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The Magnetic Field Effects on the Electrolysis of Hexacyanoferrate(II) Oxidation and Hexacyanoferrate(III) Reduction

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The effects of a magnetic field on electrolytic currents in hexacyanoferrate(II) and hexacyanoferrate(III) solutions were studied under various conditions by means of potentiometry. These effects were observed for a wide range of current densities (10^{-6}—10^{-3} A/cm^2). The results were interpreted in terms of the magnetohydrodynamic effect, including a change in the solution density during electrolysis. The present observation suggests that a magnetohydrodynamic flow strongly affects the electrochemical processes on an electrode surface.

Studies regarding magnetic field effects on chemical reactions have attracted the attention of many chemists because of their novelity as a phenomenon and their wide utility and potentiality such as for the regulation of reaction products, the elucidation of a reaction mechanism, and isotope separation.[1] Some of the present authors have studied the magnetic field effect on various photochemical reactions taking place in solutions.[2] As an extension of our research program, we have undertaken to study magnetic field effects on electrochemical reactions in solutions.

A number of studies has, hitherto, been carried out on magnetic field effects on electrolytic properties,[3] electrolytic mass transport,[4] electrode kinetics,[5] and others.[6] However, only a few papers have been published concerning magnetic field effects upon electrochemical reactions, including the electron transfer processes in which we are much interested.

In this paper, we report several electrochemical reactions which were undertaken by means of potentiometry in the presence and absence of an external magnetic field. The magnetic field is known to remarkably affect the electrolytic reduction of Fe^{3+} and the oxidation of Fe^{2+} in the high current-density region where the reaction is diffusion-controlled.[5] We have succeeded in observing the magnetic field effect even in a low current-density region (10^{-5}—10^{-6} A/cm^2), where the process is usually believed to be reaction-controlled. All the results have been interpreted in terms of the magnetohydrodynamic effect.

Experimental

Figure 1 is a schematic diagram of the present experimental set-up. An electrolytic cell and electrodes were placed between the poles of an electromagnet (Tohoku Kinzoku Kogyo Co., model SEE-15). A magnetic field did not affect the potential of a saturated calomel electrode (SCE) used as a reference electrode.

Two orientations of the magnetic field with respect to the working electrode were employed for electrolysis as schematically shown in Figs. 2, 3, and 4. One side of the working electrode (5×10 mm Pt plate) was covered with epoxide glue. The electrode plate was always kept parallel to the magnetic flux, and only the polarity of the magnetic field was changed (by alternating the direction of the electromagnet's current).

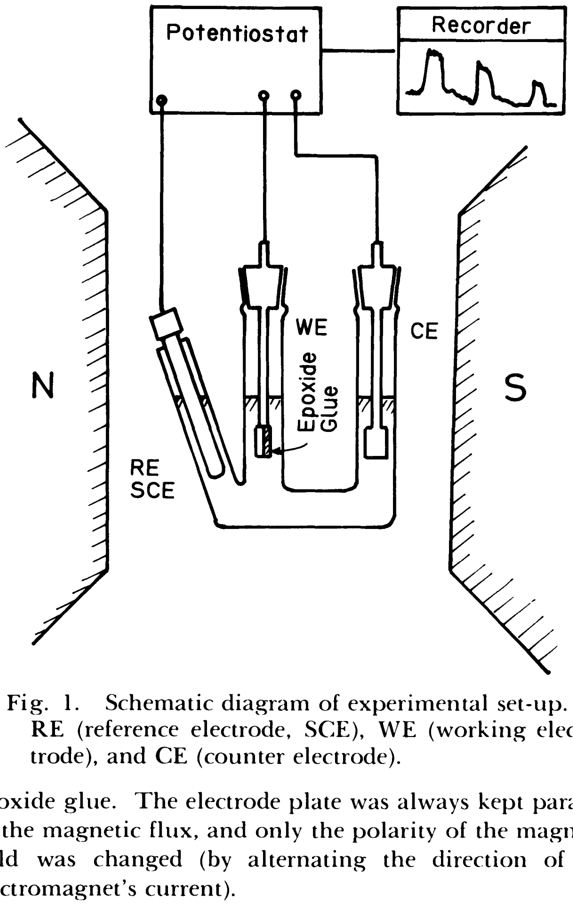

Fig. 1. Schematic diagram of experimental set-up. RE (reference electrode, SCE), WE (working electrode), and CE (counter electrode).

