[4] H. Jahnke, M. Schonborn and G. Zimmerman in 'Topics of Current Chemistry', Vol. 61, Springer-Verlag, Heidelberg (1975) pp. 133.
[5] J. S. R. Van Veen and J. F. Van Baar, *Rev. Inorg. Chem.* **4** (1982) 293.
[6] D. A. Scherson, S. B. Yao, E. B. Yeager, J. Eldridge and R. W. Hoffman, *J. Phys. Chem.* **87** (1983) 932.
[7] P. Rothemund and A. R. Menotti, *J. Am. Chem. Soc.* **70** (1948) 1808.
[8] G. D. Dorough, J. R. Miller and F. M. Huennekens, *J. Am. Chem. Soc.*, **73** (1951) 4315.
[9] D. W. Thomas and A. E. Martell, *Arch. Biochem. Biophys.* **76** (1958) 286.
[10] D. M. Drazic, Z. V. Ladinski, S. K. Zecevic, *J. Appl. Electrochem.* **13** (1983) 337.
[11] H. G. Jahnke, M. F. Schonborn and G. Zimmerman in 'Electrocatalysis' (edited by M. W. Breiter) Electrochemistry Society, Princeton (1974) pp. 303.
[12] V. S. Bagotzky, M. R. Taraservich, K. A. Radyushkina, O. A. Levina and S. I. Andrusyova, *J. Power Sources* **2** (1977) 233.
[13] J. A. R. Van Veen and C. Visser, *Electrochim. Acta* **24** (1979) 921.
[14] R. Manoharan, D. D. Sarma and A. K. Shukla, submitted to *J. Power Sources*.
[15] M. Zerner, M. Gouterman and H. Kobayaski, *Theoret. Chim. Acta* **6** (1966) 363.
[16] K. Sherwood, E. R. Gilliland and S. W. Ing, Jr., *Ind. Eng. Chem.* **52** (1960) 601.
[17] H. Meier, W. Tschirwitz, E. Zimmerhackl, E. Albrecht and G. Zeitler, *J. Phys. Chem.* **81** (1977) 712.
[18] C. A. Melendres, *J. Phys. Chem.* **84** (1980) 1938.
[19] S. Maroie, M. Savy and J. J. Verbist, *Inorg. Chem.* **18** (1979) 2560.
[20] D. A. Sherson, S. L. Gupta, C. Fierro, E. B. Yeager, M. E. Kordesch, J. Eldridge, R. W. Hoffman, J. Blue, *Electrochim. Acta* **28** (1983) 1205.
[21] J. A. R. Van Veen, J. T. Van Baar, C. J. Krolse, *J. Chem. Soc., Faraday Trans. I*, **77** (1981) 2827.
[22] K. A. Radyuskina, O. A. Levine, M. R. Tarasevich, R. Kh. Burshstein, B. D. Berezin, L. P. Shormenova, O. I. Koifman, *Sov. Electrochem.* **11** (1975) 916.

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SHORT COMMUNICATION

# *A model for correlating mass transfer data in parallel plate gas sparged electrochemical reactors*

G. H. SEDAHMED
*Chemical Engineering Department, Faculty of Engineering, Alexandria University, Alexandria, Egypt*

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## Nomenclature

| | |
|---|---|
| $a$ | cross-sectional area of the cell (cm$^2$) |
| $c$ | dimensionless constant |
| $C$ | concentration of electroactive species (mol cm$^{-3}$) |
| $C_b$ | bulk concentration (mol cm$^{-3}$) |
| $C_i$ | interfacial concentration (mol cm$^{-3}$) |
| $D$ | diffusivity of electroactive species (cm$^2$ s$^{-1}$) |
| $E$ | input of mechanical energy to the cell (dyn s$^{-1}$) |
| $e$ | energy dissipated per unit mass of liquid (cm$^2$ s$^{-3}$) |
| $F$ | Faraday constant |
| $g$ | acceleration due to gravity (cm s$^{-2}$) |
| $h$ | height of the gas liquid dispersion in the cell (cm) |
| $K$ | mass transfer coefficient (cm s$^{-1}$) |
| $l$ | active electrode height (cm) |
| $N$ | rate of mass transfer (mol cm$^{-2}$ s$^{-1}$) |
| $\Delta P$ | gas pressure drop in the cell (g cm$^{-2}$) |
| $Q$ | volumetric flow rate of gas (cm$^3$ s$^{-1}$) |
| $t$ | time (s) |
| $\bar{t}$ | contact time (s) |
| $u$ | viscosity of the solution (poise) |
| $V$ | velocity parameter of small scale eddies (cm s$^{-1}$) |
| $V_g$ | gas superficial velocity (cm s$^{-1}$) |
| $x$ | length parameter of small scale eddies (cm) |
| $y$ | distance perpendicular to electrode surface (cm) |
| $St$ | Stanton number ($K/V_g$) |
| $Sc$ | Schmidt number ($v/D$) |
| $Re$ | Reynolds number ($\varrho V_g l/u$) |
| $Fr$ | Froude number ($V_g^2/lg$) |
| $Sh$ | Sherwood number ($Kl/D$) |
| $Gr$ | Grashaf number ($gl^3\varepsilon/v^2(1-\varepsilon)$) |
| $\varrho$ | density of the solution (g cm$^{-3}$) |
| $v$ | kinematic viscosity (cm$^2$ s$^{-1}$) |
| $\varepsilon$ | gas hold up (void fraction) |
| $\varepsilon_L$ | liquid hold up in the cell |

