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MODELING AND TECHNICAL USE OF GAS EVOLVING ELECTRODES. PART II. MODELING OF GAS-EVOLVING ELECTROLYZERS WITH FREE ELECTROLYTE CIRCULATION

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Translation of "Modellierung und Technische Nutzung Gasentwickelnder Elektroden. Teil II: Modellierung Gasentwickelnder Elektrolyseure mit Freier Kreislaufstromung des Elektrolyten", Chemische Technik (Leipzig), Vol. 34, No. 5, 1982, pp. 250-252

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16. Abstract

In an electrochemical reactor with gas-evolving electrodes, the transporting action of the gas bubbles can be used to move the electrolyte in a cycle flow, when the structure of the flow channels is suitable. For an electrolysis cell with such a circulation system a mathematic model was set up and evaluated. It is shown that in this manner, a rapid flow through the electrode gap can be achieved without additional energy consumption, in addition to a low gas fraction and a low cell voltage. The cell voltage and the attainable cycle spped are investigated as a function of the geometric parameters for their optimum values.

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LIST OF SYMBOLS

Symbol	Meaning	Unit
A_1, B_1, b_1	Dimensionless figures	--
c	Concentration	mol/m^3
c_0	Gas volume density (gas volume generated per charge unit)	$m^3/A \cdot s$
d	Gap width	m
F	Faraday constant	$A \cdot s/mol$
g	Acceleration of gravity	m/s^2
h	Cell height	m
i	Current density	A/m^2
l	Cell width	m
p	Pressure	Pa
p_0	Normal pressure	Pa
r_0	Slope of the current-voltage characteristic line	$V \cdot m^2/A$
r_1, r_2	Electrode resistances	V/A
U	Voltage	V
ΔU	Voltage drop	V
v_2	Speed of electrolyte	m/s
v_B	Speed of slip	m/s
v_0	Speed of inlet flow	m/s
V_0	Volume flow	m^3/s
z	Height coordinate	m
ε	Gas volume fraction	--
ζ	Coefficient of friction	--
η	Viscosity of electrolyte	$kg/m \cdot s$
$\varkappa$	Electrical conductance of electrolyte	$A/V \cdot m$
λ	Friction index	--
ϱ	Density of the electrolyte	kg/m^3
φ	Current yield	

MODELING AND TECHNICAL USE OF GAS EVOLVING ELECTRODES
Part II.

M. Schleiff, W. Thiele, H. Matschiner

Report from the Martin-Luther University, Halle-Wittenberg, Section of Mathematics (M. Schleiff) and Chemistry (H. Matschiner) and the Eilenburg Chemie-Werk of Buna Chemical Plant, R & D Division (W. Thiele).

The evolution of gas occurring in an electrochemical process /250*
leads to gas bubbles in the electrolyte which increase the electrical resistance and thus the power loss. Since the gas quantity in vertically arranged electrodes increases toward the top, an increase in the electrolyzer is also subject to tight limits. In a force-fed electrolysis cell the gas fraction can be kept low by means of a high inlet speed, but this requires additional energy. Now the transporting effect of the gas bubbles can be used to attain a fast electrolyte recirculation by running the electrolyte through a return duct back into the cycle (Mammut pump principle, natural recirculation principle.) In this manner, a fast rate of flow of the electrode gap can be obtained without additional energy consumption and thus a lower gas fraction, a low cell voltage and favorable material transport properties will result. Through different hydrodynamic linkage of the circulating systems in the individual electrolysis cells (parallel or sequential) and through the selection of the rate of feed to the entire electrolyzer, acceptable conditions can be had for the electrolysis process being performed.

Information on the modeling of such electrolyte circulating systems is found in Rousar [1], Hertwig et al. [2] and in an earlier report [3]. Technical applications are summarized by Vogt [4].

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*Numbers in the margin refer to pagination in the original text.

Model of the Cycle Flow

The flow in the electrode gap is described precisely as in the cell with forced circulation, thus the same model equations apply as in the first part [5] of this report.

For the gas phase and for the liquid phase, the balance equations become:

$$\frac{d}{dz}\left[p\,\varepsilon\,(v_2 + v_B)\right] = p_0\, c_0\, \frac{i}{d}\,,\quad \frac{d}{dz}\left[(1-\varepsilon)\, v_2\right] = 0 \tag{1}$$

For the pulse density we have the following expression (neglecting the pulse of the gas phase):

$$\frac{d}{dz}\,(p + \varrho\,(1-\varepsilon)\, v_2^2) + \lambda v_2\,\eta\, d^{-2} = -\,\varrho\,(1-\varepsilon)\, g \tag{2}$$

In the voltage balance equation:

$$\frac{d}{dz}\left[U'(i) + i\,\frac{d}{\varkappa}\, f(\varepsilon)\right] + r_2\,\bar{i} - \frac{d}{c_0\, p_0}\, p\,\varepsilon\,(v_2 + v_B)\cdot \cdot (r_1 + r_2) = 0 \tag{3}$$

we find the voltage drop linearized in the calculation by $U'(i) = U_0 + r_0 i$ outside the electrolyte and the amplification factor $f(\varepsilon)$ for the resistance as a result of the gas fraction. Since there is no gas at the lower end of the cell and since ambient pressure prevails at the upper end, the boundary conditions below will apply:

$$\varepsilon(0) = 0,\quad p(h) = p_0 \tag{4}$$

Through integration of the first equation of (1) from 0 to the cell height h, we obtain the condition:

$$\varepsilon(h)\,[v_2(h) + v_B] = \frac{c_0\,\bar{i}}{d} \tag{5}$$

which represents an overall balance of the gas phase at a given, average current density $\bar{i}$. In the still-missing fourth boundary condition, the special conditions of the cycle flow are taken into account in a pressure balance. The pressure difference between input and outlet of the cell is equal to the hydrostatic pressure in the recirculation channel, decreased by the frictional pressure loss of the recirculation:

$$p(0) - p_0 = \varrho\, g h - \zeta\,[v_2(0)]^2\,\varrho \tag{6}$$

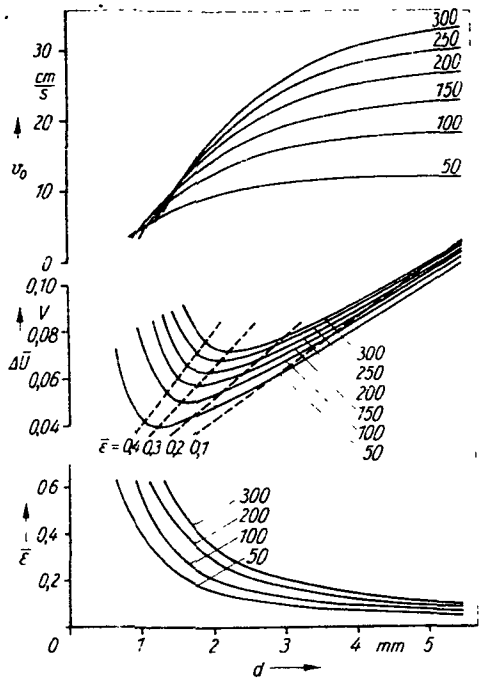

Fig. 1: Average Gas Fraction, Voltage Drop and Cycle Speed as a Function of the Gap Thickness for Various Cell Heights (in cm)

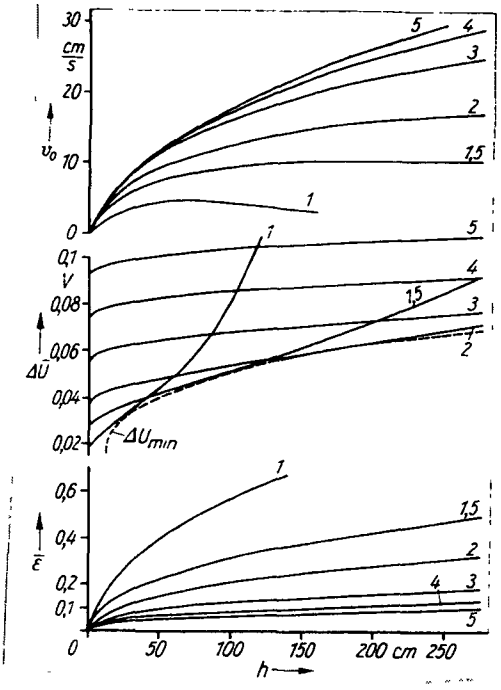

Fig. 2: Average Gas Fraction, Voltage Drop and Cycle Speed as a Function of the Cell Height for Various Gap Thicknesses (in cm)

If we insert the Maxwell relation $f(\varepsilon) = (1 + \varepsilon/2)/(1 - \varepsilon)$ for $f(\varepsilon)$ and neglect the friction loss in the recirculation channel ($b_2 = 0$), then (11) goes into the approximated model presented and discussed in [3]. The equations (10) and (11) thus generalize the results of [3] and permit a smooth post-calculation of the most important characteristic values of a cycle flow in a gas-evolving electrolyzer as a function of the two dimensionless parameters b_1 and b_2 defined in (9).

Discussion of the Results

In figures 1 and 2 the average voltage drop, the average gas fraction and the cycle speed v_0 were plotted as a function of the gap thickness d and the cell height h, as they resulted through numerical solution of the complete model equations. In this case the calculations were based on the values $v_B = 0.5$ cm/s, $c_0 = 0.127$ cm³/A·s,

always greater than the optimum gap thickness which minimizes the voltage drop. The volume flow defined by:

$$\dot{V}_0 = d\,l\,v_0 \tag{15}$$

of the circulating electrolyte increases with increasing gap by $d^{1/3}$ and thus has no maximum. As figure 2 shows, the cycle speed and thus also the volume flow at small cell height increase with increasing h; at very large cell heights the arriving gas quantity is no longer sufficient to compensate the greater friction resistance.

The circulation speed attainable in the cycle flow depends on the coefficient of friction ζ in the recirculation channel. This dependence can be used conversely to adapt the model to the measured values through suitable selection of ζ when measured values for the cycle speed are known. The measured values given in [3] for v_0 are reproduced qualitatively correct by the model; but the incomplete quantitative agreement (Measured values smaller than computed values) may have less to do with the imprecise /252
description of the flow in the recirculation channel, than with the incomplete formation of the presumed, undisturbed laminar flow in the electrode gap during the measurements. To achieve high circulation speeds in the range of 0.6 to 1.5 m/s, as were cited by Fleck [6] and Wintzer [7] for chlorate electrolysis cells, an additional ascent tube was placed over the actual electrolysis cell here.

The end-concentration c of the product attainable in an electrolysis process can be varied by the input volume flow. If $\dot{V}$ denotes the input volume flow, then we have:

$$c = \frac{i\,h\,l}{n\,F\,\dot{V}} = \frac{\bar{i}\,h}{n\,F\,v_0\,d} \cdot \frac{\dot{V}_0}{\dot{V}} \tag{16}$$

Through the selection of the geometric parameters (height, width and gap of the cell) and of the input volume flow, a desired end-concentration can be obtained regardless of the circulation speed in the cell determining the cell voltage. In general, the input

a mathematic model was set up and evaluated. It is shown that in this manner, a rapid flow through the electrode gap can be achieved without additional energy consumption, in addition to a low gas fraction and a low cell voltage. The cell voltage and the attainable cycle speed are investigated as a function of the geometric parameters for their optimum values.