Effects of Operating Conditions on LSM-Based SOFC Cathodes: EIS Analysis

Chenxin Deng, Madeleine McAllister,
Mark R. De Guire & Arthur H. Heuer

Department of Materials Science and Engineering,
Case Western Reserve University

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Outline

- Background & objectives
  - Cell specifications; testing conditions
- New results since last PRM (Apr. 2019)
  - ***1,000-h test*** in air
  - Testing under ***low*** p_{O2}
  - ***Aging*** tests — baseline for effects of *T*, *t*
- Electrochemical impedance spectroscopy (EIS
  - Equivalent circuit fitting
  - Distribution of relaxation times (DRT) analysis
- Conclusions

Background

- What drives ***microstructural change*** in LSM*-based SOFC cathodes during operation?
  - ***Temperature***
  - ***Current density*** ← **DE-FE0023476**
  - ***Cathode atmosphere*** ← **current project (DE-FE0031189)**
- Studying long-term performance loss in shorter time frames: Testing under ***aggressive conditions***
  - Show effects of non-ideal operating conditions
  - Replicate effects of much longer conventional operation?
- What role does ***Mn excess*** play in these effects?

*) LSM: lanthanum strontium manganite

Overall objectives

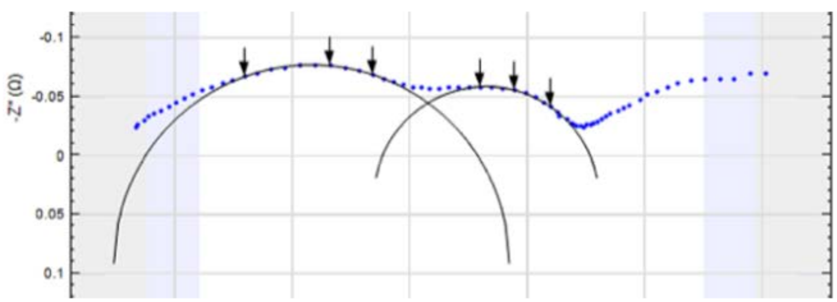
- ***Monitor changes*** in performance and microstructure
- ***Seek correlations*** between
  - composition
  - microstructure
  - performance
  - operating conditions

  and ***obtain mechanistic understanding*** of their interrelationships
- This presentation emphasizes progress in ***electrochemical characterization***

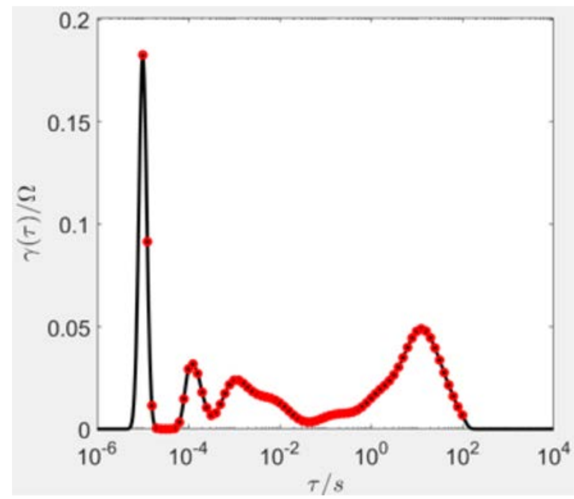
Background

- ***Measures of performance*** studied:
  - Change in area specific resistance ***(ASR)*** during extended testing
  - *I–V* curves (linear sweep voltammetry, LSV)
  - Electrochemical impedance spectroscopy ***(EIS)*** analysis

every 24–48 h



Equivalent circuit modeling
— Nova, Circle Fit



Distribution of relaxation times
(DRT) — DRTtools

Cell specifications; testing conditions

This study:

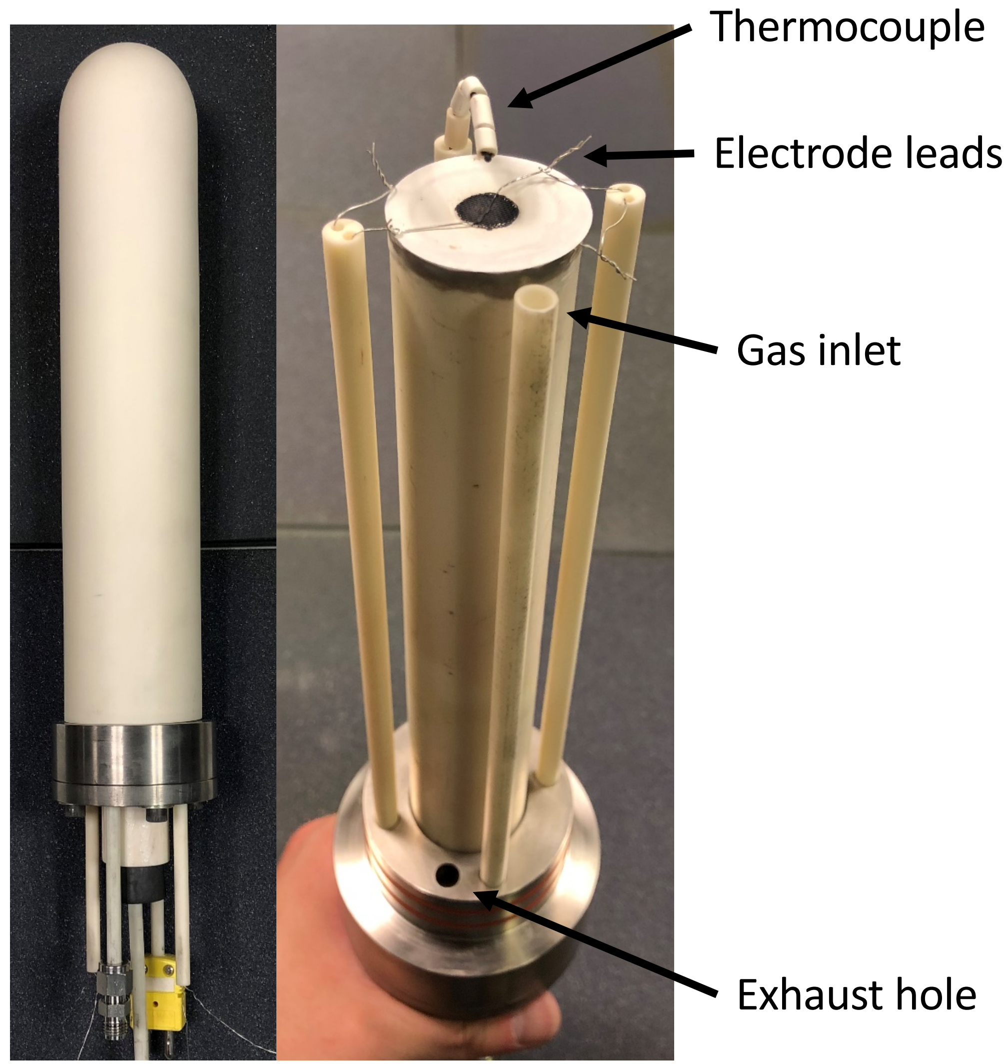
- Durability and aging tests
- Conventional or aggressive conditions
- LSV sweeps and EIS runs ⇒ ***current cycling*** every 24 h

