The Effects of High Magnetic Field on the Deposition of Silver

Akio Katsuki, Shin-ichi Watanabe, Ryoko Tokunaga, and Yoshifumi Tanimoto*
Department of Chemistry, Faculty of Science, Hiroshima University, Higashi-Hiroshima, Hiroshima 739

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Deposition of silver was observed under a high gradient magnetic field. When a copper wire was placed on a piece of filter paper which was wet with silver nitrate aqueous solution (0.5 mol dm^{-3}), the deposition of silver grew uniformly around the wire at zero field. In the presence of the magnetic field (B_{max} = 8 T), the area of the deposition at the center of the magnetic field decreased. Diffusion of ions generated in the reaction seems to be affected by the high gradient field.

Effects of high magnetic fields upon chemical reactions are an emerging and growing area of research which is attractive from both fundamental and applied points of view. This is partly because superconducting magnets, which can generate magnetic fields as high as ca. 10 T, become popular in chemists and partly because a magnetic field provide us a potential tool to control various chemical and physical processes. In the last few years, we have investigated effects of high homogeneous magnetic fields upon primary photochemical process of organic molecules by using a pulsed-magnetic-field laser photolysis apparatus. In the case of biradicals and radical pairs, the reversion of the magnetic field effect was observed for their lifetimes in magnetic fields higher than 1-2 T.[1]

In order to research effects of high magnetic fields on inorganic redox reaction, we have studied the effects upon deposition of silver from silver nitrate aqueous solution. It was shown that a high gradient field affected the redox reaction significantly.

Silver nitrate (Nacalai, GR grade), filter paper (Whatman, chromatography paper, 1Chr), were used as supplied. Deionized water was used. Copper wires (99.9%, 6 ϕ) were polished mechanically and chemically before use.

Magnetic fields were applied by using a superconducting magnet (Oxford Instruments, Spectromag 1000). Its bore (50 ϕ × 370 mm) was installed horizontally. Distribution of the magnetic field was approximated with a Gaussian distribution (Figure 1).

In a plastic vessel (40 mm × 380 mm × 10 mm), a copper wire (6 ϕ × 250 mm) was placed on a piece of filter paper (40 mm × 300 mm) which was wet with a silver nitrate solution (0.5 mol dm^{-3}), as shown in Figure 1.[2,3] The vessel was then placed in a bore of the magnet, so that the center of the vessel coincided with that of the magnetic field. The reaction was carried out for 3 h at room temperature. The deposition was washed twice with dilute hydrochloric acid and 0.1 mol dm^{-3} sodium thiosulfate solution and dried. It is known that a fluid solution is attracted to or repelled from a high gradient magnetic field, depending on the sign of its magnetic susceptibility.[4] In order to avoid this effect, a silver nitrate solution was soaked into a piece of filter paper. Furthermore, a piece of filter paper was used because of easiness for handling silver deposition on it.

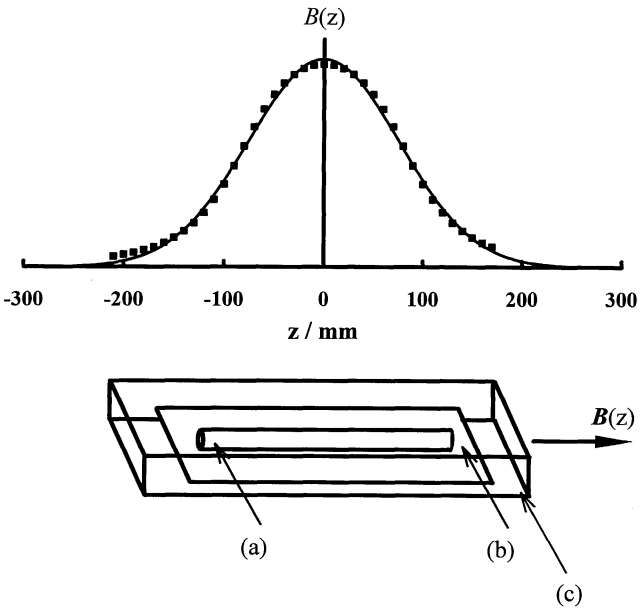

Figure 1. Distribution of magnetic field in a bore (top) and the outline of experimental handling (bottom) (a) a copper wire (6 ϕ × 250 mm), (b) a sheet (40 mm × 300 mm)of filter paper soaked with silver nitrate solution (0.5 mol dm^{-3}), and (c) a plastic vessel (40 mm × 380 mm × 10 mm).

