

# Supporting Information

## **Behavior of Ba(Co, Fe, Nb)O<sub>3-δ</sub> Perovskite in CO<sub>2</sub>-Containing Atmospheres: Degradation Mechanism and Materials Design**

Jianxin Yi,<sup>1,\*</sup> Michael Schroeder,<sup>1,\*</sup> Thomas Weirich<sup>2,3</sup>, Joachim Mayer<sup>2</sup>

<sup>1</sup> Institute of Physical Chemistry, RWTH Aachen University, Landoltweg 2, 52056, Aachen, Germany

<sup>2</sup> Central Facility for Electron Microscopy, RWTH Aachen University, Ahornstrasse 55,  
52074 Aachen, Germany

<sup>3</sup> Institute of Crystallography, RWTH Aachen University, Jaegerstrass 17-19, 52066 Aachen, Germany

## **Sample preparation**

$\text{BaCo}_{1-x-y}\text{Fe}_x\text{Nb}_y\text{O}_{3-\delta}$  ( $x=0.2-0.8$ ,  $y=0.2-0.5$ ) perovskite powders were synthesized by the conventional solid state reaction method. Appropriate amounts of  $\text{BaCO}_3$ ,  $\text{Co}_3\text{O}_4$ ,  $\text{Fe}_3\text{O}_4$  or  $\text{Fe}_2\text{O}_3$ , and  $\text{Nb}_2\text{O}_5$  were weighed according to the cation stoichiometry and mixed, followed by ball-milling in isopropanol. The powder mixture was calcined at  $1050^\circ\text{C}$  for 15 h and then  $1100^\circ\text{C}$  for 15 h with intermittent grinding. The calcined powders were uni-axially pressed at 30 MPa into disk-shaped pellets, which were successively cold iso-statically pressed at 300 MPa. Sintering of the green disks was performed in air at  $1200^\circ\text{C}$  for 10 h for the Co-containing compositions, or at  $1350^\circ\text{C}$  for 10 h for the Co-free compositions. Polished pellets and powders from crushing the sintered ceramics were pre-equilibrated in air, annealed in flowing pure  $\text{CO}_2$  at  $900^\circ\text{C}$ , and subsequently quenched in the same atmosphere. In order to study the influence of the gas stream composition on the degradation process, annealing in 33 vol.%  $\text{CO}_2/\text{Ar}$  and 33 vol.%  $\text{CO}_2/\text{O}_2$  was also carried out at  $900^\circ\text{C}$ . In these cases, the samples were pre-equilibrated in Ar or 33 vol.% Ar/ $\text{O}_2$ , respectively.

## **X-ray Diffraction**

Phase analysis was conducted by means of X-ray Diffraction (XRD) at a step size of  $0.04^\circ$  and a step-counting time of 60 s under ambient conditions. For powder samples, a STOE STADI-P transmission diffractometer with Cu  $\text{K}_{\alpha 1}$  radiation ( $\lambda=0.15406$  nm) delivered by a curved Ge (111) primary monochromator was used. Pellet samples were investigated with a STOE Theta-Theta reflection diffractometer with Cu  $\text{K}_{\alpha}$  radiation ( $\lambda=0.15418$  nm). Both diffractometers were equipped with scintillation counter and graphite secondary monochromator. Indexing and lattice parameter refinement was performed by using a Werner's TREOR program (STOE WinXPOW).

## **Oxygen permeation**

Oxygen permeation measurements were conducted with a home-made setup. A disk-shaped membrane was positioned between two alumina tubes and sealed to gas-tightness by gold rings. During the permeation measurements, synthetic air and Ar/CO<sub>2</sub> (or He/CO<sub>2</sub>) mixtures were fed to the feed side and sweep side of the membrane, respectively. The volume flows of the feed and sweep streams were 350 ml/min and 50 ml/min, respectively. Composition of the permeate effluent was analyzed by a calibrated Balzers OmniStar<sup>TM</sup> mass spectrometer (Ar/CO<sub>2</sub> as sweep gas), or Agilent 7890A gas chromatograph (He/CO<sub>2</sub> as sweep gas). During some measurements using the mass spectrometer where pure CO<sub>2</sub> was used as sweep gas, a slow increase of the intensity of the oxygen ( $m/z=32$ ) signal with time was observed in the mass spectrum. This behavior is ascribed to recombination of oxygen atoms generated by fragmentation of CO<sub>2</sub> in the ion source of the mass spectrometer. This was confirmed by a blank experiment in which pure CO<sub>2</sub> was fed directly into the mass spectrometer. The influence of this artifact on the results of this work is insignificant when compared with the amount of oxygen permeated through the membrane, and thus neglected. The gas chromatograph was equipped with a HP-PLOT-Q capillary column to separate CO<sub>2</sub> from O<sub>2</sub> and N<sub>2</sub>, and a HP-PLOT-5A capillary column to separate O<sub>2</sub> from N<sub>2</sub>. Gas leakage from the surrounding air through the membrane or the gold seals was monitored by measuring the N<sub>2</sub> signal in the permeate effluent, however, no significant leakage was observed in the present work.