temperature [°C]	current density [mA cm^{-2}]	cathode p_{O_2}
900	380	0.2
	OCV (aging)	
1000	760	
	OCV (aging)	
900	380	0.1
	OCV (aging)	
1000	760	
	OCV (aging)	

Button cells:

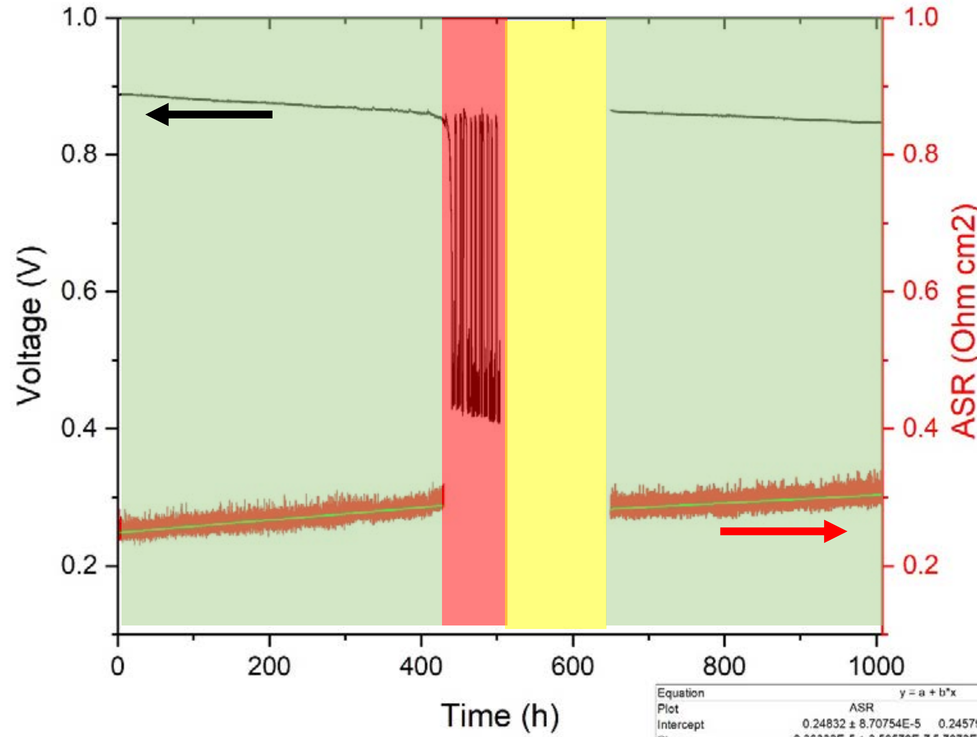
- 8YSZ electrolyte
- Ni/8YSZ anode
- Cathodes: porous LSM / 8YSZ
  - $(La_{\mathbf{0.85}}Sr_{0.15})_{\mathbf{0.90}}MnO_{3\pm\delta}$ (LSM 85-90) — ***11%*** Mn excess
  - $(La_{\mathbf{0.80}}Sr_{0.20})_{\mathbf{0.95}}MnO_{3\pm\delta}$ (LSM 80-95) — ***5%*** Mn excess
  - $(La_{\mathbf{0.80}}Sr_{0.20})_{\mathbf{0.98}}MnO_{3\pm\delta}$ (LSM 80-98) — ***2%*** Mn excess

Test fixture for controlled cathode atmosphere



New results: **1,000-h** aggressive durability test in air, LSM 85-90

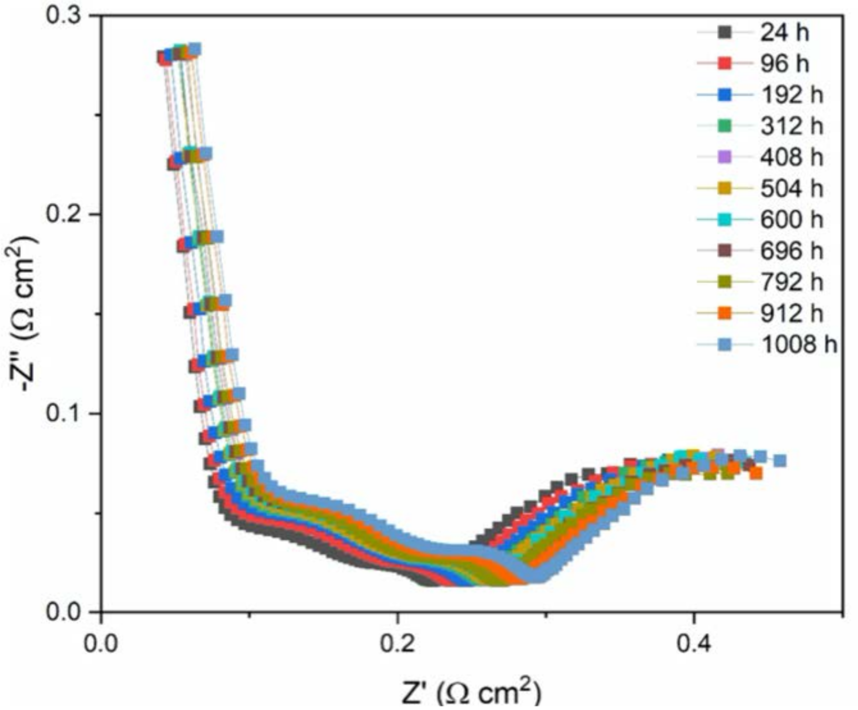
- ***11% Mn excess*** (LSM 85-90), ***thin*** electrolyte, ***1,000 °C, 760 mA cm^{-2}***
- ***0 – 430 h: normal output;*** moderate degradation (37.7% per kh)
- ***430 – 500 h: sharp, erratic drops***, with periods of normal voltage
- ***500 – 650 h:*** OCV (zero current)
- ***650 – 1,008 h: resume load***
  - Moderate degradation (23.5% per kh)
- Overall excellent performance:
  - ***858 h*** at 760 mA cm^{-2}
  - Initial total ASR ***0.25 Ω cm^2*** (~best in this project)
  - Final total ASR ***0.30 Ω cm^2*** comparable to best results of ***500-h*** tests

