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Limiting current density and specific energy consumption in electrochemical cells with inert turbulence promoters

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Electrochemical cells with inert turbulence promoters (ITP) and plain cells of the same geometry have been compared with respect to their productivity and specific energy consumption. As cathode reaction the diffusion controlled copper ion deposition process has been used, while the anode reactions were either metal dissolution or oxygen evolution on a stable anode. It has been found that in the ITP cells with an insoluble anode the contribution of ITP to the mass transfer enhancement is higher. The relationship between pumping energy and process energy has also been analysed as a function of hydrodynamic conditions for each cell separately. The application of ITP cells has significant advantages in electrowinning and plating processes, while they are not suitable, from an energy perspective, in galvanising processes, in which soluble anodes are used. In the case of electrowinning the minimum energy consumption is found to be in the region of 0.1–1 g dm^{-3} of reacting ions, depending on the kind of cell used.

List of symbols

C_b	concentration of reacting ions in the bulk electrolyte (mol dm^{-3})
d, d_p	cylinder and particle diameter respectively (m)
d_e	hydraulic diameter (m)
D	diffusion coefficient (cm^2 s^{-1})
E_0	specific energy of electrochemical process, defined by Equation 7 (Wh mol^{-1})
E_p	specific pumping energy, defined by Equation 10 (Wh mol^{-1})
E_t	total energy, defined by Equation 8 (Wh mol^{-1})
f_e, f_i	energy factor and intensification factor, respectively
F	Faraday constant (96 500 C mol^{-1})
g	acceleration due to gravity (m s^{-2})
Δh	interelectrode space (m)
i	current density (A m^{-2})
i_L	limiting current density (A m^{-2})
k_L	mass transfer coefficient (m s^{-1})
L	electrode length (m)
ΔP	pressure drop in the cell (N m^{-2})
u	electrolyte velocity (m s^{-1})
U	cell voltage (V)
U_0	decomposition potential (V)
X_e, X_F	fraction of process energy and pumping energy, defined by Equation 11
z	number of electrons exchanged

Greek letters

α	defined by Equation 9
ϵ	bed porosity
η_a	anode overpotential (V)
η_d	diffusion overpotential (V)
η_p	pumping power efficiency factor
ϕ	fluid distributor characteristic
χ	electrolyte conductivity (Ω^{-1} cm^{-1})
λ	friction factor
μ	electrolyte viscosity (Pa s)
ρ, ρ_p	electrolyte and particle density, respectively (kg m^{-3})

Similarity criteria

Re	Reynolds number
Sc	Schmidt number
Sh	Sherwood number
j_D	Chilton–Colburn factor

1. Introduction

Many attempts have been made to increase cell productivity in diffusion controlled cathodic electrochemical processes, by increasing either the specific surface area or convective mass transport of reacting ions from the bulk electrolyte to the electrode. One possible approach is the use of inert turbulence promoters (ITP) situated in the interelectrode space [1–5]. Among the turbulence promoters investigated are glass beads in the form of fixed [1] or fluidized beds [2], plastic meshes [3], bars, cylinders or similar shapes [4, 5], which produce eddies in the vicinity of the electrode thus reducing the diffusion boundary layer thickness. Gas sparging has also been utilized to improve mass transfer [6, 7] in electrochemical cells.

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2. Developing of the model

To improve mass transfer in an electrochemical cell it is necessary to expend energy; this aspect, however, has not been adequately investigated. The relation between energy expended and corresponding mass transfer enhancement, the relationship between energy consumed in the electrochemical process and energy used in electrolyte pumping, how parameters determining the mass transfer influence energy consumption and what kind of side effects may appear using ITP, are among some of the questions not yet fully addressed. The main question, from an engineering point of view, is what kind of cell with ITP is the most suitable for a given electrode reaction and under which conditions is it possible to obtain the best cell performance.

The aim of the present work is the consideration of energy consumption and mass transfer enhancement relationships in cells with flat electrodes and with ITP in the interelectrode space. These cells include: a fixed bed of glass beads (filled randomly); a fluidized bed of glass beads; and a cylinder packed bed (cylinders are placed in defined order as shown in Fig. 1).

