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Carbon fibre cloth as an electrode material: electrical conductivity and mass transfer

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Abstract

The paper deals with carbon fibre cloth electrodes, employed in the fabrication of composite materials. The electrical conductivity of single bundles, groups of bundles and cloth is studied. Ohm's law applies to the electrical conduction in the direction of the fibre length, but bundle conductivity decreases with the number of fibres in the bundle. Electrochemical mass transfer between a flowing electrolyte and a cloth arranged as a flow-through or a flow-by porous electrode indicates the existence of double porosity in the material. Due to double porosity, only the external surface of the cloth works as an electrode. This finding shows that the material is not suitable for such an application.

List of symbols

d_h	channel hydraulic diameter (m)
D	molecular diffusion coefficient (m^2 s^{-1})
I	current (A)
I_L	limiting diffusion current (A)
$(I_L)_{cloth}$	limiting diffusion current at the fibre cloth electrode (A)
$(I_L)_{sheeet}$	limiting diffusion current at the nickel sheet electrode (A)
$\bar{k}_d$	mean mass transfer coefficient (m s^{-1})
L	length of a cloth bundle (m)
M	charge over the cloth (kg)
n	number of identical bundles connected to the current feeders
n'	number of identical bundles parallel to the current feeders
N	total number of fibres connected to the current feeders
Re	Reynolds number, $(\bar{v}d_h/v)$
S	fibre cross sectional area (m^2)
Sc	Schmidt number, (v/D)
$\overline{Sh}$	mean Sherwood number, $(\bar{k}_d d_h/D)$
$\bar{v}$	electrolyte velocity in the empty channel (m s^{-1})
V	potential drop (V)

Greek symbols

α	resistance per unit of length (Ω m^{-1})
ρ	electrical resistivity (Ω m)
v	kinematic viscosity (m^2 s^{-1})

1. Introduction

Few materials are useful for making stable porous anodes. Many researchers, interested in carbon or graphite felts [1–7], realized that various difficulties appear while using such material as electrodes. The fact that the material conductivity depends on compression [8, 9] restricts its usefulness to laboratory experiments. Another material, reticulated vitreous carbon (RVC), is brittle and difficult to feed with current; its industrial use is also doubtful.

Several years ago, the use of cloth fibres as electrodes was considered [10]. Attention was drawn to the fact that, owing to the use of the material in the production of light weight reinforced plastics (composite materials), the availability of this inexpensive material on a commercial scale would be promising. It seems that no new study has been published on the subject, in spite of currently large commercial access to the material. Mass transfer between a flowing liquid and a single fibre and a bundle of fibres was studied [10]; one extremity of the bundle (containing 10^4 to 10^5 fibres, depending on the type of material) was attached to the current feeder, and the rest of the bundle extended freely into the flow. Thus, except at the fixation point, there was no contact between the fibres, which were free to orient themselves along the liquid flow streamlines.

The aim of the present work was to explore whether individual cloths could serve as electrodes.

2. Experimental details

2.1. *Cloths and tissues of carbon fibres*

Reinforcing materials made of carbon fibres provide plastics with interesting mechanical characteristics. The long carbon fibres, 5 to 7 μm in diameter, are produced by thermal decomposition of acrylic fibres. The 'unit fibres', not usable as such, are joined together in a bundle which can be woven. As in traditional weaving there are several ways to set the bundles. In the present work only the modes shown in Figure 1 were considered, using two materials quite different in the number of fibres per bundle. These were supplied by Porcher Industries, France: namely, cloth 3872 ('Cloth' type; Figure 1(a), with 48000 HR (highly resistive) fibres per bundle and cloth 3257 ('Serge' type; Figure 1(b), with 3000 HR fibres per bundle.

2.2. *Electrical conductivity*

For the purpose of producing electrodes, the first important property to study is the electrical conduction of the material. In carbon felts, made of short fibres, interfibre electrical conduction is complex. As stated above, it depends on the applied pressure [8, 9] as known for the microphone effect between carbon particles [11]. In the present case, the fibres are long, but due to their pattern in a cloth (Figure 1), several modes of electrical conduction can be considered:

(i) longitudinal conduction in a single fibre.
(ii) longitudinal conduction in a bundle or in several bundles arranged in a parallel mode.
(iii) longitudinal conduction in a cloth exposed to compression.
(iv) apparent conduction in the direction normal to the cloth and its dependence on the pressure applied over the cloth.

