Challenges in Solid Oxide Fuel Cell Technology

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Outline

- SOFC
- Anode-supported Planar for IT-SOFC
- CGCRI's Current Activities
- Challenges
- Summary

Advantage of Solid Oxide Fuel Cell

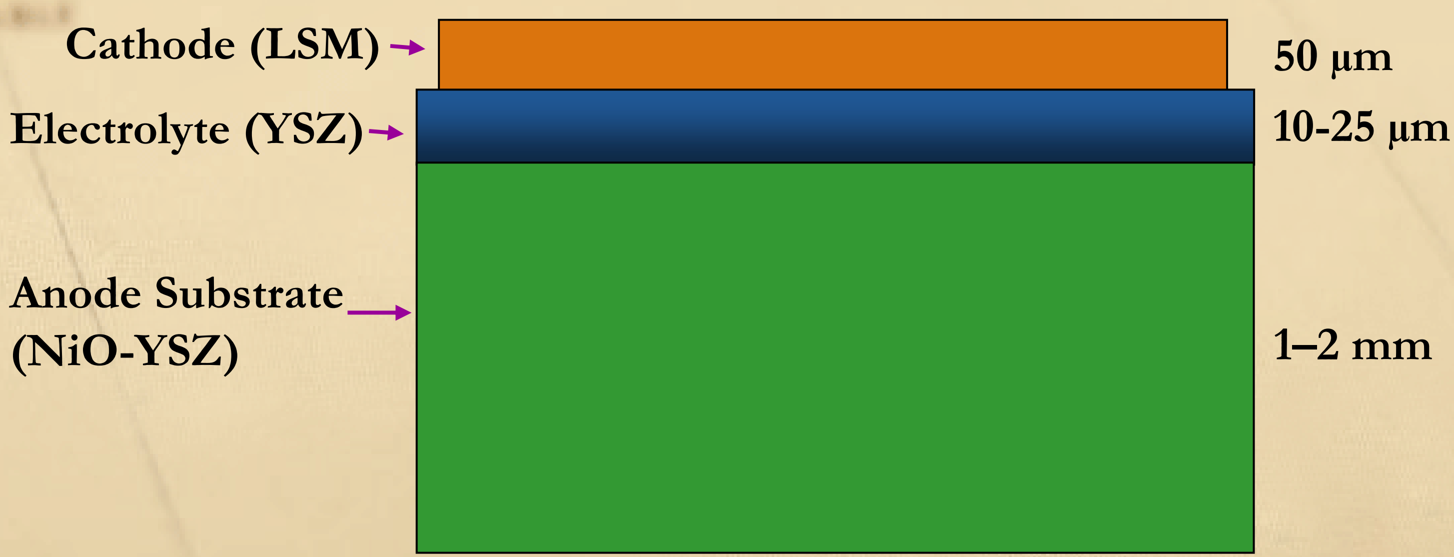
- Environment Friendly
  -- No NOx,SOx and particulate emissions
  -- Quiet
- High operation temperature (650-800^{o}C)
- Fuel to electricity efficiency ~ 35-40%(without recycling); With recycle heat ~ 60%

- All solid state
- Modularity
- Multifuel Capability
- Low in maintenance costs

	AFC/ PEMFC	PAFC	MCFC	SOFC
temperature	low	→		high
materials	noble	→		less noble
gas	ultra pure gas	→		less pure gas
costs	high	→		decreasing
stage of development	high	→		decreasing

Development of Planar IT-SOFC Technology

CGCRI Approach



Operating Temperature: 700-800^{o}C

- Thin electrolyte reduces internal resistance and operating temperature
- Sealing materials less stringent at between 700 and 800^{o}C
- Use of metal alloy (Ferritic Steel) as interconnect
- Cost-effective technology

LSM – Sr-substituted $LaMnO_3$; **YSZ** – 8mol% yttria stabilized ZrO_2

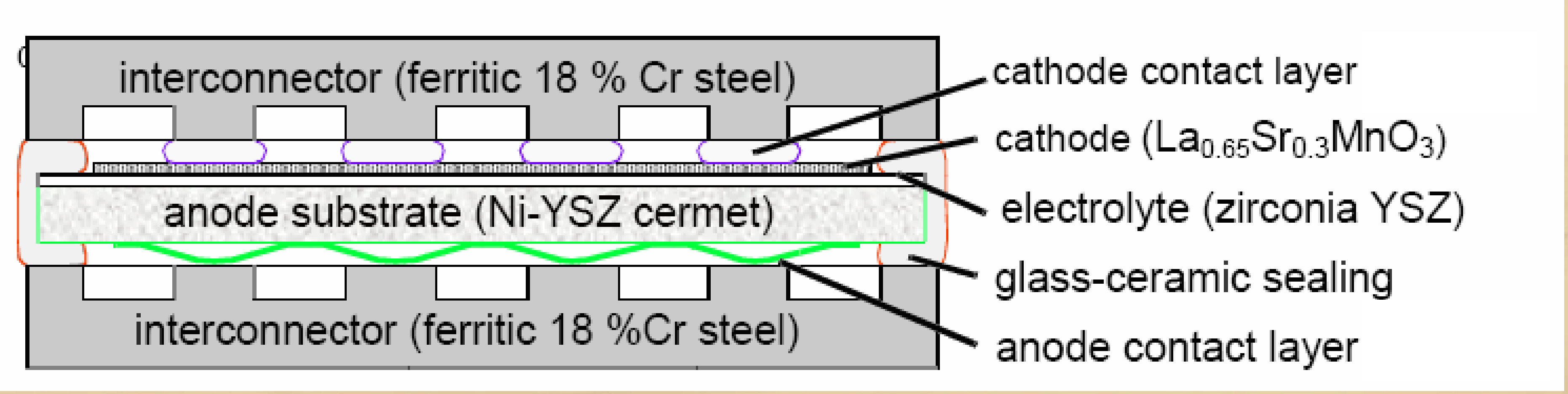
State-of-the-art Materials

Electrolyte: ZrO_2 + 8mol% Y_2O_3 (YSZ)

Cathode: $La_{0.65}Sr_{0.35}MnO_3$ (LSM)

Anode: 40vol% Ni + 60vol% YSZ (Ni-YSZ)

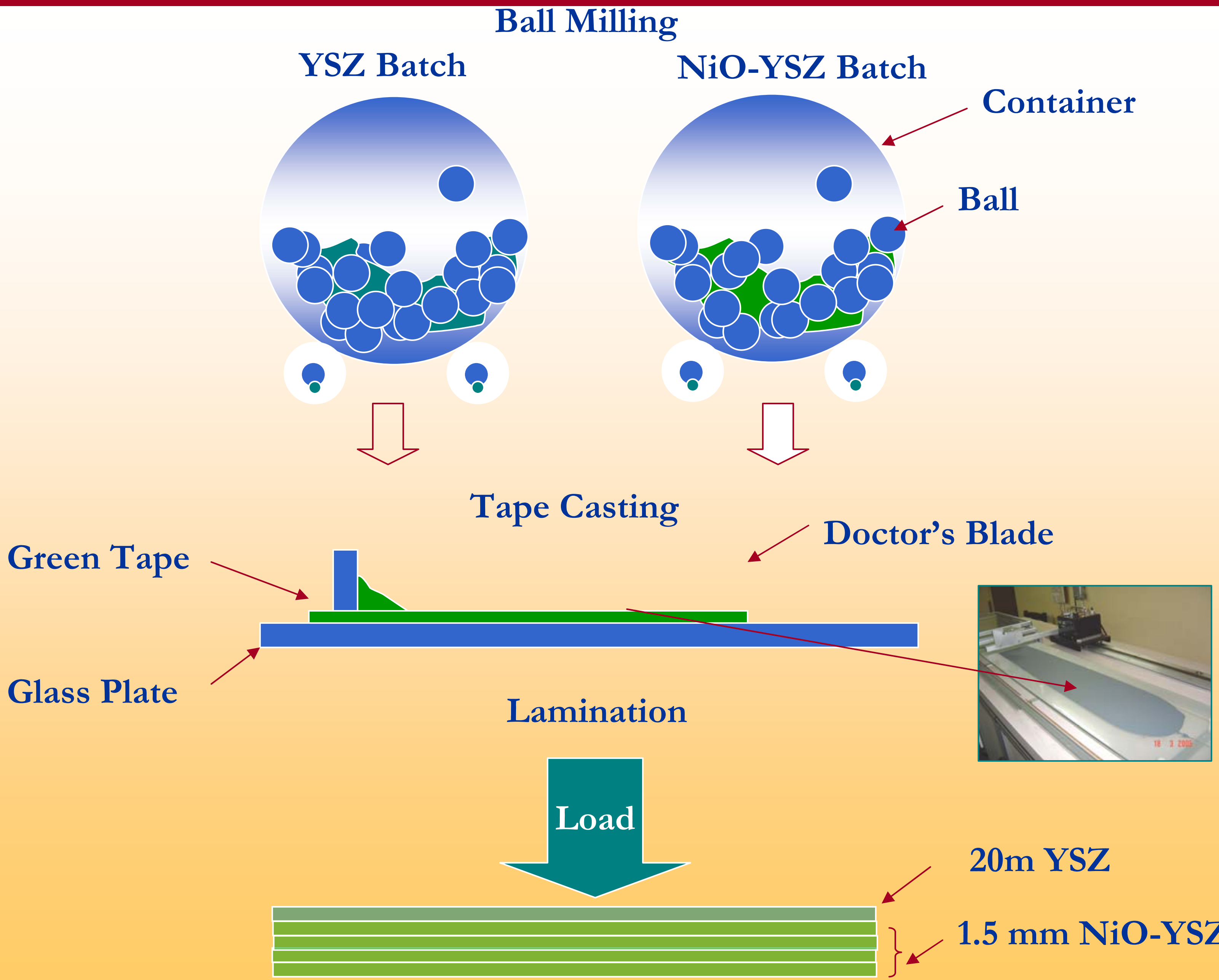
Interconnect: $La_{0.70}Ca_{0.30}CrO_3$ (LCR) / Ferritic Steel



Fabrication…

SOFC Designs	SOFC PROCESSING TECHNIQUES			
	Cathode (LSM)	**Electrolyte** (YSZ)	**Anode** (NiO-YSZ)	**Interconnect** **(LCR / Ferritic Steel)**
Cathode-supported Tubular	Extrusion	EVD/Slurry-coating/EPD/ Thermal Spray	Slurry-coating/EPD/ Thermal Spray	Slurry-coating/EPD/ Thermal Spray
Anode-supported Planar	Wet-powder spraying/ Screen printing	Vacuum slip casting/Tape-calendering/Slurry coating/EPD/ Tape casting	Tape casting/ Warm pressing	Precise Machining / Welding
Metal-supported Planar	Plasma spraying/ Screen printing	Plasma spraying/ Tape casting	Plasma spraying/ Screen printing	Precise Machining / Welding

