

X-ray Diffraction patterns of STN95, BCZY27, and BS27_5050

Plots of x-ray diffraction (XRD) data for calcined STN95 and BCZY27 materials are given below in figure S1. STN95 was calcined in air for 4 h at 1300 °C. BCZY27 was calcined in air for 24-48 h at 1430 – 1500 °C.¹

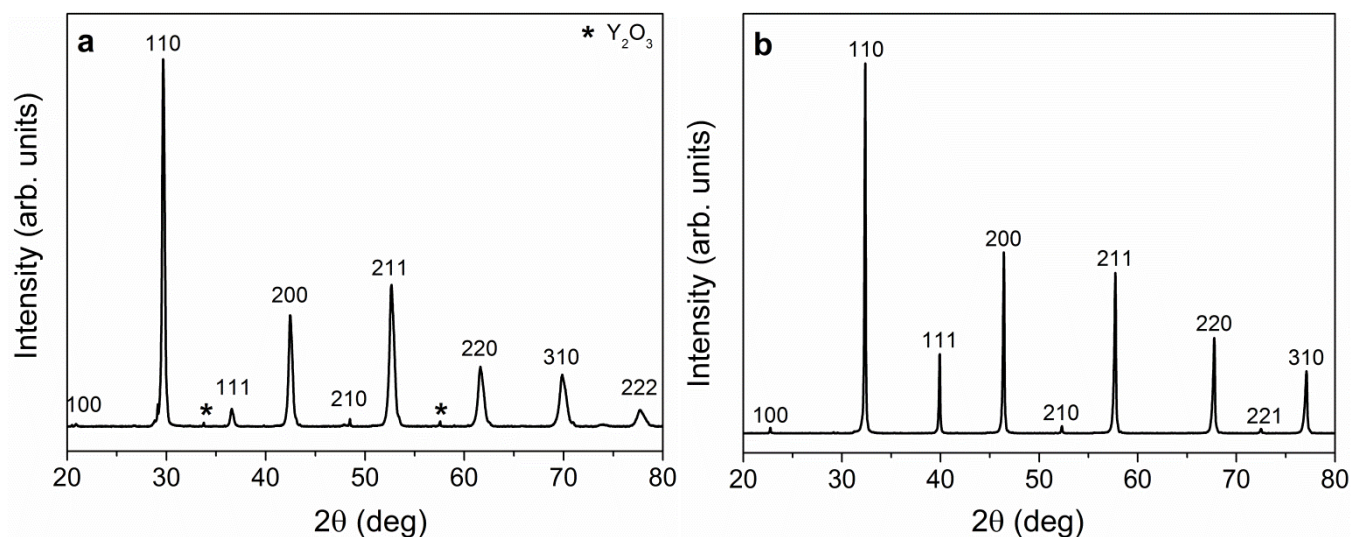


Fig. S1: Indexed XRD patterns for **a** calcined BCZY27 and **b** calcined STN95. Traces of Y₂O₃ were observed in BCZY27, but were not considered significant to the overall phase composition, due to their low intensity. Figure credit: reference S1.

A plot of a typical XRD pattern for BS27_5050 is given below as figure S2. Impurity phases corresponding to Ba/Ti-doped SrZrO₃ and Sr-doped BaTiO₃ were observed. These phases were not quantified, nor accounted for in the electrical properties model.

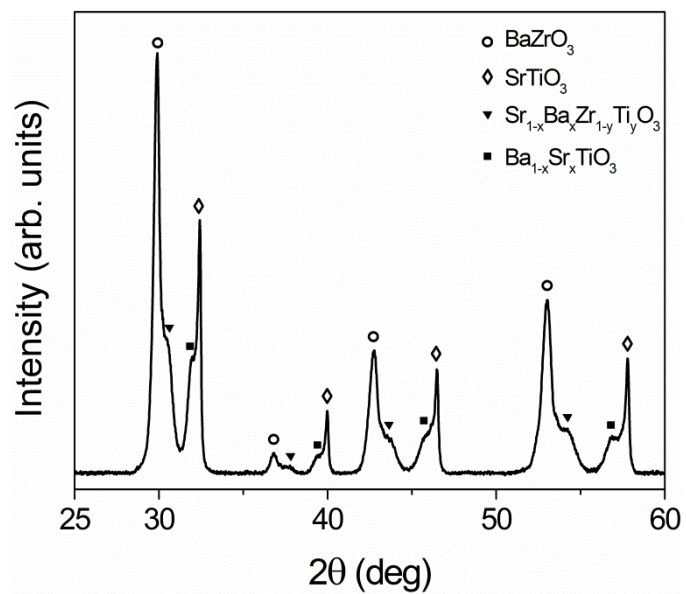


Fig. S2: Typical XRD pattern for BS27_5050 sintered sample, ground and polished flat before analysis. The x-axis has been truncated to show the overlapping peaks at each STN95 and BCZY27 peak location more clearly. Figure credit: reference S1.

