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Effect of High Magnetic Field on Copper Deposition from an Aqueous Solution

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Deposition of copper metal from a Cu^{2+}/Zn liquid–solid redox reaction is studied in a high magnetic field gradient. A zinc wire is placed on a chromatography paper strip with a copper(II) chloride aqueous solution. At zero field, copper dendrite grows uniformly around the wire. In the presence of a magnetic field gradient (ca. 410 $T^2\,m^{-1}$), the dendritic pattern changes drastically. The yields of copper dendrite and consumed copper ion increase by ca. 50% in the magnetic field. The results are interpreted in terms of the magnetic force-induced convection of the solution.

Recently, the effects of high magnetic field (> 2 T) on chemical and physical processes have attracted much attention of chemists and physicists. This is because unexpected magnetic phenomena which have potential for application have been discovered in a high magnetic field. In the case of organic photochemical reactions in *homogeneous* high magnetic fields (< 30 T), reversal of the magnetic field effects (MFEs) has been observed above 1—2 T.[1,2] In the MFEs on hydrogen-ferromagnetic compounds, the Gibbs free energy change which is induced by *homogeneous* high magnetic field results in a change in the chemical equilibrium.[3] Fibrin fiber,[4,5] polymers,[6] and organic crystals[7—9] are oriented under *homogeneous* magnetic fields. Deposition and electro-deposition patterns of silver metal from an Ag^+/Cu redox reaction are affected by a high *homogeneous* magnetic field (8 T).[10,11]

Study of magnetic field *gradient* effects on chemical reactions in condensed phase is rare, though effects of *homogeneous* magnetic fields have been studied very extensively, as mentioned above. In a previous paper, we have reported the effect of a high magnetic field *gradient* on an Ag^+/Cu liquid–solid redox reaction.[12—14] The dendritic pattern and yield of silver metal deposited by the reaction are affected significantly by the high field *gradient.* A magnetic force on a paramagnetic *product*, Cu^{2+}, is considered to induce convection of the solution. It is urgent to verify experimentally the mechanism proposed in the above-mentioned reaction by examining the effect of magnetic field *gradient* on a different type of reaction, since little is known about the effect of magnetic field *gradient.*

In this paper, we report the effect of a high magnetic field *gradient* on the deposition of copper metal from a copper(II) chloride aqueous solution. In this reaction, paramagnetic ions (Cu^{2+}) are involved as a *reactant*, in good contrast with the Ag^+/Cu reaction where Cu^{2+} ions are involved as a *product*. Dendritic pattern of copper metal as well as its yield are affected drastically by the magnetic field *gradient*, though the pattern of copper metal is very different from that of silver metal in the Ag^+/Cu reaction. A high magnetic field *gradient* induces convection in a thin layer of the solution by attracting a paramagnetic *reactant*, Cu^{2+}, dissolved in it. It is confirmed that the magnetic field effects on the liquid–solid redox reactions involving paramagnetic ions as both a *reactant* and a *product* can be interpreted with the same mechanism.

Experimental

The magnetic fields were applied using a superconducting magnet (Oxford Instrument, Spectromag-1000) with a horizontal $50\phi \times 375$ mm bore. Distribution of the magnetic field $B(z)$ is given in Fig. 1, where the direction of the magnetic field is taken along the bore tube (z-axis). The maximum value of the magnetic field ($B_{\max}$) is 8.0 T at $z = 0$ and the magnetic field gradient, $B(z)\mathrm{d}B(z)/\mathrm{d}z$, is ca. 410 $T^2\,m^{-1}$ at $z = \pm 65$ mm. In the following, for simplicity, $B_{\max}$ was used as the representative value of the magnetic field.

Copper(II) chloride (Nacalai, GR grade) and chromatography paper (Whatman, 1Chr) were used as supplied. Deionized water was used. Zinc wire (Nilaco, 99.99%) was polished mechanically and chemically before use.

