STATE-OF-THE -ART IN SOFCs SCIENCE & TECHNOLOGY

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LAMAR

The Innovation Week on R.E.S.
July 01 - 12, 2012, TEI- Patras, Greece

*** O U T L I N E ***

✓- INTRODUCTION

✓- MARKET AND APPLICATIONS

✓- SOFC CERAMIC MATERIALS

❖ - SCIENCE and BASIC RESEARCH

❖ - SOFCs TECHNOLOGY

❖- FORECAST for SOFCs and R.E.S.

✓- LAMAR FACILITIES

CONCLUSIONS

I N T R O D U C T I O N

- **- UNIVERSITIES**

  - Science and Basic Research

- **-R&D ORGANIZATIONS**

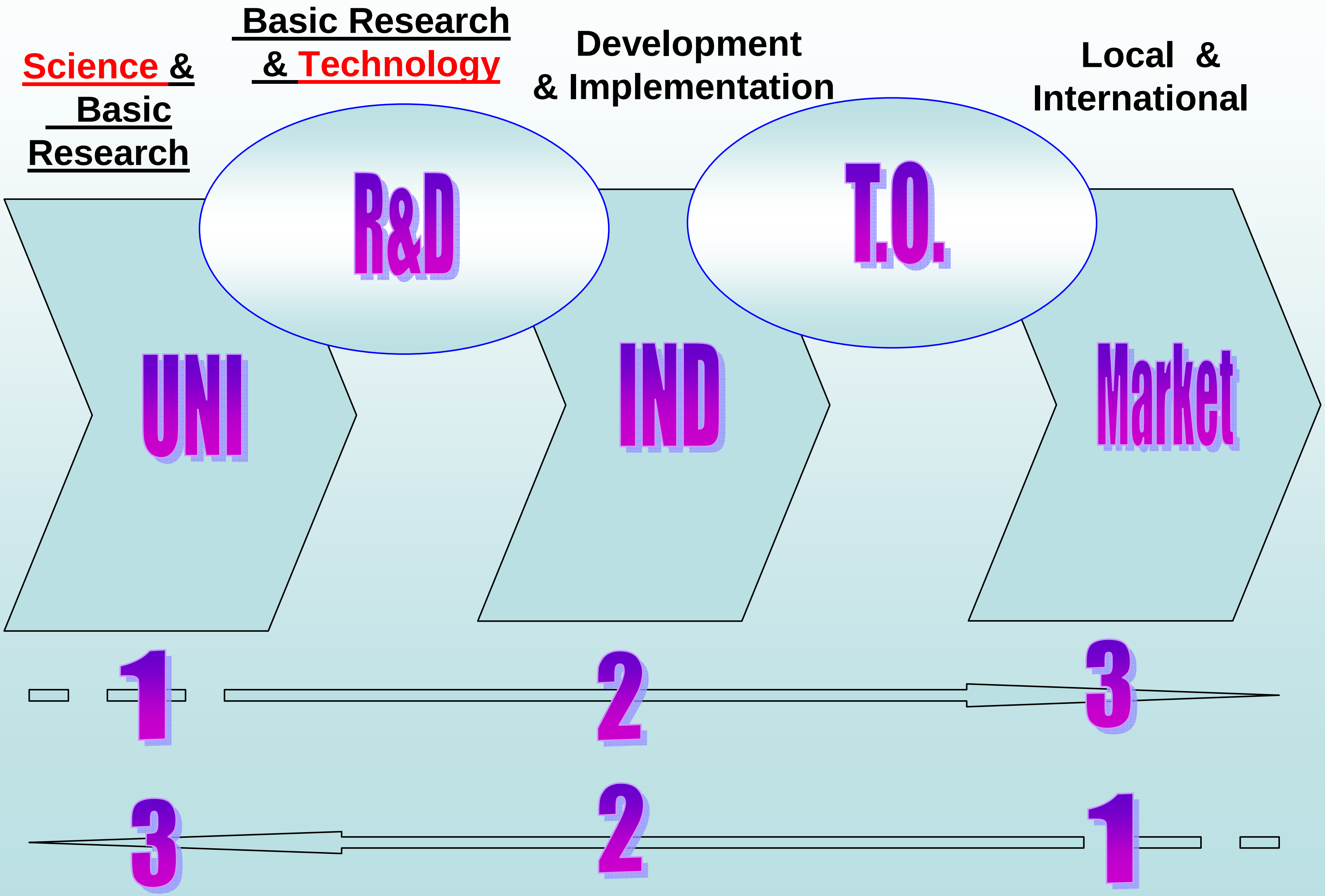
  -Basic Research and Technology Development

- **- INDUSTRIES incl. SME**

  - Development, Validation and Implementation,

  (Function of the MARKET)

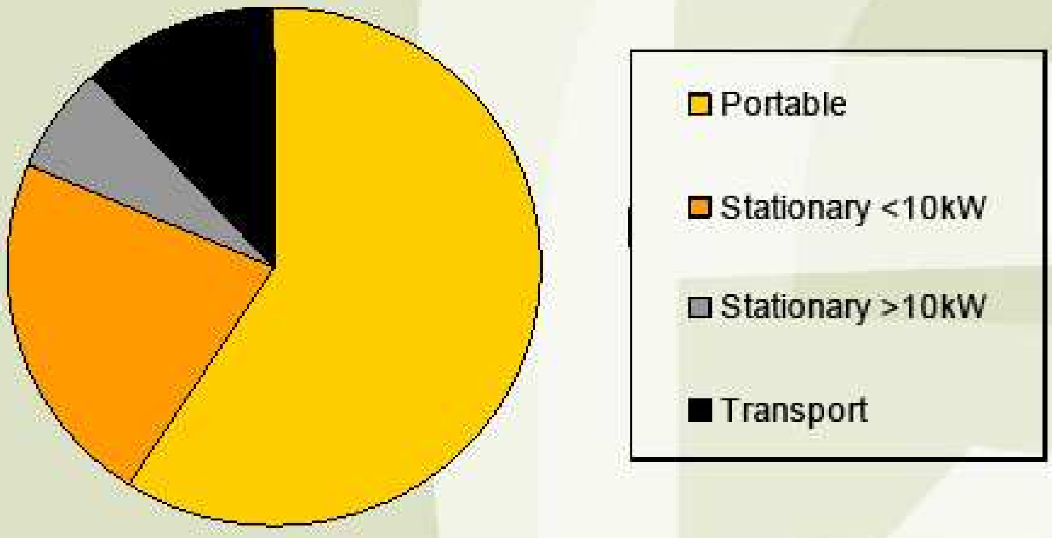
RELATIONS & IMPORTANCE



FUEL CELL TODAY

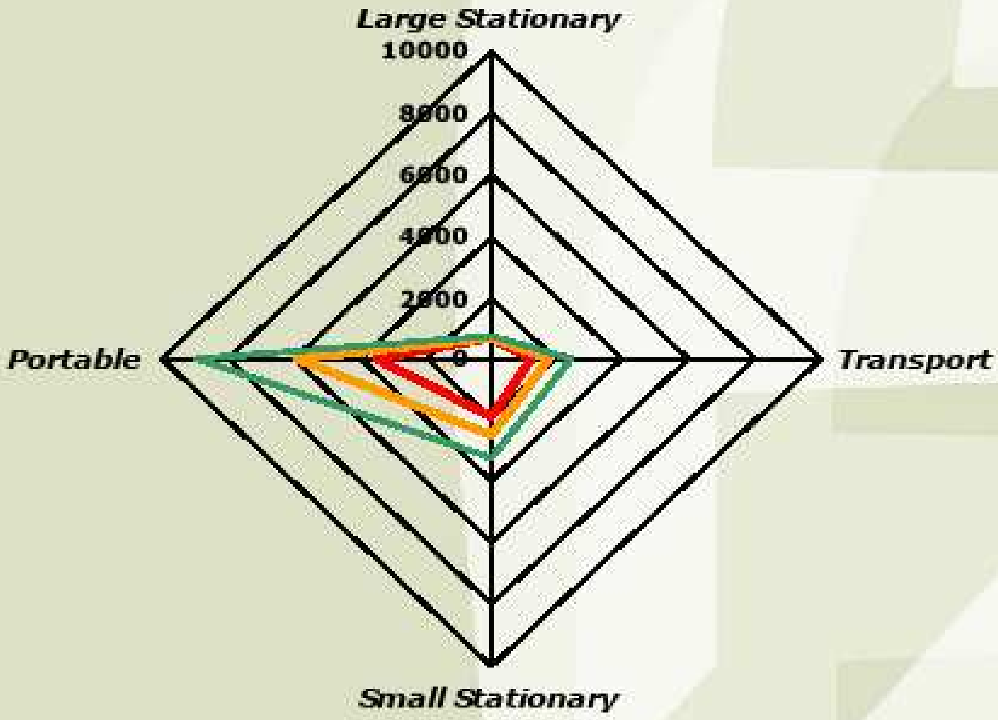
Fuel Cell Applications

All systems built, application



FUEL CELL TODAY

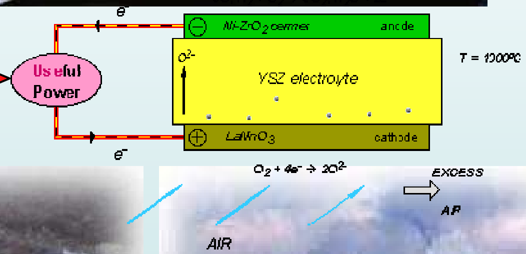
Market Growth 2003 - 2005



www.fuelcelltoday.com

APPLICATION

Civil



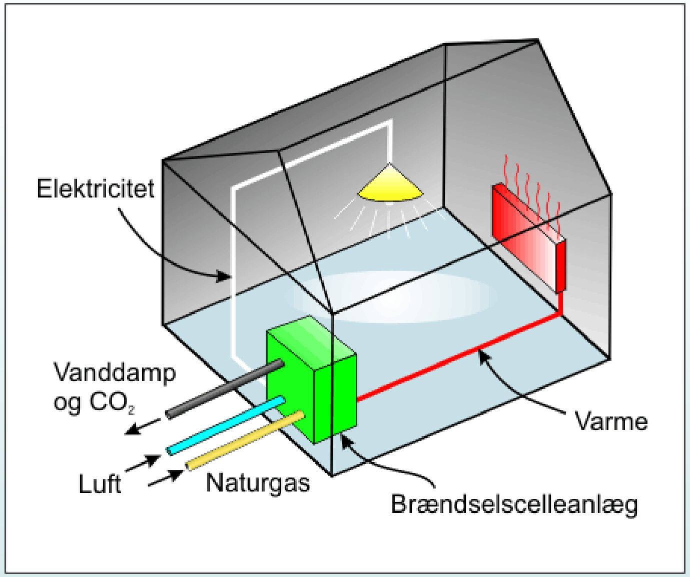
Energy Supply of Houses

Hexis/CH (1 kW), Haldor Topsoe/Dk, Siemens Power, GE /US, McDermott/Cummings/US, FCE/ Versa Power/ GTI

Military

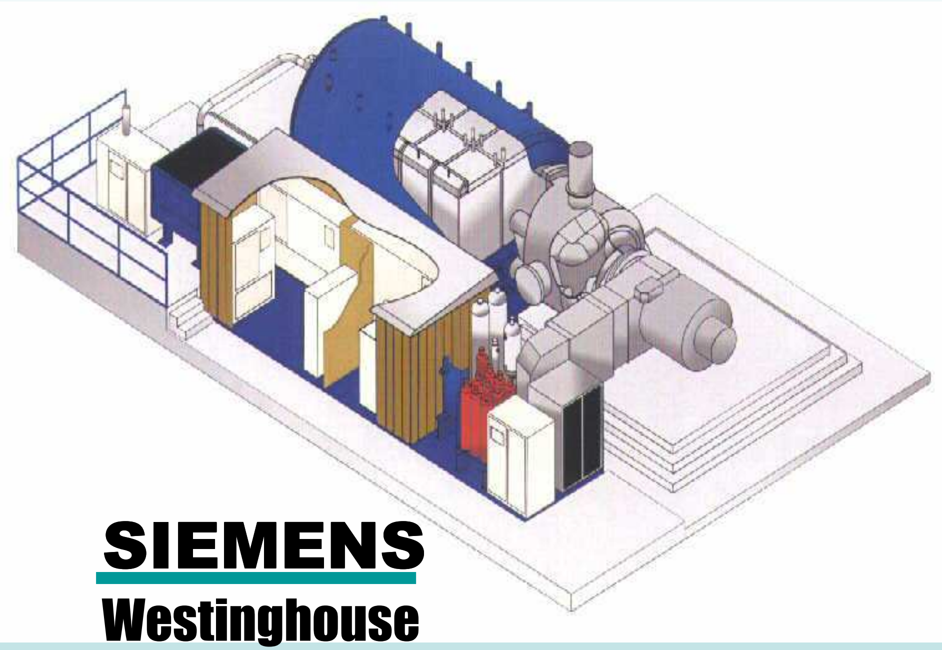
Applications / system size

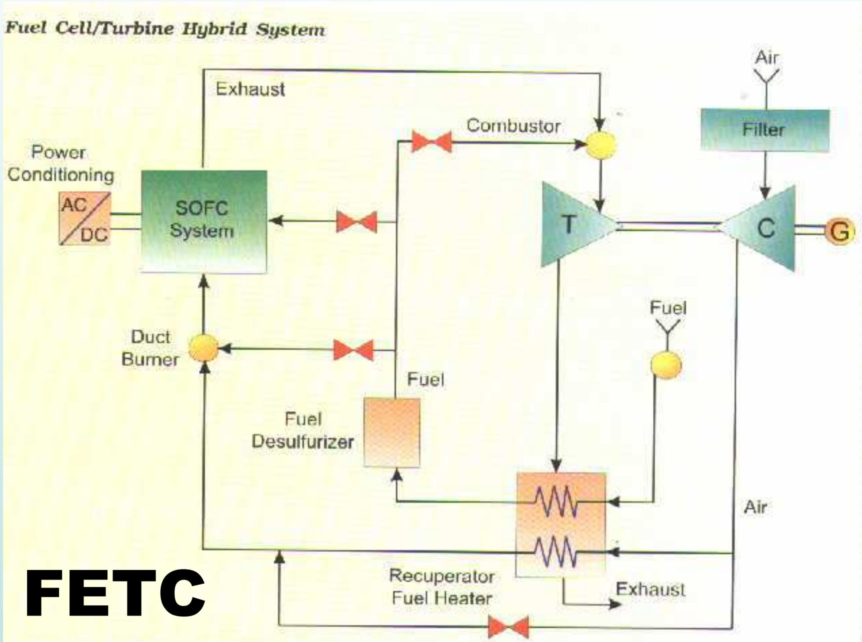
- **< 1 kWe:**
  - mobile power, e.g. military
- **1-5 kWe:**
  - µ-CHP FC for single houses
  - recreational, e.g. camping
- **5-10 kWe:**
  - APUs
  - hybrid vehicles
- **50-250 kWe:**
  - on-site generation, e.g. marine, hospitals, residential
  - back-up power
- **> 1 MWe** (preferably as gas turbine hybrids):
  - power generation



