

Iridium-Ruthenium Oxide for the Oxygen Evolution Reaction: Correlation between Calcination Temperature–Morphology–Activity Interplay

Claudelle Anensong Djadock

Nelson Mandela University

Anele Nzimeni

Nelson Mandela University

Shawn Gouws

`shawn.gouws@mandela.ac.za`

Nelson Mandela University

Research Article

Keywords: IrRuOx catalysts, Thermal treatment, P-XRD, HR-TEM, Oxygen Evolution Reaction, Acidic medium (0.5 M)

Posted Date: October 13th, 2026

DOI: <https://doi.org/10.21203/rs.3.rs-11062740/v1>

License:   This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

Additional Declarations: No competing interests reported.

Iridium-Ruthenium Oxide for the Oxygen Evolution Reaction: Correlation between Calcination Temperature–Morphology–Activity Interplay

Claudelle Sybilline Anensong Djadock ^{a*}, Anele Nzimeni ^a, Shawn Gouws ^{a*}

^a *Department of Chemistry, Nelson Mandela University, Summerstrand, Gqeberha, 6001, South Africa*

Corresponding author: shawn.gouws@mandela.ac.za

Abstract

A key challenge in water electrolysis is establishing structure–activity relationships to understand and improve IrRuOx-based catalysts for the oxygen evolution reaction (OER) in a PEM water electrolyser. We report a simple, scalable modified Adams fusion method for preparing highly OER-active IrRuOx with various sizes and shapes. This practical approach enables investigation of how heat treatment affects particle size, morphology, and the nature of surface species, and how these factors influence the OER activity of IrRuOx. P-XRD, HR-TEM/SEM-EDS, and TGA/DSC studies indicate a transition from an amorphous hydrated oxide (IrRuOx@350) to a crystalline hydrated phase (IrRuOx@400 °C, IrRuOx@450 °C, IrRuOx@500 °C, and IrRuOx@520 °C), with surface species strongly linked to OER activity. IrRuOx synthesized at 500 °C, consisting of 22.22 nm particles with an electrochemical surface area of 903 cm², shows the highest OER activity in 0.5 M H₂SO₄ (E = 220 mV and a Tafel slope of 24.41 mV/dec at 10 mA/cm²). In contrast, amorphous IrRuOx synthesized at 350 °C shows better stability at a potential of 1.27 V. A variation in intrinsic OER activity was associated with the predominant termination of rod-shaped particles by highly ordered (110) and (200) facets.

These results highlight the important role of calcination temperature in achieving the best balance between activity and durability of materials towards OER in PEMWE applications.

Keywords: IrRuOx catalysts, Thermal treatment, P-XRD, HR-TEM, Oxygen Evolution Reaction, Acidic medium (0.5 M)

Introduction

Electrochemical water splitting, EWs, commonly known as water electrolysis, is one of the most studied concepts in the field of energy . In the near future, EWs are expected to become the primary energy source once coal and hydrocarbons are fully consumed . In EWs, two critical electrochemical processes occur at the cathode and anode, namely the hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER) . The OER mechanism involves a four-electron transfer, which requires more energy than the HER, i.e., the cathodic reaction, where only two electrons are expected . Therefore, the OER process governs the overall efficiency of electricity-driven water electrolysis, which can be operated under either acidic or alkaline conditions. OER under acidic conditions is favoured by the higher ionic conductivity of acidic electrolytes and the ability to operate at higher current densities. However, practical application is significantly hindered by sluggish OER kinetics and the limited stability of existing electrocatalysts .

Ruthenium dioxide (RuO_2) has been considered as a standard OER catalyst for acidic conditions . Still, its poor stability leads to the dissolution of Ru and, therefore, to the participation of the lattice oxygen in the acidic OER mechanism, which remains problematic for RuO_2 as a sustainable catalyst for OER . To improve the performance of RuO_2 electrocatalysts, tuning the electronic structure of Ru sites by doping has been demonstrated to be an effective strategy. Fundamental research has proposed a series of approaches, including bimetallic oxide, alloy, and solid-solution phase formation. Consequently, to date, incorporating iridium is regarded as the most promising benchmark OER catalyst for practical PEM systems, owing to its superior durability. For instance, Zhu *et al.* (2023) reported that an Ir-incorporated RuO_2 catalyst forming 2D $\text{Ru}_{0.5}\text{Ir}_{0.5}\text{O}_2$ solid significantly improves both the activity and stability of the ruthenium center. Ting *et al.* (2025) reported a ruthenium-iridium alloyed oxide catalyst with remarkable catalytic stability, about 1600 h at a current density of 2.0 A/cm^2 for PEM-WE at industrial current density . This results were reinforced by the report of Thy *et al.*. Therefore, state-of-the-art IrRu oxide OER catalysts have been studied from component dependence and optimization of bimetallic oxide nanostructures to modifications of electronic properties . At the same time, it becomes progressively challenging to establish structure-activity relationships for the OER due to the complex nature of the surface species. Along the way, several preparation methods have been reported for synthesizing electrocatalysts, including the Adams method.

This technique has also been adopted for the preparation of metal-based oxide catalysts. Several synthesis parameters in the Adams fusion technique including heat treatment can affect catalyst properties, including crystallinity, oxidation state, metallic oxide or alloy, morphology and surface area. The effect of heat treatment on the OER performance of the unsupported IrO₂/RuO₂ or IrRu oxide catalysts was investigated. The fundamental study of Ilva *et al.* (2017) emphasizing a strong relationship between structural properties and electrocatalytic performance, which can be attributed to the presence of a mixture of amorphous and crystalline IrO₂. Specifically, calcination temperature and resulting catalyst crystallinity affect dissolution rate, with stability changing with variations in heat treatment and phase transition.

In this work, we investigate the Adams fusion method for producing IrRu oxide catalysts, and systematically study the resulting physicochemical properties and their relationship to OER activity and stability. Specifically, we examine the effect of heat treatment (350, 400, 450, 500, and 550 °C) on the morphology, structure, and performance of the catalysts. Insights from advanced characterization techniques (P-XRD, HR-TEM/SEM-EDS, and TGA/DSC) and electrochemical analyses (linear sweep voltammetry, cyclic voltammetry, and Chronopotentiometry) are integrated to elucidate the relationship between structure and properties in electrocatalytic OER in 0.5 M H₂SO₄.

2. Experimental Section

2.1. Reagents and Chemicals

All chemicals and reagents were obtained from commercial suppliers and used as received without further purification.

Metal precursors such as iridium(III) chloride hydrate (IrCl₃·xH₂O) and ruthenium(III) chloride (RuCl₃·xH₂O) were purchased from Alfa Aesar and Sigma-Aldrich Chemicals, respectively. Sodium nitrate (NaNO₃), isopropanol, and 98% sulfuric acid (H₂SO₄) were procured from Minema Chemicals and Associated Chemical Enterprises.

2.2. Synthesis of the IrRu oxides catalysts

The IrRuO_x catalysts were synthesized following the Adam fusion method. In a typical synthesis, the respective similar ratio metal precursors IrCl₃·xH₂O and RuCl₃·xH₂O were dissolved in 6 mL of isopropanol to achieve a total metal concentration of 8×10^{-2} M. The solution was magnetically stirred for 18 hours to ensure complete dissolution of the precursors. Subsequently, 5 g of finely ground NaNO₃ was added to the solution. The mixture was heated

at 90 °C in an open-air vessel until dry, yielding a solid residue containing NaNO₃ and the metal salts. The dried mixture was then transferred to a ceramic crucible and calcined in a preheated furnace at temperatures ranging from 350, 400, 450, 500, to 520 °C for 30 minutes each. After calcination, the resulting salt oxide powder was allowed to cool slowly to room temperature. The product was washed several times with hot deionized water to remove excess of salt before being recovered by centrifugation. The final product was dried at 90 °C in air to afford catalysts **1** (350 °C), **2** (400 °C), **3** (450 °C), **4** (500 °C) and **5** (520 °C)

2.3. Materials Characterization

2.3.1. Structural analysis

P-XRD analysis was conducted using a PANalytical Aeris PXRD diffractometer equipped with a Co K α radiation source ($\lambda \approx 1.788$ Å). Typical conditions included operating at 36 kV and 36.0 mA, and recording patterns over a 2θ range of 10°–80° with a step size of 0.022° at a scan speed of 36.72 s/step. Phase identification was carried out by means of the X'Pert accompanying software program PANalytical HighScore Plus in conjunction with the standard ICDD Powder Diffraction database and the Crystallography Open Database (COD, 2024). The peaks at the different diffraction angles were integrated using OriginPro software for data plotting and comparison purposes. The crystallite size was estimated using the Scherrer Equation 1. The analysis confirmed the formation of mixed metal oxides or alloy phases depending on the heat treatment.

$$t = 0.9\lambda/\beta\cos\theta \dots\dots\dots (1)$$

Morphological and elemental mapping was performed using scanning and transmission electron microscopy. Backscattered Electron (BSE) Scanning electron microscopy (SEM) imaging and energy-dispersive X-ray spectroscopy (EDS) analyses were carried out on mounted powders with a JEOL JSM 7001F FEG-SEM (15 kV, 10 mm WD) fitted with an Oxford XMax 100 EDS detector. SEM-EDS elemental mapping and further BSE imaging were performed on polished cross-sections of the powders with a filament-based JEOL JSM-IT210 SEM (15 kV, 10 mm WD) fitted with a standard JEOL 60 mm² SDD EDS detector. The SmileView Lab software was used for acquisition and processing.

