Microstructural Effects on the Oxygen Exchange Kinetics of $La_{0.7}Sr_{0.3}MnO_3$ Thin Films

Department of Materials Science and Engineering, Carnegie Mellon University
Lu Yan and Paul Salvador

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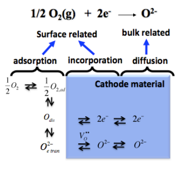
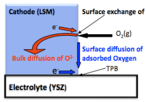
Introduction

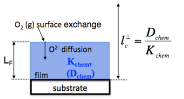
To improve the total performance of solid oxide fuel cells (SOFCs), it is desirable to reduce the losses on the cathode side of the cell. The oxygen reduction reaction (ORR) takes place in the SOFC cathode and it is rather complex; it involves a variety of sub-reactions, such as surface adsorption, dissociation, election transfer, incorporation, and bulk diffusion. Although a considerable amount of effort has been expended in correlating processing / microstructural features to cathode performance, there is relatively little known about the fundamental properties of oxide surfaces, how they are affected by surface chemistry, and how they are related to overall cathode activity. We use thin film approaches to isolate the surface response from the bulk properties and to control structural perturbations / surface chemistry. The aim is to understand the fundamental surface activity of the most commonly used cathode material $La_{0.7}Sr_{0.3}MnO_3$ (LSM). Here we investigated the relative contribution of the native surface and of the grain boundaries intersecting the surface to the chemical surface exchange of LSM thin films. This research shed light on the activity of nanoscale infiltrates used as surface modifications to improve cathode performance.

Cathode Reactions and Pathways





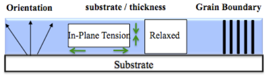
It's important to understand the impact of:
surface chemistry / structure
on activity / stability of cathode.

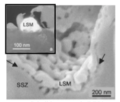


Project Objectives

Overarching Goal:

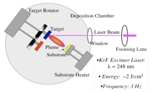
Use thin films to probe the fundamental surface chemistry/structure and their relationship to SOFC cathode reaction activity.



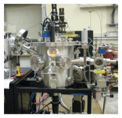


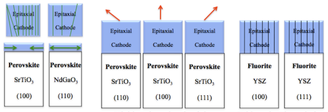
Scholklapper et al. (LBL), *Electrochem. Solid-State Lett.*, **10**, B74 (2007)

Oxide Thin Film Growth



- *KrF Excimer Laser: λ = 248 nm*
- *Energy: ~2 J/cm²*
- *Frequency: 3 Hz*

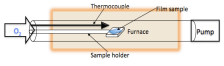




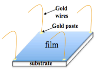
Strained and relaxed — Highly oriented, epitaxial — With variant boundaries

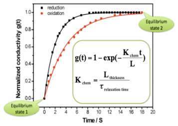
Experiments

Electrical Conductivity Relaxation (ECR) Measurements



Yan et al, Mat. Res. Soc. Symp. Proc. 1255 (2010).

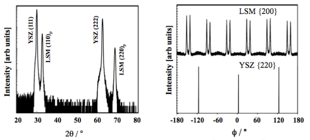




Results and Discussion

XRD patterns of $La_{0.7}Sr_{0.3}MnO_3$ (LSM) on 8%Y_2O_3-ZrO_2 (YSZ)

600nm LSM on YSZ (111), deposited at 750°C, annealed at 850 °C for 24 hr

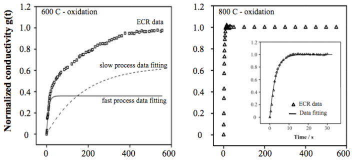


out of plane: $[110]_{LSM} \parallel [111]_{YSZ}$

in plane: $([\bar{1}11]_{LSM}$ and $[1\bar{1}1]_{LSM}) \parallel ([1\bar{1}0]_{YSZ}, [0\bar{1}1]_{YSZ}$ and $[\bar{1}01]_{YSZ})$

6 degenerate variants in the LSM film, many boundaries between the individual variants.

ECR curve and curve fitting of LSM on YSZ



$$g(t) = \frac{\sigma_t - \sigma_{final}}{\sigma_{final} - \sigma_{initial}} = 1 - A\exp(-\frac{K_{1,chem}t}{L}) - (1-A)\exp(-\frac{K_{2,chem}t}{L})$$

< 800 °C, A≠1, two K_{chem} : a fast and a slow processes.
≥ 800 °C, A=1, one K_{chem} : faster response at 600 °C diminishes with ↑ temperature.

