Anodes for Direct Hydrocarbon Solid Oxide Fuel Cells (SOFC's)

Challenges in – materials selection and deposition

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Barriers to the hydrogen economy

- How to make hydrogen (SR, electrolysis, Solar, Borohydride)?
- Loss of efficiency in making hydrogen
- Storage and Transportation?
- SOFC’s can work with any ‘fuel’
- Let us work in parallel with the Hydrogen advocates by using hydrocarbons directly with SOFC’s
- Do not forget – well to wheels efficiency!

DIRECT OXIDATION OF HYDROCARBONS AND OXYGENATES

Reactions:

Cathode: $(x + y/4 - z/2)\ O_2 + (4x + y - 2z)\ e \longleftrightarrow (2x + y/2 - z)\ O^{2-}$

Anode: $C_xH_yO_z + (2x + y/2 - z)\ O^{2-} \longleftrightarrow (y/2)\ H_2O + x\ CO_2 + (4x + y - 2z)\ e$

Overall: $C_xH_yO_z + (x + y/4 - z/2)\ O_2 \longleftrightarrow (y/2)\ H_2O + x\ CO_2$

Natural Gas, Propane/ Butane (LPG), Naphtha, Diesel, Alcohols, Syngas (from coal and biomass)

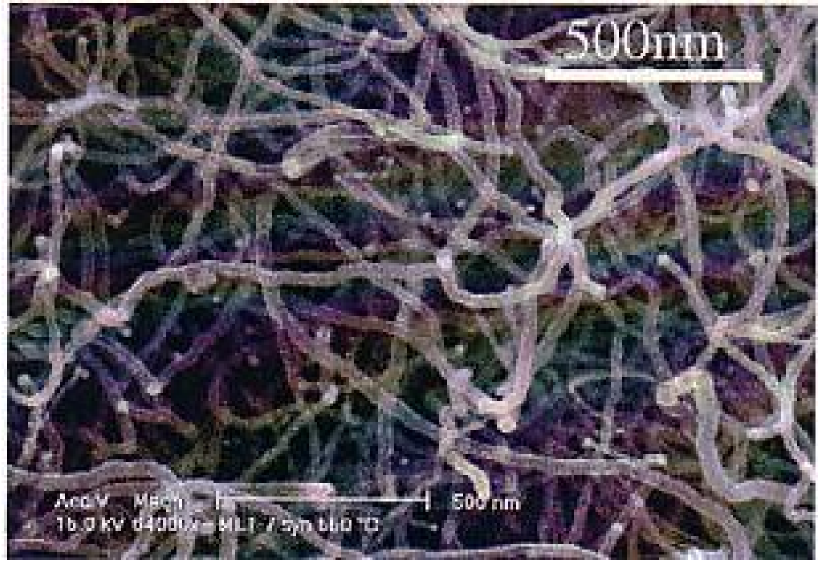
WHAT HAPPENS IN THE ANODE IN SUCH CASES ?

- **Direct oxidation;** $CH_4 + 4O^{2-} \rightarrow CO_2 + 2H_2O + 4e$
- **Internal reforming;** $CH_4 + H_2O \Leftrightarrow CO + 3H_2$
- **Syngas oxidation;** $CO + H_2 + O^{2-} \rightarrow CO_2 + H_2O$
- **Coke deposition (thermal, catalytic);** $CH_4 \Leftrightarrow CH_x + H_2$

WHY DO WE NEED NEW ANODES

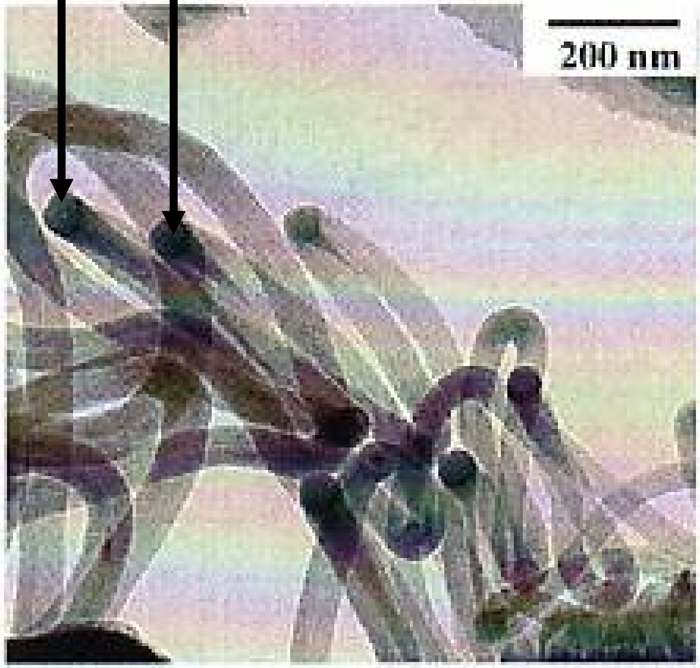
- Incompatibility of Ni-YSZ anodes with any fuel other than H_2 – reforming essential; coking with dry hydrocarbons → *Reference: Toebes et al.*
- Poisoning of Ni-YSZ by sulfur compounds
- Poor Redox tolerance of Ni-based anodes
- YET, must satisfy the basic needs of SOFC anodes –
  - Electronic conductivity
  - Ionic conductivity
  - Good catalytic activity
  - Compatibility of CTE's with that of electrolyte

EFFECT OF COKING ON Ni-YSZ ANODES



20% CO/7% H_2
550°C. Ni particles

Toebes et al. (2002)



In H_2, 800°C, 3 hrs

In CH_4, 800°C, 3 hrs

Coking due to decomposition and/or Bouduard Reaction

ALTERNATIVE ANODES ?

$Cu/CeO_2/YSZ$ *Gorte et al. (2000)*

$Ce_{0.9}Gd_{0.1}O_{1.95}$ combined with

$(La_{0.8}Sr_{0.2})\,(Cr_{0.8}Mn_{0.2})O_{3-\delta}$

Barnett et al. (2002)

Irvine et al. (2001)

Titania-Niobia, Nb_2TiO_{7-x}

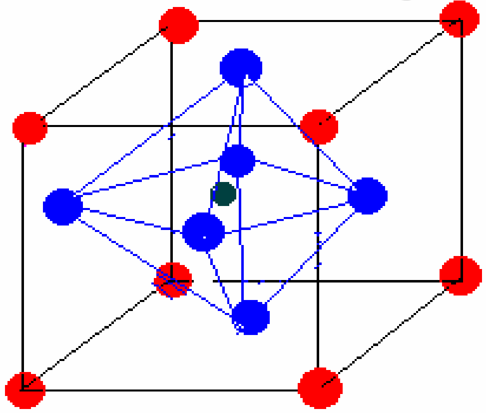
Irvine et. al. (2003) –

$(La_{0.8}Sr_{0.2})\,(Cr_{0.5}Mn_{0.5})O_{3-\delta}$

Perovskites, Irvine et al.
Boukamp, et al.

● Lanthanides/ Alkali earth Metal ions
● Oxygen ions
● Transition metal ions

ABO_3



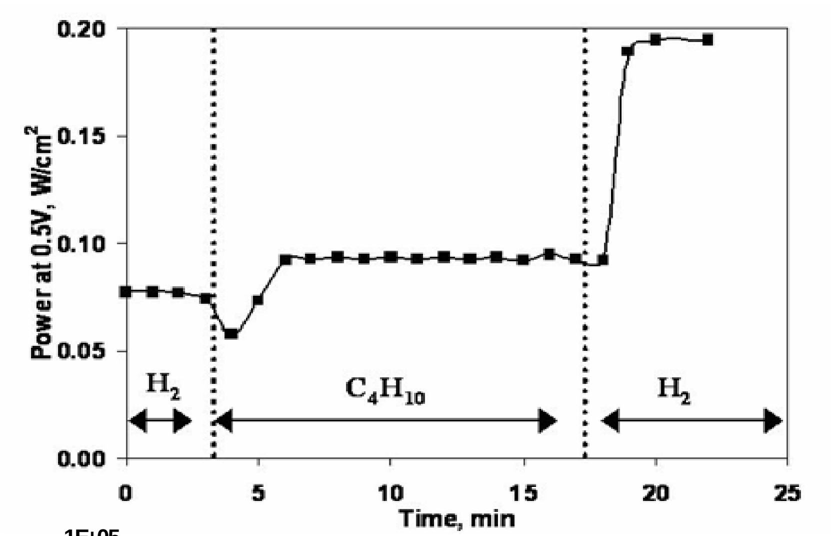
Why perovskites???

