Operating Stresses and their Effects on Degradation of LSM-Based SOFC Cathodes

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Abstract

The objectives of this project are to understand the influence of aggressive conditions on performance of solid oxide fuel cells (SOFCs) with cathodes of lanthanum strontium manganite (LSM, $(La_{1-x}Sr_x)_{1-y}MnO_{3\pm\delta}$) and to relate the operating conditions and cell performance to the microstructure changes and performance degradation.

LSM-based fuel cells with different levels of excess Mn underwent durability or aging tests under combinations of aggressive versus conventional conditions: 1,000 vs. 900 °C; 760 vs. 380 mA cm^{-2}; and reduced partial pressure of oxygen (p_{O2} = 0.10, 0.15) versus air (p_{O2} = 0.21) on the cathode side. Electrochemical impedance spectroscopy (EIS) was carried out every 24 h during durability testing to study the evolution of cell resistance over time. EIS data were analyzed in two complementary ways:

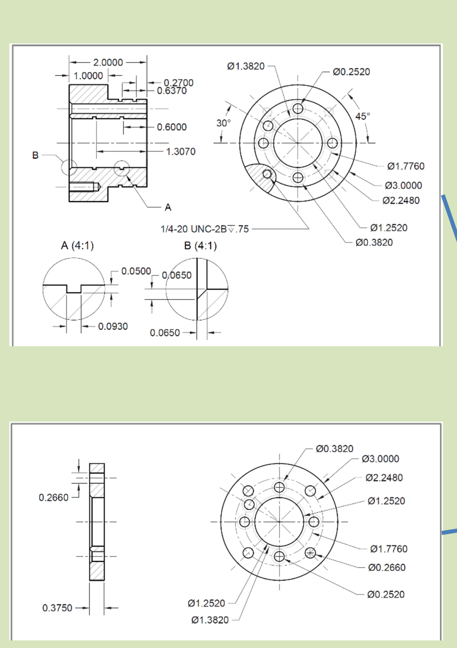
- Distribution of relaxation times (DRT) analysis, to identify possible electrochemical reactions in certain frequency ranges;
- Equivalent circuit analysis, to track the evolution of frequency-dependent (parallel) and frequency-independent (series) components of the impedance, and to correlate these results with changes in area specific resistance (ASR) during durability testing.

