

Mass transfer at carbon fibre electrodes

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Mass transfer at carbon fibre electrodes has been studied using the mass transfer controlled reduction of potassium hexacyanoferrate(III) to potassium hexacyanoferrate(II). Different geometrical configurations have been assessed in a flow-by mode, namely bundles of loose fibres with liquid flow parallel to the fibres, carbon cloth with flow parallel to the cloth and carbon felt with liquid flow through the felt. For comparison, mass transfer rates at a single fibre have been measured; the experimental data fit the correlation $Sh = 7 Re^{0.4}$. The same correlation can be used as a first approximation for felts. Mass transfer for fibre bundles and cloth under comparable conditions is much lower owing to channelling.

Nomenclature

c	reactant concentration (mol m^{-3})
c_0	reactant concentration at $x = 0$ (mol m^{-3})
c_L	reactant concentration at $x = L$ (mol m^{-3})
d	fibre diameter (m)
D	diffusion coefficient ($\text{m}^2 \text{s}^{-1}$)
F	Faraday number (96 487 C)
h	depth of the electrode (m)
i	current density (A m^{-2})
I	current (A)
k	mass transfer coefficient (m s^{-1})
L	length of the electrode (m)
n	number of electrons
S	specific surface area ($\text{m}^2 \text{m}^{-3}$)
u	(superficial) velocity (m s^{-1})
V_R	reactor volume (m^3)
w	width of electrode (m)
x	distance in flow direction (m)
β	current efficiency
η	electrode efficiency
λ	characteristic length (m)
ν	kinematic viscosity ($\text{m}^2 \text{s}^{-1}$)
q_s^n	normalized space velocity ($\text{m}^3 \text{m}^{-3} \text{s}^{-1}$)
Re	Reynolds number (ud/ν)
Sh	Sherwood number (kd/D)
Sc	Schmidt number (ν/D)

1. Introduction

During the last decade a great many novel

electrochemical reactors have been proposed for the treatment of dilute, mostly aqueous, solutions. Much attention has been paid to the electrolytic deposition and recovery of metals from waste waters from plating industries [1-3]. By contrast, electrochemical treatment of dilute waste solutions containing toxic or non-biodegradable organic compounds has received much less attention. The concentrations of compounds to be removed from either type of waste water are often so low that three-dimensional electrodes are needed if electrochemical treatment is to be economic.

One problem in the practical application of electrochemical treatment is the presence of dispersed particles in the stream. If electrodes are not to be clogged by such particles their design has to meet special demands.

In view of their high surface to volume ratio and their availability in various electrode configurations that may allow treatment of waste waters with dispersed solids, we have chosen carbon fibres as the electrode material. (Although a number of measurements have been made with graphite fibres, we shall in this report use the name carbon fibre for short.) Carbon fibres usually have a diameter of about $10 \mu\text{m}$ and therefore present a very high specific surface area (about $4 \times 10^5 \text{m}^{-1}$). They are produced in ever larger quantities for production of light-weight reinforced plastics and so are expected to

fall in price. When used in a flow-by mode (electric current perpendicular to fluid flow) they may enable the development of electrode systems less sensitive to clogging by small solid particles. An example of such an electrode is a bundle of fibres with the flow of liquid parallel to them.

Several companies and research groups are already using or studying the use of carbon fibre electrodes [4–11]. In spite of this, the literature contains few data (needed for the design of electrochemical reactors) on the mass transfer properties of various electrode geometries. We therefore considered it opportune to investigate the mass transfer properties of some configurations of carbon fibre bundle electrodes and of commercially available carbon fibre fabrics and felt.

The study was performed with a mass transfer controlled reaction, namely the reduction of potassium hexacyanoferrate(III) to potassium hexacyanoferrate(II). The configurations, which have all been studied in the flow-by mode, are:

- (i) Bundles of carbon fibres with liquid flow parallel to the fibres.
- (ii) Cloth, woven of carbon fibre yarn, with liquid flow parallel to the cloth.
- (iii) Felt made of carbon fibres with liquid flowing through the felt in the longitudinal direction.

