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Supplementary information

Strain Effects on Co Oxidation State and the Oxygen Dissociation Activity in Barium Lanthanum Cobaltite Thin Films on Y_2O_3 stabilized ZrO_2

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Target substrate preparation

Barium Lanthanum Cobaltite is synthesised via a sol-gel route. $La(NO_3)_3*H_2O$ (Wako Pure Chemical Industries), $Ba(NO_3)_3$ (Kishida Chemistry), $Co(NO_3)_3*H_2O$ (Kishida Chemistry) and citric acid (Wako Pure Chemical Industries) with molar ratios of 5:5:10:20 are dissolved in deionised water, making in total a solution of 200 ml, and 6-10 ml of ethylene glycol (Wako Pure Chemical Industries) is added. The solution is stirred and heated at 200°C until a dry powder is obtained. The dry powder is heated to 400°C for 2h with a heating and cooling rate of 200°C/h. After grinding the powder, it is sintered at 1200 °C with heating and cooling rates of 200°C/h. From this BLC powder and SDC powder (Daiichi Kigenso Kagaku Kogyo Co.), pellets are pre-pressed for 5 min, then in a hydraulic press at 300 MPa for 30 min. The BLC and SDC pellet is sintered at 1200°C for 6h, with heating and cooling at 200°C/h.

The BLC pellet shows a lattice constant of 3.89 A, like reported in literature for the target composition of $Ba_{0.5}La_{0.5}CoO_{3-d}$.

Compositional Analysis

Rutherford backscattering (RBS) and particle induced x-ray emission (PIXE) measurements were carried out to analyse the elemental ratios of the thin films, using a 2 MeV helium ion beam. Within the error bars, there are no significant differences, nor are there in comparison to fabrication batches.

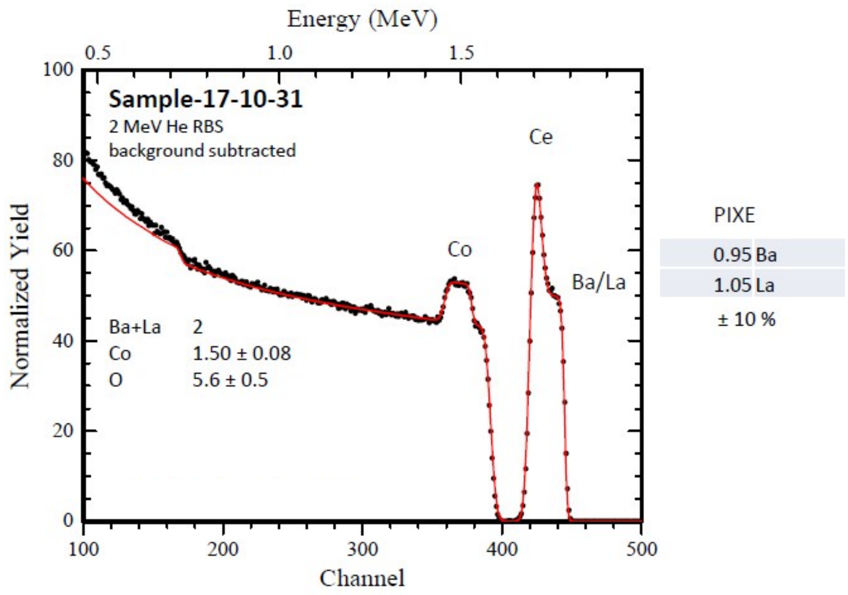

Figure S1: RBS and PIXE. The RBS measurement is shown for a 100 nm film on SDC-YSZ. On the right, the PIXE results for the Ba to La ratio is indicated.

