

Measurement of local and overall mass-transfer coefficients to a sphere in a quiescent liquid using a limiting current technique

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Abstract

The mass-transfer rate to a sphere in a quiescent ferri–ferrocyanide solution was determined from measurement of the limiting current through the spherical cathode. Mass-transfer rates to local areas on the sphere, without mass transfer to the rest of the sphere, were also measured. Convective movement of the electrolyte was observed visually although the experimental apparatus was jacketed for maintaining a constant temperature. Under this condition, the experimental Sherwood number for mass transfer to the whole sphere was 110 rather than 2 as for pure diffusion. The local Sherwood number for a 2 mm spot on the sphere was 275, which was about 1.7 times that of a 8 mm spot on the sphere. The local mass-transfer rate, in the absence of mass transfer to the rest of the sphere surface used in the present study, did not change significantly with the angular position to the upward vertical as it does when mass transfer occurs over the whole sphere simultaneously. The transient transfer approached steady state at the dimensionless time (tu/d) of about 20. The mass-transfer rate did not vary significantly with the distance between the two electrodes varied from 2.5 to 11 radii of the spherical cathode. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Mass-transfer coefficients; Ferri–ferrocyanide solution; Sherwood number

1. Introduction

Under certain conditions, the current going through an electrolytic cell is independent of the applied voltage, but is a function of mass transfer only [1–3]. This transport phenomenon has been widely used to investigate mass transfer in various systems, such as a flow in a pipe, an agitated vessel, and a solid wall. This experimental technique is also known as the electrochemical technique. Selman and Tobias [4] gave a thorough review of mass transfer studies for various geometries using the electrochemical technique.

Various electrolytes have been utilized and reported in literature [5]. Copper deposition at a cathode using a cupric sulfate and sulfuric acid solution gives a large density difference between the solution at the cathode surface and the adjacent bulk liquid. The sulfuric acid acts as a support electrolyte that eliminates the ionic migration in the electrolyte. The mass transfer is thus due to the concentration gradient of the transferring species, the cupric ions. Schutz [6], using this solution, investigated natural-convection

mass transfer to a whole sphere over a range of Rayleigh numbers ($Ra=Gr \times Sc$) from 2.29×10^8 to 1.51×10^{10} .

Another commonly used electrolyte is the ferri–ferrocyanide solution with the sodium hydroxide as a supporting electrolyte. This solution does not have a density variation between the liquid at the surface of the cathode and the bulk liquid due to chemical reactions since these are redox reactions where only electrons are transferred. This electrolyte is often used in studying forced-convection mass transfer. Noordsij and Rotte [7] measured mass-transfer coefficients to a rotating sphere and a vibrating sphere in a ferri–ferrocyanide solution [7]. The authors reported the limiting Sherwood number of 60–70 for a still sphere (no rotation or vibration), which was much higher than the Sherwood number of two for pure diffusion to a sphere. This was due to natural convection of the bulk electrolyte under a quiescent state (no forced flow). This mode of mass transfer was different from natural-convection mass transfer generated by the concentration-induced change of the density of the liquid at the surface of the cathode, such as in the chemical deposition of copper. This indicated that a significant contribution to the overall mass transfer to a sphere was due to natural convection of the bulk motion of the solution. The convective motion of the fluid could be generated by a temperature

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Nomenclature

A	transfer area (m^2)
C_b	the bulk concentration of ferricyanide (mol m^{-3})
C_0	concentration of ferricyanide at the surface of the spherical cathode (mol m^{-3})
d	diameter of the sphere (m)
D_{AB}	diffusivity of ferricyanide in the electrolyte ($\text{m}^2 \text{s}^{-1}$)
F	Faraday number (96 487 C/mol)
g	gravitational acceleration (m s^{-2})
Gr	Grashof number ($d^3 \rho g \Delta \rho / \mu^2$)
i_L	limiting current (A)
k_c	mass-transfer coefficient (m s^{-1})
n	valency change of the cathodic reaction ($n = 1$ for the present study)
N	molar flux of ferricyanide ($\text{mol m}^{-2} \text{s}^{-1}$)
P	image of the distance traveled by the dye streak (mm)
Q	the length of the image of the mirror on the photograph (mm)
Re	Reynolds number ($d \rho u / \mu$)
Sc	Schmidt number ($\mu / [\rho D_{AB}]$)
Sh	Sherwood number ($k_c d / D_{AB}$)
t	time (s)
u	fluid velocity (m s^{-1})
Z	actual distance traveled by the dye (mm)
<i>Greeks</i>	
μ	liquid viscosity ($\text{kg m}^{-1} \text{s}^{-1}$)
ρ	liquid density (kg m^{-3})
$\Delta \rho$	difference between the density of the liquid at the sphere surface and the bulk liquid (kg m^{-3})

gradient in the bulk liquid. Natural-convection mass transfer to a sphere by the concentration-induced density difference between the fluid at the solid–liquid interface and the adjacent bulk solution has been studied extensively. Recently, Sedahmed et al. [8] also made use of the copper-deposition technique to investigate natural-convection mass transfer in a fixed bed of Raschig rings. However, natural-convection mass transfer to a sphere or a bed of particles, which is due to the thermal-induced motion of liquid, has not been accounted for.

