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MASS TRANSFER COEFFICIENT IN PACKED BEDS AT LOW REYNOLDS NUMBERS

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AT LOW REYNOLDS NUMBERS

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(M. S. Thesis)

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MASS TRANSFER COEFFICIENT IN PACKED BEDS AT LOW REYNOLDS NUMBERS

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ABSTRACT

Liquid-phase mass transfer rates for a packed bed in the Reynolds numbers range of 0.01 to 0.1 were obtained by taking advantage of the packed bed characteristics of a porous flow-through electrode. The model reaction chosen for the study was the reduction of ferricyanide at a porous flow-through electrode made of packed SS 440C spheres. The flow solution was made up of a ferri-ferrocyanide redox system with potassium nitrate as excess supporting electrolyte.

Limiting current curves for the cathodic reduction of ferricyanide were obtained at several catholyte flow rates. It was observed that the limiting current plateau became less distinct as the flow rate was increased. The experimental dimensionless mass transfer coefficient $\varepsilon k_m/aD$, obtained showed the same power dependence on Reynolds numbers as Geankoplis' correlation.17

Further investigation, however, is needed to determine the effect of electrode surface condition on results and length of plateau. New techniques must be developed to extend the Reynolds numbers range in both directions.
I. INTRODUCTION

In recent years, considerable efforts\textsuperscript{1-4,9,10} have been devoted to porous flow-through electrode for industrial applications. A porous electrode in the electrochemical cell makes a highly selective reaction possible and compensates for the slow reaction rate by means of the large surface area per unit volume. Very often the reaction can be carried out without high temperature and pressure.

Bennion et al.\textsuperscript{1} used an electrochemical cell equipped with two porous electrodes made of packed carbon flakes to remove and concentrate toxic copper ions from industrial wastes associated with electroplating industries. Gendron et al.\textsuperscript{2} investigated the performance of a porous flow-through cathode which consisted of a packed bed of lead spheres as a means of carrying out often slow electro-organic reactions such as the electro-reduction of quinoline to dihydroquinoline in sulphuric acid electrolyte and p-chlorobenzaldehyde to p-p' dichlorohydrobenzoin in alcoholic-KOH electrolyte. Both applications take advantage of the packed bed nature of a porous flow-through electrode, which is characterized by its high surface area for convective mass transfer per unit electrode volume.

The objective of the present study is to make use of the packed bed characteristics of a porous flow-through electrode to determine the mass transfer coefficient in a packed bed at Reynolds numbers below unity.

The model reaction chosen for this study is the cathodic reduction of ferricyanide in a ferri-ferrocyanide redox couple.
The redox couple is ideal for this work because no reaction products are deposited on the electrode surface, thus the mechanical condition of the surface remains constant. Besides, at low solute concentrations, the transport properties of the electrolyte stay essentially unaltered due to its redox nature. Furthermore, the exchange current density, $i_o$, of this reaction is high so that the limiting current plateau remains well defined.
II. THEORY

A. Background

Before going into the modeling of a porous electrode, it is convenient to describe the type of porous electrode in consideration. The porous electrode, which in the present study is a cathode, consists of a packed bed of metal spheres in mechanical contact with each other forming the matrix phase of the electrode. The anode or counter electrode is identical to the cathode except for the reactant concentration in the anolyte. The electrolyte feed splits between the electrodes and flows through each electrode separately. Connection to the external circuit is achieved by a metal plate at the back of the electrode, which serves as the current collector. Figure 1 is a schematic diagram of such an electrochemical model.

B. Model

Mass transport in a porous electrode can be described with models developed for packed-bed chemical reactors. From the mass transport point of view, the electrolysis in a porous electrode with flowing solution closely resembles the action of such a reactor.

For inhomogeneous reactions, a material balance for a small volume element of the porous electrode leads to the differential conservation equation

$$\frac{\partial e(c_i)}{\partial t} = - \nabla \cdot (\vec{N}_i) + a(j_i) \tag{1}$$
where \( \langle N_i \rangle \) = the flux of species \( i \) averaged over the cross section of the electrode cutting matrix and pores

\[ \langle c_i \rangle \] = the solution phase concentration averaged over the solution in the pores

\[ \langle j_i \rangle \] = the flux of species \( i \) into the pore solution at the pore-matrix interface, averaged over the interfacial area in a small volume of the electrode

For a dilute solution, the flux equation is

\[
\frac{\langle N_i \rangle}{\varepsilon} = - (D_i + D_a) \nabla \langle c_i \rangle - z_i \mu_i \nabla \Phi_2 + \frac{V}{\varepsilon} \langle c_i \rangle 
\]

(2)

where \( \frac{\langle N_i \rangle}{\varepsilon} \) = the average flux in the solution phase

\( D_a \) = axial dispersion coefficient

\( \frac{V}{\varepsilon} \) = average velocity inside the pores

\( D_i \) and \( \mu_i \) should be obtained from diffusivity and mobility of the species with a correction for tortuosity. The second term on the right side of Eq. (2) represents the effect of ionic migration under a potential gradient \( \nabla \Phi_2 \).