Single Cell Fabrication



SOFC Single Cell Fabrication

Ball Milling

↓

Tape Casting

↓

Lamination

↓

Co-Firing of Laminated Blocks

↓

Half Cell

↓

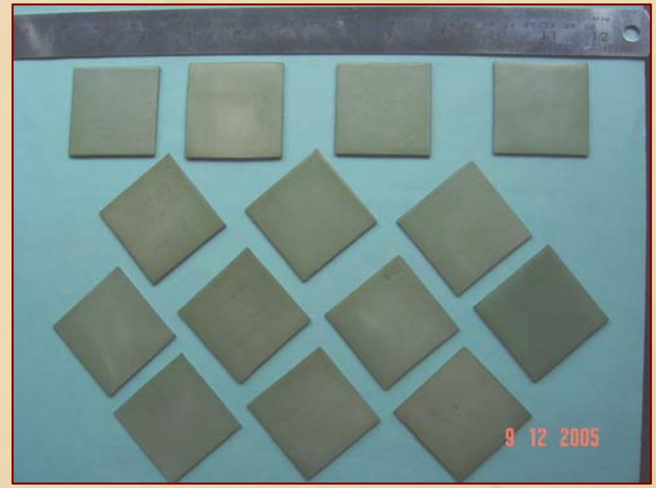
LSM Screen Printing

↓

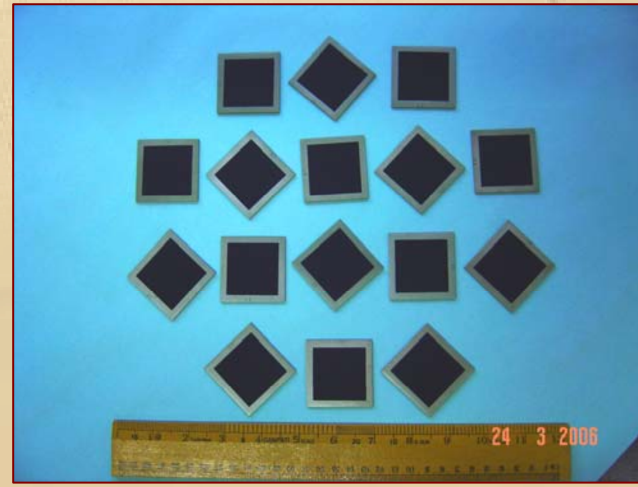
Heat Treatment

↓

SOFC Single Cell



Flat Half Cells (5 cm x 5 cm)

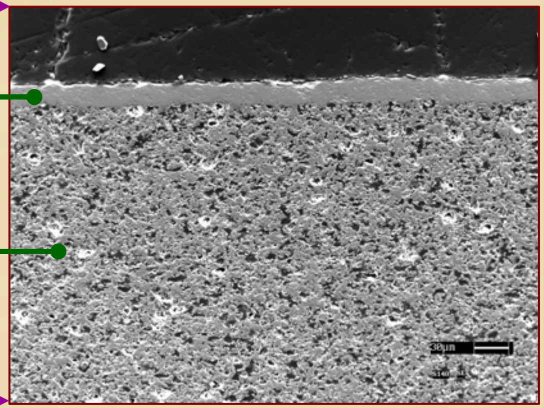


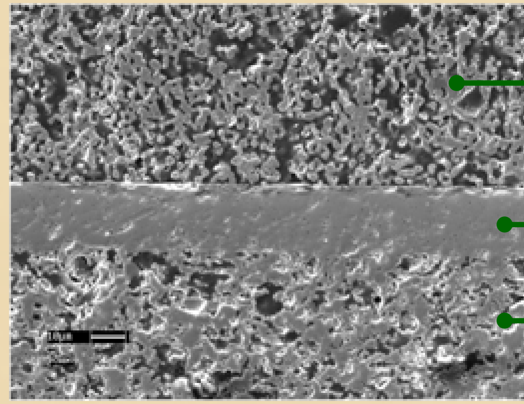
Single Cells (5 cm x 5 cm)

CGCRI Developed Anode Supported Cells

YSZ Electrolyte (20 µm)

NiO-YSZ Anode (1.5 mm)

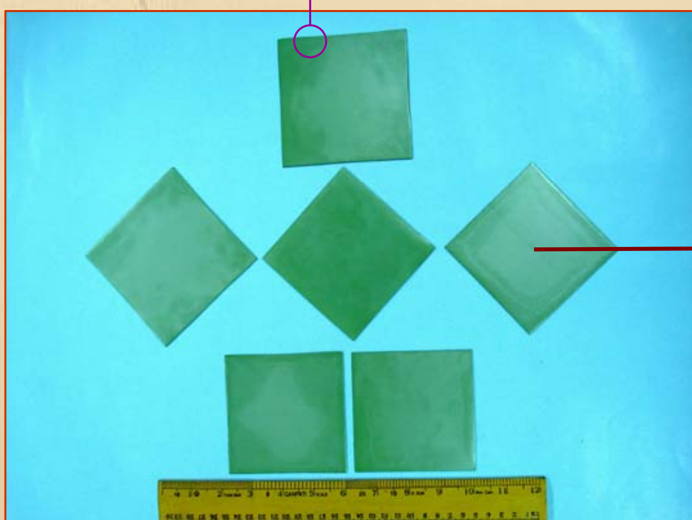




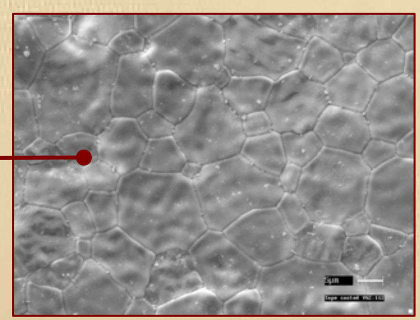
LSM Cathode (50 µm)

YSZ Electrolyte (20 µm)

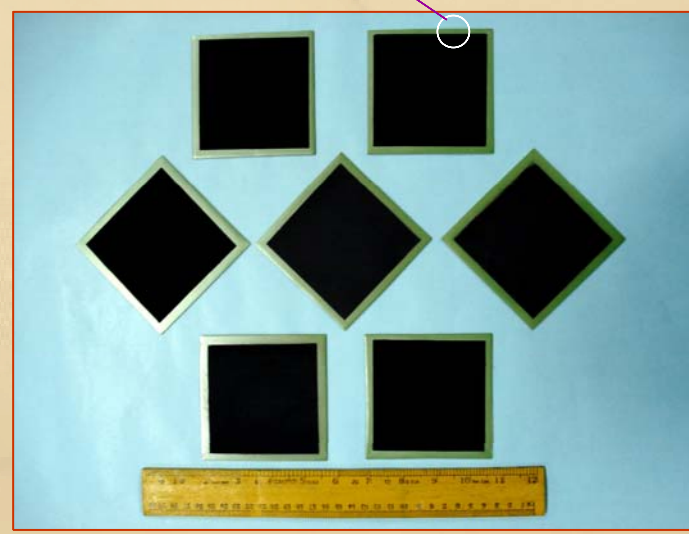
NiO-YSZ Anode (1.5 mm)



10 cm x 10 cm x 1.5 mm (Half cell)



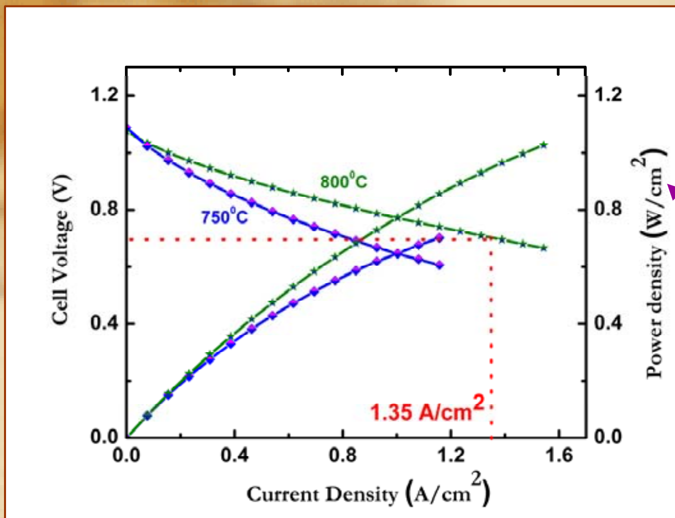
YSZ Electrolyte (Surface)



10 cm x 10 cm x 1.5 mm (Single cell)

