Solid Oxide Fuel Cell Technology Development in BARC

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BARC

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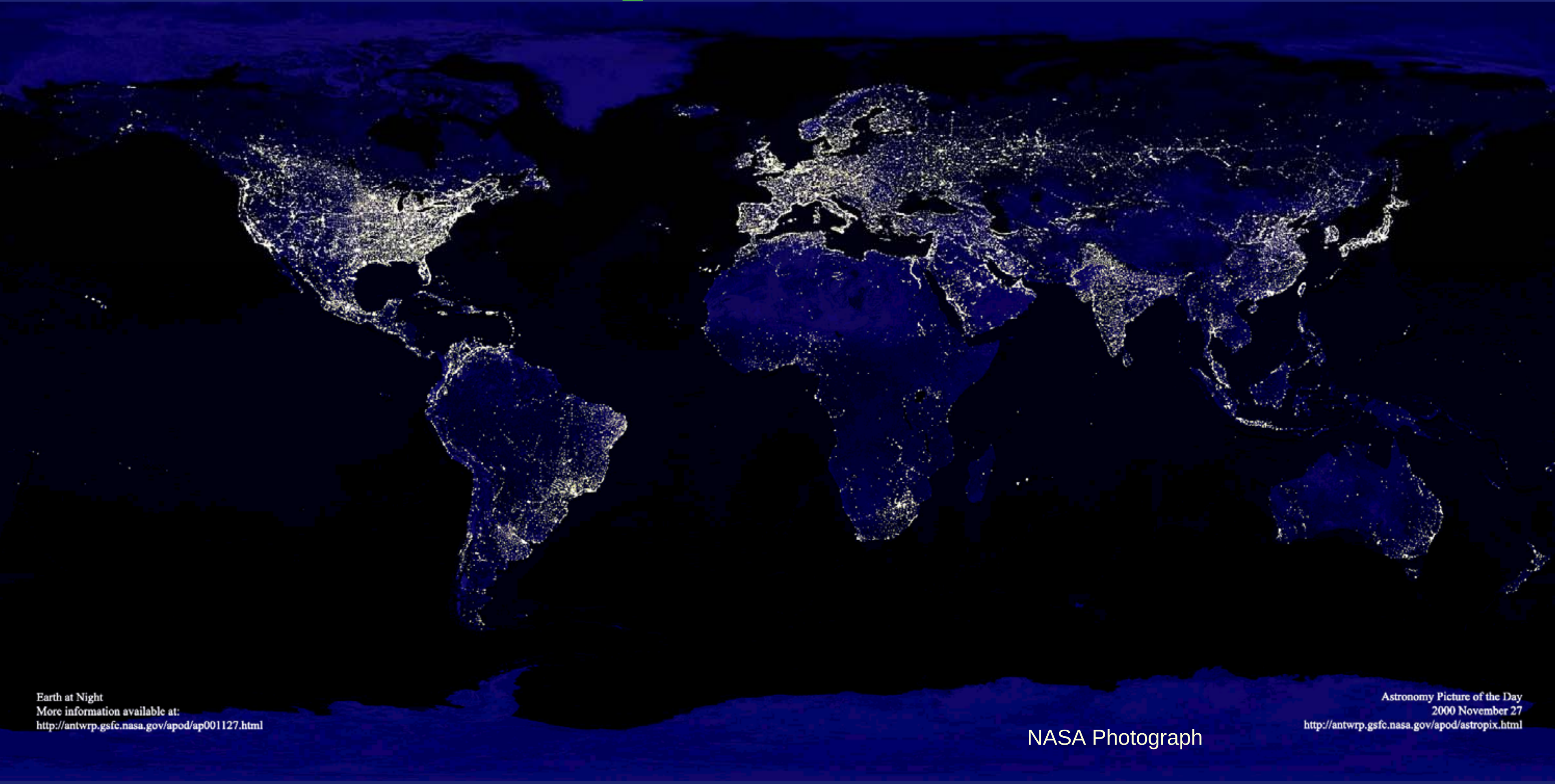
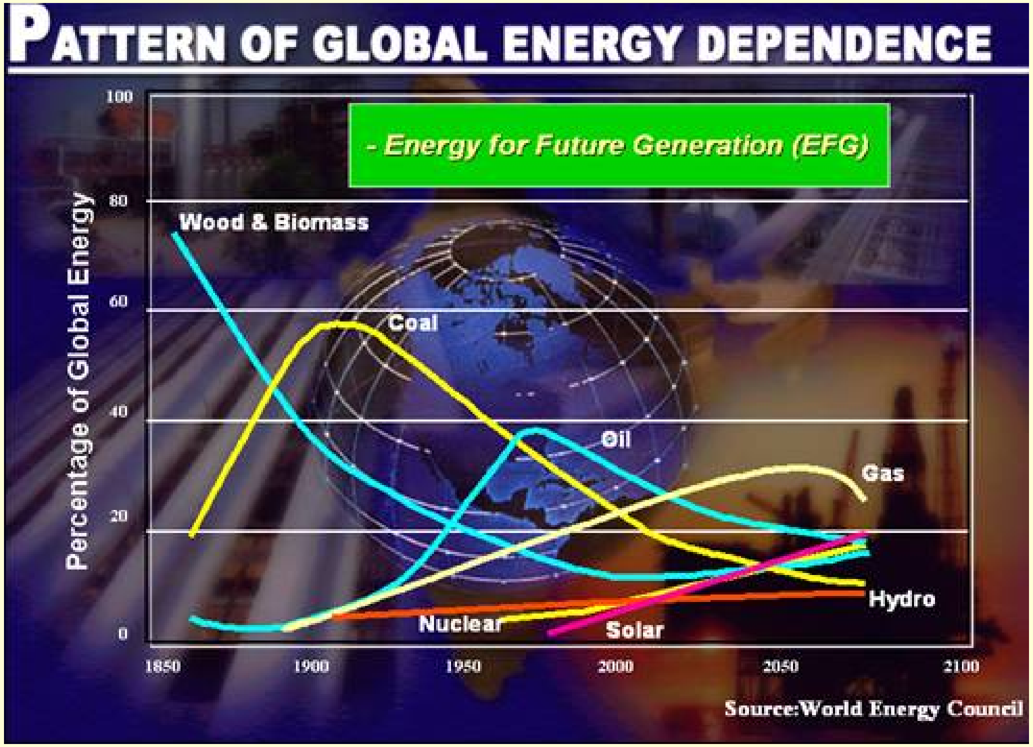


Earth at Night
More information available at:
http://antwrp.gsfc.nasa.gov/apod/ap001127.html

Astronomy Picture of the Day
2000 November 27
http://antwrp.gsfc.nasa.gov/apod/astropix.html

NASA Photograph

B. P. Sharma, A. K. Suri, S. K. Mitra, P. Ragunathan, P. K. Sinha, John T. John, and A. Ghosh



Source:World Energy Council

Future energy systems

- Solar
- Hydrogen-based
- Nuclear etc.

Outline of the Presentation

Hydrogen as future energy carrier

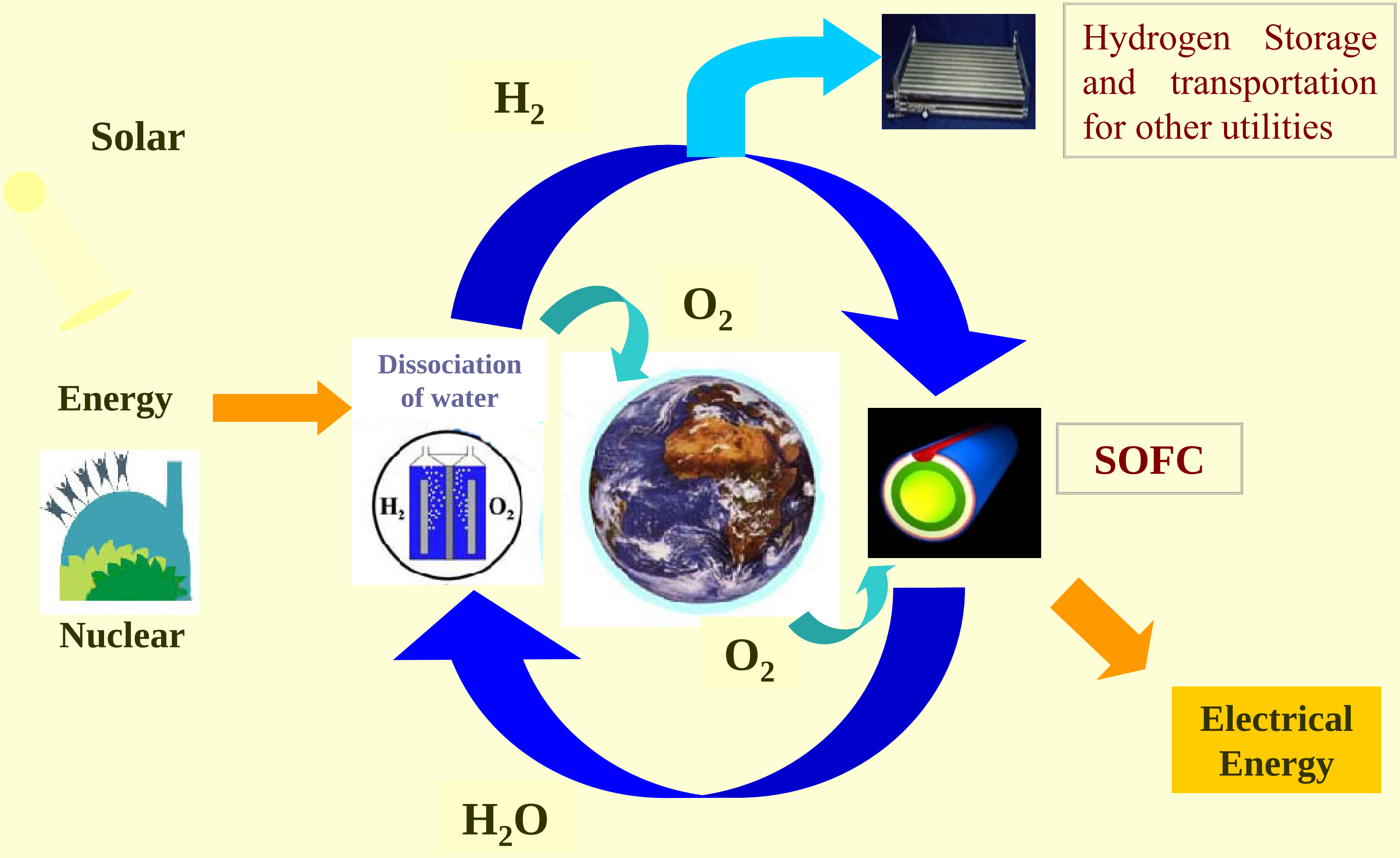
Production of hydrogen

Hydrogen storage

Direct conversion of hydrogen energy through solid oxide fuel cell

- ***Materials***
- ***Cell Design***
- ***Fabrication Techniques***

Complete Hydrogen Cycle



H_2

Hydrogen Storage and transportation for other utilities

Solar

O_2

Energy

Dissociation of water

SOFC

Nuclear

O_2

Electrical Energy

H_2O

Hydrogen Fuel: Technological Challenges

-Production and delivering hydrogen at low cost

Pyrolysis, Electrolysis, Photolysis

-Storage system (Compact, light wt., safe, efficient, low cost)

Pressurized Gas, liquid, Solid Absorbents

-Efficient conversion

Fuel Cells (Direct Conversion of Chemical Energy to electrical energy)

Materials Design Safety

Production of Hydrogen

Hydrogen from Water

Hydrogen produced from water alone can serve the purposes of an ideal, sustainable and environment friendly clean energy economy

Prospective water based hydrogen production techniques are:

1) Electrochemical production (Water electrolysis)
2) Electrothermal water decomposition (Steam electrolysis)
3) Thermochemical water splitting (Thermo chemical cycles)

Hydrogen Production by Water Electrolysis

- Alkaline Water Electrolyser: 10 Nm^3/h capacity is developed by BARC: Technology is available for production

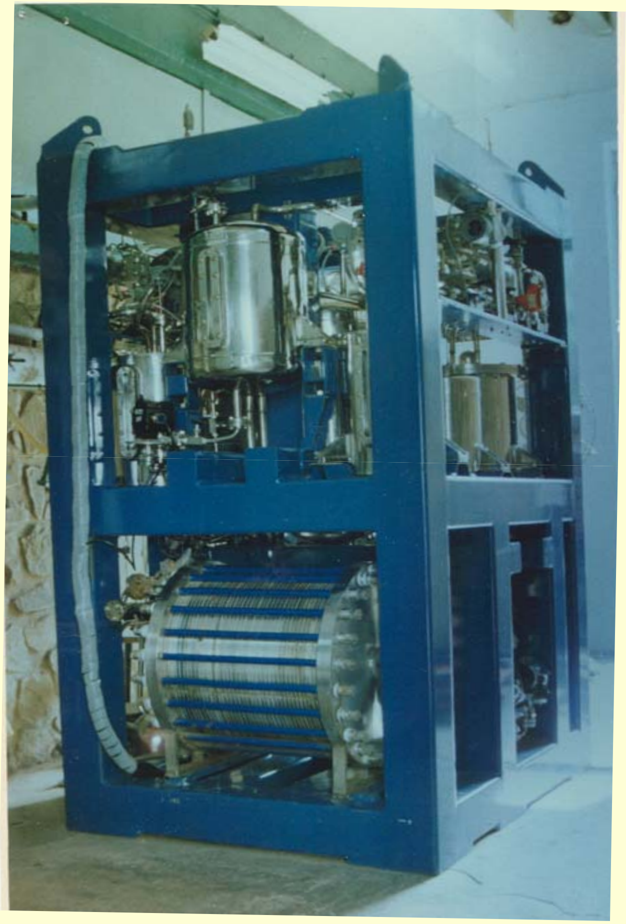
- Alkaline Water Electrolyser of 30 Nm^3/h is being developed (Time frame: 2005-08)

