Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Identification of intermediates of a molecular ruthenium catalyst for water oxidation using *in-situ* electrochemical X-ray absorption spectroscopy

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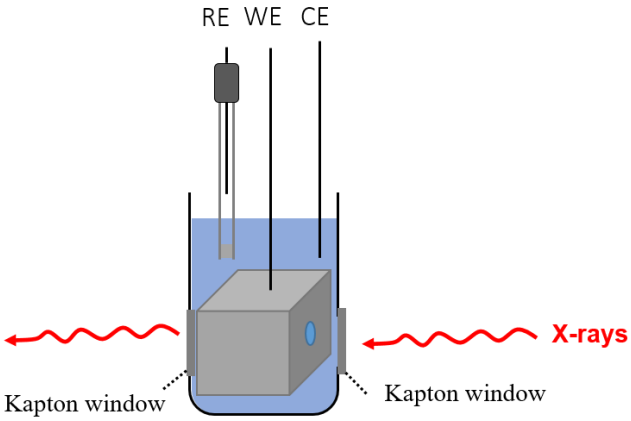

Figure S1. Illustration of in situ electrochemical cell. The cell contains a Kapton film as a window, which allows X-ray pass through. The working electrode (WE), reference electrode (RE), and counter electrode (CE) are glassy carbon foam, Ag/AgCl, and Pt respectively.

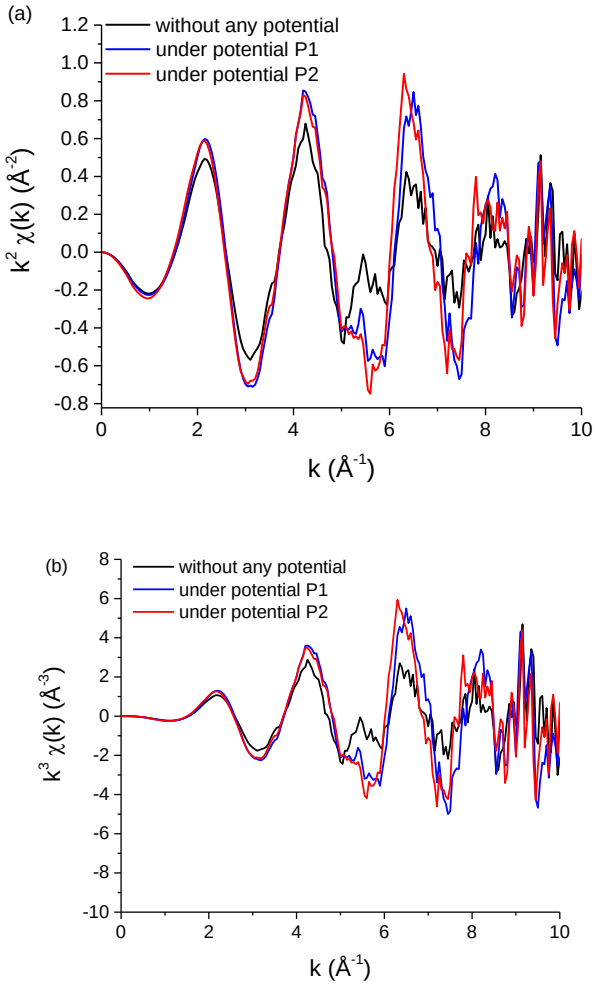

Figure S2. (a) k^2-weighted and (b) k^3-weighted EXAFS data $k^2\chi(k)$ of complex 1 in 0.1 M HNO_3 under no controlled potential (black line), under potential P1 (blue line) and potential P2 (red line).

Table S1. Best-fit parameters obtained from the EXAFS Ru K-edge of complex **1** in 0.1 M HNO_3 under no controlled potential and under potentials P1 and P2

Fit	Shell, N[a]	R[b], Å	$\sigma^2(10^{-3})$[c]	R-factor	Reduced χ-square
No potential	Ru—N, 4 Ru—O, 2	2.17 2.42	4 2	0.01	165
P1	Ru—N, 4 Ru—O, 3	2.12 2.17	13	0.03	382
P2	Ru—O3, 1 Ru—O2, 2 Ru—N3, 4	2.02 2.10 2.15	10	0.07	233

[a]coordination number per Ru center, [b]Ru-backscatter distance, [c]Debye-Waller factor. R-factor and reduced χ-square are the goodness of the fit parameters. Amplitude reduction factor S_0^2 = 1 was used in all the fits.

