Supporting Information:
How to get mechanistic information from partial pressure dependent current-voltage measurements of oxygen exchange on mixed conducting electrodes

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Samples

Figure S1: Cross section SEM image of a LSF film (100 nm) on top of a YSZ single crystal (100) substrate.

Figure S2: Sketch of the three-electrode setup used in this study.
Impedance spectroscopy

Impedance spectra were measured at oxygen partial pressures from $2.5 \times 10^{-4}$ bar to 1 bar to determine the electrolyte resistance $R_{\text{offset}}$. Figure S3 displays the impedance spectra and the corresponding fits to the equivalent circuit shown in the inset. A CPE element with impedance $Z_{\text{CPE}} = -i(\omega T)^{-P}$ was used to model an imperfect capacitance. The fit results are listed in table S1 and the polarization resistance is also plotted in figure S4 versus the oxygen partial pressure. At low $p_{\text{O}_2}$ the data can be fit to a power law with an exponent of -0.73. Above 20 mbar the polarization resistance increases with $p_{\text{O}_2}$. This is consistent with the bend found for both anodic and cathodic current voltage curves in the same pressure region.

Figure S3: Impedance spectra (1 MHz to 100 mHz, 5 points per decade) measured between an LSF thin film electrode and the reference electrode at 600°C in various oxygen partial pressures. Symbols are measured data, lines are fits to the equivalent circuit shown in the inset. Only the low frequency semicircles/arcs were included in the fits.
Figure S4: Polarization resistance of a LSF film at 600 °C versus oxygen partial pressure (symbols) and fit to power law (line).

Table S1: Fit results for impedance spectra in different atmospheres between $2.5 \times 10^{-4}$ bar and 1 bar oxygen. Only the low frequency semicircle/arc was fitted.

| $p_{O_2}$ (bar) | $R_{\text{offset}}$ (Ω) | $R_{\text{pol}}$ (Ω) | $CPE_{\text{chem}} - T(\text{mF}^{1/P}\text{S}^{1-1/P})$ | $CPE_{\text{chem}} - P$ |
|-----------------|-------------------------|----------------------|---------------------------------|------------------|
| $2.5 \times 10^{-4}$ | 69.68 ± 0.11 | 1395.00 ± 11.47 | 2.317 ± 0.004 | 0.965 ± 0.001 |
| $5.0 \times 10^{-4}$ | 68.14 ± 0.06 | 671.50 ± 1.75 | 2.129 ± 0.003 | 0.964 ± 0.001 |
| $1.0 \times 10^{-3}$ | 65.79 ± 0.10 | 375.50 ± 1.15 | 1.824 ± 0.005 | 0.962 ± 0.001 |
| $2.5 \times 10^{-3}$ | 63.65 ± 0.10 | 187.50 ± 0.52 | 1.534 ± 0.006 | 0.963 ± 0.002 |
| $5.0 \times 10^{-3}$ | 63.04 ± 0.08 | 117.60 ± 0.21 | 1.343 ± 0.005 | 0.966 ± 0.001 |
| $1.0 \times 10^{-2}$ | 62.67 ± 0.04 | 85.16 ± 0.11 | 1.229 ± 0.004 | 0.969 ± 0.001 |
| $2.5 \times 10^{-2}$ | 62.15 ± 0.04 | 44.89 ± 0.06 | 1.054 ± 0.004 | 0.969 ± 0.001 |
| $5.0 \times 10^{-2}$ | 61.35 ± 0.02 | 38.04 ± 0.03 | 0.944 ± 0.003 | 0.969 ± 0.001 |
| $1.0 \times 10^{-1}$ | 60.53 ± 0.01 | 41.22 ± 0.03 | 0.808 ± 0.002 | 0.971 ± 0.001 |
| $2.0 \times 10^{-1}$ | 59.97 ± 0.03 | 50.38 ± 0.06 | 0.671 ± 0.003 | 0.976 ± 0.001 |
| $5.0 \times 10^{-1}$ | 59.72 ± 0.06 | 102.30 ± 0.15 | 0.575 ± 0.003 | 0.985 ± 0.001 |
| 1.0 | 60.36 ± 0.09 | 285.30 ± 0.41 | 0.547 ± 0.002 | 0.991 ± 0.001 |
Deduction of a rate equation

Charge transfer at aqueous electrolyte|electrode interfaces is frequently studied and detailed models have been established, describing the corresponding current-voltage characteristics according to Butler-Volmer’s equation:\(^{S1,S2}\)

\[
 j = j_0 \cdot \left( e^{\frac{\alpha z |e\eta}{kT}} - e^{\frac{(\alpha - 1)z |e\eta}{kT}} \right). \tag{1}
\]

Here, \( j \) denotes the net current density, \( j_0 \) is the exchange current density and includes the reactant concentrations, \( \eta \) is the overpotential, \( \alpha \) represents the symmetry factor — for electronic transfer it is often close to 0.5 — and \( z \) is the charge number of the transferred species.

