Mass Transfer to and Electrode Area of a Nanostructured Nickel Electrode in a Rectangular Flow Channel

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ABSTRACT

Nanostructured nickel was electrodeposited on a stainless steel plate. The convective-diffusion mass transfer to this nanostructured electrode was compared to that of a planar, mirror polished solid nickel electrode using the limiting current technique, for the reduction of ferricyanide (hexacyanoferrate III) ion in an undivided cell. The effect of introducing a turbulence promoter into the electrolyte channel was also evaluated for each electrode under steady state conditions. At Reynolds number of 700, the product of mass transfer coefficient and electrode area, $k_L A$ for the nanostructured nickel electrode increases over 4 times compared to the mirror polished planar nickel electrode. In the presence of a turbulence promoter the nanostructured nickel electrode shows an increase of the $k_L A$ product of ca. 8 times compared with the planar mirror polished nickel electrode. The dimensionless mass transfer correlations $Sh = aRe^b Sc^d Le^e$ are compared to others in the literature.

Key words: active electrode area, ferricyanide ion, mass transfer coefficient, enhancement factor, nanostructured, nickel.

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INTRODUCTION

A number of factors should be considered during the design of an electrochemical reactor including: reactor size and geometry, fluid flow and electrode kinetics, current, potential and concentration distributions, heat transfer, cost, reliability, suitability and simplicity. It is usually necessary to compromise between these factors to maximise a desired characteristic. For example, the incorporation of a porous electrode can increase the electrode area per unit volume of the reactor but it can give rise to a high pressure drop leading to increased pumping costs. Other factors to consider are the current and potential distributions affecting the reaction engineering characteristics within the reactor [1]. Mass transfer in electrochemical reactors is often characterised by evaluating the average mass transfer coefficient, k_L , determined by the limiting current technique under convective-diffusion of an electroactive species in a fixed electrolyte under conditions of known reactant concentration and a constant geometric electrode area [2]. The evaluation of this coefficient can be used to compare its performance against similar reactors and assess its suitability for a particular electrochemical process. The coefficients are used to calculate dimensionless parameters that are useful during the scale-up of the reactor and to select a suitable electrode configuration.

Figure 1 shows a typical current vs. potential curve for the reduction of $\text{Fe}(\text{CN})_6^{3-}$ ion at a polished planar nickel electrode fitted into a rectangular, parallel plate electrochemical cell. The three characteristic zones of charge-, mixed- and mass-transfer control of the electroactive species can be clearly distinguished, followed by the reduction of water. In the mass transfer controlled region, the reaction depends on

the rate of reactant supply to the electrode surface and is characterised by the product of mass transfer coefficient, k_L , and active electrode area, A :

$$k_L A = \frac{I_L}{nF\Delta c} \quad (1)$$

Where I_L is the limiting current, A is the active surface area of the electrode, Δc is the concentration difference between the bulk and the surface concentration of the electroactive species, n is the number of electrons exchanged in the reaction and F is the Faraday constant.

For simplicity and to facilitate performance comparisons, the electrode area is normally taken as the geometrical surface area of the electrode and, if different mass transfer regimes and/or turbulence promoters are used, the mass transfer coefficient can be increased for electrodes that have the same geometrical area. The electrochemical surface area could be between two to three times larger if the microscopic texture of the electrode surface is considered [3] and depends on the electrode surface pre-treatment and the roughness factor, which expresses the ratio of actual electrode area to the geometric one. In this paper, a method to increase the electrochemical surface area, via the electrodeposition of nanostructured nickel, on a flat stainless steel electrode is presented as a means of increasing the limiting current, hence the overall rate of the electrochemical reaction. Other approaches to increase the limiting current include: use of three-dimensional electrodes to increase the active electrode area per unit volume [4], enhancement of the relative electrode/electrolyte movement, incorporation of turbulence promoters into the flow channel, increasing the electrolyte flow rate or bubbling a gas through the electrolyte [5].

Nanostructured materials have a strong influence on hardness, electrical resistance, specific heat, density and magnetic properties [6] electrocatalysis [7], batteries, supercapacitors and fuel cells [8] and hydrogen production [9-12].