To gain a better understanding of the results, values for the mass transfer at single carbon fibres in a flowing liquid were also measured.

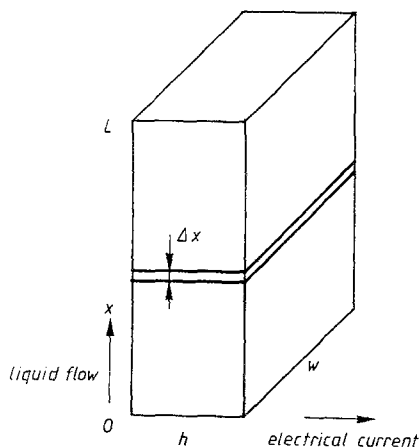


Fig. 1. Electrode dimensions.

2. Theoretical

The model used to study the mass transfer properties of carbon fibre electrodes is similar to that used before for packed and fluidized bed electrodes (see e.g. [12]). It is assumed that the solution flows through the material at a steady uniform velocity and that no back-mixing takes place (plug flow). The rate of decrease of the concentration depends on the mass transfer coefficient and the specific surface area of the three-dimensional electrode. For a mass transfer controlled reaction the concentration in different places in the bed can be calculated from the mass balance for a differential element, dx , of the electrode (Fig. 1.)

For the liquid phase this microbalance equation reads:

$$kSc = -u \frac{dc}{dx} \quad (1)$$

Integration of Equation 1 over a height x of the bed gives:

$$c = c_0 \exp(-kSx/u) = c_0 \exp(-x/\lambda) \quad (2)$$

where c_0 is the initial concentration and $\lambda (= u/kS)$ is the characteristic length (also called unit of reaction), i.e. the distance in which the concentration of reactant is lowered by 63% ($c = c_0/e$). The conversion per pass for an electrode of length L is given by

$$1 - \frac{c_L}{c_0} = (1 - \exp(-L/\lambda)) \quad (3)$$

The local current per unit electrode volume with depth h and width w (see Fig. 1) is

$$di = nFkchwSdx \quad (4)$$

The total current for an electrode of length L can be calculated from Equations 2 and 4 by integration:

$$I = nFhwc_0u (1 - \exp(-L/\lambda)) \quad (5)$$

From Equation 3 it can be seen that a small value of λ gives a high conversion per pass. For this reason, λ has been chosen as a characteristic number for the purpose of comparing the mass transfer properties of the various carbon fibre configurations.

In order to compare the performance of carbon fibre electrodes for use in the treatment of waste waters, we have also used a 'figure of merit', proposed by Kreysa [13]. This so-called normalized space velocity, q_s^n , is defined as

$$q_s^n = \frac{I\beta}{(c_0 - c_L)V_R nF} \log \frac{c_0}{c_L} \quad (6)$$

q_s^n refers to the volume of waste water for which the concentration of the reactant can be reduced by a factor of 10 per unit of time and per unit of reactor volume. Kreysa has chosen this figure of merit because it strongly correlates with investment costs, which are the dominating costs in the electrolytical treatment of waste waters.

As has already been mentioned in the introduction, mass transfer equations for fibres are scarce. For a single platinum fibre ($d = 10 \mu\text{m}$) embedded in a non-conducting felt, Bek and Zamyatin [8] found:

$$k = 1.90 \times 10^{-2} u^{0.352} \text{cm s}^{-1} \\ \times (0.02 < Re < 0.15) \quad (7)$$

Transformed into dimensionless form, Equation 7 reads

$$Sh = 6.1 Re^{0.352} (0.02 < Re < 0.15) \quad (8)$$

For a carbon felt composed of fibres of diameter $10 \mu\text{m}$, they found that the same relation applied.

