IV.A.4 SOFC Cathode Surface Chemistry and Optimization Studies

Prof. Paul A. Salvador (Primary Contact), Joanna Meador, Balasubramaniam Kavaipatti
Carnegie Mellon University
Department of Materials Science and Engineering
Pittsburgh, PA 15213
Phone: (412) 268-2702; Fax: (412) 268-7596
E-mail: paul7@andrew.cmu.edu

DOE Project Manager: Lane Wilson
Phone: (304) 285-1336; Fax: (304)285-4638
E-mail: Lane.Wilson@netl.doe.gov

Collaborators: Drs. Paul Fuoss, Jeff Eastman, Dillon Fong, and Peter Baldo
Argonne National Laboratory (ANL)
9700 South Cass Avenue
Argonne, IL 60439-4837
Phone: (630) 252-3289; Fax: (630) 252-9595
E-mail: fuoss@anl.gov

Objectives

- To determine the key correlations between surface features and electrochemical performance for solid oxide fuel cell (SOFC) cathodes.
- To develop and to employ a high throughput chemical screening methodology that provides a sensitive measure of activity/stability in operational conditions.
- To develop thin film samples having specific surface structures and chemistries using thin film preparation methods.
- To determine the stability of engineered surface chemistries as a function of thermodynamic parameters (temperature [T], pressure [P], ε, and electrochemical parameters).
- To determine the effects of engineered surface chemistries on oxygen uptake kinetics in thin film samples.

Accomplishments

- Epitaxial thin films of $LaMnO_3$, $SrMnO_3$, $La_{0.7}Sr_{0.3}MnO_3$ (LSM) were grown on various substrates, both with and without different surface layers and with and without epitaxial strain. These serve as the basis for providing samples to other tasks and collaborators.
- Epitaxial thin films were investigated with X-rays using the Advanced Photon Source (APS) at ANL and both the bulk structure of the films and their surface chemical compositions were determined as a function of T and P. These provide the initial understanding of the physicochemical response of LSM to various thermodynamic parameters.
- Showed that films exhibited superstructures consistent with unit cells doubled in all three dimensions (as compared to the simple perovskite) and exhibiting a complex microtwinning; the superstructure/microtwins persisted from room temperature to 700°C.
- Demonstrated that the surface of LSM films are Sr-rich and that Sr surface segregation is a function of P. Sr segregation was observed to increase with decreasing P.

Introduction

The cathode in SOFCs is responsible for the reduction of O_2 gas and its incorporation into the electrolyte. To accomplish this, most SOFCs use a three-phase composite for the active cathode region. The three phases are commonly: LSM and yttria-stabilized zirconia (YSZ) as solid phases and O_2 as a gas in pores. When SOFCs are operated at specific current densities/voltages, the oxygen incorporation (or uptake) process can contribute significantly to the losses of the cell, thereby limiting the performance of the SOFC system. Two major options exist for improving the cathode performance by specifically targeting the oxygen incorporation process: changing the component solid materials or adding yet another material (a catalyst) to the existing frameworks. We aim to address both approaches in this work by: (1) developing an experimental program that allows us to probe the nature of atomic scale surface chemistry and its role in oxygen incorporation in LSM and related cathode materials, and (2) determining the optimal catalyst chemistry from both an activity and stability perspective. Realizing these goals will lead to improved cathode performance in SOFCs and an acceleration of introduction of new materials into SOFCs to allow for the DOE Solid State Energy Conversion Alliance (SECA) program to meet performance metrics.

Generally speaking, the limitations in designing highly active cathodes for oxygen incorporation arise from the general lack of direct correlations between surface/interface chemistry/structure and performance of SOFC cathode materials. In other words, very little is quantitatively known about why specific materials/surfaces behave the way they do in SOFC operating conditions. To fill this gap, one must probe the nature of atomic scale surface chemistry or interface

crystallography in fuel cell operating conditions. In this work we aim to realize this by: (1) developing a high throughput screening methodology that will provide a sensitive measure of activity/stability in operational conditions, and (2) determining key correlations between structure (solid state atomic, electronic, crystallographic, and chemical) and electrochemical performance (mass and charge transfer) parameters in surface engineered samples. Several important collaborations have been developed to realize these goals, including that between Carnegie Mellon University (CMU) and ANL, where thin film samples developed at CMU are investigated using high-energy synchrotron X-ray techniques at the APS. This project began in May 2007 and, since it is only a few months old, we will describe in some detail the experiments that are being developed as well as initial observations. Results from detailed structural investigations carried out at CMU and ANL will be highlighted in this initial report.

