## Supplementary Information

# Elucidating the Origin of the Electrochemical Capacity in a Proton-Based Battery H<sub>x</sub>IrO<sub>4</sub> via Advanced Electrogravimetry

Pierre Lemaire<sup>†,‡,§</sup>, Ozlem Sel<sup>¦,\*</sup>, Daniel Alves Dalla Corte<sup>†,§</sup>, Antonella Iadecola<sup>§</sup>, Hubert Perrot<sup>¦</sup>, Jean-Marie Tarascon<sup>†,§,\*</sup>

<sup>+</sup> Chimie du Solide et de l'Energie, UMR 8260, Collège de France, 11 Place Marcelin Berthelot, 75231 Paris Cedex 05, France

<sup>‡</sup> Sorbonne Université, 4 Place Jussieu, 75005 Paris, France

<sup>§</sup> Réseau sur le Stockage Electrochimique de l'Energie (RS2E), CNRS FR 3459, 33 Rue Saint Leu, 80039 Amiens Cedex, France

<sup>1</sup> Sorbonne Université, CNRS, Laboratoire Interfaces et Systèmes Electrochimiques, LISE, 75005 Paris, France

\* Corresponding authors

Jean-Marie Tarascon: jean-marie.tarascon@college-de-france.fr Ozlem Sel: ozlem.sel@upmc.fr



## Part I: X-ray Absorption Spectroscopy.

Figure S1. Operando XAS data treatment and experimental setup. a Picture of the lab-made electrochemical cell for operating operando XAS experiments, using carbon paper loaded with 7

 $mg/cm^2_{geo}$  of  $H_x IrO_4$  as working electrode, porous graphite rod as counter electrode and  $Hg/Hg_2SO_4$  (saturated  $K_2SO_4$ ) as reference electrode. b Determination of the White Line energy thanks to derivative of the normalized absorption spectrum with the binding energy for which the curve is equal to zero.



Figure S2. Follow-up of the White Line energy (fingerprint of the Ir oxidation state) thanks to the derivative of the normalized absorption spectra as a function of the galvanostatic charge/discharge of the  $H_x$ IrO<sub>4</sub> phase in acidic electrolyte.

## Part II: Diffusion coefficient determination.

Diffusion coefficient of the involved species was determined by Galvanostatic Intermittent Titration Technique (GITT) on self-standing PTFE electrodes in three-electrode PFA Swagelock cell. The GITT procedure consists of a series of current pulses at 1C during 2 minutes, each followed by a relaxation time of 30 minutes, in which no current passes through the cell. During a discharge, the cell potential quickly fells to a value proportional to ohmic drop (iR), where R is the sum of the uncompensated and charge transfer resistances. Then, the potential slowly decreases, due to the galvanostatic discharge pulse, in order to maintain a constant concentration gradient. During the relaxation time, the composition in the electrode tends to become homogeneous by protons diffusion. Consequently, the potential suddenly increases by a value proportional to iR, and then it slowly increases, until the electrode is in equilibrium (i.e., when dE/dt  $\approx$  0) and the open circuit potential of the cell is reached.

Then, the following galvanostatic pulse is applied, followed by current interruption. This sequence of discharge pulse followed by a relaxation time is repeated until the battery is fully discharged. The chemical diffusion coefficient can be calculated at each step, with the following formula<sup>1</sup>:

$$D = \frac{4}{\pi} \left(\frac{iV_m}{z_A FS}\right)^2 \left[\frac{\frac{dE}{d\delta}}{\frac{dE}{d\sqrt{t}}}\right]^2 \qquad Equation S1$$

With i the current (A),  $V_m$  the molar volume of the active material (cm<sup>3</sup>/mol),  $z_A$  the charge number, F Faraday's constant (96485 C/mol), S the electrode/electrolyte contact area (cm<sup>2</sup>), dE/d $\delta$  the slope of the coulometric titration curve and dE/dVt the slope of the linearized plot of the potential during the current pulse of duration. If sufficient small currents are applied for time intervals, so that dE/dVt can be considered linear and the coulometric titration curve can be also considered linear over the composition range involved in that step, the previous equation can be simplified into:

$$\frac{D}{R^2} = \frac{4}{9\pi\tau} \left(\frac{\Delta E_s}{\Delta E_t}\right)^2$$
 Equation S2

With  $\tau$  the duration of the current pulse (s), R the particle radius with the assumption of spherical particles,  $\Delta E_s$  the steady-state voltage change, due to the current pulse and  $\Delta E_t$  is the voltage change during the constant current pulse. This following formula has been applied to each steps in order to obtain the D/R<sup>2</sup> ratio during the discharge, the results are depicted in the following Figure S3.



