III.A.7 Local Electronic Structure and Surface Chemistry of SOFC Cathodes

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Objectives

- Determine the key correlations between the stable structural and electronic bonding properties at $La_{1-x}Sr_xMnO_3$ (LSM) and $La_{1-x}Sr_xCoO_3$ (LSC) thin film cathode surfaces, in the presence of inhomogeneities such as grain boundaries, segregate particles and crystallographic domains.
- Examine the role of strain state in the cathode film introduced by the substrate and film thickness, and use this information to design favorable cell geometries.
- Link the spatially resolved local surface electronic behavior and topological inhomogeneities measured with scanning tunneling microscopy and spectroscopy (STM, STS) at ambient conditions and at high temperature to the electrochemical behavior.
- Identify and explain the differences in the electronic transport characteristics between LSM and LSC.
- Correlate the structure and chemical state with those determined by synchrotron X-ray measurements at Argonne National Laboratory (ANL) and provide the needed understanding of *in situ*-ex situ correlations.
- Utilize the results on prototype cathode structures to propose favorable cathode structures with high efficiency and stability at intermediate temperatures.

Accomplishments

- Probed the surfaces of the initial set of LSM and LSC dense cathode films grown on 0.7%Nb-$SrTiO_3$ (0.7Nb-STO) and Y_2O_3 stabilized ZrO_2 (YSZ) substrates at three different thicknesses before and after electrochemical treatment, using STM and identified their current-voltage (I-V) characteristics.
- Characterized the electrochemical features of the LSM and LSC cathode films grown on YSZ single crystal substrates at three different thickness. Found out that surface reactions were the rate-limiting transport process in nearly all cathode films.
- Identified the Mn-enrichment and La-depletion on the surface of the 100 nm-LSM cathode films on 0.7Nb-STO using Auger electron spectroscopy (AES) with depth profiling. Such segregation behavior is contrary to the La- and Sr-segregation on LSM on YSZ, and is likely to impact the surface electronic properties and the electrochemical activity of the cathode films.
- Using the STM, found that fine segregate particles of few-nm size exist on the surfaces of the 100 nm-LSM film, and a clear re-texturing of the cathode films takes place upon high temperature electrochemical treatment.

Introduction

Lowering the operation temperature of the solid oxide fuel cell (SOFC) systems without sacrifice from electrochemical activity is important for maximizing the long-term stability and performance. The surface structure has a major role on the electrocatalytic activity and stability of the cathodes. For this purpose, at MIT, we are investigating the correlations of the crystallographic structure and strain to the electronic structure, defect chemistry, and electronic and ionic transport characteristics of SOFC cathode surfaces. The presence and understanding of the activity at the inhomogenities on the surfaces, namely grain boundaries and surface segregates [1,2], is especially important for our research. The effectiveness of these surface inhomogeneties is essential for the design of infiltrated cathodes, where both the solid-gas and solid-solid interfaces play an important role for cathode activity and stability. The information gathered from our characterization work will serve to demonstrate the prototype of favorable structures to promote higher activity in oxygen electrocatalysis on SOFC cathodes.

Approach

We employ STM and STS in our research as an analytical agent to probe the localized topological and electronic properties at the nanoscale confined features and inhomogeneities on the cathode surfaces. The

STM/STS analysis has two phases of characterization: 1) at room temperature and ambient pressure at MIT, and 2) at high temperature and ultra-high vacuum (UHV) and non-UHV conditions at the Center for Nanoscale Systems (CNS) at Harvard University. We correlate the surface structure and electronic properties found by STM/STS to electrocatalytic activity using electrochemical characterization in a high-temperature furnace set-up. Our prototype structures include the epitaxial single crystal and textured polycrystalline dense thin-films in the presence of nano-scale grain boundaries. The samples consisted of three different thicknesses, 200 nm, 50 nm and 10 nm for LSM and LSC, on YSZ and 0.7Nb-STO substrates, and were provided by Carnegie Mellon University.

