

## IN SITU X-RAY AND ELECTROCHEMICAL STUDIES OF SOLID OXIDE FUEL CELL / ELECTROLYZER OXYGEN ELECTRODES

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### ABSTRACT

The governing reaction mechanisms, and the electrode material compositions and structures, that controls the efficiency of the solid oxide fuel cells (SOFC) and solid oxide electrolysis cells (SOEC) need to be identified and well-understood for significant technological improvements. Our study on the oxygen electrodes focuses on specifically the effect of electrode crystal structure and morphology on its electrochemical performance, and the evolution of the electronic and structural properties of the electrodes while under electrochemical conditions and high temperature. We found through electrochemical impedance spectroscopy experiments that the different crystal orientations in a given oxygen electrode material, for example  $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_{3+d}$  (LSM), can show different initial performance, dissimilar processes governing the oxygen reaction mechanism, and different electrochemical activation behavior under DC bias at a given temperature in air. Our *in-situ* x-ray and electrochemical measurements at the Advanced Photon Source have identified the chemical states of the main components of the doped lanthanum manganite electrodes. We found that the bias and time dependent changes in the concentration and in the electronic state of the La (the A-site element of the perovskite) occurring only at the top air-electrode film interface can be responsible from the electrochemical improvement of the electrode under DC current. Our observation related to the La chemical state change is unexpected and probably unique to the electrochemical current-conditioning of the oxygen electrodes.

### INTRODUCTION

Uncertainties in our understanding of the oxygen reaction (OR) mechanism at solid oxide electrolysis and fuel cell electrodes still remain due to the complexity of the OR mechanism under steady-state conditions and to the influence of processing and operating conditions and the polarization history of the electrode. Numerous studies have shown that cathodic or anodic dc polarization of the solid oxide cell oxygen electrodes results in a long-term or permanent enhancement of the oxygen reduction and evolution rate, and that this enhancement can remain even when returning to lower electrode polarization. This phenomenon has been termed current-conditioning or activation of the electrode. An understanding of the causes of this phenomenon can lead to better comprehension of the OR kinetics, and thus, to ways to improve its performance. In addition, the non-stationary improvement due to the activation of the electrode can provide new metrics to assess the cell performance instead of comparing only the initial stationary cell performance. Determination of the relationship between the structure and chemical composition of the oxygen electrode and oxygen electrode/electrolyte interface under dc polarization can provide information for the rational design of electrodes with improved

performance. The effect of the electrode crystal structure on the oxygen reaction kinetics of SOECs and SOFCs has not been fully investigated previously and remains an unknown, although it can significantly influence the electrochemical activity of the electrode.

Current-conditioning has been observed for several oxygen electrode materials, including platinum, lanthanum strontium manganite (LSM), lanthanum strontium manganite/yttria-stabilized zirconia composite, and lanthanum strontium iron cobaltite. Several theories have been postulated in the literature to explain the reaction rate enhancement upon dc polarization of the oxygen electrodes; however, a general and clear explanation of this phenomenon has not yet been achieved. The suggested underlying mechanism and the resulting magnitude of improvement upon activation vary significantly, even for the widely-studied electrode material LSM. Some of the theories proposed to explain the origin of the current-conditioning of LSM electrodes are reduction of the transition metal, Mn, to form oxygen ion vacancies in the perovskite lattice [1]-[3], removal of phases that block oxygen adsorption on the electrode surface [4][5], increase of electrode active surface or interfacial area due to roughening [6], formation of secondary phases at the electrode-electrolyte interface [7], and movement of charged species at the interfaces, such as cation diffusion [8].

All of the theories proposed for the electrode activation were based on ex situ electron or atomic force microscopy or ex situ x-ray photoelectron spectroscopy, which have limited usefulness for characterizing buried material. Thus, to obtain information on the electrode-electrolyte interface or on material buried under the surface of the electrode, the cell must be removed from its operating atmosphere and cross-sectioned. On the other hand, in situ x-ray studies of the SOEC and SOFC electrodes can allow determining the governing chemical, compositional and structural processes at a fundamental level. Synchrotron-based hard x-ray techniques enable in situ investigation of buried material, because absorptive interactions with high energy x-rays are weak enough to permit deep penetration into most materials yet strong enough to deliver surface- or interface- sensitive information. This unique penetrability/interaction allows examination of the critical interfaces under realistic operating conditions (i.e., at high temperatures and in air).

