Characterization of perovskite-YSZ Electrodes (by impregnation)

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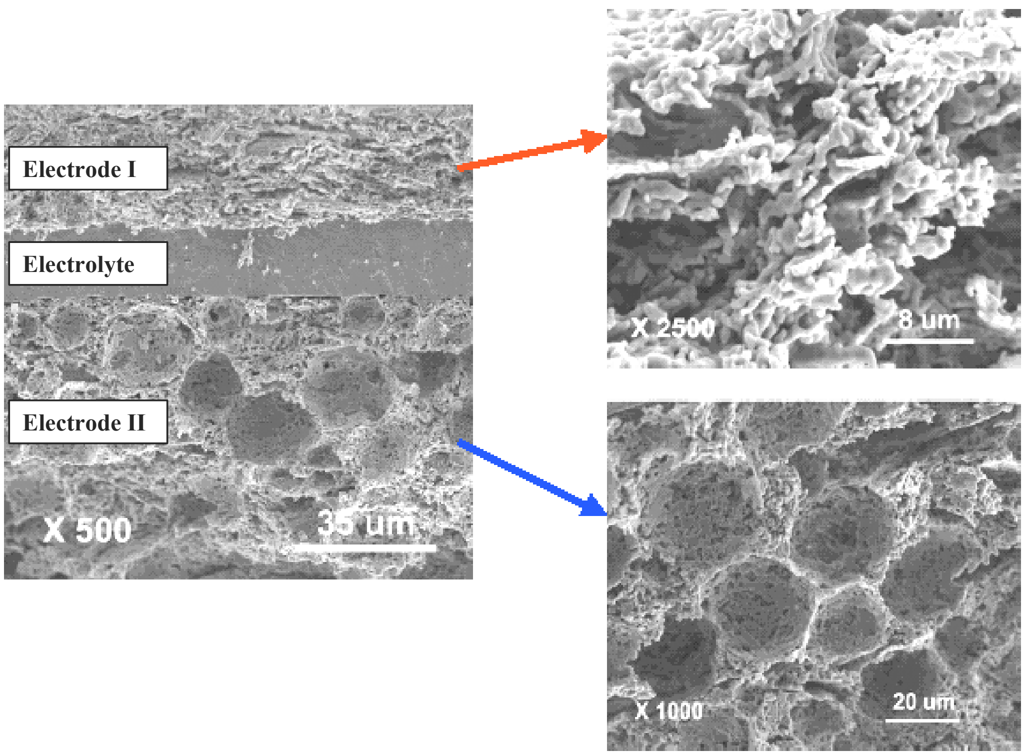
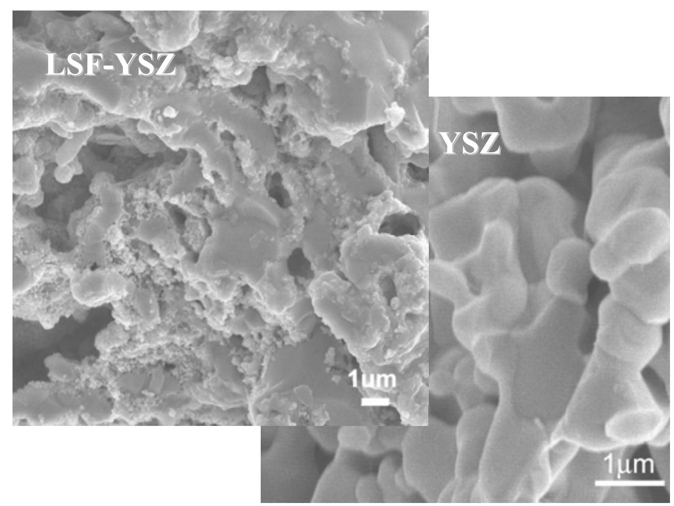
Tape casting with pore formers



Impregnate active components using

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



Advantages:

1. Separate firing temperatures for YSZ and perovskite.

   Avoids solid-state reactions between perovskite & YSZ.

   JECS, 151 (2004) A646-A651; JECS, 152 (2005) A1347-53

2. Composite structure is not random; perovskite coats pores.

   a) High conductivity at loadings below the percolation threshold.

      JACerS, 87 (2004) 331-336

   b) CTE is that of YSZ backbone.

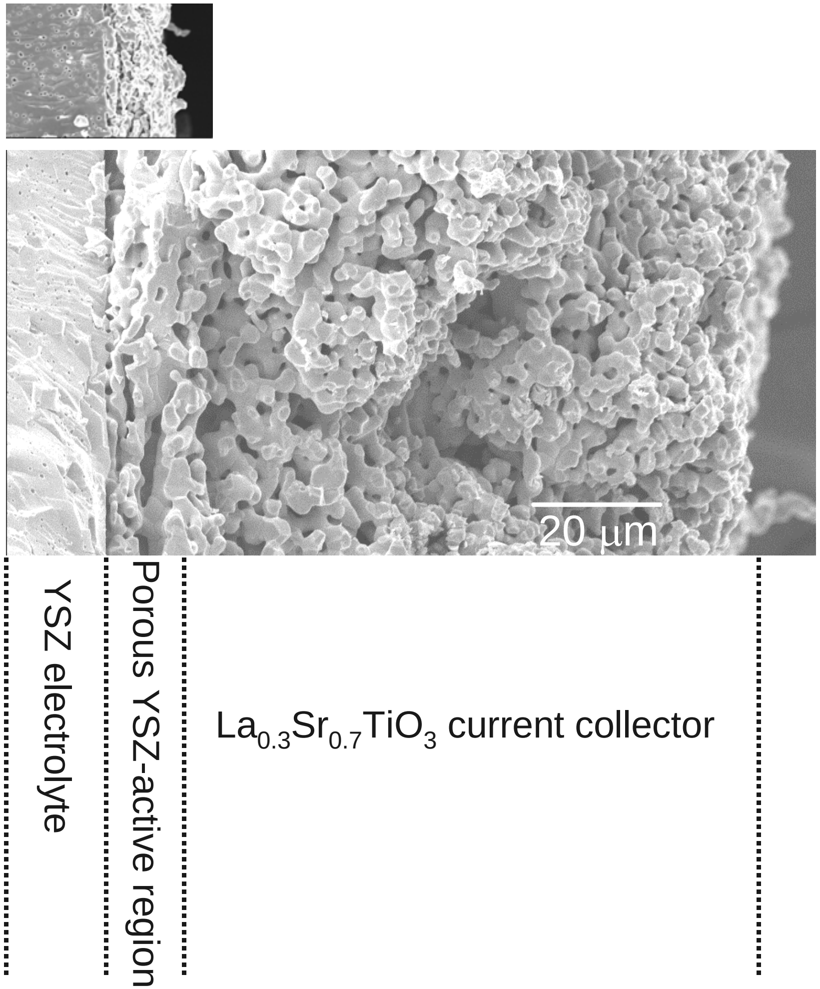
      JES, 151 (2004) A1592-1597

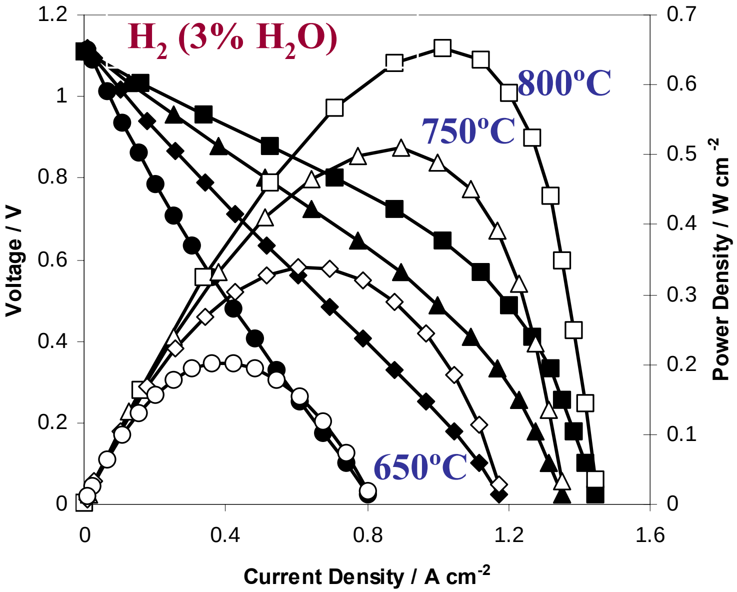
3. High-performance cathode–supported cells possible.