LSM – Sr-substituted $LaMnO_3$; **YSZ** – 8mol% yttria stabilized ZrO_2

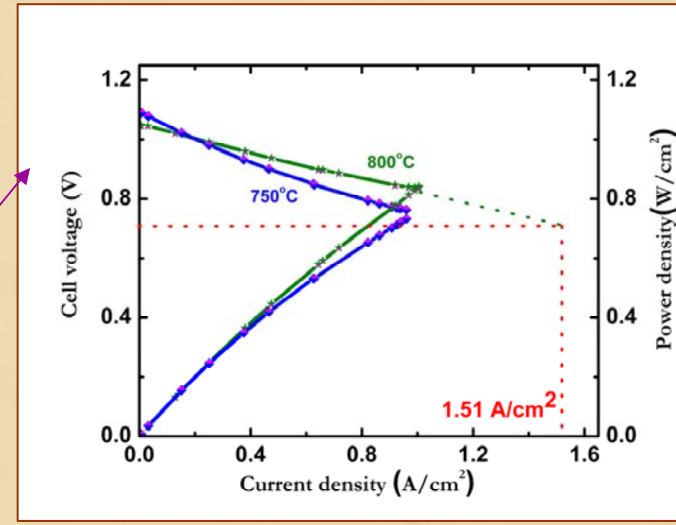
Electrochemical Performance



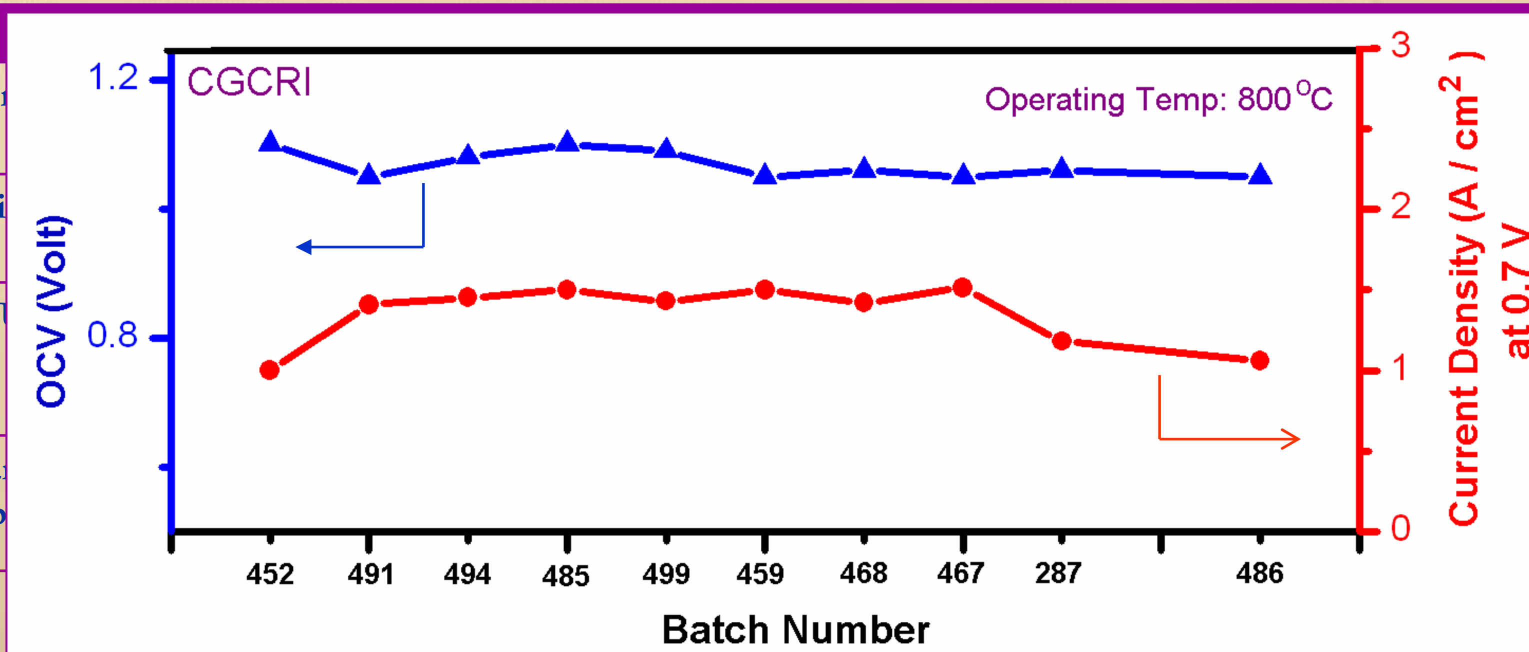
FZJ

CGCRI Single Cell

CGCRI



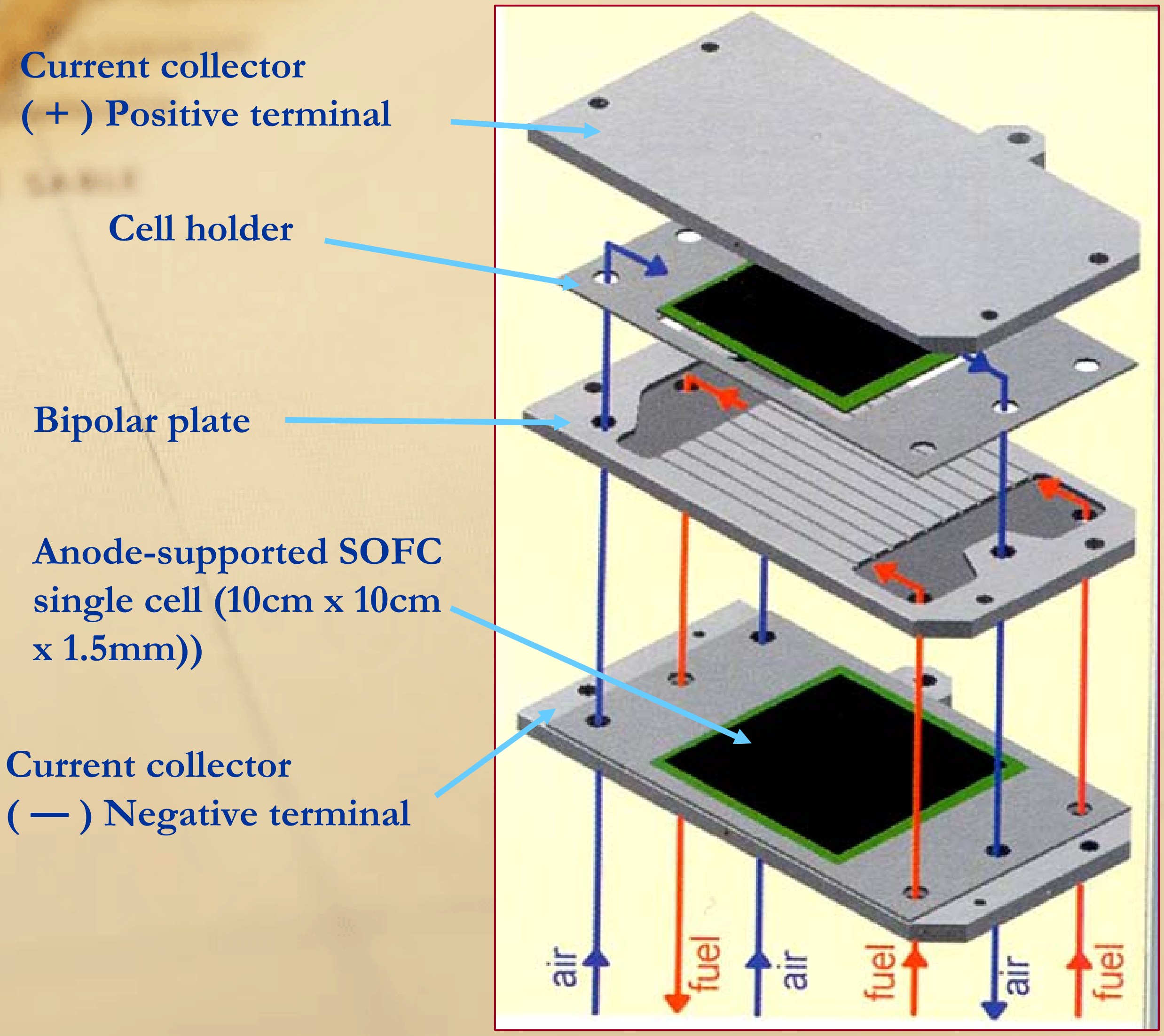
	ance
GE Hybr Systems	7V,
FZJ (Jüli	7V, 1.0
PNNL (	7 V, < Natural ne
H.C. Sta off comp	0.85V,
CGCRI,	0.7V, 2



CGCRI’s Processing Techniques…

- Simple
- Inexpensive
- Up-scalable

CGCRI's Proposed SOFC Stack Design



<u>**Total Power: 250W**</u>

Cell size: 10 cm x 10 cm

No. of cells: 6

Current Density: 0.5A/cm^2

Sealant: Glass-ceramics

Interconnect: SS 430

Fuel : H_2

Oxidant : Air

Temperature : 800^{o}C

Target : March 2007

Accomplishments (2004 - till date)

- Large scale (Kg-level) powder preparation of the SOFC cell components
- 20 μm thin fully dense YSZ (8mol% yttria stabilized ZrO_2) electrolyte on porous anode (NiO-YSZ) substrate
- Microstructural studies and He-leak test confirms gas-tightness in sintered YSZ film
- 5 cm x 5 cm x 1.5 mm – Developed and Performance tested
- 10 cm x 10 cm x 1.5mm – Initiated (Present Activity)
- Designing of SOFC stack – Initiated (Present Activity)

Project: CSIR-NMITLI

CGCRI SOFC Programme

DEC. 05

5 x 5 single cell

MARCH 06

- Complete Electrical and Electrochemical characterization of 50 x 50 cells
- Fabrication of 10 x 10 cells
- Complete Electrical characterization of 10 x 10 cells

SEPT 06

- Complete Electro-chemical charac-terization of 10 x 10 cells
- Fabrication of multiple stack with internal manifold

MARCH 07

Fully charac-terized 250W stack

JUNE 07

Fully charact-erized 500W stack

SEPT 07

Fabrication of 1 kW stack

Major Facilities at FCB, CGCRI

Challenges….

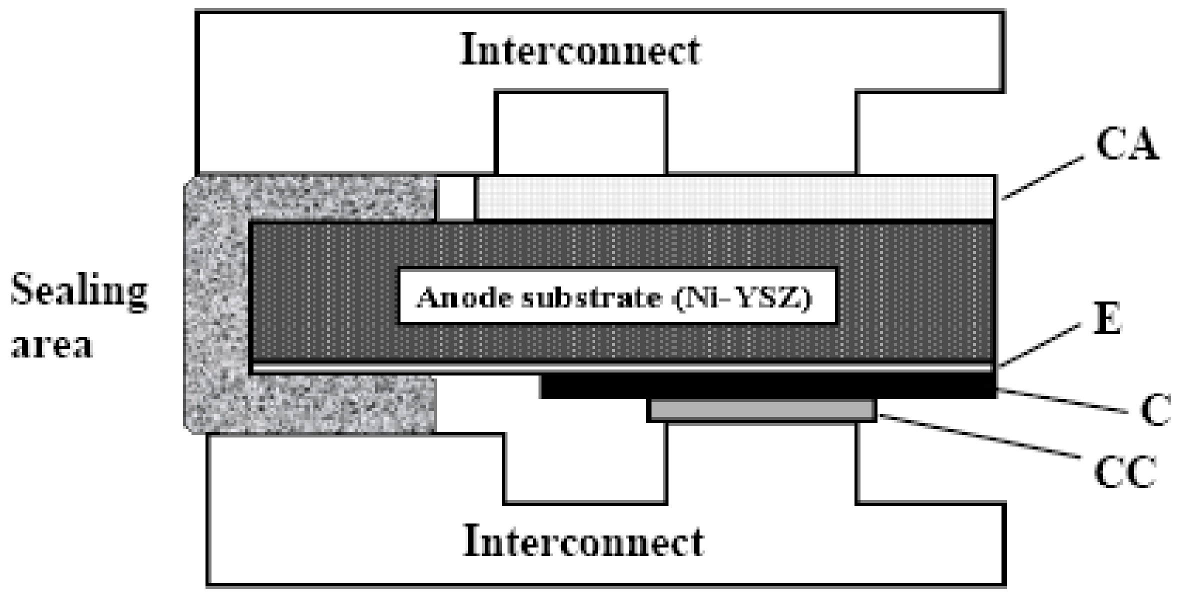
Planar (IT SOFC)

- ➢ **Glass Sealing**
- ➢ **Cell Degradation**

- ❑ **Materials, Fabrication and System Integration**
- ❑ **Cost Reduction**

Why Sealants?...

