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Magnetic Field Effects on Anodic Oxidation of Potassium Iodide

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External magnetic fields ($\leqq$ 6 kG) significantly increase yields of I_3^- and H_2 as well as oxidation currents in anodic oxidation of potassium iodide. The Lorentz force on ions in the solution induces convection of solution, resulting in acceleration of the entire reaction rate. This is further confirmed from the observation that reddish-brown streams of I_3^- in the solution, moving downward at zero field, undergo turbulent motion in magnetic fields.

Very recently, effects of magnetic fields on chemical, physical and biological systems have attracted much attention of many scientists and engineers.[1] This is partly because helium-free superconducting magnets, by which one can generate high magnetic fields without liquid helium, are commercially available and partly because magnetic fields are nowadays recognized as a clean and conventional tool to control various processes. As for electrode reactions, a large number of studies have been reported.[2–15] Most of the effects have been interpreted in terms of a magnetohydrodynamics (MHD) mechanism where the Lorentz force on ions in solution induces convection of solution. For example, one of the present authors has examined the magnetic field effects (MFEs) on inorganic and organic electrode reactions. He and his collaborators showed that the electrolytic currents in anodic oxidation of Fe^{3+} and reduction of Fe^{2+} were affected by the external magnetic fields.[11] In the anodic oxidation of gold, an external magnetic field induced the dissolution of corrosion on the anode surface.[12] In the anodic oxidation of phenyl acetate ions, the yield of benzaldehyde increased by application of a magnetic field of 0.6 T.[13] All the results are interpreted in terms of the MHD mechanism. Very recently, Mogi and his coworkers showed that the MFEs on electrode deposition of silver metal[14] and electropolymerization of pyrole[15] could be explained by the MHD mechanism. As briefly mentioned above, there are many reports about the MFEs on electrode reactions. However, most of them have been concerned with the effects on a part of a reaction, i.e., anodic current or product yield. We believe that it is very important to examine the effects at various steps in a reaction to fully understand the mechanism of the effects.

In this paper we have studied the anodic oxidation of potassium iodide in detail, in order to clarify how an external magnetic field affects an *entire* electrode reaction. This reaction is a simple and important reaction to determine the Coulomb number of an electrode reaction.[16] We have chosen this reaction since we can easily detect product yields at two electrodes as well as electrolytic current and since it is suitable to visualize hydrodynamics of the electrolytic solution in magnetic fields.

Experimental

Potassium iodide (Wako, GR grade) was used as supplied. Water was distilled. Figure 1 shows a schematic diagram of the present experimental set-up. Our electrolysis cell (92 mm × 96 mm × 47 mm) was equipped with a working electrode (WE; 10 mm × 6 mm × 0.2 mm, Pt) whose one surface was covered with epoxy resin, a counter electrode (CE; 15 mm × 20 mm × 0.2 mm, Pt), a reference electrode (RE; Ag/AgCl), and an electrolytic solution (1 M KI, 200 ml). The cell was placed between poles of an electromagnet (TOKIN, SEE-10, pole diameter 45 mm). The distance between WE and CE was about 50 mm. The surface of WE was parallel to the magnetic flux. A magnetic field did not affect the RE potential. The electrolysis was carried out using a potentiostat/galvanostat (Hokuto Denko, HA-301) at room temperature. Yields of I_3^- were calculated from the absorbance of I_3^-, its molar extinction coefficient at 500 nm being assumed to be 281 M^{-1} cm^{-1}. Yields of H_2 were measured by collecting the H_2 gas at CE. Hydrodynamics of the solution in magnetic fields were recorded by a video camera.

Results

The pathways of anodic oxidation of KI are as follows:

$$2I^- \rightarrow I_2 + 2e^- \qquad \text{(at anode)} \qquad (1)$$

$$I_2 + I^- \rightarrow I_3^- \qquad (2)$$

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \qquad \text{(at cathode)} \qquad (3)$$

The reaction is composed of oxidation of I^- to I_2 at WE and reduction of H_2O to H_2 at CE. I_3^- is formed by the reaction of I_2 and I^- near WE. I_3^- is reddish-brown and its density is heavier than that of the 1 M KI solution. Therefore, the MFEs are studied on the yields of anodic current, I_3^- ion (anode) and hydrogen gas (cathode). Furthermore, the hydrodynamics of solution can be visually observed.