In addition, reported local mass-transfer coefficients are for cases with the concentration boundary layer developed over the entire surface of a sphere such as a dissolving sphere. On the other hand, without the concentration boundary development over the whole sphere, local mass-transfer rates are expected to be higher than those for a dissolving sphere or a sphere in an electrolyte with the whole spherical surface activated. Local mass transfer, in the absence of mass transfer to the rest of the sphere surface, has an application

in mass transfer from a single opening on a coated sphere such as coated fertilizers (e.g. sulfur-coated urea) [9]. The objective of this study was thus to investigate mass transfer to a local area on a sphere (without mass transfer to the rest of the spherical surface) using the electrochemical technique. This was achieved by activating the local area on the sphere where the limiting current was measured while the rest of the sphere was inactivated. The overall mass transfer to the whole sphere was measured as well. An analysis of the effect of the motion of the bulk liquid on local and overall mass-transfer rates is also presented.

2. Experimental method

A sphere (5.0 cm diameter) was machined out of a brass rod. The sphere was divided into five segments (constituting a hemisphere) and a whole hemispherical segment as shown in Fig. 1. A small hole was drilled into the top segment. A small pin of a 2 mm diameter was inserted into the hole. The pin was electrically insulated from the top segment. Each segment was bored into a ring. This provided an opened space for running the electrical wires, one for each segment, from inside the sphere to a switch box. The whole sphere or a particular segment on the sphere was used as a cathode where the mass transfer was measured.

Before assembling all the segments, they were plated with nickel. All segments were insulated electrically from one another by inserting a thin disk of insulation between segments. The segments were bonded together with epoxy. This allowed measurements of mass transfer to individual segments. The whole spherical assembly was supported horizontally with two polymer-coated stainless-steel tubes. One end of the supporting tube was inserted into the sphere at the equator level and sealed with epoxy. The other end of the tube was passed through the walls of two concentric cylindrical PVC vessels. The supporting tube was connected to a pointer for setting the angular position of an active spot on the sphere using a semicircular graduation. The electrical wires were run inside the tube to the outside electrical circuit without any contact to the electrolyte. The inner vessel

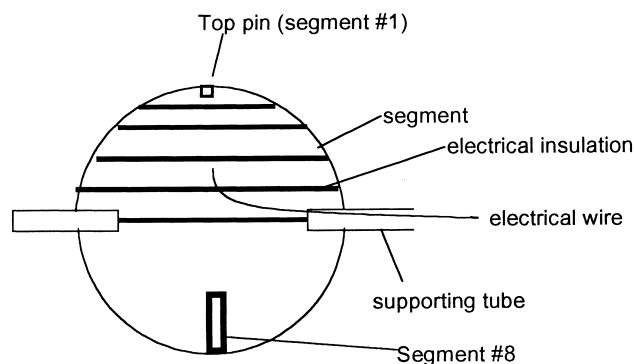


Fig. 1. Sectioned sphere.

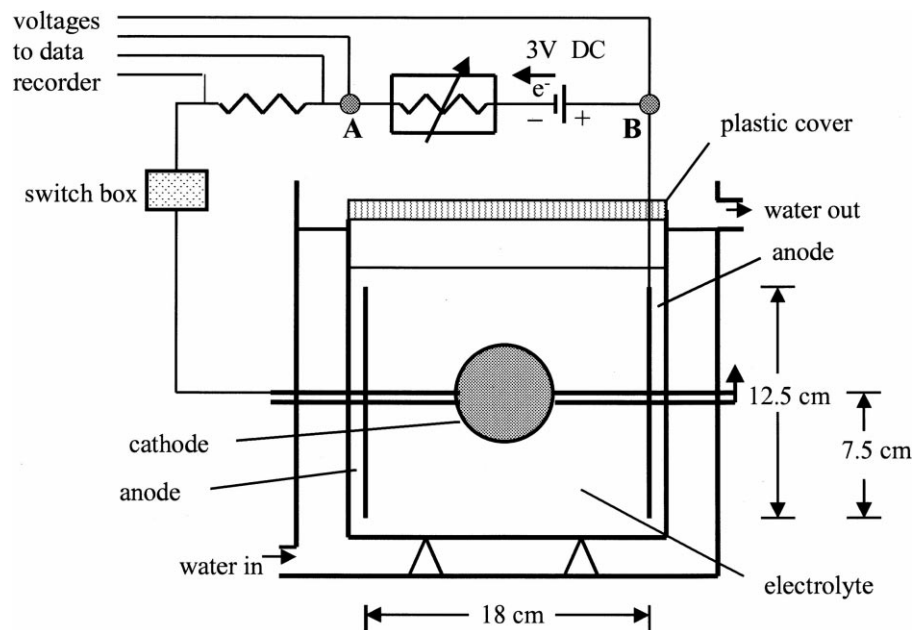


Fig. 2. Experimental set-up for mass-transfer measurements using the electrochemical technique.

contained the electrolyte. The outer vessel acted as a jacket for the inner one. Water at 30°C was pumped through the annular space between the walls and bottoms of the two concentric vessels as shown in Fig. 2. This was done to keep the electrolyte in the inner vessel at a constant temperature.

