

Electronic Supplementary Information

High performance three-dimensionally ordered macroporous composite cathodes for intermediate temperature solid oxide fuel cells

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Experimental section

1. Synthesis. Polystyrene (PS) spheres with the diameter of 596 ± 9 nm were synthesized by emulsifier-free emulsion polymerization.¹ YSZ electrolytes were prepared from commercial YSZ powders (40 nm, Tosoh) by uniaxially pressing at 300 MPa and sintering at 1500 °C for 6 h, obtaining 0.7 mm thick samples with relative density higher than 96%. The PS templates were assembled on the YSZ electrolytes via the vertical deposition method, using a procedure adapted from the literature.² The SEM micrographs of the monodispersed PS spheres and the face-centered-cubic close packing PS template are shown in Fig. S1A and B, respectively. Other raw materials were all analytical grade and used as received without further purification.

The precursor sol for LSM was prepared by dissolving certain amount of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Sr}(\text{NO}_3)_2$ and $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ in de-ionized water according to the stoichiometry of $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_{3-\delta}$. Subsequently, citric acid was added and the solution was heated to 80 °C under stirring until it became a transparent sol. Mole ratio of citric acid to total metal cations (abbreviated as C/M) was 1.5. In the course of our experiment, it was found that ethanol allows better permeation and surface wetting than water, and causes less disruption to the PS template during infiltration. Thus, due to the small size of the PS spheres, high permeation of the voids was achieved by dissolving stoichiometric ratios of $\text{Zr}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ in ethanol to form the 8mol% Y_2O_3 doped ZrO_2 . The solution was heated at 70 °C until a transparent sol was formed which was aged at ambient temperature for 24 h. LSM and YSZ precursor sols were mixed together and the weight ratio of LSM and YSZ was 5:5 in the composite.

Dip coating was carried out to fill the voids of the PS template with the LSM/YSZ precursor solution. Before dip-coating, the PS template was heated to 80 °C for 2 h to improve its adhesion to the YSZ support. Then, the PS template was vertically immersed into the mixed solution for 2 min, and slowly pulled up at a rate of 2 mm s^{-1} . During this process, the solution was drawn into the voids of the template by capillary force. After drying at room temperature, the sample was calcined at 700 °C for 4 h to remove the PS spheres and crystallize the solids, producing the 3-DOM LSM/YSZ skeleton. The heating rate was $1 \text{ }^\circ\text{C min}^{-1}$, and the furnace was held at 350 °C for 3 h to completely remove the PS template. Subsequently, a fast firing step was carried out at 1000 °C for 2~30 min, with the heating and cooling rate of $200 \text{ }^\circ\text{C min}^{-1}$, to enhance the contact between the 3-DOM LSM/YSZ skeleton and the YSZ electrolyte.

2. Characterization. Formation of the LSM and YSZ phases were confirmed by Rigaku D/max-IIIB X-ray diffraction (XRD) using Cu K α radiation. Morphology and microstructure of the samples at different stages were characterized by the scanning electron microscope (SEM, FEI Quanta 200f, Netherland). Electrochemical Impedance Spectroscopy (EIS) measurements were performed on a Parstat 2273 advanced electrochemical system in the frequency range mainly from 100 kHz to 10 mHz at an amplitude of 10 mV. A three-electrode setup was used with the as-prepared 3-DOM LSM/YSZ cathode as working electrodes (WE), as described in our previous paper.³ For all samples, the cathode area was 0.25 cm². Measurements were taken in air at 650 °C and 700 °C, at zero bias. The spectra were fitted using the analysis software (ZSimpWin, PerkinElmer Instruments).

