cm first stage shrouds**
**96 per full set - 160 MW machine**

>1900 hrs, 342 starts
*2006- Continuing*
*JEA, Florida*

>2000 hrs, 15 starts
*2011- Continuing*

# Turbine Performance Benefit Verified




**Measured benefits attributed to the CMC shrouds exceeded the expectation for increase in power output and met expectations for reduction in heat rate (increase in efficiency)**

# Publicly Announced CMC Components

GE-Rolls Royce F136 engine for the Joint Strike Fighter

GE F414 engine for F/A-18E/F Super Hornet

GE LEAP-X for narrow body aircraft

# Commercialization Challenges

## Design of Components

- Adequate attachment compliance to account for thermal expansion mismatch
- Adequate part sealing to realize cooling air flow and leakage goals

## Life of MI-CMC Components

- Industrial applications require tens of thousands of hours
- Damage propagation after initial damage
- Requires minimization of processing defects in components

## Coating Life

- Required minimum of 24,000 hours
- Damage propagation after FOD or otherwise localized damage

## Component Cost

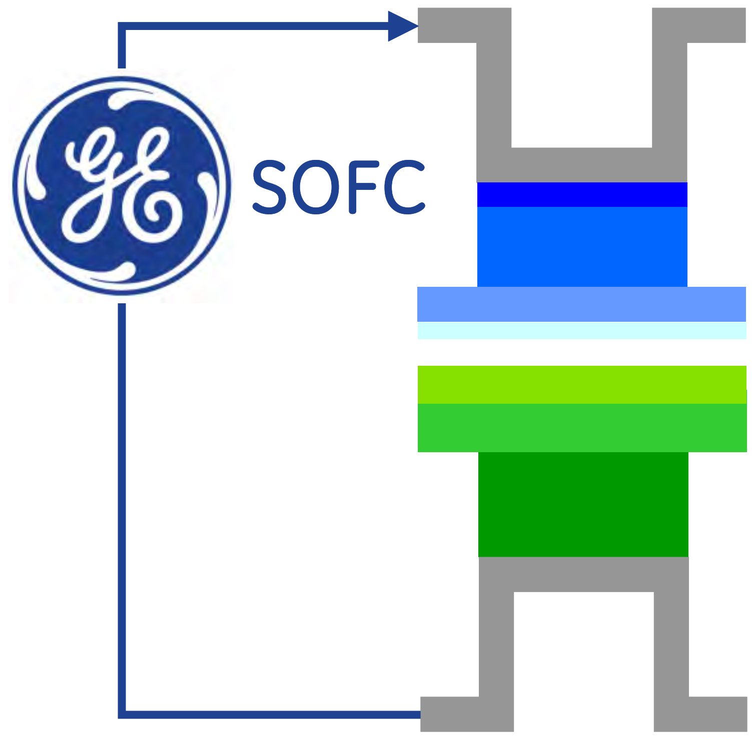
- Target is 1 - 2 times the metallic component cost

# CMC Summary

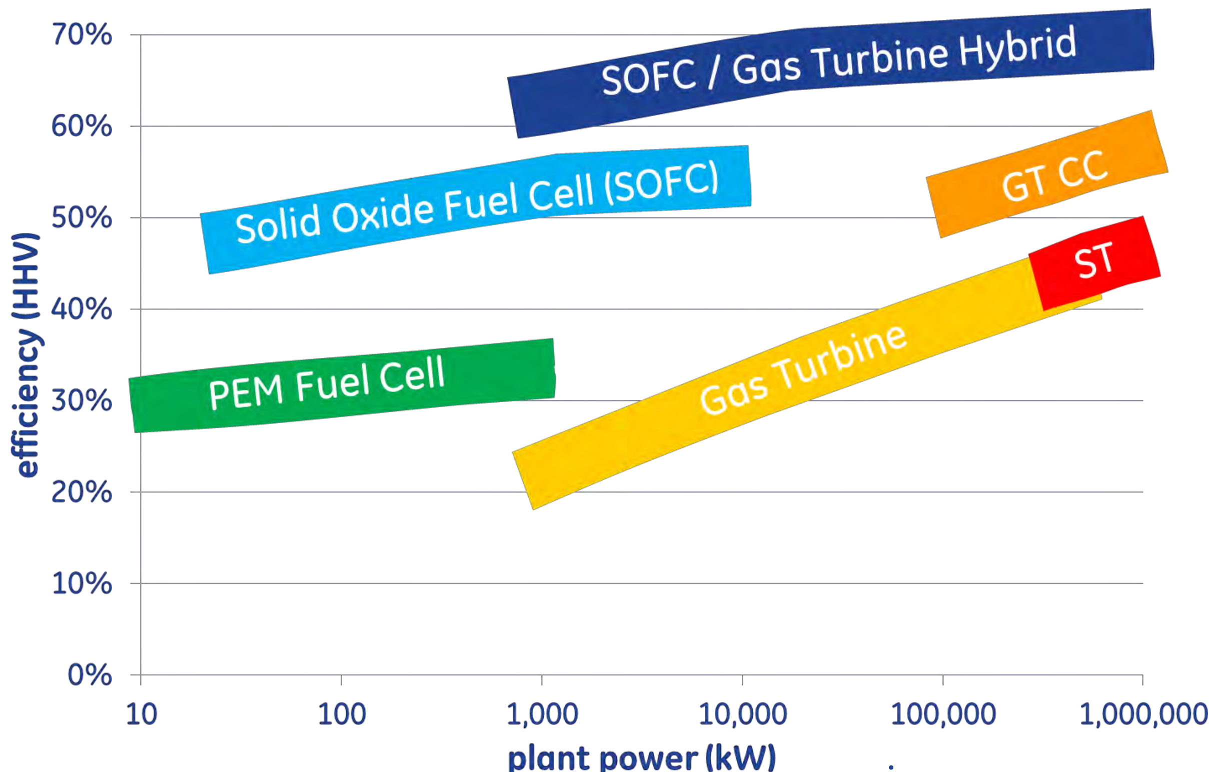
- Melt Infiltrated SiC/SiC composites (HiPerComp®) are attractive for high temperature applications in industrial gas turbines & aircraft engines
  - Low matrix porosity: high thermal conductivity, high proportional limit, high interlaminar strengths, superior oxidation resistance
- Key Attributes
  - Light weight & high temperature capability make them attractive for hot stage components of gas turbines
- Several successful field engine tests
  - Small engine shroud for >1,000 hours
  - Small engine combustor for >12,000 hours
  - Large engine partial shroud set for >5,000 hours
  - Large engine full shroud set for >1,100 hours and >800 hours continuing
- Remaining hurdles to commercialization include CMC material cost and demonstration of full component life

# SOFCs

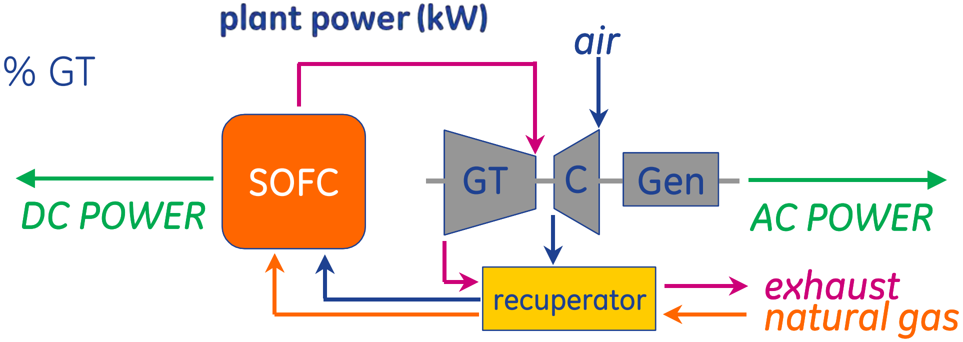
- Benefits/system
- Challenges
- Status



# Why SOFC?




Power: 80% SOFC / 20% GT
<1ppm NOx, SOx




High efficiency power generation

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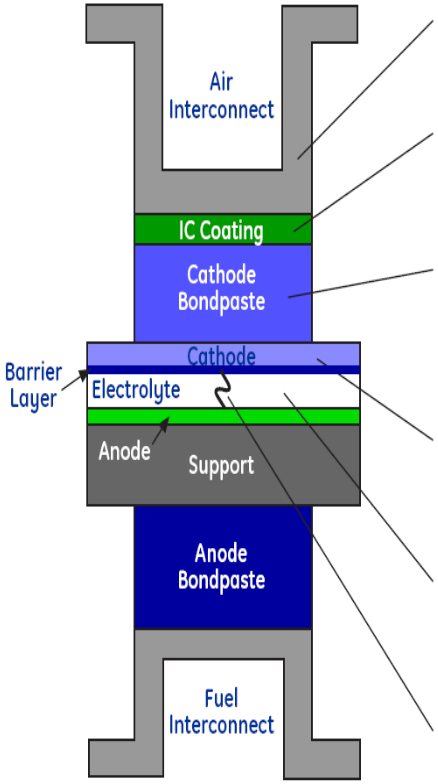
# Anode Supported Solid Oxide Fuel Cell




