

# Mass Transfer Measurements in a Parallel Disk Cell Using the Limiting Current Technique

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**Abstract.** Mass transfer measurements in electrochemical cell using a different design and Reynolds numbers have been made in a parallel plate cell of disk geometry. The cell has only one inlet and exit, which produces extremely complex hydrodynamics in the cell. The mass-transfer coefficient was obtained using limiting diffusion current technique based in ferricyanide ion reduction, also overall mass transfer coefficients were correlated to the Reynolds number range between 80 to 1039. Here, we have made a theoretical approximation of the mass-transfer coefficient for disk geometry using the Levique relation. Finally, the disk design cell has showed improvements in the mass transfer coefficient.

**Keywords:** Electrochemical cell; limiting diffusion current technique; Mass transfer coefficient; Engineering parameters.

**Resumen.** Las mediciones de transferencia de masa usando una celda electroquímica con un diseño diferente al usual han sido realizadas. Asimismo, fueron calculados los números de Reynolds con esta celda de placas paralelas con geometría de disco. La celda tiene solamente una entrada y una salida, la cual produce una hidrodinámica compleja. El coeficiente de transferencia de masa se obtuvo usando la técnica de la corriente límite basada en la reducción del ión del ferricianuro, asimismo, los coeficientes totales de la transferencia de masa fueron correlacionados al número de Reynolds en un rango de 80 a 1039. Aquí, se realizó una aproximación teórica del coeficiente de transferencia de masa para la celda con una geometría de disco usando la relación de Levique. Finalmente, el nuevo diseño de celda mostró un incremento en el coeficiente de transferencia de masa.

**Palabras clave:** Celda electroquímica; técnica de la corriente límite de difusión; coeficiente de transferencia de masa; parámetros de ingeniería.

## List of symbols

$A$	electrode surface area ( $m^2$ )
$C$	bulk species concentration ( $\text{mol m}^{-3}$ )
$D$	diffusion coefficient ( $m^2 s^{-1}$ )
$d_e$	equivalent diameter (m), $d_e = 2ws/(w + s)$
$F$	faradaic constant ( $96\,487\text{ C mol}^{-1}$ )
$I_L$	electrolysis limiting current (A)
$K$	mass transfer coefficient ( $m s^{-1}$ )
$L$	electrode length (m)
$Re$	Reynolds number
$s$	inter-electrode distance (m)
$S_c$	Schmidt number
$S_h$	Sherwood number, based on cell or channel equivalent diameter
$w$	section of cell or channel ( $m^2$ )
$z$	electrons exchanged in electrode reaction
$u$	mean fluid velocity in cell or channel ( $m s^{-1}$ )
$Q$	volumetric flow rate ( $m^3 s^{-1}$ )

## Greek letters

$\rho$	fluid density ( $\text{kg m}^{-3}$ )
$\nu$	kinematic viscosity ( $m^2 s^{-1}$ )
$\mu$	dynamic viscosity ( $\text{kg s}^{-1} m^{-1}$ )

## Introduction

Many electrochemical processes are operated under limiting or near limiting current conditions to maximize the time of the electrolyte on the cell. Mass transport therefore determines the rate of conversion of reactant to product and it is common to use inert turbulence promoters, baffles, and/ or high fluid velocity to enhance the mass transport to the electrode surface and hence, the cell current density [1]. Cells consisting of planar electrodes in a parallel plate configuration are the most frequently used industrial type of electrochemical reactor. Such reactors combine simplicity of design, manufacture and versatility, which enables them to be used for several process. However, the increase of the mass transfer coefficient ( $K$ ) may be encountered resulting from complex combinations of geometry and hydrodynamics, especially in entry and exit regions of the cell. The relationship between a parallel plate cell geometry, the cell flow conditions and mass transfer performance has been described for some specific cases [2]. Goodridge *et al.* [3] studied mass transfer in different sizes of baffled cells using the electrochemical limiting current measurement method. Wragg and Leontaritis [4] described measurements of local mass-transfer and current distributions in a parallel plate cell, of similar dimensions of the Goodridge and Mamoor cells. Wragg *et al.* [5] studied mass-transfer distributions near cell entries and corners in the electrochemical flow

cell, while Bengoa *et al.* [6] carried out flow visualization studies and modeling of a filter press type electrochemical reactor. Oduoza and Wragg [1] also studied the effects of baffle length on mass transfer in a parallel plate rectangular electrochemical cell. Several studies [7-14] have been made about the experimental conditions, phenomena interactions, inert turbulence promoters, design of cell, combinations geometry on the electrochemical cell, mathematical models and others parameters that have had a very important role in the hydrodynamic improvement and advantage of the cell. Also different types of cell constructions have been designed during recent years. Efficient cells design have been directed towards optimizing of the space time yield modifying specific electrode area  $A$  and/or large mass transport coefficient  $K$  [15].

