Novel Approaches for the Electrolysis of Water in Solid Oxide Electrolyzers

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Support: DOE-BES (H_2 program)

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Solid Oxide Electrolyzer (SOE)

Ceramic membrane reactor in which electrical energy is used to dissociate water into H_2 and O_2.

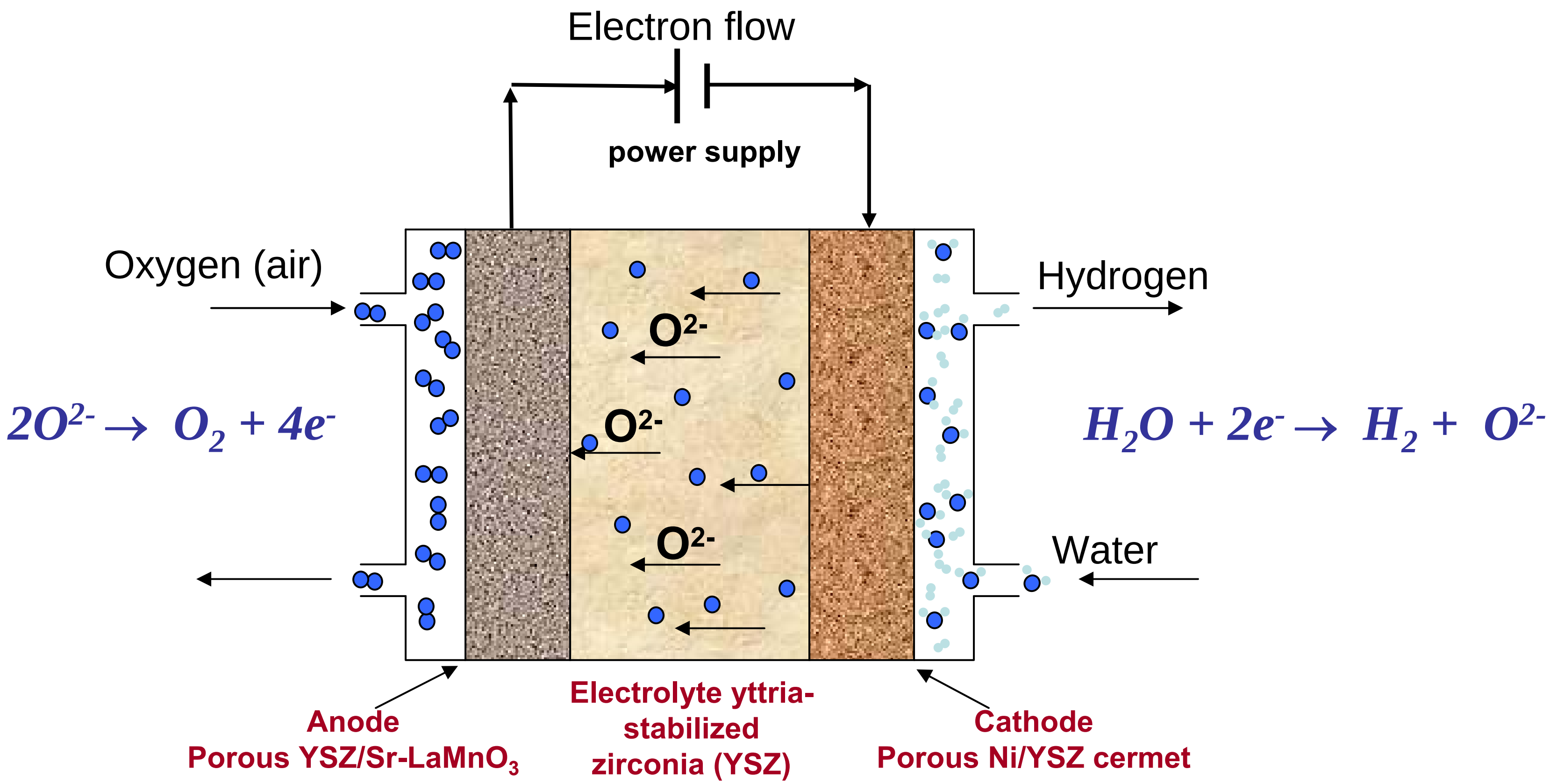
Advantages:

- Produces H_2 diluted only in H_2O
- Can produce H_2 at elevated pressures
- No green house gas emissions if powered by electricity from nuclear, solar, or wind.
- Could be used in distributed H_2 production systems

Talk Outline

- Introduction to SOE
- Materials issues in SOE cell fabrication
- Materials for conventional anodes
- Materials for hydrocarbon assisted anodes

Solid Oxide Electrolyzer



Temperature: 700 - 1000°C

Current Density: 0.1 - 1.0 W/cm^2

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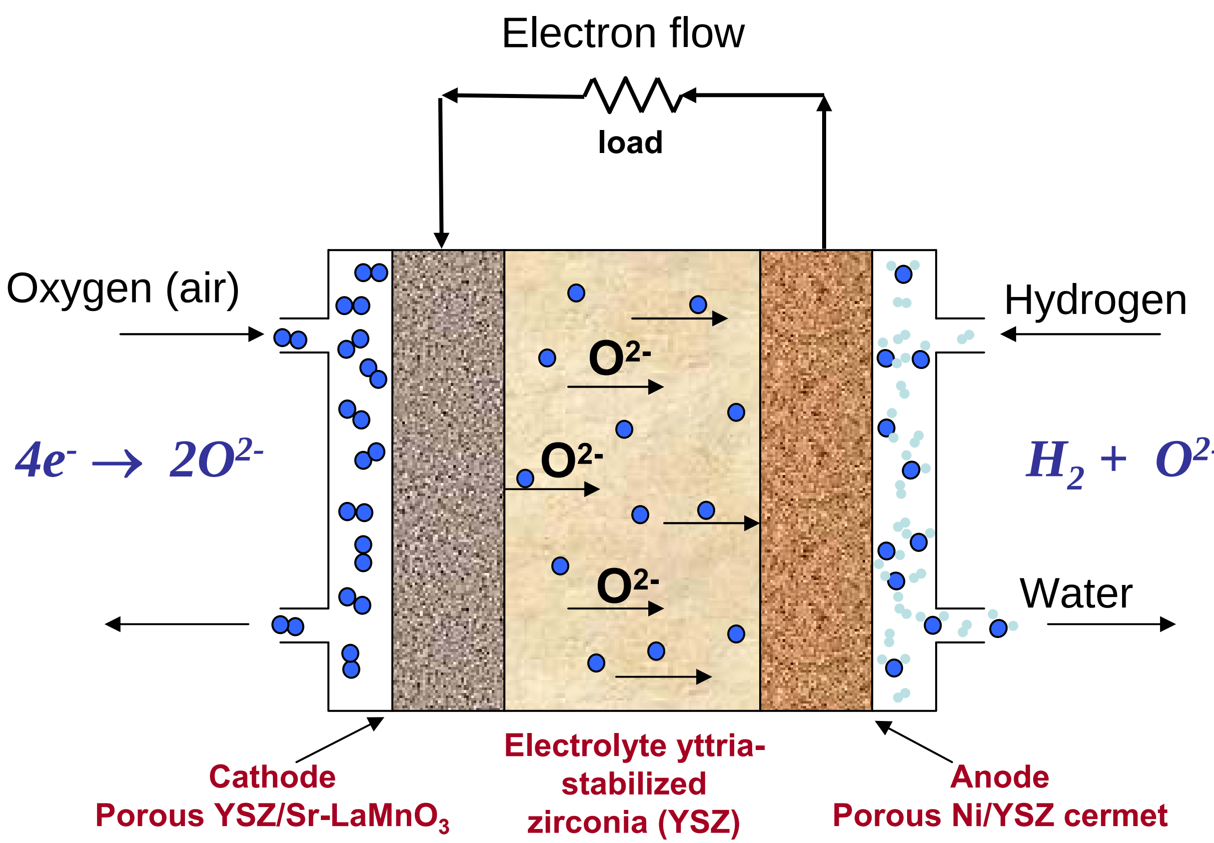
Solid Oxide Fuel Cell



$$O_2 + 4e^- \rightarrow 2O^{2-}$$

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

Temperature: 700 - 1000°C

Current Density: 0.1 - 1.0 W/cm^2

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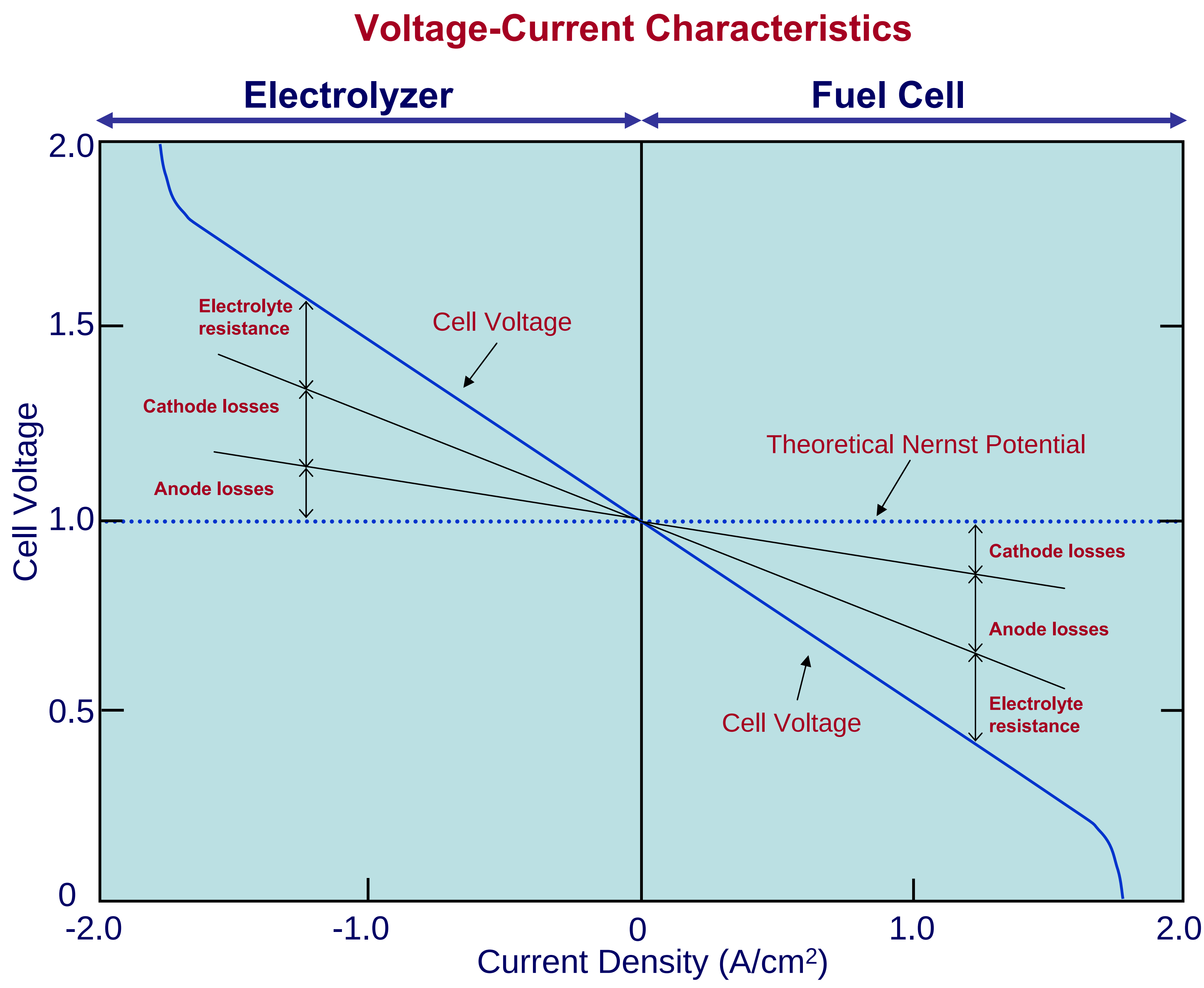
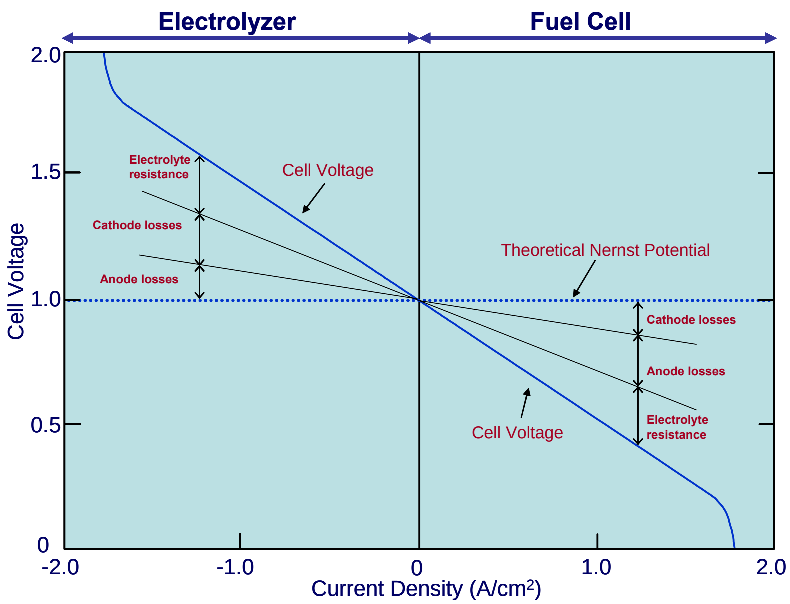


Voltage-Current Characteristics
Electrolyzer
Fuel Cell
2.0
1.5
1.0
0.5
0
Cell Voltage
Electrolyte resistance
Cathode losses
Anode losses
Cell Voltage
Theoretical Nernst Potential
Cathode losses
Anode losses
Electrolyte resistance
Cell Voltage
-2.0
-1.0
0
1.0
2.0
Current Density (A/cm2)

