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1 First electrochemical Couette-Taylor reactor for studying the influence of transport 2 phenomena on electrochemical kinetics

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9 Highlights

- 10 • The first electrochemical multi-electrodes Couette-Taylor reactor was developed
- 11 • Electrochemical responses to flow regimes were experimentally characterized
- 12 • Strictly turbulent and turbulent vortex flow gave similar electrochemical behavior
- 13 • Vortices and turbulence are the main driving forces of electrochemical reactions

14 Abstract

15 Electroactive biofilms are powerful catalysts of many electrochemical reactions of interest. Their
16 development and electrochemical efficiency can be considerably dependent on the solution
17 hydrodynamics. Unfortunately, analytical devices that are suited to the study of the effects of
18 hydrodynamics on electroactive biofilms are still lacking. This study presents an electrochemical
19 Couette-Taylor reactor (eCTR), which meets this objective. It integrated 20 large-sized
20 electrodes individually addressed and exposed to the same hydrodynamics. Fluid dynamics was
21 controlled by rotating the inner cylinder of the eCTR at speeds from 1 to 200 RPM. The device
22 was characterized in abiotic condition using hexacyanoferrate (III/II) as model reactive species.
23 The limiting currents (I_L) recorded with different concentrations of hexacyanoferrate and at
24 different rotation speeds of the inner cylinder (ω) were used to calculate the Nernst diffusive
25 layer thickness (δ_N), which ranged from 14.6 to 423 μm . Two hydrodynamic regimes were
26 identified: the wavy vortex flow for ω from 1 to 10 RPM and the turbulent vortex flow for ω
27 values higher than 15 RPM, which corresponded to the correlations $\delta_{N_{WVF}} \propto \omega^{-0.44}$ and
28 $\delta_{N_{TVF}} \propto \omega^{-0.66}$, respectively. The second correlation confirmed the theoretical equation
29 established by Gabe and Robinson for turbulent flow. In contrast, the wavy vortex flow was a

30 specific regime, which cannot be approached by the laminar or turbulent hypothesis.
31 Dimensionless correlations gave comparable results between eCTR and rotating cylinder
32 electrodes under turbulent vortex flow and confirmed the specific behavior of the Couette-Taylor
33 wavy vortex flow.

34 **Keywords**

35 Electrochemical layer thickness – Turbulent flow – Vortex flow – Hydrodynamics –
36 Electroactive biofilm – Microbial electrochemical technology

37 **Abbreviations**

B	Constant parameter
b	Constant parameter
CTR	Couette-Taylor reactor
C_b	Concentration in the bulk (mol.m^{-3})
C_i	Concentration of the species i (mol.m^{-3})
C_s	Concentration on the electrode surface (mol.m^{-3})
CV	Cyclic Voltammetry
D_i	Diffusive coefficient of the species i ($\text{m}^2.\text{s}^{-1}$)
D_{turb}	Apparent eddy viscosity ($\text{m}^2.\text{s}^{-1}$)
eCTR	Electrochemical Couette-Taylor reactor
F	Faraday constant (C.mol^{-1})
I	Current (A)
I_L	Limiting current (A)
I_p	Current at the peak (A)
K	Constant from log regression
K_L	Convective mass transfer coefficient (m.s^{-1})
L	Characteristic length (m)
M	Width of the electrode (m)
n	Exponent of the shear rate
n_e	Number of electrons
N_i	Molar flux density of species i ($\text{mol.s}^{-1}.\text{m}^{-2}$)
PVC	Polyvinyl Chloride
R^2	Coefficient of determination
r	Distance from the inner cylinder surface (m)
RCE	Rotating cylinder electrode

Re	Reynolds Number
R_i	Inner cylinder radius (m)
R_o	Outer cylinder radius (m)
RPM	Revolution Per Minutes
S	Electrode surface (m ²)
Sc	Schmidt number
SCE	Saturated Calomel Electrode
Sh	Sherwood number
TVF	Turbulent vortex flow
Ta	Taylor Number
Ta_c	Taylor critical value
U	Flow velocity (m.s ⁻¹)
WVF	Wavy vortex flow

Greek letters

α	Exponent of the angular velocity
Γ	Gamma function
$\dot{\gamma}$	Shear rate (s ⁻¹)
ΔV	Volt interval (V.rot ⁻¹)
δ_I, δ_{II}	Diffusive layer thicknesses (m)
δ_N	Nernst diffusion layer thickness (m)
μ	Dynamic viscosity (Pa.s)
ν	Cinematic viscosity (m ² .s ⁻¹)
σ	Scan rate (V.s ⁻¹)
τ	Shear stress (Pa)
ω	Angular velocity (rad.s ⁻¹)
ω_c	Critical velocity

38

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45 1. Introduction

46 Electrochemical systems are used in many industrial applications [1–4] and microbial
47 electrochemical technologies constitute an emerging field with multiple promising applications
48 for power generation, resource recovery, chemicals production and sensing [5–12]. In such bio-
49 electrochemical systems, multi-species biofilms play the role of the catalyst since they are able to
50 exchange electrons with electrodes on which they develop [13,14]. The influence of electrolytes,
51 electrode materials [15] or electrochemical parameters (applied current density and voltage or
52 potential [16]) on the reaction associated with different physical parameters such as temperature,
53 conductivity, pH or hydrodynamics are often studied to optimize those technologies [17,18].
54 However, the impact of fluid dynamics on electroactive biofilms was poorly investigated despite
55 its major influence on their growth [19–21] and current density generation [22,23].

56 The experimental requirements to adequately study the influence of hydrodynamics on biofilm
57 growth and long-term maturation are indeed numerous: (i) the electrodes size needs to be
58 sufficient in order to allow recovery of biofilm samples in sufficient quantity for complete
59 microbial characterization, (ii) the set-up should allow the continuous feeding and a
60 homogeneous repartition of substrate all along the surface of the electrodes, (iii) multiple
61 electrodes exposed to the same controlled hydrodynamics conditions need to be present to allow
62 a sufficient level of replication of the measurements, which is mandatory considering the
63 intrinsic experimental variability of biological systems under complex and variable media
64 conditions during long term experiments.

65 Some experimental systems have actually been designed to study the impact of hydrodynamics
66 on biofilms in continuous flow such as flow cells [22–25]. They were used to study precise
67 hydrodynamics in microfluidic channels where the shear stress is induced by the flow rate [26].
68 In the specific case of electroactive biofilms, they could be developed on small electrodes
69 implemented in the cell (generally up to 1 cm²) allowing having the same applied shear stress on
70 the whole surface. Experiments were run at daily or weekly scale [27]. They were often couple
71 with non-invasive imaging technologies such as microscopy to analyze biofilm structural
72 parameters overtime (thickness, density, porosity, etc. [28,29]). Thus they allow a great
73 characterization of the biofilm but some limitation appeared considering their small size, which
74 does not allow biofilm sampling overtime or having replicates under the identical operating
75 conditions.

76 Other systems were employed for the study of fluid dynamics impact on electrochemical
77 technologies [30,31]. The most well-known systems are the rotating disk electrodes described by

78 Levich [32]. Electrochemical reactions take place on the surface of a small rotating electrode
79 (lower than 1 cm²) and the current is expressed as a function of the rotation speed. Nonetheless,
80 only a few studies have shown biofilm development on rotating disk electrodes [33]. Some
81 variants such as the rotating cylinder electrodes (RCE) implement a cylinder-electrode immersed
82 in the electrolyte as described by Eisenberg *et al.* [34]. They were adapted to larger surfaces of
83 electrodes (> 10 cm²) [35–37] but RCE have mainly been described considering abiotic mass
84 transfer and not for the study of electroactive biofilms [34].

85 Couette-Taylor reactors (CTR) have a perfectly described hydrodynamic profile and have been
86 often used for the study of biofilm development for scale-up purposes [38–40]. They are
87 composed of two concentric cylinders, with a rotating inner cylinder and a fixed outer cylinder
88 (respectively characterized by the radii R_i and R_o). The main differences of CTR in comparison
89 to RCE are the various hydrodynamic conditions from well-known Couette flow to 3D typical
90 vortices flows or turbulent flows induced by the specific influence of the stationary outer wall
91 [40]. CTR may apply a higher range in terms of shear stress induced on the surface of the inner
92 cylinder classically from 0.1 to 10 Pa in aqueous media [38,41], compared to rotating electrodes
93 under high shear stress and turbulent flows [42,43]. In previous studies, CTR were used to study
94 hydrodynamics influence on physical biofilm properties and allowed characterization and
95 sampling of biofilm along time (density, thickness, porosity, etc.) [44–47]. However, no
96 adaptation to such reactor was made for the integration of electrodes in the set-up in order to
97 study electroactive biofilms.

98 In fact, some work has been done to couple electrochemistry analysis with CTR hydrodynamics.
99 Sobolík *et al.* [48] introduced a single three-segment electrodiffusion probe in two different CTR
100 with radius ratio R_i/R_o of 0.84 and 0.7 respectively. They have thus characterized components
101 of the shear rate on the outer wall under wavy vortex flows. Berrich *et al.* [49] have
102 characterized a Couette-Taylor-Poiseuille flows (for vortex and wavy vortex regimes) in an
103 larger CTR (radius ratio of 0.86) implementing 39 microelectrodes distributed along the
104 circumference and a vertical segment of the outer cylinder. Legrand *et al.* [50] have performed
105 one of the first characterization of the mass transfer occurring in Couette-Taylor-Poiseuille flows
106 for wavy vortex flows thanks to electrochemical measurement in CTR (radius ratio of 0.78).
107 Their reactor integrated a 3 segments inner cylinder (composed of the cathode framed in the
108 anode). Nevertheless, those methodologies were developed to study hydrodynamics and mass
109 transfer in CTR and were not dealing with electrodes allowing biofilm development: (i)
110 microelectrodes for Sobolík *et al.* [48] and Berrich *et al.* [49] and (ii) nickel-cathode covered by

111 platinum and gold for Legrand *et al.* [50] which are not the preferred materials for biofilm
112 growth [51].

113 In this study, the first electrochemical CTR is presented. The main specificities of this reactor are
114 (i) 20 graphite electrodes included in the inner rotating cylinder allowing to have replicates in
115 exactly the same hydrodynamic conditions, with a (ii) large surface (20 cm²) under uniform well-
116 known hydrodynamics, allowing (iii) spontaneous biofilm development in real conditions
117 including complex effluents but with (iv) independent electrical connections for each electrode.

