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Scale-up of bipolar electrode stack dimensionless numbers for current bypass estimation

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New electrochemical reactors with high specific electrode surface area and low investment and operation cost are needed for the industrial application of electrochemistry. Due to its high productivity and low cost, the bipolar electrochemical reactor is a very promising candidate for industrial application. The main disadvantage of the bipolar electrochemical reactor is the presence of parasitic electrical currents, or current bypass at the lower and upper parts of the electrode stack. For the scale-up, a relation between the current bypass (Ψ) and two dimensionless numbers (*Gb* and *Bn*) has been derived.

$$\Psi = Gb(Bn + 1)$$

The bipolar number *Bn* depends on the electrochemical system used and on the process parameters (σ, i_0) in contrast to the geometric number *Gb*, which depends only on the geometry of the bipolar reactor. Measured current bypass in a bipolar electrode stack demonstrates the validity of the scale-up relation for $\Psi \leqslant 0.68$.

List of symbols

A	electrode area (m^2)
e	interelectrode gap (m)
F	Faraday constant ($C\,mol^{-1}$)
Gb	dimensionless number given by Equation 7
H	electrode length (m)
I_0	feeding current (A)
i_0	feeding current density ($A\,m^{-2}$)
L	length of the electrolyte manifold insulating channel (m)
L_e	unitary equivalent length (m)
l	electrode width (m)
n	number of elements
P	pressure (Pa)
R	ohmic resistance in electrolyte feeder/collector channel (Ω)
$\mathscr{R}$	gas constant ($J\,mol^{-1}\,K^{-1}$)
R_i	ohmic resistance in electrolyte feeder channel (Ω)
R_0	ohmic resistance in electrolyte collector channel (Ω)
T	temperature (K)
V_c	constant potential in the n elements (V)
V_d	decomposition voltage (V)
Bn	dimensionless bipolar number
$\dot{V}_{exp}$	experimental gas flow rate ($m^3\,s^{-1}$)
$\dot{V}_0$	theoretical gas flow rate (equation 21) ($m^3\,s^{-1}$)

Greek symbols

ϵ_p	electrolyte porosity due to a packing in the manifold channels (-)
Ψ	current bypass (portion of lost current) (-)
σ	electrolyte conductivity ($\Omega^{-1}\,m^{-1}$)
σ_p	apparent electrolyte conductivity with a packing in the manifold channels ($\Omega^{-1}\,m^{-1}$)

1. Introduction

Through the years, a great deal of published information about synthetic and mechanistic aspects of organic electrochemistry has accumulated. Nevertheless, only a limited number of reactions have been commercialized [1]. The main reason is the complex nature of the electrochemical reactor compared with the chemical reactor; the latter is usually a simple stirred-tank.

This paper concentrates on a bipolar undivided electrochemical reactor with flat parallel electrodes. Two major attractions of the bipolar reactor are the saving in floor space that a compact design allows, and the lower cost of the electrical equipment. No busbars are required inside the electrode stack and the reactor operates at a much higher voltage and a much lower current than its monopolar analogue.

The main disadvantage of this electrochemical reactor is the presence of parasitic electrical currents, or bypass currents, in the electrolyte inlet and outlet of the electrode stack. This results in a faradaic efficiency loss, a nonhomogenous potential and current distributions and, consequently, poor selectivity, in addition to increased corrosion of the electrodes. The current bypass depends on the geometric configuration of the reactor, the current density, the conductivity of the electrolyte, the type of electrochemical

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reaction, the flow rate of the electrolyte and the number of elements in the reactor.

For the scale-up of an electrochemical process, a relation between current bypass and the mentioned parameters must be derived. Many authors have treated the subject of bipolar electrochemical reactors using an electrical analogy [2–6] or by solving directly the Laplace equation [7–10].

In spite of the large number of papers relative to this field, the experimental verification of the proposed models is relatively limited and the studied cases contain relatively few experimental results. In a previous paper, a simple method was proposed for the estimation of current bypass from current/potential curves measured for a bipolar electrochemical reactor and with one elemental cell of similar geometry [11].

The present purpose is to use dimensionless groups, as an industrial design tool for bipolar reactors. For the derivation of scale-up equations, the relation opposed by Burnett and Danly [2] for the filter press electrochemical reactor has been adapted for the configuration used. An experimental validation with the electrolysis of water in caustic media (KOH solution) is also provided.

