

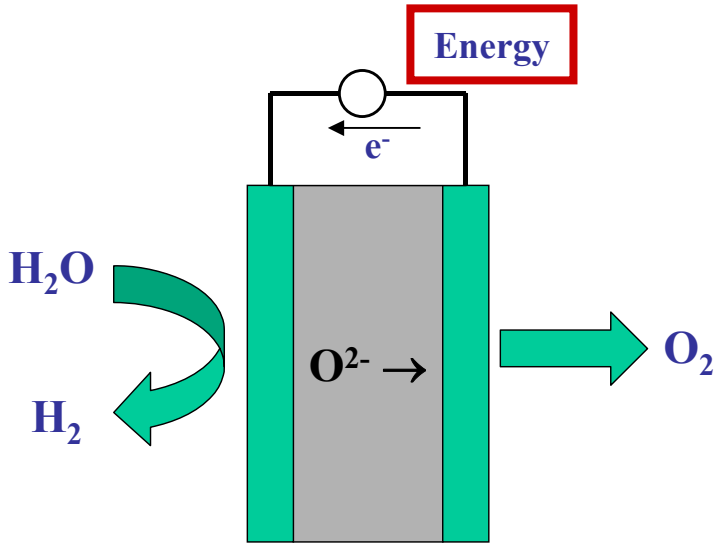
# **Electrodes for Solid Oxide Electrolysis (SOE) and Natural-Gas Assisted Steam Electrolysis (NGASE)**

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# SOE

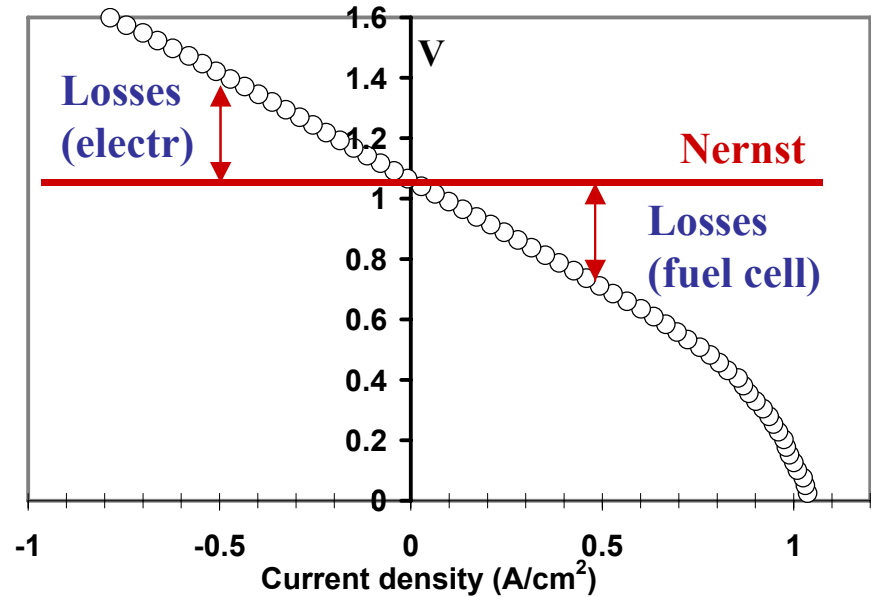


Electrolysis requires  $V > V_{\text{Nernst}}$   
SOE are more efficient

- (1) lower Nernst Potential (TAS)
- (2) low electrode losses
- (3)  $\text{CO}_2$  can be electrolyzed too.

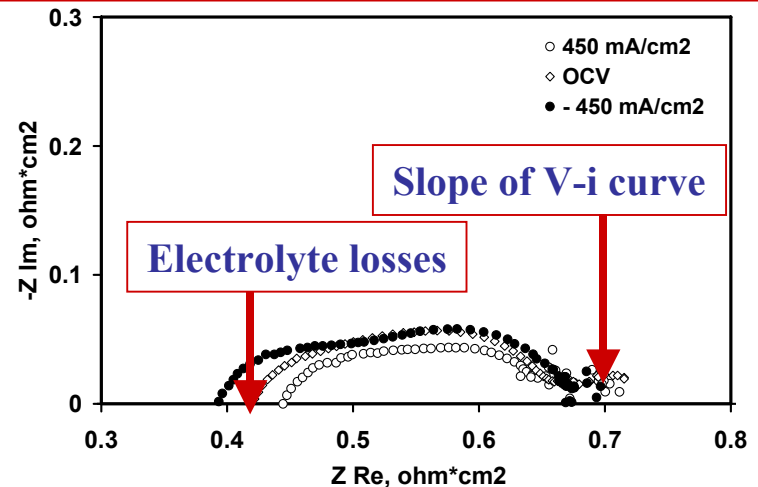
(1)

90%  $\text{H}_2$ -10%  $\text{H}_2\text{O}$  || air, 700°C



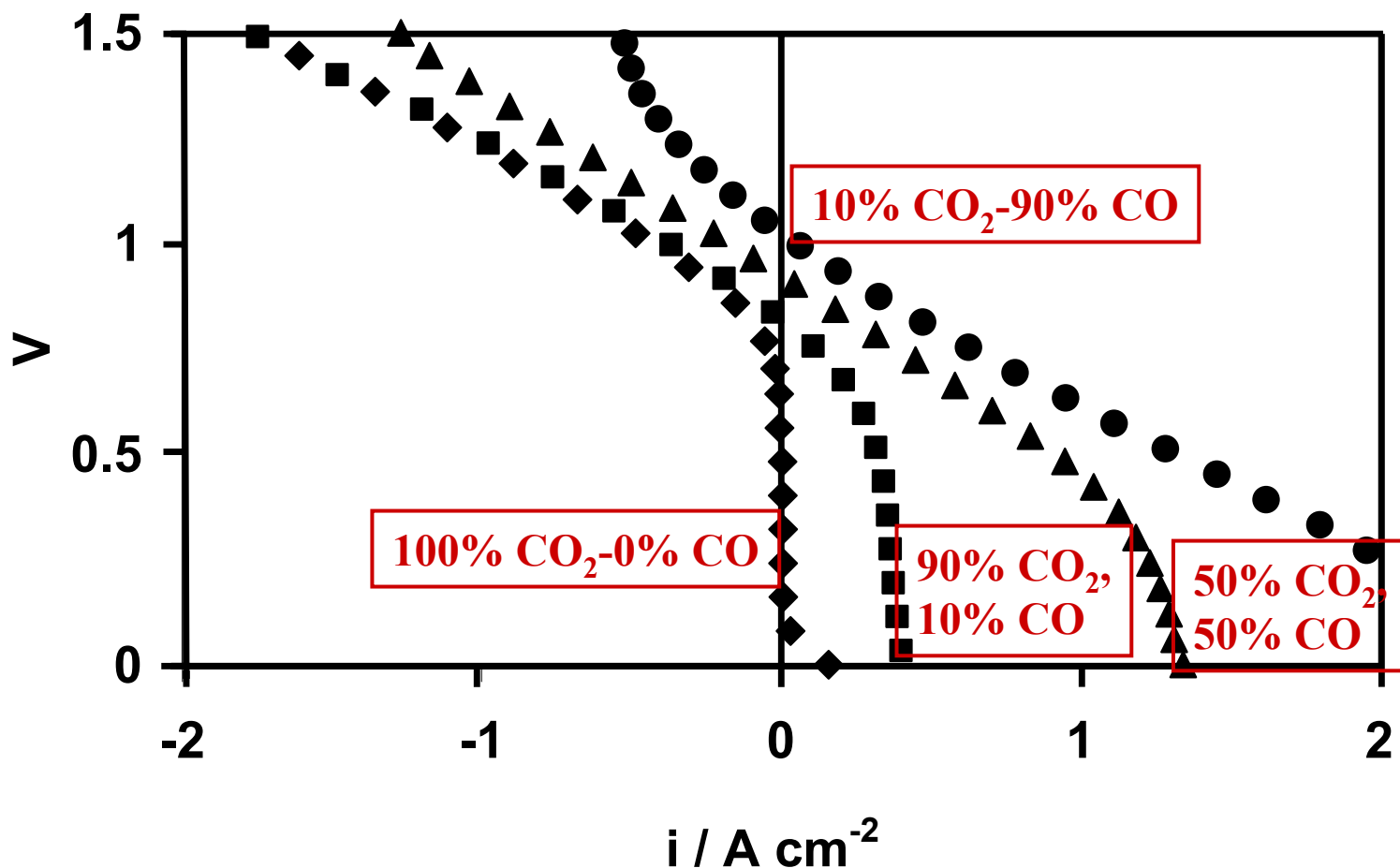
(2)

Electrode losses are low in this example!