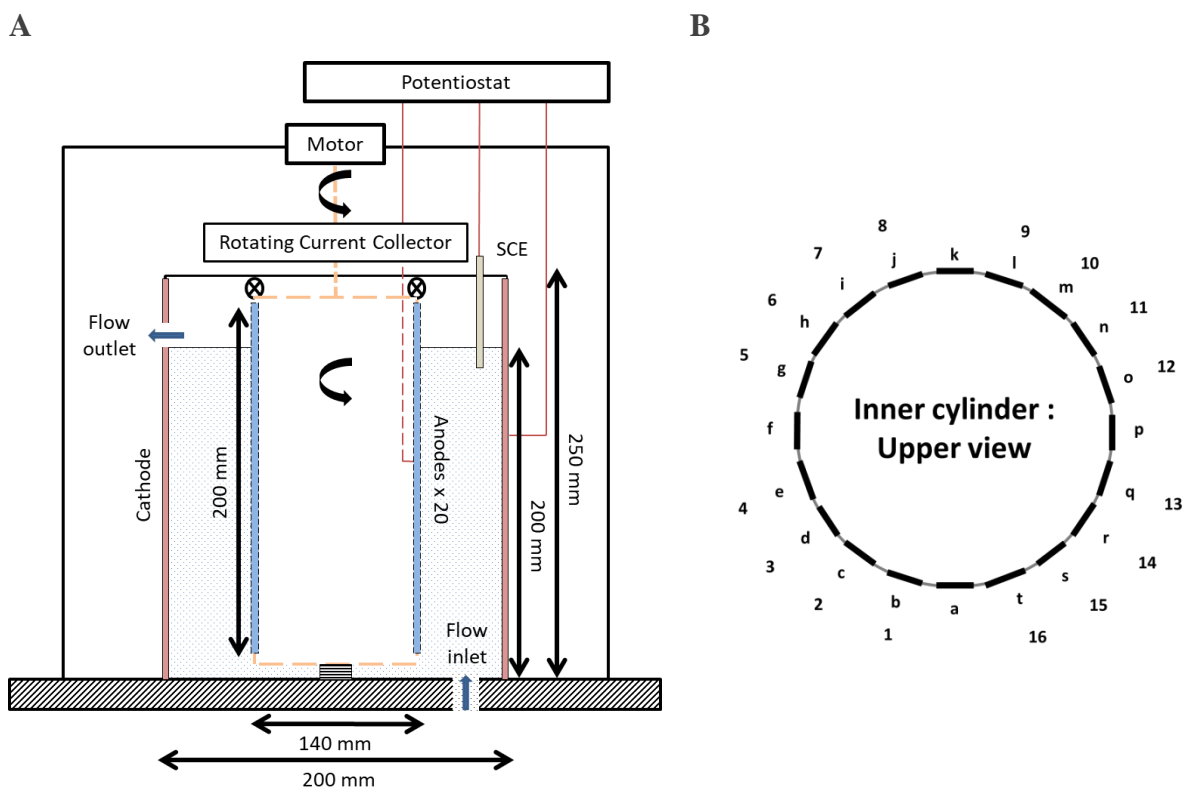
118 The reactor is characterized experimentally for various operating conditions under wavy and
119 turbulent vortex flows without biofilm development considering (i) electrochemical parameters,
120 (ii) small ascendant flow rate, (iii) concentration of the electroactive species and (iv) effect of the
121 rotation speed of the inner cylinder. Then, the results are interpreted in light of previous
122 theoretical analysis of Gabe & Robinson [52,53], which describes the relation between current
123 intensity and the flow velocity in laminar [52] and turbulent flow regimes [53]. Finally the
124 results are compared to previous studies on different hydrodynamic regimes (Eisenberg *et al.*
125 [34] and Legrand *et al.* [50]) and the potential application of the electrochemical CTR for future
126 studies is discussed.

127 **2. Materials and Methods**

128 **2.1. Electrochemical Couette-Taylor Reactor (eCTR)**

129 The Couette-Taylor reactor was composed of two coaxial cylinders of 25 cm height (Figure 1A).
130 The rotating inner cylinder, of 7 cm radius, includes 20 graphite-plate (Sigriform HLM,
131 Graphitech) working electrodes inlaid in the PVC cylindrical core. Each working electrode had a
132 surface of 20×1 cm² and was immersed by 18 cm. The active projected area of each working
133 electrode was thus 18 cm². Each electrode was individually connected to the external electrical
134 circuit thanks to a rotating collector (SVTS C 03-S-A-00/18). The central axis of the inner
135 cylinder was mechanically connected to a motor (APM-SA01) by means of a speed reducer
136 (PLGE12/1 i=9) and could thus be rotated at speeds from 1 to 200 RPM. The non-mobile outer
137 cylinder, made of stainless steel (316L) of 10 cm radius, was used as the auxiliary electrode. A
138 calomel reference electrode (SCE, BioLogic, +0.244 V/SHE) was positioned between the two
139 cylinders about 1.5 cm from the outer cylinder. The lid and the base of the reactor as made from
140 PVC. The reactor was set in a solution circulation loop equipped with a peristaltic pump
141 (Gilson), which provided a flow rate of 700 mL.h⁻¹ (axial solution velocity in the reactor of 4.38
142 cm/h). The flow inlet was at the reactor bottom and the outlet ensured a water level of 20 cm, i.e.

143 a volume of solution in the reactor of 3.6 L. All experiments were conducted in a 25°C
144 temperature-regulated room.



145 Figure 1: A) Diagram of electrochemical Couette-Taylor reactor and B) visualization in top view
146 of the inner cylinder with position of the electrodes.

147 Up to 16 working electrodes could be individually addressed with a multi-channel potentiostat
148 (VMP-3, Biologic). Two Nstat boxes (Biologic) were used to integrate each working electrode in
149 a 3-electrode set-up with the single SCE as the reference electrode and the fixed outer cylinder as
150 the auxiliary electrode. Each working electrode was identified by a letter from *a* to *t* (Figure 1B).
151 Electrodes *b* to *j*, excluding electrode *f*, were connected via an Nstat to the tracks 1 to 8 of the
152 potentiostat. The other group, from *l* to *t*, excluding electrode *p*, were connected to the tracks 9 to
153 16 via the other Nstat. Four electrodes (*a*, *f*, *k*, and *p*) were not electrochemically connected.
154 They will serve as controls in future experiments that will be devoted to the study of microbial
155 electroactive biofilms.

156 Cyclic Voltammeteries (CV) were performed with scan rates from 1 to 100 $\text{mV}\cdot\text{s}^{-1}$ in the range of
157 -0.35 to +0.65 V/SCE. Three successive cycles were systematically performed. The first cycle
158 was sometimes slightly different from the second and third cycles, which were always identical.
159 All the data reported in the present study were extracted from the second CV cycles.

160 2.2.Solutions

161 Solutions of equimolar potassium hexacyanoferrate (III) and hexacyanoferrate (II) ($\text{Fe}(\text{CN})_6^{3-}$
 162 $/\text{Fe}(\text{CN})_6^{4-}$) were used at different concentrations, from 1 mM to 20 mM. Hexacyanoferrate was
 163 chosen as model electroactive species because it ensured fast electron transfer with carbon-based
 164 electrodes. The solution was supplemented with mono-basic and di-basic phosphate (NaH_2PO_4
 165 and Na_2HPO_4) 100 mM. The potassium, sodium and phosphate ions provided thus the main part
 166 of ion migration in solution and the migration contribution can be neglected in the mass transport
 167 of hexacyanoferrate.

168 The diffusive coefficient of hexacyanoferrate (II) is given by the relation of Stokes-Einstein at
 169 25°C and is equal to $5.09 \times 10^{-10} \text{ m}^2 \cdot \text{s}^{-1}$.

170 3. Theoretical description

171 3.1. Hydrodynamic modelling

172 The flow regimes in CTR are described according to the dimensionless Taylor number (Ta) [54]
 173 which characterizes the centrifugal force applied to the liquid in relation to the viscous force the
 174 liquid opposes to the motion:

$$175 \quad Ta = \frac{\omega \sqrt{R_i(R_o - R_i)^3}}{\nu} \quad (1)$$

176 where ω is the angular velocity ($\text{rad} \cdot \text{s}^{-1}$), R_i and R_o the radii of the inner and the outer cylinder
 177 (m) and ν the cinematic viscosity ($\text{m}^2 \cdot \text{s}^{-1}$). The Ta number can be considered as a form of the
 178 Reynolds number Re adapted to the specific geometry of the CTR:

$$179 \quad Ta = Re \sqrt{\frac{(R_o - R_i)}{R_i}} \quad (2)$$

$$180 \quad \text{where } Re = \frac{\omega R_i (R_o - R_i)}{\nu}$$

181 The Ta number allows describing the different flow regimes according to the value it takes
 182 regarding a critical value Ta_c [55,56] :

$$183 \quad Ta_c = 20.65 \frac{R_o \left(1 + \frac{R_i}{R_o}\right)^2}{R_i \sqrt{\left(1 - \frac{R_i}{R_o}\right) \left(3 + \frac{R_i}{R_o}\right)}} \sqrt{\frac{R_o - R_i}{R_i}} \quad (3)$$

184 For the eCTR designed in this study, $R_o = 0.10 \text{ m}$, $R_i = 0.07 \text{ m}$ (corresponding to a radius ratio
 185 of 0.7) and $\nu = 10^{-6} \text{ m}^2 \cdot \text{s}^{-1}$ give $Ta_c = 53.0 [-]$, which corresponds to the critical velocity value
 186 ω_c of $0.039 \text{ rad} \cdot \text{s}^{-1}$ (0.37 RPM). The correspondences between Ta values, the flow regimes and
 187 ω values are given in table 1. The reactor was operated with different values of ω from 1 to 200

188 RPM (respectively 1, 3, 5, 6.5, 8, 10, 15, 25, 50, 100, 150 and 200). This choice was made
 189 considering the capacity of the motor to ensure stable rotating velocity values and in order to
 190 cover the largest velocities ranges and associated flow regimes (from vortex to turbulent vortex
 191 regimes, according to Table 1).