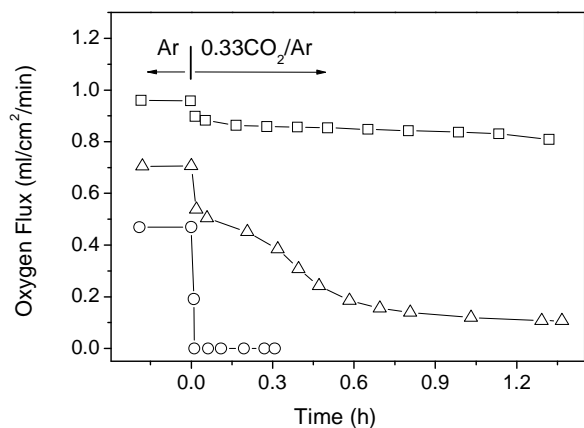


Figure S1. Time dependence of oxygen permeation flux of 1 mm thick BaCo<sub>0.4</sub>Fe<sub>0.4</sub>Nb<sub>0.2</sub>O<sub>3-δ</sub> membrane with 33%CO<sub>2</sub>/Ar as sweep gas at (□) 1000 °C, (Δ) 900 °C, and (○) 800 °C.

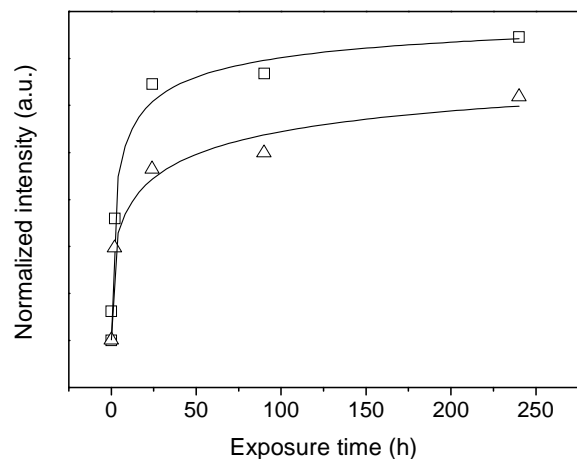


Figure S2. Intensity of the reflection (111) for BaCO<sub>3</sub> (□) and reflection (200) for CoO (Δ) as a function of CO<sub>2</sub> annealing time for BaCo<sub>0.4</sub>Fe<sub>0.4</sub>Nb<sub>0.2</sub>O<sub>3-δ</sub> powders at 900 °C. The values were normalized to that of the reflection (110) for the perovskite phase. Solid lines are guides to the eye.