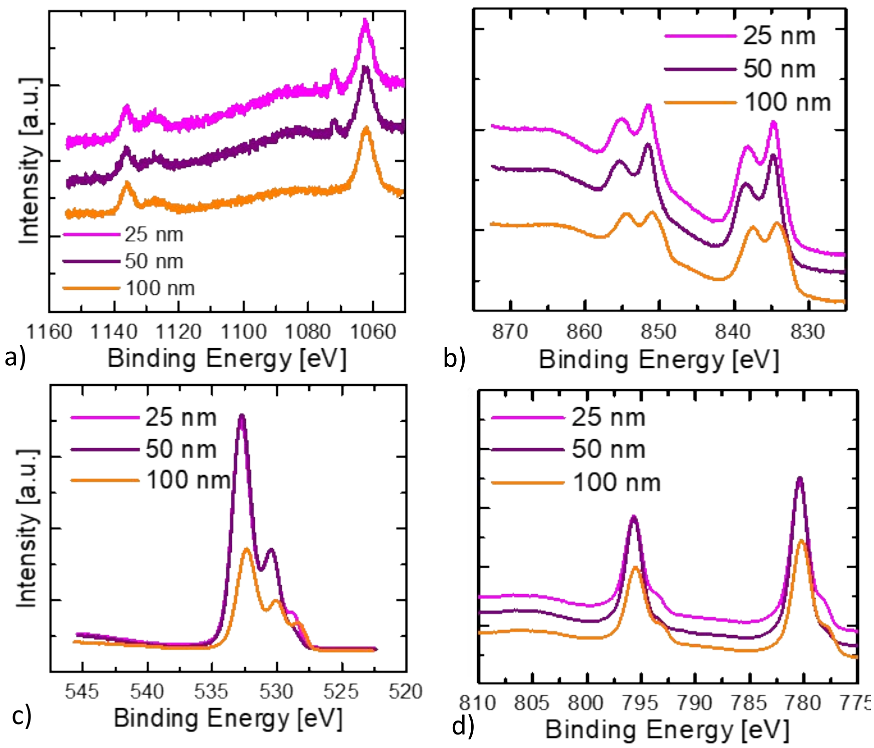

Figure S2: XPS analysis – examples for 25, 50 and 100 nm thick BLC films. a) La 3p and Ba3p, b) La3d, c) O1s, d) Co2p and Ba3d.

The measurement data is calibrated using C1s and a Shirley-type background is substratcted. For obtaining the elemental ratios displayed in the main text, figure 2, the following parts of the spectra are used: Co2p3/2, Ba3p, La3d3/2. For the Co2p fit, also the Ba3d was fitted as shown in the example in figure S3.

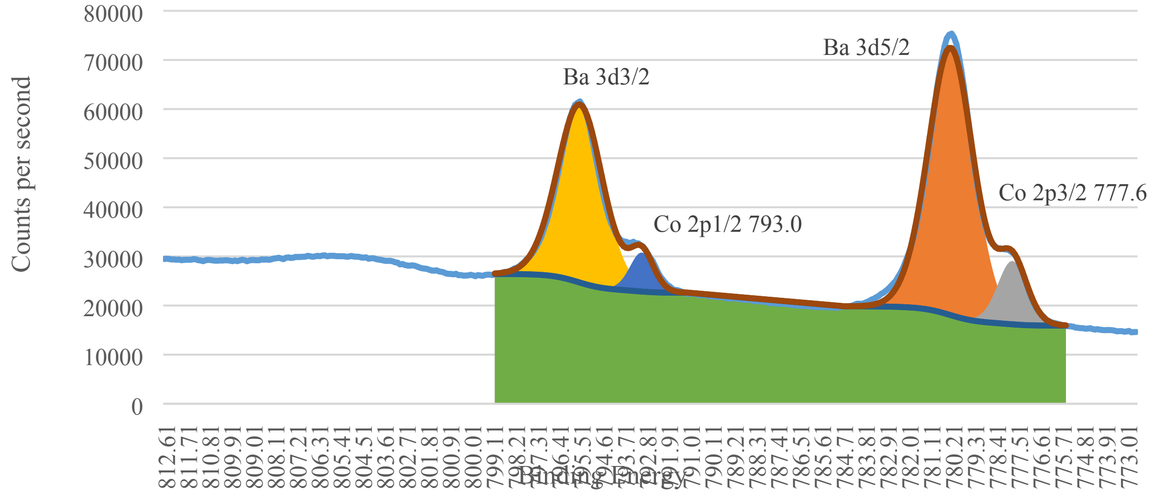

Figure S3: Example of fitting Co2p – Ba3d Spectra. This example shows the measurement of the 100 nm BLC film. The Shirley background is indicated in green.

<u>Setup for Conductivity Relaxation Studies</u>

Figure S3 shows important components of the measurement set-up. The gas inlet tube ends ~1 mm above the sample surface. To ensure a fast switching between gases, a 4 way valve is used, where Channel 1 goes to the cell and channel 2 to the exhaust or *vice versa*.

