

## Experimental Section

The  $(\text{Bi}_{0.75}\text{Y}_{0.25})_{0.93}\text{Ce}_{0.07}\text{O}_{1.5\pm\delta}$  (BYC) and  $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$  (LSM) single-phase powders were synthesized by the citric acid complexation-combustion method. In brief, the appropriate amounts of the metal salts/oxide and citrate were added into de-ionized water and mixed in a breaker with stirring. After the water was evaporated, the resultant gel was combusted to remove the organic compounds, and then calcined in air at various temperatures. The 60 wt.% BYC-40 wt.% LSM dual-phase composite powders were prepared by hand mixing (grinding in a mortar for 1 h) and in-situ synthesis method. The BYC powder was calcined at 700 °C for 4 h, while the LSM and in-situ BYC-LSM powders were heat treated at 900 °C for 5 h.

The performances of composite cathodes consisted of hand-mixed and in-situ BYC-LSM were evaluated in both symmetrical cells and single cells with  $\text{Zr}_{0.84}\text{Y}_{0.16}\text{O}_{1.92}$  (YSZ, Tosoh Corporation, Japan) and/or  $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$  (GDC, Fuel Cell Materials, USA) as electrolytes. Briefly, the cathode ink comprised of BYC-LSM and V-006 at a weight ratio of 1:2 was screen-printed onto both sides of the dense thick (~1 mm) electrolyte disk, subsequently fired at 900 °C for 2 h to obtain the symmetrical cell. For the anode supported single cell, the bilayer (including the Ni-GDC anode and GDC electrolyte) was prepared by a combination of dry-pressing, dip-coating and co-sintering methods, followed by the screen-printed cathode. Detailly, the green anode substrate was first pre-calcined at 1000 °C for 2 h, then dip-coated with electrolyte slurry, finally co-sintered at 1450 °C for 5 h. The effective surface areas of the electrodes were around 0.84 cm<sup>2</sup>. The silver meshes and pastes as current collectors were applied onto both sides of the cells and cured at 600 °C for 0.5 h.

The phase structures of the cathode materials were determined by X-ray diffraction (XRD, D8 Advance, Bruker-AXS, with Cu K $\alpha$  radiation) in the  $2\theta$  range 20-80° with a step width of 0.02°. The refinement of XRD data was

performed by using TOPAS 6 software (Bruker AXS). Surface morphologies of powders and single cell were observed by a field-emission scanning electron microscopy (FESEM, JEOL JSM-7600F) operated at 5 kV. The elemental distributions of BYC-LSM powders were analyzed by energy dispersive X-ray spectroscopy (EDXS) at 20 kV. The in-situ BYC-LSM powder was also investigated at incident electron energy of 200 kV in a field-emission transmission electron microscopy (FETEM, JEOL JEM-2100F). The microscope was equipped with a light-element energy-dispersive x-ray spectrometer of the type Oxford Instrument INCA 200 TEM. The microscope was operated as scanning TEM (STEM) and high-resolution TEM (HRTEM). Moreover, the polarization resistances of BYC-LSM in symmetrical cells and performances of anode-supported single cells were examined with a Solartron electrochemical station consisting of 1470 multichannel potentiostat and 1255B frequency response analyzer. The symmetrical cells were measured in a temperature range from 500 °C to 750 °C by heating up (2 °C/min) in stagnant air, and the samples were hold 30 min at each temperature before collecting the data. For single cell tests, a humidified (~3% H<sub>2</sub>O) hydrogen flow at 100 sccm and ambient air were applied as the fuel and oxidant gas, respectively. Additionally, for all the electrochemical impedance measurements, the frequency was swept in a range of 10<sup>6</sup>-0.01 Hz with a perturbation alternating current amplitude of 10 mV at open circuit condition. The obtained spectra were deconvoluted by ZSimpWin software.

