

**Supporting Information: *In-situ* techniques reveal the true capabilities of
SOFC cathode materials and their sudden degradation due to omnipresent
sulfur trace impurities**

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1 XPS spectra of LSC electrode during AP-XPS measurements:

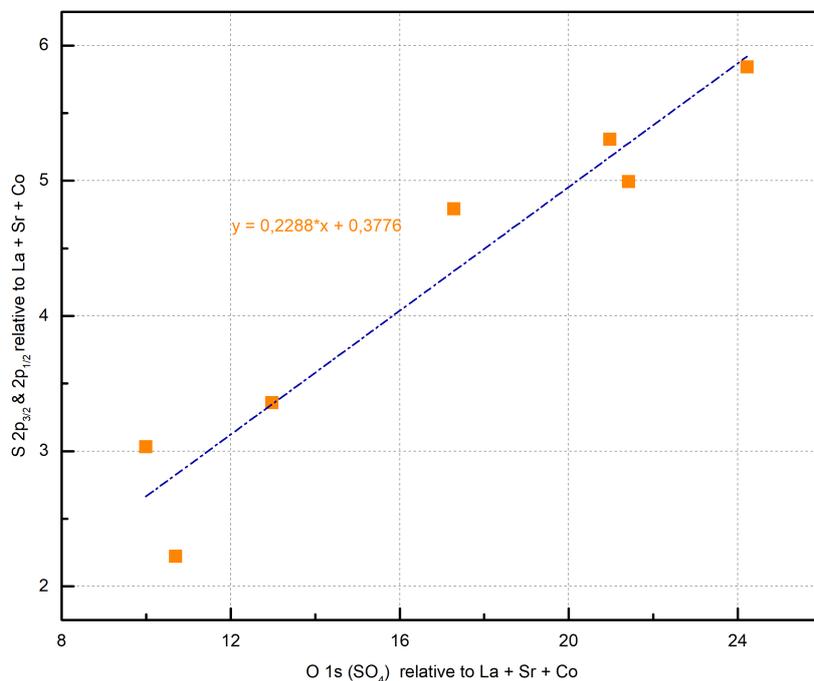


Figure S1: Linear correlation between the S 2p peak area (relative to La + Sr + Co) plotted versus the O 1s (SO₄) area (relative to La + Sr + Co). The observed slope corresponds well with the stoichiometric ratio of SO₄

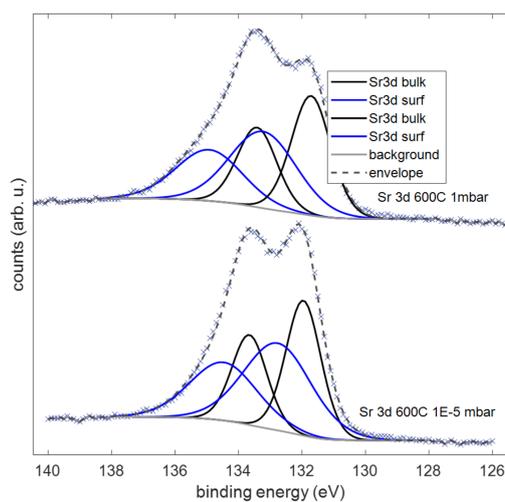


Figure S2: Spectra in the Sr 3d binding energy region of the LSC electrode.

In Figure S1 the S 2p peak area is plotted versus the O 1s area. Linear fitting of the data points yields a slope of 0.228, which corresponds well to the stoichiometric ratio observed in SO₄. More-

over, in Figure S2 the Sr 3d binding energy region is plotted. The measurements revealed that no significant change in the Sr 3d binding energy region occurred over time, which allows us to exclude Sr segregation as reason for the strong performance loss observed in our measurements. The Sr-3d spectra recorded at 10^{-5} mbar were measured on a pristine SO_4 free surface, whereas a significant SO_4 coverage was detected when conducting the measurements at 1 mbar. Mostly likely the counter ion for SO_4 is a surface strontium ion. Therefore the surface strontium ions undergo a chemical transition from SrO-like to SrSO_4 -like surface terminations, which is reflected by a change in the binding energy of the Sr-3d component.

