

Mass transfer at packed-bed, gas-evolving electrodes

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Mass transfer rates were measured for the cathodic reduction of potassium ferricyanide at a H₂-evolving electrode consisting of a packed bed of spheres. Variables studied were bed height, H₂ discharge rate and ferricyanide concentration. It was found that the mass transfer coefficient (K) is related to the H₂ discharge rate (V) by the equation

$$K = aV^{0.325}$$

Bed height and electrolyte concentration were found to have little effect on the mass transfer coefficient. A mathematical model based on the surface renewal theory was formulated to explain the mechanism of mass transfer at gas-evolving electrodes.

Nomenclature

A	electrode area (cm ²)	R	gas constant (J mol ⁻¹ K ⁻¹)
a, b, B	constants	\bar{t}	time (s)
C	concentration of K ₃ Fe(CN) ₆ (mol cm ⁻³)	T	temperature (K)
D	diffusivity of electroactive ion (cm ² s ⁻¹)	u	velocity parameter of the fluid element responsible for surface renewal (cm s ⁻¹)
F	Faraday's constant	V	gas discharge rate (cm ³ cm ⁻² s ⁻¹ or cm s ⁻¹)
g	acceleration due to gravity (cm s ⁻²)	X	length parameter of the fluid element responsible for surface renewal (cm)
i	current consumed in ferricyanide reduction (A)	y	distance in the direction of mass transfer (cm)
I_{H_2}	current consumed in H ₂ evolution (A)	z	number of electrons involved in the reaction
K	mass transfer coefficient (cm s ⁻¹)	ϵ	gas hold-up
n	exponent of the gas velocity in Equations 11 and 12	ν	kinematic viscosity (cm ² s ⁻¹)
P	pressure (Pa)		

1. Introduction

In view of their large specific surface area and high mass transfer coefficient, fixed-bed electrodes are well suited for the processing of dilute solutions, e.g. the recovery of metals from industrial waste solutions. Under such conditions H₂ evolution is likely to take place simultaneously with metal deposition at the cathode, especially when depositing metals which are less noble than H₂ such as nickel, cadmium, lead and zinc. The evolving H₂ bubbles contribute significantly

to the enhancement of the rate of mass transfer, along with forced convection especially at low flow rates. The overall mass transfer coefficient needed for the design and operation of gas-evolving electrodes operated under forced convection can be calculated in terms of the mass transfer coefficient due to gas evolution and the mass transfer coefficient due to forced convection [1, 2]. Little work has been performed on the effect of gas evolution on the rate of mass transfer at fixed-bed electrodes. In an earlier report [3]

the effect of H_2 evolution on the rate of mass transfer at a fixed bed composed of graphite particles supported on a horizontal nickel disc was studied. It was found that H_2 evolution isolated the graphite particles electrically from the feeder disc with a serious loss of the active electrode area. However, the evolving H_2 bubbles gave momentum to the graphite particles which acted as turbulence promoters and enhanced the rate of mass transfer at the feeder electrode by a factor ranging from 1.5 to 4.5. Sedahmed and Shemilt [4] studied the effect of H_2 and O_2 evolution on the rate of mass transfer at a gas-evolving electrode made of an array of parallel screens. They found that gas evolution enhances the rate of mass transfer to a degree depending on the nature of the gas, the gas discharge rate and the bed thickness. The objective of the present work is to study the effect of H_2 evolution on the rate of mass transfer at a packed-bed electrode made of closely packed spheres. The present work also seeks to extend the surface renewal model, previously applied to gas-sparged electrodes [5, 6] to gas-evolving electrodes. Previous models include the penetration model [7], the microconvection model [8] and the hydrodynamic model [9, 10]. In the penetration model it is suggested that the detachment of a bubble from the electrode surface creates a void which is filled by fresh solution through which unsteady state diffusion of the electroactive ion takes place to the electrode surface until a new bubble is formed. The microconvection model is based on the fact that the growing bubble induces a liquid flow past the electrode surface. The hydrodynamic model postulates that the rise of a swarm of bubbles near the electrode causes liquid flow which is responsible for the enhancement of the rate of mass transfer. Both the penetration model and the microconvection model lead to a $\log K/\log V$ value of 0.5, while the hydrodynamic model leads to a value of 0.33. The penetration model was modified by Rousar and Cezner [11] and more recently by Janssen and Van Stralen [12] and Ngoya and Thonstad [13]. Alkire and Lu [14] suggested that the penetration effect and macroconvection occur simultaneously. Sedahmed and Shemilt [4] proposed a laminar flow natural convection model to explain the low value of $\log K/\log V$

observed in the case of noncoalescing gases at low gas discharge rates. None of these models is valid for all conditions and each model has its limitations as described elsewhere [2]. The difference between the penetration model of Ibl and the present surface renewal model is that the penetration model is based on the detachment of bubbles from the electrode surface while the present model is based on the movement of detached bubbles in the solution and has nothing to do with attached bubbles.

