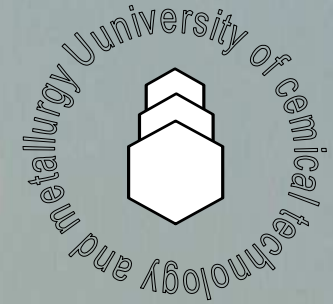


STATE-OF-THE -ART IN **SOFCs** SCIENCE & TECHNOLOGY



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< www.uctm.edu >

LAMAR



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

***** OUTLINE *****

- ✓ - INTRODUCTION
- ✓ - MARKET AND APPLICATIONS
- ✓ - SOFC CERAMIC MATERIALS
- ❖ - SCIENCE and BASIC RESEARCH
 - ❖ - SOFCs TECHNOLOGY
- ❖ - FORECAST for SOFCs and R.E.S.
 - ✓ - LAMAR FACILITIES

CONCLUSIONS

INTRODUCTION

❖ - UNIVERSITIES

- Science and Basic Research

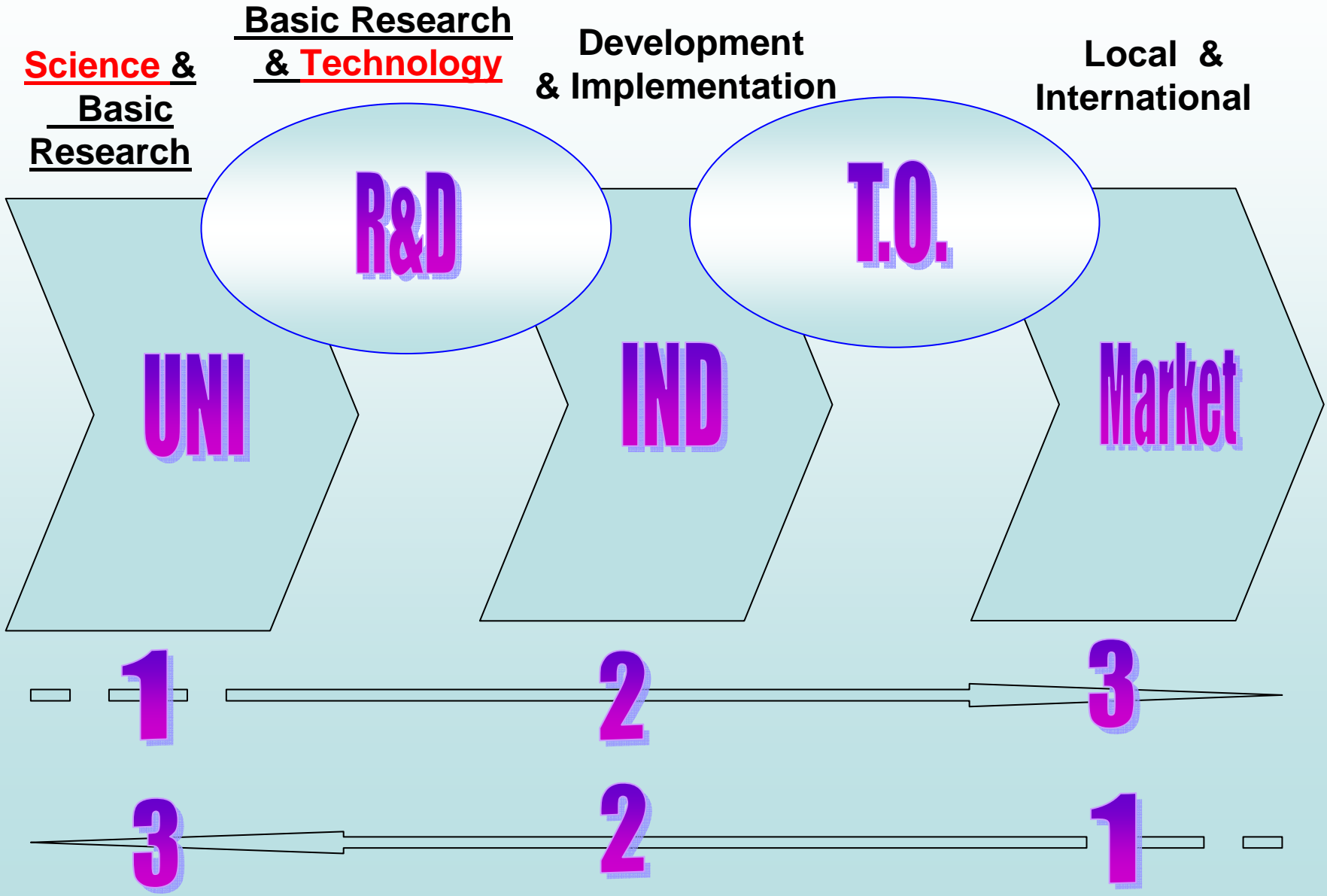
❖ -R&D ORGANIZATIONS

- Basic Research and Technology Development

❖ - INDUSTRIES incl. SME

- Development, Validation and Implementation,
(Function of the MARKET)

RELATIONS & IMPORTANCE

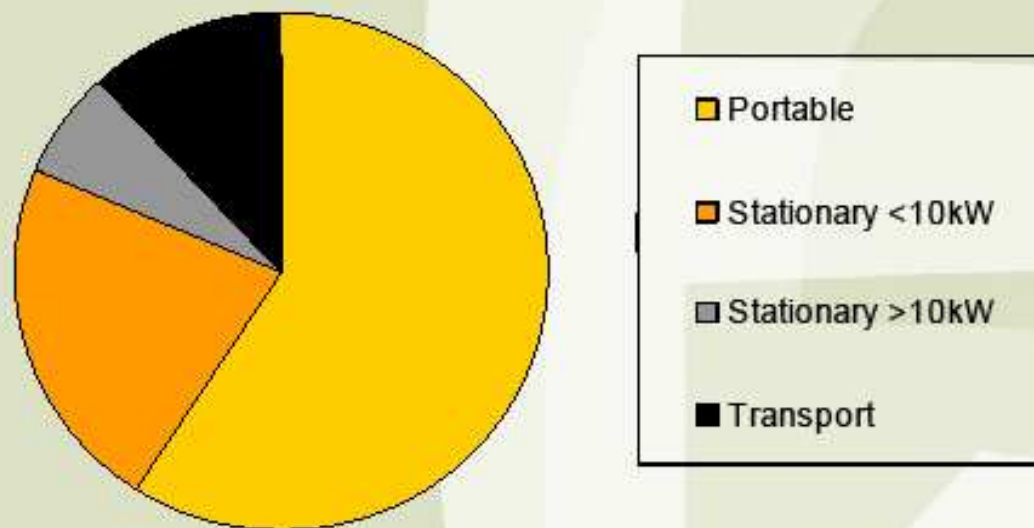




FUEL CELL TODAY

Fuel Cell Applications

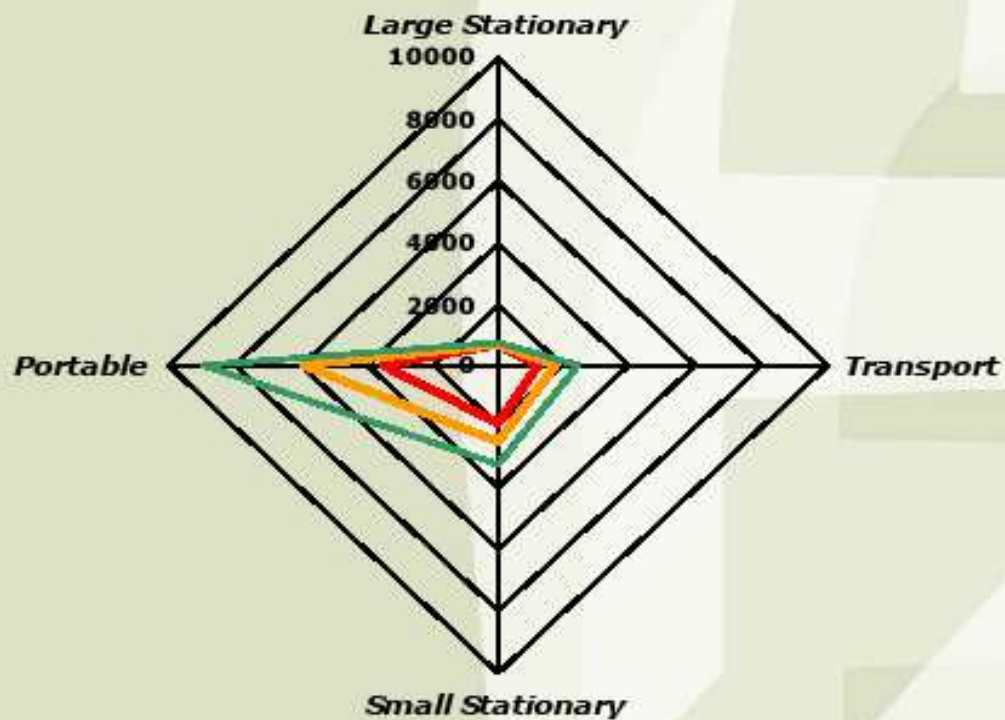
All systems built, application

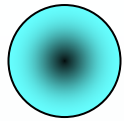




FUEL CELL TODAY

Market Growth 2003 - 2005





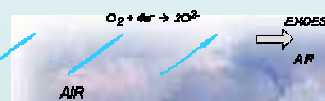
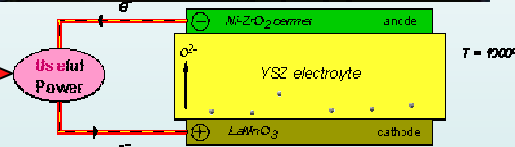
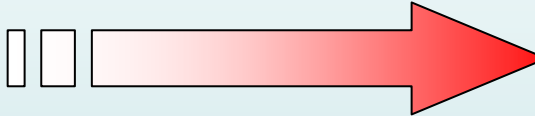
APPLICATION



