

# Comparison between primary and secondary current distributions in bipolar electrochemical reactors

E. R. Henquín · J. M. Bisang

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**Abstract** The primary and secondary current distributions in bipolar electrochemical reactors with recessed electrodes are compared. When the electrolyte of the different reactors of the stack is connected, and thus a leakage current is possible, the secondary current distribution is more pronounced than the primary one for the cases of industrial importance. In the absence of a leakage current the usual behavior of a monopolar system is observed.

**Keywords** Bipolar electrodes · Current distribution · Electrochemical reactors · Laplace equation · Leakage current

## List of symbols

$A$	Interelectrode gap–recess depth (m)
$b_i$	Tafel slope of the $i$ th reaction (V)
$e$	Interelectrode gap (m)
$E_0$	Reversible electrode potential (V)
$H$	Distance from the electrode end to the reactor bottom (m)
$j_{i,k}$	Current density of the $i$ th reaction ( $i = a$ or $c$ ) at the $k$ th electrode ( $k = A, B$ or $C$ ) ( $A\ m^{-2}$ )
$j_{\text{mean}}$	Mean current density at the terminal electrodes ( $A\ m^{-2}$ )
$j_{B,\text{mean}}$	Mean current density at the bipolar electrode ( $A\ m^{-2}$ )
$j_{0,i}$	Exchange current density of the $i$ th reaction ( $A\ m^{-2}$ )
$I$	Total current (A)

$I^*$	Leakage current (A)
$I_B$	Total current at the bipolar electrode (A)
$L$	Electrode length (m)
$R$	Bypass resistance ( $\Omega$ )
$S$	Electrode surface area ( $m^2$ )
$U_0$	Reversible cell voltage (V)
$U_A$	Potential at the terminal anode (V)
$U_C$	Potential at the terminal cathode (V)
$W$	Electrode width (m)
$Wa_{Bi}$	Bipolar Wagner number = $(b_a + b_c)/(RI)$
$x$	Axial coordinate (m)
$y$	Axial coordinate (m)

## Greek characters

$\eta$	Overpotential (V)
$\rho$	Electrolyte resistivity ( $\Omega\ m$ )
$\sigma$	Standard deviation
$\phi$	Potential (V)
$\phi_0$	Potential in the solution phase adjacent to an electrode surface (V)

## Subscripts

$a$	Anodic reaction
$A$	Terminal anode
$B$	Bipolar electrode
$c$	Cathodic reaction
$C$	Terminal cathode
$m$	Metal phase
$P$	Primary
$s$	Solution phase
$S$	Secondary

## 1 Introduction

Electrochemical reactors for the production of substances are often designed so that the current distribution is

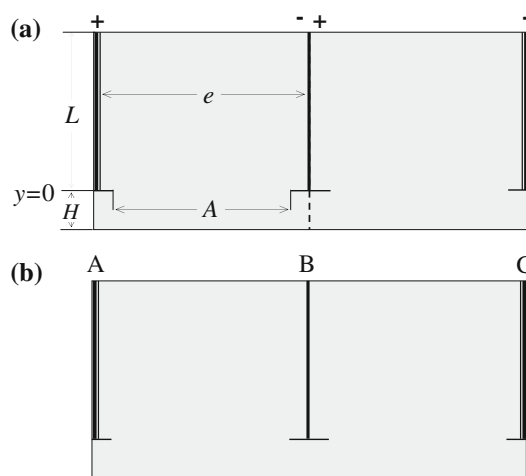
E. R. Henquín · J. M. Bisang (✉)  
Programa de Electroquímica Aplicada e Ingeniería  
Electroquímica (PRELINE), Facultad de Ingeniería Química,  
Universidad Nacional del Litoral, Santiago del Estero 2829,  
3000 Santa Fe, Argentina  
e-mail: jbisang@fiq.unl.edu.ar

uniform over the electrode surface. This enables better quality in the products and prevents the existence of underutilized electrode regions, unwanted products or corrosion zones in the electrode. According to Newman and Thomas-Alyea [1], the primary distribution represents the more pronounced case for monopolar electrodes because kinetic limitations, if present, would tend to make the current distribution more uniform. Hine et al. [2] analyzed the effect of the side and back walls of electrolytic cells on the primary current distribution in rectangular reactors with parallel and flat plates as electrodes, which represents a usual configuration in the electrochemical industry. Thus, the ratio between the current at the inner and outer surfaces of the electrodes is shown graphically; in order to achieve a uniform current distribution, it is important that the electrolyte be confined to the interelectrode gap. However, this requirement cannot be achieved in some industrial electrochemical reactors. Therefore, in tank electrolyzers used in electrowinning or electrorefining of metals, the electrodes protrude some distance above the surface of the electrolyte but they do not touch the bottom of the tank in order to reserve some clearance under the electrodes where the anode slime or sludge can settle and accumulate. The anodes are often smaller than the cathodes and the cell width is larger than the electrode width. Likewise, the sides of the electrodes are furnished with insulating plastic edge strips with the aim of facilitating the stripping of the deposit [3]. Bouzek et al. [4] studied the current distribution, both experimentally and theoretically, at the monopolar electrodes in zinc electrowinning cells. Important variations in the secondary current distributions were reported when the cathode is moved along the cell width. A similar situation is observed in some flow

