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

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Abstract

Goals: a) Understand how aggressive operating conditions affect the 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 yttria-stabilized zirconia (YSZ, $(Zr_{1-z}Y_z)O_{2\pm\delta}$); b) Understand the relationship between microstructural changes after operation and performance degradation.

This project extends previous studies of performance and microstructure changes in LSM-based SOFC cathodes after 500 h or more of durability testing at 1,000 °C and 760 mA cm^{-2} with air in the cathode atmosphere. The new investigation includes:

1) ***Reduced*** p_{O_2} on the cathode side: to escalate the degradation of cathode;
2) ***Aging tests***: to evaluate the effects of operating temperature and cathode atmosphere at open circuit voltage;
3) ***Current load cycling***: to understand the influence of interrupting the durability and aging tests with regular I–V sweeps and electrochemical impedance spectroscopy (EIS) measurements.

As in the prior work, cells will undergo detailed microstructural characterization, using transmission electron microscopy (TEM), energy-dispersive x-ray spectroscopy (EDXS), and three-dimensional reconstruction (3DR), with sample preparation via focused ion-beam scanning electron microscopy (FIB/SEM), focusing on the following phenomena:

1. ***Changes in phase fraction and their distribution*** across the cathode, particularly densification/loss of porosity near the interfaces of the cathode with the electrolyte and the cathode current collector (CCC);
2. Formation and distribution of ***manganese oxides*** ***(MnO_x)*****;**
3. Changes in total and ***active three-phase boundary (TPB) density.***

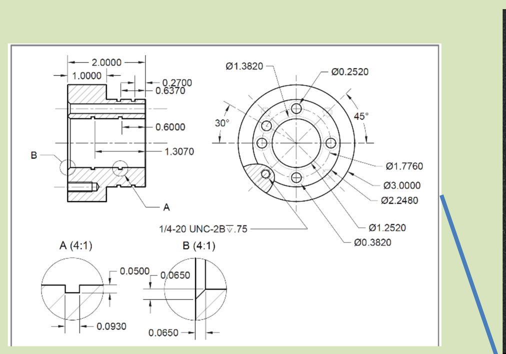
These changes were most pronounced, and degradation of performance was highest, with cathodes having 11% Mn excess. Meanwhile, the change in area specific resistance (ASR) with time as measured by EIS shows good agreement with that obtained from durability testing. The EIS analysis shows that the rise of total ASR during testing mainly comes from increases in the series resistance. By elucidating microstructural causes of cell degradation, the new studies have the potential to improve the reliability and lifetime of SOFC technology.