In this work, we are reporting the electrochemical and *in situ* x-ray reflectivity and spectroscopy analysis of the electrode bulk, electrode-air interface, and the near-interface regions under realistic operating conditions of the cells. Model dense, thin-film doped-lanthanum manganite electrodes fabricated by pulsed laser deposition on single crystal polished yttria-stabilized zirconia (YSZ) electrolyte were used for our analysis. Electrode overpotentials of 0.3-1V under anodic and cathodic polarization were applied to achieve the electrochemical activation. We are combining the in situ x-ray measurements, taken during polarization in an air atmosphere at temperatures ranging from 700 to 800°C, with simultaneous electrochemical impedance spectroscopic measurements to determine the sources of oxygen electrode activation. To the best of the authors' knowledge, this study is the first in situ x-ray and electrochemical analysis of the solid oxide cell electrodes; though prior in situ studies on low temperature fuel cell cathodes have been conducted (e.g. [9],[10]).

## EXPERIMENTAL APPROACH

*Sample preparation:* Dense thin-film  $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_{3+\delta}$  (LSM) and  $\text{La}_{0.8}\text{Ca}_{0.2}\text{MnO}_{3+\delta}$  (LCM) deposited on polished single crystal YSZ with (100) orientation were used as model electrodes in our study. In order to identify the favorable crystal structure for enhanced surface exchange and bulk diffusion of oxygen at the SOFC and SOEC oxygen electrodes, we have

fabricated model dense, thin-film perovskite oxygen electrodes on single crystal YSZ electrolyte substrates. Dense oxygen electrodes allow precise control of the surface, interface, and geometric properties, which allow one to probe the electrode and electrolyte surfaces using x-ray techniques which are discussed in later sections of this report. The YSZ substrates were single crystals cut at the (100) plane and polished to 0.5nm roughness. The use of polished single crystal substrates enhanced the x-ray reflectivity of the substrates which enabled x-ray measurements of the LSM films at grazing incident angles allowing sensitivity to the LSM-air interface. It also allows deposition of crystallographically oriented films with respect to the substrate. The thin-film model electrodes were deposited on the YSZ substrates using pulsed laser deposition (PLD) technique at a substrate temperature of 700-780°C, and were patterned to have a reference electrode for ex situ measurements in a 3-electrode configuration. The electrodes deposited at 780°C were epitaxial with (110) out-of-plane orientation. The dense film electrodes were 20-500nm thick. Porous Pt was painted and sintered on the back side of the electrolyte as a counter electrode.

*Electrochemical measurements:* Electrochemical impedance spectroscopy (EIS), cyclic-voltammetry and potentiostatic measurements were performed using a Solartron 1255 frequency response analyzer and a Princeton Applied Research 273A potentiostat. The Pt electrical contacts were attached to the surface of the electrode on the sides and in the middle, parallel to the incoming x-ray beam in order to not obstruct the beam pathway. A 50µm-diameter fine Pt wire was attached to the middle of the dense thin-film electrode in order to ensure the electrical activation of the film at its middle region, where the x-ray beam is incident on the electrode. A schematic drawing of the *in situ* electrochemical cell is shown in Figure 1. The electrode / electrolyte samples were attached to an alumina support tube for mounting on the six-circle goniometer at the APS. The electrochemical measurements were performed in air at 700-800°C. The *in situ* electrochemical cell was heated using a parabolic infrared heater with openings drilled in the heater housing to allow access of the incoming x-rays to the sample and exit of the reflected and fluorescent x-rays.

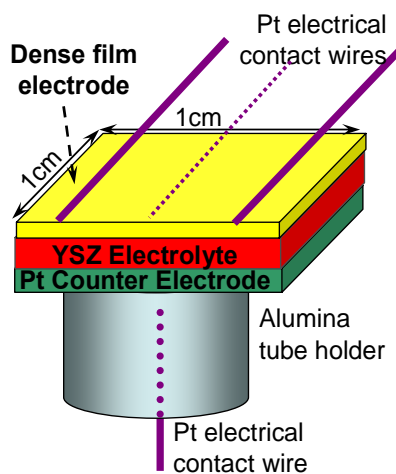


Figure 1: *In situ* electrochemical cell schematics. (Drawing not to scale.)

*X-ray reflectivity and spectroscopy:* X-ray reflectivity and x-ray fluorescence techniques were used to examine the electrochemical cell during polarization in an air atmosphere at high temperatures. The x-ray experiments were performed at Argonne National Laboratory's Advanced Photon Source (APS), which provide highly-focused and highly-brilliant hard x-rays.

