

Mass transfer at gas-evolving electrodes at forced convection

Citation for published version (APA):

Janssen, L. J. J., & Barendrecht, E. (1985). Mass transfer at gas-evolving electrodes at forced convection. In E. Zieringiebel (Ed.), *Technische Elektrolysen : Vorträge von der Tagung der Fachgruppe Angewandte Elektrochemie der GDCh vom 17. - 19. Oktober 1984, [Leverkusen]* (pp. 463-478). (Dechema Monographien; Vol. 98). Verlag Chemie.

Document status and date:

Published: 01/01/1985

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
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Mass transfer at gas-evolving electrodes at forced convection

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Summary

Mass transfer of indicator ions to a gas-evolving electrode at forced convection has hardly been investigated. No useful relations describing the effect of current density i of gas evolution and velocity of bulk solution, v_s , upon the mass transfer coefficient for indicator ions, k_i , to gas-evolving electrodes are available.

In this investigation k_i have been determined for hydrogen-evolving and for oxygen-evolving electrodes in 1 M KOH and at 298 K. A standard mass transfer coefficient k_N , being k_i for an indicator ion with a diffusion coefficient of $10^{-9} \text{ m}^2 \text{ s}^{-1}$, has been introduced to obtain more useful relations. It has been found, that for a hydrogen-evolving electrode,

$$k_{N,H} = [2.06 + 8.6 v_s + 0.42 i_H \exp(-3.1 v_s)] 10^{-5} \text{ m s}^{-1}$$

and for an oxygen-evolving electrode

$$k_{N,O} = [0.84 + 6.7 v_s + 3.6 i_O^{0.85} \exp(-1.6 v_s)] 10^{-5} \text{ m s}^{-1}$$

where i_H and i_O are given in kA m^{-2} and v_s in m s^{-1} .

Zusammenfassung

Der Stofftransport von Indikator-Ionen zu einer gasentwickelnden Elektrode bei erzwungener Konvektion, ist bisher nur wenig untersucht worden. Es gibt praktisch keine Veröffentlichungen über brauchbare Beziehungen, zwischen der Stromdichte, i , der Gassetwicklung, der Geschwindigkeit des Elektrolyten, v_s , einerseits und dem Stofftransportkoeffizienten der Indikator-Ionen, k_i , zur gasentwickelten Elektrode andererseits. Bei unseren Untersuchungen wurde k_i für eine Wasserstoff- und Sauerstoff- entwickelnde Elektrode in ein 1 m KOH und bei 298° K bestimmt. Ein Standardstofftransportkoeffizient k_N , d.h. k_i für ein Indikator-Ion mit dem Diffusionskoeffizienten $10^{-9} \text{ m}^2 \text{ s}^{-1}$, wurde eingeführt, um die Gleichungen zu vereinfachen.

Es ist experimentell bestimmt worden dass für eine wasserstoffentwickelnde Elektrode

$$k_{N,H} = [2.06 + 8.6 v_s + 0.42 i_H \exp(-3.1 v_s)] 10^{-5} \text{ m s}^{-1}$$

und für eine sauerstoffentwickelnde Elektrode

$$k_{N,O} = [0.84 + 6.7 v_s + 3.6 i_O^{0.85} \exp(-1.6 v_s)] 10^{-5} \text{ m s}^{-1}$$

wobei i_H und i_O ausgedrückt sind in KA m^{-2} und v_s in m s^{-1} .

Résumé

On a peu examiné le transfert d'ions indicateurs vers une électrode à dégagement gazeux sous une convection forcée. Aussi, ne disposant pas de corrélation quantitative, nous tâchons d'en trouver; en experiment k_i , le coefficient de transfert, en fonction de la densité de courant, i , et de la vitesse, v_s , du liquide.

Dans nos recherches, k_i a été obtenu d'une solution de KOH, 1 m à 298°K, pour le dégagement d'hydrogène comme pour celui d'oxygène. Accomodé pour un ion indicateur avec un coefficient de diffusion de $10^{-9} \text{ m}^2 \text{ s}^{-1}$, k_i devient un coefficient de transfert standardisé k_N ; ici k_{NH} respectivement k_{NO} . Nous avons trouvé

$$k_{N,H} = [2.06 + 8.6 v_s + 0.42 i_H \exp(-3.1 v_s)] 10^{-5} \text{ m s}^{-1}$$

et

$$k_{N,O} = [0.84 + 6.7 v_s + 3.6 i_O^{0.85} \exp(-1.6 v_s)] 10^{-5} \text{ m s}^{-1}$$

où i_H et i_O sont représenté en KA m^{-2} et v_s en m s^{-1} .