The magnetic field dependence (MFD) of anodic currents is determined at 5 min after each potential is applied, when the current becomes stationary. The currents are approximately 27 (0.4 V), 58 (0.5 V), 75 (0.6 V), 76 (0.7 V), and 75 mA/cm^2 (0.8 V) at zero field, and these increase with increasing magnetic

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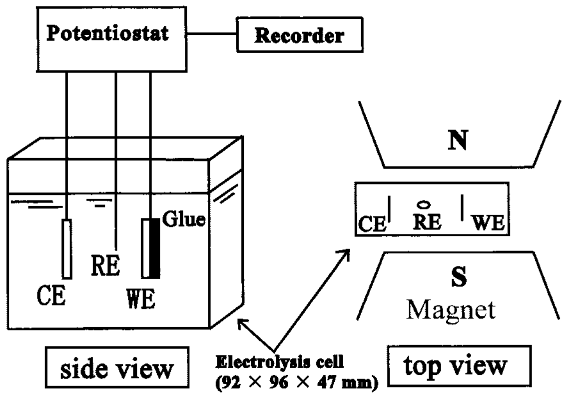

Fig. 1. Schematic diagram of the experimental setup. WE, working electrode; CE, counter electrode; RE, reference electrode

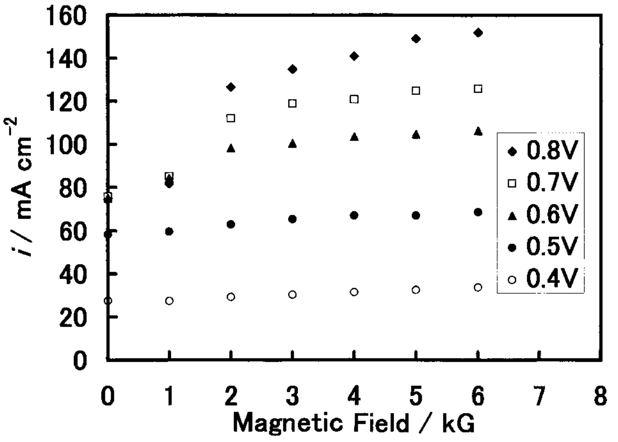

Fig. 2. Magnetic field dependence of the anodic current at several electrode potentials.

field, as shown in Fig. 2. When the potential is 0.8 V, the anodic current at 6 kG is about two times larger than that at zero field. The currents around 1 kG are always slightly smaller than the values estimated from those at high fields. In the case of the current at 0.4 V, a very shallow dip (1–2%) is observed around ca. 1 kG, though it is not apparent in the figure. These unusual behaviors are attributable to the convection induced by the Lorentz force on ions, as discussed later.

The MFEs are further analyzed on the yields of I_3^- and H_2 gas at the potential of 0.7 V where significant effects are observed. Figure 3 shows the MFD of the yield of I_3^- at 0.7 V after a reaction time of 5 min. The yield is ca. 1.2×10^{-4} mol at zero field and it increases with increasing the magnetic field. The change is about 125% at 6 kG.. The yield at zero field is in agreement with the value (1.1×10^{-4} mol) estimated from the quantity of electricity in the 5 min reaction.

Figure 4 shows the MFD ($\leqq$ 2 kG) of the yield of H_2 gas at 0.7 V. We could not collect the gas in the magnetic field above 2 kG because of convection of the solution, as discussed later. The yield after 5 min reaction is 1.3×10^{-4} mol at zero field, which is in agreement with the values obtained from both the quantity of electricity and the I_3^- yield. The yield also increases with increasing the magnetic field (140% at 2 kG).

