Decoupling structure-sensitive deactivation mechanisms of Ir/IrOₓ electrocatalysts toward oxygen evolution reaction

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ABSTRACT

Deterioration of intrinsic activity of Ir-based electrocatalysts during the oxygen evolution reaction (OER) has received much less attention compared to the metal dissolution. Combining chronocoulometry with operando electrochemical impedance spectroscopy and cyclic voltammetry, we show that the deactivation via active site phase transformation from hydrous Ir oxide/hydroxide into anhydrous Ir oxide, is concomitant with the dissolution-induced loss of electrochemical surface area. The relative contributions from these deactivation paths were found to be structure sensitive. Systematic evaluation of different Ir-based catalysts at identical electro-oxidative conditions showed that hydrous IrOₓ with structural short-range order exhibited an initial minor degradation of intrinsic activity but the most significant dissolution after the extended stability test. In contrast, newly-reported Ir superstructures with higher crystallinity and larger proportion of low-index crystal terminations exhibited enhanced resistance to dissolution but a major degradation of intrinsic activity, as the performance-relevant hydrous oxide/hydroxide species developed only on the surface of metallic Ir. The Ir/IrOₓ catalyst regeneration was demonstrated.

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1. Introduction

Water electrolysis is an electrochemical process that could convert intermittent renewable energy into storable chemical fuels [1]. The slow kinetics of oxygen evolution reaction (OER) and the insufficient catalyst durability however limit the conversion efficacy and larger-scale application of the process [2, 3]. Substantial efforts have been devoted to developing highly efficient, durable, and cost-effective OER electrocatalysts. Although a wide range of non-noble metal catalysts exhibit impressive activity and durability in alkaline conditions [4–8], OER electrocatalysts for use in acidic conditions continue to remain at the center of intense research [9–13] because at the device level, acidic polymer electrolyte membrane (PEM) water electrolyzers still outperform alkaline electrolyzers [14–16]. Under highly electro-oxidative conditions in acidic environments, precious metal Ir and its oxides are considered the most suitable materials to exhibit appreciable catalytic activity toward OER along with acceptable stability [17]. RuOₓ, though also considered to be a benchmarking catalyst for OER, is substantially less stable than IrOₓ under high anodic potential [18].

Many efforts have been directed toward enhancing the OER electrocatalytic activity and durability of Ir/IrOₓ electrocatalysts, by developing advanced catalyst supports [19–21] and using material design strategies such as well-defined extended surfaces of thin-film model systems [22, 23], lattice strain engineering [24, 25], alloy-based catalysts with skeleton or nanoporous surfaces [26–28], shape-controlled nanocrystals [29, 30], superstructures [31], and hollow particles including nanoframes [32, 33] and nanocages [34, 35]. To facilitate cross-comparison of the durability of various electrocatalysts, benchmarking studies on OER catalysts have proposed using controlled current electrolysis, i.e., chronopotentiometry (CP) [36, 37]. This method has been frequently used since then in many studies, such as in references [4, 7, 10, 21, 25, 27, 30, 31, 34].

While CP analysis may be an excellent screening method for catalyst durability, the obtained results could be dominated by catalyst activity rather than corrosion stability, as controlled current electrolysis does not evaluate catalysts under identical electro-oxidative conditions. At a constant current, a more active catalyst is likely to be more durable by operating at lower electrode potentials. For electrocatalysts with substantially different mass-specific surface areas, researchers have employed modified CP analysis using controlled current densities, normalized to the catalyst initial surface area [23]. However, determining the electrochemical surface area (ECSA) on Ir/IrOₓ is challenging because the methods...
typically used to estimate Ir ECSA are ineffective on oxides and can be sensitive to surface oxidation on Ir metals [38]. Different Ir/IrOx catalysts may also exhibit quite different surface-area-specific activities [9,23,25,31,32,35]. Consequently, it remains challenging to fairly compare the catalyst stability using either CP method. The limitations of CP analysis for proper stability evaluation have driven the current research on OER electrocatalysts to focus more on the activity aspect of the electrocatalytic performances.

In addition, durability tests using controlled current electrolysis are unable to provide sufficient physical insight regarding the deactivation mechanisms of the OER electrocatalysts. From the potential versus time curve of a CP analysis, it is difficult to distinguish whether the catalytic deactivation is dominated by either the loss of ECSA or the deterioration of intrinsic catalytic activity. It has been hypothesized that Ir/IrOx electrocatalysts deactivate in two steps: (1) a gradual increase in anodic potential due to the depletion of intrinsic activity, followed by (2) a sharp increase in anodic potential due to the loss of ECSA through Ir dissolution [39]. More work is needed to decouple the two deactivation mechanisms, as identifying the predominant deactivation path may be helpful to the future design of Ir-based OER electrocatalysts with improved stability. In particular, there is a lack of emphasis on the deterioration of intrinsic activity for OER electrocatalysts in acidic environments. Most studies on catalyst stability have focused on the degradation through anodic dissolution [28,40–42]. The influence of Ir surface phase transformation on intrinsic activity during the OER has only recently received increasing attention [43].

Herein, combining controlled potential electrolysis, i.e., chronoamperometry (CA), with operando electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV), we demonstrate an analytical procedure to decouple the deactivation mechanisms of Ir/IrOx electrocatalysts toward OER. The deactivation behaviors of different OER electrocatalysts should be properly compared under identical electro-oxidative conditions. We systematically investigated a list of Ir/IrOx electrocatalysts, including a newly reported pompom-like Ir superstructure, 2 nm Ir nanoparticles (NPs), and state-of-the-art commercial Ir black and IrOx. The four electrocatalysts investigated here exhibit different chemical and structural properties, which motivated us to study the structure sensitivities in deactivation behaviors [40,43–45]. We selected a commercially available quasi-amorphous IrOx over the crystalline IrOx as the baseline. Recent studies have explicitly identified the quasi-amorphous hydrous iridium/III/IV oxide/hydroxide species as the performance-relevant phase for acidic OER, highlighting the absence of long-range order, the amount of hydroxyl groups, and the mixed Ir oxidation states as the keys to superior OER electrocatalytic activity [39,46–50]. As will be demonstrated, the selected commercial IrOx shows the characteristic reduction feature of the highly active hydrous Ir oxide/hydroxide phase [39].

The results of our stability tests show that the relative contributions from the loss of ECSA and from the deterioration of intrinsic activity are highly dependent on the nature of the electrocatalysts. By connecting the microstructural and chemical properties of the Ir/IrOx electrocatalysts with their associated deactivation behaviors, we discussed the structure sensitivities in catalytic deactivation due to anodic dissolution or active site phase transformation. These results advance the fundamental understanding of the deactivation of Ir/IrOx OER electrocatalysts and highlight the intrinsic activity degradation induced by phase transformation of the active sites and/or the surface passivation.

