# Electronic Structure Determination of $La_xSr_{1-x}MnO_3$ films for Solid Oxide Fuel Cell Cathodes

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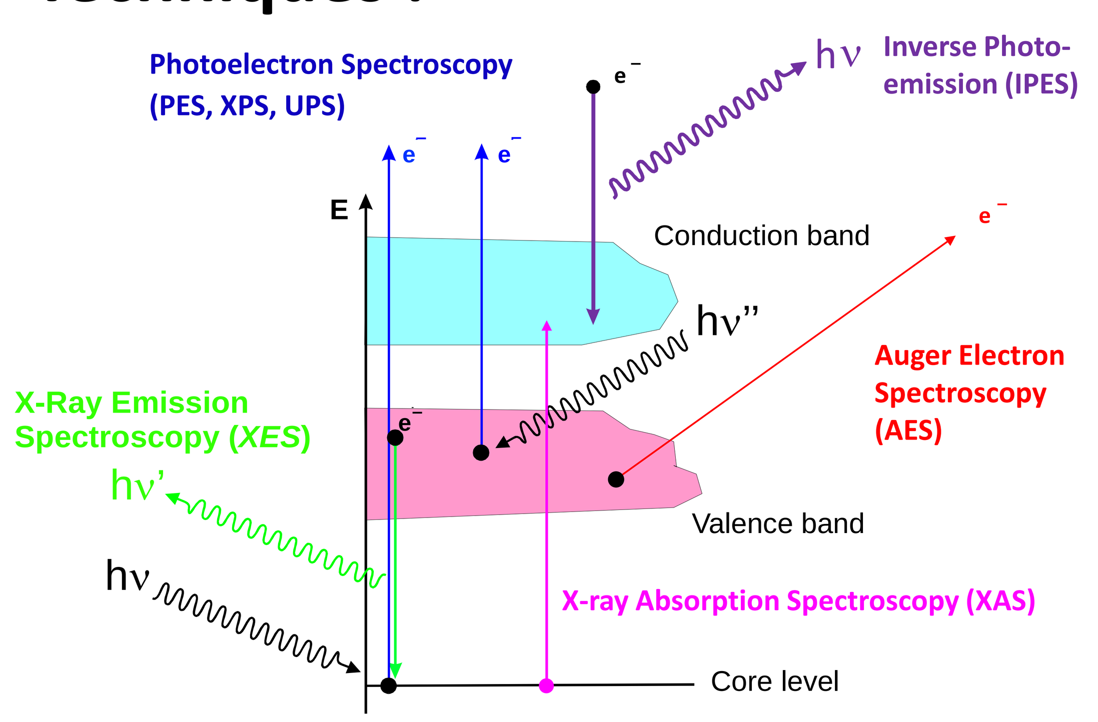
## Introduction

### Techniques :




| | XPS | XAS | XES |
|---|---|---|---|
| **Excitation** | X-ray (constant hν) | X-ray (varied hν) | X-ray (constant hν) |
| **Measured** | Photoelectron kinetic energy | Transmitted X-rays (same hν as above), fluorescent X-rays, or sample current | Emitted X-rays (varied hν) |
| **Information Depth (1/e)** | 0.5 - 3 nm | 10 nm-1 µm | 10-100 nms |
| **Information Gathered** | Elemental composition, Chemical state | Chemical state (element specific) | Chemical state (element specific) |

### Materials :

$La_xSr_{(1-x)}MnO_3$ (LSMO) is an $ABO_3$ type perovskite, where La and Sr share the A-site and Mn fills the B-site.

