**Supplementary Information** 

## Single crystalline pyrochlore nanoparticles with metallic conduction as

an efficient bi-functional oxygen electrocatalysts for Zn-air batteries

Joohyuk Park,<sup>a</sup> Marcel Risch,<sup>b,c</sup> Gyutae Nam,<sup>a</sup> Minjoon Park,<sup>a</sup> Tae Joo Shin,<sup>d</sup> Suhyeon Park,<sup>a</sup> Min Gyu Kim<sup>\*</sup>,<sup>d</sup> Yang Shao-Horn<sup>\*b,e</sup> and Jaephil Cho<sup>\*a</sup>

<sup>a</sup>School of Energy and Chemical Engineering, Ulsan National Institute of Science and Technology (UNIST), 50, UNIST-gil, Ulsan 44919, Republic of Korea

<sup>b</sup>Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, United States

<sup>c</sup>Institute of Materials Physics, University of Göttingen, Göttingen, 37077, Germany

<sup>d</sup>Beamline Research Division, Pohang Accelerator Laboratory (PAL), Pohang 790–784, Republic of Korea

<sup>e</sup>Department of Materials Science and Engineering & Research Laboratory of Electronics, Massachusetts Institute of Technology, Cambridge, MA 02139, United States

\*Corresponding author: E-mail: mgkim@postech.ac.kr, shaohorn@mit.edu, jpcho@unist.ac.kr

## **MATERIALS AND METHODS**

**Preparation of pyrochlore oxide catalysts.** To prepare the pyrochlore oxide catalysts, a buffer solution was required. The buffer solution, NH<sub>4</sub>–EDTA, was made with a mixture of 10 g anhydrous ethylenediaminetetraacetic acid ( $\geq$  99% titration, Sigma-Aldrich), 1 M ammonia solution (28.0–30.0%, Samchun chemical), and 1.5 mL nitric acid (HNO<sub>3</sub>, ACS regent 70%, Sigma-Aldrich) at a solution pH of 7. To prepare Pb<sub>2</sub>Ru<sub>2</sub>O<sub>6.5</sub>, 8.22 × 10<sup>-4</sup> mol lead (IV) acetate (reagent grade 95%, Sigma-Aldrich), 8.22 × 10<sup>-4</sup> mol ruthenium (III) nitrosyl nitrate solution (1.5 wt% Ru, Sigma-Aldrich), and 10 g anhydrous citric acid (99%, Sigma-Aldrich) were dissolved and stirred with the buffer solution for 24 h at 150 °C. At this point, gelation was observed. The gelled solution was transferred to an oven at 200 °C for 6 h drying. The prepared powder was calcined in air at 650 °C for 5 h. To prepare Sm<sub>2</sub>Ru<sub>2</sub>O<sub>7</sub>, a similar process was used except that the A-site metal precursor was 8.22 × 10<sup>-4</sup> mol of samarium (III) nitrate hexahydrate, respectively, and the final calcination temperature was 1050 °C.

**Preparation of the catalyst inks and working electrode.** The catalyst inks were prepared with mixture of 16 mg of the pyrochlore catalyst series powder, 4 mg of ketjenblack carbon (EC 600JD), 200  $\mu$ L of the 5wt% of Nafion in mixture of lower aliphatic alcohols and H<sub>2</sub>O (Sigma-Aldrich), and 800  $\mu$ L of ethanol. Briefly, the catalyst inks were prepared by ultrasonically mixing in distilled water for 1 h to make homogeneous mixture. The portion of 5  $\mu$ L of inks were loaded on the glassy carbon of rotation ring disk electrode (RRDE) as the working electrode. The area of RRDE was 0.1256 cm<sup>2</sup>. As a result, the loading levels of the pyrochlore catalyst series were 0.637 mg<sub>cat</sub> cm<sup>-2</sup>. For the loading level of 79.6  $\mu$ g<sub>pt</sub> cm<sup>-2</sup> benchmarking catalyst, 10 mg of Pt/C on Vulcan XC 72 (20wt%, Premetek Co.) was dispersed in 200  $\mu$ L of the 0.05% titrated Nafion solution and 800  $\mu$ L of ethanol. After that, this catalyst ink was prepared by ultrasonically mixing in distilled water for at least 1 h to make homogeneous ink. Then, 5