1. INTRODUCTION

Mass transfer at gas-evolving electrodes has been studied extensively over the last twenty years because of its great importance in various industrial processes, e.g. chlorine, aluminium and zinc electrolysis. In particular, the mass transfer of indicator ions to a gas-evolving electrode at natural convection has been thoroughly investigated. A recent survey has been published by Vogt /1/. The mass transfer coefficient k_i , defined by D_i/δ , for indicator ions to a gas-evolving electrode is generally given by the correlation

$$k_i = a_1 v_g^{b_1}$$

where v_g is the volumetric rate of gas evolution per unit geometrical surface area of the electrode and the factors a_1 and b_1 depend on various parameters /1,2/.

Forced convection of solution is applied increasingly in industrial electrolyses, e.g. chlorate, hypochlorite and copper electrolysis and, especially, in many new organic electrochemical processes.

Only few experimental results on mass transfer of indicator ions to a gas-evolving electrode at forced convection of solution have been published /3,4/. Some empirical correlations for the mass transfer coefficient k_i have also been proposed, for instance,

$k_i = k_{f,i} + k_{d,i}^0$ /3/. The purpose of this study is to obtain more reliable experimental results on k_i for application in industrial electrolyses and thus a more useful correlation for k_i . The newly proposed correlation for k_i will be related to the one deduced theoretically for the convection-penetration model /5/.

2. EXPERIMENTAL

2.1. Electrolytic cell and electrolyte circuits

The electrolytic cell used for all mass transfer experiments is a two-compartment acrylate cell, the compartments being separated by an ion-exchange membrane (Naphion, type 427). The experimental set-up with two separated circuits of solution are sketched in Fig. 1. Parts of the electrolytic cell are schematically shown in Fig. 2. The inner dimensions of both compartments are the same: height 100 mm, width 30 mm and depth, the distance from the membrane to the inner back wall of the rectangular compartment, 10 mm. In each compartment the solution inlet and outlet are at the bottom and top, respectively. Unless otherwise stated, an acrylate support of the working electrode was placed in the

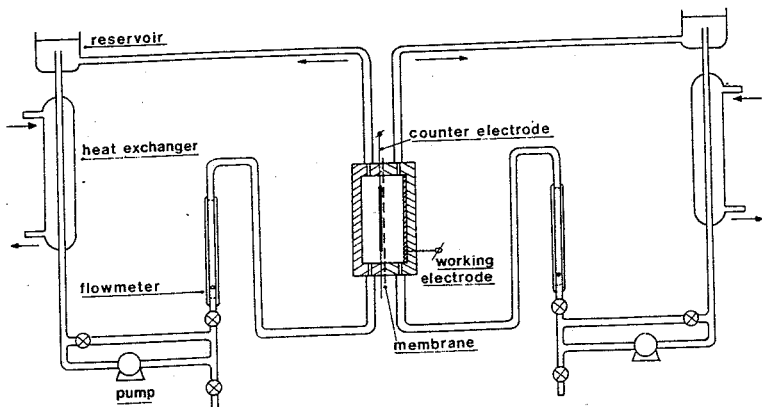


Fig. 1 Schematic diagram of experimental set-up for mass transfer experiments.

working-electrode compartment, so that the cross-section of solution flow at the level of the working electrode was 100 mm^2 and the distance from the working electrode to the membrane 7.5 mm. The working electrode was 8.0 mm in width and 60 mm in height; it was insulated at the rear. The counter electrode, made of Veco gauze, had the same geometrical dimensions and was pressed against the membrane just opposite the working electrode.

The thermostatted solutions were pumped through the electrode compartments, their volumetric flow rates were measured with a calibrated flowmeter (Fischer and Porter Tube: 3 F-3/8-25-5, Float SS-38, float material: stainless steel, density 8.02 g/cm^3). The flow rate in the counter-electrode compartment was smaller by a factor of 2 than that in the working-electrode compartment. The sizes of the solution reservoirs were sufficient to allow all bubbles to escape from the circulating solutions.

2.2. Electrolyte, analysis and procedure

A 1 M KOH solution was used as supporting electrolyte for all experiments. To determine the mass transfer coefficients for the oxygen-evolving electrode and the hydrogen-evolving electrode, respectively, $\text{K}_4\text{Fe}(\text{CN})_6$ and $\text{K}_3\text{Fe}(\text{CN})_6$ were added to the supporting electrolyte /2/. At the beginning of a series of experiments the concentration of the indicator ion was about 0.05 M, unless otherwise stated. The

