

Towards Electrochemical Iridium Recycling in Acidic Media: Effect of the Presence of Organic Molecules and Chloride Ions – Supplementary Information

L. Moriau^{a, b *}, K. Stojanovski^c, P. Jovanovič^a, D. Escalera-López^c, S. Cherevko^c, N. Hodnik^{a, d}

^a Department of Materials Chemistry, National Institute of Chemistry, 1000 Ljubljana, Slovenia.

^b Center of Excellence Low-Carbon Technologies, 1000 Ljubljana, Slovenia.

^c Helmutz-Institute Erlangen Nürnberg for Renewable Energy (IEK-11), Forschungszentrum Jülich GmbH, Erlangen, Germany.

^d University of Nova Gorica, 5000 Nova Gorica, Slovenia.

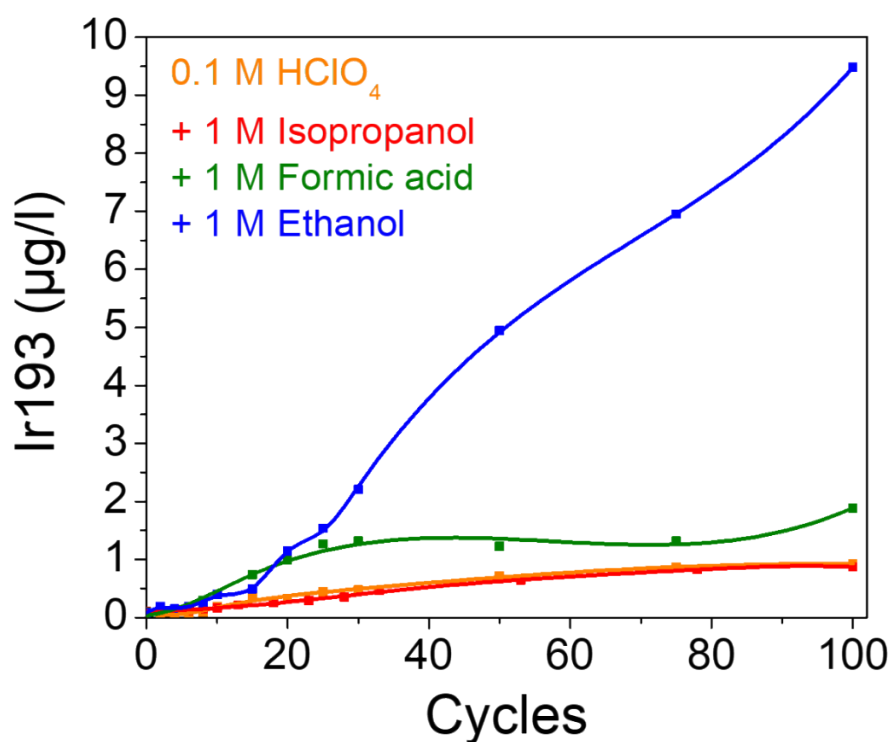


Figure S1. Comparison of the iridium dissolution in 0.1 M HClO₄ electrolyte and 1 M of different organics, ethanol in blue, formic acid in green and isopropanol in red.