2. Modelling

2.1. *Derivation of the scale-up relation*

The derivation of the scale-up relation is based on the equation derived by Burnett and Danly, using a resistance network model (Fig. 1) for computing the bypass Ψ in a bipolar reactor [2]:

$$\Psi = \frac{V_c}{12I_0}\left(\frac{1}{R_i}+\frac{1}{R_0}\right)(n^2-1) \qquad (1)$$

This simple model, considering a constant potential V_c in all the n elements can simulate the current bypass in a bipolar reactor over a wide range of values with some simple modifications [8].

Equation 1 can be simplified considering the ohmic resistances in the electrolyte feeder R_i and collector R_0

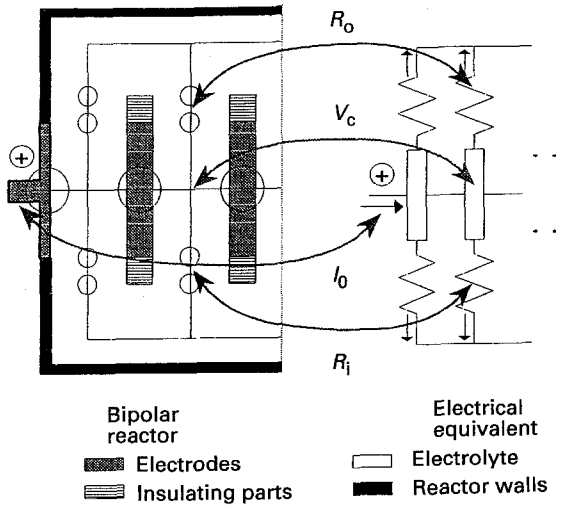

Fig. 1. Schematic view of the modelled reactor and its resistance network model.

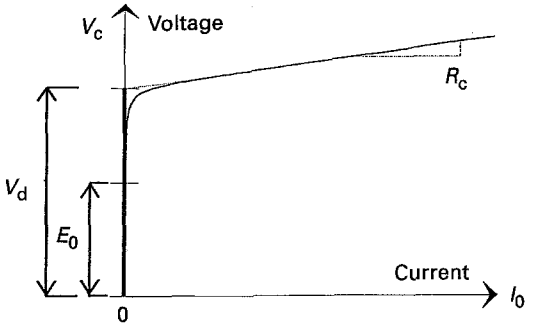

Fig. 2. Graphical representation of Equation 4 and of its parameters, the decomposition voltage, V_d, the ohmic resistance of the compartment R_c and the equilibrium potential E_0.

as equal and identical to R

$$R = R_i = R_0 \qquad (2)$$

$$\Psi = \frac{V_c}{12I_0}\left(\frac{2}{R}\right)(n^2-1) \qquad (3)$$

To take into account the potential drop at the electrode/electrolyte interfaces, a global ohmic behaviour for each element is assumed: thus, the average voltage, V_c, for each element is related to the feeding current, I_0, by the equation

$$V_c = V_d + R_c I_0 \qquad (4)$$

where R_c is the electrolyte ohmic resistance of the compartment and V_d the decomposition voltage. V_d is a value with no exact theoretical significance, but frequently used in practical electrochemistry, to describe the smallest voltage to generate a net faradaic current. It includes the sum of the thermodynamic potentials of the redox couple of the electrochemical reaction (equilibrium potential E_0) and the major part of the kinetic overpotentials, assumed as independent of the current. The decomposition voltage is a function of the electrodes, the electrolyte, the temperature and the pressure. The ohmic resistance R_c takes into account only the compartment geometry and the electrolyte properties. The graphical representation of Equation 4, including parameters V_d, R_c, E_0 is shown in Fig. 2.

Introducing Equation 4 into Equation 3

$$\Psi = \frac{(V_d + R_c I_0)}{6I_0 R}(n^2-1) \qquad (5)$$

After rearrangement, simplification and introduction of the feeding current density, i_0, passing through one element electrode area A,

$$\Psi = \frac{R_c}{6R}(n^2-1) + \frac{V_d}{6RAi_0}(n^2-1) \qquad (6)$$

The definition of two dimensionless numbers

$$Gb = \frac{R_c}{6R}(n^2-1) \qquad (7)$$

$$Bn = \frac{V_d}{AR_c i_0} \qquad (8)$$

changes Equation 6 into

$$\Psi = Gb(Bn+1) \qquad (9)$$

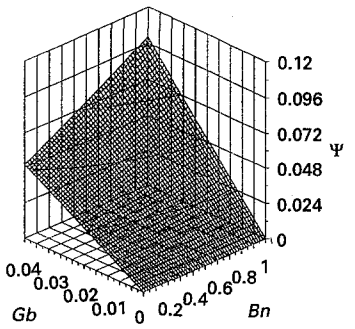

Fig. 3. Variation of bypass Ψ (Equation 9) as a function of the bipolar number *Bn* and the bipolar reactor geometry number *Gb*.