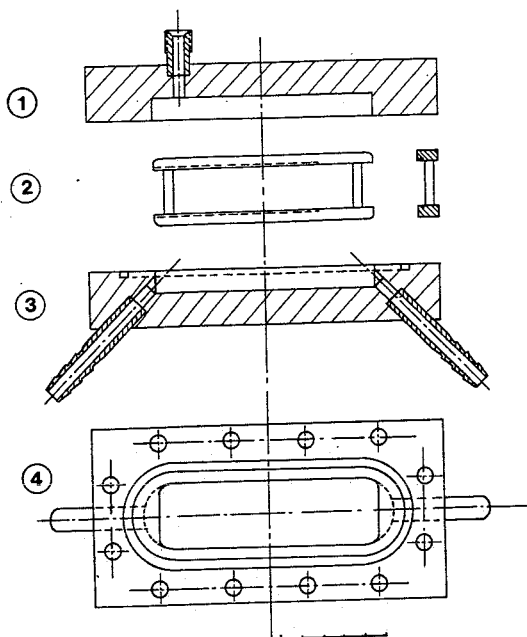


Fig. 2 Schematic diagram of electrolytic cell for mass transfer experiments.

1. cross-section A-B of working electrode compartment.
2. top view of electrode support.
3. cross-section A-B of counter electrode compartment.
4. top view of counter electrode compartment.

quantity of $\text{Fe}(\text{CN})_6^{3-}$ formed during the oxygen evolution was determined iodometrically and the quantity of $\text{Fe}(\text{CN})_6^{4-}$ formed during the hydrogen evolution was obtained by titration with Ce^{4+} /6/.

The rate of mass transfer was determined for series of experiments in sequence of decreasing current density at constant solution flow velocity or increasing solution-flow velocity at constant current density. The following procedure was applied as a general rule. Before each series of experiments the working electrode was polarized in the supporting electrolyte for 60 minutes at the highest current density of the

projected series of experiments, unless otherwise stated. After this pre-electrolysis and, without current switch-off, a calculated quantity of solution containing 1 M KOH and 1 M $K_3Fe(CN)_6$ or 1 M $K_4Fe(CN)_6$ was added to the working-electrode compartment to obtain an indicator ion concentration of 0.05 M.

As soon as the solution was homogeneous, a 25cm³ sample of solution was taken and analysed. After a polarization time of 20 minutes, the next projected current in the series of experiments was adjusted and a 25cm³ sample was taken again. The same procedure was applied for the subsequent currents in the series of experiments. No current interruption occurred during the whole series of experiments. The series of experiments with various solution-flow velocities were carried out analogously.

The maximum decrease in $K_4Fe(CN)_6$ or $K_3Fe(CN)_6$ concentration for an experiment in a series was about 6%. For the hydrogen experiments the increase in $Fe(CN)_6^{4-}$ concentration was practically equal to the decrease in $Fe(CN)_6^{3-}$ concentration. A similar result was found for the oxygen experiments. During a series of experiments, the volume of the solution in the working-electrode compartment became smaller because of sample taking.

In the calculation of the mass transfer coefficient, the decrease in volume of the solution in the working-electrode compartment and the decrease in concentration of the indicator ion were taken into account.

3. RESULTS

In describing the mass transfer of indicator ions to a gas-evolving electrode, the mass transfer coefficient k_i for the indicator ion is preferred to the thickness of the Nernst diffusion layer

$$\delta_i = D_i/k_i.$$

For hydrogen-evolving as well as oxygen-evolving electrodes it has been found that, at both forced and natural convection, and from a very low current density i_g of gas evolution the mass transfer coefficient k_i can be presented by the relation

$$k_i = k_{e,i} + a_1 \frac{i_g^b}{i_l} \exp(-a_2 v_s) \quad (1)$$

where $k_{e,i} = k_i$ at $i_g = 0 \text{ kA/m}^2$ obtained by extrapolation of the k_i/i_l^b curve. Moreover, $k_{e,i}$ can be given by

$$k_{e,i} = k_{e,i}^0 + a_3 v_s \quad (2)$$

3.1. Hydrogen-evolving electrode

3.1.1. Rate of gas evolution

For a vertical nickel electrode in 1 M KOH and 298 K, Fig. 3 shows the results of a series of experiments at a bulk flow velocity $v_s = 0.36 \text{ m s}^{-1}$ and those of two series of experiments at $v_s = 0.12 \text{ m s}^{-1}$. From this figure it follows that the k_{fi}/i_H curves are straight, even from very low i_H , viz. 0.04 kA/m^{-2} at $v_s = 0.12 \text{ m s}^{-1}$. This linear behaviour was also found up to 10 kA/m^{-2} . Unpublished results for a vertical platinum disk-electrode of 10-mm diameter [2] showed that, for i_H from 0.75 to 8 kA m^{-2} , $k_{fi} = (2.0 + 0.080 i_H) 10^{-5} \text{ m s}^{-1}$ where i_H is given in kA m^{-2} . For the same electrode in horizontal position a clear deviation from the linear relationship was already obtained at $i_H < 0.80 \text{ kA m}^{-2}$.

