

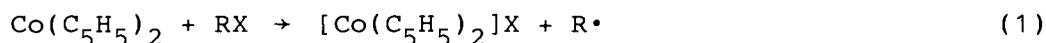
Electrocatalytic Synthesis of a Cobaltocenium/ferrocene Bilayer-like Film
Acting as a Solid State Diode

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Two-step electropolymerization involving reduction of $\text{Fe}(\text{C}_5\text{H}_4\text{CH}_2\text{Cl})_2$ catalyzed by a poly[$\text{Co}(\text{C}_5\text{H}_4\text{CCl}=\text{CHCHO})_2$]^{+/0} electrode film affords a cobaltocenium/ferrocene bilayer-like film. A device fabricated by sandwiching this film between electrodes shows diode-like i-V characteristics under a dry nitrogen atmosphere.

Design of new functional electronic devices using redox molecules has attracted much recent attention in view of their application to future technologies such as neurocomputer.¹⁾ We have previously reported a fabrication of solid state redox diode comprising a cobaltocenium/ferrocene bilayer film by automatical polymerization of $\text{Fe}(\text{C}_5\text{H}_4\text{CHClCH}_3)_2$ on an electropolymerized $[\text{Co}(\text{C}_5\text{H}_4\text{CCl}=\text{CHCHO})_2]^+$ film.²⁾ This diode fabrication involves some difficulties in reproductive formation of uniform interface between the layers and in controlling the amount of electroactive sites in the ferrocene polymer. Here we report a new fabrication method of solid state diode by means of two-step electropolymerization aiming at exclusion of the disadvantages of the previous method as mentioned above.

In general, two-step electropolymerization is effective when a precoated film is electroactive or conducting at the polymerization potential of the second monomer. Another possible case is when the precoated polymer catalyzes the electropolymerization of the second monomer. This electrocatalytic reaction is utilized in this study. It has been known that cobaltocene, $\text{Co}(\text{C}_5\text{H}_5)_2$, reacts with alkyl halides, RX , to form cobaltocenium ion and alkyl radical, as represented in Eq. 1.³⁾



This equation leads to an idea of electrocatalytic reduction of $\text{Fe}(\text{C}_5\text{H}_4\text{CH}_2\text{Cl})_2$ at a poly[$\text{Co}(\text{C}_5\text{H}_4\text{CCl}=\text{CHCHO})_2$]^{+/0}-coated electrode at the reduction potential of the cobaltocenium to form $\text{Fe}(\text{C}_5\text{H}_4\text{CH}_2\cdot)_2$, which can

act as an initiator of the polymerization (Eqs. 2 - 4).

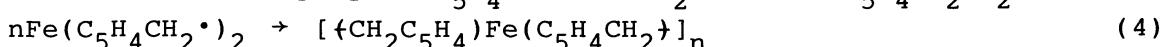
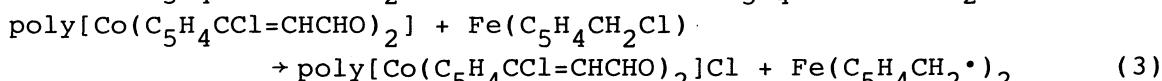
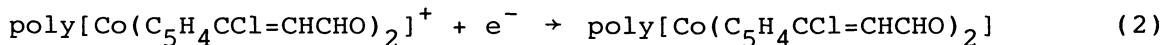


Figure 1(a) displays a cyclic voltammogram for a $\text{Fe}(\text{C}_5\text{H}_4\text{CH}_2\text{Cl})_2$ solution at a glassy-carbon (GC) electrode coated with $\text{poly}[\text{Co}(\text{C}_5\text{H}_4\text{CCl}=\text{CHCHO})_2]^+$. The redox wave at $E^0' = 0.185$ V vs. Ag/Ag^+ ($10 \text{ mol dm}^{-3} \text{ AgClO}_4$ in $0.1 \text{ mol cm}^{-3} \text{ Bu}_4\text{NBF}_4$ -MeCN, 0.27 V vs. SCE) grows with the number of cyclic scans, and this wave can be attributed to the $\text{poly}[\text{Fe}(\text{C}_5\text{H}_4\text{CH}_2\text{Cl})_2]$ deposited on the electrode surface.⁴⁾ As the reduction potential of $\text{Fe}(\text{C}_5\text{H}_4\text{CH}_2\text{Cl})_2$ at a bare GC electrode is ca. -2.7 V,⁴⁾ this result indicates a significant role of the cobaltocenium sites as the electrocatalyst as we have expected.