Voltage-Current Characteristics



Open Circuit Voltage:

$$V = \frac{\Delta G_{rxn}}{nF} = \text{Nernst Potential}$$

Electrolyte Losses:

$$\Delta V = i \cdot R_{electrolyte}$$

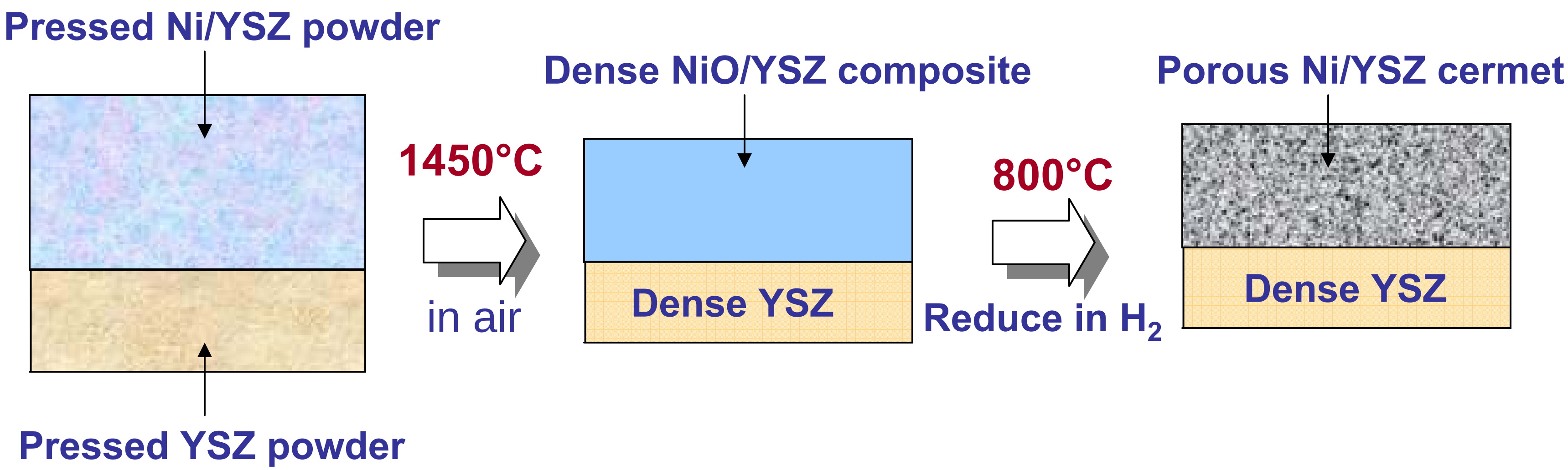
Electrode Losses:

$$\Delta V = \eta_{overpotential} = i \cdot R_{electrode}$$

$R_{electrode}$ accounts for:
- Reaction Kinetics
- Diffusion

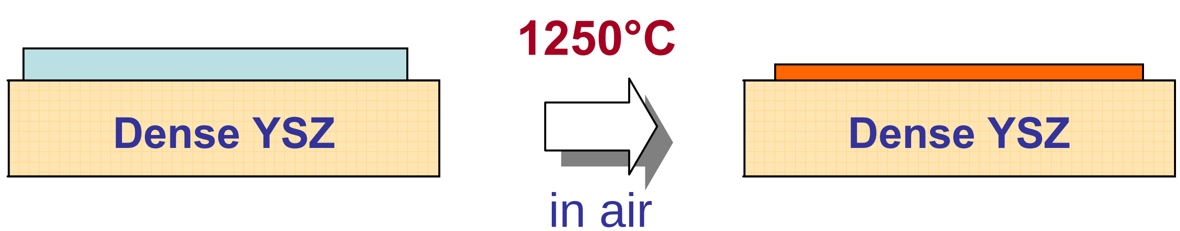
“Traditional” Cell Fabrication

- **Fuel electrode and electrolyte**



- **Air electrode**

Screen print LSM-YSZ slurry and anneal at 1250ºC



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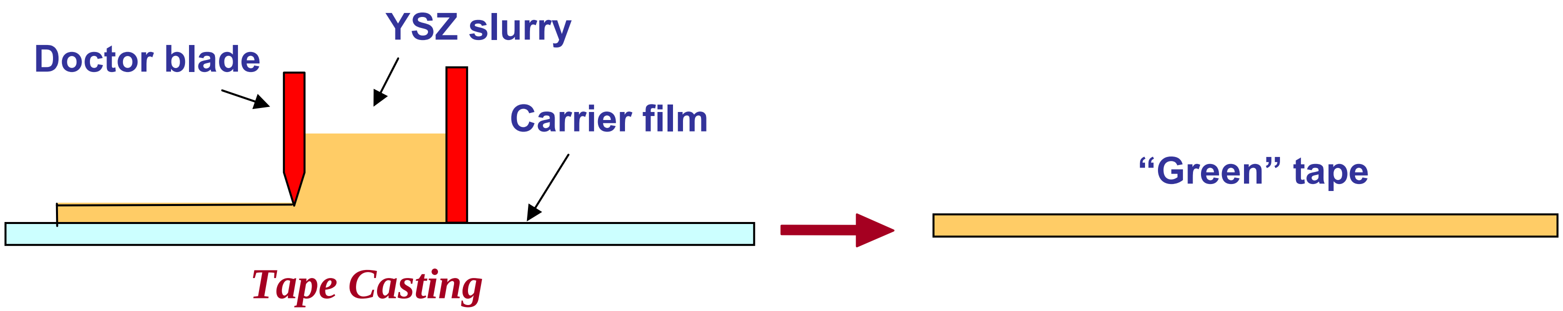
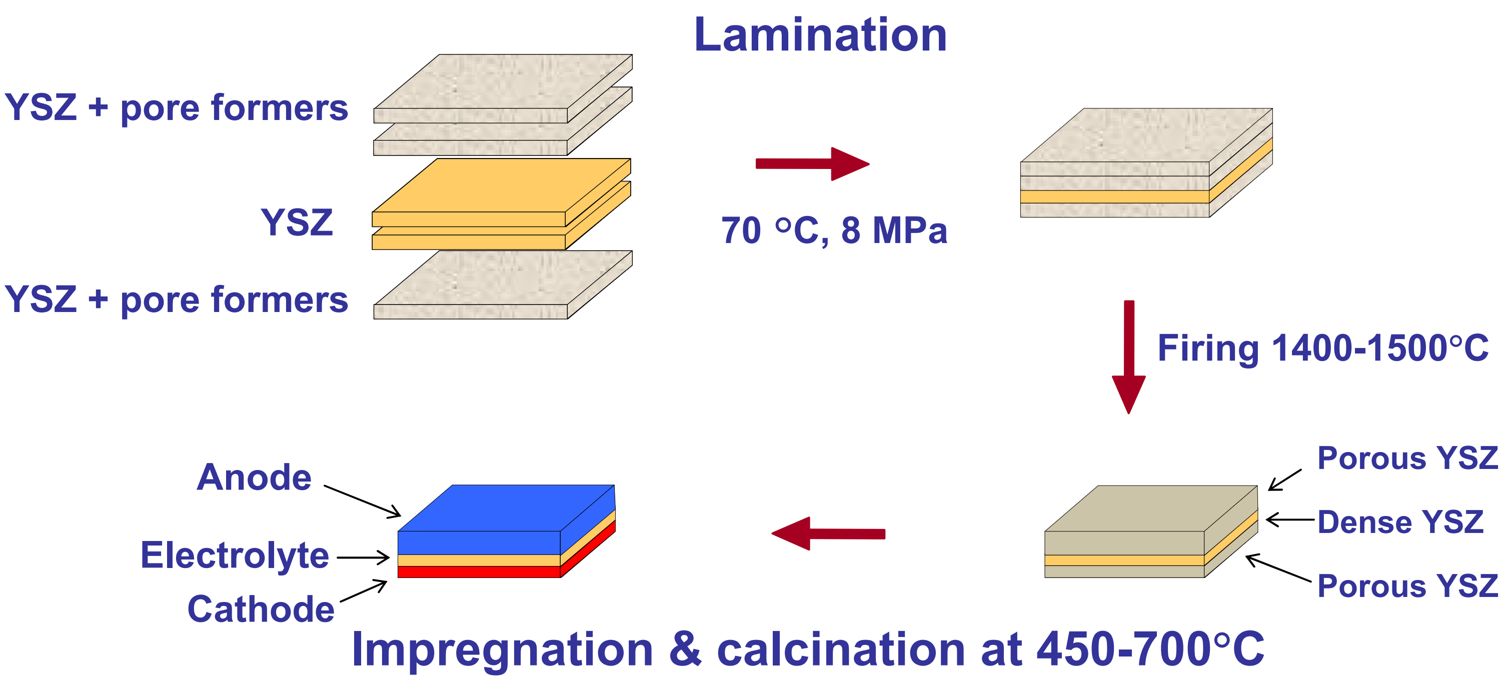
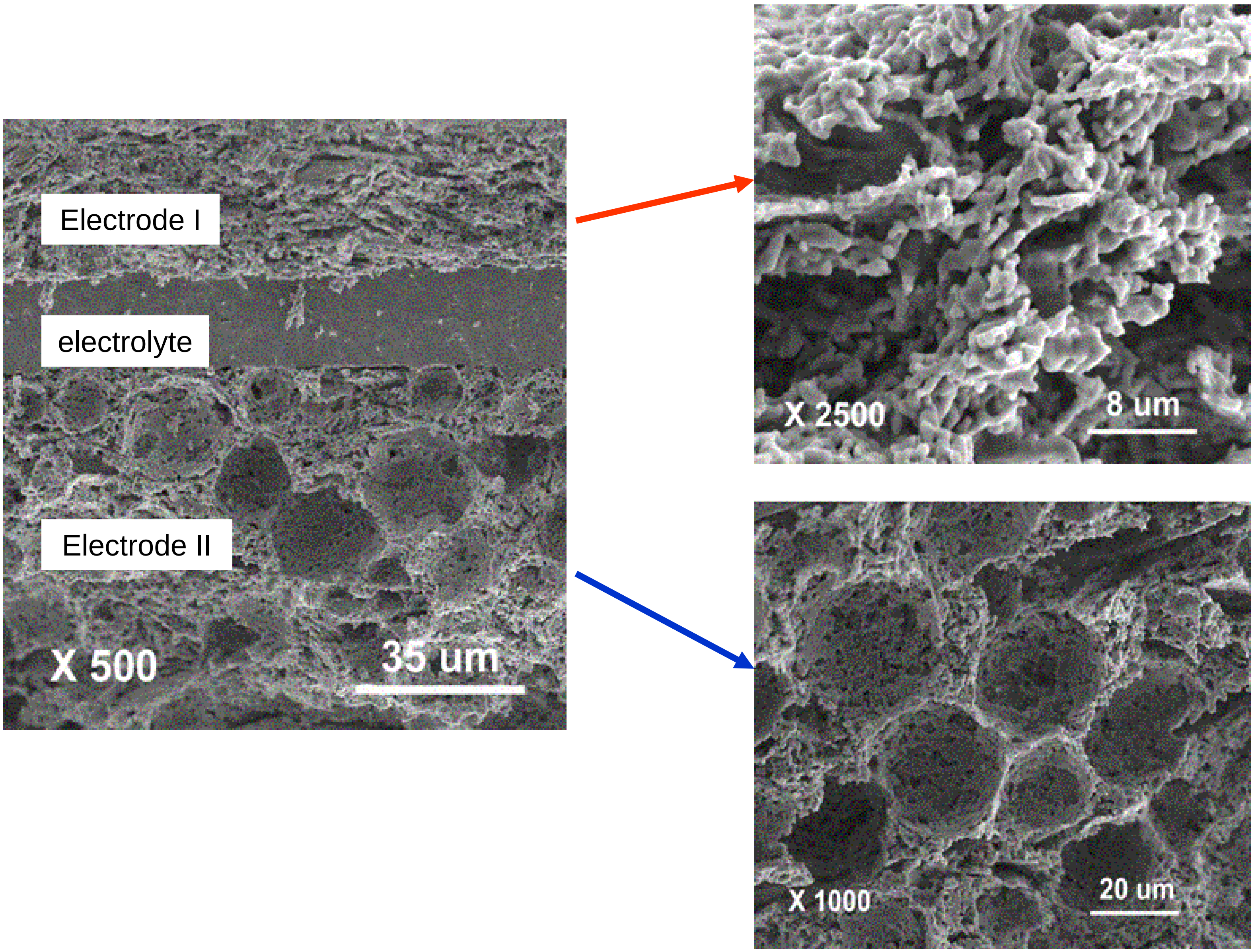
Cell fabrication using laminated tapes and impregnation



