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Electrochemical Active Surface Area Determination of Iridium-Based Mixed Oxides by Mercury Underpotential Deposition

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In Memoriam of Prof. Jean-Michel Savéant

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Abstract: The electrochemical surface area (ECSA) is a critical property to describe, analyze and compare electrocatalysts. The determination of the mass activity of a given catalyst is associated with this parameter which can thus lead to materials benchmarking. Reliable and robust methods to measure ECSA are needed, and those have to accommodate different structures, morphologies and compositions. In this study we investigate mercury underpotential deposition (Hg_{UPD}) as a way to estimate ECSA for ultraporous electrocatalysts based on iridium and iridium-molybdenum electrocatalysts for the oxygen evolution reaction. Results reveal a clear agreement between physisorption measurements and Hg_{UPD} with excellent reproducibility. The method shows also that pre- and post-catalysis surface area measurements are not affected by the catalytic process on short timescale, opening the possibility of electrocatalyst stability and degradation monitoring.

1. Introduction

Characterization of electrocatalysts for small molecules activation in bulk, in situ or operando conditions is of essential importance to evaluate, compare, and interpret reactivities of catalytic materials.^[1] Unlike molecular electrocatalyst,^[2] structural and morphological analysis of amorphous or crystalline materials can be more challenging, requiring numerous analytical techniques which can be costly in terms of money and sample required. Among the key parameters to fully describe a given electrocatalyst the electrochemical active surface area (ECSA) allows to draw a connection between the active catalytic sites of the material and its activity, supporting catalysts comparison and benchmarking.^[3] Physisorption measurement is the method of choice to characterize porosity and surface area. The major drawback comes from the fact that, depending on the actual specific surface area of the electrocatalyst, this method may require up to several hundreds of milligrams of material to give reliable values and this technique is not always available in all electrochemical laboratories. Furthermore, this technique is

not an actual measure of the number of electroactive centres in the material and it cannot be used easily in all the experimental conditions (e.g. film characterization, electrodeposition or post-electrolysis analysis). Electrochemical techniques, such as carbon monoxide stripping^[4] or underpotential deposition of hydrogen^[5] or transition metal^[6] can be of interest as they allow a direct measurement of the ECSA of the material (electrodeposited or coated) onto the electrode. These techniques only require very limited quantities of material, typically in the order of microgram to milligram. Limitations of underpotential deposition analysis can arise from the selectivity of the adsorbed atoms/molecules, and great care has to be taken when choosing those to reach reliable values of ECSA.

Pivovar and co-workers recently reported mercury underpotential deposition (Hg_{UPD}) on iridium and iridium oxide to measure ECSA in coated electrocatalytic film for the oxygen evolution reaction (OER) in a three-electrode setup.^[7] The surfaces estimated compared very favourably with values calculated from BET processing of physisorption data, unlike hydrogen underpotential deposition or CO stripping for which iridium oxide nanoparticles were electrochemically silent or not reliable. This method has already been described in the past for polycrystalline iridium materials,^[8] but its extension to iridium oxide allowed wider applications for pre- and post-catalysis analysis of OER electrocatalyst materials.

We previously reported the synthesis of ultraporous materials based on iridium-oxide^[9] and iridium-molybdenum oxide^[10] as electrocatalysts for OER using the spray-drying technique. The porosity of those IrO_2 particles was estimated around $75 \pm 5\%$, and surface areas measured by physisorption were found to be around $30 \text{ m}^2 \text{ g}^{-1}$ for samples obtained at 450°C , decreasing down to $10 \text{ m}^2 \text{ g}^{-1}$ when calcined at 800°C . We followed the evolution of ECSA through the double layer capacitance, but this method was not satisfactory as it only gave a trend rather than an actual surface area for the different materials investigated.^[9] Herein we report the expansion of the method reported earlier for iridium and iridium oxide materials to ultraporous iridium-based mixed oxide materials, examining the case of a transition metal, molybdenum, as a substitute for iridium. We are able to

prepare iridium-molybdenum mixed oxides ($\text{Ir}_{1-x}\text{Mo}_x\text{O}_y$ oxides, with $x = 0, 0.1, 0.3$, and 0.5) following the spray-drying method and estimate their ECSA with mercury underpotential deposition before and after OER. We then compare those data to BET values and capacitance measurements and show that similar values and trends can be obtained, validating this method for evaluating reliable numbers for ECSA.