## 1. Introduction

Gas stirring of electrochemical reactors has recently received attention as a means of enhancing rates of mass transfer [1–13]. One may distinguish three kinds of gas stirring: (i) electrodes stirred by gases which evolve simultaneously at the working electrode along with the main reaction (gas evolving electrodes) [1, 2], (ii) electrodes stirred by gases which evolve at the counterelectrode [3–9], (iii) electrodes stirred by gas sparging where the gas is introduced from outside into the cell by means of a porous distributor (gas sparged electrodes) [9–13]. Among the three modes of gas stirring, gas sparged electrodes have received the least attention despite their practical importance in electrowinning, electrorefining of metals and electro-organic synthesis. Ibl *et al.* [10] studied the effect of $N_2$ sparging on the rate of mass transfer of the cathodic reduction of $K_3Fe\ (CN)_6$ at vertical nickel plates ranging in height from 20 to 100 cm. $N_2$ was introduced into the cell through a porous frit placed at the bottom of the cell at a rate ranging from 0.067 to 3.33 cm $s^{-1}$. Ibl *et al.* came to the following conclusions:

(a) The increase in the rate of mass transfer due to gas sparging is higher than the value predicted from the hydrodynamic boundary layer under the same hydrodynamic conditions. Therefore the mechanism governing mass transfer at gas sparged electrodes is different from that of single phase forced convection mass transfer.

(b) The limiting current and mass transfer coefficient are uniform all over the electrode height.

(c) For the same rate of mass transfer, gas stirring is much cheaper than mechanical stirring.

Ettel *et al.* [9] conducted a similar study by measuring the mass transfer coefficient of copper deposition from acidified copper sulphate solution using a parallel plate cell with an electrode height of 110 cm. The cell was stirred by introducing air into the cell through a perforated tube placed at the bottom of the cathode at a rate ranging from 0.025 to 0.75 cm $s^{-1}$. The perforated tube sparger was made of PVC with 40 mm vertical holes set at 5 cm spacing. The results of Ettel *et al.* confirmed the findings of Ibl *et al.* concerning the uniformity of the mass transfer coefficient over the electrode height and the cheapness of gas stirring compared to mechanical stirring. Neither Ibl *et al.* or Ettel *et al.* correlated their data.

In a more recent study Sigrist *et al.* [11] studied the combined effect of gas sparging and electrolyte flow on the mass transfer coefficient for the cathodic reduction of $K_3Fe\ (CN)_6$ using a parallel plate cell. They found that gas stirring is most effective in enhancing the rate of mass transfer at low electrolyte flow rates; as the electrolyte flow rate increases the effect of gas sparging decreases. They correlated their data by an equation similar to that used in turbulent flow natural convection mass transfer, namely

$$Sh = 0.19(Sc\ Gr)^{0.33} \qquad [1]$$

The drawback of the above equation is that it requires *a priori* measurement of the gas void fraction to calculate *Gr*. The object of the present work is to derive an overall correlation which predicts the rate of mass transfer in gas sparged electrochemical reactors (with no electrolyte flow). The model used in the present work is similar to that used by Deckwer [14] to predict the rate of heat transfer in bubble columns.