A variable DC power supply (Model D-612T, Electro Products, Chicago, IL) was used to provide the overpotential across the whole circuit between nodes A and B as shown in Fig. 2. The positive terminal of the power supply was connected to the anode. The anode was made of a copper cylinder coated with nickel. At the anode ferrocyanide ions were oxidized to give off one electron per ion and converted to ferricyanide ions. Those ferricyanide ions then diffused back to the electrolytic solution. The nickel layer on the anode stayed intact, i.e. there was no dissolution or passivation of the nickel layer. Therefore, nickel-plated or nickel electrodes have been widely used by many researchers in studying mass transfer with the ferri-ferrocyanide solution [10–13].

To ensure that the anodic reaction was not a limiting factor of the mass-transfer process, the surface area of the anode was much larger than that of the spherical cathode (about 20 times the cathode surface). The negative terminal was connected to a resistor of a known resistance, which was in turn connected to a selected segment of the spherical cathode via a switch box. The switch box allowed a selection of any of the segments on the sphere to be connected individually. The current, which went through a segment, was measured by means of the voltage drop across the resistor. For mass-transfer measurements, the applied voltage was set at 500 mV and the current was recorded once every second for 2000 s using a Champ II data acquisition system (Merlan Scientific, Georgetown, Ont., Canada).

In addition, an equimolar ferricyanide (cathodic reactant) and ferrocyanide (anodic reactant) solution is often used so that the ferricyanide ions consumed at the cathode (reduced to ferrocyanide ions) is completely replenished by the oxidation of ferrocyanide ions to ferricyanide ions at the anode. A typical composition of the electrolyte used in this study was 0.025 kmol m⁻³ potassium ferricyanide [K₃Fe(CN)₆], 0.025 kmol m⁻³ potassium ferrocyanide [K₄Fe(CN)₆], and 3.0 kmol m⁻³ sodium hydroxide [NaOH]. The sodium hydroxide was used to eliminate the ionic migration in the electrolyte [14]. Thus, mass transfer from the electrolyte to the spherical cathode was due to diffusion and/or convection.

The limiting current, i_L , can be written as

$$i_L = nFNA \quad (1)$$

where A is the transfer area, F the Faraday number, n the valency change of the cathodic reaction (one for this case), and N the molar flux of ferricyanide ions from the bulk solution to the cathode. The flux of ferricyanide ions can be expressed as

$$N = k_c(C_b - C_0) \quad (2)$$

where k_c is the mass-transfer coefficient, C_b the bulk concentration of ferricyanide, and C_0 the concentration of ferricyanide at the cathode surface that is approximately zero. The overall bulk concentration of ferricyanide is constant since the depletion of ferricyanide at the cathode is made up by the oxidation of ferrocyanide ions to ferricyanide ions at the anode.

From Eqs. (1) and (2), the mass-transfer coefficient (k_c) is

$$k_c = \frac{i_L}{nFAC_b} \quad (3)$$

Multiple anodes were also used in some experiments. Local mass-transfer rates at varied angular positions were measured using segment #1. For a single cylindrical anode as shown in Fig. 2, the mass-transfer rate to the segment oriented at 0° and 180° to the vertical was 18% lower than those at other orientations. However, when two additional anodes were installed above and below the sphere, the mass-transfer rate was relatively the same for all segment orientations. For the whole spherical cathode, additional anodes did not affect the mass-transfer rate significantly. For visual observation, one cylindrical anode was used throughout the present study.

To investigate the convective motion in the bulk electrolyte, a flow visualization experiment was carried out. Potassium permanganate (KMnSO_4) was used as a dye for a visual observation of the bulk motion of the electrolyte. The electrolyte had been kept in the vessel for 24 h before performing the flow visualization experiment. This was done to ensure that the electrolyte reached a preset temperature, and no residual movement existed due to the transfer of the electrolyte from a mixing container to the electrolytic vessel. Small pieces of potassium permanganate were pasted with silicone. When silicone was dried, it helped to keep the solid dye speck from sinking into the electrolyte. Thus, the dye dissolved slowly and moved with the bulk motion of the electrolyte.

