Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.
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Hierarchically ordered porous Ni-based cathode-supported solid oxide electrolysis cells for stable CO_2 electrolysis without safe gas

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Supporting information

Experimental

1.1 SOEC preparation

Microchanneled cathode supports were prepared via a mesh-templating phase-inversion process [1]. Typically, 60 g of NiO and 40 g of $(Y_2O_3)_{0.08}(ZrO_2)_{0.92}$ (YSZ, Fuelcellmaterials, Ohio, USA) were added into Polyethersulfone /1-Methyl-2-pyrrolidinone (Sigma-Aldrich, Australia) solution (weight ratio of 17.7/100), and 0.07g of Polyvinylpyrrolidone (PVP, MW=40000, Sigma-Aldrich, Australia) was used as dispersant. The mixture was ball-milled in a planetary ball mill machine (MTI Corporation, USA) for 48 h to form a uniform slurry. The slurry was turned into a cathode support green body in a mould when water, as a coagulant, was applied on the top of the mould to induce phase-inversion. With the aid of a stainless steel mesh, microchannels were formed and then opened. The green body was pre-sintered at 1100 °C for 5 h to remove polymer and reach sufficient mechanical strength. For comparison, the cathode supports without channels were also prepared by adjusting the mesh position. As described in the previous study[2], an electrolyte film was prepared on the cathode supports by dip-coating into an YSZ slurry and subsequently sintered at 1350 °C for 6 h. Then, a slurry containing $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ (LSCF-HP, Fuel Cell Materials, Ohio, USA) and $Gd_{0.1}Ce_{0.9}O_{1.95}$ (GDC-TC, Fuel Cell Materials, Ohio, USA) with the weight ratio of 7/3 was sprayed onto the YSZ electrolyte, and an LSCF/ GDC anode layer was formed after sintering at 1000 or 1050 °C for 2 h. The anode area is about 0.6 cm^2.

1.2 catalyst preparation

A 0.2 M GDC solution was prepared by dissolving $Ce(NO_3)_3.6H_2O$ and $Sm(NO_3)_3.6H_2O$ in *N*, *N*-Dimethylformamide, and then $Pd(NO_3)_2.2H_2O$ was dissolved in the solution to reach the Pd^{2+} concentration of 0.2 M. Pd/GDC catalyst were prepared on the cathode scaffold via impregnation. The catalyst precursor solution was infiltrated into the porous cathode supports, followed by vacuum outgassing to improve impregnation effectiveness. After repeating the above process, the SOEC with catalyst precursor was calcined at 700 °C for 2 h. The above process was repeated once to increase catalyst loading. The catalyst loading was roughly calculated according to SOEC weight gains. Pd catalyst was prepared using the same process as Pd/GDC catalyst catalyst preparation without using $Ce(NO_3)_3.6H_2O$ and $Sm(NO_3)_3.6H_2O$. Chemicals for catalyst preparation were purchased from Sigma-Aldrich, Australia.

1.3 cell testing and characterisation

The SOECs were sealed onto a stainless steel tube with a ceramic adhesive (552-VFG, Aremco Products Inc., USA) for conducting CO_2 electrolysis at 800 °C. Pt paste was brushed on anode surface to form a porous layer for collecting current. Initially, hydrogen was introduced to the cathode side to reduce the NiO for 1 h. Then, the input gas was switched to CO_2 with a flow rate of 40 ml/min to test cell resistances and subsequently commenced electrolysis at 0.5 A/cm^2, controlled by an electrochemical workstation (Reference 3000, Gamry). The porosity and pore size distribution of the Ni/YSZ cathode supports was tested by mercury porosimetry (Quantachrome, PoreMaster-60, USA). The microstructure of the cathode was observed by a SEM (Zeiss Neon 40EsB FIBSEM).