Dimensionless group correlations

Mass transfer to an electrode in the side wall of a rectangular channel can be characterised by a number of dimensionless groups, namely the Sherwood (Sh), Reynolds (Re), Schmidt (Sc) and dimensionless length (L_e) numbers. These groups can be defined as:

$$Sh = \frac{k_L d_e}{D}, \quad (2)$$

$$Re = \frac{\nu d_e}{\nu}, \quad (3)$$

$$Sc = \frac{\nu}{D}, \quad (4)$$

$$L_e = \frac{d_e}{L}, \quad (5)$$

where L_e is the aspect ratio between the equivalent diameter, $d_e = 2BS/(B+S)$ and the length of the electrode L (cm), B and S are the width and the inter-electrode gap of the electrodes, D (cm² s⁻¹) is the diffusion coefficient, ν (cm² s⁻¹) is the kinematic viscosity of the electrolyte, and ν (cm s⁻¹) is the mean linear electrolyte velocity.

Table 1 shows the values of these parameters used in this work.

The relationship between the above four dimensionless groups at constant temperature, can be expressed as a correlation of the form [13-17]:

$$Sh = aRe^b Sc^d Le^e \quad (6)$$

106

107 where a is a constant associated to the geometry and cell dimensions, b depends on
 108 the hydrodynamic regime, d is taken to be 0.33 from hydrodynamic theory and e
 109 varies with the aspect ratio of the electrolyte channel. In fully developed laminar flow
 110 through a rectangular channel when $L/d_e \leq 35$ and the aspect ratio S/B is $\ll 1$,
 111 equation (6) can be expressed as [18, 19]:

112

$$Sh = 1.85\gamma(Re Sc Le)^{0.33} \quad (7)$$

114

115 The term γ is a geometrical correction factor which is significant when $S/B > 0.05$ [18].
 116 The aspect ratio (S/B) of the electrolyte channel in the flow cell used in this work is
 117 0.165 and a correction factor of 0.948, can be estimated from the literature [17]. For
 118 fully developed turbulent flow when L/d_e is < 7.5 , the appropriate mass transfer
 119 correlation for short electrodes has been suggested to be [18]:

120

$$Sh = 0.145 Re^{0.66} Sc^{0.33} Le^{0.25} \quad (8)$$

122

123 **EXPERIMENTAL DETAILS**

124 *Mass transfer experiments*

125 An undivided electrochemical flow cell consisting of three Perspex plates of $15 \times 9 \times$
 126 0.66 cm was used. The two end plates held the electrodes while the middle one had a
 127 rectangular space machined in the centre to form the electrolyte channel. Flat silicone
 128 rubber gaskets between the Perspex plates were used to seal the cell. Figure 2 shows
 129 an expanded view of the cell and the location of the electrolyte entrance and exit. A

carbon plate was used as a counter electrode while a mirror polished nickel plate or a nanostructured nickel deposited on a stainless steel plate was used as the working electrode. The geometrical area of the electrodes exposed to the electrolyte was 30 cm². The electrode potentials were measured against an Ag/AgCl reference electrode through a Luggin capillary tube inserted at the exit of the electrolyte manifold and located close to the working electrode. The nickel solid plate electrode was wet polished with silicon carbide paper grades 400, 800 and 1200 and a diamond powder of 6 µm then rinsed with deionised water before each set of experiments. The electrolyte contained 0.001 mol dm⁻³ K₃Fe(CN)₆ and 0.01 mol dm⁻³ K₄Fe(CN)₆ in 1 mol dm⁻³ Na₂CO₃. Sodium carbonate was chosen as the background electrolyte due to its more reliable limiting current behaviour than other electrolytes such as KOH [13, 20]. The characteristics of the flow cell and the electrolyte are shown in Table 1.

Preparation of the nickel electrodes

Two nickel electrodes of 30 cm² geometrical areas were used in the flow cell: a solid nickel plate 99.2 % purity and 0.5 cm thickness (ASME SB 162 UNS NO2200) or nickel electrodeposited on a stainless steel (SS) plate (type 904 L of 0.1 mm thickness). Electrodeposition of nanostructure nickel on the stainless steel electrode was carried out in a rectangular cross-section polypropylene container of 10 cm × 10 cm × 15 cm dimensions and followed a four-step procedure: 1) immersion in 50 % wt. H₂SO₄ for 10 seconds to eliminate the thin oxide film on the surface, 2) anodic-degreasing in 45 % wt. NaOH followed by immersion in a solution containing 30 cm³ dm⁻³ of an industrial alkaline cleaner (Percy, Henkel) in deionised water at a current density of 15 mA cm⁻² for 30 seconds, 3) electrodeposition of a very thin layer of Ni from a 'Woods strike' bath containing 100 cm³ dm⁻³ concentrated HCl and 240 g dm⁻³

NiCl₂ at a current density of -100 mA cm⁻² for 60 seconds and 4) electrodeposition of nickel from a Watts bath containing 260 g dm⁻³ NiSO₄, 50 g dm⁻³ NiCl₂ and 30 g dm⁻³ of HBO₃, at -100 mA cm⁻² for 180 seconds.