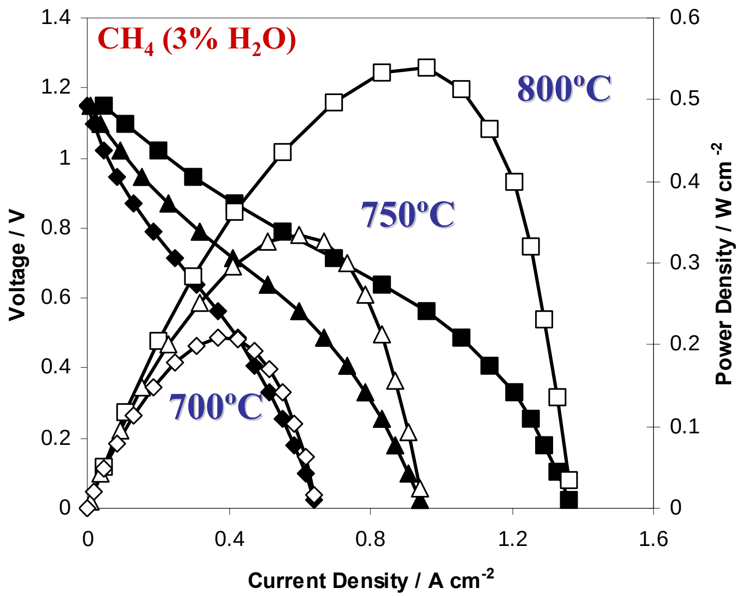
Cathode-supported cells enable alternative anodes:

LSF-YSZ(300 μm)│YSZ(75 μm)│ceramic anode

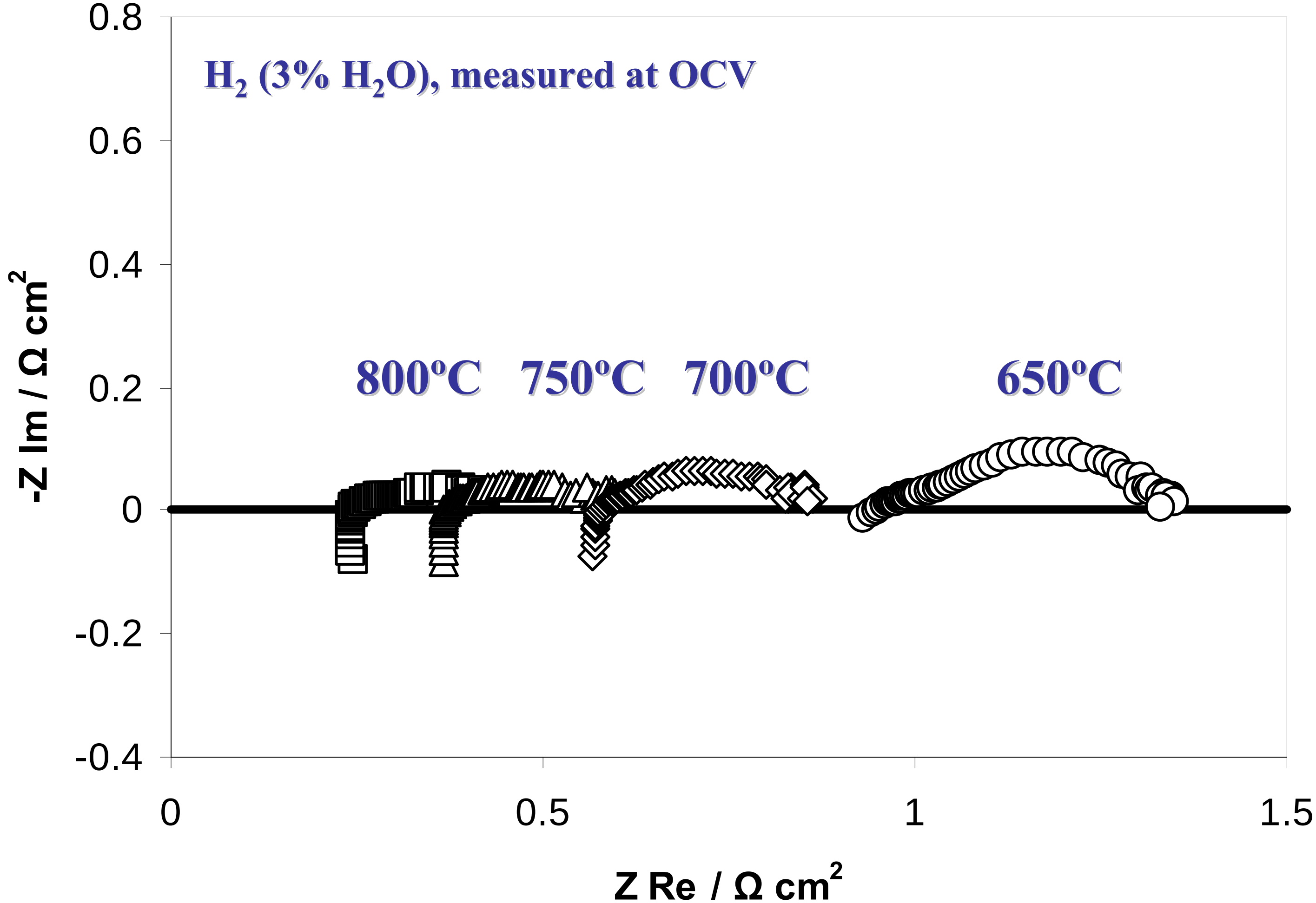
Anode: metal-doped ceria in YSZ │LST







Performance of test cells limited by electrolyte:



@650ºC, $R_{anode} + R_{cathode} < 0.5\ \Omega\cdot cm^2$

@800ºC $< 0.2\ \Omega\cdot cm^2$

1. Methods to fabricate LSM-YSZ cathodes

ESSL, 9 (2006) A237-240

Minimum Requirement:
Need 30 to 40 wt% perovskite

a) Nano-particles (●)
20 wt% in butandiol

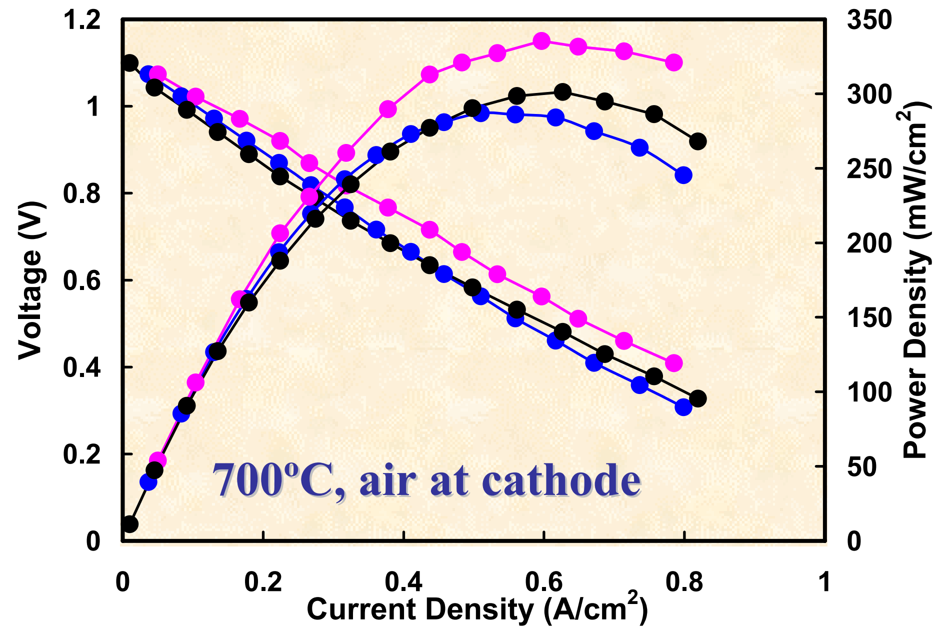
b) Aqueous solutions (●)
1.6 molar, nitrate solution

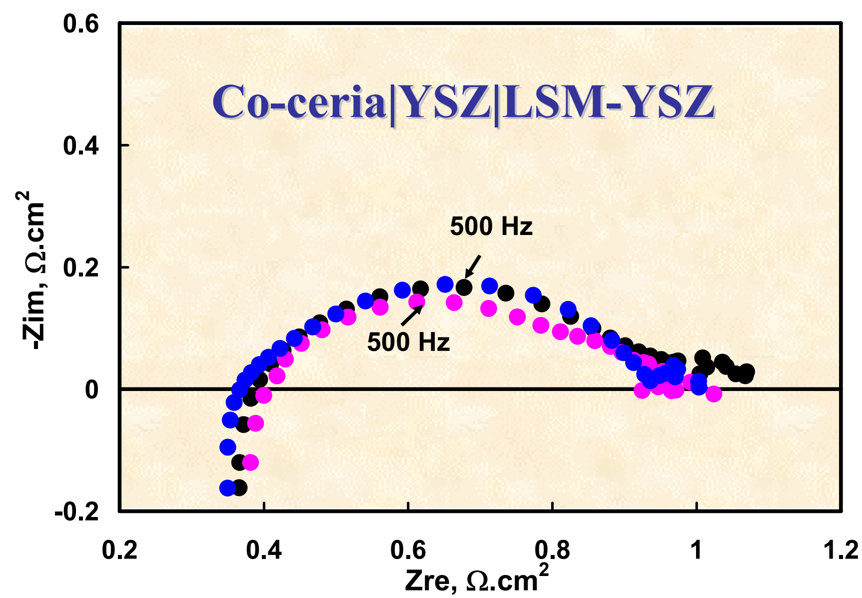
c) Molten salts (●)