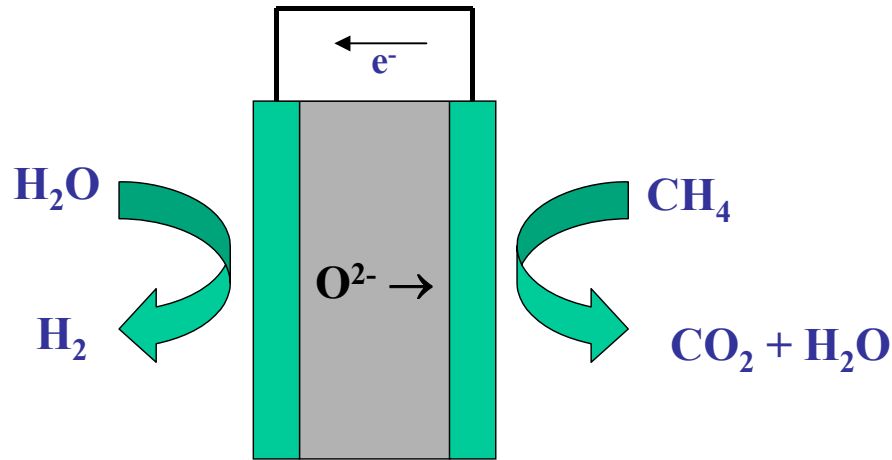


### (3) $\text{CO}_2$ Electrolysis as a function of $\text{CO}/\text{CO}_2$ : $800^\circ\text{C}$

- Used thick electrolyte ( $65\ \mu\text{m}$  YSZ)
- $\text{CO}_x$  electrode is ceramic, redox stable, & conductive in oxidizing and reducing environments.
- Collaboration with J. T. S. Irvine, St. Andrews

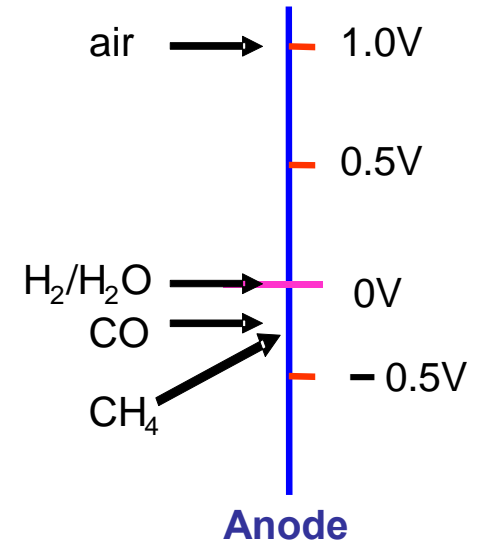


# NGASE



## Nernst Potential

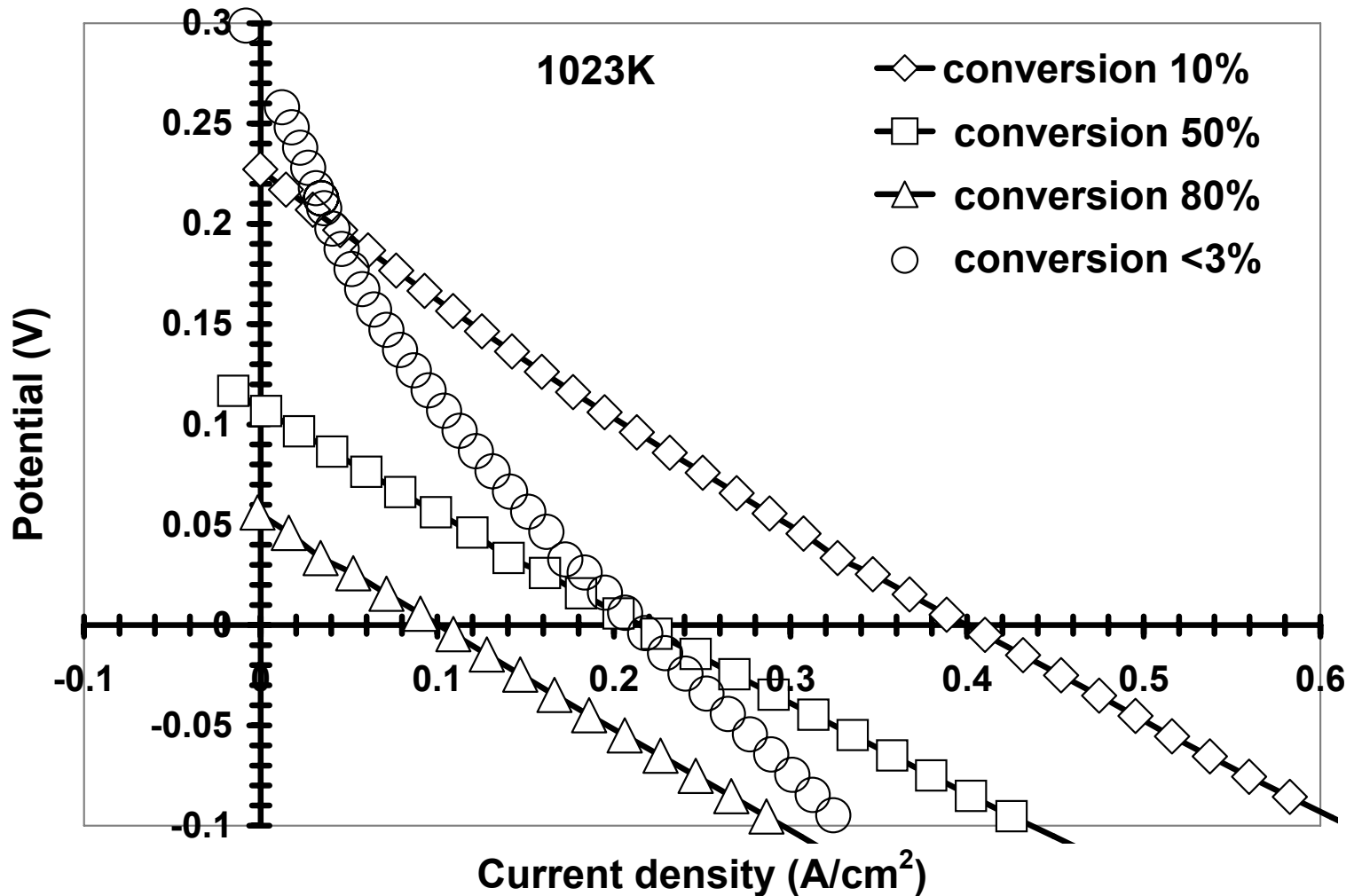
Cathode:  $\text{H}_2/\text{H}_2\text{O}$



- 1) No external power required.
- 2) Overall reaction same as reforming but produces pure  $\text{H}_2$ .
- 3) Very high efficiency possible (you use  $\Delta G$  driving force as reaction proceeds.).
- 4) Membrane can be mixed conducting (CTP Hydrogen Corp)

# NGASE Works!

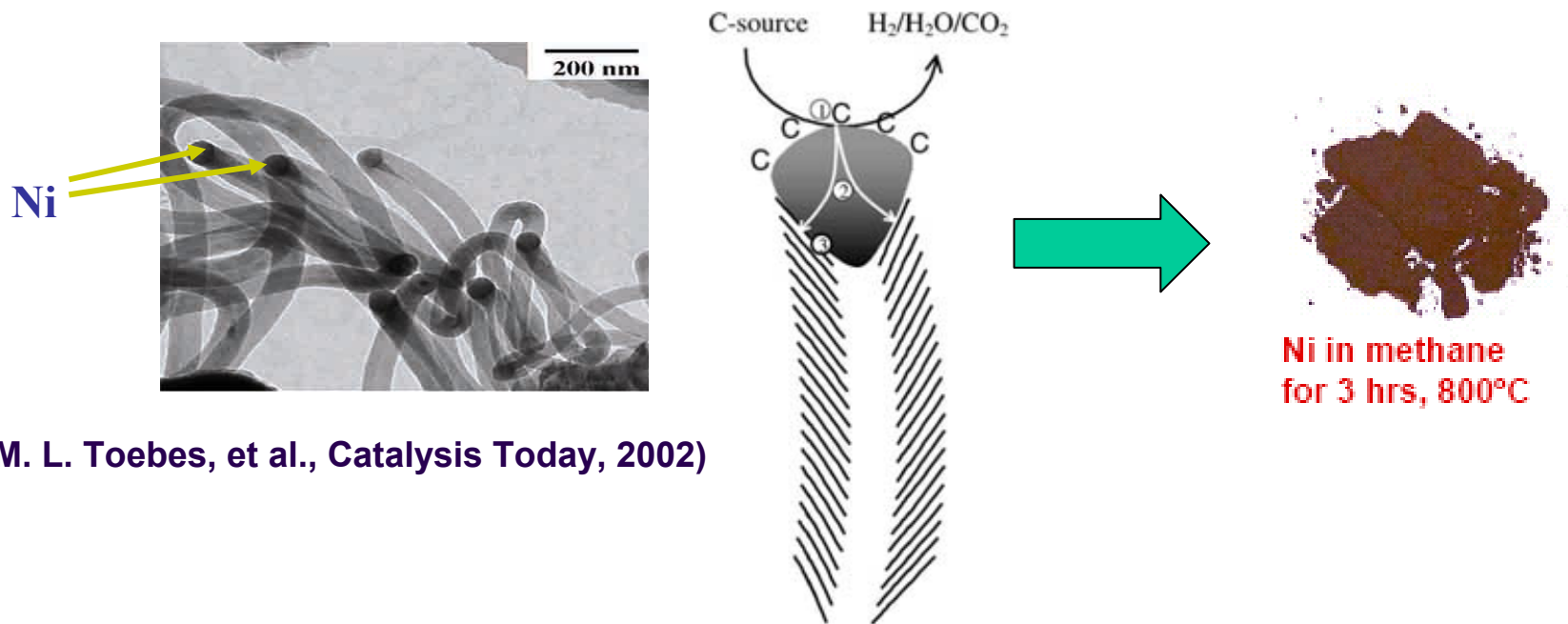
60% H<sub>2</sub>O, 4% H<sub>2</sub>, Co/ceria | YSZ(50 μm) | Pd/ceria, CH<sub>4</sub>



## Research Issues:

1) For NGASE, electrodes must be able to utilize methane.