HR-STEM and STEM-EDS analysis was carried out on a JEOL JEM-ARM200F TEM operated at 200 kV and equipped with an Oxford XMax 100 EDS detector. Annular Dark-Field (ADF) and Bright Field (BF) STEM imaging was performed with detector acceptance semi-

angles of 34-137 mrad and 0-12 mrad, respectively. Gatan's DigitalMicrograph™ software was used for STEM image analysis and Aztec software for EDS spectrum acquisition and processing.

Thermal analysis (TGA/DSC) of the samples was performed using a TA Instruments SDT Q600 apparatus. The samples were heated from 30 to 800 °C at a constant rate of 10 K/min in N₂.

2.3.2. Electrochemical Measurements

The OER performance of the five catalysts was evaluated using a standard three-electrode configuration controlled by an Autolab motor controller unit (MCUR) with a rotator (RDE-2). A platinum wire (5 mm diameter) served as the counter electrode, a commercial Ag/AgCl electrode as the reference, and a glassy carbon electrode (GCE, 5 mm diameter) coated with catalysts **1-5** served as the working electrode.

A catalyst ink was prepared by dispersing 5 mg of each of the five catalysts, respectively, in a mixture of 300 µL isopropanol and 10 µL of a 5.0 wt% Nafion solution. The mixture was sonicated for 1h and stirred for 1h. A portion of this ink was then drop-cast onto the GCE surface to achieve a catalyst loading of 0.003–0.005 g/cm².

The OER activity was primarily assessed via Linear Sweep Voltammetry (LSV) in N₂-saturated 0.5 M H₂SO₄ at room temperature. Scans were performed from 0 to + 1.5 V vs. Ag/AgCl at a scan rate of 5 mV/s. All measured potentials were converted to the reversible hydrogen electrode (RHE) scale using the Nernst equation (Equation 2):

$$E_{(\text{RHE})} = E_{(\text{Ag/AgCl})} + 0.059 \times \text{pH} + E^0_{(\text{Ag/AgCl})} \dots \dots \dots (2)$$

The overpotential (η) and Tafel slope were derived from the LSV curves using Equations 3 and 4:

$$\eta = E - 0 \text{ V vs RHE} \dots \dots \dots (3)$$

$$\eta = a + \frac{2.3RT}{\alpha nF} \log(j) \dots \dots \dots (4)$$

Respectively, where j is the current density, F is Faraday's constant, and α is the charge transfer coefficient.

Cyclic voltammetry (CV) was employed to probe redox behavior. Measurements were conducted in N₂-saturated 0.5 M H₂SO₄ over a potential window of – 0.25 to +1.5 V vs. Ag/AgCl. Double-layer capacitance (C_{dl}) was determined by measuring the CV in the non-faradaic region. CVs were recorded at different scan rates (50, 100, 200, 300, 400, 500 and

600 mV/s) in 0.5 M H₂SO₄ media. The slope of the resulting linear plot was used to determine the C_{dl} based on the following Equation 5.

$$C_{dl} = \frac{\Delta j}{\Delta v} \dots \dots \dots (5)$$

The ECSA (Equation 6) was then calculated using C_{dl} , where C_s is depicted as the specific surface capacitance (0.035 μF cm⁻²), and A_{GC} is the geometric area of the electrode (0.196 cm²).

$$ECSA = \frac{C_{dl}}{C_s} \dots \dots \dots (6)$$

The anodic (I_a) and cathodic (I_c) peak currents were calculated from the CV data at varying scan rates.

Chronopotentiometry (CP) measurements were performed at a constant current density of 10 mA/cm² for 24 h in 0.5 M H₂SO₄ to evaluate the durability of the modified electrode. The corresponding voltage changes were recorded throughout the experiment to assess the durability.

3. Results and Discussion

3.1. Synthesis and Structural Characterization

The iridium-to-ruthenium heat treatment was systematically varied based on the following target temperatures: **1** (350 °C), **2** (400 °C), **3** (450 °C), **4** (500 °C), and **5** (520 °C). The total concentration was maintained at 8×10^{-2} M, with a precursor ratio of 0.5. For brevity, the synthesized catalyst materials in this study follow the notation IrRuO_x@T, where x denotes the oxide ratio and T the sintering temperature. In general, the synthesized materials were a mixture of mixed oxides or solid solutions of IrRuO_x and Ir-Ru alloy. The applied method permitted the synthesis of a broad range of crystallinity, size and morphology-controlled IrRuO_x catalysts.

P-XRD analysis was used to scrutinize the evolution of the crystal-like structure of the IrRuO_x catalysts with increasing calcination temperature, and the corresponding diffraction patterns are shown in Figure 1 and Figure S1. The reflections at 350°C (Figure S1a) can be assigned exclusively to the mixed tetragonal and orthorhombic phase of the iridium and ruthenium oxide (see Figure 1a), which demonstrates that this iridium oxide phase is X-ray amorphous. An additional phase starts to grow at 400 °C (Figure S1b), identifiable by a small broad reflection at around 32.75° (see Figure 1b). These reflections grow in integral intensity and narrow with increasing calcination temperature, demonstrating the formation of a more

crystalline phase with larger crystallite sizes (Figures S1a-e). This phase can be identified as a rutile-type oxide based on the additional reflections. The patterns also confirmed the absence of other phases, such as metallic Ir or Ru, and the presence of mixed oxides IrRuO_x as well as IrRu alloy, which is slightly present in all catalysts.

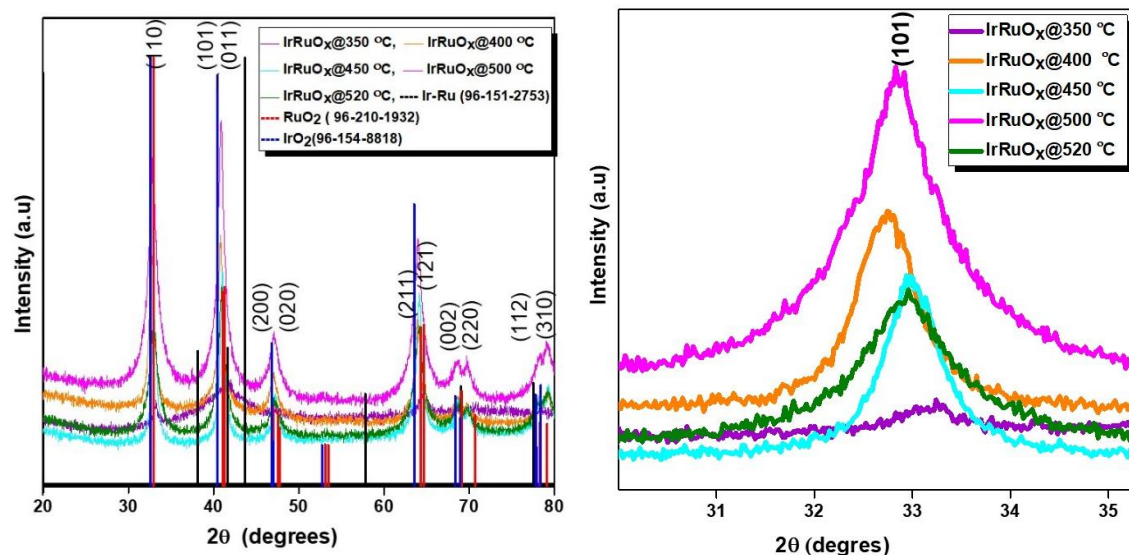
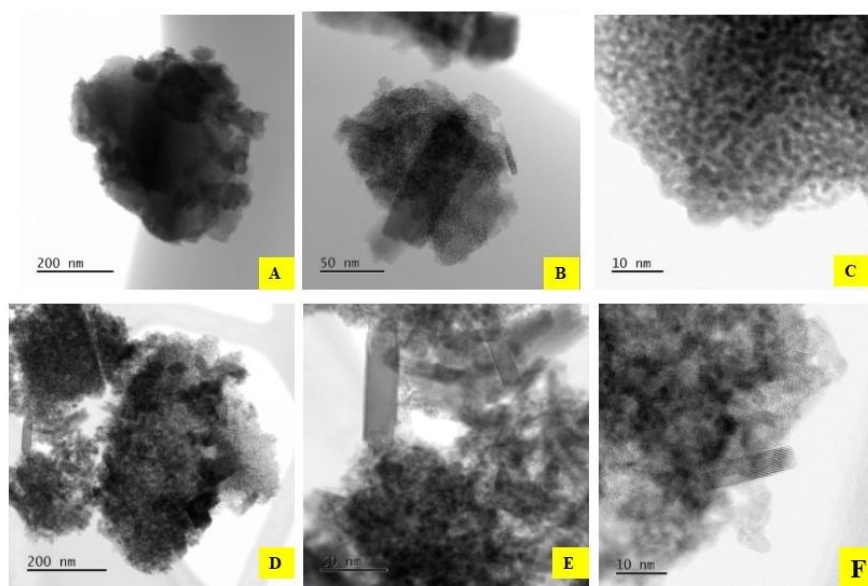


Figure 1. Powder XRD patterns of IrRuO_x catalysts from 20° to 80° 2θ (a) and with linear background correction from 30° to 35° 2θ (b) to magnify the (101) reflection of the rutile-type oxides. Reference patterns from the powder diffraction file (PDF) of the International Center of Diffraction Data are provided for comparison.

