Solid Oxide Fuel Cell Cathodes: Unraveling the Relationship between Structure, Surface Chemistry and Oxygen Reduction.

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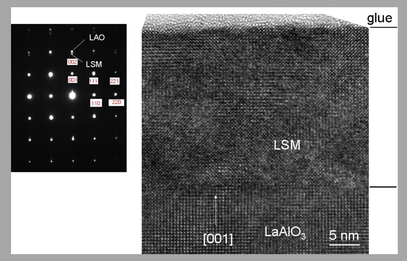
Motivation:

- Cathode surfaces vary in structure and composition with changes in operating history
- Can examine these changes by combining traditional electrochemistry with soft and hard x-ray spectroscopy techniques.

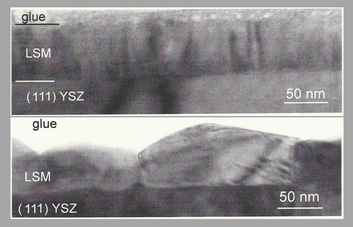
Heteroepitaxial Film Characterization

Film: LSM-20 on LAO [001]



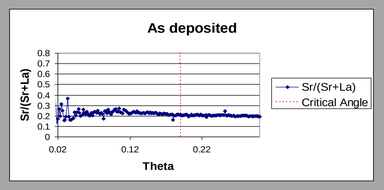
LSM on LAO [001]. Left: electron diffraction patterns. Right: HREM micrograph.

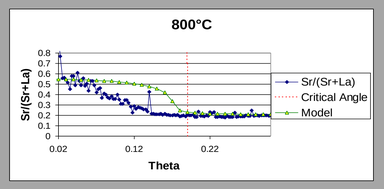
Film: LSM-20 on YSZ [111]



Top: As deposited films show ~30nm wide columnar grain growth. Bottom: Annealing at 1100°C for 4 hr introduces grain growth (~150 nm) and surface roughening.

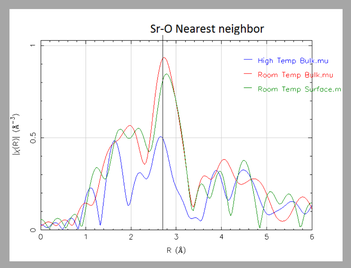
Total Reflection X-Ray Fluorescence (TXRF)





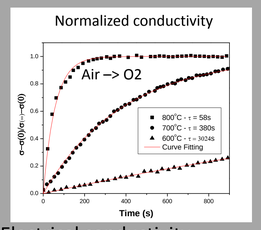
- Monitor fluorescence signals from strontium, lanthanum and manganese simultaneously.
- Total Reflection X-ray Fluorescence (TXRF) data was taken as a function of angle to probe composition ratios as a function of depth.
- Evidence of strontium enrichment on surface upon annealing. Process is not reversible.
- Sr segregation in different circumstances has been reported by Argonne groups: K. Chang, B. et al., Proc. 2008 MRS Fall Meeting, Symposium S: Solid-State Ionics. 1128S08-10, T.T. Fister et al., Appl. Phys. Lett. 93 (15) (2008) 151904.
- Shape not what we expect for segregation to the surface with simple exponential decay into material.

Extended X-Ray Absorption Fine Structure (EXAFS)

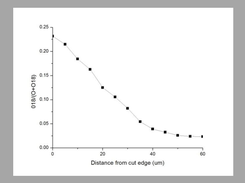


- Extended X-ray Absorption Fine Structure spectrum taken at strontium and manganese edges.
- A t current level of accuracy data shows no differences between grazing surface sensitive and more bulk sensitive modes.
- High temperature data shows a diminished Sr-O peak. Could be actual O loss or due to increased vibrations at high temperature.
- Working on data collected in June with better statistics.

