

A membrane free electrochemical cell using porous flow-through graphite felt electrodes

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Abstract This work describes the development and characterisation of an electrochemical cell which can be used to give high reactant conversion without the need for a membrane. The undivided cell uses two high porosity flow-through graphite felt electrodes, with the products flowing through the back of each electrode. A series of tests have been conducted using an equimolar mixture of potassium hexacyanoferrate (II) and potassium hexacyanoferrate (III) to characterise the cell design and identify suitable operating conditions. It has been shown that high reactant conversion (in excess of 90%) can be achieved for high concentrations of redox species at low flow rates (superficial velocities of around 0.1 mm s^{-1}). However, the cell voltage required to achieve high conversions increased with increasing concentration.

Keywords Undivided cell · Flow-through electrodes · Redox species · Potassium hexacyanoferrate (II) · Potassium hexacyanoferrate (III)

Nomenclature

a	Specific surface area ($\text{m}^2 \text{ m}^{-3}$)
C_0	Feed concentration (mol dm^{-3})
C_0	Outlet concentration (mol dm^{-3})
E_{cell}	Cell potential (V)
F	Faraday constant ($96,487 \text{ C mol}^{-1}$)
I	Cell current (A)
k_m	Mass transport coefficient (m s^{-1})
L	Porous electrode thickness (m)

L_a	Active electrode thickness (m)
n	Number of electrons transferred per mole of reactants
Q	Volumetric flow rate of electrolyte ($\text{cm}^3 \text{ s}^{-1}$)
Re	Reynolds number
u	Mean flow velocity (m s^{-1})
V	Total volume of electrolyte reacted (m^3)
W.E	Working electrode
X	Reactant conversion

Greek symbols

α	$= k_m a / u$ (m^{-1})
ϕ	Current efficiency
κ	Electrolyte conductivity (S m^{-1})

1 Introduction

Membrane-free electrochemical reactors have been studied extensively [1–8]. Laboratory-scale undivided cells have been used for studying mass transfer effects on porous electrodes [1–2] while other reactors have been employed for the destruction of pollutants from industrial wastewaters [3–7], such as textile effluents [7]. In addition, an undivided reactor has been used for a flowing soluble lead battery application [8]. In this study we are concerned with the use of an undivided electrochemical cell employing two flow-through porous electrodes. This concept was patented by a French scientist, Hulin in the 1890s [9]. Hulin referred to the electrodes he used in his process as filters whereby the products of electrolysis were formed at the electrode and extracted through the back of the electrode and discharged for further processing.

Porous three-dimensional electrodes have been used in a range of applications including electrochemical synthesis,

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energy storage and environmental engineering [10]. In spite of the obvious benefits of eliminating the requirement for a membrane, the application of flow through porous electrodes to achieve high conversion in a single pass has been relatively limited. In the flow-through porous electrode configuration the electrolyte flows in a parallel direction to the current. In many cases, a relatively high flow rate through the electrode is used to enhance mass transfer rates, reducing the potential for achieving high conversion. In addition, the effective electrode bed depth may be limited by the potential drop in the electrolyte, which can restrict the conversion per pass achieved in practice [11]. The scale-up and practical applications of this arrangement have thus been limited compared to the ‘flow-by’ arrangement, where current and electrolyte flows are perpendicular.

A wide range of porous electrode structures and materials have been studied, including packed beds [12]; reticulated carbons and metals [13]; cloths and felts [14]; and sintered metals [15]. Low porosity sintered metal electrodes may be suitable for achieving high conversion in a single pass since these materials give a high pressure drop and hence uniform flow rate. However, the energy loss associated with a high pressure drop is undesirable and is likely to be prohibitive for some applications such as redox flow batteries. Furthermore, high porosity graphite felt materials have been successfully used for electrosynthesis with high conversion achieved in a single pass [16–17]. In this study, suitable operating conditions for achieving high single-pass conversion at both anode and cathode using flow-through graphite felt electrodes are investigated. This approach, as illustrated in Fig. 1, would enable charging of a mixed electrolyte redox flow battery system in a single pass.