2. Experimental technique

The apparatus used consisted of a cell and electrical circuit (Fig. 1). The cell was made of a cylindrical glass container (1 dm^3) of inner diameter 10.5 cm, divided into two compartments by a porous cylindrical PVC diaphragm of inner diameter 3.75 cm. The bottom of the diaphragm was held firmly to the bottom of the glass beaker by a wax layer, 0.5 cm thick. The inner packed-bed electrode (cathode) was made of closely packed, nickel-plated steel spheres supported on a nickel disc of diameter 3.7 cm, each sphere having a diameter of 0.7 cm. Three bed heights were used: 0.7, 1.4 and 2.1 cm, which contained 30, 60 and 90 spheres respectively. The packed-bed was fed by current through a wire welded to the bottom of the supporting disc. The bottom and sides of the supporting disc as well as the feeder wire were electrically insulated with epoxy resin. The outer electrode (anode) was a cylindrical stainless steel screen of diameter 10 cm. Current was drawn from a 6 V d.c. power supply by means of a voltage regulator and measured on a multirange ammeter connected in series with the cell. A voltmeter was connected in parallel with the cell. Before each run the inner compartment was filled with electrolyte up to a height of 6 cm. Care was taken that the level of the electrolyte was the same in both compartments. The solution used was composed of 2N NaOH as a supporting electrolyte and potassium ferricyanide; three concentrations of $K_3Fe(CN)_6$ were used, i.e. 0.1, 0.15 and 0.2M. Electrolysis was conducted at $22 \pm 1^\circ \text{C}$ for a time sufficient to produce a 5–7% $K_3Fe(CN)_6$ concentration change. After each run the solution in the inner

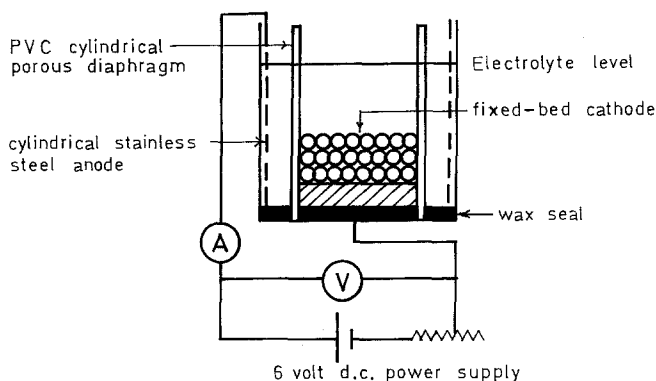


Fig. 1. Cell and electrical circuit.

compartment was analysed for ferricyanide using iodometry [15]. The mass transfer coefficient was calculated using the equation

$$K = \frac{i}{AZFC} \quad (1)$$

The current consumed in reducing ferricyanide ion was calculated using Faraday's law and the analytically determined decrease in ferricyanide concentration. The current consumed in H_2 evolution was calculated by subtracting the current consumed in reducing $K_3Fe(CN)_6$ from the total current passing. Values of V were calculated from the equation

