Microstructural Investigations of Cathode – Barrier Layer – Electrolyte Interface in a SOFC

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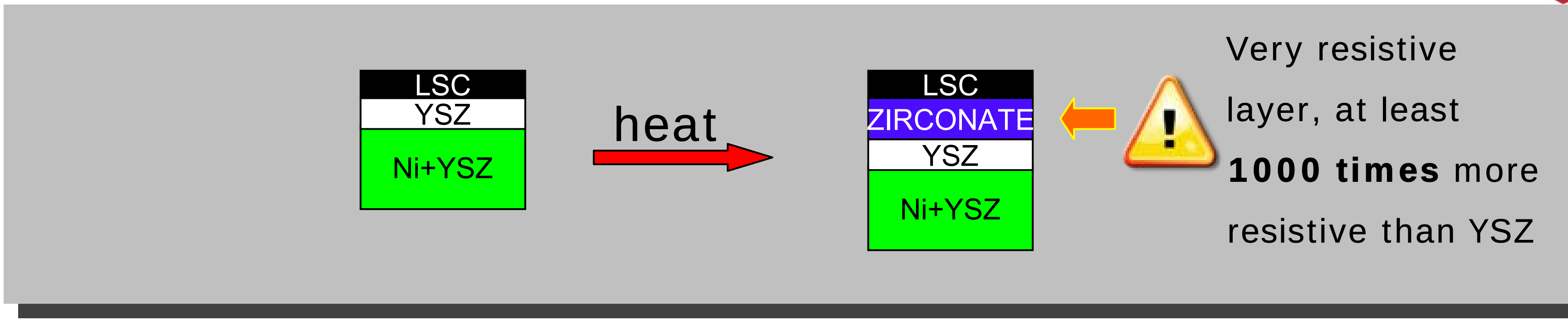
CGO Barrier Layer

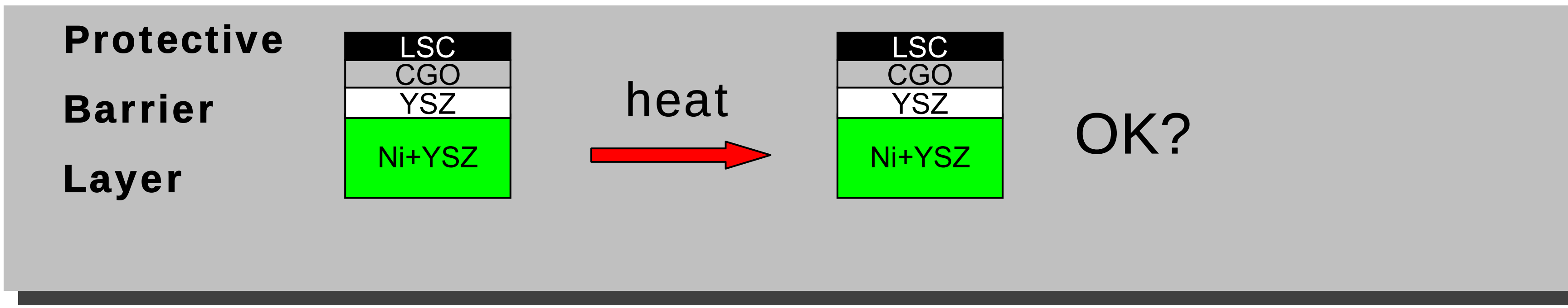
1) Introduction – motivation for investigation

2) Electron Microscopy Charaterisation of PLD CGO Barrier layers
    - Scanning Electron Microscopy (SEM)

