Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A

Supporting information

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1) Microscopic study of the asymmetric membranes

A microscopic study of the asymmetric membrane developed by freeze-casting and screen printing and developed by Jülich has been realized to get information about the microstructure and the organisation of the porosity. The Scanning electron Microscopic used is a Jeol Model JSM-5410.

a) Freeze-cast membrane

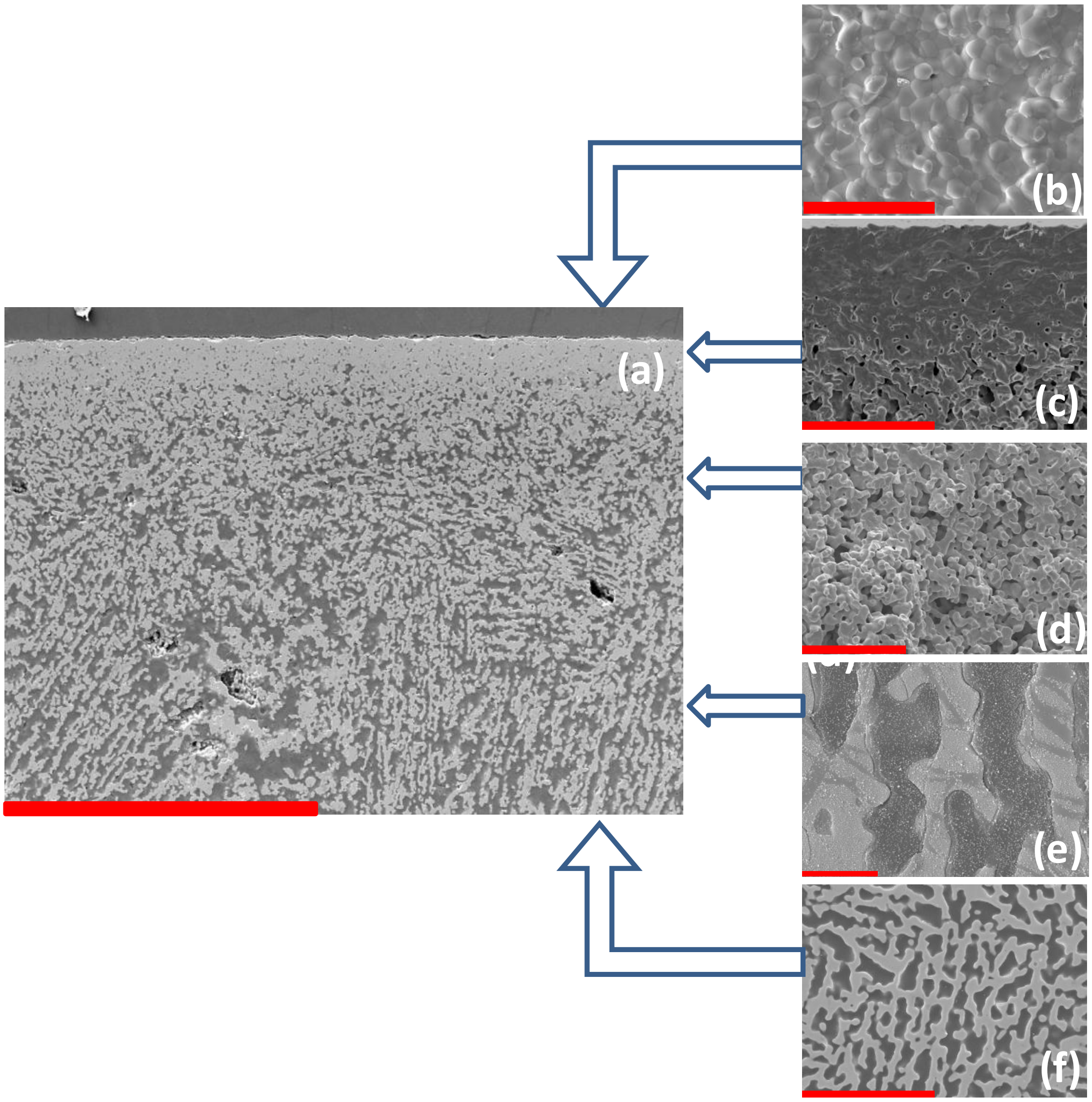


Figure S1. Microscopic study of the asymmetric membrane. (a) Asymmetric membrane: Porous support + dense top-layer, scale bar 400 µm; (b) surface of the dense top layer, scale bar 30 µm; (c) cross-section of the dense top-layer, scale bar 80 µm; (d) cross section of the non-oriented random porosity, scale bar 50 µm; (e) cross section of the hierarchically-oriented porosity, scale bar 10 µm; (f) surface of the hierarchically-oriented porosity, bottom of the asymmetric membrane, scale bar 60 µm

