

Supplementary Information for

Enhanced oxygen storage capacity of cation-ordered cerium-zirconium oxide induced by titanium substitution

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1. Experimental section

1.1 Material synthesis

Polycrystalline samples of $\text{Ce}_{0.5}\text{Zr}_{0.5-x}\text{Ti}_x\text{O}_2$ ($x = 0, 0.1, 0.2, 0.3, 0.4,$ and 0.5) were synthesized following the solution combustion method, using $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ (99.5%, Alfa Aesar, US), $\text{ZrO}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ (99.99%, Sigma-Aldrich, US), $\text{TiO}(\text{NO}_3)_2$ aqueous solution, and glycine (99.0%, Wako Chemicals, Japan) in a $0.5:(0.5-x):x:2$ molar ratio. $\text{TiO}(\text{NO}_3)_2$ aqueous solution was prepared by filtering the precipitate $\text{TiO}(\text{OH})_2$, which was obtained by hydrolyzing $\text{Ti}(\text{OC}_3\text{H}_7)_4$ (95%, Wako Chemicals, Japan) in deionized water, and subsequently dissolving it in a minimum amount of HNO_3 aqueous solution (65%, Wako Chemicals, Japan). All reagents were dissolved in minimum amounts of deionized water in crucibles and heated to $400\text{ }^\circ\text{C}$ at a rate of $2\text{ }^\circ\text{C}/\text{min}$. In order to compare it with $\text{Ce}_{0.5}\text{Zr}_{0.4}\text{Ti}_{0.1}\text{O}_2$, a polycrystalline sample of $\kappa\text{-Ce}_2\text{Zr}_2\text{O}_8$ was synthesized by reduction of $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$ at $1200\text{ }^\circ\text{C}$ for 4 h under CO flow and a subsequent oxidation at $500\text{ }^\circ\text{C}$ for 3 h under air. $\text{Pt}/\text{Ce}_{0.5}\text{Zr}_{0.5-x}\text{Ti}_x\text{O}_2$ and $\text{Pt}/\kappa\text{-Ce}_2\text{Zr}_2\text{O}_8$ were prepared by impregnation with $\text{Pt}(\text{NO}_3)_2(\text{NH}_3)_2$ aqueous solution (Tanaka Kikinzoku Kogyo, Japan) followed by calcination at $500\text{ }^\circ\text{C}$ for 3 h under air. The Pt loading amount on the metal basis was 1 wt%.

1.2 Characterization

X-ray diffraction (XRD) measurements were conducted at room temperature using an Ultima IV X-ray diffractometer (Rigaku, Japan) with $\text{Cu K}\alpha$ radiation ($\lambda = 1.54056\text{ \AA}$). Patterns were collected in the 2θ range of 10° to 80° in steps of 0.01° . Inductively coupled plasma-optical emission

spectrometry (ICP-OES) analysis was carried out using a CURIOUS 120EOP (Rigaku, Japan). Electron diffraction (ED) patterns were collected from the samples supported on copper grids using field emission transmission electron microscope (TEM; HF-2100, Hitachi, Japan) operating at 200 kV. The specific surface areas (SSAs) were estimated by the single point Brunauer-Emmett-Teller (BET) analysis^{S1} at $-196\text{ }^{\circ}\text{C}$ using an automatic surface analyzer (Micro Sorp 4232III, Micro Data, Japan). Pretreatment of the samples was carried out at $250\text{ }^{\circ}\text{C}$ for 20 min under N_2 flow in order to remove any residual water and gases.