2. Experimental section

Synthesis of pompom-like Ir superstructures (Ir PPs): Ir PPs were synthesized using a facile one-step wet-chemical reaction, using glucose as the reducing agent, hexadecyltrimethylammonium bromide (CTAB) as the surfactant, and oleylamine as the solvent. Recently, a similar approach, except using cetyltrimethylammonium chloride (CTAC) as the surfactant, was reported to synthesize zigzag-like PtFe nanowires [51]. In a typical synthesis for Ir PPs, 20 mg Ir(acac)3 (Sigma–Aldrich, 97%), 20 mg d-(+)-glucose monohydrate (Sigma–Aldrich, product number: 16301), 40 mg CTAB (Sigma–Aldrich, ≥ 98%) and 7 mL oleylamine (Sigma–Aldrich, 70%) were added into a small glass vial. The mixture was ultrasonicated for 1 h to facilitate dissolution, yielding a transparent yellow/greenish solution. The capped vial was then placed into an oil bath preheated to 200 °C. The vial was kept in the oil bath for 2–6 h until a colloidal dispersion of Ir PPs was obtained without any precipitate. The colloidal dispersion gradually turned from transparent light-brown to dark-brown and to black, depending on the reaction time. Stirring was unnecessary for the reaction because the resulting nanostructures with and without stirring were similar. Hexane and isopropyl alcohol were used to wash the nanoparticles with centrifugation at 8500 rpm/10 min (Fisher Scientific, accuSpinTM 400). The washing procedure was repeated 10 times. The washed Ir PPs were dispersed in 5 mL isopropyl alcohol. After the dispersion was ultrasonicated for 1 h, 2 mL of the catalyst suspension was dried and weighted for mass calibration. The remaining catalyst suspension was stored for further use.

Synthesis of 2 nm Ir nanoparticles (Ir NPs): Ir NPs with mean particle diameter ~2 nm were synthesized using a modified procedure for alcohol reduction of Ir precursor, with Naﬁon as the stabilizer [52]. In a typical synthesis reaction, 25 mg H2IrCl6·xH2O (Sigma–Aldrich, 99.98%) and 15 mg of 5 wt.% Naﬁon solution (Ion Power, LQ-1105) were dissolved in 17 mL ethanol/water solution (ethanol concentration = 40 vol.%) in a 50 mL single-neck round-bottom flask. The Naﬁon-Ir4+–ethanol/water solution was stirred and refluxed for 3 h in air, obtaining a transparent dark-brown colloidal dispersion of Ir NPs without any precipitate. After the dispersion was ultrasonicated for 1 h, 2 mL of the catalyst suspension was dried and weighted for mass calibration. The remaining catalyst suspension was stored for further use.

The commercial Ir/IrOx catalysts: Two state-of-the-art commercial OER electrocatalysts were included as the baseline. The Ir black was supplied by Umicore (product number: 3000020267), with supplier-certified Ir metal purity of 97.65%. The supplier noted that the Ir black surface area is 25 m2 g−1, as determined by BET surface area analysis. The IrOx was supplied by Tanaka Kikinzoku Kogyo (product number: SA = 100), hereafter denoted as TKK IrOx. The supplier stated that TKK IrOx has Ir content of 75.23 wt.% and a surface area of 100 m2 g−1, as determined by BET surface area analysis.

Catalyst ink and electrode preparation: For Ir PPs, Umicore Ir black, and TKK IrOx, a typical catalyst ink was prepared by suspending catalyst containing 5 mg of Ir in 3.75 mL of isopropanol, 1.25 mL of Milli-Q water, and 20 μL of 5 wt.% Naﬁon solution. For the 2 nm Ir NPs, the as-prepared colloidal dispersion was directly used as the catalyst ink, though additional Naﬁon solution was added to match the Naﬁon loading in the other three catalyst inks. After being ultrasonicated for 1 h, catalyst ink containing 10 μg Ir was drop-casted onto a mirror-polished glassy-carbon (GC) disk electrode 5.0 mm in diameter and dried in air, which was employed as the working electrode for the electrochemical measurement. The geometric area of the GC electrode surface was 0.196 cm2. The iridium loading on the electrode was 0.05 mg cm−2 on a geometric-area basis.

Electrochemical testing: Electrochemical measurements were carried out using an electrochemical test station (Biologic Science Instruments SP-200), a standard rotating-disk electrode (RDE) system (PINE Research MSR Rotator), and a three-electrode
electrochemical cell. A helical Pt wire and a double-junction silver chloride (Ag/AgCl) electrode were used as the counter and reference electrodes, respectively. Sulfuric acid (H₂SO₄ optima grade, Fisher Scientific) diluted with Milli-Q water (18.2 MΩ·cm) to 0.5 M was the electrolyte in all cases [23,36]. All electrochemical measurements were carried out at room temperature using research-grade gases (99.999%, Praxair). The reported potentials are specified relative to the reversible hydrogen electrode (RHE) scale by using the equation E(RHE) = E(Ag/AgCl) + 0.199 + 0.059pH. The ionization constant of HSO₄⁻ is taken as 0.01 [53].

Cyclic voltammetry (CV) was carried out in N₂-saturated electrolyte and recorded with a scan rate of 40 mV s⁻¹, unless otherwise stated. The electrochemical surface area (ECSA) of metallic Ir was estimated by averaging the integral charges of underpotentially deposited hydrogen (Hupd) and its desorption areas of the CV profiles in the potential range of 0–0.35 V versus RHE, including a correction for double-layer charging. The electrical charge constant associated with a fractional coverage of H on Ir was assumed to be 179 μC cm⁻² [38,54]. As the upper potential limit of CV scan reaches a potential relevant to the OER, the metallic Ir surface quickly evolves to a state at which hydrogen adsorption and desorption no longer occur. A similar effect of the upper potential limit of potential cycling on the CV of iridium has been reported earlier in references [55,56]. The ECSA of metallic Ir catalysts after OER measurements and the ECSA of the TKK IrOₓ were estimated by using the double layer corrected total anodic charges of the CV profiles in the potential range of 0.4–1.25 V versus RHE, as briefly discussed in references [28,42,57]. The electrical charge constant associated with the anodic processes within this potential range was assumed to be 440 μC cm⁻² ECSA obtained from a slope of a linear fit, as discussed in the “Results and discussion” section.

Anodic linear sweep voltammetry (LSV) from 0 to 1.6 V versus RHE was conducted in an O₂-saturated electrolyte to measure the OER at a rotational speed of 1600 rpm using a scan rate of 10 mV s⁻¹. iR compensation was applied using the Biologic EC-Lab software while recording CV and LSV. The software provides a technique to measure the uncompensated resistance with a high-frequency impedance measurement at 100 kHz with 20 mV amplitude about the open-circuit potential (OCP). After determining the uncompensated resistance, it will be compensated in the techniques linked afterward. Our typical electrochemical setup and catalyst electrode resulted in an overall series resistance of ~5 Ω in 0.5 M H₂SO₄ [37]. The reported CV, LSV, and activity values were averaged from multiple independent catalyst measurements.

The catalytic durability of the electrocatalysts was first evaluated using chronopotentiometry (CP) at 10 mA cm⁻², as suggested in references [36,37] as a benchmarking method for screening catalyst durability. The procedure of a CP analysis was stopped if the electrode potential reached 1.9 V versus RHE. The particularly sharp increase in potential around 1.7 V and above was recently associated with a fractional coverage of H on Ir was assumed to be 179 μC cm⁻² ECSA obtained from a slope of a linear fit, as discussed in the “Results and discussion” section.

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The corrosion stability of the electrocatalysts was evaluated using chronoamperometry (CA) at either 1.53 V or 1.6 V versus RHE. At these selected potentials, the rate of passivation for the GC electrode was reported to be slow [58]. By using identical electrode potentials, the corrosion stability of the different electrocatalysts were evaluated under the same electro-oxidative conditions. To investigate the change of charge transfer resistance during controlled potential electrolysis, operando electrochemical impedance spectroscopy (EIS) measurements were conducted, with minimal interference in the applied potential of a CA analysis. At the potential of a CA analysis, the EIS of the electrochemical cell was measured in the frequency range from 200 kHz to 30 mHz, with a potential perturbation amplitude of 10 mV. The impedance spectra were fitted using a simplified Randles cell as the equivalent circuit. The equivalent series resistance (R₁) of the electrochemical cell can be obtained from the real component value of the impedance at the minimum of the Nyquist plot. The diameter of the semicircle observed in the high-to-medium frequency region represents the charge transfer resistance (Rct) of the electrocatalytic OER. For CP, CA, and the operando EIS measurements, all procedures were conducted in an O₂-saturated electrolyte at a rotational speed of 1600 rpm. CP and CA measurements were carried out without iR compensation.