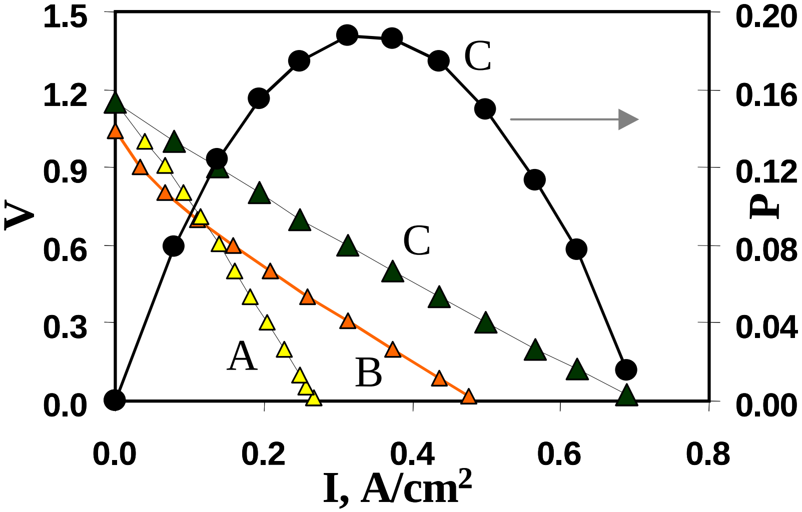
- Ionic and electronic conductivity can be tailored
- Good Hydrocarbon oxidation catalytic activity has been reported.
- No coking
- Good thermal and redox stability
- And yet, concern remains – do we have adequate electronic conductivity under reducing conditions?

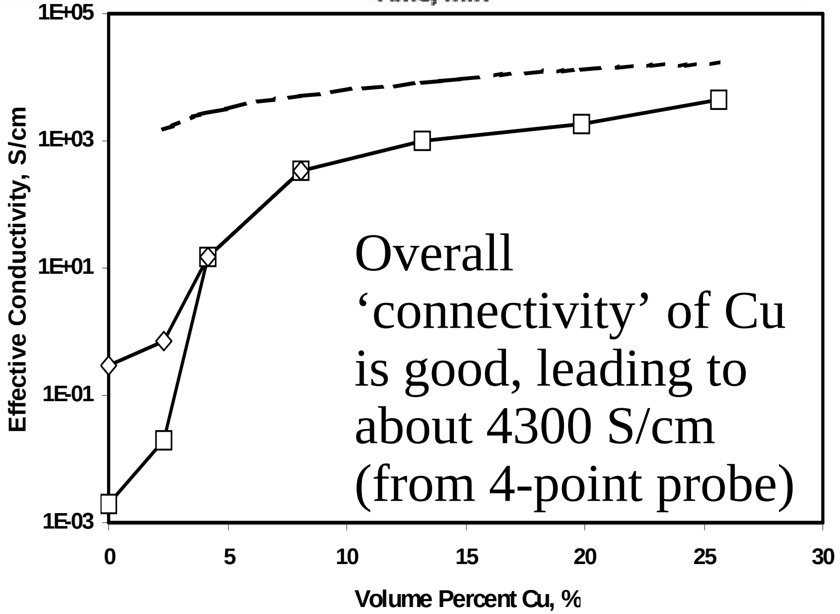
Review of work on alternate anodes - Gorte et al.

- Anodes based on Copper – conductor; Ceria – electrocatalyst
  - Cu and CeO_2 deposited on pre-formed porous anode substrates
  - Intermediate temperature SOFC's
- Considerable data on butane, methane, diesel, propane –
  - Anode stable over long periods of time
  - Direct electrochemical Oxidation observed in button cells
  - Workable with fuel with existing sulfur levels
- Technology transfer to Franklin Fuel Cells, PA, US
  - Demonstration level, with diesel, gasoline and ethanol
- Performance tends to be lowered due to Copper sintering; enhancement necessary by carbon deposition
- Little/ no data on redox tolerance (deposition technique may be advantageous, use of Vol % < 20%)

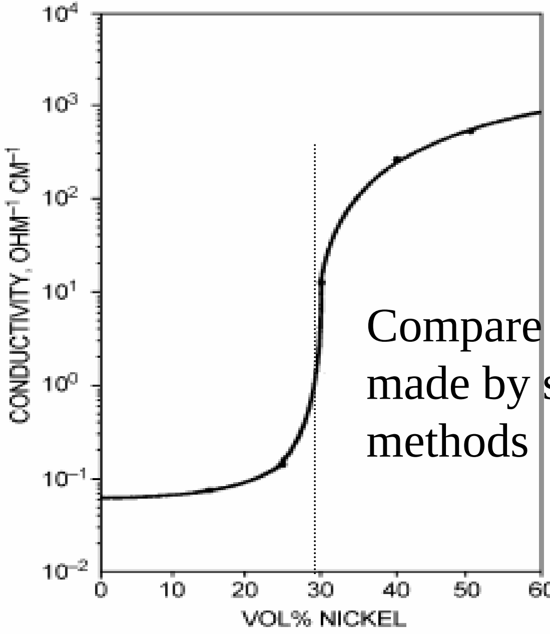
Gorte et al., cont’d





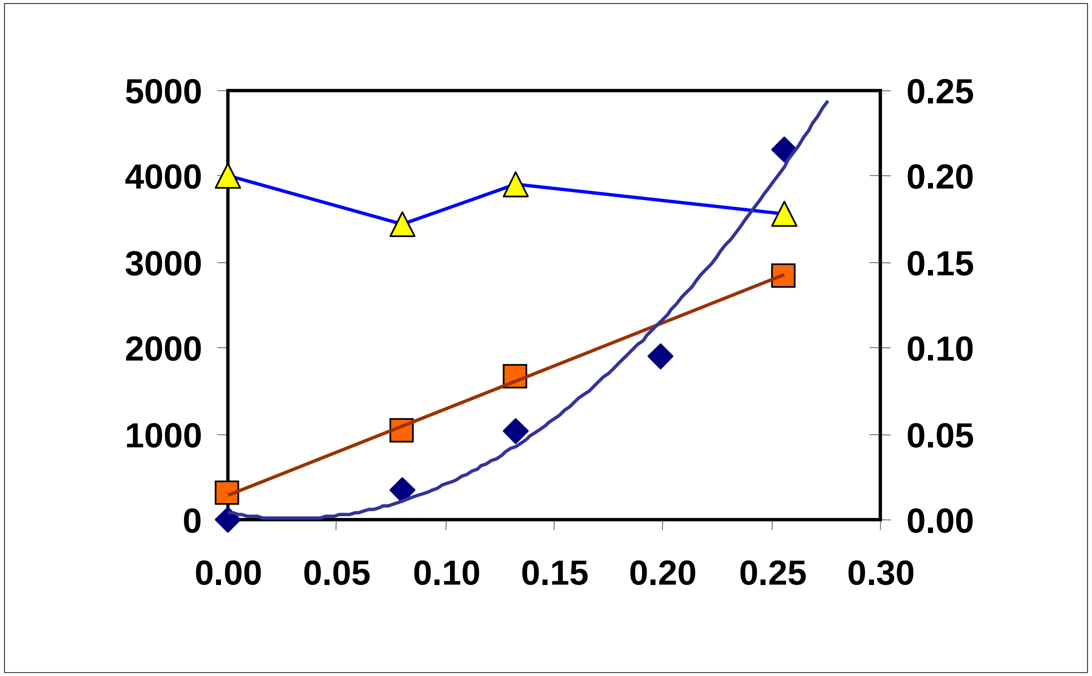


Overall ‘connectivity’ of Cu is good, leading to about 4300 S/cm (from 4-point probe)



