Supplementary Information for "An in Situ XAS Study of High Surface-Area IrO_2 Produced by the Polymeric Precursor Synthesis"

Anita Hamar Reksten^{*} Frode Seland Svein Sunde[†]

Department of Materials Science and Engineering, Norwegian University of Science and Technology (NTNU) NO-7491 Trondheim, Norway

> Andrea E. Russell and Peter W. Richardson Stephen J. Thompson Department of Chemistry, University of Southampton

> > Southampton SO17 1BJ, England

Karina Mathisen Department of Chemistry, Norwegian University of Science and Technology (NTNU), NO-7491 Trondheim, Norway

March 26, 2020

S.1 XAS in situ cell

The cell used for the in situ XAS measurement of PPS Ir powder is shown in Figure S.1.

^{*}Current address: SINTEF Sustainable Energy Technology, NO-0373 Oslo, Norway

 $^{^{\}dagger}$ Corresponding author. Tel.: +47 73594051; fax: +47 73591105, *E-mail address:* Svein.Sunde@material.ntnu.no



Figure S.1: Cell used for in situ XAS measurements from two different angles.

S.2 EXAFS parameters from ex situ XAS of $Ir-IrO_2$

EXAFS parameters from ex situ XAS of Ir-IrO_2 are given in Table S.1.

ne p.1	$\Lambda_{\rm lr}$ -1 ch s	10u, 10-16	1001-31.10, K-lange	10Λ ,	$E_0 - 3($
	Shell	\mathbf{CN}	Bond length / Å	$\mathbf{DW} / \mathbf{\mathring{A}}^2$	
	Ir-O	1.7(3)	1.97(1)	0.003(2)	
	Ir-Ir, $Met1$	6.3(3)	2.706(3)	0.0067(2)	
	Ir-Ir, Ox1	0.6(2)	3.15(1)	0.003(2)	
	Ir-Ir, Ox2	1.3(2)	3.534(9)	0.003(1)	
	Ir-Ir, $Met2$	3.3(6)	3.831(9)	0.006(1)	
	Ir-Ir, Met3	10(1)	4.708(7)	0.0085(8)	

Table S.1: $X_{Ir}=1$ ex situ, R-factor=31.16, k-range 2 - 18 Å⁻¹, $E_0=-9(1)$

S.3 EXAFS parameters from in situ potential cycling of $Ir-IrO_2$

The experimentally obtained bond lengths as function of potential cycling of the sample prepared by the A-synthesis are shown in Fig. S.2. A reference bond length is not provided for the oxygen shell, Fig. 2(a), as this shell represents a mix of two different oxygen shells, one at 1.94 Å of two atoms and one at 2.00 Å of four atoms, but these have been refined as one shell consisting of six oxygen atoms. The bond lengths obtained are more or less stable over the cycling, with some exceptions. The first elemental metal shell, Fig. 2(b), and the second metal oxide shell, Fig. 2(d), show the largest deviation from the reference values, and both show a contraction over the course of cycling.

The coordination numbers obtained from EXAFS for the sample prepared by the A-synthesis are shown in Fig. S.3 as function of the number of cycles. Since only a small decrease in the fraction of elemental iridium as a function of the number of cycles is demonstrated by LCF of the XANES spectra, any significant change in the coordination numbers as a function of potential cycling is not to be expected. Corrected multiplicities suggested by Martens et al. [1, 2] were introduced in order to estimate what the coordination numbers would have been if either the oxide or elemental metal phase were the sole phase present. The experimentally obtained coordination numbers were corrected by the fractions obtained from LCF of the XANES from fits in which Ir^{+3} were excluded ("Corrected multiplicities 1") and included ("Corrected multiplicities 2").



Figure S.2: Experimentally obtained bond lengths for the sample prepared by the A-synthesis as function of potential cycling, (a) the oxygen shell, (b) the first elemental metal shell, (c) the first metal oxide shell, (d) the second metal oxide shell, (e) the second elemental metal shell and (f) the third elemental metal shell. Reference value for the bond lengths are indicated by the red lines.



Figure S.3: See caption next page.



Figure S.3: Experimentally obtained coordination numbers and coordination numbers corrected by reduced fraction $(N_{\rm corr} = N_{\rm exp}/f_{\rm ph})$ for the sample prepared by the A-synthesis as function of cycling, (a) the oxygen shell, (b) the first elemental metal shell, (c) the first metal oxide shell, (d) the second metal oxide shell, (e) the second elemental metal shell and (f) the third elemental metal shell. Corrected multiplicity 1 and 2 are experimentally obtained Ndivided by the elemental metal and oxide fraction found without and with Ir⁺³ included in the LCF of XANES, respectively. Reference values for the coordination number are indicated by the red lines.

Fig. S.4 shows the corresponding Debye-Waller factors as a function of cycling.

The EXAFS parameters resulting from the refinements of the A-synthesis sample as function of potential cycling are given in table S.2 to S.5.

