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Role of mass transfer on hydrogen evolution in aqueous media

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The process of hydrogen evolution during alkaline electrolysis of aqueous solutions is governed by mass transfer, growth of hydrogen bubbles and removal of hydrogen from the cathode. Two mechanisms are decisive for hydrogen removal: (i) hydrogen dissolved in the solution is carried off from the cathode surface by diffusion and convection, and (ii) gas bubbles are transported by a two-phase flow. The paper describes experiments to determine the local concentration of dissolved hydrogen and the void fraction of hydrogen bubbles in aqueous solutions. Measurements were performed in a flow channel by varying the height of the cathode (40–400 mm), the current density (up to $6250\,\mathrm{A\,m^{-2}}$) and the mean velocity of the electrolyte (up to $0.95\ \mathrm{m\ s^{-1}}$). Two operating regimes of the electrolyser are found. At high current densities a back flow is observed leading to an increase in the electrolyte resistance. Traces of dissolved oxygen are detected at high current densities. At low current densities the two-phase flow is confined to a thin layer along the cathode surface, the concentration of dissolved hydrogen being small.

Keywords: *hydrogen evolution*, *mass transfer*, *bubble growth*, *flow channel*, *two-phase flow*, *dissolved hydrogen*

Nomenclature

c	concentration
E	electrical potential
F	Faraday constant
I	electrical current
K	Henry coefficient
N	number of moles
$\dot{N}$	flow rate
p	pressure
R	electrical resistance
R_m	universal gas constant
T	temperature in K
U	voltage
w	mean velocity of electrolyte

Greek symbols

ε	void fraction
ϑ	temperature in °C

Subscripts

AgCl	silver/silver chloride reference electrode
El	electrolyte
H^+	hydrogen ion
H_2	hydrogen molecule
0	without gas bubbles
sat	saturated

1. Introduction

Modelling hydrogen production at a gas evolving electrode requires a detailed knowledge of the mass transfer mechanisms. The mass transfer depends mainly on the concentration of the reaction products, which can be ascertained reliably only by experiment. Such experiments are difficult to perform, and only one experimental study, dealing with concentration profiles of hydrogen at a gas evolving cathode, seems to exist [1]; by contrast, a greater number of publications are devoted to mass transfer at hydrogen evolving electrodes [2–4]. All these experiments were performed with a tracer. The transfer of the tracer to the electrode was measured, instead of the mass transfer of the reaction product from the electrode into the liquid bulk.

Müller *et al.* [1] investigated the concentration profile with a platinum wire electrode as a function of the cathode distance. They assumed the solution to be saturated with hydrogen at a distance of about 500 μm and correlated the measured potentials of the supersaturated solution at smaller distances by the Nernst equation. The potential was measured against the cathode, under the assumption that it can be described as a function of the measured *IR*-drop and the Nernst potential. We suggest a similar method to determine the hydrogen concentration with a platinum wire electrode. However, we use a reference electrode, measure the voltage between these electrodes, and determine the concentration without any assumptions.

The influence of gas bubbles on the electrical resistance and methods of minimizing the resistance

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have been previously investigated [5–16]. The pioneering paper was that of Tobias [5]. Hine *et al.* [6–9] investigated the resistance of the electrode as a function of current density, temperature, volume rate and channel geometry. Two simple gas-bubble distribution-functions were suggested: a linear decrease of the void fraction with the cathode distance or a quasihomogenous two-phase flow region with a bubble-free liquid outside this region. Sillen *et al.* [10, 11], Janseen *et al.* [12–16] and Bongenaar-Schlenter *et al.* [17–19] studied the electrical resistance and the behaviour of gas bubbles during alkaline electrolysis. They also investigated optically the distribution of bubbles perpendicular to the electrode surface. However, these methods are not applicable to high current densities resulting in a high hydrogen production rate.

Theoretical models for calculating the electrical resistance of an electrolyser assume a constant void fraction perpendicular to the electrode-surface [21, 22]. Vogt [20] suggested a model which is based on variable void fraction.