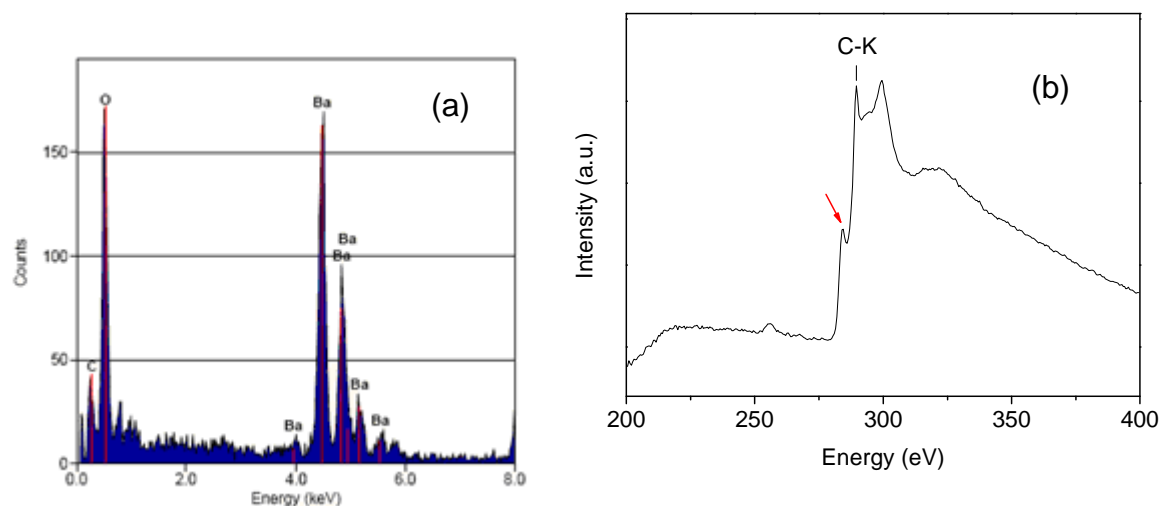


Figure S3. EDX spectrum (a) and carbon K edge EELS spectrum (b) taken from the surface layer of a  $\text{BaCo}_{0.4}\text{Fe}_{0.4}\text{Nb}_{0.2}\text{O}_{3-\delta}$  membrane exposed to  $\text{CO}_2$  at 900 °C for 2 h. The arrow in (b) shows a pre-peak of the carbon K-edge at ~ 284 eV, which is characteristic for conjugated  $\pi$  electron systems, e.g. the flat  $\text{CO}_3$  anion present in  $\text{BaCO}_3$ .

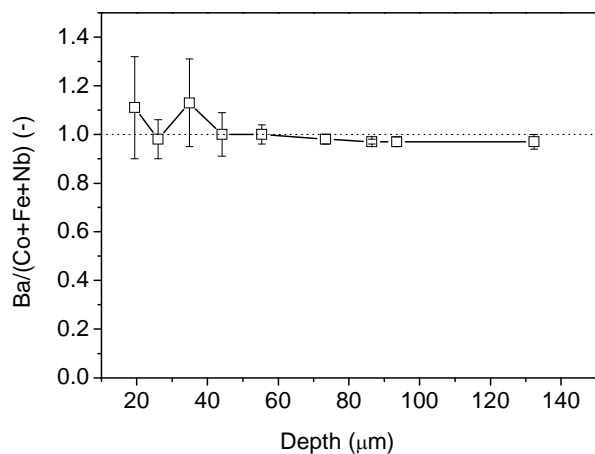


Figure S4. Atomic ratio of A-site to B-site cation of the  $\text{Ba}(\text{Co,Fe,Nb})\text{O}_{3-\delta}$  perovskite in the decomposed zone versus sample depth for the  $\text{BaCo}_{0.4}\text{Fe}_{0.4}\text{Nb}_{0.2}\text{O}_{3-\delta}$  membrane annealed in  $\text{CO}_2$  for 240 h at 900 °C. Values are normalized to that of an untreated  $\text{BaCo}_{0.4}\text{Fe}_{0.4}\text{Nb}_{0.2}\text{O}_{3-\delta}$  reference.

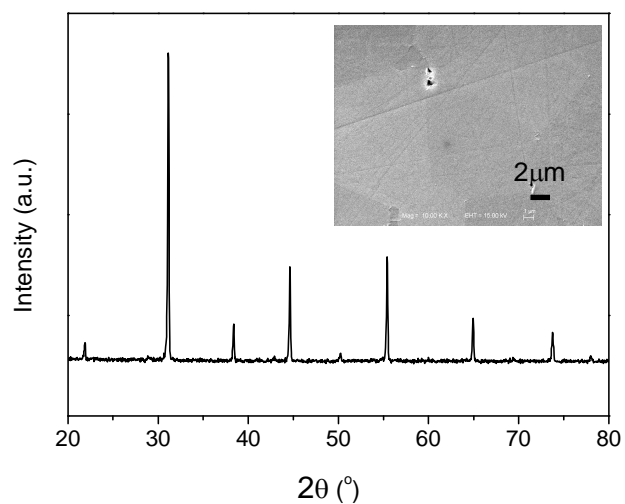


Figure S5. X-ray diffraction pattern for powders and SEM image for membrane (inset) of BaFe<sub>0.5</sub>Nb<sub>0.5</sub>O<sub>3-δ</sub> annealed at 900 °C in CO<sub>2</sub> for 90 hours. The cubic perovskite structure was retained and no formation of BaCO<sub>3</sub> or other secondary phase was found.