- Performance independent of LSM precursor
- Impregnated LSM indistinguishable from screen-printed LSM/YSZ

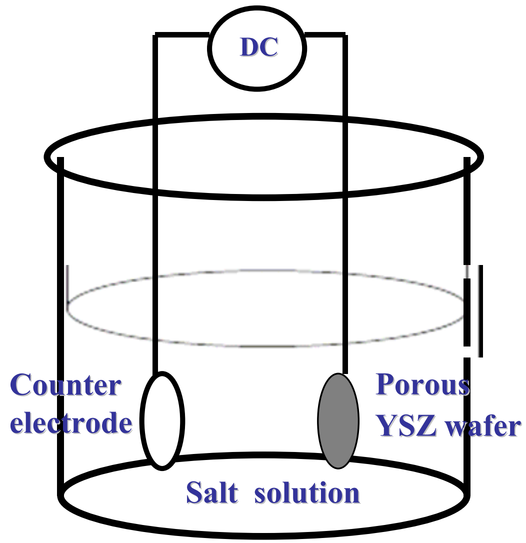
# of steps	1	2	3	4
Aqueous solutions	12 wt%	21 wt%	28 wt%	35 wt%
Molten salts	20 wt%	30 wt%		

20 steps required to reach 40 wt% with nanoparticles





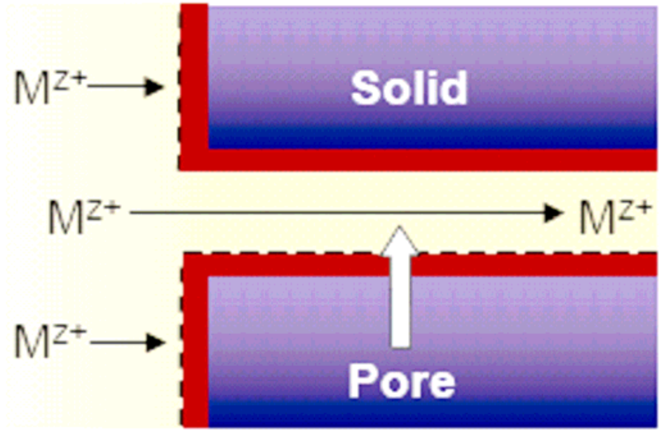
d) Electrodeposition



i) Form conductive carbon film by pyrolysis.

ii) Electroplate $LaMnO_3$ (Therese & Kamath, Chem. Matl. 10 (1998) 3364.

iii) Key is to deposit evenly throughout the pores



We have successfully deposited Cu, Co, Cr, and Ni:

1. Cu: JECS, 153 (2006) A1539-43.
2. Cr: JECS, 153 (2006) A1386-90
3. Co: Electrochimica Acta, in press.
4. Ni: in preparation.

Impregnated electrodes can be cheap and manufacturable.

2. Modification of LSM-YSZ cathodes by Co and $LaCoO_3$

JECS, 153 (2006) A951-55.

a) Mixed perovskites: $Sr_{0.2}La_{0.8}Mn_xCo_{(1-x)}O_3$

After 900ºC calcination, $Sr_{0.2}La_{0.8}Mn_{0.8}Co_{0.2}O_3$ *slightly* better than LSM

After 1200ºC calcination, LSM showed the best performance; Co-containing cells showed increased ohmic contribution.

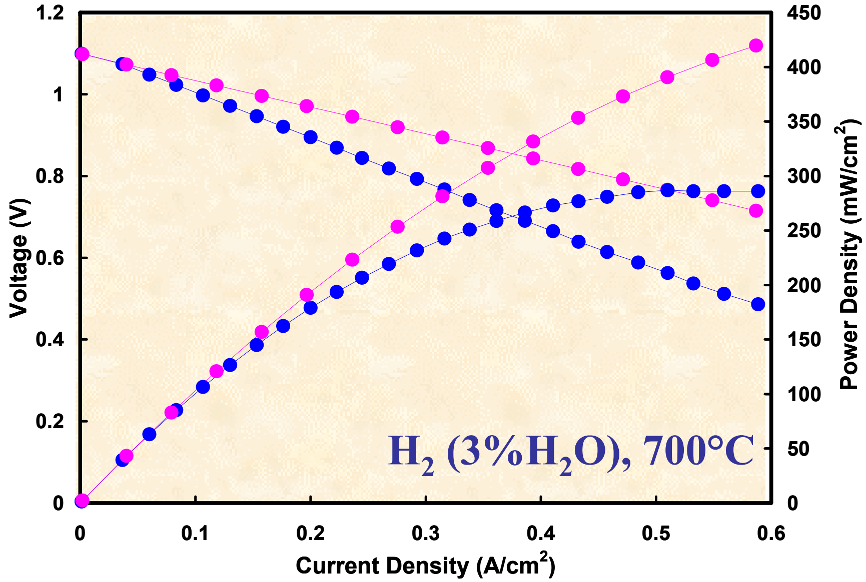
b) Co-modified LSM:

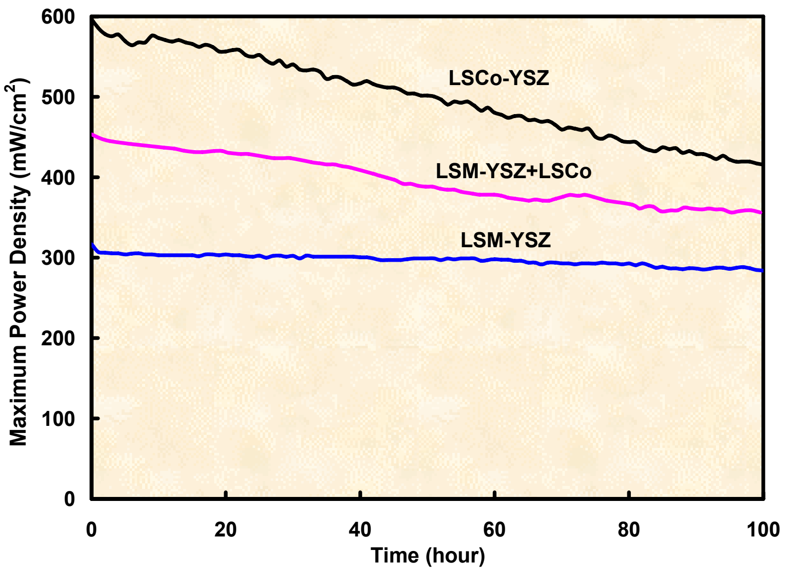
Electrodes with up to 10-wt% CoO_x were indistinguishable from that of LSM. No effect of adding CoO_x.

c) LSCo-modified LSM:

- 20%LSCo-80%LSM mixture very different from $Sr_{0.2}La_{0.8}Mn_{0.8}Co_{0.2}O_3$
- The LSCo-LSM mixture *dramatically* better than *LSM*.
- *However*, Co-containing cathodes were unstable.

