

Reaction mechanism for oxygen evolution on RuO<sub>2</sub>, IrO<sub>2</sub>, and RuO<sub>2</sub>@IrO<sub>2</sub>  
core-shell nanocatalysts

Z. Ma, J. X. Wang

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D. V. Matyushov

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# Reaction mechanism for oxygen evolution on RuO<sub>2</sub>, IrO<sub>2</sub>, and RuO<sub>2</sub>@IrO<sub>2</sub> core-shell nanocatalysts

Zhong Ma<sup>a</sup>, Yu Zhang<sup>a</sup>, Shizhong Liu<sup>a</sup>, Wenqian Xu<sup>b</sup>, Lijun Wu<sup>a</sup>, Yu-Chi Hsieh<sup>a</sup>

Ping Liu<sup>a</sup>, Yimei Zhu<sup>a</sup>, Kotaro Sasaki<sup>a</sup>, Julie N. Renner<sup>c</sup>,

Katherine E. Ayers<sup>c</sup>, Radoslav R. Adzic<sup>a,\*</sup>, and Jia X. Wang<sup>a,\*</sup>

<sup>a</sup>Brookhaven National Laboratory, Chemistry Division, Energy & Photon Sciences Directorate, Upton, NY 11973, USA

<sup>b</sup>X-ray Science Division, Advanced Photon Source, Argonne National Laboratory, Argonne, IL 60439, USA

<sup>c</sup>Proton OnSite, 10 Technology Drive, Wallingford, CT 06492, USA

In memoriam of Professor Roger Parsons

Abstract

Iridium dioxide, IrO<sub>2</sub>, is second to the most active RuO<sub>2</sub> catalyst for the oxygen evolution reaction (OER) in acid, and is used in proton exchange membrane water electrolyzers due to its high durability. To improve the activity of IrO<sub>2</sub>-based catalysts, we prepared RuO<sub>2</sub>@IrO<sub>2</sub> core-shell nanocatalysts using carbon-supported Ru as the template. At 1.48 V, the OER specific activity of RuO<sub>2</sub>@IrO<sub>2</sub> is threefold that of IrO<sub>2</sub>. While the activity volcano plots over wide range of materials have been reported, zooming into the top region to clarify the rate limiting steps of most active catalysts is important for further activity enhancement. Here, we verified theory-proposed sequential water dissociation pathway in which the O-O bond forms on a single metal site, not via coupling of two adsorbed intermediates, by fitting measured polarization curves using a kinetic equation with the free energies of adsorption and activation as the parameters. Consistent with theoretical calculations, we show that the OER activities of IrO<sub>2</sub> and RuO<sub>2</sub>@IrO<sub>2</sub> are limited by the formation of O adsorbed phase, while the OOH formation on the adsorbed O limits the reaction rate on RuO<sub>2</sub>.

KEYWORDS: Electrolysis; RuO<sub>2</sub>; IrO<sub>2</sub>; Core-shell; Oxygen evolution reaction mechanism.

Corresponding Authors \*E-mail addresses: [jia@bnl.gov](mailto:jia@bnl.gov) (JX Wang) [adzic@bnl.gov](mailto:adzic@bnl.gov) (RR Adzic)

## 1. Introduction

The core-shell nanoparticles were widely studied over the past decade for various applications in catalysis, energy storage, sensors, and in biology [1]. With the advanced technologies for their synthesis and structural characterization, an atomic level control of core-shell structures were achieved for Pt shells on other metals or metal-alloys cores [2–4]. Utilizing 1- to 2-monolayer-thick Pt shells maximizes the surface area per Pt mass, and enables fine tuning of the surface properties with suitable core metals and Pt shell thicknesses. Coupled with progress in density functional theory (DFT) calculations [5], the rational design of core-shell nanocatalysts became a practical approach. For example, Pd and Co- or Ni-containing alloys are suitable cores [2,6,7] for oxygen reduction reaction (ORR) [2,6,7], and well-ordered Ru@Pt core-shell nanocatalysts are more active than are Pt nanoparticles for hydrogen oxidation reaction (HOR) and hydrogen evolution reaction (HER) [8], especially in alkaline environments [9]. The enhancements in specific activities of these metallic core-shell particles are ascribed to optimized binding energies for the adsorbed reaction intermediates, O and OH for the ORR [2,6] and H for the HOR-HER [9,10].

Like Pt, Ir is expensive and is even rarer than is Pt in the Earth's crust [11]. Thus, considerable research efforts were made to lower the IrO<sub>2</sub> loading without compromising the OER performance [12–14]. A threefold enhancement in Ir mass activity was reported for the IrNi@IrO<sub>x</sub> catalysts, which have a metal@metal-oxide hybrid core@shell architecture, prepared by surface oxidation of the IrNi alloy nanoparticles, the surface of which were Ir-enriched by electrochemical de-alloying Ni [15]. Since non-noble metals are prone to dissolution in acid, Ru, a significantly cheaper noble metal, was a common choice in developing mixed oxide nanocatalysts for the OER in PEM water-electrolyzers [16–22]. RuO<sub>2</sub> is known to be the most active for the OER in acids [23,24], but not sufficiently durable, and thus, Ru-Ir mixed oxides were studied for enhancing the OER activity and catalysts' durability. Recently, the stability of Ru<sub>0.5</sub>Ir<sub>0.5</sub>O<sub>2</sub> catalyst was found to be four times higher after treatment to enrich Ir at its surface [25]. In this study, we prepared RuO<sub>2</sub>@IrO<sub>2</sub> core-shell nanocatalysts, which exhibit a threefold enhancement in specific activity at 1.48 V compared to IrO<sub>2</sub>.

Several OER mechanisms have been proposed for metal dioxides in acids, which can be categorized by whether it involves a reaction that combines two adsorbed oxygen species (either OH, or O, or OOH) at neighboring sites [26]. The coupling pathway with the O-O bond formation via a non-electron-transfer reaction of two surface species was preferred in early studies<sup>27-31</sup> because the observed potential- and catalyst-dependent Tafel slopes were qualitatively interpreted by having a reaction step with its rate independent of potential. Later in the 2000s, however, DFT studies suggested sequential water dissociation as the favorable pathway, in which the O-O bond forms at a single surface site by adding the second O to a previously adsorbed O [32-36]. Taking RuO<sub>2</sub> as an example, the DFT calculated reaction barrier for the coupling pathway has been found higher than that for the sequential pathway [37]. This distinctly differs from that hydrogen evolution reaction on Pt, where the Volmer-Tafel pathway in which two adsorbed H species combine to form H<sub>2</sub> is dominant. In this study, following the theoretic insight, we derived a kinetic equation based on a sequential pathway to fit measured OER polarization curves over a wide potential region using adsorption and activation free energies as the adjustable parameters. The non-linear polarization curves in the Tafel plot for RuO<sub>2</sub>, IrO<sub>2</sub>, and RuO<sub>2</sub>@IrO<sub>2</sub> were well reproduced by the best fits. The results demonstrated that small and gradual changes in Tafel slopes are not necessarily caused by a coupling pathway involving O-O bond formation via two adsorbed intermediates. In addition, we present DFT-calculated results in Theoretical section, which provide insight on the effect of O adsorption energy on the rate-limiting steps and the OER activity trend.

## 2. Materials and methods

### 2.1. Preparation of RuO<sub>2</sub> and RuO<sub>2</sub>@IrO<sub>2</sub> nanocatalysts

In a typical synthesis of a RuO<sub>2</sub> nanocatalyst, commercial carbon-supported Ru metal nanoparticles (40 wt% Ru/C, E-Tek) were calcined in air at 400 °C for 1 h using a tube furnace. An antistatic gun (Zerostat, SPI Supplies) was used to neutralize static charges whilst transferring the sample. For preparing RuO<sub>2</sub>@IrO<sub>2</sub> nanocatalysts, hydrogen hexachloroiridate(IV) hexahydrate (H<sub>2</sub>IrCl<sub>6</sub>·6H<sub>2</sub>O, 40% Ir, Acros Organics) was dissolved in anhydrous ethanol (200 proof, ACS/USP Grade, Pharmco Aaper). The ethanolic H<sub>2</sub>IrCl<sub>6</sub> solution was heated in an oil bath at 80 °C for 1 h until the solution color changed from brown to light yellow. Then, carbon-supported Ru metal nanoparticles (20 wt% Ru/C, E-Tek) were added into

the solution at 40 °C with stirring, and the solvent was evaporated by heating the mixture in an oil bath at 85 °C. The dry mixture was crushed into fine powder, and calcined in air at 400 °C for 1 h in a tube furnace.