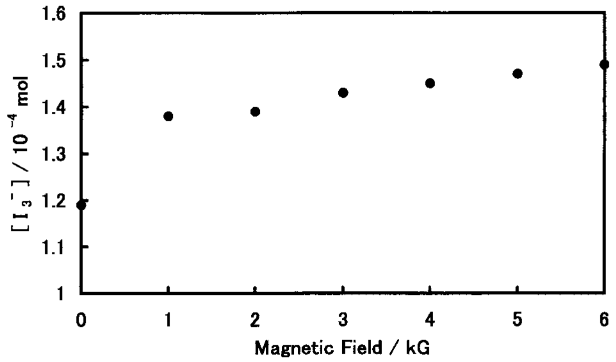

Fig. 3. Magnetic field dependence of I_3^- yield after 5 min reaction at 0.7 V.

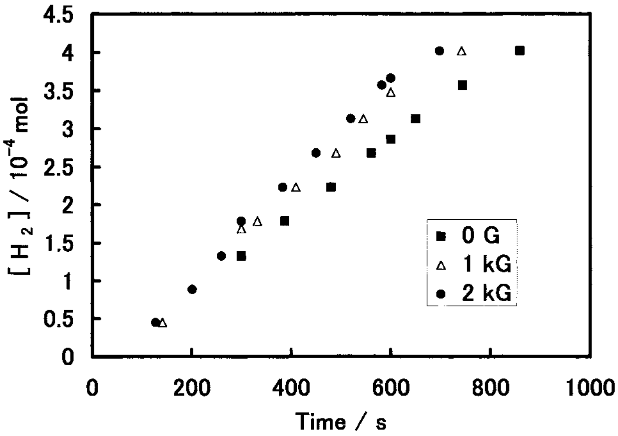

Fig. 4. Magnetic field dependence of H_2 yield at 0.7 V.

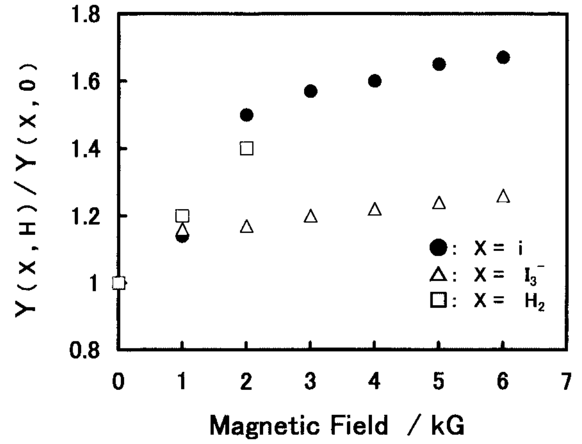

Fig. 5. Magnetic field dependence of the ratios of the anodic current and product yields. Y(X, H) and Y(X, 0) are the yield of X (i.e., anodic current, I_3^-, or H_2) in the presence and absence of a magnetic field, H.

Figure 5 summarizes the results shown in Figs. 2–4. For the purpose of comparison, the ratios of each product yield and the current in the presence or absence of a magnetic field are taken as the ordinate in the figure. The product yields at both WE (I_3^-) and CE (H_2) as well as the anodic current increase in the presence of the magnetic fields, indicating that the overall re-