Figure S3. GITT discharge curve of  $H_x$  IrO<sub>4</sub> with the estimation of the chemical diffusion coefficient of the involved species in the phase

The proton diffusion coefficient has also been determined in the electrolyte 0.5 mol/L HClO₄ thanks to the Nernst-Einstein equation:

$$D = \frac{\sigma RT}{z^2 F^2 C}$$
 Equation S3

The electrolyte conductivity has been measured with a Mettler Toledo SevenCompact S230. The obtained value was equal to 137.8 mS/cm given rise to a diffusion coefficient of  $7.33 \times 10^{-5} \text{ cm}^2/\text{s}$ .

#### Part III: Study of the film viscoelasticity by EQCM with dissipation monitoring

To ensure that the mechanical properties of the spray casted electrodes were compatible with the EQCM or *AC*-electrogravimetry measurements, the viscoelastic properties of the film were verified by EQCM with dissipation monitoring thanks to the protocol developed by the group of M.D. Levi and D. Aurbach.<sup>2–4</sup> The measurements were performed using AWS A20+ (Advanced Wave Sensors) from the 3<sup>rd</sup> to the 11<sup>th</sup> overtone on a spray casted film on a 14 mm diameter Au-coated resonator with fundamental frequency of 5 MHz. The electroactive geometric surface area was equal to 1 cm<sup>2</sup> while the the gravimetric active surface area was equal to 0.196 cm<sup>2</sup>. The volume of casted slurry was selected to obtain a loading between 40-60 µg/cm<sup>2</sup>. The resonant frequency, *f*, and the absolute dissipation factor, *D*, was recorded at the different overtones during the passage from air to the electrolyte solution (HClO<sub>4</sub> 0.5 mol/L in water) under Open-Circuit Potential (OCP). The Figure S4.a depicts the introduced protocol where the absolute dissipation factor has been replaced by the resonant width thanks to the relation:  $W = f \times D$ . Shifts of frequency and resonance widths are calculated to that of the coating in air rather than to the bare crystal and are normalized by overtone order as well as by  $\rho_l f_0^2$  where  $\rho_l$  is the density of the liquid (approximated to the water density) and  $f_0$  is the fundamental frequency (n = 1) (Figure S4).



Figure S4. a Normalized shifts of frequency  $\Delta f / n$  (negative) and resonance width  $\Delta W / n$  (positive) at different overtones (n = 3 to n = 11) as a function of time when the composite film is transferred from air to electrolyte. b Normalized (by overtone order as well as by  $\rho_l f_0^2$ ) shifts of frequency  $\Delta f / n$  (blue) and resonance width  $\Delta W / 2n$  (red) as a function of the penetration depth. Shifts are referenced to that of the film in air rather than to the bare crystal.

Apart from the  $\Delta W/n$  at the 11<sup>th</sup> overtone,  $\Delta f/n$  and  $\Delta W/n$  are demonstrated a non time-dependent behavior and decrease algebraically with the overtone order. These data indicate rigid behavior of the prepared film under OCP and changes of frequency and dissipation factors are solely attributed to hydrodynamic solid-liquid interactions.<sup>2</sup>

The combination of the Kanazawa and Gordon equation,<sup>5</sup> which describes the hydrodynamic interaction between a film with flat surface and a Newtonian liquid, and the Navier-Stocks equation leads the normalized frequency and resonance width shifts to solely depend on the penetration depth  $\delta$ .

