

# Experimental investigation of combined mass transfer at gas-evolving electrodes with superposition of electrolyte flow

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**Abstract**—Experiments were conducted for mass transfer at a hydrogen-evolving electrode with superimposed electrolyte flow parallel to the electrode, a case which is of interest for the basic understanding of processes as well as for industrial applications. Results were compared with two conflicting design equations from the literature. One of them was clearly found superior from experimental data thus confirming more general considerations on the particular concentration conditions of dissolved gas in the vicinity of gas-evolving electrodes.

## 1. INTRODUCTION

IT HAS occasionally been stated that mass transfer due to gas evolution at an electrode is more effective than macroconvective mass transfer due to liquid flow past the electrode. This may be true for many cases but it is not generally correct. Mass transfer at gas-evolving electrodes is controlled by two effects which mutually interfere: microconvective and macroconvective mass transfer.

For large current densities and small flow velocities of electrolyte past an electrode, the microconvective effect due to bubble growth and departure predominates, and substantial errors are not introduced when using mass transfer equations which consider this effect only. Macroconvective mass transfer is negligible. The situation is reversed for large values of the electrolyte velocity (e.g. induced by pumping) and simultaneous low current density. Microconvective mass transfer becomes unimportant and hydrodynamic flow past the electrode governs mass transfer virtually alone. However, in most cases of industrial electrolysis the operational conditions are of such a kind that both effects are of the same order of magnitude, and both act jointly on mass transfer. Contrary to gas bubble-sparged electrodes, where a superimposed electrolyte flow may impede mass transfer due to bubble sparging [1], the combined mass transfer coefficient at gas-evolving electrodes is obviously always larger than any one of the individual coefficients. However, the mode of how to take account of the joint action of both effects is still an unsettled question. The problem was discussed generally in refs. [2, 3].

## 2. THE TWO DESIGN EQUATIONS

Fifteen years ago, Beck [4] suggested that the overall mass transfer coefficient is the summation of the

individual coefficients

$$k \equiv \frac{D}{\delta_N} = k_1 + k_2. \quad (1)$$

It was only in 1977 that a first attempt was made to verify experimentally equation (1) in a divided parallel plate cell [5]. Birkett and Kuhn found excellent agreement between experimental data and equation (1) under laminar flow conditions, but disagreement for large values of the flow velocity.

Based on the analogy with heat transfer where the same problem of superposition of macro- and microconvective transfer occurs in boiling and where a satisfactory correlation by Kutateladze [6] had been available, a corresponding correlation for combined mass transfer at gas-evolving electrodes was proposed [7]

$$k = (k_1^2 + k_2^2)^{0.5}. \quad (2)$$

Equation (2) involves a mutual interaction of both mechanisms. Contrary to equation (1) the effect of one of the individual mass transfer coefficients is decreased as the other one increases.

At present, there is indecision over which of the two equations should be considered superior. Both are used in electrochemical engineering [8, 9] and the choice depends on the subjective preference of the user. A clear criterion for their serviceability is missing. A closer look on the interaction of both mechanisms can be used to evaluate the situation.

## 3. INTERACTION OF THE TWO MECHANISMS

As is known from experiments by Shibata, the concentration of dissolved gas in electrolyte at the electrode-electrolyte interface is affected by stirring the electrolyte bulk, i.e. by the macroconvection conditions of electrolyte. It was shown that increased stirring of electrolyte bulk (or increased macro-

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## NOMENCLATURE

$D$	diffusion coefficient of transferred species [m <sup>2</sup> s <sup>-1</sup> ]	$k_2$	mass transfer coefficient due to microconvection [m s <sup>-1</sup> ]
$j$	current density [A m <sup>-2</sup> ]	$n$	exponent in equation (3)
$k$	combined mass transfer coefficient [m s <sup>-1</sup> ]	$v$	electrolyte velocity [m s <sup>-1</sup> ]
$k_1$	mass transfer coefficient due to macroconvection [m s <sup>-1</sup> ]	$\delta_N$	Nernst diffusion-layer thickness [m].

convective flow velocity) lowers the interfacial concentration of dissolved gas [10]. As is known from nucleation equilibrium, this will lower the number of active nucleus sites which, in turn, act on the mechanism of microconvection. Therefore, it was concluded that under this condition the electrolyte flow does not only enhance macroconvective mass transfer but also impedes the microconvective one [11].