192 The Sherwood number (Sh) characterizes the ratio of the convective and diffusive mass transport
 193 [57]:

$$194 \quad Sh = \frac{K_L L}{D_i} \quad (4)$$

195 where K_L is the convective mass transfer coefficient ($\text{m}\cdot\text{s}^{-1}$), $L = R_o - R_i$ the characteristic
 196 length in Couette-Taylor reactors, which is the gap between the inner and the outer cylinder (m)
 197 and D_i is the effective diffusive coefficient ($\text{m}^2\cdot\text{s}^{-1}$).

198 The Sherwood number is generally expressed as a function of the Reynolds number (Re) and the
 199 Schmidt (Sc) number defined by $Sc = \nu/D_i$, according to experimental correlations.

200 Table 1: Couette-Taylor flow regimes, and corresponding Ta , rotation speed equivalent
 201 boundaries and shear stress values

Regime	Ta range	Ta values	ω ($\text{rad}\cdot\text{s}^{-1}$)	ω (RPM)	τ (mPa)
Couette Laminar	$Ta < Ta_c$	$Ta < 53$	$\omega < 0.039$	$\omega < 0.37$	$\tau < 0.039$
Vortex	$Ta_c < Ta < 1.27 Ta_c$	$53 < Ta < 67$	$0.039 < \omega < 0.049$	$0.37 < \omega < 0.47$	$0.039 < \tau < 0.049$
Wavy Vortex	$1.27 Ta_c < Ta < 40 Ta_c$	$67 < Ta < 2120$	$0.049 < \omega < 1.55$	$0.47 < \omega < 14.8$	$0.049 < \tau < 27$
Turbulent Vortex	$40 Ta_c < Ta < 700 Ta_c$	$2120 < Ta < 37100$	$1.55 < \omega < 27$	$14.8 < \omega < 258$	$27 < \tau < 4300$
Turbulent	$Ta > 700 Ta_c$	$Ta > 37100$	$\omega > 27$	$\omega > 258$	$\tau > 4300$

202

203 Under laminar flow conditions (Table 1), the velocity of a Couette-Taylor flow U ($\text{m}\cdot\text{s}^{-1}$) only
 204 depends on the distance from inner cylinder r and is given by [43]:

$$205 \quad U = \omega R_i^2 \frac{\left(\frac{1}{r} - \frac{r}{R_o^2}\right)}{\left(1 - \frac{R_i^2}{R_o^2}\right)} \quad (5)$$

206 The fluid shear stress is a function of the fluid velocity and the dynamic viscosity according to:

$$207 \quad \tau = \mu \operatorname{div} U \quad (6)$$

208 where τ is the shear stress applied on the cylinder wall (Pa), μ is the dynamic viscosity (Pa.s) and
209 U the fluid velocity (m.s⁻¹).

210 Under laminar flow conditions, the velocity profile (equation 5) used in equation 6 gives the
211 shear stress on the surface of the inner cylinder ($r = R_i$):

$$212 \quad \tau = \mu \omega \quad (7)$$

213 Former work in the literature [54] describes the expression of the shear forces applied to the
214 rotating inner wall as function of the Reynolds number under Couette-Taylor flows:

$$215 \quad \tau = 2.13 \frac{(R_i/R_o)^{3/2}}{[(R_o-R_i)/R_o]^{7/4}} Re^{1.445} \frac{\rho v^2}{2\pi R_i^2} \quad \text{For } Re > 800 \ (\omega > 3.65 \text{ RPM}) \quad (8)$$

$$216 \quad \tau = 0.113 \frac{(R_i/R_o)^{3/2}}{[(R_o-R_i)/R_o]^{7/4}} Re^{1.764} \frac{\rho v^2}{2\pi R_i^2} \quad \text{For } Re > 10^4 \ (\omega > 47 \text{ RPM}) \quad (9)$$

217 where ρ is the fluid density (kg.m⁻³).

218 **3.2.Relation between fluid velocity and current**

219 The molar flux density of a solute i is the sum of 3 components due to diffusion, migration and
220 convection [57]. Generally, solutions used in electroanalytical studies contain a supporting salt
221 and/or a charged buffer compound at high concentration, as it was the case here (NaH₂PO₄ and
222 Na₂HPO₄), so that the migration flux can be neglected for solutes. Furthermore, for low
223 concentration of solutes, the diffusion flux can be expressed according to the Fick's law. So the
224 molar flux density (\vec{N}_i , mol.s⁻¹.m⁻²) of a solute i at low concentration can be written as:

$$225 \quad \vec{N}_i = -D_i \overrightarrow{\operatorname{grad}} C_i + C_i \vec{U} \quad (10)$$

226 where D_i is the effective diffusive coefficient (m².s⁻¹), C_i is the concentration (mol.m⁻³) and \vec{U} is
227 the fluid velocity (m.s⁻¹).

228 At steady state and in the absence of reaction in solution, the differential mass balance equation
229 for the species i is:

$$230 \quad \operatorname{div} \vec{N}_i = 0 \quad (11)$$

231 and leads to:

232
$$\text{div}(-D_i \overrightarrow{\text{grad}} C_i + C_i \overrightarrow{U}) = 0 \quad (12)$$

233 At steady state, the current \vec{I} (A) is proportional to the molar flux of the electroactive species at
 234 the electrode surface. When only one electroactive species i is oxidized at the electrode surface,
 235 as it was the case here, the current is expressed as:

236
$$\vec{I} = n_e F S \vec{N}_i|_{\text{electrode}} \quad (13)$$

237 where n_e is the number of electrons produced per molecule of electroactive species, F is the
 238 Faraday constant (96 485 C.mol⁻¹) and S is the surface area of the electrode (m²).

239 3.2.1. Nernst model

240 The Nernst model divides the solution space into two zones: a stagnant boundary layer against
 241 the electrode surface and a perfectly stirred bulk beyond the stagnant layer (Figure 2A). The
 242 concentration is uniformly equal to C_b in the bulk. Equation 12 can thus be solved very simply in
 243 the stagnant layer, in which $U = 0$, and, combined with equation 13, gives:

244
$$I = n_e D_i F S \frac{C_b - C_s}{\delta_N} \quad (14)$$

245 where C_b and C_s are the concentrations of the electroactive species in the bulk and at the
 246 electrode surface, respectively (mol.m⁻³) and δ_N is the thickness of the Nernst layer (m). The
 247 limiting current I_L is defined as the maximal value of the current that can be reached when only
 248 the diffusion transport is rate-limiting, i.e. when the electrochemical reaction is so fast in relation
 249 to mass transport that the electroactive species reacts at the electrode surface as soon as it
 250 reaches it, resulting in $C_s = 0$. According to equation 14, in the framework of the Nernst's
 251 model, the limiting current is:

252
$$I_L = n_e F S \frac{D_i}{\delta_N} C_b \quad (15)$$

253 Nernst model allows expressing the convective mass transfer coefficient K_L as a function of δ_N
 254 according to:

255
$$K_L = \frac{D_i}{\delta_N} \quad (16)$$

256 In a CTR, the Nernst layer thickness δ_N depends on the rotation speed. More sophisticated
 257 models are needed to obtain a theoretical relationship between the layer thickness and the
 258 rotation speed.

259 3.2.2. Gabe and Robinson model for laminar flow

260 Under laminar flow conditions, Gabe & Robinson [52] considered that the annulus geometry of a
 261 CTR can be approached as a straight channel for a small length M ($M \ll 2\pi R_i$) parallel to the
 262 flow. They defined the x- and y-axes as parallel and perpendicular to the channel length,
 263 respectively. They assumed that mass transport was ensured only by the fluid flow along the x-
 264 axis and only by diffusion along the y-axis, so that equation 12 becomes:

$$265 \quad -D_i \frac{d^2 c_i}{dy^2} + U \frac{dc_i}{dx} = 0 \quad (17)$$

266 in which the fluid velocity U is given by equation 5. They used a change of variable to transform
 267 the equation in one dimension. Then, they obtained an expression for the current:

$$268 \quad I = \frac{3^{4/3}}{2\Gamma(1/3)} n_e F S D_i^{2/3} (c_b - c_s) M^{-1/3} \left(\frac{1+R_i^2/R_o^2}{1-R_i^2/R_o^2} \right)^{1/3} \omega^{1/3} \quad (18)$$

269 where Γ is the Gamma function and M the width of the electrode (m). Under laminar flow
 270 conditions, the limiting current according to the Gabe & Robinson [52] approach is
 271 consequently:

$$272 \quad I_L = \frac{3^{4/3}}{2\Gamma(1/3)} n_e F S D_i^{2/3} c_b M^{-1/3} \left(\frac{1+R_i^2/R_o^2}{1-R_i^2/R_o^2} \right)^{1/3} \omega^{1/3} \quad (19)$$

273 Comparing with the Nernst expression (equation 15) allows extracting an expression of an
 274 equivalent Nernst layer in laminar condition ($\delta_{N-Gabe\ lam}$):

$$275 \quad \delta_{N-Gabe\ lam} = \frac{2\Gamma(1/3)}{3^{4/3}} D_i^{1/3} M^{1/3} \left(\frac{1+R_i^2/R_o^2}{1-R_i^2/R_o^2} \right)^{-1/3} \omega^{-1/3} \quad (20)$$

276 Sherwood number could then be expressed according to equation 16 and 20 as:

$$277 \quad Sh = Re^{1/3} Sc^{1/3} \frac{3^{4/3}}{2\Gamma(1/3)} \left[\frac{(R_i - R_o)^2 (1 + R_i^2/R_o^2)}{R_i M (1 - R_i^2/R_o^2)} \right]^{1/3} \quad (21)$$

