

# Modeling and Investigation of Oxygen Reduction Activity of Mixed Ionic-Electronic Conductors for SOFC Cathodes

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## Introduction

- The porous cathode is one of the components currently needing the improvement to enable widespread commercialization
- Candidate mixed ionic-electronic conducting (MIEC) materials for cathodes:
  - $\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$  (LSCF) - Good electronic/ionic conductivity but poor chemical stability
  - $\text{La}_{2-x}\text{Sr}_x\text{MnO}_{3-\delta}$  (LSM) - Good catalytic activity and chemical stability but poor ionic conductivity, mitigated through the formation of a composite porous electrode with an electrolyte such as  $\text{Y}_{0.08}\text{Zr}_{0.92}\text{O}_2$  (YSZ)
- Infiltrated electrodes (Figure 1a)
  - LSCF forms the backbone, providing large ionic and electronic conductivity
  - LSM is infiltrated as a thin film/particulate coating on LSCF, providing chemical stability and catalytic activity
  - Performance and stability are both enhanced by infiltration (Figure 1b)

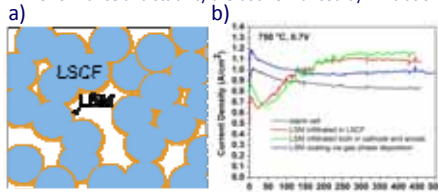


Figure 1: a) Schematic of an LSM-infiltrated LSCF cathode. b) Performance of a full cell without infiltration (blank) and with several methods of infiltration.

- The performance enhance is likely intricately related to the oxygen reduction activities of LSCF and LSM
- Hypotheses for enhancement
  - $\text{O}_2$  adsorption Enhancement
  - Large cathodic activation
  - Surface stabilization
  - Transport mitigation

## Oxygen Reduction Kinetics

Oxygen reduction on an MIEC surface is a complex process involving the gas phase, the surface (active sites), and the bulk defect chemistry (oxygen vacancies, electron holes). The elementary steps can generally be divided into adsorption and incorporation of oxygen. Such processes can be described by phenomenological chemical kinetics.<sup>1</sup>

### Adsorption

If the adsorption is characterized by dissociation of the oxygen molecule and partial reduction of the monatomic oxygen, then

$$\text{adsorption reaction: } \frac{1}{2}\text{O}_2 + * \leftrightarrow \text{O}^- + h$$

rate equation (1):

$$r_{\text{ads}} = \tilde{k}_{\text{ads}} p\text{O}_2^{1/2} \Gamma (1-\theta) \exp\left(-\frac{\alpha F}{RT} \chi_{\text{ms}}\right) - \tilde{k}_{\text{des}} \Gamma \theta \exp\left(\frac{(1-\alpha)F}{RT} \chi_{\text{ms}}\right)$$

### Incorporation

Adsorbed oxygen occupies a surface oxygen vacancy and is fully reduced

Incorporation reaction:

$$\text{O}^- + V_{\text{O}} \leftrightarrow \text{O}_{\text{O}}^2 + h + *$$

rate equation (2):

$$r_{\text{inc}} = \tilde{k}_{\text{inc}} \Gamma \theta c_v \exp\left(+\frac{\alpha F}{RT} \chi_{\text{ms}}\right) - \tilde{k}_{\text{inc}} \Gamma (1-\theta) c_{\text{O}} c_h \exp\left(-\frac{(1-\alpha)F}{RT} \chi_{\text{ms}}\right)$$

### Surface-Specific Modeling

Neglecting sheet-resistance or ionic transport impedances, at steady state, the current can be computed from the rate of oxygen adsorption and incorporation, which should be equal to one another

current equation (3):

$$i = z_h F r_{\text{ads}} + z_h F r_{\text{inc}}$$

The cathodic overpotential,  $\eta$ , can be linked to the current through the effective oxygen partial pressure and the Nernst equivalence

overpotential equation (4):

$$\eta = \frac{RT}{nF} \ln \left( \frac{p_{\text{O}_2}^{\text{eff}}}{p_{\text{O}_2}^0} \right)$$

The concentration of solid-state defects (oxygen vacancies, electron, electron holes) at the surface under a cathodic polarization are set equal to the concentration of defects at an equivalent oxygen partial pressure and are then used in the rate equations.

