Determination of Oxide Ion Conductivity in Ba-doped LaYbO₃ Proton Conducting Perovskite via Oxygen Isotope Exchange Method

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Table S1. Structural parameters for $La_{0.95}Ba_{0.05}YbO_3$ at room temperature obtained by Rietveld refinement. The lattice constants and the atomic positions were set as the variables. The occupancy, *g*, was fixed at the nominal values for cations, and 1 for oxide ions. The isotropic atomic displacement factors, B_{iso} , are also fixed at 0.5 for cations and 1 for anions, respectively.

Atom	site	g	X	у	Z.	$B_{\rm iso}$ / Å ²
La	4 <i>a</i>	0.95	0.05019(19)	0.4863(4)	0.4975(8)	0.5
Ba	4 <i>a</i>	0.05	=x(La)	=y(La)	=z(La)	$=B_{iso}(La)$
Yb	4 <i>a</i>	1	0.0038(13)	-0.0051(9)	0.7509(7)	0.5
01	4 <i>a</i>	1	0.307(5)	0.194(5)	0.705(3)	1
O2	4 <i>a</i>	1	0.329(5)	0.182(5)	0.328(4)	1
O3	4 <i>a</i>	1	0.047(19)	0.1262(19)	1.009(6)	1

Space group: $Pna2_1$, a = 6.3029(12) Å, b = 5.83622(10) Å, and c = 8.4142(16) Å, $R_{wp} = 8.46\%$, $R_p = 4.05\%$, $S (= R_{wp}/R_p)$: 2.09.



Figure S1. Powder X-ray diffraction pattern of La_{0.9}Ba_{0.1}YbO₃. The inset expands the 2θ region from 41 to 44 degrees. The black and blue marks represent the Bragg positions for LaYbO₃ phase and monoclinic Ba₄Yb₂O₇ phase, respectively. The error factors, R_{wp} and $S (= R_{wp}/R_p)$, were 4.74 % and 1.79, respectively. The secondary phase of Ba₄Yb₂O₇ was sometimes formed when the doping level attains around 10 mol%. The formation of Ba₄Yb₂O₇ phase strongly depends on the sample lot, indicating the low reproducibility. This suggests that the doping level of 10 mol% is quite close to the solubility limit. Similar results are pointed out previously.¹ To avoid the effect of secondary phase formation, we selected the doping level of 5 mol% in this study.



Figure S2 Proton concentration calculated by the assumption with and without inactive oxygen vacancies. The solid and dashed blue lines show the calculated results with $[V_{O(2)}^{\bullet}] = 0.02$ and 0, respectively. The circles show the experimental results. The dotted black line shows the theoretical maximum. The used ΔH_{hyd} and ΔS_{hyd} for $[V_{O(2)}^{\bullet}] = 0$ were -64 kJmol⁻¹ and -75 Jmol⁻¹K⁻¹, respectively, which are obtained from the fitting to the results in temperature region from 892 to 1200 °C.

Combining the results of oxygen diffusion kinetics in the main text, we can see the lower saturation limit than the theoretical maximum is not due to the slow kinetics of hydration reaction. If $[V_{O(2)}^{"}] = 0$, the expected proton concentration from the hydration thermodynamics is 0.018 at 700 °C. This proton concentration corresponds to the weight change of 0.45 mg, a sufficient amount to detect by TGA (Figure 2a). Using the oxygen diffusivity, we can predict how far the incorporated oxide ions by hydration diffuse into the particles from the correlation of $L_{\rm D} = 2\sqrt{D^*t}$. Here, $L_{\rm D}$, D^* , and t is the diffusion length, the tracer diffusivity, and the duration time, respectively. At 700 °C, the tracer diffusivity is 7.5×10^{-11} cm²s⁻¹ (Figure 5a). After the duration time of 30 min in TGA apparatus, the oxide ion diffuses ~7 µm in the particles. Considering the sizes of hand-crushed powders with a mortar, typically ranged in 1-5 µm, this retention time in TGA is long enough for the incorporated oxide ions to reach the particle core, suggesting that our experimental condition was sufficient for attaining the equilibrium. Thus, we conclude that there are inactive oxygen vacancies for hydration in Ba-doped LaYbO₃.



Figure S3. Impedance spectra for $La_{0.95}Ba_{0.05}YbO_3$ measured at a) 300, b) 500, and c) 900 °C. *R* and *X* in the axes denote the real and imaginary part of the impedance, respectively. The red circles and blue lines show the experimental and fitted results, respectively. The number beside each closed symbol corresponds to the exponent, *n*, of the base ten, 10^n , in frequency. The spectra are recorded under the 1% H₂ with the water partial pressure of 0.019 atm.

REFERENCES

1. Sakai, T.; Isa, K.; Matsuka, M.; Kozai, T.; Okuyama, Y.; Ishihara, T.; Matsumoto, H., Electrochemical hydrogen pumps using Ba doped LaYbO₃ type proton conducting electrolyte. *Int. J. Hydrogen Energy* **2013**, *38* (16), 6842-6847.