Simultaneous Observation of Faradaic and Tunneling Current at a Flat Surface Using Tunneling-Current-Based Constant-Distance Scanning Electrochemical Microscopy with a Platinum Nanoelectrode

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ABSTRACT
A conical-shaped Pt nanoelectrode whose tip apex features an effective electrode area was fabricated and used as a probe for scanning electrochemical microscopy (SECM). Nanoelectrodes were prepared by electroplating Pt in porous pyrolyzed polydimethylsiloxane filled into the tip of a quartz nanopipette. The current–distance curves were obtained by acquiring raw (without a low-pass filter) and low-pass-filtered (10 Hz) current simultaneously while a tip approached a flat Pt substrate. The raw-current approach curve showed the transition from faradaic feedback current to electron tunneling between the tip of the probe and the substrate. Alternatively, in the low-pass-filtered approach curve, a faradaic current with an improved signal-to-noise ratio was obtained without a transient increase of the tunneling current. From scanning electron microscopy observations, voltammograms, approach-curve measurements, and digital simulations of the response of a nanoelectrode, we deduced that only the apex of the conical-shaped electrode exhibited electrochemical activity and acted as an effective electrode. The constant-distance SECM imaging of an Au-sputtered polycarbonate membrane with sub-micrometer pores and Pt nanoparticles deposited on a highly oriented pyrolytic graphite (HOPG) was successfully demonstrated using the tunneling-current-based standing approach mode.

Keywords: SECM, STM, Nanoelectrode, Nanoparticle

1. Introduction

Scanning electrochemical microscopy (SECM) is widely used for the characterization of solid–liquid and liquid–liquid interfaces. Recent advances have enabled the distance between sample surfaces and probes to be controlled with nanometer-level accuracy using shear force, intermittent contact, ion conductance, atomic force, and tunneling current. Furthermore, with advances in probe miniaturization technology, the resolution of SECM has been improved to the nanometer scale. Consequently, a method is needed for the facile and reproducible preparation of nanoelectrodes.

Nanoelectrodes with a small insulator-to-electrode diameter (RG) ratio are suitable for SECM applications. Carbon nanoelectrodes in which the carbon is formed in a quartz nanocapillary via thermal pyrolysis of hydrocarbons have been reported. Simultaneous analysis of the topographic features and electrochemical properties of sample surfaces has been demonstrated using a double-barreled nanoelectrode in which one barrel is filled with pyrolyzed carbon and the other is filled with an electrolyte solution. This type of carbon nanoelectrode has been fabricated with good reproducibility.
however, carbon can deposit not only inside the capillary but also on its outer surface.

We previously fabricated Pt nanoelectrodes with etched Pt wires coated with glass and used them for SECM observations of nanometer-scale defects in alkanethiol monolayers.\textsuperscript{26} Although these electrodes were robust and reusable, the fabrication procedure was complicated and unsuitable for mass production. The fabrication of Pt nanoelectrodes by simultaneously pulling a Pt wire and a glass tube has also been reported.\textsuperscript{27,28} Furthermore, a geometry-controlled and reproducible procedure for the fabrication of disk-shaped Pt electrodes with RG > 4 has been investigated.\textsuperscript{29} Researchers have also fabricated small-RG-ratio nanoelectrodes by electropolishing\textsuperscript{30} and electroless-plating\textsuperscript{31} of metals inside nanopipette walls. Platinum deposition over nanometer sized electrodes has been reported for STM/SECM tips\textsuperscript{32}, SEC/MICM tips\textsuperscript{33} to enhance electrochemical responses.

In the present study, by electrophoresis in porous pyrolyzed polydimethylsiloxane (PDMS) filled into a quartz glass nanopipette, we fabricated a conical-shaped Pt nanoelectrode whose tip apex features an effective electrode area. We also characterized the fabricated nanoelectrodes electrochemically. The obtained nanoelectrodes were successfully used as SEC/M probes for constant-distance simultaneous topographic and electrochemical imaging using the tunneling-current-based standing approach (SA) mode.

