Highly efficient electrocatalysts for oxygen reduction reaction†

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Highly efficient and chemically compatible $Ln_xSr_{1-x}CoO_{3-\delta}$ (Ln = La, Sm, Gd, …)/Co_3O_4 electrocatalysts for oxygen reduction reaction are presented and the very low cathode polarization resistances and excellent performances implied their promising application for developing intermediate-temperature solid oxide fuel cells (SOFCs), as well as potential application for oxygen separation membranes.

As an energy-conversion device, solid oxide fuel cells (SOFCs) with high efficiency and low or zero emission have received a great attention in the past 20 years.[1–6] However, serious problems associated with high temperature operation (>800 °C), such as degradation of cell components, high cost of fabrication and poor durability, make the conventional high temperature SOFCs economically uncompetitive in the marketplace. In order to improve the practicality and competitiveness of SOFCs, it is becoming increasingly important to reduce the operation temperature to intermediate temperature (500–700 °C). The lowering of the operation temperatures results in the increase of the ohmic and cathode polarization and this consequently leads to a rapid decrease in the performance of the fuel cells. Usually, there are two main approaches to lower the operation temperature: one method is to decrease the electrolyte thickness or adopt electrolyte materials with higher ionic conductivity in order to decrease the ohmic polarization resistance of the fuel cells.[7–9] Another method is to exploit efficient cathode electrocatalysts so that the cathode polarization resistances can be decreased considerably.[10–12] Considering reliability of thin-film fuel cells, there exist severe limitations for decreasing the electrolyte thickness, thus, exploiting highly active and compatible cathode electrocatalysts may be the most promising method to lower the operation temperature.

It is generally recognized that mixed electronic and ionic conductors (MIEC) as cathode electrocatalysts extend the electrochemically active area from just the triple phase boundary (TPB) to the entire MIEC surface, consequently, there is a decrease in cathode polarization resistance of cathodes.[13,14] As hardly any actual single-phase cathode electrocatalysts possess enough ionic conductivity and electronic conductivity simultaneously, appropriate amount of ionic or electronic conductive-phase is added to ameliorate ionic or electronic conductivity of single-phase cathode electrocatalysts in practice.[15–18] Obviously, much attention has been paid to oxygen-ionic and electronic transference number, and total electrical conductivities of cathode electrocatalysts in order to exploit a high performance cathode electrocatalyst. Since the primary function of the cathode of a cell is to electrochemically reduce molecular oxygen to oxygen ion, much attention should be paid to the oxygen-reduction ability of cathode electrocatalysts. Some simple metal oxide catalysts (such as manganese oxides, iron oxides and cobalt oxides) which show good catalytic reduction abilities of oxygen,[19–21] may be an effective component for composite cathode electrocatalysts. In this report, we have demonstrated for the first time to our knowledge, that simple metal oxide Co_3O_4 could be used as an effective oxygen reduction catalyst and a chemically compatible component in the manufacture of highly efficient $Ln_xSr_{1-x}CoO_{3-\delta}$ (Ln = La, Sm, Gd, …)/Co_3O_4 composite cathode electrocatalysts, in which the cathode polarization resistances are very low, accordingly, the maximum power density of the cell is greatly improved (~2 times higher) compared with the corresponding original single-phase cathode electrocatalysts.

Based on $Sm_{0.2}Ce_{0.8}O_{1.9}$ (SDC) electrolyte, the polarization resistances of the $Sm_{0.5}Sr_{0.5}CoO_{3-\delta}$ (SSC)/Co_3O_4 composite cathode were first measured using a symmetric cell: SSC-Co_3O_4, SDC/SSC |SDC|SDC-SSC, SSC-Co_3O_4, in which the cathode interlayer SDC-SSC was applied for narrowing the difference of thermal expansion coefficients between the electrolyte and the cathode. As shown in Fig. 1, the area specific resistance (ASR) of the SSC/Co_3O_4 composite cathode was as low as 0.451, 0.163 and 0.073 Ω cm^2, respectively, at 500, 550 and 600 °C. The ASR of the composite cathode reported here is very low and comparable to the lowest ASR value which was reported previously.[12,18] The