1.3 High-resolution synchrotron XRD measurements

Synchrotron XRD measurements were performed using a Debye-Scherrer camera with a two-dimensional detector (PILATUS 100K) in the BL5S2 beamline at the Aichi Synchrotron Radiation Center. The incident beams from the bending magnet were monochromatized to $\lambda = 0.689591\text{ \AA}$. The capillaries were rotated during the measurements to reduce any preferential orientations. The collected XRD patterns were analyzed with the Rietveld method using the program JANA2006 (Institute of Physics, Praha, Czech Republic).^{S2}

1.4 X-ray absorption near edge structure (XANES) measurements

XANES spectra were recorded in transmission mode at the BL33XU in Spring-8, JASRI. The incident beams from the bending magnet were monochromatized using Si(111) for the Ce L_3 -edge. Samples mixed with boron nitride were pressed into disks (10 mm in diameter, 0.1 mm in thickness) and introduced to an in situ cell with a gas switching system. Spectra were collected 5 min after the atmosphere inside the in situ cell was changed from 3% O_2/He to 3% H_2/He at $600\text{ }^{\circ}\text{C}$. The time-resolved changes in the edge positions were recorded every 0.2 s after the atmosphere was changed.

1.5 Oxygen storage/release capacity (OSC) measurements

OSCs were estimated using a thermogravimeter (TGA-50, Shimadzu, Japan) connected to a dual gas supplying system. Samples (10 mg) were put into platinum pans and heated to the target temperatures at a rate of $50\text{ }^{\circ}\text{C}/\text{min}$ under 5% O_2/N_2 flow. Then, the weight changes of the samples were monitored upon switching between 5% O_2/N_2 and 5% H_2/N_2 flow every 5 min. The OSCs were estimated from the average of 5 measurements of the weight losses of the samples.

2. Supplementary figures

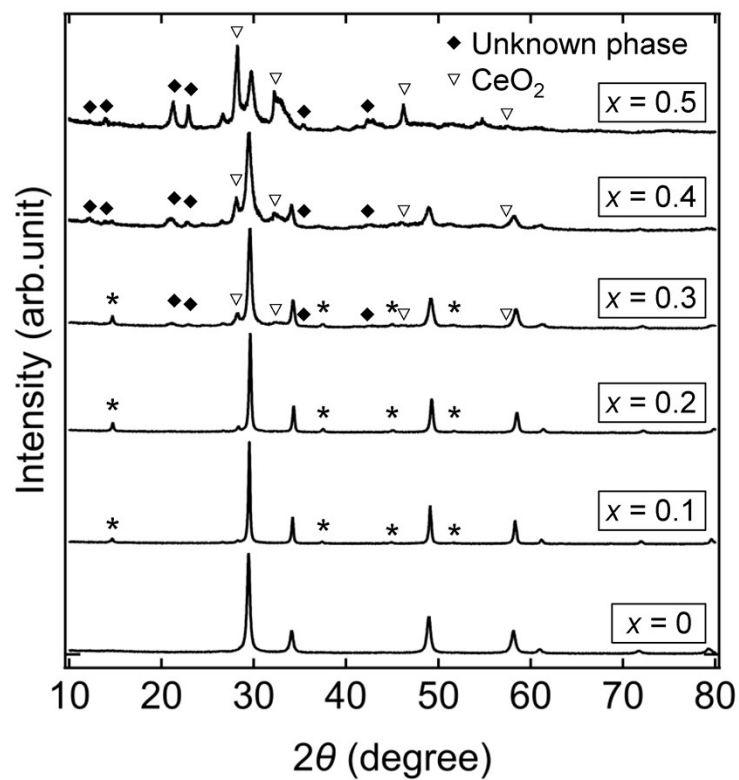


Fig. S1. X-ray diffraction patterns of the obtained samples for $\text{Ce}_{0.5}\text{Zr}_{0.5-x}\text{Ti}_x\text{O}_2$ ($0 \leq x \leq 0.5$) as target compositions at room temperature. Asterisks (*) indicate peaks arising from the superstructure. CeO_2 and an unknown phase are contained in the samples of $x = 0.3$, 0.4 , and 0.5 .

