Supplementary Information

All porous solid oxide fuel cell (SOFC): a bridge technology between dual and single chamber SOFC

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Experimental

Fuel cell fabrication: Electrolyte, anode and cathode starting materials are commercial powders. $Gd_{0.1}Ce_{0.9}O_{1.9}$ (CGO) electrolyte was fabricated using uniaxial pressing at 300 MPa pressure by mixing CGO powder (Marion Technologies) with Sigmacell Type 20 cellulose (Sigma-Aldrich) followed by tableting. Then the electrolyte was sintered at 1350 ^{o}C for 5 h to obtain a substrate of the electrodes. After sintering, the substrate of 2 mm thickness and 25 mm diameter showed a porosity of 42% and pore size of 2-3 µm. Electrode layers were prepared by screen printing. The powders, $Ba_{0.5}Sr0_{.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF, Marion Technologies)+CGO (BSCF/CGO=70/30 by weight) for the cathode, and NiO (Sigma-Aldrich)+CGO (NiO/CGO=60/40 by weight) for the anode, were respectively mixed with commercial binder (ESL V400, 0.5 g per gram of powder) and solvent (ESL T404, 8 drops per gram of powder) to obtain inks with the desired viscosity. The obtained inks were then deposited directly onto the two sides of sintered CGO pellets, with a semi-automatic AUREL C890 screen printing machine, using a 180-mesh mask. Four layers of anode were first deposited by screen printing on the CGO pellet and annealed at 1200 °C during 2 h; two layers of cathode were then coated on the other side of the CGO pellet and annealed at 1100 °C for 2 h. The thickness of the resulting NiO+CGO anode and BSCF+CGO cathode is 55 and 25 µm (18 mm diameter), respectively. Finally, a gold mesh (1 mm line space) used as current collector was deposited on the surface of the cathode using screen printing followed by sintering at 900 ^{o}C for 2 h.

Nitrogen permeance measurement: The fabricated fuel cell was sealed in a homemade three atmosphere-type reactor using gold O-rings at 975 ^{o}C under mechanical pressure for 1 h. The temperature was then decreased to 700 ^{o}C for the N_2 permeance test. On the cathode side of

the cell, pure N_2 gas was used with a flow rate of 100 mL min^{-1} (STP), while on the anode side, no sweep gas was used under atmospheric pressure. The pressure of the cathode side was controlled between 1 and 1.35 bar by closing the valve of the outlet in a stepwise fashion. Analysis of N_2 on the anode side was carried out using gas chromatography (Agilent HP 5890).

Electrochemical characterization: After the N_2 permeance test, the performances of the all-porous CGO-supported cell were studied in the anode atmosphere of 4% CH_4-96% He while the cathode was exposed to 4% O_2-96% N_2 at flow rates of 100 mL min^{-1} (STP). The I-V polarization curves were collected using a Bio-Logic potentiostat/galvanostat (EPP-400/4000) with EC-Lab software. The electrochemical impedance measurements were performed using a Solartron 1260A frequency analyzer with an AC amplitude of 200 mV under open-circuit conditions from 10^5 to 0.01 Hz.

Calculation of viscous and Knudsen flow

In the gas phase, there are at least two mechanisms involved in the porous CGO electrolyte transport process: viscous flow (Π_v) and Knudsen diffusion (Π_k).[1] The total N_2 permeance can be expressed as the sum of the viscous flow and Knudsen flow in the following equation:[2]

$$\Pi = \Pi_v + \Pi_k = \frac{\varepsilon r^2}{8\eta\tau RTL} Pm + \frac{2\varepsilon r}{3\tau\theta_k L}\sqrt{\frac{8}{\pi RMT}}$$

where ε is the porosity, r is the modal pore radius of the medium, R is the gas constant per mole, T is the temperature, L is the thickness of the porous medium, τ is the tortuosity factor, η is the viscosity of the gas, Pm is the mean pressure, M is the molar mass of the gas and θ_k is the parameter coefficient of "hardness" of the walls that reflects how the gas molecule "bounces" on the wall.

For the Knudsen diffusion, permeance does not depend on the differential pressure (ΔP), whereas for the viscous flow, the permeance is proportional to the pressure. Thus, the Π_v and Π_k were calculated as shown in Table S1.