## *2.2. Structural characterization of the metal oxide nanocatalysts*

Transmission electron microscope (TEM), scanning transmission electron microscopy (STEM) imaging and electron energy-loss spectroscopy (EELS) were carried out using the double aberration-corrected JEM-ARM200CF microscope with a cold-field emission gun and operated at 200 kV. The microscope is equipped with JEOL and Gatan HAADF detectors for incoherent STEM-HAADF (Z-contrast) imaging, Gatan GIF Quantum ER Energy Filter with dualEELS for EELS. Powder X-ray diffraction (PXRD) measurements were carried out on Beamline 17-BM ( $\lambda = 0.75009 \text{ \AA}$ ) of the Advanced Photon Source at Argonne National Laboratory. Sample powder was packed in 0.5 mm inner diameter Kapton® capillaries and measured in transmission geometry with PerkinElmer® amorphous Si flat panel detector.

## *2.3. Preparation of gas diffusion electrodes*

The catalyst inks were prepared by dispersing metal oxide nanoparticles in a solution of deionized water, iso-propanol, and Nafion® (perfluorinated resin, equivalent weight 1000, Aldrich). Typically, the dry mass of Nafion® is equal to 5% of the weight of the catalyst. The volume ratio for water to iso-propanol was 3:1. We used a Mixer Mill MM 400 (Retsch) to shake the mixture at a frequency of  $12 \text{ s}^{-1}$  for 1 hour, and sonicated it in an ice bath for 5 - 10 min before each use. Inks of 10 to 40  $\mu\text{L}$  were pipetted on to  $1 \text{ cm}^2$  area at one end of a  $1 \times 4 \text{ cm}^2$  strip of a Ti-based gas diffusion layer (from Proton OnSite) to obtain the desired catalyst loadings.

## *2.4. Electrochemical measurements*

All electrochemical measurements were performed with a three-electrode cell using a Volta PGZ402 potentiostat (Voltalab, Radiometer Analytical) at room temperature. The Ti gas diffusion electrode strips were held vertically with the catalyzed part ( $1 \times 1 \text{ cm}^2$ ) immersed in 0.5 M  $\text{H}_2\text{SO}_4$  solution facing a Pt flag counter electrode at a distance of 1 – 2 cm. Potentials were measured using a leak-free (Ag/AgCl, 3M NaCl) reference electrode, and converted to the

reversible hydrogen electrode (RHE) scale using measured open-circuit potential of the Pt flag in the H<sub>2</sub>-saturated electrolyte. Chronopotentiometry at 200 mA cm<sup>-2</sup> was carried out for 1 h to eliminate the samples having easy-to-fall-off catalysts under oxygen bubbling condition. It was followed by measurement of electrochemical impedance at 1.8 V versus RHE with a peak-to-peak perturbation of 20 mV with an AC frequency from 10 kHz to 0.1 Hz to determine the high frequency resistance (HFR) that is typically about 1 Ω cm<sup>2</sup>. The ohmic-loss corrected potential,  $E - iR$ , denotes applied potential  $E$  minus the product of measured current  $i$  and  $HFR$ . Quasi-static polarization curves were obtained by averaging the currents measured during a positive and a negative potential sweep at 20 mV s<sup>-1</sup>. The integrated charge from 0.4 to 1.23 V in a voltammetry curve was obtained by averaging the two values obtained from positive and negative sweeps.

## 2.5. Computational method

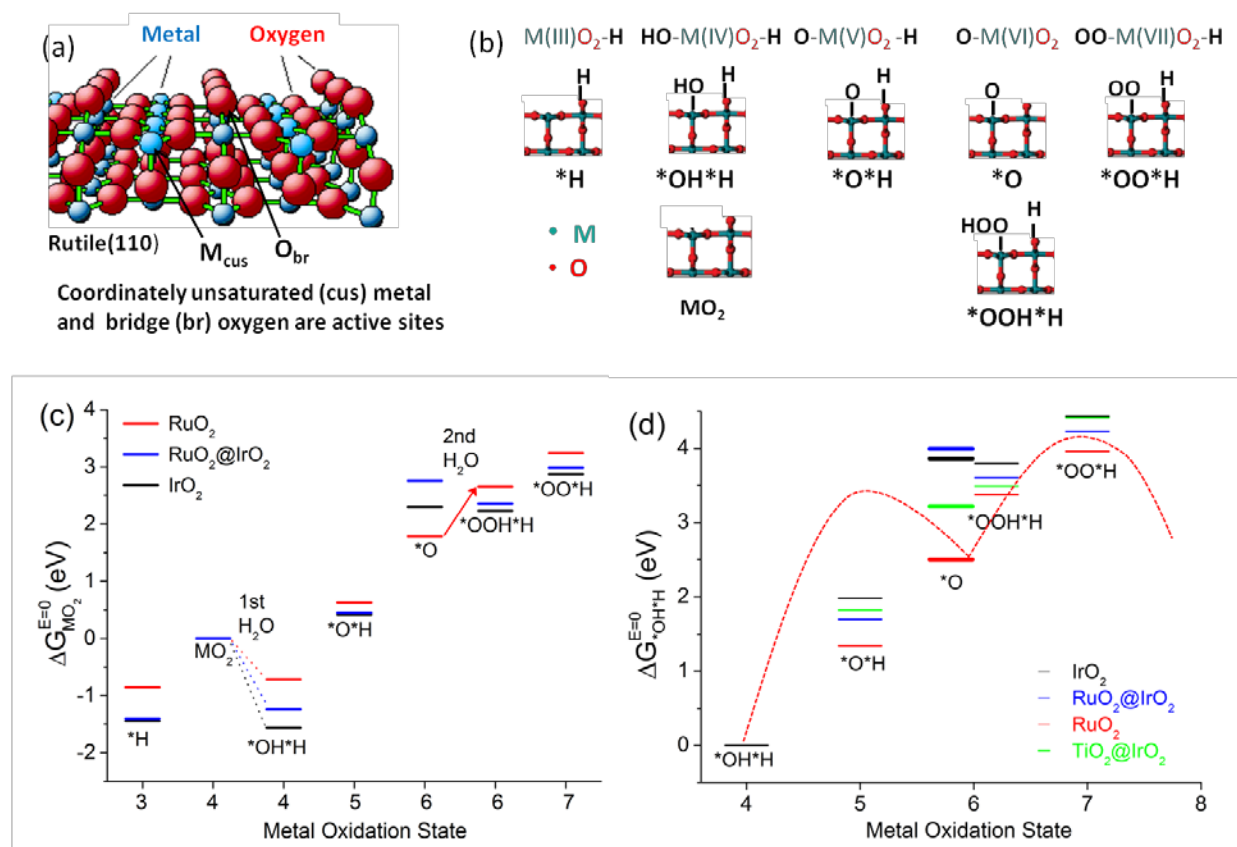
Spin-polarized DFT calculations were performed using the CASTEP code.[38,39] The generalized gradient approximation (GGA) [40] with the Perdew–Burke–Ernzerhof functional (PBE) [41] was used to describe the exchange and correlation potential. The cutoff energy for the plane-wave basis set was set at 380 eV in all calculations. The Monkhorst-Pack [42] mesh k-points ( $4 \times 4 \times 1$ ) were used for the slab calculations. To model the rutile IrO<sub>2</sub>(110), RuO<sub>2</sub>(110), and TiO<sub>2</sub>(110) surfaces, four O-Ru(Ir,Ti)-O trilayers with a ( $2 \times 2$ ) array in each layer were used, wherein the bottom two trilayers were fixed at the bulk position and the rest of the atoms were allowed to relax with the adsorbates. This setup is the same as used in the previous DFT calculations for the OER on metal oxides [33]. For the RuO<sub>2</sub>@IrO<sub>2</sub> and TiO<sub>2</sub>@IrO<sub>2</sub> catalysts, Ru and Ti, respectively, were replaced by Ir in the top layer of the oxide models. A vacuum gap of 15 Å in the z-direction was introduced to separate two subsequent slabs. The free energies for each reaction intermediate involved in the OER,  $\Delta G = \Delta E + \Delta ZPE - T\Delta S$ , were calculated based on the method reported previously [32]. It involves setting the reference potential to be that of the standard hydrogen electrode so that the chemical potential (the free energy per H) for (H<sup>+</sup> + e<sup>-</sup>) in solution can be related to that of ½ H<sub>2</sub> in gas phase. The entropies and zero point energies were from those given in the reference [32].

