Magnetic Enhancement of Electrochemical Current over Interdigitated Dot Electrodes

Rashko S. Rashkov,†,††,††† Ryoichi Aogaki,†† and Seiichiro Nakabayashi*†
†*Department of Chemistry, Faculty of Science, Saitama University, Urawa, Saitama 338-8570*
††*National Research Laboratory for Magnetic Science, JST, Kawaguchi, Saitama 333-0848*
†††*Institute of Physical Chemistry, Bulgarian Academy of Sciences, Sofia 1040, Bulgaria*

(Received December 2, 1998; CL-980894)

Current over interdigitated dot electrodes increased under magnetic field. Mach-Zehnder laser interferometer revealed that the magnetic field tilted the fluid motion over the dot electrodes. This induced lateral movement enhanced the mass transport including redox cycling among the electrodes and consequently, the current.

Much has been reported on the micro-electrode and micro-band-array electrodes.[1-6] These are the powerful electro-analytical tools for such as chemical sensing for very dilute compounds *in vivo*[1] as well as *in vitro*.[2] These features are supported by the fact that the mass transport over these small electrodes is perfectly different from the one over the conventional large scale electrode.[3-6] The electrochemical response of these electrodes is ascribed to the motion of the electrolyte over the electrode surface.[4-6] In this letter, we have tried to control the fluid movement under relatively weak magnetic field in order to increase the current sensitivity of these electrodes. This motion was directly observed by Mach-Zehnder laser interferometric microscopy.[6-8]

Three types of the electrodes were used; these consisted of thirty Pt wires with a diameter of 100 μm which were separated each other by the distance of 100, 200 and 300 μm, filling with an insulator. Every first wire and every second ones were connected as the working electrode and the counter electrode, respectively. The surface of this electrode assemble was smoothly polished and this was placed in glass cell between AR-coated quartz windows. The diameters of these windows were 10 and 20 mm and the thickness of the electrolyte was ca. 1.5 mm. The magnet used was a hand-made Helmholtz coil and the electrochemical cell was set at the center of the coil. Under this geometry, directions of the magnetic flux and of the current over the electrode arrays were orthogonal, then magnetohydrodynamic force was expected along the direction of the array.[9-13]

The investigations were carried out under potentiostatic conditions. An electrolyte used was an aqueous solution of 0.35 M $K_4Fe(CN)_6$ and 0.2 M $K_3Fe(CN)_6$, containing 1 M KCl. After starting the electrolysis, the interferogram was projected on the screen while the potential was kept to -200 mV vs. Ag/AgCl reference electrode.[6] This optics made the interferograms obtained up-side-down.

The time course of the current was shown in Figure 1. The electrode surface was faced to upward. The current obtained without magnetic field was plotted by open rectangles as shown in Figure 1 (a). The closed rectangles and triangles, as shown in Figure 1 (b) and (c), respectively, present the value under magnetic field; 187 Gauss, where the direction of the magnetic field was opposite for each other. In the initial period, less than 100 s, the three currents gradually decreased as a function of the time. This is caused by the increase of the diffusion layer thickness and the decrease of the ion flux to the electrode. However, in the region longer than 100 s, there was clear difference between the time course of the current obtained under no-magnetic field and the ones under 187 Gauss. The current obtained without magnetic field reached the steady states after 400 s. But, the ones under the magnetic field gradually increased form 100 s and almost saturated at 600 s. After the termination of the magnetic field, the currents decreased back to the one of the steady state obtained without the magnetic field.

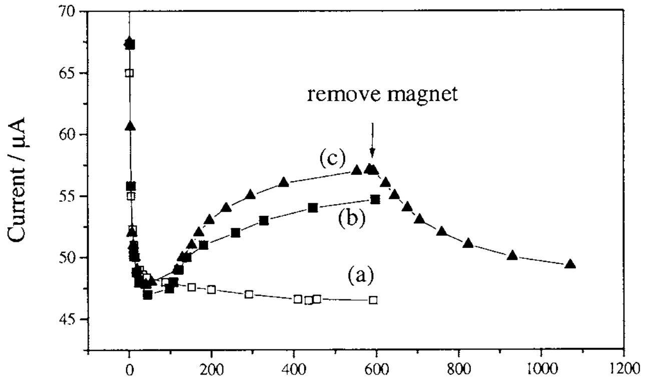

Figure 1. Time courses of the currents obtained under no-magnetic field (a), and the ones under magnetic field; (b) and (c), where the polarities of the magnet were opposite.

