The effect of anodic bubble formation on cathodic mass transfer under natural convection conditions

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The enhancing effect of gas bubbles generated at an anode, on the ionic mass transport rate at the associated cathode is analysed by means of an experimental laboratory-scale copper electrowinning cell in which the bubbles were (a) permitted to rise freely in the entire cell and (b) restricted in their motion by a copper baffle-plate placed between the two electrodes. The improvement in mass transfer observed in the unrestricted case has been correlated via statistical regression analysis to the intensity of bubble motion and pertinent cell parameters.

Nomenclature

b	Distance of anode–cathode separation; m
D	Electrolyte diffusivity, $m^2\,s^{-1}$
D_e	Cell equivalent diameter; m
F	Faraday constant; $9\cdot6487 \times 10^4\,C\,mol^{-1}$
g	Acceleration due to gravity, $m\,s^{-2}$
h	Active electrode height, m
i	Limiting current density; $\bar{i}$ average limiting current density; $A\,m^{-2}$
L	Electrode width, m
n_a	Number of electrons involved in the anode reaction for production of one mole of gas
p_a	Atmospheric pressure, Pa
Q	Volumetric gas bubble rate, $m^3\,s^{-1}$
(Re_g)	Gas-phase Reynolds number defined in Equation 4
(Sc)	Schmidt number; $(Sc) = \nu D^{-1}$
(Sh)	Sherwood number; $(Sh) = ih/n_c FDc_0$; n_c number of electrons involved in cathode reaction, c_0 bulk electrolyte concentration, $mol\,m^{-3}$
T	Electrolyte temperature, K
Z	Co-ordinate along electrode height, m
α, β, γ	Regression coefficients in Equation 5
ν	Electrolyte kinematic diffusivity, $m^2\,s^{-1}$

Subscript

B	Denotes experimental conditions where the electrodes are separated by a conducting baffle-plate

1. Introduction

The effect of bubble formation at a given electrode, due to the discharge of an ionic species to gas, on mass transport rates has been reviewed by Ibl [1]; Roušar and co-workers have recently discussed this effect where gas evolution is the result of an electrode reaction involving a second ionic species [2, 3]. Of potential technical interest is the utilization of the bubble formation effect via air-spurging through metal electrowinning cells [4] permitting operation at elevated current densities, whose distribution has also been studied by various researchers [5]. In none of these instances were the bubble formation at one electrode and simultaneous ionic mass transfer at the other electrodes studied.

In this paper the effect of bubble formation at an anode, due to the discharge of an anion, on the mass transfer rate of a cation discharging simultaneously at the cathode is described. The experimental cell is a close laboratory facsimile of a convential copper electrowinning cell where copper is deposited on the copper cathode and oxygen is generated at the indifferent (6% Sb–Pb) anode. It is shown that when the path of the evolving gas in the electrolyte is not restricted, the cathodic mass transfer rate increases with respect to its magnitude observed under restricted conditions. A quantitative relationship is proposed via statistical regression analysis of the experimental data which may be of practical interest for improved cell design.
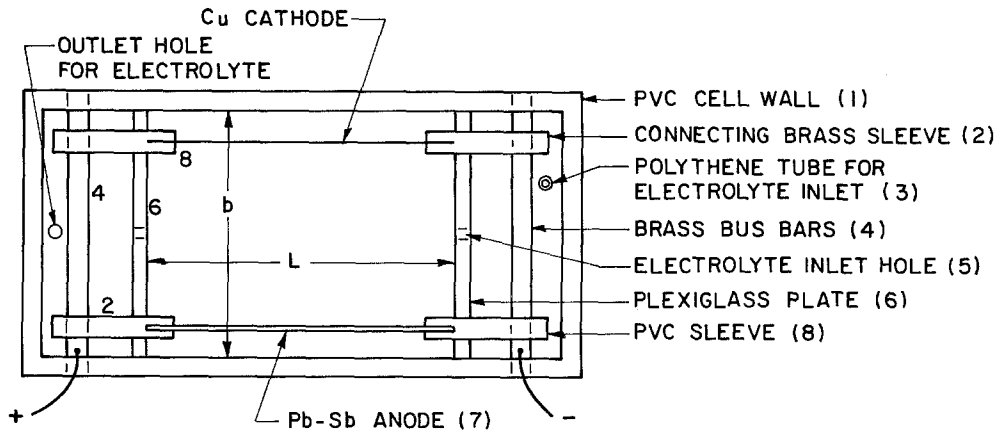
Fig. 1. Top view of the experimental electrolytic cell.

