

## 3D Printing the Next Generation of Enhanced Solid Oxide Fuel and Electrolysis Cells

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### Supplementary information

#### S1.1 Microstructural characterization of printed electrolytes

XRD analysis and Raman spectroscopy were performed on printed electrolytes in order to confirm that the 3D printing process is able to produce pieces with the proper microstructural properties to be used as electrolyte in SOCs.

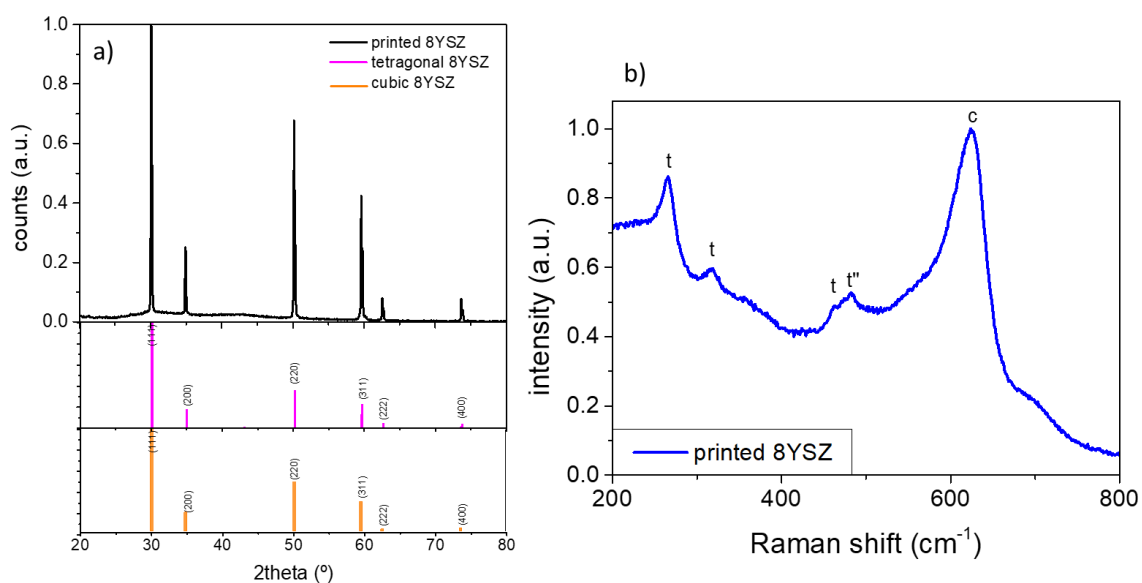


Figure S1: a) XRD of printed electrolytes, tetragonal 8YSZ reference pattern: 01-070-4431, cubic reference pattern: 01-070-4436; b) Raman spectra, wavelength laser: 532 nm

The geometry of the complex printed pieces have been determined using 3D mapping capabilities of a confocal microscope (PLu neox from Sensofar, Spain). The analysis highlights the finishing resolution and the proper reproduction of the CAD design (Figure S2).

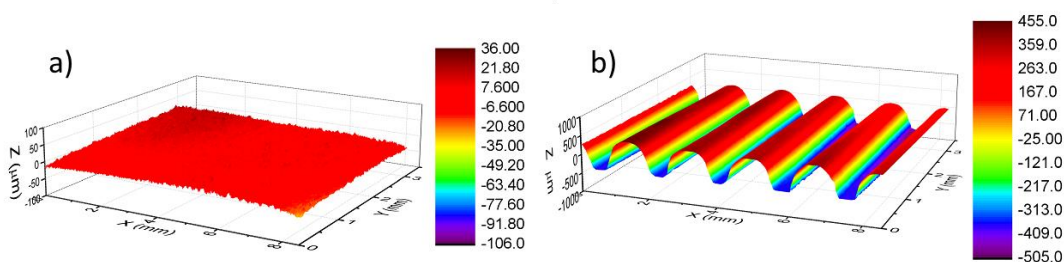


Figure S1: Optical topography of a) planar and b) corrugated electrolytes.

