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# Mixed iridium-nickel oxides supported on antimony-doped tin oxide as highly efficient and stable acidic oxygen evolution catalysts

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# Abstract

Proton exchange membrane (PEM) water electrolysis represents a promising technology for green hydrogen production, but its widespread deployment is greatly hindered by the indispensable usage of platinum group metal catalysts, especially iridium (Ir) based materials for the energy-demanding oxygen evolution reaction (OER). Herein, we report a new sequential precipitation approach to the synthesis of mixed Ir-nickel (Ni) oxy-hydroxide supported on antimony-doped tin oxide (ATO) nanoparticles (IrNi<sub>v</sub>O<sub>x</sub>/ATO, 20 wt.% (Ir + Ni), y = 0, 1, 2, 3and 3), aiming to reduce the utilisation of scarce and precious Ir while maintaining its good acidic OER performance. When tested in strongly acidic electrolyte  $(0.1 \text{ M HClO}_4)$ , the optimised IrNi<sub>1</sub>O<sub>x</sub>/ATO shows a mass activity of 1.0 mA  $\mu g_{Ir}^{-1}$  and a large turnover frequency of 123 s<sup>-1</sup> at an overpotential of 350 mV, as well as a comparatively small Tafel slope of 50 mV dec<sup>-1</sup>, better than the IrO<sub>x</sub>/ATO control, particularly with a markedly reduced Ir loading of only 19.7  $\mu$ g<sub>Ir</sub> cm<sup>-2</sup>. Importantly, IrNi<sub>1</sub>O<sub>x</sub>/ATO also exhibits substantially better catalytic stability than other reference catalysts, able to continuously catalyse acidic OER at 10 mA  $cm^{-2}$ for 15 h without obvious degradation. Our *in-situ* synchrotron-based x-ray absorption spectroscopy confirmed that the  $Ir^{3+}/Ir^{4+}$  species are the active sites for the acidic OER. Furthermore, the performance of IrNi<sub>1</sub>O<sub>x</sub>/ATO was also preliminarily evaluated in a membrane

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electrode assembly, which shows better activity and stability than other reference catalysts. The  $IrNi_1O_x/ATO$  reported in this work is a promising alternative to commercial  $IrO_2$  based catalysts for PEM electrolysis.

Supplementary material for this article is available online

Keywords: mixed oxides, oxygen evolution reaction, polymer electrolyte membrane, antimony doped tin oxide, membrane electrode assembly

# 1. Introduction

The global energy demand has been increasing exponentially since the 16th century, and it is set to keep rising at a similar rate in the future [1]. In this context, continuous consumption of fossil fuels becomes non-sustainable as this will not only deplete the limited reserves of fossil fuels but also cause ever-increasing environmental exacerbation [2]. Hence, there is a pressing need for widespread deployment of renewable energy that can fulfil the society's energy demand, and concurrently reach the carbon-neutrality goals pledged by many countries worldwide. To this end, water electrolysis (WE) technologies and the associated electrocatalysts [3–7], have become increasingly important because they allow the surplus electricity obtained from intermittent renewable sources to be stored as hydrogen (commonly referred to as 'green' hydrogen) [8], which can then be dispensed upon demand. Among the low-temperature WE technologies developed so far, proton exchange membrane WE (PEM-WE) has shown many advantages over the more mature alkaline WE (AWE), such as much lower gas crossover and accordingly higher purity of hydrogen, ability to operate at high current densities with lower ohmic losses, faster response under fluctuating power input (typical of renewable energy), ease of being pressurised, and more compact designs [9, 10]. However, the harsh oxidising conditions at the anode and the local strongly acidic environment at the electrode-electrolyte interface limit the catalysts candidates to virtually only iridium (Ir)-based materials. Ir is one of the scarcest and the most expensive metals [11], therefore, to enable PEM electrolysers to be deployed on multi-GW scale as planned to meet the demand for green hydrogen production [11-13], Ir must be more efficiently utilised without compromising its activity and stability towards the oxygen evolution reaction (OER).

A common strategy to increase the Ir mass activity is to disperse the noble metal onto a conductive support. Among many explored supports, different carbon materials have been broadly employed for a range of electrocatalytic applications. However, they generally suffer from electro-oxidation under harsh, corrosive, and oxidative conditions during acidic OER [14]. Besides various carbon materials, antimony-doped tin oxide (ATO) has been proposed as a better alternative for use as a support of Ir-based catalysts for its quasi-metallic n-type conductivity and significantly higher acid resistance than carbon materials [15–19]. Moreover, ATO is relatively cheaper

than other conductive metal oxides such as indium-doped tin oxide (ITO) [11], and its synthesis is more sustainable than fluorine-doped tin oxide (FTO) [20, 21]. In addition to improving Ir dispersion, the use of ATO is also expected to meliorate the catalyst stability through the strong metal/metal-oxide support interaction [15, 22, 23].

Massué et al reported the synthesis of amorphous iridium oxy-hydroxides  $(Ir(O)_x(OH)_z)$ , generally denoted as  $IrO_x$  for simplicity) supported on ATO (35 wt.% Ir) [24], and they found that annealing leads to crystallisation of  $IrO_x$  towards rutile IrO<sub>2</sub>, followed by a notable decrease in activity and faster degradation during the OER. This was attributed to the loss of surface –OH groups and the oxidation of  $Ir^{3+}$  to  $Ir^{4+}$ species. The loss of activity upon annealing agrees with the decrease in the electrochemically active surface area (ECSA) reported by Karimi et al over IrO2/ATO (20 wt.% Ir) catalysts [16], and it is also in line with several other reports on the effect of annealing over Ir-based catalysts for the OER [25-29]. The better activity of  $IrO_x$  catalysts compared to crystalline rutile  $IrO_2$  towards the acidic OER [30–32] is usually attributed to their higher structural flexibility, the co-existence of Ir<sup>3+</sup>/Ir<sup>4+</sup> species, and concomitant electrophilic O<sup>-</sup> sites prone to nucleophilic attack by water molecules and the formation of O-O bonds [33-39], but crystallisation would diminish these favourable properties of  $IrO_x$ . Therefore, it is highly desirable to synthesise Ir-based OER catalysts in the form of  $IrO_x$  and with improved catalytic stability by regulating the  $IrO_x$ -support interaction.

Besides dispersion on supporting materials, the dilution of Ir with abundant transition metals in the form of secondary (or ternary) mixed oxides is another widely employed strategy to improve the Ir utilisation. To this end, nickel (Ni) has been widely employed as diluent [40], although other metals such as copper (Cu) [41-43] and cobalt (Co) [44-46] were also explored. The transition metal(s) introduced into the subsurface can modify the electronic structure of IrO<sub>2</sub>, and accordingly the absorption energy of oxygenate intermediates, leading to improved activity. For instance, Moghaddam et al observed a progressive increase in the Ir mass activity of IrO<sub>x</sub> colloids from 129 to 203 A  $g_{Ir}^{-1}$  (at 1.48  $V_{RHE}$ ) by replacing 1/8 of the Ir atoms with Ni. However, a further increase in the Ni proportion resulted in a loss of mass activity [47]. During the OER, most of non-noble metals at the surface would leach out giving rise to an amorphous-like and hydroxide-rich surface with enhanced porosity, and hence, to an increase in the surface area. Meanwhile, the generated cationic vacancies in the lattice lead to the formation of oxygen 2p holes (electrophilic O<sup>-</sup> species) and the concomitant generation of Ir<sup>3+</sup> species, associated with the higher activity observed for  $IrO_x$  [48–51]. However, with excessive nonnoble metal leaching, the generated under-coordinated  $IrO_x$ species are also more prone to dissolution, compromising the overall catalyst stability [50]. Recently, Nong et al reported the loading of IrNi<sub>x</sub> nanoparticles (NPs) on high-surface-area carbon, and an Ir-rich surface was obtained by electrochemical Ni dealloying, followed by surface oxidation. Compared to pure Ir NPs, a three-fold enhancement in the OER activity was observed for the IrNi3,3 counterparts. Yet, the authors only assessed the stability at 1 mA cm<sup>-2</sup> to minimise carbon corrosion [52]. Later on, the same group further managed to load IrNi3 NPs on mesoporous ATO (20 wt.% Ir), followed by Ni dealloying and surface oxidation, and obtained a mass activity of ca. 87  $\mu$ A  $\mu$ g<sub>Ir</sub><sup>-1</sup> and longer stability of 20 h at  $1 \text{ mA cm}^{-2}$  with no apparent deactivation [53], which verified IrNi's potential as highly active and durable electrocatalysts for the acidic OER.