### 3. Theoretical Calculation

We employed DFT to calculate the free energies for the stable reaction intermediates involved in the OER on the rutile (110) metal dioxide surfaces (Fig. 1a), including RuO<sub>2</sub>(110), IrO<sub>2</sub>(110), and IrO<sub>2</sub> monolayer on RuO<sub>2</sub>(110) and TiO<sub>2</sub>(110). TiO<sub>2</sub> itself is rather inactive for the OER, but it is stable in acid. In addition, TiO<sub>2</sub> has larger, while RuO<sub>2</sub> has smaller, lattice constants than IrO<sub>2</sub> does. So the effects of these two oxide cores can show whether a lattice-mismatch-induced surface expansion or contraction is more beneficial in promoting the OER activity on the IrO<sub>2</sub> surface. Similar to Pt(111) being used to represent polycrystalline Pt and Pt nanoparticles in DFT calculations, we chose rutile (110) surface, like previous DFT studies [33,34,37], because it is the most stable facet of these dioxides. This approximation was made for studying material effect in the activity trend, and thus, our comparisons with experimentally derived free energies for nanocatalysts with multiple facets were not meant for absolute values, but for linear correlation in trend among the catalysts of different metal oxides on the surface and in the core.

The most stable adsorbates for each of the nominal metal oxidation states from 3 to 7 are identified as shown in Fig. 1b. In the short notations, the asterisk indicates the following species having a bond with the surface. Since the nominal oxidation state is the hypothetical charge for a surface metal atom assuming all bonds with different elements were 100% ionic, it is +4 for bare MO<sub>2</sub> and varies by adding 2 for each O atom and subtracting 1 for each H atom in the adsorbed species. Thus, proton desorption is oxidative as it leads to higher oxidation states, while water dissociative adsorption does not affect the nominal oxidation state because the effect of adding two H cancels out that of adding one O.

Using bare oxide surfaces and free water molecules as the zero energy references, the reaction free energies for forming these adsorbed phases at E = 0 V versus RHE are shown in Fig. 1c. The dotted lines leading to the \*OH\*H phase are all downward indicating that water dissociation is exothermic on the three oxides, which result in a \*OH on the coordinately unsaturated metal site (cus), M<sub>cus</sub> and an \*H on the bridge oxygen, O<sub>br</sub> (Fig. 1a). With a similar free energy as the \*OH\*H phase does, the \*H phase is expected to co-exist with the \*OH\*H below the oxygen reversible potential of 1.23 V. In simplification, earlier DFT study termed the surface being OH covered at potentials below the OER region [33].



**Figure 1.** (a) Atomic model of a rutile (110) metal dioxide surface. (b) Energetically favorable adsorbates from water dissociation and the OER in acid for each of the metal oxidation states from 3 to 7. (c,d) DFT-calculated reaction free energies at  $E = 0$  V vs. RHE with energy zero referenced to an adsorbates-free oxide surface labeled as  $\text{MO}_2$  in (c) and referenced to the  $\text{*OH*H}$  phase in (d). The red dotted curves in (d) schematically illustrate a kinetic model with two major steps for the OER on  $\text{RuO}_2$ .

For the OER at high potentials, oxidative deprotonation occurs preferably from the  $\text{*OH}$  group forming the  $\text{*O*H}$  phase, and then, from the  $\text{*H}$  on the  $\text{O}_{\text{br}}$  site forming the  $\text{*O}$  phases. With the  $\text{O}_{\text{br}}$  site freed by  $\text{*H}$  desorption, the second water dissociation can occur on the  $\text{*O}$  phase, forming  $\text{*OOH}$  on the  $\text{M}_{\text{cus}}$  and  $\text{*H}$  on the  $\text{O}_{\text{br}}$  sites. This reaction is endothermic on  $\text{RuO}_2$  (upward red arrow), while it remains exothermic for the  $\text{RuO}_2@ \text{IrO}_2$  and  $\text{IrO}_2$ . Before  $\text{O}_2$  evolution, a proton firstly desorbs from the  $\text{*OOH}$  group to form the  $\text{*OO*H}$  phase. For  $\text{RuO}_2@ \text{IrO}_2$  and  $\text{IrO}_2$ , the exothermic water dissociation on O adsorbed metal site results in a facile formation of the O-O bond on single metal site, and thus, clearly supports the sequential pathway. The endothermic water dissociation on O-adsorbed  $\text{RuO}_2$  questions on whether forming the O-O bond via coupling two  $\text{*O}$  could have lower activation barrier. As found by a

previous DFT study, the barrier is higher for coupling two adsorbed O than for the sequential pathway on RuO<sub>2</sub> [37].

To describe the OER kinetics, we plotted the reaction free energies in Fig. 1d using the \*OH\*H phase to set energy zero reference because this is the dominant phase at the oxygen reversible potential with the lowest energy state. The \*O phase plays a central role as it is the precursor for the O-O bond formation. As shown by the thick bars, the reaction free energies for the \*O phase, which are higher in the order of RuO<sub>2</sub> (2.50 eV) < TiO<sub>2</sub>@IrO<sub>2</sub> (3.22 eV) < IrO<sub>2</sub> (3.86 eV) < RuO<sub>2</sub>@IrO<sub>2</sub> (4.00 eV), indicating a weakening of O adsorption. The particularly strong O adsorption on RuO<sub>2</sub> results from a large structural distortion of the more flexible RuO<sub>2</sub> surface as compared to other surfaces. Compared to bulk IrO<sub>2</sub>, the O adsorption on the IrO<sub>2</sub> monolayer is weakened by a RuO<sub>2</sub> substrate, while it is strengthened by TiO<sub>2</sub>. These effects are understandable based on lattice-mismatch-induced contraction and expansion. Relative to the two in-plane lattice constants for Ir-O and Ir-Ir, those for Ru-O and Ru-Ru are smaller by -0.44% and -0.67%, respectively, and larger by 1.86% for Ti-O and 0.38% for Ti-Ti.[43] The results provide a case of lattice-mismatch effects on adsorption energies for oxides, similar to the well-known cases for metal surfaces, which were utilized for enhancing the activities of fuel cell catalysts for HOR [9] and ORR [44,45].

In identifying the rate-limiting step and predicting the relative activities of the four oxide surfaces, we calculated the energy gaps for the reactions leading to the nominal oxidation state of 5, 6, and 7, i.e., the \*O\*H phase, the \*O or \*OOH\*H phase (whichever is lower in energy), and the \*OO\*H phase. Choosing the lower of the two, rather than always taking the free energy for \*O and ignoring that for \*OOH\*H, appears more reasonable because the intermediate with lower energy should have higher coverage, and thus, plays a more important role in determining reaction kinetics. The largest energy gaps among the three reactions for each of the catalysts are 1.46 (\*OO\*H, RuO<sub>2</sub>) < 1.83 (\*O\*H, TiO<sub>2</sub>@IrO<sub>2</sub>) < 1.91 (\*OOH\*H, RuO<sub>2</sub>@IrO<sub>2</sub>) < 1.98 (\*O\*H, IrO<sub>2</sub>) eV. The higher is a barrier for the rate-limiting step, the lower OER activity of the catalyst. Thus, the DFT calculations found the OER activity decreasing in the order of RuO<sub>2</sub> > TiO<sub>2</sub>@IrO<sub>2</sub> > RuO<sub>2</sub>@IrO<sub>2</sub> > IrO<sub>2</sub>. All three IrO<sub>2</sub>-based catalysts have the rate-limiting step in either the first or second deprotonation process toward the formation of the \*O phase, while the

reaction rate on RuO<sub>2</sub> is limited by the formation of \*OO\*H that involves an endothermic water dissociation on the \*O phase in forming the O-O bond followed by deprotonation.

Detailed in Section 5, the theoretical results on the activity trend and rate-limiting steps are consistent with the conclusions based on kinetic analysis of measured polarization curves using a simplified kinetic model that involves \*O as the single reaction intermediate and two major reaction steps. As schematically illustrated by the red dotted curves in Fig. 1d, using RuO<sub>2</sub> as an example, the first step leads to the formation of \*O phase and the second step results in its removal via O<sub>2</sub> formation and desorption from the catalysts' surface.

