JOURNAL OF APPLIED ELECTROCHEMISTRY 15 (1985) 517–526

*Modelling of gas evolving electrolysis cells. I. The gas voidage problem**

G. KREYSA, M. KUHN

Dechema-Institut, Theodor-Heuss-Allee 25, 6000 Frankfurt/Main 97, Germany

Received 9 November 1984

A critical review of experimental gas voidage data for gas–liquid mixtures available in the literature yields the result that these data cannot be explained by known theories of the gas hold-up. Based on the empirical experience that bubble coalescence is hindered in electrolyte solutions, new equations are derived for the calculation of the gas voidage as a function of the superficial gas velocity by introducing a coalescence barrier model. Experimental investigations confirm the theoretical prediction of the existence of a limiting gas voidage which is a characteristic quantity of each gas–electrolyte combination.

Nomenclature

A	area (cm^2)
a_m	minimum bubble distance (cm)
E	energy (J)
F	Faraday constant (A s mol^{-1})
G	volumetric gas flow rate (cm^3 s^{-1})
h	height (cm)
L	volumetric liquid flow rate (cm^3 s^{-1})
p	pressure (Pa)
R	gas constant (J mol^{-1} K^{-1})
T	temperature (K)
u	rise velocity (cm s^{-1})
u^0	superficial flow velocity (cm s^{-1})
γ	surface tension (J cm^{-2})
ϵ	voidage (1)
ϵ_m	limiting voidage (1)
χ	conductivity (S cm^{-1})
ν_e	number of electrons (1)

Subscripts

b	bubble
g	gas phase
l	liquid phase
s	single bubble
sw	bubble swarm

1. Introduction

In modelling gas evolving cells, a subject which will be treated in more detail in part II of this communication, the local conductivity of the gas–liquid mixtures in the electrolyte chambers has to be calculated. Some of the equations available in the literature [1–9] for this purpose are listed in Table 1. A further model assuming a higher gas voidage in a layer near the electrode has been published recently by Bongenaar-Schlenter *et al.* [10]. In Fig. 1 the relative conductivity according to the expressions listed in Table 1 is shown as a function of the gas voidage. The deviations between these various equations are quite small and nearly always less than 10%. A number of electrochemical papers [8, 9, 11–16] discuss these and other equations critically and the Maxwell and the Bruggemann equations are mainly recommended as being reliable.

All conductivity equations require knowledge of the gas voidage which depends on the volumetric gas flow rate for a stationary liquid. Therefore the gas voidage is a function of the superficial gas velocity. The actual rise velocity of the gas bubbles within the electrolyte is defined by the following equation.

---

[*] Paper presented at the International Meeting on Electrolytic Bubbles organized by the Electrochemical Technology Group of the Society of Chemical Industry, and held at Imperial College, London, 13–14 September 1984.

0021-891X/85 $03.00 + .12

Table 1. Conductivity equations for gas–liquid mixtures

Conductivity equation	*Author*
$\frac{\chi}{\chi_0} = \frac{1-\epsilon_g}{1+\epsilon_g}$	Rayleigh [1]
$\frac{\chi}{\chi_0} = \frac{1-\epsilon_g}{1+(\epsilon_g/2)}$	Maxwell [2], Nader [3]
$\frac{\chi}{\chi_0} = \frac{8(2-\epsilon_g)(1-\epsilon_g)}{(4+\epsilon_g)(4-\epsilon_g)}$	Tobias [4, 5]
$\frac{\chi}{\chi_0} = (1-\epsilon_g)^{3/2}$	Bruggeman [6]
$\frac{\chi}{\chi_0} = 1-1.5\epsilon_g+0.5\epsilon_g^2$	Prager [7]

$$u_b = u_g^0/\epsilon_g \tag{1}$$

Rearranging gives,

$$\epsilon_g = (1/u_b)u_g^0 \tag{2}$$

and this shows that the dependence of the gas voidage on the superficial gas velocity is mainly determined by the manner in which the bubble velocity itself depends on the gas voidage. Treatment of this point is not unique in the literature and different assumptions have been introduced by several authors [11, 17–22]. Tobias [17] has assumed that the gas rise velocity is independent of the gas voidage. This corresponds to the straight line 1 in the schematic ϵ_g versus u_g^0 diagram shown in Fig. 2. As is easily seen this can only be a reasonable approximation for small gas voidages because the gas voidage cannot be larger than 1. According to the well known fact that the rise velocity of a bubble swarm is smaller than that of a single bubble, Vogt [22] has suggested that the bubble rise velocity decreases with increasing gas voidage. This corresponds to curve 2 in Fig. 2. Contrary to curves 1 and 2 a behaviour as indicated by curve 3 should be expected taking into account the gas voidage converging to 1. Comparing curve 3 with Equation 2 results in the conclusion that the bubble rise velocity u_b should increase with increasing gas voidage. This discussion shows that for reliable modelling of gas evolving electrolysis cells more attention should be drawn to the problem of how the gas voidage depends on the superficial gas velocity.