Mode (i) is difficult to investigate and is outside the scope of this study. The problem in mode (iii) is to determine to what extent conduction between bundles at their 'criss–cross' junctions contributes to the apparent global conduction, and how it depends on the pressure applied over the criss–cross. For mode (iv) conduction normal to the fibre length in a bundle (i.e., laterally from one fibre to another fibre) is likely to be an important component for electrodes made in stacks but analysis is difficult.

In summary, electrical conduction in the cloths is complex: since stacks of cloths were not studied in the present experimental work, conduction components (i) and (iv) were not considered.

2.2.1. *Longitudinal conduction in a bundle*

The d.c. intensity (I) against potential drop (V) curve for length L of cloth bundle 3257 shows that Ohm's law applies at small currents; above a certain current, the apparent global resistance decreases, probably due to conduction between neighbouring fibres. The measurements were made using a single bundle of fixed length and hanged vertically between two small Mohr's clamps; the tension was generated by the weight of the lower clamp. In the domain where Ohm's law applies, the apparent resistance of the bundle is proportional to its length L (Figure 2(a)).

Concerning cloth 3872, the same method shows that Ohm's law applies in a more extended domain of current variation (Figure 2(b)). It is to be noted that the number of fibres in the bundle was 16 times higher than in the case of cloth 3257.

Measurements on systems containing several identical parallel bundles clamped in two parallel current feeders were made to determine the effect of the number of fibres N (length L) on the apparent longitudinal electrical resistance of the bundle. In the experiments, three values of N were considered, one of which ($N = 120\,000$) was produced with 40 parallel bundles of material 3257. Table 1 gives the values taken by $\alpha = V/IL$ for these three values of N.

As the N fibres in a bundle are also electrical resistances arranged in a parallel mode, the apparent resistance between the extremities of the bundle is equal to the ratio of the apparent resistance of a single fibre (considered as electrically independent of the others) to

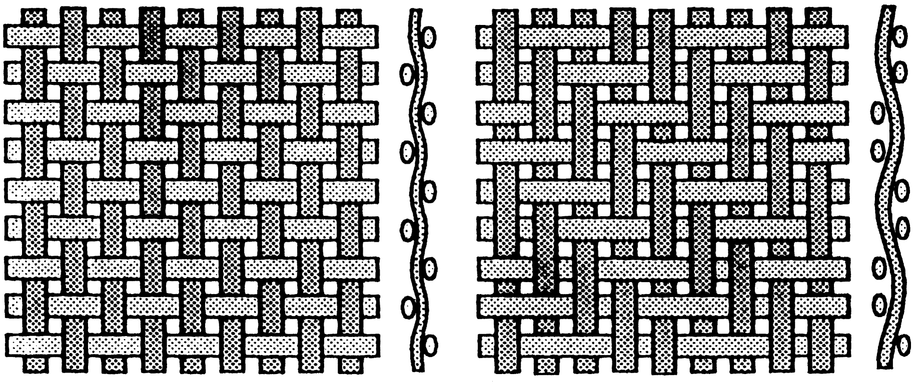
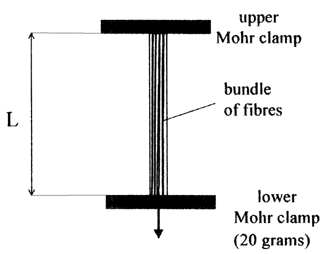


Fig. 1. Examples of bundle weaving: (a) cloth and (b) serge.