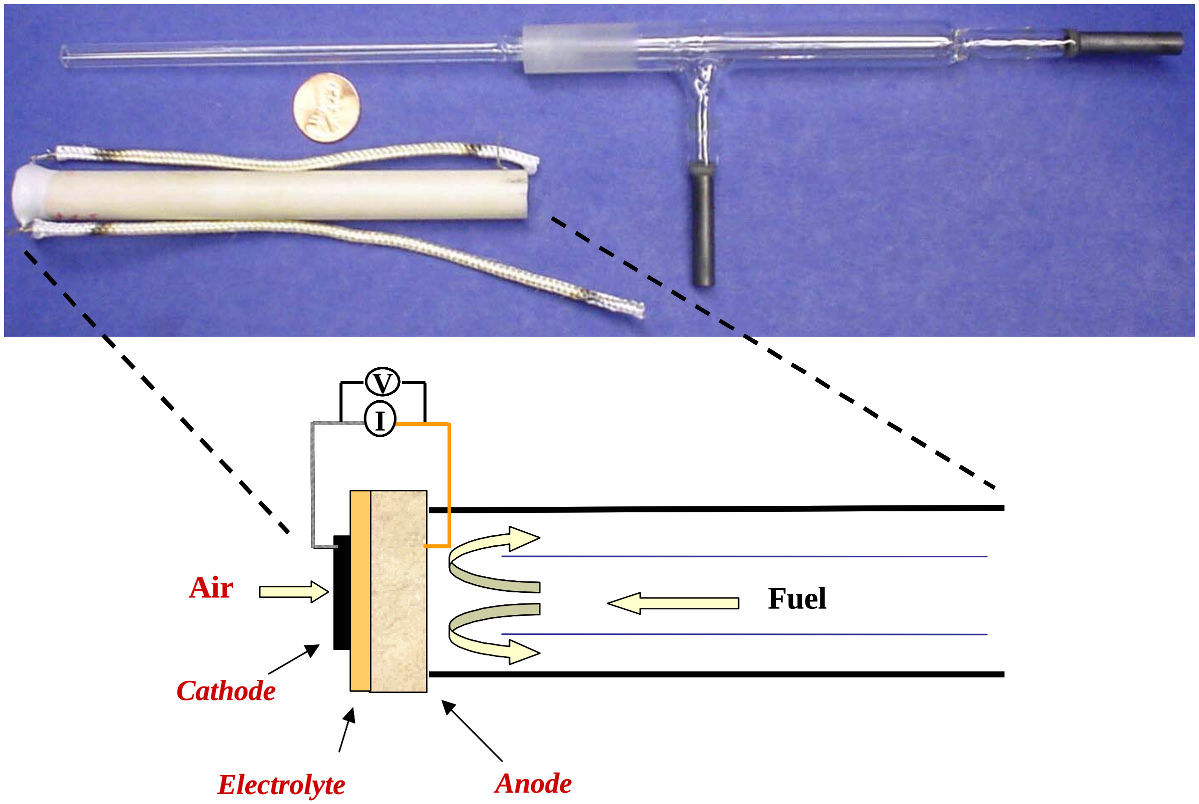


- Only one high-T sintering step is required.
- Impregnation of anode and cathode provides flexibility in choice of materials.

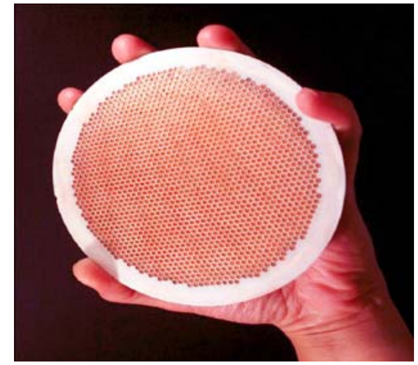
Cell Microstructure:



Lab Scale



Commercial



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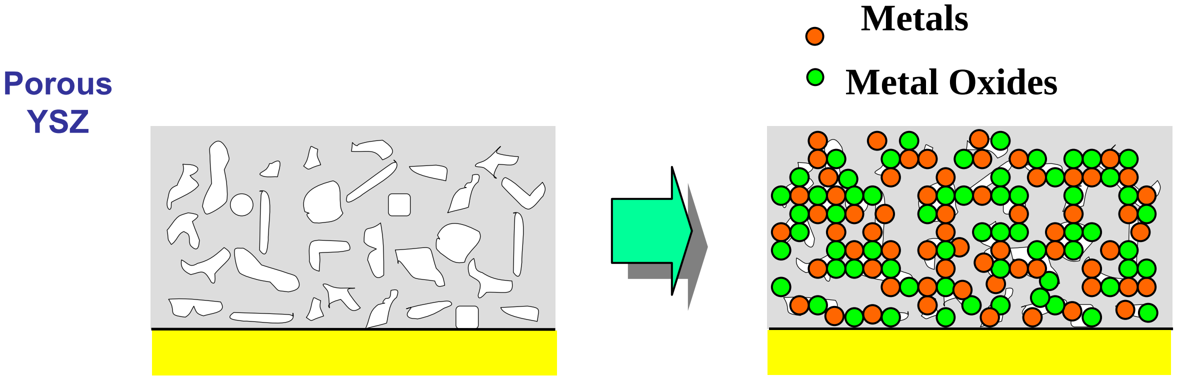
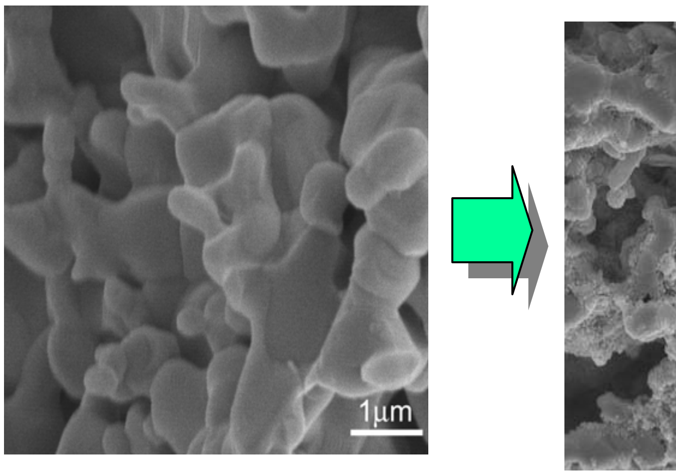
Electrode Fabrication

Active phase added separately

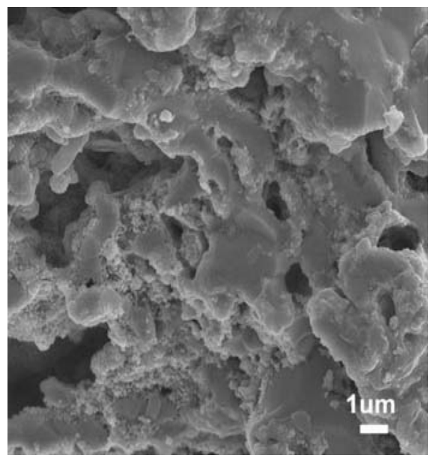


Impregnation with aqueous salt solutions followed by oxidation or reduction

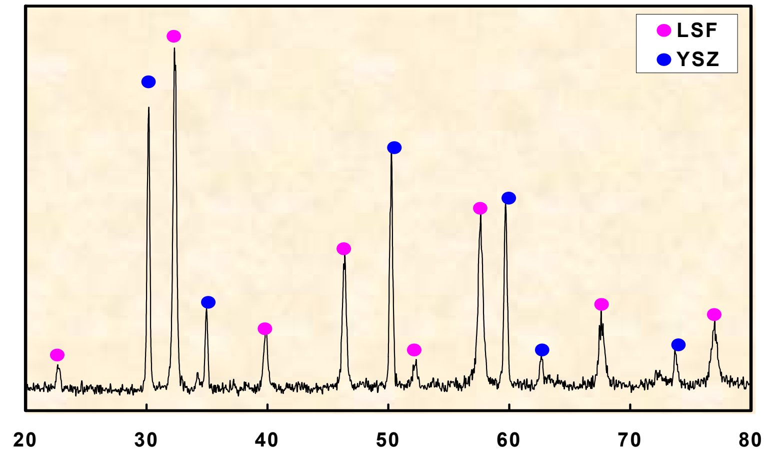
Porous YSZ



After addition of 40 wt% $La_{0.8}Sr_{0.2}FeO_3$



XRD



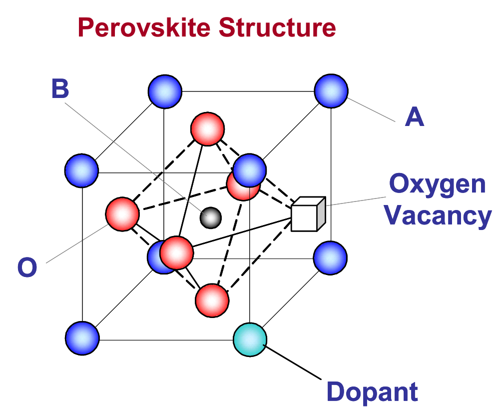
Materials for Air Electrode

SOFC Cathode

SOE Anode

- Electronically conducting perovskites (ABO_3) are used for SOFC cathodes

Composition	*CTE* $(10^{-6}K^{-1})$	*Electrical Conductivity (S/cm) at 700°C*	*Oxygen Diffusivity, at 700°C, (cm^2s^{-1})*
$La_{0.8}Sr_{0.2}MnO_3$	11.2	200	3.1×10^{-16}
$La_{0.8}Sr_{0.2}FeO_3$	13	120	4×10^{-8}
$La_{0.6}Sr_{0.4}CoO_3$	20	1800	1.04×10^{-8}



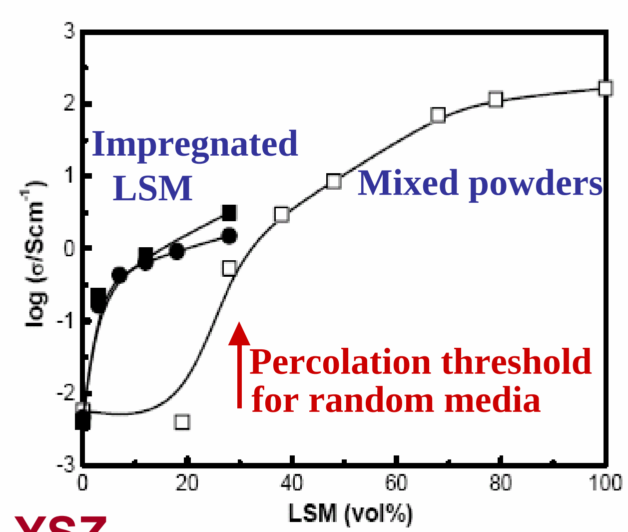
- A composite of YSZ and LSM is generally used as the cathode in an SOFC. Poor performance at low T, but easy to process.
- LSCo and LSF have higher electronic and ionic conductivity than LSM but they also have a larger CTE mismatch with YSZ and are more reactive toward YSZ
- Little data on the performance of these materials as anodes for SOEs

Advantages of Impregnated Electrodes:

- **Separate firing temperatures for YSZ and active phase.**
  - **- Avoids reactions between LSF, LSCo & YSZ.**
  - **- Can use low-melting solids (e.g. Cu).**

- **Composite has non-random structure.**

  - Electrical conductivity of LSM-YSZ



700°C in air

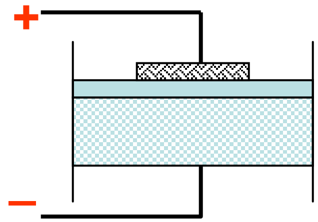
electrode calcined at 1523 K.

- CTE of LSCo-YSZ

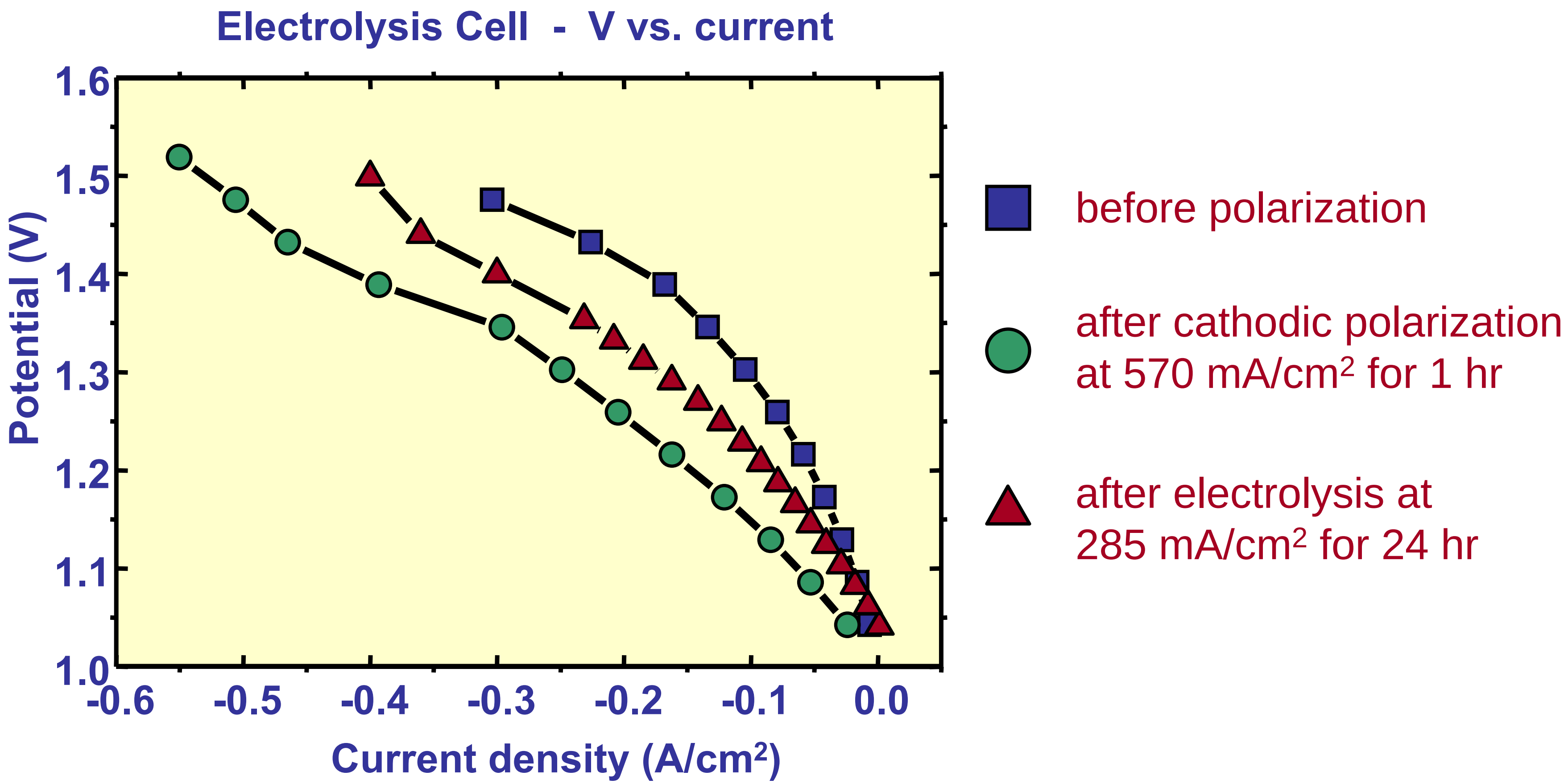
LSCo Weight Fraction in YSZ	0%	35%	45%	55%
CTE (10^{-6}/K), 300 to 1073 K	10.3	11.7	12.6	12.6