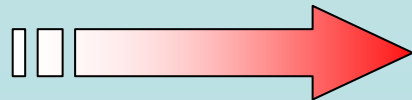
Energy Supply of Houses

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

Civil



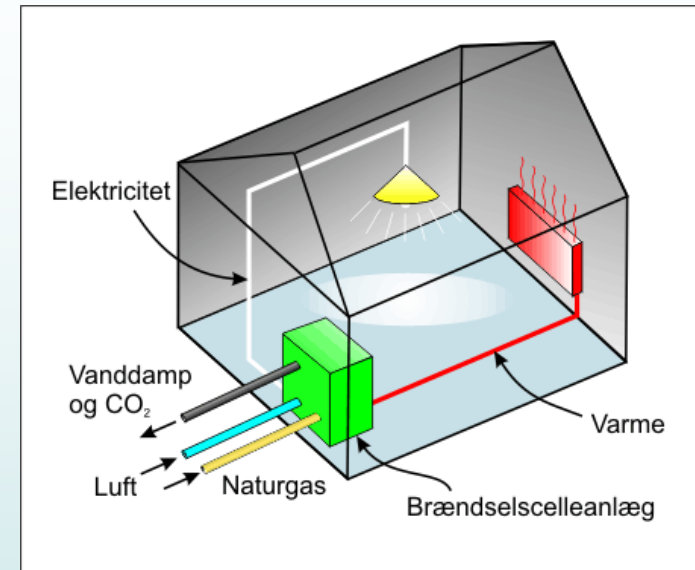
Military



Applications / system size

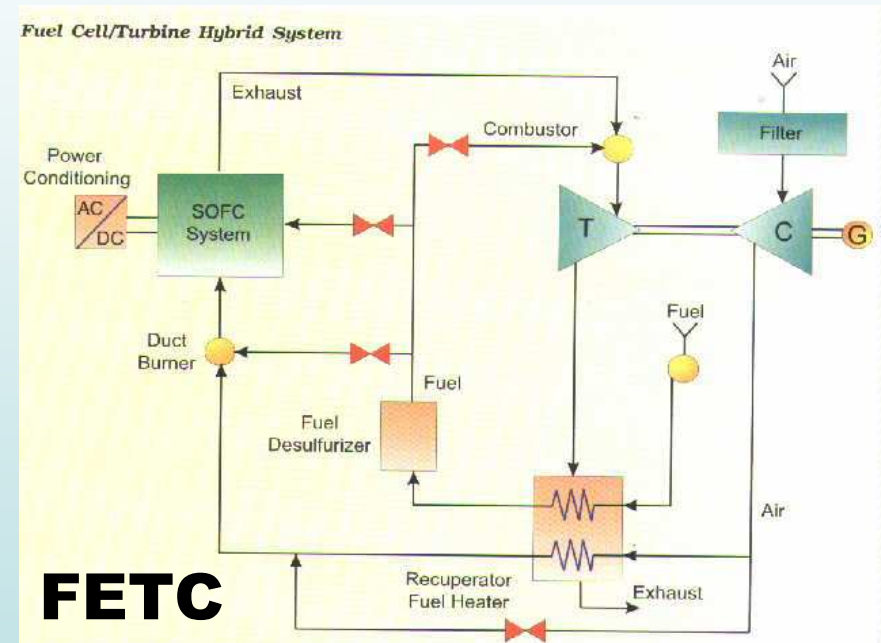
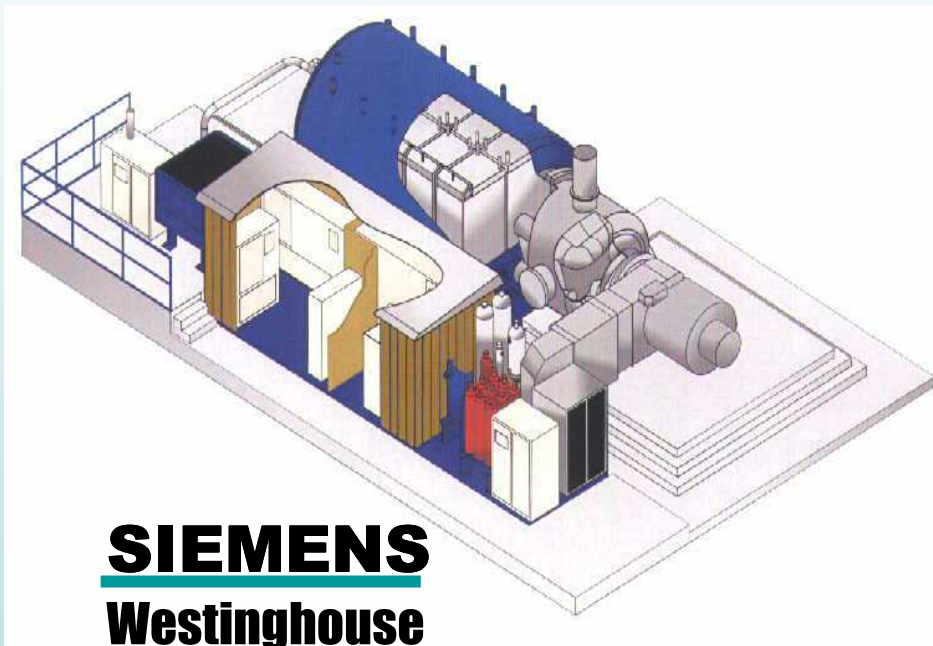
RISO

- **< 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, EGN, 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

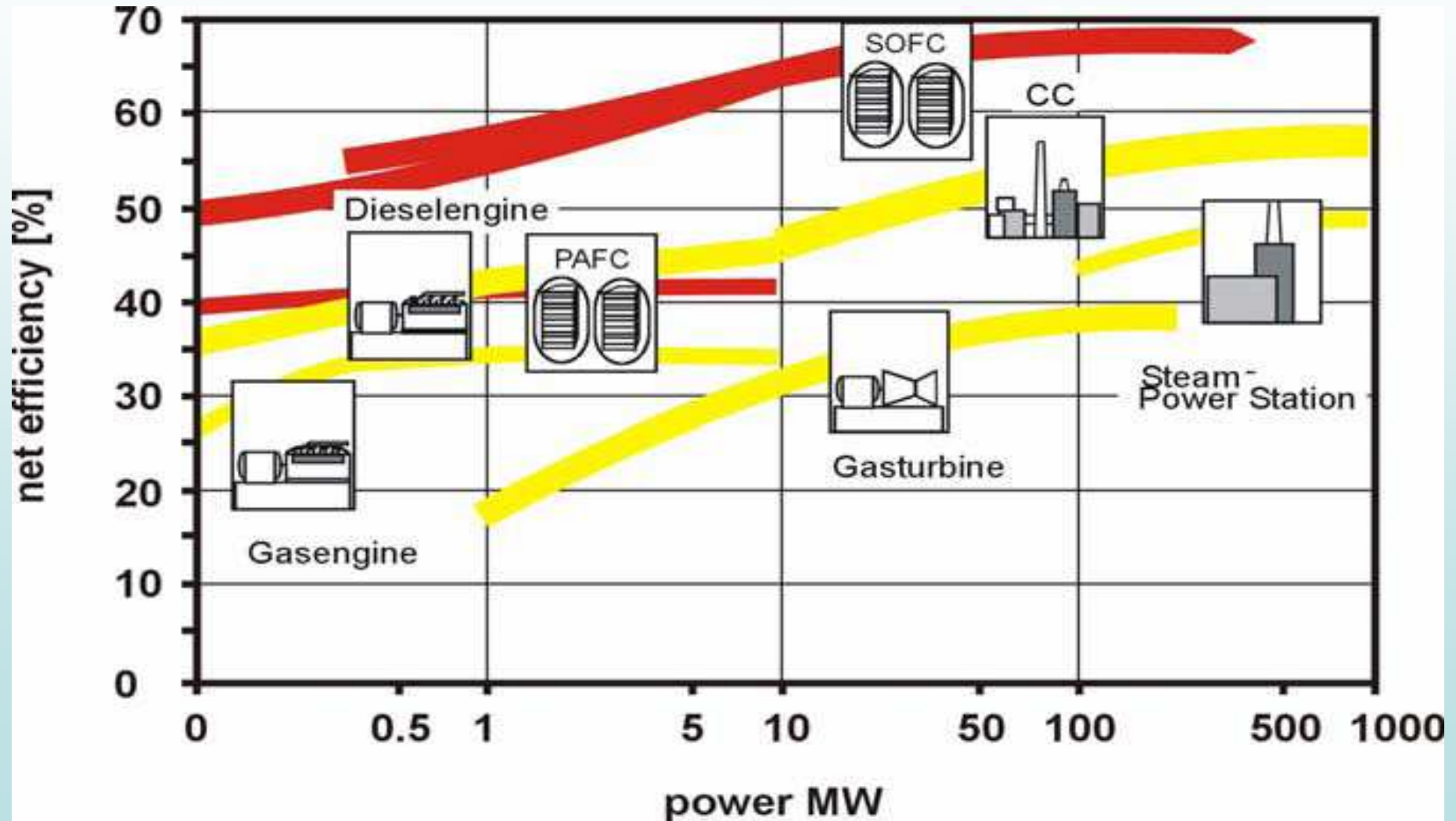
SYSTEM INTEGRATION

Efficiency: > 70% for the market 2010

Efficiency: > 80% for the market 2015

MOTIVATION

Efficiency of Different Power-Technologies





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

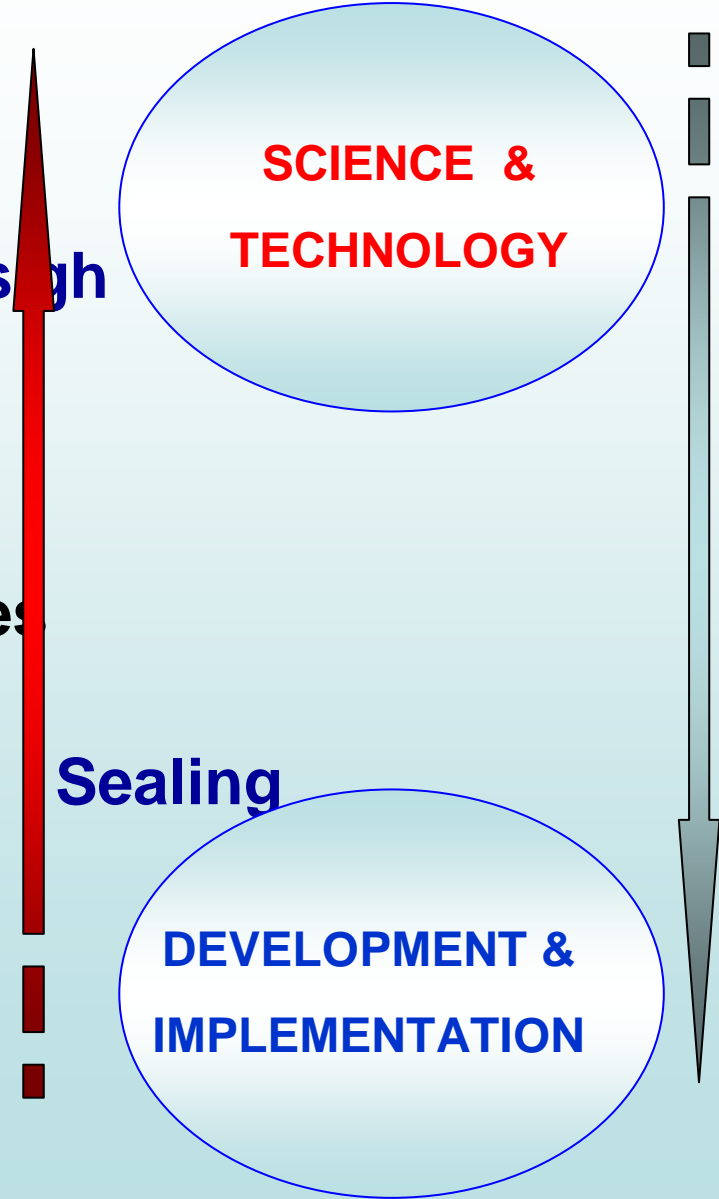
- Problem 3: Fuel Cell Production
 - Only few companies
 - Not yet mass produced
 - Learning curve: Production gets cheaper
- Problem 4: Macro Scale
 - Not enough support (funding and incentives)
 - Lack of awareness
 - Governments begin to support technology
 - Demonstration projects help raise awareness

