Enhancement of La$_{0.6}$Sr$_{0.4}$Co$_{0.2}$Fe$_{0.8}$O$_{3-\delta}$ Durability and Surface Electrocatalytic Activity by La$_{0.85}$Sr$_{0.15}$MnO$_{3\pm\delta}$ Investigated using a New Test Electrode Platform

Electronic Supplementary Information

Section ESI 1 Cell Design of Model Electrode

It is well established that the intrinsic surface catalytic properties of an electrode in both bulk and thin-film forms are difficult to investigate. The state-of-the-art electrochemical characterization techniques have difficulty distinguishing ionic transport from surface oxygen reduction occurring in porous electrodes under the polarization conditions, though some unique methods have been employed to study the surface of electrodes at equilibrium. Thin-film electrodes could minimize the contribution of bulk transport; however, they can dramatically enhance the effect of sheet resistance and might be complicated by the electrocatalytic activity of current collectors. Nevertheless, geometrically well-defined electrodes hold many advantages over the traditional electrode in investigation of electrochemical properties.$^1$

Therefore, we proposed a test cell platform to investigate the intrinsic surface catalytic properties of an electrode (Fig. 1a). The backbone LSCF serves here as both an ionic transport pathway as well as a current-collecting layer, with larger relative thickness than the surface LSM layer. With this design, the surface of the working electrode can be readily studied under equilibrium and non-equilibrium conditions with fewer uncertainties stemming from the sheet resistance, current collection, and bulk ionic transport.
transport because the underlying current collector layer provides adequate electronic conductivity while being sufficiently thin to provide sufficient oxygen vacancy transport.

The buried current collector layer has several functions. First, it acts as the current collector to minimize or eliminate the effect of sheet resistance; this becomes critical when the surface layer is very thin. Second, it will not complicate the surface of the electrode material to be studied since it is buried under the surface layer without exposure to air. Third, it also provides an ionic pathway needed for the electrode reactions.

We used LSCF as the buried layer and found that the LSM thin film at the nanoscale demonstrated increased surface electrocatalytic activity upon polarization, resulting in faster surface exchange kinetics relative to uncoated LSCF. This phenomenon is very different from the long-standing concept that LSCF possesses better surface catalytic activity than LSM which has been normally demonstrated under equilibrium conditions. It effectively combined fast electronic/ionic transport of bulk LSCF with rapid surface reactions of the LSM thin film. In addition, the thin LSM coating was demonstrated to have improved electrochemical durability and performance, further recommending this novel electrode architecture.

Section ESI 2 Surface Layer Stability Analysis

TEM micrographs of the as-deposited sol-gel coated flat, polished LSCF surface are given in Fig. ESI1. They indicate that the LSM layer was crystalline and epitaxial with the underlying LSCF prior to long-term annealing.
Fig. ESI1: TEM micrographs of the as-prepared LSM-coated LSCF pellet by the sol-gel method with one hour anneal at 900˚C. The zone-axis lattice fringes in the a) surface and b) Fourier-filtered image of the light-blue rectangle in (a) show that the LSM film is crystalline, with perovskite structure. c) HRTEM image at the interface between the two phases, showing epitaxy between the underlying LSCF and deposited LSM. (d) and (e) are Fourier-filtered images of the red and green rectangles in (c) in the two phases near their interface. The lattice fringes of LSM extend from the bottom to the top of the film indicates that the film is single-crystalline throughout the entire thickness.

TEM micrographs of the sol-gel coated flat, polished LSCF surface after long-term annealing are given in Fig. ESI2. They indicate a loss of crystallinity in the top 40
nm of the coated film, but preservation of crystallinity and epitaxy in the bottom 10 nm portion that is on the interface with the underlying LSCF.

Fig. ESI2: TEM micrograph of the pellet surface after long-term annealing (850°C, 900 h). a) Z-contrast image of the interface. b) CBED indicating amorphous structure in the top 40 nm of the surface layer. Crystallinity is retained in bottom 10 nm near the LSCF interface. c) HRTEM image of the interface region. The yellow dashed curve marks the termination of lattice fringes on the LSM(C) side. The red dashed line corresponds to the interface seen in Figure 3(b) and the Z-contrast image in (a). d) and e) are Fourier-filtered images of the green and red rectangles in (c). The zone-axis lattice fringes in (d) indicate that epitaxial, perovskite crystal structure is retained in the bottom (crystalline) portion of the LSM(C) on the interface. e) The zone-axis lattice fringes in the bulk LSCF indicate that the perovskite structure is preserved.
Fig. ESI3 gives the Raman spectra collected in air from blank LSCF and LSM-coated LSCF sputtered model electrodes before and after application of cathodic polarization at a cell voltage of -0.8 V. It is known that the peak centered around 550 cm$^{-1}$ for LaMO$_3$ (M=Co, Fe, Mn) is assigned to the M-O bonds, especially reflecting Co/Fe ratio in LSCF cathode. No change in Raman shift was observed for the LSM-coated sample, indicating no significant loss of Co and Fe during polarization. However, a main peak at 646 cm$^{-1}$ in the untreated LSCF cathode undergoes a relatively large red shift after applying a DC bias, occurring at 653 cm$^{-1}$.