2 LSC and PCO electrodes directly after *i*-PLD measurements:

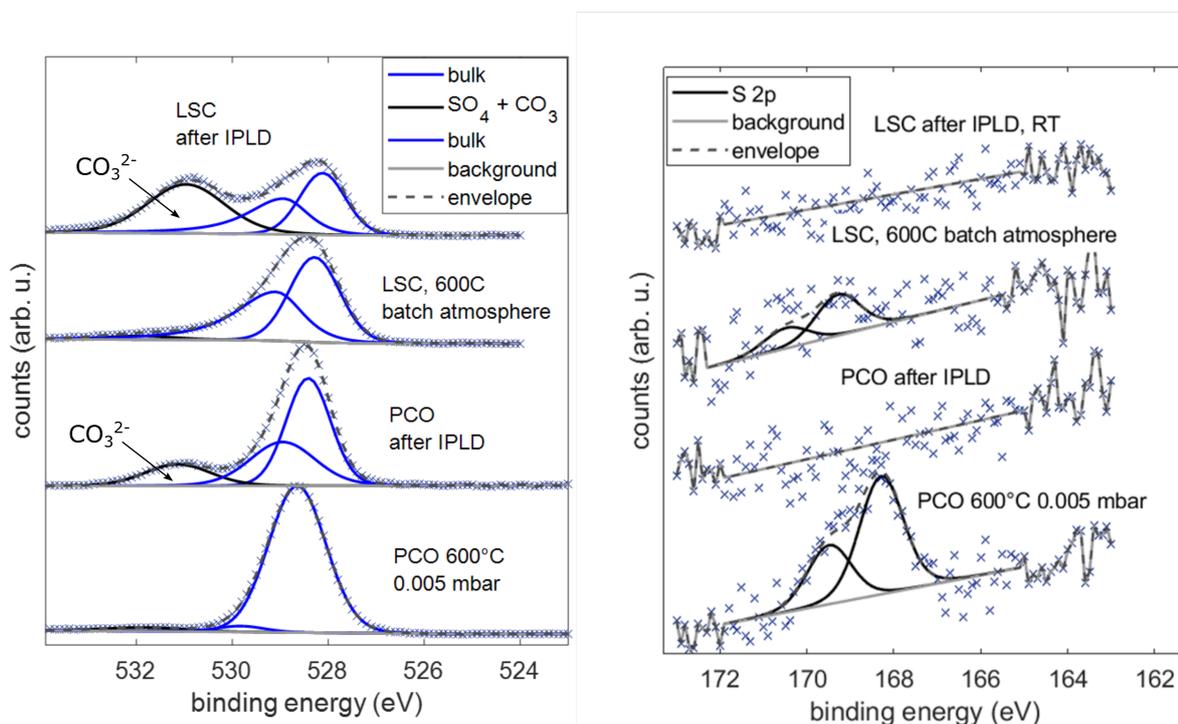


Figure S3: Spectra of O 1s and S 2p binding energy of an LSC and PCO electrode directly after *i*-PLD measurements.

The investigated LSC and PCO electrodes were annealed at 600 °C in synthetic air in the *i*-PLD for 12 h. As visible in figure S3, conducted XPS measurements revealed sulfur free surfaces directly after the *i*-PLD. After heat up of the electrodes to 600 °C in the setup of the AP-XPS, sulfur contaminations were detected on the electrode surface. This is in excellent accordance to the superior oxygen exchange kinetics observed during *i*-PLD measurements.

3 X-ray fluorescence spectroscopy (XRF):

In Figure S4 the powder obtained from the PLD walls was analyzed by X-ray fluorescence spectroscopy (XRF). XRF found that the powder was mostly composed of La (20,4 %), Mn (18,6 %), Co (13,2 %) and Sr (11,8 %). It was not possible to detect residual amounts of sulfur as the emission lines of sulfur overlap with emission lines of Co.

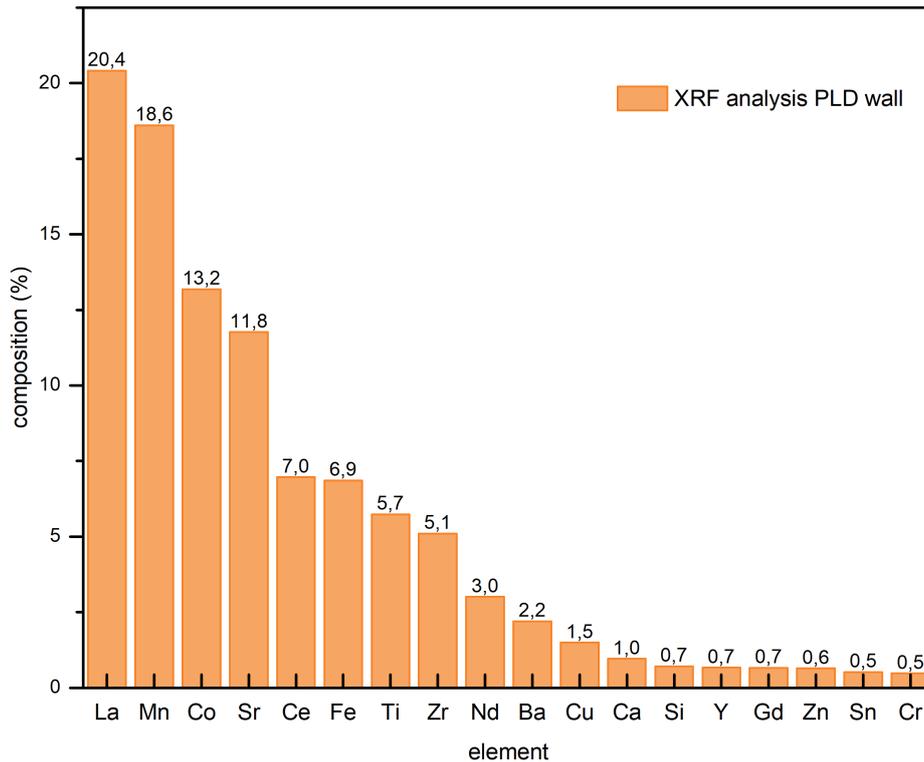


Figure S4: Analysis of powder scraped from the PLD wall.