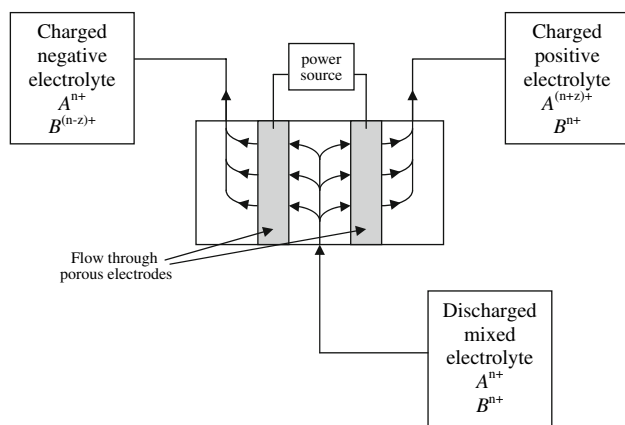


Fig. 1 Schematic diagram showing charging of a mixed electrolyte redox flow battery system using two flow through porous electrodes

2 Theoretical considerations

For a flow through electrode, the maximum achievable conversion is obtained under limiting current conditions. For plug flow conditions, the maximum achievable conversion is given by:

$$X = [1 - \exp(-\alpha L)] \quad (1)$$

where L is the thickness of the porous electrode and

$$\alpha = \frac{k_m a}{u} \quad (2)$$

where k_m is the mass transport coefficient, u is the superficial velocity of the electrolyte and a is the specific surface area of the electrode. Thus to achieve a target conversion X the required electrode thickness can be calculated:

$$L = \frac{-\ln(1 - X)}{\alpha} \quad (3)$$

For a similar graphite felt, a correlation for $(k_m a)$ with flow velocity was determined by Doherty for the reduction of ferricyanide ions [18]:

$$k_m a = 5.11u^{0.493} \quad (4)$$

Thus to achieve conversions of greater than say 90% using a 1 cm thick graphite felt electrode, it can be calculated that the flow velocity must be less than 0.5 mm s^{-1} and less than 0.1 mm s^{-1} for greater than 99% conversion. This velocity is outside the range used to determine the correlation in Eq. 4, so the accuracy of these flow velocities cannot be relied upon. However this calculation gives an indication of the order of magnitude of the required flow velocity.

A low flow velocity is not sufficient to ensure that high conversions are achieved. Significant potential drop can occur in solution, reducing the overpotential and limiting the active thickness of the electrode. In a highly conducting flow through electrode operating under mass transport limited conditions, the potential drop in solution for an anodic process is given by [19]:

$$\Delta\phi = \frac{nFuC_0}{\alpha\kappa} [1 - (1 + \alpha L) \exp(-\alpha L)] \quad (5)$$

where C_0 is the inlet concentration and κ is the electrolyte conductivity. Under conditions of high conversion Eq. 5 shows that the potential drop in the porous electrode is limited to:

$$\Delta\phi_{\text{mx}} = \frac{nFuC_0}{\alpha\kappa} \quad (6)$$

For a 1 cm thick graphite felt electrode, with typical values of the other parameters ($\kappa = 0.10 \text{ S cm}^{-1}$; $n = 1$; $u = 0.1 \text{ mm s}^{-1}$; and $C_0 = 0.01 \text{ mol dm}^{-3}$), this limit is around 19 mV.

