Anion ordering enables fast $\text{H}^-$ conduction at low temperatures

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The introduction of chemical disorder by substitutional chemistry into ionic conductors is the most commonly used strategy to stabilize high-symmetry phases while maintaining ionic conductivity at lower temperatures. In recent years, hydride materials have received much attention owing to their potential for new energy applications, but there remains room for development in ionic conductivity below 300°C. Here, we show that layered anion-ordered $\text{Ba}_2\text{H}_3$-$\text{X}$ ($X = \text{Cl}$, $\text{Br}$, and $\text{I}$) exhibit a remarkable conductivity, reaching 1 mS cm$^{-1}$ at 200°C, with low activation barriers allowing $\text{H}^-$ conduction even at room temperature. In contrast to structurally related $\text{BaH}_2$ (i.e., $\text{Ba}_2\text{H}_4$), the layered anion order in $\text{Ba}_2\text{H}_3$-$\text{X}$, along with Schottky defects, likely suppresses a structural transition, rather than the traditional chemical disorder, while retaining a highly symmetric hexagonal lattice. This discovery could open a new direction in electrochemical use of hydrogen in synthetic processes and energy devices.

INTRODUCTION

Solid-state materials with fast ionic conductivity find diverse applications such as batteries, sensors, and fuel cells. Reducing operating temperatures is an important issue, but some materials drastically lose their ionic conductivity by undergoing a structural phase transition to lower-symmetry structure upon cooling (1, 2). The best-known example is cubic $\text{ZrO}_2$ suppresses the transition to a tetragonal phase upon cooling. For example, in yttria-stabilized zirconia (YSZ), a $\text{Y}^{3+}$-$\text{for-} \text{Zr}^{4+}$ substitution for the cubic $\text{ZrO}_2$ suppresses the transition to a tetragonal or monoclinic form and induces oxide ion conductivity (1). Likewise, the hexagonal HT phase of $\text{Li}$(CB$_9$H$_{10}$) can be stabilized by forming a solid solution with Li(CB$_9$H$_{12}$), which enables a fast lithium ion conductivity at room temperature (3). Other host materials that have successfully stabilized HT forms via chemical disorder include AgI (1), $\text{O}^{2-}$ conductors [e.g., $\text{Ba}_3\text{In}_2\text{O}_5$ (1, 2) and $\text{La}_2\text{Mo}_2\text{O}_6$ (4)], $\text{Li}^+$ conductors [e.g., $\text{Li}_2\text{La}_2\text{Zr}_2\text{O}_7$ (5) and $\text{LiBH}_4$ (6)], and $\text{Na}^+$ conductors [e.g., $\text{Na}_2\text{B}_2\text{H}_3\text{H}_2$ (7) and $\text{Na}_2\text{Zn}(\text{PO}_4)_2$ (8)].

Hydride materials have raised recent interest due to the unique characteristics of $\text{H}^+$ ions such as high lability, high polarizability, and high compressibility, which have opened up new synthesis routes (9, 10) and lead to novel properties including catalysis (11, 12). In view of the light mass of $\text{H}^+$, its monovalence, and the redox potential of $\text{H}_2/\text{H}^+$ ($\approx 2.23$ V versus standard hydrogen electrode), hydride ion conductivity appears promising as next-generation electrochemical energy storage systems with high voltage and high energy density (13, 14). In 2015, $\text{BaH}_2$ with a hexagonal close packing (hcp) of Ba cations (Fig. 1A) was shown to achieve a $\text{H}^-$ conductivity of 0.04 to 0.2 S cm$^{-1}$ at 450°C to 630°C, an order of magnitude higher than that of typical oxide ion conductors and proton conductors (e.g., YSZ and Nd-doped BaCeO$_3$) (15). However, its conductivity drops rapidly at 450°C when it undergoes a transition to an orthorhombic phase with a distorted hcp (Ba) lattice (Fig. S1). Subsequent studies of $\text{H}^-$ conduction have shifted to oxyhydrides including $\text{Li}_2\text{Zr}_2\text{O}_7$ (6), $\text{Ba}_3\text{H}_2\text{O}_3$ (16, 17), and $\text{LaH}_3\text{O}_4$ (18, 19). Although the inclusion of oxide ions may improve thermal stability, high $\text{H}^-$ conductivity over $10^{-3}$ S cm$^{-1}$ is only reached above 300°C.

