Supplementary information

Single-step fully 3D printed and co-sintered Solid Oxide Fuel Cells

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S1. Characterization of the solid loading used for the robocasting ink formulations

The solid content, used for the development of the RC inks for the fabrication of SOFC electrodes, was characterized in terms of the particle size using the laser diffraction analysis (Mastersized 200, Malvern Panalytical, UK). The corresponding particle size distributions are presented in the Fig. S1.

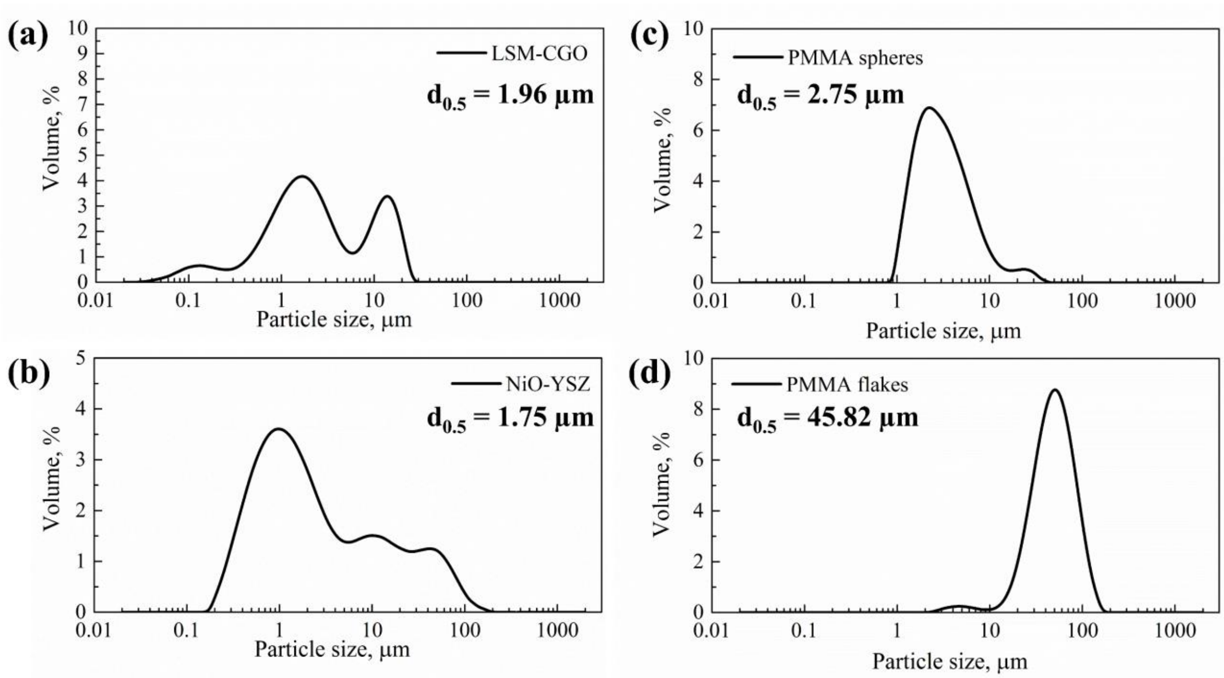

Fig. S1 Particle size distribution of the materials used as a solid loading for the RC SOFC electrode feedstock formulations: LSM-CGO applied for the oxygen electrode RC inks (a); NiO-YSZ applied for the fuel electrode RC inks (b); PMMA spheres (c) and flakes (d) applied as pore-forming agents for both ink formulations.

The LSM-CGO composite was fabricated via mixing of the LSM and CGO commercial powders in a mass ratio of 50:50 wt.%, which allowed obtaining a ceramic powder with an average particle diameter of ~2.0 µm (Fig. S1a). However, the distribution is not uniform in the presence of particles of ~2 µm in diameter, which could be related to one phase, and larger particles with the dimensions in the range of 10 – 20 µm, which could possibly represent another phase of the composite. Similarly, the 60:40 wt.% NiO-YSZ powder was characterized by an average particle size of ~1.7 µm with the presence of two fractions with a diameter of ~1 µm and ~10 – 100 µm, respectively (Fig. S1b). The RC ink compositions include PMMA spheres with an average diameter of ~2.8 µm and PMMA flakes of ~45.8 µm (Fig. S1c and S1d), which allows the creation of an interconnected open porosity due to the combination of different particle shapes and dimensions.

S2. Printability evaluation of the RC inks for 3D printing of SOFC electrodes

The rheological behavior of the RC inks represents a key aspect for the evaluation of their printability within the developed hybrid multi-material 3D printing process. One of the factors that could significantly affect the viscosity of the elaborated feedstock is the ratio between the ceramic and pore-forming content in the total solid loading of the ink. Thus, the rheological behavior of two acrylate-based RC ink formulations with 70:30 wt.% and 50:50 wt.% ceramic:pore-former ratios is investigated using HR-2 Rheometer (TA Instruments, USA).