- BARC is also developing Solid Polymer Electrolyte (SPE) Water Electrolyser (Time frame: (2005- 08)

- BARC is also working on High Temperature Steam Electrolyser:

  Experimental studies with single tube cell are planned during 2005 - 08 and with multi-tube cell are planned in 2008 –12

HIGH CURRENT DENSITY COMPACT ELECTROLYSER



Compact electrolyser of filter press type

A 40-cell electrolysis module (weighing 900 kg) incorporating Porous Nickel Electrode operates at a high current density of 4500 Am^{-2} which is much higher than conventional cells in the market (1500 Am^{-2} or below)

- The electrolyser operates at 55^0 C and 0.16 MPa to produce 10 Nm^3/h of hydrogen

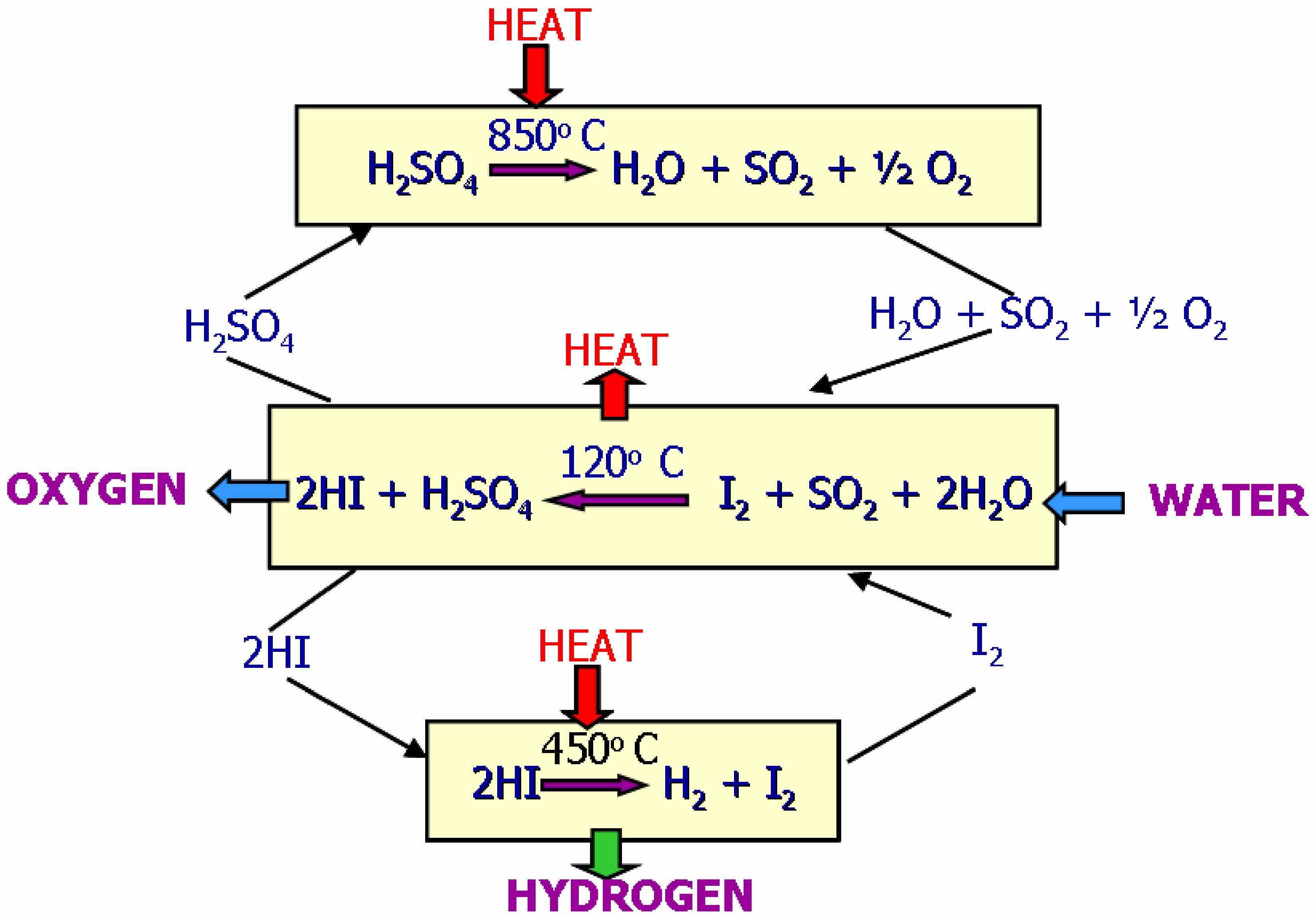
HYDROGEN FROM WATER

Comparison Of Thermo Chemical Processes

	I-S Process	Ca-Br Process	Cu-Cl Process
Efficiency (%)	57	40	41
Operating temperature	950˚ C	760˚ C	550˚ C
Process Streams	Liquid & gas	Solid & gas	Solid, liquid & gas
Development stage	Fully flow sheeted	Fully flow sheeted	R&D stage
Demonstration	Pre pilot plant	Pilot plant	Not demonstrated
Corrosion	High	High	low
Capital Cost	Low	High	NA

Hydrogen from Water: Thermochemical Process

Iodine-Sulfur (IS) Process – Reaction Scheme



HEAT

$$H_2SO_4 \xrightarrow{850^o\,C} H_2O + SO_2 + \tfrac{1}{2}\,O_2$$

H_2SO_4

$H_2O + SO_2 + ½\ O_2$

HEAT

OXYGEN

$$2HI + H_2SO_4 \xleftarrow{120^o\,C} I_2 + SO_2 + 2H_2O$$

WATER

2HI

HEAT

I_2

$$2HI \xrightarrow{450^o\,C} H_2 + I_2$$

HYDROGEN

Hydrogen Storage

Hydrogen storage

- **High-pressure storage:**

  heavy and bulky vessels

- **Liquefied hydrogen:**

  attractive weight and volume

  requires energy to liquefy

  the storage system has potential risks

- **Solid Absorbents**

  Metal hydrides
  Complex Hydrides
  Microporous materials

Absorption under ambient conditions of Temp and Pressure

Desorption occurs at elevated Temp

Metal Hydrides

- Hydrogen is distributed compactly throughout the metal lattice.
- Metal hydrides, therefore, represent an exciting method of storing hydrogen.
- They are inherently safer then compressed gas or liquid hydrogen
- They have higher hydrogen storage capacity. In fact, certain hydrides can store more than twice the amount of hydrogen that can be stored in the same volume of liquid hydrogen.
- The key to practical use of metal hydrides is their ability to both absorb and release same quantity of hydrogen many times without deterioration.

Hydrogen Storage Capacity

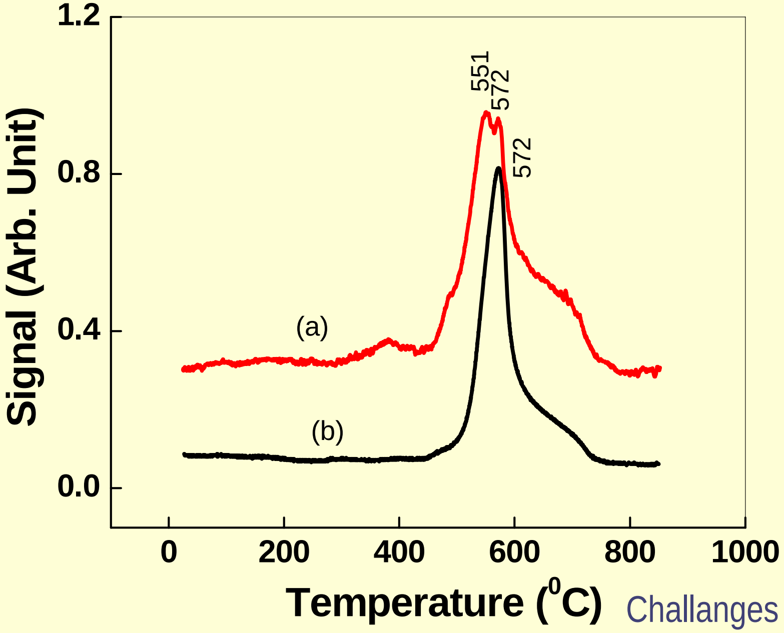
Storage media	Hydrogen storage By weight (%)	Energy density By weight (cal/g)	Energy Density By volume (cal/ml)
Gaseous H_2	**100**	**33,900**	**271**
Liquid H_2	**100**	**33,900**	**2373**
MgH_2	**7.6**	**2373**	**3423**
Mg_2NiH_4	**3.3**	**1071**	**2745**
VH_2	**3.8**	**701**	**3227**
$FeTiH_2$	**1.9**	**593**	**3254**
$LaNi_5H_6$	**1.4**	**464**	**3017**

The standard set by US Department of Energy (DOE) requires

A system-weight efficiency (the ratio of stored hydrogen weight to system weight) of 6.5-wt % of hydrogen and a volumetric density of 62 kg H_2/m^3

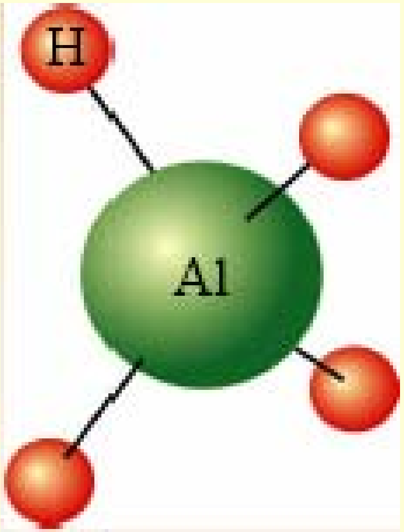
Hydrogen Storage in TiH_2

- Ti sponge absorbs hydrogen at room temperature below one atmospheric pressure forming TiH_2
- Ti-hydride desorbs hydrogen at around 534° C
- These properties of titanium sponge are ideally suitable for a getter material for handling and storage of hydrogen and its isotopes



Temperature programmed desorption (TPD) plots of (a) TiH_x and (b) TiD_x

Complex Aluminum Hydrides



Examples	Capacity* (Wt%)
$Na(AlH_4)$	5.6
$Li(AlH_4)$	7.9
$Zr(AlH_4)_2$	3.9
$Mg(AlH_4)_2$	7.0

* *Reversible Theoretical Capacity*

Hydrogen Storage in Carbon Nano Structures

Hydrogen storage in carbon nanostructures is a very attractive topic owing to the low density of carbon and its high potential storage capacities.

Challenges:

1. **The mass production of carbon nanotubes at a reasonable cost.**
2. **Purification and surface functionalisation of carbon nanotubes.**
3. **Understanding the adsorption/desorption mechanisms and the volumetric capacity of carbon nanostructures.**

Direct Conversion of Hydrogen Energy

Solid Oxide Fuel cell

Direct Conversion of Chemical Energy to Electrical Energy

…Carnot Cycle is not the limitation

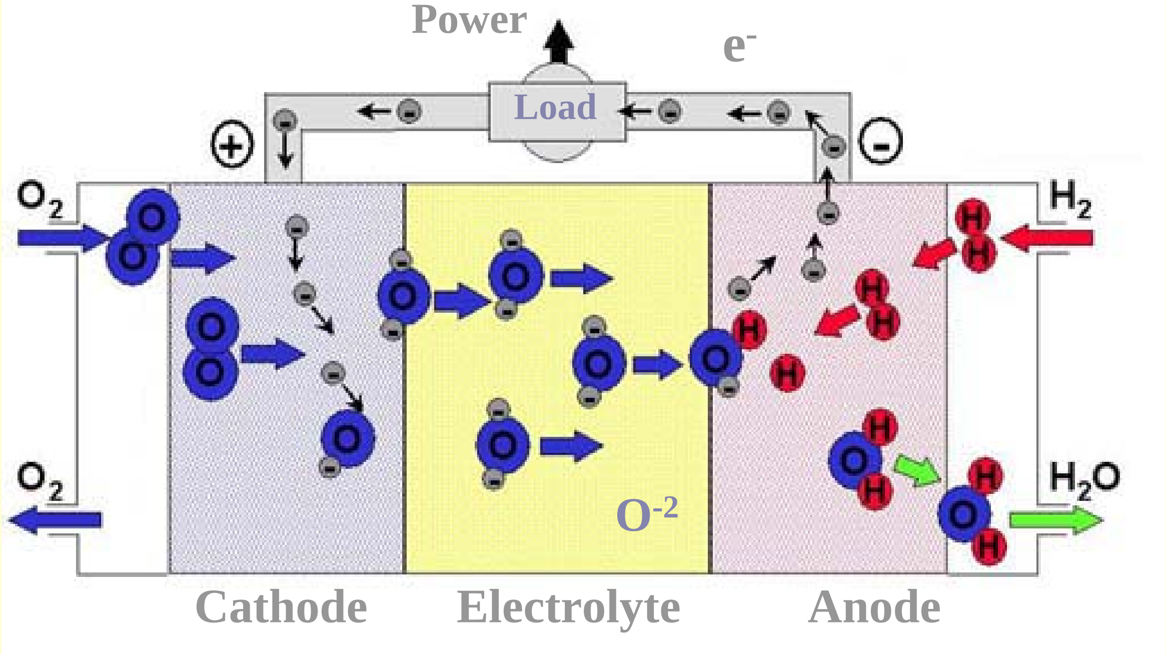
Comparison of different Fuel Cells

	PAFC	**MCFC**	**SOFC**	**PEMFC**
Electrolyte	Phosphoric Acid	Molten Carbonate Salt	Ceramic	Polymer
Operating temperature	190°C	650°C	800-1000°C	80°C
Charge Carrier	H^+	CO_3^{-2}	O^{-2}	H^+
Fuels	Hydrogen (H_2) Reformate	H_2/CO/ Reformate	$H_2/CO_2/CH_4$ Reformate	H_2 Reformate
Reforming	External	External/ Internal	External/ Internal	External
Prime Cell component	Graphite-based	Stainless steel	Ceramic	Carbon based