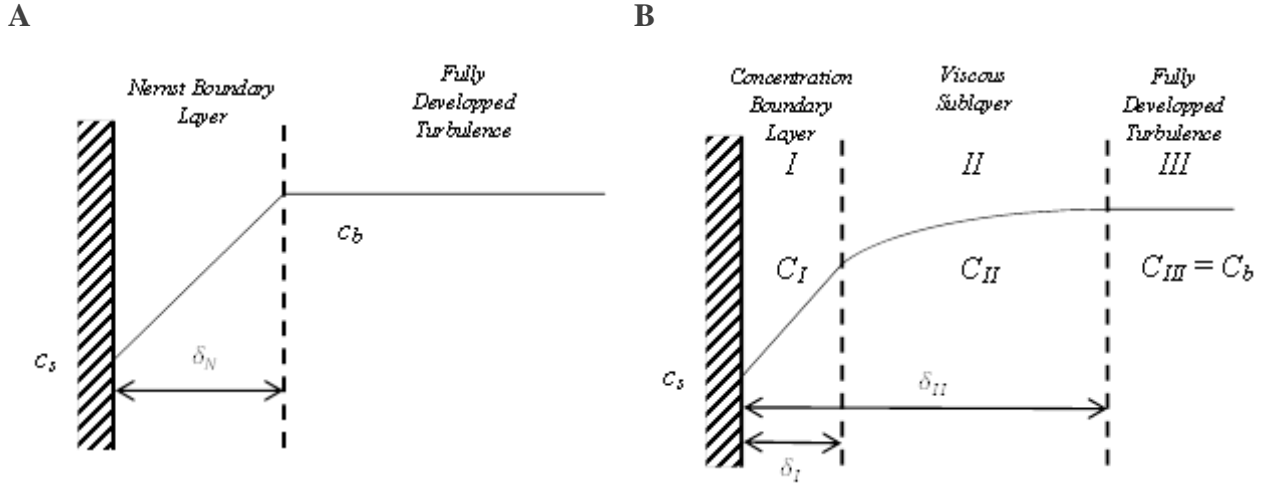
278 **3.2.3. Gabe and Robinson model for turbulent flow**

279 Under turbulent flow conditions, Gabe & Robinson [53] used the 3-zone model from Prandtl-von
 280 Karman (Figure 2B), in which the layer next to the electrode surface (zone I) is considered as a
 281 Nernst boundary layer and the zone III, the furthest from the electrode surface, is considered in
 282 fully developed turbulence. Considering a planar geometry, the Nernst approach applied to zone
 283 I gives:

$$284 \quad I = n_e F S D_i \frac{c_I - c_s}{r} \quad (22)$$

285 where C_I is the concentration ($\text{mol}\cdot\text{m}^{-3}$) of the electroactive species in zone I at the distance r (m)
 286 from the electrode surface. This equation gives the concentration profile in zone I:

$$287 \quad C_I = C_s + \frac{I r}{n_e F S D_i} \quad (23)$$



288 Figure 2: Models of mass transport near the electrode surface. The electrode is the surface of the
 289 inner cylinder of the CTR. A) Nernst model. B) 3-zone model according to Prandtl-von Karman
 290 (from [53]).

291 In the intermediary viscous layer (zone II), Gabe & Robinson [53] assumed that mass transport is
 292 achieved by convection and eddy diffusion, so that equation 10 is transformed to:

$$293 \quad \text{div} (-D_{turb} \overrightarrow{\text{grad}} C_i + C_i \overrightarrow{U}) = 0 \quad (24)$$

294 where D_{turb} ($\text{m}^2\cdot\text{s}^{-1}$) is the apparent eddy viscosity and varies with the flow velocity. Assuming
 295 that U is constant in zone II and equal to ωR_i , D_{turb} could be expressed as:

$$296 \quad D_{turb} = \frac{b r^3 \omega^2 R_i}{\nu} \quad (25)$$

297 where r is distance from the electrode surface (m), ν the cinematic viscosity ($\text{m}^2\cdot\text{s}^{-1}$) and b a
 298 constant. Solving equations 23 gives the concentration profile in zone II:

$$299 \quad C_{II} = C_b + \frac{I \nu}{2 n_e F S b \omega^2 R_i} \left(\frac{1}{\delta_{II}^2} - \frac{1}{r^2} \right) \quad (26)$$

300 where δ_{II} is the thickness of the zone II. At the interface between the zones I and II, i.e. at $r =$
 301 δ_I , the equations 23 and 26 must give the same concentration value. Writing this gives a
 302 relationship between δ_I and δ_{II} and considering that $\frac{\delta_I^3}{\delta_{II}^2} \ll \delta_I$ leads to the expression of the
 303 current as:

304
$$I = n_e FS \left(\frac{BR_i}{\nu} \right)^{1/3} (\omega D_i)^{2/3} (C_b - C_s) \quad (27)$$

305 where $B = \left(\frac{2}{3} \right)^3 b$. The limiting current I_L is consequently:

306
$$I_L = n_e FS \left(\frac{BR_i}{\nu} \right)^{1/3} D_i^{2/3} C_b \omega^{2/3} \quad (28)$$

307 Comparing with the Nernst expression (equation 15) allows extracting an equivalent Nernst layer
308 in turbulent condition ($\delta_{N-Gabe turb}$) as:

309
$$\delta_{N-Gabe turb} = \left(\frac{D_i \nu}{BR_i} \right)^{1/3} \omega^{-2/3} \quad (29)$$

310 which gives the Sherwood number according to equation 16 and 29:

311
$$Sh = Re^{2/3} Sc^{1/3} \left(\frac{B(R_o - R_i)}{R_i} \right)^{1/3} \quad (30)$$

312 **4. Results**

313 **4.1. Preliminary characterization of the reactor**

314 **4.1.1. Influence of the inlet flow without rotation**

315 The eCTR was equipped with electrodes of large surface areas, which covered the entire inner
316 (working electrode) and outer (auxiliary electrode) cylinders. The electrochemical reactions can
317 consequently drastically affect the concentration of the reactive species, so that the stationary
318 state may not be reached in batch conditions. It was therefore necessary to feed the reactor
319 continuously with solution in order to keep the concentration of the reactive species constant and
320 allow the establishment of steady state. The first objective of the eCTR characterization was to
321 verify that the continuous axial flow induced by the recirculation did not significantly disturb the
322 hydrodynamics. This check was carried out without rotation of the internal cylinder in order to
323 be in the most sensitive conditions possible.

324 Cyclic voltammeteries (CV) were performed at $5 \text{ mV} \cdot \text{s}^{-1}$ in phosphate solution that contained
325 hexacyanoferrate (III) and hexacyanoferrate (II) each at 1 mM. The CV records (current intensity
326 as a function of potential) were compared using the oxidative part ($I > 0 \text{ A}$) because the
327 reductive part may be biased by the reduction of oxygen, which occurs in a similar potential
328 range as the reduction of hexacyanoferrate (III). The CV records were compared with two
329 characteristic values: the current at the peak (I_p) and the limiting current (I_L) measured at upper
330 limit of the potential scan from 0.55 to 0.6 V/SCE (see Figure 4). Eight electrodes were
331 individually addressed in this experiment (electrodes c-e-h-j-m-o-r-t, see Materials and Methods

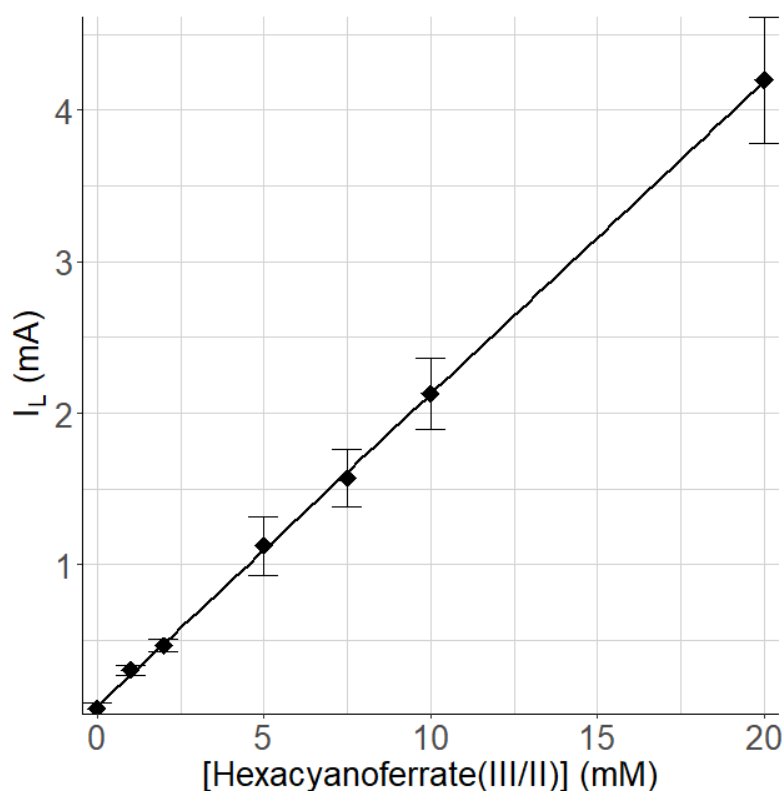
332 section). The 8 electrodes gave highly reproducible CV records (Figure S1 in Supplementary
333 data) with standard deviation lower than 4% and 5% for the I_p and I_L values, respectively.

334 CV were recorded in batch condition (no solution flow) and in continuous flow of 700 mL.h⁻¹
335 (corresponding to a superficial velocity of 4.4 cm.h⁻¹). No significant difference was observed on
336 the general shape of the CV recorded with or without continuous flow. In batch condition, I_p and
337 I_L were 2.8 ± 0.2 and 0.74 ± 0.07 mA, respectively; while, in continuous mode they were
338 2.8 ± 0.2 and 0.71 ± 0.07 mA, respectively. The small difference between the batch and the
339 continuous mode on the I_p and I_L values can be neglected according to the overlap of the
340 standard deviations. It can be concluded that the small axial velocity of 4.4 cm.h⁻¹ due to the
341 solution flow had no significant effect on the current produced by the electrodes.

342 Consequently, all the experiments were conducted with a continuous solution flow of 700 mL.h⁻¹
343 ¹, assuming that the convective part of the mass transport was fully controlled by the rotation of
344 the inner cylinder and neglecting the influence of the small axial flow.

345 **4.1.2. Nernst layer thickness without rotation**

346 CV were performed at 1 mV.s⁻¹ in phosphate solution that contained hexacyanoferrate (III) and
347 hexacyanoferrate (II) at equal concentrations ranging from 0 to 20 mM. The Figure 3 shows a
348 correct linear relationship between the I_L values extracted from the CV curves and the
349 hexacyanoferrate (II) concentrations, with a slope of 0.21 A.m³.mol⁻¹. According to the Nernst
350 hypothesis, this slope value corresponds to a Nernst diffusion layer thickness δ_N of 423 μ m
351 (equation 15 with 5.09×10^{-10} m².s⁻¹ for the hexacyanoferrate (II) diffusion coefficient and 18
352 cm² for the electrode surface area).