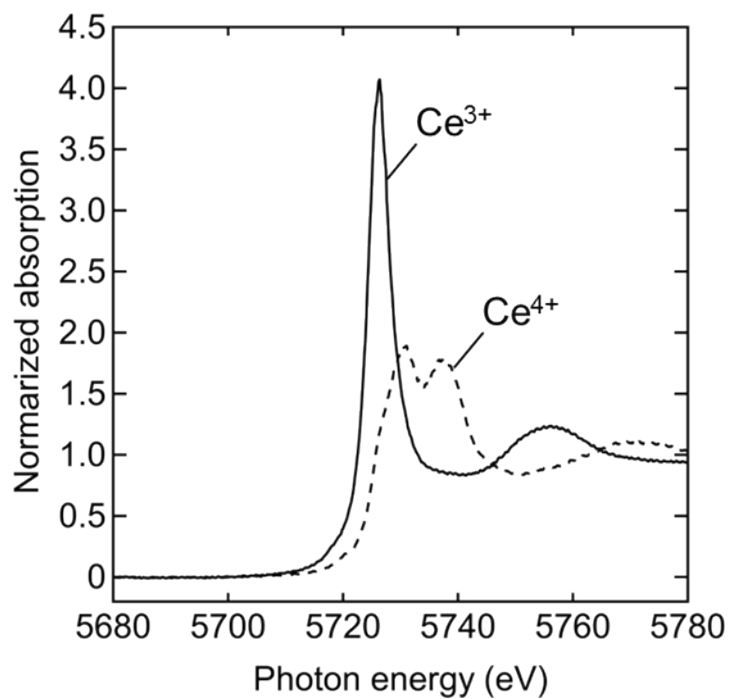


Fig. S2. Ce L₃-edge XANES spectra for CeO₂ (dashed line) and Ce(NO₃)₃·6H₂O (solid line) at room temperature.

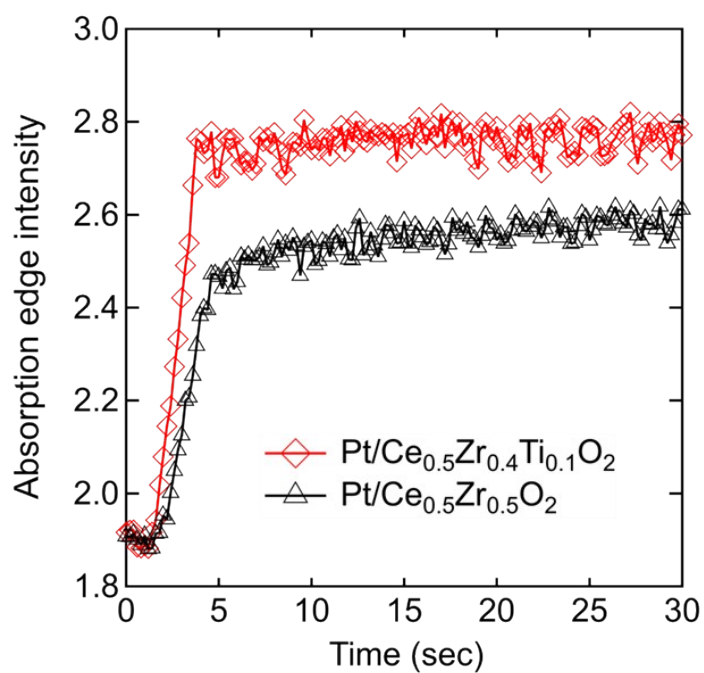
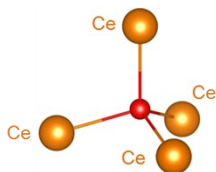


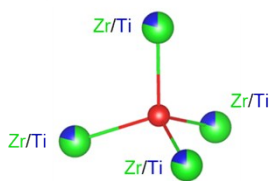
Fig. S3. Time-resolved absorption edge intensities in Ce L₃-edge XANES spectra after switching the atmosphere from 3% O₂/He to 3% H₂/He at 600 °C. Data were collected every 0.2 s.

