Multiple Oxygen Incorporation Processes in Porous Lanthanum Strontium Ferrite Thick Films Observed by the Curvature Relaxation (κR) Technique

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1. Introduction

$La_{0.6}Sr_{0.4}FeO_{3-\delta}$ (LSF) is a mixed ionic electronic conductor (MIEC) usually used as cathode in Solid Oxide Fuel Cells (SOFCs). Under operating conditions, LSF easily undergoes the following reaction [1]:

$$\frac{1}{2}O_2 + 2Fe'_{Fe} + V_O^{\cdot\cdot} \rightarrow 2Fe_{Fe} + O_O^x$$

The defect reaction expands the lattice, introducing chemical stress into the material. This mechano-chemical reaction can be described by the following equation[2]:

$$\epsilon_c = \alpha_c \Delta\delta$$

where ϵ_c represents the chemical strain, α_c represents the chemical expansion coefficient, and δ represents the oxygen nonstoichiometry. Therefore, with an oxygen partial pressure change, a LSF film on an inert substrate will produce a change in sample curvature as the LSF equilibrates to a new level of oxygen nonstoichiometry.

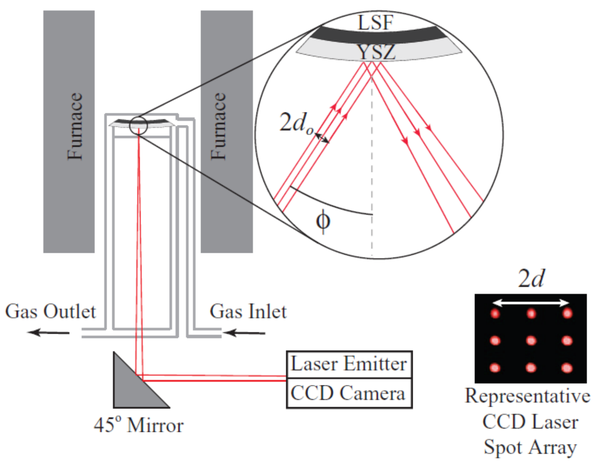
For a dense thin film | inert substrate bilayer sample [3]:

$$\frac{\kappa - \kappa_0}{\kappa_\infty - \kappa_0} = \frac{\delta - \delta_0}{\delta_\infty - \delta_0} = 1 - \exp\left(-\frac{kt}{h_f}\right)$$

For a porous thick film | inert substrate bilayer sample [4,5]:

$$\frac{\kappa - \kappa_0}{\kappa_\infty - \kappa_0} = \frac{\delta - \delta_0}{\delta_\infty - \delta_0} = 1 - \exp\left(-\frac{kt}{\frac{1 - V_V}{S_V}}\right) = 1 - \exp\left(-\frac{t}{\tau}\right)$$

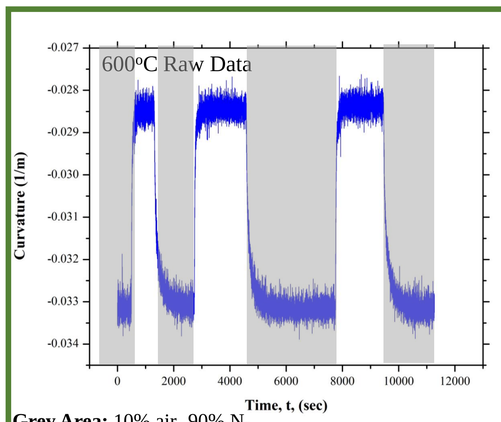
where t represents time; h_f represents the film thickness; κ represents the instantaneous curvature; κ_0 represents the initial curvature; κ_∞ represents the final curvature after po_2 equilibration; S_V represents the volume specific pore surface area; V_V represents the volume fraction porosity and τ represents the time constant for curvature relaxation.