COMPANIES & SYSTEMS

- **Europe:** Siemens AG & FZ Jülich GmbH, British Gas, R-R, EdF, ECN,Sulzer,
- **North America:** Argonne N.L., S. Westinghouse Co., Texaco, Ballard
- **Asia-** ASIA Pacific F.C. & Toto, Toho Co, Tokyo Electric Power and etc.





Classification: 1MWs SOFC/GT Hybrid Power System
Output: AC Electric Power, Hot Water, Continuous
Efficiency: ~ 60%
Noise & Emission: < 70dBA; <0.01kg/MWh

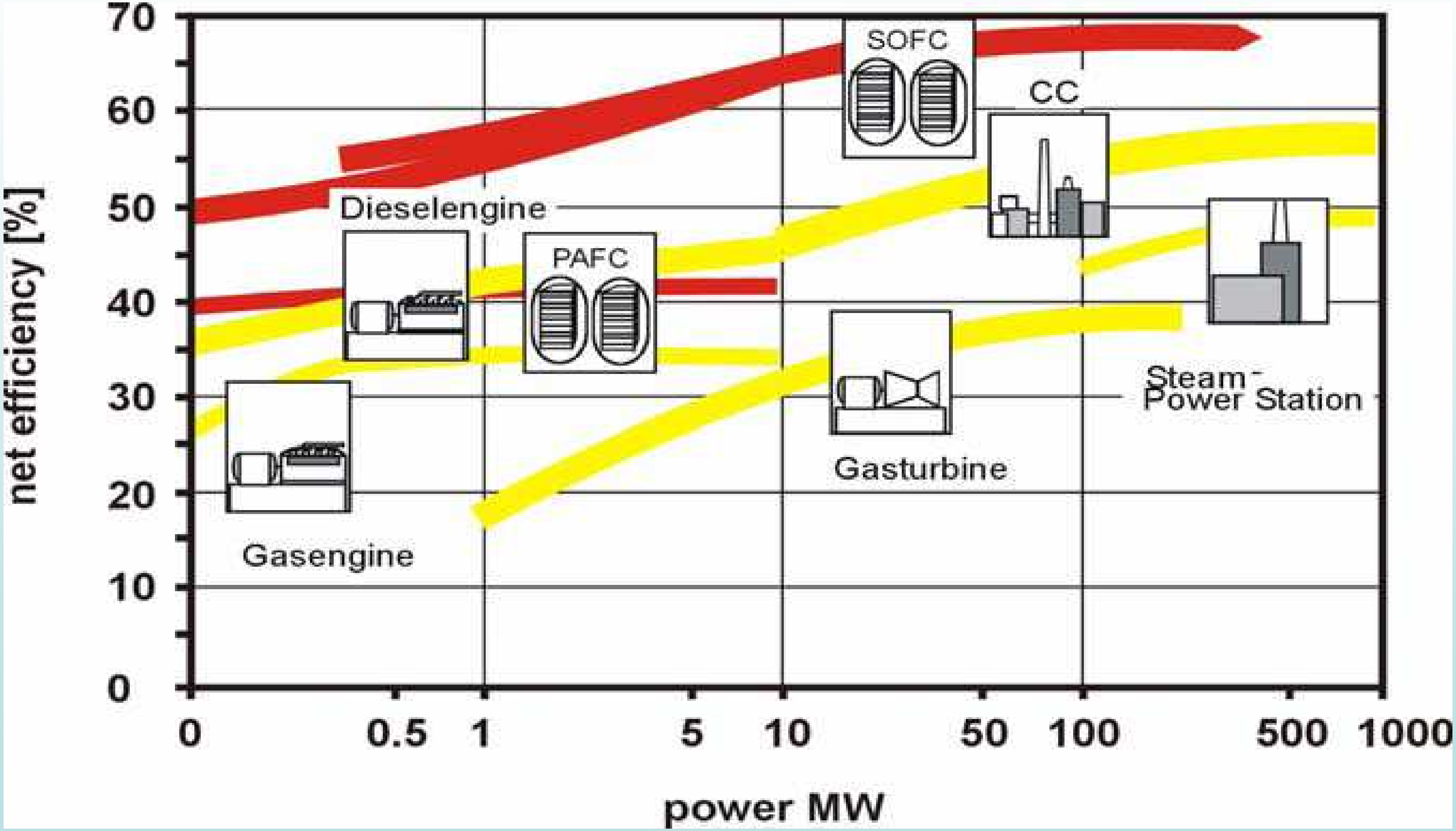
SYSTEM INTEGRATION

Efficiency: > 70% for the market 2010

Efficiency: > 80% for the market 2015

MOTIVATION

Efficiency of Different Power-Technologies



FUEL CELL TODAY

Challenges and the future

- Problem 1: Technology
  - Fuel cell use some expensive materials
  - Technology not yet 100% developed
  - Use of expensive material reduced, substituted
  - Constant improvements of technology
- Problem 2: Infrastructure
  - Hydrogen filling stations not available
  - Small scale infrastructure not in place
  - Plans for local networks (Iceland, California etc.)
  - Co-operations with lighter manufacturers

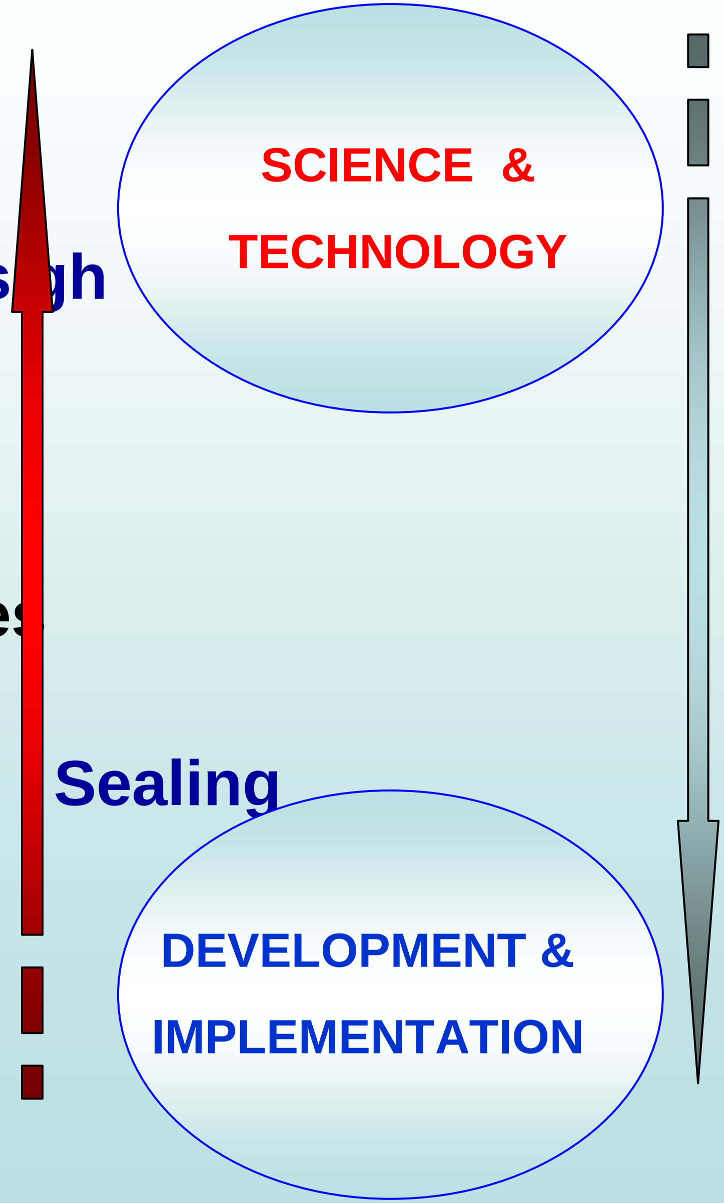
Challenges and the future

- Problem 3: Fuel Cell Production
  - Only few companies
  - Not yet mass produced
  - Learning curve: Production gets cheaper

- Problem 4: Macro Scale
  - Not enough support (funding and incentives)
  - Lack of awareness
  - Governments begin to support technology
  - Demonstration projects help raise awareness

SOFC CERAMIC MATERIALS

- Raw Materials (Powders)
- SOFCs Components and Desigh
  - Cathodes
  - Electrolytes
  - Anodes
  - Functional Cathodes/Anodes
  - Cell Desigh
- Interconnects, Coatings and Sealing
- Small Stacks
- Test rig (unit)
- Demonstration unit / system



SCIENCE & BASIC RESEARCH

❖- SOFCs BECKGROUND CONCEPTS

C. Vayenas, '**Introduction to Fuel Cells: Fundamentals of Electrochemical Kinetics and Thermodynamics**' *Uni. Patras,* 1st Summer School on SOFC Technology September 6, 2004, University of Patras, CD-ROM available

M.Ormerot '**Catalysis and Electrocatalysis in SOFCs: Internal Reforming and Chemical Cogeneration,** *Keel Univ., UK,* 1st Summer School on SOFC Technology September 6, 2004, University of Patras, CD-ROM available

SOFC - Materials Properties & Performance, Eds. J. Fergus, R. Hui, X. Li, J. Zhang, CRC Press, N.Y, London (2009)

T. Kawada, and H. Yokokawa, **Materials and Characterization of Solid Oxide Fuel Cells**, Key Eng. Materials v.125-126 (1997) 187

SCIENCE & BASIC RESEARCH

A. McEvoy , 'SOFC- Background Concepts' *EPFL, Swiss,* 1st Summer School on SOFC Technology September 6, 2004, University of Patras,GR

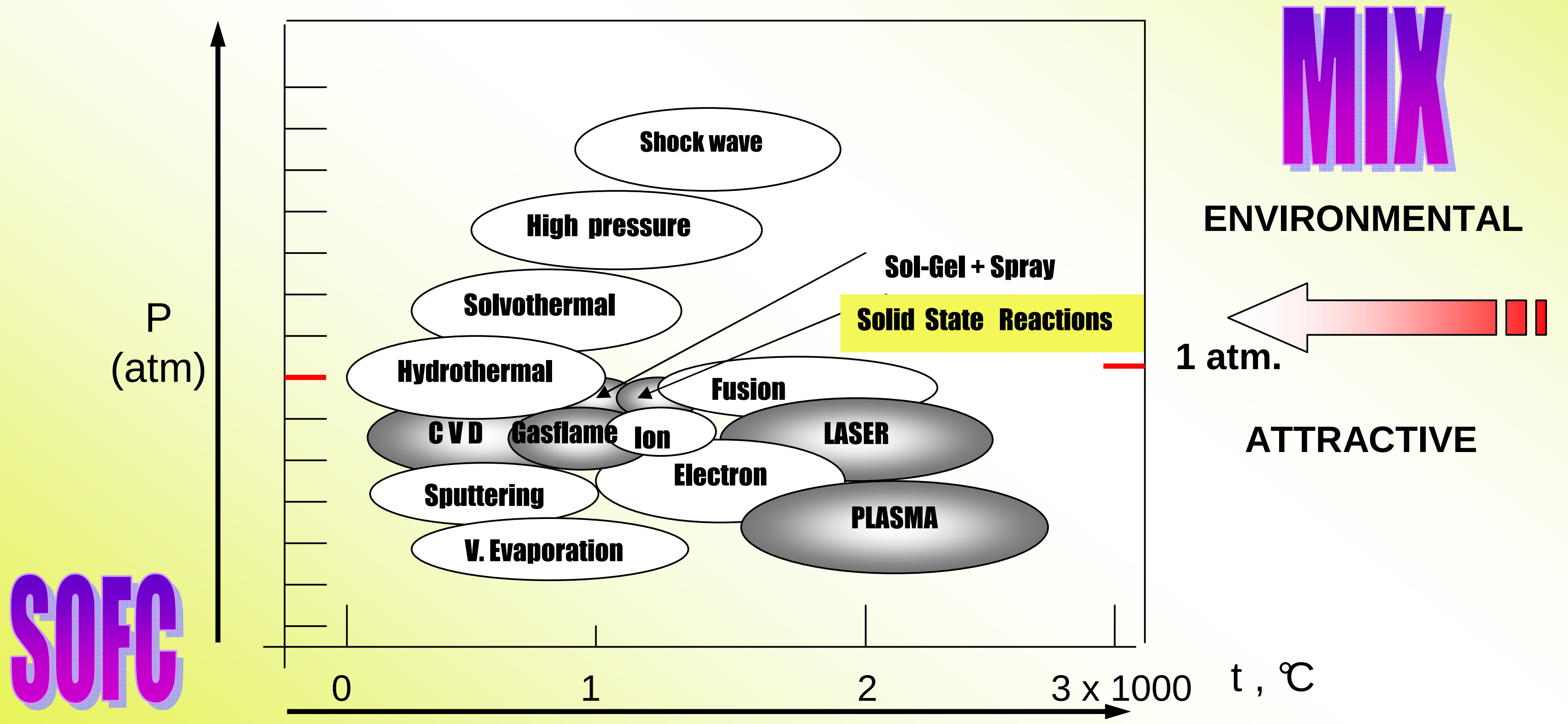
A. Atkitson, 'Solid State Chemistry of Solid Electrolytes" *Imperial College, UK,* 1st Summer School on SOFC Technology September 6, 2004, University of Patras, GR