The printing conditions are represented as a range of shear rates, which is calculated using the following equations, considering the cylindrical shape of the deposition tip [1]:

$$\dot{\gamma}_{max} = \frac{4\dot{Q}}{\pi r^3} \qquad \text{(S2.1)},$$

$$\dot{Q} = Sr^2 \qquad \text{(S2.2)},$$

where $\dot{\gamma}_{max}$ is a maximal shear rate, which is reached on the nozzle walls in the moment of the deposition; $\dot{Q}$ is a volumetric flow rate; S is a printing speed, and r is a nozzle diameter.

Assuming the target thickness of the robocast electrode layer as 150 µm in a green state, the printing speed was selected in the range of 10 – 60 mm/s depending on the composition of the electrode ink, while the radius of the tip was 0.51 mm. Thus, the printing conditions correspond to the shear rates from 50 to 300 s^{-1}.

In this work, following criteria were selected to quantitatively assess possible printability of the ceramic-based robocasting inks with different composition [2,3]:

$$Flow\ Transition\ Index\ (FTI) = \frac{\tau_f}{\tau_y} < 20 \quad \text{(S2.3)},$$

$$Figure\ of\ merit\ \Phi = \frac{G'_{eq}}{\tau_f} > 20 \qquad \text{(S2.4)},$$

where G'_{eq} is an elastic modulus value obtained within the linear viscoelastic region (LVR), τ_y is a yield stress, and τ_f is a flow stress. These ratios have been proposed to evaluate the extrudability of the ink to ensure a minimal deformation and lateral deflection of the printed structures.

Fig. S2a presents flow curves of the LSM-based robocasting inks with different ceramic-pore-former content, which were obtained in the shear rate range of 10^{-1} to 10^{3} s^{-1}. Both formulations exhibited shear-thinning behavior as it is required for the extrudability of the robocasting inks [4], while the viscosity increased with the rise of the pore-formers mass fraction at lower shear rates (3 Pa×s, and 46 Pa×s at 30 s^{-1} for 70:30 wt.%, and 50:50 wt.%, respectively). At the same time, the ink with dominant ceramic solid loading presented minor changes of the viscosity values within the printing shear rate range, while the drop of the approximately ~5 times was observed for the compositions with the equal ceramics:pore-former content within the same high shear rate interval. This behavior could be attributed to the reorientation of the flakes with non-spherical shapes in the direction of shear at higher rates, resulting in an amplified shear-thinning effect [5].