This phenomenon is due probably to mass deficiency in the lattice caused by transformation of LSCF from cation stoichiometry to A-site deficiency. The segregation of Sr to the surface of LSCF has been identified as a possible mechanism for performance degradation. It is thus reasonable to conclude that Sr segregation occurred on the LSCF cathode surface under high cathodic polarization. These observations are in good agreement with recent XPS studies that Co/Fe ratio remained fairly constant and Sr was greatly enriched on the surface. Outward diffusion of Sr dopant inevitably causes the reduction of surface oxygen vacancies, affecting surface catalytic properties including adsorption and incorporation. Thus, the presence of Sr enrichment on the surface would be expected to contribute significantly to the observed degradation. However, no obvious change in Raman shift was experienced for LSM-coated LSCF cathode after polarization, representing superior stability of this new cathode. Since LSM has stable electrical and chemical characteristics, it is very likely that LSM thin layer inhibits the outward diffusion of Sr.
Fig. ESI3: Raman spectra of cathode before and after cathodic polarization a) blank LSCF cathode b) LSM-coated LSCF cathode
Section ESI 3 Bulk Cathodic Activation Model

The model of section 2.1 links current simply to oxygen vacancy concentration. We justify this simplistic kinetic treatment because the oxygen reduction process via the bulk pathway of the MIEC is generally regarded as requiring oxygen vacancies for incorporation into the bulk as well as, in some cases, for promoting oxygen adsorption/dissociation onto the surface.\(^6\)\(^-\)\(^8\) Focusing only on the surface and neglecting all other sources of impedance such as mass transport, electronic resistance, and loss over the electrolyte-MIEC phase boundary, then the cathodic overpotential, \(\eta\), can be linked to the change in the effective internal oxygen partial pressure, \(p_{O_2}^{\text{internal}}\), of the MIEC

\[
\eta = \frac{RT}{nF} \ln \left( \frac{p_{O_2}^{\text{internal}}}{p_{O_2}^0} \right) \tag{S1}
\]

where \(p_{O_2}^0\) is the gas-phase equilibrium oxygen partial pressure and \(n=4\) is the number of electrons associated with oxygen reduction. Equation S1 can be rearranged to give \(p_{O_2}^{\text{internal}}\) as a function of \(\eta\). This is a well-known approximation in solid state ionics.

Point defect concentrations of La\(_{0.6}\)Sr\(_{0.4}\)Co\(_{0.2}\)Fe\(_{0.8}\)O\(_{3-\delta}\) and La\(_{0.8}\)Sr\(_{0.2}\)MnO\(_{3+\delta}\) used for this analysis are represented in the Brouwer diagram in Fig. ESI4 and computed using published models.\(^9\),\(^10\) Note that both models describe LSCF and LSM as hopping-type semiconductors.

In order to determine the point defect concentration at some \(\eta\), the value of \(p_{O_2}^{\text{internal}}\) associated with \(\eta\) (Equation S1) was used as the x-axis variable of the Brouwer diagram to determine the steady state defect point defect concentrations under the bias.
The equilibrium point defect concentration were those dictated by the temperature and \( p_{O_2}^0 \). The concentrations under \( \eta \) were those dictated by temperature and \( p_{O_2}^{\text{internal}} \).

Fig. ESI4: Brouwer diagrams showing computed bulk point defect equilibrium at 700°C of a) LSCF 6428 (according to its published defect model\(^9\)) and b) LSM 8020 (according to its published defect model\(^10\)). Both models assume semiconducting small polaron electronic states.