CTE of LSCo is $23x10^{-6}$/K

Performance of LSM during Electrolysis

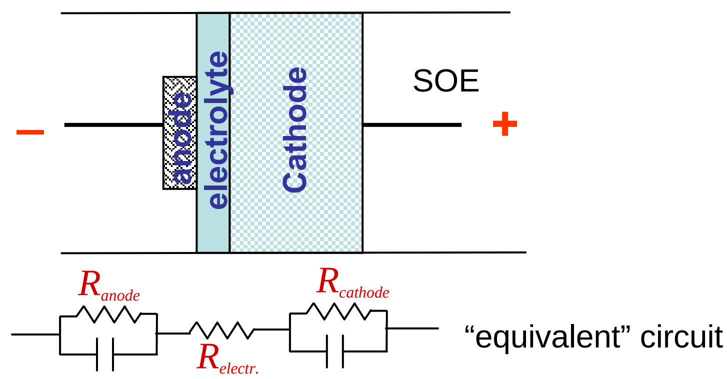


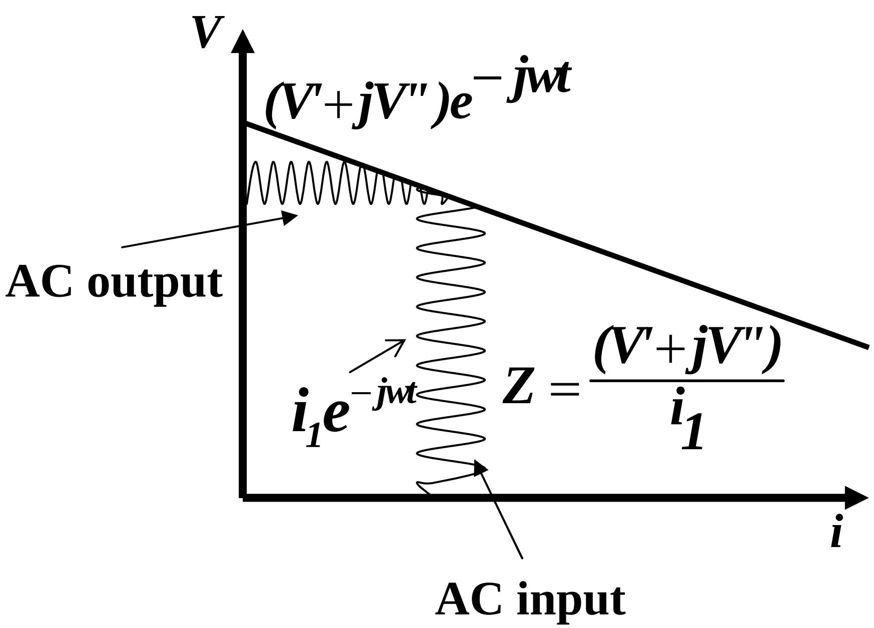
Anode:	LSM-YSZ, air
Electrolyte:	YSZ
Cathode:	CeO_2-Co, 85%H_2+15%H_2O

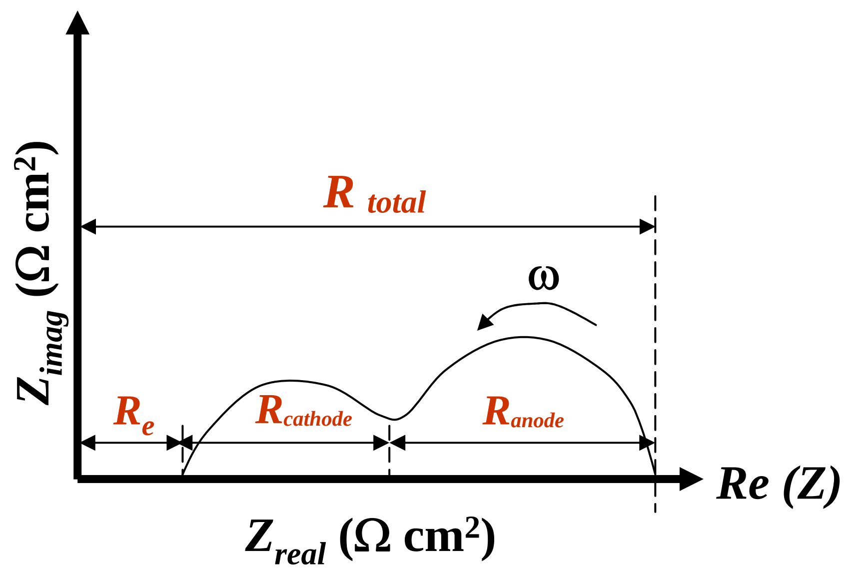


Analysis of Electrode Resistances

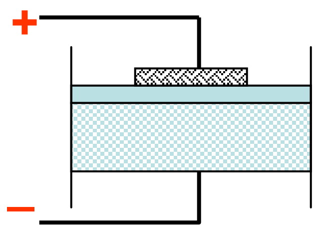
Electrochemical impedance spectroscopy (EIS)





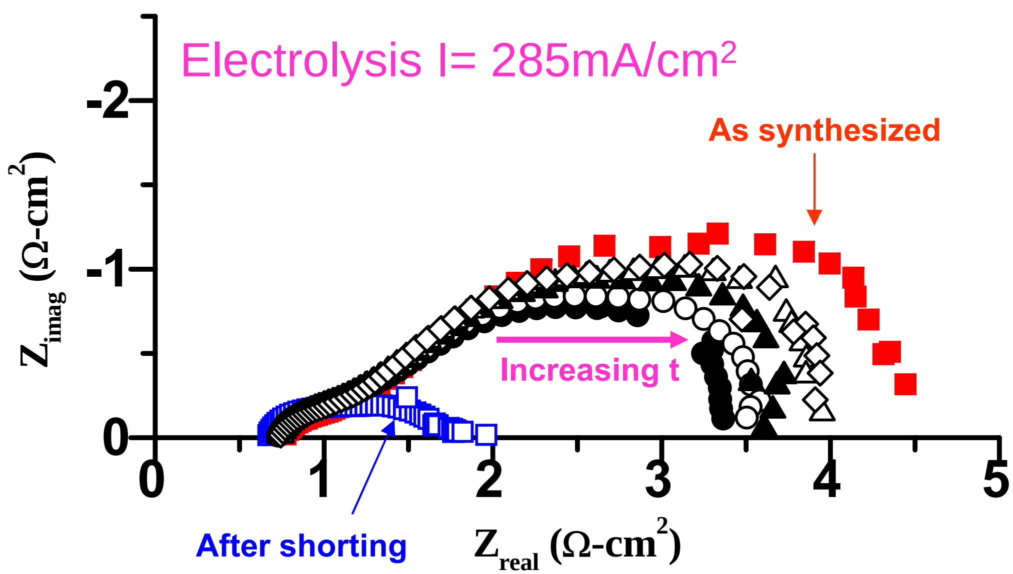


Performance of LSM during Electrolysis

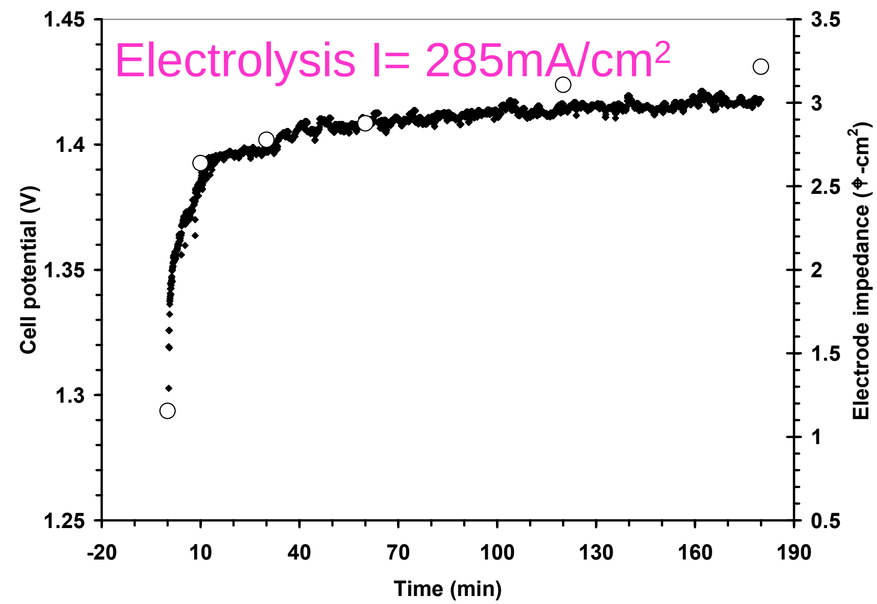


Anode: LSM, air
Electrolyte: YSZ
Cathode: CeO_2-Co, 85%H_2+15%H_2O

Impedance vs. polarization history



Cell potential vs. time



The performance of LSM is polarization-dependent

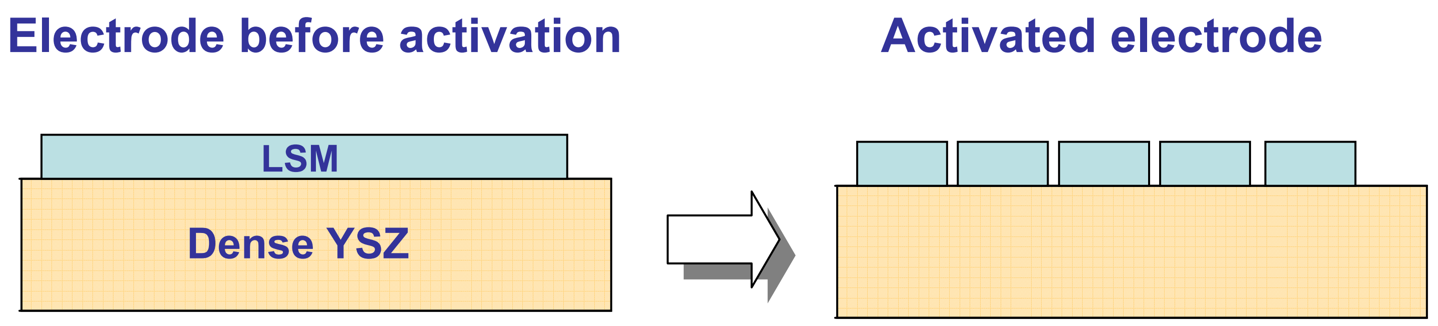
- Activated under cathodic polarization (fuel cell operation)
- Deactivated under anodic polarization (electrolysis operation)
- Reversible and time-dependent

BET Surface Area of 40 wt% LSM in YSZ

Sample	*Surface Area (m^2/g)*	*Average Pore Size (μm)*
Porous YSZ without LSM	0.77	1.6
LSM-YSZ 850ºC	2.53	
LSM-YSZ 1250ºC	0.38	0.58
LSM-YSZ 1250ºC reduced	0.78	

Polarization Activation of LSM - Mechanism?