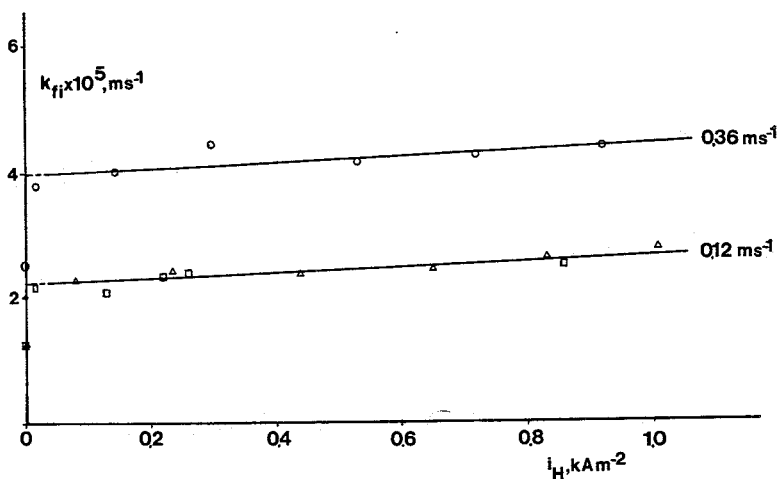


Fig. 3 Mass transfer coefficient for $\text{Fe}(\text{CN})_6^{3-}$ to a hydrogen-evolving nickel electrode in 1 M KOH and at 298 K and two different bulk solution flow velocities v_s is plotted versus the current density of hydrogen evolution. For $v_s = 0.12 \text{ m s}^{-1}$, the results of two series of experiments are given.

3.1.2. Solution flow velocity

The effect of the bulk solution flow velocity, v_s , on k_{fi} was determined by carrying out the series of experiments at increasing v_s and at $i = 0.53$ and 6.37 kA . The rate of mass transfer of indicator ions

changed with increasing v_s during a series of experiments at constant current density. Consequently, i_H has to change too. Because of this change, k_{fi} at i_H , being almost the average i_H for a series of experiments, is calculated using the dependence of k_{fi} on i_H at a constant v_s obtained from the series of experiments at $i = 0.53$ and 6.37 kA.

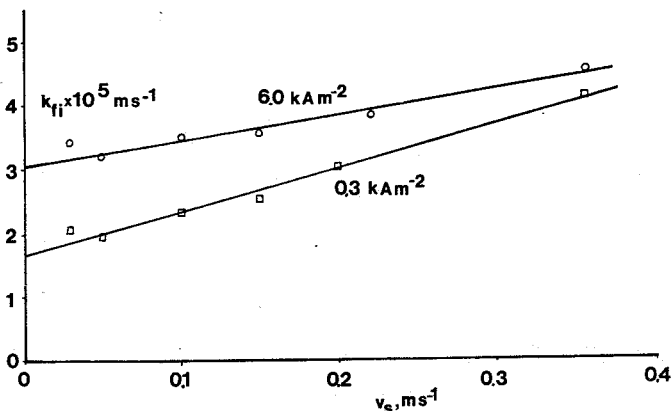


Fig. 4 Mass transfer coefficient for $\text{Fe}(\text{CN})_6^{3-}$ to a hydrogen-evolving nickel electrode in 1 M KOH and at 298 K and two different current densities i_H of hydrogen evolution, is plotted versus the bulk flow velocity v_s .

In Fig. 4, k_{fi} is plotted versus v_s for $i_H = 0.30$ and 6.0 kA m^{-2} . This curve shows an increasing effect of v_s at decreasing i_H .

To obtain a relation for k_{fi} as a function of i_H and v_s and starting from the relation for k_{fi} at a constant v_s , viz. $k_{fi} = k_{e,fi} + h_{fi} i_H$, the dependence of $k_{e,fi}$ and h_{fi} on v_s has to be determined. These dependences are obtained from the results of Fig. 4. It has been found that the logarithm of the slope h_{fi} of the k_{fi}/i_H curves plotted versus v_s gives a straight line, represented by

$$h_{fi} = 0.26 \times 10^{-5} \exp(-3.1 v_s) \text{ m}^3 \text{ s}^{-1} \text{ kA}^{-1}.$$

The dependence of $k_{fi,e}$ on v_s can also be obtained from Fig. 4. From experimental results it follows that $k_{e,fi} = k_{e,fi}^0 + a_3 v_s$, viz. $k_{e,fi} = 1.6 \times 10^{-5} + 6.7 \times 10^{-5} v_s \text{ m s}^{-1}$.

