Development of Accelerated Test Protocols and Investigation of Cathode/Electrolyte Interfaces

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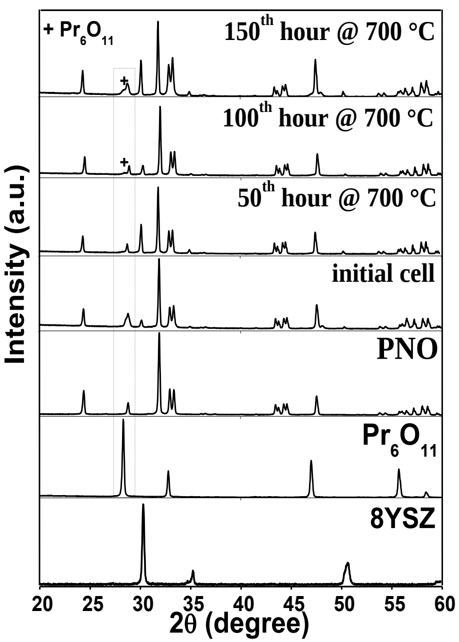
Highlights of the Accomplishments

1. **Role of the interlayer chemistry on the cathode performance**
   The chemistry of doped ceria buffer is of critical importance in determining the activity and stability of cathode. The addition of Pr into the doped ceria interlayer, e.g. (Pr,Gd)-doped CeO_2, improves the stability and activity for nickelates, LSCF, and LSM.
2. **Phase transition during the electrochemical operation**
   Introduced the role of electrochemical operation on the chemical activity and structural stability in cathodes.
3. **Accelerated test protocols (ATPs)**
   More than 200 single cells were examined to develop reproducible and relevant accelerated test protocols for solid oxide fuel cells. **The following parameters were studied: current density, operation temperature, moist level, sintering temperature, accelerated test frequency, operation time, and cathode composition.** These measurements enable a systematic and quantitative analysis of the applicability of accelerated test protocols, which can be adopted to measure all type of cathodes.

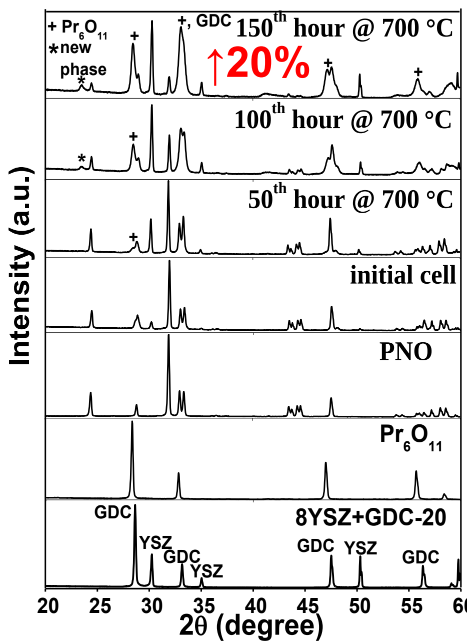
Role of Interlayer on the Phase Evolution - Case of Nickelates

PNO

Interlayer absent

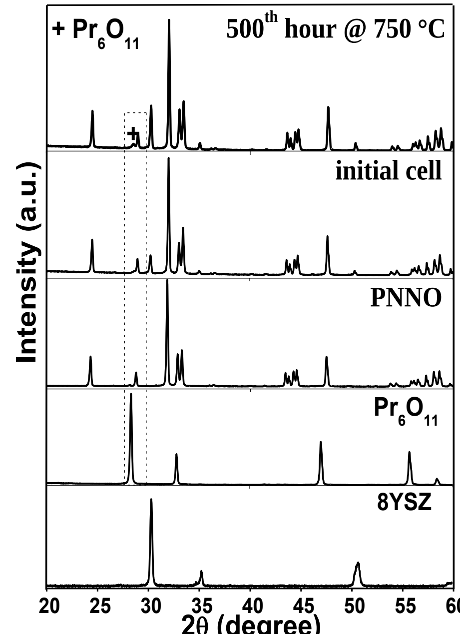


GDC-20

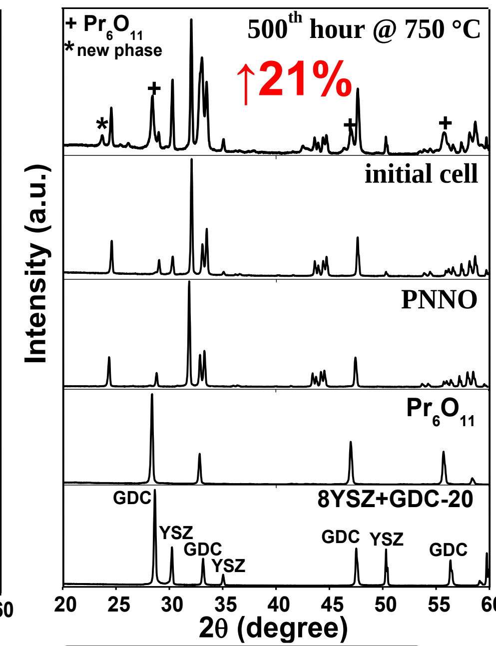


PNNO50-50

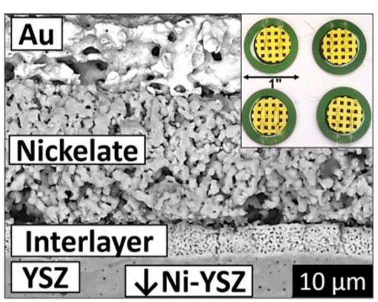
Interlayer absent



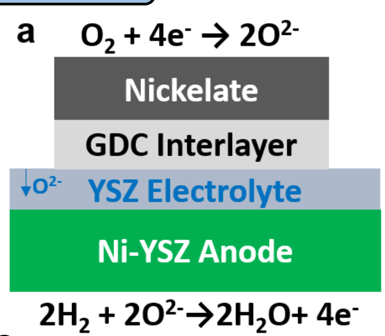
GDC-20



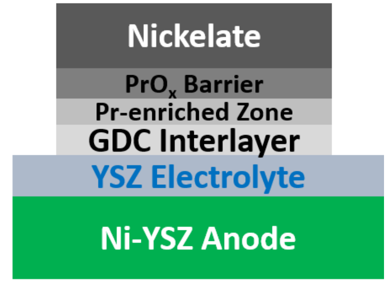
Standard



GDC cells

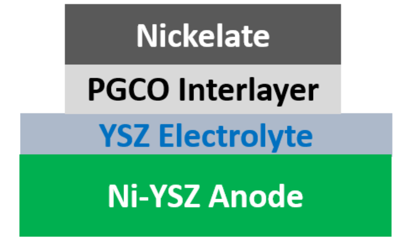


Thin PrO_x Film



PrO_x-GDC cells

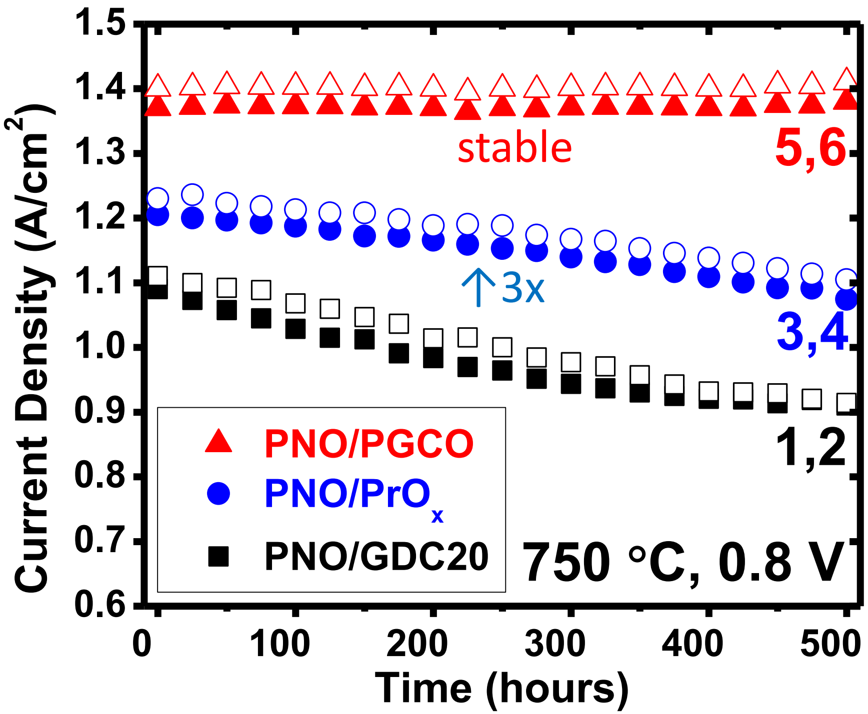
New Chemistry

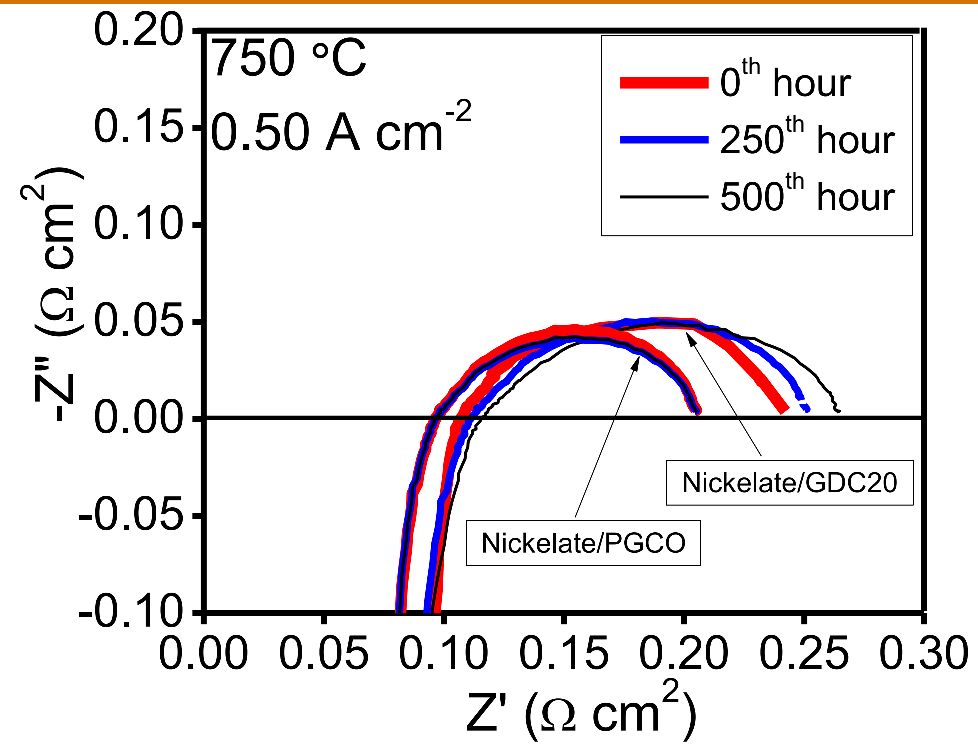


PGCO cells

PGCO: $Pr_{0.10}Gd_{0.10}CeO_{1.90\pm\delta}$

Performance Stability vs. Interlayer Chemistry – Case of Nickelates





Points to take:

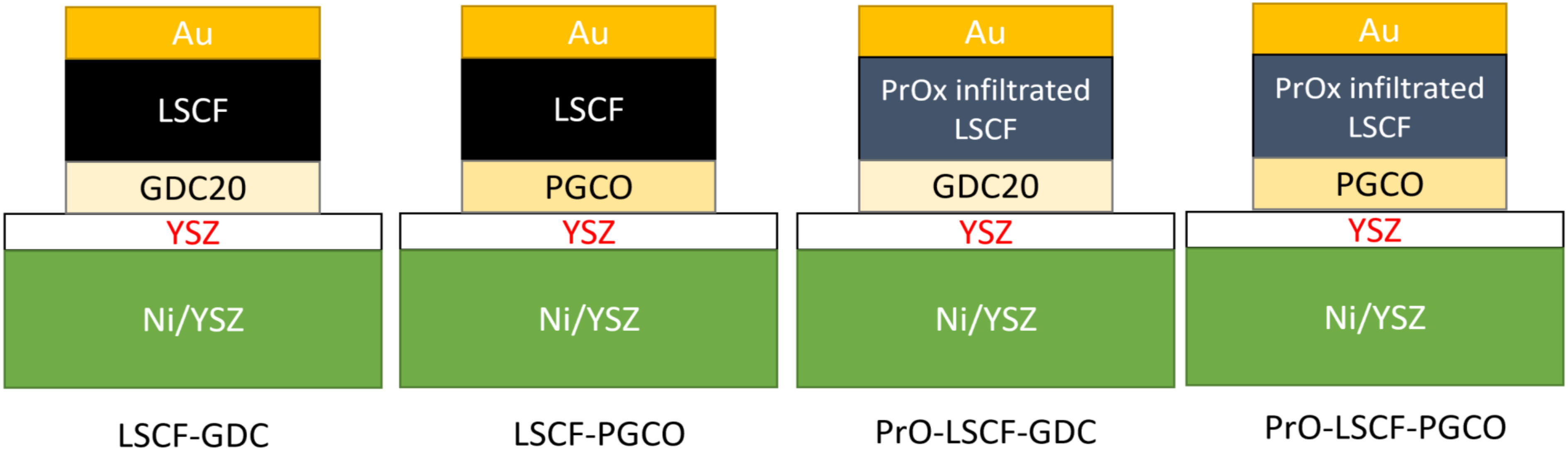
- Multiple cells for each condition for both PNO and PNNO electrodes
- 3x reduced performance degradation in PNO/PrO_x cells.
- Stable operation was measured on multiple sets of cells and cathode compositions with the **(Pr,Gd) doped CeO_2 (PGCO)** interlayer.
- Reduced R_{pol} (↑MIEC → ↑σ_e) due to extended rxn. zone.
- Reduced Rohm (↓Rgb with [Pr]↑)[1]

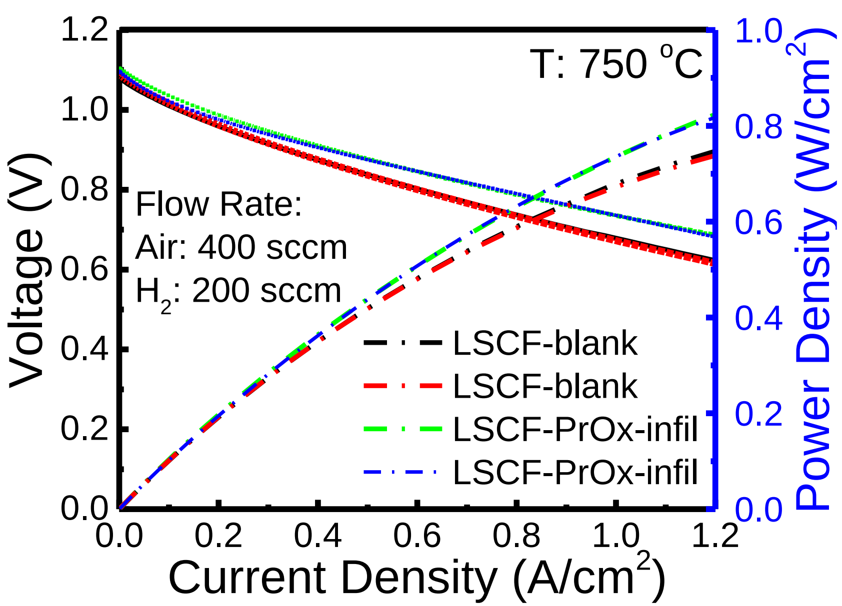
Summarized ASR vs. GDC cells.

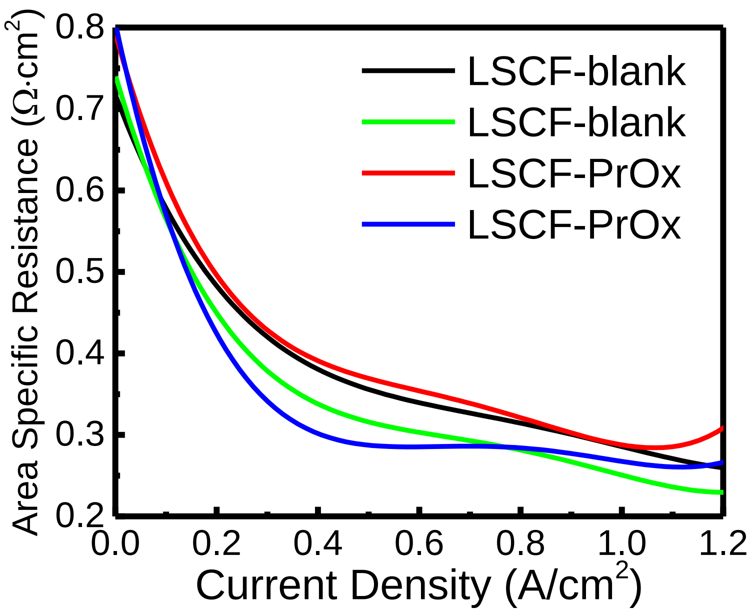
ASR	Ohmic	Electrode	Total
PrOx-GDC 500th hour	7%↓	22%↓	15%↓
PGCO 500th hour	16%↓	28%↓	22%↓

[1]S. Lübke et al. *SSI*, **117**, p.229 (1999).

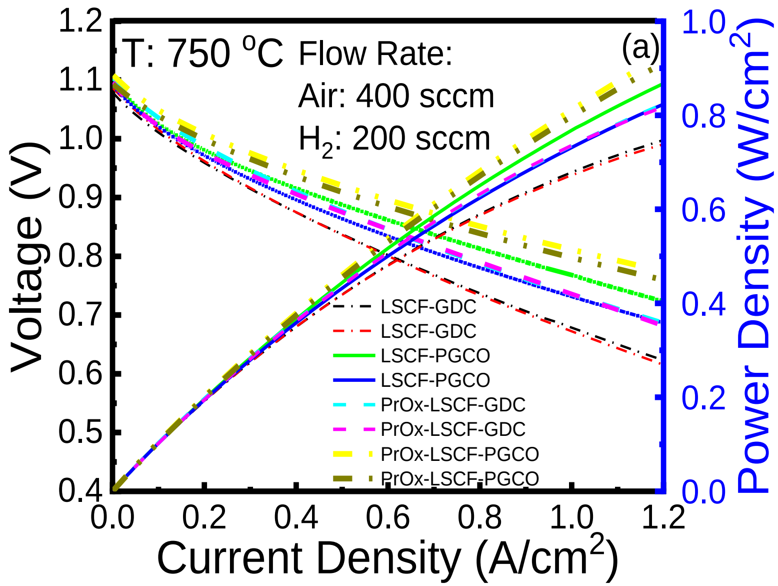
Role of Interlayer on the Cathode Performance - Case of LSCF

