Electropolymerization of *o*-Mercaptoaniline Monolayer Self-assembled on an Au Electrode

Naotake Sato and Tsutomu Nonaka*
Department of Electronic Chemistry, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226

(Received May 22, 1995)

An electroactive monolayer of poly(*o*-mercaptoaniline) was prepared by electrooxidatively polymerizing *o*-mercaptoaniline self-assembled on an Au electrode.

It is well known that electropolymerization of aromatic compounds dissolved in electrolyte solutions is a very useful method for preparing the corresponding multilayered polymer films on the electrodes. The initial process of polymerization involves local nucleation and growth of polymers.[1] Therefore, it is generally difficult to prepare uniform monolayers of the polymers by this method.

The uniform monolayers can be prepared by electropolymerizing Langmuir-Blodgett (LB) and self-assembled monolayers of amphipathic and thiol compounds, respectively. In fact, there have been many reports of polymerization of LB monolayers.[2] On the other hands, the polymerization of self-assembled monolayers of thiol compounds has been rarely reported so far. In 1994, Ataka *et al.*[3] reported on *in situ* IR-spectroscopic study on electropolymerization process of a self-assembled monolayer of *p*-mercaptophenol on an Au electrode. Subsequently, a stable monolayer of poly[N-(mercaptoalkyl)pyrrole] was prepared by Willcut and McCarley.[4]

A variety of practical utilization of multilayers of polypyrroles and polyanilines have already been developed, while those of their monolayers have not been found at present. However, electrochemical properties of the monolayers should be unique compared with those of the multilayers, since electron and mass transfers on electroactive monolayer-coated electrodes should be much less affected by polymer bulk properties than those on the multilayer-coated electrodes.

Viewed the above light, we report here the preparation of monolayer of polyaniline on an Au electrode and its electrochemical properties.

An Au electrode (5 x 5 mm) was polished with alumina powder (0.6 μm), then was washed with conc. H_2SO_4 and 0.2 mol dm^{-3} NaOH, and finally was rinsed with distilled water in an ultrasonic cleaning bath. Self-assembly of a monolayer of *o*-mercaptoaniline was accomplished by soaking the Au plate in a 10 mmol dm^{-3} *o*-mercaptoaniline / CH_3CN solution for 60 min in the ultrasonic cleaning bath and the resulting Au plate was used as a working electrode for polymerizing *o*-mercaptoaniline self-assembled monolayer after being rinsed with acetone and hexane in the cleaning bath. The counter electrode was a Pt plate (10 x 10 mm). For polymerization of *o*-mercaptoaniline, the Au electrode was repeatedly potential-scanned between −0.2 and 1.0 V *vs*. SCE at 0.1 V s^{-1} of scan rate in 0.5 mol dm^{-3} H_2SO_4. A set of redox peaks was observed around 0.4 V, was increased by repeating the scan, and was saturated at the tenth scan, as shown in Figure 1(a).

Redox properties of the poly(*o*-mercaptoaniline) monolayer prepared above were examined by cyclic voltammetry at various scan rates. Figure 1(b) indicates that the anodic and cathodic peak currents (*I*pa and *I*pc, respectively) are proportional to the scan rate, while the anodic and cathodic peak potentials (*E*pa and *E*pc, respectively) are independent on the scan rate as shown in Figure 1(c). The formation of poly(*o*-mercaptoaniline) monolayer could be reconfirmed by these facts.

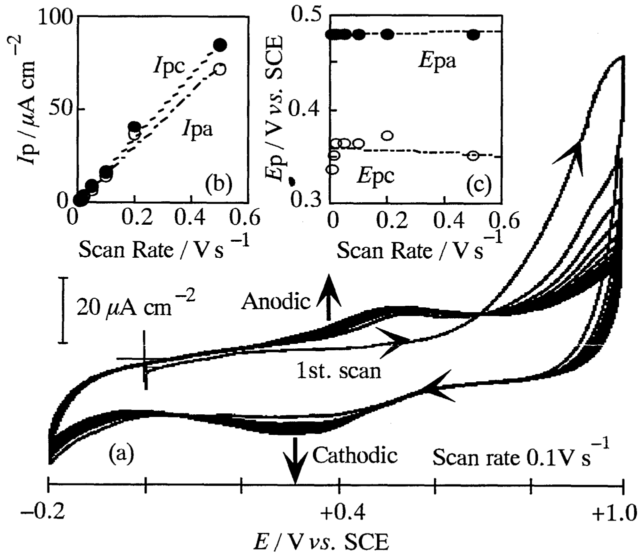

Figure 1. Cyclic voltammetric data of (a) *o*-mercaptoaniline monolayer self-assembled, and (b) and (c) poly(*o*-mercaptoaniline) monolayer polymerized on an Au electrode in 0.5 mol dm^{-3} H_2SO_4.

Integration of the anodic and cathodic peaks indicates that surface coverages with aniline units are estimated to be 5.9 and 6.0 x 10^{-10} mol cm^{-2}. These values seem to be reasonable as those for monolayers on an Au electrode,[5] and also indicate a high reversibility for redox of the poly(*o*-mercaptoaniline) monolayer prepared.

