Enhancement of electrolytic mass transfer around spheres by applying static magnetic fields

ENHANCEMENT OF ELECTROLYTIC MASS TRANSFER AROUND SPHERES BY APPLYING STATIC MAGNETIC FIELDS

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Key Words: Electrolysis, Mass Transfer Coefficient, Dimensionless Correlation, Natural Convection, Magnetic Field, MHD Flow, Spherical Cathode

The effect of applying a static magnetic field on mass transfer rate in diffusion-controlled electroreduction was studied experimentally around single spheres of diameters 8 to 14 mm under the condition of laminar natural convection. The electrolytic solution of the system $K_3Fe(CN)_6$–$K_4Fe(CN)_6$ with a supporting electrolyte was employed and the magnetic field was applied to the cathode in the horizontal or vertical direction and up to 336 mT in flux density.

By applying the magnetic field in every direction, the mass transfer rate was enhanced more than 50 % at the highest magnetic flux density, compared to the simple natural convection case. From the obtained data of mass transfer coefficients, dimensionless regression equations for each direction of the applied magnetic field were derived where the magneto-diffusion factor was introduced so as to express the contribution of the applied magnetic flux density.

Introduction

Early advances in investigations on chemical reactions in magnetic field were reviewed by Steiner and Ulrich[16] and Tanimoto[17].

The MHD flow induced by a magnetic field is well known to enhance or depress electrochemical reaction rates, depending on the direction of the applied magnetic flux[6]. This phenomenon can be explained by the fact that interference between the developments of hydrodynamic boundary layer and the MHD flow depends on the direction of the MHD force (*i.e.*, Lorentz force). Recently the maximum likelihood method was applied by Fahidy[4] to data regression of the mass transfer enhancement due to the MHD effect in magnetoelectrolysis but no recommendable correlation equation was determined.

Although electrode geometries such as a cylinder or sphere are more useful and practical from an industrial viewpoint, a number of studies on magnetoelectrolysis have been concentrated for electrolytic mass transfer only around a vertical flat plate or rotating disc electrode.

On the other hand, the MHD effect on flow pattern around electrodes with various geometries has been dealt with by many investigators[8-10, 14]. However, the MHD flow has rarely been analyzed quantitatively to date[13].

Most recently, electrolytic mass transfer around an inclined cylindrical cathode in the static magnetic field in the horizontal or vertical direction was studied experimentally for a $K_3Fe(CN)_6$–$K_4Fe(CN)_6$ system with supporting electrolyte[12]. The obtained mass transfer coefficient was correlated well by using a new dimensionless parameter, the "magneto-diffusion factor," to account for the effect of magnetic flux density.

In the present paper, mass transfer around a spherical cathode in diffusion-controlled magnetoelectrolysis is investigated experimentally and the experimental data of the mass transfer coefficient are correlated to obtain a dimensionless regression equation by using the magneto-diffusion factor.

1. Experimental Procedure

By using the limiting current technique, experiments were performed in a manner similar to that in the previous study[12] for the following electrolytic reduction with a supporting electrolyte:

$$Fe(CN)_6^{3-} + e^- \rightarrow Fe(CN)_6^{4-}$$

The mass transfer rate for a spherical cathode was measured.

An electrolytic cell with inside dimensions of 50 mm cube made of acrylic resin plate was used in the experiments and a brass sphere plated with platinum was located in the center of the cell as the working electrode. The sphere was 8.0, 10.0 or 14.0 mm in diameter. Every brass sphere was manufactured to a diameter precision of 20 μm and its surface was polished by lapping with fine abrasive compound. The spheres thus obtained had surface roughnesses of about 0.1 μm and sphericity of less than 40 μm. The anode, in the shape of a short square duct and 45 mm square × 45 mm long, was made of thin platinum plate and set so as to surround the cathode sphere.

