

## Supporting information

### Novel B-site Ordered Double Perovskite $\text{Ba}_2\text{Bi}_{0.1}\text{Sc}_{0.2}\text{Co}_{1.7}\text{O}_{6-x}$ for Highly Efficient Oxygen Reduction Reaction

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#### Experimental Section

**Powder Preparation.**  $\text{Ba}_2\text{Bi}_{0.1}\text{Sc}_{0.2}\text{Co}_{1.7}\text{O}_{6-x}$  (BBSC) powder was synthesized by a combined EDTA-citrate complexing process.  $\text{Ba}(\text{NO}_3)_2$  (99.99+%, Sigma-Aldrich),  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  (99.99+%, Sigma-Aldrich),  $\text{Sc}(\text{NO}_3)_3$  (99.9%, Metall Rare Earth Limited, China) and  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (98.0+%, Sigma-Aldrich) were used as the raw materials for metal sources. Stoichiometric amounts of these metal nitrates were mixed in deionized water and heated at 80°C. Dissolution of  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  was performed by adding the required amount of  $\text{HNO}_3$  (67%). EDTA (99.9%, Sigma-Aldrich) and anhydrous citric acid (99.5%, Fluka) were then added as the complexing agents. The molar ratio of total metal nitrates, EDTA and citric acid in the solution was 1:1:2. To ensure complete complexation, solution pH was adjusted to 6 by adding  $\text{NH}_3$  aqueous solution (28%); resulting in violet transparent aqueous solution. After evaporation of water at 120°C, a dark purple gel was recovered. The gel was pretreated on the furnace at 250°C for 8 hours to form a solid precursor. The solid precursor was then ground onto powder and calcined at 1050°C for 5 hours in air. As calcined powder were ball-milled in a planetary mill (Pulverisette 5, Fritsch) at 800rpm for 2 hours before characterization and testing.

**Characterization.** The crystal structure of the BBSC powder was determined by x-ray diffraction (XRD, Bruker AXS D8 Advance) with filtered Cu-K $\alpha$  radiation at 40 kV and 40 mA and a receiving slit of 0.2-0.4 mm. The diffraction patterns were collected at room temperature by step scanning in the range of  $10^\circ \leq 2\theta \leq 90^\circ$  with the scan rate of  $2^\circ \text{ min}^{-1}$ . Rietveld refinements on the XRD patterns were carried out using DIFFRAC<sup>plus</sup> Topas 4 software.<sup>1</sup> All initial parameters for BBSC structure were taken from ICSD#189 for  $\text{Ba}_2\text{MnWO}_6$ .<sup>2</sup> During refinements, general parameters, such as the scale factor, background parameters and the zero point of the counter were optimized. Profile shape calculations were carried out using the Thompson-Cox-Hastings function implemented in the program by varying the strain parameter. The cell

parameter and the isotropic thermal parameters ( $B_{eq}$ ) were refined with all atomic positions kept constant. The initial isotropic thermal parameters for Ba, Bi, Sc, Co and O were set to 10. Transmission electron microscopy was conducted at 200kV with a Philips Tecnai T30F field emission instrument equipped with a 2k-CCD camera. Energy dispersive x-ray spectroscopy was carried out by a light-element detector using the ZAF technique. Raman spectra were recorded in the backscattering mode at room temperature using a Renishaw inVia micro-Raman system equipped with an optical microscope comprising a 50× objective lens. The radiation source was a He-Ne laser with beam of wavelength 780 nm operated at 1% power which was focused on a spot of 5  $\mu\text{m}$  in size at 1.0 mW. Before measurement, the micro-Raman system was calibrated using the 520  $\text{cm}^{-1}$  peak of polycrystalline Si.

