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Calculation of local current densities and terminal voltage for a monopolar sandwich electrolyser: application to chlorate cells

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Chemical engineering calculations are performed for a new type of monopolar electrolyser with power leads located on its sides, used for chlorate production. The calculation gives the value of the total cell voltage as well as of local current densities for given current load and given electrode dimensions, inter-electrode gap etc. On this basis the optimization of the system is possible.

List of symbols

		Values used for calculation
a_A	constant a for the calculation of anode potential, see Equation 2a (V)	1·412 8
a_K	constant a for the calculation of cathode potential, see Equation 2b (V)	1·238 1
b_A	constant b for the calculation of anode potential, see Equation 2a (V)	0·030 438
b_K	constant b for the calculation of cathode potential, see Equation 2b (V)	0·059 704
a'_A, a'_K	constants in linearized Equations 3a and 3b (V)	1·345 99 1·107 05
b'_A, b'_K	constants in linearized Equations 3a and 3b (Ω cm^2)	0·100 55 0·197 22
d	electrode distance (cm)	0·4
D_G	average diameter of bubbles at pressure P_0 (cm)	0·05
F	Faraday's constant; 964 96 C	
F_G, F_E	effective cross-section of inter-electrode channel for the flow of gas and the electrolyte, respectively (cm^2)	
F_p	cross-section occupied by current leads placed in inter-electrode channel for one cell (cm^2)	
F_T	total cross-section of inter-electrode channel for one cell (cm^2)	22·43
F_R	cross-section for one copper rod outside the cell (cm^2)	
g	acceleration due to gravity; 981 cm s^{-2}	
I_o	total current (A)	40 000
I_T	current flowing through one cell $= I_o/n_c$ (A)	2000
I_x	current flowing through an electrode strip at a height x and a distance y from the origin (A)	

		Values used for calculation
$I_{T,x}$	current flowing through an electrode strip at a height x and $y = 0$ (A)	
$I_{p,x}$	current consumed by electrochemical reaction at a height x between $y = 0$ and $y = y$ (A)	
$i_{x,y}$	local current density (A cm^{-2})	
$\bar{i}_x$	average current density at a height x (A cm^{-2})	
$\bar{i}$	average current density $= I_T/wL$ (A cm^{-2})	0·302 73
K_1	criterion cf. Equation 32	
$K_{1,x}$	criterion cf. Equation 25	
K_2	criterion cf. Equation 26	
K_3	criterion cf. Equation 22	
$K_{3,x}$	criterion cf. Equation 21	
K_4	criterion cf. Equation 33	
$K_{4,A}$	criterion cf. Equation 27	
$K_{4,K}$	criterion cf. Equation 28	
$K_{4,L}$	criterion cf. Equation 29	
K_5	criterion cf. Equation 38	
L	height of electrode (cm)	143
L_A, L_K	length of copper rods outside the electrolyser (cm)	
n_A	number of equivalents per mole for anodic process yielding a gaseous phase	2
n_C	number of cells in electrolyser	20
n_K	number of equivalents per mole for cathodic process yielding a gaseous phase	2
n_r	number of copper rods outside the electrolyser	
P	local pressure (atm)	
P_o	pressure on top of electrolyser (atm)	1
P_w	pressure of water vapour in equilibrium with electrolyte (atm)	0·148
R	gas constant (cm^3 atm [mol° K]$^{-1}$)	
$(Re)_G$	Reynolds number for bubbles	
S_A	anode thickness (cm)	0·2; 0·3; 0·4
S_K	cathode thickness (cm)	0·7
s_E	specific gravity of electrolyte (g cm^{-3})	
s_G	specific gravity of gas (g cm^{-3})	
s_M	specific gravity of gas-electrolyte mixture (g cm^{-3})	
T	absolute temperature (° K)	333
U_A, U_K	ohmic voltage drops in anode and cathode, respectively (V)	
U_{LA}, U_{LK}	ohmic voltage drop in anode and cathode leads, respectively (V)	
U_M	ohmic voltage drop in the electrolyte in the z direction (V)	
U_T	cell voltage (V)	
U_{AB}, U_{CD}	ohmic voltage drop between copper rods and electrodes, see Fig. 5 (V)	
v_E	rate of electrolyte flow in inter-electrode channel (cm s^{-1})	
v_{ET}	rate of electrolyte flow in inter-electrode channel at the top (cm s^{-1})	
v_G	rate of gas flow in inter-electrode channel (cm s^{-1})	
v_{GT}	rate of gas flow in inter-electrode channel at the top (cm s^{-1})	
v_R	velocity of bubbles corresponding to buoyance (cm s^{-1})	
V_E	volume flow rate of electrolyte in inter-electrode channel (for one cell) (cm^3 s^{-1})	