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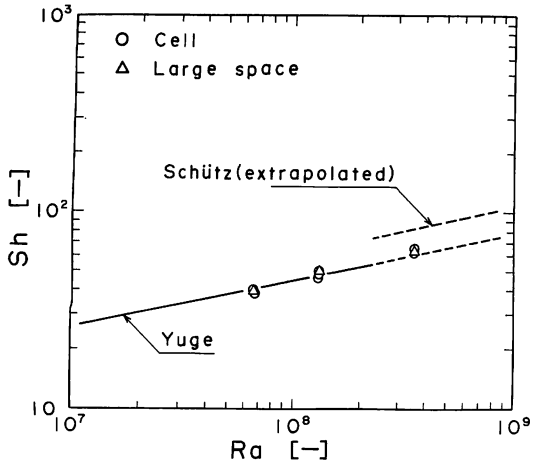

Fig. 1 Comparison of mass transfer coefficient observed for a case of natural convection to previous work

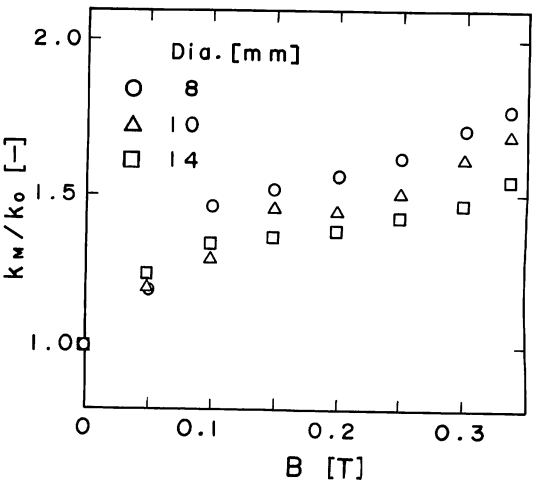

Fig. 2 Enhancement of mass transfer coefficient with magnetic flux density (Horizontal magnetic field)

A static magnetic field was applied to the cell in the horizontal or vertical direction. The density of the applied magnetic flux was varied up to 336 mT by adjusting the electric current charged to an electromagnet. In the central region of the gap space of size 50 mm square and 60 mm wide between the magnet poles, at least 45 mm cube, the magnetic field was confirmed to be uniform within a few percent deviation by using a gaussmeter.

To evaluate the mass transfer rate, the limiting current was measured by a potentiostat at 0.3 V cell voltage which brought a diffusion-controlled condition under any magnitude of magnetic flux density for every cathode.

The prepared electrolyte was 0.15 M equimolar aqueous solution of $K_3Fe(CN)_6$ and $K_4Fe(CN)_6$ with 1.0 M NaOH.

To avoid thermal disturbance caused by heat generation in the coil, an electric fan was employed to cool both magnet coil and cell and the room temperature was kept constant at 23.0 ± 0.2 °C, by an air-conditioning system. The temperature of the electrolyte solution was monitored by a calibrated thermocouple.

After the charged electrolyte solution was confirmed to be stationary and at constant temperature, specified voltage was applied to the cell. First, a limiting current in free convection was recorded at steady state by an autograph recorder. Then, the magnetic field was applied at a specified flux density and the steady limiting current was measured. Finally, the magnetic field was switched off and the resulting value of limiting current was re-confirmed to be the same as the initial one for simple free convection. This procedure was repeated for different values of magnetic flux density.

The mass transfer coefficient was calculated from a well-known relation, Eq. (1), based on the measured limiting current.

$$k = \frac{I}{zAFC} \tag{1}$$

The enhancement of mass transfer rate was evaluated as

$$k_M / k_0 = I_M / I_0 \tag{2}$$

where the subscripts M and 0 imply values with and without the magnetic field, respectively.

2. Results and Discussion

To ensure that the situation for a spherical cathode in the cell is similar to that in an infinite space, several experiments were carried out preliminarily to examine the effect of cell size without magnetic field. The mass transfer coefficient obtained in the cell and that in a one liter beaker are compared in **Fig. 1** with the following empirical correlations: the first, Eq. (3), for free convection mass transfer around a sphere given by Schuetz[15] for electrodeposition of copper; and the second, Eq. (4), derived analogously from that obtained by Yuge[18] for heat transfer from sphere to air.

$$Sh = 2 + 0.59\, Ra^{1/4} \qquad (2.3 \times 10^8 < Ra < 1.5 \times 10^{10}) \tag{3}$$

$$Sh = 2 + 0.392\, Gr^{1/4} \qquad (1 < Gr < 10^5) \tag{4}$$

(or modified to give $Sh = 2 + 0.427\, Ra^{1/4}$)

Since no appreciable differences between the data obtained for the cell and the beaker are observed in Fig. 1, the effect of the cell size is found to be negligible, at least under simple free convection. The present data are in good agreement with the analogous equation of Yuge's and about 20% smaller than the extrapolation of Schuetz's equation, Eq. (3). In the low Ra region, Schuetz's experimental results might include the influence of induced recirculation flow.