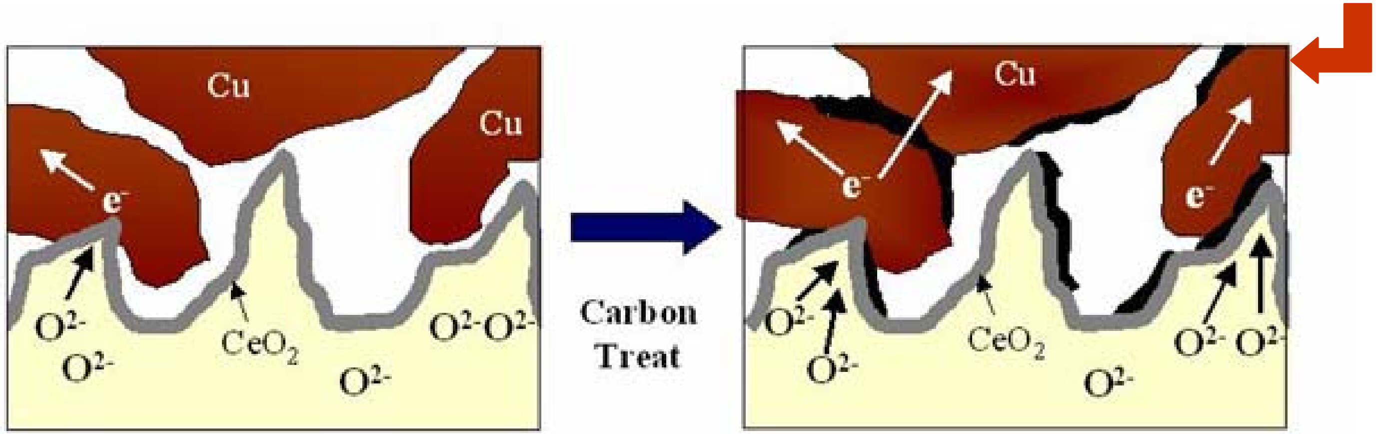
Compare with Ni-YSZ made by solid state methods

Performance, Conductivity with Cu content

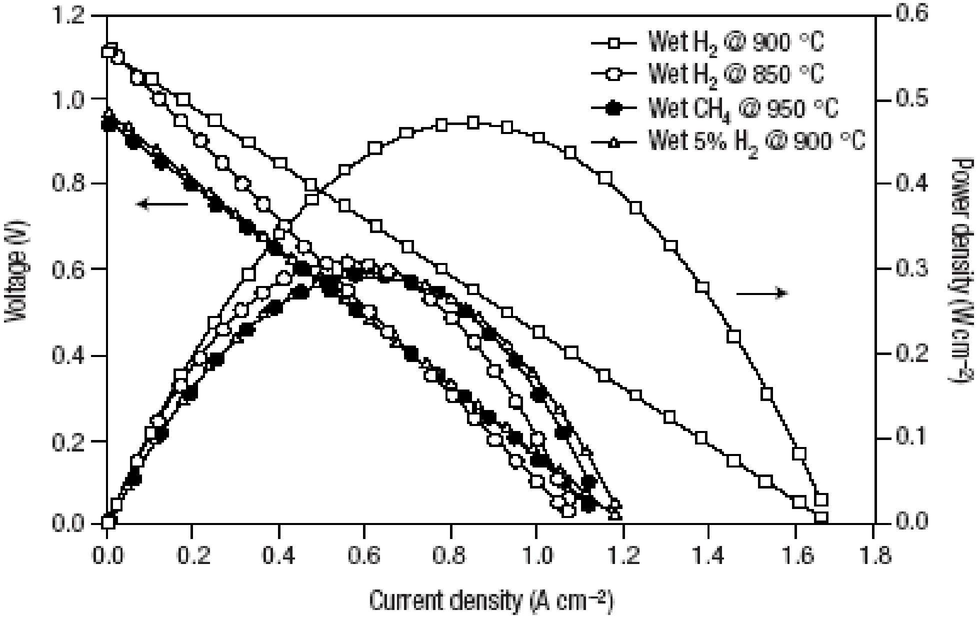


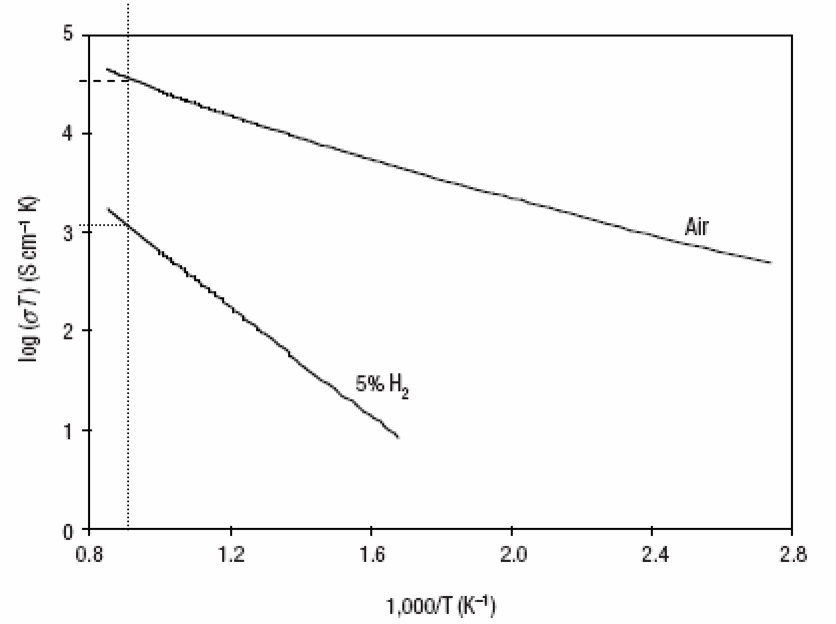
- Carbon enhancement occurs even at 25% Vol Cu; constant, independent of Cu
- But sufficient conductivity is attained with less than 10% volume

Overall conductivity not the problem; the issue is proper ‘connectivity’ at the 3-phase boundary



Irvine et al. (2003) ($La_{0.75}\,Sr_{0.25}\,Cr_{0.5}\,Mn_{0.5}\,O_{3-\delta}$), LSCM





Max. P. D. (W/cm^2) = 0.47, 900^{o}C
Max. P. D. in Methane = 0.3 W/cm^2
(at 950^{o}C)

Conductivity of perovskite at 850^{o}C
- in air, 28 S/cm
- in reducing atmosphere, 1.12 S/cm

Irvine et al., Niobia-Titania rutile system (2001)

- Max. conductivity under reduction, 300 S/cm
- Good catalytic activity towards methane Oxidation

$$Nb_2TiO_7 \xrightarrow[\text{Reduction}]{} Nb_{0.67}Ti_{0.33}O_2$$

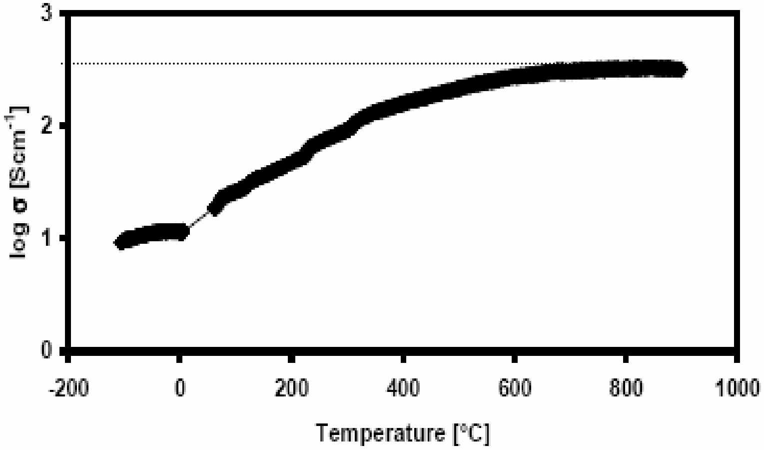


Fig. 3 Conductivity in the system "Nb_2TiO_{7-x}" as a function of temperature (in H_2 atmosphere, 75% theoretical density of the polycrystalline pellet).

