Electronic Supplementary Material (ESI) for Chemical Communications

A ternary cathode composed of LSM, YSZ and $Ce_{0.9}Mn_{0.1}O_{2-\delta}$ for the intermediate temperature solid oxide fuel cells

Li Liu[a,b,c], Zhe Zhao[a,b,c], Xiaomin Zhang[a,b,c], Daan Cui [a,b], Baofeng Tu[a,b], Dingrong Ou[a,b], Mojie Cheng[a,b,*]

a Division of Fuel Cells, Dalian National Laboratory for Clean Energy, Dalian 116023, China

b Laboratory of Fuel Cell, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China

c University of Chinese Academy of Sciences, Beijing, 100049, China

Experimental

Single cells fabrication

Anode-supported fuel cells were fabricated by tape casting method.[1] YSZ (Tosoh-Zirconia; TZ-8Y) and NiO (from J.T.Baker) powders in a 50:50 wt% were mixed thoroughly, and then organic binders and n-butanol solvent were added to form the NiO-YSZ slurry. The slurry was fabricated into anode substrate by tape-casting. A thin layer of YSZ powder was fabricated on one side of the anode substrate by a slurry coating method, then the bilayer was cut into circular disks and sintered at 1300 °C for 3 h in air to obtain a dense YSZ electrolyte. The sintered discs were ~ 21 mm in diameter and ~ 450 μm in thickness. The thickness of the YSZ electrolyte film was ~ 15 μm.

The ternary cathode was composed of LSM, YSZ and Ce-Mn-O. $(La_{0.8}Sr_{0.2})_{0.9}MnO_{3-\sigma}$ (LSM) was synthesized by ammonium citrate method[2,3] with $La(NO_3)_3.6H_2O$ (99.95%), $Sr(NO_3)_2$ (99.95%) and $Mn(NO_3)_2$ solution (49-51%) as raw materials, and calcined at 1100 °C for 2 h to form pure perovskite phase. LSM and YSZ in a 60:40 wt% as cathode were mixed through grinding in a mortar. Then, the powders were deposited on the electrolyte with an active area of 0.5 cm^2, sintered at 1100 °C for 2 h and the thickness was ~20 μm. Pure LSM was used as the current collector, deposited on the surface of LSM-YSZ, and calcined at 1200 °C for 2 h. The Ce-Mn-O solution was infiltrated into LSM-YSZ cathode before testing to form the ternary cathode.

The $Ce_{0.9}Mn_{0.1}O_{2-\delta}$ precursor solution of 2.0 M was composed of appropriate amounts of $Ce(NO_3)_3.6H_2O$ (99.99%), $Mn(NO_3)_2$ solution (49-51%) with citric acid (the ratio of citric acid : cations was 0.5). The solution was pipetted into the LSM-YSZ composite cathode at 60 °C. The amount of $Ce_{1-x}Mn_xO_{2-\delta}$ was varied by the volume of solution, and the cells were calcined at 600 °C for 1 h between each impregnation step. The powder composed of LSM and YSZ in a 60:40 wt% was calcined at 1100 °C for 2 h, infiltrated by 10 wt% $Ce_{0.9}Mn_{0.1}O_{2-\delta}$ precursor solution, and then calcined at 600 °C for 2 h. The $Ce_{0.9}Mn_{0.1}O_{2-\delta}$ precursor solution was heated and evaporated on a hot plate to remove the water and organic compounds, and then calcined at 600 °C for 2 h in air.

Single cells testing

The single cells were evaluated in an alumina test housing placed inside the furnace. The measurements were undertaken using the two-electrode four-wire measurement from 800 °C to 600 °C in 100 ml min^{-1} humid H_2 (3% H_2O) and 100 ml min^{-1} O_2. Au mesh at the cathode side and Ni mesh at the anode were used as current collectors. The electrochemical impedance spectra was measured under open circuit conditions using a Solartron 1260 frequency response analyzer with Solartron 1287 electrochemical interface. The frequency ranged from 10^6 Hz to 0.08 Hz with amplitude of 10 mA.

Characterization of materials

The microstructures of the ternary cathodes after the testing were examined by a Quanta 200 FEG (FEI Company) scanning electron microscope equipped with energy dispersive X-ray (EDX) spectroscopy. X-ray powder diffraction (XRD) patterns were collected with a Rigaku D/Max-2500/PC X-ray diffractometer with Cu Kα radiation in the 2θ range of 20-80°.

