

***In situ* X-ray, Electrochemical, and Modeling Investigation of the Oxygen Electrode Activation**

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Abstract

Oxygen electrodes of solid oxide electrochemical cells have been shown to improve under strong cathodic and anodic polarization. Our study investigates the mechanism causing such improvement, using *in situ* x-ray and electrochemical characterization and electrochemical impedance modeling of the oxygen electrodes. Several porous and dense thin-film model electrodes of $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ (LSM) and $\text{La}_{0.8}\text{Ca}_{0.2}\text{MnO}_3$ (LCM) on single crystal yttria-stabilized zirconia (YSZ) electrolytes have been analyzed *in situ* at the Advanced Photon Source (APS) using x-ray reflectivity and x-ray absorption near edge spectroscopy (XANES) at the Mn *K*-edge and La *L*_{II}-edge. *In situ* x-ray reflectivity analysis show that no clear correlation between the polarization of the electrode and any further changes in the roughness of the LSM/YSZ interface exist. XANES measurements illustrate that the cathodic or anodic dc polarization at high temperature induces no detectable changes in Mn chemical state either in the bulk or at the surface of the LCM and LSM electrodes on YSZ, while the La chemical state changes reversibly at the electrode surface. This field-induced chemical change of La at the surface of electrodes is assumed to be a cause of the electrochemical activation through enhanced surface exchange of oxygen on the doped lanthanum manganite electrodes.

Introduction

Uncertainties in our understanding of the oxygen reduction mechanism (ORR) at solid oxide fuel cell (SOFC) cathodes still remain due to the complexity of the ORR mechanism under stationary conditions, as well as the influence of the processing and operating conditions, and polarization history of the electrode. Numerous studies have shown that cathodic or anodic dc polarization of the solid oxide fuel 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 ORR kinetics, and thus, to ways to improve its performance. In addition, the non-stationary improvement due 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.

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 govern the current-conditioning of LSM electrodes are reduction of the transition metal, Mn, to form oxygen ion vacancies in the perovskite lattice [1][2], removal of phases that block oxygen adsorption on the electrode surface [3][4], increase of electrode active surface or interfacial area due to roughening [5], formation of secondary phases at the electrode-electrolyte interface [6], movement of charged species at the interfaces, such as cation diffusion [7].

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 SOFC must be removed from its operating atmosphere and cross-sectioned. On the other hand, *in situ* x-ray studies of the 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 *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. 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 SOFC cathodes; though prior *in situ* studies on low temperature fuel cell cathodes have been conducted (e.g. [8],[9]).

Realistic powder cathodes of doped-lanthanum manganite, and 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 the analysis. Electrode overpotentials of 0.3-1V under cathodic and anodic polarization were applied to achieve the electrochemical activation. The results of the structure, composition, and impedance analyses provide input for the modeling of the electrode reaction mechanisms. The modeling is based on predicting the electrochemical impedance by simulating the kinetics of the reaction mechanisms governing the electrode and electrolyte behavior at the molecular level [10].

Experimental Approach

Sample preparation: The first set of oxygen electrode materials in this analysis were porous $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_{3+\delta}$ of about 20-30 μm thickness sintered at 1000 °C on polished single

crystal YSZ of 10 x 10 x 0.5 mm, with (100) orientation. The porous electrodes were used for representing the conventional SOFC cathodes in this analysis. The second set of materials were 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. The LSM thin-film electrodes were prepared using a sol-gel technique and the LCM thin-film electrodes were prepared using the pulsed laser deposition (PLD) technique at a substrate temperature of 700°C. The dense film LCM electrodes were 20-500nm thick. Porous Pt was sintered on the back side of the electrolyte as a counter electrode.

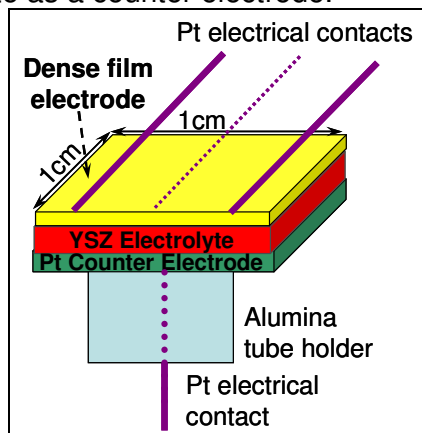


Figure 1 *In situ* electrochemical cell schematics. (Drawing not to scale.)