Herein, we report the synthesis of ATO supported Ir-Ni oxy-hydroxide catalysts  $(IrNi_v(O)_x(OH)_z/ATO, y = 0, 1, 2,$ and 3) through sequential precipitation of NiCl<sub>2</sub> and IrCl<sub>3</sub> in the form of oxy-hydroxides over commercially available ATO NPs. Different from previously reported synthetic approaches, such sequential precipitation would allow more Ir to appear at the surface of catalysts ensuring efficient usage of precious Ir. The influence of Ni content on the acidic OER was comprehensively investigated. For the sake of simplicity, the  $IrNi_{v}(O)_{r}(OH)_{r}$  catalysts synthesised in this work will be denoted as  $IrNi_vO_x$  in the following of the paper. We found that the IrNi<sub>1</sub>O<sub>x</sub>/ATO catalyst with an Ir loading of 19.7  $\mu$ g<sub>Ir</sub> cm<sup>-2</sup> shows an apparent OER activity similar to the unsupported IrO<sub>x</sub> with a substantially higher Ir loading of 75.6  $\mu$ g<sub>Ir</sub> cm<sup>-2</sup>, well below the EU Ir loading target of 400  $\mu$ g<sub>Ir</sub> cm<sup>-2</sup> set for PEM electrolysers by 2035 [12]. Additionally, no significant performance decay was observed for IrNi1Ox/ATO during the chronopotentiometric test at 10 mA cm<sup>-2</sup> for 15 h. In contrast, IrNi<sub>2</sub>O<sub>x</sub>/ATO and IrNi<sub>3</sub>O<sub>x</sub>/ATO suffer from fast degradation under the same testing conditions, though their apparent and mass activities are better than those of  $IrNi_1O_r/ATO$ . The good stability of IrNi<sub>1</sub>O<sub>x</sub>/ATO may arise from the homogeneous dispersion of  $IrO_x$  at the surface of the  $\beta$ -Ni(OH)<sub>2</sub> phase that prevents Ni from dissolution. Furthermore, the performance of IrNi<sub>1</sub>O<sub>x</sub>/ATO catalysts was also evaluated in a membrane electrode assembly (MEA), which outperforms both commercial  $IrO_2$  and home-made  $IrO_x$ /ATO control catalysts.

# 2. Methods

Reagents: All chemicals and materials used in this work, including iridium chloride hydrate (IrCl<sub>3</sub>·xH<sub>2</sub>O, Alfa Aesar, 99%), nickel chloride hexahydrate (NiCl<sub>2</sub>·6H<sub>2</sub>O, Sigma Aldrich, 99%), lithium carbonate (Li<sub>2</sub>CO<sub>3</sub>, Merck, 99%), antimony-doped tin oxide (ATO, Sigma Aldrich, <50 nm), Nafion solution (Sigma Aldrich, 5 wt.%), isopropanol

(Honeywell, 99%), and perchloric acid (HClO<sub>4</sub>, Sigma Aldrich, 70%), were commercially available and employed as received without further purification or treatment.

#### 2.1. Catalyst synthesis

2.1.1.  $IrO_x$  synthesis. Unsupported  $IrO_x$  was synthesised as a control when assessing the OER performance of  $IrNi_yO_x/ATO$  samples. The synthesis of  $IrO_x$  was carried out as follows:  $IrCl_3 \cdot xH_2O$  (159 mg, 0.45 mmol) and four equivalents of  $Li_2CO_3$  (133 mg, 1.8 mmol) were dissolved at room temperature under constant magnetic stirring for 16 h in 50 ml of deionised (DI) water (resistivity:  $\geq 18.2 \text{ M}\Omega$  cm). Under continuous stirring, the slurry was heated to reflux for 3 h. The mixture was then lifted from the oil bath and naturally cooled down to room temperature, and the precipitate was collected and washed with DI water by centrifuge (40 ml  $\times$  6 times). The solid powder was subsequently placed in a filter paper and dried on a bench at room temperature for 16 h. *ca.* 100 mg of catalysts could be obtained in one synthetic batch.

2.1.2. IrNi<sub>v</sub>O<sub>x</sub>/ATO synthesis. The synthesis of IrNi<sub>v</sub>O<sub>x</sub>/ATO (25 wt.% (Ir+ Ni), y = 0, 1, 2, and 3) mixed oxides is exemplified through the description of  $IrNi_1O_x/ATO$  catalysts. Specifically, IrCl<sub>3</sub>·xH<sub>2</sub>O (88 mg, 0.25 mmol) and Li<sub>2</sub>CO<sub>3</sub> (74 mg, 1 mmol) were firstly dissolved in 25 ml of DI water under constant magnetic stirring for 16 h. In a separate flask, NiCl<sub>2</sub>·6H<sub>2</sub>O (59 mg, 0.25 mmol) and Li<sub>2</sub>CO<sub>3</sub> (74 mg, 1 mmol) were dissolved in 25 ml of DI water. Under vigorous stirring, the NiCl<sub>2</sub> solution was heated to 95 °C for 1 h, and the IrCl<sub>3</sub> solution was then added into the NiCl<sub>2</sub> solution dropwise. Afterwards, the whole solution was stirred for 30 min. Subsequently, the ATO powders (188 mg) were added slowly into the solution under constant stirring. The slurry was then heated to reflux for 3 h and cooled naturally down to room temperature. The product was collected and washed in DI water by centrifuge (40 ml  $\times$  6 times), and afterwards placed on a filter paper for drying at room temperature for 16 h. The amounts of precursors required for the synthesis of IrNi<sub>0</sub>O<sub>x</sub>/ATO (denoted as IrO<sub>x</sub>/ATO hereafter), IrNi<sub>2</sub>O<sub>x</sub>/ATO and IrNi<sub>3</sub>O<sub>x</sub>/ATO are given in the Supporting Information (table S1). ca. 150-200 mg of catalysts could be collected in one synthetic batch.