| | Layer | Function | Material | Thickness |
|---|---|---|---|---|
| Air Side | Interconnect | Gas & Electron Transport | Ferritic Stainless Steel | 500 µm |
| | Protective Coating | Prevent interconnect Cr from poisoning cathode | $(Mn,Co)_3O_4$ | 10 µm |
| | Cathode Contact Paste | Electrically connect cell with air interconnect | $(La,Sr)CoO_3$ | 100 µm |
| | Cathode | Air electrode | $(La,Sr)(Co,Fe)O_3$ | 40 µm |
| | Barrier Layer | Prevent cathode Sr from reacting with electrolyte Zr | GDC $(Ce_{0.8}Gd_{0.2})O_2$ | 10 µm |
| | Electrolyte | Permit $O^{2-}$ transport, prevent air/fuel mixing | YSZ $(ZrO_2 + 8 \text{ mol } Y_2O_3)$ | 10 µm |
| Fuel Side | Functional Anode | Fuel electrode | NiO/YSZ | 20 µm |
| | Anode Support | Mechanically supports Anode & Electrolyte | NiO/YSZ | 200 µm |
| | Anode Contact Paste | Electrically connect cell with fuel interconnect | NiO | 100 µm |
| | Interconnect | Gas & Electron Transport | Ferritic Stainless Steel | 500 µm |

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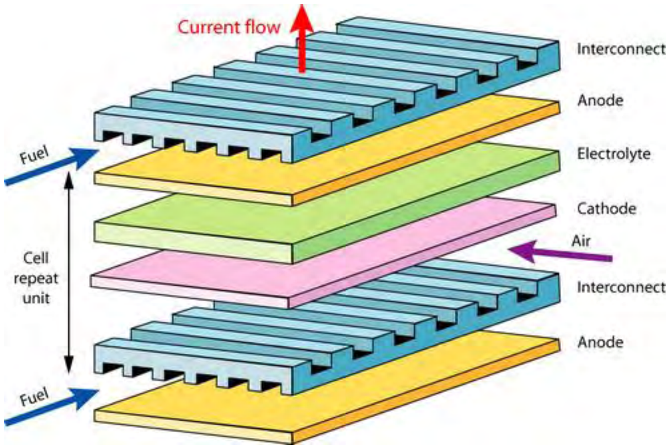
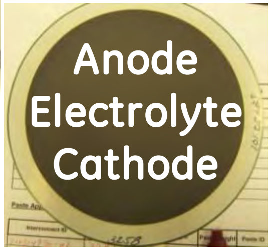
# Solid Oxide Fuel Cells at GE




Planar SOFC

Anode
flow field




Cell operates at ~0.8V (DC)

Stack series of cells sum voltage



SOFC 5kW
Prototype

System stacks in parallel

# Commercialization Challenges

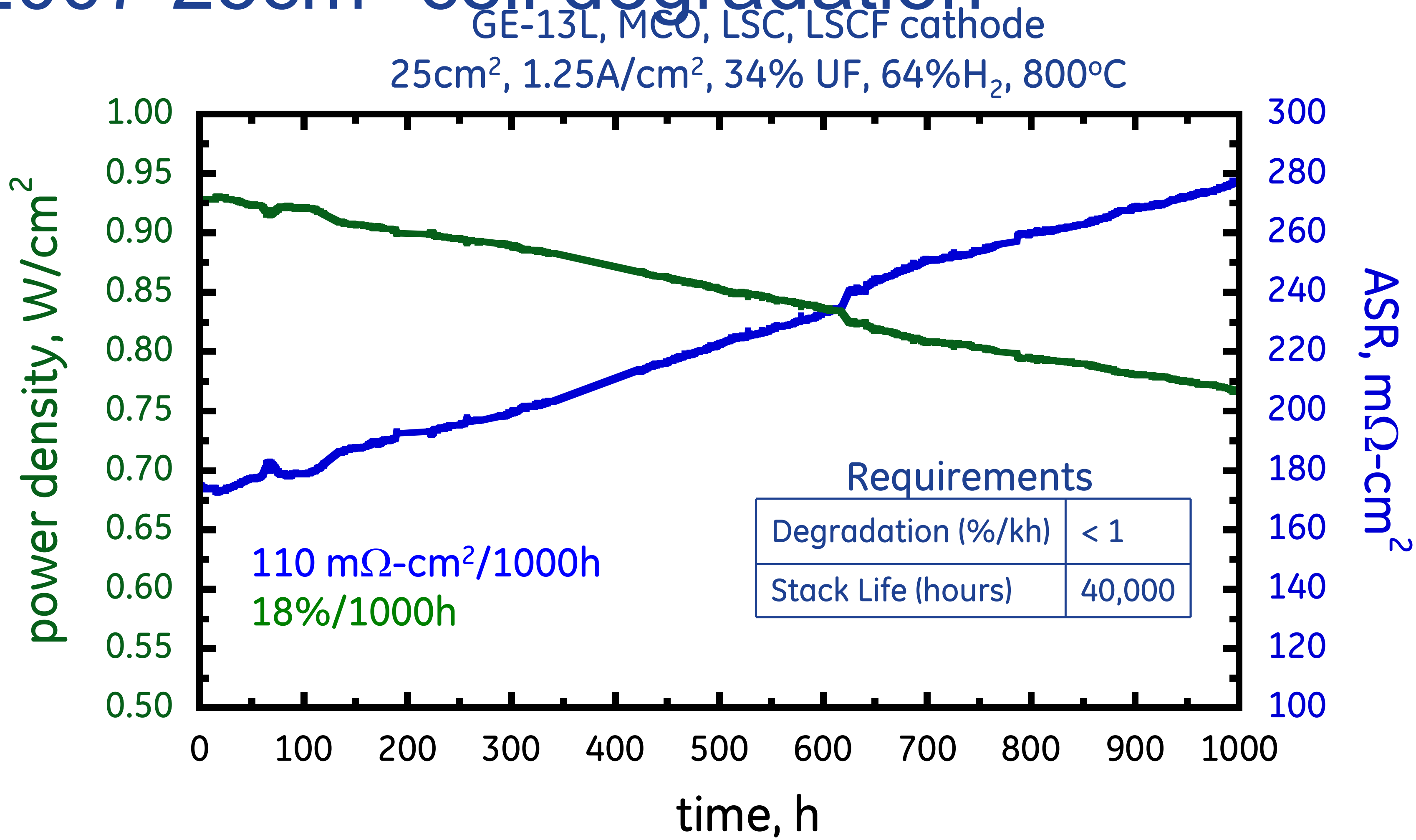
**Key Requirements**

- Life: >40,000 hrs
- Cost: Cost of Electricity (COE) at par with existing Power Generation systems (<10 cents per KWH)

**Approach**

- Life
  - Limited by Materials Issues (Chemical and structural)
- Cost
  - Installed Cost
    - Low Cost Materials (Innerconnect alloy, rare earths, …)
    - High performance materials set (Increased power density)
    - Low Cost Manufacturing (Thermal spray for processing of electrolyte & electrodes)
    - Operating Cost (Increased system efficiency & Increased life)