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



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

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

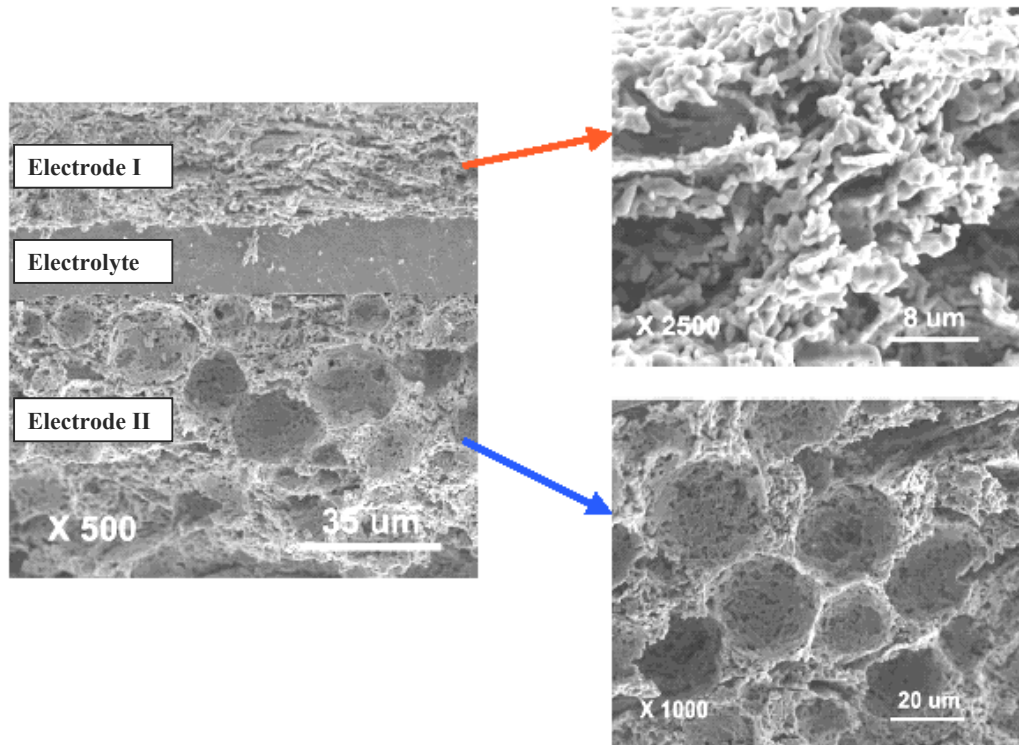
**The common air electrode,  $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ , changes with polarization.**

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

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

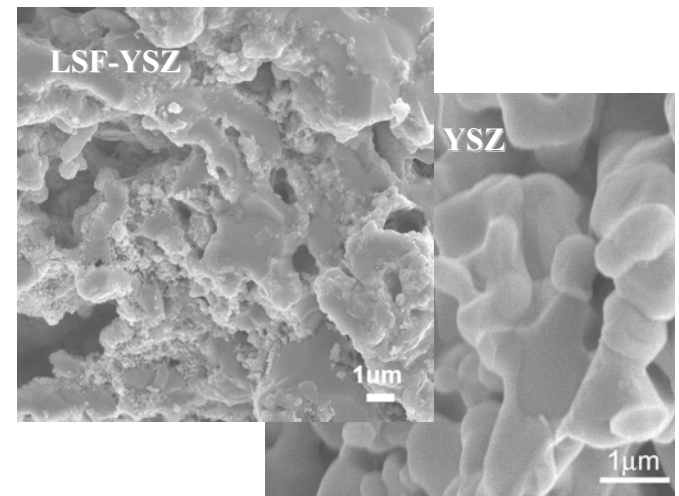
# Electrode and Cell Fabrication at Penn:

## Tape casting/lamination with pore formers



## Infiltrate active components using

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

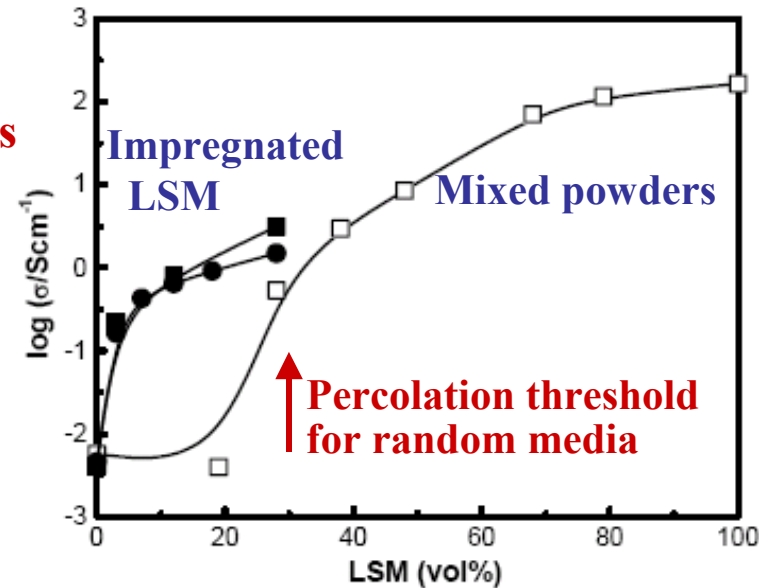


# Advantages:

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

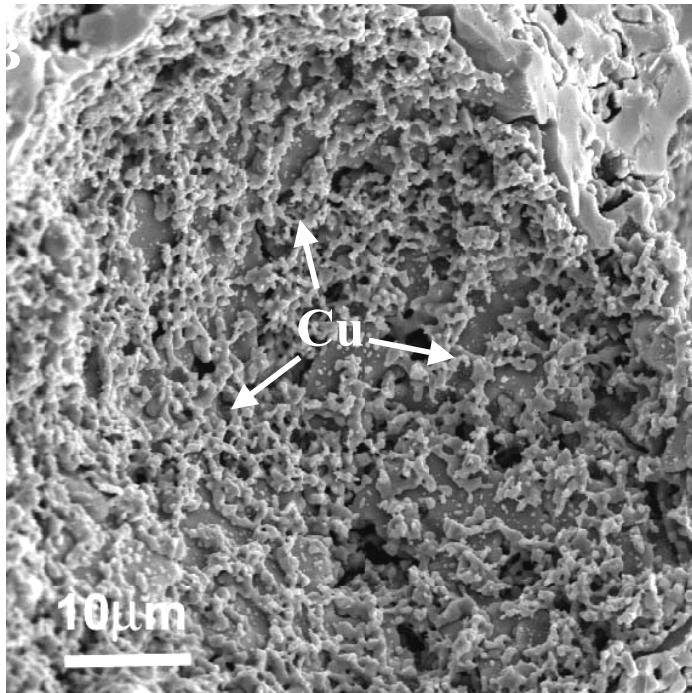
LSCo Weight Fraction in YSZ	0%	35%	45%	55%
CTE ( $10^{-6}/\text{K}$ ), 300 to 1073 K	10.3	11.7	12.6	12.6

CTE of LSCo is  $23 \times 10^{-6}/\text{K}$

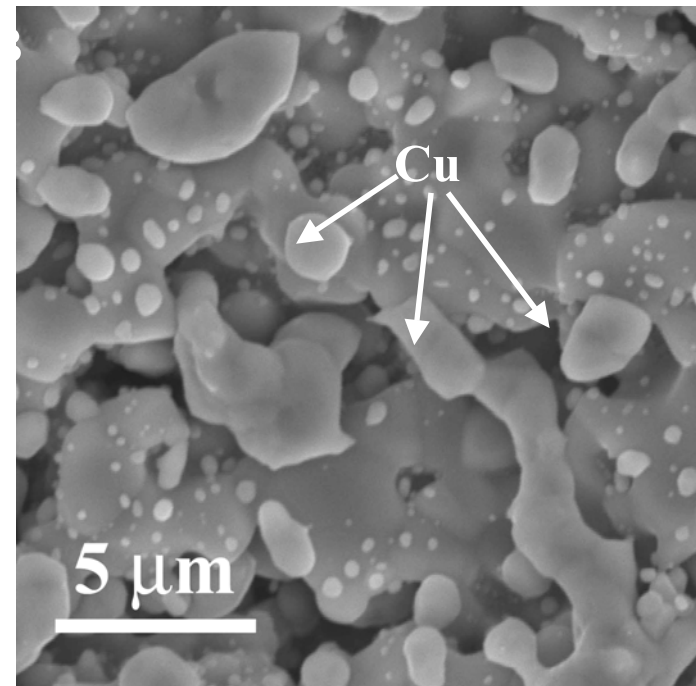
# Cu-based anodes are stable in hydrocarbons but not suitable for CH<sub>4</sub> utilization

