Novel $Mn_{1.5}Co_{1.5}O_4$ spinel cathodes for intermediate temperature solid oxide fuel cells

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Experimental

Preparation of cathode powder

$Mn_{1.5}Co_{1.5}O_4$ (MCO), $Sm_{0.2}Ce_{0.8}O_{1.9}$ (SDC) and $Sm_{0.5}Sr_{0.5}CoO_3$ (SSC) powders were synthesized by a citrate and EDTA process.[1] Stoichiometric amounts of the metal nitrates were dissolved in deionized water, and then a combination of EDTA and citric acid equal to the total number of moles of the metal ions as complexing agents. The mixed solution was slowly heated to combustion point to form the precursor ash. The ash was fired in air for 4 h at 800 ^oC for MCO and SDC and 900 ^oC for SSC.

Fabrication of Anode- supported SOFCs

Anode substrate YSZ-NiO (50 %:50 % weight ratio) were by grinding in a mortar, then suitable organic binders and n-butanol solvent were added, and the mixture was fabricated via a tape-casting process.[2] A colloidal YSZ suspension was then applied to one side of the anode substrate by a slurry coating method. The anode/electrolyte discs thus obtained sintered at 1400 ^oC for 2 h in air. The sintered discs were about 21 mm in diameter and 450 μm in thickness. The thickness of the YSZ electrolyte film was approximately 13 μm. A cathode paste of MCO, MCO-SDC (mechanical mixing 50%:50%, weight ratio), SSC or LSM-YSZ (mechanical mixing 50%:50%, weight ratio) dispersed in terpineol was applied to the electrolyte surface by doctor blade processing (a convenient method for cathode fabrication).[3, 4] The cells were then fired at 1100 ^oC for 3 h in air, except for the one with the LSM-YSZ cathode fired at 1200 ^oC. The final cathode was about 30 μm thick and with about 0.33 cm^2 effective area

for each layer.In this study, the cathode current collectors of the fuel cell are the cathode materials themselves, that is to say there is no Ag / Pt or other noble metal paste as the cathode current collector. Ag wires on the electrodes were used both as current and voltage probes.

Electrochemical Measurement

Anode-supported thin-film fuel cells placed between two quartz tubes were tested under ambient pressure, while humidified hydrogen (3 vol. % H_2O) (100 ml min^{-1} at STP) was supplied to the anode as fuel gas and ambient air as oxidant (300 ml min^{-1} at STP). The ohmic resistances and the polarization resistances of the electrodes were typically measured under cell-testing condition by impedance spectroscopy using a Solartron 1287 electrochemical interface and a Solartron 1260 frequency response analyzer interfaced to a computer in the frequency range from 10^{-2} Hz to 10^{5} Hz. The current-voltage characteristics of the cells were monitored by the Solartron 1287 interfaced to a computer.

Microstructure of Cell Components

Scanning electron microscopy (SEM) images and energy-dispersive X-ray spectroscopy (EDX) scan analysis (linear or map) were performed on a FEI Quanta 200F scanning electron microscope.

Table S1. Ohmic resistances (R_{ohm} / Ω cm^2), polarization resistances of electrodes (R_p / Ω cm^2) and peak power densities (P_{peak} / mW cm^{-2}) of fuel cells with different cathodes on YSZ electrolyte at different temperatures*

	650ºC			700ºC			750ºC			800ºC		
	R_{ohmic}	R_p	P_{peak}	R_{ohmic}	R_p	P_{peak}	R_{ohmic}	R_p	P_{peak}	R_{ohmic}	R_p	P_{peak}
MCO	1.38	7.52	57	0.40	2.56	139	0.31	1.11	248	0.29	0.70	386
MCO-SDC	1.62	7.62	42	1.23	3.41	77	0.95	1.85	126	0.85	1.30	151
MCO-SDC, SSC	0.31	3.52	166	0.26	1.35	394	0.17	0.57	707	0.15	0.50	912
LSM-YSZ	0.29	4.07	150	0.22	1.89	253	0.18	0.94	383	0.15	0.60	551

* These fuel cells were fabricated by the same cell preparation procedure and tested under the same conditions (humidified H_2 (3 vol. % H_2O) at 100 ml min^{-1} (at STP) in the anode and air at 300 ml min^{-1} (at STP) in the cathode). Note that the weight ratio of MCO and SDC or LSM and YSZ is equal to 50:50% by mechanical mixing.

