Supporting Information

Hierarchical Porous Cobalt-Free Perovskite Electrode for Highly Efficient Oxygen Reduction

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Experimental

Fabrication of SNF-3D cathode: Dewaxed cotton fiber was immersed in 67 wt% concentrated nitric acid for 2 h, washed with deionized water three times and dried at 100 °C to form the activated cellulose fiber. Stoichiometric amounts of Sr(NO$_3$)$_2$, Fe(NO$_3$)$_3$ and (NH$_4$)$_3$NbO(C$_2$O$_4$)$_3$ were combined to form a mixed aqueous solution (total metal ions concentration of 2 mol L$^{-1}$), to which glycine was then added (mole ratio of glycine: total metal ions is 2:1) as the fuel. The mixed solution was then heated at 80 °C to result in a sol, which was then carefully and slowly dropped over the activated cellulose until the cellulose was soaked. After the cellulose was dried at 80 °C for several hours, a solid precursor was obtained, which was then heated at 250 °C in an electrical oven to trigger its auto combustion and result in a carbon-oxides precursor with the morphology of the initial cellulose fiber. The carbon-oxides precursor ink was prepared by mixing the precursor with a premixed solution of glycerol, ethylene glycol, and isopropyl alcohol, which was followed by the rapid mixing and ball milling of the mixture at 400 rpm for 0.5 h. The SNF-3D cathode was fabricated by spraying the ink onto the surface of the SDC electrolyte and subsequently performing calcination at 800°C for 2 h under an air atmosphere. Silver paste was painted on the surface of the electrode to collect current.

Preparation of SDC pellets and SDC/NiO-supported SDC bi-layers: To obtain the dense SDC electrolyte substrate (1.0 mm thickness, 13 mm diameter), the SDC powder was pressed into pellets using a stainless steel die under a hydraulic pressure of 10 MPa. The pellets were then sintered at 1400°C for 5 h in air. The SDC/NiO-supported SDC bi-layer was fabricated via dual co-pressing for the single fuel cell test. [34] Anode powders consisting of 60 wt% NiO and 40 wt % SDC were prepared by mixing NiO and SDC in an agate mortar. The well-mixed SDC/NiO powder was then pressed as a substrate, onto which the SDC powder was
added and pressed again to form a bi-layer pellet. The pellet was then sintered in air at 1450 °C for 5 h for densification of the electrolyte layer.

**Structural and thermal characterizations:** A high temperature in-situ X-ray diffractometer (Philips, X’Pert) with Cu Kα₁ radiation (λ = 0.154056 nm) was used to check the lattice thermal stability across the temperature range of approximately 50-1000 °C. Le Bail and Rietveld refinements on the XRD patterns were conducted using the DIFFRACplus Topas 4.2 software. During these refinements, general parameters, such as the scale factor, background parameters and the zero point of the counter, were optimized. The average valences of iron in SNF were determined by iodometry. The TGA of the carbon-oxides precursor was performed in a DTA/TA (NETZSH, STA 449 F3) under synthetic air at temperatures ranging from room temperature to 950 °C. The Brunauer-Emmett-Teller (BET) surface area was estimated using N₂-adsorption measurements on samples pre-treated for 3 hours at 220 °C.

The morphologies of the powders and cathodes were examined using a JEOL JSM-6300 field emission scanning electron microscope and a JEOL JEM-2100 transmission electron microscope operated at an accelerating voltage of 200 kV and equipped with an energy dispersive X-ray spectrometer (for TEM and HRTEM images). The samples were dispersed in a mixture of ethanol and isopropanol and sonicated before being deposited on a holey carbon film deposited on a Cu grid.

**Electrochemical characterizations:** The electrochemical impedance spectroscopy (EIS) of the symmetrical cell was investigated via an AC impedance method using an electrochemical workstation (Solartron 1260A frequency response analyzer and a Solartron 1287 potentiostat) at a temperature range of 500-750°C under ambient air. The applied frequency ranged from 0.01 Hz to 100 KHz, and the signal amplitude was 10 mV under open-cell voltage conditions. The data from the impedance spectra were analyzed by Z-plot 3.0c software.

To test the performance of the single fuel cell, the cell was sealed onto the top of a quartz tube reactor with silver paste and fixed inside the furnace. Pure H₂ was fed into the
anode chamber as fuel at a flow rate of 80 mL min$^{-1}$ (STP), and the cathode was exposed to ambient air. A Keithley 2420 Source Meter with a four-probe configuration was used for I-V and I-P polarization tests under the approximate temperature range of 450-600$^\circ$C. The power density was calculated based on the active area of the cathode, which was approximately 0.48 cm$^2$. 
Figure S1. The SNF powders prepared by solid state reaction calcined at 1250 °C for 20 h.
Figure S2. The SEM image of the cross-section of SNF cathode on SDC electrolyte heated at 1000°C for 2h.
Figure S3. TGA-DSC curves of carbon-oxides precursor in air from room temperature to 1050 °C. The carbon content is estimated to be ~13 wt% in carbon-oxides precursor.
Figure S4. Phase development of SNF perovskite from carbon-oxide precursor studied by HT-XRD in air. The SNF phase formed at 550 °C.
Figure S5. X-ray diffraction profiles of the SNF powder after heating carbon-oxides precursor at 800 and 1000 °C for 5 h. Observed (blue circles), calculated by the Le Bail method (red line), difference (gray line), and calculated Bragg positions (green vertical bar) for each phase are presented. The SNF shows cubic structure with space group Pm-3m, while a tetragonal phase with space group P4mm formed after heating at 1000 °C.
Figure S6. HT-XRD patterns of SNF at 800-1050 °C heated from the carbon-oxides precursor. The gradual splitting of the reflections at approximately 45.5 and 56.5° occurs at 900 °C indicates the phase transition from cubic (Pm-3m) to tetragonal (I4/m). The I4/m phase can transfer to P4mm phase when the temperature is cooled down to RT.
Figure S7. Thermal evolution of the ASRs of the SNF-3D cathode compared with those of other cobalt-free (a) and cobalt-containing cathodes (b).
Figure S8. ASRs of the SNF cathodes fabricated at 800, 900 and 1000 °C.
**Figure S9.** I-V and I-P plots of the single SOFC based on the SNF-3D cathode from 450 to 600 °C.