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Supporting Information

Direct synthesis of barium titanium oxyhydride for use as a hydrogen permeable electrode

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Experimental details

To obtain mechanochemically synthesized $BaTiO_{3-x}H_x$ powder, BaH_2 (Mitsuwa Chemical, 95 %), BaO (Aldrich, 99.99%), TiO_2 (FUJIFILM Wako Pure Chemicals, 99.9%), and TiH_2 (Kojundo Chemical Laboratory Co., Ltd.) were used as starting materials. BaO powder was pre-crushed using a ball mill (Pulverisette-7, Fritsch) to make fine powder. Those materials were mixed in an Ar-filled glovebox with an agate mortar, in accordance with the following equation (1) with nominal composition $x_{\mathrm{nom}} = 0.1, 0.25, 0.5, 1$. In the case of $x_{\mathrm{nom}} = 2$, TiH_2 was used following the equation (2).

$$xBaH_2 + (1 - x)BaO + TiO_2 \rightarrow BaTiO_{3-x}H_x + 0.5xH_2 \qquad (1)$$

$$BaO + TiH_2 \rightarrow BaTiOH_2 \qquad (2)$$

The mixtures of 1g were sealed in a ZrO_2 container together with 16 ZrO_2 balls of diameter 10 mm. Mechanical activation was performed at 600, 800, and 1100 rpm for 90 min without intervals using a high-energy ball mill (Emax, Retsch).

Laboratory powder X-ray diffraction (XRD) were carried out with a diffractometer (Rigaku, MiniFlex 600) with Cu-Kα radiation. Synchrotron XRD (SXRD) data of $x_{\mathrm{nom}} = 0.25$ 0.5 was collected at the BL02B2 beamline at SPring-8 in Japan. Incident beams were monochromatized to $\lambda = 0.42015$ for $x_{\mathrm{nom}} = 0.5$, 0.41984 for $x_{\mathrm{nom}} = 0.25$ Å. The powder samples were loaded in a Lindemann glass capillary tube with an inner diameter of 0.2 mm. Neutron diffraction (ND) data for the sample of $x_{\mathrm{nom}} = 0.25, 0.5$, was acquired using a time-of-flight (TOF) neutron powder diffractometer, SPICA, at J-PARC in Japan. Approximately 1.2 g of samples were loaded in vanadium cans. The obtained SXRD and ND data were refined by Rietveld method using RIETAN-FP and Z-Rietveld software, respectively.[1,2] Thermal desorption spectroscopy (TDS) was conducted with 60 ºC/min from 27 to 1000 ºC under high vacuum conditions (~10^{-7} Pa) (ESCO, Ltd.). Particle morphology was observed by scanning electron microscope (SEM, Hitachi High-Tech, SU6600).

Electrode property of mechanochemically

synthesized $BaTiO_{3-x}H_x$ was evaluated by electrochemical impedance spectroscopy (EIS). A three-layered pellet was composed of solid electrolyte $LaSrLiH_2O_2$ sandwiched by $BaTiO_{3-x}H_x$ ($x_{nom} = 0.5$). Polycrystalline $LaSrLiH_2O_2$ was prepared by sintering under ambient pressure, according to previous literature.[3] The 6.1 mmϕ layered pellet was prepared by hot-press sintering at 400 ºC for 1h under uniaxial 300 MPa in an argon-filled glovebox. The relative densities of $BaTiO_{2.5}H_{0.5}$ and $LaSrLiH_2O_2$ were approximately ~66 and ~72%, respectively. The weight of the solid electrolyte, $LaSrLiH_2O_2$, was adjusted to be 1.5 and 3 times that of $BaTiO_{2.5}H_{0.5}$, and symmetric cells with different electrolyte thicknesses were fabricated. The thickness of each component for the thin and thick cells were ~0.4 mm for $BaTiO_{2.5}H_{0.5}$ in both cells, and ~0.6 and ~1.2 mm for $LaSrLiH_2O_2$, respectively. The ionic conductivities for $LaSrLiH_2O_2$ were determined by alternating current (AC) impedance spectroscopy under H_2 gas flow, using a frequency response analyzer (Biologic, MTZ-35) at an applied voltage of 10-100 mV and a frequency range from 35 MHz to 0.5 mHz. The obtained impedance spectra were fitted with electrical equivalent circuits using the EC-Lab software. The electrical resistivity of the hot-pressed $BaTiO_{3-x}H_x$ pellet was measured by the AC impedance and DC polarization methods.

