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Electronic Supplementary Information

La₂(Nb_{1-x}Y_x)₂O_{7-δ}: Discovery of a Novel Fluorite Structure Based Ionic Conductor

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Experimental

Material preparation

In this work, samples with different nominal composition of $La_2(Nb_{1-x}M_x)_2O_{7-\delta}$ (M = Sc, Y, In, Nd, Sm, Gd, Yb), as listed in **Table S1**, were prepared by a conventional solid state reaction method. Starting materials of La_2O_3 , Nb_2O_5 and M_2O_3 (M = Sc, Y, In, Nd, Sm, Gd, Yb) were mixed at the desired ratios, and ball-milled for 24 h. Mixtures were then pelletized under 9.8 MPa and heat-treated at 1000 °C in ambient atmosphere for 10 h. After ball-milling for 10 h, the samples were pelletized under 9.8 MPa again, and kept at 1300 °C in ambient atmosphere for 10 h for synthesizing. The as-synthesized samples were ball-milled for 50 h, and mixed with a binder (NCB-166, DIC Corporation, Tokyo, Japan). After being pelletized at 392 MPa, the samples were heat-treated at 1600 °C for 8 h to remove the binder. The thereby prepared pellet-like samples were heated at 1600 °C for 24 h in oxygen atmosphere for sintering, besides the Sc or In-contained sample, which was found to melt at 1600 °C, but be sintered at 1500 °C.

Characterization

Powder X-ray diffraction (XRD) measurements were performed using Cu K_{α} radiation with X'Pert PRO MPD and monochromatic Cu $K_{\alpha 1}$ radiation with X'Pert PRO Alpha-1 (PANalytical, Almelo, Netherland). High temperature XRD (HT-XRD) measurements were performed using a HTK 1200N high-temperature chamber (Anton Paar, Graz, Austria) attached to the PANalytical X'Pert PRO MPD diffractometer. Dry or wet ($p_{H_{2}O} = 0.031$ atm) argon gas was fed through the hightemperature chamber. HT-XRD patterns were collected during cooling from 1000 to 30 °C at an average cooling rate about 1.06 °Cmin⁻¹. Detailed procedures of HT-XRD measurements were described in our previous work. [S1, S2] Rietveld refinement was carried out utilizing a commercial software X'Pert HighScore Plus to simulate the XRD patterns. Microstructures were observed by electron probe microanalyzer (EPMA) with JXA-8230 (JEOL, Tokyo, Japan). Wavelength-dispersive X-ray spectroscopy (EPMA-WDS) was used to determine the composition. Karl-Fischer titration method was applied to determine water content. The pellet-like samples heattreated at 1600 °C for sintering were broken into pieces about 2 mm in length, and hydrated in wet Ar with a water partial pressure of 0.05 atm for at least 6 days at 300 or 600 °C. Readers are referred to our previous works [S3, S4] for detailed procedures. CO_2 and water vapor tolerance was evaluated by keeping powder samples in Ar – 10% $CO_2 - 5\%$ H₂O for 100 h at 500, 600 and 700 °C with the XRD patterns collected after such heat-treatment.

Electrochemical Measurements

Conductivity measurements of the pellet-like samples with sputtered platinum (Pt) electrodes were performed in dry or wet atmosphere of H_2 or O_2 . The partial pressure of water vapor in the wet atmosphere was 0.05 or 0.3 atm by passing the gas through deionized water kept at 33 or 70 °C. Pt plates wiped with silver mesh were used as current collector. Pt wire was used to lead the current to a frequency response analyzer (Solartron SI 1260, Solartron Analytical, Farnborough, UK). The impedance spectra were collected in the frequency range from 10 Hz to 7 MHz with applied voltage of 100 mV during cooling from 700 to 100 °C at 0.2 °Cmin⁻¹.

Transport numbers of different charge carriers (protons, oxide ions, electronic holes and electrons) in humid hydrogen or oxygen atmospheres were determined with the electromotive force (EMF) method performed at 600 and 700 °C. Hydrogen concentration cell, oxygen concentration cell, and water vapor concentration cell were established with the EMF values collected. The partial pressure of water vapor ($p_{\rm H_{20}}$) in the hydrogen and oxygen concentration cells was kept constantly as 0.0312 atm. And $p_{\rm H_{20}}$ in the water vapor concentration cells was 0.0312 and 0.0086 atm at the two opposite electrodes. The detailed information on the EMF measurements can be found in our previous works [S5, S6]. But, in this study, the transport numbers evaluated in the oxygen atmosphere were not compensated by taking the effect of electrode polarization into consideration.

References

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Table S1 Preparation results of $La_2(Nb_{1-x}M_x)_2O_{7-\delta}$ (M = Sc, Y, In, Nd, Sm, Gd, Yb). The Sc or In-contained samples were finally sintered at 1500 °C. The other samples were finally sintered at 1600 °C. The meaning of the symbols in this table is as following: \circ for a single phase; Δ for close to a single phase but with minor peak belonging to a second phase; \times for not a single phase. The compositions not prepared are marked with a horizontal line.

Cation		Cation content, x					
species, M	0.5	0.55	0.6	0.65	0.7	0.75	0.8
Sc	Δ	-	×	-	×	-	-
Y	×	×	0	0	0	×	×
In	-	-	-	-	×	-	-
Nd	-	-	-	-	×	-	-
Sm	-	-	-	-	×	-	-
Gd	×	-	×	-	×	-	-
Yb	×	-	×	-	×	-	-



Fig. S1 Powder XRD patterns of the samples with the composition listed in **Table 1**, except those of $La_2(Nb_{1-x}Y_x)_2O_{7-\delta}$ (x = 0.6, 0.65, 0.7). The Sc or In-contained samples were finally sintered at 1500 °C. The other samples were finally sintered at 1600 °C.

