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# The Effect of Very High Magnetic Fields on Cyclic Voltammetry

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The cyclic voltammetry of ferrocene and *p*-benzoquinone in *N*,*N*-dimethylformamide and acetonitrile was inverstigated under very high magnetic fields up to 140 kOe (1 kOe=(1/4π)×10³ A m⁻¹). Plateaus of limiting currents were observed on cyclic voltammograms, and the limiting currents were remarkably enhanced by magnetic fields. These results were explained as the enhancement of mass transfer, which is caused by a magnetohydrodynamic convection. This effect was found to be pronounced at the slow potential scan rate of 10 mV s$^{-1}$ in a low viscosity solvent like acetonitrile, where the current is controlled by not only mass transfer but also the electron transfer rate. The current enhancement was also observed in anodic stripping on the cyclic voltammogram of $Cu^{2+}$ above 100 kOe.

The application of a high magnetic field to studies of chemical reactions is of great interest in connection with the magnetic field effect on a biological system. In some chemical reactions including organic radicals, the rate of intersystem crossing between triplet and singlet states is appreciably affected by magnetic fields.[1,2] However, there have been only a few papers dealing with fields exceeding 100 kOe: An example is concerned with the chemical equilibrium of the $LaCo_5$–H system.[3]

On the other hand, the effect of magnetic fields on electrolytic redox behavior has been investigated by many workers.[4–7] For electrolysis on a steady electrode, the enhancement of a limiting diffusion current was observed in the presence of a relatively weak magnetic field below 10 kOe.[7] The result is interpreted as a consequence of the magnetohydrodynamic (MHD) effect on electrolytic solution. When an external magnetic field is imposed on electrolytic cell, the Lorentz force causes streams and enhances the rate of mass transfer. Fahidy[8] predicted that the current could be wholly convective in very high magnetic fields up to 150 kOe. In addition, Gak and Rokhinson[9] proposed the application of the MHD effect with high magnetic fields to controlling a convective transfer velocity in electrolytes. However, electrochemical measurements have not been carried out in such a high magnetic fields.

In this paper, we first investigate cyclic voltammetry in very high magnetic fields up to 140 kOe. If a diffusion current turns into a convective one in a high magnetic field, the cyclic voltammogram is expected to change into a limiting current curve. In order to examine this, we deal with the reversible redox systems of ferrocene and *p*-benzoquinone in aprotic solvents. In addition, we report the high magnetic field effect on anodic stripping in cyclic voltammetry of $Cu^{2+}$.

## Experimental

**Reagents.** All reagents used in the present experiments are guaranteed ones of Kanto Chemicals. Molecular sieves were used to eliminate water from nonaqueous solvents of *N*,*N*-dimethylformamide (DMF) and acetonitrile.

**Apparatus and Procedures.** The experiments with high magnetic fields were performed at the High Field Laboratory for Superconducting Materials of Tohoku University. Magnetic fields were produced by the water-cooled resistive magnet, so-called Bitter magnet, with the maximum field of 150 kOe in a 80 mm bore at room remperature.

The diagram of the measurement of cyclic voltammetry in a magnetic field is shown in Fig. 1. A Pt-disk electrode with the diameter of 1.6 mm was used as a working electrode (WE), and a Pt-wire was used as a counter electrode (CE). An applied magnetic field $H_0$ was perpendicular to the surface of the working electrode. The reference electrode (RE) was a AgCl/Ag electrode. Cyclic voltammograms were obtained with a Nikko Keisoku potentiogalvanostat model NPGFZ-2501A containing a function generator and a YEW type-3086

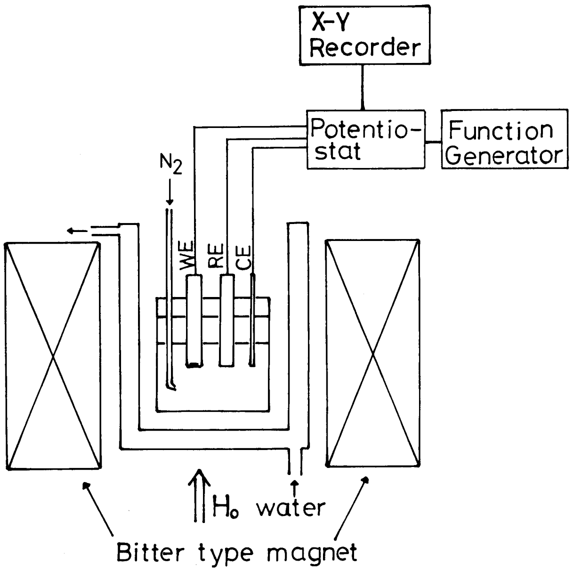

Fig. 1. Schematic diagram of the experiment for cyclic voltammetry in very high magnetic fields $H_0$. WE; working electrode, RE; reference electrode, CE; counter electrode.