2. Theory

At the surface of a hydrogen electrode electrons in the platinum electrode, hydrogen ions in solution, and dissolved molecular hydrogen are in equilibrium. The concentration of the dissolved hydrogen is normally an independent variable [23]. When equilibrium is maintained and when the partial pressure of hydrogen in the gas phase is fixed, the potential of the hydrogen electrode is given through the well known expression (e.g. [23]).

$$E_{\text{hydrogen - electrode}} = \frac{R_m T}{F} \ln \frac{c_{H^+}}{c_{0,H^+}} - \frac{R_m T}{2F} \ln \frac{p_{H_2}}{p_{0,H_2}} \quad (1)$$

The standard conditions are defined by $c_{H^+} = 1\,\text{M}$ and $p_{H_2} = 1$ bar. The partial pressure p_{H_2} in Equation 1 can be replaced by the concentration of the dissolved gas using the relation for phase equilibrium. Henry's law $(p_{H_2} = Kc_{H_2})$ is suitable for low partial pressures $(p_{H_2} < 2$ bar and $\vartheta = 25\,^\circ\text{C})$. The proportionality constant, K, has a value of $= 1.723$ bar m^3 mol^{-1} in 1M potassium hydroxide [24]. Thus, assuming equilibrium between dissolved molecular hydrogen and the hydrogen ions, the voltage between a platinum electrode and a silver/silver chloride reference electrode is a function of the amount of dissolved gas. From Equation 1 for a one molar hydroxide solution $(c_{H^+} = 10^{-14}\,\text{M})$, as used in the experiments,

$$U_{\text{Pt,AgCl}} = E_{\text{Pt}} - E_{\text{AgCl}} = -1.029 - \frac{R_m T}{2F} \ln c_{H_2} \quad (2)$$

where c_{H_2} is given in mol m^{-3} and $U_{\text{Pt,AgCl}}$ in V. The equation is only valid for constant concentration of H$^+$. At large values of current density deviations can occur if the concentration is strongly affected by mass transfer to the electrode [25]. At the surface of an inert metal electrode placed in a solution, containing hydrogen molecules and hydrogen ions, equilibrium does not exist, and a potential defined by Equation 2 cannot be assumed. Therefore, the metal has to act as catalyst adsorbing hydrogen atoms. Because of the term $\ln c_{H_2}$ in Equation 2 small concentrations of dissolved hydrogen can be detected. However, small concentrations of impurities can also influence or govern the voltage. In order to verify the validity of Equation 2 we checked the correlation between voltage and concentration experimentally.

3. Experiments

The experimental setup to verify Equation 2 is shown in Fig. 1. It consists mainly of two electrodes, a platinized platinum wire (1) as redox and a silver/silver chloride (2) as reference electrode. Both electrodes were arranged in a closed plexiglass tank filled with 8.2 dm^3 of 1M potassium hydroxide solution, initially saturated with air. The voltage between the two electrodes (3) was measured as a function of time for a given constant hydrogen flow rate. Hydrogen was produced at the cathode (4), its area being 0.02 m^2. A magnetic stirrer (5) assured a homogenous distribution of the hydrogen in the potassium hydroxide solution. A heater (6) kept the temperature constant at 25 °C, and a constant current of 20 mA was imposed from the power supply (7), leading to a constant hydrogen flow rate of $\dot{N}_{H_2} = 1.04 \times 10^{-7}$ mol s^{-1}. The circuit was completed with an anode (8) arranged in an open tank and a PTFE-tube (9) filled with KOH solution. Diaphragms arranged between the tanks prevented mixing of dissolved gases.

A catalytic layer of black platinum on the platinum wire was prepared with a solution of hexachloro-platinum acid.

The volumetric void fraction of hydrogen and its distribution in forced convection flow was determined by measuring the electrical resistance of the two-phase mixture flowing up a vertical channel of rectangular cross section. The apparatus used in these experiments is shown in Fig. 2. It consists of two closed circuits, one for hydrogen and the other for oxygen. The gases were evolved on ten electrode pairs mounted in the upper section of the electrolyser. Cathodes and anodes were made of nickel, their size was 4 cm × 2 cm. The channel was divided vertically by a diaphragm into two subchannels, and the electrolyte pumped through the electrolyser at velocities up to 1.0 m s^{-1}. At the end of the channel, the two separated two-phase flows streamed into reservoirs where the liquids were purged from gases. The electrolyte then passed through a heat exchanger, where the temperature was regulated in the range from 20 to 60 °C. The whole electrolyte volume amounted to about 100 dm^3.

