

Estimation of the effectiveness factor of an outer-sphere redox couple ($\text{Fe}^{3+}/\text{Fe}^{2+}$) using rotating disk Ti/IrO₂ electrodes of different loading

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Abstract The effectiveness factor; E_f , defined as the fraction of the surface that participates effectively in a given reaction, is an important parameter when operating three-dimensional (3D) electrodes. The rotating disk electrode (RDE) technique with the $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox couple as a probe reaction has been used for the evaluation of the effectiveness factor of 3D Ti/IrO₂ electrodes with different IrO₂ loading. For this purpose, steady-state polarization measurements using Ti/IrO₂ rotating disk electrodes in 0.5 M $\text{Fe}^{3+}/\text{Fe}^{2+}$ in 1 M HCl were carried out under well-defined hydrodynamic conditions. The low-field approximation relation has been used for the estimation of the exchange current densities j_0 , of the $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox couple. It was found for this redox couple that the effectiveness factor is very low (<2%) and essentially the 2D electrode surface area works effectively in the steady-state polarization measurements.

Keywords Ti/IrO₂ electrodes · Rotating disk electrode (RDE) technique · $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox couple · Effectiveness factor

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1 Introduction

The effectiveness factor E_f is well known in heterogeneous catalysis as the measure of how much the reaction rate is lowered because of the resistance to catalyst pore diffusion [1]. In 1976, Coeuret et al. [2] presented the effectiveness factor E_f for the first time in electrochemistry for a 3D electrochemical reaction. These authors attributed the observed decrease of effectiveness with increasing electrode thickness to an overpotential distribution within the porous electrode and defined the effectiveness factor as the ratio of the measured electrolytic current and the current obtained with an electrode whose overpotential is maintained constant. The application of this is in the electrolytic treatment of diluted solutions for the recovery of metal ions using a 3D porous electrode. Later, Savinell et al. [3] used the effectiveness factor E_f for the investigation of the DSA[®] electrodes.

In this paper, the effectiveness factor E_f , defined as the fraction of the surface which participates effectively in the investigated reaction, has been determined for Ti/IrO₂ electrodes. The outer-sphere redox couple $\text{Fe}^{3+}/\text{Fe}^{2+}$ (which is a fast reaction) was used as a probe. Conditions of low overpotential and high concentration have been chosen in order to minimize the effect of bulk diffusion.

2 Experimental

In order to determine the exchange current density of the Ti/IrO₂ electrodes, the rotating disk electrode (RDE) technique, in which with this configuration the hydrodynamic properties and the mass transport kinetics are well defined, is used.

2.1 Preparation of the Ti/IrO₂ rotating disk electrodes

Sandblasted titanium wire ($\phi = 4$ mm) was used as substrate for the deposition of the IrO₂ coatings. The Ti/IrO₂ rotating disk electrodes have been prepared by thermal decomposition of H₂IrCl₆ (99.9% ABCR) precursor at 500 °C in air. The aqueous precursor solution of 46 mM was applied by brush application of the Ti substrate that was previously treated in boiling 1 M oxalic acid ($\geq 97\%$ Fluka) solution. The lateral insulation of the Ti/IrO₂ rotating disk electrodes was done by Teflon as in the case of commercial RDEs. The resulted IrO₂ loading has been estimated from the cyclic voltammetric charge measured under identical conditions as proposed by Savinell et al. [3], namely, in 1 M H₂SO₄ at a scan rate of 20 mV s⁻¹ in the potential range of 0.05–1.00 V versus SCE. In fact, the voltammetric charge (either anodic or cathodic) obtained for a large series of IrO₂ electrodes prepared by the above method showed a good linear correlation with the loading to give an average specific charge of 24 ± 3 mC mg⁻¹ IrO₂ [4]. Despite the somewhat different conditions of the preparation, this value is in reasonably good semi-quantitative agreement with that (31 ± 3 mC mg⁻¹ IrO₂) reported in [3], which allows us to also adopt the value of specific surface area (102 ± 6 cm² mg⁻¹ IrO₂) proposed in [3] on the basis of Zn²⁺ ion adsorption measurements. Four Ti/IrO₂ rotating disk electrodes of different loadings ($E_{0.62}$, $E_{1.97}$, $E_{2.46}$, and $E_{4.92}$) were prepared this way; where E represents the electrode and the number in subscript represents the loading in mg IrO₂ cm⁻².