A combination of CA, operando EIS, and CV analyses were used to decouple the deactivation mechanisms of the Ir/IrOₓ OER electrocatalysts. The stability test protocol can be described as follows: After saturating the electrolyte with oxygen, the EIS before the stability test was measured at 1.53 V (1.6 V) at a rotational speed of 1600 rpm. The catalyst stability was then evaluated using CA analysis at 1.53 V (1.6 V) for 3 h, while EIS was measured periodically with minimal interference in the applied potential of the CA analysis. Following the 3-h controlled potential electrolysis, the electrolyte was purged with nitrogen while the electrode was held at open-circuit potential (OCP). After about 10 min, CV was recorded in the potential range of 0–1.53 V. The aforementioned procedure was repeated for more iterations.

Materials characterization: Conventional bright-field transmission electron microscopy (TEM), high-resolution TEM (HRTEM), selected area electron diffraction (SAED), high-angle annular dark field (HAADF) and energy dispersive X-ray spectroscopy (EDS) analyses in scanning mode (STEM) were conducted on a JEOL JEM-ARM200CF S/STEM, which was operated at 200 kV accelerating voltage. The microscope was equipped with a cold field-emission gun (cFEG) and a probe spherical aberration corrector. The commercial software Crystal Maker™ was used to simulate the crystal structure of the materials in this work. Diffraction-Ring-Profiler [59] was used to simulate the electron diffraction patterns and to obtain the azimuthally averaged electron diffraction intensity profiles [60,61]. X-ray diffraction (XRD) analysis of the TKK IrOₓ was carried out on a Bruker AXS diffractometer (Discover 8) equipped with a Histar general-area two-dimensional detection system (GADDS) using Cu-Kα radiation (λ = 0.15406 nm). Temperature-programmed reduction (TPR) of the TKK IrOₓ was performed on an AutoChem II 2920HP Instrument (Micromeritics) equipped with a thermal conductivity detector (TCD). The measurement was performed in 10 vol% H₂/Ar stream with a flow rate of 25 mL min⁻¹ in a temperature range of room temperature to 500 °C at a heating rate of 6 °C min⁻¹. 15.4 mg of the TKK IrOₓ was diluted in 138.6 mg of α-Al₂O₃ and packed in a quartz U-tube with quartz wool placed on both sides of the catalyst bed. Prior to the TPR experiment, the sample was kept under Ar flow (25 mL min⁻¹) at room temperature for 1 h to eliminate physically adsorbed water. X-ray photoelectron spectroscopy (XPS) measurements were performed on a Kratos Ultra spectrometer under ultrahigh vacuum (10⁻⁸ Torr) using monochromated Al Kα radiation (hv = 1848.6 eV) operated at 210 W. All XPS spectra were calibrated using the universal hydrocarbon contamination C 1s peak at 284.8 eV. Inductively coupled plasma mass spectrometry (ICP-MS) analysis was conducted on a Perkin Elmer Elan6000 quadrupole ICPMS, with a detection limit concentration of 0.00004 ppm. This detection limit was calculated based on 3 times standard deviation of 11 measurements on a standard solution with 1 ppb concentration. The typical measured concentration in this work was at least 0.001 ppm, which is 2 orders of magnitude higher than the detection limit.
3. Results and Discussion

3.1. Catalyst microstructure

Fig. 1 compares the microstructures of the newly reported Ir superstructure, the 2 nm Ir NPs, the Umicore Ir black, and the TKK IrO$_x$. To systematically investigate the deactivation behaviors of various forms of Ir/IrO$_x$ for acidic OER, all electrocatalysts were studied without being dispersed onto support materials. This experimental consideration is important, given the insufficient corrosion stabilities of the high-surface-area carbons under OER-relevant conditions and the metal/metal-oxide support interactions observed from the interface of Ir and some commonly used oxide support materials [62,63].

As shown by low-magnification HAADF-STEM micrographs (Figs. 1a and S1a), the Ir superstructure appears to be spherical, with a quite uniform size distribution. Higher-magnification TEM micrographs (Figs. 1a inset and S1b) show that each Ir superstructure is composed of dozens of primary building blocks of Ir nanodendrites growing radially outwards, similar to the corrosion stabilities of the high-surface-area carbons under OER-relevant conditions and the metal/metal-oxide support interactions observed from the interface of Ir and some commonly used oxide support materials [62,63].

Fig. 1. Microstructural characterizations for the electrocatalysts. (a) HAADF-STEM micrograph of the pompon-like Ir superstructure with a mean diameter of 50 nm. The inset shows the TEM micrograph of an individual 50 nm Ir PP. (b) SAED of the Ir PPs, with the inset showing the simulated diffraction pattern of polycrystalline iridium. (c) HRTEM micrograph of a nanodendrite of the Ir PPs. (d) TEM micrograph, (e) SAED, and (f) HRTEM micrograph of the 2 nm Ir NPs. (g) TEM micrograph, (h) SAED, and (i) HRTEM micrograph of the Umicore Ir black. (j) TEM micrographs, (k) SAED, and (l) HRTEM micrograph of the TKK IrO$_x$. 

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structure/morphology of a pompon. Energy-dispersive X-ray spectroscopy (EDS) analysis shows that the as-synthesized Ir superstructure is metallic, with negligible bulk content of oxygen (Fig. S1c). The selected area electron diffraction (SAED) of the Ir superstructure (Fig. 1b) shows that the intensity of the (200) Bragg diffraction for a face-centered cubic crystal structure is relatively weak, in comparison to the simulated electron diffraction of polycrystalline iridium (FM-3m [225]). This observation is consistent with the HRTEM micrographs shown in Figs. 1c and S1d. For each nanodendrite, the presence of CTAB seems to suppress the grain growth in the (001) directions. Earlier studies demonstrated that the binding of CTAB to specific crystal facets leads to the anisotropic one-dimensional growth of gold nanocrystals [64–67]. The development of a pompon-like Ir superstructure may be explained in two ways. First, the anisotropic growth of Ir nanocrystals and the subsequent/spontaneous self-assembling into a superstructure may be driven by the surface energy minimization while being synthesized in a relatively high-temperature solution. In this case, the underlying growth mechanism of the pompon-like Ir superstructure may be similar to that of an ultrathin laminar Ir superstructure, as reported in reference [31]. Alternatively, or in parallel, the development of the dendritic nanostructure may be mediated by a nanocrystal core, which involves a kinetically controlled process in which atoms are deposited quickly but with slow surface diffusion [68]. In this latter case, the underlying growth mechanism of the pompon-like Ir superstructure may be similar to that of the two-step seed-mediated approach used to synthesize Pd-Pt or other bimetallic nanodendrites [69–71]. Further details regarding the size control and the control experiments to determine the effects of various synthesis parameters on the structure and morphology of the Ir superstructure can be found in Figs. S2–S5 in the Supporting Information. Considering the potential surface area and the yield of catalyst synthesis, a pompon-like Ir superstructure with a mean diameter of 50 nm was selected for evaluating the OER electrocatalytic performance. For simplicity, the pompon-like Ir superstructure is hereafter denoted as 50 nm Ir PPs.