Table S.2: Parameters from refinement of EXAFS data for synthesis series A as recorded in situ after n=0 cycles. R-factor=41.38, k-range 2 – 18 Å⁻¹, E_0 =-9(2) CN = coordination number. DW = Debye-Waller factor.

Shell	\mathbf{CN}	Bond length / Å	$\mathbf{DW} / \mathbf{\AA}^2$
Ir-O	1.7(5)	1.97(2)	0.002(3)
Ir-Ir, Met1	6.3(4)	2.704(4)	0.0058(3)
Ir-Ir, Ox1	0.6(5)	3.18(4)	0.005(5)
Ir-Ir, Ox2	1.3(4)	3.53(2)	0.003(2)
Ir-Ir, $Met2$	3.3(8)	3.81(1)	0.006(2)
Ir-Ir, Met3	10(2)	4.70(1)	0.007(1)

Table S.3: Parameters from refinement of EXAFS data for synthesis series A as recorded in situ after n=25 cycles. R-factor=35.43, k-range 2 – 18 Å⁻¹, E_0 =-8(1) CN = coordination number. DW = Debye-Waller factor

Shell	\mathbf{CN}	Bond length / Å	$\mathbf{DW} / \mathbf{\AA}^2$
Ir-O	2.1(6)	1.97(2)	0.006(4)
Ir-Ir, Met1	6.3(3)	2.701(3)	0.0058(3)
Ir-Ir, Ox1	0.6(2)	3.18(1)	0.001(2)
Ir-Ir, Ox2	1.2(2)	3.53(1)	0.0009(9)
Ir-Ir, Met2	3.2(7)	3.84(1)	0.005(1)
Ir-Ir, Met3	9(1)	4.709(8)	0.0073(8)

S.4 High-resolution TEM imaging

An image of an IrO_2/Ira sample synthesized by synthesis A is shown in Fig. S.5. The image shows little contrast. However, Fig. S.6 shows a high-resolution TEM image of a less denser part of the sample. The lattice fringes correspond to a distance between lattice planes approximately equal to 3.3 Å. In another image (not shown) similar lattice fringes appeared at a distance 3.18 Å apart.



Figure S.4: Debye-Waller factors for the sample prepared by the A-synthesis as function of potential cycling, (a) the oxygen shell, (b) the first elemental metal shell, (c) the first metal oxide shell, (d) the second metal oxide shell, (e) the second elemental metal shell and (e) the third elemental metal shell.

Shell	CN	Bond length / Å	$\mathbf{DW} / \mathbf{A}^2$
Ir-O	2.0(5)	1.96(2)	0.005(3)
Ir-Ir, Met1	6.5(3)	2.700(4)	0.0063(3)
Ir-Ir, Ox1	0.6(2)	3.15(2)	0.002(2)
Ir-Ir, Ox2	1.1(2)	3.52(2)	0.002(2)
Ir-Ir, Met2	2.9(6)	3.81(1)	0.004(1)
Ir-Ir, Met3	9(2)	4.696(9)	0.008(1)

Table S.4: Parameters from refinement of EXAFS data for synthesis series A as recorded in situ after n=100 cycles. R-factor=37.16, k-range 2 – 18 Å⁻¹, E_0 =-8(2). CN = coordination number. DW = Debye-Waller factor

Table S.5: Parameters from refinement of EXAFS data for synthesis series A as recorded in situ after n=150 cycles. R-factor=37.16, k-range 2 – 18 Å⁻¹, E_0 =-8(2) CN = coordination number. DW = Debye-Waller factor.

Shell	\mathbf{CN}	Bond length / Å	$\mathbf{DW} \ / \ \mathbf{A}^2$
Ir-O	2.0(6)	1.97(2)	0.004(3)
Ir-Ir, Met1	6.6(4)	2.70(4)	0.0067(3)
Ir-Ir, Ox1	0.5(2)	3.15(2)	0.001(23)
Ir-Ir, Ox2	1.0(2)	3.52(1)	0.0004(16)
Ir-Ir, Met2	2.6(5)	3.84(1)	0.003(1)
Ir-Ir, Met3	9(1)	4.710(8)	0.006(8)



Figure S.5: TEM image of an $\rm Ir/IrO_2$ catalyst (as made).



Figure S.6: High-resolution TEM image of an $\rm Ir/IrO_2$ catalyst (as made). The distance between the lattice fringes is approximately 3.3 Å.

References

- J. H. A. Martens, R. Prins, and D. C. Koningsberger. Controlled oxygen chemisorption on an alumina supported rhodium catalyst. The formation of a new metal-metal oxide interface determined with EXAFS. *The Journal of Physical Chemistry*, 93(8):3179–3185, 1989.
- [2] Anita Hamar Reksten, Andrea E. Russell, Peter W. Richardson, Stephen J. Thompson, Karina Mathisen, Frode Seland, and Svein Sunde. Strategies for the analysis of the elemental metal fraction of Ir and Ru oxides via XRD, XANES, and EXAFS. *Phys. Chem. Chem. Phys.*, 21(23):12217–12230, JUN 21 2019.