Figures

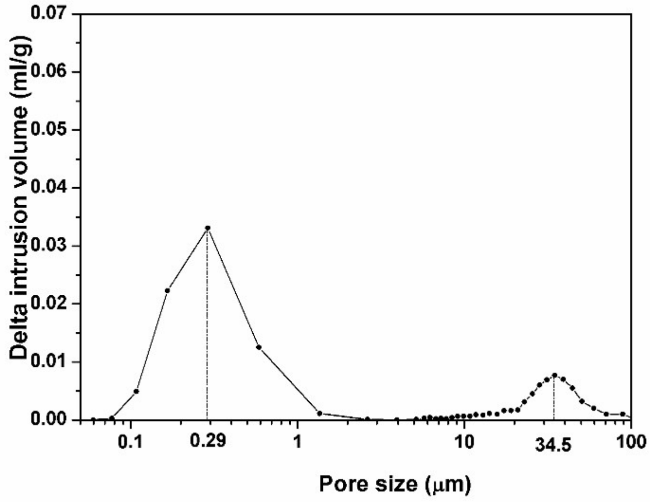

Figure S1. The pore size distribution of microchanneled Ni/YSZ cathode support.

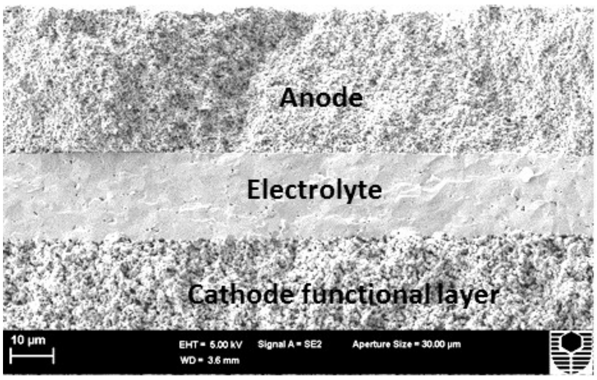

Figure S2. SEM image of SOEC three layers. Scale bar is 10 µm.

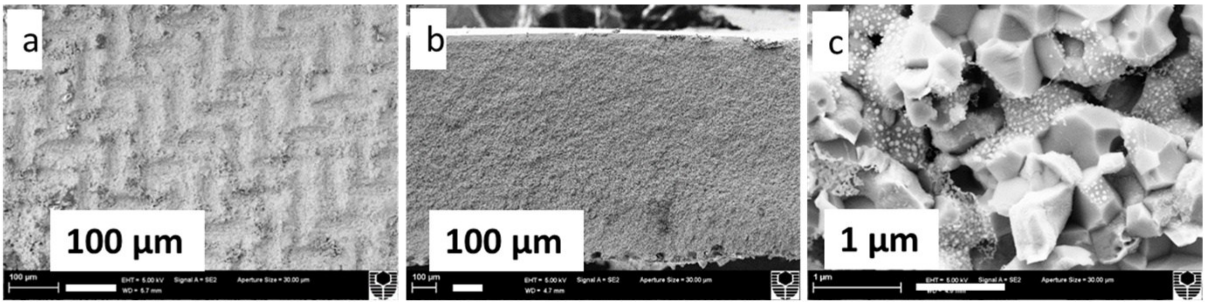

Figure S3. SEM images of cathode without channels: a, surface; b, cross section; c, Pd/GDC catalyst on cathode scaffold.

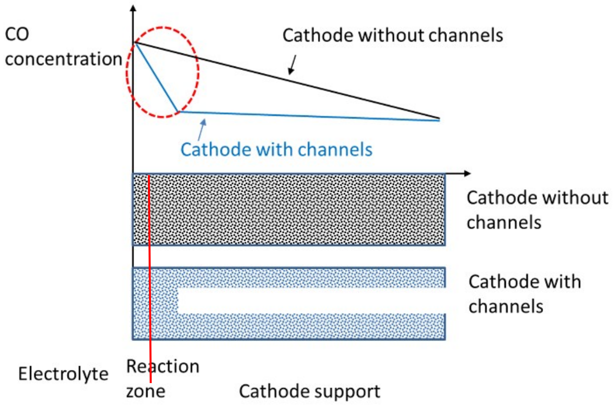

Figure S4. CO concentration profiles within cathode supports with and without channels