Chemical state of cobalt in BBSC was analyzed using a Kratos Axis ULTRA X-ray Photoelectron Spectrometer incorporating a 165 mm hemispherical electron energy analyzer. The incident radiation was monochromatic Al  $K\alpha$  X-rays (1486.6 eV) at 150 W (15 kV, 15 mA). Narrow high-resolution scans were run to obtain Co 2p level spectra with 0.05 eV steps and 250 ms dwell time. Base pressure in the analysis chamber was  $1.0 \times 10^{-9}$  torr and during sample analysis was  $1.0 \times 10^{-8}$  torr. All binding energies were referenced to the C 1s peak (285 eV) arising from adventitious carbon. The oxygen nonstoichiometry of BBSC powder between room temperature to 950°C was measured by thermal gravimetric analysis using a Shimadzu TGA-50 with a ramping rate of 2°C  $\text{min}^{-1}$  under air flow rate of 20  $\text{ml min}^{-1}$ . The oxygen nonstoichiometry at room temperature was measured by iodometric titration.<sup>3</sup> BBSC powder was dissolved in a solution of potassium iodide heated in an O<sub>2</sub>-free atmosphere. HCl was added to dissolve the powder completely. The valence state of Sc was effectively fixed at 3+. On the other hand, reaction with iodide reduced Co ions, e.g. Co<sup>4+</sup> and/or Co<sup>3+</sup> to Co<sup>3+</sup> and/or Co<sup>2+</sup> with simultaneous formation of I<sub>2</sub>; the amount of which was quantified by titration with thiosulfate. The average B-site cation valence and oxygen vacancy stoichiometry were then calculated based on the amount of I<sub>2</sub> formed. Thermal expansion data were collected with a dilatometer (Netsch DIL 402C/3/G) from room temperature to 1000°C on a 2 mm × 5 mm × 12 mm BBSC bar (previously sintered at 1050°C in air).

**Electrical conductivity testing.** BBSC bars for conductivity testing were prepared by pressing the BBSC powder into disk followed by sintering at 1050°C and polishing into bar shape. Ag paste was painted on the square cross-sectional edges and two circumferential surfaces of the bar to form the current and voltage electrodes. The electrical conductivities were measured by a four-probe DC technique using an Autolab, PGSTAT30 electrochemical workstation.

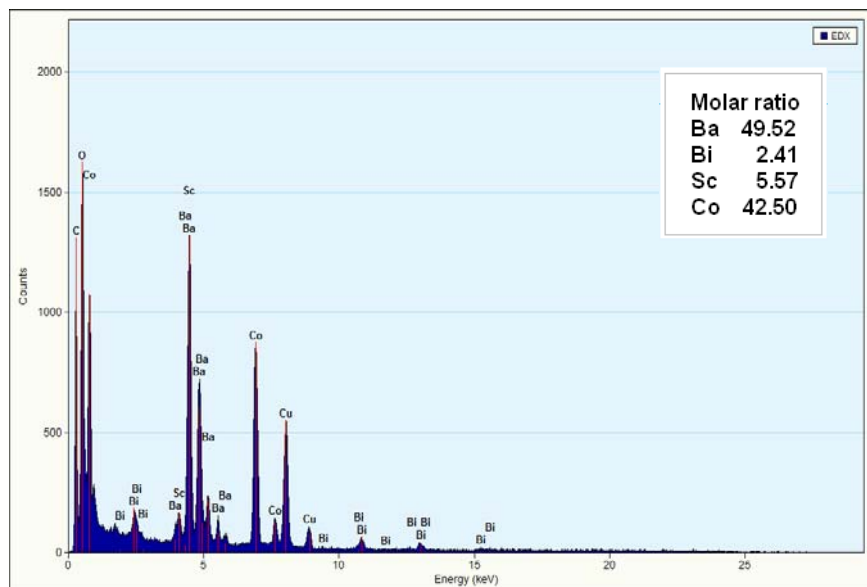
**Fabrication of symmetric cells.** BBSC slurry for spray deposition was prepared by dispersing BBSC powder with a premixed solution of glycerol, and isopropyl alcohol followed by rapid mixing and milling in an agate mortar for 0.5 hours. Symmetrical cells of electrode|Sm<sub>0.2</sub>Ce<sub>0.8</sub>O<sub>1.9</sub>(SDC)|electrode configuration were fabricated by spraying BBSC slurry onto both surfaces of SDC disk in a symmetric

configuration and calcining the sprayed cells at 900-1050°C for 2 hours in air.