b) Asymmetric membrane developed by Jülich

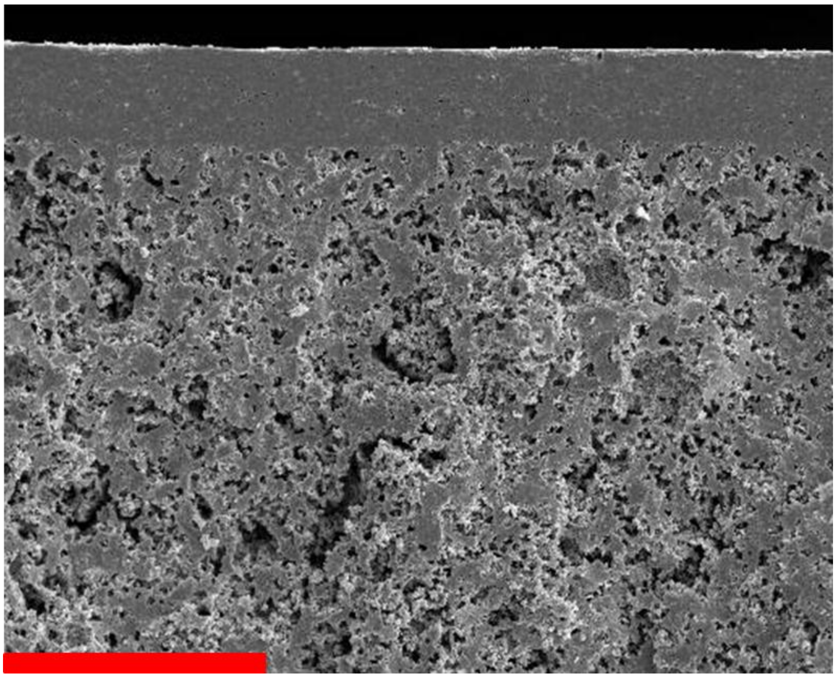
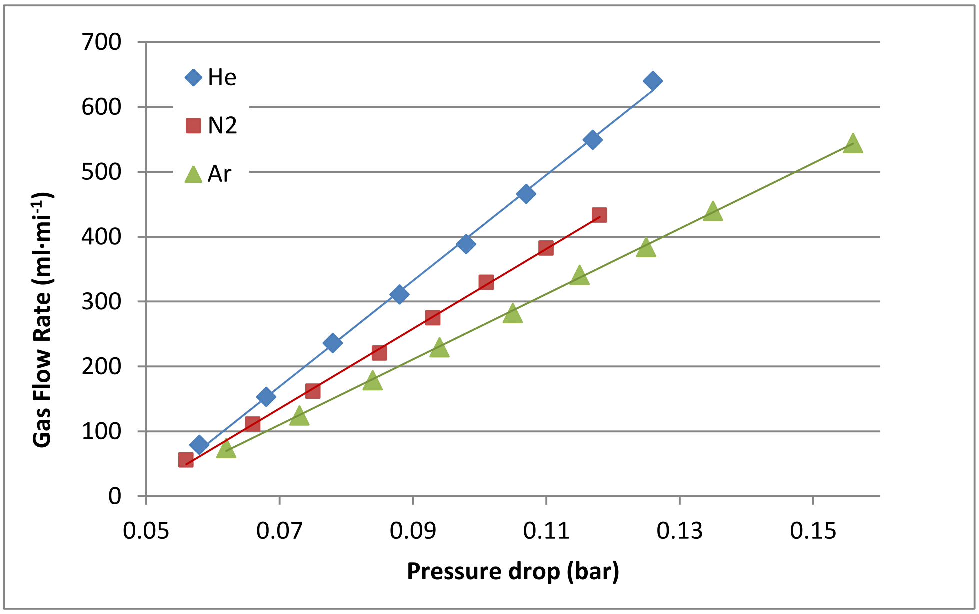