Proposed Model

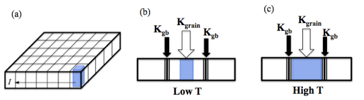


Figure. Schematics of two proposed mechanisms for oxygen exchange of LSM films: (a) schematic of grain boundaries networks inside the film, dashed line indicates in plane current direction (b) and (c) schematic of two possible oxygen flux pathways on the surface at different temperatures

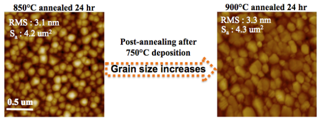
Grains ≈ 100 nm x 600 nm. Grain boundaries are interconnected, dense and intersect the surface uniformly. The equilibrium state is achieved when all of the paths come to their new value.

We propose:

1) The grain boundaries exchange oxygen quickly, low Ea, $K_{gb} = K_{chem,2(fast)}$;
the native surfaces exchange oxygen slowly, higher Ea, $K_{grain} = K_{chem,1(slow)}$.

2) The two mechanisms act in parallel, the A value changes with temperature.

600 nm LSM on YSZ (111) with different grain size

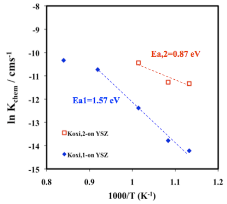


Grain size: ≈ 100 nm — Grain size: ≈ 150 nm

Temp / K	883	923	986	1088	1191
$A_{small\ grain}$	0.6	0.7	0.8	1	1
$A_{big\ grain}$	0.7	0.75	0.84	1	1

K_{chem} values for the fast process and the slow process are the same for both grain sizes.

Temperature dependence of surface exchange coefficients K_{chem}



Our data agree with literatures:

K_{chem} is on the order of 10^{-5}cm/s.[1-5]

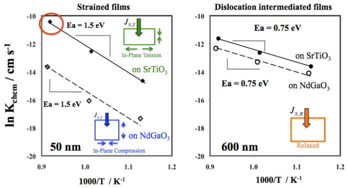
Ea1: 1.48 eV for microelectrode[1], 1.32 eV dense pellet[2],

Ea2: 0.8 eV (100) and (111) on STO[3], 0.07-0.8 eV powder[4].

1. *la O' et al, J. Electrochem Soc. (2009).*
2. *De Souza et al, Mater. Lett. (2000).*
3. *Yan et al, Solid State Ionics. (2011).*
4. *Kan et al, J. Solid state Ionics. (2010).*
5. *Yasuda et al, J. Solid State. Chem. (1996).*

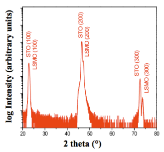
Previous Results

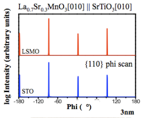
Thickness and substrate effects on $K_{chem,red}$ of LSM (100)

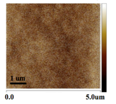


Two activation energy: 1.5 eV (50nm) and 0.75 eV (600nm).
Substrate effects on K_{chem}: $K_{STO} > K_{NGO}$
Fully tensile strained, LSM (100) on $SrTiO_3$: highest K_{chem}, at high T.

$La_{0.7}Sr_{0.3}MnO_3$ film deposited on $SrTiO_3$(100)

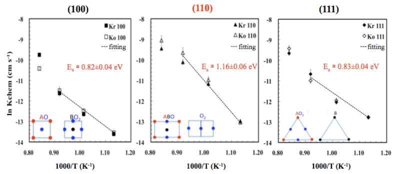






Yan et al, Mat. Res. Soc. Symp. Proc. 1255 (2010).

Orientation effect on K_{chem} of $La_{0.7}Sr_{0.3}MnO_3$ on $SrTiO_3$



Up to 70% surface anisotropy were observed.
L. Yan et al, Solid State Ionics (2011).

At high T, $K_{chem}(110) \geq K_{chem}(111) > K_{chem}(100)$;
At low T, $K_{chem}(111) \geq K_{chem}(110) > K_{chem}(100)$;

Compare with literatures:

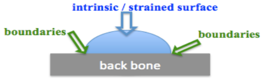
- ΔE_a for surface anisotropy is comparable to YSZ.
- B site is the preferential adsorption site on the surface.
- Surface energy calculations show *(100) < (111) ≤ (110).*

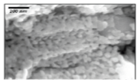
Sasaki et al, Solid State Ionics (2003).
Kotomin et al, Phys. Chem. Chem. Phys. (2008).
Choi et al, Chem. of Mater. (2007).

Conclusion

Microstructrual effects
(including orientation, strain and grain boundaries)
strongly influence the oxygen surface exchange process on LSM.

Grain boundaries are important incorporation sites for LSM: triple or two phase boundaries.
What is the optimized infiltration material (10 to 100 nm) ?





Chao, Gerdes, Kitchin, Salvador, Electrochem. Soc. Trans. (2011).

Mesoporous LSM infiltration on LSCF / YSZ