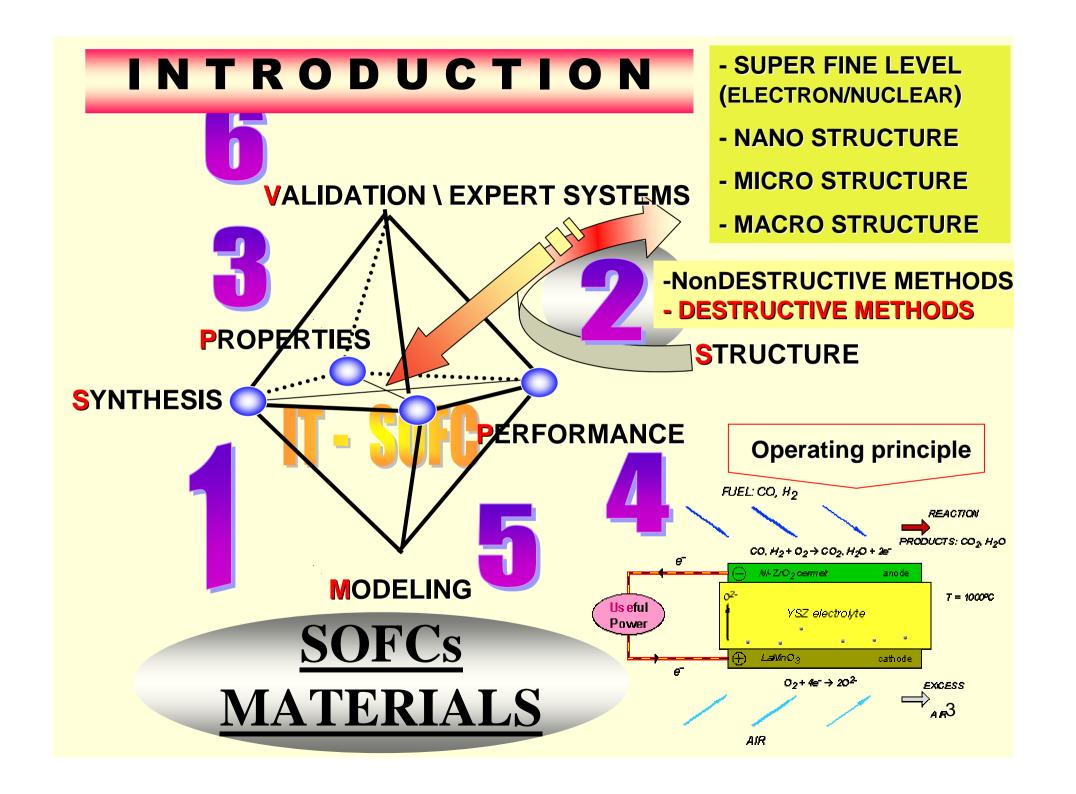
SUFFS - PHYSICAL-CHEMICAL CHARACTERIZATION METHODS

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The Innovation Week on R.E.S.
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INTRODUCTION **PHYSICAL VALIDATION \ EXPERT SYSTEMS * CHEMICAL** PROPERTIES SYNTHESIS PÉRFORMANCE FUEL: CO, H2 REACTION PRODUCTS: CO 2, H2O CO, $H_2 + O_2 \rightarrow CO_2$, $H_2O + 2e^-$ **MODELING** Ni-ZrO ₂ cermet $T = 10000^{\circ}$ **Us et al** YSZ electrolyte Power cathode **SOFCs MATERIALS** $O_2 + 4e^- \rightarrow 20^2$ **EXCESS** AIR



2

INTRODUCTION

NON-DESTRUCTIVE METHODS

The online Journal of Nondestructive Testing < http://www.ndt.net/ >

Divided into various methods on the base on a particular scientific principle:

- □ ULTRASONIC INSPECTION TECHNIQUES
- ☐ IR AND THERMAL TESTING METHODS
- **□ RADIOGRAPHIC TESTING**
- □ VISUAL AND OPTICAL TECHNIQUES
- ☐ LASER TECHNIQUES

X-ray tomography





*** DESTRUCTIVE METHODS**

2-STRUCTURE (METHODS)

RESONANCE METHODS

√- NMR (NQR), ESR, MÖS

OPTICAL & X-RAY SPECTROSCOPY

✓-OESp (UPS,XPS) ICP-AES, AASp, UV-VIS, IR Sp,Raman Sp,X-Ray Sp

DIFRACTION METHODS

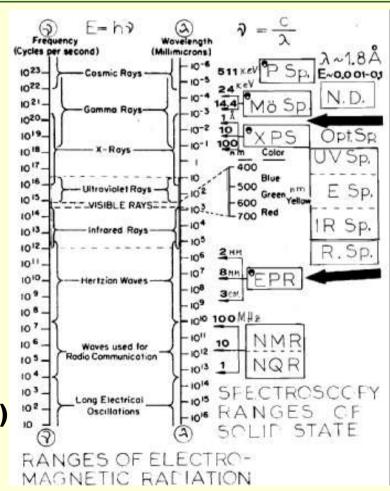
√- XRD, ED, ND, SAXS, SANS

METHODS ON SPUTTERING & SCATTERING

√- SIMS, RBackScSp

OTHER METHODS (METALLOGRAPHIC)