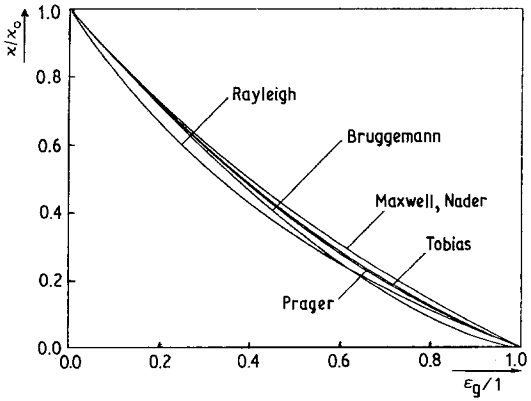

Fig. 1. Relative conductivity of gas–liquid mixtures.

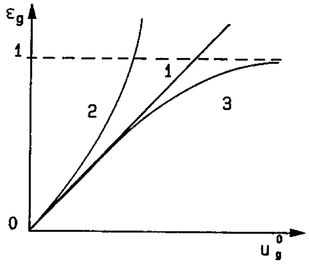

Fig. 2. Schematic dependence of gas voidage on superficial gas velocity (1–constant bubble rise velocity, 2–rise velocity decreases with ϵ_g, 3–expected behaviour).

A first attempt to overcome this situation has been made by Nicklin [23, 24], who derived an equation

$$u_b = u_g^0 + u_l^0 + u_{sw} \tag{3}$$

showing that the bubble rise velocity is determined by three components: the superficial gas velocity, the superficial liquid velocity and a rise velocity due to buoyancy corresponding to the swarm rise velocity. Several equations are available from the literature [8, 25–28] for the calculation of the rise velocity of bubble swarms and these are listed in Table 2. In Fig. 3 the relative velocity of bubble swarms is plotted as a function of the gas voidage. In contrast to the conductivity equations the deviations of these equations are much higher. Calculation of the absolute rise velocity of a bubble swarm requires a knowledge of the rise velocity of a single bubble. Some of the equations available for this are summarized by Brauer [29].

2. Critical discussion of the Nicklin equation

Introducing Equation 1 into Equation 3 and rearranging yields:

Table 2. Equations for the rise velocity of bubble swarms

Equations	*Author*
$u_{sw} = u_s \left\{ 1 \middle/ \left[1 + \frac{\epsilon_g}{(1-\epsilon_g)^2} \right] \right\} \left\{ (1-\epsilon_g) \middle/ \left[1 + \frac{1.05}{(1 + 0.0685/\epsilon_g^2)^{0.5} - 0.5} \right] \right\}$	Kaskas [25]
$u_{sw} = u_s \frac{(1-\epsilon_g)^2}{1-\epsilon_g^{5/3}}$	Marucci [26]
$u_{sw} = u_s (1-\epsilon_g)^{4.65}$	Richardson–Zaki [27]
$u_{sw} = u_s \left\{ (1-\epsilon_g) \middle/ \left[1 + \frac{1.05}{(1 + 0.0685/\epsilon_g^2)^{0.5} - 0.5} \right] \right\}$	Brauer [28]

$$\epsilon_g = \frac{1}{1 + [(u_l^0 + u_{sw})/u_g^0]} \qquad (4)$$

From this equation it is seen that ϵ_g converges to 1 for an infinite superficial gas velocity as expected. A similar equation has also been derived by Funk and Thorpe [18]. The importance of the Nicklin equation with respect to the conductivity of gas–liquid mixtures was firstly recognized by Ibl and coworkers [30]. However, in that paper there are some results which are not consistent with the Nicklin equation. In Fig. 6 of [30] the authors have shown, in a plot of experimental bubble velocities as a function of the sum of the superficial gas and liquid velocity, that all points fall together onto a straight line. In terms of Equation 3 this would mean that the rise velocity, u_{sw}, is independent of the gas voidage which is not true. Since for $\epsilon_g = 1$ the bubble velocity is equal to the superficial gas velocity it follows from Equation 3 that u_l^0 and u_{sw} must be zero.