Figure S2. Cross section of the asymmetric membrane developed by Forschungszentrum Jülich, scale bar 100 μm

2) Gas permeation study of the porous support

This study is carried out using porous support without any top layer. For this purpose, the freeze-cast support was sintered without coating a top layer and subsequently the non-oriented porous volume was removed by grinding. The pressure drop of the porous support prepared by freeze-casting has been evaluated at high temperatures using the same set-up as the permeation test and using a ceramic cement to seal the outer support area to the quartz tube. Argon, helium and nitrogen were and the pressure drop ΔP across the membrane was recorded as a function of the inlet gas flow rate and temperature.



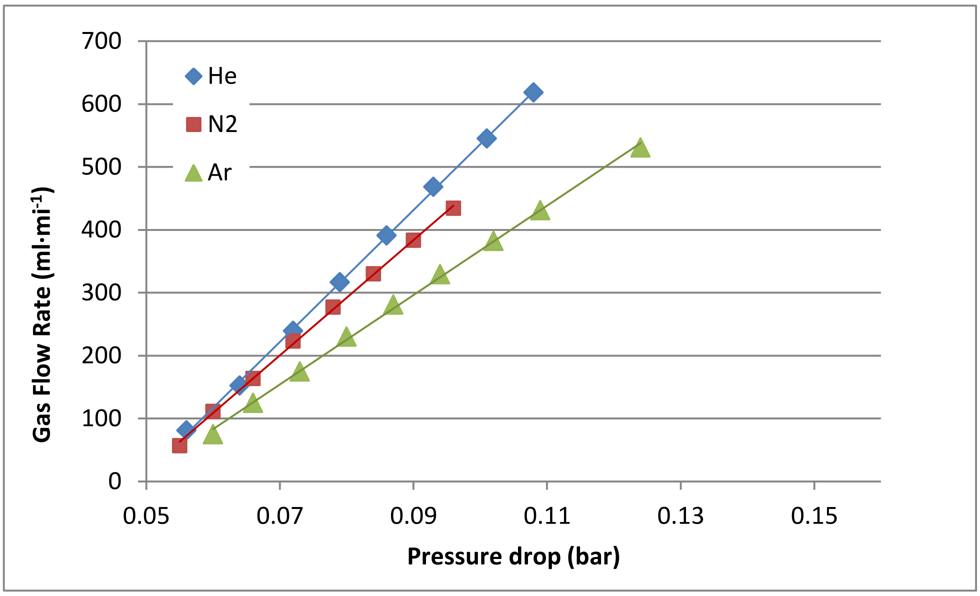


Figure S3. ΔP across the porous support as a function of the gas flow rate at (top) 800 ºC and 900 ºC (down) for a 1.5 mm –thick tape-cast support made of LSCF.

Table S1. Results of the linear fit Π=a. ΔP +b of the Ar single gas permeance as a function of the ΔP for the freeze-cast and tape-cast supports. * Note: determined at Q_{Ar}= 250 ml·min^{-1}

Temperature (ºC)	a factor (mol.Pa^{-2}.s^{-1}.m^{-2}) freeze-cast	b factor (mol. .Pa^{-1}.s^{-1}.m^{-2}) freeze-cast	$\Pi_{v/}$ Π_k * % freeze-cast	a factor (mol.Pa^{-2}.s^{-1}.m^{-2}) tape-cast	b factor (mol. .Pa^{-1}.s^{-1}.m^{-2}) tape-cast	$\Pi_{v/}$ Π_k * % tape-cast
600	1,8.10^{-9}	8,8.10^{-4}	2%	3,0·10^{-10}	1.0·10^{-4}	10%
700	2,0.10^{-9}	9,2.10^{-4}	2%	3.7·10^{-10}	1.2·10^{-4}	12%
800	9,6.10^{-9}	0,010	6%	5.0·10^{-10}	1.5·10^{-4}	13%
900	1.5.10^{-8}	0,016	4%	nd	nd	Nd

The argon permeance can be written by the following equation:

$$\Pi = a.\ \Delta P + b$$

Where a and b are the viscous flow (*Poiseuille*) Π_v and the *Knudsen* flow Π_k contributions, respectively [1]. The fitting of the four permeance measurements are summarized in the Table S1 for both porous supports, where both a and b factors are given. Irrespective of the temperature, the *Knudsen* flow appears to be the most important mechanism in the gas.