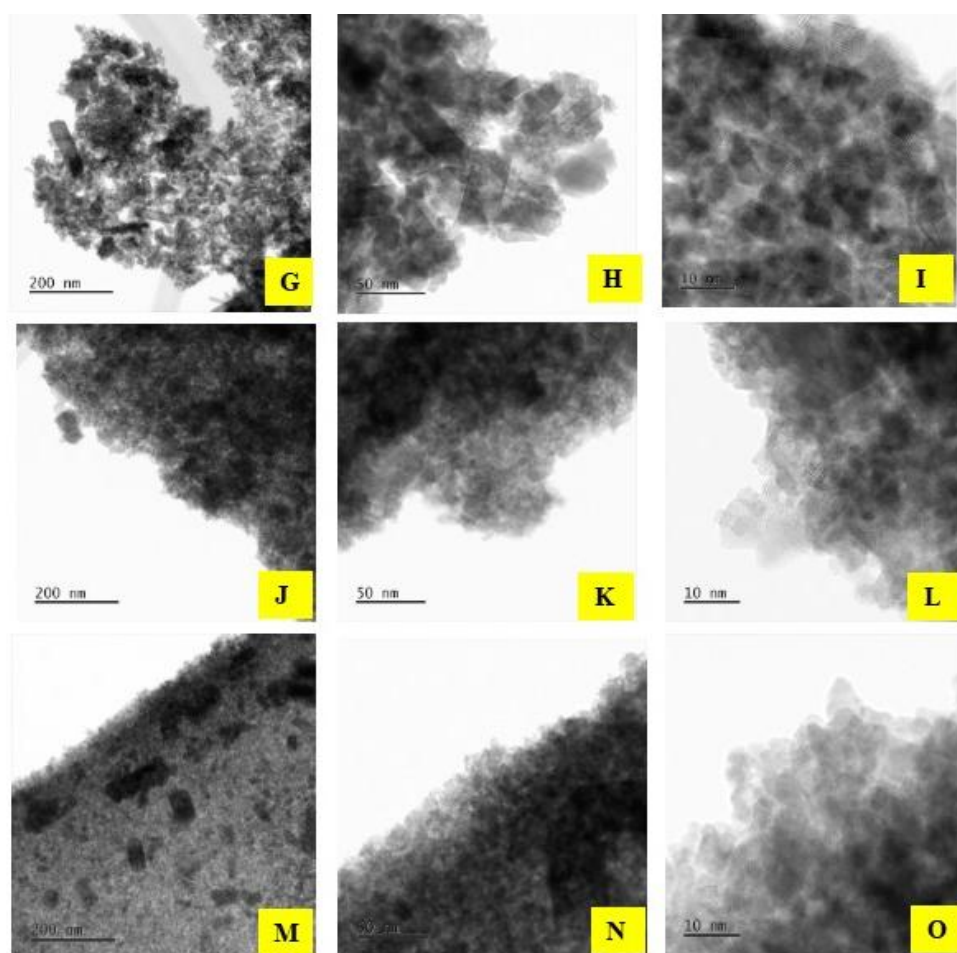
Interestingly, the similar (110), (101), (011), (200), (020), (211), (121) (002), (220) (112), and (310), reflection peaks for the catalysts have a predominant mixed oxides or solid solutions of IrRuO_x in accordance with the JCPDS database for the tetragonal IrO₂ (JCPDS No. 96-154-8818), and the orthorhombic RuO₂ crystallographic pattern (JCPDS No. 96-210-1932). However, the (101) and (220) peaks match the orthorhombic Ir-Ru alloy ICCD file No. (96-151-2753). The angular shifts compared to those of IrO₂ and RuO₂ indicate the successful incorporation of IrO₂ into RuO₂. Therefore, the crystal lattice parameters of the solid-solution or mixed-oxide catalysts vary considerably depending on the heat treatment (Fig. S1). This is mostly due to the cationic radii of ruthenium and iridium, which are 0.625 Å and 0.620 Å, respectively. Thus, the lattice parameters are very similar for these two oxides, as can be found in the JCPDS database. So, during IrRuO_x formation, the Ru or Ir atoms can be randomly substituted among each other's positions in the lattice. Consequently, a solid solution forms with smaller lattice parameters, leading to a shift in the diffraction peak observed in the XRD patterns (see Figures 1 and S1). Using the Scherrer equation 1, the average crystallite size of

the IrRuO_x catalysts is estimated from the XRD patterns at the (101), (200), (111), (210), and (211) peaks. The crystallite sizes are 16.3 nm, 18.9 nm, 20.7 nm, 22.25 nm, and 16.04 nm for **1** (350 °C), **2** (400 °C), **3** (450 °C), **4** (500 °C), and **5** (520 °C), respectively. As the heat treatment increased, the crystallite size of the mixed materials increased, which may imply the introduction of tensile strain and possible generation of hydrophilic group vacancies. While the crystallite sizes of the solid-solution catalysts increase with increasing heat treatment, changes in the morphology and particle distribution of the catalyst samples are observed by SEM and HR-TEM. SEM images of catalysts, displayed in Figures S2-S6, seem to have irregular, tightly porous, and visible networks of interconnected pores or voids between the granules. The catalyst particles are significantly influenced by the fractional time (T = 30 min) of heat treatment. For instance, at lower calcination temperatures of 350 °C (**1**), the highly porous structure changes to larger crystallized particles (**2**, **3**, **4**, and **5**). This morphological progression, observed under identical synthetic conditions, aligns with a previous structural XRD study (Figures 1 and S1). To observe clear morphological characteristics of the catalyst, high-resolution transmission electron micrographs (HR-TEM/STEM) were obtained and are shown in Figure 2.

In general, all catalyst samples show smaller particles with darker contrast, probably due to the presence of hydrophilic groups or species, which are distributed on the surface of each catalyst. The particles, however, had rough, unclear edges and lacked a specific shape, indicating an amorphous structure, as previously confirmed from XRD patterns (Figure S1). Calcination at 350 °C (**1**) and 400 °C (**2**) (Figure 2a) reveals a slight change in the morphology, with well-observed rectangular or nanorod-like and amorphous particles. HR-TEM images of the catalyst calcined at higher temperatures of 450, 500, and 520 revealed a transformation in the physical morphology of the catalyst. The existing small darker contrast on particles grew to the size of IrRuO_x particles. Also, the particles developed clearer grain boundaries with a more distinct shape, which is evidence of developing a crystalline structure. This conversion is more evident in Figure 2b. The change in the physical structure from amorphous to crystalline has been discussed in the XRD section.



(a) HR-TEM images of catalysts **1** (A-C) and **2** (C-E)



(b) HR-TEM images of catalysts **3** (G-I), **4** (J-L), and **5** (M-O).

Figure 2. HR-TEM images of catalysts **1-5** from high (200 nm) to low (10 nm) magnification

In all the catalysts, the arrangement of these particles creates a highly sponge-like structure, which suggests a high surface-area-to-volume ratio, generally favourable for catalytic activity. However, the mean particle size could not be reliably determined due to the agglomeration of these nanoparticles. Consistently, the high-angle annular dark-field scanning transmission electron microscopy (Figure 3a) image of IrRuO_x displays well-defined lattice fringes with interplanar distances of 0.321 nm, 0.228 nm and 0.277 nm at a sintering temperature of 350 °C (**1**, Figure 3A). At 400 °C (**2**), the corresponding lattice spacings are 0.316 nm, 0.260 nm and 0.338 nm (Figure 3B), while at 450 °C (**3**, Figure 3C), the interplanar distances are 0.318 nm, 0.317 nm, 0.264 nm, 0.231 nm and 0.226 nm. The corresponding lattice fringes of 0.314 nm, 0.317 nm, 0.279 nm, and 0.244 nm were found at 500 °C (**4**, Figure 3D), as well as 0.327 nm, 0.313 nm, 0.274 nm, 0.264 nm, and 0.258 nm at 520 °C (**5**, Figure 3E). These measured *d*-spacing values, which are relatively broader than those of RuO₂ (0.315 nm) and IrO₂ (0.318 nm), further demonstrate the expanded RuO₂ lattice after introducing IrO₂. The corresponding lattice fringes reveal coincidence with the *d*-spacing of (110), (101), (011), (020), and (200) within the lattices of each catalyst found in the P-XRD pattern (see Figure 1).

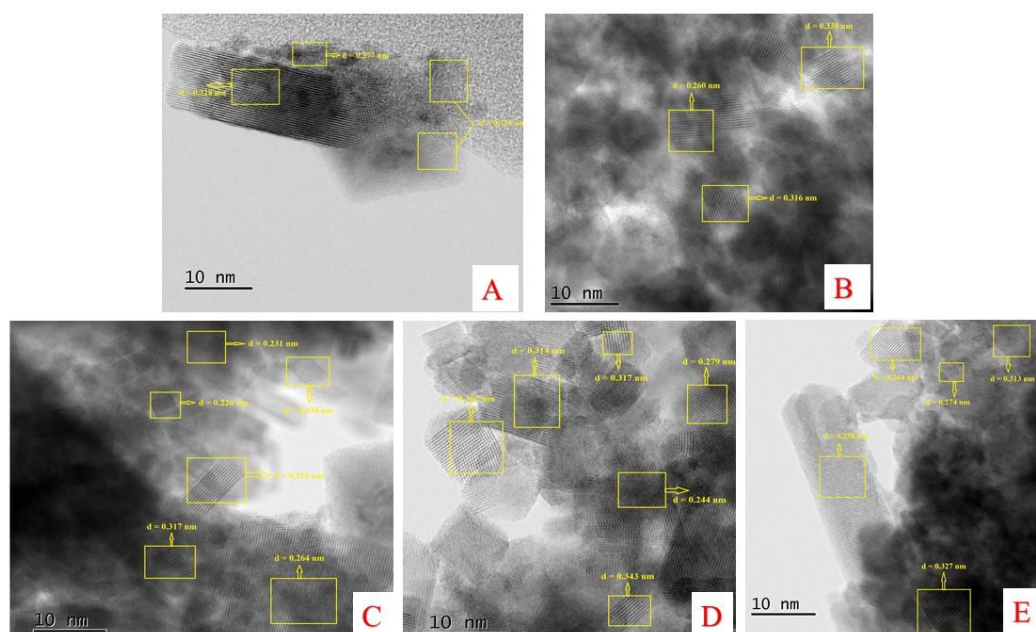


Figure 3. HR-TEM images of corresponding lattice fringes of catalysts **1**(A), **2**(B), **3**(C), **4**(D) and **5**(E)

Measurements of the interplanar spacing indicate that the nano-rod particles predominantly grow in the (110) and (200) directions of the rutile unit cell. In addition, energy-dispersive X-ray spectroscopy (EDS) elemental maps of the catalysts confirmed the presence of Ir, Ru, O, Na, and Cl within the particles (Figure S7). Figure 4A- B shows the elements Ir, Ru, and O

from the IrRuO_x catalysts at 400 °C (2), 500 °C (4), and 520 °C (5), respectively, confirming that all elements are present on the surface and distributed throughout the area.

