In-Situ Synchrotron and Electrochemical Measurements of Heteroepitaxial Thin-Films of SOFC Cathode

Lincoln Miara[1], Jacob Davis[1], Kevin Smith[3], Uday B. Pal[1,2], Karl Ludwig[1,3], Soumendra Basu[1,2], Srikanth Gopalan[1,2]

[1]Division of Materials Science and Engineering, [2]Department of Mechanical Engineering, [3]Department of Physics, Boston University, Boston, MA 02215

Motivation:

Development of state of the art Solid Oxide Fuel Cells (SOFCs) has to overcome costs that are still considerably higher and operating lifetimes that are considerably shorter than conventional power generating systems. This requires an understanding of some of the fundamental science behind certain fuel cell processes.

Goals:

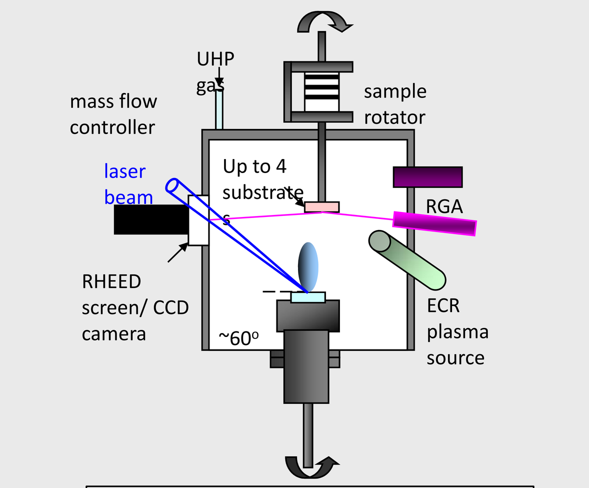
Understand the fundamental physics of the reactions occurring at the cathode surface. This will be achieved by:

•Growth of epitaxial thin films of SOFC cathodes of various thicknesses on different single crystal substrates by Pulsed Laser Deposition; and complete characterization of these samples by XRD and TEM.

•Design and construction of a heated synchrotron chamber capable of various oxygen partial pressures and temperatures that has the capability of making electrochemical measurements.

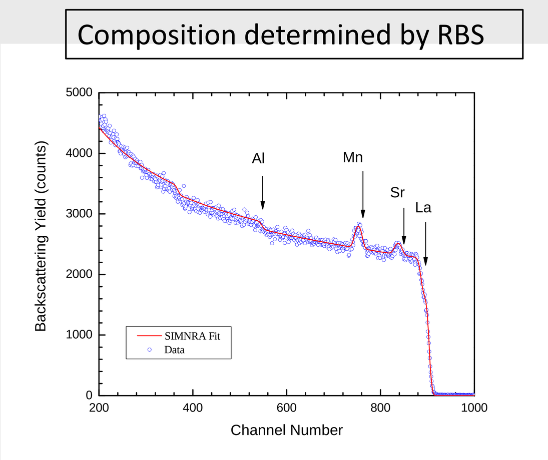
•Use the chamber to characterize the crystalline and electronic structure of the cathode material, and determine in-situ changes.