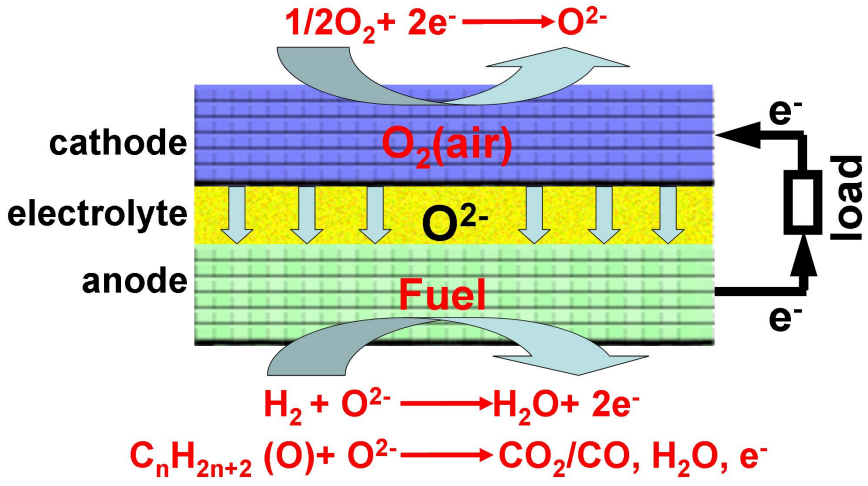

Figure S1. Scheme of the solid oxide fuel cell. *

*The fuel cell, a sandwich structure, is constructed with two porous electrodes and a dense electrolyte. When an oxygen molecule from air contacts the triple-phase-boundary (electronic-ionic-gas) interface, it catalytically acquires four electrons from the cathode and decomposes into two oxygen ions. The oxygen ions diffuse into the electrolyte material and migrate by oxygen vacancies to the anode. The oxygen ions meet the fuel (e.g. hydrogen, hydrocarbon) at the anode/electrolyte interface and react catalytically, giving off water, carbon dioxide, heat, and electrons. The electrons transport through the anode to the external circuit and back to the cathode, providing a source of useful electrical energy in an external circuit. And then it finishes a cycle and continues the cycles.

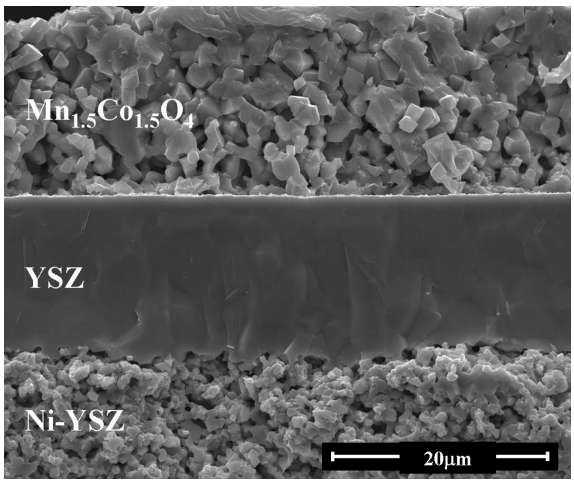

Figure S2. Cross-section SEM image of MCO cathode on YSZ electrolyte after electrochemical test. *

*The MCO particles after test are obvious bigger than the ones before test, since sintering of MCO spinel had been occurring during electrochemical test. There is no cracking or delamination between two neighbor layers.

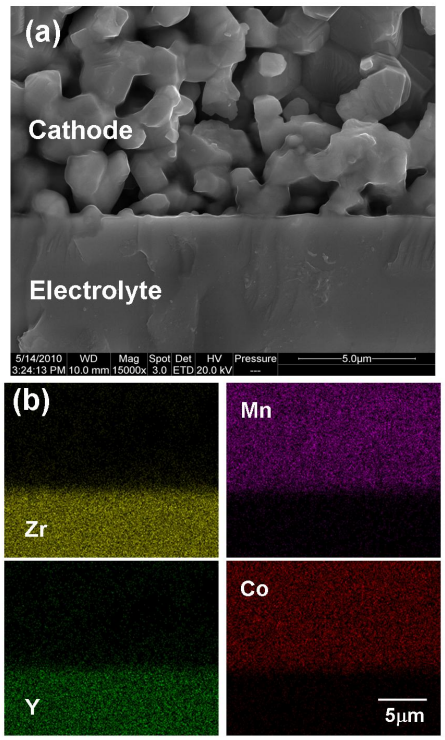

Figure S3. a) Cross-section SEM image of MCO cathode on YSZ electrolyte, and b) EDX map scan analysis of the whole region in image a).