The bulk point defect chemistries of LSM versus LSCF are markedly different from one another. Though both materials have been described by a small polaron model for their electronic defects,\(^9\)-\(^11\) the magnitude of the oxygen vacancy concentrations and their behavior under sub-atmospheric pO\(_2\)’s are quite different. Namely, the oxygen vacancy concentration of LSCF is quite high, leading to high tracer diffusivity and oxygen surface exchange, and may be directly measured by techniques such as TGA or
coulometric titration. LSM, in contrast, has very low oxygen vacancy concentration and is generally regarded as superstoichiometric with respect to oxygen at equilibrium partial pressures because the A- and B-site vacancy concentrations are large. The exact equilibrium oxygen vacancy concentration is experimentally inaccessible in LSM precisely because of the large cation vacancy concentration and so only estimates of it are available from models.\textsuperscript{10-13}

Despite the small oxygen vacancy concentration, there is evidence of an appreciable bulk pathway contribution from LSM in the literature.\textsuperscript{14-17} The bulk pathway is especially activated under a large cathodic bias,\textsuperscript{16, 17} an effect attributed to a large addition of oxygen vacancies to the LSM under polarization. Koep demonstrated that the contribution of the bulk increased with decreasing film thickness,\textsuperscript{14} showing that the bulk pathway of LSM depends in part on diffusion limitation. Thus, it seems possible for the LSM coating to be strongly activated under cathodic polarization due to large relative oxygen vacancy concentration increase with the requirement that it be very thin in order to mitigate oxygen vacancy transport losses.

The Brouwer diagram offers a guide to the strong activation of LSM. Oxygen vacancy concentration increases steadily with decreasing pO\textsubscript{2}. LSCF in contrast has a much larger oxygen vacancy concentration at near-atmospheric pO\textsubscript{2}, but the concentration does not increase as much relative to its initial value as pO\textsubscript{2} decreases. The change in oxygen vacancy concentration with pO\textsubscript{2} is directly proportional to the quantity commonly referred to as the thermodynamic factor of vacancies.

Fig. ESI5 is a plot of the oxygen vacancy concentration versus pO\textsubscript{2} without log-scale y-axis. Note that the LSM curve is concave up over the entire region. The LSCF
curve has an inflection point at approximately 10^{-3} \text{ atm}, where the sign of the second derivative of $c_v$ changes.

![Graph showing equilibrium oxygen vacancy concentration for LSCF 6428 and LSM 8020 predicted from the bulk models as a function of oxygen partial pressure.]

Fig. ESI5: Equilibrium oxygen vacancy concentration for LSCF 6428 and LSM 8020 predicted from the bulk models as a function of oxygen partial pressure.

Putting together the proportionalities for overpotential (Equation S1) and current (main text Equation 1) shows that $R_i$ is proportional to the inverse of the slope of the curves in Fig. ESI5.

\[
R_i \propto \frac{\partial \ln(pO_{2\text{int}})}{\partial c_v} = \left( \frac{\partial c_v}{\partial \ln(pO_{2\text{int}})} \right)^{-1} 
\]

(S2)

Since LSM has a positive second derivative over all relevant $pO_2$ values, $R_i$ continuously decreases with decreasing $\log(pO_{2\text{internal}})$. Since the $c_v$ curve of LSCF initially has a positive second derivative near OCV, $R_i$ initially decreases with decreasing $\log(pO_{2\text{internal}})$. $R_i$ increases again at the inflection point of the $c_v$ curve.

Fig. 4a shows these $R_i$ values calculated by finite differences for both LSM and LSCF as a function of effective cathodic overpotential, normalized to their respective values at OCV. LSM resistance decreases monotonically as the overpotential becomes
more negative – strong activation caused by cathodic polarization. The resistance of LSCF does not decrease very much before it starts to increase again.

Now, examine the following thought experiment. Suppose that the bulk defect chemistry of LSCF is computed according to reference. With this defect chemistry is associated some standard free energy of oxygen reduction, $\Delta G_{\text{red}}^0$, which corresponds to the following standard bulk point defect equilibrium written in Kröger-Vink notation

$$\frac{1}{2} O_2 + V^-_O + 2B^+_B \leftrightarrow O^+_O + 2B_B$$

(S3)

where $B_B$ is an electron hole and $B^+_B$ is a neutral B-site (B refers to the ABO$_3$ perovskite structure). A very negative $\Delta G_{\text{red}}^0$ shifts the reaction in favor of oxygen reduction and a lower equilibrium concentration of oxygen vacancies. A less negative $\Delta G_{\text{red}}^0$ shifts it in favor of oxygen production and in favor of high oxygen vacancy concentration. The former case is similar to LSM.