$$V = \frac{RT}{PzFA} I_{H_2} \quad (2)$$

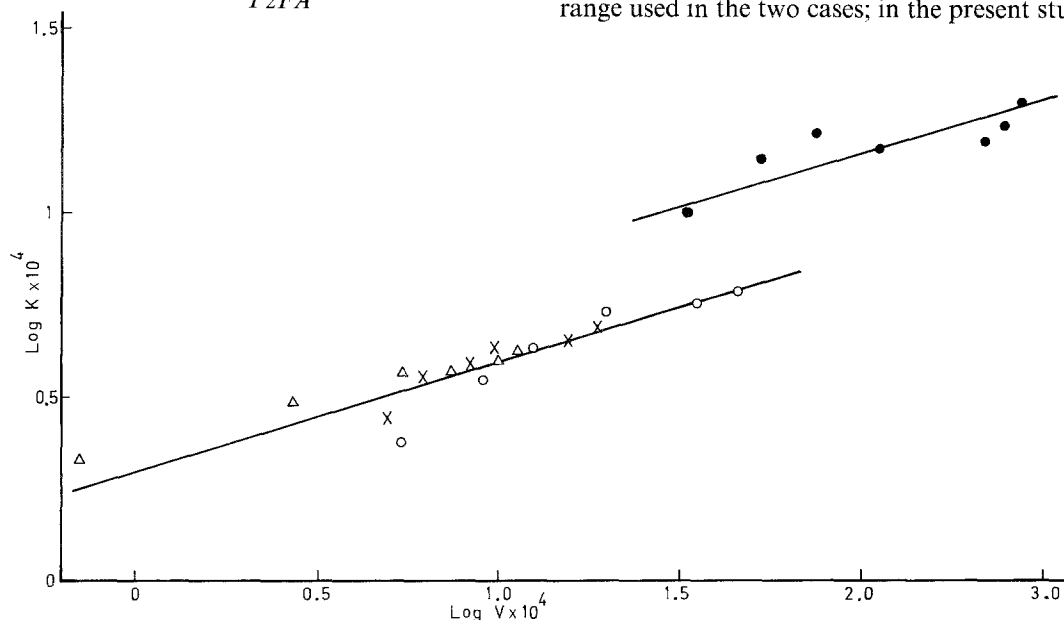


Fig. 2. Effect of H_2 discharge rate on the mass transfer coefficient at different bed heights. ●, Supporting disc; ○, height 0.7 cm; ×, height 1.4 cm; △, height 2.1 cm. $K_3Fe(CN)_6$ concentration, 0.2 M.

3. Results and discussion

Fig. 2 shows that the mass transfer coefficient at the packed-bed electrode can be related to the H_2 discharge velocity by the equation

$$K = aV^{0.325} \quad (3)$$

Fig. 2 also shows that the mass transfer coefficient at the supporting disc can be related to the H_2 discharge rate by a similar equation, but with a coefficient higher than the value of a . The $\log K/\log V$ slope of the disc of 0.325 is higher than the value of 0.25 obtained by Fouad and Sedahmed [16] for horizontal electrodes using the same system. The discrepancy may be attributed to the difference in the current density range used in the two cases; in the present study

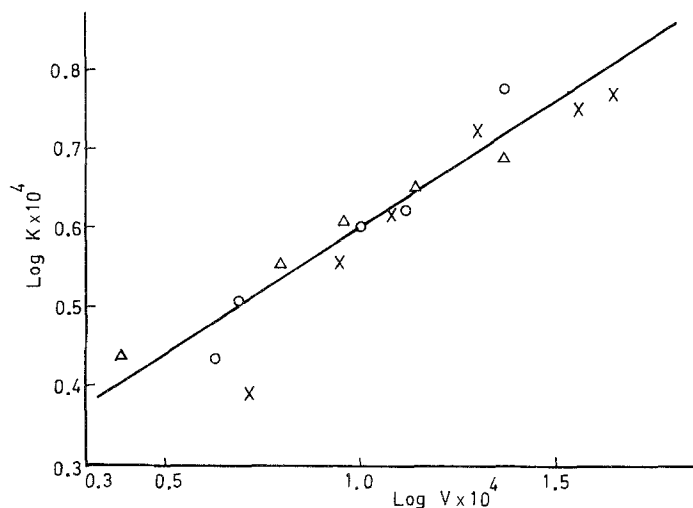


Fig. 3. Effect of H_2 discharge rate on the mass transfer coefficient at different $K_3Fe(CN)_6$ concentrations: x, 0.2 M; o, 0.15 M; Δ , 0.1 M. Bed height, 1.4 cm.

the range is $0.047\text{--}0.257\text{ A cm}^{-2}$ while that used by Fouad and Sedahmed was $0.018\text{--}0.105\text{ A cm}^{-2}$. The variation of the $\log K/\log V$ slope with current density range was also observed by Janssen and Hoogland [9, 10]. The present slope agrees with the value obtained by Janssen and Hoogland [10] for a horizontal, H_2 -evolving electrode in alkaline solution. The fact that for the same H_2 discharge rate of mass transfer at the supporting disc is higher than that at the fixed-bed electrode may be ascribed to the resistance offered to the moving gas-liquid dispersion by the bed and the pronounced blanketing of the lower half of each sphere by H_2 bubbles. Fig. 2 also shows that bed height has no effect on the mass transfer coefficient probably because of the turbulent nature of the flow and/or the attainment of fully developed flow. Fig. 3 confirms Equation 2 at different ferricyanide concentrations.