The electrolysis was carried out without stirring using a potentio/galvano stat (Hokuto Denko, model HA-102). Values of electrolytic current in the presence and absence of a magnetic field (represented hereafter I_H and I_O, respectively) were measured at a controlled potential of the working electrode. Argon gas was passed through the electrolytic solution to purge any dissolved oxygen before electrolysis took place.

Special grade $K_4[Fe(CN)_6]$ and $K_3[Fe(CN)_6]$, and a nonfluorescent grade glycerol were used without further purification. Potassium sulfate, which was used as a supporting electrolyte, was recrystallized from water. All the chemicals were obtained from Katayama Chemical Industries Co., Ltd.

Results

The effects of a magnetic field upon the potential/current curves of hexacyanoferrate(II) oxidation and hexacyanoferrate(III) reduction in a 1.0×10^{-1} mol/dm^3

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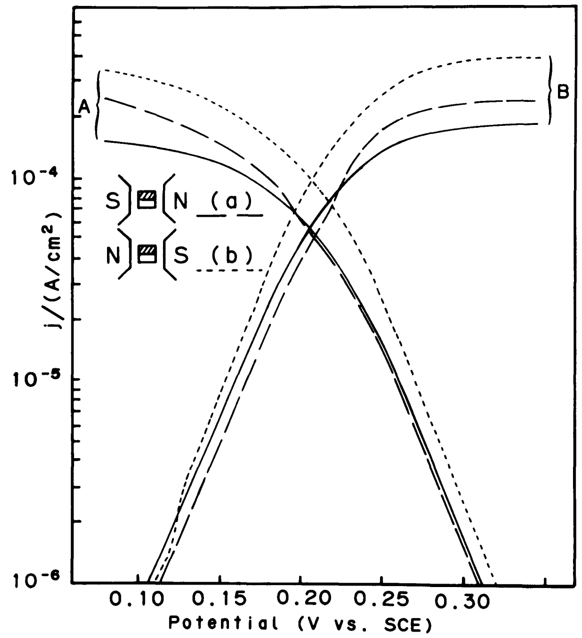

Fig. 2. Potential/current curves for (A) reduction of $K_3[Fe(CN)_6]$ (1.0×10^{-2} mol/dm^3) and (B) oxidation of $K_4[Fe(CN)_6]$ (1.0×10^{-2} mol/dm^3). Concentration of K_2SO_4 supporting electrolyte is 1.0×10^{-1} mol/dm^3). (——), at the residual magnetic field (6.2 mT); (— —), magnetic field orientation-(a) at 1.7 T; (·····), magnetic field orientation-(b) at 1.7 T. Top view of two magnetic field orientations with respective to the working electrode are also illustrated in the figure. ▨ and ▭ indicate epoxide glue and platinum plate of the electrode, respectively.

potassium sulfate aqueous solution were measured. The results are shown in Fig. 2. When a magnetic field was applied, the electrolytic current gradually changed for several tens of minutes and then reached a constant value. The magnetic field effects were observed in a limiting current (diffusion-controlled) region as have been reported in the literature.[4,5] The same is true for the low current density (reaction-controlled) region.

The effect of hexacyanoferrate(II) concentrations on a magnetic field-induced change in a limiting current is shown in Fig. 3. As the concentration increases, the ratio $R(=I_H/I_0)$ increases in magnetic field orientation-(b), while in orientation-(a) it decreases gradually to 0.8, and then increases rapidly up to 2.5. At the higher concentration, the ratio seems to become almost constant. In order to investigate the influence of the viscosity of a solution upon the current in the presence and absence of a magnetic field, a measurement was made with a 1.0×10^{-2} mol/dm^3 hexacyanoferrate(II) aqueous solution containing 3.0 mol/dm^3 glycerol. The results are also shown in Fig. 3.

The influences of the external magnetic field on the anodic current in various concentrations of hexacyanoferrate(II) are presented in Fig. 4. The curves for 3.0×10^{-2} mol/dm^3 or 1.0×10^{-2} mol/dm^3 in Fig. 4 are very similar in their shapes to the corresponding ones with regard to the magnetic field orientations in Fig. 3B. This means that the dependence of R upon the concentration is similar to that upon the magnetic field.