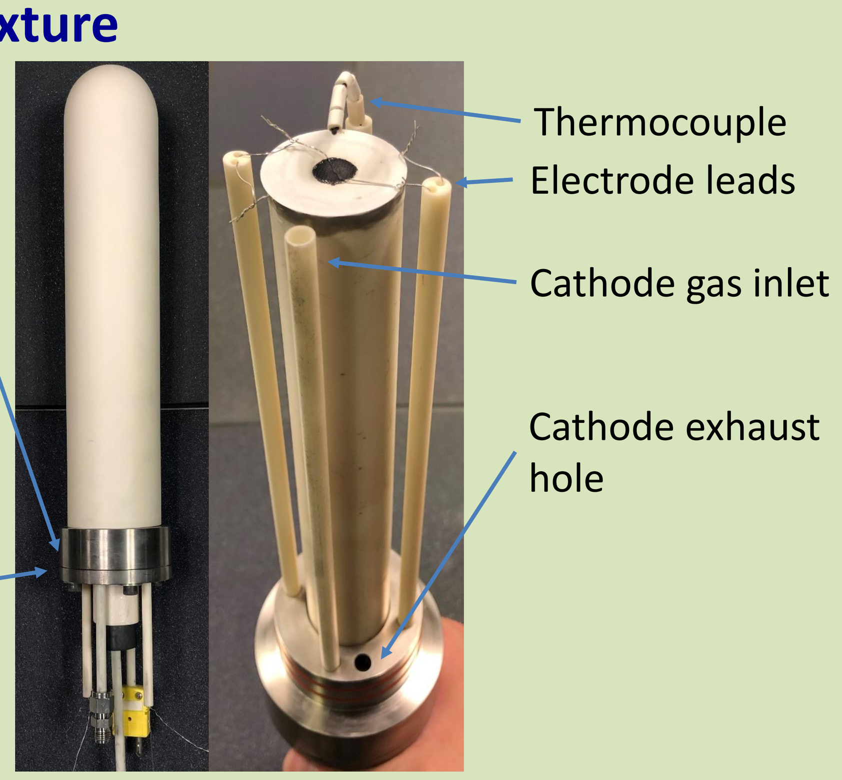
Cell specification; testing procedures

- Button cells:
  - 8YSZ electrolyte • NiO-8YSZ anode
  - Cathodes: LSM + 8YSZ
    - $(La_{0.85}Sr_{0.15})_{0.90}MnO_{3\pm\delta}$ *(LSM 85-90)*
    - $(La_{0.80}Sr_{0.20})_{0.95}MnO_{3\pm\delta}$ *(LSM 80-95)*
    - $(La_{0.80}Sr_{0.20})_{0.98}MnO_{3\pm\delta}$ *(LSM 80-98)*
- Test conditions:
  - Durability and aging tests
  - Conventional or aggressive conditions
  - LSV sweeps + EIS runs ⇒ current cycling every 24 h

temperature [°C]	current density [mA cm^{-2}]	cathode p_{O2}
900	380	0.21
	OCV (aging)	
1000	760	
	OCV (aging)	
900	380	0.1/0.15
	OCV (aging)	
1000	760	
	OCV (aging)	