To measure the curvature from the detector spot spacing[5]:

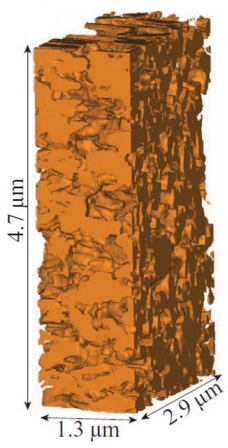
$$\kappa = \left(\frac{cos\emptyset}{2L}\right)\left(1 - \frac{d}{d_0}\right)$$

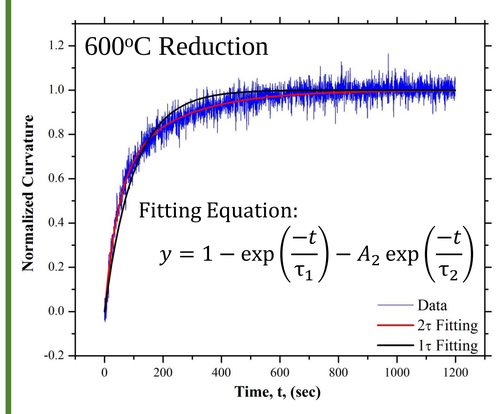
2. LSF κR Data Processing



Grey Area: 10% air- 90% N_2
White Area: air

FIB-SEM 3D Reconstruction





Porosity (V_V):
50.7%
Surface area/Unit Volume(S_V)
:0.024nm^{-1}[5]

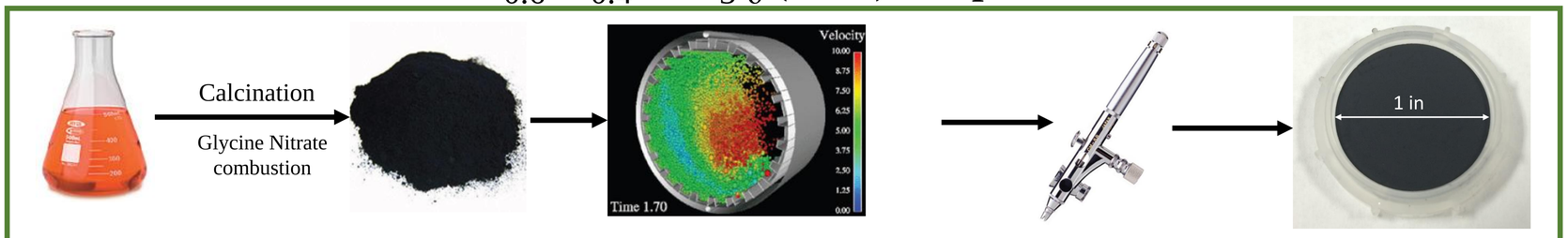
Using Relationship:

$$\tau = \frac{k_{chem}}{\frac{1 - V_V}{S_V}}$$

Get k_{chem} value

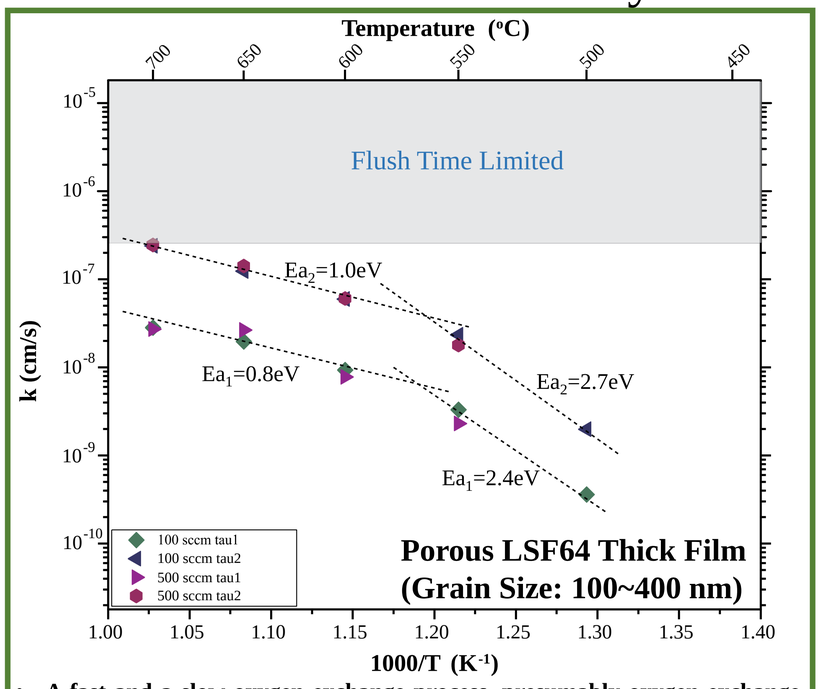
- **Two time constants are needed to fit the curvature relaxation curve**