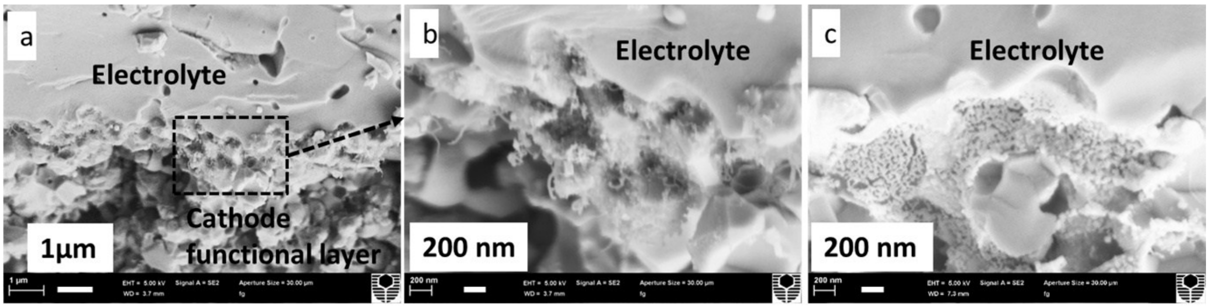

Figure S5. Comparison of carbon formation at the interface between electrolyte and cathode without channels (a and b) and with channels (c)

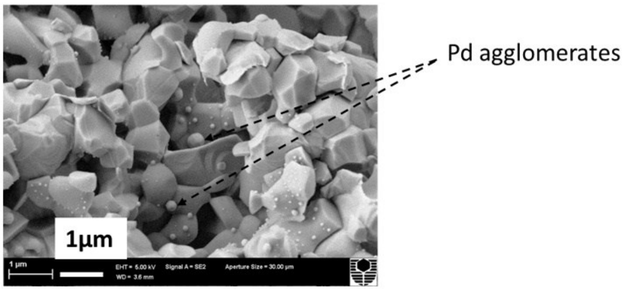

Figure S6. SEM image of Pd agglomerates on Ni/YSZ cathode scaffold

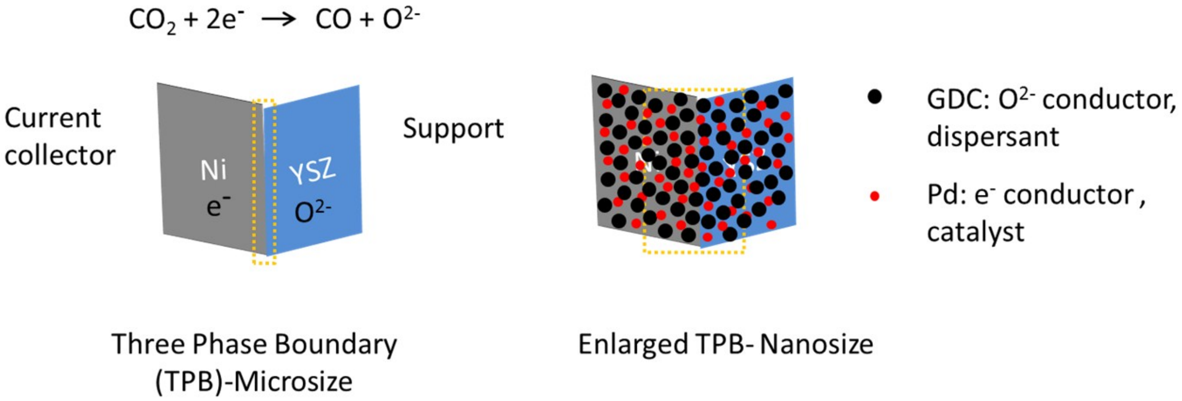

Figure S7. Schematic representation of nanosized TPB over Pd/GDC-coated Ni/YSZ cathode.