A mirror was positioned at 45° to the horizontal in the electrolytic vessel. A video camera was set to face the electrolyte–air interface as shown in Fig. 3. Therefore, any vertical movement of the dye was projected onto the mirror and captured in a videotape. Photographs of the dye movement over a period were then obtained. The velocity of the dye, which was pulled along by the bulk motion of the electrolyte, was then determined. The distance, which the dye traveled over a known interval, was estimated using the following equation [15]:

$$Z = \left(\frac{P}{Q} \right) 150 \cos(45^\circ) \quad (4)$$

where Z is the actual distance traveled by the dye, P the distance swept by the dye image (projected on the mirror) in the photograph, and Q the length of the image of the mirror

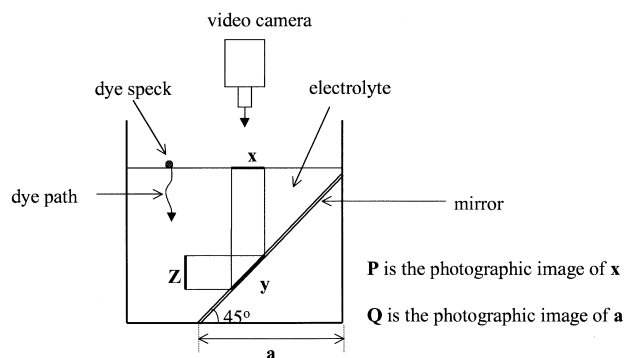


Fig. 3. Experimental set-up for flow visualization of natural convection in the electrolyte.

in the photograph. The constant in Eq. (4) is the actual length of the mirror of 150 mm. From Eq. (4) and the photographs of the dye movement, the velocity of the bulk motion of the electrolyte was determined.

3. Results and discussion

3.1. Evaluation of the experimental method

To determine an applied potential that was suitable to obtain the limiting current, a polarization curve was established. The current going through the cathode was measured at each applied potential that was reset to a new value at 3 min intervals. A smooth polarization curve was achieved as shown in Fig. 4. For applied potentials from 200 to 1000 mV, a stable limiting current was obtained. Therefore, the applied voltage of 500 mV was chosen for all experiments thereafter. The smooth polarization curve obtained also indicated that the limiting current measured by means of the voltage drop across a known resistor is satisfactory.

Once the appropriate applied voltage was determined, experiments with various ferricyanide concentrations from 0.01 to 0.03 M were carried out to evaluate the reproducibility of the experimental results. Equimolar concentrations of ferrocyanide were also used. When the concentration of ferricyanide was increased, the mass-transfer rate increased as expected. However, the mass-transfer coefficient (k_c) remained relatively constant. Thus, the corresponding Sherwood numbers did not change significantly with ferricyanide concentrations from 0.01 to 0.03 M as shown in Table 1. This indicated that the results obtained were reproducible.

In addition, these experiments were done to make sure that the whole surface of the spherical cathode was active evenly throughout. If the surface of the cathode were active unevenly, such as a dirty surface, the limiting current would not have changed proportionally with the concentration of ferricyanide; hence, the Sherwood number would have varied. When the concentration of ferricyanide was increased, the limiting current increased proportionally, and the mass-transfer coefficient remained constant. This indicated a uniformly active cathode.

Table 1
Effect of the concentration of potassium ferricyanide in a 3.0 M sodium hydroxide solution on mass transfer to a sphere at 30°C (with equimolar concentration of potassium ferrocyanide)^a

Run No.	Ferricyanide concentration (M)	Limiting current density (mA cm^{-2})	Sh
WH1	0.0092	0.093	109
WH2	0.0205	0.208	109
WH3	0.0281	0.290	110
WH4	0.0305	0.318	112

^a Diffusivity of ferricyanide in a 3.0 M sodium hydroxide solution at 30°C is $4.995 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ [19].

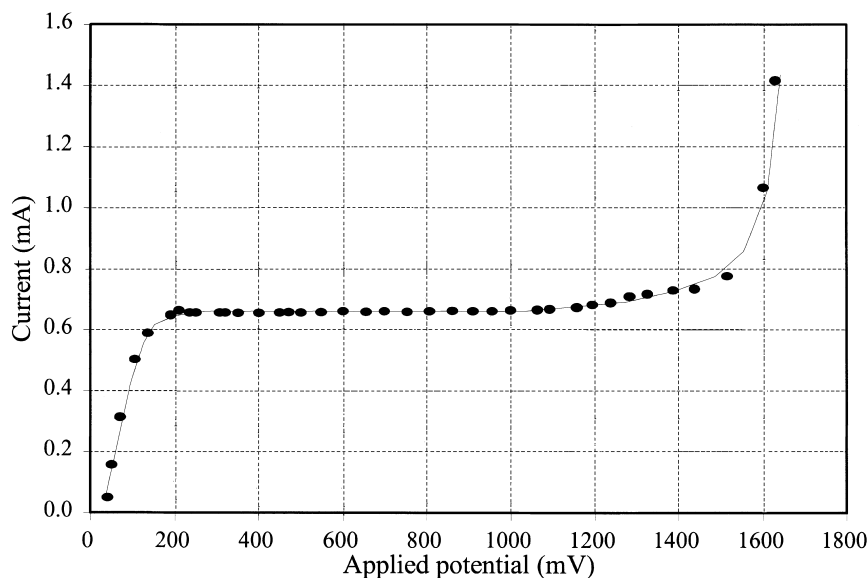


Fig. 4. A typical polarization curve for an electrolytic cell with 0.0092 M ferri-ferrocyanide in 3.0 M sodium hydroxide solution.