SOFC CERAMIC MATERIALS

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

SCIENCE &
TECHNOLOGY

DEVELOPMENT &
IMPLEMENTATION



SCIENCE & BASIC RESEARCH

❖- SOFCs BACKGROUND 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

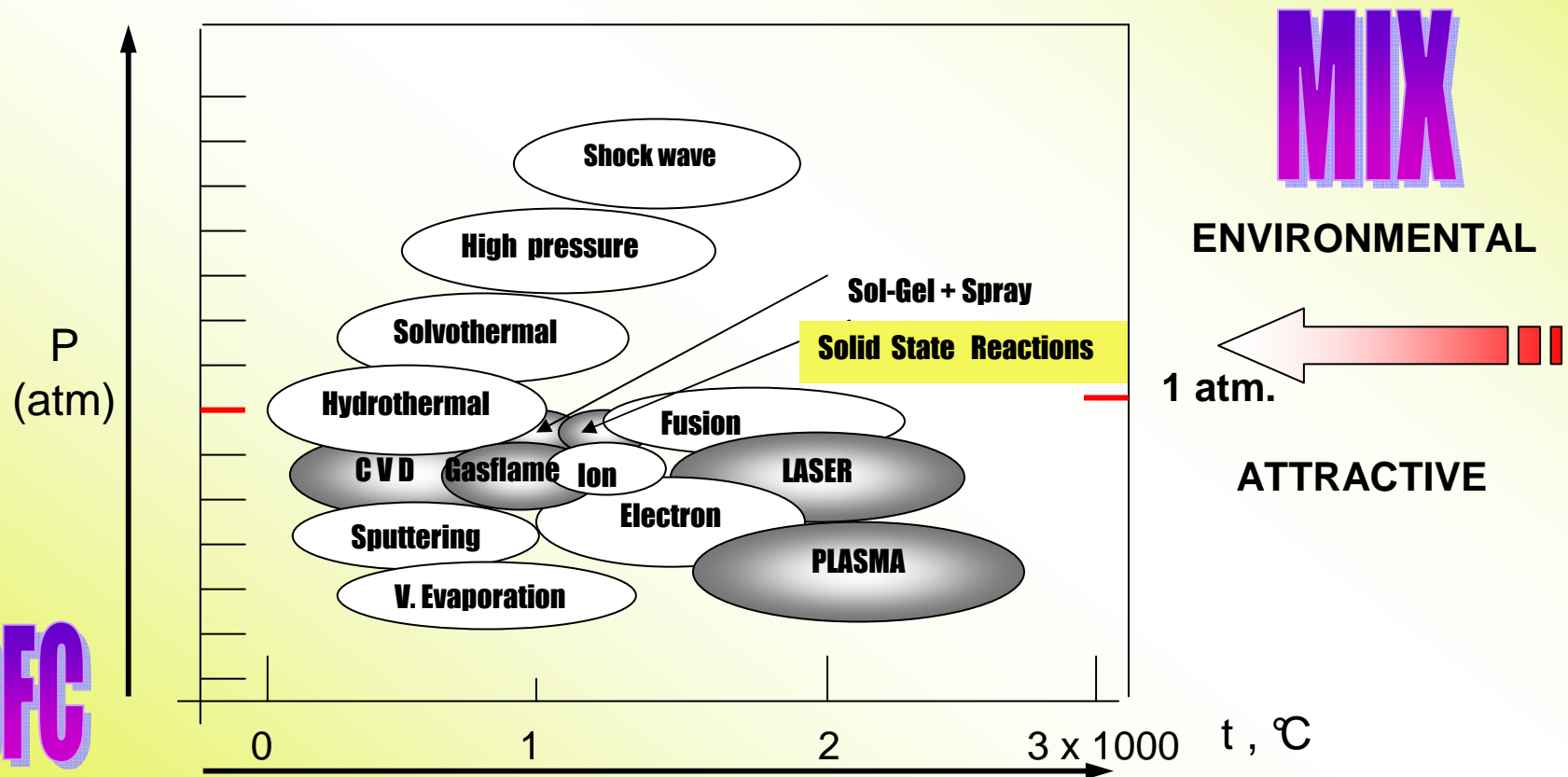
A. Atkinson, **'Solid State Chemistry of Solid Electrolytes'** Imperial College, UK, 1st Summer School on SOFC Technology September 6, 2004, University of Patras, GR

❖ - 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 & templating 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

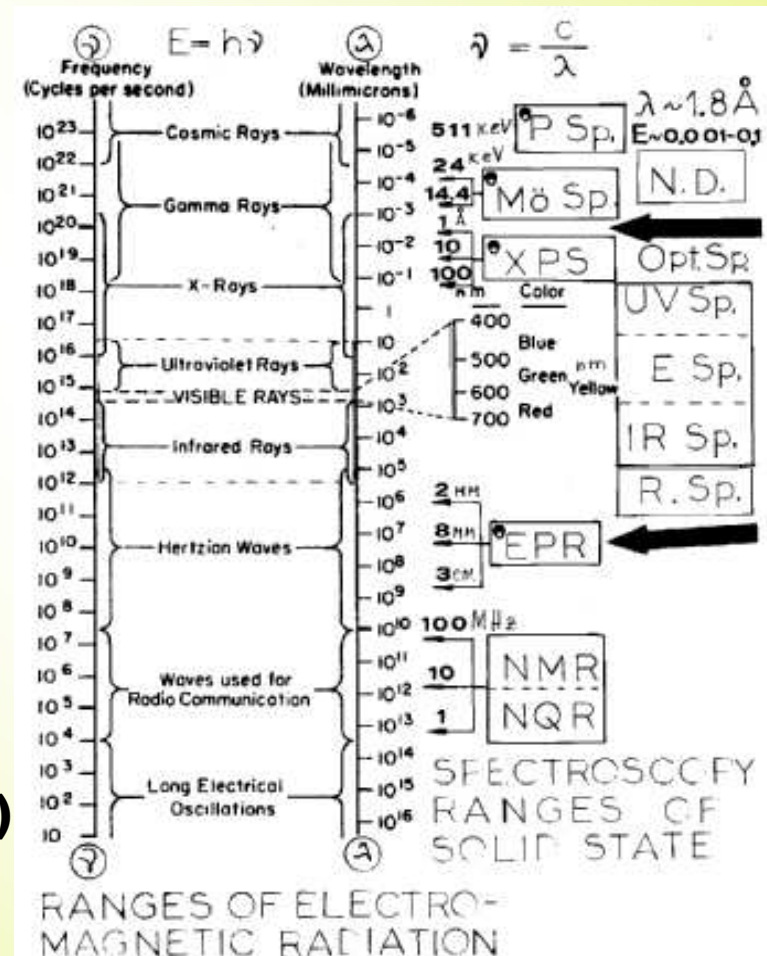
- ✓ - XRD, ED, ND, SAXS, SANS

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

TECHNIQUES FOR

PHYSICOCHEMICAL

CHARACTERIZATION

STANDARDS

4- SOFC TESTING (BEHAVIOUR)

AGEING BEHAVIOUR

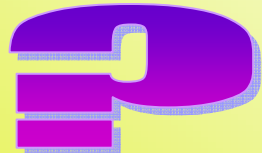
- ✓ - Ageing under various atmospheres, temperatures and current loads (influence of the water vapour)

PERFORMANCE CHARACTERISTICS

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

SURFACE & INTERFACIAL PHENOMENA

- ✓ - Thermodynamics and kinetics of Cr evaporation



PHYSICAL & CHEMICAL

TECHNIQUES



STANDARDS

Tubular Design – Siemens Westinghouse SWPC

- 190 kW at 950°C with NG/air



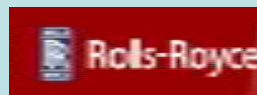
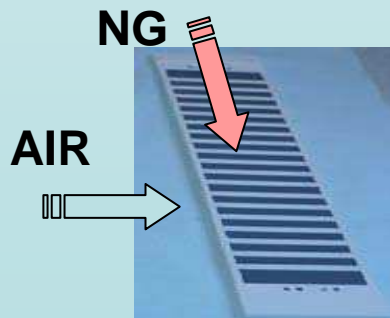
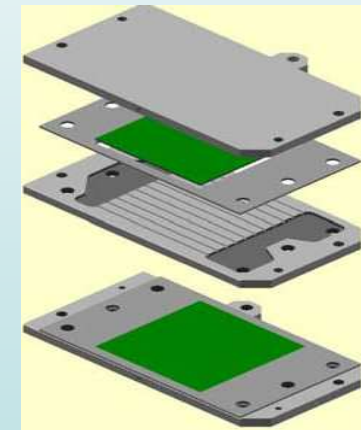
TOTO and Mitsubishi Heavy Industries MHI - 21 kW at 900°C with NG/air



Planar Design: Hexis – Swiss

(Heat Exchanger Integrated System => HEXIS)