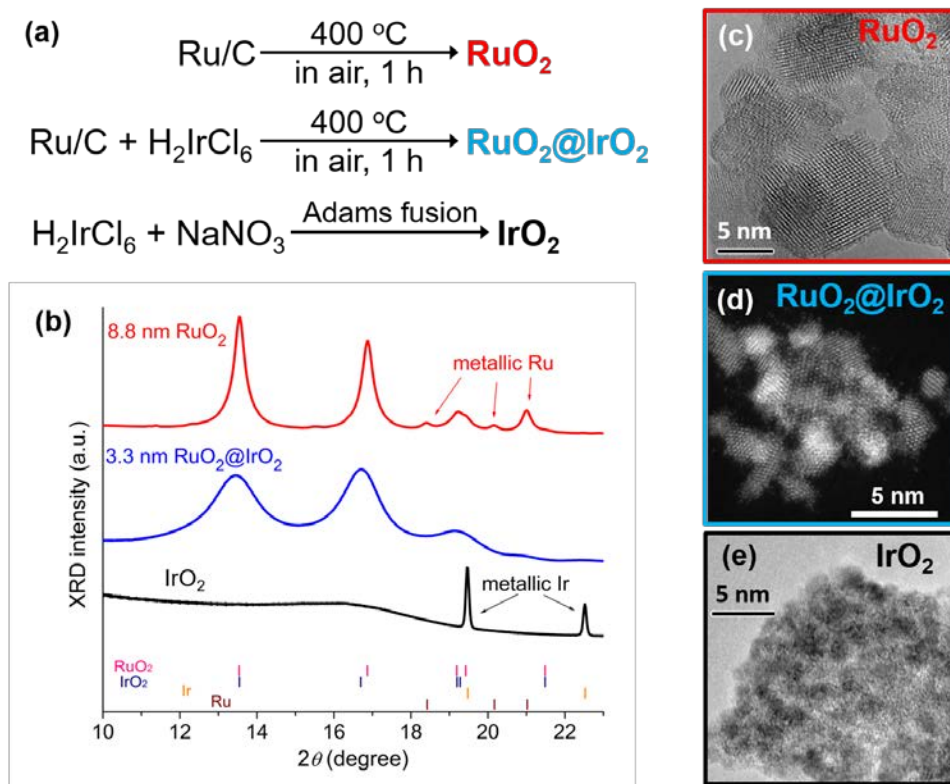
## 4. Results

### 4.1. Catalyst synthesis and structural characterization

Figure 2 shows the synthesis methods, X-ray diffraction profiles, and the TEM images for the RuO<sub>2</sub> and RuO<sub>2</sub>@IrO<sub>2</sub> (Ir:Ru atomic ratio 1.17:1.0 or 0.54:0.46) nanocatalysts we prepared in comparison with those for the commercial IrO<sub>2</sub> nanocatalyst used in PEM water electrolyzers. The Adams fusion method used in commercial production of unsupported IrO<sub>2</sub> catalyst involves mixing the H<sub>2</sub>IrCl<sub>6</sub> precursor with NaNO<sub>3</sub>, heating the dried mixture in air at 350 - 500 °C for 0.5 - 2 h, and washing off remaining salts (NaNO<sub>3</sub> and NaCl) [46,47]. The produced IrO<sub>2</sub> catalysts usually contain aggregates of small, amorphous IrO<sub>2</sub> nanoparticles as shown by the TEM image in Fig. 2e. A few large metallic Ir particles may coexist as indicated by the sharp XRD spikes (black line in Fig. 2b). We take this IrO<sub>2</sub> sample as the baseline reference for performance comparison because the catalyst is industrial standard for PEM water electrolyzers and it exhibits the typical characteristics of IrO<sub>2</sub> in voltammetry and polarization measurements [23,48].

We prepared RuO<sub>2</sub> and RuO<sub>2</sub>@IrO<sub>2</sub> nanocatalysts using well-dispersed Ru nanoparticles on a carbon support (Ru/C) as the precursor of RuO<sub>2</sub>, and using H<sub>2</sub>IrCl<sub>6</sub> as the precursor of IrO<sub>2</sub> shell (Fig. 2a). The carbon support as a template in the Ru/C (20 or 40 wt%) was burnt off during calcinations at temperatures between 350 and 450 °C in air, yielding unsupported metal dioxide nanoparticles as ready-to-use OER catalysts. In Table S1, we list the weights of samples made with different Ru/C ratios and at different calcining temperatures. All but one that was made with 10 wt% Ru/C weigh as expected for unsupported metal dioxides (within 5% of the values

calculated from the amount of metals in the precursors). It appears that Ru nanoparticles catalyze carbon combustion, and thus, a higher Ru weight percentage on a carbon support facilitates the complete elimination of carbon. The catalytic effect of Ru in removing carbon is supported by the findings in a study of preparing Pt-RuO<sub>2</sub>/C catalysts [49], in which the weight loss from a Pt-RuO<sub>2</sub>/C sample started around 350 °C while the carbon-only sample showed a weight loss above 500 °C.



**Figure 2.** (a) Synthetic schemes. (b) Synchrotron XRD profiles of the RuO<sub>2</sub> (red), RuO<sub>2</sub>@IrO<sub>2</sub> (blue), and IrO<sub>2</sub> (black) catalysts with the reference peak positions marked by the bars.  $\lambda = 0.75009 \text{ \AA}$ . Particle sizes are determined using the Scherrer equation. (c) TEM image of RuO<sub>2</sub>. (d) STEM image of RuO<sub>2</sub>@IrO<sub>2</sub> particles. (e) TEM image of a commercial IrO<sub>2</sub> catalyst.

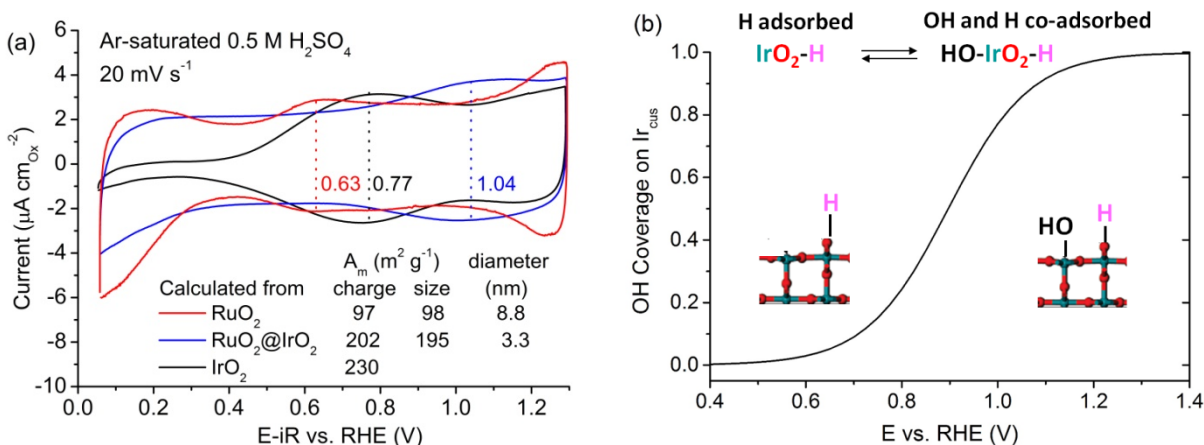
The synchrotron XRD profiles for a RuO<sub>2</sub> sample made with 40 wt% Ru/C and a RuO<sub>2</sub>@IrO<sub>2</sub> sample made using 20 wt% Ru/C with H<sub>2</sub>IrCl<sub>6</sub> (Fig. 2b) exhibit the major XRD peaks at the positions for RuO<sub>2</sub> and IrO<sub>2</sub> rutile structures (space group P4<sub>2</sub>/mnm). The average sizes of the particles are 8.8 and 3.3 nm, respectively, consistent with the TEM images shown in Figs. 1c and 1d. They differ, partly due to the larger Ru particles in the 40 wt% than those in the 20 wt% Ru/C used as the starting materials, and partly because Ir diffuses more slowly than Ru

does, which likely facilitated the formation of smaller RuO<sub>2</sub>@IrO<sub>2</sub> particles. Suggested by the weak XRD peaks at the metallic Ru positions for the 8.8 nm RuO<sub>2</sub> particles, the inner core of the Ru particles may not be as fully oxidized as the 3.3 nm RuO<sub>2</sub>@IrO<sub>2</sub> particles. With an Ir/Ru atomic ratio of 1.17/1, the thickness of IrO<sub>2</sub> is close to one monolayer for 3.3 nm particles when the distribution is uniform. Quantifying the degree of core-shell structure was difficult because rather weak intensity contrast was expected in STEM-HAADF and EELS measurements to distinguish a monolayer shell on small nanoparticles. Indirectly, we show, in the next section, that the RuO<sub>2</sub>@IrO<sub>2</sub> sample exhibited distinct voltammetry feature suggesting the core-shell nanoparticles being dominant.