X–Y recorder. Temperature was controlled at 25.0±0.1 °C by the water circulating system. The test solutions were deaerated for ca. 20 min with nitrogen gas before measurements. The working electrode was polished each time at the measurements of anodic stripping. Supporting electrolytes were 0.1 mol dm$^{-3}$ tetrabutylammonium perchlorate (TBAP) in the nonaqueous solutions and 0.1 mol dm$^{-3}$ sodium perchlorate in the aqueous solution.

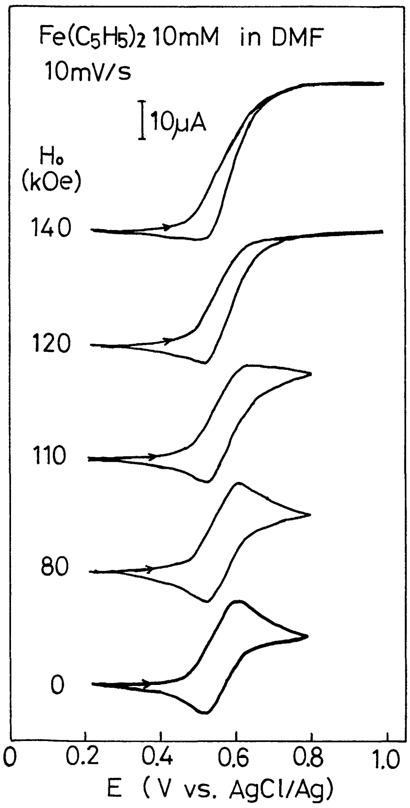

Fig. 2. Cyclic voltammograms of 10 mmol dm$^{-3}$ ferrocene in *N*,*N*-dimethylformamide under various magnetic fields $H_0$. The supporting electrolyte is 0.10 mol dm$^{-3}$ tetrabutylammonium perchlorate. The potential scan rate is 10 mV s$^{-1}$.

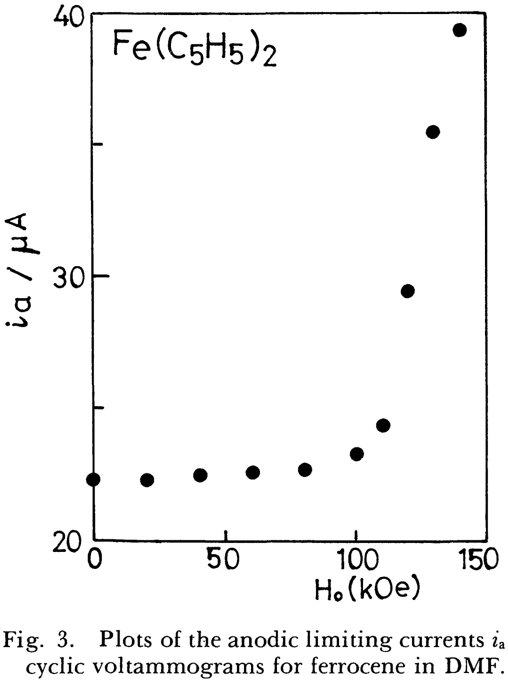

Fig. 3. Plots of the anodic limiting currents $i_a$ of the cyclic voltammograms for ferrocene in DMF.

## Results and Discussion

**Ferrocene.** Ferrocene and ferricinium ion are one of the most typical redox couples. Figure 2 shows the cyclic voltammograms of 10 mmol dm$^{-3}$ ferrocene in DMF at the scan rate of 10 mV s$^{-1}$ under various magnetic fields. The anodic limiting currents $i_a$ are plotted in Fig. 3. A remarkable change in the voltammogram was not observed below 100 kOe, except that $i_a$ slightly increases with the magnetic field. When the magnetic field increases above 120 kOe, a plateau of the anodic limiting current appears and the voltammogram approaches a limiting current curve. In such a field region, $i_a$ increases rapidly with the magnetic field.