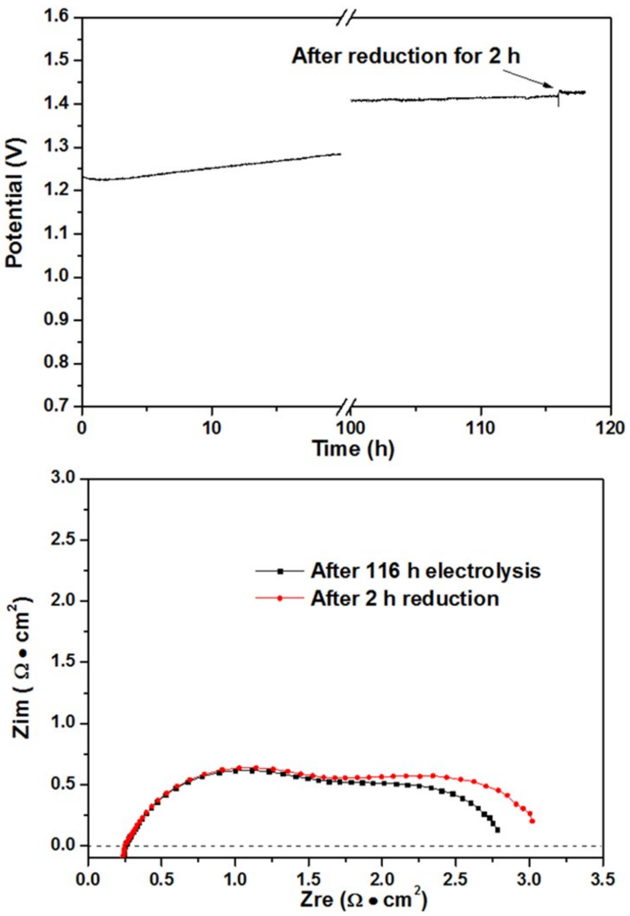

Figure S8. The effect of cathode reduction on CO_2 electrolysis performance: a, applied potential at 0.5 A/cm^2; b, Impedance spectra tested at the OCV (about 0.68 V) in CO_2: the first test was immediately after 116 h-electrolysis. Then, the cathode was reduced in H_2 for 2 h. Subsequently, the second impedance test was conducted after switching input gas to CO_2. Anodes were sintered at 1050 °C.

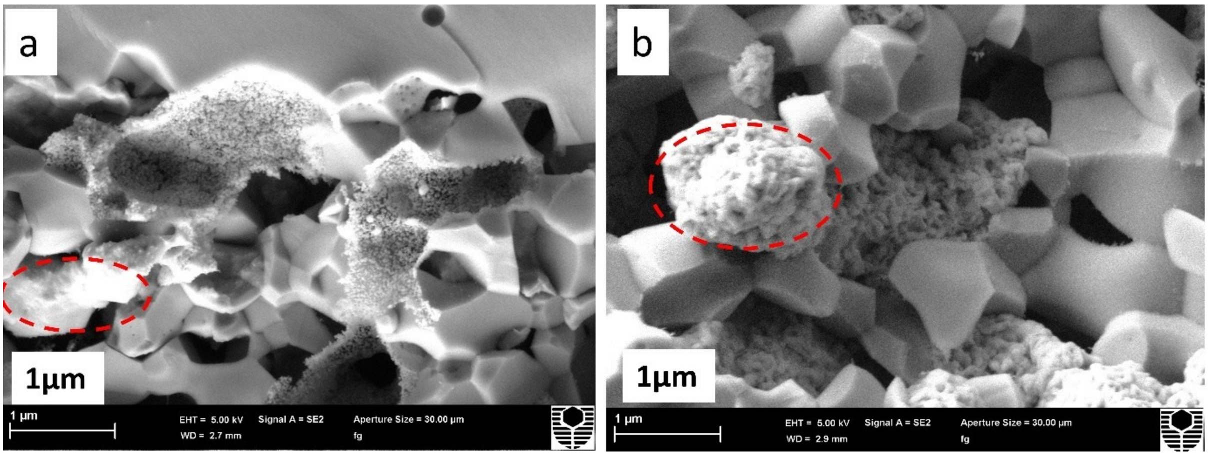

Figure S9. SEM images of Ni surface (marked with red line) in cathode after reduction (a) and electrolysis test (b): smooth surface after the reduction and porous surface after the test due to redox process.

References

[1] X. Shao, D. Dong, G. Parkinson, C.-Z. Li, *J. Mater. Chem. A* 2013, 1, 9641.

[2] D. Dong, X. Shao, K. Xie, X. Hu, G. Parkinson, C.-Z. Li, *Electrochem. Commun.* 2014, 42, 64.