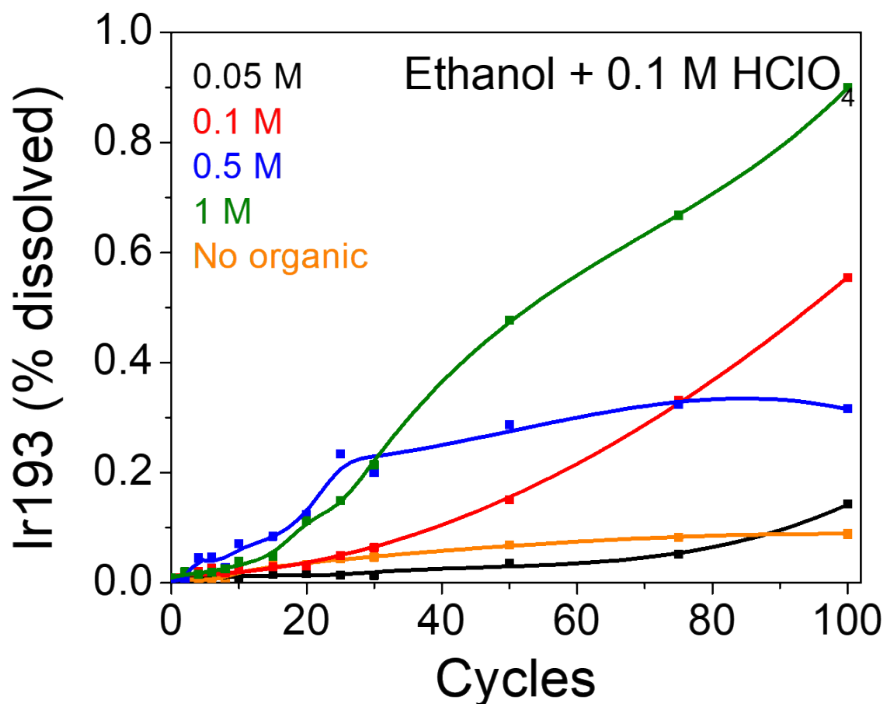


Figure S2. Percent of the iridium dissolved in 0.1 M HClO₄ electrolyte and different amounts of ethanol.

Discussion about the cyclic voltammetry of iridium in presence of formic acid and ethanol in HClO₄.

The CVs were recorded in a three-electrodes set-up. An Ag/AgCl electrode was used as a reference electrode and was previously calibrated against RHE while a carbon rod was utilized as the counter electrode. The working electrode was prepared by drop-casting 20 μ L of a 1mg/mL suspension of iridium (Iridium Black, Alfa Aesar). The suspension was sonicated before the drop-casting process to assure good homogeneity. The electrochemical protocol consisted of 10 cycles between 0.05 and 1.45 V_{RHE} at 10 mV/s followed by 3 cycles between 0.05 and 1.6 V_{RHE} at 5 mV/s under N₂ atmosphere. The electrolytes were saturated with N₂ during all the process. The experiments were reproduced three times. The resistance of the solution was compensated by 90%.

The cyclovoltammogram (CV) of iridium in HClO₄ present the characteristic features of iridium (Figure S3a)¹⁻³. Namely, the redox peak of the couple Ir(III)/Ir(IV) is observed at around 0.8 V_{RHE} while further oxidation of iridium (couple Ir(IV)/Ir(V/VI)) is visible after 1.2 V_{RHE}. These two reactions are reversible as the oxidation peaks are paired with reduction peaks at around the same potential. The layer formed is stable under oxygen evolution reaction as seen in Figure S3b. and the onset of the reaction is around 1.46 V_{RHE}.

The addition of formic acid in the solution leads to a different behaviour (Figure S3c). During the first cycle, an oxidative peak is also observed around 0.9 V_{RHE} followed by a steady increase in potential at 1.4 V_{RHE} (onset 1.23 V_{RHE}). The first oxidative peak overlap with the Ir(III)/Ir(IV) observed in HClO₄ but the higher current indicates another process is undergoing, i.e. Ir (IV) reacts with the forming acid and get directly chemically reduced back to Ir(III), which can be oxidized again leading to a higher current. The absence of reduction peak during the return scan is a proof of the discussed

mechanism. This indicates an electrochemical-chemical mechanism. Specifically, a first step is happening (first oxidative peak) where a specie (A: metallic iridium) is transformed during an electro-reaction into another specie (B: iridium-oxide/iridium-hydroxide). This is followed by the reaction between the newly formed specie (B) with another reactant (C: formic acid) in a chemical step. Afterwards, the specie B is not electrochemically converted back to A as indicated by the absence of reduction peak. In addition, only few cycles are sufficient to limit the first step (no more oxidation peak) as well as decreasing the second step. This could suggest that the specie B is blocked by the product or consume during its reaction with C and thus is not further available for reduction and for further reaction with C. Oppositely, when the upper limit is increased to $1.6 V_{RHE}$, the CVs are stable (Figure S3d). Moreover, the current is higher compared to pure $HClO_4$ electrolyte and the onset of reaction happens at lower potential. This is due to the combination of oxygen evolution reaction and organic oxidation reaction.

