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Electrodes for Solid Oxide Electrolysis (SOE) and Natural-Gas Assisted Steam Electrolysis (NGASE)

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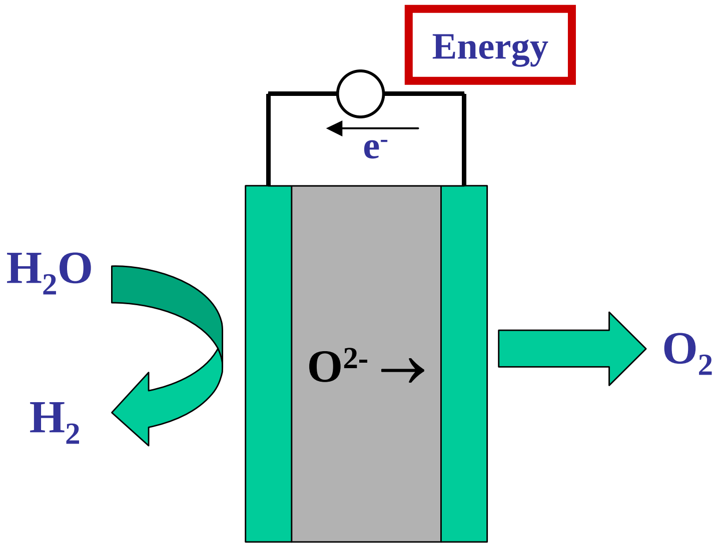
SOE

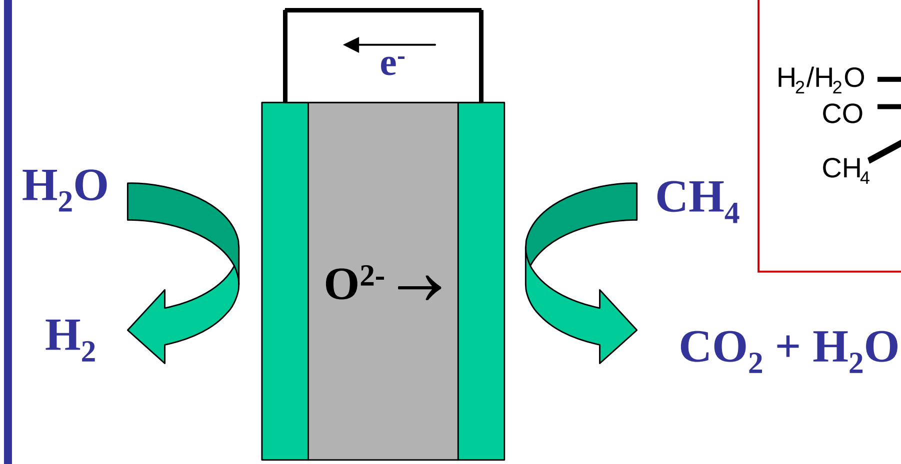


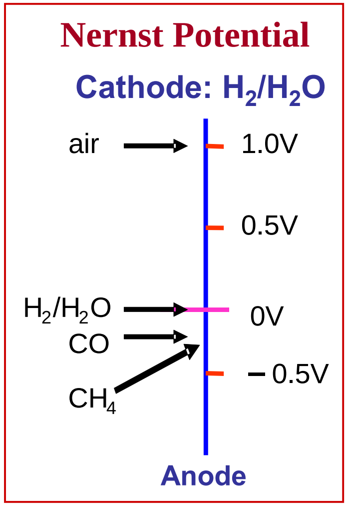
Electrolysis requires $V > V_{Nernst}$

SOE are more efficient

- low cathode losses
- lower Nernst Potential ($T\Delta S$)

NGASE





No external power required.

Produces pure H_2.

High efficiency possible.

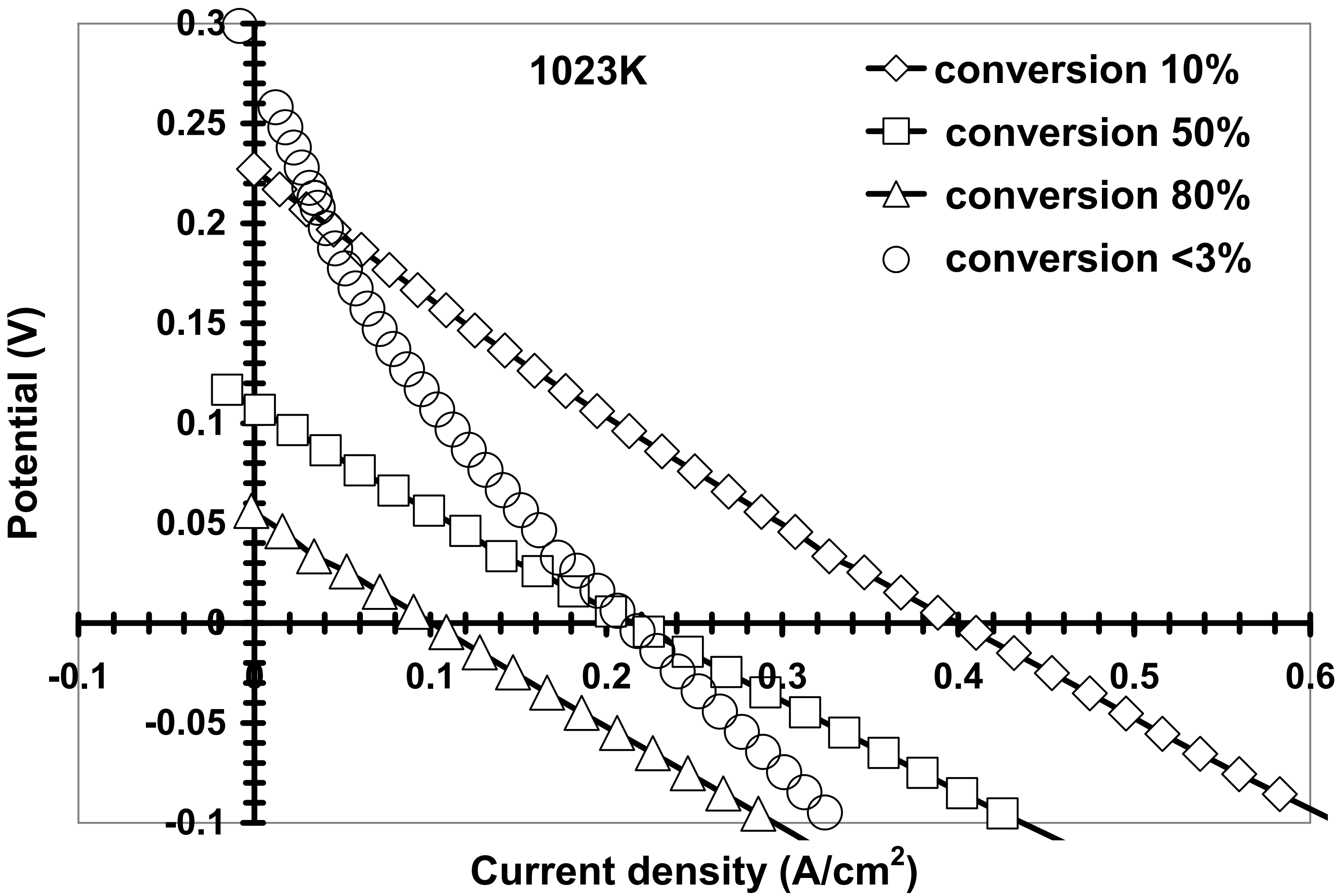
Membrane can be mixed conducting

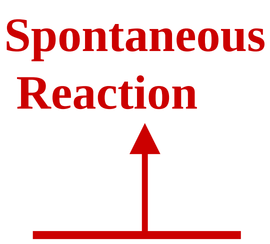
CTP Hydrogen Corp:

www.ctphydrogen.com

NGASE Works!

60% H_2O, 4% H_2, Co/ceria | YSZ(50 μm) | Pd/ceria, CH_4



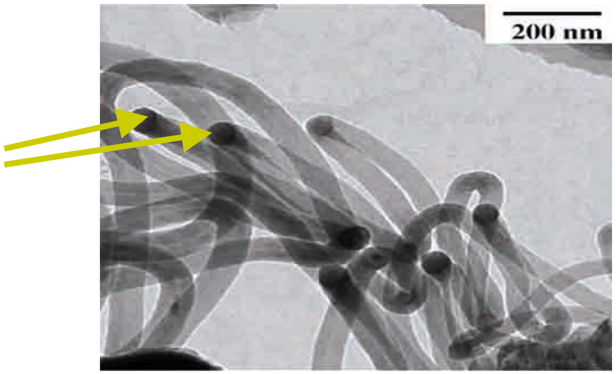


Research Issues:

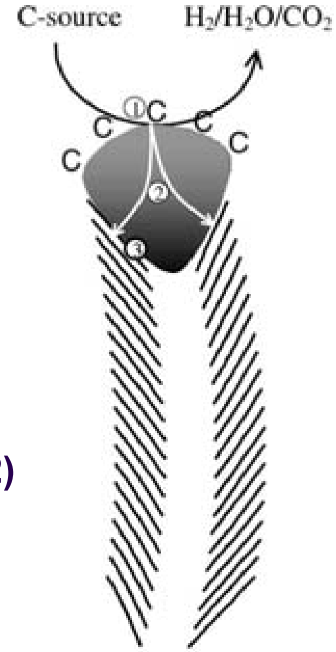
1) We need electrodes capable of utilizing methane.