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

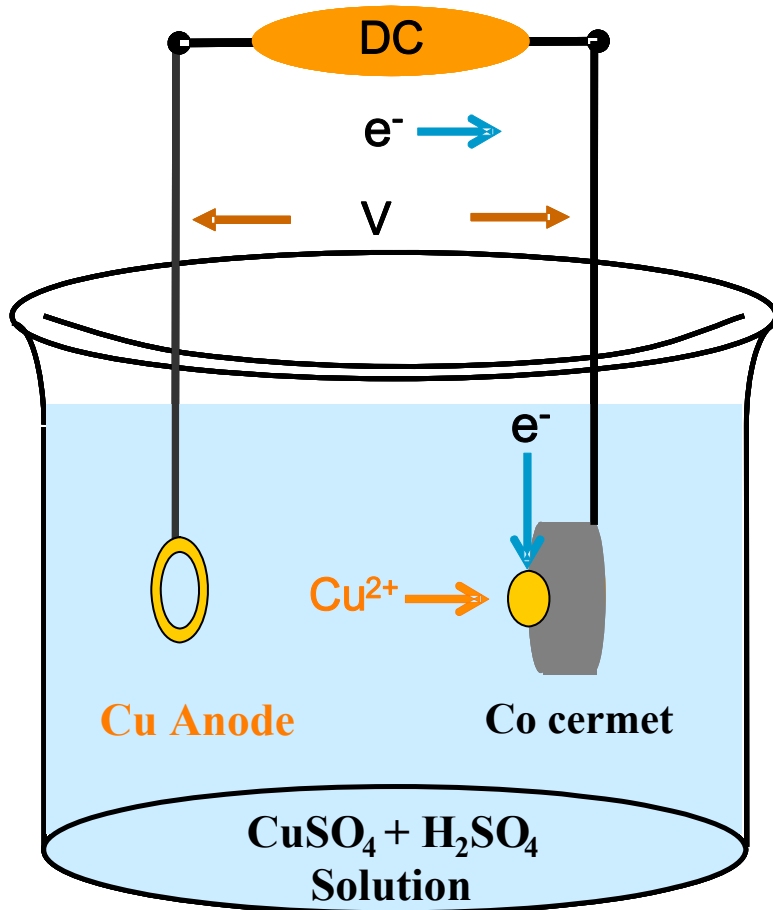
700°C



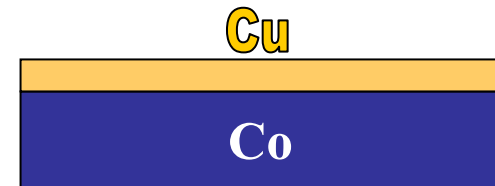
900°C



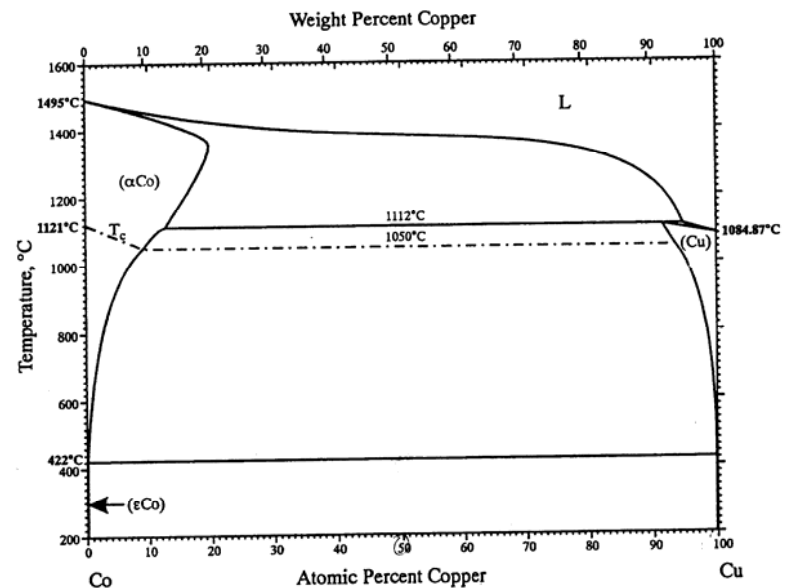
# Solution 1: Electroplate Cu onto Co cermets



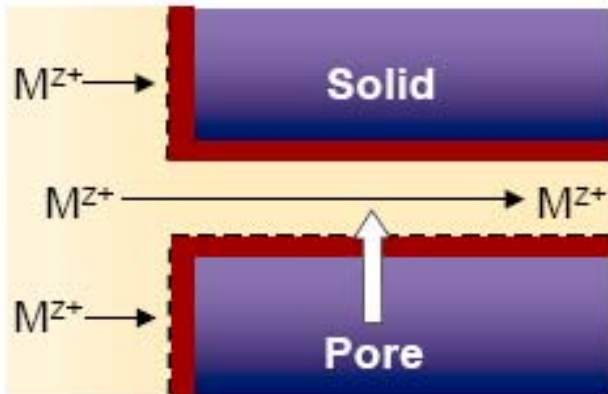
Idea: “Coat” thermally stable Co with chemically stable Cu:



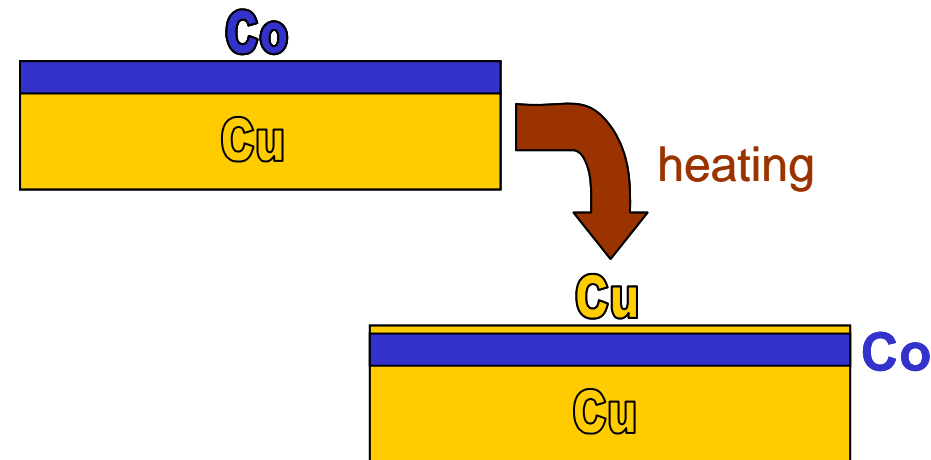
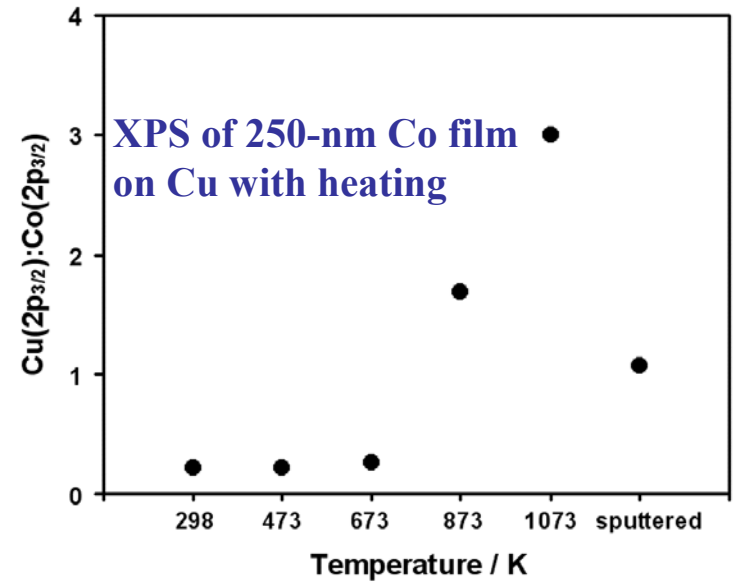
Cu and Co do not form alloys



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



But Cu segregates to Co surface



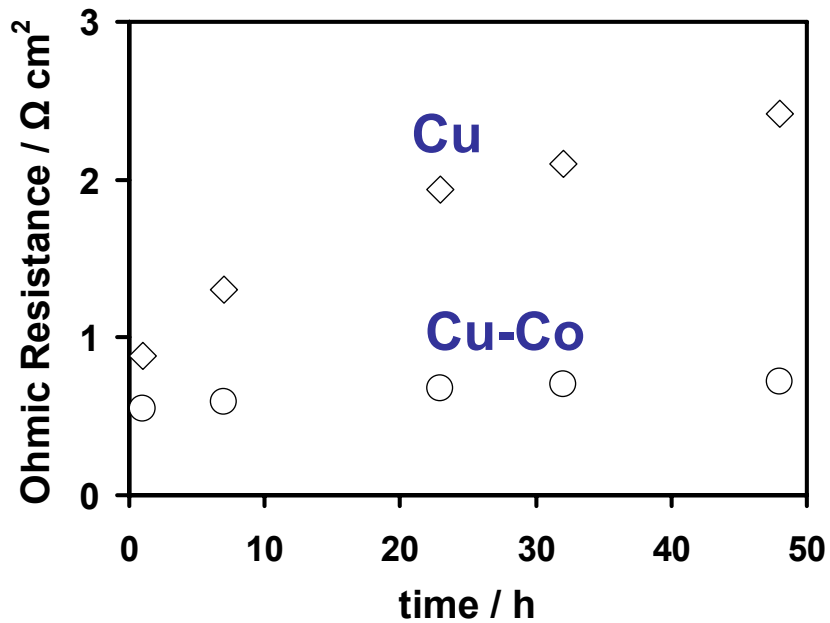
Co plated Cu stable in  
 $\text{CH}_4$  at  $800^\circ\text{C}$  for 3 h