Approach

A key part of an experimental program that can address the above stated goals is the development of samples that allow both for controlled changes in surface chemistry and for screening experiments to be carried out upon them. Epitaxial and textured thin films are ideal samples for these experiments. To screen for structure-performance correlations, we will produce single-crystal and textured thin film samples using pulsed laser deposition (PLD) and hybrid (laser or standard) molecular beam epitaxy (MBE) approaches to produce thin, flat films having surfaces of specific terminations. Figure 1a shows a schematic of a surface engineered thin film sample. The green inner layer represents the bulk of the thin film or, in oxygen uptake experiments, the reservoir to be filled. The red outer layer represents the surface of the thin film or, in oxygen uptake experiments, the active surface being investigated. By systematically depositing various surface (red) layers on specific bulk (green) layers, we can achieve the goals listed above - determining key correlations between surface structure and electrochemical performance. Figure 1b is a structurally-engineered sample of related composition to LSM: praseodymium strontium manganate (PSM) where the sample is separated into layers of praseodymium manganese oxide (PMO) and strontium manganese oxide (SMO) two unit cells thick [1], demonstrating that such engineering is stable for a length of time to make structural and physical property measurements. In the future, we will develop several physical property measurement techniques that monitor the kinetics of oxygen uptake for a specific reservoir layer as a function of the composition of the surface-active layer. By combining such observations with detailed structural analyses we will develop the above-described key correlations. By generating a large number of

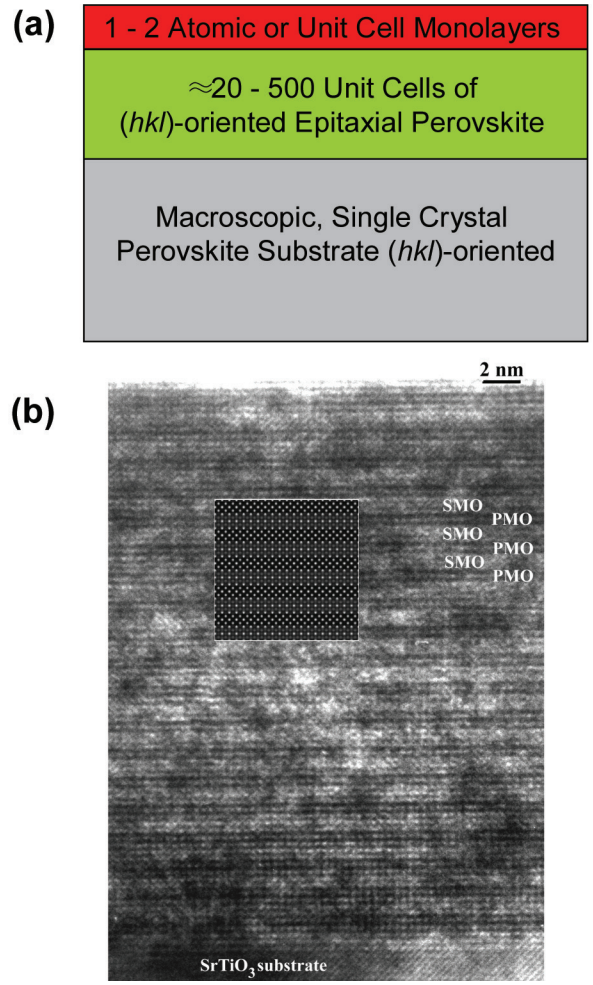

FIGURE 1. Engineered thin film samples of (a) a schematic of a surface engineered thin film cathode material, where the red layer is the surface active layer a few unit cells thick and the green layer is the bulk reservoir in which the oxygen concentration is being altered. (b) A TEM image of a PMO/SMO engineered film [1] made with PLD-MBE having spatially separated regions only two unit cells thick.

well-controlled thin film samples, we will have a high-throughput screening process that probes the identified key correlation.

To establish a baseline in understanding the bulk and surface structure of LSM, epitaxial LSM samples were grown using PLD on different single crystal perovskite substrates ($SrTiO_3$, $NdGaO_3$, YSZ, and $DyScO_3$). The films were characterized for their growth rate, surface roughness, and structural nature at CMU using X-ray techniques and atomic force microscopy (AFM). Certain representative samples were sent to ANL and were characterized at the APS using *in situ* X-ray scattering observations, while the films were exposed to various T and P environments. An environmental chamber was used that allowed for grazing incidence X-ray scattering and depth sensitive

X-ray fluorescence measurements to be made over a T range from room temperature (RT) to 700°C and a P range from 0.01 to 100 Torr. The observations made on these epitaxial films provide a basic scientific understanding for how LSM behaves and provide important structural information that will enable a better understanding to interpret physical property observations.