$$\delta = \sqrt{\frac{\eta}{\pi n f_0 \rho}}$$
 Equation S4

Moreover a flat rigid surface in contact with liquid should be expressed by straight lines for all overtone orders and in contact with different liquids. To verify that our film behaves as a flat surface in contact with the electrolyte,  $\Delta f/n$  and  $\Delta W/2n$  were plotted as a function of the penetration depth  $\delta$  of the transverse wave. The Figure S4.b depicts two straight lines of  $\Delta f/n$  and  $\Delta W/2n$  in function of  $\delta$  demonstrating the rigid behavior of the film and that it can be assimilated to a flat surface under OCP. Nevertheless these findings do not prove the film rigidity retention during the material cycling. To this end the motional resistance was measured during the cyclic voltammetry of the H<sub>x</sub>IrO<sub>4</sub> phase, the results are plotted in the Figure S5.



*Figure S5. Cyclic voltammetry and simultaneously measured motional resistance at 5 mV/s in acidic electrolyte* 

The motional resistance, R, shows a variation of 5  $\Omega$  between the lower and higher resistance during the cycling at a scan rate of 5 mV/s corresponding to a motional resistance change below 2 %. The motional resistance variations were always lower than 10  $\Omega$  independently of the applied scan rate; consequently the viscosity changes at the vicinity of the H<sub>x</sub>IrO<sub>4</sub> coated electrode during cycling were supposed to be negligible. As mentioned in M.D. Levi and D. Aurbach's works,<sup>6</sup> this criterium can be employed to prove the rigidity of the prepared film during the proton release/uptake and therefore the gravimetric regime of the QCM response.

#### Part IV: AC-electrogravimetry model.<sup>7–11</sup>

AC-electrogravimetry measurements were carried out by using a four-channel frequency response analyzer (Solartron 1254 FRA) and a lab-made potentiostat and QCM. The QCM was used under dynamic regime, working electrode (gold patterned quartz resonator) was polarized at a selected potential, and a small-amplitude potential perturbation (40 mV rms) was superimposed. The frequency range was between 63 kHz and 10 mHz. The microbalance frequency change,  $\Delta f_m$ , corresponding to the mass response,  $\Delta m$ , of the working electrode was measured simultaneously with the AC response,  $\Delta I$ , of the electrochemical system. The resulting signals were sent to the four-channel Frequency Response Analyzer (FRA), which allowed the electrogravimetric transfer function  $(\Delta m/\Delta E)(\omega)$  and the classical electrochemical impedance  $(\Delta E/\Delta I)(\omega)$  to be obtained simultaneously at a given potential. Then the experiemental  $(\Delta q/\Delta E)(\omega)$  was calculated from electrochemical impedance thanks to the Equation S17 and Equation S18. A model that involves the transfer of one cation, one anion and one free solvent at the Electrode-Electrolyte Interface has been used in this work and fitted our experimental *AC*-electrogravimetry data. A schematic of a deposited film on a gold EQCM electrode in contact with an electrolyte is represented in the Figure S6. Ionic transfer occurs at the interface between the active material and the electrolyte. The flux of species i (c: cation, a: anion, s: solvent)  $J_i$ , is considered positive if the species is expulsed from the active material:



Figure S6. Schematic of the EQCM electrode / Active material / Electrolyte stacking

If both cations (c), anions (a) and solvent (s) are involved in the charge compensation process directly or indirectly, the associated mass variation,  $\Delta m$  and the charge variation per surface unit,  $\Delta q$ , which flows through the interface between the gold electrode and the active material, are equal to:

$$\Delta m = m_c \Delta \xi_c + m_a \Delta \xi_a + m_s \Delta \xi_s \qquad \qquad \text{Equation S5}$$

$$\Delta q = -F(\Delta \xi_c - \Delta \xi_a) \qquad \qquad Equation S6$$

where  $m_i$  and  $\xi_i$  are the molar mass and the quantity of moles of species *i* exchanged, respectively. The generalized mechanism for insertion or electroadsorption by a cation or an anion in a free site  $\langle \rangle$  can be described by the following reactions:

$$\langle \rangle + e^{-} + C^{+} \underset{k_{c}}{\overset{k_{c}}{\leftarrow}} \langle C^{+} \rangle \text{ and } \langle \rangle + A^{-} \underset{k_{a}}{\overset{k_{\prime}a}{\leftarrow}} \langle A^{-} \rangle + e^{-}$$
 Equation S7