## S2.2 Characterization of electrochemical behaviour of cells based on printed electrolytes

Printed electrolytes have been functionalized for the electrochemical characterization. Firstly, a symmetrical cell based on printed electrolyte is fabricated, LSM-YSZ ink (Fuelcell materials, USA) is deposited on both sides and gold paste is used as current collector. The purpose of this symmetric cell is to confirm that the ionic conductivity under synthetic air atmosphere is comparable to the one reported in literature. The sample was assembled to a ProboStat™ (NorECs AS, Norway) and placed on a high temperature sandwich furnace. The characterization is performed recording the EIS spectra in the range 1 MHz-0.1 Hz, with an amplitude of 50 mV, using a galvanostat frequency response analyser (Alpha-A, Novocontrol, Germany) from 900°C to 500°C with steps of 50°C to obtain the dependence of the ionic conductivity with the operation temperature and the activation energy.

The measured resistive behaviour is stated in a Nyquist plot (inset of Figure S3) and the different contributions are fitted with the described equivalent circuit. Obtained values are reported in the Arrhenius plot of the Figure S3. The increase of the conductivity of the 3D printed electrolyte with the increase of the temperature is shown and compared with reference values<sup>1</sup> (dot-dash line). The conductivity of the printed electrolytes is close to theoretical expected values ( $4.5 \cdot 10^{-2}$  S/cm for the reference vs  $3.2 \cdot 10^{-2}$  S/cm for the printed electrolyte at 800°C). The activation energy of the oxygen conduction process in YSZ is around 0.9-1.0 eV, according to the bibliography while the obtained value for the printed sample is 1.02 eV for temperatures lower than 600°C. Slight differences with the reference, at higher temperatures, can be attributed to slight different preparation processes, attachment temperatures and the different contribution of the electrodes. The accordance with the values of the literature proves the suitability of 3D printing process to produce electrolytes for SOCs.

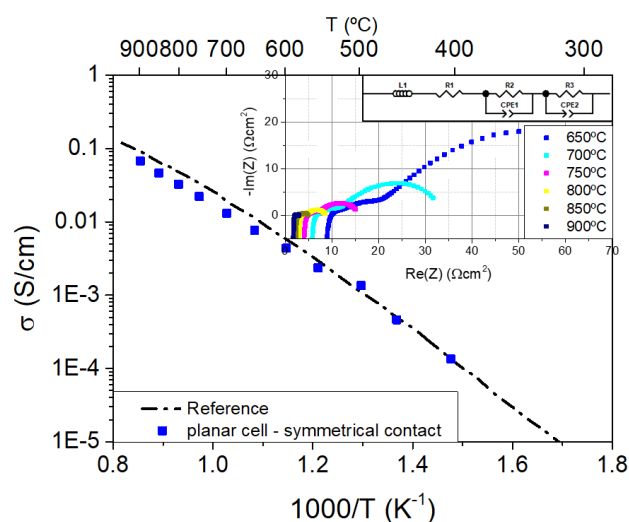


Figure S2: Arrhenius plot of ionic conductivity of tested symmetric and full cells compared with literature<sup>1</sup>. A detail of the operation temperatures of the full cells as an inset.

In order to improve the attachment between electrodes and electrolyte roughness layers of 8YSZ (Kceracell, Korea) were deposited by wet powder spray (airbrushing) and sintered at 1150°C on top of the sintered electrolytes, to reduce the reported attachment issues<sup>2,3</sup>. Subsequently, the different electrodes were deposited. Firstly, the fuel electrode was deposited in the form of NiO-YSZ ink (Fuelcell materials, USA) and attached at 1400°C for 3 hours. Afterwards the air electrode was deposited based on LSM-YSZ ink (Fuelcell materials, USA) is

deposited, on top of the previously deposited roughness layer and attach at 1200°C for 1 hour. Reported attachment temperatures for both electrodes were chosen according to a previous optimization process (results are not discussed in the paper) by minimization of the ohmic resistance contribution of different symmetrical cells prepared with both electrodes and attached at different temperatures.