 $\mu$ L of ink was loaded on the glassy carbon of working electrode that the loading level of 20% Pt/C and the pure Pt were 0.398 mg<sub>(20% Pt/C)</sub> cm<sup>-2</sup> and 79.6  $\mu$ g<sub>Pt</sub> cm<sup>-2</sup>, respectively.

**Electrochemical measurements.** A three-electrode cell was used to measure the electrocatalytic activities of the pyrochlore catalyst series. Rotating ring disk electrode (RRDE) (ALS Co., Ltd) tests were carried out based on the pyrochlore catalyst series film (loaded on the glassy carbon of RRDE) for the working electrode in O<sub>2</sub>-saturated 0.1 M KOH alkaline electrolyte. Platinum wire and Hg/HgO were used as the counter and reference electrodes, respectively. Electrochemical characterizations were conducted using a bipotentiostat (IviumStat). The scan rate of 10 mV s<sup>-1</sup> was swept from 1.13 V to 0.26 V (vs. RHE) for oxygen reduction reaction (ORR) and from 1.23 to 1.82 V (vs. RHE) for oxygen evolution reaction (OER). The ORR capacitance were corrected by averaging current of cyclic voltammetry plots (CVs) in O<sub>2</sub>- and Ar-saturated electrolytes. The OER CVs were capacitive-corrected by averaging current of the forward and backward sweeps. The capacitive-corrected ORR and OER currents were ohmically corrected with the measured ionic resistance ( $\approx 45 \Omega$ ).

In addition, a ring potential of 0.4 V (vs. Hg/HgO) was applied to oxidize peroxide during ORR. The collection efficiency (N) was determined under Ar atmosphere using 10 mM  $K_3[Fe(CN)_6]$ , which is around 0.41. This value is similar to the theoretical value of 0.42. The peroxide yield (H<sub>2</sub>O<sup>-</sup>) and the number of transferred electrons (n) were calculated from the below equations.

$$H_2 O^-(\%) = 100 \frac{2I_r/N}{I_d + I_r/N}$$
(1)

$$n = 4 \frac{I_d}{I_d + I_r/N} \tag{2}$$

Primary Zn-air batteries tests. For primary Zn-air batteries tests based on the pyrochlore catalyst

series, 0.75 g of zinc granular is used as an anode and 200 µL of 6 M KOH was used as an electrolyte. A nylon membrane was used as a separator. The air electrode which is a cathode was prepared by uniformly loaded gas diffusion layer (GDL) (the catalyst ink formulation: 16 mg of catalyst, 4 mg of ketjenblack, 200 µL of the 5wt% of the Nafion solution and 800 µL of ethanol on nickel mesh. Thickness of the electrode is around 500 µm. The assembled primary Zn-air batteries were tested at discharge current densities at 20 mA cm<sup>-2</sup>. The GDL was prepared from a mixture of activated charcoal (Darco G-60A, Sigma-Aldrich) and PTFE binder (60 wt% PTFE emulsion in water, Sigma-Aldrich) at a weight ratio of 7:3 with about 450 µm of thickness to ensure proper gas distribution and sufficient current collection. This prepared GDL was used as the reference for comparison to confirm enhanced performance of air electrode based on catalysts in polarization curves of the Zn-air batteries.

**Rechargeable Zn-air batteries tests.** For primary Zn-air batteries tests based on pyrochlore oxide catalyst series, 0.5 g of zinc plate is used as an anode and 2 mL of 6 M KOH with 0.2 M ZnO as an electrolyte. Preparation method of air electrode with the catalysts is same as primary Zn-air batteries except nickel mesh. Thickness of the electrode is around 950  $\mu$ m. In this case, nickel foam is used for air electrode instead of mesh. The assembled rechargeable Zn-air batteries were tested at discharge/charge current densities at 10 mA cm<sup>-2</sup>.