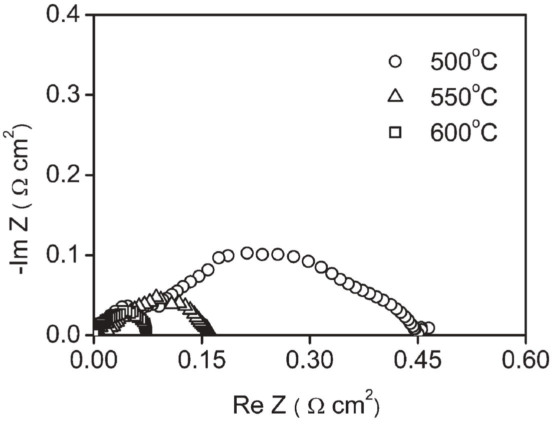

Fig. 1 The cathode polarization resistances of SSC/Co_3O_4 composite electrocatalyst, measured under ambient air in different temperatures, using a 1 mm thick SDC electrolyte symmetric cell: SSC-Co_3O_4, SDC-SSC |SDC|SDC-SSC, SSC-Co_3O_4.

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single-phase SSC cathode was fabricated and tested similarly for comparison and the results are shown in Fig. S1, ESI.† The ASR of the SSC cathode reached 1.653 Ω cm^2 at 500 °C, 0.571 Ω cm^2 at 550 °C, 0.233 Ω cm^2 at 600 °C and 0.102 Ω cm^2 at 650 °C. It was clearly indicated that the cathode polarization resistances of SSC greatly decreased by a factor of three to four by adding an appropriate amount of Co_3O_4.

Using the $NiO/Gd_{0.2}Ce_{0.8}O_{1.9}$ (GDC) anode and SDC electrolyte assembly, the performance of SSC/Co_3O_4 cathode in a conventional anode supported thin film electrolyte fuel cell was then investigated with humidified hydrogen (3 vol% H_2O) as fuel and stationary air as oxidant. As shown in Fig. 2, the maximum power densities (P_{max}) of the cell achieved are 650, 1033 and 1662 mW cm^{-2} at 550, 600 and 650 °C respectively, which is almost two times higher than the performance of a fuel cell with only SSC as cathode (Fig. S2, ESI†), *i.e.*, 330, 595 and 882 mW cm^{-2} at 550, 600 and 650 °C respectively. The cross section of the fractured fuel cell after testing (Fig. S3, ESI†) showed that SDC electrolyte, of about 25 μm thickness, although without perforations, was not entirely densified. Thus, the power density of fuel cells with the composite cathode may be further improved by the application of more densified and thinner electrolyte.

An energy-dispersive X-ray spectroscopy (EDX) linear scan analysis (Fig. S3, ESI†) was performed along the cathode/electrolyte cross-section of the cell without SDC/SSC cathode interlayer in order to examine the chemical compatibilities of the composite electrocatalyst with SDC electrolyte during cathode high-temperature sintering and the results are shown in Fig. 3. It was clearly demonstrated that there are no other element interdiffusions except a gentle diffusion of Co element into the electrolyte within ∼2 μm in depth. Furthermore, similar EDX analysis demonstrated that such slight Co element diffusion could be eliminated by applying a porous SDC/SSC cathode interlayer in the cells.

The chemical compatibility of SSC and Co_3O_4 in the composite electrocatalyst was also checked by XRD analysis (Fig. 4). When compared with the spectra of an SSC/Co_3O_4 mixture (70 : 30 wt%) at room temperature, no new peak was found in the spectra of SSC/Co_3O_4 (70 : 30 wt%) after 3 h treatment at 1100 °C. This result clearly showed that no new phase was formed in the composite electrocatalyst during high-temperature treatment because of their good chemical compatibilities.