On the other hand, the supersaturation at the electrode-electrolyte interface is strongly dependent on the current density which affects the number of active nucleous sites and, hence, the gas bubble coverage of the electrode surface. The rate of microconvection, therefore, acts on the macroconvective mass transfer by shielding a varying fraction of the electrode surface and, moreover, by a varying amount of hydrodynamic obstacles formed by the adhering bubbles [12]. Microconvection thus interferes with macroconvection in such a way that increasing microconvective mass transfer impedes the macroconvective one. It was further shown that macroconvective mass transfer even affects the rate of gas evolution at electrodes [13, 14]. It becomes evident that there is a mutual action of both mass transfer mechanisms: an increase of each of them lowers the other one. These reasons speak against equation (1) which simply describes the combined mass transfer coefficient as the sum of both individual coefficients. Equation (2) avoids this drawback and appears, if not as a good, at least as the better equation.

In fact, when testing equations (1) and (2) on the basis of data for mass transfer with superimposed macro- and microconvection obtained by Roald and Beck [15] nearly 25 years ago, equation (2) was clearly found to be superior [7]. However, it was argued with good reason that equation (2) had only been verified for one particular set of data [16]. Indeed, the old experimental data are not representative from today's point of view.

Roald and Beck used a simple stirred-beaker arrangement for dissolving magnesium in hydrochloric acid under the formation of hydrogen bubbles. The gas evolution was not the result of electrolysis nor was the geometry of the beaker comparable with that of an industrial electrochemical reactor. Kuhn and Hamzah compared both equations on the basis of data obtained in a hypochlorite cell [16] where

the cathodic reduction of hypochlorite is diffusion controlled and its rate is affected by both mechanisms. However, clear evidence of the superiority of one of the two equations could not be given: experimental data were closer to equation (1) at short reaction times and closer to equation (2) at longer times.

The reason may be seen partially in the method of comparing experimentally obtained mass transfer coefficients with data calculated from equations for pure micro- and macroconvective mass transfer, respectively [17]. Since inaccuracies of these under particular operating conditions (e.g. effect of the leading edge, real rate of gas evolution at a given current density) will directly increase the inaccuracy of the outcome, an improved procedure has to be found to test equations (1) and (2).

It is the objective of this report to compare both equations using mass transfer data obtained at a laboratory cell with gas-evolving electrodes and definite flow conditions of electrolyte. Operational conditions are varied in such a way as to ensure the combined mass transfer coefficient  $k$  as well as individual coefficients  $k_1$  and  $k_2$  are obtained from experiment in one and the same cell. Any reference to mass transfer equations to calculate individual coefficients becomes unnecessary.

## 4. EXPERIMENTAL

The object of investigation was a hydrogen-evolving cathode operating at various current densities and various electrolyte velocities of flow parallel to the surface.

The test cell used was equipped with planar, vertical platinum electrodes,  $48 \times 18 = 864 \text{ mm}^2$ , forming a part of the wall of a rectangular flow channel with a cross-sectional area  $20 \times 3 = 60 \text{ mm}^2$ , Fig. 1. Catholyte and anolyte were divided by a permselective membrane. Centrifugal pumps were used for both separate electrolyte systems. Mean flow velocities were 0.01, 0.18, and  $0.44 \text{ m s}^{-1}$ . Flow condition in the cell channel was always laminar. The distance covered from the electrolyte entrance into the cell to the electrode was 25 times the equivalent diameter to ensure developed flow profile when reaching the cathode. Current density was varied between 23 and  $5800 \text{ A m}^{-2}$ . The electrolyte was a solution of 2 M