For ideal Knudsen diffusion, the selectivity coefficients of gases, for example, nitrogen with respect to oxygen, could be expressed by the following equation:

$$\alpha_k\left(N_2/O_2\right) = \frac{\sqrt{M_{O_2}}}{\sqrt{M_{N_2}}} = 1.07$$

Supporting Tables and Figures

Table S1. The calculated viscous flow (Π_v) and Knudsen diffusion (Π_k) by the equation as a function of the differential pressure at 700°C.

ΔP (bar)	Π_v ($\times 10^7$)	Π_k ($\times 10^6$)	Π ($\times 10^6$)	Π_k/Π (%)
0.05	0.32	6.64	6.96	95.4
0.07	0.45	6.64	7.09	93.6
0.10	0.64	6.64	7.28	91.2
0.13	0.84	6.64	7.48	88.8
0.15	0.97	6.64	7.61	87.3
0.17	1.09	6.64	7.73	85.9
0.20	1.29	6.64	7.93	83.8
0.23	1.48	6.64	8.12	81.8
0.25	1.61	6.64	8.25	80.5
0.27	1.74	6.64	8.38	79.3
0.30	1.93	6.64	8.57	77.5
0.33	2.12	6.64	8.76	75.8
0.35	2.25	6.64	8.89	74.7

Table S2. The calculated oxygen concentration in the anode side of the fuel cell under different current at 700 ^{o}C. The cathode atmosphere is 4% O_2-96% N_2 and pure He is applied to the anode chamber.

Cell compartment	Cathode	Anode		
		I = 0 mA	I = 50 mA	I = 100 mA
Oxygen concentration %	4.00	1.66	1.75	1.86
Enhancement by O^{2-} diffusion %	--	--	5.42	12.05

Table S3. The calculated OCV values of the all porous fuel cell obtained from the Nernst equation as a function of the differential pressure at 700 ^{o}C.

ΔP (bar)	Po_2 in the cathode (bar)[a]	Po_2 in the anode (bar)[b]	Calculated OCV (V)[c]
0	0.040	1.00E-21	0.94606
0.03	0.041	1.00E-21	0.94668
0.05	0.042	1.00E-21	0.94709
0.07	0.043	1.00E-21	0.94748
0.10	0.044	1.00E-21	0.94806
0.13	0.045	1.00E-21	0.94863
0.15	0.046	1.00E-21	0.94899
0.17	0.047	1.00E-21	0.94935
0.20	0.048	1.00E-21	0.94989
0.23	0.049	1.00E-21	0.95040
0.25	0.050	1.00E-21	0.95074
0.27	0.051	1.00E-21	0.95107
0.30	0.052	1.00E-21	0.95156
0.33	0.053	1.00E-21	0.95204
0.35	0.054	1.00E-21	0.95235

[a] $Po_2=P_{cathode}\times Xo_2$, $P_{cathode}$ is the pressure of cathode, Xo_2 is oxygen concentration in the cathode atmosphere.
[b] Po_2 is set as a fixed value of 1.00E-21 according to references.[3, 4]
[c] The OCV is calculated by the Nernst equation of $E_r = \frac{RT}{nF}\left(\frac{P_{O_2},cathode}{P_{O_2},anode}\right)$, where n=4.

