Supporting Information

Hydride Conductivity in an Anion-ordered Fluorite Structure LnHO with an Enlarged Bottleneck

Hiroki Ubukata,^a Thibault Broux,^a Fumitaka Takeiri,^{b,c} Kazuki Shitara,^d Hiroki Yamashita,^a Akihide Kuwabara,^e Genki Kobayashi,^{b,c} and Hiroshi Kageyama*^a

- a. Graduate school of Engineering, Kyoto University, Kyoto 615-8510, Japan.
- Department of Materials Molecular Science, Institute for Molecular Science, Aichi 444-8585, Japan.
- c. SOKENDAI (The Graduate University for Advanced Studies), Aichi 444-8585, Japan
- d. Joining and Welding Research Institute, Osaka University, Osaka 567-0047, Japan.
- e. Nanostructures Research Laboratory, Japan Fine Ceramics Center, Nagoya 456-8587, Japan.

Corresponding Author

*E-mail: kage@scl.kyoto-u.ac.jp

Methods

Hebb-Wagner polarization method

Electrical conductivities were measured using the Hebb-Wagner polarization method¹ with an asymmetric (–)Pd/NdHO/Au(+) cell. The Pd reversible hydrogen electrode and the ion blocking Au electrode were deposited on the pellet by either thermal deposition. Measurements were carried out using a Bio-Logic VSP-300 frequency response analyzer in a flow of H₂ gas at 300 °C, with an applied potential between 0.2 and 2.0 V. Figure S7 shows the Hebb-Wagner polarization *i-V* curve at 300 °C. The total electrical conductivity (electrons σ_e + holes σ_h) at the irreversible Au/NdHO interface of the cell is given by the following equation:

$$\sigma_{\rm e} + \sigma_{\rm h} = (L/A)(d|I_{\rm e,h}|/dE)$$
 (eq. S1)

where *L* represents the electrolyte thickness, *A* the electrolyte-electrode surface area, $|I_{e,h}|$ the absolute value of the total electronic current, and *E* the polarization voltage. As shown in Fig. S7, the total electrical conductivity ($\sigma_e + \sigma_h$) at 300 °C calculated by the linear fitting of *i*-*V* curve between 0.6-1.6 V gave 2.15 × 10⁻⁷ S cm⁻¹. This electronic contribution is negligible given the total conductivity determined by the ac impedance method.

First-principles calculation

We considered point defects of vacancy and octahedral interstitial atoms of each element (La, O and H), and anti-site atoms of O and H in anion-ordered LaHO. The 2*b*, 2*c*, and 4*d* sites were considered for the interstitial sites. For the La vacancy, we considered 2*a*, 2*c*, and 4*e* sites. The formation energies of point defects, $E_f(D^q)$ are given by

$$E_f(D^q) = \{E(D^q) + E_{corr}(D^q)\} - E(perfect) - \sum_i n_i \mu_i + q\{(\varepsilon_{VBM} + \Delta \nu) + \Delta \varepsilon_F\} \quad (eq. S2)$$

where $E(D^q)$ and E(perfect) are the total energies of the supercell with a defect D in charge state of qand the perfect supercell without any defect, respectively. n_i is the number of removed ($n_i < 0$) or added ($n_i > 0$) i atoms to make the defects and μ_i is the chemical potential of atom i. ε_{VBM} is the energy level of the valence band maximum, $\Delta \varepsilon_{\text{f}}$ is the Fermi level referenced to ε_{VBM} . $E_{\text{corr}}(D_q)$ and Δv correspond to the image-charge correction and potential alignment correction, respectively. $E_{\text{corr}}(D_q)$ and Δv were calculated by extended FNV scheme.² μ_{H} was taken as the hydrogen-rich limit ($\mu_{\text{H}} = 1/2\mu_{\text{H2(molecule)}}$) and LaH₃ was considered as an equilibrium phase ($\mu_{\text{La}} = \mu_{\text{LaH3(bulk})} - 3\mu_{\text{H}}$) and $\mu_{\text{O}} = \mu_{\text{LaHO(bulk})} - \mu_{\text{La}} - \mu_{\text{H}}$).