As a reference cell an empty channel with parallel flat plate electrodes was used. To unify the conditions under which the cells work, the following assumptions were made:

(i) all cells were with rectangular cross section and with the same electrode dimension and interelectrode distance;

(ii) the diffusion controlled cathode reaction of copper deposition was used as a model system while the anodic reactions were either metal dissolution or oxygen evolution;

(iii) electrolyte flow was perpendicular to the current flow;

(iv) ITP were placed in the interelectrode space as schematically presented in Fig. 1;

(v) the current efficiency was assumed to be 100%. Data used in the calculation are summarized in Table 1.

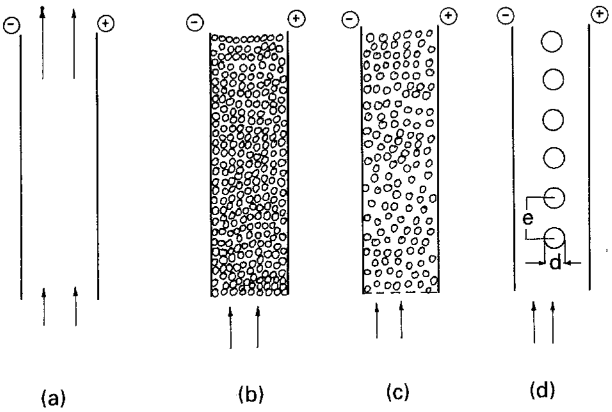

Fig. 1. Schematic view of considered cells.(a) empty cell, (b) fixed bed ITP cell, (c) fluidized bed ITP cell, and (d) cell with inert cylindrical promoters.

3. Mass transfer enhancement: limiting current density

The maximum productivity of an electrochemical cell corresponds to the limiting current density, which may be described by the following equation:

$$i = zFk_L C_B \tag{1}$$

Equation 1 is valid for electrolytes in which an excess amount of supporting electrolyte is added, so that the ionic migration of the reacting species can be neglected.

The mass transfer coefficient, k_L, in Equation 1 depends on the geometry of the electrode and ITP and also the electrolyte characteristics and flow conditions.

Its value may be calculated using equations of the form:

$$j_D\epsilon = \text{constant}\left(\frac{Re}{1-\epsilon}\right)^m \tag{2}$$

Equation 2 is a relationship which is commonly used to describe convective mass transport in fixed and fluidized beds. For an empty cell, as well as for the cell with packed cylinders, bars etc., the following general dimensionless correlation is recommended:

$$Sh = \text{Constant} \times Re^a Sc^b \left(\frac{d_e}{L}\right)^c \tag{3}$$

where a, b, and c are experimentally determined exponents. In Equation 3 Sherwood and Reynolds numbers are defined based on the electrode length, while in Equation 2 the dimension in the Reynolds number is the particle diameter. Values of the constants and the exponents in Equations 2 and 3 are characteristic of a given cell, in particular the flow conditions, and may be found in the literature [8, 9].

Using numerical data from Table 1, values for

Table 1. Data for computing

Electrolyte characteristics	*ITP characteristics*	*Other data*
$D = 5.57 \times 10^{-10}\,\mathrm{m^2\,s^{-1}}$	$d_p = 1\,\mathrm{mm}$	$U_0 = 0.828\,\mathrm{V}$
$\eta = 1.1 \times 10^{-3}\,\mathrm{Pa\,s}$	$\rho_p = 2650\,\mathrm{kg\,m^{-3}}$	$a_a = 0.5\,\mathrm{V}$
$\rho = 1070\,\mathrm{kg\,m^{-3}}$	$d = 8\,\mathrm{mm}$	$b_a = 0.12\,\mathrm{V}$
$\nu = 1.037 \times 10^{-6}\,\mathrm{m^2\,s^{-1}}$	$e = 25\,\mathrm{mm}$	$z = 2$
$\chi = 50\,\Omega^{-1}\,\mathrm{cm^{-1}}$	Cell geometry	$F = 96\,500\,\mathrm{C\,mol^{-1}}$
$Sc = 1860$	$L = 1\,\mathrm{m}$	$T = 298\,\mathrm{K}$
Composition	$B = 1\,\mathrm{m}$	
$CuSO_4 + H_2SO_4$	$\Delta h = 1\,\mathrm{cm}$	