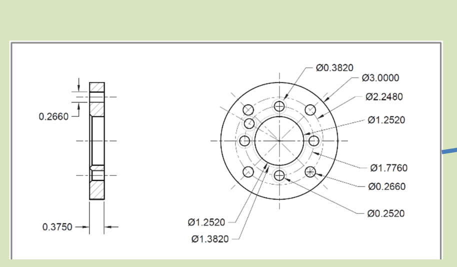
Cell specification; testing procedures

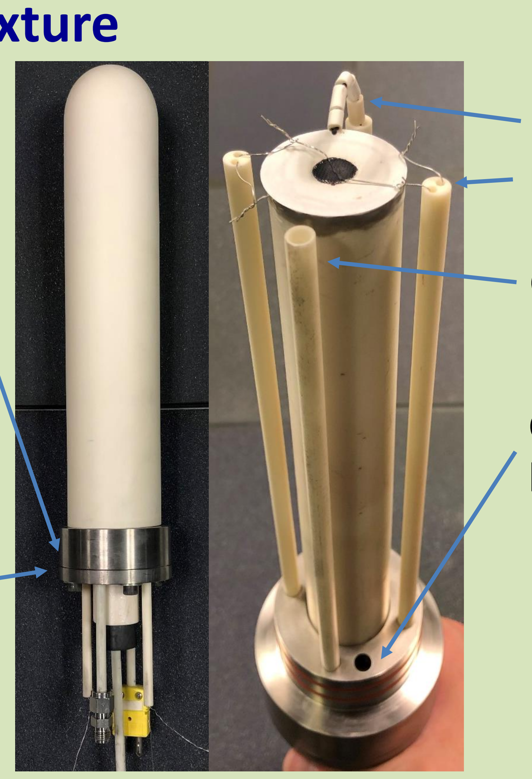
- Button cells:
  - 8YSZ electrolyte • NiO-8YSZ anode
  - Cathodes: LSM + 8YSZ
    - $(La_{0.85}Sr_{0.15})_{0.90}MnO_{3\pm\delta}$ *(LSM 85-90)*
    - $(La_{0.80}Sr_{0.20})_{0.95}MnO_{3\pm\delta}$ *(LSM 80-95)*
    - $(La_{0.80}Sr_{0.20})_{0.98}MnO_{3\pm\delta}$ *(LSM 80-98)*
- Test conditions:
  - Durability 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_{O_2}
900	380	0.2
	OCV (aging)	
1000	760	
	OCV (aging)	
900	380	0.1
	OCV (aging)	
1000	760	
	OCV (aging)	