Solid Oxide Fuel Cell (SOFC)

Fuel cell utilizes hydrocarbon/hydrogen as fuel which reacts electrochemically with oxygen

Principle of SOFC



Cathodic Reaction : $\frac{1}{2} O_2 + 2e^- \longrightarrow O^{2-}$

Anodic Reaction : $H_2 + O^{2-} \longrightarrow H_2O + 2e^-$

Salient Features of SOFC

- Highly efficient electric power generation system (can be as high as 70-80%)
- Effective utilization high temperature waste heat
- Direct reforming of gaseous fuel in 1000° C operating SOFC
- Environmental friendly power generation
- All ceramic component---- A Challenge in Materials and Manufacturing Technology

Target: Low cost of SOFC system by achieving

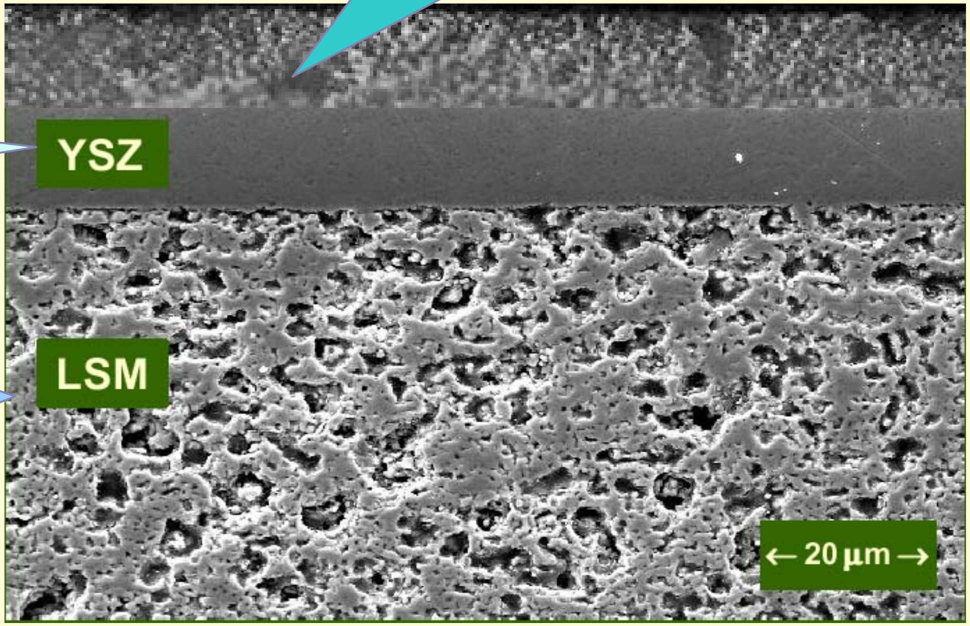
- High power density (0.5 W/cm^2)
- Improved durability
- Low material and manufacturing cost

Microstructural Requirements

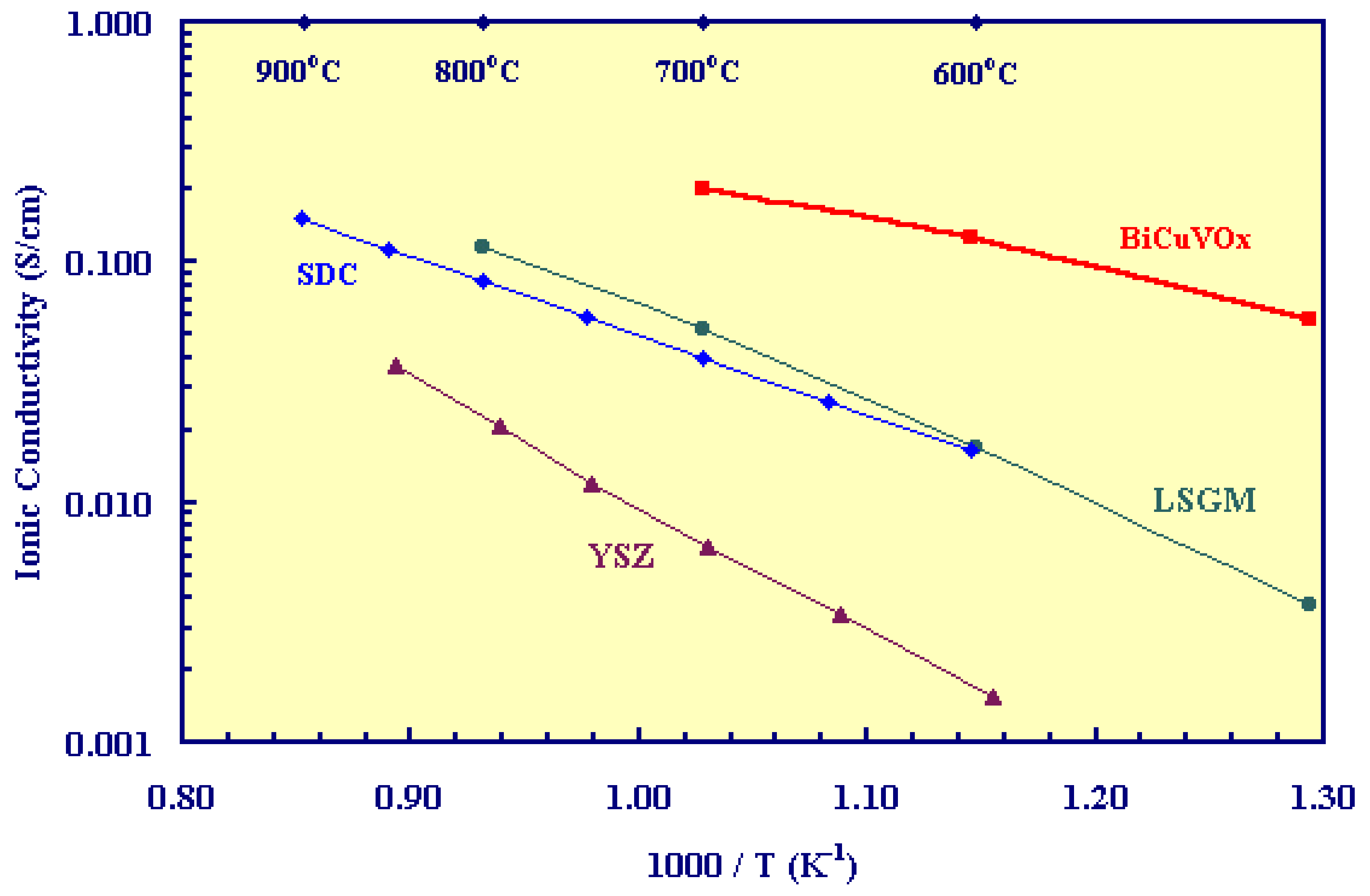
Electronic Conductor
30-40% Porous
Stability, Matching TCE
No chemical interaction

Ionic Conductor
Fully Dense

Mixed conductor
Porous (30 -40 %)
Stability
No chemical interaction
Matching TCE

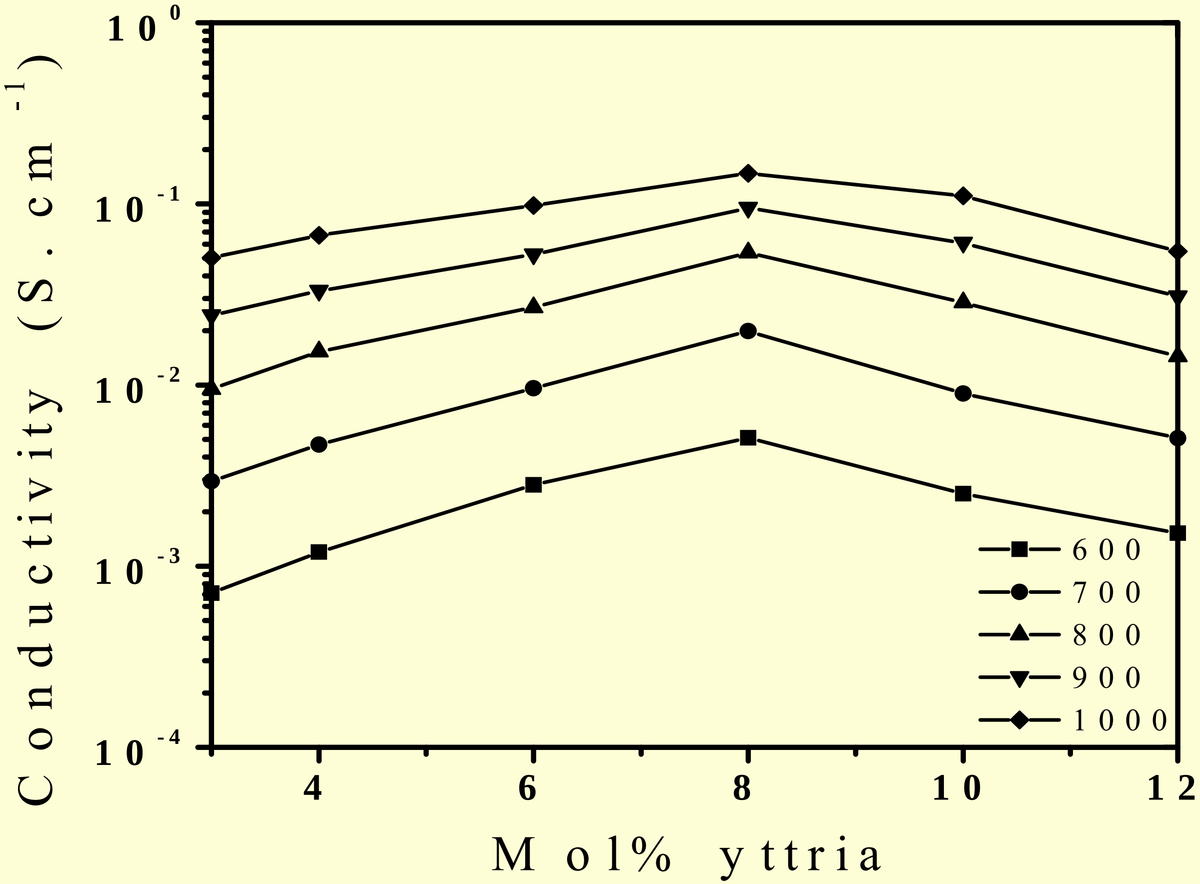


Ionic Conductivity of different Electrolyte



Zirconia based	Ceria based	Lanthanum oxide based	Bismuth oxide based
Excellent Stability in oxidizing and reducing environment **Excellent Mechanical stability (3YSZ)** **Well studied material**	**Good compatibility with cathode Materials**	**Good compatibility with cathode Materials** **High Conductivity**	**High Conductivity**
Lower Ionic Conductivity	**Electronic conduction at low pO_2** **Poor mechanical strength**	**Ga evaporation at low pO_2** **Formation of stable secondary phases** **Incompatible with NiO** **Poor mechanical strength**	**Thermodynamic instability in reducing atmosphere** **Volatilization of Bi_2O_3** **High corrosion activity** **Poor mechanical strength**

Total conductivity of YSZ at different temperatures as a function of yttria content



In YSZ the maximum conductivity is for 8 mol% Yttria doping

Fuel Cell Development at BARC

The Fuel Cell Development Program at BARC aims at

- Technology Development and Demonstration for **5 kW tubular SOFC** and **1 kW Planar Multi-cell PEMFC systems** complete with fuel generator and power conditioner
- Setting up of facilities and infrastructure for fabrication/ integration of fuel cell components and other subsystems, specially **thin ceramic films for SOFC** and **Membranes and MEA (Membrane Electrode Assembly) for PEMFC**
- Modular Cell design for standardization and Scale up

State-of-the-art SOFC
Bench mark properties for component materials

1. Cathode

Composition : LSM ($La_{0.9}Sr_{0.1}MnO_3$)
Porosity : 40% (pore size 20-50 μm)
Conductivity : 100 S/cm at 1000° C
TEC : 10 – 12 ppm/$^{\circ}$ C
Dimensions : ID-14mm, Wall -2mm, L-160mm