If the value of $\Delta G_{\text{red}}^0$ is made more negative systematically and the defect equilibrium equations are solved for each value, the resulting trend of oxygen vacancies as a function of effective cathodic overpotential is shown in Fig. ESI6. As $\Delta G_{\text{red}}^0$ becomes more negative the equilibrium oxygen vacancy concentration not only decreases, but the overpotential at which the inflection point occurs is shifted to more negative cathodic overpotentials. From the prior analysis, it was shown that the inflection point leads to an increase in the resistance with further decrease of the cathodic overpotential. Therefore, the tighter oxygen binding associated with decreased $\Delta G_{\text{red}}^0$ forces the increase in resistance to more extreme cathodic overpotentials and thus causes better
cathodic activation. The normalized resistances associated with these values of $\Delta G_{red}^0$ are shown in Fig. 4b.

Fig. ESI6: Oxygen vacancy concentration versus effective cathodic overpotential for LSCF 6428 and LSCF with modified $\Delta G_{red}^0$.

Of course, the exact trend of $R_i$ is very dependent upon the precise kinetics used in the current expression. In fact, changing the expression does change the slope of the LSCF $R_i$ curve as well as the location of its minimum. The preceding argument is intended to illustrate the strikingly different behavior of oxygen vacancies with cathodic polarization in LSM and LSCF and how it dramatically impacts the bulk pathway. A surface layer that is strongly activated under cathodic polarization has the potential to be somewhat blocking at OCV but much more active toward oxygen reduction under cathodic polarization.

Section ESI 4 Promoted Adsorption/Dissociation Model

The model presented in section 3.3.3 links solid-phase point defect and adsorbed oxygen concentrations expected under a steady state cathodic polarization to the rate of oxygen reduction via Equations 6-8 in the main text. The model is surface-specific in
that it neglects sources of losses not associated with the air-MIEC surface. The intention of this section is to provide supporting details for that model.

In the rate equations, the surface potential difference across the surface, \( \chi_{ms} \), was approximated using a parallel plate capacitor model

\[
\chi_{ms} = \frac{dQ}{\varepsilon_0} = \frac{dF}{2\varepsilon_0} (2\gamma + \theta)
\]

(S4)

where \( Q \) is the surface charge per unit area, \( \Gamma \) is the density of surface adsorption sites, \( d \) is the distance of separation between the adsorbates and surface, and \( \varepsilon_0 \) is the permittivity of free space. The values of these quantities are listed in Table ESI1.

Table ESI1: Blank LSCF parameters specified for the simulation.

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<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
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<tr>
<td>( k_{ads.f} )</td>
<td>4.5x10^0</td>
<td>mol m^-2 s^-1 atm^-1</td>
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<tr>
<td>( k_{ads.b} )</td>
<td>1.7x10^-10</td>
<td>m^4 mol^-1 s^-1</td>
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<tr>
<td>( k_{diss.f} )</td>
<td>5.0x10^-3</td>
<td>m s^-1</td>
</tr>
<tr>
<td>( k_{diss.b} )</td>
<td>3.4x10^-10</td>
<td>m^4 mol^-1 s^-1</td>
</tr>
<tr>
<td>( k_{inc.f} )</td>
<td>2.8x10^-3</td>
<td>m s^-1</td>
</tr>
<tr>
<td>( k_{inc.b} )</td>
<td>1.1x10^-9</td>
<td>m^4 mol^-1 s^-1</td>
</tr>
<tr>
<td>( c_{O/site} )</td>
<td>7.9x10^4</td>
<td>mol m^-3</td>
</tr>
<tr>
<td>( \Delta G_{red}^{0(LSCF)} )</td>
<td>-1.0x10^9</td>
<td>eV</td>
</tr>
<tr>
<td>( \Delta G_{ads}^{0(LSCF)} )</td>
<td>-3.0x10^-1</td>
<td>eV</td>
</tr>
</tbody>
</table>
The rate equations were developed with the implicit assumption that elementary steps preceding and following the rate limiting step were at equilibrium. The adsorption reaction was assumed to proceed as follows:

\[
O_2(g) + s \leftrightarrow O_2(s) \quad (S5)
\]

\[
*_{rls} \quad O_2(s) \leftrightarrow O_2^-(s) + h^-
\]

\[
O_2^-(s) \leftrightarrow O_2^{2-}(s) + h^-
\]

where the second step is rate-limiting. Equilibrium of the reactant and product in the second step with preceding and subsequent steps leads to the rate expression of Equation 6. A further assumption was that the surface site fractions \([O_2(s)]\) and \([O_2^-(s)]\) are minimal and may be neglected when expressing the concentration of free surface sites as \((1-\gamma-\theta)\). Finally, we neglected the role of neutral B-sites in Equation 6-8, including only the mass-action effect of electrons holes associated with B-sites. Mass action of neutral B-sites may be important in the rate of reaction of hopping-type, small-polaron conductors but there is very little literature discussing it and is still a matter under theoretical investigation.