Hypothesis

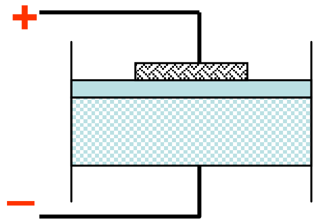


- Dense layer of LSM covers YSZ electrolyte
- Performance limited by oxygen diffusion through LSM layer

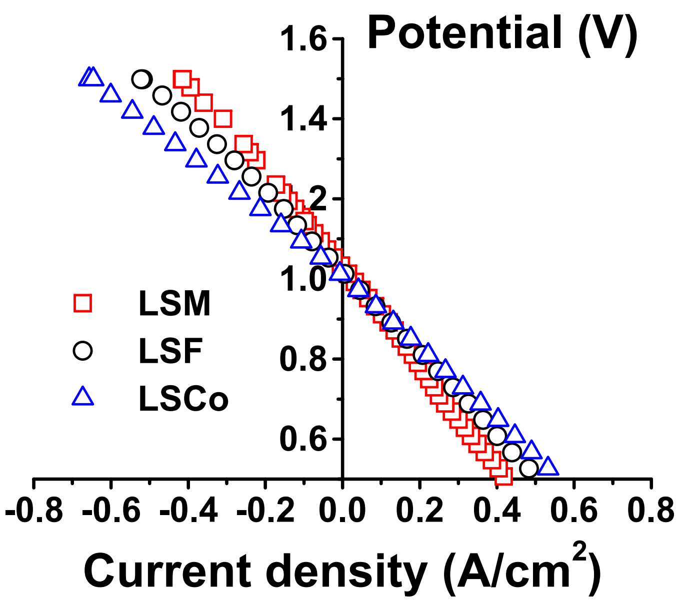
- Gaps in LSM layer are formed upon reduction
- Oxygen diffusion limitations are reduced

Process driven by interactions at the LSM-YSZ interface and the local $P(O_2)$

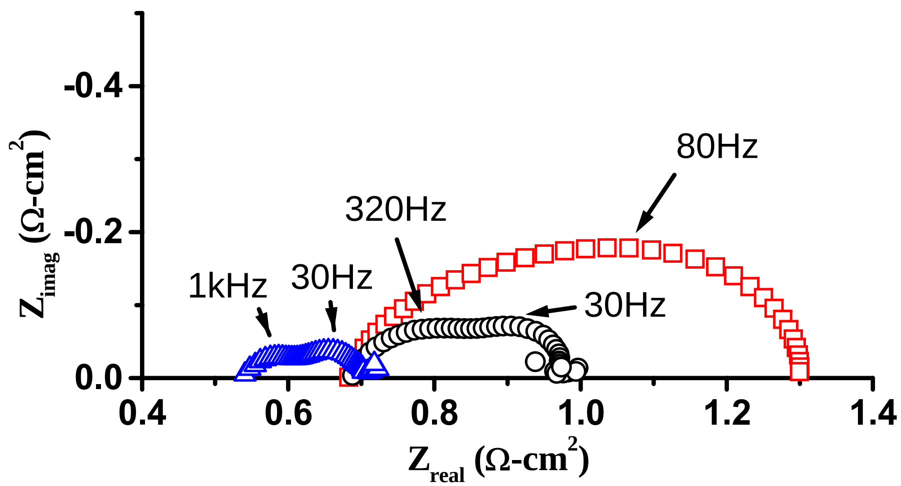
Comparison of LSM, LSF, and LSCo



Cathode: CeO_2+Co, 85%H_2+15%H_2O
Temperature: 700°C



V-I Curve

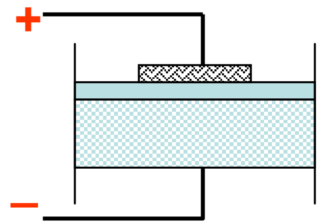


Total Impedance

Total polarization loss:
LSCo < LSF < LSM

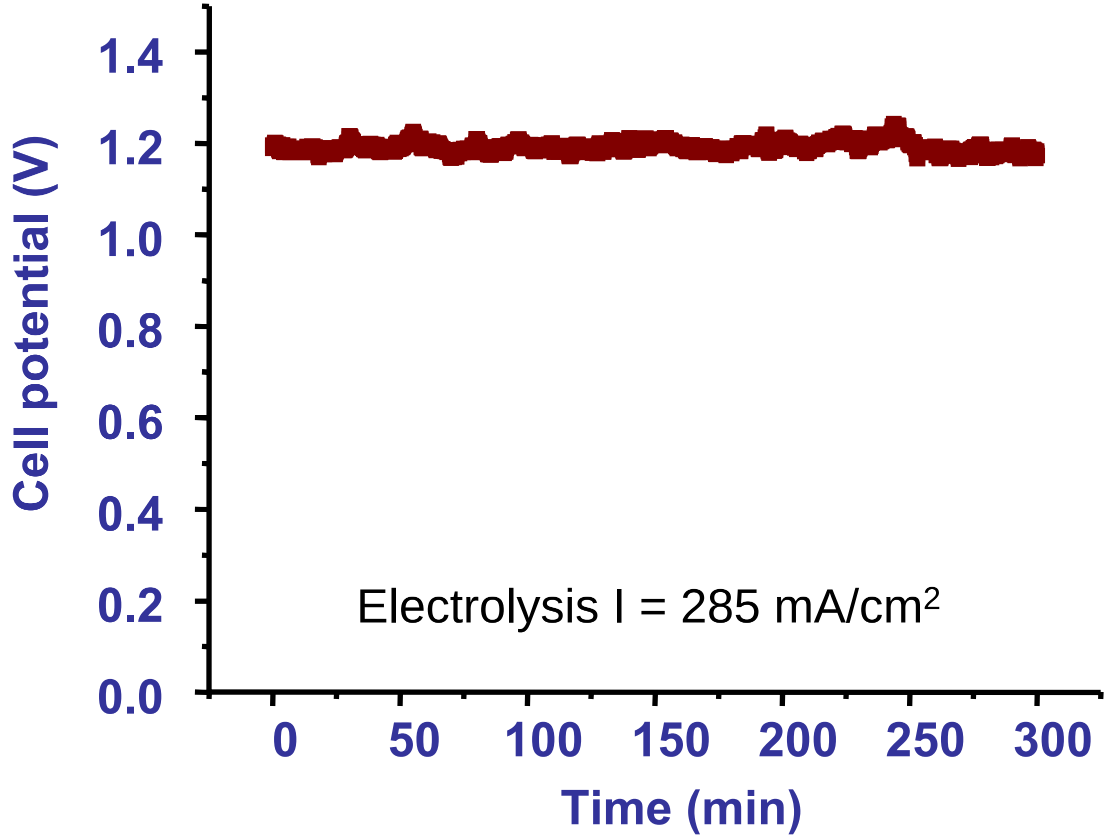
Total electrode loss:
LSCo < LSF < LSM

Performance of LSF during Electrolysis



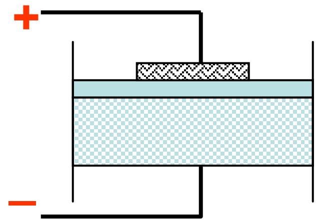
Anode : LSF, air

Cathode: Ceria-Co, 85%H_2+15%H_2O

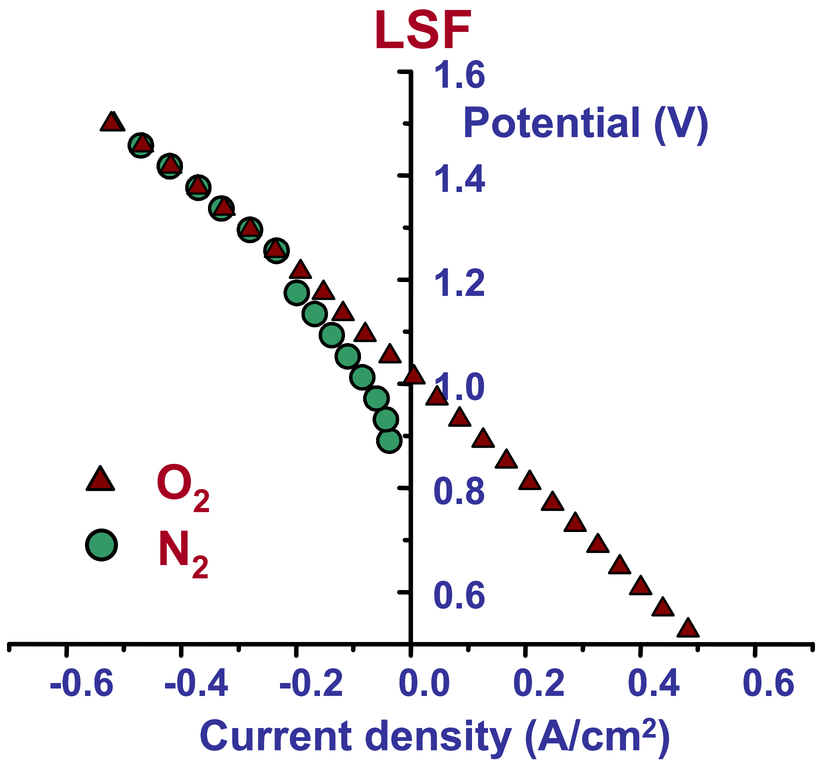


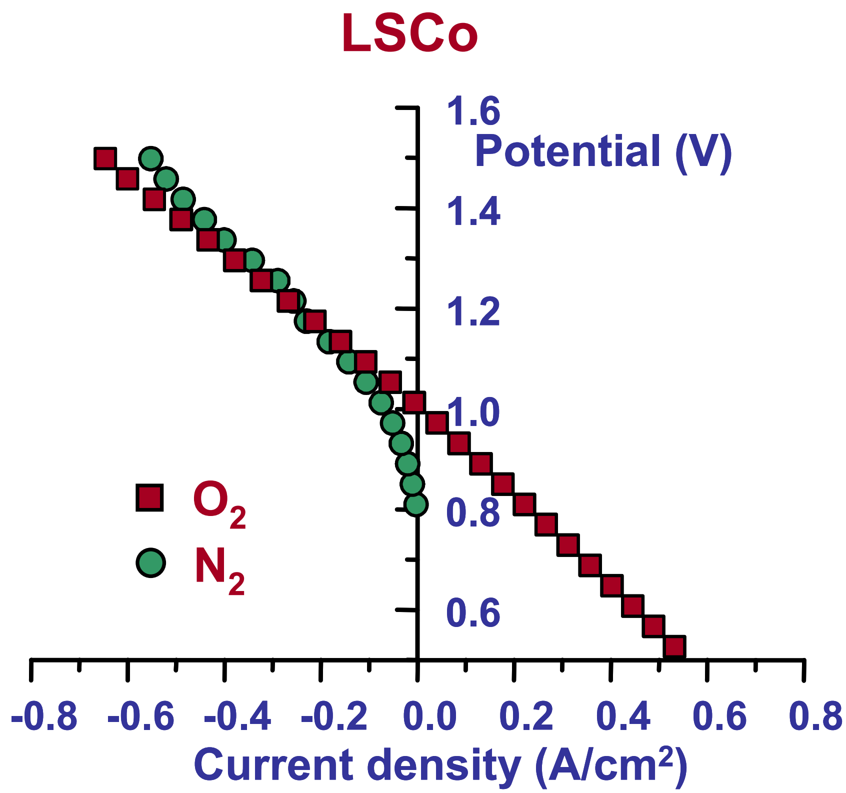
LSF electrodes do not exhibit activation polarization and are stable during electrolysis

Influence of P_{O_2} on Anode Performance



Cathode: CeO_2+Co, 85%H_2+15%H_2O
Temperature: 700°C





Performance of LSCo anode *increases* at high P_{O_2}

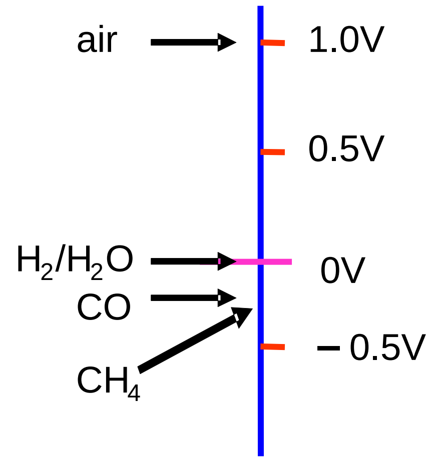
Increasing Efficiency: Hydrocarbon Assisted Electrolysis

Expose anode to reducing gases

- Reduces the oxygen chemical potential at the anode and decreases the open circuit voltage.
- Reduces required power input.
- May reduce cost since price of natural gas is ~1/3 that of electricity of equivalent energy value.
- Requires hydrocarbon tolerant anode

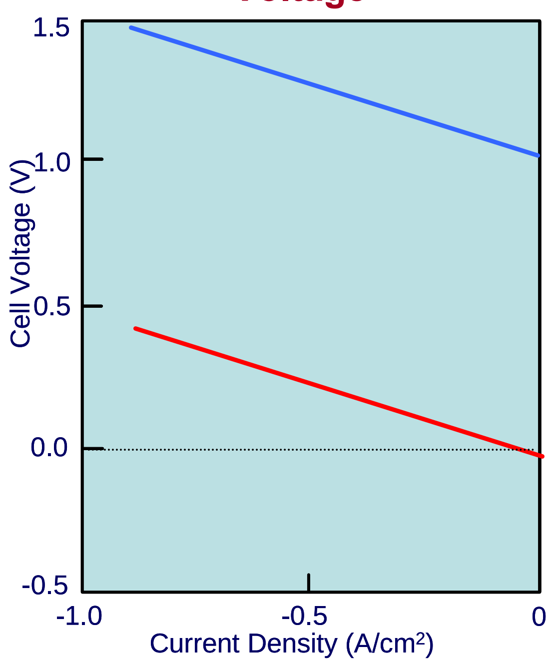
Cathode: H_2/H_2O

OCV



Anode

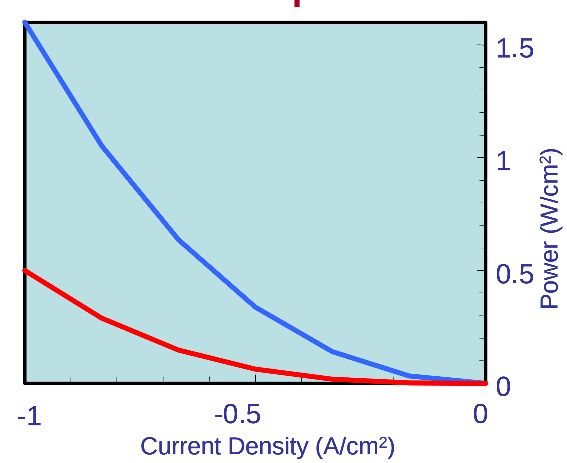
Voltage



Cathode: H_2O/H_2

Anode: Air CH_4

Power Input



Natural Gas Assisted Steam Electrolysis - NGASE

First demonstrated by researchers at Lawrence Livermore National Lab.

Martinez-Frias et al., *Int. J. Hydrogen Energy*, **28**, 483 (2003).