Test fixture







Thermocouple

Electrode leads

Cathode gas inlet

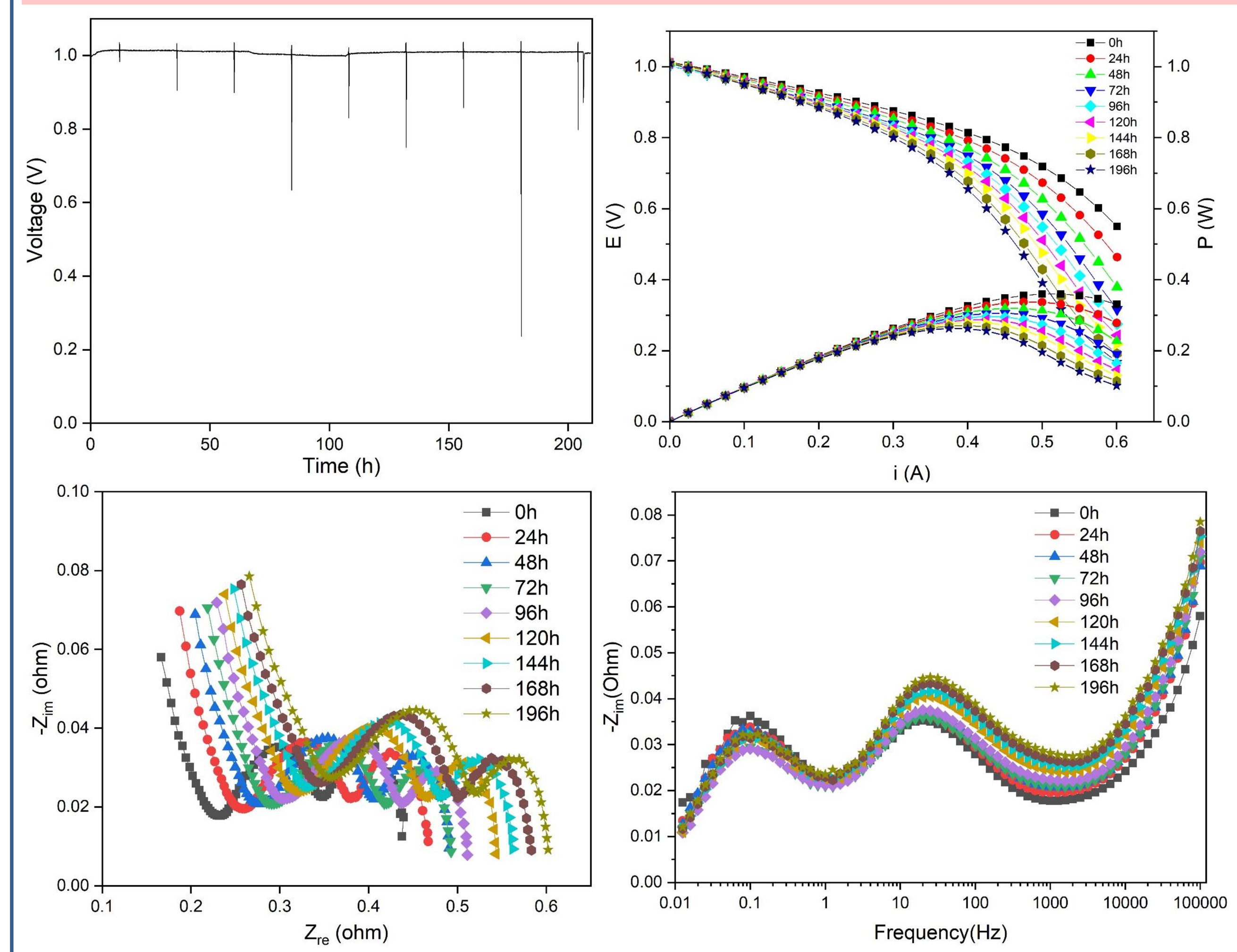
Cathode exhaust hole

Testing at low p_{O_2} is in progress

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 the 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.

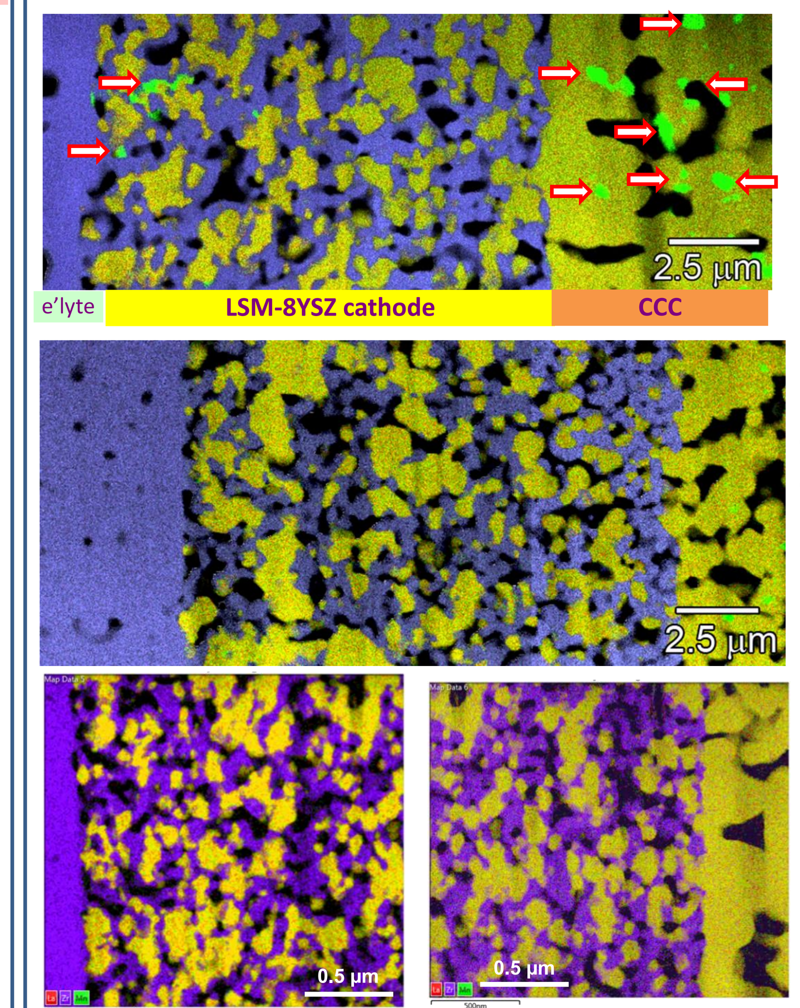
Aging test result (LSM85-90, 208h, 20% O_2)



The open-circuit voltage ranged from 1.00 to 1.01V. (LSV and EIS readings taken every 24 h account for the sharp drops.)

The Nyquist plots (left) showed an expected increase in real and imaginary impedance with time. The Bode plots (right) showed little change in peak frequency with time.