Other measurements on carbon felts (fibres of diameter $25 \mu\text{m}$), have been published by Kinoshita and Leach [9] who proposed

$$Sh = 1.29 Re^{0.72} (0.01 < Re < 0.25) \quad (9)$$

for a felt 0.25 cm thick and

$$Sh = 1.01 Re^{0.61} (0.02 < Re < 0.25) \quad (10)$$

for a felt 0.175 cm thick. The dependence of these results on electrode thickness and especially the high exponent of Re are rather unexpected for the (laminar) flow regime in question. Furthermore, values for Sh are much lower than those found by Equation 8. The explanation is that Kinoshita and Leach calculated Sh directly from the total current without correcting for the degree of conversion. In calculating Sh as we define it, dropping this correction is only permitted for very low degrees of conversion.

Oren and Soffer [10] have also conducted measurements on felts. They found the variation between limiting current and flow rate to be linear, owing to the near-completeness of conversion under the conditions of their experiments. For this reason we did not calculate a Sherwood–Reynolds relation from the results of their experiments. For bundles of fibres and cloth with liquid flow in the length direction of the fibres or cloth, no usable relations were found in the literature.

Processes and equations in heat transfer being comparable with those in mass transfer (Chilton–Colburn analogy), we have also searched the literature on the former. Most literature concerns heat transfer on wires. For the range of Re studied we found only experimental equations for single wires. Transformed into a mass transfer equation, the most suitable equation for fibres appears to be [14]:

$$Sh = 0.9 Re^{0.385} Sc^{0.31} (0.1 < Re < 50) \quad (11)$$

For aqueous diluted solutions, $Sc \cong 1400$ (for $D = 7.10^{-10} \text{m}^2 \text{s}^{-1}$), resulting in

$$Sh = 8.5 Re^{0.385} (0.1 < Re < 50) \quad (12)$$

This relation has been found to be valid for flow perpendicular to a wire; for flow parallel to the wire it is stated [14] that values 40% lower should be taken, giving

$$Sh = 5.1 Re^{0.385} \quad (13)$$

Both relations agree reasonably well with the relation found by Bek and Zamyatin (Equation 8). Equations 8, 12 and 13 are used for comparison with the present results of mass transfer measurements for the various fibre geometries; this comparison affords an estimate of the efficiency or utilization factor of the multi-fibre electrodes. This utilization factor (η) will be defined as the ratio of the λ value calculated from the measurements at a single fibre to the λ value calculated from the measurements on the multi-fibre electrode. From $\lambda = u/kS$ it follows that the utilization factor is also equal to the ratio of the kS values.

3. Experimental details

3.1. The single fibre cell

Experiments with single fibres were conducted in

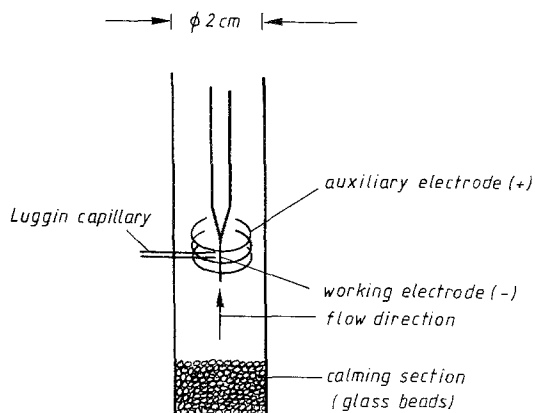


Fig. 2. Single fibre cell.

the set-up shown in Fig. 2. The fibre was fixed in a drawn-out glass capillary with epoxy resin. Electrical contact with the fibre was made by a mercury drop. The exposed length of the fibre in solution was 0.5 cm and 1 cm, respectively. The test solution was passed along the fibre. A helical platinum wire served as an auxiliary electrode. The fibre potential was controlled with a Luggin capillary connected to a saturated calomel electrode (SCE).

3.2. The multi-fibre cell

A diagram of the multi-fibre cell is shown in Fig. 3. The cell accepts various fibre configurations (bundles, cloth, felt). These are usually clamped to a platinum strip connected with an electrical power source; an insulating material is used for the clamping. The cathodic compartment in which the configurations to be investigated are clamped is 10 cm high, 2 cm wide and 0.5 cm deep. Incorporated in the clamping unit are holes to give an equal flow along the width of the electrode. The counterelectrode (platinum gauze) is separated from the working electrode by a cation selective membrane (Nafion 425), which serves to prevent both electrical and hydraulic short circuiting.