Cathode reaction: $H_2O + 2\,e^- \rightarrow H_2 + O^{2-}$

Anode reaction: $CH_4 + 4\,O^{2-} \rightarrow CO_2 + 2\,H_2O + 8\,e^-$

Overall reaction: $CH_4 + 2\,H_2O \rightarrow CO_2 + 4\,H_2$

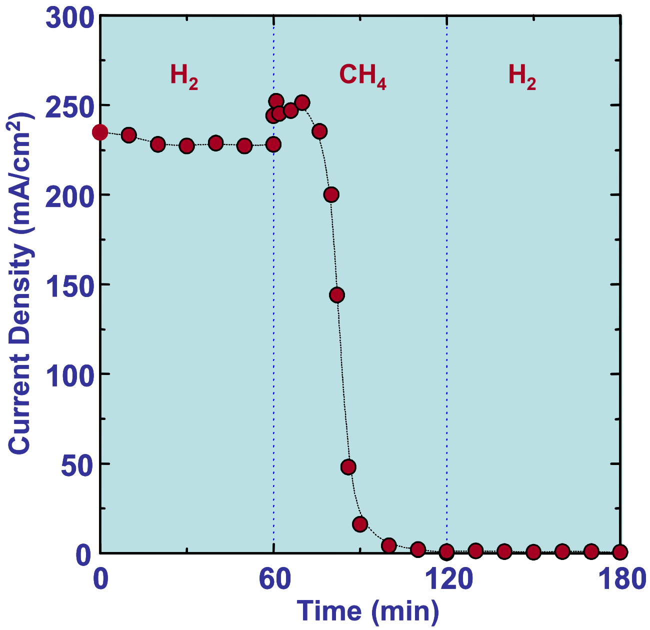
- Overall reaction is the same as steam reforming of CH_4
- H_2 produced at cathode is diluted only in H_2O
- H_2 may be produced at high pressures by increasing applied voltage. 0.1 V corresponds to ~9 atm
- An overall efficiency comparable to that of a large, steam reforming plant is feasible

Hydrocarbon Assisted Electrolysis – Materials Issues

Anode Requirements

- Stable under reducing conditions and in hydrocarbons
  - Ni and most transition metals are not stable in hydrocarbons (see below)
  - LSM, LSCo, LSF are not stable under reducing conditions
- Catalytic activity for hydrocarbon oxidation
- Thermally stable

H_2/CH_4 SOFC cell performance - Ni cermet anode



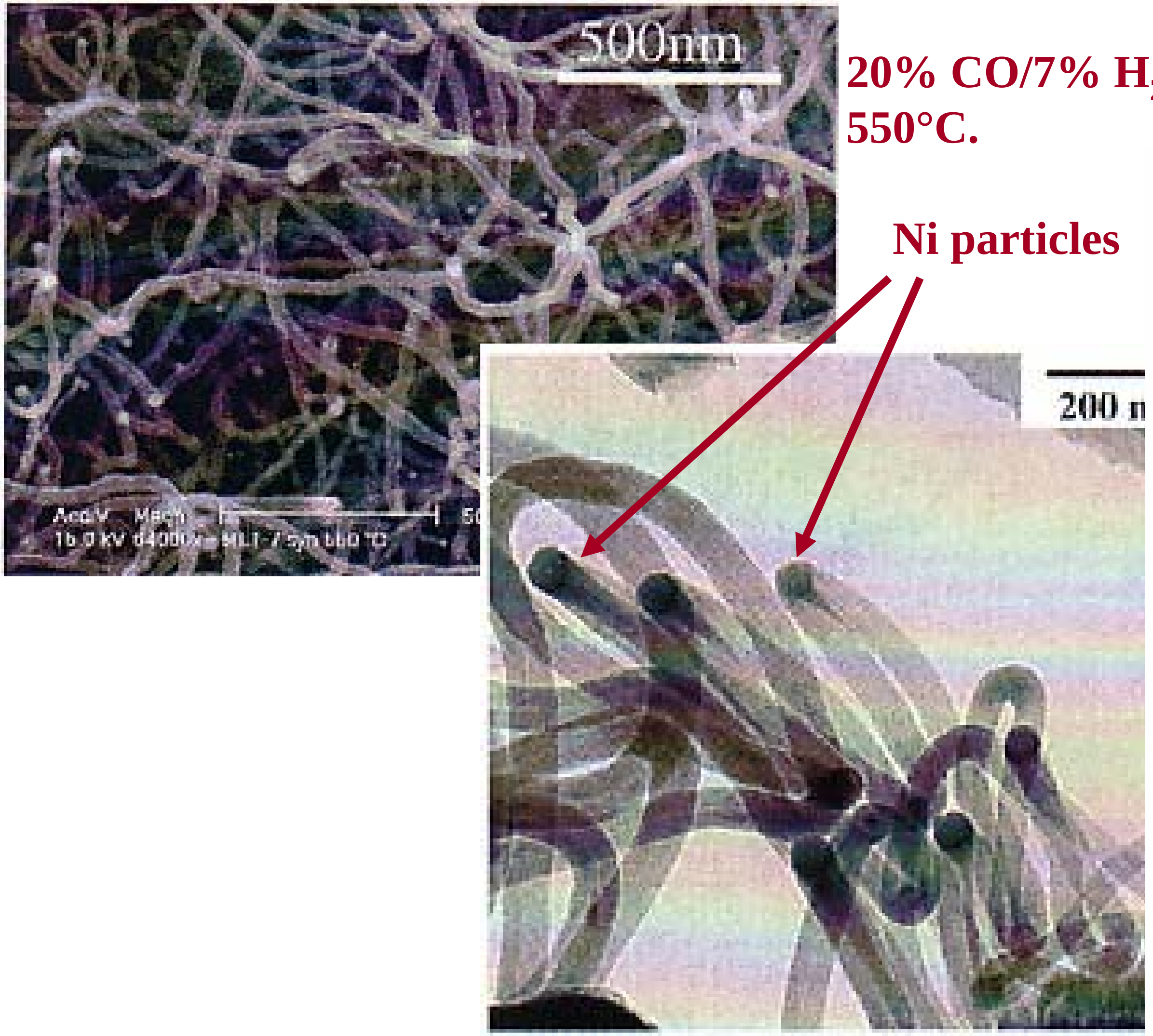
230 mm thick YSZ, 800°C, 0.5 Volts

Ni/YSZ exposed to H_2 for 3 hrs, 800ºC

Ni/YSZ exposed to CH_4 for 3 hrs, 800ºC

$C_xH_y \xrightarrow{Ni}$ Graphite + H_2

Carbon Formation on Ni



20% CO/7% H_2
550°C.

Ni particles

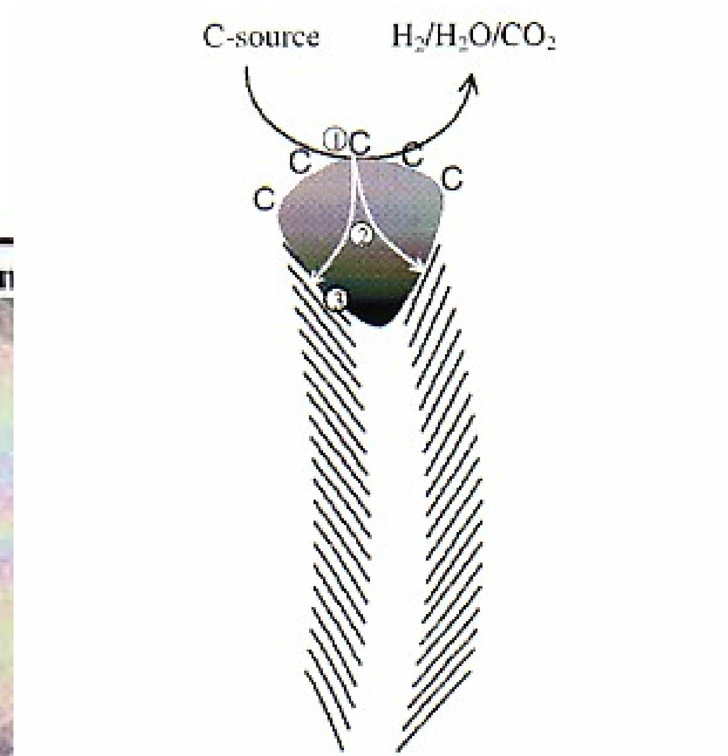


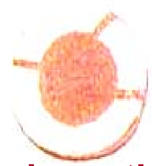
Fig. 8. Schematic representation of the catalytic growth of a CNF using a gaseous carbon-containing gas. Step 1: decomposition of carbon-containing gases on the metal surface. Step 2: carbon atoms dissolve in and diffuse through the bulk of the metal. Step 3: precipitation of carbon in the form of a CNF consisting of graphite.

From M. L. Toebes, et al., *Catalysis Today*, 2002

Two Approaches for Direct Hydrocarbon Anodes

1st Method

- Replace Ni with other metals such as Cu or Cu alloys which do not promote carbon deposition



Cu in methane
for 3 hrs, 800ºC

Cu in toluene
for 3 hrs, 700ºC

- Must include oxidation catalyst – ceria

2nd Method

- All ceramic anode

- Use oxide-based catalysts and a conducting ceramic as the current collector

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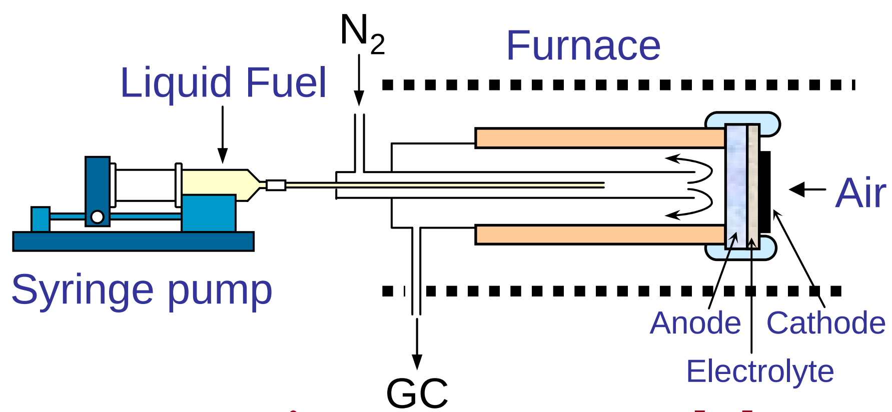
Hydrocarbon Tolerant Anodes

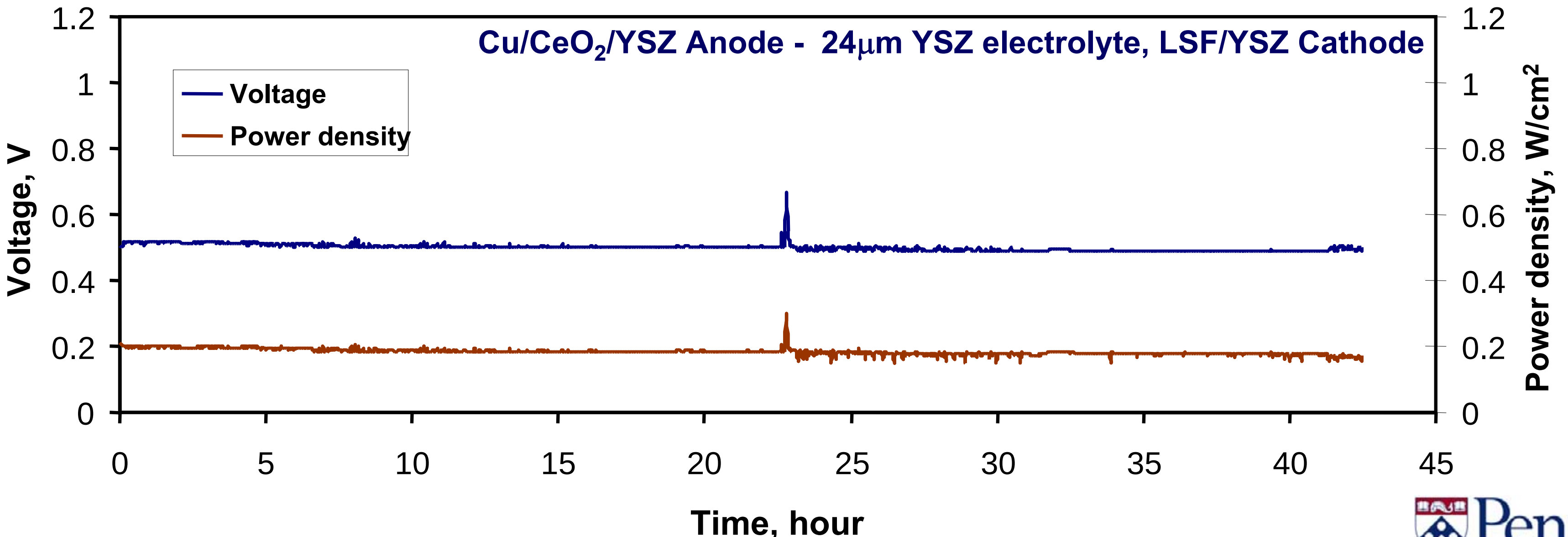
We have previously demonstrated Cu-ceria impregnated anodes

- **Cu provides electronic conductivity**
- **Ceria provides catalytic activity**

Cu-ceria composite anodes work with real fuels!