For the reaction of a minor ionic species in a solution with excess supporting electrolyte, it should be permissible to neglect the contribution of the ionic migration term in Eq. (2). Substituting Eq. (2) into Eq. (1) gives

\[
\frac{\partial \varepsilon \langle c_i \rangle}{\partial t} + \nabla \cdot [\varepsilon \langle c_i \rangle] = \alpha \langle j_i \rangle + \nabla \cdot [(D_i + D_a) \varepsilon \langle c_i \rangle] 
\]

(3)

Equation (3) can be used for a packed bed chemical reactor as well as a porous electrode.
For convective transport through a porous electrode or packed bed, the rate of mass transfer of the reacting species to the surface at the interface can be expressed as

\[ a(j_r) = -ak \frac{c_b - c_w}{m} \]  

(4)

thus defining the mass transfer coefficient, \( k \). \( c_b \) and \( c_w \) represent the bulk reactant concentration and the reactant concentration at the interface.

If we assume \( \varepsilon \) and \( a \) are uniform, and axial diffusion is negligible, and a uniform velocity profile exists across the electrode, then we can construct a steady state one dimensional model for the porous electrode (refer to Fig. 1). It is expressed as

\[ \frac{\partial}{\partial y} (v_y c_b) = -ak \frac{c_b - c_w}{m} \]  

(5)

If the concentration of reactant at the interface, \( c_w \), is zero, as in the case of operation at limiting current for a maximum driving force, Eq. (5) becomes

\[ v \frac{dc_b}{dy} = -ak \frac{c_b}{m} \]  

(6)

after dropping the subscript \( y \) in \( v_y \).

Faraday's law relates the concentration to solution phase current, \( i_2 \), by

\[ v \frac{dc_b}{dy} = -\frac{1}{nF} \frac{di_2}{dy} \]  

(7)

The solution phase potential distribution, \( \phi_2 \), then follows from the current distribution by Ohm's law.
Fig. 1
Schematic diagram of a porous electrode model.
The boundary conditions to Eqs. (6), (7) and (8) are

\[
\begin{align*}
\text{for } y = 0, & \quad c_b = c_o \quad \text{(9)} \\
\text{for } y = L, & \quad i_2 = 0 \quad \text{(10)} \\
\text{for } y = 0, & \quad \phi_2 = 0 \quad \text{(11)}
\end{align*}
\]

These boundary conditions imply that the metal backing which serves as the current collector must be located at \( y = L \) with free solution entering at \( y = 0 \).

With the B. C. specified, the solution to the Eqs. (6), (7) and (8) yields

\[
\frac{c_b}{c_o} = \exp \left[ - \frac{\alpha k m y}{v} \right] \quad \text{(12)}
\]

\[
i_2 = nFv c_o \left[ \exp(-\alpha y) - \frac{c_L}{c_o} \right] \quad \text{(13)}
\]

\[
\phi_2 = \frac{nFv^2 c_o}{ak m} \left[ \exp(-\alpha y) - 1 + \alpha y \frac{c_L}{c_o} \right] \quad \text{(14)}
\]

where

\[
\alpha = \frac{ak m}{v}
\]

Since at \( y = 0, \ i_T = i_2 \), it follows from Eq. (13) that the total current flowing through the external circuit is given by

\[
I_T = nFv c_o A \left( 1 - \frac{c_L}{c_o} \right) \quad \text{(15)}
\]

or

\[
\frac{c_L}{c_o} = 1 - \frac{I_T}{nFv c_o A} \quad \text{(15a)}
\]

where

\[
c_b = c_L \text{ at } y = L
\]
For an electrode thickness, \( L \), Eq. (12) becomes

\[
\frac{c_L}{c_0} = \exp \left[ -\frac{a k L}{v} \right] \tag{16}
\]

\( c_L/c_0 \) can be calculated from Eq. (15), once the other parameters in the equation are experimentally determined. Substituting the value for \( c_L/c_0 \) into Eq. (16) will yield \( k_m \) for the specified velocity.

From Eq. (15a) it is realized that as \( c_L/c_0 \) approaches unity as in a thin bed, it might be difficult to distinguish \( c_L \) from \( c_0 \) by analytical methods with sufficient accuracy. Conversely, if \( c_L/c_0 \) is allowed to approach zero, as in the case of thick bed, \( I_T/nFc_0 v A \) will tend to unify. \( I_T \) will become relatively large so that a small error in its measurement may result in great error in \( c_L/c_0 \). For example, if the fraction \( I_T/nFc_0 v A \) equals 0.99 with \( \pm 0.01\% \) uncertainty in the fraction, then \( c_L/c_0 \) equals 0.01 with \( \pm 1\% \) uncertainty. The relative uncertainty is increased by two orders of magnitude.

To avoid unnecessary propagation of experimental error, the ratio \( c_L/c_0 \) must be kept close to 0.5. For the present study, experimental accuracy is ensured within limits by imposing

\[
0.3 < c_L/c_0 < 0.7 \tag{17}
\]

as a design criterion.

Another phenomenon that can affect experimental accuracy is the hydrogen evolution reaction (HER). If Eq. (14) is solved for electrode thickness \( L \), the solution phase potential drop across the electrode is

\[
\Phi_{L2} - \Phi_{O2} = \Delta\Phi_2 = \frac{nF c_v^2}{\kappa k_m} \left[ \exp(-\alpha L) - 1 + \alpha L \frac{c_L}{c_0} \right] \tag{18}
\]
The effective conductivity $\kappa$ in the electrolyte inside the porous packing is given by

$$\kappa = \kappa_0 \varepsilon^{1.5}$$  \hspace{1cm} (19)

The principle that determines the permissible flow rate and bed thickness is the allowable solution phase potential drop within the porous electrode, $\Delta \phi_2$ in Eq. (18). Figure 2 shows, schematically, the cathodic potentials, $\phi$, as a function of electrode position, $y$. Although the electrode matrix is considered to be at a uniform potential, a potential difference exists between the electrode surface and the electrolyte. The absolute magnitude of the potential difference between the solid matrix and the solution, $|\phi_1 - \phi_2|$, should be large enough to ensure limiting current throughout the electrode length, but not so large that HER occurs. Should there be HER, it will occur first at the front of the electrode. It is important in the design of this porous electrode to ensure limiting current at $y = L$ while avoiding HER at $y = 0$.