**Materials characterizations.** The material morphologies were examined using SEM (VERIOS 460, FEI), high-resolution transmission electron microscopy (HR-TEM) (JEM-2100F, JEOL) operating at 200 kV. Powder analysis was performed using an X-ray diffractometer (XRD) (D/Max2000, Rigaku). X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) were collected on BL10C beam line at the Pohang light source (PLS-II) with top-up mode operation under a ring current of 200 mA at 3.0 GeV.



**Figure S1.** (a) SEM image of  $Sm_2Ru_2O_7$ . The primary particles of the pyrochlore catalyst showed angular shapes with average sizes of ~200 nm. (b) HR-TEM FFT image along the [110] zone axis with indexed unit spots of  $Sm_2Ru_2O_7$ . The indexed points refer to the lattice planes of (-11-1), (-220), (-111) and (002) in clockwise order. (c) Lattice scale STEM-HAADF image with d-spacing of  $Sm_2Ru_2O_7$ . 0.306 nm and 0.511 nm denote the lattice spacing indicated by yellow arrows and lines, on the (111) and (002) planes, respectively. Scale bars are 1 µm and 2 nm in (a) and (c), respectively.



**Figure S2.** STEM-HAADF-EDS images of  $Pb_2Ru_2O_{6.5}$  and elemental maps of (a) all elements, (b) Pb, (c) Ru and (d) O. Scale bars are 500 nm in (a), (b), (c) and (d).



**Figure S3.** (a) STEM and (b) EDS of  $Pb_2Ru_2O_{6.5}$  at different point. Scale bar is 500 nm in (a).



**Figure S4.** STEM-HAADF-EDS images of  $Sm_2Ru_2O_7$  and element maps of (a) all elements, (b) Sm, (c) Ru and (d) O. Scale bars are 500 nm in (a), (b), (c) and (d).



Figure S5. (a) STEM and (b) EDS of Sm<sub>2</sub>Ru<sub>2</sub>O<sub>7</sub> at different points. Scale bar is 500 nm in (a).



**Figure S6**. Photograph of three electrodes half-cell for *in situ* XAS analysis. The half-cell consists of the pyrochlore series based air electrode as working electrode, Hg/HgO reference electrode and Pt wire as counter electrode in 0.1 M KOH electrolyte.



**Figure S7**. Chronoamperometric tests of (a)  $Pb_2Ru_2O_{6.5}$  and (b)  $Sm_2Ru_2O_7$  in 0.1 M KOH at 0.7 V, 0.5 V and 0.3 V (vs. RHE) for *in situ* XAF analysis during the ORR. Chronoamperometric tests of (c)  $Pb_2Ru_2O_{6.5}$  and (d)  $Sm_2Ru_2O_7$  in 0.1 M KOH at 1.3 V, 1.5 V and 1.7 V (vs. RHE) for *in situ* XAS analysis during the OER.



**Figure S8**. Discharge and charge cycling curves of rechargeable Zn-air batteries at the current density of 10 mA cm<sup>-2</sup> in short cycle periods (600 sec per cycle) with ambient air based on (a)  $Pb_2Ru_2O_{6.5}$  and (b)  $Sm_2Ru_2O_7$ . Discharge and charge cycling curves of rechargeable Zn-air batteries at the current density of 10 mA cm<sup>-2</sup> in long cycle periods (2 h per cycle) with ambient air based on (c)  $Pb_2Ru_2O_{6.5}$  and (d)  $Sm_2Ru_2O_7$ .



**Figure S9**. Durability tests of pyrochlore oxide catalysts. (a) Normalized Ru K-edge XANES for pristine (solid line) and 100<sup>th</sup> cycled (dashed line) pyrochlore catalysts. (b) Fourier-transformed radial distribution function of Ru K-edge EXAFS for pristine and 100<sup>th</sup> cycled pyrochlore catalysts. (c) XRD patterns for 100<sup>th</sup> cycled pyrochlore catalysts.

