Electronic Supplementary Material (ESI) for Nanoscale.


**Electrochemical stability of (La,Sr)$CoO_{3-\delta}$ in (La,Sr)$CoO_{3-\delta}$/(Ce, Gd)$O_{2-\delta}$ heterostructures**

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## 1. Electrical measurement cycling and thermal history

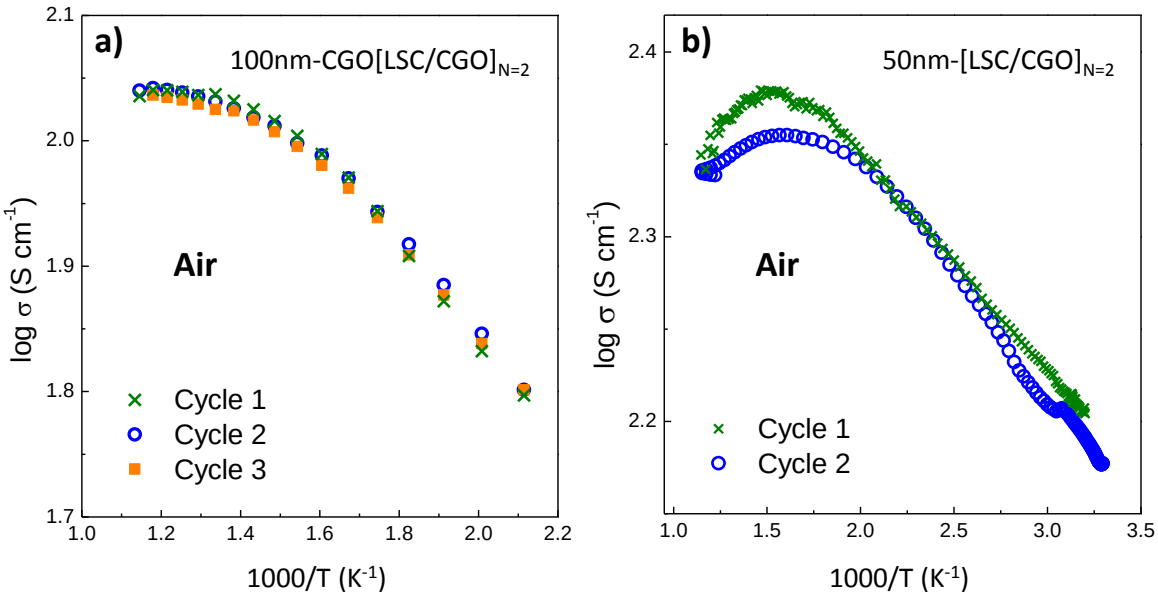


**Figure S1.** Arrhenius plot of (a) 100nm-CGO[LSC/CGO]$_{N=2}$ and (b) 50nm-CGO[LSC/CGO]$_{N=2}$ heterostructures measured in air after different thermal cycles of ca. 10 hours in the RT-600 ºC temperature range.

CGO-terminated samples are stable after different thermal cycles of thermal cycles of ca. 10 hours in the RT-600 ºC temperature range (Figure S1a), however, LSC-termination samples suffer from superficial carbonation and the electrical measurements are not reproducible (Figure S1b).