The standard electrode potential of ferrocyanide to ferricyanide is 0.36 V. The electrode potentials of HER and oxygen evolution are pH dependent and they are illustrated in Fig. 3. An estimate of the allowable $\Delta \phi_2$ between ferri-ferrocyanide electrode potential and HER is 1.18 V in an alkaline medium and is 0.78 V in a neutral medium. This $\Delta \phi_2$ represents the maximum desirable solution potential variation in the electrode due to ohmic drop and concentration overpotential contribution. Note also that in neutral or alkaline media the $\Delta \phi_2$ between oxygen evolution and the redox reaction is relatively smaller than for HER. Therefore we would expect oxygen evolution to occur first at the anode.
Fig. 2

Solution phase and solid matrix phase potentials as a function of cathode position.
Fig. 3

Electrode potential vs pH diagram.
Before we can carry out the design of the electrode with the equations discussed earlier, we need to establish an estimate for \( k_m \). Newman applies Graetz analysis and arrives at

\[
\frac{\varepsilon k_m}{aD} = 0.914
\]

for \( k_m \) beyond the entrance region. This Graetz solution predicts an infinite mass transfer rate at the entrance region and accounts for a functional dependence of \( k_m \) on electrode position, \( y \).

Bird et al. suggest the following correlation (designated here as BSL)

\[
\frac{k_m}{aD} = 0.91 \left( \frac{\partial \nu}{a \mu \psi} \right)^{0.49} \psi^{2} \text{Sc}^{1/3}
\]

for Reynolds numbers, \( Re \), below 50. \( \psi \) is a shape factor and is equal to unity for spheres. However, we suspect that at extremely low \( Re \), much less than 50, Eq. (21) will not be valid. Instead, for such low Reynolds numbers, we suspect the dimensionless mass transfer coefficient, \( \varepsilon k_m/aD \), becomes a constant, as predicted by Eq. (20) (Graetz solution). There may be a transition zone between the two correlations.

Figure 4 represents what might be the correlation for fully developed mass transfer coefficient over a range Reynolds number below 50. It is also the intent of this experiment to determine \( k_m \) over a similar range and compare the results with these correlations to confirm or disprove our postulate.

Another system parameter that must be specified before actual design of the electrode is the concentrations of the ferri-ferrocyanide working solution. The criteria for selecting concentration are:
Postulated dimensionless mass transfer coefficient as a function of Reynolds numbers.
1. The concentration of reactants must be low enough so that natural convection effects are negligible.

2. From Eq. (17) it is apparent that a low $c_o/\kappa$ ratio will decrease $\Delta \Phi_2$. This can be accomplished by a low ratio of the reactants concentrations to the supporting electrolyte concentration.

3. The reactant concentrations must not be so low that the current measurement becomes a problem. Equation (15) can be applied to estimate the total current.

The concentration of ferricyanide was chosen to be 0.01 M, at which no detectable natural convection effects were reported. Ferrocyanide concentration was at 0.03 M. The 3 to 1 concentration ratio of ferrocyanide to ferricyanide is an effort to eliminate oxygen evolution at the anode. Potassium nitrate at 2 M was employed as excess supporting electrolyte, which was about 200 times the concentration of the cathodic reactant.

C. Design of Electrode

The design of the porous-electrode electrochemical cell was based on several design criteria. These design criteria are:

1. The operation of the electrode must be such that the ratio, $c_L/c_o$, be within the limits set by the inequality Eq. (17). As mentioned earlier, this is to minimize error in measurement.

2. As indicated before, the ohmic potential drop, $\Delta \Phi_2$, must be within the estimated limit, so that HER does not occur.

3. The minimum thickness of the electrode must not be less than two sphere diameters, because at such low electrode thickness entrance effect may come into play. The maximum thickness is governed by the allowable $\Delta \Phi_2$, and the limitation that $c_L/c_o$ must be greater than 0.3.
4. Besides being limited by the $\Delta \phi_2$, the maximum flow rate is restricted by the fact that there is a limited supply of working solution. Too high a flow rate will reduce cell operating time tremendously. A reasonable range may be a flow up to 40 ml/min, provided that all other criteria are met.

5. The desired range of Reynolds numbers to be studied is from $10^{-1}$ to $10^{-3}$.

With the concentrations of the working solution specified, there are three major design parameters we can control to meet all the design criteria. They are the flow rate, $Q$; the bed thickness, $L$; and the sphere diameter, $D_p$. The relative ease of control in descending order is $Q$ to $L$ to $D_p$. The flow rate, $Q$, can be varied in a continuous manner whereas both $L$ and $D_p$ change in discrete steps.

The design procedure involved choosing a probable sphere size, $D_p$. Using Eq. (16), a series of operating lines $c_L/c_o$ vs $Q$ were plotted for different electrode thickness, $L$. Figure 5 shows a series of operating line for sphere size, $D_p$ equal 0.4 cm. From Fig. 4, we could determine the bed thickness and the range of flow rate most suited for measuring $k_m$ at, say, the higher range of $Re$, and at the same time meet the criterion that $c_L/c_o$ was still within the 0.3 and 0.7 limits.