At the upper end of the channel, just above the last electrode pair, nine platinum electrodes (Pt-E1) were mounted perpendicular to the cathode surface, Fig. 3. The electrical current through the last electrode pair consisted of a direct current superimposed on an alternating current of small amplitude. A bipolar

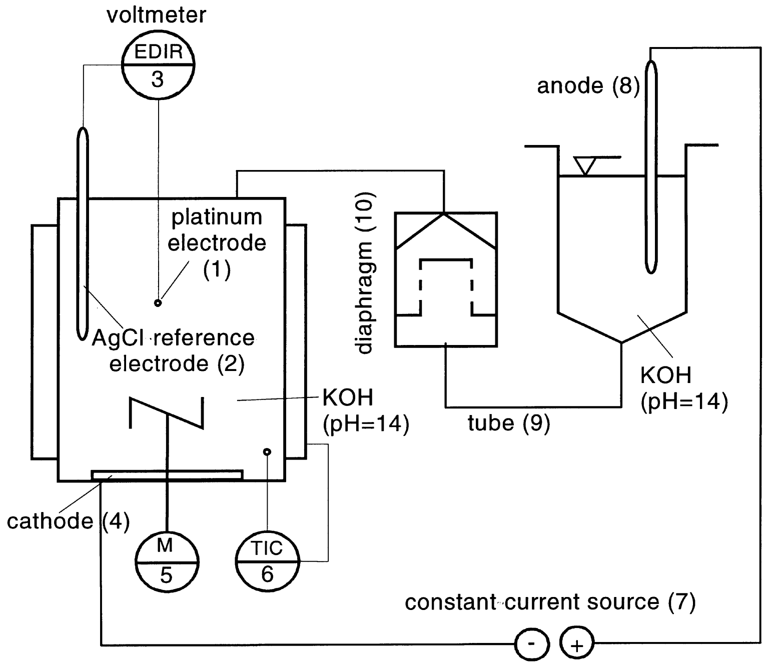

Fig. 1. Experimental setup.

operational amplifier (BOP) served as current source. The frequency of the alternate current corresponded to the frequency of an external alternating voltage, supplied by the oscillator of a lock-in amplifier, used to measure the a.c.-voltage between neighboured platinum electrodes at the frequency of the oscillator. The frequency of 1.1 kHz was high enough to avoid polarizing effects on the electrodes. With this technique, the electrical resistance of the fluid was measured as a function of distance. The location of the platinum electrodes (diameter 100 μm) was determined from the electrolyte resistance without gas bubbles.

As is well known, the resistance of the electrolyte depends on the void fraction. Several relations correlate the resistance and the void fraction ε. Kreysa and Kuhn [26] examined the different relations and recommended those derived by Bruggemann [27] and Maxwell [28]. Since these equations differ only slightly from each other, we used the Maxwell equation

$$\frac{R_{\mathrm{El}}}{R_{0,\mathrm{El}}} = \frac{1+\varepsilon/2}{1-\varepsilon} \tag{3}$$

where R_{El} represents the electrical resistance with, and $R_{0,\mathrm{El}}$ without, gas bubbles.

When determining the concentration of dissolved hydrogen the d.c. voltage between platinum electrode and reference electrode must be considered to consist of two additive parts. One is caused by the electrical current through the electrolyte. This part, $R_{\mathrm{El}}I$, is the product of the total current produced by the BOP and the resistance between the two electrodes (platinum and reference) which is also measured. The second part is the difference between the e.m.f.'s of the two electrodes, given by Equation 2. Determination of dissolved hydrogen therefore requires a measurements of the d.c. voltage between the platinum electrode and the reference electrode. From the voltage is then obtained c_{H_2} (see Equation 2).