❖ - SOFCs DEGRADATION

H. Yokokawa et al. 'Introduction of Fundamental Mechanism' *AIST,* Intern. Workshop on Degradation Issues of Fuel Cells, 19-21September, 2007,Crete, Greece

B. Iwanschitz, A. Mai, T. Hocker, 'Origin and mechanisms of anode degradation, *Helix AG, Züricher Hochschule Winterthur, Swiss*, Intern. Workshop on Degradation Issues of Fuel Cells, 19-21September, 2007,Crete, Greece

1- SYNTHESIS (METHODS)



Deposition of thin-film electrolyte and nano- structured electrodes by combustion CVD, sol-gel, slurry coating & templateing synthesis methods are actual at present.

2- STRUCTURE (METHODS)

RESONANCE METHODS

✓- **NMR (NQR), ESR, MÖS**

OPTICAL & X-RAY SPECTROSCOPY

✓- **OESp, ICP-AES, AASp, UV-VIS, IR Sp, Raman Sp, X-Ray Sp**

DIFRACTION METHODS

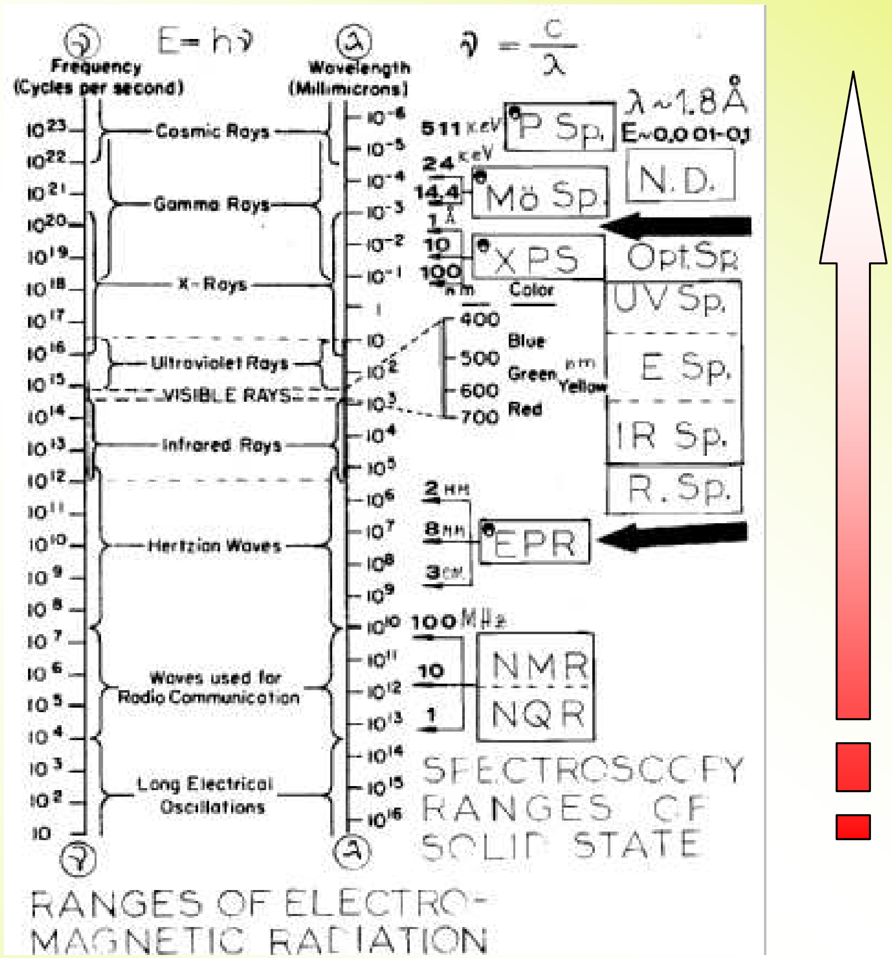
✓- **XRD, ED, ND, SAXS, SANS**

METHODS ON SPUTTERING & SCATTERING

✓- **SIMS, RBackScSp**

OTHER METHODS **(METALLOGRAPHIC)**

✓- **XPS, UPS, TEM, SEM, EDX, LEED, AFM, STM, PSp, etc.**



3 - CHARACTERIZATION (PROPERTIES)

THERMAL PROPERTIES

✓-T.EXPANSION, CONDUCTIVITY etc.

ELECTRICAL & MAGNETIC PROPERTIES

✓-E. CONDUCTIVITY, TRANSPORT BEHAVIOUR, DIELECTRIC etc.

MECHANICAL PROPERTIES

✓-ELASTICITY, ADHESION,CRACK PROPAGATION etc.

SURFACE & INTERFACIAL PHENOMENA

✓- SURFACE TENSION & CAPILLARITY, TPB etc.

OTHER (COMPLEX) PROPERTIES

PHYSICAL & CHEMICAL

THECHNIQUES FOR PHYSICOCHEMICAL CHARACTERIZATION

STANDARDS

4 - SOFC TESTING (BEHAVIOUR)

AGEING BEHAVIOUR

✓- Ageing under various atmospheres, temperatures and current loads (influence of the water vapour)

PERFORMANCE CHARACTERISTICS

✓- short (performance) and long term (durability) tests

SURFACE & INTERFACIAL PHENOMENA

✓-Thermodynamics and kinetics of Cr evaporation

?

PHYSICAL & CHEMICAL

THECHNIQUES

STANDARDS

Tubular Design – Siemens Westinghouse SWPC

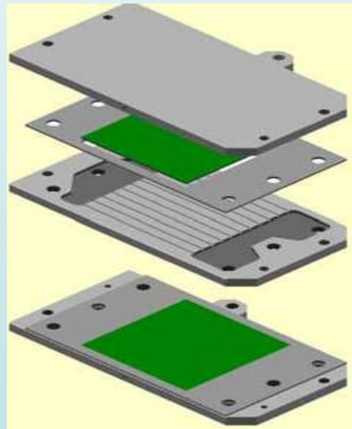
- 190 kW at 950℃ with NG/air

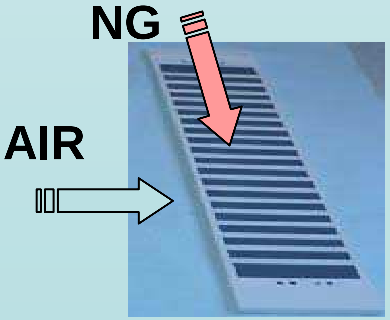
TOTO and Mitshubishi Heavy Industries MHI - 21 kW at 900℃ with NG/air

Planar Design: Hexis – Swiss

(Heat Exchanger Integrated System => HEXIS)