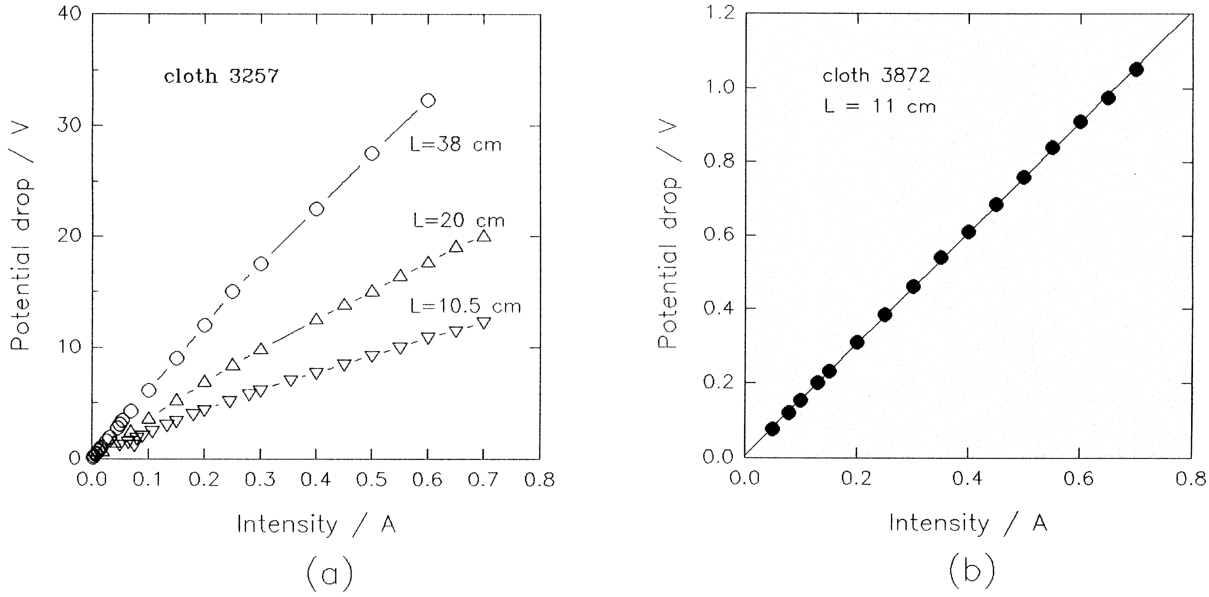


Fig. 2. Results for electrical conduction in a bundle: (a) cloth 3257 and (b) cloth 3872.

N. In other words, the quantity $\alpha = V/IL$ is equal to the product of $1/N$ by the ratio ρ/S of the apparent single fibre longitudinal electrical resistivity (ρ), to the individual fibre cross sectional area S. Linear graphical representation of α against $1/N$ may appear to be logical, but the extent of variation of $1/N$ in the present experiments would not yield an accurate and useful plot (Table 1). The best plot would be a representation of αN against N. With a system behaving electrically as N parallel single fibres without any longitudinal electrical contact, αN has to be a constant. Table 1 shows that αN increases with N instead of being a constant. This clearly indicates that the apparent electrical resistance of a bundle could be increased by longitudinal fibre–fibre contacts.

The plot of αN against N would be a line, the extrapolation of which to $N \approx 0$ yields 4.6×10^5 Ω m^{-1} for a single fibre.

Table 1. Experimental data for the longitudinal conduction in parallel bundles

N	$10^5 \times (1/N)$	$\alpha = (V/(IL)$ / Ω m^{-1}	αN / Ω m^{-1}
3000	33.3	157.9	663×10^3
48 000	2.083	13.82	473.67×10^3
120 000	0.833	8.03	963×10^3

2.2.2. *Longitudinal conduction in a cloth*

In the case of material 3257, the charge M over the entire cloth does not affect the global resistance measured in the direction of the bundles, at least at small values of the charge (Figure 3(a)). Ohm's law applies in the explored domain of both Figures. The same observation was made when, the number n being constant under a high charge, the number n' of bundles parallel to the current feeder was changed (Figure 3(b)). This means that electrical conduction takes place essentially through the bundles normal to the current feeders and connected to them, and that the criss–cross regions do not influence it.

It can be concluded from these measurements that Ohm's law applies to conduction which takes place essentially through the bundles placed in the general direction of the current; also, for identical bundles, the apparent global resistance increases with the number of fibres in the bundle.

2.3. *Mass transfer in the flow-through configuration*

The cell shown in Figure 4 was used to study mass transfer at a flow-through porous electrode disc made of material 3257 (dia. 2 cm). The liquid of the storage tank was pumped by a peristaltic pump to a constant level reservoir, from which it flowed towards the cell through a circuit containing a valve, a rotameter and a calming