Hydride-based antiperovskites with a soft anion sublattice have recently shown promise as alkali ion conductors (20). The use of soft anions compared to oxide ions would also be beneficial for hydride conductivity. Thus, we aimed to investigate $\text{Ba}_2\text{H}_3\text{X}$ hydride-halides ($X = \text{Cl}, \text{Br}, \text{I}$) with the anti-$\text{Li}_3\text{LaSb}_2$ structure (space group: $P\bar{3}m1$) (21, 22), which consists of alternating stacking of face-sharing $\text{H}^+$ and $\text{X}^-$ octahedral layers along the hexagonal $c$ axis, with additional hydride anions in a distorted tetrahedral [$\text{H}^+$] environment (Fig. 1B). It can be also considered anion-ordered HT-$\text{BaH}_2$ in which half of $\text{H}^+$ is replaced by $\text{X}^-$ (see Fig. 1). We found that the “stabilization” of the HT-$\text{BaH}_2$ structure at low temperature by anion ordering makes $\text{Ba}_2\text{H}_3\text{X}$ excellent $\text{H}^-$ conductors together with low activation energies (ca. 35 to 50 kJ mol$^{-1}$). The highest conductivity was achieved for $X = \text{I}$ with $1.4 \times 10^{-3}$ S cm$^{-1}$ at 200°C. This result could open new avenues for hydride-based energy devices and material conversion systems that operate at low temperatures.

RESULTS

Crystal structure and nonstoichiometry

Polycrystalline $\text{Ba}_2\text{H}_3\text{X}$ ($X = \text{Cl}, \text{Br}, \text{I}$) samples were prepared by reacting stoichiometric quantities of $\text{BaH}_2$ and $\text{BaX}_2$ at 650°C for 20 hours in an $\text{Al}_2\text{O}_3$ tube loaded into an evacuated silica tube. All the powder specimens obtained are white, and their bandgaps were estimated from the diffuse reflectance spectrum to be around 3.1 eV,
which are in agreement with those from first-principles calculations (Fig. 2A and fig. S2). The synchrotron x-ray diffraction (SXRD) pattern for $X = I$ (Fig. 2B) could be indexed by a hexagonal lattice of $a = 4.51276(4)$ Å and $c = 8.0832(10)$ Å. These values are in reasonable agreement with those of the single crystal $\text{Ba}_2\text{H}_3\text{I}$ [$a = 4.5186(12)$ Å and $c = 8.118(2)$ Å] (21), although they are slightly different. The lattice constants for $X = \text{Cl}$ and Br are also compatible with the reported values (table S1) (22). Note that each SXRD profile contains a minor impurity $\text{BaH}_X$ ($< 5\%$).

In the previous studies (21, 22), the structure of $\text{Ba}_2\text{H}_3\text{X}$ was determined by single-crystal x-ray diffraction, and the hydrogen positions (1a and 2d) were only deduced from the analysis of the Madelung potentials and the bond valence sum. We therefore measured neutron powder diffraction (NPD) using the deuterated sample $\text{Ba}_2\text{D}_3\text{I}$ and performed the Rietveld refinement. This readily converged with reasonable reliability factors ($R_p = 4.51\%$ and $R_{wp} = 6.61\%$), but with large residual peaks (e.g., 101 at $d \sim 3.5$ Å), as shown in fig. S3. No improvement in the fit assuming different
crystallographic sites for each atom suggests a nonstoichiometric composition, such as hydride vacancies that generate F-centers. However, given the sample color (white) and the bandgap of 3.1 eV (Fig. 2A), it is unlikely that electrons trapped in impurity levels are present. Furthermore, the absence of sizable defect-induced electrons is supported by the very small and nearly temperature-independent magnetic susceptibility (fig. S4). These results strongly suggest that under our synthetic condition, charge-neutral Schottky defects of Ba$^{2+}$ and 2H~ are generated, thus resulting in the composition of Ba$_2$–H$_3$–2δX.

