Pulsed laser deposition (PLD) was performed using a 248 nm Kr-F-excimer laser (Compex Pro 201F, Coherent Lambda, Germany) operating 5 Hz pulse rate and 400 mJ pulse energy.

The oxygen background pressure in the PLD chamber and the substrate temperature (measured by pyrometer, (Heitronics, Germany)) and deposition time for each material are given in Table S1.

| Material          | temperature (°C) | pressure (mbar) | deposition time (min) | desired film thickness |
|-------------------|------------------|-----------------|-----------------------|------------------------|
| La$_{0.6}$Sr$_{0.4}$FeO$_{3-δ}$ | 650              | 0.04            | 45                    | 300 nm                 |
| La$_{0.6}$Sr$_{0.4}$CoO$_{3-δ}$ | 650              | 0.04            | 30                    | 300 nm                 |
| SrTi$_{0.7}$Fe$_{0.3}$O$_{3-δ}$ | 620              | 0.02            | 30                    | 300 nm                 |

Target preparation

LSF: commercial La$_{0.6}$Sr$_{0.4}$FeO$_{3-δ}$ powder (Sigma-Aldrich).

STF: solid state reaction of properly weighed SrCO$_3$, TiO$_2$ and Fe$_2$O$_3$ powders (STF73).

LSC: Pechini’s method[1].

All powders were isostatically pressed and sintered at 1200°C.

Phase purity of the targets was confirmed by powder XRD.
XPS spectra of Ti and La

XPS spectra of Ti (in STF) and La (in LSC and LSF) do not show changes of their oxidation states or distinct bulk and surface components. Only the binding energy is shifting as a function of the oxygen partial pressure.

The Ti 2p peaks show doublet splitting of 5.7 to 5.8 eV and a binding energy (Ti 2p$_{3/2}$) of 457.4 eV in oxidizing and 458.4 eV in reducing atmosphere. Typical binding energies reported for SrTiO$_3$ lie between the oxidizing and reducing value$^{[2]}$. Also the effective oxygen partial pressure in UHV lies between the used oxidizing and reducing atmosphere. The Ti 2p$_{1/2}$ peak is strongly broadened, which is typical for Ti 2p spectra.

The La peaks have a complex shape. In addition to the doublet splitting ($\Delta \approx 18$ eV) also strong satellites at 838 and 856 eV can be observed. These features can be attributed to charge transfer from the ligand atoms$^{[3]}$.

![Figure S1. XPS spectra of the Ti 2p (a) and La 3d peaks (b). The Ti 2p$_{1/2}$ peak is strongly broadened, which is typical for this component. Also the La 3d region shows doublet splitting and in addition strong satellite features (at 838 and 856 eV). These are caused by a charge transfer to a neighbouring atom. When the atmosphere is changed from oxidizing to reducing, the binding energy increases by roughly 0.9V, due to a Fermi level shift.](image-url)
The O1s surface component – effects of beam damage and polarization

The intensity of the surface oxygen component on the LSC and STF samples slowly decreases with irradiation time. When the beam spot is moved to another sample position, the initial surface oxygen intensity is almost restored (Figure S2 a-b). On these two materials, electrochemical polarization did not influence the surface oxygen intensity.

In contrast, on LSF the surface oxygen component irreversibly vanishes after an initial cathodic polarization.

Figure S2. O 1s spectra of LSC (a) and STF (b) in 0.5 mbar O₂ as a function of beam irradiation time. After 6-7 hours of irradiation the high binding energy component – probably OH groups – has decreased in intensity. After moving to a new position, the previous intensity is almost restored. This effect is stronger on STF.

(c) Subsequently recorded (top to bottom) XPS spectra of the O 1s region in LSF. The high binding energy (surface) component irreversibly disappears during an initial cathodic polarization, the effect of beam damage could therefore not be explicitly studied – the indicated potential is the set voltage, not η.
Electrochemical characteristics: Chemical capacitance

The impedance spectra of the electrodes were recorded also under polarization and fitted to a simplified equivalent circuit that uses an offset resistance and a parallel connection of resistor ($R_{\text{surface}}$) and constant phase elements ($Q_{\text{chem}}$) for the electrode arc. The impedance function of a constant phase element reads

$$Z_{CP} = \frac{1}{T(\omega)^p} \quad (S1)$$

From this fit, a chemical capacitance can be calculated\(^4\), using the relation

$$C_{\text{chem}} = (R_{\text{Surface}} \cdot 1-pT_{\text{chem}})^{\frac{1}{p}}. \quad (S2)$$