Results

Figure 2 shows the calibration experiments carried out at CMU that demonstrate the high quality of the films; this film is an LSM film deposited on $SrTiO_3$(100) at 700°C in 50 mTorr O_2 and cooled in 300 Torr O_2; it has a thickness of 310 Å. Figure 2a shows an AFM image of the film which has an rms roughness of 4.4 Å, or about one unit cell. This image indicates that unit-cell rough films can easily be obtained for the bulk of the film. It also implies that, by depositing two or more unit cells atop the bulk, the surface chemistry can be easily modified (as also shown in Figure 1b). It should be noted that small particulates are sometimes observed in the films, as is well known for PLD produced films. These can be removed by optimizing processing; in the future we will explore their effects on the results and remove them as necessary. Figure 2b shows the X-ray reflectivity scan and a refined fit to the scan. The excellent agreement between fit and data allows for structural parameters to be established with confidence: the thickness of this film was 310 Å and the X-ray roughness was 3.1 Å, in agreement with the AFM roughness. The growth rate was determined to be 0.115 Å/pulse, and this allows us to design specific thicknesses of the bulk-layer and surface layers in engineered thin films. Finally, Figure 2c shows the Θ-2Θ X-ray diffraction scan for this film, demonstrating that a single out-of-plane orientation exists, corresponding nominally to the expected cube-on-cube epitaxy considering both the substrate and the film are perovskites. Such observations provide the routine information that ensure films used in the high-throughput screening experiments, and other physical property measurements, are of high-quality and are similar to other samples.

It should be noted that similar results have been obtained on other substrates (high quality film growth with flat surfaces and cube-on-cube arrangements) for $LaAlO_3$, $NdGaO_3$, and $DyScO_3$. The latter two are of extreme interest because they have very high crystal qualities (much lower dislocation densities than $SrTiO_3$) and contain no similar elements to the targeted cathode materials, both of which improve our ability to understand the native surface activity of materials. Films of different thicknesses had different levels of strain states and phi scans are also routinely carried out to quantify the strain state of the films. Nevertheless, it is challenging to obtain a full X-ray data set that allows for the determination of the detailed structure of our films using this type of X-ray source.