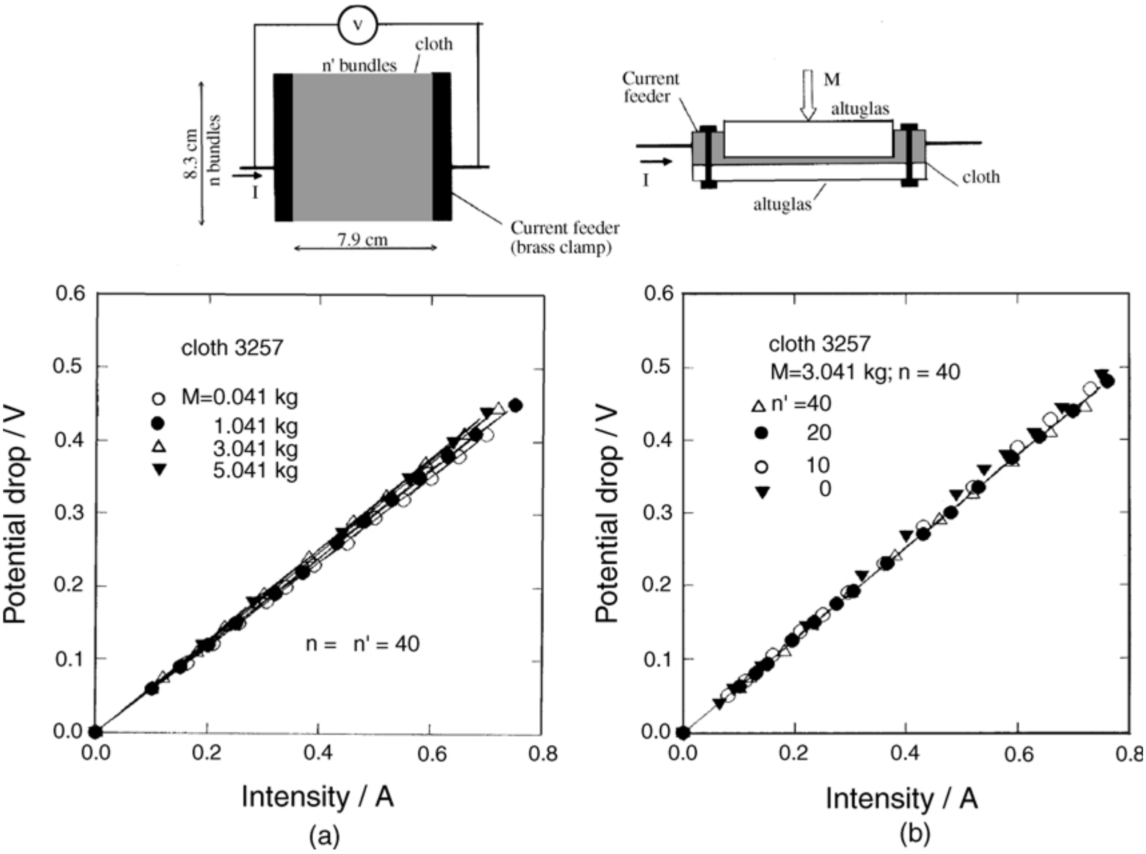


Fig. 3. Results for electrical conduction under a charge: (a) when $n = n'$; (b) variable n'.

section made of a chemically inert reticulated material. The liquid left the cell at its lateral top and returned to the storage tank.

Mass transfer to the disc was studied with the electrochemical method using the reduction of ferricyanide ions in an alkaline medium [12]. The liquid (electrolyte) was an aqueous solution of 0.5 N NaOH containing 0.005 M $K_3Fe(CN)_6$ and 0.05 M $K_4Fe(CN)_6$. Its temperature was maintained at 25 °C in the storage tank. The disc of carbon cloth was a cathode while the anode was a large diameter disc of nickel foam located as shown in Figure 5, with an S.C.E. reference electrode immersed. The three-electrode potentiostatic circuit contained a Tacussel PRT-Potentiostat associated with a Tacussel–Servovit pilot unit, and a Sefram recorder.

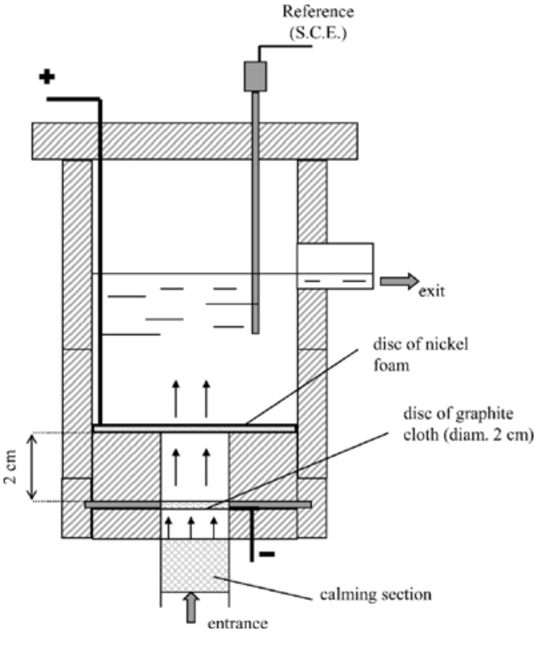


Fig. 4. View of the cell used for the flow-through configuration.