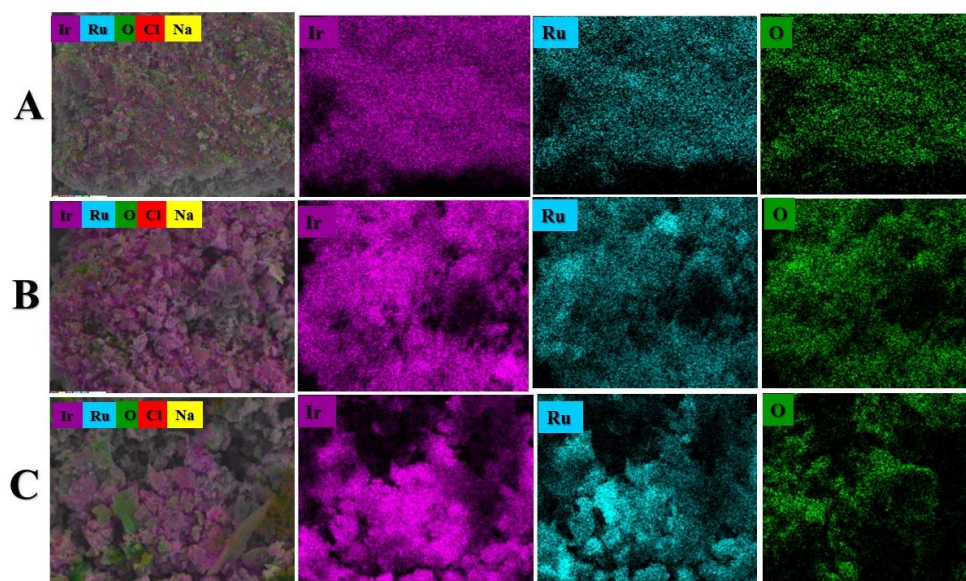


Figure 4. EDS elemental mapping of Ir, Ru, and O elements for IrRuO_x@400 °C (2), IrRuO_x@500 °C (4), IrRuO_x@520 °C (5),

In studies of the preparation of IrRuO_x catalyst with the Adams fusion method, it was found that the calcining temperature influences their thermal behaviour. The results of TGA and DSC measurements are shown in Figure 5.

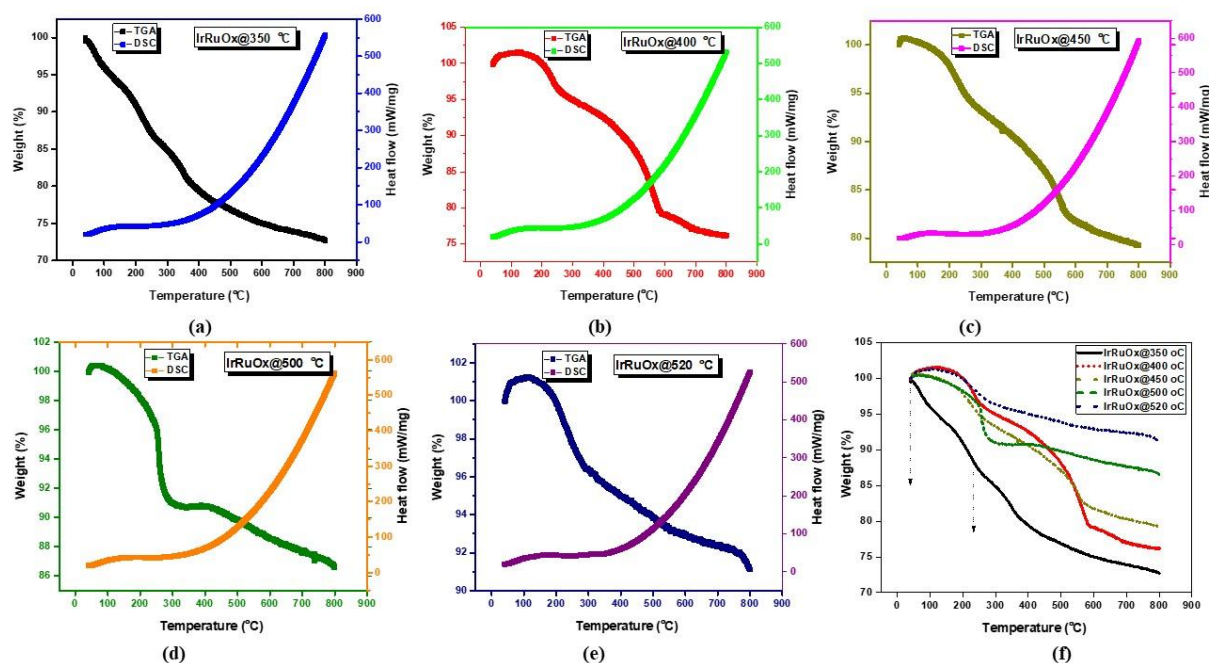


Figure 5. TGA and DSC curves of the as-synthesized IrRuO_x@350 °C (1), IrRuO_x@400 °C (2), IrRuO_x@450 °C (3), IrRuO_x@500 °C (4), IrRuO_x@520 °C (5).

Distinct temperature regions are present in all metal oxide catalysts. The first weight loss observed between ~ 35 – 293 °C (calc value: 5.07%) was attributed to chemical dehydration. Whereas the second one, attributed to a phase transition of IrRuO_x from an amorphous to a crystalline structure, as confirmed by the XRD pattern (Figure 1), was observed in the range ~ 293 – 417 °C. This was also accompanied by a slight weight loss due to the breakdown of -OH (calc value: 4.75 %) or oxygen (calc value: 4.47 %) groups, possibly forming a sub-stoichiometric oxide in the amorphous material. The low decrease in weight is accompanied by an indiscernible exothermic peak on the DSC curves. When increasing the calcination temperature of the catalysts, the weight loss (%) assigned to water, -OH group or oxygen loss, as well as the phase transition from amorphous to crystalline, changes gradually. Above ~ 417 °C, the final weight percentages are attributed to the remaining oxide particles. Considering that oxygen represents 14.2 % and 24.0 % of the total mass of the IrO_2 and RuO_2 , respectively, the weight % values of 53 % and 28 % would be expected if metallic ruthenium and iridium particles were formed, respectively. The TGA/DSC values are lower, which supports the solid-solution oxide nature of the particles, largely at their surfaces.

3.2. Catalytic performance towards acidic Oxygen Evolution Reaction (OER)

3.2.1. Surface Electrochemistry

After gaining a broad understanding of the structural and morphological outcomes of IrRuO_x , we carried out electrochemical OER studies in N_2 -saturated and 0.5 M H_2SO_4 solution as the electrolyte. CV was performed on the calcined catalysts, and during the potential scan, the oxidation states of iridium/ruthenium may change; thus, well-defined current peaks are identified on the studied electrodes. Figure 6 shows the first cycle of a series of cyclic voltammograms for $\text{IrRuO}_x@350$ °C (1), $\text{IrRuO}_x@400$ °C (2), $\text{IrRuO}_x@450$ °C (3), $\text{IrRuO}_x@500$ °C (4), $\text{IrRuO}_x@520$ °C (5), and commercial RuO_2 and IrO_2 recorded at 50 mV/s.