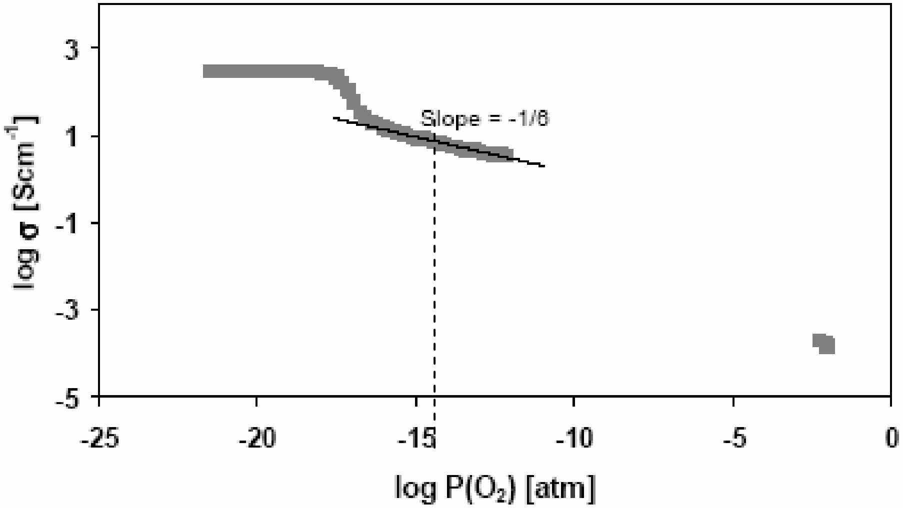


Fig. 4 Conductivity in the system "Nb_2TiO_{7-x}" as a function of oxygen partial pressure pO_2 (at 930 °C, 75% theoretical density of the pellet), measured on reoxidation.

Barnett et al. (2002) – LSCM-GDC composite

Small qty of Ni +

$Ce_{0.9}Gd_{0.1}O_{1.95}$ – ionic conduction

$(La_{0.8}Sr_{0.2})(Cr_{0.8}Mn_{0.2})O_{3-\delta}$ – electronic conduction

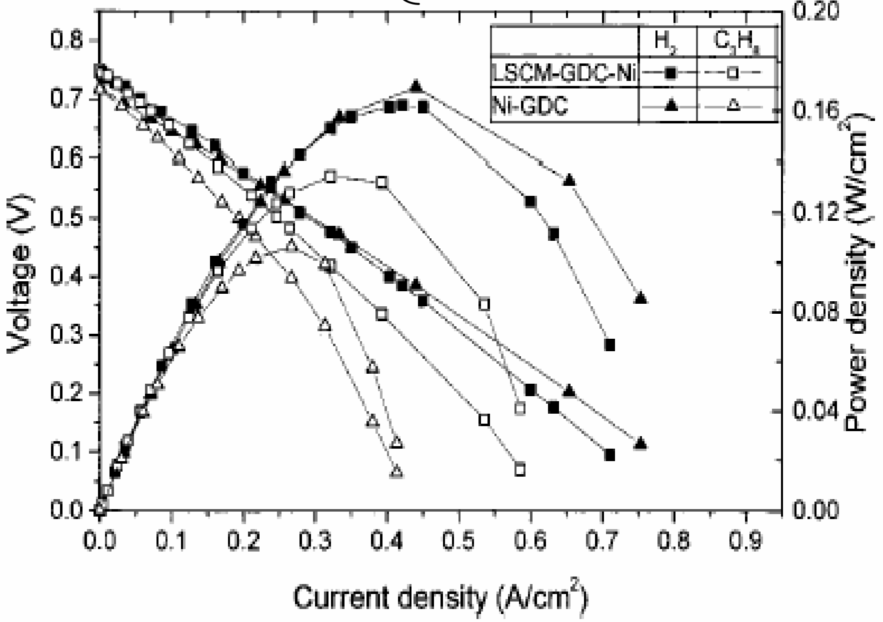


Figure 1. Voltage and power density *vs.* current density for SOFCs with LSCM-GDC-Ni and Ni-GDC anodes, operated at 750°C with air as the oxidant and either H_2 or C_3H_8 fuel.

- Usage of LSCM – high electronic conductivity in reducing conditions, as well
- Compatible with GDC electrolytes

Compared to Ni-GDC, performance in C_3H_8 is significantly higher

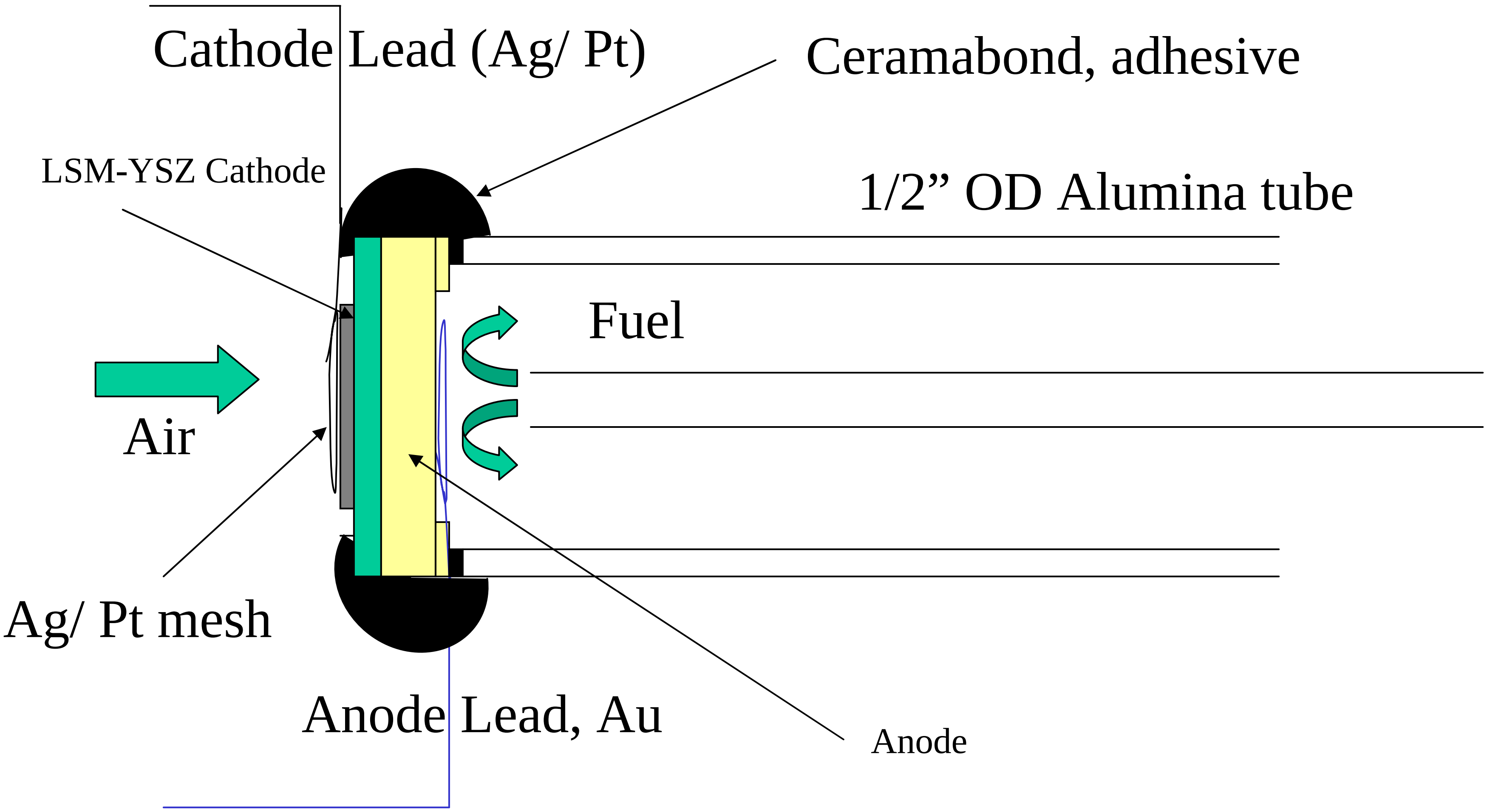
Focus of research at Chemical Eng. Dept., IIT-D

