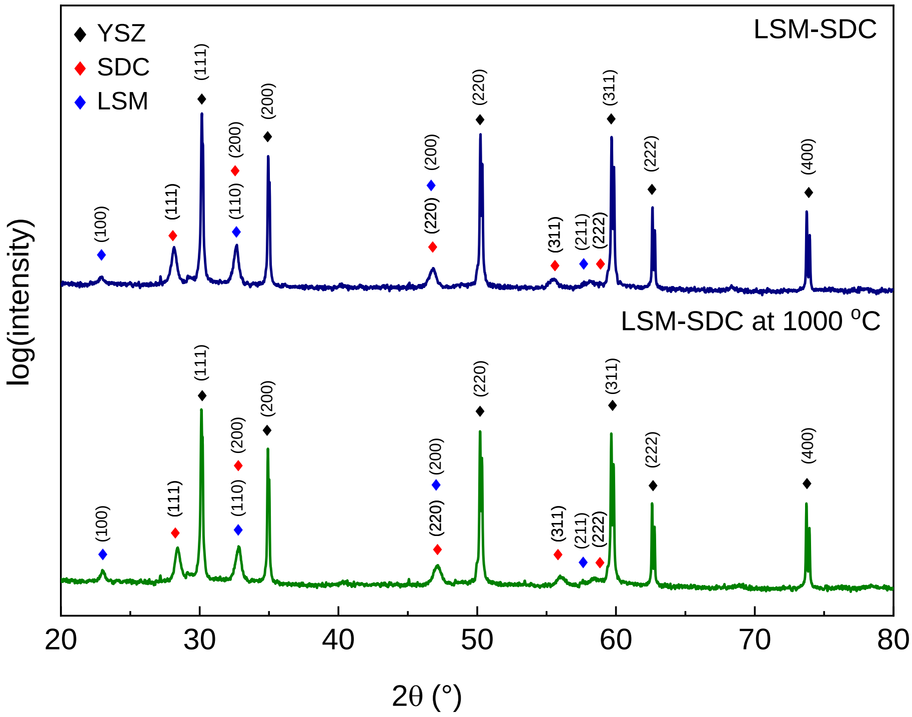
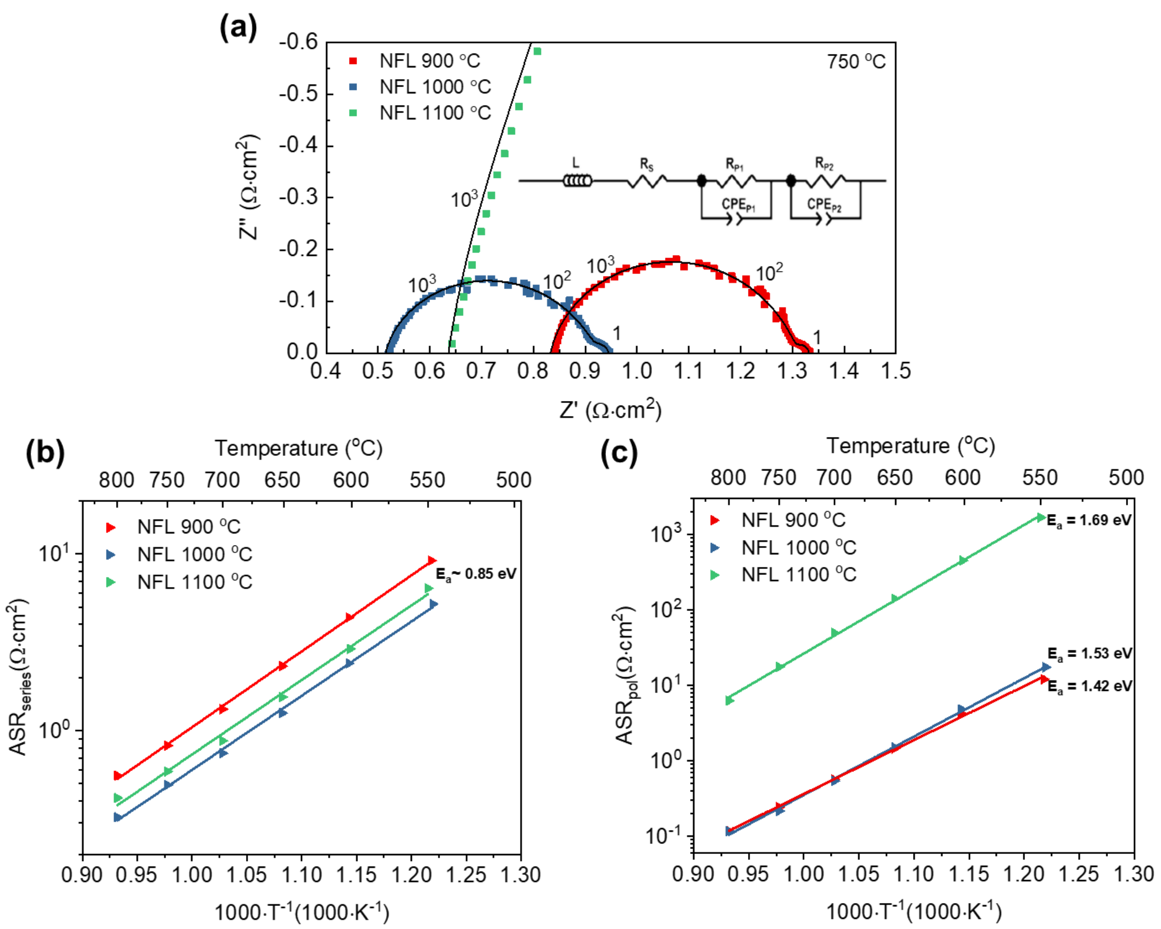
SUPPLEMENTARY INFORMATION