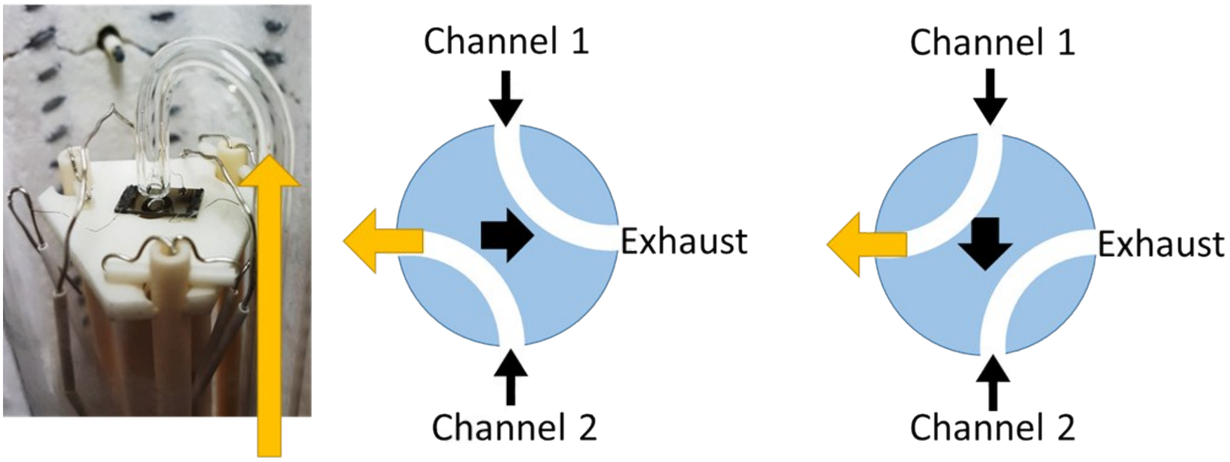

Figure S4: Sample holder and gas mixer sketch. A photograph of the sample holder is shown on the left, while the principle of the 4-way valve is sketched on the right.

While switching from N_2 to O_2 shows a kink in the R(t) curve, R(t) when switching from air to O2 and back is described well by equation…. As shown in the manuscript

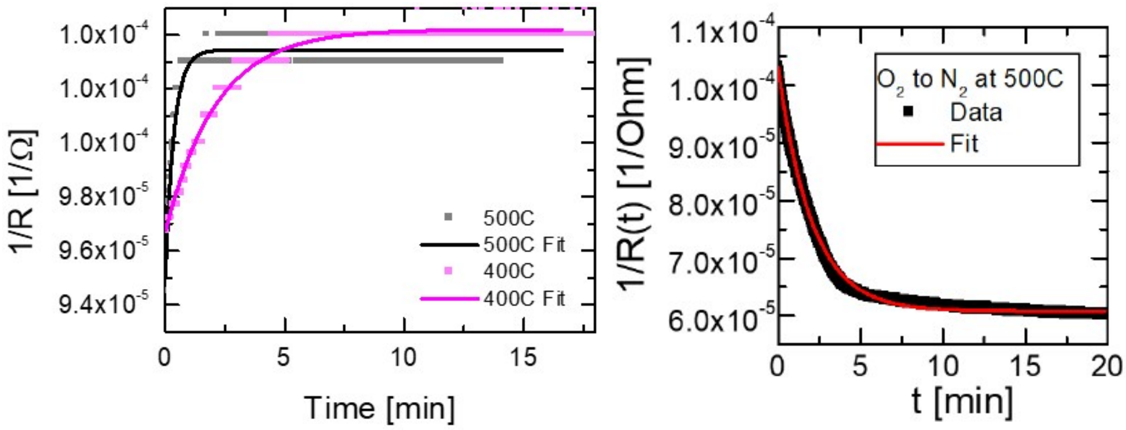

Figure S5: Fitting of ECR Measurements.

In the air-O2 switching regime, different sample positions with respect to the gas inlet do not affect the measurement result and neither does a change in the total flow rate between 50 and 100 sccm (maximum). Therefore, we conclude that the interdiffusion between the two gases can be neglected.

Python script for fitting ECR measurements

```
import os
import numpy as np
from lmfit import Parameters, Model
file_in = "C:/filepath/directory/filename.txt"
#2 column file:
#column1 = time [min] from gas switching
#column2 = 1/R [1/Ohm]
Rzero= resistance in gas 1 [Ohm]
h= film thickness [nm]
data = np.loadtxt(file_in)
t = data[:, 0]*60  #in seconds
oneoverR = data[:, 1]
# Data is recorded in 2s intervals, which is not accurate enough to
define the time of gas switching when k_chem is high. Therefore
tzero is introduced as an additional fitting parameter to correct
this. Units of k_chem: cm/s
def func(t, Rinf, tzero, k):
    return (1/Rinf-(1/Rinf-1/Rzero)*np.exp(-k*(t+tzero)/(h*1E-7)))
pv = Parameters()  #examples for starting values are inserted below
pv.add('Rinf', value=3000, vary=True)
pv.add('k', value=1E-7, vary=True)
pv.add('tzero', value=0, vary=True)
ymodel = Model(func)
result = ymodel.fit(oneoverR, t=t, params=pv)
```