Likewise, the dissociation reaction was divided into elementary steps as

<table>
<thead>
<tr>
<th>(\Delta G_{\text{diss}}^{0(\text{LSCE})})</th>
<th>-1.4x10^{-1}</th>
<th>eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>(T)</td>
<td>9.73x10^{2}</td>
<td>K</td>
</tr>
<tr>
<td>(\Gamma)</td>
<td>1.0x10^{-3}</td>
<td>mol m^{-2}</td>
</tr>
<tr>
<td>(d)</td>
<td>1.0x10^{-10}</td>
<td>m</td>
</tr>
</tbody>
</table>
\[ \text{*rls} \quad O_2^-(s) + V_o^- \leftrightarrow O_o^+ + O^-(s) \quad (S6) \]

\[ O_o^+ \leftrightarrow O_o^+ + h^- \]

and the incorporation reaction divided as

\[ \text{*rls} \quad O^-(s) + V_o^- \leftrightarrow O_o^+ + ^* \quad (S7) \]

\[ O_o^+ \leftrightarrow O_o^+ + h^- \]

in order to generate the reaction rates in Equations 7-8.

Of course, assuming different elementary steps or a different set of overall adsorption, dissociation, or incorporation reactions would result in different kinetics. We justify our assumptions because we are aware of no conclusive identification of LSCF surface reaction mechanisms but do note that vacancy mediated adsorption/dissociation has been suggested for LSF\textsuperscript{6,7} and LSM.\textsuperscript{18}

The rate expressions for adsorption associated with a total current, \( i \), of oxygen reduction on the surface was

\[ i = -4F \dot{r}_{\text{ads}} \quad (S8) \]

In order to use the rate expressions for \( r_{\text{ads}} \) and \( r_{\text{inc}} \) corresponding to a given \( \eta \), the concentration of solid-state point defects (oxygen vacancies, electron holes) at the surface as well as the surface oxygen coverage (\( \gamma, \theta \)) should be known. Values of \( c_v \) and \( c_h \) were determined from the Brouwer diagram, as described in section ESI 3.

Having established the point defect concentrations inside the MIEC surface at equilibrium and under a bias, \( \gamma \) and \( \theta \) should then be determined. If the rate constants are
specified (equivalent to specifying $\Delta G_{\text{ads}}^{\text{eq}}$), then the equilibrium value, $\gamma_0$ and $\theta_0$, can be computed simply by setting the equilibrium rate of adsorption and incorporation to zero and solving the set of nonlinear equations.

Under bias, the reaction rates are not zero and so the surface species cannot be determined from a single set of forward and backward rates. Instead, steady state requires that the rate of these reactions be the same, e.g. $r = r_{\text{ads}} = r_{\text{diss}} = r_{\text{inc}}$ where $r$ is the overall oxygen reduction rate. Imposing that condition allows the solution of

$$0 = r_{\text{ads}} - r_{\text{diss}} \quad \text{(S9)}$$

$$0 = r_{\text{diss}} - r_{\text{inc}} \quad \text{(S10)}$$

for $\gamma$ and $\theta$ under bias.

With the concentrations at equilibrium and under a bias known, $i$ can be computed from Equation S8. The overall interfacial resistance, $R_i$, is computed from the change of current and overpotential at steady state by Equation 2 of the main text. We approximated this derivative by calculating $i$ at discrete values of $\eta$ using the link to defect chemistry and surface coverage already examined and then using finite differences.

The parameters used in the simulation of the blank LSCF appearing in Fig. 4c and d are listed in Table ESI1. The values of the quantities derived from them are listed in Table ESI2.
Table ESI2: Blank LSCF derived quantities, solved for based upon specified parameters at $pO_2 = 0.21$ atm.

<table>
<thead>
<tr>
<th>Parameter Name</th>
<th>Value</th>
<th>Units</th>
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<tr>
<td>$c_v^0$</td>
<td>$2.0 \times 10^2$</td>
<td>mol m$^{-3}$</td>
</tr>
<tr>
<td>$c_h^0$</td>
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<td>mol m$^{-3}$</td>
</tr>
<tr>
<td>$\gamma_0$</td>
<td>$7.0 \times 10^{-3}$</td>
<td>unitless</td>
</tr>
<tr>
<td>$\theta_0$</td>
<td>$2.0 \times 10^{-2}$</td>
<td>unitless</td>
</tr>
<tr>
<td>$k_{ads}^0$</td>
<td>$1.0 \times 10^{-1}$</td>
<td>mol m$^{-2}$ s$^{-1}$</td>
</tr>
<tr>
<td>$k_{diss}^0$</td>
<td>$6.3 \times 10^{-4}$</td>
<td>mol m$^{-2}$ s$^{-1}$</td>
</tr>
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<td>$k_{inc}^0$</td>
<td>$1.0 \times 10^{-1}$</td>
<td>mol m$^{-2}$ s$^{-1}$</td>
</tr>
</tbody>
</table>

Based upon the surface exchange coefficient$^{10}$ and assuming that oxygen dissociation is the rate limiting step at equilibrium.