2.2 Steady-state polarization measurements using RDEs

Steady-state polarization measurements (scan rate 0.1 mV s⁻¹) with the Fe³⁺/Fe²⁺ redox couple (0.5 M FeCl₃ + 0.5 M FeCl₂ in 1 M HCl) were carried out at 25 °C in a three-electrode cell using either a Ti/IrO₂ or a commercial Pt rotating disk electrode ($\phi = 4$ mm; exposed geometric surface area: 0.125 cm²) as working electrode (WE), Pt wire (Goodfellow 99.99%) as a counter electrode (CE) and MSE (Hg/Hg₂SO₄/K₂SO₄sat. Radiometer REF621) as a reference electrode (RE). The latter was equipped with a Luggin capillary and placed at a distance of 3 cm from the working electrode. It was experimentally confirmed that increasing the RE to WE distance above 3 cm no longer affected the obtained steady-state current—overpotential response, indicating invariant uncompensated ohmic drop. A computer-controlled EcoChemie potentiostat (model Autolab[®] PGSTAT 30) and a RDE equipment E.G.&G Parc model 616 were used at five rotation rates: 100, 500, 1,000, 1,500, and 2,000 rpm. Overpotentials are

Fig. 1 Ohmic drop-corrected steady-state (0.1 mV s⁻¹) polarization curves of Ti/IrO₂ rotating disk electrodes of different loading: **a, b** $E_{0.62}$, **c, d** $E_{1.97}$, **e, f** $E_{2.46}$ and **g, h** $E_{4.92}$, recorded at different rotation rates: $\omega = 100, 500, 1,000, 1,500,$ and $2,000$ rpm. *Left (a, c, e, g):* $I-\eta$ curves. *Right (b, d, f, h):* $III_{\text{lim}}-\eta$ curves (with $I_{\text{lim}} = I$ taken at ± 0.3 V). Electrolyte: 0.5 M Fe³⁺ + 0.5 M Fe²⁺ in 1 M HCl. T = 25 °C

with respect to the standard potential of the Fe³⁺/Fe²⁺ redox couple (0.77 V vs. NHE).

The steady-state polarization curves were corrected for the uncompensated potential drop ΔE [V] between WE and RE, estimated according to Eq. (1) [5]:

$$\Delta E = \frac{I}{4 \cdot \gamma_0 \cdot r} \quad (1)$$

where I is the measured current [A], γ_0 the conductivity of the electrolyte [Ω^{-1} cm⁻¹] and r the disk radius [cm]. A value of $\gamma_0 = 0.8 \Omega^{-1}$ cm⁻¹ was used, estimated from literature data [3, 6].

2.3 Estimation of the effectiveness factor of Ti/IrO₂ electrodes

The effectiveness factor is calculated with the exchange current density j_0 of the Fe³⁺/Fe²⁺ redox couple using Eq. (2):

$$E_f = \frac{(j_0)_{3D}}{(j_0)_{2D} \gamma_{3D}} \quad (2)$$

where $(j_0)_{3D}$ is the exchange current density (measured current reported to 1 cm² projected area) for a (three-dimensional) IrO₂ electrode with a given loading, $(j_0)_{2D}$ is the exchange current density measured with a polished (two-dimensional) Pt electrode and γ_{3D} is the 3D roughness factor of the IrO₂ electrode with the given loading. The charge transfer with the Fe³⁺/Fe²⁺ redox couple being an outer-sphere reaction $(j_0)_{2D}$ can be measured, in principle, with any polished electrode.

The 3D roughness factor γ_{3D} of Ti/IrO₂ electrodes described in [4] is calculated using Eq. (3):