2. Experimental

The details of construction are shown in Fig. 1.
The rectangular cell size is 25 cm × 10 cm × 25 cm.
Made of polyvinylchloride, it contains a refinery-
quality copper cathode sheet, a 6% Sb–Pb anode
sheet and the $CuSO_4/H_2SO_4$ electrolyte. The gen-
erated bubbles are kept inside the electrolyte space
by two plexiglass plates set perpendicularly to and
at the end of the electrodes. The height of the
electrolyte level and the distance between the two
electrodes are adjusted arbitrarily in order to span
an h/b range of 1 to 6. Electrolysis was carried out
in two experimental modes, one without and one
with a copper baffle-plate of the same kind as the
cathode between the two electrodes. In this latter
configuration, the plate behaves as a bipolar elec-
trode and there are, of course, no bubbles within

Fig. 2. Illustration for the concept of (Re_g).

the cathode–baffle space. From conventional cath-
ode current density versus cell voltage drop curves
the pertinent limiting current density values were
determined. The two experimental modes were
successively performed and duplicated at a given
electrolyte composition in order to keep other
variables constant.

3. Analysis and discussion

Table 1 contains the summary of the experimental
data; in the last two columns pertinent gas-phase
Reynolds numbers and Sherwood numbers are
given. In establishing the concept of the former
quantity the following simplified approach was
employed (refer to Fig. 2).

At any arbitrary height, z, of the electrolyte
the volumetric rising rate of the bubbles generated
at the anode may be written as

$$Q_z = 8 \cdot 206 \times 10^{-5} \frac{TL}{n_a F} \frac{p_a}{p_a + (h-z)\rho g} \int_0^z i(z) \mathrm{d}z. \tag{1}$$

Assuming that the hydrostatic pressure vari-
ation over the distance $0 \leqslant z \leqslant h$ is minimal, the
pressure correction term may be replaced by its
average value, whence it follows that the expression

$$Q_h \cong 1 \cdot 0256 \times 10^{-5} \frac{TL}{F} \frac{2 p_a + h\rho g}{p_a + h\rho g} \int_0^h i(z) \mathrm{d}z \tag{2}$$

is an acceptable approximation to the total rate of
bubble formation (n_a for oxygen formation at
anode is 4). The integral may be replaced by the
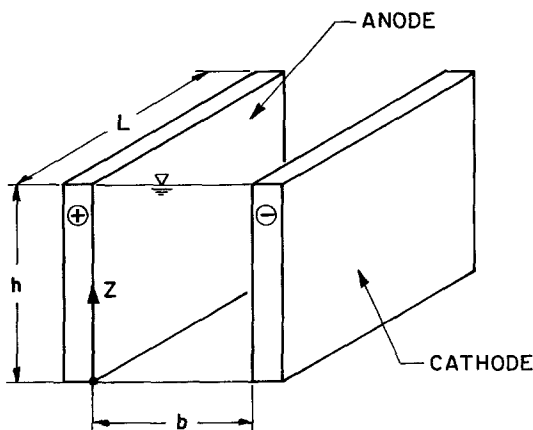current density averaged over the electrode surface,

Table 1. Summary of the experimental data.