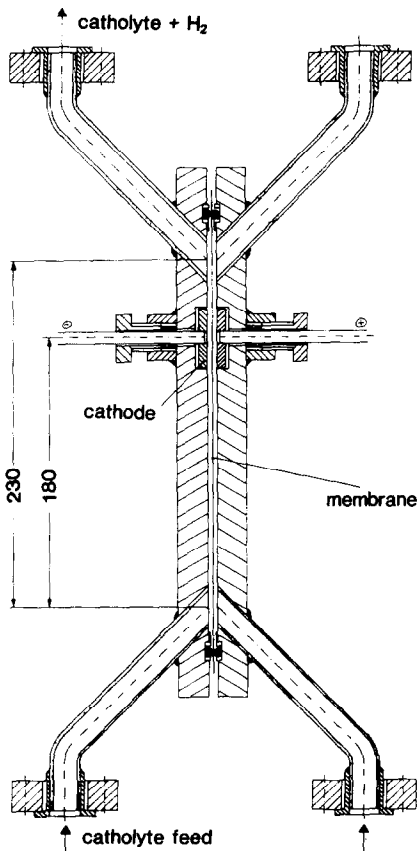


FIG. 1. Cross-sectional view of the experimental cell.

$\text{KOH} + 0.03 \text{ M } \text{K}_3\text{Fe}(\text{CN})_6 + 0.03 \text{ M } \text{K}_4\text{Fe}(\text{CN})_6$  maintained at  $25^\circ\text{C}$ . The rate of mass transfer at the cathode was measured by potentiometric titration of catholyte solution with cerium sulfate. Since the total catholyte volume in the system was 1500 ml it was necessary to run the plant for 60 min to obtain one data point. With this time-consuming procedure, the accuracy thus obtained in titration was within  $\pm 1.6\%$ .

## 5. RESULTS

Mass transfer coefficients at the gas-evolving electrode with superimposed electrolyte flow were determined for varied values of the current density and of the electrolyte velocity. Data points obtained following the procedure outlined in Section 4 are plotted in Fig. 2.

For the lowest possible mean velocity ( $0.01 \text{ m s}^{-1}$ ) and current density values up to  $1000 \text{ A m}^{-2}$ , the mass transfer coefficient increases with the square-root of the current density—in agreement with theory [3]. This operational case is considered to represent pure microconvective mass transfer. On the other hand, it is seen for velocities much larger than zero that when lowering the current density the combined mass transfer coefficient approaches a limiting value representing the case of pure macroconvective mass transfer. This result is in agreement with the observation made by Roald and Beck [15]. Experimental values for pure macroconvective and pure microconvective mass transfer, respectively, are thus available. They permit one to calculate combined mass transfer coefficients from equations (1) and (2) and to compare the results with the value obtained from experiment.

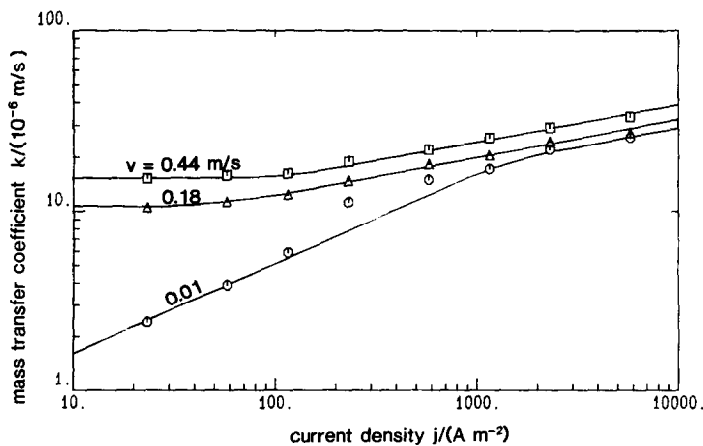
This method is considered superior to the methods used by other authors because in our case none of the mass transfer coefficients used for comparison between theoretical and empirical need be based on available design equations. The values used in this paper are obtained from the particular equipment they are applied to.

## 6. DISCUSSION

The conflicting equations (1) and (2) can both be expressed uniformly by

$$\frac{k}{k_1} = \left[ 1 + \left( \frac{k_s}{k_1} \right)^n \right]^{1/n} \quad (3)$$

where  $n = 1$  for equation (1) and  $n = 2$  for equation (2).


 FIG. 2. Mass transfer coefficient as a function of the current density  $j$  and the liquid velocity  $v$ .