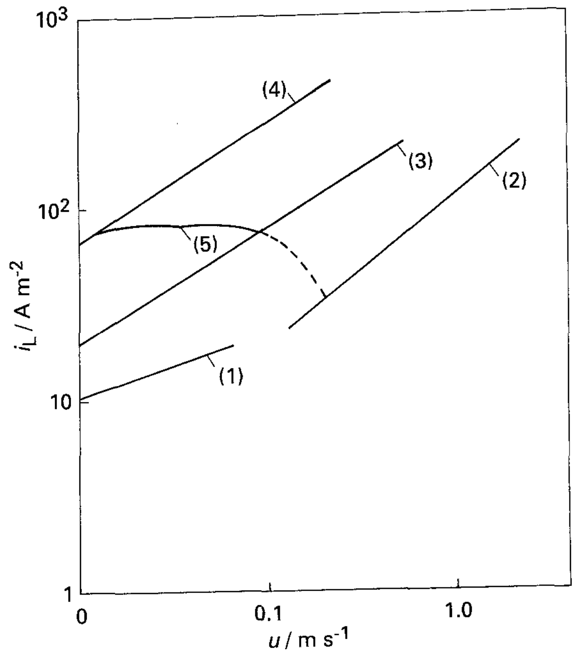

Fig. 2. Change of limiting current density with electrolyte flow-rate: (1) empty cell (laminar flow), (2) empty cell (turbulent flow), (3) cell with packed cylinders, (4) fixed bed ITP cell, and (5) fluidized bed ITP cell.

limiting current density were obtained and plotted against the electrolyte velocity in Fig. 2.

ITP clearly cause an increase in limiting current density. For example, the limiting current density of about 80 A m^{-2}, obtained in a fluidized bed at velocities in the range 2–3 cm s^{-1}, may be reached in the empty cell only with vigorous electrolyte flow i.e. at velocities of approximately two orders of magnitude higher than that in the fluidized bed. In some electroplating plants, electrodeposition occurring at very high electrolyte velocity of about 1–2.5 m s^{-1} lessens the processing time. The same effect could be obtained in a fluidized bed cell of inert particles at much lower flow rates.

The highest productivity may be obtained in the cell with the fixed bed since the greatest limiting current density is obtained.

The contribution of inert turbulence promoters to the mass transfer enhancement may be presented by introducing an intensification factor as the ratio of the limiting current density in a cell with inert turbulence promoters to that in an empty cell [10]:

$$f_i = \frac{i_L}{i_{L_0}} \tag{5}$$

where the subscript '0' relates to the empty cell. Calculated data for f_i are shown in Fig. 3 as a function of electrolyte velocity.

f_i is seen to increase continuously with electrolyte velocity for the cell with fixed and packed bed of ITP while in the case of the fluidized bed cell f_i passes through a maximum. This is in accordance with mass transfer behaviour with the increase in bed porosity [10, 11], and is an important criterion for determining the optimal cell working conditions.

4. Specific energy consumption

The energy requirement to provide a certain degree of mass transfer enhancement is a vital factor, particularly in the comparison with that for the empty cell.

The specific energy consumption per unit of obtained product is the sum of the specific energy for the electrochemical process and for electrolyte pumping:

$$E_T = E_e + E_P \tag{6}$$

The energy consumed in the process may be expressed as

$$E_e = zFU \tag{7}$$

The total cell voltage is

$$U = U_0 + \frac{\alpha i_L \Delta h}{\epsilon^n} + |\eta_d| + |\eta_a| \tag{8}$$

Since a cell usually works at a constant operating current less than limiting current density, α represents the ratio of the actual current density to the limiting current density i.e.

$$\alpha = i/i_L \tag{9}$$

The second term on the right side of Equation 8 represents the ohmic voltage drop in the cell. The presence of ITP in the interelectrode space causes an increased resistivity of the interelectrode space. This phenomenon has already been described by Le Goff *et al.* [12].