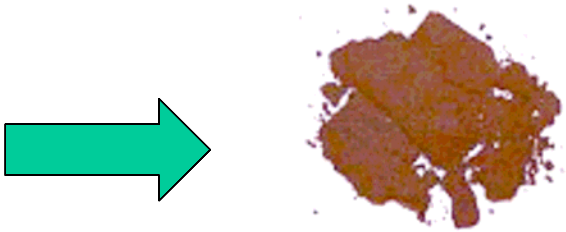
Ni electrodes ubiquitous but form carbon fibers; we need alternatives.

Ni



(M. L. Toebes, et al., Catalysis Today, 2002)





Ni in methane
for 3 hrs, 800°C

2) We need to understand the effect of polarity on electrodes.

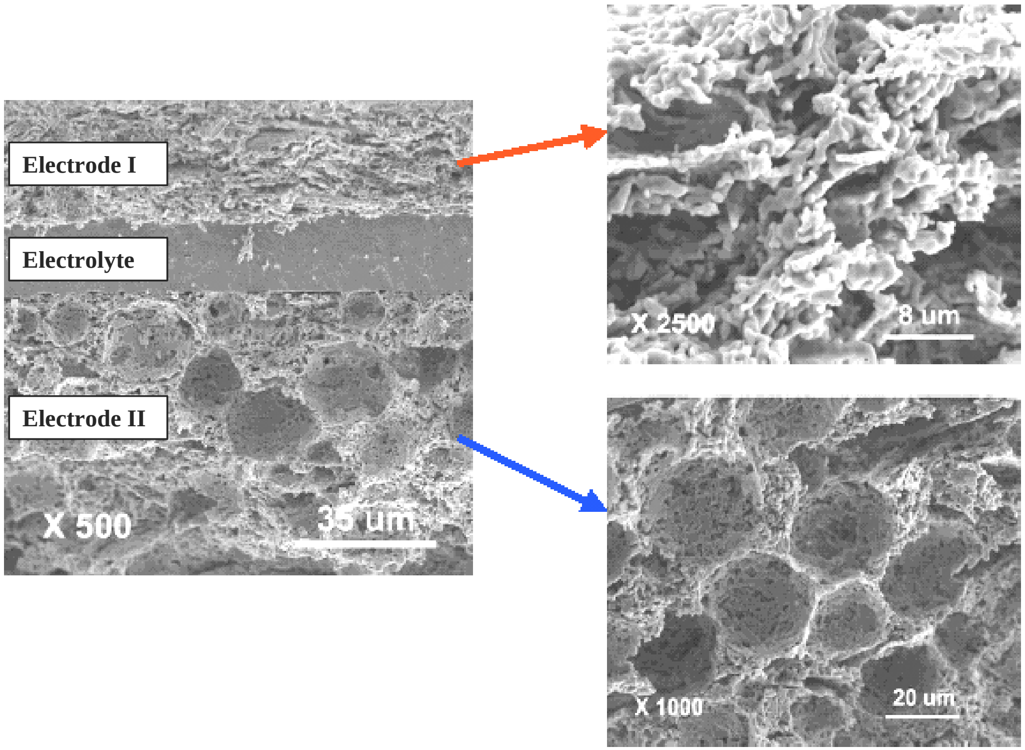
The common air electrode, $La_{0.8}Sr_{0.2}MnO_3$, changes with polarization.

a) LSM is activated by cathodic (fuel cell) polarization.

b) LSM is deactivated by anodic (SOE) polarization.

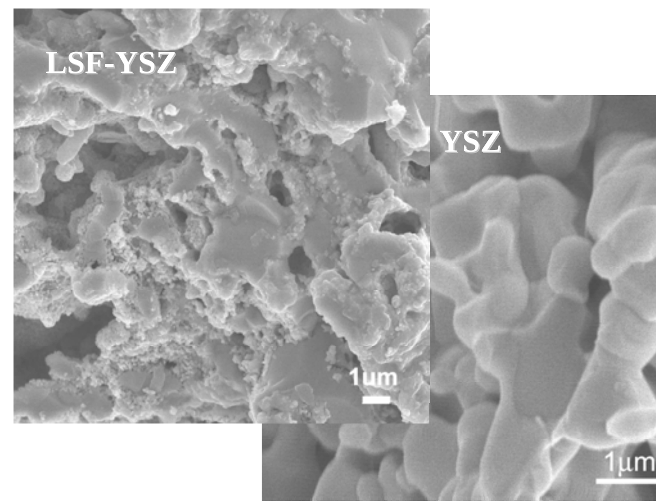
Electrode and Cell Fabrication:

Tape casting/lamination with pore formers



Impregnate active components using

1. Aqueous salt solutions
2. Perovskite nanoparticles
3. Molten salts
4. Electrodeposition

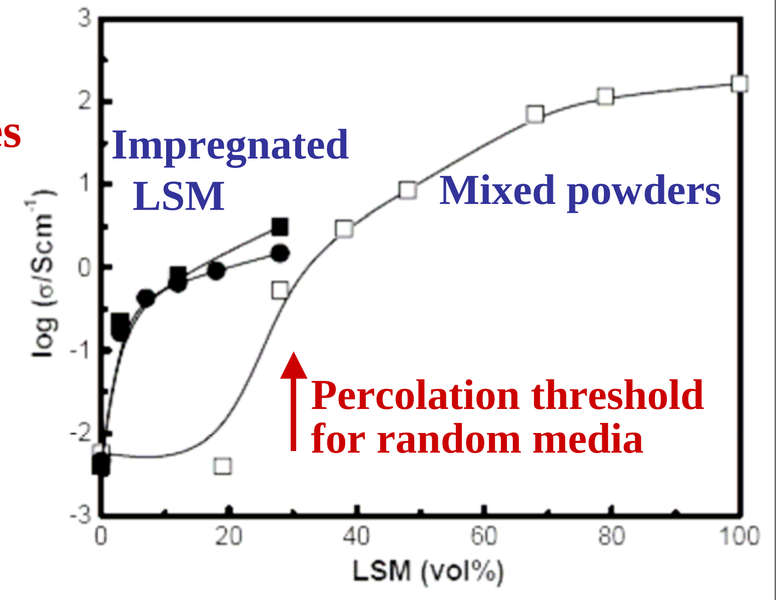


Advantages:

1. Separate firing temperatures for YSZ and active phase.
   - Avoids solid-state reactions between LSF & YSZ.
   - Can use low-melting solids (CuO).
2. Composite is non-random structure.

a) Electrical conductivity of LSM-YSZ

700°C in air, composites calcined at 1523 K.



b) CTE of LSCo-YSZ

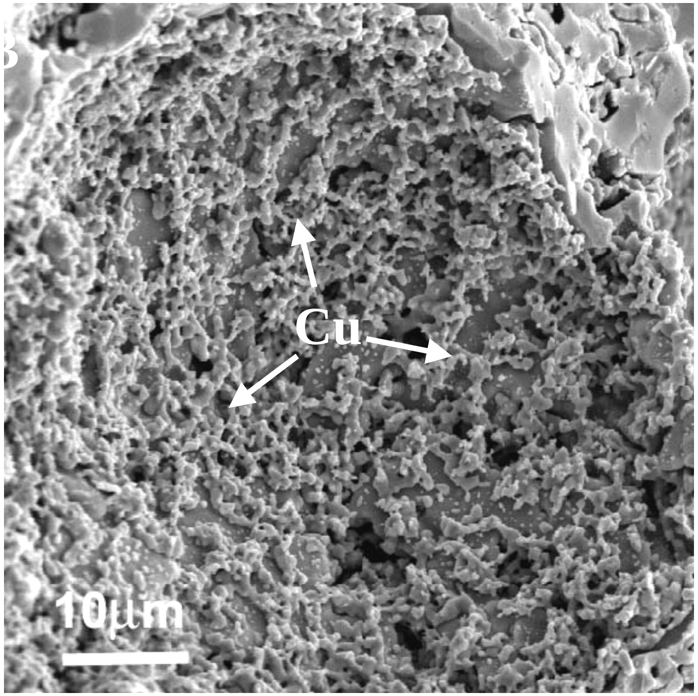
LSCo Weight Fraction in YSZ	0%	35%	45%	55%
CTE (10^{-6}/K), 300 to 1073 K	10.3	11.7	12.6	12.6