- **Circular cells with a diameter of 120 mm**
- **1.1. kW at 900℃ with NG/air**

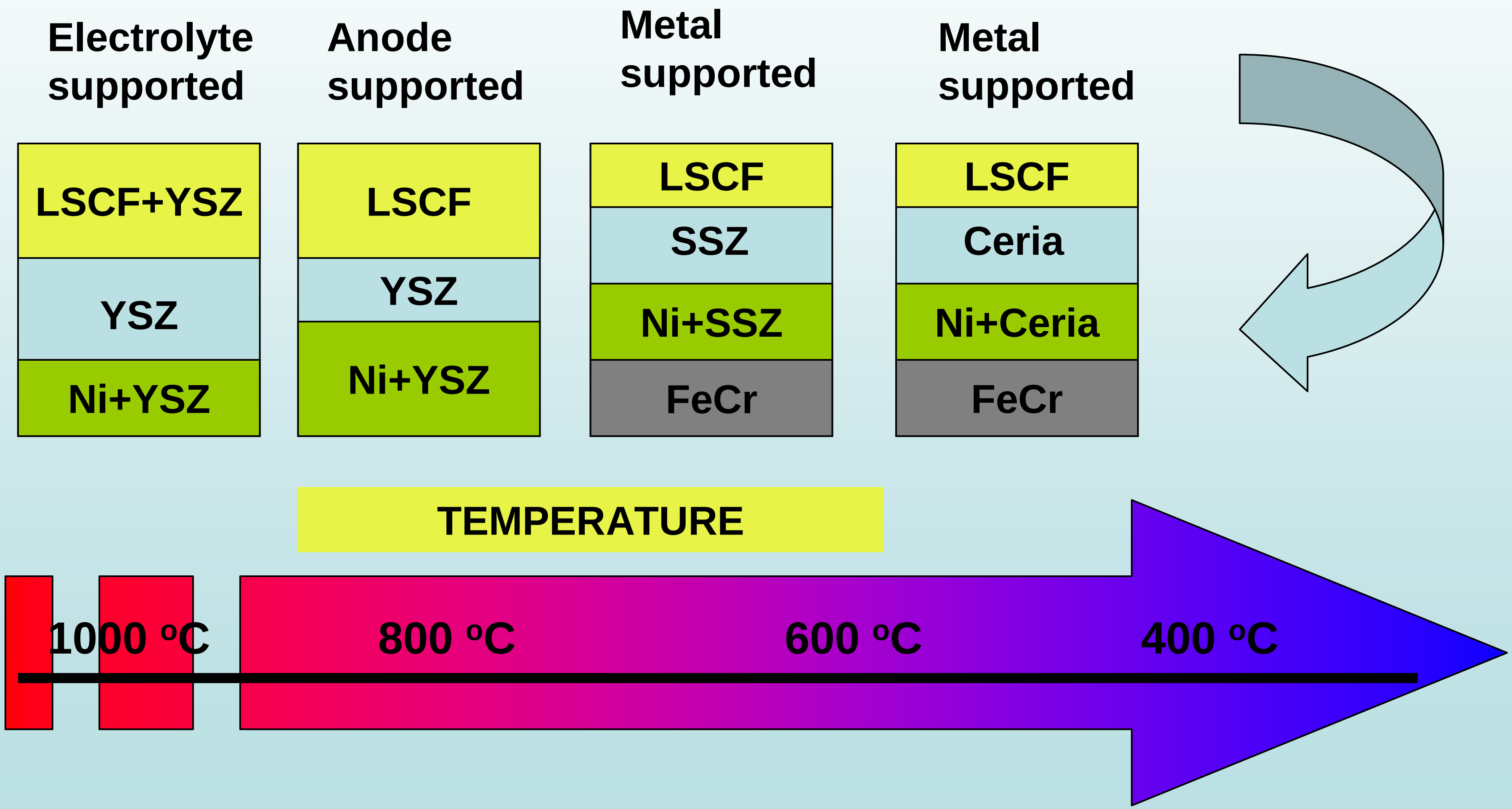




Planar Design: Rolls Royce IP SOFC (Integrated Planar) - 50 W module

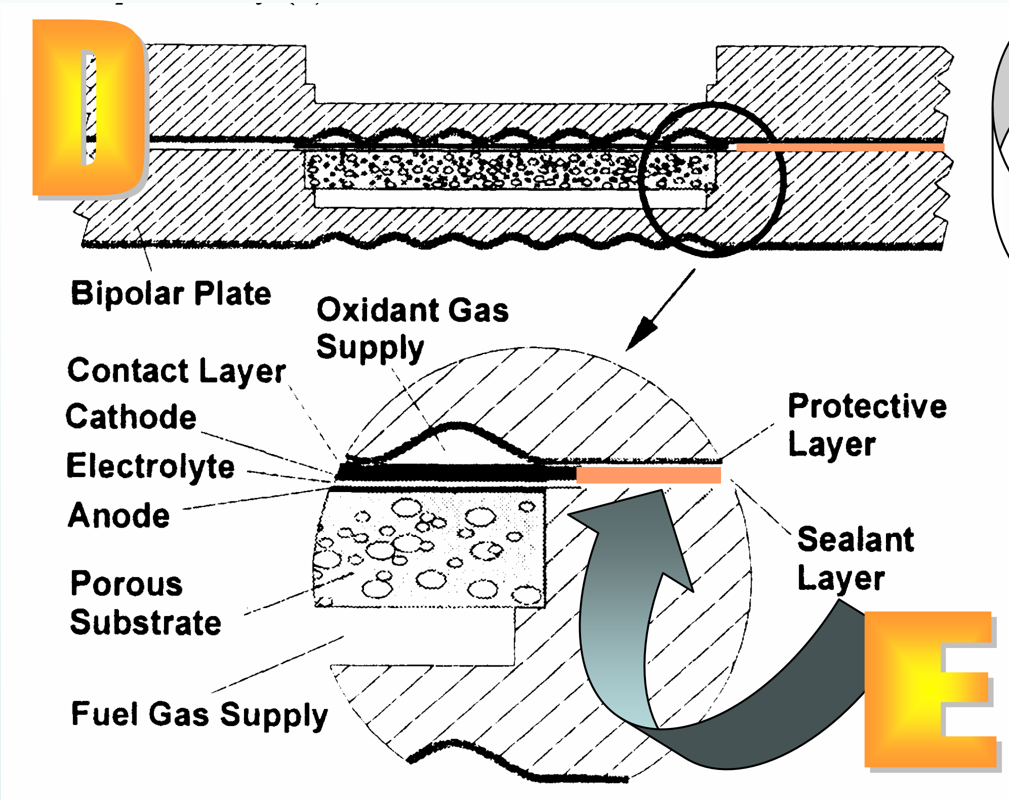
SOFCs REQUIREMENTS

Operation temperature & Materials

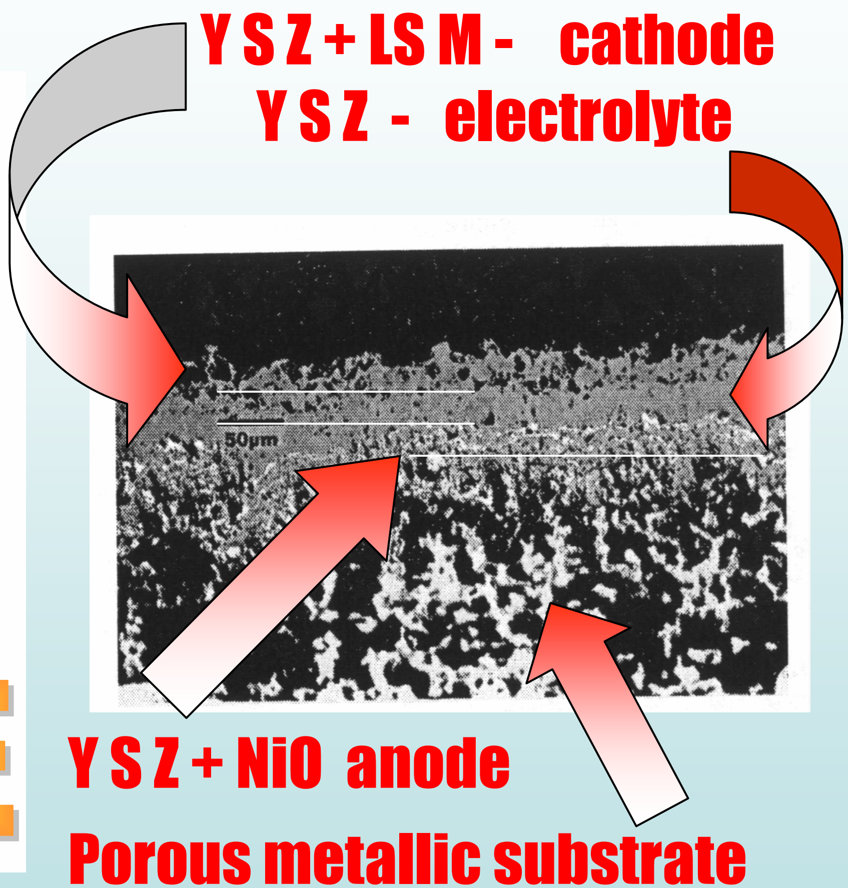


BIPOLAR PLATE APPLICATION

G. Schiller, Deutsches Zentrum fur Luft- und Raumfahrt (DLR), Stuttgart, Germany



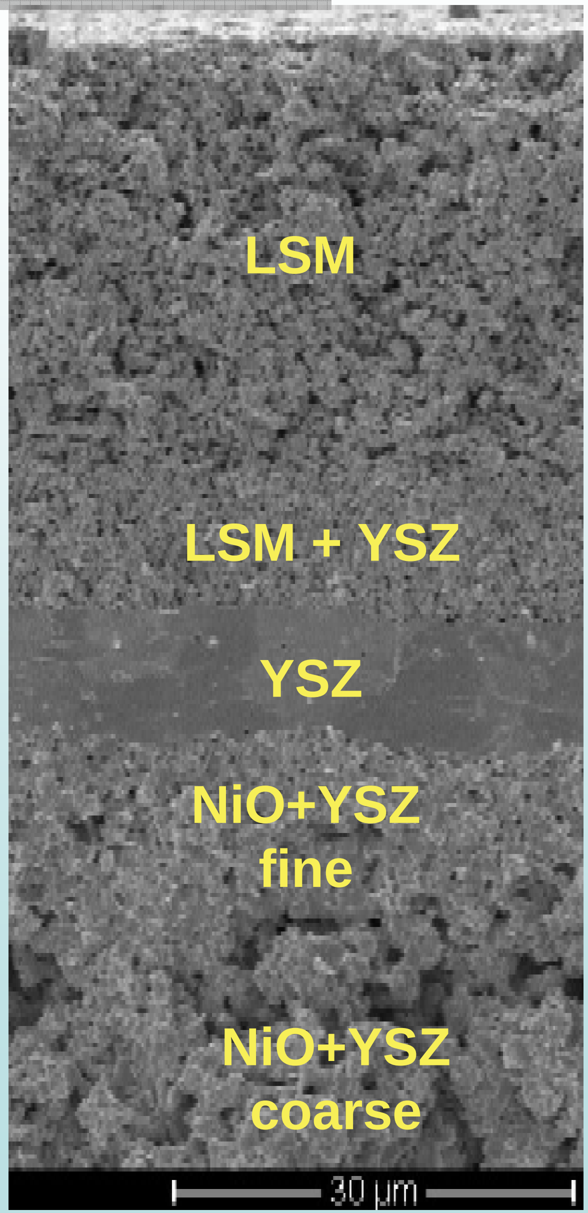
Principle of SOFC design according to GAC- spray concept



Plasma sprayed thin film cell

State-of-the-Art of SOFCs Layer Structures

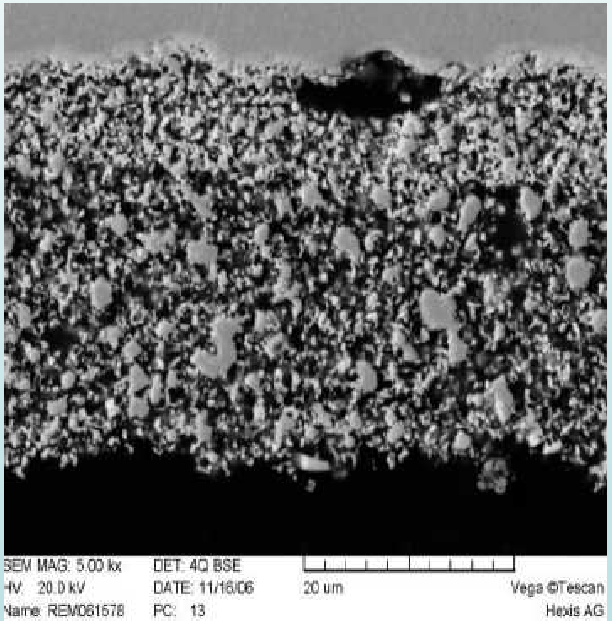
porosity	graine d_{50}	σ S/cm	
45%	10µm	50	Cathode Current Collector 30 – 70 µm
20%	1-3µm	25	Cathode Functional Layer 10 - 15 µm
0%	2-5µm	0.01	Electrolyte Layer 5 - 10 µm
20%	1-4µm	1000	Anode Functional Layer ~ 5 - 10 µm
35%	3-5µm	500	Anode Substrate < 1500 µm
open	size	800°C	

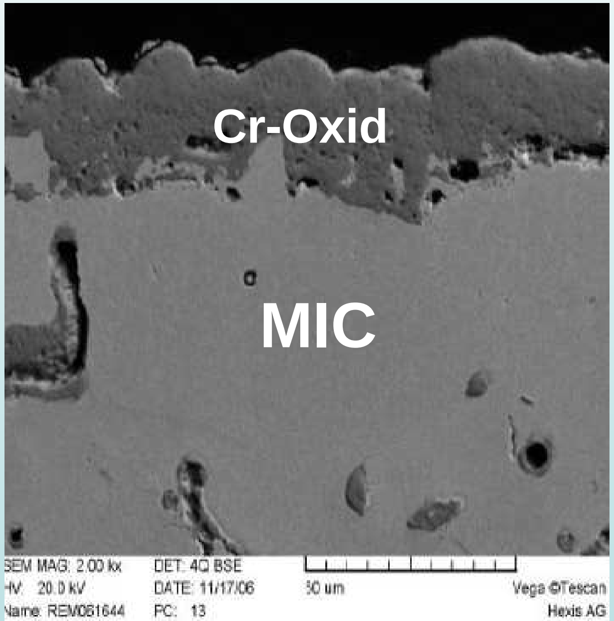


B. Iwanschitz, A. Mai, T. Hocker, 'Origin and mechanisms of anode degradation, *Helix AG, Züricher Hochschule Winterthur, Swiss*, Intern. Workshop on Degradation Issues of Fuel Cells, 19-21September, 2007,Crete, Greece

Besides **cost** and **performance**, **lifetime** is the key issue for the commercial use of SOFCs .

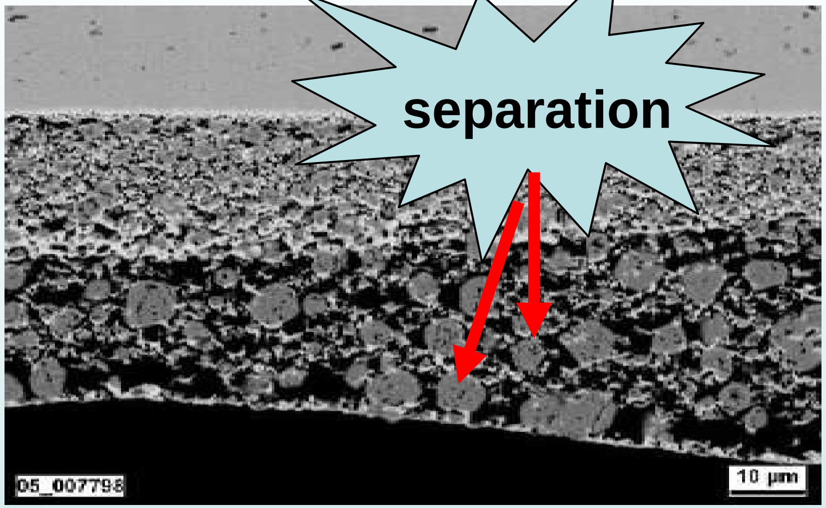
Cell materials degradation | **Design, Contacting, Cr-evaporation** | **Thermomechanical stress**