Liquid–solid redox reaction was carried out in a plastic vessel (40 mm × 385 mm × 10 mm) at room temperature (Fig. 1). A zinc wire ($5\ \phi \times 250$ mm) was placed on a strip of chromatography paper (37 mm × 300 mm) with a copper(II) chloride aqueous solution (0.5 mol dm^{-3}, 2.6 ml). The vessel was then placed in a magnet bore, its center at $B_{\max}$. A copper(II) chloride solution was soaked into a strip of chromatography paper, since a fluid solution is attracted to or repelled from a high magnetic field *gradient* due to its magnetic susceptibility.[15]

The patterns of copper dendrite and unreacted Cu^{2+} on a strip of chromatography paper were recorded by a camera after exposing the paper to ammonia. The area of the paper where Cu^{2+} remained turned blue, since the tetraamminecopper(II) complex ($[Cu(NH_3)_4]^{2+}$) had an absorption band at ca. 630 nm.

Dendritic patterns of copper metal were also obtained by an alternative method. The copper dendrite deposited on the paper was

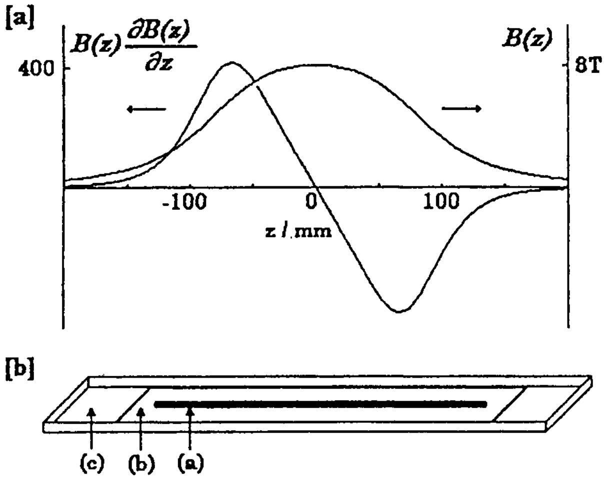

Fig. 1. [a] The distribution of the magnetic field $B(z)$ and the magnetic field gradient $B(z)\mathrm{d}B(z)/\mathrm{d}z$ in the magnet bore. z is the distance along the magnetic axis from the center of the magnetic field. [b] The outline of experimental handling. (a) a zinc wire (5ϕ×250 mm), (b) a strip (37 mm×300 mm) of chromatography paper soaked with 0.5 mol dm^{-3} copper chloride aqueous solution (2.6 ml), and (c) a plastic vessel (40 mm×385 mm×10 mm).

washed twice with dilute hydrochloric acid, 0.1 mol dm^{-3} sodium thiosulfate solution and water, dried, and stored for recording by a camera and for measurements of its chemical yield.

The yield of copper metal was determined by gravimetry. The relative yield of consumed Cu^{2+} was determined using the reaction with ammonia. After the Cu^{2+}/Zn redox reaction, the Cu^{2+} adsorbed by the chromatography paper was extracted with water. Ammonia water was added to the extract and the relative yield of consumed Cu^{2+} was calculated from the absorbance of $[Cu(NH_3)_4]^{2+}$ at 630 nm.

The electromotive force was measured using a high-impedance electric recorder. As shown in Fig. 2, the two sets of zinc wire (5ϕ×50 mm×4 pieces) were placed on a strip of chromatography paper at z = 0 and z = 125 mm. Magnetic field values were 8.0 (z = 0) and 1.9 T (z = 125 mm).

In order to examine the magnetic field-induced drift of ions, an aqueous solution (0.5 mol dm^{-3}, 2 μl) of Cu^{2+} (Zn^{2+}) was impregnated at z = 50 mm on a strip of chromatography paper with water (2.6 ml). The magnetic field gradient was 350 $T^2\,m^{-1}$ at z = 50 mm. After 1 h, the distance between the impregnated point and the center of the diffused solution was measured.

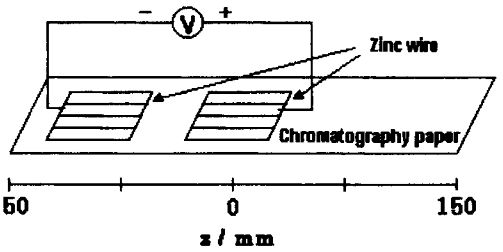

Fig. 2. Experimental setup for the electromotive force. Two sets of zinc wire (5ϕ×50 mm×4) were placed on a strip of chromatography paper at z = 0 and z = 125 mm.