The electrolytic vessel was covered with a plastic lid as shown in Fig. 2. Natural convection of the electrolyte was observed visually. The plastic lid was then replaced by a styrofoam cover for a better thermal insulation. Natural convection, however, was present still. Thus, the experimental apparatus was then modified to have constant-temperature water at 30°C covering all around the electrolytic vessel. This was done so the temperature of the electrolyte would be uniform. The experiment was then carried out in the same way as before. The bulk motion in the electrolyte still existed. The average Sherwood number of 98 was obtained.

Despite all the attempts, the convective movement of the electrolyte remained. The average Sherwood numbers ranged from 96 to 110 for various apparatus configurations. The convective motion of the bulk electrolyte was confirmed visually by the movement of the dye obtained from the flow visualization experiment as typically shown in Fig. 5.

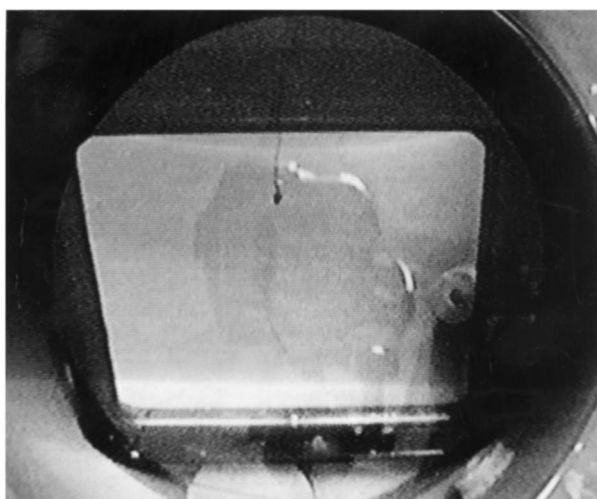
3.2. Effect of the convective motion of the bulk electrolyte on mass transfer to the sphere

The average Sherwood number obtained with the whole sphere ranged from 96 to 110. This was much higher than the limiting Sherwood number of two for pure diffusion to a sphere in a perfectly stagnant fluid. This indicated that the bulk motion existed in the quiescent electrolyte. In an investigation of mass transfer to a rotating sphere and a vibrating sphere using the same electrolyte, Noordsij and Rotte [7] obtained the Sherwood numbers of 60–70 with a still sphere (no rotation or vibration). It is noticed that the distance between the two electrodes used in Noordsij and Rotte's work [7] was about 4.5 radii of the spherical cathode. On the other hand, a distance of 2.5 radii of the spherical cathode was used in the present study. The distance

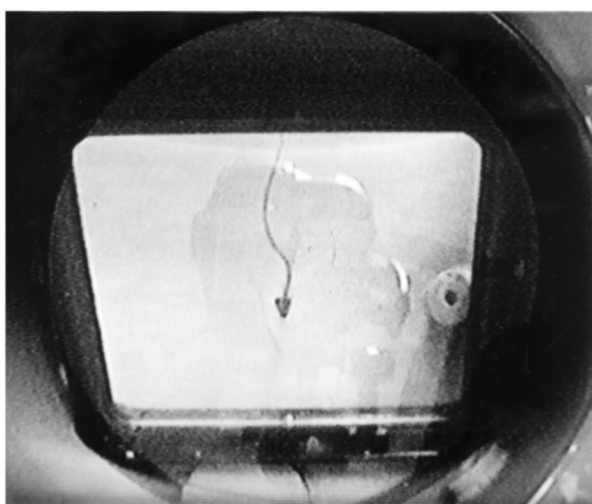
between the anode and the spherical cathode might have some influence on the mass-transfer rate to the sphere.

To assess the effect of the distance between the spherical cathode and the anode on the mass-transfer rate, a larger electrolytic vessel of a 61.0 cm (2 ft) diameter was built and used to run the experiment again. The distance between the anode and the cathode was 11 radii of the 5.0 cm spherical cathode. The Sherwood number obtained was about 120, which was slightly higher than that obtained previously with the smaller vessel. This indicated that there was no consistent trend of variation of the Sherwood number with the distance between the two electrodes in the electrolytic cell. It was actually more difficult to maintain a uniform liquid temperature in a larger vessel containing a quiescent liquid; hence, natural convection of the bulk electrolyte was slightly higher. However, the mass-transfer rate to the sphere did not change significantly with the distance between the two electrodes when this distance was increased from 2.5 to 11 radii of the spherical cathode. The difference between the Sherwood number obtained and that given by Noordsij and Rotte [7] might be due to different magnitudes of natural convection conditions in the bulk electrolyte for the two cases.