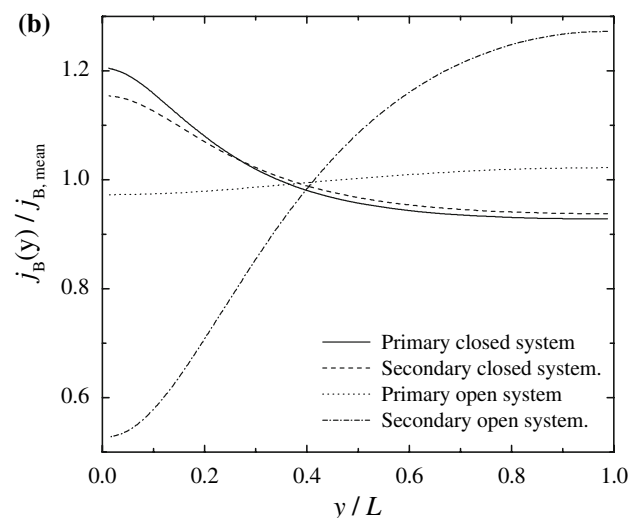
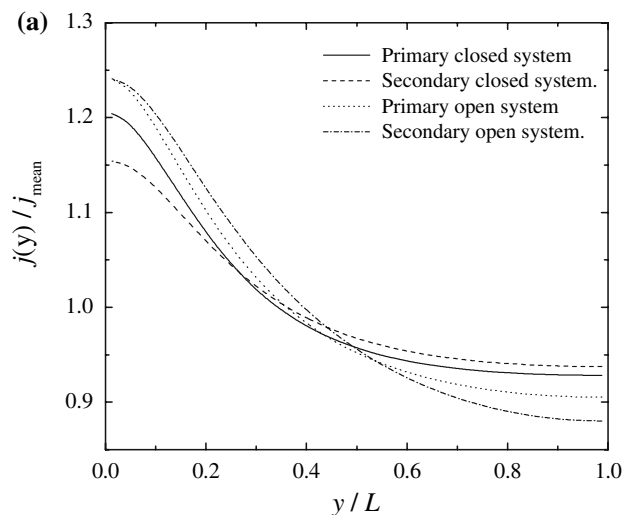
electrolyzers of filter press configuration employed in organic or inorganic electrosynthesis where the electrodes are embedded in a frame and the presence of channels for the inlet or outlet of the electrolyte generates an additional electrolyte volume. Thus, in the above reactors the electrodes are recessed and there is electrolyte outside the interelectrode gap, which affects the current distribution.

**Table 1** Physicochemical properties and kinetic parameters used in modeling

$\rho$ ( $\Omega$ m)	$3 \times 10^{-2}$
$U_0$ (V)	1.23
$b_a = b_c$ (V)	0.04
$j_{0,a} = j_{0,c}$ ( $A\ m^{-2}$ )	$1 \times 10^{-2}$



**Fig. 1** Schema of a bipolar stack with recessed electrodes. **a** Solution phase of both reactors not connected. **b** Solution phase of both reactors connected. **■**: terminal electrodes, **—**: bipolar electrode, **■**: electrolyte, **—**: insulating electrode edge, **- -**: insulating wall



**Fig. 2** Comparison of the current distributions for the closed and open configurations of bipolar electrochemical reactors.  $e/L = 1.225$ ,  $e/H = 4.9$ ,  $A/e = 67.35\%$ .  $j_{\text{mean}} = 0.3\ A\ \text{cm}^{-2}$ . **a** Terminal electrodes. **b** Bipolar electrode

The current distribution at monopolar recessed electrodes has been studied in the literature. Thus, West and Newman [5] analyzed the primary current distribution on disk electrodes recessed in insulating planes with the aim of designing a cell that would have an approximately uniform current distribution. It is graphically shown that, for aspect ratios (defined as the ratio of the recess depth to the disk radius) greater than 0.5, the deviation of the current density at the edge of the electrode from the average current density was less than 10%, and (as expected) a uniform current distribution is achieved when the aspect ratio approaches infinity. Dinam et al. [6] performed an experimental investigation of the current distribution on a recessed rotating disk electrode and have experimentally corroborated that the recess dramatically improves the uniformity of the primary current distribution. Likewise, it was reported that, for a mass-transfer-controlled reaction, the current density was uniform near the centre of the electrode but decreased rapidly towards the edge of the electrode, and the current density distribution was more uniform when the aspect ratio decreased. This behavior was attributed to the effect of the recess on the hydrodynamics of the system. Diem et al. [7] studied theoretically the influence of both the angle between the electrode and isolator and the depth to which the electrode is recessed on the primary current distribution for a two-dimensional slotted electrode.