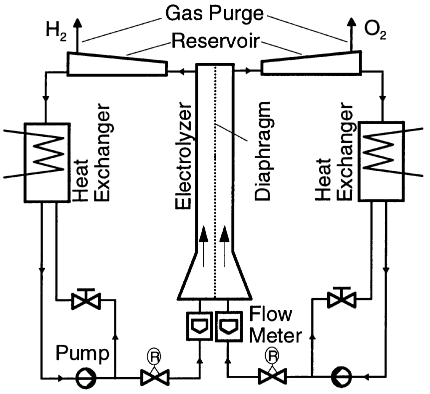

Fig. 2. Apparatus for two-phase experiments.

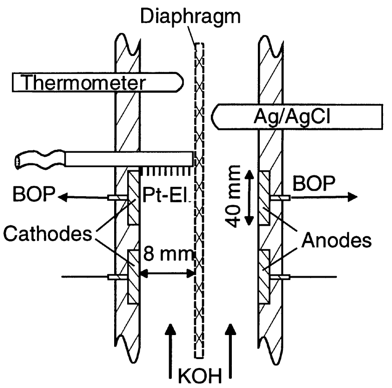

Fig. 3. Upper part of the channel.

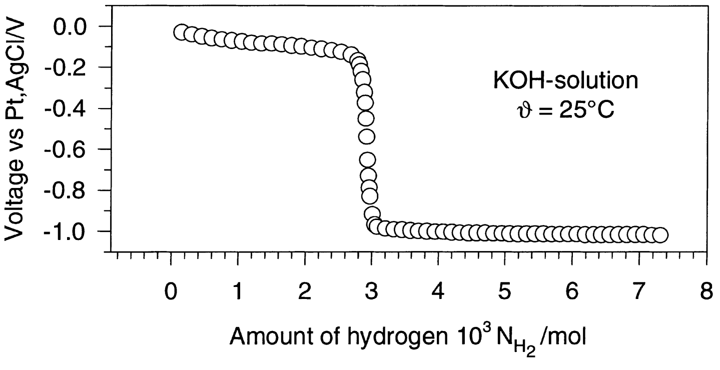

Fig. 4. Voltage between platinum electrode and silver/silver chloride reference electrode in 1 M KOH solution as function of the amount of hydrogen.

4. Results

The voltage between the platinum electrode and the silver/silver chloride reference electrode is plotted in Fig. 4 as a function of the amount of hydrogen. Such a curve is typical for a redox titration. It can roughly be divided into three sections. The first part is characterized by a flat slope and a point of inflection. Then follows a short transitional region with a steep decrease passing through another inflection point. Finally, the voltage decreases slowly. The slow decrease of the voltage in the first section is caused by an oxidizing agent, which reacts with the reducing agent hydrogen. The reduction is completed at amounts of hydrogen 3×10^{-3} mol. After this, a further supply of hydrogen leads to an increase in the hydrogen concentration causing a slight decrease in the voltage with the amount of hydrogen.

Figure 5 shows the measured voltage as a function of the hydrogen concentration together with values calculated by Equation 2. The hydrogen concentration follows from

$$c_{H_2} = \frac{N_{H_2} - 3.0 \times 10^{-3}\ \text{mol}}{V_{KOH}} \tag{4}$$

according to which, at $N_{H_2} \leq 3 \times 10^{-3}$ mol hydrogen content, the concentration c_{H_2} in the solution is zero. As can be seen from the Figure, experiment and theory agree well. Equation 2 can thus be used to determine the concentration of dissolved hydrogen at a voltage below −0.7 V.

As the experiments showed, hydrogen reacts first with an oxidizing agent. This is dissolved oxygen. In the solution of distilled water and potassium hydroxide saturated with air the solubility amounts to 0.926 mol m^{-3} at a partial pressure of oxygen of 1 bar [24]. The amount of oxygen is 1.5×10^{-3} mol at a partial pressure of 0.2 bar in 8.2 dm^3 of solution. Hydrogen reduces oxygen on the platinum surface according to $O_2 + 2H_2 \rightarrow H_2O$. Therefore, twice as much hydrogen is consumed as oxygen is initially present in the solution. Since no hydrogen is present in the tank at the beginning of the titration, the voltage cannot be determined from Equation 2. The voltage near the inflection point corresponds to the standard potential of the titrated redox couple and, as Fig. 6 shows, amounts to −84 mV.