3) Long-term Degradation of PLD CGO Barrier Layers

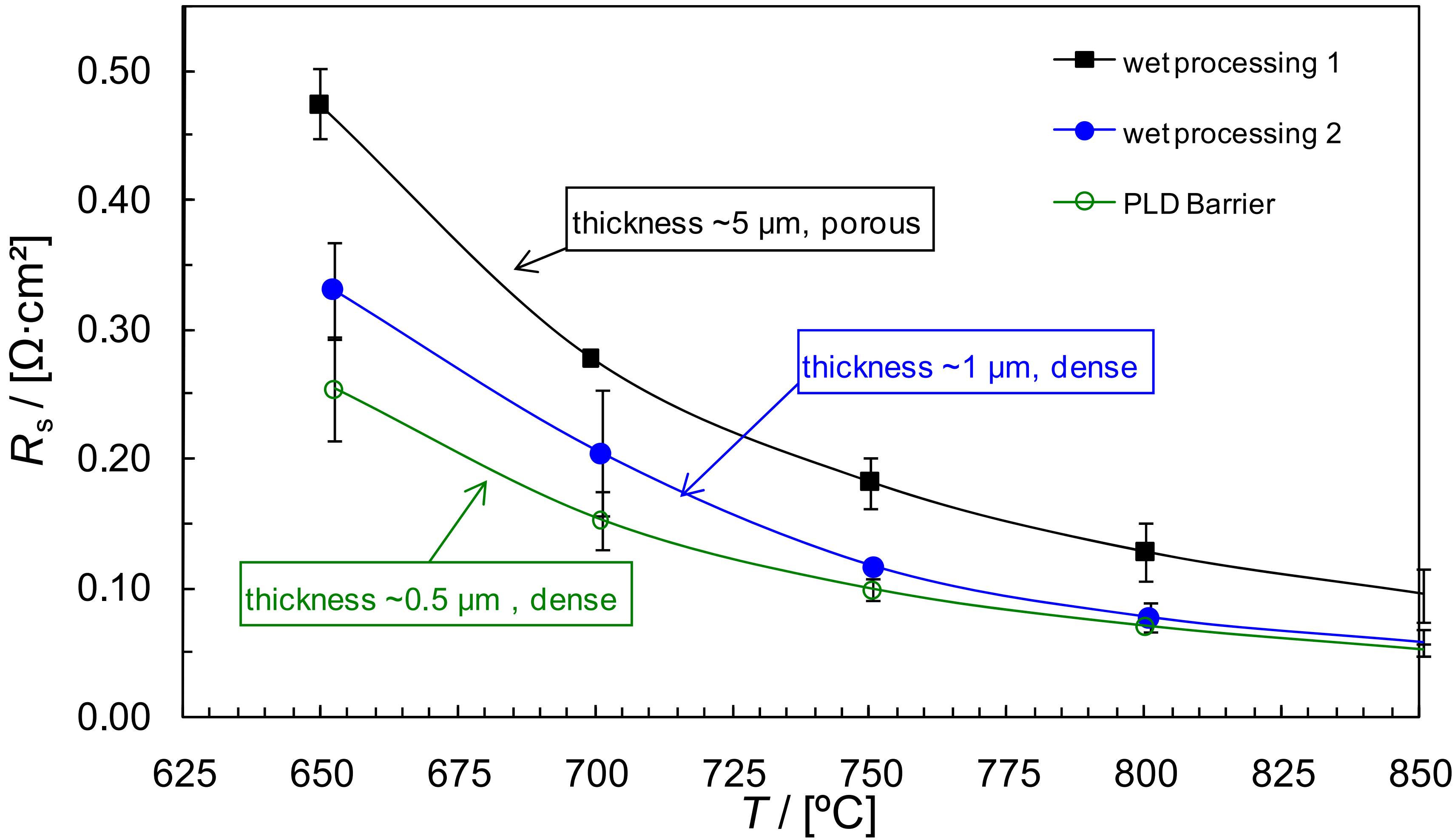
CGO Barrier Layer - Motivation



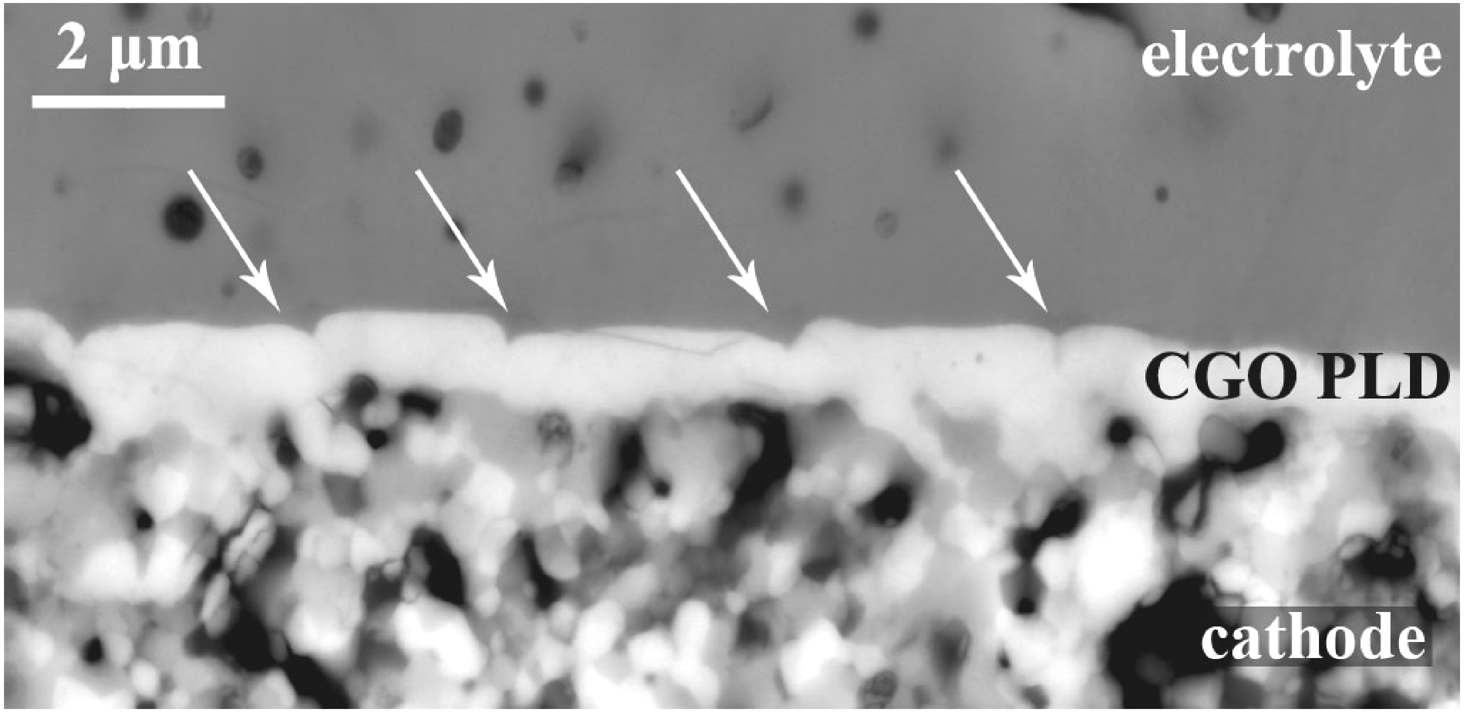


- LSC highly reactive with YSZ electrolyte
  - Barrier layer required between the YSZ electrolyte and LSC cathode– Gd-doped Ceria (CGO)
- YSZ-CGO interdiffusion, (T >1100°C) - low conductivity CGO/YSZ solid solution
  - Low temperature deposition technique required – physical vapour deposition (PVD) e.g. pulsed laser deposition (PLD)

CGO Barrier Layer – Rs Comparison



SEM across CGO barrier layers



SEM

- periodic $SrZrO_3$ formation at CGO-YSZ interface - imaging and EDS
- no obvious interaction of CGO with YSZ electrolyte - EDS
- CGO barrier layer – thin, dense