		Values used for calculation
V_G	volume rate of gas flow in inter-electrode channel (for one cell) ($cm^3 s^{-1}$)	200, 400, 500 600, 700
V_{GT}	volume rate of gas flow in inter-electrode channel at the top ($cm^3 s^{-1}$)	
w	width of the active surface of an electrode (cm)	46·2
w_A	width of the inactive part of an anode (cm)	10·0
w_K	width of the inactive part of cathode (cm)	10·0
w_{AE}	width of the inactive part of an anode embedded in electrolyte (cm)	5·0
w_{KE}	width of the inactive part of a cathode embedded in electrolyte (cm)	5·00
x, y, z	length in the direction of co-ordinates	
α, α_T	volume fraction of bubbles at a height x and at the top	
ϵ_A, ϵ_K	anodic and cathodic potentials	
η_A	anodic current efficiency for gas evolution	0
η_K	cathodic current efficiency for gas evolution	1
ν	kinematic viscosity of electrolyte ($cm^2 s^{-1}$)	0·009 508 8
ρ_A	specific resistance of an anode (Ω cm)	$5{\cdot}76 \times 10^{-5}$
ρ_K	specific resistance of a cathode (Ω cm)	$1{\cdot}21 \times 10^{-5}$
ρ_E	specific resistance of electrolyte (Ω cm)	3·04
ρ_M	specific resistance of a gas-electrolyte mixture between electrodes (Ω cm)	
ξ_A	ratio of active anode surface to the product wL	1·0
ξ_K	ratio of active cathode surface to the product wL	1·0

Note. The values of a_A, b_A, a_K, b_K and of kinematic viscosity (ν) were measured at 60°C in an electrolyte containing 100 g NaCl, 480 g $NaClO_3$ and 10 g Na_2CrO_4 dm^{-3}. The cathodes were made from mild steel, the anodes from titanium sheet activated with RuO_2/TiO_2. Specific resistivities ρ_A and ρ_K were found in [9].

1. Introduction

The present paper is a continuation of a series devoted to electrolysers for chlorate production [1–4]. An electrolyser of this type has been used by Jakšić [5].

For constant temperature and constant composition of the electrolyte, the calculation of local current densities in an electrochemical reactor is based on a simultaneous solution of three Laplace equations: for the anode and cathode bodies and for the inter-electrode gap. The boundary conditions depend on the nature of the electrode processes. In the case when the electrode processes are independent of the transport of electroactive species to the electrode surface, we can assume that they are only activation controlled. Then the solution leads to the so-called secondary current distribution. Also, for electrode reactions with complex mechanisms, where the activation-controlled electrode reaction is only a part of the whole reaction path (e.g. hydrogen evolution, chlorine evolution), the secondary current distribution is obtained.

Simultaneous solution of three Laplace equations is a rather difficult task (even using very fast computers), and this is why we have made a number of additional assumptions:

(a) The Laplace equation for the electrode body can be replaced by Ohm's law.

(b) Instead of solving the Laplace equation for the inter-electrode gap, we assume that the current lines are perpendicular to the electrode surface.

(c) The boundary condition, e.g. the relationship between electrode potential and local current density, can be expressed in a linear form.

Using (a) it is necessary to solve two ordinary differential equations simultaneously with one

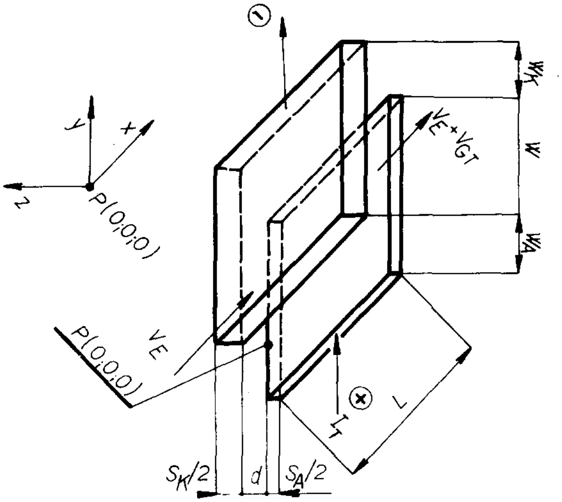

Fig. 1. One cell of the sandwich type electrolyser. The abbreviations are explained in the list of symbols and P(0,0,0) = origin of co-ordinates x,y,z.

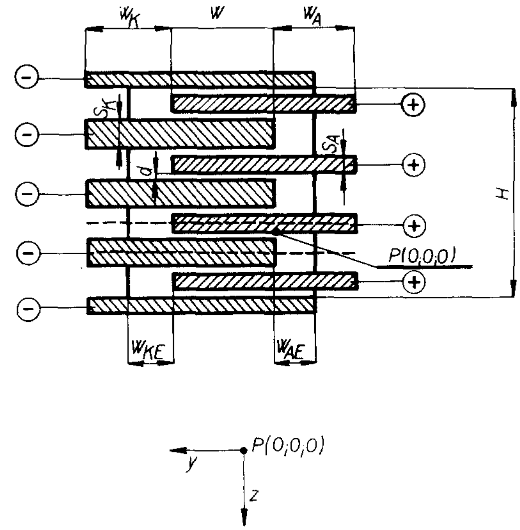

Fig. 2. The sandwich type electrolyser (top view). The abbreviations are explained in the list of symbols and d = the distance between boundaries for one cell.

eliptic partial differential equation. Using (a) and (b) we would obtain one ordinary differential equation of the second order, which must usually be solved by trial and error. Using (a–c) allows one to solve the problem analytically.

The relationship between electrode potential, or overvoltage, and current density (c.d.) is usually expressed by a Tafel equation. The assumption (c) involves a reduction of the differences between the highest and the lowest local current densities existing in the system. It means that the calculated local current densities are spread more uniformly around the average c.d. in comparison with those calculated using only the first two assumptions.

