Journal of Applied Electrochemistry **29**: 1155–1159, 1999.

Instability of the two-phase flow in vertical interelectrode gaps

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Received 2 March 1998; accepted in revised form 1 June 1998

Key words: bubble street, flow instability, gas evolving electrode, gas fraction, two-phase flow

Abstract

In vertical gaps between electrode and membrane, the smooth upward flow of the gas–liquid dispersion near the electrode in the form of a bubble street may be upset under certain conditions. At a certain channel height, a downward flow develops near the membrane resulting in a more or less uniform distribution of gas bubbles over the whole cross-sectional area. The controlling conditions of the conversion of the regular bubble street flow into irregular downward flow were analysed quantitatively in a previous theoretical model, the results of which are now compared with experimental data confirming the theory. The experimental data are further used to derive a relationship for the distribution of the volume fraction of gas.

List of symbols

A	electrode surface area (m^2)
F	Faraday constant ($F = 96\,487$ A s mol^{-1})
f_G	gas evolution efficiency
g	acceleration due to gravity (m s^{-2})
H	height (m)
I	current (A)
j	nominal current density, $j = I/A$ (A m^{-2})
K_4	numerical constant, Equation 13
K_5	numerical constant, Equation 14
m	exponent, Equation 4
n	charge number
p	pressure (kg m^{-1} s^{-2})
R	universal gas constant ($R = 8.3143$ kg m^2 s^{-2} mol^{-1} K^{-1})
T	temperature (K, °C)
v	velocity (m s^{-1})
$\dot{V}_G$	volume flow rate of gas (m^3 s^{-1})
$\dot{V}_L$	volume flow rate of liquid (m^3 s^{-1})
W	channel width (m)
x	coordinate in main flow direction (m)
y	coordinate orthogonal to main flow direction (m)
Y	electrode–membrane distance (m)
Y^*	equivalent channel thickness (m)
Fr	Froude number, Equation 6
Re	Reynolds number, Equation 7

Greek symbols

δ	bubble layer thickness (m)
ε	volume fraction of gas
ε^*	current efficiency
Θ	fractional bubble shielding of the electrode surface
v	stoichiometric number
η_L	dynamic liquid viscosity (kg m^{-1} s^{-1})
ρ_L	liquid density (kg m^{-3})

Subscripts

c	critical
G	gas
L	liquid
0	zero distance from elecrode

1. Introduction

In interelectrode spaces, between a vertical gas-evolving electrode and a membrane, an unwanted phenomenon may occur. Under certain conditions, the smooth upward flow of the gas–liquid dispersion near the electrode in the form of a bubble street is upset, and the gas exhibits a downward flow near the membrane filling the whole cross-sectional area with a dispersion, as shown in Fig. 1. This phenomenon is detrimental to the ohmic interelectrode resistance and should be avoided in design and operation of electrochemical reactors.

The phenomenon has been described by Fouad and Sedahmed [1], Krenz [2] and Giron et al. [3] and was experimentally studied by Sigrist [4], using a physical model cell where the gas evolving electrode was simulated by a frit through which gas was pressed. It was found that the point of onset of the downward flow is well defined and its position depends on the flow velocity, the current density and the gap width [5, 6].

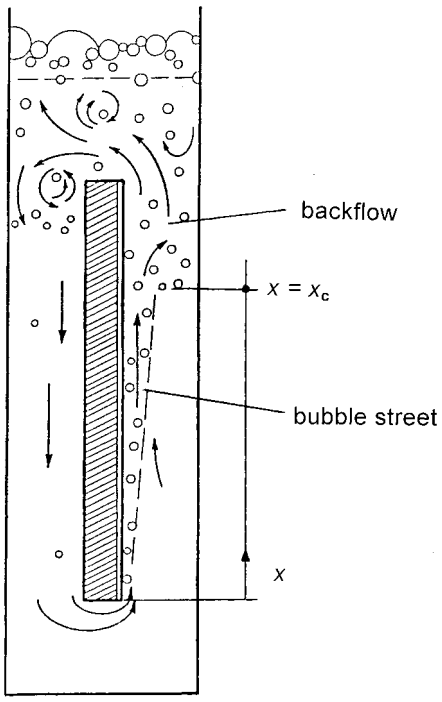

Fig. 1. Bubble street close to a gas-evolving electrode (simulated in the experimental set-up of Sigrist [4]).