Argon, helium and nitrogen were used as gas to measure the pressure drop ΔP across the membrane as a function of the inlet flow. As a comparison, the same experiment was performed with the support of the asymmetric membrane prepared by tape-casting

[1] R.J.R. Uhlhorn, K. Keizer, A. J. Burgraaf, J. Memb. Sci. 46 (1995) 2131

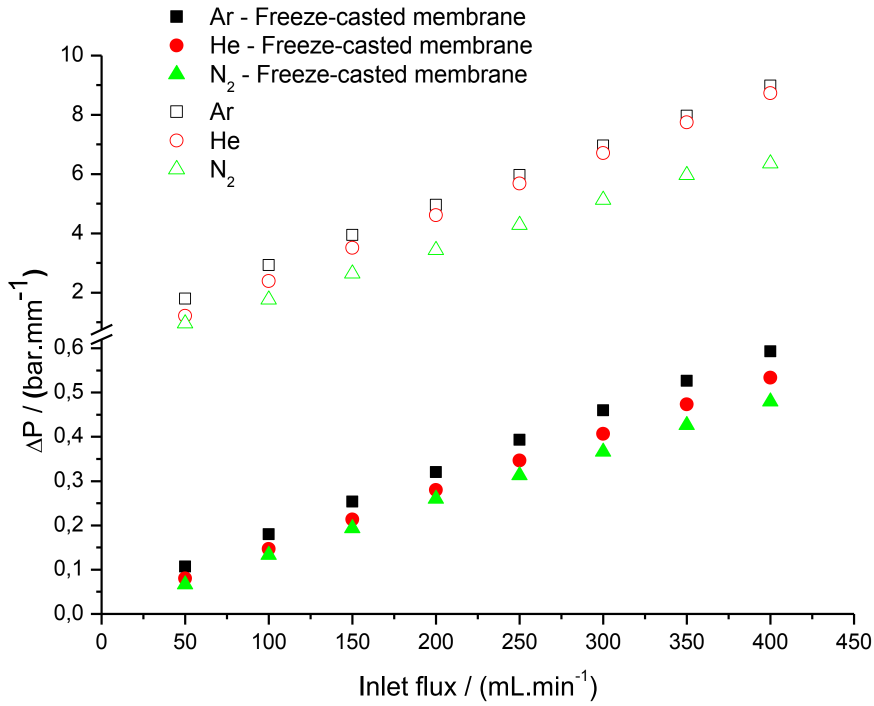
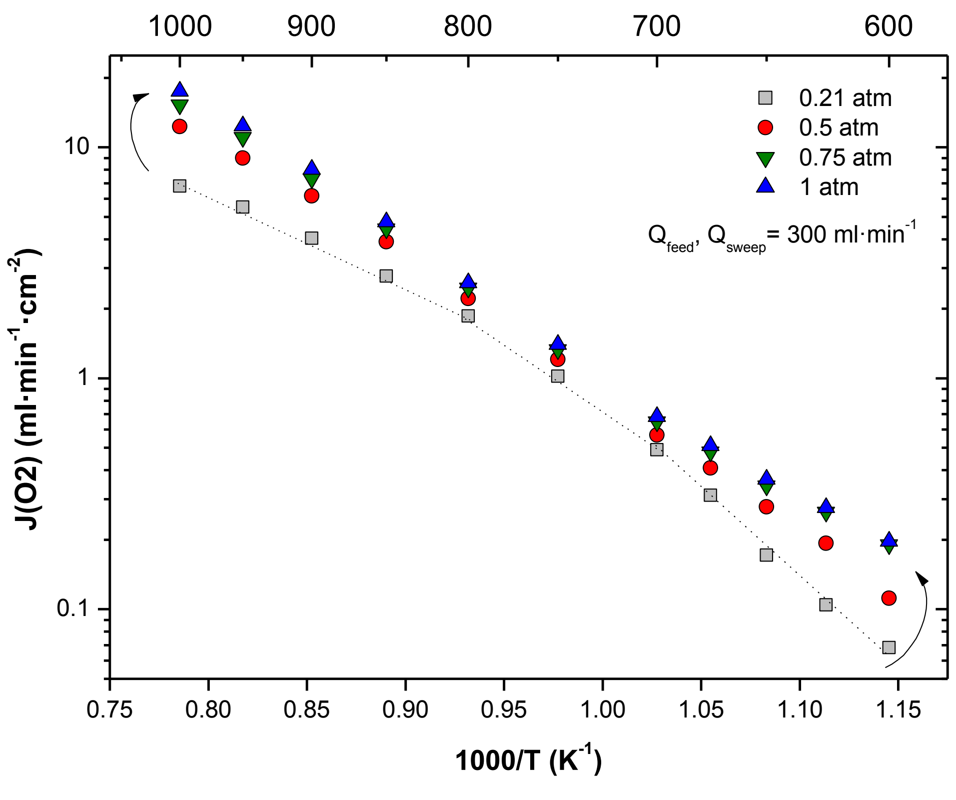