(a) $\text{Ce}_{0.5}\text{Zr}_{0.4}\text{Ti}_{0.1}\text{O}_2$

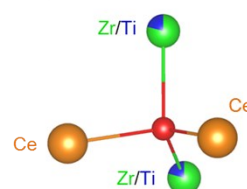
O1, O2 sites



O3, O4 sites

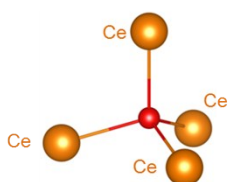


O5, O6 sites

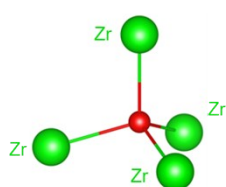


(b) $\kappa\text{-Ce}_2\text{Zr}_2\text{O}_8$

O1, O2 sites



O3, O4 sites



O5 – O8 sites

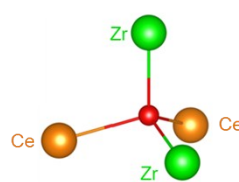


Fig. S4. Coordination geometries around the O sites in (a) $\text{Ce}_{0.5}\text{Zr}_{0.4}\text{Ti}_{0.1}\text{O}_2$ and (b) $\kappa\text{-Ce}_2\text{Zr}_2\text{O}_8$.

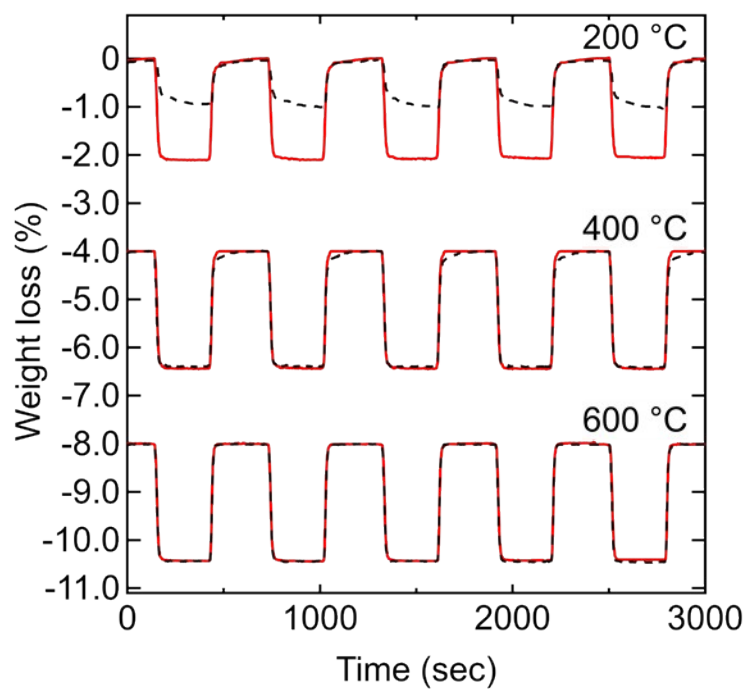


Fig. S5. Thermogravimetric analysis curves of Pt/Ce_{0.5}Zr_{0.4}Ti_{0.1}O₂ (red solid lines) and Pt/κ-Ce₂Zr₂O₈ (black dashed lines) upon switching the atmosphere from 5% O₂/N₂ to 5% H₂/N₂ every 5 min at various temperatures.