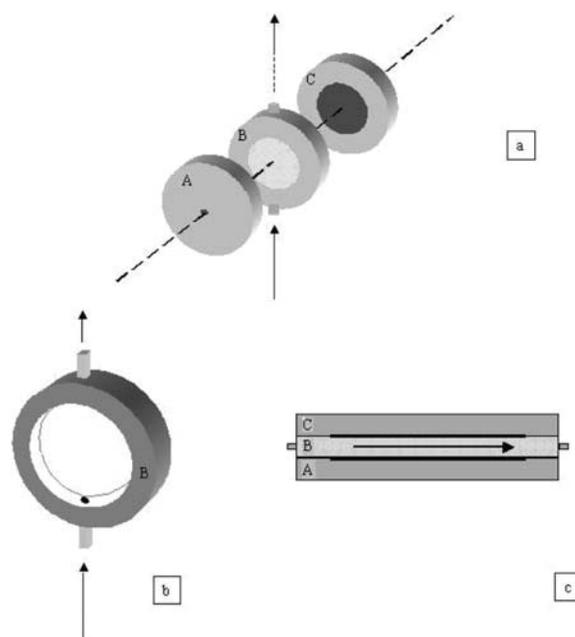
In the wastewater treatments, the electrochemistry offers interesting approaches for the incineration of the organics compounds [14], such as the versatility of the process and the simplicity of the reactors in terms of construction and management. Usually, the reactors employed in the electrochemical oxidation are single body cell type and rectangular cells. The electrochemical oxidation process is an example where the continuous advances in reactor designs and construction are necessary. This process promising versatility, environmental compatibility and potential cost effectiveness in degradation of the organic pollutants [16]. The electrochemical oxidation method has been proposed for the destruction or/and conversion of mixed waste, when the wastewater contains refractory organic pollutants or toxic substances. However the design and efficiency of the reactor is a significant parameter for the process optimization. For this reason, the constants and several studies realized about the electrochemical cell have permitted advances on the optimization.

The aim of this work is to carry out the characterization of the electrochemical cell using the limiting diffusion current technique based in ferricyanide ion reduction for determination of the mass transfer coefficient  $K$ . This is a key parameter for understanding the use of the electrochemical cell before of the electrochemical oxidation application. Also, a comparison has been made between the experimental  $K$  obtained for disk geometries and calculated  $K$ . The latter was obtained through a theoretical approximation using Levique relation because no attempts to determinate mathematical  $K$  for the disk-type cell geometry by alternative mathematical methods have been published yet. Finally, the disk design cell has showed improvements in the mass transfer.

## Experimental

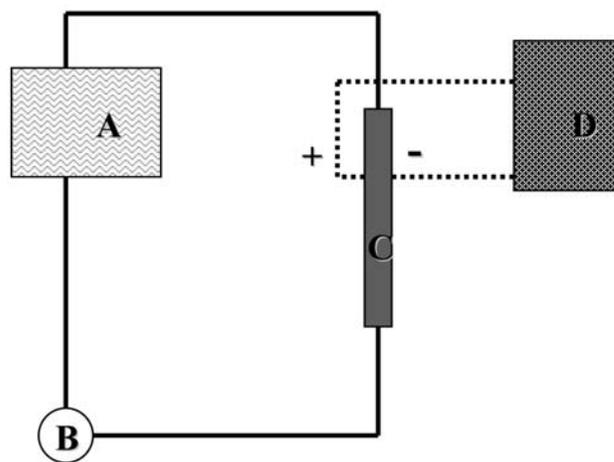
### a. Cell and Electrodes

The experiments were made in a one compartment electrolytic flow cell with parallel plate electrodes as the schematic diagram of the flow and cell are shown as Figure 1. The cell is formed with parallel disk plate electrodes which were made of nickel sheets 0.5 mm thick and each had a total active area of 63.5 cm<sup>2</sup>, with an interelectrode gap of 10 mm. A saturated



**Fig. 1.** Design of the electrochemical cell. 1a) Different compartments of the cell: A) anodic compartment, B) electrolysis compartment and C) Cathodic compartment. 1b) Electrolysis compartment: One inlet and outlet section. 1c) Electrolyte distribution in the central compartment and toward electrode surfaces.

calomel electrode (SCE) was used as the reference electrode. The cell has only one inlet and exit; the central compartment cell was provided for electrolyte circulation through the parallel disk cell using a peristaltic pump. The cell compartments were made of PVC constructed to accommodate the disk electrodes. The electrolyte was stored in a glass tank and circulated through the electrolytic cell (Figure 1B). The electrolyte flow rate was kept at 165 dm<sup>3</sup> h<sup>-1</sup>. The system used for this research is shown in Figure 2.