3.3. Electrode materials

For the experiments with single fibres, Le Carbone Lorraine AGT/F10 000 fibres with a diameter of $8\ \mu\text{m}$ were used. Table 1 lists the

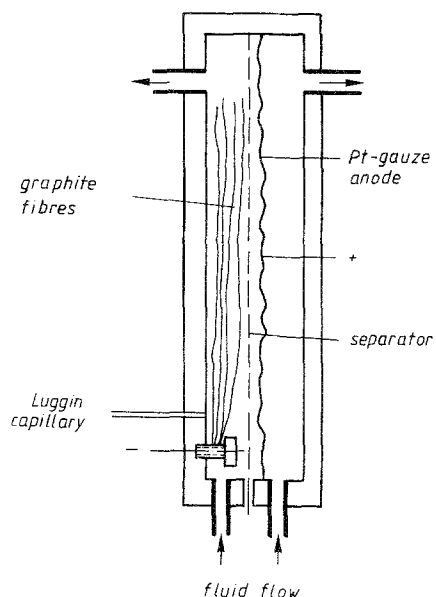


Fig. 3. Multi-fibre cell.

materials used in the multi-fibre experiments and some of their properties. The (external) porosity is the percentage of free liquid-filled space between the fibres, assuming the fibres are equally spread in the cathodic compartment. The total length of the fibre electrodes in the cathodic compartment is 8.3 cm, leaving 1.7 cm free space at the outflow side. The thickness of the felt (0.5 cm) and the seven layers of cloth is such that they completely fill the cathodic compartment.

3.4. Flow circuit

The flow circuit is shown in Fig. 4. All experiments discussed here have been conducted in a single pass mode. Velocities have been chosen in a range that will be used in practice (some dm s^{-1}).

3.5. Model reaction

In studying the performance of the fibre electrodes, the mass transfer controlled reduction of potassium hexacyanoferrate(III) to potassium hexacyanoferrate(II) was used. Reactant concentrations were 10^{-4} to $10^{-2}\ \text{M}$ in 1 M KOH solutions. All measurements were conducted at room temperature.

Table 1. Types and properties of carbon fibre electrodes used

Configuration	Number or quantity of fibres	Calculated surface area for $L = 8.3 \text{ cm}$ (m^2)	Specific surface area (m^{-1})	Porosity (%)
Parallel bundles (a)	10 000	0.019	2 500	99.5
	50 000	0.096	12 600	98
	200 000	0.385	50 400	90
	500 000	0.962	126 000	75
Cloth (b)	7 layers	0.631	82 500	83
Felt (c)	1 layer	0.087	11 300	96

(a) Le Carbone Lorraine AGT/F 10 000, graphite fibres $8 \mu\text{m}$ in diameter.

(b) UCAR WCA – graphite cloth, fibre diameter $8 \mu\text{m}$.

(c) UCAR WDF – graphite felt, fibre diameter $15 \mu\text{m}$.

3.6. Instrumental

The potential of the single fibre electrode was controlled by means of a PAR 174 Polarographic Analyzer, and that of the multi-fibre electrode by a Wenking potentiostat 68TS10 in conjunction with a voltage scan generator VSG72 (both from G. Bank Electronics). The current voltage relations were recorded on a Philips PM 8041 x - y recorder. The scan rate was 1 mV s^{-1} .

After constant potential electrolysis in the multi-fibre cell, the potassium hexacyanoferrate(II) concentrations were determined by

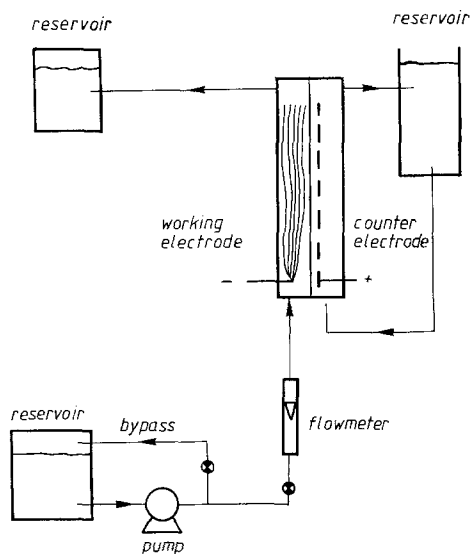


Fig. 4. Diagram of flow circuit.

potentiometric titration with cerium(IV) sulphate using a Metrohm 636 Titroprocessor and a platinum indicator electrode.