2. Experimental

2.1 Preparation of pyrolyzed PDMS carbon nanoelectrodes

Nanoelectrodes were prepared using a lab-fabricated heating furnace, as shown in Supporting Information Fig. S1. A quartz tube (Q150-75-10, Sutter, Novato) was pulled with a P-2000 puller (Sutter, Novato) so that the outer diameter (o.d.) of the tip of the nanopipette was 100–300 nm. Two-step pulling was used to obtain a short taper nanopipette. The following pulling parameters were used: (line 1) Heat 965, Fil, 4, Vel 50, Del 130, and Pull –; (line 2) Heat 965, Fil 4, Vel 50, Del 115, and Pull 80–90. The taper length of the nanopipette was ~5 mm. Under observation using a Micro Forge MF-900 optical microscope (Narishige, Tokyo), the tip of the nanopipette was immersed in a droplet of PDMS precursor (Sylgard 184, Dow Corning, Midland), and the precursor was drawn 2–3 μm into the tip. The nanopipette was then inserted into a quartz tube furnace and heated to 900°C at a heating rate of 2°C/minute under flowing H₂ in the capillary, and the quartz tube furnace was evacuated using a rotary pump (GHD-031A, ULVAC KIKO, Tokyo). After the PDMS in the tip was cured and pyrolyzed, the tip of the nanopipette was pyrolyzed to form a porous material under application of a conductive coating.

The pyrolyzed PDMS (p-PDMS) carbon nanoelectrode was recrystallizing the product twice from water. Hexachloroplatinate(IV) acid (Tokyo Kasei, Tokyo) was used as received.

The potential, referenced against a Ag/AgCl quasi-reference electrode, was controlled using a potentiostat (HA1010m2B, Hokuto Denko, Tokyo) for electrochemical measurements.

In this study, a pyrolyzed PDMS carbon nanoelectrode was used: (line 1) Heat 965, Fil, 4, Vel 50, Del 130, and Pull –; (line 2) Heat 965, Fil 4, Vel 50, Del 115, and Pull 80–90. The tip was approached to a Pt layer on a glass substrate (counter electrode part of an interdigitated array (IDA) electrode, 012263, BAS, Tokyo) at a rate of 1 μm/s while measuring the low-pass-filtered current (Ch1) until the raw current signal (Ch2) increased sharply because of the onset of tunneling between the tip and the sample surface. The raw and filtered current were sampled at 3.0 ms intervals to acquire the approach curves.

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2.2 Pt plating and electrochemical measurements

(Ferrocenylmethyl)trimethylammonium perchlorate was synthesized by adding saturated sodium perchlorate solution to a solution of (ferrocenylmethyl)trimethylammonium bromide (Tokyo Kasei, Tokyo) and recrystallizing the product twice from water. Hexachloroplatinate(IV) acid (Tokyo Kasei, Tokyo) was used as received.

The potential, referenced against a Ag/AgCl quasi-reference electrode, was controlled using a potentiostat (HA1010m2B, Hokuto Denko, Tokyo) for electrochemical measurements.

The pyrolyzed PDMS (p-PDMS) carbon nanoelectrode was polarized at −0.1 or −0.3 V in 5 or 25 mM hexachloroplatinate(IV) acid/0.1 M HCl solution. The potential was applied until a sudden increase in the reduction current was observed.

Cyclic voltammetry and SEC/M measurements were performed in 1.0 mM (ferrocenylmethyl)trimethylammonium (FA⁺)/0.14 M NaCl aqueous solution.