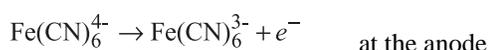
**Fig. 2.** Design of system A) Electrolyte reservoir, B) peristaltic pump, C) electrochemical cell and D) power supply.

The electrochemical oxidation experiments were carried out at PbO<sub>2</sub> electrode, with chloranilic acid (C<sub>6</sub>H<sub>2</sub>Cl<sub>2</sub>O<sub>4</sub>) in solution at 100 ppm of concentration.

### b. Techniques and Instrumentation

Characterization of the flow cell, was achieved in an aqueous solution of potassium ferro/ferricyanide considering the range from 20 to 80 mM in 0.5 M NaOH (K<sub>3</sub>Fe(CN)<sub>6</sub>/K<sub>4</sub>Fe(CN)<sub>6</sub>/NaOH-H<sub>2</sub>O). The ferrocyanide concentration was double the ferricyanide concentration to ensure a limiting reaction rate at the cathode. The physical properties of the electrolyte are shown in Table 1 [4].

The reactions in this system are as follows:



Mass-transfer coefficients were determined through the diffusion limiting current technique [5, 17], from these curves were obtained the limiting current values at different redox couple concentrations. Data was also obtained in the cell with the following equation:

$$K = \frac{I_L}{zFAC_\infty} \quad (1)$$

which was used to calculate mass transfer coefficient from the limiting current values.

## Results and Discussion

### a. Mass transfer coefficient

Polarization curves for the cell in the disk configuration are shown in Figure 3; the reported data was obtained at a constant flow rate ( $Q = 4.6 \times 10^{-5} \text{ m}^3/\text{s}$ ) but at different ferro/ferricyanide concentrations (from 20 to 80 mM, in 0.5 M NaOH). Figure 4 presents the obtained limiting current values as a function of the ferro/ferricyanide concentration. As expected, a linear dependence was obtained, which allowed the calculation of the experimental mass transfer coefficient  $K$  for the disk-type cell, by means of equation 1 and a value of  $2.1 \times 10^{-5} \text{ m s}^{-1}$  could be obtained.

In addition to the mass transfer coefficient increase, the characteristics of the cell allow a better flow control, increasing the effective distribution of the electrolyte onto the elec-

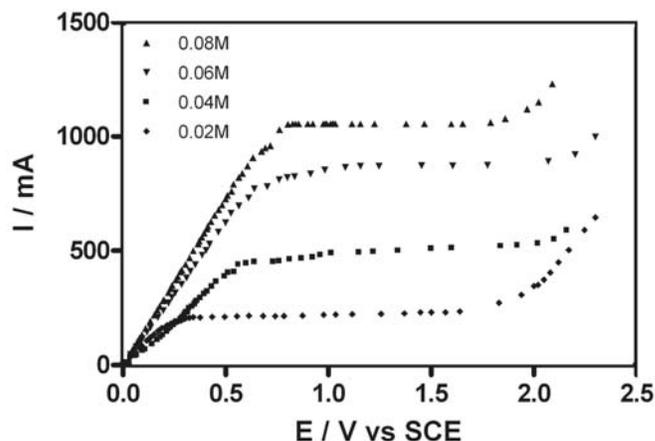


Fig. 3. Polarization curves for the mass transfer characterization of the electrochemical cell, using the ferro/ferricyanide redox couple (30 mM, in 0.5M NaOH).