4. Results and discussion

4.1. Single fibre electrodes

Polarization curves of a single fibre electrode at different rates of flow (exposed length 0.5 cm) are given in Fig. 5. This shows that the reaction

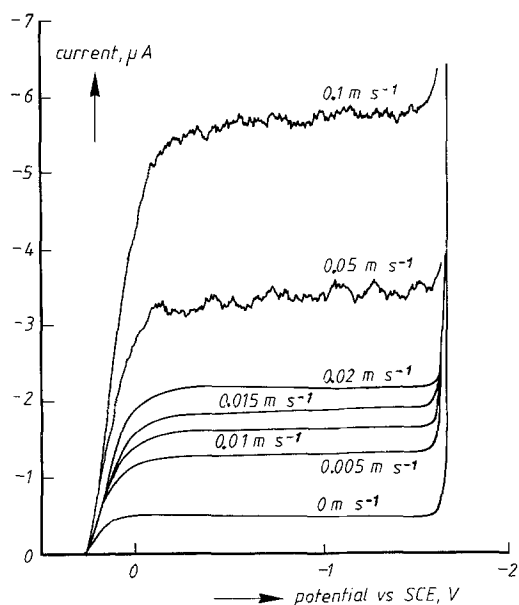


Fig. 5. Polarization curves for a single fibre electrode at different flow velocities ($10^{-3} \text{ M K}_3\text{Fe}(\text{CN})_6$ in 1 M KOH , $L = 0.5 \text{ cm}$).

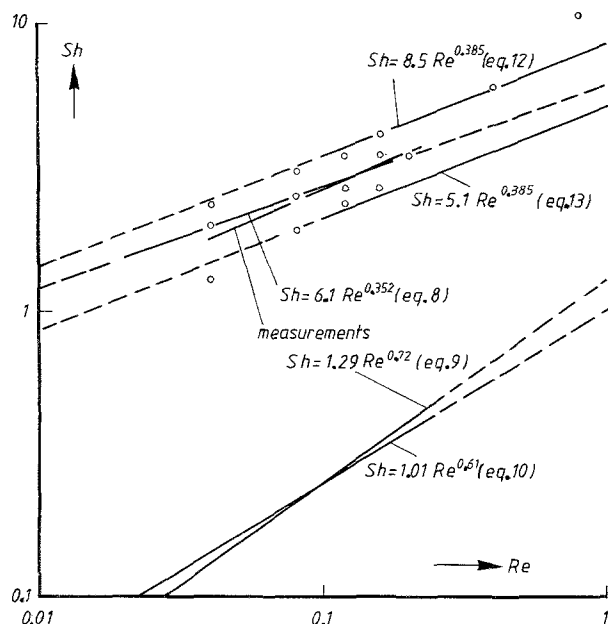


Fig. 6. Mass transfer correlations. —, literature equations; ----, extrapolated; O, measured in present study.

at the fibre electrode is mass transfer-controlled over a wide range of potentials, namely from about 0 V to -1.6 V versus SCE. The fluctuations in the current at higher velocities are caused by the transition from laminar to turbulent flow in the tube, leading to movement of the fibre in the flow (at 0.05 m s^{-1} , Re based on the tube diameter is 10^3).