Sigrist [4] recognized that the destruction of the bubble street flow is caused by a flow instability. The abrupt change of the flow pattern occurs if the gradient of the velocity at the wall opposite to the electrode, that is, at the membrane, equals zero. A further minute increase in the flow height results in backflow. By means of a mathematical model Vogt [7] made an attempt to describe the instability problem in quantitative terms. It was shown that if the upward flow exceeds a certain value (depending on the rate of gas evolution, the dimensions of the interelectrode space and on the liquid flow rate), the enlarged flow of the dispersion near the electrode cannot be balanced by the liquid flow rate, and the back flow develops. These results will be reviewed briefly.

2. Theory

The critical condition has been expressed by a critical ratio of the flow rates of gas (at a particular height) and of liquid,

$$\left[\frac{\dot{V}_G}{\dot{V}_L}\right]_c = \left(\frac{K_4}{K_5} - 1\right)^{-1} \tag{1}$$

where

$$K_4 \equiv \frac{1}{3\delta/Y} - \frac{1}{m+3} \tag{2}$$

$$K_5 \equiv \frac{\varepsilon_0}{m+2}\left[\frac{(1-\delta/Y)^2}{m+1} - \frac{(\delta/Y)^2}{m+3} + \frac{m+1}{2m+3}\right] \tag{3}$$

where ε_0 is the void fraction at zero distance from the electrode, $\varepsilon = \varepsilon_0$ at $y = 0$, and m denotes the exponent in the distribution of the fraction of gas in the dispersion (void fraction).

$$\varepsilon = \varepsilon_0\left(1 - \frac{y}{\delta}\right)^m \tag{4}$$

The relative thickness of the bubble street in regular flow, δ/Y, of a cell with an electrode–membrane distance Y may be eliminated by means of the ratio of the Froude number and the Reynolds number of the liquid [7]

$$\frac{Fr}{Re} = \left[\frac{1 - \frac{1.15\,(m+2)\varepsilon_0}{2m+1}}{\frac{(m+1)\,(m+2)}{\varepsilon_0\,(\delta/Y)^2} - 4.6}\right]\left(\frac{\delta}{Y}\right)(K_4 - K_5) \tag{5}$$

with the definitions

$$Fr \equiv \frac{v^2}{Y^* g} \tag{6}$$

$$Re \equiv \frac{vY^*\rho_L}{\eta_L} \tag{7}$$

where the average velocity of the gas-free liquid is

$$v = \frac{\dot{V}_L}{WY}$$

and Y^* denotes the equivalent channel thickness equal to twice the cross-sectional area of the channel divided by its perimeter:

$$Y^* \equiv 2\frac{WY}{2(W+Y)} = \frac{Y}{1 + Y/W} \tag{9}$$

to result in

$$\frac{Fr}{Re} \equiv \frac{\dot{V}_L\eta_L}{WY^3\rho_L g}\left(1 + \frac{Y}{W}\right)^2 \tag{10}$$

The bracket is an extension of the original equation [7] which was based on the assumption of a channel width W being large compared to the channel thickness Y, $Y/W \ll 1$.

By this means it is possible to obtain an interrelation between the ratio of the critical flow rates, Equation 1, and Fr/Re, representative of the liquid flow rate, the controlling properties and the cell geometry.

$$\left[\frac{\dot{V}_G}{\dot{V}_L}\right]_c = f\left(\frac{Fr}{Re}\right) \tag{11}$$

Equation 11 has not been expressed in analytical form, but was shown in a diagram [7]. It generally answers the question of the admissible flow rate of evolved gas with a certain liquid flow rate and cell geometry. The

relationship opens up the possibility to calculate the critical electrode height not to be exceeded in a cell with vertical gas-evolving electrodes.

3. Comparison with experimental results

At the time the theory was published it was not possible to check the validity of the theoretical relationships in comparison with experimental data. However, recently, Riegel [8, 9] (without knowledge of the theoretical analysis [7]) conducted experiments of the local distribution of the volume fraction of gas and studied the onset of the backflow. His investigations [8] allow a quantitative check of Equation 11, and for this purpose, the results are interesting in two respects.