X-ray reflectivity and fluorescence analysis were used for studying the structure, oxidation state, and the electron density profile of the material at the air-cathode interface, and in the bulk of the electrode. X-ray reflectivity is the ideal technique with which to study and monitor the electrode interfaces and the near-interface region. Like visible light, a beam of x-rays follows the Fresnel law of reflectivity, refracting at the interface between materials with different indices of refraction. At or near the critical angle of total external reflection, the x-ray electric field decays rapidly inside the substrate (the electrolyte in our case) and gets strongly enhanced outside of the substrate due to the constructive interference between the incoming and reflected beams. This enhancement property allows us to measure fluorescence arising from the material (e.g., Mn, Co, La or Ni) mainly at interface of interest, but also into the electrode. Low incident angles in specular reflectivity geometry allow us to perform measurements sensitive to the bulk of the thin-film materials of our experiments. When the grazing incidence angle lower than the critical angle for a given thin-film material is used, the measurements are sensitive to approximately 1nm material at the air-electrode interface. The reflectivity measurements and the x-ray absorption spectroscopy in fluorescence mode used in our experiments are depicted in Figure 2.

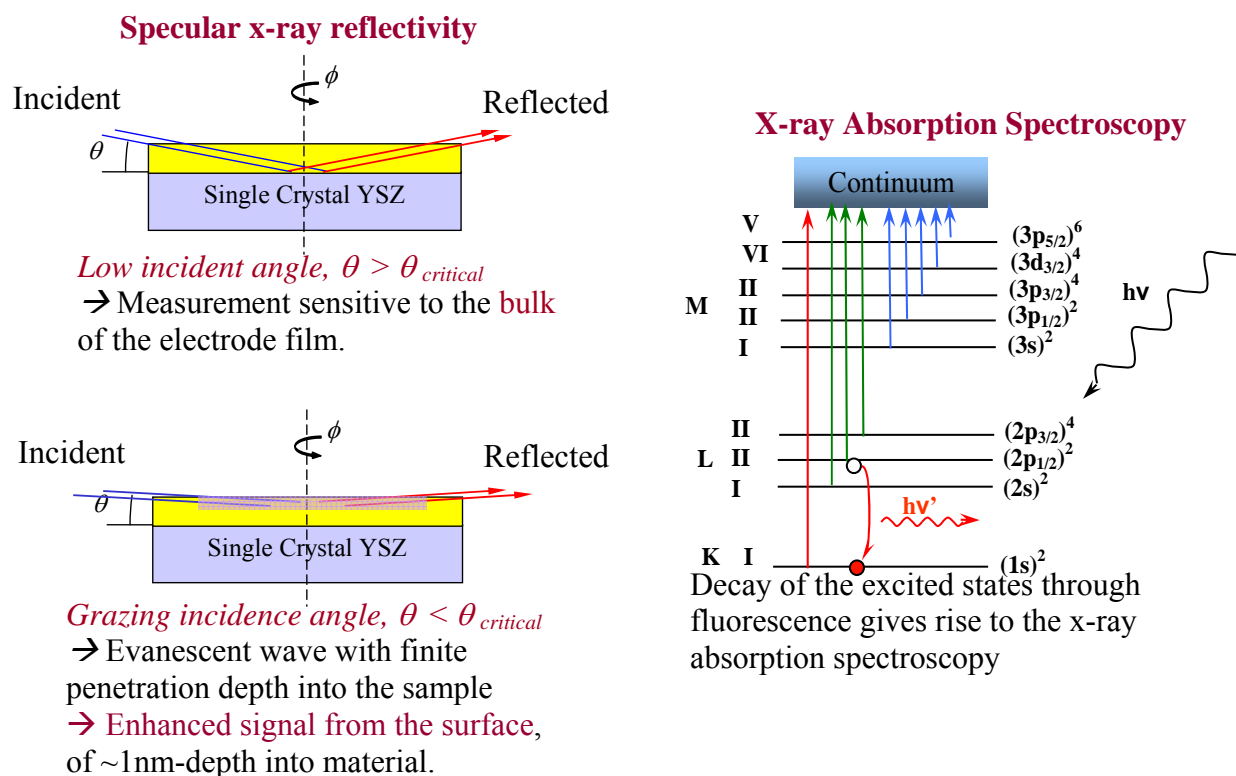


Figure 2: Schematics of grazing incidence angle X-ray reflectivity and x-ray absorption spectroscopy

X-ray reflectivity and x-ray absorption near edge spectrum (XANES) measurements of the cathode material components at its bulk and surface using the *in situ* electrochemical cell were performed at the Materials Research Collaborative Access Team (MR-CAT) insertion device beam-line at the APS. The *in situ* electrochemical setup and the incident x-ray beam path are shown in Figure 3.

