

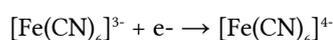
This study investigates a well-defined electrochemical system with the C-Flow LAB cell to show the versatility and ease of use of this device for making electrochemical measurements.

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The one electron reduction of ferricyanide to ferrocyanide was chosen as this redox couple exhibits a nearly reversible electrode reaction with no complications of proceeding or post chemical reactions and has therefore become a popular choice as a standard for the demonstration of cyclic voltammetry (CV).<sup>1</sup>

In this case study two types of experiments were carried out. One was a typical cyclic voltammetry (CV) experiment to show the effect of scan rate and a second featured linear sweep voltammetry to determine the limiting current density at different flow rates which then allowed calculation of mass transfer coefficients for ferricyanide reduction. Linear sweep voltammetry was carried out with a flat two dimensional nickel electrode, with the addition of HDPE mesh to show the effect of added turbulence,<sup>2</sup> and with the addition of a nickel foam to increasing the electrode surface area.<sup>3</sup>

The cathode reaction for the reduction of ferricyanide is:



The CV portion of this experiment could also be carried out in a beaker but using the cell gives a well defined electrode surface area with electrodes at a controlled distance from each other, with no issues of interface potentials or the need to de-gas with nitrogen and allows easy connection to current collectors. The ability to carry out hydrodynamic experiments also makes it possible to calculate mass transfer coefficients, understand turbulence effects and the behaviour of three dimensional electrodes.

1 J. Bard, L. R. Faulkner, *Electrochemical Methods: Fundamentals and Applications*, 2<sup>nd</sup> Ed., John Wiley and Sons, Inc., 2001

2 Pletcher et al, *Journal of Applied Electrochemistry* **24** (1994) 95-106

3 Ponce De Leon C et al 2014, *Chemical Engineering Transactions*, **41** (2014) 1-6. DOI 10.3303/CET1441001

## Apparatus

A 6 x 4 cm C-Flow cell was used for the purposes of this case study and is shown in Figure 1 ("C-Flow LAB 6x4"). This experiment was run with an undivided cell so part no. 8 (the membrane/separator) was omitted.

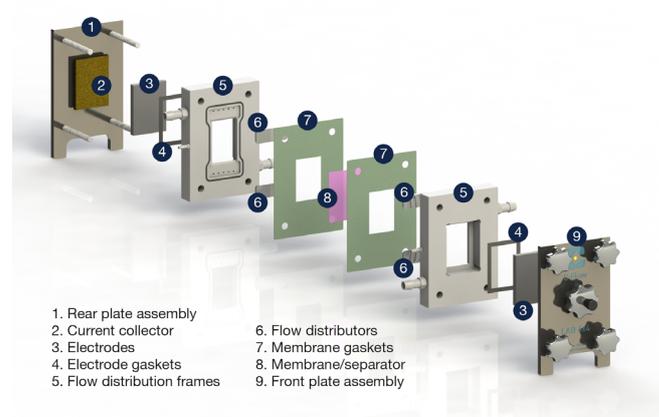


Figure 1 – Expanded view of the C-flow cell

Figure 2 shows the polypropylene cell frames and flow distribution inserts that direct the electrolyte flow into the cell space close to the electrode surfaces. Figure 3 shows the dimensions.

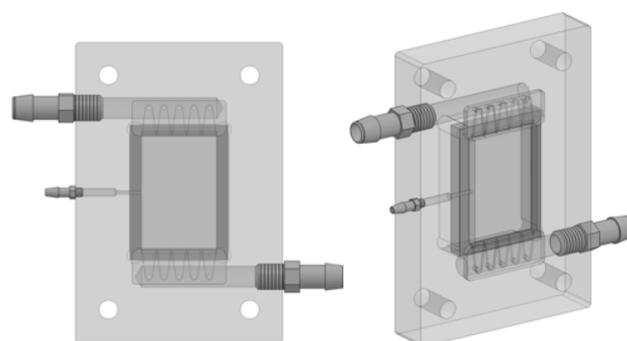
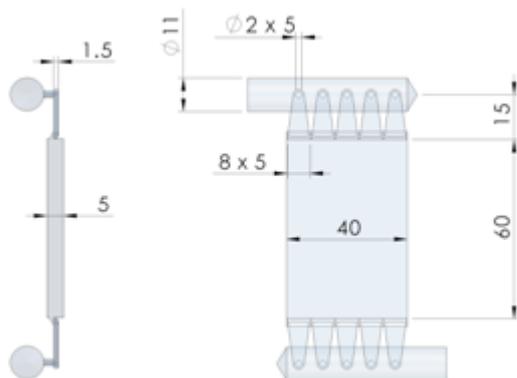