Fig. 1d and f show the TEM micrographs of the 2 nm Ir NPs. Unsupported 2 nm Ir NPs aggregate considerably, which are likely to form a dense catalyst layer, leading to less effective utilization of the Ir surface area. As shown in Fig. 1e, the SAED of the 2 nm Ir NPs is similar to the simulated diffraction pattern of polycrystalline iridium. This is expected, since the 2 nm Ir nanocrystals have no preferred growth direction.

Fig. 1g shows the TEM micrograph of the Umicore Ir black. The morphology of Umicore Ir black is not particulate but flake-like. The dimensions of each flake are about 100–200 nm, while the flake thickness is about 10–20 nm. Unlike the simulated diffraction pattern of polycrystalline iridium, the intensities of the (200), (220), and (311) Bragg diffractions from the SAED of the Umicore Ir black are relatively strong, in comparison to the intensity of the (111) Bragg diffraction (Fig. 1h). This observation suggests that the Ir flakes contain larger proportions of the (100)Ir and high-index crystal terminations. Fig. 1i shows a typical HRTEM micrograph of the Umicore Ir black characterized along the zone axis of [001].

Fig. 1j and the inset show the TEM micrographs of the TKK IrOx. As evidenced by the various mass-thickness contrasts in the bright-field TEM micrographs, the surface of TKK IrOx appears to be corrugated and rich in pores, in accordance with the high BET surface area (100 m² g⁻¹) provided by the supplier. The SAED of the TKK IrOx can be easily distinguished from that of metallic iridium but cannot be indexed to a single phase (Fig. 1k). Fig. S6 shows the X-ray diffraction (XRD) pattern of the TKK IrOx. The material is X-ray amorphous, in agreement with the XRD of quasi-amorphous hydrous iridium(III/IV) oxide/hydroxide, as reported in references [39,47,49]. As shown by HRTEM analysis (Fig. 1l), the TKK IrOx is indeed quasi-amorphous, featuring structural short-range order. Fig. S7 shows the temperature-programmed reduction (TPR) profile of the TKK IrOx. A sharp reduction peak is observed at 89 °C, with detected H₂ consumption starting at approximately 35 °C. Previous studies have suggested that such low-temperature reduction is one of the characteristic fingerprints of the highly active hydrous Ir oxide/hydroxide phase formed under hydrothermal conditions [39,47]. The TPR profile of crystalline IrO₂ should show one main reduction peak at 239 °C [47]. As the TPR profile of TKK IrOx does not show a second reduction peak at higher temperatures, the TKK IrOx can be assumed to be a quasi-amorphous hydrous Ir oxide/hydroxide baseline.

The four electrocatalysts investigated here exhibit three pairs of features, which will be shown to be important in the following catalysis sections. (1) The 50 nm Ir PPs, the 2 nm Ir NPs, and the Umicore Ir black are metallic, while the TKK IrOx is composed entirely of hydrous iridium(III/IV) oxide/hydroxide. (2) HRTEM analyses show that the microstructures of the 2 nm Ir NPs and the TKK IrOx are nanocrystalline or quasi-amorphous, with structural short-range order, whereas the Umicore Ir black and the 50 nm Ir PPs possess enhanced crystallinity, probably as a result of high-temperature synthesis. (3) For metallic Ir catalysts, the (100)Ir and high-index facets (e.g., (220)Ir and (311)Ir) are more prevalent in the Umicore Ir black than in the 50 nm Ir PPs and 2 nm Ir NPs. The different proportions of Ir crystal terminations may be more obvious by plotting the azimuthally averaged SAED diffraction intensities versus the d-spacing (Fig. 2). Considering the compositional, structural and morphological effects, the different properties listed above may have profound impacts on the intrinsic OER activity and the corresponding corrosion stability, as assessed below.

![Fig. 2. Azimuthally averaged electron diffraction profiles of the 50 nm Ir PPs, the 2 nm Ir NPs, the Umicore Ir black, and the TKK IrOx.](image-url)
3.2. Initial electrocatalyst activity

Cyclic voltammetry (CV) and rotating-disk-electrode (RDE) linear sweep voltammetry (LSV) were used to investigate the initial catalytic properties of the electrocatalysts. CV was measured in N₂-saturated 0.5 M H₂SO₄ solution using a scan rate of 40 mV s⁻¹. OER polarization curves were measured at 1600 rpm in O₂-saturated electrolyte using a scan rate of 10 mV s⁻¹. Fig. 3a compares the initial CV profiles of the four catalyst electrodes, with the upper potential limit not exceeding 1.05 V versus RHE. As can be seen, the underpotential deposition of hydrogen (Hupd) only occurs on the surface of metallic Ir catalysts. The initial electrochemical surface area (ECSA) of the 50 nm Ir PPs, the 2 nm Ir NPs, and the Umicore Ir black was therefore estimated using the integral charges of Hupd. The ECSA estimation using Hupd was validated by comparing the obtained ECSA to the BET surface area of the Umicore Ir black. As provided by the supplier, the surface area of the Umicore Ir black is 25 m² g⁻¹. This value is in agreement with our estimated ECSA, which is 21 ± 5 m² g⁻¹.

Fig. 3b compares the CV profiles of the four catalyst electrodes, with the upper potential limit reaching 1.53 V versus RHE. These CV profiles were recorded after the 10 preconditioning cycles as shown in Fig. S8. The initial ECSA of the TKK IrOₓ was estimated by using the total anodic charges of the CV profile between 0.4 and 1.25 V versus RHE, corrected for double layer charging. The anodic charges in such a potential range are due to the chemisorption of the upper potential limit of the CV must be kept low to retain a reversible surface state of metallic Ir so that Hupd will still occur. As the upper potential limit was set to 1.53 V during the preconditioning cycles, the hydrogen adsorption–desorption peaks quickly diminish as the metallic Ir surface oxidizes. Such potential-dependent irreversible surface oxidation of metallic Ir during potential cycling was also reported earlier [55,56]. These studies suggested the formation of stable hydrous Ir oxide/hydroxide phase, which is not reduced in the cathodic branch of the CV. Thus, it can be assumed that after electrochemical cycling, the metallic Ir catalysts and the TKK IrOₓ share a similar surface chemical state in situ, which is most likely the quasi-amorphous hydrous iridium(III/IV) oxide/hydroxide phase. This argument was further confirmed by the X-ray photoelectron spectroscopy (XPS) analysis. As shown in Fig. S9, the Ir 4f XPS spectrum of the 50 nm Ir PPs after the preconditioning cycles contains the features of both the metallic Ir (as-synthesized 50 nm Ir PPs) and the as-received TKK IrOₓ.

Fig. 3b compares the CV profiles of the four catalyst electrodes, with the upper potential limit reaching 1.53 V. These CV profiles were recorded after the 10 preconditioning cycles as shown in Fig. S8. The initial ECSA of the TKK IrOₓ was estimated by using the total anodic charges of the CV profile between 0.4 and 1.25 V versus RHE, corrected for double layer charging. The anodic charges in such a potential range are due to the chemisorption of...
oxygenated species and the deprotonation of the hydrous Ir oxide/hydroxide [56,57,72]. An electrical charge constant associated with these anodic processes is needed to calculate the ECSA. The charge constant can be obtained by assuming that the ECSA of a metallic Ir catalyst remains unchanged before and after the hydrous oxide/hydroxide is formed on the surface through the preconditioning cycles. By plotting the total anodic charges between 0.4 and 1.25 V (for CV, such as those shown in Fig. 3b) versus the integral charges of Hupd (for CV, as shown in Fig. 3a) for numerous metallic Ir catalyst electrodes, a charge constant was obtained from the slope of a linear fit (see Fig. S10). The ECSA estimation method, using the anodic charges between 0.4 and 1.25 V, was validated by comparing the obtained ECSA to the BET surface area of the TKK IrOx. As provided by the supplier, the surface area of the TKK IrOx is 100 m² g⁻¹. This value satisfactorily agrees with our estimation of ECSA, which is 84 ± 5 m² g⁻¹.

