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SHORT COMMUNICATION

Mass transfer to a rotating horizontal cylinder electrode with full and partial immersion

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Nomenclature

d	cylinder diameter
D	diffusion coefficient
E	potential
I_l	limiting current
k	mass transfer coefficient
t	time
v	peripheral cylinder velocity
θ	angle (measured from the top of a cylinder)
ρ	density
ν	kinematic viscosity
Gr	Grashof number, $g\Delta\rho d^3/\nu^2\rho$
Re	Reynolds number, vd/ν
Sc	Schmidt number, ν/D
Sh	Sherwood number, kd/D

1. Introduction

A reactor with a rotating horizontal cylinder electrode has been used in the printing industry [1], in the production of metal sheets and foils [2], solid organic products [3], and metal powders [4, 5], but its characteristics have not been fully described in the literature. Some preliminary results of mass transfer investigations are presented in this paper, for a cylinder with both full and partial immersion in the electrolyte.

2. Experimental details

The investigations were performed on a laboratory reactor model with a carbon-paste working electrode which was conveniently formed into the desired profile and exhibited the properties of a metal electrode for the ferricyanide ion reduction reaction [3, 6, 7].

A Teflon cylinder (Fig. 1) fitted with the ring carbon-paste electrode (9 cm diameter, 1 cm length) and two electrically independent segment electrodes (1 cm in the rotation direction, 4 cm length), was placed in a 9000 cm^3 vessel. A cylindrically bent steel sheet positioned at a distance 10 cm from the working electrode was used as the counter-electrode, and a saturated calomel electrode (SCE) served as reference electrode. Measurements were performed by observing the cathodic reduction of ferricyanide ion in a solution of 1×10^{-2} mol dm^{-3} ferri- and ferro-cyanide in 0.5 mol dm^{-3} KOH. The value of the diffusion coefficient, $D = 0.732 \times 10^{-5}$ cm^2 s^{-1}, was taken from the literature [8]. Prior to each series of measurements, nitrogen was bubbled through the solution for about 10 h, while during the measurements it was introduced only into the space above the solution.

The current–potential relations were determined using a Metaloscan-Amel device at a potential change rate of 0.33–0.66 mV s^{-1}. The curves were recorded by means of an x–y recorder (Goerz-Electro). Due to considerable oscillations of the limiting current, the values used in the calculations were determined graphically as mean current values.

The degree of immersion was varied by

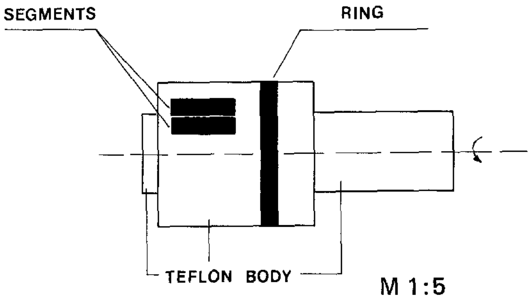

Fig. 1. The rotating horizontal cylinder electrode.

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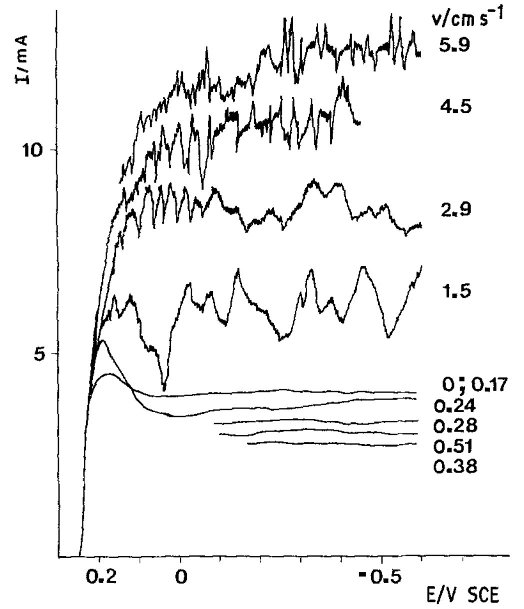

Fig. 2. The voltammetric curves of $Fe(CN)_6^{3-}$ reduction on the ring electrode at complete immersion.

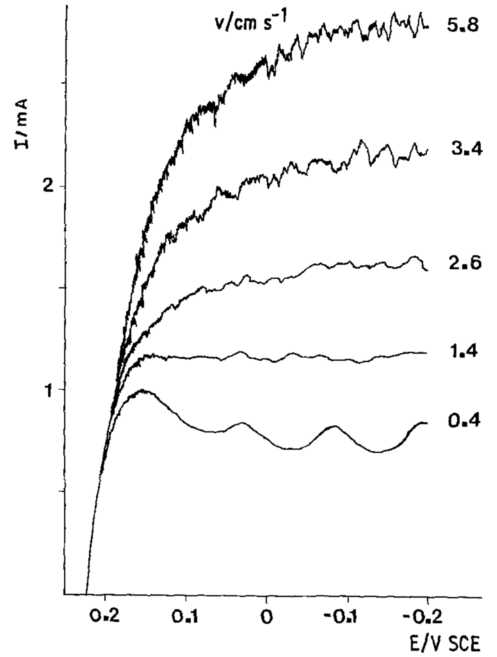

Fig. 3. The voltammetric curves of $Fe(CN)_6^{3-}$ reduction on the segment at complete immersion.

changing the solution level in the vessel. Measurements were taken at complete and partial immersion (2/3, 1/2, 1/3, 1/6) within the rotation rate range $v = 0\text{–}6\ \mathrm{cm\ s^{-1}}$ ($Re = 0\text{–}5300$).

