

Electrochemical comparison of IrO₂ prepared by anodic oxidation of pure iridium and IrO₂ prepared by thermal decomposition of H₂IrCl₆ precursor solution

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Abstract Surface redox activities, oxygen evolution reaction (OER), oxidation of formic acid (FA), and anodic stability were investigated and compared for IrO₂ electrodes prepared by two techniques: the thermal decomposition of H₂IrCl₆ precursor (TDIROF) and the anodic oxidation of metallic iridium (AIROF). Surface redox activities involved on the AIROF were found to be much faster than those involved on the TDIROF. Concerning the oxygen evolution reaction, both films show a similar mechanism and specific electrocatalytic activities. The situation seems to be different for FA oxidation. In fact, on TDIROF, the oxidation of FA and the OER compete involving the same surface redox couple Ir(VI)/Ir(IV) contrary to FA oxidation on AIROF, where the Ir(V)/Ir(IV) surface redox couple is involved. Finally, electrode stability measurements have shown that contrary to TDIROF, which are very stable under anodic polarization, the AIROF are rapidly corroded under anodic treatment. This corrosion is enhanced even further in the presence of formic acid.

Keywords TDIROF · AIROF · Surface redox activity · Oxygen evolution · Formic acid oxidation · Anodic stability

1 Introduction

Iridium dioxide electrodes form part of the dimensionally stable anodes (DSA[®]), which are widely used in industry for metal electro-winning, cathodic protection, and electro-organic synthesis [1–4].

The first iridium dioxide electrodes, as described in the corresponding patents [5, 6], were thermally decomposed iridium oxide films (TDIROF) produced by thermal decomposition of the appropriate precursor solution on an inert substrate such as titanium or tantalum.

Later, other techniques of conductive IrO₂ film formation such as the anodic oxidation of metallic iridium were considered. In fact, it has been shown that pure iridium and mostly the corresponding anodic iridium oxide film (AIROF) formed through potential cycling exhibit some interesting electrochemical properties and especially toward the oxygen evolution reaction (OER) [7–9].

Although the activity and stability of AIROF and TDIROF toward OER have been widely studied [1–4, 10–12], the mechanisms involved in the process are still a matter of discussion.

More recently, the electro-catalytic activity of TDIROF toward the oxidation of organics has been described. However, little is known about the surface redox activity and stability during the oxidation of organics on AIROF.

However, as the participation of the TDIROF coating via the IrO₃/IrO₂ redox couple during OER and the oxidation of formic acid in acidic media has been proved

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recently using DEMS [13, 14], the aim of the present study is to compare an IrO₂ electrode prepared by anodic oxidation of pure Ir (AIROF) with an IrO₂ electrode prepared by thermal decomposition of a precursor solution (TDIROF) by investigating the surface redox activities in the water stability potential region as well as during the OER and the oxidation of formic acid as model organic compound.

2 Experimental

All electrochemical experiments were performed in a classical three-electrode cell (70 mL) using an Autolab PGSTAT 30. The counter electrode was a Pt wire; the reference electrode was Hg/Hg₂SO₄/K₂SO₄ (sat.) (MSE; 0.65 V vs. SHE) and two different working electrodes were used:

- Anodic iridium oxide film electrode (AIROF): An iridium film (0.1 μm) was deposited by sputtering on p-Si (0.0054 mm²) using a thin (0.02 μm) tantalum interlayer (p-Si/Ir). The anodic iridium oxide film (AIROF) was formed through potential cycling of this electrode between -0.05 and 1.45 V.
- An IrO₂ electrode prepared by thermal decomposition of a precursor (TDIROF): the IrO₂ film (0.35 mg cm⁻²) was deposited on disc-shaped sandblasted p-Si (182.25 mm²) by the thermal decomposition of a H₂IrCl₆ (99.9%, ABCR) precursor solution in air at 500° (TDIROF). The presence of iridium dioxide on the substrate was verified using XPS measurements (not presented).

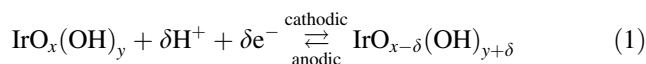
All potentials in this work are with respect to the standard hydrogen electrode (SHE).