TEM & EDXS results: effect of Mn excess

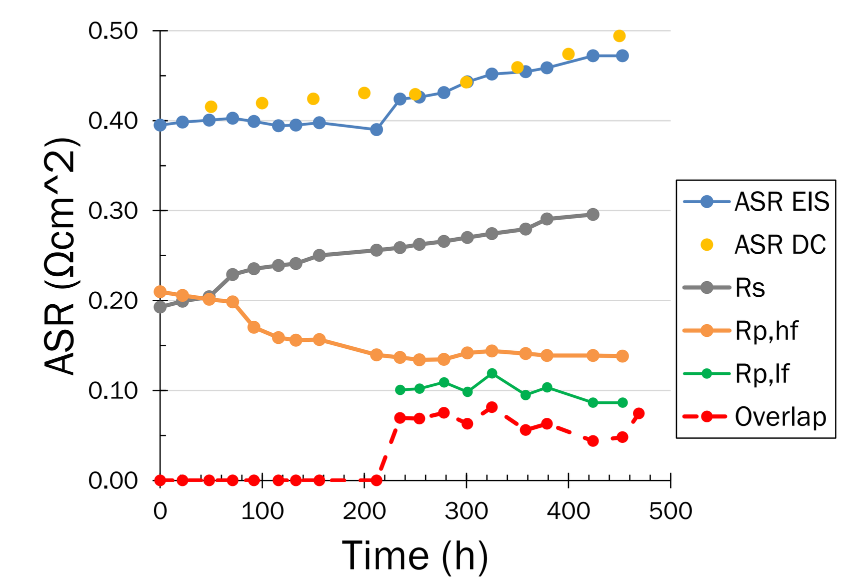


LSM 85-90, 493 h aggressive test:
- MnO_x near cathode-electrolyte interface
- MnO_x coarsened in cathode current collector

LSM 80-95, 500 h aggressive test:
- MnO_x is rarely seen in cathode
- No evidence of localized densification of MnO_x at cathode-electrolyte interface

LSM 80-98, 500 h aggressive test:
- MnO_x is not seen in cathode and cathode current collector

EIS analysis

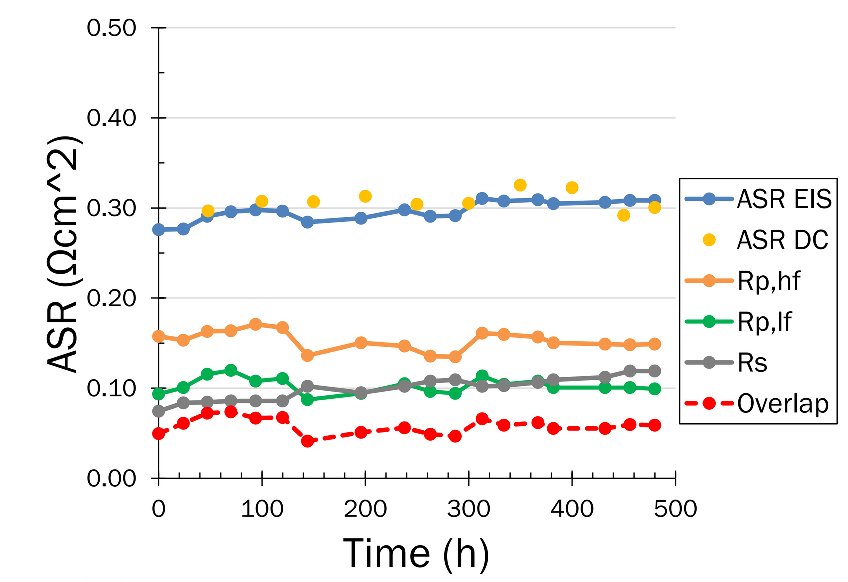


LSM 85-90 (11% Mn excess), aggressive, air on cathode side:

a) ASR EIS is the sum of the gray, orange, and green, minus red curves.

b) **ASR EIS gave good agreement with ASR DC** from durability testing (±0.02 Ω cm^2).