**Cu-Co**

**Co only**

$R_\Omega$  as a function of time at  $900^\circ\text{C}$

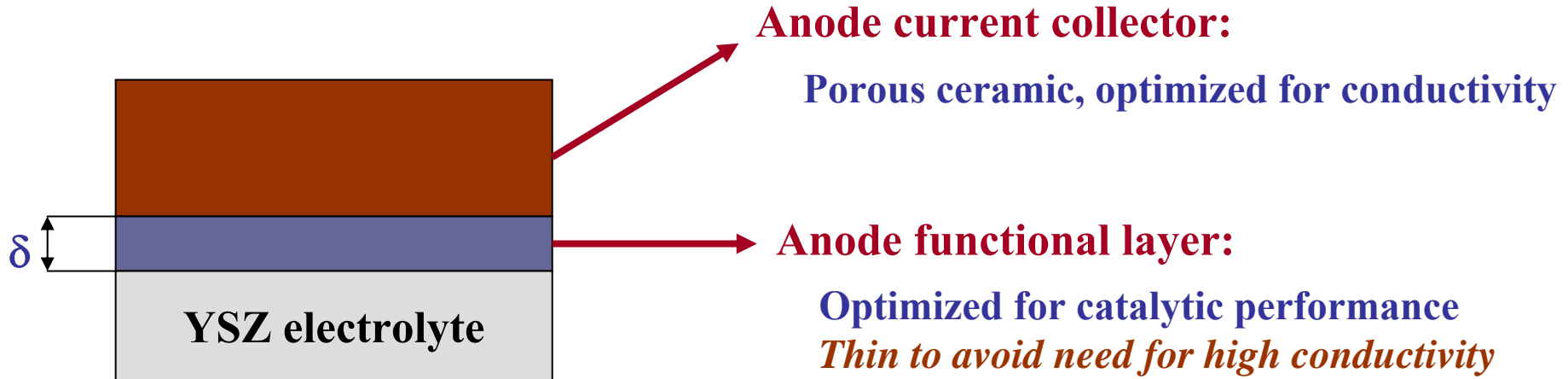


Dramatic increase in thermal  
stability with Cu-Co

## Solution 2: Ceramic fuel-side electrodes

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

**Concept:** Separate the two required functions



**Key point:**

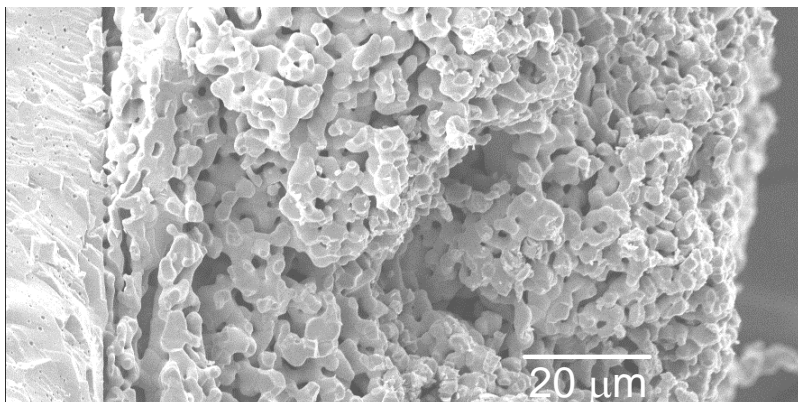
If  $\delta = 10 \mu\text{m}$  and  $R_{\text{ohmic}}$  must be  $< 0.1 \Omega \cdot \text{cm}^2$ ,  
 $\sigma$  need only be  $0.01 \text{ S/cm}$ !

**Current collector:**



**Functional layer:**

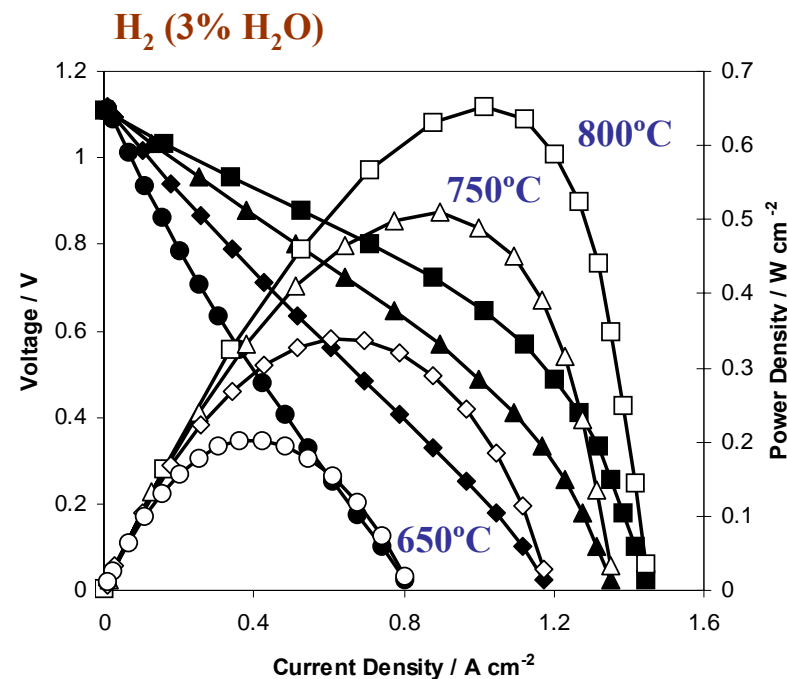
**1wt%Pd-40wt% ceria in YSZ**



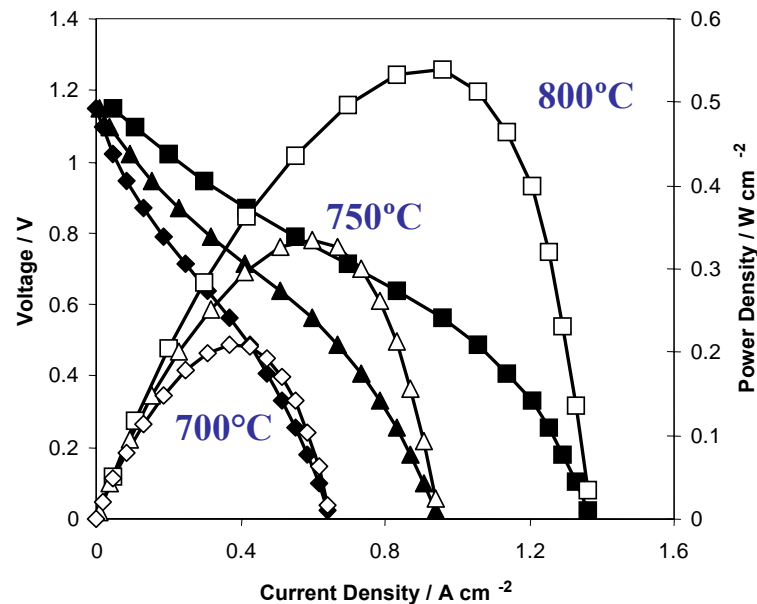
YSZ electrolyte

Porous YSZ-active region

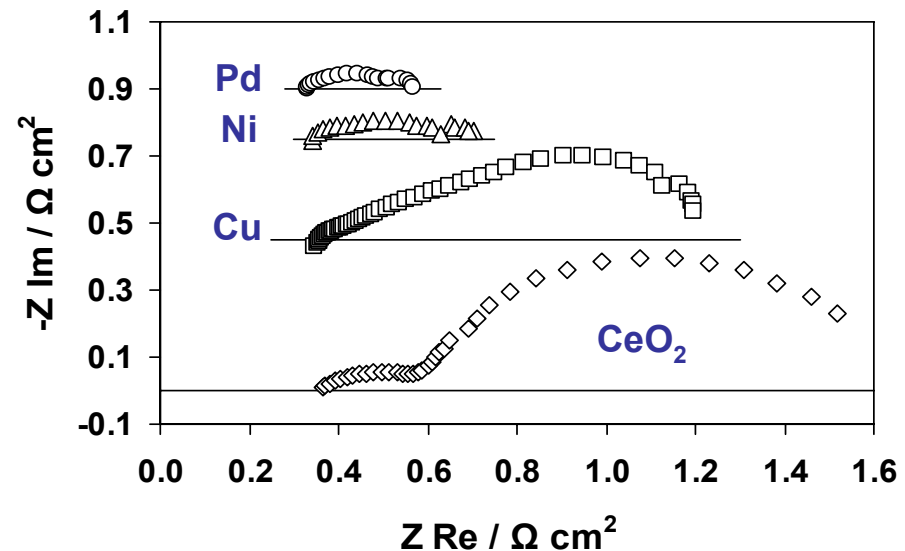
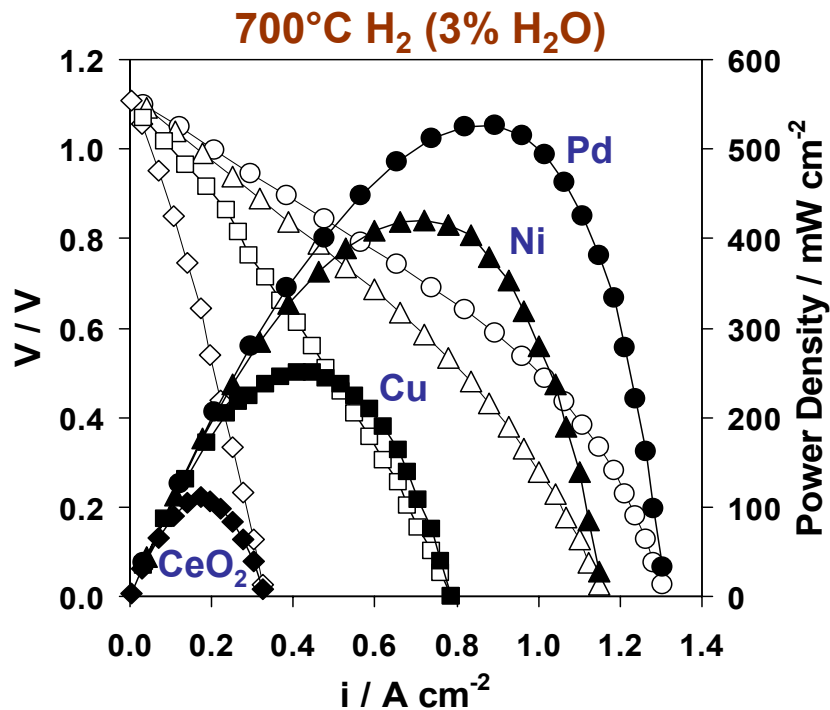
$\text{La}_{0.3}\text{Sr}_{0.7}\text{TiO}_3$  current collector