Consequently, the molar flux of species (c, a or s) is  $J_i = \frac{d\xi}{dt}$  and the concentration of species I in the active material film of thickness  $d_f$  can be written under the form:

$$C_i = \frac{\xi_i}{d_f}$$
 Equation S8

The species transfers at the Electrode-Electrolyte Interface are only taken into account as rate-limiting steps since the species transports inside the active material and in the solution are supposed to be fast enough as deduced by GITT and conductivity measurements. By using the laws of heterogeneous kinetics and reaction formulae, the flux of cations and anions are:

$$J_a(d_f) = -d_f \frac{dC_a}{dt} = k_a (C_a - C_{a,min}) - k'_a (C_{a,max} - C_a) C_{a,sol} \qquad \text{Equation S9}$$

$$J_c(d_f) = -d_f \frac{dC_c}{dt} = k'_c (C_c - C_{c,min}) - k_c (C_{c,max} - C_c) C_{c,sol} \qquad \text{Equation S10}$$

By using the Hillman solvation model<sup>12</sup>, the same relationship can be used for the solvent flux:

$$J_s(d_f) = -d_f \frac{dC_s}{dt} = k'_s(C_s - C_{s,min}) - k_s(C_{s,max} - C_s)$$
 Equation S11

Where:

- C<sub>i</sub> is the concentration of species i in the film, C<sub>i,sol</sub> is the concentration of species i in the solution by assuming that the diffusion of the ions in solution does not limit the global kinetics.
- $(C_{i,max} C_i)$  is the concentration in free sites for species i at time t, with  $C_{i,max}$  is the maximum concentration of the free sites in the film for species i.
- $(C_i C_{i,min})$  is the concentration of species i in the film, where  $C_{i,min}$  is the minimum concentration of species i in the film.

The two kinetic constants can be defined as:

$$k_i = k_{i_0} e^{[b_i(E - E^\circ_i)]}$$
 and  $k'_i = k'_{i_0} e^{[b'_i(E - E^\circ_i)]}$ 

Where *E* is the potential,  $E_i^{\circ}$  is the apparent normal potential,  $(E - E_i^{\circ})$  is the overvoltage,  $k_{i_0}$ ,  $k'_{i_0}$ ,  $b_i$  and  $b'_i$  are constants.

Under the effect of a sinusoidal potential perturbation with low amplitude,  $\Delta E$ , imposed to the gold surface/film/electrolyte system, sinusoidal fluctuations of concentration,  $\Delta C_i$ , and flux,  $\Delta J_i$ , are observed such as:

$$\Delta J_i = -d_f \frac{dC_i}{dt} = -j\omega d_f \Delta C_i \qquad Equation S13$$

The expression of the global insertion/expulsion flux,  $\Delta J_i$ , which depends on the concentration and potential perturbations, at the film/electrolyte interface is:

$$\Delta J_{i} = \frac{\partial J_{i}}{\partial C_{i}}\Big|_{E} \Delta C_{i} + \frac{\partial J_{i}}{\partial E}\Big|_{C_{i}} \Delta E = K_{i} \Delta C_{i}(d_{f}) + G_{i} \Delta E \qquad Equation S14$$

where  $\omega$  is the angular frequency equal to  $2\pi f$ , f is the perturbation frequency and  $K_i$  and  $G_i$  are the partial derivatives of the flux,  $J_i$ , with respect to the concentration and the potential,  $K_i = \left(\frac{\partial J_i}{\partial C_i}\right)_E$  and  $G_i = \left(\frac{\partial J_i}{\partial E}\right)_{C_i}$ .  $K_i$  is the kinetic rate of transfer and  $G_i$  is the inverse of the transfer resistance,  $Rt_i$ , of the species at the film/electrolyte interface:  $Rt_i = \frac{1}{FG_i}$ . For each transferred species, the ionic transfer resistance is a good estimation of the ease of the transfer.