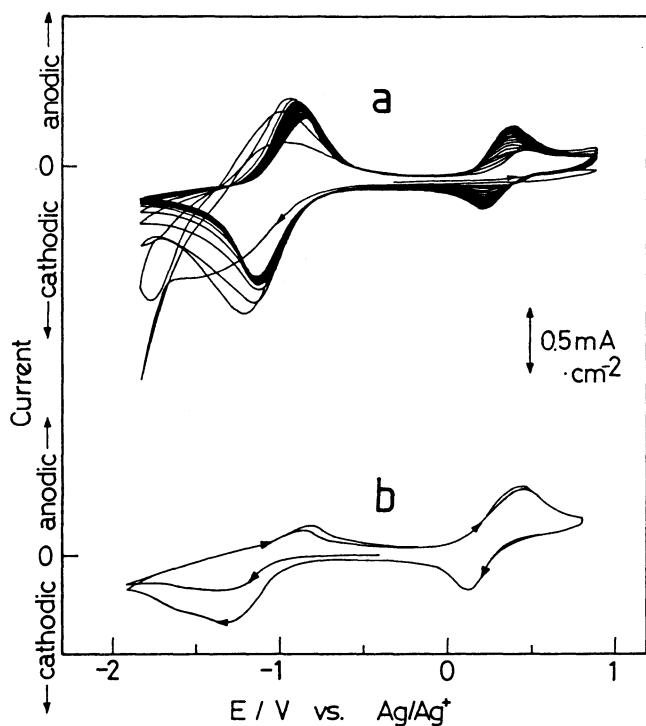


Fig. 1. (a) Cyclic voltammetry for a 5 mol dm^{-3} solution of $\text{Fe}(\text{C}_5\text{H}_4\text{CH}_2\text{Cl})_2$ in $0.1 \text{ mol dm}^{-3} \text{ Bu}_4\text{NBF}_4$ -MeCN at 0.1 V s^{-1} at $\text{poly}[\text{Co}(\text{C}_5\text{H}_4\text{CCl}=\text{CHCHO})_2]^+/\text{GC}$ by consecutive potential scans between 0.8 and -1.9 V vs. Ag/Ag^+ . (b) Cyclic voltammetry of the electrode thus treated in $0.1 \text{ mol dm}^{-3} \text{ Bu}_4\text{NBF}_4$ -MeCN at 0.1 V s^{-1} .

Figure 2 also displays this electrocatalytic activity of the polycobaltocenium film, where the redox wave of the polyferrocene

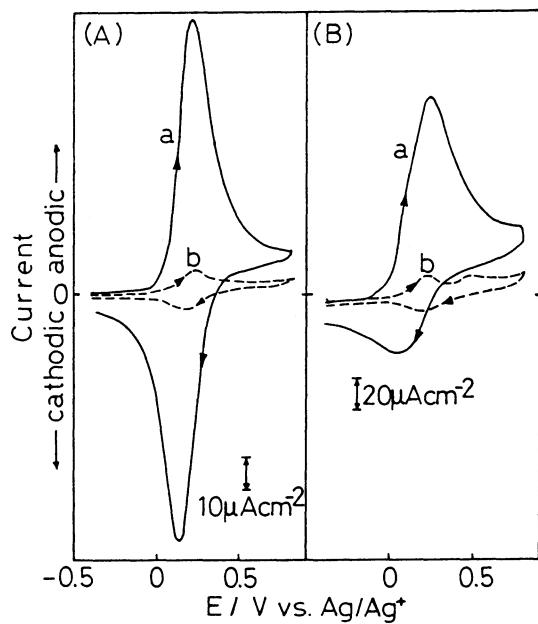


Fig. 2. Cyclic voltammograms of $\text{poly}[\text{Fe}(\text{C}_5\text{H}_4\text{CH}_2\text{Cl})_2]$ formed by controlled potential electrolysis at -1.9 V vs. Ag/Ag^+ for 60 s in 3 mol dm^{-3} solution of the monomer at a $\text{poly}[\text{Co}(\text{C}_5\text{H}_4\text{CCl}=\text{CHCHO})_2]^+$ -coated (a) and uncoated (b) SnO_2 (A) and GC (B) electrodes.