The inclusion of the Schottky defects in the refinement substantially improved the agreement ($R_p$ = 3.29% and $R_{wp}$ = 4.41%; Fig. 2, C and D, and table S2) and gave Ba$_{1.764(3)}$D$_{2.529(3)}$I ($\delta$ = 0.236). The occupancy factor of the tetrahedral (H2) site is higher than that of the octahedral (H1) site. Furthermore, the Ba/I ratio of 1.73 estimated by ion chromatography (IC) agrees well with the value from NPD. The refinements for X = Cl and Br with the Schottky defects resulted in Ba$_{1.724(3)}$D$_{2.447(2)}$Cl ($\delta$ = 0.276) and Ba$_{1.812(4)}$D$_{2.618(3)}$Br ($\delta$ = 0.188), with the same tendency in the hydride occupancy (figs. S5 and S6 and tables S3 and S4). IC measurements also showed consistent Ba/X ratios of 1.60 (Cl) and 1.64 (Br). The formation of the Schottky defects of Ba$^{2+}$ and 2H~ probably causes the discrepancy in the lattice parameters between the single crystals (21, 22) and our powder samples. We found a linear relationship between the Ba/I ratio and the lattice volume in Ba$_2$–H$_3$–2δX (fig. S7). However, such lattice variation (or the amount of Schottky defects) does not substantially affect the ionic conductivity, at least within the range examined. It should be noted that the hydride vacancies in BaH$_2$–δ (δ ~ 0.2) determined from NPD are similar to our compound, although the resulting electrons were assumed to be localized as F-centers (13).

To obtain further insight into the Schottky defects, we estimated the formation energies of point defects under hydrogen-rich conditions using first-principles calculations, but the results did not fully explain the experimental observations (fig. S8). For example, in Ba$_2$H$_3$I, the formation energies of V$_{Hi}$ and V$_{Ba}$, which are found as major defects, are only 0.2 eV lower than that of H$_i$. This implies the presence of H$_i$ to some extent, but hydrogen was not detected at the H$_i$ site within the experimental accuracy by neutron diffraction. In addition, although the binding energy of a V$_{Hi}$ and V$_{Ba}$ pair is reasonably high (e.g., 0.37 eV for $X = I$), the formation energy of the associated defect of a pair of V$_{Hi}$ and V$_{Ba}$ is also high (e.g., 0.69 eV for $X = I$). Considering the high concentration of Schottky defects observed in Ba$_2$–H$_3$–2δX, interactions among Schottky defects (clustered Schottky defects) may be taken into account, as reported in TiO$_2$ (23) and UO$_2$ (24). We also point out that some low-energy phonon vibrations of hydride anions are involved in the defect formation, as seen in hydrogen storage alloys (25) and Li$_3$HCh and Na$_3$HCh (Ch = S, Se, and Te) (20).

**Hydride conductivity**

The ionic conductivities of Ba$_2$–H$_3$–2δX (δ ~ 0.2) were measured by electrochemical impedance spectroscopy (EIS) for 20° to 400°C using as-synthesized pellets. Note that there is no noticeable change in the XRD profiles before and after the EIS experiments (figs. S9 and S10 and table S5). Figure 3A displays the representative Cole-Cole plots at 200°C with a semicircle in the high-frequency region and a sharp rise in the low-frequency region, corresponding to the contribution from the bulk/grain boundary and the electrode, respectively (details in fig. S11 and table S6). The temperature evolution of total conductivity ($\sigma_{total}$) for Ba$_2$–H$_3$–2δX, calculated from the sum of the bulk and grain boundary resistances, is shown in Fig. 3B. The Hebb-Wagner polarization (26) for $X = I$ was measured to identify the charge carriers. We obtained a sufficiently small electronic conductivity $\sigma_{eh} = 7.98 \times 10^{-6}$ S cm$^{-1}$ at 200°C (fig. S12), indicating that the main contribution to the observed conductivity is ionic, with a transport number of $t_{ion} = (\sigma_{total} - \sigma_{eh})/\sigma_{total}$ ~ 0.99. The high total conductivity observed in the relatively low-temperature region is hardly conceivable for the divalent Ba$^{2+}$ conduction. Negligible halide ion conduction is supported theoretically by the much higher formation energy of V$_X$ (1.3 eV) compared to that of V$_{Hi}$ (fig. S8) and experimentally by the higher conductivity for the larger $X^-$, along with a lower concentration ($X/H \sim 1/3$). Overall, these factors indicate that the H~ ion is the only carrier.

