CERAMIC MATERIALS FOR

SOFCs

CURRENT STATUS

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LAMAR

The Innovation Week on R.E.S.

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

✓- INTRODUCTION & AIM

✓- SOFC CERAMIC MATERIALS

A - CATHODE MATERIALS

B - ELECTROLYTE MATERIALS

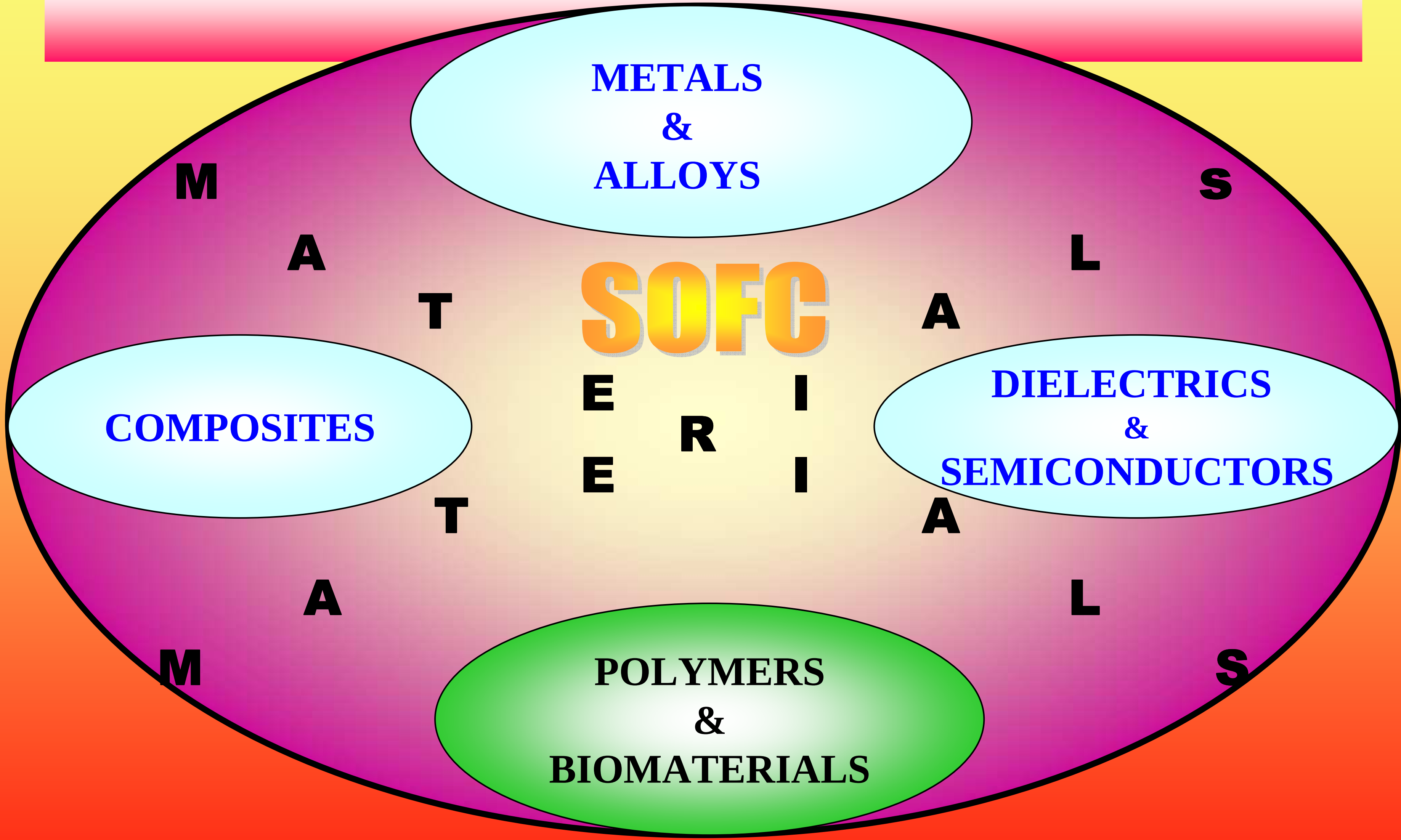
C - ANODE MATERIALS

D - INTERCONNECT (SEPARATOR)

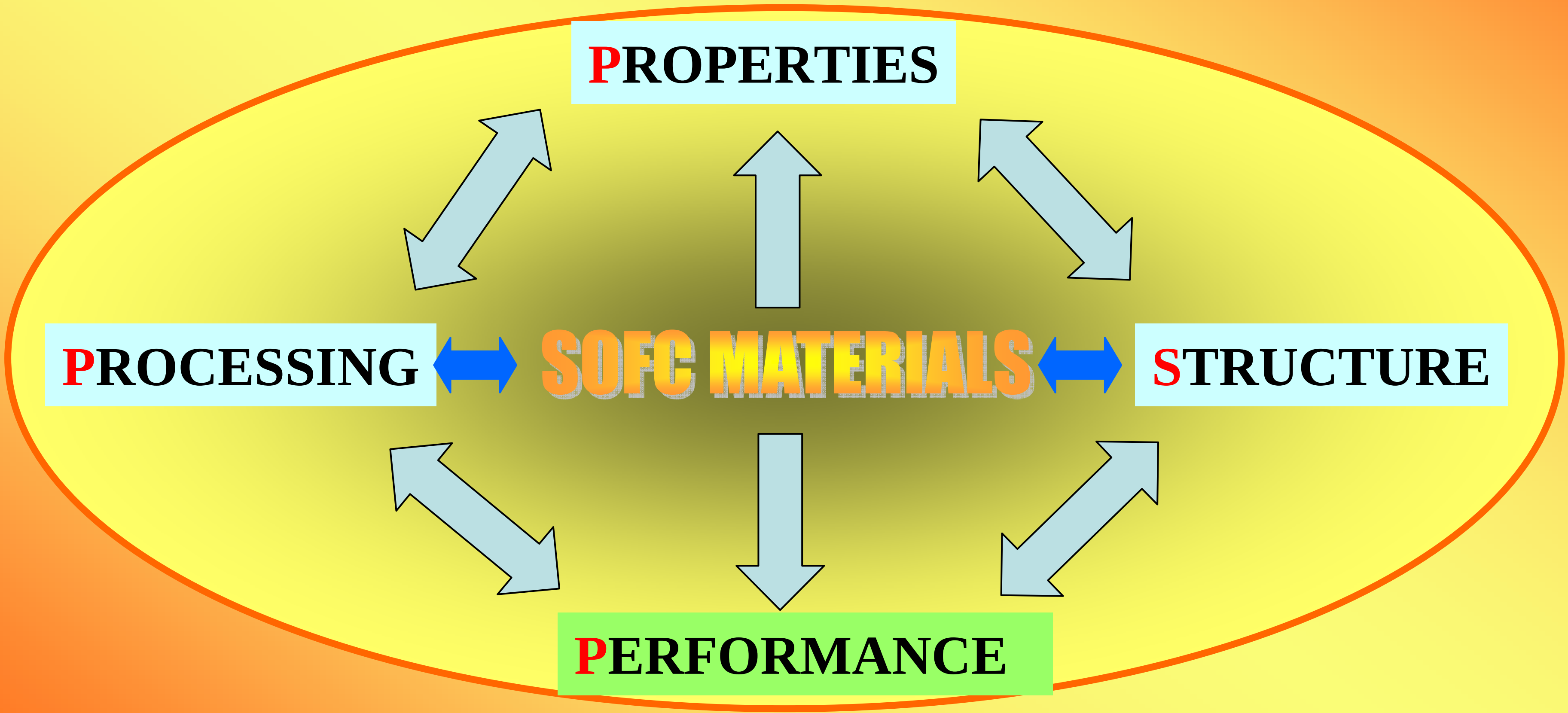
E - SEALING MATERIALS

CONCLUSIONS

INTRODUCTION



INTRODUCTION

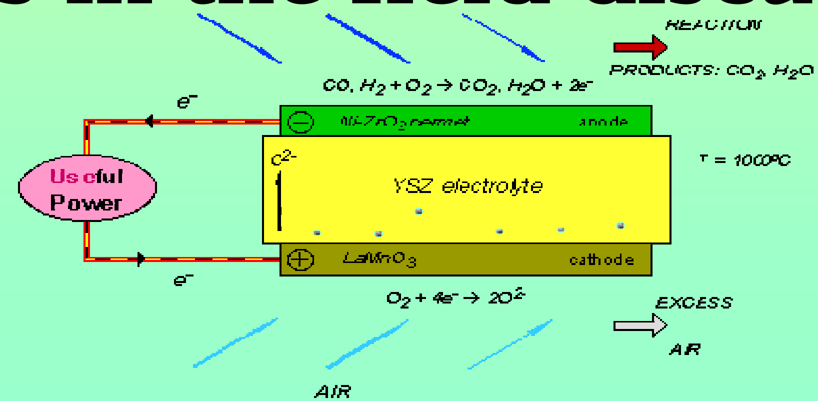


*** AIM ***

Current status of research and development regarding the

ceramic materials

used for SOFCs and IT- SOFCs during the last years using selection of examples taken from actually key papers in the field discussed .



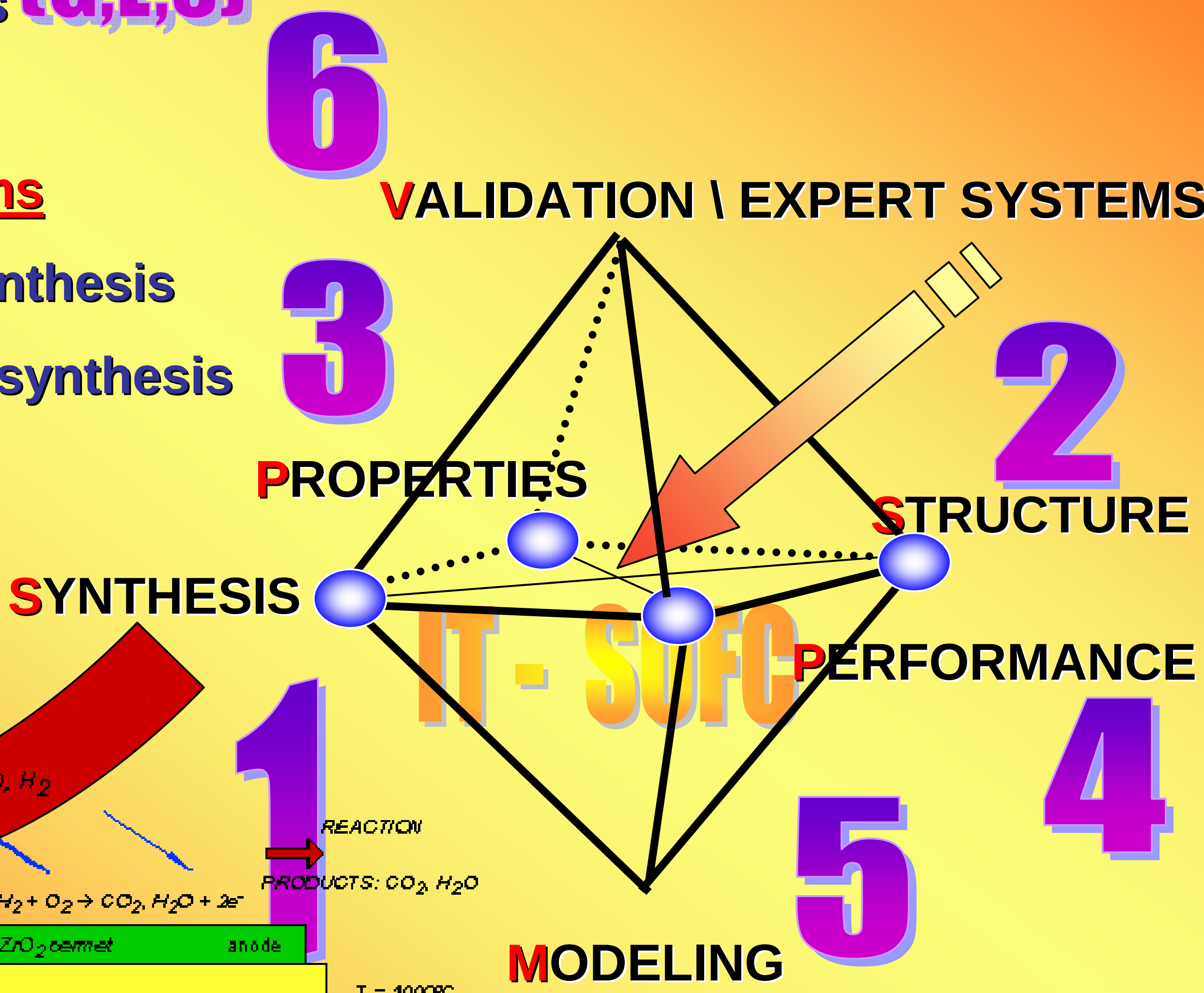
Raw materials (G,L,S)

