CHEMISTRY LETTERS, pp. 301-304, 1989.

Microvoltammetric Measurements in a Single Microcapsule

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microcapsule (radius ; 1.6 mm) were made by using a carbon fiber microelectrode. The permeability coefficient of $Mo(CN)_8^{4-}$ through the capsule wallwas determined by the variation of the concentration with time and found to be $(1.6 \pm 0.1) \times 10^{-4}$ cm/s. The electrochemical measurement insidea smaller microcapsule (radius ; ca. 100 μm) was also performed.

Microvoltammetric electrodes have attracted our considerable interest in electrochemistry.[1-12] To date, microelectrodes have found various applications such as voltammetric measurements in highly resistive solutions,[3,4] of fast electron transfer reactions[5,6] and fast coupled chemical reactions,[7,8] and of growth of metal nuclei.[9] Microdisk electrodes have also been used in vivo measurements.[10,11] Potentiometric investigations of the in vivo systems have been carried out extensively by using glass microelectrodes[12] and patch clamp pipettes.[13] The most interesting advantage of microdisk electrodes is their capability of amperometric measurements, which will provide useful information on the reactions occurring in vivo circumstances.

We reported here the measurement of voltammetric behavior in a single microcapsule as a model system for a cell, using a minute carbon microdisk electrode.

The microdisk electrode was fabricated by drawing a heated soft glass tube containing a carbon fiber (UCC Pitch Fiber, diameter of 10 μm) in it using the micro capillary puller (NARISHIGE model PD-5). Figure 1 shows a typical scanning electron micrograph of a carbon fiber electrode cracked with a knife. It can be seen that the thickness of the sealed glass is a few micrometers. The electrode was polished with 0.05 μm alumina powder and rinsed with distilled water. Microcapsules were prepared

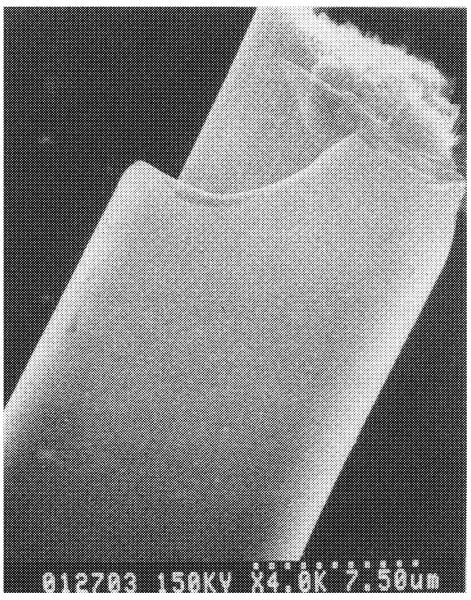

Fig. 1. A scanning electron micrograph of a carbon microelectrode. The photograph was taken at a magnification of 4000.

by dropping[14] a sodium alginate solution (0.2 g sodium alginate dissolved in 20 ml of 0.1 M Na_2SO_4 and 0.01 M $K_4Mo(CN)_8$ aqueous solution) into 0.15 M $Ca(NO_3)_2$ aqueous solution. This procedure created insoluble calcium alginate at the interfacial region of the droplet, resulting in a microcapsule formation. The diameter of microcapsules were controlled by using a micro cylinder.

A two electrodes configuration without a potentiostat was employed for the electrochemical measurements. An Ag/AgCl electrode immersed in the outer solution of 25 ml 0.15 M $Ca(NO_3)_2$ was used as a counter electrode. Small currents were measured with a high speed current amplifier (Keithley model 427). During the experiment, the outer solution was bubbled by N_2 gas.