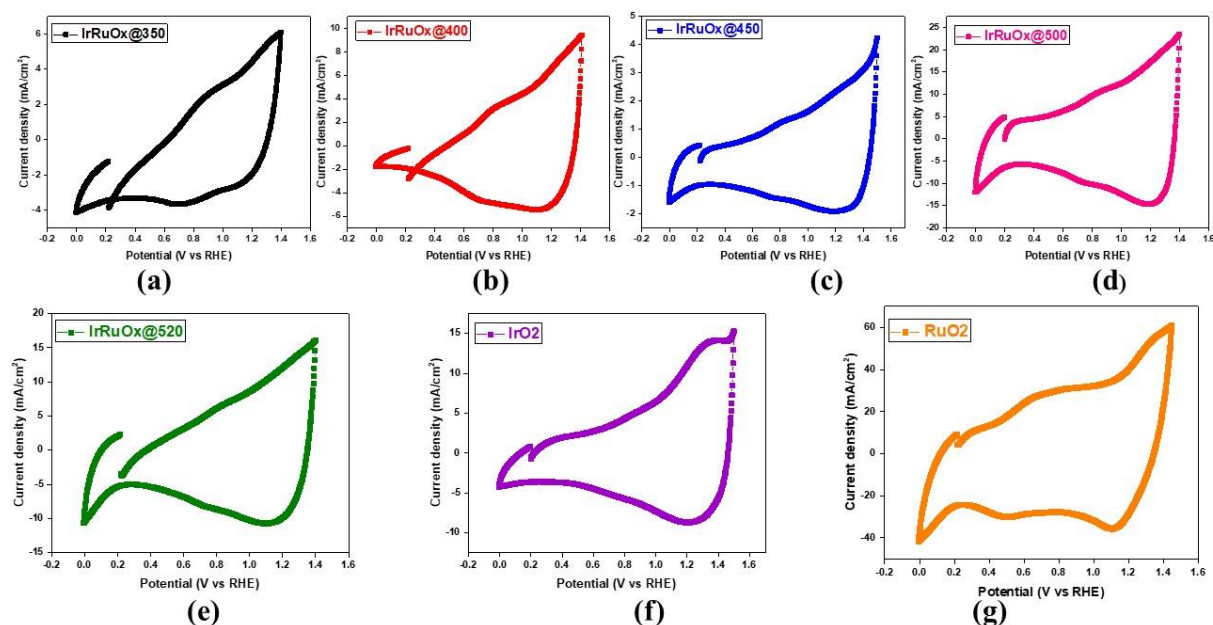


Figure 6. Cyclic voltammograms of IrRuOx @350 °C (1), IrRuOx@400 °C (2), IrRuOx@450 °C (3), IrRuOx@500 °C (4), IrRuOx@520 °C (5), and commercial RuO₂ and IrO₂ recorded in 0.5 M H₂SO₄ at a scan rate of 50 mV/s

On the voltammograms of IrO₂ (Figure 6f), two well-defined peaks are discernible. By analogy, the peaks at 0.84 and 1.33V vs. RHE are reasonably attributed to the Ir(III)/Ir(IV) and Ir(IV)/Ir(VI) redox transitions, respectively. For the RuO₂ (Figure 6g), the broad reversible peaks at 0.69 V vs. RHE are attributed to the Ru(III)/Ru(IV) redox couple. In contrast, the small shoulders at 0.89V and 1.08V vs. RHE correspond to the redox transitions Ru(IV)/Ru(VI) and Ru (VI)/Ru(VIII), respectively. For our mixed ruthenium-iridium oxide catalysts, the voltammogram shapes differ with increasing heat treatment and become larger than those of IrO₂, which is considered characteristic of Ru-rich catalysts. However, the current densities are lower, which reveals that the material is still amorphous but that the particles are partially dehydrated, leading to a decrease in their capacitive properties, as confirmed in structural section 3.1.

After annealing at 350 °C and 400 °C, both samples lead to very similar voltammograms in terms of shape achieved over the whole potential range of experiments. However, they are different from those obtained on samples annealed at 450 °C, 500 °C, and 520 °C. When increasing the annealing temperature up to 450 °C, the current densities decrease, indicating an increase in the crystallinity of the materials compared to the electrocatalyst calcined at 400 °C. Simultaneously, with increased heat treatment to 500 °C and 520 °C, the current densities increase, indicating a decrease in the crystallinity of the materials compared to the

electrocatalyst calcined at 450 °C. Even if the crystalline nature of the catalysts was observed from 400 °C on XRD patterns (see Figure 1), this voltammetric peak is only observed on samples annealed at temperatures higher than 350 °C. This indicates that between 400 °C and 520 °C, the particles are crystalline (according to XRD measurements) but hydrated (according to electrochemical measurements), which could confer good capacitive and OER properties to such oxide materials. These results are comparable to the discussion revealed by HR-TEM analysis.

Although all redox transitions remain visible and occur near the potentials, the voltammogram shapes for the mixed oxide catalysts are less well defined due to the overlap of both Ir and Ru redox processes. Nevertheless, for all catalysts, at low cathodic potentials (below 0.25 V vs RHE), atomic hydrogen absorption into the oxide lattice is observed. So, differences in CV shapes are observed for samples annealed at intermediate temperatures, indicating that the morphological and crystalline changes are not only dependent on the annealing temperature, but also depend on the metal oxide or hydroxide phase. Consequently, the electrochemical activity of the solid solution catalysts improves, which may be caused by a change in the structure and/or the smaller size of the oxide/hydroxide catalyst particles. For a better understanding of the charge transfer between the electrode-electrolyte interfaces, the intrinsic activity is quantified by calculating the electrochemical surface area (ECSA)-normalized current densities. Figure S8 and Figures 7a-b show the scan rate versus current density, revealing interesting findings. In all the electrocatalysts, as the scan rate increases, the current densities increase, whereas the voltammogram shape remains the same. The redox transitions described and attributed previously are accompanied by proton transfer, which is a faradaic process occurring only on the material surface, along with the formation of hydroxide surface species .

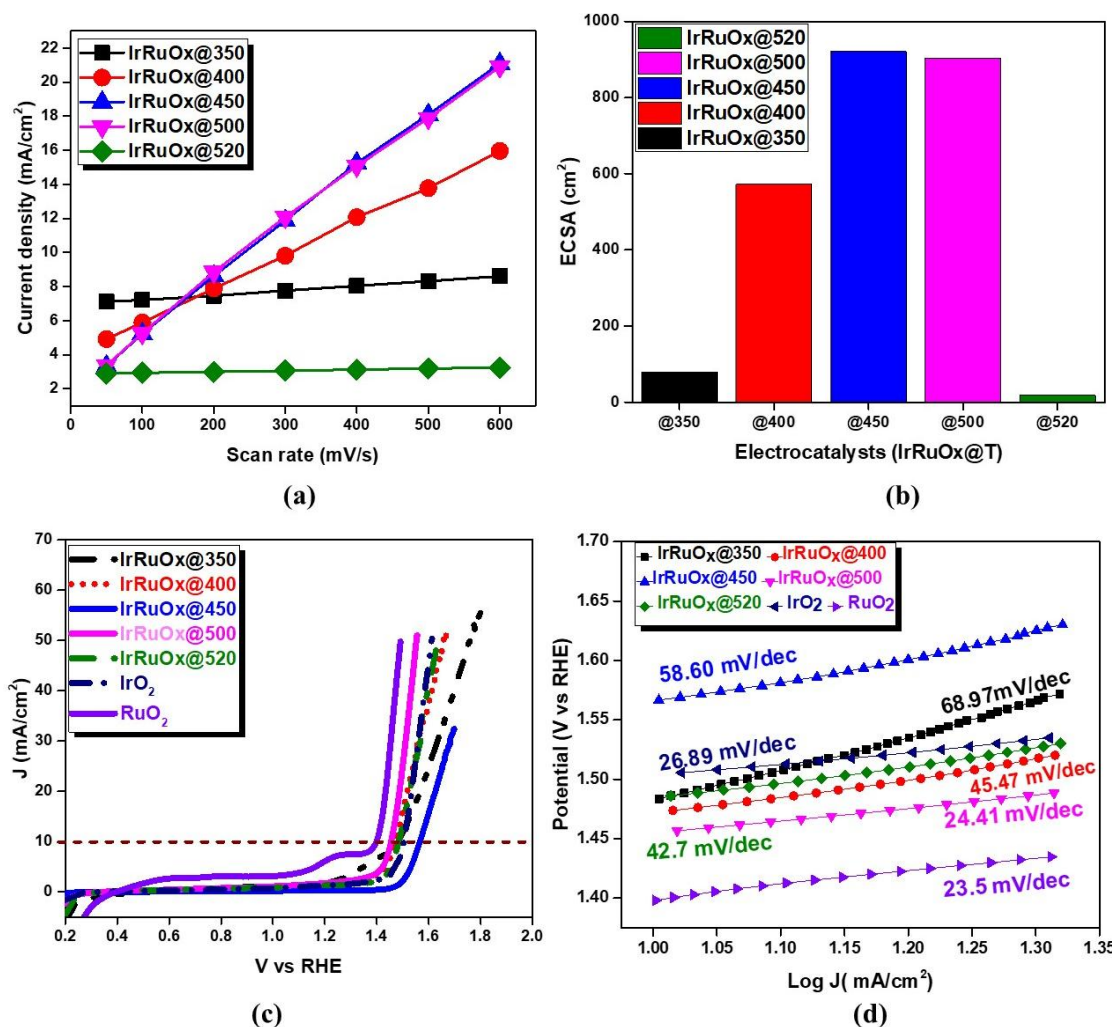


Figure 7. (a) Capacitance double layer (C_{dl}) and (b) Electrochemical Surface Area (ECSA), (c) LSV and (d) Tafel curves of IrRuO_x @350 °C (1), IrRuO_x@400 °C (2), IrRuO_x@450 °C (3), IrRuO_x@500 °C (4), IrRuO_x@520 °C (5) recorded in 0.5 M H₂SO₄

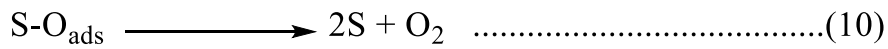
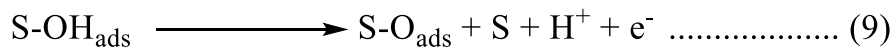
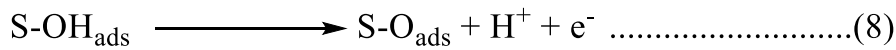
As summarised in Figures 7a-b, IrRuO_x@350 °C (1) and IrRuO_x@520 °C (5) exhibit a lower C_{dl} of 2.75 F/cm² and 0.63 F/cm², corresponding to an ECSA of 78.57 cm² and 18 cm², respectively. Whereas a high C_{dl} of 20.03 F/cm², 32.23 F/cm² and 31.63 F/cm² for IrRuO_x@400 °C (2), IrRuO_x@450 °C (3), and IrRuO_x@500 °C (4), along with their ECSA of 572.29 cm², 920 cm² and 903.71 cm², respectively. ECSA is also an important factor for catalysts in the electrocatalytic process, as the number of active sites on the surface directly depends on its value. As shown in Table S1, the order of the ECSA for the catalysts is: IrRuO_x@450 °C (3) > IrRuO_x@400 °C (2) > IrRuO_x@500 °C (4) > IrRuO_x@350 °C (1) > IrRuO_x@520 °C (5). This indicates that with the heat treatment at 450 °C, multiphase structures may be present, which leads to a high number of available active sites, thereby increasing the ECSA. Consequently, the sintering temperature affects the specific surface area of IrRuO_x@Temp/GC, depending on

the amorphous and multiple or mixed phases, which in turn causes a change in ECSA. This provides a clear understanding of the structural behaviour and morphology, which impacts the activity and stability of the electrocatalysts in an acidic medium.