Based on Fig. 5, Table I is a sample design result that satisfies all the criteria for the given sphere size. By varying the flow rate, $Q$, over three different electrode thickness, we should be able to determine $k_m$ over a range of Reynolds numbers from $10^{-3}$ to about $10^{-1}$. If some of the criteria were not met, a new sphere size, $D_p$, would be picked and the design procedure repeated. It should be pointed out that by
Fig. 5

Design $c_L/c_o$ vs $Q$ (operating lines for $D_p = 0.4$ cm).
reducing the sphere size, we can approach still lower values of Reynolds numbers.
Table I. Design result for Dp = 0.4 cm

<table>
<thead>
<tr>
<th>Dp (cm)</th>
<th>L (cm)</th>
<th>Layers of Spheres</th>
<th>Range of Q (ml/min)</th>
<th>Range of Re</th>
<th>ΔΦ2 max (volt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.4</td>
<td>0.74</td>
<td>2</td>
<td>1&lt;Q&lt;6</td>
<td>2.0×10⁻³&lt;Re&lt;1.3×10⁻²</td>
<td>-0.01</td>
</tr>
<tr>
<td>1.3</td>
<td>4</td>
<td>3</td>
<td>3&lt;Q&lt;20</td>
<td>6.5×10⁻³&lt;Re&lt;4.3×10⁻²</td>
<td>-0.06</td>
</tr>
<tr>
<td>2.0</td>
<td>6</td>
<td>6</td>
<td>6&lt;Q&lt;40</td>
<td>1.3×10⁻²&lt;Re&lt;8.6×10⁻²</td>
<td>-0.18</td>
</tr>
</tbody>
</table>

Conditions: c_o = 0.01 M

D = 5×10⁻⁶, cm²/sec

κ_o = 0.088, mho/cm

k_m ≡ estimated with Eq. (21), cm/sec
III. EXPERIMENTAL APPARATUS

A. Cell Design

The experimental cell, constructed for this study, closely followed the cell design adopted by Bennion in his work in copper ion removal. The principal features were two porous metallic electrodes made of stainless steel spheres. The spheres were 5/32 in. O.D. SS 440C type steel provided by Atlas Company as bearing balls. The cell was made of plexiglas housing the two electrodes, which were separated by a feed ring where the feed solution entered. Sealing was ensured by "O" rings at joints. Figure 6 shows the cell design.

Each electrode was held in place by a plastic perforated plate on the feed side. The perforated plate was held in place by a stainless steel tightening rod, through which the bed could be compressed by pulling and tightening the lock nut at the end. To ensure good liquid distribution, polypropylene non woven fabric filter paper ("Webril" by Kendall Company) and a 0.5 cm sintered glass plate were employed to prevent channeling. The outlet side of the electrode is contained by a stainless steel back plate containing 60 holes of 0.2 cm I.D. This back plate served as the current collecting plate for the electrode and also provided electrical connection to the external circuit through a 0.3 cm O.D. rod threaded into the plate. On operation, the anode stayed on the top side so that oxygen bubbles could escape should there be any.

Plexiglass support rings could be added into the tubular section to help bring the electrodes closer towards each other. In this way the ohmic drop across the feed ring electrolyte was minimized. A 2 cm and a 4 cm tall support ring were available depending on the thickness of
Fig. 6

Cell design.
the electrode. The thickness of the porous electrode could be varied from a maximum of 6 cm to a minimum of one layer of spheres by adjusting the tightening lock nut. The position of the electrode could be altered by the addition of different sizes of support rings.

B. Flow System

Figure 7 is a schematic diagram of the flow system. The feed solution from a stainless steel storage tank (50 L in capacity) supplied solution to the cell through a constant head overflow bottle. The bottle and the tygon tubing were screened from day light with black tape. The pressure in the storage tank was kept at atmospheric at all times by supplying nitrogen and venting nitrogen to the atmosphere at a slow rate through a wash bottle half filled with water to prevent back flow of air into the tank. The constant head overflow allowed a steady gravity flow of feed solution into the cell. It could maintain constant the volumetric flow rate to no better than 3 or 4%. The over flowed liquid was drained to a storage bottle.

Downstream of the constant head flow bottle, there is an in line filter made of a glass bulb filled with polypropylene filter fabric. This device picked up particulate suspended in the solution which otherwise would deposit on the distributor filter plugging up the pore and resulting in channeling.

The feed solution entered the feed ring and split up its flow to form the catholyte and anolyte streams. Both flows were controlled by Nupro micrometer valves. The relative variations in flow were monitored by two glass flowmeters (Gilmont, range 0.4-42 ml/min). The actual volumetric flow rate was determined by measuring a known volume of product in a graduated cylinder over a period of time with a stop watch.
Fig. 7

System flow diagram.
A gas vent line allowed gas bubbles, which were swept into the feed ring, to leave the cell. The gas bubbles and some solution would end eventually in the wash bottle. For the sake of convenience in detecting bubbles trapped in any of the feed or product lines, tygon tubing was used in all flow system lines. Tube flexibility allowed easy bubble removal. It was learned during experimental runs that any bubble trapped in the feed or product streams could cause pulsation of flow and consequently could jeopardize the accuracy of current and voltage measurements.