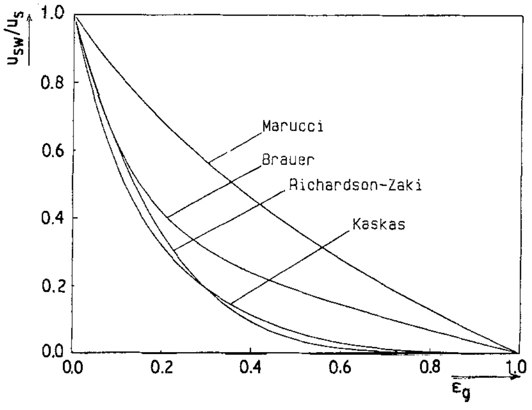

Fig. 3. Relative rise velocity of bubble swarms.

Ibl and coworkers [30] have also published experimental voidage data measured at various superficial gas and liquid flow velocities. In Fig. 4 the bubble velocity calculated from these data using Equation 1 is plotted as a function of $u_g^0 + u_l^0$. Contrary to the prediction of the Nicklin Equation 3 not all points fall together onto one curve but every data group for a certain superficial liquid velocity forms a separate curve.

In Fig. 5 gas voidage data measured by Siemes [31] for air in water are plotted as a function of the superficial gas velocity. These experiments were carried out in a stationary liquid phase. For the sake of comparison a theoretical line calculated using Equation 4 is also plotted. Comparing the theoretical and experimental shape of the curves a large difference is seen. In contrast to the Nicklin equation experimental gas voidage data do not converge to 1 but to a certain value less than 1. This result is of great significance and has important consequences for modelling of electrolysis cells as will be shown later. The experimental result that with increasing superficial gas velocity there exists a limiting gas voidage, as also confirmed by our investigations, requires a modification of the Nicklin equation by an additional model. Such a model is suggested in the following.

3. The coalescence barrier model

It is well known that coalescence of gas bubbles in electrolyte solutions takes place to a much less extent than in pure water. If two bubbles of diameters d_1 and d_2 are coalescing, a new bubble of diameter d_n is formed. The change of surface energy due to this process is given as

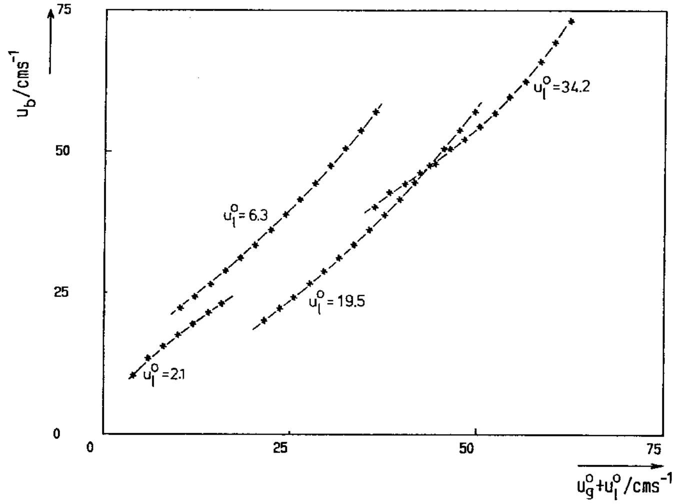

Fig. 4. Bubble velocity as function of $u_g^0 + u_l^0$ evaluated from experimental data given by Ibl *et al.* [30].

$$\Delta E = \gamma_{gl}\Delta A \tag{5}$$

Since the surface area of the new bubble is always smaller than that of the two small bubbles this energy change is always negative. However, in electrolyte solutions coalescence is obviously not a spontaneous process as indicated by this negative change of surface energy. Therefore an activation energy barrier for coalescence must exist. Two physical reasons may be responsible for this activation barrier. Liquid molecules near the gas liquid interface are attracted by the liquid bulk due to their asymmetric surrounding resulting in a small layer of increased pressure around the gas bubble. This leads to a certain repulsion if two gas bubbles come close together. Recently it has been reported [32] that gas bubbles in electrolyte solutions have a negative surface charge due to an excess of $\mathrm{OH^-}$ near the interface. This means that an electrostatic repulsion also retards the coalescence. Assuming such a coalescence barrier yields the conclusion that gas bubbles in a swarm are separated from each other by a minimum distance a_m. From elementary geometric considerations for various lattice types of bubble arrangement the following equation

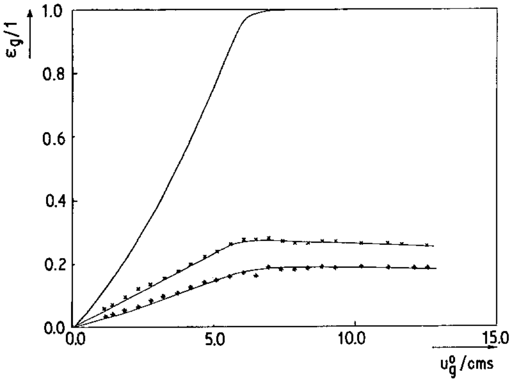

Fig. 5. Experimental gas voidage data (+, *) given by Siemes for two different gas distributors [31] and theoretical curve (plain line) according to the Nicklin equation.

$$\epsilon_m = \epsilon_l\left[\frac{1}{1+(a_m/d_b)}\right]^3 \tag{6}$$

for the maximum gas voidage can be derived. The factor ϵ_l is a characteristic constant for a certain lattice type (Table 3). Equation 6 shows that the limiting gas voidage depends mainly on the ratio of the minimum bubble distance to the bubble diameter. Until now the minimum bubble distance has not been predicted theoretically and therefore has to be determined empirically by measurements in various systems.