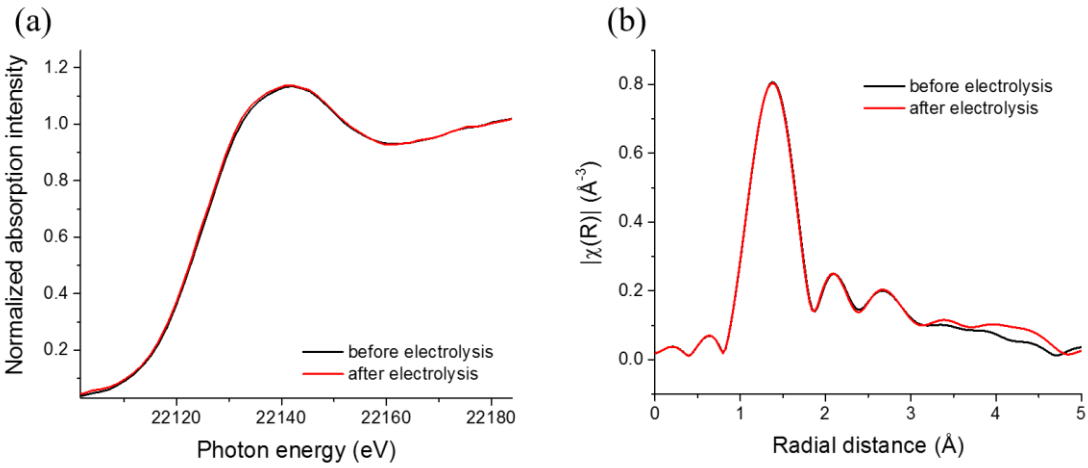

Figure S3 (a). Normalized XANES at Ru K-edge and (b) Fourier transformed EXAFS spectra of complex 1 in 0.1 M HNO_3 before and after electrolysis.

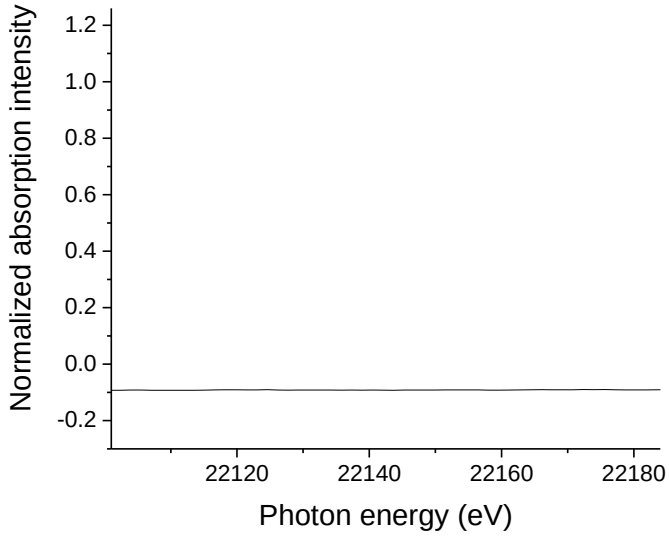

Figure S4. Normalized XANES at Ru K-edge and working electrode 0.1 M HNO_3 after experiment.

Table S2. Fit parameters obtained from EXAFS Ru K-edge of complex 1 in 0.1 M HNO_3 under no controlled potential, under potential P1 and potential P2.

Fit	Shell, N	R, Å	$\sigma^2(10^{-3})$	ΔE_0	ΔR	Reff	R-factor	Reduced χ-square
under no controlled potential The crystal structure used for EXAFS fitting is from reference 1[1] 1-7.3 k-space, 1-2.4 R-space								
1	Ru—N, 6	2.19	25	2.36	0.10	2.09	0.08	609
2	Ru—N1, 1 Ru—N2, 1 Ru—N4, 2	2.07 2.11 2.24	3	7.47	0.16 0.16 0.17	1.91 1.94 2.07	0.14	885

	Ru—O2, 1 Ru—O3, 1	2.39 2.35			0.18 0.18	2.17 2.21		
3	Ru—N, 4 Ru—O, 2	2.17 2.42	5	7.47	0.23 0.25	1.95 2.17	0.02	581
4	Ru—N, 4 Ru—O, 2	2.17 2.42	5 3	7.85	0.23 0.25	1.95 2.17	0.02	381
0.8-8 k-space, 1-2.4 R-space								
5	Ru—N, 4 Ru—O, 2	2.17 2.42	4 2	7.67	0.23 0.25	1.95 2.17	0.01	165
under no controlled potential The crystal structure used for EXAFS fitting is from reference 2[2] 1-7.3 k-space, 1-2 R-space								
6	Ru—N, 6	2.18	25	2.57	0.08	2.10	0.06	1337
7	Ru—N1, 2 Ru—N2, 2 Ru—O1, 2	2.06 2.22 2.33	3	7.47	0.14	1.92 2.08 2.32	0.12	2400
8	Ru—N2, 4 Ru—O, 2	2.17 2.27	15	6.94	0.08	2.08 2.18	0.08	1876
9	Ru—N1, 4 Ru—O, 2	2.18 2.44	3	8.57 8.57	0.25	1.92 2.18	0.02	375
under potential P1 1-7.3 k-space, 1-2 R-space								
10	Ru—N, 6	2.11	12				0.071	5631
under potential P1 The crystal structure used for EXAFS fitting is from reference 2[2] 1-10 k-space, 1-1.86 R-space								
11	Ru—N2, 2 Ru—O2, 1 Ru—O3, 1 Ru—N3, 2	2.09 2.14 2.14 2.17	9	4.61	0.09	1.99 2.04 2.04 2.07	0.03	408
12	Ru—N2, 2 Ru—O2, 2 Ru—O3, 1 Ru—N3, 2	2.09 2.14 2.15 2.18	13	5.03	0.10	1.99 2.04 2.04 2.07	0.03	385
13	Ru—N2, 1 Ru—O2, 2 Ru—O3, 1 Ru—N3, 2	2.08 2.12 2.13 2.16	10	4.61	0.08	1.99 2.04 2.04 2.07	0.03	417
14	Ru—N2, 2 Ru—O2, 2 Ru—O3, 1 Ru—N3, 1	2.09 2.14 2.14 2.17	10	4.61	0.09	1.99 2.04 2.04 2.07	0.03	417
15	Ru—N2, 4 Ru—O2, 3	2.12 2.17	13	5.03	0.12	1.99 2.04	0.03	382