Terms for anode, η_a, and cathode, η_d, overpotentials are well known.

The mechanical energy per unit of product is given by

$$E_P = \frac{zF\Delta pu\Delta h}{\alpha i_L L \eta_P} \tag{10}$$

where η_P is the pumping power efficiency factor.

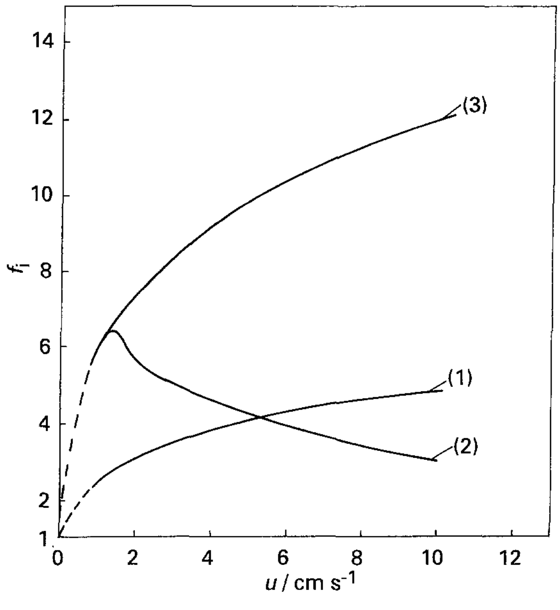

Fig. 3. Intensification factor behaviour against electrolyte velocity. (1) cell with packed cylinders, (2) fluidized bed ITP cell, and (3) fixed bed ITP cell.

Table 2. Cell pressure drop equations

Cell	Equation	Reference
Empty cell		
laminar flow	$\Delta p = \frac{u^2\rho}{2}\lambda\frac{L}{d_e}; \quad \lambda = \frac{96}{Re}$	[14]
turbulent flow	$\Delta p = \frac{u^2\rho}{2}\lambda\frac{L}{d_e}; \quad \lambda = 0.027\, Re^{-0.22}$	[13]
Packed bed	$\Delta p = \frac{u^2 r}{2}\cdot\frac{L}{\Delta h}\left(\frac{176}{Re}+0.57\right)$	[4]
Fixed bed fluidized bed	Ergun's equation $\Delta p = Lg\,(1-\epsilon)(\rho_p-\rho) + \frac{0.5(1-\phi^2)u^2\rho}{C^2\phi^2}$ with $\phi = 0.03 \quad c = 0.8$	[14]

The pressure drop, Δp, in Equation 10 may be calculated for each considered cell separately using appropriate equations. In Table 2 the explicit form of the pressure drop equations are given.

In the case of the fluidized bed and the fixed bed cell a pressure drop through the electrolyte distributor should also be considered and these pressure losses are taken into the count in Table 2 as the second term in the equations.

Figure 4 shows calculated results for the pressure drop against the electrolyte velocity. The pressure drop in the empty and packed bed cell is negligible for laminar flow conditions in comparison to the fluidized and, particularly, the fixed bed cell. Pumping energy losses become significant only for velocities that indicate vigorous flow conditions and which are not usual in practice.

The total energy specified by Equation 6, was calculated and is presented in Fig. 5. The specific energy consumption changes slightly with electrolyte flow rate only in the lower velocity region for all cells considered, except the fixed bed cell, for which the energy is seen to increase rapidly with increase in electrolyte flow rate. A lower increase in specific energy is obtained for the packed bed cell and the empty cell in the turbulent region.

