Magnetic Field Effect on Electron Transfer Process in Electrochemical Reaction(Crystal Growth, Chemical Reaction and Biology)

Magnetic Field Effect on Electron Transfer Process in Electrochemical Reaction*

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Synopsis

A new method with MHD electrode (MHDE) to analyze the electrochemical reaction under the magnetic field is applied to the copper reduction. The Tafel plots obtained at the magnetic field up to 13T show that there is no change in the slopes but drastic decrease of the current density in comparison with the results in the no or low magnetic field.

I. Introduction

Magnetic field effects on living organisms, especially on biochemical reactions have been the subject of many studies in recent years.However, the phenomena themselves have been not fully investigated. The reason can be partly attributed to the complexity of the biochemical reactions and the difficulty of reproducibility in the experiments. We, therefore, paid attention to simpler reactions, i.e., electrochemical reactions, which also play important role in the field of biochemistry. In an electrochemical system, externally applied magnetic field yields a solution flow induced by Lorentz force to enhance the mass transfer process, which is well known as the magnetohydrodynamic (MHD) effect [1-3]. On detecting the effect on the electron transfer processes, a difficult problem is revealed that the MHD effect is inevitable in electrode reaction under external magnetic field. Therefore, even if we observe some magnetic field effect on electrolytic current, it can not directly be identified with the effect on the electron transfer processes. At least, one part is attributable to the change in the diffusion process, i.e., the MHD effect. So far as such effect is not removed, pure magnetic field effect on the electron transfer process can not be detected. In stead of suppressing the MHD effect, we rather attempted to positively employ it for separating only electron transfer process from overall reaction.

In this study, with the electrodes using the MHD effect (MHDE), the electron transfer process in copper reduction in the magnetic field was examined.

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Ⅱ Theoretical

Figure 1 shows a MHDE cell, which is made of a channel with two open ends. A pair of plane copper electrodes, working and counter electrodes, are embedded face to face on the top and bottom inner walls, respectively. To regulate the potential of the working electrode, a Luggin capirally is inserted from behind of the electrode through a drilled small hole, conjugating the tip position with the electrode surface. Inside the channel, electrolytic current flows vertically to the magnetic field. Whole cell system is immersed in a large volume of 1.0M H_2SO_4 containing a given amount of $CuSO_4$.

Then, the solution starts to move by the induced electromagnetic force, entering the inlet of the channel and leaving from the outlet. Inside the channel, the movement is retarded by the friction of the inner walls, so that hydrodynamic boundary layers develop along the electrode surfaces. Figure 2 schematically represents the boundary layer flow.

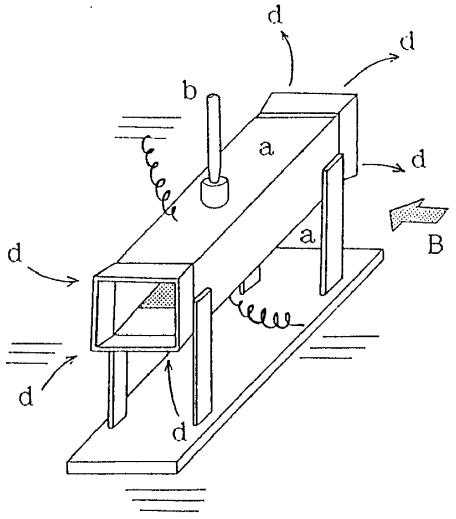

Fig.1 Electrode cell configration

a: working and counter electrodes
b: Luggin capillary
d: streamline
B: magnetic flux density

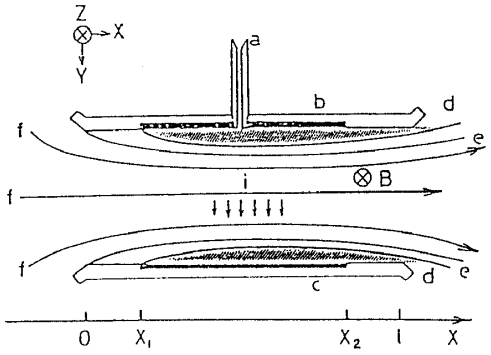

Fig.2 Boundary layer and resulting diffusion layer formed inside the channel

a: Luggin capillary
b: working electrode
c: counter electrode
d: diffusion layer
e: boundary
f: streamline