Thus, the change of the concentration,  $\Delta C_i$ , of each species with potential  $\Delta E$  can be calculated using:

$$\frac{\Delta C_i}{\Delta E}(\omega) = \frac{-G_i}{j\omega d_f + K_i}$$
 Equation S15

The charge/potential transfer function can be calculated:

$$\frac{\Delta q}{\Delta E}(\omega) = -Fd_f\left(\frac{\Delta C_c}{\Delta E}(\omega) - \frac{\Delta C_a}{\Delta E}(\omega)\right)$$
  
=  $-Fd_f\left(\frac{-G_c}{j\omega d_f + K_c} + \frac{G_a}{j\omega d_f + K_a}\right)$   
Equation S16

The Faradaic impedance relative to the global ionic transfer of charged species involved in the charge compensation is:

$$Z_F(\omega) = \frac{\Delta E}{\Delta I_F}(\omega) = \frac{1}{j\omega \frac{\Delta q}{\Delta E}(\omega)}$$

$$= \frac{1}{j\omega F d_f \left(\frac{G_c}{j\omega d_f + K_c} - \frac{G_a}{j\omega d_f + K_a}\right)}$$
Equation S17

Finally, the classical electrochemical impedance can be estimated incorporating the electrolyte resistance  $R_{el}$  and the interfacial capacitance  $C_{dl}$ :

$$\begin{split} \frac{\Delta E}{\Delta I}(\omega) &= R_{el} + \frac{1}{j\omega C_{dl} + \frac{1}{Z_F(\omega)}} \\ &= R_{el} \\ &+ \frac{1}{j\omega C_{dl} + j\omega F d_f \left(\frac{G_c}{j\omega d_f + K_c} - \frac{G_a}{j\omega d_f + K_a}\right)} \end{split}$$
 Equation S18

The second main transfer function can be calculated theoretically taking also into account the charged and uncharged species:

$$\frac{\Delta m}{\Delta E}(\omega) = d_f \left( m_c \frac{\Delta C_c}{\Delta E}(\omega) + m_a \frac{\Delta C_a}{\Delta E}(\omega) + m_s \frac{\Delta C_s}{\Delta E}(\omega) \right)$$
$$= -d_f \left( m_c \frac{G_c}{j\omega d_f + K_c} + m_a \frac{G_a}{j\omega d_f + K_a} \right)$$
Equation S19
$$+ m_s \frac{G_s}{j\omega d_f + K_s} \right)$$

To illustrate what the experimental AC-electrograviemtry data may look like, the  $\Delta q/\Delta E(\omega)$  and  $\Delta m/\Delta E(\omega)$  transfer functions are shown schematically in Figure S7.



Figure S7: Representation of the possible experimental transfer functions for a  $\Delta q/\Delta E(\omega)$  and b  $\Delta m/\Delta E(\omega)$  in the case of two charged species. c Example of  $\Delta m/\Delta E(\omega)$  TF for one anion (ClO<sub>4</sub><sup>-</sup>) and one cation (H<sup>+</sup>) plus the participation of one uncharged species (H<sub>2</sub>O) in the same direction as the cation flux.

For a single ion transfer at the Electrode Electrolyte interface, a typical cation and anion contribution appear characteristically on the 3<sup>rd</sup> and 1<sup>st</sup> quadrant (Cartesian system) of the mass/potential TF, respectively. It is important to note that the mass/potential TF is the only TF that can discriminate between the cations or anions and identify them by their molar mass ( $m_i$  in Equation S19). In a more complex electrochemical process, where a multi-ion transfer occurs, the above mentioned TFs may look like as shown in Figure S7.a,b. The contribution of two charged species may translate into two loops in  $\Delta q/\Delta E(\omega)$  (Figure S7.a) if the the respective time constants of the participating ions are different enough. However, the four different configuration given in the Figure S7.a result in the same response in terms of  $\Delta q/\Delta E(\omega)$  TF. The strength of the mass/potential TF is more evident in the Figure S7.b, where four possibilities of ionic transfers (two anions, an anion/cation, two cations and a cation/anion) can be distinguished, with further kinetic resolution depending on the dynamics of interfacial transfer.