Catalysts	Synthetic	Crystalline	Half-cell	Full-cell	Reference
	procedure	phase			
$Pb_2Ru_2O_{6.5}$	Sol-gel 650 °C	Pure	ORR OER	Zn-air batteries	This work
Sm <sub>2</sub> Ru <sub>2</sub> O <sub>7</sub>	Sol-gel	Pure	ORR	Zn-air	This work
	1050 °C		OER	batteries	
Pb <sub>2</sub> Ir <sub>2-x</sub>	Solid state	n/a	ORR	n/a	J. Am. Chem.
Pb <sub>x</sub> O <sub>7-y</sub>	reaction		OER		Soc.
	850 °C				<b>1990</b> , 112, 2076
$Bi_2[Ru_{2-x}]$	Precipitation	n/a	ORR	n/a	J. Electrochem.
Bi <sub>x</sub> ]O <sub>7-y</sub>	200 °C		OER		Soc.
					<b>1983</b> , 130, 1851
$Pb_2[Ru_{2-x}]$	Solid state	n/a	ORR	n/a	J. Am. Chem.
$Pb_{x}^{4+}]O_{6.5}$	reaction		OER		Soc.
	850 °C				<b>1990</b> , 112, 2076
$Pb_2[Ru_{2-x}]$	Precipitation	n/a	ORR	n/a	J. Electrochem.
$Pb_{x}^{4+}]O_{6.5}$	200 °C		OER		Soc.
					<b>1983</b> , 130, 1851
$Pb_2[Ru_{2-x}]$	Solution	Pure	n/a	Li-air	Nat. Chem.
$Pb_{x}^{4+}]O_{6.5}$	100 °C			batteries	<b>2012</b> , 12, 1004
$Pb_2Ru_2O_{6.5}$	Solid state	n/a	OER	n/a	Bull. Korean
	reaction				Chem. Soc.
	900 °C				<b>1997</b> , 18, 972
Pb <sub>2</sub> Ru <sub>2</sub> O <sub>6.5</sub>	Precipitation	Pure	ORR	n/a	J. Electrochem.
	300 °C		OER		Soc.
					<b>1999</b> , 146, 4145
$Pb_2Ru_2O_{6.5}$	Precipitation	Pure	OER	n/a	J. Mater.
	272atm				Chem. A.
	45 °C				<b>2015</b> , 3, 10819
$\operatorname{Bi}_{2.4}\operatorname{Ru}_{1.6}\operatorname{O}_7$	Precipitation	Impure	OER	n/a	J. Mater.
	300-500 °C				Chem. A.
					<b>2015</b> , 3, 10819
$Bi_2Ru_2O_7$	Solid state	n/a	OER	n/a	Bull. Korean
	reaction				Chem. Soc.
	900 °C				<b>1997</b> , 18, 972
Bi <sub>2</sub> Ru <sub>2</sub> O <sub>7</sub>	Sol-gel	Impure	n/a	SOFC	RSC Advances
	600-900 °C				<b>2013</b> , 3, 19866
$Pb_2Ru_2O_{7-x}$	Precipitation	Impure	ORR	n/a	J. Electrochem.
	700 °C				Soc.
					2015, 162, 129

 Table S1. Reported pyrochlore oxide electrocatalysts either ORR or OER.

**Table S2.** Percent composition and atomic ratios of Pb and Ru in  $Pb_2Ru_2O_{6.5}$  at different points (Figure S3).

Catalyst	Sites	Pb (wt %)	Ru (wt %)	Pb/Ru (At. %)
$Pb_2Ru_2O_{6.5}$	1	58.70	28.92	1.01
	2	62.61	28.38	0.93

**Table S3.** Percent composition and atomic ratios of Sm and Ru in Sm<sub>2</sub>Ru<sub>2</sub>O<sub>7</sub> at different points (Figure S5).

