Fabrication and Characteristic Responses of Integrated Microelectrodes in Polymer Channel Chip

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(Received May 1, 2000; CL-000412)

A polymer microchannel (width = 100 μm and depth = 20 μm) chip integrated with band Au electrodes (47 × 100 μm) was fabricated on the basis of photolithography/etching and imprinting techniques, and its characteristic electrochemical responses have been demonstrated.

Microchannel chips have now received wide interests in various research fields. As an example, they have been applied to a microfluidic device for liquid chromatography, flow injection analysis, electrophoreisis and so forth.[1] Channel chips play important roles in microreactors and micro-total analysis systems as well.[1] Although chips are fabricated mostly on silicon or glass substrates, polymer solids have also several advantages as a chip material; they are easily processed by an appropriate method such as molding, casting, or imprinting.[1] In practice, several research groups have reported fabrication of polymer microchannel chips.[2] However, a polymer chip integrated with various chemical and physical functions has been scarcely reported. In this letter, we report here a novel approach to fabricating a polymer microchannel chip integrated with metal electrodes and, demonstrate unique and characteristic responses of the electrodes in the microchannel.

A polymer microchip is made of channel- and electrode-substrates (Figure 1a). A channel-substrate was fabricated on a polystyrol plate (Tamiya Co. Ltd., 1.5 × 3.0 cm) by an imprinting method.[3] A micromachined Si substrate was used as a template for imprinting and, a single-line microchannel with the width and depth of 100 and 20 μm, respectively, was fabricated on the substrate by pressing the template onto the polymer at 108 °C for 25 min. An electrode-substrate was fabricated as follows. A gold thin-film (thickness ~100 nm) was vacuum deposited directly onto a polystyrol substrate. A photoresist (Tokyo Ooka Co. Ltd., OFPR800) was spin-coated on the Au/polymer substrate and exposed to a W-lamp through a photomask, whose structure was printed on a transparency film by using a conventional computer software package. The resist layer was developed (Tokyo Ooka Co. Ltd., MMD-3) and the exposed Au layer was etched in an aqueous I_2/NH_4I solution. The resist layer on Au was then removed with acetone. As shown in Figure 1b, dual band microelectrodes acted as a working electrode (WE; width = 47 μm, edge-to-edge interelectrode distance = 68 μm) and the relevant bonding pads for connection with an external electrochemical analyzer (ALS Co. Ltd., model 701) were fabricated on the polymer. Au counter and Ag reference electrodes were also fabricated on the same substrate. The electrodes/polymer substrate was then clamped between two glass plates and heated at 108 °C for 25 min to bury the electrodes into the polymer. The electrode-substrate was covered and bonded with the channel-substrate by heating at 108 °C for 25 min, with two substrates being clamped tightly between glass plates. The spatial geometry of the electrodes was designed so as to each electrode being bisected the microchannel (Figure 1c). The chip and a syringe pump (Harvard, model 44) were connected with a glass capillary tube to introduce an aqueous solution of 1-hydroxyethylferrocene (FeCp–OH, 1×10^{-3} M (= mol/dm^3)) and KCl (0.1 M).

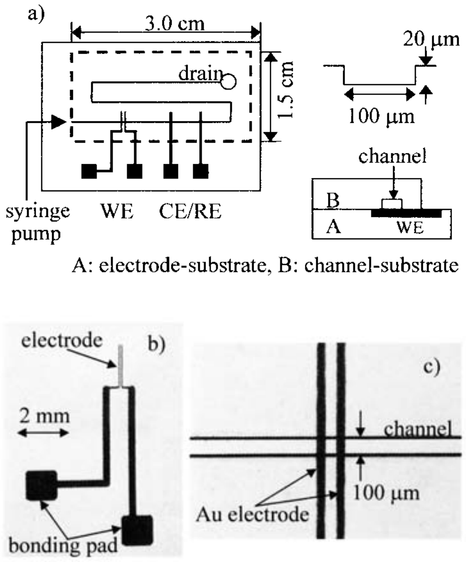

Figure 1. Illustration of an integrated polymer microchannel chip (a). Photographs of Au electrodes (b) and a microchannel (c).

Cyclic voltammograms (CV) of FeCp–OH at several sweep rates (v) are shown in Figure 2. In the experiments, one of the dual Au electrodes was used as WE. Since the electrode was not small enough (width = 47 μm, length (= channel width) = 100 μm), the CV was not sigmoidal, but exhibited a peak potential. Although the peak separation of each CV (65 mV) was slightly larger than 59 mV, the oxidation potential of FeCp–OH agreed well with that determined in a bulk solution by a disk electrode (164 mV vs. Ag). Furthermore, the current (i_p) increased linearly with $v^{1/2}$, indicating the semi-infinite diffusion response of the electrode in the channel. Since the channel depth is 20 μm, a thin-layer cell type response might be expected ($i_p \sim v$).[4] However, this was not the case in the present experiments, since the lateral dimension of the channel was very large compared to the channel depth. Thus, a semi-infinite diffusion field in the direction of the channel is dominant. This is the general characteristics of an electrode in a microchan-