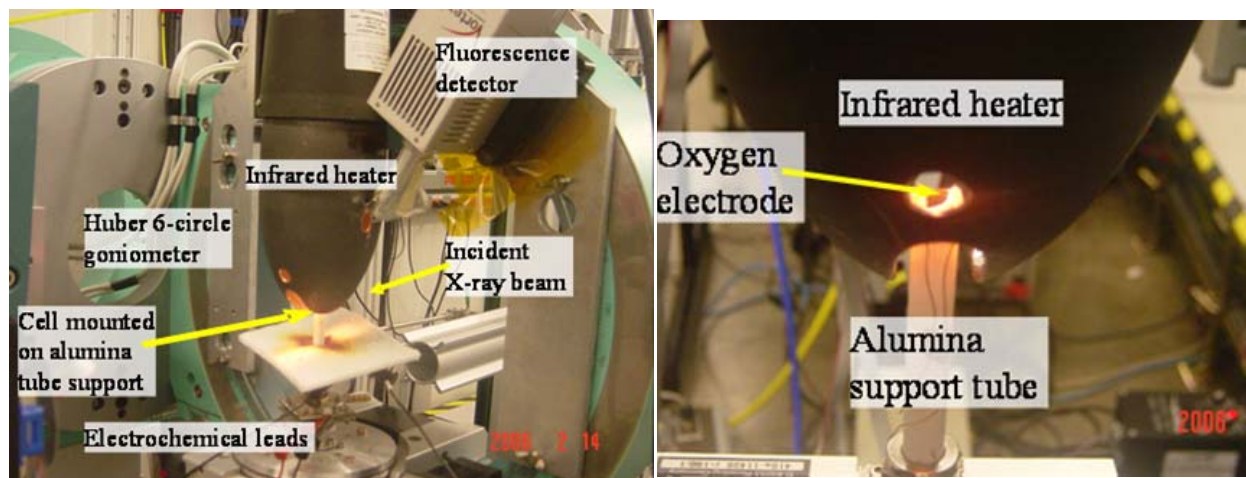


Figure 3: The in situ electrochemical cell set-up at MR-CAT beam-line of the APS, for x-ray reflectivity and x-ray fluorescence analysis of the SOFC oxygen electrodes.

## RESULTS AND DISCUSSION

### Effect of Crystal Structure on Electrochemical Impedance

The total electrochemical impedance (in terms of area specific resistance, ASR) of 100nm-thick epitaxial dense thin-film  $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_{3+d}$  (LSM) and 100nm-thick non-epitaxial LSM on single crystal YSZ (100) electrolyte under 10mV DC anodic bias is shown in Figure 4. The thick YSZ electrolyte contributes partially to the measured ASR. We find that the performance of the two structures are comparable at and above 800°C, while the non-epitaxial film shows better activity for the oxygen evolution reaction below 800°C. This indicates that the surface exchange and bulk diffusion properties of the two different structures of LSM are clearly different. A specific crystal structure present in the non-epitaxial LSM makes this electrode more active as an oxygen electrode especially at lower temperatures. The dissimilar dependence of total impedance on temperature for the two cases also implies that different processes (with dissimilar activation energies of 1.24eV for the No-Epitaxy and 2.04eV for the Epitaxial (110)) are controlling the oxygen evolution kinetics at LSM as an SOEC anode. In addition, we find that the performance of these two different LSM structures vary differently when subject to representative SOEC anodic current densities, as shown in Figure 5. The electrochemical activation of the non-epitaxial LSM electrode is significantly stronger than the (110) oriented LSM film electrode, yielding a more efficient electrode structure.

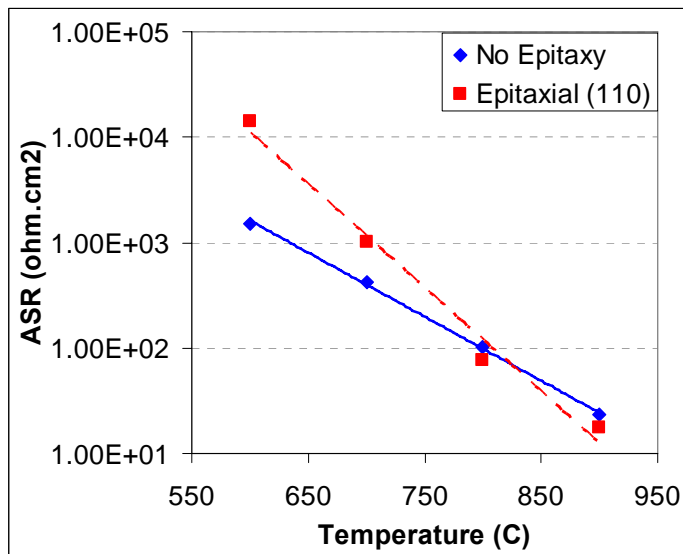


Figure 4: Total impedance of the epitaxial (110) and non-epitaxial dense thin-film LSM electrodes on single crystal YSZ (100) electrolyte, in three-electrode configuration, measured with 10mV DC bias and 10mV AC amplitude in air, as a function of temperature.