The standard potentials of some platinum/platinum oxide couples [29] are also presented in Fig. 4. None of them fits the experiments. Obviously, a

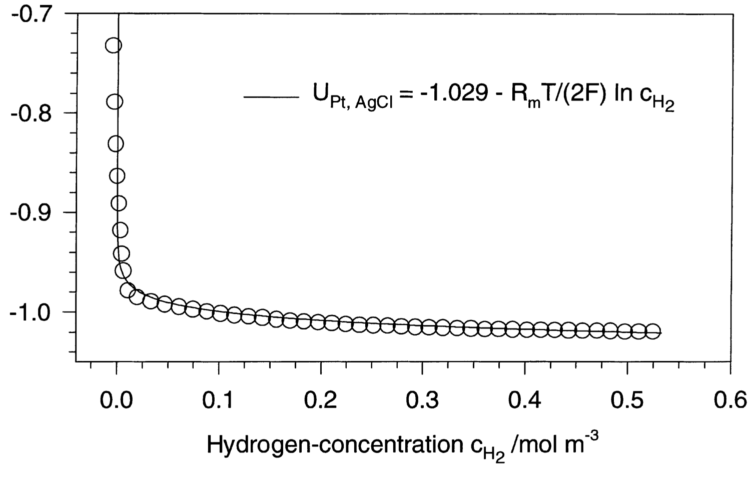

Fig. 5. Voltage between platinum electrode and silver/silver chloride reference electrode as a function of the hydrogen concentration. The figure represents a comparison of measured and calculated data.

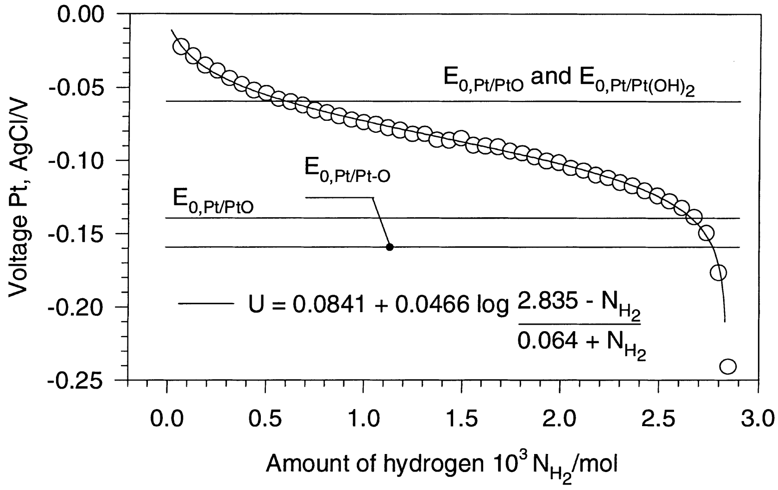

Fig. 6. Voltage between platinum electrode and silver/silver chloride reference electrode as a function of the supplied amount of hydrogen. The voltage is governed by oxygen initially dissolved in the solution.

mixture of oxygen compounds exists on the surface, so that a mixed potential arises, as already stated by Hoare [29].

Figure 7 shows the void fraction, ε, for several current densities as a function of the cathode distance. The measurements were made with a 1 M potassium hydroxide solution at a mean velocity of 0.69 m s^{-1} and a temperature of 50 °C. The first three electrode pairs below the platinum electrodes were operated at current densities noted in the Figure. The void fraction decreases with increasing cathode distance and vanishes at the diaphragm surface ($x = 8$ mm). Increasing current density results in a higher void fraction at the cathode surface.

Figure 8(a) shows the influence of the number of electrode pairs on the void fraction as a function of distance. The void fraction increases with the number of electrodes. This effect is more pronounced at small cathode distances. Figure 8(b) shows a contour plot of these results. Along the boundary between single-phase and two-phase flow, the void fraction is 1%. The white area represents single-phase flow. The thickness of the two-phase boundary increases with the number of electrode pairs.