# 2007 25cm$^2$ cell degradation




High power density and high degradation rate

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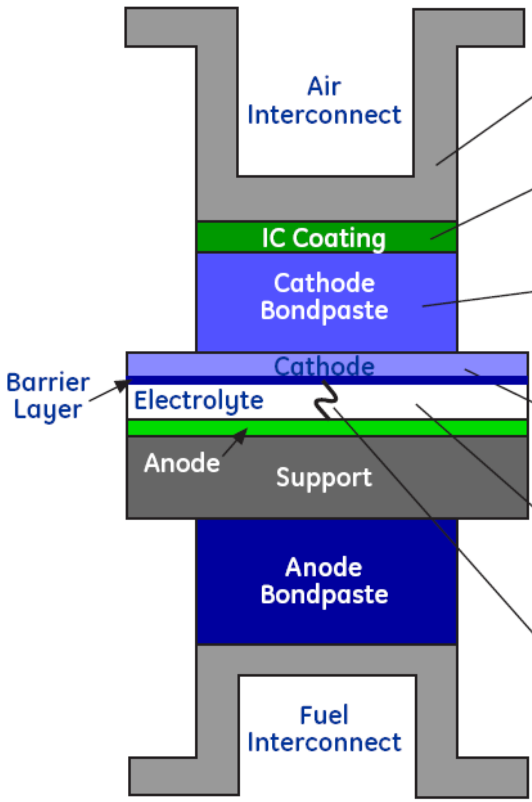
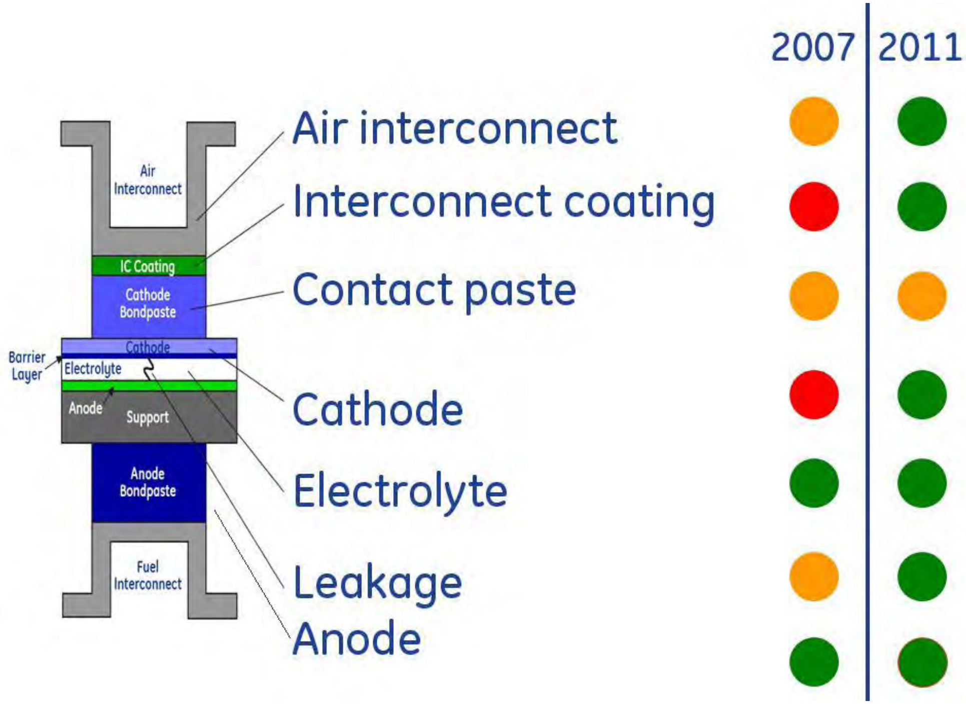
# SOFC degradation - phenomenological approach

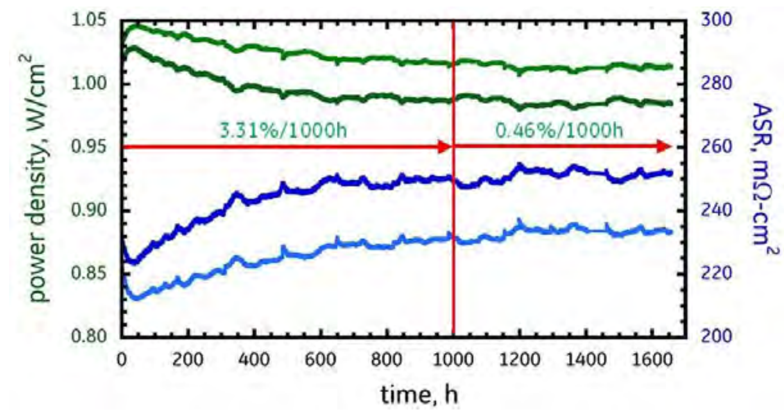



| Mechanism | Type |
|---|---|
| **Air Interconnect** | |
| • *Chromia scale resistance ($Cr_2O_3$)* | *Chemical* |
| • *Insulating scale growth ($SiO_2$)* | *Chemical* |
| **Protective Coating** | |
| • *Coating resistance (MnCo spinel)* | *Chemical* |
| **Cathode Bondpaste/Coating Interface** | |
| • *$SrCrO_4$ layer resistance* | *Chemical* |
| • *$SrMnO_3$ layer resistance* | *Chemical* |
| • *'Other' reaction phase formation* | *Chemical/Structural* |
| • *Mechanical delamination* | *Structural* |
| **Cathode** | |
| • *Chromia poisoning* | *Chemical* |
| • *Coarsening* | *Structural* |
| **Cathode/Electrolyte/ Barrier Layer Interface** | |
| • *Zirconate resistive layer* | *Chemical* |
| • *Cathode poisoning* | *Chemical* |
| • *Delamination* | *Structural* |
| **Leakage-Driven Degradation** | |
| • *Cathode reduction* | *Chemical/Structural* |
| • *Anode oxidation* | *Chemical/Structural* |
| • *Combustion thermal* | *Chemical/Structural* |

With a 'fixed' materials set: Focus on cathode side, high-impact degradation mechanisms

# Degradation reduction




Degradation mechanisms identified and mitigation strategies validated

-Developed interconnect coating
-Stabilized cathode
-Validated low-cost interconnect alloy

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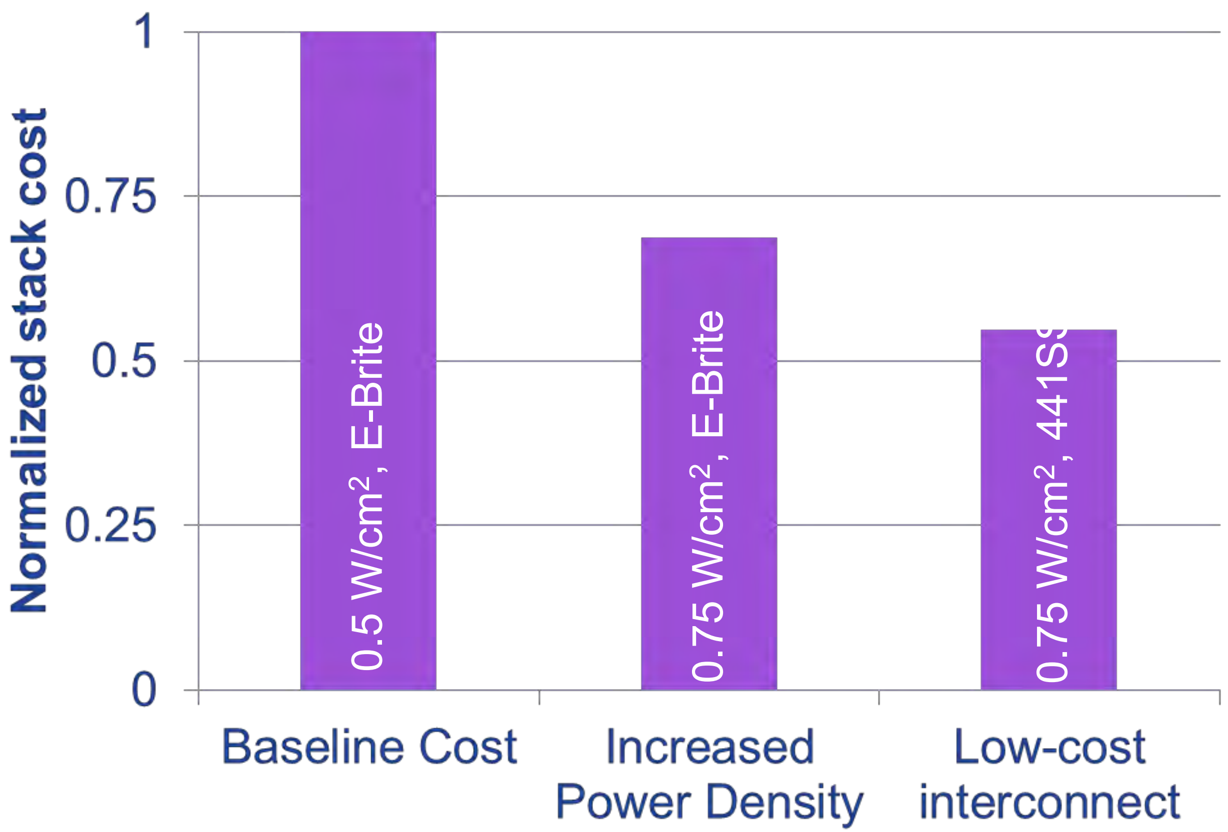
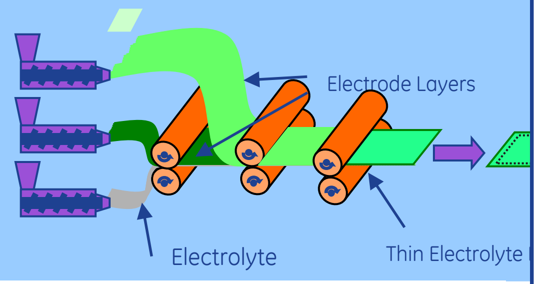
# Cost reduction