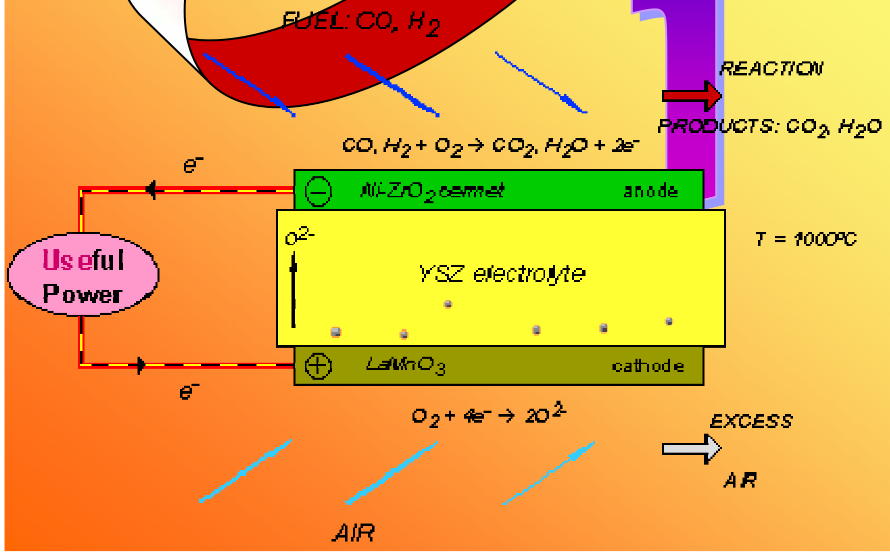
Compositions

Phase diagrams

Methods of synthesis

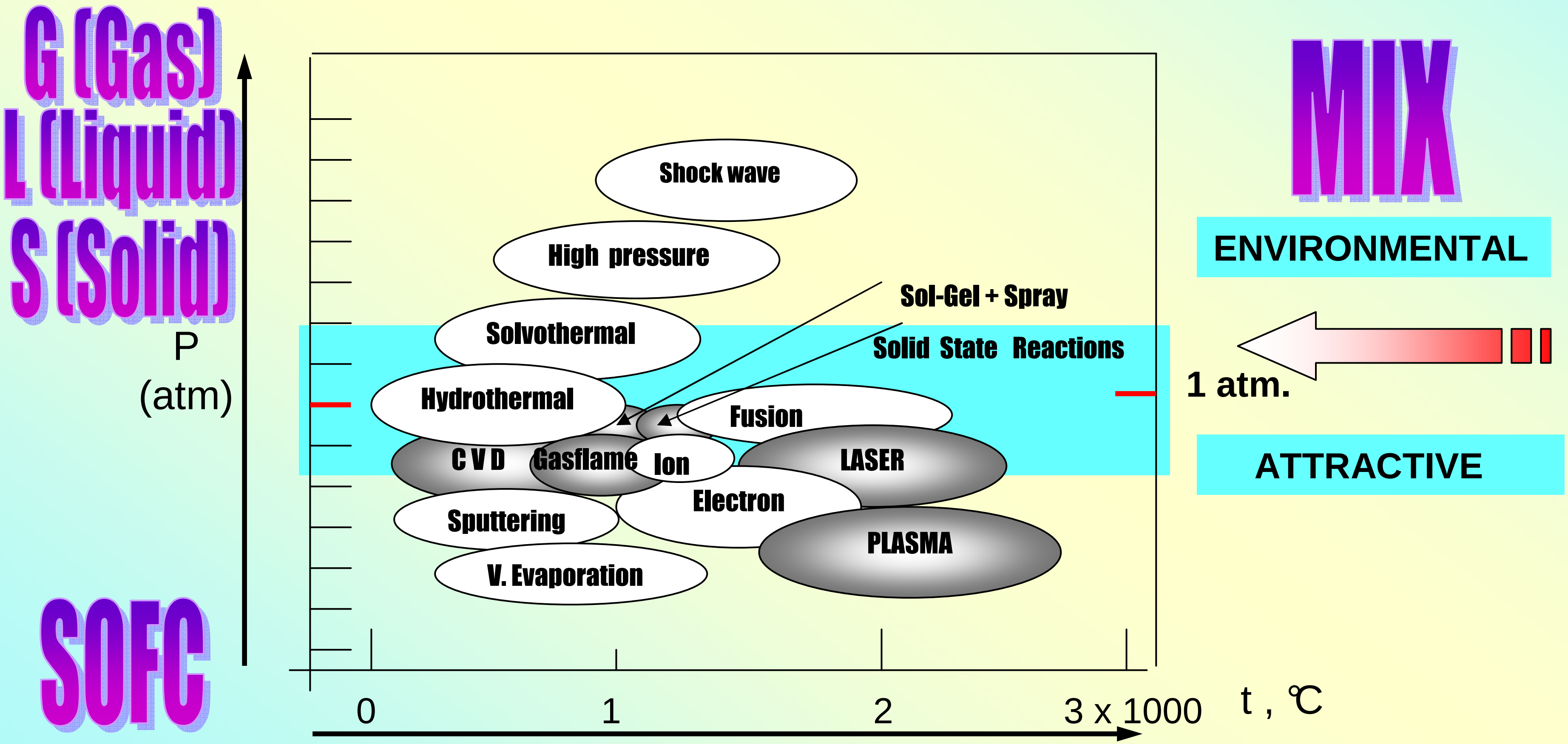
Conditions of synthesis





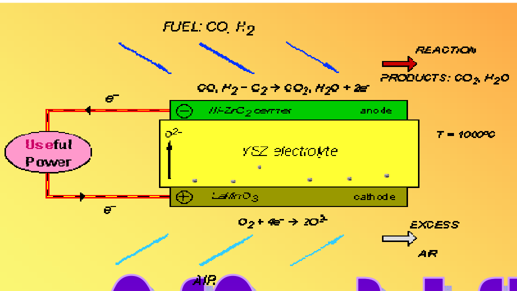
SOFCs MATERIALS

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.

1 :



Raw materials G (Gas), L (Liquid), S (Solid)

❖ **Compositions** → Multicomponent

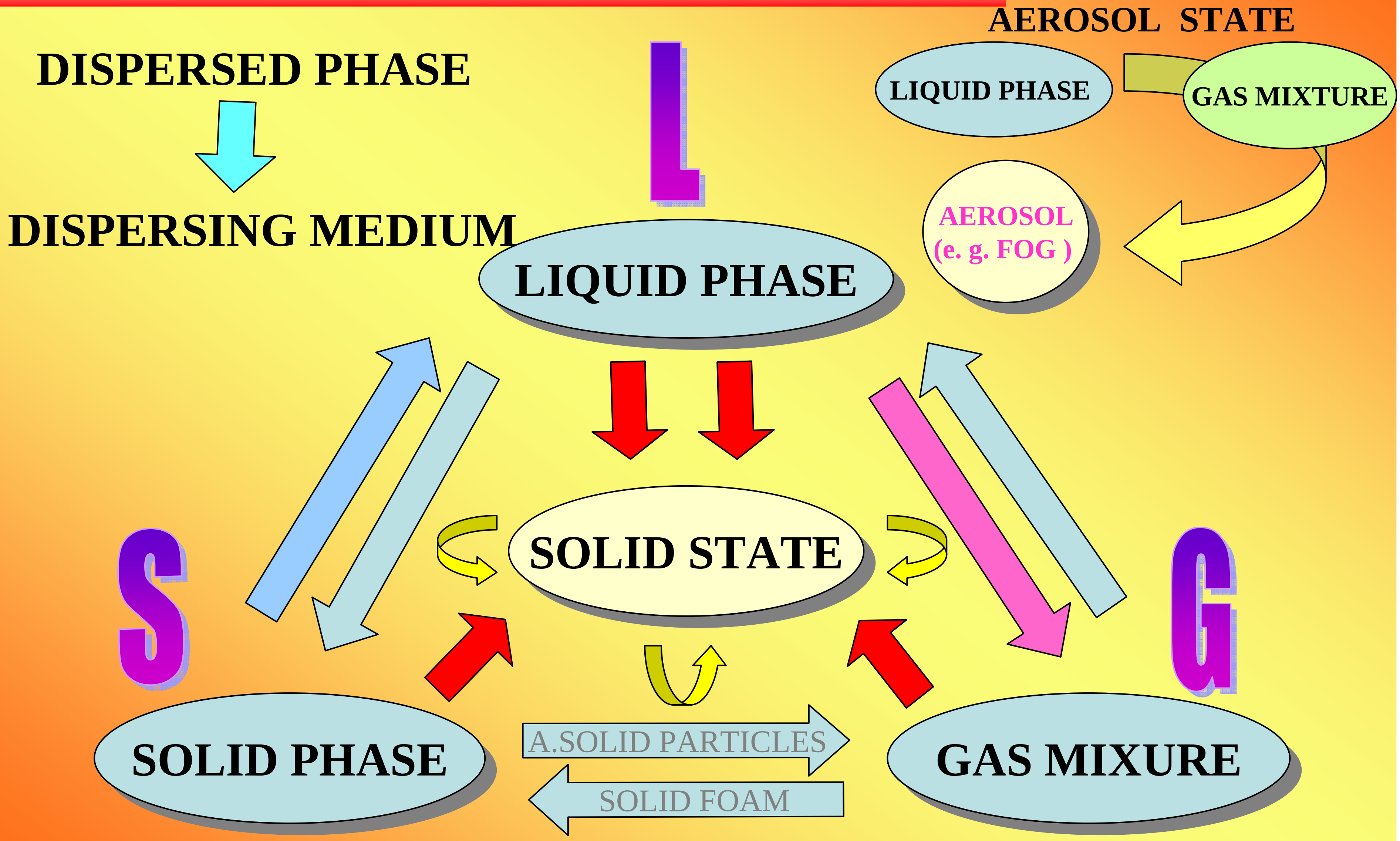
Phase diagrams $C = f(T)$; isopletes

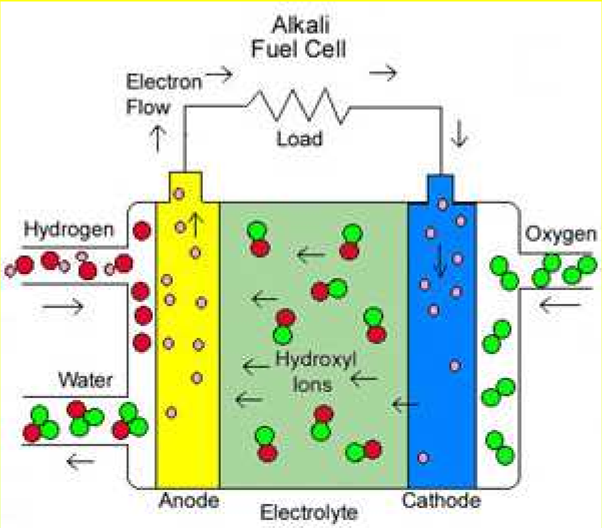
Methods of synthesis Raw materials, Compositions

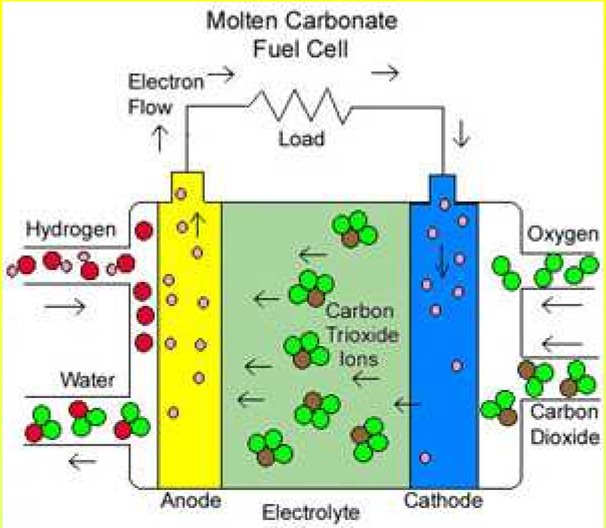
Conditions of synthesis Atmosphere , Pressure etc.

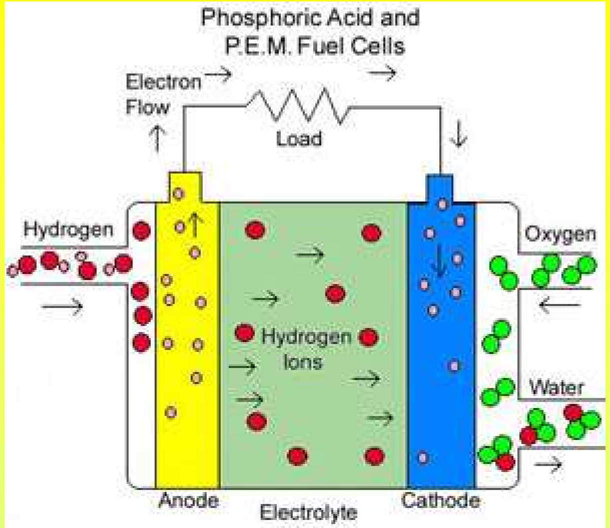
THE METHODS OF PROCESSING

Raw materials







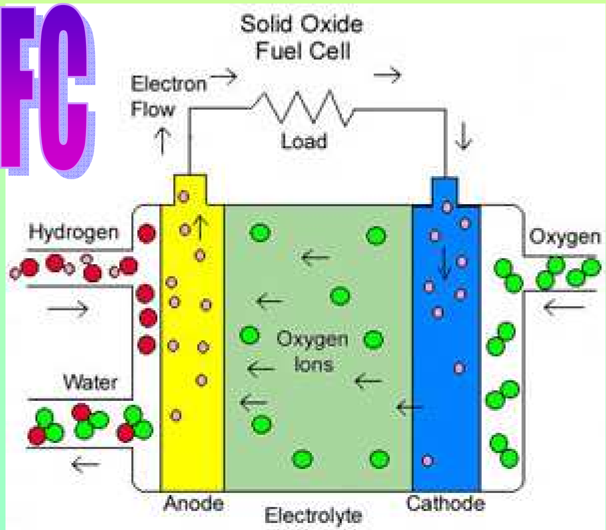


Drawing of an alkali cell

Molten carbonate cell

Phosphoric acid and PEM FC operation principle

SOFC

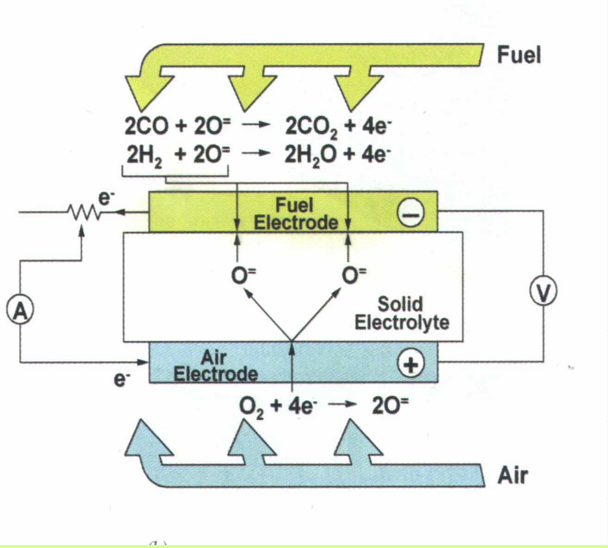


$$2H_2 + 2O^{2-} \rightarrow 2H_2O + 2e^-$$

Cell elements	Moderate T	Low T
Electrolyte	Yttria Stabilized Zirconia (YSZ)	Doped Ceria
Cathode	$(La,Sr)MnO_3$	(La,Sr)(Co,Fe)O (LSCF)
Anode	Ni-YSZ	Ni-Ceria
Interconnect (IC)	$(La,Sr)CrO_3$ (LSC)	LSC
Support	Partially Stabilized Zirconia (PSZ)	MgO

A fuel cell is a device that generates electricity by a chemical reaction.