**CH<sub>4</sub> (3% H<sub>2</sub>O)**



# Catalysis is crucial!



**40 wt% CeO<sub>2</sub>**

**Pd 1 wt%**

**Ni 1 wt%**

**Cu 5 wt%**

**Need combination of  
ceria and metal**

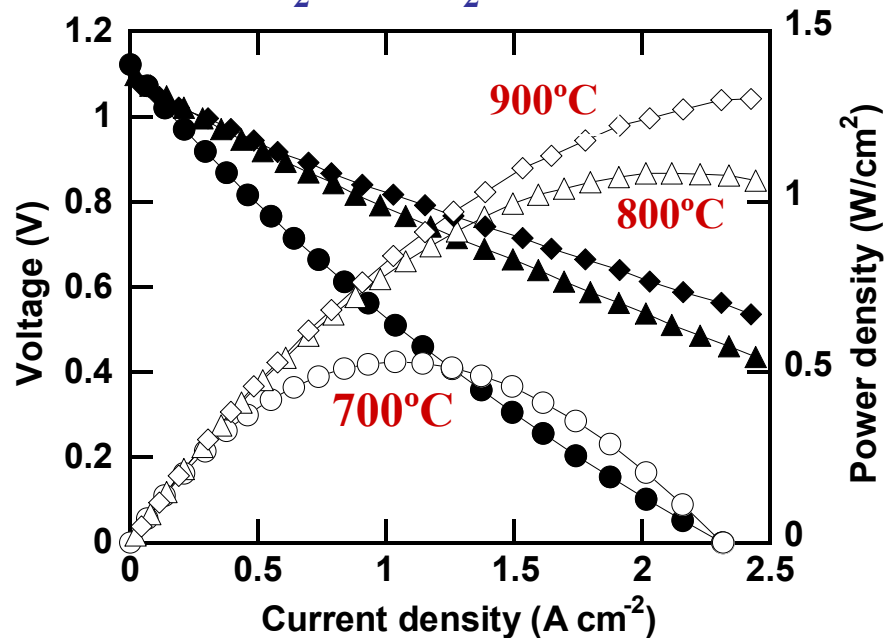
# Improved conductivity with LSCM ( $\text{La}_{0.8}\text{Sr}_{0.2}\text{Cr}_{0.5}\text{Mn}_{0.5}\text{O}_3$ ):

**Anode: 45-wt% LSCM, 5-wt% ceria, 0.5-wt% Pd**

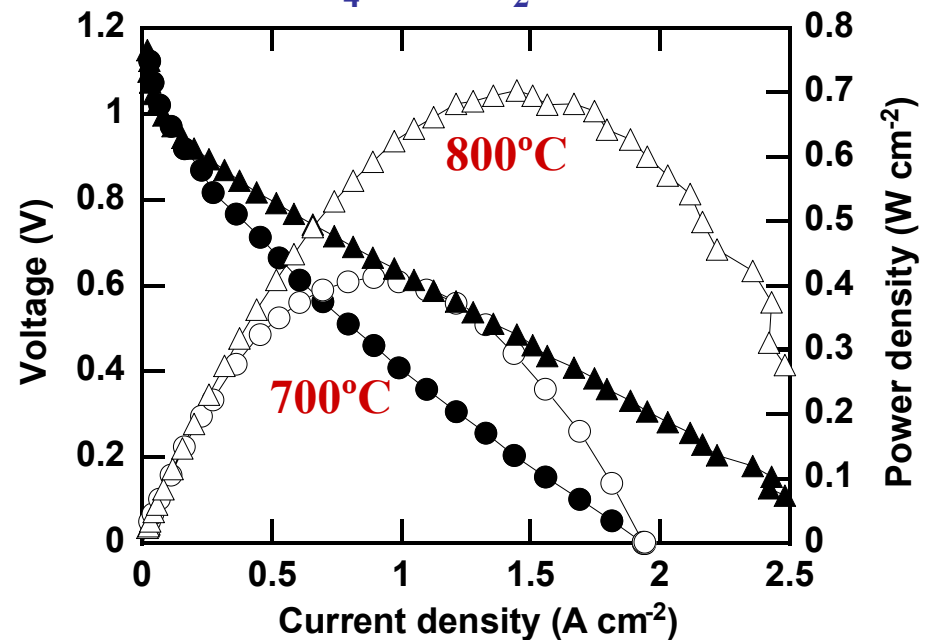
**Cathode: 40-wt% LSF**

**Electrolyte: 60 micron YSZ**

**97%  $\text{H}_2$ -3%  $\text{H}_2\text{O}$**



**97%  $\text{CH}_4$ -3%  $\text{H}_2\text{O}$**

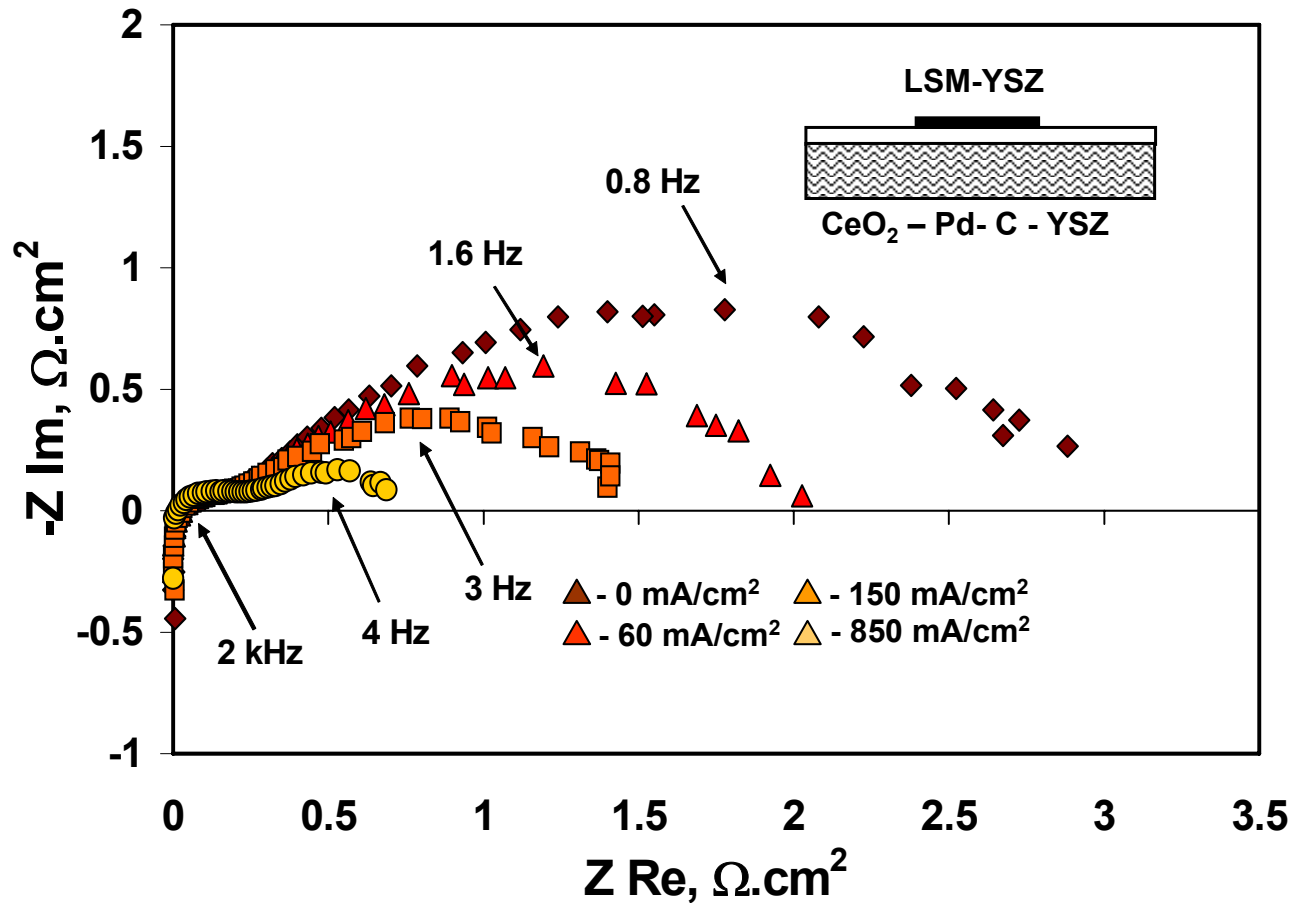


# How does polarity affect electrodes?

## LSM-YSZ: Show activation under fuel cell load.

ESSL, 7 (2004) A111-A114.

700°C, H<sub>2</sub>/3%H<sub>2</sub>O, OCV after applying current



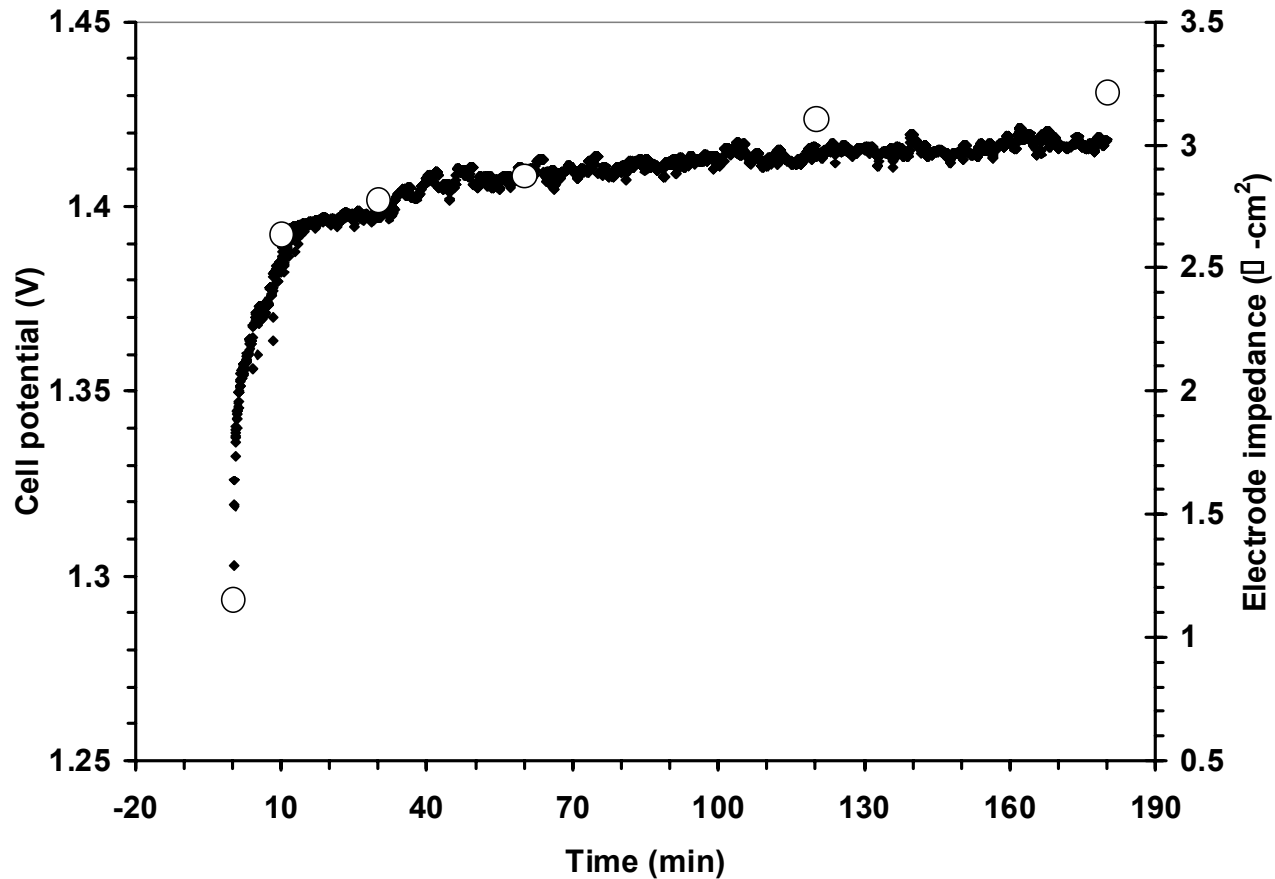
**Note: These changes are reversible.  $\tau \sim 120$  minutes.**