Origin of R_s in 2.5G SOFC - Calculated

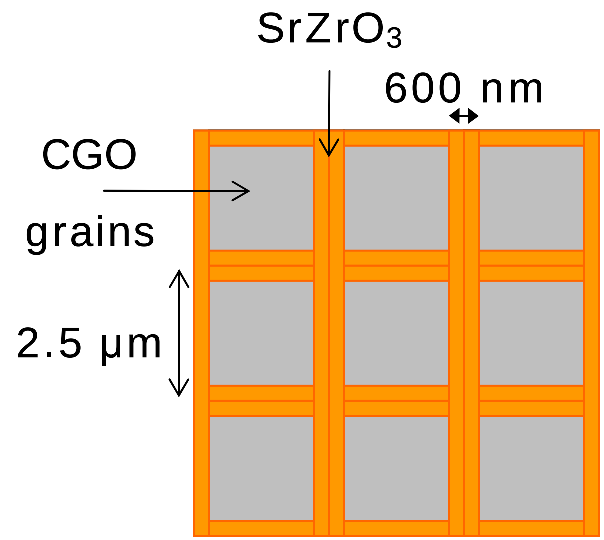
Ionic conductivity at 650°C

CGO – 1.78 x 10^{-2} S/cm

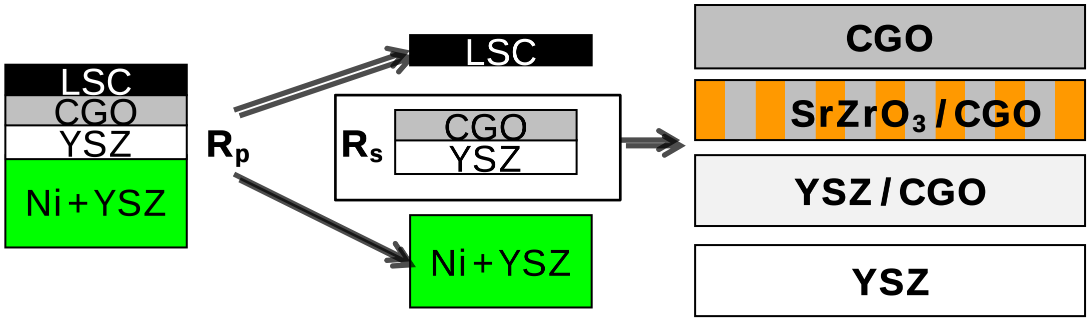
YSZ – 9.81 x 10^{-3} S/cm

CGO/YSZ – 5.78 x 10^{-4} S/cm

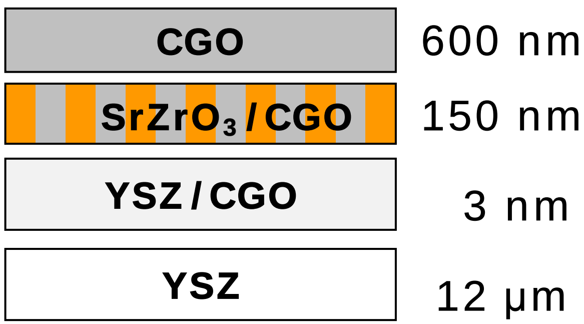
$SrZrO_3$ – 3.16 x 10^{-5} S/cm (1200°C)



Top View - Schematic



Origin of R_s in 2.5G SOFC - Calculated



PLD Barrier Layer Cell
R_s ($\Omega.cm^2$)

YSZ – 1.2 x 10^{-1}
CGO– 3.4 x 10^{-3}
$SrZrO_3$/CGO– 1.7 x 10^{-3}
YSZ-CGO – 5.2 x 10^{-4}
Total R_s – 1.3 x 10^{-1}

PLD CGO Interface

- PLD layer
  - thin (600 nm) + dense; reduced the interaction of CGO with YSZ; small amount of $SrZrO_3$ formation.
- No major interaction between CGO-YSZ

- By mitigating $SrZrO_3$ formation major contributor to R_s is the YSZ electrolyte