# 2.2. Catalyst characterisation

X-ray powder diffraction (XRD) patterns were obtained on an X'Pert PRO diffractometer (PANalytical) working at 45 kV and 40 mA with Cu K $\alpha$  radiation ( $\lambda = 1.541$  874 Å) and a PIXcel detector. Data were collected with the Bragg–Brentano configuration in the  $2\theta$  range of  $10^{\circ}$ – $80^{\circ}$  at a scan speed of  $0.01^{\circ}$  s<sup>-1</sup>. X-ray photoelectron spectroscopy (XPS) characterisation was carried out on an ESCALAB 250Xi instrument with an Al K $\alpha$  x-ray source (1486.6 eV). Scanning electron microscopy (SEM) was performed on a FEI Quanta 650 FEG microscope. Transmission electron microscopy (TEM) characterisation was conducted on a Titan Themis TEM (Thermo-Fisher Scientific) equipped with both probe and image  $C_s$  correctors and a Super-X energy-dispersive x-ray spectroscopy

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(EDS) detector, operated at 200 KeV. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) was done on a Shimadzu ICPE-9000 spectrometer. Catalyst digestion was performed by dissolving 1-2 mg of materials in 2.5 ml of pre-heated aqua regia (3:1 HCl to HNO<sub>3</sub>) at 60 °C. To facilitate the digestion, the acid solution was placed in an ultrasound bath at short intervals (10-30 s) until complete dissolution (Note: to avoid the formed bubbles from overflowing the vial, the vial should be left open). The digestion was then diluted to 100 ml with DI water, and possible particles in suspension were removed with an HPLC filter prior to analysis. Thermogravimetric analyses (TGA) were performed on a TG209 F1 iris (NETZSCH) instrument under nitrogen flow  $(30 \text{ ml min}^{-1}, 30 \degree \text{C}-1000 \degree \text{C}, 2 \degree \text{C} \text{min}^{-1})$ . Nitrogen adsorption isotherms were obtained on a Quantachrome Autosorb AS-1 surface area analyser at -196 °C. Prior to analysis, samples were degassed under vacuum at 200 °C for 4 h. The x-ray absorption spectroscopy (XAS) was conducted at the BL22-CLAESS beamline, ALBA Synchrotron in Barcelona, Spain. Catalyst powders were diluted with cellulose, thoroughly grinded for 45 min and then pressed (2 ton, 30 s) into 8 mm pellets. Data were acquired at room temperature using a Si(111) double crystal monochromator. The Ir L<sub>3</sub>-edge spectra were collected in transmission mode, and 5 scans were averaged to reduce the signal to noise ratio. For the in-situ XAS analysis IrNi<sub>1</sub>O<sub>x</sub>/ATO was loaded onto a carbon paper (spectracarb 2050A-0850, Fuel Cell Store) at a concentration of 0.85  $mg_{cat}$  cm<sup>-2</sup> and then measured in fluorescence mode on a PECC-1 photoelectrochemical cell (Zahner). Data were analysed with the Demeter software package [54].

#### 2.3. Electrochemical testing

For electrochemical testing on a three-electrode configuration, the catalyst ink was prepared as follows: 2.5 mg of  $IrNi_vO_x/ATO$  (or unsupported  $IrO_x$ ) were dispersed in a mixture of 740  $\mu$ l H<sub>2</sub>O, 250  $\mu$ l isopropanol and 10  $\mu$ l Nafion<sup>®</sup> solution, and subsequently sonicated for 30 min. Then, 9.48  $\mu$ l of the catalyst ink (4.74  $\mu$ l  $\times$  2) were drop-cast onto a glassy carbon (GC) slide electrode (Tokai Carbon Europe) with a predefined exposed area of 0.238 cm<sup>-2</sup>. The OER was performed in a conventional 3-electrode configuration in stirred 0.1 M HClO<sub>4</sub> electrolyte using a BioLogic VPM3 potentiostat as the source meter. Prior to each reaction, catalysts were preactivated by cyclic voltammetry (CV) in the potential range of 0.8–1.4  $V_{\rm RHE}$  at 50 mV s<sup>-1</sup> for 20 cycles. The catalytic activity was obtained from the reduction branch of CV curves (0.8-1.6  $V_{\rm RHE}$ , 5 mV s<sup>-1</sup>, the 2nd scan) to avoid any overcompensation, whilst the catalyst stability was assessed by chronopotentiometry (CP) at 10 mA  $\text{cm}^{-2}$  for 2 h and 15 h.

To assess the OER performance in a MEA, the catalyst ink was sprayed onto a commercial Nafion<sup>®</sup> 115 membrane with a constant Ir loading of 0.5 mg<sub>Ir</sub> cm<sup>-2</sup>. Catalyst inks were prepared by dispersing the required amount of catalysts (8.8, 20.0 and 22.0 mg for IrO<sub>2</sub>-Pk, IrO<sub>x</sub> and IrNi<sub>1</sub>O<sub>x</sub>/ATO, respectively) in the mixture of H<sub>2</sub>O (4 ml), isopropanol (4 ml) and 5 wt.% Nafion<sup>®</sup> solution (210  $\mu$ l). A platinum (Pt)-coated titanium (Ti) porous transport layer (PTL, Fuel Cell Store, ref 592815) was employed at the anode side, whilst a gas diffusion electrode (GDE, Fuel Cell Store, ref 1610025) with a Pt/C (40 wt.% Pt) loading of 0.3 mg<sub>Pt</sub> cm<sup>-2</sup> was employed at the cathode side. The as-prepared MEAs were tested at 60 °C under 1 bar on a single-cell electrolyser (QuinTech, EC-EL-05) with 5 cm<sup>2</sup> of active area using an in-house designed test station.

# 3. Results and discussion

#### 3.1. Structural and morphological characterization

The IrNi<sub>v</sub>O<sub>v</sub>/ATO (y = 0, 1, 2, and 3) catalysts were synthesised through sequential precipitation of NiCl<sub>2</sub> and IrCl<sub>3</sub> in alkaline media, following a method adapted from previous reports [30, 55]. The Ir and Ni loading mass for the as-prepared samples was confirmed by ICP-AES (table S2). Commonly reported methods for Ir-based catalyst synthesis (excluding electrodeposition techniques) typically require a heat treatment step in order to generate the active phase (e.g. Adams fusion [25], Ir-based precursor's decomposition [56–58], ligand or templating agent removal [28], and surface metal oxidation [27]). For the methods involving thermal treatment, the OER activity normally shows a 'volcano'like trend with the heating temperature, with the peak relating to the formation of amorphous iridium oxy-hydroxide  $(Ir(O_x)(OH)_y)$ , hereafter denoted as  $IrO_x$ ). Lower temperatures do not accomplish the formation of preferable  $IrO_x$ , whilst higher temperatures would lead to the crystallisation of IrO<sub>x</sub> to rutile IrO<sub>2</sub>, and accordingly the concomitant activity loss [24, 25], as mentioned in Introduction section. The same trend in OER activity with heating temperature was also reported for IrNi-based catalysts [40, 53]. Thus, direct precipitation of  $IrNi_vO_x$  phase without the need for any heat treatment, meanwhile employing commercially available precursors and following easily-scalable routes, is highly desired. Moreover, the sequential precipitation of NiCl<sub>2</sub> and IrCl<sub>3</sub> precursors enables to concentrate Ir at the catalyst surface, which allows for optimising Ir's utilisation.

XRD was employed to assess the crystal phases of asprepared  $IrNi_vO_x/ATO$  catalysts. Only peaks arising from the ATO (ICDD No. 01-075-8100) support were observed (figure S1(a)). No peaks related to crystalline Ir, Ni or IrNi phases were detected for any catalyst, suggesting that Ir and Ni are likely present in amorphous phases or as thin flakes/tiny aggregates beyond the detection limit of XRD (<2 nm). For comparison, the synthesised unsupported  $IrO_x$  and commercial rutile IrO2 from Alfa Aesar (IrO2-AA) and Premetek (IrO<sub>2</sub>-Pk) were also characterised by XRD (figure S1(b)). No distinct features were observed for  $IrO_x$  confirming its amorphous nature, in accordance with previous reports [30]. The XRD pattern for IrO<sub>2</sub>-AA is consistent with the standard diffraction pattern of rutile IrO<sub>2</sub> (ICDD No. 00-015-0870); while for IrO2-Pk, a significant presence of rutile IrO2 was also observed, but the main crystalline phase seems to arise from metallic Ir (ICDD No. 00-006-0598).