Test fixture

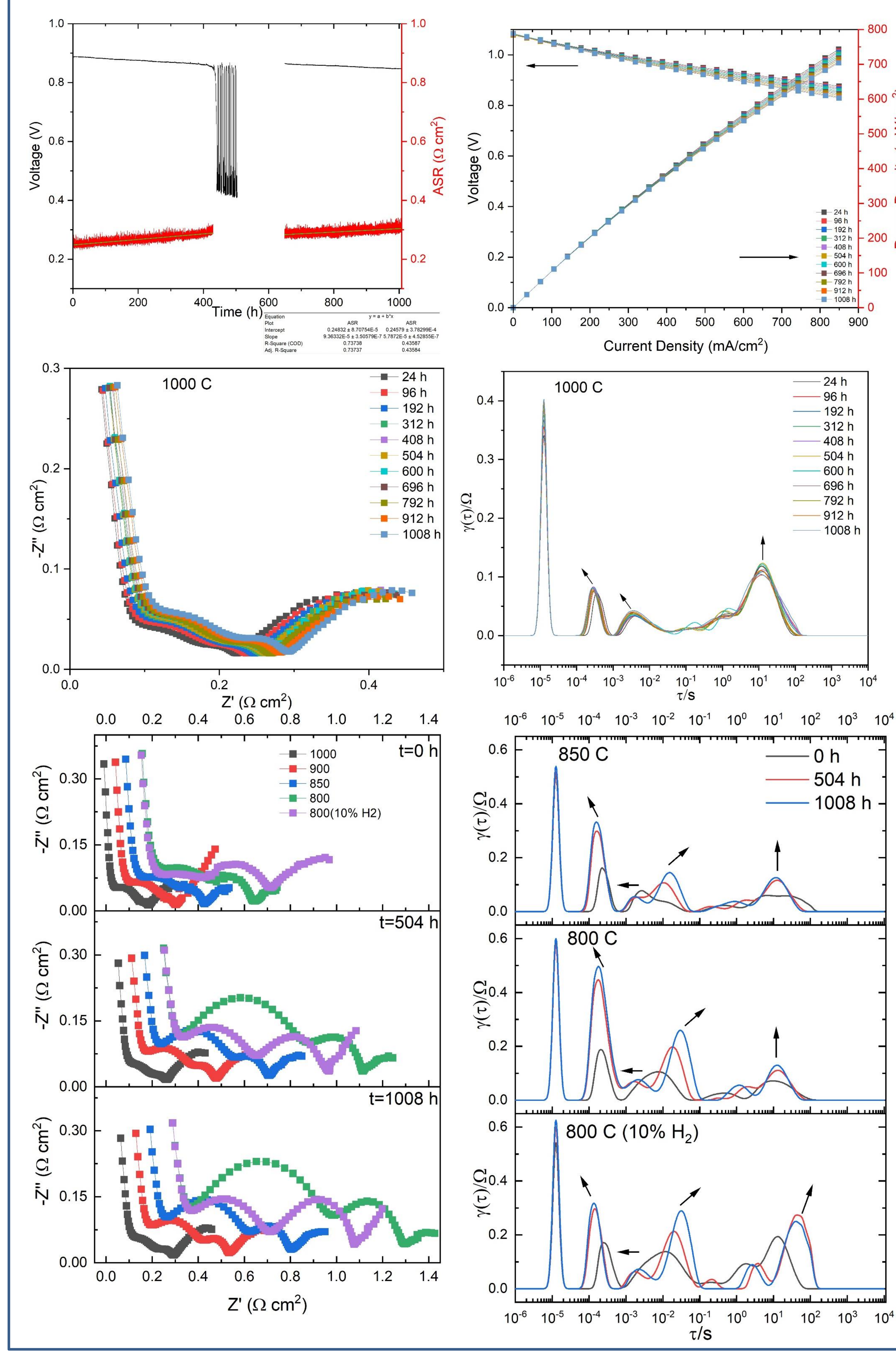




Test stand

- A light-weight titanium fixture is used to hold ceramic tubes in position.
- The type K thermocouple was replaced by type R thermocouple to minimize Cr contamination.
- A closed-end tube and gas inlet tube are used to control the partial pressure of O_2, which enables use of different cathode atmospheres than air.