The electrochemical characterization of the optimised complete cells was also performed in a commercial ProboStat™ (NorECs AS, Norway) station. The cells were characterized at 800°C (Figure S4), 850°C (Figure S5) and 900°C (discussed in the manuscript). Gold meshes and gold ink were employed as current collector for both electrodes. Ceramabond™ (Aremco, USA) sealant paste was applied to ensure gas tightness between the anodic and the cathodic chambers. The fuel side is fed with 22.2ml/min·cm<sup>2</sup> of hydrogen under SOFC mode and 696 Nmg/h·cm<sup>2</sup> of water with 5.55 Nml/min·cm<sup>2</sup> of CO<sub>2</sub> and 2.22 Nml/min·cm<sup>2</sup> of H<sub>2</sub> under co-electrolysis mode. The air electrode is fed with synthetic air at 55ml/min·cm<sup>2</sup> under SOFC mode and 45 Nml/min·cm<sup>2</sup> of air under co-SOEC mode. The electrochemical performance is evaluated through V-j polarization curves performed by a potentiostat/galvanostat (Parstat 2273, PAR, USA). The voltage is measured at each current step up to a maximum potential of 0.6 V in SOFC mode and 1.4 V in co-SOEC to limit degradation. The polarization curves in SOFC mode are extrapolated up to 0.4V to show the maximum power output. Electrochemical Impedance Spectroscopy (EIS) is also carried out using a potentiostat/galvanostat frequency response analyser (Parstat 2273, PAR, USA) in the frequency range of 100 kHz down to 100 mHz and an amplitude of 50 mV under OCV and operative conditions, respectively at 0.7 V and 1.3 V.

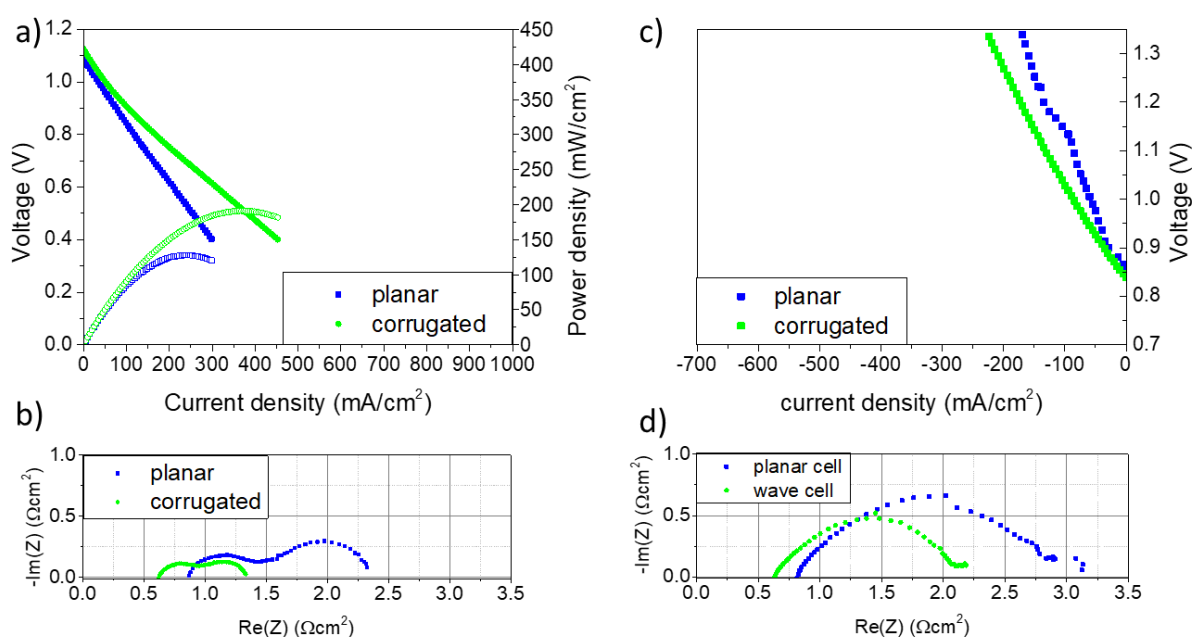


Figure S4: a) j-V curves in SOFC mode at 800°C and b) relate EIS at 0,7V, c) j-V curves in co-SOEC mode at same temperature, and related EIS at 1,3 V.