SOFCs ARCHITECTURES



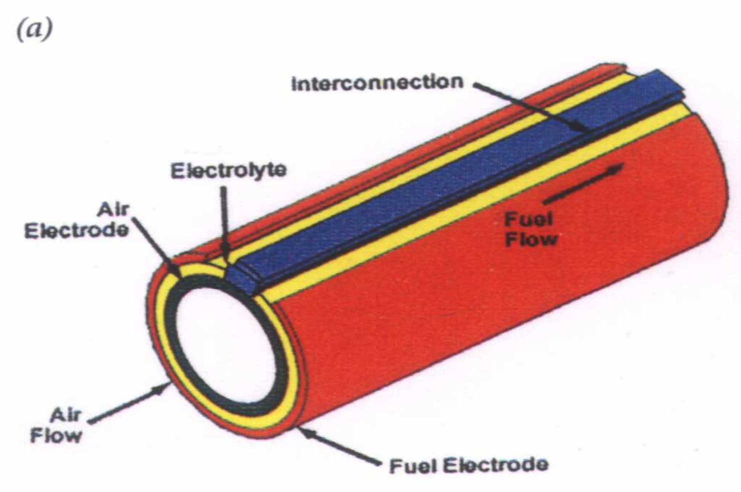
Operating principle

Electrochemistry of a Direct Methanol Fuel Cell

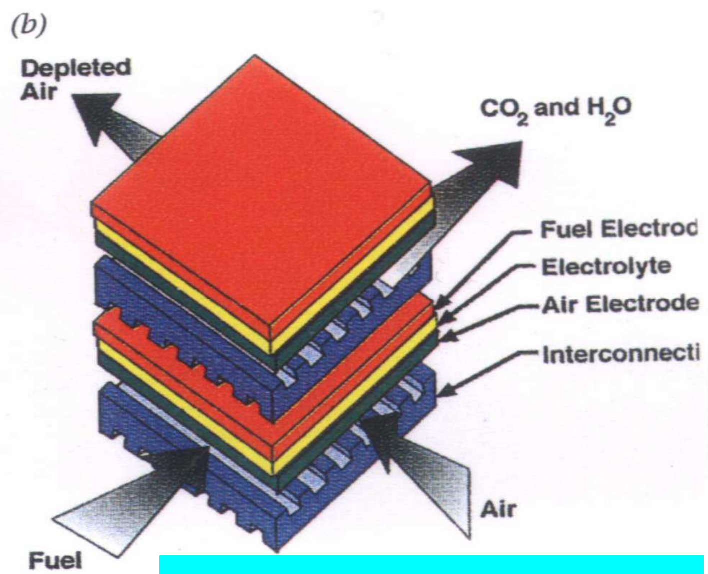
Anode: $CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-$

Cathode: $3/2\ O_2 + 6H^+ + 6e^- \rightarrow 3H_2O$

Cell Reaction: $CH_3OH + 3/2\ O_2 \rightarrow CO_2 + 2H_2O$

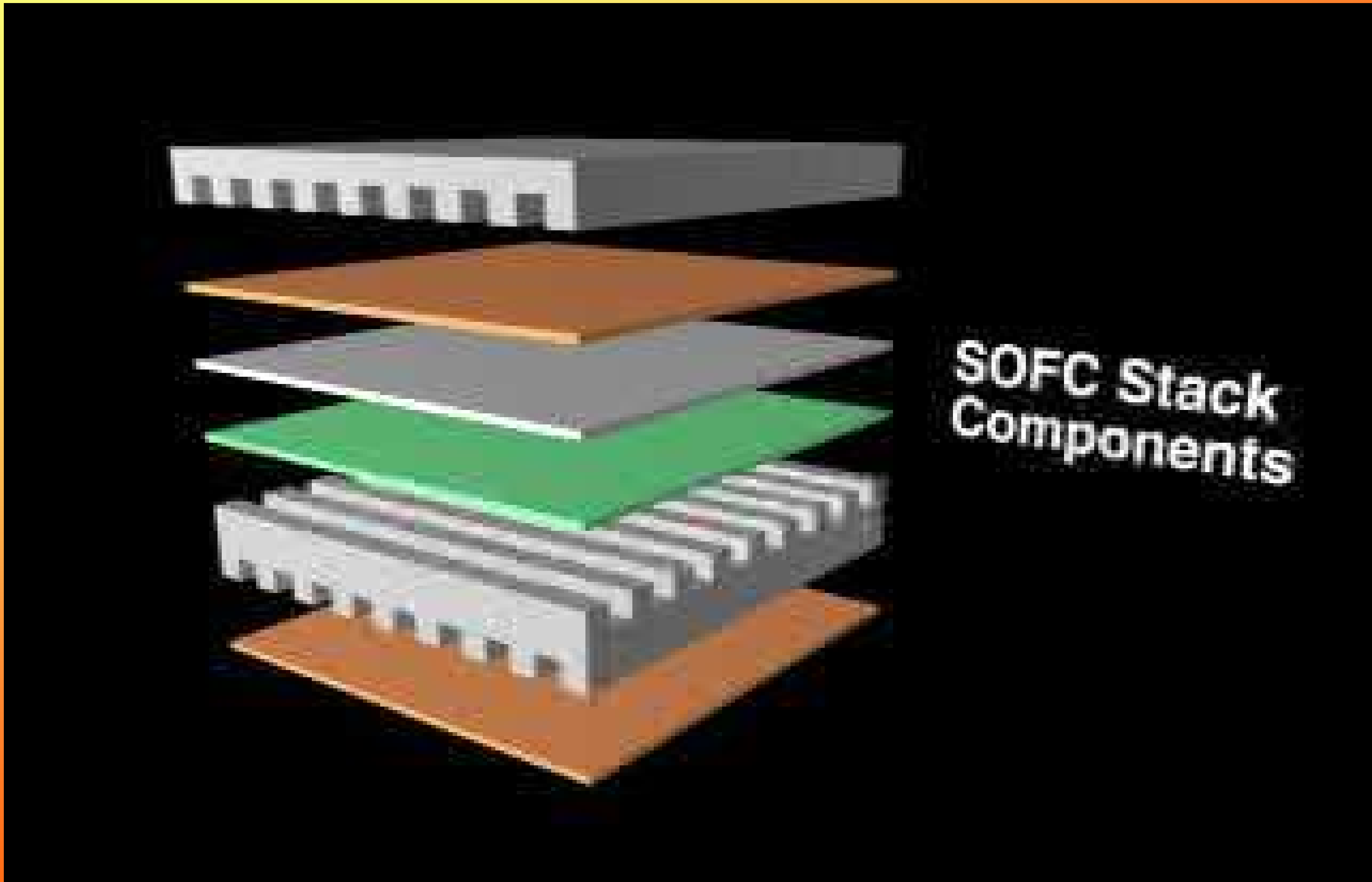


Tubular design



Planar design

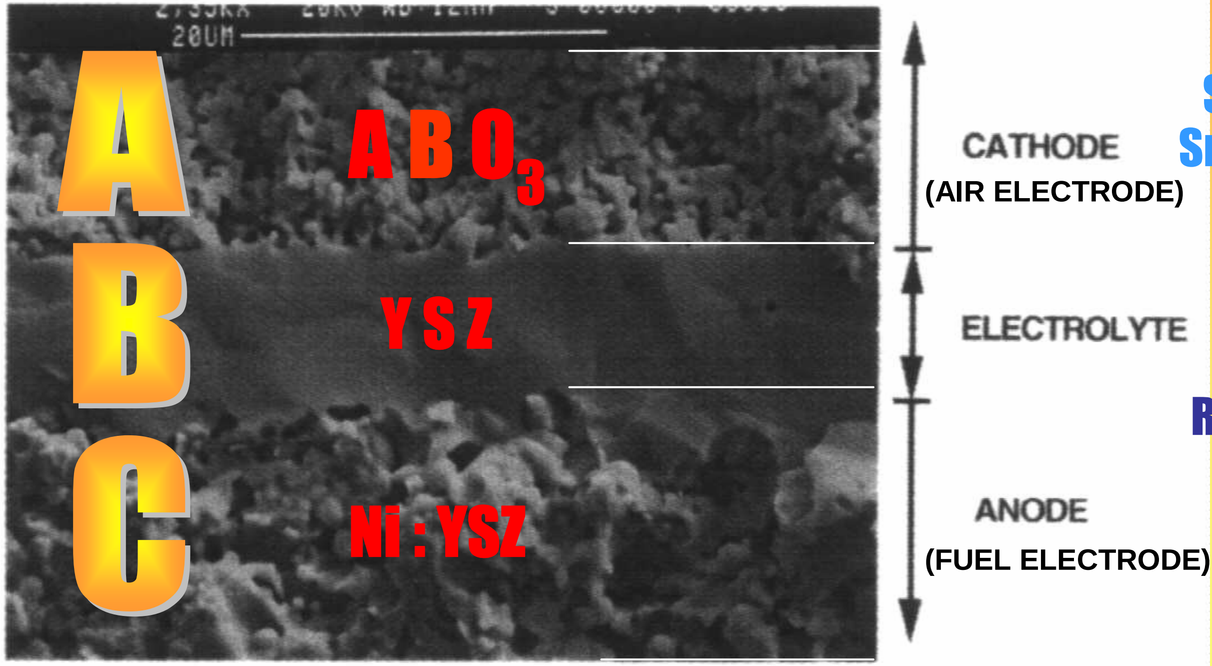
PRINCIPLE OF THE SOFCs WORK



COMPOSITIONS

ALTERNATIVE

A B C D E



$LaFeO_3$, $LaCoO_3$, $LaNiO_3$,

$SrFeCo_{0.5}O_{0.35}$, $Gd_{1-x}Sr_xCoO_3$

$SmCoO_3$,$La_{0.8}Sr_{0.2}Co_{0.8}Fe_{0.2}O_3$,

SSC – 30%SDC composite

$Sm_{0.5}Sr_{0.5}CoO_3$ (SSC)

$La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\delta}$

$RE_{9.33}(SiO_4)_6O_{26}$, $Bi_2Ru_2O_{7.5}$

$Ce_{1-x}Gd_xO_{2-\delta}$

$SrTi_{1-y}Nb_yO_3$,$La_xSr_{1-x}NbO_3$

Ytria- Doped Ceria [YDC]

Ni: perovskites

<u>INTERCONNECT</u> (SEPARATOR) OR BIPOLAR PLATE

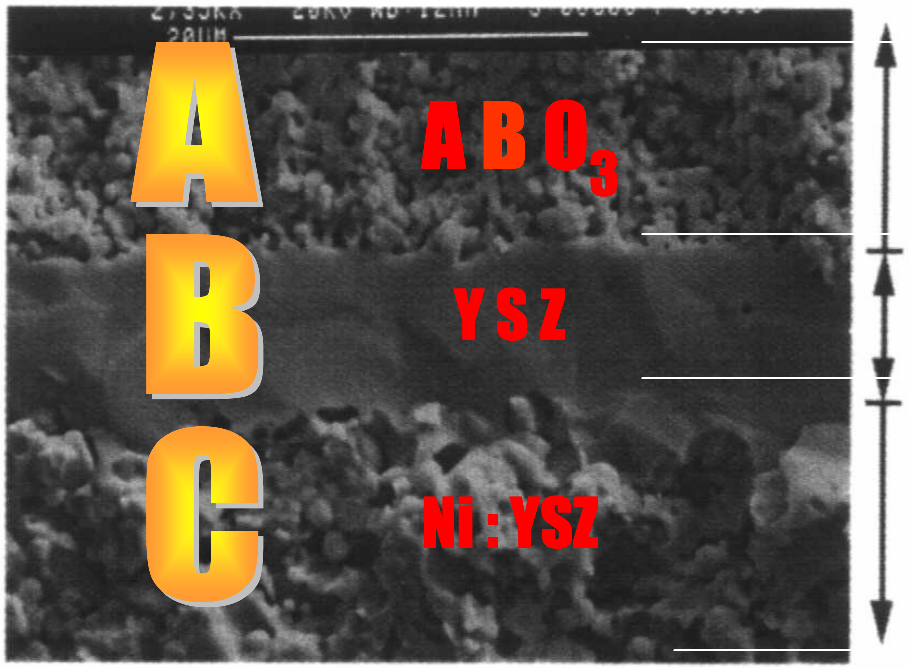
La_2O_3- Cr_2O_3 , alloys > Fe--Cr- $La_{0.8}Sr_{0.2}Cr_{1-x}Ti_{0.1}M_xO_3$

<u>SEALING MATERIALS</u> FOR STACK COMPONENTS

“3.3” borosilicate glass MICA, GLASSCERAMICS

HIGH TEMPERATURE CONDUCTING CERAMICS.

COMPOSITIONS



LSCF

Gadolinia doped Ceria

CGO

Ni- Ceria

cermet

HT - SOFC

LSM / YSZ / Ni :YSZ

IT - SOFC

LSCF / CGO / Ni :Ceria

HIGH TEMPERATURE CONDUCTING CERAMICS.

SOFC materials have to meet the following requirements:

A

- **CATHODE** – To possess high electronic conductivity in oxidizing atmosphere (> 100 S.cm-1) ; Effective ionic (oxygen) conductivity (~10-1 S.cm-1), Stability in oxidizing atmosphere; Electrocatalyst for oxygen reduction charge-transfer reaction, Compatibility and minimum reactivity with the electrolyte and the interconnect

B

- **ANODE** – High electrical conductivity and stability in reducing atmosphere; To possess high catalytic activity RE: fuel oxidation charge-transfer reaction; To be porous, electronically conducting media and with redox (corrosion) cycling stability.

C

- **ELECTROLYTE** – High oxygen ion conductivity ; Stability in oxidizing and reducing atmospheres; Thermal phase stability and low thermal expansion coefficient (< $10.10^{-6}.^{o}C^{-1}$); Dense and not gas permeation phenomena.

D

- **INTERCONNECT** – High electrical conductivity in oxidizing atmosphere; Corrosion stability to both oxidation and reduction atmospheres.

E

- **SEALING** - High chemical and thermal stability, To possess good isolating effect and not exhibit any gas (especially to O2 & H2) permeability; The thermal expansion coefficient could be matched the other components.