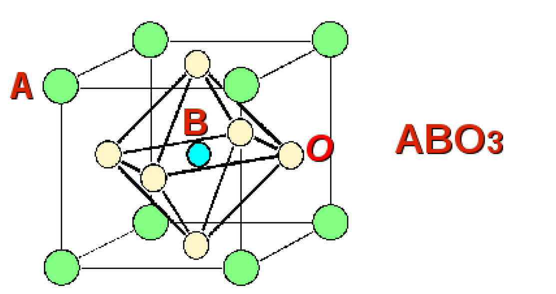
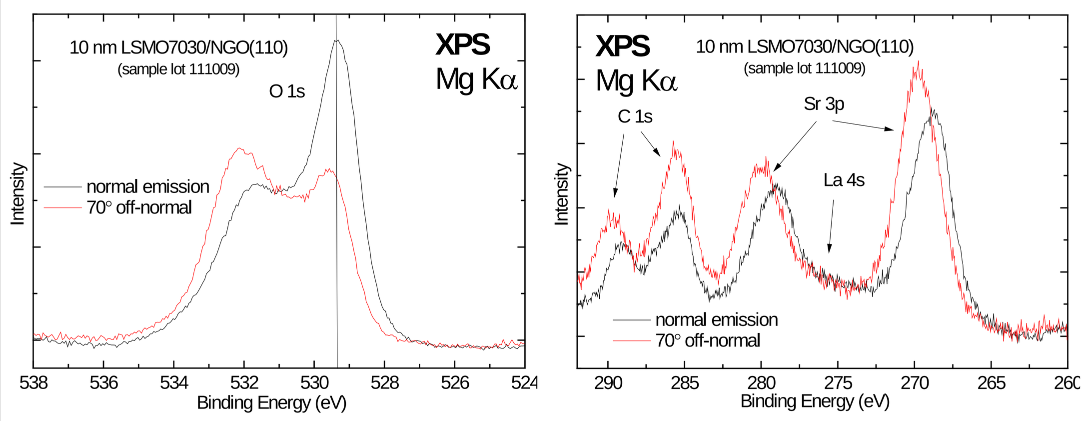



Image from website of Trivedi group, Ohio State University

- Known symmetries include cubic, rhombohedral, orthorhombic and tetragonal.
- Sr addition changes the lattice constant and crystal symmetry and increases the Mn oxidation state.
- Sr likely segregates to the surface, forming SrO or $SrCO_3$.
- $O_2$ is effectively transported through the LSMO film by the movement of O vacancies.
- LSMO films are used as cathodes for solid oxide fuel cells because of the combination of sufficiently high electronic conductivity, surface activity, and stability with the electrolyte at operating temperatures (600 °C – 1000 °C).