#### 4.2. Voltammetry curves and oxide surface area

The typical voltammetry curves for the RuO<sub>2</sub>, RuO<sub>2</sub>@IrO<sub>2</sub>, and IrO<sub>2</sub> nanocatalysts in acid are shown in Fig. 3a with the current normalized to the oxide surface area. The rather high, near constant currents between 0.4 and 1.23 V distinctly differ from the voltammetry curves on Pt and Au metal surfaces, in which a low current region is free of chemically adsorbed species. This is because water dissociation is exotic on the oxide surfaces, while H and OH adsorption on noble metals occurs only at sufficiently low and high potentials, respectively. Using IrO<sub>2</sub> as an example, we show schematically in Fig. 3b that the dissociative water adsorption leads to an OH and H co-adsorbed phase (HO-IrO<sub>2</sub>-H) that likely dominates near 1.23 V; lowering the potential causes a gradual loss of the OH from the unsaturated metal sites, M<sub>cus</sub>, while the bridge oxygen sites, O<sub>br</sub>, remain covered by H (Fig. 1a). This simplified surface phase diagram is based on the comparable free energies for the \*H and \*OH\*H phases at low potentials and the general trend of higher coverage of more oxygenated phase at higher potentials. Recently, a Pourbaix diagram for the IrO<sub>2</sub> (110) surface was constructed theoretically using machine learning to handle a large number of possible adsorption configurations [50]. The essential feature presented in the abstract is that the \*H phase is the most stable at low potentials, followed by a \*OH and \*H mixed phase, and then the \*OH phase with increasing potential. That is consistent with our estimated phase diagram presented in terms of coverage at the potentials below the potential for the \*OH dominant phase. Below 0.4 V, the voltammetry behavior is not well understood. For RuO<sub>2</sub>, an experimental study suggested the formation of Ru(II) phase at 0.4 V [51]. However, the surface phase diagram constructed from DFT calculations only confirmed the phases with Ru oxidation

state above (III) [52]. We exclude the region below 0.4 V in the following comparison of the catalysts.



**Figure 3.** (a) Voltammetry curves with current normalized to the oxide surface areas estimated from the charge integrated between 0.4 and 1.23 V, which was obtained by averaging the absolute charges in the positive and negative potential sweeps. The specific areas ( $A_m$ ) calculated from charge-deduced area and particle-size-dependent area are given with the average diameter of the nanoparticles. The metal oxide loadings were the same as those given in Fig. 4a. (b) Schematic illustration of the reversible Ir(III)/Ir(IV) redox reaction on the IrO<sub>2</sub> rutile (110) surface in acid, which involves OH adsorption/desorption on the Ir surface sites while H adsorbs on the bridge O site over the whole potential region. Green dots are Ir and red dots are oxygen in the IrO<sub>2</sub> surface model.

A catalyst-specific voltammetry feature is the potential for a pair of broad, nearly reversible current peaks as marked by the dotted vertical lines in Fig. 3a, which increases in the order of RuO<sub>2</sub> (0.63 V) < IrO<sub>2</sub> (0.77 V) < RuO<sub>2</sub>@IrO<sub>2</sub> (1.04 V), indicating the surface phase transition from \*H to \*OH\*H or metal surface oxidation from (III) to (IV) is increasingly more difficult in that order. The fact that the RuO<sub>2</sub>@IrO<sub>2</sub> is not in the middle between RuO<sub>2</sub> and IrO<sub>2</sub> signifies a surface property of core-shell nanoparticles because one cannot generate such a feature by mixing RuO<sub>2</sub> and IrO<sub>2</sub> particles. In addition, near the high potential limit at 1.23 V, the current rises most on RuO<sub>2</sub>, signaling the onset of \*OH phase formation on RuO<sub>2</sub>. The absence of this feature for the RuO<sub>2</sub>@IrO<sub>2</sub> sample indicates that majority RuO<sub>2</sub> cores were covered by IrO<sub>2</sub> shells. In contrast, the voltammetry curve for Ru-Ir mixed oxide is similar to the average of the curves for RuO<sub>2</sub> and IrO<sub>2</sub> [53].

For estimation of mass-normalized oxide surface area,  $A_m$ , we used two methods. The results are consistent as given in Fig. 3a. One method estimates the surface area from the

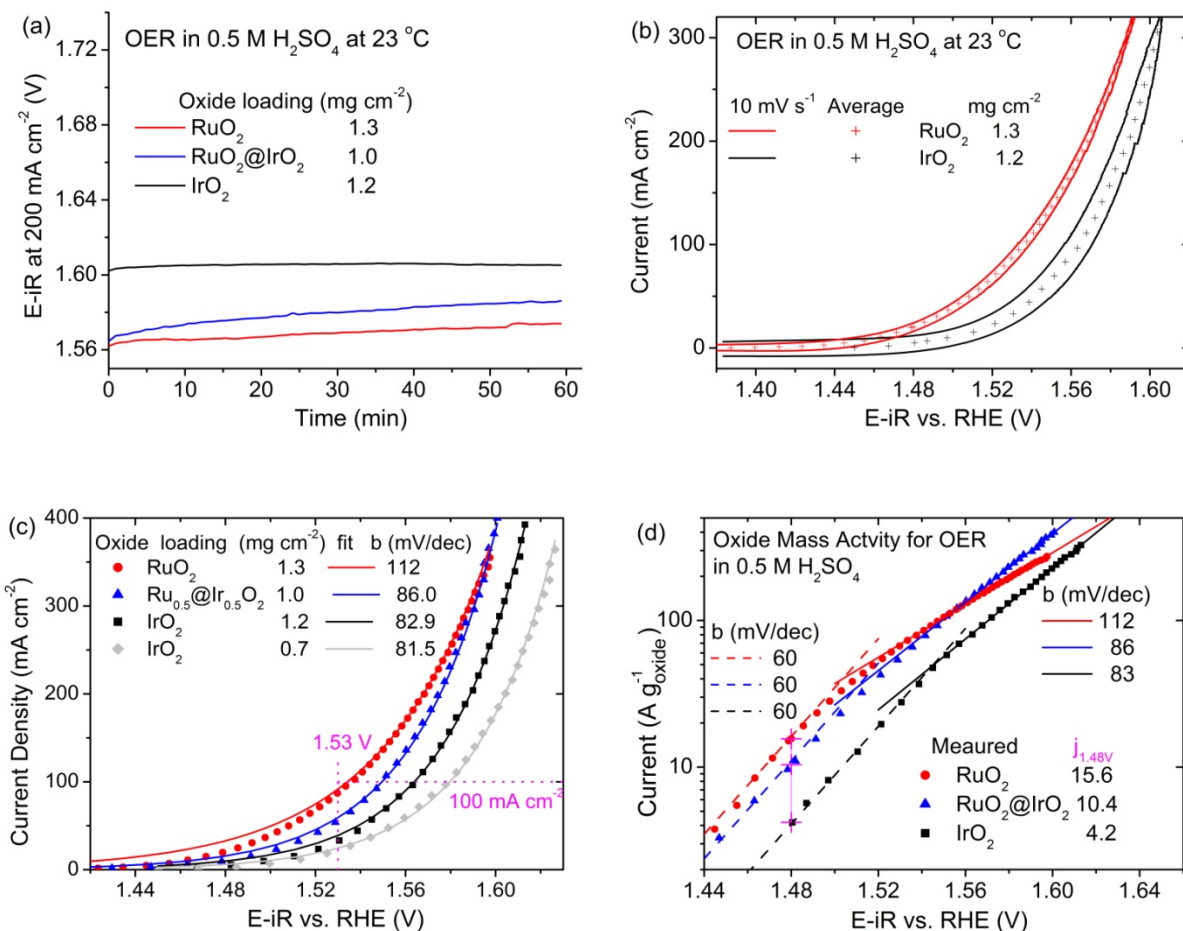
integrated charges of the voltammetry curves between 0.4 and 1.23 V, using a charge density of  $0.10 \text{ mC cm}^{-2}$ . This value is based on the atomic density of the surface metal atoms and the assumption of a  $1e/\text{metal-atom}$  redox reaction. The values for the rutile (110) and (100) facets are listed in Table S2. For nanoparticles with both facets, the averaged charges for  $1e/\text{metal-atom}$  redox were about the same  $0.10 \text{ mC cm}^{-2}$  for  $\text{IrO}_2$  and  $\text{RuO}_2$ . This value is about half of the commonly used charge density of  $0.21 \text{ mC cm}^{-2}$  for polycrystalline Pt because metallic Pt has a facet-averaged atomic density about twice of those for  $\text{IrO}_2$  and  $\text{RuO}_2$  (Table S3). Based on the same  $1e/\text{metal-atom}$  assumption, a study using the (110) and (100) surfaces of rutile  $\text{RuO}_2$  and  $\text{IrO}_2$  showed that the atomic densities estimated from the charges integrated between 0.3 to 1.25 V are higher by 12% to 21% than the values calculated from the lattice constants [48]. Better agreements would be obtained using a smaller potential range, supporting the choice of potential range from 0.4 and 1.23 V.