Reference

1 F. Izumi and K. Momma, in *Solid State Phenomena*, Trans Tech Publ, 2007, vol. 130, pp. 15–20.

2 R. Oishi, M. Yonemura, Y. Nishimaki, S. Torii, A. Hoshikawa, T. Ishigaki, T. Morishima, K. Mori and T. Kamiyama, *Nucl. Instruments Methods Phys. Res. Sect. A Accel. Spectrometers, Detect. Assoc. Equip.*, 2009, **600**, 94–96.

3 A. Watanabe, G. Kobayashi, N. Matsui, M. Yonemura, A. Kubota, K. Suzuki, M. Hirayama and R. Kanno, *Electrochemistry*, 2017, **85**, 88–92.

Table S1. Refined structure parameters for ND data of $x_{\mathrm{nom}} = 0.5$.

Atom	Site	g	x	y	z	B / Å^2
Ba	1a	1	0	0	0	0.302(15)
Ti	1b	1	0.5	0.5	0.5	0.737(14)
O	3c	0.8588(12)	0	0.5	0.5	0.371(9)
H	3c	0.1413(18)	0	0.5	0.5	= B(O)

Unit cell: Cubic $Pm\bar{3}m$, $a = 4.02525(5)$

$R_{\mathrm{wp}} = 2.2785$ %, $R_{\mathrm{p}} = 1.8152$ %, $R_{\mathrm{e}} = 1.1048$ %, $S = 2.0625$, $R_{\mathrm{B}} = 4.4740$ %, $R_{\mathrm{F}} = 4.5743$ %

Table S2. Refined structure parameters for SXRD data of $x_{\mathrm{nom}} = 0.5$.

Atom	Site	g	x	y	z	B / Å^2
Ba	1a	1	0	0	0	0.55(13)
Ti	1b	1	0.5	0.5	0.5	0.74(1)
O	3c	0.859(4)	0	0.5	0.5	0.79(5)

Unit cell: Cubic $Pm\bar{3}m$, $a = 4.0256(3)$

$R_{\mathrm{wp}} = 6.070$ %, $R_{\mathrm{p}} = 4.179$ %, $R_{\mathrm{e}} = 8.984$ %, $S = 2.2633$, $R_{\mathrm{B}} = 1.108$ %, $R_{\mathrm{F}} = 0.432$ %

Table S3. Refined structure parameters for ND data of $x_{\mathrm{nom}} = 0.25$.

Atom	Site	g	x	y	z	B / Å^2
Ba	1*a*	1	0	0	0	0.474(13)
Ti	1*b*	1	0.5	0.5	0.5	0.949(12)
O	3*c*	0.9030(11)	0	0.5	0.5	0.483(6)
H	3*c*	0.0954(17)	0	0.5	0.5	= *B*(O)

Unit cell: Cubic $Pm\bar{3}m$, $a = 4.02296(3)$

$R_{\mathrm{wp}} = 3.5358$ %, $R_{\mathrm{p}} = 2.8439$ %, $R_{\mathrm{e}} = 1.3443$ %, $S = 2.6302$, $R_{\mathrm{B}} = 5.3855$ %, $R_{\mathrm{F}} = 4.3455$ %

Table S4. Refined structure parameters for SXRD data of $x_{\mathrm{nom}} = 0.25$.

Atom	Site	g	x	y	z	B / Å^2
Ba	1*a*	1	0	0	0	0.86(2)
Ti	1*b*	1	0.5	0.5	0.5	0.11(2)
O	3*c*	0.883(6)	0	0.5	0.5	0.66(8)

Unit cell: Cubic $Pm\bar{3}m$, $a = 4.0267(2)$

$R_{\mathrm{wp}} = 6.763$ %, $R_{\mathrm{p}} = 4.907$ %, $R_{\mathrm{e}} = 3.427$ %, $S = 1.9732$, $R_{\mathrm{B}} = 1.619$ %, $R_{\mathrm{F}} = 0.896$ %