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 Fig. 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.

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. The width of the strong

enhancement varies with the angle of incidence. This feature allows depth-sensitive measurement of the oxidation state of the electrode's constituent metal oxides located a few to a few hundred nanometers from the interface.

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 cell set-up and the incident x-ray beam path are shown in Fig. 2.

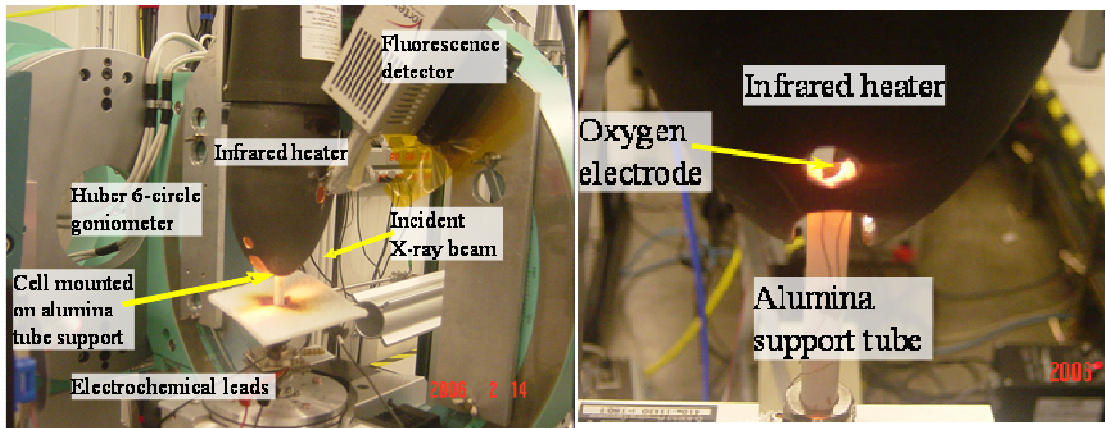


Figure 2 The *in situ* electrochemical cell set-up at MR-CAT beam-line of the APS, for x-ray reflectivity and x-ray fluorescence analysis of the SOFC oxygen electrodes.

Results and Discussion

Porous $La_{0.8}Sr_{0.2}MnO_{3+\delta}$ electrodes

EIS of the porous LSM electrodes in half-cell configuration at 800°C show the following typical features in our analysis before, during, and after current-conditioning (Fig. 3): 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