c) Rise in ASR DC with time comes from **series resistance R_S**, not from R_p

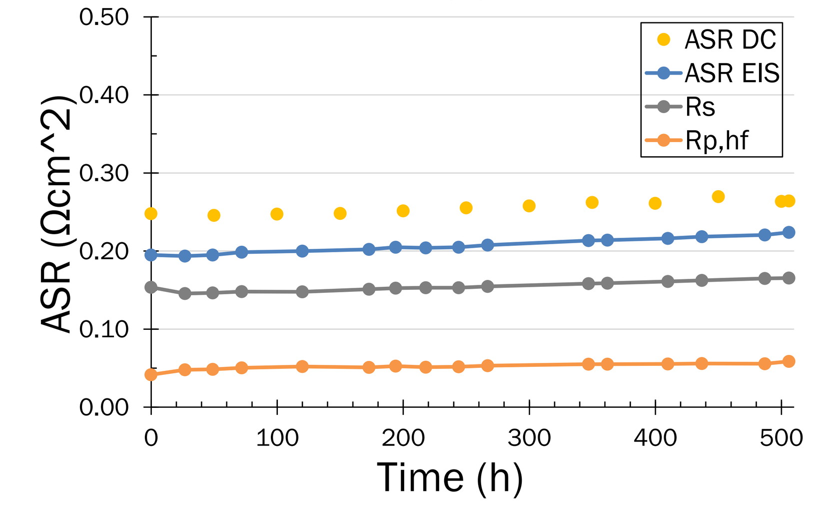


LSM 80-95 (5% Mn excess), aggressive, air on cathode side:

a) ASR EIS is the sum of the gray, orange, and green, minus red curves.

b) **ASR EIS gave good agreement with ASR DC** from durability testing (±0.03 Ω cm^2).

c) Rise in ASR DC with time comes from **series resistance R_S**, not from R_p



LSM 80-98 (2% Mn excess), aggressive, air on cathode side:

a) LSM 80-98 had the lowest ASR under these conditions.

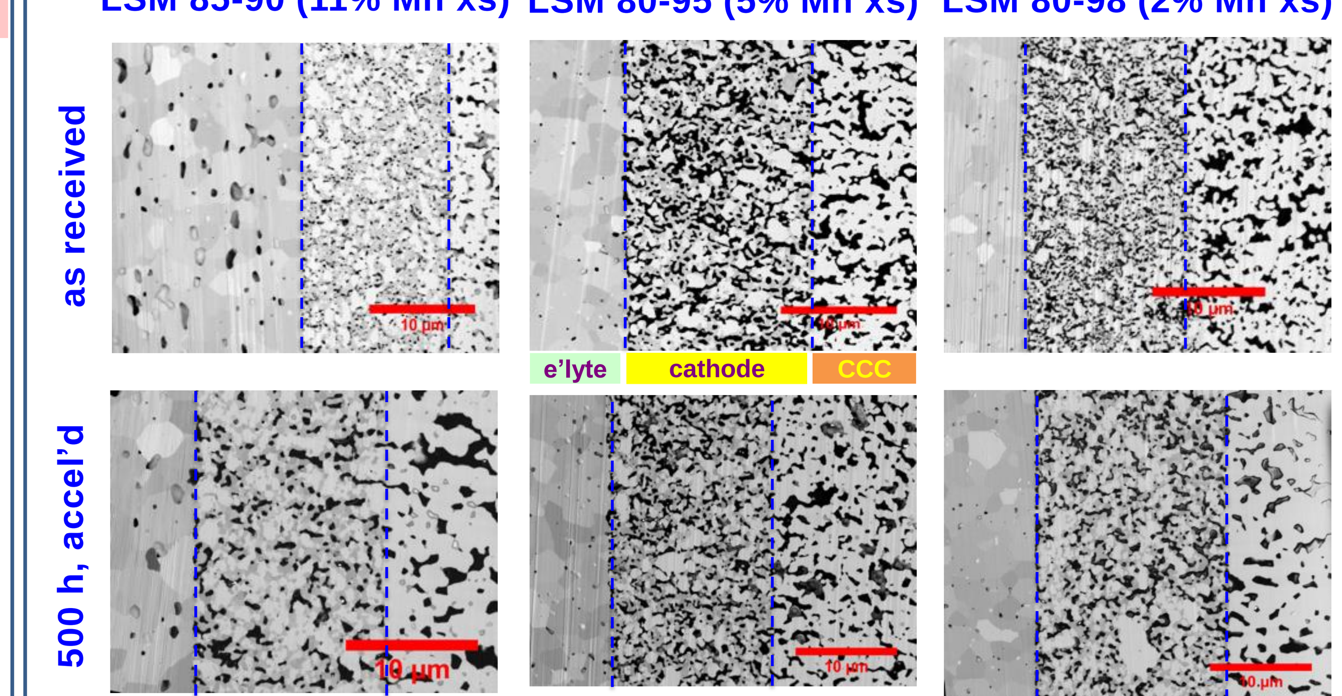
b) Inductance affected the high frequency peak (not shown here), potentially also impacting the low frequency peak.