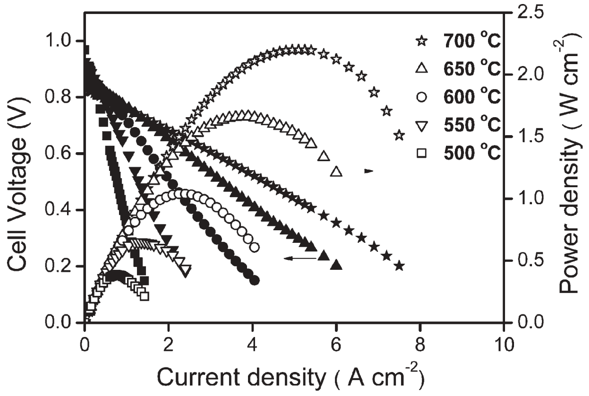

Fig. 2 Cell voltages and power densities as a function of current density for the cell NiO-GDC|SDC|SDC-SSC, SSC-Co_3O_4, tested in humidified H_2 (3 vol% H_2O) at 100 ml min^{-1} in the anode and air at 400 ml min^{-1} in the cathode in different temperatures.

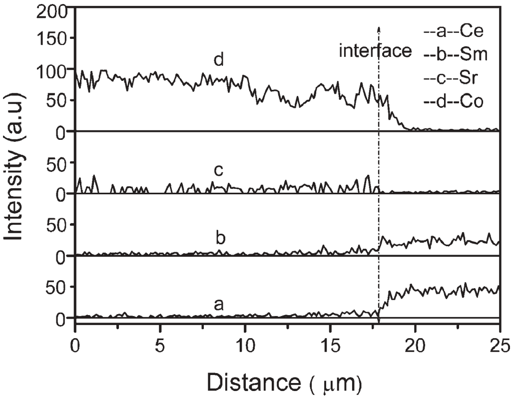

Fig. 3 The relative density of the element distribution *vs.* the distance of the EDX analysis (EDX linear scan analysis performed from cathode to electrolyte over a 25 μm range).

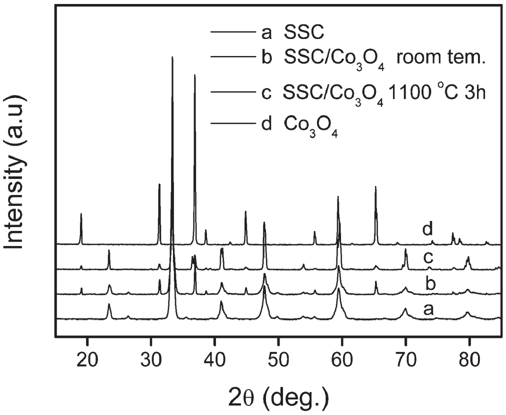

Fig. 4 X-Ray powder diffraction analysis for: (a) $Sm_{0.5}Sr_{0.5}CoO_{3-\delta}$; (b) $Sm_{0.5}Sr_{0.5}CoO_{3-\delta}/Co_3O_4$ (70 : 30 wt%) mixture at room temperature; (c) $Sm_{0.5}Sr_{0.5}CoO_{3-\delta}/Co_3O_4$ (70 : 30 wt%) mixture after 3 h treatment at 1100 °C; (d) Co_3O_4.

Due to the limitation of XRD for detecting possible instability of the cathode *in situ* during cell operation, the time dependence of maximum power density of the fuel cell was investigated at 600 °C (Fig. S4, ESI†). No deterioration of cell performance appeared even though the fuel cell continued discharging in a very high current density (2.4 A cm^{-2}, corresponding to the value at maximum power density) within the test period of 100 h, which indicated that the SSC/Co_3O_4 composite electrocatalyst is also essentially stable under working condition.