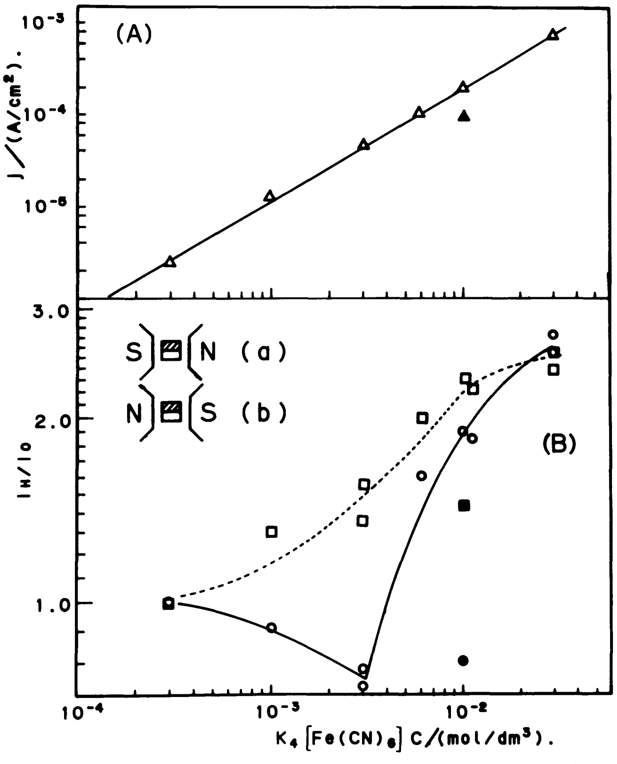

Fig. 3. Concentration dependence of $K_4[Fe(CN)_6]$ in the prssence of 1.0×10^{-1} mol/dm^3 K_2SO_4 at 0.45 V *vs.* SCE.

(A) Limiting current density in the absence of a magnetic field; (—△—). ▲ shows the value of j for the solution containing 3.0 mol/dm^3 glycerol, 1.0×10^{-2} mol/dm^3 $K_4[Fe(CN)_6]$ and 1.0×10^{-1} mol/dm^3 K_2SO_4.

(B) Ratio of limiting currents. I_H and I_0 show intensities of limiting currents in the presence and absence of magnetic field, respectively. (—○—), magnetic field orientation-(a) at 1.7 T, (···□···), magnetic field orientation-(b) at 1.7 T. ● and ■ represent the ratios I_H/I_0 with orientation-(a) and -(b) for the solution containing glycerol, respectively.

Discussion

An increase in the electrolytic current in the presence of a magnetic field has already been interpreted in terms of a magnetohydrodynamic model where the magnetohydrodynamic force induces a flow of the solution and enhances the rate of diffusional mass transfer.[4,5]

According to Aogaki *et al.*[7] under the conditions where the magnetohydrodynamic flow is mostly predominant, the ratio R is proportional to the 1/3 power of the magnetic field strength B and to the 1/3 power of the electrolyte concentrations. The concentration dependence of R in Fig. 3B and the magnetic field dependence of R in Fig. 4 seem to agree with this theoretical prediction in the high concentration region ($\geq 5\times10^{-2}$ mol/dm^3) and in the strong magnetic field strength ($\geq$ 0.5 T), respectively.