Figure 5 presents cathodic current-potential curves at several percolation flow-rates. The reduction wave does not exhibit a well-defined horizontal plateau, contrary to that observed by Schmal et al. [10] with fibres which were not in a bundle. The curves of Figure 5 were obtained at the scanning rate of 1 mV s^{-1}. After each curve had been obtained, a long time was necessary to reach stabilization near equilibrium, probably because molecular diffusion of electroactive ions was occuring from the electrolyte bulk to the interior of the bundles. Reverse diffusion from the bundle to the electrolyte bulk could explain the 'camel-back' portions of the curves at small percolation flow-rates. Thus, with such a material made of bundles of fibres, a situation similar to that observed with a sintered metal electrode [13] may exist, and the reaction current is the sum of the reaction current at the bundle external surface and of the current

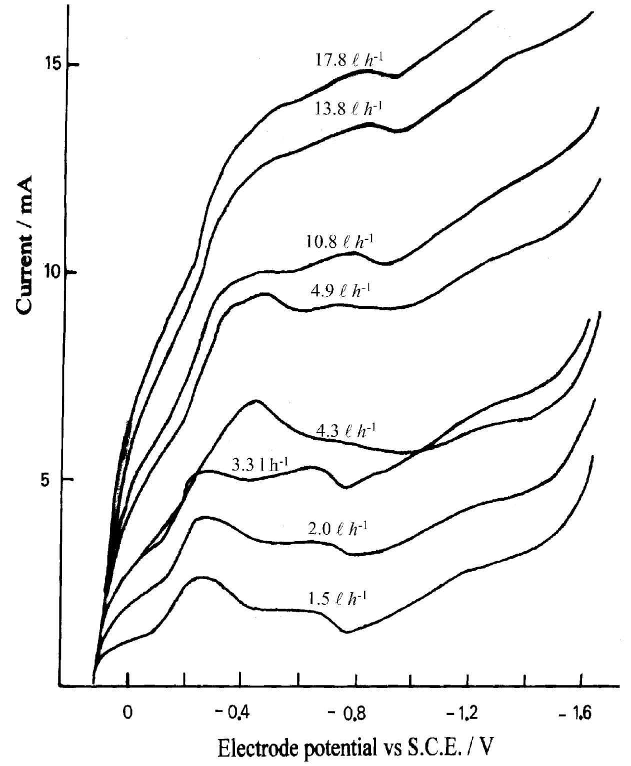


Fig. 5. Cathodic waves obtained for material 3257 in the flow-through configuration.

corresponding to the reaction within the porous bundle. Depending on hydrodynamic conditions which determine the former current contribution, the latter contribution may or may not be negligible. In any event, it seems clear that percolation only exists between the bundles and not through the bundles which exhibit an approximately non-porous behaviour.

2.4. *Mass transfer in the flow-by configuration*

The cell of Figure 6, constructed with Altuglas elements, was used for studying mass transfer when longitudinal flow occured along the cloth located at the wall of the cell channel packed with a plastic grid. The rectangular channel was 6 cm large, 3 cm wide and 0.3 cm thick. The anode was a 2.9 cm × 3.8 cm nickel surface delimited with M-Coat D (Vishay Micromesures) on a nickel sheet. The cathode was a piece of carbon cloth with siliconed borders; cloth 3257 had an active projected surface 3.2 cm long and 3 cm wide. The 2 mm free channel gap between anode and cathode was packed with a piece of commercial garden-type plastic net. The electrolyte entered the cell through a rectangular slot, flowed first through a rectangular chemically inert reticulated plastic sheet acting as a calming and equalizing section, then flowed upward between anode and cathode through the plastic net, and left the cell at its top, also through a horizontal rectangular slot. The closed flow circuit was similar to that used in experiments reported in Section 2.3. Through a small hole located just below the cathode, an electrolyte bridge was made to a saturated calomel reference electrode.