Thermogravimetric analysis of STN95

Data for the TGA experiment on a sample of STN95-CS is given below as figure S3.

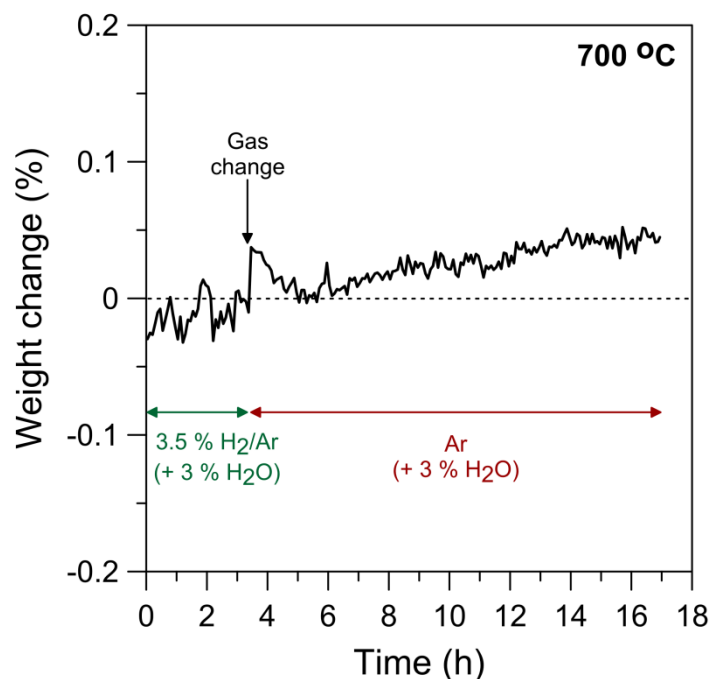


Fig. S3: TGA data for STN95 sample held at 700 °C in moist dilute H₂/N₂ and in moist Ar to study the potential for oxidation under hydrogen separation sweep conditions.

The weight increase of 0.05 % to a 150 mg sample of STN95 was assumed to be entirely due to oxygen incorporation into vacancies, amounting to $\sim 75 \mu\text{g}$. This mass was converted into 4.7×10^{-6} mol O. The mass is treated as atomic oxygen because molecular oxygen is not known to incorporate into the structure of STN95. The molecular weight of STN95 is $183.6 \text{ g}\cdot\text{mol}^{-1}$, yielding a value of 8.2×10^{-4} mol STN95.

Electronic carriers in STN95 are produced by substitution of Nb⁵⁺ onto Ti⁴⁺ sites, a process which, when combined with the reducing sintering atmosphere, causes reduction of Ti⁴⁺ ions to Ti³⁺ ions.² Conduction-band electrons, n , of concentration $[n]$, equivalent to $[\text{Ti}^{3+}]$, which in turn is equivalent to $[\text{Nb}^{5+}]$, are generated. In the case of the STN95 TGA sample, n

lost to re-oxidation was calculated to be 8.2×10^{-5} mol electrons. Since oxygen vacancies are doubly-ionized, written as $V_O^{\bullet\bullet}$ in the Kroger-Vink formalism, for each vacancy filled, two conduction-band electrons must be consumed to maintain electroneutrality. Thus, the fraction of Ti^{3+} ions re-oxidized in the TGA experiment, eliminating as many conduction-band electrons, is given by equation (S1):

$$n_{\text{lost}} = Ti^{3+}_{\text{re-ox}} = \frac{4.7 \times 10^{-6} \text{ mol } O_{\text{inc}}}{8.2 \times 10^{-5} \text{ mol } Ti^{3+}_{\text{total}}} \cdot \frac{1 \text{ mol } V_O^{\bullet\bullet}_{\text{filled}}}{1 \text{ mol } O_{\text{inc}}} \cdot \frac{2 \text{ mol } e'}{1 \text{ mol } V_O^{\bullet\bullet}_{\text{filled}}}, \quad (\text{S1})$$

where O_{inc} refers to the incorporated atomic oxygen equivalent to the 0.05 % weight increase of the STN95 sample. Utilizing equation (S1), ~11 % of the conduction-band electrons were calculated to be consumed during the TGA experiment.

Hydrogen flux testing by GC: calibration and raw data example

A thermal conductivity detector (TCD), which demonstrates a linear response between chromatograph peak area and sample concentration across a broad range, was used to measure H_2 flux in the BS27 experiments. Based on the literature from the GC manufacturer (Agilent), the TCD response was assumed to be linear across all conditions used in the current work.