Cathode (60 μm) | YSZ(45 μm) | Co-ceria-YSZ anode (600 μm)





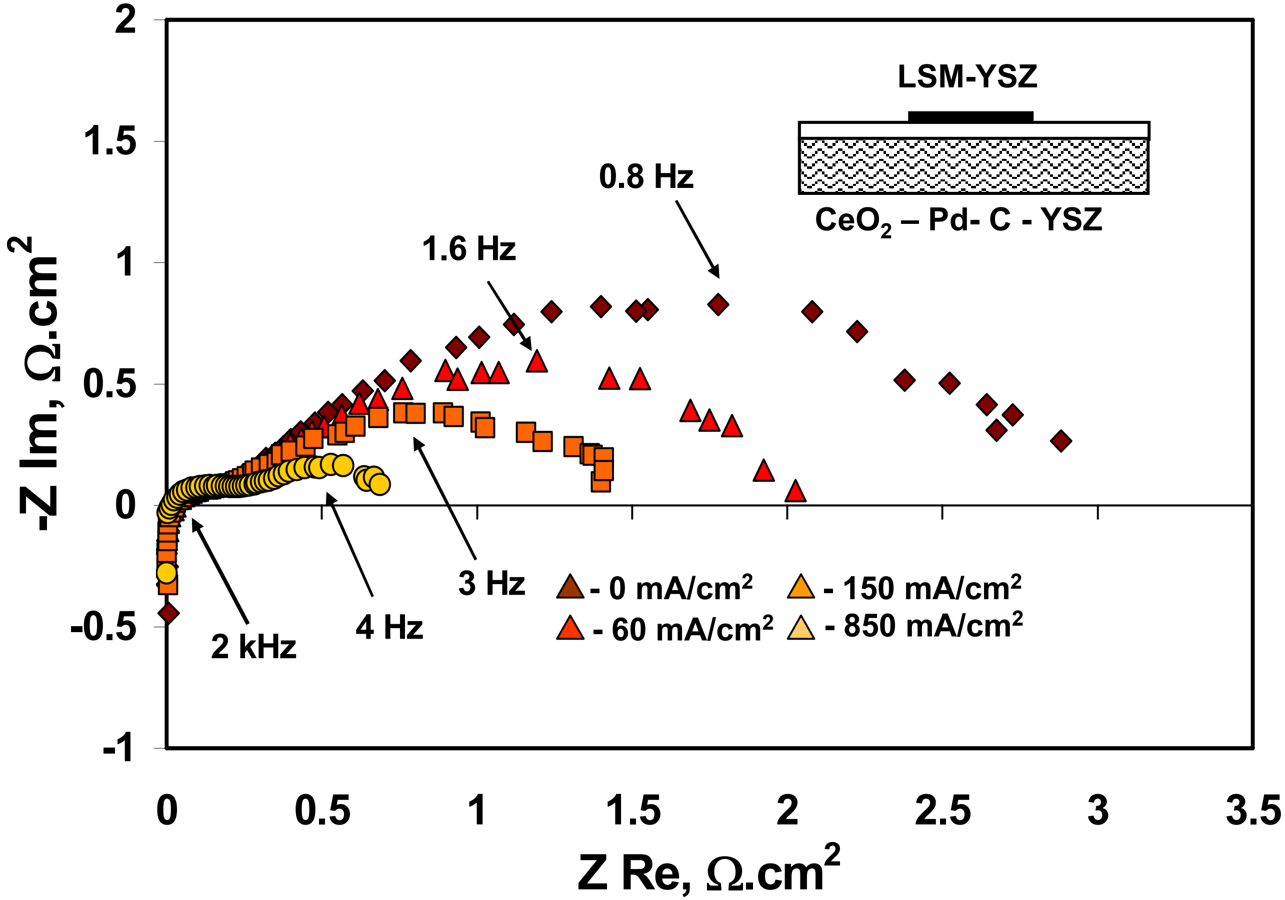
Cathode: ● LSM-YSZ

● LSM-YSZ + LSCo

3) Progress on understanding polarization activation in LSM-YSZ

ESSL, 7 (2004) A111-A114.

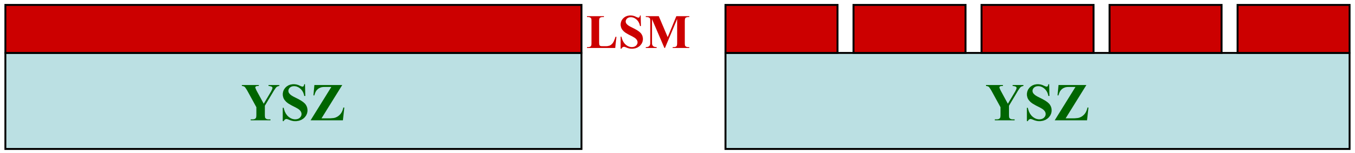
700°C, $H_2/3\%H_2O$, OCV after applying current



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

What we believe is happening:

Electrode before activation | Activated Electrode



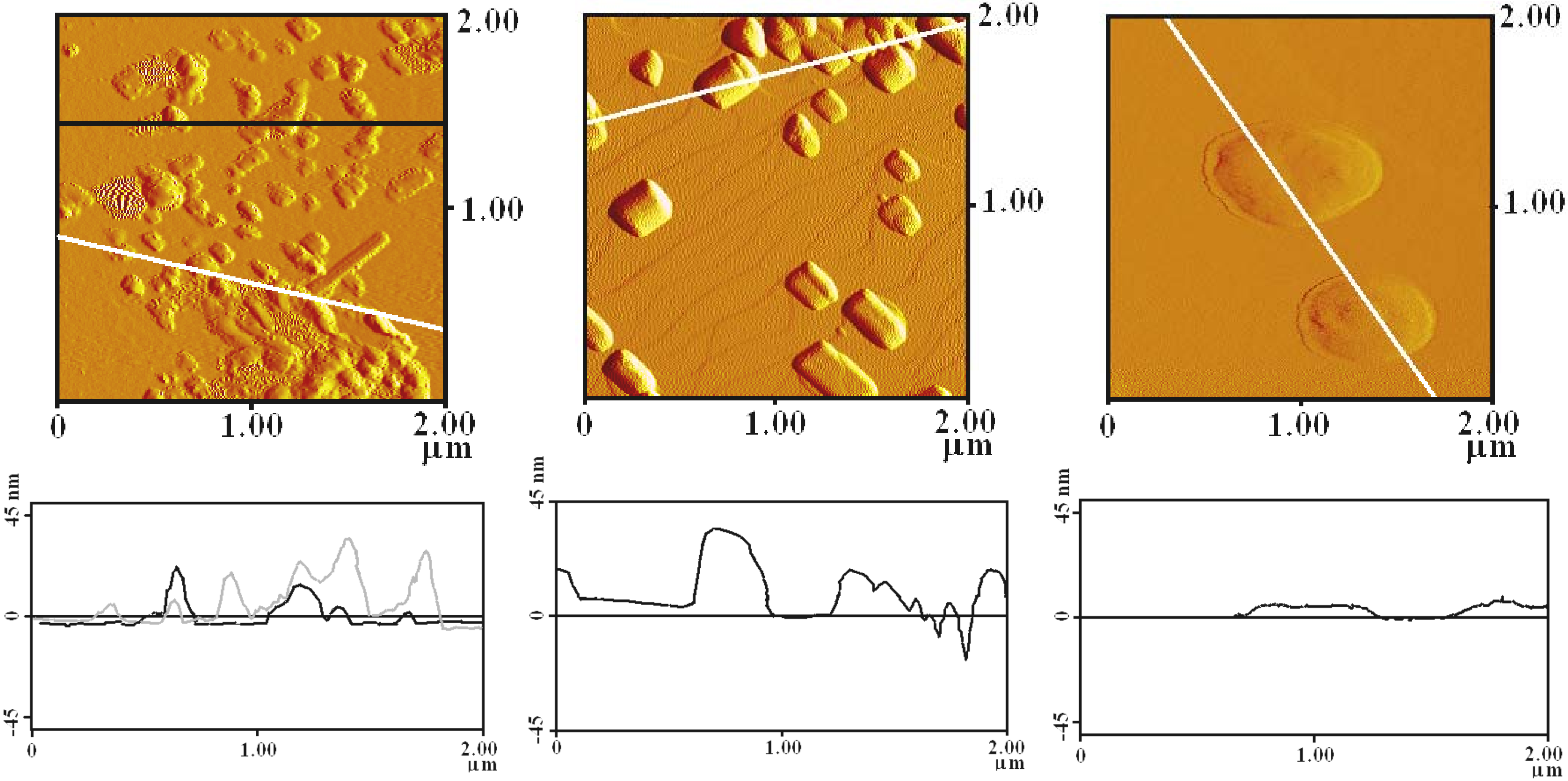
1) Dense LSM covers YSZ — Gaps in LSM film caused by reduction