Figure S1. Laboratory XRD patterns of LnHO-AP (Ln = Nd, Gd, and Er). The presence (absence) of the 101 reflection in NdHO (GdHO and ErHO) indicates anion order (anion disorder).



Figure S2. Laboratory XRD patterns of LnHO-HP (Ln = La, Nd, Gd, and Er). The presence (absence) of the 101 reflection for Ln = La and Nd (Ln = Gd and Er) indicates the anion order (anion disorder).

Table S1. Lattice parameters derived from Le Bail analysis using XRD data of LnHO (La, Nd, Gd, Er) prepared under high pressure (LnHO-HP) and ambient pressure (LnHO-AP) method. The reported data are also shown.^{3–5}

Material	Space group	<i>a</i> (Å)	<i>c</i> (Å)
LaHO-HP	P4/nmm	8.07783(7)	5.7343(1)
LaHO ³	P4/nmm	8.074(1)	5.739(1)
NdHO-HP	P4/nmm	7.8574(2)	5.5461(2)
NdHO-AP	P4/nmm	7.8501(2)	5.5476(3)
NdHO ⁴	P4/nmm	7.8480(5)	5.5601(8)
GdHO-HP	$Fm\overline{3}m$	5.3889(1)	-
GdHO-AP	$Fm\overline{3}m$	5.39397(3)	-
GdHO ⁵	$Fm\overline{3}m$	5.4035(1)	-
ErHO-HP	$Fm\overline{3}m$	5.2453(2)	-
ErHO-AP	$Fm\overline{3}m$	5.24467(4)	-
ErHO ⁵	$Fm\overline{3}m$	5.2473(1)	-



Figure S3. The photos of (a) ErHO-AP, (b) ErHO-HP, (c) NdHO-AP, and (d) NdHO-HP. The dark color for ErHO-AP indicates the presence of conduction electrons derived from hydrogen deficiency.

Tables S2. Crystallographic data for ErHO-HP from powder neutron diffraction at room temperature.

Atom	Site	x	У	Ζ	$B_{\rm iso}$ (Å ²)	g
Er	4 <i>a</i>	0	0	0	0.430(8)	1
Ο	8 <i>c</i>	1/4	1/4	1/4	0.53(3)	0.505(1)
Н	8 <i>c</i>	1/4	1/4	1/4	0.53(3)	0.494(3)

Space group: $Fm\overline{3}m$, a = 5.2490(1) Å, $\chi^2 = 10.8$, $R_p = 3.17\%$, $R_{wp} = 3.88\%$, $R_{exp} = 1.17\%$.

Atom	Site	x	У	Ζ	$B_{\rm iso}$ (Å ²)	g
Nd1	2a	3/4	1/4	0	0.71(1)	1
Nd2	2c	1/4	1/4	0.9479(3)	0.71(1)	1
Nd3	4 <i>e</i>	0	0	1/2	0.71(1)	1
0	8 <i>i</i>	1/4	0.5086(3)	0.7463(3)	1.02(2)	0.985(4)
Н	8 <i>i</i>	1/4	0.5263(5)	0.2556(7)	1.37(7)	0.706(9)
Space grou	up: P4/nmm,	a = 7.8513	59(3) Å, $c = 5.5554$	41(5) Å, $\chi^2 = 9.6$, <i>R</i>	$p_{\rm p} = 2.10\%, R_{\rm wp} =$	$= 2.67\%, R_{exp}$
Space grou	up: P4/nmm,	a = 7.8513	59(3) Å, $c = 5.5554$	41(5) Å, $\chi^2 = 9.6, R$	$P_{\rm p} = 2.10\%, R_{\rm wp} =$	= 2.67%, <i>R</i>

Table S3. Crystallographic data for NdHO-HP from powder neutron diffraction at room temperature.

= 0.87%.