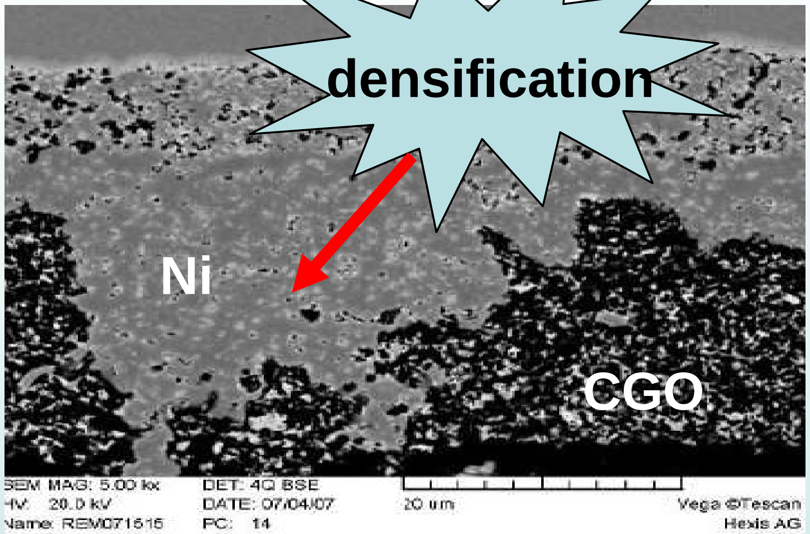


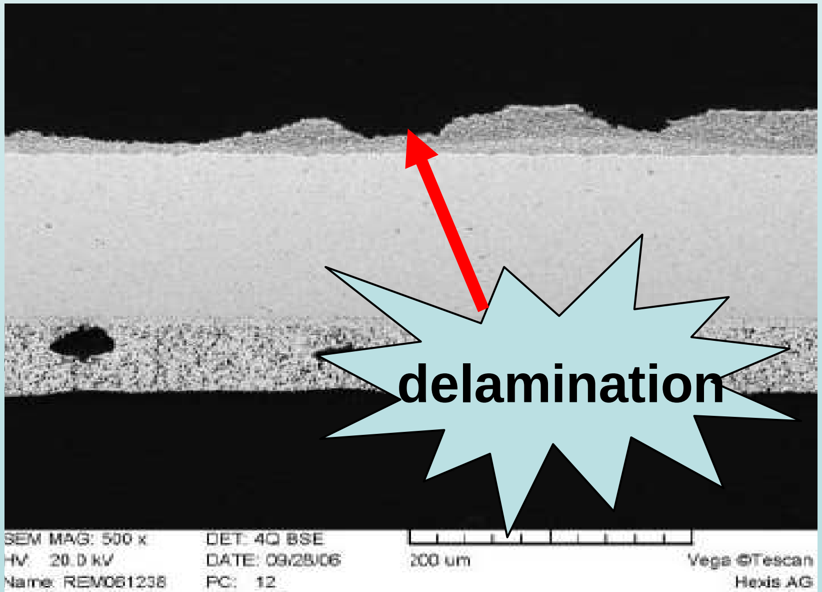


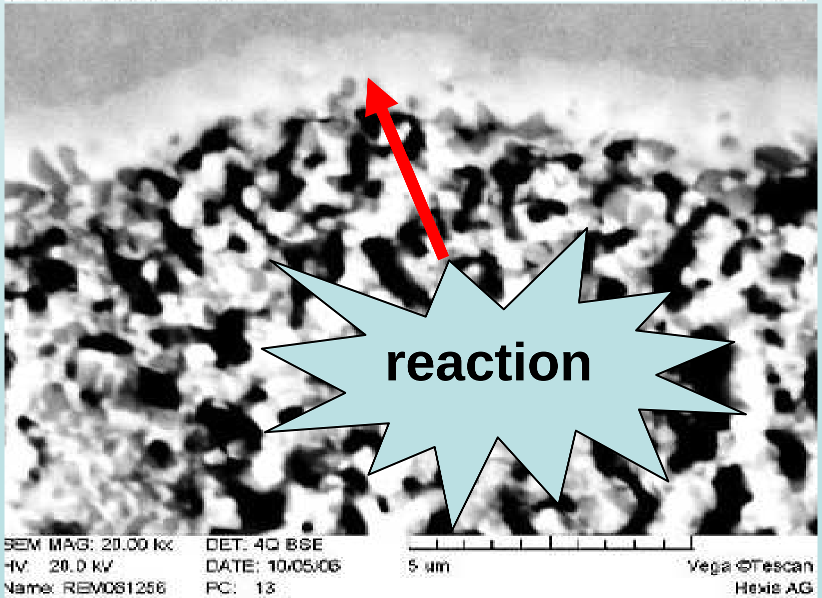
CELL → **STACK** → **SYSTEM**

Microstructural degradation









Stability / Degradation of Anodes

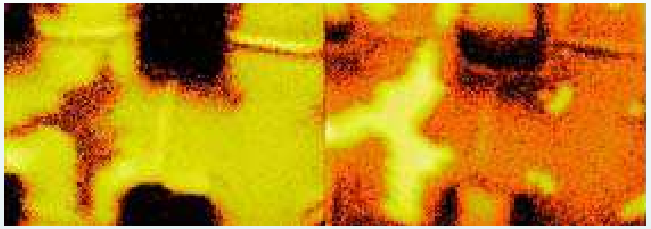
- **Ni sintering**
  -Temperature influence
  - Ni-C liquid formation
  - Water vapors (Ni(OH) vapor)

- **Ni Sulfur poisoning**
  - H_2S (COS) concentration
  - S Coverage over Ni/ dissolution into Ni
  - Ni-S liquid formation

- **Redox stability**
  - Effect Water Vapors(?)
  - Temperature increase on oxidation

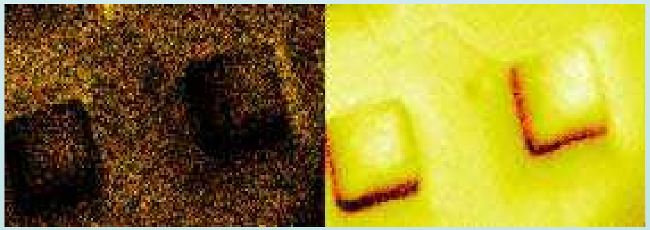
SIMS image

^{12}C ^{16}O



Ni/YSZ

^{12}C ^{16}O



Ni/SDC

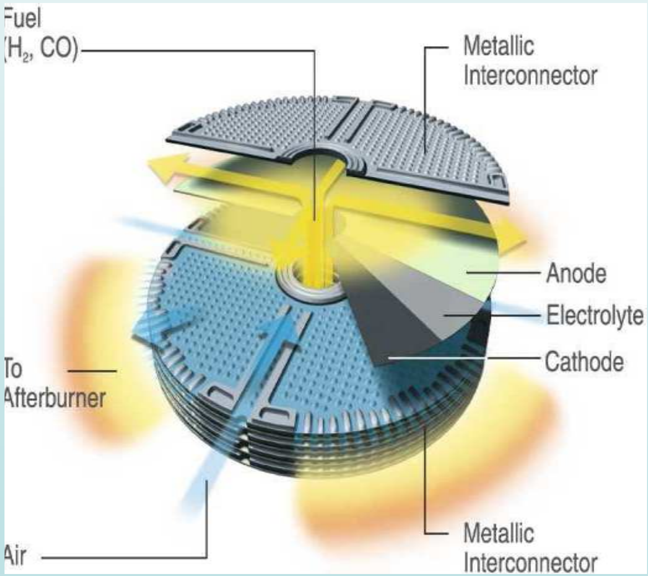
Important role of water vapor pressures (EIS)
O, H and C atoms are dissolved into Ni (dynamic SIMS)

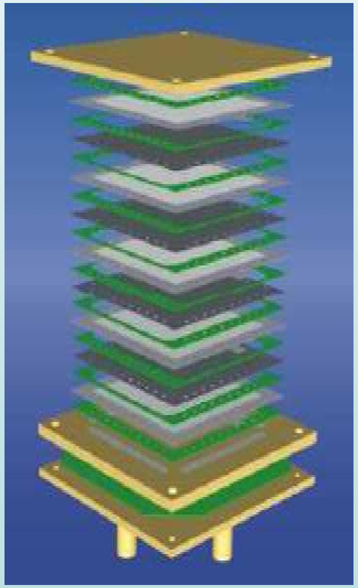
AIST

SOFCs TECHNOLOGY

D. Eyler, '**Recent Advances in SOFC Technology**' ***ALPHEA Co.***, 1st Summer School on SOFC Technology September 6, 2004, Patras, GR.

R. Steinberger, **Worldwide Activities in SOFC: Developers, Manufacturers & Concepts**'' ***FZJ, Germany***, 4 Summer School "Manufacturing SOFC- from the laboratory to the industry-SOFC-2007" September 5-10, 2007,Ct.Constantin and Elena ,Varna, Bulgaria CD-ROM available





CELL **STACK** **SYSTEM**

SOFC Power Plant Concept

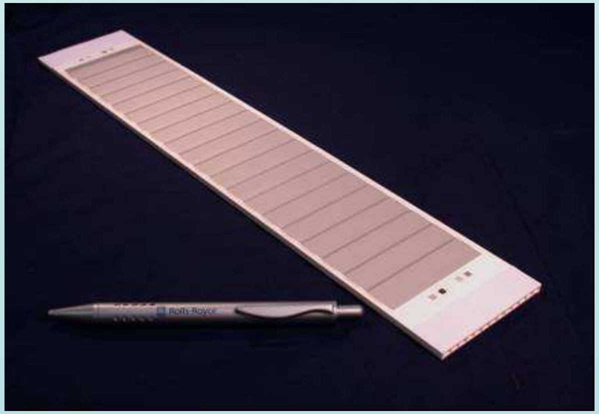
Big Plants:
SWPC/US (250 to 1000 kW) and RollsRoyce/UK (planning 1 MW)
up to 50 kW: SWPC with Fuel Cell Technologies/C, Prototech/N, Honeywell/US, McDermott/US, Global/C, CFCL/AUS

Targets => INDUSTRY & TECHNOLOGY

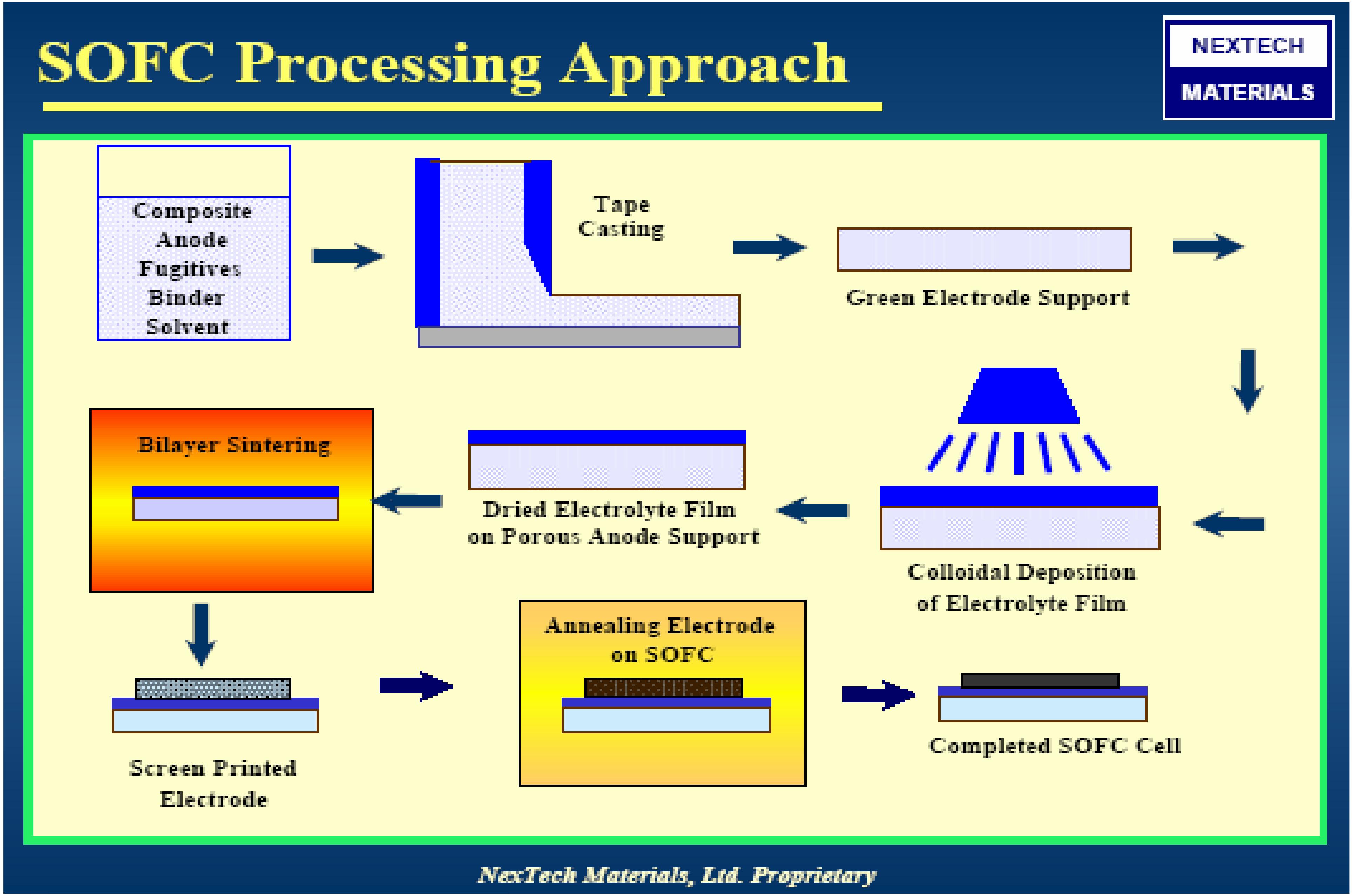
- **Costs**
- **Manufacturability**
  - No manual operation
  - Wide window of process parameters
- **Reproducibility**
  - Quality