2. Results and Discussion

2.1. Material synthesis and characterization

Iridium-based mixed oxides were prepared using spray-drying following the procedure reported earlier.^[9,10] The ratio between the metal precursors was adjusted to obtain the desired composition between 0 and 50% atoms of molybdenum, and the composition of each sample was confirmed by X-ray fluorescence. The morphology of the materials is characteristic of the synthesis technique and consists in highly porous hollow microspheres with diameter ranging from 500 nm to a few microns. A typical scanning electron microscopy (SEM) image is represented in Fig. 1a. X-ray diffraction (XRD) analysis of the calcined powders confirm the formation of a single phase corresponding to a rutile-type structure (ICSD: 98-008-4577) as exemplified in Fig. 1b. By varying the calcination temperature or the preparation procedure, we were able to prepare materials with similar compositions but tunable specific surface area. We have then used these materials to investigate the applicability of the determination of the ECSA by mercury underpotential deposition in the case of iridium-based mixed oxides.

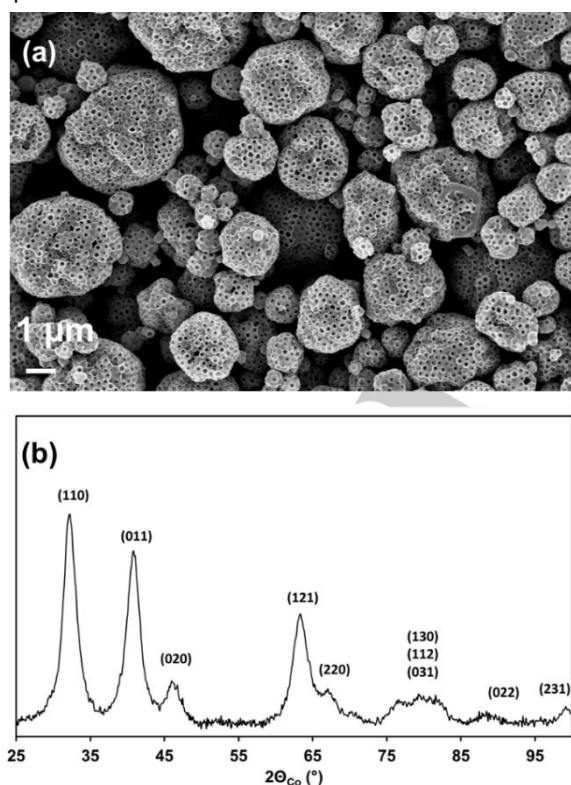


Figure 1. (a) Typical SEM image and (b) corresponding X-ray diffractogram of a sample prepared with 30% Mo and calcined at 550 °C.

2.2. Electrochemical characterization

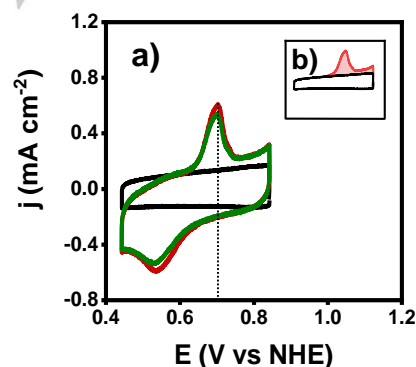
Electrochemical experiments were performed in a three-electrode setup. Results are presented in experimental order to demonstrate coherence among the tests as well as to ensure reproducibility. Each experiment for mercury underpotential deposition was performed at least 3 times to ensure good reproducibility.