The dimensionless number *Gb* (Equation 7) depends only on the geometry of the bipolar reactor, in contrast to the dimensionless number *Bn* (bipolar number), which depends on the electrochemical system (V_d), the electrolyte resistance (R_c), the electrode area (A) and the operating current density i_0. *Bn* expresses the ratio between the potential drop at the metal/solution interface (V_d) and the ohmic drop in the electrolyte compartment (AR_ci_0).

Relation 9 can be considered in two limiting cases:

(i) $Bn \ll 1$ or $V_d \ll AR_ci_0$.
In this case, *Bn* can be neglected relative to unity in Equation 9 and Ψ is given by

$$\Psi = Gb \tag{10}$$

Thus, the dimensionless number *Gb* can be defined as the so-called geometric bypass, obtained in the absence of any potential drop at the electrode/electrolyte interface. This is the primary current distribution, the most homogenous for the bipolar reactor. *Bn* tends to zero when operating at high current density (i_0) using electrolyte with high electrical resistance (R_c) and an electrochemical system with low V_d values.
(ii) $Bn \gg 1$ or $V_d \gg AR_ci_0$.
In this case, unity can be neglected relative to *Bn* and Equation 9 becomes

$$\Psi = Gb\,Bn \tag{11}$$

This situation corresponds to operation at low i_0, when V_d is a significant contribution to the potential drop. This is the case of secondary current distribution.

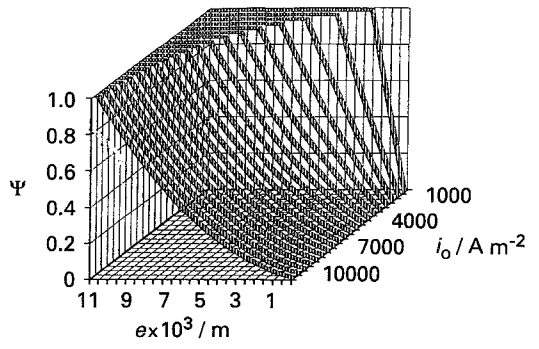

Fig. 4. Influence of the interelectrode gap *e* and the current density i_0 on the bypass Ψ. Parameters values are: $V_d = 1.4\,V$; $\sigma = 29.17\,\Omega^{-1}\,m^{-1}$; $n = 15$; $H = 0.4\,m$; $L = 0.015\,m$.

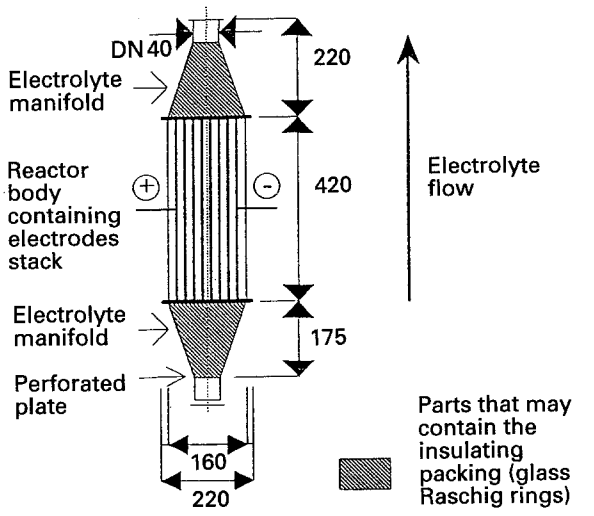

Fig. 5. Schematic view of the electrochemical bipolar reactor containing eight elements.

These two limiting cases clearly show the meaning of Equation 9: Ψ is expressed as the lowest bypass, given by *Gb*, obtained in a bipolar reactor with pure primary current distribution, corrected by the factor $(Bn + 1)$ for secondary current distribution. This factor is necessarily bigger than 1 and increases with the influence of the secondary current distribution.