Fig. 3c reports the initial specific ECSA of the electrocatalysts. The TKK IrOx showed the highest specific ECSA of 112 m² g⁻¹, followed by the 50 nm Ir PPs at 49 m² g⁻¹, the 2 nm Ir NPs at 37 m² g⁻¹, and last the Umicore Ir black at 21 m² g⁻¹. The trend obtained for the ECSA is consistent with the trend in the microstructure, as shown in Fig. 1. It is noteworthy that the 50 nm Ir PPs better utilized the Ir surface area compared to the other metallic Ir electrocatalysts. The three-dimensional pompon-like superstructure mitigates the necessity of using high-surface-area catalyst support, by featuring nanoscale sub-units and a large number of pores for effective mass transport.

Fig. 3d shows the iR-corrected OER polarization curves. All catalyst electrodes investigated here were quite active toward OER, with onset potentials lower than 1.45 V versus RHE. To achieve 10 mA cm⁻²geo, the TKK IrOx catalyst electrode required an initial overpotential of 250 mV, which is better than the values of 265 mV, 273 mV, and 288 mV for the 50 nm Ir PPs, Umicore Ir black, and 2 nm Ir NPs catalyst electrodes, respectively. These values are reported as the initial performance indicators of the catalyst electrodes in the top panel of Fig. 3e. The surface-specific activities, which represent the intrinsic catalytic efficacies of the electrocatalysts, were calculated through normalization by ECSA. Fig. 3f plots the initial surface-specific activities as a function of the applied potentials. To reach 1 mA cm⁻²geo, the Umicore Ir black electrocatalyst required an initial overpotential of 274 mV, which is lower than the 289 mV, 292 mV, and 310 mV required for the 50 nm Ir PPs, TKK IrOx, and 2 nm Ir NPs electrocatalysts, respectively. These values are reported as the initial performance indicators of the electrocatalysts in the bottom panel of Fig. 3e.

As shown in Fig. 3g, the electrocatalysts investigated here exhibit Tafel slopes of ~50 mV dec⁻¹ between 1.45 and 1.50 V, suggesting similar reaction mechanisms toward OER. Fig. 3h reports the initial surface-specific activities of the electrocatalysts, measured at 1.53 V. The higher initial intrinsic activity of the Umicore Ir black may be attributed to the larger proportion of high-index facets, which were found to possess more active catalytic sites for various noble metal nanocrystals [73]. The combined contributions from the ECSA and the surface-specific activities lead to the initial mass activities, as reported in Fig. 3i.

3.3. Catalytic durability

The catalytic durability of the electrocatalysts was evaluated using chronopotentiometry (CP) at 10 mA cm⁻²geo (Fig. 4a). The 50 nm Ir PPs exhibited a gradual increase in anodic potentials required to reach the set value of the current density, registering a catalytic durability of ~4.5 h before the electrode potential reached 1.9 V versus RHE. The TKK IrOx was able to maintain a
fairly stable electrode potential over a period of 8 h, but it experienced a particularly sharp increase in anodic potential once 1.6 V versus RHE was reached. The 2 nm Ir NPs and the Umicore Ir black showed rapid increases in anodic potentials, with the electrode reached 1.9 V in less than 1 h. From the results of the CP analyses, the TKK IrO\(_x\) appeared to have superior catalytic durability. However, the CP analysis actually imposed a much less corrosive condition on the TKK IrO\(_x\) catalyst electrode, due to its higher initial ECSA and mass activity, and as evidenced by the lower starting potential required to reach 10 mA cm\(^{-2}\) \(\text{O}_2\)-geo. Close inspection of Fig. 4a reveals that the TKK IrO\(_x\) actually showed a shorter lifetime in the potential range of 1.55–1.65 V, compared to the 50 nm Ir PPs (Fig. S11). Hence, it can be argued that under the condition of controlled current electrolysis, the measured durability is not entirely equivalent to the catalyst corrosion stability. The “apparent” durability of the TKK IrO\(_x\), as shown in Fig. 4a, may have been dictated by its substantially larger initial ECSA and mass activity. To minimize the influence of surface area on the evaluation of catalytic durability, CP analyses were also performed with the controlled current densities normalized to the initial ECSA.

Fig. 5. Evaluation of corrosion stability using chronoamperometry (CA) at 1.53 V versus RHE. (a) Normalized electrode current densities as a function of time during the controlled potential electrolysis. (b) Electrochemical impedance spectroscopy (EIS), measured periodically at time points of I to VIII, during the first 3-h CA analysis with minimal interference in the applied potential of the CA analysis. CA and EIS were measured at room temperature, at 1600 rpm, and in \(\text{O}_2\)-saturated 0.5 M \(\text{H}_2\text{SO}_4\) solution. (c) CV profiles measured before the stability test and after each 3-h CA analysis. CV was recorded after holding the electrode at open-circuit potential (OCP) for about 10 min while saturating the electrolyte with nitrogen. (d) Comparison of EIS before and after CV-2 measurement. (e) Normalized \(1/R_{\text{ct}}\) and (f) normalized ECSA as a function of time during the stability test.
compares the potentials required to reach 1 mA cm$^{-2}$ between the 50 nm Ir PPs and the TKK IrO$_x$. The starting potentials to reach 1 mA cm$^{-2}$ are slightly different between the two catalyst electrodes, consistent with the initial overpotentials shown in Fig. 3e. At 1 mA cm$^{-2}$, the catalytic durability of the two electrocatalysts was evaluated in a similar potential range of 1.55–1.9 V. Here, the TKK IrO$_x$ showed a catalytic durability of only 2 h, which was 76% shorter than its durability at 10 mA cm$^{-2}$. Conversely, the 50 nm Ir PPs exhibited a catalytic durability of 3.6 h, which was just 23% shorter than its durability at 10 mA cm$^{-2}$. The results of CP analyses at 1 mA cm$^{-2}$ versus at 10 mA cm$^{-2}$ highlight the limitations of the controlled current electrolysis experiment for proper comparison of the catalyst durability. The difference in durability between the 50 nm Ir PPs and the TKK IrO$_x$ at 1 mA cm$^{-2}$ may be due to the higher dissolution rate of the TKK IrO$_x$ from 1.55 to 1.65 V, as evidenced by ICP-MS analysis shown in Fig. 4c and d.

It is worth mentioning that the lifetime of the OER electrocatalyst, as measured using controlled current electrolysis, could actually be limited by the passivation of the GC backing electrode, which has been recently shown to be the cause for the sharp potential increase observed at the end of each CP analysis [58]. However, as the four electrocatalysts were all studied on a GC electrode and exhibited dramatically different degradation behaviors within a lower potential range of 1.5–1.65 V, where the rates of passivation for GC electrode was reported to be slow [58], it is likely that the degradation behaviors are due to the different chemical and structural properties of the four electrocatalysts.

3.4. Corrosion stability, deactivation mechanisms, and activity regeneration

To properly compare the corrosion stability, we propose evaluation of the catalysts under identical electro-oxidative conditions. Here, the corrosion stability and deactivation mechanisms of the Ir/IrO$_x$ OER electrocatalysts were systematically studied using a combination of chronoamperometry (CA), operando electrochemical impedance spectroscopy (EIS), and cyclic voltammetry (CV). The stability test procedure has been detailed in the experimental section. Fig. 5 summarizes the results of the stability test at 1.53 V, for the 50 nm Ir PPs, the 2 nm Ir NPs, the Umicore Ir black, and the TKK IrO$_x$.