Figure S4. Normalized pressure drop ΔP across two porous support (filled symbol: support elaborated by freeze-casting, empty symbol: support of the asymmetric membrane developed by tape-casting) as a function of the inlet flux and for three different gases at 800ºC

Figure S4 represents the normalized ΔP across the porous support elaborated by freeze-casting and across the support of the asymmetric membrane developed by Jülich as a function of the inlet flux and at 800ºC. Whatever the gas and the inlet flux, the porous support elaborated by freeze-casting presents a lower pressure drop than the other support. For example, when N_2 is chosen as gas, the pressure drop of the freeze-cast support does not exceed 0.48 $bar.mm^{-1}$ for an inlet flow of 400$mL.min^{-1}$ while it already reaches 0.89 $bar.mm^{-1}$ for an inlet flow of only 50 $mL.min^{-1}$ with the other support.

3) Additional O_2 permeation results

Figure S5 presents the evolution of the permeation flux as a function of temperature and the oxygen partial pressure of the gas feed. The partial pressure was achieved by using different mixtures of N_2 and O_2. A very important improvement in the flux is achieved at both high and low operating temperatures. Indeed, at 1000 ºC a peak flux of ~18 ml·min^{-1}·cm^{-2} is observed when using pure O_2. On the other hand, a relatively higher improvement is achieved at 600 ºC, reaching a flux of ~2 ml·min^{-1}·cm^{-2} when using 75% O2 in the feed. Moreover, the strong changes in the apparent activation energies are in full agreement with previous observations using the tape-cast LSCF membrane [33] and are related to the progressive change of the rate limiting steps as a function of the



oxygen partial pressure (and temperature).

Figure S5. Thermal evolution of the oxygen flux as a function of the oxygen partial pressure in the feed gas, made of mixture of O_2 and N_2. The total feed pressure was slightly above the atmospheric.