2. Electrolyte

Composition : YSZ [$(ZrO_2)_{0.92}(Y_2O_3)_{0.08}$]
Porosity : Nil, permeability should be zero
Conductivity : Ionic ~ 0.1S/cm
TEC : 10.5 ppm/$^{\circ}$ C
Dimensions : Film thickness ~ 50 μm, L~125mm

State-of-the-art SOFC
Bench mark properties for compositions

3. Anode

Composition : Ni-YSZ cermet (Ni- 60% by wt)
Porosity : 40% (pore size 20-50 μm)
Conductivity : 1000-1500 S/cm
TEC : 10 – 12 ppm/^{O}C
Dimensions : OD- 18.1 mm, t~ 100 μm, L~125 mm

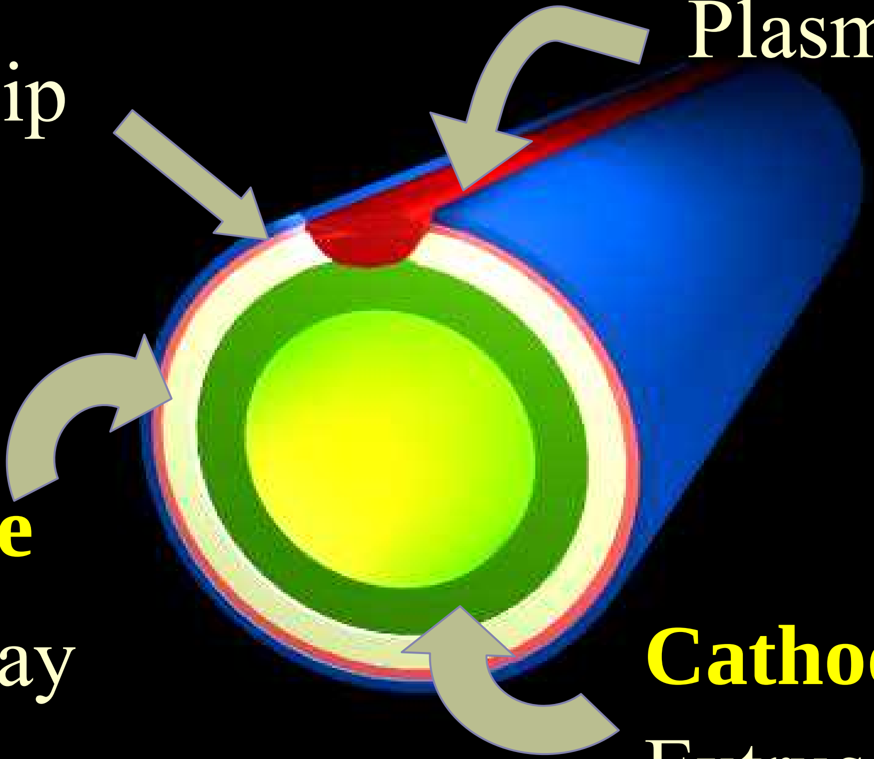
4. Interconnect

Composition : LCM [$La_{0.95}Mg_{0.05}(CrO_3)$]
Porosity : Nil, permeability should be zero
Conductivity : 5-10 S/cm at 1000^{O} C
TEC : 10-12 ppm/^{O} C
Dimensions : W- 5mm, L- 125mm, t~100 μm

SOFC: Designs

1. **Tubular Design**
    - Pioneered by Siemens- Westinghouse
2. **Planar Design**
    - Conventional ‘electrolyte supported’ concept
    - Cathode supported design
    - Newer – Anode supported concept
3. **Monolithic design**

SOFC Development



Anode

Screen printing/Dip Coating

Interconnect

Plasma Spray

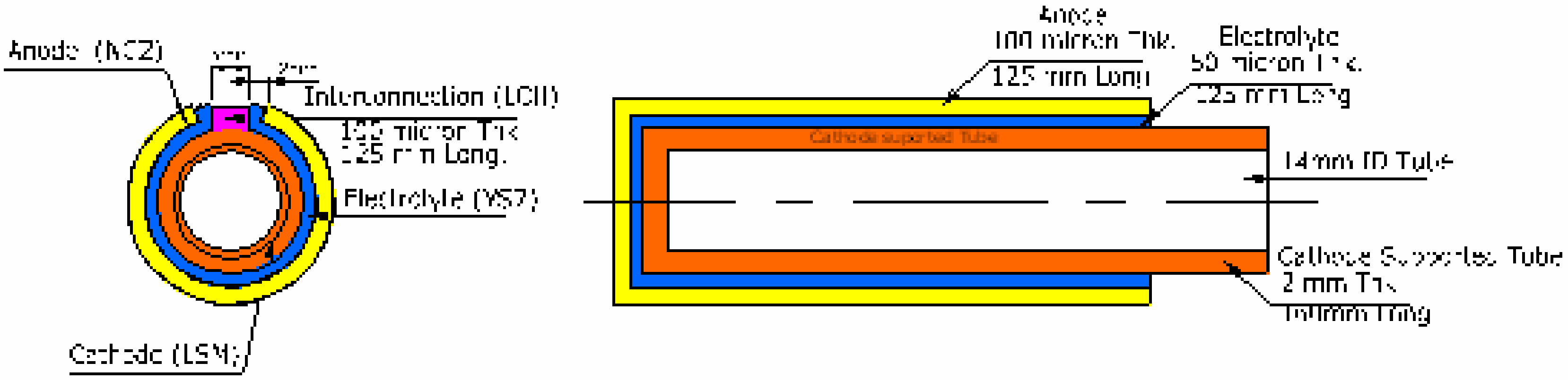
Electrolyte

EVD / Spray coating / Gel Coating/ Dip Coating

Cathode Tube

Extrusion / CIP

Cell Dimension and Design of Tubular SOFC at BARC



Single Tube Cell

HWD/SKM/pillai 27.3.02

Powder Preparation

Solution synthesis route a promising approach

- Citrate gel
- Oxalate precipitation
- Hydrothermal Synthesis
- Combustion Synthesis
- Spray drying

Synthesis of 8YSZ by Hydrothermal Technique

$ZrOCl_2$

$Y(NO_3)_2$

Mixed at stoichiometric ratio (0.1M)

Added PEG

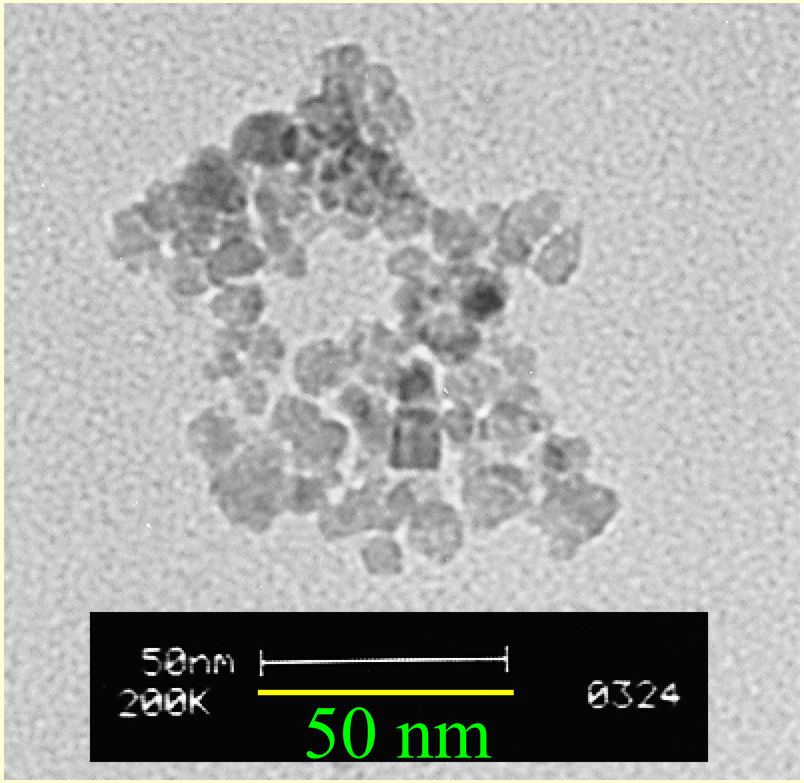
Coprecipitated in excess Ammonia

Precipitate is made Chloride free

Hydrothermal treatment at 150°C and ~100 PSI in 0.5 wt% Ammo. Polyacrylate for 24h

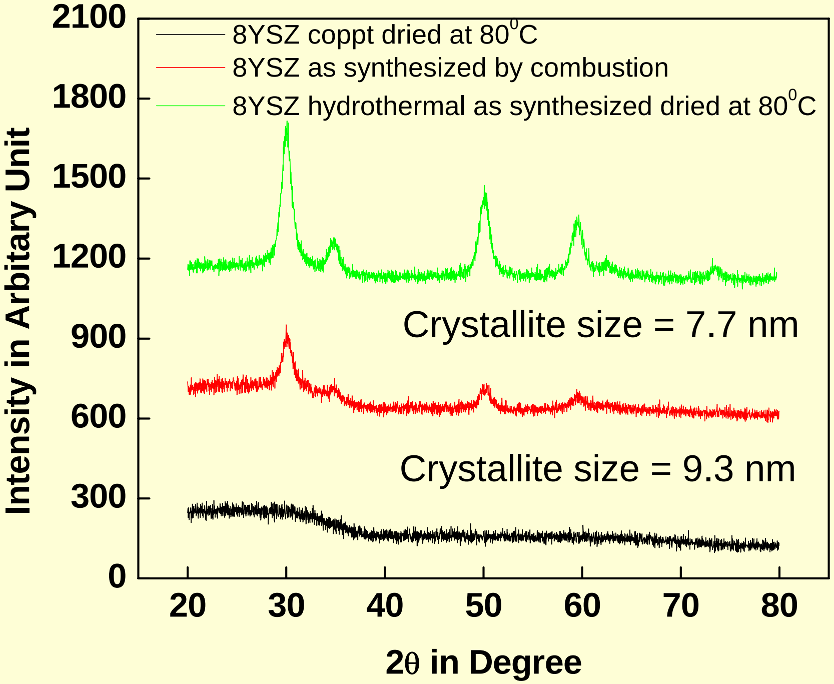
Dried at 80°C then crushed

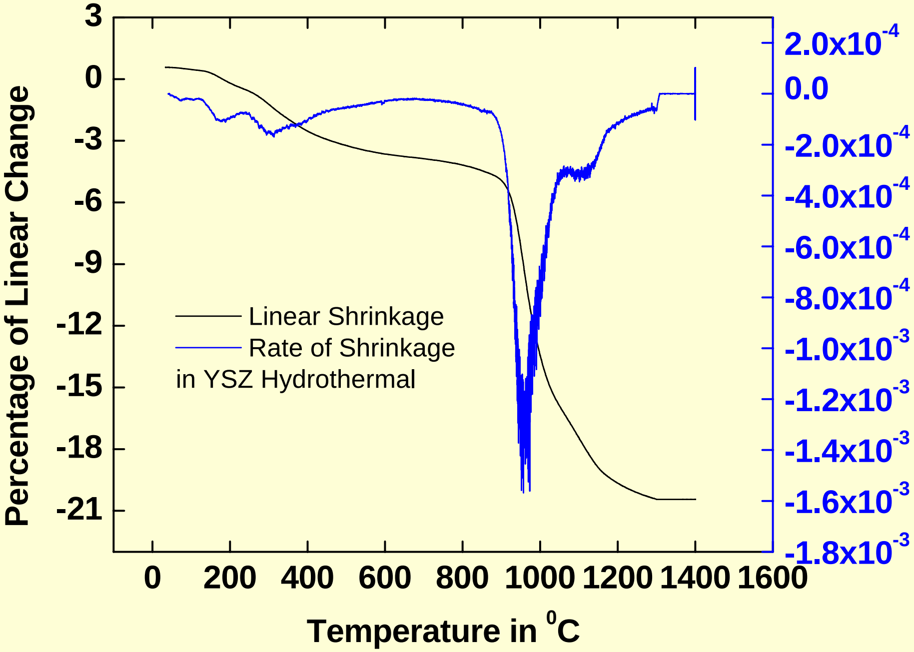
Ball milled for < 1hr

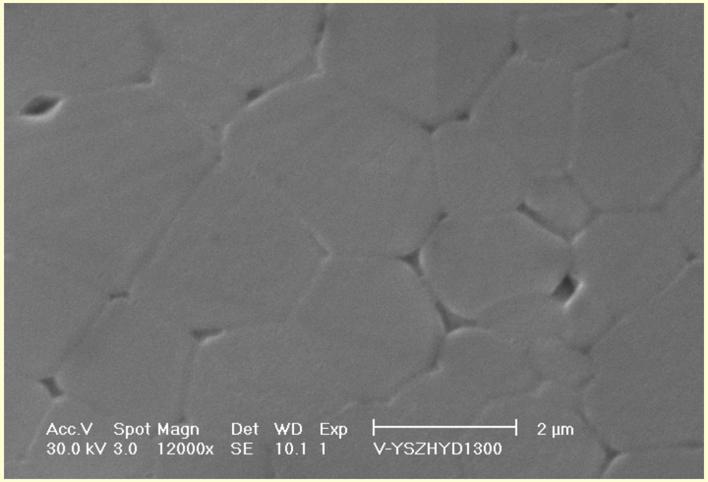


Crystallite Size = 4 to 6 nm
Surface Area = 166 m²/gm
(BET Technique)