Catalyst	Sites	Sm (wt %)	Ru (wt %)	Sm/Ru (At. %)
$Sm_2Ru_2O_7$	1	51.22	28.47	1.2
	2	47.15	26.18	1.14

**Table S4.** Tafel slopes (mV dec<sup>-1</sup>) of the pyrochlore oxide catalysts and Pt/C for the ORR at different voltages.

Catalysts	Slope at low $\eta$ (mV dec <sup>-1</sup> )	Slope at high $\eta$ (mV dec <sup>-1</sup> )
$Pb_2Ru_2O_{6.5}$	56	126
$Sm_2Ru_2O_7$	62	125
Pt/C	60	120

**Table S5**. Electrocatalytic activities of the pyrochlore oxide catalysts and reported metal-oxide based electrocatalysts for ORR in O<sub>2</sub>-saturated 0.1 M KOH. Abbreviation of Ketjenblack, acetylene black, and carbon black are KB, AB, and CB, respectively.

Catalysts	Loading $(mg.cm^{-2})$	Onset Potential	Half-wave Potential	Current	Reference
	(Ing chi )	$(V_{VS}, PHE)$	(V vs	$(m\Lambda cm^{-2})$	
	rate (rpm)	$(\mathbf{v}, \mathbf{v}\mathbf{s}, \mathbf{K}\mathbf{n}\mathbf{E})$			
			KIIL)		
				(vs. KIIE)	
$Pb_2Ru_2O_{6.5}$	0.637	0.89	0.81	-1.28	This work
/KB	/1600			@ 0.85 V	
Sm <sub>2</sub> Ru <sub>2</sub> O <sub>7</sub>	0.637	0.78	0.65	-0.01	This work
/KB	/1600			@ 0.85 V	
20% Pt/C	0.319	1.08	0.85	-3.02	This work
	/1600			@ 0.85 V	
LaCu <sub>0.5</sub> Mn <sub>0.5</sub> O <sub>3</sub>	0.3	0.85	n/a	n/a	Nat. Chem.
/AC					<b>2011</b> , 3, 546
LaMnO <sub>3</sub>	0.3	0.87	0.66	-0.02	Nat. Chem.
/AC				@ 0.85 V	<b>2011</b> , 3, 546
LaCoO <sub>3</sub>	0.3	0.83	0.67	-0.03	Nat. Chem.
/AC				@ 0.85 V	<b>2011</b> , 3, 546
LaSrMnO <sub>3</sub>	n/a	0.88	n/a	n/a	Energy
					Environ. Sci.
					<b>2013</b> , 6, 1582
BSCF-5528_Ar	0.639	0.76	0.63	0.0375	Adv. Energy
/KB	/1600			@ 0.85 V	Mater.
					<b>2015</b> , 5,
					1501560
BSCF-5582_Ar	0.639	0.75	0.62	-0.256	Adv. Energy
/KB	/1600			@ 0.85 V	Mater.
					<b>2015</b> , 5,
					1501560
La <sub>0.7</sub> -50 nm	0.64	0.77	0.68	-0.163	Energy
/KB	/1600			@ 0.85 V	Environ. Sci.
					<b>2016</b> , 9, 179
Pb <sub>2</sub> Ru <sub>2</sub> O <sub>7-x</sub>	0.5	0.89	0.73	-0.383	J. Electrochem.
/CB	/3600			@ 0.85 V	Soc.
					<b>2015</b> , 162, 129

**Table S6**. Electrocatalytic activities of the pyrochlore oxide catalysts and reported metal-oxide based electrocatalysts for OER in O<sub>2</sub>-saturated 0.1 M KOH.