Fuel Cell Degradation

Testing Conditions

Duration: 1500 hours

Temperature: 650°C

Current Density: 0.75 A/cm^2

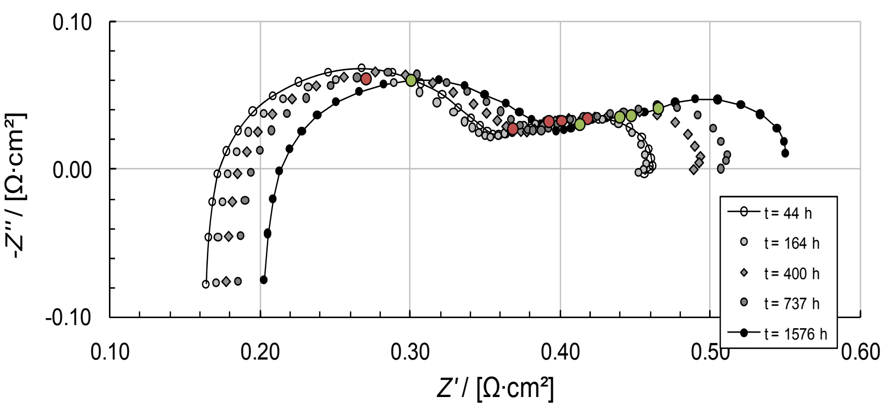
Active Area: 16 cm2.

Fuel Electrode: H2:CO2 (4:1)

Air Electrode: Air

Utilisation: 20%.

Impedance degradation under current

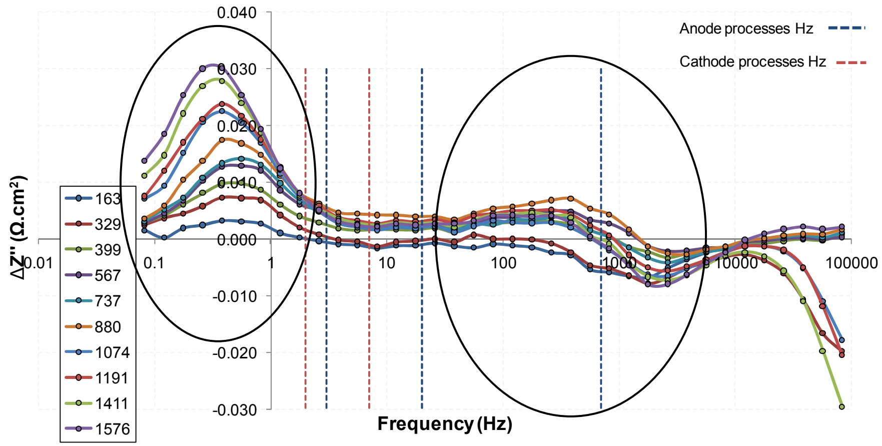


Rs, Rp degradation with time

	Initial	Degradation	
	mΩ·cm²	%/ 1000hrs	mΩ·cm²/ 1000hrs
R_s	159	17	27
R_p	316	9	29

Rp degradation – Characteristic Hz

ΔZ'' change with time



	Initial	Degradation	
	mΩ·cm²	%/ 1000hrs	mΩ·cm²/ 1000hrs
R_s	159	17	27
R_p	316	9	29

	Summit Frequency
Anode Polarisation	0.7 kHz
Anode Gas Diffusion	20 Hz
Anode Gas Conversion	3 Hz
Cathode Polarisation	7 Hz
Cathode Gas Related	2 Hz