2.2.1. Double layer capacitance

Electrochemical double layer capacitance (C_{dl}) was measured to give a trend for the ECSA evolution between the different materials. A first scan at 25 mV s^{-1} in the range -0.2 V to $+1.24 \text{ V}$ vs NHE was performed in order to determine the non-Faradaic region, which correspond to the region between $+0.89 \text{ V}$ to $+1.09 \text{ V}$ vs NHE. CVs were run at various scan rates from 10 mV s^{-1} up to 200 mV s^{-1} in order to obtain the charging current of the electrodes at each scan rate (Figure S1) and the C_{dl} (Figure S2). Figure S3 shows the evolution of the C_{dl} , with maxima shifting towards higher calcination temperatures when the amount of molybdenum is increased in the material. A summary of the values for the corresponding samples and temperatures are presented in Table 2.

2.2.2. Mercury underpotential deposition

The protocol proposed by Pivovar and co-workers was slightly adapted to our electrochemical setup to study mercury underpotential deposition (see the Experimental Section).^[7] We started to evaluate the ECSA on pure iridium oxide samples to



validate the applicability of this method on ultraporous materials calcined in the range 400 – 800 °C (Figure S4). Cyclic voltammograms in all samples containing the mercury nitrate solution showed an anodic desorption peak at ca. $+0.7 \text{ V}$ vs. NHE, corresponding to the mercury monolayer (Figure 3a).

Figure 3. Cyclic voltammogram of $\text{IrO}_2@450$ recorded at a scan rate of 50 mV s^{-1} in 0.1 M HClO_4 (black), and 0.1 M HClO_4 containing 1 mM mercury nitrate solution (red: before OER, green: after OER); inset: area of the charge current corresponding to the anodic peak.

The charge of the anodic peak was estimated from the integration of the peak area (Figure 3b), before and after OER characterization. Cathodic peaks could as well be used, but as noted by Pivovar *et al.* the integration limits are not as defined as for anodic peaks.^[7] Cyclic voltammogram backgrounds were recorded in the absence of mercury nitrate and subtraction of this background current provides the measurement without other charging phenomenon than mercury desorption. Electrochemical conditioning involving 10 cycles over the OER region (+1.24 to +1.54 V vs. NHE) was performed prior and after the CVs in order to observe potential changes regarding mercury adsorption (Figure S5), and very little variations were observed (Table S1). ECSA values presented in Table 1 are comparable to the ones previously determined by physisorption measurement.^[9] Those results were encouraging to further investigate ECSA Hg_{UPD} determination for iridium oxide heterometallic samples.

We first had to determine that pure ultraporous molybdenum oxide particles were also subject to mercury adsorption and gave an electrochemical response. Figure 4 shows the cyclic voltammogram of molybdenum oxide MoO_3 calcined at 550 °C in the absence (black) and in the presence (red) of mercury nitrate. A peak in the same range as for pure iridium oxide was found around +0.7 V vs. NHE, allowing a potential match when investigating the substitution of iridium by molybdenum.

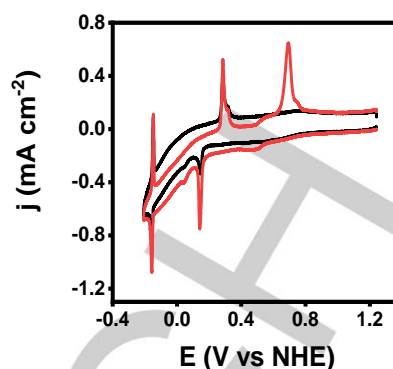


Figure 4. Cyclic voltammograms of $MoO_3@550$ recorded at 20 mV s⁻¹ in a 0.1 M $HClO_4$ (black) and in a 0.1 M $HClO_4$ containing 1mM mercury nitrate solution (red).