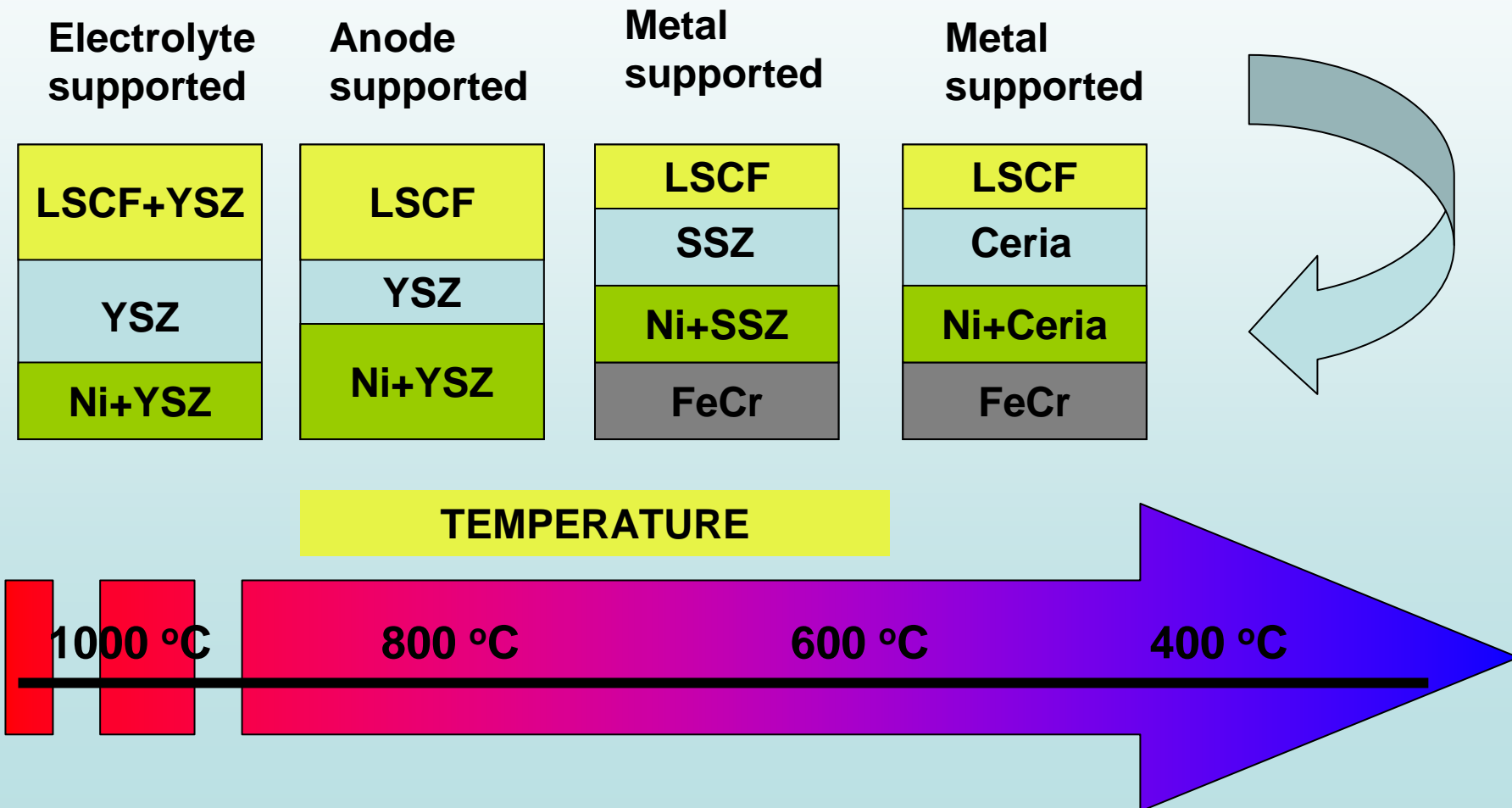
- Circular cells with a diameter of 120 mm
- 1.1. kW at 900°C with NG/air



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

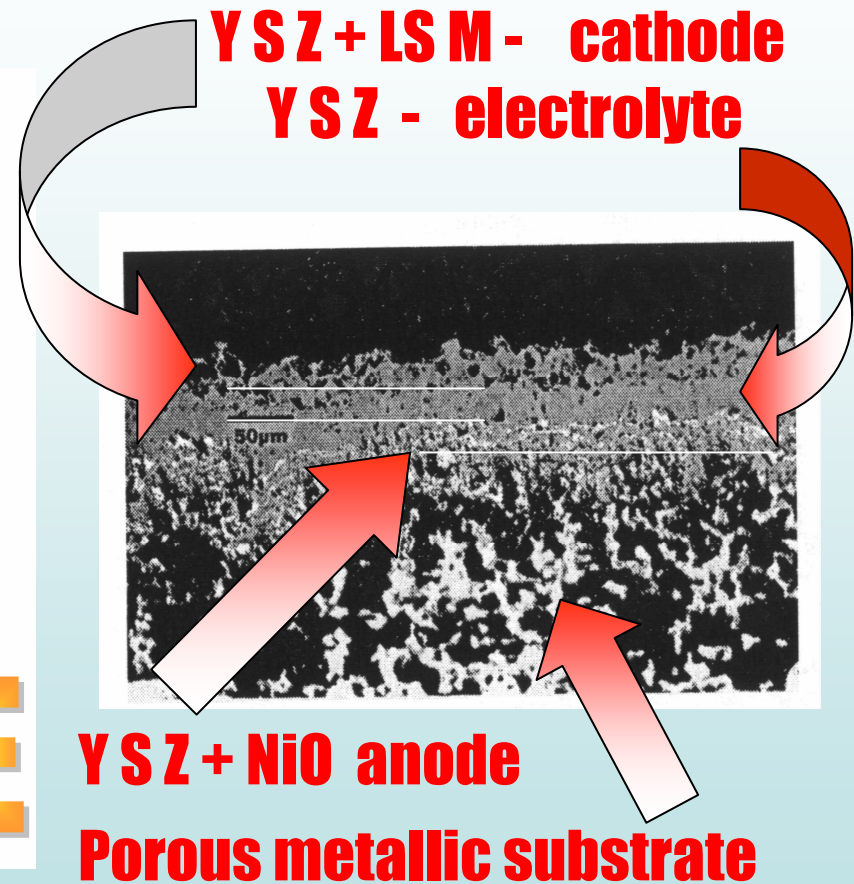
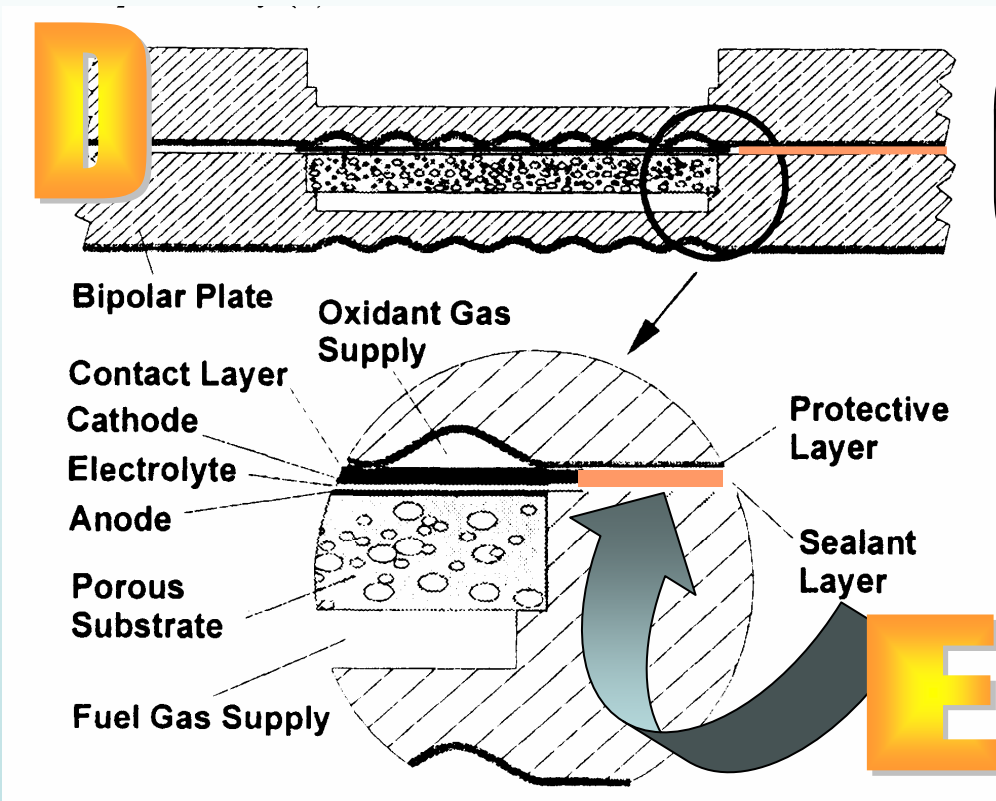
SOFCs REQUIREMENTS

Operation temperature & Materials



BIPOLAR PLATE APPLICATION

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



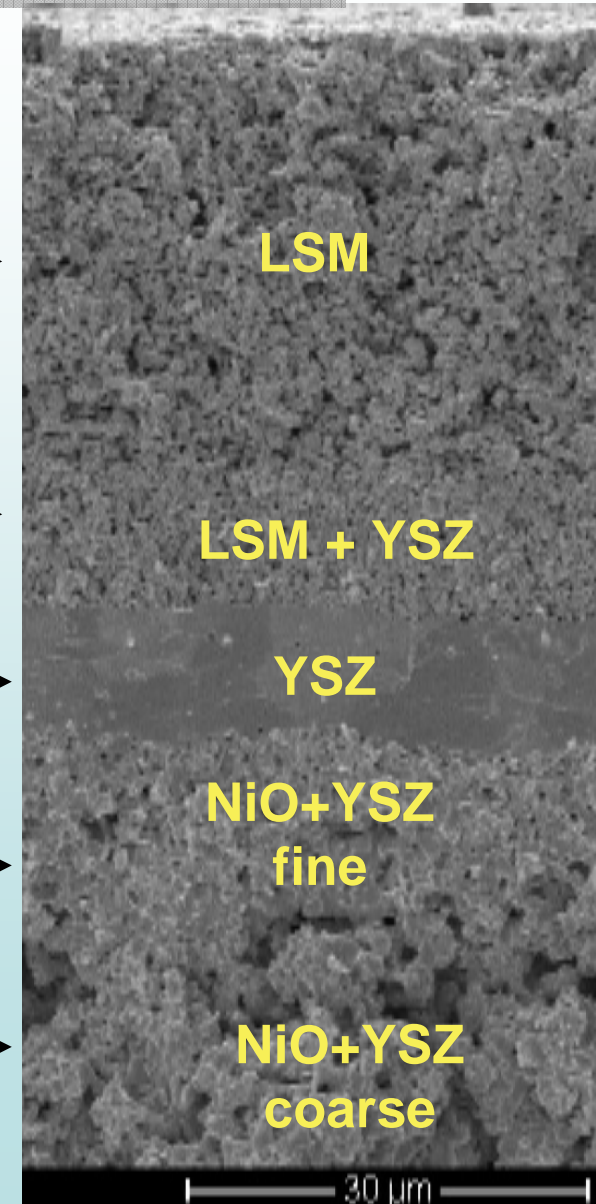
Principle of SOFC design
according to GAC- spray concept

Plasma sprayed thin film cell



State-of-the-Art of SOFCs Layer Structures

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

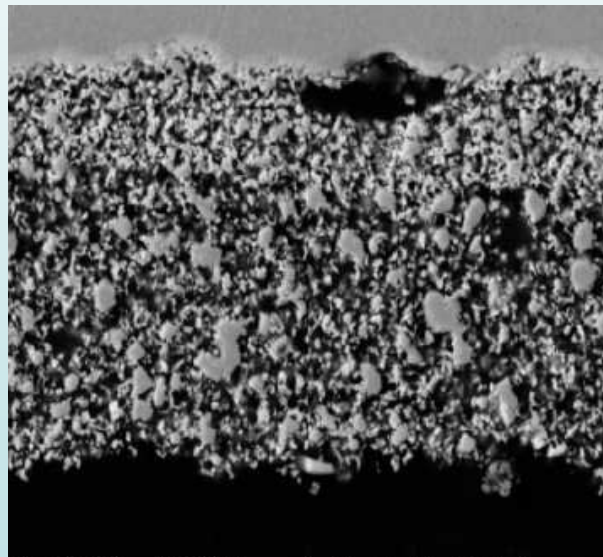


B. Iwanschitz, A. Mai, T. Hocker, 'Origin and mechanisms of anode degradation, Helix AG, Züricher Hochschule Winterthur, Swiss, Intern. Workshop on Degradation Issues of Fuel Cells, 19-21 September, 2007, Crete, Greece



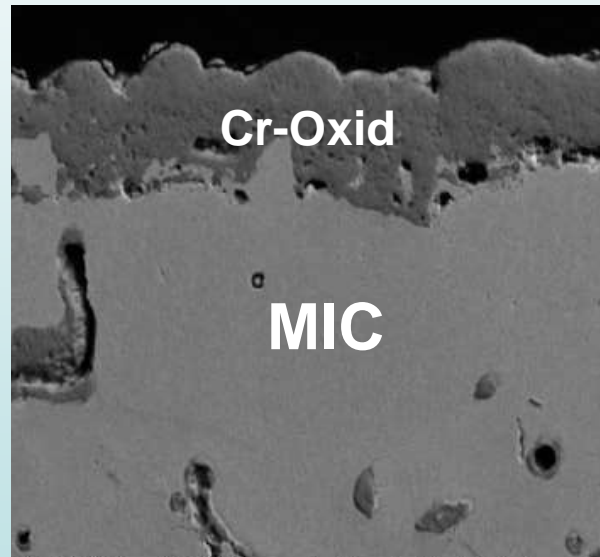
Besides **cost** and **performance**, **lifetime** is the key issue for the commercial use of SOFCs .