formed by controlled potential electrolysis at -1.9 V vs. Ag/Ag⁺ is much larger at a polycobaltocenium coated electrode than at a bare electrode.

Depth profiles of the elements, cobalt and iron, in the film were measured with X-ray photoelectron spectroscopy (XPS) with Ar⁺ sputtering, and the results are shown in Fig. 3. Peaks appearing at the binding energy of 779 (A) and 709 eV (B) can be assigned to Co(2P_{3/2}) of the polycobaltocenium and Fe(2P_{3/2}) of the poly-ferrocene, respectively.⁵⁾ The Co(2P_{3/2})/Fe(2P_{3/2}) peak intensity ratio is plotted against the etching time and given in Fig. 4. The intensity ratio increases gradually with the etching time, indicating that the

cobaltocenium sites in the film exist mainly near the GC electrode and the ferrocene sites in the surface region of the film, supporting the bilayer-like structure of the film. However, the profile seen in Fig. 4 denotes that the cobaltocenium and ferrocene sites coexist in a wide range in the middle part of the film, even if the resolution of the XPS technique is taken into consideration.⁶⁾

In order to judge whether this bilayer-like film shows a redox diode behavior or not, current-voltage characteristics of a device fabricated by depositing Au vapor on the cobaltocenium/ferrocene polymer coated

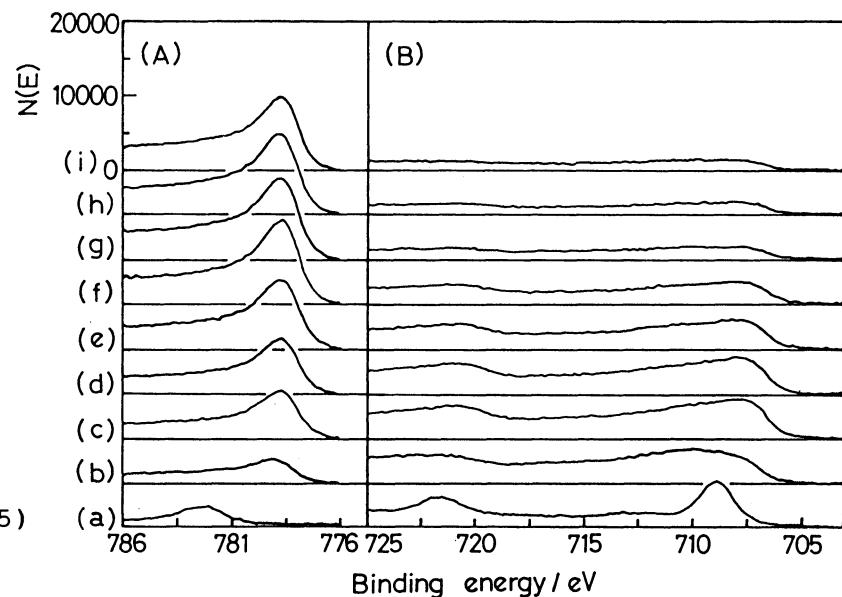


Fig. 3. Depth profiles in XPS spectra of Co(2P_{3/2}) (A), Fe(2P_{1/2}), Fe(2P_{3/2}) (B) for the bilayer-like film coated GC electrode when the etching time is 0 (a), 2 (b), 122 (c), 242 (d), 422 (e), 602 (f), 782 (g), 962 (h), and 1142 s (i).