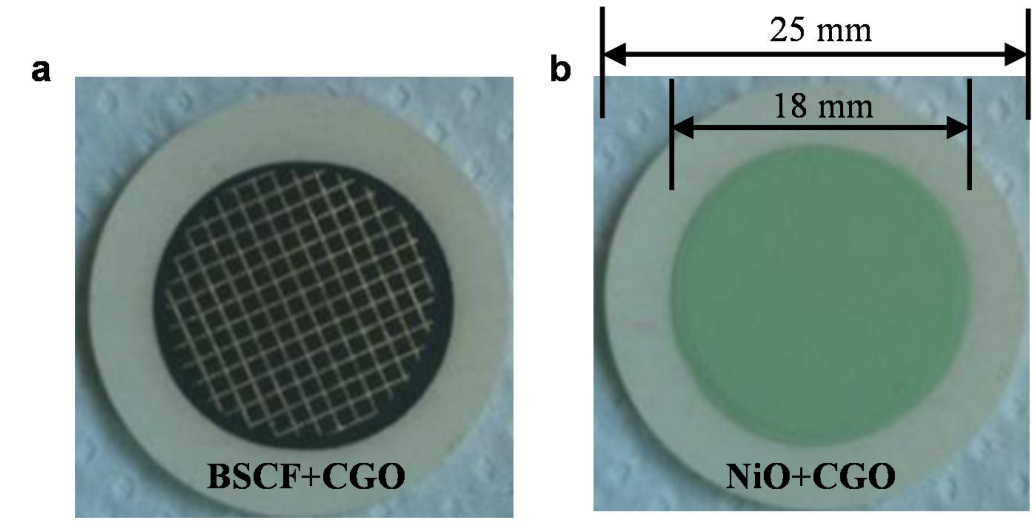

Fig. S1 Digital photos of the fabricated all porous fuel cell: (a) BSCF+CGO cathode side with gold mesh as current collector. The thickness is 25 µm and the surface area is 2.54 cm^2; (b) NiO+CGO anode side without current collector. The thickness is 55 µm and the surface area is 2.54 cm^2.

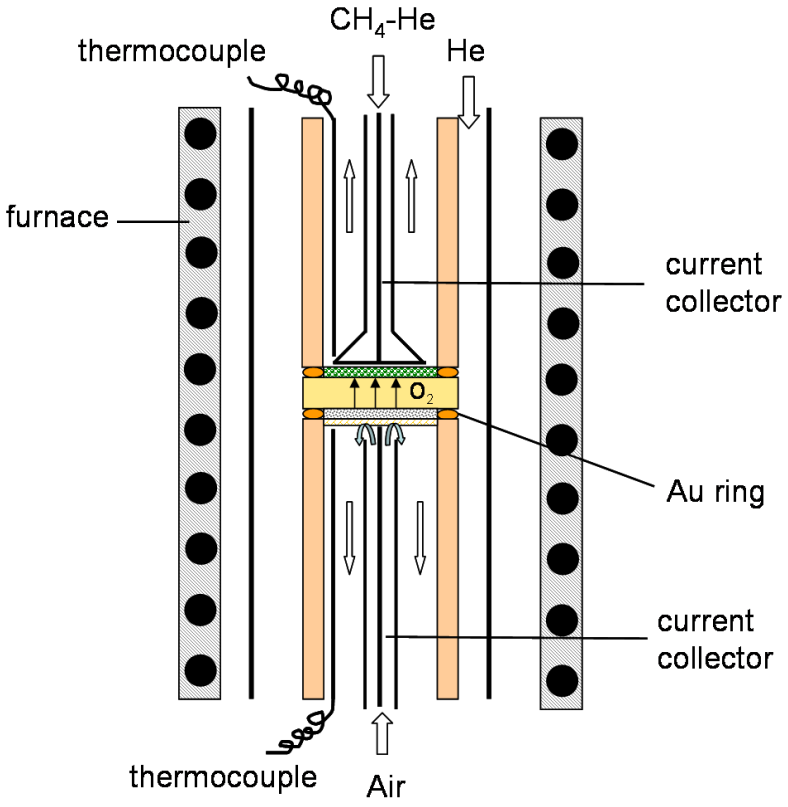

Fig. S2 Shematic diagram of three atmosphere-type reactor developed at LEPMI, France.