The equilibrium surface coverage, $\gamma_0$ and $\theta_0$, relate to the free energies of reaction of the adsorption and dissociation steps as follows:

$$K_{ads} = \exp\left( -\frac{\Delta G_{ads}^{0(LSCF)}}{RT} \right) = \frac{\gamma_0}{(1-\gamma_0-\theta_0)} x_h^2 pO_2^{-1} \exp\left( \frac{2F}{RT} \chi_m^\gamma \right) \quad (S11)$$

$$K_{diss} = \exp\left( -\frac{\Delta G_{diss}^{0(LSCF)}}{RT} \right) = \frac{\theta_0 x_O^0}{\gamma_0 x_v} x_h \exp\left( -\frac{F}{RT} \chi_m \right) \quad (S12)$$

where $x_h$ is the site fraction of electron holes associated with B-sites, $x_v$ and $x_O$ are site fraction of oxygen vacancies and filled oxygen sites, respectively, and the 0 superscript or subscript indicates the equilibrium value.

Likewise, the overall oxygen reduction equilibrium was written (see Equation S3)$^9$
\[
K_{\text{red}} = \exp\left( -\frac{\Delta G_{\text{red}}^{\text{LSCF}}}{RT} \right) = \frac{x^0_O}{x^0_{B_x}} \left( \frac{x^0_{B_x}}{x^0_{B_x}} \right)^2 pO_2^{-1/2}
\] (S13)

The quantities \(k_{\text{ads}}^0\) and \(k_{\text{inc}}^0\) in Table ESI2 indicate the forward/backward rate of oxygen adsorption and incorporation, respectively, at equilibrium (OCV). They were computed according to the following equations (c.f. Equations 6-8):

\[
k_{\text{ads}} = k_{\text{ads},f} pO_2 (1 - \gamma_0 - \theta_b) \exp\left( -\frac{\alpha_a F}{RT} \chi_{ms}^0 \right) = k_{\text{ads},b} \gamma_0 (c_v^0)^2 \exp\left( \frac{(2 - \alpha_a) F}{RT} \chi_{ms}^0 \right) \] (S14)

\[
k_{\text{diss}} = k_{\text{diss},f} \gamma_0 c_v^0 \exp\left( \frac{\alpha_d F}{RT} \chi_{ms}^0 \right) = k_{\text{diss},b} \gamma_0 c_O^0 c_h^0 \exp\left( \frac{(1 - \alpha_d) F}{RT} \chi_{ms}^0 \right) \] (S15)

\[
k_{\text{inc}} = k_{\text{inc},f} \theta_b c_v^0 \exp\left( \frac{\alpha_i F}{RT} \chi_{ms}^0 \right) = k_{\text{inc},b} (1 - \gamma_0 - \theta_b) c_O^0 c_h^0 \exp\left( \frac{(1 - \alpha_i) F}{RT} \chi_{ms}^0 \right) \] (S16)

In order to mimic LSM modification of the surface in Fig. 4c and d, we adjusted the parameters as a function of changes to bulk point defect concentrations, \(\theta\), and \(\gamma\) in that order, shifting them from their values associated with blank LSCF toward what we suspected for LSM. We assumed that if the concentration of an oxygen vacancy or either surface adsorbed species changed, the equilibrium exchange rate changed in direct proportion to it.

The use and modification of LSCF bulk defect chemistry and surface properties serves only as an instructive guide to the possible trends arising from an LSM coating. Over the long-term as the LSM(C) hybrid coating forms, the properties may be expected to be between these two extremes. The adjusted \(\Delta G_{\text{red}}^0\) mimicked the behavior of LSM in that the concentration of oxygen vacancies at OCV was much less than LSCF 6428 and the surface was more activated under bias. The standard free energy of adsorption, \(\Delta G_{\text{ads}}^0\),
and dissociation, $\Delta G_{diss}^0$, were also made more negative, simulating the suspected more energetically favorable adsorption/dissociation\textsuperscript{20} and consequently providing the surface with a larger adsorbed oxygen concentration.

