Electrochemical Measurement of Dissolved Oxygen from Atmosphere in a Highly Homogeneous Magnetic Field

Shin-ya Kishioka,*[†,††] Akifumi Yamada,[†] Ryoichi Aogaki,[††] Tsukasa Kiyoshi,[†††] Atsushi Goto,[†††] and Tadashi Shimizu[†††]
[†]*Department of Chemistry, Faculty of Engineering, Nagaoka University of Technology, 1603-1 Kamitomioka, Nagaoka, Niigata 940-2188*
[††]*National Research Laboratory for Magnetic Science, Japan Science and Technology Corporation, 1-1-56 Shimoshiba, Kawaguchi, Saitama 333-0848*
[†††]*National Research Laboratory for Metal, 3-13 Sakura, Tsukuba 305-0003*

(Received March 2, 2000: CL-000210)

In a very highly homogeneous magnetic field generated by the 270 MHz high resolution NMR magnet system, the accelerated dissolution of atmospheric oxygen into water was confirmed.

Using a magnetic force induced by a highly homogeneous magnetic field for experiments such as the crystallization of proteins has attracted much attention as an alternative method for a non-gravitational environment in the Space Shuttle.[1,2] It is due to the development of the superconducting magnet for NMR spectroscopy which has a highly homogeneous magnetic flux density in the magnetic center, followed by advances in superconducting technology.[3] We measured the acceleration process of the dissolution of oxygen from the atmosphere into a liquid using a magnetic field gradient[4] in the bore of a High-Temperature super conducting (HTSC) magnet using an electrochemical method.[5] Furthermore, we postulated that even in a homogeneous magnetic field, the magnetic force caused by the gradient in the magnetic susceptibility of the paramagnetic oxygen in the solution generated the accelerated dissolution process phenomenon and clarified it in a relatively homogeneous magnetic field in the bore of the HTSC magnet.[6] In this case, however, the three-dimensional distribution of the magnetic field in the bore was measured by a Gauss meter with a hole probe and the position in the bore where the experimental cell was placed was determined, so that there existed a slight nonuniformity in the magnetic flux density, especially in the perpendicular direction though it was an inherent feature of the HTSC magnet. Therefore, it is important to confirm this phenomenon in a highly uniform magnetic field. A superconducting magnet for NMR spectroscopy has provided a uniform magnetic field for long time, therefore, it is appropriate to investigate the reaction process in a highly homogeneous magnetic field. For example, an NMR magnet was used to investigate the effect of a magnetic field gradient and homogeneous field up to 9.4 Tesla (T) on the electrode reaction using microdisk electrodes by Ragsclale et al.[7]

In this communication, we describe the initial dissolution process of atmospheric oxygen into water using an NMR magnet.

The 270 MHz high resolution NMR system designed for liquid and solid state NMR (Oxford Instruments Co.) was employed. This magnet generates 6 T at its magnetic center in a persistent mode, which has an 89 mm diameter bore in the perpendicular direction. Since uniformity of the magnetic field at the magnetic center in the bore was guaranteed to be 7 ppm for 10 mm in the horizontal direction, a glass cell of 22 mm diameter was used for the homogeneous magnetic field. The experimental cell without a cover, which was filled with 10 mL of pure water degassed with nitrogen, was placed in the bore center of the NMR magnet, and the gas-solution interface was vertically adjusted to the point where the uniformity of the magnetic field was the highest. After the water was exposed to the 6 T magnetic field for 10 min and then stirred with a cover, the steady state voltammograms were obtained using a microdisk electrode outside the NMR magnet for quantification of the dissolved oxygen. Electrochemical measurements were carried out using a conventional three-electrode potentiostat (Nikko Keisoku Co., NPGS-2501-10 nA), a function generator (Toho Technical Research Co., FG-20) and an X-Y recorder (Rikin Denshi Co., Model F-45). A platinum disk microelectrode with 30 μm diameter, which was locally constructed, was used as the working electrode. Platinum wires were used as the auxiliary and the quasi-reference electrodes. The reduction potential of the oxygen was confirmed by a comparison with the data using an Ag/AgCl reference electrode. The experimental setup is indicated in Figure 1. The NMR magnet has a magnetic flux density distribution in the vertical direction as shown in Figure 2. The point of the magnetic center at a distance of

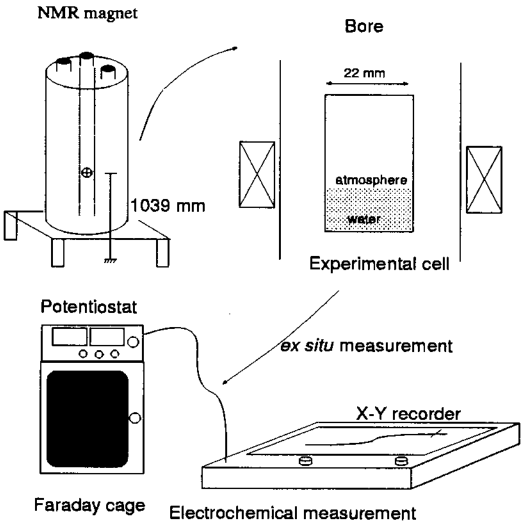

Figure 1. Schematic representation of the experimental setup.