In the range 0·05–1·2 A cm^{-2}, Tafel equations give an adequate description of the chlorate process for both electrodes. For the purpose of calculating the local c.d. values the side reactions, e.g., Foerster's reaction at the anode and ClO$^-$ reduction at the cathode, are included in the values of η_A and η_K representing the anodic and the cathodic current efficiency for gas evolution, respectively. Chlorine dissolution in the electrolyte is a very fast reaction and therefore the value η_A should represent only the oxygen originating by Foerster's reaction; for industrial conditions η_A = 0·02–0·04. The hydrogen gas evolution is lowered by ClO$^-$ reduction to the value η_K = 0·94–0·96. No other effects of the side reactions are significant enough to warrant their consideration in our calculations.

2. The model system

In a monopolar, sandwich-type electrolyser the electrolyte is introduced at the bottom; a mixture of bubbles and electrolyte leaves the cell at the top and enters the bubble separation section located above the cell. The current leads are located at the sides of the electrodes (Figs. 1 and 2). The whole assembly can be divided into η_c identical cells (neglecting the fact that in the first and last cell one electrode is located on the wall of the electrolyser). In this case the total voltage for one cell (U_T) equals the total voltage for the whole electrolyser. In this paper the calculation procedures are shown which yield the desired value of U_T as well as the c.d. distribution over the surface of the electrodes.

3. Mathematical description for one cell

Suppose that the cell is isothermal and that processes on both electrodes are controlled by the rate of the electrode reaction. When the electrodes are large, the distance between them is small, and b_A and b_K in the Tafel equations are large. It can be assumed that the lines of force in the electrolyte are perpendicular to the electrode surface. Then the local current densities at a height and a distance y from the origin are the same for both the electrodes. The voltage distribution in the cell is given by:

$$U_\mathrm{T} = \epsilon_\mathrm{A} - \epsilon_\mathrm{K} + U_\mathrm{A} + U_\mathrm{K} + U_\mathrm{M} + U_\mathrm{LA} + U_\mathrm{LK}. \tag{1}$$

The anode and the cathode relationship between current density and potential are described by the Equations:

$$\epsilon_\mathrm{A} = a_\mathrm{A} + b_\mathrm{A} \ln i_{x,y} \tag{2a}$$

$$-\epsilon_\mathrm{K} = a_\mathrm{K} + b_\mathrm{K} \ln i_{x,y} \tag{2b}$$

Equations 2a and b must be linearized to permit an analytic solution of Equation 1. For small deviations of $i_{x,y}$ from the mean current density $\bar{i}$ we have:

$$\epsilon_\mathrm{A} = a'_\mathrm{A} + b'_\mathrm{A}\, i_{x,y} \tag{3a}$$

$$-\epsilon_\mathrm{A} = a'_\mathrm{K} + b'_\mathrm{K}\, i_{x,y} \tag{3b}$$

where

$$a'_\mathrm{A} = a_\mathrm{A} - b_\mathrm{A} + b_\mathrm{A} \ln \bar{i};$$

$$a'_\mathrm{K} = a_\mathrm{K} - b_\mathrm{K} + b_\mathrm{K} \ln \bar{i};$$

$$b'_\mathrm{A} = b_\mathrm{A}/\bar{i}; \quad b'_\mathrm{K} = b_\mathrm{K}/\bar{i}.$$

Usually the anode and cathode plates are perforated by holes of small diameter. Introducing the ratio ξ_A or ξ_K which equals active anode (or cathode) surface to the product wL, then

$$a'_\mathrm{A} = a_\mathrm{A} - b_\mathrm{A} + b_\mathrm{A} \ln (\bar{i}/\xi_\mathrm{A})$$

and

$$a'_\mathrm{K} = a_\mathrm{K} - b_\mathrm{K} + b_\mathrm{K} \ln (\bar{i}/\xi_\mathrm{K}).$$

The mean current density $\bar{i}$ is given by $\bar{i} = I_\mathrm{T}/wL$.

Assuming now that the current proceeds only in the y-direction, it is possible to calculate the current density distribution in the direction of the y-axis for a section (strip) of the electrode at the height x. The height of the electrode section (strip) is denoted Δx, the power load for this section is $I_{\mathrm{T},x}$, and the mean current density at the height x is given by

$$\bar{i}_x = \frac{I_{\mathrm{T},x}}{\Delta x w} \tag{4}$$

$I_{\mathrm{T},x}/\Delta x$ can also be denoted as a part of the total current I_T which enters the electrode at height x in the direction of the y-axis.