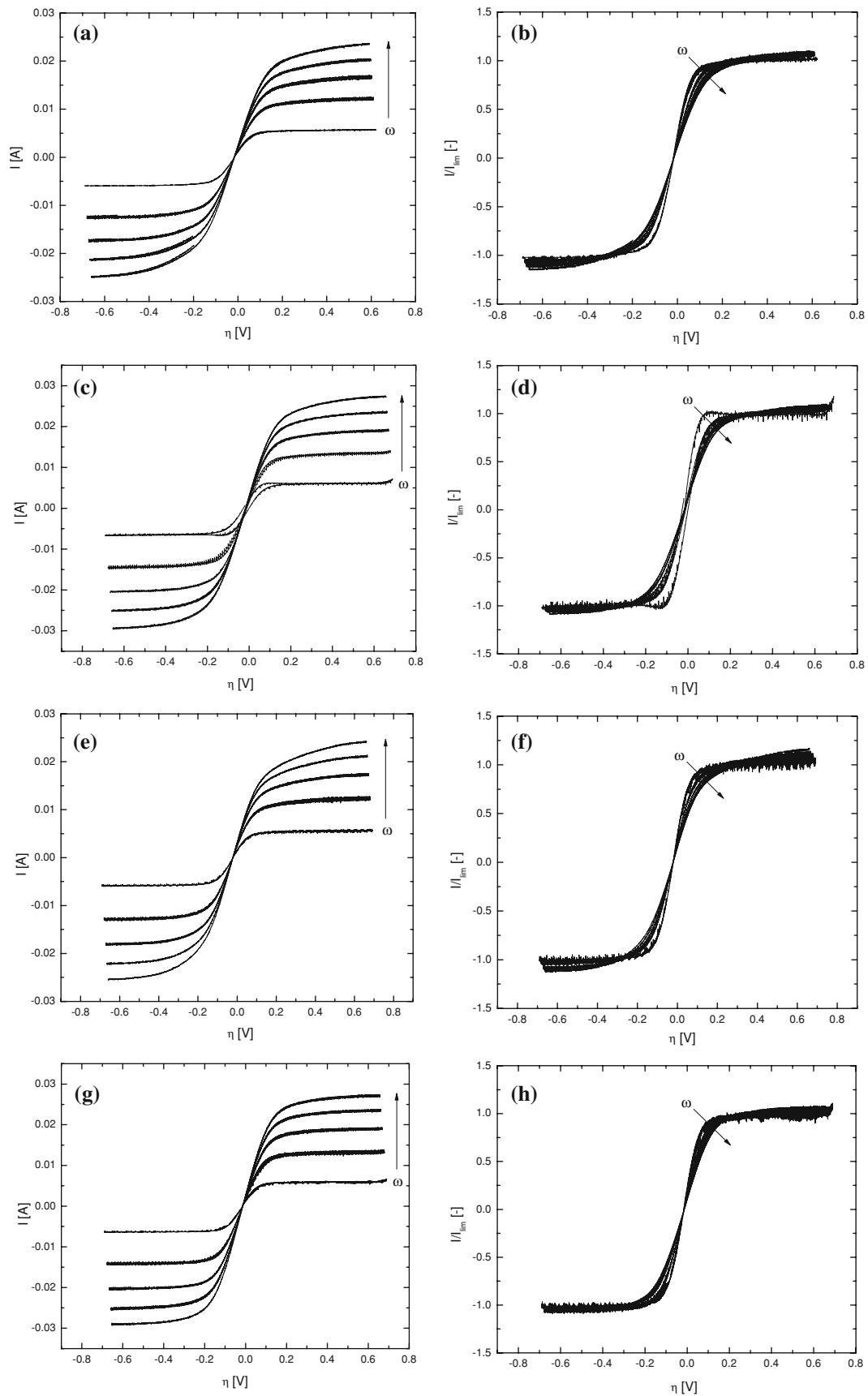
$$\gamma_{3D} = a_{\text{sp}} \cdot m_{\text{sp}} \quad (3)$$

where a_{sp} is the specific surface area (102 ± 6 cm² mg⁻¹ IrO₂) of the coating taken from [3] and m_{sp} is the specific loading [mg IrO₂ cm⁻²].

3 Results and discussion

3.1 Polarization curves

Figure 1 shows ohmic drop corrected, steady-state (0.1 mV s⁻¹) current—overpotential, $I-\eta$, curves and