Sample Growth by PLD



PLD Growth Chamber Schematic

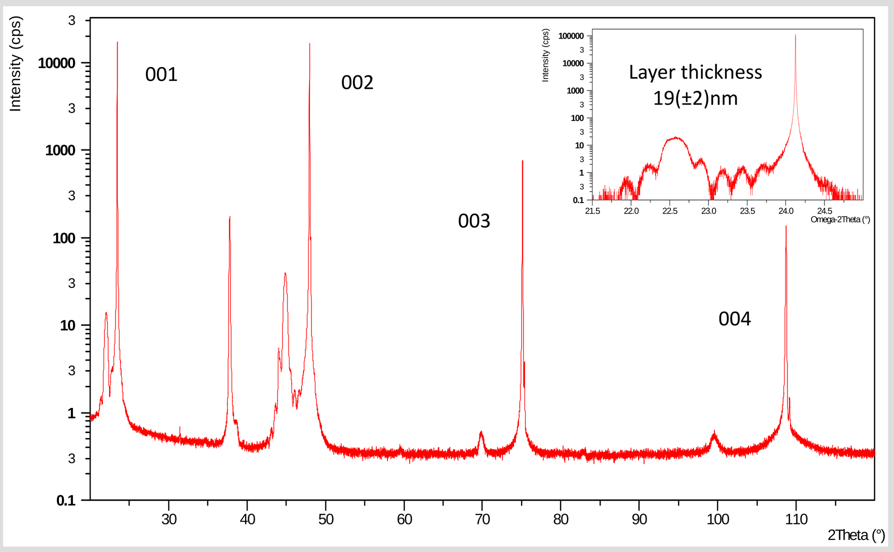
Composition determined by RBS

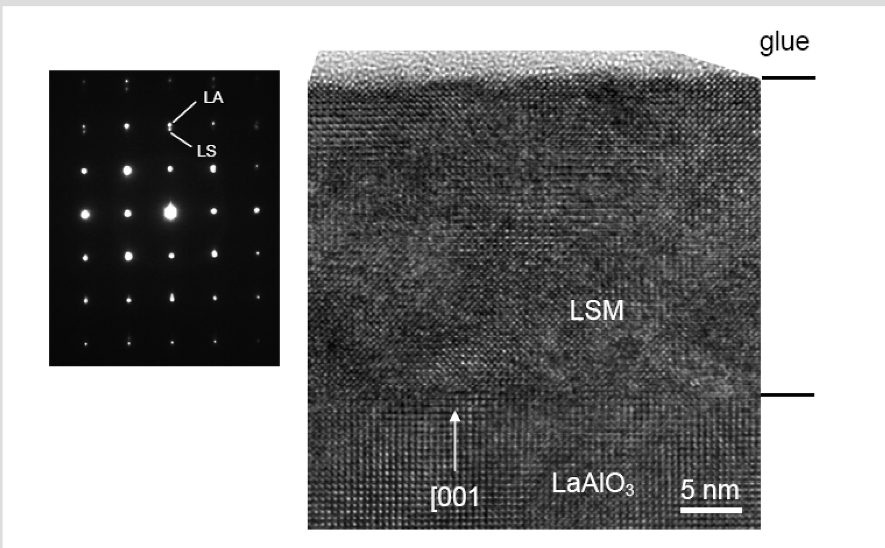


RBS Results:
Target Composition: $(La_{0.8}Sr_{0.2})_{0.97}MnO_{3\pm\delta}$
Film Thickness: 35.2 nm
Cation Ratios: Sr/(La +Sr) = 0.21 Mn/(La + Sr) = 0.95
Film composition: $(La_{0.79}Sr_{0.21})_{0.95}MnO_{3\pm\delta}$