3.4.1. Overall deactivation behavior

Fig. 5a depicts the normalized electrode current densities as a function of time during several iterations of controlled potential electrolysis. The current densities are expressed in percentage, normalized to the initial value at the beginning of the stability test. From the first 3-h CA analysis at 1.53 V, the percentage of activity degradation increases in the order of TKK IrO$_x$, 50 nm Ir PPs < 2 nm Ir NPs < Umicore Ir black. The measured catalytic deactivation is accompanied by a gradual increase in the charge transfer resistance ($R_{ct}$), as evidenced by the increasing diameter of the semicircle observed from the Nyquist plots shown in Fig. 5b. The fitted results of the impedance spectra using the simplified Randles cell as the equivalent circuit are listed in Table S1. When the normalized 1/$R_{ct}$ is plotted as a function of time (Fig. 5e), the trend observed is similar to the trend in catalytic deactivation (as shown in Fig. 5a). For TKK IrO$_x$, which exhibits a lower percentage of activity degradation during the first 3-h CA analysis, the decrease in 1/$R_{ct}$ was found to be lower than the other cases. The results of CA and operando EIS analyses show a direct correlation between the increase in $R_{ct}$ and catalytic deactivation of the Ir/IrO$_x$ OER electrocatalysts. It should be mentioned that all catalyst electrodes investigated here show negligible changes in the equivalent series resistance ($R_{es}$) over the period of the stability test.

CV analyses after every 3 h of controlled potential electrolysis were used to track the change in ECSA over the course of the stability test. As discussed above, the total anodic charges in the potential range of 0.4–1.25 V were used to estimate the ECSA for the electrocatalysts after being tested for OER. Fig. 5c shows the evolution of voltammograms during the stability test. The CV profiles of the 50 nm Ir PPs show minimal changes overall, followed by the CV of the 2 nm Ir NPs. The CV profiles of the Umicore Ir black show considerable decreases in size after the first 3-h CA, but then are essentially unchanged after the second and third CA analyses. For the TKK IrO$_x$, the CV profiles show moderate decreases during the first 3 h, but suffer tremendous degradation during the second and third CA analyses, leading to an almost negligible ECSA after 9-h electrolysis at 1.53 V. After extended stability testing, TKK IrO$_x$ showed the most deterioration in OER activity. In contrast, the 50 nm Ir PPs exhibited good retention of ECSA, which in turn led to the best activity retention overall.

It is interesting to note that the degraded OER activity resulting from the controlled potential electrolysis can be partially restored by performing a CV measurement. The capacity for such activity regeneration is also different for each electrocatalyst. The dotted lines in Fig. 5a are used to guide the observation of recoverable activities at the beginning of each 3-h CA analysis. The trends observed for the dotted lines are similar to the trends in the normalized ECSA, plotted as a function of time (Fig. 5f). Hence, the part of OER activity that is not recoverable is presumably due to the loss of ECSA, which is likely to be an irreversible process. The partial activity regeneration is accompanied by a partial recovery of $R_{ct}$, as shown by the impedance spectra before and after the CV measurement procedure (Fig. 5d). For each electrocatalyst, the activity regeneration and recovery of $R_{ct}$ show similar magnitudes (Fig. 5a and e). This observation once again points to the underlying connection between the change in $R_{ct}$ and the variation in catalytic activity.

The observation of activity regeneration has been validated by ruling out two possible experimental artifacts: (a) redeposition of dissolved Ir from the electrolyte while holding the electrode at OCP, and (b) degradation of water transport properties through Nafion, which was used as a binder of the electrocatalysts. Control experiments were conducted for validation by (a) replacing the electrolyte with fresh solution immediately after each 3-h CA analysis, and (b) performing the stability test using a catalyst electrode with one-third of the Nafion loading. The results of validation testing (shown in Figs. S12 and S13) exhibit similar activity regeneration.

3.4.2. Structure sensitivity in the loss of ECSA due to anodic dissolution

The results of stability tests at 1.6 V (Fig. S14) are analogous to the results at 1.53 V, as mentioned above. At a higher anodic potential, all electrocatalysts show more substantial losses in ECSA (Fig. S14c and f), leading to further degradation of OER activities. Specifically, the CV profiles and OER activities of the TKK IrO$_x$ and the 2 nm Ir NPs become almost negligible after 6 h of electrolysis at 1.6 V. The poor stability of the two electrocatalysts at high anodic potentials may be related to their quasi-amorphous/nano crystalline microstructures, which are short-range ordered with a high density of surface defects. It is generally accepted that OER is accompanied by steady-state dissolution of the elements comprising the catalyst due to the high electro-oxidative conditions present [28,40,74]. Previous studies on thin-film model systems revealed that the onset potential of Ru and Ir dissolution is reduced on more defective surfaces [22,40]. Another study on IrO$_x$ electrocatalysts also reported that smaller particles with a diameter of ~1.7 nm are significantly more sensitive to dissolution, though the observation was ascribed to the presence of unstable hydroxide species [45]. As observed from the stability tests at both 1.53 and
1.6 V, the Umicore Ir black shows a major degradation during the first 3-h electrolysis, with its performance being stabilized during the following stability test. Our hypothesis for the two-stage corrosion behavior of the Umicore Ir black is that the Ir flakes contain a bimodal distribution of both low-index and high-index crystal terminations. The high-index facets of Ir may be unstable at the potentials relevant to OER due to their high surface energies [51, 68]. This hypothesis is supported by comparing the SAED of the Umicore Ir black before and after a 6-h CA analysis at 1.53 V (Fig. S15). Relative to the intensity of the (111) Bragg diffraction, the intensities of the (200), (220) and (311) Bragg diffractions were reduced significantly after the stability test. It is remarkable that the 50 nm Ir PPs exhibit a much smaller change in ECSA with a better retention of the OER activity after a 9-h stability test at either 1.53 or 1.6 V. Considering the high rate of anodic dissolution from electrocatalysts with structural short-range order and high-index facets, we argue that the enhanced crystallinity and larger proportion of low-index crystal terminations on Ir PPs account for the better resilience under high electro-oxidative conditions. This is in line with the observation that a single-crystalline Ir (111) surface is much more stable than a polycrystalline Ir electrode [40].

To seek direct evidence regarding Ir dissolution, ICP-MS analysis was used to measure the Ir ion concentration in the electrolyte, which allows us to calculate the percentage of dissolution from the catalyst electrode during stability tests. The trends in the percentage of Ir dissolution, normalized to the initial Ir amount drop-casted on the electrode as a function time (Fig. S16), are consistent with the changes in ECSA (Figs. 5f and S14f). However, we expect some discrepancies between the two magnitudes, considering agglomeration, electrochemical Ostwald ripening and physical detachment of catalyst nanoparticles from the electrode, which are concomitant processes of the cation dissolution [75]. A recent study using online electrochemical mass spectrometry also reported the formation of gaseous IrO3 under the operation conditions of the OER [41].

3.4.3. Intrinsic activity degradation due to active site phase transformation

As can be seen in Figs. 5 and S14, the deactivation of the Ir/IrOx electrocatalysts cannot be solely explained through the loss of ECSA. A large component of activity degradation that is also partially recoverable may therefore be related to the change of intrinsic activity of the OER electrocatalysts. Our analysis shows that such deterioration or regeneration of intrinsic activity can be captured by concomitant changes in the Rct. Because charge transfers are involved in the electrocatalytic OER, an increase in the Rct is likely to involve a change of the active sites, presumably due to a phase transformation and/or a passivation of the electrocatalyst surface. As suggested above, the quasi-amorphous hydrous Ir oxide/hydroxide is the performance-relevant phase for both the metallic Ir catalysts and the TKK IrOx. At OER-relevant potentials, multiple steps of deprotonation of the hydrous Ir oxide/hydroxide will occur, leading to higher oxidation states of Ir [49, 56, 57, 72, 76]. If the highly active hydrous Ir(III/IV) oxide/hydroxide is not regenerated following an OER catalytic cycle as previously proposed [41, 48, 57, 76, 77], a decay of the intrinsic activity is expected, as the performance-relevant species will eventually be depleted on the catalyst surface.