Finally, when ethanol is added in the $HClO_4$ solution, the couple oxide/reduction peak is still visible at around $0.8 V_{RHE}$ which slowly decreases with cycling and a sharp increase in current is visible from 1.2 to $1.4 V_{RHE}$. Nonetheless, a higher oxidative current is observed than for pure $HClO_4$, implying towards the consumption of some iridium oxide during organic oxidation, but less intense than in presence of FA. Also, the presence of the reduction peak means that the transient dissolution of iridium is still happening, oppositely that in presence of FA. In addition, the current during cycling to higher potential decreases quickly albeit the onset of reaction is at lower potential, i.e. $1.38 V_{RHE}$. Therefore, in presence of ethanol, both dissolution during organic oxidation and the transient dissolution during oxidation/reduction of iridium are present.

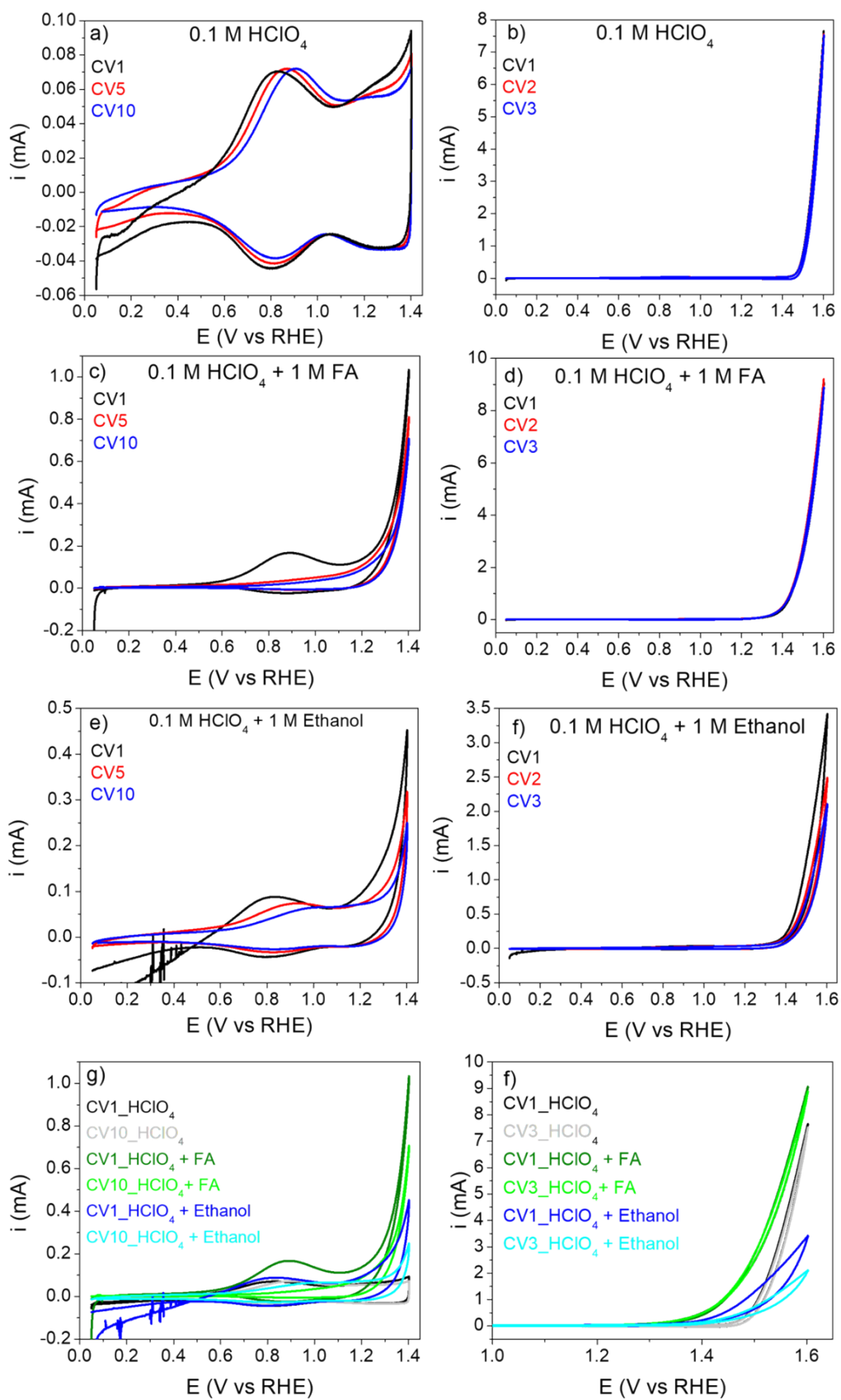


Figure S3. CVs of iridium in different electrolytes and in two different potential windows. Left column, 10 cycles between 0.05 and 1.45 V_{RHE} at 10 mV/s under N_2 atmosphere. Cycles 1, 5 and 10 are displayed. Right column, 3 cycles between 0.05 and 1.6 V_{RHE} at 5 mV/s under N_2 atmosphere. a

and b) CVs in 0.1 M HClO₄. c and d) CVs in 0.1 M HClO₄ + 1M Formic acid. e and f) CVs in 0.1 M HClO₄ + 1 M Ethanol. g and h) Comparison of the CVs in the different electrolytes.

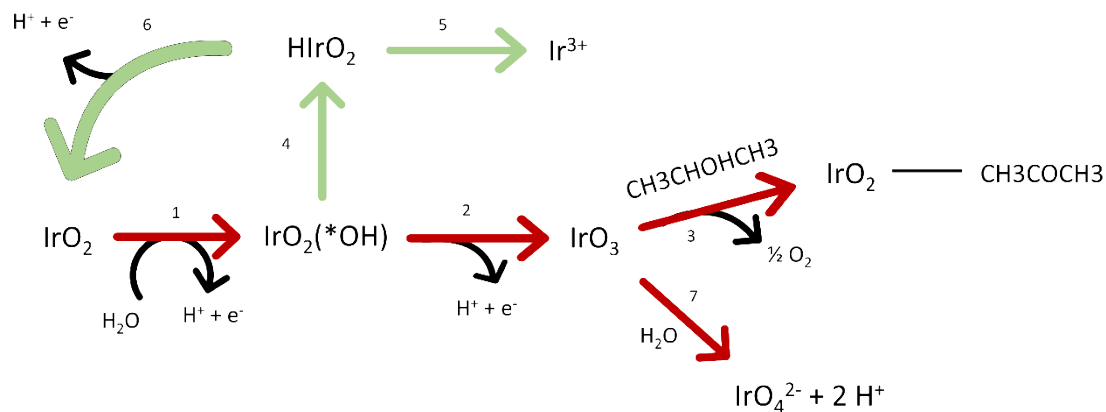


Figure S4. Scheme of the combined OOR and OER pathways for isopropanol.

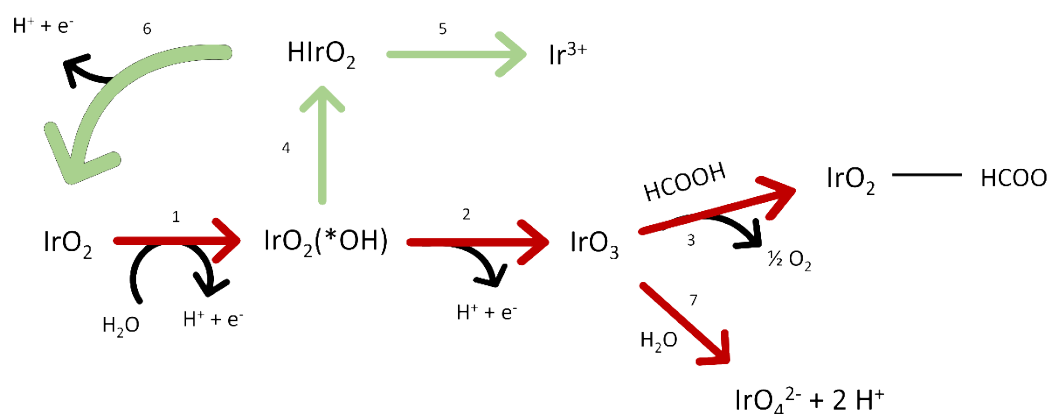


Figure S5. Scheme of the combined OOR and OER pathways for formic acid.

