Electrochemical Measurement of Dissolved Oxygen from Atmosphere under a Magnetic Field Gradient

Shin-ya Kishioka and Ryoichi Aogaki*
National Research Laboratory for Magnetic Science, Japan Science and Technology Corporation, Kawaguchi, Saitama 333-0848

(Received October 5, 1998; CL-980766)

Electrochemical measurement using a steady state voltametry with a microdisk electrode revealed the effect of magnetic field on the acceleration of the dissolution of the atmospheric oxygen molecule into water containing tetraethylammonium-perchlorate as a supporting electrolyte in the initial state.

In recent years, further progress in magnetic science and chemistry for materials of very small magnetic susceptibility has been made, accompanied by successful development of the superconducting magnets with high performance cryocoolers. However, some of these results have been discussed because they seem to lack scientific evidence, especially quantitative one. In order to apply the magnetic field effects to chemical processes, quantitative analyses as well as reliable data are indispensable. On the one hand, there were many reports that a magnetic field affected the concentration of dissolved oxygen in water.[1] From detailed study, as predicted by the thermodynamic theory it was pointed out that the magnetic field influences not the concentration of saturated oxygen but the dissolution rate.[2] For this interesting phenomenon, a qualitative mechanism that the magnetic field gradient in the bore of the superconducting magnet induces the motion of water to increase the dissolution rate of oxygen has been proposed.[2] It might be difficult to measure precisely the concentration of dissolved oxygen during its initial stage by a simple method such as a dissolved oxygen meter using Clark-type oxygen electrode because of the low detection limit. Microelectrode voltammetry is thought on the other hand of great advantage for detecting such trace amount of electroactive molecules.

In the present communication, we will report the voltammetric results in steady state with a microdisk electrode for measuring the concentration of trace amount of oxygen of which dissolution rate is accelerated by the high magnetic field.

Electrolytic solution was prepared with 25 mL of water purified by the passage through a Milli-Q purification train and 0.1 moldm^{-3} tetraethylammonium perchlorate (Wako Pure Chemical) as a supporting electrolyte. The solution was deaerated with Ar gas before the measurements. High-Tc superconducting (HTSC) magnet (7 Tesla type, Sumitomo Electric Industries) was used and the measurement of the distribution of the magnetic field was carried out with a Gauss meter (A. D. S. Co., MODEL HGM 8300-1). A platinum disk microelectrode (BAS Co.) with 15 μ m in diameter and platinum wires were used as the working, the auxiliary and the quasi-reference electrodes, respectively. Electrochemical measurements were performed outside the magnet using a conventional three-electrode potentiostat (NIKKO KEISOKU Co., NPGS-2501-10nA), a function generator (TOHO TECHNICAL RESEARCH Co., FG-02) and an X-Y recorder (RIKEN DENSHI Co., Model F-45). Reduction potential of oxygen was confirmed by the comparison with the data using an Ag/AgCl reference electrode. An experimental setup is shown in Figure 1.

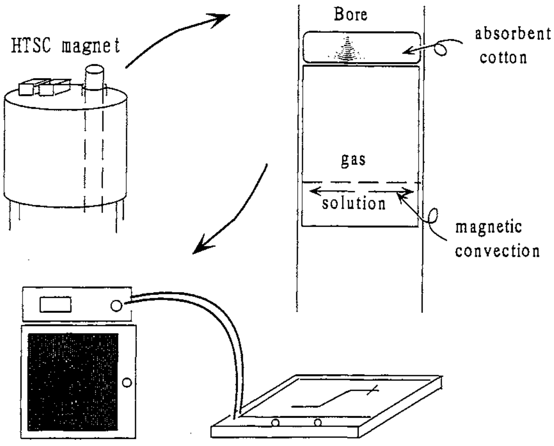

Figure 1. Schematic representation of an experimental setup.

The magnetic field in the magnet bore showed three-dimensional distribution; for the highest value of 7 T at the bore center, as shown in Figure 2(a) the magnetic flux density was changed in z-direction (vertical direction). Figure 2(b) exhibits the distribution of magnetic flux density in x-direction (horizontal distribution) at the maximum point in z-direction. However, since the thickness of the diffusion layer of dissolved oxygen is very thin, we can neglect the vertical change of the magnetic fields, that is, we can assume the uniform distribution in vertical direction, so that only the diffusion process under horizontal distribution of the magnetic field shown in Figure 2(b) is considered. The experimental cell without a cover was settled in the bore center of HTSC magnet, and the gas-solution interface was vertically adjusted to the magnetic

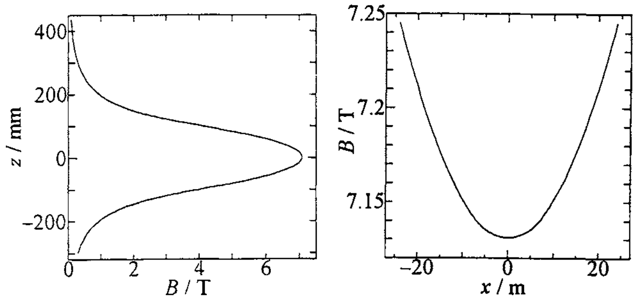

Figure 2. Magnetic field distributions along (a) the perpendicular and (b) horizontal axes of the High-Tc superconducting magnet.

maximum point. After the solution was exposed to magnetic fields up to 7 T for 10 min. and then stirred enough with a cover , steady state voltammograms were measured with a microdisk electrode outside the HTSC magnet.

