Electronic Supplementary Information

Cubic perovskite-type Sm_{0.3}Sr_{0.7}Nb_{0.08}Co_{0.92}O_{3-δ} as a novel cathode material for

intermediate temperature solid oxide fuel cells

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Experimental Section

Preparation of powder

 $Sm_{0.2}Ce_{0.8}O_{1.9}$ (SDC) and $Sm_{0.3}Sr_{0.7}CoO_{3-\delta}$ (SSC) were synthesized by a citrate and EDTA process. 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.

 $Sm_{0.3}Sr_{0.7}Nb_{0.08}$ Co_{0.92}O_{3- δ} (SSNC) powder was synthesized by a solid-phase reaction process. Analytical grade Sm_2O_3 , $SrCO_3$, Nb_2O_5 and Co_3O_4 were weighed and well mixed by ball milling under ethyl alcohol medium for 2 h. The dried powder mixture was then sintered at 1200 °C in air for 24 h to acquire perfectly crystallized cathode material.

Fuel-cell fabrication

The anode-supported thin-film electrolyte fuel cells were fabricated using co-pressing method. SDC (50 wt %) and commercial NiO (50 wt %) powder were mixed and ground with ethyl alcohol. The dried mixed powder was first isostatically pressed into a disk at 100 MPa as a substrate. SDC foam powder was then added and pressed onto the substrate at 200 MPa. The green bi-layer pellets were subsequently sintered at 1500 °C for 4 h in air, resulting in a SDC film of about 20 μ m by controlling the amount of foam powder. Cathode slurry, the mixture of cathode material powder and appropriate moment of terpineol, was applied on the electrolyte surface by a doctor blade processing. The cell was then fired at 1000-1100 °C for 3 h in air. The final cathode was about 50-100 μ m thickness, with an effective area of ~0.33cm².

Symmetrical cells, which be used for the electrochemical impedance spectroscopy research, were prepared by dry pressing. SDC electrolyte powder was first dispersed and ground in ethyl alcohol medium with additive of ethylene glycol and polyvinylpyrrolidone. The dried mixture was then isostatically pressed into a disk at 300 MPa as green pellet, which was subsequently fired at 1550 °C for 6 h in air. After the sintered disks were polished to 0.2 mm thick, cathode slurry was painted onto both sides of the SDC electrolyte disks. The cell was then fired at 1000-1100 °C for 3 h under air atmosphere, with an about 0.33cm² effective electrode area.

Electrochemical measurements

Both the film single cell and symmetric cell were evaluated on an in-house test station. The cell was sealed on alumina tube with ceramic paste and the silver meshes were used as current collector. The performances of thin film fuel cells were tested under ambient pressure, in which, humidified hydrogen (3 vol % H₂O) was fed into the anode chamber as fuel at a flow rate of 100 ml min⁻¹(STP) and air was fed into the cathode chamber as oxidant at a flow rate of 400 ml min⁻¹ (STP). Current-voltage (I-V) characteristics of the cells were measured at

various current densities by changing the external load.

Based on symmetric cell, the electro-catalytical activities of cathode materials were investigated by the AC impedance technology using CHI 660E electrochemical workstation under ambient air. The frequency range applied was from 1 Hz to 10 kHz with signal amplitude of 10 mV under the open circuit condition. The overall impedance data were fitted by a complex non-linear least square fitting program in the Zsimpwin32 software.

The electrical conductivity of the sintered samples ($4mm \times 4mm \times 15mm$) was measured in air using Keithley 2000 multimeter by the standard four-probe DC method. Measurements were performed at intervals of 10 °C from 50 °C to 900°C with a heating rate of 3°C min⁻¹ under ambient atmosphere. As four-probe method schematic diagram showing, silver paste was painted and sintered as contact electrode while platinum wire as lead wire. When constant current was applied between two outer contact electrodes, the terminal voltage between two inner contact electrodes was measured, and electrical conductivity can be calculated as following equation.



Schematic diagram of electrical conductivity test using four-probe method

Other characterization

The oxygen nonstoichiometry of the cathode material at room temperatures was determined by thermogravimetric analysis. Sample material was pretreated under air atmosphere with 60 ml min⁻¹ at 950 °C for 1 h to remove trace water. When the temperature was decreased to room temperature, a mixture atmosphere of 5% H_2 and 95% N_2 with 60 ml min⁻¹ adjusted by mass flow controller was switched to reduce the sample by increasing the temperature to 900 °C at 10 °C min⁻¹. The sample material was treated at 900 °C for 3h to ensure complete reduction before the temperature was cooled to room temperature again, thus the oxygen nonstoichiometry δ_0 could be calculated according the mass difference between the reduced and unreduced sample material at room temperature. During hydrogen reduction, the starting material underwent the following decomposition¹⁻³:

$$Sm_{0.3}Sr_{0.7}Nb_{0.08}Co_{0.92}O_{3-\delta_0}(w_0) \rightarrow (0.15Sm_2O_3 + 0.7SrO + 0.08NbO_2 + 0.92Co)(w_r) + \frac{1.69 - \delta_0}{2}O_2(g)$$
⁽²⁾

where w_0 presents molar mass of the starting material and w_r presents nominal molar mass of reduced material, and oxygen nonstoichiometry at room temperature δ_0 could be calculated by following equation:

$$\frac{W_0 - W_r}{W_0} = \frac{27.04 - 16\delta_0}{216.09 - 16\delta_0} = \text{loss rate}$$
(3)

