Impact of Ir-Valence Control and Surface Nanostructure on Oxygen Evolution Reaction over a Highly Efficient Ir–TiO2 Nanorod Catalyst

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ABSTRACT: Iridium oxide (IrOx)-based materials are the most suitable oxygen evolution reaction (OER) catalysts for water electrolysis in acidic media. There is a strong demand from industry for improved performance and reduction of the Ir amount. Here, we report a composite catalyst, IrOx–TiO2–Ti (ITOT), with a high concentration of active OH species and mixed valence IrOx on its surface. We have discovered that the obtained ITOT catalyst shows an outstanding OER activity (1.43 V vs RHE at 10 mA cm–2) in acidic media. Moreover, no apparent potential increase was observed even after a chronopotentiometry test at 10 mA cm–2 for 100 h and cyclic voltammetry for 700 cycles. We proposed a detailed OER mechanism on the basis of the analysis of the in situ electrochemical X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) measurements as well as density functional theory (DFT) calculations. All together, we have concluded that controllable Ir-valence and the high OH concentration in the catalyst is crucial for the obtained high OER activity.

KEYWORDS: Ir-oxide catalyst, iridium-valence-engineering, oxygen evolution reaction (OER), in situ electrochemical XANES and EXAFS

1. INTRODUCTION

To develop reliable renewable energy technologies is always the prevailing strategy to balance the mismatch between energy supply and demand. Water electrolysis is a potentially effective method to address the issues of environmental emissions and energy sustainability,1,2 but it has the challenge of a sluggish oxygen evolution reaction (OER).3,4 IrOx-based materials are regarded as the most promising candidates in acidic media, but they are still limited because of the high cost of the Ir metal.5–7

To solve this problem, it is crucial to design and fabricate a new catalyst with a very high OER performance and a reduced Ir amount. One solution for this goal is to regulate the microstructures of the IrOx catalysts with a high specific surface area8 by fabricating ultrathin laminar structures,9 core–shell nanoparticles (NPs),10 nanodendrites,11 nanofibers,12 subnanometer clusters,13 and so on. However, the key factors for the OER activity should be active species bonded to the catalysts’ surfaces together with the intrinsic features of the catalysts.14–18 Hence, some amorphous iridium oxides or iridium oxohydroxides were prepared in order to obtain a high concentration of the OH species, but their long-term stability was not clearly determined.19–21 Well-crystallized IrOx catalysts with a high stability were also synthesized by a high-temperature process (≥400 °C);22–24 however, their activity was reduced by this calcination treatment. Therefore, to ensure both OER activity and stability, technical issues with respect to the Ir-based OER catalyst design still remain.
Another approach is to disperse the IrO$_x$ on an electronically conductive substrate for increasing the efficient utilization of the noble metal. Typically, carbon is a widely used substrate material for electrocatalysts, but there are still problems of low long-term stability and weak interaction between the carbon support and the deposited catalysts.\textsuperscript{23–27} To address this issue, several alternatives have been reported, for example, titanium, silicon, and tantalum carbides\textsuperscript{28–31} are potentially suitable substrates, but high-temperature annealing is necessary to form a strong contact between these carbides and the deposited catalysts. Among other alternatives, metal oxides, such as TiO$_2$,\textsuperscript{32–34} Ta$_2$O$_5$,\textsuperscript{35} SnO$_2$,\textsuperscript{27,36} and so on, are expected to be the most favorable support materials; meanwhile, it is still worthwhile to develop an appropriate structure design between the metal oxides and IrO$_x$ to provide both a high OER activity and long-term durability.

We recently fabricated a Ti mesh-supported TiO$_2$-nanorods (TOT) material with a high surface area.\textsuperscript{37–39} Inspired by this structure, we designed a new OER catalyst with a 3D structure, schematically presented in Figure 1, in which IrO$_x$ nanoparticles are deposited on the surface of Ti-based nanorods. The obtained IrO$_x$–TiO$_2$–Ti (ITOT) shows an excellent OER activity and long-term stability in acidic media. In this study, we have examined the active species bonded to the ITOT surface and the unique Ir valence state in the ITOT catalyst. According to in situ X-ray absorption spectroscopy (XAS) measurements, we have clearly revealed the dynamic change in the Ir oxidation states and experimentally demonstrated the variable Ir valence during the OER. Furthermore, we have carried out density function theory (DFT) calculations on small trinuclear Ir–O$_2$ clusters, and we explored the influence factor of the Ir valence state. On the basis of these experimental and simulation results, we have proposed a catalytic mechanism with respect to the high activity and durability of the obtained ITOT catalyst.

2. EXPERIMENTAL SECTION

Synthesis of Materials. The Ti mesh (Manabe Industry, Co.), NaOH (Kanto Chemical), and HCl (Kanto Chemical) were used as purchased. IrCl$_3$·xH$_2$O and ethylene glycol (EG) were purchased from Tokyo Chemical Industry Co., Ltd., and Wako Pure Chemical, Ltd., respectively.