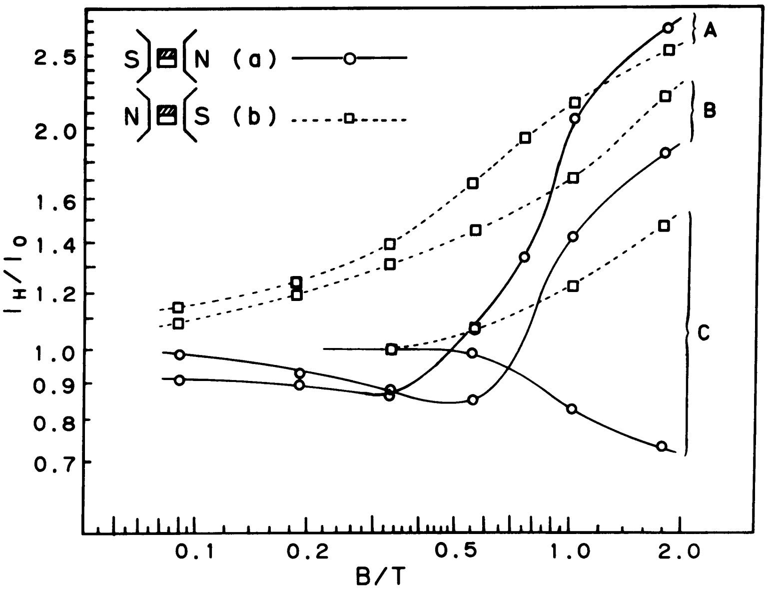

Fig. 4. Magnetic field dependence for $K_4[Fe(CN)_6]$ aqueous solution at 0.45 V *vs.* SCE. The concentration of K_2SO_4 is 1.0×10^{-1} mol/dm^3. (A), 3.0×10^{-2} mol/dm^3 $K_4[Fe(CN)_6]$ (B), 1.0×10^{-2} mol/dm^3 $K_4[Fe(CN)_6]$ and (C), 3.0×10^{-3} mol/dm^3 $K_4[Fe(CN)_6]$. (—○—) magnetic field, orientation-(a) (···□···), magnetic field orientation-(b).

Thus, under these conditions, the magnetic field effect on the electrolytic current can be explained in terms of the magnetohydrodynamic mechanism.

On the other hand, in the low concentration region or in a weak magnetic field, we observed not only an increase in the current under the magnetic field but also its decrease (shown in Figs. 2, 3, and 4).

In the case of hexacyanoferrate(II) oxidation in Fig. 2, upon electrolysis a density of the electrolyte solution localized near the working electrode may become smaller than that of the bulk solution, because the specific gravities of potassium hexacyanoferrate(III) and potassium hexacyanoferrate(II) aqueous solution are 1.002_4 at 3.0×10^{-2} mol/dm^3 and 1.003_9 at 2.7×10^{-2} mol/dm^3, respectively.[8] Therefore, the solution on the surface of the electrode may flow upward. On the other hand, the direction of the magnetohydrodynamic force is downward in magnetic field orientation-(a). This means that the magnetohydrodynamic force prevents a natural convection flow under these conditions, and the anodic current may decrease under the field in the low current density region (10^{-5}—10^{-6} A/cm^2), where the magnetohydrodynamic force is smaller than the natural convection force. In the high current density region ($>10^{-4}$ A/cm^2), the magnetic field increases the current density because the flow due to the magnetohydrodynamic force is much stronger than for convective flow. The magnetic field in orientation-(b) always increases the electrolytic current, because the direction of a magnetohydrodynamic force is parallel to that of the natural convective flow. Thus, we can explain the magnetic field effects upon the potential/current curves of hexacyanoferrate(II) oxidation as shown in Fig. 2. This interpretation is supported by the slow response of the electrolytic current to an applied magnetic field.

The potential/current curves of hexacyanoferrate(III) reduction in Fig. 2 are explained in a manner similar to that of the hexacyanoferrate(II) oxidation mentioned above. In this case, both the directions of the magnetohydrodynamic force and the natural convection flow become opposite. This can be compared with the case for hexacyanoferrate(II) oxidation. Therefore, a decrease in the electrolytic current density in the presence of a magnetic field was observed also for magnetic field orientation-(a).

According to the relation $\boldsymbol{F}=\boldsymbol{j}\times\boldsymbol{B}$ (where $\boldsymbol{F}$ is a magnetohydrodynamic force and $\boldsymbol{j}$ is a electrolytic current density), the concentration dependence and the magnetic field dependence of R should resemble each other. As shown in Figs. 3B and 4, our observations are in good agreement with this prediction. This confirms our interpretation that all results presented here can be explained in terms of magnetohydrodynamics.

A magnetohydrodynamic flow velocity is affected by the viscosity of a solution. Figure 3 shows the measured results for a solution containing 1.0×10^{-2} mol/dm^3 hexacyanoferrate(II) and 3.0 mol/dm^3 glycerol, the viscosity of which is higher than that of the glycerol-free solution by a factor of 2.3. From this figure we can see that the limiting current density and R decrease for a viscous solution containing glycerol compared with a corresponding glycerol-free solution.

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