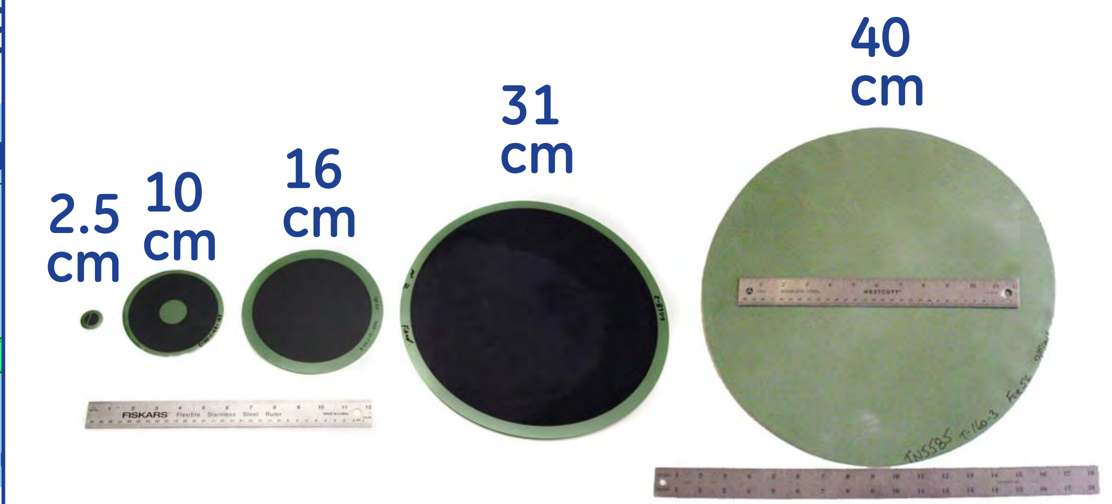


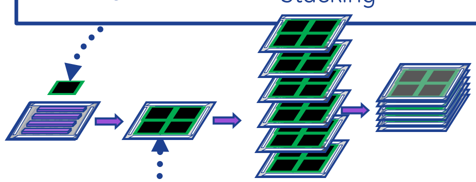

**Increased power density and decreased steel cost lead to significant cost reductions**

# Low-cost manufa

## Sintered Cell Manufactu

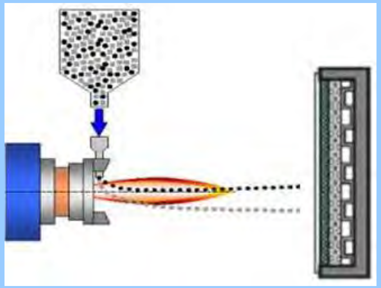



Larger area
Simplified sealing
Low capex

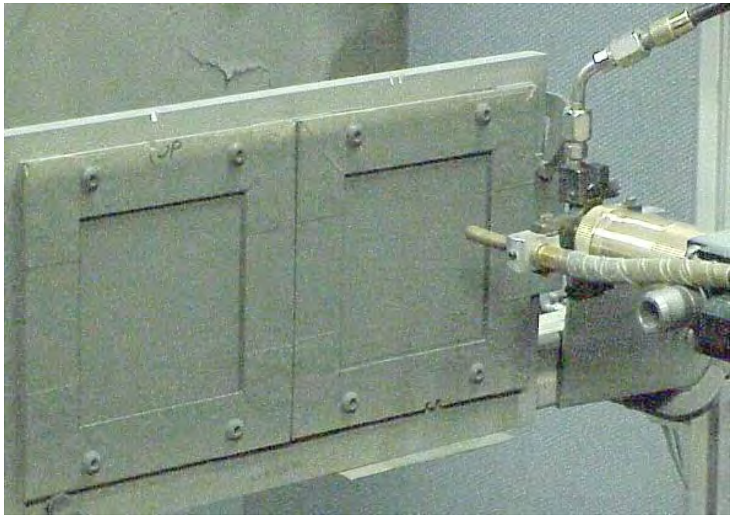
## Thermal Spray

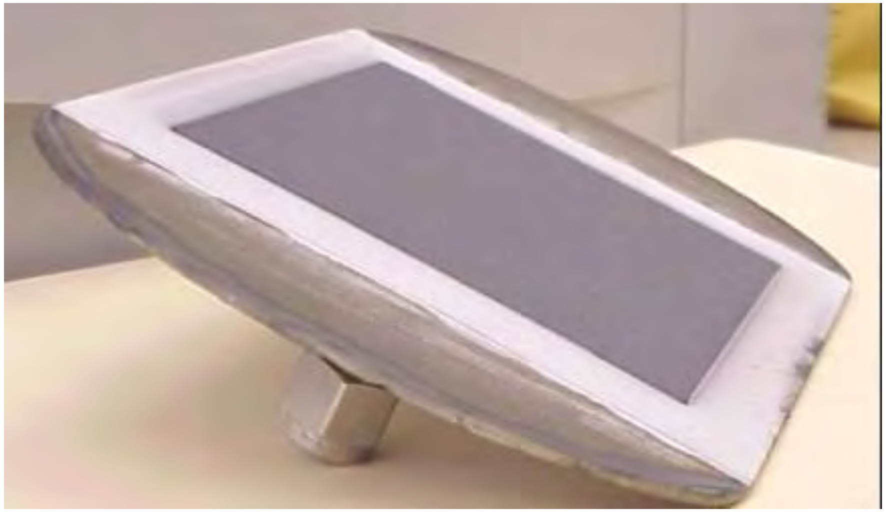


Leverage GE thermal spray expertise

# Deposition Technology Progress

- High throughput, many different structures/ compositions can be easily fabricated
- Cell and stack design tailored to deposition processes
- Performance reaching sintered cell levels
- Scale-up to 4" and 12" cell on-going



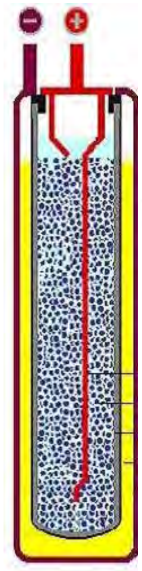


# SOFC Summary

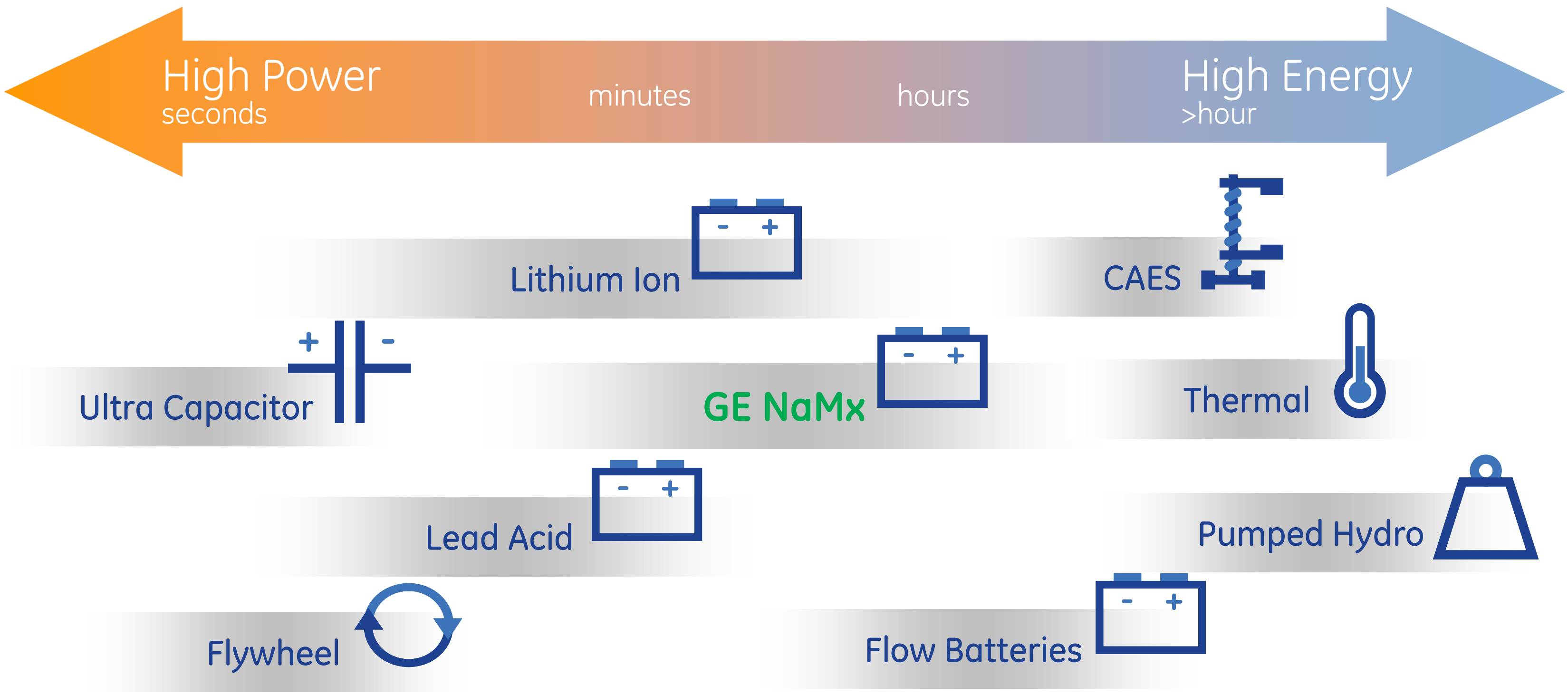
- SOFCs offer opportunities for high efficiency systems
- Significant progress made in past several years
- Life & Cost are key challenges in commercializing SOFCs
  - GE pursuing low cost plasma spraying technique for processing of electrolye for anode supported SOFCs