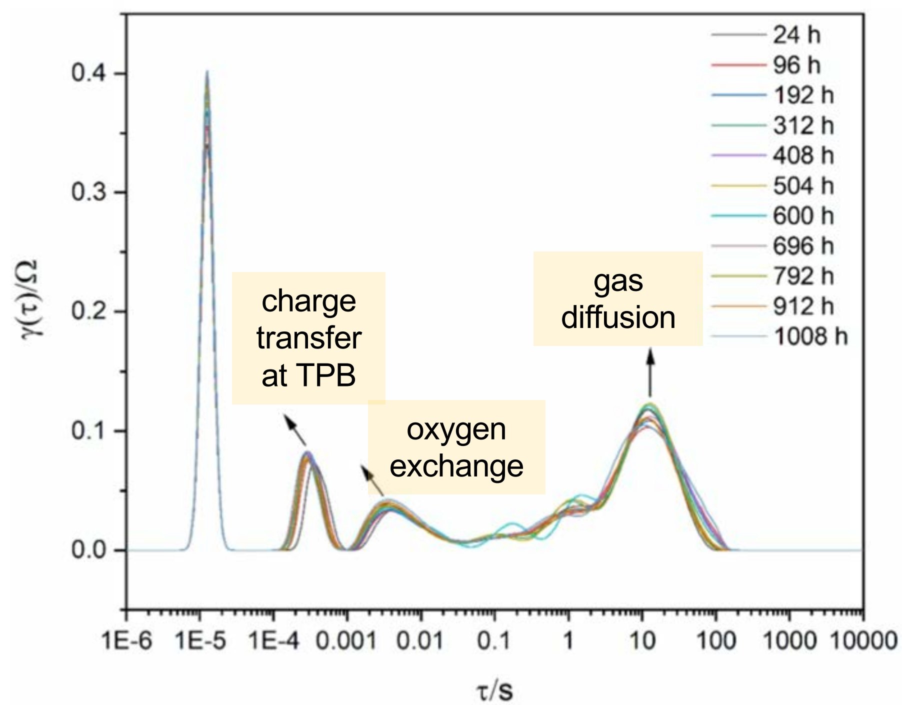


Equation	y = a + b*x	
Plot	ASR	ASR
Intercept	0.24832 ± 8.70754E-5	0.24579 ± 3.78299E-4
Slope	9.36332E-5 ± 3.50579E-7	5.7872E-5 ± 4.52855E-7
Residual Sum of Square	1.22121	0.98179
Pearson's r	0.85871	0.6602
R-Square (COD)	0.73738	0.43587
Adj. R-Square	0.73737	0.43584

New results: **1,000-h** aggressive durability test in air, LSM 85-90

- ***EIS,*** 24 – 1,008 h, 1,000 °C, 0.76 A cm^{-2}





Steady, small ↑ in Z' & Z'' as t ↑

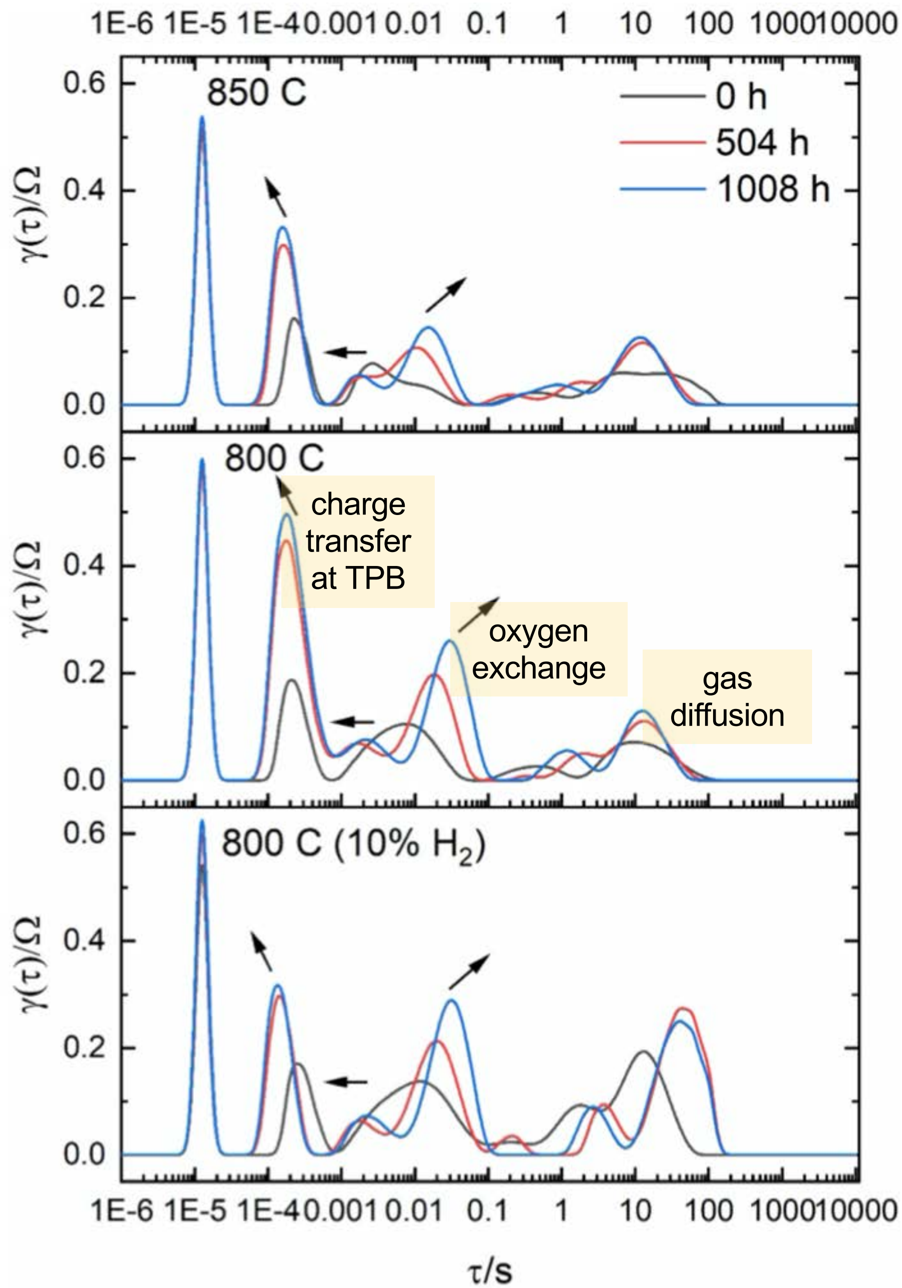
All major loss peaks ↑ as t ↑

- ***Gradual degradation across all aspects of cell performance***
- Microstructural analysis underway