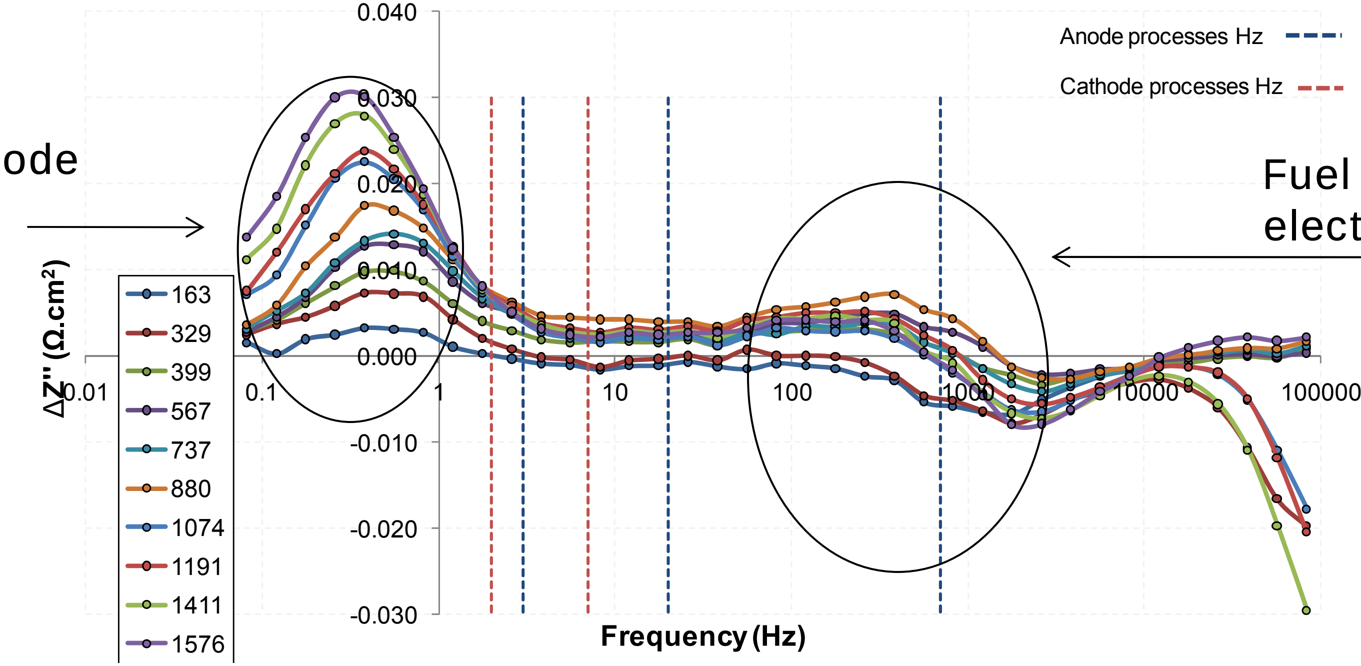
Hjelm, J. *et al. ECS Transactions 13(26):285-299, 2008.*