The raw data consisted of chromatograph plots interpreted by the software (OpenLAB ChemStation). The results were reported as text files tabulating areas under the curves for H_2 and He peaks together with the corresponding concentrations of each gas calculated from a calibration. The GC was calibrated using well-defined mixtures of H_2 and He in Ar and, for each mixture concentration, its value in ppm was assigned to the measured area under the observed peak. A linear relationship between chromatograph peak area and concentrations of H_2 and He was achieved and used as an external standard to calculate ppm concentrations of

H₂ and He observed during BS27 membrane tests. The linear equations obtained from the calibration process are given in table S1.

Table S1: Calibration equations for interpreting GC experiment data on BS27 membranes.

Gas	Calibration Equation
He	He (ppm) = [Peak (area) + 9879.8]/258.1
H ₂	H ₂ (ppm) = [Peak (area) - 1722.7]/440.8

Using the concentrations calculated from table S1, and knowing the flow rate of the gas through the system, a flow of H₂ output from the membrane in mL/min was determined. A flux of H₂ was then calculated by dividing this flow over the known area (cm²) of the membrane. Conversion to a molar flow rate was done to compare with other experiments in the literature citing the same metric. GC runs were taken every five minutes at a given temperature and gas condition until equilibration was achieved. A typical GC result text file representing the raw output for the BS27_5050 sample coated with 100 nm Pd layers is given below as table S2.

Table S2: GC results for BS27_5050+Pd test at 700 °C after 30 minute equilibration

Peak	Retention Time (min)	Concentration (ppm)	Peak Area (μV/min)
He	0.39	20092	5168548
H ₂	0.42	2685	1185225

The GC software utilized the equations given in table S1 together with the peak areas in column 4 of table S2 to generate the concentration values in ppm for H₂ and He during a given GC run.

Hydrogen flux leak correction

Leaks in the hydrogen flux measurements were corrected using the theory of binary gas mixtures developed by independently Chapman and Enskog.^{3,4} Their formula for calculating effective diffusion coefficients for such mixtures is given by:

$$D_{eff} = \frac{1.86 \times 10^{-3} T^{3/2} \left(\frac{1}{M_1} + \frac{1}{M_2} \right)^{1/2}}{p(\sigma_{12})^2 \Omega}, \quad (S1)$$

where T is the temperature, M_1 and M_2 are the molecular weights of the gases, p is the pressure, σ_{12} is the Lennard-Jones (L-J) potential between the gases, and Ω is the collision integral, which represents an estimated cross-sectional area of the gas molecule dependent on temperature and transport energy. The L-J and Ω parameters for H₂ and Ar were taken from textbook literature.⁴ Values for helium were acquired from a separate source.⁵

Interactions between H₂ and Ar and between He and Ar must be taken into account to correct the raw flux data for any leaks. Equation (S1) was used to calculate D_{eff} values for H₂-Ar and He-Ar. The D_{eff} for H₂-Ar was divided by the D_{eff} for He-Ar, thereby obtaining a unitless factor which could be used to determine the magnitude of the H₂ leak during flux testing. The values of the unitless factor, dubbed D^* , were 1.097, 1.094, and 1.092 for temperatures of 600, 700, and 800 °C, respectively. Thus, the H₂ signal output from the GC was ~10 % higher than the value expected if both H₂ and He were to diffuse through a leak at equivalent rates.

With the correction factors from equation (S2) and knowing the H₂ fraction present in the feed gas, the amount of H₂ coming through the membrane setup as a leak was determined by equation (S3):

$$J_{\text{H}_2, \text{corr}} = \frac{f_{\text{H}_2}}{D^*} \cdot J_{\text{H}_2, \text{obs}}, \quad (\text{S3})$$

where $J_{\text{H}_2, \text{corr}}$ is the corrected H_2 flux, f_{H_2} is the fraction of H_2 in the feed gas, e.g., 0.09 for the 9 % H_2/He gas used in this work, D^* is the binary gas mixture correction factor, and $J_{\text{H}_2, \text{obs}}$ is the total observed H_2 flux from the GC. The observed flux was calculated from the calibration equation in table S1 based on the total H_2 peak in the raw data.

Supplementary References:

- 1 J. S. Fish, S. Ricote, F. Lenrick, L. R. Wallenberg, T. C. Holgate, R. O'Hayre and N. Bonanos, *J. Mater. Sci.*, 2013, **48**, 6177-6185.
- 2 P. Blennow, A. Hagen, K. K. Hansen, L. R. Wallenberg and M. Mogensen, *Solid State Ionics*, 2008, **179**, 2047-2058.
- 3 S. Chapman and T. G. Cowling, *The Mathematical Theory of Non-uniform Gases*, Cambridge University Press, Cambridge, UK, 1991.
- 4 E. L. Cussler, *Diffusion: Mass Transfer in Fluid Systems*, Cambridge University Press, Cambridge, UK, 2009.
- 5 S. W. Van Scriver, in *International Cryogenics Monograph Series*, eds. K. D. Timmerhaus and C. Rizzuto, Springer, New York, 2nd edn., 2012.