The polarization resistance may be computed from the change of current and overpotential at steady state

polarization resistance equation (5):

$$R_p = \frac{\partial \eta}{\partial i} = \frac{1}{2F} \frac{\partial \eta}{\partial r}$$

### Thin-Film Investigation

To better investigate the surface properties, LSCF films were sputtered onto an electrolyte substrate and left blank or then covered with a layer of sputtered LSM. The polarization resistance of the LSM-coated LSCF is larger at OCV, but decreases faster towards cathodic polarization.



## Promoted Adsorption

One possible mechanism for enhancement is more facile adsorption of oxygen onto the oxide surface. Easier adsorption leads to a larger supply of adsorbed oxygen available for incorporation and for easier replenishment of adsorbed oxygen under a bias. The underlying LSCF provides a source of oxygen vacancies. Recently, DFT calculations showed that adsorption energy is lower (more favorable) on LSM than on LSF or LSCF due to the presence of the Mn cation (Figure 3a).

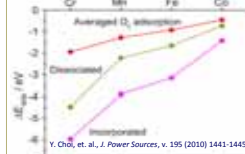


Figure 3: Oxygen adsorption energies associated with the presence of different transition metal cations in  $\text{La}_{0.5}\text{Sr}_{0.5}\text{BO}_{2.75}$ , where  $B = \text{Cr}, \text{Mn}, \text{Fe}, \text{or Co}$ . "Averaged" corresponds to the average energy of super-/peroxo- molecular adsorption, "Dissociated" corresponds to dissociated oxygen, "Incorporated" corresponds to one of the oxygen atoms incorporated into an oxygen vacancy. Image reproduced from ref. 2.

Despite more strongly adsorbing oxygen, LSM has a much smaller surface oxygen exchange coefficient than LSCF.<sup>3,4</sup> A thin LSM coating on LSCF therefore might be modeled with a larger forward adsorption rate constant (Equation 1) and a smaller forward incorporation rate constant (Equation 2) compared to blank LSCF, leading to larger equilibrium surface coverage, but lower equilibrium rate of oxygen incorporation for the LSM-coated LSCF.

Such a case is simulated in Figure 4. The polarization resistance ( $R_p$ ) at open-circuit voltage (OCV) is initially larger for the case of LSM coating due to smaller incorporation at OCV (Figure 4a). However,  $R_p$  decreases more quickly as cathodic overpotential becomes more negative and eventually decreases to below that of the blank LSCF. The superior performance of the LSM-coated LSCF at large cathodic overpotentials can be attributed in

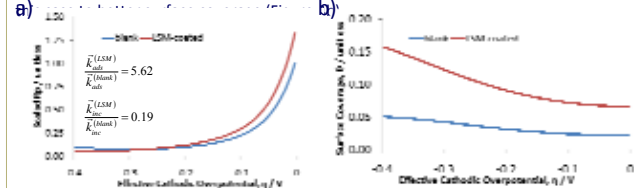


Figure 4: a) Simulated polarization resistance versus effective cathodic overpotential for blank and LSM-coated LSCF.  $R_p$  is scaled to the value of the blank LSCF at OCV. b) Simulated surface coverage versus effective cathodic overpotential. Coverage increases at more cathodic overpotentials because the concentration of electron holes decreases (see Equation 1).

## Bulk Cathodic Activation

A large increase in oxygen vacancy concentration results from cathodic polarization of an MIEC, which may be linked to the change in effective oxygen partial pressure in the interior of the MIEC. Therefore Brouwer diagrams are helpful for interpreting the response to polarization through the use of the Nernst equivalence (Equation 4).