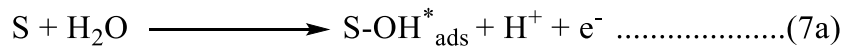
3.2.1. Polarisation curves and Tafel slope

The OER performance of IrRuO_x was tested using linear sweep voltammetry in 0.5 M H₂SO₄. For significant comparison, the OER activities of IrRuO_x, RuO₂ and IrO₂ were tested under identical conditions. Figures 7c-d show the polarisation and the Tafel curves of these catalysts in acidic OER. From the curves above, the starting potentials of the OER are summarised in Table S1. The RuO₂ catalyst is the most active for the oxygen evolution reaction, with an overpotential of 167 mV at a current density of 10 mA/cm². In the presence of ruthenium, the potentials of the IrRuO_x@T catalysts are lower than those of the IrO₂ catalyst (273 mV). This may be due to the presence of Ir in the lattice, as seen in XRD patterns, which forms a common valence band with RuO₂ and promotes the OER on the active nucleus. It is apparent from Figure 7a that catalyst activity varies as the calcination temperature increases. The overpotential of 251 mV for the catalyst calcined at 350 °C was reduced by 9 and 27 mV when the catalyst was calcined at 400 °C and 500 °C, respectively. This variation in activity with calcination temperature is due to the reduction in the available ECSA and the amorphous-to-crystalline phase transition, as discussed previously. The decrease in performance was more evident when the calcination temperature was increased from 350 to 450 °C, i.e., a drop in overpotential by 84 mV. So, Pfeifer *et al.* (2016) investigated one crystalline and one amorphous IrO₂ for OER in 0.5 M H₂SO₄, and they found that the amorphous IrO_x catalyst exhibits significantly better performance than the crystalline rutile IrO_x catalyst. Further, Fatemeh *et al.* (2017) report that calcination temperature affects the morphological and electrochemical characteristics of supported IrO_x electrocatalysts for the PEM electrolyzer anode. The polarisation curves for the catalysts calcined at 250 and 350 °C had comparable performance, similar to this work for 350, 400, 500 and 520 °C, but the performance decreased when the catalyst was calcined at 450 °C. This indicates that the iridium active sites in the catalysts calcined at 450 °C had lower activity for the OER. Iridium species in the catalyst calcined at 400-520 °C have a partially crystalline or hydrated structure, compared to 350 °C. It could be concluded that amorphous or crystalline iridium-based species, mixed IrO₂ and RuO₂, and alloy obtained during the calcination temperature promote the change in the activity of the catalyst toward OER, since the loading is not constant for all catalysts.

The best performance is obtained for the catalyst annealed at 500 °C, and it is worth noting that higher performance is reached for the crystallite size of 22.5 nm, which could also indicate a size effect in the catalytic behavior . To further examine the activity of the catalysts, the OER Tafel slopes for the catalysts were estimated. The Tafel values vs. calcination temperatures are summarised in Table S1 and Figure 8b. The Tafel slope in the range of 25-60 mV/dec, common for iridium and ruthenium oxides , was observed for all the catalysts. However, these samples tend to show a slightly high degree of crystallinity, while lower Tafel slopes indicate a hydrous surface, usually associated with surface amorphisation. Due to the complex reaction involving a 4-electron transfer for water oxidation, several mechanisms (Equations 7- 10) were considered with different rate-determining steps, starting from the water adsorption on the active site (S) with a charge transfer leading to intermediate hydroxyl species.



For the Tafel slope values of 120 mV/dec, Equation (7) is the rate-determining step; for 40 mV/dec, Equation (8) is the rate-determining step; and this value can be slightly different due to the intervention of the step described by Equation (9), leading to values close to 30 mV/dec; and finally, for 15 mV/dec, the rate-determining step is described by Equation (10) . Still, substitution steps can take place depending on the bond strength of the intermediate species to the active sites, which can vary with the catalytic layer arrangement. They thus can lead to different Tafel slope values. Thus, the step described in Equation (7) can be dissociated into two reactions, Equations (7a) and (7b):



Where the intermediate species $S-OH_{ads}$ and $S-OH^*_{ads}$ have the same chemical structure, as is the case in this work, but different bond strengths depending on the active site nature. Both steps can occur alternatively or in parallel, and the Tafel slope value is then 60 mV/dec if they are the rate-determining steps. Table S1 shows that the Tafel slopes of catalysts calcined at 350

and 450 °C are close to 60 mV/dec, which might be due to the formation of S-OH_{ads} and S-OH^{*}_{ads} of different energy states, which correspond to Equations (7a-b) as the rate-determining step. For the catalysts annealed at 400 and 520 °C, the Tafel values are close to 45 mV/dec, indicating that Equation (8) of the general mechanism is the rate-determining step. Whereas the Tafel value of the catalyst calcined at 500 °C is 24.41 mV/dec, which means that the rate-determining step of the mechanism could have changed from Equation (8) to Equation (9). It is important to recognise, however, that the Tafel behaviour of all samples is representative of a hydrous surface, regardless of the heat-treatment temperature. Although slightly higher, the values obtained are consistent with those reported in the literature at room temperature for the OER with IrRu-based catalysts.

3.2.2. Stability of the catalyst using a three-electrode system

To evaluate stability, the catalysts were tested in 0.5 M H₂SO₄. Activity before and after the stability test was compared, and the loss in activity was quantified from the LSV curves, as shown in Figure S9. Activity loss is lower in all catalysts; however, this difference can be attributed to the low decomposition of the hydrophobic group as well as the change in phase transition. IrRuO_x@500 (3), which shows the best OER performance, also exhibited significant activity degradation under the same conditions compared to IrRuO_x@350 °C (1), IrRuO_x@400 °C (2), and IrRuO_x@500 °C (4). This observation aligns with a prior study suggesting an inverse relationship between catalyst activity and stability. The durability test was performed by fixing the current density at 10 mA/cm² for 24 h, and the change in potential was tracked, as seen in Figure 8. Interestingly, it is clearly shown that the potential at the end of 24 h of electrolysis is 1.27 V for IrRuO_x@350 °C (1), 1.35 V for IrRuO_x@400 °C (2), and 1.37 V for IrRuO_x@500 °C (4). At the same time, IrRuO_x@450 °C (3) is 1.39 V during 12 h of electrolysis. This clearly reveals that the amorphous catalyst IrRuO_x calcined at 350 °C (1) shows better stability at a lower potential.

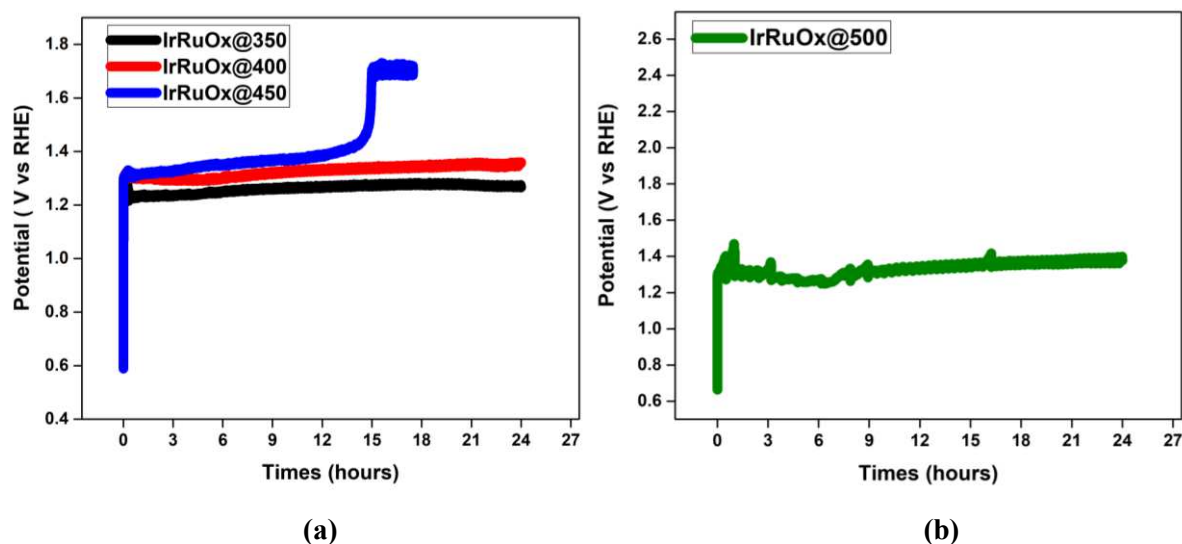


Figure 8. Chronopotentiometry test at 10 mA/cm² for 24 hours of electrolysis of the anode catalyst: (a) IrRuOx@350 °C (1), IrRuOx@400 °C (2), and IrRuOx@450 °C (3), and (b) IrRuOx@500 °C (4).