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

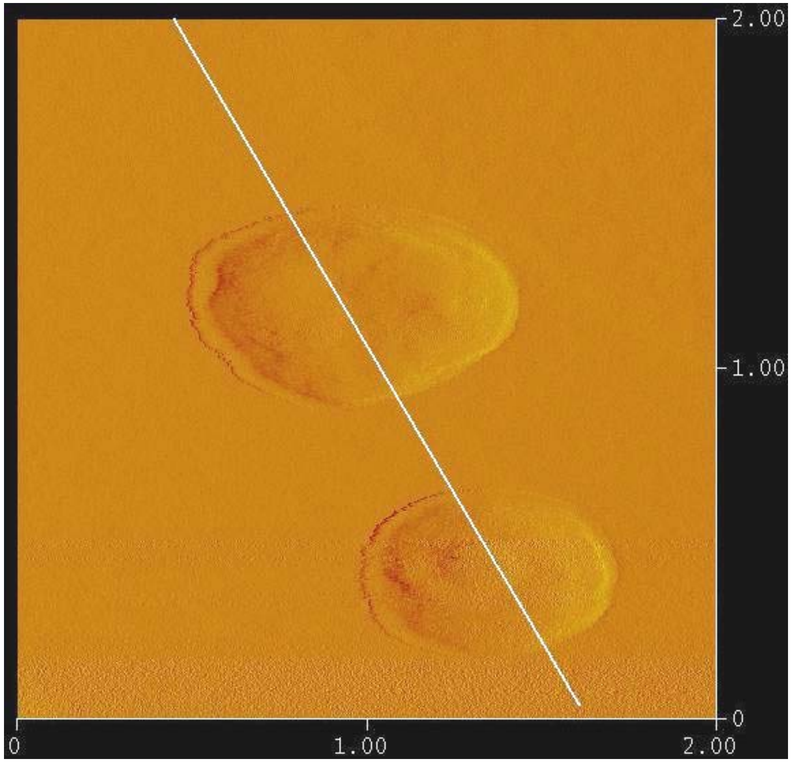
ESSL, 9 (2006) A237-240



850°C 1050°C 1150°C

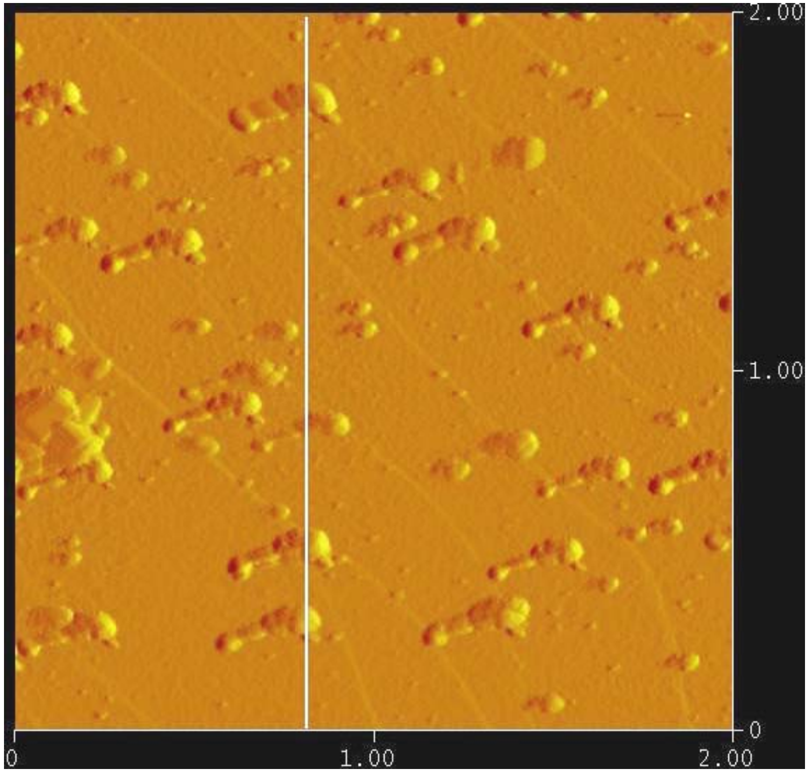
Movement of particles is reversible:

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.

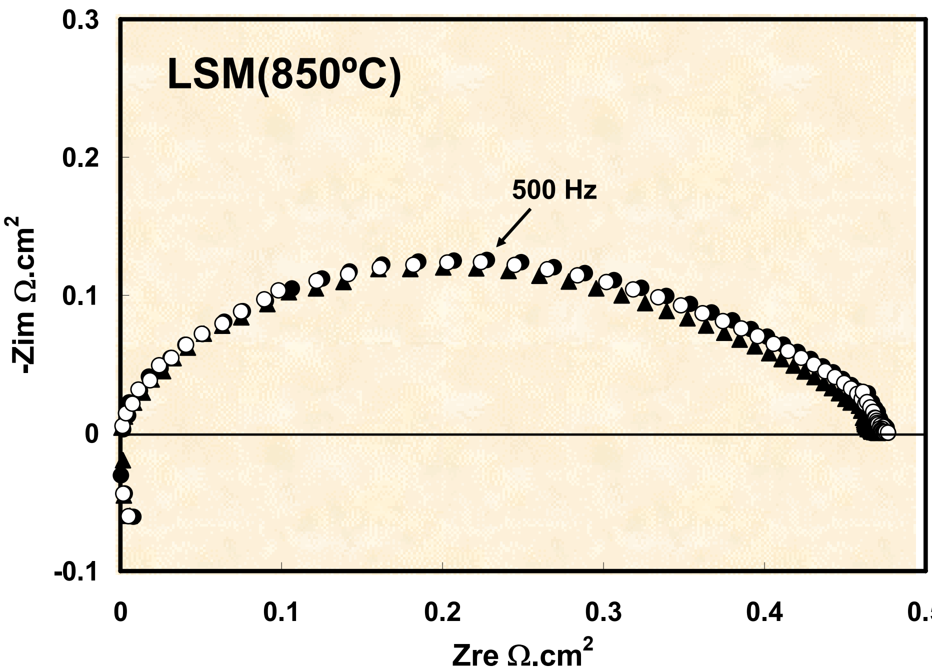
2) Reducing LSM-YSZ electrode "activate" it.

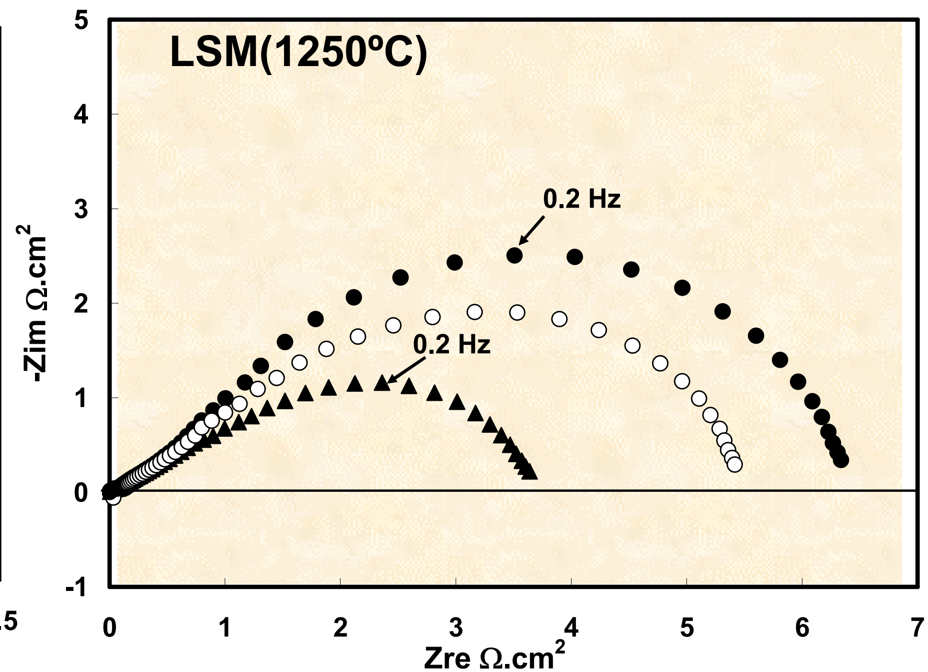
Activation affected by calcination temperature

JECS, 152 (2005) A1347-53.

40-wt% impregnated LSM-YSZ, fired to 850ºC or 1250ºC
Measurement at 700ºC in air at OCV.

(●) – Initial spectrum.
(▲) – After applying 250 mA/cm^2 for 10 minutes.
(○) – 5 h after applying current.