Due to their physical meaning, values of Ψ and *Gb* are smaller or equal to unity (Ψ and $Gb \leqslant 1$) and $Bn \geqslant 0$. These constraints are satisfied by the following relations:

$$\frac{1}{Gb} \geqslant Bn + 1 \tag{12}$$

$$6R \geqslant R_c(n^2 - 1) \tag{13}$$

Figure 3 clearly demonstrates that it is necessary to have low values of *Gb* and *Bn* to keep the bypass in a suitable range ($\Psi < 0.1$).

2.2. *Application to the channel-type configuration*

2.2.1. Evaluation of the ohmic resistances. For the bipolar electrolyser in the channel-type configuration (Figs 5 and 6), the ohmic resistances R_c and R are

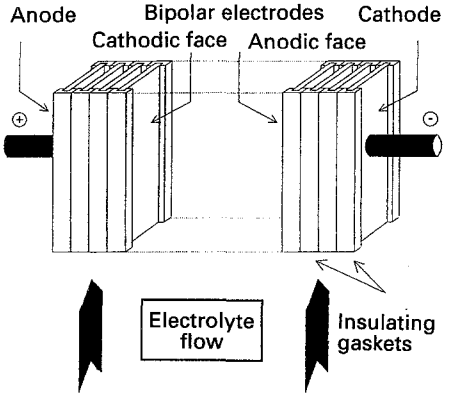

Fig. 6. Schematic representation of the bipolar electrodes stack.

given by the relations:

$$R_c = \frac{1}{\sigma}\left(\frac{e}{Hl}\right) \quad (14)$$

$$R = \frac{1}{\sigma}\left(\frac{L}{el}\right) \quad (15)$$

where the symbols σ, L, e, H and l are explained at the commencement of this paper.

Protection against bypass current can be realized by placing an insulating random packing, like glass Raschig rings, in the manifold (Fig. 5). The resulting electrolyte porosity, ϵ_p, induces an apparent electrolyte conductivity, σ_p, in the channels calculated according to the Bruggeman equation

$$\sigma_p = \sigma(1 - \epsilon_p)^{1.5} \quad (16)$$

to be used in Equation 15.

Introducing Equations 14, 15 and 16 in Equations 7, 8 and 13, we obtain the dimensionless numbers *Gb* and *Bn* for the channel type configuration:

$$Gb = \frac{e^2}{6HL}(1 - \epsilon_p)^{1.5}(n^2 - 1) \quad (17)$$

$$Bn = \frac{V_d \sigma}{e i_0} \quad (18)$$

In this work, the electrodes in the bipolar stack are not terminated with insulating plates. For this configuration, a hypothetical channel equivalent length is defined as the product of a unit equivalent length L_e and the number of elements n.

$$L = nL_e \quad (19)$$

L_e depends on the geometry of the electrolyte manifold and is determined by fitting *Gb* in such a way that a linear relation between Ψ and $Bn + 1$ is obtained (Equation 9).

2.2.2. Design. The two major constraints in the design of a bipolar reactor are the bypass Ψ, which must be as low as possible, and the bipolar number *Bn*, which is very often imposed. The latter is a function of the process parameters fixed at the bench scale step. Equation 9 is then used to determine the number *Gb*, leading to the cell geometry.

To obtain low values of *Gb*, long electrodes (*H*) and insulating channels in the manifold (*L*) are required, especially when the number of elements n is large. If needed, a random insulating packing, with a porosity ϵ_p, put in the electrolyte manifolds, reduces the current losses. The interelectrode gap, e, must be chosen with care: at high values of *Bn*, e causes an increase in Ψ in Equation 9. Figure 4 shows this influence of e, using i_0 as parameter. If i_0 is small, a larger e increases Ψ much more than for a big i_0; the ohmic path for shunt currents is clearly preferred to that through the electrode stack.

Finally, the length of the insulating channels is very often the only remaining parameter which is free.

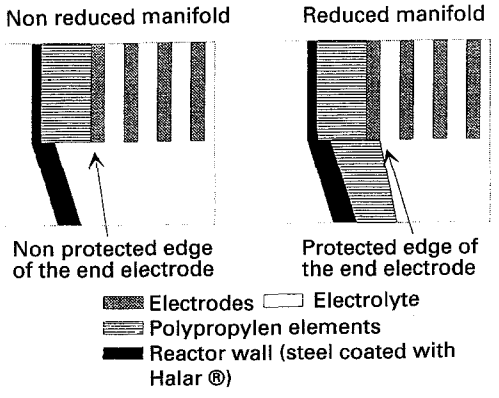

Fig. 7. Schematic view showing the protection mode of the end electrodes edges in the electrolyte manifold.