Results

MFE on Patterns of Copper Dendrite and Copper Ion. The liquid–solid redox reaction studied here is given by the following equation:

$$Cu^{2+} + Zn \rightarrow Cu\downarrow + Zn^{2+}. \quad (1)$$

Because of the ionization tendency, the dendrite of copper metal deposits from a copper(II) chloride aqueous solution when a zinc wire is placed on the paper. Figure 3 shows the effect of a magnetic field on patterns of copper dendrite and unreacted copper ion after the 1 h reaction. In the absence of the magnetic field, the copper dendrite grows uniformly around the zinc wire and the area where the dendrite grows coincides with that where copper ion is consumed. In the presence of the magnetic field (B_{max} = 8.0 T), the copper metal deposits preferentially in the neighborhood of the center of the wire, whereas copper ions near the edges are consumed preferentially.

Figure 4 shows the magnetic field dependence of the patterns of copper dendrite recorded by the alternative method. A remarkable change of the pattern is observed for magnetic fields above 3.0 T.

MFE on the Yields of Copper Metal and Copper Ion. The MFE on the yield of copper metal was determined by gravimetry. The yield after the 1 h reaction is 56±12 mg in the presence of a magnetic field (B_{max} = 8.0 T), whereas it is 36±2 mg at zero field. The yield increases by ca. 50%. Figure 5 shows the effect of the magnetic field (B_{max} = 8.0 T) on the relative yield of consumed Cu^{2+} by the reaction. The yield after the 1 h reaction increases by about 50% in the magnetic field. By application of the magnetic field, the net yields of both the deposited copper metal and consumed copper ions increase, even though the deposition of copper metal seems to be localized in the neighborhood of the center of the wire.

Electromotive Force. The present redox reaction in the magnetic field gradient generates an electromotive force. It

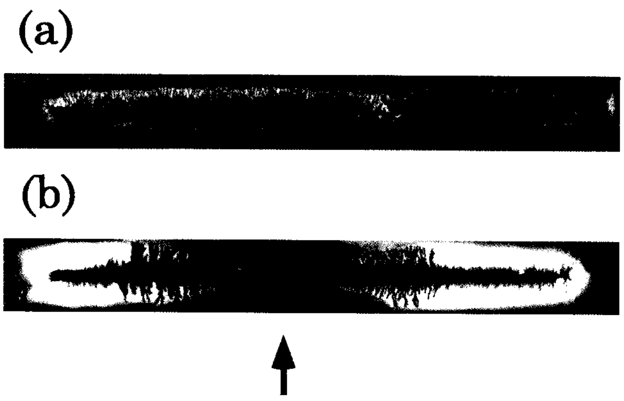

Fig. 3. The patterns of copper dendrite and Cu^{2+} after the 1 h reaction in (a) the absence and (b) presence of a magnetic field (B_{max} = 8.0 T). An arrow indicates the position at z = 0 mm. The area where unreacted Cu^{2+} ions remained is shown by blue color of $[Cu(NH_3)_4]^{2+}$.

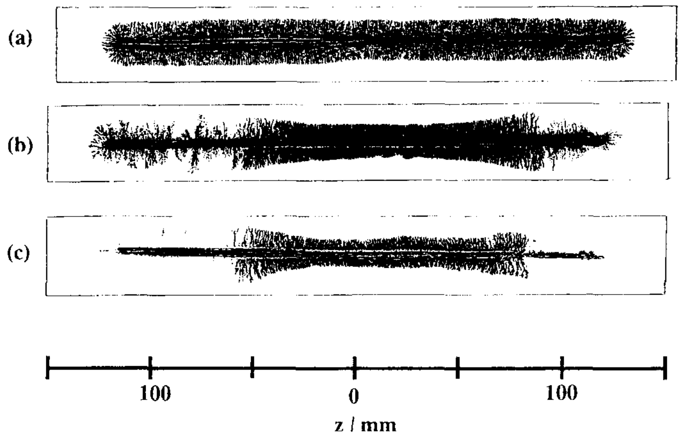

Fig. 4. Magnetic field dependence of the pattern of copper dendrite after the 1 h reaction obtained by the alternative method (see text). (a) $B_{max} = 0$ T, (b) $B_{max} = 5.0$ T, (c) $B_{max} = 8.0$ T.