✓- OM, 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

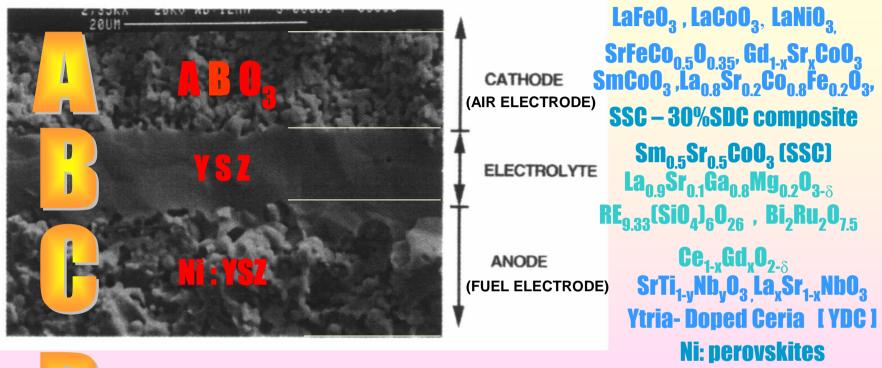
CHARACTERIZATION

STANDARDS



COMPOSITIONS

ALTERNATIVE





INTERCONNECT (SEPARATOR) OR BIPOLAR PLATE

 $La_2O_3-Cr_2O_3+ (alloys)$

La_{0.8}Sr_{0.2}Cr_{1-x}Ti_{0.1}M_xO₃

SEALING MATERIALS FOR STACK COMPONENTS

"3.3" borosilicate glass

MICA, GLASSCERAMICS



HIGH TEMPERATURE CONDUCTING CERAMICS.

DATA BASE & STANDARDS

DATA BASE of physical properties and technical papers for SOFC materials

The work is supported by METI - Japan:

- Thermal and physical properties of materials for SOFC and PEFC
- Literature database of oxide interconnectors in SOFC
- > Source [2004 Fuel Cell Group, EEI, AIST, Japan]

FUTURE: Standardized database for SOFC

material properties EXPERT SYSTEMS

STANDARDS

Creation of "SOFC MATERIALS TESTS OBSERVATORY"

STANDARDS SITUATION



(Catalogue of European Norms)

Management center held by Belgium, available via http://www.cenorm.be

On-line Catalogue of European Standards

[AT] • ON [BE] • IBN/BIN [CH] • SNV [CZ] • CSNI

[DE] • DIN [DK] • DS [ES] • AENOR [FR] • AFNOR

[GB] • BSI [GR] • ELOT [IT] • UNI [NL] • NEN

and ETC.

STANDARDS SITUATION



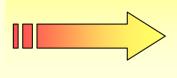


International Standards Organization



Secretariat held by Swiss,

available by http://www.iso.ch



ISO - A network of national standards institutes from 140 countries



STANDARDS SITUATION





American Standards Tests and Measurements



Secretariat held by USA,

On line by http://www.astm.org



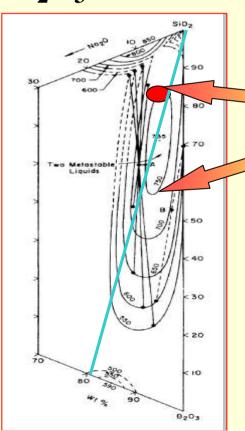
US Participation in ISO and ISO/IEC JTC 1 Activities



An US Resource for Global Standards Accredited by - ANSI

THECHNICAL PROPERTIES OF THE GLASSES

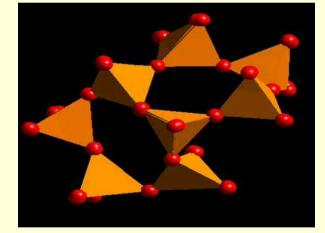
COMPOSITION: SiO₂ from 79.5 to 80.5; B₂O₃ from 12.0-13.0, Al₂O₃ from 2.0 to 2.8, Na₂O from 4.5 to 5.5; K₂O from 0 to 1.5



System SiO₂-B₂O₃-Na₂O

PYREX α =3,3.10-6





TRADE MARKS: Pyrex 7740 (USA), K-33 Kimble (Canada); Terex (Japan); EU – Duran-50 (Germany), Symax (Czech), Termisil (Poland), Nufe (Sweden);