353

354 Figure 3: Experimental relation between I_L and the hexacyanoferrate (II) concentration without
 355 rotation of the inner cylinder; I_L values were obtained from the CV recorded at $1 \text{ mV}\cdot\text{s}^{-1}$; average
 356 values and standard deviations resulted from CV performed on 15 electrodes. The regression line
 357 corresponds to $I_L = 0.07 + 0.21C_b$ with $R^2 = 0.9995$.

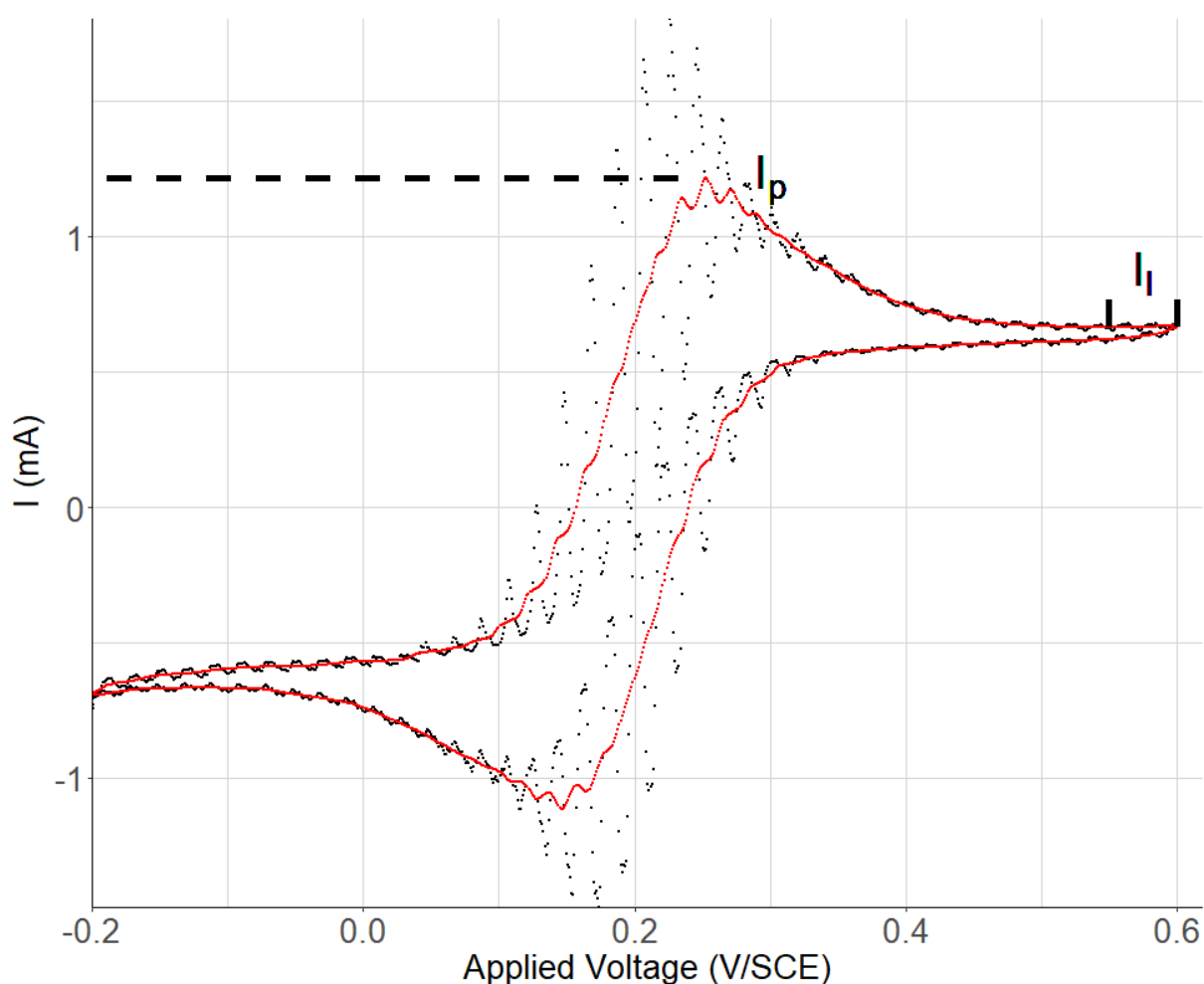
358 In fact, from a fully rigorous theoretical standpoint, the Nernst hypothesis should not be used in
 359 the absence of stirring, as it was the case here, but the equation of semi-infinite linear diffusion
 360 should be applied. Nevertheless, the estimation of a Nernst layer thickness is a relevant criterion
 361 for evaluating possible hydrodynamic disturbance at the electrode surface. In quiescent solution,
 362 parasite stirring may occur due to natural convection or parasitic motion, vibrations transmitted
 363 to the reactor for example. In quiescent condition, the thickness of the Nernst layer is typically in
 364 the range of a few hundreds of μm ; values ranging from 100 to 500 μm have been reported in the
 365 literature [58–60]. The high value of 423 μm obtained here confirmed that the continuous
 366 solution flow did not induce parasitic motion of the solution near the electrode surface.

367 4.2. Impact of hydrodynamics on the current produced by hexacyanoferrate (II) 368 oxidation

369 4.2.1. Correction of the effect electrode rotation on the current measured

370 With the rotation of the inner cylinder, the CV records were of extremely poor quality because of
 371 large discrepancy in the values of the current measured. By increasing the measurement

372 frequency in order to monitor the rapid current variations, it was observed that the current was
373 disturbed in a regular periodic way, with a period corresponding to the time for a complete
374 rotation of the cylinder. The reference electrode was located at a fixed point in the crown
375 between the inner and outer cylinders (Figure 1). Each working electrode, 1 cm wide,
376 represented a small section of the inner cylinder. As the cylinder rotated, the distance of each
377 working electrode from the reference varied from about 2 cm, when facing the reference, to half
378 a circumference (around 24 cm) when facing the opposite direction. The periodic variation of the
379 distance of the working electrode from the reference induced the periodic variation of the
380 potential of the working electrode, which was responsible for the periodic variation of the current
381 measured.



382

383 Figure 4: Numerical processing of the CV records. Raw data (black) obtained from the second
384 CV cycle of the anode *i* immersed in hexacyanoferrate (III/II) 1mM with supporting electrolyte,
385 with a flow rate of 700 mL.h⁻¹. CV was performed using a scan rate of 1 mV.s⁻¹ and the inner
386 cylinder rotated at 3 RPM. Fitted curve (red) after applying a moving average on $\Delta V = 20$
387 mV.rot⁻¹. Value of I_p and I_L represented.

388 This periodic perturbation of the current was corrected by numerically processing the raw data.
389 On Figure 4, an example of raw data is given (black points) and the same curve is represented
390 after applying a moving average correction (red curve). The moving average correction was
391 performed on the Volt interval ΔV , which corresponded to the potential range that was scanned
392 during one rotation of the inner cylinder. ΔV expressed in $V \cdot \text{rot}^{-1}$ corresponded to the ratio of the
393 scan rate σ ($V \cdot s^{-1}$) to the rotation speed of the inner cylinder ω (RPM):

$$394 \quad \Delta V = \frac{\sigma \times 60}{\omega} \quad (31)$$

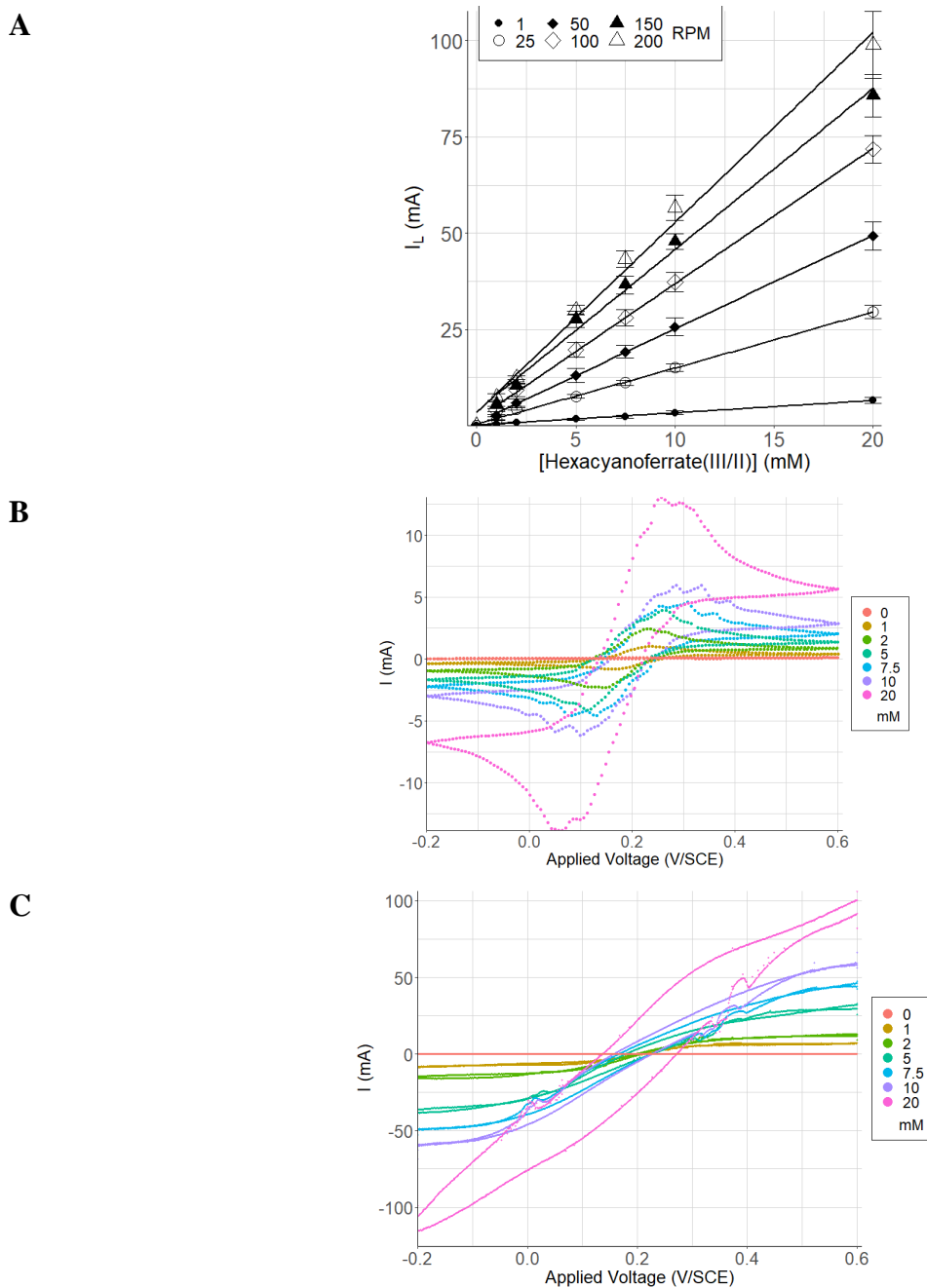
395 This correction was systematically used to interpret the CV records and extract the characteristic
396 values I_p and I_L .