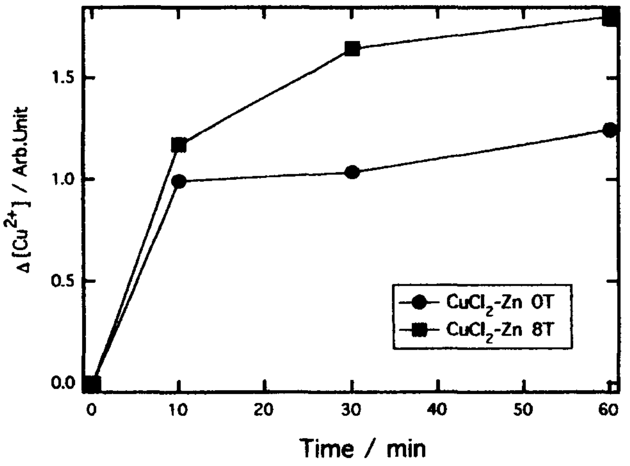

Fig. 5. The relative disappearance yield ($\Delta[Cu^{2+}]$) of copper ions vs. time in the absence (●) and presence (■) of a magnetic field ($B_{max} = 8.0$ T).

is measured using the experimental setup depicted in Fig. 2. As shown in Fig. 6, no electromotive force is generated in the absence of a magnetic field. When a magnetic field ($B_{max} = 8.0$ T) is applied, an electromotive force of 200—250 mV is generated between two sets of identical wires. The force is not induced immediately on application of the magnetic field but increases gradually with a time constant of a few minutes.

Drift Distance of Ions. The magnetic field-induced drift distance of Zn^{2+} and Cu^{2+} is examined in the presence of a magnetic field gradient of 350 $T^2\,m^{-1}$. In the case of the 0.5 mol dm^{-3} Cu^{2+} solution, the distance is 11±2 mm, whereas no appreciable drift is observed in the case of the 0.5 mol dm^{-3} Zn^{2+} solution. Paramagnetic Cu^{2+} is attracted to the higher field, whereas diamagnetic Zn^{2+} is not. Furthermore, a chromatography paper was lifted up from the vessel so that it is out of contact with the bottom of the vessel. Under this circumstance, paramagnetic Cu^{2+} does not drift to the higher field.

Discussion

In a previous paper, the MFEs on the deposition of silver metal formed by the reaction:

$$2Ag^{+} + Cu \rightarrow 2Ag\downarrow + Cu^{2+}, \tag{2}$$

have been discussed in detail.[12—14] In this reaction, the following observations are made about the magnetic field gradient ($B_{max} = 8.0$ T). (a) Silver dendrite deposits preferentially near the edges of a copper wire. (b) The chemical yields of both silver dendrite and copper ions increase by about 40%. (c) The magnetic field induces an electromotive force of ca. 200 mV. In reaction (2), the product Cu^{2+} is only para-

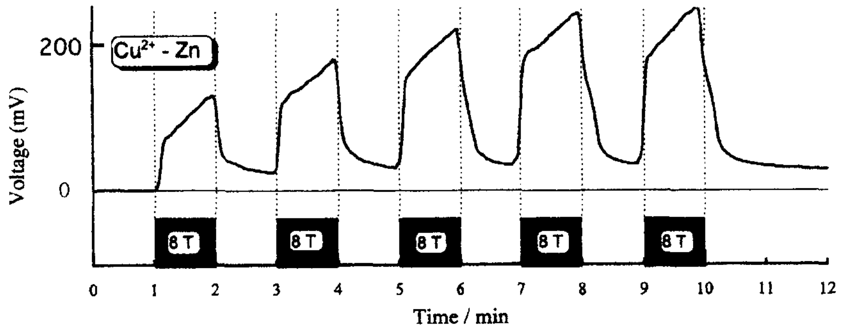

Fig. 6. Electromotive force for the Cu^{2+}/Zn redox reaction induced by a magnetic field ($B_{max} = 8.0$ T). A closed box $\boxed{8\ T}$ indicates the time period when the reaction system is exposed to the magnetic field. Unless otherwise noted, the reaction is carried out at zero field. Experimental setup is given in Fig. 2.

magnetic and the results are interpreted by the magnetic force on Cu^{2+} formed by the reaction. The force is considered to induce convection of the solution. Present observations mentioned above are in parallel with those for the Ag^+/Cu redox reaction and, therefore, should be explained analogously by the magnetic force on the paramagnetic Cu^{2+}, which is involved as a reactant in the reaction. The dendritic pattern of copper metal is indeed different from that of silver metal; this difference will be explained later.