Properties of Hydrothermally produced 8YSZ





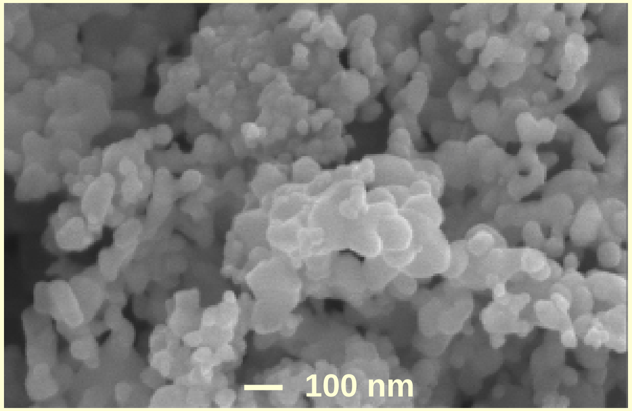


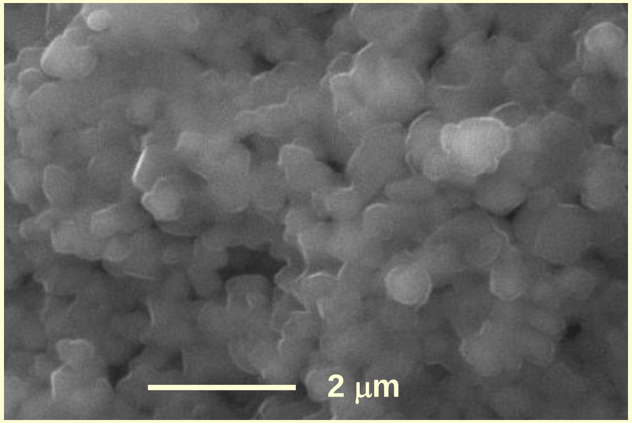
Sintered at 1300°C

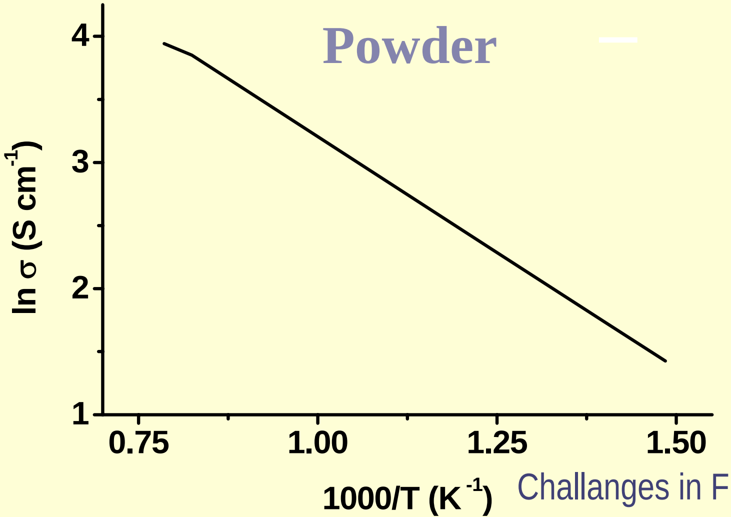
~96% ρ_{Th}

Low temperature sintering of nano-crystalline La(Ca)CrO_3 (LCR) interconnect prepared through controlled gel combustion processes

EDTA-nitrate combustion synthesis of $La_{0.70}Ca_{0.30}CrO_3$







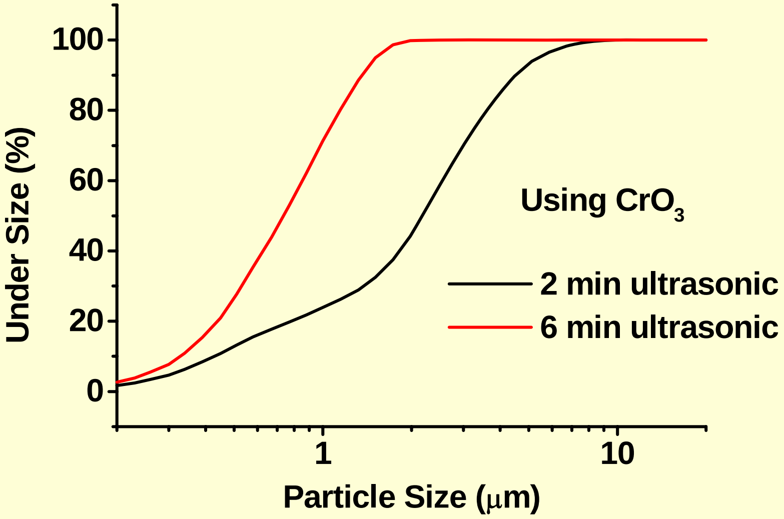
Powder

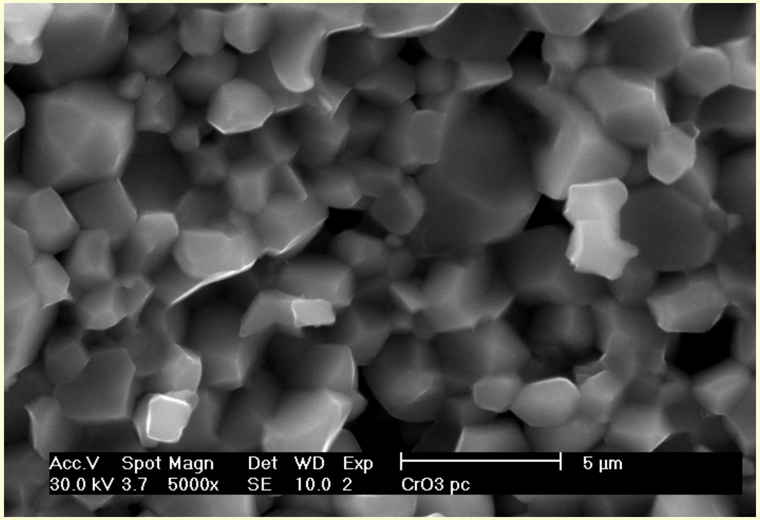
Sintered at 1250 °C

Conductivity at 1000 °C: 51 Scm^{-1}

TEC: 10.3×10^{-6} °C^{-1}

Glycine-nitrate combustion synthesis of LCR interconnect





Sintered at 1200 °C

(Fractured surface)