CTE of LSCo is 23×10^{-6}/K

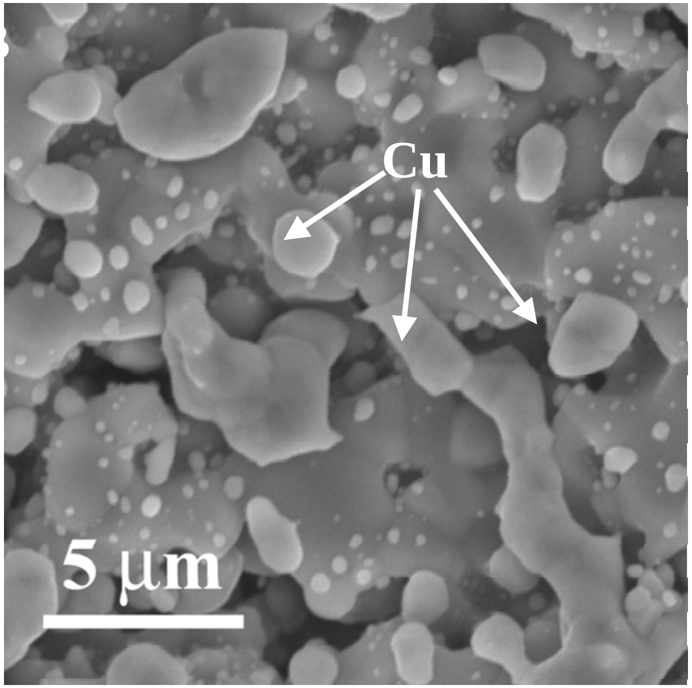
Cu-based anodes are stable in hydrocarbons but not suitable for CH_4 utilization

- Low catalytic activity (ceria is the catalyst)
- Limited to use at lower temperatures; sintering causes loss of electrode conductivity.

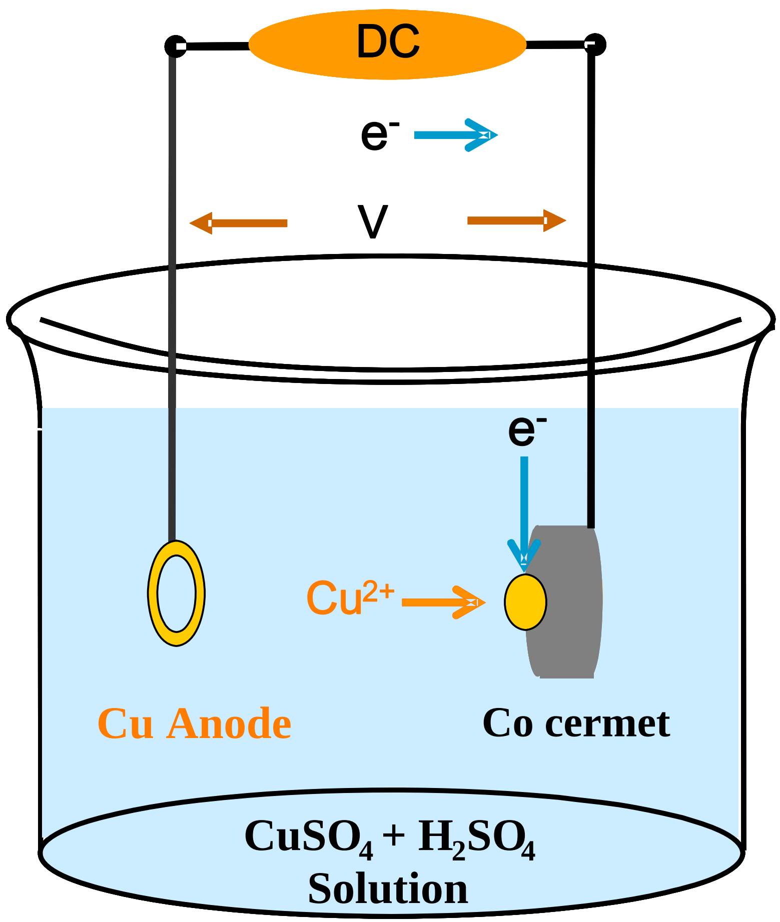
700ºC



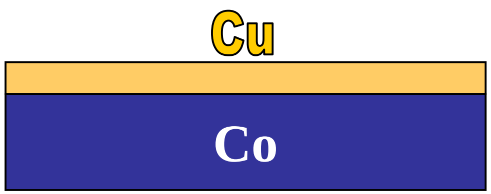
900ºC



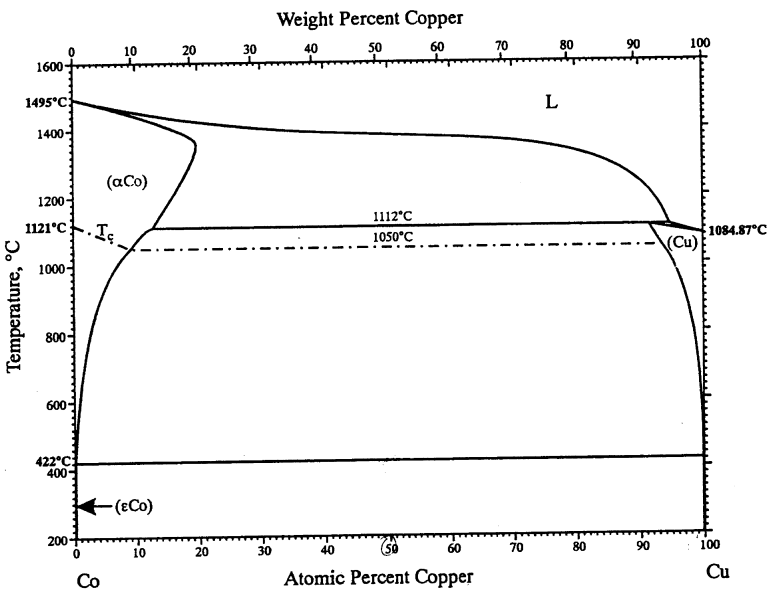
Solution 1: Electroplate Cu onto Co cermets



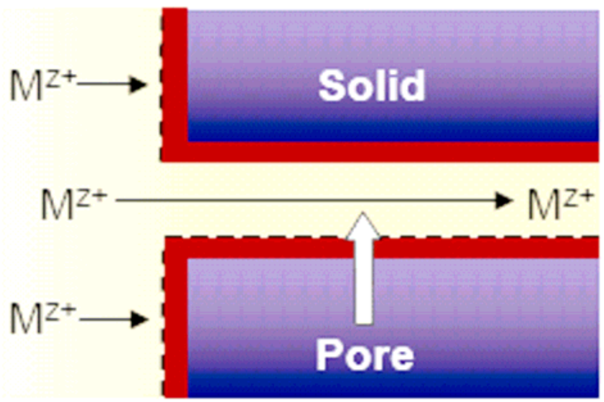
Idea: "Coat" thermally stable Co with chemically stable Cu:



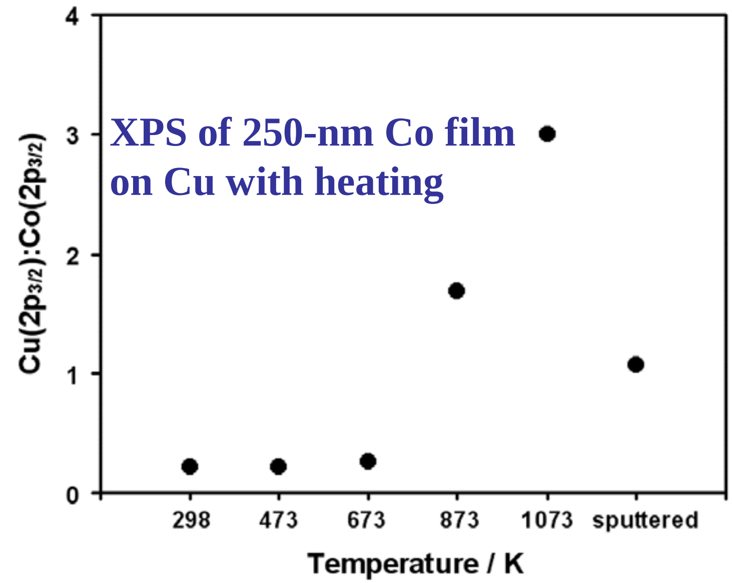
Cu and Co do not form alloys

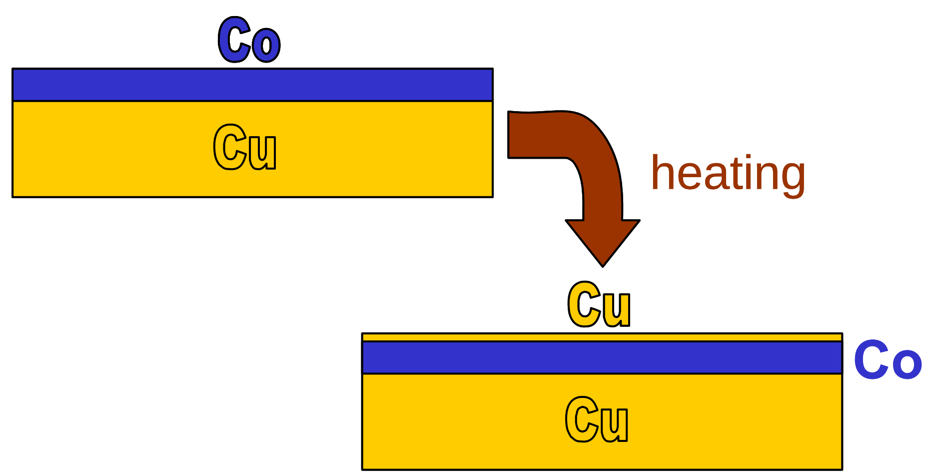


Key is to deposit evenly throughout the pores; Co plating is much easier than Cu



But Cu segregates to Co surface

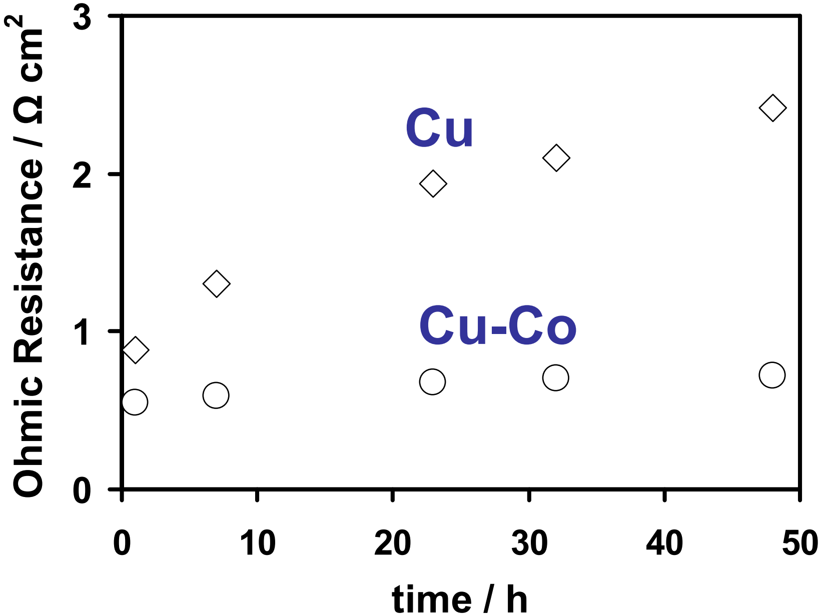




Co plated Cu stable in CH_4 at 800ºC for 3 h

Cu-Co **Co only**

R_Ω as a function of time at 900ºC

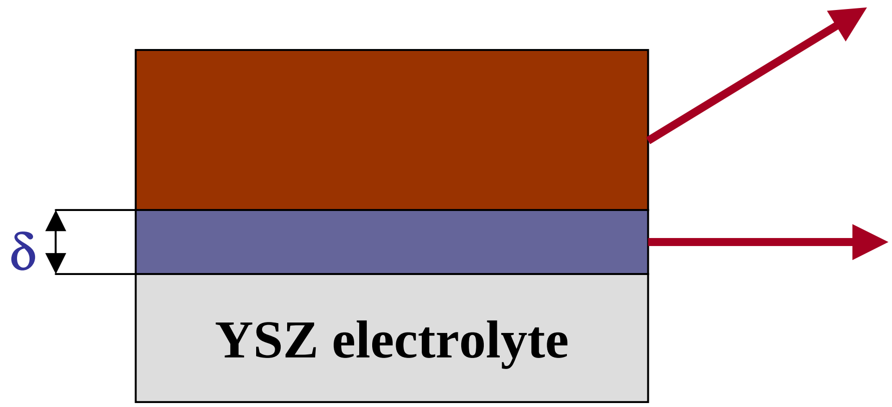


Dramatic increase in thermal stability with Cu-Co

Solution 2: Ceramic anodes

Problem: Oxides have either poor conductivity at low $P(O_2)$ or poor catalytic activity

Concept: Separate the two required functions



Anode current collector:

Porous ceramic, optimized for conductivity

Anode functional layer:

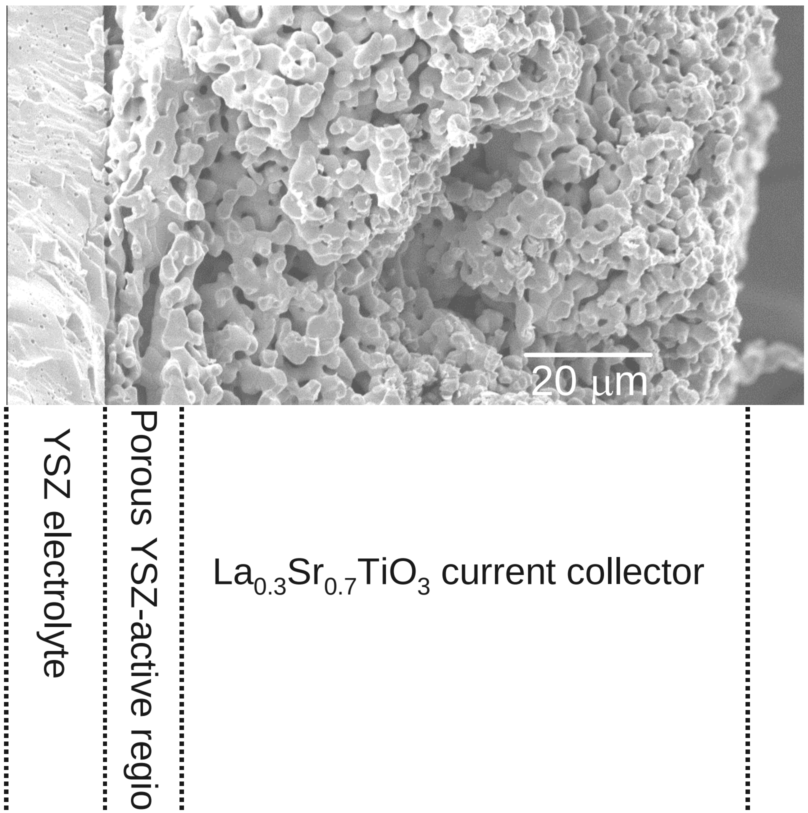
Optimized for catalytic performance

Thin to avoid need for high conductivity

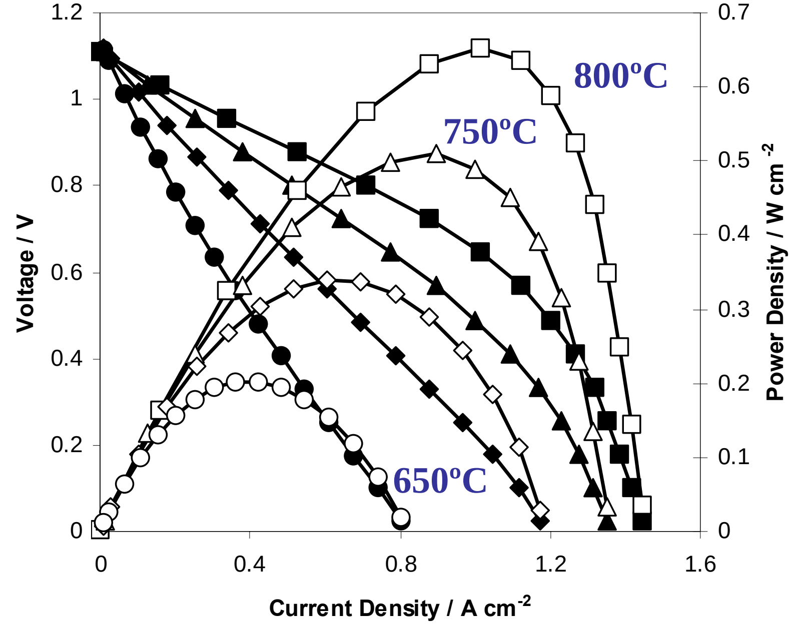
Key point:

If δ = 10 μm and R_{ohmic} must be < 0.1 $\Omega \cdot cm^2$,
σ need only be 0.01 S/cm!