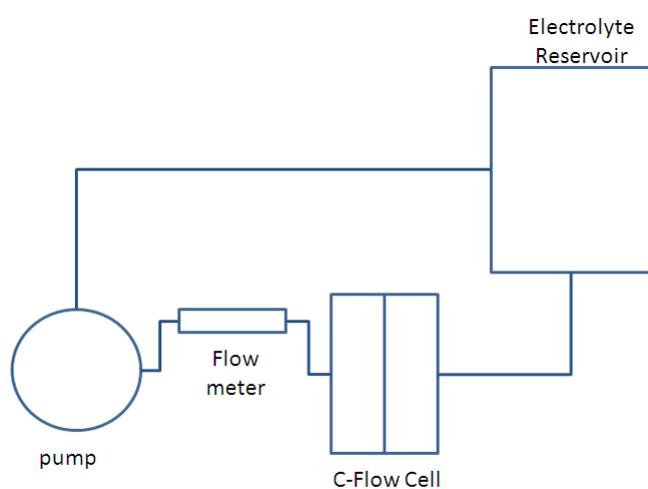
Figure 2 – Cell frames and flow distribution inserts





**Figure 3: Dimension of flow channels in C-Flow LAB 6x4 cell**

The apparatus was set up as shown in Figure 4.



**Figure 4: C-flow test set up**

The C-Flow LAB cell was assembled using flat nickel plate electrodes for both anode and cathode. These were 7.2 cm x 5.2 cm rectangles cut from commercially available nickel sheet (Ni200, 1.2 mm thick), giving an active electrode area of 6 cm x 5 cm. The cell was leak tested with water at 0.5 bar. Subsequent experiments used other cell configurations. To investigate the effects of turbulence in the cell three pieces of HDPE mesh (NetLon, 6mm diamond 2.4 mm thick) were inserted into the cell. In a third configuration a 6 cm x 4 cm piece of nickel foam in electrical contact with the nickel cathode was included (nickle foam from Linyi Gelon LIB Co Ltd, 90ppi, dimensions 300 x 400 x 1.6 mm, density 320 g/

m<sup>2</sup>). In this configuration the effect of additional electrode surface area on the mass transfer coefficients could be determined.

Electrolyte: A 10mM potassium ferricyanide (AnalR Lot #3512110L) in 1M potassium carbonate solution (Sigma-Aldrich batch #0281MH) with a 5x molar excess of potassium ferrocyanide (Sigma Lot MKBR6235V) was made with de-ionised water from a Millipore purification system. An excess of ferrocyanide was used to ensure that the anode reaction did not become rate determining. For the CV experiments the solution contained only 10mM ferrocyanide.

Electrochemical measurements: All electrochemical experiments were carried out with a Biologic potentiostat model SP150 with all potentials in this study measured against a Directlon Hg/HgSO<sub>4</sub> reference electrode. CV was carried out at stationary flow, i.e. the electrolyte was pumped into the cell and then the pump switched off and were initially at 1V to -1V where it was found that the reduction peak was measured at 0.175V and the oxidation peak at 0.245V versus Hg/HgSO<sub>4</sub> at ambient temperature. The values measured depend on the nature of the electrolyte, pH, temperature etc.<sup>4</sup> CV traces were then measured at 0V-0.5V versus Hg/HgSO<sub>4</sub> for future experiments, at varying scan rates. Linear sweep voltammetry was carried out from OCV (near 0V) to -1.4V versus Hg/HgSO<sub>4</sub> at a scan rate of 3mV/s and at different electrolyte flow rates from 40-2000ml/min. The limiting current was obtained at approximately -0.8V versus the reference.

## Results

### 1. Investigation of Different Scan Rates

Cyclic voltammetry with increasing scan rates is shown in Figure 5. Note from the figure the position of the maximum current, with the peak occurring at approximately the same voltage regardless of scan rate. This is a characteristic of this redox couple which is known to have rapid electron transfer kinetics at the electrode. The maximum currents

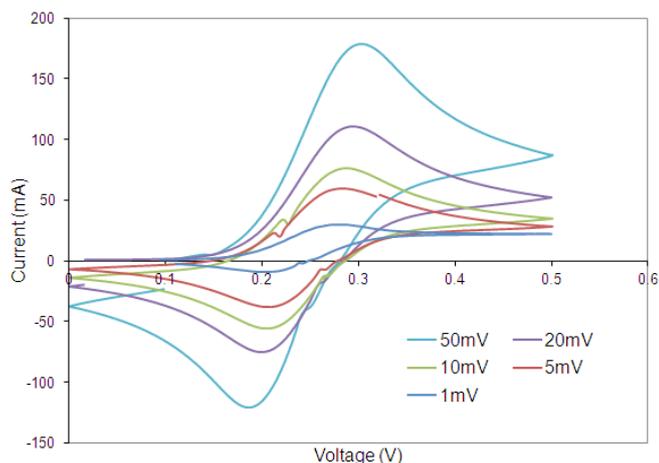
<sup>4</sup> Rock, P.A et al, *J. Phys. Chem.*, 70 (1996), 576-580