2.1 Horizontal magnetic field

The dimensionless mass transfer coefficient, k_M/k_0, is plotted against the magnetic flux density, B, at different

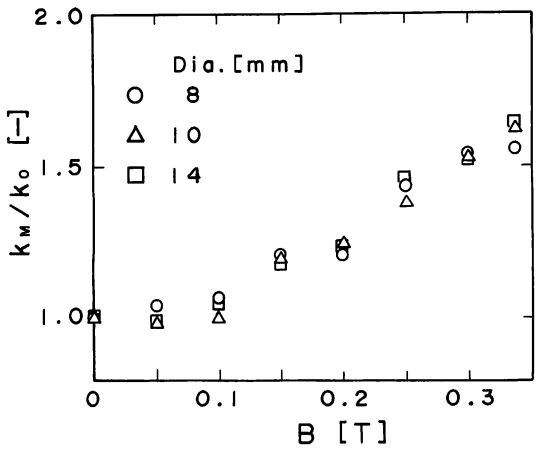

Fig. 3 Enhancement of mass transfer coefficient with magnetic flux density (Vertical magnetic field)

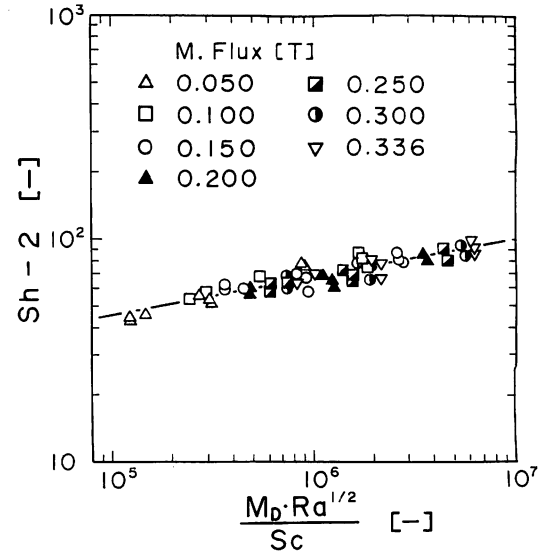

Fig. 4 Correlation of mass transfer coefficient for horizontal magnetic field

diameters of the spherical cathodes, $d = 8.0$, 10.0 and 14.0 mm (**Fig. 2**). This figure shows that k_M/k_0 increases rapidly with B below 100 mT and in the region of higher B, the dependency becomes rather weak. This non-linear dependency on magnetic flux density is similar to previous studies[1-5, 7, 11], though the dependency of k_M/k_0 tends to increase again with B beyond about 250 mT. In addition, k_M/k_0 becomes gradually larger with a decrease in sphere diameter.

2.2 Vertical magnetic field

Figure 3 shows enhancement of the mass transfer coefficient obtained in the vertical magnetic field against the magnetic flux density with the parameter of the sphere diameter.

The tendency of these results for the vertical magnetic field is considerably different from those for the horizontal one. Application of the vertical magnetic flux has almost no enhancing effect on mass transfer rate up to 100 mT and, with a further increase in B, k_M/k_0 increases up to an extent similar to those for the horizontal magnetic field case. There is, however, no appreciable dependency on the sphere diameter, different from the case for the horizontal magnetic field.

The discrepancy between the dependencies of k_M/k_0 on the sphere diameter due to the directions of the applied magnetic fields can be explained qualitatively as follows. In the horizontal magnetic field case, the MHD flow is induced peripherally around the sphere in the vertical plane. This flow interacts with the development of natural convection caused by the body force due to the density difference. Such an interacting MHD flow becomes intenser and consequently the enhancement of the mass transfer becomes larger with a decrease in sphere diameter because generally the current density on the sphere surface due to natural convection increases as the diameter decreases. On the contrary, in the vertical magnetic field case, the induced MHD flow is in the horizontal plane and this flow would be independent of the development of natural convection in the vertical direction as far as the MHD flow is not so intense as to predominate the entire flow field. The mass transfer due to rotational flow induced by the vertical magnetic field does not depend appreciably on the sphere diameter because the diffusion layer due to the MHD flow develops not peripherally but radially and its thickness is very thin in comparison with the sphere diameter.