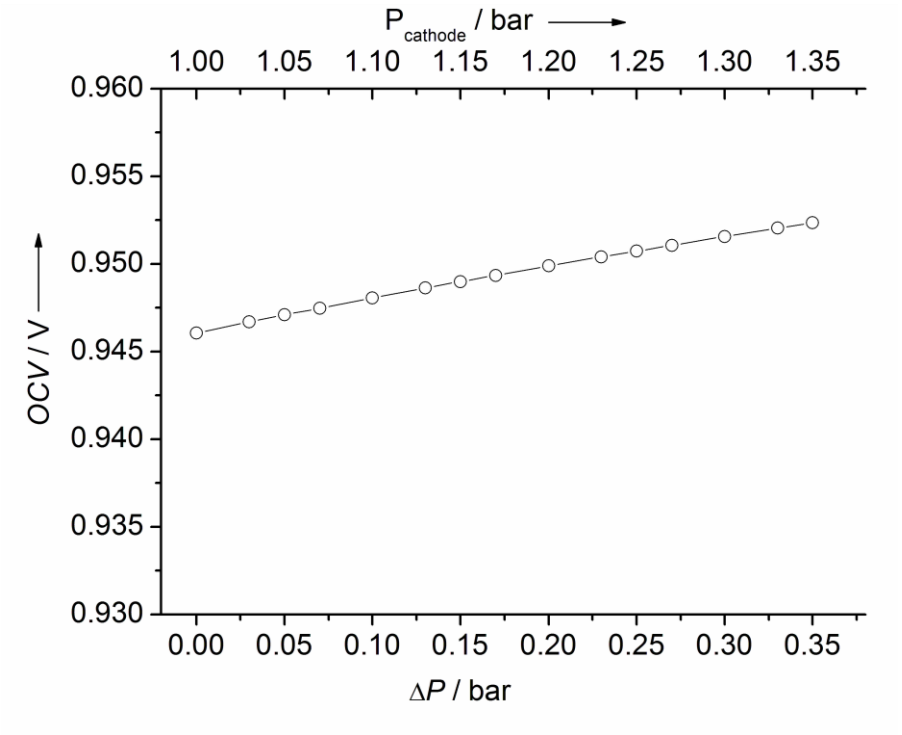

Fig. S3 Open circuit voltage of the all porous fuel cell obtained from the Nernst equation as a function of the differential pressures at 700 ^{o}C.

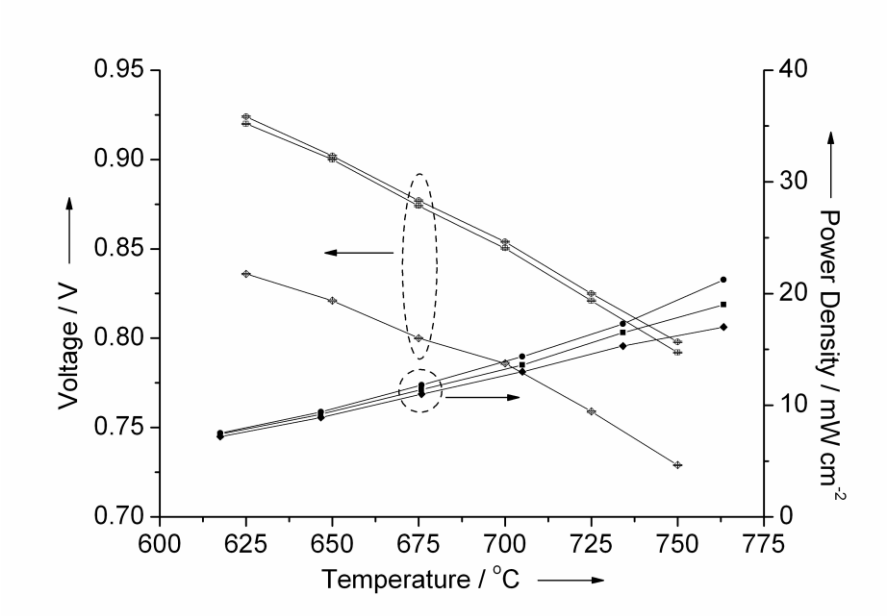

Fig. S4 Open circuit voltage and power density of the all porous fuel cell at different ΔP (■ ΔP=0.05 bar, ● ΔP=0.15 bar, ♦ ΔP=0.30 bar).