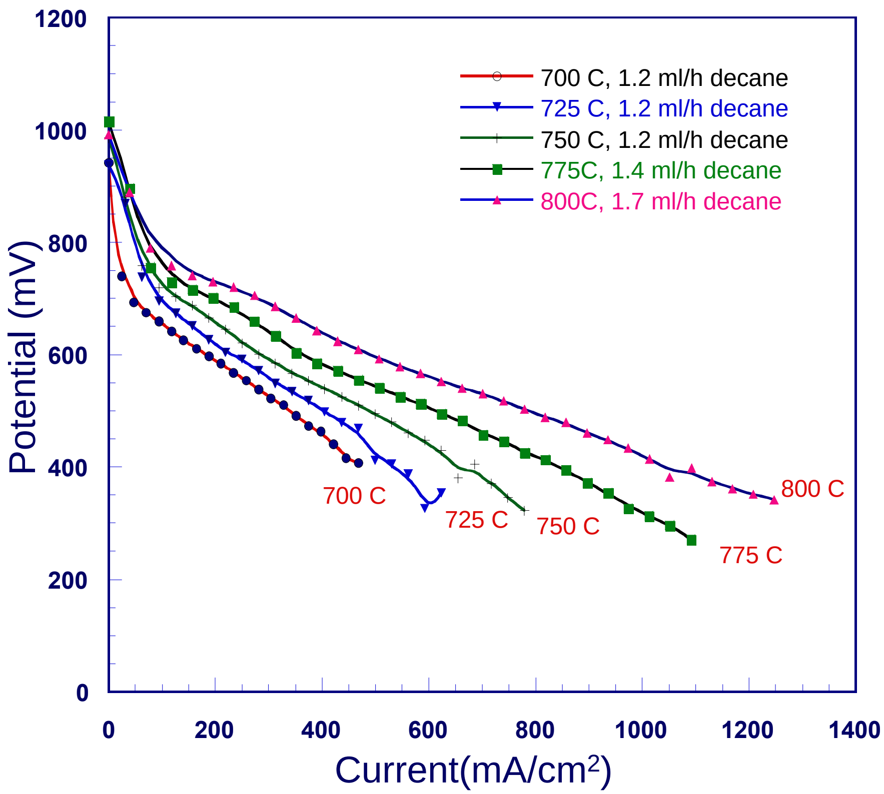


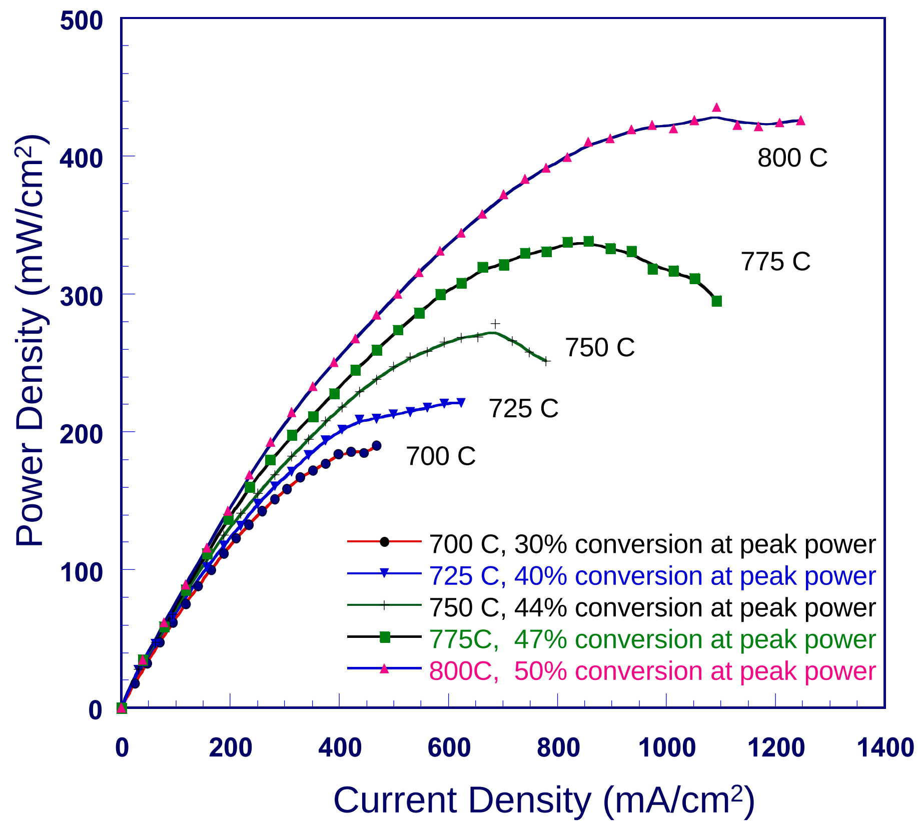
SOFC operation on Heavy Naphtha at 700°C.



High power densities can be obtained in optimized cells:

Fuel: pure n-Dodecane





Data from SRI
Cell area 6.4 cm^2

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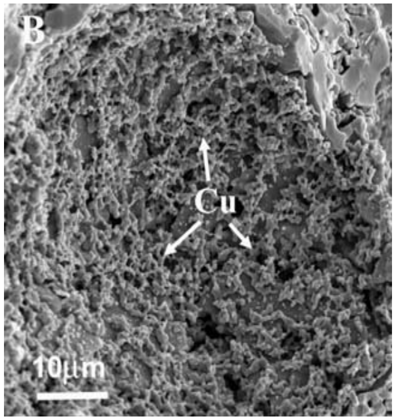
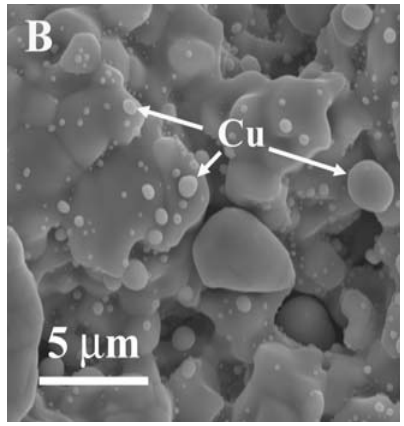
Anode Thermal Stability

Impregnated Cu/YSZ Cermet

700°C



900°C



Cu/YSZ anode stability

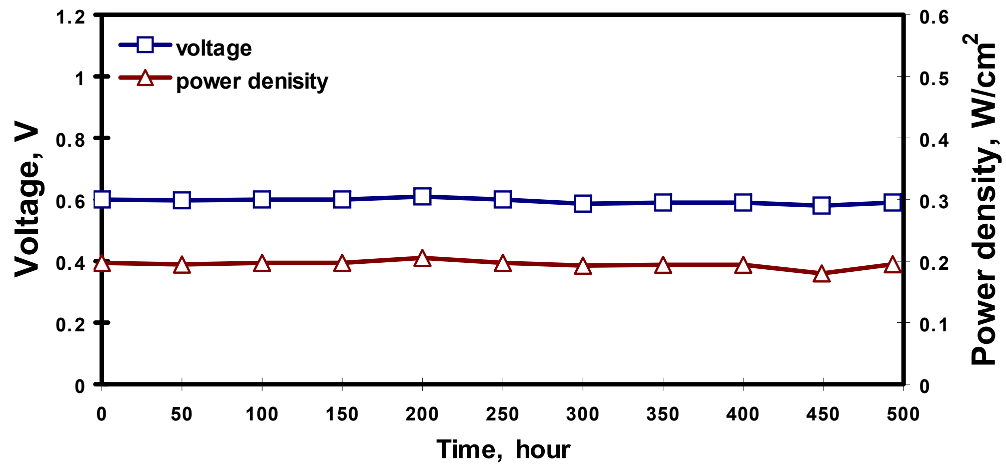
- Cu sinters at T > ~850°C
- Cu use limited to lower temperatures

Cu can be alloyed with a more refractory metal to increase thermal stability

Cu-Co composites exposed to CH_4 at 800ºC for 2 hours:

% Cu	100	50	0
% Co	0	50	100

SOFC - dry CH_4, 800ºC - 50:50 Co-Cu anode

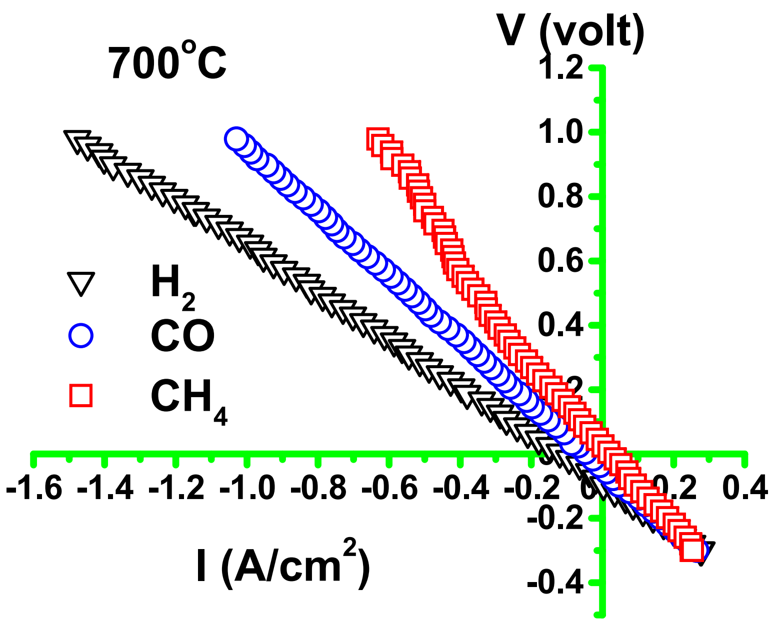


Bimetallic Fuel Electrodes

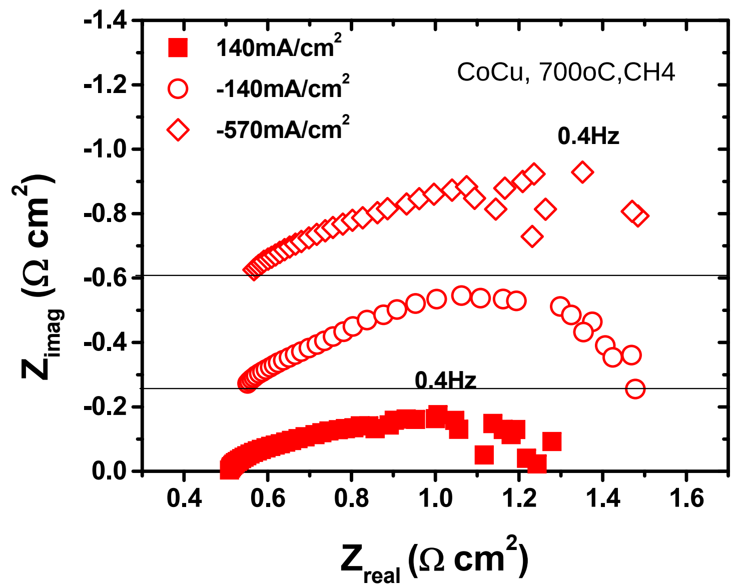
Steam electrode: Ceria-Co, 85%H_2+15%H_2O

Fuel electrode : Cu-Co-CeO_2-YSZ

Cu:Co=1:1, co-impregnated



V-I Curve

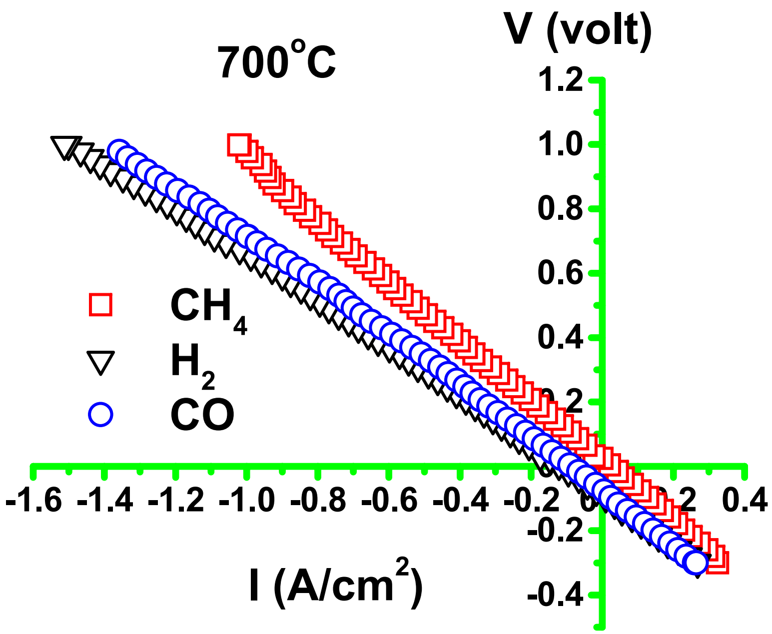


Total Impedance for CH_4

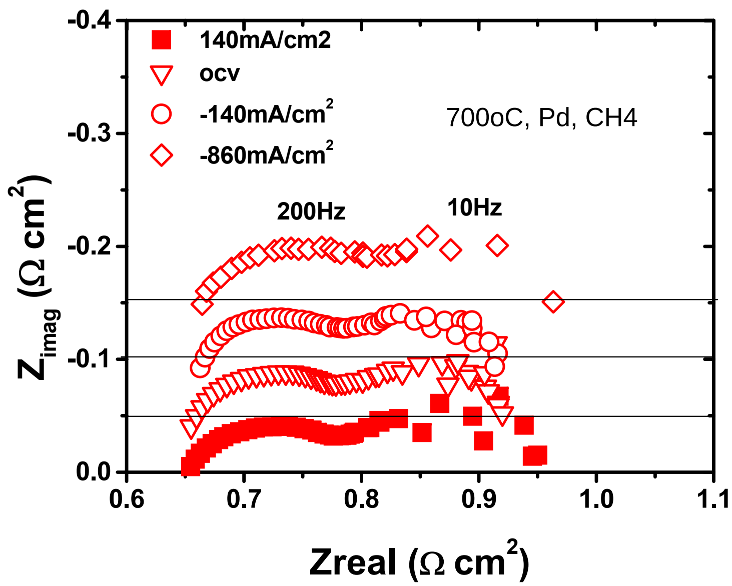
- Cu and Co do not form an alloy
- The bimetallic mixture depresses carbon deposition and Cu sintering and improves catalytic activity

Enhancing Catalytic Activity - Carbon-1%Pd-CeO_2-YSZ Fuel electrode

- Fuel electrode: C-1%Pd-CeO_2-YSZ
- Steam electrode: YSZ-Ceria-Co, 85%H_2+15%H_2O
- C was deposited by exposing to butane for 20mins



V-I Curve



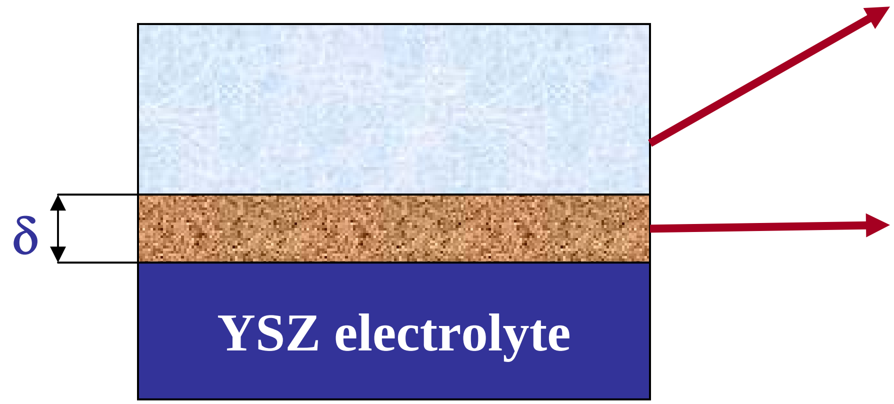
Total Impedance for CH_4

- C provides electronic conduction
- Precious metal enhances catalytic activity for hydrocarbon oxidation

All ceramic anodes

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

Concept: Separate the two required functions



Anode current collector

- Porous ceramic, optimized for electronic conductivity

Anode functional layer

- Optimized for catalytic performance
- Thin to avoid need for high conductivity

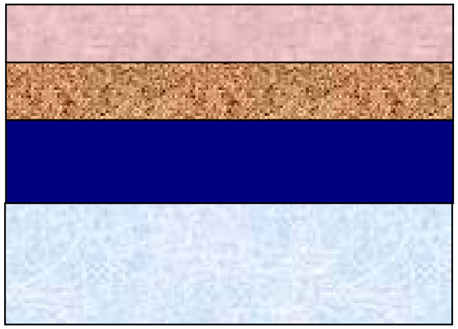
Key point:

If $\delta = 10\ \mu m$, R_{ohmic} must be < $\sim 0.1\ \Omega \cdot cm^2$ to obtain high performance

This can be achieved if σ of the active layer is only 0.01 S/cm.

