Support information

**XRD**

*Fig. 1s.* Portion of the LSCF XRD patterns calculated in the rhombohedral R-3 C H (black) and cubic Pm3m (red) space group. The arrows point out the reflections belonging to the rhombohedral crystallographic arrangement. The (113) reflection is evident only in the rhombohedral calculated pattern.

**EXAFS discussion**

The X-ray Absorption Near Edge Structure (XANES) spectra of the samples LSCF0.2Pd and LSCF0.8Pd (samples B and D) together with the reference Pd foil and PdO spectra are reported in Figure 2s. An attempt to reproduce the main features of the experimental spectra by weighing up the
measured Pd foil and the Pd metal oxide is also reported (green line): due to the sharp features of
the Pd foil, the only way to obtain some agreement with the data was that of underestimating the
metal contribution with respect to the EXAFS analysis reported in the main paper. Despite this
expedient, it is clear that the overall fitting is definitely unsatisfactory. Moreover, it is worth
noticing that the shift of the Pd K-edges toward higher energies, showed in detail in the left panel
enlargement of the Figure 2s, indicate an average Pd oxidation state higher than 2+. This is not
surprising because metal ions are known to be able to exist in such unusual oxidation states in the
perovskite structure.  

![Figure 2s](image)

**Figure 2s.** XANES spectra of samples LSCF0.2-Pd (B) and LSCF0.8-Pd (D), respectively, are
showed. The arrows in the right panel part indicate the bump due to the presence of contribution of
the metal component in the edge region. The arrow (in the left part) shows the $E_0$ of the Pd foil at
24350 eV.

In line with the XANES simulation, an EXAFS data analysis carried out by weighing up the
contributions of metallic and PdO phase was also exploited. Assuming that the palladium metal
clusters have an fcc structure, two $\gamma^2$ terms taking into account the first and second coordination shell were used. The first-shell Pd–Pd (R1) distance is linked to the fcc a-axis length $a$ by $R1 = a/(2)^{1/2}$, while the second neighbors are placed at a distance $R2$. The higher shells were calculated according to three-body contributions $\eta^3$: the third-shell term ($R3$), at $R3 = a(3)^{1/2}/2$, is relative to an isosceles triangle with two first neighbors constituted by $R1$ sides at an angle $\theta = 120^\circ$. The fourth shell contribution ($R4$), involving particularly strong multiple scattering contributions, is obtained from the degenerate ($\theta = 180^\circ$) triangle formed by three aligned first neighbors. Consequently, the lattice constant $a$ and the Debye–Waller factor ($\sigma^2$) were the only parameters needed to calculate the Pd metal environment.

Concerning the palladium oxide, it has a tetragonal space group (D4h9 – P44/mmc), where each Pd atom is surrounded by a slightly distorted square of oxygen atoms at 2.02369 Å. The four oxygens are actually in the form of a rectangle with sides 3.0434 and 2.682 Å. So, two $\gamma^2$ terms were considered to take into account the first (2.02369 Å) and second coordination shell (four Pd-Pd distance at 3.03 Å; moreover, one three-body configuration $\eta^3$ Pd-O-Pd was allowed, representing an isosceles triangle with two first-shell Pd-O distances as sides and an angle $\theta = 170^\circ$, involving a Pd-Pd distance of 3.34 Å. In the fitting procedure, a Pd-O first shell coordination number of 4 was fixed on the basis of the PdO crystal structure. However, this value was not able to reproduce the correct amplitude of Pd-O distance. When this parameter was released in the fitting process, its value increased up to 6, suggesting that the Pd cation has a local environment different from that of palladium(II)oxide. Moreover, the Pd-Pd distances in the oxide structure are, respectively, 3.03 and 3.34 Å, while no evidence of these distances is detectable in the spectrum. Details of this analysis are reported Figure 3s.
Figure 4s. EXAFS data analysis on the sample LSCF08-Pd performed by using Pd metal and Pd oxide (N=4) components respectively. The arrows indicate the most evident signals that are missing in this model.

XPS discussion on La and Sr components.

For all samples, the Sr 3d region shows two distinct 3d5/2 - 3d3/2 doublets at 132.5 and 134 eV respectively (see Fig. 5s and Fig. 6s, Fig. 7s, Fig. 8s). These two components have been already observed for all La-Sr based perovskites but the correct attribution is not clear. One hypothesis is that the higher binding energy component at around 134 eV is due to Sr in the perovskites lattice while the low energy component at 132.5 eV could be attributed to Sr\(^{2+}\) ions surrounded by vacancies in the oxygen-deficient perovskite structure.\(^{52}\)