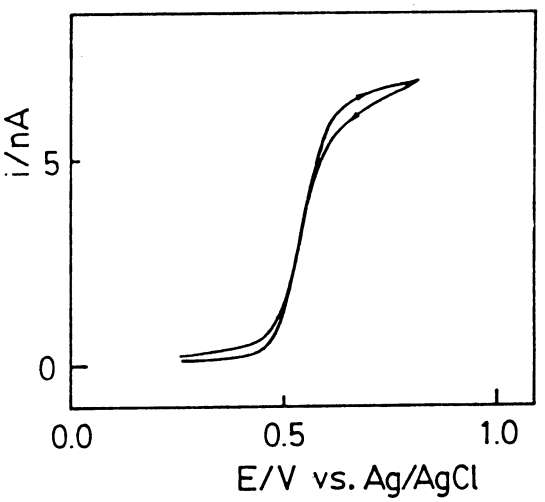

Fig. 2. A cyclic voltammogram of $Mo(CN)_8^{4-}$ in a microcapsule at a carbon microelectrode. An electrode diameter is 10 μm. Scan rate is 50 mV/s.

Figure 2 shows a typical cyclic voltammogram (CV) for $Mo(CN)_8^{4-}$ inside a microcapsule using a carbon fiber microdisk electrode with the diameter of 10 μm. The radius of a microcapsule is 1.6 mm. A plot of $\log[(I_d-I)/I]$ vs. potential (E) showed a slope of 58 mV. The half-wave potential ($E_{1/2}$) was 0.55 V vs. Ag/AgCl which is nearly in accord with the reported value.[15] No variation of $E_{1/2}$ was observed during the measurements. The above results demonstrate that it is possible to carry out the electrochemical measurement in a single microcapsule.

Thereupon, the permeation of $Mo(CN)_8^{4-}$ through the capsule wall of a calcium alginate was investigated by measuring the voltammetric response of the microdisk electrode. Figure 3 showed time dependence of $Mo(CN)_8^{4-}$ concentration inside the microcapsule. The concentration of the redox species was estimated from the steady-state current (I_d) of the CV using the following equation,

$$I_d = 4nFCDa \qquad (1)$$

where n, C, D, and a are the number of electrons per mole, the concentration of the electroactive species, the diffusion coefficient, and the radius of the disk electrode, respectively. It can be seen in Fig.3 that the concentration of $Mo(CN)_8^{4-}$ inside the microcapsule decreases with

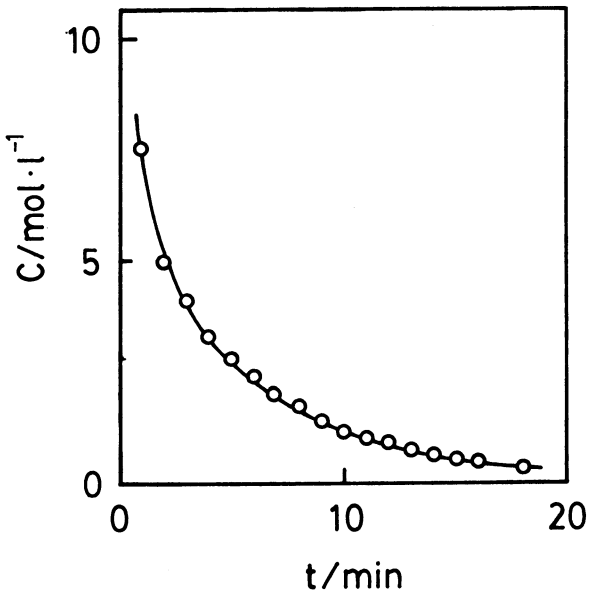

Fig. 3. Time dependence of $Mo(CN)_8^{4-}$ concentration in a microcapsule. The radius of a microcapsule is 1.6 mm.

time. The permeability coefficient of redox species through the capsule wall is estimated according to the following equation,

$$P = -2.303\ V_i\ \log(C^t/C^0)/AKt \qquad (2)$$

where V_i, A, K, t, C^t, and C^0 are the inner volume of a microcapsule, the total surface area of a microcapsule, distribution coefficient, the initial and intermediary (at time t) concentrations of redox species in the microcapsule, respectively. From the plot of $\log(C^t/C^0)$ against time, the permeability coefficient of $Mo(CN)_8^{4-}$ found to be $(1.6 \pm 0.1) \times 10^{-4}$ cm/s. The permeability coefficient was also estimated by monitoring the concentration of $Mo(CN)_8^{4-}$ in the outside solution. The concentrations were determined from the absorbance at 370 nm and from the electrochemical measurement using a Pt microdisk electrode with a 15 μm diameter. As a result, the permeability coefficients obtained from two different measurements gave the values similar to that described above. The agreement of the permeability coefficient strongly indicates that the microdisk electrode should be applicable to monitoring the electroactive species inside a single microcapsule.