Care must be taken in order to assure thermodynamic consistency with this approach. A chief concern is properly preserving the relationship between the forward and backward rate constants:

$$K = \frac{k_f}{k_b} \quad \text{(S17)}$$

A representative example of the surface parameter modification is given here for the dissociation reaction:

$$k_{diss}^0 \quad (^{(1)}_1) = k_{diss}^0 \quad (^{(0)}_0) \quad \frac{c_v^{(0(1))}}{c_v^{(0(0))}} \quad k_{diss,f}^{(1)} = k_{diss,f}^{(0)} \quad k_{diss,x}\quad (^{(1)}_1) = k_{diss,x}\quad (^{(0)}_0) \quad \frac{k_{diss}^{(1)}}{\theta_0^{(1)}} \quad \frac{c_{O}^{(0(1))} c_{h}^{(0(1))} \exp \left( \frac{-(1-\alpha_d)F}{RT} \chi_{ms}^{(0(1))} \right)}{c_v^{(0(0))}}$$

$$k_{diss}^{(0(2))} = k_{diss}^{(1)} \quad \frac{\theta_0^{(2)} \exp \left( \frac{-(1-\alpha_d)F}{RT} \chi_{ms}^{(0(2))} \right)}{\theta_0^{(1)} \exp \left( \frac{-(1-\alpha_d)F}{RT} \chi_{ms}^{(0(1))} \right)}$$

$$k_{diss,f}^{(2)} = \frac{k_{diss}^{(2)}}{\gamma_0^{(2)} c_v^{(0(2))} \exp \left( \frac{\alpha_d F}{RT} \chi_{ms}^{(0(2))} \right)} \quad k_{diss,x}\quad (^{(2)}_2) = k_{diss,x}\quad (^{(1)}_1)$$
The (0) superscript indicates the blank LSCF quantity and the (3) superscript indicates the final quantity used in Fig. 4c and d. The (1) superscript indicates changing the bulk defect concentration by manipulating $\Delta G_{\text{red}}^0$, the (2) superscript indicates changing $\theta_0$ by manipulating $\Delta G_{\text{ads}}^0$, and the (3) superscript indicates changing $\gamma_0$ by manipulating $\Delta G_{\text{ads}}^0$. Note that $c_v^{(0)(3)}=c_v^{(0)(2)}=c_v^{(0)(1)}$ because $c_v$, as a bulk quantity, is only changed from (0) to (1). The same logic applies to $\theta_0$ (changed in step 2) and $\gamma_0$ (changed in step 3) as well. The final quantities (3) are shown in Tables ESI3 and ESI4.

Table ES13: Modified LSCF derived quantities corresponding to Fig. 4c, solved for based upon specified parameters at $pO_2 = 0.21$ atm.

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<td>mol m$^{-3}$</td>
</tr>
<tr>
<td>$c_h^{(0)}$</td>
<td>$1.1 \times 10^4$</td>
<td>mol m$^{-3}$</td>
</tr>
<tr>
<td>$\gamma_0$</td>
<td>$9.8 \times 10^{-3}$</td>
<td>unitless</td>
</tr>
<tr>
<td>$\theta_0$</td>
<td>$2.5 \times 10^{-2}$</td>
<td>unitless</td>
</tr>
<tr>
<td>$k_{\text{ads}}^{(0)}$</td>
<td>$3.2 \times 10^{-1}$</td>
<td>mol m$^{-2}$ s$^{-1}$</td>
</tr>
<tr>
<td>$k_{\text{dis}}^{(0)}$</td>
<td>$2.1 \times 10^{-4}$</td>
<td>mol m$^{-2}$ s$^{-1}$</td>
</tr>
<tr>
<td>$k_{\text{inc}}^{(0)}$</td>
<td>$2.2 \times 10^{-2}$</td>
<td>mol m$^{-2}$ s$^{-1}$</td>
</tr>
</tbody>
</table>
Table ESI4: Modified LSCF derived quantities corresponding to Fig. 4d, solved for based
upon specified parameters at pO\textsubscript{2} = 0.21atm.

