—コミュニケーション—

Electrochemical Response of Poly(1,1'-ferrocenylene) - Modified Electrode

Noboru OYAMA*, Yumiko TAKIZAWA†, Hiroaki MATSUDA†,
Takakazu YAMAMOTO** and Kenichi SANECHIKA**

Received June 7, 1988 ; Accepted July 15, 1988

1 INTRODUCTION

Analysis of electrochemical response of polymer-modified electrode and its application are the subject of recent interest (1-3). We previously reported preparation of poly-(1,1'-ferrocenylene), PF, and rapid exchange of electron on Mössbauer time scale between Fe(II) and Fe(III) in a partly oxidized PF adduct of TCNQ (4,5). We now report electrochemical response of PF-modified electrode. Although a number of reports have been published on electrochemical studies of ferrocene and its derivatives, preparation of the PF-modified electrode and report on its electrochemical response have no precedent.

2 EXPERIMENTAL

Poly(1,1'-ferrocenylene) (PF) was prepared as previously reported (4,5), and hexane-extractable fraction (molecular weight = ca. 900) was used for the present study. Two methods were used to prepare the PF-modified electrode. Method A: PF was electrochemically deposited on a platinum or gold electrode ($\phi = 0.1$ mm, $l = 1.0$ cm) from a CH_2Cl_2 solution containing saturated PF and 0.20 M of $[\text{Bu}_4\text{N}][\text{ClO}_4]$. The electrochemical deposition was carried out at 1.0 V vs. SSCE (sodium chloride saturated calomel electrode). Method B: A graphite electrode (basal plane pyrolytic graphite) was coated with PF dispersed in poly(vinylidene fluoride) by drying up a CH_2Cl_2 solution of poly(vinylidene fluoride) and PF. Poly(vinylferrocene) (PVF) was purchased from Merck Co. Ltd.

3. RESULTS AND DISCUSSION

We first measured cyclic voltammogram of PF in a CH_2Cl_2 solution of PF containing $[\text{Bu}_4\text{N}][\text{BF}_4]$ as the electrolyte. As shown in Fig. 1, redox reaction of PF occurs over a wide range of potential between 0.1 V and 0.8 V vs. SSCE. In contrast to PF, PVF shows only one redox potential at ca. 0.47 V vs. SSCE. The multiple oxidation of PF indicates that the electron in PF is delocalized along the polymer chain and oxidation of one Fe(II) center to Fe(III) affects the oxidation of the next Fe(II) in the same polymer chain.

Fig. 1. Cyclic voltammogram for PF (0.98 mM) at a gold electrode in a CH_2Cl_2 solution of $[\text{Bu}_4\text{N}][\text{BF}_4]$. Scan rate: (1) 380; (2) 190; (3) 74 mV s^{-1} .

----Fe(II)-Fe(II)-Fe(II)-Fe(II)----

first oxidation → ----Fe(III)-Fe(II)-Fe(II)-Fe(II)----

second oxidation → ----Fe(III)-Fe(II)-Fe(III)-Fe(II)----, etc.

Department of Applied Chemistry for Resources, Tokyo University of Agriculture & Technology (2-24-16 Nakamachi, Koganei 184). †Department of Electronic Chemistry, Tokyo Institute of Technology (4259 Nagatsuta, Midori-ku, Yokohama 227). ††Research Laboratory of Resources Utilization, Tokyo Institute of Technology (4259 Nagatsuta, Midori-ku, Yokohama 227)

Key words: Poly(1,1'-ferrocenylene). Modified Electrode.

The cyclic voltammetric result is consistent with the Mössbauer spectroscopic results which demonstrate that rapid exchange of electron between Fe(II) and Fe(III) in the partly oxidized PF occurs on Mössbauer time scale (10^{-7} s) at room temperature (5).

Figure 2 shows cyclic voltammogram of the PF-modified electrode prepared by Method A. A voltammogram of a PVF-modified electrode is also shown in Fig. 2 for comparison. The PF film overlaid on the electrode was stable in the solvent. As seen in Fig. 2, the PF-modified electrode shows multiple redox potential in a range of 0.1-0.8 V vs. SSCE. The PF-modified electrode prepared at longer time of electrodeposition gave larger electric current, but the shape (redox potentials) of the voltammogram was invariant. Both i_p^a and i_p^c were roughly proportional to square root of potential scan rate, indicating that the charge-transport process within the PF film was diffusion-controlled apparently (3). As shown in Fig. 2, the PVF-modified electrode shows only one redox potential at about 0.35 V vs. SSCE, revealing that electronic interaction between the ferrocene centers in the PVF film is not so significant as in the PF film. The PF film on the electrode prepared by Method B was often released from the graphite electrode when the PF-modified electrode was dipped in organic solvent. However, this PF-modified electrode was stable in an aqueous medium containing 0.2 M of NaClO₄ and showed cyclic voltammetric behavior similar to that shown in Fig. 2. Since the PF-modified electrodes show redox response over the wide range of potential, they may serve as a unique electrode, e.g., for organic synthesis or amperometric sensor. The electroactive ferrocene centers having different redox potentials will serve multiple electron-transfer mediating catalysts to accelerate slow reactions.

Fig. 2. Cyclic voltammograms for electro-deposited PVF(1) and PF(2) films on a Pt electrode in a CH₂Cl₂ solution of [Bu₄N][ClO₄] (0.1 M). Electrolysis time for the deposition of films: 3 min. Scan rate: 190 mV s⁻¹.

This work was partially supported by Grant-in-Aid for Scientific Research on Priority Area "Macromolecular Complex", No. 62612504 for N. Oyama and No. 62612002 for T. Yamamoto, for the Ministry of Education, Science and Culture, Japan.

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