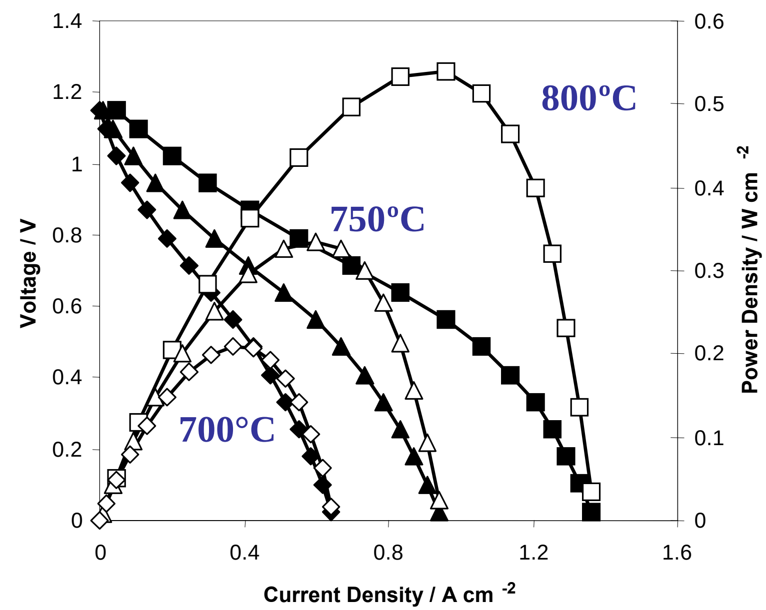
Current collector:
$La_{0.3}Sr_{0.7}TiO_3$
Functional layer:
1wt%Pd-40wt% ceria in YSZ



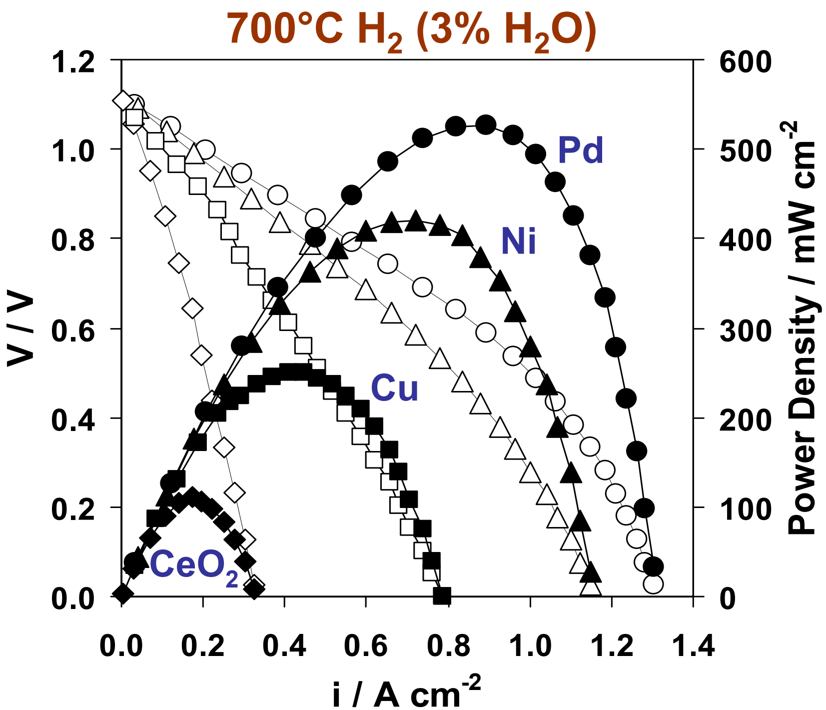
H_2 (3% H_2O)

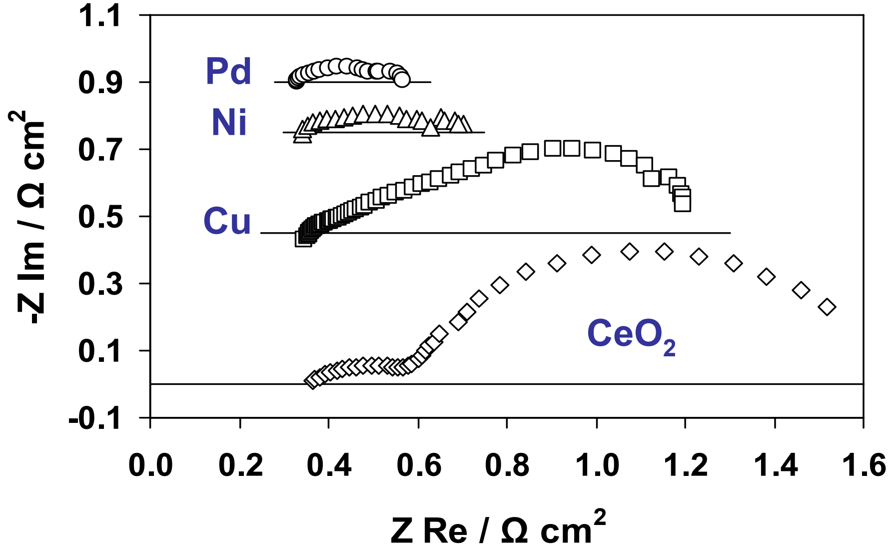


CH_4 (3% H_2O)



Catalysis is crucial!





40 wt% CeO_2
Pd 1 wt%
Ni 1 wt%
Cu 5 wt%

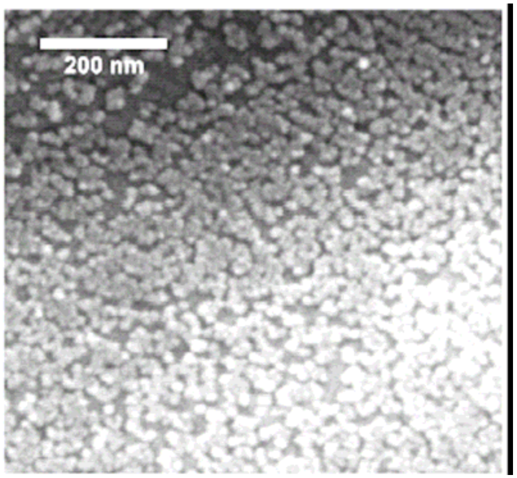
Need combination of ceria and metal

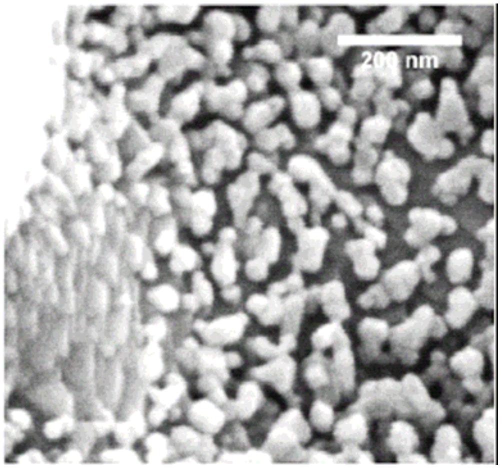
A remaining issue:

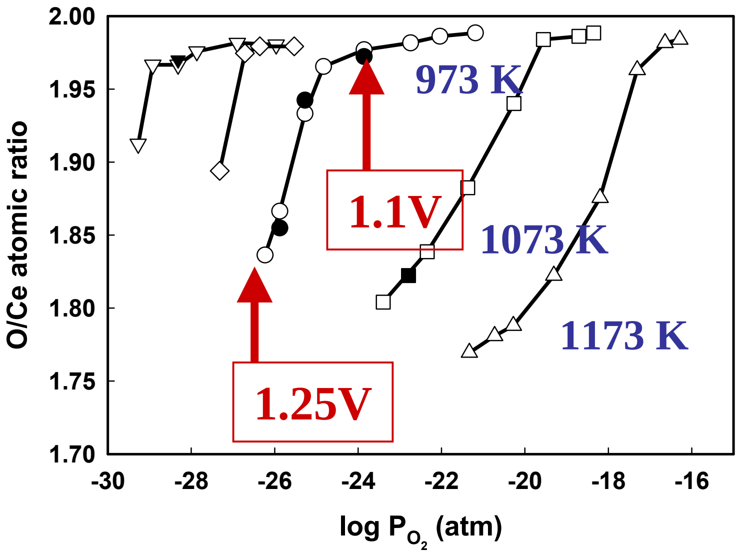
Conductivity of ceria layer is not stable at low $P(O_2)$:

Ceria film in porous YSZ

Wet H_2 at 973 K (1.1 V) **Methanol (1.25 V)**







J. Power Sources 164 (2007) 42

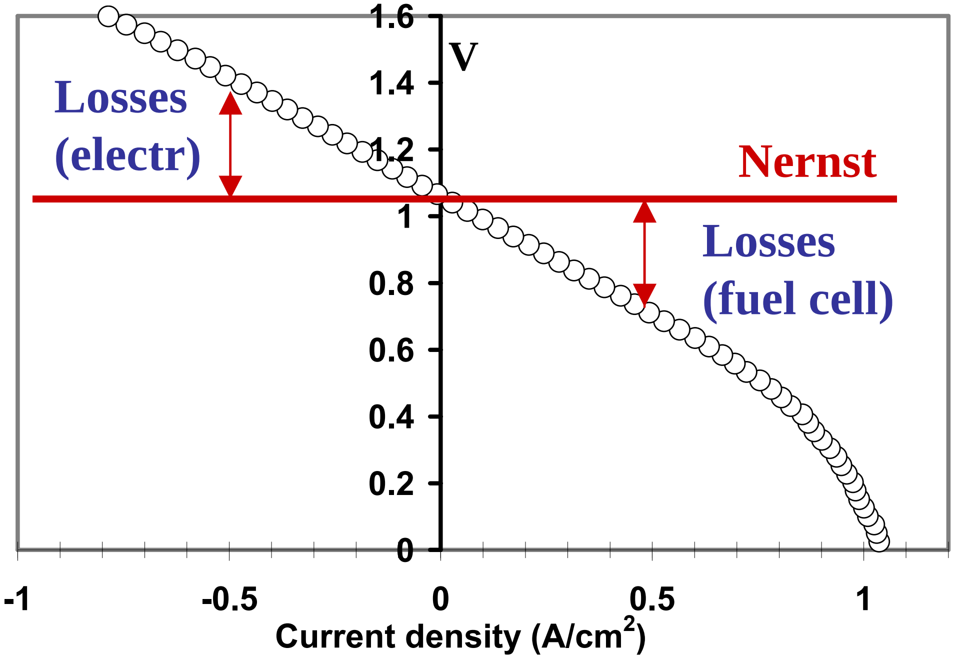
IECR 45(2006) 5561

Need to develop other ways to make functional layer conductive:

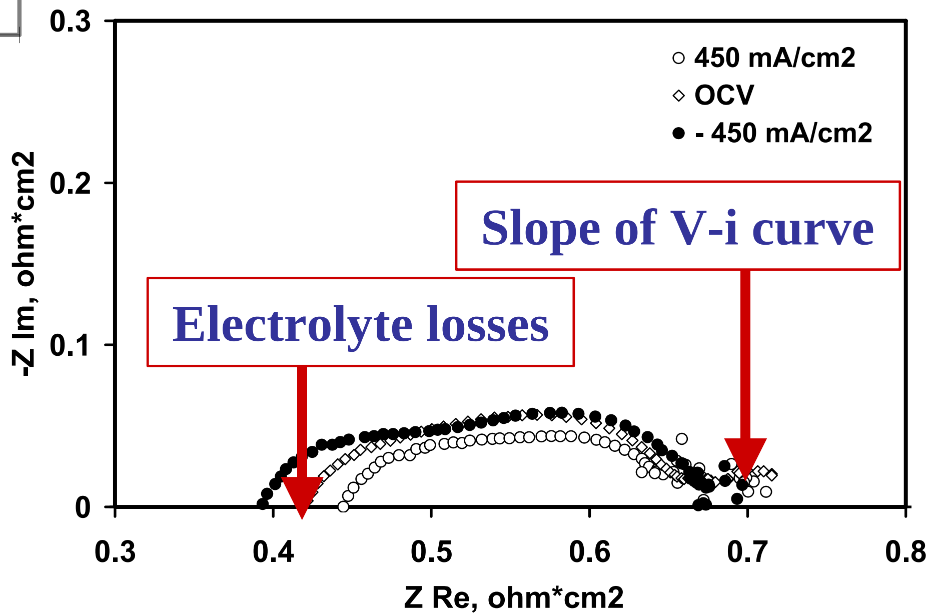
1) Use composites of YSZ with doped $SrTiO_3$
2) Dope the YSZ with Ce, Ti, or Nb.

How does polarity affect electrodes?

Characterization:



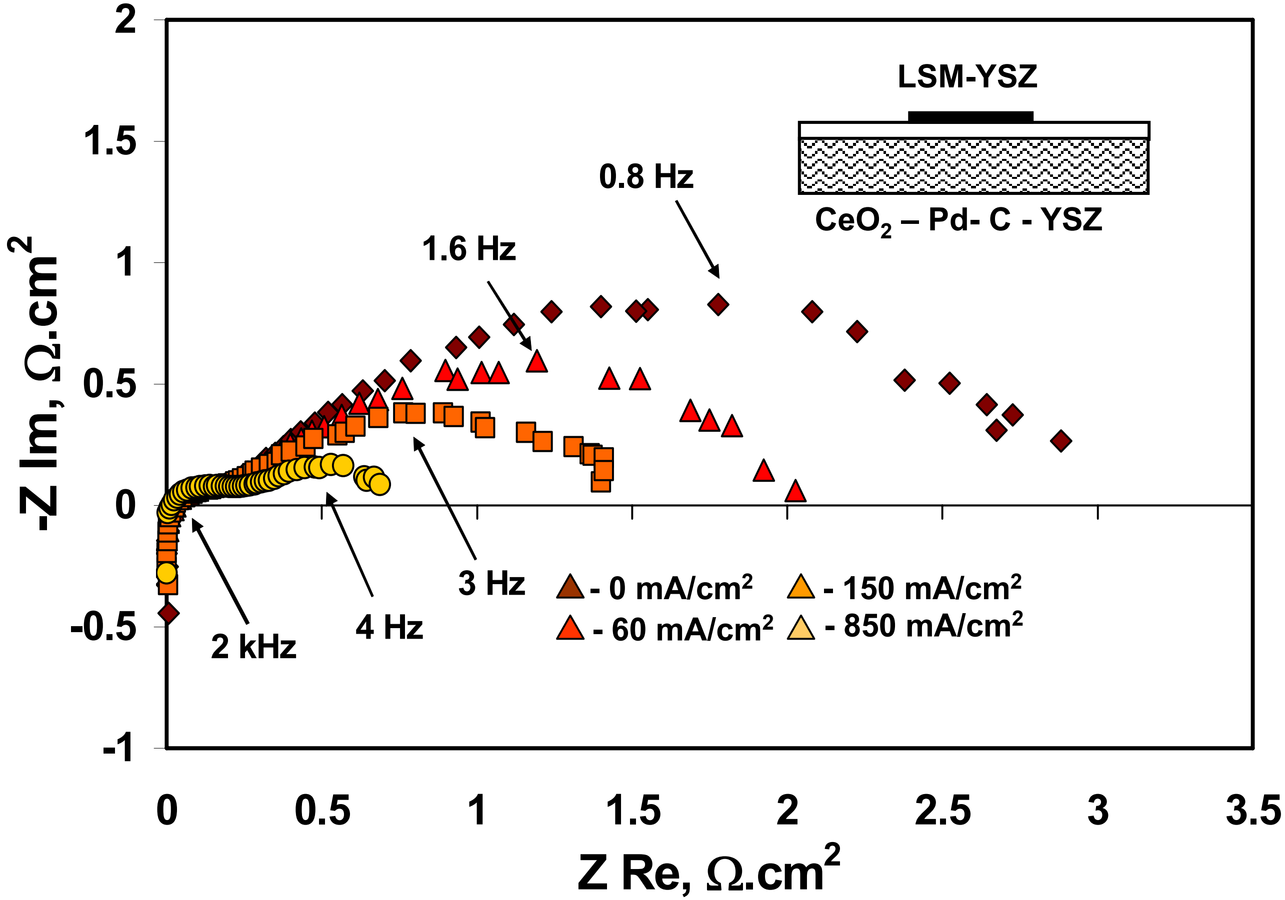
Impedance spectroscopy allows separation of electrode and electrolyte losses:



Polarization activation with LSM-YSZ

ESSL, 7 (2004) A111-A114.

700°C, H_2/3%H_2O, OCV after applying current

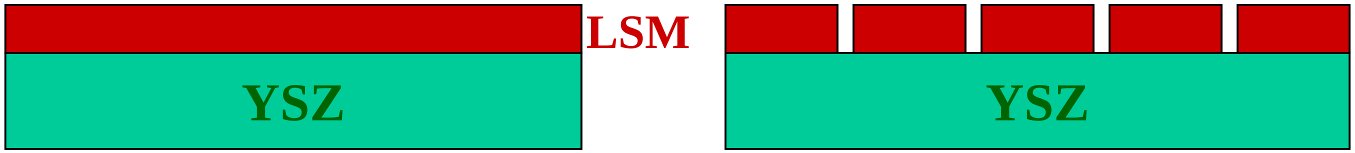


Note: These changes are reversible. τ ~ 120 minutes.

What we believe is happening:

Electrode before activation

Activated Electrode



1) Dense LSM covers YSZ
2) Performance limited by oxygen diffusion.

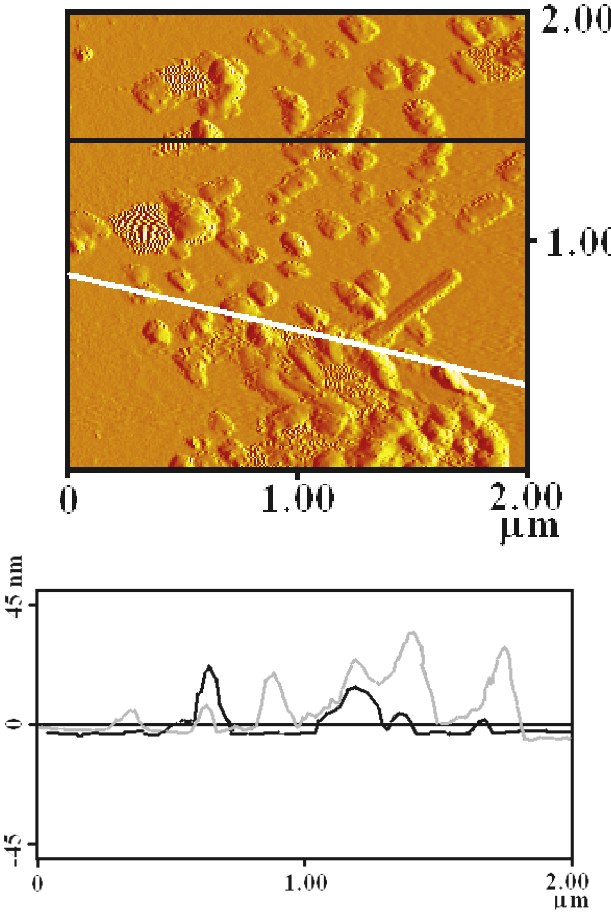
Gaps in LSM film caused by reduction

Gas can get to YSZ interface.