In recent years there has been increasing interest in the use of bipolar reactors for industrial processes. However, one disadvantage of this electrical connection is the presence of leakage currents, flowing through the connecting manifolds and pipes, which can modify the current distribution in the reactor. Thus, in previous works from this laboratory [8–10] the primary and secondary current distributions were analyzed and the theoretical results were compared with experimental data. A satisfactory concordance between them was reported.

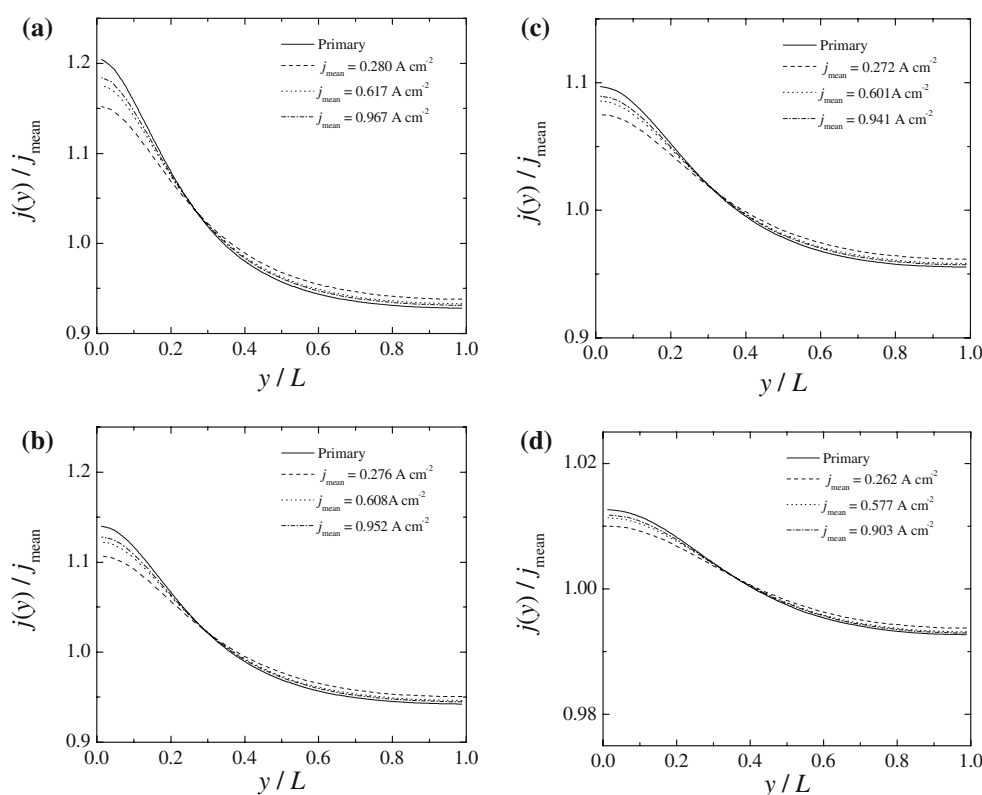
The aim of the present work is to compare the primary and secondary current distributions in bipolar electrochemical reactors with recessed electrodes in the presence or absence of leakage currents.

### 2 Theoretical considerations

Figure 1 shows a schematic representation of bipolar electrochemical reactors with recessed electrodes. In Fig. 1a the electrolytes of both reactors of the stack are not interconnected, a so-called closed system, and the leakage current is hindered. However, the reactor sketched in Fig. 1b allows a leakage current, which bypasses the bipolar electrode, a so-called open system.

In the following mathematical treatment some simplifying assumptions are made:

**Fig. 3** Current distributions for an electrochemical reactor of the type sketched in Fig. 1a, closed system.  $e/L = 1.225$ ,  $e/H = 4.9$ . **a**  $A/e = 67.35\%$ , **b**  $A/e = 59.18\%$ , **c**  $A/e = 51.02\%$  and **d**  $A/e = 18.36\%$



- (1) The metal phase of the electrodes is isopotential.
- (2) The current distribution in the direction of the electrode width can be neglected.
- (3) The effect of the gases generated at the electrodes on the electrolyte resistivity can be disregarded.