16	Ru—N2, 4 Ru—O2, 2	2.12 2.17	9	4.89	0.12	1.99 2.04	0.03	420
17	Ru—N2, 3 Ru—O2, 3	2.11 2.15	10	4.89	0.11	1.99 2.04	0.03	429
18	Ru—O2, 3 Ru—N3, 4	2.13 2.16	14	5.34	0.08	2.04 2.07	0.03	392
19	Ru—O2, 2 Ru—N3, 4	2.11 2.15	10	4.61	0.07	2.04 2.07	0.03	406
20	Ru—O2, 3 Ru—N3, 3	2.11 2.15	10	4.61	0.07	2.04 2.07	0.03	414
21	Ru—N2, 4 Ru—O3, 3	2.12 2.17	13	5.03	0.12	1.99 2.04	0.03	382
22	Ru—N2, 4 Ru—O3, 2	2.12 2.17	8	4.89	0.12	1.99 2.04	0.03	419
23	Ru—N2, 3 Ru—O3, 3	2.11 2.16	9	4.89	0.11	1.99 2.04	0.03	429
under potential P1 The crystal structure used for EXAFS fitting is from reference 2[2] 1-10 k-space, 1-1.92 R-space								
24	Ru—N2,4 Ru—O2,2	2.08 2.19	5	3.51 3.69	0.005	2.08 2.19	0.064	597
25	Ru—N2,4 Ru—O2,3	2.07 2.18	8	3.44 3.61	- 0.005	2.08 2.19	0.064	556
under potential P1 The crystal structure used for EXAFS fitting is from reference 3[3] 1-10 k-space, 1-1.92 R-space								
26	Ru—N1, 2 Ru—O1, 2 Ru—N2, 2	2.06 2.12 2.14	7	4.07 4.20 4.24	0.07	1.99 2.05 2.07	0.062	597
27	Ru—N1, 2 Ru—O1, 3 Ru—N2, 2	2.06 2.13 2.15	11	4.20 4.33 4.37	0.07	1.99 2.05 2.07	0.061	552
28	Ru—N1, 4 Ru—O1, 2	2.1 2.12	9	4.41 4.45	0.05	2.05 2.07	0.064	605
29	Ru—N1, 4 Ru—O1, 3	2.09 2.15	10	4.32 4.45	0.09	1.99 2.05	0.062	554

under potential P2 The crystal structure (Ru^{IV} dimer) used for EXAFS fitting is from reference 1 1-7.6 k-space, 1-1.92 R-space								
30	Ru—N, 6	2.10	9	1.14	-0.002	2.10	0.016	1981
31	Ru—O3, 1 Ru—O2, 2 Ru—N3, 4	2.01 2.09 2.13	9	7.47	0.050 0.052 0.053	1.96 2.03 2.08	0.025	3418
32	Ru—O3, 1 Ru—O2, 1 Ru—N3, 4	2.00 2.08 2.13	6	7.07	0.042 0.044 0.045	1.96 2.03 2.08	0.018	3414
under potential P2 The crystal structure (Ru^{IV} dimer) used for EXAFS fitting is from reference 1 1-10 k-space, 1-1.92 R-space								
33	Ru—O3, 1 Ru—O2, 2 Ru—N3, 4	2.02 2.10 2.15	10	8.01	0.063 0.065 0.067	1.96 2.03 2.08	0.079	233

N, coordination number for per Ru center. R, Ru-backscatter distance. σ^2, Debye-Waller factor. ΔE_0, the energy shift parameter. ΔR, change in half-path length. Reff, initial half path length. R-factor and Reduced χ-square are the goodness of the fit parameters. Amplitude reduction factor $S_0^2 = 1$ was used in all fits.

References:

1. Duan, L.; Fischer, A.; Xu, Y.; Sun, L., *J. Am. Chem. Soc.* **2009,** 131, 10397-10399.
2. Duan, L.; Wang, L.; Inge, A. K.; Fischer, A.; Zou, X.; Sun, L., *Inorg. Chem.* **2013,** 52, 7844-7852.
3. Concepcion, J. J.; Zhong, D. K.; Szalda, D. J.; Muckerman, J. T.; Fujita, E., *Chem. Commun.* **2015,** 51, 4105-4108.