The electrolyte was the same as in Section 2.3, with the following properties: molecular diffusion coefficient of ferricyanide, $D = 5.57 \times 10^{-10}$ m^2 s^{-1}; kinematic viscosity, $\nu = 1.024 \times 10^{-6}$ m^2 s^{-1}; Schmidt number, $Sc = 1846$. In some experiments, the nickel sheet was used as a cathode in order to compare with published data on mass transfer in the presence of turbulence promoters, and to test the experimental set-up.

2.4.1. *Mass transfer to the nickel sheet*

The mean flow velocity in the empty channel, $\bar{v}$, varied between 0.25 and 23.6 cm s^{-1}. The mass transfer results,

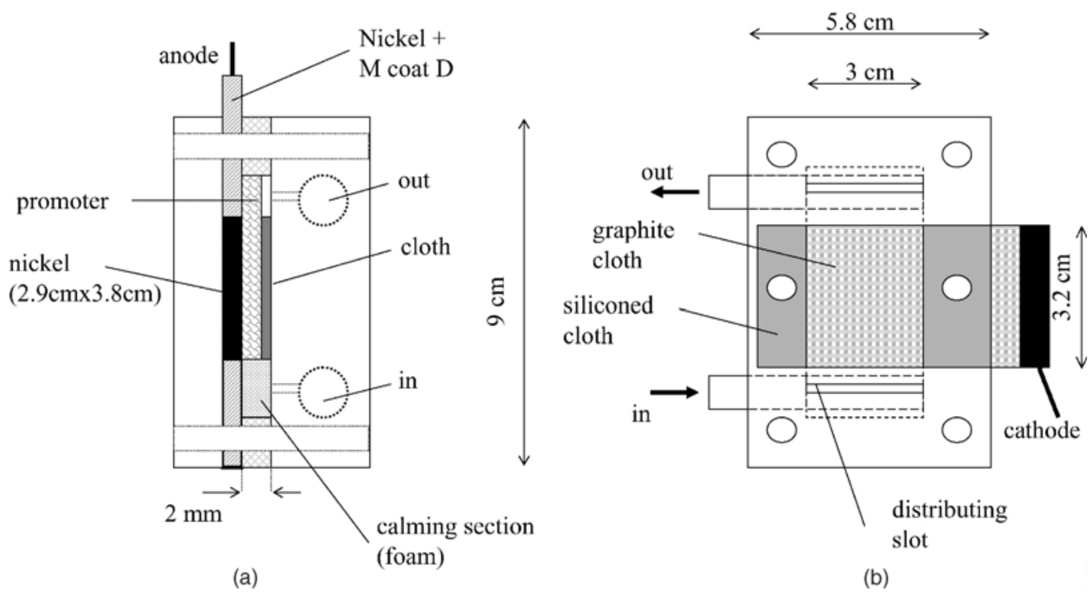


Fig. 6. Views of the cell used for the flow-by configuration: (a) general arrangement and (b) element supporting the cloth electrode.

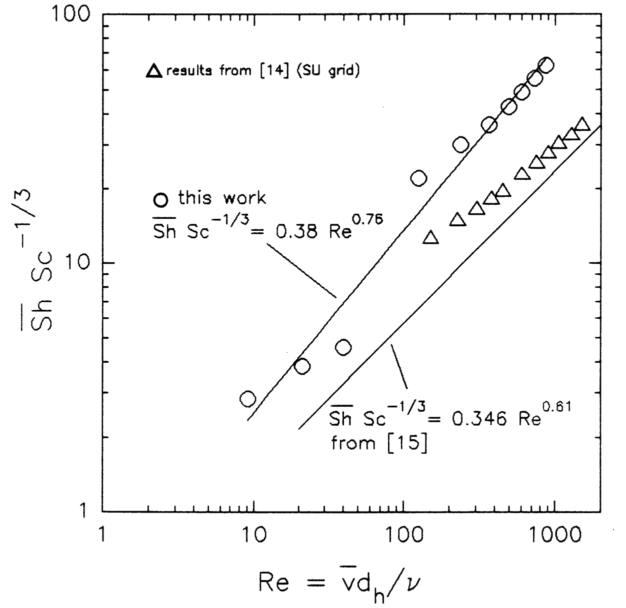


Fig. 7. Results for mass transfer to the nickel sheet in presence of the grid.

plotted in Figure 7 as $\bar{Sh}\ Sc^{-1/3}$ against *Re*, are correlated as:

$$\bar{Sh}\ Sc^{-1/3} = 0.38\ Re^{0.76} \tag{1}$$

in the $10 \leqslant Re \leqslant 1000$ range.