R = 0.5 Ωcm^2
Not activated

R = 6.5 Ωcm^2
Activated by polarization

BET Surface Areas (40 wt% LSM in YSZ)

	Surface Area (m^2/g)
Porous YSZ without LSM	0.77±0.02
LSM(850°C)-YSZ	2.53
LSM(1250°C)-YSZ	0.38±0.02
LSM(1250°C)-YSZ w/ 700°C reduction	0.78±0.03

$$\delta = \frac{4\,\varepsilon}{[\alpha\,(1-\varepsilon)\,\rho]}$$

ε= porosity
α= surface area
ρ= YSZ density

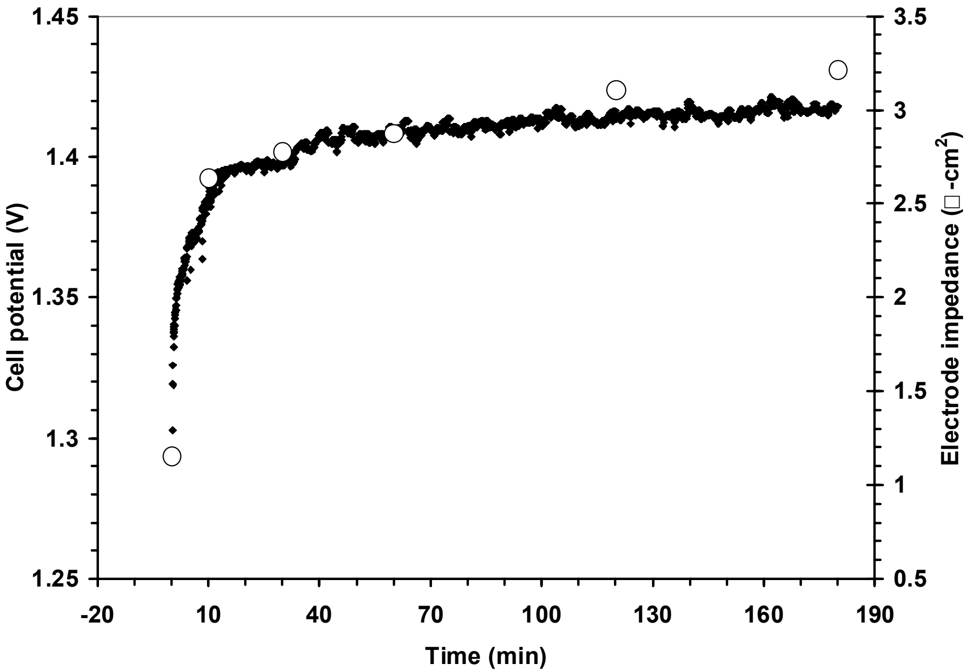
α= 0.77 $m^2/g \Rightarrow \delta$ = 1.6 microns
α= 0.38 $m^2/g \Rightarrow \delta$ = 0.58 microns
$\Rightarrow$ dense LSM film on YSZ pores

Consequences for electrolysis (anode environment is oxidizing):

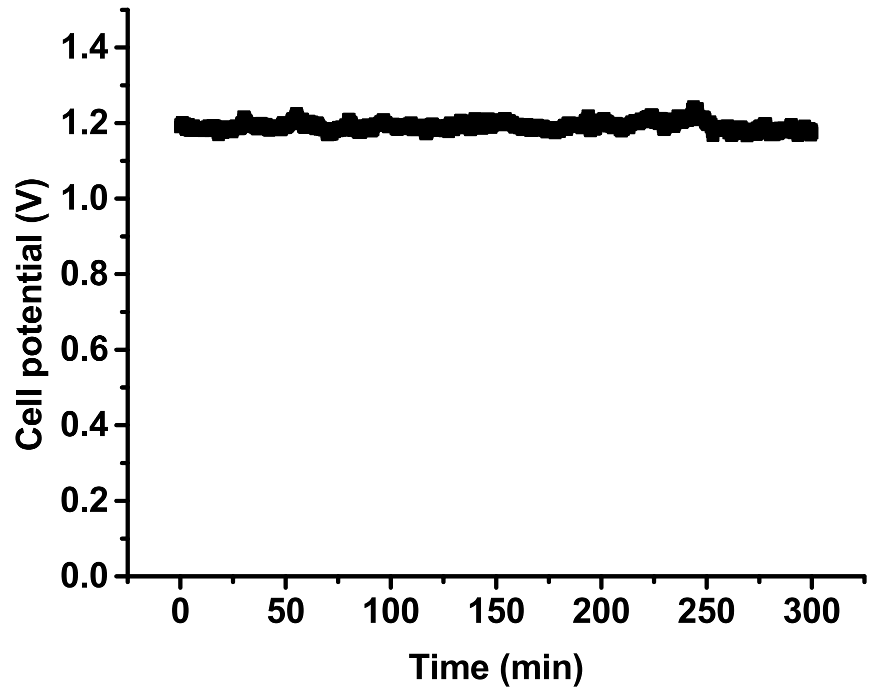
JECS, in press.

285 mA/cm^2; 700^{o}C; 85%H_2-15%H_2O| air

LSM-YSZ anode



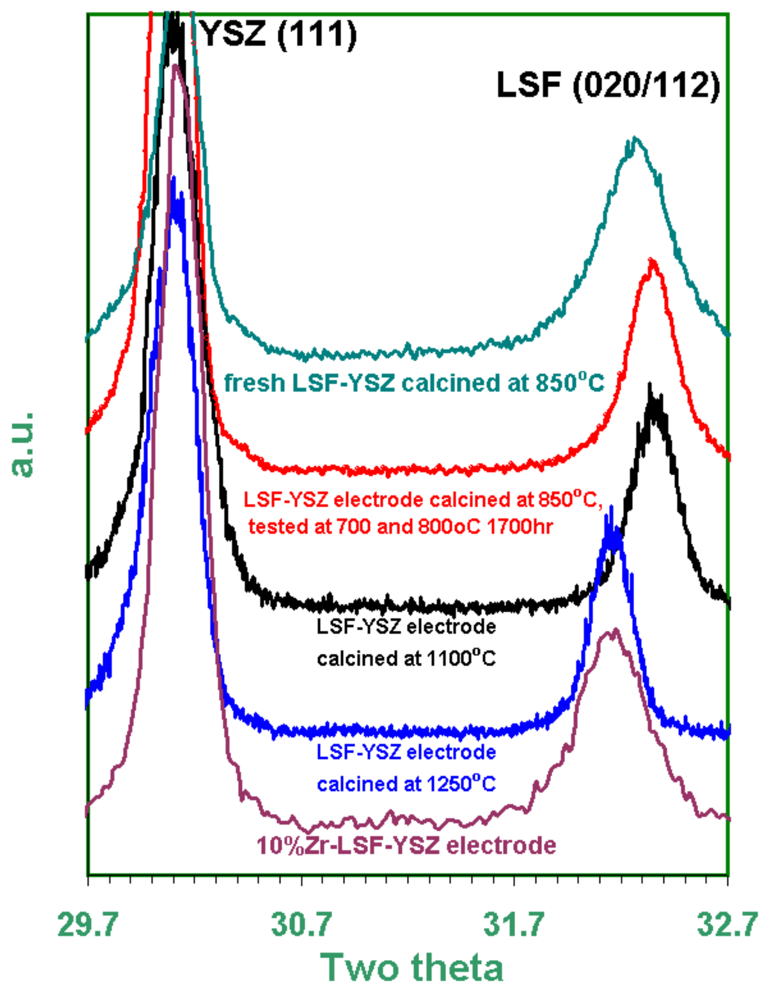
LSF-YSZ anode



4) Progress on understanding stability of LSF-YSZ

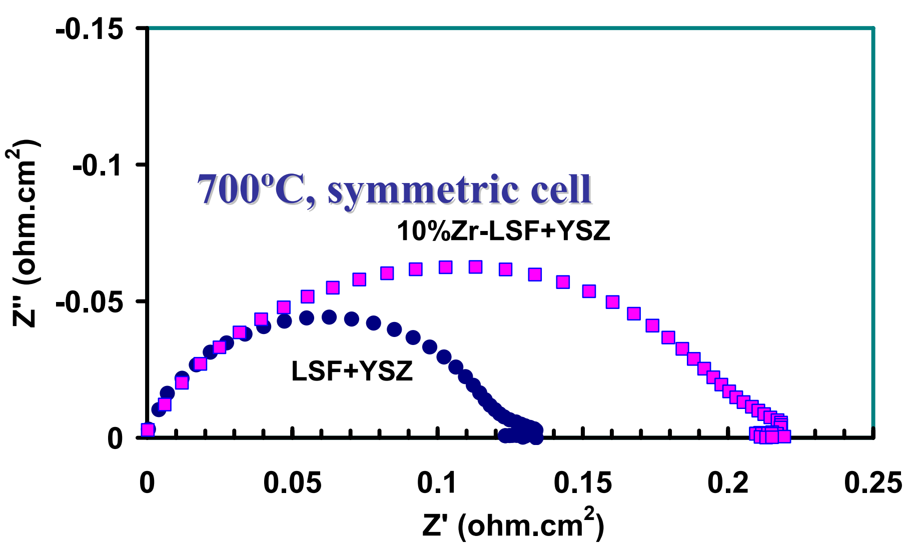
Observations:

1) See no additional phases with calcination temperature (Very different from $LaCoO_3$)



2) Formation of Zr-doped $LaFeO_3$ only above 1200°C

3) Zr doping is not a deactivation process.