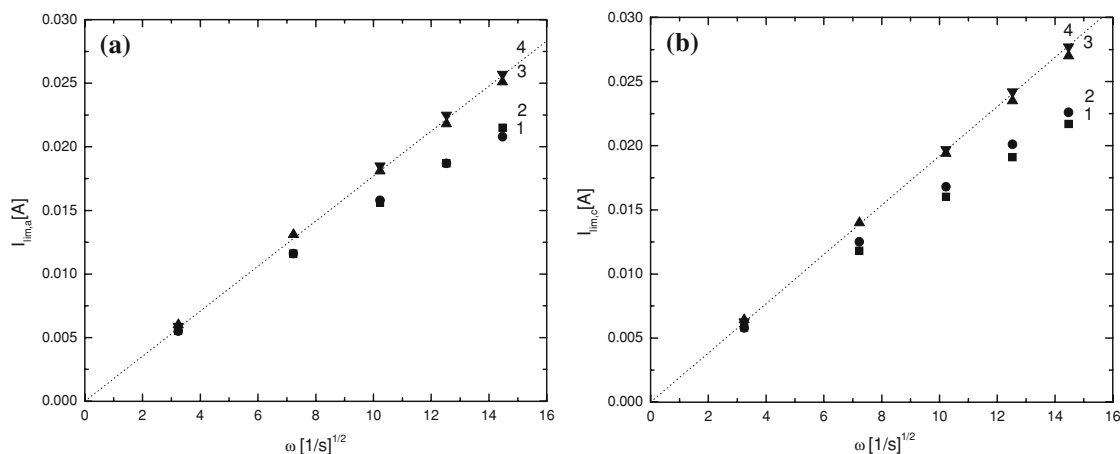


Fig. 2 Plot of the **a** anodic and **b** cathodic limiting current, $I_{\text{lim,a}}$ and $I_{\text{lim,c}}$ (taken at $\eta = +0.3$ and -0.3 V, respectively), as a function of the square root of the rotation rate, $\omega^{1/2}$ for Ti/IrO₂ rotating disk

electrodes of different loading: 1: $E_{0.62}$, 2: $E_{1.97}$, 3: $E_{2.46}$, and 4: $E_{4.92}$. Experimental conditions as in Fig. 1

$I/I_{\text{lim}}-\eta$ curves (the limiting currents, I_{lim} being taken at $\eta = \pm 0.3$ V) obtained at different rotation rates (100, 500, 1,000, 1,500, and 2,000 rpm) using four electrodes of different loading ($E_{0.62}$, $E_{1.97}$, $E_{2.46}$ and $E_{4.92}$). The anodic and cathodic limiting currents plotted as a function of the square root of rotation rate for the four investigated electrodes are shown in Fig. 2.

From Figs. 1 and 2, the following points should be noted:

- The normalized ($I/I_{\text{lim}}-\eta$) polarization curves do depend on rotation rate (see Fig. 1).
- At low loading and high rotation rates, even in the range of high overpotentials, the current continues to increase slightly with the applied potential without reaching a limiting value (see Fig. 1).
- At low loading and high rotation rates, the $I_{\text{lim}}-\omega^{1/2}$ curves deviate from linearity (series 1 and 2 in Fig. 2).

These anomalies observed at high rotation rates and low loading might be explained by the surface roughness of the investigated electrodes. Electrodes of low loading have higher surface roughness factors inherent to the preparation procedure of the used Ti substrate. In fact, Ti has a very rough surface after sandblasting. Increasing loading seems to decrease the surface roughness of the electrode. At high rotation rates, where the thickness of the diffusion layer goes down to a few micrometers (see in Table 1), the

behavior of rough electrodes do not follow the theory of RDE, developed considering perfectly polished surfaces, because the diffusion layer thickness approaches the scale of surface roughness. Note that possible contribution of a local turbulence, born at higher rotation rates to the observed anomalies, also cannot be excluded. Elucidation of the reasons of this behavior is out of scope of this paper.

From the slope of the obtained straight lines in Fig. 2 (considering the two high loadings), the diffusion coefficient of both Fe³⁺ and Fe²⁺ were calculated using the Levich equation (Eq. 4):

$$I_{\text{lim}} = 0.62 \cdot nFAD^{2/3}\omega^{1/2}\nu^{-1/6}C \quad (4)$$

where I_{lim} is the limiting current [A], n the number of exchanged electrons ($=1$), F the Faraday constant ($=96,500$) [Cmol⁻¹], A the geometrical surface of the RDE [cm²], D the diffusion coefficient [cm² s⁻¹], C the concentration [molcm⁻³] of the electroactive species (Fe³⁺ or Fe²⁺), ω the angular velocity [s⁻¹] and ν the kinematic viscosity ($=1 \times 10^{-2}$) [cm² s⁻¹]. For the species Fe³⁺ and Fe²⁺, respectively, diffusion coefficients of $(3.6 \pm 0.1) \times 10^{-6}$ and $(3.3 \pm 0.1) \times 10^{-6}$ cm² s⁻¹ were calculated, in reasonable good agreement with the respective literature values (5.4×10^{-6} and 4.4×10^{-6} [7]) and with those (3.2×10^{-6} and 2.8×10^{-6} cm² s⁻¹) obtained under the same experimental conditions using a polished platinum RDE.