A TOT mesh was prepared by a two-step hydrothermal method as already described.\textsuperscript{37} The Ti mesh (area: 2 cm × 2 cm) was put in a Teflon-lined autoclave with 30 mL of a 1 M NaOH aqueous solution and then heated at 220 °C for 12 h to grow H$_2$Ti$_2$O$_5$·H$_2$O on the electrode as the first step. The obtained Ti mesh was then washed with water and immersed in a 0.1 M HCl aqueous solution for 10 min followed by washing with water and ethanol. After it was dried in air, the treated Ti mesh was placed in the Teflon-lined autoclave again with 40 mL of water and kept at 200 °C for 24 h to convert H$_2$Ti$_2$O$_5$·H$_2$O to the anatase TiO$_2$ on the surface. After it was washed and dried, the TOT mesh was measured. The weight and area were recorded as $M_1$ and $S$, respectively.

Then this mesh was immersed into an IrCl$_3$ solution under an N$_2$ atmosphere for 6 h in an oil bath (140 °C) and refluxed to deposit IrO$_x$ nanoparticles on the surfaces of the TOT mesh (for details, see the Supporting Information). After it was washed and dried, the obtained ITOT mesh was weighed and recorded as $M_2$. The deposition amounts of the IrO$_x$ can be determined by the concentration of the IrCl$_3$ solution and calculated by the formula of $\frac{M_2 - M_1}{S}$.

Characterization of Materials. SEM images were acquired using an SU9000 (Hitachi High-Technologies) operated at 30 kV. The high-resolution TEM and EDX-STEM images were taken by a JEM-ARM200F instrument (JEOL Ltd.) at 200 kV.

X-ray photoelectron spectroscopy (XPS) spectra were obtained by an AXIS-ULTRA DLD (Shimadzu, Co., Japan). X-ray diffraction analysis (XRD) was conducted using a SmartLab (Rigaku Corp.) instrument. The synchrotron radiation experiments were performed at BL44B2 in SPring-8 with the approval of RIKEN. The data were acquired using the Debye–Scherrer camera equipped with an imaging plate as an X-ray detector. The incident wavelengths were 0.80024 Å, which were obtained by calibration using CeO$_2$ as a standard powder sample. The X-ray beam was collimated by a 0.5 mm by 3.0 mm double slit. Powder samples were sealed in a 3.0 mm double slit.
borosilicate glass capillaries under ambient air. The samples were irradiated by X-rays at 300 K.

The X-ray absorption fine structure (XAFS) spectra were recorded for the Ir L$_{III}$-edge Ti K-edge at the BL 06 (Kyushu University beamline) of the SAGA-LS (Saga, Japan) with a storage ring operating at the energy of 1.4 GeV. The energy range of this light source (bending magnet) was 2.1–23 keV. A silicon (111) double-crystal monochromator was used to obtain the incident X-ray beam. The typical photon flux was $10^9$ photons/sec. The intensities of the fluorescence X-rays were monitored by a silicon drift detector. Powder samples of the Ir, IrO$_2$, and TiO$_2$ were diluted with boron nitride to provide the optimum concentration and then pressed into a tablet with a diameter of 1 cm. The spectra of the prepared pellet samples were measured in the transmission mode, and the spectra of the mesh electrodes were measured using the fluorescence and conversion electron yield modes. Data processing was carried out by Athena and Artemis included in the Iffit package.

In situ electrochemical XAS measurements were performed by employing a three-electrode system connected to a VersaSTAT4 potentiostat using a laboratory-prepared polypropylene cell with a polyethylene cap. The cuboid polypropylene cell has a measurement window of 1.6 $\times$ 1.6 cm at a side wall where a Kapton film (7.5 μm thickness) covered the whole window area, and the ITOT electrodes were fixed at a distance of two millimeters from the Kapton film inside the cell. An aqueous electrolyte solution of 0.05 M H$_2$SO$_4$ was added to the cell, and Ag/AgCl reference and Pt counter coil electrodes were placed inside the cell. While the electrochemical reactions were conducted by application of constant anode potentials with vigorous stirring under ambient air, in situ XAS measurements were conducted in the fluorescence mode. The in situ electrochemical measurements were conducted on the pristine ITOT catalyst at various fixed potentials between 1.05–2.2 V, and each potential remained constant during each step. We also used the 350 °C calcined (2 h) ITOT catalyst in the same way. The XAFS spectra under application of various potentials were collected using the identical uncalcined and calcined ITOT electrodes without change in the electrolyte solution.