In Fig. 3C, we compare the thermal evolution of total conductivities of Ba$_2$–H$_3$–2δX (δ ~ 0.2) with those of the reported H~ conductors (13–19, 27). The conductivities in the range of 10$^{-3}$ to 10$^{-2}$ S cm$^{-1}$ above 300°C are comparable to those of known representative materials such as BaH$_2$ (~5 × 10$^{-2}$ S cm$^{-1}$ at 420°C) (13) and LaH$_{2.52}$O$_{0.24}$ (2.6 × 10$^{-2}$ S cm$^{-1}$ at 342°C) (18). Ba$_2$–H$_3$–2δX exhibit excellent total conductivities below 300°C. Even at 200°C, the total conductivity is...
as high as $10^{-4}$ to $10^{-3}$ S cm$^{-1}$. It is also worth noting that the H$^-$ conductivity can be measured down to room temperature in all samples, where a distinct semicircle is consistently observed at high frequencies (fig. S11 and table S6). Clearly, such fast conduction over a lower-temperature range is enabled by the low activation energy (35 to 50 kJ mol$^{-1}$), in contrast to LaH$_2$O$_{0.24}$ with an activation energy of 125 kJ mol$^{-1}$ (18).

**DISCUSSION**

The key to understanding the superior H$^-$ conductivity of Ba$_{2-\delta}$H$_{3-2\delta}X$ becomes clearer by comparing it with the structurally related BaH$_2$. As mentioned above, the rapid decrease in the conductivity of BaH$_2$ at 450°C results from the structural transition from the hexagonal structure (Fig. 1A) to the distorted orthorhombic one (fig. S1) (13). Extrapolation of the conductivity of the HT phase of BaH$_2$ to low temperatures (broken line in Fig. 3B) is roughly in agreement with that of Ba$_{2-\delta}$H$_{3-2\delta}X$. This observation strongly suggests that the superior conductivity in Ba$_{2-\delta}$H$_{3-2\delta}X$ is achieved by “stabilizing” the HT-BaH$_2$ structure through ordered anion substitution with halide anions (Fig. 1), in stark contrast to the introduction of chemical disorder applied to conventional ionic conductors including YSZ (1, 2). One might be surprised to see the correspondence in conductivity between Ba$_{2-\delta}$H$_{3-2\delta}X$ and the ”hypothetical” HT-BaH$_2$ (broken line in Fig. 3B), because the latter has a three-dimensional (3D) H$^-$ network and contains ca. 33% more H$^-$ ions. However, this result is coherent with the preferential 2D conduction that is proposed in HT-BaH$_2$ based on the large anisotropic thermal vibrations of H1 (13).

From the crystal structure of Ba$_{2-\delta}$H$_{3-2\delta}X$, it is evident that the H$^-$ migration occurs within the Ba$_{2-\delta}$H$_{3-2\delta}$ slab. This was also verified by the climbing image nudged elastic band (CI-NEB) calculations for Ba$_3$H$_2$X. Among the possible H$^-$ vacancy hopping routes, the lowest migration energy of 0.22 eV ($X = \text{Cl}$), 0.20 eV ($X = \text{Br}$), and 0.17 eV ($X = \text{I}$) is found for the nearest-neighbor H1–H2 path (Fig. 4, fig. S13, and table S7). Given the relatively lower values compared to the experimental activation energy (0.37 to 0.5 eV), the binding energy of a V$_{\text{H1}}$ and V$_{\text{H2a}}$ pair must be considered. The sum of the migration energy and the binding energy is 0.63 eV ($X = \text{Cl}$), 0.64 eV ($X = \text{Br}$), and 0.54 eV ($X = \text{I}$), which is higher but comparable to the experimental activation energy. This overestimation is probably due to the effects of phonon vibrations and interactions among multiple point defects as described above. For a more quantitative analysis, these effects need to be taken into account in the calculations. The higher ionic conductivity in the order of $X = \text{Cl} < \text{Br} < \text{I}$ (e.g., 0.23, 0.63, and 1.4 mS cm$^{-1}$ at 200°C) is not simply explained in terms of the size effect, because both H1–H2 distance and bottleneck size for H$^-$ diffusion hardly depend on X species (fig. S14). Important here could be the softness of anions (Cl$^-$ < Br$^-$ < I$^-$) (28), as underlined in Li$^+$ conductors such as LGPS (Li$_{10}$GeP$_2$S$_{21}$) and argyrodite (Li$_x$PS$_{32}$X; $X = \text{Cl}$, Br, and I) (29–31).