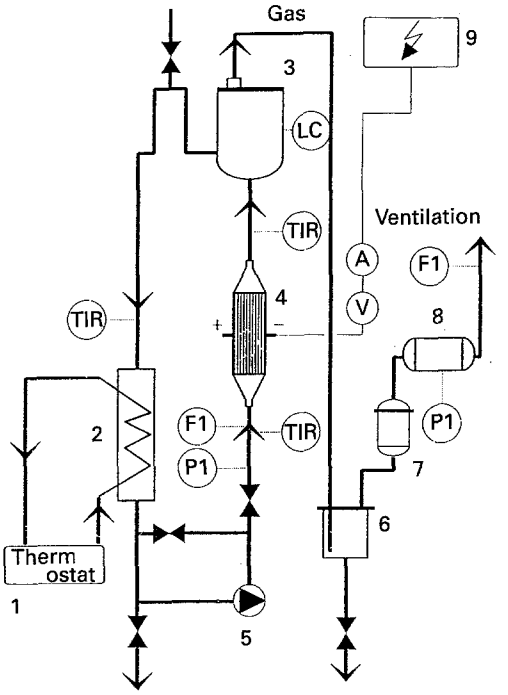

Fig. 8. Schematic presentation of the equipment used. (1) Thermostat, (2) heat exchanger, (3) gas-liquid separator, (4) bipolar reactor, (5) circulation pump, (6) liquid separator, (7) alumina bed, (8) gas measures, and (9) current rectifier.

3. Experimental details

3.1. *Equipment*

The bipolar reactor (Fig. 5) was built in steel coated with Halar to achieve a good rigidity, chemical resistance and electrical insulation. The electrode stack (Fig. 6) contained from 4 to 25 nickel bipolar plates (396 mm × 17 mm × 2 mm) and two nickel end plates (same size) as current feeders; the electrodes were separated from each other by insulating gaskets (Neoprene) with a fixed gap e of (3.3 mm), making 5 to 26 elements for a total electrode area between 0.034 and 0.175 m^2. The insulating packing (glass Raschig rings with a porosity ϵ_p of 0.37), when used, was placed in the manifold as shown in Fig. 5. Two kinds of manifolds (Fig. 7), *nonreduced* and *reduced* (the flow section of the manifold reduced to the stack size), characterized by nonprotected or protected edges of the end electrodes, were used.

Figure 8 is a schematic view of the installation used.

The electrolyte pumped through the electrode stack with an average velocity of $0.5\,m\,s^{-1}$. The temperature was kept constant using a thermostat (Lauda LTH 100) connected to a glass heat exchanger (Sovirel, $1\,m^2$). The electric current was provided by a rectifier (Electronic Measurements Inc.; SCR-100-100-200 000; range: 0–100 V, 0–100 A) driven by computer.

3.2. *Method of determination of current losses*

The electrochemical reaction used for the experimental determination of current bypass of the bipolar reactor is water electrolysis in alkaline medium (0.1 to, 1.0 M KOH).

$$2H_2O \longrightarrow 2H_2 + O_2$$

Electrolysis was effected at constant current density and temperature (50° C), the evolved gas was dried on an alumina bed, its flow rate ($\dot{V}$) was measured using a bubble flow meter. The current bypass, Ψ, was calculated using the relation

$$\Psi = \frac{\dot{V}_0 - \dot{V}}{\dot{V}_0} \tag{20}$$

where $\dot{V}_0$ is the theoretical volumetric flow rate of gas in absence of current bypass ($\Psi = 0$) and is given by

$$\dot{V}_0 = \left(0.75\frac{\mathscr{R}T}{FP} I_0\right) n \tag{21}$$

The key parameters were: The electrolyte conductivity σ in the range of $3-30\,\Omega^{-1}\,m^{-1}$ (changing the KOH concentration), the current density ($0.6-10\,kA\,m^{-2}$) and the geometry of the bipolar reactor (number of elements n, presence of insulating packing in the manifold).