Turbulence promoters

In order to compare the mass transfer characteristics of the nickel solid plate and the nanostructured nickel electrodes with other strategies used to increase the mass transfer, a PTFE turbulence promoter type “D” which occupies approximately 17 % of the overall channel volume, described in reference [14] was used. The characteristics of this turbulence promoter are provided in Table 1.

Morphological characterization of the nickel surface

The surface morphology of the electrodes was characterized by atomic force microscopy (AFM), using a Nanoscope IIIa (Veeco) operated in the intermittent contact mode. Silicon cantilevers (Veeco) with a nominal force constant of 40 N m⁻¹ were employed. The images consisted of 512 x 512 pixels with a typical acquisition time of 4-5 minutes.

Electrochemical voltammetry

The solid nickel plate and the nanostructured nickel electrodes were characterized in the flow cell using the reduction of ferricyanide ions by linear sweep voltammetry between 0.2 V and -1.1 V vs. Ag/AgCl at a potential sweep rate of 2 and 5 mV s⁻¹. Since no difference was observed between the two linear sweep voltammetry rates we only report experiments at 5 mV s⁻¹. The mean linear electrolyte velocity varied between 6 and 38 cm s⁻¹.

RESULTS AND DISCUSSION

Surface morphology

Figure 3a and 3b show the characteristic images of the nickel solid plate after polishing and the nanostructured electrode, respectively. The polished surface is relatively smooth (with a root mean square, rms, and surface roughness of 4 nm) and displays the characteristic morphological features of the polishing process, i.e. long and oriented structures together with small nanostructures. In contrast, the nanostructured surface displays a larger rms roughness (close to 100 nm). Both morphologies are compared in figure 3c where the two characteristic profiles are displayed at the same scale. The roughening induced by the nanostructuring process is then evident. Moreover, this process also induces strong changes at the nanoscale. Figure 3d shows a characteristic image at a higher magnification of the polished surface. Essentially, the main surface features described above are also observed and the rms roughness is just 2 nm. However, figure 3e displays at the same scale the corresponding image obtained on the nanostructured electrode. Clearly, the electrode surface of the latter is formed by highly packed nanostructures, which are uniformly distributed, forming a compact layer with an increased surface roughness (around 15 nm). These nanostructures have lateral sizes in the 30-90 nm range, which implies a density of ~ 400 nanostructures μm^{-2} (i.e. 4×10^{10} nanostructures cm^{-2}). Finally, the difference between the surface morphology of both electrodes at the nanoscale can be clearly appreciated in the comparison of figure 3f.

Mass-transfer characteristics

Figure 4 shows linear sweep voltammetry curves for the reduction on: a) solid mirror polished flat plate nickel and b) nanostructured nickel on stainless steel, at a sweep

potential rate of 5 mV s^{-1} . The curves for both electrodes show the expected increase in current with increase in velocity. The limiting current values measured at $-0.80 \text{ V vs. Ag/AgCl}$ at a flow velocity of 6 cm s^{-1} were -3 mA and -13 mA for the mirror polished solid nickel plate and the nanostructured Ni deposit electrodes, respectively. At the highest electrolyte velocity (38 cm s^{-1}) the limiting currents at the same potential in the mirror polished and in the nanostructured nickel electrodes were -10 mA and -21 mA , respectively, indicating the enhanced activity of the latter.

In the charge transfer controlled region at an electrode potential of $+0.150 \text{ V vs. Ag/AgCl}$, the voltammograms in Figures 4a and 4b show that the current at the planar mirror polished nickel electrode is -1.86 mA while at the nanostructured electrode is -11.3 mA . The high current observed in the nanostructured nickel is attributable to its larger surface density observed in the AFM analysis.