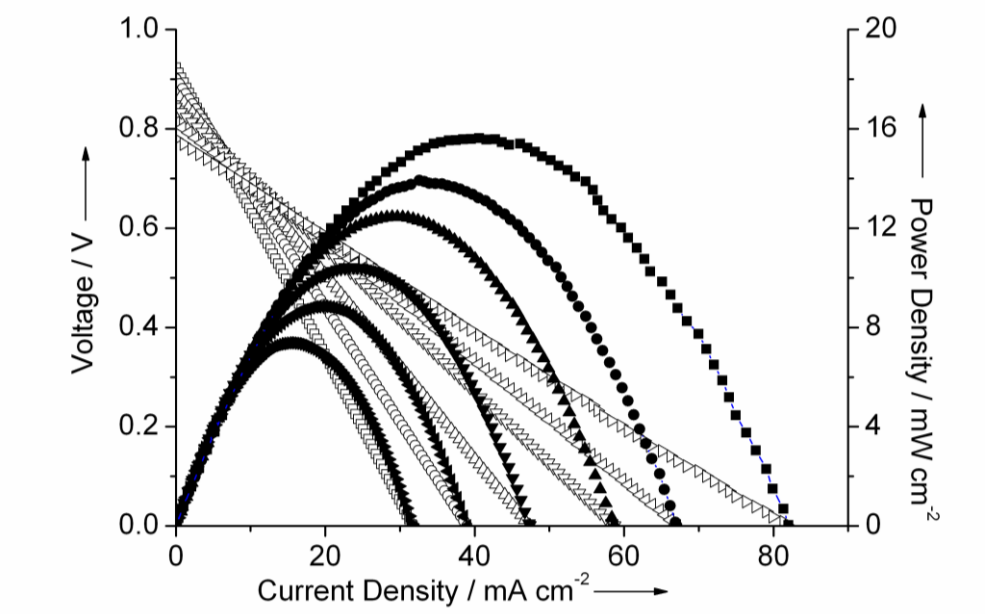

Fig. S5 *I-V* curves of the all porous fuel cell under 4% CH_4-96% He / 20% O_2-80% N_2 atmosphere. The cell voltage and power density are presented as functions of current density at various temperatures (■ 750 °C, ● 725 °C, ▲ 700 °C, ▼ 675 °C, ◀ 650 °C, ► 625 °C).

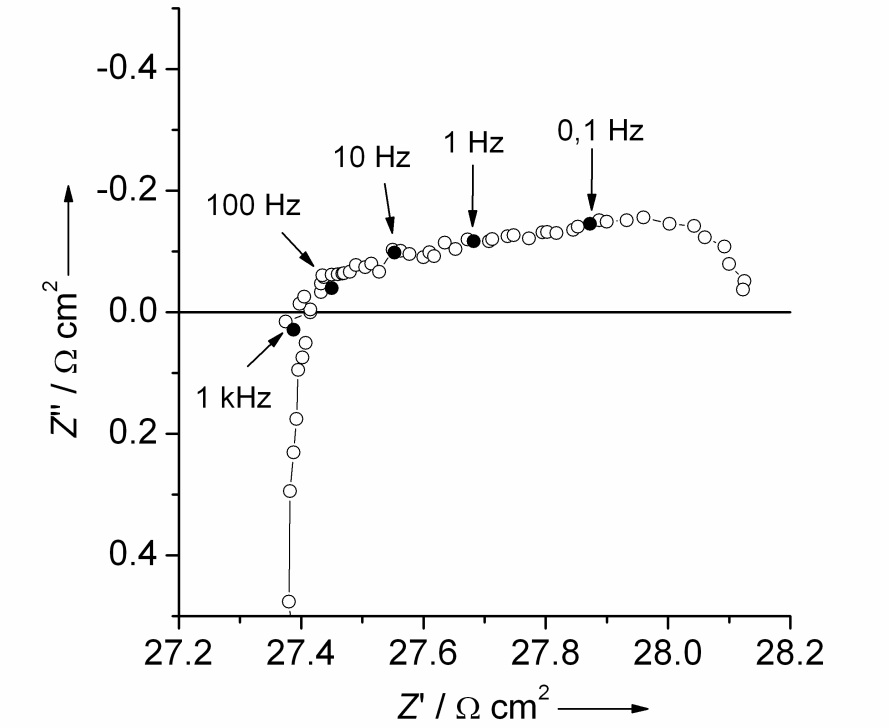

Fig. S6 Electrochemical impedance spectroscopies of the all porous fuel cell under 4% CH_4-96% He/4% O_2-96% N_2 atmosphere at 625 °C. The test was made under open circuit

condition. The AC amplitude is 200 mV and the frequency range is from 10^5 to 0.01 Hz. Flow rates for the anode and the cathode are 100 ml min^{-1} (STP), respectively.