To assist in estimating the economic feasibility of using packed-bed, gas-evolving electrodes in practice, cell characteristics under H_2 evolving conditions were determined as shown in Fig. 4. For a given current density the cell voltage at the packed-bed electrode is much higher than at the supporting electrode, especially at high current densities, because of the ohmic drop caused by the bubbles adhering to the spheres and the bubbles present in the gas-liquid dispersion. The presence of gas bubbles between spheres may also cause a marked increase in contact resistance between spheres.

Since packed-bed electrodes are operated, in practice, under forced convection conditions the deleterious effect of bubbles on cell voltage is expected to be less than that observed in the present work by virtue of the sweeping effect of the flow on the gas bubbles [17, 18].

3.1. Application of the surface renewal model to gas-evolving electrodes

Studies on the effect of gas sparging on the rate of mass [19] and heat transfer [20] have revealed that the hydrodynamic boundary layer theory underestimates the rate of heat or mass transfer. Kast [20] attributed the high rates of transfer to the fact that the rising gas bubbles not only induce axial flow but also induce radial eddy momentum transfer which reaches the transfer surface with a fresh supply of bulk fluid. This postulate was confirmed experimentally by the tracer technique [21] where it was found that the radial dispersion coefficient in bubble columns is about three to four times larger than the axial dispersion coefficient. In the case of gas-evolving electrodes it is possible that the detached gas bubbles induce radial momentum transfer which reaches the electrode surface with a fresh supply of bulk solution. It is reasonable to assume that a radially flowing fluid element will stay for a certain contact time (\bar{t}) at the electrode surface and then leave it and enter the bulk fluid again. This situation can be treated by the Higbie surface renewal model [22] where unsteady

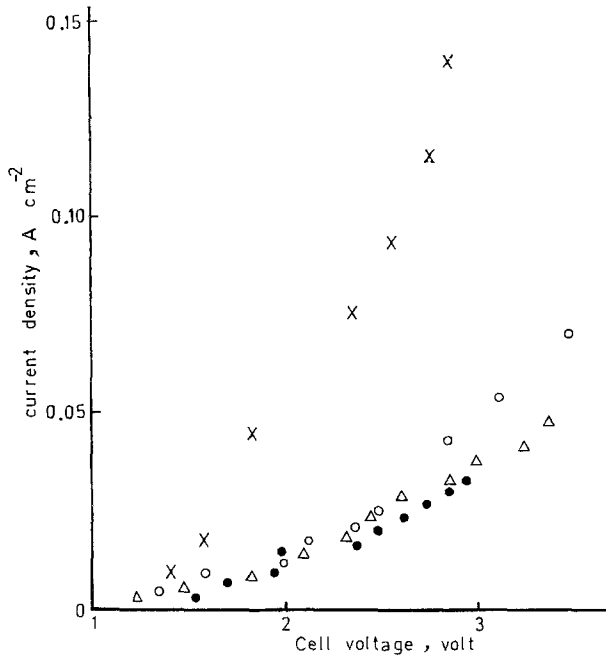


Fig. 4. Current density versus cell voltage for different bed heights. x, Supporting disc; o, 0.7 cm; Δ, 1.4 cm; ●, 2.1 cm. $K_3Fe(CN)_6$ concentration, 0.1 M.

