



# Electronic Structure, Surface Chemistry and Activity of $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ Thin Film Cathodes at Elevated Temperatures

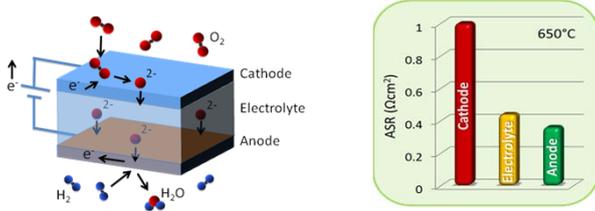
Wonyoung Lee,<sup>1</sup> Helia Jalili,<sup>1</sup> Michael Weir,<sup>2</sup> Clemens Heske,<sup>2</sup> Lu Yan,<sup>3</sup> Paul Salvador<sup>3</sup> and Bilge Yildiz<sup>1</sup>

<sup>1</sup>Laboratory for Electrochemical Interfaces, Department of Nuclear Science and Engineering, Massachusetts Institute of Technology,

<sup>2</sup>Department of Chemistry, University of Nevada-Las Vegas, <sup>3</sup>Department of Materials Science and Engineering, Carnegie Mellon University

## Motivation and Objective

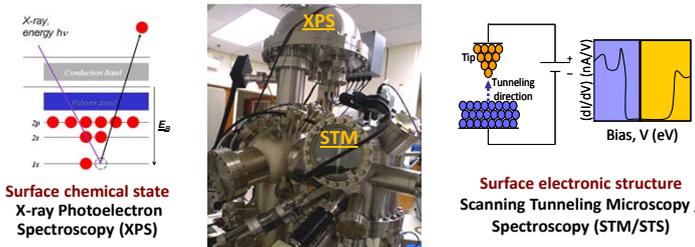
Oxygen reduction at cathode of solid oxide fuel cell is a key barrier to achieve higher power output and enable more economic functionality at intermediate temperatures.



The oxygen reduction reactivity depends on the **electronic structure and surface chemistry** driven by temperature, oxygen pressure, and lattice strain.

**Goal** - Identify the correlations of temperature, oxygen pressure, and strain to the electronic and chemical state and reactivity on the surface of epitaxially-grown  $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$  thin films. In particular, focus on the Sr segregation, energy gap, and density of states (DOS) near  $E_F$ .

**Approach** - *In situ* measurements to reveal the surface electronic structure and chemistry under the operating conditions of cathodes at elevated temperatures and oxygen pressures.

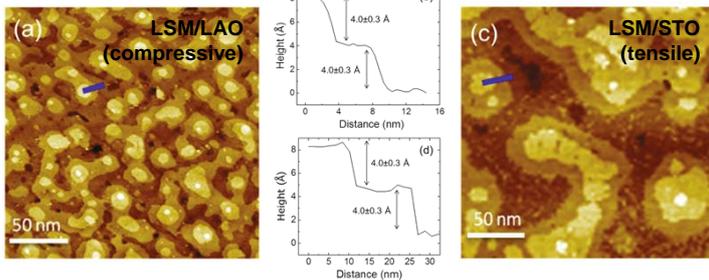


Surface chemical state  
X-ray Photoelectron Spectroscopy (XPS)

Surface electronic structure  
Scanning Tunneling Microscopy / Spectroscopy (STM/STS)

## Results: Strain effects

### Surface structures

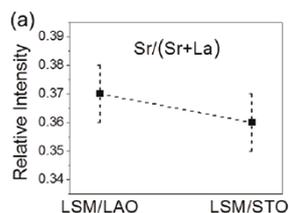


| Compound  | Lattice parameters                |
|---|-----------------------------------|
| <sup>1</sup> $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ | $a=b=c= 3.88 \text{ \AA}$         |
| <sup>2</sup> $\text{SrO}$                                 | $a=b=c=5.16 \text{ \AA}$          |
| <sup>3</sup> $\text{SrCO}_3$                              | $a=5.1, b=8.4, c=6.0 \text{ \AA}$ |
| <sup>4</sup> $\text{La}_2\text{O}_3$                      | $a=b= 3.4, c=6.1 \text{ \AA}$     |
| <sup>5</sup> $(\text{La,Sr})_2\text{MnO}_4$               | $a=b=3.84, c=12.5 \text{ \AA}$    |

Both films show similar surface morphologies of a layer-by-layer structure with height difference of  $4.0 \pm 0.3 \text{ \AA}$ .