4. Results and discussions

For the experimental verification of the theoretical model (Equation 9), the current bypass Ψ has been measured in a wide range of *Gb* (Equation 17) and *Bn* (Equation 18) values. *Gb* and *Bn* have been varied by changing the geometry of the bipolar reactor

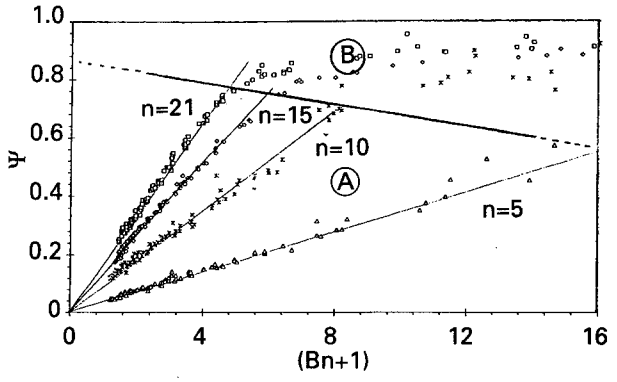

Fig. 9. Variation of experimental current bypass (Ψ) as a function of the distribution factor ($Bn + 1$) with a bipolar reactor having different numbers of elements ($n = 5, 10, 15, 21$). Domain A corresponds to the normal running mode and Domain B to the partial running mode of the bipolar stack.

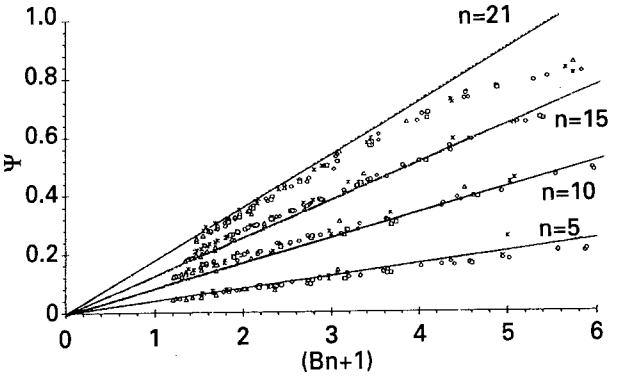

Fig. 10. Experimental and predicted (continuous line) current bypass (Ψ) as a function of the distribution factor ($Bn + 1$). Configuration used: Bipolar reactors with nonreduced manifolds (Fig. 7). Parameters: $L_e = 5.6 \times 10^{-4}$ m; $V_d = 1.67$ V; $\sigma = 3-20\,\Omega^{-1}\,m^{-1}$; $n = 5, 10, 15, 21$.

(number of elements n, presence of insulating packing in the electrolyte manifold) and by changing the process parameters (σ and i_0), respectively.

4.1. *General behaviour of the system*

Figure 9 shows a plot of the current bypass Ψ against the distribution factor ($Bn + 1$) obtained with a bipolar reactor having a different number of elements ($n = 5$, 10, 15, 21) and different electrolyte conductivity ($3-30\,\Omega^{-1}\,m^{-1}$). A linear relation between Ψ and ($Bn + 1$) was obtained only for a small number of elements in the bipolar stack ($n = 5$). For a higher number of elements deviation from linearity occurs at high ($Bn + 1$) values (transition point). The higher the number of elements in the bipolar stack, the lower is the ($Bn + 1$) value at which transition occurs. The linear domain (Domain A in Fig. 9) corresponds to the normal running mode of the bipolar stack in which the potential of all the elements in the stack is higher than the decomposition voltage V_d. In this domain, Equation 9 is applicable and *Gb* is the slope of $\Psi = f\,(Bn + 1)$ linear relation.

In the other domain (Domain B in Fig. 9) for higher *Bn* values, the reactor works in the partial running mode in which only a fraction of the elements works at potentials higher than the decomposition voltage V_d. In this domain, Equation 9 is not valid due to the fact that the model proposed in this paper is based on the assumption that the potential of all the elements in the bipolar stack is higher than the decomposition voltage V_d (Equation 4).