Electrochemical reactions at mixed conducting oxide electrode|gas interfaces, however, differ from aqueous reactions in several respects, making the analysis in terms of equation (1) unsuitable. First, the applied overpotential changes the oxygen chemical potential in the electrode bulk and thus modifies the concentration of point defects, i.e. the reacting species. Second, despite the possibly existing electrostatic potential difference \( \chi = \varphi_{\text{ode}} - \varphi_{\text{ads}} \) between the electrode bulk (\( \varphi_{\text{ode}} \)) and the adsorbate layer (\( \varphi_{\text{ads}} \)), an applied overpotential does not directly translate to a change of this surface potential. If \( \chi \) is caused by charged adsorbates, any overpotential driven change of this surface potential is correlated with a change in adsorbate concentration, and the resulting \( \chi - \eta \) relation can become quite non-trivial.\(^{S3}\)

Owing to these differences, a modified approach is required to describe the current-voltage characteristics of electrochemical reactions at solid electrode|gas interfaces. In the following we deduce such a model, i.e. a rate equation, for an exemplary mechanism and this can then be generalized. This mechanism is not necessarily the most realistic one, rather it is chosen for the sake of clarity.

Let us assume that the reaction consists of a reductive adsorption of molecular oxygen to form adsorbed \( \text{O}_2^- \) (2), followed by dissociative incorporation into the electrode (3) and
reduction to oxide ions (4), and let steps (2) and (4) be sufficiently fast compared to step (3), such that (3) is the rate determining step (rds).

\[ O_2 \leftrightarrow O_2^- + h^* \]  \hspace{1cm} (2)

\[ O_2^- + 2V_0^{\bullet\bullet} \rightarrow O_0^\bullet + O_0^{\bullet\bullet} \]  \hspace{1cm} (3)

\[ O_0^\bullet + O_0^{\bullet\bullet} \rightarrow 2O_0^{\bullet\bullet} + 3h^* \]  \hspace{1cm} (4)

Equations (2) and (4) include holes (h*) in the valence band but could also be formulated with electrons (e') from the conduction band, due to equilibrium of (2) and electron hole formation. The reaction rates of the rate limiting forward (\( \rightarrow r \)) and backward (\( \leftarrow r \)) ion transfers are then given by

\[ \rightarrow r = \tilde{k} \cdot [O_2][V_0^{\bullet\bullet}]^2 \]  \hspace{1cm} (5)

\[ \leftarrow r = \tilde{k} \cdot [O_0^{\bullet\bullet}][O_0^\bullet] \]  \hspace{1cm} (6)

with the surface potential dependent rate constants \( \tilde{k} \) and \( \tilde{k} \), and the normalized reactant concentrations \([O_2], [V_0^{\bullet\bullet}], [O_0^{\bullet\bullet}]\) and \([O_0^\bullet]\). The net reaction rate \( r \) is the difference between forward and backward reaction rates. Owing to equilibrium of the fast steps (2) and (4) the electrochemical potentials \( \tilde{\mu} \) of all species are related by

\[ \tilde{\mu}_{O_2} + \tilde{\mu}_{h^*} = \tilde{\mu}_{O_2} \]  \hspace{1cm} (7)

\[ 2\tilde{\mu}_{O_0^\bullet} + 3\tilde{\mu}_{h^*} = \tilde{\mu}_{O_0^\bullet} + \tilde{\mu}_{O_0^{\bullet\bullet}} \]  \hspace{1cm} (8)
Assuming $\bar{\mu}_i = \mu_i^0 + kT \ln [i] + z_i e \varphi_i$, yields (with $p_{O_2} = [O_2]$)

$$[O_2] = \frac{p_{O_2}}{[h^*]} \exp \left( \frac{\mu_{O_2}^0 - \mu_{h^*}^0 - \mu_{O_2}^0}{kT} \right) \exp \left( \frac{-z_{O_2} e \varphi_{ads} - z_{h^*} e \varphi_{ode}}{kT} \right) = \frac{p_{O_2}}{[h^*]} K_1 \exp \left( -\frac{e \chi}{kT} \right)$$