**Fabrication of anode-supported SOFCs.** A tape casting process was used to prepare anode substrates. The slurry for tape casting was prepared by two-step milling process in a planetary mill (Pulverisette 5, Fritsch) at 800rpm. Initially, NiO, (ZrO<sub>2</sub>)<sub>0.92</sub>(Y<sub>2</sub>O<sub>3</sub>)<sub>0.08</sub> (YSZ), starch, triethanolamine (as a surfactant) and organic solvents (ethanol and acetone) were milled for 24 hours. Subsequently, polyvinyl butyral (PVB) and polyethylene glycol (PEG) (both as binders) and dibutyl o-phthalate (DOP) (as plasticizers) were added into the initial slurry followed by another milling for 24 hours. The final slurry was subjected to absolute vacuum pressure of 200 mBar to remove trapped gases and casted onto the polymer carrier on a tape casting machine. The tape was then dried for 24 hours before detached from the polymer carrier. Disk-shaped anode substrates with 16 mm diameter were punched from the tape followed by sintering at 1150°C in air to remove organic materials. The SDC|YSZ double electrolyte layers were prepared via wet powder spraying. The YSZ and SDC suspensions were sprayed onto the anode substrate in sequence using a spraying gun with a nozzle diameter of 0.35 mm. Nitrogen was used as a carrier gas at a working pressure of 1.5 atm. The spraying gun was aligned vertically to the anode substrate leaving a 10 mm distance between them. The spray speed was controlled at about 0.005 g s<sup>-1</sup>. The spray process was carried out at a substrate temperature of ~200°C by contacting the substrate with hot plate. The resulting green three-layered disks were fired at 1450°C for 5 hours in air at a ramping rate of 3°C min<sup>-1</sup>. BBSC slurry was then sprayed onto the center of the disk electrolytes and fired at 950°C for 2 hours in air. The resulting coin-shaped film cathodes had a thickness of 10-20 μm and an area of 0.26 cm<sup>2</sup>.

**Electrochemical evaluation and fuel cell testing.** The electrochemical impedance spectra (EIS) of the symmetric cells were obtained using an Autolab, PGSTAT30 electrochemical workstation. The frequency range was 0.01 Hz to 100 kHz and the signal amplitude was 10 mV under open cell voltage conditions. The coin-shaped fuel cell was mounted onto an alumina tube and sealed by ceramic paste at 150°C before heated for testing. H<sub>2</sub> was fed into the anode side as a fuel at a flow rate of 60 ml (STP) min<sup>-1</sup> while the cathode side was exposed to air. The current-voltage curves of the fuel cells operated between 600-750°C were obtained using an Autolab, PGSTAT30 electrochemical workstation. Electrodes and electrolyte polarization resistance were obtained from the EIS of the fuel cell obtained in a frequency range of 100 kHz to 0.1 Hz with signal amplitude of 50 mV under open circuit voltage (OCV).

## Results



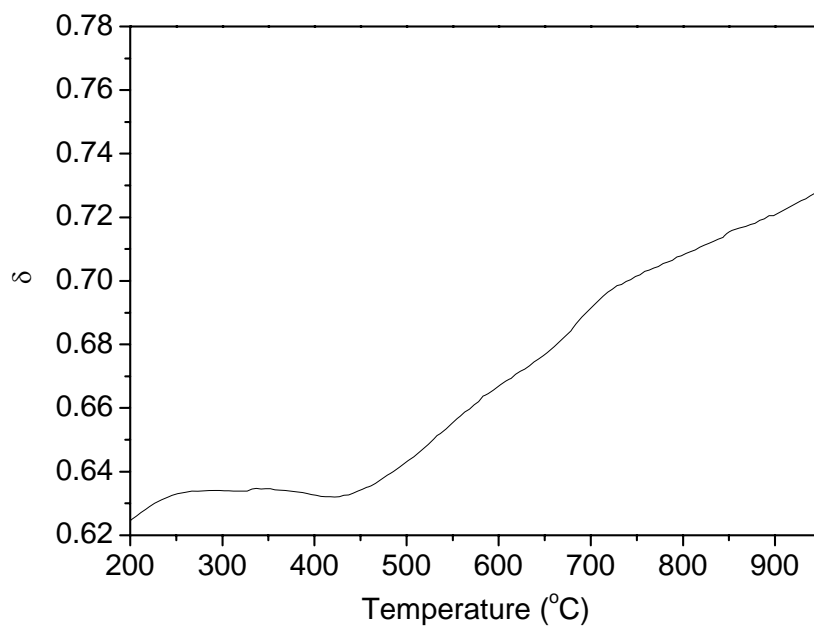
**Figure S1.** Energy dispersive x-ray (EDX) diffraction spectra and quantitative composition of BBSC.