Lowest sintering temperature

ever reported

Conductivity at 1000 °C: 58 Scm^{-1}

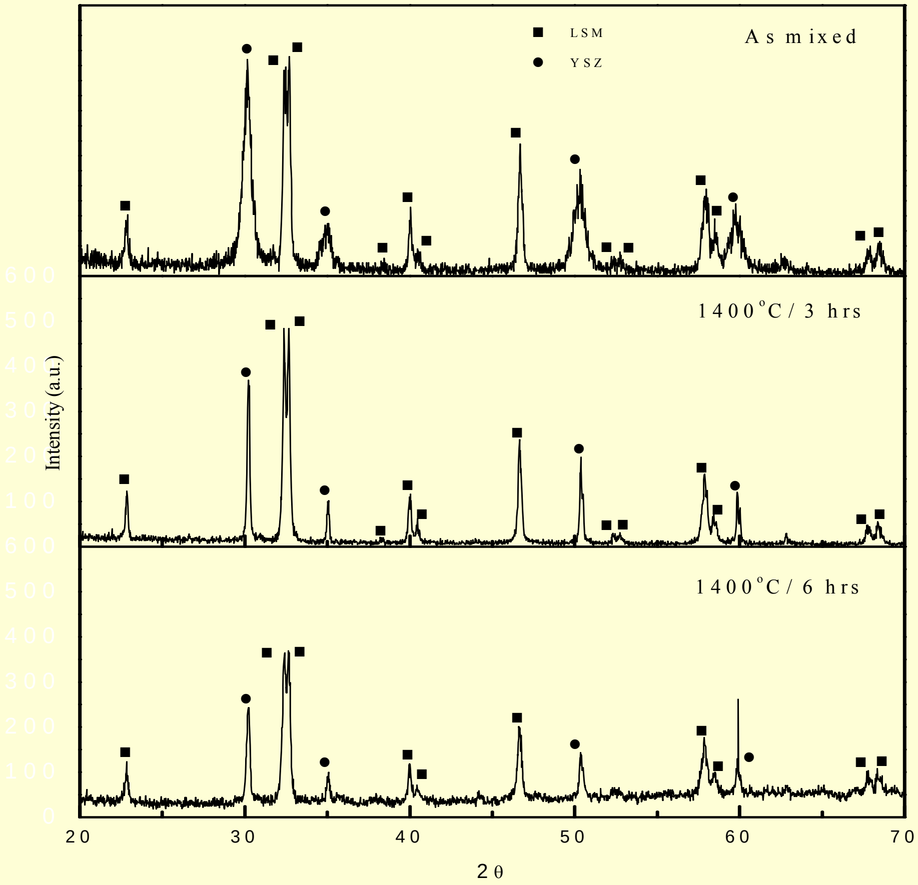
Chemical compatibility of LSM with YSZ

Powder mixture compact

- Phase analysis
- X-ray maps

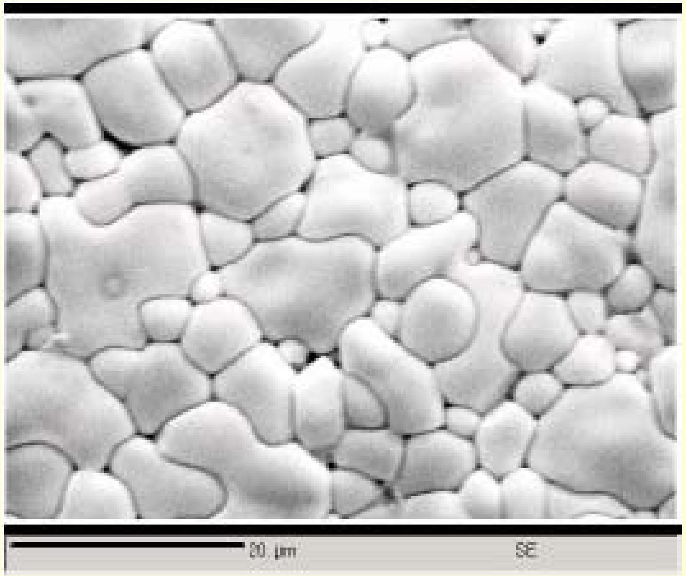
Temperature range

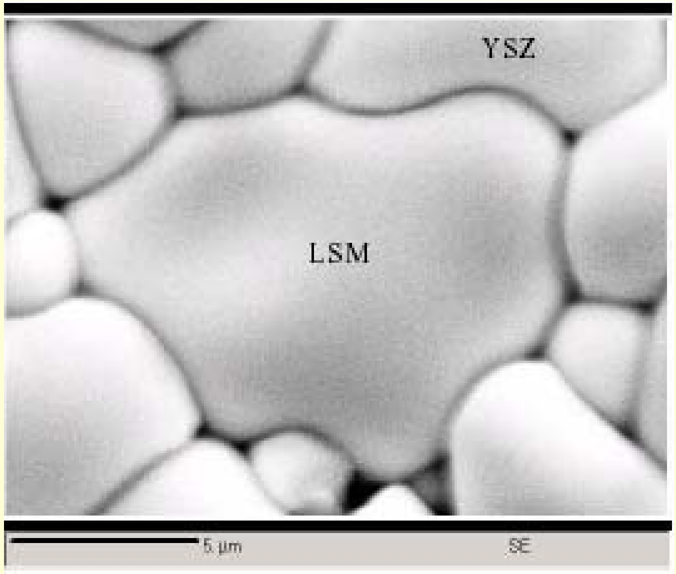
1000 – 1400° C

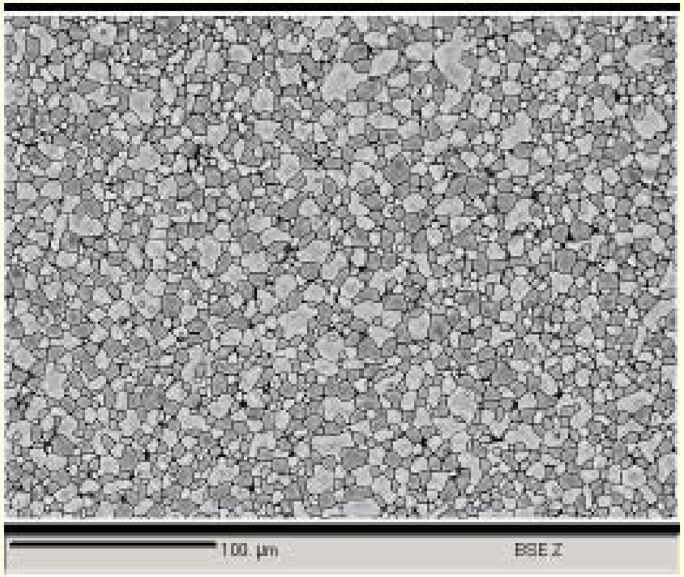


No reaction products even at 1400° C

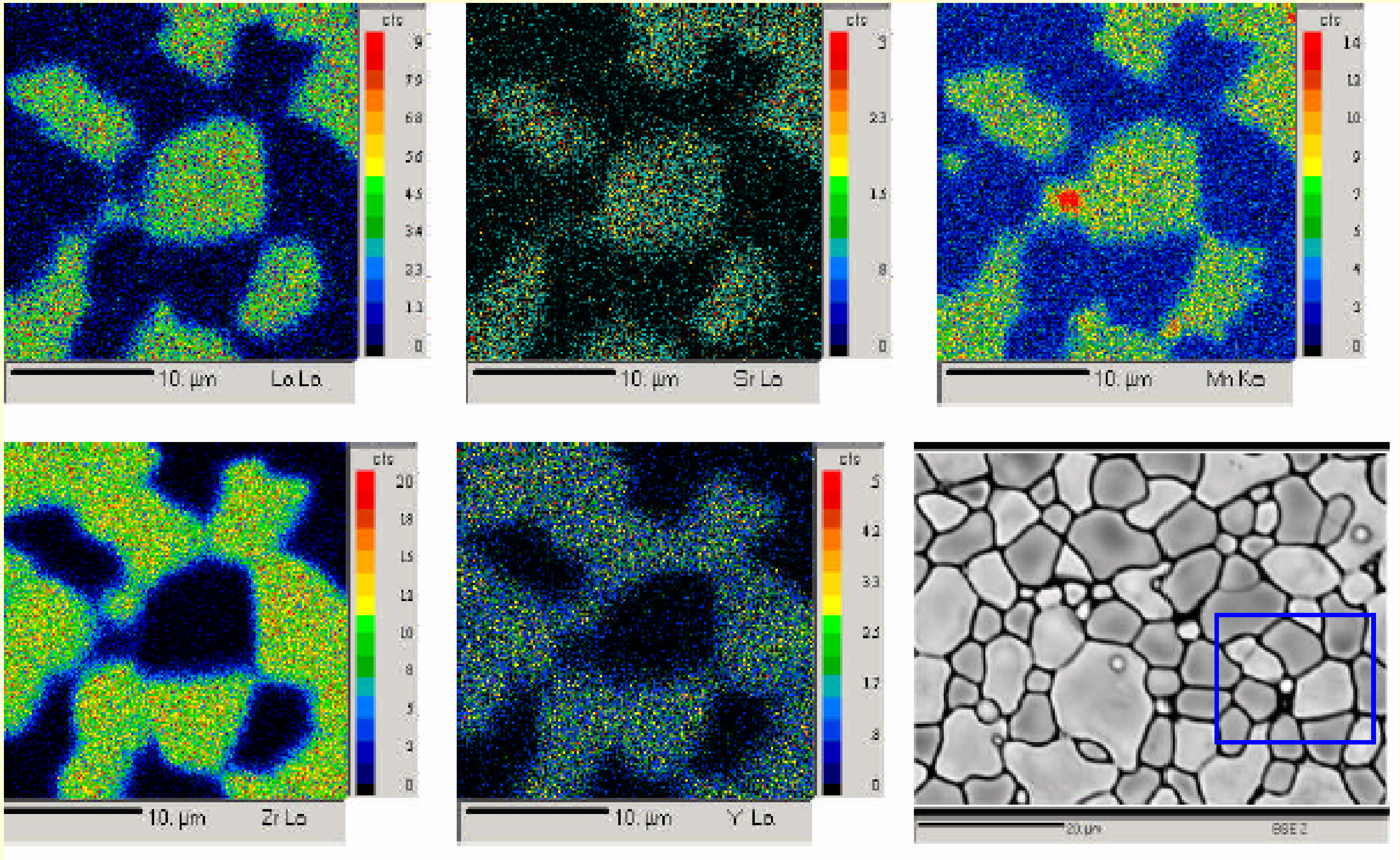
Microstructural study of YSZ-LSM: Chemical Compatibility







Electron Microprobe Micro analysis of YSZ-LSM



Sharp interface between YSZ and LSM

Shape Forming

Fabrication of support tube (tubular SOFC)

- Extrusion
- Cold Isostatic Press

Fabrication of thin/thick films

- Tape casting
- Vacuum slip casting

LSM Cathode fabricated at ECMS through CIP

$La_{0.7}Sr_{0.2}MnO_3$

Graphite (19.5 μm)

Slurry mixing

Compaction

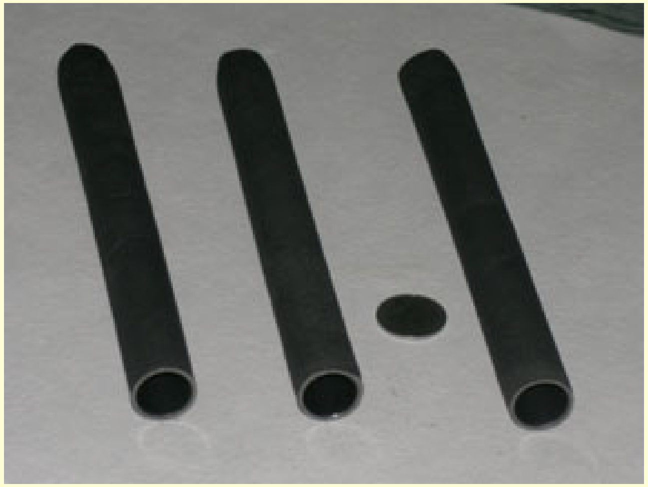
Die filling and CIP at 145 MPa

Green tube

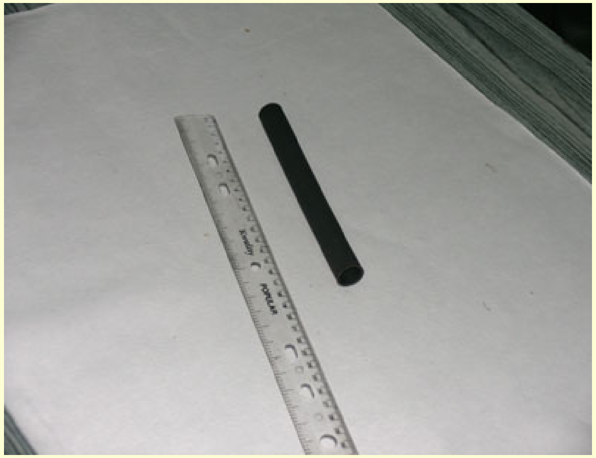
Sintering

Finished tube

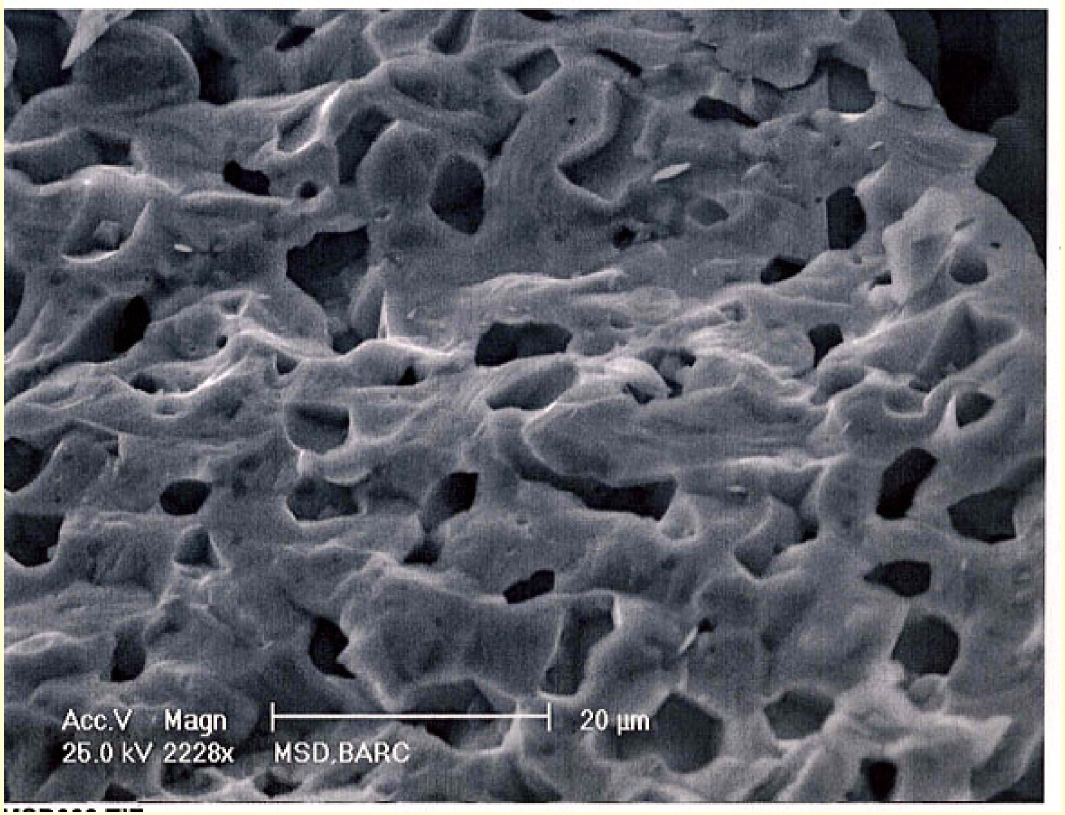
Green Tube



Sintered Tube



Microstructure of Sintered Porous LSM tube



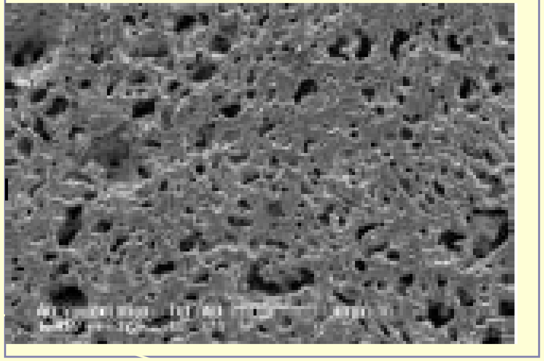
Pore size 5-15 µm

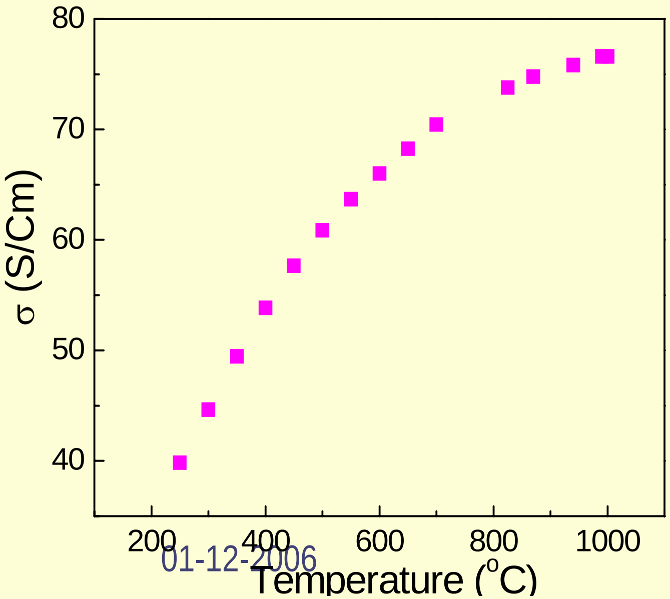
Graphite was added as the pore former

Shape Fabrication Extrusion Technique

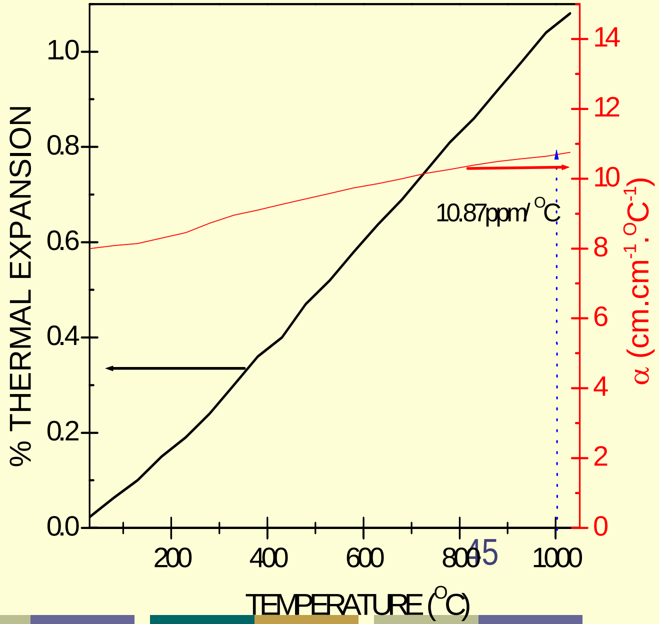
Sintered LSM tube (35% porous)