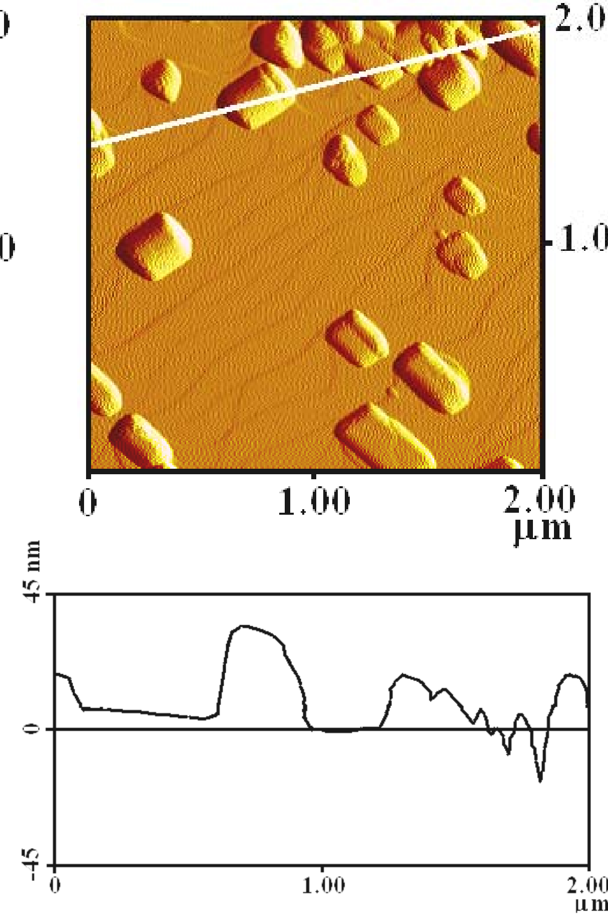
Process driven by surface interactions between LSM & YSZ

LSM Particles on YSZ (100): Effect of calcination temperature

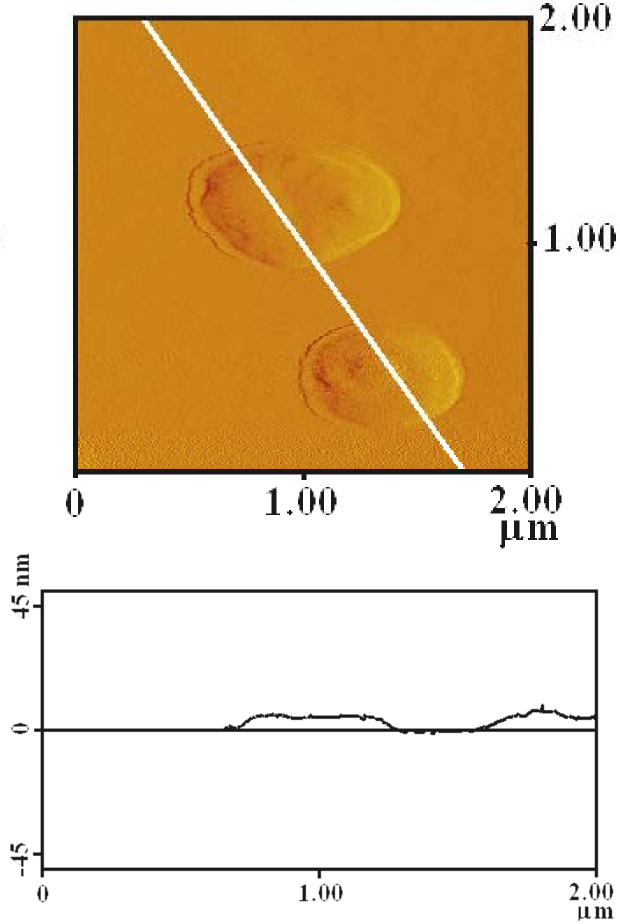
ESSL, 9 (2006) A237-240



850°C



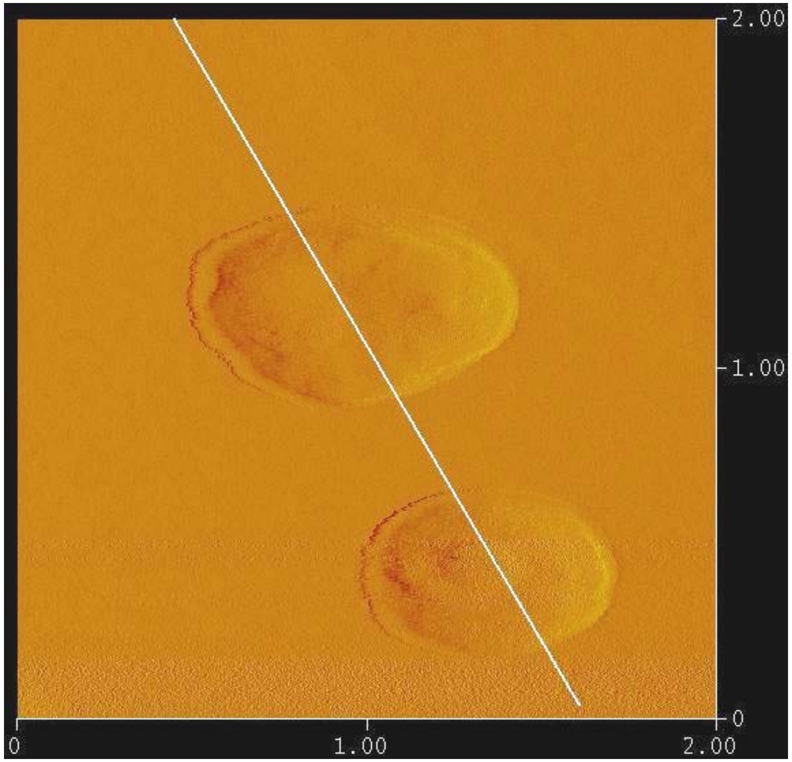
1050°C



1150°C

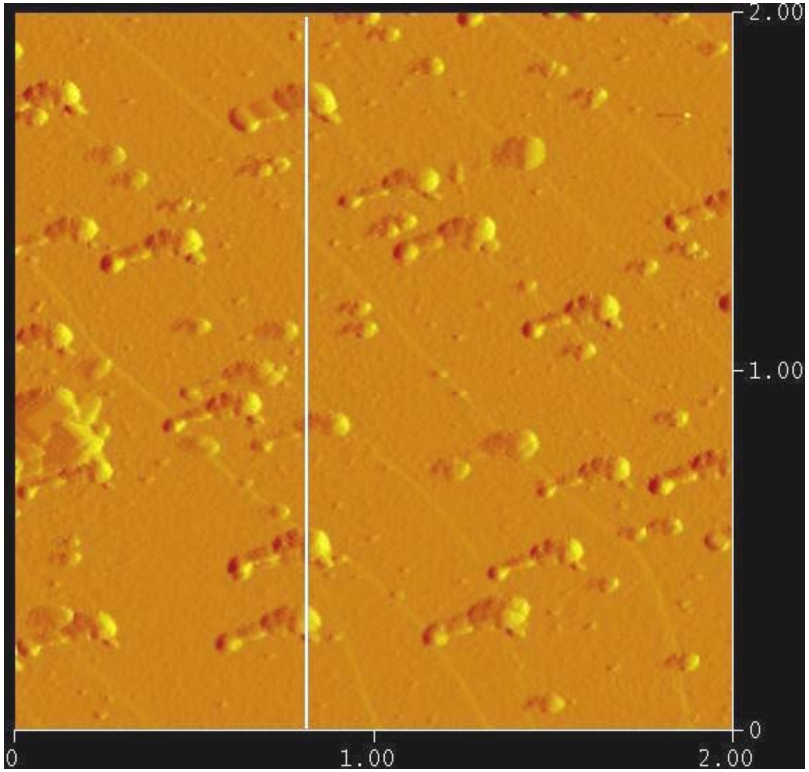
Movement of particles is reversible:

Calcination at 1150°C



Reduced in H_2 (10%H_2O) at 700°C

2 μm x 2 μm



1) LSM is stable in 10%H_2O-90% H_2 at 700ºC.

