Supporting Information

Impact of Ir-Valence Control and Surface Nanostructure on Oxygen

Evolution Reaction over a Highly Efficient Ir-TiO₂ Nanorod Catalyst

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Note regarding electrochemical active area (ECSA) of ITOT catalyst

Measuring ECSA is useful to estimate the electrochemically active surface area of Ptbased catalysts, which is obtained from the reversible adsorption and desorption of hydrogen on Pt. During the measurement, Pt remains metallic phase. In the case of IrO_x , however, the hydrogen desorption peak of the ECSA of an IrO_x -carbon support catalyst rapidly disappeared as the Ir oxidation increased, as was reported in the previous work by our group members¹. The same trend was also reported by Oh et al.,² in which the Ir black showed an obvious hydrogen desorption peak in the ECSA curves, while after oxidation, it disappeared. Furthermore, once Ir is oxidized, it would not be electrochemically reduced during the CV operation. Hence, in this study, we are not able to provide ECSA-normalized specific activities of the IrO_x based catalysts.

The experimental evidence for the above mentioned response to the comment is shown in Figure A. We measured CV to obtain ECSA value of our ITOT catalyst according the well-known method for ECSA evaluation of Pt catalysts. We recognize that the CV curves of the ITOT are quite different from that of conventional Pt-based catalysts. In our catalyst, we see no evident hydrogen desorption area in the CVs, and such results are very similar to the oxidized Ir catalysts discussed above^{1,2}. Therefore, ECSA is not appropriate to evaluate the electrochemical activity of our ITOT catalyst because the Ir nanoparticles on the surface are easily oxidized during the CV cycling processes.

Based on the references and the obtained results, we conclude that ECSA is not suitable to evaluate ITOT catalysts.



Figure S1. CV curves of the ITOT catalyst measured at room temperature (25 °C) in $0.05 \text{ M H}_2\text{SO}_4$ electrolyte solution.

Synthesis of ITOT catalyst

IrCl₃ is soluble in an ethylene glycol (EG)-water mixture solution. The solution amount of EG+H₂O is 75 mL. Before the reaction, IrCl₃ was pre-dispersed and sonicated for ~1h to dissolve in the solvent. In this study, we used IrCl₃·xH₂O purchased from Tokyo Chemical Industry Co., Ltd. We have prepared ITOT catalyst with different IrO_x loading (from 0.08 to 0.58 mg cm⁻²), which is controlled by changing the amount of IrCl₃·xH₂O (from 6 mg to 24 mg). The actual IrO_x loading amounts were determined by the formula of (M₂-M₁)/S, where M₁ and M₂ are the mass of TOT mesh before and after the reflux process, S is the surface area of TOT mesh, for details, see in Experimental Section). The loading of IrO_x = 0.58 mg cm⁻² was chosen for further mechanism study.

Temperature 140 °C is the azeotropic temperature of the EG+H₂O (6:4) mixture solution. Only in the azeotropic condition, the N₂ gas can be involved in the reaction and reflux occurs. Actually, the temperature from 140 to 160 °C is feasible and we finally did at 140 °C in this experiment.

 IrO_x on the TOT mesh is the mixture of Ir nanometal particles and IrO_2 . In this research, we have obtained ITOT with different IrO_x loadings (0.08, 0.33, 0.38, 0.44 and 0.58 mg cm⁻²) and chosen $IrO_x = 0.58$ mg cm⁻² for further mechanism study.

Note regarding the CV curves shape of ITOT catalyst

We discuss about CV curve shape of our catalyst. If the catalyst is pure IrO₂, the doublelayer capacitance should be very small³. In this case, no apparent Ir(III)/Ir(IV) waves were observed during the OER. This is consistent with the results for calcined ITOT catalyst, which is mainly IrO_x. If the amount of IrO_x is very low in the catalyst, such as film-coated $IrO_x(OH)_y^4$, TiO₂ supported IrO_x^5 , and SnO_2 supported IrO_x^6 , the Ir(III)/Ir(IV) waves are not obvious and the double-layer capacitance would exist, just like our pristine ITOT catalyst. One reason for this phenomenon is that the amount of IrO_x is very low, and IrO_x is almost in the surface, suggesting that it is already oxidized at the initial state. Another reason is that these IrO_x -based catalysts are Ir hydrated oxides, like $IrO_x(OH)_y$ and the double-layer capacitance is derived from the OH species on the surface. The faint surface Ir(III)/Ir(IV) wave is already overlapped by this double-layer capacitance. The amount of IrO_x in our pristine ITOT is very low and the surface OH species are very high, so the double-layer capacitance is remained while the Ir(III)/Ir(IV) wave is not obvious.

