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

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$Mn_{1.5}Co_{1.5}O_4$ spinel oxide as a cathode or one component of a composite cathode presents no visible reaction with an Y_2O_3-stabilized ZrO_2 electrolyte. The low electrode polarization resistances and good performance compared with traditional Sr-doped $LaMnO_3$–YSZ composite cathodes imply promising application for the next generation of intermediate-temperature solid oxide fuel cells.

Solid oxide fuel cells (SOFCs) (Fig. S1, ESI†) are electrochemical devices for the direct conversion of chemical energy to electrical energy with high system efficiencies and environmental benefits.[1,2] To date, there has been significant progress in decreasing SOFCs operating-temperature,[3] optimizing anode,[4,5] electrolyte[6] and cathode[7] structures–compositions, and enhancing the power output.[8,9] Below 800 °C, the interconnection of SOFC stacks using metallic interconnections can significantly reduce the cost of SOFC devices and has an ideal projected service lifetime of ~40 000 h, longer than the working lifetime of fuel cells using electrolytes other than the YSZ electrolyte.[10–12] Although other solid electrolytes for SOFCs have higher conductivities, most of them either exhibit electronic conduction under reducing conditions or react with commonly used electrode materials.[7,13]

The traditional cathode material for an Y_2O_3-stabilized ZrO_2 (YSZ) electrolyte is a composite of Sr-doped $LaMnO_3$ (LSM) and YSZ. This composite cathode provides stable power output during long-term testing; however, its catalytic activity decreases sharply and leads to a relatively high polarization resistance below 800 °C.[1] The polarization resistances of cathodes made from mixed conducting perovskites, such as Sr-doped $LaCoO_3$ (LSCo),[14] $LaFeO_3$ (LSF),[15] or $LaCo_{1-x}Fe_xO_3$ (LSCF),[16] can be much lower. However, the standard preparation method for these alternative electrodes is accompanied by a solid-state reaction with YSZ at the required calcination temperatures (~1100 °C). In this communication, we intend to explore a novel cathode material which is thermally and chemically compatible with the YSZ electrolyte and metallic interconnections.

Spinel oxides materials have been extensively studied in the field of SOFCs as protective layers coated onto stainless steel interconnections to reduce the contact resistance between the interconnections and the cathode and inhibit the transfer of Cr from the steel interconnections to the cathode.[17,18] This work depends on their high conductivity and the matching of thermal expansion coefficients (TEC, *e.g.* $(Co, Mn)_3O_4$ equal to 11–12 × 10^{-6} K^{-1})[19,20] with that of the steel interconnections (11.5–14 × 10^{-6} K^{-1})[11] and other parts of the fuel cell (10.5–12.5 × 10^{-6} K^{-1}).[1,7] It has been reported that a $Mn_{1.5}Co_{1.5}O_4$ (MCO) spinel protection layer on the stainless steel interconnections is the best of the $(Mn Co)_3O_4$ spinel series because of its excellent electronic conductivity (~60 S cm^{-1} at 800 °C in air) and good thermal and structural stability.[21,22] Although all these features imply that MCO spinel oxide may be a potential cathode material, there have been no reports on power output of such SOFCs.[23] Here we show a fuel cell with a spinel MCO as cathode on an YSZ electrolyte for intermediate temperature of SOFCs.

After calcination at 1100 °C for 3 h or electrochemical test, the MCO cathode and the YSZ electrolyte are well adhered to each other, with no cracking or delamination, as determined by scanning electron microscopy (SEM), as shown in Fig. 1a and Fig. S2, ESI.† The TEC of MCO is reported to be 11.7 × 10^{-6} K^{-1},[21] close to that of YSZ (10.8 × 10^{-6} K^{-1})[7] in the range 20–800 °C. It reveals that the MCO cathode and the conventional electrolyte YSZ show good thermal

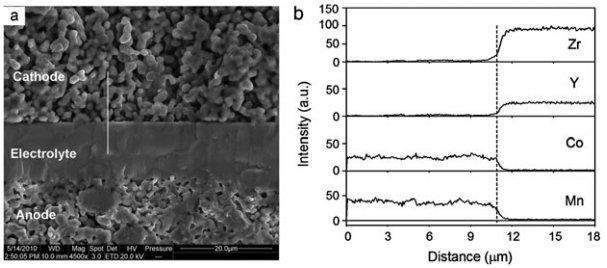

Fig. 1 (a) Cross-section SEM image of the fuel cell before testing, and (b) EDX linear scan analysis of the relative density of the element distribution along the white line shown in an image. The linear scan analysis performed from the cathode to electrolyte over an 18 μm range.