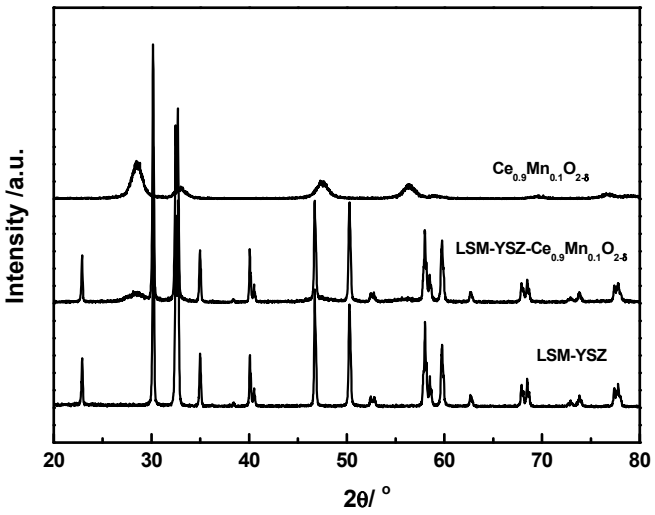

Fig. S1 The XRD patterns of LSM-YSZ powders with and without 10 wt% $Ce_{0.9}Mn_{0.1}O_{2-\delta}$, and $Ce_{0.9}Mn_{0.1}O_{2-\delta}$ powders calcined at 600 °C for 2 h.