The potential distribution was obtained by solving the Laplace equation

$$\frac{\partial^2 \phi_s(x, y)}{\partial x^2} + \frac{\partial^2 \phi_s(x, y)}{\partial y^2} = 0 \tag{1}$$

subject to the following boundary condition at the insulating walls:

$$\left. \frac{\partial \phi_s(x, y)}{\partial x} \right|_{\text{insulating walls}} = \left. \frac{\partial \phi_s(x, y)}{\partial y} \right|_{\text{insulating walls}} = 0. \tag{2}$$

For primary current distribution at the terminal anode it must hold that

$$\phi_s = U_A, \tag{3}$$

and at the terminal cathode,

$$\phi_s = U_C. \tag{4}$$

Likewise, at the electrode surfaces the current density can be calculated as

$$j_{i,k}(y) = - \left. \frac{1}{\rho} \frac{\partial \phi_s(x, y)}{\partial x} \right|_{k\text{th electrode surface}}, \tag{5}$$

where  $i$  indicates the anodic or the cathodic reaction, and  $k$  the electrode.

For secondary current distribution the boundary conditions at the electrode surfaces are obtained combining Eq. 5 with the kinetic expression. Therefore, in these calculations we assumed a Tafel equation for the kinetics at each electrode surface according to:

$$j(y) = j_0 \exp \left[ \frac{\eta(y)}{b} \right], \tag{6}$$

where

$$\eta(y) = \phi_m - \phi_0(y) - E_0. \tag{7}$$

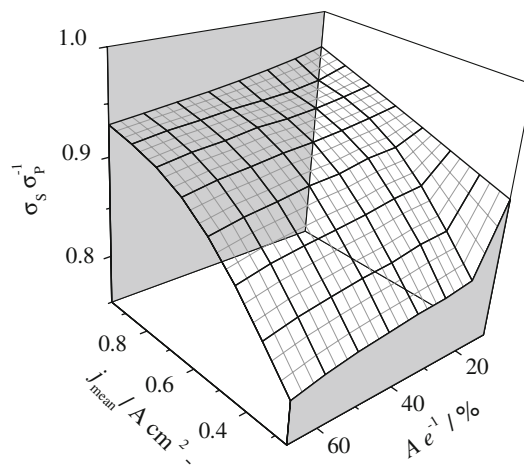
The current drained at each electrode surface was calculated as

$$I_k = W \int_0^L j_{i,k} dy, \tag{8}$$

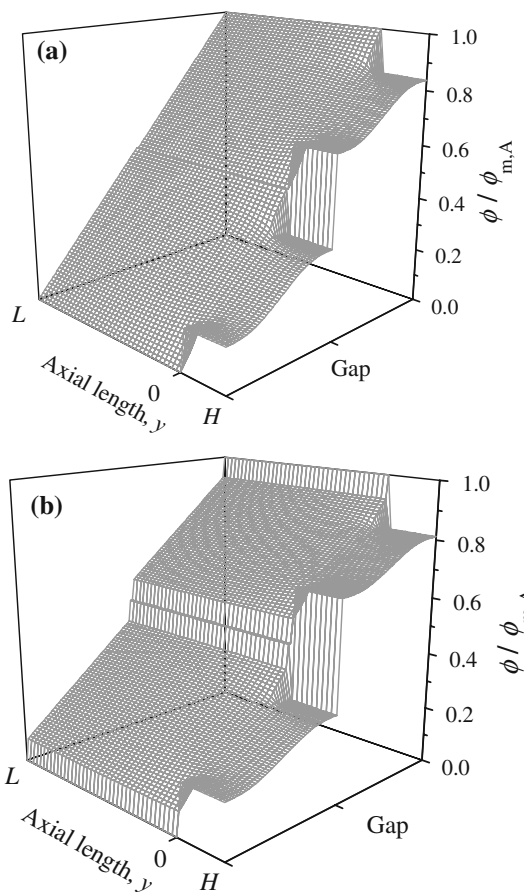
and the leakage current is given by

$$I^* = I_{A \text{ or } C} - I_B. \tag{9}$$

The calculation procedure was described in detail for the primary case in [9] and for the secondary distribution in [10]. Table 1 summarizes the kinetic and physicochemical parameters used in the modeling.