Description of RRFCS SOFC manufacturing concept

- Extrusion
- Screen printing
- Firing

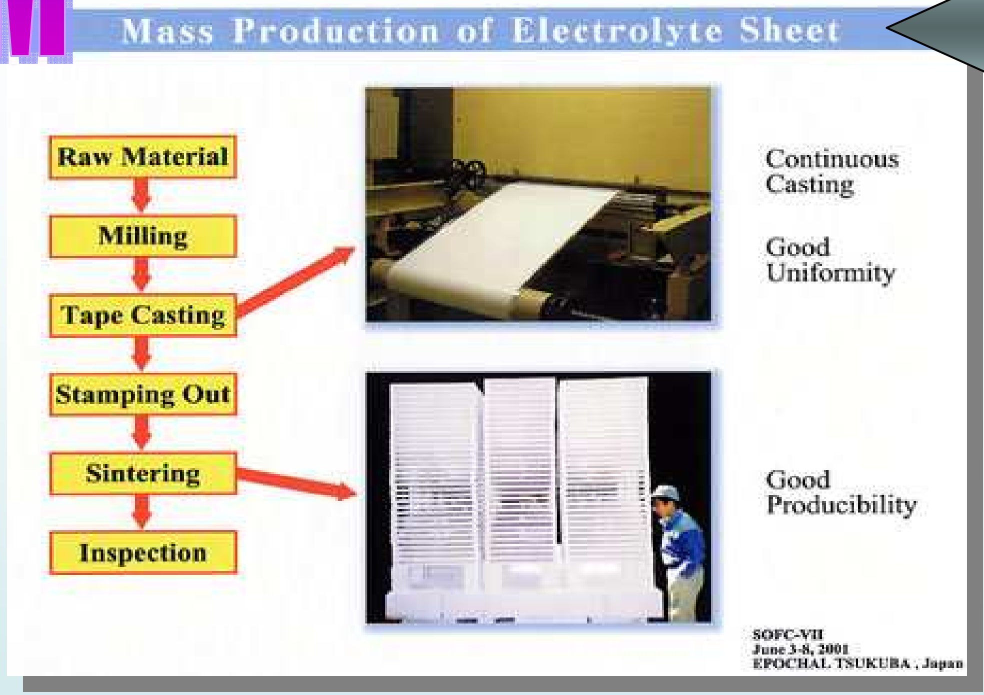


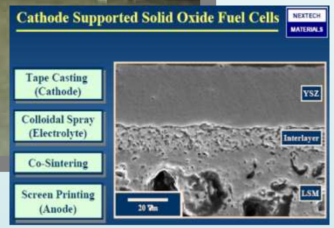
SOFC FABRICATION

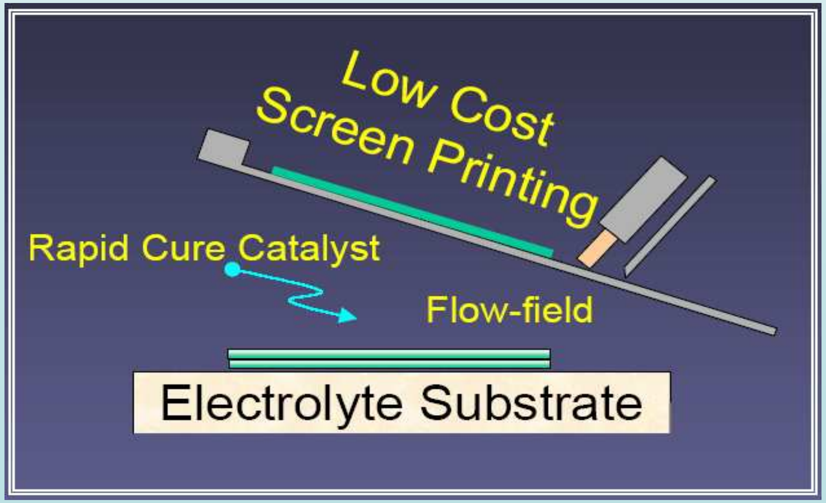


Simple & cost-effective fabrication processes

NIPPON SHOKUBAY



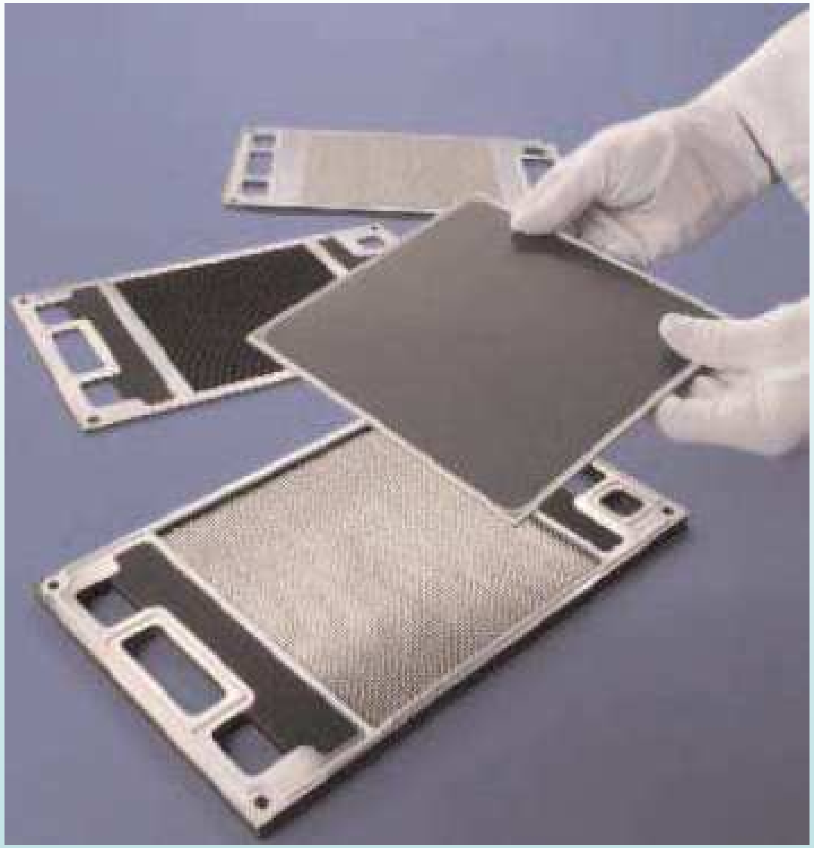




P. Ennis, Properties and Production of Steels for SOFC Applications, 4-th REAL-SOFC Summer School, 3 – 7 September 2007, Varna, BG

SOFCs

STEELS



Ceramic cells and metallic interconnector plates

The choice of a suitable interconnect alloy depends on the SOFC design

In anode-supported designs, promising results have been obtained by vacuum induction (VIM) melting ferritic, high Cr interconnector steels (Crofer 22 APU)

Important research issues for further steel development and qualification

- behaviour in C- containing fuel gases and redox atmosphere
- resistance under frequent, long-term thermal cycling
- stability of very thin interconnects
- reducing formation of volatile Cr species
- improvements in mechanical properties (creep strength)

SUMMARY

REQUIREMENTS OF SOFC FABRICATION METHODS

RECOM.

- **TAPE CASTING METHODS:** Tight control of particle size distribution is important; relatively low surface areas needed for high green density.
- **CO-SINTERING PROCESSES:** Lower sintering temperatures are desired; control of sintering shrinkage rates is essential.
- **COLLOIDAL DEPOSITION:** Dispersion chemistry is critical; higher surface areas can be tolerated; tailored particle size distributions are beneficial.
- **PLASMA- SPRAY METHODS:** Large particle size and spherical powder morphology are required for optimum flow characteristics.
- **EXTRUSION:** Lower surface areas needed for dimensional control and green strength; particle size requirements vary by developer > (t-SOFCs)
- **ULTRASONIC SPRAY PYROLYSIS:** Lower yield production value is needed to increase; suitable for multilayer /functional deposition process

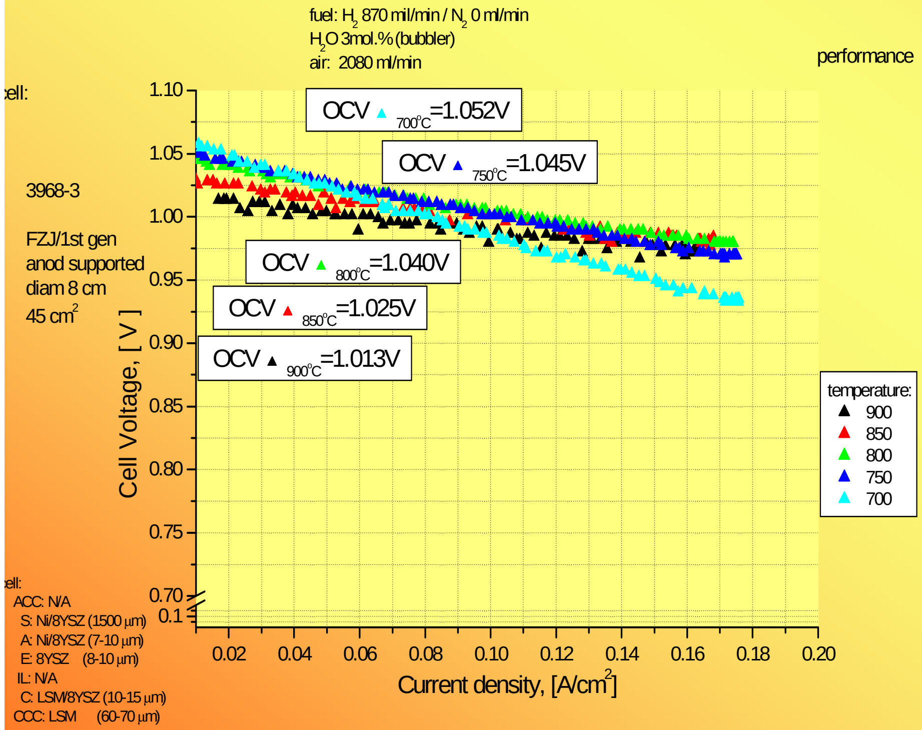
➢**The best method** is this one which is low cost, high- volume manufacturing method (one step production track in air), low temperature method suitable for automation, PC control of the technological parameters for multilayer deposition and on- line robotisation process:

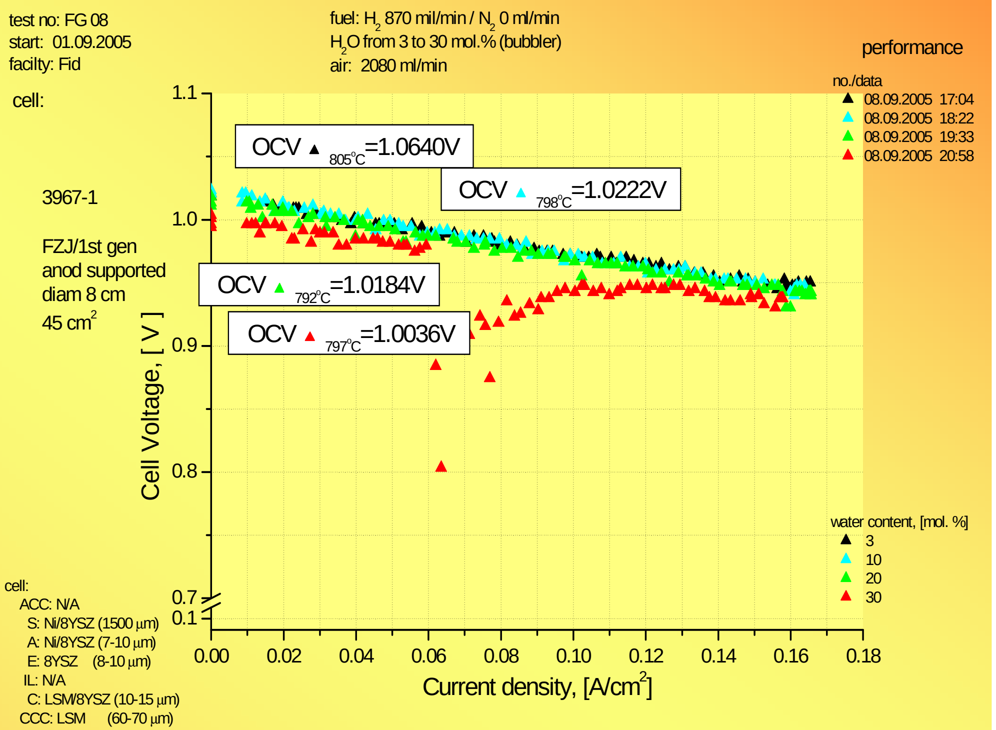
i.e. : **To adopt** low-cost microelectronic fabrication techniques to SOFC component production ;

: **To develop** a low- cost tape casting/lamination/screen printing technique for fabricating anode- supported SOFCs.

CELL PERFORMANCE

Study of water vapour pressure influence on V-I characteristics at 800°C (short term experiments with different water content (3, 10, 20, 30 mol. %H2O) in fuel at temperatures 700°C and 900°C.