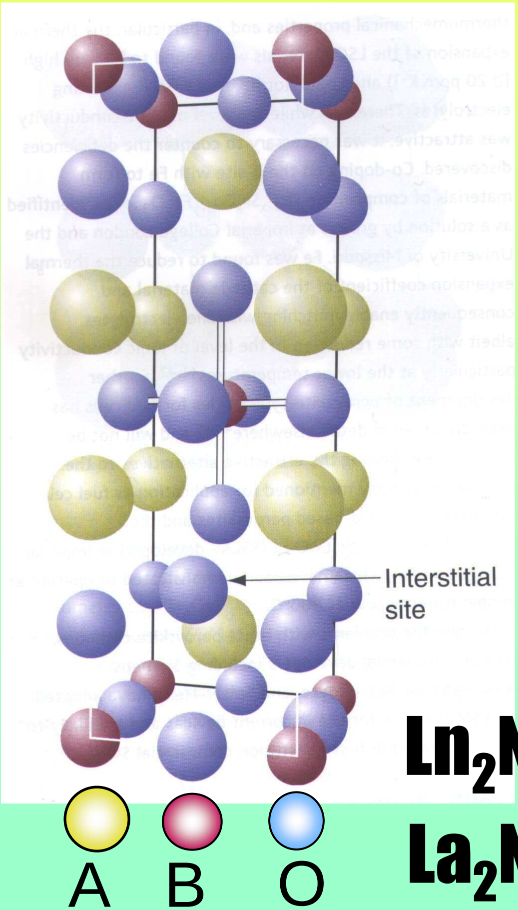
NATURE OF THE PEROVSKITES

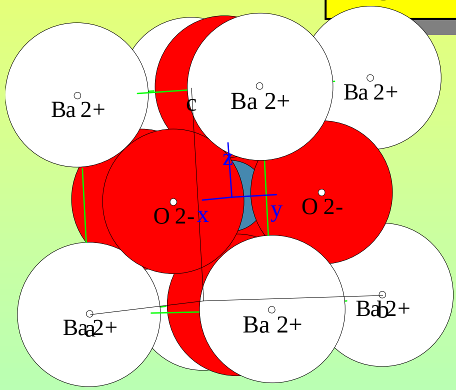
A.Wels, *Structural Inorganic Chemsitry*, **Fifth Edition. vol.2, Moscow, Mir, (1987) p. 300 (Russian Edition)**

A B O_3

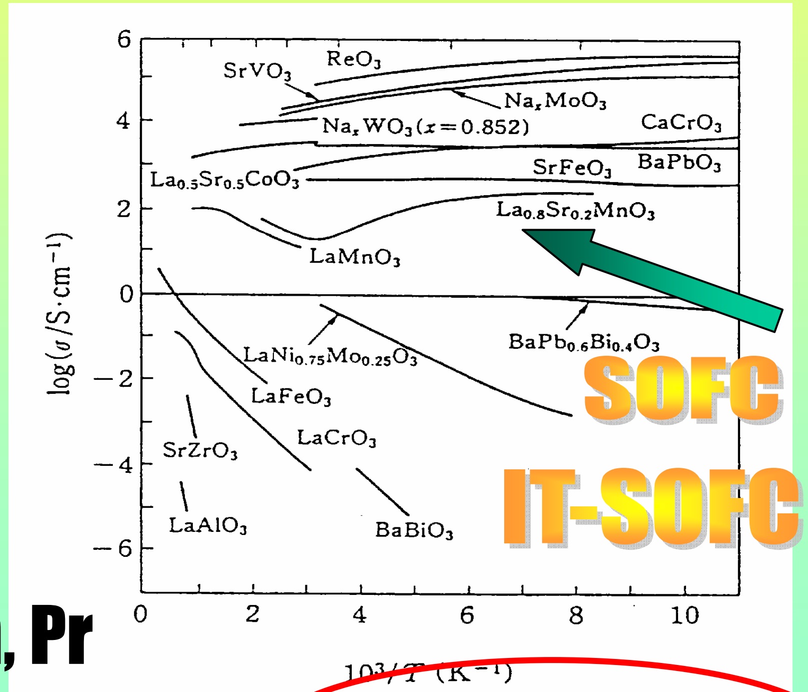
$BaTiO_3$ (tetragonal) ; space group № 123 (P4/mmm)
a = 3.993 Å; c = 4.033Å Ba 2+ (0,0,0); Ti 4+ (1/2,1/2,1/2) ;
O 2- (0,1/2,1/2),(1/2,1/2,1),(1/2,1/2,0)

Properties and applications of perovskite- type oxides, Eds. L.Tejuca, J.Fierro, **Marcel Dekker, Inc New York, Basel, Hong Kong , (1993) p.1- 377**





$A_2BO_{4+\delta}$



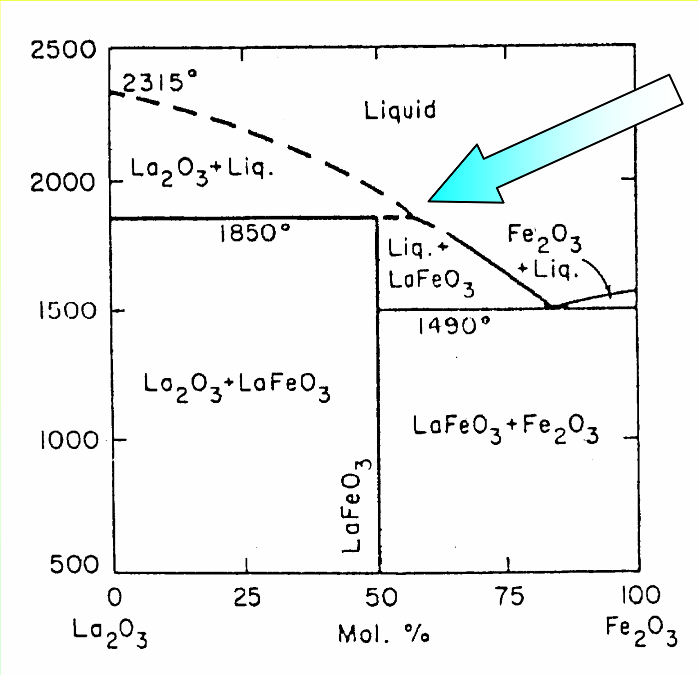
$Ln_2NiO_{4+\delta}$ Ln = Nd, Sm, Pr

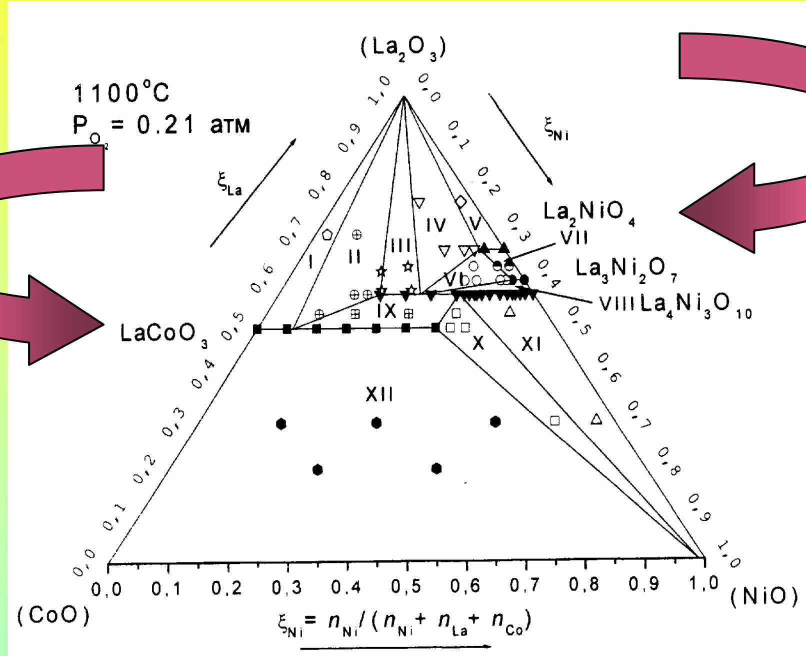
$La_2Ni_{1-x}Fe_xO_{4+\delta}$ $La_2Cu_{1-x}Co_xO_{4+\delta}$

$La_2Ni_{0.5}M_{0.5}O_{4+\delta}$
(M= Co, Cu)

PHASE EQUILIBRIUM DIAGRAMS

[28] *Phase Equilibrium Diagrams, CD Data base*, **NIST, The Amer. Ceram. Soc. ISBN: 0-944904-93-9 (1993) Selection: Fig 61, Fig. 340.**





$LaCoO_{3-\delta}$, La_2NiO_4, $La_3Ni_2O_7$, $La_4Ni_3O_{10}$
and

SS → **$LaCo_{1-x}Ni_xO_{3-\delta}$** ($0 \leq x \leq 0.6$),
$La_2Ni_{1-y}Co_yO_{3-\delta}$ ($y = 0.1$),
$La_3(Co_{1-y}Ni_y)_2O_7$ ($0 \leq y \leq 0,025$)
$La_3(Co_{1-x}Ni_x)_3O_{10}$ ($0 \leq y \leq 0,6$)

Incongruent melting compound

A **$LaFeO_3$- perovskite** **A,B**

La1-x SrxMnO3-δ **La1-x SrxCo1-yFeyO3-δ**

PHASE EQUILIBRIUM DIAGRAMS

LSCF/CGO/Ni:Ceria

A,B

La-Fe-O
La-Sr-O
La-Co-O
Sr-Fe-O
Sr-Co-O
La-Sr-Fe-O
La-Sr-Co-O
La-Co-Fe-O
La-Sr-Co-Fe-O

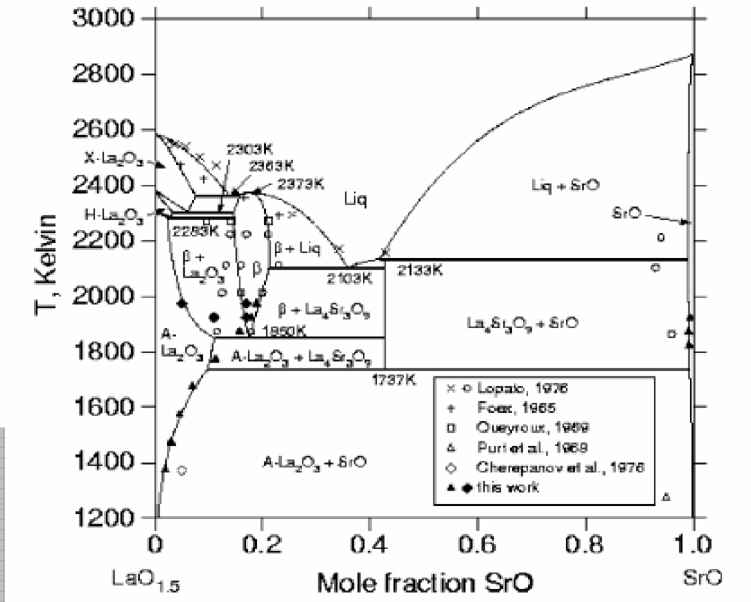
E. Filonova ,A. Demina,E. Kleibaum, L.Gavrilova A. Petrov**, *Phase equilibria in the system $LaMnO_{3+\delta}$ - $SrMnO_3$-$LaFeO_3$- $SrFeO_{3-\delta}$.*** Inorg.Mat(Rus) 2006, **42**, 4, pp. 497

Isothermal Sections at 1100-1300ºC

A. Fossdal, M. Einarsrud, T.Grandew

Phase Relations In the System La_2O_3–SrO–Fe_2O_3

J. Am. Cer. Soc.,88(2005) 1988



Calculated La_2O_3 - SrO,

A. Grundy , B. Hallstedt, L. Gauckler,

Acta Materialia 50 (2002) 2209–2222

CALPHAD XXXIV 2005 conference

D. Sedmidubský, J. Leitner, A. Strejc, O. Beneš and M. Nevřiva
Phase equilibria modelling in Bi–Sr–Mn–O system

ALTERNATIVE CATHODE MATERIALS

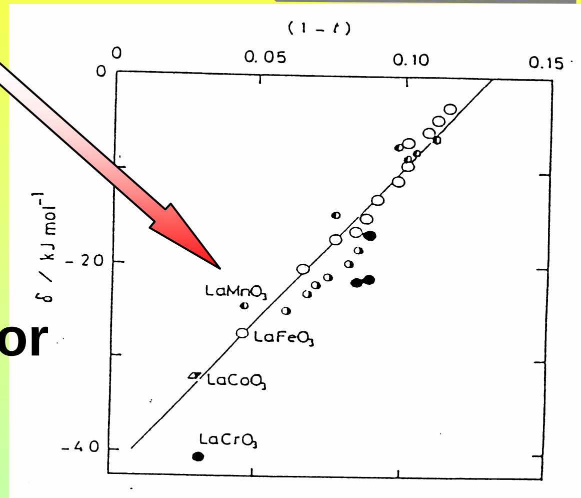
SOFC

- ✓ SS of $La_{1-x}Sr_xCoO_{3-\delta}$ are mixed conducting ceramic materials.
- ✓ The perovskites from the binary system $La_2O_3 – Me_nO_m$

→ La_2O_3 - Fe_2O_3 system, $LaFeO_3$, $LaCoO_{3-\delta}$, $LaNiO_3$

A → $La_{0.8}Sr_{0.2}CoO_3$ **A,B** → $La_{0.8}Sr_{0.2}Co_{0.8}Fe_{0.2}O_3$

- ✓ Novel cathode $SrFeCo_{0.5}O_{0.35}$, $Gd_{1-x}Sr_xCoO_3$ Ref. [35]
- ✓ New data for $SmCoO_3$ – perovskite+ Pt particles [36]



$La_{0.8}Sr_{0.2}MnO_3$ (LSM) is an excellent cathode material for higher operating temperature SOFCs (800- 1000°C)

The stabilization energy of perovskites vs. the tolerance factor defined from the ionic configuration properties

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IT-SOFC

LSM-LSGM composite
LSCF ($La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_3$)
LSCF – LSGM composite
LSCF – GDC composite

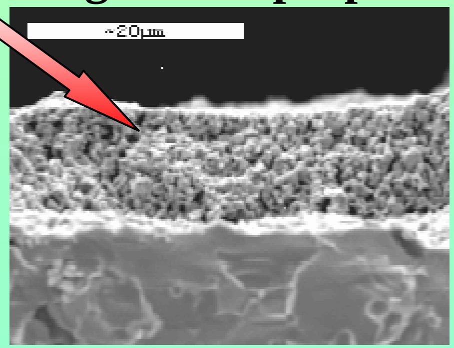
$Sm_{0.5}Sr_{0.5}CoO_3$ (SSC)
SSC – 10%SDC composite
SSC – 30%SDC composite
SSC – 40%SDC composite