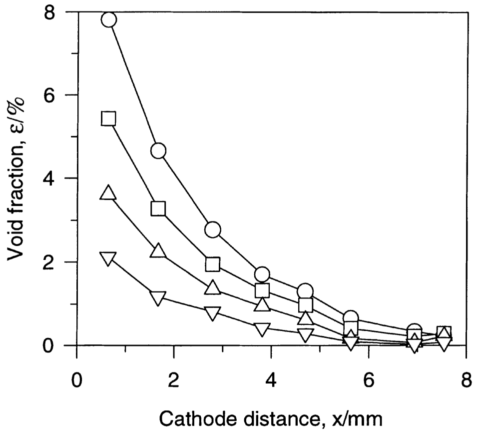

Fig. 7. Void fraction as a function of distance. Temperature 50 °C, mean velocity 0.69 m s^{-1}. Current density: (○) 6250, (□) 3250, (△) 1500 and (▽) 500 A m^{-2}.

Figure 9 shows results at smaller mean electrolyte velocity ($w = 0.16$ m s^{-1}), and for a current density $i = 3250$ A m^{-2}. Here the gas bubbles are spread over the channel. In the upper region the void fraction as a function of the cathode distance has a minimum in the centre between cathode and diaphragm. This is caused by backflow of the electrolyte close to the diaphragm, resulting in higher void fractions and electrical resistances. In a commercial electrolyser backflow must be avoided. It seemed worthwhile therefore to study the conditions for the onset of backflow as a function of current density, number of electrode pairs and mean velocity. Figure 10 shows the results. The current I is obtained from the product of the current density, the number of electrodes and the area of a single electrode.

At working conditions right of the line backflow is avoided. A current I (A) at given mean velocity w (m s^{-1}) smaller than

$$I = -3.79 + 128\ w \tag{5}$$

should be chosen. This equation is a result of linear regression of the measured values at mean velocities above 0.03 m s^{-1}.

The concentration of dissolved hydrogen was determined as follows. The voltage $U_{\mathrm{Pt,AgCl,sat}}$ between a platinum electrode and reference electrode in potassium hydroxide saturated with hydrogen at 50 °C was measured, followed by the voltage $U_{\mathrm{Pt,AgCl}}$ at the unknown concentration. This voltage difference results in

$$U_{\mathrm{Pt,AgCl}} - U_{\mathrm{Pt,AgCl,sat}} = -\frac{R_{\mathrm{m}}T}{2F}\ln\frac{c_{\mathrm{H_2}}}{c_{\mathrm{H_2,sat}}} \tag{6}$$

In the case of a saturated solution the voltage difference disappears. Increasing voltage differences correspond to a decreasing hydrogen concentration. Figure 11 shows some results as a function of cathode distance. The distance has no significant influence on the voltages. The dissolved gases are, in contrast to the void fraction, homogeneously distributed over the investigated cross section. The current density, how-

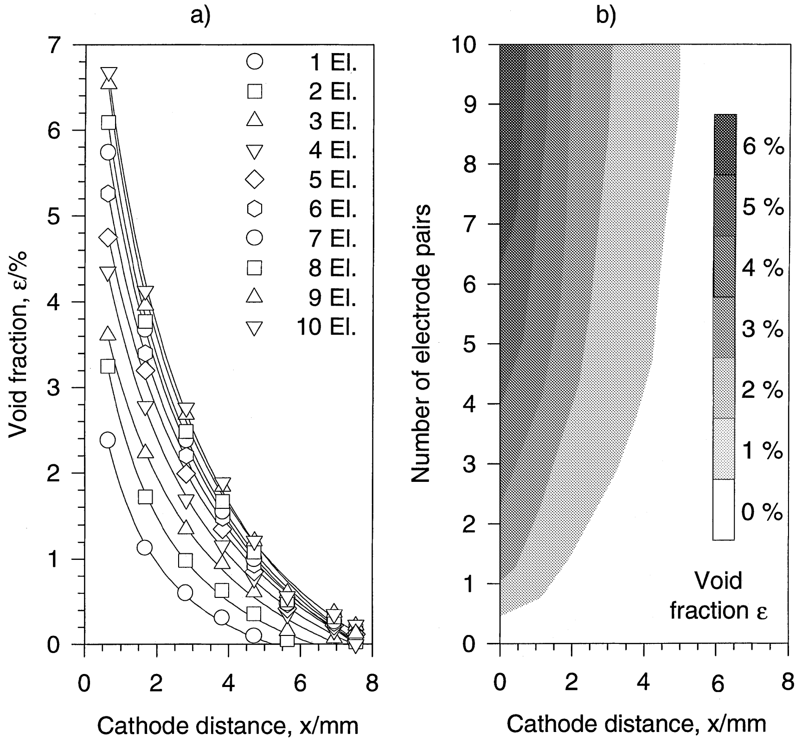

Fig. 8. Void fraction as a function of distance and number of electrodes. Current density, i = 1500 A m^{-2}; mean velocity, w = 0.69 m s^{-1}; temperature, ϑ = 50 °C.