In the mass transfer controlled region, under limiting current conditions, the product of mass transfer coefficient and electrode area $k_L A$ for each electrode was calculated using equation (1). Figure 5 shows $k_L A$ vs. the velocity for the two nickel electrodes in the presence and in the absence of a turbulence promoter. The curves can be expressed by the equation: $k_L A = \alpha v^b$. At a potential sweep rate of 5 mV s^{-1} , which allows steady state conditions, the expressions for each electrode at linear flow velocities lower than 20 cm s^{-1} are:

$$k_L A = 0.007 v^{0.71} \quad \text{Mirror polished planar nickel} \quad (9)$$

$$k_L A = 0.01 v^{0.62} \quad \text{Mirror polished planar nickel in the presence of a turbulence promoter} \quad (10)$$

$$k_L A = 0.08 \nu^{0.23} \quad \text{Nanostructured nickel deposit} \quad (11)$$

$$k_L A = 0.16 \nu^{0.14} \quad \text{Nanostructured nickel deposit in the presence of a turbulence promoter} \quad (12)$$

The “ b ” values for the mirror polished electrode in the presence and in the absence of turbulence promoter are similar to those reported in the literature for the FM01 laboratory electrolyser which generally report values of ≈ 0.7 for an empty channel [15]. The value of the constant α in the relationship $k_L A = \alpha \nu^b$ when the nanostructured nickel electrode was used with respect to the mirror polished nickel electrode is approximately 9 times larger while when the turbulence promoter was used in combination with the nanostructured electrode a value of 18 was measured. Some authors consider this constant as the increase of the term $k_L A$ [15]. The increase in the product of mass transfer coefficient and electrode area $k_L A$, due to the use of the nanostructured nickel electrode with respect to the mirror polished nickel electrode is approximately 11 while if the turbulence promoter is used in combination with the nanostructured electrode a factor of ca. 22 was measured. The increase of $k_L A$ due to the turbulence promoter on the mirror polished nickel electrode is 1.5 which is close to the value of 1.7 obtained by Brown et al. [15] for the FM01-LC laboratory electrolyser. The larger mass transfer increase observed for such a nanostructured nickel deposit does not appear to have been previously quantified.

Another useful way to analyse the increase in $k_L A$ is the enhancement factor, δ which can be defined as [16]:

$$\delta = \frac{k_L A_{enhanced}}{k_L A_{smooth \ Ni \ plate}} \quad (13)$$

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255 where $k_L A_{enhanced}$ is the mass transfer coefficient obtained using different electrode
256 configurations such as fitting the turbulence promoter or the use of a nanostructured
257 nickel in the absence and in the presence of a turbulence promoter. $k_L A_{smooth Ni plate}$ is
258 the mass transfer coefficient with the mirror polished nickel plate electrode in an
259 empty channel, the latter having been used by many workers.

260

261 The log-log plot shown in Figure 6 indicates that the enhancement factor, δ decays
262 with the electrolyte velocity for the three systems mentioned above. When the mirror
263 polished solid nickel flat plate electrode was fitted with the turbulence promoter, an
264 increase in the mass transfer coefficient of approximately 23 % was achieved at low
265 velocities. This trend agrees with other works reported in the literature where the
266 same turbulence promoter was used during the reduction of ferricyanide ion at a
267 nickel electrode [16]. Analysis of the log-log plot for this electrode shows a
268 relationship between the enhancement factor δ , and the velocity, v , as $\delta = 1.5v^{-0.097}$
269 which indicates that the enhanced factor is projected to reach 1 when the velocity of
270 the electrolyte reaches 61 cm s^{-1} . This velocity is almost twice that found by Griffiths
271 et al. [16] who estimated a value of 33 cm s^{-1} as the value when the mass transfer
272 would not benefit from an increase in the electrolyte velocity in a flow cell using a flat,
273 64 cm^2 electrode area. The larger area of the cell used in this reference and the
274 different entrance electrolyte manifolds in the cell are the most likely reasons for this
275 difference. Entrance/exit effects due to the manifolds are normally observed in all
276 practical parallel plate filter-press cells and it is well known that smaller
277 electrochemical cells, such as the one used in this work, show effects that dominate
278 the hydrodynamic behaviour of the electrolyte.