XPS analysis was used to verify our interpretation of the phase transformation-induced intrinsic activity deterioration. Fig. 6a and b show the Ir 4f XPS spectra of the 50 nm Ir PPs and the TKK IrOx, respectively, in their as-synthesized (as-received) state, after preconditioning cycles, and after a stability test. (c-f) Fitting of Ir 4f spectrum for (c) TKK IrOx - as received, (d) TKK IrOx - post CA 1.53 V 3hr, (e) 50 nm Ir PPs - as synthesized, and (f) 50 nm Ir PPs - post CA 1.6 V 9 hr.
guided by the green, red and blue dashed lines. While the green and red dashed lines mark the peak positions of the as-synthesized 50 nm Ir PPs and the as-received TKK IrO₃, respectively, the blue dashed line marks the position of a shoulder peak, which becomes more prominent in both electrocatalysts upon continuous holding at OER-relevant potentials. To obtain a quantitative description of the catalyst surface after a stability test, careful analyses of the Ir 4f spectra were performed according to the fit models of metallic Ir and amorphous IrO₂ as described in references [47,78]. These works showed that the Ir(III) species is in fact at higher binding energies than the Ir(IV) species, based on synchrotron X-ray absorption and photoemission spectroscopies coupled with theoretical calculations. While the detailed fit parameters can be found in Tables S2–S5, the order of the analyses is noted to be: TKK IrO₂ as received (Fig. 6c), TKK IrO₂ post CA 1.53 V 3hr (Fig. 6d), 50 nm Ir PPs as synthesized (Fig. 6e), and 50 nm Ir PPs post CA 1.6 V 9hr (Fig. 6f). This sequence allowed us to first determine the fit parameters of Ir(IV), Ir(III), Ir(0), as well as their associated shake-up satellite peaks, which will be fixed to deconvolute the XPS spectrum of an electrocatalyst after a stability test.

The deconvolution of Ir 4f spectra confirms a common phase, labelled as Ir(post-OER), which was detected on the surface of both Ir and IrO₂ electrocatalysts after holding at OER-relevant potentials. For hydrous Ir oxide/hydroxide, the Ir 4f spectrum of "TKK IrO₂ – post CA 1.53 V 3hr" can be deconvoluted to Ir(IV), Ir(III), and Ir(post-OER) with its Ir 4f/2 and Ir 4f/2 main lines located at binding energies of 63.0 and 66.0 eV, respectively (Fig. 6d). For metallic Ir, the Ir 4f spectrum of "50 nm Ir PPs – post CA 1.6 V 9hr" can be deconvoluted to Ir(0), Ir(IV), Ir(III), and Ir(post-OER) with its main lines also located at 63.0 and 66.0 eV (Fig. 6f). The binding energies of Ir(post-OER) are 0.9 and 0.3 eV higher than the binding energies of Ir(IV) and Ir(III), respectively. Considering the atypical trend of binding energies for Ir(III) and Ir(IV), respectively. Considering the atypical trend of binding energies for Ir(III) and Ir(IV), respectively. Considering the atypical trend of binding energies for Ir(III), the CL shift to a higher binding energy – as observed in Ir(post-OER) – is indicative of an overall higher oxidation state than the initial Ir(III/IV), based on the general understanding of CL binding energy shift. Previous studies have reported that dehydration of hydrous Ir oxide/hydroxide, either in situ in the TEM [49] or by higher calcination temperature [39,81,82], results in an increased oxidation state of Ir and a sharp decrease in the OER activity. A recent study based on operating X-ray absorption spectroscopy revealed that the hydrous Ir (III/IV) oxide/hydroxide transforms into dehydrated Ir(IV) oxide under OER conditions [45]. Another study using ex-situ atom probe tomography coupled with XPS was also able to show that the surface layer of metallic Ir, consisting of non-stoichiometric Ir-O species bounded with hydroxy-groups and water molecules, gradually transforms into rutile IrO₂ during electrolysis between 1.54 and 1.64 V [43]. Based on these reported results, the observed intrinsic activity deterioration may be induced by a progressive surface phase transformation from hydrous Ir(III/IV) oxide/hydroxide into anhydrous Ir(IV) oxide. As Ir(post-OER) in our XPS analyses is positioned at a binding energy higher than both Ir(IV) and Ir(III), the formation of Ir(post-OER) is also likely. The detection of surface phase transformation by ex-situ methods suggests that the performance-relevant active sites of hydrous Ir oxide/hydroxide are not fully regenerated during the OER following the catalytic cycle of Ir(III)-Ir(IV). This reaction cycle has been suggested for more active Ir catalysts, including reactively sputtered Ir oxide [41] and electrochemically formed hydrous Ir oxide [57,79]. Compared to hydrous Ir oxide/hydroxide, the anhydrous Ir oxide surface may be lacking in the electrophilic O¹⁻ species, which were suggested to facilitate the O–O bond formation during electrocatalytic OER [48,83]. The anhydrous oxide surface is also unlikely to have proton conductivity, which has been suggested as a unique property of the hydrous Ir oxide/hydroxide, rendering a three-dimensional electrocatalysis for OER [57,84].

It is worth discussing that one may propose dissolution of active sites as an alternative scenario to explain the intrinsic activity deterioration. We argue that such interpretation may be more applicable to a thermally prepared IrO₂ electrocatalyst with the presence of hydrous oxide/hydroxide surface species as the performance-relevant active sites. As bulk IrO₂ is generally accepted to be less active but more stable, in this case one may not be able to separate between a deterioration induced by active sites dissolution and one induced by surface phase transformation from hydrous Ir oxide/hydroxide into anhydrous Ir(IV) oxide. Thermally-prepared IrO₂ is however not targeted in our study. For the four electrocatalysts studied here, the active sites are shown to be hydrous Ir oxide/hydroxide, with the three metallic Ir catalysts containing a metallic core, and the TKK IrO₂ being composed entirely of hydrous Ir oxide/hydroxide. If dissolution of active sites is the only mechanism, XPS spectrum of the metallic Ir catalysts, with a clear shoulder peak of hydrous oxide/hydroxide after the preconditioning cycles, should revert back to the as-synthesized metallic state after a stability test, and XPS spectrum of the TKK IrO₂ should remain essentially unchanged. This is however not the case, as shown in Fig. 6. Hence, it can be argued that our interpretation of phase transformation-induced intrinsic activity deterioration is more plausible, at least to the electrocatalysts investigated in this study.