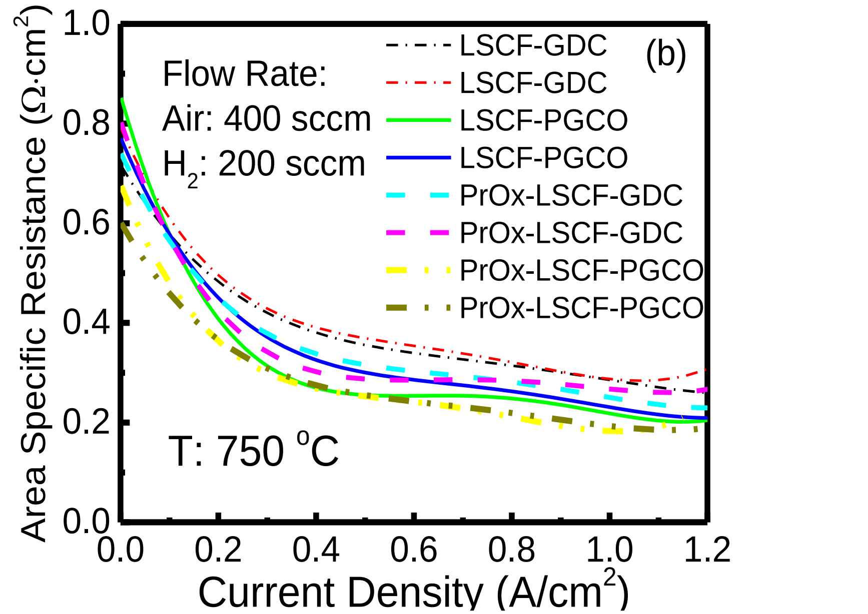


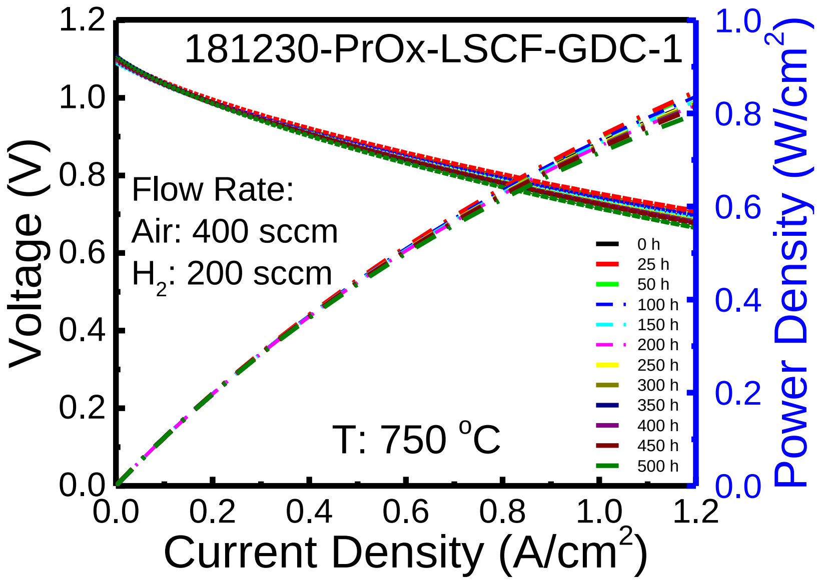


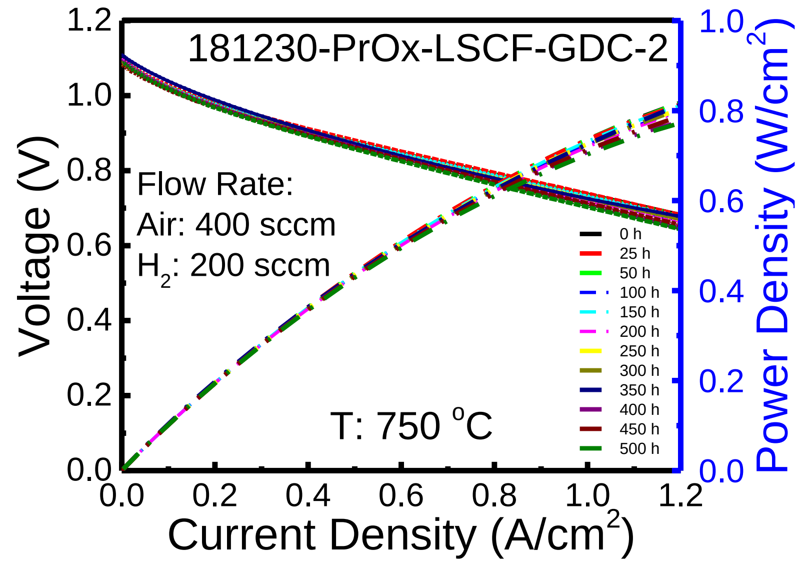


Role of Interlayer on the Cathode Performance - Case of LSCF

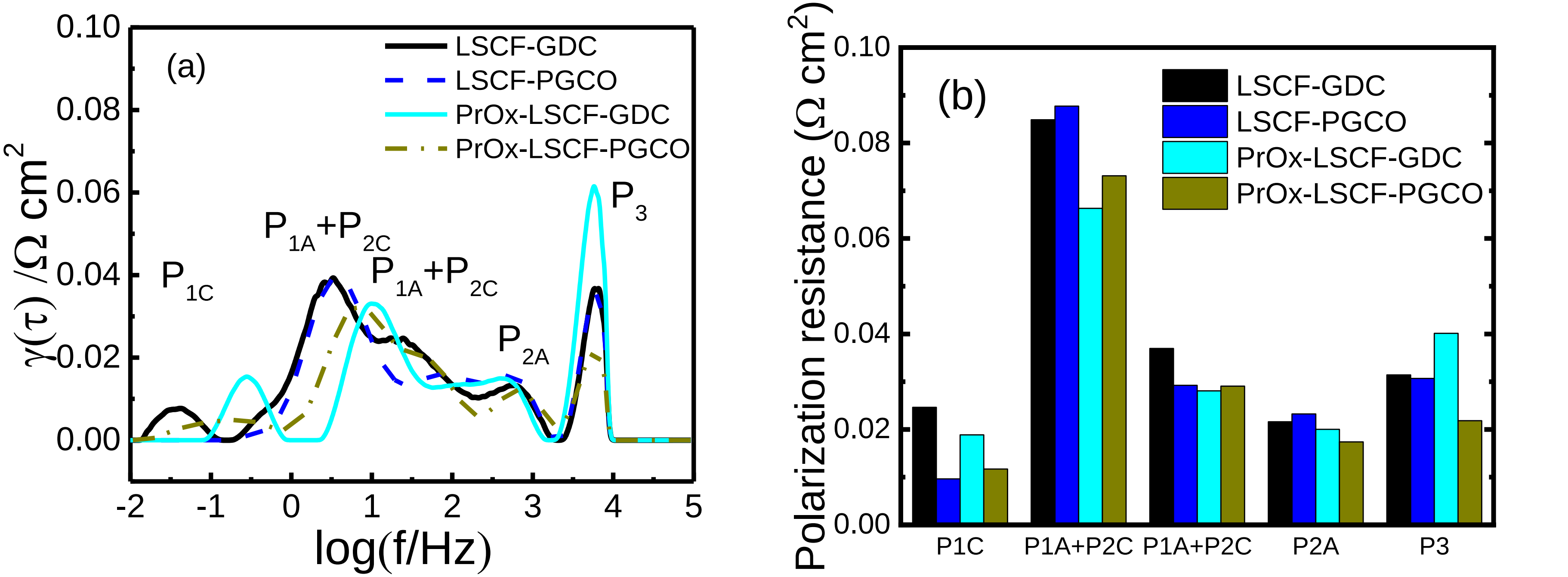








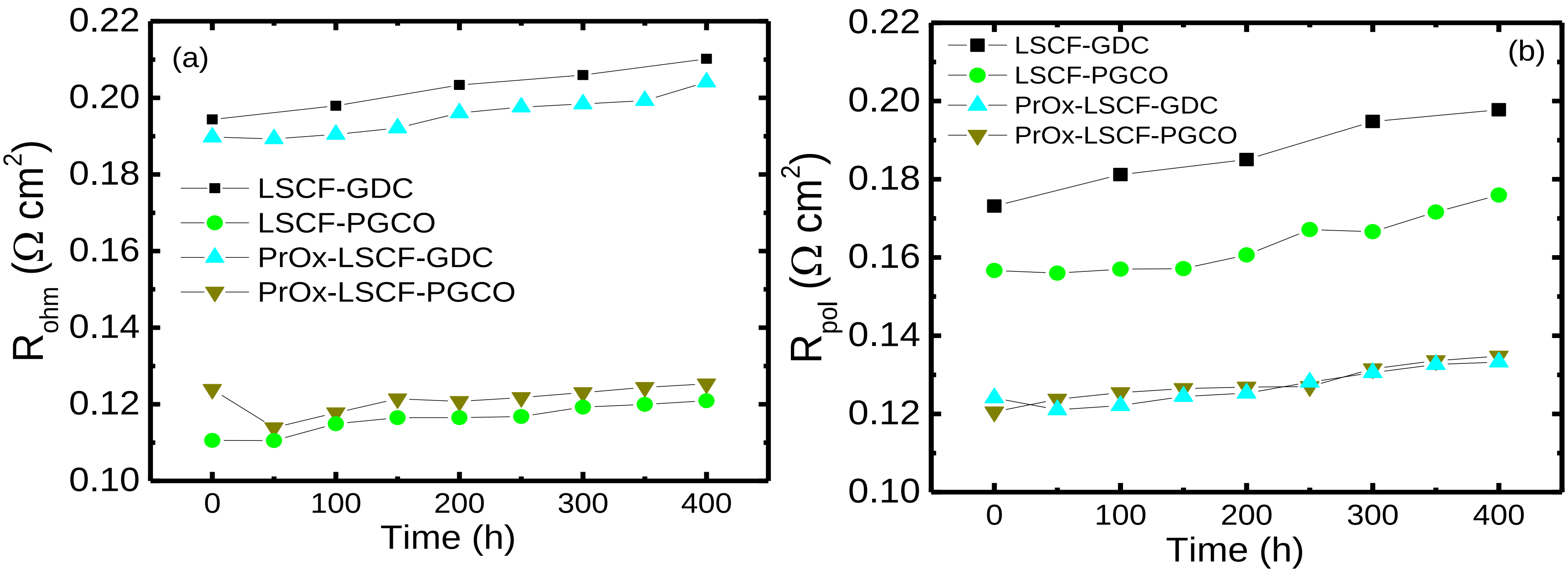
Role of Interlayer on the Cathode Performance - Case of LSCF



Points to Take

- P_{1C} at ~ 0.1 Hz, related to gas transport in LSCF electrodes. Infiltrated electrode shows a higher resistance than the one without infiltration with the same ceria interlayer.
- P1A determined by the gas diffusion at the anode; while P2C strongly dependent on the oxygen reduction reaction kinetics, which can be promoted by PrOx infiltration.
- Peaks P2A at ~ 1 kHz, strongly affected by p(H_2O) in the anode gas and related to hydrogen oxidation kinetics in Ni/YSZ anode.
- P3 at 10 kHz can be related to high frequency cathode process.

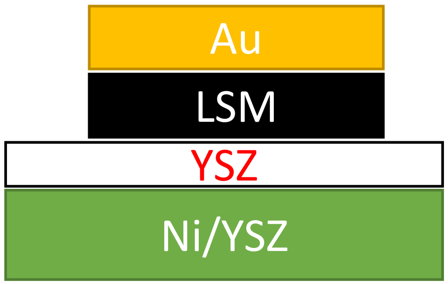
Role of Interlayer on the Cathode Performance - Case of LSCF



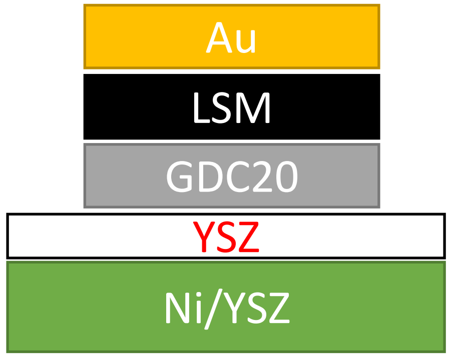
Points to Take

- PGCO interlayer can suppress the ohmic degradation. By replacing the GDC layer with a PGCO layer, the ohmic polarization reduces from 0.016 $\Omega\cdot cm^2$ to 0.01 $\Omega\cdot cm^2$.
- PrOx provides additional active sites for ORR in LSCF. The infiltration of PrOx to LSCF backbone leads to a decrease of R_{pol} from 0.02 $\Omega\cdot cm^2$ to 0.014 $\Omega\cdot cm^2$ at the 400th hour.
- The increasing R_{pol} of the infiltrated electrode likely due to the coarsening of infiltrated catalysts.