- Nature of work essentially fundamental - ‘button cells’
- Aim is to contribute to existing knowledge ‘pool’, via publications and patents by addressing problems involving Electrochemistry, Materials and Catalysis
- We look forward to collaborate with ‘developmental laboratories’, e.g., test our ideas on a larger scale – CGCRI, BHEL R&D

What we are involved in -

- SOFC component fabrication – tape casting, sintering, painting, impregnation
- Characterization of components – bi-layers, catalysts – SEM, SA/PSD, Porosity, XRD, Thermal Analysis
- Testing of Electrical Conductivity
- Fuel Cell Testing

FUEL CELL REACTOR AND OPERATION



Cathode Lead (Ag/ Pt)

Ceramabond, adhesive

LSM-YSZ Cathode

1/2” OD Alumina tube

Fuel

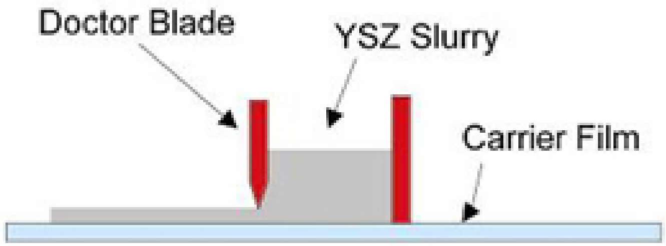
Air

Ag/ Pt mesh

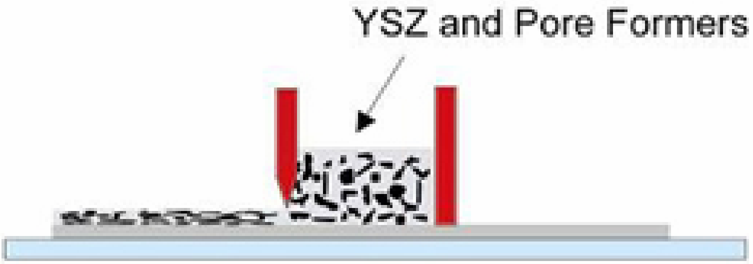
Anode Lead, Au

Anode

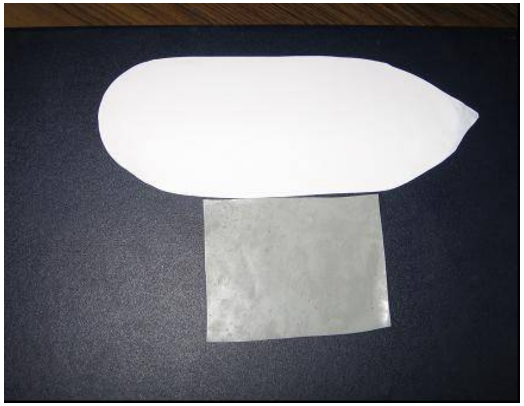
Tape Casting (non-Aq)



Tape casting



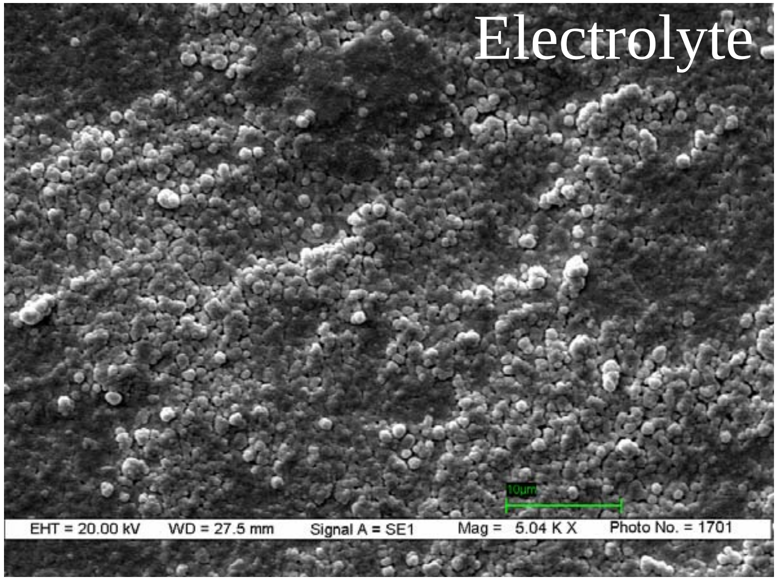
Multilayer Tape casting



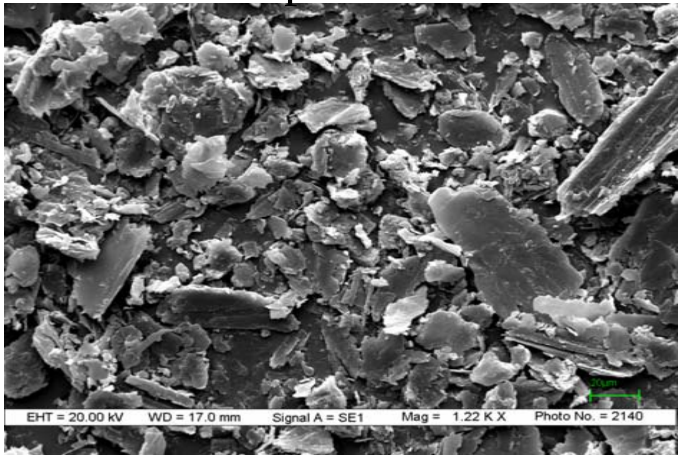
Component function	Component	Quantity
Powder	YSZ	15g
Solvent	MEK	20mL
	EtOH	10mL
Dispersant	Oleic Acid	0.5mL
Binder	PVB	2.0g
Plasticizer	PEG	1.2mL