Porosity ~35 %

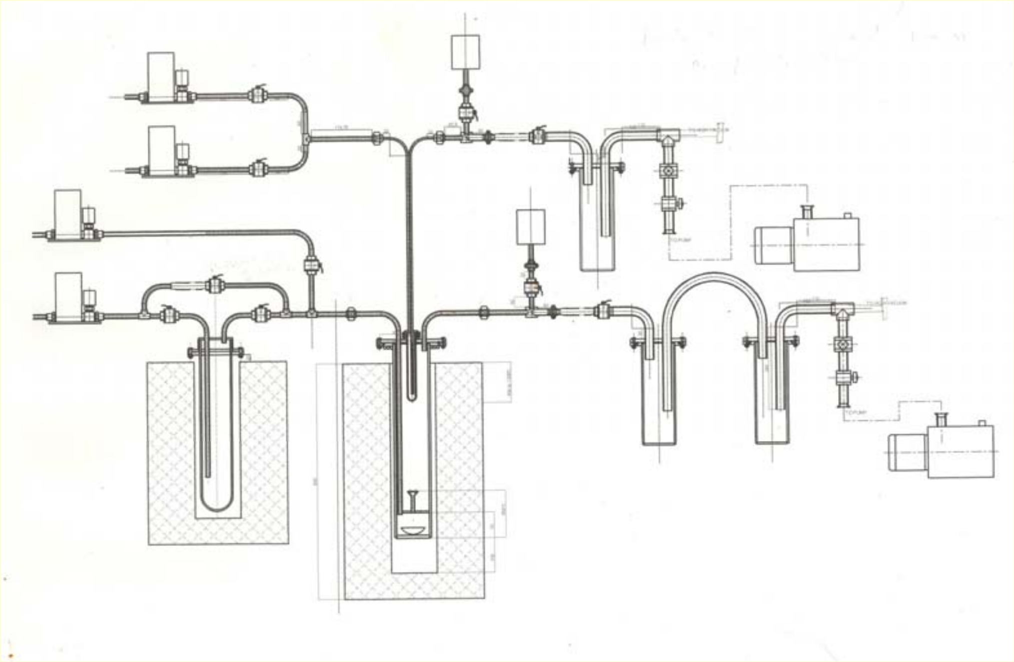




Cathode for SOFC



Schematic diagram of the CVD system



For coating of LSM tube by YSZ

CVD process

Gas stream I $ZrCl_4 + H_2O \rightarrow ZrO_2 + 2HCl$

$2YCl_3 + 3H_2O \rightarrow Y_2O_3 + 6HCl$ at 1000- 1300^{0}C

Gas stream II $CO_2 + H_2 \rightarrow H_2O + CO$

Electrochemical Reaction $2YCl_3 + 3\,O^{2-} + 3H_2 \rightarrow Y_2O_3 + 6HCl + 6\,e^-$

$ZrCl_4 + 2O^{2-} + 2H_2 \rightarrow ZrO_2 + 4HCl + 4e^-$

- Fraction of Y_2O_3 in ZrO_2 is decided by the composition of the vapor.

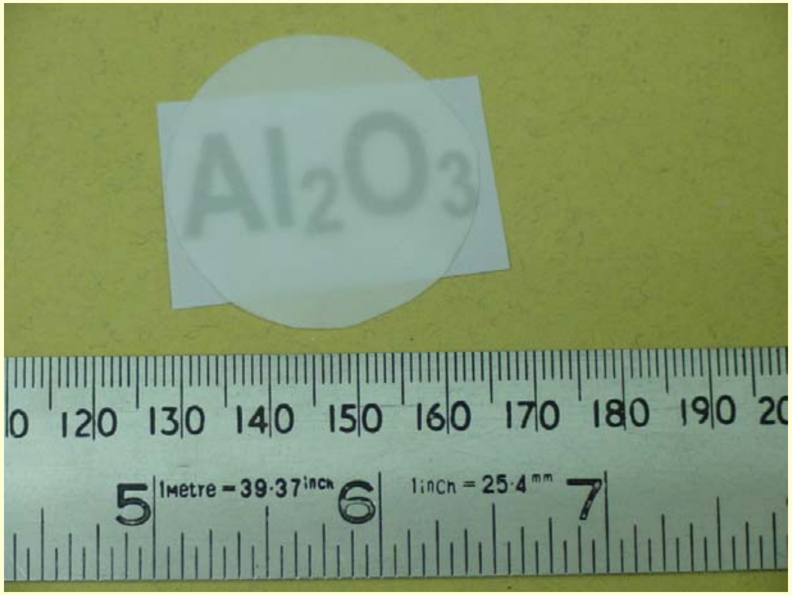
  1. Independent control on the temperature of $ZrCl_4$ and YCl_3 baths.
     $ZrCl_4$ between 150 - 185^{0}C
     YCl_3 between 550 - 650^{0}C
  2. Independent gas steams

- Optimization of pressure to get coating at the outer surface.

R

EVD Setup for depositing YSZ electrolyte film on porous LSM cathode tube

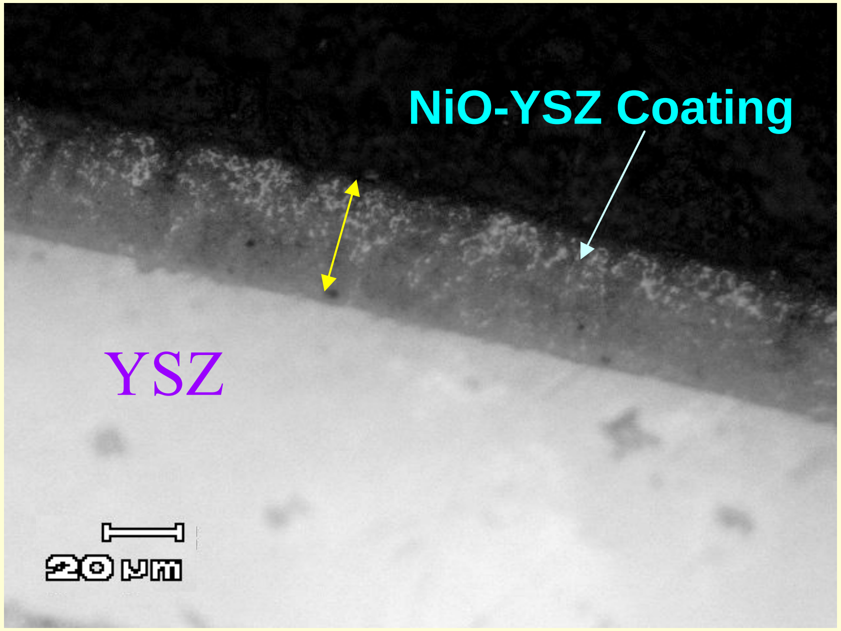
Sintered ceramic tapes



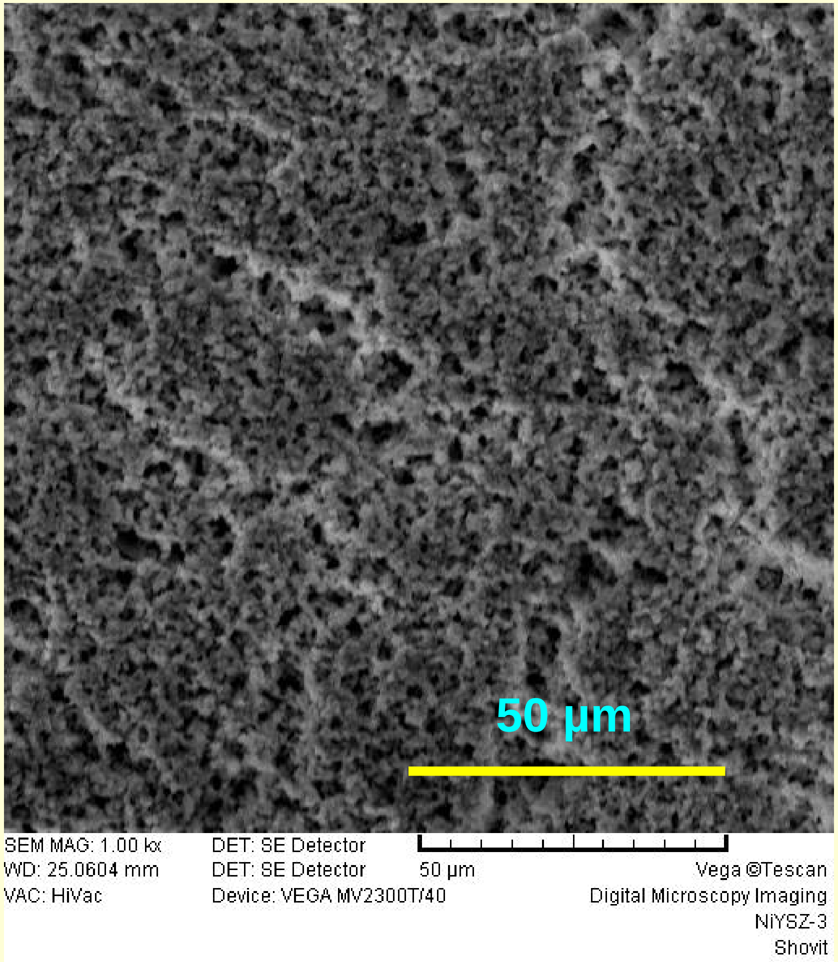

Flexing of sintered 20 um thick electrolyte sheet

3YSZ flexible ceramic tapes (Corning corporation, USA)

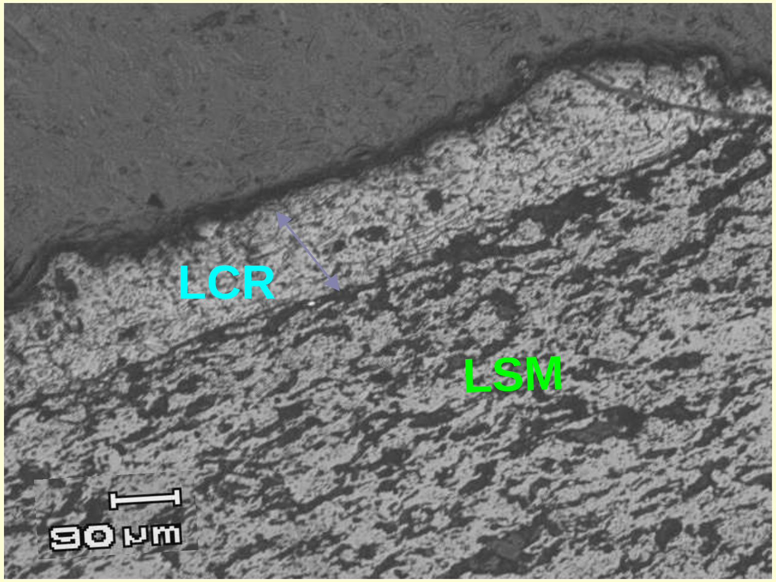
Cross sectional view of NiO-YSZ coating on YSZ tube