Catalysts	Loading (mg cm <sup>-2</sup> ) /Rotation rate (rpm)	Potential (V vs. RHE) @ 2.5 mA cm <sup>-2</sup>	Current density (mA cm <sup>-2</sup> ) @ ~ (vs. RHE)	Reference
$Pb_2Ru_2O_{6.5}$	0.637	1.56	6.2	This work
	/1000	1 (7	<i>a</i> 1.0 v	This mode
	/1600	1.07	1.44 @ 1.6 V	T IIIS WOLK
IrO <sub>2</sub>	0.637	1.61	3.26	This work
/KB	/1600		@ 1.6 V	
De-LiCo <sub>0.33</sub>	0.1	1.52	10	Nat. Commun.
Ni <sub>0.33</sub> Fe <sub>0.33</sub> O <sub>2</sub> /CB			@ 1.55 V	<b>2014</b> , 5, 4345
BSCF-5528_Ar	0.639	1.62	2.1	Adv. Energy
/KB <sup>–</sup>	/1600		@ 1.6 V	Mater.
				<b>2015</b> , 5,
				1501560
BSCF-5582_Ar	0.639	1.71	2.0	Adv. Energy
/KB	/1600		@ 1.6 V	Mater.
				<b>2015</b> , 5, 1501560
BSCF-5582_O <sub>2</sub>	0.64	1.69	0.78	Adv. Mater.
/KB	/1600		@ 1.6 V	<b>2015</b> , 27, 266
BSCF-5582	0.64	1.77	0.45	Adv. Mater.
/KB	/1600		@ 1.6 V	<b>2015</b> , 27, 266
La <sub>0.7</sub> -50 nm	0.64	1.54	10	Energy
/KB	/1600		@ 1.8 V	Environ. Sci.
				<b>2016</b> , 9, 179
$Pb_2Ru_2O_{6.5}$	0.2	1.41	28	J. Mater.
	/1600		@ 1.5 V	Chem. A.
	<u> </u>	1.50		<b>2015</b> , 3, 10819
$B_{1_{2.4}}Ru_{1.6}O_7$		1.53	9.1	J. Mater.
	/1600		@ 1.6 V	Chem. A.
				2015, 3, 10819

**Table S7.** Tafel slopes (mV dec<sup>-1</sup>) of the pyrochlore oxide catalysts and RuO<sub>2</sub> for the OER at different voltages.

Catalysts	Average slope (mV dec <sup>-1</sup> )
$Pb_2Ru_2O_{6.5}$	114.2
$Sm_2Ru_2O_7$	100.8
RuO <sub>2</sub>	115.9

	Applied potential	Energy shift (eV)	Interatomic distance (Å)	Coordination number	Debye- Waller factor (x 10 <sup>-3</sup> Å <sup>2</sup> )	R-factor*
Initial a	at OCV**	1.50 (±1.15)	1.967 (±0.004)	5.81 (±0.42)	3.05	0.018
	0.7 V	-1.51 (±1.12)	1.953 (±0.004)	5.75 (±0.36)	3.05	0.015
ORR	0.5 V	-2.84 (±1.13)	1.947 (±0.004)	5.81 (±0.36)	3.05	0.016
_	0.3 V	-2.01 (±1.18)	1.948 (±0.004)	6.07 (±0.42)	3.05	0.019
	1.3 V	-2.77 (±1.78)	1.944 (±0.006)	5.24 (±0.48)	3.05	0.021
OER -	1.5 V	1.77 (±1.21)	1.966 (±0.005)	5.74 (±0.42)	3.05	0.019
	1.7 V	-0.57 (±1.19)	1.953 (±0.005)	5.85 (±0.36)	3.05	0.022
$\sum_{n=1}^{\infty} (D_{n}A_{n}(l))^{2} + I_{n}A_{n}(l)^{2} / \sum_{n=1}^{\infty} (D_{n}A_{n}(l))^{2} + I_{n}A_{n}(l)^{2} + I_{n}A_{n}(l)^{2$						

**Table S8.** EXAFS structural parameters of Ru K-edge  $k^3$ -weighted EXAFS spectra for Pb<sub>2</sub>Ru<sub>2</sub>O<sub>6.5</sub>.

\* The Goodness of fit:  $\sum \{Re\Delta\chi(k)^2 + Im\Delta\chi(k)^2\} / \sum \{Re(\chi(k)_{data})^2 + Im(\chi(k)_{data})^2\}$ 

\*\* The value means pyrochlore electrode sample is wetted in 0.1M KOH solution at open-circuit voltage (OCV), i.e. without applied voltage.