# NaMx Battery

- Application Space
- Materials Needs



# Power/Energy Spectrum




**Power -** needed to drive at high speeds, Fast charge/discharge
**Energy -** needed to provide range, distance and power over extended periods

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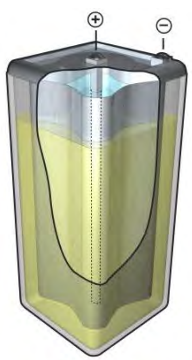
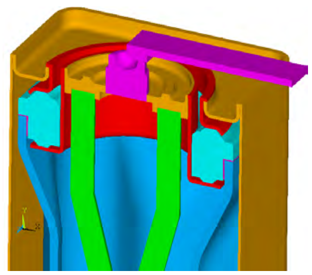
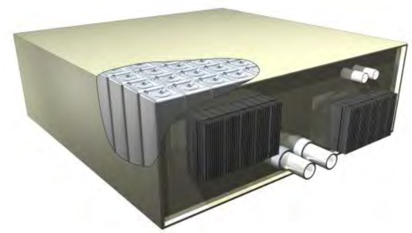
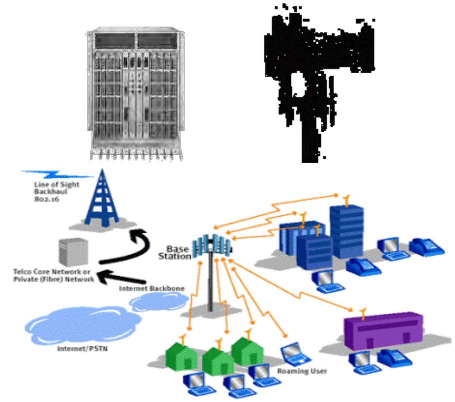
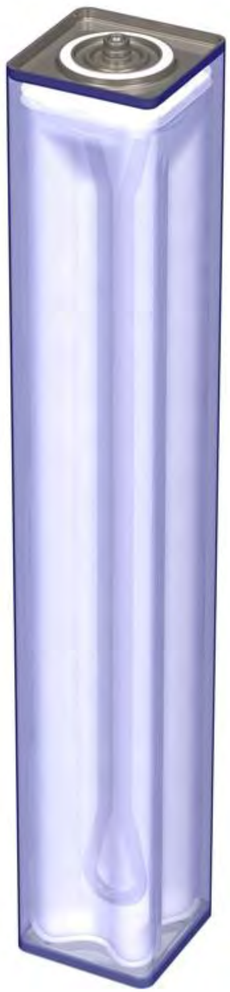
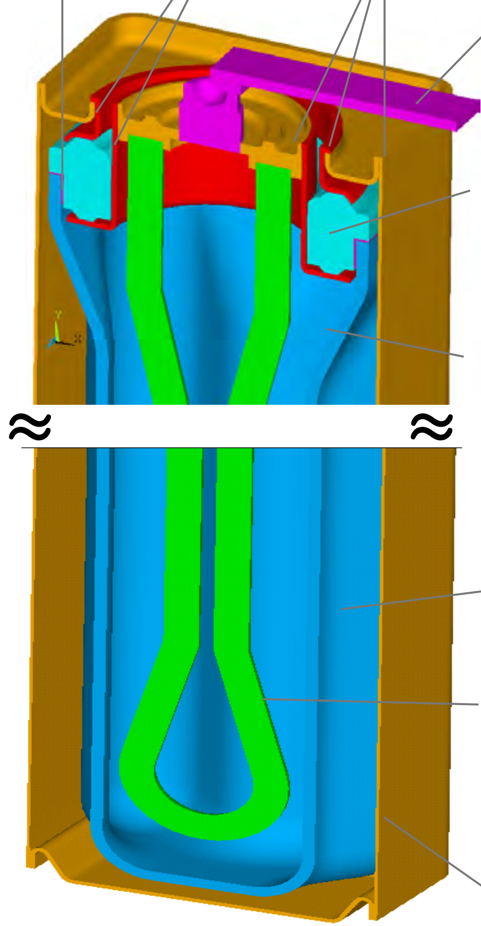
# Technology areas for Na-Metal Halide Batteries

| Chemistry | Materials | Battery pack | System Integration |
|---|---|---|---|
|  |  |  |  |
| • Cathode chemistry<br>• Performance maintenance<br>• Modeling/diagnostics | • Beta''-alumina<br>• Sealing materials<br>• Joining processes<br>• Corrosion | • Thermal management<br>• Vibration hardening<br>• Packaging materials<br>• FE modeling | • Control<br>• System optimization |

**Key drivers/tradeoffs: Performance – Reliability - Cost**

# Na-$NiCl_2$ cell basic structure

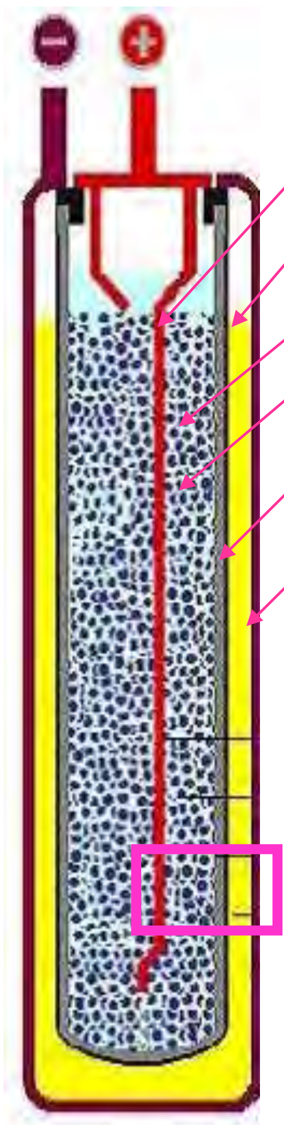





**Key materials**

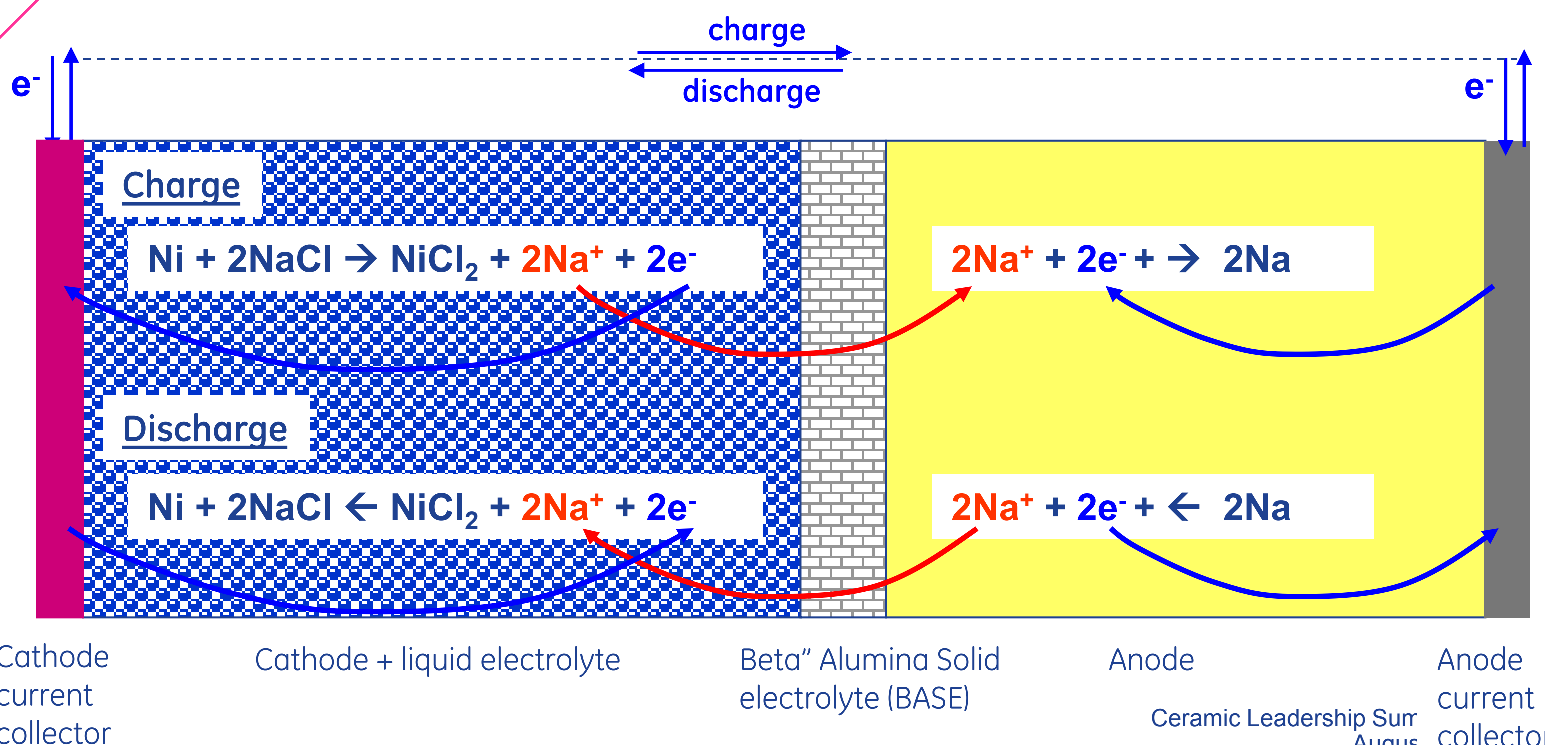
- Stable cathode mix
- Solid electrolyte (Beta"-Alumina)
- High-temperature seals
- Metal to Ceramic bonding
- Corrosion resistant metals and alloys
- Low resistivity current collectors