Table 1. Comparison between BET theory surface area of IrO_2 ^[9] and ECSA values obtained by Hg_{UPD}

Temperature (°C)	$S_{BET} IrO_2$ (m ² g ⁻¹) ^[9]	$S_{Hg} IrO_2$ (m ² g ⁻¹)
400	32	30 ± 1.3
450	30	28 ± 2.5
500	29	26 ± 1.4
550	17	17 ± 2.2
800	13	14 ± 1.5

A similar protocol was performed on all IrMo-mixed oxides to estimate their ECSA. The evolution of the CV shape and characteristic anodic peak at ca. +0.7 V vs NHE for 10%-Mo is shown in Figure 5 (see Figure S6 for the CVs of 30%-Mo and 50%-Mo). A double hump is observed on the anodic scan and only one peak is observed on the cathodic scan.

A comparison of the behaviour of the Hg_{UPD} charge current as function of the temperature for 10%-Mo at different calcination temperatures is represented in Figure 6 (see Figure S6 for 30 and 50 % Mo). Similarly, as for pure IrO_2 , a Coulombic charge of 138.6 $\mu C cm^{-2}$ was used as a conversion factor to obtain the ECSA values.^[7] To ensure the stability of the material and the robustness of the procedure we measured ECSA after OER cycling, with no significant variations observed (Figure 6 and S7). ECSA values obtained before OER for the mixed samples are summarized in Table 2 (see Table S2 for values after OER).

Table 2. Summary of surfaces obtained by BET, Hg_{UPD} and C_{dl} measurements (before OER).

Temperature (° C)	10%Mo				30%Mo				50%Mo			
	S_{BET} (m ² g ⁻¹)	S_{Hg} (m ² g ⁻¹)	$ Δ $ (%)	C_{dl} (μF cm ⁻²)	S_{BET} (m ² g ⁻¹)	S_{Hg} (m ² g ⁻¹)	$ Δ $ (%)	C_{dl} (μF cm ⁻²)	S_{BET} (m ² g ⁻¹)	S_{Hg} (m ² g ⁻¹)	$ Δ $ (%)	C_{dl} (μF cm ⁻²)
450	64	52±1.2	19	19.10	50	46±5.8	8	10	24	31±0.7	23	5.7
500	49	38±1.3	22	6.2	74	74±13	0	14	27	31±3.4	13	8.7
550	29	28±0.6	3	3.8	40	32±2.8	20	5.7	55	57±2.1	4	13.1
600	22	18±2.5	18	2.5	76	62±18	18	8.3	29	32±2.2	10	11.9

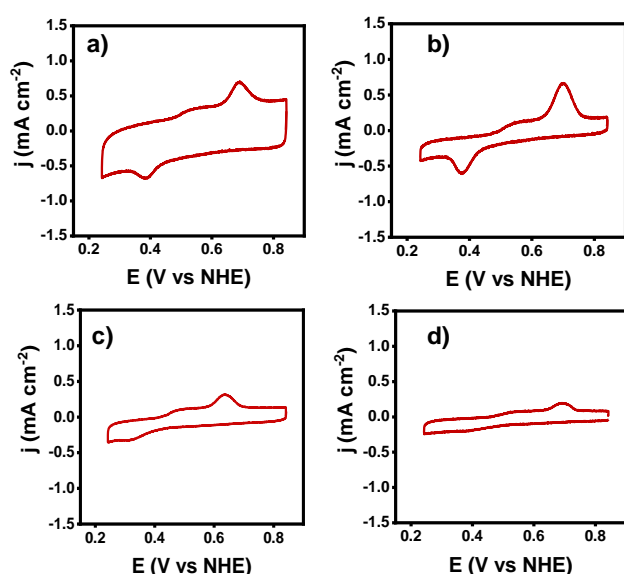


Figure 5. Cyclic voltammograms of 10% Mo samples calcined at a) 450, b) 500, c) 600 and d) 800 °C recorded at 25 mV s⁻¹ in a 0.1 M HClO₄ containing 1 Mm mercury nitrate solution.