**Electrochemical Measurements.** The OER performances of the ITOT catalysts were measured using a three-electrode system. The electrochemical characterization and Nyquist plots were conducted by a Model 760E Electrochemical Analyzer (ALS Co., Ltd.) at room temperature (25 °C) in 0.05 M H$_2$SO$_4$ electrolyte solution. All potentials reported in this paper were normalized with respect to the reversible hydrogen electrode (RHE). The IR-compensated OER polarization curves were collected in a N$_2$-saturated electrolyte at the sweep rate of 10 mV s$^{-1}$. The potential vs.
Ag/AgCl was converted to the reversible hydrogen electrode (RHE) scale by the following equation:

$$E_{\text{vs RHE}} = E_{\text{vs Ag/AgCl}} + 0.197 + 0.059V \times \text{pH}$$

For the durability test, the electrodes were held at a constant current density of 10 mA cm$^{-2}$. The potentials were recorded as a function of time and after IR-compensated. All of the impedance data are recorded at open circuit voltage. We described the specific activity of ITOT in the Supporting Information (Figure S1).

**Theoretical Calculations.** Ir$_3$ (Ir$_3$O$_{14}$H$_{16}$) cluster models were created by cutting out from the IrO$_2$ rutile lattice so they contain three Ir with octahedral coordination and an O bridge between them. In the crystalline IrO$_2$, Ir$-$O$-$Ir chains are formed in the x/y directions, while Ir$-$O$_2$-$Ir chains occur in the z direction. Our computational models were chosen so they contain both of these Ir$-$O$-$Ir and Ir$-$O$_2$-$Ir bridges, and the remaining coordination of Ir was capped with $\text{OH}$ and $\text{OH}_2$ groups. Three nuclear clusters were chosen as they contain bridging Ir$-$O$-$Ir, I$-$O$_2$-$Ir as well as terminal Ir$-$OH/Ir$-$OH$_2$ groups. To determine the stoichiometry of the clusters (thus the number of $\text{OH}_{2}$ ligands), we assumed that all the three Ir are in Ir(IV) state and the clusters are neutral. For the calculation, we used the DFT method as implemented in DMOl3 using the PBE (GGG) functional and DNP (4,4) basis set. The convergence criteria for geometry optimization were $1.0 \times 10^{-5}$ Ha and $1.0 \times 10^{-6}$ Ha for the SCF. Because of the large number of states around the HOMO-LUMO gap, SCF convergence was only possible with thermal smearing ($0.01S$). The accuracy of the calculations was assessed compared to calculations with the B3LYP hybrid functional, leading to the same geometry and equivalent charges.

3. RESULTS AND DISCUSSION

We selected Ti mesh as the framework and then synthesized the TOT mesh via a hydrothermal method. After the hydrothermal process, the black Ti mesh was covered by Ti-based nanorods (see the photo and SEM in Figure S2). We synthesized the ITOT catalyst by a wet-process reduction method in order to avoid an annealing treatment.

**Nanoscale Structure of the Catalyst (ITOT).** The microscopic images of the obtained ITOT catalyst are shown in Figure 2. In the catalyst, uniform nanoparticles were homogeneously deposited on the surfaces of the support nanorods (see Figure 2a,b). On the basis of a high-resolution transmission electron microscopy (HRTEM) image (Figure 2c), the lattice spacing of the nanorods was determined to be 0.35 nm, which corresponds to the (101) crystal face fringes of the anatase TiO$_2$. High-angle annular dark field STEM (HAADF-STEM) images are shown in Figure 2d,e, in which the lattice space of 0.22 and 0.23 nm, 0.26 nm correspond to the (111) crystal face of Ir and (200), (101) crystal face of IrO$_2$ respectively, suggesting the coexistence of the Ir metal and IrO$_x$ clusters in the ITOT catalyst. We also observed some lattice distortions, which would be formed by the interaction between the Ir-containing nanoparticles and TiO$_2$ support. The energy-dispersive spectroscopy (EDS) of the sample (Figure 2f–h) shows that the existence of elements Ti and Ir quite agreed with the TEM and STEM results.
OER Activity and Stability of the ITOT Catalyst in Acidic Media. The electrocatalytic activity for the OER was evaluated by cyclic voltammetry (CV). We first measured the CV curves of the ITOT with different IrOx loadings (see Figure S3). The OER activity was significantly improved with the increase in the amounts of IrOx. The catalyst with the loading of IrOx = 0.58 mg cm\(^{-2}\) exhibited a potential of \(E_{\text{OER}} = 1.43\) V vs RHE at 10 mA cm\(^{-2}\), indicating a remarkably high OER performance when compared to the state-of-the-art Ir(Ru)-based catalysts (see Table S1). The Tafel plot of the ITOT catalyst is shown in Figure 3a in which the slope is \(\sim 48\) and 66 mV dec\(^{-1}\) in the higher and lower potential regions, respectively.

In order to explore the mechanism for such a high OER performance of the obtained ITOT catalyst, we examined the effect of the annealing treatment on the OER activity. An ITOT mesh sheet was cut into four pieces, and three pieces were separately calcined at 350 °C for 10, 30, and 60 min. As shown in Figure 3b, with the increase in the calcination time, the electrochemical double layer capacitive current and their OER performances drastically decreased. The note about the CV curve shape is provided in the Supporting Information.