(9)

$$[O_0^\circ][O_0^*] = [h^*]^3[O_0^\circ]^2 \exp \left( \frac{2\mu_{O_3}^0 + 3\mu_{h^*}^0 - \mu_{O_0}^0 - \mu_{O_0}^{\circ*}}{kT} \right) = [h^*]^3[O_0^\circ]^2 K_3.$$  

(10)

Here, $\chi = \varphi_{ode} - \varphi_{ads}$ is the electrostatic potential difference between electrode bulk and adsorbate layer, $\mu_i^0$ is the standard chemical potential and $z_i$ is the charge number of species $i$ ($z_{O_2} = -1$ and $z_{h^*} = 1$). $K_1$ and $K_3$ are the purely chemical equilibrium constants of the preceding and succeeding equilibria without the factor due to the equilibrium surface potential. Combining equations (9), (10) with equations (5) and (6) yields

$$\overrightarrow{r} = k \frac{p_{O_2} [V_0^\circ]^2}{[h^*]} K_1 \exp \left( -\frac{e \chi}{kT} \right)$$

(11)

$$\overleftarrow{r} = \frac{k}{[h^*]^3}[O_0^\circ]^2 K_3.$$  

(12)

The rate determining transfer of $O_2^-$ from the adsorbate layer to the electrode bulk can be considered a jump of the $O_2^-$ ion over a spatial energy barrier, where initial and final state are at different electrostatic potentials $\varphi_{ads}$ and $\varphi_{ode}$, respectively. The activation barrier for this ion jump consists of a purely chemical term ($\overrightarrow{E}_{a,c}^\circ$ and $\overleftarrow{E}_{a,c}^\circ$) and an additional component due to the potential difference between the two phases ($\alpha z_{O_2} e \chi$ and $- (1 - \alpha) z_{O_2} e \chi$). The surface potential $\chi = \chi_0 + \Delta \chi$ includes the equilibrium surface potential $\chi_0$ and its deviation under current $\Delta \chi$; $\alpha$ reflects the symmetry of the energy barrier, see figure S5. Thus, we get

$$\overrightarrow{k} = k^0 \exp \left( -\frac{\overrightarrow{E}_{a,c}^\circ}{kT} \right) \exp \left( \frac{\alpha e \chi}{kT} \right)$$

(13)

$$\overleftarrow{k} = k^0 \exp \left( -\frac{\overleftarrow{E}_{a,c}^\circ}{kT} \right) \exp \left( -\frac{(1 - \alpha) e \chi}{kT} \right).$$  

(14)
with the pre-exponential factors $k^0$ and $k^0$ of the forward and backward ion transfer. As sketched in figure S5, the change in surface potential upon current $\Delta \chi = \chi - \chi_0$ modifies the equilibrium activation barriers by $\alpha z O_2 e \Delta \chi$ and $-(1-\alpha) z O_2 e \Delta \chi$ for the forward and backward reaction, respectively; a possible $\chi$ dependence of $\alpha$ is neglected. Combining equations (11) to (14) leads to

$$ \dot{r} = k^0 \exp \left( -\frac{E_{eq}}{kT} \right) \exp \left( \frac{\alpha e \chi_0}{kT} \right) \exp \left( \frac{\alpha e \Delta \chi}{kT} \right) K_1 \frac{pO_2^2 [V_{O^2}^\ast]^2}{[h^\ast]} \exp \left( -\frac{e (\chi_0 + \Delta \chi)}{kT} \right) \tag{15} $$

$$ \dot{r} = k^0 \exp \left( -\frac{E_{eq}}{kT} \right) \exp \left( -\frac{(1-\alpha) e \chi_0}{kT} \right) \exp \left( -\frac{(1-\alpha) e \Delta \chi}{kT} \right) K_3 [h^\ast]^3 [O^\ast]_O^2 \tag{16} $$