3. Porous Thick Film $La_{0.6}Sr_{0.4}FeO_{3-\delta}$ (LSF) Preparation



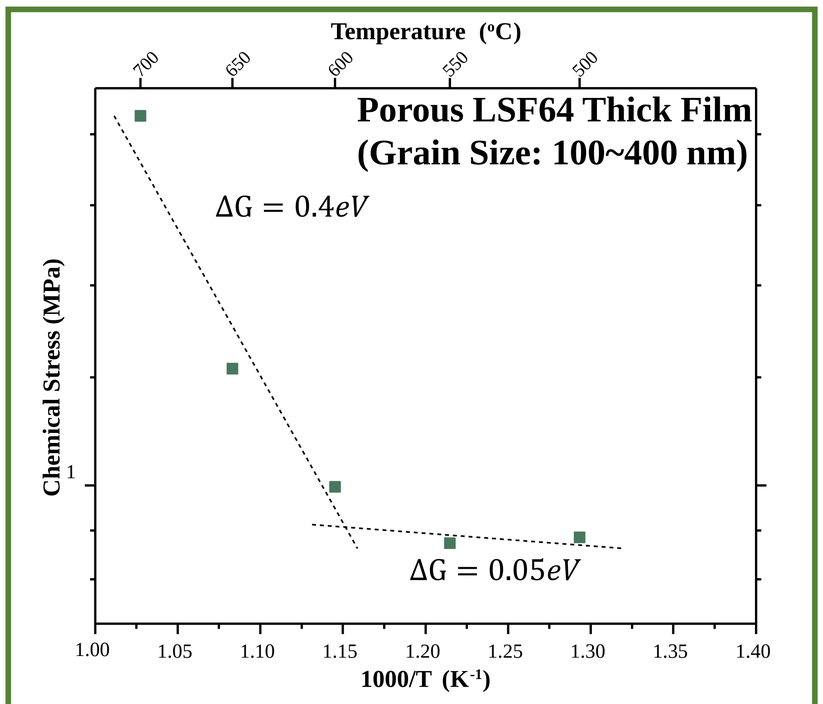
Nitrate precursor Solution | Phase Pure LSF powder | Ball Milling with Dibutyl Phthalate and 2-Propanol | Spray Deposition on (100) $(Y_2O_3)_{0.13}(ZrO_2)_{0.87}$ Single Crystal | Porous LSF | YSZ

4. LSF k Data vs. Thermal Cycle



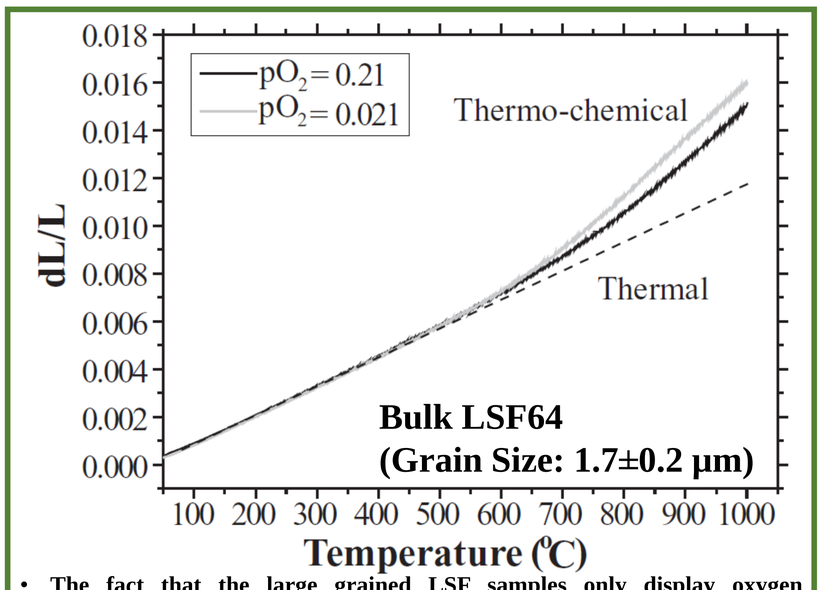
- **A fast and a slow oxygen exchange process, presumably oxygen exchange into different crystallographic directions, are observed at all temperatures**
- **A transition in the dominant oxygen exchange mechanisms occurs at ~575°C**

