Electronic Structure Determination of La$_x$Sr$_{1-x}$MnO$_3$ films for Solid Oxide Fuel Cell Cathodes

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Introductions

**Techniques:**
- Photoelectron Spectroscopy (PES, XPS, UPS)
- Auger Electron Spectroscopy (AES)
- X-ray Absorption Spectroscopy (XAS)
- Inverse Photoemission Spectroscopy (IPES)
- X-ray Emission Spectroscopy (XES)

Materials:
- La$_x$Sr$_{1-x}$MnO$_3$ (LSMO) is an ABO$_3$ type perovskite, where La and Sr share the A-site and Mn fills the B-site.
- 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.

**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 measurements with shallower penetration. The differences between the measurements indicate that the surface of this film is terminated by SrCO$_3$.
- Thinner films are more likely to show substrate effects.
- Significant differences in chemical composition and state.
- 0.1 nm peak shows several different chemical environments.
- The 100 nm sample has the strongest deviations: less Mn, more La, and different line shape for Sr 3d.
- No thickness dependent trends.

**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(STO100) 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.

**Film Thickness:**
- Ex Situ analysis.
- O K-edge XAS and O K-edge XES.

**Results**

**Current Work**

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

Measurements:
- Weak XPS signal through gases.
- XAS and XES signals penetrate further through gas.
- Experiments use synchrotron as X-ray source.
- Advanced Light Source, Lawrence Berkeley National Laboratory.
- Soft X-ray spectroscopic measurements are able to measure chemical and electronic differences in LSMO films caused by experimental variations including film thickness, substrate material and annealing conditions.

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.