To illustrate the case introduced in the main paper, the Figure S7.c has been represented. In the high frequency domain, the loop found in the 1<sup>st</sup> quadrant is characteristic of the contribution of one anion. The molar mass associated to this loop is equal to the perchlorate one (ClO<sub>4</sub><sup>-</sup>). The difficulty lies in the awarding of the contributions of the 3<sup>rd</sup> quadrant. The Figure S7.c depicts the contributions of one cation (H<sup>+</sup>) and one free solvent (H<sub>2</sub>O) (in the same flux direction as the cation) where the time constants associated to each species are so close that theses two contributions give rise to one big single loop in the 3<sup>rd</sup> quadrant.

Partial mass/potential TF can be also estimated by removing the cation contribution, calculating  $\Delta m/\Delta E^{a,s}(\omega)$ .

$$\frac{\Delta m^{a,s}}{\Delta E}(\omega) = \frac{\Delta m}{\Delta E}(\omega) + \frac{m_c}{F}\frac{\Delta q}{\Delta E}(\omega) \qquad \text{Equation S20}$$

$$\frac{\Delta m^{a,s}}{\Delta E}(\omega) = d_f\left((m_a + m_c)\frac{\Delta C_a}{\Delta E}(\omega) + m_s\frac{\Delta C_s}{\Delta E}(\omega)\right) \qquad \text{Equation S21}$$

This TF acts as a cross-check procedure to discriminate between two possible cations or to amplify the anion contribution as its apparent molar mass is  $m_a + m_c$ . In our experiment, the partial

mass/potential TF is calculated by removing the cation contribution either proton (Figure S8.a) or hydronium ion (Figure S8.b) thanks to the Equation S21.



Figure S8. Partial mass/potential transfer functions  $\frac{\Delta m^{a,s}}{\Delta E}(\omega)$  at 0.15 V vs. Hg/Hg<sub>2</sub>SO<sub>4</sub> where a the proton or b the hydronium ion contribution has been removed, both experimental and theoretical curves are given.

The Figure S8 shows that the partial TF where the proton contribution has been removed demonstrates the best adjustment in terms of shape and frequency similarities between the experimental and theoretical curves in comparison with the TF without the hydronium ion contribution. This data analysis permits to favor the proton over the hydronium ion contribution in our proposed model.

The derivative of the concentration for each species with respect to the potential can be calculated by considering the low frequecy limit of  $\frac{\Delta C_i}{\Delta E}(\omega)$ .

$$\frac{\Delta C_i}{\Delta E}(\omega) = \frac{-G_i}{j\omega d_f + K_i} \xrightarrow{\omega \to 0} -\frac{G_i}{K_i}$$
 Equation S22

Then  $\Delta C_i$  is obtained by integrating  $-\frac{G_i}{K_i}$  with respect to the potential. To finish,  $\Delta m_i$  is acquired by multiplying  $\Delta C_i$  by the volume of active material. The global mass variation at each potential can therefore be calculated with the sum of each  $\Delta m_i$  in order to be compared with the classical EQCM measurement.

The different parameters collected by the fitting of the *AC*-electrogravimetry at each stationary potential are gathered in the following Table S1.