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compatibility with each other. An energy-dispersive X-ray spectroscopy (EDX) linear scan analysis (see Fig. 1b) was performed through the cathode/electrolyte cross-section of the fuel cell to examine the chemical compatibility between the MCO cathode and the YSZ electrolyte. The linear scan shows that there is almost no elemental inter-diffusion between these two layers in the error range of the instrument (Note that the spatial resolution of the EDX-instrument used for image characterization is about 1 μm.) Additionally, a clear-cut interface (see Fig. S3a and S3b, ESI†) between the electrolyte and the cathode reveals that no visible reaction has taken place to form high-resistance zirconate phases in the triple phase boundaries (TPBs) of the interface between the MCO cathode and the YSZ electrolyte. This phenomenon arises from the fact that MCO has neither rare-earth element nor alkaline-earth species in its chemical composition. Therefore, MCO and YSZ are also chemically compatible with each other, and there will be no problem when the fuel cells with the MCO cathode directly connect with the ferric steel stainless interconnects. This is the first time a feasible procedure for fabricating a single cell with a MCO cathode well-adhered on an YSZ electrolyte without any reaction *via* standard electrodes preparation has been demonstrated.

The current–voltage characteristics and the corresponding power densities of a fuel cell with the MCO cathode in a conventional anode supporting a ~13 μm thick YSZ electrolyte fuel cell were then investigated with humidified hydrogen (3 vol% H_2O) as fuel and air as oxidant. As shown in Fig. 2, the open circuit voltages achieve ~1.1 V, which reveals that the electrolyte is dense. The peak power densities (P_{peak}) of the fuel cell are 57, 139, 248, 386 mW cm^{-2} at 650, 700, 750, 800 °C, respectively. Although we first demonstrate that this single cell with the MCO cathode can be operated with the power output, these values of P_{peak} at each temperature point are not satisfying. Through analysis of existing data, we found that the polarization resistance of the electrodes dramatically reduced to 0.70 Ω cm^2 at 800 °C from 2.56 Ω cm^2 at 700 °C (Note that we use the term area specific resistance (ASR) to describe all resistance terms and measured the resistance of electrodes by single fuel cells, not symmetric cells). However, the difference of the ohmic resistance is only 0.11 Ω cm^2 from 0.40 Ω cm^2 at 700 °C to 0.29 Ω cm^2 at 800 °C (see Table S1 and Fig. S4, ESI†). It indicates that the performance of the cell is primarily limited by the high polarization resistance of the electrodes, which results from the TPBs only locating at the interfaces of the electrolyte and cathode in view of negligible oxygen ion conductivity of the MCO (less than 10^{-3} S cm^{-1} at 800 °C,[21] close to the value of LSM).[24] Therefore, to enhance the cell performance, it is necessary to add an ionic conducting phase to make the TPBs length extend to the entire cathode area, so as to decrease the cathode polarization resistance.

Considering that the ionic conductivity of YSZ is lower than that of the samaria-doped ceria (SDC) at intermediate temperatures, a composite MCO–SDC cathode (weight ratio 1 : 1) has been made on the YSZ electrolyte to extend the TPBs from simply the interface between the YSZ electrolyte and the MCO cathode to the entire cathode area (see Fig. S5, ESI†). However, the performance of the cell with the MCO–SDC cathode decreases significantly in comparison to that of the MCO cathode. For example, P_{peak} is 42, 77, 126, 151 mW cm^{-2} at 650, 700, 750, 800 °C, respectively (see Fig. S6, ESI†). Furthermore, it is noted that the resistances increase considerably (see Fig. 3 and Table S1, ESI†), especially the ohmic resistances. The reason for this result is that the electronic conductivity of the MCO–SDC composite cathode is significantly lower than that of the MCO cathode, which leads to difficulty in current collecting for the cathode.[4] Therefore, it is necessary to coat a current collector onto the MCO–SDC composite cathode. Perovskite oxide $Sm_{0.5}Sr_{0.5}CoO_3$ (SSC) is an appropriate choice in terms of its excellent mixed electronic–ionic conduction.[25–28] After coating the SSC onto the MCO–SDC composite cathode (see Fig. S7, ESI†), the performance is greatly enhanced and confirmed by the significant reduction of both ohmic and polarization resistances (see Table S1 and Fig. S8, ESI†). Fig. 4 shows that the observed P_{peak} of this single cell reaches 166, 394, 707, 912 mW cm^{-2} at 650, 700, 750, 800 °C, respectively, which are higher than those for the cell with the MCO cathode, the MCO–SDC composite cathode, or even the LSM–YSZ composite cathode measured in our laboratory (see Table S1, ESI†). The results confirm that a current-collecting layer