Results

For the first stage of our investigation at MIT, we carried out STM/STS analysis on epitaxial (100) LSM films grown on 0.7Nb-STO and YSZ. The morphologies we retrieved from our analysis are shown in Figure 1. A retexturing of the film in the form of small rectangular islands has occurred after electrochemical treatment at 300 mA/cm^2 and 800°C (Figure 1a-b). The reason for the restructuring can be related to the preferential stabilization of an in-plane crystallographic epitaxy domain that LSM and LSC can form on the YSZ upon electrochemical treatment. Furthermore, using the UHV-STM at CNS, we found that fine segregate particles of few-nm size exist on the surfaces of the 100 nm-LSM film (Figure 1-c).

Following the surface topography scans, we calculated the tunneling conductances at small bias near the Fermi level using the I-V measurements on different regions of the surface on each sample. The I-V behavior of the samples are not yet correlated to the specific sites or surface features in these experiments. Figure 2 presents a summary of the characteristic Fermi level tunneling conductance data from the surfaces of LSM films on 0.7Nb-STO compiled in the form of histograms. The Fermi level conductances of the sample surfaces exhibited a clear trend with varying thickness. The comparison of the three histograms clearly indicate that the 10 and 50 nm samples have low near-Fermi level tunneling conductances compared to the 100 nm sample, while the 100 nm sample displays a large spread in the number of sites with dI/dV greater than zero. Given these results, we expect that the 100 nm thick sample have more available electronic states to exchange electrons with oxygen in the vicinity of the surface, and thus higher activity. Non-zero tunneling conductances on the 100 nm-LSM film could also indicate a relatively high density of free carriers that depend on defect density, deviation from exact stoichiometry, and the local and overall strain states at a given temperature. Furthermore, the band-gap values found from the I-V

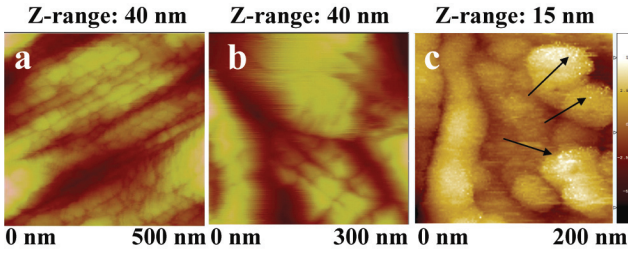

FIGURE 1. The surface topography scans of (a) 200 nm thick LSC (b) 200 nm thick LSM after electrochemical treatment at 800°C, and (c) 200 nm LSM after ½ hour annealing at 500ºC. We acquired the scan in (c) at CNS of Harvard using the Omicron VT-STM under UHV conditions. The segregated speckles on some of the grains are shown with arrows.

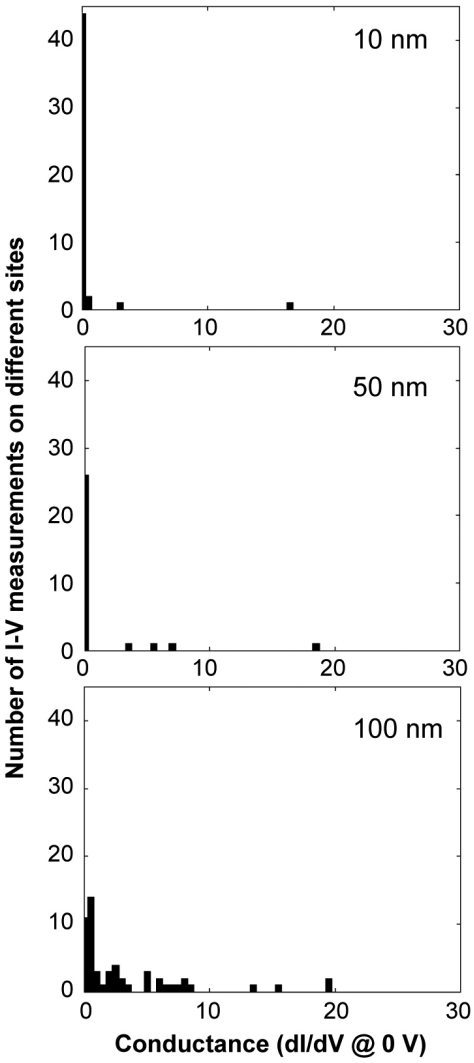

FIGURE 2. The Fermi level conductance histograms compiled from various measurements at ambient conditions on different sites on the 10 nm, 50 nm and 100 nm thick LSM films grown on (100) 0.7% Nb-SrTiO$_3$.

