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An experimental study of a single layer packed bed cathode in an electrochemical flow reactor

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Experimental measurements are reported for a packed bed electrode consisting of a single planar layer of uniform copper plated spheres located between platinum anodes and restrained by two plane porous PVC diaphragms. Two mass transfer controlled reactions, namely the reductions of *m*-nitrobenzene sulphonic acid and copper sulphate, were investigated and the electrochemical mass transfer data in the range $23 < Re < 520$ correlated by the equation

$$Sh\, Sc^{-\frac{1}{3}} = 0{\cdot}83\, Re^{0{\cdot}56},$$

the Reynolds and Sherwood numbers being defined in terms of a particle diameter. Variations of electrode potential throughout the bed were found to be small enough to ensure reaction selectivity in the system.

List of symbols

A	Electrode area (m^2)
C	Reactant concentration (kmol m^{-3})
D	Molecular diffusivity ($m^2\ s^{-1}$)
d	Particle diameter (m)
F	Faraday ($C\,mol^{-1}$)
I_L	Limiting current (A)
n	Number of electrons per molecule
u	Superficial velocity (ms)
ν	Kinematic viscosity ($m^2\ s^{-1}$)
ϕ	Electrode potential (V)
Re	ud/ν
Sc	ν/D

1. Introduction

The scale up of an electrochemical process nearly always requires the ratio of electrode area to cell volume to be preserved. Consequently the scale factor for such a system is much greater than for conventional reactors and process equipment. This fact has been discussed a good deal and attempts have been made to increase the available electrode area for a given cell volume by the use of electrodes consisting of large numbers of metal particles through which the electrolyte flows. Systems in which the particles are fluidized have now been extensively investigated notably by Goodridge *et al.* [1–3] and Fleischmann *et al.* [4–7], however the packed bed system where the particles are not in motion has received rather less attention [1,8].

The main drawback to the use of packed beds is that spacial electrode potential variations can be so large that loss of reaction selectivity results. This problem could possibly be substantially overcome by the use of a single layer of uniform particles with suitable current feed and plane counter electrodes in a parallel plate type of assembly as in Fig. 1. At first sight it would, of course, appear that such a system has only a modest increase in area over a plane electrode of similar overall dimensions. However, it has been calculated [9] that a current up to thirty times greater than for a plane electrode of similar dimensions could be obtained for a given flow rate with mass transfer controlled reactions. This situation arises due to much higher limiting currents because of the large interstitial electrolyte velocities and indicates that such a system may have merit.

This paper reports experimental work on a

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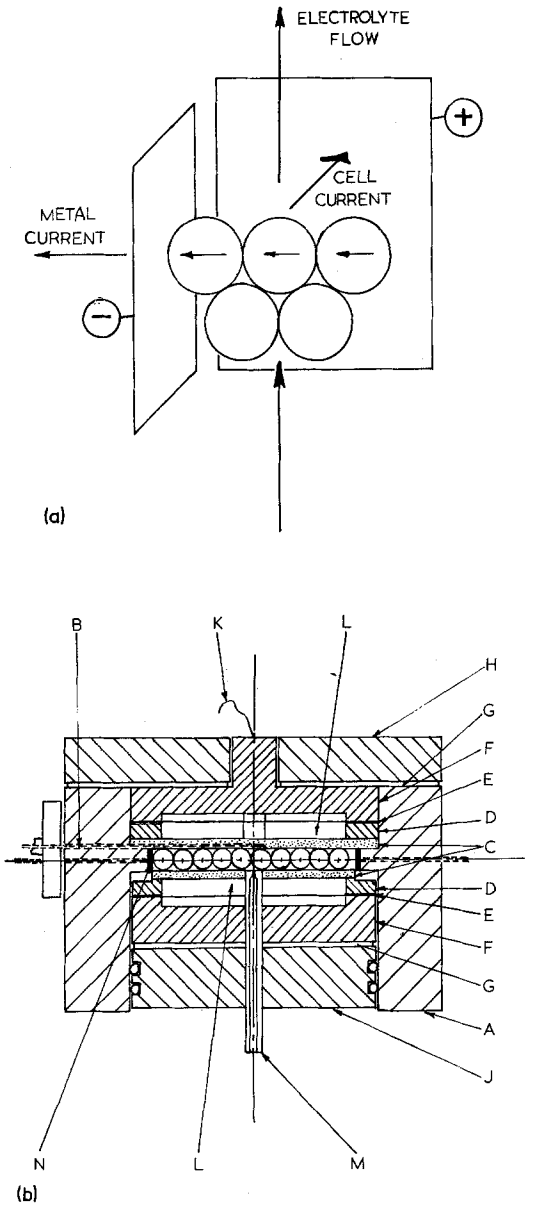