The solid-liquid redox reaction studied here is given by the following reaction,

$$2Ag^{+} + Cu \longrightarrow 2Ag\downarrow + Cu^{2+} \quad (1)$$

Because of the order of ionization tendency, silver metal deposits from the silver nitrate solution soaked into a piece of filter paper when a copper wire is placed on the paper. Figure 2 shows the effects of magnetic fields on deposition of silver. At zero field, silver metal deposited uniformly around the copper wire. In the presence of the magnetic field (5 T) the deposition at the center of the wire decreased slightly. When the reaction was carried out in the magnetic field of 8 T, the yield of silver decreased drastically in the neighborhood of the center of the wire. No specific change of pattern was observed at the position of z = 0, where $d\boldsymbol{B} / dz = 0$. The fine shapes of the deposition pattern at $z \approx \pm 50$ mm slightly depended on each run.

For the purpose of comparison, similar solid-liquid redox reactions shown below were examined,

$$2Ag^{+} + Sn \longrightarrow 2Ag\downarrow + Sn^{2+} \quad (2)$$

$$2Ag^{+} + Zn \longrightarrow 2Ag\downarrow + Zn^{2+} \quad (3)$$

$$Cu^{2+} + Sn \longrightarrow Cu\downarrow + Sn^{2+} \quad (4)$$

When tin and zinc wires were used (Reactions 2 and 3), silver metal deposited uniformly regardless of a magnetic field (8 T). On the other hand, in the case of copper deposition (Reaction 4), copper metal deposited mainly at the center of the wire when the field was applied.

Now let us consider the mechanism of magnetic field effect (MFE) shown in Figure 2. Generally speaking there are three mechanisms to explain the effect. The first is the magnetohydrodynamics (MHD) mechanism, the second is the difference in the Gibbs free energies in the magnetic fields,[5] and the third is the magnetic force caused by a gradient magnetic field.[4]

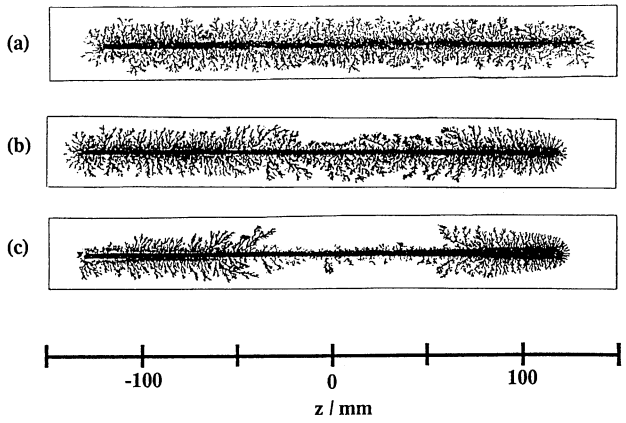

Figure 2. The depositions of silver metal under magnetic fields. B_{max} are (a) 0 T, (b) 5 T, and (c) 8 T, respectively.