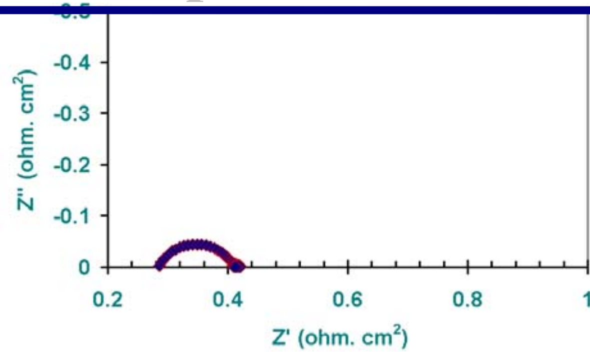


Time & calcination temperature have similar effect:

Symmetric Cells

Calcine @ 850ºC

t = 0 h @700 º C

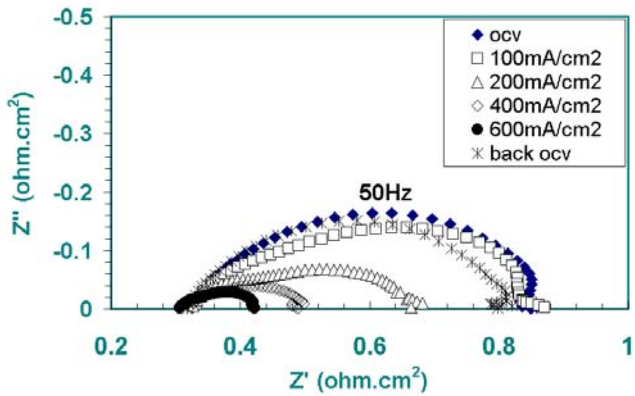


R_Ω = expected value for YSZ electrolyte

R_P = 0.12 Ω cm² @ 700ºC independent of *i*

Calcine @ 850ºC

t = 2500 h @700ºC



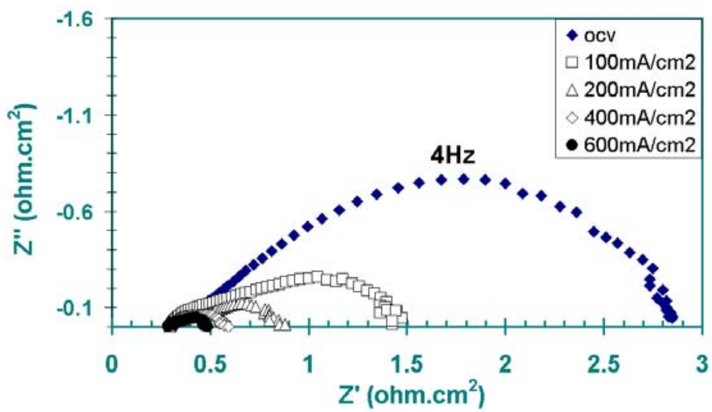
R_Ω = expected value for YSZ electrolyte

R_P = 0.6 to 0.1 Ω cm², *depends strongly* on *i*

No hysteresis! Not like LSM.

Calcine @ 1100ºC

t = 0 h



R_Ω = expected value for YSZ electrolyte

R_P = 2.5 to 0.1 Ω cm², *depends strongly* on *i*

No hysteresis.

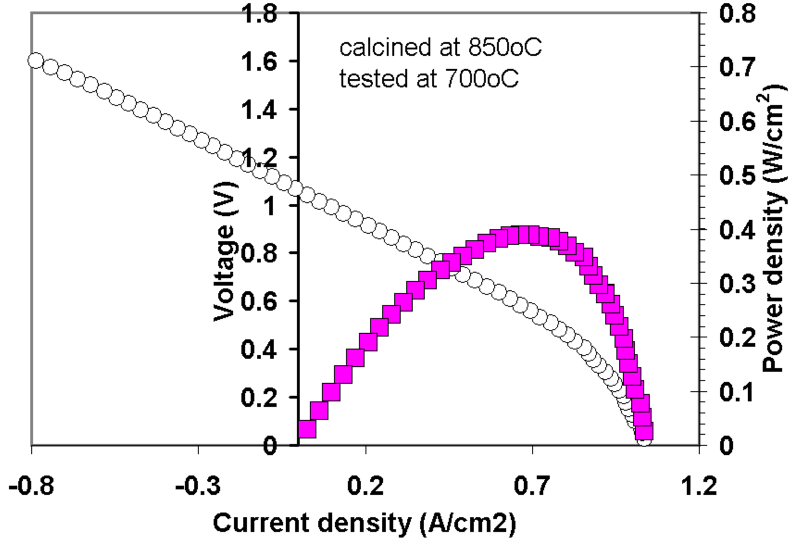
Effect of Calcination Temperature, Performance @ 700ºC

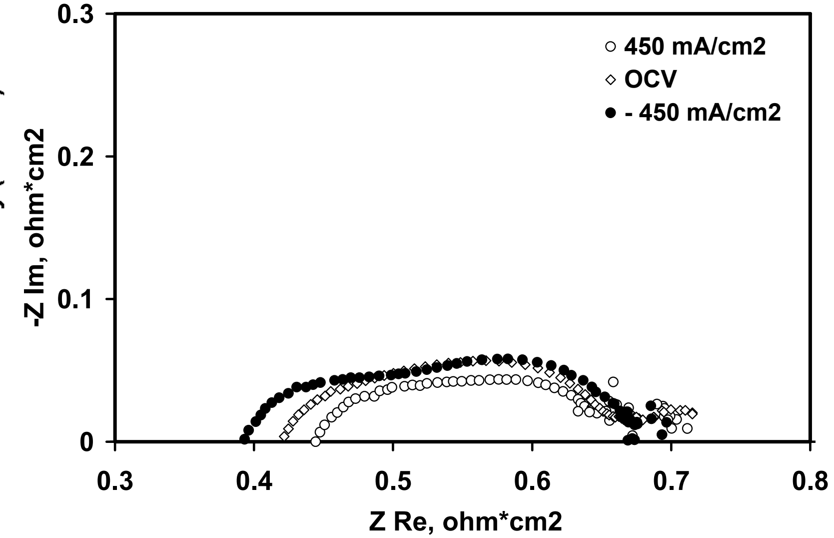
Anode: metal-doped ceria-YSZ│Ag, 50 μm YSZ electrolyte