In all cases, the samples exhibit mixed amorphous and crystalline particles with a one-phase nanorod-like morphology as evidenced by the XRD and HR-TEM analysis. This is also further supported by the fact that the surface areas increase with charge capacitance, but the electrochemical OER activity does not. If one compares the trend between stability (normalised current density after 24 h of electrolysis (see Figure 9), and activity (η at $J = 10 \text{ mA/cm}^2$, see Figure 8a), then it is clear that the resemblance is remarkably similar. The stability of the measured catalysts scales with activity and surface area, indicating that stability is directly related to the available active sites. IrRuOx@500 °C (4) shows the lowest stability and degrades more after 24 hours. Although this sample shows high OER activity, it comes at the cost of catalyst stability. This further supports the assertion in the literature, that activity and stability are correlated to one another. Therefore, higher electrochemical OER activity is associated with lower electrocatalyst stability and vice versa.

4. Conclusion

In this work, IrRu oxide materials have been synthesized by the Adams' fusion method followed by a calcination treatment under an air atmosphere. The physicochemical and electrochemical characterizations have shown that the main effect of the heat treatment is the modification of the transition phase from an amorphous hydrated oxide to a crystalline hydrated phase.

It has been found that higher catalytic activities towards the OER were obtained at a lower overpotential of 224 mV along with a Tafel slope of 24.41 mV/dec at high temperatures, *i.e.*, 500 °C. Although the catalyst at 450 °C has a high overpotential (335 mV) and a larger ECSA among the catalysts, its mesoporosity can lead to the entrapment of gas bubbles within the pores of the material during OER in the catalyst layers, thereby blocking some of the electrochemically active surface area. In terms of stability, it was shown that the amorphous IrRuOx@350 °C (**1**) show the better stability at a lower potential of 1.27 V. Any enhancement due to the formation of additional surface hydroxide species in catalysts **2**, **3**, **4** and **5** seems to be outweighed by the loss in electrochemically active surface area that inevitably occurs as the catalyst degrades and lowers their stability compared to **1**. It is unclear if the decreased stability is directly related to the presence of Ru³⁺ or Ir³⁺ sites, although the relationship between activity and stability suggests that this is a possibility. This work thus shows that iridium-ruthenium oxide materials with a hydroxide surface layer participate in the OER. Therefore, tuning the calcination temperature is important to obtain the best balance between activity and durability of materials towards OER in PEMWE applications.

Statements & Declarations

Funding

This work was supported by Nelson Mandela University for granting Dr Claudelle Sybilline Anensong Djadock and Anele Nzimeni in completing a post-doc fellowship and Master's dissertation, respectively, in the Green Hydrogen Research Group, Department of Chemistry, hosted by InnoVenton. Financial support also comes from NRF (CSUR) and the Technology Innovation Agency (TIA) for seed funding for the project.

Competing Interests

The authors declare that there are no conflicts of interest.

Author Contributions

All authors have contributed to writing and reviewing the manuscript.

Data Availability

The datasets generated during and/or analysed during the current study are available from the corresponding author on reasonable request.

References

- [1] S. Anantharaj, S. R. Ede, K. Sakthikumar, K. Karthick, S. Mishra, S. Kundu, Recent trends and perspectives in electrochemical water splitting with an emphasis on sulfide, selenide, and phosphide catalysts of Fe, Co, and Ni: A Review, *ACS Catalysis*. **6**(12), 8069–8097 (2016). doi:<https://doi.org/10.1021/acscatal.6b02479>
- [2] Q. Feng, Z. Y. Xiao, L. Gaoyang, W. Bing, Z. Zhen, L. Hui, A review of proton exchange membrane water electrolysis on degradation mechanisms and mitigation strategies, *J. Power Sources*. **366**, 33-55 (2017). doi:<https://doi.org/10.1016/j.jpowsour.2017.09.006>
- [3] Q. N. Wu, Y. N. Wang, K. X. Zhang, Z. B. Xie, K. Sun, W. An, X. Liang, X. Zou, Advances and status of anode catalysts for proton exchange membrane water electrolysis technology, *Mater. Chem. Front.* **7**(6), 1025 (2023). doi:<https://doi.org/10.1039/d3qm00010a>.
- [4] M. Ali, E. Pervaiz, T. Noor. O. Rabi. R. Zahra, M. Yang, "Recent Advancements in MOF-Based catalysts for applications in electrochemical and photoelectrochemical water splitting: A Review, *I. J. Energy Research*. **45**(2) 1190-1226 (2021). doi:<https://doi.org/10.1002/er.5807>
- [5] R. Huang, Y. Z. Wen, P. Miao, W. J. Shi, W. Z. Niu, K. Sun, Y. Y. Li, Y. J. Ji, B. Zhang, Constructing the oxygen diffusion paths for promoting the stability of acidic water oxidation catalysts, *Chem. Catal.* **3**(7), 100667 (2023). <https://doi.org/10.1016/j.checat.2023.100667>
- [6] S. H. Chang, J. G. Connell, N. Danilovic, R. Subbaraman, K.-C. Chang, V. R. Stamenkovic, N. M. Markovic, Activity-stability relationship in the surface electrochemistry of the oxygen evolution reaction, *Faraday Discuss.* **176**, 125- 133 (2015). doi:<https://doi.org/10.1039/c4fd00134f>
- [7] N. Danilovic, R. Subbaraman, K.-C. Chang, S.H. Chang, Y.J. Kang, J. Snyder, A. P. Paulikas, D. Strmcnik, Y.-T. Kim, D. Myers, V.R. Stamenkovic, N. M. Markovic, Activity–Stability Trends for the Oxygen Evolution Reaction on Monometallic Oxides in Acidic Environment, *J. Phys. Chem. Lett.* **5**, 2474–2478 (2014). doi:<https://doi.org/10.1021/jz501061n>
- [8] H. Over, Surface chemistry of ruthenium dioxide in heterogeneous catalysis and electrocatalysis: from fundamental to applied research, *Chem. Rev.* **112**(6) 3356–3426 (2012). <https://doi.org/10.1021/cr200247n>
- [9] G. Simon, K. Olga, L. Marc, P. Enrico, M. M. Andrea, T. F. Wen, D-M. Oscar, L. Zhizhong, O. Tobias, F. Luc, L. Alfred, J. J. M. Karl, T.M. Koper, C. Serhiy, The stability number as a metric for electrocatalyst stability benchmarking, *Nat. Catal.* **1**, 508–515 (2018). <https://doi.org/10.1038/s41929-018-0085-6>
- [10] Z. Caixia, H. Bing, L. Xuwei, W. Hao, L. Guan, Mn-doped RuO₂ nanocrystals with abundant oxygen vacancies for enhanced oxygen evolution in acidic media, *Inorg. Chem. Front.* **11**(6), 1912-1922 (2024). doi:<https://doi.org/10.1039/D4QI00013G>
- [11] K. Jaemin, S. Pei-Chieh, Y. Qi, A-B, Zaid, S. Cheng-Jun, Y. Hong, "A Porous Pyrochlore Y₂[Ru_{1.6}Y_{0.4}]O_{7-δ} Electrocatalyst for Enhanced Performance towards the Oxygen Evolution Reaction in Acidic Media, *Angew. Chem. Int.* **57** (42), 13877-13881 (2018). doi:<https://doi.org/10.1002/anie.201808825>
- [12] M. Escudero-Escribano, A. F. Pedersen, E. A. Paoli, R. Frydendal, D. Friebe, P. Malacrida, J. Rossmeisl, I. E. L. Stephens, I. Chorkendorff, Importance of surface IrO_x in stabilizing RuO₂ for oxygen evolution reaction, **122**(2), 947 (2018).doi:<https://doi.org/10.1021/acs.jpcc.7b07047>