To obtain an equation describing the gas voidage as a function of the operating parameters a cross-section A as shown schematically in Fig. 6 is considered. A part of this cross-section $(1 - \epsilon_m)A$

Table 3.

Lattice type	ϵ_l
Simple cubic structure	0.524
Face-centred cubic structure	0.740
Body-centred cubic structure	0.680

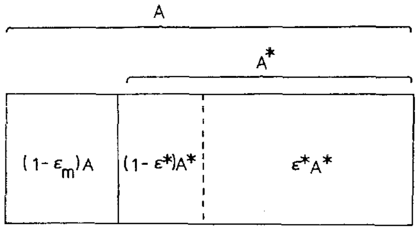

Fig. 6. Cross-section considered for derivation of Equation 13.

is not available for the gas phase. Only the cross-section A^*

$$A^* = A\epsilon_m \tag{7}$$

can be partially occupied by the gas bubbles. A gas voidage ϵ^* can be introduced which is related to the cross-section A^*

$$\epsilon^* = \frac{\epsilon_g}{\epsilon_m} \tag{8}$$

Applying Nicklin's considerations [24] to the gas in the available cross-sections A^* yields

$$\frac{G}{\epsilon^* A^*} = \frac{G}{A^*} + \frac{L^*}{A^*} + u_{sw}(\epsilon^*) \tag{9}$$

L^* is that part of the volumetric liquid flow rate which flows through the cross-section A^*. It can be written as:

$$L^* = L\,\frac{1 - \epsilon^*\epsilon_m - (1 - \epsilon_m)}{1 - \epsilon^*\epsilon_m} \tag{10}$$

Simplification leads to:

$$L^* = L\,\frac{\epsilon_m - \epsilon^*\epsilon_m}{1 - \epsilon^*\epsilon_m} \tag{11}$$

Introducing this expression into Equation 9 and eliminating A^* and ϵ^* by Equations 7 and 8 yields:

$$\frac{G}{\epsilon_g A} = \frac{G}{A\epsilon_m} + \frac{L}{A\epsilon_m}\left(\frac{\epsilon_m - \epsilon_g}{1 - \epsilon_g}\right) + u_{sw}\left(\frac{\epsilon_g}{\epsilon_m}\right) \tag{12}$$

Introducing the superficial velocities yields the characteristic equation for the suggested coalescence barrier model.

$$\frac{u_g^0}{\epsilon_g} = \frac{u_g^0}{\epsilon_m} + u_l^0\left[\frac{1 - (\epsilon_g/\epsilon_m)}{1 - \epsilon_g}\right] + u_{sw}\left(\frac{\epsilon_g}{\epsilon_m}\right) \tag{13}$$

It should be mentioned that the swarm rise velocity term u_{sw} is not related to the actual gas voidage ϵ_g but to the voidage ϵ^* related to the gas in the available cross-section A^*. Due to the fact that u_{sw} is not a simple function of ϵ_g (see Table 4) Equation 13 cannot be resolved with respect to ϵ_g. However, rearranging Equation 13 yields an expression

$$\epsilon_g = \frac{\epsilon_m}{1 + \left\{\left[u_l^0\left(\frac{\epsilon_m - \epsilon_g}{1 - \epsilon_g}\right) + \epsilon_m u_{sw}\left(\frac{\epsilon_g}{\epsilon_m}\right)\right] \Big/ u_g^0\right\}} \tag{14}$$

which is similar to Equation 4. This equation can be used on a computer as an iteration formula for the calculation of ϵ_g as a function of the superficial gas and liquid velocities. It can be easily seen that the gas voidage converges to the limiting gas voidage ϵ_m for infinite superficial gas velocity. For $\epsilon_m = 1$ this equation is equal to Equation 4 and therefore contains the Nicklin equations as a special case.