ever, is of great influence on the concentration. At 100 A m^{-2} and 500 A m^{-2} oxygen can be detected. Only at the two highest current densities of 3250 A m^{-2} and 6250 A m^{-2} can dissolved hydrogen be measured.

Figure 12 shows the average values of the voltage over a cross section as a function of number of electrode pairs. The voltage difference (hydrogen concentration) becomes smaller with increasing number of electrode pairs. It is noteworthy that the voltage difference does not disappear. The smallest value is 30 mV, corresponding to a maximum concentration of $c/c_{\mathrm{sat}} = 12\%$, see Equation 6.

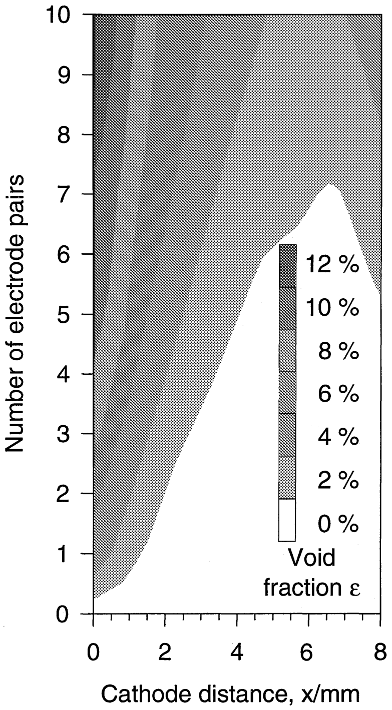

Fig. 9. Void fraction as a function of distance and number of electrodes. Current density, $i = 3250$ A m^{-2}; mean velocity, w = 0.61 m s^{-1}; temperature, ϑ = 50 °C.

Such a low value is not surprising, because the platinum electrodes were then completely surrounded by hydrogen bubbles, so that saturated solution can be assumed. In this case each platinum electrode acts as a hydrogen electrode. Its potential is shifted positively in the presence of dissolved oxygen. The platinum electrode can be used as a detector for oxygen impurities. Lorch [30] investigated the influence of oxygen on the e.m.f. of a hydrogen electrode. Assuming electrolyte saturated with hydrogen an amount of oxygen corresponding to $0.058\,c_{\mathrm{H_2,sat}}$ is determined from the results of Lorch.

5. Summary

The concentration of hydrogen dissolved in an aqueous KOH solution can be determined using a platinum electrode and a reference electrode. The voltage between the two electrodes depends on the concentration according to Equation 2, valid in the absence of oxygen. This condition is justified in the presence of a catalyst for the reaction $2H_2 + O_2 \rightarrow 2H_2O$, and when voltages are below −0.7 V. When a solution is saturated with hydrogen the e.m.f. of platinum electrode can be used to determine the concentration of traces of oxygen. The gas voidage in a flow channel was determined from the electrical resistance between neighboured platinum electrodes. At small current