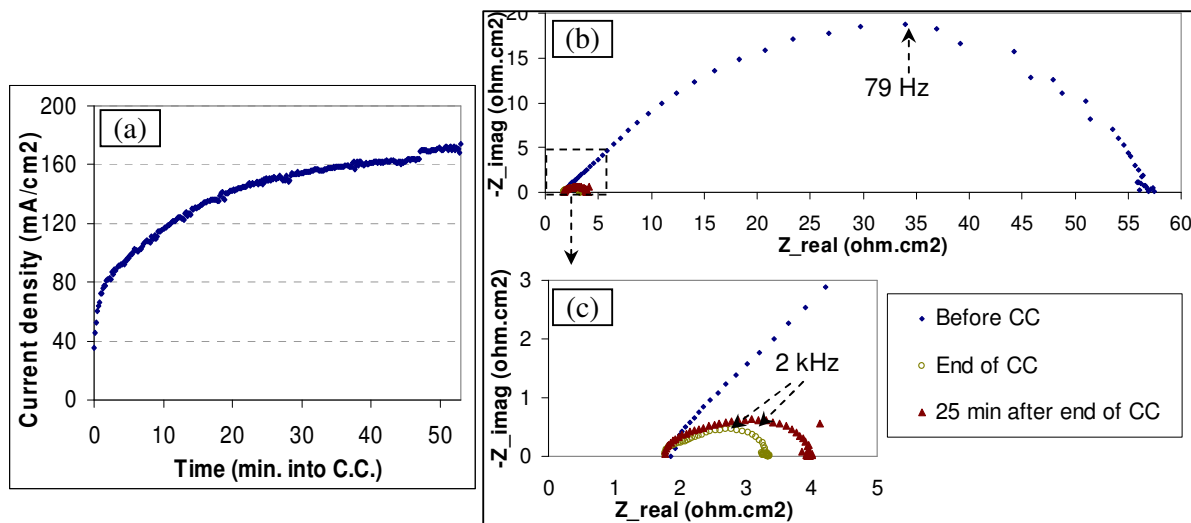


Figure 3 (a) Current density from the porous LSM electrode during current-conditioning (C.C.) at -0.6V at 800°C. (b) EIS at open circuit potential before the CC, at the end of a 55min CC, and 25 minutes after the end of C.C. shown in (a). (c) Inset of (b) showing the lower impedance values.

current-conditioning, and multiple overlapping impedance arcs in intermediate-frequency regions after current-conditioning. The intermediate-frequency impedance arc(s) relax back slowly after the dc polarization is removed. In accordance with literature [11], 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 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 [12]. A change in the chemical state of Mn under electrical polarization can lead to higher amount of oxygen vacancies or active sites at 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 the bulk of several lanthanum strontium manganite (LSM) porous cathodes of ~10-30 μm thick on single-crystal yttria-stabilized zirconia (YSZ) electrolytes operating at 800 °C under dc polarization (Fig.4). Measurements on the porous LSM electrodes were not performed using an interface sensitive configuration, and showed that the Mn oxidation state in the bulk of the LSM electrode did not change with either cathodic or anodic polarization, although significant electrode activation was observed, as depicted in Fig. 3.

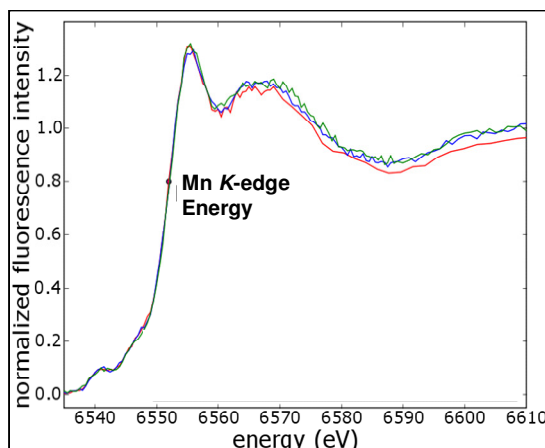


Figure 4 Mn K-edge XANES of the porous doped-manganite electrode before, during, and after polarization at 800 °C.

However, the fraction of the ~10-30 μm thickness of these realistic fuel cell electrodes that is active during the electrochemical reaction is unknown. If only a thin layer near the electrolyte-electrode interface or at the electrode-air interface (surface) is activated during polarization, the remaining large bulk material of the LSM that is not activated may limit the sensitivity of the XANES measurements to changes in the Mn oxidation state. Therefore, we propose that the Mn oxidation state in porous LSM electrodes (of tens of μm thick) either doesn't change under electrochemical polarization, or that its change is limited to a layer of material that is smaller than the sensitivity limit of our XANES measurements.

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:

In order to enhance the sensitivity of the x-ray measurements to the surface and bulk of the electrode material, dense thin-film doped-lanthanum manganite model electrodes were analyzed in reflectivity geometry. Similar to the 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. Fig. 5 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 before and after current-conditioning at -0.8V for 15 minutes.

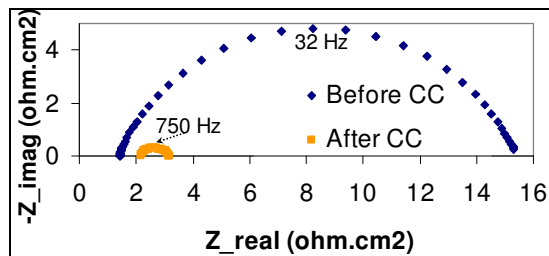


Figure 5 EIS at open circuit potential before and at the end of C.C. at -0.8V, 800°C for 15min for the 150nm-thick dense LCM electrode.