YSB

YSB- Ag

$Bi_2V_{0.9}Cu_{0.1}O_{5.35}$ – BICUVOX

Bismuth Oxide based Cathodes

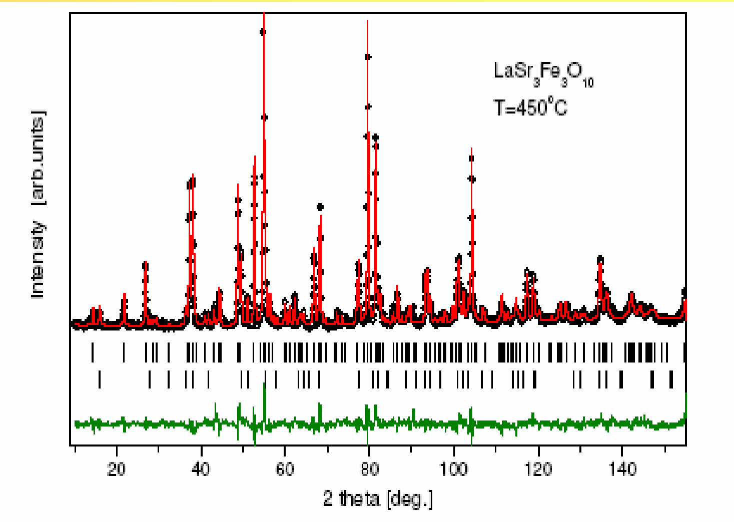


C. Xia., Y. Lang, G. Meng,
Development of Low-Temperature SOFC
Fuell Cells , 4 (2004) 41

ALTERNATIVE CATHODE MATERIALS

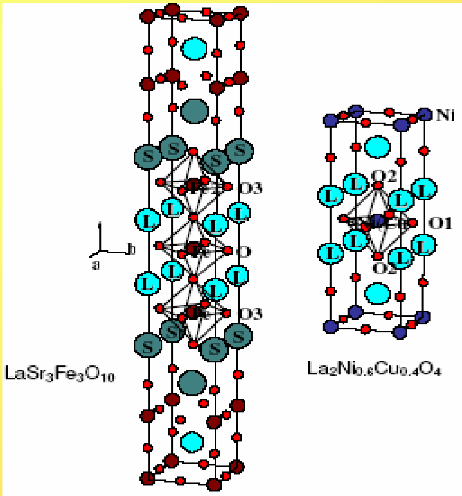
IT- SOFC

LSCF ($La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_3$), SSC – 30%SDC composite, **$SrFeCo_{0.5}O_{0.35}$, $Ba_{0.5}SrO_{0.5}CoFeO_3$, $LaSr_3Fe_3O_{10}$** and other new layer phases from **Ruddlesden–Popper perovskite family can be treated as potential effective cathode materials for IT- SOFCs .**

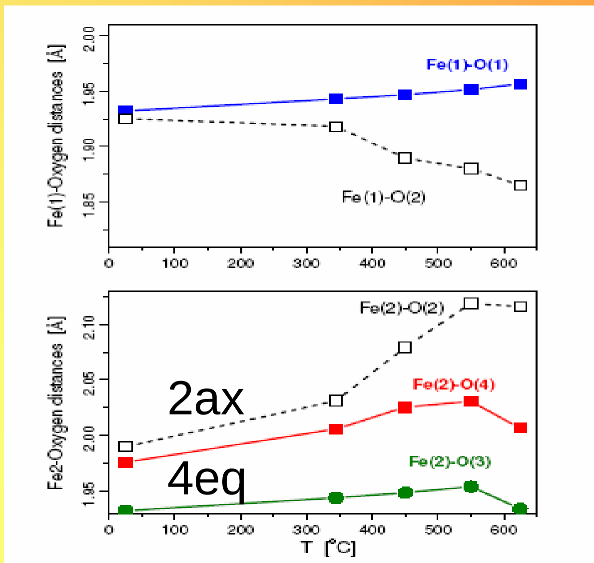


Neutron diffraction spectrum of $LaSr_3Fe_3O_{10}$ phase

(T = 450±C)



Crystal structure of *n*=3 $LaSr_3Fe_3O_{10}$ and *n*=1 $La_2(Ni,Cu)O_4$ R-P phases.



Temperature dependence of Fe(1)-O and Fe(2)-O distances in FeO6-octahedra.

ELECTROLYTE MATERIALS

FLUORITE

AO_2

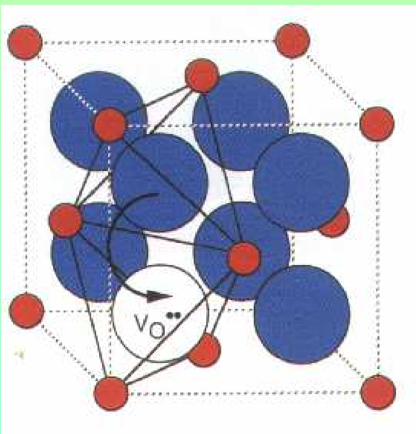
YSZ

$Zr_{1-x}Sc_xO_{2-\delta}$

$Ce_{1-x}Gd_xO_{2-\delta}$

SS - **BIMEVOX** type

$Bi_2Mg_xV_{1-x}O_{5.5-3x/2-\delta}$



PEROVSKITE

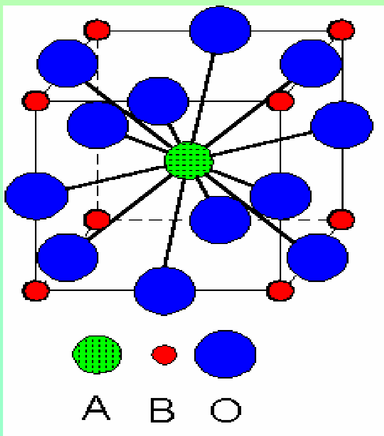
ABO_3

SS from $LaGaO_3$ base

$La_{1-x}Sr_xGa_{1-y}Mg_yO_{3-\delta}$

$CaTi_{1-x}Al_xO_{3-\delta}$ and

$CaTi_{1-x}Mg_xO_{3-\delta}$



PYROCHLORE

$A_2B_2O_7$

SS -

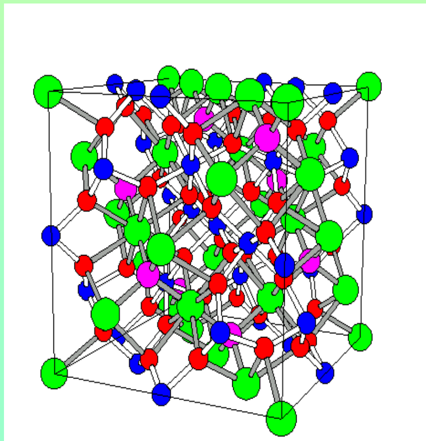
$Gd_2(Zr_xTi_{1-x})_2O_7$

$Y_2(Zr_xTi_{1-x})_2O_7$

$Bi_2Ru_2O_{7.5}$

A-8 B-6

O-4 X-4



APATITE

$A_{10}B_6O_{26}$

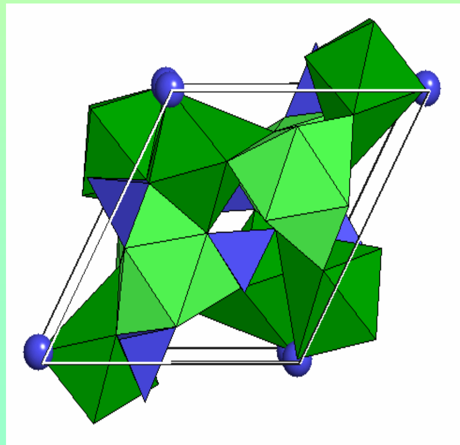
$(La/Sr)_{10-x}Si_6O_{26+y}$

$(La/Sr)_{10-x}Ge_6O_{26+y}$

$La_9SrGe_6O_{26.5}$

LAMOX

$La_2Mo_2O_9$

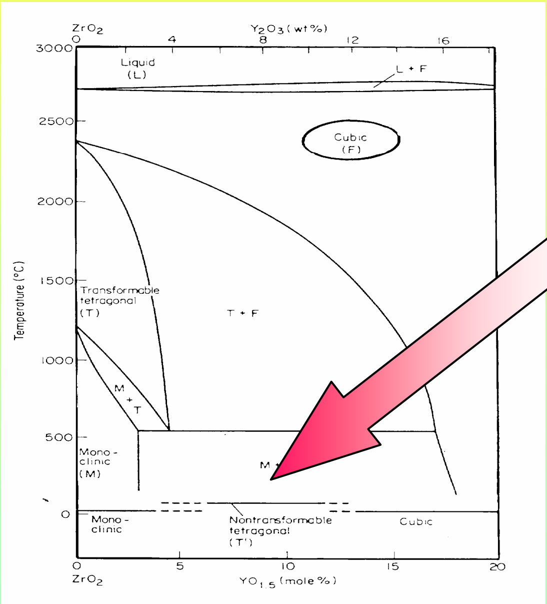


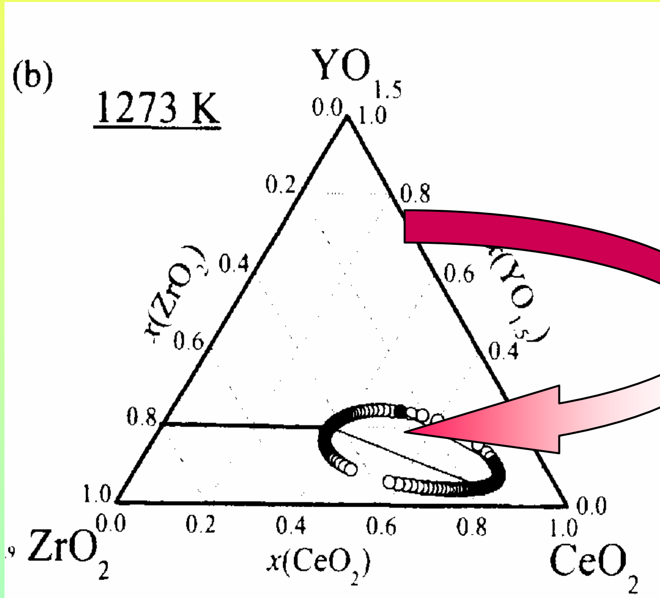
ELECTROLYTE

Usually are used fluorite- structured oxide materials like YSZ, rare earth doped bismuth oxide and rare earth doped ceria.

[28] *CD ROM Data base*, **NIST, ISBN: 0-944904-93-9 (1993)**

H.Yokokawa, *Proceed. SOFC-VII, Tsukuba*, **v. 2001-16 , (2001) p.339**





Above 8 % Y_2O_3 – doped leads to cubic phase stabilization, parallel with Vö - creation , equivalent for every mole of Y_2O_3 amount.

Calculated miscibility gap and the tie lines in the ZrO_2-CeO_2- $YO_{1.5}$ system

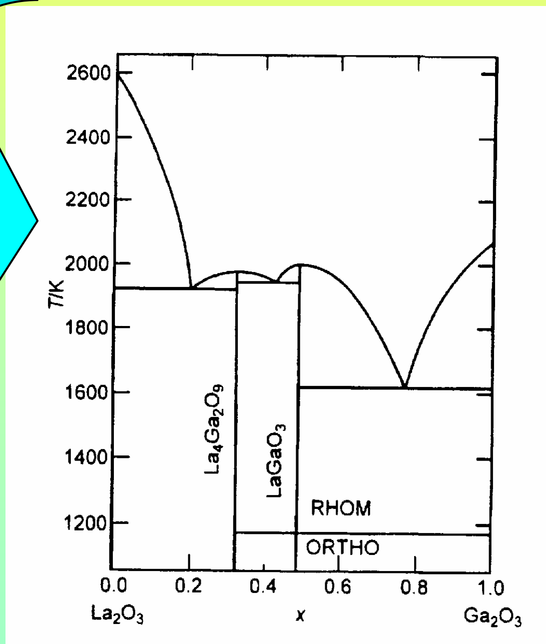
PHASE EQUILIBRIUM DIAGRAMS

[39] A. Matraszek , *Proceed. of SOFC-VII*, **Eds. H. Yokokawa, S. Singhal , Electrochem Soc. , vol. 2001 - 16, (2001) p. 319**

[40] M. Mizuno, T. Yamada and T. Ohtake, *Yogyo- Kyokai- Shi* **93, 295 (1985)**

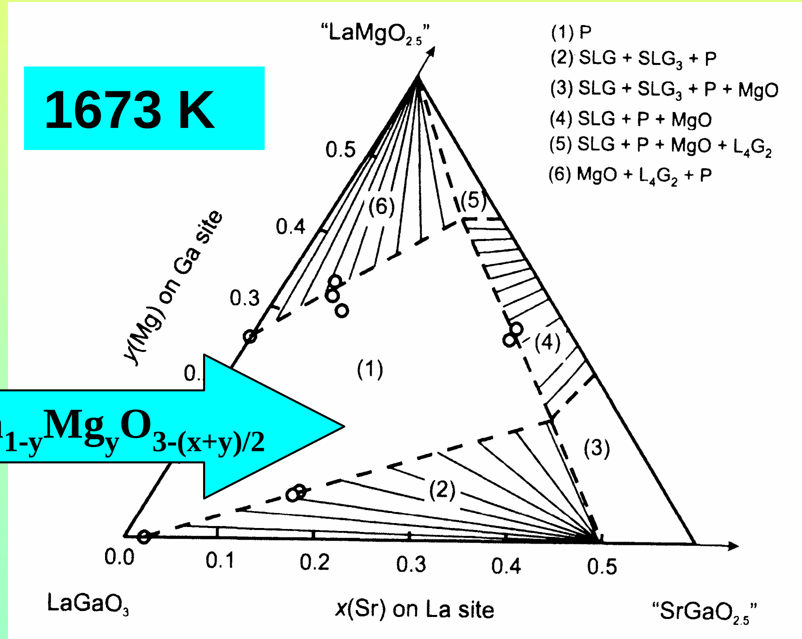
Phase relations in quasi-ternary system:

$LaGaO_3$- $SrGaO_{2.5}$ - $LaMgO_{2.5}$



Phase equilibrium diagram

La_2O_3 - Ga_2O_3

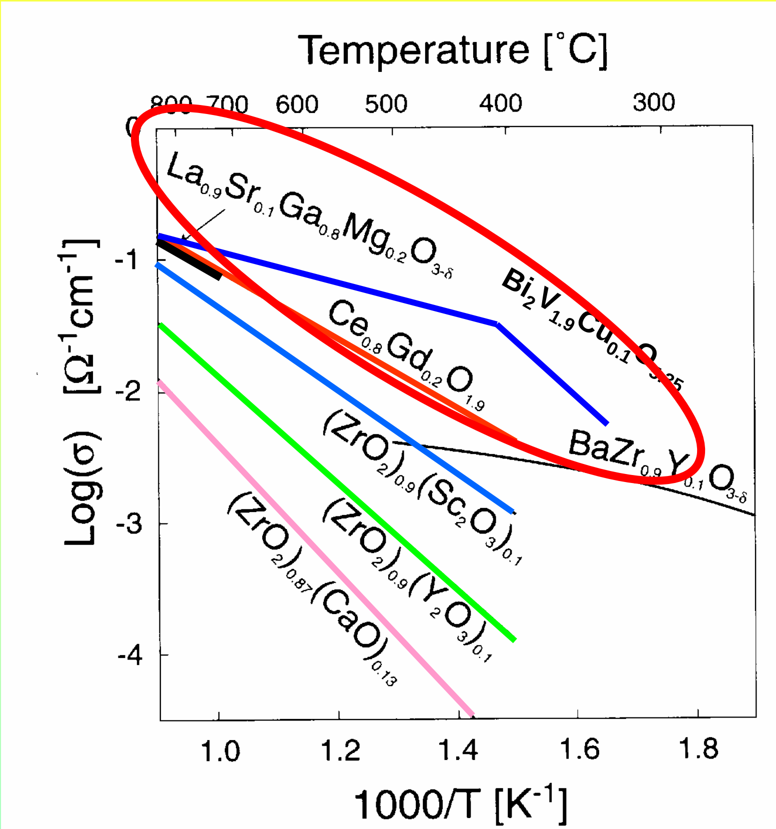


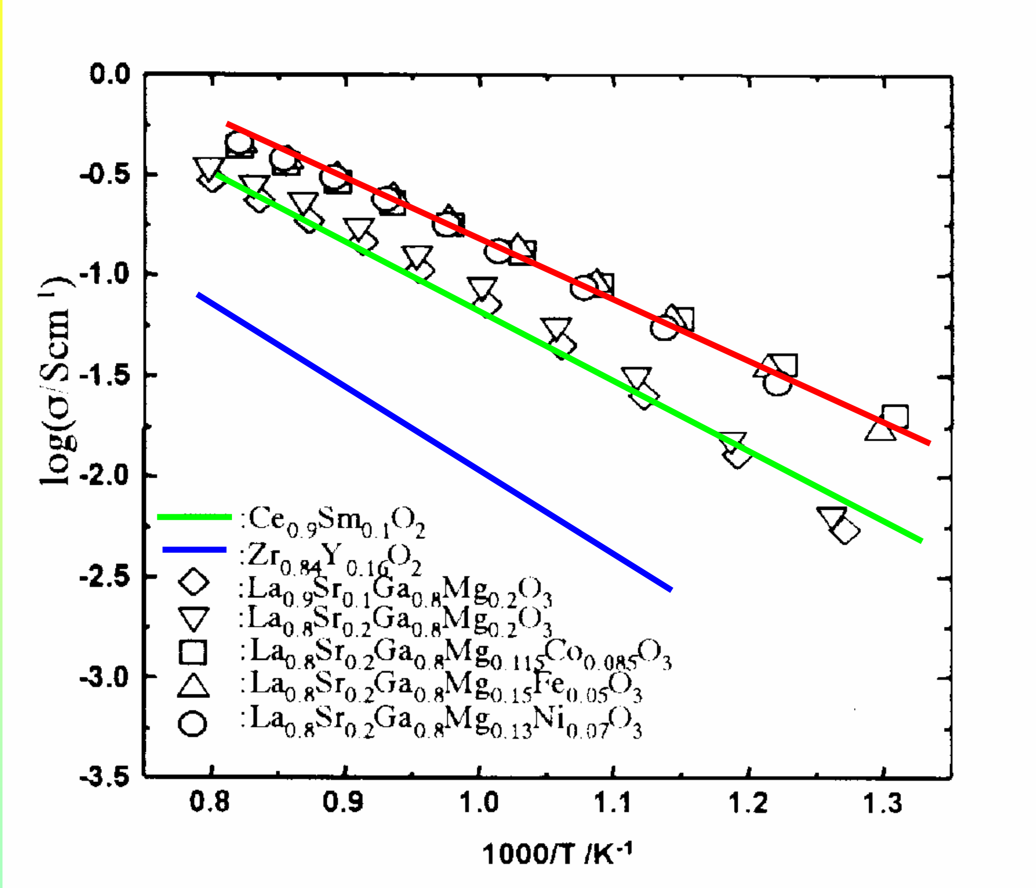
$La_{1-x}Sr_xGa_{1-y}Mg_yO_{3-(x+y)/2}$

(LSGM)

In lit. the phase $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ is an object of interest of synthesis

CONDUCTIVITY OF ELECTROLYTES

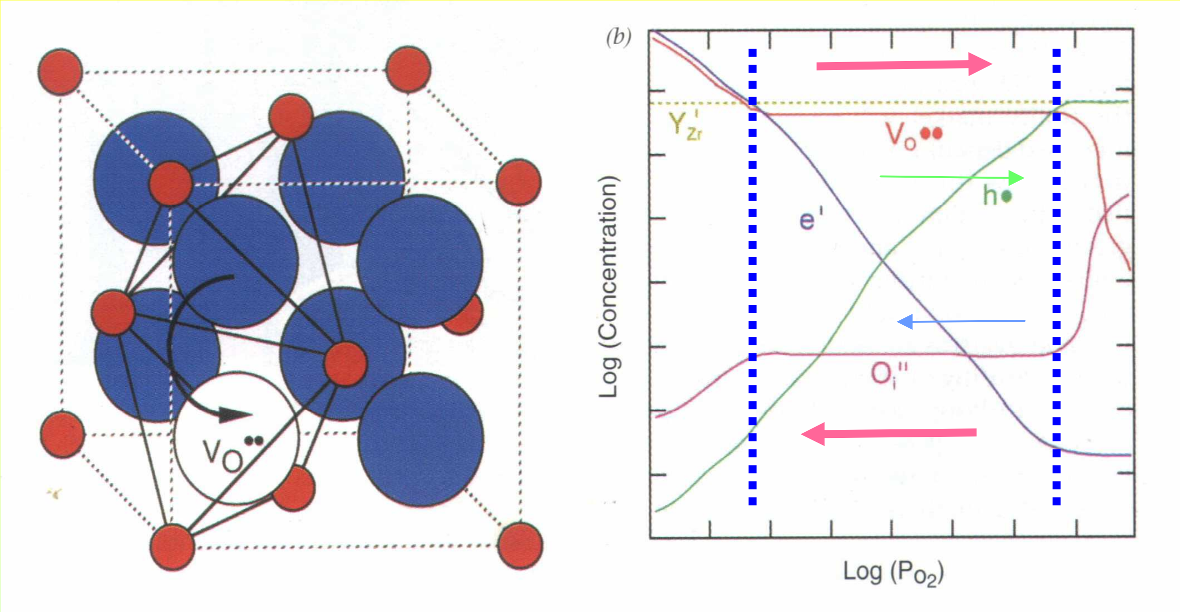




S. Haile, *Materials today* (6)
March 2003, 24

T. Ishihara, Y. Tsuruta, H. Nishiguchi, Y. Takita, *2000 Fuel Cell Seminar*, **Portland, 550, 2000**

OXYGEN TRANSPORT



The mechanism of the oxygen transport from one occupied anion lattice site to a vacant anion site in a fluorite oxide and defect concentration in YSZ vs. P_{O2}. The diagram shows **3** regions: *low, intermediate and high P_{O2}*. Each of the mobile species is then transported through the material in response to an applied chem. potential due to ΔP_{O2} or electrical one [4].

The δ- Bi_2O_3 exhibits the highest oxygen- ion conductivity, due to its open crystal structure.

Bi^{3+} → Bi^0

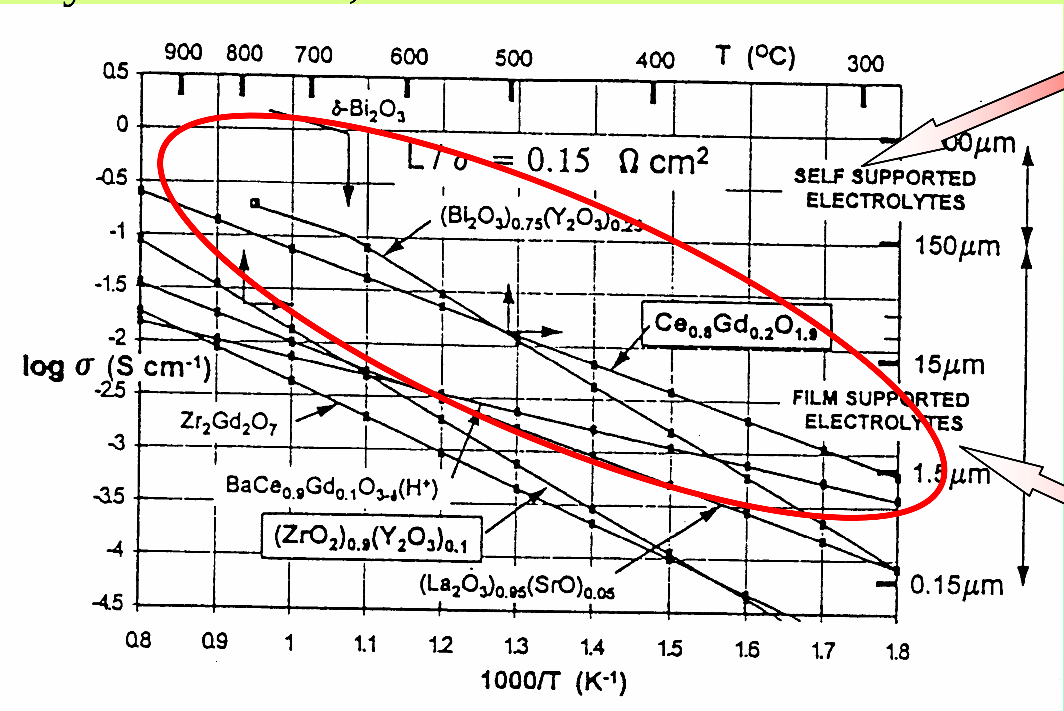
Ceria doped with alkaline earths (e.g. Ca- , Mg-) or rare earths (e. g. Ga- (CGO) and Sm – oxides) samples are attractive .

Ce^{4+} → Ce^{3+}

e^- - conductivity will appear

ALTERNATIVE ELECTROLYTES

- ✓ New lanthanum gallate system **$LaGaO_3$, $SrGaO_{2.5}$ $LaMgO_2$** [39]
- ✓ **$La_{1-x}Sr_xGa_{1-y}Mg_yO_{3-(x+y)/2}$** (LSGM) perovskite phase **$La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\delta}$**
- ✓ 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].
- ✓ **$La_{0.9}Sr_{0.1}$]$M^{III}O_{3-\delta}$** (where M^{III} is **Al, Ga, Sc and In**) perovskites [K. Nomura]
- ✓ New rare- earth silicates (**$RE_{9.33}(SiO_4)_6O_2$**) for medium operating temperature by Ch. Barthet,



1

2

Summing up of ionic conductivity of CeO_2 and Bi_2O_3 based electrolytes

REQUIREMENTS TO SOFC ANODE

The anode as the part of a SOFC is obviously crucial for a high performance of the cell/system. In particular, the following requirements are actual :

- **Catalytic activity:** the anode must have a high catalytic activity for fuel oxidation (high level of fuel utilization must occur).
- **Conductivity:** a maximum electrical conductivity under a large variety of operating conditions is desired to minimize the ohmic losses (i.e. n- type conductor).
- **Compatibility and Stability:** the anode must be chemically (redox), thermally, and mechanically stable and compatible with the other fuel cell components.
- **Porosity:** the porosity of the anode must be tailored with regard to mass transport considerations as well as mechanical strength.
- **Tolerance:** Tolerance to the impurities: CO,S,Cl,H_2O must exists.
- **Cost:** Cheaper (non or low Pt content) catalysts are recommended.

