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]:

$$\frac{1}{2} \text{O}_2 + 2\text{Fe}^{3+} + \text{V}^{\text{O}}_0 \rightarrow 2\text{Fe}^{4+} + \text{O}_2$$

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

$$\varepsilon_c = \alpha_c \Delta \delta$$

where $\varepsilon_c$ represents the chemical strain, $\alpha_c$ represents the chemical expansion coefficient, and $\Delta \delta$ 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 $\Delta \delta$ inert substrate bilayer sample [3]:

$$\kappa = \kappa_0 = 1 - \exp \left( \frac{kT}{\Delta \delta} \right)$$

And for a porous thin film $\Delta \delta$ inert substrate bilayer sample [4,5]:

$$\kappa = \kappa_0 = 1 - \exp \left( \frac{kT}{\Delta \delta} \right)$$

where $\kappa$ represents time; $h_0$ represents the film thickness; $\kappa$ represents the instantaneous curvature; $\kappa_0$ represents the initial curvature; $\kappa_0$ represents the final curvature after poeq; equilibration; $S_0$ represents the volume specific pure surface area; $V_4$ represents the volume fraction porosity and $t$ represents the time constant for curvature relaxation.

2. LSF $\kappa R$ Data Processing

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

$$\kappa = \frac{\cos \beta}{2 \lambda} \left( \frac{d}{d_0} \right)$$

3. Porous Thick Film La$_{0.6}$Sr$_{0.4}$FeO$_{3-\delta}$ (LSF) Preparation

Calcination

Glycine Nitrate combustion

Phase Pure LSF powder

Ball Milling with Dibutyl Phthalate and 2-Propanol

Spray Deposition on (100) $\text{Y}_{0.23315}\text{La}_{0.76685}\text{O}_3\text{La}_2\text{O}_3$ Single Crystal

4. LSF $k$ Data vs. Thermal Cycle

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

5. Chemical Stress

&Delta;G = 0.4eV

&Delta;G = 0.05eV


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

7. XRD Characterization

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

9. Conclusions

- Porous $k_{chem}$ 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 $k_{chem}$ technique also detects oxygen vacancy concentration changes at lower temperatures due to its higher resolution limit.
- In the future, the $k_{chem}$ 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

11. Acknowledgements