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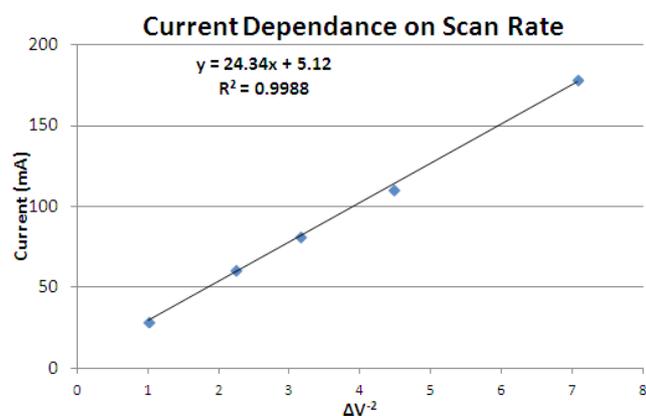
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**Figure 5 Ferri/Ferrocyanide CV's in C-Flow cell at different scan rates**

Figure 6 shows that the peak currents are proportional to the square root of the scan rate, which is as predicted by the Randles-Sevcik equation. This is due to the change in the thickness of the diffusion layer with changing scan rate. At slower scan rates, the diffusion layer grows much further from the electrode than with faster scan rates and as a consequence the flux toward the electrode surface is greater at faster scan rates, resulting in greater currents.



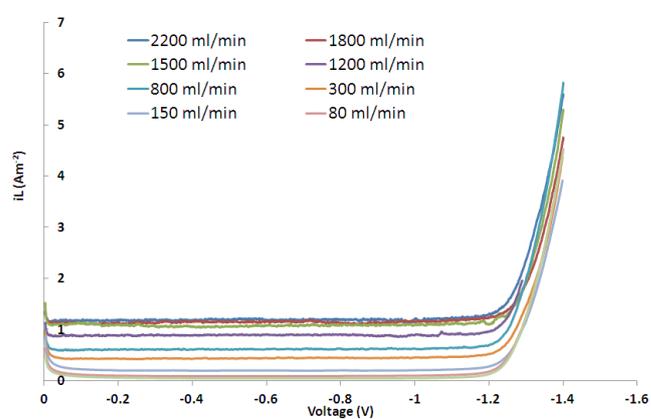
**Figure 6: Correlation between scan rate and peak current**

## 2. Determination of Mass Transfer Coefficient

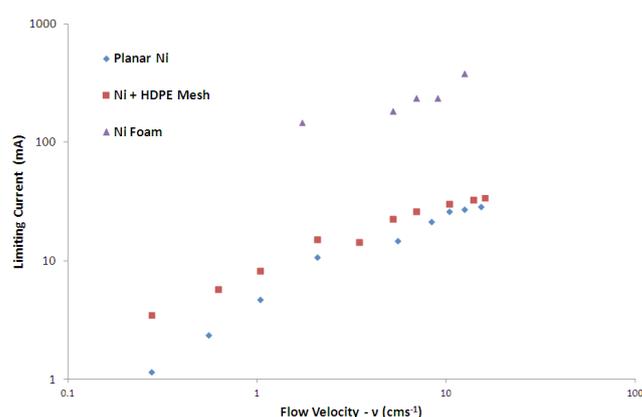
Current-potential curves were recorded for ferricyanide in 1M potassium hydroxide solution at increasing electrolyte flow rates with a planar Ni electrode and then with addition of non electro-active HDPE mesh to promote turbulence in the cell and finally with a Ni foam

to increase electrode surface area.

Reduction sweeps with a limiting plateau extending over approximately 1V were obtained for all cell configurations as shown in Figure 7. The limiting currents,  $i_L$ , were measured at 0.8V versus Hg/HgSO<sub>4</sub> reference electrode. Figure 8 shows the limiting current as a function of flow velocity. This shows that at high flow rates there is little difference between the current measured with and without the addition of mesh whereas at lower flow rates the addition of mesh does improve the limiting current somewhat. The use of the nickel foam in contact with the planar nickel electrode has the effect of increasing the limiting current measured by an order of magnitude due to the greatly increased surface area at the electrode.



**Figure 7: Linear Sweep Voltammetry - HDPE mesh added to Ni electrode example**



**Figure 8: Limiting currents as a function of flow velocity for (i) a flat Ni plate electrode (ii) with HDPE mesh for turbulence promotion and (iii) a Ni foam electrode**

Reduction of the ferricyanide at the nickel electrode is



mass transport controlled and the mass transfer coefficient for electrode of specified area can be calculated from the following equation:<sup>5</sup>

$$IL = nk_LFC_b \quad (1)$$

Where IL is the limiting current, n is the number of electrons in the reaction,  $k_L$  is the mass transfer coefficient, F is the Faraday constant and  $C_b$  is the bulk concentration. At the lowest flow measured in this experiment the mass transfer coefficients were calculated as:

Electrode set-up	Mass transfer coefficient $k_L$ (cm/s)
Planar nickel	$5 \times 10^{-8}$
Planar nickel with HDPE mesh	$1.5 \times 10^{-7}$
Planar nickel with nickel foam at the cathode	$6.4 \times 10^{-6}$

## Conclusions

Two types of electrochemical measurements have been made with the ferri/ferrocyanide redox couple in a C-Flow LAB cell. Experimental data showed the expected relationship between scan rate and peak current in cyclic voltammetry. Mass transfer coefficients for different cell configurations were obtained from the measured values of limiting currents.

<sup>5</sup> Pletcher et al, *Journal of Applied Electrochemistry* **24** (1994) 95-106



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