397 **4.2.2. Determination of the limiting currents as a function of rotation speed**

398 CV were recorded at $1 \text{ mV} \cdot \text{s}^{-1}$ in phosphate solutions that contained equal concentrations of
399 hexacyanoferrate(II) and hexacyanoferrate(III) ranging from 0 to 20 mM. The eCTR was
400 continuously fed with the solution at $700 \text{ mL} \cdot \text{h}^{-1}$. The inner cylinder rotated at different speeds
401 from 1 to 200 RPM, which gave complete picture of the wavy vortex and turbulent vortex flow
402 regimes (Table 1). The limiting current I_L was measured as the mean value of the oxidative
403 plateau of the CV records observed at the upper values of the potential. I_L was represented as a
404 function of the concentration of hexacyanoferrate(II) in the bulk for different rotation speeds
405 (Figure 5A). The average values and standard deviations were calculated from the measurements
406 obtained from the 15 individually addressed electrodes, which were implemented for each
407 experimental condition.

408 In most cases, the CV records presented the well-known current peaks (in both oxidation and
409 reduction parts of the CV), which showed the transient rate-limiting effect of mass transfer
410 during the potential scan (Figure 5B). Considering the oxidation part ($I > 0 \text{ A}$), during the scan in
411 the positive direction, when the potential applied to the working electrode became higher than
412 the equilibrium potential, oxidation at the electrode surface consumed the electroactive species,
413 leading to the formation of the diffusive layer. When the applied potential increased quickly,
414 high transient currents were produced, but mass transfer was not able to provide a sufficiently
415 high flow of electroactive species to balance the electrochemical consumption, and consequently
416 the current decreased. This is the reason of the current peak observed at low hexacyanoferrate
417 (II) concentrations and low rotating speeds. In contrast, at high hexacyanoferrate (II)
418 concentrations and high rotating speeds, mass transport was more efficient and able to
419 compensate the consumption of the electroactive species, so that a stationary state was reached in

420 a large range of the potential scan. The transient peak vanished as the concentration and the
421 rotating speed increased (Figure 5C).



422 Figure 5: CV recorded with various hexacyanoferrate (III/II) concentrations and various rotating
423 speeds of the inner cylinder; only 6 rotation speeds are plotted among the 13 tested; equation of
424 the regression lines and the R^2 values are given in Supplementary Data Table S1. A) I_L values as
425 a function of hexacyanoferrate (II) concentration; average and standard deviations resulted from
426 the measures of 15 electrodes. B) CV curves from electrode *c* at 1 RPM and C) at 200 RPM.

427 In any cases, when the potential is high enough, only mass transfer was rate-limiting and the
428 value of the current did no longer depend on the value of the potential; the current displayed a
429 horizontal plateau on the CV records. Obtaining the I_L value was not obvious for the highest

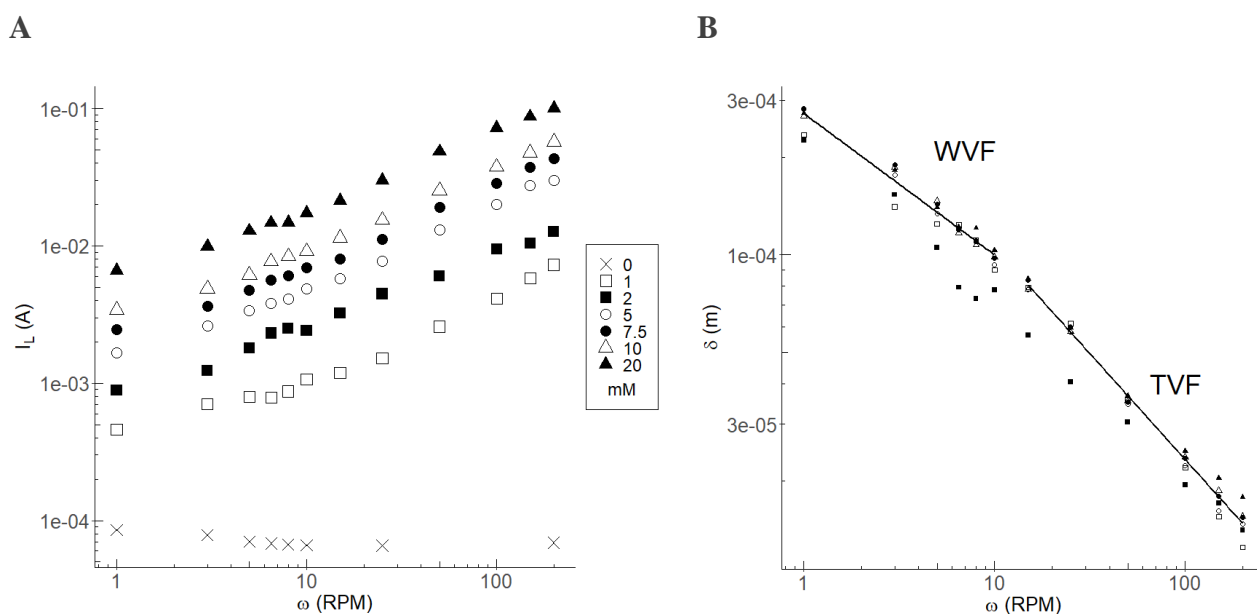
430 concentration (20 mM) and at high rotating speed (≥ 150 RPM) because, in these conditions,
431 mass transport tended to be less rate-limiting. The potential of the upper limit of the CV scan
432 was not high enough to rigorously reach the horizontal plateau that characterizes the limiting
433 current (Figure 5C). Nevertheless, it was not possible to use higher values of potential without
434 reaching the water oxidation range. In this case, I_L was assessed as the value of the current at the
435 highest potential value. I_L tended thus to be slightly underestimated for the highest concentration
436 value at the highest rotating speeds. Nevertheless, it can be observed in Figure 5A that the
437 deviation from the linear regression was very limited. These values were consequently kept for
438 further analysis but some precautions were taken when using these data.

439 **4.3. Evolution of the diffusive layer thickness with hydrodynamics: evidencing the** 440 **impact of wavy (WVF) and turbulent vortex flow (TVF)**

441 The eCTR was operated in the rotation speed range from 1 to 200 RPM, corresponding to Taylor
442 numbers from 144 to 28,793 (i.e. $2.7Ta_c < Ta < 544Ta_c$) allowing to cover different
443 hydrodynamic regimes from the wavy vortex to turbulent vortex flows (see Table 1). To analyze
444 the impact of the hydrodynamic regime on the electrochemical reactions, the limiting current I_L
445 was represented as a function of ω using a log scale for the different selected concentrations of
446 hexacyanoferrate (II) (Figure 6A).

447 Without any electroactive species, the velocity had no significant effect on the limiting current
448 ($I_{L0mM} \approx 70 \mu\text{A}$ for each ω), showing that the residual currents were likely due to adsorbed
449 species rather than soluble species contained in solution. For each concentration from 1 to 20
450 mM, a log-linear increase of the limiting current with the rotation speed was observed,
451 highlighting the decrease in the limitation due to mass transfer. To illustrate the influence of
452 hydrodynamics independently of the concentration of the reactive species, the Nernst-diffusive
453 layer thickness (δ_N) is calculated using equation 15 (Figure 6B) and by considering $I_L - I_{L0mM}$
454 for the calculation. Figure 6B presents the diffusion layer thickness δ_N calculated from the
455 experimental data as a function of the rotation speed ω using a log scale. A significant difference
456 is observed between the curve for a concentration of hexacyanoferrate (II) of 2 mM and the other
457 concentrations. This difference could be linked to an experimental bias for intermediate rotation
458 speed from 5 to 50 RPM. Consequently, this concentration is no longer considered for further
459 data exploitation.

460



461 Figure 6: A) Effect of the angular velocity on the I_L value obtained on CV at various
 462 concentrations of hexacyanoferrate (II) B) Effect of the angular velocity on the diffusive layer
 463 thickness. Data recorded at 2 mM are represented in the graph but they were excluded from the
 464 regressions. WVF: Wavy Vortex Flow; TVF: Turbulent Vortex Flow. Data are represented on a
 465 log scale; each point is the average value obtained from 15 electrodes.

466 The increase in the rotation speed of the inner cylinder induced a velocity profile gradient along
 467 the gap between the two cylinders with a maximum velocity near the inner cylinder where the
 468 anodic reaction was located. As expected, δ_N decreased with higher rotation speed.

469 Moreover, by considering the experimental points for all concentrations, two distinct linear
 470 evolutions are observed, with a modification of the slope for a rotation speed in the range from
 471 10 to 15 RPM. This slope break showed the transition between the wavy vortex and the turbulent
 472 vortex flows, and confirms the boundary of $40 Ta_c$ (corresponding to 14.8 RPM).