3 Results and discussion

3.1 Surface redox activities

The cyclic voltammetry measurements of IrO₂ films prepared by the thermal decomposition technique (TDIROF), recorded for three potential windows in the potential range between 0.0 and 1.4 V and presented in Fig. 1, show two main features:

- The charge involved in the anodic scan is completely recovered during the cathodic scan ($q_+ = q_-$) for all the scan rates investigated (10–500 mV s⁻¹). However, the CV shows an axial symmetry (around the potential axis) only if the lower potential limit is higher than 0.4 V. In fact, at lower potential limits, a strong distortion of the CV around the potential axis is observed. This is an indication that the surface processes involved at low potentials (<0.4 V) are slow.
- The TDIROF are completely inactive toward the electrochemical reduction of dissolved oxygen (aerated and de-aerated solutions give the same CV).
- Furthermore, from measurements of the apparent activation energy (E_a) for the charging/discharging process using TDIROF reported in a previous paper [15], we have to consider two contributions. The first contribution is due to a fast (instantaneous) process with zero activation energy related to the charging of the electrical double-layer at the electrode–electrolyte interface and the second is related with the slow diffusion of protons within the IrO₂ coating inducing surface redox activities (Eq. 1) with an activation energy around 2.4 kJ mol⁻¹ [15].



The cyclic voltammetry measurements of IrO₂ films prepared by the anodic oxidation of metallic iridium

Fig. 1 Cyclic voltammograms using TDIROF (IrO₂ loading: 0.273 mg cm⁻²) at 100 mV s⁻¹ for different potential windows *a* between 0.3 and 1.1 V, *b* between 0.3 and 1.4 V, *c* between 0 and 1.4 V. Supporting electrolyte: 1 M HClO₄. *T* = 25 °C

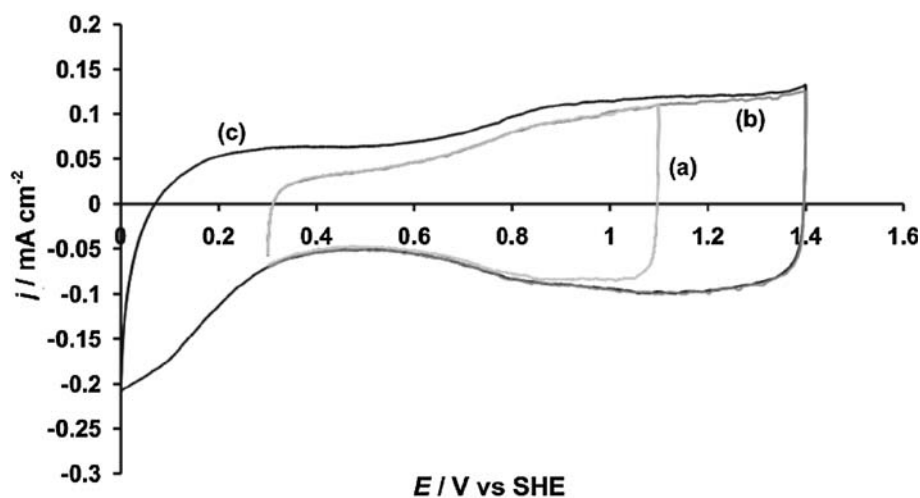
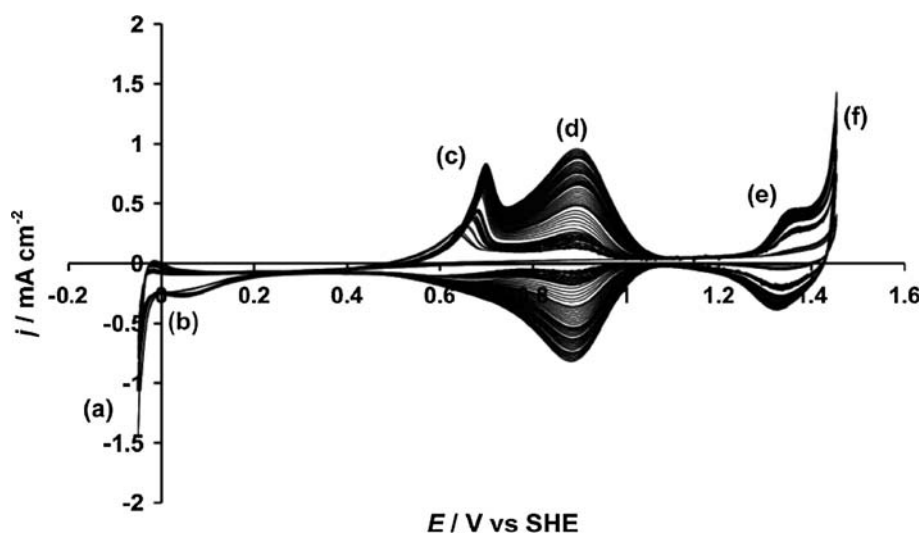