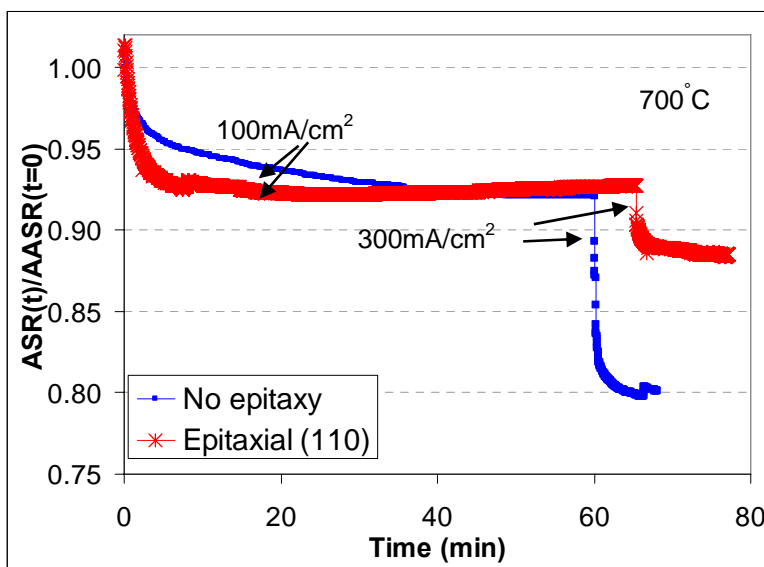


Figure 5: Relative reduction in total impedance, with time at two current densities, of the epitaxial (110) and non-epitaxial dense thin-film LSM electrodes on single crystal YSZ (100) electrolyte in air at 700°C.

In order to fully identify and utilize the crystal structure in the non-epitaxial electrode film, we will expand our analysis to several different film orientations (other than (110)) in the manganite electrode, and in cobaltite electrodes. Due to small effective surface area of our model electrodes as compared to realistic electrodes, the electrode impedance in these experiments is large, as shown in Figure 4. However, once identified, the more active structure can be incorporated into novel electrode morphologies with high effective surface area for

attaining much enhanced performance for the oxygen evolution reaction in SOECs, especially with reduced temperature operation.

In situ x-ray studies of the dense thin-film  $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_{3+\delta}$  (LSM) and  $\text{La}_{0.8}\text{Ca}_{0.2}\text{MnO}_{3+\delta}$  (LCM) Electrodes

Dense thin-film doped-lanthanum manganite model electrodes were analyzed in reflectivity geometry in order to enhance the sensitivity of the x-ray measurements to the surface and bulk of the electrode material. Similar to porous realistic LSM electrodes, electrochemical activation during the cathodic and anodic dc polarization yielded significant improvement of the electrode performance. Therefore, we expect that the same phenomena can govern the electrochemical activation of both the porous electrodes and the idealized model dense thin-film electrodes. In fact, the dense film electrode can be viewed as representing a large-aspect ratio particle in the porous electrode. Figure 6 presents the typical electrochemical impedance spectra for the dense model electrodes. The EIS data is for a 150nm-thick LCM electrode on single crystal YSZ electrolyte tested in the *ex situ* set-up before and after current-conditioning at -0.8V for 15 minutes. A high-frequency intercept that is influenced by current-conditioning only to a small extent, a low-frequency region main impedance arc that is significantly reduced in magnitude during current-conditioning, and multiple overlapping impedance arcs in intermediate-frequency regions after current-conditioning are observed. The intermediate-frequency impedance arc(s) relax back very slowly after the dc polarization is removed. In accordance with literature [12], this medium to low frequency region of the electrochemical impedance spectrum can be attributed to the oxide ion diffusion on the surface or the bulk of the LSM electrode and/or the surface exchange and reduction of oxygen on LSM. The transient activation of the electrode represented as the decrease in the total impedance was shown in Figure 5 for 700°C. The x-ray measurements presented here are in accordance with the time dependence of electrochemical activation of the electrodes shown in Figure 5.

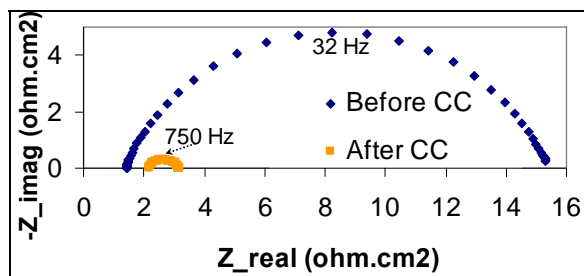


Figure 6: EIS at open circuit potential before and at the end of C.C. at -0.8V, 800°C for 15min for the 150nm-thick dense LCM electrode.

