

ESI (Supporting information)

Experimental procedure

For preparing a porous pellet, SrZrO₃ powders were crushed into fine particles using a planetary ball mill (pulverisette 6; Fritsch GmbH) with suspension in *iso*-propanol. The rotation was conducted at 300 rpm for 15 min, with a successive 10 min pause and re-rotation at 300 rpm for 15 min. After evaporation of *iso*-propanol, SrZrO₃ powders were pressed at 130 kN for 30 min with vacuum aspiration. The obtained pellet was sintered at 1523 K for 12 h with the heating ramp rate of 5 K/min in air. The calcined sample diameter and thickness were, respectively, 19.30 mm and 1.1 mm. The relative density was calculated from weight and geometry as approximately 60%. Finally, circular Pt electrodes were painted on both sides of the pellet using Pt ink (Pt ink no. 356010; The Nilaco Corp.) and annealed at 1173 K for 1 h with the heating ramp rate of 4 K/min in air. For preparing a dense SrZrO₃ sample, crushing of SrZrO₃ powders using the planetary ball mill was conducted. Six cycle rotations were conducted at 600 rpm for 30 min, followed by a 15 min pause. After evaporation of *iso*-propanol, SrZrO₃ powders were pressed with vacuum aspiration after 41 drops of a binder had been mixed uniformly with the powder. The powders were pressed at 180 kN for 90 min and were sintered at 1703 K for 28 h with the heating ramp rate of 2 K/min in air. The calcined sample diameter and thickness were, respectively, 17.75 mm and 1.5 mm. The relative density was calculated as approximately 90% from weight and geometry. Then, circular Pt electrodes were painted on both sides of the pellet similarly to the porous pellet. The crystalline phases in the synthesized powder and pellets were analyzed using X-ray diffraction (XRD, $\lambda = 1.5418 \text{ \AA}$, MiniFlex600 with Cu-K α radiation sources; Rigaku Corp.). The pellet morphologies were studied using scanning electron microscopy (SEM, 15 kV, S4500S; Hitachi Ltd.). All electrochemical impedance spectroscopy (EIS) measurements were taken in a measurement cell (ProboStat; NorECs AS, Norway) using a two-electrode four-wire setup connected to an impedance spectrometer (alpha-A; Novocontrol Technologies) with a ZG4 interface. The impedance spectra were recorded at frequencies of 10⁶–10⁻³ Hz using an oscillation amplitude of 100 mV RMS (root mean square). Temperature dependences of electrical conductivity were examined under N₂ atmosphere at 423–723 K and under N₂: H₂=1: 3 at 348–723 K. The total flow rate of the supply gas was 60 SCCM. Under the N₂ atmosphere, no measurement could be taken below 398 K because the resistance was too high to describe the semi-circle. Before measurement under the N₂: H₂=1: 3 atmosphere, pre-reduction was conducted at 723 K for 2 h. Partial pressure of hydrogen (P_{H_2}) dependence of electrical conductivity was assessed under $P_{\text{H}_2} = 10^{-5} - 1 \text{ atm}$ (N₂ balanced) at 723 K. H/D isotope effects were evaluated under N₂: H₂(D₂) = 1: 3 at 423–723 K. Then impedance data were analyzed using ZView equivalent circuit fitting software (ver. 3.5a; Scribner Associates Inc.). The impedance spectra were fitted using a [(RC)(RC)]C_{stray}

equivalent circuit model, as presented in Fig. S1. The (RC) components were assigned to the series-connected bulk and grain boundary transport. Also, C_{stray} denotes parallel-connected parasitic capacitance.

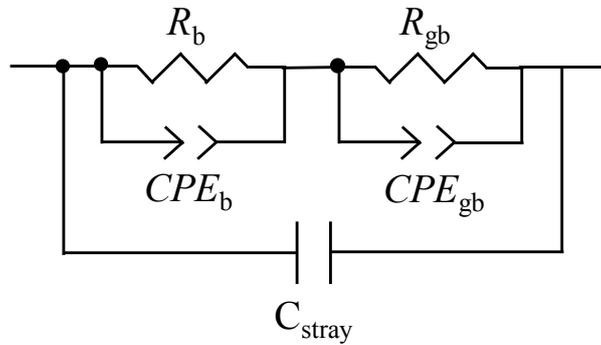


Fig. S1. Equivalent circuit with series-connection of bulk and grain boundary: R denotes resistance, CPE denotes the constant phase element, C_{stray} represents the parasitic capacitance, b and gb respectively stand for the bulk and the grain boundary.

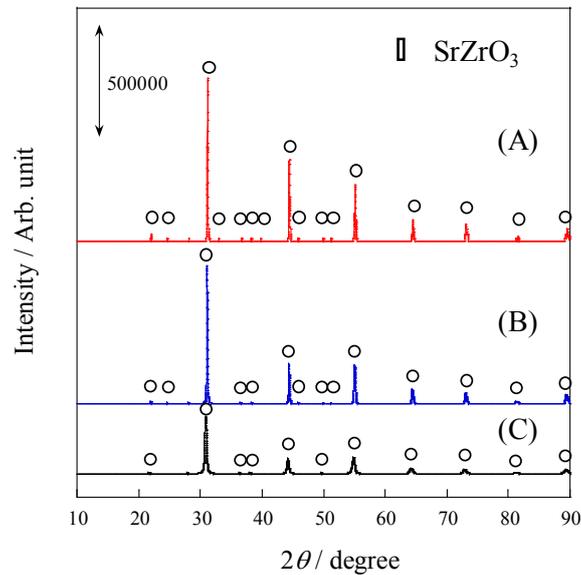


Fig. S2. XRD patterns of SrZrO_3 : (A) dense pellet (R.D. = 90%), (B) porous pellet (R.D. = 60%), and (C) synthesized powder.

Table S1 Geometry factors of porous and dense SrZrO₃ pellets

	Porous SrZrO ₃	Dense SrZrO ₃
Relative density / %	59.2	92.0
Weight / g	1.05	1.88
Diameter / mm	19.3	15.8
Thickness / mm	1.10	1.50
Pore size / μm	6.11	5.99