Cell materials degradation



SEM MAG: 5.00 kx DET: 4Q BSE HV: 20.0 kV DATE: 11/16/06 20 um Vega ©Tescan Hexis AG Name: REM081678 PC: 13

Design, Contacting, Cr-evaporation



SEM MAG: 2.00 kx DET: 4Q BSE HV: 20.0 kV DATE: 11/17/06 50 um Vega ©Tescan Hexis AG Name: REM081644 PC: 13

Thermomechanical stress

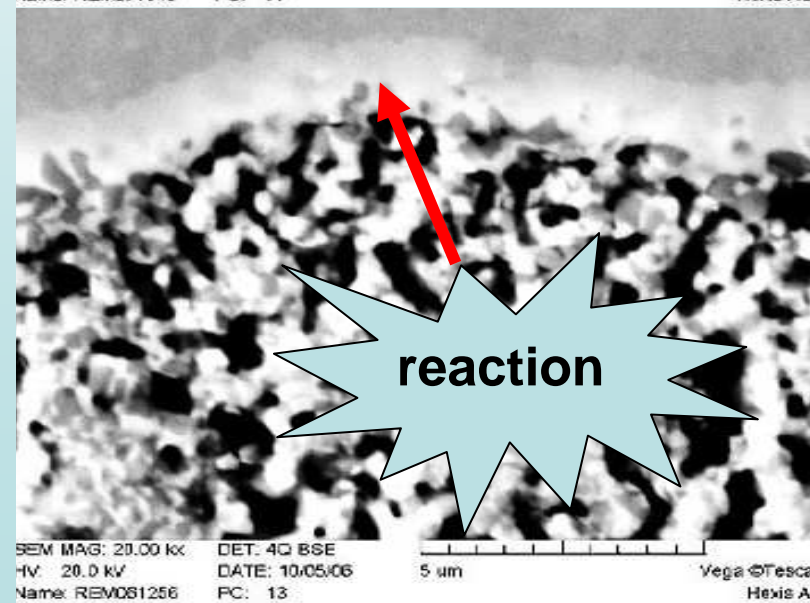
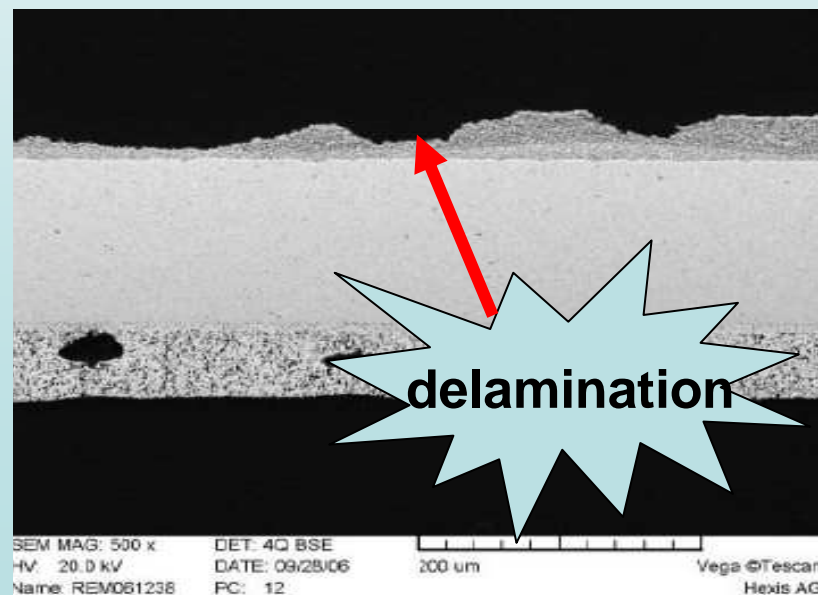
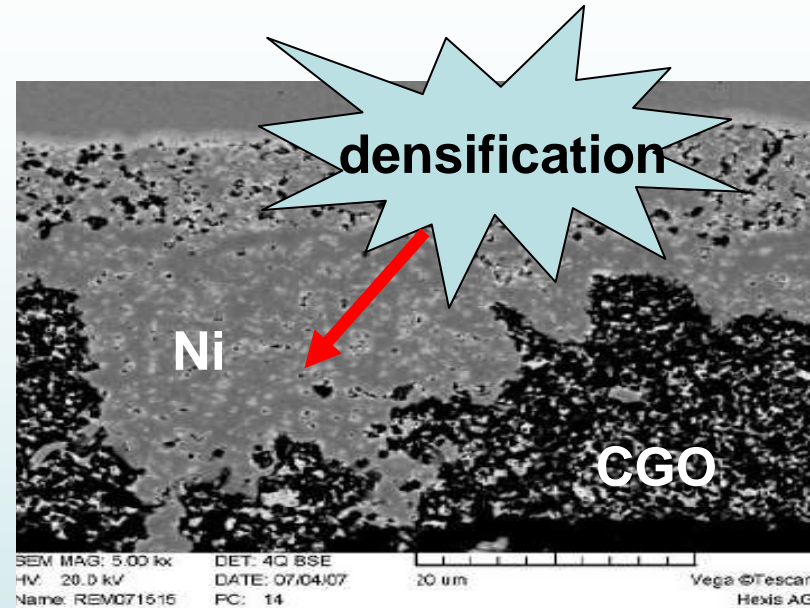
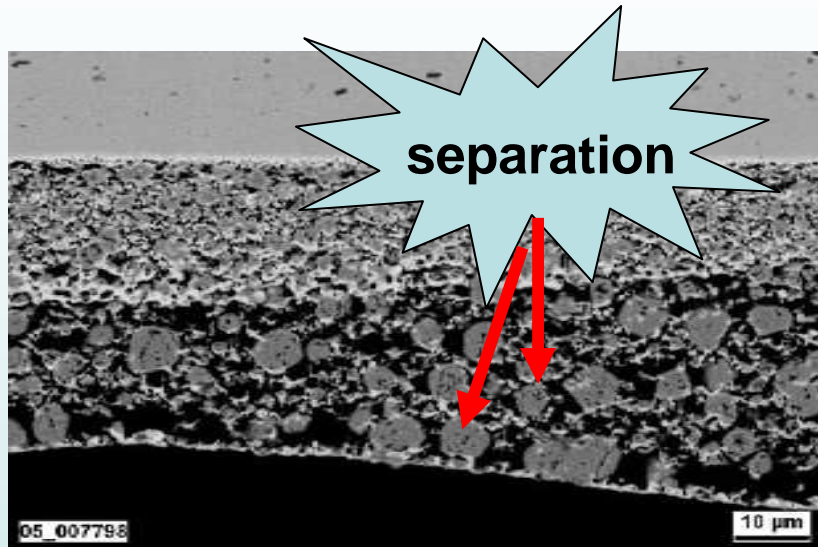


CELL

STACK

SYSTEM

Microstructural degradation



Stability / Degradation of Anodes

- **Ni sintering**

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

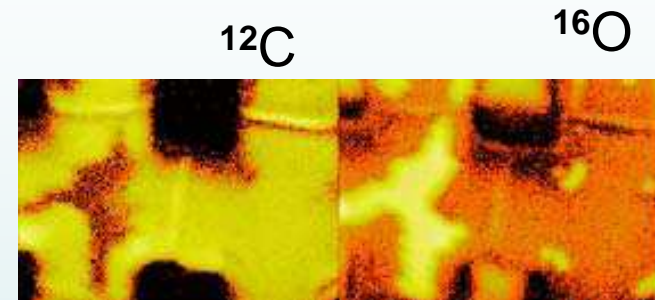
- **Ni Sulfur poisoning**

- H₂S (COS) concentration
- S Coverage over Ni/ dissolution into Ni
- Ni-S liquid formation

- **Redox stability**

- Effect Water Vapors(?)
- Temperature increase on oxidation

SIMS image



Ni/YSZ



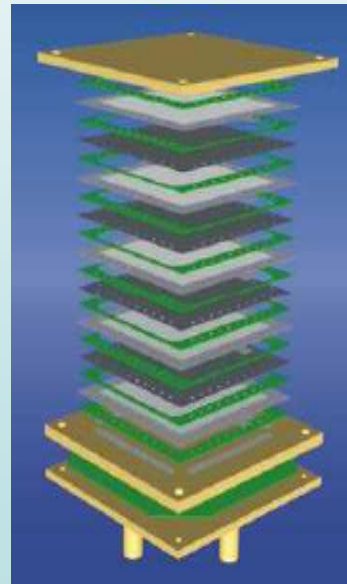
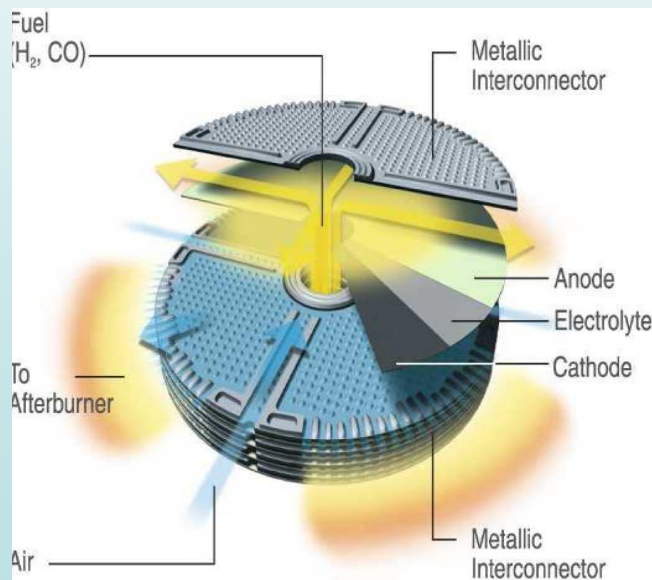
Ni/SDC