Fig. 1. (a) Schematic view of cell. (b) Cross section of experimental cell. A – cell body; B – traversing potential probe; C – Vyon diaphragms; D – spacer; E – platinum anode; F – anode mount; G – neoprene gasket; H – backing plate; J – adjustable backing plate; K – platinum wire; L – anode compartment; M – Luggin capillary; N – cathode feeder strips.

single layer bed electrode for two mass transfer controlled reactions, namely the reduction of sodium meta-nitrobenzene sulphonate and copper sulphate on a copper electrode.

2. Experimental

A full description of the system has been given by Stanmore [9], the pertinent details being included below.

2.1. *Cell and electrodes*

A cross sectional arrangement of the cell is shown in Fig. 1b. The cell body was made of perspex and consisted essentially of two main parts. The first comprised the main body and one anode compartment bolted together, the second being the other anode compartment which was easily removable and could be adjusted by means of a yoke/screw thread arrangement. Each anode compartment held pieces of platinum gauze 150 X 60 mm to act as anodes. These were connected at the edges to rubber sheet to provide rigidity and a liquid seal. The sheets were clamped between a perspex mount and spacer. Two 2·5 mm thick Vyon diaphragms were cemented to the spacers to provide sealed anode compartments. Each assembly was bolted to a backing plate fitted with QVF inlet and outlet stubs. Electrical connection was by means of platinum wires located in slots cut into two of the cylindrical spacing plugs between the mount and diaphragm. In the moveable anode compartment were two perspex Luggin capillaries with openings flush with the diaphragm surface for potential measurement. These were 100 mm apart and equidistant from the centreline. Bolted to the side of the cell body was a traversing stainless steel hypodermic potential probe insulated with Lacomit solution which ran in a groove in the diaphragm and allowed potentials to be measured to the centreline. The probe could be positioned at two points 25 mm on either side of the centreline, so that in all four points were available for potential measurements in the flow direction. To support the particles inside the cell, a perspex bridge with square section slots cut into it was placed across the cell bottom. Current was taken from the particles at either side of the cell by three copper wires each fixed to a 1·5 mm thick x 5 mm wide copper strip cemented into steps in the cell walls so as not to shield any of the anode area. Catholyte inlet and outlet connections were connected to the flow circuit and bolted on to the cell body.

The bed particles were steel balls with a layer of

phosphor bronze electroplate. The balls were exactly 1/4 in (6·35 mm) diameter with an electroplate not more than 0·03 mm thick. Copper was barrel plated on to these spheres before every run and good surfaces and reproducible over-potential data were obtainable.

2.2. *Flow and electrical circuits*

The flow circuits for both anolyte and catholyte, which were solutions of identical composition, are shown in Fig. 2. Flow to the cell was from the constant head tank via one of two rotameters. The anode compartments were run stagnant where possible. However, at high catholyte flow rates, flow across the diaphragm from the anode compartment occurred so that a partial vacuum could be applied to the anode compartment by means of a reservoir evacuated by a water pump. Anolyte flowed from the cell by an air lift which removed the gas formed by electrolysis; it was replenished by flow from the bottom of the reservoir which was controlled by a globe valve.

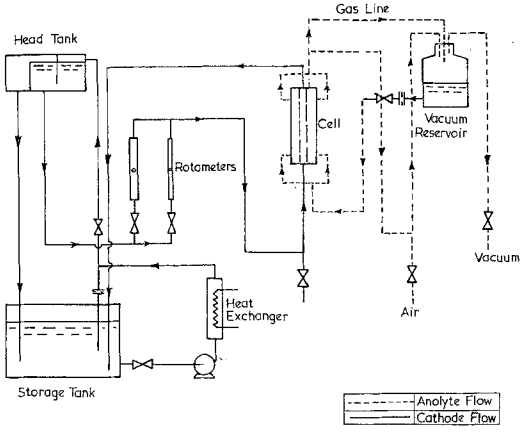

Fig. 2. Flow Circuit.

The main electrical circuit contained an Advance Industrial Electronics Type PM20 stabilised power supply of 20 A capacity at 7·5 V. The circuit on the cathode side contained an Avometer and five resistors to enable a maximum current of 20 A to be measured on a recorder.