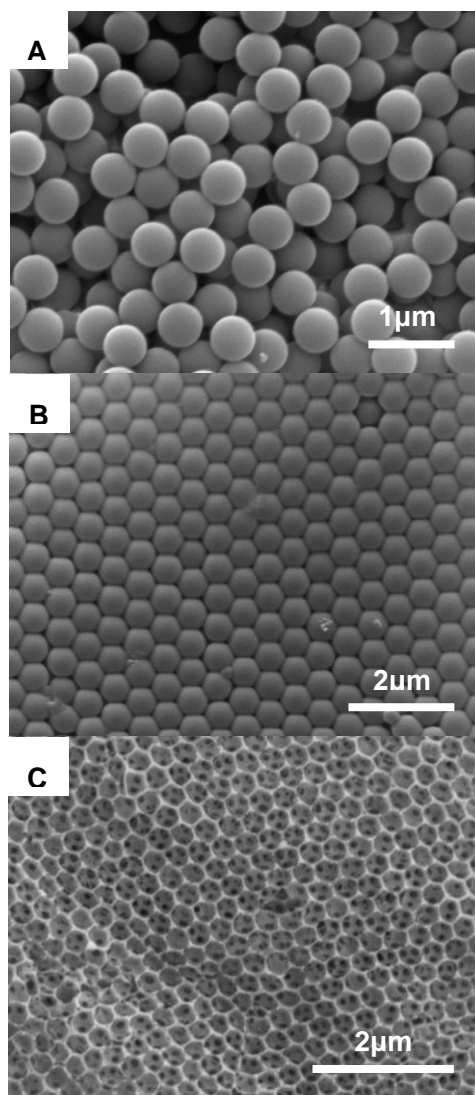


Figure S1. SEM images of the (A) monodispersed PS spheres, (B) PS colloidal crystal self-assembled by the vertical deposition method and (C) 3-DOM LSM/YSZ skeleton calcined at 700 °C for 4 h.

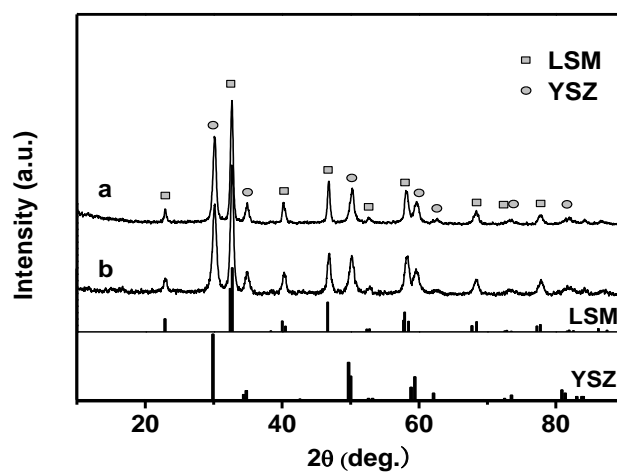


Figure S2. XRD patterns for the 3-DOM LSM/YSZ composites fast-firing at 1000 °C for (a) 15 min and (b) 5 min.

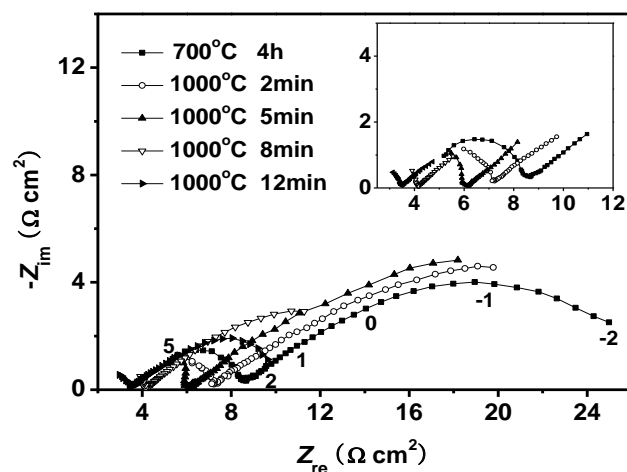


Figure S3. Nyquist plots of the 3-DOM LSM/YSZ composite cathodes fast firing at 1000 °C for 0~12 min, operating at 650 °C, the inset shows the magnified high-frequency section.