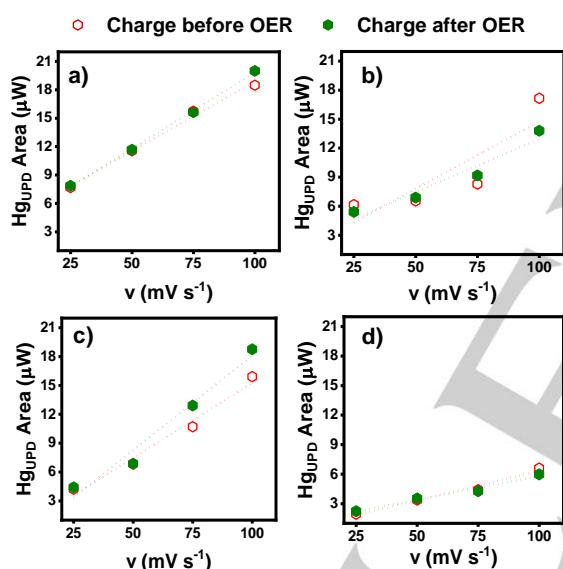


Figure 6. Charges before and after electrochemical conditioning of OER on 10% Mo samples at a) 450, b) 500, c) 550 and d) 600 °C recorded at multiple scan rates in a 0.1 M HClO₄ containing 1Mm mercury nitrate solution.

2.3. Discussion

Cyclic voltammetry in 0.1 mol L⁻¹ HClO₄ with or without mercury nitrate solution was used to characterize and compare the mixed oxide electrocatalysts calcined at different temperature for their ECSA. At first it was necessary to consider pure ultraporous IrO₂ particles,^[9] and demonstrate that mercury underpotential deposition was an appropriate method for these ultraporous materials. From the comparison between BET and Hg_{UPD} measurements we can see an excellent agreement along the series of materials regardless of the temperature of calcination (Table 1). The trend shows a decrease of the surface area from ca. 30 m² g⁻¹ to ca. 14 m² g⁻¹ when increasing the thermal treatment from 400 to 800 °C. From those measurements we can estimate that the ultraporous structure allows mercury ions to diffuse freely and react at the surface and inside the pores of

the material to accurately probe the ECSA of IrO₂ particles. This is valid if we consider that: i) physisorption and Hg_{UPD} measurements give access to the same adsorption sites for N₂ and mercury; ii) physisorption gives access to all the adsorption sites.

We then decided to investigate the effect of the incorporation of molybdenum within the structure on the surface area. As the nature of the material can greatly affect the underpotential deposition process, we had to assess that mercury was indeed reacting with pure molybdenum oxide prior to examine the different mixed oxides. We can observe from Figure 4 that several adsorption and desorption peaks can be observed for the MoO₃ reference sample endorsing mercury as good candidate for ECSA to analyze these heterometallic materials.

Hg_{UPD} measurement for Ir_{1-x}Mo_xO₂ samples are showing a slightly different behavior than for pure IrO₂ particles, with two peaks in the anodic part of the cyclic voltammogram, probably resulting from the difference between iridium and molybdenum desorption sites for mercury. This is nevertheless difficult to attribute with this set of electrochemical measurements, and it would require further investigation – beyond the scope of this study – to fully understand the peak pattern observed.