Summarizing the preceding discussion on dependences of k_{fi} on v_s and i_H , the mass transfer coefficient

$$k_{fi} = [1.6 + 6.7 v_s + 0.26 i_H \exp(-3.1 v_s)] 10^{-5} \text{ m/s where } v_s \text{ is given in } \text{m s}^{-1} \text{ and } i_H \text{ in } \text{kA m}^{-2}.$$

Assuming that all gas formed is evolved as bubbles on the electrode and taking into account $v_{g,H} = V_H i_H / 2F$, that is

$1.268 \times 10^{-4} i_H \text{ m s}^{-1}$ at 298 K where i_H is given in kA m^{-2} , the mass transfer coefficient can also be given by

$$k_{fi} = [1.6 + 6.7 v_s + 0.20 \times 10^{+4} v_{g,H} \exp(-3.1 v_s)] \times 10^{-5} \text{ m s}^{-1}$$

where v_s and $v_{g,H}$ are given in m s^{-1} .

3.1.3. Electrode geometry

To study the effect of the electrode geometry, a part of the experiments was carried out in an electrolysis cell similar to the one used for investigating the other parameters. In this case, the electrodes except the flat-plate electrode were pressing against an ion exchange membrane (Naphion 4257). The flat-plate electrode was placed against the back wall of the compartment of the working electrode. The distance between the flat-plate electrode and the membrane was about 10 mm. No pre-polarisation of the working electrode was applied and the series of

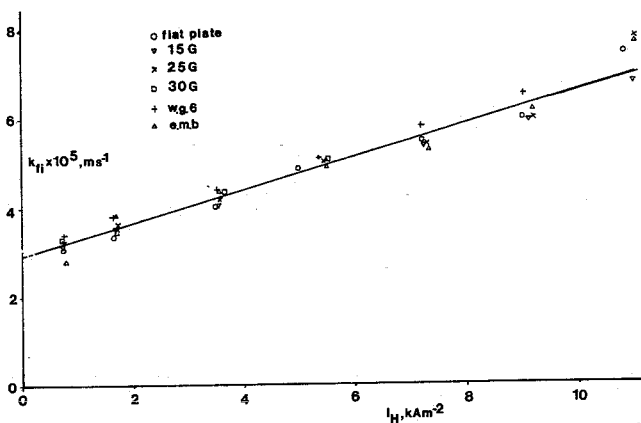


Fig. 5 Mass transfer coefficient for $\text{Fe}(\text{CN})_6^{3-}$ to a hydrogen-evolving nickel electrode in 1 M KOH and at 298 K and a bulk solution flow velocity of 0.03 m s^{-1} , is given as a function of current density i_H of hydrogen evolution for various electrode geometries. The working electrodes, except the flat-plate electrode, were pressed against the membrane.

experiments started with the highest current. In Fig. 5 the mass transfer coefficient k_{fi} is plotted versus i_H for various types of electrodes [flat plate, woven gauze, (w.g.6. /2/), expanded metal gauze (e.m.b. /2/) and perforated plate, (Veco type 15G, 25G and 30G)]. To calculate k_{fi} , the geometrical surface area of the electrodes was taken into account. Fig. 5 shows that for all the investigated geometries, the mass transfer coefficient can be given by $k_i = k_{e,i} + a_4 i_H$ where the factor a_4 does not depend on the electrode geometry. The obtained differences in $k_{e,i}$ may be attributed to differences in the nature of the electrode surface, since there was no close correlation between $k_{e,i}$ and $k_{f,fi}$, where $k_{f,fi}$ is the mass transfer coefficient k_{fi} at forced convection in the absence of bubble formation. It has been found that in the investigated range for v_s from 0.003 to 0.04 $m\ s^{-1}$ there is no significant effect of v_s on k_{fi} at $i_H = 0.7$ and 4.2 $kA\ m^{-2}$.

3.2. Oxygen-evolving electrode

3.2.1. Rate of gas evolution

The mass transfer coefficient k_{fo} is given as a function of i_o in Fig. 6 for an oxygen-evolving electrode in 1 M KOH and at 298 K and

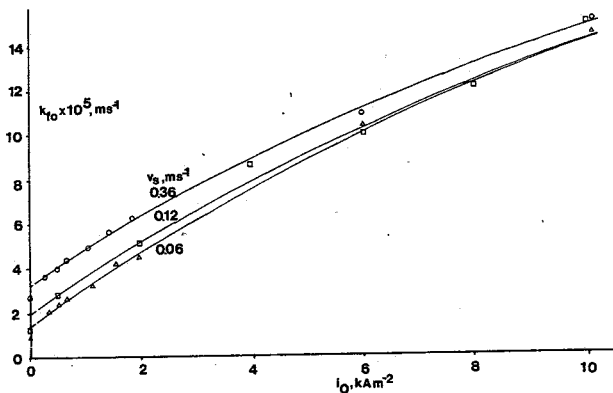


Fig. 6 Mass transfer coefficient for $Fe(CN)_6^{4-}$ to an oxygen-evolving nickel electrode in 1 M KOH and at 298 K and three different bulk solution velocities is plotted versus the current density of oxygen evolution.

various bulk solution flow velocities v_s . From the results of Fig. 6 it can be deduced that $k_{fo} = k_{e,fo} + a_4 i_0^{b_2}$ where b_2 is practically independent of v_s and $b_2 = 0.85$. It has been found that, in the investigated range of v_s , viz. from 0.06 to 0.36 m s^{-1} , $k_{e,fo}$ is only slightly less than $k_{f,fo}$.