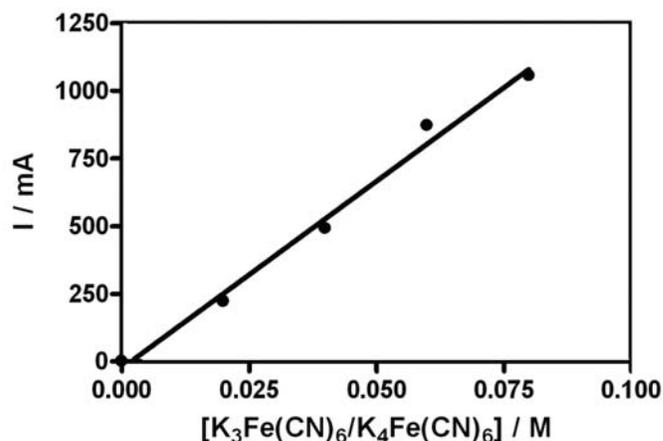


Fig. 4. Dependence of the limiting current on the ferro/ferricyanide concentration.

trode surface with respect to the usual single body cell. An approximation of the mass transfer coefficient was also obtained theoretically, on the basis of the definition of the Sherwood parameter [18], which relates  $S_h$  with  $K$ . This taking profits from the relationship proposed by Leveque (equation 3 below), for a laminar flow in a rectangular channel [19], and of the definitions of Reynolds (Re) and Schmidt ( $S_c$ ) parameters [18]:

$$S_h = \frac{K \cdot d_e}{D} \quad (2)$$

$$S_h = 1.85 \left[ \text{Re} \cdot S_c \cdot \frac{d_e}{L} \right]^{1/3} \quad (3)$$

Table 1. Physical properties of the electrolyte at 20°C [4].

Density	1020.5	Kg m <sup>-3</sup>
Viscosity	$1.105 \times 10^{-3}$	Kg m <sup>-1</sup> s <sup>-1</sup>
Kinematic viscosity	$1.083 \times 10^{-6}$	m <sup>2</sup> s <sup>-1</sup>
Diffusivity of ferricyanide ion	$6.631 \times 10^{-10}$	m <sup>2</sup> s <sup>-1</sup>
Schmidt number	1633	

where:

$$Re = \frac{ud_e}{\nu} \quad (4)$$

$$S_c = \frac{\nu}{D} \quad (5)$$

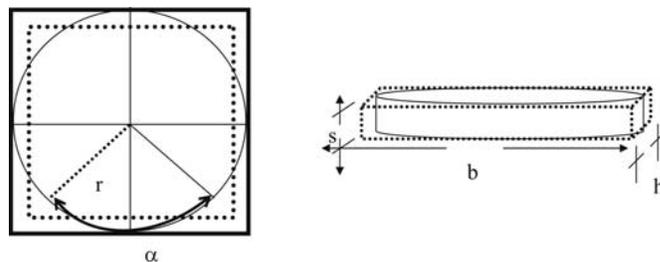
$$d_e = \frac{2(b \times s)}{(b + s)} \quad (6)$$

Nevertheless, in these equations the characteristic length parameter ( $d_e$ ) is considered for a rectangular cell and for this reason, in the planar disk geometry it was necessary to consider the radius for realizing the approximation of ( $d_e$ ). To use the Leveque relationship, the present electrochemical cell, with planar disk electrodes having a diameter of 9 cm, has been approximated to a rectangular channel considering the circumference arc denominated in this work as  $\alpha$ , and a height of 10 mm (inter-electrode gap); hence:

$$\alpha = \frac{\pi \times r}{4}$$

$$w = b \times s = 3.53 \times 10^{-4} \text{ m}^2 \quad d_e \approx 1.559 \times 10^{-2} \text{ m}$$

Due to the differences between rectangular and disk cells, the radius were considered for the approximation of  $b$  according to Figure 5, where  $b$  in the rectangular channel cell relatively represents the circumference arc obtained from the cylindrical form. This value of  $b$  represents an approximation of a rectangular cell that can include the disk, represented by the outlined line in Figure 5. Once the characteristic length parameter ( $d_e$ ) is known, the theoretical mass transfer coefficient for this electrochemical cell can be estimated. For an electrolyte flow of  $4.6 \times 10^{-5} \text{ m}^3 \text{ s}^{-1}$ ,  $Sh_h$  and  $Re$  numbers of 123 and 1040 are respectively obtained (equations 3 and 4); the  $K$  value, calculated using equation 2, results therefore to be  $5.06 \times 10^{-6} \text{ m s}^{-1}$ . Interestingly, the experimentally determined value of  $K$  is more than three times higher than the theoretical value just obtained. This discrepancy has to be ascribed to an inhomogeneity of the flow in the cell; certain zones of the electrode could have a higher coefficient of local transfer (inlet



**Fig. 5.** Disk geometry and the rectangular cell with equivalent dimensions, for determining the mass transfer coefficient through a theoretical approximation using Leveque relation.

