Oxygen Permeability of Surface-modified Poly(dimethylsiloxane) Characterized by Scanning Electrochemical Microscopy

Hitoshi Shiku,*[1] Takeshi Saito,[1] Ching-Chou Wu,[1] Tomoyuki Yasukawa,[1] Masaki Yokoo,[2] Hiroyuki Abe,[2] Tomokazu Matsue,*[1,2] and Hiroshi Yamada[3]

[1]*Graduate School of Environmental Studies, Tohoku University, Aramaki Aoba 6-6-11, Sendai 980-8579*

[2]*Tohoku University Biomedical Engineering Reseach Organization (TUBERO), Sendai 980-8579*

[3]*Department of Applied Chemistry, National Defense Academy, Kanagawa 239-8686*

(Received November 18, 2005; CL-051434; E-mail: shiku@bioinfo.che.tohoku.ac.jp, matsue@bioinfo.che.tohoku.ac.jp)

Scanning electrochemical microscopy (SECM) was employed to quantitatively characterize the oxygen permeation behaviors of poly(dimethylsiloxane) (PDMS) and surface-modified PDMS. The mass-transfer process of oxygen from the PDMS substrate to the tip electrode is diffusion limited, whereas the oxygen permeability of PDMS subjected to oxygen plasma treatment or albumin adsorption is critically restricted. Our results suggest that the oxygen permeability of PDMS is possibly affected by O_2 plasma irradiation and albumin adsorption at the PDMS surfaces.

Poly(dimethylsiloxane) (PDMS) is recognized as an ideal material for manufacturing microdevices in the biomicroelectromechanical systems (bio-MEMS), because of its significant characteristics to easily design relatively complicated three-dimensional structures and biocompatibility.[1,2] The surface modification of PDMS has been a focus of attention to explore application of the PDMS microdevices. Recently, protein analysis on the PDMS device has become available by resolving the protein adsorption issue through the control of PDMS surface energy. PDMS microdevices have also been utilized in microculture, microcirculation, or complicated operations involving various living cells, and tissues.[3–6] The modification of PDMS surfaces to promote or restrict the interactions between the cells and the microdevice substrate has thus become a key technology.

PDMS is a material that possesses high oxygen permeability; this property facilitates the application of its microdevices in cell culture. However, the oxygen permeability of PDMS may change with its surface condition. Although many studies on the gas-transport characteristics of PDMS in the gas phase[7–9] have been conducted, research on the quantitative analysis of the oxygen mass transfer at the water/PDMS interface is limited.

SECM has been applied to analyze kinetics including electron transfer and mass transfer at solid/liquid, liquid/liquid, and gas/liquid interfaces.[10–15] A tip microelectrode is positioned near the interface where mass transfer does not occur. After the set-up, electrochemical reaction at the microelectrode induces mass transfer within the very small space between the tip and the sample interface. In this paper, we report the quantitative characterization of the oxygen permeation behavior of PDMS and surface-modified PDMS by SECM.

PDMS (Sylgard 184, Dow Corning) and a curing agent were mixed in a 60 mm polystyrene culture dish and cured at 75 °C for 1 h.[6] Oxygen plasma treatment was conducted with a plasma asher (100 W, 13.6 MHz). A Pt-disk microelectrode with a radius of 6 μm and a seal radius of 12 μm was used as the SECM probe ($a = 6\,\mu m$, $r_g = 12\,\mu m$). The SECM measurements were performed in a PBS solution (25 mM Na_2HPO_4, 25 mM NaH_2PO_4, 100 mM KCl, pH 7.0) by scanning the microelectrode placed very close to the PDMS substrate. The tip potential was maintained at −0.5 V vs. Ag/AgCl in order to monitor the oxygen reduction current.[5] All the current–distance plots shown in this paper were recorded when the tip approached the PDMS surface at $1\,\mu m\,s^{-1}$.

The partitioning equilibrium of oxygen between water and PDMS can be represented as

$$O_2(\text{water}) \underset{k_2}{\overset{k_1}{\rightleftarrows}} O_2(\text{PDMS}), \tag{1}$$

where k_1 and k_2 are the heterogeneous mass-transfer constants (first-order interfacial rate constant) of oxygen from the water phase and PDMS phase, respectively. The oxygen flux at the water/PDMS interface ($flux_{O_2}$) is expressed as follows:

$$flux_{O_2} = k_2[O_2]^{PDMS} - k_1[O_2]^{water}. \tag{2}$$

Under steady state condition,

$$k_1/k_2 = [O_2]^{PDMS}/[O_2]^{water} = K_p, \tag{3}$$

where K_p is the partition coefficient of oxygen between water and PDMS. The oxygen concentration in PDMS has been reported as 2 mM,[7] whereas that in PBS is 0.204 mM. The diffusion coefficient of oxygen in PDMS is reported as 5.2×10^{-6} to $3.4 \times 10^{-5}\,cm^2\,s^{-1}$;[4,8,9] this value is essentially in the same order as that in PBS, $2.1 \times 10^{-5}\,cm^2\,s^{-1}$.