## 2. Evolution of the Sr-enriched species in the heterostructure without CGO termination.

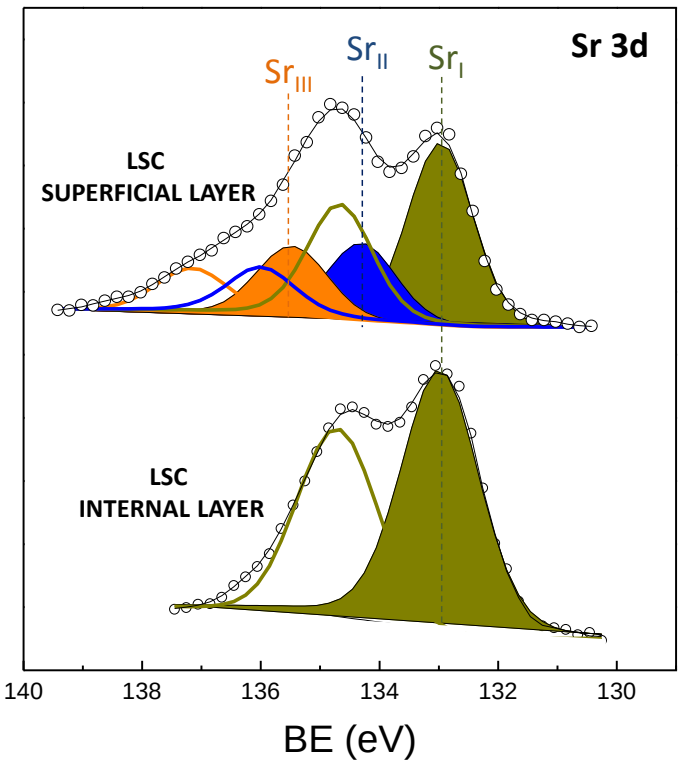


**Figure S2.** Sr 3d region of the photoelectron spectra for the superficial and internal LSC layer of the the 50nm-[LSC/CGO]$_{N=2}$ heterostructure (without CGO termination).

The chemical instability of the samples without CGO termination after the electrochemical test in air from RT to 600 °C is corroborated by XPS analysis. The measurement in depth-profile shows a Sr-enriched species at the top layer only. The inner layer does not segregate as result of the nano-confinement in the CGO heterostructure.

## 3. Morphological characterization of NGO[CGO/LSC]$_N$CGO heterostructures

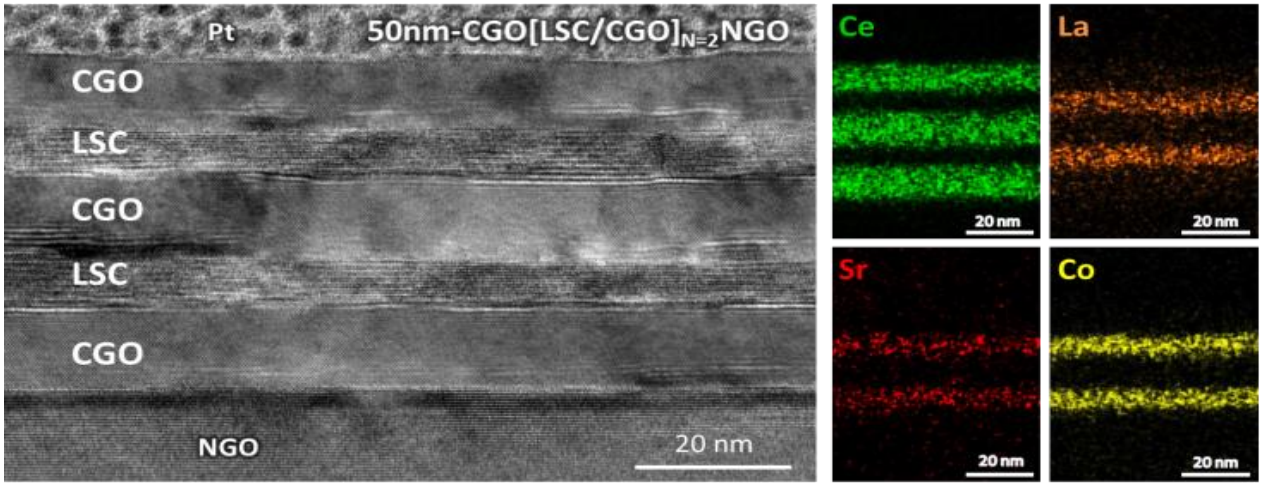


**Figure S3**. Cross section HR-TEM micrograph and EDS elemental mapping of the 50nm-CGO[LSC/CGO]N=2NGO heterostructure after thermal cycles (aged sample/post mortem). The Pt protective layer (top-layer in Figure) was deposited by focused ion beam (FIB) to the area of interest prior to ion beam milling in order to preserve the sample and avoid ion beam damage during lamella preparation.

To check the stability of the samples, microstructural and chemical measurements were carried by STEM analysis on post-mortem image and elemental mapping of the 50nm-CGO[LSC/CGO]$_{N=2}$NGO heterostructure. This reveals an alternating layered heterostructure on a NGO (110) single-crystal substrate. **Figure S1** shows that the samples terminated with CGO were stable. The analysis is representative of a larger scale of the sample after test, where neither pinholes nor inclusions, *e.g.* macro-particulate from the PLD, were detected. Both CGO and LSC single layer phases at the heterostructures can be clearly identified. Probably due to the low statistics at the STEM, elements did not appear sharply defined at the interfaces, where lanthanum and strontium exhibit a slight interdiffusion throughout the layers.