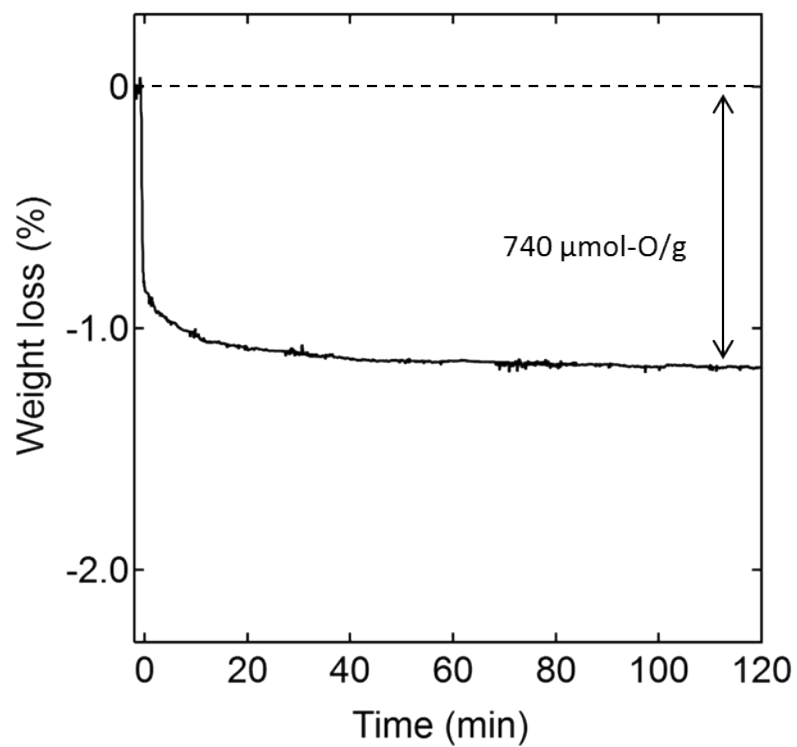


Fig. S6. Thermogravimetric analysis curves of Pt/ κ -Ce₂Zr₂O₈ in 5% H₂/N₂ at 200 °C.

3. Supplementary tables

Table S1. Structural parameters of $\text{Ce}_{0.5}\text{Zr}_{0.4}\text{Ti}_{0.1}\text{O}_2$ obtained from the Rietveld refinement of the synchrotron X-ray diffraction pattern at room temperature.^a

Atom	Site	<i>g</i>	<i>x</i>	<i>y</i>	<i>z</i>	U_{iso} (Å ²)
Ce	16 <i>e</i>	1	0.1252(1)	0.1252(1)	0.1252(1)	0.00436(6)
Zr	16 <i>e</i>	0.8	0.6233(2)	0.6233(2)	0.6233(2)	0.0174(2)
Ti	16 <i>e</i>	0.2	0.6233(2)	0.6233(2)	0.6233(2)	0.0174(2)
O1	4 <i>a</i>	1	0	0	0	0.0179(7)
O2	4 <i>c</i>	1	0.25	0.25	0.25	0.0179(7)
O3	4 <i>b</i>	1	0.50	0.50	0.50	0.0179(7)
O4	4 <i>d</i>	1	0.75	0.75	0.75	0.0179(7)
O5	24 <i>f</i>	1	0.2820(6)	0	0	0.0179(7)
O6	24 <i>g</i>	1	0.4445(5)	0.25	0.25	0.0179(7)

^a Space group *F*-43*m* (No. 216), $a = 10.50439(5)$ Å, $R_{\text{wp}} = 6.46\%$, $R_{\text{p}} = 4.23\%$, GOF = 0.80.

Table S2. Bond valence sums calculated for various anion sites.

Atom	$\text{Ce}_{0.5}\text{Zr}_{0.4}\text{Ti}_{0.1}\text{O}_2^a$		$\kappa\text{-Ce}_2\text{Zr}_2\text{O}_8^b$	
	Site	BVS	Site	BVS
O1	4 <i>a</i>	-2.03	4 <i>a</i>	-1.94
O2	4 <i>c</i>	-2.08	4 <i>a</i>	-2.31
O3	4 <i>b</i>	-1.61	4 <i>a</i>	-1.59
O4	4 <i>d</i>	-1.37	4 <i>a</i>	-1.68
O5	24 <i>f</i>	-1.82	12 <i>b</i>	-2.02
O6	24 <i>g</i>	-2.46	12 <i>b</i>	-2.39
O7	-	-	12 <i>b</i>	-1.76
O8	-	-	12 <i>b</i>	-1.94

^a Calculated from the crystallographic data obtained by the Rietveld refinement. ^b Calculated from the crystallographic data reported in reference S3.

4. References

S1 S. Brunauer, P. H. Emmett and E. Teller, *J. Am. Chem. Soc.*, 1938, **60**, 309.

S2 V. Petříček, M. Dušek and L. Palatinus, *Z. Kristallogr. - Cryst. Mater.*, 2004, **229**, 345.

S3 H. Kishimoto, T. Omata, S. Otsuka-Yao-Matsuo, K. Ueda, H. Hosono and H. Kawazoe, *J. Alloys Compd.*, 2000, **312**, 94.