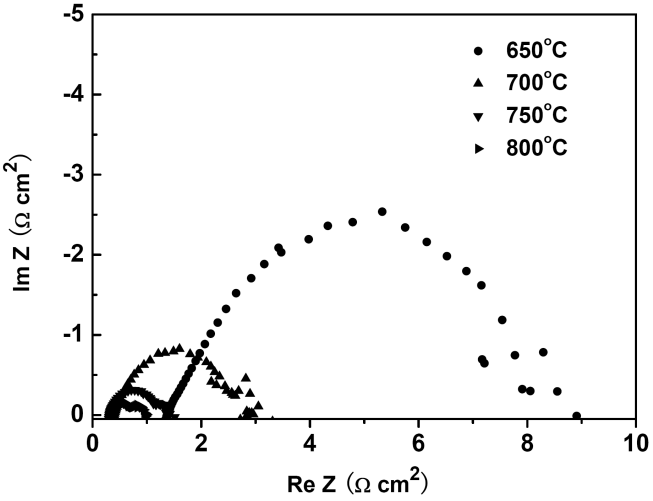

Figure S4. Impedance spectra of the single cell with MCO cathode measured under open-circuit conditions at different temperatures.*

*The intercept with the real axis at high frequencies represents the ohmic resistance of the electrolyte, electrodes and silver wires, whereas the difference between the high-frequency and low-frequency intercepts with the real axis represent the sum of the electrode polarization resistances of the fuel cell (primarily cathode). Above 700 ^{o}C, the difference of the ohmic resistances at different temperatures is smaller than the one of polarization resistances, which implies the performance of this fuel cell is primarily limited by the high polarization resistance of the electrodes.

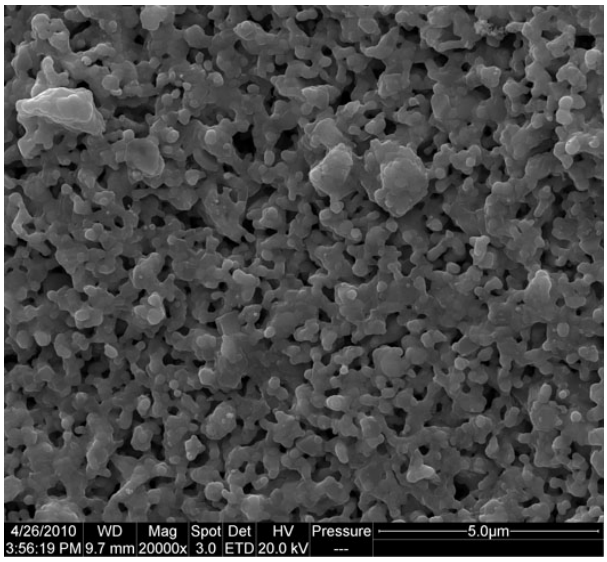

Figure S5. SEM image of cathode surface for the fuel cell: Ni-YSZ | YSZ | MCO-SDC.*

*The MCO-SDC cathode is porous and particles well connected to each other and with sizes in the range 0.4-1 μm, clearly smaller than the particles of the MCO cathode.

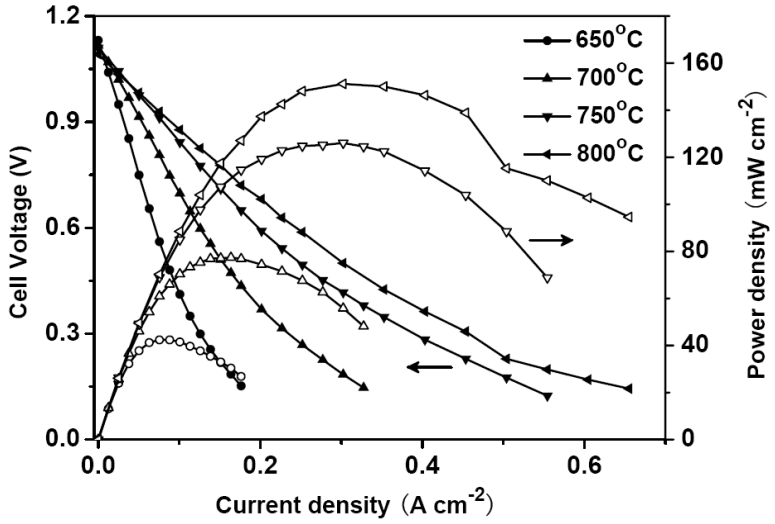

Figure S6. Cell voltages and power densities as functions of current density for the fuel cell: Ni-YSZ | YSZ | MCO-SDC tested in humidified H_2 (3 vol. % H_2O) at 100 ml min^{-1} (at STP) in the anode and air at 300 ml min^{-1} (at STP) in the cathode at different temperatures.