The chemical capacitance of a mixed conducting SOFC electrode is - in analogy to an electrostatic capacitance - the derivative of electronic charge in the working electrode ($Q_{\text{electron}}^{WE}$) by the overpotential ($\eta$). In order to maintain electroneutrality, this charge is compensated by a change in the oxygen ion content. It can therefore be seen as a measure for reducibility of the material under the investigated conditions.

$$C_{\text{chem}} = \frac{dQ_{\text{electron}}^{WE}}{d\eta} = -\frac{dQ_{\text{ion}}^{WE}}{d\eta} = -Vc_{\text{lattice}} \cdot z \cdot e \cdot \frac{d(3-\delta)}{d\eta}. \quad (S3)$$

$V$ is the sample volume, $c_{\text{lattice}}$ is the volume density of ABO\(_3\) unit cells, $z$ is the charge number of the mobile ion (-2 for oxygen), $\eta$ the overpotential of the electrode and $\delta$ the oxygen vacancy concentration per formula unit, e.g. La\(_{0.6}\)Sr\(_{0.4}\)FeO\(_3\)\(_{-\delta}\).

For surface limited electrode kinetics the overpotential can be used to calculate the oxygen partial pressure in the electrode bulk ($p_{O_2}$), using Nernst's equation

$$\ln\left(\frac{p_{O_2}}{p_{O_2}^0}\right) = \frac{\eta \cdot AE}{k_B T} \quad (S4)$$

where $p_{O_2}^0$ is the atmospheric oxygen partial pressure. Consequently, also the chemical capacitance can be written as function of the oxygen partial pressure. Using the simplifications $d(3-\delta) = -d$ and $d \ln\left(\frac{p_{O_2}}{p_{O_2}^0}\right) = d \ln(p_{O_2})$.

$$C_{\text{chem}} = Vc_{\text{lattice}} \cdot \frac{Be^2}{k_B T d\ln(p_{O_2})} \quad (S5)$$

The oxygen partial pressure in the oxide bulk can be changed by application of a bias according to eqn. S4. This way, the chemical capacitance can be plotted as a function of the oxygen partial pressure. Measurements in oxidizing and reducing atmospheres can be included in a single plot, by setting the atmospheric $p_{O_2}$ ($p_{O_2}^0$) to 0.5 mbar in oxidizing and to $3 \times 10^{-21}$ mbar\(^5\) in our reducing conditions. This leads to Figures S3 and S4 for LSF and STF, respectively.
In the case of LSF, the oxygen nonstoichiometry can be well described with a model assuming non-interacting point defects[6]. Using equation S3, the defect model can be used to calculate the chemical capacitance, indicated as a line in Fig. S3. The capacitances of this model correspond very well to the measured chemical capacitance.

Figure S3. Measured chemical capacitance of the LSF electrode as function of the effective oxygen partial pressure, according to eqn. S4. The open circuit \( p_{O_2} \) is 0.5 mbar in oxidizing and \( 3 \times 10^{-21} \) mbar in reducing conditions. The increased scatter under reducing conditions is probably connected with the segregation of Fe\(^0\). Solid line: calculated chemical capacitance of idealized LSF bulk (volume: 300 nm thickness, 11 mm\(^2\) area), using a defect chemical model from ref [6]. The different defect regimes correspond well with the measured chemical capacitance.
The chemical capacitance of SrTi_{0.7}Fe_{0.3}O_{3-\delta} was also measured during polarization and in different atmospheres. For comparison with literature, the oxygen nonstoichiometry data from ref [7] was taken and fitted to a simple point defect model, similar to LSF\[^6\], considering following defects:

- Oxygen vacancies \(V'_O\)
- \(\text{Fe}^{2+} (Fe'^{''}_{Ti})\), \(\text{Fe}^{3+} (Fe'_{Ti})\) and \(\text{Fe}^{4+} (Fe^{x}_{Ti})\)

These defects are coupled by following equilibrium reactions and equilibrium constants at 615°C:

- Oxygen exchange reaction
  \[
  \frac{1}{2}O_2 + 2Fe'^{''}_{Ti} + V'_O \rightleftharpoons O'_O + 2Fe'_{Ti} \quad K_{red} = \frac{\sqrt{pO_2[Fe'^{''}_{Ti}]^2[V'_O]}}{[O'_O][Fe'_{Ti}]^2} = 9 \times 10^{-18} \sqrt{\text{bar}}
  \]

- Disproportionation of iron (or electron hole pair generation)
  \[
  2Fe'_{Ti} \rightleftharpoons Fe^{x}_{Ti} + Fe'^{'}_{Ti} \quad K_{i} = \frac{[Fe^{x}_{Ti}][Fe'^{'}_{Ti}]}{[Fe'_{Ti}]^2} = 2.1 \times 10^{-8}
  \]

And following conservation laws:

- Conservation of Fe content (30 % doping)
  \[
  [Fe'^{''}_{Ti}] + [2Fe'^{'}_{Ti}] + [Fe^{x}_{Ti}] = 0.3 \text{ c}_{lattice}
  \]

- Conservation of oxygen lattice sites
  \[
  [V'_O] + [O'_O] = 3\text{c}_{lattice}
  \]

- Charge neutrality
  \[
  2[V'_O] = 2[Fe'^{'}_{Ti}] + [Fe^{x}_{Ti}]
  \]

The resulting calculated and measured chemical capacitances (Figure S4) show reasonable agreement, especially the intrinsic point where \([Fe'^{''}_{Ti}] = [Fe^{x}_{Ti}]\) fits perfectly to the measured values.

![Chemical capacitance of STF](image)

Figure S4. Measured chemical capacitance of the LSF electrode as function of the effective oxygen partial pressure, according to eqn. S4. The open circuit \(pO_2\) is 0.5 mbar in oxidizing and \(3 \times 10^{-21}\) mbar in reducing conditions. Solid line: calculated chemical capacitance of idealized STF bulk (volume: 300 nm thickness, 11 mm\(^2\) area), using oxygen nonstoichiometry data from ref [7]. The different defect regimes correspond well with the measured chemical capacitance.
Electrochemical characteristics: Current-voltage curves in 0.5 mbar O₂

Current-voltage characteristics in reducing atmosphere are given in the main text (Fig. 9). Here, DC characteristics in oxidizing conditions are shown for the sake of completeness. The current was normalized to the electrochemically active area of each electrode.

Figure S5. Current-voltage characteristics in oxidizing atmosphere. The electrochemical current density is highest for LSC, whereas LSF and STF lead to similar values. The higher catalytic activity of cobaltite perovskites has already been observed in literature. Also strong non-linearity in cathodic and anodic branches for all materials is clearly visible. The overpotential η is calculated by subtracting ohmic losses in the electrolyte from the applied potential.

Supporting references

1. Pechini, M., Method of Preparing Lead and Alkaline earth Titanates and Niobates and Coating Method using the same to form a Capacitor. *US patent US 3330697 A*, 1967.
2. Yoo, S.E., et al., Preparation of Strontium Titanate Thin Film on Titanium Metal Substrate by Hydrothermal-Electrochemical Method. *J. Am. Ceram. Soc.* 1990, 73, 2561-2563.
3. Sunding, M., et al., XPS Characterisation of In Situ Treated Lanthanum Oxide and Hydroxide Using Tailored Charge Referencing and Peak Fitting Procedures. *J. Electron Spectrosc. Relat. Phenom.* 2011, 184, 399-409.
4. Hirschorn, B., et al., Determination of effective capacitance and film thickness from constant-phase-element parameters. *Electrochi. Acta*, 2010, 55, 6218-6227.
5. Yao, Y., T. Xie, and Y. Gao, Handbook of physical chemistry. *Science and Technology Press, Shanghai*, 1985, 677.
6. Kuhn, M., et al., Oxygen nonstoichiometry, thermo-chemical stability and lattice expansion of La₀.₆Sr₀.₄FeO₃–δ. *Solid State Ionics*, 2011, 195, 7-15.
7. Kuhn, M., et al., Oxygen Nonstoichiometry and Defect Chemistry of Perovskite-Structured Ba₅Sr₁₋ₓTiₓ₋ₓFeₓO₃₋ₓ/₂₊δ Solid Solutions. *Chem. Mater.* 2013, 25, 2970-2975.