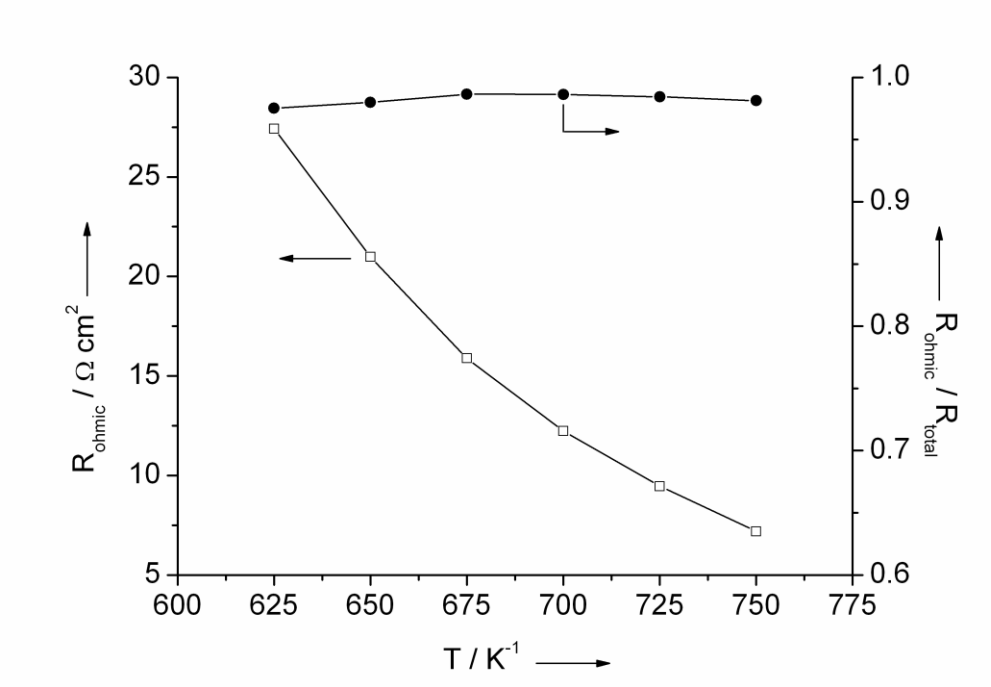

Fig. S7 Ohmic resistance (○) and ratio (●) of ohmic resistance and total resistance of the all porous fuel cell under 4% CH_4-96% He/4% O_2-96% N_2 atmosphere at various temperatures. Flow rates for the anode and the cathode are 100 ml min^{-1} (STP), respectively. The ohmic resistance was calculated from electrochemical impedance spectroscopy of the cell under open circuit condition based on the thickness of the porous CGO electrolyte (2 mm). The total resistance is the sum of ohmic resistance and polarization resistance.