# $Na\text{-}NiCl_2$ cell basic chemistry



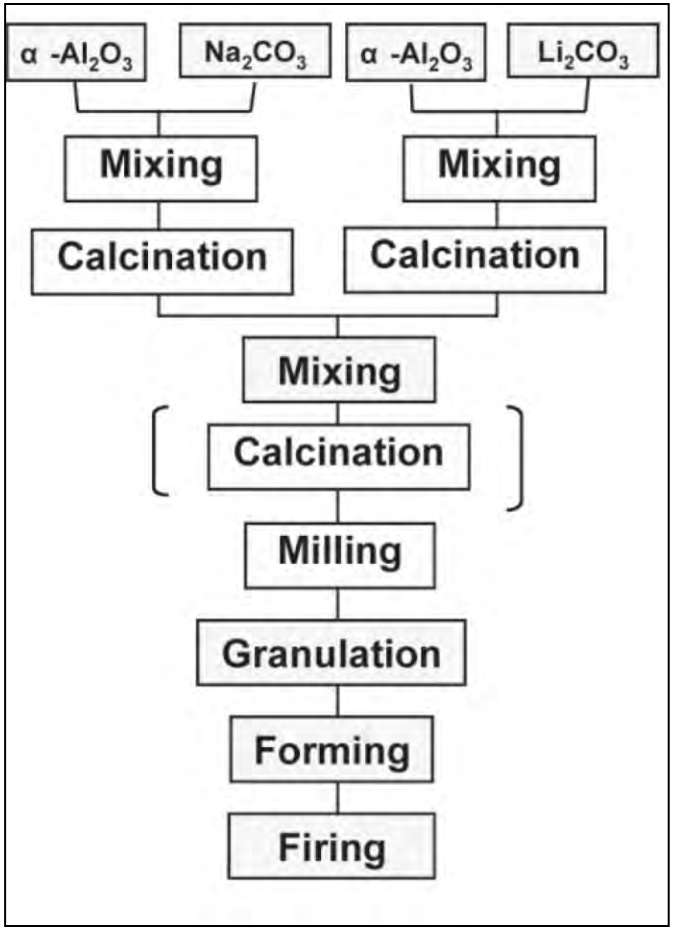

## Cell operating conditions

- Temperature ~ 270C-350C
- Voltage ~ 1.8-3.4V (OCV: 2.58V)
- Current ~ 20-100A
- Cell power ~ 100-200W
- Resistance (initial) ~ 7-10mΩ
- Pressure 1-2 bar

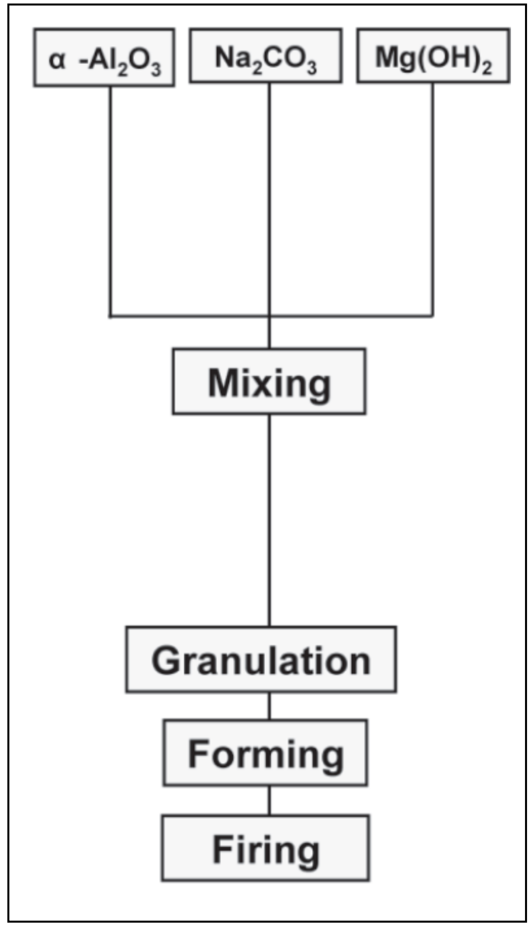


# **Beta"-Alumina:** Various processing routes

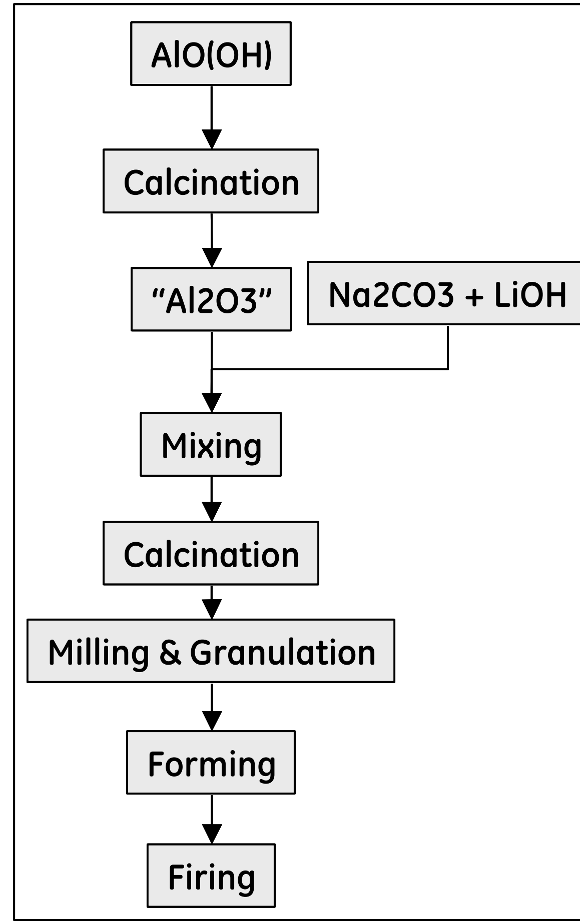
*After T. Oshima et al**




*After T. Oshima et al**




*After J. Sudworth***




*T. Oshima et al, Int J. Appl. Ceram. Tech., 1 (3) 269-76 (2004).