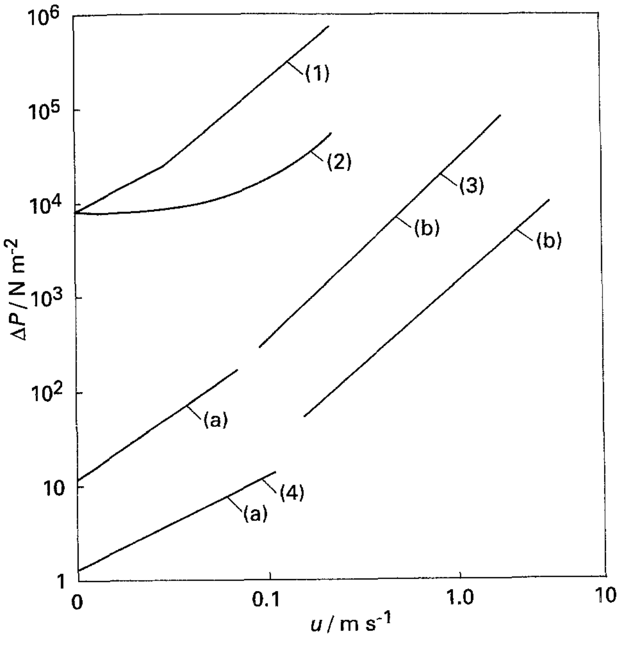

Fig. 4. Pressure drop vs. electrolyte velocity: (1) fixed bed ITP cell, (2) fluidized bed ITP cell, (3) cell with packed cylinders (laminar *a* and turbulent flow *b*), (4) empty cell (laminar *a* and turbulent flow *b*).

Since the limiting current density is also a function of the electrolyte flow rate, as shown in Fig. 2, it is of interest to establish the relationship between specific energy consumption and limiting current density, which is presented in Fig. 6.

An increase in limiting current density up to the value of about 200 A m^{-2} corresponds to a slight increase in total energy. Exceeding this i_L value total energy increases dramatically, thus indicating the area of ITP cell applicability in which a reasonably small amount of energy per unit of product would be consumed. The data show that this relationship is valid for every type of cell considered.

It is of interest to establish how the specific energy consumption E_T is distributed between process and pumping energy in the cell considered. Introducing the fractional terms X_e and X_P defined as

$$X_e = E_e/E_T \quad \text{and} \quad X_P = E_P/E_T \tag{11}$$

and noting that

$$X_P + X_e = 1 \tag{12}$$

the distribution indicated in Fig. 7 is obtained.

The pumping energy fraction is very small in both

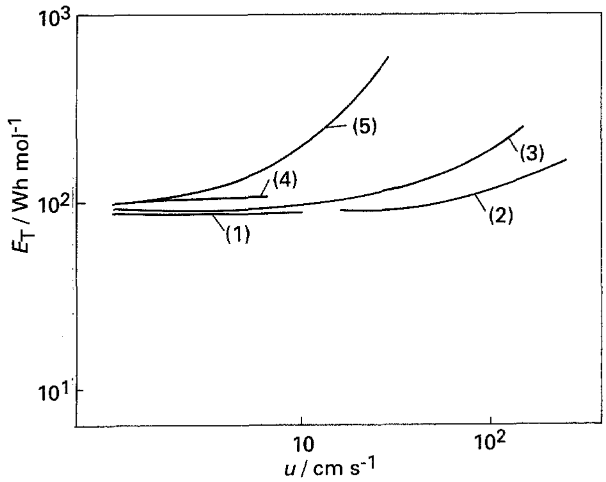

Fig. 5. Change of specific energy consumption with electrolyte velocity: (1) empty cell (laminar flow), (2) empty cell (turbulent flow), (3) cell with packed cylinders, (4) fluidized bed ITP cell, and (5) fixed bed ITP cell.