3.1. *Distribution of the volume fraction of gas*

This finding contributes to the clarification of an old problem. The distribution of the gaseous phase in the interelectrode space has attracted attention for a long time, because an ascertained knowledge is the precondition of every estimation of the ohmic potential drop in the interelectrode space. The oldest and most simple models are based on the strongly simplifying assumption of a uniform distribution of the gas phase in each horizontal cross-section [10, 11]. An improvement was made possible by introducing a layer with larger void fraction adhering to the electrode in addition to a space with constant void fraction in the rest of the gap [12]. Sillen [13] distinguished three zones: a first layer with large void fraction adhering to the electrode, a second zone with a substantially lowered void fraction, each being independent of y, and a third zone being free of bubbles. Following a proposal of Bongenaar–Schlenter [14] a nonlinear distribution according to Equation 4 was introduced [7]. Other linear or nonlinear distributions were used by Janssen and Visser [15] and Czarnetzki [16]. The experimental investigations of Riegel [8, 9] on the gas fraction ε were conducted through measuring the ohmic resistance at various distances from the gas-evolving electrode and with variable height of the operating gas-evolving electrode. So he obtained a two-dimensional distribution of the gas fraction in the total electrode-membrane gap. Typical data are shown in Figs 2 and 3 evidencing that the profile may be approximated by Equation 4 with an exponent $m = 2.5$. Then Equations 2, 3 and 5 simplify to

$$\frac{Fr}{Re} = \left[\frac{1 - 0.86\,\varepsilon_0}{\frac{15.75}{\varepsilon_0(\delta/Y)^2} - 4.6}\right]\left(\frac{\delta}{Y}\right)(K_4 - K_5) \tag{12}$$

$$K_4 = \frac{1}{3\delta/Y} - \frac{1}{5.5} \tag{13}$$

$$K_5 = \frac{\varepsilon_0}{4.5}\left[\frac{(1-\delta/Y)^2}{3.5} - \frac{(\delta/Y)^2}{5.5} + \frac{3.5}{8}\right] \tag{14}$$

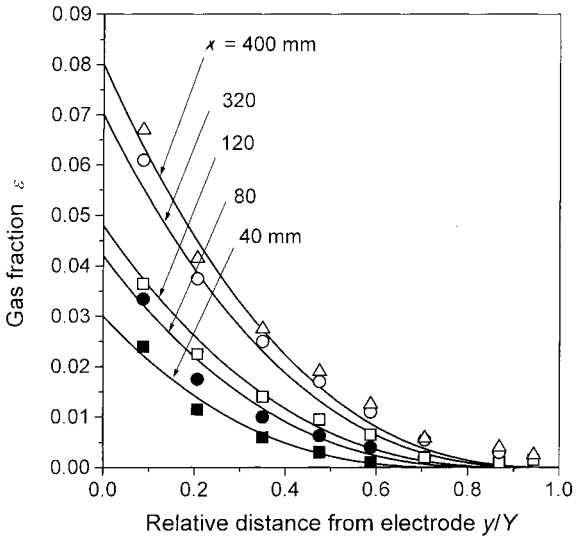

Fig. 2. Distribution of the volume fraction of gas in the gap. Comparison of Equation 4, $m = 2.5$, with experimental data of Riegel [8, 9] for various heights of electrode, $Y = 8\,\text{mm}$, $v = 0.69\,\text{m s}^{-1}$, $j = 1500\,\text{A m}^{-2}$.

The volume fraction of gas in the bubble layer adhering to the electrode was originally assumed as $\varepsilon_0 = 0.5$, because the value represents approximately the closest irregular configuration of spheres [7]. Then the relationship may be approximated with satisfactory accuracy in the whole range $0 \leq \delta/Y \leq 1$ by

$$\left[\frac{\dot{V}_G}{\dot{V}_L}\right]_c = 3.1\left(\frac{Fr}{Re}\right)^{0.5}\left(1 + 163\frac{Fr}{Re}\right) \tag{15}$$

Equation 15 may be applied by calculating the volume flow rate of gas from Faraday's law