C. Electrical Circuit

Figure 8 shows a schematic diagram of the electrical circuit. The cell was powered by a regulated D.C. power supply (Power Design, Inc., Model 5015-S) whose voltage output could be adjusted by means of two controls to give voltage increment of 0.05 V. The voltage output by the power supply was monitored by a Weston Voltmeter (0-3 volts range), which would be connected only when precise cell voltage was required. The positive terminal of the power supply was attached to the anode of the cell and the grounded negative terminal was connected to the cathode.

The power lead first went to a Weston D.C. milliammeter (with ranges 0-30 mA, 0-300 mA and 0-3000 mA). To observe trends and establish steady state of the total current, $I_T$, the potential drop across a Decade Resistor box (General Radio Co., type 1432-U), was measured and recorded by a Sargent Recorder (Model SRG).

The potential, $\eta_c$, across the Beckman saturated Calomel Electrode in the catholyte stream vs the cathode was measured on an electrometer (Keithly type 602) and was recorded on a Sargent Model SR recorder via the 1 mA output attenuating adapter in the electrometer. The recorder
Electrical circuit.

Fig. 8
helped to observe trends and established when steady state was reached.

Care was taken to make sure all instruments were grounded at the same point of the circuit in order to avoid ground loop currents.
IV. EXPERIMENTAL PROCEDURES

A. Preparation of Electrolyte

In preparing a redox solution of 0.01 M $K_4Fe(CN)_6$ and 0.03 M $K_4Fe(CN)_6$ in excess supporting $KNO_3$, certain precautions should be taken. Potassium ferrocyanide decomposes on long exposure to light by the reactions:

$$\text{Fe(CN)}_6^{4-} + H_2O \xrightarrow{\text{light}} \left[\text{Fe(CN)}_5H_2O\right]^{3-} + CN^-$$ (22)

$$CN^- + H_2O \xrightarrow{\text{dark}} HCN + OH^-$$ (23)

It is apparent from the second reaction that a high pH tends to prevent decomposition by shifting the equilibrium to the left. Unfortunately, the supporting electrolyte we employed is neutral and cannot help stabilize decomposition.

Moreover, dissolved oxygen reacts at the cathode in the same potential range as that of the ferricyanide ions.

It is, therefore, expedient to prepare the redox solution as quickly as possible so as to avoid unnecessary exposure to light and air.

Weighed portions of ferricyanide, ferrocyanide and potassium nitrate were added into a 10 l glass tank to give the desired concentrations. To accelerate dissolution, an electric stirrer was used. Several batches of solution were made to prepare a total of 50 liters of electrolyte in the storage tank. When the lid of the reservoir was tightened, nitrogen gas was allowed to bubble into the electrolyte to provide mixing and saturation with nitrogen in an effort to expel dissolved oxygen. The storage tank was kept in an inert atmosphere at all times by a blanket of $N_2$ on the top of the solution.
The concentrations of the final working solution were analytically determined by titrations. Ferricyanide was by potassium iodide and sodium thiosulphate iodiometry.\textsuperscript{12} Ferrocyanide was by titration against ceric sulphate in sulphuric acid using Ferroin indicator.\textsuperscript{13} This method of titration for ferrocyanide gave a much sharper end point than titration against potassium permanganate.\textsuperscript{12}

The potassium nitrate was determined gravimetrically by evaporating a 100 ml solution to dryness at room temperature in a vacuum. The weight of the crystals minus the contribution due to potassium ferricyanide and potassium ferrocyanide would give the concentration of KNO\textsubscript{3} in the 100 ml sample. As a check, the concentration of potassium ion was determined gravimetrically by precipitating with tetraphenyldiboro sodium.\textsuperscript{14} The nitrate concentration would be calculated knowing the potassium ion concentration due to other species present.

B. Packing Porous Electrode

Special attention must be paid to packing porous electrode correctly in order to obtain a tight porous matrix with good electrical contact and an even electrode thickness. Bubbles trapped inside the porous matrix of the electrode would reduce the total bed surface area. While large bubbles trapped in the tubing would cause pulsation of flow rate which could be detected as a current or overpotential-voltage surge, if the system is in operation, bubbles found between the two porous electrodes in the feed ring would cause nonuniform distribution of flow into the electrode and thus result in nonuniform current distribution across the cross-section of the electrode. The technique of packing will be based upon the above philosophy.
Before packing the electrode, the stainless steel back plate and all the spheres were cleaned in distilled water and then methanol. Without drying the methanol, the back plate was immersed in the water-filled plexiglas cell as shown in Fig. 9. In this way, bubbles would not stick to the surface of the metal.

The porous electrode should be "wet packed". The water level should be adjusted such that the spheres were just covered with water. The surface tension helped keep the spheres together allowing earlier packing. The spheres were in a regular close pack arrangement—the Rhombohedral packing where each second layer of spheres is placed in the hole formed by the contacting spheres of the first layer.

The regular packing provided a very stable electrode so that on tightening the packed bed, little rearrangement of the spheres would result. A randomly packed electrode bed tended to redistribute and very often resulted in uneven bed thickness.

To achieve rhombohedral regular packing, the spheres were arranged in parallel rows, but always starting from the centre closest to the tightening rod towards the wall. This procedure provided a maximum number of spheres per layer and also the most stable configuration. Once the first layer of spheres was set, the subsequent layers are much easier to set because the spheres tended to fall into the stable saddle points.