We have also examined to measure the concentration in a small microcapsule with the diameter of sub mm using a microdisk electrode. Since such small microcapsules could not be fabricated by using a micro cylinder, the fabrication of microcapsules was performed by using an atomizer. Figure 4 shows a microphotograph of the electrochemical measurement inside a small microcapsule using a carbon fiber microdisk electrode with a diameter 10 μm. The diameter of the microcapsule is estimated to be about 100 μm compared with the diameter of a carbon microdisk electrode. The cyclic voltammogram indicated a quite normal shape and the concentration of a redox species determined from the limiting current coincided with that of the original concentration of a redox species in alginate solution used for preparation of the microcapsule.

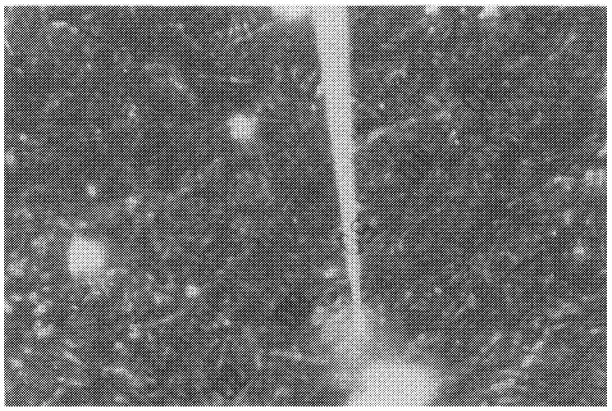

Fig. 4. A microphotograph of the electrochemical measurement in a small microcapsule using a carbon microelectrode.

The above results suggest the feasibility of the voltammetric measurement inside a single cell if we can use the more minimal electrode including insulator. We have previously reported the preparation of ultra microdisk electrodes with a radius less than a few thousand angstroms using an electropolishing method.[16,17] At present, we are investigating the voltammetric measurement using ultra microdisk electrodes inside a single cell.

References

1) R. M. Wightman, Anal. Chem., 53, 1125A (1981).
2) S. Pons and M. Fleischmann, Anal. Chem., 59, 1391A (1987).
3) A. M. Bond and A. P. Lay, J. Electroanal. Chem., 199, 285 (1986).
4) M. J. Pena, M. Fleischmann, and N. Garrard, J. Electroanal. Chem., 220, 31 (1987).
5) O. J. Howell and R. M. Wightman, J. Phys. Chem., 88, 3915 (1984).
6) O. J. Howell and R. M. Wightman, Anal. Chem., 56, 524 (1984).
7) A. Fitch and D. H. Evans, J. Electroanal. Chem., 202, 83 (1986).
8) R. S. Robinson and R. L. McCreery, J. Electroanal. Chem., 182, 61 (1985).
9) B. Scharifker and G. J. Hills, J. Electroanal. Chem., 130, 81 (1981).
10) H. Y. Cheng, J. Schenk, R. Huff, and R. N. Adams, J. Electroanal. Chem., 100, 23 (1979).
11) G. Nagy, G. A. Gerhardt, A. F. Oke, M. E. Rice, and R. N. Adams, J. Electroanal. Chem., 188, 85 (1985).
12) M. Lavallee, O. F. Schanne, and N. C. Hebert, "Glass Microelectrode," John Wiley & Sons, Inc., NewYork, London, Sydney, Toronto (1969).
13) B. Sakmann and E. Neher, Ann. Rev. Physiol., 46, 455 (1984).
14) A. M. Rosenthal and T. M. S. Chang, J. Membr. Sci., 6, 329 (1980).
15) T. Saji, Y. Maruyama, and S. Aoyagi, J. Electroanal. Chem., 86, 219 (1978).
16) K. Itaya, T. Abe, and I. Uchida, J. Electrochem. Soc., 134, 1191 (1987).
17) T. Abe, K. Itaya, and I. Uchida, Chem. Lett., 1988, 399.

(Received October 27, 1988)