The oxygen nonstoichiometry of the cathode material at other temperatures also could be acquired by thermogravimetric analyzer (TA TGA55). Measurement was carried out up to 700 °C at 5 °C min⁻¹ under air atmosphere with 60 ml min⁻¹, thus, the oxygen nonstoichiometry δ could be calculated based on the TG data at different temperatures. Under ordinary TGA (air atmosphere), niobium retains constant pentavalence in SSNC sample, weight loss only derives from cobalt valence alteration and can be present as following:

$$Sm_{0.3}Sr_{0.7}Nb_{0.08}Co_{0.92}O_{3-\delta_0}(w_0) \to Sm_{0.3}Sr_{0.7}Nb_{0.08}Co_{0.92}O_{3-\delta}(w) + \frac{\delta-\delta_0}{2}O_2(g) \quad (4)$$

where w presents molar mass of partial mass loss sample, and oxygen nonstoichiometry δ could be calculated by following equation:

$$\frac{W_0 - W}{W_0} = \frac{16(\delta - \delta_0)}{216.09 - 16\delta_0} = \text{loss rate}$$
(5)

The crystallographic structure of cathode material, as well as chemical compatibility of between component materials, was examined by XRD analysis based on Rigaku ultima IV diffractometer. Rietveld refinements on the XRD patterns were carried out using *FULLPROF* software. The line shape of the diffraction peaks was generated by a pseudo-Voigt function and the background refined to a fifth-degree polynomial. During refinements, general parameters, such as the scale factor, background parameters and the zero point of the counter were optimized. The cell parameter, occupancy and the isotropic displacement (temperature) parameters (Biso) were refined. The cross-section of the fuel cells after tested was performed on Sigma HD scanning electron microscope.

Oxygen vacancy concentration was determined by cell volume and oxygen nonstoichiometry δ value. SSNC cell parameter adopted refinement results while SSC cell parameters were taken from ISCD # 413478 for Sm_{0.3}Sr_{0.7}CoO_{3- δ}. TEC value of 20×10⁻⁶ K⁻¹ was employed for both samples to consider cell volume variation due to temperature change.

Reference:

- (1) S.Kim, Y.L.Yang, A.J.Jacobson, B. Abeles, Solid State Ionics., 1998, 106,189
- (2) H.H.Wang, Y.Cong, W.S.Yang., Journal of Membrane Science., 2002, 210, 259
- (3) A. Aguadero, C. de la Calle, J. A. Alonso, M. J. Escudero, M. T. Fernandez-Diaz and L. Daza, *Chem. Mat.*, 2007, **19**, 6437

Atom	Wyckoff-site	Х	У	Z	Occ	$B_{iso}(Å^2)$
Sm	1b	0.5	0.5	0.5	0.30	1.11(5)
Sr	1b	0.5	0.5	0.5	0.70	1.23(4)
Nb	1a	0	0	0	0.08	1.01(2)
Co	1a	0	0	0	0.92	0.97(3)
0	3d	0	0	0.5	0.90(4)	2.

Table S1.: The powder X-ray Rietveld refinement results for $Sm_{0.3}Sr_{0.7}Nb_{0.08}Co_{0.92}O_{3-\delta}$ ($\chi 2 = 0.431$; $R_p = 7.7\%$; $R_{wp} = 7.38\%$; $R_{exp} = 9.13\%$; $R_{Bragg} = 1.89\%$; a = 3.8452(5) Å; space group = Pm-3m)

Table S2.: Oxygen vacancy concentration for $Sm_{0.3}Sr_{0.7}Nb_{0.08}Co_{0.92}O_{3-\delta}$ and $Sm_{0.3}Sr_{0.7}CoO_{3-\delta}$ under d different temperature (unit : 10^{21} cm⁻³)

Sub	RT	400 °C	450 °C	500 °C	550 °C	600 °C	650 °C
SSNC	5.54	6.07	6.35	6.64	6.92	7.19	7.41
SSC	3.77	5.36	5.54	5.73	5.92	6.13	6.33



Figure S1. Temperature dependence of electrical conductivity of SSNC and SSC cathode materials measured under ambient atmosphere.



Figure S2. Nyquist plots of the SSC cathode with SSC|SDC|SSC symmetrical cell under ambient atmosphere at 500, 550 and 600 °C.



Figure S3. The evolution of polarization resistance with oxygen partial pressure pO₂ at 550 °C.



Figure S4. Cross-section SEM image for the fuel cell: NiO-SDC|SDC|SSNC.



Figure S5. Voltage and power density as functions of current density for the cell: NiO-SDC|SDC|SSC, tested in 3% H₂O humidified H₂ at 100 ml min⁻¹ in the anode and air at 400 ml min⁻¹ in the cathode at different temperature.



Figure S6. X-ray powder diffraction analysis. a) $Sm_{0.2}Ce_{0.8}O_{2.\delta}$; b) $Sm_{0.3}Sr_{0.7}Nb_{0.08}Co_{0.92}O_{3.\delta}$; c) $Sm_{0.2}Ce_{0.8}O_{2.\delta}$ / $Sm_{0.3}Sr_{0.7}Nb_{0.08}Co_{0.92}O_{3.\delta}$; c) $Sm_{0.2}Ce_{0.8}O_{2.\delta}$ / $Sm_{0.3}Sr_{0.7}Nb_{0.08}Co_{0.92}O_{3.\delta}$; c) $Sm_{0.2}Ce_{0.8}O_{2.\delta}$ /



Figure S7. Time dependence of power density under 0.7V terminal voltage for a fuel cell: NiO-SDC|SDC|SSNC, 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 550 °C. Fuel cell continued discharging within the test period of 120 hours.