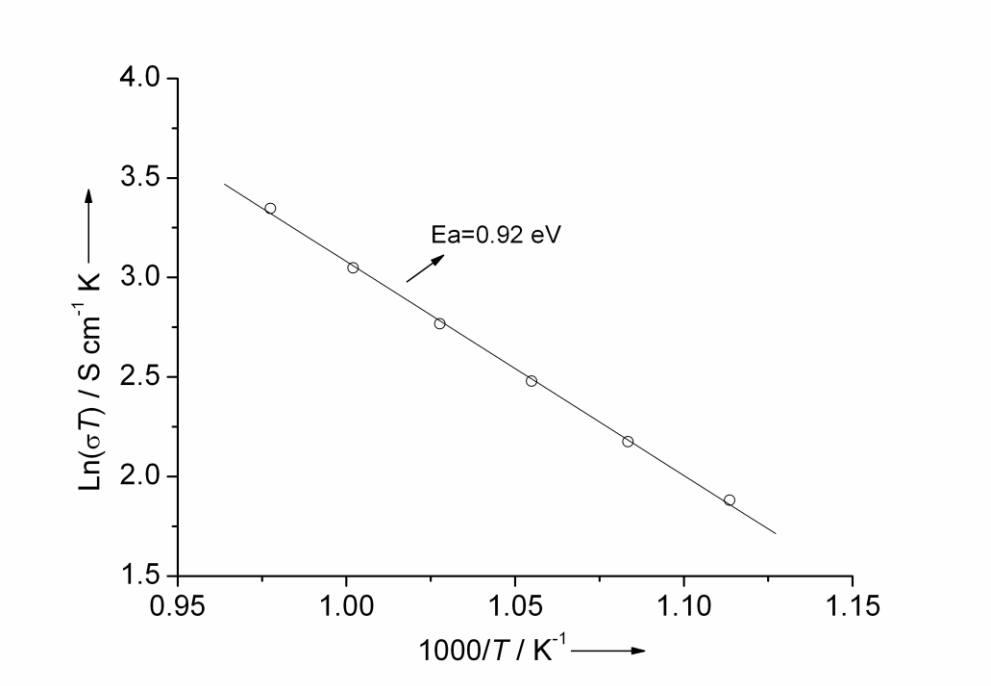

Fig. S8 Arrhenius plot of the ionic conductivity versus 1/T for the porous CGO electrolyte under operating atmosphere. Flow rates for the anode and the cathode are 100 ml min^{-1} (STP), respectively. The ionic conductivity was calculated by the ohmic resistance and the thickness of the porous CGO electrolyte (2 mm) at corresponding temperature.

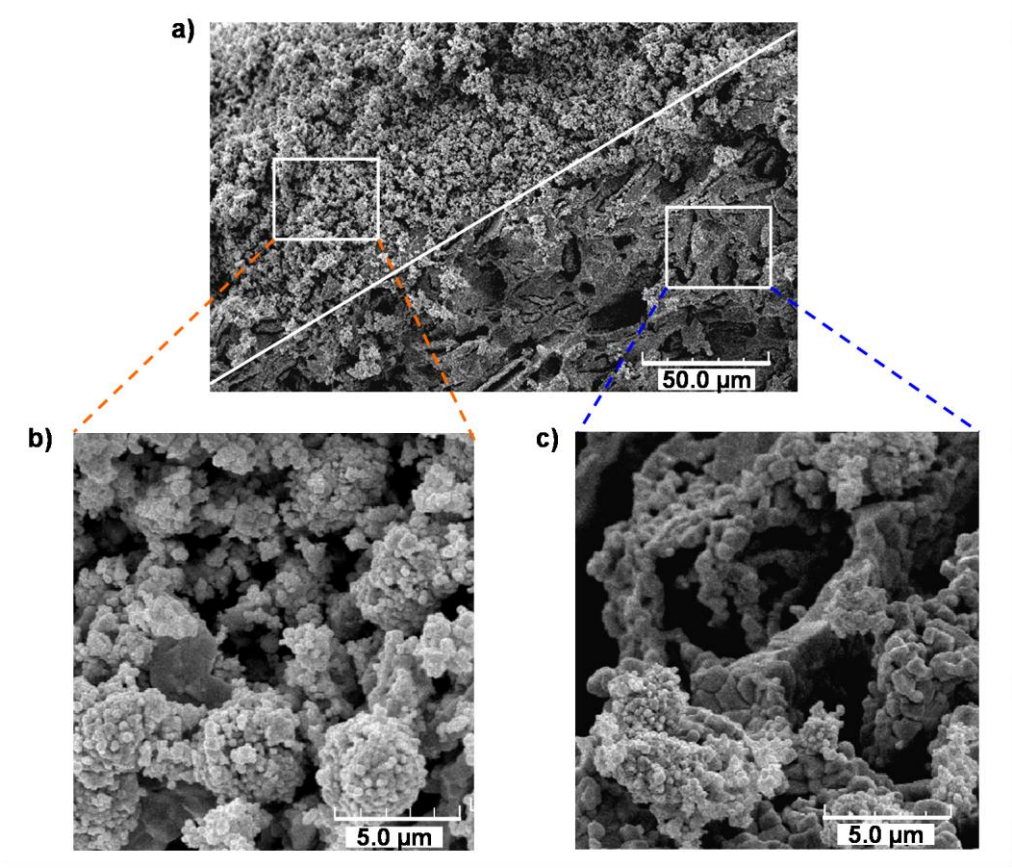

Fig. S9 SEM images of the tested all porous fuel cell composed of NiO+CGO (NiO/CGO=60/40 by weight) anode, porous CGO electrolyte and BSCF+CGO (BSCF/CGO=70/30 by weight) cathode, after 2000 h operating in CH_4 containing atmosphere: (a) Cross-sectional image of electrolyte and anode with scale of 50 μm; (b) SEM image of the Ni-CGO anode with scale of 5 μm; (c) SEM image of the porous CGO electrolyte with scale of 5 μm.

References

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