New results: **1,000-h test** in air, LSM 85-90, 0.76 A cm^{-2}

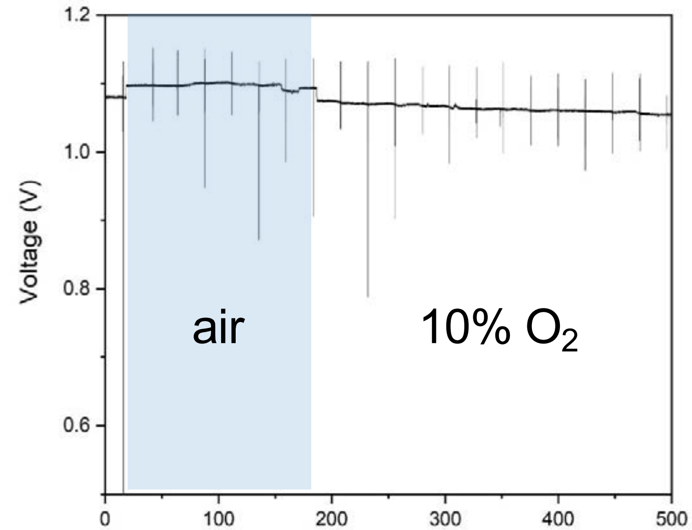
DRT analysis at 850 & 800 °C
after 0, 504, and 1,008 h testing at 1,000 °C

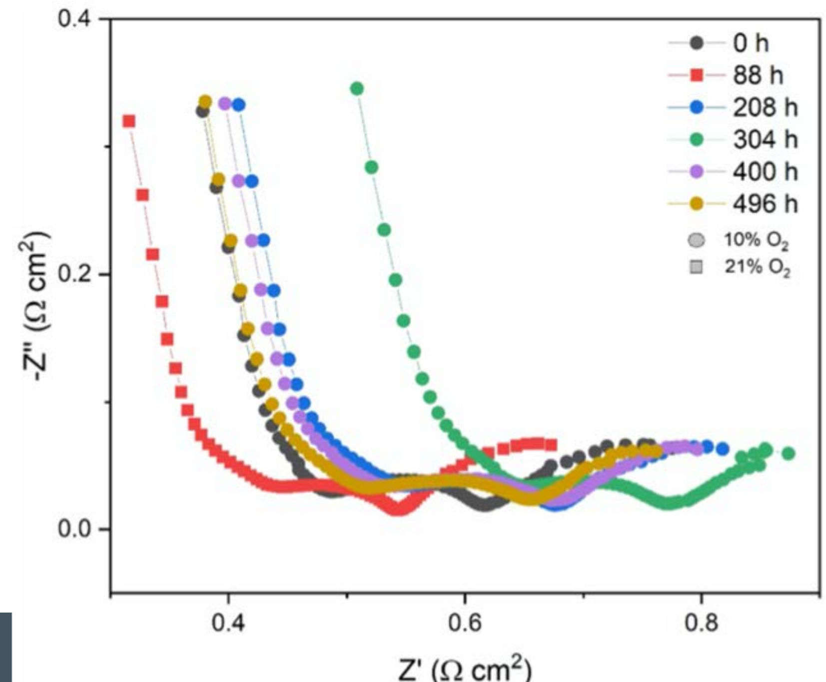
- ***As t*** ↑ :
  - ***All major peaks*** ↑ , more pronounced than at 1,000 °C
  - ***Peak separation*** in middle frequencies ($10^{-3} < \tau < 10^{-2}$ s, $10^{-1} < \tau < 10^{2}$ s)
- ***As T*** ↓ :
  - ***All major peaks*** ↑
  - Shift of oxygen exchange peak to longer τ
- In ***low H$_2$,*** 800 °C, as *t* ↑:
  - Charge transfer losses ↓
  - Gas diffusion losses ↑ and shift to higher τ



New results: aging test, LSM 80-98, ***900 °C, 10% O_2, 0 A cm^{-2}***

- 0 – 19 h, ***10% O_2***: ASR ↑ (data not shown)
  - ⇒ ***Degradation*** at low p_{O2}, zero load
- 19 – 187 h: ***lab air,*** 20 sccm
  - ASR ↓ for ~100 h
    — ***"repair"*** of degradation?
  - … then ASR ↑
    — "normal" thermal degradation?
- 187 – 500 h: ***10% O_2***
  - *Z´* ↑ to 304 h, then ↓
  - *Z´* ↑ remained higher than in air