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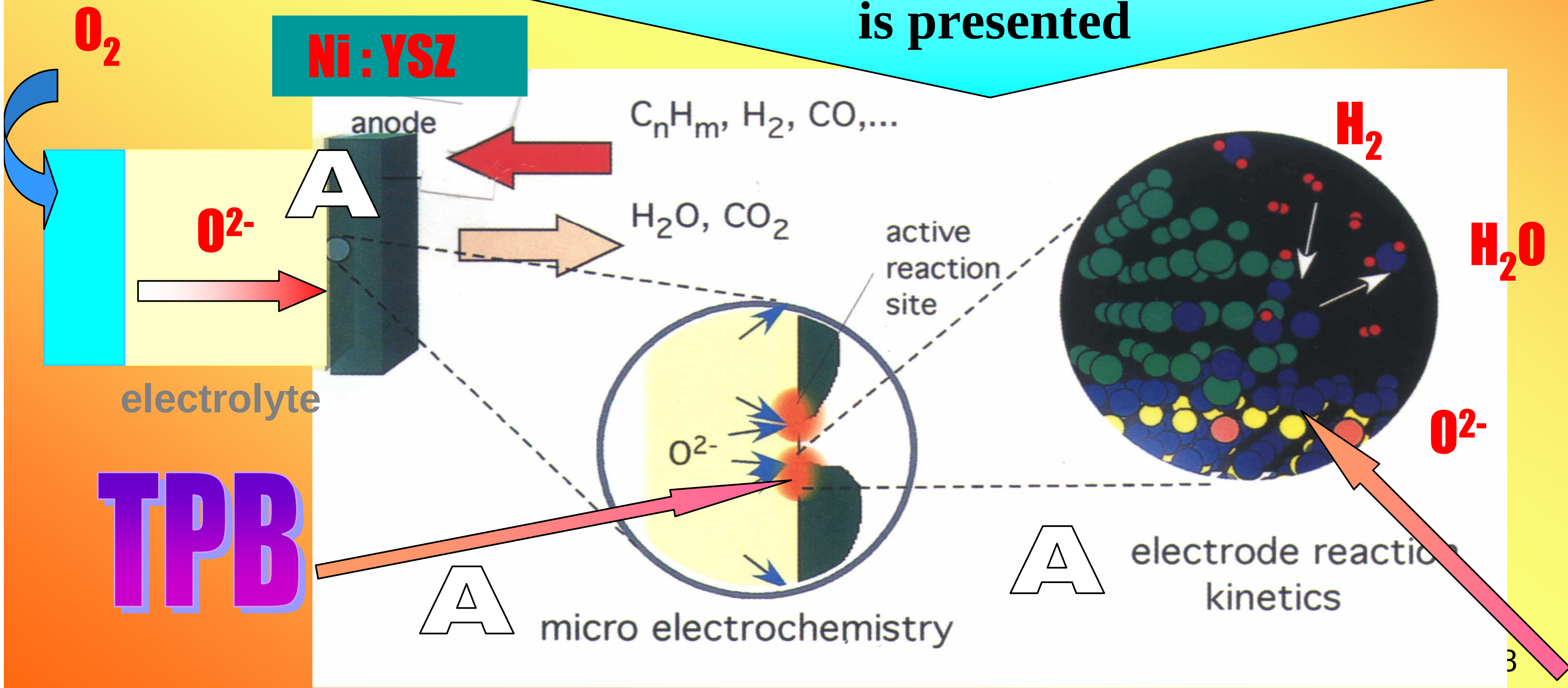
ANODE REACTION

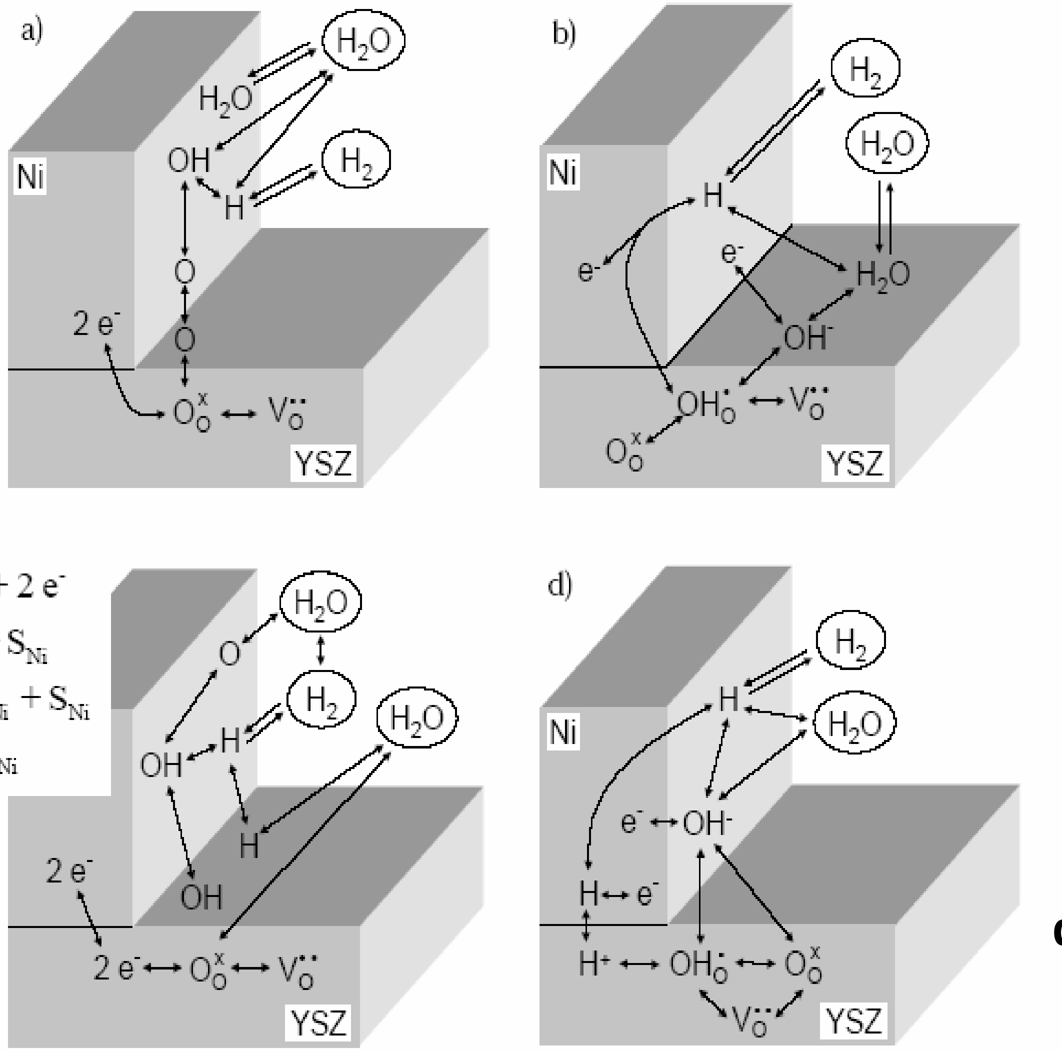
According to Mizusaki's Labs investigations a conception and idea of the electrolyte / fuel electrode interface fuel oxidation reaction

$$O^{2-} + H_2 = H_2O\ (g) + 2e^-$$

is presented



TPB models



a) Mizusaki

b) de Boer

c) Jiang

d) Holtappels

step 1 $H_{2_{gas}} + 2\,S_{Ni} \rightleftarrows 2\,H_{Ni}$

step 2 $O_O^x + S_{Ni} \rightleftarrows O_{Ni} + V_O^{\bullet\bullet} + 2\,e^-$

step 3 $H_{Ni} + O_{Ni} \rightleftarrows OH_{Ni} + S_{Ni}$

step 4 $H_{Ni} + OH_{Ni} \rightleftarrows H_2O_{Ni} + S_{Ni}$

step 5 $H_2O_{Ni} \rightleftarrows H_2O_{gas} + S_{Ni}$

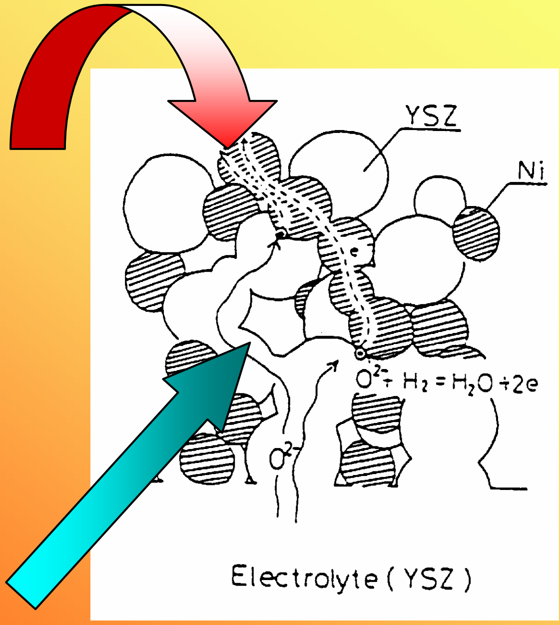
Different EC models predicted for the kinetics of SOFC anodes

Anja Bieberle, The Electrochemistry of SOFC Anodes: Experiments, Modeling, and Simulations, 2000, ETH- Zurich , CH

A N O D E

[6]T.Kawada&H.Yokokawa,*Materials and Characterization of SOFC,* **Key Eng. Materials v. 125 - 126 (1997) p. 187**

Ni:YSZ - cermet anode is used (Ni is 50 ± 10vol.%); possess a high interface thermal,mechanical and corrosion stability.

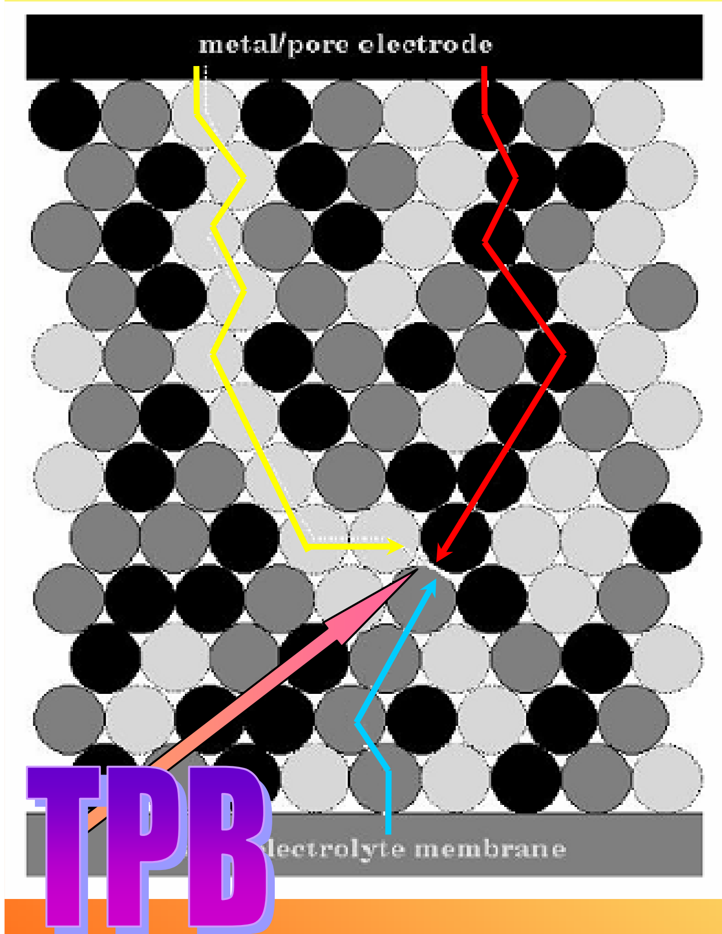


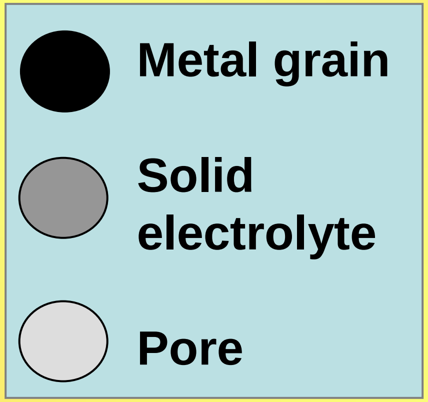
Schematic view of Ni : YSZ - cermet

According to [6] the most important point in the processing of Ni: YSZ electrode is to keep nickel- to- nickel contact. The size ratio of Ni- particles to YSZ is an important factor to make better Ni contacts.

It is also important to keep the ionic path through YSZ to YSZ contact to make a high O^{2-} transport and good performance electrode.

STRUCTURE AND TRANSPORT





Model of three phase boundary in the cermet [5]

SEM image of Ni/YSZ cermet anode [6, 7]

ALTERNATIVE ANODE MATERIALS

Ni-based anodes	CeO_2-based anodes *	$SrTiO_3$-based anodes	La_2O_3-based anodes	Other anodes
Ni-Ti-YSZ Ni-Cr-YSZ	Ni- CeO_2 based cermet	$La_xSr_{1-x}TiO_3$ (x= 0.1÷0.4)	$LaCrO_3$ doped with Mg, Ca or Sr	$(Mg,Ni/Co/Fe/Mn)TiO_4$
Ni-Mn-YSZ		$SrTi_{0.97}Nb_{0.03}O_3$	$(La,Sr)(Cr,Mn)O_3$ (LSCM)	$(Ba/Sr,Sr/La/Ca)_{0.6}(Ti,Nb)O_3$
Ni/perovskites Ni/ $SrTi_{0.93}Mg_{0.07}O_3$	Ru/GDC (50% containing of Ru)	$Sr_{1-1.5x}Ln_xTiO_3$ (Ln= Nd, Eu, Sm)	LSCM-GDC and LSCM-Ni-GDC	$(Nb,Ti, Fe)O_2$
Ni/YSZ, covered with Pt or Au	$Cu/CeO_2/YSZ$	$La_4Sr_8Ti_{12-x}Mn_xO_{38-z}$	LSC doped with Fe, Co, Ni, Cu	Bi_2O_3–Ta_2O_5 mixtures
Ni/ $Sc_{0.18}Zr_{0.82}O_2$	Ni- CeO_2 cermet	$(La,Sr)TiO_3$ doped with transition metals (Ni, Co, Cu, Cr, Fe) and Ce	$LaNi_{1-x}M_xO_3$ (M =Ti, V, Nb, Mo, W)	Ti-doped $NdCrO_3$ Cu/YSZ
Pd-doped Ni/SDC	Ce- doped LST	$Sr_{1-1.5x}Y_xTiO_3$	$La_{0.8}Sr_{0.2}Cr_{0.97}V_{0.03}O_3$ (LSCV)–YSZ	$Ba_{0,5-x}A_xNbO_3$ (A=Ca, Sr)
Ni(MgO)/CeO_2 cermet		$(Sr_{1-x}Ba_x)_{0.6}Ti_{0.2}Nb_{0.8}O_{3-\delta}$	(La,Sr)VO3 H_2S	$Gd_2Ti_{2-x}Mo_xO_7$ (x=0-2) Gd_2TiMoO_7

ALTERNATIVE ANODE MATERIALS

✓ **Ni: [ceria-samaria (CSO)]** cermet; ⟶ Ce^{4+} tends to reduce Ce^{3+}

✓ **Cerium- gadolinium** anodes and correlation with **Ni: YSZ** ones, are object of study in **[48]** (600ºC to 800ºC). It was established that **Ni:CGO** anodes are superior to **Ni:YSZ** anodes especially at **low temperature operation and when CH_4 is used.**

✓ High performance electrode for medium- temperature on **Ytria-Doped Ceria (YDC)** anode + dispersed **Ru** electro catalyst is object of study in **[49]. YDC - $(CeO_2)_{1-x}(Y_2O_3)_x$ (x=0.2 and 0.3)** exhibit about 3 times higher σ_e than that of SDC, while its value of σ_{ion} is moderate.