The temperature dependence of electrical conductivity for SSC, Co_3O_4 and SSC/Co_3O_4 (70 : 30 wt%) composite is shown in Fig. S5, ESI.† This showed that perovskite-type SSC retained high electrical conductivity over a wide range from low temperature to almost 1000 °C, while the electrical conductivity of spinel-type Co_3O_4 decreased from ∼10 S cm^{-1} at 800 °C to less than 1 S cm^{-1} at 600 °C. NiO-GDC|SDC|Co_3O_4 fuel cell was also designed and tested (Fig. S6, ESI†). The maximum power density of the cell was as low as 130 mW cm^{-2} at 600 °C, which indicated that Co_3O_4 was not appropriate as a cathode electrocatalyst alone due to its such low electrical conductivity.

Table 1 Cathode polarization resistances and maximum power densities of fuel cells with different cathode electrocatalysts at 600 °C

	GSC	GSC/Co_3O_4	LSC	LSC/Co_3O_4	SSC	SSC/Co_3O_4
OCV/V	0.89	0.887	0.88	0.882	0.913	0.893
P_{max}/mW cm^{-2}	497	705	463	821	595	1033
R_c/Ω cm^2	0.252	0.171	0.269	0.136	0.233	0.073

It is generally recognized that the overall cathode process on a MIEC cathode is a multistep process and consists of several elemental steps,[22,23] in which there exists one or more limiting steps which determine the overall performance of the cathode. For example, oxygen surface exchange processes (adsorption, dissociation and reduction) is usually the limiting step at low temperature.[17] As an excellent MIEC in a wide range of temperature, SSC still exhibits inferior performance at low temperature probably due to slow oxygen surface exchange process. In view of no foreign phase in sintered SSC/Co_3O_4 and its slightly lower electrical conductivity than that of SSC, as well as good ability of catalytic reduction of oxygen of Co_3O_4, thus, it seemed that the remarkable performance improvement of single-phase SSC by mixing an appropriate amount of Co_3O_4 simply resulted from high oxygen-reduction activity associated with an improved oxygen surface exchange coefficient of the SSC/Co_3O_4 composite.

In view of $La_{1-x}Sr_xCoO_{3-\delta}$ and $Gd_{1-x}Sr_xCoO_{3-\delta}$ also being effective cathode electrocatalysts for fuel cells,[24–26] $La_{0.7}Sr_{0.3}CoO_{3-\delta}$ (LSC) and $Gd_{0.6}Sr_{0.4}CoO_{3-\delta}$ (GSC) were selected as examples to verify whether it was feasible that the performance of perovskite $Ln_xSr_{1-x}CoO_{3-\delta}$ (Ln = La, Sm, Gd, …) cathode electrocatalysts could be greatly improved by mixing an appropriate amount of Co_3O_4. The results (Table 1) demonstrated that all composite cathode materials showed much better performances than that of the corresponding single-phase cathode electrocatalysts in spite of very different increases noted.

In summary, Co_3O_4 could be mixed with a single-phase perovskite $Ln_xSr_{1-x}CoO_{3-\delta}$ (Ln = La, Sm, Gd, …) as a chemically compatible component for cathode electrocatalysts. Due to the high oxygen reduction activity of Co_3O_4, electrocatalysts ($Ln_xSr_{1-x}CoO_{3-\delta}/Co_3O_4$) have much lower cathode polarization resistances, consequently, resulting in considerable improvement in performances of fuel cells. In particular, for $Sm_{0.5}Sr_{0.5}CoO_{3-\delta}/Co_3O_4$ electrocatalyst, the maximum power density of a SDC electrolyte based fuel cell reached 1033 and 2200 mW cm^{-2} at 600 and 700 °C, respectively, when operated with humidified hydrogen (3 vol% H_2O) as fuel and air as oxidant. As aforementioned, one of the main obstacles for developing intermediate-temperature SOFCs is to lower the high cathode polarization resistances. Thus, the highly efficient electrocatalysts presented here, fulfil the need in great part and provide a much needed promising approach in developing intermediate temperature SOFCs. In addition, the characteristics of mixed electronic and ionic conductors (MIEC) and high oxygen reduction activity of the electrocatalysts also implied their promising potential application for oxygen separation and mild oxide catalysts.

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