X-ray reflectivity and x-ray fluorescence measurements were performed on the dense thin-film model electrodes under *in situ* conditions, i.e. at 800°C and under electrochemical dc polarization. Figure 7 shows the reflectivity data of the 20nm LCM film electrode at room temperature before current-conditioning, at 800°C before and after current-conditioning, and at room temperature after the current-conditioning. A roughening of the electrode/YSZ interface was proposed in the literature as a cause of the electrode activation that lead to better adhesion of this interface, and thus faster transfer of oxide ions. As seen in Figure 7, the loss of the clear oscillations in the reflectivity data after current conditioning at 800°C indicates that the electrode/electrolyte interface was irreversibly roughened at high temperature and under dc

polarization. Nevertheless, similar roughening was observed from the reflectivity data for the electrode/electrolyte interface when the sample was subject to high temperature only, without electrical polarization, where no detectable improvement in electrochemical performance was observed. From these results, the *in situ* x-ray reflectivity data with these electrodes showed no clear correlation between the polarization of the electrode and any further changes in the roughness of the LCM/YSZ interface.

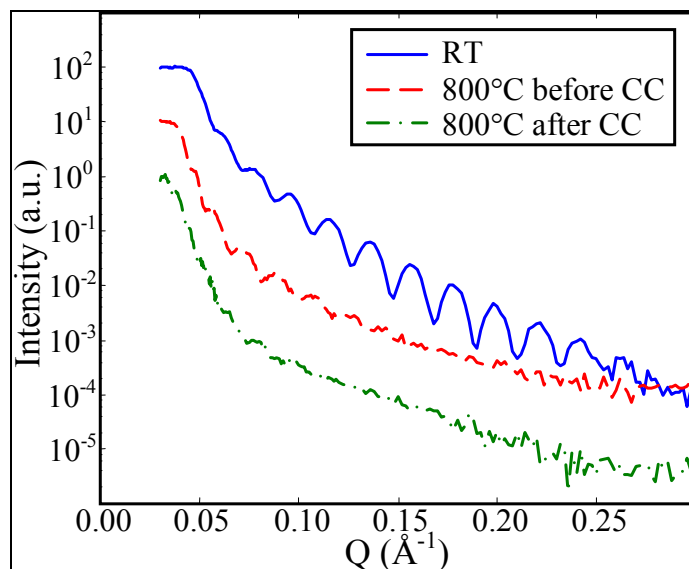


Figure 7: X-ray reflectivity of the electrode/electrolyte interface for the 20nm-thick LCM. (CC: Current conditioning.)

The current prevailing hypothesis for La-Sr based perovskite electrodes is that the A-site elements (La and Sr in this case) serve as unreactive supports for the crystal structure. Although it was never proven with *in situ* x-ray techniques, it is expected in the literature that B-site Mn surrounded by oxygen atoms must be changing its chemical state during polarization, such as during current-conditioning [13]. A change in the chemical state of Mn under electrical polarization can lead to a higher amount of oxygen vacancies or active sites in the manganite electrode, which can consequently improve the oxide ion diffusion or its surface exchange kinetics. We obtained Mn K-edge X-ray absorption near edge spectra (XANES) of several LSM and LCM dense thin-film electrodes of 20-200nm thickness on single-crystal yttria-stabilized zirconia (YSZ) electrolytes operating at 700-800°C under dc polarization (Figure 8). The Mn K-edge XANES measurements showed *no changes* for any of the dense thin-film doped lanthanum manganite electrode samples, either in the bulk or at the surface of the films, during the cathodic and anodic dc polarization-induced activation of the electrodes at high temperature. Thus, one of the intriguing findings of these studies is that the Mn oxidation state does not detectably change under polarization of the electrode, contrary to a theory postulated in the literature that cathodic polarization reduces  $Mn^{4+}$  to  $Mn^{3+}$ , or  $Mn^{3+}$  to  $Mn^{2+}$  [13], or visa versa for anodic polarization, resulting in the formation of oxygen vacancies on the electrode surface, in its bulk, or close to the interface with the YSZ electrolyte.



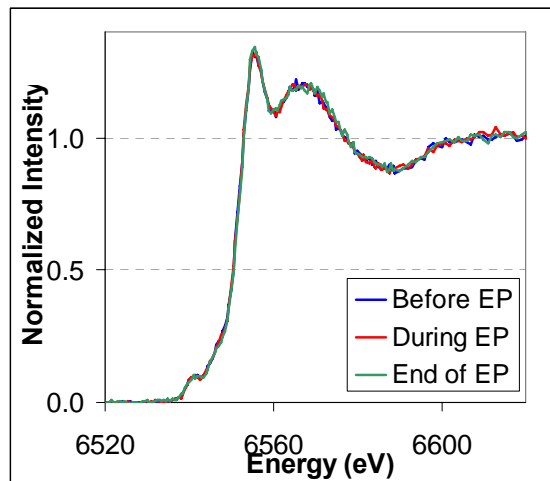


Figure 8: Mn *K*-edge XANES of the dense thin-film LSM electrode before, during, and after electrochemical polarization at 0.8V and 700°C.