Fig. 2 Successive cyclic voltammograms (three scan number intervals: from scan 1 to scan 40; from scan 90 to scan 130 and from scan 150 to scan 350) using a p-Si/Ir electrode at 50 mV s^{-1} between -0.05 and 1.45 V . Supporting electrolyte: $1 \text{ M H}_2\text{SO}_4$, $T = 25 \text{ }^\circ\text{C}$. *a* hydrogen evolution domain, *b* reduction of dissolved O_2 domain, *c* pre-peak, *d* redox couple Ir(IV)/Ir(III), *e* redox couple Ir(V)/Ir(IV) and *f* oxygen evolution reaction domain



(AIROF) are very different from those obtained using TDIROF. These anodic films are obtained by cycling the potential in the range between -0.05 and 1.45 V . Figure 2 shows three series of consecutive CV scans (from scan 1 to scan 40, from scan 90 to scan 130 and from scan 150 to scan 350) recorded at 50 mV s^{-1} in $1 \text{ M H}_2\text{SO}_4$ using a metallic iridium electrode. The results are in very good accordance with similar CV curves found in literature [11, 12]. The first voltammograms show almost no surface activity between hydrogen evolution at -0.05 V (Region (a) in Fig. 2) and oxygen evolution at 1.45 V (Region (f) in Fig. 2), which are the first signals to appear together with dissolved O_2 reduction at 0.2 V (Region (b) in Fig. 2) in aerated solution. This last reaction has been clearly identified as no activity was observed in that potential region when using de-aerated solutions.

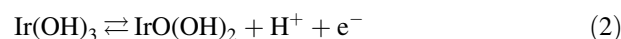
After approximately 50 scans, three anodic peaks appear at 0.65 V (peak (c) in Fig. 2), 0.9 V (peak (d) in Fig. 2) and 1.2 V (peak (e) in Fig. 2). The irreversible peak (c) (reported as pre-peak) is the first to appear followed by the reversible peaks (d) and (e) before oxygen evolution.

The pre-peak is progressively shifted toward more positive potentials with increasing scan number (from 0.65 V for scan number 50 to 0.7 V for scan number 350); however, the position of peaks (d) and (e) are only slightly shifted with increasing scan number. These shifts are certainly related to the reversibility of the surface processes involved.

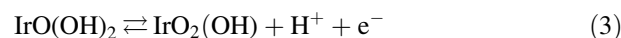
Figure 3 shows CV measurements of AIROF obtained in the potential range between -0.05 and 1.25 V then moving toward the upper potential limit with increments of 20 mV up to 1.49 V . This figure shows clearly that the reduction of dissolved oxygen at 0.2 V is strongly related with the oxygen evolution reaction, which has an onset potential of about 1.36 V .

The surface reactions related to redox couples (d) and (e) have been discussed in literature [11, 12] and are believed to be the following:

At 0.9 V , peak (d) on fig. 2:



At 1.35 V , peak (e) on fig. 2:



These cyclic voltammetry measurements show that TDIROF and AIROF have different kinetics for the involved surface redox activity. In fact, on iridium dioxide prepared through thermal decomposition (TDIROF), the surface process is slow while on the oxide film prepared anodically (AIROF), numerous fast surface redox reactions are involved. Furthermore, AIROF are active toward the reduction of dissolved oxygen contrary to TDIROF, which is inactive toward the same process.