In Fig. 7 one data set from Fig. 5 is shown again. Two theoretical curves are shown calculated using Equation 14. The parameters used are: $\epsilon_m = 0.19$, $u_s = 50\,\mathrm{cm\,s^{-1}}$. The two theoretical curves have been calculated using two extreme bubble swarm equations: the Marucci equation for curve 1, and the Richardson–Zaki equation for curve 2. A reasonable agreement with the experimental data is observed for the Marucci equation which is therefore used in the following. Nicklin [24] has published rise velocities of air bubbles in stagnant water as a function of the superficial gas velocity. These data are shown in Fig. 8 and are compared with theoretical curves according to Equation 14. The rise velocity of a single bubble has been estimated from Nicklin's own measurements to be about $25\,\mathrm{cm\,s^{-1}}$. Two lines corresponding to $\epsilon_m = 1$ and $\epsilon_m = 0.38$ are shown in Fig. 8. It is seen that the Nicklin equation ($\epsilon_m = 1$) does not reflect the experimental data whereas there is reasonable agreement for $\epsilon_m = 0.38$.

It can be stated that the coalescence barrier model as given by Equations 13 and 14 respectively reflects experimental data published by other authors [24, 31] much better than the simple Nicklin equation. However, in the literature data are mainly available for gas–water systems which

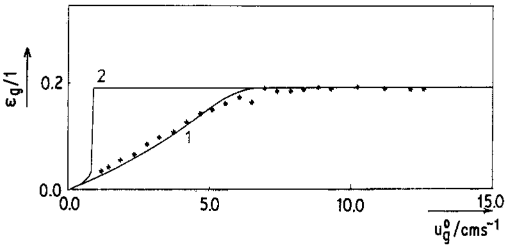

Fig. 7. Comparison between experimental gas voidage data and theoretical data calculated using Equation 14, (u_{sw} calculated with Marucci (1) and Richardson–Zaki Equations (2)).

can be used to prove the coalescence barrier model. To test this new model for gas–liquid systems which are typical of electrolytic cells some measurements have been made.

4. Experimental procedure

The gas voidage as a function of the superficial gas velocity, which is referred to here as the gas voidage function, has been measured for various systems which are of interest with respect to industrial electrochemical processes. The systems investigated are:

Hydrogen in potassium hydroxide
Oxygen in potassium hydroxide
Hydrogen in sulphuric acid
Oxygen in sulphuric acid
Chlorine in sodium chloride

Table 4. Estimated limiting voidage and rise velocity data for various gas–electrolyte systems

Gas	*Electrolyte*	ϵ_m	u_s(cm s^{-1})
H_2	20% KOH	0.26	5.0
O_2	20% KOH	0.455	5.0
O_2	30% KOH	0.31	5.0
H_2(ec)	30% KOH	0.24	3.5
H_2(ec)	20% KOH	0.27	3.5
H_2(ec)	20% H_2SO_4	0.13	10.0
O_2(ec)	20% KOH	0.13	4.5
O_2(ec)	20% H_2SO_4	0.11	4.0
Cl_2(ec)	30% NaCl	0.35	3.7

Comparative measurements have been carried out for electrogenerated gas evolution and gas distribution through a porous disc. By this means it is possible to decide whether there is a difference between the two types of gas–liquid dispersions. This is important because only very few experimental data for electrogenerated gases are available. The experimental arrangements used are shown schematically in Fig. 9. The gas inlet or the gas evolving electrode was mounted at the bottom of a perspex tube. If gas is dispersed within the stationary liquid the volume of the mixture expands. With Δh as the difference between the height of the gas–liquid mixture and the height of the pure liquid the gas voidage can be calculated according to

$$\epsilon_g = \frac{\Delta h}{h_0 + \Delta h} \tag{15}$$

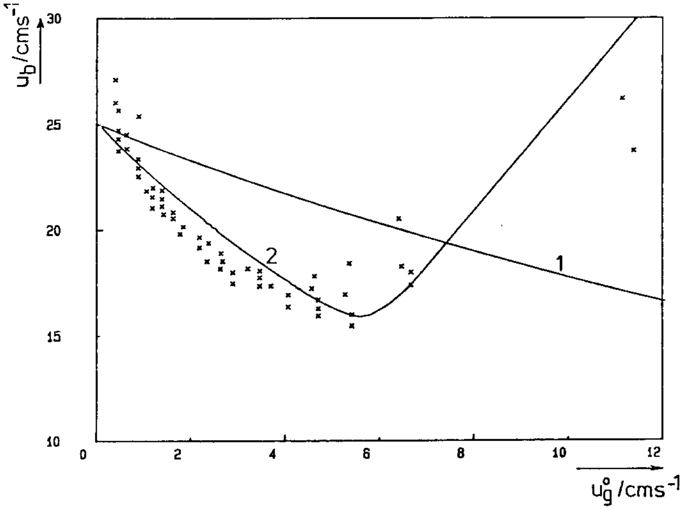

Fig. 8. Comparison of experimental gas bubble velocities with the Nicklin Equation (1) and the Coalescence Barrier Model (2) ($u_l^0 = 0$, $\epsilon_m = 0.38$, $u_s = 25$ cm s^{-1}).