Nevertheless, some form of chemical change of the electrode material is likely to take place under electrochemical polarization. Therefore, the A-site component of the doped-lanthanum manganite was investigated in our study, in spite of the current prevailing hypothesis for La-based perovskite electrodes that the A-site elements are unreactive. The La  $L_{III}$ -edge XANES behavior of several LSM and LCM model electrode samples was examined under cathodic and anodic dc polarization, at 700-800°C, using depth-sensitive glancing angle incidence for the XANES analysis. No change either in total fluorescence or in the La  $L_{III}$ -edge peak intensity was found when the measurement was performed at low angles probing the bulk of the electrode films, as shown in Figure 9-a. This indicates either that the A-site element, La, is not subject to a net change when all the electrode bulk is probed on average, or that the possible chemical changes are very localized such that the bulk measurement is not sufficiently sensitive to probe such localized changes. When the incidence angle was reduced to below the critical angle ( $\sim 0.5^\circ$  in our experiments), an increase in the total fluorescence as well as a decrease in the La  $L_{III}$ -edge peak intensity (white-line height) with the increasing degree of current-conditioning in oxygen-evolution polarization mode was observed. The overall fluorescence intensity is proportional to the concentration of La and the peak or white line intensity is sensitive to the electronic state of the La. An increase in the white-line intensity in the La  $L_{III}$  XANES indicates an increase in the number of electronic vacancies in the La 5d-band. A plot of the consequent changes in the La  $L_{III}$ -edge XANES corresponding to the surface of the LSM electrode films when anodic and open circuit potentials were repeatedly applied is shown in Figure 9-b. As seen in Figure 9-b, the La  $L_{III}$ -edge XANES changes with time under polarization approaching a steady-state trace with time. This stabilization of the La XANES data is correlated with stabilization of the area-specific resistance of the electrode, as presented in Figure 5. The A similar behavior, i.e. a reduction in the total fluorescence and a reduction in the white-line intensity, was observed for the La  $L_{III}$ -edge XANES measurements when the electrode was subject to cathodic polarization. This effect was seen repeatedly on several independently measured doped-lanthanum manganite electrodes of 100nm and 150nm thickness.