As explained in the previous papers [1-4], the diffusion current in this case is given as

$$\bar{i} = H^* (C_0 - C_s)^{4/3} B^{1/3} \qquad (1)$$

where

$$H^* = 0.753(nFD)^{4/3}(\nu/D)^{4/9}\nu^{-2/3}\rho^{-1/3} \gamma^{1/3} (\sqrt{X_2} - \sqrt{X_1})^{4/3} (X_2 - X_1)^{-1} \qquad (2)$$

Here, $\bar{i}$ the average current density, B the external magnetic flux density, and X_1 and X_2 are the x-coordinates of the upstream and downstream edges of the working electrode, respectively. Then, C_0 the bulk concentration, C_s the surface concentration, n the electron number participating the reaction, F Faraday constant, D the diffusion coefficient, ν the kinematic viscosity, the ρ solution density, and r is the cell constant.
For the limiting case of Eq.(1)

$$\bar{i}_L = H^* C_0^{4/3} B^{1/3} \qquad (3)$$

is introduced. From Eqs.(1) and (3), it follows that

$$\bar{i} / \bar{i}_L = \{(C_0 - C_s)/C_0\}^{4/3} \qquad (4)$$

If the electron transfer processes can be apparently regarded as the first order reaction concerning the surface concentration of the reactant, the average reaction current density is given, as follows,

$$\bar{i} = nFkC_s \qquad (5)$$

where k is the reaction rate constant reflecting overall reaction.
For cathodic reaction

$$k = k_0 \exp(-\alpha_c \Delta\Phi F/RT) \qquad (6)$$

and for anodic reaction,

$$k = k_0 \exp(-\alpha_a \Delta\Phi F/RT) \qquad (7)$$

where α_c and α_a are the transfer coefficients of cathodic and anodic reactions, respectively. Here, T the absolute temperature, R gas constant, $\Delta\Phi$ is the activation overpotential, and k is the reaction rate constant at equilibrium potential ($\Delta\Phi = 0$). Then, from Eqs. (4) and (5),

$$\bar{i} = nFkC_0\{1-(\bar{i}/\bar{i}_L)^{4/3}\} \qquad (8)$$

is obtained, defining

$$\bar{i} = nFkC_0, \qquad (9)$$

where $\bar{i}_k$ represents the reaction current in the absence of any mass transfer effects.

Substituting Eqs. (3) and (9) into Eq. (8), the following relationship between the current density and the magnetic flux density is derived.

$$1/\bar{i}-1/\bar{i}_k = 1/\{H^{*4/3}C_0(B\bar{i})^{1/4}\} \qquad (10)$$

In order to measure the reaction current density , we must, at first, plot $1/\bar{i}$ against $1/(B\bar{i})^{1/4}$ in terms of the experimental data of i's at various given magnetic flux densities, B's, then extrapolate the linear plot to the intercept of the ordinate, which gives the value of $1/\bar{i}_k$ at the activation overpotential of $\Delta\Phi$.

Ⅲ. Experimental

Two kinds of MHDE were used. One was a lower magnetic field type corresponding to an iron-core electromagnet up to 0.9T, of which the core was set horizontally, and another was a higher magnetic field type corresponding to a high-power water-cooled magnet up to 15T. The core of this magnet was set vertically.

Figure 1 depicts the lower magnetic field type. In the higher magnetic field type MHDE, working and counter electrodes are set on the each side wall instead of the top and bottom walls. Both copper electrods were 1 × 2cm in surface area, and the channel height was 0.5cm.