Characterization of tape

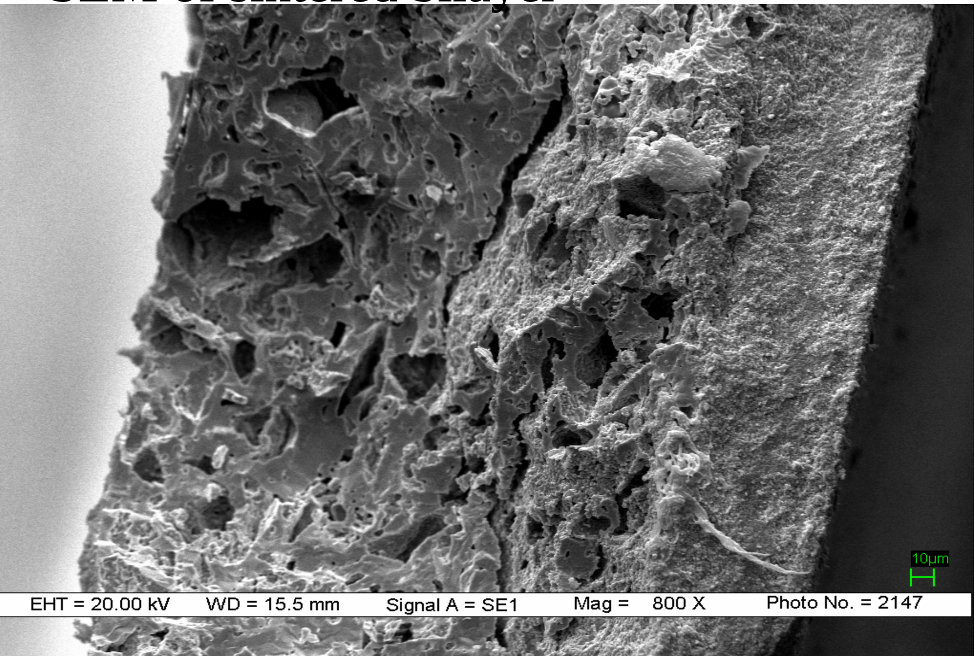
Electrolyte

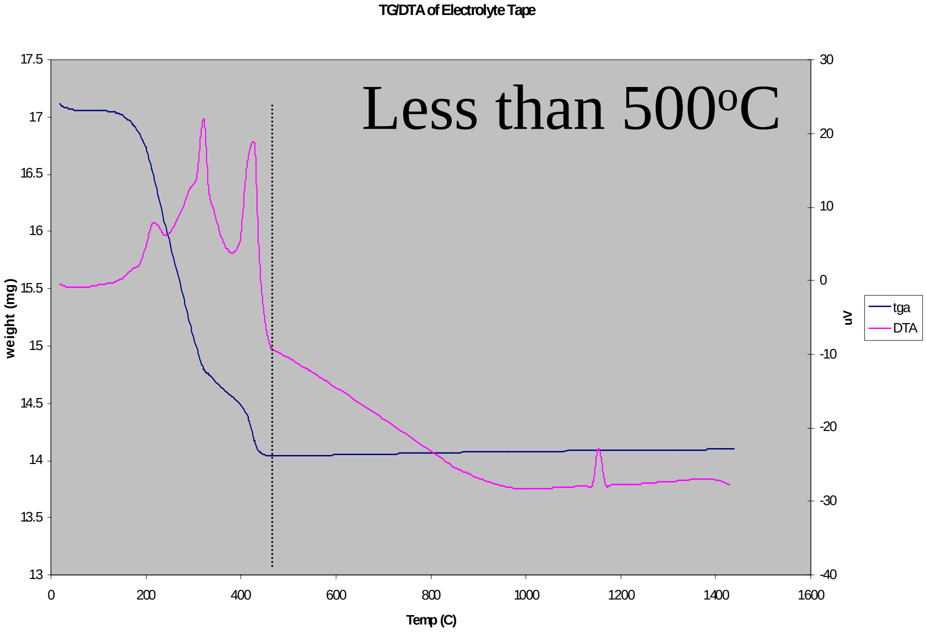


SEM of Graphite – as received



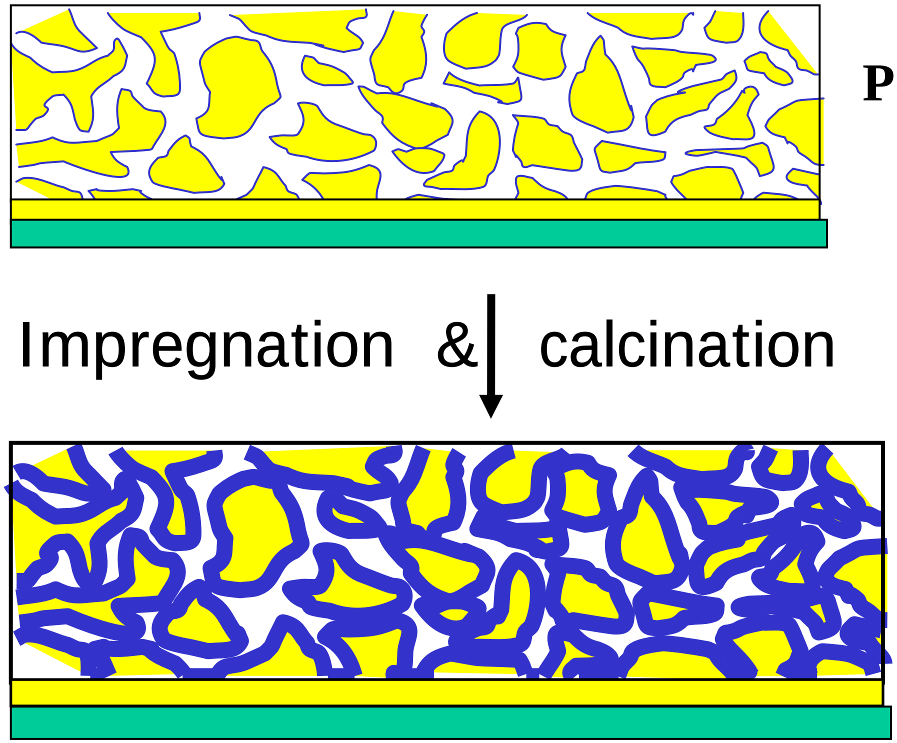
SEM of sintered bilayer





Less than 500^{o}C

Anode Preparation by Perovskite Deposition



Porous anode matrix

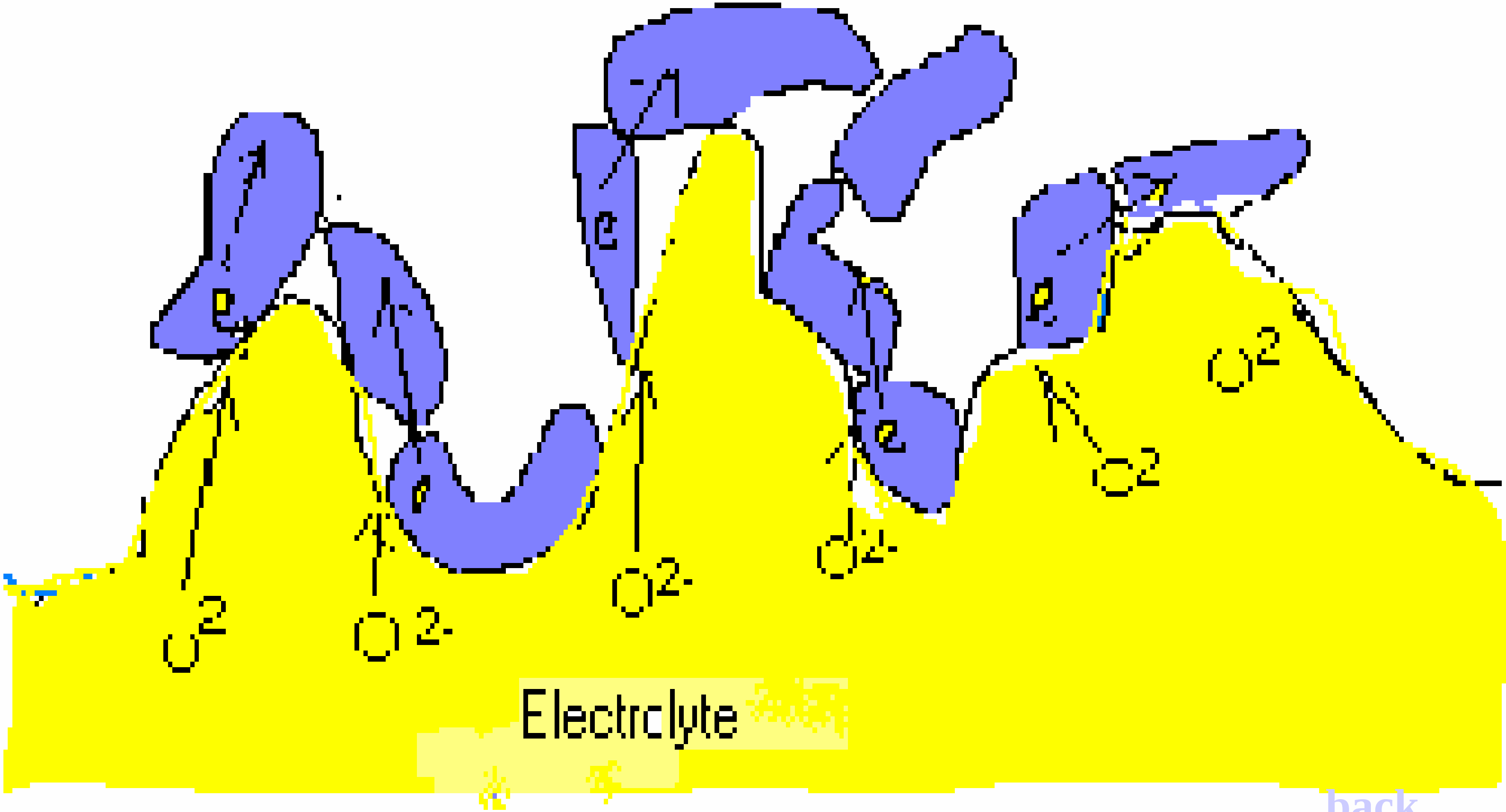
Impregnation & calcination

Final Anode Structure

This method is totally different from the mixing and solid-state synthesis techniques listed in most literature.