Table 2 Compositions of the as-sintered samples measured by EPMA-WDS area analysis which were performed for at least five times for each sample to obtain average values.

Sampla	Nominal composition / at%			Actual composition by EPMA-WDS / at%			
Sample	La	Nb	Y	La	Nb	Y	
$La_2(Nb_{0.4}Y_{0.6})_2O_{7-\delta}$	50	20	30	49.89	20.48	29.63	
$La_2(Nb_{0.35}Y_{0.65})_2O_{7-\delta}$	50	17.5	32.5	50.28	17.47	32.26	
$La_2(Nb_{0.3}Y_{0.7})_2O_{7-\delta}$	50	15	35	51.30	14.80	33.90	



Fig. S2 Comparison of the lattice constants of the as-sintered samples and the ones collected by HT-XRD measurements at 30 °C (**Fig. 2(b**)). The lattice constants of the as-sintered samples were obtained by refining the Cu $K\alpha_1$ XRD patterns shown in **Fig. 1(a)**. Cubic pyrochlore ($Fd\overline{3}m$) and fluorite ($Fm\overline{3}m$) models were used for La₂(Nb_{1-x}Y_x)₂O_{7- $\delta}$} (x = 0.6, 0.65) and La₂(Nb_{0.3}Y_{0.7})₂O_{7- δ}, respectively.





Fig. S3 Representative electrochemical impedance spectra of $La_2(Nb_{0.3}Y_{0.7})_2O_{7-\delta}$ in $H_2 - 30\%$ H_2O .



Fig. S4 Activation energy of electrical conduction in dry or wet (a) O_2 or (b) H_2 atmosphere. The partial pressure of water vapor in wet atmospheres was 0.05 or 0.3 atm. The activation energy was determined by fitting the conductivity collected below 400 °C.

Table S3 Activation energy and pre-exponential factor of electrical conduction of $La_2(Nb_{1-x}Y_x)_2O_{7-\delta}$ $_{\delta}$ (x = 0.6, 0.65, 0.7) dry or wet O_2 or H_2 atmosphere. The partial pressure of water vapor in wet atmospheres was 0.05 or 0.3 atm. The activation energy was determined by fitting the conductivity collected below 400 °C.

Composition	$La_2(Nb_{0.4}Y_{0.6})_2O_{7\text{-}\delta}$		La ₂ (Nb	$_{0.35}Y_{0.65})_2O_{7-\delta}$	$La_2(Nb_{0.3}Y_{0.7})_2O_{7-\delta}$		
Atmosphere	$E_{\rm a}$ / eV	$A / \operatorname{Scm}^{-1}K$	$E_{\rm a}$ / eV	$A / \operatorname{Scm}^{-1}K$	$E_{\rm a}$ / eV	$A / \operatorname{Scm}^{-1} K$	
Dry O ₂	1.028(3)	$7.64(42) \times 10^4$	1.022(3)	$2.74(18) \times 10^4$	1.038(9)	$7.52(126) \times 10^4$	
$O_2 - 5\% H_2O$	0.862(3)	$1.37(8) \times 10^4$	0.895(2)	$2.78(13) \times 10^4$	0.916(2)	$6.18(21) \times 10^4$	
$O_2 - 30\% H_2O$	0.853(6)	$1.24(17) \times 10^{5}$	0.856(2)	$2.08(11) \times 10^4$	0.880(2)	$6.85(25) \times 10^4$	
Dry H ₂	0.954(8)	$2.29(24) \times 10^4$	0.980(3)	$2.03(13) \times 10^4$	0.955(7)	$2.54(34) \times 10^4$	
${ m H}_2 - 5\%~{ m H}_2{ m O}$	0.888(2)	$2.72(9) \times 10^4$	0.912(3)	$3.25(17) \times 10^4$	0.913(2)	5.80(21) × 10 ⁴	
$H_2 - 30\% H_2O$	0.849(6)	9.62(125) × 10 ⁴	0.840(5)	$1.76(21) \times 10^4$	0.870(2)	$5.28(24) \times 10^4$	



Fig. S5 Arrhenius plot of total conductivities of $La_2(Nb_{0.5}Sc_{0.5})_2O_{7-\delta}$ in dry H₂ and wet H₂. The conductivity of $La_2(Nb_{0.4}Y_{0.6})_2O_{7-\delta}$ in wet H₂ is also plotted for comparison. The partial pressure of water vapor in the wet H₂ atmosphere is 0.05 atm.



Fig. S6 EMF values of (a) hydrogen concentration cell, (b) oxygen concentration cell, (c) water vapor (in hydrogen) concentration cell, and (d) water vapor (in oxygen) concentration cell with $La_2(Nb_{1-x}Y_x)_2O_{7-\delta}$ (x = 0.6, 0.65, 0.7) as the electrolyte.



Fig. S7 Powder XRD patterns of La₂(Nb_{0.3}Y_{0.7})₂O_{7- δ} after kept at (a) 700, (b) 600, and (c) 500 °C in Ar – 10 % CO₂ – 5% H₂O for 100 h, respectively. The XRD patterns of the as-sintered sample is shown in (d) for reference.