As discussed in a previous paper, there are three mechanisms which may be applicable for explaining the observed effects. They are (a) the magnetic field-induced changes in the Gibbs free energies,[3] (b) the magnetohydrodynamics (MHD) mechanism[10] and (c) the magnetic force caused by a magnetic field gradient.[16] The magnetic field-induced Gibbs free energy change $\Delta G(B)$ in a chemical reaction is

$$\Delta G(B) = (-1/2\mu_0)B^2\left[\sum_i n_i \chi_M^i - \sum_j n_j \chi_M^j\right], \tag{3}$$

where χ_M^i and χ_M^j are the molar magnetic susceptibilities of the product i and reactant j, respectively, n_i and n_j are the respective stoichiometric mole numbers, μ_0 is the magnetic permeability of vacuum and B is the applied magnetic field. When $|\Delta G(B)|$ becomes comparable with the free energy change at zero field, the chemical equilibrium of the reaction is affected by the magnetic field.

In the present reaction (1), the magnetic field value $B(z)$ is not constant but is dependent on the distance z. Since $\Delta G(B)$ at the center of the wire is different from that at the edge of the wire, the equilibrium constant of the reaction (1) might be different at two positions in the high magnetic field. Assuming that molar magnetic susceptibilities of copper, copper ion, zinc, and zinc ion are $-4\pi \times 5.46 \times 10^{-12}$, $+4\pi \times 1.03 \times 10^{-9}$, $-4\pi \times 1.14 \times 10^{-11}$, and $-4\pi \times 1.0 \times 10^{-11}$ $m^3\,mol^{-1}$, respectively (all values are described using SI units), and magnetic fields at the center ($z = 0$ mm) and the edge ($z = 125$ mm) of the wire are 8.0 and 2.0 T, respectively, $\Delta G(8\ T)$ and $\Delta G(2\ T)$ are estimated to be +0.33 J ($z = 0$ mm) and +0.02 J ($z = 125$ mm) respectively. Thus, the difference in the ΔG between the center and the edge of the wire is 0.31 J. This free energy difference is too small to explain non-uniform deposition of copper dendrite in magnetic fields shown in Figs. 3 and 4. Furthermore, the electromotive force between the two sets of zinc wire shown in Fig. 2 is estimated to be 1.6×10^{-6} V from the above-mentioned free energy difference. This value is also too small to explain the observed electromotive force (ca. 200 mV) shown in Fig. 6. The present results can not be interpreted in terms of a magnetic field-induced change in the Gibbs free energies.

The MHD force $\boldsymbol{F}_{MHD}$ is given by the following equation:

$$\boldsymbol{F}_{MHD} = e\boldsymbol{v} \times \boldsymbol{B} \tag{4}$$

where e is the electric charge, $\boldsymbol{v}$ is its velocity, and $\boldsymbol{B}$ is the homogeneous magnetic field. $\boldsymbol{F}_{MHD}$ gives charged species torque perpendicular to both $\boldsymbol{v}$ and $\boldsymbol{B}$ axes. When $\boldsymbol{v}$ and $\boldsymbol{B}$ are perpendicular to each other, $\boldsymbol{F}_{MHD}$ is maximum, whereas $\boldsymbol{F}_{MHD}$ is zero when $\boldsymbol{v}$ and $\boldsymbol{B}$ are parallel. Mogi et al. have reported that a high magnetic field affects the deposition pattern of the Ag^+/Cu redox reaction.[10] In their experiment, the magnetic field is perpendicular to a piece of chromatography paper and $\boldsymbol{F}_{MHD}$ is maximum as motion of ions is perpendicular to the magnetic field. In the present experiment, however, the direction of the flow of ions is considered to be parallel to that of the magnetic field (z-axis), since the Cu^{2+} near the two edges of the wire (lower magnetic field) disappears and Cu dendrite is formed preferentially near the center of the wire (higher magnetic field) (Figs. 3 and 4). Therefore, this mechanism does not explain the experimental results. Furthermore, in the case of the Ag^+/Zn redox reaction (5), no appreciable MFE is observed on both the deposition pattern and the yield of silver dendrite.[13]