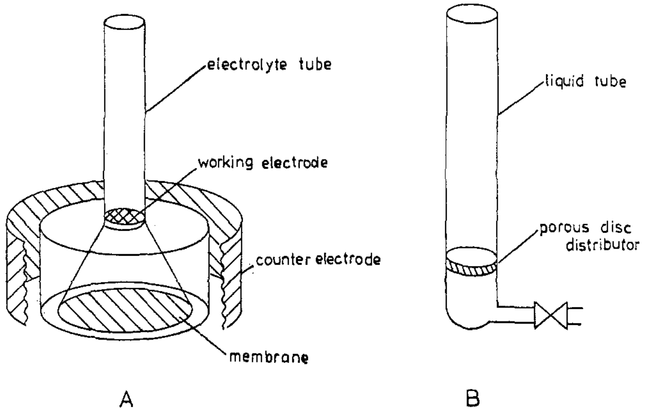

Fig. 9. Schematic experimental set-ups for measurements of gas hold-up, (A) electrochemical gas generation, (B) gas distribution through a porous disc.

In the case of gas dispersion through a porous plate the superficial gas velocity can be calculated from the volumetric gas flow rate.

$$u_g^0 = G/A \qquad (16)$$

For the electrochemical gas evolution the empty tube velocity can be calculated from the current.

$$u_g^0 = \frac{RT}{pv_eFA}I \qquad (17)$$

5. Results and discussion

Experimental gas voidage functions for electrogenerated hydrogen and oxygen in alkaline and acid solution and for chlorine in sodium chloride solution are shown in Fig. 10. Excepting chlorine, in all other cases a limiting gas voidage has been found within the investigated range of superficial gas velocities. This maximum gas voidage seems to be a characteristic quantity for each gas–electrolyte combination. Using Equation 14 and the Marucci equation for the bubble swarm velocity term the theoretical curves shown in Fig. 10 have been calculated using the experimental values for ϵ_m and fitting the single bubble rise velocity u_s.

All curves in Fig. 10 have been measured using a platinum electrode. The question arises whether the limiting gas voidage is also a function of the electrode material. Therefore gas voidage functions for electrogenerated hydrogen in 20% potassium hydroxyde have been measured at a platinum and at a stainless steel electrode. The results are shown in Fig. 11 and no significant influence of the electrode material is apparent.

For the case where the gases are not electrogenerated but distributed into the electrolyte through a porous disc, experimental gas voidage functions for oxygen and hydrogen in alkaline solution are shown in Fig. 12. Comparing these results with the corresponding curves in Fig. 10 shows that for oxygen the way in which the gas bubbles are generated in the electrolyte has a

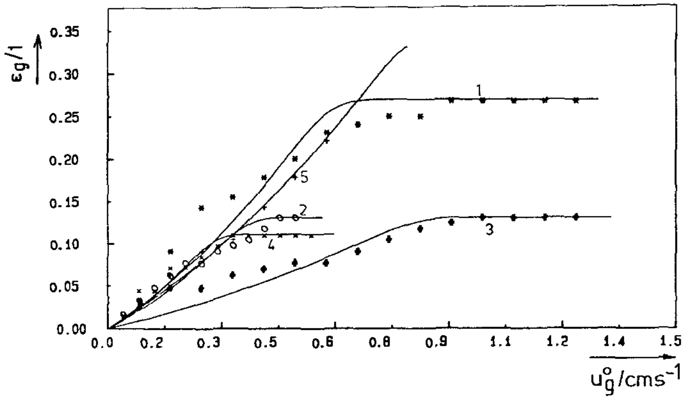

Fig. 10. Gas voidage functions for various electrogenerated gases: 1–H_2 in 20% KOH, 2–O_2 in 20% KOH, 3–H_2 in 20% H_2SO_4, 4–O_2 in 20% H_2SO_4, 5–Cl_2 in 30% NaCl.

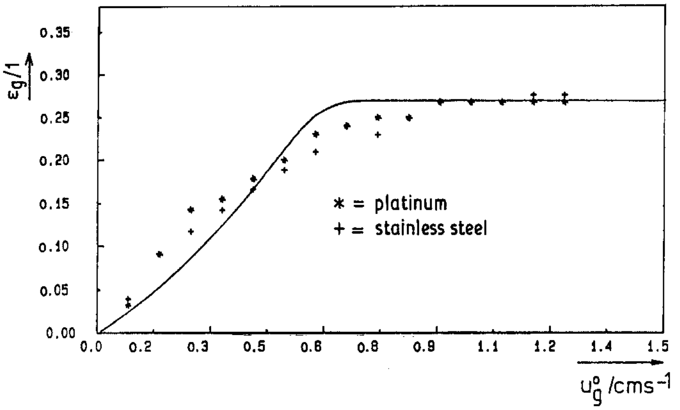

Fig. 11. Gas voidage functions for electrogenerated hydrogen in 20% KOH at different electrode materials.

strong influence. For a gas inlet through a porous disc higher limiting voidage values are observed than for electrogenerated gases. In terms of the coalescence barrier model this means that electrogenerated oxygen gas bubbles should have a higher surface charge resulting in a stronger repulsion and a larger minimum bubble distance. This conclusion is not proved absolutely by the present results but needs further investigation.