These differences are mainly due to the preparation technique of the electrode. In fact, AIROF are produced under mild conditions involving the anodic oxidation at room temperature through potential cycling of pure iridium metal. It has been shown that this method yields much more hydrated IrO_2 with higher bulk defect densities compared to TDIROF [16]. Furthermore, it has been shown that treating the AIROF at high temperature, which implies the loss of water molecules, yields to an electrode whose behavior tend to approach the one of TDIROF [8]. It is therefore clear that the observed differences in the surface processes between TDIROF and AIROF are related to the hydration of the obtained oxide.

3.2 The oxygen evolution reaction

Figure 4 shows a typical steady polarization curve for the OER on TDIROF electrodes in 1 M HClO_4 . In the same

Fig. 3 Cyclic voltammograms recorded at 50 mV s^{-1} using AIROF for different potential windows: the lower cut-off was fixed at -0.05 V while the higher cut-off varies from 1.25 to 1.49 V with increments of 20 mV . Supporting electrolyte: $1 \text{ M H}_2\text{SO}_4$. $T = 25 \text{ }^\circ\text{C}$

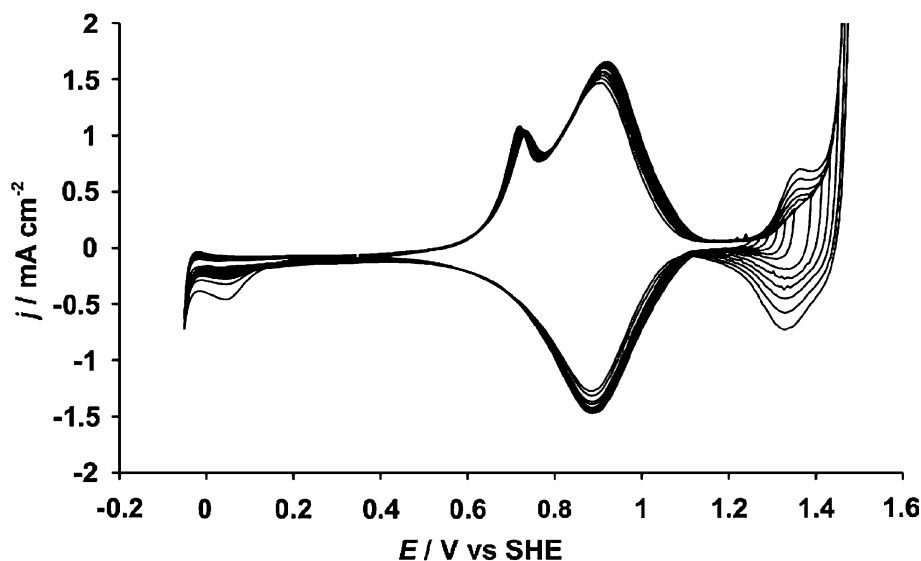
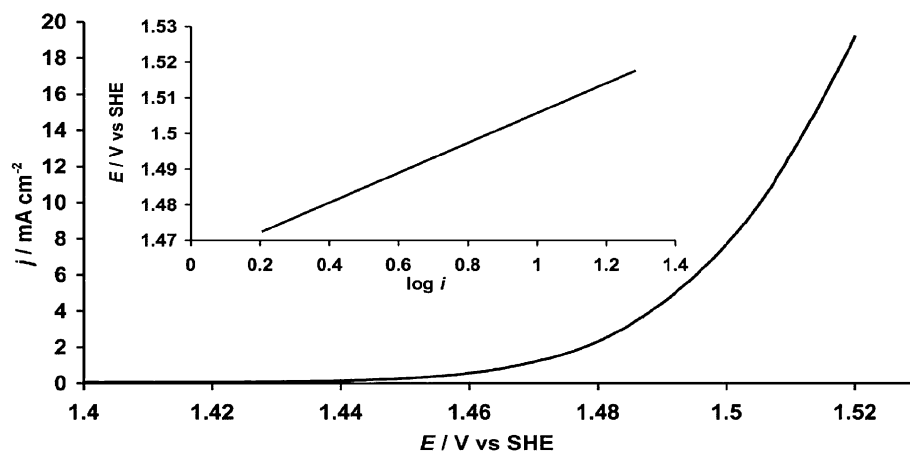