$$2Ag^+ + Zn \rightarrow 2Ag\downarrow + Zn^{2+}. \tag{5}$$

Although reactions (1), (2), and (5) are similar redox reactions, reactants and products are all diamagnetic only in the reaction (5). In reactions (1) and (2), paramagnetic Cu^{2+} is involved as a reactant or a product. Paramagnetism of chemicals involved in the reaction is essential for the MFEs. Therefore, it is inadequate to explain the present MFE in terms of the MHD mechanism.

The present results can be explained in terms of the magnetic force caused by a magnetic field gradient as discussed below. During reaction (1), the aqueous solution composed of Cu^{2+}, Zn^{2+}, Cl^-, and water (solvent) is considered to receive the magnetic force in the magnetic field. The magnetic force $\boldsymbol{F}_{mag}(z)$ in the z direction which is induced by a magnetic field gradient is given by:

$$F_{mag}(z) = (1/\mu_0)\chi_M B(z) dB(z)/dz. \tag{6}$$

Suppose the maximum value of $B(z)dB(z)/dz$ is 410 $T^2\,m^{-1}$ ($z = \pm 65$ mm), the maximum magnetic forces for Cu^{2+}, Zn^{2+}, Cl^-, and water are estimated to be +4.2, −0.04, −0.1, and −0.05 $N\,mol^{-1}$, respectively. The force for Cu^{2+} is strong enough to induce convection of the solution, since the water surrounding Cu^{2+} may move together with Cu^{2+} by collision. Paramagnetic Cu^{2+} is the key compound for the MFEs shown in Figs. 3, 4, 5, and 6. The importance of the magnetic force on Cu^{2+} is supported by the measurement of drift distance of Cu^{2+} and Zn^{2+}. As mentioned above, Cu^{2+} moves by ca. 11 mm to the higher field in a field gradient of 350 $T^2\,m^{-1}$, whereas Zn^{2+} does not.

Chemical yields of copper dendrite and consumed Cu^{2+} should increase because mass transfer to the reaction front is enhanced by the convection of the solution in a magnetic field gradient in addition to the transfer by diffusion at zero field.

The electromotive force shown in Fig. 6 can then be explained by the convection of a solution induced by the magnetic force. As discussed above, the paramagnetic solution starts to flow to the higher field as the reaction proceeds. This convection of the solution generates an electromotive force in the magnetic field gradient. It takes a few minutes to reach the maximum value in the electromotive force. This slow response time may be attributed to the time for convection of the solution to reach a steady-state flow. Electric current induced by the magnetic force is estimated to be about 4×10^{-6} A, since an electromotive force is about 200 mV and the impedance between the two electrodes is about 50 kOhm. This corresponds to a flow of 7.5×10^{-8} mol of doubly charged ions per 1 h. If Cu^{2+} is the origin of the electric current, this value corresponds to a flow of 4.7×10^{-6} g of Cu^{2+} per 1 h. Since in the experiment shown in Fig. 4 the amount of copper metal deposited is about 0.05 g after the 1 h reaction at $B_{max} = 8.0$ T, transfer of 4.7×10^{-6} g of Cu^{2+} per 1 h between two sets of the wire is easily attainable under the experimental condition shown in Fig. 2.