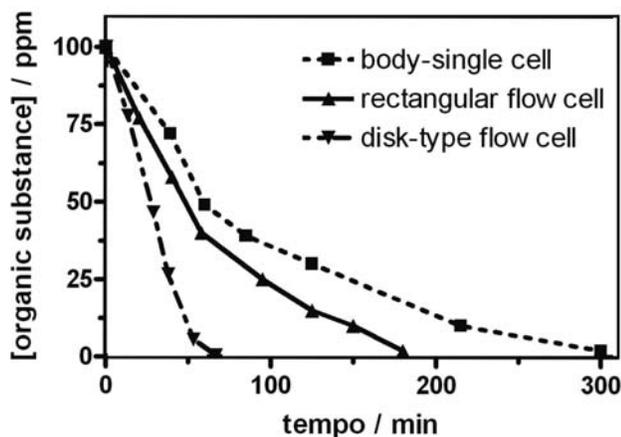
and outlet areas), whereas other parts might suffer from mass transfer limitations.

On the other hand, different values for the deciding engineering parameters can be obtained for the electrochemical cell, depending on the electrolyte flow and in turn, on the performance of the peristaltic pump. Data in Table 2 have been obtained according to the mathematical approach used for this cell geometry and thus they represent relative estimations of the possible experimental results. These results indicate that the mass transfer coefficient is dependent of flow, nevertheless at the high flows the mass transfer coefficient seem to continue in the same values; as can be seen in the Table 2. Also, the  $Re$  values shown that the flow regimen is laminar, but due to the cell geometry is possible that certain zones can be promoted local turbulence regimens.

In addition, with the results obtained in the previous experiments, we decided to probe the disk design cell's performance for the electrochemical oxidation of organics; and of chloranilic acid in particular only to demonstrate the improvements in efficiency for this cell during the electrochemical oxidation. According to results reported in Figure 6, the rate of the electrochemical oxidation of this organic substrate was increased due to an increase in the mass-transfer coefficient obtained for the disk-type cell. The cells were used at similar experimental conditions of anode area, temperature, flow, current density and concentration of chloranilic acid in solution, these conditions have permitted the comparison between these electrochemical cells. According to results obtained in this

**Table 2.** Hydrodynamic parameters for the disk-type cell design.

Flow (dm <sup>3</sup> /h)	14	27	55	82	100	130	150	160	165
Flow (m <sup>3</sup> /s)	3.9·10 <sup>-6</sup>	7.5·10 <sup>-6</sup>	1.5·10 <sup>-5</sup>	2.2·10 <sup>-5</sup>	2.8·10 <sup>-5</sup>	3.6·10 <sup>-5</sup>	4.2·10 <sup>-5</sup>	4.4·10 <sup>-5</sup>	4.6·10 <sup>-5</sup>
Re	88.2	170.2	346.6	516.84	630.3	819.4	945.4	1008.5	1039.9
Sh	54.1	67.3	85.3	97.5	104.1	113.6	119.2	121.8	123.0
K (m/s)	2.2·10 <sup>-6</sup>	2.7·10 <sup>-6</sup>	3.5·10 <sup>-6</sup>	4.0·10 <sup>-6</sup>	4.3·10 <sup>-6</sup>	4.7·10 <sup>-6</sup>	4.9·10 <sup>-6</sup>	5.0·10 <sup>-6</sup>	5.06·10 <sup>-6</sup>



**Fig. 6.** Improvements in the electrochemical oxidation of chloranilic acid ( $C_6H_2Cl_2O_4$ ) using  $PbO_2$  electrode, at similar experimental conditions of anode area =  $63.5\text{ cm}^2$ , temperature =  $25^\circ\text{C}$ , flow =  $165\text{ l/h}$ , current density =  $10\text{ mA/cm}^2$  and concentration of chloranilic acid in solution =  $100\text{ ppm}$ .

research and due to the crucial role of mass transfer in the electrochemical processes, we have proposed that this type of cell is a feasible tool for the electrochemical oxidation applications.

## Conclusions

The results have demonstrated that the mass transfer coefficient was increased with this design of the electrochemical cell and optimizing the effective electrode area. The mass-transfer coefficient is possible to be calculated with the limiting diffusion current technique based in ferricyanide ion reduction. Also if the electrochemical cell is used for other process the characteristics can permit to obtain good results or yields with this new characteristics. Additionally, the theoretical approximation with Leveque relation could be used to estimate the mass-transfer coefficient in this design, but it is necessary to realize more studies to determine a mathematical model that can give a better estimation of mass-transfer coefficient with this geometry cell. Finally, this cell can be potential tool to remove of organic pollutants from water and it can work with higher volumes.

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