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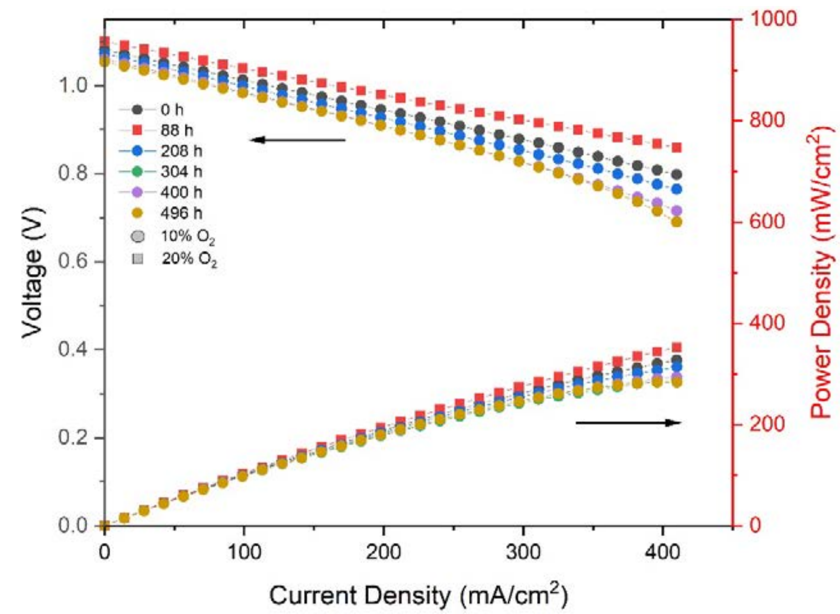
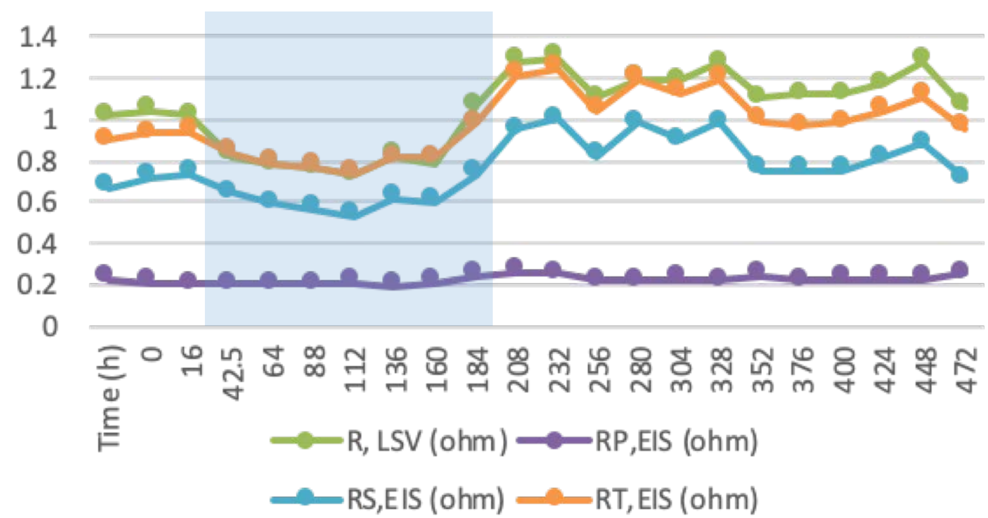
New results: aging test, LSM 80-98, ***900 °C, 10% O_2, 0 A cm^{-2}***

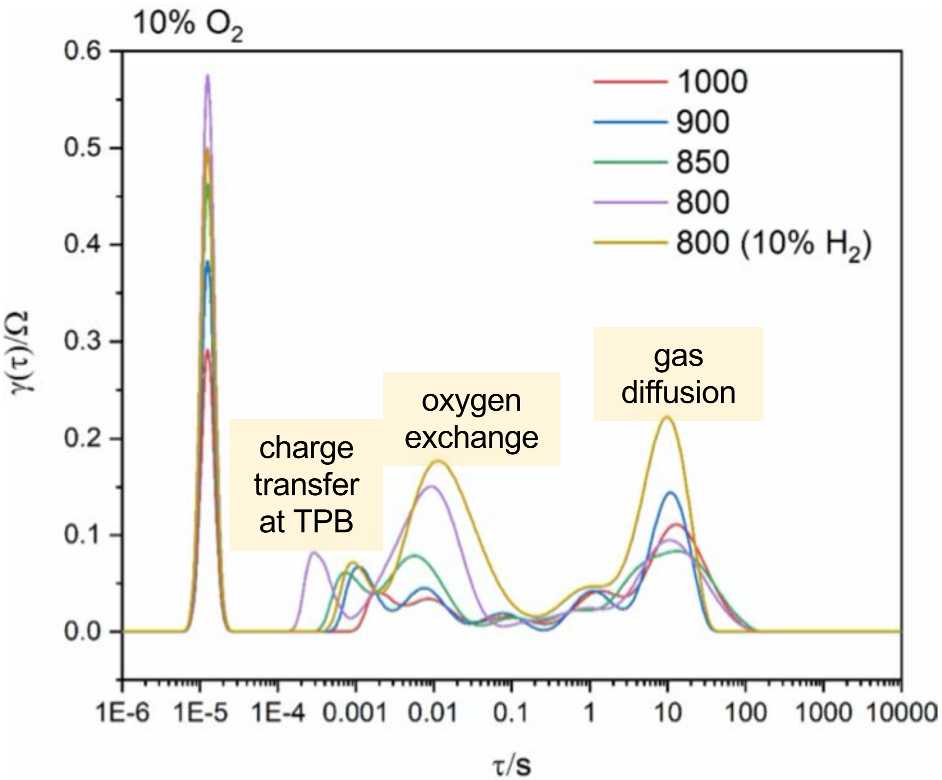
- 0 – 19 h, ***10% O_2***: ASR ↑
- 19 – 187 h: ***lab air,*** 20 sccm
  - ASR ↓ for ~100 h
  - … then rose
- 187 – 500 h: ***10% O_2***
  - overall: ***ASR ↑ , power ↓***

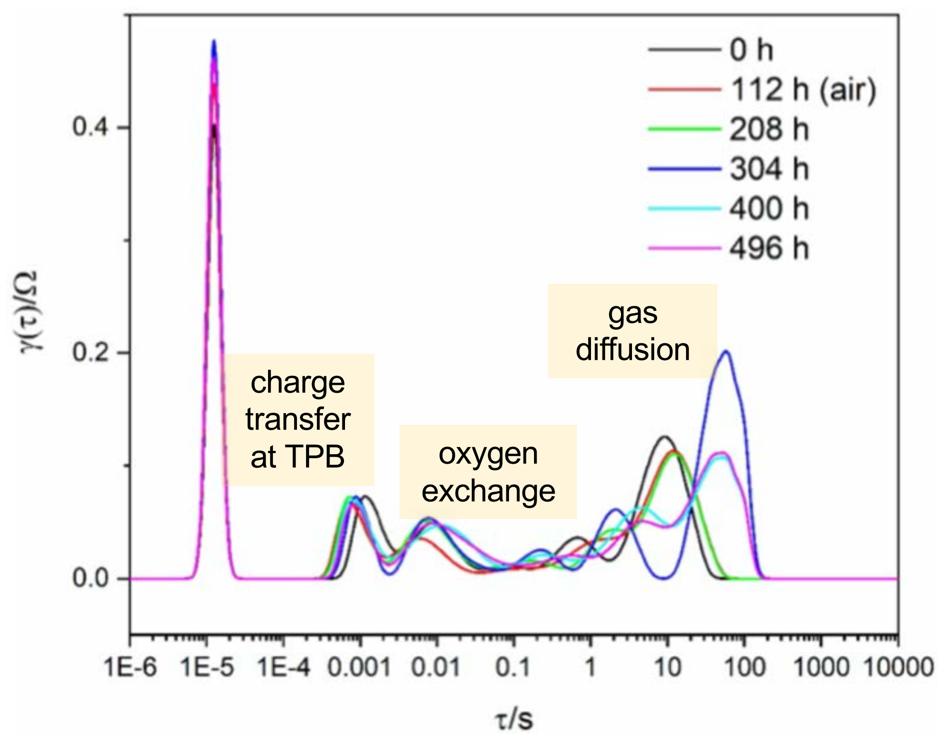


- EIS fitting (equivalent circuit):
  - *R,* LSV agreed with total *RT*,EIS from EIS fitting
  - Series *RS*,EIS tracked total resistance *R*,LSV
  - Parallel *RP*,EIS unchanged