## Supporting figures

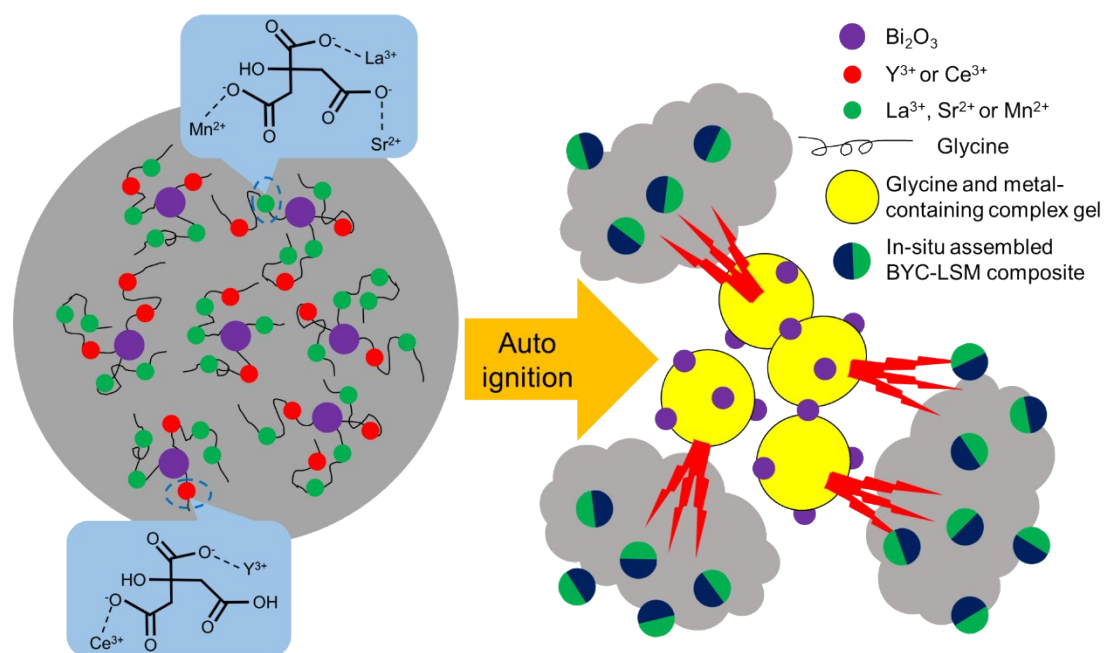


Figure S1. Schematic diagram of in-situ synthesis of BYC-LSM composite cathode.