THECHNICAL PROPERTIES OF THE GLASSES

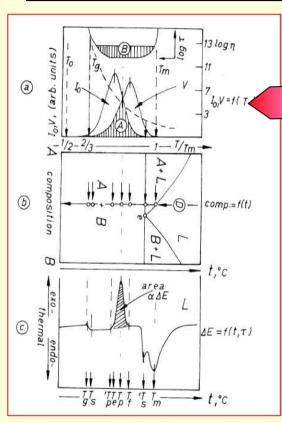
Regarding Borosilicate glasses here are well known the following base standards:

- " DIN ISO 3585/98 _ Borosilicate Glass 3.3 Properties
- " DIN ISO 3586/98_ General Rules for Testing, Handling and Use
- " DIN ISO 4704/97 _ Glass Plant Components
- " <u>BS 2598: Part 1:1991, ISO 3585/91</u> Glass plant, pipeline and fittings. Specification for properties of borosilicate glass 3.3
- " <u>BS EN 1595/97</u> Pressure equipment made from borosilicate glass 3.3. General rules for design, manufacture and testing

CHEMICAL & PHYSICAL PROPERTIES

3.1.CHEMICAL PROPERTIES

3. 1. 1. DEVITRIFICATION



[5&6] I.Gitzov, Contemp. Phys. 21 (1980) 121, Part I & II

[7] I. Gitzov, J. Schmelzer, VITREOUS STATE: Thermo - dynamics, Structure, Rheol. & Crystall., Springer Ver. (1995)

1[8] BORATE GLASSES: structure, properties, applications, Eds. L. Pye&N. Kreidl, Plenum Press (1978)

[9] BORATES GLASSES: crystals and melts, Eds. A. Wright, S. Feller, A. Hannon, Pub. Soc. Glass Tech. (1997)



ASTM-E-537/84 — utilizes techniques of DTA

& DSC-analysis; Subcommittee E27. 02 Thermal Stability

Devitrification due to the glass impurity and extended

3.1.CHEMICAL PROPERTIES

3. 1.2.CHEMICAL RESISTANCE

ASTM-E-70/77 — Standard method for pH of aqueous solution with the glass electrode

ISO-3585/76 — Glass plant, pipeline & fittings - Properties of B-Si 3.3

ISO-719/85 (DIN 12111); ISO 720/85; ISO 4802-1/88; ISO 4802-2/88 Glassware- hydrolytic resistance test methods & clasification

DIN 52339/80-1 & DIN 52339/80-2 - Autoclave method for testing the hydrolytic resistance

ASTM C-225/75 & ISO-1776/85 & DIN 12116/76 -RE: Determination of acid resistance(spectroscopic, gravimetric&classification into acid classes)

ISO-695/84 (DIN- 52 322) — Resistance to attack by boiling aqueous solution of mixed alkali: Method of test and classification

3.2. PHYSICAL PROPERTIES

3. 2.1. **DENSITY**

Two principal methods are known:

ASTM-C-693/84 & ASTM C-729/75 (Archimedes&Flotation method)

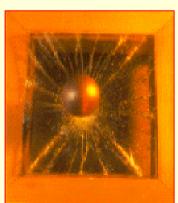
Not any SO standards are known up to date; 2.23 gcm⁻³ at 20°C

3.2.2.MECHANICAL PROPERTIES

ASTM-C-158/81 - Standard methods of flexure testing of glass (determination of module of rupture) Methods A & B

ASTM C-623/71- > Young's & Shear modulus and Poisson's ratio.

ASTM-C-730/75- > KNOOP indentation hardness of glass. **ISO TC/48**

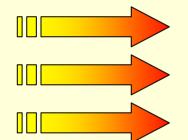


[17,18] ICG,. Strength Testing of glass and glass products: An International Survey (1974); Physical Properties of Glass (Strength, Hardness, Elasticity) (1967)

Photoelastic constant (B) is $3.5 - 3.9.10^{-6}$ MPa⁻¹; the modulus of elasticity (G) is a value of 26 500 MPa.

3.2. PHYSICAL PROPERTIES

3.2.3. THERMAL PROPERTIES



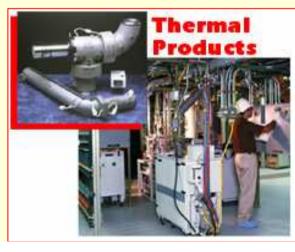
ASTM-C-149/77; ASTM E-228/71 & ASTM-C-408/82

ISO-718/90; ISO-7991/87 & ISO 3585/76

BS EN 13024-1/02; pren 13424-1 & -2 & pren 1748-1-2;

The specific heat $(c_p - J.kg^{-1}K^{-1})$, enthalpy $(\Delta H - Jg^{-1})$, thermal conductivity $(\lambda, -Wm^{-1}K^{-1})$, thermal diffusivity $(a - m^2s^{-1})$, thermal endurance (resistance to thermal shock, Δt - °C), are important thermal parameters for "3.3" glass articles; Data >[4,12,18]. There is an laser interferometric technique known.