Fig. 4 Steady-state polarization curves recorded between 1.4 and 1.52 V using TDIROF (IrO_2 loading: 0.35 mg cm^{-2}). Inset Corresponding IR drop-corrected Tafel plot. Supporting electrolyte: 1 M HClO_4 . $T = 25 \text{ }^\circ\text{C}$



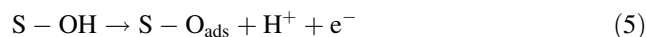
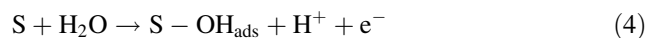
figure, the corresponding Tafel plot obtained after IR drop correction (inset of Fig. 4) is also given. It can be seen that even at high overpotentials, the IR drop-corrected Tafel plot gives a linear relation with a slope of about 40 mV/decade .

It is worthwhile to notice that these polarization measurements are reproducible even after treatment of the electrode for a long period of time (several hours) at high anodic potentials ($>1.5 \text{ V}$). This is an indication of the high anodic stability of the TDIROF.

Figure 5 shows IR drop corrected Tafel plots obtained for a fresh iridium electrode (p-Si/Ir) ((a) on Fig. 5) and for AIROF ((b) on Fig. 5) formed by potential cycling ($50 \text{ cycles at } 50 \text{ mV s}^{-1}$ between -0.05 and 1.45 V).

This figure shows clearly that the Tafel slope for the OER changes from 120 mV/decade for the Ir metal to 40 mV/decade for the AIROF indicating that the rate determining step of the OER on pure iridium differs from the one occurring on AIROF.

In acid medium, the following reaction path (Eqs. 4, 5 and 6) was proposed for the oxygen evolution reaction (OER) on active oxide electrodes [17].



where S stands for active sites and OH_{ads} , O_{ads} are adsorption intermediates.

This mechanism predicts the following Tafel slopes: 120 mV/decade if step 4 is the rate-determining step (rds), 40 mV/decade for step 5 and 30 mV/decade for step 6.

The measured Tafel slopes indicate that water discharge (step 4) is the rds for the OER on metallic iridium (Tafel slope 120 mV/decade) and formation of a higher oxide (step 5) is the rds in case of IrO_2 formed either by the anodic oxidation of metallic Ir (AIROF) or by the thermal

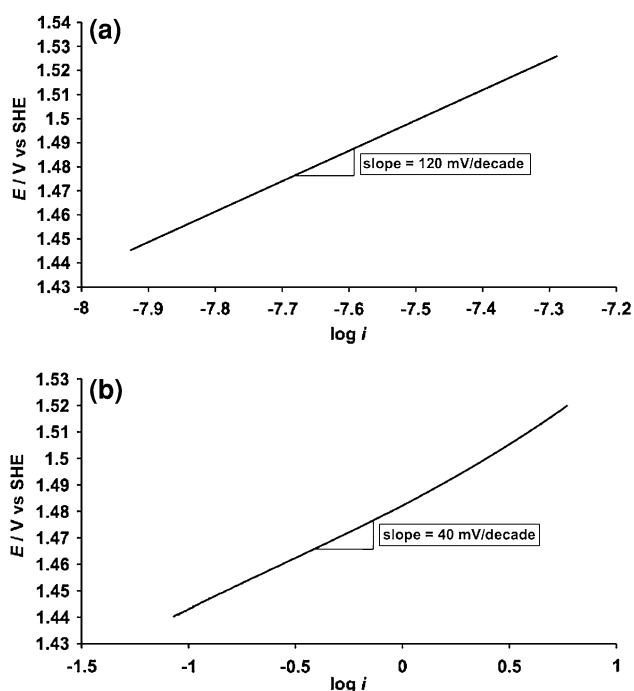


Fig. 5 IR drop-corrected Tafel slopes recorded between 1.44 and 1.52 V corresponding to: **a** fresh p-Si/Ir electrode, **b** AIROF. Supporting electrolyte: 1 M H₂SO₄. T = 25 °C

decomposition of a precursor solution (TDIROF). This is an indication that the same mechanism of OER is involved on both AIROF and TDIROF. The participation of the higher oxide in the OER on TDIROF via the IrO₃/IrO₂ redox couple has been recently demonstrated using ¹⁸O labelling together with differential electrochemical mass spectrometry (DEMS) measurements [13].