Electrolyte composition (mol dm^{-3})	h(cm)	b(cm)	Limiting current density (A m^{-2})		(Re_g)	$(Sh)-(Sh_B)$
			Without baffle (i)	With baffle (i_B)		
	9·55	6·60	405	385	2·74	35·2
	14·00	6·60	495	435	4·92	154·6
$[Cu^{2+}] = 0.542$	13·70	3·80	425	362	4·80	157·6
$[H_2SO_4] = 1.62$	13·40	2·30	337	297	4·08	98·7
$(Sc) = 2790$	13·20	7·50	322	308	2·88	34·0
	9·00	7·50	376	345	2·30	51·4
	8·10	2·30	400	364	2·92	53·7
	10·00	7·50	247	232	1·68	38·5
	10·10	2·40	260	235	2·36	64·7
$[Cu^{2+}] = 0.380$	15·00	5·00	252	229	2·92	88·5
$[H_2SO_4] = 1.60$	14·90	2·40	261	236	3·48	95·5
$(Sc) = 2938$	12·50	7·50	240	225	2·04	48·1
	12·30	2·50	248	229	2·72	59·9
	10·00	7·50	183	175	1·24	26·7
	10·10	5·00	178	165	1·40	45·5
	10·10	2·40	168	157	1·52	37·0
$[Cu^{2+}] = 0.290$	15·00	7·50	170	163	1·74	35·0
$[H_2SO_4] = 1.61$	15·10	5·00	165	155	2·02	95·6
$(Sc) = 3122$	14·80	2·31	175	157	2·34	88·8
	12·50	7·60	156	148	1·32	33·3
	12·50	5·10	176	164	1·68	50·0
	12·60	2·30	182	165	2·06	71·4
	14·90	7·50	29·9	29·6	0·30	20·2
$[Cu^{2+}] = 0.080$	14·80	5·00	28·0	27·1	0·32	13·9
$[H_2SO_4] = 1.64$	12·80	2·30	33·2	31·9	0·38	17·4
$(Sc) = 3884$	10·10	7·50	30·4	30·0	0·20	4·22
	10·20	5·00	32·3	30·1	0·26	10·60

Average electrolyte temperature: 298 K, $L = 13.55$ cm

hence

$$Q_h = 1.0256 \times 10^{-5} \frac{TL}{F} \frac{2 p_a + h\rho g}{p_a + h\rho g} h\, \bar{i}. \quad (3)$$

One can formally define, therefore, a gas-phase Reynolds number as

$$(Re_g) = \frac{Q_h}{Lb} \frac{D_e}{\nu} = \frac{2\, Q_h}{(L+b)\nu} \quad (4)$$

for the given cell geometry. The fifth column in Table 1 contains the associated numerical values of this Reynolds number, computed as $(Re_g) = 1.7038 \times 10^{-8}\, h\, \bar{i}/(L+b)\nu$ under the given experimental conditions. It is clearly seen that (Re_g) does not depend on the current distribution at the anode and can be readily computed both for laboratory and plant conditions.

The last column in Table 1 shows the beneficial effect of the rising bubbles on cathodic mass transport as manifested by the $(Sh) > (Sh_B)$ inequality. It appears that the bubbles exert a 'stirring' effect near the cathode and the convection generated, therefore, improves the associated ionic mass transfer rate, with respect to the case of restricted bubble motion. The magnitude of this effect can be related, as shown in Fig. 3, by the regression line