Moving away from the 3-phase boundary limitation to a 2-phase boundary situation

Three Phase Boundary



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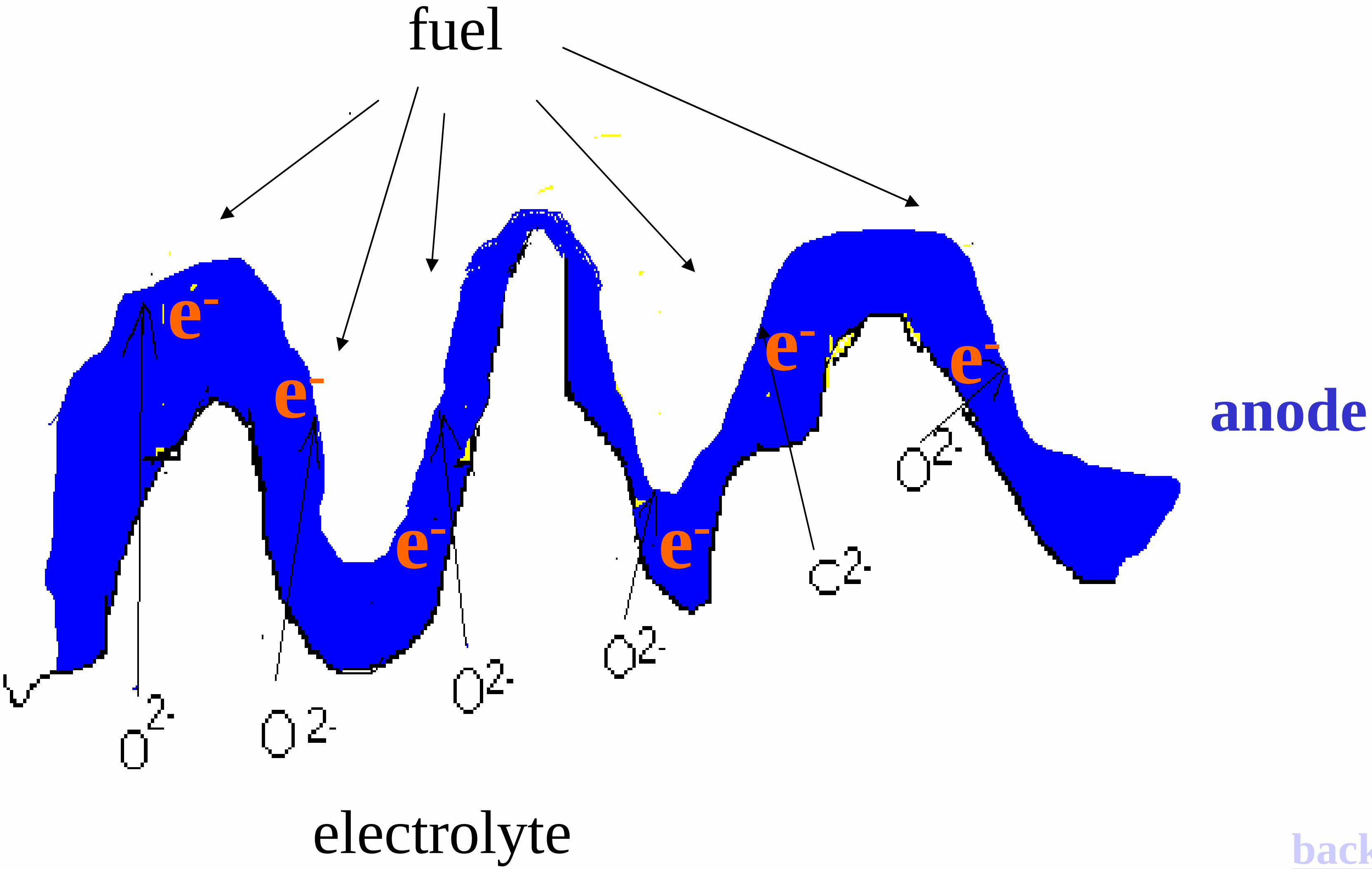
Two Phase Boundary- a new approach



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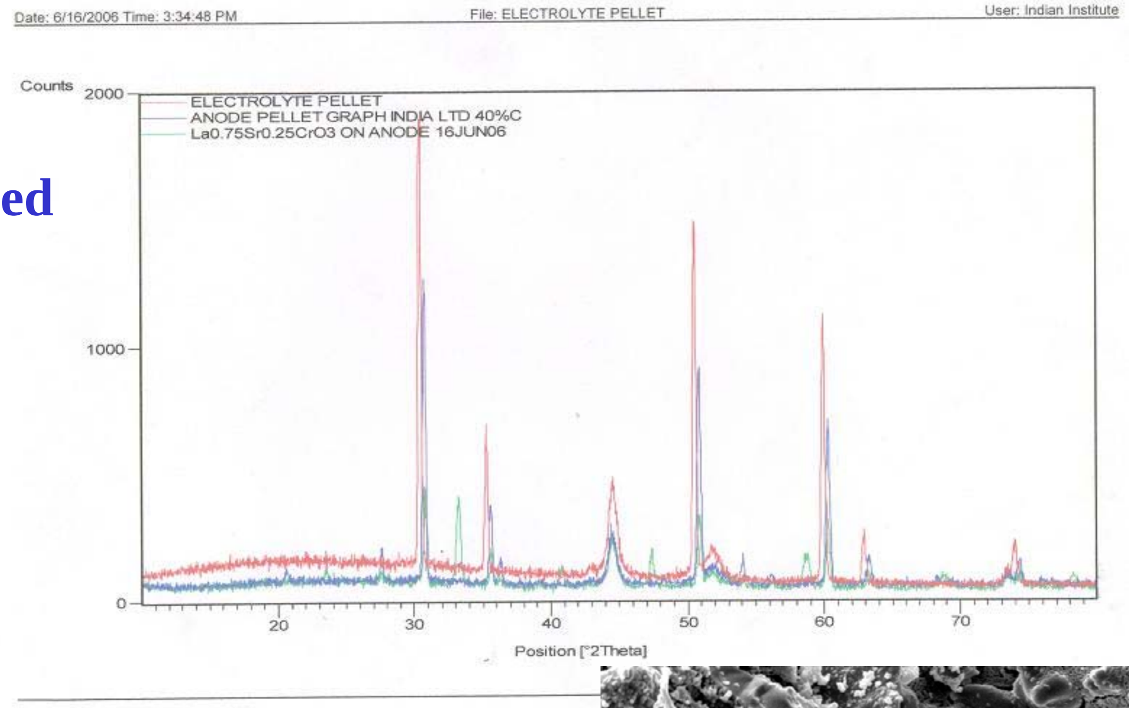
Impregnated La CrOx on preformed anodes

Perovskites deposited

$LaCrO_3$

$La_{0.75}Sr_{0.25}CrO_3$

$La_{0.9}Sr_{0.1}CrO_3$



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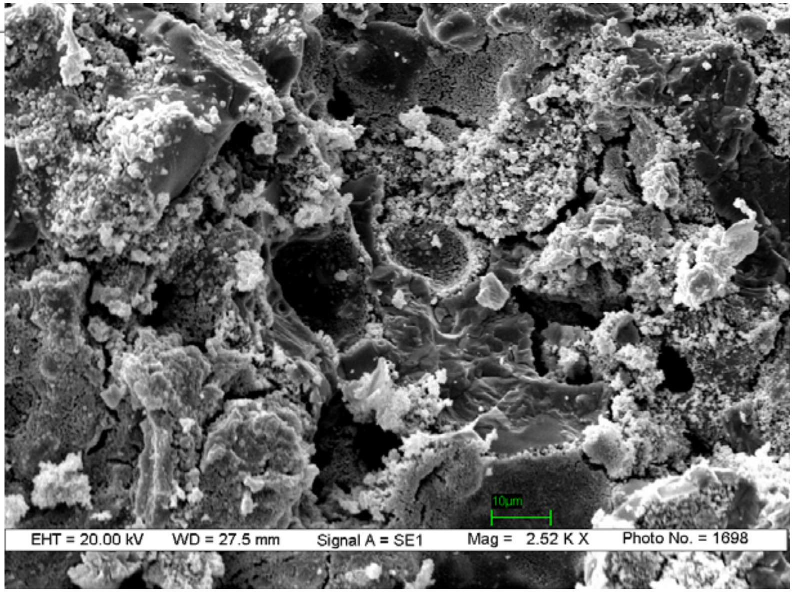
SEM and XRD both confirm that the required phase is formed inside the pores. But conductivity is very low i.e., 10^{-2} S/cm.