During the experiment, constant-temperature water at 30°C was pumped through the annular space of the double-walled vessel so the electrolyte in the vessel was kept at this temperature. However, the room air surrounding the experimental apparatus was at 25°C. The electrolytic compartment was covered with a 0.5 in. thick plastic lid. Water condensation on the lower side of the lid was observed indicating some water evaporation from the electrolytic solution. The temperature at the top section of the electrolyte was 0.3°C higher than that at the level of the sphere. Thermal-induced convection might thus exist in the bulk electrolyte. This caused the high Sherwood number observed.



At zero time



After 13.5 seconds

Fig. 5. Vertical movement of the potassium permanganate dye streak in the electrolyte.

Fig. 5 shows the image of the vertical movement of the dye projected on a mirror that appears as a square of a lighter background in the photographs. The dye path is the vertical dark blue streak on the lighter background of the mirror. From the image of the dye streak projected on the mirror over a period, the linear velocity of the dye streak, which was also the velocity of the convective current of the electrolyte, was estimated at 3.5 mm s^{-1} . The convective motion of the bulk electrolyte acted as a flow approaching the sphere. Thus, the mass transfer to the spherical cathode was in effect under a forced-convection condition. Therefore, the equation for forced-convection mass transfer to a sphere, given by Linton and Sutherland [16], was used to estimate the Sherwood number:

$$Sh = 2 + 0.582 \times Re^{1/2} \times Sc^{1/3} \quad (5)$$

Linton and Sutherland [16] used benzoic acid spheres in a water tunnel ($Sc=1200\text{--}1525$) to generate data for the correlation shown in Eq. (5). For forced-convection mass transfer from a dissolving sphere in liquid at low Reynolds numbers, the effect of natural convection on the overall mass-transfer rate might be significant. The ratio $[Gr/(Re^{1/2} \times Sc^{1/3})]$ proposed by Acrivos [17] is widely used to evaluate this effect. For the experimental conditions used by Linton and Sutherland [16], this ratio was less than 0.1 indicating that the transfer process was mainly by forced convection. In other words, the effect of natural convection on the overall mass transfer was negligible. Eq. (5) thus represents the convective mass transfer well and can be used to evaluate it in the present study.

For the electrolyte used in the present study, the Schmidt number was 2778. The fluid velocity traced from the photographs of the dye streak in Fig. 5 was 3.5 mm s^{-1} . At this velocity, Eq. (5) predicted a Sherwood number of 93 that was about 15% lower than the experimental Sherwood number. The dye streak moved in both vertical and lateral directions. The actual dye path might be longer than that observed in the photograph. Therefore, the actual fluid velocity might be larger than the value measured from the photograph; hence, the experimental Sherwood number was higher than the predicted value. When the fluid velocity was assumed to be 5 mm s^{-1} , the Sherwood number predicted from Eq. (5) was 112, which agreed well with the experimental value. The thermal-induced convective current in the quiescent electrolyte enhanced mass transfer to the sphere significantly. Consequently, the transfer process behaved as a forced-convection mass-transfer process. The Sherwood number could thus be predicted accurately from the equation for forced-convection mass transfer to a sphere given by Linton and Sutherland [16].

3.3. Transient mass-transfer analysis

From measurements of the current with time, instantaneous Sherwood numbers were normalized against the steady state value. These data are presented in Fig. 6. At the first moment after the start of the experiment, the transfer rate was very high since the concentration gradient was accordingly high. The rate then decreased as the concentration gradient dropped with time. Finally, the concentration gradient became stable. Thus, the transfer rate, hence, the Sherwood number became unchanged after 200 s. This indicated that the mass transfer from the electrolyte to the cathode was under a steady state condition after 200 s.

For a run performed immediately after a previous run, the Sherwood number approached a steady state value faster than that with the electrolyte at rest for 24 h as can be seen in Fig. 6. This was probably due to the residual concentration profile set by the previous run, which was not completely diminished after a short time.

Fluid velocities were estimated using the experimental Sherwood numbers at the steady state and Eq. (5). These