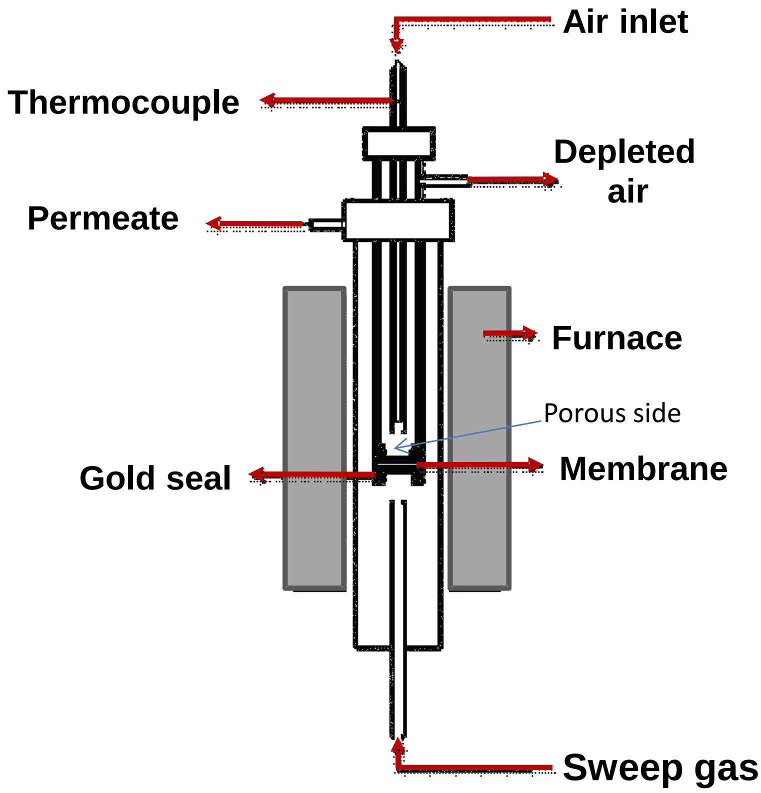


Figure S6. Experimental setup of oxygen permeation test.

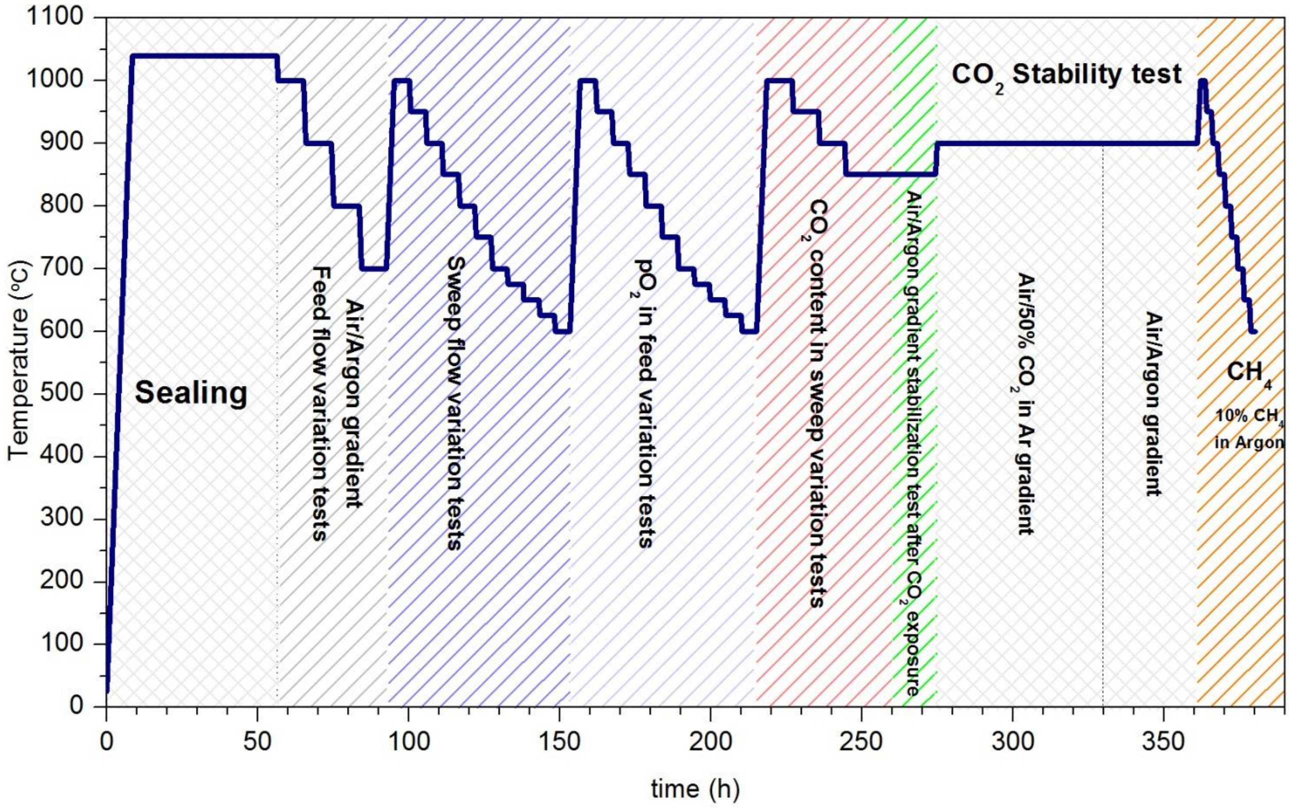


Figure S7. Thermal cycling (experimental permeation test) for the bare LSCF asymmetric tape-cast sample