The diffusion layer thickness δ [μm] was estimated using Eq. (5) taking the average diffusion coefficient of Fe³⁺ and Fe²⁺ equal to $(3.4 \pm 0.2) \times 10^{-6}$ cm² s⁻¹:

$$\delta = 1.61 \cdot D^{1/3}\omega^{-1/2}\nu^{1/6} \quad (5)$$

The estimated diffusion layer thickness at different rotation rates is given in Table 1. Furthermore, in knowledge of the

Table 1 Thickness of the diffusion layer δ at different rotation rates calculated with Eq. (5) taking the average diffusion coefficient of Fe³⁺ and Fe²⁺ equal to $(3.4 \pm 0.2) \times 10^{-6}$ cm² s⁻¹

Rotation rate (rpm)	100	500	1,000	1,500	2,000
δ (μm)	35 ± 3	16 ± 2	11 ± 1	9 ± 1	8 ± 1

Table 2 Exchange current density j_0 (referred to 1 cm² geometric area) of the Fe³⁺/Fe²⁺ redox couple at different rotation rates for Ti/IrO₂ electrodes of different specific loading m_{sp} and for a polished Pt electrode, as calculated using Eq. (6) from steady-state polarization data

Rotation rate (rpm)	j_0 (mA cm ⁻²)				Polished Pt
	m_{sp} (mg IrO ₂ cm ⁻²)				
	0.62	1.97	2.46	4.92	
100	42	36	61	48	47
500	42	46	57	59	53
1,000	44	46	56	57	52
1,500	46	47	57	59	51
2,000	47	47	55	62	51
Average ^a	45 ± 2	47 ± 1	56 ± 1	59 ± 2	52 ± 1

^a Average is taken with neglecting data obtained at the slowest (100 rpm) rotation rate

anodic and cathodic limiting currents $I_{lim,a}$ and $I_{lim,c}$ [A], the exchange current density j_0 [Acm⁻²] of the Fe³⁺/Fe²⁺ redox couple can be obtained from the slope at the origin of the $I-\eta$ curves (Fig. 1) using Eq. (6) valid for small overpotentials [8]:

$$\eta = I \frac{RT}{AF} \left(\frac{1}{j_0} - \frac{1}{j_{lim,c}} + \frac{1}{j_{lim,a}} \right) \quad (6)$$

where η is the overpotential [V], I is the measured current [A], R is the molar gas constant (=8.314) [Jmol⁻¹ K⁻¹] and T is the temperature (=298) [K].

Table 2 shows j_0 values obtained for the four investigated Ti/IrO₂ electrodes using five different rotation rates. It is seen that j_0 slightly increases with the electrode loading and it is rather independent of the rotation speed, excepting the slowest rotation rate (100 rpm) where the experimental uncertainties are the highest. In the same table, the exchange current density j_0 of the Fe³⁺/Fe²⁺ redox couple measured on polished Pt electrode is also given.

3.2 Effectiveness factor for the 3D IrO₂ electrodes

The effectiveness factor E_f was calculated from experimental data using Eq. (3). As experimental $(j_0)_{3D}$ data, the measured exchange current densities (average values calculated for rotation rates ≥ 500 rpm) were taken as reported in Table 2, for the IrO₂ (3D) electrodes of different loading. Similarly, the exchange current density (average value calculated for rotation rates ≥ 500 rpm) measured with the polished Pt (2D) electrode (see Table 2) was identified as $(j_0)_{2D}$ (Table 3).

Table 3 Characteristics of the IrO₂ electrodes of different specific loading m_{sp} used in the rotating disk electrode experiments: Average exchange current density $(j_0)_{3D}$ (see Table 2), 3D roughness factor γ_{3D} (Eq. 3), and experimental effectiveness factor E_f (Eq. 2). For the calculation of E_f , a 2D exchange current density of $(j_0)_{2D} = 52$ mA cm⁻²* was taken, measured with a polished Pt electrode

	m_{sp} (mg IrO ₂ cm ⁻²)			
	0.62	1.97	2.46	4.92
$(j_0)_{3D}$ (mAcm ⁻²) ^a	45	47	56	59
γ_{3D}	63	200	250	499
E_f	0.014	0.005	0.004	0.002

^a Reported to 1 cm² geometric (projected) area

As expected, the experimentally obtained effectiveness factor increases with decreasing loading, but its value remains very low even at the lowest used loading. It means that in all cases only the 2D surface is effectively working.

4 Conclusions

The Fe³⁺/Fe²⁺ redox couple has been used as a probe reaction in order to evaluate the effectiveness factor E_f of 3D Ti/IrO₂ electrodes of different loading. Steady-state polarization measurements using RDE electrodes in 0.5 M Fe³⁺/Fe²⁺ in 1 M HCl were performed and corrected for the uncompensated potential drop, and allowed to draw the following conclusions:

- The exchange current densities j_0 (measured current reported to 1 cm² projected area) show to increase slightly with the electrode loading and it is rather independent of the rotation speed, except at the slowest one (100 rpm), where the experimental uncertainties are the highest,
- The reaction with the Fe³⁺/Fe²⁺ redox couple takes place almost exclusively at the 2D surface shown by the very low effectiveness factors (<2%).

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