2.3 Correlation of experimental data

1) Dimensionless parameters for data regression According to the discussion in the previous study[12] on the parameters to be employed for the data regression of mass transfer coefficient obtained, based on the normalization of the relevant governing equations, the following expression is used in the present work:

$$Sh = 2 + \alpha\left(\frac{M_D\, Ra^{1/2}}{Sc}\right)^{\beta} \tag{5}$$

where, M_D, designated as "magneto-diffusion factor," is introduced instead of the Hartmann number. Since the present experimental situation is under diffusion-control, the Hartmann number is inadequate for correlating the data.

2) Correlation of data for horizontal magnetic field The data of mass transfer coefficients in horizontal magnetic field are plotted in **Fig. 4** at different magnetic flux densities to correlate them in the expression, Eq. (5). The least squares method was applied to determine the coefficient and exponent as follows:

$$Sh = 2 + 6.4\left(\frac{M_D\, Ra^{1/2}}{Sc}\right)^{0.17} \tag{6}$$

$$\text{for } 3.40 \times 10^4 \leqq M_D \leqq 7.36 \times 10^5,$$

$$\text{and } 6.70 \times 10^7 \leqq Ra \leqq 3.62 \times 10^8$$

Equation (6) is given in Fig. 4 and is found to represent well the experimental data within an error of ±15 %.

3) Correlation of data for vertical magnetic field Similar to the case of horizontal magnetic field, the regression equation Eq. (5) was fitted to the experimental data of the mass

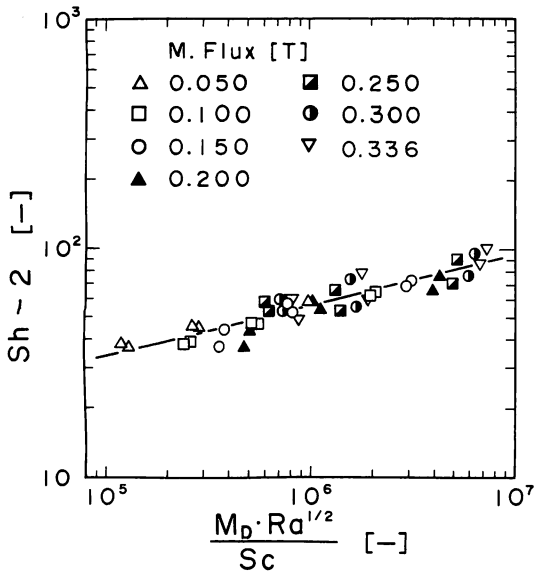

Fig. 5 Correlation of mass transfer coefficient for vertical magnetic field

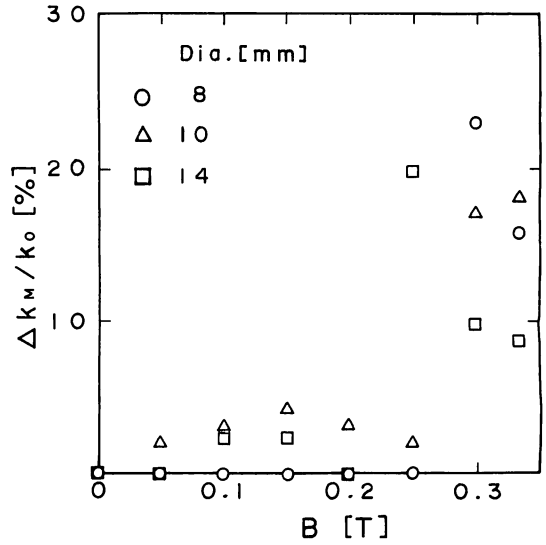

Fig. 6 Change in fluctuation of mass transfer coefficient with magnetic flux density (Vertical magnetic field)

transfer coefficient in **Fig. 5** to give Eq. (7) with the coefficient of correlation, 0.917.

$$Sh = 2 + 2.7\left(\frac{M_D Ra^{1/2}}{Sc}\right)^{0.22} \quad (7)$$

$$\text{for } 3.43 \times 10^4 \leqq M_D \leqq 7.62 \times 10^5,$$

$$\text{and } 6.80 \times 10^7 \leqq Ra \leqq 3.60 \times 10^8,$$

The straight solid line in Fig. 5 represents Eq. (7). The equation is shown to be a good expression of the experimental data with a scattering of ±20 %. Clustering around this regression line is rather loose in comparison with that for the horizontal magnetic field case. This tendency is similar to that for the inclined cylinder[12].