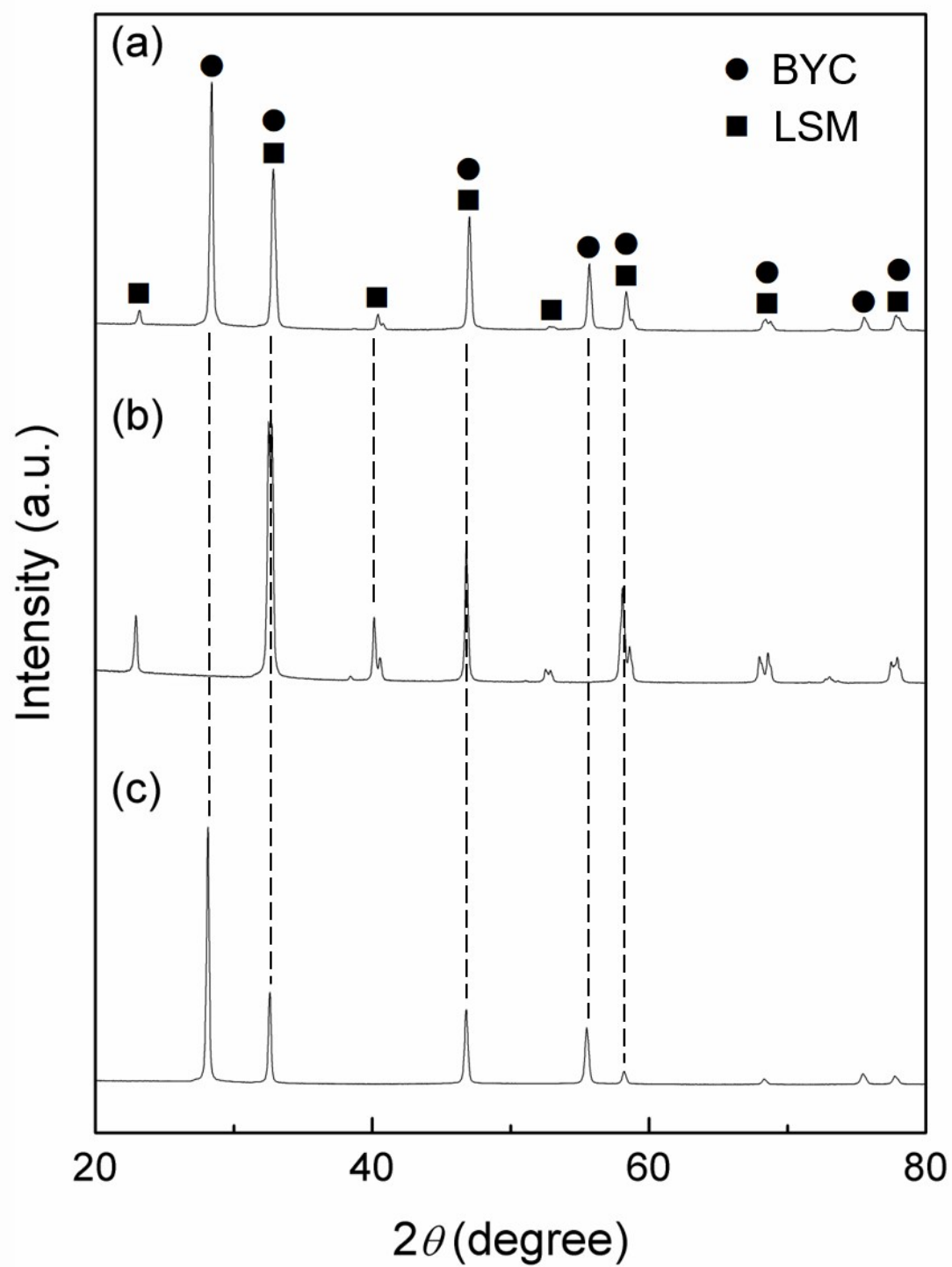


Figure S2. XRD patterns of as-prepared a) in-situ BYC-LSM powders, b) LSM powders and c) BYC powders in air at room temperature.

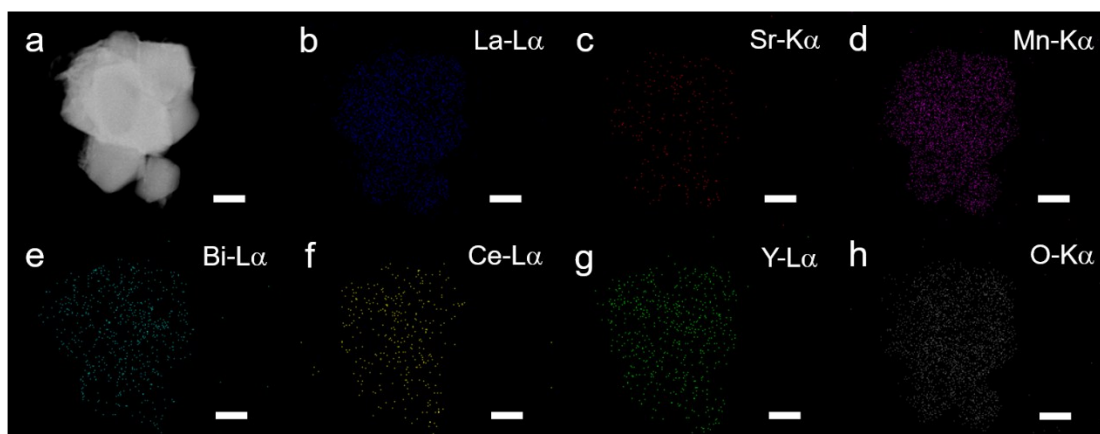


Figure S3. The sintered in-situ BYC-LSM powders. a) STEM micrograph, EDXS elemental distributions of b) La, c) Sr, d) Mn, e) Bi, f) Ce, g) Y and h) O. Scale bar: 100 nm.