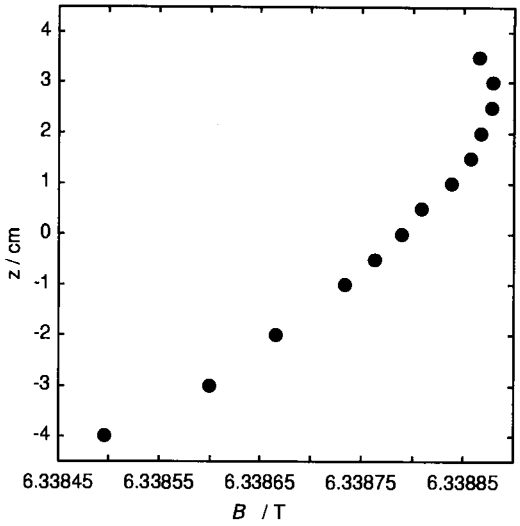

Figure 2. Magnetic field distributions along the perpendicular axis of the high resolution NMR magnet.

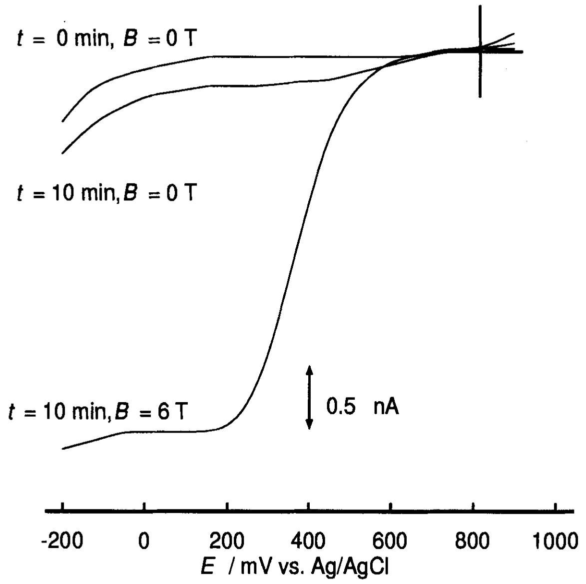

Figure 3. Steady-state voltammograms at Pt microdisk electrode in pure water.

1039 mm from a floor level in the bore of the magnet is assured to be a 7 ppm homogeneous magnetic field of 10 mm in the horizontal direction in which we placed the cell there. Determination of the dissolved oxygen was performed by an analysis of the value of the limiting currents using microelectrode voltammetry as previously noted.[5,6] Figure 3 illustrates the current-potential curves of 10 mL pure water which had been in contact with the atmosphere in the bore under a homogeneous 6 T condition for 10 min. The dissolution of oxygen increases with the 6 T homogeneous magnetic field. The limiting current corresponds to a 4-electron reduction of the oxygen molecule. The values of these limiting currents are proportional

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

to the concentration of the electroactive species, oxygen in this case, in the following equation,[8]

In order to ease the comparison between the present data and previous one,[6] we call the former case A and the latter case B for convenience. The average concentration value of dissolved oxygen was 6.2×10^{-5} mol dm^{-3} (case A). The oxygen concentration value was converted into a volume of 6.2×10^{-7} mol, indicating that this value was smaller than the previous one (1.2×10^{-6} mol in 10 mL of water, case B)[6]. These experimental conditions were almost the same except for the intensity of the homogeneous magnetic field and the diameter of the experimental cell, as we used over a 1.0 T conditions, and the amount of dissolved oxygen was almost a constant value.[6] As one probable reason for the difference in the concentration of dissolved oxygen, we can consider the difference in the diameter of the experimental cell. The diameter of the cell in case B (32.5 mm), as we previously reported, was larger than that in case A (22 mm), resulting in an area where the water contacted the atmosphere in case A being about twice that of case B. If we take into account the volume of dissolved oxygen from the stand point of the flux, f, which is normalized in time (t = 600 s) and the area of the interface ($S = \pi(r/2)^2$), the values of f_A and f_B are 6.80×10^{-11} mol cm^{-2} s^{-1} and 6.03×10^{-11} mol cm^{-2} s^{-1}, respectively. These values are in fair agreement with each other and indicate the acceleration of oxygen dissolution would occur in a highly homogeneous three-dimensional magnetic field. In addition, though the HTSC magnet had a relatively uniform magnetic field in the horizontal direction, there was a small magnetic field gradient in the perpendicular direction at the same point in case B, therefore, paramagnetic oxygen should be subject to a magnetic force in the upward direction. This can explain that the dissolution flux in case A is a slightly larger than that in the previous case B. Thus, the acceleration of atmospheric oxygen dissolution into water can certainly occur in highly homogeneous magnetic field generated by an NMR magnet.

References and Notes

1 G. Sazaki, E. Yoshida, H. Komatsu, T. Nakada, S. Miyashita, and K. Watanabe, *J. Cryst. Growth*, **173**, 231 (1997).
2 N. I. Wakayama, M. Ataka, and H. Abe, *J. Cryst. Growth*, **178**, 653 (1997).
3 T. Miyazaki, Y. Murakami, T. Hase, T. Miyatake, M. Shimada, Y. Kawate, T. Kiyoshi, K. Itoh, and H. Wada, *Cryogenic Engineering*, **33**, 724 (1999).
4 Y. Ikezoe, N. Hirota, T. Sakihama, K. Kunio, H. Uematsu, T. Honma, J. Nakagawa, H. Sugawara, and K. Kitazawa, *J. Magn. Soc. Jpn.*, **22**, 821 (1998).
5 S. Kishioka and R. Aogaki, *Chem. Lett.*, **1999**, 91.
6 S. Kishioka and R. Aogaki, *Chem. Lett.*, **1999**, 473.
7 S. R. Ragsclale, K. M. Grant, and H. S. White, *J. Am. Chem. Soc.*, **120**, 13461 (1998).
8 Y. Saito, *Rev. Polarogr.*, **15**, 177 (1968).
9 A. Yamagishi, *J. Magn. Magn. Mater.*, **90/91**, 43 (1990).