All the heterometallic samples with different molybdenum contents and calcination temperatures have been measured for Hg_{UPD}, and data are summarized in Table 2 to be compared to BET and capacitance data. Given the fact that XRD diffractograms are showing constant unit-cell parameters along the series, *i.e.* Mo atoms are replacing Ir atoms without any major structural modifications, we used a Coulombic charge of 138.6 μC cm_{Ir}⁻² and a roughness factor of 1.3 for all the materials to estimate the ECSA, as described and developed earlier in the literature for Hg_{UPD}.^[8a] We can observe an excellent agreement between Hg_{UPD} and surface area calculated from physisorption measurements using BET processing (Figure S8). Trends observed for both type of measurements are similar, and the determined surfaces are very close. The small differences observed can be explained by the quality of the electrode coating, the catalyst loading and the diffusion of mercury ions in the electrocatalytic film. Furthermore, the charge measured for the mercury desorption before and after several cycles in the OER region are not significantly affected by the catalytic process (Figure 6). Interestingly, this opens the possibility to monitor ECSA changes and degradation over longer period of electrolysis (days to weeks) for these materials, which could be complementary to post-electrolysis microscopic studies or metal leakage analysis of the electrolyte solution.

3. Conclusion

Electrocatalytic film analysis is critical in the framework of catalysts characterization and benchmarking.^[11] ECSA values are difficult to obtain, and robust and reliable methods to estimate the number of electroactive sites for different types of materials depending on their structure, morphology or composition are still critical. Mercury underpotential deposition has been previously successfully developed for iridium and iridium oxide electrocatalyst to measure surface area values comparable to BET measurements.^[7] In this study we are presenting results outlining that the Hg_{UPD} method is also relevant for porous and heterometallic materials in electrocatalytic films, with the example of ultraporous iridium

oxide and iridium-molybdenum oxide electrocatalysts. Values obtained are consistent with BET values, and the robustness of the method is evidenced with before/after OER experiments. Degradation and durability experiments can also be envisioned by monitoring the evolution of the ECSA through this method.

4. Experimental Section

CAUTION: mercury and mercury compounds are poisonous and teratogenic.^[12] Hydrated iridium (III) chloride ($\text{IrCl}_3 \cdot x\text{H}_2\text{O}$) and molybdenum (V) chloride ($\text{MoCl}_5 \cdot x\text{H}_2\text{O}$) were purchased from Sigma Aldrich. Commercial iridium (IV) oxide (IrO_2), Mercury (II) nitrate hydrate ($\text{Hg}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$), Nafion® D-521 dispersion (5% w/w), sulfuric acid (H_2SO_4) 0.1 N standardized solution, perchloric acid (HClO_4) 70% aq. solution were purchased from Alfa Aesar. Carbon Vulcan® XC72R was purchased from Cabot. The template polymethylmethacrylate (PMMA) beads were synthesized by radical polymerization following the protocol presented in reference ^[13].

Synthesis of catalysts

The mixed Ir-based oxide catalysts, $\text{Ir}_{1-x}\text{Mo}_x\text{O}_2$, were prepared at different values of x ($x = 0, 0.1, 0.3, 0.5, 0.7$), using the synthesis method described in the previously published procedure^[9] using $\text{IrCl}_3 \cdot x\text{H}_2\text{O}$ (Alfa-Aesar) and $\text{MoCl}_5 \cdot x\text{H}_2\text{O}$ (Sigma-Aldrich). The precursors solution contains the inorganic reagents, $\text{IrCl}_3 \cdot x\text{H}_2\text{O}$ and $\text{MoCl}_5 \cdot x\text{H}_2\text{O}$, and PMMA beads (300 nm bead diameter) colloidal dispersion mixed in water. After constant stirring, the solution is first sprayed to form microdroplets which are then transported by an air flux in a drying chamber where evaporation takes place, and the powder is collected to be then calcined in the range 400 – 800 °C increasing every 50 °C; above 350 °C the polymer template is removed and then iridium-molybdenum species are converted to oxides.