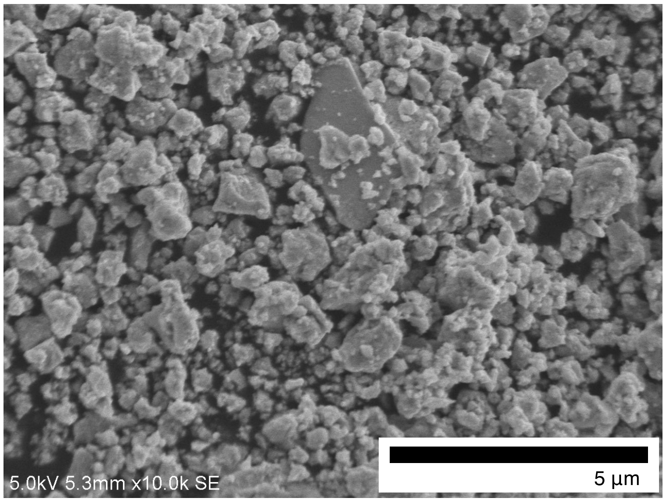

Figure S1 the morphology of $x_{\mathrm{nom}} = 0.5$ in preparation composition. Particles which have various size about 0.1-2 µm were observed, which probably results from grain growth during the rotation.

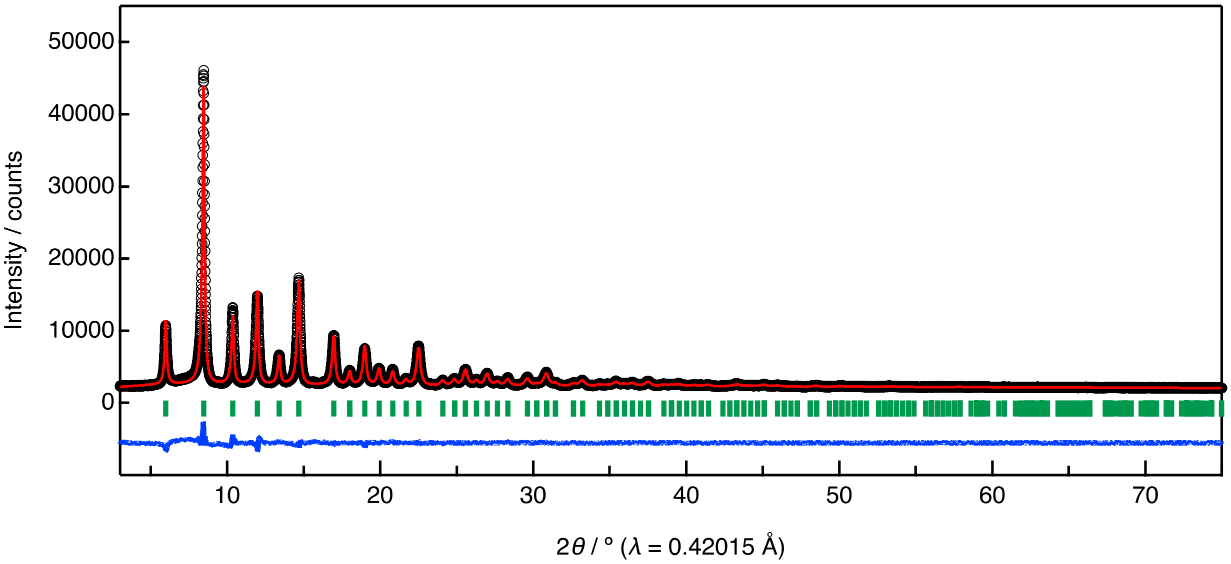

Figure S2 Rietveld refinement profile for SXRD data of $x_{\mathrm{nom}} = 0.5$. The wavelength was 0.42015 Å. Final observed calculated, and residual differences are shown in black circles, red line, and blue solid line, respectively. Green vertical marks indicate the positions of Bragg reflections.