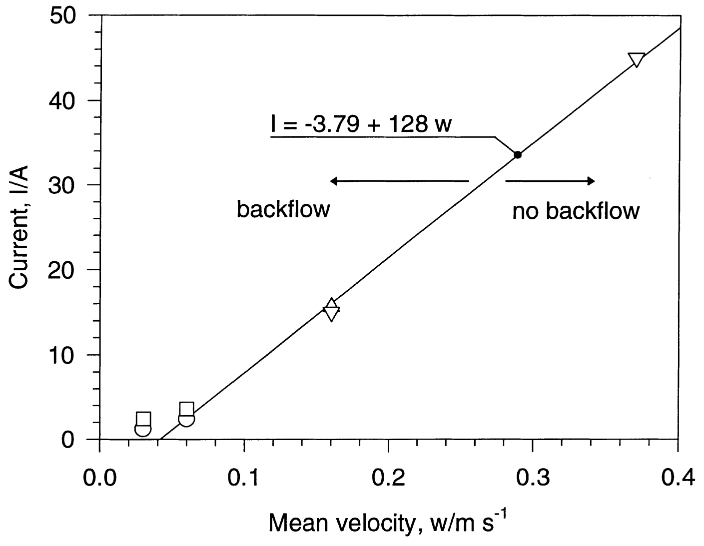

Fig. 10. Current, I, and velocity, w at onset of backflow. Current density: (○) 500, (□) 1500, (△) 3250 and (▽) 6250 A m^{-2}.

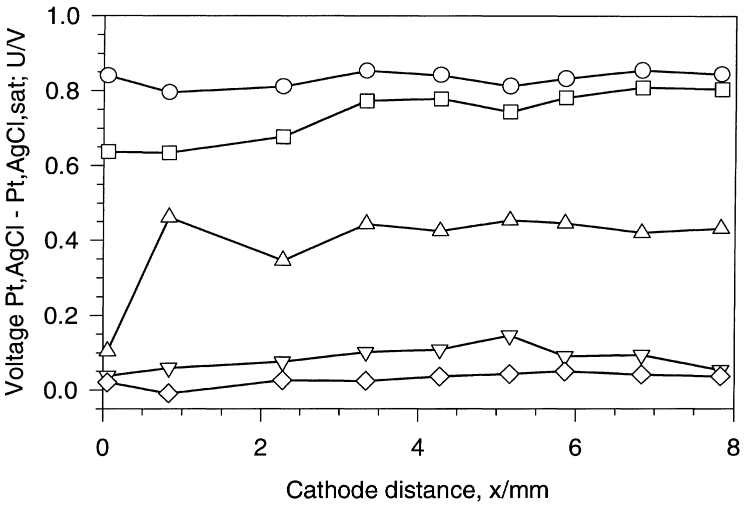

Fig. 11. Voltage $U_{\mathrm{Pt,AgCl}} - U_{\mathrm{Pt,AgCl,sat}}$ as a function of cathode distance. The first three electrodes below the platinum wires were operated at 50 °C and $w = 0.69$ m s^{-1}. Current density: (○) 100, (□) 500, (△) 1500 and (▽) 3250 and (◇) 6250 A m^{-2}.

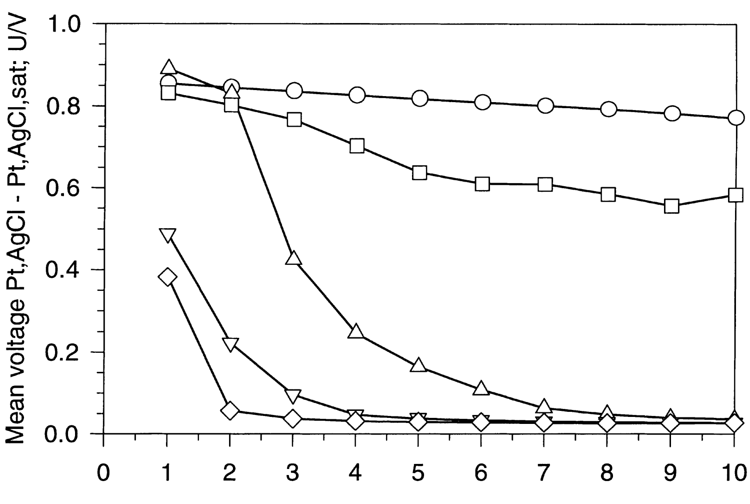

Fig. 12. Mean voltage, averaged across the channel width as a function of the number of operated electrodes at noted current densities at mean velocity $w = 0.69$ m s^{-1} and temperature $\vartheta = 50$ °C. Current density: (○) 100, (□) 500, (△) 1500, (▽) 3250 and (◇) 6250 A m^{-2}.

densities a two phase flow was observed with increasing thickness of the boundary layer along the flow path. High current densities produce a backflow close to the diaphragm, the void fraction and the electrical resistance then increase considerably. A relationship for the onset of backflow is given, with current as a function of electrolyte velocity.

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