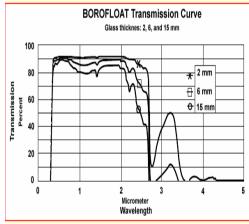


3.2. PHYSICAL PROPERTIES



3.2.4. OPTICAL PROPERTIES

ISO- 13653/96 & ISO 11421/97 - Optics and optical measurements- General optical test methods; Accuracy for optical transfer function (OTP)



The refractive index n_D of "3.3" glass is close to that of silica glass $(n_{D'3.3}) = 1.474$, $n_{D'3ilica} = 1.458$. Test method using polarizing microscope via immersion liquids- standards is also known; Abbe, Pulphrich & V-block refractometers.

- ELECTRICAL PROPERTIES



ASTM-C-657/78; ASTM D-149/44 & ASTM D-150/46

DC volume resistance; Dielectric breakdown voltage & dielectric properties

 ρ = 10¹³-10¹⁵ ohm.cm; For PyrexTM dielectric relative permittivity (ϵ_r =4.6), dissipation factor (tan δ.10⁻⁴=46) at 1 MHz and dielectric strength is 1000 KVcm⁻¹ (in air) and 10KVcm⁻¹(in oil).

Standards for ceramics materials (cathode, anode, electrolyte)

THERMAL PROPERTIES

✓-THERMAL EXPANSION, THERMAL CONDUCTIVITY, THERMAL ASPECT OF STABILITY, HEAT CAPACITY etc.

- M. White, Properties of Materials, N.Y, Oxford, Oxford Univ. Press (1999)
 - T. Kawada, and H. Yokokawa, Materials and Characterization of Solid Oxide Fuel Cells, Key Eng. Materials v.125-126 (1997) 187
- Y.S. Touloukian (Editor), 'Thermophysical Properties of Matter. The TPRC Data Series Thermal Conductivity'. Vol.3, TPRC, New York, 1970.
 - R. H. Perry, 'Perry's Chemical Engineering Handbook', 7th Edition, McGraw- Hill, New York, 1997.
 - D. R. Lide (Editor), 'CRC Handbook of Chemistry and Physics', 81st Edition, CRC Press, Boca Raton, 2000-2001

Elert Glenn. Linear thermal expansion coefficients of select materials. The Physics Hypertextbook (March 5, 2004).

http://hypertextbook.com/physics/thermal/expansion/.



THERMAL PROPERTIES

- DIN CEN/TS 1159-4/2004 Advanced technical ceramics - Ceramic composites -Thermo- physical properties - Part 4: Determination of thermal conductivity;
- DIN CEN/TS 820-5/2004 Advanced technical ceramics - Methods of testing monolithic ceramics -Thermomechanical properties - Part 5: Determination of elastic module at elevated temperatures;
- ASTM C-1470/2006 Standard Guide for Testing the Thermal Properties of Advanced Ceramics and
- ASTM C-1525/04 Standard Test Method for Determination of Thermal Shock Resistance for Advanced Ceramics by Water Quenching.

ELECTRICAL & MAGNETIC PROPERTIES

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

Conduction In Ionic Solids

Electrical conductivity, σ is defined in terms of material parameters as:

$$\sigma = n (Z_e) \mu [cm S]$$

Where,

n = concentration of the charge carriers in numbers per volume [cm³]

 $e = electronic charge [1.6 x 10^{-19} C] and$

Z = valence of the carrier

μ= mobility of the charge carrier in [m²/s.V]. It is well known that the mobility of electrons or holes are 103 times higher in comparison to ions. For more than one charge carrier, the resultant conductivity is sum of component conductivities:

$$\sigma = \sum n_i(Z_i)\mu_i$$
 [cm S]

For a mixed conductor equation can be re-written

as:
$$\sigma = \sigma_i + \sigma_e$$

Concentrations of both electronic and ionic defects tend to increase with temperature.

$$\sigma = \sigma_o \exp^{(-E/kT)}$$

 $\mathbf{E} = \mathbf{q_1} + \mathbf{q_2}$ is the activation energy.

Plasma Sprayed LSGM Layer		
Temperature ⁰ C	R Ohm	Specific conductivity S.cm ⁻¹
650	311	0.000225
700	340	0.000206
750	1.11	0.0631
800	0.82	0.0854
Sintered LSGM Pellet		
650	1.3	0.0641
700	1.2	0.0694
750	0.76	0.110
800	0.75	0.111

Comparison on resistance and conductivity of as sprayed and sintered LSGM pellets at several temperatures.