279

280 The set of data for the nanostructured nickel electrode shows that the enhancement
281 factor is around 5 at 6 cm s^{-1} and around 2 at 38 cm s^{-1} velocity with respect to the
282 nickel flat electrode in the absence of turbulence promoter. The enhancement factor
283 gradually falls with the velocity and the relationship can be expressed as: $\delta = 11.16v^{-0.47}$.
284 The analysis of this equation shows that the enhanced factor δ , will be equal to 1
285 at $v = 165 \text{ cm s}^{-1}$. Such a high flow rate might be unrealistic in practice due to the
286 high reactor pressure drops and pump size involved but it shows that the presence of
287 the nickel nanostructure enhances the overall mass transfer substantially. When the
288 nanostructured nickel electrode was fitted with a turbulence promoter, an increase of 3
289 to 8 times compared to the solid flat plate nickel electrode was observed. The
290 enhancement factor falls asymptotically as the electrolyte velocity increases and the
291 relationship between the enhancement factor and the velocity is: $\delta = 22.18v^{-0.55}$
292 indicating that the enhancement factor is projected to have a value of unity at a
293 velocity of approximately 270 cm s^{-1} .

294

295 *Comparison with the dimensionless mass transfer correlations*

296 The mass transfer coefficient data at different velocities were fitted into the
297 dimensionless equation (6). The physical characteristics used to calculate the
298 dimensionless number expressed by equations (2) to (5) are listed in Table 1. Figure 7
299 shows the log-log plot of the Sherwood vs. Reynolds numbers for the mirror polished
300 and the nanostructured nickel electrodes in the presence and in the absence of a
301 turbulence promoter (TP). The figure also shows some data taken from the literature
302 from other flow cell systems using nickel electrodes for the reduction of ferricyanide
303 ion as well as the predicted fully developed laminar and turbulent flow curves from

equations (7) and (8), respectively. The results of the experiments without turbulence promoter from this work are in fairly good agreement with literature data of references [15] and [16] that use other electrochemical parallel cells plates such as the FM01-LC, as it is shown in Table 2. The data from reference [21], where a monopolar membrane cell with nickel electrodes of 14.8×29.7 cm were used, differ slightly in the “a” value but the “b” value is fairly close and indicates a turbulent flow regime. The data obtained in the presence of a turbulence promoter for the mirror polished nickel electrode shows a small value of the coefficient “a” compared with references [15] and [16] possibly indicating the different cell design used in this work and the more influential effect of the entrance and exit manifolds in the cell. The value of the slope “b” is as high as in references [15] and [16] and indicates turbulent flow. The value of the coefficient “a” for the nanostructured nickel electrode in the absence and in the presence of turbulence promoter is fairly large compared with the other electrochemical systems, as shown in Table 2. This seems to indicate that the nanostructured electrode is an effective way to increase mass transfer at modest Re numbers. It is interesting to note that the coefficient “a” from the system described in reference [21] is also large as in the case of the nanostructured nickel electrode and the slope “b” just above the value normally accepted for laminar flow regimes. This cell has a turbulence promoter made from triangular threads of polypropylene and flow distributors at the inlet and the outlet of the cell. In contrast, the cell described in this work has no flow distributors or calming zone.

Conclusions

The product of mass transfer coefficient and electrode area, $k_L A$, evaluated for a nanostructured nickel electrode in the absence of a turbulent promoter is 11 times

larger than that calculated with a flat mirror polished nickel electrode. In the presence of a turbulence promoter the term $k_L A$ increased 22 times. The Sherwood number vs. Reynolds number correlations for the electrochemical cell used in this work fitted with a mirror polished nickel electrode are similar to those reported in the literature using the FM01-LC laboratory reactor. However, when a nanostructured nickel electrodeposit on a stainless steel plate was used, the mass transfer term associated with the electrode area increased substantially. The simple electrodeposition method used here to produce a nanostructured nickel surface is a convenient and economical way to improve the overall reaction rate on nickel electrodes and can increase the space time yield of a reactor. The larger area available for the high mass transfer rates observed might be due to the strong force at which the jets of the electrolyte impact on the electrode surface. The electrolyte jets enter perpendicular to the electrode surface causing such a turbulence that decreases the thickness of the diffusion layer to a similar scale as the nanostructured features following its profile. Work continues on characterisation of these nanostructured nickel deposits in electrosynthesis, wastewater treatment and energy conversion applications.