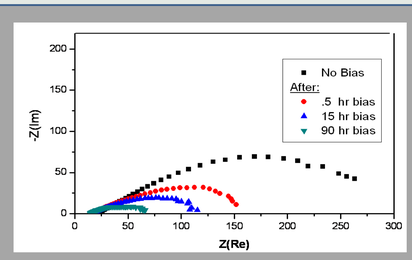
Electroc hemical Characterization



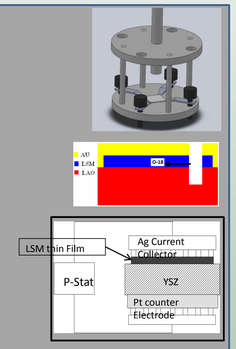
Electrical conductivity relaxation (ECR) experiments performed using Van der Pauw arrangement



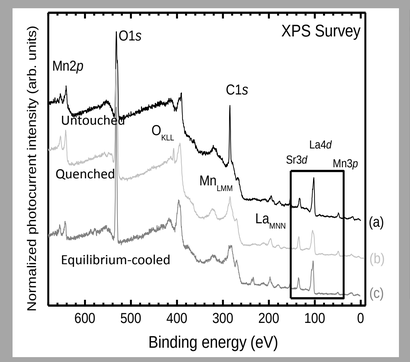
1-D 18O Tracer Diffusion measurements, analyzed with TOF-SIMS at PNNL

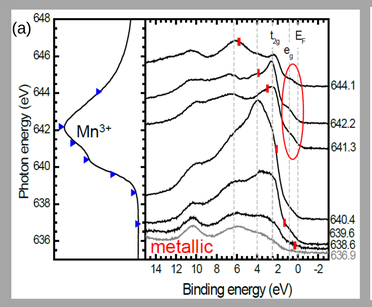


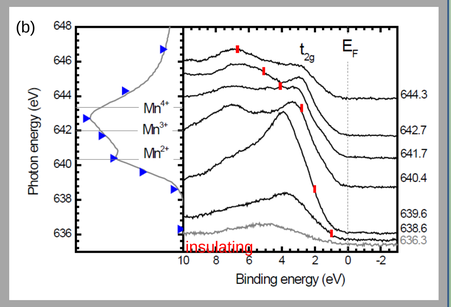
Impedance Spectra were recorded periodically while applying a 1-Volt bias. The value of Rp decreased dramatically over the 4 day treatment.

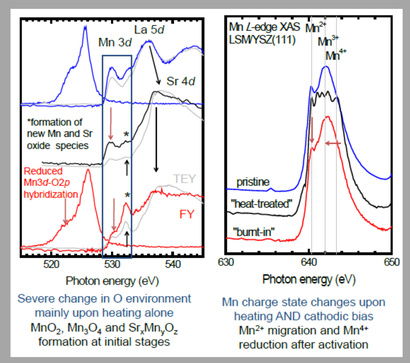


Soft X-ray Synchrotron Spectroscopies









Severe change in O environment mainly upon heating alone
MnO_2, Mn_3O_4 and $Sr_xMn_yO_z$ formation at initial stages

Mn charge state changes upon heating AND cathodic bias
Mn^{2+} migration and Mn^{4+} reduction after activation

- Four samples were tested: Untouched, equilibrium cooled, heated to 800C and quenched, and heated to 800C -1V applied bias for 4 days and quenched.
- XPS shows clear evidence of Sr enrichment nearer the surface upon heating and quenching, meanwhile the La/Sr ratio of equilibrium cooling and untouched are the same.
- Absence of e_g state → increased hole doping ($x > 0.55$) consistent with La/Sr ratio at surface for heat-treated and quenched sample.
- Mixed Mn valence states from Mn $L_{3,2}$-edge XAS, increased 4+ character consistent with Sr enrichment for quenched films.
- O *K*-edge XES/XAS provides the O 2*p partial* DOS. Severe changes in the O 2p environment upon heat-treatment may suggest formation of new Mn (Sr)O species. Subtle changes in O 2*p* PDOS following bias.
- Enhanced Mn^{3+} is seen with heated and quenched. Mn^{4+} is reduced (to Mn^{3+}) and Mn^{2+} intensity is weakened after bias treatment.

Summary:

- High quality heteroepitaxial thin-films of LSM have been grown on LAO [001], while on YSZ [111] possibly films oriented in the [110] direction are grown. Further characterization is ongoing.
- Hard x-ray techniques (TRXF, and EXAFS) are probing the *in situ* nature of the surface
- Electrochemical techniques (EIS, ECR, and tracer diffusion) characterize the in situ nature of the films.
- Soft x-ray measurements on sealed samples reveal the changing nature of the surface cations.