1,000-h test in air (21% O_2): LSM 85-90; 1,000 °C; 0.76 A cm^{-2}



Total test time: ~1,008 h (504 h + ~146 h (OCV) + 358 h).
Initial ASR: 0.245 Ω cm^2
Final ASR: 0.30 Ω cm^2

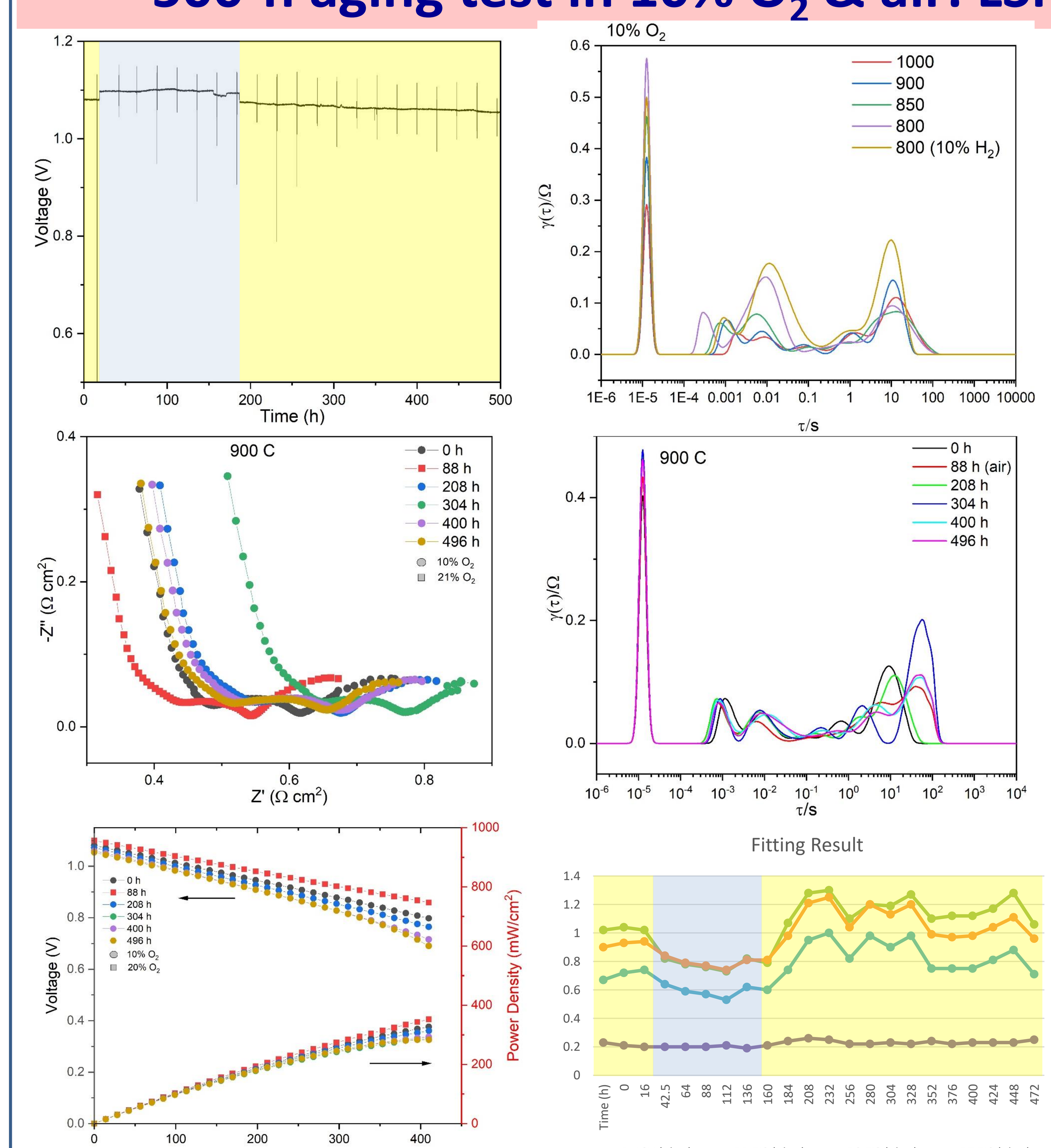
Nyquist plots (left) showed a small increase in real and imaginary impedance with time. DRT analysis (right) showed impedance increase in the 3 largest peaks.