In the case of MHD mechanism, MHD force $\boldsymbol{F}_{MHD}$ is given by the following equation,

$$\boldsymbol{F}_{MHD} = e\boldsymbol{v} \times \boldsymbol{B} \tag{5}$$

where e is the electric charge, $\boldsymbol{v}$ is its velocity, and $\boldsymbol{B}$ is the magnetic field. MHD force $\boldsymbol{F}_{MHD}$ gives charge 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 $\boldsymbol{B}$ is parallel. Therefore, this mechanism does not explain the experimental results shown in Figure 2, since the direction of the flow of ions is parallel to that of the magnetic field. Okubo et. al. applied the magnetic field perpendicular to the direction of the growth of metal depositions, and discussed the effects of MHD upon metal depositions.[6]

The difference in the Gibbs free energy ΔG, which is induced by the difference between magnetic susceptibility of ions and that of metals, is

$$\Delta(\Delta G) = -\frac{1}{2}\frac{1}{\mu_0}\Delta\chi \boldsymbol{B}(\mathrm{z})^2 \tag{6}$$

where $\Delta\chi$ is the difference between molar magnetic susceptibilities χ of ions and that of metals and μ_0 is magnetic permeability. $\boldsymbol{B}(\mathrm{z})$ is the magnetic field at the position which is z mm apart from the center of the magnetic field in the bore. The difference in the Gibbs free energy ΔG at the center and edge of the wire may induce a shift of equilibrium points of redox reaction. By assuming that molar magnetic susceptibilities of copper, copper ion, silver, and silver ion are $-4\pi \times 5.46 \times 10^{-6}$ cm^3mol^{-1}, $+4\pi \times 1.28 \times 10^{-3}$ cm^3mol^{-1}, $-4\pi \times 2.05 \times 10^{-5}$ cm^3mol^{-1}, and $-4\pi \times 2.4 \times 10^{-5}$ cm^3mol^{-1} respectively, and magnetic fields at the center and the edge of the wire are 8 T and 2 T, the difference in the free energies between the center and edge of the wire is estimated to be 9.6×10^{-2} J. Then the electromotive force was estimated to be 2.0×10^{-6} V. This value is too small to explain the MFE shown in Figure 2.

On the other hand, the magnetic force $\boldsymbol{F}_{GMF}$ induced by the magnetic field gradient is given,[7]

$$\boldsymbol{F}_{GMF} = \chi\frac{1}{\mu_0}\frac{d\boldsymbol{B}(\mathrm{z})}{dz}\boldsymbol{B}(\mathrm{z}) \tag{7}$$

If a sign of χ is positive, ions are accelerated to the higher field. In the case of a negative sign, ions are accelerated to the lower field. Silver, tin and zinc ions are diamagnetic, whereas copper is paramagnetic. Silver, tin and zinc ions are repelled by the gradient field, whereas copper ion is attracted by the field. From Equation (7) the maximum magnetic forces for copper and silver ions are estimated to be 4.9 N mol^{-1} and -9.2×10^{-2} N mol^{-1} respectively under our experimental condition (8 T). The force affect copper ion is about one-fifth of gravity. Thus, it is most reasonable to consider that paramagnetic copper ion is the key species for the MFE shown in Figure 2, since redox reactions (2) and (3) exhibited no MFE and the deposition of copper (Reaction (4)) shows the MFE opposite to the effect shown in Figure 2. If the diamagnetism of silver ions operates effectively, reactions (2) and (3) will exhibit MFE. Because of this concentration gradient, the copper wire and silver nitrate solution constitute an electric cell due to the concentration gradient. Furthermore the observed MFE does not seem to be explained solely by the acceleration of copper ion to the center. It is because the observed MFE was very small when the wire was cut into three short pieces (length = 50 mm) and placed at intervals of 50 mm. As a result the deposition of silver mainly may occur at two ends of the wire, whereas the ionization of copper may occur mainly at the neighborhood of the center of the wire. Electric current flows in the wire to compensate the electric charge generated by the reaction at two ends and the center of the wire.

In conclusion, the effect shown in Figure 2 seems to attributable chiefly to the magnetic force (Equation (7)), which attracts paramagnetic copper ions to the higher magnetic field. This may induce the difference in the ΔG between the edge and the center of the wire. Detailed analysis of the effect is now in progress and will be reported soon.

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