It is worthwhile to notice that the treatment of the AIROF at high potentials (>1.6 V) for a few minutes results in an increase of Tafel slope from 40 to 120 mV/decade. This is an indication that at these potentials, the anodically formed film is corroded as already reported by others [10, 18].

Figure 6 shows that the normalized polarization curves (the current is reported relative to the voltammetric charge measured from the CV curves between -0.05 and 1.45 V at 50 mV s⁻¹) for the OER are almost the same for both TDIROF and AIROF electrodes. This is an indication that both electrodes have almost the same specific electrocatalytic activity.

However, it is worthwhile to mention that the obtained Tafel plots for the OER using TDIROF in this work (40 mV/decade) are different from those reported by others. In fact, a Tafel slope of 60 mV/decade for the OER in acidic media has been usually reported [17, 19]. A very intriguing reaction path involving S-OH_{ads} intermediates with different energy states has been proposed by these authors in order to explain this abnormal Tafel slope

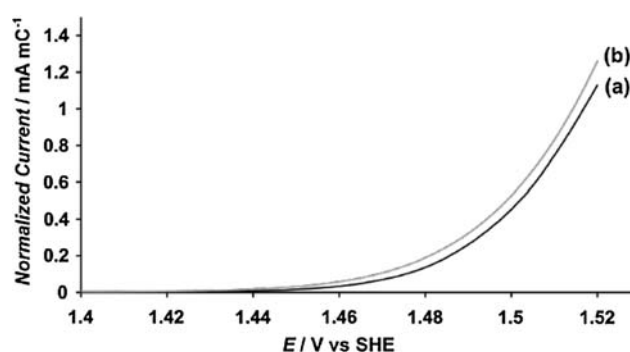


Fig. 6 Normalized steady-state polarization curves using: **a** the AIROF, **b** the TDIROF (IrO₂ loading: 0.35 mg cm⁻²). The current has been normalized relative to the voltammetric charge measured between -0.05 and 1.45 V at 50 mV s⁻¹. T = 25 °C

[17, 19]. Problems related with uncompensated IR drop correction and partial blockage of the electrode surface by the evolved oxygen are certainly related with the reported abnormal Tafel slopes. In the present study, the experiments have been carefully conducted in order to avoid these problems.

3.3 Oxidation of organics using formic acid as a model compound

Figure 7 shows steady-state polarization curves obtained on TDIROF in 1 M HClO₄ containing different concentration of Formic Acid (FA). The shift of these I-V curves toward less positive potentials in presence of FA is related with the involvement of the same redox couple IrO₃/IrO₂ in both the oxygen evolution reaction (Eq. 9) and FA oxidation (Eq. 10) competing during the process according to the reaction path given in Eq. 7–10.