measurements using STS for the 10 nm and 50 nm LSM films ranged as 1.5-2.2 V.

We performed electrochemical impedance spectroscopy (EIS) measurements to characterize the dynamic bulk electrochemical response of the LSM and LSC electrodes and to correlate the STM/STS results to electrocatalytic activity of the cathode films. There were three main observations we made in our EIS work thus far:

- We found activation energies of 1.8 eV to 2.2 eV that imply the surface reactions [3,4] being the rate-limiting process on almost all LSM films except from the 100 nm-thick LSM at the low temperature range (Figure 3a). This result is consistent with our STS characterization that revealed higher tunneling conductance on the surface of the 100 nm-LSM as shown in Figure 2.
- We observed orders of magnitude of difference between the total impedance of the LSM and LSC dense thin-film cathodes (Figure 3b).
- All samples, except from the 100 nm LSM at lower temperature range, had the surface reactions as the rate-limiting processes as there was no clear indication that the film thickness was impacting total impedance results.

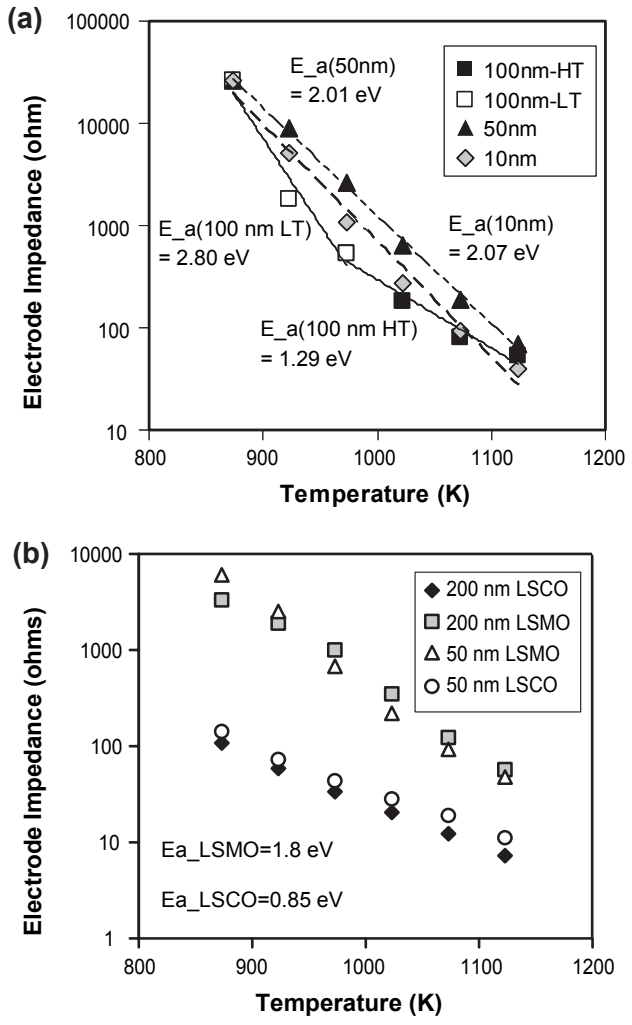

FIGURE 3. (a) The activation energy, in eV, for total impedance (Z_tot) – low-frequency intercept on the real axis (see highlighted). The data of the 100 nm thick sample were fitted both for a low temperature range and a high temperature range as it exhibits a distinct slope change around 700°C that might be an indication of change in the type of the limiting-process. HT stands for the High-Temperature Range, LT stands for Low Temperature Range. (b) Resistance vs. temperature plots of the 50 nm thick LSM and LSC, 200 nm thick LSM and LSC (resistance is given in logarithmic scale).