Now let us consider the location of the solution which moves under the influence of the magnetic force. In the present experimental condition, three types of aqueous solution may be involved. They are (a) the solution bound by the paper, (b) the solution covering the surface of the paper, and (c) the solution held in a thin space between the chromatography paper and the bottom of the plastic vessel. A strip of chromatography paper (37 mm×300 mm) can take up 2.0 ml of aqueous solution. However, no dendrite like the one shown in Figs. 3 and 4 is formed when the paper is wet with a 2.0 ml aqueous solution. The solution bound by the paper does not contribute to the formation of dendrite. In other words, in order to form the copper dendrite shown in Figs. 3 and 4, some fluid solution which can move is indispensable. In this experiment, the paper is wet with a 2.6 ml solution to form dendritic patterns of copper metal. Although an excess solution of 0.6 ml is considered to be mobile, this volume of solution is insufficient to cover the surface of the paper and it is unnecessary to take the solution covering the paper into account. Therefore, a mobile solution of 0.6 ml which can move under the influence of the magnetic force is considered to be held in a thin space between the paper and the bottom of the vessel. This consideration is supported by the drift experiment of Cu^{2+} in the magnetic field. When a strip of wet chromatography paper is lifted up from the vessel so that it is out of contact with the bottom of the vessel, paramagnetic Cu^{2+} does not drift to the higher field. This indicates that the solution which moves in the magnetic field is the solution held in the thin space between the paper and the bottom of the vessel.

The Cu^{2+}/Zn redox reaction takes place between a zinc wire and the solution bound on the chromatography paper, while the solution bound on the paper exchanges ions with the mobile solution held in the thin space between the paper and the bottom of the vessel. On application of a magnetic field gradient, convection of the solution in the thin space is induced and, therefore, the pattern of copper dendrite as well as the chemical yields are affected.

Patterns of copper dendrite and unreacted Cu^{2+} may be explained schematically by Fig. 7. At zero field, copper dendrite is formed uniformly around the zinc wire by diffusion due to the concentration gradient of Cu^{2+} (Fig. 7(a)). In the presence of a magnetic field gradient, a magnetic force induces convection of a solution to the higher field, resulting in the drift of Cu^{2+} to the higher field (Fig. 7(b)). Thus a paramagnetic solution at the lower field (area A in the Fig. 7(b)) moves to the center of the field and Cu^{2+} in it reacts at the reaction front, i.e., zinc wire and copper dendrite. For this reason copper dendrite is formed preferentially in the higher field region, in accord with consumption of Cu^{2+} in the lower field region. The solution near the center of the magnetic field (area B in Fig. 7(b)) remains unreacted. This occurs partly because the magnetic force is weak and partly because there is no space to undergo convection.

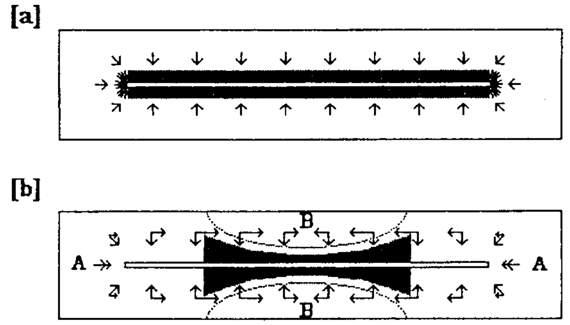

Fig. 7. Schematic model for mechanism of MFEs on the Cu^{2+}/Zn reaction (Top view). [a] $B_{max} = 0$ T, [b] $B_{max} = 8.0$ T.

In the present reaction, the paramagnetic solution as a whole receives a magnetic force simultaneously. In the case of Ag^{+}/Cu redox reaction, however, the Cu^{2+} formed by the reaction is attracted by the magnetic force. This means that only the solution near a copper wire which is rich in Cu^{2+} receives the magnetic force.[14] This difference in the pattern of the magnetic force results in the difference in the pattern of the deposited dendrite.

Summary

A Cu^{2+}/Zn liquid–solid redox reaction is carried out on a strip of chromatography paper in a magnetic field gradient of ca. 410 $T^2\,m^{-1}$. The pattern of copper dendrite is affected remarkably by the magnetic field. The chemical yield of Cu metal as well as that of consumed Cu^{2+} increases by about 50%. These MFEs are explained in terms of the magnetic field-induced convection of the solution. The magnetic force upon paramagnetic copper ions dissolved in the solution induces convection of the solution which is held in the thin space between the chromatography paper and the bottom of the vessel.

The magnetic field effect on the Cu^{2+}/Zn reaction involving paramagnetic Cu^{2+} ions as a *reactant* can be explained with the same mechanism which has been proposed in the magnetic field effect on the Ag^{+}/Cu, where Cu^{2+} ions are involved as a *product*. This confirms the proposed mechanism that the magnetic force on Cu^{2+} ions induces convection of solution.

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