In planar SOFC, fuel gas and air must be kept separate from each other to prevent decreased efficiency in producing electric energy as well as direct combustion and overheating



Schematic drawing of sealing and contact layers within the stack: CA = contact layer anode (Ni-mesh); E = electrolyte; C = cathode; CC = contact layer cathode (Basu R.N., 2006)

SOFC SEALS

Functions

- SOFC seals prevent mixing of fuel and oxidant within stack
- SOFC seals prevent leaking of fuel and oxidant from stack
- SOFC seals electrically isolate cells in stack
- SOFC seals may provide mechanical bonding of components

Requirements

While fulfilling the above functions, seal materials must remain:

- structurally stable
- chemically compatible with other stack components
- inexpensive

SOFC Seal Requirements

Functional requirements and materials selection parameters

Mechanical

- Hermetic (or near hermetic)
- Minimal CTE mismatch (or ability to yield or deform to mitigate CTE mismatch stresses)
- Acceptable bonding strength (or deformation under compressive loading)
- Thermal cycle stability
- Vibration and shock resistance (for mobile applications)

Chemical

- Long-term chemical stability under simultaneous oxidizing/wet fuel environments
- Long-term chemical compatibility with respect to the adjacent sealing surface materials
- Resistance to hydrogen embrittlement / corrosion

Electrical

- Non-conductive

Fabrication

- Low cost
- High reliability with respect to forming a hermetic seal
- Sealing conditions compatible with other stack components

Typical glass-based SOFC sealing compositions

Mica glass ceramics

Commercially available micas

Alkali silicate glasses

Na_2O-CaO-SiO_2

Li_2O-ZnO-Al_2O_3-SiO_2

MgO-ZnO-SiO_2

Alkali earth borosilicate glasses

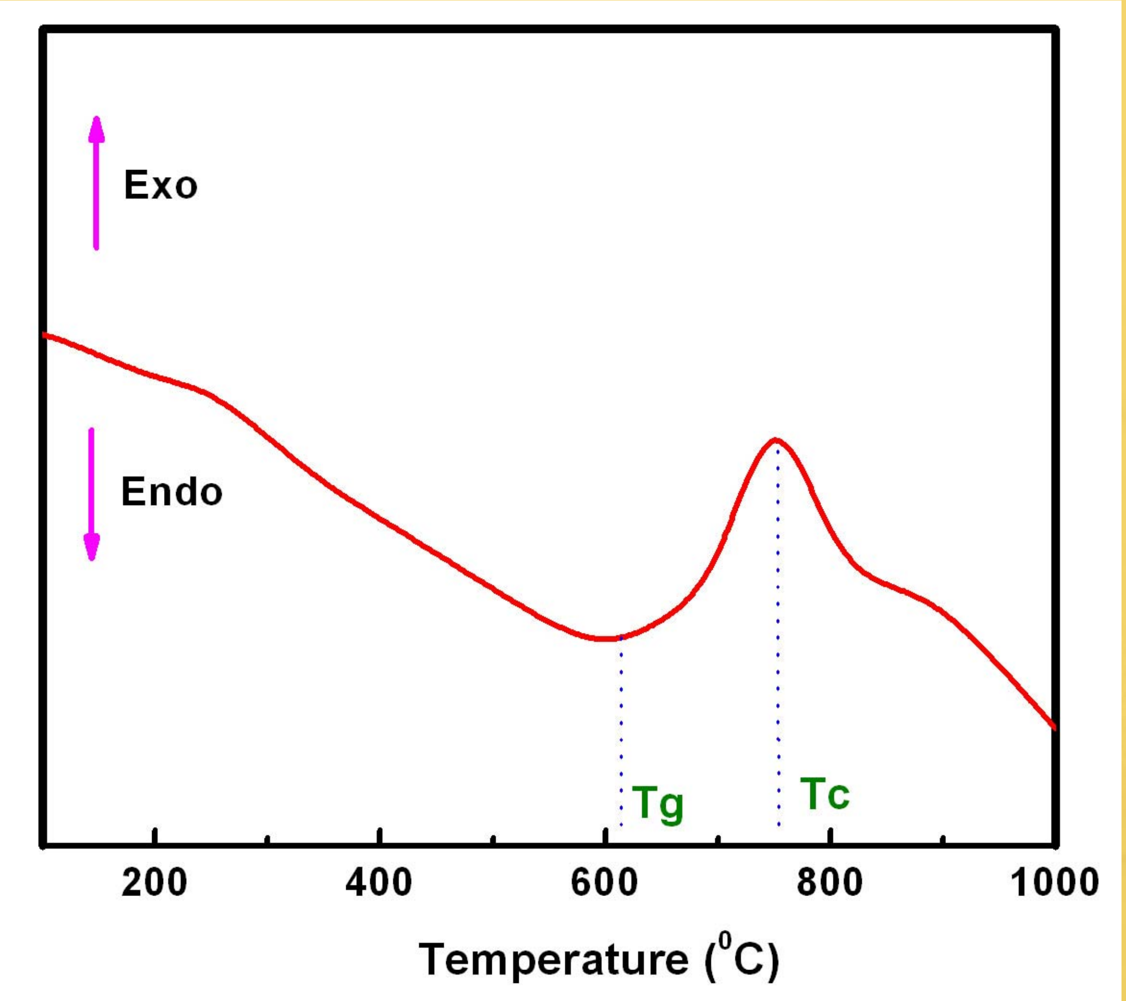
SrO-La_2O_3-Al_2O_3-B_2O_3-SiO_2

Alkali earth aluminosilicate glasses

MgO-Al_2O_3-SiO_2

CaO-Al_2O_3-SiO_2

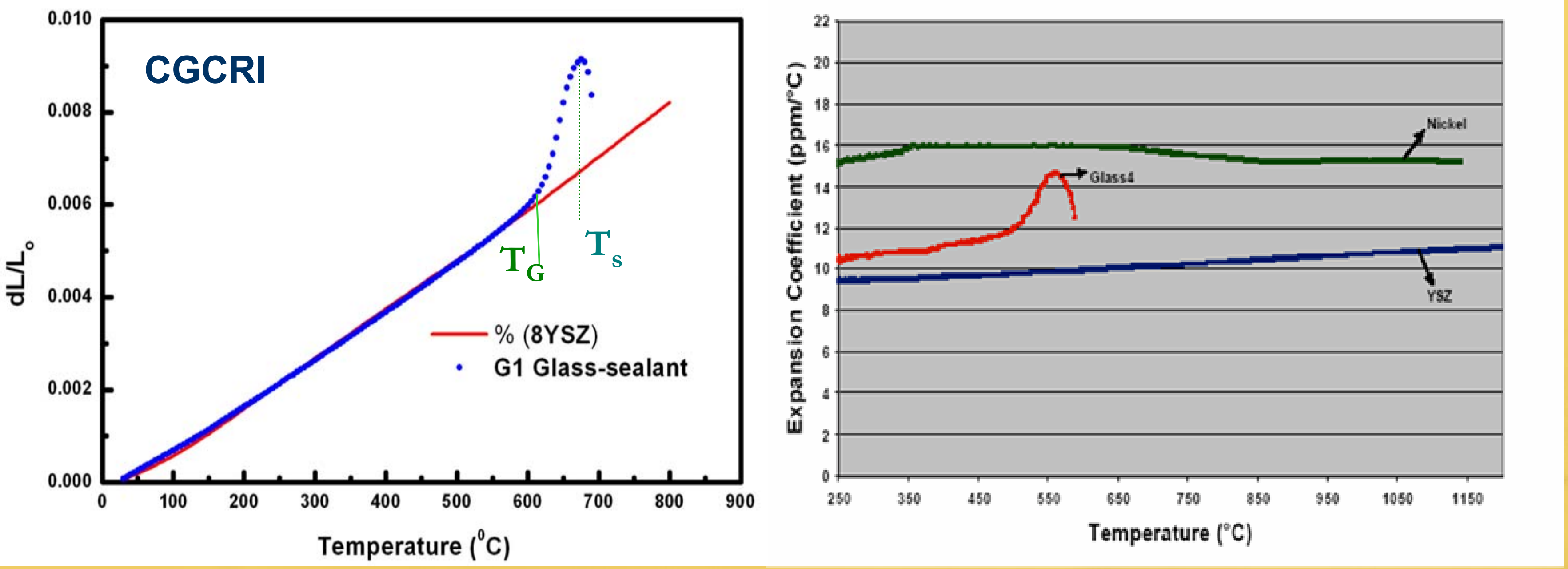
Typical DTA plot for the sealing glass (CGCRI)



T_g: Glass transition temperature T_c: Crystallization temperature

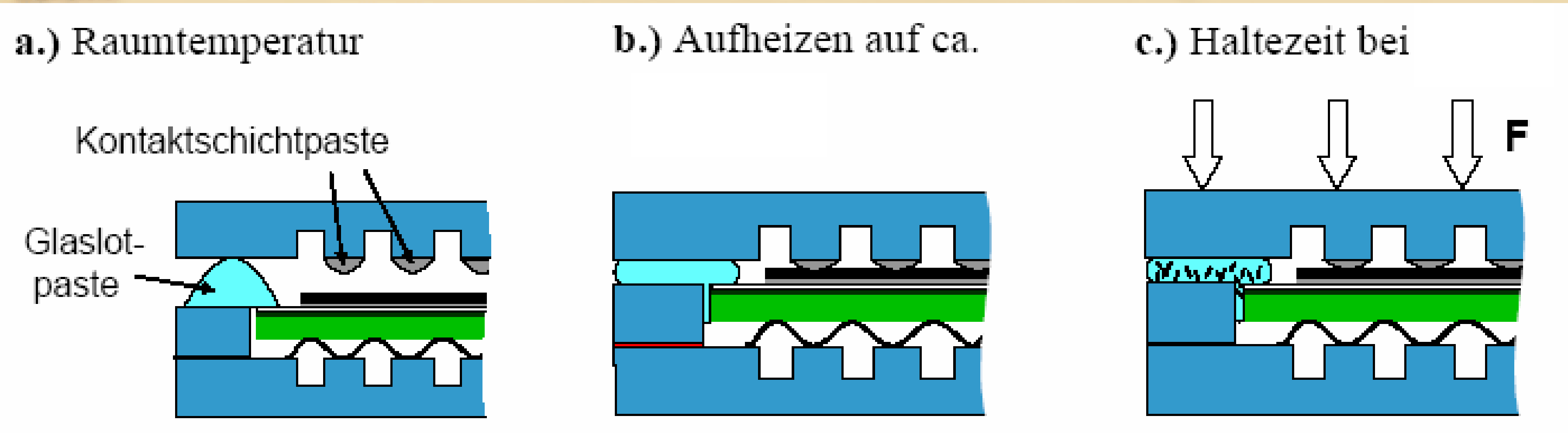
Typical thermal expansion behavior of glass-sealant