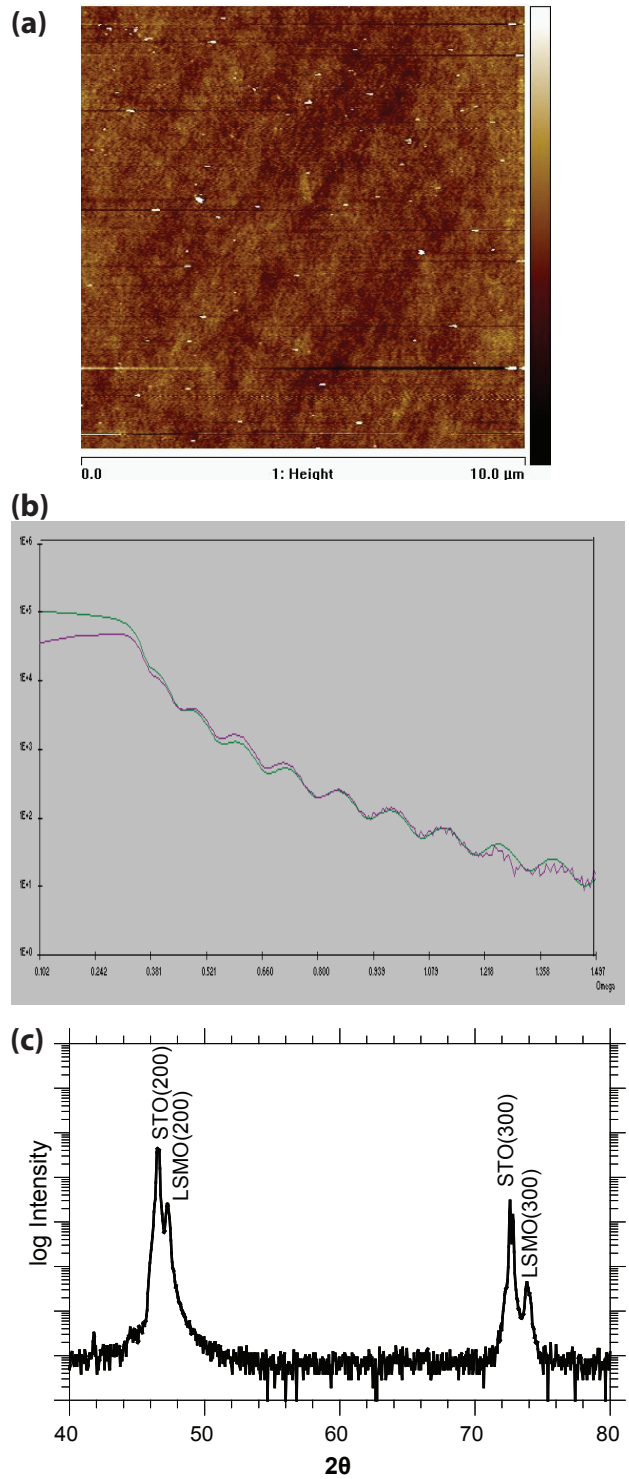

FIGURE 2. Standard calibration measurements of LSM films on $SrTiO_3$(100). (a) An AFM scan, (b) an X-ray reflectivity scan, and (c) a Θ=2Θ X-ray scan.

As a starting point for understanding the structures of surface engineered thin film samples, we explored

the nature of the bulk crystallography and surface chemistry of pure LSM single crystal epitaxial films with thicknesses of 5 to 75 nm grown by PLD on $SrTiO_3$ (001) substrates using X-ray scattering at the APS. Two important observations have been made that are relevant to our goals. First, a stable structural distortion (with respect to the basic perovskite sub-cell) was observed in the epitaxial films that was not observed in bulk powders and, second, Sr-segregation to the film surface was observed, and it was dependent on P. The former observation is of interest in determining the structural behavior of bulk layers in different thermodynamic conditions (T, P, ε) which represent the reservoir to be filled with O_2 during oxygen incorporation experiments. For epitaxial films, the strain state can be further engineered, which allows us to explore this parameter in a systematic fashion. LSM grains in active cathodes experience a range of thermal stresses and may have significant local strains. The latter observation is of interest since it implies that even pure LSM films have some spatial inhomogeneities similar to that shown in Figure 1a. In other words, the surface-active layer in LSM is of a different chemistry than the bulk of the film, and this is a function of P.

Half-order Bragg reflections (*e.g.*, 3/2, 1/2, 1/2), were observed that indicate the unit cell periodicity is double that of the normal unit cell in all three dimensions. We have also found evidence of satellites to the half-order peaks indicating another periodic long-ranged structural modulations in LSM thin films. Figure 3 shows the intensity of one such half-order peak (3/2 -1/2 1/2) as a function of temperature during cooling; satellites are also observed adjacent to these half-order peaks. Both the satellites and the half-order peak intensify as room temperature is approached. While we have not yet fully determined the atomic structure associated with these features, the unit cell doubling is consistent with an antiferrodistortive orbital ordering (albeit at much higher temperatures than typically observed in LSM) and the satellites are consistent with microtwinning (albeit exhibiting a slightly more complex domain pattern than previously reported). Figures 3b and 3c demonstrate that the symmetry of satellite distributions varies for different 1/2-order peaks, indicating a three-dimensionally-complex domain structure to the microtwins.

We also observe Sr segregation to the surface of these epitaxial single crystal LSM (001)-oriented films. Moreover, surface segregation increases with decreasing oxygen partial pressure. The near surface chemical signatures are shown in Figure 4 and one can observe that while the Sr signal increases on decreasing P, the La and Mn signals decrease. Interestingly, the structural modulations described above persist after this rearrangement takes place, implying that the surface crystal structure remains the same on changing P but that the surface chemistry does not. This type of P-dependant segregation is important to understanding both surface activity and surface stability in cathodes, both of which are essential in obtaining highly active and stable cathode materials. In the future we will correlate the surface chemistry to activity using our engineered thin film samples and explore their stabilities using the APS and other techniques, such as Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS).