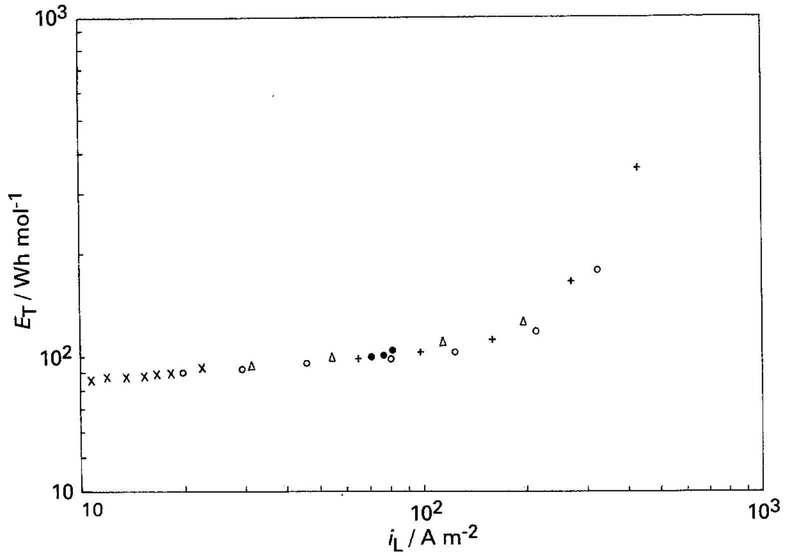

Fig. 6. Specific energy consumption against limiting current density: (×) empty cell (laminar flow), (Δ) empty cell (turbulent flow), (○) cell with packed cylinders, (●) fluidized bed ITP cell, and (+) fixed bed ITP cell.

the empty and packed bed cells and does not exceed 10% in the laminar flow region, which usually exists in cells at the industrial scale. The fixed and, particularly, the fluidized bed have a large pumping energy demand which is observed to be in the range 20–80%, depending on the electrolyte velocity. The fluidized bed consumes more mechanical energy than process energy. The reason for this is the decrease in the fluidized bed cell productivity with increase in electrolyte flow rate, as presented in Fig. 2.

To obtain a base for cell comparison it is useful to define an energy factor in a similar way as has been done with the intensification factor, i.e. as a ratio of the total energy in the cells with inert promoters and the energy necessary for the empty cell:

$$f_E = E_T/E_{T_0} \qquad (13)$$

Values of the energy factor are plotted as a function of electrolyte flow rate in Fig. 8. Two families of curves are seen: one family relates to cells in which oxygen evolution occurs as the anodic reaction on an insoluble anode, while the other family relates to cells in which the anodic reaction is metal dissolution. It is evident that in cells such as electroplating cells with a soluble anode, where deposition and dissolution of metal occurs ($U_0 = 0$), the value of the energy factor substantially exceeds the value of the intensification factor f_i. In other words, for an intensification factor of about 5–7 in such a cell, the energy factor is one order of magnitude higher or even more. But in cells with insoluble anodes ($U_0 \neq 0$), the energy factor f_E does not exceed the value of 1.2, in the investigated range of electrolyte flow rates. For this reason, cells with inert turbulent promoters may be very useful in electrowinning processes as well as in some plating processes, using insoluble anodes. The fluidized bed cell may be particularly appropriate in such electroplating processes, because, beside the increase in the process rate, the collision of particles with the cathode contributes to improved surface quality [15, 16]. Fixed and packed beds are not suitable for such purposes, since they

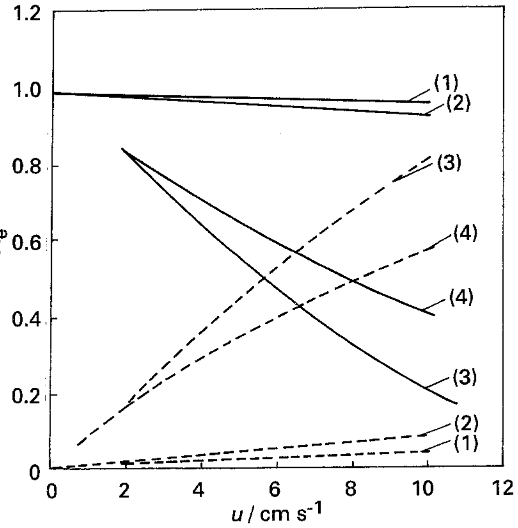

Fig. 7. Fraction of energy expended in electrochemical process (full line) and pumping energy (broken line) against electrolyte velocity: (1) empty cell (laminar flow), (2) cell with packed cylinders, (3) fluidized bed ITP cell, and (4) fixed bed ITP cell.