$$(Sh) = (Sh_B) + \alpha(Re_g)^\beta(Sc)^{1/4}(h/b)^\gamma \quad (5)$$

which offers a reasonable correlation between the intensity of bubble motion, cell geometry and cathodic mass transfer. Under the experimental conditions, $\alpha = 3.088$, $\beta = 0.77$ and $\gamma = 0.336$ with an associated confidence interval of $2.7154 < \alpha < 3.4606$ at the 95% confidence level. The (Sc)-term is included in the model (Equation 5) so as to present its true nature and the exponent 1/4 is
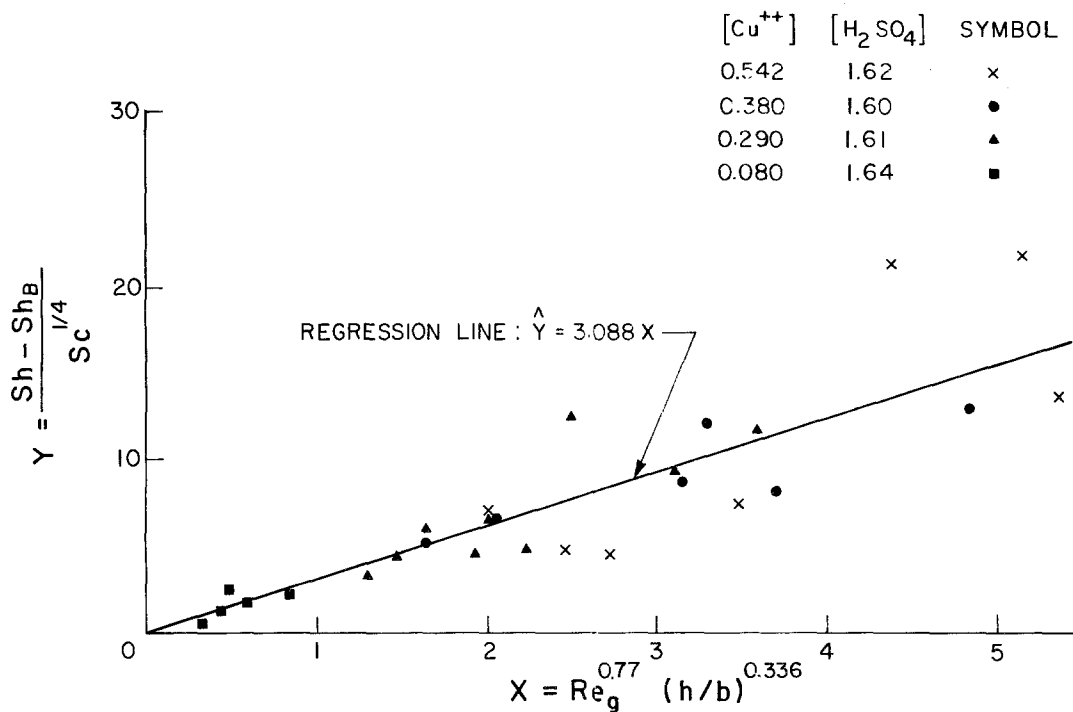
Fig. 3. Regression analysis of the experimental results.

chosen as an approximate value. In view of the relatively narrow range of the experimental Schmidt numbers, an appreciable improvement in the accuracy of the regression correlation obtained by letting the (Sc)-exponent 'float' is not likely.

The numerical value of the (Re_g)-exponent is reasonably close (12% discrepancy) to the value of 0·875 which appears in relationships hitherto proposed for forced-convection mass transfer in parallel-plate electrode cells [6–8]. This finding might be explained by the existence of turbulent conditions due to eddies formed in the vicinity of the bubbles. The positive exponent of the aspect ratio h/b indicates that

(a) The farther apart the two electrodes are separated, the smaller the portion of the bubbles which travels across the electrolyte toward the cathode, and

(b) The higher the electrode, the larger the proportion of the cathodic area effected by bubble-generated convection.

The overall effect of this convection is modest in the sense that the relative increase in cathodic mass transfer rates is apparently not more than 20%, with respect to the case of restricted bubble-motion.

It does not follow from these results, however, that high bubble rates would always be beneficial in any electrowinning cell: an important limitation to permitted bubble rates is the quality of the cathode deposit at higher current densities. However, the proposed relationship estimates the cathodic mass transfer contribution due to the bubbles evolved at anodes in a given situation.

Acknowledgement

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