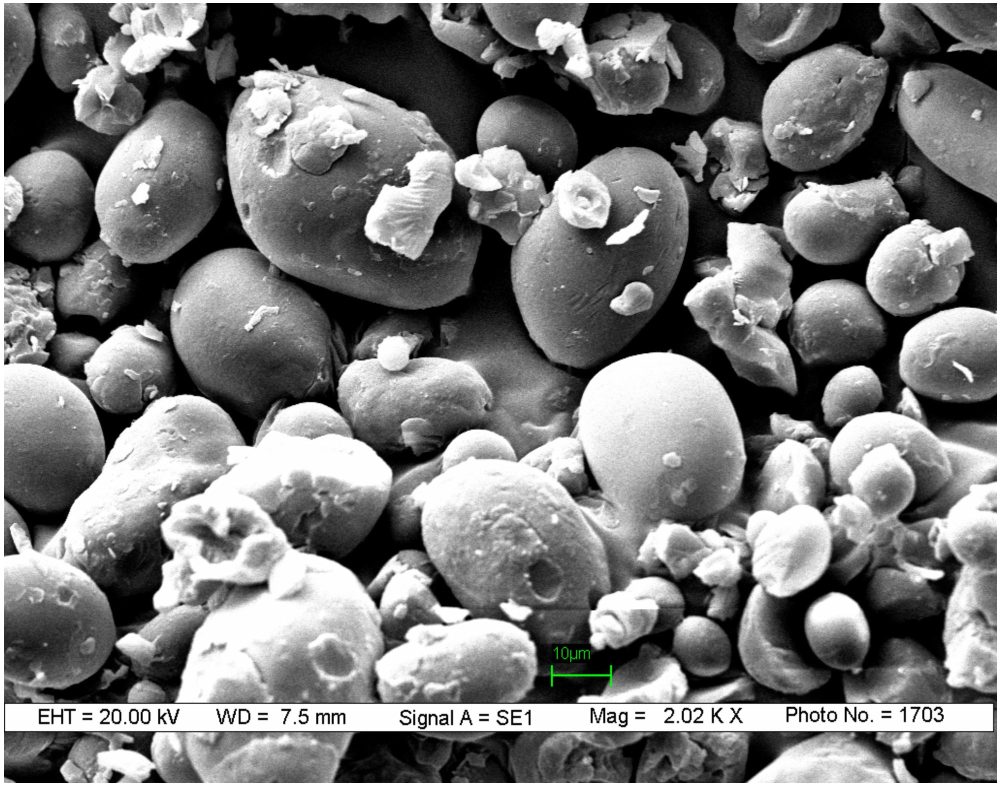
Morphology of bi-layers

- Investigation of pore sizes – choice of pore-formers, like Graphite, Starch, PMMA to name a few
- Porosity
- Pore size distribution

Which are dependent on –

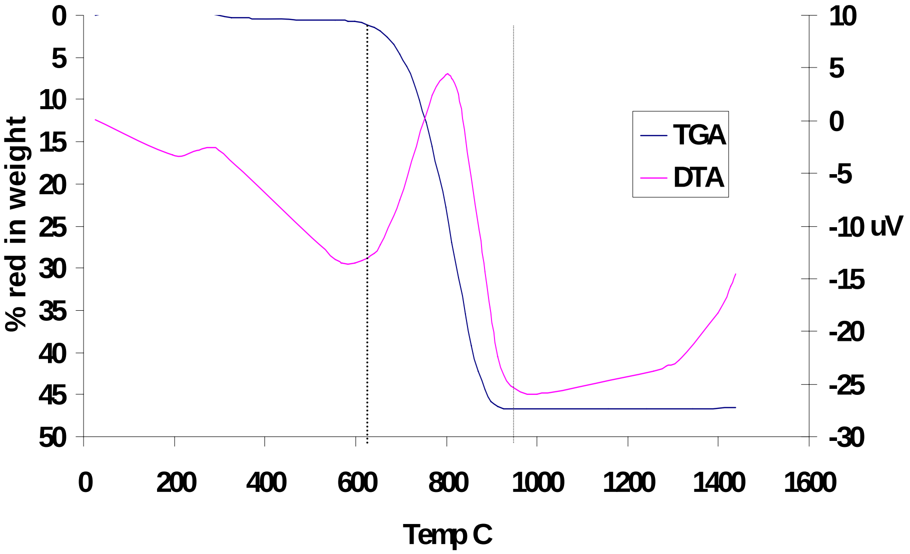
- Particle sizes
- Particle size distribution
- Particle 'shapes'

Starch



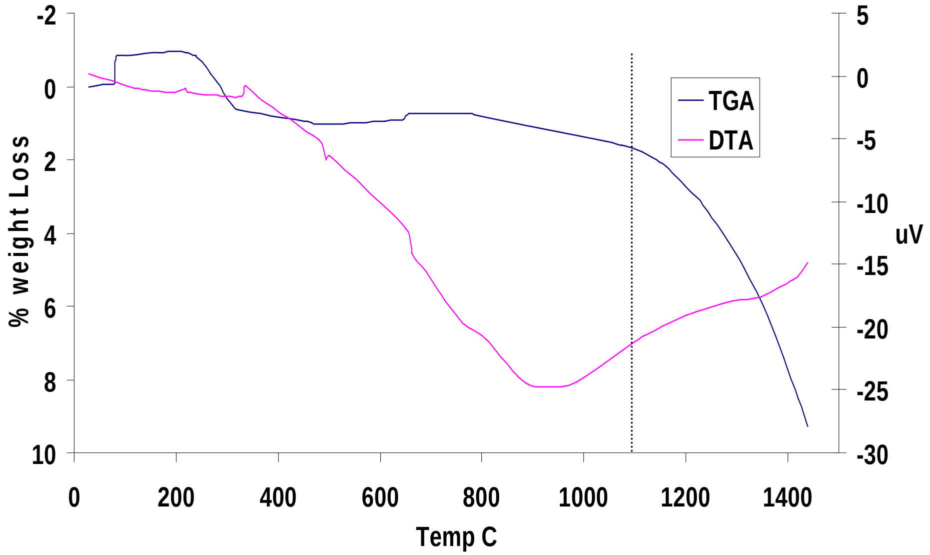
Tailoring the porosity of anode

TGA/DTA of Anode, in air;
Pore former is 50% Graphite (Alfa Aesar)



Removal of pore formers by 950^{o}C, completely

TGA-DTA of anode pellet with 30% graphite in N_2 atm



Removal of pore formers only begins at 1100^{o}C

Sintering temperature is usually 1450^{o}C up to 1550^{o}C
Pore structure may have a strong dependence on temperature of removal of pore former

Work in Progress

- Preparation and testing of – chromites, titanates, niobates and vanadates
- Impregnation of perovskites onto pre-formed anode substructure
- Conductivity data on oxides as electrocatalysts under reducing conditions – redox stability of oxides, as well
- Systematic investigation of pore and particle morphology
- Testing of anode supported cells on various fuels