From unpublished results for a vertical and a horizontal platinum disk-electrode of 10-mm diameter /2/ it followed that the mass transfer coefficient is given by, respectively, $k_{fo} = 0.5 + 2.9 i_0^{0.88}$ and $k_{fo} = 3.7 i_0^{0.83}$ where i_0 is given in kA m^{-2} .

3.2.2. Solution flow velocity

Analogously to the hydrogen-evolving nickel electrode, the effect of v_s on k_{fo} was studied for the oxygen-evolving nickel electrode. It has been found that, in particular, at high i_0 , for instance 6 kA m^{-2} , the experimental sequence in a series of experiments at various v_s strongly affects the results obtained. To eliminate this effect, k_{fi} was determined alternately at $v_s = 0.03$ and 0.36 m s^{-1} . After three alternations k_{fi} had attained a stationary value, whereupon k_{fi} was determined at 0.15 m s^{-1} . From the experiments at $i = 0.53$ and 6.37 kA

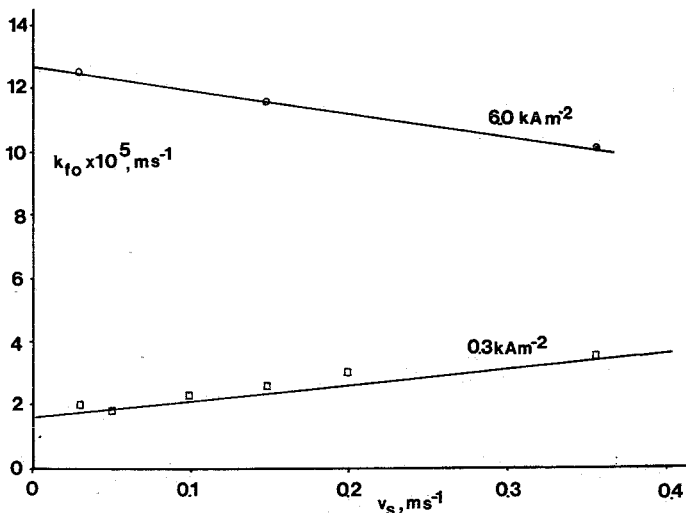


Fig. 7 Mass transfer coefficient for Fe(CN)_6^{4-} to an oxygen-evolving nickel electrode in 1 M KOH and at 298 K and two different current densities i_0 of oxygen evolution is plotted versus the bulk flow velocity v_s .

m^{-2} and various v_s , k_{fo} was determined at 0.40 and 6.0 kA m^{-2} as described in 3.1.2 for k_{fi} . The result is given in Fig. 7. This figure shows that at high i_o , k_{fo} decreases with increasing v_s and at low i_o , k_{fo} increases with increasing v_s . A relation for k_{fo} as a function of i_o and v_s is deduced by analogy with 3.1.2.

Taking into account that the increase in k_{fo} is proportional to $i_o^{0.85}$, k_{fo} from Fig. 7 was plotted versus $i_o^{0.85}$ for various v_s . The results were given by $k_{fo} = k_{e,fo} + h_{fo} i_o^{0.85}$. It has been found that $h_{fo} = 2.8 \times 10^{-5} \exp(-1.6 v_s)$ and $k_{e,fo} = 0.65 \times 10^{-5} + 5.2 \times 10^{-5} v_s$ where v_s is given in m s^{-1} . Summarizing the obtained dependences of k_{fo} on i_o and v_s , the mass transfer coefficient

$$k_{fo} = [0.65 + 5.2 v_s + 2.8 i_o^{0.85} \exp(-1.6 v_s)] 10^{-5} \text{ m/s}$$

where i_o is given in kA m^{-2} and v_s in m s^{-1} .