Independent of voltammetry measurements, we estimated the surface area per oxide mass based on the particle-size-dependent geometric areas using  $A_m = \text{area} / (\text{volume} \times \text{density}) = 6 / (d \times \rho)$  where  $d$  is the diameter of the spherical particles and  $\rho$  is the density of the dioxides (detailed in Table S4). The values for the  $\text{RuO}_2$  and  $\text{RuO}_2@/\text{IrO}_2$  samples are consistent with those obtained from measured charges as listed in Fig. 3a.

#### *4.3. Steady-state OER polarization and oxide-mass activities*

In the OER polarization measurements, we used high oxide loadings ( $\sim 1 \text{ mg cm}^{-2}$ ) on Ti gas diffusion electrodes and strong acidic electrolyte ( $0.5 \text{ M H}_2\text{SO}_4$ ) to be close to the high-current conditions in PEM water electrolyzers. Figure 4 shows the results using  $1 \text{ cm}^2$  electrode surface area with the OER currents up to 400 mA. Oxygen bubbling at high currents sometimes knocks off catalyst particles causing a sudden change of measured current or voltage. To obtain reliable steady-state polarization curves, we first ran 1 h chrono-potentiometry at  $200 \text{ mA cm}^{-2}$  to ensure at least the particles survived were well attached on the electrode in the following measurements. Figure 4a shows the voltages measured for the three catalysts were all stabilized near the end of 1 h. After impedance measurement that determined the high frequency resistance (HFR), the OER polarization curves were obtained by averaging the currents in the positive and negative potential sweeps (Fig. 4b), and correcting the uncompensated ohmic loss in potential using the

measured HFR. Averaged currents represent the steady-state reaction rates when coverage of the intermediates reaches equilibrium.



**Figure 4.** (a) Chronopotentiometry for OER at 200 mA cm<sup>-2</sup> for three oxide nanocatalysts on Ti gas diffusion electrodes in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution. (b) OER currents in positive and negative sweeps (lines) and the averaging currents (+ signs). (c) Steady-state OER polarization curves (symbols) measured after 1 h chronopotentiometry with the best fits (solid lines) using the Butler-Volmer equation with a constant Tafel slope, *b*, which reproduced the data above 1.53 V. (d) Oxide-mass-normalized polarization curves with the Tafel lines and marked mass activities at 1.48 V.

Figure 4c compares the measured polarization curves (symbols) for the RuO<sub>2</sub>, IrO<sub>2</sub>, and RuO<sub>2</sub>@IrO<sub>2</sub> catalysts. The solid lines are the best fits using the Butler-Volmer equation,  $j = j_0 e^{2.303(E-1.23)/b}$ , where  $j_0$  is the exchange current and  $b$  is the Tafel slope. The data at potentials above 1.53 V were well reproduced in all four curves by the fits using a constant Tafel slope. The fitted Tafel slopes were reproduced by samples with different catalysts' loadings, as

illustrated by the two IrO<sub>2</sub> samples. Figure 4d shows the mass-normalized current on logarithmic scale for the three catalysts. While the Tafel slopes are all about 60 mV/dec at low overpotentials, the characteristic high-overpotential Tafel slopes are considerably smaller for RuO<sub>2</sub>@IrO<sub>2</sub> (86 mV/dec) and IrO<sub>2</sub> (83 mV/dec) than for RuO<sub>2</sub> (112 mV/dec). At 1.48 V (0.25 V overpotential), the oxide mass activity of ~3 nm RuO<sub>2</sub>@IrO<sub>2</sub> (10.4 g<sup>-1</sup><sub>ox</sub>) is 2.5 times of that for the ~2 nm IrO<sub>2</sub> (4.2 A g<sup>-1</sup><sub>ox</sub>), and is 33% lower than ~9 nm RuO<sub>2</sub> (15.6 A g<sup>-1</sup><sub>ox</sub>). To gain insight on reaction mechanism, we show in next section, the analysis of surface-area-normalized polarization curves.

#### 4.4. OER specific activity and kinetic analysis

Based on the surface areas determined in Section 4.2, we plot the surface-area-normalized polarization curves in Fig. 5a, representing the OER specific activities for the three oxide catalysts. At 1.48 V, the OER specific activities of the IrO<sub>2</sub> (1.7 μA cm<sup>-2</sup><sub>ox</sub>) and the RuO<sub>2</sub> (16 μA cm<sup>-2</sup><sub>ox</sub>) samples are comparable with the values of 2 and 10 μA cm<sup>-2</sup><sub>ox</sub>, respectively, measured on rotating disk electrodes [23]. Also, the shapes of the curves are in the same trend with the Tafel slopes at high potentials being larger for RuO<sub>2</sub> than for IrO<sub>2</sub> [23]. The RuO<sub>2</sub>@IrO<sub>2</sub> (5.5 μA cm<sup>-2</sup><sub>ox</sub>) sample exhibited threefold specific activity and similar Tafel slope as compared with the IrO<sub>2</sub>.

Fitting or simulating polarization curves were commonly carried out using equations with the adsorption isotherms of reaction intermediates being derived based on the steady-state principle [54–58]. For the OER, kinetic equations involving \*OH and \*O as the reaction intermediates were derived with reaction rates and equilibrium constants as the kinetic parameters [55,58]. The results demonstrated a variety of possible Tafel slopes [58] and the ability to simulate measured OER polarization curve for IrO<sub>2</sub> [55]. However, the reaction rate and equilibrium constants for multiple reaction intermediates were not determined from fitting measured polarization curves. To facilitate comparison with DFT calculations, we derived here the OER kinetic equation using activation and adsorption free energies as the kinetic parameters. A simple kinetic model is adapted to minimize the number of parameters, which considers the sequential water dissociation pathway in two major reaction steps and one major adsorbed intermediate, O<sub>ad</sub>:



Compared to the DFT calculations, the first step here includes the elementary reactions of water dissociation on oxide surface and oxidative deprotonation to \*O\*H and \*O; the second step involves water dissociative adsorption of another O in forming \*OOH, deprotonation, and O<sub>2</sub> evolution.