New results: **aging test**, LSM 80-98, ***900 °C, 10% O_2, 0 A cm^{-2}***





At $t = 0$, 10% O_2, ***as T*** $\downarrow$:

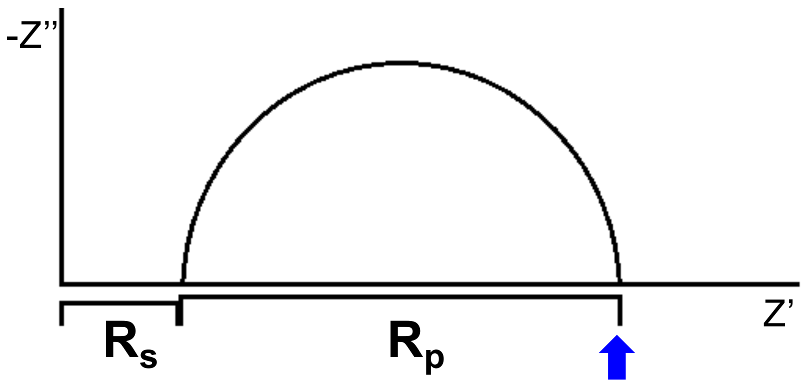
- All major peaks $\uparrow$
- Charge transfer shifts to shorter τ
- Oxygen exchange shifts to longer τ

As t $\uparrow$ at 10% O_2, 900 °C:

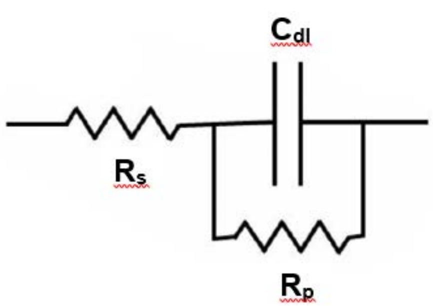
- Most major peaks $\uparrow$
- Charge transfer shifts to longer τ
- Complex effects in oxygen exchange and gas diffusion