# Consequences for electrolysis?

JECS, 153 (2006) A2066.

285 mA/cm<sup>2</sup>; 700°C; 85%H<sub>2</sub>-15%H<sub>2</sub>O| air

**LSM-YSZ anode (initially activated by polarization)**



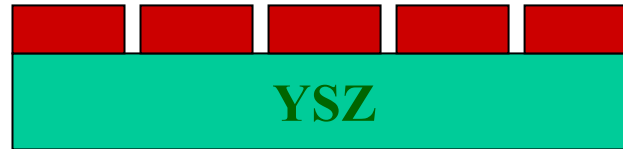
# What we believe is happening:

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**Electrode before activation**



**Activated Electrode**



**1) Dense LSM covers YSZ**

**Gaps in LSM film caused by reduction**

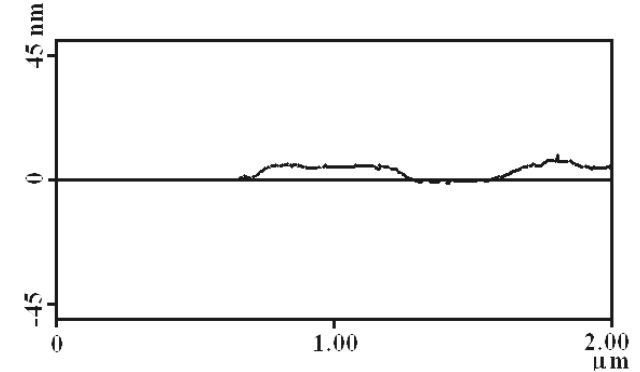
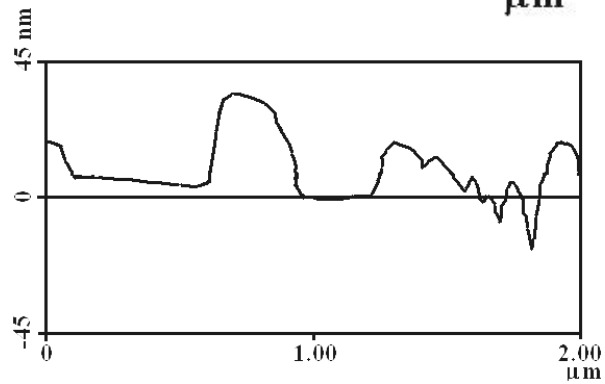
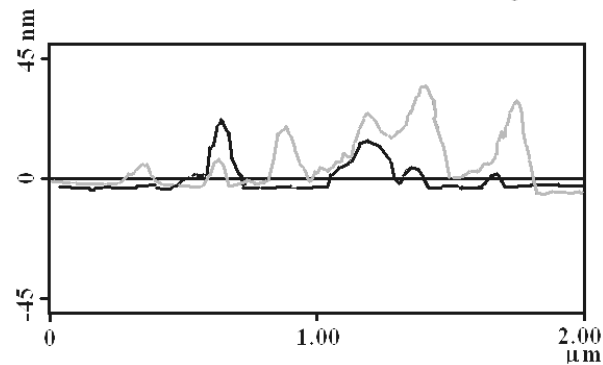
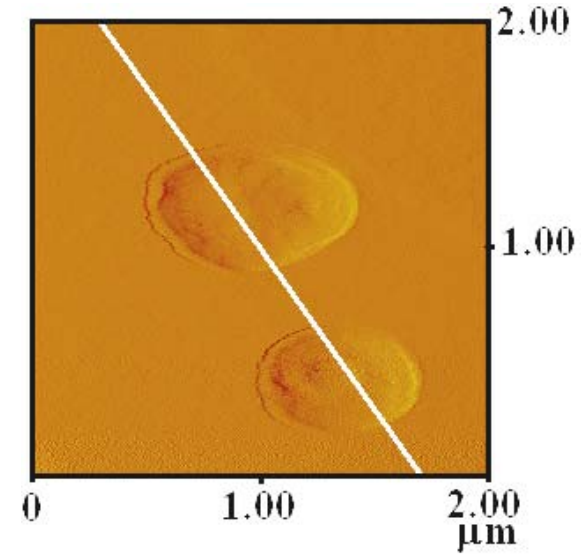
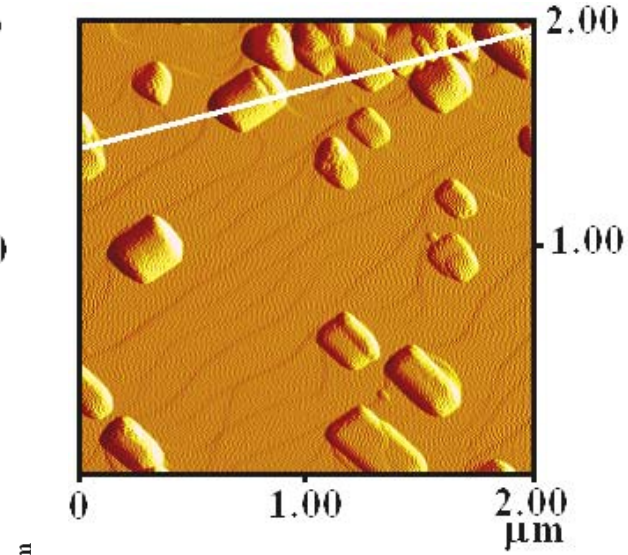
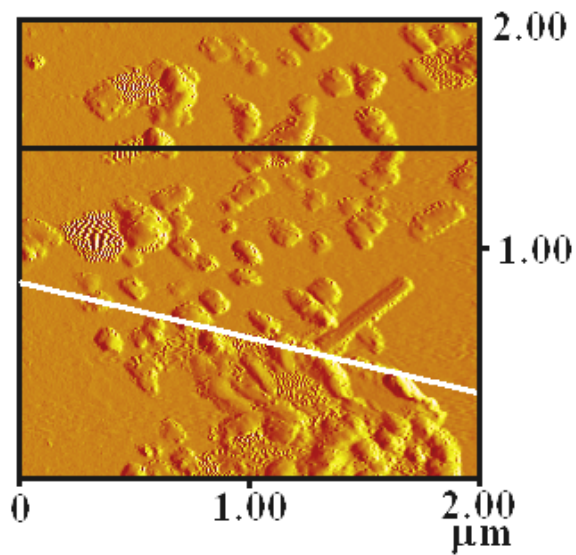
**2) Performance limited by oxygen diffusion.**