### Structure 1

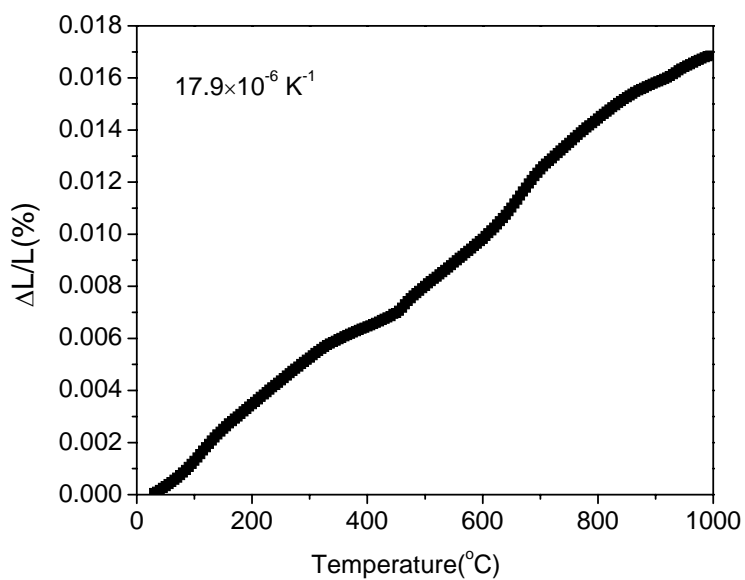
Phase name	Structure
R-Bragg	99.686
Spacegroup	Fm-3m
Scale	9.05484599e-005
Cell Mass	2002.888
Cell Volume (Å <sup>3</sup> )	546.85561
Wt% - Rietveld	100.000
Crystallite Size	
Cry size Lorentzian (nm)	166.3
Strain	
Strain L	0.0259593
Crystal Linear Absorption Coeff. (1/cm)	1584.482
Crystal Density (g/cm <sup>3</sup> )	6.082
PV_TCHZ peak type	
U	0.08060823
V	-0.03060039
W	0.01933399
Z	0
X	0.05171697
Y	0
Lattice parameters	
a (Å)	8.1775691

Site	Np	x	y	z	Atom Occ	Beq
Ba	8	0.25000	0.25000	0.25000	Ba+2 1	2.564
Co1	4	0.00000	0.00000	0.00000	Co+2 1	2.43
Co2	4	0.50000	0.50000	0.50000	Co+2 0.7	5.094
Bi	4	0.50000	0.50000	0.50000	Bi+3 0.1	6.36
Sc	4	0.50000	0.50000	0.50000	Sc+3 0.2	5.991
O	24	0.25000	0.00000	0.00000	O-2 1	6.926