When a magnetic field is applied to an electrolytic cell, the Lorentz force acting on ions induces convection of a solution, and hence decreasing the thickness of a diffusion layer. For steady state electrolysis, this MHD effect is reflected in the current enhancement. On the other hand, for cyclic voltammetry the MHD effect is reflected in the shape of a voltammogram. In the present case, an applied magnetic field is perpendicular to the surface of the working electrode. Thus, a remarkable change is not observed in the voltammogram so long as the current is controlled by diffusion. This is the case below 100 kOe. As the magnetic field increases above 120 kOe, the convection becomes so violent that the current is controlled by not only diffusion but also convection. As a result, the voltammogram approaches a limiting current curve. In such a field region, the limiting current increases with the magnetic field because the MHD flow rate is proportional to the square root of the Lorentz force.[6)]

At the scan rate of 200 mV s$^{-1}$ no change of the cyclic voltammogram was observed in the magnetic field up to 140 kOe. It is well-known that the thickness $\delta$ of a diffusion layer depends on a time $t$ as $\delta=(\pi Dt)^{1/2}$, where $D$ represents a diffusion constant. Thus, the diffusion layer at the scan rate of 200 mV s$^{-1}$ is thinner than that at 10 mV s$^{-1}$. Hence, the influence of the convection on the diffusion layer is less effective at the fast potential scan, and the cyclic voltammogram does not change even in the field of 140 kOe.

***p*-Benzoquinone.** The MHD effect should depend on viscosity of a solvent. In order to examine this, we measured cyclic voltammetry of *p*-benzoquinone in DMF and acetonitrile. Figures 4 and 5 show the magnetic field dependence of cyclic voltammograms for 10 mmol dm$^{-3}$ *p*-benzoquinone at 10 mV s$^{-1}$ in DMF and acetonitrile, respectively. *p*-Benzoquinone is reduced by one electron to a relatively stable

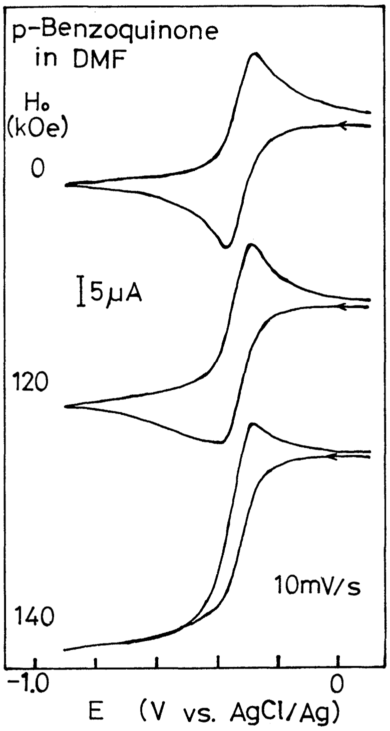

Fig. 4. Cyclic voltammograms of 10 mmol dm$^{-3}$ *p*-benzoquinone in DMF under various magnetic fields. The supporting electrolyte is 0.10 mol dm$^{-3}$ TBAP. The potential scan rate is 10 mV s$^{-1}$.

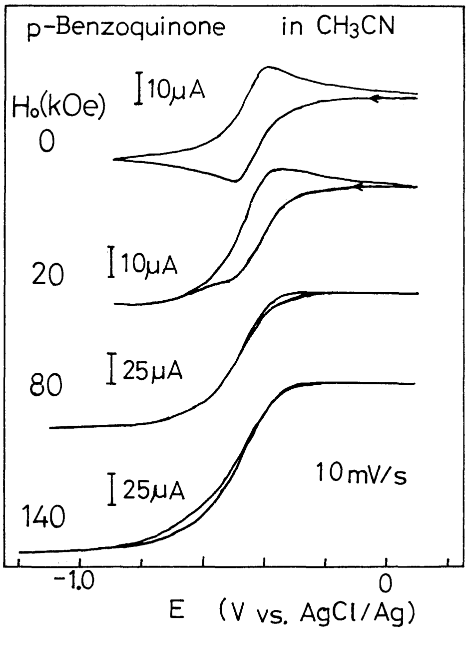

Fig. 5. Cyclic voltammograms of 10 mmol dm$^{-3}$ *p*-benzoquinone in acetonitrile under various magnetic fields. The supporting electrolyte is 0.10 mol dm$^{-3}$ TBAP. The potential scan rate is 10 mV s$^{-1}$.