To analyze the change in the surface structure during the calcination, we analyzed the X-ray photoelectron spectroscopy (XPS) spectra of the catalysts. As shown in Figure 3c, we observed the O 1s peaks at 525.1, 526.4, and 528.1 eV, which are assigned to the lattice oxygen, OH species, and absorbed H\(_2\)O, respectively.\(^{6,8,20,40,44-47}\) The relative concentration of the OH species is represented by the \(\theta\) value (\(\theta = \text{OH peak area} / \text{O 1s peak area}\)) (for details, see Table S2). The \(E_{\text{OER}@10\ mA\ cm^{-2}}\) is plotted as a function of \(\theta\) in Figure 3d. It is confirmed that the \(E_{\text{OER}@10\ mA\ cm^{-2}}\) values shifted in a negative direction with the increase in the concentration of the OH species on the catalysts. By calcination, the catalyst rapidly lost the OH species on the surface, resulting in the drastic decrease in the OER activity. Such a tendency clearly suggests that the high OH concentrations on the surface significantly benefits the OER. The XPS spectra of the Ir of the catalysts are shown in Figure 3e. The raw spectra (black curves) were deconvoluted into the metallic Ir\(^0\) (red curves), Ir\(^{III}\) (green curves), and Ir\(^{IV}\) (blue curves).\(^{16,44-47}\) The relative contents of these three Ir valences are listed in Table S3. The relations between the relative contents of the Ir\(^0\), Ir\(^{III}\), Ir\(^{IV}\) valence states and the calcination times are shown in Figure 3f, in which the relative contents of the Ir\(^0\) and Ir\(^{III}\) decreased with the increase in the calcination time. On the other hand, no apparent change in the XPS spectra of Ti has been observed for the annealed catalysts, indicating that the oxidation states of Ti in the catalysts remained during the annealing treatment (Figure S4).

We conducted a chronopotentiometry test at 10 mA cm\(^{-2}\) to evaluate the durability of the pristine ITOT catalyst. As shown in Figure 4a, the potential did not apparently change even after a 100-h durability test. Furthermore, we carried out a cycling test for the pristine ITOT catalyst. As shown in Figure 4b, the catalyst retained a very high OER performance even after 700 cycles. The \(E_{\text{OER}}\) value only increased from 1.428 V (1st cycle) to 1.461 V (700th cycle). In order to investigate the surface species of the ITOT during the cycling processes, the O 1s XPS spectra after different cycles were measured (see Figure 4c), and the relative contents of the OH species (%) are calculated and listed in Table S4. The \(E_{\text{OER}@10\ mA/cm^2}\) and the relative contents of OH species (%) as a function of the
Figure 5. Synchrotron XRD and XAS analysis of the ITOT catalysts. (a) Synchrotron radiation XRD patterns of different samples. (b,c) Ir $L_{III}$ edge XANES spectra (b) and Fourier transformed EXAFS (R-space with k-weight 2) spectra (c) of the provided Ir-based materials. For the synthesis of the Ir–Nylon, a Nylon mesh was separated from the TOT mesh in a vessel, and Ir-based nanoparticles were deposited on its surface. The prepared sample was denoted as Ir–Nylon. The oxidation state of Ir in the ITOT mesh is between Ir and IrO$_2$ and also different from Ir on Nylon mesh, indicating that the TiO$_2$ support influenced the formation state of Ir. (d,e) Ti K-edge XANES spectra (d) and their Fourier transformed EXAFS spectra (e) of different Ti species.

CV-cycles are plotted in Figure 4d, in which we observed that the $E_{\text{OER}}$ value slowly increased with the increase in the cycling number and the OH concentration only decreased by 7% even after 700 cycles. This result indicates the maintained high OH density/concentration even after 700 cycles, which contributed to the very high cycle stability of the ITOT catalyst.

Besides, the Ir 4f XPS spectra of the ITOT catalyst after the cycling test are shown in Figure 4e. The relative contents of the three valence states of Ir$^0$, Ir$^{III}$, and Ir$^{IV}$ are listed in Table S5 and plotted as a function of the cycling number in Figure 4f. The contents of the Ir$^0$ and Ir$^{IV}$ slightly changed during the first 60 cycles and almost reached stable states, while the content of the Ir$^{III}$ was stable during the entire 700 cycling test.

**Iridium Valence Change of the ITOT Catalyst during the OER.** It is crucial to determine the microstructure of the catalyst to clarify the mechanism of the obtained high OER activity. In view of this, we carried out X-ray diffraction (XRD) and in situ XAS measurements. The annealing treatment for the ITOT only promoted the crystallization of IrO$_2$ and caused no change to the anatase-TiO$_2$ (Figure S5). The synchrotron radiation XRD measurements were conducted to further distinguish the structural differences between the pristine ITOT, the ITOT calcined at 350 °C for 1h (denoted as Calcined ITOT), and the ITOT after several CV cycles (denoted as Cycled ITOT) together with the conventional Ir metal, IrO$_2$, and anatase-TiO$_2$ for comparison. Figure 5a shows that most of the main peaks are ascribed to the Ti metal and anatase-TiO$_2$ except for some weak peaks of Ir and IrO$_2$. The peaks of the IrO$_2$ that appeared at 14.4°, 17.8°, and 32.8° is the Calcined ITOT catalyst were much more clear compared with those of the pristine ITOT and Cycled ITOT catalysts. These XRD results indicated that the crystal structures of these materials are sufficiently robust.