IT-SOFC Based on Fully Integrated Plasma Sprayed Components, X. Ma & S. Hui, Inframat Corp., CT, USA

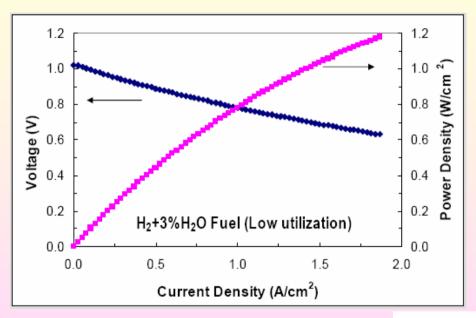
STANDARDS ELECTRICAL PROPERTIES

ceramics materials (cathode, anode, electrolyte)

- prEN 50359-1-1/00 Advanced Technical Ceramics -Part 1-1: Electrical Properties - Methods of Test for Short Term Electric Strength;
- prEN 50359-1-2/00 Advanced Technical Ceramics, Part 1-2: Electrical Properties Determination of the Surface and Volume Resistivity in the Temperature Range from 200C to 800°C,
- ASTM D-4496/2004 Standard Test Method for D-C Resistance or Conductance of Moderate Conductive Materials and
- ASTM C-483-95/00 Standard Test Method for Electrical Resistance of Conductive Ceramic Tiles.



ANODE- SUPPORTED CELL AT 800°C



D o E, Pacific Northwest National Laboratory (SECA Program)

Anode:

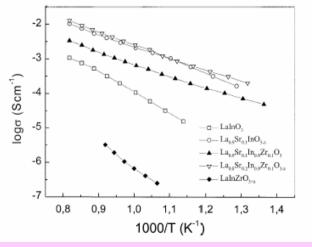
 $Ni+YSZ+AI_2O_3(600 \mu m);$

Cathode:

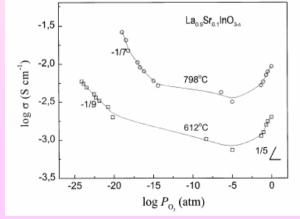
 $La_{0.8}Sr_{0.2}FeO_3(50 \mu m);$

Electrolyte:

YSZ (10µm)



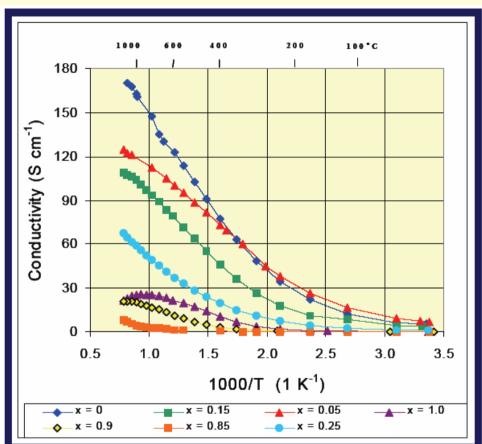
Effects of different dopants on σ -value of **LainO**₃.

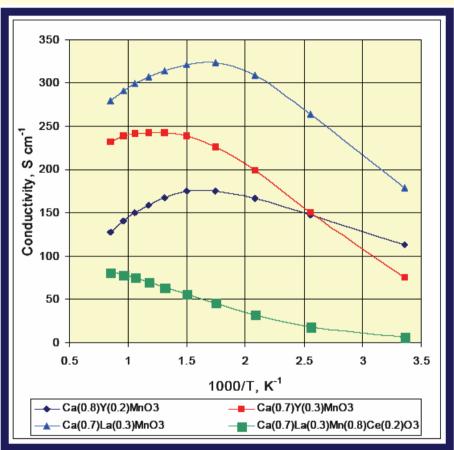


Electrical conductivity of La_{0.9}Sr_{0.1}InO₃ as functions of oxygen partial pressure and temperatures.

2

(a) (b)