Monolayer of poly(*o*-mercaptoaniline) on an Au electrode responded to redox of $Fe(CN)_6^{3-/4-}$ to give a set of redox peaks of which the peak potentials and currents are shown in Table 1 (Entry 1).

Figure 2 shows redox peak potentials and currents of $Fe(CN)_6^{3-/4-}$ on multilayers of polyaniline prepared by passing various amounts of charge in aniline / 0.5 mol dm^{-3} H_2SO_4.[6] Their values extrapolated to 0 mC cm^{-2} (exactly, ca 10^{-7} mC cm^{-2} corresponding to the monolayer formation) of charge are almost equal to those obtained for the monolayer of poly(*o*-mercaptoaniline), as shown in Table 1 (Entry 2).

Any locally-accumulated clusters[4b] of poly(*o*-mercaptoaniline) multilayers were not observed on the Au electrode by SEM (x10 000). The electrode surface was scanned with a beam (10–50 μm) of SIMS for elemental analysis of C, N and S, but they were not detected significantly from the background. This fact also suggests that the clusters of multilayers are not formed. From these results, poly(*o*-mercaptoaniline), if it is formed, may be regarded as considerably uniform monolayered film, though it can not be directly detected within sensitivities of

Table 1. Redox data of $Fe(CN)_6^{3-/4-}$ (10 mmol dm^{-3}) in 0.5 mol dm^{-3} H_2SO_4 at scan rate 0.1 V s^{-1} on mono- and multi-layers of poly(*o*-mercaptoaniline) and polyaniline, respectively

Entry	Peak potential / V *vs.* SCE		Peak current / mA cm^{-2}	
	Anodic	Cathodic	Anodic	Cathodic
1	0.42	0.31	6.3	5.7
2[a]	0.41	0.32	7.6	5.7
3[b]	0.44	0.29	6.0	5.0

a Value extrapolated to 0 mC cm^{-2} of charge passed for the polyaniline formation (See Figure 2).

b On a bare Au electrode.

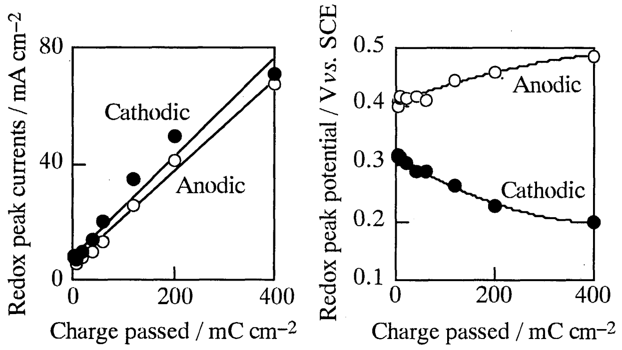

Figure 2. Redox peak currents and potentials of $Fe(CN)_6^{3-/4-}$ (10 mmol dm^{-3}) on multilayers of polyaniline prepared by passing various charges. Scan rate: 0.1 V s^{-1}.

SEM and SIMS used in this work. Although the surface coverage with aniline units seems to be a reasonable value as described above, it has not been evidently corroborated that the electrode surface is exhaustively covered with the monolayer.

Dynamic process for the polymerization of a self-assembled monolayer of *o*-mercaptoaniline was examined by SNIFTIRS. Figure 3 shows drastic changes in the spectra during potential scanning for the polymerization from –0.2 to 0.8 V *vs.* SCE. These spectra give the first IR spectroscopic information of a monolayer of polyaniline. The spectra are considerably different from those of a bulk of polyaniline[7] and their detailed investigation is in progress.

This study was financially supported by Grant-in-Aid for Scientific Research on Priority Area (New Development of Organic Electrochemistry) from the Ministry of Education, Science and Culture. The authors are grateful to Dr. Fusao Kitamura for his kind assistance in the SNIFTIRS surface analysis.

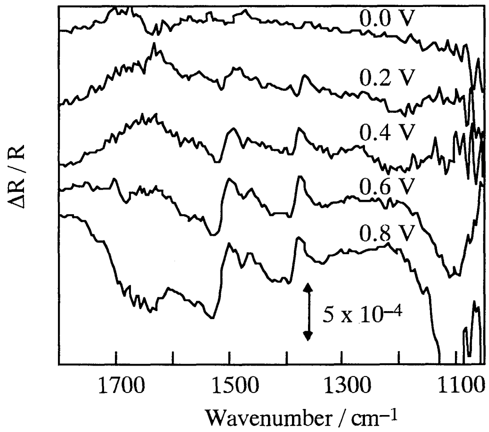

Figure 3. SNIFTIRS spectra of a self-assembled monolayer of *o*-mercaptoaniline on Au electrode in 0.1 mol dm^{-3} H_2SO_4. Reference : reflectance at –0.2 V *vs.* SCE.

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