Material characterization

The catalysts synthesized were characterized by scanning electron microscopy (SEM) using a Zeiss SUPRA 40 FESEM operating at 5 kV. Determination of the formation of single-phase materials was performed by X – ray powder diffraction (XRD) on a Panalytical X'pert pro diffractometer equipped with a Co anode ($\lambda_{\text{Co}} = 1.789 \text{ \AA}$) and a multichannel X'celerator detector. Each pattern was recorded in the $\theta - \theta$ Bragg – Brentano geometry in the range 15 – 120 ° using 2 θ step size of 0.0334° and compared to diffraction profiles reported in the ICDD (International Center for Diffraction Data) database. Physisorption studies were performed with N_2 at 77 K using a Belsorp-max apparatus from MicrotracBEL. Before analysis, the samples were outgassed at 423 K for 12 h under 0.1 Pa. The BET processing was carried out in the relative pressure range 0.05–0.25.

Electrochemical characterization

Inks were prepared by suspending 1.0 mg of $\text{Ir}_{1-x}\text{Mo}_x\text{O}_2$ and 2.0 mg of Vulcan carbon in 250 μL of Nafion® and 250 μL of deionized water (0.059 $\mu\text{S cm}^{-2}$) by sonicating in an ultrasonic bath for 30 minutes. All electrochemical tests were studied using a rotating disk electrode (RDE, Pine Research Instrumentation) with a potentiostat Autolab PGSTAT 12. The three-electrode cell setup included a saturated calomel electrode (SCE) as a reference electrode (RE), a 5 mm diameter glassy carbon (previously polish and rinsed in ethanol) as a working electrode (WE) where 8 μL of catalyst ink were deposited (dried in air and at 60° C/ 30 min in an oven), and a Pt wire as the counter electrode (CE). All experiments with the loaded WE were carried out at a constant rotating rate speed of 1600 rpm in a glass vessel containing 0.05 mol L^{-1} H_2SO_4 (ohmic drop of ca. 30 Ω) or 0.1 M HClO_4 (ohmic drop of ca. 20 Ω) as supporting electrolyte solutions. Oxygen evolution reaction measurements were carried out in a H_2SO_4 solution as follows: 50 cycles

in the range -0.2 – +1.24 V vs. NHE followed by a forward scan recorded at 10 mV s^{-1} in the potential range of +1.24 to +1.54 V vs. NHE. The double layer capacitance measurements were carried out in a 0.1 M HClO_4 solution as follows: cyclic voltammograms were measured in a non-faradaic region of the potential sweep at several scan rates (0.2, 0.15, 0.1, 0.05, 0.025 and 0.01 V s^{-1}) in the range +0.89 – +1.09 V vs. NHE. Mercury underpotential deposition tests for ECSA measurements were carried out as follows: cyclic voltammograms were taken at several scan rates (0.1, 0.075, 0.05 and 0.025 V s^{-1}) in the range +0.24 to +0.84 V vs. NHE in 0.1 M HClO_4 solution before and after dropping mercury nitrate solution into the supporting electrolyte, for a final mercury nitrate concentration of 1 mM. OER measurements were performed by 10 cycles in the range +1.24 – +1.54 V vs. NHE at 0.1 V s^{-1} as an electrochemical conditioning prior to ECSA measurements once mercury nitrate was added. All voltammograms are reported in V vs. Normal Hydrogen Electrode (NHE). To process the desorption monolayer the Coulombic charge of 138.6 $\mu\text{C cm}^{-2}$ was used as a conversion of factor.^[7]

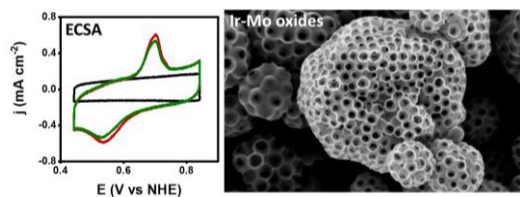
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Keywords: OER • ECSA • Mercury underpotential deposition

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Material ultraporosity characterization: Mercury underpotential deposition (Hg_{UPD}) was used to determine the Electrochemical Surface Area (ECSA) of iridium and iridium-molybdenum mixed oxides ultraporous materials. Comparison with physisorption measurements showed excellent agreement for a wide range of compositions and calcination temperatures.