3. Results and discussion

3.1. *Completely immersed cylinder*

Current–potential relations were recorded on the ring electrode and on one of the segment electrodes (Figs. 2 and 3).

It is observed that at lower rotation rates the ring current does not initially increase with an increase in rotation rate but that a drop of the current value occurs. Free convection, in a downward direction, is obviously the dominant convective mechanism at zero and low rotation rates. It is the interaction with the slow rotation-induced forced convection which produces the depression in the current values, the two forms of convection being partially co-directional and partially counter-directional. It is also noted that oscillations of the current value become greater with an increase of rotation rate. As with other systems (e.g. rotating vertical cylinder [9], fixed horizontal cylinder

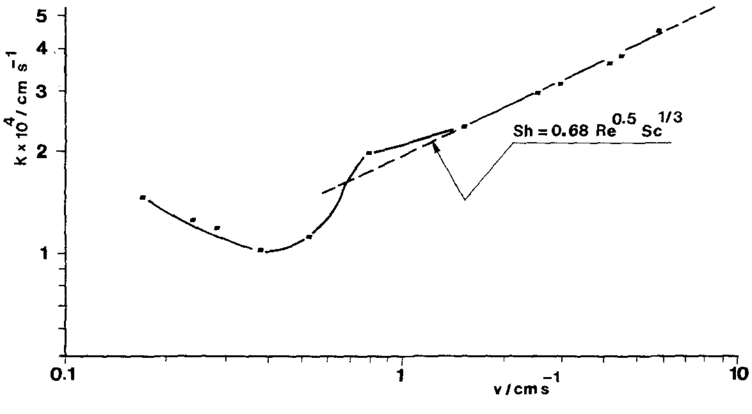

Fig. 4. Plot of mass transfer coefficient vs linear velocity for the completely immersed ring electrode.

[10], parallel-plate reactor with solution flow [11] and annular reactor [12]), the current oscillations observed on the limiting current plateau can be attributed to the occurrence of turbulence. As previously observed [13–15] with the rotating vertical cylinder the flow type tends to change rapidly ($Re > 200$) into the turbulent flow regime, which also seems to be the case with the rotating horizontal cylinder.

A change of the current value is also observed on the segment electrode, but on the lower curve ($v = 0.4\ \mathrm{cm\ s^{-1}}$) these oscillations were of a relatively regular shape (approximately sinusoidal) and are clearly due to the alternating relative direction of the forced and free convection. The oscillation pattern changes with an increase in rotation rate, assuming the form of frequent, irregular oscillations similar to those recorded on the ring electrode.

Results obtained on the ring electrode, presented in Fig. 4 as a plot of k against v, clearly indicate that the mass transfer rate decreases with an increase in rotation rate in the range up to approximately $v \approx 0.5\ \mathrm{cm\ s^{-1}}$, i.e. in the region of the combined convection. Only at higher rates, $v > 1\ \mathrm{cm\ s^{-1}}$, is the mass transfer rate dependent solely on forced convection.

On the basis of the results obtained, mass transfer to a completely immersed cylinder under the condition of forced convection can be described by the following relation:

$$Sh = 0.68 Re^{1/2} Sc^{1/3} \tag{1}$$

where $Sc^{1/3}$ was taken from literature.

For the case of natural convection on a completely immersed horizontal cylinder, the expressions of Acrivos [16] or Schütz [10] relation can be used:

$$Sh = 0.53(Gr \cdot Sc)^{1/4} \tag{2}$$

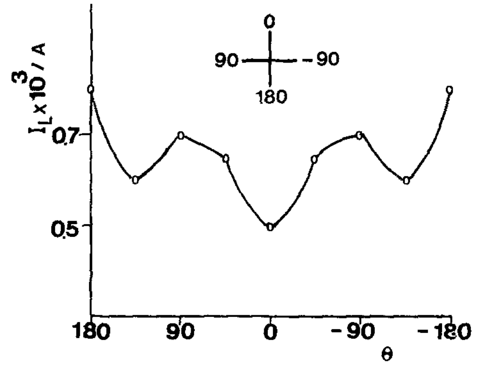

Fig. 5. Current density profile obtained with the segment electrode at different positions in free convection.

Studies of natural convection at horizontal cylinders have indicated that the local current values on the electrode are distributed symmetrically around the value obtained at the stagnation point of the cylinder [16, 17]. Similar behaviour was observed in experiments with the segment electrode (Fig. 5).