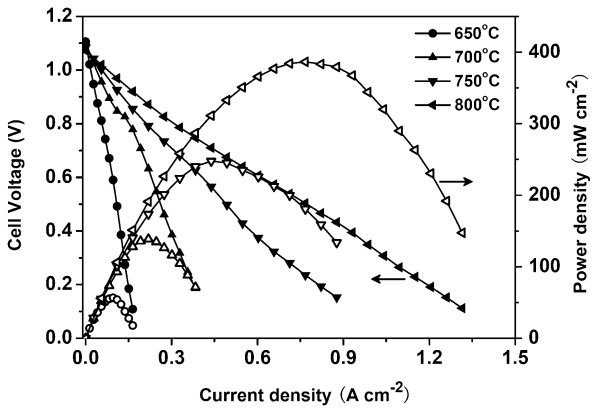

Fig. 2 Cell voltages and power densities as functions of current density for a fuel cell: Ni–YSZ|YSZ|MCO (~20 μm) tested in humidified H_2 (3 vol% H_2O) at 100 ml min^{-1} (at STP) in the anode and air at 300 ml min^{-1} (at STP) in the cathode at different temperatures.

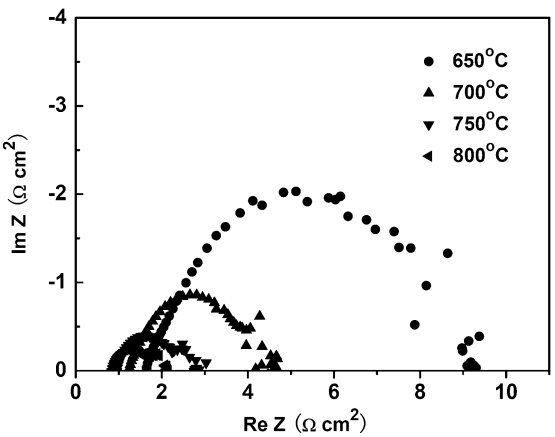

Fig. 3 A typical impedance spectrum of the single cell with the MCO–SDC composite cathode under open-circuit and performance-test conditions at different temperatures.

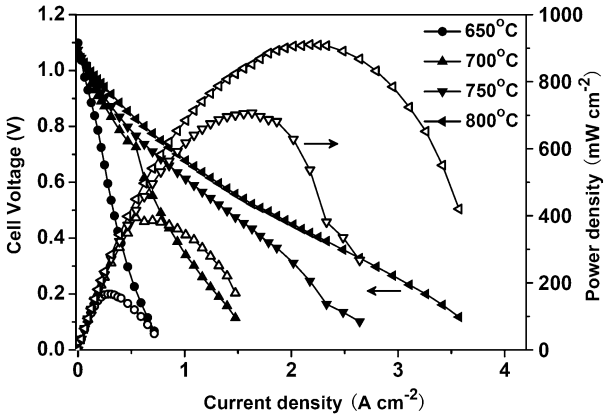

Fig. 4 Cell voltages and power densities as functions of current density obtained from a Ni–YSZ|YSZ|MCO–SDC (~20 μm), SSC (~15 μm) fuel cell. Air was supplied to the cathode (300 ml min^{-1} at STP) and humidified H_2 (3 vol% H_2O) was supplied to the anode (100 ml min^{-1} at STP). The peak power density reaches 912 mW cm^{-2} at 800 °C.

is very important for power output, especially when the electronic conductivity of the composite cathode is relatively low. Hence, it is feasible to operate SOFCs on a single cell with a MCO–SDC composite cathode and a SSC cathode current collector.

In summary, we show a potential material with a spinel structure for coating on metallic interconnection that can be used as a SOFC cathode which exhibits good electro-catalysis and chemical compatibility with YSZ. It was found that the spinel oxide $Mn_{1.5}Co_{1.5}O_4$ (MCO) itself is remarkably capable of activating oxygen molecules and a single cell with it, as the cathode shows high output power, which can be comparable with that of the traditional $La_{1-x}Sr_xMnO_3$–YSZ (LSM–YSZ) composite cathode. The output power has been further improved by making a composite cathode with a current collector (SSC), and achieves 912 mW cm^{-2} at 800 °C, which is much higher than that obtained on the LSM–YSZ composite cathode. The results demonstrate a new family of potential cathode material compatible with the YSZ electrolyte for intermediate temperature SOFCs.

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