The interferograms corresponding to Figures 1 (a), (b) and (c) were shown in Figures 2 (b), (a) and (c), respectively. These pictures were taken at 600 s form the starting of the electrolysis. At this time, the current reached the quasi-steady states as shown in Figure 1.

On the single micro-electrode, the ion flux towards the edge of the electrode is not negligible. Thus, the diffusion over the micro-electrode is spherical.[1-6] As shown in Figure 2 (b), where no magnetic field was applied, the spherical diffusion was clearly obtained over the cathodes. And, as reported previously,[6] the jet of the ion flux was seen over the anodes. The magnetic field tilted the direction of the convective jet as shown in Figure 2 (a) and (c). The direction of this tilting was changed from left to right when the polarity of the magnet was switched. The direction of the magnetic field determines the motion of the electrolyte. Under the magnetic field, the shape of the spherical diffusion on the cathode was also deformed; the field made the thickness of the diffusion layer shortened toward the vertical direction.

The current increase under the magnetic filed can be attributed to two terms; (1) the shrinkage of the diffusion layer thickness by the lateral movement of the solution, which is

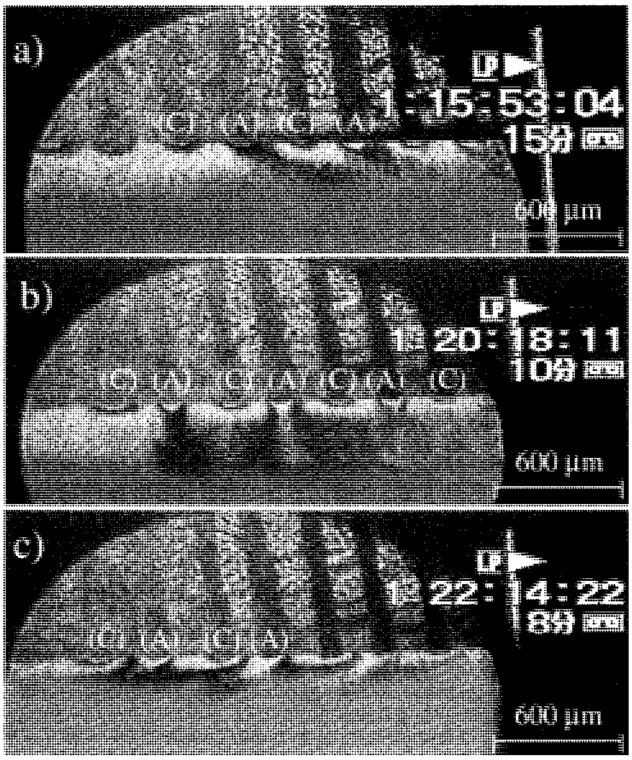

Figure 2. Interferograms obtained under no-magnetic fields, (b) and the ones under magnetic field; (a) and (c), where the directions of the field were opposite.

qualitatively identical with the effect of the agitation of the solution by, for example, a magnetic stirrer, and (2) the activation of the redox cycling over these interdigitated dot electrodes. The redox cycling occurs when the spacing between the micro-electrodes is smaller than the diffusion length.[3-6] The species generated at one electrode is electrolyzed to reverse direction at adjacent electrodes and then it diffuses back to the initial electrode. Under this condition, if the redox reaction is highly reversible as $Fe^{2+/3+}(CN)_6$, the current increases by this redox cycling mechanism. The overlapping of the diffusion layer was not perfect in these experiments because of the large distances among the electrodes, i.e., 100 to 300 µm.[6] This insufficient redox cycling was activated by magneto-hydrodynamic motion. The lateral motion induced by the magnetohydrodynamic effect was localized over the surface of the electrode, because the electrode geometry confined the current distribution close to the surface, Lorenz force tilted the interferograms as shown in Figure 2 (a) and (c). This induced motion is expected to increase the coupling among the electrodes and the redox cycling.