473 For each identified flow regimes (WVF and TVF for $\omega < 10$ RPM and $\omega > 15$ RPM
 474 respectively), the Nernst-diffusive layer thickness (and the associated limited current I_L) varied
 475 with the rotation speed according to a power law, as expected from the theory for laminar and
 476 turbulent flows in equations 19 and 28:

$$477 \quad \delta_N = 10^{-K} \omega^{-\alpha} \quad (32)$$

478 Values of K and α resulting from numerical fitting of the experimental data are provided in Table
 479 2. For 10 and 20 mM, K and α values may be underestimated considering the approximation in
 480 the calculation of the I_L value shown in 3.2.2. for high concentration and high velocities.
 481 Nonetheless, they followed the same tendency as for the other concentrations. The value of α

482 coefficient (0.44 and 0.66 for WVF and TVF respectively), is more sensitive to the modification
 483 of the flow regime than the coefficient K (3.99 and 3.97 for WVF and TVF respectively). Its
 484 dependency on the flow regime is linked to the difference in the physical nature of the flows,
 485 from a more structured one for the WVF to a more heterogeneous and chaotic flow for the TVF
 486 one. Those results help describing the two different Couette-Taylor vortex flows by estimating
 487 the Nernst-diffusive layer thickness using electrochemical tools and confirmed the boundary
 488 value between these two regimes.

489 Table 2: Values of the experimental coefficient of the log correlation of the diffusive layer and
 490 the concentration of the electroactive species $\delta_N = 10^{-K} \omega^{-\alpha}$. Values are given for each
 491 concentration, for the total dataset or by removing the 10 and 20 mM concentrations.

Hexacyanoferrate (III/II) (mM)	Wavy Vortex Flow			Turbulent Vortex Flow		
	K_{WVF}	α_{WVF}	R^2	K_{TVF}	α_{TVF}	R^2
1	4.0	0.38	0.96	3.9	0.73	1.00
5	4.0	0.47	1.00	4.0	0.66	1.00
7.5	4.0	0.47	0.99	4.0	0.66	1.00
10	4.0	0.45	0.98	4.0	0.63	1.00
20	4.0	0.42	0.99	4.0	0.60	1.00
Total set	4.0	0.44	0.96	4.0	0.66	0.99
Total set (without 10 and 20 mM)	4.0	0.44	0.96	4.0	0.68	0.99

492

493 5. Discussion

494 5.1. Flow characterization using micro-electrodes in CTR

495 The study of Couette-Taylor hydrodynamics has already been carried out using microelectrodes
 496 integrated in the outer cylinder. Sobolík *et al.* [48,61] characterized axial and azimuthal
 497 components of the shear rate on the wall of the outer cylinder of a CTR using a microelectrode.
 498 They measured the limiting current I_L with the three-segment microelectrodes on the surface of
 499 the outer cylinder and deduced the shear rate ($\dot{\gamma}$) and the associated shear stress ($\tau = \mu\dot{\gamma}$) from
 500 the rotation speed of the inner cylinder. Under laminar condition, their results confirmed the
 501 theoretical evolution of the limiting current according to shear rate $I_L \propto \dot{\gamma}^n$ (equation 18 for
 502 shear rate in the range $4 - 80 \text{ s}^{-1}$) with an experimentally determined value $n = 0.31$ (close to
 503 the theoretical value of 0.33).

504 As the fluid velocity is directly linked to shear rate τ in Couette-Taylor flows (equation 7, 8 or 9
505 depending on the flow regime), it is possible to express the limiting current obtained by Sobolík
506 *et al.* [48,61] as a function of the rotation speed for wavy vortex flows, in the form $I_L \propto \omega^\alpha$. It
507 gave $\alpha = 0.45$ considering equation 8 for the shear rate range tested. The same approach has
508 been considered by Berrich *et al.* [49] with the same parameter values n for the calculation of the
509 shear rates giving the components of the vortices on the outer wall using more electrodes.

510 Those results obtained under wavy vortex conditions showed similar values of α (0.45) than the
511 results presented here on the rotating inner cylinder (0.44). Considering non-laminar conditions
512 by comparison of the theoretical value of Gabe & Robison [52], this tends to show the major
513 effect of vortices on the electrochemical reactions next to the walls of CTR, even next to the
514 outer wall due to the divergence with laminar theoretical behavior.

515 The approach used in our work with large and numerous electrodes shows also reliable and
516 reproducible results such as the ones obtain with much precise electrodes used for precise
517 understanding of hydrodynamics in CTR.

518 **5.2.Comparison between RCE and CTR with literature experimental and theoretical** 519 **results**

520 Rotating cylinder electrode (RCE) are reactors in which a cylinder is rotating in the electrolyte
521 with no influence of the outer wall of the reactor on the flow [34]. A RCE could thus be
522 considered as a CTR with a so small radius ratio (R_i/R_o) that the impact of the outer cylinder
523 can be neglected. In comparison, CTR are characterized by the major influence of the outer wall
524 on the flow and with conversely high radius ratio. It is generally observed in literature that
525 Couette-Taylor flows appear from a radius ratio of 0.5 giving typical RCE with radius ratio
526 bellow this value [40,62]. It is still necessary to investigate those flow differences on
527 electrochemical reactions.

528 Correlations have been established on different devices between the Sherwood numbers and the
529 Reynolds numbers as shown in Figure 7. For comparison, Sherwood numbers were calculated
530 from the present work (equation 4) by using the average value of Nernst-diffusive layer for each
531 rotation speed.

532 Former work has been done to characterize the influence of mass transfer in RCE [35]. One of
533 the main study focused on hydrodynamic in RCE was proposed by Eisenberg *et al.* [34]. They
534 considered the effect of various geometries (with radius ratio from 0.2 to 0.4) and Reynolds
535 number 1,000 to 100,000 (corresponding to the range from 4.6 to 460 RPM for the eCTR

536 presented in this study). They characterized mass transfer on the rotating cylinder-electrode
537 surface. Eisenberg *et al.* [34] gave an α value only different by 6% from the data under turbulent
538 vortex flow from present study in Figure 7 (from equation 32). Thus, the present work gave
539 similar results to those in RCE for turbulent flows due to the lower influence of the fixed outer
540 cylinder on hydrodynamics at inner cylinder wall under turbulent regime.

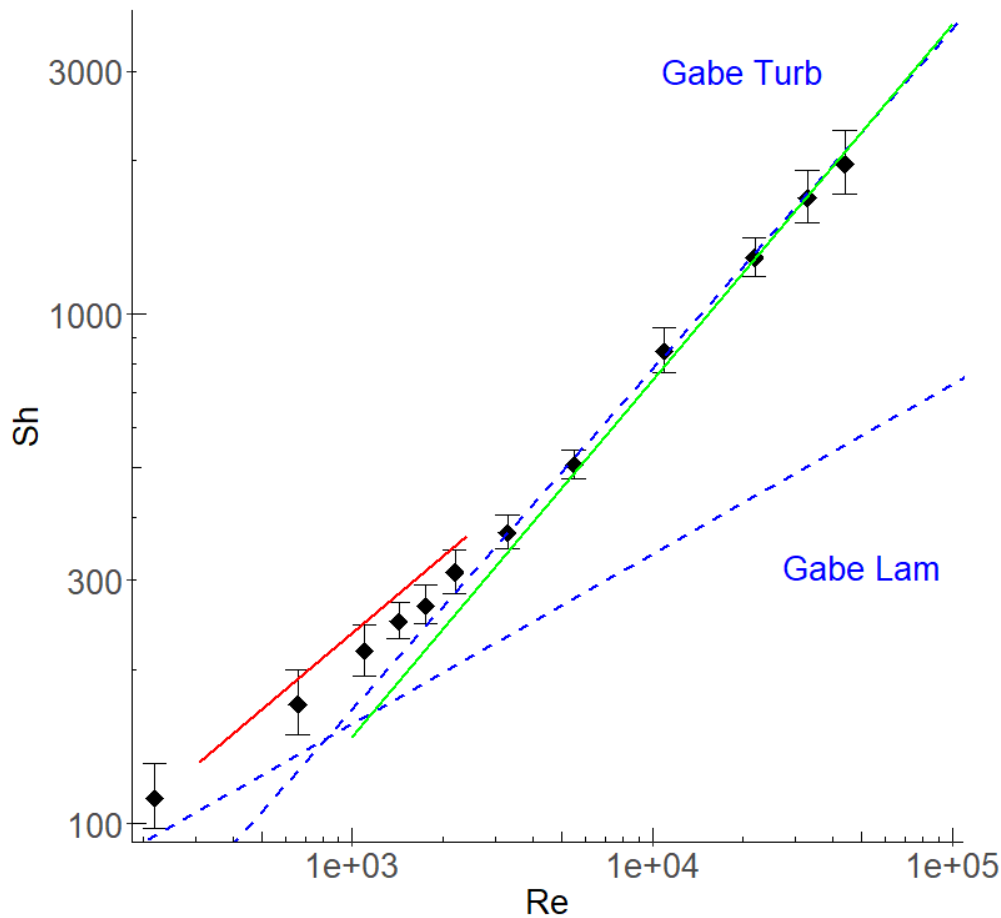
541 A mass transfer analysis of a CTR was also made electrochemically by Legrand *et al.* [50] with
542 an inner cylinder containing both cathode and anode in a device with a radius ratio of 0.8 (gap
543 between the two cylinders of 5 mm) with Ta values from 200 to 1600 (corresponding to values
544 from 1.4 to 11 RPM in this study). They followed the impact of vortices and axial flow on the
545 reduction reaction that occurred on the inner cylinder rotating electrode by measuring the
546 Sherwood number. Without axial flow, i.e. for equivalent operating conditions than in the
547 present study, Sherwood expression reveals similar behavior in the Re range corresponding to
548 wavy vortex flow ($Re < 2400$). They was a mean difference in Sherwood numbers from
549 empirical correlation of Legrand *et al.* [50] and the experimental points of 13% (with maximal
550 difference of 15% for 8 RPM) related to experimental measurement accuracy and
551 reproducibility.

552 The Sh versus Re correlations calculated from the theoretical models of Gabe & Robinson
553 [52,53] (equation 21 and 30) are also presented in Figure 7. The parameter B from equation 30
554 was estimated to $B = 5.71 \times 10^{-3}$ [-] using the experimental data under turbulent vortex flows.
555 The correlations are represented with dotted lines for a large range in terms of Reynolds number
556 even if they are only applicable in strictly laminar and turbulent flow respectively.