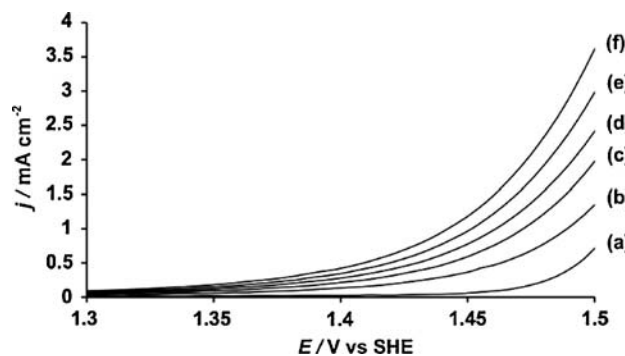
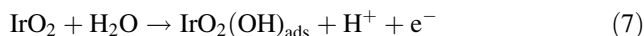
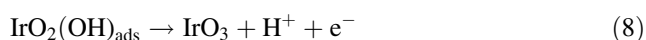
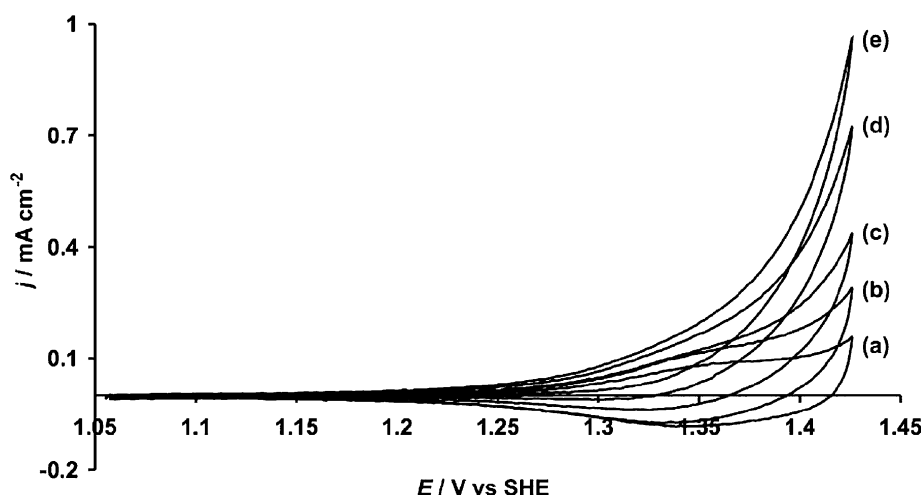


Fig. 7 Steady-state polarization curves between 1.3 and 1.5 V using TDIROF (IrO₂ loading: 0.35 mg cm⁻²) for different concentration of formic acid: **a** 0 mM, **b** 195.33 mM, **c** 387.78 mM, **d** 577.4 mM, **e** 764.25 mM and **f** 948.41 mM. Supporting electrolyte: 1 M HClO₄. T = 25 °C

Fig. 8 Cyclic voltammograms recorded at 100 mV s^{-1} between 1.055 and 1.425 V using AIROF for different concentration of formic acid: *a* 0 mM, *b* 100 mM, *c* 250 mM, *d* 500 mM and *e* 750 mM. Supporting electrolyte: 1 M H_2SO_4 . $T = 25 \text{ }^\circ\text{C}$



This mechanism has been proved recently on TDIROF electrodes using ^{18}O labelling combined with DEMS measurements [14, 20].

Figure 8 shows CV obtained on AIROF in 1 M H_2SO_4 containing different concentration of formic acid. This figure clearly shows that the reduction peak related with the redox couple Ir(V)/Ir(IV) decreases strongly with increasing FA concentration. This is an indication that this redox couple is involved during FA oxidation on AIROF.

It is worthwhile to notice that the anodic oxide film was completely corroded at the end of these experiments.

4 Conclusions

The main conclusions can be summarized below:

- The surface redox activities involved on the AIROF are much faster than those involved on the TDIROF. Formation of a highly hydrated AIROF is certainly the main reason of the high surface activity of IrO_2 film electrodes obtained by the anodic polarization of Ir metal (AIROF).
- The investigation of the oxygen evolution reaction in acid media has shown that both films show similar mechanisms (same Tafel slope of 40 mV/decade) and specific electrocatalytic activity (similar normalized I–V curves).
- The involved surface redox couple during the anodic oxidation of formic acid (FA) depends strongly on the preparation mode of the IrO_2 anodes. In fact, on TDIROF the oxidation of FA and the OER compete

involving the same surface redox couple Ir(VI)/Ir(IV). However, this is not the case on the AIROF, where the oxidation of FA involves the Ir(V)/Ir(IV) surface redox couple and is not competing with the OER.

- Electrode stability measurements have shown that contrary to TDIROF, which are very stable under anodic polarization, the AIROF are rapidly corroded under anodic treatment. This corrosion is further enhanced in the presence of formic acid.

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