In order to investigate the dominant contribution between these two terms, the ratio of the enhanced current over the steady state currents; ($\Delta i / i_{ss}$) were plotted as a function of the electrode distance in Figure 3. The geometry of the electrode was opposite for Figure 3 (a) and (b), in which the electrode surface was faced to upward and downward, respectively. The enhanced current; Δi, was defined as the value of the difference between the steady state current under the magnetic field, i_{mag} and the one without the magnetic field, i_{ss} ; $\Delta i = i_{mag} - i_{ss}$. The steady state currents obtained under no magnetic filed changed depending on the experimental geometry, such as the distance between the electrodes, the direction of the electrode and the polarities of the magnet. Although the plot was performed for only three distances, ($\Delta i/i_{ss}$) was apparently decreased proportionally to the distance from 100 µm up to 300 µm. This trend was secured at least qualitatively in all the experimental geometry consisting of the direction of the electrode and the polarities of the magnet, but the slope of the decrease were varied on each geometry. As reported in the previous letter,[6] the spatiotemporal stability of the convective motion; jet was dependent on the direction of the electrode, then the difference in the slope may be attributed to these unresolved artifacts. At this stage, we conclude that the value of ($\Delta i/i_{ss}$) changes as a function of the distance between the electrode and that it decreases to the distance up to 300 µm. This observation suggests that the current enhancement by the magnetic field is mainly contributed from the activation of the redox cycling. If the shrinkage of the diffusion layer thickness is the major origin and there is no coupling between the electrodes, the current increase must be independent of the distance. The results obtained in Figure 2 and 3 show that the coupling among the electrodes is enhanced by the magnetic field and that it is the magnetic induced redox cycling over the interdigitated dot electrode.

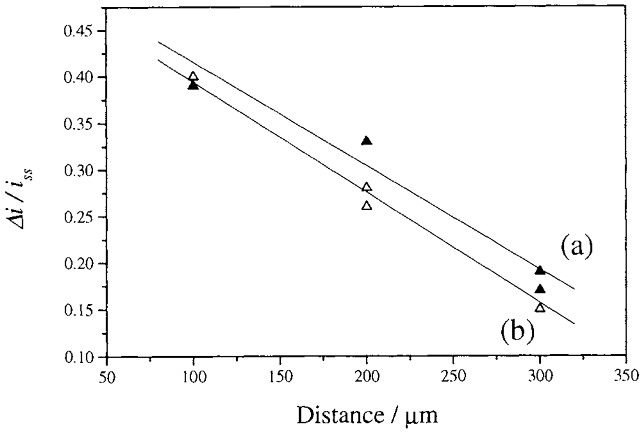

Figure 3. Relationship between the current enhancement by magnetic field ($\Delta i/i_{ss}$) and the distances of the electrode.

This work was partly supported by Grant-in-Aid for Scientific Research No. 09450312 and on Priority Area of Electrochemistry of Ordered Interfaces from Ministry of Education, Science, Sports and Culture, Japan.

References and Notes

1 J. Janat and A. Bezegh, *Anal. Chem.*, **60**, 62R (1988).
2 J.-L. Ponchon, R. Cespugllo, F. Gonon, M. Jouvet, and J.-F. Pujol, *Anal. Chem.*, **51**, 1483 (1979).
3 T. V. Shea and A. J. Bard, *Anal. Chem.*, **59**, 2101 (1987).
4 K. Aoki, M. Morita, O. Niwa, and H. Tabei, *J. Electroanal. Chem.*, **256**, 269 (1988).
5 O.Niwa, M. Morita, and H. Tabei, *Anal. Chem.*, **62**, 447 (1990).
6 R. Rashkov, R. Aogaki, and S. Nakabayashi, *Chem. Lett.*, (in press).
7 S. Nakabayashi, M. Yanagida, and K. Uosaki, *J. Phys. Chem.*, **100**, 714 (1996).
8 D. Fournier, P. Gleyzes, A. Lafosse, V. Marry, and V. Plichon, *Electrochim. Acta*, **44**, 287 (1998).
9 F. Takahashi, Y. Sakai, and T. Tamura, *Electrochim. Acta*, **28**, 1147 (1983).
10 C. Iwakura, M. Kitayama, T. Edamoto, and H. Tamura, *Electrochim. Acta*, **30**, 747 (1985).
11 I. Mogi, *Chem. Lett.*, **1996**, 419.
12 N. Leventis, M. Chen, X. Gao, M. Canalas, and P. Zhang, *J. Phys. Chem. B*, **102**, 3512 (1998).
13 S. R. Ragsdale, J. Lee, X. Gao, and H. S. White, *J. Phys. Chem. B*, **100**, 5913 (1996).