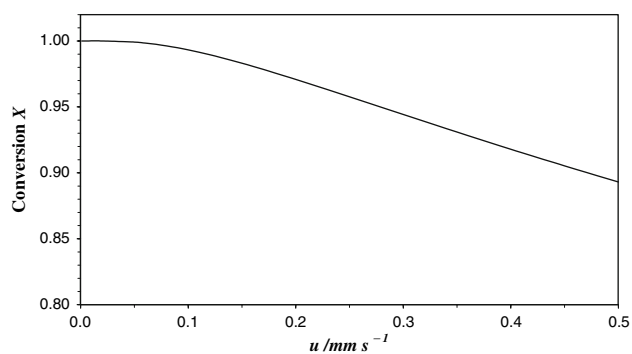


Fig. 2 Calculated reactant conversion for a flow through porous graphite felt electrode as function of electrolyte velocity for an electrode thickness of 10 mm. The conversion was calculated using Eqs. 1 and 4

In the experimental study reported in this paper, the electrode thickness was 10 mm, and the reactant conversion was measured as a function of cell voltage and electrolyte flow rate. The effect of cell voltage has not been considered in the above equations, since it was assumed that the electrode was operating under mass transport limiting conditions. If the electrode is operating under mass transport limiting conditions, then we would expect the conversion to decrease with electrolyte flow rate, as shown in Fig. 2.

3 Experimental

3.1 Electrolyte system

In order to mimic a redox flow battery, two flow through porous electrodes were used with an equimolar mixture of $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ [hexacyanoferrate(III)/hexacyanoferrate(II), also commonly known as ferricyanide/ferrocyanide]. Under suitable conditions (with no side reactions), equal conversions are expected to occur at each electrode. For a redox flow battery application it will be desirable to achieve high conversions at both electrodes, corresponding to charging of a redox flow battery system in a single pass.

The $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ [hexacyanoferrate(III)/hexacyanoferrate(II)] redox couple has been widely studied and has been reported to possess fast kinetics at a number of electrode surfaces [20–22]. Various researchers have also used this couple for evaluating mass transport conditions of electrochemical reactors using porous electrodes [15, 22–26]. A high concentration of K_2CO_3 (potassium carbonate) or Na_2CO_3 (sodium carbonate) has been recommended as a supporting electrolyte for the ferrocyanide/ferricyanide couple by a number of studies [21, 27–28]. Although, a higher conductivity can be achieved with a hydroxide

electrolyte, it has been reported that potassium carbonate provides a more stable limiting current than potassium or sodium hydroxide [28–29].

Equimolar concentrations of ferrocyanide/ferricyanide ions have been used in this study in order to obtain high conversions at both the cathode and the anode flow through electrodes. This is important for applications such as the charging of a mixed redox flow battery electrolyte. In addition, several studies have suggested that the highest values of the heterogeneous rate constant for the electrochemical conversion of ferrocyanide ion to ferricyanide ion and vice versa are obtained under equimolar conditions [24, 30–31].

Throughout this study an equimolar (0.01–0.1 mol dm^{-3}) mixture of potassium ferrocyanide and potassium ferricyanide in a 0.5 mol dm^{-3} potassium carbonate supporting electrolyte has been used. All chemicals were obtained from Merck (Reagent Grade).

3.2 Electrode material

Graphite felt was used as a low porosity high surface area material for the flow through porous electrodes. Graphite felt electrodes have found successful applications in metal recovery [14] and redox flow battery systems [32], often giving better performance than other porous electrode systems. Sigratherm[®] GFA 10 (SGL Carbon Ltd. UK) graphite felt was used throughout this study. The physical properties of this material are shown in Table 1. Each $12 \times 12 \times 1$ cm electrode was heat treated in a Gallenkamp Muffle furnace at 500 °C for 1 h prior to use. This pretreatment reduced the hydrophobic nature of the felts. The electrodes were allowed to cool to room temperature before being connected to the current feeders (stainless steel mesh) in the flow cell.

3.3 Cell design and operation

A cross-sectional view of the electrochemical cell is shown in Fig. 3. The flow area of the electrodes was 10×10 cm and the inter-electrode gap was 6 mm. Four entrance ports were used to distribute the flow across the width of the cell. The flow velocity at the entrance of the cell was 0.15 cm s^{-1} for a total electrolyte flow rate of 1.81 mL s^{-1} , with a Reynolds number of less than 10, corresponding to laminar flow conditions.