The X-ray absorption near edge structure (XANES) spectroscopy at the Ir–$L_{III}$ edge was carried out to evaluate the change in the Ir oxidation states after different types of treatments. Figure 5b shows the normalized XANES spectra at the Ir–$L_{III}$ edge of these Ir-based samples. The XANES spectra recorded at the Ir–$L_{III}$ edge (probe the electronic transitions from 2p to 5d) were found to be sensitive to the change in the Ir oxidation states. The absorption energy peak of the ITOT catalyst was observed at ~11 222.5 eV, which is between the Ir (Ir$^0$) and IrO$_2$ (Ir$^{IV}$); namely, the average Ir oxidation state of the ITOT catalyst is between the Ir$^0$ and Ir$^{IV}$. The absorption energy peak of the Calcined ITOT catalyst shifted to a slightly higher energy level, which is close to that of the IrO$_2$, indicating that the calcination enhanced the Ir oxidation states, while no obvious change was observed for the Cycled ITOT catalyst. The absorption energy peak of the Ir–Nylon appeared at ~11 221.6 eV, which is similar to the Ir metal and different from that of the ITOT catalyst, indicating that the TiO$_2$ support on the ITOT affected the Ir oxidation states.

The Fourier transformed extended X-ray absorption fine structure (EXAFS) spectra are shown in Figure 5c, from which we can obtain the local structural environments of the Ir element. The Ir–O bond distance (~1.7 Å) in the first shell has been reported to be highly sensitive to the Ir oxidation state, and the longer bond distance means the lower oxidation state. The first Ir–O bond distance of the ITOT, Cycled ITOT, and Calcined ITOT catalysts were very similar, and all of them were around 1.73 Å, which is slightly higher than that of the IrO$_2$ (~1.70 Å), suggesting that the Ir oxidation state is lower than that of the IrO$_2$, which agreed with the XPS and XANES results. On the other hand, for the Ir–Nylon mesh, less obvious peaks were observed, which would be attributed to the thin layer of the Nylon mesh. Similar XANES
and EXAFS measurements were also conducted on the Ti-based materials. As shown in Figure 5d,e, the Ti oxidation states in all the samples were similar, and there is no difference in the Ti coordination environment between these Ti-based materials, indicating that the Ti oxidation states did not change after the calcination and CV testing.

Since the conventional ex situ characteristic measurements are unable to monitor the oxidation states during the OER process, we conducted in situ electrochemical XANES and EXAFS measurements in order to investigate the dynamic change in the Ir oxidation states of the catalysts in the OER potential range of 1.05−2.2 V (for the experimental setup, see Experimental Section and Figure S6). The measurement was done as the order of the applied potentials of 1.05, 2.2, 1.2, 1.5, and 1.8 V and then at the open circuit potential. This measurement order can eliminate the effect of the previous potential on the next step. The obtained results are shown in Figure 6a−d. As shown in Figure 6a, the in situ Ir LIII-edge XANES absorption peak of the uncalcined ITOT catalyst shifted to a higher energy region with the increasing applied potentials, while no such change was observed for the calcined ITOT sample. (c,d) In situ Fourier transformed EXAFS spectra of the uncalcined ITOT (c) and calcined ITOT (d) catalysts with the k weight of 2 at the applied potentials. (e) The XANES absorption energy peak positions of the uncalcined and calcined samples at different applied potentials. (f) The EXAFS-determined Ir−O bond distance of the uncalcined and calcined samples as a function of the applied potentials.

On the basis of the obtained XANES and EXAFS results, we plotted the absorption energy peaks and the Ir−O bond distance as a function of the applied potentials in Figure 6e,f, respectively. Notably, for the uncalcined ITOT catalyst, the Ir oxidation state changed as the applied potential changed. Besides, when the applied potential was higher than the onset potential, the Ir valency became higher than IrIV. However, no such change nor high iridium valency (above Ir IV) was observed for the calcined ITOT. According to the in situ electrochemical XANES and EXAFS measurements, the controllable Ir valency by applying the potentials is possible only for the uncalcined ITOT catalyst but not for the calcined ITOT catalyst. We now emphasize that the controllable Ir valency plays a key role in the obtained remarkably high OER activity of the presented ITOT catalyst.