Supporting Figures



Figure S2. Photos of Ti (a), and TOT (b) meshes; SEM images of Ti (c) and TOT (d and e) meshes. TiO₂ nanorods were grown on the Ti mesh surfaces during the hydrothermal method to form a TOT mesh.



Figure S3. CV curves of the uncalcined ITOT catalysts with specified IrO_x loading amounts.



Figure S4. Ti 2p XPS spectra (455~468 eV range) of the ITOT before and after calcination at 350 °C for a specific time.



Figure S5. XRD diagrams of the TOT catalyst, pristine ITOT catalyst and calcined ITOT catalyst.



Figure S6. Setup for the *in situ* electrochemical XAS experiments.



Figure S7. Relationship between the bulk rutile IrO_2 structure and geometry of the trinuclear $Ir_3O_{14}H_{16}$ clusters.



Figure S8. HRTEM images of the (a) pristine ITOT catalyst after 700 CV-cycling test and (b) calcined ITOT catalyst. The insets of (a) and (b) are the distribution of particles size for the corresponding ITOT.

Figure S9. Nyquist plot of the ITOT catalyst before and after calcination at 350°C for a specific time. Their corresponding equivalent circuits are provided in the inset. The first intercept value between the Nyquist plot with the x axis represents the ohmic impedance R_0 of the measurement system. The difference between the intercepting values of the semicircular arc and the x axis generally means the charge transfer resistance R_{ct}^{7-11} .

Supporting Tables

Samples	electrolyte	Overpotential @ 10 mA cm ⁻² (mV)	E _{OER} @10mA cm ⁻² (V vs. RHE)	Tafel Slope (mV dec ⁻¹)	Reference
IrO _x @TiO ₂ - Ti mesh	0.05 M H ₂ SO ₄	200	1.43	48, 66	This work
IrO₂- RuO₂@Ru		299~312	1.51-1.53	53.1-56.2	
IrO ₂	0.5 M	317	1.55	57.3	12
Ir ₃ RuO ₃	H ₂ SO ₄	293	1.53	56.5	
IrO ₂ (CM)		318	1.54	-	
RuO ₂ (CM)		289	1.53	-	
Rulr _{0.2} O ₂	0.5 M H ₂ SO ₄	>320	-	-	13
IrO ₂ /NbTiO ₂	0.1 M HClO₄	~310	-	-	14
lrO₂ (lr−Ni)	0.5 M H₂SO₄	-	1.60	62	. 15
IrO ₂ /Ir Bulk	0.5 M H₂SO₄	-	1.64	57	
Pt–Ir alloy nano- catalysts	0.5 M H₂SO₄	-	1.57-1.58	79-96	16
IrO _x in Stabilizing RuO ₂	0.05 M H₂SO₄	356-405	1.62-1.68	-	17
Ni-Ir nano- cages	0.05 M H ₂ SO ₄	302	1.53-1.54	46.6-56.1	18
Ir nano- dendrites	0.05 M H ₂ SO ₄	280	1.63-1.72	55.6-57.7	2
IrFe alloy/C	0.5 M HClO₄	286-351	1.51-1.55	56-70	19
Cry-Ir	0.1 M HClO₄	-	1.51	76	20
Aut-IrO _x	0.5 M H ₂ SO ₄	-	1.48	-	21
leached- Ir _{0.7} Co _{0.3} O _x	0.5 M H ₂ SO ₄	≈260	1.56	40	22
Ir-Ni mixed oxide films	0.1 M HClO4	-	1.53-1.58	-	23
dtf-Ir ₂₅ Os ₇₅	0.1M HClO₄	-	≈ 1.52	-	24
Ir/M₄N	0.5 M H ₂ SO ₄	316-346	≈ 1.52	-	25
Pt/IrO ₂	0.5 M H ₂ SO ₄	-	1.52-1.57	-	26
Ir _x Mo _{1-x} O _õ	0.1 M HClO4	-	≈ 1.54	57	27
A-IrO _x -B	0.1 M HClO ₄	283	1.554	-	28
Ir ₂ Sn ₁ O _x -Ar	0.5 M H ₂ SO ₄	-	≈ 1.54	49	29

Table S1. Comparison of OER performance between the ITOT mesh and state-of-theart Ir(Ru)-based catalysts.