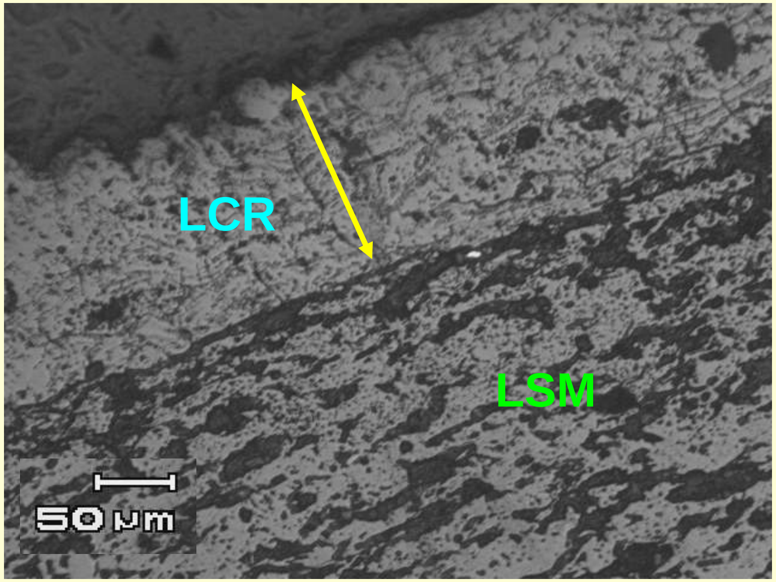


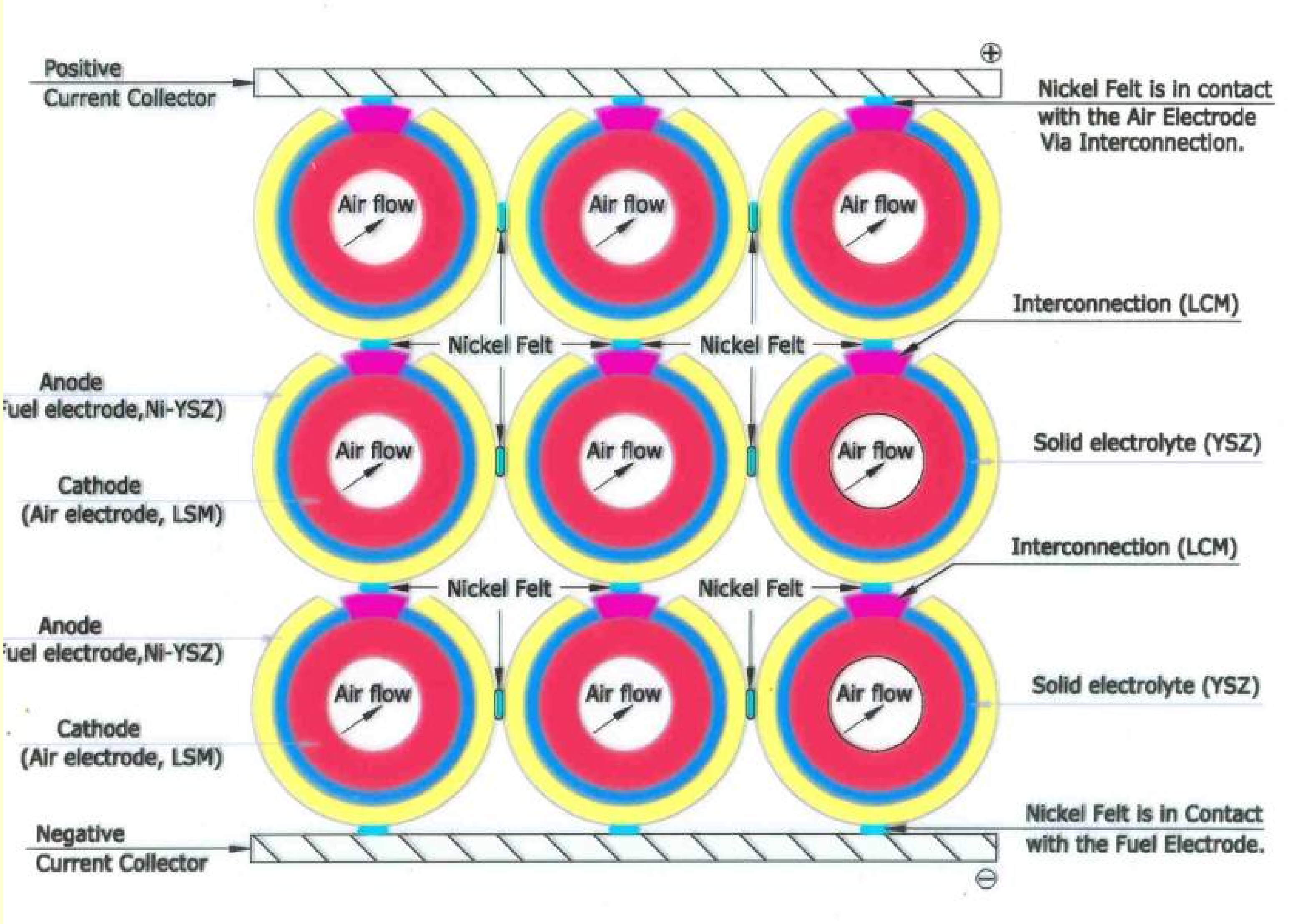
Morphology of Ni – YSZ coating



LCR Coating (Plasma Spray) on Porous LSM







SOFC Tube Assembly

Target : March 2007

Electrical Characterization Facility for SOFC

- ☐ **SOFC Single cell Self supporting YSZ electrolyte 20mm dia 700 µm thick cathode and anode are applied by brush coating**
- ☐ **Pt grid was used on the electrode contacts**

Open Circuit Voltage 0.8 V was obtained at 1000 °C.

Summary

BARC Activity on Fuel Cell Programme

- BARC has taken up development of “Compact High Temperature Reactor”
- The heat generated in the reactor may be tapped and converted to electricity and hydrogen
- Solid Oxide Fuel Cell will play a pivotal role in conversion of this hydrogen energy to electrical energy

Thank You

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Hydrogen : The Future Fuel

- *Clean energy*
  - *No air-pollution*
  - *Minimum green house gas emission*

- High energy density

- Compatible with efficient fuel cells

- Long term energy security/ diverse resources

- Can serve all sectors of economy

> ***….the first car driven by a child born today could be powered by hydrogen and pollution free.***
>
> US President, Jan. 28, 2003

Overall cell reaction is simply the oxidation of fuel. Open circuit voltage “E” is expressed as:

$$E = \frac{RT}{4F} \ln \left\{ \frac{P_{O_2}\,(\text{oxidant})}{P_{O_2}\,(\text{fuel})} \right\}$$

When a current is drawn from the cell, cell voltage V is:

$$V = E - IR - \eta_A - \eta_F$$

Fuel Cell components

- ✓ **Electrolyte**
- ✓ **Cathode**
- ✓ **Anode**
- ✓ **Interconnect (for a stack)**
- ✓ **Seals**

Requirements for the electrolyte

- **Ionically conductive - oxygen ion transport no. ~ 1**
- **Chemically stable (at high temperatures as well as in reducing and oxidizing environments**
- **Gas tight/free of porosity**
- **Uniformly thin layer (to minimize ohmic losses)**
- **Thermal expansion that match**

Different Electrolytes

Zirconia electrolytes (8YSZ,3YSZ,ScSZ,CaSZ etc.)

Ceria electrolytes (GDC, SDC, YDC, CDC etc.)

Lanthanum based electrolytes

LSGM $La_xSr_{(1-x)}Ga_yMg_{(1-y)}O_3$

$LaAlO_3$-based $La_{1-x}Ca_xAlO_3$, $La_{1-x}Ba_xAlO_3$

Bismuth oxide-based $Bi_2V_{0.9}Cu_{0.1}O_{5.5-\delta}$, $(Bi_2O_3)_x(Nb_2O_5)_{1-x}$

Pyrochlorores-based YZr_2O_7, $Gd_2Ti_2O_7$

Barium brownmillerites $BaZrO_3$, $Ba_2In_2O_5$, $Ba_3In_xAO_y$ (A = Ti, Zr, Ce, Hf), $Ba_3Sc_2ZrO_8$

Composite Electrolyte: Doped ceria + Molten Salt ???

Requirements for the cathode

- High electronic conductivity
- Chemically compatible with neighboring cell component (usually the electrolyte)
- Should be porous
- Stable in an oxidizing environment
- Large triple phase boundary
- Catalyze the dissociation of oxygen
- Adhesion to electrolyte surface
- Thermal expansion coefficient similar to other SOFC materials

Different Cathode Materials

Lanthanum cathodes

LSM $La_xSr_{(1-x)}MnO_3$

LSF $La_xSr_{(1-x)}FeO_3$

Gadolinium cathodes

GSC $Gd_xSr_{(1-x)}CoO_3$

Yittria cathodes

YSCF $Y_{(1-x)}Sr_xCo_yFe_{(1-y)}O_3$

Strontium cathodes

SSC $Sm_xSr_{(1-x)}CoO_3$

Requirements for the anode

- Electrically conductive
- High electro-catalytic activity
- Large triple phase boundary
- Stable in a reducing environment
- Can be made thin enough to avoid mass transfer losses, but thick enough to provide area and distribute current
- Thermal expansion coefficient similar neighboring cell component
- Chemically compatible with neighboring cell component
- Fine particle size
- Able to provide direct internal reforming (if applicable)
- Tolerant to sulfur in fuels (if applicable)

Requirements for the interconnect

- Stable under high temperature oxidizing and reducing environments
- Very high electrical conductivity
- High density with “no open porosity”
- Strong and high creep resistances for planar configurations
- Good thermal conductivity
- Phase stability under temperature range
- Resistant to sulfur poisoning, oxidation and carburization
- Low materials and fabrication cost
- Matching thermal expansion to other cell components

Interconnect

Ceramic Interconnect for High temperature SOFC

(High material cost, sintering difficulties)

e.g Doped Lanthanum Chormites and doped Yttrium chromites

Metallic Interconnects

(easy fabrication, high electrical and thermal conductivity)

High chrome alloys ($Cr_5Fe_1Y_2O_3$)

Ferritic stainless steel for low temperature SOFC

Iron super alloys

Nickel super alloys

Critical Issues

Chromium evaporation (in Cr based interconnects)

Requirements for the sealing materials

- Electrically insulating
- Thermal expansion compatibility with other cell components
- Chemically and physically stable at high temperatures
- Gastight
- Chemically compatible with other components
- Provide high mechanical bonding strength
- Low cost

Materials

Glass ceramic materials – $SrO\text{-}La_2O_3\text{-}Al_2O_3\text{-}SiO_2$

Mostly are under Intellectual Property Rights

Cell Design

Different Concepts

Driven by

Cell efficiency
Fabrication Technology of the component
Cost of the Material
Sealing Material Technology

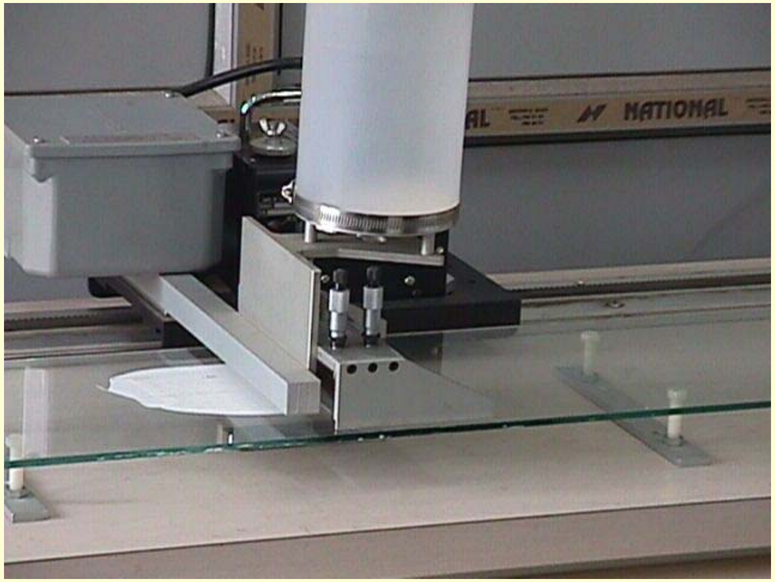
Materials Processing :

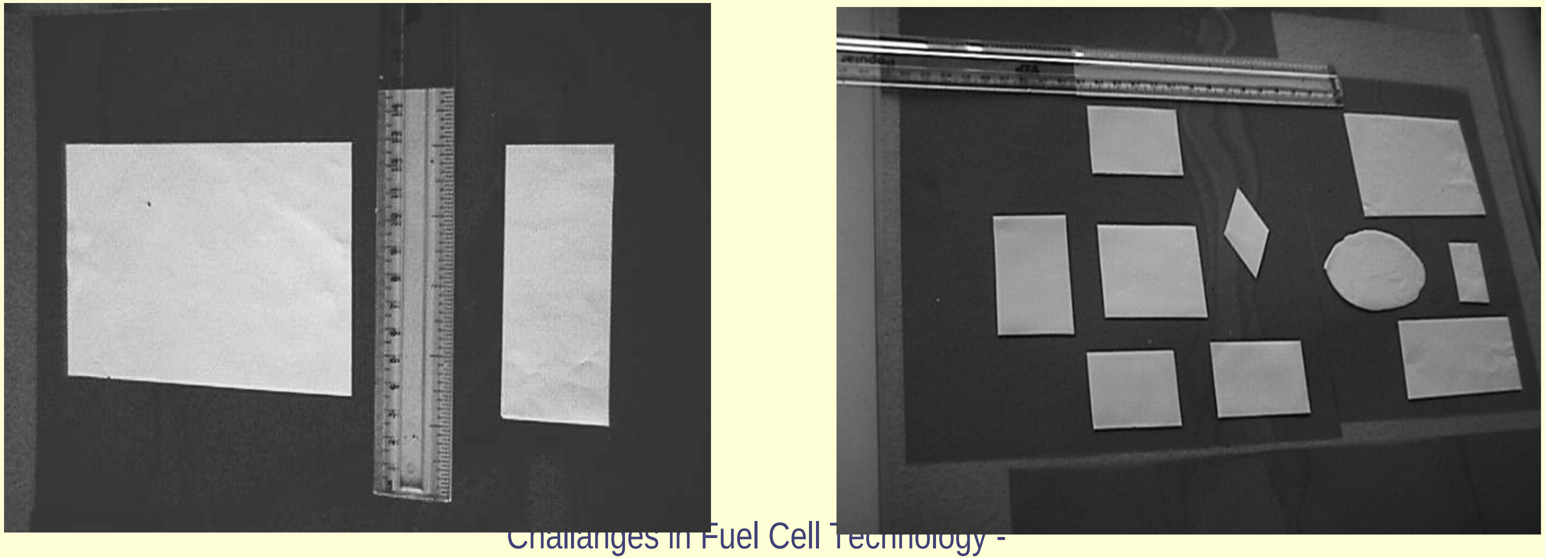
Powder Preparation
Stable Slurry
Shape Forming
Thin coating
Sintering

Tape Casting

- **Tape casting is a method for producing thin, ceramic tapes by doctor-blade process**
- **For tape-casting, first ‘Slip’ of ceramic powders is prepared. The slip is generally a fluid based on organic solvents**
- **A typical slip composition contains:**
  - **Powder**
  - **Dispersant (Acetic acid, Oleic acid etc.)**
  - **Solvent (Ethanol, MEK, TCE etc.)**
  - **Plastisizer (PEG, phthalates etc.)**
  - **Binder (PVB, PVA etc.)**

Tape-casting Facility at ECMS, Vashi Complex, BARC





Green Ceramic tapes

Thin/thick Coating

- Slurry Coating
  - Dip coating
  - Electrophoretic deposition
  - Screen printing
  - Spray Coating
- Vapour deposition
  - Chemical vapour Deposition
  - Electrochemical vapor Deposition
  - Reactive Magnetron Sputtering
  - RF sputtering
- Plasma Spraying