**Fig. 4** Ratio of the standard deviation of the secondary current distribution to the standard deviation of the primary current distribution as a function of  $j_{\text{mean}}$  and  $A/e$  for an electrochemical reactor of the type sketched in Fig. 1a.  $e/L = 1.225$ ,  $e/H = 4.9$



**Fig. 5** Potential distributions for an electrochemical reactor of the type sketched in Fig. 1a.  $e/L = 1.225$ ,  $e/H = 4.9$ .  $A/e = 67.35\%$ . **a** Primary distribution. **b** Secondary distribution,  $j_{\text{mean}} = 0.967 \text{ A cm}^{-2}$ ,  $U = 10 \text{ V}$

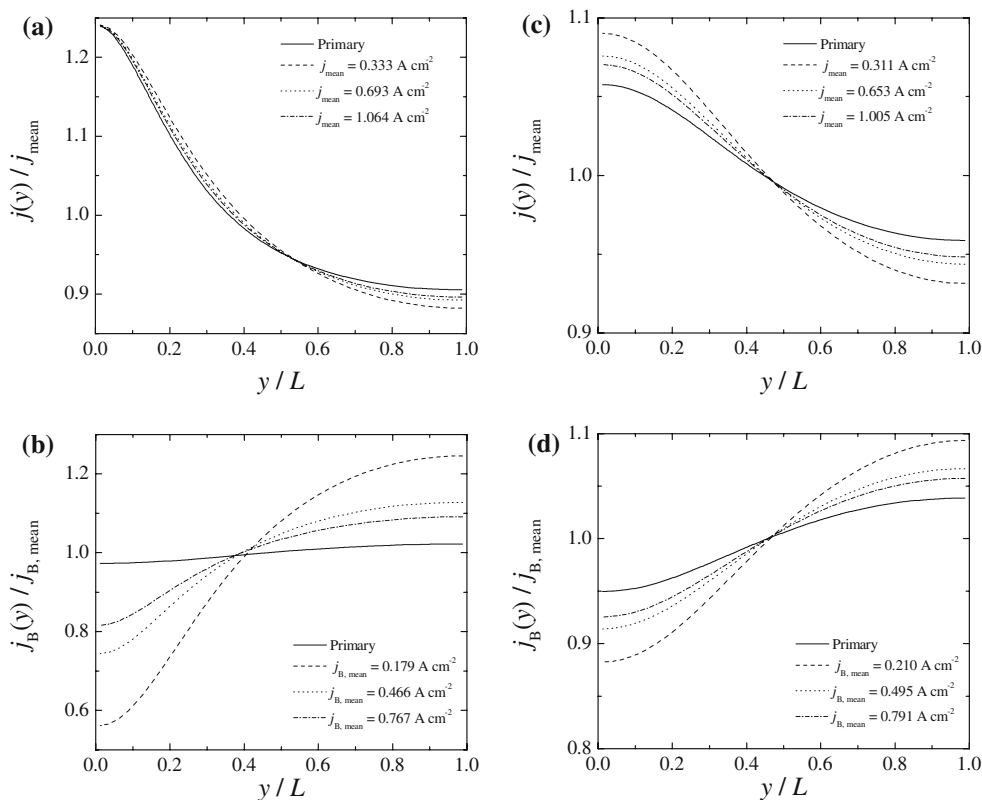
### 3 Results and discussion

Figure 2 compares typical curves of current distributions for the closed and open arrangements sketched in Fig. 1 for  $e/L = 1.225$  and  $e/H = 4.9$ , where it can be observed that the open system presents a more pronounced current distribution due to the existence of the leakage currents bypassing the bipolar electrode.

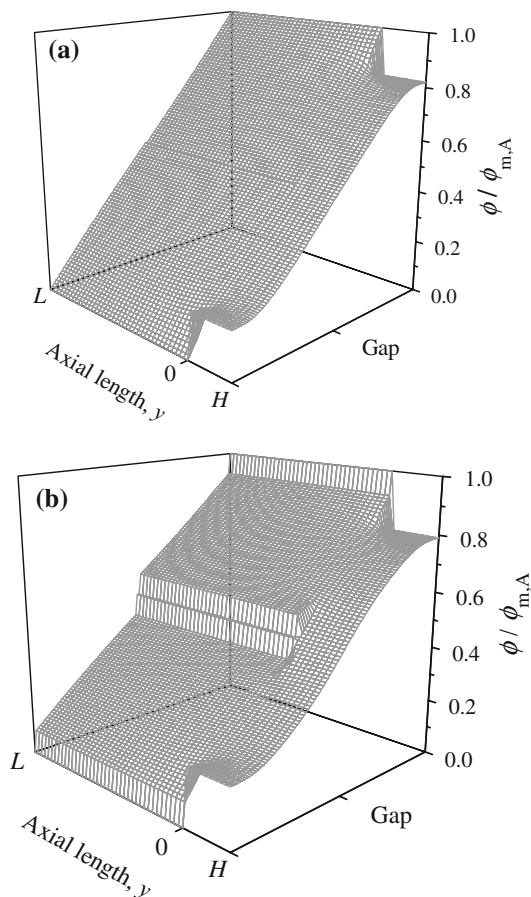
Figure 3 shows the current distributions for the schema of Fig. 1a, the closed arrangement, parametric in the ratio  $A/e$ . The secondary current distributions are given for three values of mean current density, corresponding to cell voltages of 6, 8 and 10 V, respectively. Figure 4 summarizes the results for the ratio of the standard deviation of the secondary current distribution to the standard deviation of the primary current distribution reported as a function of both the mean current density and  $A/e$ . As expected, for a closed arrangement, from Figs. 3 and 4 it can be observed that the secondary current distribution is always more attenuated than the primary one and, when the current is increased, the secondary current distribution approaches the primary case because of the decrease of the polarization resistance. Likewise, when the parameter  $A/e$  is lower than 20% the current distribution is practically uniform.