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

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

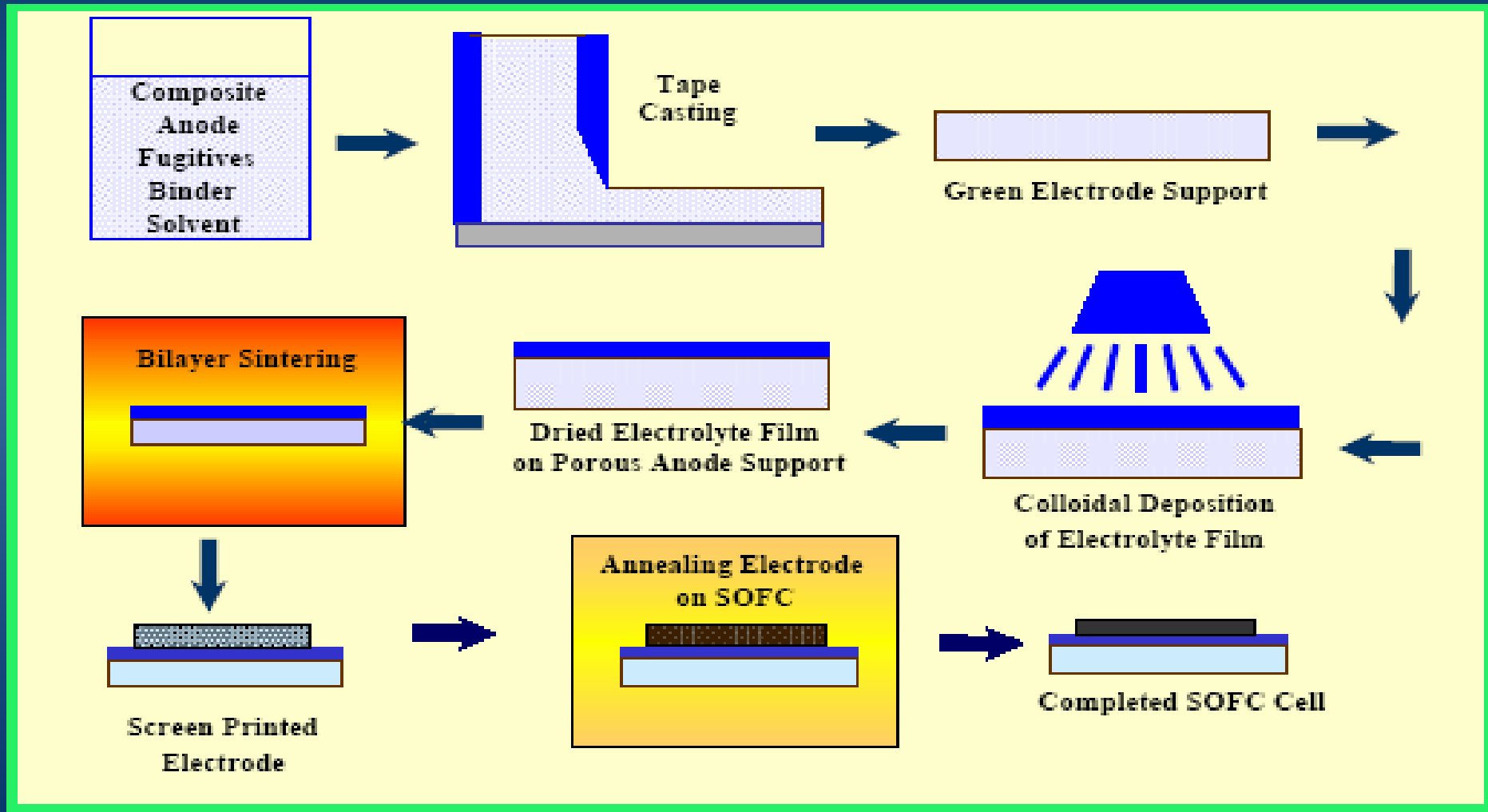
- Extrusion
- Screen printing
- Firing



SOFC FABRICATION

NEXTECH
MATERIALS

SOFC Processing Approach



M

Simple & cost-effective fabrication processes

Mass Production of Electrolyte Sheet

NIPPON SHOKUBAY

- Raw Material
- Milling
- Tape Casting
- Stamping Out
- Sintering
- Inspection



Continuous Casting
Good Uniformity



Good Producibility

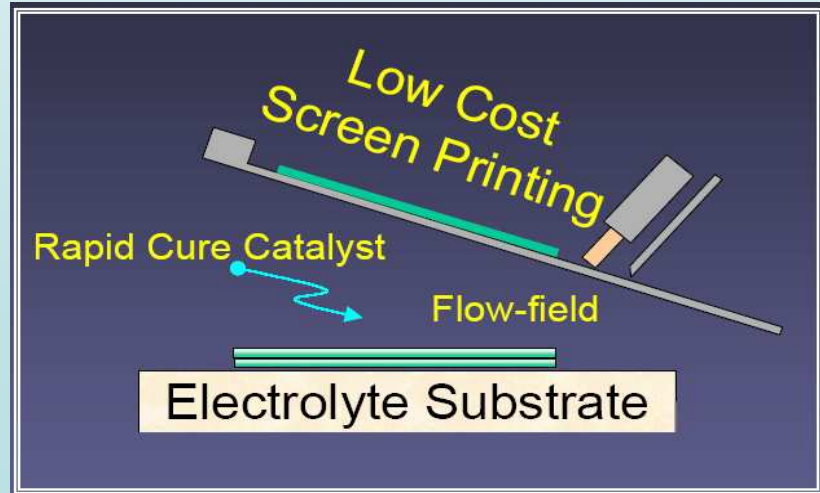
SOFC-VII
June 3-8, 2001
EPOCHAL TSUKUBA, Japan



Cathode Supported Solid Oxide Fuel Cells

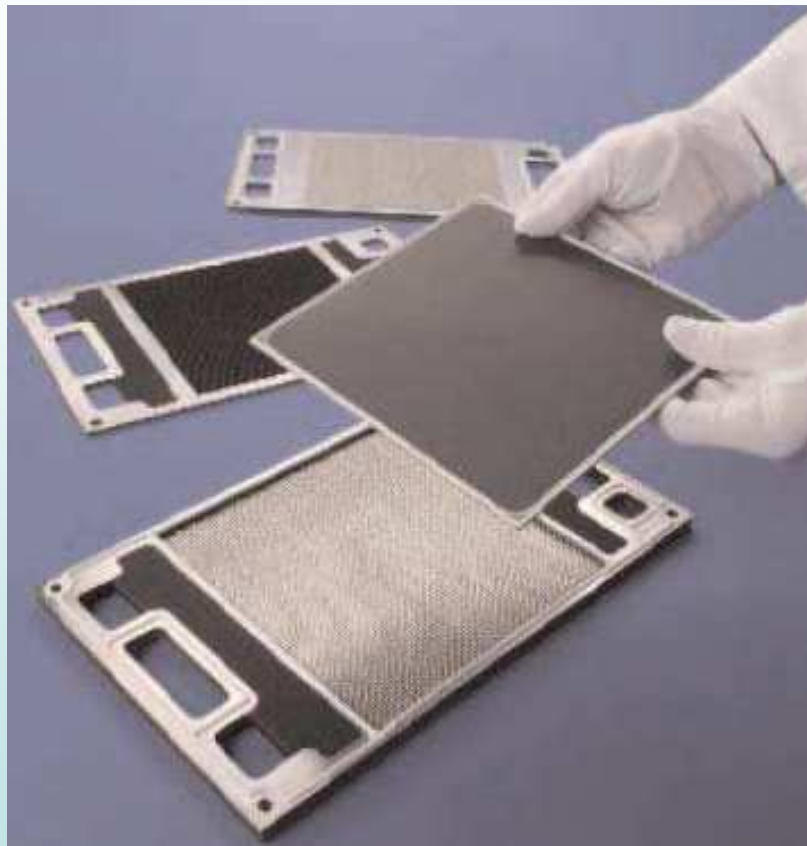
- Tape Casting (Cathode)
- Colloidal Spray (Electrolyte)
- Co-Sintering
- Screen Printing (Anode)

20 μm



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

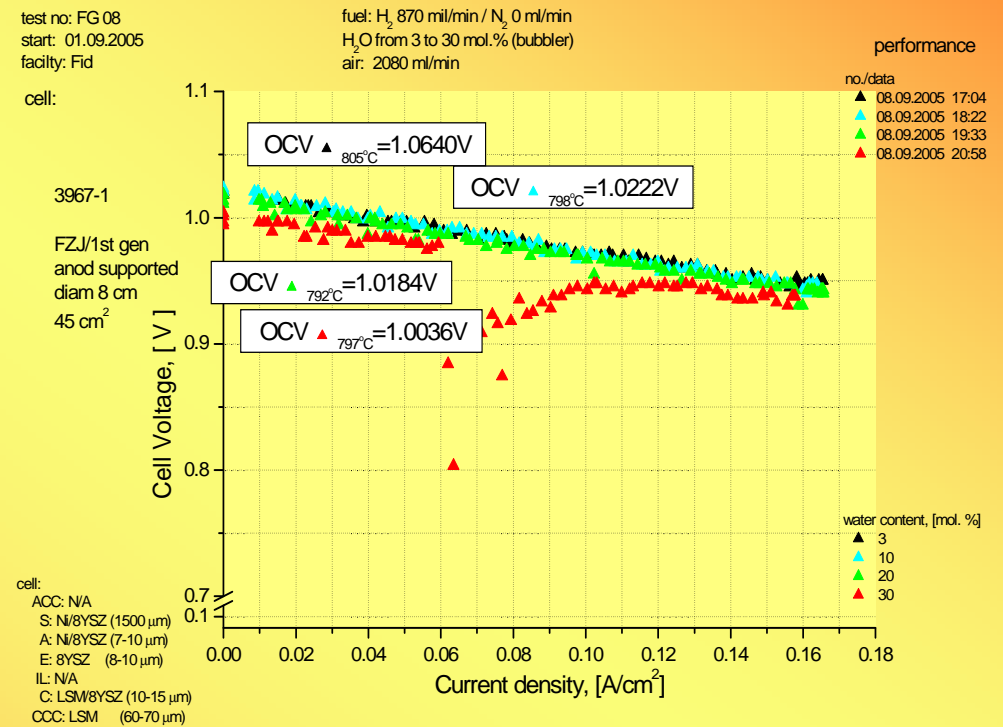
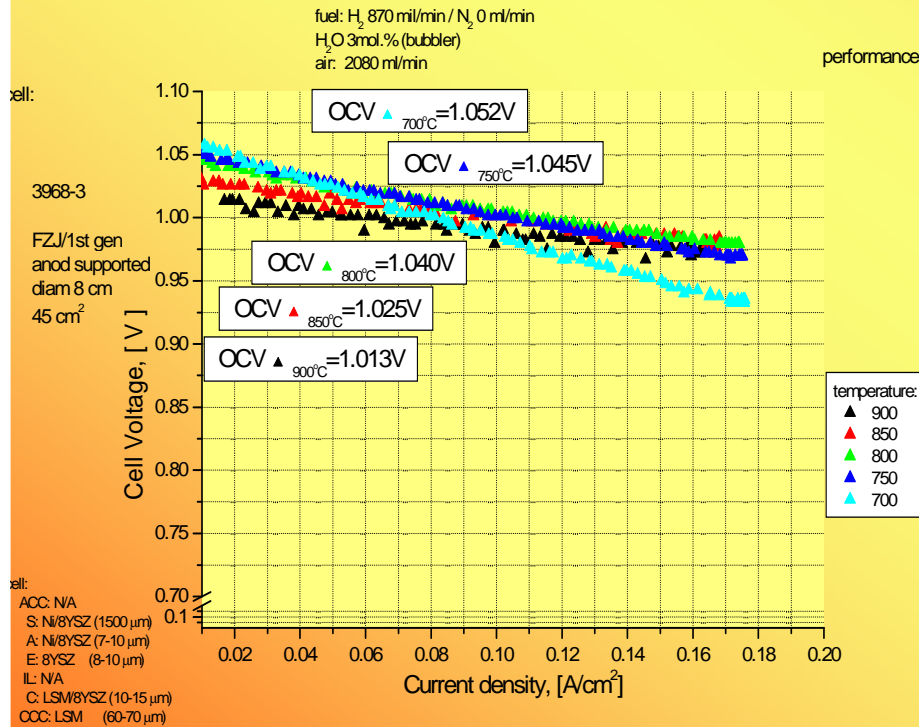
- behaviour in C- containing fuel gases and redox atmosphere
- resistance under frequent, long-term thermal cycling
- stability of very thin interconnects
- reducing formation of volatile Cr species
- improvements in mechanical properties (creep strength)