Table S4. Crystallographic data for NdHO-HP with hydride ion at all the octahedral sites (2b, 2c, and 4d) from powder neutron diffraction at room temperature.

Atom	Site	x	У	Z	$B_{\rm iso}$ (Å ²)	g
Nd1	2 <i>a</i>	3/4	1/4	0	0.74(1)	1
Nd2	2c	1/4	1/4	0.9450(3)	0.74(1)	1
Nd3	4 <i>e</i>	0	0	1/2	0.74(1)	1
Ο	8 <i>i</i>	1/4	0.5091(2)	0.7471(3)	0.93(1)	1
H1	8 <i>i</i>	1/4	0.5319(4)	0.2544(7)	2.25(6)	0.897(3)
H2	2b	1/4	3/4	1/2	2.25(6)	0.103(3)
Н3	2c	1/4	1/4	0.691(7)	2.25(6)	0.103(3)
H4	4d	0	0	0	2.25(6)	0.103(3)

Space group: *P*4/*nmm*, *a* = 7.85165(3) Å, *c* = 5.55529(5) Å, χ^2 = 9.7, R_p = 2.11%, R_{wp} = 2.69%, R_{exp} = 0.87%.

Table S5. Considered crystallographic data for NdHO-HP with hydride ion at the octahedral (2c) site from powder neutron diffraction at room temperature.

Atom	Site	x	У	Z	$B_{\rm iso}({\rm \AA}^2)$	g
Nd1	2a	3/4	1/4	0	0.79(1)	1
Nd2	2c	1/4	1/4	0.9456(3)	0.79(1)	1
Nd3	4 <i>e</i>	0	0	1/2	0.79(1)	1
Ο	8 <i>i</i>	1/4	0.5107(2)	0.7478(3)	0.93(1)	1
H1	8 <i>i</i>	1/4	0.5354(4)	0.2516(6)	2.18(5)	0.884(3)
Н3	2 <i>c</i>	1/4	1/4	0.690(2)	2.18(5)	0.46(1)

Space group: *P*4/*nmm*, a = 7.85166(3) Å, c = 5.55530(5) Å, $\chi^2 = 9.7$, $R_p = 2.11\%$, $R_{wp} = 2.69\%$, $R_{exp} = 0.87\%$.



Figure S4. Fourier difference map for NdHO-HP calculated from the ideal anion-ordered model but without hydrogen. The yellow isosurfaces indicate negative nuclear scattering length densities.



Figure S5. The lattice parameters of NdHO-HP as a function of temperature in the range of (a) 27-827 °C and (b) 27-327 °C.



Figure S6. DSC curves of NdHO-HP.



Figure S7. Cole-Cole plot for (a) GdHO-AP and (b) ErHO-AP at 300 °C. (c) Arrhenius plots for the conductivity of NdHO-AP, GdHO-AP, and ErHO-AP.

Elements	LaHO-HP	NdHO-HP
$R_{\rm c}$ (n Ω)	0.2537	4.568×10 ⁻³
$Q_{\mathrm{bluk}} \left(\mathrm{nF} \cdot \mathrm{s}^{lpha_{\mathrm{bulk}}-1} ight)$	0.3421	0.7716
$lpha_{ m bulk}$	0.800	0.751
$R_{ m bulk}$ (k Ω)	59.88	67.38
$Q_{gb}\left(\mu\mathrm{F}\!\cdot\!\mathrm{s}^{lpha_{gb}-1} ight)$	76.09×10 ⁻³	0.1713
$lpha_{ m gb}$	0.512	0.461
$R_{ m gb}$ (k Ω)	185.5	190.2

Table S6. Fitting results from EIS experiments for LaHO-HP and NdHO-HP at 300 °C.

The subscripts 'c' and 'gb' stand for circuit and grain boundary, respectively. R is resistance and Q is constant phase element (CPE).



Figure S8. Hebb-Wagner polarization curve obtained from the (-) Pd / NdHO / Au (+) cell at 300 °C.



Figure S9. Formation energy of defects in stoichiometric LaHO. For example, H_octa2b indicates an H atom at interstitial octahedral 2b site and V_H means a vacancy defect at lattice H site (8*i*).