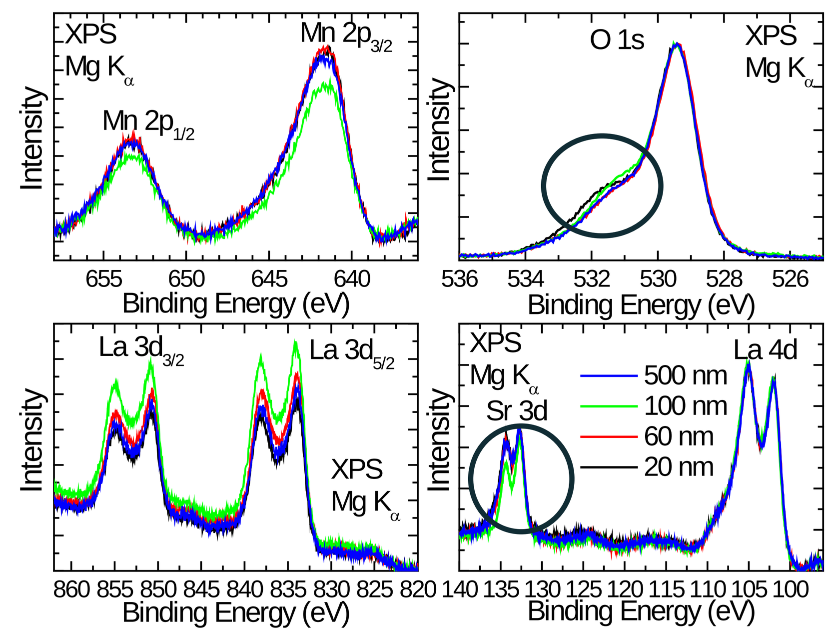
## Results

### Surface Chemistry:



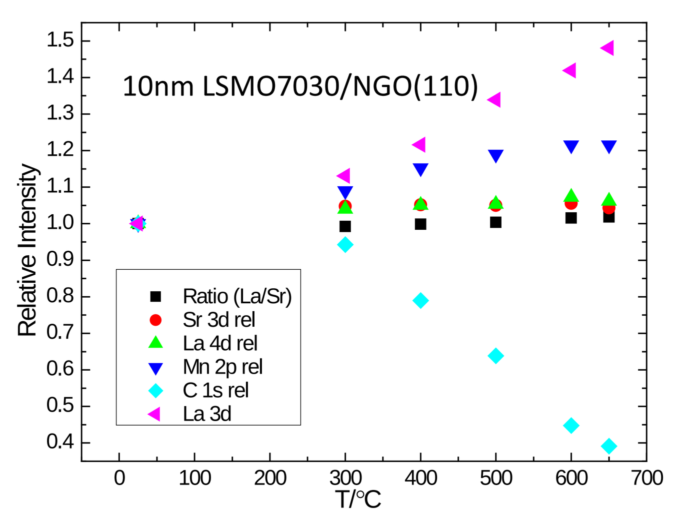

Changing the angle of the sample with respect to the detector allows measurement of different depths of the same film. In these figures, the black lines represent normal surface measurements while the red lines are much shallower measurements. The differences between the measurements indicate that the surface of this film is terminated by $SrCO_3$.

### Film Thickness:




- Thinner films are more likely to show substrate effects
- Significant differences in chemical composition and state
- O 1s peak shows several different chemical environments
- The 100 nm sample has the strongest deviations: less Mn, more La, and a different line shape for Sr 3d
- No thickness dependent trends

### *ex situ* Heating:

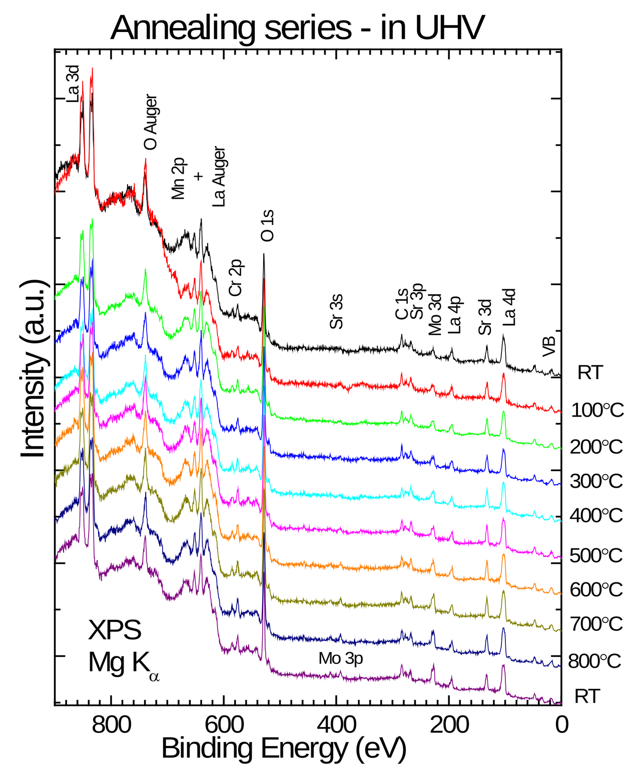



- Experiment examines the effects of temperature cycling and annealing on the films
- *ex situ* heating occurred in $pO_2$
- C 1s signal consistently decreases
- La/Sr ratio stays constant up to 500° and then increases slightly by 4%
- La 3d, Mn 2p signals increase