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351 **List of symbols**

Symbol	Meaning	Units
A	A constant associated with the geometry and cell dimensions in equation (6)	-
A	Active electrode area	cm^2
B	Reynolds number exponent in equation (6) and in the expression $k_L A = \alpha v^b$	-
B	Width of the electrode	cm
Δc	Concentration difference between the bulk and the surface concentration of the electroactive species (ferricyanide ions)	mol cm^3
D	Schmidt number exponent in equation (6)	-
d_e	Equivalent diameter of the flow channel	cm
D	Diffusion coefficient of ferricyanide ions	$\text{cm}^2 \text{s}^{-1}$
E	Dimensionless length exponent in equation (6)	-
F	Faraday constant ($96\,485 \text{ C mol}^{-1}$)	C mol^{-1}
I_L	Limiting current for reduction of ferricyanide ion	A
k_L	Mass transfer coefficient	cm s^{-1}
L	Length of the electrode in the direction of flow	cm
N	Number of electrons exchanged in the reaction	-
R_f	Roughness factor (ratio of actual active electrode area to the geometrical value)	-
S	Inter-electrode gap	cm
v	Mean linear flow velocity of the electrolyte	cm s^{-1}
Greek Symbols		
α	Constant in the expression $k_L A = \alpha v^\beta$	-
β	Exponent of the flow velocity	-
γ	A geometrical correction factor in equation (7)	-
δ	Enhancement factor defined by equation (13)	-
ν	Kinematic viscosity of the electrolyte	$\text{cm}^2 \text{s}^{-1}$
Dimensionless groups		
L_e	Aspect ratio between the equivalent diameter and the length of the electrode	dimensionless
Re	Reynolds number	dimensionless
Sc	Schmidt number	dimensionless
Sh	Sherwood number	dimensionless

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Electrode width, B	4 cm
Electrode spacing, S	0.66 cm
Electrode geometric area, $A = BL$	30 cm ²
Equivalent diameter of flow channel, $d_e = 2BS/(B+S)$	1.13 cm
Length of the electrolyte compartment, L	9 cm
Kinematic viscosity of electrolyte, ν	$9.56 \times 10^{-3} \text{ cm}^2 \text{ s}^{-1}$
Diffusion coefficient of $\text{Fe}(\text{CN})_6^{-3}$, D	$6.4 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$
Density of the electrolyte, ρ	1.0985 g cm^{-3}
Schmidt number, Sc	1494
L_e number = d_e/L	0.125
Electrolyte composition	$1 \times 10^{-3} \text{ mol dm}^{-3} \text{ K}_3\text{Fe}(\text{CN})_6$ + $10 \times 10^{-3} \text{ mol dm}^{-3} \text{ K}_4\text{Fe}(\text{CN})_6$ + $1 \text{ mol dm}^{-3} \text{ Na}_2\text{CO}_3$
Range of mean linear electrolyte velocity	6 to 38 cm s^{-1}
Temperature	302 K
Turbulence promoter (PTFE mesh type “D”) [12].	11 mm internal size of shorter and longer mesh diagonals with a volumetric porosity of 0.83.

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405 Table 1 Dimensions of the flow cell and characteristics of the electrolyte.

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System (Figure 7)	<i>a</i>		<i>b</i>		Reference
	Re < 2380	Re > 2380	Re < 2380	Re > 2380	
●) Mirror polished Ni flat plate, in the absence of TP	0.25	0.82	0.71	0.82	This work
○) Ni mirror polished flat plate in the presence of TP	0.58	0.16	0.62	0.78	This work
■) Nanostructured Ni on stainless steel in the absence of TP	28.4	7.4	0.23	0.4	This work
□) Nanostructured Ni on stainless steel in the presence of TP	86.2	22.7	0.14	0.32	This work
◆) Ni electrode in the FM01-LC in the absence of TP. Sc = 1562	0.22		0.71		[15]
◇) Ni electrode in the FM01-LC in the presence of TP. Sc = 1562	0.74		0.62		[15]
▲) Ni electrode in the FM01-LC in the absence of TP. Sc = 1494	0.18		0.73		[16]
▼) Laminar flow; equation (7)	1.75		0.33		[17-19]
▽) Turbulent flow; equation (8)	0.14		0.66		[17-19]
⊕) Ni electrode in the absence of TP. Sc = 1572	0.39		0.63		[21]
✕) Ni electrode; polypropylene TP, triangular threads. Sc = 1572.	5.57		0.4		[21]