semiquinone radical in an aprotic solvent.[10] In DMF a remarkable change is not observed below 120 kOe. The plateau of the cathodic limiting current emerges

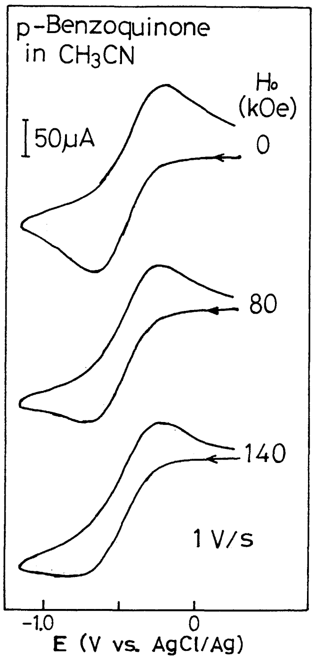

Fig. 6. Cyclic voltammograms of 10 mmol dm$^{-3}$ *p*-benzoquinone in acetonitrile under various magnetic fields. The supporting electrolyte is 0.10 mol dm$^{-3}$ TBAP. The potential scan rate is 1 V s$^{-1}$.

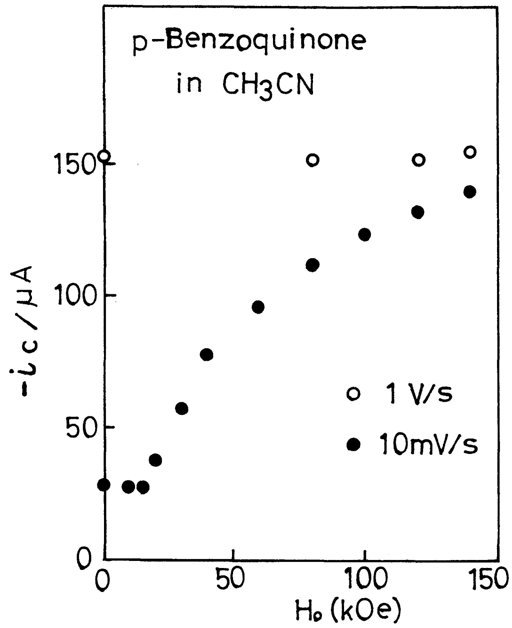

Fig. 7. Plots of the cathodic limiting currents $i_c$ of cyclic voltammograms for *p*-benzoquinone in acetonitrile.

in the high field of 140 kOe. On the other hand, the cyclic voltammogram drastically changes in acetonitrile. The plateau appears above 20 kOe and the reverse wave almost treads back on the forward wave in the field higher than 80 kOe. The potential $E_L$ that reaches the cathodic limiting current is −0.50 V at zero magnetic field. (In this case $E_L$ is equal to the cathodic

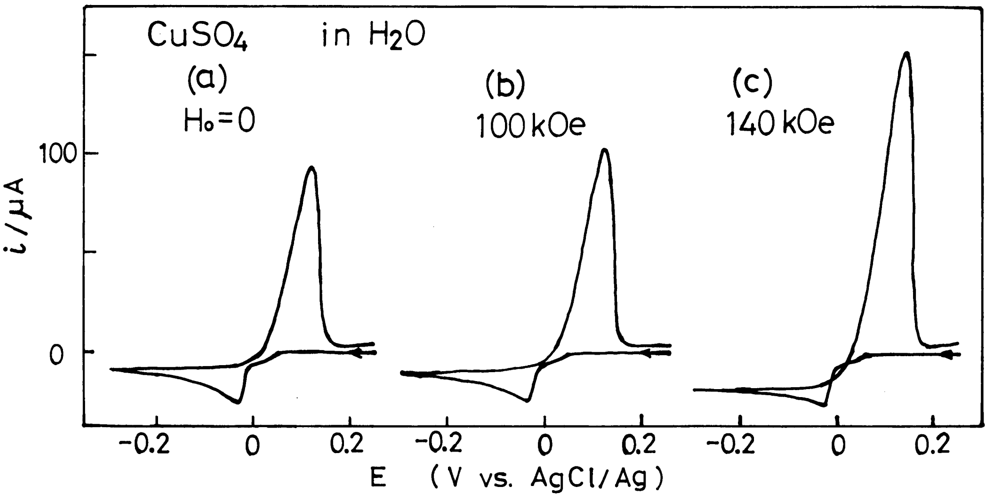

Fig. 8. Cyclic voltammograms of 5.0 mmol dm$^{-3}$ $CuSO_4$ in the aqueous solution under various magnetic fields. The supporting electrolyte is 0.10 mol dm$^{-3}$ $NaClO_4$. The potential scan rate is 10 mV s$^{-1}$.