Laminar flow conditions were required in order to minimise back mixing of the reaction products. The aim was to achieve a uniform, plug flow through each electrode. It is possible that a non-uniform flow may have occurred in the electrodes, for example with higher flow

Table 1 Properties of SGRATHERM[®] graphite felt electrodes employed in this work

Material properties	Unit	Graphite felt (GFA 10)
Thickness	mm	10
Fibre diameter	μm	10–12
Weight per unit area	g m^{-2}	950–1,100
Specific surface area (BET)	$\text{m}^2 \text{g}^{-1}$	<1.0
Specific surface area per unit volume (BET)	$\text{m}^2 \text{m}^{-3}$	<95,000–110,000
Specific surface area (geometric estimate from fibre diameter)	$\text{m}^2 \text{m}^{-3}$	~16,000
Resistivity		
Longitudinal	$\Omega \text{ mm}$	1.5–2.5
Transverse		3–4

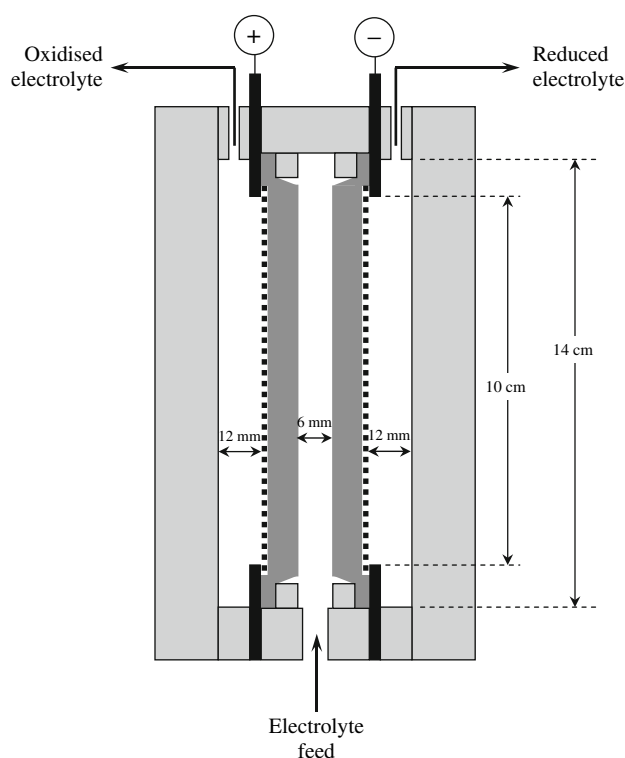


Fig. 3 Cross-sectional view of the aqueous prototype cell (simplified drawing). Reproduced from Bae [36]

velocities near the inlet. The superficial velocity in the electrodes was very low; less than 0.1 mm s^{-1} at an electrolyte flow rate of $1.81 \text{ cm}^3 \text{ s}^{-1}$. This corresponds to a Reynolds number of only 10^{-3} based on the fibre diameter or $Re = 1$ based on the felt thickness.

Although the electrodes have a relatively high porosity ($\sim 95\%$), their high surface area leads to a significantly higher pressure drop (estimated from the Ergun equation) than that in the flow channels upstream and downstream of the electrodes. Furthermore, the pressure distribution in the feed region between the electrodes will be partially compensated by that in the outlet channel behind each electrode. Thus a relatively uniform superficial velocity is

expected to occur in each electrode. However, a disadvantage of using laminar flow is the relatively low mass transport rates due to the low electrolyte velocity. This is evident when the Reynolds numbers and flow velocities are compared with other systems reported in the literature [18, 33–34].