In Fig. 6 the values of Sh calculated from the limiting currents in Fig. 5 are given as a function of Re . The lines represent the Sh values calculated from Equations 8, 9, 10, 12 and 13. The measurements on a single fibre are clearly in good agreement with both the data for heat transfer on wires (Equations 12 and 13) and the data for mass transfer on a single wire in a felt (Equation 8). The relation between Sh and Re for the data measured at velocities up to 0.02 m s^{-1} can be approximated by the linear regression method

$$Sh = 7Re^{0.4} \quad (0.04 \leq Re \leq 0.2) \quad (14)$$

with a somewhat higher exponent than that in Equations 8, 12 and 13. Sh values calculated from the individual measurements agree with those from Equation 14 to within 30% (see Fig. 6). At 0.05 and 0.1 m s^{-1} , values of Sh are higher than calculated from Equation 14, owing to the turbulence of the flow in the tube.

4.2. Multi-fibre electrodes

Fig. 7 shows some polarization curves for bundles of 200 000 fibres at various flow rates. Although at higher flow rates the current is not really constant, the figure reveals that most of the electrode is operating under limiting current conditions. In Fig. 8 the mean λ values calculated from the measured concentrations with Equation 2 are plotted as a function of flow rate

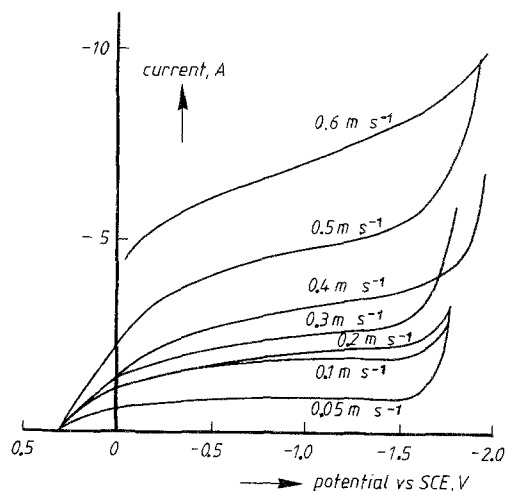


Fig. 7. Polarization curves for a bundle of 200 000 fibres at different velocities ($10^{-2} \text{ M K}_3\text{Fe(CN)}_6$ in 1 M KOH , $L = 8.3 \text{ cm}$).

for the different geometries investigated (electrode length in these experiments was 8.3 cm). From this figure it can be seen that the increase in the number of fibres in a bundle and thus in electrode surface area has relatively little influence on mass transfer: a 50-fold increase in specific surface area causes λ to decrease by a factor of only about 3. Results calculated with Equation 5 from the measured limiting currents agree within 15% with the values calculated from the measured concentration.

Obviously, most of the fibres do not take part in the reaction, probably owing to the flow between the parallel fibres being non-uniform and proceeding in preferred stream patterns (channelling). At higher velocities λ generally decreases for 50 000 and 200 000 fibres, whereas for 10 000 and 500 000 fibres it still increases. This must be due to instabilities in the flow in this range of velocities, leading to rearrangement and/or movement of the fibres which in its turn gives rise to higher mass transfer coefficients and/or exposure of a larger electrode surface area to the flowing electrolyte. This is plausible when one compares the results for fibre bundles of different histories (e.g. different sequence of experiments or different flow conditions in the preceding experiments) with those of bundles of the same history. In the first case differences in λ values at the same velocities can be as high as 50%, whereas in the second case differences are less than 20%.

The cause of these phenomena must be sought in the transition of laminar to turbulent flow that occurs at a velocity of 0.2–0.3 m s⁻¹, corresponding to *Re* values based on the hydraulic diameter of the flow channel of 1600–2400. Research into these instabilities is still in progress, one purpose being to improve mass transfer in flow-by bundle electrodes which may be important in the treatment of waste water containing dispersed solids (see Introduction).