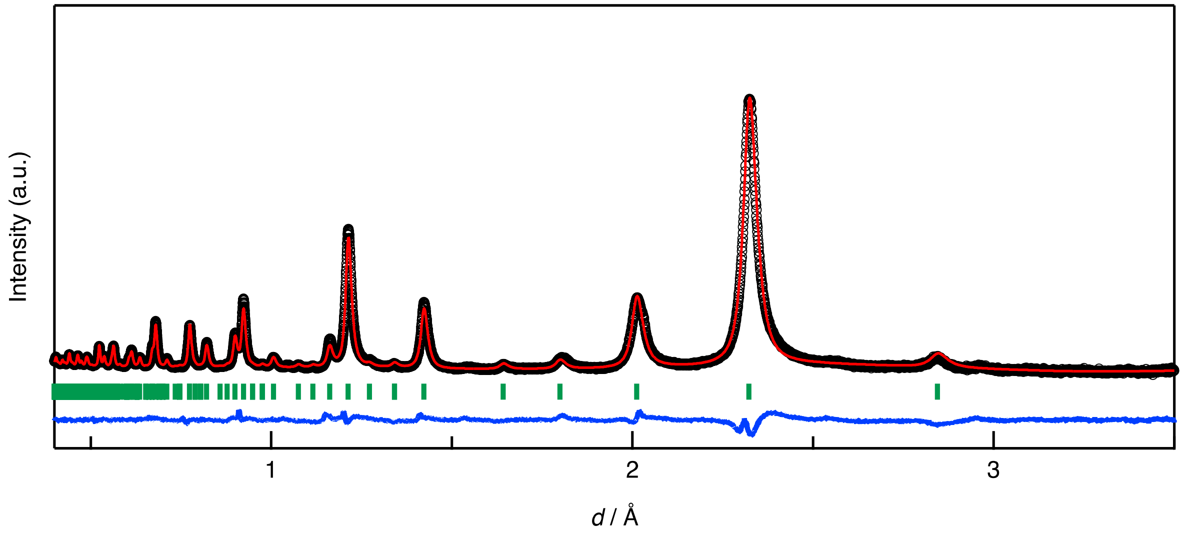

Figure S3 Rietveld refinements for ND data of x_{nom} = 0.25 product. Final observed, calculated, and residual differences are shown in black circles, red solid line, and blue solid line, respectively. Green vertical marks indicate the positions of Bragg reflections.

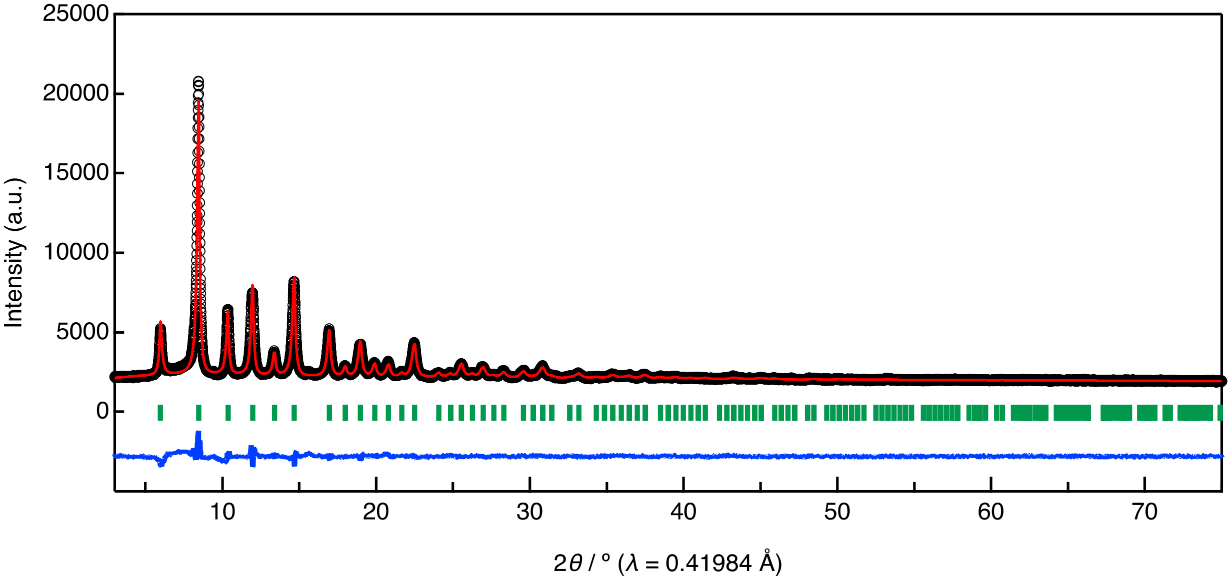

Figure S4. Rietveld refinement profile for SXRD data of x_{nom} = 0.25 product. The wavelength was 0.41984 Å. Final observed, calculated, and residual differences are shown in black circles, red solid line, and blue solid line, respectively. Green vertical marks indicate the positions of Bragg reflections.