## 2. Theory

Ibl *et al.* [10] found that mass transfer equations based on the hydrodynamic boundary layer theory underestimate the rate of mass transfer in gas sparged cells and therefore it can be inferred that mass transfer at gas sparged electrodes takes place by a different mechanism. In the area of heat transfer Kast [15] came to a similar conclusion and postulated that the high rate of heat transfer arises from the fact that the uprising gas bubbles induce a radial eddy momentum which reaches the wall with a fresh supply of bulk fluid. This postulation was confirmed experimentally by the tracer technique [16] where it was found that the radial dispersion coefficients were about 3 to 4 times larger than the axial dispersion coefficients. In addition, Buchholz [17] measured

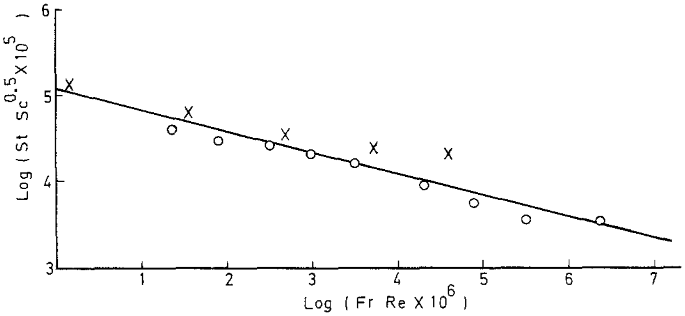

Fig. 1. Overall mass transfer correlation at gas sparged electrodes. —— equation 21; x, data of Ettel *et al.* [9]; o, data of Ibl *et al.* [10].

turbulence intensities in bubble columns and found that the radial profile of the relative turbulence intensity was approximately constant over the cross-sectional area. It is obvious that the small scale eddies extend their action towards the wall and their isotropic motion is responsible for the radial flow as proposed by Kast [15]. A fluid element will stay for a certain constant time at the electrode surface and then leave it and re-enter the bulk fluid; this situation can be treated with Higbie's surface renewal model [18] where unsteady mass diffusion takes place according to the equation

$$\frac{\delta C}{\delta t} = D\frac{\delta^2 C}{\delta y^2} \qquad [2]$$

The boundary conditions are

$$C = C_i \text{ for } y = 0 \text{ at } t > 0 \qquad [3]$$

$$C = C_b \text{ for } y \longrightarrow \infty \text{ at } t > 0 \qquad [4]$$

$$C = C_b \text{ for } y = 0 \text{ at } t = 0 \qquad [5]$$

With these boundary conditions, integration of Equation 2 leads to the relation

$$\frac{C_b - C}{C_b - C_i} = \operatorname{erfc}\left(\frac{y}{(Dt)^{\frac{1}{2}}}\right) \qquad [6]$$

The flux of the electroactive species crossing the $y = 0$ plane towards the electrode surface is expressed by

$$N = -D\left[\frac{\delta C}{\delta y}\right]_{y=0} = (C_b - C_i)\left(\frac{D}{\pi t}\right)^{\frac{1}{2}} \qquad [7]$$

The mean value of the flux over the time interval $\bar{t}$ is

$$N = \frac{1}{\bar{t}}\int_0^{\bar{t}} N\,\mathrm{d}t = 2(C_b - C_i)\left(\frac{D}{\pi\bar{t}}\right)^{\frac{1}{2}} \qquad [8]$$

Since $$N = K\,(C_b - C_i) \qquad [9]$$

then by comparing Equations 8 and 9,

$$K = 2\left(\frac{D}{\pi\bar{t}}\right)^{\frac{1}{2}} \qquad [19]$$

The contact time $\bar{t}$ can be expressed by the equation

$$\bar{t} \propto x/V \qquad [11]$$

Where $x$ and $V$ are length and velocity parameters which characterize the small scale eddies responsible for surface renewal; $x$ and $V$ can be expressed in terms of easily measurable parameters using Kolmogoroff's theory of isotropic turbulence [19–21]. According to this theory only small scale eddies are responsible for energy dissipation by viscous forces, large scale eddies contribute to a negligible extent to energy dissipation. The theory also postulates that energy dissipation by the small scale eddies is isotropic and is governed mainly by viscous forces. Accordingly the small scale energy dissipating eddies can be characterized by two parameters, namely, the kinematic viscosity ($v$) and the rate of energy dissipation per unit mass ($e$). On the basis of these two quantities Kolmogoroff [20–22] derived expressions for the length scale ($x$) and the velocity scale ($V$) of small scale eddies using the method of dimensional analysis as follows

$$x = (v^3/e)^{0.25} \qquad [12]$$

$$V = (ve)^{0.25} \qquad [13]$$

The contact time $\bar{t}$ can be obtained from Equations 12 and 13

$$\bar{t} \propto x/V \propto (v^3/e)^{0.25}/(ve)^{0.25} \propto (v/e)^{0.5} \qquad [14]$$

The rate of energy dissipation per unit mass($e$) can be calculated by considering the total mechanical energy input to the cell ($E$) which is the product of the gas pressure drop in the cell and the volumetric gas flow rate.