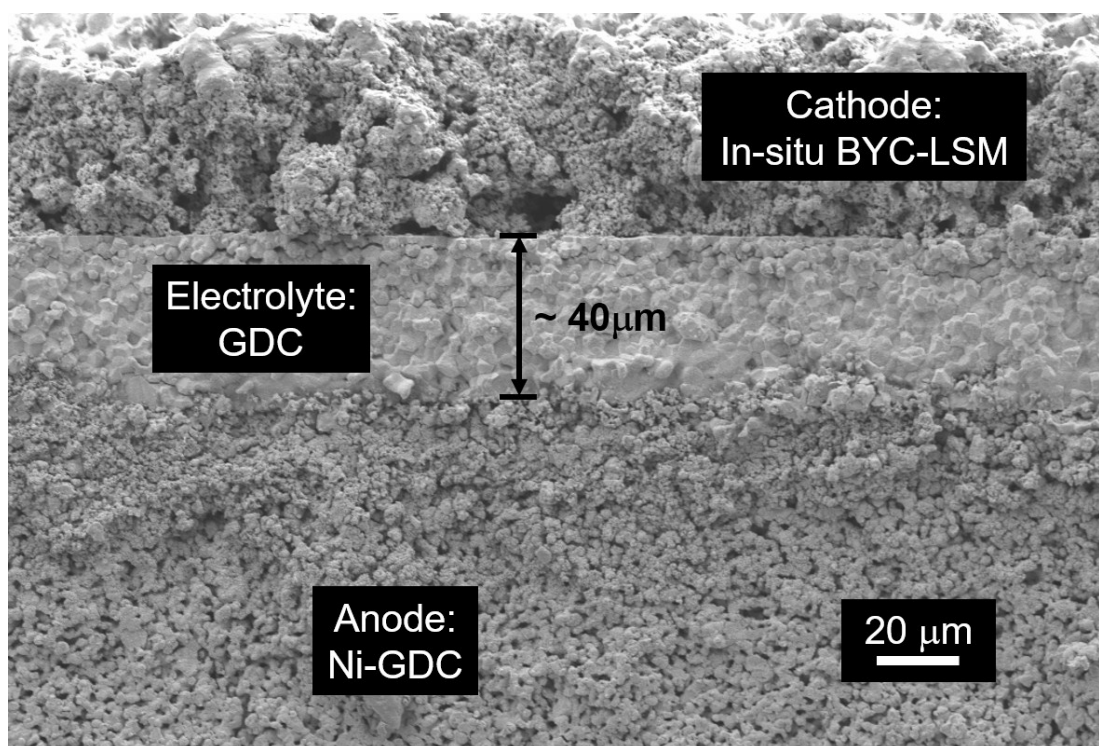


Figure S4. Secondary electron micrograph of the fractured cross-section of the anode-supported SOFC with in-situ BYC-LSM cathode after test.

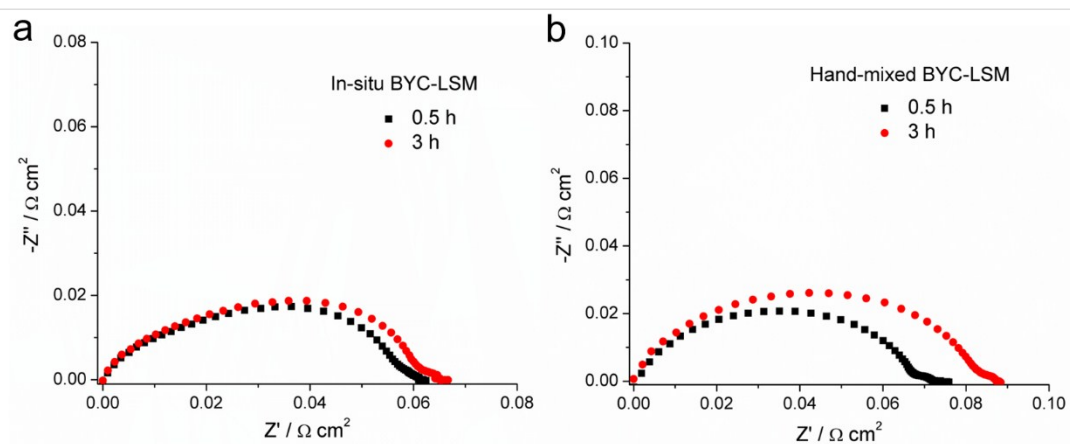


Figure S5 Electrochemical impedance spectra of the symmetrical half cells with a) in-situ BYC-LSM cathode and b) hand-mixed BYC-LSM cathode on GDC electrolyte at 800 °C in air. The ohmic contribution from GDC electrolyte has been subtracted from the overall impedance spectra.