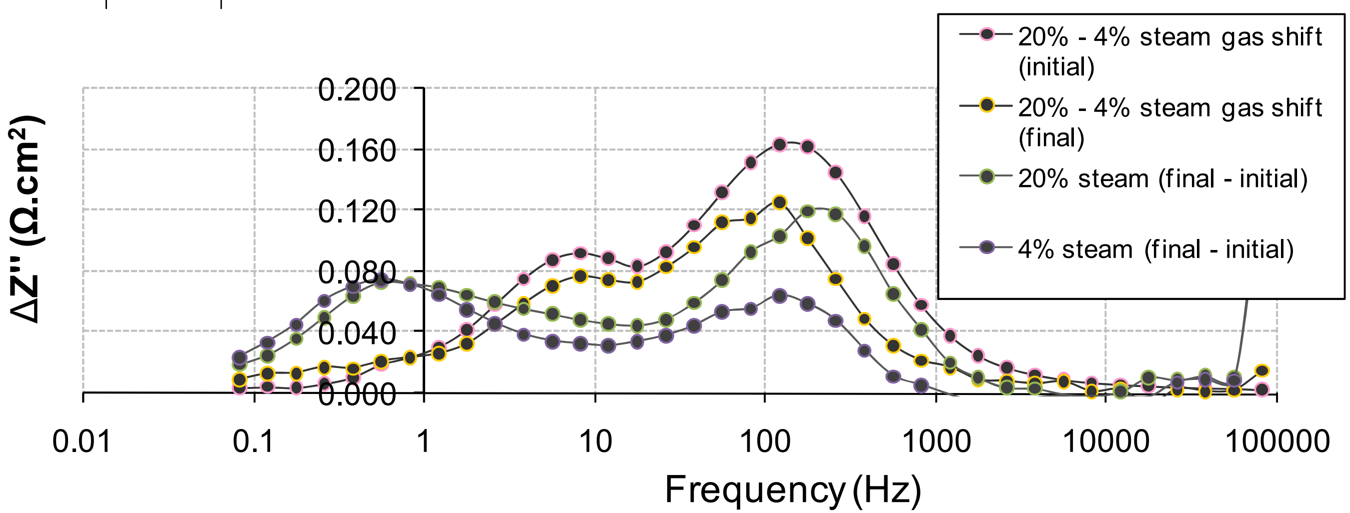
Rp degradation – Gas shift impedance

ΔZ'' change with time

Air electrode

Fuel electrode





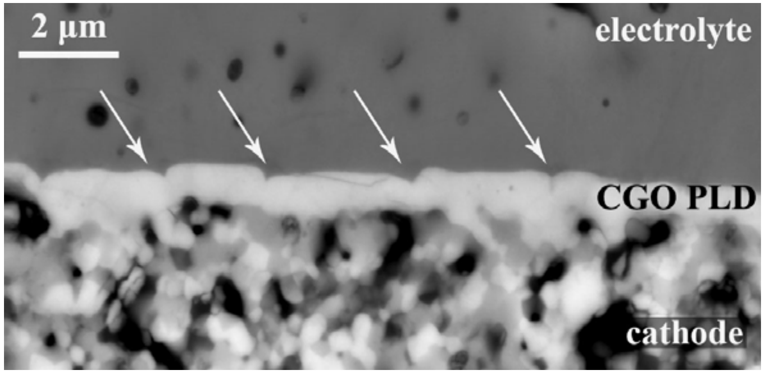
Rs degradation during testing

	Initial	Degradation	
	$m\Omega \cdot cm^2$	%/ 1000hrs	$m\Omega \cdot cm^2$/ 1000hrs
R_s	159	17	27
R_p	316	9	29

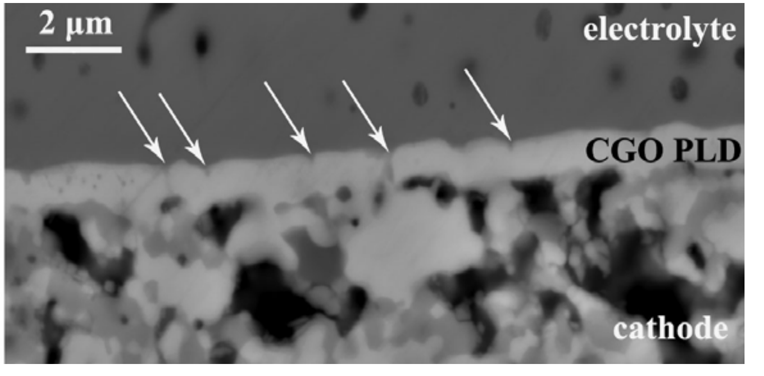
PLD Barrier Layer Cell
R_s ($\Omega.cm^2$)

YSZ (12µm) – 1.2 x 10^{-1}
CGO (600nm) – 3.4 x 10^{-3}
YSZ-CGO (3nm) – 5.2 x 10^{-4}
$SrZrO_3$/CGO (600nm) – 1.7 x 10^{-3}
Total R_s – 1.3 x 10^{-1}

Before Testing



After Testing



Kinetic Demixing - Sr depletion (Hjalmarsson, P. *et al. Solid State Ionics (179): 1422 - 1426*(2008))

Conclusions

- PLD an effective barrier layer
- Long-term testing for 1500^{+} hours
  - Cell Degradation
- Diagnostic recommendations for SOFC testing
  - Impedance and electrical characterisation provides insitu overview of cell degradation
  - Electron microscopy (EM) provides post-mortem results to support electrical characterisation
  - Area chosen for characterisation must be chosen judiciously
    - Results from EM can be sight specific
    - A suitable and representative reference must be available!

Future Work

- Reproducibility – PLD and Cathode
- Long-term degradation mechanism
- Improved Barrier Properties (Sputtered Layers)

Conclusions