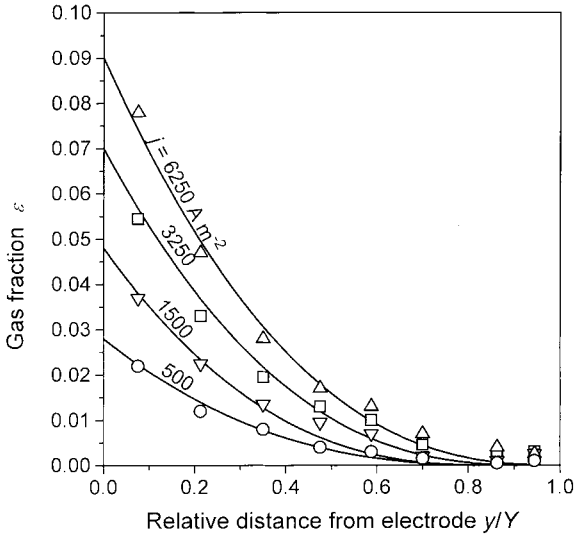

Fig. 3. Distribution of the volume fraction of gas in the gap. Comparison of Equation 4, $m = 2.5$, with experimental data of Riegel [8] for various current densities, $Y = 8\,\text{mm}$, $v = 0.69\,\text{m s}^{-1}$, $x = 120\,\text{mm}$.

$$\dot{V}_G = \frac{RT\varepsilon^* f_G}{(n/v)Fp} \int_0^H jW \, dx \tag{16}$$

where H is the height, W the width of the electrode. The gas evolution efficiency may approximately be set at $f_G \approx 1$. As a further approximation for the sake of simplicity, the current density may be assumed uniform, $j = I/A$:

$$\dot{V}_G = \frac{RT\varepsilon^* I}{(n/v)Fp} \frac{WH}{A} \tag{17}$$

3.2. *Flow pattern charts*

The charts of the distribution of the volume fraction of gas under various operational conditions [8] enable a quantitative check of Equation 15. The plots clearly indicate the configuration in a regular state of the bubble street flow and in backflow, respectively. The total of Riegel's published experimental data are shown in Fig. 4 together with some typical charts of the total electrode-membrane gap taken from [8]. Figure 4 also shows the theoretical Equation 15 indicating the boundary between regular bubble street flow and unwanted backflow. Figure 5 shows the interrelation of the values of liquid flow velocity (in the entrance cross-section) and current density to the data points of Riegel. The experimental conditions were $Y = 8$ mm, $W = 40$ mm, 1 M KOH, $T = 50\,^{\circ}$C [8].

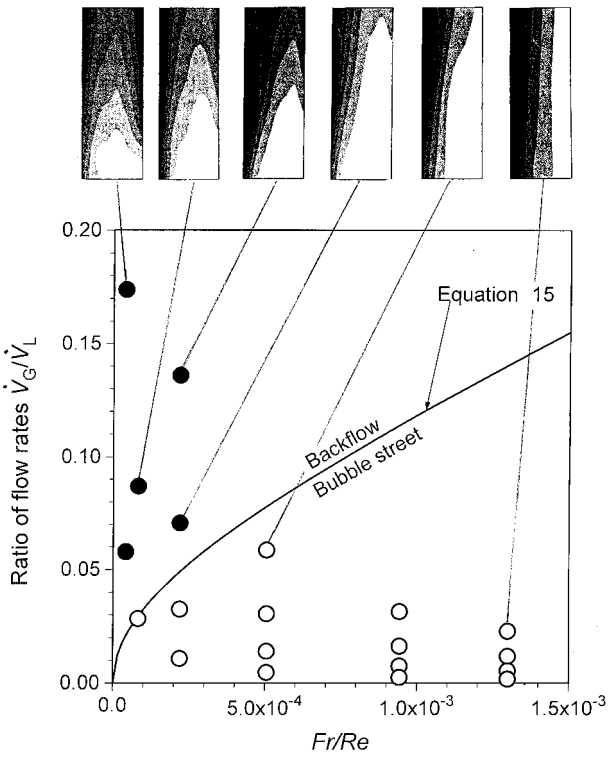

Fig. 4. Regions of flow patterns in electrode–membrane gaps. Experimental charts (top) and data points from Riegel [8]: [○] bubble street flow, [●] backflow. (—) theoretical boundary, Equation 15 with $\varepsilon_0 = 0.5$. (Charts show gap height $H = 418$ mm and electrode–membrane distance $Y = 8$ mm in different scale.)

