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
*** OUTLINE ***

✓ - INTRODUCTION
✓ - MARKET AND APPLICATIONS
✓ - SOFC CERAMIC MATERIALS

 - SCIENCE and BASIC RESEARCH
 - SOFCs TECHNOLOGY
 - FORECAST for SOFCs and R.E.S.

✓ - LAMAR FACILITIES

CONCLUSIONS
- 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

Science & Basic Research
Basic Research & Technology
Development & Implementation
Local & International

UNI  R&D  IND  T.O.  Market

1  2  3

1  2  3
Fuel Cell Applications
All systems built, application
Market Growth 2003 - 2005
Energy Supply of Houses
Hexis/CH (1 kW), Haldor Topsoe/Dk, Siemens Power, GE/US, McDermott/Cummings/US, FCE/Versa Power/GTI
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:**
  - APU
  - 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
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
- SOFCs BACKGROUND CONCEPTS


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


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


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

**DIFFRACTION 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

- **Electrolyte supported**
  - LSCF+YSZ
  - YSZ
  - Ni+YSZ

- **Anode supported**
  - LSCF
  - YSZ
  - Ni+YSZ

- **Metal supported**
  - LSCF
    - SSZ
    - Ni+SSZ
    - FeCr
  - LSCF
    - Ceria
    - Ni+Ceria
    - FeCr

**TEMPERATURE**

- 1000 °C
- 800 °C
- 600 °C
- 400 °C
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

YSZ + LSM - cathode
YSZ - electrolyte
YSZ + NiO - anode
Porous metallic substrate
State-of-the-Art of SOFCs Layer Structures

<table>
<thead>
<tr>
<th>Porosity</th>
<th>Grain Size</th>
<th>Conductivity</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>45%</td>
<td>10 µm</td>
<td>50 S/cm</td>
<td>LSM</td>
</tr>
<tr>
<td>20%</td>
<td>1-3 µm</td>
<td>25 S/cm</td>
<td>LSM + YSZ</td>
</tr>
<tr>
<td>0%</td>
<td>2-5 µm</td>
<td>0.01 S/cm</td>
<td>YSZ</td>
</tr>
<tr>
<td>20%</td>
<td>1-4 µm</td>
<td>1000 S/cm</td>
<td>NiO+YSZ fine</td>
</tr>
<tr>
<td>35%</td>
<td>3-5 µm</td>
<td>500 S/cm</td>
<td>NiO+YSZ coarse</td>
</tr>
</tbody>
</table>

- Cathode Current Collector: 30 – 70 µm
- Cathode Functional Layer: 10 - 15 µm
- Electrolyte Layer: 5 - 10 µm
- Anode Functional Layer: ~ 5 - 10 µm
- Anode Substrate: < 1500 µm

Grain porosity:
- 45% open size 800°C
Besides **cost** and **performance**, **lifetime** is the key issue for the commercial use of SOFCs.

**Cell materials degradation**

**Design, Contacting, Cr-evaporation**

**Thermomechanical stress**

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**Cr-Oxid**

**MIC**
Microstructural degradation

- separation
- densification
- delamination
- reaction

CGO
Ni
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

**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:**

M. Jorger, RRFCS report, 4-RealSOFC Summer School, 2-7 Sept 07, Varna, Bulgaria
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

SOFC Processing Approach

1. Composite Anode Fugitives Binder Solvent
2. Tape Casting
3. Green Electrode Support
4. Dried Electrolyte Film on Porous Anode Support
5. Colloidal Deposition of Electrolyte Film
6. Annealing Electrode on SOFC
7. Completed SOFC Cell

NexTech Materials, Ltd. Proprietary
Simple & cost-effective fabrication processes

Mass Production of Electrolyte Sheet

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

Continuous Casting
- Good Uniformity

NIPPON SHOKUBAY

Low Cost Screen Printing
- Rapid Cure Catalyst
- Flow-field
- Electrolyte Substrate
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.
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.

at 3% H2O – f (T)

at 800°C– f (H2O content)
Fuel/cell test: T= 800°C. Fuel is H₂/H₂O=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 La₀.₄Sr₀.₆TiO₃ (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).
Application of Nanotechnologies for Separation and Recovery of Volatile Organic Compounds

REAL - SOFC

NMP3-CT-2005-011783
MULTIPROTECT

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

SES6-CT-2003-502612

REAL - SOFC

SSA FP6-510314 - ANVOC

http://www.enfugen.net/
Map of solar cells efficiencies vs. year of R&D and companies involved
A view for the future grid of hydrogen production, transport and utilization with other R.E.S., origin from ENEA.
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.
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;
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°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);
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

Florida State University

Institute of Organic Catalysis and Electrochemistry

Boreskov Institute of Catalysis

Dalian Maritime University

Doha University

Institute of High Temperature Electrochemistry

International Cooperation College
CONCLUSIONS

✓ The progress in SOFCs science and especially in technology during the last decades is obviously high and depends on 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