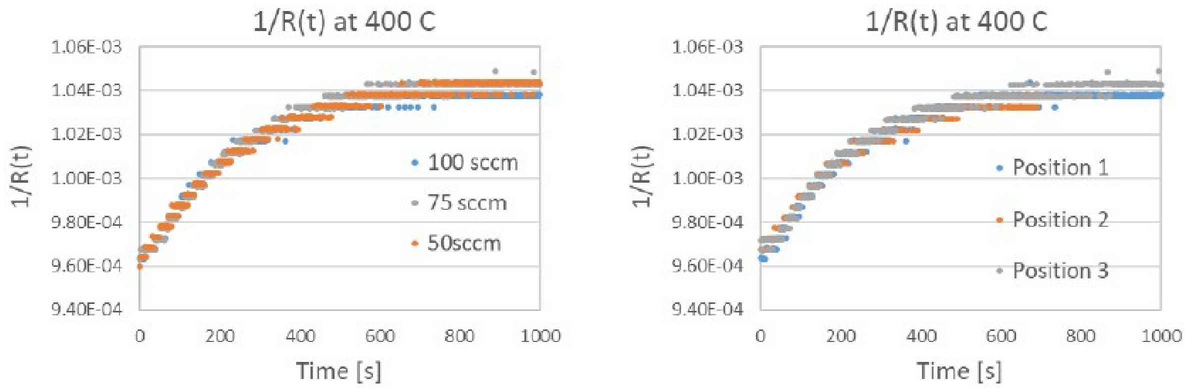

Figure S6: The influence of the total flow rate and the sample position with respect to the gas inlet. Changing the total flow from 50-100 sccm and changing the sample position within reason does not influence the conductivity relaxation measurement.

<u>Conductivity</u>

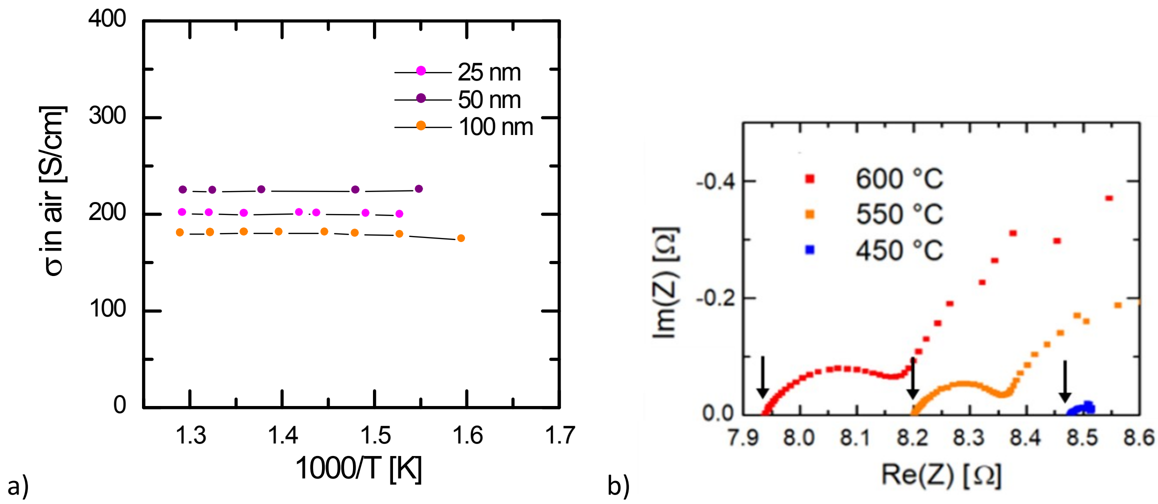

Figure S7: Conductivity in air and impedance spectroscopy. The conductivity of the three BLC films (a) is within the error bar as estimated from thickness and electrode geometry uncertainties: Assuming a 20 nm film with 200 S/cm and an electrode distance, the conductivity changes roughly by +/- 20 S/cm for a thickness error of +/-2nm, and by +/- 10 S/cm for an error in electrode distance of +/-0.2 mm. b) shows examples of impedance spectroscopy measurements in air performed on a thick film. Arrows indicate the points that correspond to the DC resistance which was used for the ECR measurements. It is noted, that Impedance Spectroscopy measurements are too slow to follow the air-O_2 switching.