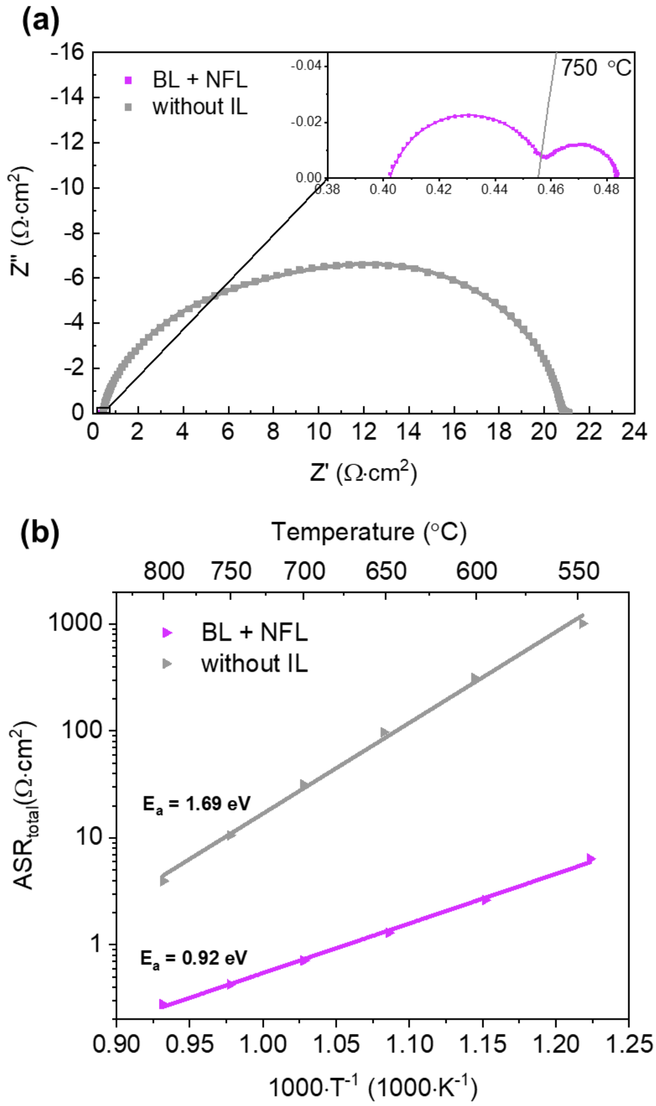
Supplementary Fig. S1 X-ray diffraction patterns of PLD layers on YSZ. Top to bottom: LSM-SDC as-deposited, LSM-SDC after heat treatment at 1000 °C.

The electrochemical properties of the symmetrical cells with thin-film interlayers were measured by EIS to define the optimal attachment temperature of the LSCF layer through the minimisation of the ASR contributions. The EIS data of symmetrical cells with the nanocomposite LSM-SDC was collected under synthetic air in the range of 550 – 800 °C for LSCF sintering temperature of 900, 1000 and 1100 °C. **Supplementary Fig. S2** (a) shows the impedance data of the samples at 750 °C. The experimental data was fitted with the equivalent circuit $LR_S(R_{P1}CPE_{P1})(R_{P2}CPE_{P2})$, where L refers to the inductive contribution due to the setup, R_S is the serial resistance ascribed to the ionic resistance of the electrolyte and to the electronic resistance from the current collection, and the electrode polarization arcs were fitted with a resistance and a constant phase element (CPE) connected in parallel ($R_{Pi}CPE_{Pi}$). The diagrams have clearly distinguishable arcs with similar frequency distributions; the first arc at high frequency is formed at around 10^3 and 10^2 Hz and the low frequency arc at around 1 Hz.