Conclusions and Future Directions

We have demonstrated that surface engineered films of cathode materials can be produced and characterized in detail for the structural and chemical properties. Even for pure epitaxial LSM films, surface segregation occurs that is a strong function of the thermodynamic variables, although the crystal structure does not appear to be strongly perturbed. As this project only began in

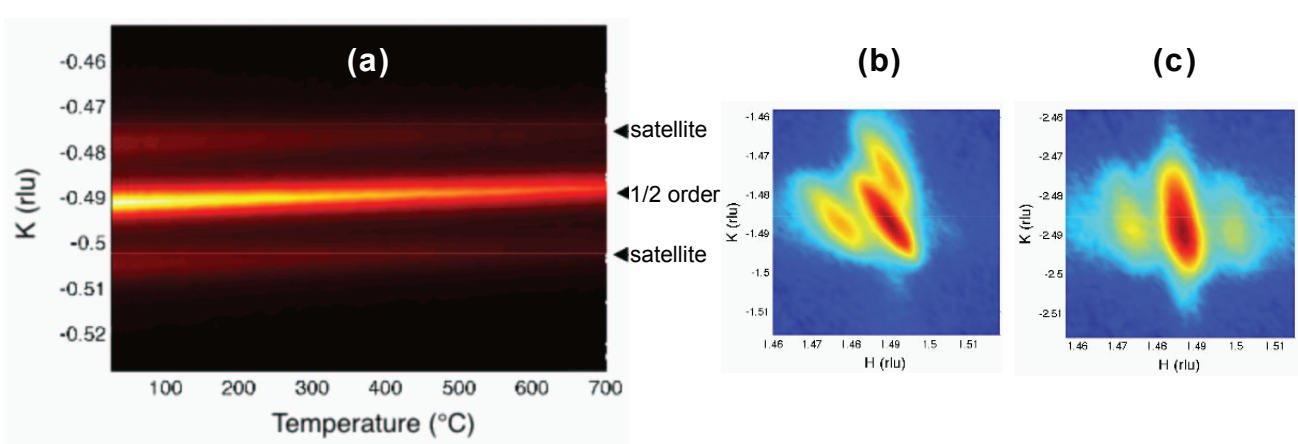

FIGURE 3. X-ray scattering data of a 5.8 nm thick LSM film grown epitaxially on $SrTiO_3$(001). (a) Temperature dependence of the 3/2 -1/2 1/2 peak and satellites. (b) and (c) In-plane reciprocal space maps centered on the 3/2 -3/2 1/2 and 3/2 -5/2 3/2 peaks.

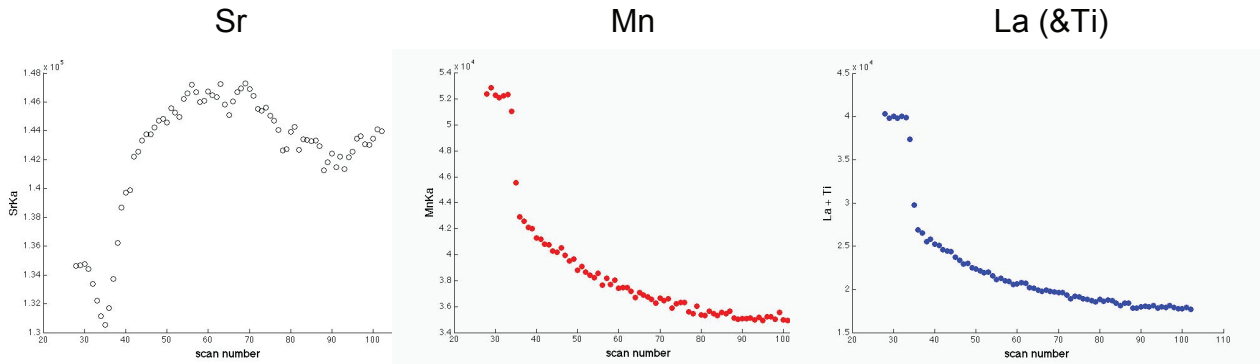

FIGURE 4. Chemical signatures using X-ray fluorescence of the near surface region on changing pO_2 from 100 Torr to 0.01 Torr. The count number is related to time. The kinetics are likely associated with the time to equilibrate the atmosphere, which was changed near count ≈30.

May 2007, significant portions of the goals remain to be realized. We will produce a series of surface engineered films and will investigate: (1) their structural properties, (2) their stabilities, (3) their oxygen uptake kinetics using specially designed crystal microbalances and electronic conductivity rigs, and (4) will investigate how electrochemical parameters affect segregation/activity. By fabricating a matrix of related materials and carrying out these measurements, we will be able to provide a large amount of data to determine the key parameters that correlate surface structure to surface activity.

Reference

1. B. Mercey *et al.*, *Journal of Applied Physics*, 94(4), 2716-2724 (2003).