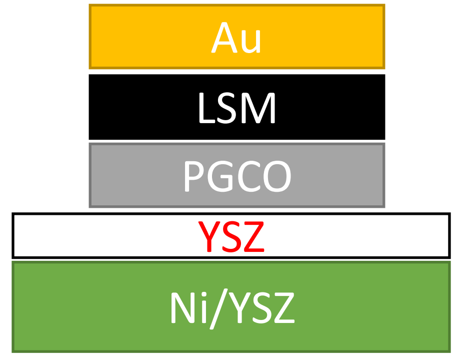
Role of Interlayer on the Cathode Performance - Case of LSM



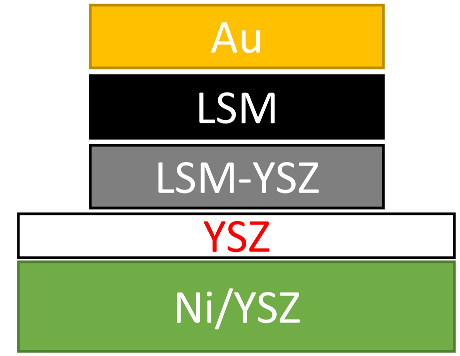
Conventional SOFC with YSZ electrolyte and LSM cathode



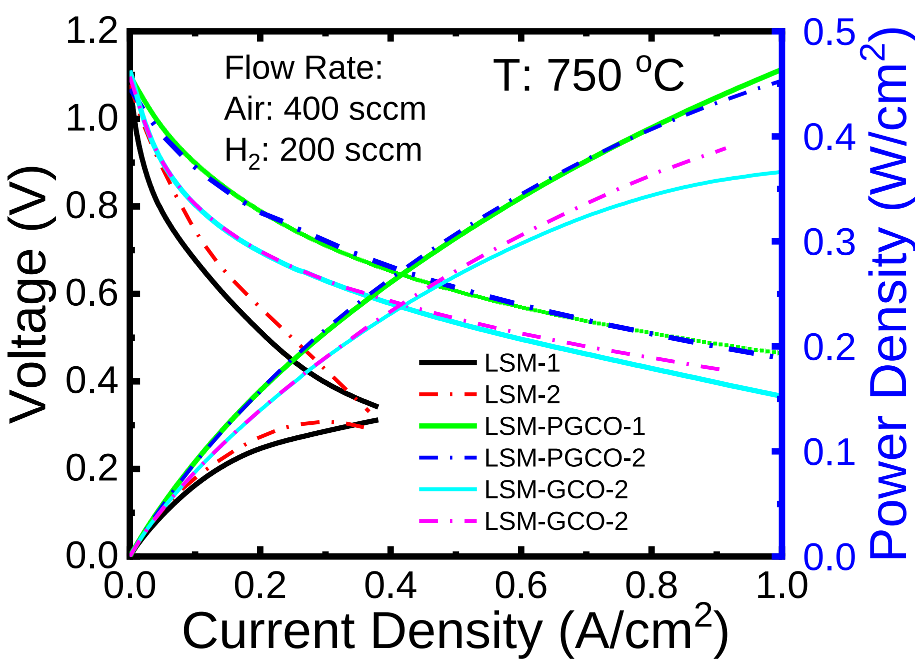
Conventional interlayer, GDC, is applied between LSM and YSM

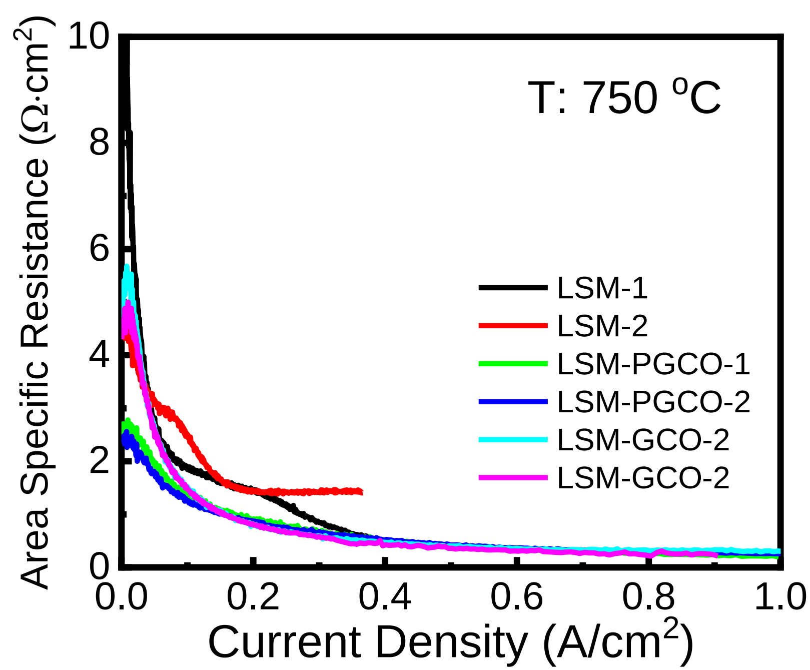


PGCO is used to study the role of interlayer chemistry on LSM performance

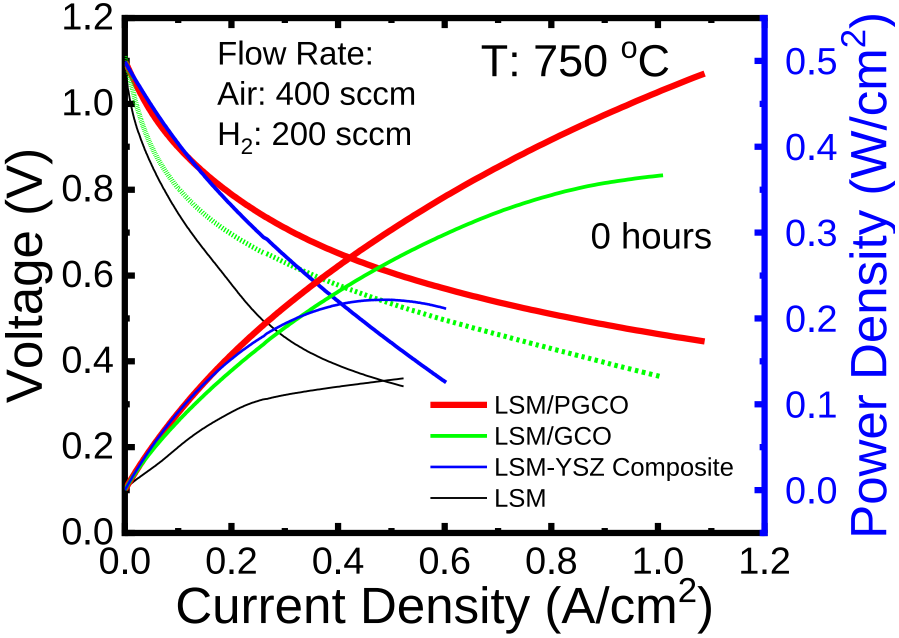


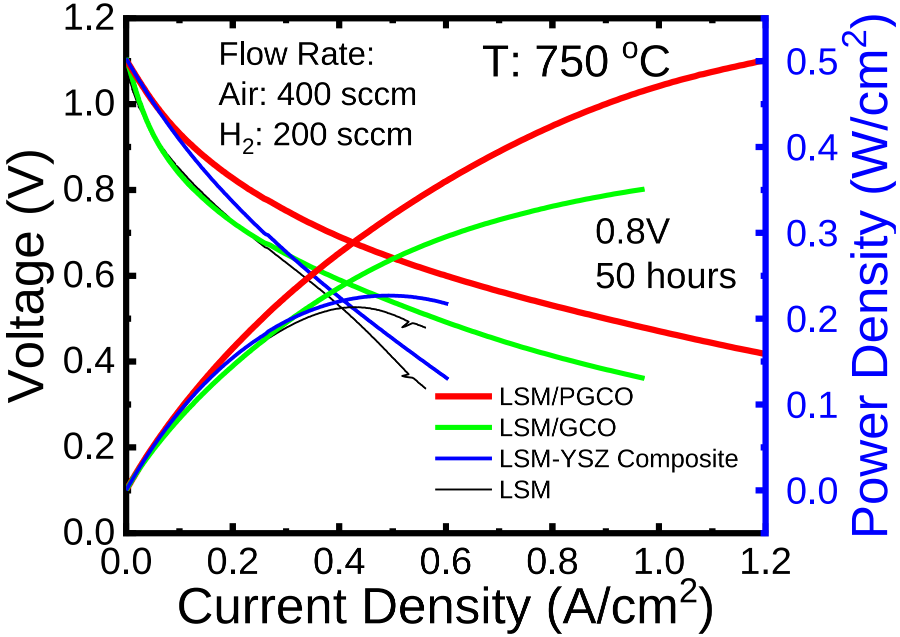
LSM-YSZ composite cathode is used as the baseline cathode