The microscopic morphology of supported samples was examined by SEM. The as-received ATO support consists of aggregates with a rough surface and a wide range of particulate size from 1  $\mu$ m to tens of  $\mu$ m. After the precipitation of Ir or IrNi oxy-hydroxides, the surface of the particulates appears smoother compared to the pristine ATO (figures S3(a)-(e)), and the formation of two distinct phases is not visible, which suggests that Ir or IrNi oxy-hydroxides are supported over or well mixed with the ATO particles. For IrNi<sub>v</sub>O<sub>x</sub>/ATO samples, the average granulate size seems to decrease compared to the pristine ATO. It is believed that this could be a consequence of the synthetic procedure, where the support was subjected to vigorous stirring in solution and reflux for 3 h, which may cause the shattering of big particles or the re-dispersion of large agglomerates. Despite of that, the average size obtained by counting over 200 particulates falls within the standard deviation of each sample (figure S2(f)). In addition, the surface area of synthesised catalysts was obtained through the Brunauer-Emmett-Teller (BET) method from the adsorptiondesorption nitrogen isotherms (table S3). The BET surface area of IrO<sub>x</sub>/ATO is comparable to that of as-received ATO (c.a. 60 m<sup>2</sup> g<sup>-1</sup>), suggesting that Ir is most likely finely dispersed at the surface of the support. The surface area for IrNi<sub>2</sub>O<sub>x</sub>/ATO and IrNi<sub>3</sub>O<sub>x</sub>/ATO is significantly smaller (c.a.  $10 \text{ m}^2 \text{ g}^{-1}$ ) than that of ATO, indicating that the precipitated mixed oxide phase is of low surface area and possibly blocks the pores of the support. In contrast,  $IrNi_1O_x/ATO$  shows a surface area of *c.a.* 90 m<sup>2</sup> g<sup>-1</sup>, manifesting that it may expose more catalytically active surface area.

The high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and high-resolution transmission electron microscopy (HRTEM) were carried out to unveil the morphology and atomic structure of  $IrO_{r}$ and IrNivOx/ATO catalysts. The ATO support was found to be highly crystalline with an average crystallite size of  $9.8 \pm 5.2$  nm, consistent with that calculated from the Scherrer equation (ca. 15 nm), and the Sb, Sn and O elements are uniformly distributed over individual particles (figure S4). According to HADDF-STEM, the unsupported  $IrO_x$  is generally amorphous and made of particles in the 50 nm range. Nevertheless, the presence of some small IrO2 crystallites (1-2 nm) at the edge of the IrO<sub>x</sub> particle was observed by HRTEM (figure S5(d), not evident by HAADF-STEM), which very likely results from the re-crystallisation of amorphous  $IrO_x$  upon the irradiation of electron beam. In fact, it is noticed that  $IrO_x$  was very sensitive to the electron beam and changed dynamically during the TEM/STEM observation. Some structural damage was also found in IrO<sub>x</sub> NPs upon long-term electron beam irradiation (bright spots in figures S5(e)-(g)). For the IrO<sub>x</sub>/ATO catalyst, the higher molecular weight of Ir compared to Sn, Sb and O makes the  $IrO_x$  phase stand out due to its higher brightness against the support (figures S6(a) and (b)). In addition, STEM-EDS elemental mapping revealed that although the  $IrO_x$  phase is well dispersed onto the support, it does not cover the ATO surface entirely (figure S6(c)). High magnification HAADF-STEM images indicate that the IrOxphase is distributed on the support as small crystallites (c.a. $1.5 \pm 0.4$  nm). Further fast Fourier transform (FFT) analysis implies that the nanocrystallites are composed of metallic Ir (figures S7 and S8), which does not align with XRD, XPS and XAS results (as discussed below), suggesting that the observed nanocrystallites most probably result from electron beam induced reduction of  $IrO_x$  and re-crystallisation.

The introduction of Ni in IrNi<sub>1</sub>O<sub>x</sub>/ATO catalysts did not give rise to a significant change in the morphology, compared to that of IrO<sub>x</sub>/ATO. In this case, a granulated phase made of small nanoclusters was observed on the surface of the ATO support (figures 1(a), (b) and S9). Additionally, a good intercalation exists between these nanoclusters and the particulate ATO support, though the nanoclusters do not fully cover ATO. STEM-EDS elemental mapping revealed that Ir and Ni are homogeneously distributed on the surface of ATO (figure 1(c)). When the Ni content increases, a similar granular phase was observed in IrNi<sub>2</sub>O<sub>x</sub>/ATO and IrNi<sub>3</sub>O<sub>x</sub>/ATO. However, higher magnification STEM imaging and EDS elemental mapping indicate that Ir and Ni seem not to form a homogeneous phase (figures S10 and S11). In particular, highcontrast bright clusters and spots, most likely originating  $IrO_x$ and atomically dispersed Ir atoms, were observed for IrNi<sub>3</sub>O<sub>r</sub> (figures 2(a)–(d)), implying phase separation on both nanometre and atomic scales. To elucidate the nature of the nickel phase, an unsupported IrNi<sub>3</sub>O<sub>x</sub> sample was synthesised following the same procedure but without adding ATO. The XRD pattern of this sample suggests that the Ni precursor precipitates as a low-crystallinity  $\beta$ -Ni(OH)<sub>2</sub> phase (ICDD No. 04-013-3641, figure S2) [59], confirming the occurrence of phase separation with a high Ni content. It is worth noting that given the metastability of  $IrO_x$  and  $IrNi_vO_x$  upon the electron beam irradiation, the observed Ir dispersion and the atomic structure may not represent the precise ones in the samples, but can to a large extent reflect how they are existent on ATO, considering that the image acquisition was fast and the atomic structure change did not occur instantaneously.

#### 3.2. Surface chemistry and electronic structure

The surface composition of catalysts was assessed by XPS. In this case, the powdery catalysts were mounted on a sticky carbon tape, which allows for calibration of all measured peaks against the C1s peak at 284.8 eV [60]. According to the survey spectra (figure S12), no chlorine (Cl) contamination was detected by XPS for any synthesised catalyst, indicating the complete conversion of metal chloride precursors into their corresponding metal oxy-hydroxides, and the efficient cleaning of the samples. The presence of lithium (Li) cannot be discerned from the survey spectra because the Li1s peak appears at a binding energy (BE) between the Ir4f and Ir4d peaks. Nevertheless, the high-resolution Ir4f spectra seem to indicate no Li contamination.

To elucidate the chemical nature of surface Ir sites on supported ATO, the Ir4f and O1s components of commercial IrO<sub>2</sub> and unsupported IrO<sub>x</sub> references were firstly analysed. Ir<sup>4+</sup> and O<sup>2-</sup> species were found to be exclusively present in commercial crystalline rutile IrO<sub>2</sub>, while co-existence of Ir<sup>3+</sup>/Ir<sup>4+</sup> species were observed in amorphous IrO<sub>x</sub>, in agreement with previous reports [33]. However, quantification of the Ir<sup>3+</sup>/Ir<sup>4+</sup> ratio from the Ir4f component turns out to be challenging due to the influence of the Ir5p<sub>1/2</sub> peak, electron



Figure 1. (a), (b) HAADF-STEM images and (c) STEM-EDS elemental maps of the as-prepared  $IrNi_1O_x/ATO$ .