$$E = gQ\Delta P = gV_g a h \varrho \varepsilon_L \qquad [15]$$

The energy dissipated per unit mass of liquid is given by

$$e = gV_g \qquad [16]$$

Introducing this expression in Equation 14 we get

$$\bar{t} \propto (\nu/gV_g)^{0.5} \qquad [17]$$

Substituting for the contact time from Equation 17 into Equation 10

$$K \propto D^{0.5} \nu^{-0.25} g^{0.25} V_g^{0.25} \qquad [18]$$

Equation 18 can be rearranged to

$$St\ Sc^{0.5} = c(V_g^3/\nu g)^{-0.25} \qquad [19]$$

or

$$St\ Sc^{0.5} = c(Fr\ Re)^{-0.25} \qquad [20]$$

Fig. 1 shows that the available experimental data (Fig. 9) of [9] and Fig. 8 of [10]) fit the equation

$$St\ Sc^{0.5} = 0.035(Fr\ Re)^{-0.25} \qquad [21]$$

Physical properties of the solution ($\nu$, $D$) used in calculating the dimensionless groups $Sc$, $Fr$, $Re$ were taken from the literature [9, 10]. Equation 21 predicts that $K \propto V_g^{0.25}$; the exponent 0.25 is less than the value obtained from the data of Ibl *et al.* and that of Ettel *et al.* However, Fig. 1 shows that the agreement between experimental data and Equation 21 is fair. The average deviation of the data of Ibl *et al.* [10] from Equation 21 is 11% and the maximum deviation is 25%. In the case of the data of Ettel *et al.* [9] the deviation is much higher, especially at high gas flow rate; this may be attributed in part to the fact that Ettel *et al.* used a perforated tube sparger which did not produce uniform gas distribution in the interelectrode gap or at the electrode surface. Ibl *et al.* used a porous frit as a gas distributor which produced uniform gas distribution in the interelectrode gap and at the electrode surface. It is probable that uniformity of gas distribution in the interelectrode gap favours the generation of isotropic eddies, whose presence is essential for the validity of the present model. Ibl *et al.* [10] found that the pore size of the frit has a negligible effect on the rate of mass transfer and therefore the pore size of the gas distributor does not limit the applicability of Equation 21. Further experimental data is needed to verify Equation 21 under different conditions of electrode geometry, physical properties of the solution and sparger design.

## References

[1] H. Vogt, in 'Comprehensive Treatise of Electrochemistry', Vol. 6 (edited by E. Yeager, J. O'M. Bockris, B. E. Conway and S. Sarangapani) Plenum Press, New York (1983) Chap. 7, p. 445.
[2] G. H. Sedahmed and L. W. Schemilt, *J. Appl. Electrochem.* **14**, (1984) 123.
[3] *Idem, ibid.* **11**, (1981) 537.
[4] *Idem, Can. J. Chem. Eng.* **60**, (1982) 767.
[5] G. H. Sedahmed, *J. Appl. Electrochem.* **10**, (1980) 351.
[6] *Idem, ibid.* **80**, (1978) 399.
[7] *Idem, ibid.* **14** (1984) 693.
[8] S. Mohanta and T. Z. Fahidy, *ibid.* **7** (1977) 235.
[9] V. A. Ettel, B. V. Tilak and A. S. Gendron, *J. Electrochem. Soc.* **121** (1974) 867.
[10] N. Ibl, R. Kind and E. Adam, *Anales de Quim.* **71**, (1975) 1008
[11] L. Sigrist, O. Dossenbach and N. Ibl, *Int. J. Heat Mass Transfer* **22**, (1979) 1393.
[12] W. W. Harvey, A. H. Miguel, P. Larson and I. S. Servi, *Trans. Inst. Min. Metall.* (Section C) **84**,(1975) 11.
[13] H. Vogt, *Fortschr. Verfahrenstechnik* **20**, (1982) 269.
[14] W. D. Deckwer, *Chem. Eng. Sci.* **37**, (1980) 1341.
[15] W. Kast, *Int. J. Heat Mass Transfer* **5**, (1962) 329.
[16] P. Gohler, Dr- Ing. Thesis, TU Berlin (1972).
[17] R. Buchholz, Dr. rer, nat. Thesis, U. Hanover (1979).
[18] R. Higbie, *Trans. Am. Inst. Chem. Eng.* **35**, (1935) 365.
[19] J. O. Hinzé, 'Turbulence', McGraw Hill, New York (1958).
[20] A. M. Kolmogoroff, *Compt. Rend. Acad. Sci. USSR* **30**, (1941) 301.
[21] *Idem, ibid.* **31** (1941) 538.
[22] *Idem, ibid.* **32** (1941) 16.