Sample Characterization by XRD and TEM

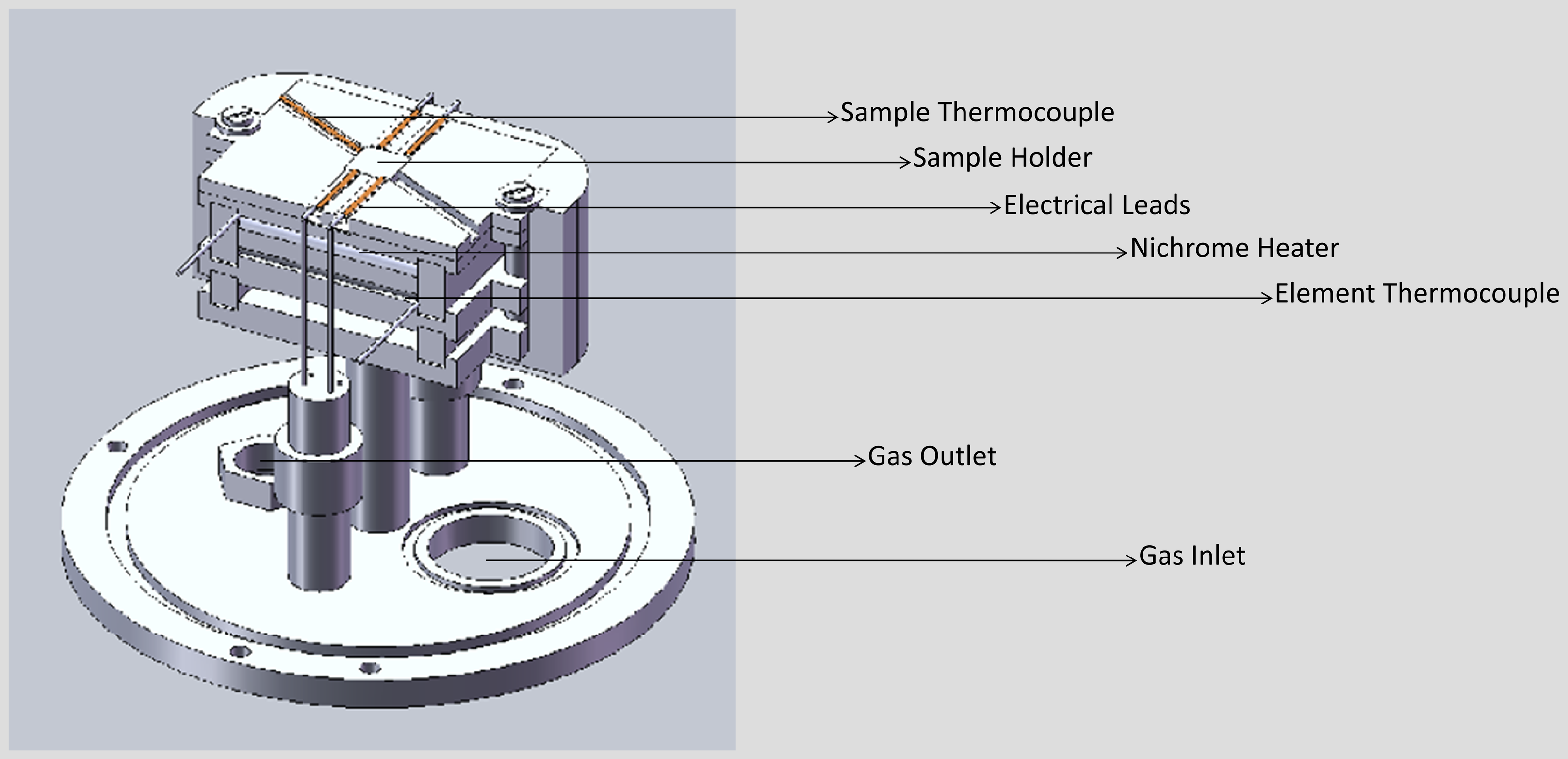
LSM on $LaAlO_3$





XRD and HRTEM analysis both reveal that the sample is heteroepitaxial. The inset [010] electron diffraction pattern clearly reveals the heteroepitaxial nature of the film. The appearance of split diffraction spots in the [001] (growth) direction, but not in the [100] direction indicates that the two lattices match up very well along the interface due to the heteroepitaxy constraints, but the film relaxes to its original lattice parameter in the growth direction due to lack of constraint.

Design and Manufacture of the In-Situ Synchrotron and Electrochemical measurement chamber

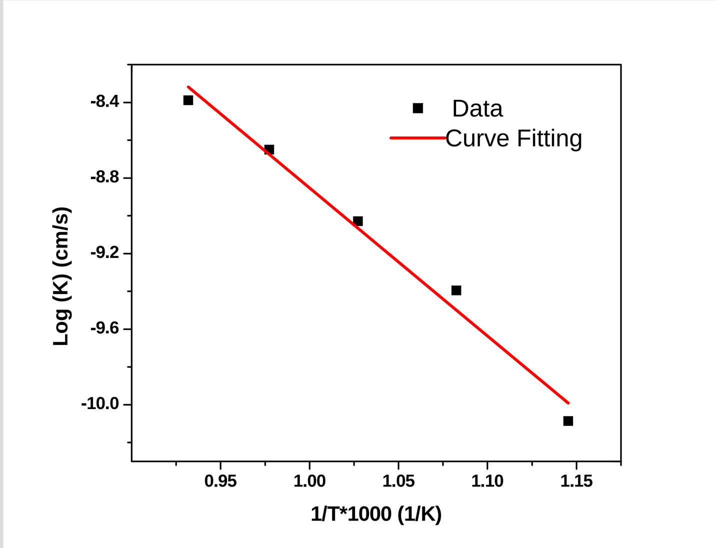


Electrochemical Performance

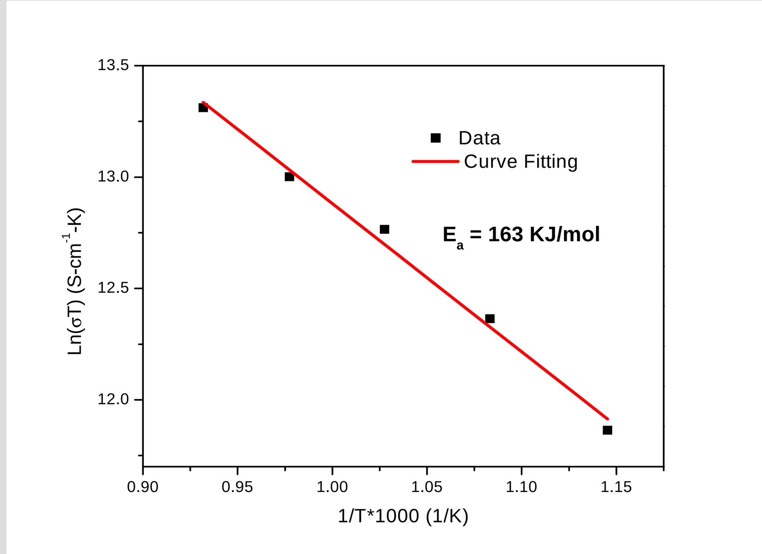
$$\frac{\sigma(t)-\sigma(0)}{\sigma(\infty)-\sigma(0)} = 1 - e^{-(t/\tau)}$$