Equivalent circuit modeling

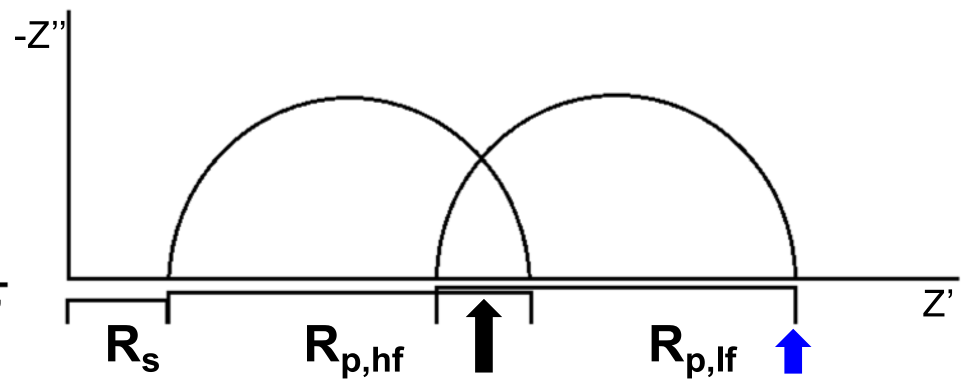
Fitting an arc with a single semicircle



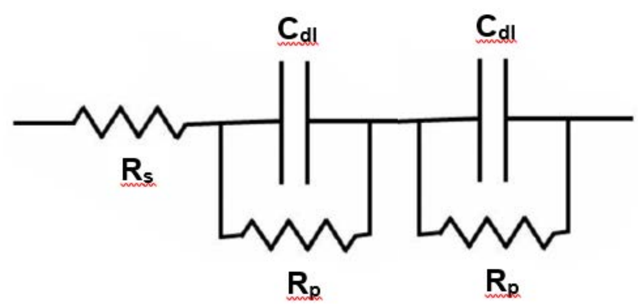
ASR_{EIS}
$= R_s + R_p$



Fitting multiple arcs with overlapping semicircles

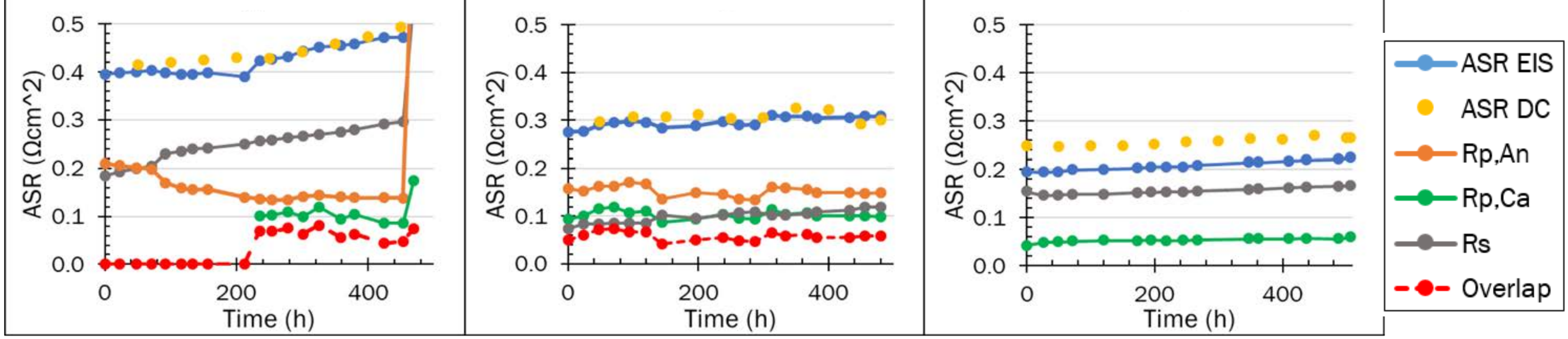


ASR_{EIS}
$= R_s + R_{p,hf} + R_{p,lf}$
– overlap



Effect of Mn excess: 1,000 °C, 0.760 A cm^{-2}, air

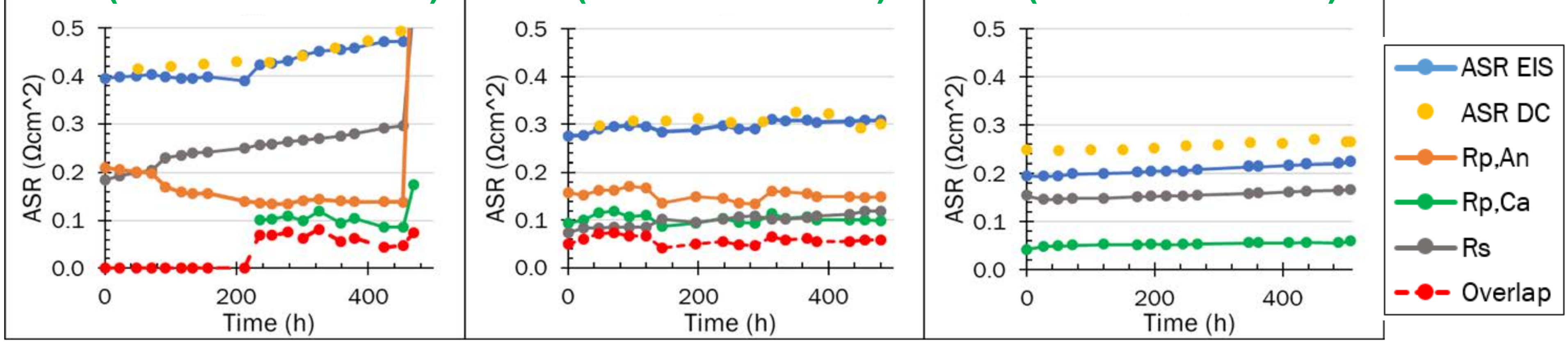
LSM 85-90 (11% Mn excess) | **LSM 80-95 (5% Mn excess)** | **LSM 80-98 (2% Mn excess)**



- **ASR EIS** is the sum of the gray, orange, and green, minus red curves.
- **ASR EIS gave good agreement with ASR DC** from durability testing:
  - ±0.02 Ω cm^2 for 11% Mn xs
  - ±0.03 Ω cm^2 for 5% Mn xs
  - – 0.06 Ω cm^2 for 2% Mn xs (effect of inductive component)
- ASR DC ↑ as t : ***from series resistance*** R_S***,*** not from R_p
- $R_{p,Ca}$ ***was a minor component*** of total ASR EIS ⇐ ***high T*** (1,000 °C)

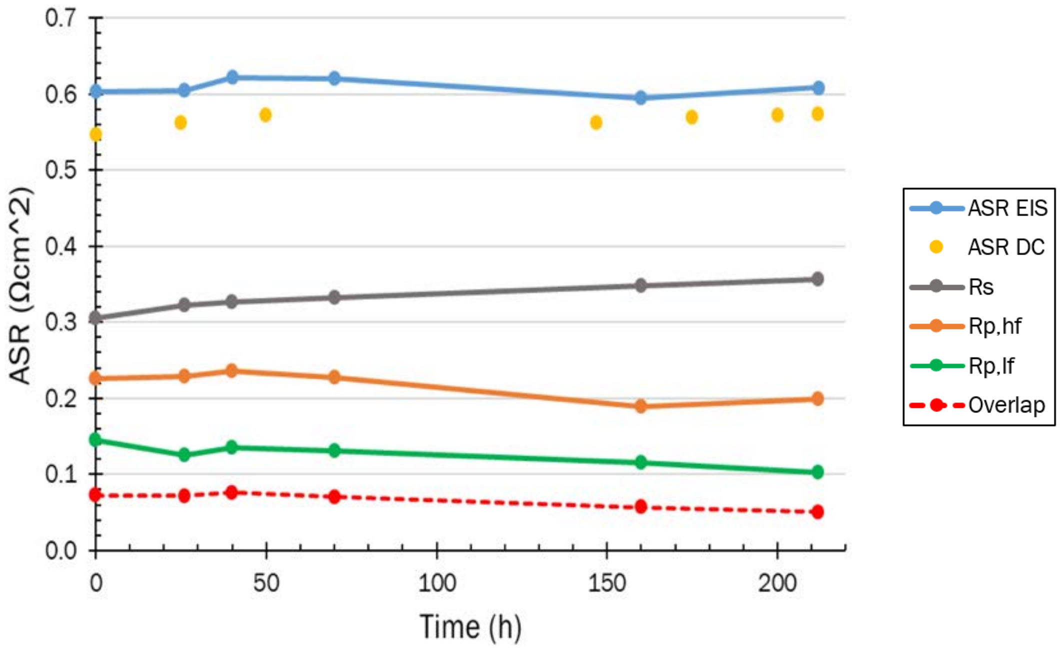
Effect of Mn excess: 1,000 °C, 0.760 A cm^{-2}, air

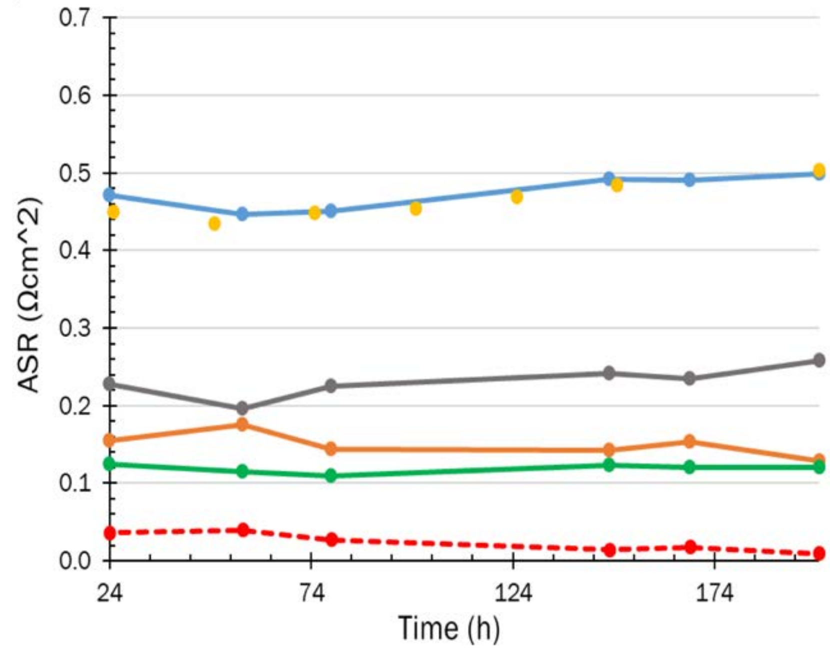
LSM 85-90 (11% Mn excess) | **LSM 80-95 (5% Mn excess)** | **LSM 80-98 (2% Mn excess)**