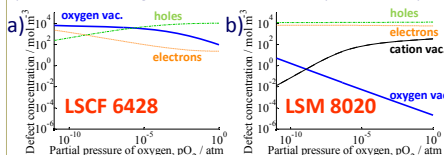


Figure 5: Brouwer diagrams for ref. 5 LSCF 6428 (computed with ref. 5 model) and LSM 8020 (computed with ref. 6 model). These diagrams show the pertinent point defect concentrations as a function of oxygen partial pressure (and cathodic overpotential, if the Nernst equivalence is used to convert).

The equilibrium oxygen vacancy concentration is much larger for LSCF 6428 than for LSM 8020. However, as the overpotential becomes more cathodic (equivalent to a decrease in effective, internal oxygen partial pressure on the Brouwer diagram) the increase in oxygen vacancy concentration in the LSCF eventually slows, reaching a plateau. The increase of oxygen vacancies in LSM does not slow.

If other mechanisms are neglected and current is simply made proportional to the oxygen vacancy concentration at steady state, then  $R_p$  associated with the LSM surface will decrease monotonically as the overpotential becomes more cathodic (Figure 6). The  $R_p$  associated with the LSCF surface will reach a minimum and begin to increase at negative overpotentials (Figure 6) because the rate of increase of oxygen vacancies with decreasing cathodic overpotential is decreased from its initial value at OCV. Therefore, under large cathodic polarization, the LSM surface is more activated with respect to its initial value at OCV than is the LSCF surface. This LSM activation phenomenon may explain the superior performance of the coated cells under operation and may also explain the increase in polarization resistance of the blank LSCF cells in Figure 2b. This approach of course neglects mass transport considerations, but may be valid when the LSM film/coating is very thin. Activation of a substantial bulk pathway in LSM under cathodic polarization has been observed experimentally.<sup>7,8</sup>

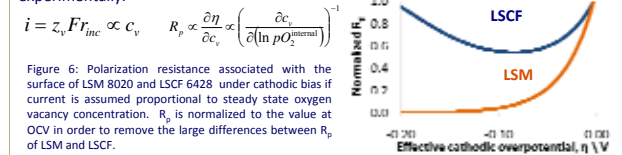


Figure 6: Polarization resistance associated with the surface of LSM 8020 and LSCF 6428 under cathodic bias if current is assumed proportional to steady state oxygen vacancy concentration.  $R_p$  is normalized to the value at OCV in order to remove the large differences between  $R_p$  of LSM and LSCF.

## Other Important Factors

### Transport Considerations

The thickness of the LSM coating is important. Since oxygen diffusion proceeds slower in LSM than in LSCF,<sup>3,4</sup> an LSM coating that is very thick could introduce large transport impedance into the system, offsetting or even overwhelming any gain from increased surface activity. Therefore, the LSM coating must be thin (less than 50 nm) in order to realize any benefit. Grain boundaries or other structural defects may also aid ionic transport through the LSM film

### Interdiffusion

Interdiffusion between the LSM and LSCF backbone during operation introduce Co and Fe ions into the surface catalyst layer, forming LSCFM (Figure 7). Therefore, the properties of the surface layer in operation are likely intermediate between LSM and LSCF. Some increased adsorption compared to blank LSM is likely present due to the Mn ions, while the oxygen vacancy concentration is likely much larger than in pure LSM due to the effects of space-charge and alteration of the defect chemistry by Co and Fe.

### Surface Stabilization

The segregation of Sr to the surface of LSCF has been identified as a possible mechanism for performance degradation over time.<sup>9-11</sup> Our TEM investigation shows that after operation, the LSM layer loses long-range order but does not appear to form an inactive layer on the surface.

## Summary

Infiltration of an LSM coating onto an LSCF backbone in a porous SOFC cathode increases performance. The increase in performance is likely related to the details of the oxygen reduction reaction including possibly superior oxygen adsorption and stronger activation of LSM under cathodic polarization. Factors such as transport limitation in the LSM coating, modification by interdiffusion with the LSCF, and stabilization of the LSCF surface are also likely important.

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