416

417 Table 2 Constants in the dimensionless correlation $Sh = aRe^b Sc^{0.33} L_e^{0.33}$.
418 TP indicates the presence of a turbulence promoter in the flow channel.
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423 **Figure captions**

424 **Figure 1** Typical current vs. potential curve for the reduction of Fe(CN)_6^{3-} in
425 $0.01 \text{ mol dm}^{-3} \text{ K}_3\text{Fe(CN)}_6 + 0.1 \text{ mol dm}^{-3} \text{ Na}_2\text{CO}_3 + 0.001 \text{ mol dm}^{-3}$
426 $\text{K}_4\text{Fe(CN)}_6$ at a nickel electrode with a electrolyte velocity of 38 cm s^{-1} .
427 Potential sweep rate: 5 mV s^{-1} . The main regions associated with
428 different types of reaction rate control are indicated. The current
429 density is based on the geometrical area of the electrode.

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431 **Figure 2** Expanded view of the electrochemical cell.

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433 **Figure 3** Tapping mode three-dimensional images ($5 \times 5 \text{ }\mu\text{m}^2$) of: (a) polished
434 and (b) nanostructured nickel electrodes. (c) Characteristic surface
435 profiles at the micro-scale of the polished (bottom profile) and
436 nanostructured (top) electrodes. $1 \times 1 \text{ }\mu\text{m}^2$ tapping mode three=
437 dimensional images of: (d) polished and (e) nanostructured nickel
438 electrodes. (f) Characteristic surface profiles at the nanoscale of the
439 polished (bottom profile) and nanostructured (top) electrodes. The
440 profile figures at the top have been shifted for comparison purposes.

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442 **Figure 4** Current vs. potential curves for the reduction of 0.01 mol dm^{-3}
443 Fe(CN)_6^{3-} in $0.1 \text{ mol dm}^{-3} \text{ Na}_2\text{CO}_3$ and $0.001 \text{ mol dm}^{-3}$ of $\text{K}_4\text{Fe(CN)}_6$
444 on different nickel electrodes at 5 mV s^{-1} : a) solid Ni plate and b)
445 nanostructured Ni deposit. Geometrical area of the working electrode:
446 30 cm^2 .

Figure 5 Log-log plot of the product of mass transfer coefficient and active electrode area $k_L A$ vs. velocity at a potential sweep rate of 5 mV s^{-1} for the reduction of $0.01 \text{ mol dm}^{-3} \text{ Fe(CN)}_6^{3-}$. $\square$) nanostructured nickel in the presence of a turbulence promoter (TP), $\blacktriangle$) nanostructured nickel in the absence of a turbulence promoter, $\bullet$) solid mirror polished flat plate nickel in the presence of a TP and $\circ$) solid mirror polished flat plate nickel in the absence of a TP. Potential sweep rate: 5 mV s^{-1} .

Figure 6 Enhancement factor vs. velocity for: $\blacktriangle$) nanostructured nickel electrodes in the presence of a TP, $\circ$) nanostructured nickel electrodes in the absence of a TP and $\bullet$) solid flat plate nickel electrode. Potential sweep rate: 5 mV s^{-1} .

Figure 7 Log Sh vs. log Re for various rectangular flow channel cells in the presence and absence of a turbulence promoter (TP): $\bullet$) nickel solid electrode, this work: no TP, $\circ$) with a TP. Nanostructured nickel deposit, this work: $\blacksquare$) no TP and $\square$) with a TP. Nickel electrode in the FM01-LC electrolyser [15]: $\blacklozenge$) no TP and $\blacklozenge$) with a TP. Nickel electrode in the FM01-LC [16]: $\blacktriangle$) in the absence of a TP. $\blacktriangledown$) fully developed laminar flow equation (7) [17] and ∇) fully developed turbulent flow; equation (8) [17]. $\oplus$) Nickel electrode in the absence of a TP and $\otimes$) with a polypropylene grid with triangular threads TP [21].

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Figure 1

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Figure 2

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Figure 3 (a) (b) and (c)

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Figure 3 (d), (e) and (f)

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Figure 4a

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Figure 4b

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528 **Figure 5**

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Figure 6

Figure 7