Since the experimental electrode surface area was not very large compared with the mesh size of the promoter, the empirical correlation (Equation 1) is not very accurate. However, as shown in Figure 7, it is in satisfactory agreement with results obtained in [14] with a grid (SU grid) used as promoter in the SU Electro-SynCell, and with the correlation established in [15] using a plastic promoter similar to that of [14]. These findings demonstrate the soundness of the experimental set-up, in spite of its small scale.

2.4.2. *Mass transfer to carbon cloths*

Figure 8(a) and (b) show cathodic waves obtained with cloths 3257 and 3872, respectively.

With cloth 3257 (Figure 8(a)), the curves have a more conventional aspect than in a flow-through configuration (Figure 5). A diffusional limitation is clearly observed, without 'camel-back regions'; this probably indicates that, even the smallest flow velocities were sufficiently high to ensure that the reaction current at the external surface of the cloth was larger than the reaction current corresponding to the inner surface of the bundles.

Similar results were obtained with cloth 3872 (Figure 8(b)), with more inclined diffusional plateaux. The lower plot shown in this Figure corresponds to a mass flow rate of 2.14 g s^{-1}. At smaller flow rates (Figure 9), the camel-back curves obtained demonstrate the existence of a depletion region in the pores of the material. Figure 9 also allows comparison of mass transfer at

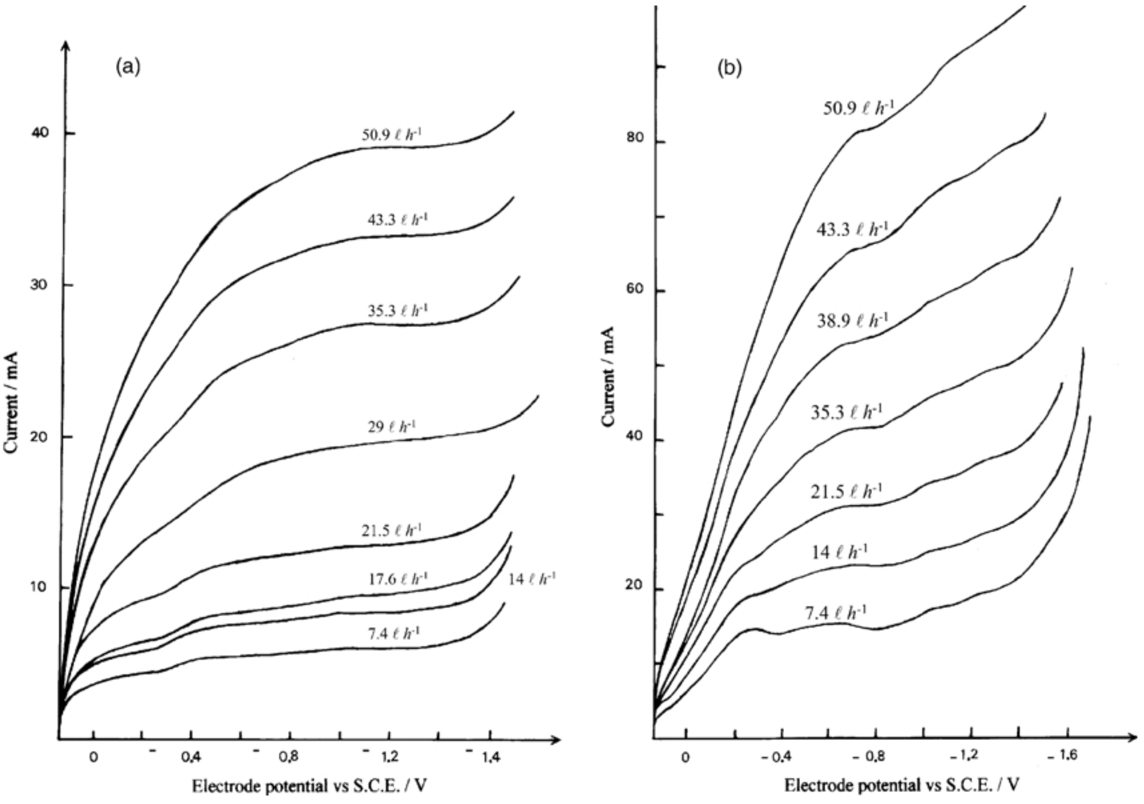


Fig. 8. Cathodic waves obtained in the flow-by configuration: (a) material 3257 and (b) material 3872.