The dependence of U_A and U_K on y can be derived in the following manner. The current $I_{\mathrm{T},x}$ enters the end of the electrode strip. At a distance y from the origin P a certain part of the current ($I_{\mathrm{p},x}$) is consumed in the electrochemical reaction and the remainder (I_x) continues to flow through the electrode. Thus

$$I_{\mathrm{p},x} = \Delta x \int_0^y i_{x,y}\, \mathrm{d}y$$

$$I_x = I_{\mathrm{T},x} - I_{\mathrm{p},x} = I_{\mathrm{T},x} - \Delta x \int_0^y i_{x,y}\, \mathrm{d}y. \tag{5}$$

The voltage drop in the electrode is given by Ohm's law in the differential form,

$$\mathrm{d}U_\mathrm{A} = I_x 2 \rho_\mathrm{A}\, \mathrm{d}y/S_\mathrm{A}\, \Delta x \xi_\mathrm{A} \tag{6}$$

where $S_\mathrm{A} \Delta x \xi_\mathrm{A}/2$ represents the mean cross-section of anode material, due to the perforation of the plates. Combining Equations 4 and 5 with 6 and integrating we obtain the voltage drop in the anode (starting at $y = 0$).

$$U_\mathrm{A} = (\rho_\mathrm{A} 2/\Delta x S_\mathrm{A} \xi_\mathrm{A})(I_{\mathrm{T},x} y - \Delta x \times \int_0^y \int_0^y i_{x,y}\, \mathrm{d}y\, \mathrm{d}y) \tag{7a}$$

$$U_\mathrm{A} = (2\rho_\mathrm{A} w^2/S_\mathrm{A} \xi_\mathrm{A}) \bar{i}_x \times \left[(y/w) - \int_0^{y/w} \int_0^{y/w} (i_{x,y}/\bar{i}_x)\, (\mathrm{d}y/w)\, (\mathrm{d}y/w) \right]. \tag{7b}$$

An analogous expression holds for the voltage drop in the cathode

$$U_\mathrm{K} = (2\rho_\mathrm{K} w^2/S_\mathrm{K} \xi_\mathrm{K}) \bar{i}_x \times \int_{v/w}^1 \int_0^{y/w} (i_{x,y}/\bar{i}_x)\, (\mathrm{d}y/w)\, (\mathrm{d}y/w) \tag{8a}$$

This can be rearranged to read

$$U_\mathrm{K} = (2\rho_\mathrm{K} w^2/S_\mathrm{K} \xi_\mathrm{K}) \bar{i}_x \times \left[\int_0^1 \int_0^{y/w} (i_{x,y}/\bar{i}_x)\, (\mathrm{d}y/w)\, (\mathrm{d}y/w) - \int_0^{y/w} \int_0^{y/w} (i_{x,y}/\bar{i}_x)\, (\mathrm{d}y/w)\, (\mathrm{d}y/w) \right]. \tag{8b}$$

The value of U_L ($= U_\mathrm{LA} + U_\mathrm{LK}$) is also calculated, yielding

$$U_\mathrm{L} = [(\rho_\mathrm{A} w_\mathrm{A}/S_\mathrm{A}) + (\rho_\mathrm{K} w_\mathrm{K}/S_\mathrm{K})]\, 2w\, \bar{i}_x \tag{9a}$$

$$U_\mathrm{LA} = 2\rho_\mathrm{A} w_\mathrm{A} w\, \bar{i}_x/S_\mathrm{A} \tag{9b}$$

$$U_{LK} = 2\rho_K w_K w \bar{i}_x / S_K. \tag{9c}$$

As can be seen from Equations 9b and c the inactive part of the anode and cathode plates are not perforated.

The voltage drop in the elctrolyte is given by the Equation

$$U_M = i_{x,y} \rho_M d \tag{10}$$

in which ρ_M is the specific resistance of the electrolyte containing bubbles. The latter parameter can be calculated using the Maxwell [6] (or Bruggeman [7], Meredith [8]) equation.

For a flowing system the modified Maxwell equation assumes the form

$$\rho_M = \rho_E(1 + 1{\cdot}5\, F_G/F_E). \tag{11}$$

We assume, that the ratio F_G/F_E depends only on x and not only on y, i.e. that it may be substituted for the average value of F_G/F_E pertaining to a given height x.

This value can be expressed as a function of the volume rates of flow of the liquid, V_E, and of the gas, V_G, and of the respective linear velocities, v_E and v_G, related to the cross-sections F_E and F_G. Thus

$$F_G = V_G/v_G \tag{11a}$$

$$F_E = V_E/v_E \tag{11b}$$

$$F_T = F_G + F_E \tag{12}$$

Here F_T is the channel cross-section for one cell:

$$F_T = d(w_{AE} + w_{KE} + w) + 0{\cdot}5(S_K w_{AE} + S_A w_{KE}) - F_p \tag{13}$$

where F_p denotes the part of the flow cross section occupied by power leads (see Fig. 5).

The volume rate of gas flow, V_G, at a given height in the cell can be calculated using Faraday's law and the equation of state of an ideal gas, yielding

$$V_G = V_{GT} F_1 \int_0^{x/L} (\bar{i}_x/\bar{i})\, dx/L \tag{14}$$

where

$$V_{GT} = [RT/(P_0 - P_w)](I_T/F) \times [(\eta_A/n_A) + (\eta_K/n_K)] \tag{15}$$

and

$$F_1 = (P_0 - P_w)/(P - P_w). \tag{16}$$

Here F_1 is a correction factor representing the dependence of the pressure on the x-co-ordinate.

The quantity P in Equation 16 denotes the actual pressure in the bubbles. In calculating this quantity it is necessary to consider the hydrostatic pressure at the given depth in the electrolyser; the increase of pressure due to friction of liquid and to surface tension can be neglected. Hence,

$$P = P_0 + 0{\cdot}9869 \times 10^{-6} g \int_x^L s_M\, dx$$

$$= P_0 + (0{\cdot}9869 \times 10^{-6} g L s_E)(1 - x/L) \times (1 - 0{\cdot}5\alpha_T - 0{\cdot}5\alpha)$$

$$\alpha_{max} = \alpha_T.$$

If the height of the electrolyser is small it is possible to use P_0 instead of P and then $F_1 = 1$.