The experimental setup is shown in Fig. 4. A 5 dm^3 reservoir was used as the feed tank for the electrolyte. The reservoir was fitted with a feed for purge gas, a vent, and a sampling point, and was covered to prevent the photo-degradation of ferrocyanide ions. Two 2.5 dm^3 reservoirs were used to collect converted electrolytes from the cell outlets. These were fitted with a feed for purge gas, a vent and sampling points. A peristaltic pump was used to supply the electrolyte at a constant rate. The use of a peristaltic

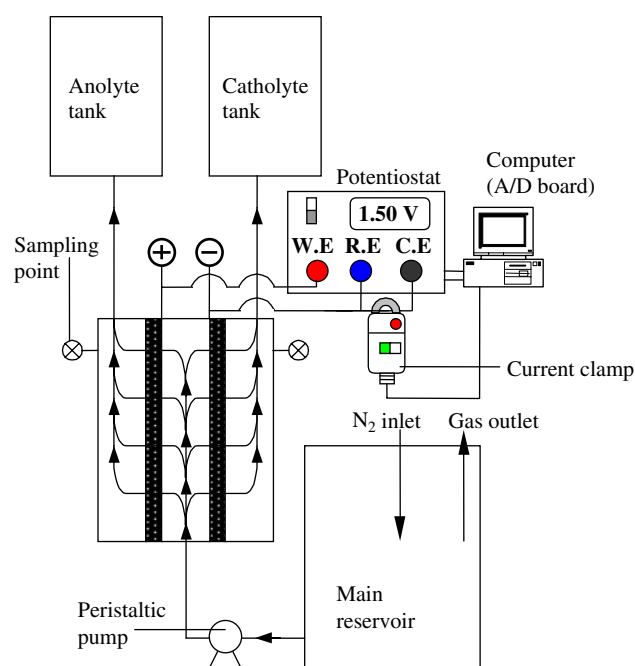


Fig. 4 Schematic diagram showing the principle of the electrochemical separation of a mixture of $\text{Fe}(\text{CN})_6^{4-}$ and $\text{Fe}(\text{CN})_6^{3-}$ using the membrane-free electrochemical cell [36]

pump will lead to some flow pulsation, and although this may lead to undesirable back mixing, it has the advantage that mass transfer rates in porous electrodes can be intensified by pulsating the flow [35].

The fresh electrolyte was sparged with nitrogen gas for 1 h to ensure effective de-aeration prior to each experiment, and an initial sample was taken from the feed tank. A potentiostat (Sycopel, Ministat Potentiostat 259E) was used to apply a constant cell potential and a data logger and current clamp (LEM HEME PR200) were used to monitor the current and cell potential throughout each experiment.

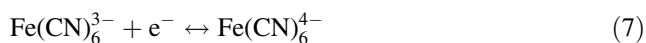
Three control parameters (concentration, cell potential and electrolyte flow rate) were varied to observe their effect on the current efficiency and electrochemical conversion of ferrocyanide ion at the anode and ferricyanide ion at the cathode. The cell potential was applied at the start of the experiment, before the cell had been filled with electrolyte. Once the current was observed to be approximately constant (signifying steady-state), samples were collected from both the anodic and cathodic sampling points (illustrated in Figs. 3 and 4). The experiment was terminated after 4.5 dm³ of electrolyte had passed through the cell. All experiments were carried out at room temperature (~20 °C).

3.4 Sample analysis

UV/Visible Spectrophotometry was used as the analytical technique for determining the concentrations of ferrocyanide and ferricyanide ions in the samples collected. All samples were stored in the dark to prevent the photo-oxidation of ferrocyanide ion and were diluted to one thousandth of their original concentration with de-ionised water before analysis. A method was developed to determine the concentration of the two ions in each sample using measurements of absorption at 420 and 260 nm [36–37]. The accuracy of this method was found to be around ±4% using standard solutions.

4 Results and discussion

At the anode surface, ferrocyanide ions are oxidised to ferricyanide ions while at the cathode ferricyanide are reduced to ferrocyanide.



Although no voltametric studies have been carried out in this study, previous work suggests that the kinetics of this reaction on graphite felt are fast, and can be considered to be reversible [38].