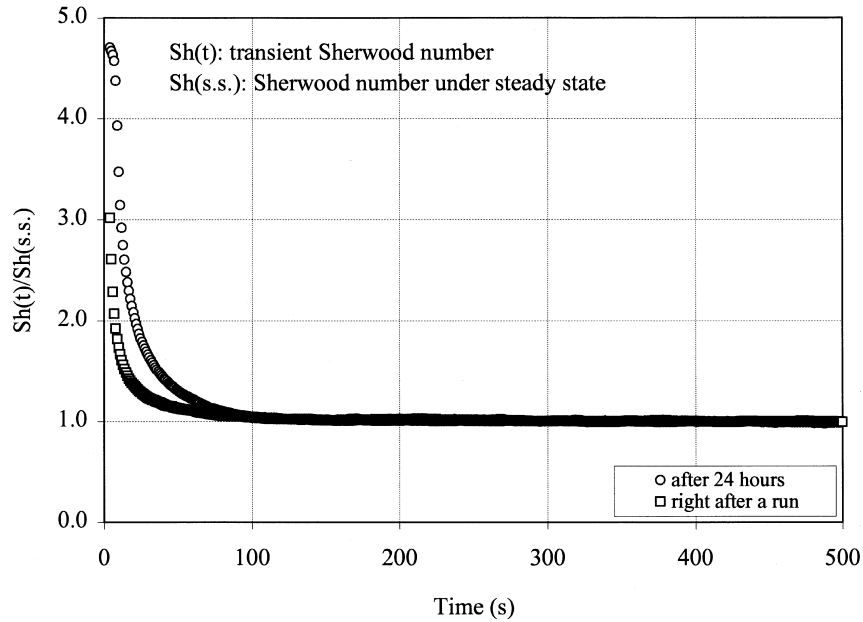


Fig. 6. Transient mass transfer to a sphere in the electrolyte.

velocities were used to calculate the dimensionless time that was defined as tu/d . The physical and transport properties and the Schmidt number are the same for all runs since the same electrolytic system was used. At a given time, the transfer rate is thus solely dependent on the fluid velocity. Therefore, the data for different fluid velocities should fall into the same trend with respect to the dimensionless time. For various fluid velocities, the plots of the normalized Sherwood number versus the dimensionless time indeed converge together as shown in Fig. 7, indicating a high consistency of the experimental data obtained. This also showed that the

mass-transfer process in this system approached the steady state at the dimensionless time of about 20.

It may be noticed that there was an anomalous increase of the Sherwood number at the beginning of the experiment (Fig. 7). The Sherwood number should have been highest at the start of the experiment. However, there was a delay in the system. The transfer rate was not at the highest value initially but increased for a few seconds before dropping. This might be due to a delay for the DC power supply to be fully charged after it was switched on at the start of the experiment. However, this period was less than 5% of the

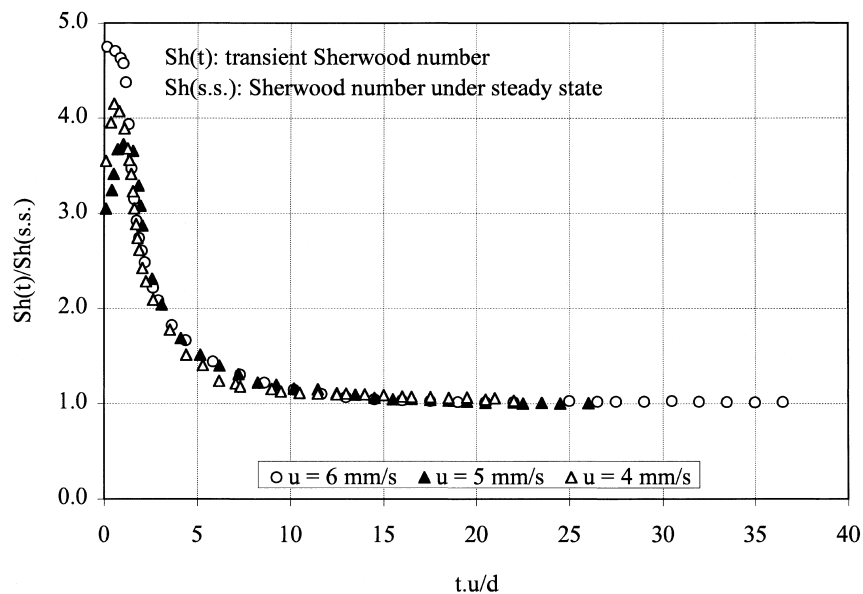


Fig. 7. Transient mass transfer to a sphere in the electrolyte versus dimensionless time for various fluid velocities.