The λ values calculated from the measurements with bundles of fibres of length 1 cm are not given in Fig. 8; within the measuring accuracy they are the same as those for the longer fibres. This provides additional confirmation that most of the fibre electrode operates under a mass transfer-controlled regime. Fig. 8 also shows the results for several layers of cloth. The λ values

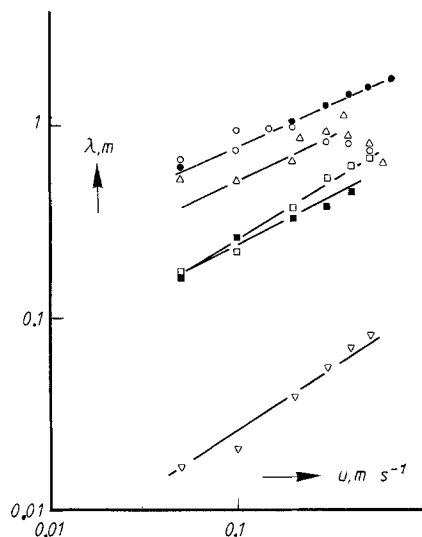


Fig. 8. Characteristic length for the different fibre configuration at different flow velocities: ●, 10 000 fibres; ○, 50 000 fibres; △, 200 000 fibres; □, 500 000 fibres; ■, cloth (seven layers); ▽, felt.

are of the same order as those for 500 000 fibres. The total surface area of the seven layers is equal to that of a bundle of 330 000 fibres. The λ values for the felt (see also Fig. 8) are much smaller than those for the bundles and cloth, indicating a much higher rate of mass transfer. This can be expected because the fibres in a felt are always in contact with the flowing liquid.

The mean slope of the λ versus u curves varies from 0.4 to 0.55 for loose bundles and cloth and from 0.6 to 0.65 for the felt. From the definition of λ (u/kS) it follows that the slope for the k values (i.e. the power coefficient in the *Sh-*Re** relations) varies from 0.45 to 0.6 for bundles and cloth and from 0.35 to 0.4 for the felt. These latter values agree well with the slope found for single fibres in a felt (see Equation 8 in Fig. 6).

Table 2 compares the utilization factors (η , defined in Section 2) for a velocity of 0.05 m s⁻¹. As has already been mentioned, these factors are equal to the ratio of calculated and measured λ values. The low values of η , especially for bundles with more than 50 000 fibres and for the cloth, also indicate that flow in these configurations is far from ideal. Considering the accuracy (reproducibility) of the measurements it can be concluded that the results measured for a felt agree well with the values predicted from measurements with a single fibre.

Table 2. Utilization factors η for the different electrode geometries studied at 0.05 m s^{-1} (for a single fibre η is by definition 100%)

Geometry	λ_{meas} (Fig. 8) (m)	λ_{calc} (Equation 14) (m)	η (%)
10 000 fibres	0.60	4.8×10^{-2}	8.0
50 000	0.06	1.0×10^{-2}	1.6
200 000	0.38	2.4×10^{-3}	0.6
500 000	0.17	1.0×10^{-3}	0.6
Seven layers of cloth	0.17	1.5×10^{-3}	0.9
Felt	1.7×10^{-2}	1.5×10^{-2}	90.0

5. Comparison with other electrode geometries

Direct comparison of λ with other three-dimensional electrodes is only possible for the same superficial velocities. As an example we used the data for flow-through packed beds of 0.8–1.0 mm particles ($S = 4000 \text{ m}^{-1}$) given by Chu *et al.* [12]. At 1.43 cm s^{-1} the measured λ value was 7.3 cm. If we assume that $\lambda \propto (u)^{1/2}$ as their measurements indicated, λ at 5 cm s^{-1} should be 13.6 cm which is of the same order as the λ values measured for some fibre bundles and the cloth (see Fig. 8). Comparable values have recently been found by Simonsson [15] for a flow-by packed bed of graphite particles. The data also illustrate the relatively small degree of utilization of the total surface area. The λ values of the felt are one order of magnitude lower than those for the packed bed.

Another basis for comparison is the normalized space velocity (see Section 2). Data for different types of cells and different solutions were gathered by Kreysa [3] and are given in Table 3. Values for q_s^n calculated from our

Table 3. Normalized space velocities for different electrodes

Electrode type	q_s^n ($l l^{-1} h^{-1}$)
Rotating cylinder	20
Swiss roll	20
Porous flow-through	0.9
Fixed bed	28
Fluidized bed	30
Rotating fixed bed	250
Rolling tube	0.4