When the porous electrode was packed, the distributing elements were installed. The electrode bed was then slightly tightened by compressing with the perforated plastic plate, which was pulled by the center tightening rod.
Arrangement for packing electrode.
The electrode on the top side was packed in a similar manner, only that the first layer started on the plastic plate side. With the electrodes packed, the whole cell assembly was bolted together with four brass bolts. Care should be taken to tighten bolts diagonally and evenly to avoid air in-leakage into the beds. The porous electrodes were further compressed by slowly tightening the lock nut. This procedure was to ensure a good metal-to-metal contact between spheres and also spheres-to-back-plate contact.

All the outlets from the cell were isolated either with plugs or valves before the cell was transferred to be connected to the rest of the flow system. With the cell in horizontal position, the feed solution was introduced into the feed ring. Bubbles in the ring were vented by the gas vent line. To get rid of bubbles in the reservoirs, the cell was set vertical with the control valve wide open so that bubbles could be flushed out through the product streams. The transparent flexible tygon tubing proved to be convenient both in detecting trapped bubbles in the line and also in "directing" bubbles downstream.

C. Experimental Run

A typical run was described here.

The flow rate in each product stream was adjusted to the desired level with the micrometer valves. The catholyte and the anolyte were set at about the same flow as indicated by the flowmeter rough calibration curve. Since flow control was critical in this study, a cathetometer was employed to detect a relative change in flow rate from its original set point on the flowmeter. However, the recorded catholyte flow rate should be measured with a graduated cylinder and a stop watch.
Once the flow rates were set, the cell voltage, $\Delta V$ was increased at 100 mV increment for each step. Ten minutes at the most was actually needed for the current $I_T$, and the cathode vs calomel reference electrode potential, $\eta_c$, to respond and arrive at the new steady state value. $\eta_c$ had more sensitivity towards parameter changes and was considered the better indicator of steady state. For this study, steady state was ensured by waiting at least a half hour after each cell voltage change. Then, $I_T$, $\eta_c$, catholyte flow, $Q$, and the temperature of the feed were recorded.

Limiting current was reached when an increase in $\eta_c$ did not cause a corresponding increase in $I_T$. $\eta_c$ was not allowed to go above 1.0 V for fear that bubbles due to HER might be trapped in the porous packing thus changing the physical characteristic of the electrode. The limiting curve was checked for reproducibility by going down in cell voltage and repeating the measurements mentioned above.
V. RESULTS

A typical limiting current curve for the reduction of ferricyanide is presented in Fig. 10. The total current, \( I_T \), across the cell is the ordinate and the potential, \( \eta_c \), the abscissa. The curve started at about \(-0.2V\) and climbs rather steeply bending towards the horizontal as it rose. Between \(-0.1V\) to \(0.45V\) the slope of the curve was rather constant, and finally at about \(0.45V\) the curve began to level off as the limiting current plateau. At around \(0.85V\) the curve began to climb at a constant slope again for about \(100mV\) before it increased exponentially around \(1.0V\) as it approached hydrogen evolution region.

The relatively large overpotential, \( \eta_c \), required for the electrode to reach the limiting current plateau suggested that ohmic drop across the solution and the electrode matrix was high. This ohmic drop may be due to the formation of a yellow tarnish or coating (perhaps an oxide or cyanide ion poisoning) on the surface of the spheres. It was also observed that the limiting current curve was not reproducible if the cell voltage was allowed to decrease after reaching the limiting plateau. This was illustrated in Fig. 11. A new current curve 2 with a lower current for the same \( \eta_c \) resulted, even though it was run immediately after the curve 1. This phenomenon seemed to suggest that the surface condition of the sphere was constantly changing as if a coating was gradually building up on it. The effect of the surface condition of disk electrode on measurement was also observed by Smyrl and Newman and seemed to substantiate the argument here.
Fig. 10

Typical limiting current curve for reduction of ferricyanide in a porous flow-through electrode.
Fig. 11

Effect of electrode surface condition on limiting current.
The dependence of limiting current curves on flow rate is illustrated in Fig. 12 for Run #21. At lower flow rates (below 10 ml/min), the plateaux were long and well defined. However, at higher (above 10 ml/min) it took a higher and higher overpotential $\eta_c$ to reach limit current plateaux, which were now shorter and ill defined. The shortening of the plateau at higher flow rate was expected since the solution phase potential drop across the electrode was proportional to the square of the velocity as given in Eq. (14). At about 20 ml/min the limiting current plateau was hard to discern and therefore set an upper limit to the flow rate. The short limiting current plateau due to high flow was further complicated by the aging effect of the spheres' surface, which gave the plateau the appearance of a slight slope instead. Precise flow rate control was of absolute importance for a good limiting current plateau. $\Delta \phi_2$ for the highest flow was estimated to be 0.1V, which is much below HER.

The effect of flow rate on the ratio $c_L/c_o$ was given in Fig. 13 for the same run #21. It was obvious that only two experimental points actually met the constraint $0.3 < c_L/c_o < 0.7$. Both BSL correlation and Graetz solution predicted a higher $c_L/c_o$ ratio for the corresponding flow rate. A literature search showed that another correlation by Geankoplis et al.\textsuperscript{17} developed for a similar Reynolds number range, fit the experimental data well. The correlation is

$$k_m = \frac{1.09}{\epsilon} \left( \frac{D \rho v}{\mu} \right)^{2/3} \left( \frac{\mu}{\rho D} \right)^{-2/3} \nu$$  \hspace{1cm} (24)
The effect of flow rate on limiting current curves for cathodic reduction of ferricyanide in a porous electrode.