2.3 SEC/M apparatus

An SEC/M system (HV404, Hokuto Denko, Tokyo) was modified to enable tip positioning at nanometer resolution. The probe and the samples were moved with a piezo-driven Z-stage (PS1L60-060U, THK PRECISION, Tokyo) and XY-stage (NS4214, THK PRECISION, Tokyo), respectively. The stage controllers (NC-5000, THK PRECISION, Tokyo) were controlled with a computer (MD9000, Epson Direct, Tokyo) running homemade software made with Delphi XE2 (Embarcadero, Austin) via a DIO board (DIO-6464T-PE, Contec, Tokyo). The current output signal was amplified (100×) with a preamplifier (LJ-75A, NF Corp.) followed by an RC-low-pass filter (homemade). The current and potential signals were digitized and transferred to/from a computer via 16-bit AD/DA board [ADA16-32/2(P/C)I,F, Contec, Tokyo]. The SEC/M apparatus is illustrated in Fig. S3. The output signal of the current for the nanoelectrode is branched, and one is amplified 100× followed by low-pass filtering, the other was used as a stop trigger signal for acquiring approach curves, and as a feedback signal for constant-distance SEC/M imaging.

2.4 Approach curves and SEC/M imaging

The tip was approached to a Pt layer on a glass substrate (counter electrode part of an interdigitated array (IDA) electrode, 012263, BAS, Tokyo) at a rate of 1 μm/s while measuring the low-pass-filtered current (Ch1) until the raw current signal (Ch2) increased sharply because of the onset of tunneling between the tip and the sample surface. The raw and filtered current were sampled at 3.0 ms intervals to acquire the approach curves.

Au was sputtered onto an Isopore membrane (pore size: 0.8 μm, ATTP, Merck, Burlington) with a film coater (DI-29010SCTR, JEOL, Tokyo) for 10 min. An Au-coated membrane was glued with epoxy resin onto a polycarbonate plate with a 3.0 mm hole, and the plate was affixed to the bottom of the electrochemical cell. Highly oriented pyrolytic graphite (HOPG) (429HP-AB, Alliance Biosystems) was polarized at ~0.3 V for 60 s to deposit Pt nanoparticle at a HOPG surface in 0.1 M HCl solution.

SEC/M imaging was carried out in 1.0 mM FA⁺/0.14 M NaCl solution in the SA mode, which is similar to the hopping mode used in scanning ion conductance microscopy (SICM) and SEC/M.\textsuperscript{30} The potential of the tip (E_{tip}) was changed as shown in Supporting Information Fig. S5. Details of this mode have been described elsewhere.\textsuperscript{2} The potential of the substrates was set at open circuit potential. The tip was approached at 1 μm/s until the tunneling current reached 500 pA; the low-pass-filtered current was then immediately sampled for SEC/M imaging. The low-pass-filtered current signal was insensitive because of the delay when the sharp increase in the raw current signal was observed.

2.5 Scanning electron microscopy observations of the nanoelectrodes

Nanoelectrodes were observed by scanning electron microscopy (SEM) (JCM-6000 or JSM-7800F, JEOL, Tokyo) without the application of a conductive coating.

3. Results

3.1 Fabrication of Pt nanoelectrodes

Supporting Information Fig. S2 illustrates the fabrication and Pt-plating processes of a p-PDMS carbon electrode. The PDMS at the tip of the nanopipette was pyrolyzed to form a porous material under...
The deposition rate being limited by the mass transfer of PtCl$_6^{2-}$ in a reducing atmosphere. Pyrolysis of butane in the nanopipette produced a carbon nanoelectrode without carbon being deposited at the tip. Figure 1a shows the cyclic voltammograms for a p-PDMS carbon nanoelectrode (blue line) and a Pt nanoelectrode (red line) in 1.0 mM FA$^+/0.14$ M NaCl. Because no carbon was deposited at the tip (~2 µm from the apex of the tip was transparent), a small peak current, indicating the limited diffusion of FA$^+$ in the porous p-PDMS, was observed at the p-PDMS carbon electrode. Figure 1b shows the time dependence of the current at $-0.1$ V for the Pt plating process. A sudden increase in the current was observed at 4000 s. The deposition of Pt proceeds from the edge of carbon in the porous p-PDMS toward the aperture in the tip of the nanopipette. The steady-state oxidation current at a disk nanoelectrode is given by the equation:

$$i_\infty = 4nFc^+D\beta\gamma$$

where $n$ is the number of electrons exchanged with a mediator molecule/ion, $F$ is the Faraday constant, $D$ is the diffusion coefficient of the mediator, $\gamma$ is the radius of the electrode, $c^+$ is the bulk concentration of the mediator, and $\beta$ is a parameter dependent on the RG value, ranging from 1 (for an RG value of $\infty$) and 1.43 (for an RG value of 1). A steady-state current of $\approx 28$ pA from the oxidation of FA$^+$ ($D = 6.7 \times 10^{-6} \text{cm}^2\text{s}^{-1}$) corresponds to the steady-state current at a disk nanoelectrode.
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Figure 2. (a) Approach curves of the raw current signal at $E_{\text{tip}} = 0.5$ V when the tip was moved toward the Pt surface in 1.0 mM $\text{FA}^+$/0.14 M NaCl. (b) Expanded curves shown in (a). (c) Approach curves of the low-pass-filtered current signal at $E_{\text{tip}} = 0.5$ V simultaneously acquired with the curves shown in (a). (d) A secondary electron SEM top-view image (at a tilt angle of 90°) at an accelerating voltage of 15 kV and a schematic of the electrode geometry used for the digital simulation of the approach curves.

Because the side of the electrode was tapered, the digital simulation was carried out on the basis of the volume element model given in Fig. S4 to calculate approach curves that account for the tapered shape. The simulated approach curves for the electrode reaction of the $\text{FA}^+/\text{FA}^{2+}$ redox couple are given in Fig. 2c. Open circles represent the curves for an electrode with the geometry shown in Fig. 2d at diffusion-controlled pure positive feedback. The solid circle represents the curve at an effective standard rate constant at the substrate ($k_0$) is 2.2 × 10⁻² (solid circle). The electrical double layer (EDL) effect on the electron-transfer kinetics is substantial for nanoelectrodes when they are located in close proximity to substrates such as electrodes and/or charged surfaces. The effective standard rate constant for the positively charged redox couple such as $\text{FA}^+/\text{FA}^{2+}$ can be decreased with decreasing distance between the tip and the substrate. Although the digital simulations should have taken the EDL effects into account to solve the Nernst–Plank equation, we have not yet conducted such simulations.

3.3 SEC imaging

Figure 3 shows topographic and SECM images of the Au-sputtered Isopore membrane (a, c) and Pt nanoparticles deposited at the HOPG surface (b, d). The potential of the substrates was set at open circuit potential. The pores in the membrane were clearly observed in the topographic and SECM images. The size of the pore reasonably agrees with that observed in the SEM image (Fig. 6S). Because the tip of the nanoelectrode was ~200 nm, it could enter the pores, resulting in clearly observed depressions in the topographic image. When the tip entered the pore, no stop-trigger (tunneling current between the tip and the sample) was obtained. To prevent the tip from impacting the specimen, a travel limit of the vertical movement was prefixed at each data point. Thus, the depth of the pore in the topography represents the travel distance at which the tip enters the pore. Although the Pt particles were clearly observed in...
topographic image in Fig. 3b, the difference between the Pt particles and the HOPG surface was not observed in SECM image (Fig. 3d) due to the similar electrochemical activity for FA+/FA− at the Pt and the HOPG surfaces. The observed height of the nanoparticles (50–100 nm) have similar height reported previously.16

4. Conclusions

A conical-shaped Pt nanoelectrode, of which the apex of the tip featured an effective electrode, was fabricated and used as a probe for SECM. The volumetric experiments showed that the obtained Pt nanoelectrode was not an ideal disk shape but rather a protruded shape, as revealed by SEM observations and digital simulations of the electrochemical response of the nanoelectrode. Approach curves with improved signal-to-noised-ratios were obtained by acquiring the low-pass-filtered current while simultaneously monitoring the raw current as a stop trigger for the movement of the tip toward the surface. By using the tunneling-current-based constant distance SA mode imaging, we obtained topographic and SECM images of an Au-sputtered polycarbonate membrane with submicron pores and Pt nanoparticle at the HOPG surface.

Supporting Information

The Supporting Information is available on the website at DOI: https://doi.org/10.5796/electrochemistry.21-00013.

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