**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

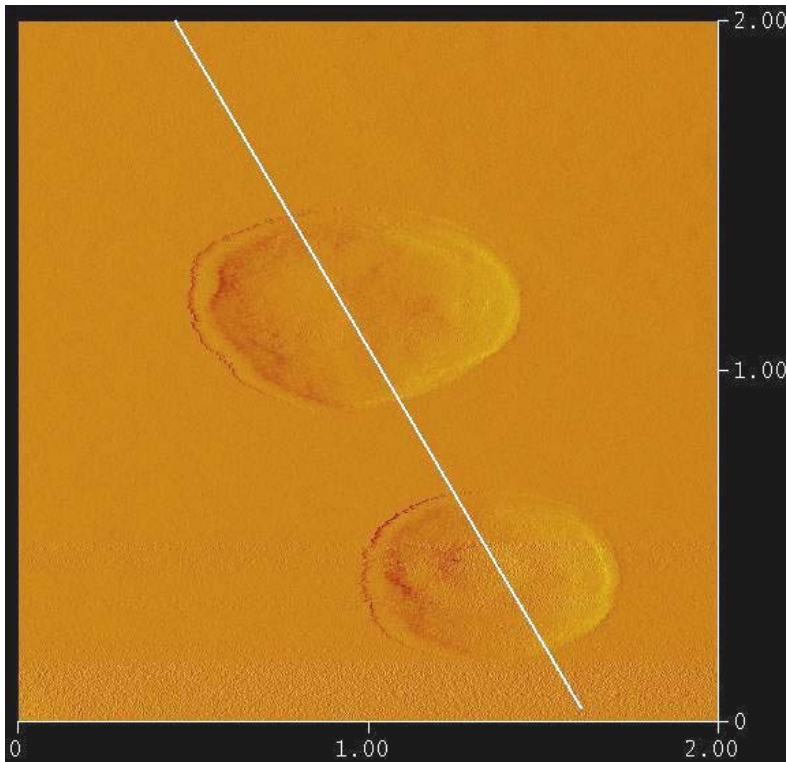
1050°C

1150°C

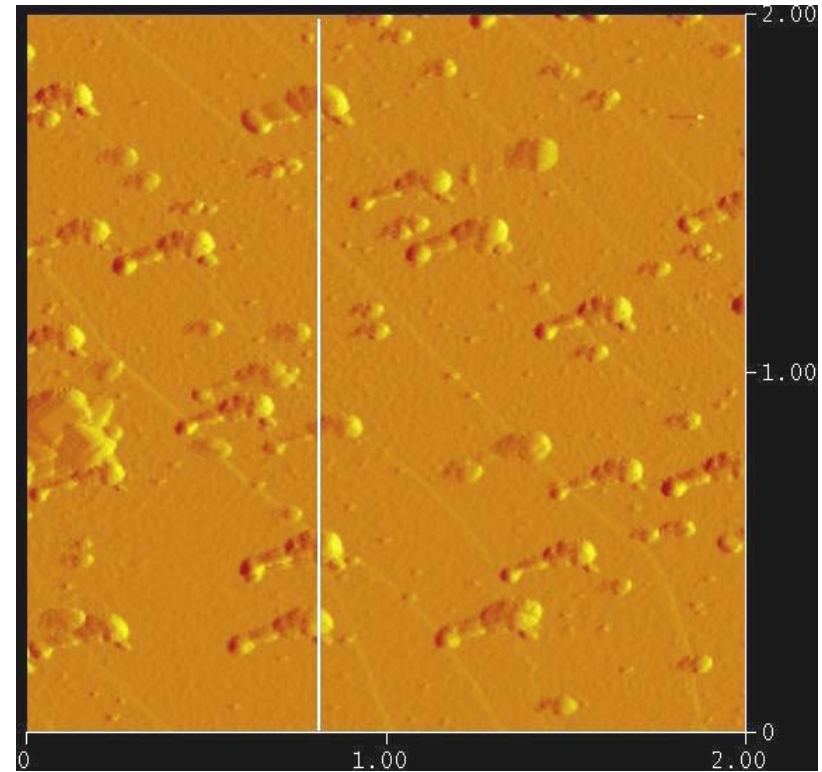
# Movement of particles is reversible:

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Calcination at 1150°C



Reduced in H<sub>2</sub> (10%H<sub>2</sub>O) at 700°C  
2 μm x 2 μm

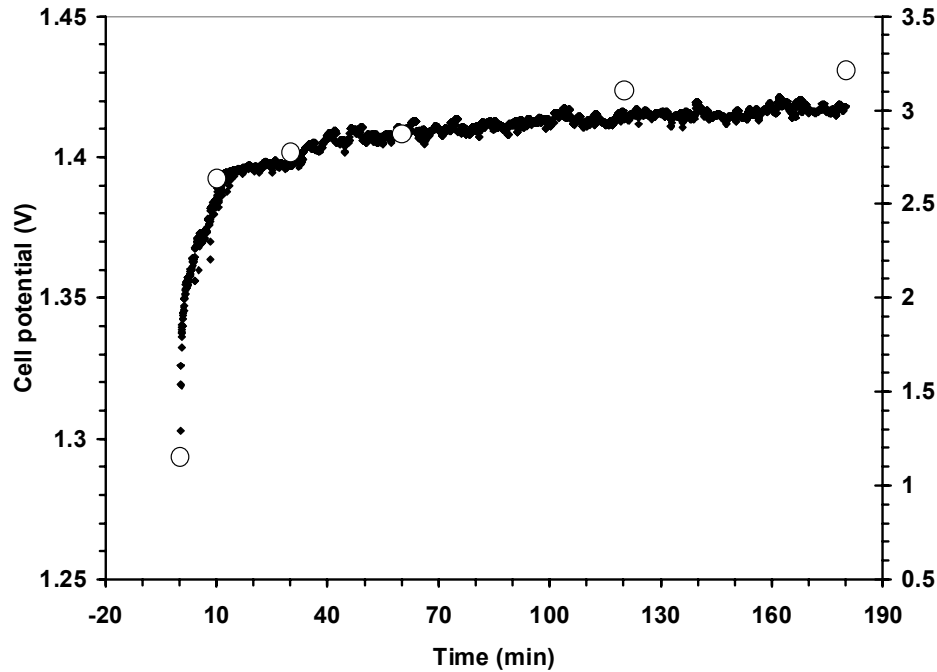


- 1) LSM is stable in 10%H<sub>2</sub>O-90% H<sub>2</sub> at 700°C.
- 2) Reducing LSM-YSZ electrode “activate” it.

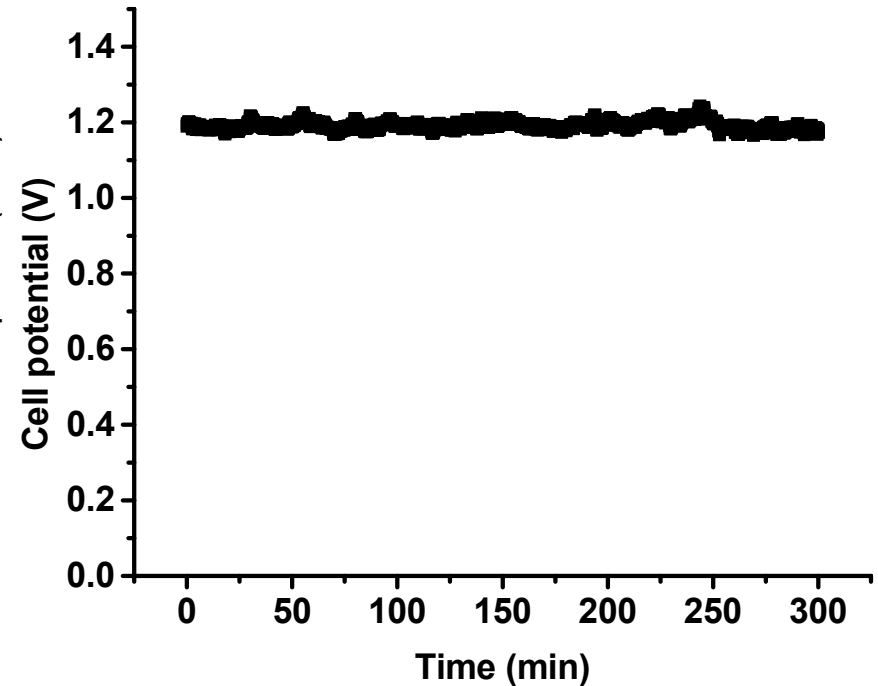
# Replace LSM to avoid this problem:

285 mA/cm<sup>2</sup>; 700°C; 85%H<sub>2</sub>-15%H<sub>2</sub>O | air

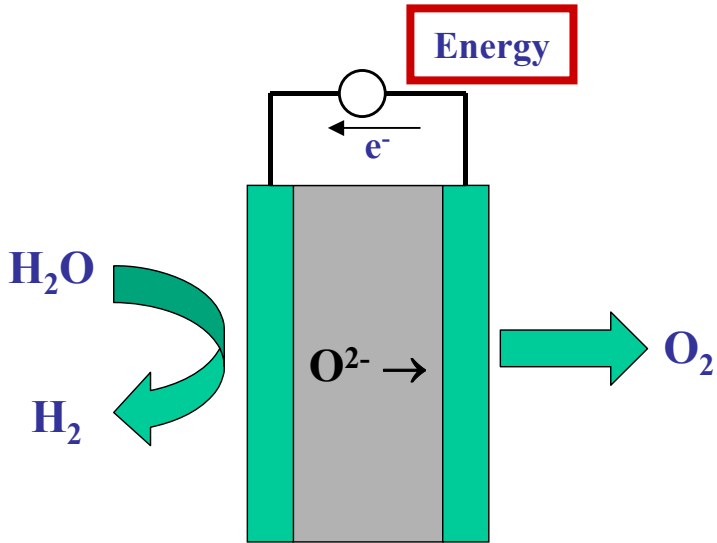
**LSM-YSZ anode (initially activated by polarization)**



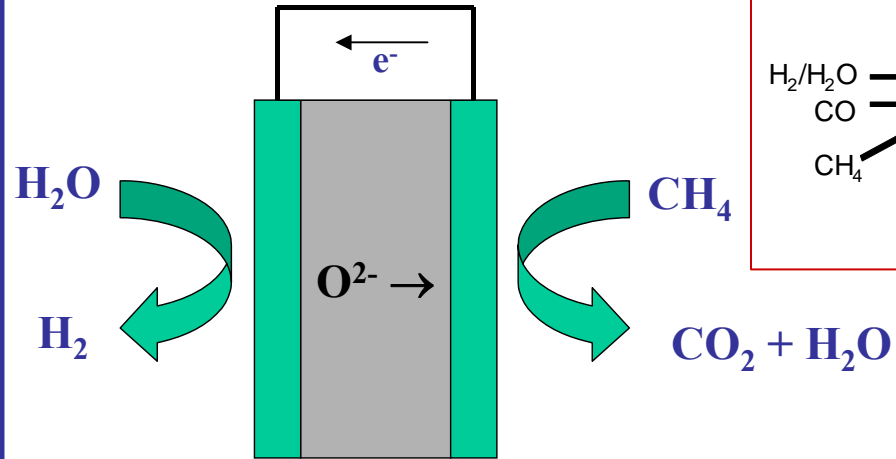
**LSF-YSZ anode**



# SOE



# NGASE



## Nernst Potential

Cathode:  $\text{H}_2/\text{H}_2\text{O}$

air  $\rightarrow$  1.0V

0.5V

$\text{H}_2/\text{H}_2\text{O}$   $\rightarrow$  0V

CO  $\rightarrow$

$\text{CH}_4$   $\rightarrow$  -0.5V

Anode

Electrolysis requires  $V > V_{\text{Nernst}}$

SOE are more efficient

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

No external power required.

Produces pure  $\text{H}_2$ .

High efficiency possible.

Membrane can be mixed conducting