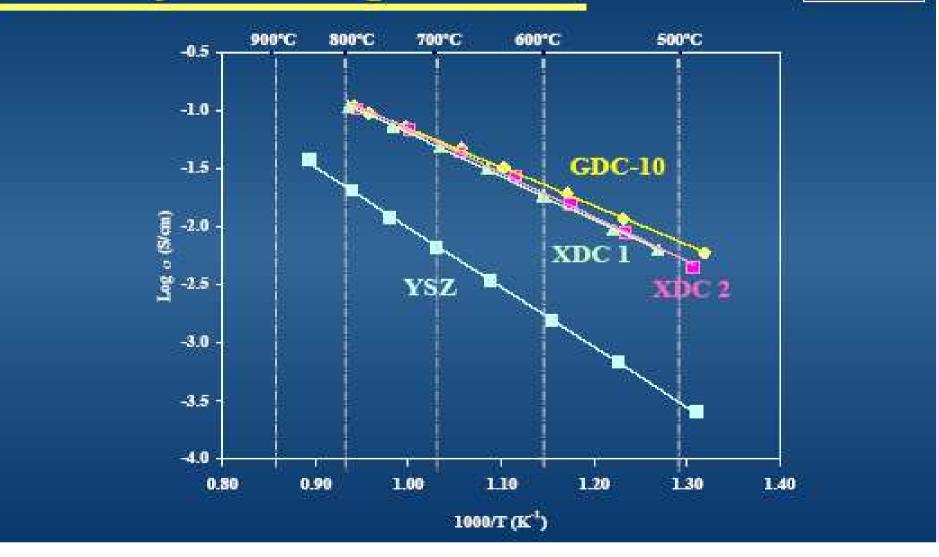
Conductivity vs. temperature in air of select compositions of promising SOFC interconnect materials, (a) the system La_{0.84} Sr_{0.16} Mn_(1-x) Fe_x O₃ and (b) Ca_(1-x) (Y/La)_x Mn_(1-y)Ce_yO₃ determined using the four-probe method.

Nano-sized powders prepared in-house and sintered to high density using (a) the Citrate Gel Process (CGP) and (b) a Modified Glycine Nitrate Process (MGNP).

ELECTROLYTE CONDUCTIVITY

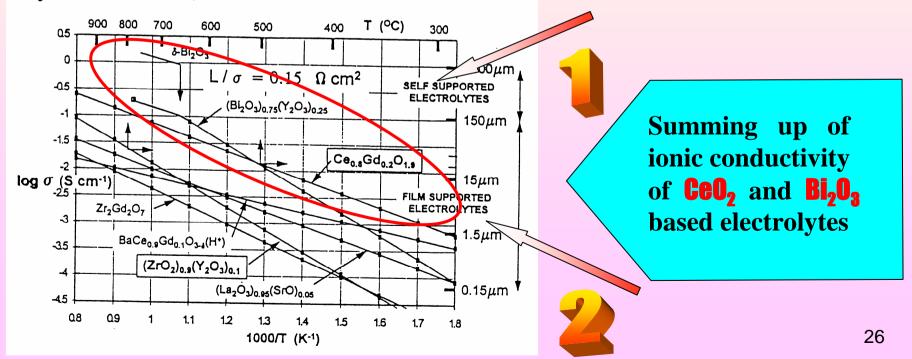
Electrolyte Development

NEXTECH MATERIALS

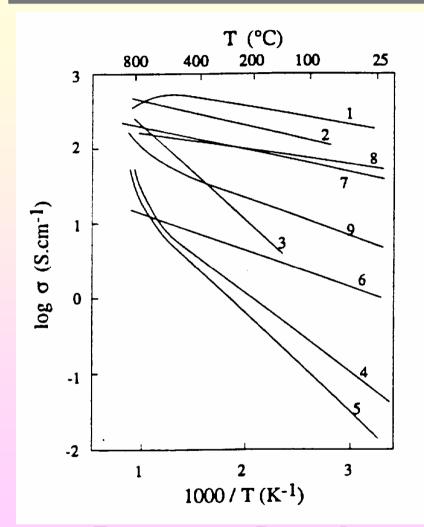


ALTERNATIVE ELECTROLYTES

- ✓ New lanthanum gallate system **LaGaO₃**, **SrGaO_{2.5} LaMgO₂** [39]
- $\sqrt{\text{La}_{1-x}\text{Sr}_x\text{Ga}_{1-y}\text{Mg}_y\text{O}_{3-(x+y)/2}}$ (LSGM) perovskite phase $\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\delta}$
- ✓ It was established that the thermal expansion coefficients increases in the order **YSZ< LSGM< CGO** and all samples possess an excellent thermal shock resistance [41].
- $\sqrt{\text{La}_{0.9}\text{Sr}_{0.1}\text{JM}^{\text{III}}\text{O}_{3-\delta}}$ (where M^{III} is Al, Ga, Sc and In) perovskites [K. Nomura]
- ✓ New rare- earth silicates ($\mathbf{RE}_{9.33}(\mathbf{SiO}_4)_{\mathbf{6}}\mathbf{O}_2$) for medium operating temperature by **Ch. Barthet**,