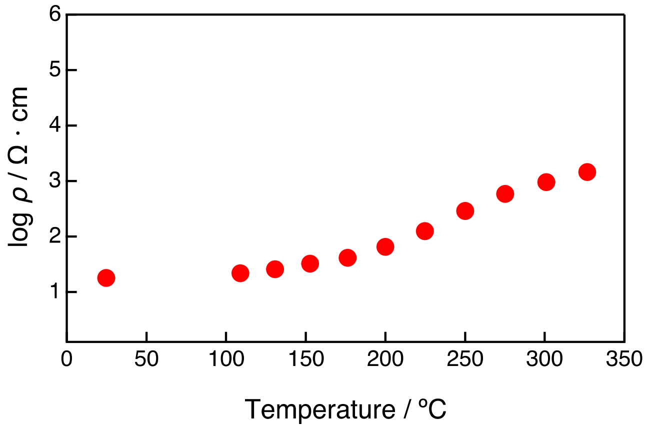

Figure S5. Electrical resistivity of $BaTiO_{2.5}H_{0.5}$ (x_{nom} = 0.5). The electrical resistivity measurement was performed with a hot-pressed $BaTiO_{2.5}H_{0.5}$ pellet by AC impedance and DC polarization method. The resistivity at room temperature was 17.9 Ω·cm, and a metallic behavior that the electrical resistivity increase with elevating temperature was observed.

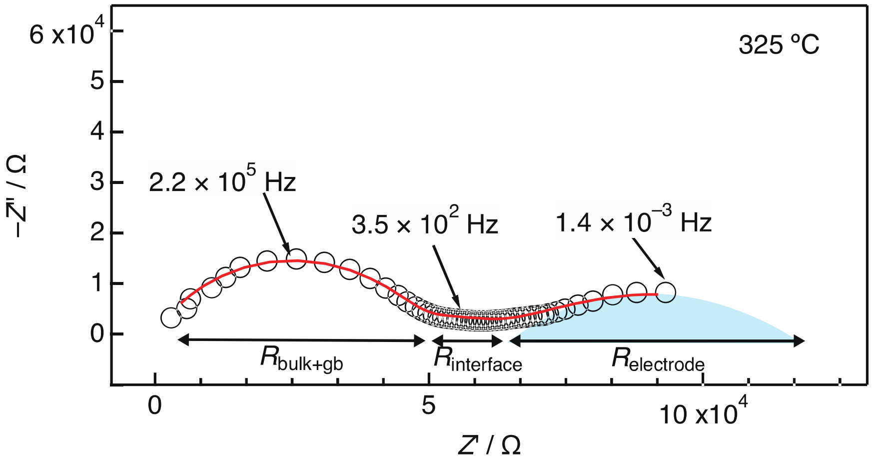

Figure S6. Impedance spectrum at 325 ºC for the symmetric cell composed with $BaTiO_{3-x}H_x$|$LaSrLiH_2O_2$|$BaTiO_{3-x}H_x$ in which the thickness of $LaSrLiH_2O_2$ is twice as that of Figure 4a. The open circle and solid red line are observed and calculated data, respectively. The sum of resistances for bulk and grain boundary ($R_{bulk + gb}$) increased nearly twofold depending on the thickness of the solid electrolyte, while the resistances of the interface ($R_{interface}$) and electrode ($R_{electrode}$) was almost the same as in Figure 4a.

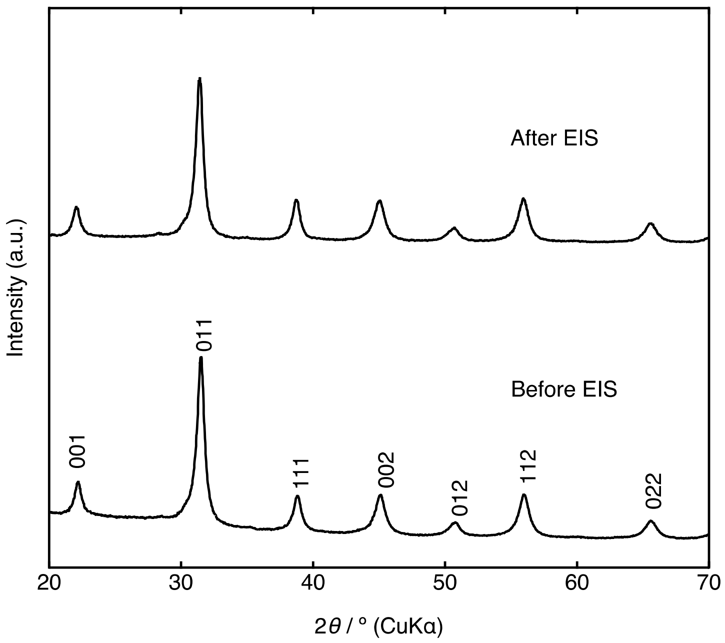

Figure S7. XRD patterns of the sample of x_{nom} = 0.5 before and after EIS at 325 ºC. The lattice constants before and after EIS are 4.0252 and 4.0233 Å, respectively. The color of the sample did not change from black as well. These results indicate the composition of the sample is maintained before and after hot pressing and EIS measurement.