Assuming that all the oxygen is evolved as bubbles on the electrode and taking into account $v_{g,o} = v_M i_o / 4F$, that is $0.634 \times 10^{-4} i_o \text{ m s}^{-1}$ at 298 K, where i_o is given in kA m^{-2} , the mass transfer coefficient k_{fo} can also be given by

$$k_{fo} = [0.65 + 5.2 v_s + 4.42 \times 10^{-4} v_{g,o}^{0.85} \exp(-1.6 v_s)] 10^{-5} \text{ m/s},$$

3.2.3. Electrode geometry

The effect of the electrode geometry on mass transfer for an oxygen-evolving electrode has been studied likewise for a hydrogen-evolving electrode. In Fig. 8 the mass transfer coefficient k_{fo} is plotted versus i_o for various unprepolarised types of electrodes [flat plate, woven gauze (w.g.6. /2/), expanded metal gauze (e.m.b. /2/) and perforated plate (Veco type 10H, 15G, 25G and 30G)]. This figure shows that the increase in k_{fo} with increasing i_o is practically independent of the electrode geometry and that $k_{e,fo}$ varies. Since there is no systematic change in $k_{e,fi}$ for the electrodes of Veco type G and the results obtained for the second series of experiments where k_{fo} was determined at a current density of 6 kA m^{-2} at various v_s did not show the same correlation between k_{fo} and the electrode geometry, it is concluded that the differences in $k_{e,fo}$ are mainly caused by differences in the nature of the electrode surface.

In the range investigated for v_s from 0.003 to 0.04 m s^{-1} , k_{fo} was practically independent of v_s at both $i_H = 0.8$ and 5.0 kA m^{-2} .

As shown in the preceding discussion, the nature of the electrode surface

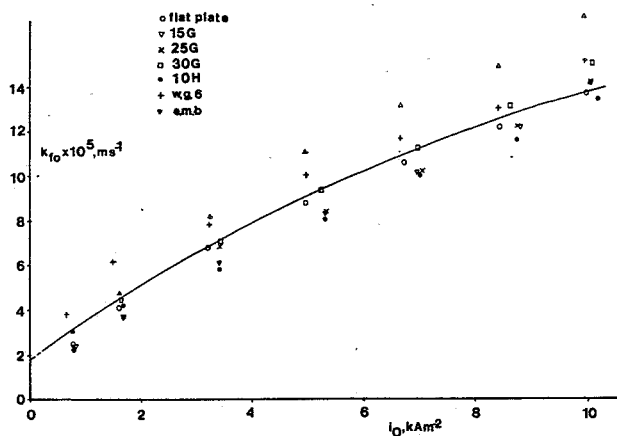


Fig. 8 Mass transfer coefficient for $\text{Fe}(\text{CN})_6^{4-}$ to an oxygen-evolving nickel electrode in 1 M KOH and at 298 K and a bulk solution flow velocity of 0.03 m s^{-1} is given as a function of current density i_0 of oxygen evolution for various electrode geometries. The working electrodes except the flat plate electrode were pressed against a membrane.

affects $k_{e,fo}$. For two electrodes of the perforated plate Veco, type 12.5G with surfaces completely different in nature - one electrode without prepolarisation and the other electrode polarised cathodically for a 3-week period in a 1 M KOH, the mass transfer coefficient k_{fo} is given in Fig. 9 as a function of i_0 . The size of the departing oxygen bubbles for the cathodically prepolarised electrode was comparable to the usual size of hydrogen bubbles. Consequently, the difference in the k_{fo}/i_0 relation is caused by a difference in the nature of the electrode surface.

In general, the behaviour of oxygen bubbles is practically the same for the normal electrode materials assuming the usual pretreatment.

4. DISCUSSION

A short survey of the relations given in literature for the mass transfer coefficient of indicator ions to a gas-evolving electrode at forced convection of bulk solution has been published by Vogt /1/.

The experimental relations given in section 3.1.2 and 3.2.2 for, respectively, hydrogen-evolving and oxygen-evolving electrodes in alkaline

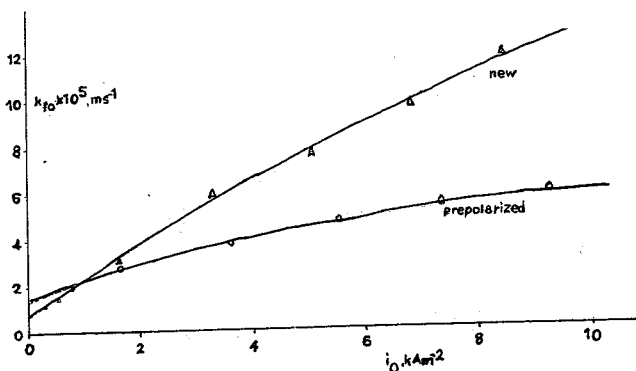


Fig. 9 Effect of nature of electrode surface on the relation between k_{fo} and i_o . One electrode was not prepolarised and the other was cathodically prepolarised for a period of about 3 weeks in a 1 M KOH solution.