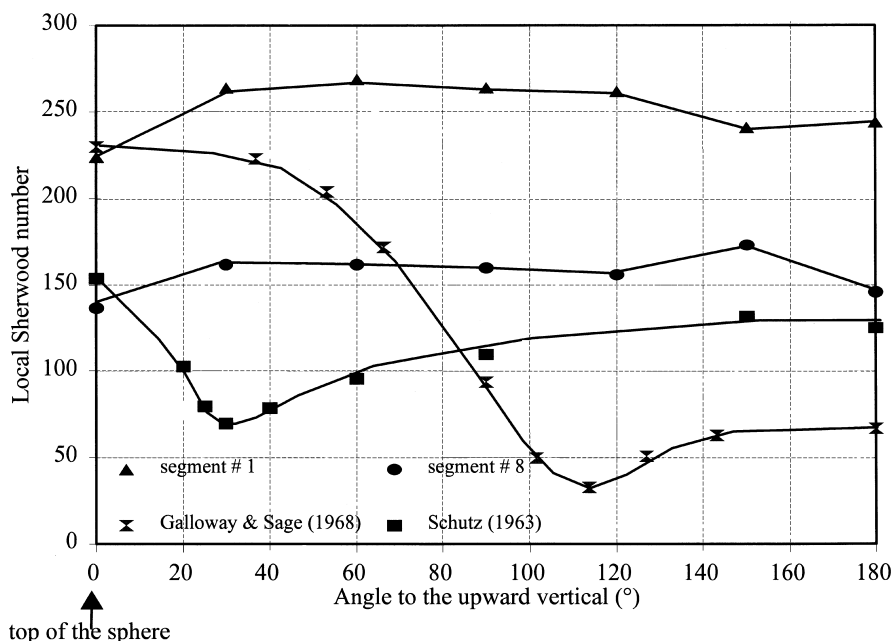


Fig. 8. Local mass transfer without the entire spherical surface activated and literature values for mass transfer over the whole sphere.

whole transient period. Thus, this imposed a negligible shift on the overall transient time. Also, this delay had no effect on the steady state value of the Sherwood number.

3.4. Local mass transfer to the sphere

The local Sherwood numbers obtained for segment #1 (2 mm diameter) and segment #8 (7.0 mm diameter) are plotted in Fig. 8 along with the local Sherwood numbers for convection mass transfer to a sphere, which were predicted from equations given by Galloway and Sage [18], and the data for natural-convection mass transfer to a sphere given by Schutz [6]. For segment #1 or segment #8, in the absence of mass transfer to the rest of the surface of the sphere surrounding the activated segment, the mass-transfer rate, hence, the Sherwood number was relatively constant at various angular positions to the upward vertical. On the other hand, for the case with mass transfer occurred over a whole sphere, the concentration boundary layer started to develop from the upper stagnation point (the top of the particle at 0° with respect to the upward vertical). The concentration boundary layer became thicker as it moved down the side of the sphere. Thus, the local Sherwood number decreased with increases in the angular position until a minimum value was reached. The Sherwood number then increased with further decreases in the angular position due to flow separation after the location of the minimum Sherwood number. This trend is presented by the curve of the local Sherwood numbers predicted from the correlations given by Galloway and Sage [18] as shown in Fig. 8.

The local Sherwood numbers given by Schutz [6] were obtained from experiments using copper deposition with the

whole spherical surface activated. For this case, the concentration boundary layer developed from the bottom of the sphere and moved upwards. This was in the opposite direction of that for the case with a dissolving sphere undergoing natural-convection mass transfer or forced-convection mass transfer with a flow approaching the top of the sphere (0° to the upward direction). The local Sherwood number given by Schutz [6] was thus higher at the bottom of the sphere and decreased in the upward direction as shown in Fig. 8.

The Sherwood number for segment #8 was substantially lower than that for segment #1 at all angular positions of the segment. The transfer area of segment #8 was larger than that of segment #1. Thus, the transfer rate to segment #8 was higher than that of segment #1 as reflected by a higher limiting current observed. However, the average mass flux to segment #8 was lower than that of segment #1 resulting in a lower Sherwood number. The concentration boundary layer started from the central region of the spot and moved outwards. The mass flux at the central region is thus higher than the adjacent region on the spot. The resultant average mass flux over the whole spot was thus smaller for a larger spot. Further increase in the surface of the segment would lead to further decrease in the Sherwood number. If the area of the spot was extended to cover the whole sphere, the Sherwood number would be decreased to that of the whole sphere ($Sh = 100\text{--}120$).

4. Conclusion

From experimental data obtained and analysis we conclude the following:

- The limiting current can be determined by measuring the voltage drop across a fixed resistor in series with the cathode (as shown in Fig. 2).
- Variation of the distance from the cathode to the anode from 2.5 to 11 radii of the spherical cathode did not affect the mass-transfer rate to the sphere significantly.
- The local Sherwood number for a spot of a 2 mm diameter, in the absence of mass transfer to the rest of the sphere, was about 2.5 times that for the whole spherical cathode of a 5 cm diameter.
- Under the effect of a thermal-induced convection in the bulk electrolyte. The Sherwood number for the whole spherical cathode was 110. This calls for some precaution in interpreting experimental data for mass transfer in a quiescent liquid or in a liquid flow at low Reynolds numbers since the thermal-induced natural convection is difficult to be eliminated and it can lead to a significant overestimation of the mass-transfer coefficient.
- The local mass-transfer rate to a spot on a sphere did not change significantly with the angular position of the spot when mass transfer did not exist over the rest of the sphere co-currently. This is in contrast to the local Sherwood number for the case with mass transfer occurred over the whole sphere simultaneously.
- Transient mass transfer to the sphere in the electrolyte was consistent for various fluid velocities. For a spherical cathode in the ferri–ferrocyanide solution, the transfer process approached steady state at the dimensionless time (tu/d) of about 20.

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