In order to study the effect of the coordination environment and surface structure on the valence variation, we carried out DFT calculations using small trinuclear Ir−Ox clusters (Ir3, for short) (for details, see Experimental Section and Figure S7). We assumed that in a fully hydrated state like the uncalcined ITOT catalyst all the Ir atoms are six-coordinated. The charge of the Ir(IV)s in the neutral clusters (Ir3O14H16) is compensated by the −O− bonds and the −OH/−(OH2) ligands. We now discuss four different isomers (Ir_a···Ir_d) distinguished by the different positions of the water ligands, as shown in Figure 7a. As expected, the DFT calculations found a large number of orbitals around the HOMO−LUMO gap of the Ir3 clusters. The small energy difference between these orbitals and the large overlap through oxygen orbitals leads to delocalization of electrons on the metal atoms. Because of these partial fillings, it is difficult to assign the oxidation states of the Ir atoms. Instead, we monitored the Mulliken charges as
an indicator of the electron density on different atoms. The geometry of the Ir3 clusters and the Mulliken charges are shown in Figure 7b. As a reference, the mononuclear Ir(III)(OH)3(H2O)µ, Ir(IV)(OH)4(H2O)2, and Ir(V)−(OH)3(H2O) complexes have 0.485, 0.625, and 0.782 Mulliken charges surrounding the central Ir atom. The Ir atoms with H2O in their coordination sphere have significantly lower Mulliken charges than the ones with only the −OH coordination in spite of the same formal Ir(IV) oxidation state. The water ligands stabilize the Mulliken charge of 0.66−0.67, with some exceptions around 0.72. The Mulliken charge of the Ir atoms without water is much higher, between 0.74 and 0.80. The extra negative charge in the ligand environment can stabilize a more positive Ir. What is more surprising is the significant difference in the charges when we compare them with the mononuclear complexes in which the electrons around the Ir in the Ir3 clusters are clearly very sensitive to protonation around the atom.

While this model is simple, it helps highlight the fact that the charge on the Ir is significantly influenced by the protonation state around the cluster oxygens, and the acid−base equilibrium can stabilize or destabilize the given valence states. Since protonation/deprotonation reactions are very fast and water/protons are in abundance around the electrode, the higher oxidation states like Ir(V) can be stabilized by deprotonation, while protonation can stabilize a lower oxidation state like Ir(III) when they are needed in the redox cycle. In short, the rapid rearrangement of protons can lower the energy difference between the intermediates with different Ir oxidation states.

When the clusters and amorphous oxide are compared to the bulk IrO2 or regular surfaces like (110), one big difference is that in the clusters and amorphous oxides, the presence of protons is a necessity for charge compensation. In the bulk IrO2 or on the crystalline surface, the number of oxygen matches with a neutral lattice and formal Ir(IV) charge. In the amorphous IrO2, the coordination number around Ir can vary; therefore, the local charge neutrality can only be achieved through protonation or alternative Ir formal charges. In the clusters, positive protons are required to compensate the extra negative charge of a high number of oxygens around the five- or six-coordinated Ir(IV) ions. Therefore, clusters and amorphous oxides have a flexibility in charges that they can accommodate compared to the bulk, crystalline IrO2. Low oxidation states can be stabilized by water coordination, while the higher oxidation states can be stabilized by deprotonation and a higher number of −OH ligands around the Ir atoms. The dynamic acid−base equilibrium and transfer of protons to different position on the surface is therefore coupled with the electron transfer/destabilization of the valence states.

**OER Mechanism of the ITOT Catalyst in Acidic Media.** As for the catalytic mechanism of metals/oxides supported noble metals/oxides, the concept of metal/metal oxide−support interactions (MMSI) between the supports and the loaded nanoparticles has recently been proven to play a key role in the Ir-based catalysts39,40 for the OER. Early reported general hypotheses for the MMSI effect is that the charge state alteration of the metal by electron transfer from/to a support leads to the improved ability to activate the reactants and thus influences the catalytic properties, which have been experimentally confirmed.58,59 Excellent OER enhancement using the IrOx−TiO2 catalysts has also been reported. For example, Ryu et al.34 fabricated a crystalline IrO2-decorated TiO2 nanofiber and found that the TiO2 support stabilized the crystalline structure and the oxidation state of the IrO2 during the OER. A similar interaction was also reported between the antimony-doped tin oxide and IrOx.27 For the Ir-based catalysts with a high performance, the presence of IrIII as well as higher oxidation states than IrIV during the OER have been reported,18,52,60,61 but the relations between the TiO2 support, iridium oxidation states, and active species together with the detail reaction pathway have not yet been well-clarified. Recently, detailed mechanistic studies have indicated that the OER activity is related to the reactive species Oad formed in the mixed-valent IrIII/IV hydrated amorphous oxyhydroxides during the OER. However, to the best of our knowledge, no report has been published describing a clear OER mechanism based on controllable Ir valence.