The figures of merit used in this study are the conversion (X) and current efficiency (ϕ), defined as follows:

$$X = \left(\frac{C_0 - C_1}{C_0} \right) \times 100\% \quad (8)$$

$$\phi = \frac{nF(C_0 - C_1)Q}{I} \times 100\% \quad (9)$$

where C_0 and C_1 are the concentrations of ferrocyanide ion or ferricyanide ion in the feed cell outlet respectively; Q is the volumetric flow rate of the electrolyte (cm³ s⁻¹) through each electrode; and I is the current measured (A) at the sampling time.

The concentrations of potassium ferrocyanide [K₆Fe(CN)₄] and potassium ferricyanide [K₆Fe(CN)₃] were varied from 0.01 to 0.1 mol dm⁻³ in order to investigate the effect of concentration on the conversion achieved with the membrane free electrochemical cell using two flow through electrodes. Other experimental conditions varied were the cell potential and the electrolyte flow rate.

In all cases the conversion measured at the cathode and anode were within a few percent, which is less than the experimental error. A plot of the instantaneous conversion as a function of the cell potential for 0.01, 0.05 and 0.1 mol dm⁻³ equimolar solutions of Fe(CN)₆⁴⁻ and Fe(CN)₆³⁻ solutions is shown in Fig. 5 for a total electrolyte flow rate of 1.81 mL s⁻¹, corresponding to a flow velocity of around 0.1 mm s⁻³. In each case the average conversion from six separate measurements is plotted.

When the cell potential was increased, the conversion of all solutions increased up to a limit of around 95%. Higher potentials were required to achieve high conversions with increasing electrolyte concentration. This is consistent with Eq. 5 and is expected since the current density increased with concentration, leading to higher ohmic losses. The observed limiting conversion may be a consequence of

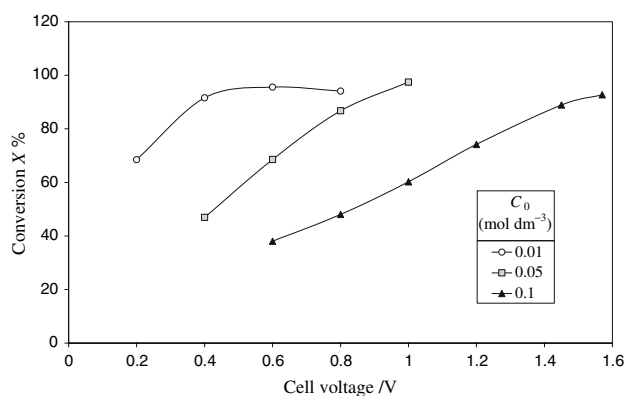


Fig. 5 Conversion versus cell potential recorded at the flow rate, $Q = 1.81 \text{ mL s}^{-1}$ in electrochemical separation of 0.01, 0.05 and 0.1 mol dm⁻³ Fe(CN)₆⁴⁻/Fe(CN)₆³⁻ mixtures dissolved in 0.5 mol dm⁻³ K₂CO₃ solutions

potential distribution, mass transport limitations or hydrodynamic effects. Potential drop within the electrolyte in the porous electrodes may have limited the active depth of the electrode (as discussed in Sect. 2), so that full conversion of the active species was not possible. However, based on the calculations in Sect. 2, it is not expected that potential distribution effects will be important at these low flow rates. Furthermore, if the potential distribution were important, it can be inferred from Eqs. 1 and 5 that the limiting reactant conversion would decrease with increasing concentration of the active species. It therefore seems unlikely that the limiting conversion is caused by potential distribution effects.

Under mass transport limiting conditions, the conversion is given by Eq. 1. Based on the correlation given by Eq. 5, Fig. 2 indicates that at a flow velocity of 0.1 mm s^{-1} , the conversion would be limited to a value of around 99%. However, the mass transport correlation cannot be relied upon at these low flow velocities. A reduction in the mass transport coefficient of only 40% would be sufficient to reduce the limiting conversion to 95%. Hydrodynamic effects such as non-uniform flow distribution or back mixing of the electrolyte would also limit the conversion due to some bypassing of unreacted electrolyte. In this case the limiting conversion would be expected to be independent of concentration, and it therefore seems likely that the observed limiting conversion of around 95% was a consequence of a combination of hydrodynamic effects and mass transport limitations.