Role of Interlayer on the Cathode Performance - Case of LSM

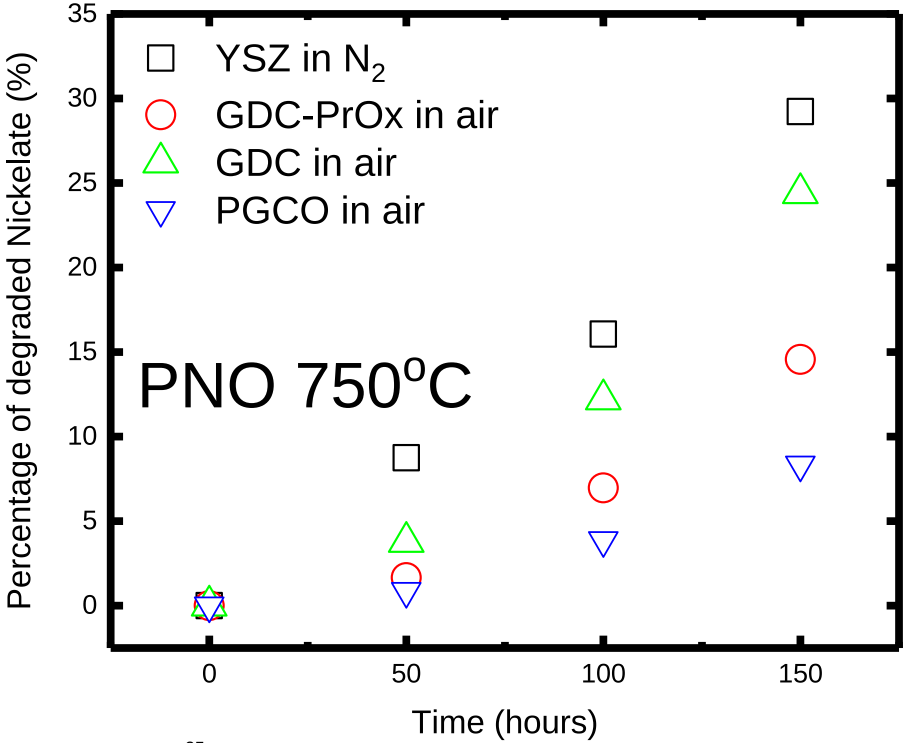


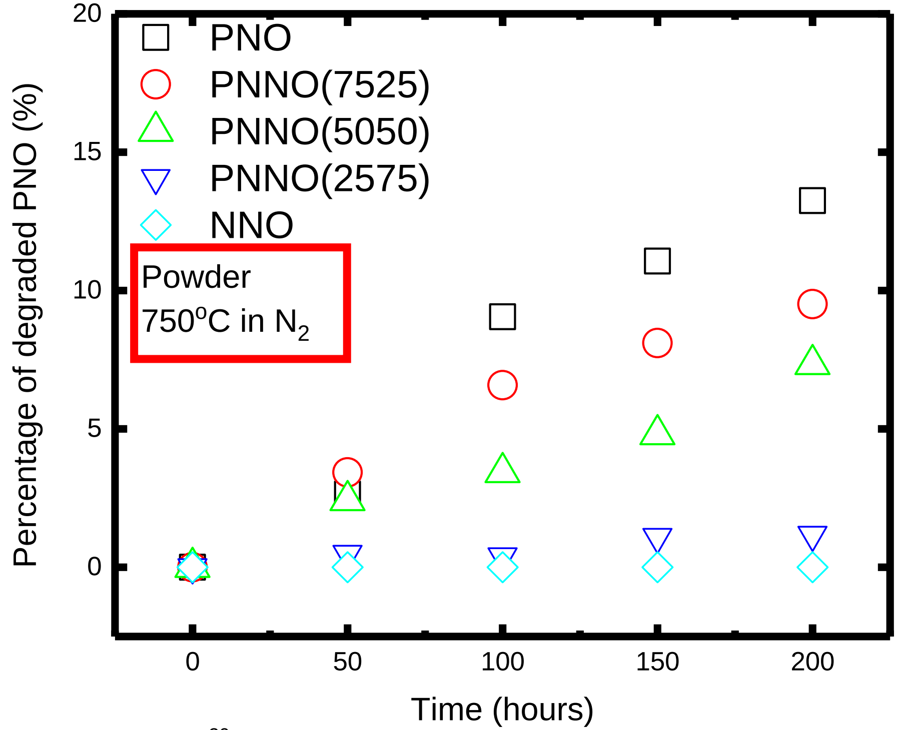


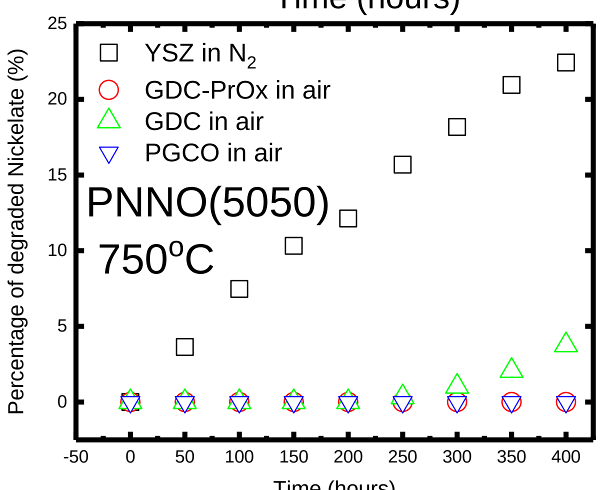
Points to Take

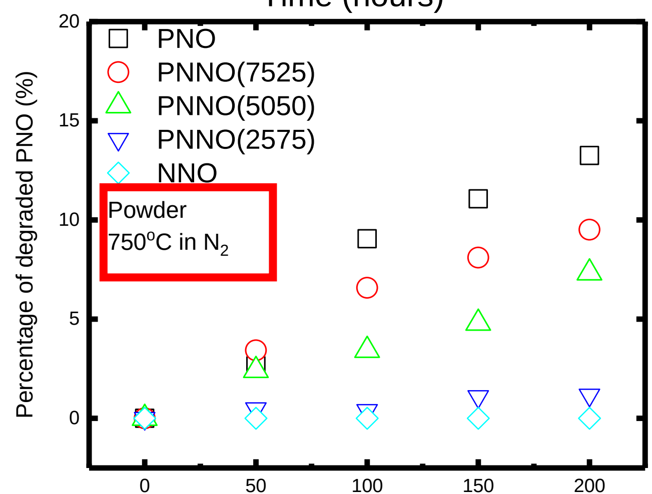
- The existence of a ceria interlayer affects the initial performance of LSM-based cells.
- By applying PGCO and GCO interlayer, the initial current density at 0.7 V increases.
- PGCO interlayer may provide extended triple phase boundaries for the oxygen reduction and lowers the cell resistance.
- The interlayer chemistry plays a significant role on the activation process of the LSM-based electrode.

Phase Transition of Nickelates in a Reducing Condition





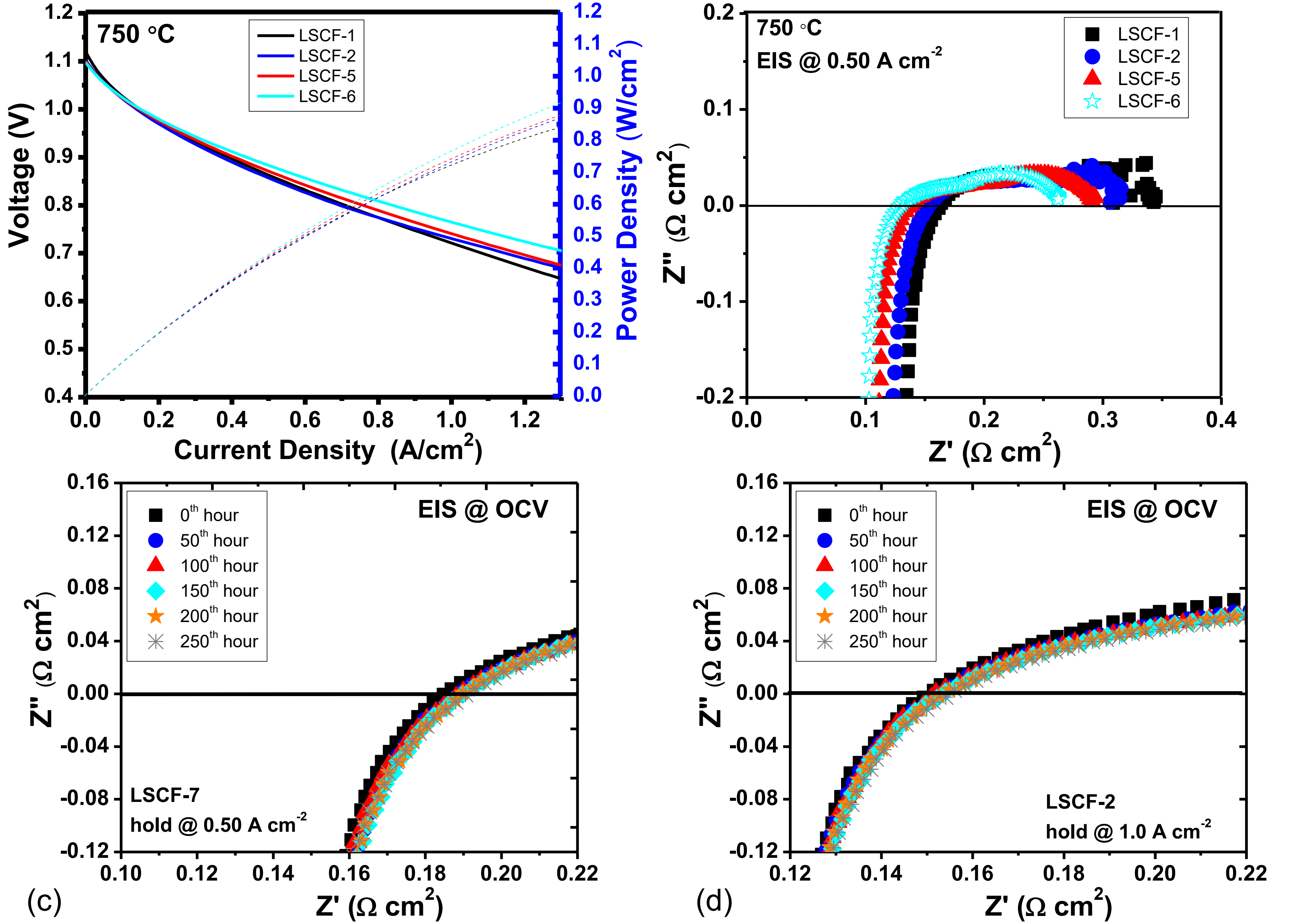




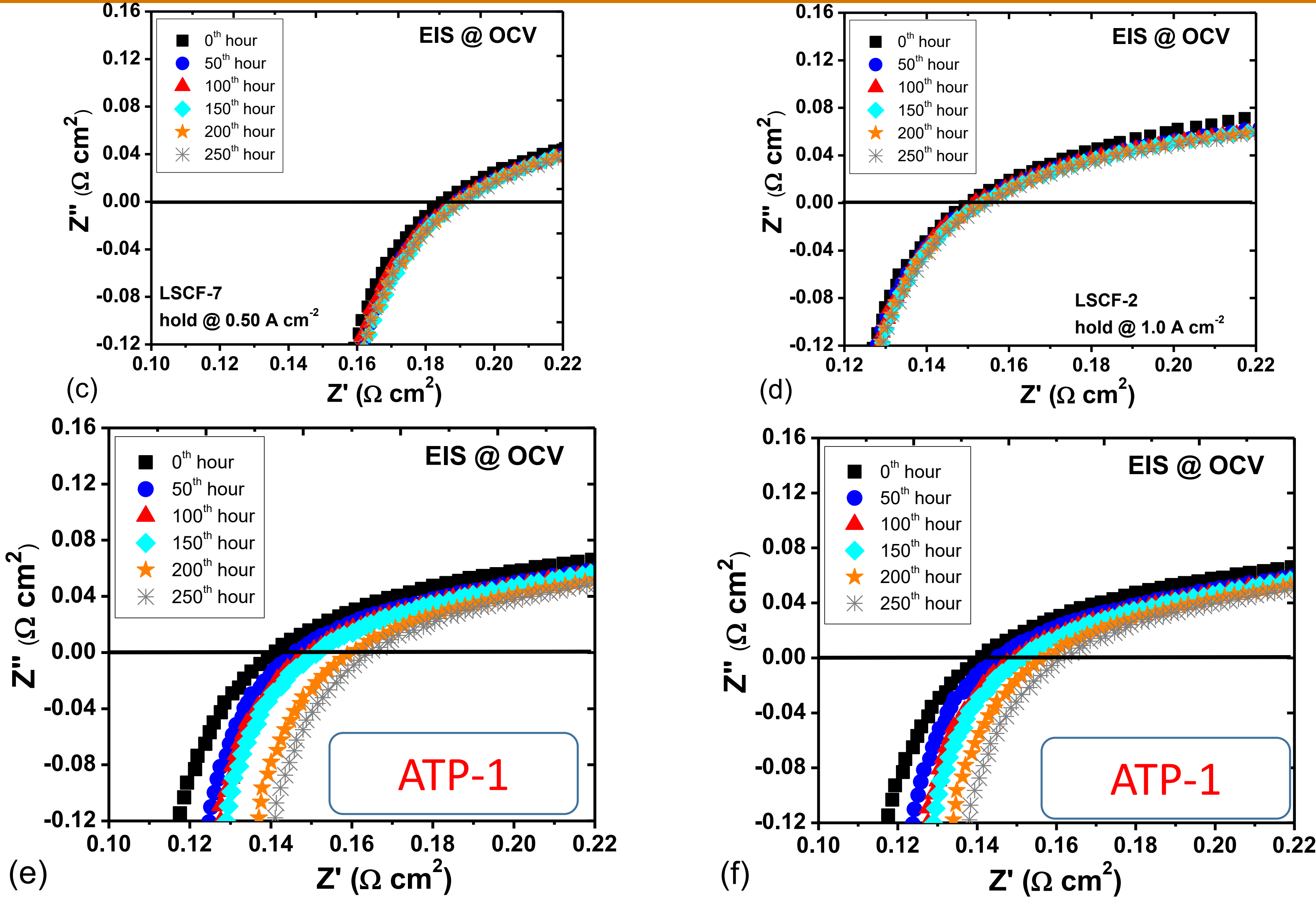
A Brief Summary of Accelerated test Protocols (ATP)