E (V vs.	K <sub>i</sub> (cm.s <sup>-1</sup> )			G <sub>i</sub> (mol.V <sup>-1</sup> .s <sup>-1</sup> .cm <sup>-2</sup> )			Rt <sub>i</sub> (Ω.cm²)		
Hg/Hg <sub>2</sub> SO <sub>4</sub> )	H <sup>+</sup>	CIO4 <sup>-</sup>	H <sub>2</sub> O	H⁺	CIO4 <sup>-</sup>	H <sub>2</sub> O	H <sup>+</sup>	CIO4 <sup>-</sup>	$H_2O$
-0.3	1.6 10 <sup>-4</sup>	3.4 10 <sup>-3</sup>	4.3 10 <sup>-4</sup>	1.6 10 <sup>-8</sup>	5.0 10 <sup>-8</sup>	7.0 10 <sup>-8</sup>	653	208	149
-0.2	1.6 10-4	3.4 10 <sup>-3</sup>	3.9 10 <sup>-4</sup>	2.8 10 <sup>-8</sup>	7.2 10 <sup>-8</sup>	3.0 10 <sup>-7</sup>	367	144	35
-0.1	1.8 10 <sup>-4</sup>	3.4 10 <sup>-3</sup>	3.4 10 <sup>-4</sup>	6.0 10 <sup>-8</sup>	8.1 10 <sup>-8</sup>	5.4 10 <sup>-7</sup>	172	128	19
0	1.8 10 <sup>-4</sup>	3.4 10 <sup>-3</sup>	2.7 10 <sup>-4</sup>	5.7 10 <sup>-8</sup>	2.4 10 <sup>-7</sup>	8.6 10 <sup>-7</sup>	183	43	12
0.05	1.8 10 <sup>-4</sup>	3.4 10 <sup>-3</sup>	2.3 10 <sup>-4</sup>	8.7 10 <sup>-8</sup>	3.3 10 <sup>-7</sup>	1.0 10-6	120	32	10
0.1	2.0 10 <sup>-4</sup>	3.4 10 <sup>-3</sup>	2.6 10 <sup>-4</sup>	1.2 10 <sup>-7</sup>	4.2 10 <sup>-7</sup>	1.1 10 <sup>-6</sup>	88	25	10
0.15	2.4 10 <sup>-4</sup>	3.4 10 <sup>-3</sup>	2.9 10 <sup>-4</sup>	1.4 10 <sup>-7</sup>	3.8 10 <sup>-7</sup>	1.1 10 <sup>-6</sup>	74	27	9
0.2	3.2 10 <sup>-4</sup>	3.4 10 <sup>-3</sup>	3.5 10 <sup>-4</sup>	1.9 10 <sup>-7</sup>	2.8 10 <sup>-7</sup>	1.1 10 <sup>-6</sup>	54	37	9
0.3	5.1 10 <sup>-4</sup>	3.4 10 <sup>-3</sup>	3.7 10 <sup>-4</sup>	2.7 10 <sup>-7</sup>	1.5 10 <sup>-7</sup>	1.0 10-6	39	67	10
0.4	1.0 10 <sup>-3</sup>	3.4 10 <sup>-3</sup>	5.8 10 <sup>-4</sup>	3.7 10 <sup>-7</sup>	1.7 10 <sup>-7</sup>	8.9 10 <sup>-7</sup>	28	61	23
0.5	1.8 10 <sup>-3</sup>	3.4 10 <sup>-3</sup>	7.8 10 <sup>-4</sup>	7.2 10 <sup>-7</sup>	1.9 10 <sup>-7</sup>	7.0 10 <sup>-7</sup>	14	54	15
0.6	2.8 10 <sup>-3</sup>	3.4 10 <sup>-3</sup>	8.2 10-4	1.5 10 <sup>-6</sup>	2.6 10 <sup>-7</sup>	5.1 10 <sup>-7</sup>	7	40	21
0.7	3.2 10 <sup>-3</sup>	3.4 10 <sup>-3</sup>	1.2 10 <sup>-3</sup>	1.9 10 <sup>-6</sup>	2.9 10 <sup>-7</sup>	3.2 10 <sup>-7</sup>	5	35	32

Table S1 : Parameters used in the fitting of AC-electrogravimetry data at each stationnary potential

Part V: Film homogeneity on gold EQCM electrode.



Figure S9. SEM image of a spray casted composite film of  $H_x IrO_4$ , Csp and PVDF on a gold EQCM electrode

## Part VI: Structural determination.

Table S2 : Crystallographic data and Atomic positions of H<sub>4</sub>IrO<sub>4</sub>, determined from Rietveld refinement of its XRD pattern

$R\overline{3}m$ ; a = 3.026(5) Å; c = 14.138(7) Å; R <sub>Bragg</sub> = 6.11%; $\chi^2$ = 1.54; $\alpha$ = 90°; $\gamma$ = 120°; vol = 112.158 Å <sup>3</sup>									
atom	Wyckoff position	x/a	y/a	z/a	B <sub>iso</sub> (Ų)	occupancy			
0	6c	0	0	0.4002(9)	4.79(5)	1			
Ir	3a	0	0	0	2.39(12)	0.25			

Due to the small scattering factor of protons for X-rays, their structural positions within the structure have not been determined but solely speculated.

## References

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