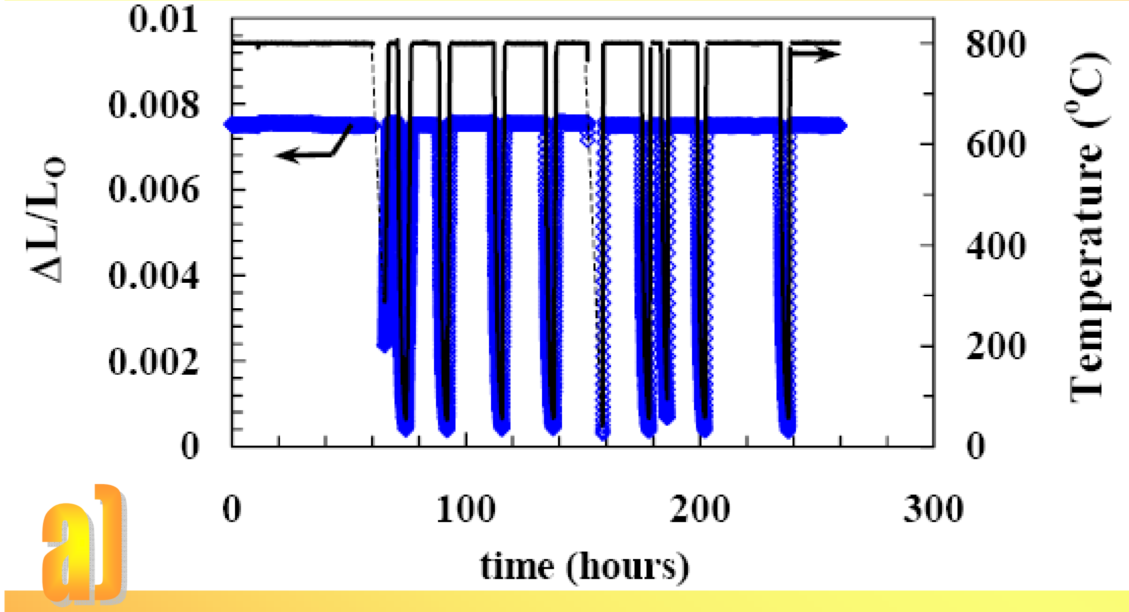


STUDY

at 3% H_2O – f (T)

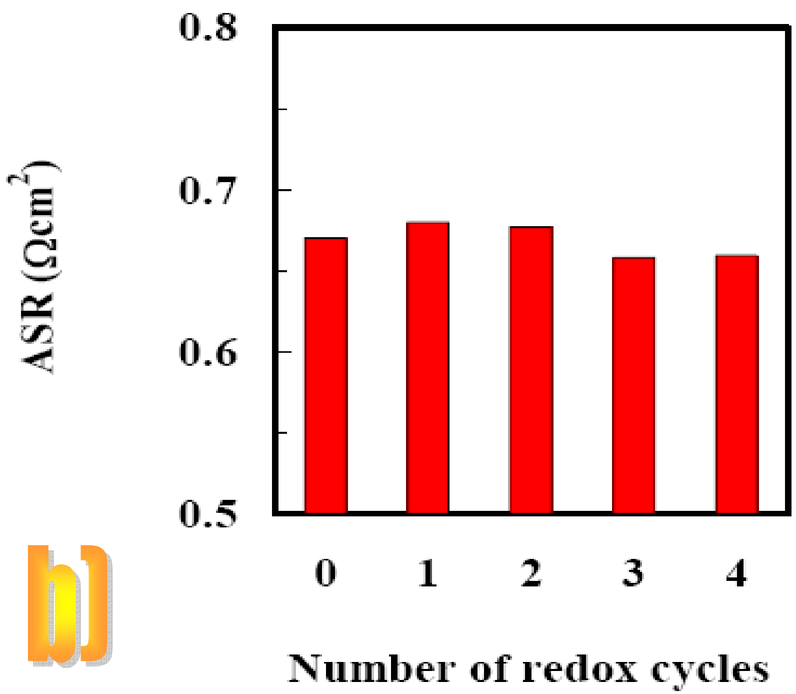
at 800°C– f (H_2O content)

RedOx STABILITY



Fuel/cell test: T= 800°C. Fuel is H_2/H_2O=97/3 ;oxidant is air.

- **No change in cell resistance after several redox cycles;**
- **No loss in dimensional stability**



Effect of reduction– oxidation cycling on relative expansion of $La_{0.4}Sr_{0.6}TiO_3$ (a) and effect of oxidation-reduction cycles on the cell area specific resistance at 0.7 V (b) [20]

- **Exposure to reducing environment at 800ºC** (corresponding to SOFC anode environment during operation);
- **Exposure to air during thermal cycling** (corresponding to conditions an unprotected anode would experience during system startup and shutdown).

2002-2006

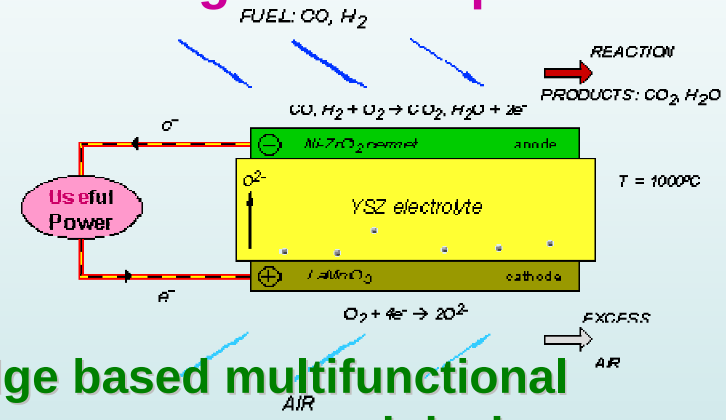
LAMAR

Sixth Framework Programme

Laboratory of Advanced Materials Research

SSA FP6- 510314 - ANVOC

Application of Nanotechnologies for Separation and Recovery of Volatile Organic Compounds



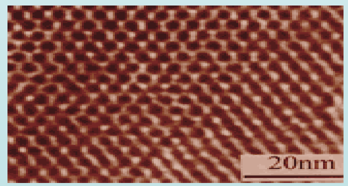
SES6-CT-2003-502612

REAL - SOFC

✓**AREA 3--NT&NS, Knowledge based multifunctional materials and new production processes and devices**