From Which: $k(chem) = l/\tau$

$$\sigma = \left(\frac{A}{T}\right) exp\left(-\frac{E_a}{RT}\right)$$



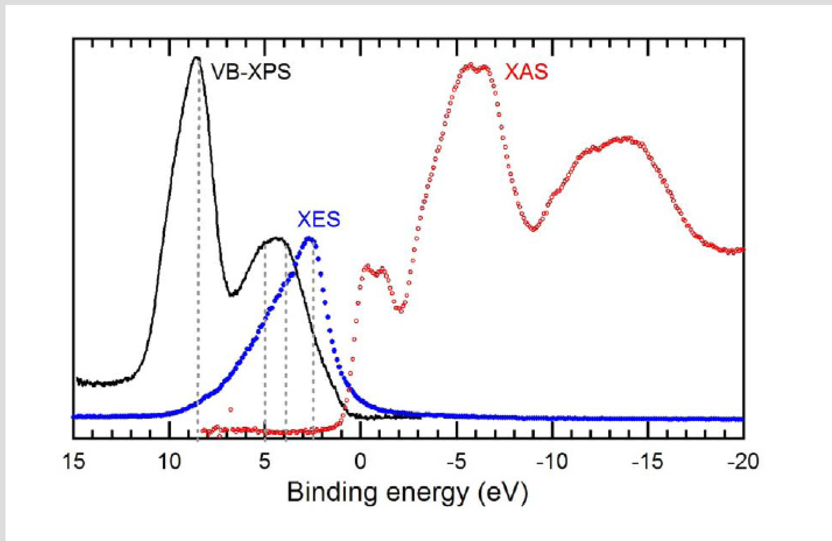
Surface exchange coefficient for 25nm LSM on LAO. Because our samples are sufficiently thin we can model the surface exchange coefficient in the above manner.



The conductivity of the samples is in good agreement with published values for LSM demonstrating the feasibility of getting quality electrochemical measurements from our thin films using the Van der Pauw arrangement.

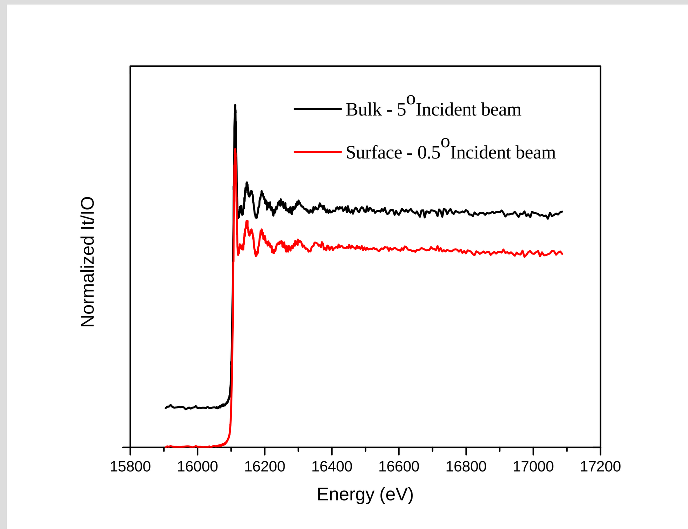
Synchrotron Results

VB-XPS of LSM on LAO (001)



The O K-edge XAS spectrum reflects the unoccupied O2p contribution to the conduction band of LSM, and is in agreement with various earlier O K-edge XAS studies of LSM with 15- 20% Sr content.

Representative EXAFS Scan of Sr K-Edge



At the NSLS surface and bulk EXAFS scans were taken at the Sr K-edge to monitor segregation from 600-725 deg C, and in different Po_2's. Additionally, as the ECR measurements were being performed we collected data from the Sr, Mn, and La K-edge energy windows to look for the in-situ effect of a step change in oxygen partial pressure.

Key Accomplishments:

•Fully developed growth conditions for heteroepitaxial growth of LSM on LAO

•Designed and built a synchrotron chamber for high temperature in-situ electrochemical and x-ray measurements.

•We used the aforementioned chamber to collect data at the National Synchrotron Light Source at Brookhaven National Lab.

Future Work:

•Grow thick films of cathode materials on YSZ substrates and study the effects of an applied bias on surface structure in-situ by combining the XAS and XPS data on very clean, heated substrates.

•Using the synchrotron and TEM characterize the two dimensional interfaces between the cathode/YSZ and cathode/gas.

•Determine the bulk and surface Mn, O, and La L-edge charge state with X-ray Absorption Spectroscopy of 800C quenched and unquenched LSM samples and obtain information on the hole concentration in surface and bulk.

•Analyze experimental results to understand and optimize SOFC cathode performance.