557 The theoretical model of Gabe & Robinson [52,53] states two different behaviors. The Figure 7
558 shows an excellent correspondence between the experimental points for turbulent vortex flows
559 and this theoretical model. The hypothesis made by to establish their equations for the turbulent
560 flows could therefore be applied to data obtained in turbulent vortex flow. In this regime, the
561 main part of the mass transport is due to the turbulence. Likewise, results from Eisenberg *et al.*
562 [34] also follow this tendency and could corroborate the negligible part of the vortex transport in
563 turbulent vortex flow.

564 A different behavior appears for wavy vortex flow, which was not described theoretically [52].
565 The data recorded at this regime match neither the theoretical curves for the laminar flow nor
566 those for the turbulent flow. It emphasizes the impact of another phenomenon than the ones
567 described theoretically for Re values that may be due to vortices. Sherwood numbers are also
568 slightly higher in the experimental approach under wavy vortex flows than in the laminar theory,

569 which corroborates the role of the vortex in increasing the transfer close to the electrode surface
570 for such rotation speeds (Figure 7).



571

572 Figure 7: Sherwood number (Sh) as a function of Reynolds number (Re). Comparison of
573 correlations from Eisenberg *et al.* [34] in green, in the CTR of Legrand *et al.* [50] in red and with
574 the theoretical equations of Gabe & Robinson [52,53] in dashed blue using $B = 5.71 \times$
575 10^{-3} [–]), versus the experimental data (\blacklozenge obtained with the 5 concentrations for the 15
576 electrodes).

577 The eCTR developed here gave results that matched the experimental and theoretical results
578 reported in the literature for identical flow regimes. Moreover, it enriches the former results by
579 characterizing the wavy vortex regimes, which were clearly distinct from the turbulent vortex
580 flows.

581 **5.3.Characterization of coupled fluid dynamics and electrochemical modelling in**
582 **Couette-Taylor vortex flows**

583 The range of Couette-Taylor flows is described in Table 3 and it allows having a new point of
 584 view on the transition between vortices and turbulence besides their impact on electrochemical
 585 reactions.

586 The present eCTR allowed the control of diffusive layer thickness going from 15 to 423 μm
 587 (Table 3). For microbial electrochemical processes, this thickness range is interesting regarding
 588 the thickness of electroactive biofilms, which commonly ranges from 20 to 250 μm [63–65].
 589 Indeed, shear stress is a promising way to control biofilm development [38,66], coupled to the
 590 control of mass transfer close to the electrode. The shear stress is also known as an important
 591 factor that influences biofilm structural properties [39,41,42]. In non-electroactive biofilms,
 592 increased shear is known to enhance particle detachment at the surface of the biofilm, which
 593 often lead to the formation of a thin and dense biofilm [38,66]. Nevertheless, such investigations
 594 are rarely done on electroactive biofilms. The eCTR developed here allowed applying a range of
 595 shear stress from 10^{-4} to 10 Pa (from equation 7 and 9) versus 10^{-1} to 10^2 for the RCE [37]. These
 596 shear stress values can be applied to up to 20 biofilm duplicates developed in exactly the same
 597 hydrodynamics condition. This should be a powerful tool to explore the influence of shear stress
 598 on the formation, maturation, electrochemical efficiency and, possibly, regeneration of
 599 electroactive biofilms [67].

600 Table 3: Key parameters of the study

Flow characteristics	Taylor range	Rotation speed (RPM)	Nernst diffusive layer thickness (μm)	Shear stress (mPa)	α value
No rotation	$Ta=0$, Axial flow ≈ 0	0	423	$\tau \approx 0$	NA
WVF	$140 \leq Ta \leq 2100$	$1 \leq \omega \leq 14.8$	$274 \geq \delta_N \geq 84.5$	$0.1 \leq \tau \leq 40$	0.44
TVF	$2100 \leq Ta \leq 29000$	$14.8 \leq \omega \leq 200$	$80.4 \geq \delta_N \geq 14.6$	$40 \leq \tau \leq 2700$	0.66

601

602 6. Conclusion

603 The proposed eCTRreactor is able to describe electrochemical kinetics in controlled
 604 hydrodynamic conditions decoupled from the flow input for low axial flow rates. Results are
 605 repeatable on the 16 electrodes connected that will help characterizing the influence of
 606 hydrodynamics on electroactive biofilms allowing performing conveniently replicates. The big

607 size planar electrodes give a large electroactive surface to develop biofilms in the same
608 hydrodynamics conditions and will allow sampling representative part of whole biofilm for
609 comprehensive analysis during long-term experiments.

610 The characterization of the electrochemical response has been made as a function of the flow
611 regime. The electrochemical diffusive layer thickness (δ_N) on the surface of the inner cylinder
612 were extracted from the limiting current values (I_L) and correlated to the rotation speed of the
613 inner cylinder. Those relations are given as function of the Couette-Taylor flow regime and are
614 then linked to the shear stress resulting from hydrodynamics. Such characterization is necessary
615 to further understand how biofilm development can affect electrochemical response.

616 The CTR vortices influence deeply electrochemical behavior for lower fluid dynamics. The
617 vortices are responsible of the main part of the mass transport under the wavy vortex flow while
618 the turbulence is responsible of most of the mass transport in the turbulent vortex flow. Results
619 of this study contribute to better understand the role of fluid dynamics on electrochemical
620 reactions in Couette-Taylor reactors.

621 **References**

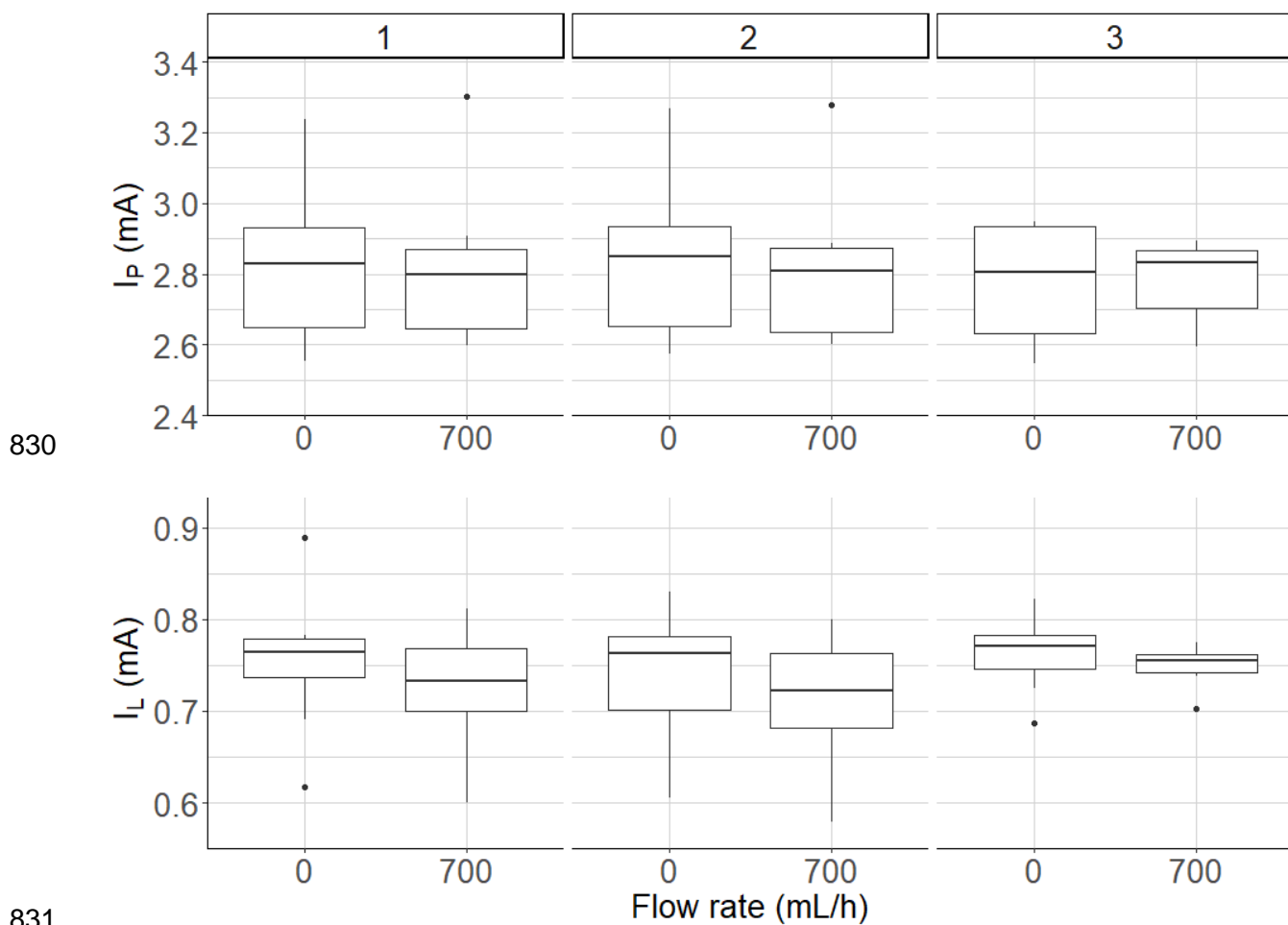
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832 Figure S1: CV cycle and recirculation effect on 8 working electrodes (c-e-h-j-m-o-r-t) acting as
833 anodes oxidizing hexacyanoferrate II, for the values of A) I_p and B) I_L calculated. I_p was
834 considered as the maximum of each anodic curve. I_L is the mean value of the oxidative plateau of
835 the curves from 0.55 to 0.6V/SCE.

836 Table S1: Correspondence of the R^2 value obtained from the correlation between I_L and
 837 hexacyanoferrate (III/II) concentration for the different rotation speeds of the inner cylinder and
 838 number of experimental points used for the correlation.

ω (RPM)	0	1	3	5	6.5	8	10	15	25	50	100	150	200
Slope	0.21	0.32	0.47	0.61	0.70	0.71	0.85	1.0	1.5	2.4	3.5	4.2	4.9
Intersect	0.07	0.1	0.2	0.2	0.3	0.5	0.4	0.6	0.4	0.8	1.7	3.8	3.4
R^2	1.00	1.00	1.00	1.00	1.00	0.99	1.00	1.00	1.00	1.00	1.00	0.99	0.99
N	105	195	105	195	105	105	195	90	105	179	180	90	105

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