The electrolytic current in steady state was measured under potentiostatic conditions. Because the overall reaction of copper is known as the first order, according to Eq.(10), the average reaction current density was obtained from the extrapolation of the magnetic flux density to infinity. Then, the Tafel plots for copper reduction in the magnetic field were made.

Finally, the plots were compared with the data measured by the chronopotentiometry using the same MHDE cell as in the above experiments in the absence of the magnetic field. Farthermore, to confirm the magnetic field effect, we also carried out the hydrodynamic voltammetry with rotating disc electrode in the absence of the magnetic field.

Ⅳ. Results and Discussion

As shown in Fig.3, in the case of mass transfer control, the current density proportionally increases with 1/3 order of the magnetic flux density according to Eq.(1).

In the case of mixed control of mass and electron transfers, as expected from Eq.(10), the current density follows the linear plot of $1/\bar{i}$ versus $1/(B\bar{i})^{1/4}$ in Figs.4 and 5.

Figures 4 and 5 show the plots corresponding to the lower and higher magnetic fields.

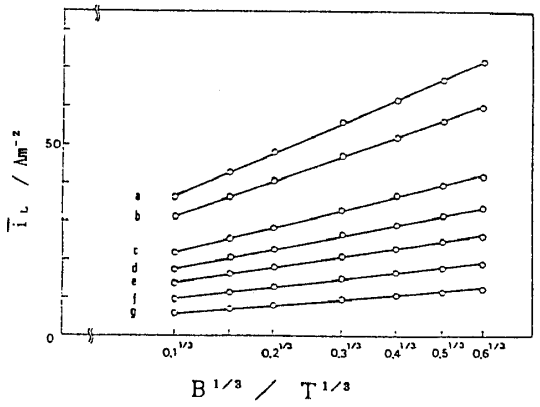

Fig.3 Dependence of the average limiting current density on the magnetic flux density. Electrodeposition of copper on the copper electrode

a : C_o =7.6 x 10 mol/m³, b : C_o =6.8 x 10 mol/m³,
c : C_o =5.2 x 10 mol/m³, d : C_o =4.4 x 10 mol/m³,
e : C_o =3.6 x 10 mol/m³, f : C_o =2.8 x 10 mol/m³,
g : C_o =2.0 x 10 mol/m³ [3]

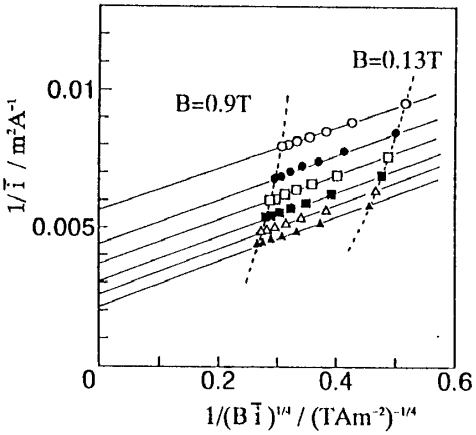

Fig.4 Plot of $1/\bar{i}$ vs. $1/(B\bar{i})^{1/4}$ for copper deposition onto copper in the lower magnetic field up to 0.9T in a solution with 0.3M $CuSO_4$ + 1M H_2SO_4
○ : E=−70mV ● : E=−80mV □ : E=−90mV
■ : E=−100mV △ : E=−110mV ▲ : E=−120mV
(E : potential vs. Ag/AgCl)

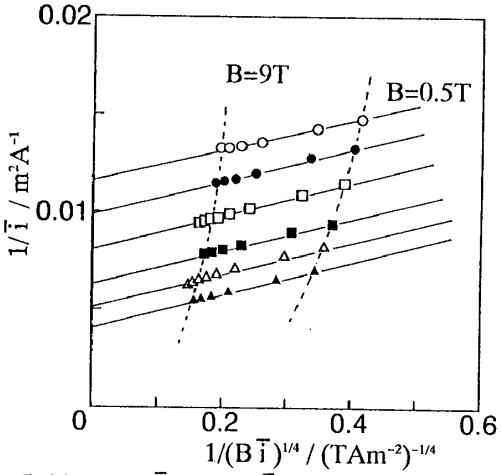

Fig.5 Plot of $1/\bar{i}$ vs. $1/(B\bar{i})^{1/4}$ for copper deposition onto copper in the higher magnetic field up to 13T in a solution with 0.3M $CuSO_4$ + 1M H_2SO_4
○ : E=−70mV ● : E=−80mV □ : E=−90mV
■ : E=−100mV △ : E=−110mV ▲ : E=−120mV
(E : potential vs. Ag/AgCl)