Figure 5 presents the potential distributions in the reactor with the closed arrangement for the primary case (Fig. 5a), and for the secondary one (Fig. 5b), when  $A/e$  is 67.35%. For the secondary case an abrupt change in potential is observed at each electrode surface. Likewise, in both distributions an approximately linear variation in potential in the interelectrode gap is detected for the region farther from the recessed part of the electrode, and in its proximity the potential distribution is altered by the electrolyte outside of the interelectrode gap.

Figure 6 shows the current distributions for the schema of Fig. 1b, the open arrangement, when  $e/L = 1.225$  and  $e/H = 4.9$  for different  $A/e$  values, parametric in the mean current density for the same cell voltages as in Fig. 3. The secondary current distribution is more pronounced than the primary one. This behavior has also been predicted by the simplified model proposed in a former paper [8] to calculate current distributions in bipolar electrochemical reactors. The secondary current distribution approaches the primary one when the total current increases. The potential distributions for the open arrangement are reported in Fig. 7 for  $A/e = 67.35\%$ . Comparison between Figs. 5 and 7 reveals the effect of the leakage current on the potential



**Fig. 6** Current distributions for an electrochemical reactor of the type sketched in Fig. 1b.  $e/L = 1.225$ ,  $e/H = 4.9$ . **a**  $A/e = 67.35\%$ , terminal electrodes. **b**  $A/e = 67.35\%$ , bipolar electrode. **c**  $A/e = 18.36\%$ , terminal electrodes. **d**  $A/e = 18.36\%$ , bipolar electrode

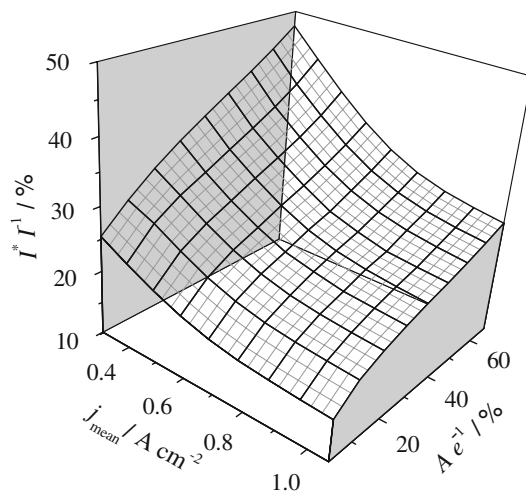


**Fig. 7** Potential distributions for an electrochemical reactor of the type sketched in Fig. 1b.  $e/L = 1.225$ ,  $e/H = 4.9$ .  $A/e = 67.35\%$ . **a** Primary distribution. **b** Secondary distribution,  $j_{\text{mean}} = 1.064 \text{ A cm}^{-2}$ ,  $j_{B,\text{mean}} = 0.767 \text{ A cm}^{-2}$ ,  $U = 10 \text{ V}$

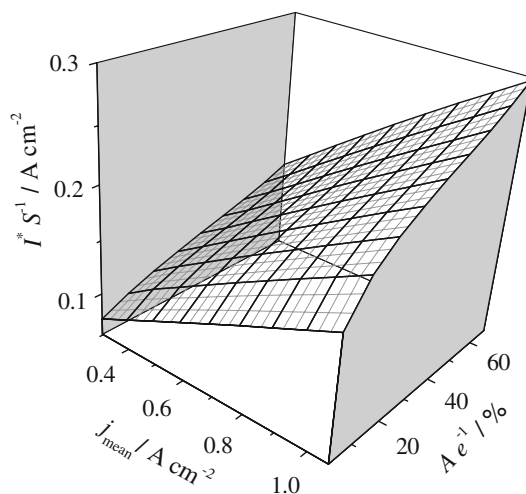
distribution: a pronounced influence is detected in the region near the recessed electrode parts.