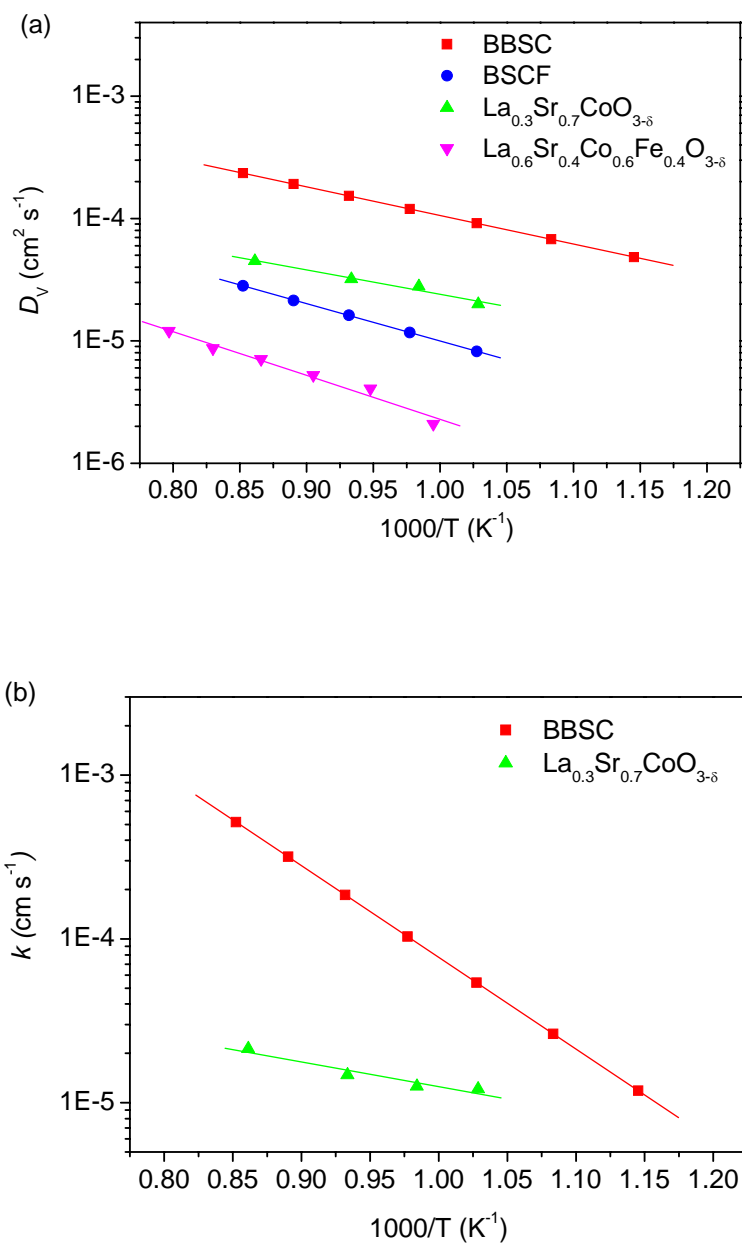
**Figure S2.** Detailed results of Rietveld refinement.



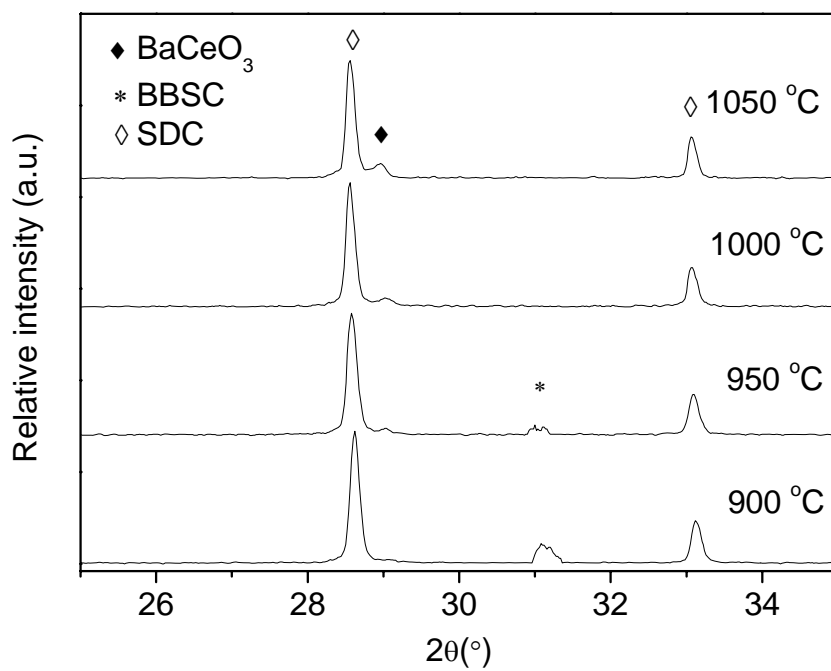
**Figure S3.** Oxygen nonstoichiometry of BBSC between room temperature to 950°C.  
 $\delta=x/2$