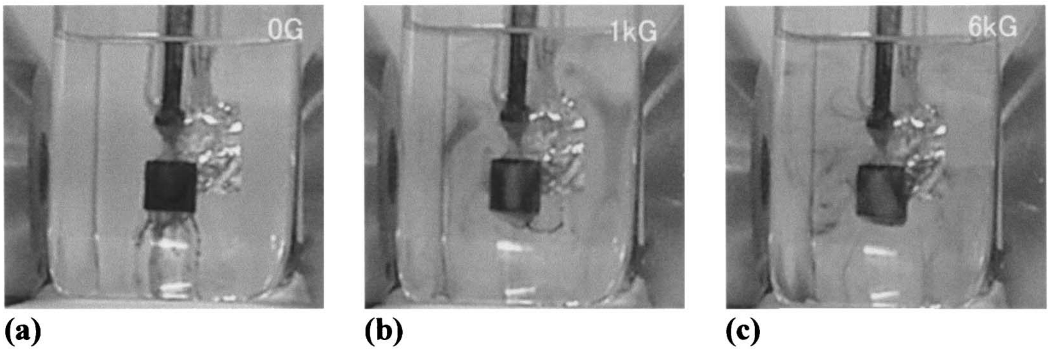

Fig. 6. Video images of the electrolyte solution in magnetic fields. (a) 0 G. (b) 1 kG. (c) 6 kG. The electrode at near side is WE and the rugged one at far side is CE. For the purpose of visual inspection, the WE surface is turned by 180 degree from the orientation schematically shown in Fig. 1.

action is certainly enhanced by the magnetic field. The MFE on the yield of I_3^- is much smaller than on that of H_2 and anodic current, as shown in Fig. 5. This occurs because of the reaction of I_3^- generated at WE and OH^- generated at CE:[16]

$$3I_3^- + 6OH^- \rightarrow IO_3^- + 8I^- + 3H_2O \tag{4}$$

In the magnetic field, the MHD-induced convection of the solution accelerates this reaction significantly. Therefore, I_3^- ions generated at WE are consumed partly by application of magnetic fields.

Finally, we visually observed the MFE on the hydrodynamics of the solution in the cell. Figure 6 shows video images of the solution electrolyzed at 0.7 V in magnetic fields. In this experiment, the WE surface is rotated by 180 degrees from the original orientation schematically shown in Fig. 1, for the purpose of visual inspection. At zero field, the WE surface gradually turns to reddish-brown after application of the electric potential of 0.7 V. Then, streams of reddish-brown solution of I_3^- formed near WE flows downward, as the material is more dense than that of the 1 M KI solution. At 1 kG the solution is partly retained near the electrode surface and partly undergoes convection in the cell. By application of the magnetic field of 6 kG, the entire solution in the cell undergoes turbulent motion intensively. The WE surface becomes bright in magnetic fields. This means that the supply of bulk solution to the WE surface and therefore the removal of product(s) from the surface are efficient in magnetic fields. From the analysis of video images, the MHD flow rate can be roughly estimated to be 16 mm s^{-1} at 6 kG, whereas the downward flow rate of I_3^- near WE is approximately 2 mm s^{-1} at zero field.

We further examined the motion of streams of I_3^- ions in a weak magnetic field of ca. 500 G, since it is slow enough to be followed visually. At 500 G, streams of I_3^- ions move by heading under WE for the far side of the cell. When the direction of the magnetic field is reversed, streams of I_3^- ions move upward and go over WE for the far side of the cell. The directions of streams of I_3^- ions in the magnetic fields are more or less similar when the WE surface is at its original orientation.

Discussion

The MFEs shown in Figs. 2–5 can be interpreted in terms of magnetohydrodynamics (MHD) mechanism.[2–4] In this mechanism, the Lorentz force $\boldsymbol{F}_\mathrm{L}$ is induced to electrolytic current density $\boldsymbol{i}$ in the presence of a magnetic field $\boldsymbol{H}$,

$$\boldsymbol{F}_\mathrm{L} = \boldsymbol{i} \times (\mu \boldsymbol{H}) \tag{5}$$

where μ is the magnetic permeability. Due to this Lorentz force on ions in solution, convection of the solution takes place by application of a magnetic field (MHD flow).