- [13] Y. Qin, T.T. Yu, S. H. Deng, X. Y. Zhou, D. M. Lin, Q. Zhang, Z. Jin, D. F. Zhang, Y. B. He, H. J. Qiu, L. H. He, F. Y. Kang, K. K. Li, T. Y. Zhang, RuO₂ electronic structure and lattice strain dual engineering for enhanced acidic oxygen evolution reaction performance, *Nat. Commun.* **13**(1), 3784 (2022). doi:https://doi.org/10.1038/s41467-022-31468-0
- [14] K. R. Yeo, K. S. Lee, H. Kim, J. Lee, S.K. Kim, A highly active and stable 3D dandelion spore-structured self-supporting Ir-based electrocatalyst for proton exchange membrane water electrolysis fabricated using structural reconstruction, *Energy Environ. Sci.* **15**(8) 3449 (2022). doi:https://doi.org/10.1039/d2ee01042a
- [15] W. X. Zhu, X. C. Song, F. Liao, H. Huang, Q. Shao, K. Feng, Y. J. Zhou, M. J. Ma, J. Wu, H. Yang, H.W. Yang, M. Wang, J. Shi, J. Zhong, T. Cheng, M. W. Shao, Y. Liu, Z. H. Kang, Stable and oxidative charged Ru enhance the acidic oxygen evolution reaction activity in two-dimensional ruthenium-iridium oxide, *Nat. Commun.* **14**(1), 5365 (2023). doi:https://doi.org/10.1038/s41467-023-41036-9
- [16] H. Ting, B. Ze-Nan, W. Cong, H. Tao, W. Yi-Fan, Ruthenium-iridium alloyed oxides with remarkable catalytic stability for proton exchange membrane water electrolysis at industrial current density, *Rare Met.* **44**(2), 1139–1146 (2025). doi:https://doi.org/10.1007/s12598-024-03004-0
- [17] S. P. Thy, H. P. Hong, L. D. Chi, T. A. N. Tuvet, A. P. Tuan, Ir_xRu_{1-x}O₂ Nanoparticles with Enhanced Electrocatalytic Properties for the Oxygen Evolution Reaction in Proton Exchange Membrane Water Electrolysis, *J. Electron. Mater.* **50**(3), 1239-1246 (2021). doi:https://doi.org/10.1007/s11664-020-08624-7
- [18] K. M. Papazisi, A. Siokou, S. Balomenou, D. Tsiplakides, Preparation and characterization of Ir_xPt_{1-x}O₂ anode electrocatalysts for the oxygen evolution reaction, *Int. J. Hydrogen Energy.* **37**, 16642–16648 (2012). doi:https://doi.org/10.1016/j.ijhydene.2012.02.118
- [19] Y. Liu, C. Wang, Y. Lei, F. Liu, B. Tian, J. Wang, Investigation of high-performance IrO₂ electrocatalysts prepared by adams method, *Int. J. Hydrog.* **43**(42), 19460-19467 (2018). doi:https://doi.org/10.1016/j.ijhydene.2018.08.196
- [20] C. Felix, B. J. Bladergroen, V. Linkov, B. G. Pollet, S. Pasupathi, Ex-Situ Electrochemical Characterization of IrO₂ Synthesized by a Modified Adams Fusion Method for the Oxygen Evolution Reaction., *Catalyst.* **9**(4), 318 (2019). doi:https://doi.org/10.3390/catal9040318
- [21] L. Guangfu, Y. Hongmei, S. Wei, D. Meiling, L. Yongkun, S. Zhigang, Y. Baolian, A Hard-Template Method for the Preparation of IrO₂, and Its Performance in a Solid-Polymer-Electrolyte Water Electrolyzer, *Chem. Sus. Chem.* **5**(5) 858-861 (2012). doi:https://doi.org/10.1002/cssc.201100519
- [22] T. Reier, H. N. Nong, D. Teschner, R. Schlögl, P. Strasser, Electrocatalytic oxygen evolution reaction in acidic environments—reaction mechanisms and catalysts, *Adv. Energy Mater.* **7**, 1601275 (2017). doi:https://doi.org/10.1002/aenm.201601275
- [23] S. Cherevko, T. Reier, A.R. Zeradjanin, Z. Pawolek, P. Strasser, K. J. J Mayrhofer, Stability of nanostructured iridium oxide electrocatalysts during oxygen evolution reaction in acidic environment, *Electrochem. Commun.* **48**, 81–85 (2014). doi:https://doi.org/10.1016/j.elecom.2014.08.027
- [24] G. C. Ilva, N. Perini, E. A. Ticianelli, Effect of temperature on the activities and stabilities of hydrothermally prepared IrO_x nanocatalyst layers for the oxygen

- evolution reaction, *Appl. Catal. B-Environ.* **218**, 287–297 (2017). doi:https://doi.org/10.1016/j.apcatb.2017.06.044
- [25] B. Angeliki, M.P. Kalliopi, Effect of Calcination Temperature on the Activity of Unsupported IrO₂ Electrocatalysts for the Oxygen Evolution Reaction in Polymer Electrolyte Membrane Water Electrolyzers, *Molecules*. **28**, 5827(2023). doi:https://doi.org/10.3390/molecules28155827
- [26] Y. Matsumoto, E. Sato, Electrocatalytic properties of transition metal oxides for oxygen evolution reaction, *Mater. Chem. Phys.* **14**, 397–426 (1986). doi:https://doi.org/10.1016/0254-0584(86)90045-3
- [27] K. Fatemeh, B. Aimy, A. P. Brant, Effect of Calcination Temperature on the Morphological and Electrochemical Characteristics of Supported Iridium Hydroxyoxide Electrocatalysts for the PEM Electrolyzer Anode, *J. Electrochem. Soc.* **164**, F464 (2017). doi:10.1149/2.0111706jes
- [28] J. C. Cruz, V. Baglio, S. Siracusano, R. Ornelas, L. Ortiz-Frade, L. G. Arriaga, V. Antonucci, A. S. Arico, Nanosized IrO₂ electrocatalysts for oxygen evolution reaction in an SPE electrolyzer. *J. Nanopart Res.* **13**, 1639–1646 (2011). DOI 10.1007/s11051-010-9917-2
- [29] T. Audichon, B. Guenot, S. Baranton, M. Cretin, C. Lamy, C. Coutanceau, Preparation and characterization of supported RuIr_(1-x)O₂ nano-oxides using a modified polyol synthesis assisted by microwave activation for energy storage applications, *Appl. Catal. B Environ.* **200**, 493-502 (2017). doi:http://dx.doi.org/10.1016/j.apcatb.2016.07.048
- [30] F. I. Mattos-Costa, P. de Lima-Neto, S. A. S. Machado, L. A. Avaca, Characterisation of surfaces modified by sol-gel derived RuIr_{1-x}O₂ coatings for oxygen evolution in acid medium, *Electrochimica Acta.* **44**,1515-1523 (1998). doi:https://doi.org/10.1016/S0013-4686(98)00275-8
- [31] T. Audichon, E. Mayousse, S. Morisset, C. Morais, C. Com-minges, T. W. Napporn, K. B. Kokoh, Electroactivity of RuO₂-IrO₂ mixed nanocatalysts toward the oxygen evolution reaction in a water electrolyzer supplied by a solar profile, *Int. J. Hydrogen Energy.* **39**, 16785-16796 (2014). doi:https://doi.org/10.1016/j.ijhydene.2014.07.170
- [32] C. C. Hu, K. H. Chang, Cyclic voltammetric deposition of hydrous ruthenium oxide for electrochemical capacitors: effects of codepositing iridium oxide, *Electrochim. Acta.* 2685-2696 (2000). doi:https://doi.org/10.1016/S0013-4686(00)00386-8
- [33] V. Pfeifer, T. E. Jones, J. J. Velez, V. C. Massue, R. Arrigo, D. Teschner, F. Girgsdies, M. Scherzer, M. T. Greiner, J. Allan, M. Hashagen, G. Weinberg, S. Piccinin, M. Havecker, A. Knop-Gericke, R. Schlogl, The electronic structure of iridium and its oxides, *Surf. Interface Anal.* **48**, 261-273 (2016).doi 10.1002/sia.5895
- [34] R. D. L. Mith, M. S. Prévot, R. D. Fagan, Z. Zhang, P. A. Sedach, M. K. J. S. S. Trudel, C. P. Berlinguette, Photochemical route for accessing amorphous metal oxide materials for water oxidation, *catalysis Science.* **340**(6128), 60-63, (2013). doi:https://doi.org/10.1126/science.1233638
- [35] T. Reier, D. Teschner, T. Lunkenbein, A. Bergmann, S. Selve, R. Kraehnert, R. Schlogl, P. Strasser, Electrocatalytic Oxygen evolution on Iridium Oxide: Uncovering Catalyst-Substrate Interactions and Active Iridium Oxide Species. *J. Electrochem. Soc.* **161**(9), F876–F882 (2014). doi:10.1149/2.0411409jes
- [36] A. Ermete, Iridium As Catalyst and Cocatalyst for Oxygen Evolution/Reduction in Acidic Polymer Electrolyte Membrane Electrolyzers and Fuel Cells, *ACS Catal.* **4**(5),1426–1440 (2014). doi:https://doi.org/10.1021/cs4011875

- [37] W. Xu, T. Jyoti, B. Suddhasatwa, S. Keith, Nano-crystalline $\text{Ru}_x\text{Sn}_{1-x}\text{O}_2$ powder catalysts for oxygen evolution reaction in proton exchange membrane water electrolyzers, *Int. J. Hydrogen Energy*. **36**(22), 14796-14804 (2011). doi:<https://doi.org/10.1016/j.ijhydene.2011.01.067>
- [38] K. A. Stoerzinger, L. Qiao, M. D. Biegalski, Y. Shao-Horn, Orientation-Dependent Oxygen Evolution Activities of Rutile IrO_2 and RuO_2 , *J. Phys. Chem. Lett.* **5**(10),1636-1641(2014). doi:<https://doi.org/10.1021/jz500610u>
- [39] M. Pourbaix, H. Zhang, A. Pourbaix, Presentation of an Atlas of Chemical and Electrochemical Equilibria in the Presence of a Gaseous Phase, *Mater. Sci. Forum.* (251-254),143-148 (1997). doi:<https://doi.org/10.4028/www.scientific.net/MSF.251-254.143>
- [40] D. F. Abbott, D. Lebedev, K. Waltar, M. Povia, M. Nachtegaal, E. Fabbri, C. Copéret, T. J. Schmidt, Iridium Oxide for the Oxygen Evolution Reaction: Correlation between Particle Size, Morphology, and the Surface Hydroxo Layer from Operando XAS, *Chem. Mater.* **28**(18), 6591–6604 (2016). doi:<https://doi.org/10.1021/acs.chemmater.6b02625>
- [41] T. Binninger, R. Mohamed, K. Waltar, E. Fabbri, P. Levecque, R. Kötz, T. J. Schmidt, Thermodynamic explanation of the universal correlation between oxygen evolution activity and corrosion of oxide catalysts, *Sci. Rep.* **5**, 12167 (2015). doi:<https://doi.org/10.1038/srep12167>

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- [SupplementalInformationSI.docx](#)