In this study, the HRTEM results showed the obvious crystalline clusters of Ir and IrO2 in the ITOT catalyst as shown in Figure 2d,e. In addition, the crystals of the nanoparticles in the ITOT after calcination and 700 CV-cycles were still clearly seen in the HRTEM images (Figure S8). There is no obvious change in the nanoparticle size between the uncalcined and the calcined ITOT samples. As the conductivity of Ir is better than that of IrOx, some Ir might be beneficial for the electron transfer during the OER. In order to analyze the interfacial charge-transfer kinetics, impedance measurements for the ITOT before and after calcination were carried out (for the Nyquist plot, see Figure S9). The R0 values of these samples were almost similar, while the Rct increased with the increasing calcination time. The Nyquist plot of the pristine ITOT catalyst showed two-continuously nonstandard arcs, while for the calcined samples, we observed only one standard arc. Such a difference is derived from the different surface structures of the pristine and calcined samples. The first arc of the pristine ITOT is due to the existence of Ir metal, which is beneficial for the charge transfer. However, some amount of amorphous iridium oxyhydroxides would generate heterogeneous interfaces, which contributed to the diffusion impedance, resulting in the second arc. Although the diffusion impedance is not advantageous for the charge transfer, their highly reactive activity is more desirable for the OER processes. After calcination, the Ir metal would decrease and the oxyhydroxides would decompose, resulting in one classic impedance arc. According to the above-mentioned results, in which the TiO2 support influences the iridium oxidation state during the synthesis process, and the Ir oxidation state was the...
mixed valency of Ir$^{III}$/Ir$^{IV}$ in the ITOT catalyst, we suggest that the MMMSI in this study is not reflected on the OER process, but rather, it is reflected in the formation of the Ir$^{III}$ valency during the refluxing process and stably loading the IrO$_2$ on the TiO$_2$ surfaces. The mixed valency of Ir$^{III}$/Ir$^{IV}$ on the TiO$_2$ surface is more active than the bulk crystalline IrO$_2$ since it is more susceptible to be attacked by a proton or H$_2$O to form hydrated amorphous oxyhydroxides with the mixed-valent Ir$^{III}$/Ir$^{IV}$, resulting in the high concentration of surface OH species, which have been revealed to be crucial for the very high OER activity (see Figure 3). The evolution process of the active species can be analyzed by the Tafel slope (see Figure 3a), which is important for evaluating the OER activity and considered to be the rate-determining step of the OER. As previously reported$^{23,62–64}$ the OER process of the active oxides includes the following four steps that involve three oxygen-adsorbed species (OH$^{\text{ad}}$, O$_2^{\text{ad}}$, and OOH$^{\text{ad}}$) together with the active sites (denoted by W$^{\text{ad}}$):

$$
W^{\text{ad}} + W^{\text{ad}} \overset{H^+ + e^-}{\rightarrow} W^{\text{ad}} + W^{\text{ad}} + H^+ + e^- \quad (120 \text{ mV dec}^{-1})
$$

$$
W^{\text{ad}} \overset{H^+ + e^-}{\rightarrow} W^{\text{ad}} + O_2 + 2H^+ + 2e^- \quad (5)
$$

The Tafel slope values are 120, 60, and 40 mV dec$^{-1}$ for the rate-determining step described by eq 1, eq 2 and eq 3, respectively. Generally, the different bond strengths of the intermediate species to the active sites can differ with the catalytic layer composition and thus leads to different Tafel slope values. The Tafel plot of the ITOT catalyst exhibited two slopes of 48 and 66 mV dec$^{-1}$ in the high and low potential regions, respectively (see Figure 3a), suggesting that the rate-limiting processes are eq 3 in the higher potential region and eq 2 in the lower region. This might be related to the change in the adsorbed OH intermediates states. Such phenomenon agrees well with the reported IrO$_x$ catalysts in acidic media.$^{11,65,66}$

The O 1s XPS result of the ITOT catalyst (see Figure 3c) indicated that the OH species has already bonded to the mixed-valent Ir$^{III}$/Ir$^{IV}$ hydrated amorphous oxyhydroxides surfaces of the ITOT catalyst prior to the OER. Hence, the rate-limiting step is not the eq 1 reaction. The Ir valency of the ITOT catalyst was controllable during the OER and changed to the higher valency (above Ir$^{IV}$) by applying a higher potential than the onset potential, which was never observed for the calcined ITOT with a much lower Ir$^{III}$ content. Therefore, the OER pathway of the ITOT catalyst can be described by the following equations:

$$
\text{Ir}^{III}O_x(OH)_{ad} \overset{\text{++} + \text{--}}{\rightarrow} \text{Ir}^{IV}O_x(OH)_{ad} + H^+ + e^- \quad (7)
$$

$$
\text{Ir}^{IV}O_x(OH)_{ad} + H_2O \overset{0}{\rightarrow} \text{Ir}^{V}O_x(OH)_{ad} + OOH_{ad} + H^+ + e^- \quad (8)
$$

$$
\text{Ir}^{V}O_x(OH)_{ad} + OOH_{ad} \overset{O_2 + H^+ + 2e^-}{\rightarrow} \text{Ir}^{III}O_x(OH)_{ad} + 2H^+ + 2e^- \quad (9)
$$

These equations have clarified the transformation pathway of the active species during the OER process, which are dominated and coordinated by the change in the Ir valency, and thereby maintain the charge and electron balance during the OER. As the computational models suggest, the stabilization of different valence states is largely assisted by the water molecules and their acid–base equilibrium in the coordination sphere of the Ir atoms. This is in agreement with the observed loss of activity upon high-temperature treatment of the anode materials.

