High Efficient Electrocatalysts for Oxygen Reduction Reaction

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Experimental Section

Preparation of powder

Sm\textsubscript{0.2}Ce\textsubscript{0.8}O\textsubscript{1.9} (SDC), Gd\textsubscript{0.2}Ce\textsubscript{0.8}O\textsubscript{1.9} (GDC), La\textsubscript{0.4}Ce\textsubscript{0.6}O\textsubscript{1.9} (LDC), Sm\textsubscript{0.5}Sr\textsubscript{0.5}CoO\textsubscript{3-\delta} (SSC), La\textsubscript{0.7}Sr\textsubscript{0.3}CoO\textsubscript{3-\delta} (LSC), Gd\textsubscript{0.6}Sr\textsubscript{0.4}CoO\textsubscript{3-\delta} (GSC) and Co\textsubscript{3}O\textsubscript{4} powders were synthesized by a citrate and EDTA process.\textsuperscript{1,2} Stoichiometric amounts of metal nitrate solutions were introduced into a beaker and equal molar of citrate and EDTA respect to total metal ions were added into the mixed solution. Then the pH value was adjusted close to 8 with ammonia. After water evaporated on a hot plate, the resulting gel was calcined at about 600 °C to remove organic compounds, and then calcined for 4 h under stagnant air at 800-950 °C.

Fuel-cell fabrication

The anode-supported thin-film electrolyte fuel cells were fabricated using co-pressing method.\textsuperscript{3} GDC (50 wt.\%) and commercial NiO (50 wt.\%) powder were mixed and ground with alcohol. The dried mixed powder was first pressed at 100 MPa as a substrate. SDC foam powder was then distributed uniformly, and pressed onto the substrate at 200 MPa. The bilayer (~22 mm in diameter and 1 mm thick) was subsequently fired at 1450 °C for 6 h in air, resulting in a SDC film of about 25μm by controlling the amount of SDC powder. A paste of LnSC (70 wt.\%) (Ln corresponding to Sm, Gd and La respectively) and LnDC (30 wt.\%) powder mixture dispersed in terpineol was applied on the electrolyte surface by a doctor blade processing, followed by a layer of LnSC or LSC/ Co\textsubscript{3}O\textsubscript{4} (70:30 wt.\%) paste prepared similarly. The cell was then fired at 1100 °C for 2 h in air. The final cathode was about 100 μm thickness, with a ~30 μm interlayer and ~0.33cm\textsuperscript{2} effective area. As for the symmetric cell, SDC electrolyte green pellets were first fired at 1550 °C for 6 h in air, and then cathode interlayer and cathode layer were fabricated identical to the anode supported thin-film cells.

Electrochemical measurements

Anode-supported thin-film fuel cells were tested under ambient pressure, while humidified hydrogen (3 vol.\% H\textsubscript{2}O) was fed as fuel and stationary air as oxidant. Current-voltage (I-V) characteristics of the cells were measured at various current densities by changing the external load. The impedance of the symmetric cells were typically measured under ambient air from 10 mHz to 10\textsuperscript{5} Hz using EG&G lock-in amplifier (model 5210) in combination with EG&G potentiostat/Galvanostat (model 263A). The conductivities of samples were measured by the four-probe direct current (dc) conductivity measurement method in air using Keithley-2000 multimeter and EG&G potentiostat /galvanostat.

Characterization

The chemical compatibility of the components within composite cathode material was examined by XRD analysis based on Rigaku D/Max-2500 diffractometer. The cross-section of fuel cells and
energy-dispersive X-ray spectroscopy (EDX) linear scan analysis were performed on FEI Quanta 200F scanning electron microscope.
Figure S1 The cathode polarization resistances of SSC single-phase electrocatalyst, measured under ambient air at different temperatures, using a 1mm thick SDC electrolyte symmetric cell: SSC, SDC-SSC|SDC|SDC-SSC, SSC.
Figure S2  Cell voltages and power densities as a function of current density for a fuel cell: NiO-GDC|SDC|SDC-SSC, SSC, tested in humidified H₂ (3 vol.% H₂O) at 100 ml min⁻¹ in the anode and air at 400 ml min⁻¹ in the cathode at different temperatures.
**Figure S3** Cross-section SEM image and EDX analysis (EDX linear scan analysis performed from cathode to electrolyte over a 25 μm range) for a fuel cell: NiO-GDC|SDC|SSC-Co$_3$O$_4$. 
Figure S4 Time dependence of maximum power density for a fuel cell: NiO-GDC|SDC|SSC-SDC, SSC-Co$_3$O$_4$, tested in humidified H$_2$ (3 vol.% H$_2$O) at 100 ml min$^{-1}$ in the anode and air at 400 ml min$^{-1}$ in the cathode at 600 °C. Fuel cell continued discharging in current density of 2.4 A cm$^{-2}$ (corresponding to the value at maximum power density) within the test period of 100 hours.
Figure S5 Temperature dependence of the electrical conductivity for: a) Co$_3$O$_4$; b) Sm$_{0.2}$Sr$_{0.5}$CoO$_{3+2\delta}$/Co$_3$O$_4$ (70:30 wt.%); c) Sm$_{0.2}$Sr$_{0.5}$CoO$_{3+2\delta}$. 
Figure S6 Cell voltage and power density as a function of current density for a fuel cell: NiO-GDC|SDC|Co$_3$O$_4$, tested in humidified H$_2$ (3 vol.% H$_2$O) at 100 ml min$^{-1}$ in the anode and air at 400 ml min$^{-1}$ in the cathode at 600 °C.

References