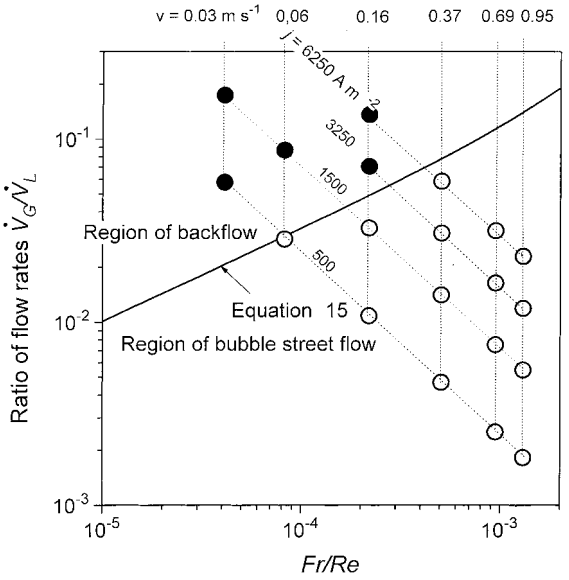

Fig. 5. Theoretical Equation 15 in comparison with experimental results of Riegel [8], H_2 evolution from 1 M KOH, 50 °C. Experimental: (○) bubble street flow, (●) backflow. Equation 15 with $\varepsilon_0 = 0.5$.

4. Discussion

Although the assumptions used to derive the instability model [7] involve inevitable deformations of reality, the result appears to be in conformity with the available experimental results.

Equation 4, although satisfactorily correlating the data of the void fraction profile, is far from accurate, as seen from the particular forms of the profiles experimentally obtained by Riegel [9] which cannot be attributed to experimental inaccuracies. However, the value of the exponent m is of little effect on the overall result evidenced by a numerical check as already stated previously [7].

Greater importance must be attributed to the value of the gas fraction at the electrode, ε_0. Riegel's charts confirm once more that the gas fraction ε_0 is not constant, but depends on the experimental conditions. In particular, the value increases with the current density and the flow length (or channel height) in agreement with previous findings by Bergner [17]. The value ε_0 is further lowered as the liquid flow rate increases. As known from the experiments of Sillen [13], an increase in the flow velocity past a gas-evolving electrode substantially lowers the bubble population density at the electrode, commonly expressed by the fractional bubble shielding Θ, i.e. the fraction of the electrode area shadowed by adhering bubbles in orthogonal projection [18]. This value is interrelated with the volume fraction of gas, ε_0, of the zone adjacent to the electrode [19–22].

For Riegel's experimental velocity of $v = 0.69\,\mathrm{m\,s^{-1}}$ the value was much smaller than the value $\varepsilon_0 = 0.5$ used in Equation 15. Smaller values of ε_0 shift the boundary between the two regions of bubble flow and downward flow, Equation 15, to smaller values of the ratio of the flow rates. However, such small ε_0 values are not representative of the *critical value* linked with the incipience of the downward flow which in no case occurred at or above $0.37\,\mathrm{m\,s^{-1}}$ under his experimental conditions. Although reliable information on the representative value of ε_0 in Equations 12 and 14 is missing, a value of about $\varepsilon_0 = 0.5$ appears applicable for the time being.

5. Conclusion

It is seen from Equations 15 and 17 that the flow pattern changes from the regular bubble street flow to backflow at a height where the ratio of the flow rates of gas and liquid exceeds a certain value Fr/Re depending on the flow rate, the density and the dynamic viscosity of the liquid and of the dimensions of the cross section.

The agreement of the theoretical Equation 15 with experimental data suggests that it may be used as a first means to predict the flow pattern of the two-phase flow in vertical electrode–membrane gaps. Equation 15 appears particularly appropriate as an attempt to answer the question of the critical condition of an abrupt change from regular bubble street flow to backflow and is expected to be helpful in the design of electrochemical reactors.

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