A further point of interest is the influence of the electrolyte concentration. In Fig. 13 gas voidage functions for the distribution of oxygen and the electrogeneration of hydrogen in potassium hydroxide electrolytes of different concentrations are given. In both cases the limiting voidage decreases with increasing electrolyte concentration. This also seems to confirm the assumption of an ionic surface charge of the gas bubbles which should increase with increasing electrolyte concentration.

All experimental curves shown in Figs. 10–13 have been simulated theoretically as described above. In Table 4 the limiting gas voidage values and the rise velocities of single bubbles are summarized. The values for chlorine are only a rough estimate since the limiting voidage could not be achieved within the available current range. In all other cases the limiting voidage data has been taken directly from the experimental curves. However, the rise velocity data are also only approximate because the influence of this value on the shape of the voidage function is not great. The rise velocities of the bubble swarms, u_{sw}, have been calculated using the Marucci equation as already mentioned. This means that the voidage functions should start with a concave curvature at low superficial gas velocities. Literature data for air–water mixtures (see Figs. 5 and 7) show this behaviour, whereas this could not be confirmed significantly for the measurements in electrolyte solutions. To

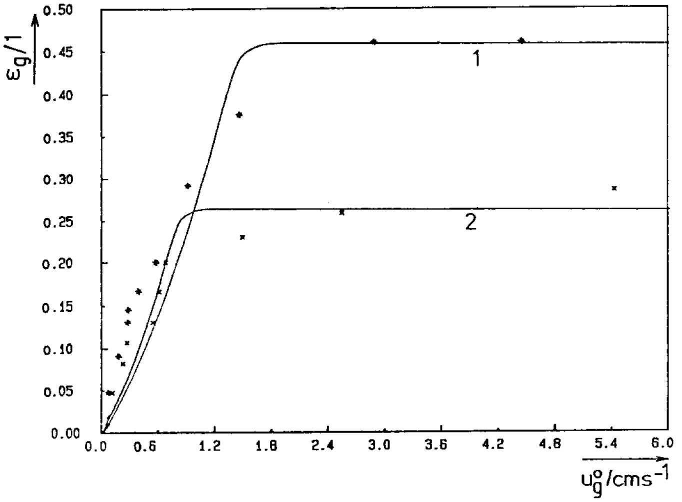

Fig. 12. Gas voidage functions for distribution of oxygen (1) and hydrogen (2) in 20% KOH.

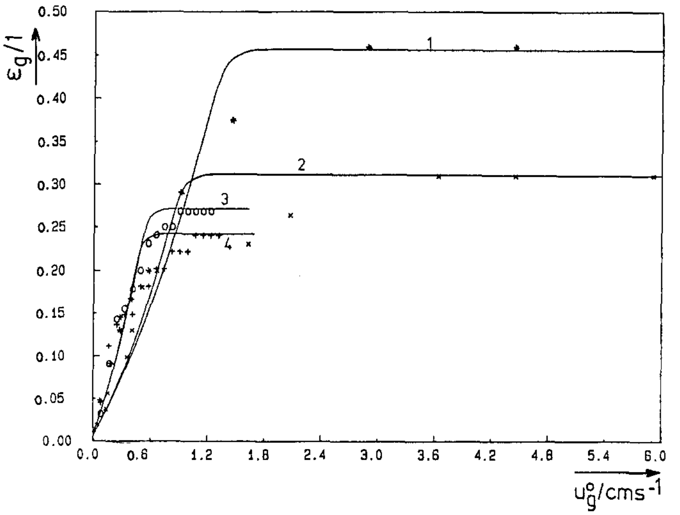

Fig. 13. Gas voidage functions for different electrolyte concentrations: 1–distribution of oxygen in 20% KOH, 2–distribution of oxygen in 30% KOH, 3–electrogenerated hydrogen in 20% KOH, 4–electrogenerated hydrogen in 30% KOH.

decide this question finally, voidage measurements of higher accuracy and independent measurements of the swarm rising velocity in electrolyte solutions are required. It may be that the Marucci equation is not valid for electrolyte solutions and has to be modified.