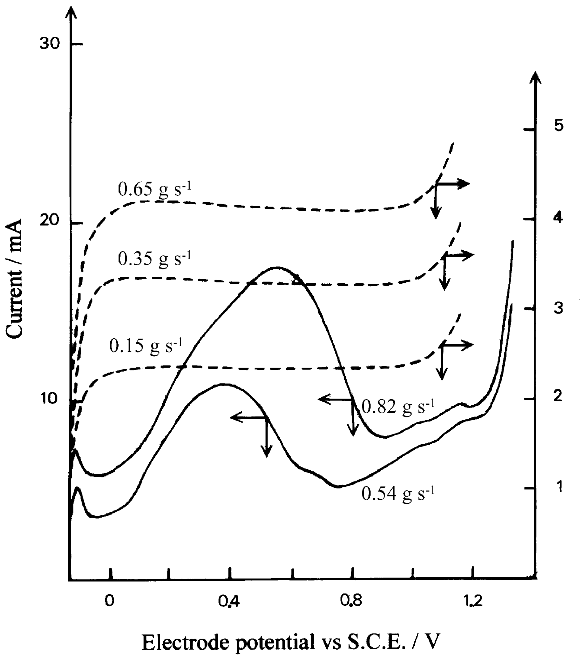


Fig. 9. Cathodic waves at small flow rates: (——) material 3872; and (- - -) nickel sheet.

material 3872 and at the nickel sheet used cathodically. Except for the camel-back regions, the limiting reaction currents which can be estimated for material 3872 ranged approximately between 5 and 8 mA, that is, with an order of magnitude comparable to that of the currents measured with the nickel sheet. This finding indicates that, once the reactive species (ferricyanide ions) contained within a bundle are consumed, only the external surface of the cloth is electrochemically accessible to the ferricyanide ions. The time necessary to reach equilibrium after one experiment would correspond to the time necessary to reach by molecular diffusion within the pores a concentration of ferricyanide ions equal to the bulk solution concentration. Again the situation found here is similar to that observed and commented in [13] for minimum mass transfer in a sintered metal electrode. Camel-back regions are not present in the curves obtained with the nickel sheet cathode. This means that the cathodic reduction of dissolved oxygen was negligible in the experiments.

Taking limiting values of the current $(I_L)_{cloth}$ from the curves of Figure 8(a), and comparing them to the limiting current measured to the sheet working cathodically, $(I_L)_{sheet}$, indicates that $(I_L)_{sheet}/(I_L)_{cloth}$ ratios at given entrance flow velocities are higher than one. From a value of about 3.5 at the smaller flow-rate, the ratio decreases progressively to reach a minimum value of 1.54 as the flow-rate is increased.

3. Discussion

Semifree carbon fibre electrodes studied in [10] are not attractive for practical applications.

The current study shows clearly, albeit indirectly, that bundles of carbon fibres exhibit double porosity: a high porosity considered relative to the bundles as nonporous, and a very small porosity within the bundles. Diffusional mass transfer from the electrolyte to the bundle of carbon fibres is not affected by this small porosity. In others words, only the external surface of the bundle can be considered to be electrochemically active, the rest of the material only acting as a current feeder. It follows that carbon fibre cloths are not suitable electrode material, in spite of the fact that very few carbon materials are eligible for use as anodes. By the same token, construction of stacks for use as percolated porous electrodes is not warranted, since the bundles behave as if they were nonporous.

Electrical conduction (and expectably thermal conduction) in the direction of the bundle length is reduced as the number of fibres in the bundle is increased; this is probably due to contact resistances between fibres existing along their entire length. It seems that electrical conduction through the criss–cross pattern between two bundles is not a limiting factor. Compression of a cloth also has a very small effect on its conducting properties. Thermal conduction problems in the fabrication of reinforced plastics using stacks of carbon cloths could be partially understood by electrical conduction data obtained in the present work.

4. Conclusions

Even if they are made of long fibres, carbon cloths do not possess good electrode properties owing to the existence of double porosity, and electrical conduction problems. The structure of the bundles prevents percolation by the electrolyte; the movement of electroactive species into or out of the bundle is due essentially to molecular diffusion. As a consequence, the apparent surface area (projected area) can only be considered as an active electrode area, hence the use of such a material as an electrode is not recommended.

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