NMP3-CT-2005-011783

MULTIPROTECT



NMP3-CT-2005-011783

ENFUGEN

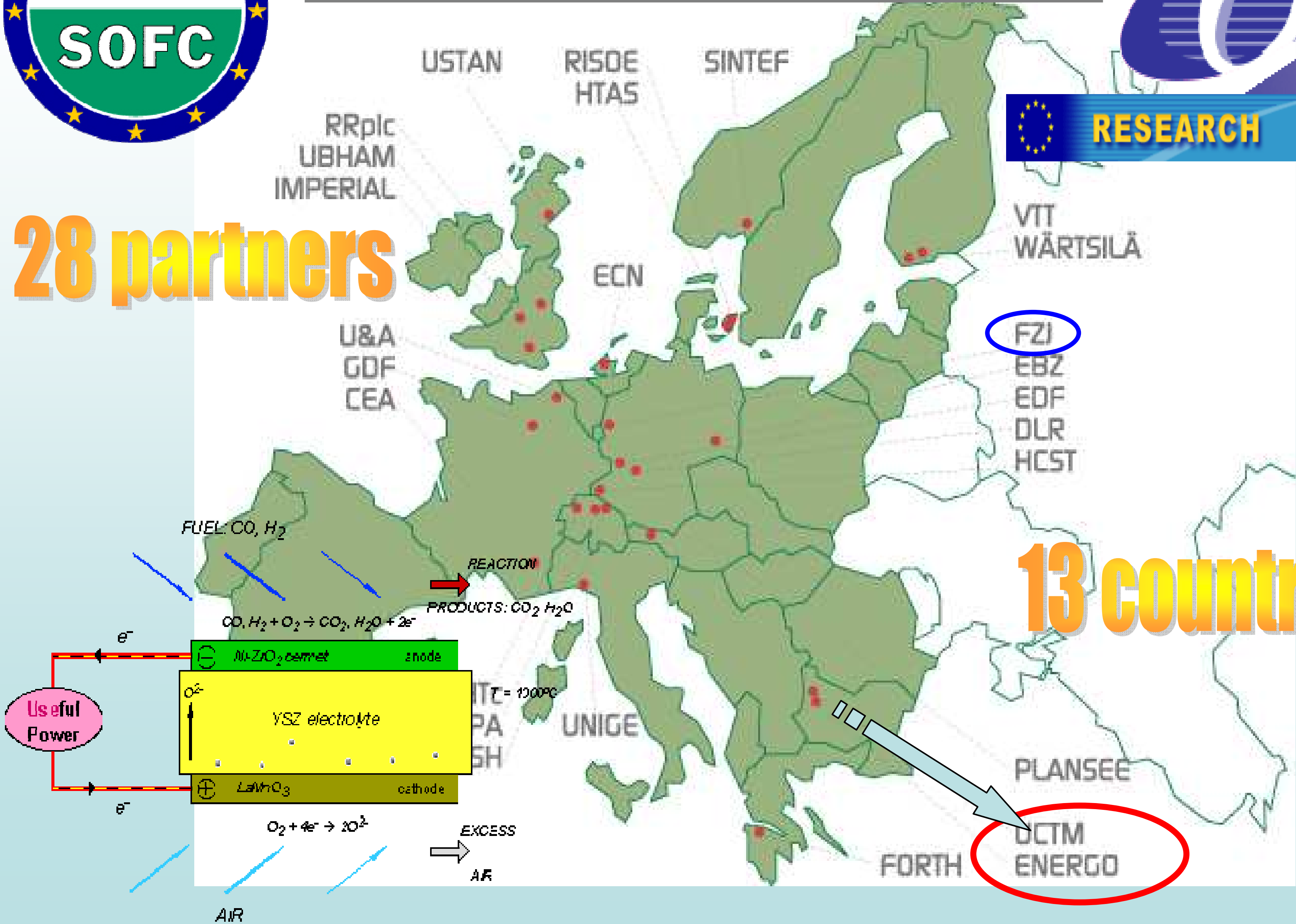
http://www.enfugen.net/

7-th FP 2007 - 2013

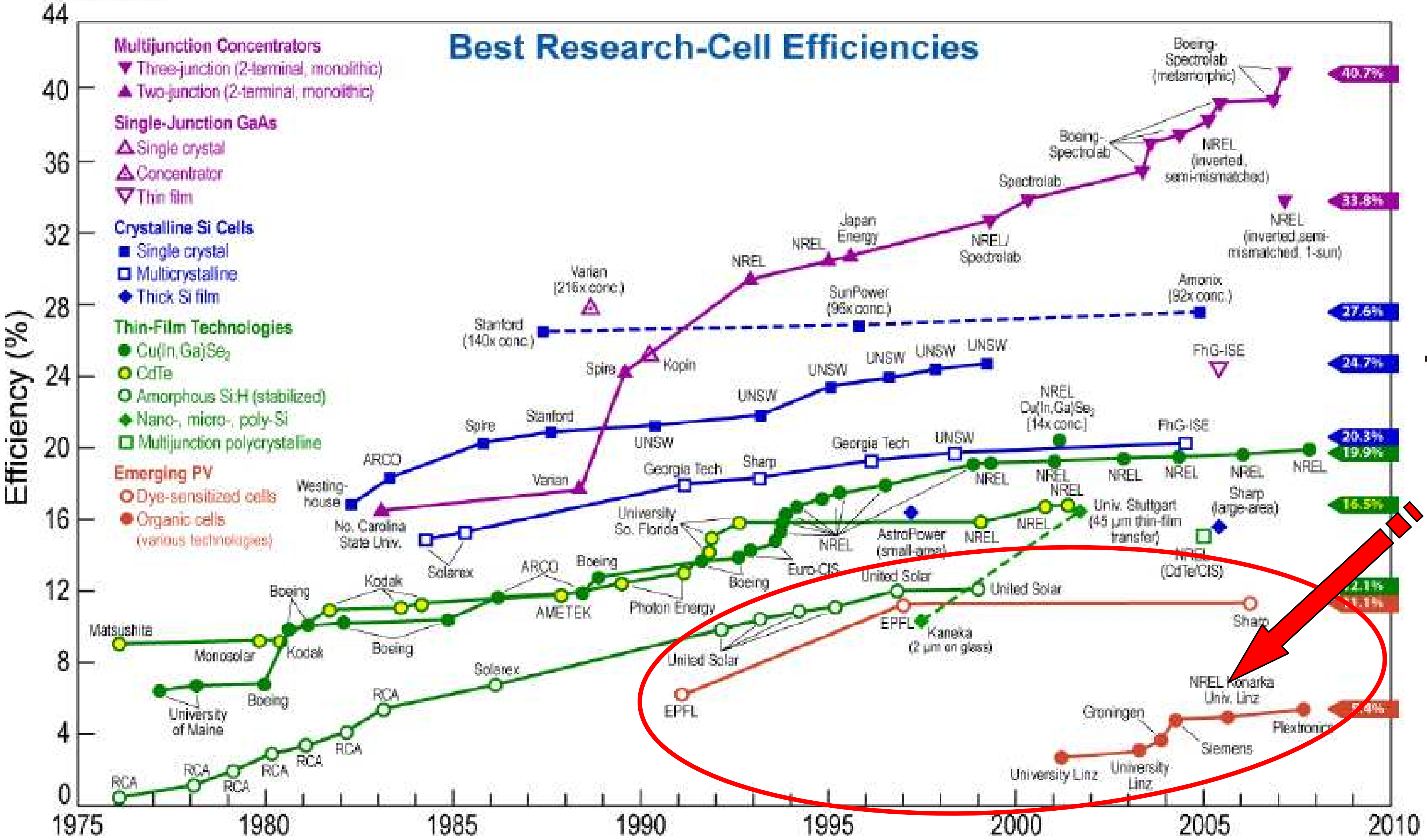
SES6-CT-2003-502612
REAL - SOFC

28 partners

13 countries

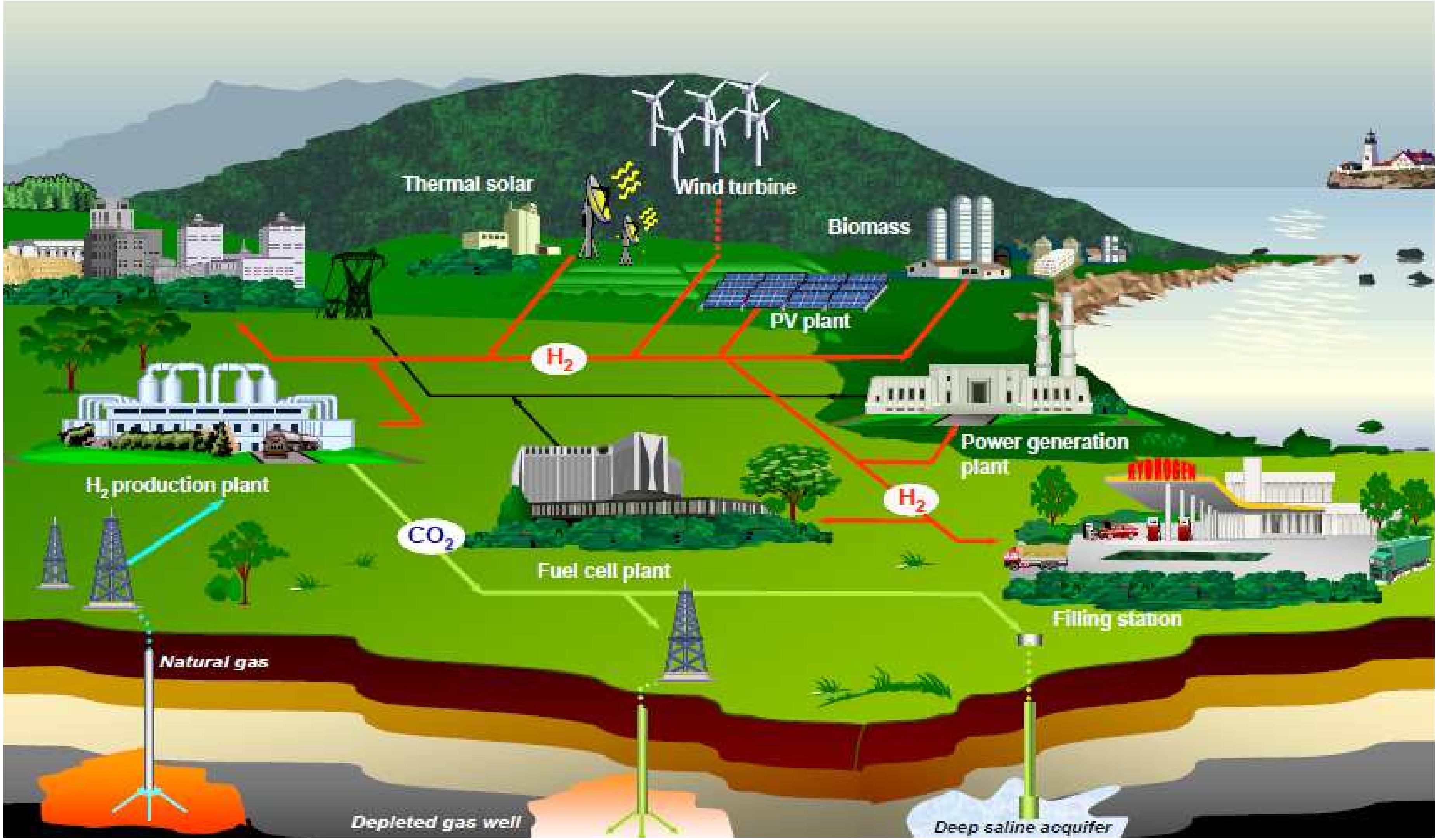


FORECAST for SOFC and RES [NREL 2011 data]



Map of solar cells efficiencies vs. year of R&D and companies involved

FORECAST for SOFC and RES



A view for the future grid of hydrogen production, transport and utilization with other R.E.S., origin from ENEA .

LABORATORY OF ADVANCED MATERIALS RESEARCH

DEPARTMENT OF SILICATE TECHNOLOGY

DEPARTMENT OF PHYSICAL CHEMISTRY

DEPARTMENT OF INORGANIC TECHNOLOGY AND ELECTROCHEMISTRY

UCTM

LABORATORY OF ADVANCED MATERIALS RESEARCH

The mission of LAMAR

To develop, identify and investigate of advanced materials and technology, including nanotechnology, in the strategic areas of **EDUCATION, RESEARCH** and **APPLICATION** . The main goal is to meet the needs of a future society, science and industry through activities as follows:

- - innovative education in frontier of the science
- - international and interdisciplinary collaboration
- - partnerships for a mutual progress
- - research on a high level of expert competence
- - application activities to the industry

i.e. target focused on the **MATERIALS** with new effects for the future components, devices and systems.

LAMAR Facilities

1- Atmosphere corrosion tests procedures:

- **Climatic tests**:
  - **Test on shock alteration of the temperature** region (-50º - +55º C).
  - **Test under dry heat treatment** > **conditions** - Test up to 100ºC
- Test in salt – spray camera > due to standard ASTM 117
- **Test under low atmosphere pressure > conditions** - Pressure from 1 to 700 torrs; Temperature range: from - 60ºC to +120ºC
- **Test under high humidity level > conditions** - Temperature from 20ºC to 65ºC; Humidity up to 95%
- **Test under impact of sun radiation > conditions** - Irradiation dose of one test cycle from 8.9 to 26.9 k Wk/m2, Irradiation intensity 1120 W/m2

2- Corrosion tests under special conditions (high temperature corrosion tests)

- Corrosion tests under special conditions (high temperature corr tests) - isothermal treatment in **the temperature range from 400o to 900ºC**, in H2 atmosphere and other supplementary conditions as the water content, that can be precisely adjusted (**N2 and/or H2 + x% H2O**); these experiments can be performed on disc-shaped samples with disc diameter not above than 120 mm and thickness limited to 1mm;

LAMAR Facilities

3. Electro-chemical measurements (according to the standards req.)

- Impedance spectroscopy (IS) measurements.
- Potentiodynamic measurements (Rp, Ecorr, Icorr and etc.)
- Electrochemical noise.

4- Mechanical corrosion test procedures (coop. lab)

- Combined properties investigation, e.g. thermo-mechanical characterization;
- Tests on stretch
- Tests on bend and flatten;
- Kick on elastic behavior at 20℃ ;
- Kick on elastic at minus/negative temperatures;
- Kick on elastic at mechanical ageing;
- Hardness for 3 marks (imprints);
- Test on hit (measurements on vertical axis)

5- Other kind of tests:

- Micro-analyses, shlif & Macro-analyses, shlif ;
- Chemical analysis and control of the materials (ICP- AES method)
- Measurements of surface defects and surface topology ;
- Supersound (0.6 MHz) capabilities for measuring of macro-defects
- Test under vibrations (sinusoidal vibrations);

LAMAR Facilities

6- Supporting and additional study with:

- **Thermodynamic tests** of stability by simultaneous TG-DSC and/or TG-DTA analysis with phase diagrams correlation; Conditions - up to 1600ºC and choice of 2 different gas atmospheres, e.g. N2 and H2; (not simultaneous mass spectroscopy or FT-IR analysis of the vapors is available, at present !)
- **Diffraction and spectroscopy tests**: X-ray diffraction, IR spectroscopy, X-ray photoelectron spectroscopy, SEM, TEM, EDX, Fe57 -Moessbauer spectroscopy, electron and/or neutron diffraction measurements (INRNE-BAS) and characterization i.e. structural characterization and morphological studies, including diagnostic behavior of the surface treatment;
- **Optical microscopy** at different magnifications;
- **AFM surface morphology** studies for selected coatings and thin films.

7- SOFCs test rig installation :

- The installation is available for **short-term (performance)** and **long-term (durability)** single SOFCs tests under different fuels and conditions. Special tests for IT- SOFCs under adjusted conditions are also possible to be executed. Experiments at temperature regions from 400o to 900ºC, and/or at isothermal treatment at H2 atmosphere and other conditions are available, as well. Tests for SOFCs disc samples at **80mm** and 120mm in diameter.

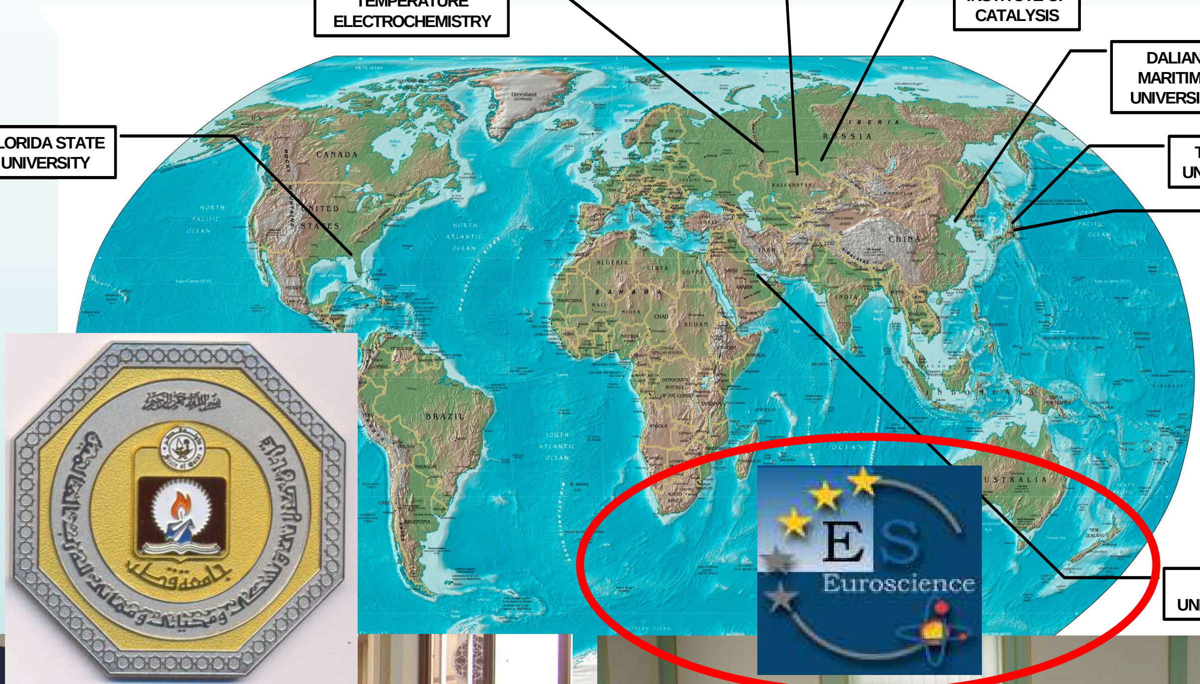
8- Additional laboratory facilities:

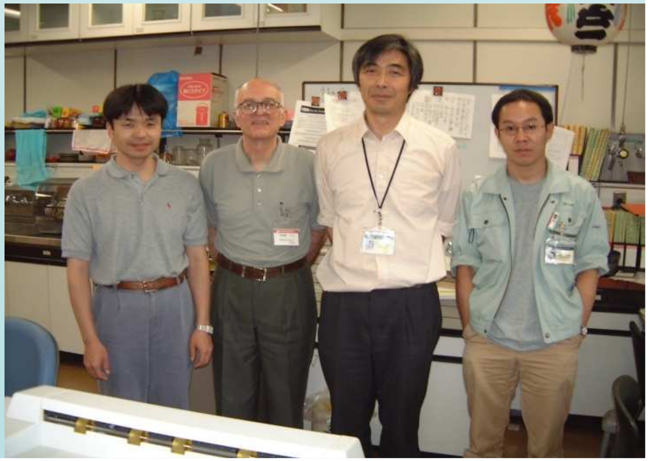
- Programmable Naber- furnaces up to 1350 oC; CO2 and He-Ne lasers; ultrasonic spray pyrolysis system; furnaces for polymer film deposition and surface treatment; Netz- milling unit, screen printing unit and UV- photopolymer deposition unit , sol- gel deposition (Deep& Spinning) and etc.

INTERCONTINENTAL COLLABORATION

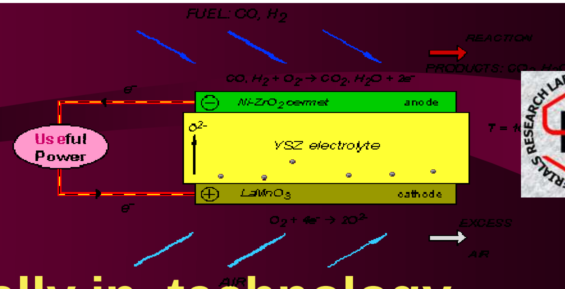
Dalian Maritime University 大连海事大学 International Cooperation College

TOHOKU UNIVERSITY





CONCLUSIONS



✓-The progress in SOFCs science and especially in technology during the last decades is obviousy high and depends of the MARKET;

✓- For the working stability of SOFCs materials the key aspect is to decide the interaction between the basic and acidic character of the substances ;

✓- Materials choices are critical issue for SOFC stacks and systems in terms of costs, reliability and on damaging of the stack ;

✓- The influences of working conditions on cathode Cr – poising mechanisms have to be better understood and to be object of study;

✓- Anode performance degradation is correlated to its microstructural Changes ;

✓ - Redox stability is one of the biggest challenge for small scale SOFC systems for residential use;

✓- To resolve problems of SOFCs components and stack degradation it is necessary to decrease working temperature to 500-600°C;

✓- System design strongly depends on the requirements of the application.

✓ - FORECAST & LAMAR

UCTM, Sofia, Bulgaria

THANK YOU FOR YOUR ATTENTION