Materials with dramatically different thermal expansion coefficients

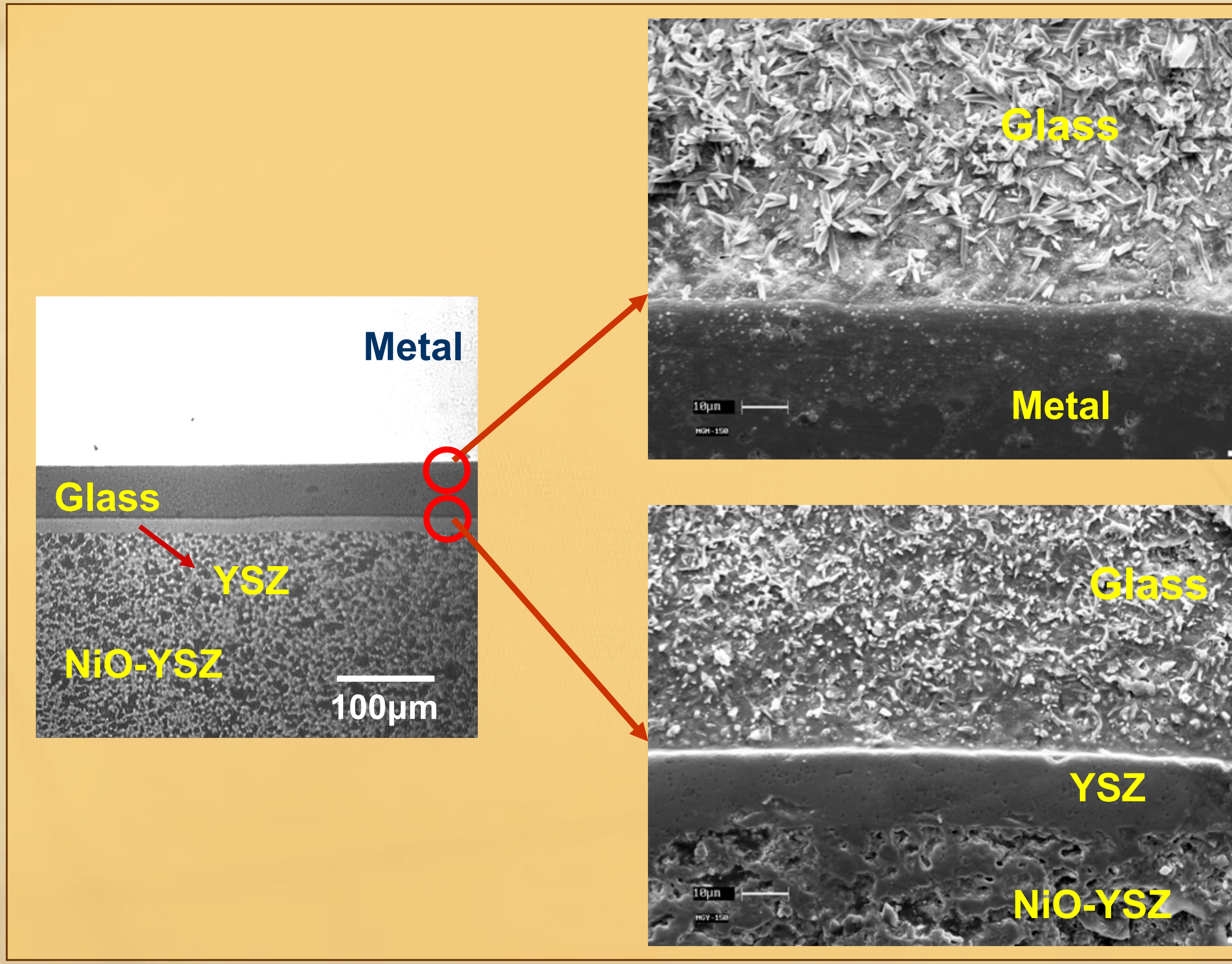


Tg values should be well within the range and are as low as possible to minimize the stress produced as the structure cools to room temperature

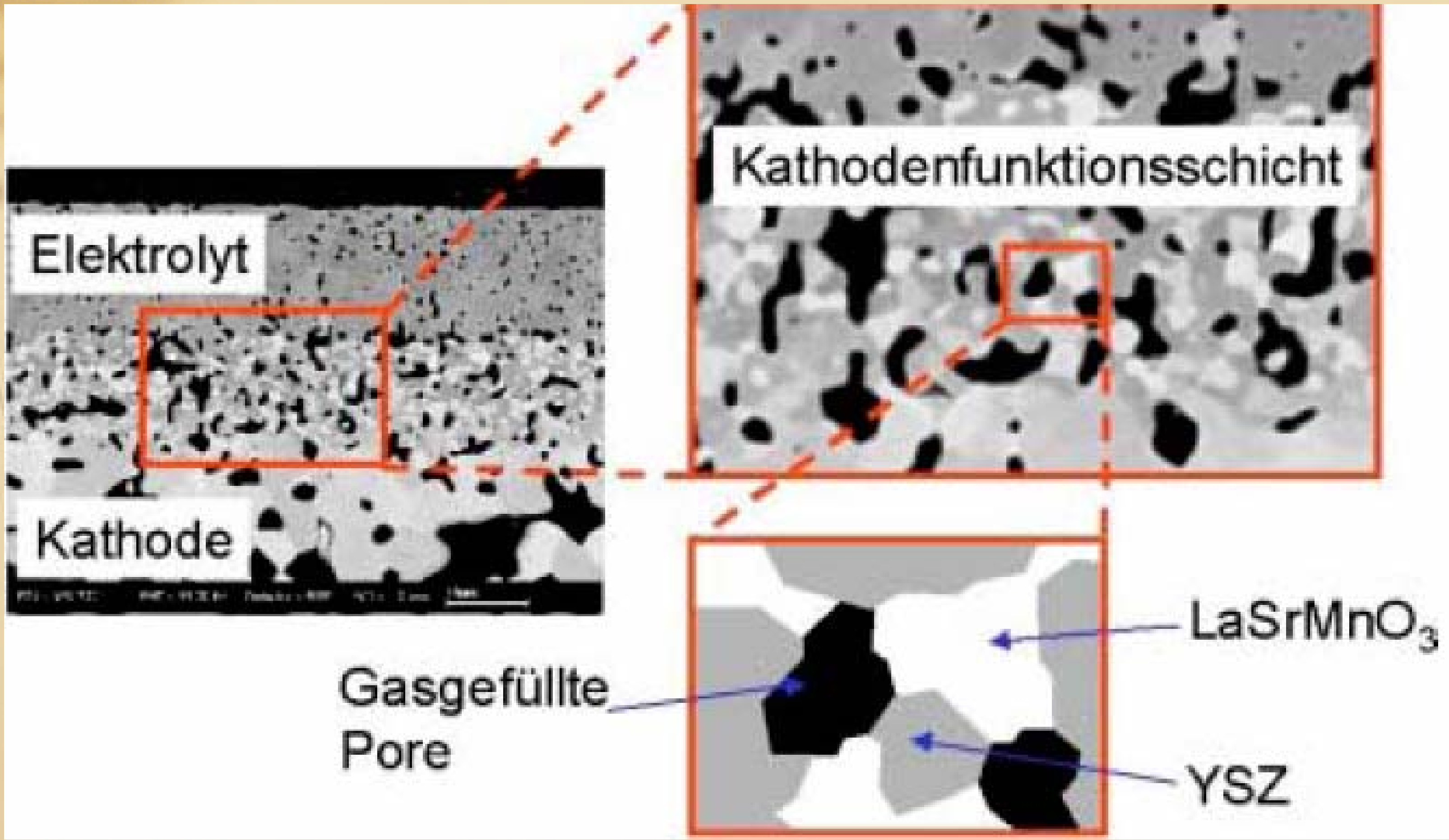
Application of Glass-based Sealants in Stack