peak potential.) It is found that $E_L$ shifts to a negative side with increasing the magnetic field and it is ca. −1.1 V at 140 kOe. In contrast with the case of ferrocene in DMF, the MHD effect on *p*-benzoquinone in acetonitrile can be distinguished even at the fast potential scan rate of 1 V s$^{-1}$, as shown in Fig. 6. The cathodic limitig currents $i_c$ in acetonitrile are plotted against the magnetic field in Fig. 7. The limiting current is independent of the magnetic field at the fast scan rate of 1 V s$^{-1}$. On the other hand, in the case of the slow scan rate of 10 mV s$^{-1}$, $i_c$ rapidly increases above 20 kOe and then tends to approach the saturation.

The coefficients of viscosity for DMF and acetonitrile are 7.96 and 3.39 millipoises, respectively. It is easy to understand that the MHD effect on the acetonitrile solution is larger than that on the DMF solution. The viscous solvent is liable to resist the MHD convection.

As mentioned above, in the case of acetonitrile at the scan rate of 10 mV s$^{-1}$, $E_L$ shifts to a negative side with increasing the magnetic field. This indicates that the rate-determining step of the electrode reaction turns from the mass transfer into the electron-transfer process. In such a case the voltammetric current is controlled by both mass transfer and the rate of electron transfer. This result is conceivable when the MHD convection of a low viscosity solution becomes violent in high magnetic fields.

**Anodic Stripping.** In electrolysis of a metal ion the reduced metal is deposited on an electrode. As mentioned above, the MHD convection enhances mass teansfer to the surface of a working electrode. Thus, it is expected that a magnetic field increases the quantity of a deposited metal, which can be measured by anodic stripping. Figure 8 shows cyclic voltammograms of 5.0 mmol dm$^{-3}$ $CuSO_4$ in an aqueous solution under various magentic fields. The peak at 0.12 V corresponds to the anodic stripping of Cu. The anodic peak currents $i_a$ are plotted against the magnetic field in Fig. 9, where $i_a$ rapidly increases above 100 kOe. Because the current of anodic stripping is proportional to the quantity of a deposited metal on a working electrode, the observed results indicate that mass transfer to the electrode surface is enhanced in the field higher than 100 kOe. In this magnetic field region the cathodic current is controlled by diffusion and the MHD convection.

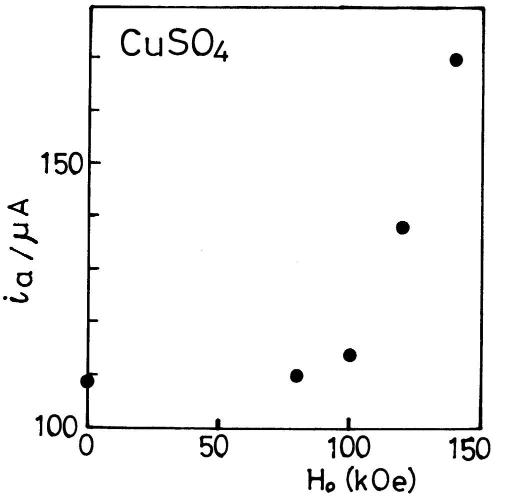

Fig. 9. Plots of the peak currents $i_a$ for anodic stripping of Cu.

## Conclusion

Our experiments are the first example of electrochemical measurements under very high magnetic fields up to 140 kOe. In cyclic voltammetry, the shape of a voltammogram depends on a magnetic field. When a magnetic field is applied perpendicular to the surface of a working electrode, the diffusive motion of electrolytes should not be influenced by the magnetic field. Thus, a remakable change should not be observed in a cyclic voltammogram so long as the current would be controlled by diffusion. As the MHD flow rate increases with the magnetic field, the current is expected to be controlled by both diffusion and convection. Then the voltammogram changes into a limiting current curve, as observed in the present experiments. It is moreover confirmed that in a low viscosity solvent like acetonitrile the rate-determining step on an electrode reaction turns from mass transfer to an electron-transfer process with increasing the magnetic field. The more quantitative analysis of the magnetic field dependence of cyclic voltammograms is the subject for a future study.

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