Figure 8 shows the ratio of the leakage current to the total current as a function of both the mean current density at the terminal electrodes and the geometric parameter  $A/e$ .  $I^*/I$  increases as  $A/e$  increases due to the decrease in the bypass resistance, and the increase in  $j_{\text{mean}}$  produces a decrease in  $I^*/I$  but an increase in  $I^*$ , as reported in Fig. 9. Furthermore, Fig. 10 shows the ratio of the standard deviation of the secondary current distribution to the standard deviation of the primary current distribution at the terminal electrodes as a function of the mean current density and the geometric factor  $A/e$  for the open arrangement. Contrary to the performance of the closed system (Fig. 4), the standard deviation of the secondary current distribution decreases as the mean current density increases.

The current distributions of the open arrangement (Fig. 1b) for  $e/L = e/H = 1.96$  and  $A/e = 67.35\%$  are reported in Fig. 11. As opposed to the behavior observed in Fig. 6, for this geometrical configuration the secondary



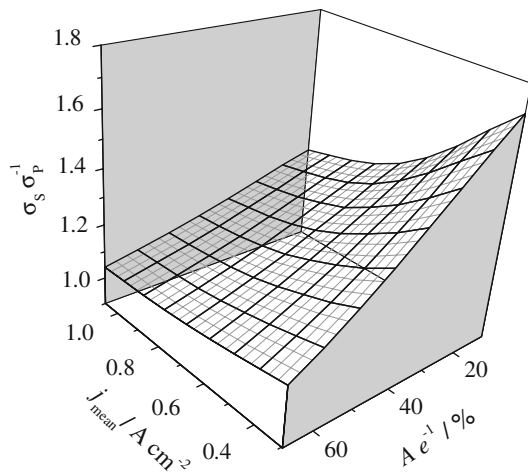
**Fig. 8** Fraction of the leakage current as a function of  $j_{\text{mean}}$  and  $A/e$ . Secondary current distribution.  $e/L = 1.225$ ,  $e/H = 4.9$



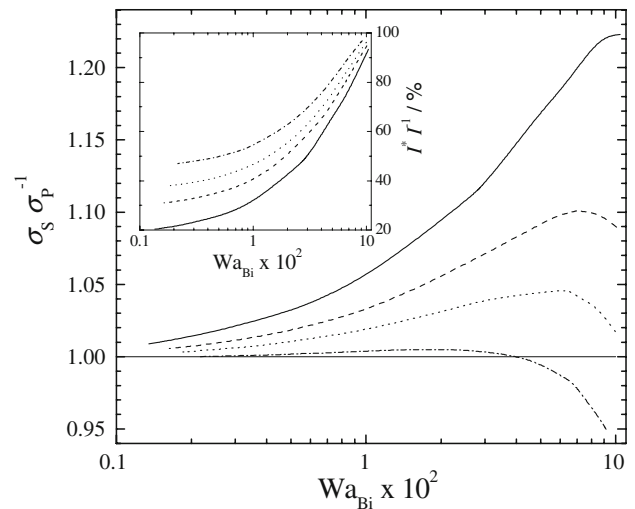
**Fig. 9** Leakage current related to the electrode surface area as a function of  $j_{\text{mean}}$  and  $A/e$ . Secondary current distribution.  $e/L = 1.225$ ,  $e/H = 4.9$

current distribution at the terminal electrodes is less pronounced than the primary one when the mean current density is low. Figure 12 shows the standard deviation of the secondary current distribution related to the standard deviation of the primary one as a function of the bipolar Wagner number [10] and parametric in the geometrical numbers characteristic of the reactors. It can be observed that in the major cases the secondary current distribution is more pronounced than the primary one. However, the inverse behavior is detected for reactors with large distance from the electrode end to the reactor bottom and low current density. Furthermore, as shown in Fig. 12, in these cases the leakage current is remarkably high and uninteresting from a practical point of view. Additional simulations performed with other geometrical parameters displayed the same tendency shown in these figures.