Following our discussion of phase transformation-induced intrinsic activity deterioration, the slower deactivation of the TKK IrO₂, compared to the metallic Ir electrocatalysts, during the initial stage of a stability test may be explained by the major difference between the availability and the initial reactivity of the performance-relevant species on the catalyst surface. It has been suggested that the migration of the performance-relevant species from sub-surface to surface may play a key role in maintaining OER activity during a stability test [48]. For the 50 nm Ir PPs, the 2 nm Ir NPs and the Umicore Ir black, the performance-relevant quasi-amorphous hydrous oxide/hydroxide species are only developed on the surface of the metallic Ir through electrochemical cycling. During a continuous electrolysis at OER-relevant potentials, a major degradation of the intrinsic activity is expected once the performance-relevant species are depleted on the surface due to a phase transformation to anhydrous Ir oxide. Although migration of metallic Ir from sub-surface to surface is possible, further development of hydrous oxide/hydroxide may be less effective under OER conditions than through electrochemical potential cycling, as direct oxidation of metallic Ir to anhydrous Ir oxide would prevail at OER-relevant potentials. For the TKK IrO₂, that is composed entirely of the hydrous Ir oxide/hydroxide phase, the active species may be able to migrate from sub-surface toward the surface until a more compact layer of anhydrous Ir oxide is formed to limit the migration process. The great availability of the performance-relevant species in the TKKIrO₂ plays a role in stabilizing intrinsic OER activity, which leads to superior catalytic durability when substantial loss of ECSA is not yet the predominant process of catalytic deactivation – for example, in the case of CP analysis at 10 mA cm⁻².

3.4.4. OER activity regeneration on Ir/IrO₂ electrocatalysts

The regeneration of OER activity, as shown in Figs. 5 and S14, and also observed though not explained in a previous study (Fig. 1A in Ref. [23]), may take place as a cathodic reduction from...
the anhydrous Ir oxide to hydrous Ir oxide/hydroxide together with transient cathodic dissolution. According to a recent study based on operando X-ray absorption spectroscopy, a dehydrated Ir oxide surface, transformed from hydrous Ir oxide/hydroxide under OER conditions, can be reduced back to the initial state during the cathodic polarization [45]. It is also known that the reduction of Ir oxide is a kinetically hindered process [56]. The transient cathodic dissolution on the other hand would facilitate the replenishment of OER active sites by exposing fresh surfaces of metallic Ir or hydrous Ir oxide/hydroxide to the electrolyte. The transient cathodic dissolution has been reported to occur at very low potentials and may be promoted by increasing the sweep rate of potential cycling. [56].

To verify activity regeneration using controlled current electrolysis, a 50 nm Ir PPs catalyst electrode was regenerated periodically during CP analysis at 10 mA cm\(^{-2}\) by (1) holding the electrode at OCP in N\(_2\)-saturated solution, (2) applying a reducing potential over time, or (3) using potential cycling at a high sweep rate. When the cathodic reduction/dissolution procedure was short (i.e., holding the electrode at OCP in N\(_2\)-saturated solution for about 10 min, followed by recoding a CV), only the superficial sites appeared to be replenished. These superficial sites are highly active, but would be quickly consumed once again by electrolysis at OER-relevant potentials (Fig. S17a). When substantially more time was spent at lower potentials for cathodic reduction/dissolution, the regenerated OER activity lasted longer and could potentially extend the lifetime of a 50 nm Ir PPs catalyst electrode by onefold, compared to the same CP analysis without any activity regeneration (Fig. S17b). When 1000 potential cycles between 0 and 1 V at a sweep rate of 500 mV s\(^{-1}\) was used to promote transient cathodic dissolution, the lifetime of a 50 nm Ir PPs catalyst electrode could also be extended considerably (Fig. S17c).

As shown in the right panel of Fig. S17, the increasing diameter of a second semicircle observed from the high-frequency region of the Nyquist plot suggests an increasing surface film impedance, possibly due to the development of a porous anhydrous oxide surface passivation layer [55,85] resulting from the repeated electrolysis–partial regeneration cycles. It is noteworthy that for the case shown in Fig. S17b, in which the regenerated activity lasted longer, there was also a low level of surface passivation, as evidenced by a small semicircle in the high-frequency region. More work is apparently needed to explore activity regeneration for Ir/IrO\(_x\) OER electrocatalysts. Considering the intermittent nature of renewable energy, the fact that a deactivated Ir/IrO\(_x\) surface can be regenerated after electrolysis may be practically important.

4. Conclusions

In this study, the OER activity and corrosion stability for a list of Ir/IrO\(_x\) electrocatalysts, including a newly reported pompom-like Ir superstructure (50 nm Ir PPs), 2 nm Ir NPs, and commercially available Ir black (Umicore Ir black) and IrO\(_x\) (TKK IrO\(_x\)), were systematically investigated. In addition to using chronopotentiometry – a benchmarking method – to evaluate the catalyst durability at a constant current density, the corrosion stabilities of the electrocatalysts were compared under identical electro-oxidative conditions, thereby decoupling the deactivation mechanisms of Ir/IrO\(_x\) electrocatalysts toward OER. By establishing the relationship between electrocatalytic performance and the microstructural/chemical properties of the electrocatalysts, the relative contributions from the loss of ECSA and from the deterioration of intrinsic activity were shown to be highly dependent on the nature of the electrocatalysts.

For the TKK IrO\(_x\) and the 2 nm Ir NPs, which have structural short-range order with a high density of surface defects, the tremendous loss of ECSA due to Ir dissolution is the predominant deactivation mechanism during a continuous electrolysis at OER-relevant potentials. For the Umicore Ir black, with its prevalent high-surface-energy high-index facets, the loss of ECSA due to rapid Ir dissolution is also the predominant deactivation mechanism. For the 50 nm Ir PPs, which exhibits a much smaller change in ECSA, the enhanced crystallinity and larger proportion of low-index crystal terminations account for its better resilience under high electro-oxidative conditions.

The stability test results highlighted the degradation of intrinsic activity, which plays a key role in the deactivation behaviors of the Ir/IrO\(_x\) OER electrocatalysts. For the 50 nm Ir PPs, the 2 nm Ir NPs and the Umicore Ir black, the performance-relevant quasi-amorphous hydrous Ir oxide/hydroxide species are only developed on the surface of the metallic Ir through electrochemical cycling. During a continuous electrolysis at OER-relevant potentials, a major degradation of intrinsic activity is expected once the performance-relevant species are depleted on the surface due to a phase transformation to anhydrous Ir oxide. For the TKK IrO\(_x\), which is composed entirely of the hydrous Ir oxide/hydroxide, greater availability of the performance-relevant species plays a role in stabilizing the intrinsic activity, leading to superior durability when substantial loss of ECSA is not yet the predominant process of catalytic deactivation.

The stability test results also demonstrated the regeneration of a deactivated Ir/IrO\(_x\) surface, taking place as a cathodic reduction from the anhydrous Ir oxide to hydrous Ir oxide/hydroxide together with transient cathodic dissolution. While the regeneration of active sites could potentially extend the lifetime of an Ir catalyst electrode, the regeneration process is shown to be kinetically sluggish. The electrolysis–partial regeneration cycles eventually lead to the development of a surface passivation layer, which may be the source of the ultimate activity fade or permanent deactivation in the Ir/IrO\(_x\) OER electrocatalysts.

To propose a rational design of Ir-based OER electrocatalysts based on the findings of structure-sensitive deactivation mechanisms, a single crystalline dendritic nanostructure with low-index crystal terminations may be ideal to achieve a balanced initial mass activity and enhanced resistance to anodic dissolution. To mitigate the degradation of intrinsic activity induced by the phase transformation of active sites and/or the surface passivation, a multimetallic Ir-based hydrous oxide/hydroxide might be feasible to achieve the availability of the performance-relevant species, and in the meantime to facilitate the generation of fresh surface to the electrolyte through controlled leaching of the secondary elements during electrolysis.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.jcat.2019.01.018.

References

Y. Pi, N. Zhang, S. Guo, J. Guo, X. Huang, Ultrathin laminar Ir superstructure as highly efficient oxygen evolution electrocatalyst in broad pH range, Nano Lett. 16 (2016) 7011–7016.