At zero field, I^- ions are supplied from a bulk solution to the WE surface, where an electrochemical reaction takes place, by such mass-transport processes as diffusion, natural convection and electrophoretic migration. In the present experiment, the surface of WE is covered with a reddish-brown layer, as visually confirmed. Thus the reaction rate at zero field is considered to be partly controlled by the rate of removal of product (I_2 or I_3^-) from the anode surface, most probably due to the natural convection. By application of a magnetic field, the MHD flow of solution is induced. In the present experimental condition, the direction of the flow is upward, as depicted in Fig. 7. This flow supplies fresh bulk solution rich with I^- ions to the surface and removes the layer of solution rich with product(s) (i.e., I_2 and/or I_3^-) covering the WE surface. As a result of magnetic convection of the solution, the net reaction rate is accelerated by the application of high magnetic fields. At the same time, the I_3^- consuming reaction Eq. 4 is enhanced. This is why the intensity of the MFE on the I_3^- is smaller than the

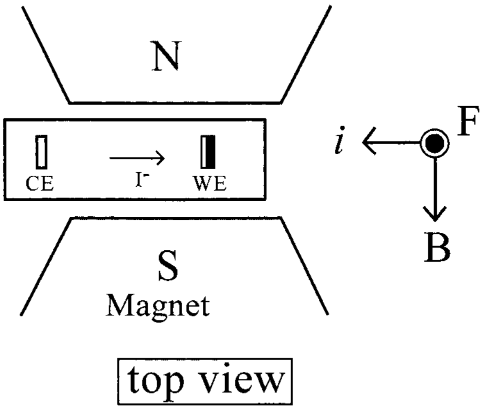

Fig. 7. Mechanism of magnetic field effects.

intensities on H_2 and anodic current in high magnetic fields (Fig. 5).

The MHD flow is visually confirmed as shown in Fig. 6. Hydrodynamic behavior of the solution changes by application of the magnetic field. Downward streams of reddish-brown I_3^- ions at zero field undergo turbulent motion by application of high magnetic fields, as expected. The relationship between the Lorentz force and the motion of streams of I_3^- ions in a magnetic field should be mentioned. As described in Results, at 500 G streams of I_3^- ions move by heading under WE for the far side of the cell. This could be explained as follows. In the magnetic field the solution between two electrodes receives the upward force and therefore flows at upper side of the solution. As a result, a counter flow occurs at the lower side of the solution because of continuity of the flow. Therefore, what we observed by streams of I_3^- ions in magnetic fields seems to be the behavior of this counter flow. If the Lorentz force on ions near WE surface contributes mainly to the convection, the direction of the flow should be downward. This is against the observation. Furthermore, the fact that directions of streams of I_3^- are similar regardless of orientation of the WE surface also supports the idea that the Lorentz force chiefly affect the motion of the solution between two electrodes. The volume of the solution between two electrodes, which is influenced by the magnetic field, would be larger than that of the solution near the WE surface in the present experimental setup. The observation that, when the direction of the magnetic field is reversed, the direction of streams of I_3^- ions is reversed, agrees well with the expectation from Eq. 5.

Finally the influence of the low magnetic field of ca.1 kG will be discussed. The direction of the Lorentz force near the anode surface is upward, which is opposite to that of natural convection due to I_3^-. Therefore, the removal of I_3^- is partly retarded when gravity and the upward weak Lorentz force on I_3^- is balanced. This effect is observed in the MFD of the anodic current density at 0.4 V as a shallow dip in the current vs magnetic field plots. From visual inspection, it is confirmed that a reddish-brown solution, moving downward at zero field, is retained partly near the anode surface by application of a magnetic field of ca.1 kG.

The *entire* solution in the cell undergoes turbulent motion in magnetic fields at the present experimental condition and therefore the MHD behavior of the solution is very complex. It would depend on the size and shape of each cell, the volume of solution, the size of electrodes and so on. Therefore, further analysis on the MHD behavior of the solution was not attempted in this study.

Conclusion

The MFEs on the entire electrode reaction of potassium iodide are studied. The anodic current and the products of anode reaction (I_3^-) and cathode one (H_2) all together increase in yield by application of magnetic fields (≤ 6 kG). These MFEs are interpreted in terms of the MHD mechanism, in which supply of reactant I^- ions from bulk solution is accelerated by the MHD-induced convection. Furthermore, the MHD-induced convection of the solution is visually confirmed via the motion of reddish-brown solution of I_3^- ions. This reaction is ideal to demonstrate the importance of the MHD flow in the electrode reaction in magnetic fields.

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