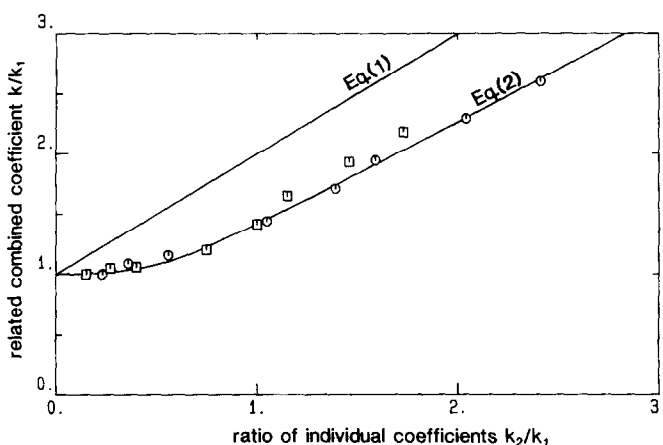


FIG. 3. Comparison of equations (1) and (2) on the basis of experimental data.  $\circ v = 0.18 \text{ m s}^{-1}$ ;  $\square v = 0.44 \text{ m s}^{-1}$ .

Experimental results are plotted in Fig. 3 in a non-dimensional form already used earlier [7]. Data points are shown in comparison with equations (1) and (2). It is seen that the experimental values fit equation (2) well and much better than (1).

This result agrees with the previous analysis [7] of the Roald and Beck data [15] and suggests that equation (2) be considered the superior equation.

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#### ETUDE EXPERIMENTALE DE TRANSFERT MASSIQUE COMBINE A DES ELECTRODES A GAZ AVEC SUPERPOSITION D'ECOULEMENT D'ELECTROLYTE

**Résumé**—Des expériences de transfert massique sont faites sur une électrode à hydrogène avec écoulement d'électrolyte parallèle à l'électrode, un cas intéressant pour la compréhension des mécanismes aussi bien que pour les applications industrielles. Des résultats sont comparés avec des équations contradictoires tirées de la littérature. L'une d'elles a été trouvée nettement supérieure à l'expérience, confirmant ainsi des considérations plus générales sur les conditions particulières de concentration du gaz dissous au voisinage des électrodes à gaz.

EXPERIMENTELLE UNTERSUCHUNG DES STOFFTRANSPORTES AN GAS-FREISETZENDEN ELEKTRODEN IN ANWESENHEIT EINER ÜBERLAGERTEN ELEKTROLYTSTRÖMUNG

**Zusammenfassung**—Der Stofftransport bei der Wasserstoff-Freisetzung an einer in Längsrichtung von Elektrolyt umströmten Elektrode wurde experimentell untersucht. Dieser Fall ist gleichermaßen für das grundlegende Verständnis der Vorgänge wie auch für die industrielle Anwendungen interessant. Die Ergebnisse wurden mit den Aussagen zweier widersprüchlicher Auslegungsbeziehungen aus der Literatur verglichen. Eine davon wird aufgrund der Versuchsdaten als die eindeutig bessere angesehen; dadurch werden allgemeinere Betrachtungen bezüglich der Konzentration von gelöstem Gas in unmittelbarer Nähe der gas-freisetzenden Elektroden bestätigt.

ЭКСПЕРИМЕНТАЛЬНОЕ ИССЛЕДОВАНИЕ СЛОЖНОГО МАССОБМЕНА У ВЫДЕЛЯЮЩИХ ГАЗ ЭЛЕКТРОДОВ В ПОТОКЕ ЭЛЕКТРОЛИТА

**Аннотация**—Проведены эксперименты по исследованию массообмена у электрода, выделяющего водород в параллельном электроду потоке электролита (случай, представляющий интерес для понимания основных закономерностей процесса, а также для промышленного применения). Результаты сравниваются с двумя различными расчетными формулами, встречающимися в литературе. Установлено, что одна из них значительно лучше описывает экспериментальные результаты, подтверждая, таким образом, более правильно общие соображения о распределении концентрации растворенного газа в непосредственной близости к выделяющим газ электродам.