Chemical disorder induced by substitution with dopants randomly distributed in the immobile ion sublattice is, apart from morphological control (32–34), a general strategy to stabilize HT phases at lower temperatures and achieve fast ionic conductivity (1–8). Such chemical substitution inevitably introduces different parameters at the same time, including changes in local bonding nature and coordination environment (35–38), that might complicate a thorough understanding of the mechanism of ionic conductivity. In marked contrast, the present study demonstrates the case where an ordered arrangement of anions can maintain the lattice free from or minimized chemical disorder, giving an ideal opportunity to study the intrinsic nature of H$^-$ conductivity. Because many mixed-anion compounds adopt layered anion-ordered structures based on the concept of HSAB (hard and soft acids and bases) and the Hume-Rothery rule (39), ordered mixed anionization will lead to a new development in a variety of ion conducting materials, not only in the hydride system.

**Perspectives**

The observation of H$^-$ conduction at low temperatures may give rise to various functions such as catalysis, not limited to ionic conductivity. For example, several oxohydrides such as BaTi(O,H)$_3$ BaCe(O,N,H)$_{3-6}$ have recently been shown as catalytically active in NH$_3$ synthesis and CO$_2$ methanation at about 300°C, indicating that the lability of the H$^-$ ions, combined with the strong basicity, is involved in these catalytic activities (II, 40, 41). An isotope experiment is a facile method to examine the exchangeability of H$^-$ ions in a solid with hydrogen species in the outer atmosphere (9, 42). To see this, the Ba$_{2-\delta}$H$_{3-2\delta}X$ powder was heated in a D$_2$ gas stream, and the downstream gas was analyzed by quadrupole mass spectroscopy (see Materials and Methods). Figure 5 shows that H/D exchange started already at 100°C, much lower than for typical oxohydride compounds [e.g., 350°C for BaTi(O,H)$_3$ (9, 42)]. Such a low temperature H/D exchange makes Ba$_{2-\delta}$H$_{3-2\delta}X$ a promising candidate material that could allow various inorganic hydrogenations under milder conditions, with much room for material optimization, e.g.,
After Ba chunks were loaded into a SUS (steel use stainless) container (Aldrich, > 99%) with deuterium gas (Taiyo Nippon Sanso, 99.8%). A total of five cycles of heating at 550°C for 30 min in 0.2 MPa of D\textsubscript{2} gas, with two intermediate grindings, were performed to investigate the band structures and the migration of V\textsubscript{H} and V\textsubscript{Ba}. The evolved gas species (X = Cl, Br, and I) samples (typically ~30 mg) were placed in an Al crucible. The evolved gas species (m/z = 2 and 3 for H\textsubscript{2} and HD) were recorded as a function of time using the Bruker MS9610 mass spectrometer.

**MATERIALS AND METHODS**

**Synthesis of Ba\textsubscript{2}H\textsubscript{3}X (X = Cl, Br, and I)**

We prepared the powder samples of Ba\textsubscript{2}H\textsubscript{3}X (X = Cl, Br, and I) using a conventional solid-state reaction. Powders of BaH\textsubscript{2} (Mitsuwa Chemical, 99.5%) and BaX\textsubscript{2} (X = Cl, Ba, and I) (Wako, 99.99%) were thoroughly ground and mixed, and then the mixture was pressed into a pellet (4 to 10 mm in diameter and 1 to 2 mm in thickness). The pellets were loaded into an alumina tube. The tube was then placed in a sealed and evacuated silica tube, followed by heating at 650°C for 20 hours. For neutron diffraction experiments, we prepared deuterated samples of Ba\textsubscript{2}D\textsubscript{3}X in the same method but using BaD\textsubscript{2}. BaD\textsubscript{2} was synthesized by reacting barium metal (Sigma-Aldrich, > 99%) with deuterium gas (Taiyo Nippon Sanso, 99.8%). After Ba chunks were loaded into a SUS (steel use stainless) container, the container was evacuated and filled with deuterium gas, which was repeated five times to remove the residual N\textsubscript{2}. The sample was heated at 550°C for 30 min in 0.2 MPa of D\textsubscript{2} gas, with two intermediate grindings. Owing to the air- and moisture-sensitive nature of the reactants and products, all handling was carried out in a nitrogen-filled glovebox. The quality of the sample was determined using a Rigaku SmartLab powder XRD apparatus.