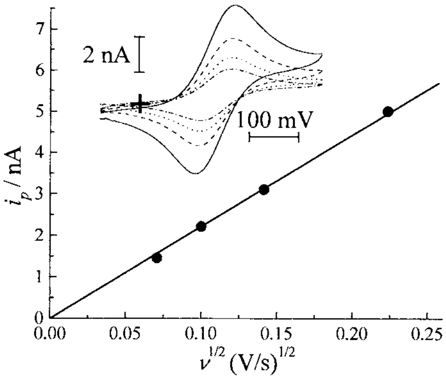

Figure 2. Potential sweep rate (v) dependencies of a cyclic voltammogram of FeCp-OH (vs. Ag) and the relevant peak current (i_p). The increasing order of i_p in the voltammograms corresponds to the data at v = 5, 10, 20, and 50 mV/s.

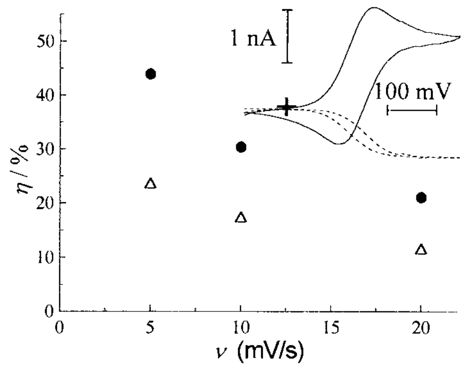

Figure 3. Cyclic voltammograms of FeCp-OH observed at generator (solid curve) and collector electrodes (broken curve), and a potential sweep rate dependence of the collection efficiency (η). Closed circles and triangles are the data obtained by the eletrodes with and without the microchannel-substrate respectively.

nel.[2b] The electrode area determined by the slope of the plot in Figure 2 (4.9×10^{-5} cm^2) agreed very well with that calculated from the electrode dimension (4.7×10^{-5} cm^2),[4] demonstrating the correct response and the precise geometry of the fabricated electrode.

Generation–collection mode experiments were conducted by the two Au microelectrodes being used as generator (***G***) and collector electrodes (***C***). A typical example of the results at v = 5 mV/s is shown in Figure 3, in which ***C*** was held at 0 V during potential sweep at ***G***. In the GC mode, FeCp–OH is oxidized at ***G*** and the resultant cation is reduced at ***C***. Therefore, the ratio of the peak current at ***G*** (i_p(***G***)) to that at ***C*** (i_p(***C***)) is a measure of a collection efficiency of the cation at ***C***: $\eta = i_p(C)/i_p(G)$. The η values determined at several v are summarized in Figure 3 (closed circles), together with those obtained by using the same electrode-substrate without a channel-cover plate (open triangles). It is worth emphasizing that, at given v, η observed in the channel is almost two-times larger than that without a channel-cover. At v = 5 mV/s, the η value was as high as 45% even for the edge-to-edge ***GC*** distance of 68 µm. Since the cation generated at ***G*** diffuses along the channel direction, η should be 50% as a maximum value. The observed η value thus indicates almost complete collection of the cation at ***C***. In the case of dual band microelectrodes, such a high collection efficiency cannot be realized with an interelectrode distance larger than 10 µm.[5] Therefore, the presence of the microchannel above ***G*** and ***C*** provides extraordinary effects on η. Although data are not shown here, i_p(***G***) at given v was larger in the absence of a channel-substrate as compared to that with the channel-substrate. This is explained by the fact that, efficient mass transport to ***G*** takes place in the absence of a channel-cover owing to cylindrical diffusion of FeCp–OH, while mass transport is limited in the channel. i_p(***G***) decreased with a decrease in v analogous to the results in Figure 2, while i_p(***C***) was almost independent of v in the channel and that without a cover-plate decreased with an increase in v. Therefore, the collection efficiency becomes larger in the channel as compared with that without a cover-substrate and, the difference in η between the electrodes with and without a channel-cover becomes larger with a decrease in v.

As preliminary experiments, furthermore, we studied a solution flow-rate dependence of η in the channel chip. Although we report detailed results in a separate publication, we have found that η depends highly on the flow-rate and, η as high as ~ 90% is realized at an optimum solution flow-rate.[6] This is another interesting characteristics of microelectrodes integrated in a microchannel chip. Polymer microdevices integrated with electrodes could be thus very promising as a high-efficient detection device for electrochemical intermediates as well as an electrochemical sensor.

The authors thank to a Grant-in-Aid from the Ministry of Education, Science, Sports and Culture, Japan (No. 11554032 and 12640578 to HBK and No.10354012 and 10207201 to NK) for the support of the research.

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