CGCRI-Developed Glass Sealants

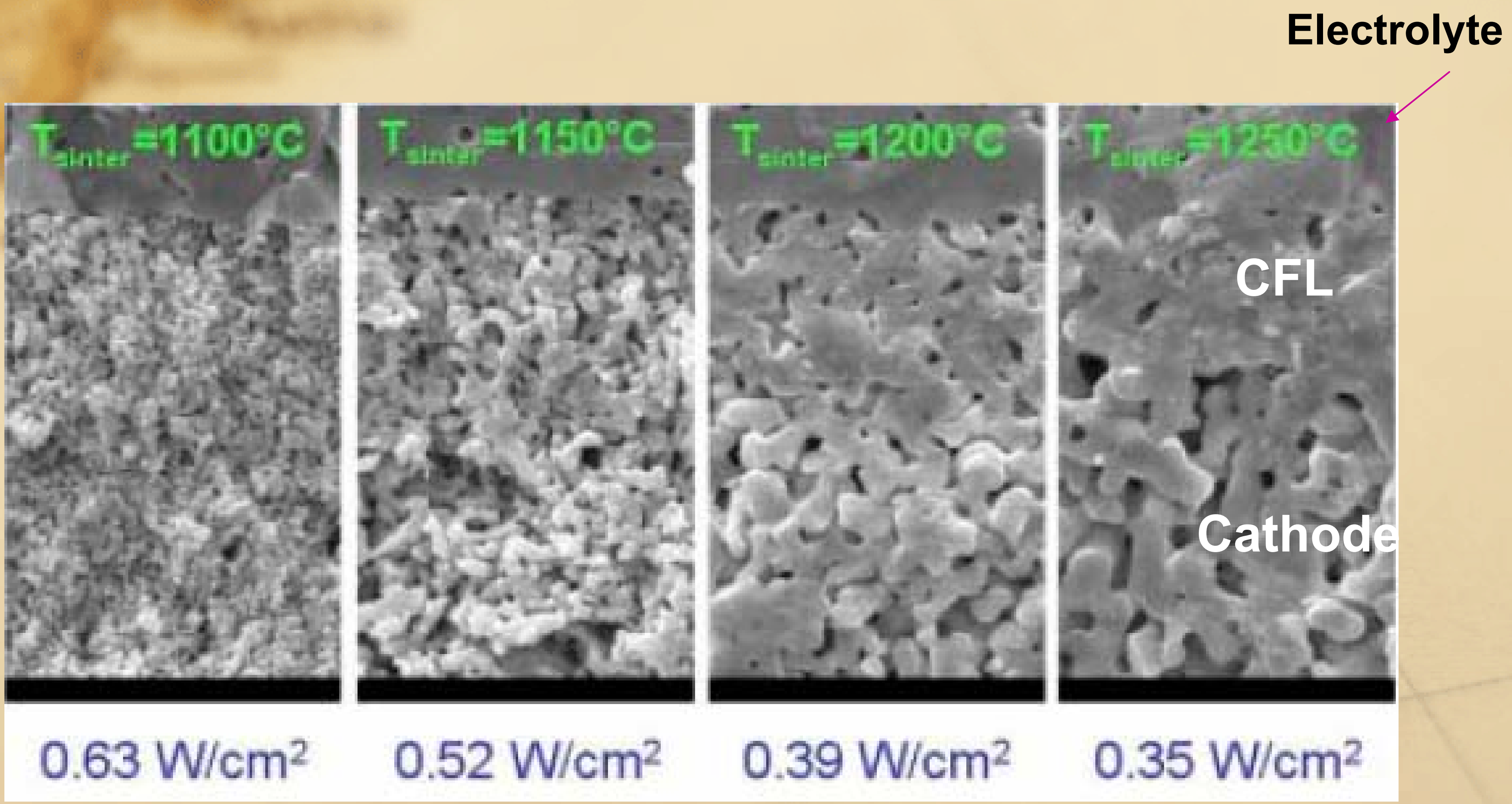


Cathode Functional Layer (CFL)

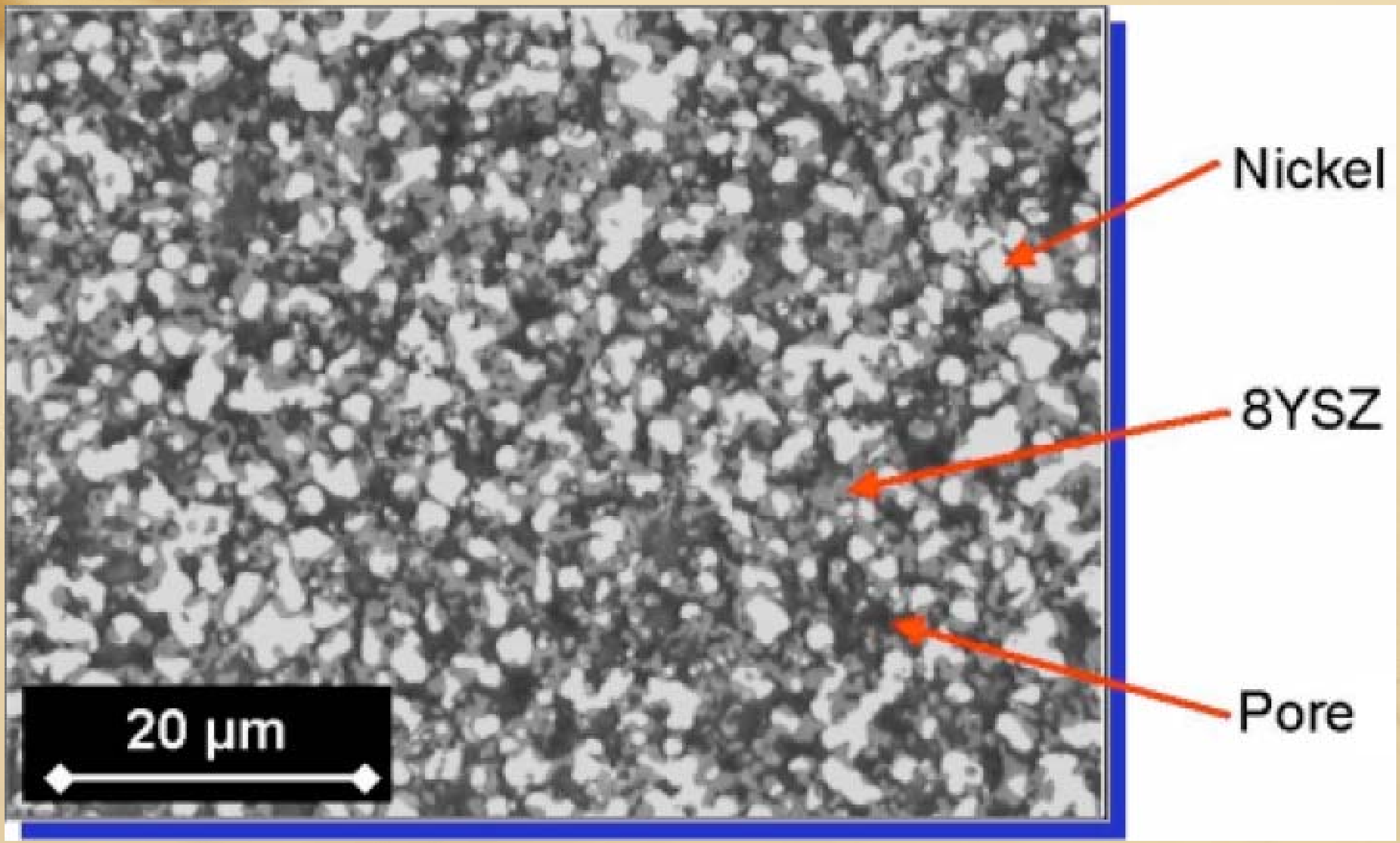


Triple phase boundary (tpb)

Microstructure of CFL



Microstructure of AFL



State-of-the-art Materials

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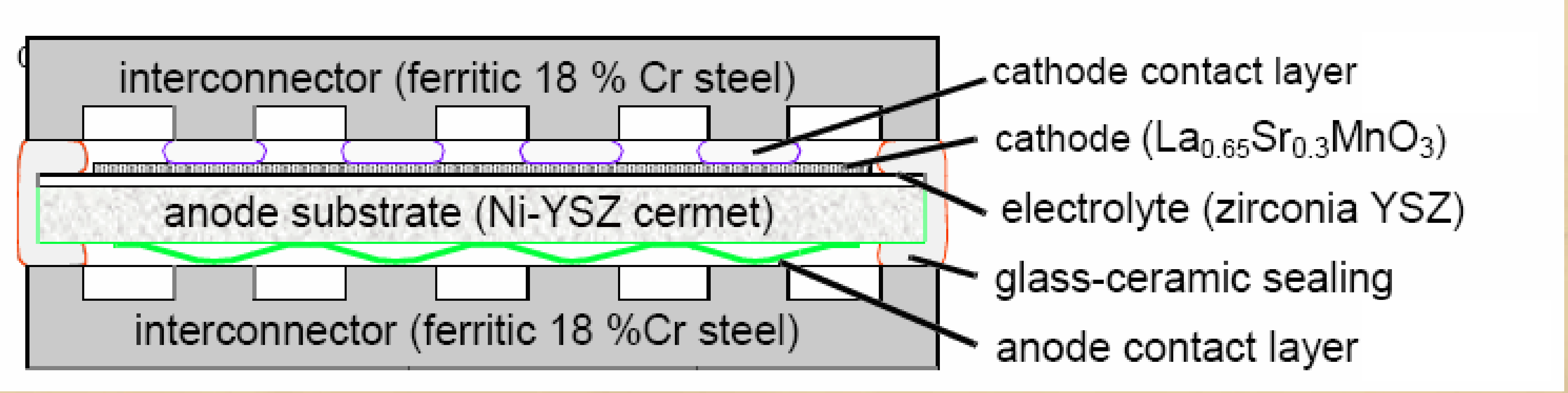
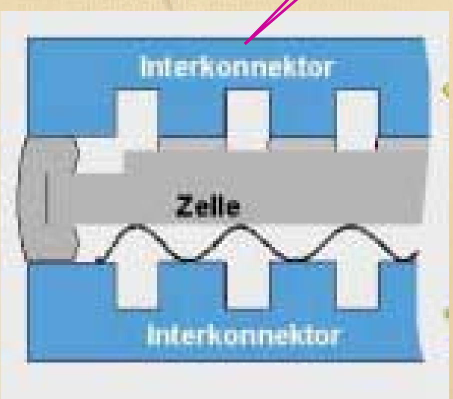