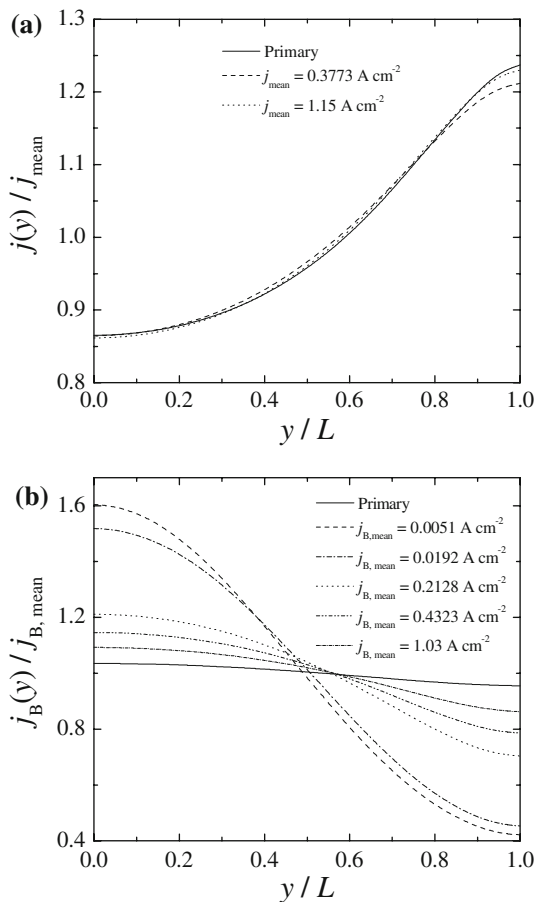




**Fig. 10** Ratio of the standard deviation of the secondary current distribution at the terminal electrodes as a function of  $j_{\text{mean}}$  and  $Ae$  for an electrochemical reactor of the type sketched in Fig. 1b.  $e/L = 1.225$  and  $e/H = 4.9$



**Fig. 12** Ratio of the standard deviation of the secondary current distribution to the standard deviation of the primary current distribution at the terminal electrodes as a function of the Bipolar Wagner number. Inset: fraction of the leakage current as a function of the bipolar Wagner number.  $Ae = 67.35\%$ . Full line:  $e/L = 1.225$ ,  $e/H = 4.9$ . Dashed line:  $e/L = 1.4412$ ,  $e/H = 3.0625$ . Dotted line:  $e/L = 1.6333$ ,  $e/H = 2.45$ . Dashed-dotted line:  $e/L = e/H = 1.96$



**Fig. 11** Current distributions for an electrochemical reactor of the type sketched in Fig. 1b.  $e/L = e/H = 1.96$ ,  $Ae = 67.35\%$ . **a** Terminal electrodes. **b** Bipolar electrode

Considering Figs. 6–12 it can be stated that, in bipolar electrochemical reactors with an open electrolyte arrangement, the secondary current distribution is frequently more pronounced than the primary one. This unexpected behavior can be explained by considering that, in an open bipolar stack, there are two paths for the flow of current: (1) the ordinary path, where the current flows through the bipolar electrodes; and (2) the bypass path, where the bipolar electrodes are excluded and thus the overpotentials at these electrodes are disregarded. When the overpotentials at the bipolar electrodes are high, more current is drained through the bypass in order to diminish the cell voltage. For the primary case the overpotentials are non-existent and the leakage current is lower, thus the primary current distribution is more uniform than the secondary one. However, for the secondary case the contribution of the leakage current to the current distribution is lower when the total current increases because, according to Fig. 8, the fraction of the leakage current decreases. Thus, the secondary current distribution becomes more uniform when the total current increases and approaches the primary one. Likewise, according to Figs. 11 and 12, for special geometrical factors of an open bipolar electrochemical system and low current density, the secondary current distribution can be more attenuated than the primary one. Under such conditions the electrochemical system behaves as a monopolar reactor because the leakage current is extremely high, as shown in the inset of Fig. 12, and thus the current drained by the bipolar electrode becomes very small.

#### 4 Conclusion

In bipolar electrochemical reactors with recessed electrodes the secondary distribution depends on two contributions: that due to the electrolyte not confined to the interelectrode gap, and the leakage current. The secondary current distribution may be more pronounced than the primary case when the leakage current is present.

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#### References

1. Newman J, Thomas-Alyea KE (2004) *Electrochemical systems*, 3rd edn, Chap 18. Wiley, Hoboken, p 424
2. Hine F, Yoshizawa S, Okada S (1956) *J Electrochem Soc* 103:186
3. Ettl VA, Tilak BV (1981) In: Bockris JO'M, Conway BE, Yeager E, White RE (eds) *Comprehensive treatise of electrochemistry*, vol 2, Chap 6. Plenum Press, New York, pp 340–345
4. Bouzek K, Børve K, Lorentsen OA, Osmundsen K, Rousar I, Thonstad J (1995) *J Electrochem Soc* 142:64
5. West AC, Newman J (1991) *J Electrochem Soc* 138:1620
6. Dinam TE, Matlosz M, Landolt D (1991) *J Electrochem Soc* 138:2947
7. Diem CB, Newman B, Orazem ME (1988) *J Electrochem Soc* 135:2524
8. Henquín ER, Bisang JM (2005) *J Appl Electrochem* 35:1183
9. Henquín ER, Bisang JM (2007) *J Appl Electrochem* 37:877
10. Henquín ER, Bisang JM (2008) *J Appl Electrochem* 38:1259