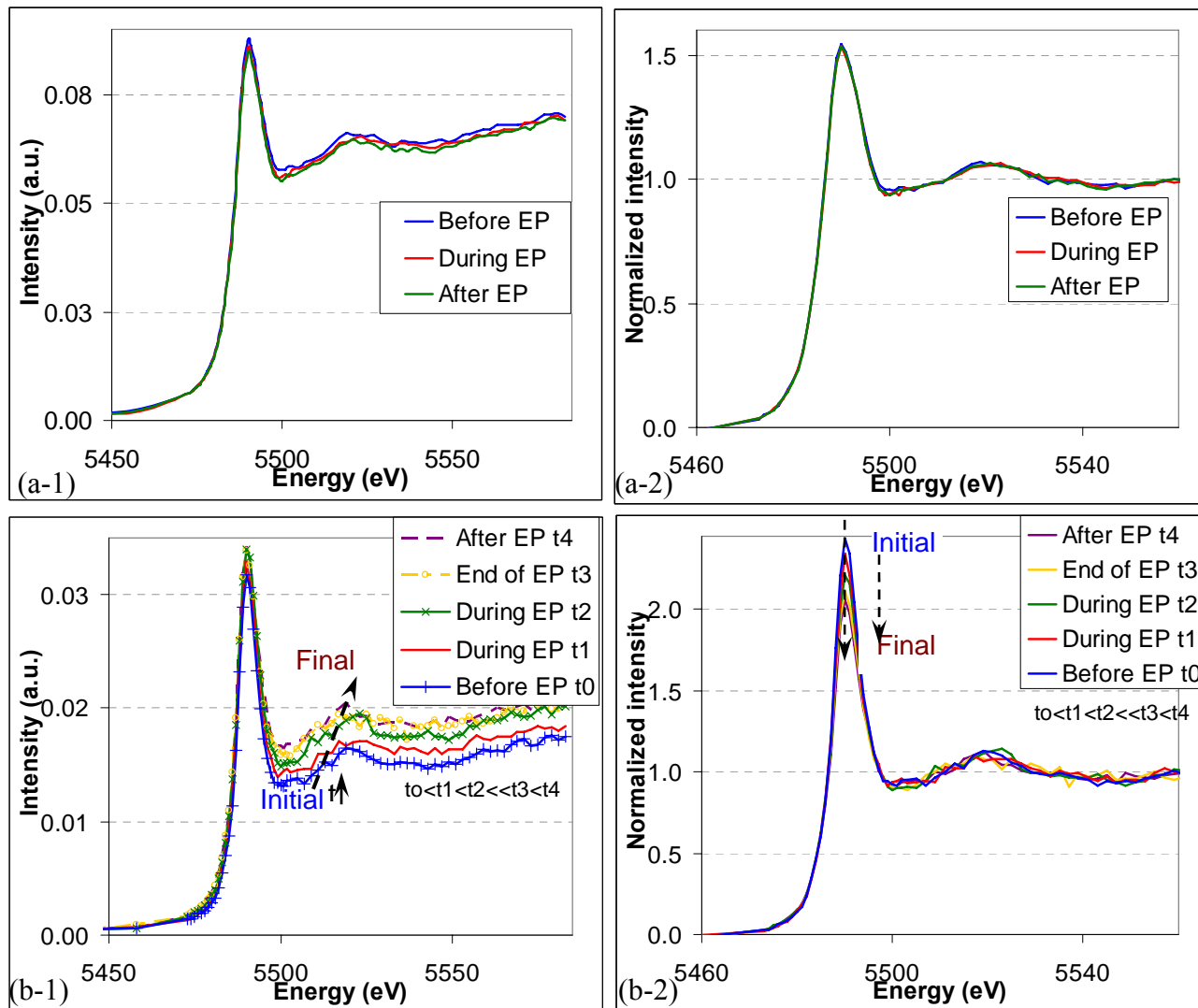


Figure 9: Grazing incidence angle XANES of La  $L_{III}$ -edge at 700°C (a) in the bulk of the dense thin-film LSM before, during, and after the anodic electrochemical polarization (EP) of 0.8V, (b) at the surface of the dense thin-film LSM before, during (at several consecutive times), and after the anodic electrochemical polarization (EP) of 0.8V. 1- Data normalized to show edge height (proportional to the concentration of La). 2- Data normalized to show changes in white-line intensity (proportional to d-band vacancy of La).

The clear change in the total fluorescence and the white-line intensity could be observed only when the x-ray incident angle was below the critical angle of reflectivity. This suggests that the increase in the concentration and the change in the electronic state of the La occurred only at the air-electrode interface. Our observation related to the La chemical state change is unexpected and probably unique to the electrochemical current-conditioning. The results can imply an active role of La in oxygen surface chemisorption and charge transfer processes, and be related to the improved oxygen reaction rate, thus faster exchange of oxygen, *at the surface of the electrodes* in electrolysis cell anodes during electrochemical polarization. It is especially interesting that such a phenomenon can control the electrochemical activation of the doped-lanthanum

manganite electrode, whose performance was thought to be limited by bulk diffusion of oxygen rather than by surface exchange of oxygen.

## CONCLUSIONS

The governing reaction mechanisms, and the electrode and electrolyte material compositions and structures, that controls the efficiency and durability of the SOECs for high temperature steam electrolysis need to be identified and well-understood for a significant improvement in SOEC performance. Our research on the oxygen electrode focused on specifically the effect of electrode crystal structure and morphology on its electrochemical performance, and the evolution of the electronic and structural properties of the electrodes while under electrochemical conditions and high temperature. We found through electrochemical impedance spectroscopy experiments that, indeed, different crystal orientations in a given oxygen electrode material, for example LSM, show different initial performance and different electrochemical activation under SOEC conditions. Optimal structures in manganite and cobaltite materials for higher oxygen surface exchange and bulk diffusion in SOEC electrodes are needed to be identified through the study of such model material systems.

Our *in-situ* x-ray and electrochemical measurements at the Advanced Photon Source of ANL have identified the chemical states of the main components of the doped lanthanum manganite electrodes. We found that the changes in the concentration and in the electronic state of the La (the A-site element of the perovskite) occurring only at the top air-electrode film interface can be responsible from the electrochemical improvement of the oxygen electrode under DC current. Our observation related to the La chemical state change is unexpected and probably unique to the electrochemical current-conditioning. The results can imply an active role of La in oxygen surface chemisorption and charge transfer processes, and be related to the improved oxygen reaction rate, thus faster exchange of oxygen, *at the surface of the electrodes* during electrochemical polarization. It is especially interesting that such a surface phenomenon can control the electrochemical activation of the doped-lanthanum manganite electrode, whose performance was thought to be limited by bulk diffusion of oxygen rather than by surface exchange of oxygen. In order to fully elucidate the role of electrode composition and chemical state at the surface, in the bulk and at the electrode-electrolyte interface on the initial and long-term electrochemical performance of SOEC anodes, further *in-situ* x-ray characterization of model oxygen electrodes for SOFCs and SOECs is needed.

## ACKNOWLEDGEMENTS

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