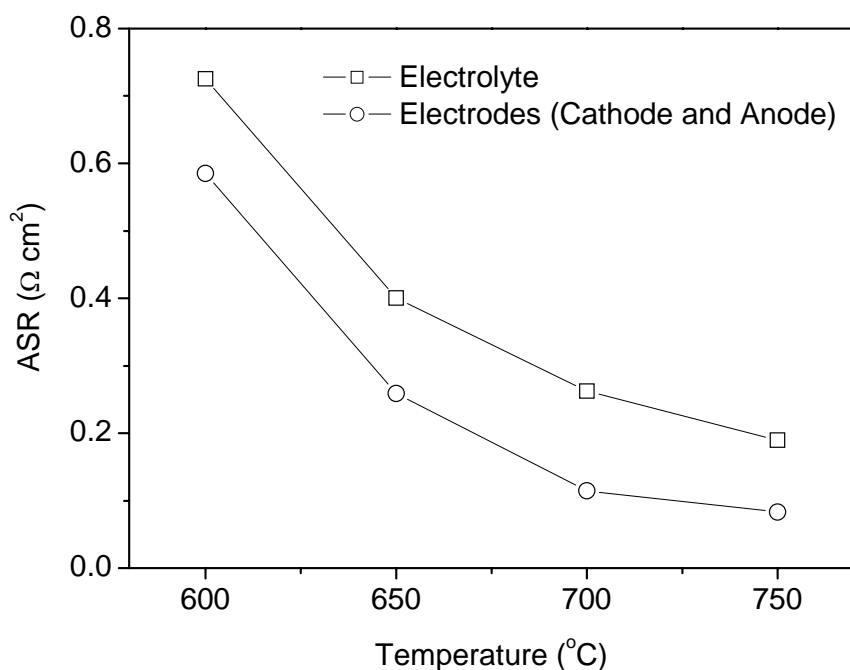
**Figure S4.** Thermal expansion behavior of BBSC.



**Figure S5.** (a) Oxygen vacancies diffusion coefficient ( $D_v$ ) and surface exchange coefficients ( $k$ ) of BBSC, BSCF<sup>4</sup>,  $\text{La}_{0.3}\text{Sr}_{0.7}\text{CoO}_{3-\delta}$ <sup>5</sup> and  $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.6}\text{Fe}_{0.4}\text{O}_{3-\delta}$ <sup>6</sup> between 600-900°C.



**Figure S6.** XRD patterns of BBSC and SDC mixtures fired between 900-1050°C.



**Figure S7.** Electrodes and electrolyte polarization resistances of the fuel cell between 600-750°C.

### References

- (1) *DIFFRAC<sup>plus</sup> TOPAS 4*; Bruker AXS GmbH, Karlsruhe, 2008.
- (2) *Find-It: Inorganic Crystal Structure Database (ICSD)*; Fachinformationszentrum (FIZ): Karlsruhe, 2010.
- (3) Zeng, P.Y.; Chen, Z.H.; Zhou, W.; Gu, H.X.; Shao, Z.P.; Liu, S.M. *J. Membr. Sci.* **2007**, *291*, 148.
- (4) Wang, H.H.; Cong, Y.; Yang, W.S. *J. Membr. Sci.* **210**, 2002, 259.
- (5) van Doorn, R.H.E.; Fullarton, I.C.; de Souza, R.A.; Kilner, J.A.; Bouwmeester, H.J.M.; Burggraaf, A.J. *Solid State Ionics* **1997**, *96*, 1.
- (6) ten Elshof, J.E.T.; Lankhorst, M.H.R.; Bouwmeester, H.J.M. *Solid State Ionics* **1997**, *99*, 15.