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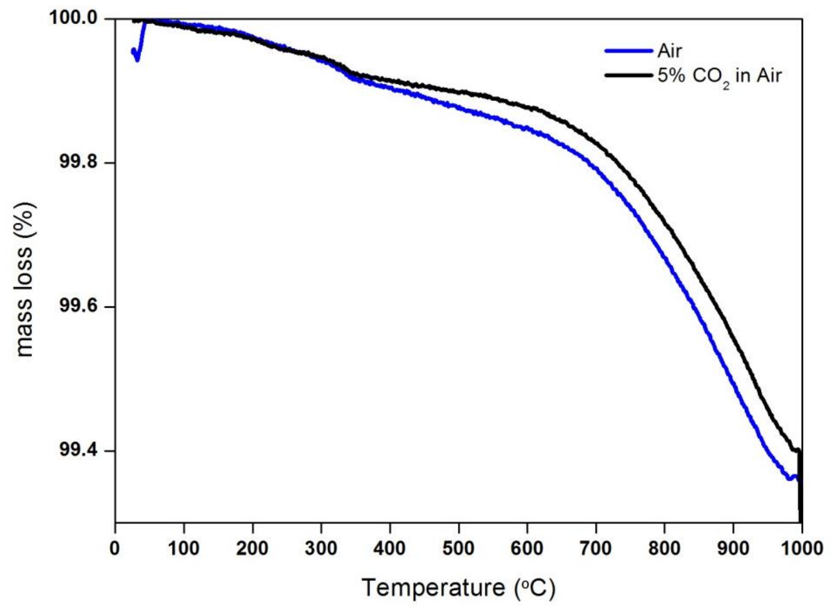

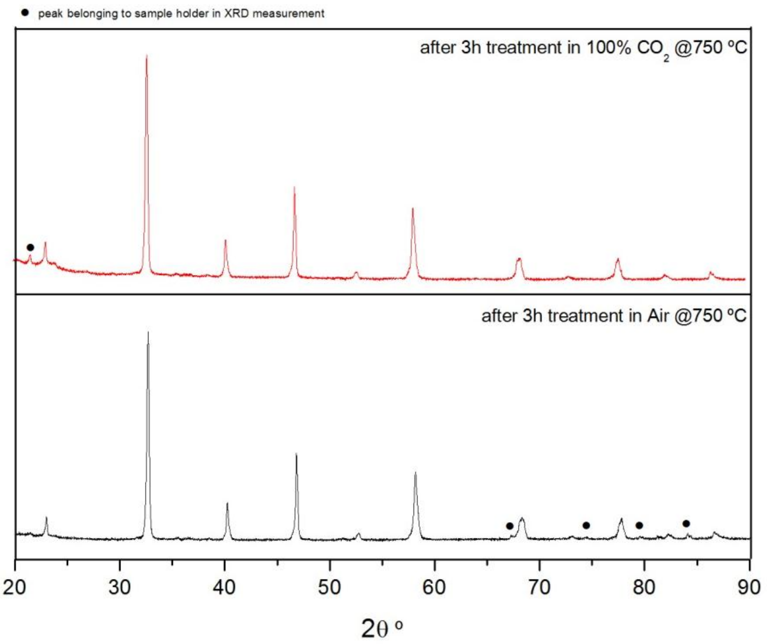

Figure S8. (top) Thermogravimetric analysis of LSCF power in air and air with 5% CO_2 and (bottom) XRD patterns of LSCF samples quenched directly from 750ºC in Air or pure CO_2 gas environment

Experimental: Thermogravimetry analysis was performed on a Mettler-Toledo StarE equipment in air with 5% CO_2 and using a heating ramp of 10 K/min. XRD measurements were carried out by a PANalytical X'Pert PRO diffractometer, using $CuK\alpha_{1,2}$ radiation and an X'Celerator detector in Bragg-Brentano geometry. XRD patterns were recorded in the 2θ range from 20º to 90º and analyzed using X'Pert Highscore Plus software