solution are much more complicated than those given in literature. The mass transfer coefficient k_i of an indicator ion depends on its diffusion coefficient. The Sherwood number is generally used to describe the mass transfer to an electrode at forced convection of bulk solution and without bubble evolution on the electrode. The Sherwood number $Sh = k_i d / D_i$ where d is the equivalent diameter of electrolysis cell. Vogt /1/ has also introduced the Sherwood number for a gas-evolving electrode at natural convection where d is a characteristic diameter for bubbles departing from the electrode surface. However, for a gas-evolving electrode at forced convection it is very difficult or even impossible to define the characteristic length d present in the relation for Sh . In order to establish a useful relation for mass transfer, a standard mass transfer coefficient k_N is equal to k_i for an indicator ion with a diffusion coefficient of $10^{-9} \text{ m}^2 \text{ s}^{-1}$. From k_{fo} (3.2.2) and $D_{fo} = 7.0 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ /2/ and using the dependence of k_i on D_i for laminar flow, with k_i proportional to $D_i^{2/3}$ /7/ it can be shown that the standard mass transfer coefficient for an oxygen-evolving electrode in 1 M KOH at 298 K is given by

$$k_{N,O} = [0.84 + 6.7 v_s + 3.6 i_o^{0.85} \exp(-1.6 v_s)] 10^{-5} \text{ m/s}$$

where i_o is given in kA m^{-2} and v_s in m s^{-1} .

Similarly, from k_{fi} (3.1.2) and $D_{fi} = 7.9 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ /2/ it can be shown that the standard mass transfer coefficient for a hydrogen-evolving electrode in 1 M KOH and at 298 K is given by

$$k_{N,H} = [2.06 + 8.6 v_s + 0.42 i_H \exp(-3.1 v_s)] 10^{-5} \text{ m/s}$$

It should be noted that k_i is proportional to $D_i^{1/2}$ for so-called semi-infinite linear diffusion, to $D_i^{2/3}$ for laminar flow and to $D_i^{3/4}$ for turbulent flow /7/.

For the relations for k_N , the standard mass transfer coefficient at natural convection, $k_{N,O}^0$ can be deduced. It can be shown that

$$k_{N,O}^0 = [0.84 + 3.6 i_O^{0.85}] 10^{-5} \text{ m/s}$$

$$\text{and } k_{N,H}^0 = [2.06 + 0.42 i_H] 10^{-5} \text{ m/s.}$$

Taking into consideration the effect of the term $3.6 i_O^{0.85}$ with respect to 0.84 in the relation for $k_{N,O}^0$ it is clear that this relation agrees very well with the experimental slope, viz. -0.87, of the $\log \delta / \log i_O$ curve at $i_O > 0.3 \text{ kA m}^{-2}$ /8/, where $\delta = D_i / k_i$.

The slopes of the $\log \delta / \log i_H$ curve show a wide spread /1/. It may be caused by a relatively small effect of the second term in the relation for $k_{N,H}^0$. Moreover, the measured range of i_H will clearly affect the slope of the $\log \delta / \log i_H$ curve.

LITERATURE

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LIST OF SYMBOLS AND UNITS

a	: proportional factor	
b	: index factor	
A_e	: surface area of electrode	(m ²)
c_i	: concentration of species i in bulk of solution	(mol/m ³)
D_i	: diffusion coefficient of species i	(m ² /s)
E	: electrode potential versus SCE	(V)
F	: = 96.487 10 ⁶ C/kmol, Faraday constant	
h_{fi}	: slope of k_{fi}/i_H curve	(m ³ /kAs)
h_{fo}	: slope of k_{fo}/i_O curve	(m ³ /kAs)
i	: electric current density	(kA/m ²)
I	: electric current	(kA)
k_i	: mass transfer coefficient of the indicator ion i	(m/s)
k_i^o	: mass transfer coefficient of the indicator ion i in absence of forced convection or in a convectionless solution	(m/s)
$k_{e,i}$: mass transfer coefficient of the indicator ion i obtained by extrapolation of k_i/i_g^b curve	(m/s)
$k_{f,i}$: mass transfer coefficient of the indicator ion i at forced convection in absence of gas bubble evolution	(m/s)
n	: number of electrons, involved in the reaction to form one molecule of a species	(l)
t	: time	(s)
T	: temperature	(K)
v_s	: solution flow velocity	(m/s)
V_M	: volume of 1 mol gas; 24.4 x 10 ⁻³ m ³ at 298K	(m ³ /mol)

SUBSCRIPTS

e	: electrode; extrapolated
f	: forced convection
fi	: ferricyanide ion
fo	: ferrocyanide ion
g	: gas, H or O
H	: hydrogen
i	: indicator ion i
N	: standard
O	: oxygen
s	: solution