The OER mechanism has been extensively studied using a computational method on slab models of IrO$_2$ surface,$^{67}$ including details like solvent effect.$^{18}$ Instead of using such slab models, we have tested the mechanism on the computational trinuclear cluster model, which allows us to study protonation effects and behavior of small clusters. We have studied three different isomers with the catalytic site in identical position while the position of an extra proton was changing (Figure 8).
localized nature of the changes on the catalytic center. The variance of charges in the care of H2 is due to conformational changes and formation of new hydrogen bond between the −OH and −OH2 groups.

The free energies of individual steps are shown in Figure 9. The overall free energy of the reaction is stepwise increasing as expected. A closer look reveals, however, that the free energies of these steps strongly depend on which isomeric form is studied. The free energy of individual steps can differ by 5−8 kcal/mol depending on the position of the extra protons. As we pointed out previously, the protons are very mobile in an aqueous solution, and one can expect that the transformation of isomers like H1, H2, and H3 to each other is easy even during a catalytic cycle. In other words, spontaneous isomerization of a proton can create different pathways to follow, with smaller energy barriers and overpotentials. This model is more of an illustrative example than an accurate simulation of the actual nanoparticle structure. However, it clearly shows that the valence states are localized on the catalytic site and that the mobility of protons can assist in stabilizing intermediates and lowering the overpotential.

On the basis of the above discussion, we propose a possible OER mechanism involving our ITOT catalyst that is shown in Figure 10, in which the TiO2 supports contribute to the formation of the incomplete iridium oxidation state, IrIII, which is unstable during the OER. The presence of IrIII forms the mixed-valent IrIII/IV hydrated amorphous oxyhydroxides, resulting in the high concentration of OH*ad species on the surfaces. During the OER process, the unstable IrIII would shift to a higher valence state (above IrIV, denoted IrV) when the applied potential is higher than the onset potential. In order to maintain the charge and electron balance, the surface OH*ad species would change to other key active species Oad and then OOHad which generates oxygen. Underlying the evolving active species during the OER, the variable iridium valence was the key factor for the observed very high OER activity, as well as high cycle stability of the ITOT catalyst. The content of the IrIII valence state was very stable after different CV cycles, indicating that the IrIII valence can go back to the initial state after each cycle ends, which is consistent with the XAS results. The controllable Ir-valence between IrIII and IrV plays a key role for the high OER activity and durability of the ITOT catalyst.

4. CONCLUSIONS

In summary, we designed and synthesized a novel IrOx−TiO2−Ti (ITOT) catalyst on which IrOx nanoparticles with ∼5 nm size were uniformly distributed. The obtained catalyst with a reduced IrOx amount exhibits an outstanding OER activity compared to the state-of-the-art Ir(Ru)-based catalysts as well as the high cyclic stability in acidic media. Some amount of Ir metal in ITOT is beneficial for the charge transfer. The high OER performance is due to a very high OH concentration generated on the catalyst surfaces. The XPS and in situ electrochemical XAS studies revealed that the TiO2 supports were beneficial for the formation of IrIII and the mixed-valent IrIII/IV hydrated amorphous oxyhydroxides, resulting in the high concentration of OH*ad species on the surfaces. Furthermore, the kinetic OER mechanism on the ITOT was clarified by in situ electrochemical XAS study. The unstable IrIII was found to shift to a higher valence state (above IrIV) during the OER. In order to maintain the charge and electron balance, the OH*ad species on the surface change to other key active species, Oad and OOHad, and subsequently transform into an oxygen molecule. As IrIII is variable during the OER, it returns to its initial state when the test ends, leading to the excellent cycle stability. The important role of the −OH species and acid/base equilibrium have also been confirmed by a computational model, in which we showed that charges on the Ir atoms can easily move around in the IrOx clusters, following the protonation of the −OH species, which
may stabilize the more positive (higher valence) electronic states.

We would like to emphasize that the in situ XAS experiments revealed the dynamic change process of the Ir valence state during the OER. In the present study, we described a very high OER performance based on the controllable Ir-valence, which provides a novel insight into the design of efficient and durable OER catalyst with reduced Ir amount as well as its use in energy conversion systems.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.9b01438.

Additional electrochemical data, XRD results, XPS analysis, in situ electrochemical XAS setup, HRTEM results, Nyquist plots, and further details concerning the DFT calculations (PDF).

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**Notes**

The authors declare no competing financial interest.

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