REQUIREMENTS OF SOFC FABRICATION METHODS

- **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.

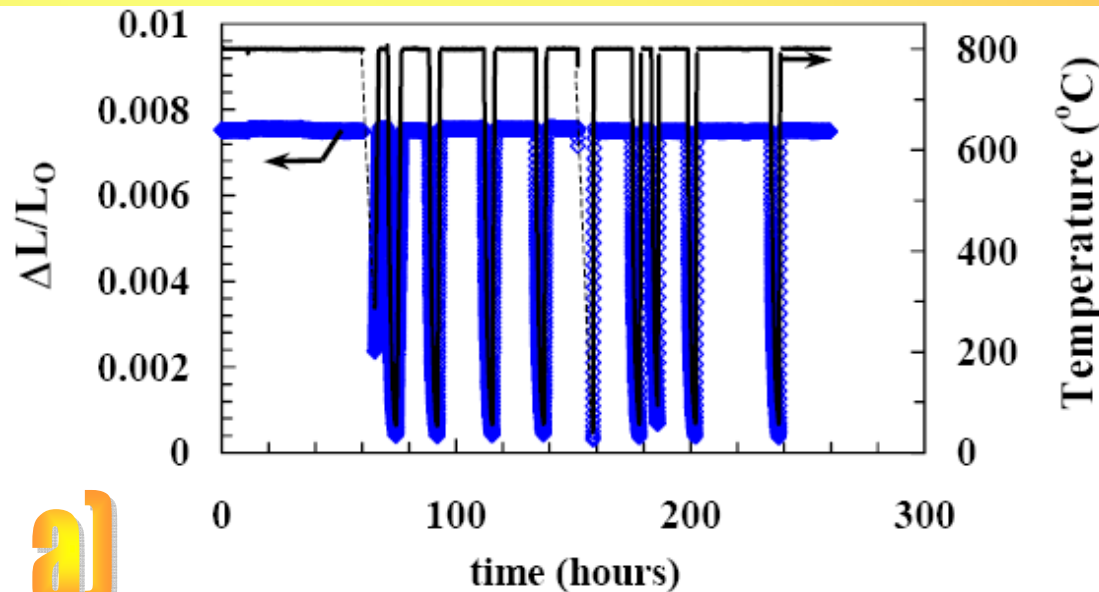


STUDY

at 3% H₂O – f (T)

at 800°C – f (H₂O content)

RedOx STABILITY



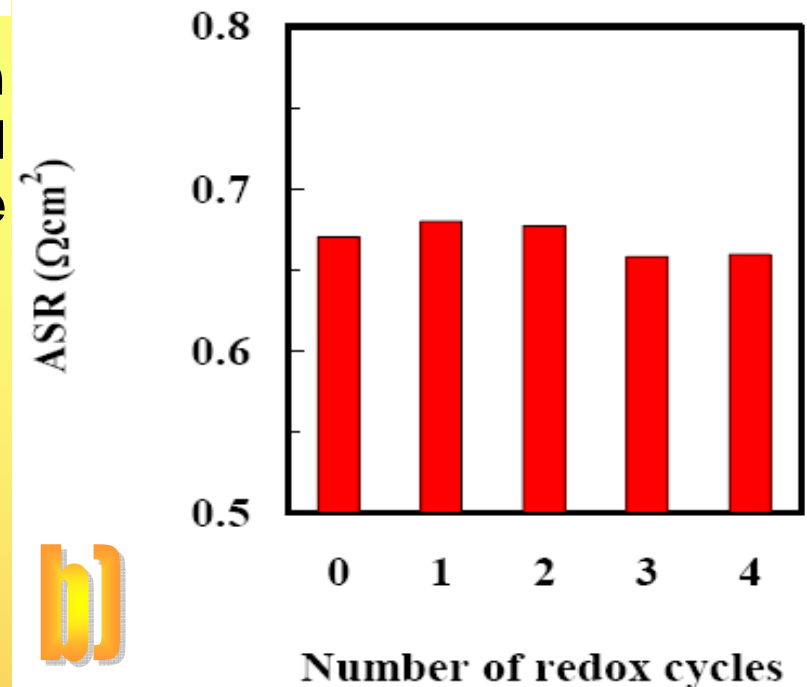
a)

Effect of reduction– oxidation cycling on relative expansion of $\text{La}_{0.4}\text{Sr}_{0.6}\text{TiO}_3$ (a) and effect of oxidation-reduction cycles on the cell area specific resistance at 0.7 V (b) [20]

- Exposure to reducing environment at 800°C (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).

Fuel/cell test: $T = 800^{\circ}\text{C}$. Fuel is $\text{H}_2/\text{H}_2\text{O} = 97/3$; oxidant is air.

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



b)



2002-2006

LAMAR



SSA FP6- 510314 - ANVOC

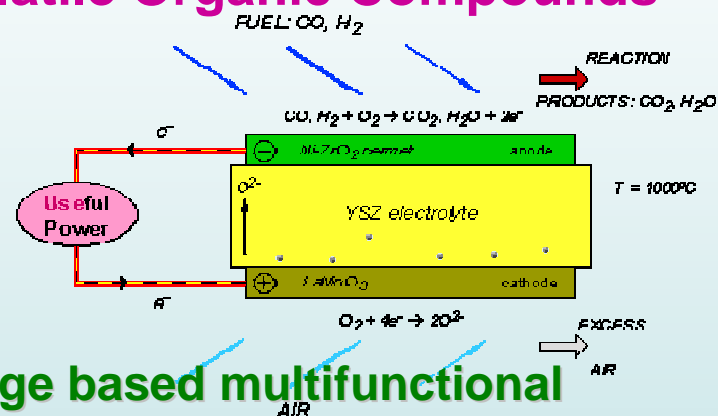


Application of Nanotechnologies for Separation and Recovery of Volatile Organic Compounds



SES6-CT-2003-502612

REAL - SOFC



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

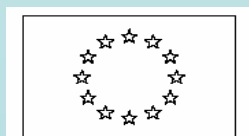
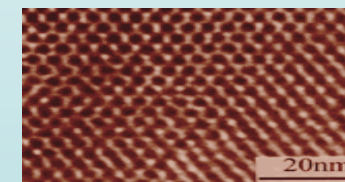
NMP3-CT-2005-011783