**J. Sudworth, MRS Bulletin March 2000

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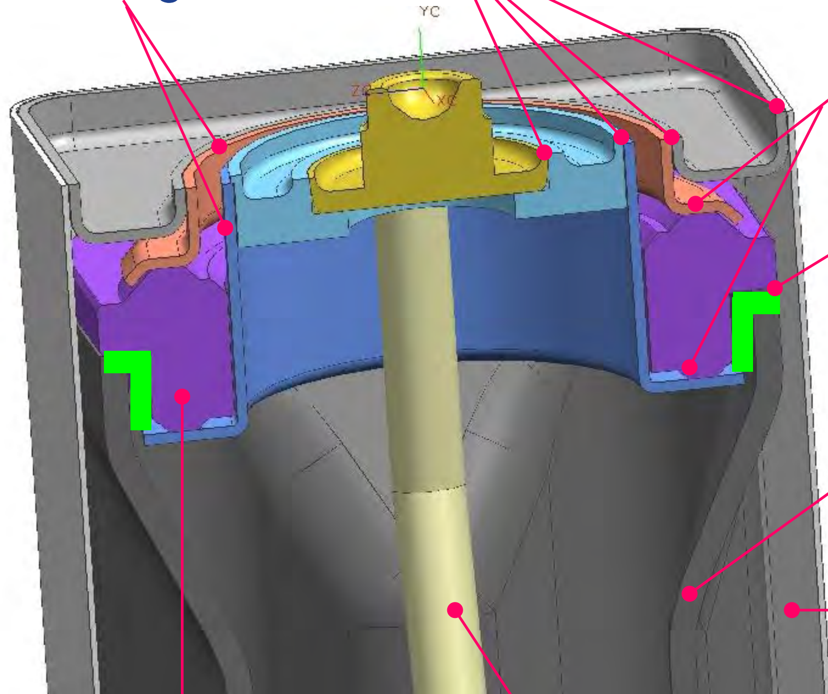
# Sealing materials & processes

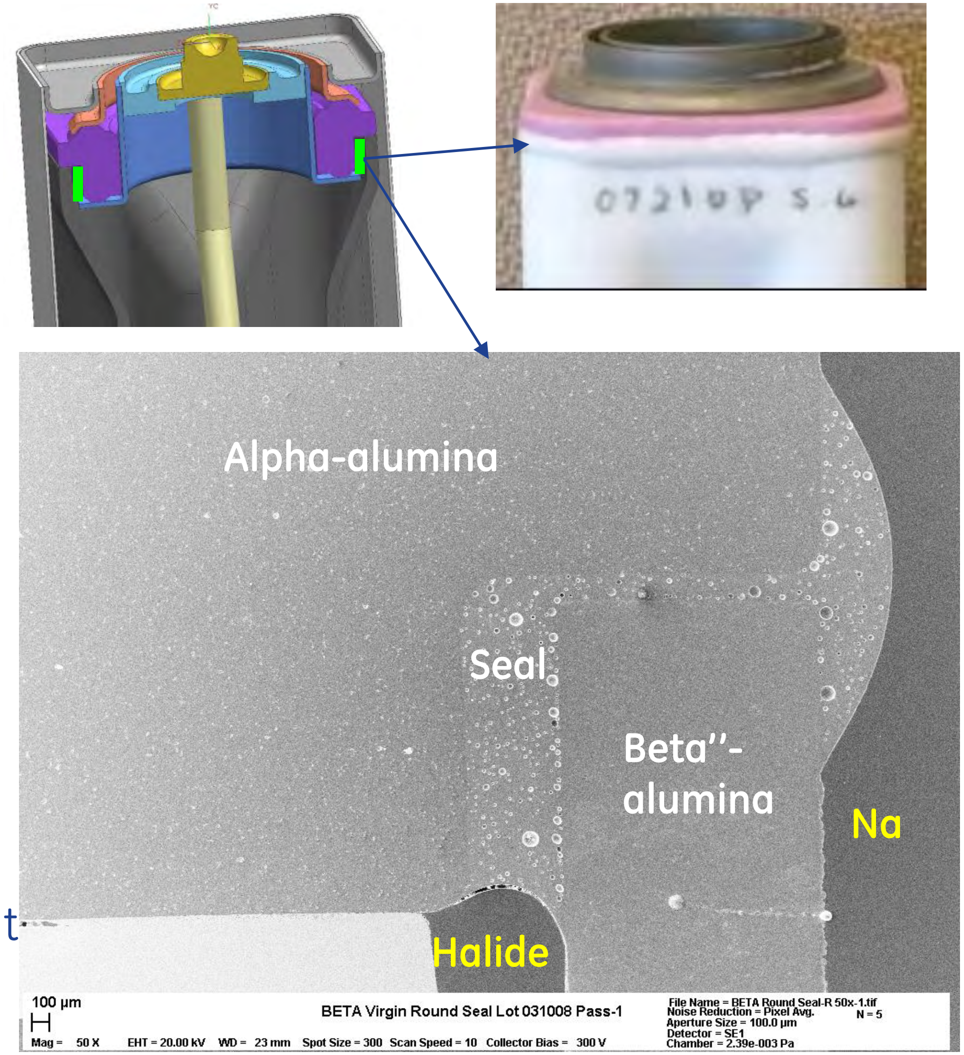
## Cell assembly steps

- $\alpha$-alumina collar metallization
- Thermal compression bond Alumina-Ni
- Seal $\alpha$-alumina-$\beta$''-alumina
- Weld subassembly to case
- Assembly to cell fill and final weld




**Bonds strength of all joints and resistance to cell chemical fill are most critical**

# Seal glass




## Requirements

- Chemical resistance to Na and halide melt
- No interaction with Beta"-alumina (ion exchange)
- High bond strength
- CTE close to β" and α-ceramics
- Hermiticity
- Low process temperature (800-1050C)

## Technology areas

- Material composition
- Corrosion mechanism in Na and halide melt
- Characterization (Properties & Bonding)
- Sealing process

**Sodium-sulfur batteries (GE)**
- Aluminoborosilicate glasses (GE 2093 and GE 2112)

→

**Sodium-Metal Halide batteries**
Improved properties for compatibility with cathode chemistry

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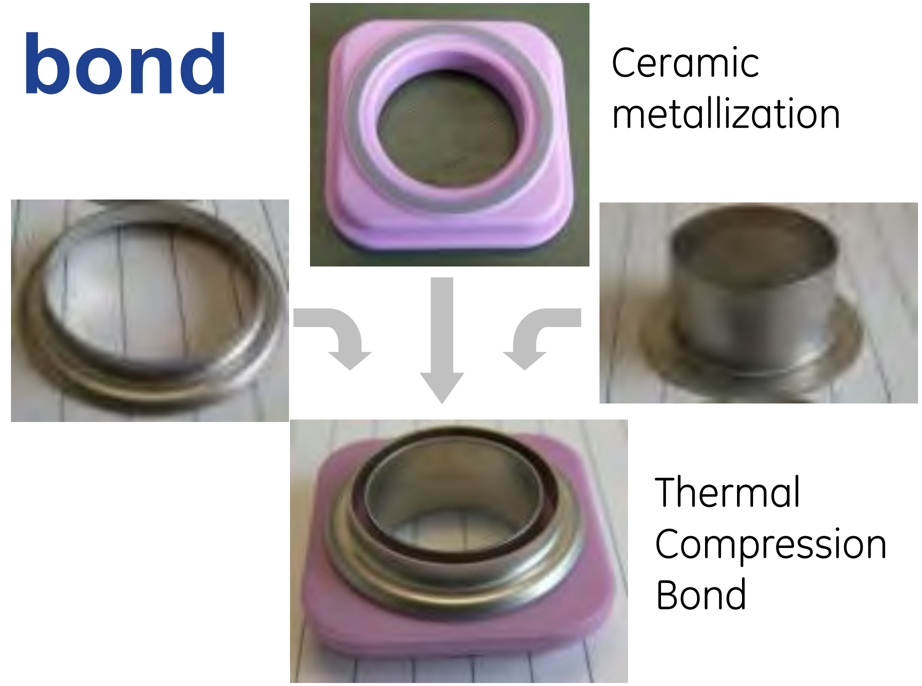
# Thermal compression bond