Table 4. Values of q_s^n for the multi-fibre electrodes

q_s^n ($l l^{-1} h^{-1}$)	u (m s^{-1})		
	0.05	0.2	0.5
10 000	135	310	505
50 000	135	310	1 110
200 000	215	465	1 065
500 000	475	850	–
Seven layers of cloth	475	950	–
Felt	4800	8 100	11 000

experiments are given in Table 4 for three different flow velocities. The values are generally much higher than those given by Kreysa. The high specific surface area of the fibre electrodes cannot be the only reason for this because λ values, and thus q_s^n values, for a packed bed electrode and fibre bundle are comparable for the same velocity. One reason for the difference is that in the present experiments and those of Chu *et al.* [12] the reaction used was ideal from the viewpoint of mass transfer, whereas the data given by Kreysa are concerned with waste waters containing metals. This is illustrated by the fact that the q_s^n value calculated from the measurements of Chu *et al.* [12] is about 30 times higher than the value given by Kreysa for a packed bed. Another reason for the differences is that the present experiments have been carried out at a relatively high velocity where mass-transfer coefficients are high (see e.g. Equation 8), leading to higher current densities and therefore to higher values of q_s^n .

6. Conclusions

The mass transfer correlation for a single fibre electrode in a flowing liquid agrees well with those found for a single fibre in a felt [8] and for heat transfer on wires [14]. The experimental mass transfer data for a single wire fit the correlation $Sh = 7Re^{0.4}$.

In fibre bundles and cloth, mass transfer in a flow-by configuration is lower than that calculated from the relation for a single fibre and the total surface area exposed. This might be due to channelling effects. However, when we compare the results of our measurements with those

obtained for other geometries (see Tables 3 and 4) it becomes clear that, even under the flow-by conditions occurring in fibre bundles and cloth electrodes, relatively high capacities for the treatment of waste water can be attained.

Felts are very attractive as electrode material in the treatment of dilute solutions (e.g. waste waters). For scaling-up purposes their mass transfer properties can be calculated directly from the relation for a single fibre and the total external surface area of the fibres in the felt.

Where felts are not suitable (e.g. in liquids containing dispersed solids, or when having unfavourable electrochemical properties), fibre bundles or cloth can give good results.

In the range of flow velocities investigated, transition from laminar to turbulent flow takes place and leads to a relatively low reproducibility of the measurements and a lowering of the characteristic length at higher velocities. For practical application it is important that, because flow is in the transition region, even simple modifications (e.g. turbulence promoters, ultrasonic vibration) can be expected to improve mass transfer greatly.

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References

- [1] A. Kuhn, *Chem. Ind.* **13** (1978) 447.
- [2] Anon., *Processing* (May 1982) 55.
- [3] G. Kreysa, *Metalloberflaeche* **35** (1981) 211.
- [4] G. I. P. Levenson, and C. J. Sharpe, *J. Photogr. Sci.* **29** (1981) 16.
- [5] B. Fleet, and S. das Gupta, U.S. Patent 4 108 754 (1978).
- [6] E. Sutzkover, C. Zur and M. Ariel *Isr. J. Chem.* **18** (1979) 99.
- [7] C. Lestrade, P. Y. Guyomar and M. Astruc, *Env. Techn. Letters* **2** (1981) 409.
- [8] R. Y. Bek, and A. P. Zamyatin, *Sov. Electrochem.* (Eng. Transl.) **14** (1978) 1034.
- [9] K. Kinoshita and S. C. Leach, *J. Electrochem. Soc.* **129** (1982) 1993.
- [10] Y. Oren and A. Soffer, *Electrochim. Acta* **28** (1983) 1649.
- [11] G. C. Mitchell, IPC Fall Meeting, Sept. 1983, Denver, CO, Technical paper, IPC-TP-472.
- [12] A. K. P. Chu, M. Fleischmann and G. J. Hills, *J. Appl. Electrochem.* **4** (1974) 323.
- [13] G. Kreysa, *Electrochim. Acta* **26** (1981) 1693.
- [14] M. Jakob, 'Heat Transfer', John Wiley, New York (1962).
- [15] D. Simonsson, *J. Appl. Electrochem.* **14** (1984) 595.