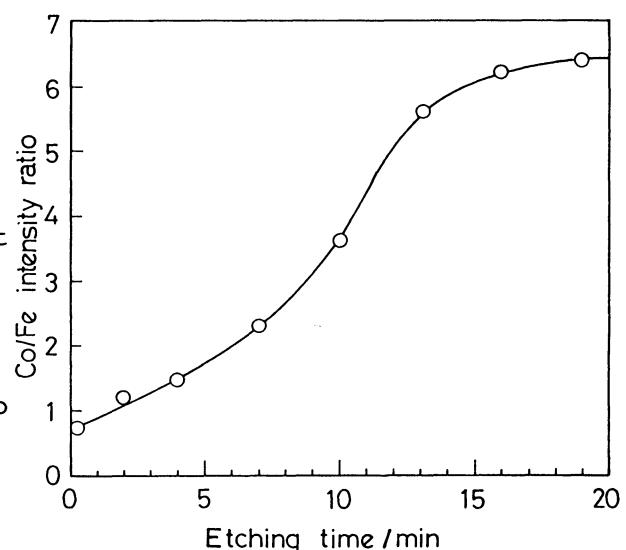


Fig. 4. Relationship between Co(2P_{3/2})/Fe(2P_{3/2}) peak intensity ratio and Ar⁺ sputtering time based on the results shown in Fig. 3.

electrode were measured under a nitrogen atmosphere. The result displayed in Fig. 5 shows an unsymmetrical diode-like characteristic, but this characteristic disappears gradually with cyclic voltage scans. The i - V curve is not wholly consistent with the ideal behavior of redox diode, where a cut-off voltage of abrupt increase in

current that corresponds to the difference in redox potentials between the two layers will appear.²⁾ The rationale of this inconsistency and synthesis of a polymer film with a more clear bilayer structure and high durability against an electric field are now under investigation.

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- 5) The shift in binding energy with Ar^+ sputtering (between (a) and (b) in Fig. 3) might be due to changes in charging effects and/or oxidation states of Co and Fe by Ar^+ ions. Cf., W. M. Riggs and J. Parker, "Methods and Phenomena 1. Methods of Surface Analysis", ed by A. W. Czanderna, Elesvier Scientific, Amsterdam (1975), Chap. 4, pp. 103-158.
- 6) The resolution of XPS is 0.5 - 3 nm and much smaller than thickness of the cobaltocenium/ferrocene film, 100 nm, corresponding to 20 min of Ar^+ sputtering time.

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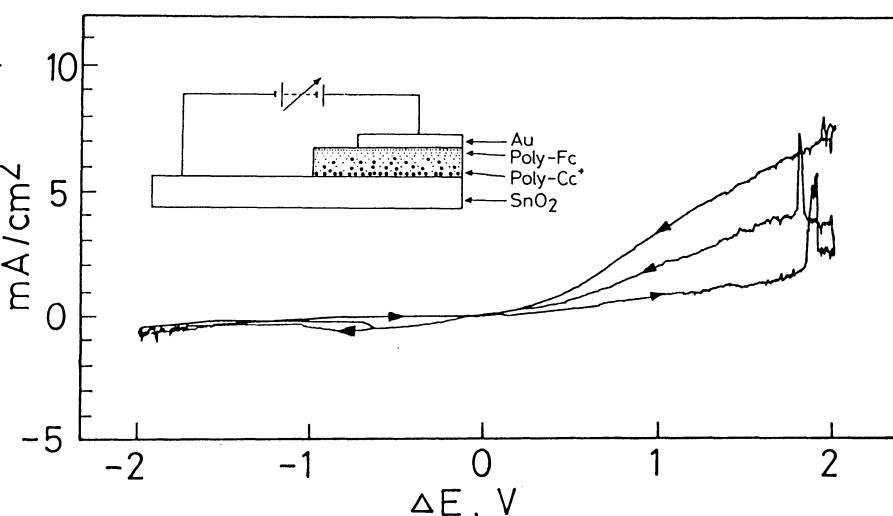


Fig. 5. Current vs. voltage curves for a Au vapor deposited bilayer-like film on SnO_2 at a potential scan rate of 20 mV s^{-1} .