On the contrary van der Heide, by studying similar surface at different take off angles, attributed the lower binding energy to the bulk component while the higher energy peak with the surface segregated strontium.\(^{53}\) Similarly Prasad associated the 132 eV components to the lattice and the high energy with the surface termination and surface secondary phases.\(^{54}\) This interpretation is in
accordance with Cai who attributed the high energy component to surface Sr(OH)$_2$-like species. As for the oxygen component, the larger differences are seen in the LSCF0.2 samples, in which an increase in the low energy component is seen upon addition of palladium. Regarding the La 3d$5/2$ region (see Fig. 6s), it is well known that the La3d spectra are split not only into two lines 3d$5/2$ and 3d$3/2$ (here not reported), but additionally each line is split due to the transfer of an electron from oxygen to La 4f, which is initially empty. The La 3d has, besides the main line, two satellites: a satellite peak SI at higher binding energy and SII towards lower binding energy. This last line, not always visible, is probably related to defects. In Table 1 the SII/M, where M is the main line, is given and, although a trend is not clearly recognizable between the different samples, it is remarkable that this SII component is quite large.

Figure 5s. Sr 3d high resolution XPS region for LSCF and LSCF-Pd samples.
Figure 6s. La 3d\textsubscript{5/2} high resolution XPS region for LSCF and LSCF-Pd samples.
Figure 7s. High resolution Co2p spectra for LSCF0.2 and LSCF0.2Pd and high resolution Fe 2p spectra for LSCF0.8 and LSCF0.8-Pd, respectively.
Figure 8s. Pd 3d high resolution region for LSCF0.2-Pd and LSCF0.8-Pd, respectively.
Table 1: H₂ (ml/g) consumption and temperatures of reduction peaks for LSCF and LSCF-Pd.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Reduction steps</th>
<th>Experimental H₂ consumption (ml/g)</th>
<th>Theoretical H₂ consumption (ml/g)</th>
<th>% of reduction for all Co/Fe species</th>
</tr>
</thead>
<tbody>
<tr>
<td>LSCF0.2</td>
<td>Co³⁺ → Co²⁺</td>
<td>39.6 (528 °C)</td>
<td>39.9</td>
<td>82.5 (Co)</td>
</tr>
<tr>
<td>1000 °C</td>
<td>Co²⁺ → Co⁰</td>
<td>59.2 (693 °C)</td>
<td>79.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Fe³⁺ → Fe⁰</td>
<td>25.2 (1006 °C)</td>
<td>29.9</td>
<td>84.3 (Fe)</td>
</tr>
<tr>
<td></td>
<td><strong>Total H₂ consumption (ml/g)</strong></td>
<td><strong>124.0</strong></td>
<td><strong>149.6</strong></td>
<td><strong>82.9 % overall reduction</strong></td>
</tr>
<tr>
<td>LSCF0.2-Pd</td>
<td>Pd⁴⁺ → Pd⁰ ∕ Co³⁺ → Co²⁺</td>
<td>42.6 (141 °C; 229)</td>
<td>42.6</td>
<td>86.4 (Co+Pd)</td>
</tr>
<tr>
<td>1000 °C</td>
<td>Co²⁺ → Co⁰</td>
<td>62.7 (690 °C)</td>
<td>79.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Fe³⁺ → Fe⁰</td>
<td>21.5 (1004 °C)</td>
<td>25.3</td>
<td>85.0 (Fe)</td>
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<tr>
<td></td>
<td><strong>Total H₂ consumption (ml/g)</strong></td>
<td><strong>126.8</strong></td>
<td><strong>147.2</strong></td>
<td><strong>86.1 % overall reduction</strong></td>
</tr>
<tr>
<td>LSCF0.8</td>
<td>Co³⁺ → Co⁰</td>
<td>18.0 (428 °C)</td>
<td>30.2</td>
<td>59.6 (Co)</td>
</tr>
<tr>
<td>1000 °C</td>
<td>Fe³⁺ → Fe⁰</td>
<td>60.5 (967 °C)</td>
<td>120.7</td>
<td>50.0 (Fe)</td>
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<td></td>
<td><strong>Total H₂ consumption (ml/g)</strong></td>
<td><strong>78.5</strong></td>
<td><strong>150.8</strong></td>
<td><strong>52.0 % overall reduction</strong></td>
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<tr>
<td>LSCF0.8-Pd</td>
<td>Pd⁴⁺ → Pd⁰ ∕ Co³⁺ → Co⁰</td>
<td>24.1 (121 °C; 445 °C)</td>
<td>33.0</td>
<td>73.0 (Co+Pd)</td>
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<td>1000 °C</td>
<td>Fe³⁺ → Fe⁰</td>
<td>65.2 (945 °C)</td>
<td>115.4</td>
<td>56.5 (Fe)</td>
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<td><strong>Total H₂ consumption (ml/g)</strong></td>
<td><strong>89.3</strong></td>
<td><strong>148.4</strong></td>
<td><strong>60.2 % overall reduction</strong></td>
</tr>
</tbody>
</table>

References

S1 M. M. Natile, F. Poletto, A. Galenda, A. Glisenti, T. Montini, L, De Rogatis, P. Fornasiero, 