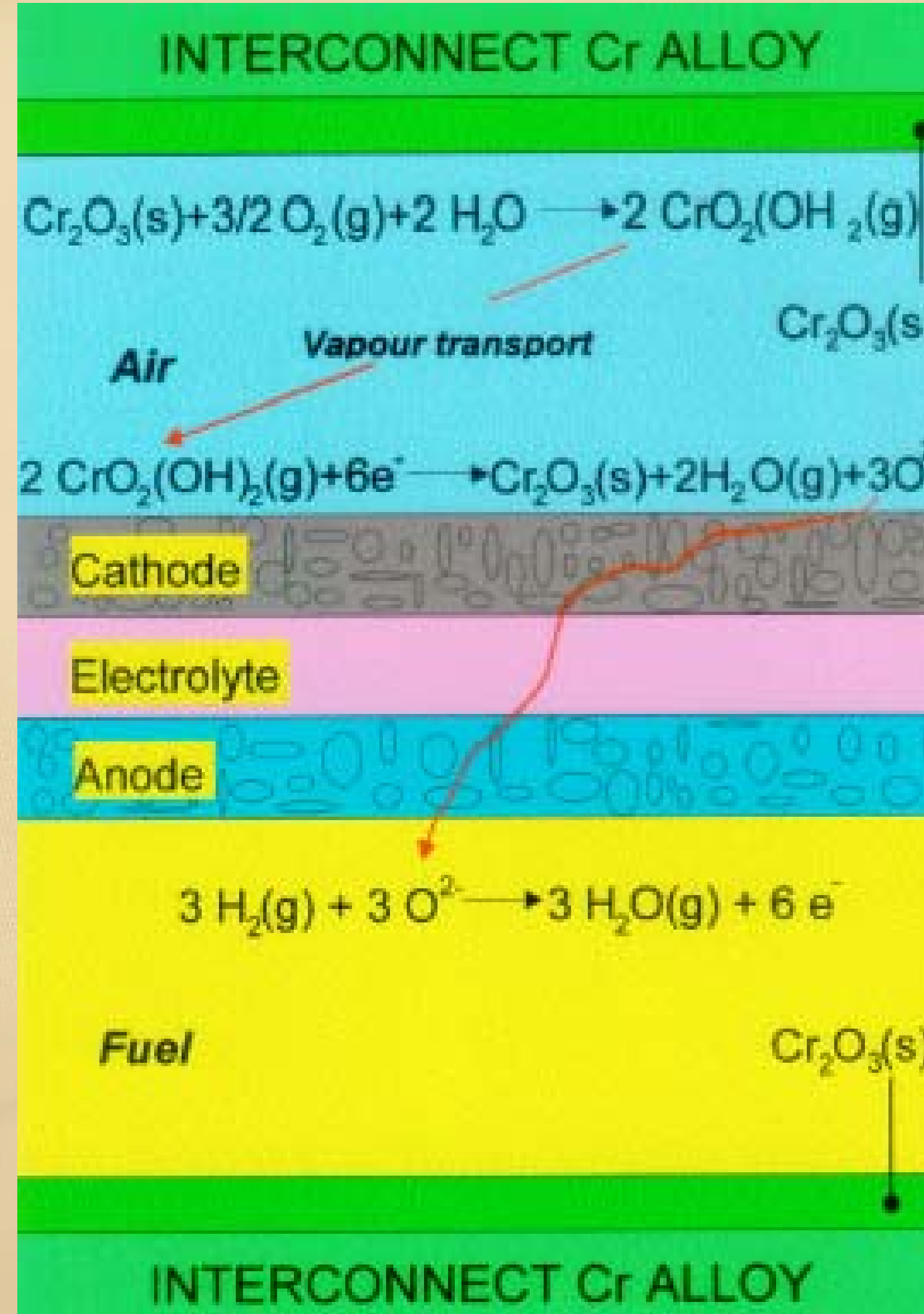
CATHODE POISINING

Stack Degradation

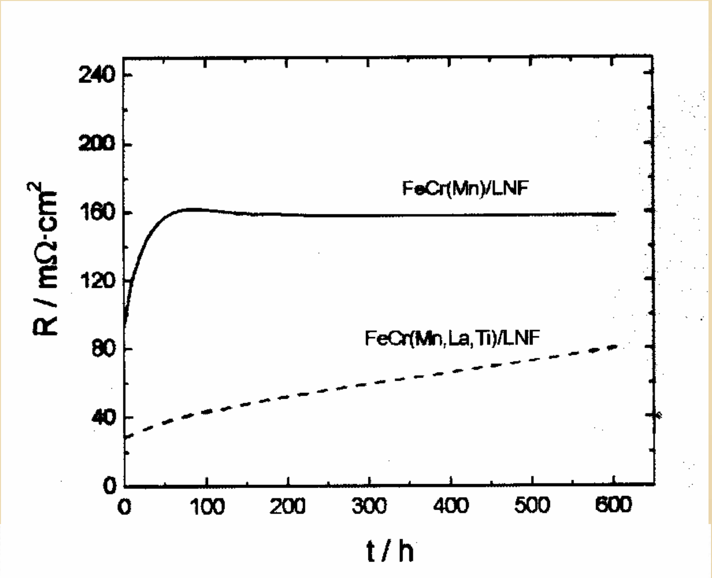


<u>Problem</u>

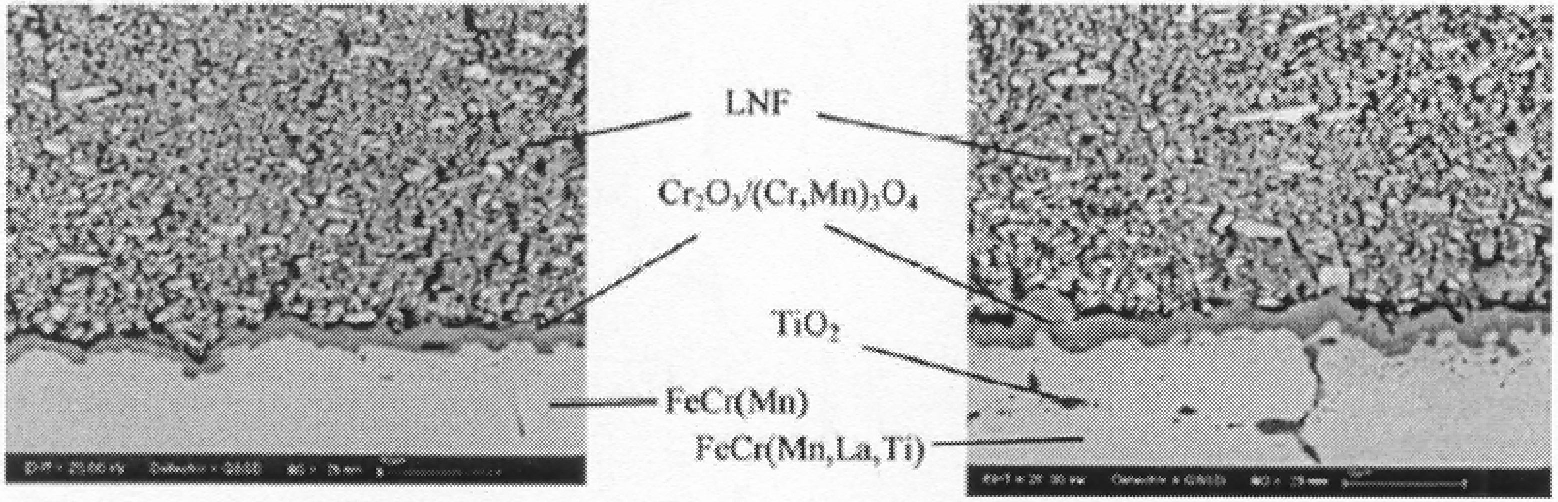
Reduces the active sites at the tpb (cathode poisoning) - Cell degrading at 700-800^{o}C



Cathode Protective Layer



ASR value depends on the particular composition of the steel used



R.N. Basu et al., J. Solid State Electrochem., 7, 416-20 (2003) and an International Patent

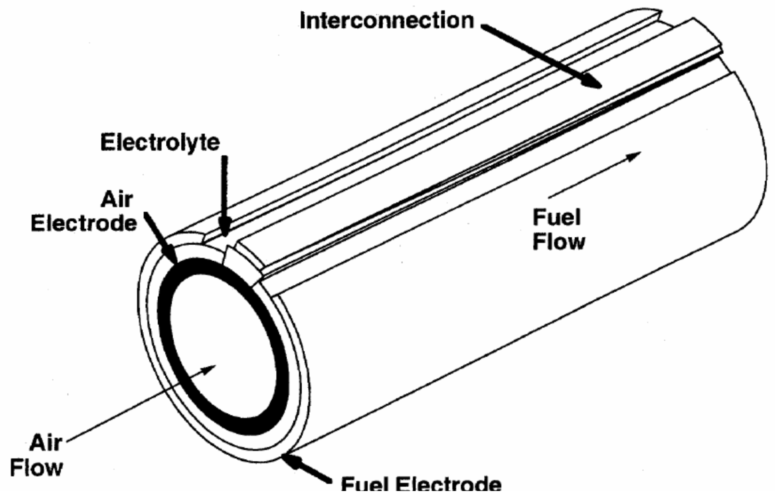
Planar Design…

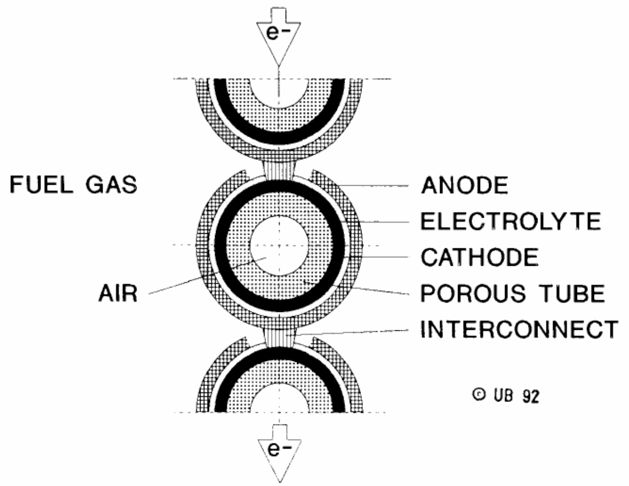
- Suitable Sealants (Thermal cyclability is a major issue)
- Supply of special steel (SS 430)
- Limited to distributed power generation (5-10kW and its multiplication) Niche Area
- System integration at least with 5x5kW SOFC Stack

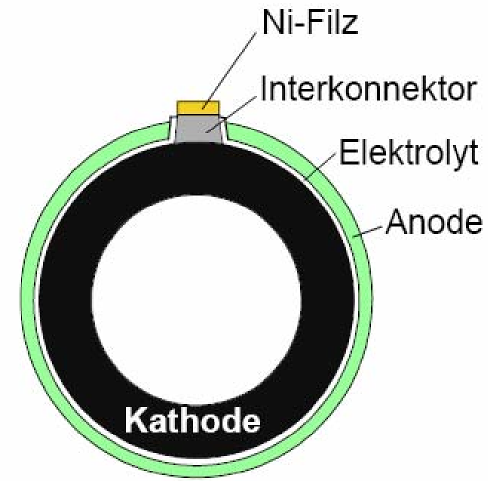
Tubular Design…

- CVD/EVD extremely sophisticated and costly (Repeatability is a major issue)
- Handling long-length tube / masking for interconnect (LCR) coating at high temperature
- High temperature operation (>950C) and low power density