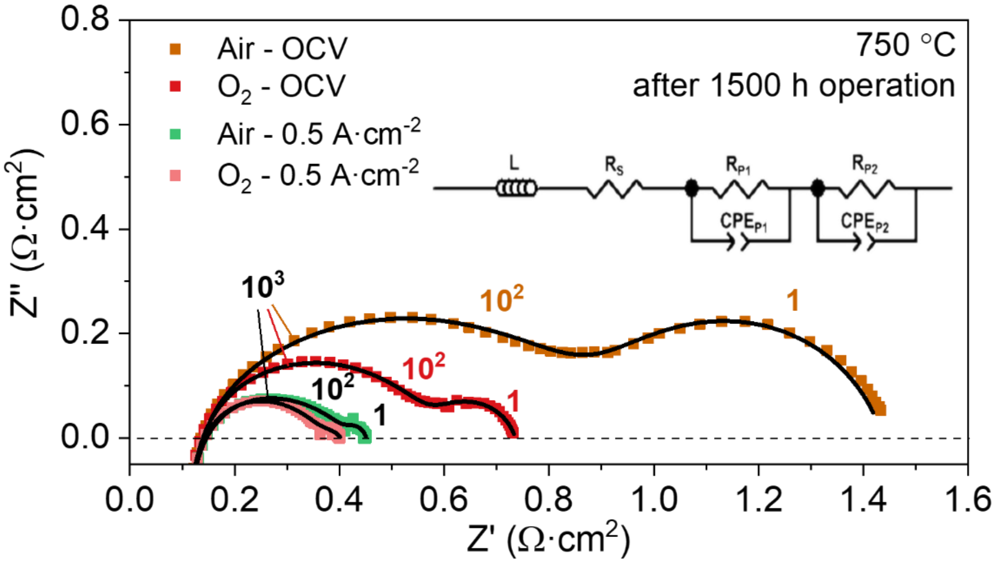
The temperature dependence of the series (ASR_{series}) and polarization (ASR_{pol}) area-specific resistances for the different cells are reported in the Arrhenius plot of **Fig. S2** (b) and (c) respectively. The activation energies for the ASR_{series} are similar for all sintering temperatures, as seen in Fig. 3 (a), but a lowest resistance is noted for the sample with the oxygen electrode sintered at temperatures of 1000 °C. From **Fig. S2** (c), it can be observed that the sample with attachment temperature of 1100 °C displays a significant increase in polarization resistance and a higher activation energy as compared to the samples submitted to lower temperatures. Such resistive behaviour can be attributed to the high temperature of 1100 °C that promotes the formation of resistive phases such as $SrZrO_3$ at the interface between the YSZ electrolyte and the LSCF cathode. This high temperature coupled with the limitation due to the very thin layer (200 nm) might activate parallel interdiffusion processes between the cathode and the electrolyte leading to the formation of insulating phases and decomposition of the electrode material [14,46]. The sample with layers attached 1000 °C has the lowest polarization and series resistance at the cell's operating temperature (700 – 800 °C). Thus, such sintering temperature was selected as the optimal one to produce the symmetrical cell with both the NFL and the BL.



Supplementary Fig. S2 (a) Impedance diagram of the symmetrical cells with YSZ support, NFL and LSCF cathode submitted to different sintering temperatures, 900, 1000 and 1100 °C, measured at 750 °C. Arrhenius plots of the series ASR (b) and of the polarization ASR (c) of the symmetrical cells.



Supplementary Fig. S3 (a) Impedance diagram of the symmetrical cell with and without BL and NFL with LSCF sintered at 1000 °C measured at 750 °C. (b) Arrhenius plot of the total area specific resistance of the symmetrical cell with BL+NFL and without intermediary layers (IL) and LSCF sintered at 1000 °C.



Supplementary Fig. S4 Impedance diagram of the anode-supported single cell with the BL+ NFL bilayers and LSCF at 750 °C under dry hydrogen with flow rate of 22.22 Nml·min1·cm^{-2} after 1500 h of operation under synthetic air and O_2 on the cathode chamber at OCV and under 0.5 A·cm^{-2}.