diffusion takes place according to the equation

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial y^2} \quad (4)$$

which upon integration using the pertinent boundary conditions [5, 6] yields

$$K = 2 \left(\frac{D}{\pi t} \right)^{1/2} \quad (5)$$

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

$$\bar{t} \propto \frac{x}{u} \quad (6)$$

where x and u are length and velocity parameters which characterize the radially moving fluid element responsible for surface renewal. Deckwer [21] and Sedahmed [5], who correlated heat and mass transfer data in bubble columns and gas-sparged cells respectively, expressed the parameters x and u in terms of the Kolmogoroff theory of isotropic turbulence. This approach, which yields a $\log K/\log V$ slope of 0.25, seems to be valid when gas is uniformly distributed in the interelectrode gap [5]. In the case of gas-evolving electrodes the approach used by Ruckenstein and Simigelschi [23], who studied heat transfer in bubble columns, seems more appropriate. Based on dimensional considerations, the

following expressions were derived for x and u :

$$x \propto v^{2/3} (g\varepsilon)^{-1/3} \quad (7)$$

$$u \propto v^{1/3} (g\varepsilon)^{1/3} \quad (8)$$

Therefore

$$\bar{t} \propto \frac{x}{u} \propto \frac{v^{1/3}}{(g\varepsilon)^{2/3}} \quad (9)$$

Substituting for the contact time in Equation 5 using Equation 9 gives

$$K \propto \frac{2D^{1/2}}{\pi^{1/2} v^{1/6} g^{-1/3} \varepsilon^{-1/3}} \quad (10)$$

The dependence of the gas hold-up, ε , on gas velocity is generally of the form [24]:

$$\varepsilon \propto V^n \quad (11)$$

Substituting for ε in Equation 10 from Equation 11 gives

$$K \propto \frac{D^{1/2} g^{1/3} V^{n/3}}{\pi^{1/2} v^{1/6}} \quad (12)$$

The value of n in Equation 11 was reported by Shah *et al.* [24] to lie between 0.7 and 1.2. Kreysa and Kuhn [25] plotted the gas hold-up data measured by Siemes [26] as a function of the superficial gas velocity (Fig. 5 of [26]). The gas hold-up was found to increase linearly with the

superficial gas velocity (i.e. $n = 1$) and then remain constant with further increase in the superficial gas velocity. Kreysa and Kuhn [25] derived a theoretical relation between the gas hold-up and the superficial gas velocity using a coalescence barrier model. The relation is complex and shows that the gas hold-up increases non-linearly with the superficial gas velocity till it reaches a limiting value at a certain superficial velocity. However, the experimental data of Kreysa and Kuhn (ϵ versus V) below the limiting hold-up can be approximated fairly by a linear relation, i.e. $n \approx 1$. Putting $n = 1$ in Equation 12 gives

$$K \propto \frac{2D^{1/2} g^{1/3} V^{1/3}}{\pi^{1/2} \nu^{1/6}} \quad (13)$$

The above equation can be written in the form

$$K = bV^{0.33} \quad (14)$$

The velocity exponent of the above equation (0.33) agrees with the present experimental value (0.325). Substituting a value of n in the range of 0.7 to 1.2, as reported by Shah *et al.* [24], in Equation 12 it follows that the $\log K/\log V$ slope should range from 0.23 to 0.4. This agrees well with the values obtained by different authors [2, 4] who worked under conditions where bubble coalescence was negligible or slight. When coalescence is heavy the $\log K/\log V$ slope increases considerably and may reach the value of 0.9 as found by Janssen and Van Stralen [12]. The present model may explain the phenomenon observed by some investigators [27–29] where the mass transfer coefficient increases with the gas discharge rate up to a certain limit and then remains constant with further increase in gas discharge rate. Based on Equation 10, which can be written in the form

$$K = B\epsilon^{1/3} \quad (15)$$

and the hold-up data of Kreysa and Kuhn, it is probable that a limiting value of the mass transfer coefficient occurs when the limiting gas hold-up is reached. Ruckenstein and Simigelschi [23], who studied heat transfer in bubble columns, found that at a certain gas velocity the heat transfer coefficient and the gas hold-up reach a limiting value at the same time. This may support the above speculation. The phenom-

enon of the attainment of a limiting mass transfer coefficient at a certain gas flow rate was also observed in the case of gas-sparged electrodes (using external gases) [1, 19, 30, 31]. Physically speaking, the occurrence of a limiting mass transfer rate at the limiting gas hold-up may be attributed to the fact that the number of active bubbles per unit volume of the gas-liquid dispersion which promote the rate of mass transfer through surface renewal becomes constant at the limiting gas hold-up. However, much work remains to be carried out to confirm the above speculation, especially on the factors affecting the gas hold-up in electrolytic cells and its role in mass transfer.

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