The volume rate of flow of the electrolyte in a cell is obtained by dividing the total volume flow rate by the number of cells. The average linear flow velocity of the gas, v_G, is equal to the vectorial sum of the velocity, v_R (due to the buoyancy force and corrected for the volume contents of the bubbles), at which the bubbles move against a stationary liquid, and of the linear flow velocity of the liquid, v_E. As both v_R and v_E are of the same directions in the given system, it follows that

$$v_G = v_E + v_R\,(1 - \alpha)^{3{\cdot}5} \tag{17}$$

where

$$\alpha = F_G/F_T \tag{18a}$$

$$1 - \alpha = F_E/F_T. \tag{18b}$$

Assuming that the average bubble diameter D_G is known and that $s_E \gg s_G$, the magnitude of v_R can be calculated as

$$v_R = g D_G^2/18\nu$$

for

$$(Re)_G = (D_G v_R/\nu) \leqslant 1{\cdot}9$$

or as

$$v_R = (4/3)^{5/7}(g D_G/18{\cdot}5)^{5/7}(D_G/\nu)^{3/7}$$

for

$$(Re)_G \in \langle 1{\cdot}9; 505 \rangle.$$

By combining Equations 11a,b; 18a,b and 17 we obtain

$$F_G = F_T \alpha = V_G/v_G$$

$$F_E = V_E/v_E = F_T(1 - \alpha)$$

$$\alpha = V_G/[V_G + V_E + F_T v_R\,(1 - \alpha)^{4{\cdot}5}]. \tag{19}$$

When Equation 19 is employed in conjunction with Equations 18 and 11a, then values of v_E are obtained which depend on V_G and thus on $\bar{i}_x$.

Nevertheless, if $V_G \ll V_E$ the value of v_E, which is calculated for the top of the cell where $V_G = V_{GT}$, may be employed in all calculations ($V_E = V_{ET}$).

Using the aforementioned assumptions we obtain

$$\rho_M = \rho_E(1 + 1{\cdot}5\, K_{3,x}) \tag{20}$$

where

$$K_{3,x} = K_3 \int_0^{x/L} (\bar{i}_x/\bar{i})\, \mathrm{d}x/L \qquad (21)$$

and

$$K_3 = (v_{\mathrm{ET}}/v_{\mathrm{GT}})(V_{\mathrm{E}})^{-1}[RT/(P_0 - P_{\mathrm{w}})] \times (I_{\mathrm{F}}/F)[(\eta_{\mathrm{A}}/n_{\mathrm{A}}) + (\eta_{\mathrm{K}}/n_{\mathrm{K}})] \qquad (22\mathrm{a})$$

using α_{T} we obtain

$$K_3 = \alpha_{\mathrm{T}}/(1 - \alpha_{\mathrm{T}}). \qquad (22\mathrm{b})$$

Upon substituting the expressions 3a, b, 7b, 8b, 9, 10 and 20 into 1, an equation is obtained which describes the potential distribution in the electrode–electrolyte system in the following integral form:

$$U_{\mathrm{T}} = a'_{\mathrm{A}} + a'_{\mathrm{K}} + (b'_{\mathrm{A}} + b'_{\mathrm{K}})i_{x,y} + (2\rho_{\mathrm{A}} w^2/S_{\mathrm{A}} \times \xi_{\mathrm{A}})\bar{i}_x[(y/w) - \int_0^{y/w}\int_0^{y/w} (i_{x,y}/\bar{i}_x)(\mathrm{d}y/w)\cdot(\mathrm{d}y/w)]$$
$$+ (2\rho_{\mathrm{K}} w^2/S_{\mathrm{K}}\xi_{\mathrm{K}})\bar{i}_x [\int_0^1\int_0^{y/w} (i_{x,y}/\bar{i}_x)(\mathrm{d}y/w) \times (\mathrm{d}y/w) - \int_0^{y/w}\int_0^{y/w} (i_{x,y}/\bar{i}_x)(\mathrm{d}y/w)(\mathrm{d}y/w)]$$
$$+ [(\rho_{\mathrm{A}} w_{\mathrm{A}}/S_{\mathrm{A}}) + (\rho_{\mathrm{K}} w_{\mathrm{K}}/S_{\mathrm{K}})] 2w\bar{i}_{\mathrm{x}} + i_{x,y}\rho_{\mathrm{E}}\mathrm{d} \times [1 + 1{\cdot}5\, K_3 \int_0^{x/L} (\bar{i}_x/\bar{i})(\mathrm{d}x/L)]. \qquad (23)$$

In order to obtain an analytical solution of Equation 23 it is necessary to introduce the assumption (in calculating the voltage drop in the electrodes) that the current distribution over the surface is practically uniform, i.e. that $i_{x,y}/\bar{i}_x \approx 1$; then

$$\int_0^{y/w}\int_0^{y/w} (i_{x,y}/\bar{i}_{\mathrm{x}})(\mathrm{d}y/w)(\mathrm{d}y/w) \approx 1/2\,(y/w)^2$$

and

$$\int_0^1\int_0^{y/w} (i_{x,y}/\bar{i}_{\mathrm{x}})(\mathrm{d}y/w)(\mathrm{d}y/w) \approx 1/2.$$