Operating conditions	Comments, Ohmic ASR and Power Density (PD)		H_2O% air	250 hour	600 hour	1100 hour
Hold @ 0.50Acm^{-2}	Baseline, low current (J)	Ohmic	0.6	1.9	2.6	4.5
		PD		1.3	2.3	3.6
Hold @ 1.0 Acm^{-2}	Baseline, high current (J)	Ohmic	0.6	2.9	3.5	7.5
		PD		1.8	4.0	6.5
ATP-2	Low J	Ohmic	0.6	11.0	13.7	18.2
		PD		4.2	8.4	13.3
ATP-2	Low J	Ohmic	0.6	14.4	18.5	22.0
		PD		4.2	8.3	13.2
ATP-1	High J	Ohmic	0.6	17.0	24.1	31.2
		PD		5.6	11	17.4
ATP-1	High J	Ohmic	0.6	16.0	26.5	36.0
		PD		5.6	11	17.5
ATP-3	High J	Ohmic	0.6	8.4	10.1	14.0
		PD		2	4.5	7.8
ATP-3	High J	Ohmic	0.6	7.9	10.3	14.4
		PD		2.3	5.0	8.2
ATP-4	High J, **wet air**	Ohmic	3.0	20.1	31.5	39.5
		PD		9.2	18.9	23.1
Hold @ 1.0 A·cm^{-2}	Constant & high J, wet air	Ohmic	3.0	5.3	7.1	9.2
		PD		1.8	3.6	5.2
ATP-5	Fast cycle; high J, **dry air**	Ohmic	0	9.4	18.4	21.6
		PD		4.4	7.6	9.9
Hold @ 1.0 A·cm^{-2}	Constant & high J, dry air	Ohmic	0	1.1	2.9	3.9
		PD		1.1	1.4	1.4

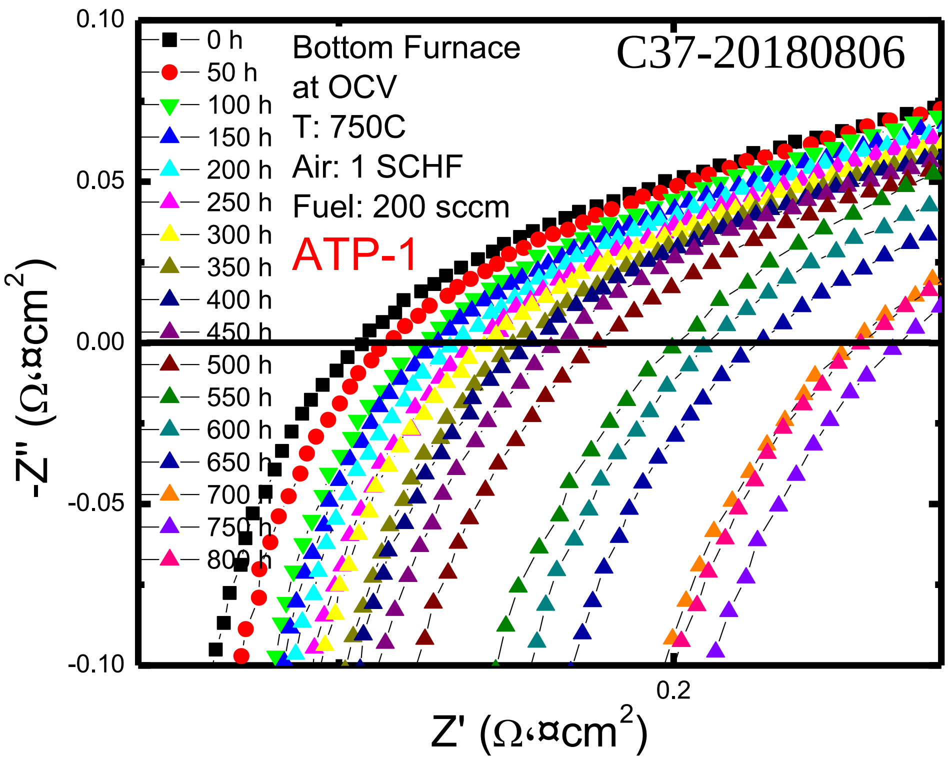
Reproducible Cell Performance Under the Steady-State Operation