Following the conventions detailed in our previous derivation of the dual-pathway kinetic equation for the HER-HOR [9,56], and the double-trap kinetic equation for the ORR [57], the currents for first and second reactions in the forward (+) and backward (-) directions can be written as

$$j_1 = j_{+1} - j_{-1} = j^* e^{-\Delta G_{+1}/kT} (1 - \theta) - j^* e^{-\Delta G_{-1}/kT} \theta \quad (3)$$

$$j_2 = j_{+2} - j_{-2} = j^* e^{-\Delta G_{+2}/kT} \theta - j^* e^{-\Delta G_{-2}/kT} (1 - \theta) \quad (4)$$

where  $j^* = 1000 \text{ A cm}^{-2}$  is a fixed reference pre-factor [56],  $kT = 25.51 \text{ meV}$  at  $23 \text{ }^\circ\text{C}$ ,  $\theta$  is the fractional coverage of the reaction intermediate,  $\text{O}_{\text{ad}}$ , and  $\Delta G_i$  is the activation free energy for the reaction labeled by the subscript  $i$ . The activation free energies vary with the overpotential  $\eta = E_{\text{RHE}} - E^0$ , where  $E^0$  is the oxygen reversible potential, as given below:

$$\Delta G_{+1} = \Delta G_1^0 - \alpha_1 e \eta \quad (5)$$

$$\Delta G_{-1} = \Delta G_1^0 - \Delta G_{\text{ad}}^0 + (1 - \alpha_1) e \eta \quad (6)$$

$$\Delta G_{+2} = \Delta G_2^0 - \Delta G_{\text{ad}}^0 - \alpha_2 e \eta \quad (7)$$

$$\Delta G_{-2} = \Delta G_2^0 + (1 - \alpha_2) e \eta \quad (8)$$

In which,  $\alpha$  is the transfer coefficient, superscript <sup>0</sup> means at zero overpotential relative to  $E^0$ . Here, we define the standard activation free energies  $\Delta G_1^0 \equiv \Delta G_{+1}(\eta = 0)$ ,  $\Delta G_2^0 \equiv \Delta G_{-2}(\eta = 0)$ , and the standard adsorption free energy  $\Delta G_{\text{ad}}^0 \equiv -\ln(\theta^0 / (1 - \theta^0))$  as the independent

parameters. Figure S1 illustrates the relationship among the activation barriers for the two reactions in two directions, and the three independent free energy parameters.

Based on the steady-state principle, the total kinetic current,  $j_k$ , and the coverage of the intermediate,  $\theta$ , are invariant with time at any potential, so that the net reaction rate of the first reaction that adds  $O_{ad}$  on the surface must equal the net reaction rate of the second reaction that removes  $O_{ad}$  from the surface. Therefore, we have  $j_1 = j_2$  and thus the kinetic equation can be expressed using either  $j_1$  or  $j_2$ .

$$j_k = j^* e^{-\Delta G_{+1}/kT} (1 - \theta) - j^* e^{-\Delta G_{-1}/kT} \theta = j^* e^{-\Delta G_{+2}/kT} \theta - j^* e^{-\Delta G_{-2}/kT} (1 - \theta) \quad (9)$$

Rearranging this steady-state equation gives us the adsorption isotherm expressed as a fractional coverage of the OER intermediate,

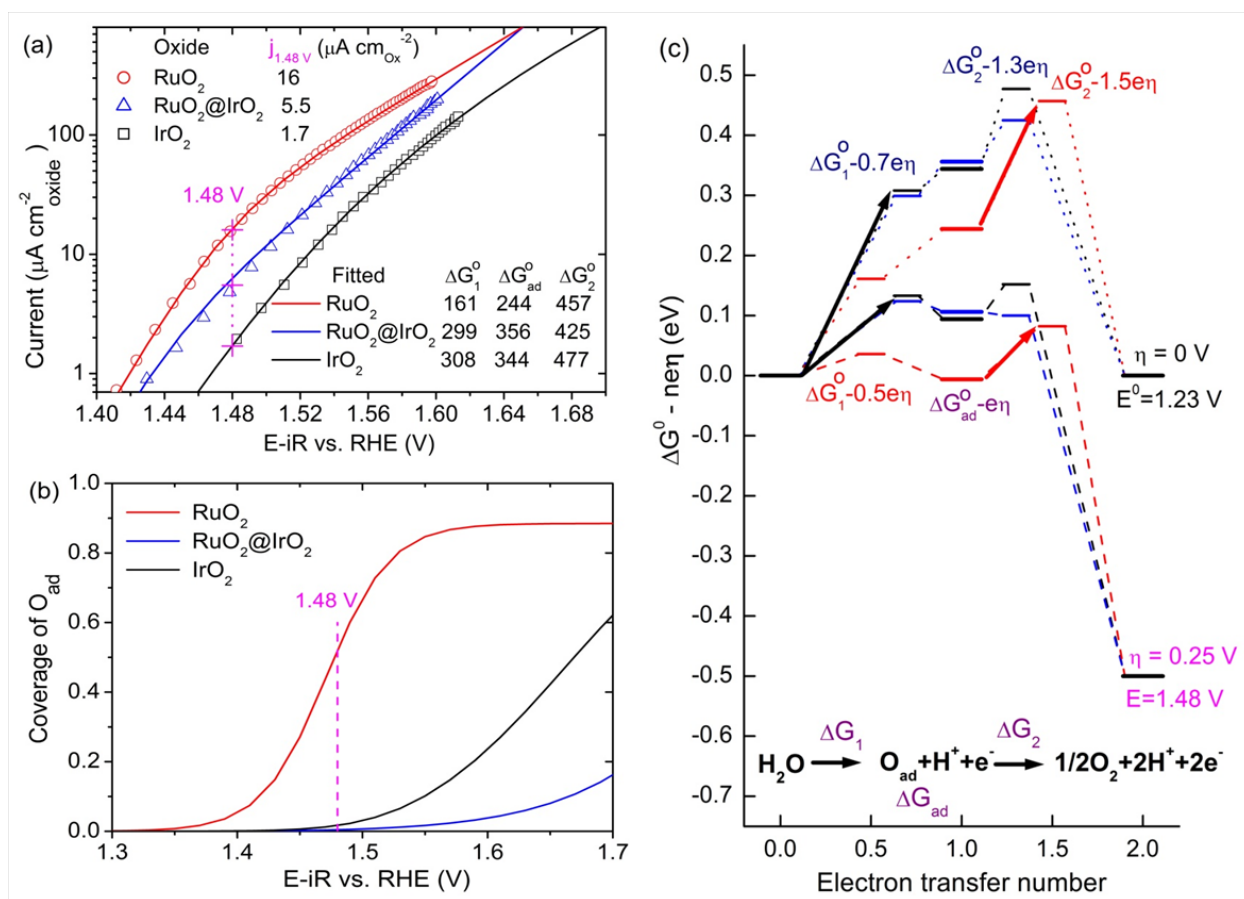
$$\theta = \frac{g_{+1} + g_{-2}}{g_{+1} + g_{-1} + g_{+2} + g_{-2}} \quad (10)$$

where  $g_i = e^{-\Delta G_i/kT}$  with  $\Delta G_i$  given in Eqs. 5-7.

In fitting the measured polarization curves in Fig. 5a using above derived kinetic equation, we allowed the two activation free energies  $\Delta G_1^0$  and  $\Delta G_2^0$  to vary during fitting with fixed  $\alpha_1$ ,  $\alpha_2$  and  $\Delta G_{ad}^0$  values, and reset the fixed parameters for each run. As shown by the solid lines in Fig. 6a, the entire polarization curves were well reproduced by the best fits. The transfer coefficients need to be  $\alpha_1 = \alpha_2 = 0.5$  for the  $RuO_2$  and  $\alpha_1 = 0.7$  and  $\alpha_2 = 0.3$  for the  $IrO_2$  and  $RuO_2@IrO_2$ . Good fits can be obtained with a range of  $\Delta G_{ad}^0$  values with adjusted  $\Delta G_1^0$  and  $\Delta G_2^0$ . The uniqueness of the best fits would increase if experimentally determined adsorption isotherms  $\theta(E)$  were also available for fitting. We report here the sets of parameters for the three catalysts obtained with  $\Delta G_{ad}^0$  at the low end of the range (listed in Fig. 5a).

