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

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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$_{3-\delta}$ (LSM) was synthesized by ammonium citrate method$^{2,3}$ with La(NO$_3$)$_3$.6H$_2$O (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$_2$O (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$_{1-x}$MnxO$_{2-\delta}$ 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$_2$O) 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 K$\alpha$ radiation in the 20 range of 20-80°.
Fig. S1 The XRD patterns of LSM-YSZ powders with and without 10 wt% Ce₉₀Mn₀₁O₂·₅, and Ce₀₉Mn₀₁O₂·₅ 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$_2$O) 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.\textsuperscript{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