<table>
<thead>
<tr>
<th>Parameter Name</th>
<th>Value</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>(c_v^0)</td>
<td>1.1 \times 10^1</td>
<td>mol m\textsuperscript{-3}</td>
</tr>
<tr>
<td>(c_h^0)</td>
<td>1.1 \times 10^4</td>
<td>mol m\textsuperscript{-3}</td>
</tr>
<tr>
<td>(\gamma_0)</td>
<td>9.8 \times 10^{-3}</td>
<td>unitless</td>
</tr>
<tr>
<td>(\theta_0)</td>
<td>2.5 \times 10^{-2}</td>
<td>unitless</td>
</tr>
<tr>
<td>(k_{ads}^0)</td>
<td>3.2 \times 10^{-4}</td>
<td>mol m\textsuperscript{-2} s\textsuperscript{-1}</td>
</tr>
<tr>
<td>(k_{diss}^0)</td>
<td>2.6 \times 10^{-4}</td>
<td>mol m\textsuperscript{-2} s\textsuperscript{-1}</td>
</tr>
<tr>
<td>(k_{inc}^0)</td>
<td>6.8 \times 10^{-3}</td>
<td>mol m\textsuperscript{-2} s\textsuperscript{-1}</td>
</tr>
</tbody>
</table>

The assumption that underlies this scheme is that when the reactant appears as a
first order term, e.g. \(c_v^0\) in one direction, it modifies the equilibrium exchange rate in
direct proportion to its change and also that the associated rate constant is not changed. If
the species is on the surface, then the surface potential term is included as well. Since the
associated rate constant is not changed, the activation energy barrier in that direction is
unchanged and therefore all changes to the rate of reaction in that direction are
configurational, not energetic.

As previously mentioned, the rate constant in the opposing direction is related via
the equilibrium constant for the step. Since the equilibrium constant changes due to a
change in the step free energy of reaction but the forward rate constant does not, then the
backward rate constant must change as shown. This modification means that the
opposing direction activation energy is modified.
Constant activation energy in one direction while requiring the activation energy in the other direction to change is somewhat arbitrary. Unfortunately, no information is available about the comparative nature of the transition states. Therefore, the most straightforward approach is to ignore any change to the activation energy in the direction that directly involves the modified quantity while allowing thermodynamics to dictate the reverse quantity.

The effect of varying the different parameters is shown in Fig. ESI7, assuming that the dissociation reaction is rate-limiting in the case of blank LSCF. The equilibrium concentration of $O^-(s), \theta_0$, has little effect upon the interfacial resistance except at large polarization (part a). However, increasing the equilibrium concentration of $O^{2-}(s), \gamma_0$, has a significant effect in lowering the interfacial resistance at all bias (part b). A more negative $\Delta G_{\text{red}}^0$ and hence fewer oxygen vacancies (part c) causes $R_i$ to increase near OCV, but its superior activation causes $R_i$ to be decrease to less than the blank value at large overpotential.

We also examined the effect of lowering the activation energy barrier in both directions by modifying the equilibrium exchange rates $k_{\text{ads}}^0$ and $k_{\text{diss}}^0$. This change in reaction barrier would be expected to increase the equilibrium rate of exchange by increasing the forward and backward rate constants in proportion to one another but leaving the overall reaction free energy the same. This corresponds to a true catalytic enhancement on the surface due to LSM coating. Increasing the adsorption exchange rate (part d) has little effect except at large overpotential because adsorption is not rate limiting near OCV. Increasing the dissociation rate constant (part e), in contrast, suppresses $R_i$ significantly near OCV.
Fig. ESI7: Normalized resistance plots for the case of increased a) $\theta_0$, b) $\gamma_0$, c) more negative $\Delta G_{\text{red}}^0$, d) increased equilibrium exchange rate for adsorption, $k_{\text{ads}}^0$, and e) increased equilibrium exchange rate for dissociation, $k_{\text{diss}}^0$.

Fig. 4c and d of the main text shows the results of putting these different LSCF surface modifications together. Fig. 4c shows how an adjustment to the concentrations of oxygen vacancies and adsorbed surface species affects the performance. The trend is
very similar to that observed experimentally, with $R_i$ of the modified surface greater near OCV but less at large overpotential.  Fig. 4d incorporates a modification of $k_{diss}^0$ and a further modification of $\Delta G_{red}^0$.  A surface simulation with all of the chemical equilibria shifted toward those suspected for LSM from those associated with blank LSCF demonstrates electrochemical response similar to that observed experimentally, namely inferior performance near OCV but superior performance at moderate to large cathodic overpotentials.

When we shifted these reactions from their starting points associated with LSCF in the direction we suspected for LSM, the resulting simulations showed behavior that was qualitatively similar to the experimental results.  Interfacial resistance for the modified surface was larger than the blank LSCF at OCV but decreased more rapidly as cathodic overpotential increased, resulting in superior performance at larger cathodic overpotential.  This behavior resulted from more favorable and faster oxygen adsorption/dissociation kinetics despite more sluggish oxygen incorporation kinetics.  Similar behavior might be expected for an LSM(C) hybrid layer, though it may lie between the two extremes.
Electronic Supplementary Information References:


19. S. J. Benson, PhD, Imperial College, 1999.