Using the fitted parameters, we show in Fig. 5b the corresponding adsorption isotherms,  $\theta(E)$ , and in Fig. 5c the OER free energy diagrams at 0 V (dashed lines) and 0.25 V (dotted lines) overpotentials. The fractional coverage of  $O_{ad}$  is closely correlated to the O adsorption free energy. The high  $\Delta G_{ad}^0$  for all three oxide surfaces prohibit the formation of  $O_{ad}$  phase, and thus,

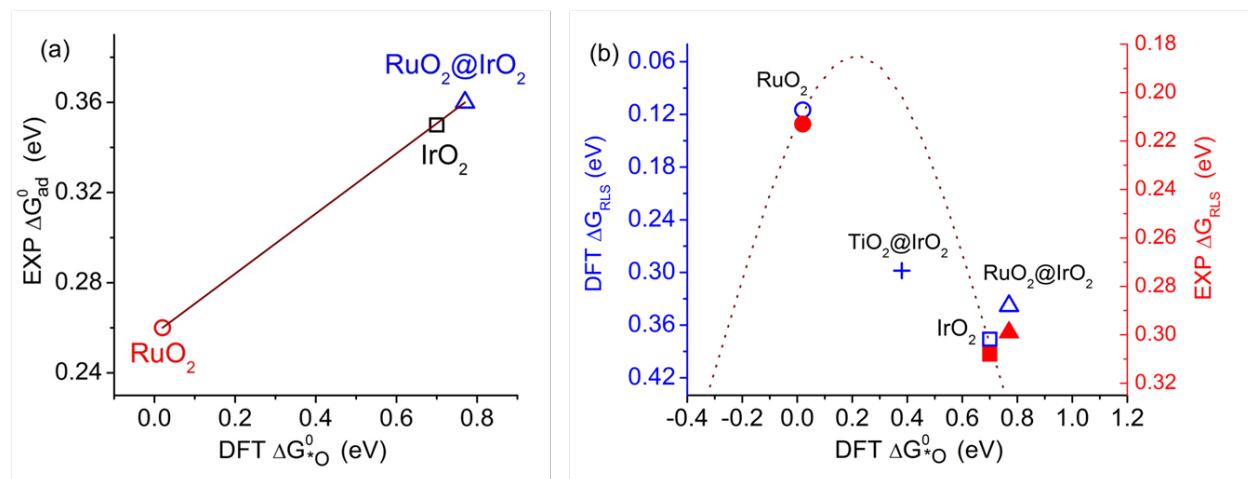
any OER activity at 1.23 V. At 1.48 V (or 0.25 V overpotential), the fractional coverage of  $O_{ad}$  on the  $RuO_2$  surface rises to about 0.5 when its  $\Delta G_{ad}$  ( $= \Delta G_{ad}^0 - 0.25$  eV) is lowered to near 0. The  $\Delta G_{ad}^0$  values are considerably higher for  $IrO_2$  and  $RuO_2@IrO_2$ , so the  $O_{ad}$  coverage rises more gradually. The rate-limiting steps are identified by the highest barriers. For the  $IrO_2$  and  $RuO_2@IrO_2$ ,  $\Delta G_1^0$  is larger than  $\Delta G_2^0 - \Delta G_{ad}^0$ . Thus, the formation of the  $O_{ad}$  phase is the rate-limiting step (black arrows). In contrast,  $\Delta G_1^0$  is smaller than  $\Delta G_2^0 - \Delta G_{ad}^0$  for  $RuO_2$ , so the reaction rate is limited by the second step (red arrows) involving the O-O bond formation before  $O_{ad}$  desorbs from the surface.



**Figure 5.** (a) Surface-area-normalized polarization curves (symbols) obtained using the same metal oxide loadings as in Fig. 4a and the best fits (lines) using the sequential OER kinetic equation. The fitted kinetic parameters are the standard free energies given in unit of meV. (b) Adsorption isotherm for the OER intermediate  $O_{ad}$  calculated, and (c) OER free energy diagrams at 0 and 0.25 V overpotentials constructed, using the standard free energies listed in (a). Color schemes:  $RuO_2$  (red),  $RuO_2@IrO_2$  (blue), and  $IrO_2$  (black).

## 5. Discussion

Comparisons of experimental and theoretical results are shown in Fig. 6. For the three oxide catalysts, Fig. 6a shows the experimental  $\Delta G_{ad}^0$  (zero is defined at the oxygen reversible potential,  $E = 1.23$  V vs. RHE, for  $\text{H}_2\text{O} = 1/2\text{O}_2 + 2\text{H}^+ + 2\text{e}^-$ ) versus the DFT-calculated  $\Delta G_{*O}^0$ , which equals  $\Delta G_{*O} / 2 - 1.23$  eV, where  $\Delta G_{*O}$  is the reaction free energy (shown by the thick bars in Fig. 1d) calculated for  $2\text{H}_2\text{O} = \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$  (thus dividing by 2) at  $E = 0$  ( $1\text{e} \times 1.23$  V = 1.23 eV). A linear relationship is demonstrated for the three oxide catalysts, which supports the use of  $\Delta G_{*O}^0$  (or  $\Delta G_{*O}$ ) as the descriptor for the OER activities of the oxide catalysts.



**Figure 6.** (a) Linear relationship between experimental and theoretical adsorption free energies at oxygen reversible potential ( $\eta = 0$  V,  $E = 1.23$  V). (b) Comparison of activation barriers for the rate-limiting step obtained from DFT calculations (blue symbols, left axis) and kinetic analyses (red solid symbols, right axis).

In Fig. 6b, we plot the activation barrier for the rate-limiting step (open symbols in blue, left axis) based on DFT-calculated reaction free energies in comparison with the values derived experimentally (solid symbols in red, right axis). The conversion of the DFT barriers for the rate-limiting steps (1.46, 1.83, 1.91, and 1.98 eV discussed in Section 3) involves dividing by 2 (the reaction formula used in kinetic analysis and DFT calculation differ by a factor 2) and subtracting 0.625 eV (a transfer coefficient of 0.5 with a potential shift of 1.23 V). We plot the lower activation barriers upward in Fig. 6b as they represent higher activities. The relative activities of RuO<sub>2</sub>, IrO<sub>2</sub> and RuO<sub>2</sub>@IrO<sub>2</sub> estimated by the DFT calculations (blue open symbols)

are consistent with the trend determined experimentally (red solid symbols). Based on the rate-limiting step being after and before the formation of \*O for RuO<sub>2</sub> and IrO<sub>2</sub>, respectively, a volcano curve (dotted line) is drawn, having RuO<sub>2</sub> on the left side of the optimal  $\Delta G_{*O}^0$  and the IrO<sub>2</sub> on the right side. Both TiO<sub>2</sub>@IrO<sub>2</sub> and RuO<sub>2</sub>@IrO<sub>2</sub> are on the right side, consistent with their rate-limiting step being the same as that of IrO<sub>2</sub>.

Relative to IrO<sub>2</sub>,  $\Delta G_{*O}^0$  increases on the IrO<sub>2</sub> shell with a RuO<sub>2</sub> core and decreases with a TiO<sub>2</sub> core. The effects can be explained by the general trend of core-induced surface contraction and expansion, respectively, since the lattice constants are in the order of RuO<sub>2</sub> < IrO<sub>2</sub> < TiO<sub>2</sub>. For the activation barrier of the rate-limiting step along the y-axis, however, the calculated values (blue plus and triangle) are not exactly on the volcano curve. As the experimental result is consistent with the calculated barrier for the RuO<sub>2</sub>@IrO<sub>2</sub> core-shell catalyst, we can consider the volcano curve as a main trend, and use the calculated barriers as detailed prediction and guidance in designing and optimizing oxide core-shell nanocatalysts. Interestingly, the activation barrier for the rate-limiting step for the TiO<sub>2</sub>@IrO<sub>2</sub> (blue plus in Fig. 6b) was found lower than those for IrO<sub>2</sub> and RuO<sub>2</sub>@IrO<sub>2</sub>. This can be important for developing advanced OER catalysts for PEM water electrolysis because TiO<sub>2</sub> is stable in acid and Ti is not a precious metal.

## 6. Conclusion

This study shows a feasible synthesis method to prepare active RuO<sub>2</sub> and RuO<sub>2</sub>@IrO<sub>2</sub> nanocatalysts for the OER in acids, and elucidates the OER mechanism in acid on most active metal dioxides. Both DFT calculated and experimentally derived free energy diagrams support the reaction mechanism with the O-O bond forming via sequential water dissociative adsorption on a single metal site. To be highly active for the OER, the \*O phase needs to be stable enough so that it can be formed at low overpotentials, but also needs to be reactive enough for water dissociation on adsorbed O in forming the O-O bond. From this viewpoint, the formation of the \*O phase by oxidative desorption of two protons following water dissociative adsorption is slightly too hard on IrO<sub>2</sub>, while the more easily forming \*O phase on RuO<sub>2</sub> is slightly too stable, and thus, not reactive enough to facilitate water dissociative adsorption in forming the \*OO\*H phase. Based on the DFT calculations, the effect of a RuO<sub>2</sub> core on the IrO<sub>2</sub> monolayer shell

slightly reduces the \*O adsorption strength, which is not ideal, and TiO<sub>2</sub> is likely a more suitable oxide core than RuO<sub>2</sub>. The insight can help developing more active OER catalysts.

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