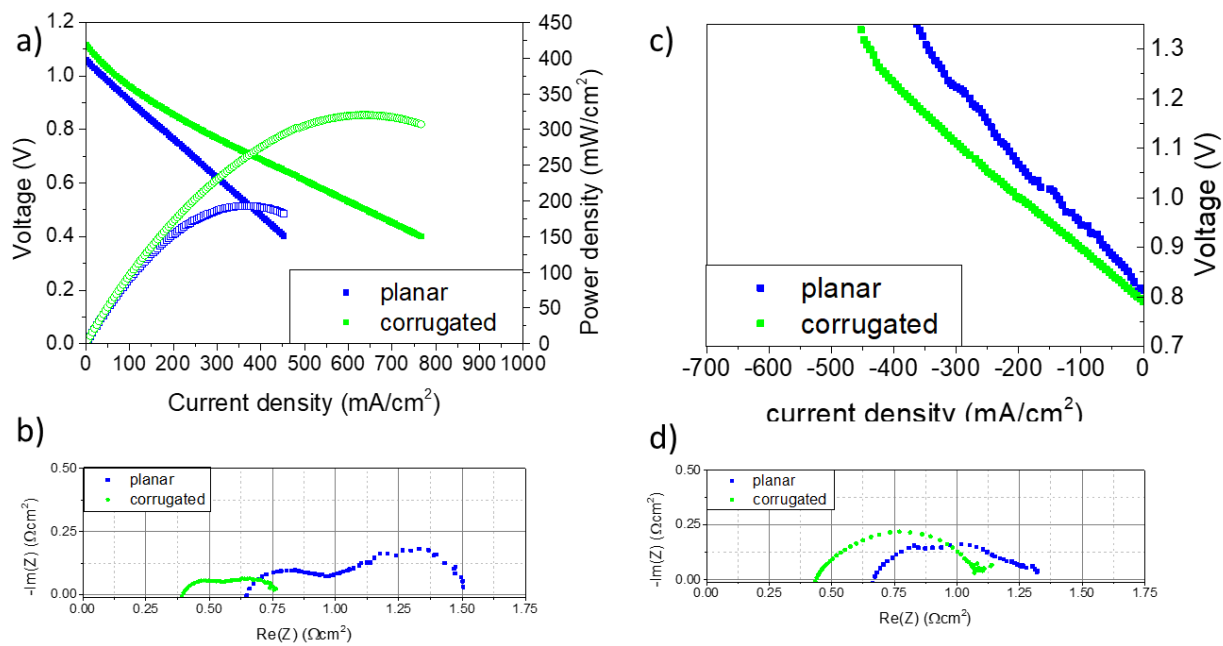


Figure S5: a)  $j$ -IV curves in SOFC mode at 850°C and b) relate EIS at 0,7V, c)  $j$ -V curves in co-SOEC mode at same temperature, and related EIS at 1,3 V.

## References

- 1 C. Ahamer, A. K. Opitz, G. M. Rupp and J. Fleig, *J. Electrochem. Soc.*, 2017, **164**, F790–F803.
- 2 J. A. Cebollero, R. Lahoz, A. Larrea, *J. Power Sources* 2017, **360**, 336-344.
- 3 J. A. Cebollero, R. Lahoz, M. A. Laguna-Bercero, J. I. Peña, A. Larrea, V. M. Orera, V. M. *Int. J. Hydrogen Energy* 2017, **42**, 13939-13948.