Potential measurements were made by connecting the bed capillaries to three saturated calomel electrodes via agar bridges. To avoid polarizing the electrode the output was amplified before being measured. All measurements of potentials and currents were made on a Pye Ether 70568 six channel recorder of 50 mV full scale with a thirty second printout interval. The overall cell voltage was measured by a voltmeter across the power supply. The power supply incorporated an external programming capability at 100 Ω V^{-1}, so a ten-turn 250 Ω wire-wound potentiometer driven by a small synchronous motor was put in series with the voltage control to provide an automatic sweep characteristic giving 25 mV min^{-1} potential increase across the cell.

2.3. *Procedure*

Two electrolytes were used during the work. The first consisted of analytical grade *m*-nitrobenzene sulphonic acid sodium salt (m NBSA) dissolved in 1 M sulphuric acid to give concentrations from 0·004 – 0·0315 M in m NBSA. The copper sulphate solutions (0·013 – 0·0102 M) were also made up in 1 M sulphuric acid from analar reagents. Before commencing each series of runs with either electrolyte, the solution was purged with oxygen-free nitrogen and analysed as described elsewhere [9].

The spheres were prepared by barrel plating at 5 A m^{-2} for 20 min, then water washed and dried with cotton wool. They were then packed into the cell. Entry lengths of glass ballotini of the same nominal diameters as the electrode spheres were provided to bring the first row of plated spheres level with the feeder. Packing of the spheres was regular, the spheres being in rows across the cell, producing an equilateral triangular pitch. The total cathode area in all runs was 320 cm^2 corresponding to twenty-eight rows of spheres in the flow direction. The adjustable anode compartment was then screwed down lightly until zero electrical resistance from feeder to feeder was obtained.

After assembly and adjustment of catholyte flow rate the rest potential was allowed to steady and the overall cell voltage set at about 1·4 V which was sufficient to produce a small current. After allowing the electrode to stabilize, the sweep was started and continued until hydrogen was evolved at about 600 mV cathodic overpotential. The voltage was then returned to zero, the rest potential measured and a new run started. After three runs, the cell was dismantled for electrode replating and electrolyte analysis.

The variables measured were overall bed current and electrode potentials at various points in the bed. Potential profiles were constructed by comparing values at the Luggin points selected. On some runs, the potential across the bed was measured by the traversing probe at various fixed current densities. The range of flowrates used corresponded to a range of $Re = 23$ to 520.

The contributions of the cell feeder strips to the overall current were established by runs in which the cell was packed with glass spheres. The potential in this instance was measured by the traversing probe located in the plane of the feeder.

3. Results and discussion

For m NBSA, data on density, viscosity and molecular diffusivity were obtained from Postlethwaite *et al.* [10]. That for copper sulphate was obtained from [11] which is a collection of data from various sources. From the measured flow rates, superficial velocities and Reynolds numbers were determined. The limiting currents were used to evaluate average Sherwood numbers from Equation 1.

$$Sh = \frac{I_L\, d}{nFACD} \qquad (1)$$

Runs done with the cell packed with glass spheres enabled mass transfer at the wall feeder strips to be correlated by the equation

$$Sh = 0{\cdot}725\, Re^{0{\cdot}56}\, Sc^{\frac{1}{3}}. \qquad (2)$$

The Sherwood and Reynolds numbers were calculated in Equation 2 by using a particle diameter as the characteristic length in order to be consistent with the bed definitions. Since Equation 2 was found *'a posteriori'* to predict values of *Sh* comparable with those of the bed, the feeder strips, whose area never exceeded 4% of the total electrode area, were regarded as additional sphere surface.

Table 1. Typical Experimental Results

Re	*C* (kmol m^{-3})	*Sc*	I_L (A)	I_L A^{-1} (A m^{-2})
41	0·0044	2830	0·38	11·9
63	0·0112	2890	1·68	52·7
99	0·0108	2880	1·84	57·7
140	0·0121	2890	2·90	91·0
194	0·0298	3040	6·70	210
314	0·0105	2880	3·62	113

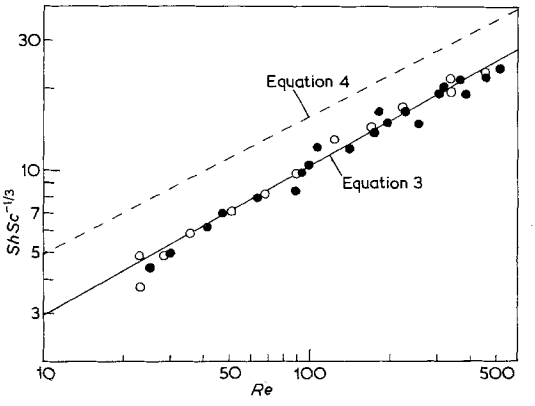

Fig. 3. Plot of $ShSc^{-\frac{1}{3}}$ versus Re for mNBSA, $CuSO_4$.