Table S2. Values of relative content of OH species (θ) and the E_{OER} of the ITOT catalysts after calcination for a specific time. The value of θ is calculated by the equation: $\theta = \frac{OH \ peak \ area}{O \ 1s \ peak \ area}$, which comes from the XPS curve area in Fig. 3c. The value of E_{OER} is the potential at the 10 mA/cm⁻² current density on the CV curves shown in Fig. 3b. The η value can represent the concentration of OH species. The lower E_{OER} value corresponds to a higher OER performance. The relevant contents of the

Different calcined samples	Relative percentage of OH species (θ)	<i>E</i> _{OER} @10mA cm ⁻² (V vs. RHE)
Pristine ITOT	60%	1.428
Calcined ITOT 10 min	45%	1.473
Calcined ITOT 30 min	43%	1.487
Calcined ITOT 60 min	41%	1.507

concentration of the OH species and the E_{OER} values are shown in Fig. 3d.

Table S3. Relative contents of different Ir valences states calculated from their peak area in Ir 4f XPS spectra. As shown in Fig. 3e, the relative content of Ir^0 is calculated

by the equation: $\eta_{Ir0} = \frac{red \ curves \ area}{Ir \ 4f \ curve \ area}$. Similarly, $\eta_{Ir} = \frac{green \ curves \ area}{Ir \ 4f \ curve \ area}$, $\eta_{Ir} \ N$

 $=\frac{blue\ curves\ area}{lr\ 4f\ curve\ area}.$ These η values can represent the relative contents of the Ir valence

states in different calcined samples, which are intuitively presented in Fig. 3f.

Different calcined	Relative content of Ir ⁰	Relative content of Ir	Relative content of Irv	
samples	$\eta_{Ir^{0}}$	Ŋırıı	Ŋırw	
Pristine ITOT	51%	32%	18%	
Calcined ITOT 10min	49%	29%	22%	
Calcined ITOT 30min	42%	28%	30%	
Calcined ITOT 60min	39%	23%	38%	

Table S4. Values of relative percentage of OH species (θ) and the E_{OER} of the ITOT meshes after CV-cycling tests. The value of θ is calculated by the equation: θ

 $=\frac{OH \ peak \ area}{O \ 1s \ peak \ area}$, which comes from the curves area in Fig. 4c. The value of E_{OER} is the

potential at the 10 mA/cm⁻² current density on the CV curves, shown in Fig. 4b. The relative contents of the OH species (%) obtained by the O 1s XPS curves and $E_{OER}@10$ mA/cm² as a function of the provided CV-cycles are shown in Fig. 4d.

Different CV cycles	Different CV cycles Relative percentage of OH species (θ)	
After 5 cycles	60%	1.428
After 60 cycles	55%	1.445
After 120 cycles	55%	1.446
After 300 cycles	54%	1.455
After 700 cycles	53%	1.461

Table S5. Relative contents of different Ir valences calculated from their peak areas in Ir 4f XPS spectra. As shown in Fig. 4e, the relative content of Ir⁰ was calculated by the equation: $\eta_{Im} = \frac{red \ curves \ area}{whole \ curves \ area}$. Similarly, $\eta_{Im} = \frac{green \ curves \ area}{whole \ curves \ area}$, $\eta_{Im} = \frac{blue \ curves \ area}{whole \ curves \ area}$. These η values represent the relative contents of different Ir valence states in the samples after the given CV cycles, which are presented in Fig. 4f.

Different CV cycles	Relative content of Ir ⁰	Relative content of Ir	Relative content of Irv	
	$\eta_{{\scriptscriptstyle Ir}{\scriptscriptstyle 0}}$	Ŋırıı	Ŋırw	
After 5 cycles	51%	33%	17%	
After 60 cycles	43%	33%	24%	
After 120 cycles	46%	31%	22%	
After 300 cycles	44%	34%	22%	
After 700 cycles	44%	35%	22%	

Table S6. Coordination environment of the Ir atoms in the computational models: number of different ligands around various Ir atoms.

	-OH	-OH2	Ir-O(-Ir)		
<u>Ir3 a</u>					
Ir1	4	0	2		
Ir2	2	1	3		
Ir3	2	1	3		
<u>Ir3 b</u>					
Ir1	3	1	2		
Ir2	2	1	3		
Ir3	3	0	3		
<u>Ir3 c</u>					
Ir1	4	0	2		
Ir2	2	1	3		
Ir3	2	1	3		
<u>Ir3 d</u>					
Ir1	3	1	2		
Ir2	2	1	3		
Ir3	3	0	3		

	<u>lr3_a</u>	<u>lr3_b</u>	<u>lr3_c</u>	<u>lr3_d</u>
lr1	0.802	0.679	0.803	0.718
lr2	0.653	0.718	0.656	0.670
lr3	0.659	0.739	0.666	0.771

Table S7. Mulliken charge of Ir atoms in the computational models.

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