The kinetic parameters for oxygen permeation at the water/PDMS interface were determined by a digital simulation.[10–16] The space between the tip electrode and the sample was divided into small volume elements, and the mass transfer for each element was calculated by considering the partition coefficient of oxygen for water/PDMS and heterogeneous kinetic constants at this interface. The typical grid numbers of the tip electrode, tip insulator, distance between the tip and the water/PDMS interface, and diffusion layers for the water and PDMS phases were 8, 8, 6–22, and 30, respectively. The partition coefficient $K_p = 10$, and the diffusion coefficients of oxygen in water and PDMS phases were assumed as $D_{O_2}{}^{water} = D_{O_2}{}^{PDMS} = 2.1 \times 10^{-5}\,cm^2\,s^{-1}$. The digital simulation employs the fast quasi-explicit finite difference method (FQEFD).[17]

Figure 1 shows the approach curves (normalized current (i/i^*) versus the distance between the tip and the sample surface) for various samples. The oxygen reduction current was normalized to that obtained in bulk (i^*). When the tip approaches the polystyrene substrate, the current at a distance less than 30 μm reduces. This is because polystyrene barely permeate oxygen. On the other hand, the current near the PDMS substrate drasti-

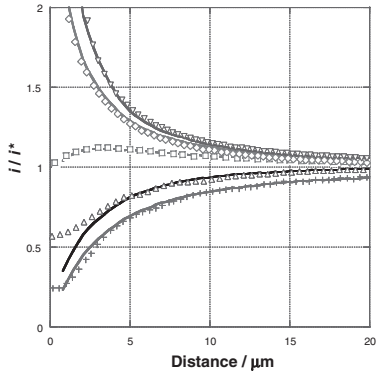

Figure 1. Plots of normalized current (i/i^*) vs. distance for various samples: PDMS (rev-triangle), O_2-treated PDMS (O_2 plasma irradiation for 5 s (diamond), 1 min (square), and 5 min (triangle)), and polystyrene (cross). Solid lines represent theoretical results for $k_1 = 1$, 0.2, 4×10^{-2}, 4×10^{-3}, and 0 cm s^{-1} (from top to bottom).

cally increases because PDMS serves as an effective oxygen reservoir. It was reported that in the approach curve, the oxygen reduction current at the water/1,2-dichroloethane and water/air interfaces was remarkably amplified.[10,11] The apparent heterogeneous rate constant (k_1) at the water/PDMS interface was estimated to be at least 1 cm s^{-1}.

Figure 1 also shows the approach curves of PDMS after the O_2 plasma treatment. The SECM measurements were carried out within one hour after the plasma treatment. Although the PDMS surfaces that were treated for 5 s to 5 min exhibited excellent wettabilities and were no difference, the oxygen permeation of the surface-modified PDMS was changed significantly. The oxygen-transfer barriers at the water/PDMS interfaces subjected to plasma treatments for 5 s, 1 min, and 5 min are no less than 5-, 25-, and 250-fold of those at the original water/PDMS interface, respectively. The k_1 values at the water/PDMS interfaces after plasma treatment for 5 min was estimated to be 4×10^{-3} cm s^{-1}; this value might be sufficiently high to apply O_2 plasma-treated PDMS to microchannel devices for various microculture living cell systems. However, the parameters described in the present work will be essential for designing systems that require sufficient oxygen supply.

Figure 2 shows the approach curves of PDMS treated with BSA. The SECM measurements were carried out in a PBS solution containing 1% (w/v) BSA (Fraction V, SIGMA) after the BSA-incubation for 20 min to 10 h. The current increases as the tip-sample distance reduces. The k_1 values at the water/PDMS interface after the BSA treatment for 20 min and 10 h were 0.2 and 7×10^{-2} cm s^{-1}, respectively. Since many types of proteins including BSA can be adsorbed on the PDMS surface during cell culture within a PDMS microdevice,[1] further investigations are required to quantify the oxygen permeability using actual PDMS-based microfluidic devices or a model system with similar surface conditions. The type and quantity of proteins adsorbed on the PDMS surface can be varied with the modified PDMS surfaces. The present results clearly indicate that the oxygen permeability of a surface-modified PDMS substrate significantly differs from that of the original PDMS.

There is another aspect of the application of PDMS membranes as an oxygen permeable membrane of biosensors:[18]

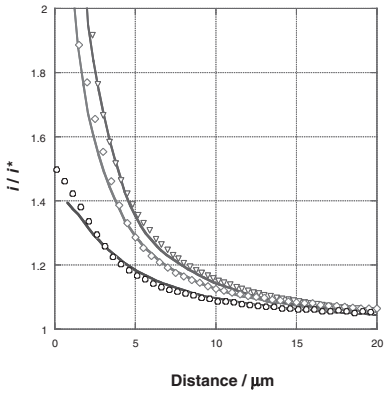

Figure 2. Plots of (i/i^*) vs distance for BSA-treated PDMS (20 min (diamond) and 10 h (circle)). The plot of the original PDMS is the same as that in Fig. 1. Solid lines represent theoretical results for $k_1 = 1$, 0.2, and 7×10^{-2} cm s^{-1}.

PDMS membranes have been applied to a separator or protector to prevent the undesired adsorption of proteins in biosensors based on oxygen sensors.[6,18] In these sensors, the outer side of the membrane can be easily contaminated with proteins in the sample solution, thereby reducing the oxygen permeation and degrading the sensor response. In the present study, it is suggested that the surface modification of PDMS can affect not only oxygen permeability but also the affinity against proteins. Since these surface modifications often occur in a set of the device fabrication procedure, the oxygen-permeation properties of PDMS and modified PDMS should be considered carefully for designing PDMS-based devices.

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