correlation and spin-orbit coupling on the electronic structure. Moreover, changes in the oxidation state of Ir-compounds typically only translate in a small variation in the BE of the Ir4f peak [61-63]. Hence, it is better to employ a model to fit the Ir4f peak highlighting changes in the peak shape without attempting to quantify the  $Ir^{3+}/Ir^{4+}$  ratio, for non-synchrotron based XPS characterisation [61]. Typically, the co-existence of Ir<sup>3+</sup>/Ir<sup>4+</sup> species associated with amorphous iridium oxyhydroxide would result in a broadening of the Ir4f peak due to the variation in the atomic separation compared to rutile IrO2. In addition, the Ir4f spectrum of rutile IrO2 has a distinctive asymmetric shape, whilst a more symmetric peak envelope is the characteristic of  $IrO_x$  that contains even minor  $Ir^{3+}$ sites [64]. In our experiments, the Ir4f peak for IrO<sub>2</sub>-AA is centred at 61.9 eV, within the range of BE reported for rutile IrO<sub>2</sub> (61.7–61.9 eV) [34, 39, 64, 65], and it can be fitted with a model developed for commercial rutile IrO2 measured by laboratory XPS facilities (figure 3(a)) [64]. The Ir4f peak for IrO<sub>2</sub>-Pk shows a red shift by 0.2 eV compared to IrO<sub>2</sub>-AA (figure S13(a)), in agreement with the co-existence of  $IrO_2$  and metallic Ir in IrO<sub>2</sub>-Pk, as evidenced by XRD characterisation (figure S1(b)). Nevertheless, the O/Ir ratio obtained from XPS quantification for IrO<sub>2</sub>-AA (2.1) and IrO<sub>2</sub>-Pk (2.2) indicates that the surface of both samples consists of rutile IrO<sub>2</sub>, and that the metallic Ir in IrO<sub>2</sub>-Pk lies in the core of IrO<sub>2</sub> NPs. Besides, the O1s XPS spectra of commercial IrO2 catalysts show the characteristic asymmetric peak centred at 530.1 eV (figure S13(b)), ascribed to the pure oxide nature of rutile IrO<sub>2</sub>. In contrast, the Ir4f peak for the unsupported IrO<sub>x</sub> catalyst appears more symmetric, exhibits a blue shift, and broadens compared to the IrO<sub>2</sub>-AA. Besides, the Ir4f peak can be well fitted with a model developed for commercial IrO<sub>x</sub> (figure 3(a)) [64], suggesting the co-existence of Ir<sup>3+</sup>/Ir<sup>4+</sup> species commonly associated with amorphous iridium oxy-hydroxides [34, 39, 64, 65]. The presence of Ir<sup>3+</sup> species is usually ascribed to high surface hydration, as indicated by the O1s peak centred at 531.2 eV (figure 3(b)) that confirms –OH groups dominate on the surface of IrO<sub>x</sub>. Additionally, physi-sorbed water was observed in the O1s XPS spectra of IrO<sub>x</sub> as a shoulder at 533.2 eV [62]. Quantitative XPS analysis revealed an O/Ir ratio of 4.3 for IrO<sub>x</sub>, corroborating the high hydration degree of IrO<sub>x</sub> compared to rutile IrO<sub>2</sub> (O/Ir = 2).

Considering the overlap of the Ir4f and Ni3p peaks, the O1s and Sb3d<sub>5/2</sub> peaks, and the fact that both the ATO support (SnO<sub>2</sub> and Sb<sub>3</sub>O<sub>5</sub>) and metal oxy-hydroxides (IrO<sub>x</sub> and  $\beta$ -Ni(OH)<sub>2</sub>) contribute to O1s, the XPS analysis of IrNi<sub>y</sub>O<sub>x</sub>/ATO catalysts is fairly tricky. Hence, the nature of Ir species in IrNi<sub>y</sub>O<sub>x</sub>/ATO will be mainly discussed from the perspective of Ir4f peak shape with respect to that of rutile IrO<sub>2</sub> and IrO<sub>x</sub>, and peak fitting is not performed to avoid any misinterpretation. For IrO<sub>x</sub>/ATO, the Ir4f peak is centred at 61.9 eV and resembles that of IrO<sub>x</sub> in terms of broadening (figure S14), indicating that the nature of IrO<sub>x</sub> was not altered upon being loaded on the ATO support. The Ir4f peak of



Figure 2. (a)-(d) High-magnification HAADF-STEM images of IrNi<sub>3</sub>O<sub>x</sub>/ATO catalyst.

IrNi<sub>1</sub>O<sub>x</sub>/ATO shows a BE and line shape comparable to that of  $IrO_x$ , suggesting that  $Ir^{3+}$  and  $Ir^{4+}$  species co-exist after the introduction of Ni. The presence of Ni was also confirmed by the shoulder appearing at ca. 67.3 eV (figure 3(c)), which results from the Ni3p component [66]. The attempt to make a Gaussian peak fitting at 67.3 eV to integrate the Ni3p contribution did not give rise to a satisfactory result, implying that the close proximity of Ni might have modified the electronic structure of IrOx. For IrNi2Ox/ATO and IrNi3Ox/ATO, the shoulder peak originating from Ni3p becomes more pronounced, as expected by the higher concentration of Ni in these samples compared to that in IrNi<sub>1</sub>O<sub>x</sub>/ATO (figure S15). No significant peak broadening or BE shift was observed in the Ir4f spectra of IrNi<sub>2</sub>O<sub>x</sub>/ATO and IrNi<sub>3</sub>O<sub>x</sub>/ATO, compared to the IrNi<sub>1</sub>O<sub>x</sub>/ATO catalyst, which indicates that the Ir chemical states in all  $IrNi_vO_x/ATO$  catalysts are possibly similar.

Interpreting the Ni2p XPS spectra is challenging because multiple peaks are required to fit each oxidation state (e.g. 5 and 6 components for NiO and Ni(OH)<sub>2</sub>, respectively) [67]. Nevertheless, the chemical shift, indicative of the Ni species, can be used for rough analysis. For instance, Ni, NiO and Ni(OH)<sub>2</sub> show a BE value of 852.6, 853.7 and 855.6 eV, respectively [60]. The Ni2p peak for  $IrNi_1O_x$ /ATO is centred at 855.5 eV, indicating that Ni in IrNi<sub>1</sub>O<sub>x</sub>/ATO may exist mainly in the form of Ni(OH)<sub>2</sub> [67]. The predominant presence of  $Ni(OH)_2$  is in line with the high hydration degree observed in the Ir4f and O1s spectra, and is also reasonable considering the absence of heat treatment during the catalyst synthesis. In fact, Reier et al also observed that incorporating Ni into the IrO<sub>2</sub> lattice in  $Ir_{x}Ni_{1-x}O$  films favoured the formation of surface hydroxide groups, instead of a metal oxide surface [50]. For IrNi<sub>2</sub>O<sub>x</sub>/ATO and IrNi<sub>3</sub>O<sub>x</sub>/ATO, no significant changes in the



**Figure 3.** High-resolution (a) Ir4f and (b) O1s XPS spectra of IrO<sub>x</sub> and IrO<sub>2</sub>-AA. (c) Comparison of Ir4f XPS spectra of IrO<sub>x</sub>/ATO and IrNi<sub>1</sub>O<sub>x</sub>/ATO. (d) High-resolution Ni2p XPS spectra of IrNi<sub>y</sub>O<sub>x</sub>/ATO.

Ni2p peak were observed compared to the IrNi<sub>1</sub>O<sub>x</sub>/ATO catalyst (figure 3(d)), implying that Ni in these samples is likely existent in Ni(OH)<sub>2</sub> as well. This also agrees with XRD phase analysis of the unsupported IrNi<sub>3</sub>O<sub>x</sub> reference (figure S2). The Ir4d and Ni2p peaks were employed to quantify the surface composition of the IrNi<sub>y</sub>O<sub>x</sub> phase. For all three IrNi<sub>y</sub>O<sub>x</sub>/ATO (y = 1, 2, and 3) samples, an excess of Ni compared to the nominal value on the surface of catalysts was observed (table S4). For IrNi<sub>2</sub>O<sub>x</sub>/ATO and IrNi<sub>3</sub>O<sub>x</sub>/ATO, such Ni enrichment may result from the exposure of subsurface Ni, given that HAADF-STEM imaging revealed a phase separation on nanometre/atomic scale, where IrO<sub>x</sub>/Ir is present in the form of tiny clusters or single atoms.