Figure S10. Enlarged view of low formation energy region in Figure S9.



Figure S11. (a) is the bottleneck proposed by Kilner.⁶ (b) The geometrical concept where A and l_{A-A} represent cation and the distance between A cations, respectively. r_{bn} and r_A indicate the bottleneck radius and cation radius.



Figure S12. Considerable hydride ion conduction pathways in anion ordered LnHO (*P4/nmm*). Blue circles and white circles indicate $T_{8i}^{\rm H}$ sites and *O* sites, respectively. White line, dark blue line and light blue line indicate $T_{8i}^{\rm H} - O_{2b}$, $T_{8i}^{\rm H} - O_{2c}$ and $T_{8i}^{\rm H} - O_{4d}$, respectively. Black dot lines represent unit cells.



Figure S13. Migration energies for interstitial hydride ions, via (a) indirect interstitial mechanism, (b) direct interstitial mechanism, and (c) vacancy mechanism. NN and 2NN in (c) indicate the middle position between nearest-neighboring 8i sites and between 2nd-nearest-neighboring 8i sites, respectively. For indirect interstitial mechanism, each migration state for $O_{2b} - O_{2c}$, $O_{2b} - O_{4d}$ or $O_{4d} - O_{4d}$ pathway was optimized to a structure with hydrogen in remaining interstitial sites.

Table S7. Formation and migration energies yielded by the first-principles calculations. The activation energies for hydride ion conduction based on three mechanisms (indirect interstitial, direct interstitial, and vacancy) were calculated as the sum of the formation energy and the migration energy. For the direct and indirect interstitial mechanisms, the formation energy of interstitial hydride at 4*d* site was employed. For the vacancy mechanism, the formation energy of hydride vacancy was used.

Mechanism	Formation energy (eV)	Migration energy (eV)	Activation energy (eV)
Indirect interstitial	0.3	0.7	1.0
Direct interstitial	0.3	1.3	1.6
Vacancy	0.5	1.8	2.3



Figure S14. Crystal structures of γ -LaHO (PbCl₂-type, Space group *Pnma*) and δ -LaHO (Fe₂P-type, Space group $P\overline{6}2m$).



Figure S15. Proposed hydride ion diffusion pathways (light blue or dark blue lines) in (a) γ -LaHO and (b) δ -LaHO.

References

- Neudecker, B. J.; Weppner, W. Li₉SiAlO₈ : A Lithium Ion Electrolyte for Voltages above 5.4 V. J. Electrochem. Soc. 1996, 143, 2198–2203.
- Kumagai, Y.; Oba, F. Electrostatics-Based Finite-Size Corrections for First-Principles Point Defect Calculations. *Phys. Rev. B - Condens. Matter Mater. Phys.* 2014, 89, 19.
- 3. Malaman, B.; Brice, J. F. Etude Structurale de l'hydruro-Oxyde LaHO Par Diffraction Des Rayons X et Par Diffraction Des Neutrons. *J. Solid State Chem.* **1984**, *53*, 44–54.
- Widerøe, M.; Fjellvåg, H.; Norby, T.; Willy Poulsen, F.; Willestofte Berg, R. NdHO, a Novel Oxyhydride. J. Solid State Chem. 2011, 184, 1890–1894.
- Yamashita, H.; Broux, T.; Kobayashi, Y.; Takeiri, F.; Ubukata, H.; Zhu, T.; Hayward, M. A.; Fujii, K.; Yashima, M.; Shitara, K.; Kuwabara, A.; Murakami, T.; Kageyama, H. Chemical Pressure-Induced Anion Order–Disorder Transition in LnHO Enabled by Hydride Size Flexibility. *J. Am. Chem. Soc.* 2018, *140*, 11170–11173.
- Kilner, J. A.; Brook, R. J. A Study of Oxygen Ion Conductivity in Doped Non-Stoichiometric Oxides. *Solid State Ion.* 1982, 6, 237–252.