Table S1. Chemicals used for electrolyte solutions.

Chemicals	Purity	Provider
HClO ₄	Suprapur (98-100%)	Merck
HCl	Suprapur (98-100%)	Merck
Isopropanol	99.5+ %	Merck
Formic acid	> 98 %	Merck
Ethanol	99.9 %	Merck

Discussion S1. Calculation of the percent dissolution of an iridium monolayer.

To be able to calculate the percent dissolution of an iridium monolayer, two specific characteristics of the catalyst needs to be known: the ECSA (m^2/g) and the weight of one monolayer (ng/cm^2). The latter was assumed in a previous study to be $400 \text{ ng}/\text{cm}^2$ based on similarities between surface density of platinum and iridium atoms⁴.

In the case of ECSA, the supplier (Alfa Aesar) states that it is over $20 \text{ m}^2/\text{g}$ but does not provide an exact number. Therefore, a rough estimation was made based on nanoparticles sizes. The particle size of the particles was found to be between 3 and 5 nm based on TEM analysis. Therefore, if we assume that the particles are perfectly spherical, the surface area of one particle can be determined by the formula

$$A = 4\pi r^2$$

And thus, A is between 27.27 and 78.54 nm^2 for single particles between 3 and 5 nm, respectively.

In order to know the total surface area, the number of nanoparticles in the deposited catalysts need to be determined.

First, the volume of one nanoparticle is determined by

$$V = \frac{4}{3}\pi r^3$$

Resulting in a volume of 14.14 to 65.45 nm^3 for particles of 3 to 5 nm.

Knowing the density of iridium ($22.56 \text{ g}/\text{cm}^3$), the mass of one nanoparticle can be found to be $3.18 \cdot 10^{-19}$ to $1.48 \cdot 10^{-18}$ (for 3 to 5 nm).

As $22 \mu\text{g}$ of catalyst was deposited on the FTO, the number of nanoparticles is between

$$\frac{3.18 \cdot 10^{-19}}{22 \cdot 10^{-6}} = 6.9 \cdot 10^{13}$$

And

$$\frac{1.48 \cdot 10^{-18}}{22 \cdot 10^{-6}} = 1.49 \cdot 10^{13}$$

As we previously determined the surface area (A) of one nanoparticle, the total surface area of the deposited catalyst can be calculated and is 0.0019 to 0.0012 m^2 for 3 to 5 nm particles. Now, the ECSA can be determined by dividing the total surface area by the mass of catalyst loaded and 85.5-53.2 m^2/g was found.

These values are overestimated as they do not consider the surface of the particles that are not available, i.e. because of contact between particles, which explain the 2.5 to 4 times the value provided by the supplier ($>20 \text{ m}^2/\text{g}$). Similarly, Ioroi et al. measured a surface area of $44 \text{ m}^2/\text{g}$ on the same Ir-black by BET measurements⁵. On the other hand, Alia et al. measured a surface area of $29.4 \text{ m}^2/\text{g}$ for Ir-black (from Johnson Matthey) by mercury underpotential deposition⁶.

Finally, the total mass of one monolayer can be determined by multiplying the ECSA by 400 ng/cm² from literature⁴ to find the total mass of one monolayer. Therefore, the percent of monolayer can be calculated. Table S2 summarized the percent found for the different ECSA. The value from Ioroi et al. was selected as the most precise and presented in the article.

Table S2. Percent of an iridium monolayer dissolved based on the electrolyte and on the calculated ECSA.

Electrolyte	0.1 M HClO ₄	0.1 M HClO ₄ + 1 M Ethanol	0.1 M HCl	0.1 M HCl + 1 M Ethanol
Mass % of Ir dissolved	0.08	0.9	0.91	3.2
ECSA				
21 m ² /g From AA (>20)	1.04	10.71	10.87	35.34
29.4 m ² /g ⁵	0.74	7.65	7.77	25.24
44 m ² /g ⁶	0.50	5.12	5.19	16.87
53.2 m ² /g (5 nm particles)	0.42	4.23	4.29	13.95
85.5 m ² /g (3 nm particles)	0.26	2.63	2.67	8.68

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