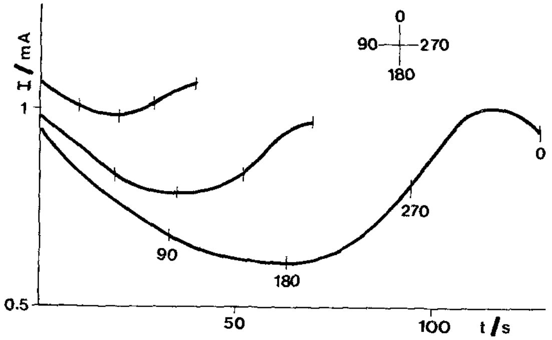

Fig. 6. Sinusoidal behaviour of current on the segment electrode at different rotation rates of the cylinder. Current vs time per one full circle.

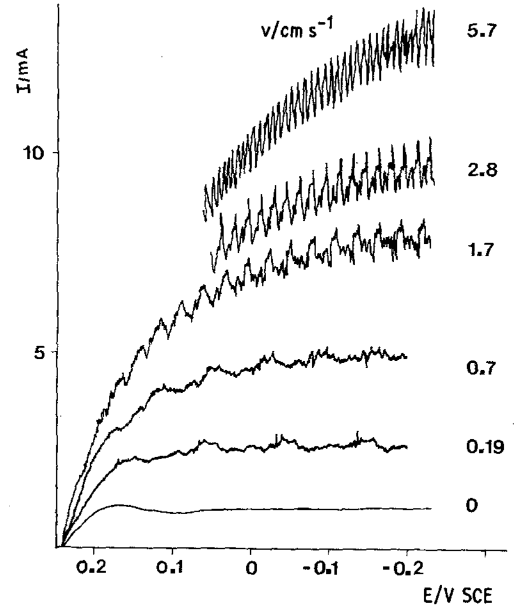

Fig. 7. The voltammetric curves of $Fe(CN)_6^{3-}$ reduction on the ring electrode at 1/6 immersion.

At very low rotation rates (Fig. 6) 'sine curves' of I against t were obtained at the limiting current plateau potential with the segment electrode. This

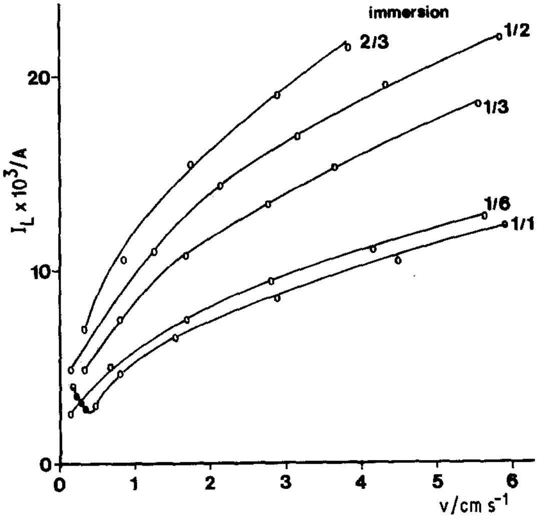

Fig. 8. Dependence of I_l on v for the ring electrode at different degrees of immersion.

is attributed to the interaction of natural and forced convection [18] but a theoretical treatment of this complex situation has not yet been achieved.

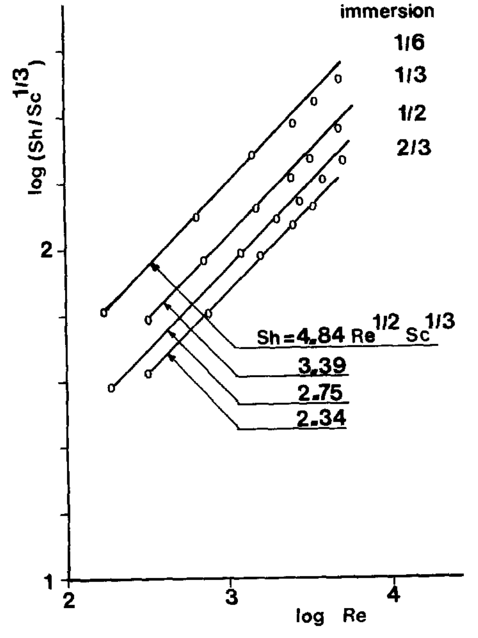

Fig. 9. Dependence of log ($Sh/Sc^{1/3}$) on log (Re) for the ring electrode at different degrees of immersion.

3.2. *Partially immersed cylinder*

Data obtained from the 2/3, 1/2, 1/3 and 1/6 immersed ring electrodes also showed oscillations of the current value. A representative current–potential plot for 1/6 immersion is given in Fig. 7. Results obtained, presented by a plot of I vs v (Fig. 8), indicate that the currents obtained are higher than for the case of the completely immersed cylinder.

If the limiting current density is calculated on the basis of the immersed part of the electrode only, data presented here as a plot of log ($Sh/Sc^{1/3}$) vs log Re (Fig. 9) shows that the limiting current density increases when the degree of immersion is diminished.

However, it must be noted that it is likely that a part of the non-immersed section of the electrode is electrochemically active due to electrolyte film pick-up. Further work is necessary to clarify this point.

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