To further explore the electronic and structural differences among  $IrNi_yO_x/ATO$  catalysts, XAS examination was performed at the Ir-L<sub>3</sub> edge (2p to 5d electronic transition). Information about the relative oxidation state can be obtained from the white line (WL) position, intensity and shape of the x-ray absorption near-edge structure (XANES). The adsorption edge energy was obtained from the first derivative (figure S16), and the XANES spectra were normalised using Athena from the Demeter software package [54]. The absorption edge is 11221.1 eV for IrO<sub>2</sub>-AA, which can be assigned to a formal bulk oxidation state of Ir<sup>4+</sup>, in line with previous reports on commercial crystalline IrO<sub>2</sub> [33, 34] and in agreement with the above XPS and XRD results. The WL position of  $IrO_x$  shifts towards lower energy compared to that of IrO<sub>2</sub>-AA, indicating an overall oxidation state lower than  $Ir^{4+}$ . This confirms the coexistence of  $Ir^{3+}$  and  $Ir^{4+}$  species throughout the bulk of catalysts, consistent with our previous XPS analysis. However, the lack of Ir<sup>3+</sup> standards prevents the exact determination of the average oxidation state for the synthesised samples. No shift in the WL position was observed for  $IrO_x/ATO$  with respect to the unsupported  $IrO_x$ , suggesting a comparable chemical environment and a similar Ir<sup>3+</sup>/Ir<sup>4+</sup> ratio. In contrast, a blue shift in the absorption energy is observed in IrNi1Ox/ATO and IrNi2Ox/ATO relative to  $IrO_r/ATO$  (figure 4(a)), manifesting that the introduction of Ni increases the overall bulk oxidation state of Ir and makes it closer to  $Ir^{4+}$ . The difference in the WL peak intensity between IrO2-AA and IrNi2Ox/ATO may be related to variations in symmetry and ligand environment among samples, as suggested by different electron scattering paths observed in q-space (figure S17) [68]. The local environment of Ir sites was further investigated by the extended x-ray absorption fine structure (EXAFS) spectroscopy. Ir centres of all samples are expected to have an octahedral coordination, i.e.  $[IrO_6]$ , with O interconnected through corner- and edge-sharing positions. In rutile [IrO<sub>6</sub>], octahedra are interconnected in the most thermodynamically stable configuration leading to a rigid structure, whilst in amorphous samples, the [IrO<sub>6</sub>] octahedra are usually assembled in a



**Figure 4.** XAS characterisation for  $IrO_2$ -AA,  $IrO_x$  and  $IrNi_yO_x/ATO$ : (a) normalised XANES spectra and (b) phase corrected EXAFS spectra.

more flexible configuration [31, 37]. The average Ir–O bond distance (Ir-O<sub>av</sub>) was obtained by fitting the first coordination shell with a distorted octahedron containing two Ir-O axial (Ir-Oax) and four Ir-O equatorial (Ir-Oeq) bonds using IFEFFIT with Artemis from the Demeter software package (tables S5 and S6) [54]. An Ir-O<sub>av</sub> bond distance of 1.97 Å and 2.01 Å was obtained for  $IrO_2$ -AA and  $IrO_x$ , respectively, in accordance with distances previously reported for rutile IrO2 and iridium oxy-hydroxides [62, 69]. The Ir-O<sub>av</sub> bond distance for the supported  $IrO_x/ATO$  is further elongated compared to the  $IrO_x$  sample, which might be attributed to a wider Ir–O bond length distribution, although comparable Debye-Waller factors ( $\sigma^2$ ) suggest a similar structural disorder for both samples. For IrNi1Ox/ATO and IrNi2Ox/ATO, Ir-Oav bond distances comparable to that of  $IrO_x$  were obtained (figure 4(b) and table S5), indicating that even though the XANES spectra suggest a bulk oxidation state close to Ir<sup>4+</sup>, Ir centres in these two samples remain a disordered structure.

#### 3.3. Electrocatalytic performance towards the acidic OER

The acidic OER performance of unsupported  $IrO_x$  and  $IrNi_yO_x/ATO$  was evaluated in a conventional three-electrode configuration in 0.1 M HClO<sub>4</sub> electrolyte (pH = 1). Prior to each measurement, catalysts were conditioned by CV in the potential range of 0.8–1.4  $V_{RHE}$  at 50 mV s<sup>-1</sup> for 20 cycles. The apparent activity was obtained from the reduction branch of CV curves (0.8–1.6  $V_{RHE}$ , 5 mV s<sup>-1</sup>) to avoid any over-compensation. As shown in figure 5(a), comparable apparent activity was obtained for IrO<sub>x</sub>, IrO<sub>x</sub>/ATO and IrNi<sub>1</sub>O<sub>x</sub>/ATO catalysts (ca. 1.54  $V_{RHE}$  at 10 mA cm<sup>-2</sup>), even though the Ir loading on the electrode was reduced from 71.2  $\mu$ g cm<sup>-2</sup> for unsupported IrO<sub>x</sub> to 21.8  $\mu$ g cm<sup>-2</sup> for IrO<sub>x</sub>/ATO and 19.7  $\mu$ g cm<sup>-2</sup> for IrNi<sub>1</sub>O<sub>x</sub>/ATO, highlighting the advantage of dispersing Ir on a support to improve the metal utilisation.

For IrNi<sub>2</sub>O<sub>x</sub>/ATO and IrNi<sub>3</sub>O<sub>x</sub>/ATO with further decreased Ir/Ni ratio, a progressive increase in the overpotential (n) was found. For comparison, commercial IrO2-Pk was also assessed towards OER under the same conditions (It was very challenging to disperse IrO<sub>2</sub>-AA in a solution, and hence, IrO<sub>2</sub>-AA was not tested because of the great error associated with its irregular loading). It is known that crystalline rutile IrO<sub>2</sub> catalysts are generally less active than amorphous iridium oxyhydroxides [30–32]. This is also the case for  $IrO_2$ -Pk, which required a potential of 1.59  $V_{\text{RHE}}$  ( $\eta = 360 \text{ mV}$ ) to reach a current density of 10 mA  $cm^{-2}$ , higher than all other catalysts. Furthermore, the mass activity of all catalysts was assessed and compared. The Ir loading of supported catalysts was measured by ICP-AES, while the Ir loading of unsupported  $IrO_x$  and IrO<sub>2</sub>-Pk was determined by TGA (figure S18). The Ni content was not considered because Ni suffers from fast corrosion in acidic electrolyte, though it is active towards OER in alkaline media. At  $\eta = 350$  mV, the IrO<sub>x</sub>/ATO (0.9 mA  $\mu$ g<sub>Ir</sub><sup>-1</sup>) shows a markedly improved mass activity compared to the unsupported IrO<sub>x</sub> (0.3 mA  $\mu g_{Ir}^{-1}$ ), indicating the benefit of supported catalysts over the unsupported ones (figure S19). The introduction of Ni further increases the Ir mass activity, amounting to 1.0 mA  $\mu g_{Ir}^{-1}$  for IrNi<sub>1</sub>O<sub>x</sub>/ATO and 1.5 mA  $\mu g_{Ir}^{-1}$  for IrNi<sub>2</sub>O<sub>x</sub>/ATO at  $\eta = 350$  mV, owing to the further reduced Ir loading. Assuming that all Ir atoms on the electrode are equivalent and active towards OER, the turnover frequency (TOF) of all catalysts was calculated at  $\eta = 350 \text{ mV}$  (table 1). The TOF value for IrO<sub>x</sub>/ATO (108 s<sup>-1</sup>) is >3 times higher than that of  $IrO_x$  (34 s<sup>-1</sup>). For  $IrNi_vO_x$ /ATO catalysts, although  $IrNi_2O_x/ATO$  (180 s<sup>-1</sup>) and  $IrNi_3O_x/ATO$  (152 s<sup>-1</sup>) show a higher initial TOF value than  $IrNi_1O_x/ATO$  (123 s<sup>-1</sup>), they suffer from fast degradation, which suggests that the current density used for TOF calculations cannot be solely attributed to the OER and it may contain the contribution from catalyst corrosion.