Complementary with the structural, electronic, and electrochemical characterization is the surface chemical analysis. At MIT, we carried out our first preliminary AES on the 100 nm thick LSM on a 0.7 %Nb-STO substrate. The analysis consisted of depth profiling of the La, Sr, Mn and O elements using a 3 keV incident electron beam (Figure 4). Presently, the AES results are not fully quantitative. However, it is clear that there is an enrichment of Mn (B-site). The *La* (A-site main cation) signal gets stronger with depth, implying a depletion of this element near the surface. In this preliminary analysis, we cannot conclude whether Sr is enriched or depleted near the surface because the 1.6 keV electrons can penetrate from the subsurface region, too. Such segregation behavior is contrary to the A-site segregation on the surface of LSM on YSZ substrate, and is likely to impact the surface electronic properties and the electrochemical activity of the cathode.

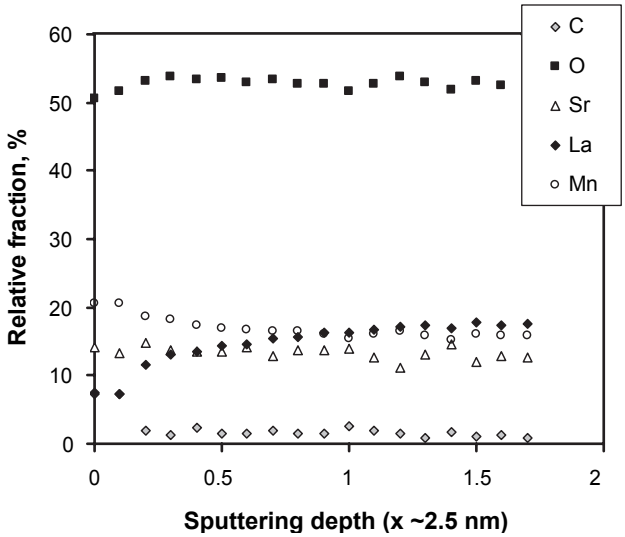

FIGURE 4. Near-surface depth profile of the 100 nm thick LSM composition using Auger Electron Spectroscopy. The analysis was terminated when the relative change in concentrations reached a constant ratio. The predicted sputtered depth corresponds to approx. 5 nm. (Source of carbon is the overall carbon-contamination of surface of the films due to prior handling of films.)

Conclusions and Future Directions

- Electronic and topological characterizations show that thinner LSM films (10-50 nm thick) have lower near-Fermi level conductance on their surface than 100 nm samples. Consistently with this result, EIS measurements indicate that the diffusion of oxide ions dominates the electrode impedance for the 100 nm film while resistive surface processes dominate for the thinner electrodes.
- We identified the LSC films grown on YSZ to be much more active than the LSM films on YSZ. We will compare the electronic behavior of the surfaces of the LSC and LSM electrodes using the STM/STS.
- AES and STM results imply that surface enrichment of A-site or B-site elements in fine segregate particles is possible and can impact the surface electronic states of the cathode film. We will identify the origin and consequences of these surface segregates and whether they form during growth, annealing or electrochemical conditions will be sought.
- We will evaluate the ex situ AES and STM data in the light of the synchrotron X-ray measurements by the ANL group at the Advanced Photon Source to provide and understanding of *in situ*-ex situ correlations.
- We will expand our STM/STS analysis from ambient conditions to high temperature (up to 1,000 K) under UHV and non-UHV (mild-UHV) conditions using the Omicron VT STM at the National Science Foundation facility of Center for Nanoscale Systems.

FY 2008 Publications/Presentations

1. Progress Report to ANL as of January 2008.

2. Progress Report to ANL as of March 2008.

3. Quarterly Report to SECA for the second calendar quarter, April 25 2008.

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