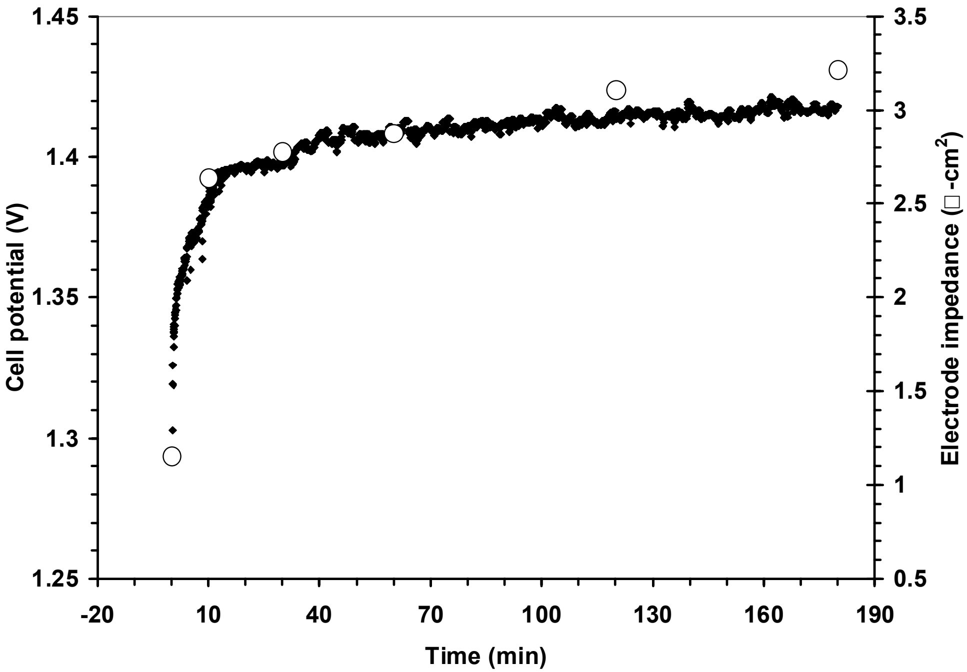
2) Reducing LSM-YSZ electrode “activate” it.

Consequences for electrolysis (anode environment is oxidizing):

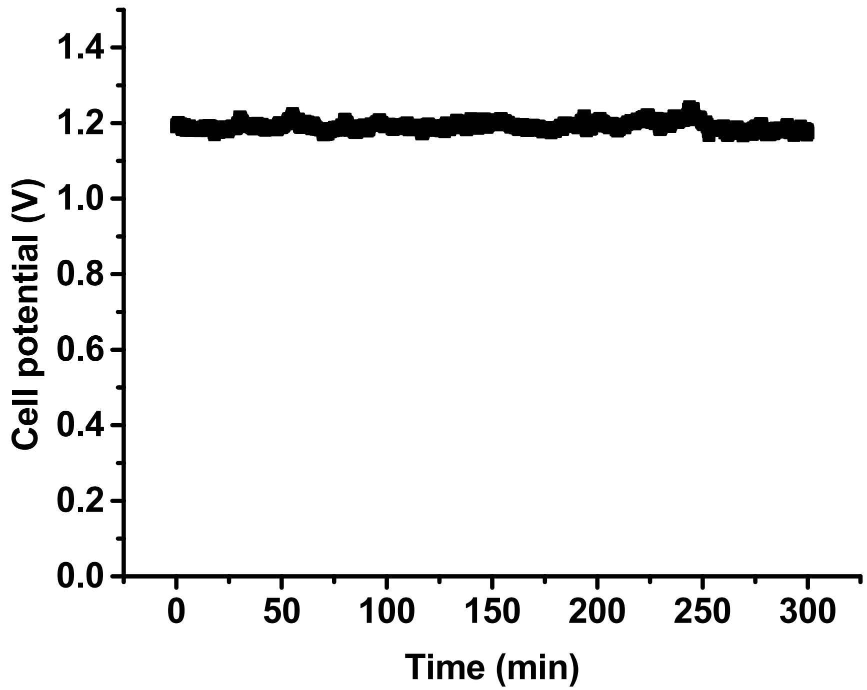
JECS, 153 (2006) A2066.

285 mA/cm^2; 700ºC; 85%H_2-15%H_2O| air

LSM-YSZ anode



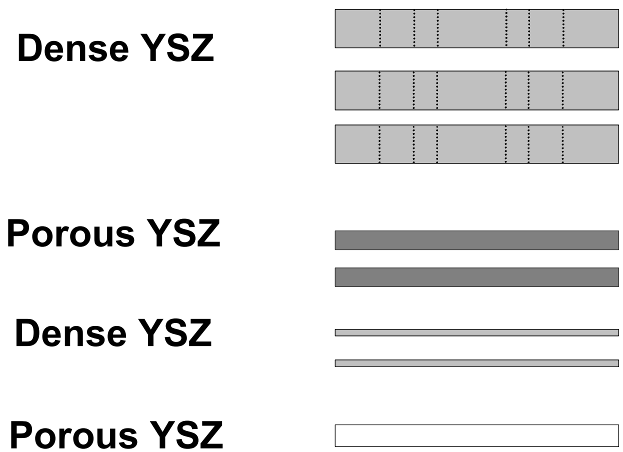
LSF-YSZ anode



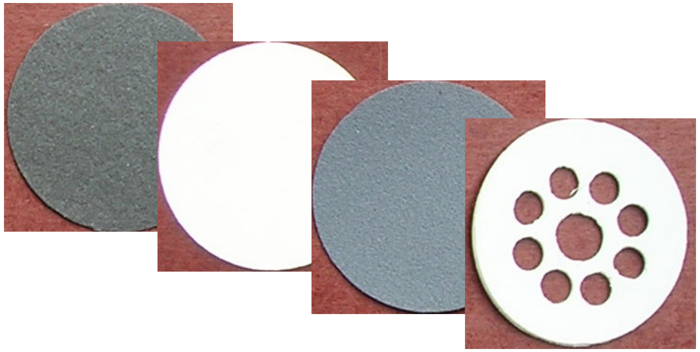
Publications Citing DOE Support (2006 -)

1. "Electrodeposition of Cu into a Highly Porous Ni/YSZ Cermet", S. Jung, M. D. Gross, R. J. Gorte, and J. M. Vohs, Journal of the Electrochemical Society, 153 (2006) A1539-43.
2. "Enhanced Thermal Stability of Cu-Based, SOFC Anodes by Electrodeposition of Cr", M. D. Gross, J. M. Vohs, and R. J. Gorte, Journal of the Electrochemical Society, 153 (2006) A1386-90.
3. "A Comparison of LSM, LSF, and LSCo for Solid Oxide Electrolyzer Anodes", Wensheng Wang, Yingyi Huang, Sukwon Jung, John M. Vohs, and Raymond J. Gorte, Journal of the Electrochemical Society, 153 (2006) A2066-70.
4. "A Study of Thermal Stability and Methane Tolerance of Cu-Based SOFC Anodes with Electrodeposited Co", M. D. Gross, J. M. Vohs, and R. J. Gorte, Electrochimica Acta, 52 (2007) 1951.
5. "A strategy for achieving high-performance with SOFC ceramic anodes", M. D. Gross, J. M. Vohs, and R. J. Gorte, Electrochemical and Solid State Letters, 10 (2007) B65-69.
6. "The Stability of LSF-YSZ Electrodes Prepared by Infiltration", W. Wang, M. D. Gross, J. M. Vohs, and R. J. Gorte, Journal of the Electrochemical Society, 154 (2007) B439-45
7. "Impedance characterization of a model Au/YSZ/Au electrochemical cell in varying oxygen and NO_x concentrations", L. Y. Woo, L. P. Martin, R. S. Glass, and R. J. Gorte, Journal of the Electrochemical Society, 154 (2007) J129.
8. "Multilayer High Performance Ceramic Anodes", M. D. Gross, R. J. Gorte, and J. M. Vohs, ECS Transactions - Solid Oxide Fuel Cells, Volume 7, accepted.
9. "Hydrogen Production via CH_4 and CO Assisted Steam Electrolysis", W. Wang, J. M. Vohs, and R. J. Gorte, Topics in Catalysis, accepted.
10. "An examination of SOFC anode functional layers based on ceria in YSZ", M. D. Gross, J. M. Vohs, and R. J. Gorte, Journal of the Electrochemical Society, accepted.
11. "Recent Progress in SOFC Anodes for Direct Utilization of Hydrocarbons", M. D. Gross, J. M. Vohs, and R. J. Gorte, Journal of Materials Chemistry, accepted.

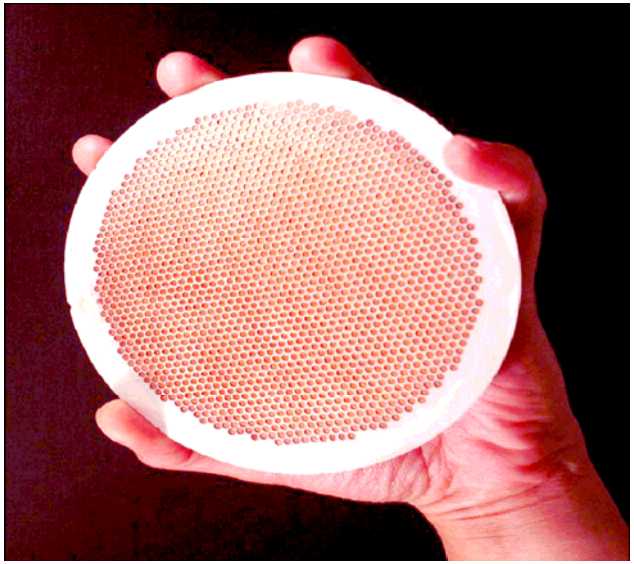
Support Layers can be added for strength:



Laminated cell



Final Product



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