All Ceramic Anode

Cell with thin ceria/YSZ anode and Ag current collector

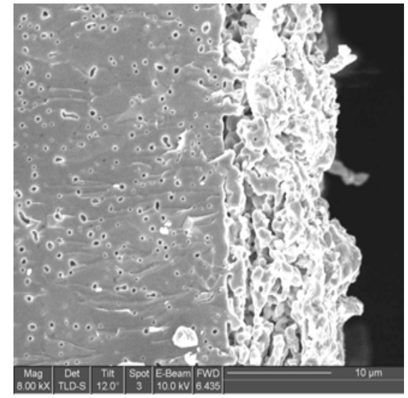


Current collector, Ag paint

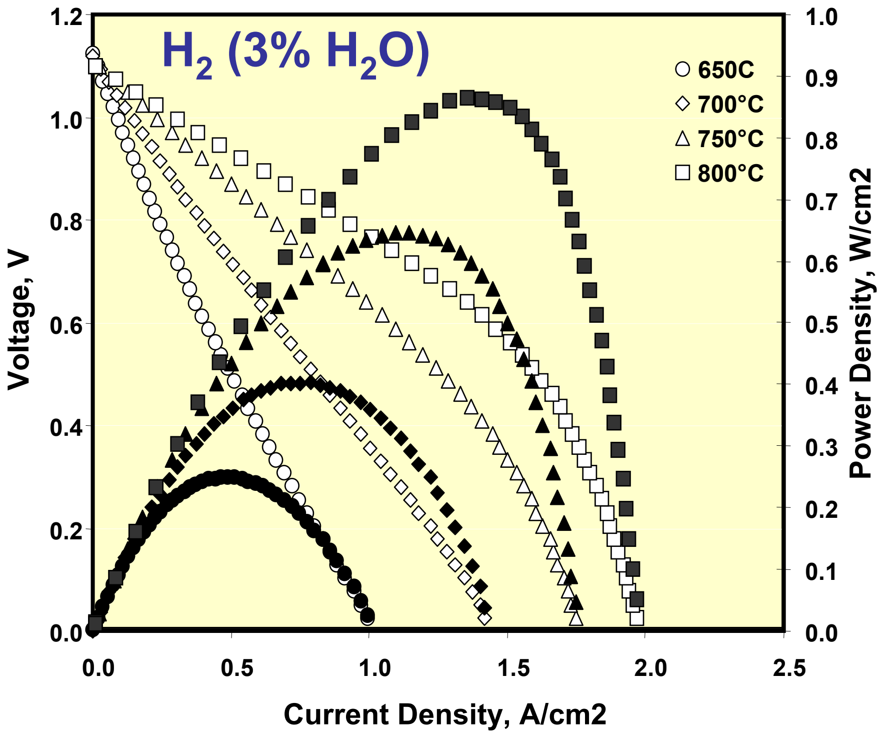
Anode, 10 μm Pd-Ceria/YSZ

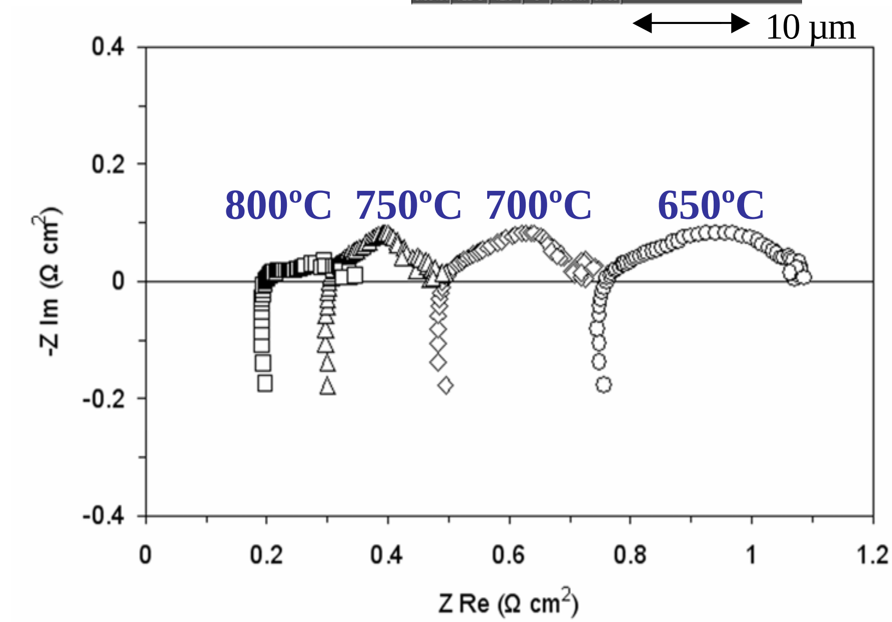
75 μm YSZ electrolyte

300 μm LSF-YSZ cathode (300



10 μm

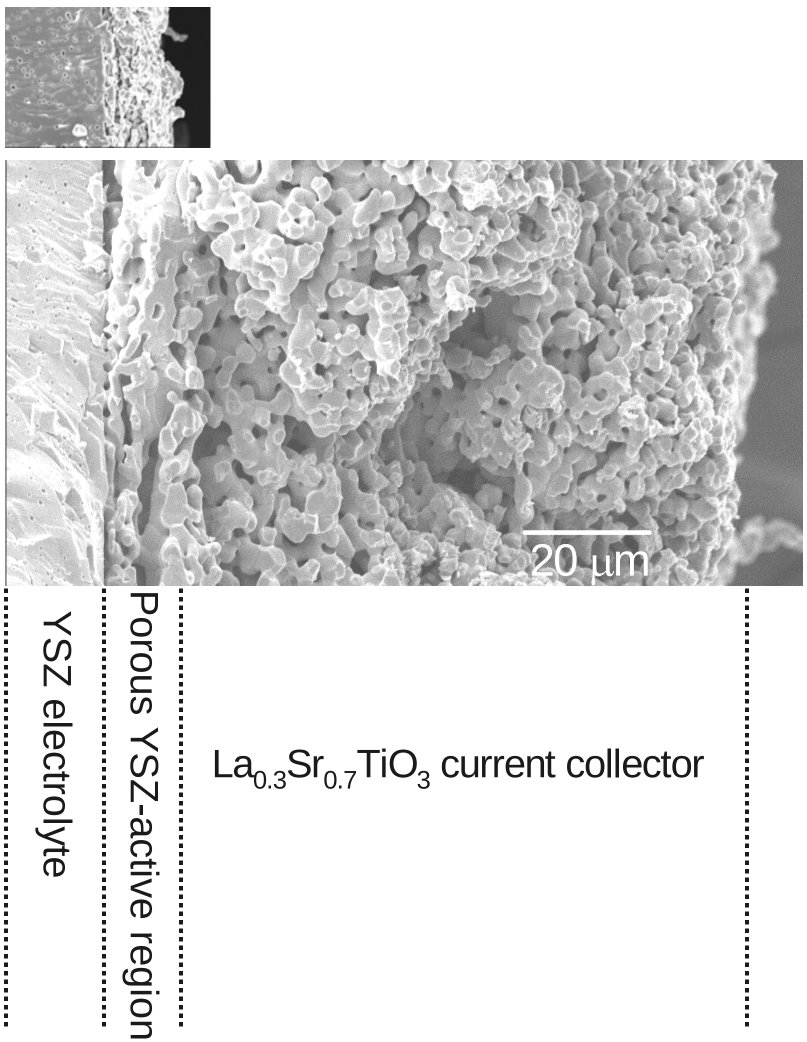




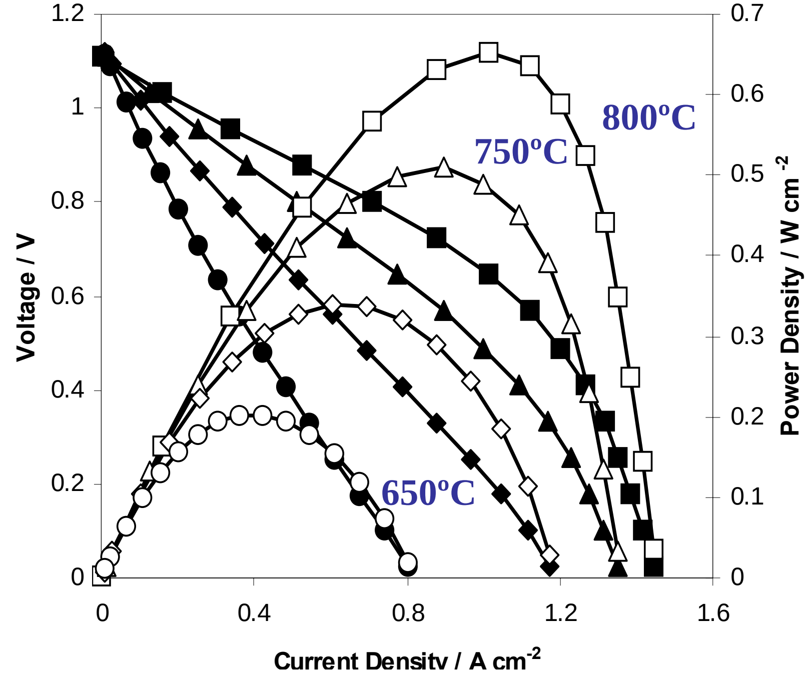
- Cell exhibits excellent performance
- High electrical conductivity not required for thin functional layer

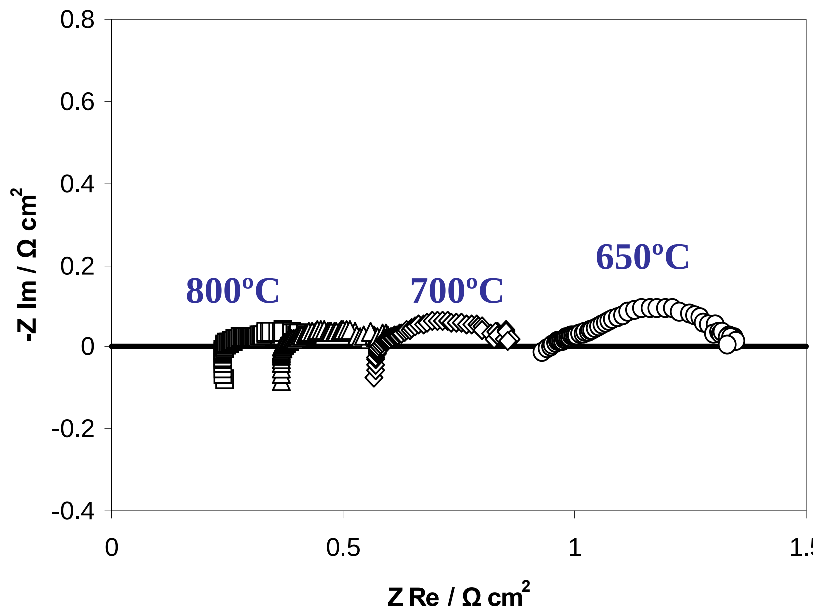
All Ceramic Anode

$La_{0.3}Sr_{0.7}TiO_3$, an electronically conducting ceramic, can be used as the current collector



H_2 (3% H_2O)





Summary

- Materials science will play a critical role SOE development
- Materials functions and challenges are similar in SOEs and SOFCs but there are also some differences

  example: LSM electrodes

  - Activated by cathodic polarization
  - Deactivated by anodic polarization
- Novel approaches to ceramics processing are needed to optimize electrode structure and composition

  example: Impregnated porous YSZ electrodes

  - Lowers processing temperature for active component
  - Expands the range of materials that can be used (LSF, LSCo, Cu, etc.)
- Hydrocarbon assisted electrolysis may have advantages for some applications (e.g. distributed H_2 generation), but requires the development of hydrocarbon stable electrodes.

  examples: Cu/CeO_2/YSZ electrodes

  All ceramic anodes