**Figure 5.** (a) Apparent OER activity obtained from the reduction branch of CV curves at a scan rate of 5 mV s<sup>-1</sup>. (b) Tafel slope obtained from LSV at 0.5 mV s<sup>-1</sup>. (c) Catalytic stability assessed by CP at 10 mA cm<sup>-2</sup> for IrO<sub>2</sub>-Pk, IrO<sub>x</sub> and IrNi<sub>y</sub>O<sub>x</sub>/ATO catalysts.

Table 1. The OER activity of all catalysts measured in 0.1 M HClO<sub>4</sub> electrolyte.

| catalyst                              | $E_{\rm RHE}$ at 10 mA cm <sup>-2</sup> | J (mA $\mu g_{Ir}^{-1}$ ) at $\eta = 350 \text{ mV}$ | TOF/s <sup>-1</sup> at $\eta = 350 \text{ mV}$ | Tafel slope/mV dec $^{-1}$ | ECSA/cm <sup>2</sup> |
|---------------------------------------|---|--|--|----------------------------|----------------------|
| IrO <sub>2</sub> -Pk                  | 1.59                                    | 0.10   | 10   | 60                         | 157                  |
| $IrO_x$                               | 1.54                                    | 0.29   | 34   | 50                         | 197                  |
| IrO <sub>x</sub> /ATO                 | 1.55                                    | 0.90   | 108  | 49                         | 257                  |
| IrNi <sub>1</sub> O <sub>x</sub> /ATO | 1.54                                    | 1.02   | 123  | 50                         | 191                  |
| IrNi <sub>2</sub> O <sub>x</sub> /ATO | 1.56                                    | 1.52   | 180  | 58                         | 143                  |
| IrNi <sub>3</sub> O <sub>x</sub> /ATO | 1.57                                    | 1.26   | 152  | 62                         | 180                  |

Tafel analysis was carried out to compare the OER kinetics of the synthesised catalysts.  $IrO_x$ ,  $IrO_x/ATO$  and  $IrNi_1O_x/ATO$ catalysts show a Tafel slope of ca. 50 mV dec<sup>-1</sup> (figure 5(b) and table 1), in agreement with previous results reported for iridium oxy-hydroxides (35–55 mV dec<sup>-1</sup>) [31, 56, 65, 70]. In comparison,  $IrO_2$ -Pk exhibits a Tafel slope of 60 mV dec<sup>-1</sup>, consistent with the values reported for rutile  $IrO_2$  (ca. 60 mV dec<sup>-1</sup>) [65, 70–73] and in line with the slower OER kinetics over crystalline  $IrO_2$  compared to amorphous iridium oxy-hydroxides. The Tafel slope of  $IrNi_2O_x/ATO$  and  $IrNi_3O_x/ATO$  is closer to 60 mV dec<sup>-1</sup>, which could be associated with the lower concentration of Ir species at the surface and the higher overall oxidation state close to  $Ir^{4+}$  compared to  $IrNi_1O_x/ATO$ , as demonstrated by the above XPS and XAS results.

To assess the possible active sites involved during the OER, a CV scan in the 0.3–1.4  $V_{\text{RHE}}$  range was recorded (figure S20). The commercial IrO<sub>2</sub>-Pk showed no distinct redox transition as typically observed for crystalline IrO<sub>2</sub> with a low OER activity [74]. By contrast, IrO<sub>x</sub>, IrO<sub>x</sub>/ATO and IrNi<sub>1</sub>O<sub>x</sub>/ATO all exhibited typical redox pairs of Ir<sup>3+</sup>/Ir<sup>4+</sup> at ca. 0.95  $V_{\text{RHE}}$  and Ir<sup>4+</sup>/Ir<sup>4+δ</sup> at ca. 1.25  $V_{\text{RHE}}$ , associated with active amorphous iridium oxy-hydroxides [56, 63, 75], corroborating the presence of Ir<sup>3+</sup> species as suggested by XPS and XAS. For IrNi<sub>2</sub>O<sub>x</sub>/ATO and IrNi<sub>3</sub>O<sub>x</sub>/ATO, a peak at ca. 0.65 V<sub>RHE</sub> was observed, which can be attributed to a redox process on Ni(OH)<sub>2</sub> [76]. This indicates that the surface of these catalysts contains Ni species that is likely corroded during the acidic OER, which in turn would compromise the overall catalytic stability. To confirm that the OER activity only relates to Ir sites, in-situ XAS was conducted for the IrNi1Or/ATO catalyst at the Ir-L<sub>3</sub> edge and Ni-K edge. For the XAS spectra recorded at Ir-L<sub>3</sub> edge, a blue-shift of 1.54 eV in the WL position was observed when increasing the anodic potential from 0.8  $V_{\rm RHE}$ to 1.6  $V_{\text{RHE}}$  (figure 6(a)). This energy shift with the increasing potential into the OER regime relates to surface deprotonation and a concomitant increase in the oxidation state of Ir centres that promotes the OER process [31, 63, 65, 68]. Such a change in Ir oxidation state was found to be reversible, as confirmed by the recovery of the WL to its original position when the polarisation came back to 0.8  $V_{\rm RHE}$ . In contrast, no evident changes in the Ni-K edge spectra were observed when the anodic potential increased to the OER regime (figure 6(b)). The XAS characterisation of the oxidation of  $Ni(OH)_2$  to NiOOH and NiO upon the OER has been well-documented previously [77, 78], so the fact that no change occurs at the



**Figure 6.** In situ XAS characterisation at the (a) Ir-L<sub>3</sub> edge and (b) Ni-K edge for  $IrNi_1O_x/ATO$ .

Ni K-edge during the OER indicates that Ni centres were not involved during the reaction.

The ECSA of IrO<sub>2</sub>-Pk, IrO<sub>x</sub>, and IrNi<sub>y</sub>O<sub>x</sub>/ATO was estimated by electrochemical double-layer capacitance from CV measurements at different scan rates from 2 to 100 mVs<sup>-1</sup> in a non-Faradaic potential region (0.47–0.57  $V_{RHE}$ ). It is noted that such estimation varies largely depending on the reference specific capacitance ( $C_s$ ) adopted and the presence of pseudocapacitance and chemical capacitance [79–81]. Hence, it is only used to make comparison among the catalysts synthesised in this work (figures S21, S22 and table S7), but not to compare to other catalysts reported in the literature. Supporting IrO<sub>x</sub> onto ATO resulted in a higher ECSA, in agreement with the enhanced Ir dispersion; while for the IrNi<sub>y</sub>O<sub>x</sub> samples, a reduced ECSA was observed, which may be attributed to the inactive Ni introduced.