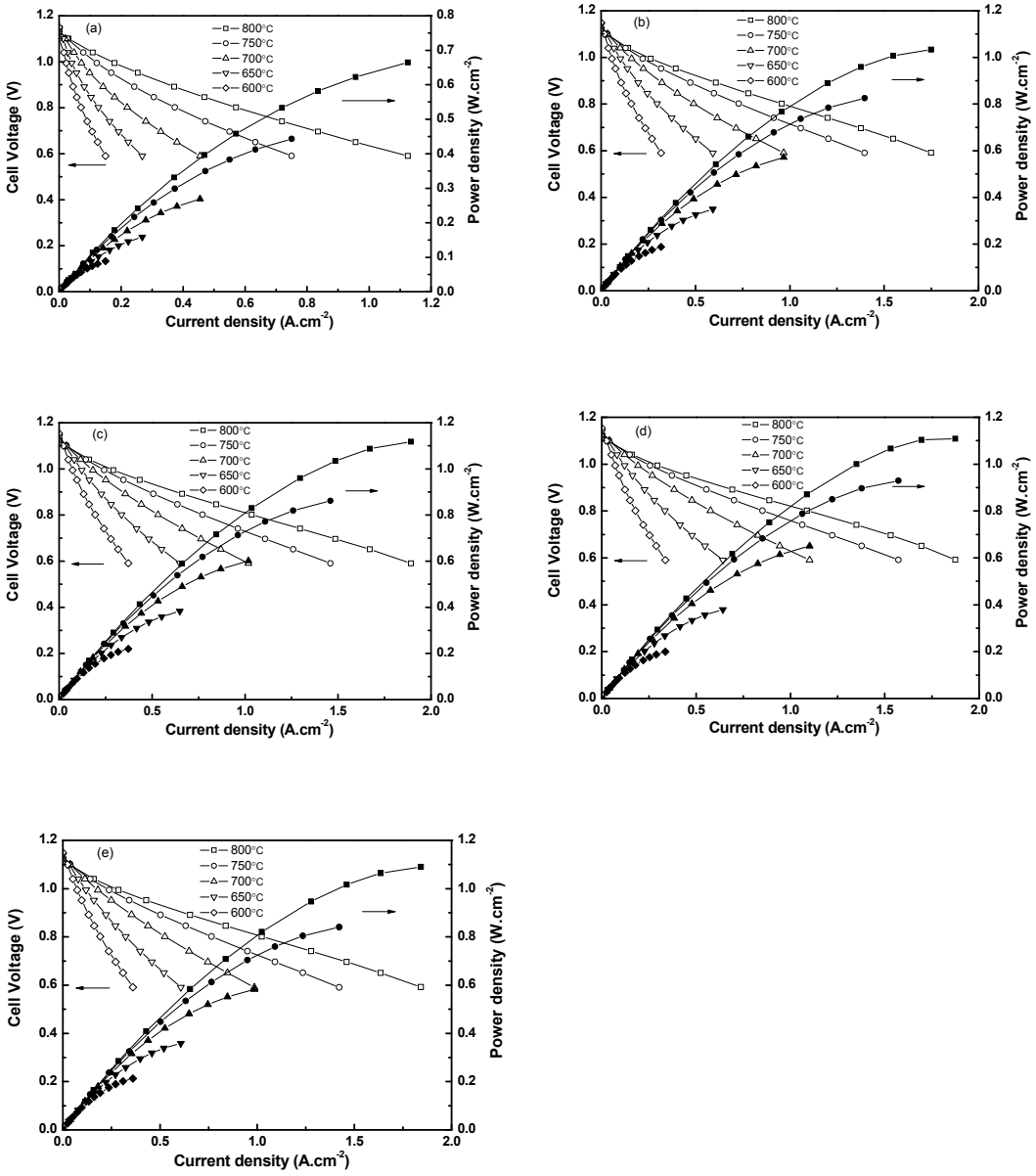

Fig. S2 I-V curves and the corresponding power densities of single cells with composite cathodes of (a) LSM-YSZ, (b) LSM-YSZ-5 wt% $Ce_{0.9}Mn_{0.1}O_{2-\delta}$, (c) LSM-YSZ-10 wt% $Ce_{0.9}Mn_{0.1}O_{2-\delta}$, (d) LSM-YSZ-20 wt% $Ce_{0.9}Mn_{0.1}O_{2-\delta}$, (e) LSM-YSZ -30 wt% $Ce_{0.9}Mn_{0.1}O_{2-\delta}$.*

*These cells with Ni-YSZ as anode and YSZ as electrolyte were fabricated by the same fabrication conditions and tested in humidified H_2 (3 vol. % H_2O) at 100 ml min^{-1} (at STP) in the anode and O_2 at 100 ml min^{-1} (at STP) in the cathode.