**Sample characterizations**

High-resolution SXRD experiments were performed at room temperature using a large Debye-Scherrer camera installed at SPring-8 BL02B2 with λ = 0.420344(1) Å. Powder samples were loaded into the container, which was evacuated and filled with deuterium gas, with two intermediate grindings. Owing to the air- and moisture-sensitive nature of the reactants and products, all handling was carried out in a nitrogen-filled glovebox. The quality of the sample was determined using a Rigaku SmartLab powder XRD apparatus.

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**Electrochemical characterizations**

Electrochemical measurements were carried out on sintered pellets of Ba\textsubscript{2}H\textsubscript{3}X (X = Cl, Br, and I) specimens with the relative density of around 80% (4 to 10 mm in diameter and 1 to 2 mm in thickness) using a Bio-Logic MTZ-35 frequency response analyzer. Ionic conductivity was measured by AC impedance methods with an applied frequency of 0.1 Hz to 35 MHz using gold electrodes for both sides in a flow of H\textsubscript{2} gas for 27°C to 400°C. The temperature in the measurement was controlled by a TOYO Corporation HT-Z3-800 furnace control system. The obtained impedance spectra were analyzed using the EC-Lab software. The equivalent circuits used in the analysis were described in the Supplementary Materials. Electrical conductivities were estimated by the Hebb-Wagner polarization method (26) using an asymmetric (−)Pd/Ba\textsubscript{2}H\textsubscript{3}I/Au(+) cell, where Pd electrode was used as a reversible electrode for H\textsubscript{2}. The measurement was carried out using a Bio-Logic VSP-300 multichannel potentiostat in a flow of H\textsubscript{2} gas at 200°C, with an applied potential between 0.3 and 1.9 V.

**H/D exchange experiment**

H/D exchange experiments were performed at heating rate of 5°C min\textsuperscript{-1} over the temperature range of 20°C to 350°C under flowing 5% D\textsubscript{2}/Ar. The Ba\textsubscript{2}H\textsubscript{3}X (X = Cl, Br, and I) samples (typically ~30 mg) were placed in an Al crucible. The evolved gas species (m/z = 2 and 3 for H\textsubscript{2} and HD) were recorded as a function of time using the Bruker MS9610 mass spectrometer.

**First-principles calculations**

First-principles calculations based on the density functional theory were performed to investigate the band structures and the migration energies using the projector augmented-wave method implemented in the Vienna Ab initio Simulation Package (VASP) code (45–48). The band structures were calculated using the unit cell of Ba\textsubscript{2}H\textsubscript{3}X (X = Cl, Br, and I) shown in Fig. 1B. The supercell containing 3 × 3 × 2 unit cells was constructed to calculate point defect formation energies (49, 50) of Ba vacancy (V\textsubscript{Ba}), H vacancy (V\textsubscript{H}), X vacancy (V\textsubscript{X}), interstitial H (H\textsubscript{i}), and interstitial X (X\textsubscript{i}). The binding energy (51) of a pair of V\textsubscript{H} and V\textsubscript{Ba} was also estimated in Ba\textsubscript{2}H\textsubscript{3}X. All the symmetrically independent structures including one V\textsubscript{H} and one V\textsubscript{Ba} were calculated. On the basis of the results of the experimental crystal structure
analysis and the calculation of defect formation energies, the migration energies were calculated for the diffusion paths of H₁–H₁, H₁–H₂, and H₂–H₂ sites of H⁺ ion vacancy with the charge state +1, V⁺. In the calculation models, the vacancy concentration of 1.85% (1/5), corresponding to δ ~ 0.04 in Ba₂−δH₃−2δX, was used. This concentration is lower than the experimentally obtained value of δ ~ 0.2, but it is known that the migration energy obtained from a model with low defect concentration usually agrees well with the experimental results for samples with high degree of defects (52, 53). The exchange-correlation term was treated with the Heyd-Scuseria-Ernzerhof hybrid functional (HSE06) (54) for the calculation of the band structure and Generalized Gradient Approximation and Perdew-Burke-Ernzerhof functional (GGA-PBE) (55) for the point defect formation and migration energies. The plane-wave cutoff energy was set to 520 eV. The integration in the reciprocal space was performed using 6 × 6 × 3 and 2 × 2 × 2 Γ-centered grids for the unit cell and the supercell, respectively. Structure optimization was carried out until that all residual forces acting on each atom become less than 0.002 eV/Å. The migration energies of H⁺ ion via vacancy mechanisms were calculated using the CI-NEB method with three intermediate images (56, 57).

SUPPLEMENTARY MATERIALS
Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/7/23/eabf7883/DC1

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