Using the above equations and rearranging Equation 23 we obtain

$$K_{1,x} = (i_{x,y}/\bar{i}_{\mathrm{x}})(K_2 + 1 + 1{\cdot}5\, \mathrm{K}_{3,x}) + K_{4,\mathrm{A}} \times [(y/w) - 1/2(y/w)^2] + K_{4,\mathrm{K}} \times [(1/2) - (1/2)(y/w)^2] + K_{4,\mathrm{L}} \qquad (24)$$

where

$$K_{1,x} = [U_{\mathrm{T}} - (a'_{\mathrm{A}} + a'_{\mathrm{K}})]/\bar{i}_{\mathrm{x}} d\rho_{\mathrm{E}} \qquad (25)$$

$$K_2 = (b'_{\mathrm{A}} + b'_{\mathrm{K}})/d\rho_{\mathrm{E}} \qquad (26)$$

$$K_{4,\mathrm{A}} = 2\rho_{\mathrm{A}} w^2/S_{\mathrm{A}} d\rho_{\mathrm{E}}\xi_{\mathrm{A}} \qquad (27)$$

$$K_{4,\mathrm{K}} = 2\rho_{\mathrm{K}} w^2/S_{\mathrm{K}} d\rho_{\mathrm{E}}\xi_{\mathrm{K}} \qquad (28)$$

$$K_{4,\mathrm{L}} = [(\rho_{\mathrm{A}} w_{\mathrm{A}}/S_{\mathrm{A}}) + (\rho_{\mathrm{K}} w_{\mathrm{K}}/S_{\mathrm{K}})](2w/\rho_{\mathrm{E}} d). \qquad (29)$$

The current density distribution at the given height x is described by Equation 24. In order to evaluate the unknown value $K_{1,x}$ it is necessary to use the equation

$$\int_0^1 (i_{x,y}/\bar{i}_{\mathrm{x}})\, \mathrm{d}y/w = 1. \qquad (30)$$

Upon combining Equations 24 and 30 and integrating we obtain

$$K_{1,x} = 1 + 1{\cdot}5\, K_{3,x} + K_2 + [(K_{4,\mathrm{A}} + K_{4,\mathrm{K}})/3] + K_{4,\mathrm{L}}. \qquad (31)$$

Now the criteria K_1 and K_4 can be introduced:

$$K_1 = [U_{\mathrm{T}} - (a'_{\mathrm{A}} + a'_{\mathrm{K}})]/\bar{i}\, d\rho_{\mathrm{E}} \qquad (32)$$

$$K_4 = [(K_{4,\mathrm{A}} + K_{4,\mathrm{K}})/3] + K_{4,\mathrm{L}} \qquad (33)$$

and Equation 31 can be rearranged to

$$K_1 = (\bar{i}_x/\bar{i})[1 + K_2 + K_4 + 1{\cdot}5\, K_3 \times \int_0^{x/L} (\bar{i}_x/\bar{i})\, \mathrm{d}x/L]. \qquad (34)$$

Equation 34 describes the distribution of $\bar{i}_{\mathrm{x}}$ over the height of the electrode in an integral from. Furthermore we know that

$$\int_0^1 (\bar{i}_x/\bar{i})\, \mathrm{d}x/L = 1. \qquad (35)$$

The solution of Equation 34, together with 35, results in the following expressions:

$$\bar{i}_x/\bar{i} = (K_5 - 0{\cdot}5)/[(K_5 - 1)^2 + (2K_5 - 1)x/L]^{1/2} \qquad (36)$$

and

$$K_1 = 1 + K_2 + 0{\cdot}75\, K_3 + K_4 \qquad (37)$$

where

$$K_5 = (1 + K_2 + K_4 + 1{\cdot}5\, K_3)/1{\cdot}5\, K_3. \qquad (38)$$

Using Equation 36 we obtain for $K_{3,x}$

$$K_{3,x} = K_3\{1 - K_5 + [(K_5 - 1)^2 + (2K_5 - 1)\,x/L]^{1/2}\}.$$

Equation 36 describes the distribution of $\bar{i}_{\mathrm{x}}$ over the height of the electrode and Equation 37 permits us to calculate U_{T} (using criteria K_2, K_3 and K_4):

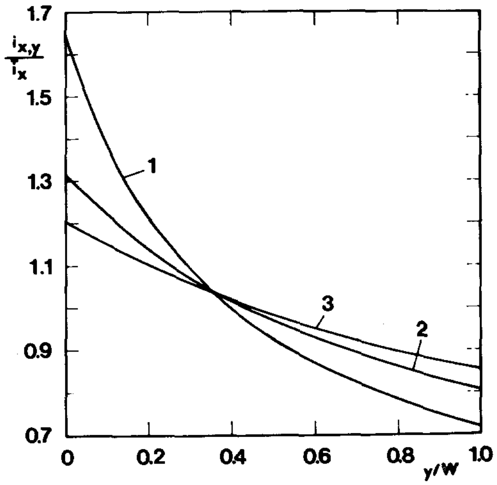

Fig. 3. The dependence of relative local current density on y/w. $K_1 = 3{\cdot}066\ 72$; $K_2 = 0{\cdot}247\ 82$; $K_3 = 1{\cdot}630\ 14$; $K_4 = 0{\cdot}596\ 30$; $K_{4A} = 1{\cdot}023\ 20$; $K_{4K} = 0{\cdot}061\ 41$ and $K_{4L} = 0{\cdot}234\ 76$. Curve 1: $x/L = 0$; $K_{3x} = 0$; $K_{1x} = 1{\cdot}8441$; curve 2: 0·5; 0·9715; 3·3014; and curve 3: 1·0; 1·6301; 4·2893 respectively.