The current efficiency versus cell potential for all cases is shown in Fig. 6. Although there is no clear trend, in most cases the current efficiency obtained was around 95% or higher. For this system a current efficiency of less than 100% may be due to hydrodynamic (back mixing) effects as well as side reactions. The results show that high single-

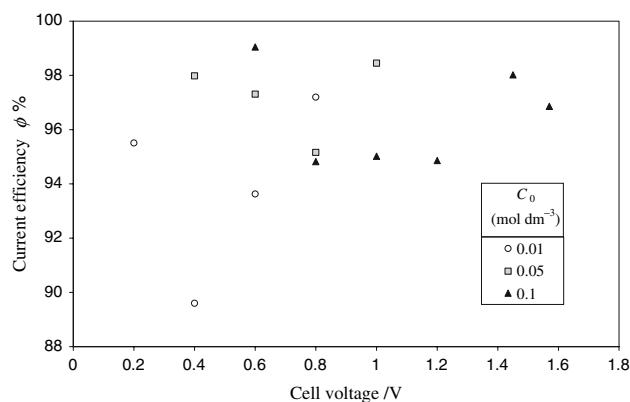


Fig. 6 Current efficiency versus cell potential recorded at the flow rate, $Q = 1.81 \text{ mL s}^{-1}$ in electrochemical separation of 0.01, 0.05 and 0.1 mol dm^{-3} $\text{Fe(CN)}_6^{4-}/\text{Fe(CN)}_6^{3-}$ mixtures dissolved in 0.5 mol dm^{-3} K_2CO_3 solutions

pass conversion with high current efficiency at both the anode and cathode can be achieved with an undivided cell using two flow through porous electrodes.

When the flow rate was increased from 1.81 to 2.95 mL s^{-1} , the conversion for 0.05 and 0.1 mol dm^{-3} solutions decreased (see Fig. 7). The conversion for 0.05 and 0.1 mol dm^{-3} solutions show an approximately linear increase with cell potential at low cell potentials for both flow rates (Figs. 5 and 7). Under these conditions the porous electrode is not operating under mass transport limiting conditions (as assumed in Eq. 1), and the linear relationship between conversion and cell potential suggests that ohmic effects are controlling the conversion in this regime. As the current density increases with flow rate, lower conversion can be expected at higher flow rates. For 0.01 mol dm^{-3} solutions, the potential required to achieve the limiting conversion was observed to increase due to the increased ohmic losses associated with higher current density.

These effects can be confirmed with a plot of conversion versus flow rate at the maximum cell potentials applied for each solution (see Fig. 8). The conversion at the maximum applied potential for the 0.05 and 0.1 mol dm^{-3} solutions decreases as the electrolyte flow rate increases. In this case the limiting conversion has not been reached and increasing flow rate leads to higher currents and thus lower conversion. It is possible that the 0.05 mol dm^{-3} solution is operating under mass transport limiting conditions, since the observed decreasing conversion is consistent with Fig. 2. However, since higher conversions are observed at the lower concentration of 0.01 mol dm^{-3} this seems unlikely.

The conversion for the 0.01 mol dm^{-3} electrolyte was observed to increase slightly with flow rate at the maximum applied cell potential, $E_{\text{cell}} = 0.8 \text{ V}$. This effect is