c) For the low frequency peak, **all resistances increased with time.**

d) **ASR EIS still gave fair agreement with ASR DC** (≤ 0.06 Ωcm^2).

Microstructure change

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

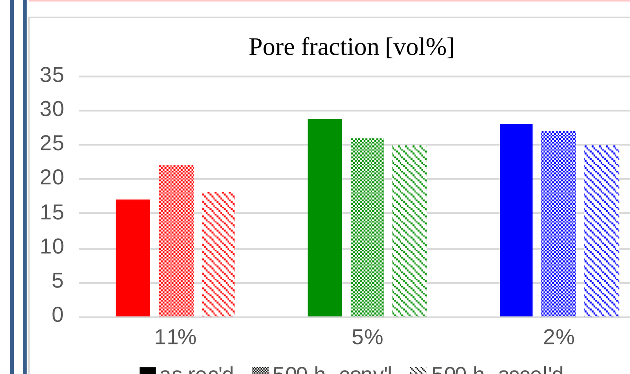


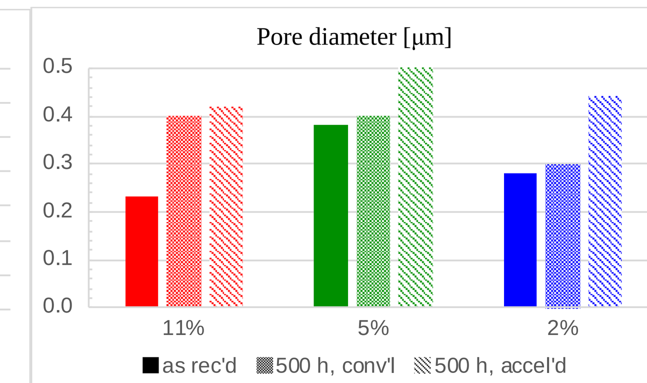
- Coarsening of pores & LSM
- Densification of CCC

- Highest overall microstructural stability

- Coarsening of pores & LSM
- Densification of CCC

Microstructure parameters from 3DR

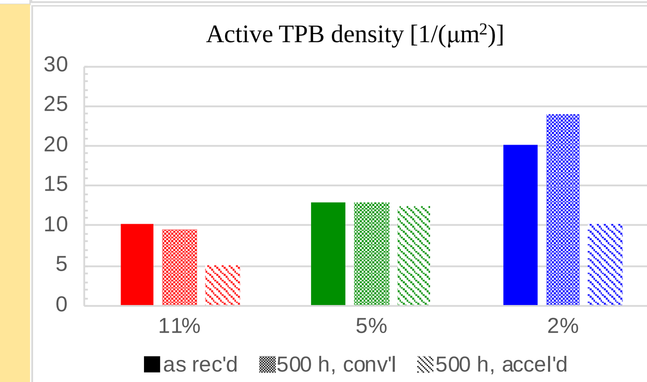




11% Mn excess:
- Pore coarsening; lowest TPB density

5% Mn excess:
- Some pore coarsening; stable TPB density

2% Mn excess:
- Pore coarsening; drop in TPB density



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