Fig. 12
Experimental $c_L/c_o$ vs $Q$.
A log-log plot of the dimensionless mass transfer coefficient $\frac{\varepsilon k_m}{aD}$ vs the Reynolds number for Run #21 is given in Fig. 14. The experimental data are compared with the correlations of Eq. (2) and Eq. (21). BSL correlation shows a steeper slope than the experimental data. Graetz solution implies there is no dependence on Reynolds number. Geankoplis' correlation has a very similar slope as the experimental data. This confirmed the Reynolds number dependence of the experimental mass transfer coefficient.

The major parameters of Run #21 are given in Table II. The viscosity was measured with a viscometer. The density of the solution at similar conditions was measured with a pycnometer. The thickness of the porous cathode was measured with a cathetometer. The diffusion coefficient was calculated from the Stokes-Einstein relation $\frac{\mu D}{T} = 2.76$ (Ref. 18) for potassium nitrate supporting electrolyte.
Fig. 14
Dependences of experimental dimensionless mass transfer coefficient on Reynolds number.
Table II. Major system parameters for run #21

<table>
<thead>
<tr>
<th>A. Concentrations:</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Fe(CN)}_{6}^{3-} = 0.009769 \text{ M} )</td>
</tr>
<tr>
<td>( \text{Fe(CN)}_{6}^{4-} = 0.02927 \text{ M} )</td>
</tr>
<tr>
<td>( \text{KNO}_{3} = 1.65 \text{ M} )</td>
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</table>

<table>
<thead>
<tr>
<th>B. Solution Properties (at 22°C):</th>
</tr>
</thead>
<tbody>
<tr>
<td>( D = 8.585 \times 10^{-6} \text{ cm}^2/\text{sec} )</td>
</tr>
<tr>
<td>( \mu = 0.009175 \text{ poise} )</td>
</tr>
<tr>
<td>( \rho = 1.1217 \text{ g/cm}^3 )</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>C. Physical Dimensions:</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A = 60.8 \text{ cm}^2 )</td>
</tr>
<tr>
<td>( a = 9.67 \text{ cm}^{-1} )</td>
</tr>
<tr>
<td>( \varepsilon = 0.355 )</td>
</tr>
<tr>
<td>( L = 1.433 \text{ cm (cathode)} )</td>
</tr>
</tbody>
</table>
VI. DISCUSSION OF RESULT  

A. Sources of Error  

The range of Reynolds number in the experiment is set at the upper limit by the maximum velocity at which a discernable limiting current plateau can be obtained and the lower limit by the constraint \( \frac{c_L}{c_o} > 0.3 \). The accuracy of the \( k_m \) therefore, also depends on how well the plateau can be defined. The shorter the plateau, the harder it is to obtain a good limiting current. The problem is further complicated by the gradually changing surface of the spheres, which make the plateau less flat. The accuracy of the physical properties of the solution contributes another source of error to \( \frac{ek_m}{aD} \). The diffusivity \( D \) is believed to lie within the vicinity of \( 5 \times 10^{-6} \) cm/sec. An increase in \( D \) will shift the experimental line in Fig. 14 down without changing the slope. This means the power dependence on the Reynolds number will be preserved despite inaccuracy in transport properties measurement. A change in the viscosity will shift curve form left to right or vice versa, again without affecting the slope of the curve.

Similarly, error in "c" and therefore "a" measurement, will introduce a factor in the dimensionless coefficient shifting the experimental line up or down. Although the experimental data presented in Fig. 14 may appear to fit the Geankoplis' correlation, it should be pointed out that the only conclusion we can make is that the slope and therefore the power dependence of Reynolds number matches. More experimental results must be gathered to prove this point.

The distribution of liquid as it enters the packed bed is of vital importance to the absolute magnitude of \( k_m \). Channeling may cause
localized hydrogen evolution. The thin bed may introduce entrance effect into the result.

It was observed that the orientation of the cell (i.e. cathode above or below anode) has considerable influence in the current measured. It was decided here to use the anode on top for the reason that the chance of exceeding the oxygen evolution overpotential at the anode is higher than HER at the cathode. Oxygen evolution may set up an undesirable convection pattern and bubble formation in the cell if the anode is below the cathode. Moreover, the densification due ferrocyanide is larger than that due to ferricyanide, so that the redox reaction makes the catholyte denser and anolyte less dense.

B. Proposed System Improvements

The problems mentioned in the result and discussion can be partially corrected by improving the existing system.

1. Flow system

Flow control has proved to be an absolute necessity to obtain reasonable measurement. The overflow system used in the present apparatus can keep the drift of flow rate to 3-4% without adjusting the micrometer value. To avoid such down drift of flow rate and to avoid the need of adjustment of flow during long period operation, a pump with variable speed control can be used to provide a better constant head overflow. The flow scheme is shown in Fig. 15. The extra line connecting the surge tank and the constant head overflow tank is for pressure equalization in the two tanks.

A finer flowmeter with better resolution can help detect variations of flow rate more easily. The present resolution is approximately 0.5 ml/min.
Proposed flow diagram of the improved system.
However, the final flow measurement will still have to be measured quantitatively with a graduated cylinder.

The distribution of fluid in the bed should not be overlooked. Glass beads can be used as inert spheres to provide more even distribution than the perforated-plate-sintered-glass assembly. Several layers of such glass beads, whose size is similar to the metal spheres, can be packed in between the plastic plate and the metallic porous electrode.