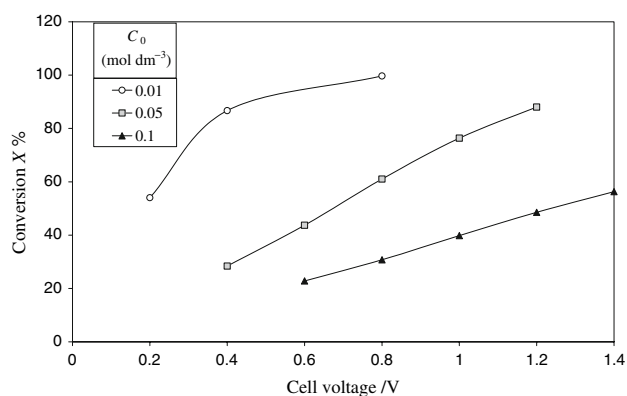


Fig. 7 Conversion versus cell potential recorded at the flow rate, $Q = 2.95 \text{ mL s}^{-1}$ for electrochemical separation of 0.01, 0.05 and 0.1 mol dm^{-3} $\text{Fe(CN)}_6^{4-}/\text{Fe(CN)}_6^{3-}$ mixtures dissolved in 0.5 mol dm^{-3} K_2CO_3 solutions

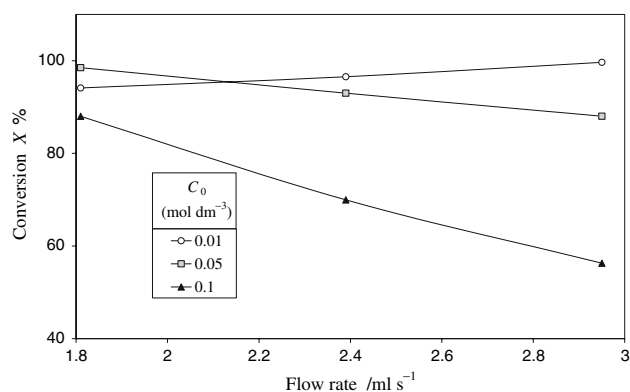


Fig. 8 Conversion versus flow rate recorded at fixed cell potential in electrochemical separation of 0.01, 0.05 and 0.1 mol dm⁻³ Fe(CN)₆⁴⁻/Fe(CN)₆³⁻ mixtures dissolved in 0.5 mol dm⁻³ K₂CO₃ solutions. The fixed potentials of each solution are 0.8, 1.2 and 1.4 V, respectively

small and its magnitude is close to the experimental error. If this increase is a real effect, it is difficult to explain, but may be due to side reactions such as the generation of oxygen and hydrogen gas bubbles. The presence of gas bubbles will influence the mass transport coefficient and electrolyte conductivity. Other possibilities are a strong sensitivity of the mass transport coefficient to flow velocity at these low flow rates or effects associated with potential losses in the graphite felt electrode.

It can be concluded that with a low flow rate corresponding to a superficial velocity of around 0.1 mm s⁻¹, high conversion (>90%) can be obtained at both anode and cathode with over 90% current efficiency for moderate concentrations of electrolyte using an undivided electrochemical cell with two flow-through graphite felt electrodes. However, the cell potential required to achieve high conversion increases significantly with electrolyte concentration.

5 Conclusions

High porosity graphite felt materials can be used to achieve high reactant conversion at both electrodes with relatively low pressure drop. As the cell potential was increased the conversion approached a limiting value of around 95%. Since this limit was apparently independent of electrolyte concentration, it has been concluded that the limit was a consequence of mass transport limitations or hydrodynamic effects (i.e. back mixing or short circuiting of electrolyte). The flow velocity used is consistent with predictions of flows suitable to achieve high conversion assuming plug flow and mass transport limiting conditions. However, further work is needed to confirm the mass transport coefficients at low superficial velocities.

Although it was possible to achieve high conversion with relatively high feed concentrations (0.1 mol dm⁻³), a high cell potential was required, suggesting that the approach would not be suitable for applications such as redox flow batteries. Since at high concentrations the electrode kinetics would be expected to be faster, the increase in cell potential with concentration is almost certainly associated with ohmic losses at the increased current densities. It would be possible to reduce the ohmic losses in the cell by reducing the inter-electrode gap, although this could influence the flow distribution. In addition it is likely that some of the observed overpotential was occurring within the flow-through porous electrodes.

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