$$U_{\mathrm{T}} = a'_{\mathrm{A}} + a'_{\mathrm{K}} + \bar{i}\rho_{\mathrm{E}} d\,(1 + K_2 + 0{\cdot}75\,K_3 + K_4) \tag{39a}$$

or, going back to the inlet variables

$$\begin{aligned} U_{\mathrm{T}} &= (a'_{\mathrm{A}} + a'_{\mathrm{K}}) + \bar{i}\rho_{\mathrm{E}} d\,(1 + 0{\cdot}75\,K_3) \\ &+ \bar{i}\,\{(2/3)[(\rho_{\mathrm{A}} w^2/S_{\mathrm{A}}\xi_{\mathrm{A}}) + (\rho_{\mathrm{K}} w^2/S_{\mathrm{K}}\xi_{\mathrm{K}})] \\ &+ 2w\,[(\rho_{\mathrm{A}} w_{\mathrm{A}}/S_{\mathrm{A}}) + (\rho_{\mathrm{K}} w_{\mathrm{K}}/S_{\mathrm{K}})]\}. \end{aligned} \tag{39b}$$

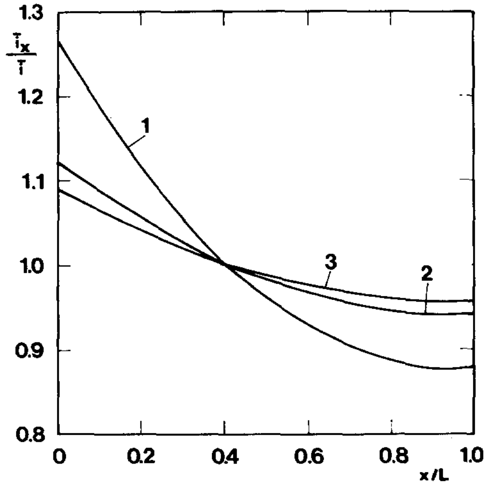

Fig. 4. The dependence of relative mean current density in given height on x/L. $K_2 = 0{\cdot}247\ 82$ and $K_4 = 0{\cdot}596\ 30$ curve 1: $K_3 = 1{\cdot}630\ 1$; $K_1 = 3{\cdot}066\ 72$; curve 2: 0·785 46; 2·433 21; and curve 3: 0·511 94; 2·228 07 respectively.

4. Discussion of Equations 24 and 36

The relative local c.d. ($i_{x,y}/\bar{i}_x$) distribution over the relative width (y/w) of the electrode at a given height (x) is given by Equation 24. This relationship is considerably influenced by the values of $K_{4,\mathrm{A}}$ and $K_{4,\mathrm{A}}$. If these values are equal to each other, then a minimum of local current densities exists near the centre ($y = 0{\cdot}5w$) of the electrode

Table 1. Dependence of local values of potentials and voltage losses in anode, cathode and electrolyte on the x and y values (position of the electrode)

X/L	Y/W	i_x (A cm^{-2})	$i_{x,y}$ (A cm^{-2})	ϵ_{A} (V)	$-\epsilon_{\mathrm{K}}$ (V)	U_{A} (V)	U_{K} (V)	U_{LA} (V)	U_{LK} (V)	U_{M} (V)
0·000	0·000	0·503	0·637	1·410	1·233	0·000	0·019	0·134	0·008	0·765
0·000	0·500	0·503	0·485	1·395	1·203	0·232	0·014	0·134	0·008	0·538
0·000	1·000	0·503	0·443	1·390	1·194	0·310	0·000	0·134	0·008	0·532
0·200	0·000	0·367	0·430	1·389	1·192	0·000	0·014	0·098	0·006	0·871
0·200	0·500	0·367	0·358	1·382	1·178	0·169	0·010	0·098	0·006	0·726
0·200	1·000	0·367	0·339	1·380	1·174	0·226	0·000	0·098	0·006	0·686
0·400	0·000	0·303	0·343	1·380	1·175	0·000	0·011	0·081	0·005	0·917
0·400	0·500	0·303	0·297	1·376	1·166	0·140	0·008	0·081	0·005	0·794
0·400	1·000	0·303	0·284	1·375	1·163	0·186	0·000	0·081	0·005	0·759
0·600	0·000	0·264	0·294	1·376	1·165	0·000	0·010	0·070	0·004	0·944
0·600	0·500	0·264	0·260	1·372	1·158	0·122	0·007	0·070	0·004	0·835
0·600	1·000	0·264	0·250	1·371	1·156	0·162	0·000	0·070	0·004	0·805
0·800	0·000	0·237	0·260	1·372	1·158	0·000	0·009	0·063	0·004	0·923
0·800	0·500	0·237	0·233	1·370	1·153	0·109	0·007	0·063	0·004	0·864
0·800	1·000	0·237	0·226	1·369	1·152	0·145	0·000	0·063	0·004	0·836
1·000	0·000	0·216	0·236	1·370	1·154	0·000	0·008	0·058	0·003	0·976
1·000	0·500	0·216	0·214	1·368	1·149	0·100	0·006	0·058	0·003	0·885
1·000	1·000	0·216	0·208	1·367	1·148	0·133	0·000	0·058	0·003	0·860