As pointed out in the preceding section, in the vertical magnetic field case, scattering of the data around the correlation equations is somewhat large in comparison with that in the horizontal magnetic field case. To discuss this difference between clusterings of the data for two cases, the time fluctuation in the mass transfer coefficient is examined in detail in the next section.

4) Fluctuation of mass transfer coefficient Though the mass transfer coefficient shown above as the *Sh* number was calculated from time-averaged values of the limiting current, appreciable fluctuation in its recorded curve was observed occasionally. The maximum value of the fluctuation with lapse of time from the time-averaged mass transfer coefficient was measured relatively based on the mass transfer coefficient for the simple free convection. The obtained data for the case of the vertical magnetic field are plotted against the applied magnetic flux density in **Fig. 6.** The fluctuation is at most 4 % up to 200 mT but increases abruptly in the higher region of the magnetic flux density, depending on the sphere diameter. This result suggests that induced MHD flow and natural convection due to gravity force do not influence each other in the region of low magnetic flux density because of perpendicularly intersecting directions of both flows and that in the region of higher magnetic flux density the intensely induced MHD flow causes an interaction and unstable turbulence in both flows.

For the case of the horizontal magnetic field, it was found that the maximum fluctuation is at most 4 %, even for the highest magnetic flux density and that the relative fluctuation tends to decrease with a decrease in the sphere diameter.

Conclusions

The mass transfer rate around a sphere in a static magnetic field in the horizontal or vertical directions was studied experimentally by using the limiting current technique for a $K_3Fe(CN)_6$–$K_4Fe(CN)_6$ system with supporting electrolyte, NaOH. The experiments were performed for a spherical cathode of 8, 10 or 14 mm diameter for magnetic flux densities up to 336 mT.

The mass transfer rate was found to be promoted more than 50% by applying the magnetic field in every direction, compared with that for the original natural convection case. The mass transfer coefficient data obtained were correlated to give the dimensionless regression equations Eqs. (6) and (7) by using the magneto-diffusion factor so as to account for the applied magnetic flux density. Very good clustering of the present data around the regression equations is observed, showing the usefulness of the magneto-diffusion factor.

In the present study, a general equation that accounts for the applied direction of the magnetic field has not been established. Further research is required to clarify the configuration effect on the magnetoelectrolysis.

Acknowledgments

The authors wish to express their deep gratitude to Prof. Y. Tanimoto,

Hiroshima University, for valuable discussions and to Messrs. A. Ueda, T. Sasai and K. Sawamoto for their assistance in the experiments and the data processing.

The electromagnet employed in the present experiments was provided by the Laboratory of Magnetic Field Control and Applications, Kanazawa University.

Nomenclature

A	=	surface area	[m^2]
B	=	magnetic flux density	[T]
C	=	bulk concentration of ion	[mol/m^3]
ΔC	=	concentration difference between bulk solution and electrode interface	[mol/m^3]
D	=	diffusion coefficient	[m^2/s]
d	=	diameter of spherical cathode	[m]
F	=	Faraday constant	[C/eq.]
g	=	gravity acceleration	[m/s^2]
Gr	=	Grashof number, defined as $g\zeta\Delta Cd^3/\nu^2$	[-]
I	=	limiting current	[A]
k	=	mass transfer coefficient	[m/s]
M_D	=	magneto-diffusion factor, defined as $zFB\Delta Cd^2/(\rho\nu)$	[-]
Ra	=	Rayleigh number, defined as $GrSc$	[-]
Sc	=	Schmidt number, defined as ν/D	[-]
Sh	=	Sherwood number, defined as kd/D	[-]
z	=	valency of ion	[eq./mol]
ζ	=	densification factor	[m^3/ mol]
ν	=	kinematic viscosity	[m^2/s]
ρ	=	density	[kg/m^3]

<Subscripts>

M	=	with magnetic field
0	=	without magnetic field

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