→This increase may be due to the removal of C surface species

## Results

### *in situ* Heating:




- Experiment performed in vacuum
- *in situ* heating allows examination of reversible changes
- Reversible changes identified by STM at MIT
- 100 nm LSMO8020/STO(100) was heated in steps of 100°C up to 800°C
- Temperature scale calibrated with infrared pyrometer
- Secondary electron background (high binding energy) changes in the first annealing step and then stays constant
- C 1s signal retained despite heating

## Current Work

**Objective:**

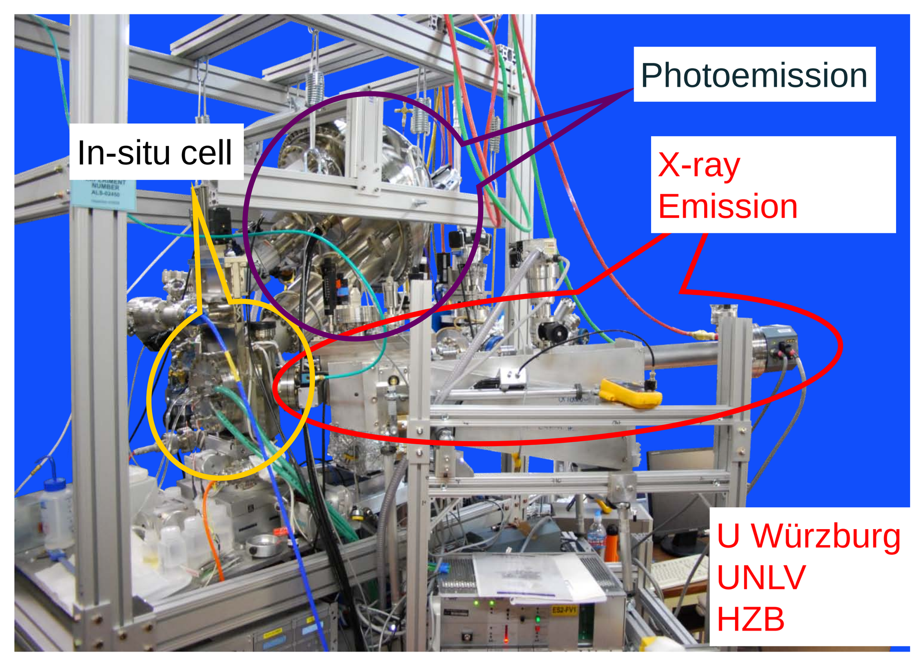
Measure the electronic structure of LSMO films under realistic SOFC operating conditions (1 atm, 800 °C)

**Measurements:**

- Weak XPS signal through gasses
- XAS and XES signals penetrate further through gas
- Experiments use synchrotron as X-ray source
- Advanced Light Source, Lawrence Berkeley National Laboratory
- SXF endstation at beamline 8.0 also used *in vacuo*

**SALSA endstation:**

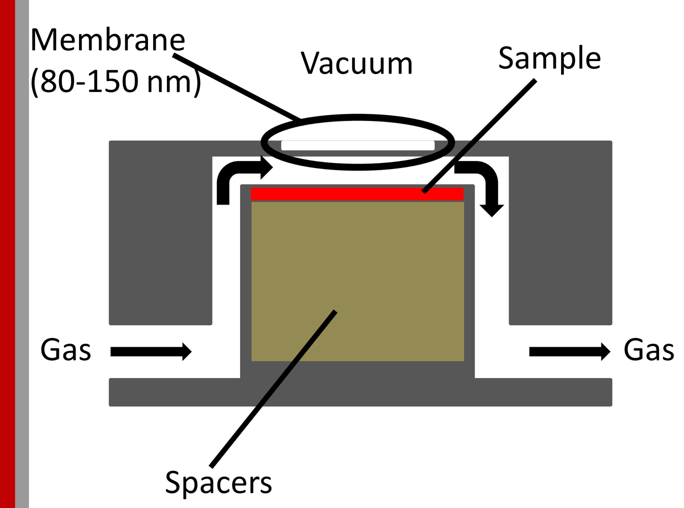
- Currently used for analysis of solid and *in situ* liquid samples
- Beamline 8.0
- VLS spectrometer measures energies between 120 and 650 eV
- XPS measurements possible, particularly for solid samples
- New *in situ* cell designed for high temperature and high pressure