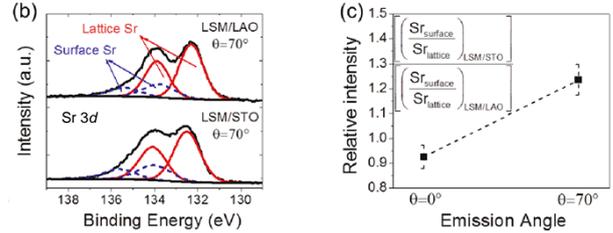
→ LSM perovskite itself is the most appropriate surface structure, no secondary phase on the surface.

### Surface chemistry



Emission angle of  $70^\circ$  (surface sensitive)  
Both films are larger than the bulk ratio of 0.3.  
→ Sr-rich in near-surface region  
→ The total Sr fraction on the A-site within the top surface is the same regardless of the sign or magnitude of strain.

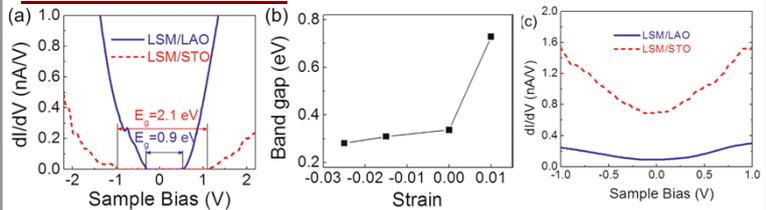
### Surface chemistry



Surface-Sr : under-coordinated Sr or Sr-OH on the perovskite.

→ More enrichment of surface-Sr driven by the tensile strain state in LSM/STO.

### Electronic structures



(a) Tunneling spectra measured at RT in UHV ( $10^{-10}$  mbar).

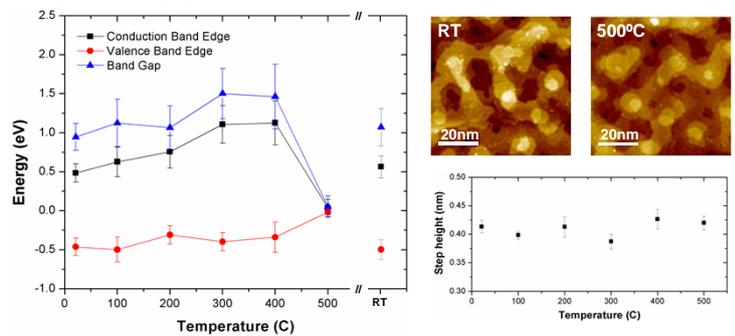
(b) DFT calculations of total density states as a function of strain

(c) Tunneling spectra measured at  $500^\circ\text{C}$  in  $10^{-3}$  mbar of oxygen.

→ Tensile: @ RT,  $E_g$  large ; @  $500^\circ\text{C}$ ,  $\text{DOS}_{E_F}$  large, higher activity<sup>6</sup>.

## Results: Temperature effects

### Gap to no-gap transition



Reversible electronic structure transition from a semiconducting state to a metallic-like state between  $400^\circ\text{C}$  and  $500^\circ\text{C}$  in  $10^{-5}$  mbar of oxygen.

No change in surface structure or step height difference.

Possible mechanisms: oxygen vacancy formation<sup>7</sup>, surface reconstruction<sup>8</sup>.

## Conclusion

- ✓ Lattice strain: Sr-rich and larger band gap when tensile strained.
- ✓ Temperature: Transition from gap to no-gap in DOS at elevated temperature, higher DOS near  $E_F$  when tensile strained.
- ✓ These results demonstrate the important role of lattice strain and temperature in understanding and controlling the electronic structure and cation chemistry, and thus oxygen reduction activity of the cathode, for attaining higher power density in SOFCs.

## References

- [1] R. L. Martin, *Phys. Rev. B*, **53**, 15501, 1996.
- [2] R. Bertacco, J. P. Contour, A. Barthlemy, J. Olivier, *Surf. Sci.*, **511**, 366, 2002.
- [3] T. Thongtem, N. Tipcompor, A. Phuruangrat, S. Thongtem, *Mater. Lett.*, **64**, 510, 2010.
- [4] C. Hu, H. Liu, W. Dong, Y. Zhang, G. Bao, C. Lao, Z. L. Wang, *Adv. Mater.*, **19**, 470, 2007.
- [5] F. Zheng, L. R. Pederson, *J. Electrochem. Soc.*, **146**, 2810, 1999.
- [6] P. J. Feibelman, D. R. Hamann, *Phys. Rev. Lett.*, **52**, 61 1984.
- [7] Y.-L. Lee, D. Morgan, *ECS Trans.*, **25**, 2769, 2009.
- [8] K. Fuchigami, Z. Gai, T. Z. Ward, L. F. Yin, P. C. Snijders, E. W. Plummer, J. Shen, *Phys. Rev. Lett.*, **102**, 066104/1, 2009.