The robustness of catalysts is very important towards practical applications. Rutile IrO2 is reported to be the state-of-theart catalyst for the acidic OER due to its outstanding stability against corrosion in acidic conditions. However, the stability comparison between crystalline IrO<sub>2</sub> and IrO<sub>x</sub> is controversial [82]. Mom and co-workers, through online Ir dissolution studies combined with operando XAS and XPS characterisation, reported that during the OER the deprotonation of -OH intermediates, which precedes O-O coupling, occurs at the outermost surface over crystalline samples, while the deprotonation over amorphous  $IrO_x$  happens on both outermost and sub-surface [61]. This can explain the higher activity usually observed for  $IrO_x$  compared to rutile  $IrO_2$ , but at the expenses of higher Ir dissolution [27, 61]. However, recent works also pointed out that the higher activity of  $IrO_x$  is not always correlated with compromised stability [24, 31, 32, 83, 84]. The contradictory activity-stability trends reported earlier might correlate with the interplay of several Ir dissolution pathways [83, 85], the existence of different types of  $IrO_x$  [30, 37], and other physical factors that influence O<sub>2</sub> gas bubble formation and detachment [86, 87]. In our experiment, no evident rapid degradation was observed by CP (10 mA cm<sup>-2</sup>) during a 2 h test for IrO<sub>x</sub>, IrO<sub>x</sub>/ATO, IrNi<sub>1</sub>O<sub>x</sub>/ATO and IrNi<sub>2</sub>O<sub>x</sub>/ATO catalysts (figure 5(c)). In contrast, a gradual increase in anodic potential up to 1.9  $V_{\rm RHE}$  was observed for the IrNi<sub>3</sub>O<sub>x</sub>/ATO catalyst, indicative of catalyst degradation, which might be related to the presence of excess Ni that is prone to dissolution in acidic conditions. Furthermore, rapid degradation was also observed for IrO2-Pk, which mainly resulted from partial delamination of catalysts from the glassy carbon substrate. The catalytic stability was further appraised by comparing the polarisation curves before and after the CP test (figure S23). The initial polarisation curves of unsupported  $IrO_x$ ,  $IrO_x/ATO$  and  $IrNi_yO_x/ATO$  (y = 1 and 2) nearly overlap with those after the 2 h CP test, demonstrating reasonably good catalytic stability. By comparison, a large positive shift of polarisation curves was observed for IrNi<sub>3</sub>O<sub>x</sub>/ATO and IrO2-Pk after the CP test, which corroborates the instability of these catalysts. Given the observed good stability, unsupported IrO<sub>x</sub>, IrO<sub>y</sub>/ATO, IrNi<sub>1</sub>O<sub>y</sub>/ATO and IrNi<sub>2</sub>O<sub>y</sub>/ATO catalysts were further tested at  $10 \text{ mA cm}^{-2}$  for 15 h (figure S24). While unsupported IrO<sub>x</sub>, IrO<sub>x</sub>/ATO and IrNi<sub>1</sub>O<sub>x</sub>/ATO all survived the long-term stability test, only IrNi<sub>1</sub>O<sub>x</sub>/ATO showed insignificant sign of performance decay in the 15 h stress test. In contrast, IrNi<sub>2</sub>O<sub>x</sub>/ATO became deactivated after 5 h.

# 3.4. Performance assessment in membrane electrode assemblies

To evaluate the potential of the synthesised catalysts for use in PEM-WE, a MEA was further fabricated using the  $IrO_x/ATO$  and  $IrNi_1O_x/ATO$  as the anode catalysts and commercial Pt/C (40 wt.% Pt) as the cathode catalysts, whose performance was tested in a single-cell electrolyser using the harmonised testing conditions proposed by the EU Joint Research Centre (60 °C, 1 bar) [88]. For comparison, the catalytic activity



**Figure 7.** Polarisation curves (a) and chronopotentiometry (b) obtained for  $IrO_2$ -Pk,  $IrO_x/ATO$  and  $IrNi_1O_x/ATO$  catalysts on a MEA single cell configuration.

of commercial IrO2-Pk was also assessed. At a comparable Ir loading of 0.5  $mg_{Ir}$  cm<sup>-2</sup>, IrNi<sub>1</sub>O<sub>x</sub>/ATO, IrO<sub>x</sub>/ATO and IrO<sub>2</sub>-Pk reached a current density of 1 A cm<sup>-2</sup> at 2.03, 2.26 and 2.46 V, respectively (figure 7(a)). Assuming that the cell voltage is limited by the OER activity at the anode, the activity trend obtained in the MEA configuration aligns well with results obtained in the three-electrode configuration. The stability of MEAs was measured through chronopotentiometry at the current density initially required to reach 1.8 V (0.4 and 0.6 A cm<sup>2</sup> for IrNi<sub>1</sub>O<sub>x</sub>/ATO and IrO<sub>x</sub>/ATO, respectively). An upper limit of 2 V was applied to the cell voltage, according to the EU's harmonised PEM-WE testing protocol [88]. Based on the first 60 h of accelerated stress test, a  $0.7 \text{ mV h}^{-1}$  degradation rate was observed for IrNi1Ox/ATO, whilst the degradation rate was 70% higher for  $IrO_x/ATO (1.2 \text{ mV h}^{-1})$ . For both IrO<sub>x</sub>/ATO and IrNi<sub>1</sub>O<sub>y</sub>/ATO catalysts, a sharp increase in cell voltage was seen after 70 and 90 h of operation (figure 7(b)), which might be attributed to a combination of catalyst degradation, agglomeration, delamination, membrane cracking and increased mass transport resistance as common causes reported for PEM-WE cell degradation [89, 90]. Further optimisation will be carried out to improve the performance of IrNi<sub>1</sub>O<sub>x</sub>/ATO for PEM-WE.

# 4. Conclusions

In summary, we report a new sequential precipitation method for preparing  $IrNi_yO_x/ATO$  catalysts with an aim to reduce Ir utilisation while maintaining its good OER performance for PEM-WE. We systematically investigated how the Ni content influences the morphology, microstructure, surface chemistry and electrocatalytic performance using advanced physicochemical characterisation techniques. We found that phase separation exists in all  $IrNi_yO_x/ATO$  (y = 1, 2, and 3) samples, but  $IrNi_1O_x/ATO$  shows a favourable Ir-rich surface and has a mixture of  $Ir^{3+}$  and  $Ir^{4+}$  species on its surface. As a result,  $IrNi_1O_x/ATO$  exhibits reasonably good OER performance in terms of apparent activity, mass activity and turnover frequency. Importantly, it shows an outstanding catalytic stability compared to other reference catalysts under investigation. The good performance of  $IrNi_1O_x/ATO$  has also been validated preliminarily in membrane electrode assemblies. Given the easy and potentially cost-effective synthetic approach, the  $IrNi_1O_x/ATO$  shows substantial promise for use as highperformance alternative anode catalysts in PEM electrolysers.

# 5. Future perspective

Iridium is currently indispensable for use as anode catalysts in a practically usable PEM electrolyser. Although considerable research effort was also made to develop iridium- and even platinum group metal-free materials able to catalyse the anodic OER under acidic conditions, the unsatisfactory electrochemical stability of these materials in acid hardly allow them to be employed in practice. Hence, it is anticipated that iridium will still be a material of choice for industrial PEM electrolysers in the near to medium term. In this case, efficient usage of precious and scarce iridium becomes particularly important, considering the projection of large-scale deployment of PEM electrolysers in the coming decades for energy transition. Reducing iridium loading by introducing secondary inexpensive transition metals and enhancing effective exposure of active sites by loading iridium-based mixed oxides/oxy-hydroxides on acid-stable supports are promising approaches to improving the catalytic performance for PEM-WE and lowering materials costs. The powdery supported mixed oxide/oxy-hydroxide catalysts are also compatible with the fabrication techniques of MEAs currently being used to make PEM electrolysers. Notwithstanding some progress, the long-term stability of the supported mixed oxide/oxy-hydroxide catalysts should be further improved and their performance needs to be comprehensively assessed under various working conditions, before their usage in commercial PEM electrolysers.

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# Author's contribution

J R E was responsible for project management, catalyst synthesis, characterisation, testing and manuscript writing. A P L performed STEM characterisation. H J, Z P Y and A A contributed equally and helped in acquiring the XAS data, and they also ensured the smooth operation of the electrochemical test station, and the laboratory in general including the maintenance of working, counter and reference electrodes. R M and A M were responsible of MEA preparation and testing. L L proposed the concept, secured funding, supervised the research, and wrote the final version of the manuscript.

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