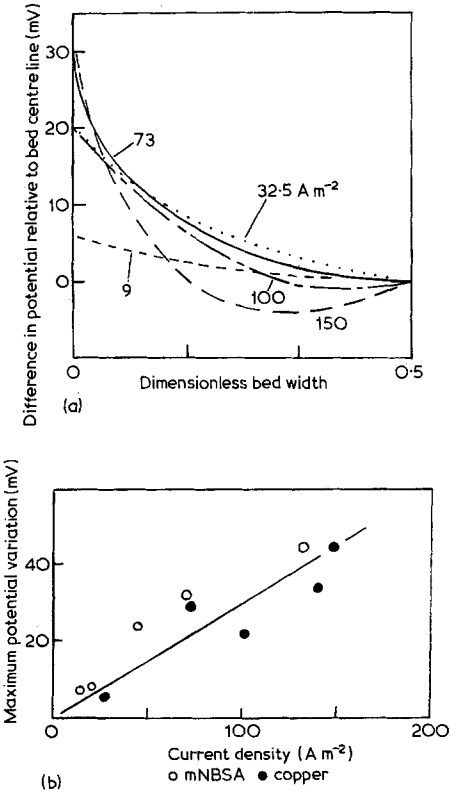

Fig. 4. (a) Variation of potential difference across bed for various current densities. (b) Variation of maximum solution potential difference with current density.

Data are presented in Table 1 for mNBSA and plotted for both electrolytes in Fig. 3 as $Sh/Sc^{\frac{1}{3}}$

versus *Re*. Both sets of data can be correlated to within about ±10 by an equation.

$$Sh = 0{\cdot}83\, Re^{0{\cdot}56}\, Sc^{\frac{1}{3}} \qquad (3)$$

which is shown in Fig. 3. Also presented as a comparison is a typical packed bed mass transfer correlation [12] corrected for the bed voidage (0·40).

$$Sh = 1{\cdot}54 Re^{\frac{1}{2}} Sc^{\frac{1}{3}} \qquad (4)$$

and it is evident that the present data fall far below conventional packed bed mass transfer data.
It is interesting to note however that the Reynolds number power is very close to that found by Wegner *et al.* [13] for arrays of regularly packed spheres in a bed. The discrepancies between Sherwood numbers calculated from Equations 3 and 4 are of course to be expected. Due to the open structure of the electrode a good deal of channelling will occur in the bed and was indeed observed during the measurement of electrolyte residence times [9], particularly at Reynolds numbers above 100. This would give rise to reduced mass transfer coefficients in the centre of the bed compared with the edges. Since the effective electrode area is less at the edges for a given volume a reduction in total current would most likely result.

The variation of electrode potential throughout the bed would produce a certain amount of variation in local current densities. The most severe variations were found not unexpectedly in the direction orthogonal to the flow from the bed centreline to the feeder and this is consistent with the observations of Goodridge [1]. Experimental measurements of the potential across the bed are shown in Fig. 4a and the dependence of the potential change on the mean current density demonstrated in Fig. 4b. It appears that there are no significant differences between the two electrolytes but a tendency exists for greater potential variations as the current density (and electrolyte velocity) increases. This is consistent with observations that charge transfer becomes more significant at higher flow rates with the two electrochemical reactions used [9] resulting in increasing current variation over a given potential range. The differences exhibited however are of the order of 45 mV maximum compared to a centre line potential of around 550 mV so that for this range, significant differences in local current density are not too likely. In the longitudinal (flow) direction, potential gradients were found to be small. Indeed about 80% of all the runs exhibited only about 10 mV maximum variation along the bed. When changes did occur they were consistent from run to run with unchanged packing. With repacking a rise or fall of potential in the flow direction appeared random.

The question of potential variation around the surface of an individual sphere has been considered [9] but it is unlikely to be too significant when the majority of the potential drop occurs in the diffusion layer and not in the bulk of the electrolyte [14]. It may be that the distortion of the diaphragm around the spheres could result in some inactive electrode area but this should be small.

The overall extent of the potential variations in the structure are encouraging from the point of view of the reaction selectivity of such systems. A model for this system has been developed, and its application to a charge transfer controlled reaction is being considered to further elucidate some of the above points [14].

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