All the data exhibit good straight lines in Fig.4, the extrapolation to the ordinate gives the value of $\bar{i}_k$ at the magnetic field up to 0.9T. With the higher magnetic field type MHDE, the same kind of plot gives the data of $\bar{i}_k$ up to 13T in Fig.5. Then, all the data of $\bar{i}_k$ allow us to make the Tafel plots at the magnetic field and to compare them with the data in the absence of the magnetic field.

Figure 6 shows the transfer coefficients in the presence and absence of the magnitic field. All the data take almost the same value, 0.44. However, the satndard exchange current density drastically changes in the magnetic field. As shown in Fig.7, the exchange current density decreases to about 1/4 in the high magnetic field. In the low magnetic field, we can not see any difference of the value in the absence of the magnetic field.

These results seem consistent with the recent report on the same theme using radiotracer[5]. In the report, it was concluded that there is no change in the current density. This may be attributed to the fact that the too weak magnetic field, i.e, 0.4T to detect such effect was used in the experiments of the report.

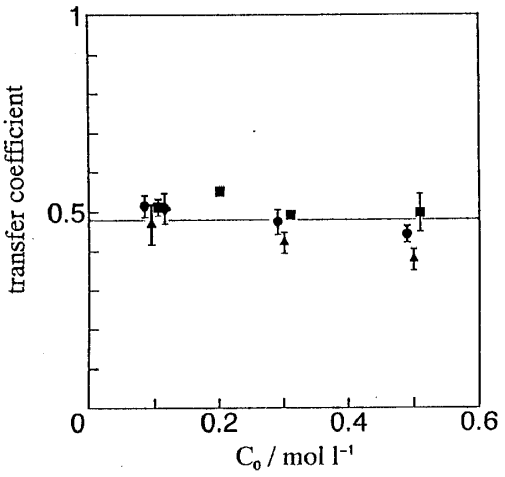

Fig.6 Dependence of the transfer coeficient on the bulk concentration

● : data at 0T (chronopotentiometry)
▲ : extrapolated data in the lower magnetic field
■ : extrapolated data in the higher magnetic field
◆ : data from the rotating disk electrode method

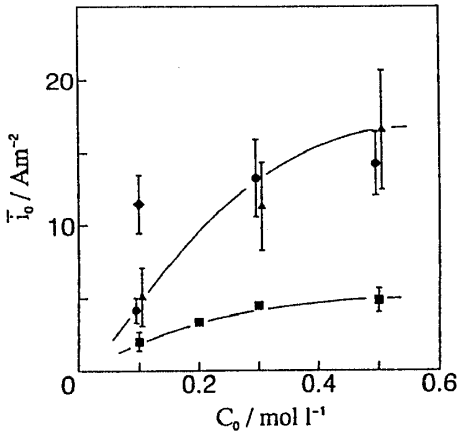

Fig.7 Dependence of the standard exchange current density on the bulk concentration

● : data at 0T(chronopotentiometry)
▲ : extrapolated data in the lower magnetic field
■ : extrapolated data in the higher magnetic field
◆ : data from the rotating disk electrode method

V. Conclusions

Using MHDE, the Tafel plots for copper reduction in the magnetic field were obtained.

Though we could not detect the change in the slope of the plot even in the high magnetic field up to 13T, it was observed that the Tafel line shifts to lower side of the current density, therefore, the exchange current density decreases to about 1/4 in the high magnetic field up to 13T.

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