It is indicated that the ohmic and polarization resistances of the samples sharply decrease as the dwell time of the fast firing thermal treatment increases from 2 to 12 min. Furthermore, an additional arc at high frequency is only observed when the dwell time is shorter than 12 min and the magnified plot of the high frequency section is shown inset in [Fig. S3](#). Due to the weak contact at the cathode/electrolyte interface, the additional depressed arc should be ascribed to the interface resistance, which is the impedance concerning the ion-transfer processes at the cathode/electrolyte interface.⁴

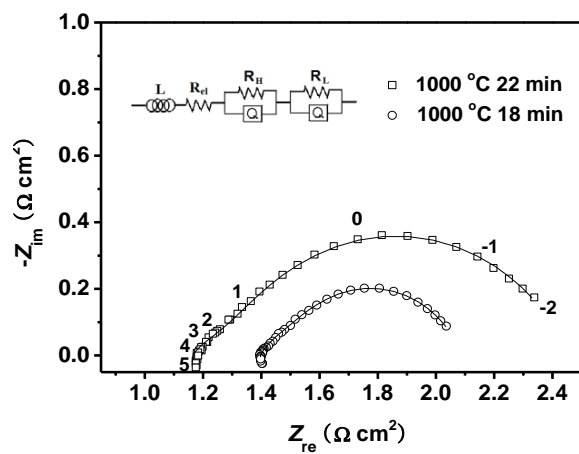


Figure S4. Nyquist plots of the 3-DOM LSM/YSZ composite cathodes fast firing at 1000 °C for 18 min and 22 min, operating at 650 °C.

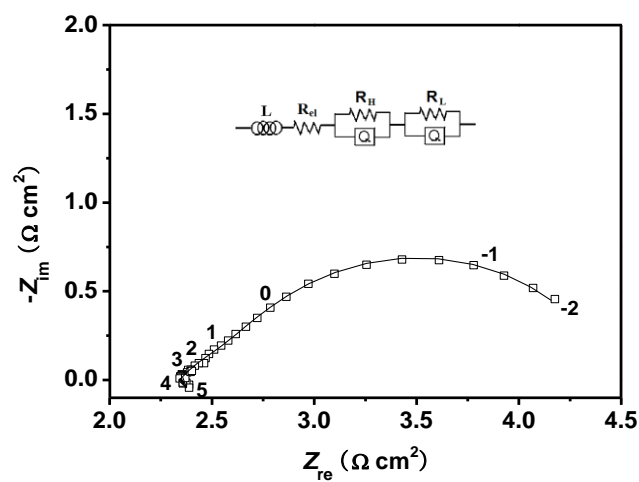


Figure S5. Nyquist plot of the 3-DOM LSM/YSZ composite cathode fast-firing at 1000 °C for 30 min, operating at 650 °C.

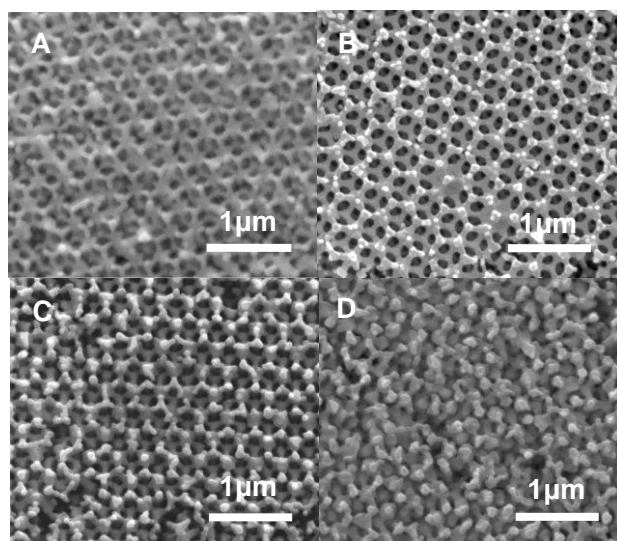


Figure S6. Surface SEM images of the 3-DOM LSM/YSZ composite cathodes fast-firing at 1000 °C for (A) 10 min, (B) 15 min, (C) 20 min and (D) 30 min.

References

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- S3 Q. Fu, K. Sun, N. Zhang, X. Zhu, S. Le and D. R. Zhou, *J. Power Sources*, 2007, **168**, 338.
- S4 S. B. Adler, *Solid State Ionics*, 1998, **111**, 125.