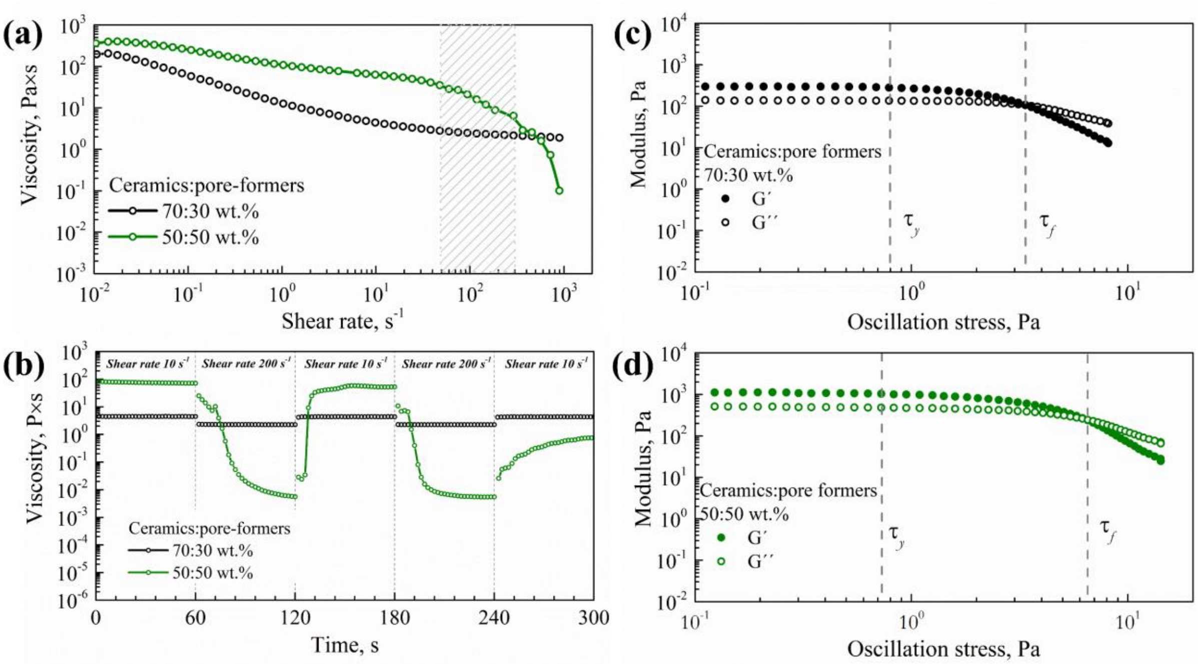

Fig. S2 Rheological characterization of the LSM-based ink formulations for the robocasting of SOFC oxygen electrodes with two different ratios between ceramic and pore-former loadings: flow curves, where the grey shadowed area represents the potential printing conditions under the printing speed of 10 – 60 mm/s (a); thixotropy test, which includes the measurement of the viscosity values under the periodical application of the fixed shear rates of 10 s^{-1} and 200 s^{-1} for 60 seconds (b); amplitude oscillation test, presented as a dependence of storage and loss moduli on the oscillation stress, τ_y is a yield stress and τ_f is a flow stress, respectively (c-d).

The thixotropy test was performed by the periodical application of the constant shear rates of 10 s^{-1} and 200 s^{-1} for 60 seconds while the viscosity values were measured (Fig. S2b). The RC ink with primary ceramic solid loading demonstrated thixotropic behavior with a fast recovery speed, while the formulation with higher pore-former loading, required more time to reach stable viscosity values under 200 s^{-1} shear rate, and then to recover the initial viscosity after the shear rate switch. The stabilization period attributed to the higher pore-former content was estimated as 60 s interval, while the ink exhibited 70% of the initial viscosity reached after 34s during the recovery period. Moreover, when the ceramic powder and pore-former were loaded in equal parts, the second switch after the shear rate resulted in only ~1% structural recovery within a 60 s time range. This could be explained by differences in the mobility of particles, since the restructuration of particles with irregular shapes (such as flakes) is delayed due to the contact and locking of the closest particles, which are not able to immediately slide and rotate to return the initial configuration [6].

The amplitude oscillation study was carried out in the strain range of 0.01 – 20% and an angular frequency of 10 rad/s. Both inks demonstrated a solid-like behavior (G´>G´´) within the LVR, while an increase of the $G_{eq}^{'}$ from ~290 Pa to ~1000 Pa was observed for the composition with the highest pore-former loading (Fig. S2c and S2d). The increase of the pore-former content up to 50 wt.% of the solid loading led to an extension of the "breaking" range between yield and flow points, which indicates higher resistance to flow owing to the friction between spherical particles and flakes. Both ink compositions satisfy the selected printability criteria, with an increase of the figure of merit Φ from 87 to 172, corresponding to the rise of the pore-former content. At the same time, the increase of FTI from 4 to 9 is well correlated with the thixotropy behavior of the inks.

Overall, the ratio of approximately 70:30 wt.% was selected for the feedstock compositions for the robocasting of the oxygen and fuel SOFC electrodes, which was related to the fast recovery of the viscosity values observed during the thixotropy test, aiming to improve the control of the electrode shape after the RC deposition.

S3. 3D printing parameters for the fabrication of SOFC electrodes

A series of printability tests was performed to investigate the influence of the parameters applied during the robocasting and curing of the developed electrode inks on the geometry and homogeneity of the printed layers. Finally, the following conditions for the SOFC electrode robocasting were selected to obtain the uniform fuel and oxygen electrode layers with a thickness of 150 µm in a green state (Table S3.1). The addition of the pore-formers to the RC ink formulations led to an increase of the viscosity values, which could complicate the extrusion through the tip with a small diameter. Thus, the pressure was set at 0.8 bar, while the gap distance between the printing nozzle and the building platform was fixed at 150 µm, creating the continuous flow of the RC inks. The printing speed of 20 mm/s was used for the production process, resulting in the deposition of the sufficient amount of the electrode material on building platform. The choice of the 0.5 mm spacing, which represented a distance between two individual lines of the extruded material, correlated with the diameter of the selected nozzle.

Table S3.1: Parameters of the robocasting applied for the 3D printing of SOFC electrodes.

Parameter	Value
Nozzle diameter	0.51 mm
Nozzle/building platform gap distance	150 µm
Pressure	0.8 bar
Spacing	0.5 mm
Speed	20 mm/s

As the next printing step, the solidification of the deposited electrode layer is required, which is done by thermo-curing with the emission of IR laser, installed on the retractable robotic arm. The parameters of polymerization were optimized to reach the complete homogeneous solidification of the material (Table S3.2). Note that similarly to the robocasting process, thermo-polymerization required the selection of the spacing parameter, which represented the distance between the individual laser passes. Considering the diameter of the IR laser spot (< 1mm), the uniform surface of the printed electrode layer was obtained with the spacing of 0.05 mm.

Table S3.2: Parameters of the thermo-curing of 3D printed SOFC electrodes via IR laser.

Parameter	Value
Laser/building platform distance	9 cm
Number of laser passes	2
Spacing	0.05 mm
Speed	1.5 mm/s

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