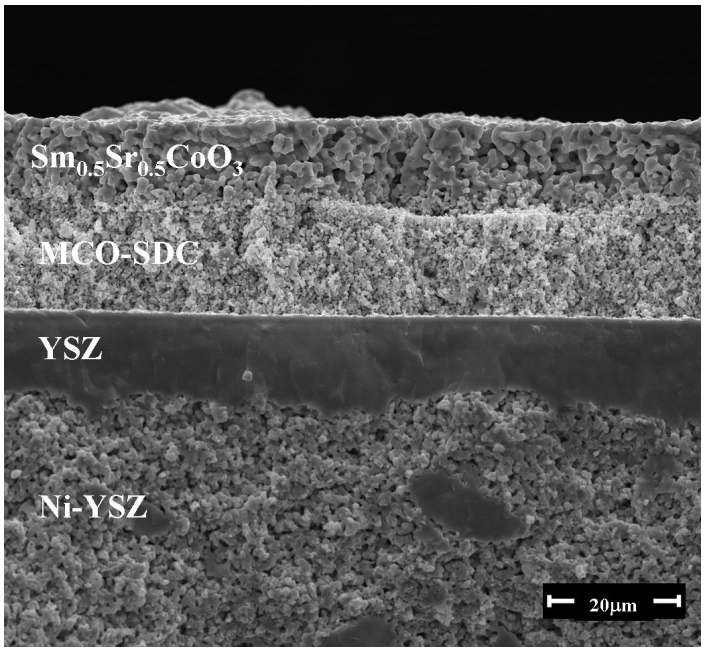

Figure S7. SEM cross sectional image of the cell with cathode: | MCO-SDC, SSC, after electrochemical test. *

* There is no cracking or delamination between two neighbor layers before or after electrochemical test. The sintering temperature of SSC is lower than that of composite MCO-SDC, so the sizes of the SSC particles are obvious larger than that of MCO-SDC. But there is no growth of the particles of MCO-SDC or SSC during electrochemical test.

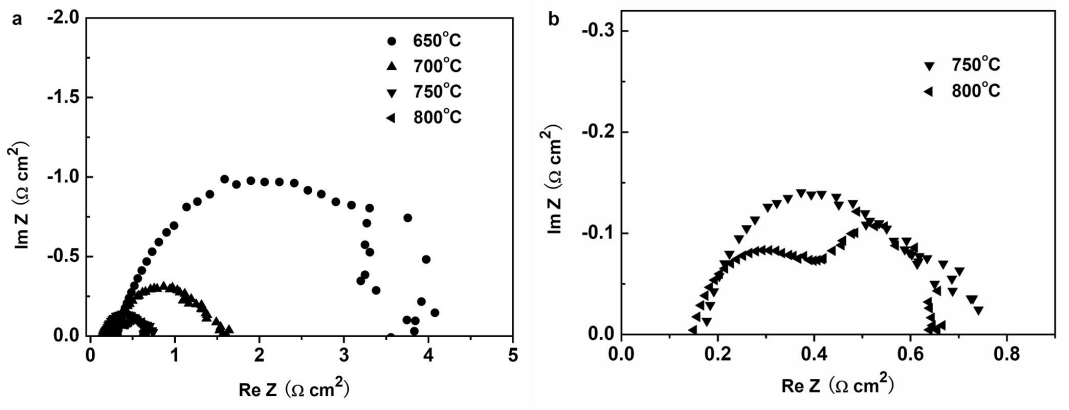

Figure S8. a) Impedance spectra of the single cell: Ni-YSZ | YSZ | MCO-SDC, SSC measured under open-circuit conditions at different temperatures, and b) the values for 750 and 800 ^{o}C.

References

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2 M. Zhang, M. Yang, Z. F. Hou, Y. L. Dong, M. J. Cheng, *Electrochim. Acta* 2008, **53**, 4998.

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4 H. Z. Zhang, H. Y. Liu, Y. Cong, W. S. Yang, *J. Power Sources*, 2008, **185**, 129.