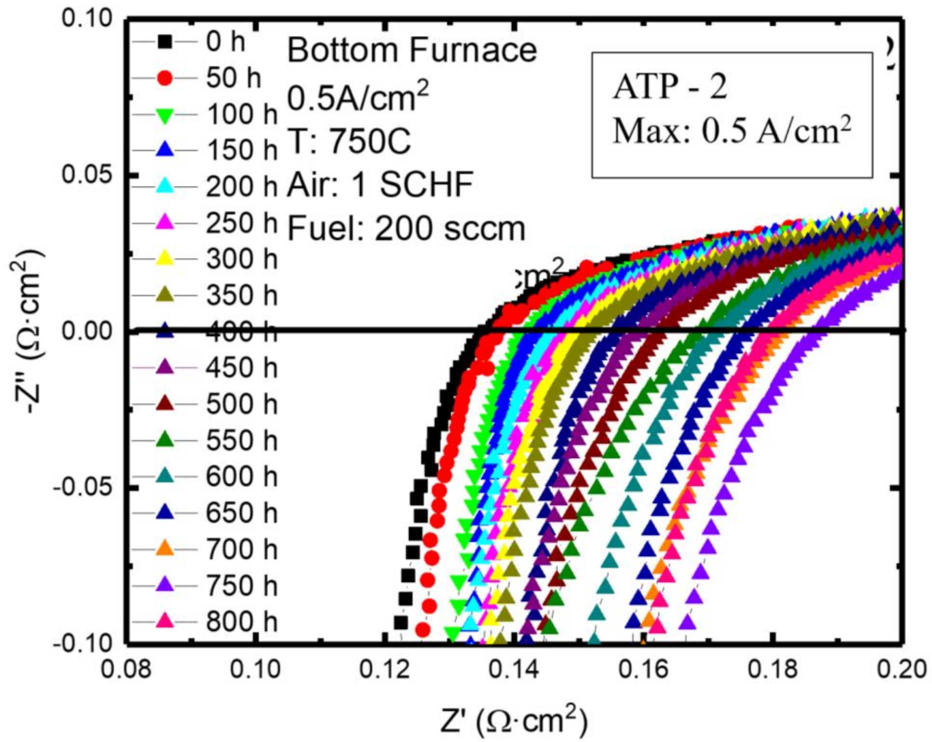


Accelerated Increases in Ohmic Resistance



Accelerated Measurements at a New Location

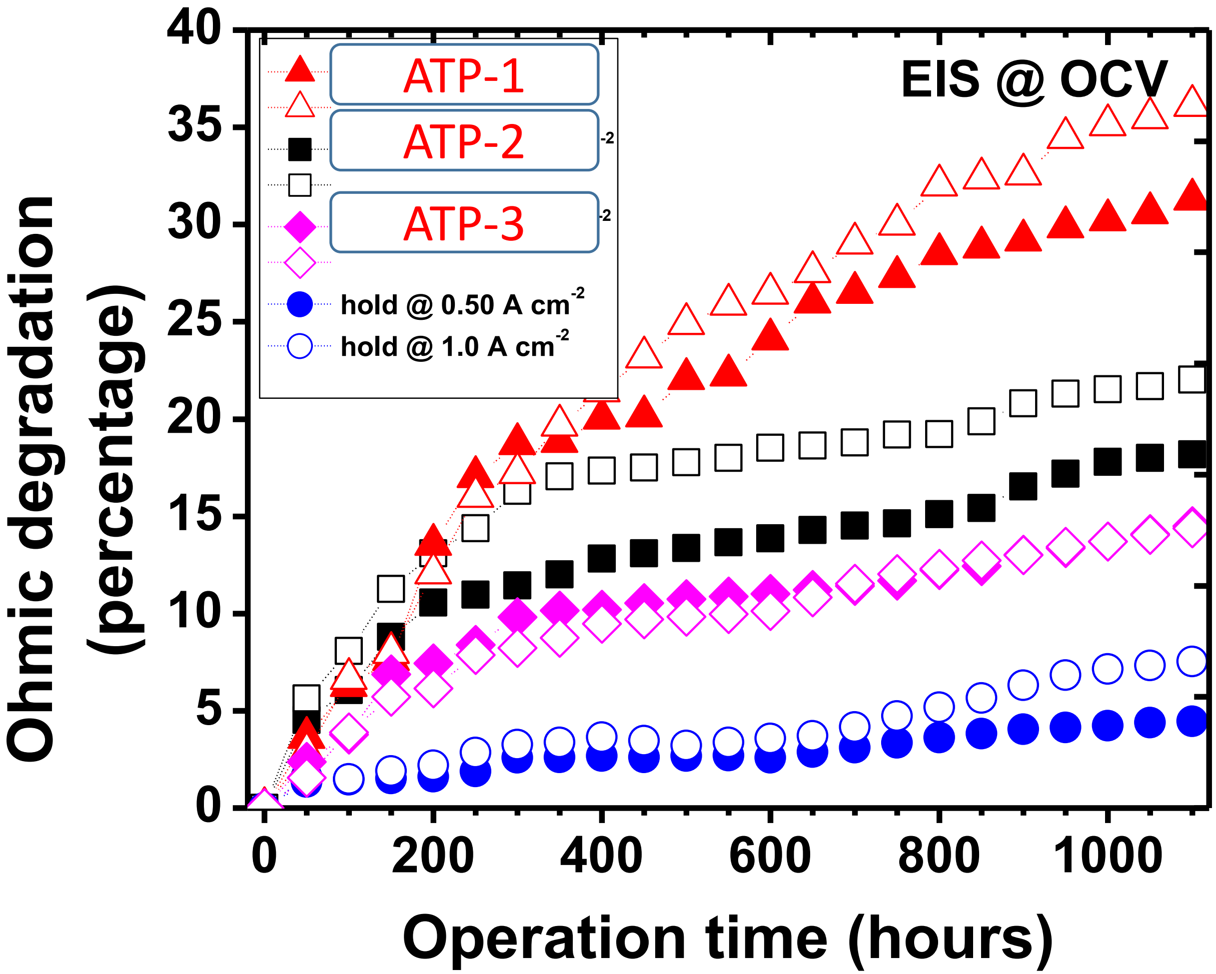




Points to Take

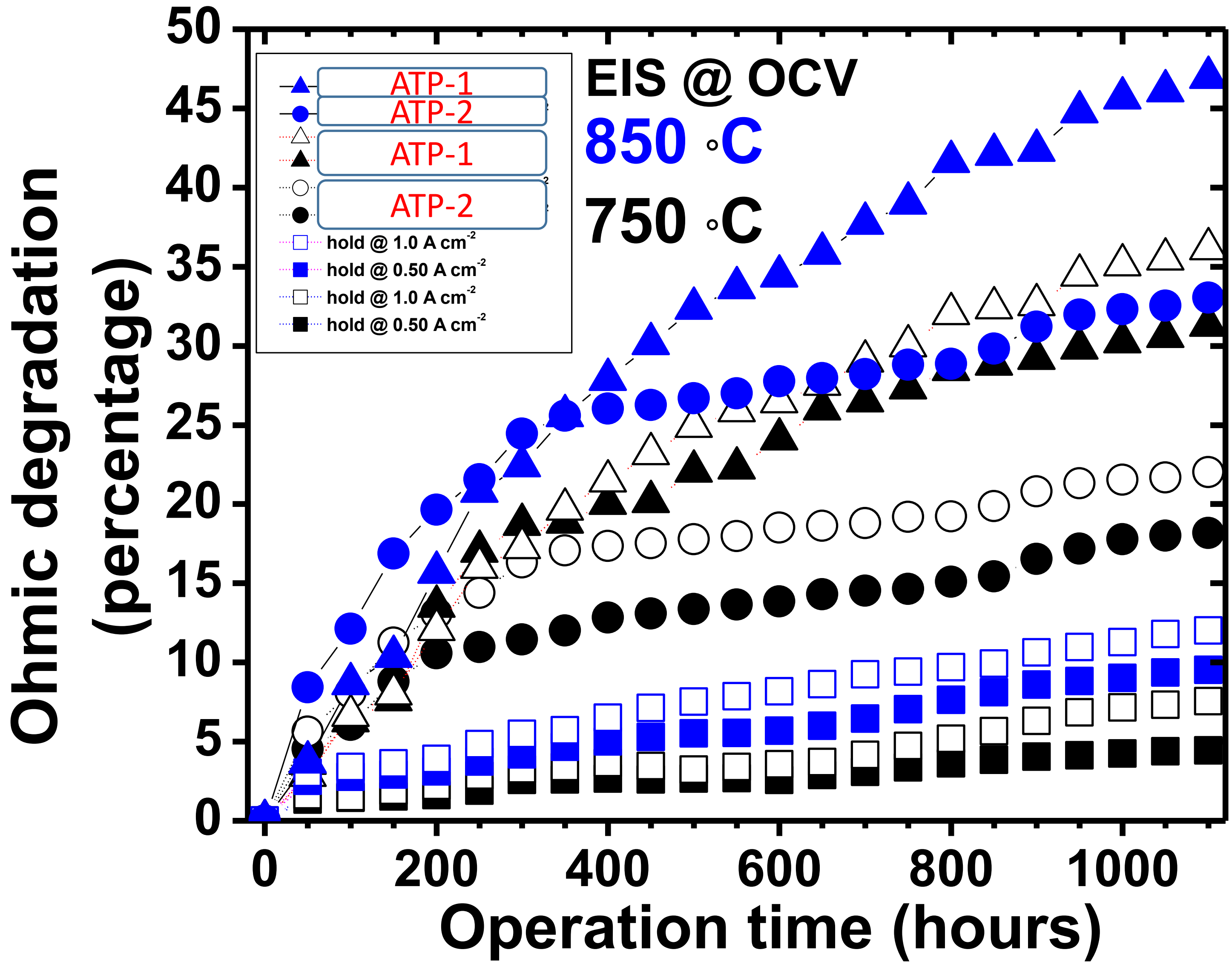
- The accelerated test protocols were adopted at various locations.
- The following parameters were studied: current density, operation temperature, moist level, sintering temperature, accelerated test frequency, operation time, and cathode composition.
- Results were reproducible.

Ohmic Resistance During the Accelerated Tests

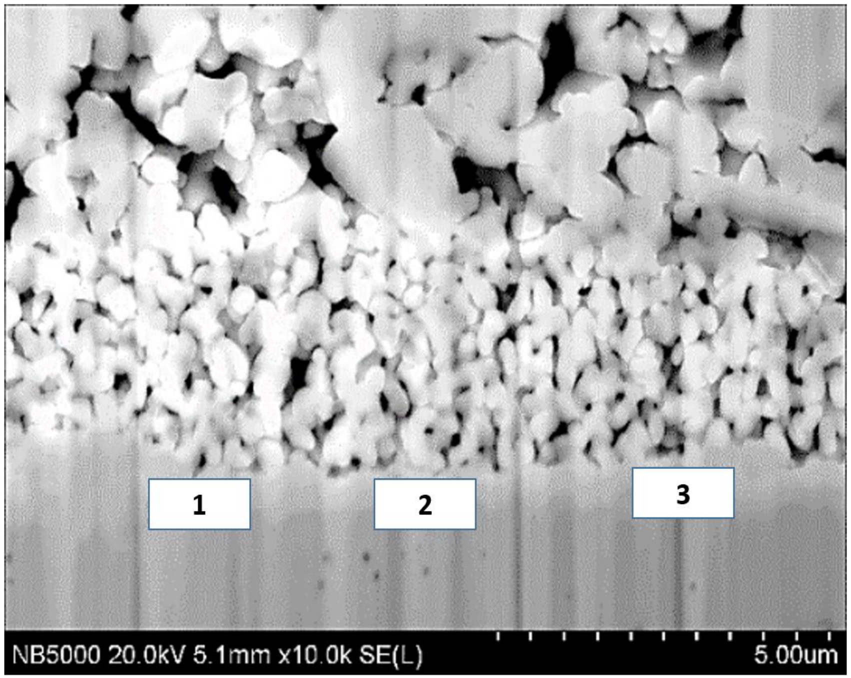


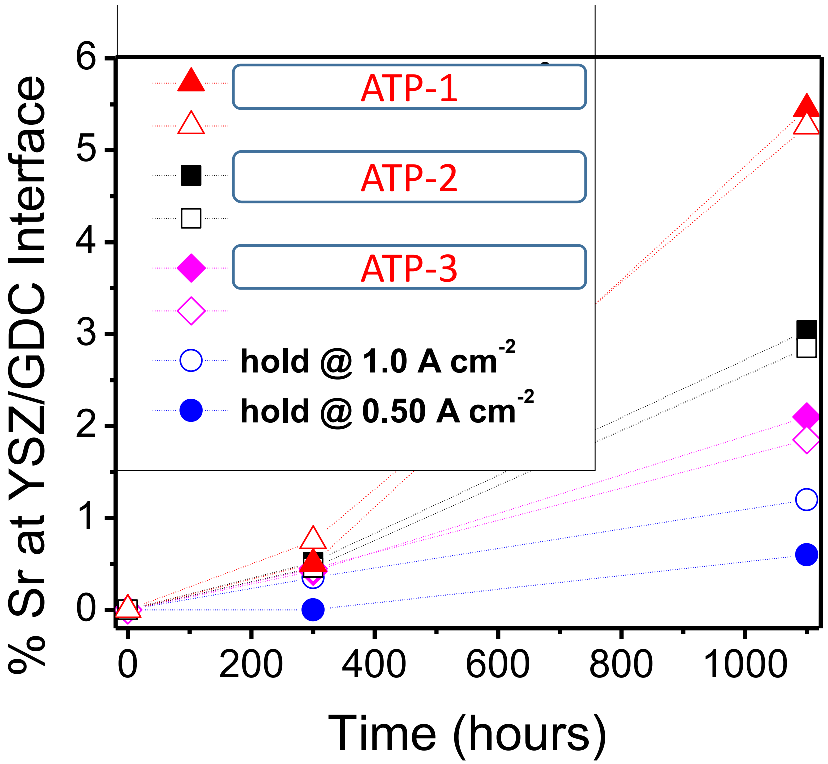
- Steady-state operation: the role of J on ohmic loss is small initially, but increases with time
- Strong correlation of J and ohmic change (Sr segregation) during accelerated test
- ~ 7x larger degradation for fast cycling at 1.0 A/cm2 vs. constant current (process accelerated ~7x)