2. Temperature Control

Although not proven, it was noticed that the shift of 1 to 2 °C in solution temperature will set current and potential recorders adrift to a new equilibrium position, therefore affecting the accuracy of measurement. Moreover, heat dissipated to the solution by the proposed pump may very slowly shift the solution temperature. To make sure there is no temperature variation, the solution is passed through a stainless steel coil immersed in a constant temperature bath.

3. Solution

The ferricyanide and ferrocyanide in neutral excess supporting electrolyte tend to decompose to form cyanide ion, which poisons the electrode surface. An alkaline excess supporting electrolyte though more corrosive, may provide a stable plateau, i.e. unaffected by pH changes associated with HER and oxygen evolution. This will provide a more discernable plateau specially at the higher flow rate range.

4. Cell Mechanism

The present electrode tightening mechanism may crack the perforated plastic front plate as well as the two end disks. One single centre-pulled tightening rod may not be able to keep the porous electrode
uniform in thickness. A better mechanism preferably with more than one tightening rod is desired.

Clamped connections of tygon tubing to the cell often leak. Swagelok connection may be more reliable against leak as well as convenient to disconnect the cell from the rest of the system.
VII. CONCLUSION

This study has demonstrated the feasibility of determining the mass transfer coefficient of a packed bed using the electrochemical limiting current method. It has been shown how an electrochemical cell equipped with two porous flow-through electrodes made of packed beds of SS440C spheres can be designed and used, with considerable success, to perform chemical reactions. The choice of SS440C spheres in this work over lead spheres, which were used by Gendron et al. in their investigation of porous flow-through electrodes for electro-organic reactions, has the distinct advantage of much less surface aging problem, and therefore should be considered as a better material for long periods of continuous operation. The fact that SS440C bearing balls are commercially available in a wide range of sizes from 1/32" to 2" at 1/32" increment has further increased design flexibility. By varying $D_p$ and $L$, measurement of $k_m$ can be extended to much higher Reynolds numbers, which if dependent on flow rate alone, is limited by the potential drop through the electrode.

There are still areas that need further investigations in order to understand the operation of a porous electrode. The effect of electrode surface condition on limiting current must be looked into further. A cleaning procedure is in order. This may be accomplished by buffing the spheres with tin oxide in a rock tumbler or by chemical and cathodic treatment of the spheres before usage. However, questions like how long can the spheres be in service before recleaning is required still remain to be answered.
A different $c_L/c_o$ detection scheme is required if the $k_m$ is to be extended to $Re$ less than $10^{-2}$. The method of current detection does not prove accurate at very low $c_L/c_o$ under the present design.
ACKNOWLEDGEMENTS

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NOMENCLATURE

\(a\) surface area per unit packed bed volume, \(\text{cm}^{-1}\)

\(A\) cross section of the electrode, \(\text{cm}^2\)

\(c_o\) ferricyanide feed concentration, \(\text{mole/cm}^3\)

\(c_L\) ferricyanide concentration in catholyte effluent, \(\text{mole/cm}^3\)

\(c_b\) bulk concentration of ferricyanide in porous electrode as a function electrode position, \(\text{mole/cm}^3\)

\(D_p\) sphere diameter, \(\text{cm}\)

\(D\) diffusion coefficient of ferricyanide, \(\text{cm}^2/\text{sec}\)

\(F\) Faraday's constant, coulomb/equivalent

\(i_s\) solution phase current density, \(\text{ampere/cm}^2\)

\(I_T\) total circuit current, ampere

\(k_m\) mass transfer coefficient, \(\text{cm/sec}\)

\(L\) thickness of porous electrode, \(\text{cm}\)

\(<j_i>\) the flux of species \(i\) into the pore solution at the pore-matrix interphase, averaged over all the interfacial area in the electrode

\(<N_i>\) the flux of species \(i\) averaged over the cross section of the electrode cutting matrix and pores, \(\text{mole/cm}^2\cdot\text{sec}\)

\(Re\) Reynolds number, \(\frac{\rho v}{\mu}\)

\(Sc\) Schmidt number, \(\frac{\mu}{\rho D}\)

\(v\) superficial velocity of the catholyte across the electrode, \(\text{cm/sec}\)

\(Q\) catholyte flow rate, \(\text{ml/min}\)

\(z_i\) ionic charge of species \(i\)

\(\varepsilon\) void fraction of porous electrode

\(\kappa\) effective conductivity of catholyte, \(\text{mho/cm}\)
<table>
<thead>
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<th>Symbol</th>
<th>Definition</th>
<th>Unit</th>
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<tr>
<td>( \kappa_0 )</td>
<td>electrical conductivity of the feed solution</td>
<td>mho/cm</td>
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<tr>
<td>( \mu )</td>
<td>viscosity of feed solution</td>
<td>poise</td>
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<tr>
<td>( \rho )</td>
<td>density of feed solution</td>
<td>gm/cm³</td>
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<tr>
<td>( \phi_1 )</td>
<td>solid matrix potential</td>
<td>volt</td>
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<td>( \psi )</td>
<td>particle shape factor</td>
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<tr>
<td>( \alpha )</td>
<td>( a k_m / \nu ), cm(^{-1})</td>
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<tr>
<td>( \gamma )</td>
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<tr>
<td>( \eta_c )</td>
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REFERENCES


4. C. L. Mantell, Chemical Engineering, 74 (6), 128 (1967).


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