Calcine

@ 850°C

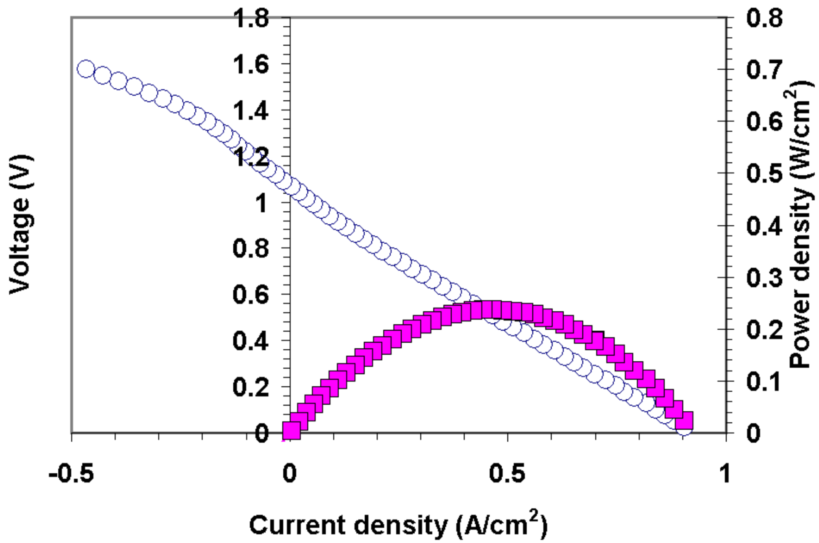
t = 0 h

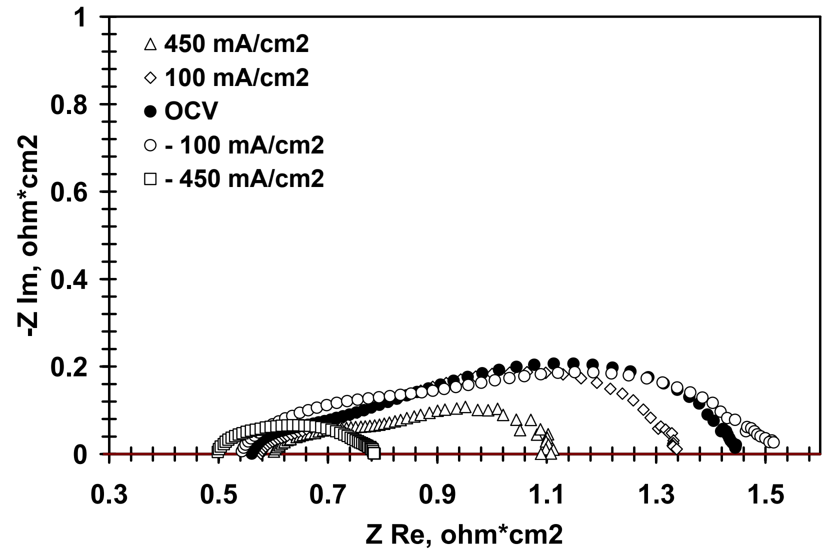




Calcine

@ 1100°C



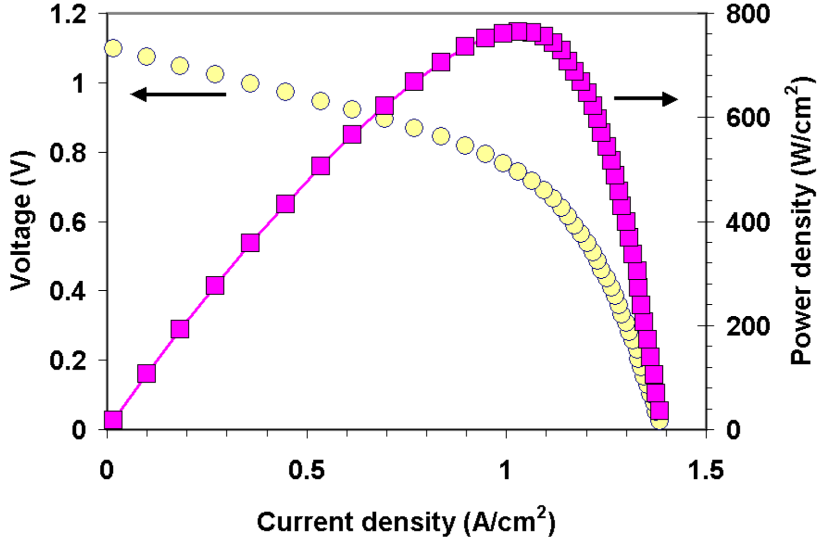


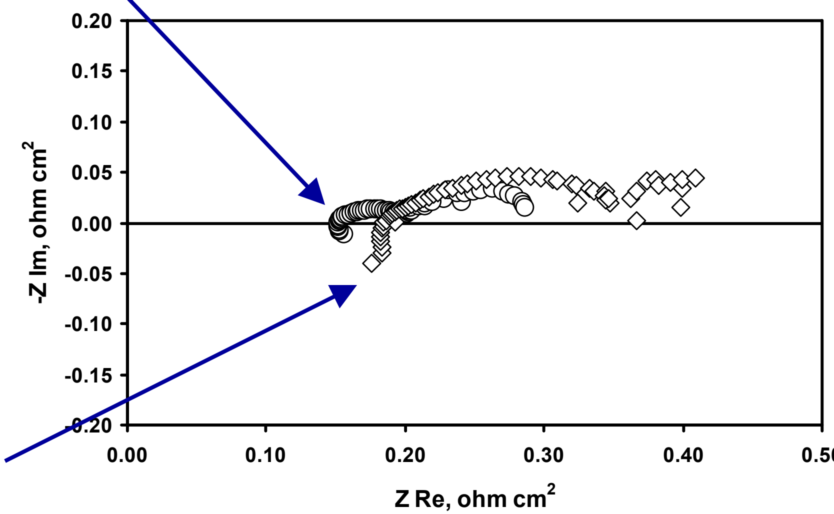
Effect of Calcination Temperature, Performance @ 800ºC

Calcine

@ 850C

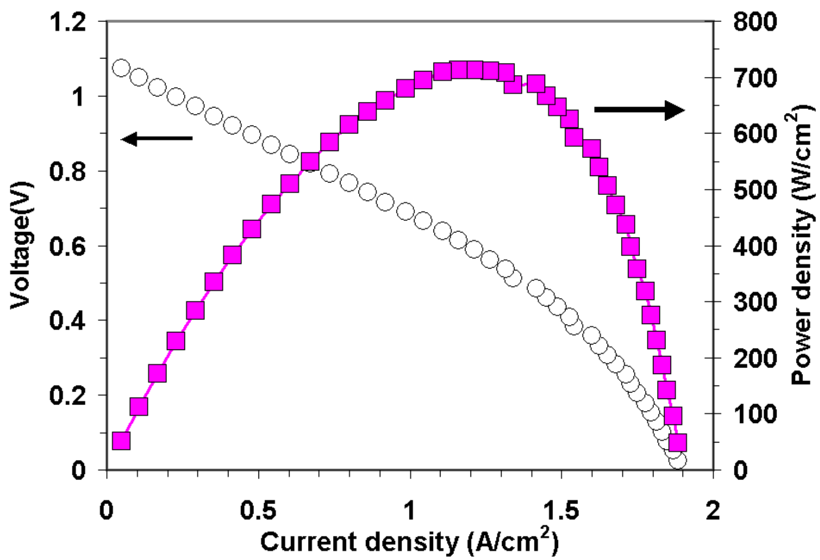
t = 0 h





Calcine

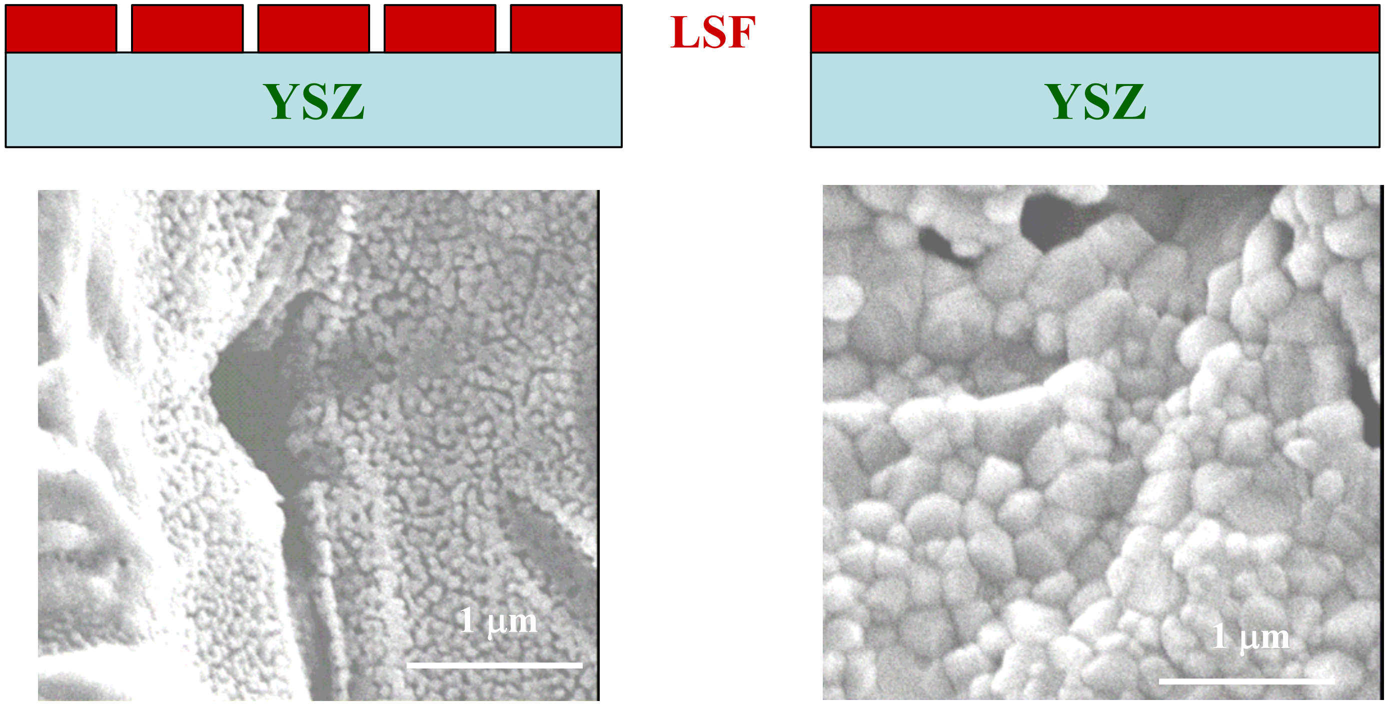
@ 1100C



Proposed deactivation mechanism:

850ºC calcination

1100ºC



Implications:

1. Deactivation is structural, not associated with interfacial reactions
2. Interlayers will probably not be effective
3. With LSM, activation of very good electrodes less important – use same concepts for stabilizing LSF?