Table S9. EXAFS structural parameters of Ru K-edge  $k^3$ -weighted EXAFS spectra for Sm<sub>2</sub>Ru<sub>2</sub>O<sub>7</sub>.

	Applied potential	Energy shift (eV)	Interatomic distance (Å)	Coordination number	Debye- Waller factor (x 10 <sup>-3</sup> Å <sup>2</sup> )	R-factor
Initial at OCV		-0.37 (±0.97)	1.988 (±0.004)	6.66 (±0.24)	2.70	0.011
	0.7 V	4.78 (±0.73)	2.011 (±0.003)	5.58 (±0.24)	2.70	0.011
ORR	0.5 V	3.43 (±0.43)	2.004 (±0.002)	5.46 (±0.12)	2.70	0.004
	0.3 V	2.93 (±0.87)	2.001 (±0.003)	5.64 (±0.18)	2.70	0.012
	1.3 V	0.97 (±0.61)	1.988 (±0.002)	5.52 (±0.24)	2.70	0.006
OER -	1.5 V	1.46 (±0.36)	1.990 (±0.001)	6.18 (±0.12)	2.70	0.003
	1.7 V	3.89 (±0.96)	2.004 (±0.004)	4.92 (±0.30)	2.70	0.012

## Note S1. Ru K-edge EXAFS data analysis

Using AUTOBK module in UWXAFS package,<sup>1</sup> the  $k^3$ -weighted Ru K-edge EXAFS spectra,  $k^3\chi(k)$ , have been obtained through background removal and normalization processes on the edge jump of ~ 22130 eV. In order to present effective radial distribution functions (RDF) for each sample during various electrocatalytic reactions, the  $k^3 \chi(k)$  spectra have been Fourier-transformed (FT) in the k range between 2.5 and 13.0 Å<sup>-1</sup> The experimental Fourier-filtered  $k^{3}\gamma(k)$  spectra have been inversely Fouriertransformed with the *hanning* window function in the r space range between 1.0 and 2.0 Å. To determine the structural parameters for the first Ru-O bond pair, the curve-fitting process has been carried out by using the single bonding model. Theoretical scattering path of octahedral Ru-6O single shell has been calculated with FEFF8 code under the space group of Fd-3m for the well-known cubic pyrochlore model.<sup>2,3</sup> In the EXAFS curve fitting process with FEFFIT module, total amplitude reduction factor,  $S_i^2$ , were fixed to 0.85 for the central Ru atom. The EXAFS structural parameters for each voltage-cutoff spectra, energy shift ( $\Delta E$ ), bond distance (R) and coordination numbers (N), have been determined with of allowed R-factor value which is quality the fit determined with  $\sum \{Re\Delta\chi(k)^2 + Im\Delta\chi(k)^2\} / \sum \{Re(\chi(k)_{data})^2 + Im(\chi(k)_{data})^2\}, \text{ where } \chi(k) \text{ is EXAFS-function}\}$ and  $\Delta \chi(k)$  means  $\chi(k)_{data} - \chi(k)_{best-fitted}$ . On the other hand, Debye–Waller factors ( $\sigma^2$ ) for voltage-cutoff

electrocatalytic reactions in each pyrochlore sample were fixed in the EXAFS fitting process.

## References

- 1 E.A. Stern, M. Newville, B. Ravel, Y. Yacoby, & D. Haskel, The UWXAFS analysis package: philosophy and details, *Physica B* **117**, 208-209, (1995).
- 2 A.L. Ankudinov, B. Ravel, J.J. Rehr, & S.D. Conradson, FEFF8: Real Space Multiple Scattering Calculation of XANES, *Phys. Rev. B* **58**, 7565 (1998).
- J. J. Rehr & R. C. Albers, Theoretical Approaches to X-ray Absorption Fine Structure, *Rev. Mod. Phys.* **72**, 621 (2000).