Up to the present it was generally agreed that in electrolysis cells with gas evolving electrodes the local gas voidage increases along the length of the electrode. A modification of this idea seems to be necessary according to the present results. An increase of the local gas voidage should be expected only within the lower part of a cell. At a certain height of the electrode the limiting gas voidage should be reached and this remains constant in the upper part of the cell. A practical consequence of this is that the influence of the electrode height on the cell voltage is not as strong as previously expected. The consequences of the coalescence barrier model to modelling of the axial current distribution in electrolysis cells with gas evolving electrodes will be reported in part II of this communication. Further experiments to test the hypothesis discussed here for larger electrolysis cells are in progress.

Acknowledgement

The authors acknowledge Arbeitsgemeinschaft Industrieller Forschungsvereinigungen (AIF) and Fonds der Chemischen Industrie for financial support of this work. Experimental measurements were carried out by U. Huber and the authors would like to thank Dr G. Linzbach and Dipl.-Chem. W. Kochanek for helpful discussions.

References

[1] Lord Rayleigh, *Philos. Mag.* **34** (1892) 481.
[2] J. C. Maxwell, 'A Treatise on Electricity and Magnetism', 2nd ed., Vol. 1, Clarendon Press, Oxford (1881) p. 435.
[3] G. H. Neale and W. K. Nader, *AIChE J.* **19** (1973) 112.
[4] R. E. De la Rue and C. W. Tobias, *J. Electrochem. Soc.* **106** (1959) 827.
[5] R. E. Meredith and C. W. Tobias, *ibid.* **108** (1961) 286.
[6] D. A. G. Bruggemann, *Ann. Phys.* **24** (1935) 636.
[7] S. Prager, *Physica* **29** (1963) 129.
[8] H. Vogt, 'Gas-evolving Electrodes', in 'Comprehensive Treatise of Electrochemistry', Vol. 6, Plenum Press, New York (1983) p. 471.
[9] P. J. Sides, *AIChE* Symposium Series No. 229, **79** (1984) 226.
[10] B. E. Bongenaar-Schlenter, L. J. J. Janssen, S. J. D. van Stralen and E. Barendrecht, *J. Appl. Electrochem.* **15** (1985) 537.
[11] F. Hine and K. Murakami, *J. Electrochem. Soc.* **127** (1980) 292.
[12] P. J. Sides and C. W. Tobias, *ibid.* **129** (1982) 2715.
[13] L. J. J. Janssen and E. Barendrecht, *Electrochim. Acta* **28** (1983) 341.
[14] L. J. J. Janssen, J. J. M. Geraets, E. Barendrecht and S. D. J. van Stralen, *ibid.* **27** (1982) 1207.
[15] O. Lanzi and R. F. Savinell, *J. Electrochem. Soc.* **130** (1983) 799.
[16] L. Sigrist, Dissertation ETH Nr. 6286. Zürich (1978).
[17] C. W. Tobias, *J. Electrochem. Soc.* **106** (1959) 833.

[18] J. E. Funk and J. F. Thorpe, *ibid.* **116** (1969) 48.

[19] S. Nagy, *J. Appl. Electrochem.* **6** (1976) 171.

[20] I. Rousar, *J. Electrochem. Soc.* **116** (1969) 676.

[21] I. Rousar, V. Cezner, J. Nejepsová, M. M. Jaksić, M. Spasojević and B. Z. Nikolić, *J. Appl. Electrochem.* **7** (1977) 427.

[22] H. Vogt, *Electrochim. Acta* **26** (1981) 1311.

[23] D. J. Nicklin, J. D. Wilkes and J. F. Davidson, *Trans. Instn. Chem. Eng.* **40** (1962) 61.

[24] D. J. Nicklin, *Chem. Eng. Sci.* **17** (1962) 693.

[25] A. A. Kaskas, Dissertation, TU Berlin (1971).

[26] G. Marucci, *Ind. Eng. Chem. Fundam.* **4** (1965) 224.

[27] J. F. Richardson and W. N. Zaki, *Trans. Instn. Chem. Eng.* **32** (1954) 35.

[28] H. Brauer and H. Thiele, *Chem. Ing. Tech.* **45** (1973) 909.

[29] H. Brauer, Grundlagen der Einphasen- und Mehrphasenströmungen, Verlag Sauerländer, Frankfurt/M. (1971) p. 295f.

[30] L. Sigrist, O. Dossenbach and N. Ibl, *J. Appl. Electrochem.* **10** (1980) 223.

[31] W. Siemes, *Chem. Ing. Tech.* **26** (1954) 614.

[32] N. P. Brandon, G. H. Kelsall, S. Levine and A. L. Smith, *J. Appl. Electrochem.* **15** (1985) 485.