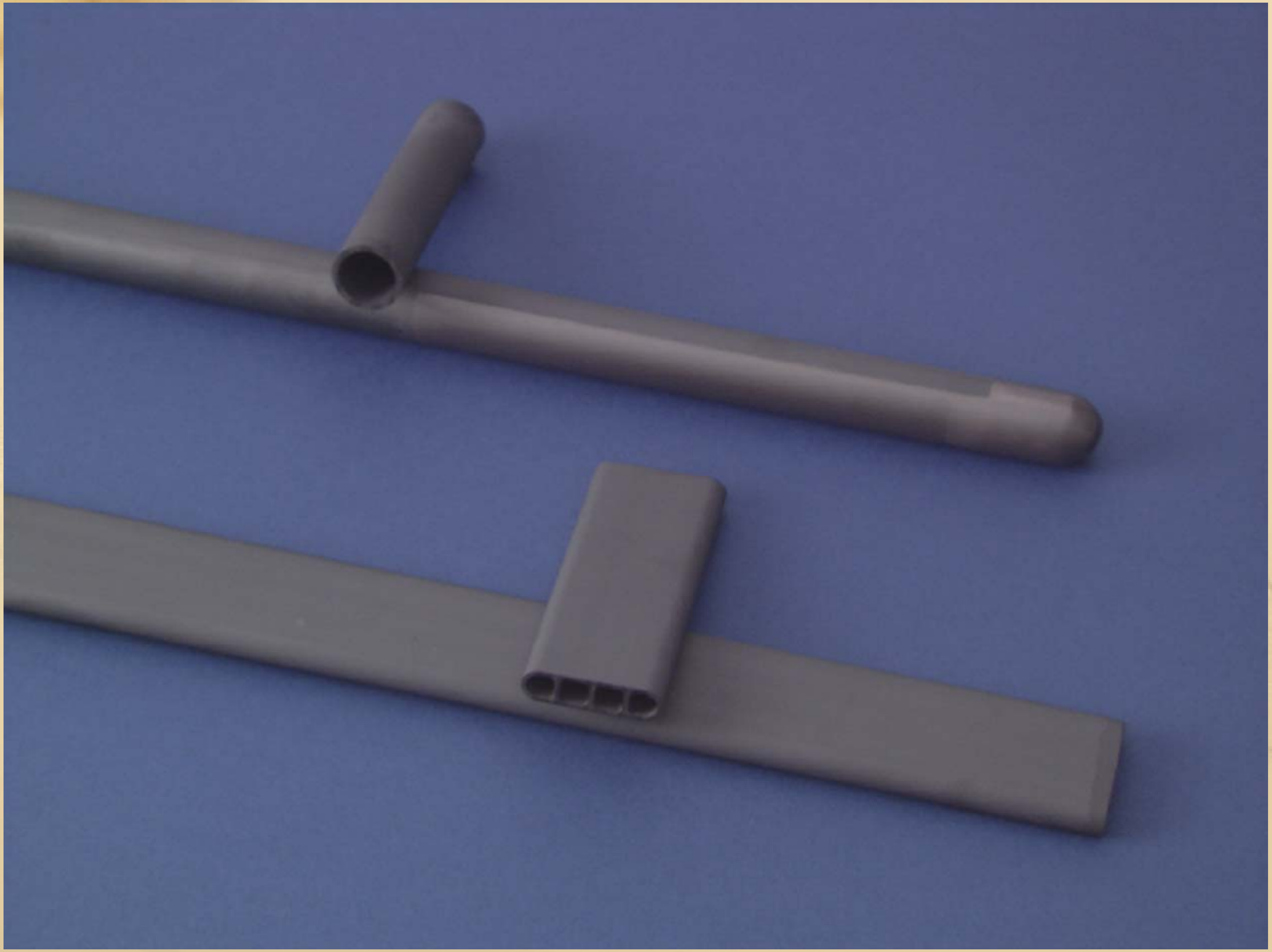
Tubular Design





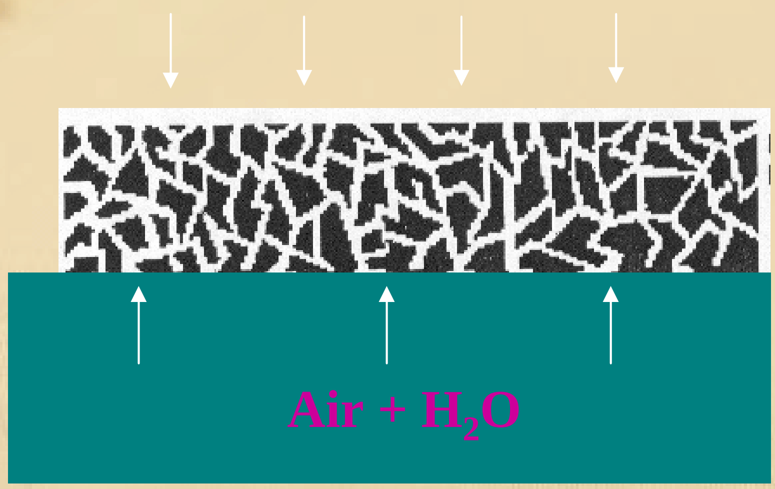


Westinghouse Tubes

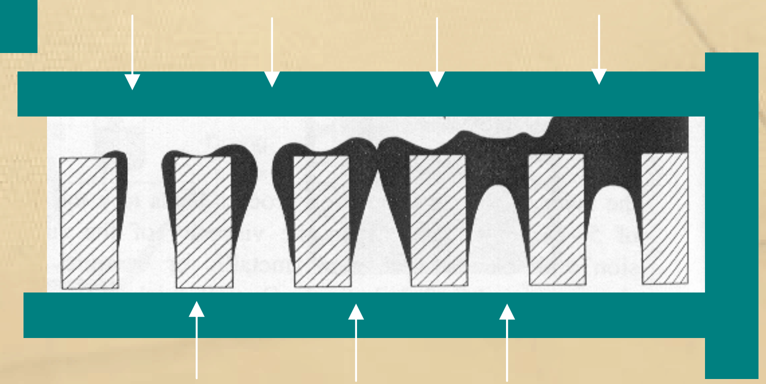


Siemens Westinghouse 1.5mts. LSM Tubes

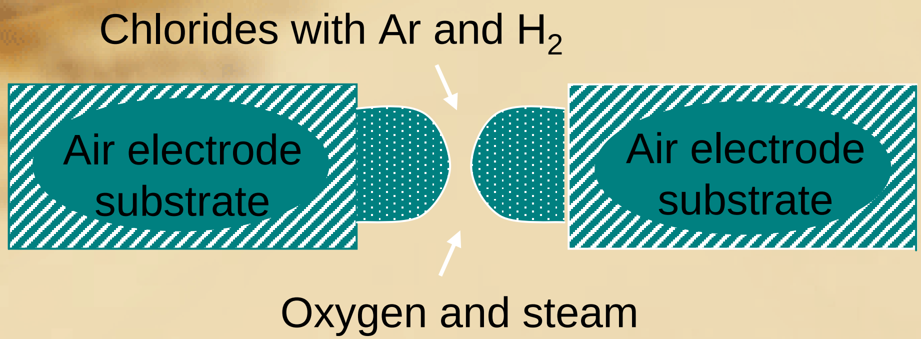
Electrochemical Vapour Deposition (EVD)



Step 1 (CVD) + Step 2 (EVD)

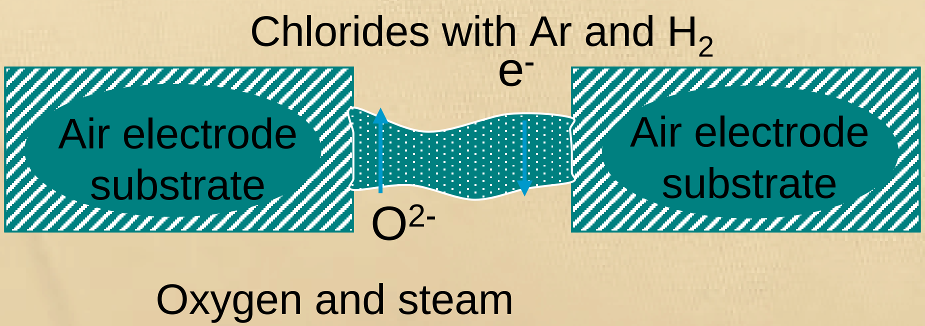


Step 1
(CVD)



$$MeCl_x + x/2\ H_2O \longrightarrow MeO_{x/2} + x\ HCl \qquad (1)$$

Step 2
(EVD)



$$MeCl_x + x/2\ O^- \longrightarrow MeO_{x/2} + x/2\ Cl_2 + xe^- \qquad (2)$$

$$x/2\ H_2O + xe^- \longrightarrow x/2\ H_2 + x/2\ O^- \qquad (3)$$

Film Thickness:

$$L^2 = 2k_p t$$

k_p = Rate constant
t = Deposition time

Wagner Oxidation process

Deposition rate for YSZ film:

At 1000°C, 1μm/min.

Where,

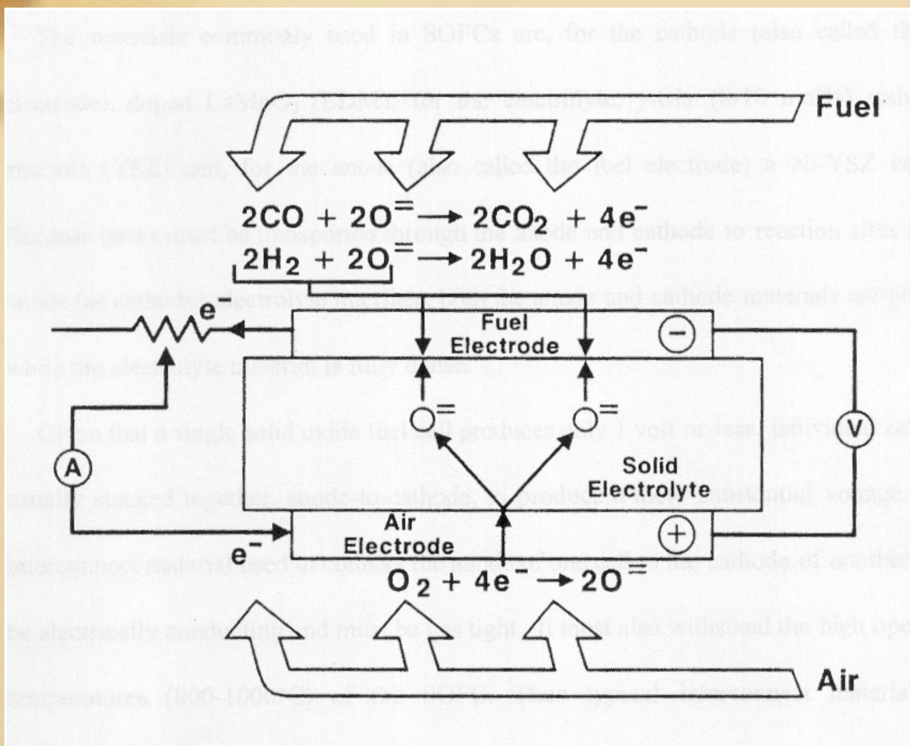
Me = Zr, Y, La, Sr, Ga and Mg etc.

Summary

- To overcome materials/fabrication related issues including scaling-up issues
- For anode-supported IT-SOFC we must have our own Glass-based sealant
- Ferritic steel-based technology, our own stack and gas-manifold design including up-gradation
- Up-scaling and System Integration (BHEL)
- Modeling and simulation (IIT-B)

Thank You

SOFC Working Principle



When a current (I), passes through the cell, the cell voltage V is given by:

$$V = E_r - IR - \eta_A - \eta_F \qquad (1)$$

Where, R = Electrical Resistance of the cell

η_A and η_F = Polarization voltage losses at the air and fuel side respectively.

$$E_r = \frac{RT}{4F} \ln\left(\frac{pO_{2(c)}}{pO_{2(a)}} \right)$$