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. Fig. 6 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 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 Fig 6., the loss of the clear oscillations at 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.

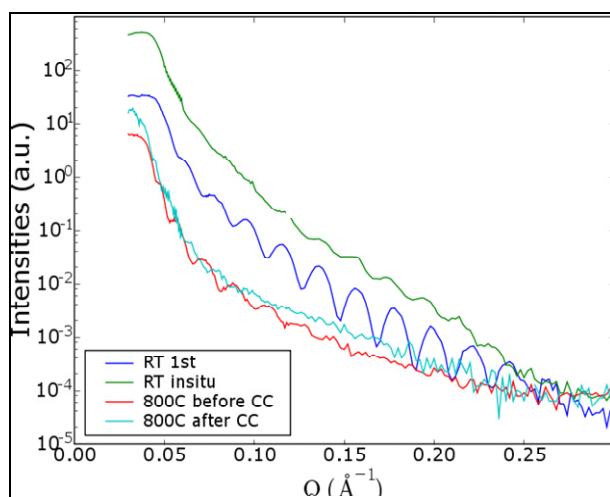


Figure 6 X-ray reflectivity of the electrode/electrolyte interface for the 20nm-thick LCM.

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. The resulting Mn *K*-edge XANES were the same as those shown in Figure 4. 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 Mn⁴⁺ to Mn³⁺, or Mn³⁺ to Mn²⁺ [12], resulting in the formation of oxygen vacancies on the electrode surface or in its bulk.

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*_{II}-edge XANES behavior of several LCM model electrode samples was examined under cathodic and anodic dc polarization, at 800°C, using depth-sensitive glancing angle incidence for the XANES analysis. A decrease in the La *L*_{II}-edge peak intensity with the increasing degree of current-conditioning in both oxygen-reduction and oxygen-evolution polarization modes was observed. A plot of the corresponding changes in the La *L*_{II}-edge XANES when cathodic and open circuit potentials were repeatedly applied is shown in Fig. 7. After 30-minute intervals of maintaining the sample at open circuit with no polarization, the La *L*_{II}-edge peak relaxed back to its initial intensity, which correlated with an increase of the electrochemical impedance back to its initial value. This effect was seen repeatedly on two independent LCM electrodes of 100nm and 150nm thickness.

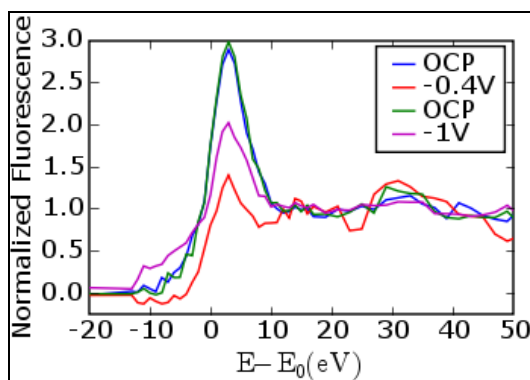


Figure 7 Grazing incidence angle XANES of La *L*_{II}-edge at initial OCP before C.C., at -0.4V during 1st C.C., at OCP after the 1st C.C., and at -1.0V during the 2nd C.C. at 800°C for the 150nm-thick LCM electrode.

The clear change in 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 change in the chemical state or concentration of the La occurred only at the top air-LCM film 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 adsorption and charge transfer processes, and be related to the improved oxygen adsorption and reduction rate, thus faster exchange of oxygen, at the surface of the electrodes in fuel cell cathodes 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.