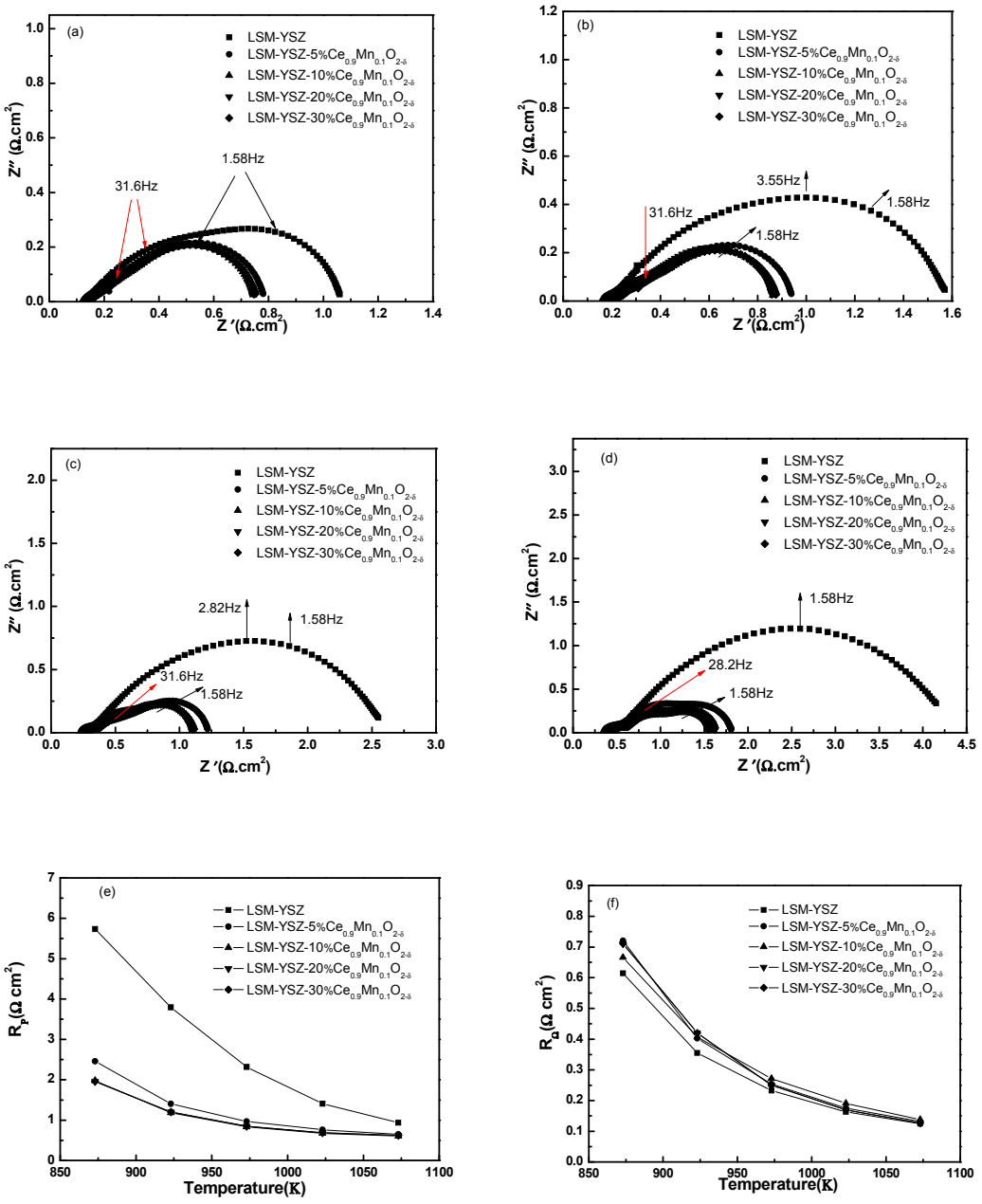

Fig. S3 Comparison of impedance spectra for the cells with LSM-YSZ-5, 10, 20,30 wt% $Ce_{0.9}Mn_{0.1}O_{2-\delta}$ ternary cathodes or LSM-YSZ binary cathode measured under open circuit conditions at 800 °C(a); 750 °C(b); 700 °C(c); 650 °C(d); ASRs of the electrodes (sum of anode and cathode contributions) (e); ohmic resistances of the cells with different cathodes(f)*

*The high frequency intercept on real axis represents the overall ohmic resistances R_{ohm} from the electrolyte, the electrodes (including the cathode and anode), the interfaces of electrodes/electrolyte and the connection wires. The distance between the high-frequency and low-frequency intercepts with the real axis represents the electrodes polarization resistances R_p (sum of anode and cathode contributions). The polarization of O_2 reduction on the LSM-YSZ cathode is much higher than that of H_2

oxidation on Ni-YSZ anode, so the impedance spectra for a single cell mainly reflect the properties of the cathodes.[4]

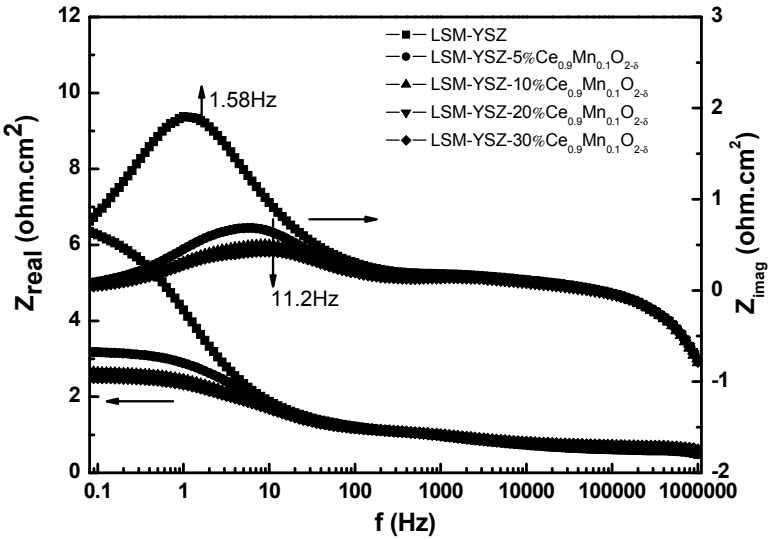

Fig. S4 Bode plots of single cells with LSM-YSZ-5, 10, 20, 30 wt% $Ce_{0.9}Mn_{0.1}O_{2-\delta}$ ternary cathodes or LSM-YSZ binary cathode at 600 °C.

References

1 M. Zhang, M. Yang, B. Liu, Z. Hou, Y. Dong, M. J. Cheng, *J. Power Sources*, 2008, 175, 739.

2 R. A. De Souza, J. A. Kilner, *Solid State Ion.*, 1998, **106**, 175.

3 K. Yamahara, C. P. Jacobson, S. J. Visco, X. F. Zhang, L. C. De Jonghe, *Solid State Ion.*, 2005, **176**, 275.

4 Yi Jiang, Anil V. Virkar and Feng Zhao, *J. Electrochem. Soc.*, 2001, **148**, A1091.