- $10^{-4} < \tau < 10^{-3}$ s: anode charge transfer (TPB)
- $10^{-3} < \tau < 10^{-1}$ s: oxygen exchange, anode & cathode
- $10^{-1} < \tau < 10^{2}$ s: gas diffusion, anode & cathode

With decreasing temperature, Nyquist plots (left) showed normal increases in resistance. DRT analysis (right) at 850 °C, 800 °C, and 800 °C (10% H_2) showed:

- increases in all major peaks with increasing t and decreasing T,
- peak separation in middle frequencies ($10^{-3} < \tau < 10^{-2}$ s, $10^{-1} < \tau < 10^{2}$ s)

500-h aging test in 10% O_2 & air: LSM 80-98, 900 °C



OCV, 500 h (left); cathode gas was 90%N_2/ 10%O_2, except for 19–187 h (air).

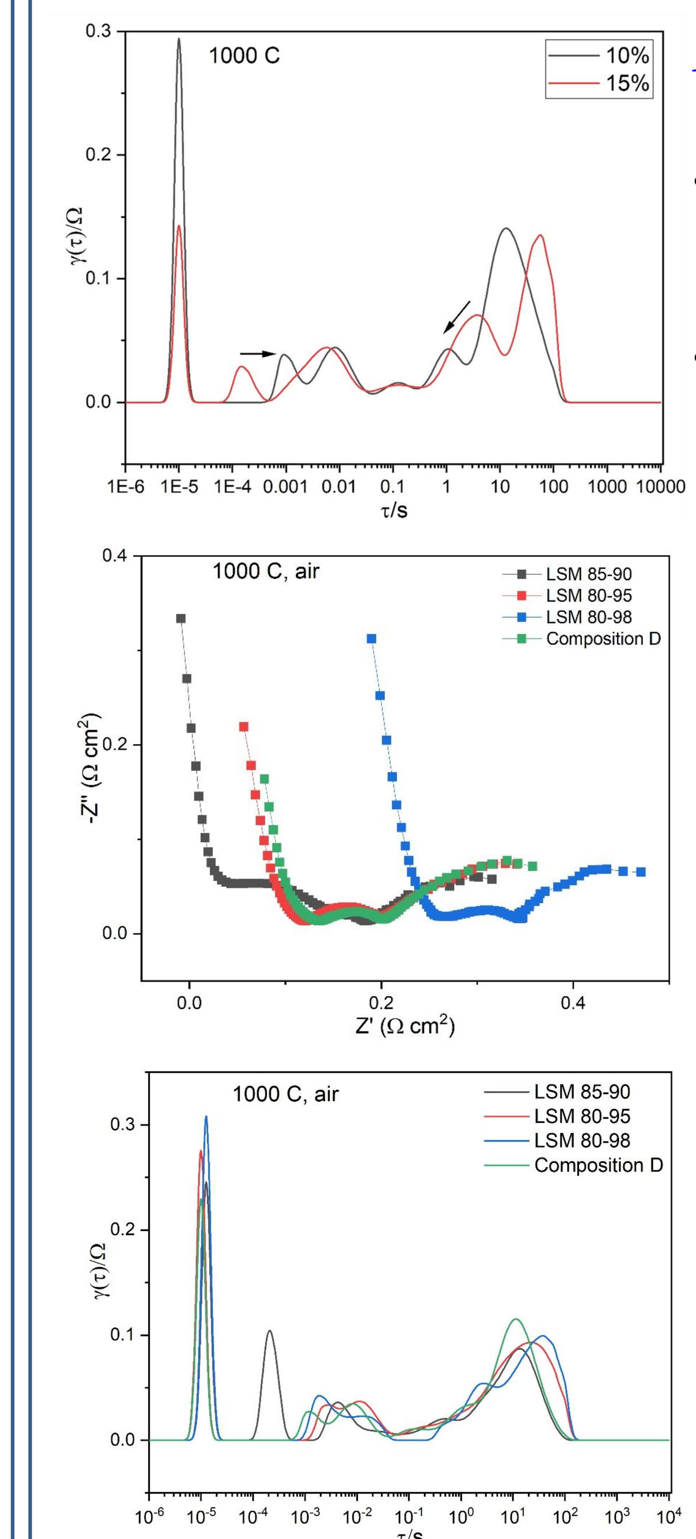
DRT analysis (right) at t=0 h, shows splitting and growth of the low-τ peaks, and growth of the high-τ peaks, as T decreased.

In air:

- ASR dropped in Nyquist plots (left, 88 h).
- Peaks shrank and shifted to lower τ in DRT analysis.

- ASR was always higher in 10% O_2 than in air.
- ASR from LSV (left) agreed with the total ASR (RT,EIS) from EIS fitting (right).
- Series resistance (RS,EIS) tracked total ASR.

Effects of p_{O2} and cathode composition



LSM 80-98, 1,000 °C, t = 0; 10% O_2 and 15% O_2

- DRT analysis reveals effects of cathode atmosphere, independent of differences in series resistance.
- Peak splits, shifts, and growth with changes in p_{O2} will be studied further.

Four cathode compositions, 1,000 °C, t = 0

- LSM 85-90: ***11%*** Mn excess
- LSM 80-95: ***5%*** Mn excess
- LSM 80-98: ***2%*** Mn excess
- Differences in series resistance can make interpretation of Nyquist plots difficult.
- DRT analysis:
  - Facilitates comparisons of mechanisms with distinct relaxation times
  - Peak splits, shifts, and growth with changes in p_{O2} will be studied further.

Conclusions

- DRT analysis was introduced into this project.
  - In a 1,000-h durability test in air at 1,000 °C and 0.760 A cm^{-2}:
    - All major loss mechanisms (charge transfer, oxygen exchange, and gas transport) steadily increased with time.
    - Brief thermal excursions to 850 and 800 °C showed:
      - Increases in all major loss mechanisms as temperature decreased;
      - Separation of loss mechanisms (peak splitting) in middle frequencies ($10^{-3} < \tau < 10^{-2}$ s, $10^{-1} < \tau < 10^{2}$ s);
      - In low-hydrogen anode atmosphere, charge transfer losses dropped, but gas diffusion losses rose and shifted to longer relaxation times.
- Equivalent circuit modeling accounts for changes in total cell resistance in terms of changes in series and parallel resistances, in this case during aging in cathode p_{O2} = 0.10.
- Low p_{O2} on the cathode side (0.10, 0.15) strongly reduces cell life.

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