$U_{\mathrm{T}} = 3{\cdot}5685$ V; $S_{\mathrm{A}} = 0{\cdot}2$ cm; $V_{\mathrm{E}} = 200$ cm^3 s^{-1}; $K_3 = 1{\cdot}630\ 14$; $\bar{i} = 0{\cdot}302$ A cm^{-2}

Table 2. Dependence of the total voltage and voltage losses in the electrolyte on the anode thickness and electrolyte flow

S_A (cm)	V_E ($cm^3 s^{-1}$)	K_3	U_T (V)	$U_{M, max}$ (V)	$U_{M, min}$ (V)
0·2	200	1·630 14	3·568 5	0·976 2	0·531 8
0·2	400	0·785 46	3·338 1	0·724 9	0·421 9
0·2	500	0·620 10	3·293 0	0·673 2	0·400 4
0·2	600	0·511 94	3·263 5	0·638 6	0·386 4
0·2	700	0·436 11	3·242 8	0·613 9	0·376 5
0·3	200	1·629 74	3·500 2	0·931 3	0·583 7
0·3	400	0·784 91	3·269 8	0·683 7	0·455 2
0·3	500	0·619 56	3·224 6	0·633 1	0·430 1
0·3	600	0·511 44	3·195 1	0·599 4	0·413 6
0·3	700	0·435 66	3·174 5	0·575 4	0·402 1
0·4	200	1·629 35	3·466 0	0·908 5	0·612 8
0·4	400	0·784 36	3·235 5	0·662 8	0·473 4
0·4	500	0·619 03	3·190 4	0·612 8	0·446 1
0·4	600	0·510 94	3·160 9	0·579 5	0·428 2
0·4	700	0·435 20	3·140 2	0·555 9	0·415 7

width. If $K_{4,K} \leqslant K_{4,A}$, this minimum is shifted to the end of the anode ($y = w$). As can be seen from Equations 27 and 38, this condition is fulfilled for $\rho_K/S_K \leqslant \rho_A/S_A$; this condition can be interpreted as a small resistance of cathode material in comparison to the resistance of anode material. For this case the curves are shown in Fig. 3 for different values of $K_{3,x}$.

Equation 36 is used in calculating the distribution of c.d. over the height of the electrode. Here the c.d. is maximum at the bottom of the electrode as the electrolyte adjacent to the bottom is free of bubbles. On the contrary, the c.d. is minimum on the top of the electrode, owing to the maximum content of bubbles in the adjacent electrolyte, see Fig. 4 and Table 1. The dependence of the total voltage U_T on the electrolyte flow rate and the anode thickness is shown in the Table 2. The two columns on the right of Table 2 represent the maximum and minimum values of ohmic drops in the electrolyte–gas emulsion for the given system. These data indicate that the deviations of local current densities from the average value will be kept small as long as thick anodes and a high electrolyte flow rate are used. For such a system the total voltage is very low too. Nevertheless, the investment costs of electrodes increase with electrode thickness and the operation costs increase with increasing pumping rate. The best economy of the process may be calculated using any common optimization technique.

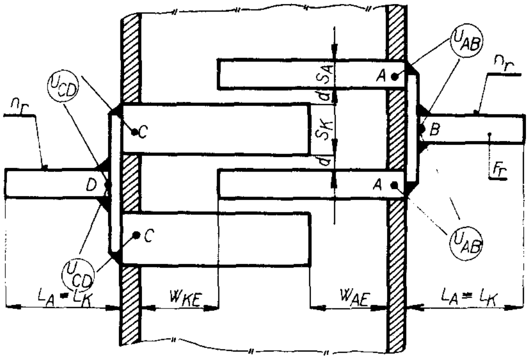

Fig. 5. The view of the assembly of four cells. The abbreviations are explained in the list of symbols.

Appendix

In practical cases the electrodes are mutually connected by means of copper rods (located outside the electrolyser). Thus the equivalent length w_A, w_K can be calculated as follows: first the resistance of the whole system (outside the electrolyser) and the current flowing through this resistance are calculated; subsequently the values of w_A and w_K are calculated using the Equations A.1 and A.2. Here the calculation of w_A and w_K is shown for an actual case depicted in Fig. 5. For two cells there is only one row of copper rods outside the cell. Thus

$$(\rho_A w_A/S_A)(2w\bar{i}) = (2\rho_A w_{AE}/S_A)\bar{i}w + U_{AB} + [(\rho_{Cu} L_A w L \bar{i} 2)/n_R F_R] \quad (A.1)$$

$$(\rho_K w_K/S_K) 2w\bar{i} = (2\rho_K w_{KE}/S_K)\bar{i}w + U_{CD} + [(\rho_{CU} L_K w L \bar{i} 2)/n_R F_R)] \quad (A.2)$$

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