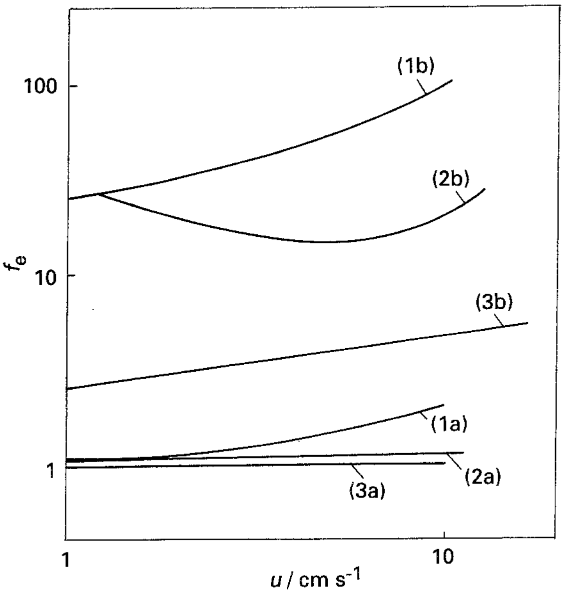

Fig. 8. Plot of energy factor against electrolyte velocity. (1) fixed bed ITP cell, (2) fluidized bed ITP cell, and (3) cell with packed cylinders. Subscripts: (a) cells with insoluble anodes, and (b) cells with soluble anodes.

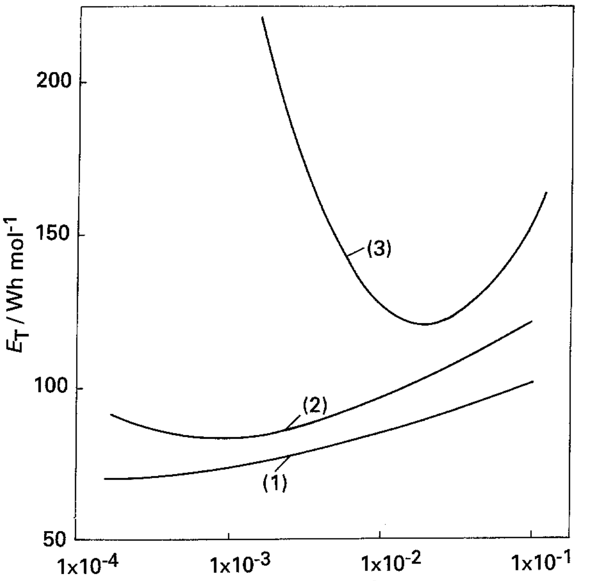

Fig. 9. Plot of specific energy consumption vs. concentration of reacting ions. (1) empty cell (laminar flow), (2) fluidized bed ITP cell, and (3) fixed bed ITP cell.

produce nonuniform local values of mass transfer coefficient over the surface, caused by flow disturbances due to the presence of ITP in the interelectrode space.

For metal winning processes from nonconventional electrolyte, ITP cells may be useful since they intensify the process rate, thus decreasing investment cost. A side effect, which may appear in electrowinning, is the inclusion of some particles of the fixed bed in the deposited metal. Using packed or fluidized bed cell this disadvantage may be avoided.

It is also of interest to demonstrate the influence of the reacting ion concentration on the specific energy consumption of the considered cells working in a batch recirculating mode of operation, assuming constant hydrodynamic conditions corresponding to the maximum value of f_i for the fluidized bed cell. It is also assumed that k_L does not change significantly with ion concentration. Since the limiting current density is directly proportional to the concentration, the operating current was kept at a constant level of 0.75 i_L. The energy consumed in the process was calculated and plotted against Cu^{2+} ion concentration. The results are presented in Fig. 9.

Since the energy for the electrochemical process decreases with concentration and pumping energy increases, the curves pass through a minimum. These minima are less prominent for the fluidized and packed beds than for the fixed bed with ITP. Actually, for the packed bed the minimum is not reached in the analysed range of concentrations, as expected. Figure 9 allows determination of the concentration region in which the cells work with a minimum energy consumption.

5. Conclusion

The presence of ITP in the interelectrode space of cells results in an increase in the limiting current density. The measure of this increase depends on the kind of promoters and the hydrodynamical conditions in the cells.

Intensification of the electrochemical process by ITP causes an increase in specific energy consumption, which is a function of the electrolyte velocity, the current density and the cell itself.

Use of ITP in cells with insoluble anodes has a positive energy effect but its magnitude depends on the nature of the anodic reaction.

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