Thus, we get

$$ \dot{r} = r^0 pO_2 \frac{[V_{O^2}^\ast]^2}{[h^\ast]} \exp \left( \frac{(\alpha - 1) e \chi_0}{kT} \right) \exp \left( \frac{(\alpha - 1) e \Delta \chi}{kT} \right) \tag{17} $$

$$ \dot{r} = r^0 [h^\ast]^3 [O^\ast]_O^2 \exp \left( \frac{(\alpha - 1) e \chi_0}{kT} \right) \exp \left( \frac{(\alpha - 1) e \Delta \chi}{kT} \right) \tag{18} $$

with $r^0 = K_1 k^0 \exp \left( -\frac{E_{eq}}{kT} \right)$ and $r^0 = K_3 k^0 \exp \left( -\frac{E_{eq}}{kT} \right)$. One peculiar feature of this specific mechanism is the fact that forward and backward reaction have the same surface potential dependency, i.e both reaction rates decrease with increasing surface potential. The reason for this behavior is that in forward direction, the thermodynamic term of the preceding equilibrium $(-e \chi_0, -e \Delta \chi)$ adds to the kinetic term of the rate limiting ion transfer $(\alpha e \chi_0, \alpha e \Delta \chi)$ resulting in the same surface potential dependency as the kinetic factor of the backward reaction $((\alpha - 1) e \chi_0, (\alpha - 1) e \Delta \chi)$. The succeeding equilibrium does not contribute a surface potential dependency since no charge is transferred between the two phases. Equal surface potential dependencies of forward and backward rate can occur if a preceding equilibrium involves a charge transfer with the opposite direction of the charge transfer in the rate determining step. In general, however, different dependencies of $\dot{r}$ and $\dot{r}$ result.
This example shows how an expression for the reaction rate can be derived for a given mechanism. The same approach can be applied to different mechanisms, leading to rate equations of the generalized form

\[
\dot{r} = r_0 \rho_{O_2} \nu_c D \nu_D \exp\left(\frac{-\beta e\chi_0}{kT}\right) \exp\left(\frac{-\beta e\Delta\chi}{kT}\right)
\]

(19)

\[
\dot{\nu} = \nu_0 \rho_{O_2} \nu_c D \nu_D \exp\left(\frac{-\beta e\chi_0}{kT}\right) \exp\left(\frac{-\beta e\Delta\chi}{kT}\right)
\]

(20)

where \(r_0\) and \(\nu_0\) are prefactors including chemical equilibrium constants of the pre- and succeeding reactions as well as pre-exponential factors and chemical activation energies of the rate determining step. \(D\nu_c\) represents the product of defect concentrations with their corresponding reaction orders, \(\rho_{O_2}\) describes the oxygen partial pressure dependency via adsorbate species and \(\beta\) and \(\nu\) are factors depending on the mechanism. The equilibrium surface potential \(\chi_0\) generally depends on the oxygen partial pressure, since it is (partly) caused by charged adsorbates.\(^{3,5}\)

Since reaction rates are proportional to current densities we finally get

\[
j_c = -j_c^0 \rho_{O_2} \nu_c \nu_D \exp\left(\frac{-\beta_c e\chi_0}{kT}\right) \exp\left(\frac{-\beta_c e\Delta\chi}{kT}\right)
\]

(21)

\[
j_a = j_a^0 \rho_{O_2} \nu_a \nu_D \exp\left(\frac{-\beta_a e\chi_0}{kT}\right) \exp\left(\frac{-\beta_a e\Delta\chi}{kT}\right)
\]

(22)

for the anodic \((j_a)\) and cathodic \((j_c)\) current densities. As detailed above for the specific mechanism, \(\beta_a\) and \(\beta_c\) have non-trivial meanings, since they combine a thermodynamic effect of \(\chi\) (via steps in equilibrium) with the kinetic charge transfer effect of the rate limiting step.
Figure S5: The incorporation of an $O_2^-$ ion can be considered an ion jump over an activation barrier. Under equilibrium this energy barrier consists of a purely chemical energy contribution (1) with the activation energies $E_{eq,a,c}$ and $E_{eq,a,c}$ and an electrostatic potential term ($e\chi_0$) due to charged adsorbates (2). This potential term causes a modified energy barrier (4) with activation energies $E_{a,c} = E_{eq,a,c} - \alpha e\chi_0$ and $E_{a,c} = E_{eq,a,c} + (1 - \alpha) e\chi_0$. Under current flow, the surface potential changes from its equilibrium value (3), and this further modifies the energy barrier (5) and leads to activation energies of $E_{a} = E_{eq,a,c} - \alpha e\chi_0 - \alpha e\Delta\chi$ and $E_{a} = E_{eq,a,c} + (1 - \alpha) e\chi_0 + (1 - \alpha) e\Delta\chi$ for the forward and backward reaction.
References

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