4.2. *Experimental verification of the model*

Comparison of experimental results with those predicted using Equation 9 has been carried out in the absence and presence of glass Raschig in the electrolyte manifolds. In the absence of glass Raschig in the electrolyte manifolds, the channel equivalent length (L) has been calculated using Relation 19 in which the unitary equivalent length (L_e) has been calculated by fitting *Gb* in such a way that a linear

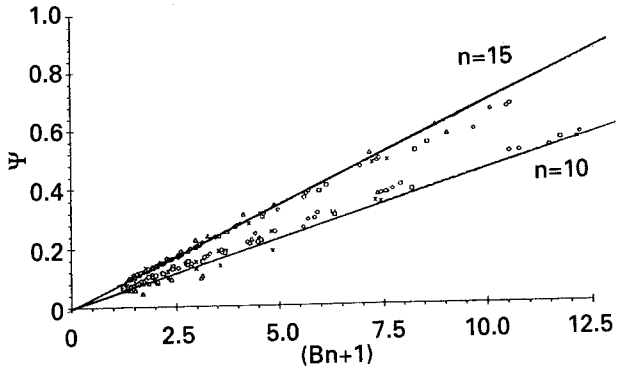

Fig. 11. Experimental and predicted (continuous line) current bypass (Ψ) as a function of the distribution factor ($Bn + 1$). Configuration used: Bipolar reactors containing glass Raschig in the electrolyte manifolds (Fig. 5). Parameters: $\epsilon_p = 0.37$; $V_d = 1.67$ V, $\sigma = 3$–$20\,\Omega^{-1}\,m^{-1}$; $n = 10, 15$.

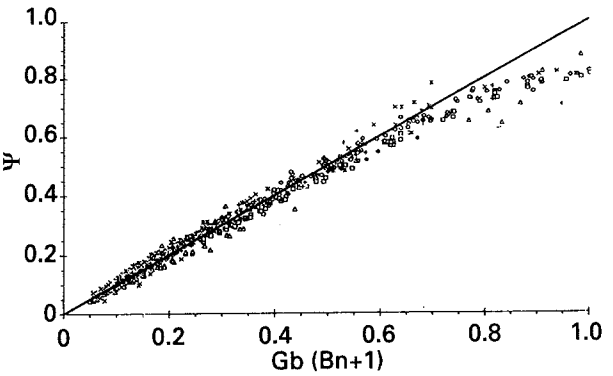

Fig. 12. Experimental current bypass (Ψ) plotted against the calculated values using Equation 9.

relation between Ψ and $(Bn + 1)$ is obtained. Figure 10 shows a plot of the current bypass Ψ against the distribution factor $(Bn + 1)$ for four different reactor configurations ($n = 5$, 10, 15 and 21 elements) with nonreduced manifolds (Fig. 7); the unitary equivalent length (L_e) used in this case is $L_e = 5.3 \times 10^{-4}$ m. This figure shows that there is a good agreement between experimental and theoretical values obtained for $n = 5$, 10 and 15.

The deviation of the experimental values from those predicted by the model for a bipolar electrode stack with 21 elements ($n = 21$) is due to the fact that in this configuration the reactor works in the partial running mode in which only a fraction of the elements in the stack works at potentials higher than V_d.

Similar results are obtained with a bipolar stack having reduced manifolds (Fig. 7) with the only difference that the unitary equivalent length (determined by fitting Gb in such a way that a linear relation between Ψ and $Bn + 1$ is obtained) is longer ($L_e = 6.4 \times 10^{-4}$ m) than those obtained with a bipolar stack having a reduced manifold ($L_e = 5.3 \times 10^{-4}$ m). This increase of L_e is due to the increase of the ohmic resistance in the electrolyte manifold as expected with this geometry (Fig. 7).

Figure 11 shows a plot of Ψ against $(Bn + 1)$ plot obtained in the presence of glass Raschig (porosity $\epsilon_p = 0.37$) in the electrolyte manifolds. In this case, the apparent electrolyte conductivity in the electrolyte manifolds has been estimated using Bruggeman equation (Equation 16).

Finally, in Fig. 12, the experimental current bypass Ψ (measured with different geometries of the bipolar reactor and with different process parameters) has been plotted against the calculated Ψ values obtained from Equation 9. A good agreement between experimental and theoretical Ψ values obtained in a region of bypass Ψ lower than 0.68. The observed deviation from the model at higher bypass is due to partial running mode of the bipolar reactor.

5. Conclusion

This paper presents a scale-up equation (Equation 9) for the estimation of current bypass, which takes into account the potential drop at the electrode–electrolyte interfaces as a decomposition voltage.

Two dimensionless numbers are introduced: the bipolar number Bn which depends on the electrochemical system used and Gb number which depends only on the geometry of the bipolar reactor.

According to the scale-up equation, low bypass can be obtained working at high current density and using long electrodes in the bipolar electrode stack.

Finally, the validity of the scale-up equation has been experimentally demonstrated for the current bypass $\Psi \leqslant 0.68$.

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