Intermediate Temperature Solid Oxide Fuel Cell (IT- SOFC) [51]

✓ **Perovskite/ perovskite/ Ni: perovskite** oxide cermet anodes $La_{0.4}Ba_{0.6}CoO_3$ (cathode)/ $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.15}Co_{0.05}O_3$ / **Ni: cermet** (anode) as **(Ni; Ni/ $SrTi_{0.93}Mg_{0.07}O_3$; Ni/ $Sc_{0.18}Zr_{0.82}O_2$; Ni/$La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.15}Co_{0.05}O_3$ and etc.)** are useful for methane processing.

MATERIALS FOR INTERCONNECTS

Two classes of interconnect materials are currently applied:

CERAMIC

✳ Suitable for high temperature operation (900-1000ºC)
✳ Problem with the electronic conductivity as strong function of temperature.

METALLIC

✳ Suitable for 650 -800ºC operation temperature
✳ Problem with oxidation stability at higher temperature.

REQUIREMENTS

The main requirements for Interconnect MATERIALS include as following :

✳ Excellent electrical conductivity with ~100% electronic conduction.

✳ High Stability (Chemical, Phase, Microstructure and Dimensions**) at high temperatures operating process in both oxidation and reduction atmospheres.**

✳ Excellent impermeability for oxygen and hydrogen.

✳To possess thermal expansion coefficient (TEC**) match well to those of the another stack components (**Anode, Cathode, Electrolyte **).**

✳ Fairly good thermal conductivity.

✳Mechanical compatibility and adequate strength and creep resistance at operating conditions .

✳ Easy to fabricate at a low cost

CERAMIC INTERCONNECTS

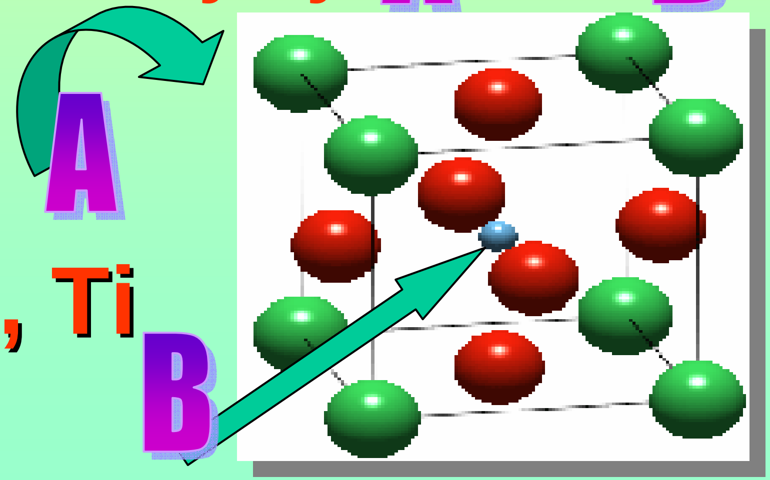
Last decades ceramic materials as lanthanum chromite (perovskite) $LaCrO_3$ are applied. These materials demonstrate reasonably high electronic conductivity, moderate stability and fairly good compatibility with the other cell components.

In order to improve the electrical conductivity as well as modify the thermal expansion coefficient lanthanum chromite usually is doped on A , B or both position.

$LaCrO_3$ ⇨ substitution usually by A and B

A = Sr, Ca

B = Mg, Fe, Ni, Co, Cu, Ti



D INTERCONNECT (ALTERNATIVE)

[57]M. Mori, *Air-sintering characteristics of Ti-doped lanthanum strontium chromites*, **Symp. SOFC-VII Eds. H. Yokokawa, S. Singhal, Proceed. v,. 2001-16, Electroch. Soc., Inc. Pennington, (2001) p. 855**

Usually materials from the La_2O_3- Cr_2O_3 system are used :

✓ **There are limiting data checked on other alternative bipolar plates on ceramic base. The effect of B- site dopants in the :**

$La_{0.8}Sr_{0.2}Cr_{0.9}Ti_{0.1-y}Co_yO_3$ ($0.15 \leq x \leq 0.20$ and $0 \leq y \leq 0.02$)

$La_{0.8}Sr_{0.2}Cr_{1-x}Ti_{0.1}M_xO_3$ (M = V and Ni ; $0 \leq x \leq 0.05$) is studied on samples prepared from powders made by the Pechini method.

The authors proposed composition $La_{0.8}Sr_{0.2}Cr_{0.88}Ti_{0.1}V_{0.02}O_3$ as a promising candidate material for SOFC separators.

✓ **Separators can be applied using metal alloys. The metals and alloys possess a big problem regarding corrosion stability and protection (via thin oxide films) at high temperature treatment.**

METALLIC INTERCONNECTS

The materials most frequently used for SOFC interconnects are based on binary alloys from Fe – Cr system. For improvement of oxidation resistance and thermo-mechanical properties of Fe-Cr- based alloys additives like Y, Ce, La, Mn and Zr are used.

ThyssenKrupp VDM

CROFER 22 APU

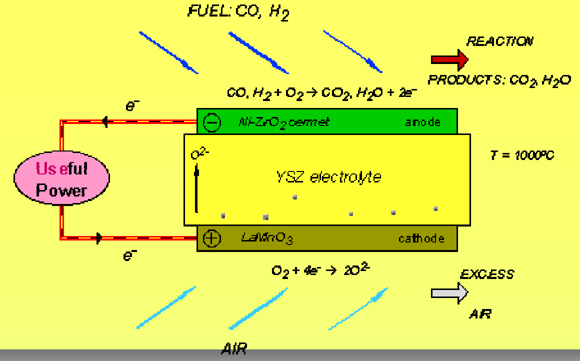
CROFER 22 APU Material Specification :

Analysis: **Fe / Cr 22 / Mn 0.8 / Ti 0.2 / La 0.2**
Density: 7,67 g/cm3
Resistivity: 0,54 Ohm* mm2/m
Tensile Strength: 450 –550 MPa
Elongation: 30 –40 %

Table 1. Composition of the interconnect steel samples (wt%)

	Fe	Cr	Mn	Ni	Al	Si
1.4016	82.5	16.1	0.23	0.25	<0.01	0.26
1.4742	80.0	17.0	0.38	0.19	1.13	1.09
1.4509	77.1	20.9	0.42	0.26	<0.01	0.54
1.4749	70.8	25.4	0.64	0.22	<0.01	0.55
ZMG232	74.3	22.0	0.51	0.30	0.24	0.34
JS-3	77.6	22.6	0.39	0.16	0.11	0.10

COMPARISON



ELECTRICAL CONDUCTIVITY

DOPED $LaCrO_3$ INTERCONNECTS

- **p- type** electronic conductor with hole charge carriers
- **CONDUCTION MECHANISM:**

Small polaron hopping

$\sigma = (A/T)\exp(-Ea/kT)$ (< 1100ºC)

- **OHMIC LOSSES** cannot be neglected: They are much larger than those of electrode materials, but not smaller than that of electrolyte materials .
- **SUITABLE** only for hight temperature SOFCs (HT-SOFCs)

METALLIC INERCONNECTS

- **n- type** electronic conductor with electron charge carriers
- **CONDUCTION MECHANISM:**

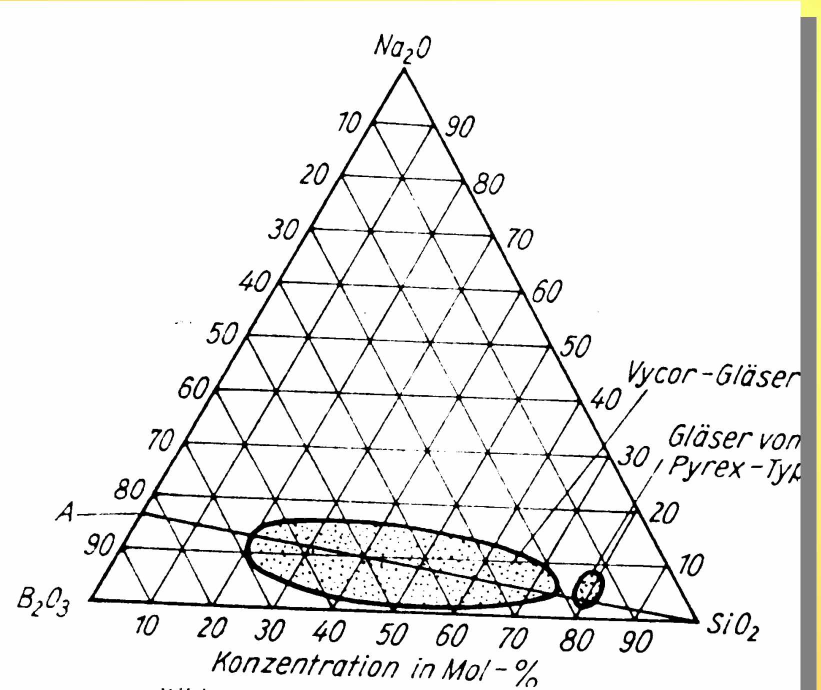
Electron hopping

$\sigma = A\exp(-Ea/kT)$ (< 1100ºC)

- **OHMIC LOSSES** are the least among SOFC components and can be neglected.
- **SUITABLE** for both Intermediate and High temperature SOFCs. (IT&HT-SOFC)

SEALING MATERIALS

[59] B. Altken et al. ,
EP 0603 620 A1,
Corning Inc., H01M 8/24 (1993)



GFR in the SiO_2-B_2O_3-Na_2O system

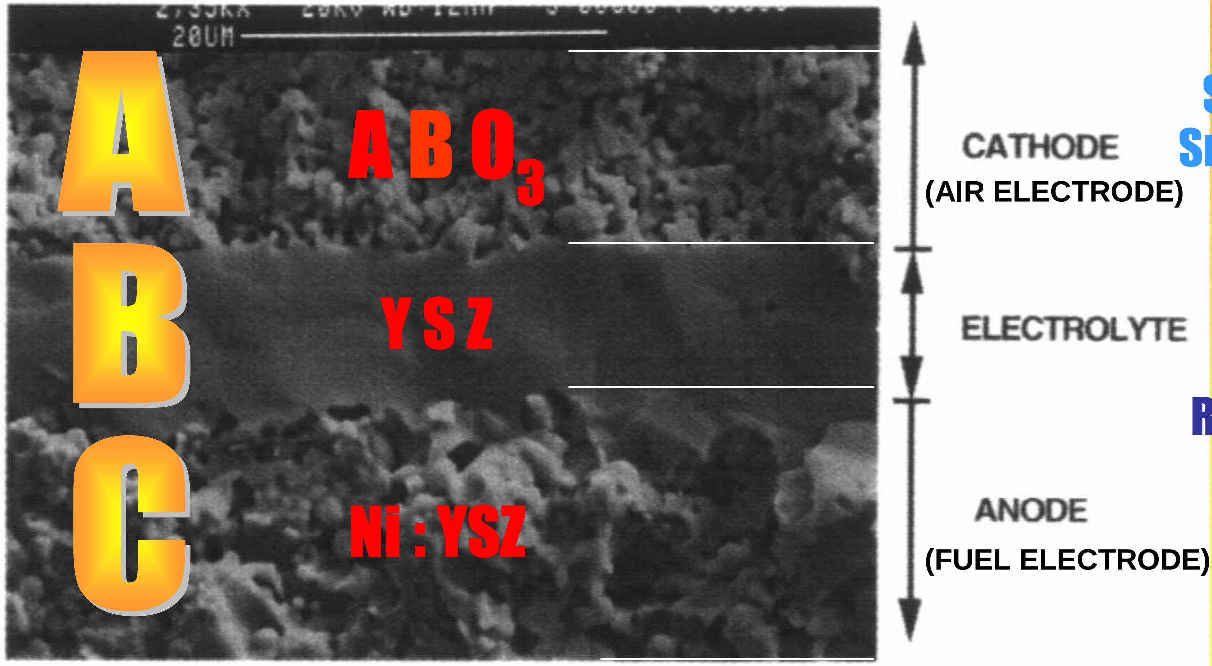
✓- **Borosilicate glasses : "Pyrex, Simax, Duran 8330 and etc." are suitable to be used as a base. It is necessary to modify by rare- earth and Sr, Ba, Mg – oxides incorporation into the vitreous structure. May be the best materials are glass-ceramics compositions.**

✓- **There is a patent [59] relates to rare- earth silicate glasses with appropriate coefficient of thermal expansion and good adhesion effect.**

✓-**The System SiO_2-Ba-Ca-/MeO**

CONCLUSIONS

ALTERNATIVE



A B C D E

$LaFeO_3$, $LaCoO_3$, $LaNiO_3$,

$SrFeCo_{0.5}O_{0.35}$, $Gd_{1-x}Sr_xCoO_3$

$SmCoO_3$,$La_{0.8}Sr_{0.2}Co_{0.8}Fe_{0.2}O_3$,

SSC – 30%SDC composite

$Sm_{0.5}Sr_{0.5}CoO_3$ (SSC)

$La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\delta}$

$RE_{9.33}(SiO_4)_6O_{26}$, $Bi_2Ru_2O_{7.5}$

$Ce_{1-x}Gd_xO_{2-\delta}$

$SrTi_{1-y}Nb_yO_3$,$La_xSr_{1-x}NbO_3$

Ytria- Doped Ceria [YDC]

Ni: perovskites

INTERCONNECT (SEPARATOR) OR BIPOLAR PLATE

La_2O_3- Cr_2O_3 + [alloys] $La_{0.8}Sr_{0.2}Cr_{1-x}Ti_{0.1}M_xO_3$

SEALING MATERIALS FOR STACK COMPONENTS

“ 3.3” borosilicate glass MICA, GLASSCERAMICS

HIGH TEMPERATURE CONDUCTING CERAMICS.

CONCLUSIONS

The following general conclusions may be drawn:

❋ It appears that the materials synthesis for SOFCs application is now maturing (2nd,3rd G) and the leading companies are focusing on stack and systems application to the market .

❋Study of phase equilibrium diagrams is actual, synthesis is carried out by methods starting from G, L, S state.

❋ IT-SOFC study materials increase and recent development are on perovskite type and bismuth oxide based cathodes, cerium base electrolytes and redox stable anodes.

❋ As alternative anode materials for SOFC the attention is focused on Ce- based, SrTiO3- based, La2O3-based,bronzes and etc. IT-SOFC study materials increase and recent development are redox stable anodes.

Acknowledgement

THANK YOU FOR YOUR ATTENTION