5. Chemical Stress



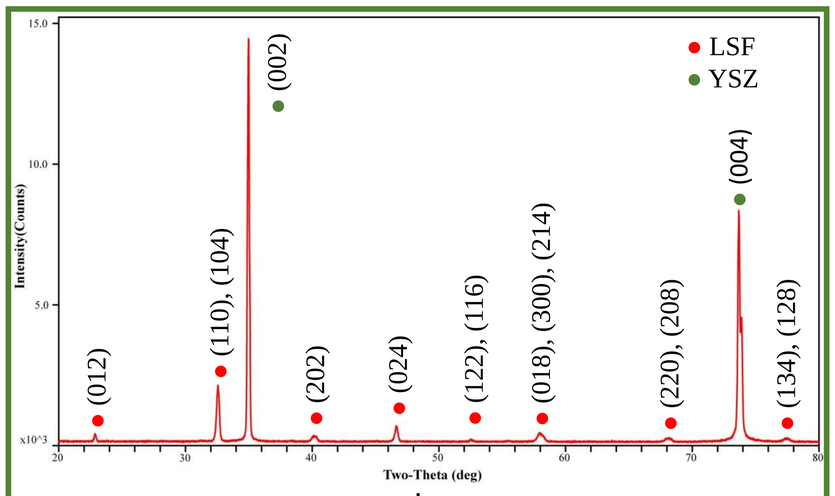
- **A transition in the dominant chemical stress generating mechanism also occurs at ~575°C**

6. Dilatometer Measurement [5]



- **The fact that the large grained LSF samples only display oxygen nonstoichiometry changes above ~575°C suggests that the dominant LSF oxygen exchange incorporation into the bulk, while below ~575°C it is oxygen incorporation in the grain boundaries**

7. XRD Characterization

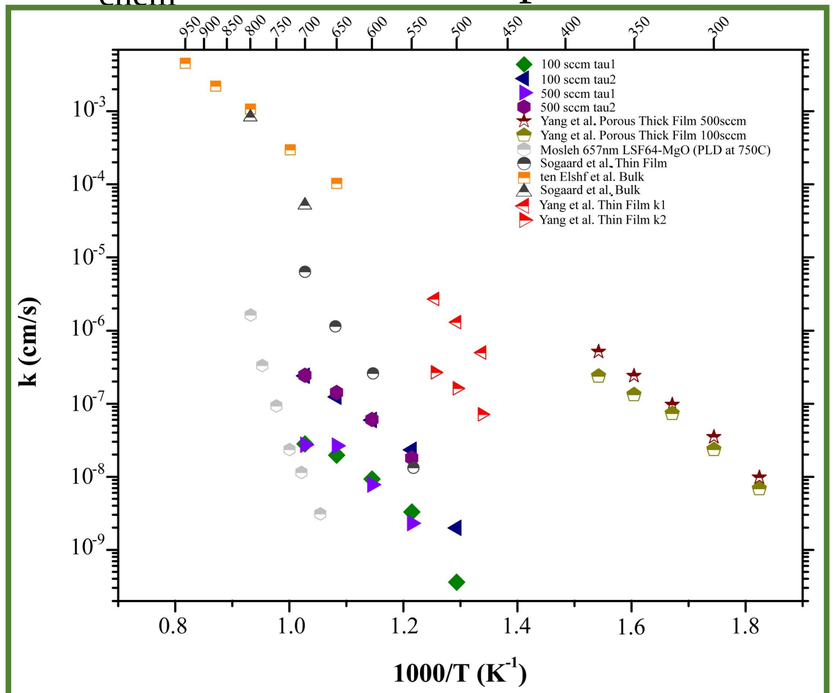


XRD Spectra of LSF64 | YSZ Bilayer after Testing

XRD peak indexing was done with the aid of LSF64 JCPDS PDF # 01-082-1961 and YSZ JCPDS PDF # 01-077-2114

- **LSF64 remains phase pure after deposition and testing**

8. k_{chem} Literature Comparison [6-9]



- **The kchem values fall within the range of previously measured values**

9. Conclusions

- Porous kchem values can be obtained via a new, electrode-free, *in-situ* curvature relaxation technique.
- Two different physical processes, which are presumed to represent oxygen incorporation into the bulk above 575°C and into the grain boundary below 575°C, control the oxygen surface exchange coefficient and the chemical stress.
- While both bulk sample dilatometry and porous film chemical stress measurements detect changes in the bulk oxygen vacancy concentration at ~575°C and higher, the κR technique also detects oxygen vacancy concentration changes at lower temperatures due to its high resolution limit.
- In the future, the kR technique will be used to help identify self-passivating braze alloys by measuring the oxygen exchange kinetics of oxides forming on metal brazes.

10. References

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11. Acknowledgements

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