Figure 3 indicates the current-potential curves measured above. Limiting currents corresponding to 4-electron reduction of oxygen molecule as follows,

$$O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$$

As shown in Figure 3, the dissolution rate of oxygen increases with magnetic flux densities. The values of these limiting currents are proportional to the concentration of electroactive species in the following equation,[3]

$$I_{ss} = 4nFc^*Da$$

where I_{ss} the limiting current, n the number of electron, F Faraday constant, c^* the concentration of species O_2, D the diffusion constant and a is the diameter of a microdisk electrode. From this relation, we can obtain the concentration of dissolved oxygen. In the present study, we adopted 2.07 × 10^{-5} cm^2s^{-1} as the value of D.[4] The dependence of the total amount of oxygen dissolved during initial 10 min. on the intensity of the magnetic field is shown in Figure 4. Considerable increase of the concentration was observed at the magnetic field higher than 4 T shown in dots (a). Under high magnetic fields, as well as the solution, the change in magnetic susceptibility of the atmosphere causes convection of air, which results from the differences in composition or temperature.[5] For the open cell without any cover, such a convection would conversely affect the dissolution process of oxygen inside the cylindrical bore of the HTSC magnet. In contrast loosely stuffing a piece of absorbent cotton above the cell in the bore can remove the effect by the convection as shown in Figure 4(b); the dissolution process of atmospheric oxygen into solution is also promoted by convection of air inside the cylindrical bore, which is induced by magnetic field and in this process, the concentration of oxygen is not directly proportional to the magnetic flux density as expected by intuition. We are now developing the theoretical approach in order to clarify the magnetic field effect on this acceleration process quantitatively.

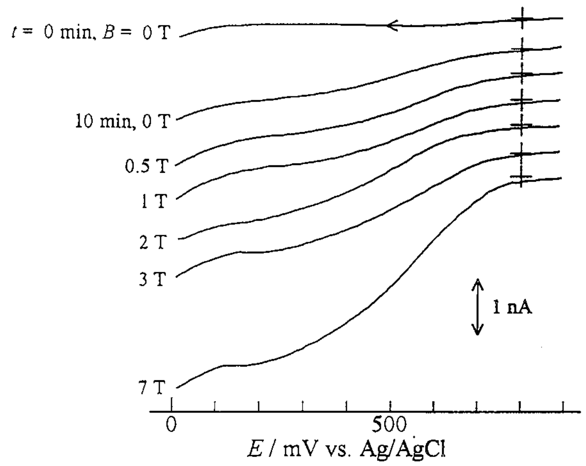

Figure 3. Steady-state voltammograms at Pt microdisk electrode in aqueous solution containing 0.1 moldm^{-3} TEAP exposed to the atmosphere.

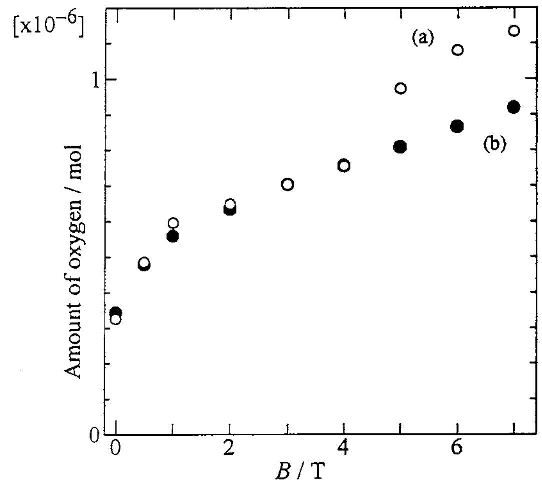

Figure 4. The relationship between the total amount of dissolved oxygen and the intensity of the magnetic field in the absence (a) and presence (b) of absorbent cotton in the bore.

References and Notes

1 For example, S. Ueno, M. Iwasaka and G. Furukawa, *IEEE Trans. Magn.*, **31**, 4259 (1995).

2 Y. Ikezoe, N. Hitora, T. Sakihama, K. Kunio, H. Uematu, T. Honma, J. Nakagawa, H. Sugawara, and K. Kitazawa, *J. Magn. Soc. Jpn.*, **22**, 821 (1998).

3 L. Sinru, J. Osteryoung, J. J. O'Dea, and R. A. Osteryoung, *Anal. Chem.*, **60**, 1135 (1988).

4 M. Tsushima, K. Tokuda, and T. Ohsaka, *Anal. Chem.*, **66**, 4551 (1994).

5 H. Uetake, J. Nakagawa, N. Hirota, and K. Kitazawa, *J. Magn. Soc. Jpn.*, **22**, 833 (1998).