Electrochemical Modeling

Electrochemical impedance spectroscopy modeling analysis for the cathodic activation of the dense thin-film model doped lanthanum manganite electrodes was based on our ORR model developed and validated for similar model electrode/electrolyte systems [10]. This

modeling approach includes the coupled influence of oxygen surface-adsorption, electronation, and diffusion at the surface and in the bulk of LSM, and diffusion in the electrolyte using the reaction rates in continuum electrochemical kinetics. As discussed, the *in situ* x-ray analysis of the cathode activation under polarization indicated a surface chemical state change due to changes in the La L_{II} -edge measured for the surface of the LCM dense film electrodes. Therefore, we evaluated the influence of the surface properties on the EIS for our model systems using the ORR model applied to the geometry of the model systems here. Two important physicochemical properties pertaining to the surface activity of the electrode materials are the concentration of available sites for oxygen adsorption (N), and the rate constant for the oxygen adsorption/reduction reaction. The electrochemical model of our analysis indicates a strong correlation between the total impedance and the surface properties of the thin-film LCM electrodes, as shown in Fig. 8.

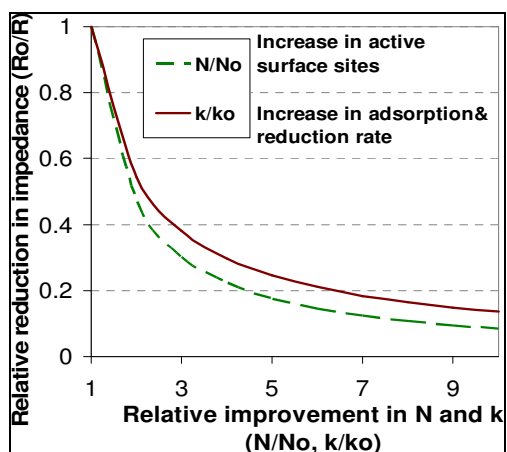


Figure 8 Relative influence of the surface oxygen vacancy site concentration, N , and adsorption/reduction rate constant on the impedance at 800 °C for the 150nm thick LCM electrode. Subscript 'o': values before the current conditioning.

If no change in site activity due to a change in metal composition is imposed on the electrode surface during polarization, a two- to ten-fold decrease in the total impedance after dc polarization would require about a two- to eight-fold increase in the concentration of oxygen vacancy sites. On the other hand, independent of the oxygen vacancy site concentration change, the same improvement would require a similar magnitude of increase in the reaction rate constant for the oxygen adsorption/reduction process due to La-related chemical and/or compositional changes. We assume that both phenomena, separately or together, are likely to take place under dc polarization and can govern the electrochemical activation of the electrode during current conditioning.

Conclusion

This study investigated the mechanism causing electrochemical activation of the SOFC cathodes, porous and dense-thin film electrodes of $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ (LSM) and $\text{La}_{0.8}\text{Ca}_{0.2}\text{MnO}_3$ (LCM), using *in situ* x-ray and electrochemical characterization and electrochemical impedance modeling. To the best knowledge of the authors, this is the first *in situ* x-ray and electrochemical investigation of the SOFC electrodes' behavior. *In situ* x-ray reflectivity analysis show that no clear correlation between the polarization of the electrode and any further changes in the roughness of the LSM/YSZ interface exist. XANES measurements at the Mn K -edge and La L_{II} -edge illustrate that the cathodic or anodic dc polarization at high temperature induces no detectable changes in Mn chemical state either in the bulk or at the surface of the LCM and LSM electrodes on YSZ, while the

La chemical state changes reversibly at the electrode surface only. This field-induced chemical change of La at the surface of electrodes is assumed to be a cause of the electrochemical activation through faster surface exchange of oxygen on the doped lanthanum manganite electrodes. Investigation of the chemical and compositional properties at the electrode/electrolyte interface and the near-interface region is also needed and would be complementary to this study, for the understanding of the role of both interfaces of the electrode on the electrochemical activation under dc polarization.

Acknowledgements

We acknowledge Dr. Beihai Ma for preparing the dense thin-film $\text{La}_{0.8}\text{Ca}_{0.2}\text{MnO}_3$ electrodes for this study and Dr. Bruce Ravel for facilitating the set up for our experiments at MRCAT. MRCAT operations are supported by the Department of Energy (DOE) and the MRCAT member institutions. This research was financially supported by the Laboratory Directed Research and Development Program at US-DOE's Argonne National Laboratory.

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