Crystallographic Anisotropy of Oxygen Surface Exchange in (La,Sr)MnO_3 Thin Films

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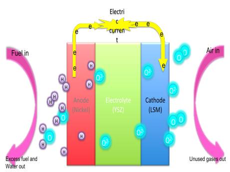
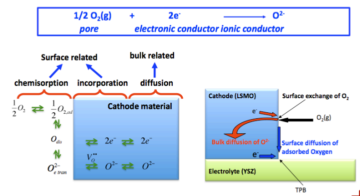
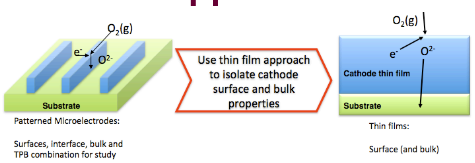
Introduction

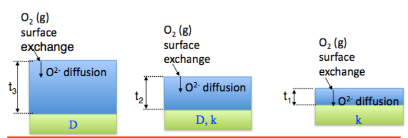


The oxygen reduction reaction (ORR) takes place in the solid oxide fuel cell (SOFC) cathode and the overall reaction is rather complex; it involves a variety of sub-reactions, such as surface adsorption, dissociation, election transfer, incorporation, and bulk diffusion. Although a considerable amount of effort has been expended in correlating processing / microstructural features to cathode performance, there is unfortunately relatively little known about the fundamental surface properties of oxide surfaces and their relation to cathode activity. In this study, to avoid the complex structural perturbation on the oxygen uptake pathways, we adopted the thin film approach to isolate the surface response from the bulk properties. The aim of this research is to understand the fundamental surface activity of cathode materials, including $La_{0.7}Sr_{0.3}MnO_3$, and to shed light onto the utility and stability of potential infiltrate materials as surface modifications to improve cathode performance.



Approach

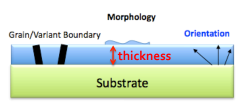




To isolate the surface influence on oxygen exchange process, film thickness should be smaller than critical value.

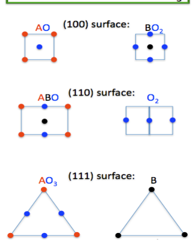
Objectives

1. Isolate oxygen uptake
   - Surface or bulk control
   - Further distinguish sub-steps
   - Correlate chemistry/structure to activity



2. Prepare high quality epitaxial films:
   - With controlled surface properties
   - As proxy for bulk crystals

Perovskite surfaces: ABO_3



3. How sensitive is uptake to orientation?
   - Is there any surface anisotropy?
   - How much surface anisotropy?

Experiments and results

I. Film Growth

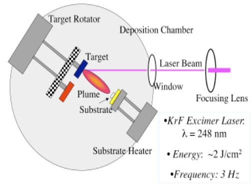


Fig. Sketch of Pulsed laser deposition process

Smooth and similar surfaces make the films comparable to each other.

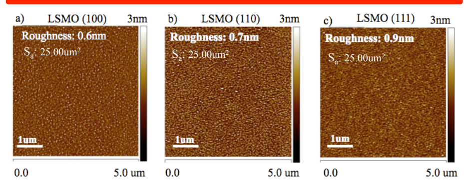


Figure . AFM images of 600nm thick $La_{0.7}Sr_{0.3}MnO_3$ films on $SrTiO_3$ substrates in 3 orientations.

The films are of good expitaxial and crystallographic qualities.

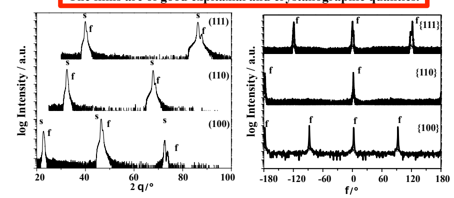


Figure . XRD patterns of 600nm thick $La_{0.7}Sr_{0.3}MnO_3$ films on $SrTiO_3$ substrates in 3 orientations: (left) 2q scan show out of plane film orientations; (right) f scan give in plane epitaxial alignments.

II. Electrical Conductivity Relaxation (ECR) and Kelvin Probe (KP) Measurements

LSMO films are good proxy for the bulk materials.

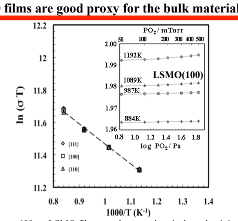


Figure . 600nm LSMO films steady-state electrical conductivity dependency on temperature and oxygen partial pressure.

600nm thick films have a surface controlled response.

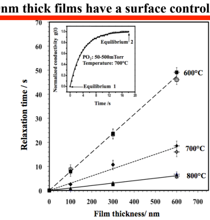


Figure . Linear relaxation time dependency on LSMO film thickness: oxidation state is in open marker, reduction is in close marker. (inset) shows ECR data fitting curve for calculation of relaxation time and chemical surface exchange coefficient.

Reduction

Temperature / K	Kr (100) $\times10^{-6}$/cm•s^{-1}	Kr (110) $\times10^{-6}$/cm•s^{-1}	Kr (111) $\times10^{-6}$/cm•s^{-1}
883	1.22	2.31	2.84
986	3.24	14.2	5.92
1088	8.93	40.7	23.2
1191	*57.9*	*79.1*	*63.9*

Oxidation

Temperature / K	Ko (100) $\times10^{-6}$/cm•s^{-1}	Ko (110) $\times10^{-6}$/cm•s^{-1}	Ko (111) $\times10^{-6}$/cm•s^{-1}
883	1.30	2.18	2.83
986	3.74	17.2	6.40
1088	10.1	64.3	16.9
1191	*29.8*	*118*	*80.3*

Table . Summary of K_{chem} under different temperatures in 3 orientations.

Significant surface anisotropy was observed in this study.

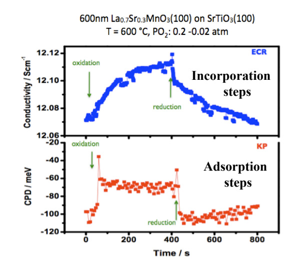


Figure . Comparison of ECR and KP measurements under the same conditions: results reveal the two measurements complement one another.

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

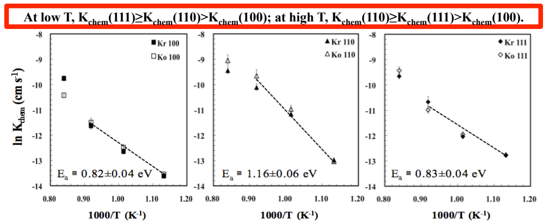


Figure . Chemical surface exchange coefficient K_{chem} for 600nm LSMO of 3 orientations under various temperatures. E_a is the activation energy as calculated from data fitting. (PO_2 between 50mTorr to 500mTorr.)

Differences of activation energy for surface anisotropy is comparable to YSZ in literatures.
K. Sasaki, J. Maier, Solid State Ionics 161 (2003)

Conclusion

1. 600nm thick $La_{0.7}Sr_{0.3}MnO_3$ films have a surface dominated respond to oxygen exchange; thin films are good proxy for bulk/single crystals.
2. There are 2 steps in transient response to PO_2 change:

   Kelvin Probe measurement is sensitive to fast adsorption step;
   Electrical conductivity relaxation measurement is likely related to incorporation step.
3. There is significant crystallographic anisotropy in LSMO to surface response:

   at high T: $K_{chem}(110) > K_{chem}(110) > K_{chem}(100)$
   at low T: $K_{chem}(111) \geq K_{chem}(110) > K_{chem}(100)$

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