Effect of Operating Temperature on the Accelerated R_{ohm}



Accelerated Sr Segregation

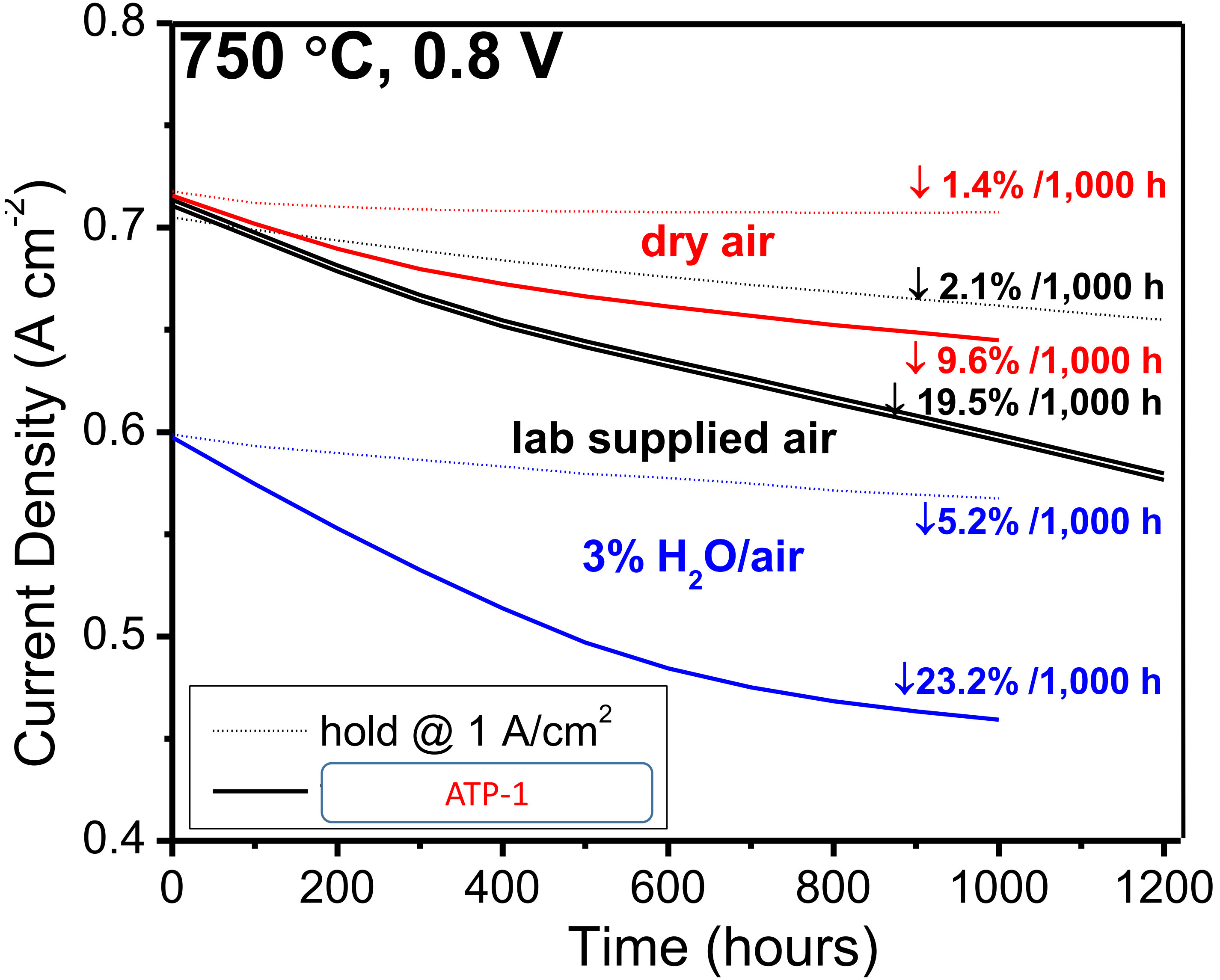




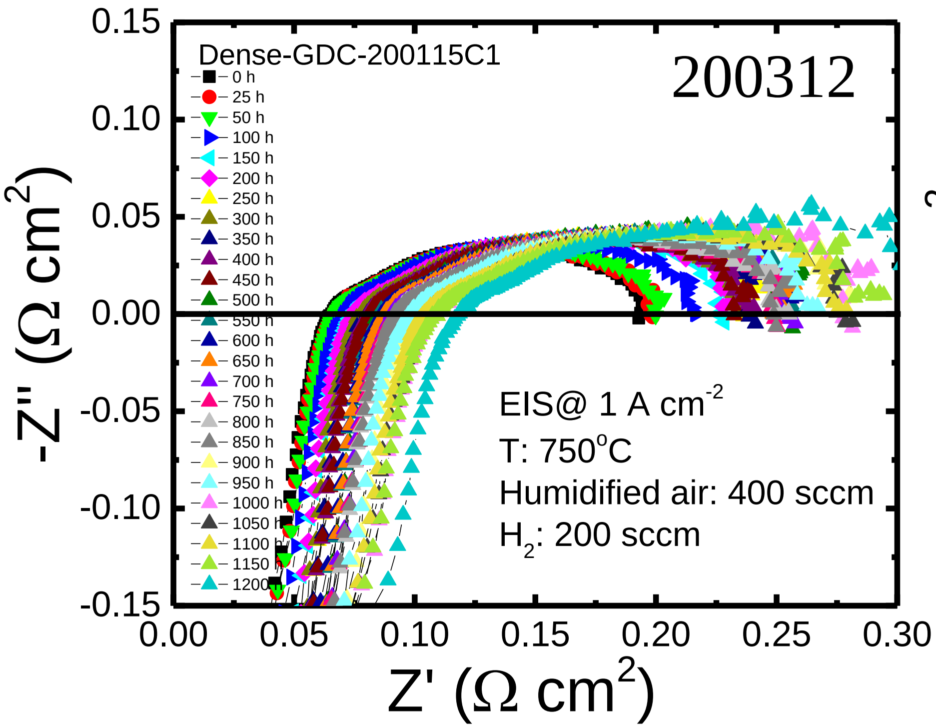
Points to Take

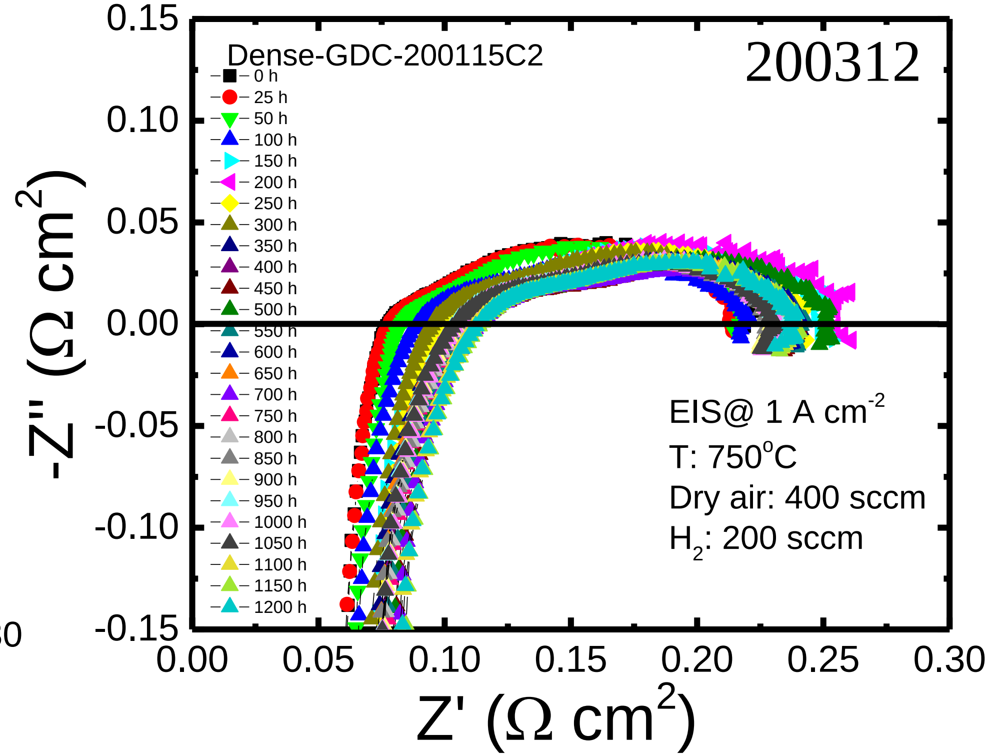
1. An example cross-sectional image of LSCF-based cells. Analysis was done at the GDC/YSZ interfaces.
2. Sr concentration at the interfaces as a function of time in various operation conditions

Effect of Humidity on the Applicability of Accelerated Test



Role of Humidity and GDC Porosity on the Applicability of Accelerated Test

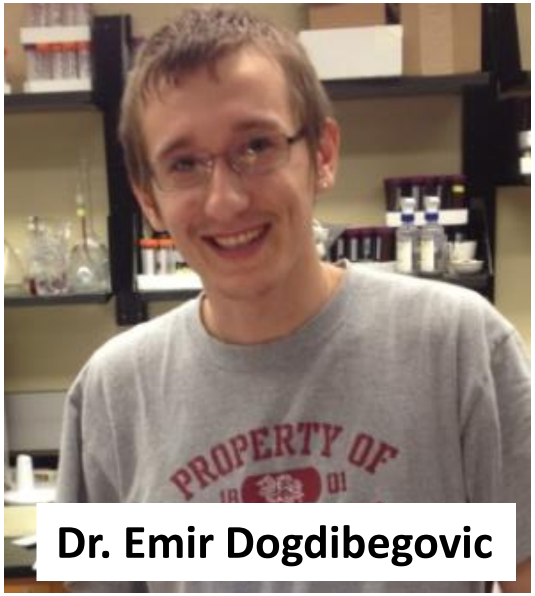




Points to Take

- Humidified air on cathode side promotes an increase in ohmic loss. (faster degradation within first ~300h)
- Additional strontium species deposits at YSZ interfaces when humidified air is used, leading to an increase in ohmic loss.
- A dense interlayer may suppress the performance degradation. More post-analysis is being carried out to establish the microstructure-property relationship.

Team Members Contributing to This Presentation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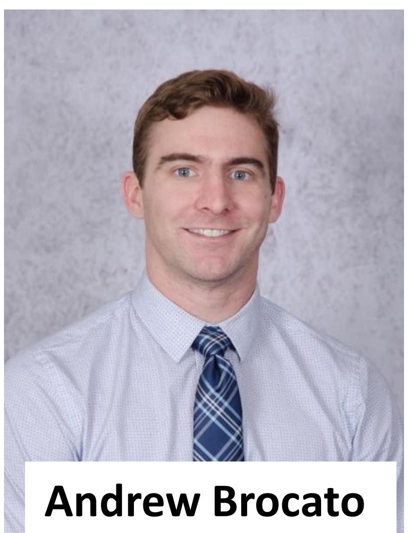
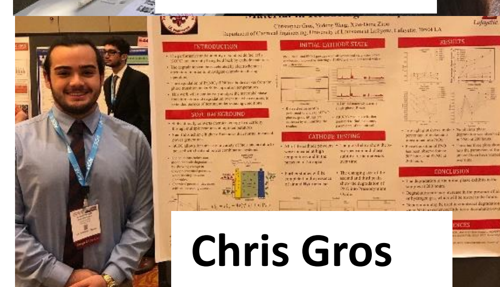

Andrew Brocato

Tom Clause


Austin Schilling


Josh Wilson


Chris Gros

Development of High Efficiency Cathodes and Accelerated Test Protocols for SOFCs

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