MULTIPROTECT

NMP3-CT-2005-011783

ENFUGEN

<http://www.enfugen.net/>



7-th FP 2007-2013



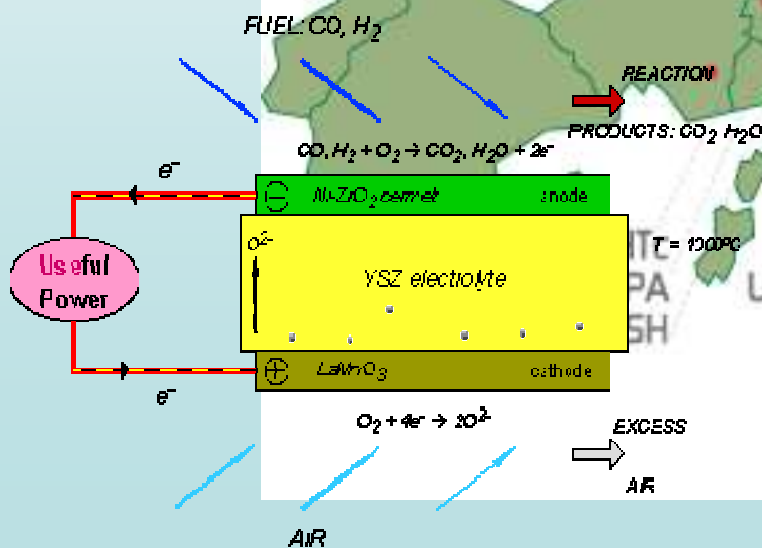
SES6-CT-2003-502612 REAL - SOFC



28 partners

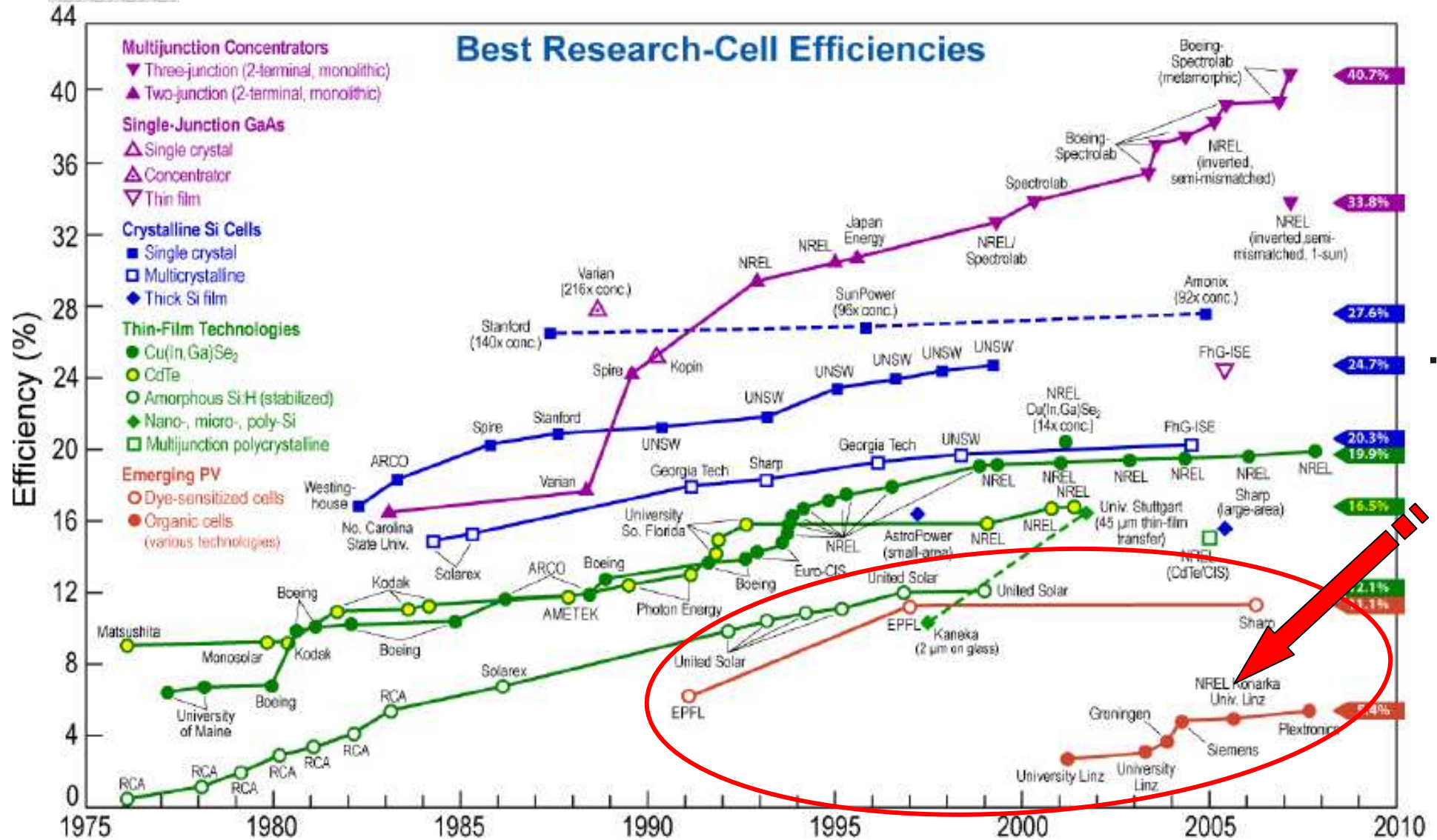


13 countries





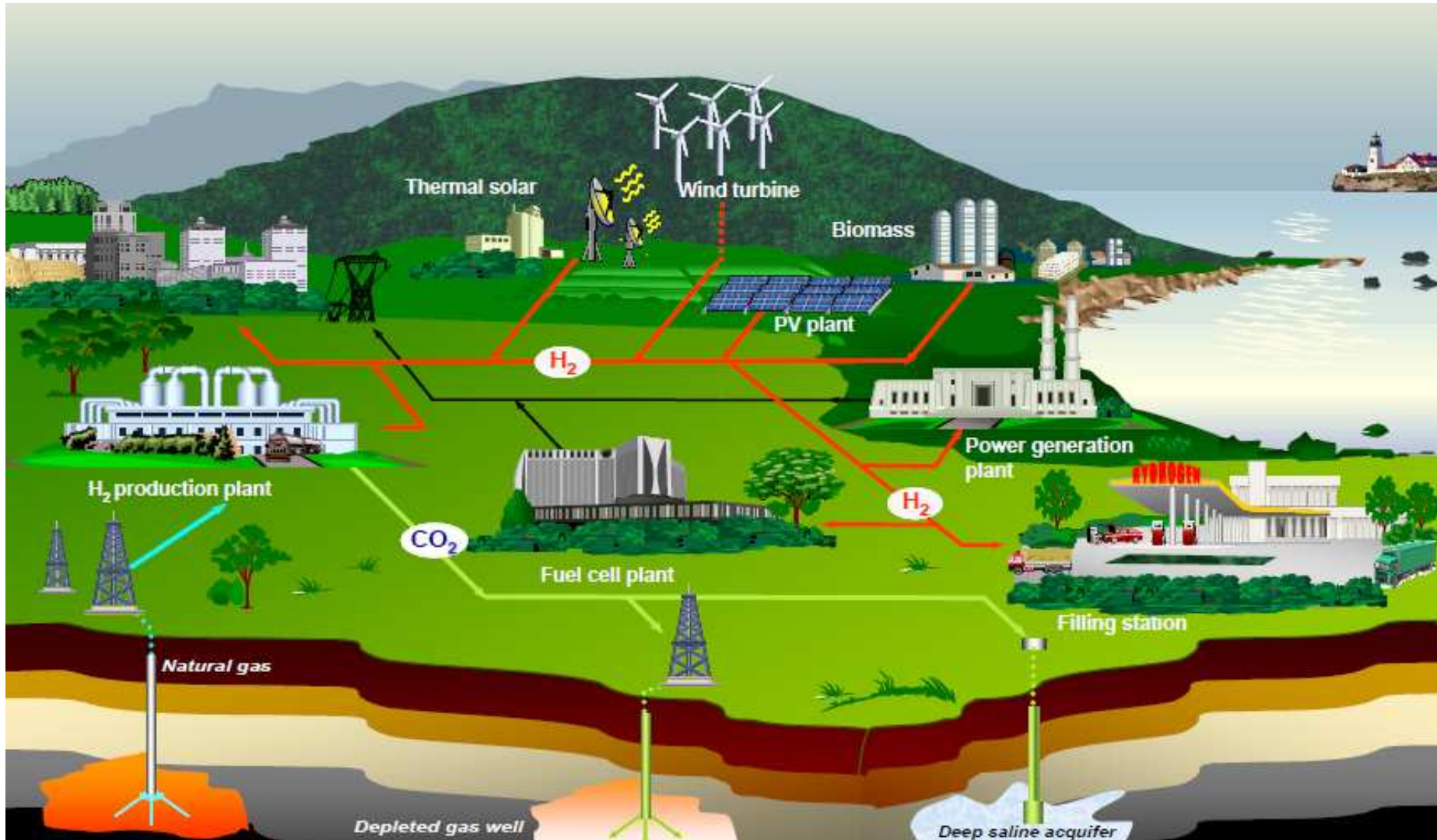
FORECAST for SOFC and RES [NREL 2011 data]



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 (-50° - $+55^{\circ}$ C).
 - Test under dry heat treatment > conditions - Test up to 100° C
- 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 -60° C to $+120^{\circ}$ C
- Test under high humidity level > conditions - Temperature from 20° C to 65° C; 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 900°C**, 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 (R_p , E_{corr} , I_{corr} 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°C ;
- 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 1600°C 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 -Moesbauer 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 900°C, 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



大连海事大学
Dalian Maritime University

International Cooperation College



TOHOKU UNIVERSITY

INSTITUTE OF HIGH TEMPERATURE ELECTROCHEMISTRY

INSTITUTE OF ORGANIC CATALYSIS AND ELECTROCHEMISTRY

BORESKOV INSTITUTE OF CATALYSIS

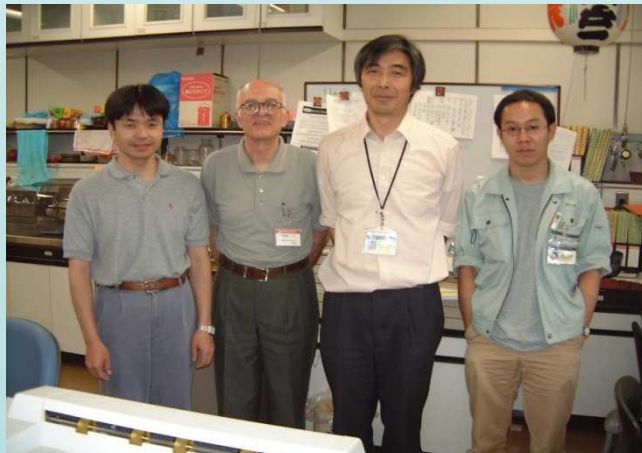
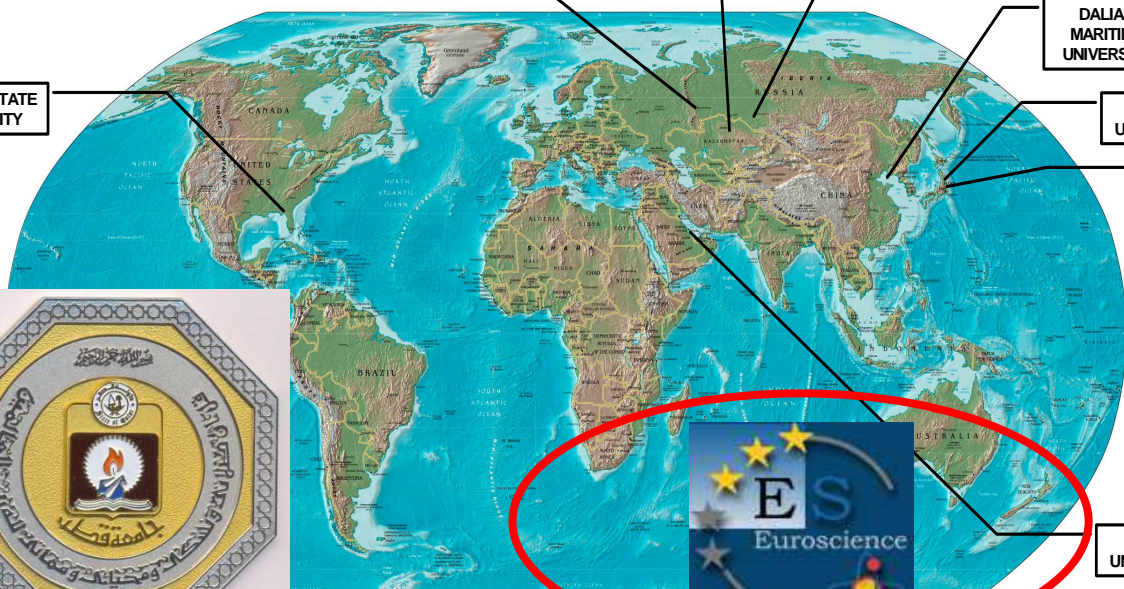
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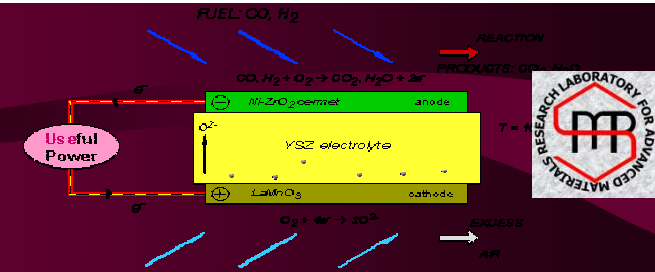
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FLORIDA STATE UNIVERSITY



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CONCLUSIONS



- ✓ - The progress in SOFCs science and especially in technology during the last decades is obviously 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 – poisoning 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