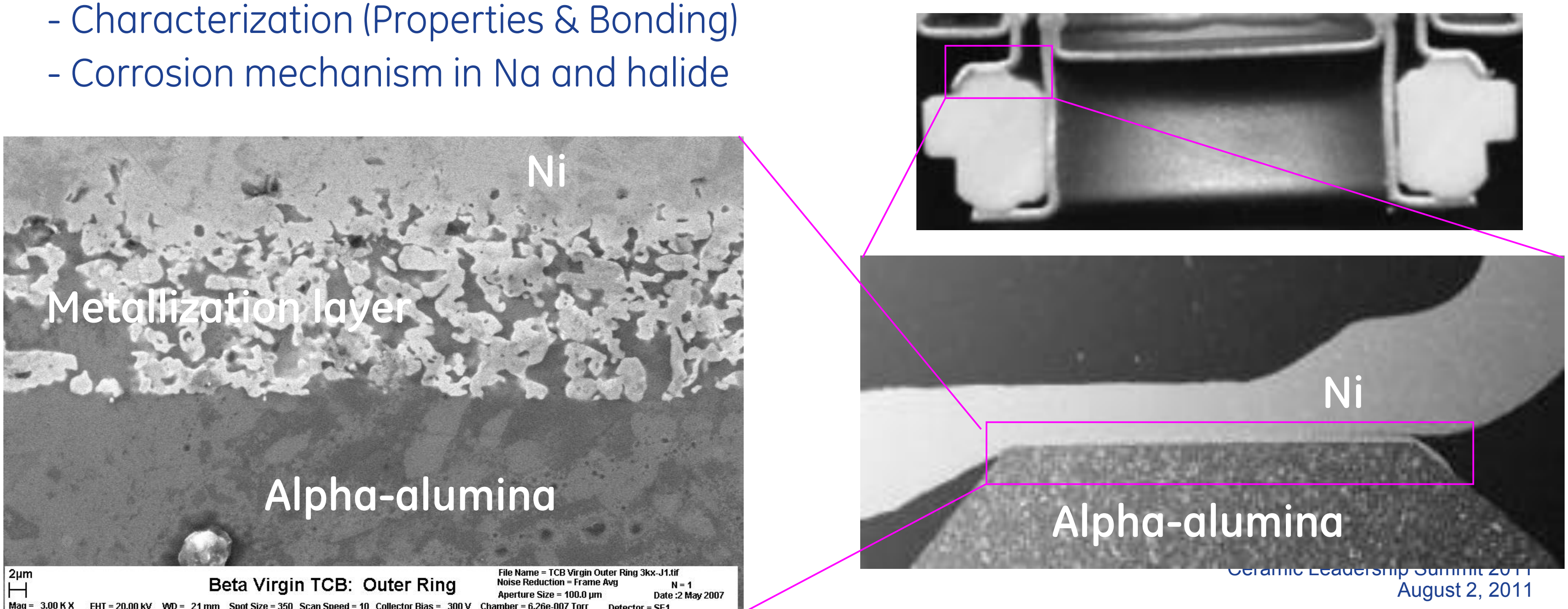
## Requirements

- Chemical resistance to Na and halide
- High bonding strength
- CTE close to α-alumina
- Hermiticity

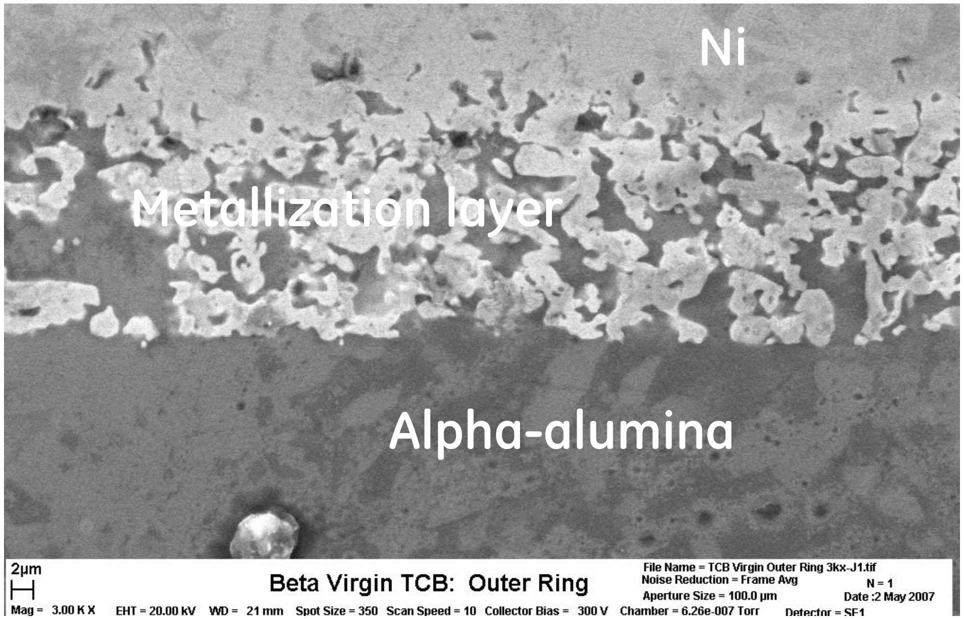
## Technology areas

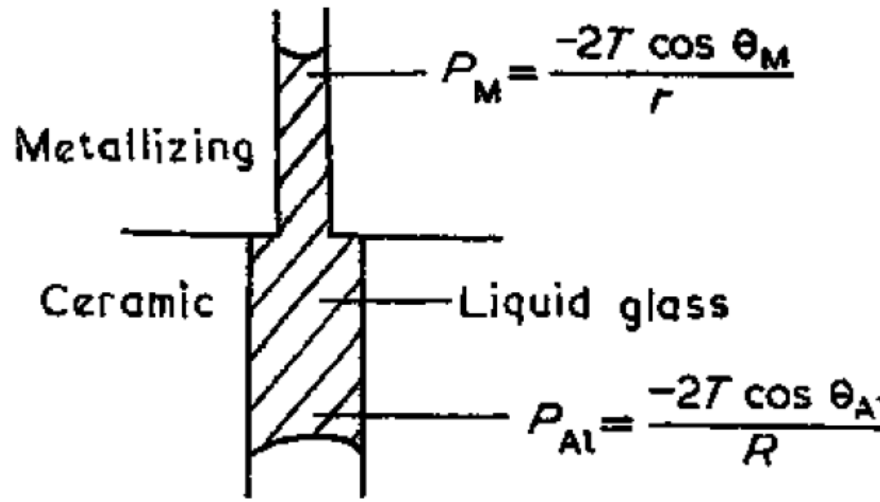
- Metallization material composition
- Sintering and TCB processes
- Characterization (Properties & Bonding)
- Corrosion mechanism in Na and halide



# Ceramic metallization




**Good conditions for glass wicking**

- Small pore size in metallization layer
- Large grain size in ceramic

# Materials interaction with cell chemistry

## Challenge

Ability to predict material life in cell environment without testing the cell for years

## Accelerated life test

- Accelerate corrosion by increasing temperature and/or using liquid phase vs vapor without introducing “un-real” failure mechanisms
- Establish stress-life curves through test data
- Estimate material life & degradation rate

## Thermodynamic modeling

- Proven to be effective in several materials applications where thermochemical data are available
- Limited data for Sodium-Metal Halide battery materials and chemistry

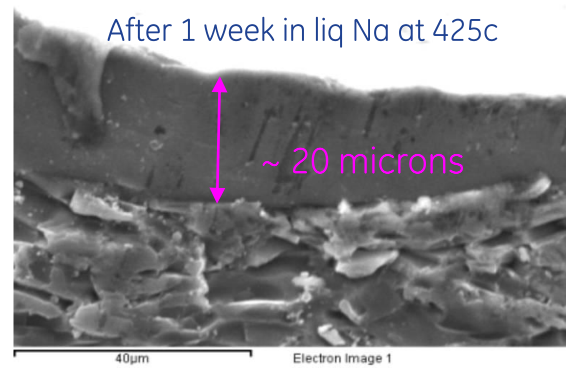
Pristine seal sample

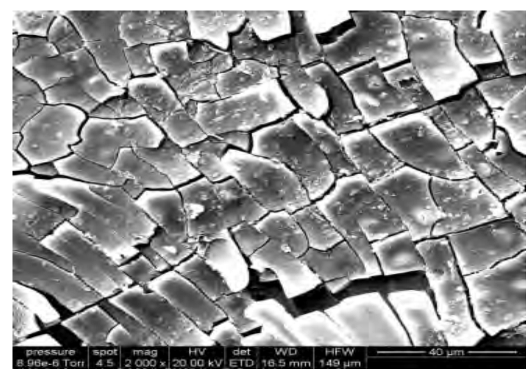
After 1 week at 425 C

In Liquid Na

In Liquid halide

After 1 week in liq Na at 425c

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# Manufacturing Investment

New York Battery Plant

GE Energy Schenectady Campus

- Repurpose existing facility
- 190,000 ft$^2$ factory
- Workforce of 350

NaMx

# NaMx Battery Summary

- NaMx Batteries are demonstrated to be suitable for a wide spectrum of energy applications (Transportation, Power infrastructure)

- Advanced materials (cathode, ceramic electrolyte and seals) are key enablers for the performance and life of NaMx batteries

# Summary & Conclusions

- Ceramics offer tremendous opportunities for improved efficiency of many gas generation systems
  - SOFCs, Batteries, CMCs, Ceramic Cores
- Life & Cost are key challenges in commercializing ceramic components
- GE actively working on commercializing many ceramic components
  - CMCs & NaMx batteries offer opportunities within 5 years
- Materials research key to addressing commercialization challenges
- Many companies, including GE, are actively recruiting in ceramics areas

# Acknowledgements


- CMC and SOFC work were partly funded by DOE (DOE contracts DE-FC26-00CH11047& DE-NT0004109)
- Key Contributors
  - CMCs: Greg Corman
  - SOFC: Matt Alinger
  - NaMx Battery: Mohamed Rahmane


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