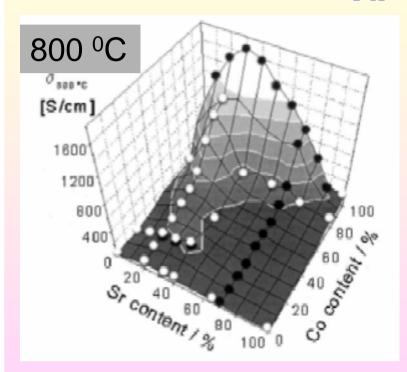


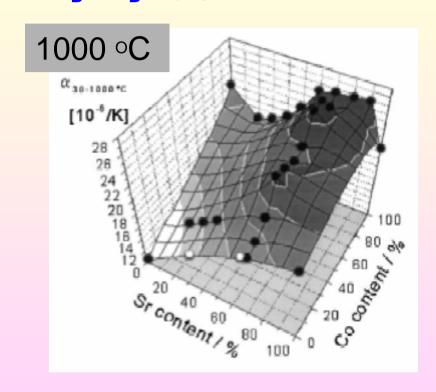
PEROVSKITE CONDUCTIVITY





Temperature Dependence of selected La_{1-x}Sr_xMeO₃



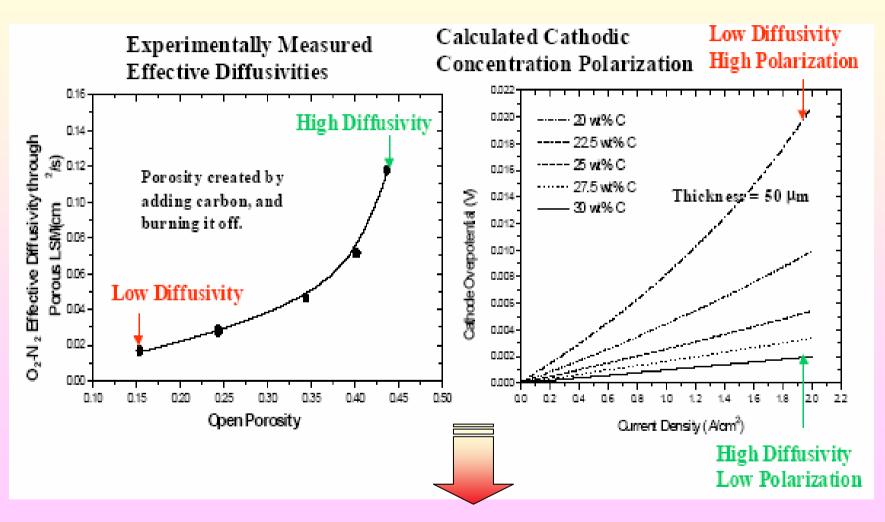


A. Petric, P. Huang and F. Tietz; Evaluation of La-Sr-Co-Fe-O perovskites for solid oxide fuel cells and gas separation membranes,

B. Solid State Ionics, 135 (2000) 719-725

O₂-N₂ Effective Diffusivity through Porous LSM and Cathodic Concentration Polarization





Cathode Concentration Polarization is Small When the Porosity is High 29

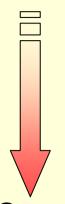
MECHANICAL PROPERTIES

✓-ELASTICITY, ADHESION, CRACK PROPAGATION etc.

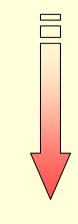
Fracture Phenomena Related to SOFC

- Because SOFC systems are formed by layering and bonding of different materials, stresses unique to layered systems arise due to differential thermal-elastic properties.
- Some layers will contain biaxial **compresses** stress, while other must contain biaxial **tensile** stresses.
- In addition, the extension of cracks from one layer to another depend on the residual stresses within each layer, and the volume fraction of the porosity.
- > Residual stresses within layered structures; internal and surface
- > Crack extension and failure in layered structures
- > Crack extension in porous ceramics
- Crack Extension in Brittle Materials
- Background for stress, stain, their relation
- Background to crack instability (fracture)
- Understanding and predicting failure under conditions of sub-critical crack growth

MECHANICAL ENGINEERING 30



STANDARDS MECHANICAL PROPERTIES

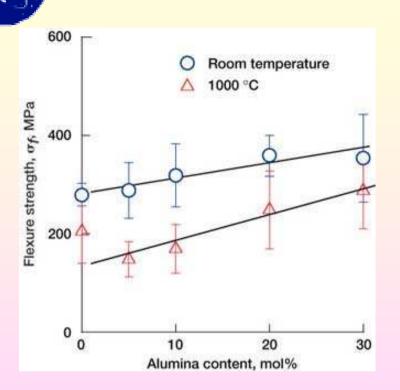


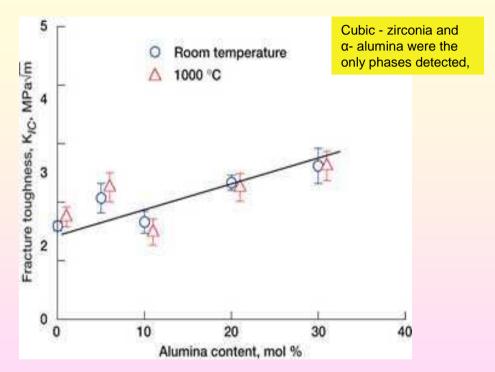
Generally ASTM standards have been object of issue:

- ASTM WK8344 06/2005- Flexural Strength of Advanced Ceramics with Engineered Porosity and Cellular Structures at Ambient Temperatures;
- ASTM C-1211/01- Test Method for Flexural Strength of Advanced Ceramics at Elevated Temperatures;
- ASTM C-1465/2006 Test Method for Determination of Slow Crack Growth Parameters of Advanced Ceramics by Constant Stress-Rate Flexural Testing at Elevated Temperatures;
- ASTM C-1368/2006 Test Method for Determination of Slow Crack Growth Parameters of Advanced Ceramics by Constant Stress-Rate Flexural Testing at Ambient Temperature and
- ASTM C-1366/04 Standard Test Method for Tensile Strength of Monolithic Advanced Ceramics at Elevated Temperatures.

< http://www.grc.nasa.gov/WWW/RT2001/5000/5130bansal.html>(ZCETProgram)

SAMPLES: Zirconia- alumina composites (0 to 30 mol% of alumina) fabricated by hot pressing.





Left: Effect of <u>alumina additions on the strength</u> of 10YSZ electrolyte at room temperature and 1000 ℃ measured in four-point flex ure in ambient atmosphere with 20/40- mm spans [ASTM C1161 & 1211] at a loading rate of 50 MPa/sec in ambient air.

Right: Effect of <u>alumina additions on fracture toughness</u> of 10YSZ electrolyte at room temperature and 1000 ℃.. Measurements were conducted in fourpoint flexure with 20/40- mm spans by the single- edge V- notched beam 32 method in ambient atmosphere at a loading rate of 0.5 mm/min.

MICRO-MECHANICAL PROPERTIES OF CERAMIC COATINGS

TESTING OF COATINGS

- Results of ceramic coatings MMT on metallic / non-metallic substrates
- Standard microhardness HV
- Integrated microhardness HVJ
- Evaluation of coating fracture toughness

STANDARDS

RECOMMENDATIONS FOR COATING DEPOSITION PROCESS







OTHER (COMPLEX) PROPERTIES

Chemical Degradation Phenomena

The water, as product of combustion, reacts with several of the materials used in SOFCs. For example, Ca, Y, Mg- oxides in solid-solution with zirconia is know to form a hydroxide at the surface. For Y this reaction appears to be most rapid at 250 ℃.

For some rare- earth zirconia materials, the decrease in yttrium at the surface can stimulate a phase transformation that eventually cause catastrophic failure of the cell.

Water reacts with the glass at crack tips to produce a phenomena know as **subcritical crack growth**. Sub- critical crack growth leads to time dependent failure at low stresses.

i.e. there is a **Destabilization of Zr(Y)O2 by water!**

- Time dependent failure in glass & glass ceramics
- Reaction of silicates with water; RedOx behaviour

THERMO- MECHANICAL THERMO- CHEMICAL THERMO- ELECTRICAL

STANDARDS

for interconnect (stack component)

There are few standards for corrosion of Cr-containing steels for SOFC stacks interconnect as follows:

- DIN 50905 P1/87- Corrosion of Metals; Corrosion Testing; Principles;
- ISO 7539-6/2003- Corrosion of metals and alloys-Stress corrosion testing- Part 6: Preparation and use of pre- cracked specimens for tests under constant load or constant displacement;
- ISO 3651-2/98- Determination of resistance to intergranular corrosion of stainless steels- Part 2: Ferritic, austenitic and ferritic- austenitic (duplex) stainless steels- Corrosion test in media containing sulfuric acid,
- ASTM G-111/97- Guide for Corrosion Tests in High-Temperature or High-Pressure Environment!

CONCLUSIONS



- ❖- For advanced SOFC application and performance the physical chemical properties of the materials and their test methods, are of high level of importance.

 - **√- THERMAL PROPERTIES**
 - **✓- ELECTRICAL & MAGNETIC PROPERTIES**
 - **V- MECHANICAL PROPERTIES**
 - **V-SURFACE AND INTERFACIAL PROPERTIES**
 - **✓- CHEMICAL PROPERTIES & THERMAL CORROSION BEHAVIOUR**
 - **❖-** For new SOFC materials study and application the complex of properties are of vital position to investigate. There are namely:
 - **√- ELECTRO- CHEMICAL**
 - **√- THERMO- MECHANICAL**
 - **V- THERMO- ELECTRICAL**
 - **√- THERMO- CHEMICAL**



❖ - All properties are function of the THERMAL history of the materials used; Respectively: composition and phase relations according to the phase diagrams, methods of synthesis, nature of the structure on fine-, nano-, micro- a macro- level. UCTM, Sofia, Bulgaria