- LSM 85-90:
  - Thicker electrolyte ⇒ anomalously high R_S
  - Even when corrected to thinner electrolyte, these cells had highest ASR
  - ***On normal electrolyte,*** LSM 85-90 lasted ***1 kh*** (earlier slides), ***lower ASR after 1 kh*** than LSM 80-95 and LSM 80-98 after ***500 h***
- LSM 80-95:
  - Distinct anode (high-*f*) and cathode (medium-*f*) parallel resistances
  - Moderate ASR overall
- LSM 80-98: lowest overall ASR in 500-h comparisons

Reproducibility: LSM 85–90, 1,000 °C, 0.760 A cm^{-2}, air



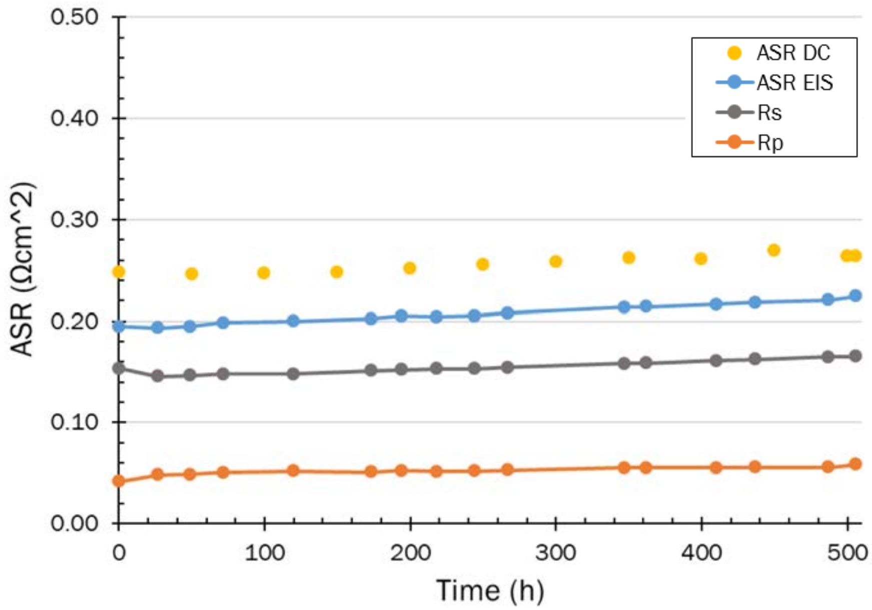


- ***ASR EIS*** **gave good agreement with ASR DC** (~ –0.04 Ω cm^2).
- ***ASR EIS*** **gave excellent agreement with ASR DC** (± 0.01 Ω cm^2).

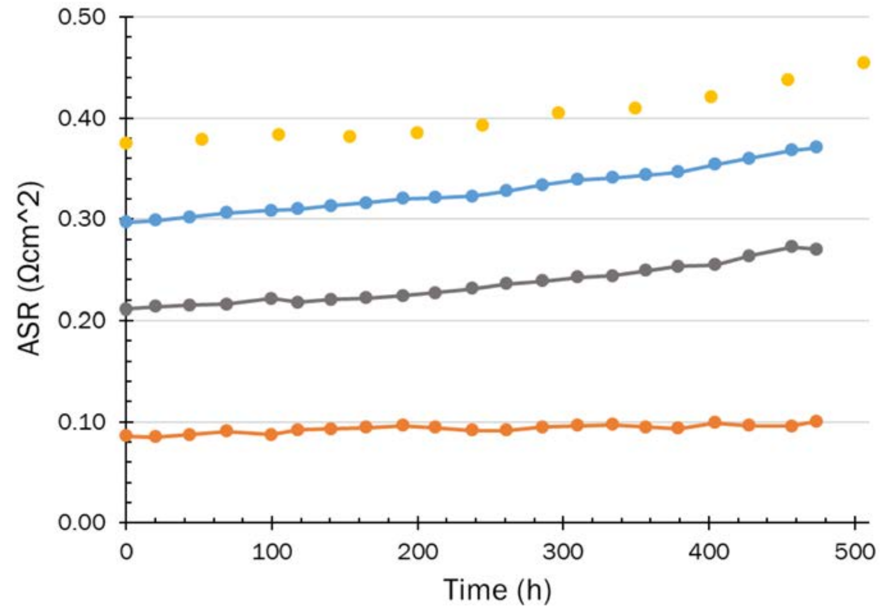
~20% difference in total ASR (0.1 Ω cm^2) between identical cells

Aggressive vs. conventional: LSM 80–98 (2% Mn xs)

1,000 °C, 760 mA cm^{-2}, air



900 °C, 380 mA cm^{-2}, air



- ***All ASR components rose ~50%*** at 900 °C vs. 1,000 °C
- All ASR components ***rose with t***, but more strongly at 900 °C
- High frequency: inductive component ⇒ lower ASR EIS vs. ASR DC
- ASR EIS and ASR DC still agree within 0.06 Ωcm^2

Conclusions (prior project): ASR, microstructure, EIS

- ***EIS analysis:*** a complement to durability testing
  - Equivalent circuit modeling
    - EIS ASR tracks DC ASR closely
    - Rise in R_s accounts for rise in ASR
    - Low-frequency R_p (usu. assigned to cathode) was not the major source of ASR at 1,000 °C — expected at high T
  - Distribution of relaxation times (DRT modeling)
    - All major loss mechanisms ↑ as time ↑
    - All major loss mechanisms ↑ as temperature ↓
    - Enables resolution of mechanisms at different frequencies
    - In 10% H_2 (anode), charge transfer losses dropped, while gas diffusion losses rose and shifted to lower frequencies

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