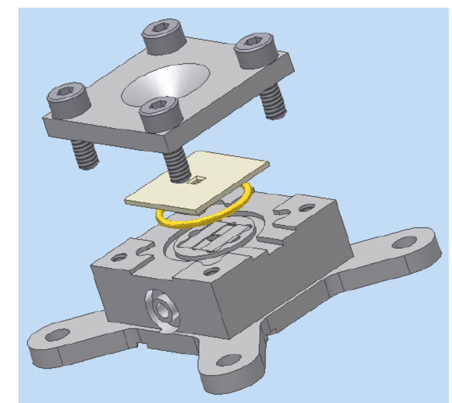



## Current Work

**_in situ_ cell design parameters:**

- Heats cell up to 600 °C
- Gas inlet may be pre-heated
- Pressures from 50 mbar to 1 bar
- Flow cell design with thin layer of gas over sample
- Primary design and construction through Univ. of Würzburg



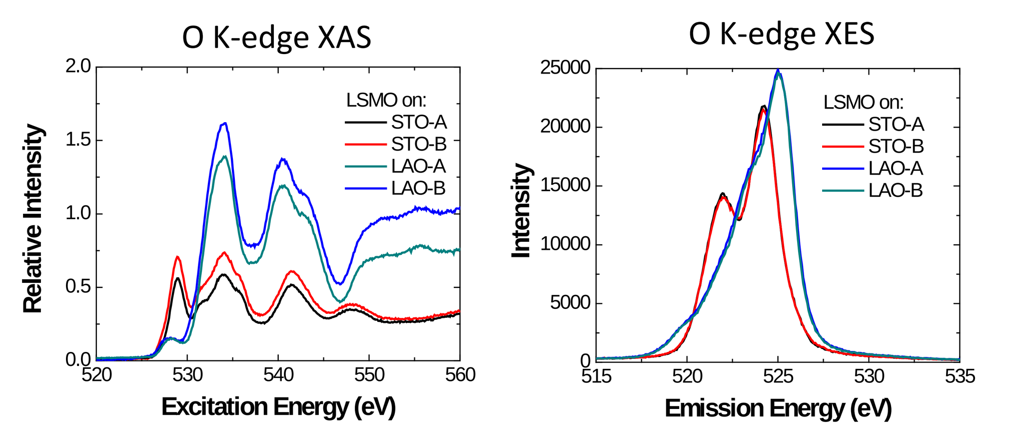



**Initial results:**

XAS and XES measurements of four samples, 2 each of :

- 10 nm $La_{0.7}Sr_{0.3}MnO_3$ on $SrTiO_3$
- 10 nm $La_{0.7}Sr_{0.3}MnO_3$ on $LaAlO_3$

Measurements were made *in vacuo* as controls.




For films on the same substrate, the features are similar (XAS) or practically identical (XES)

Significant differences between films on different substrates are likely due to measuring both the film and the substrate

## Summary and Future

Soft X-ray spectroscopic measurements are able to measure chemical and electronic differences in LSMO films caused by experimental variables including film thickness, substrate material and annealing conditions.

Our methods have expanded to include *in situ* measurements at elevated temperatures. Recent work includes progress toward simultaneous control of temperature and atmosphere.

Future work includes investigation of temperature-based transitions and modifications of the *in situ* gas cell leading to measurements at operating conditions.