Charge-transfer Complex Formation Promoted by an Electric Field at the Interface of a Ferrocene–Cobaltocenium Bilayer Film

Yoshiyuki Ando, Hiroshi Nishihara,* and Kunitsugu Aramaki

Department of Chemistry, Keio University, Hiyoshi, Yokohama 223, Japan

In the electron transport process of the chemical diode comprising a ferrocene/cobaltocenium bilayer film, an absorption band at *ca.* 500 nm is observed, which can be attributed to charge-transfer complex formation at the film/film interface.

We have recently demonstrated a chemical diode consisting of ITO/PBCFVC/PBCEF/ITO where ITO, PBCFVC, and PBCEF are an In–Sn oxide coated glass, a polymer formed by electrochemical reduction of poly[1,1′-bis(1-chloro-2-formylvinyl)cobaltocenium hexafluorophosphate], and a polymer formed from poly[1,1′-bis(1-chloroethyl)ferrocene] in air, respectively.[1] The overall electron transport process in this diode is composed of electron hopping in the two films and electron transfer at the film/film interface. It is of considerable interest to clarify the mechanism to yield the diode characteristics. Here we report the results of spectroelectrochemical properties of the chemical diode, which indicate the importance of charge transfer complexation at the film/film interface throughout the electron transfer process.

Spectroelectrochemical properties of PBCFVC and PBCEF by themselves are shown in Figures 1 and 2 for comparison with those of the chemical diode. Figure 1 shows spectral changes for PBCFVC/ITO in 0.1 M Bu_4NBF_4/MeCN in the process of electrochemical reduction of cobaltocenium sites in PBCFVC, showing two absorption maxima at 440 ($\varepsilon = 907$) and 560 nm ($\varepsilon = 1109$ mol^{-1} dm^3 cm^{-1}) which can be

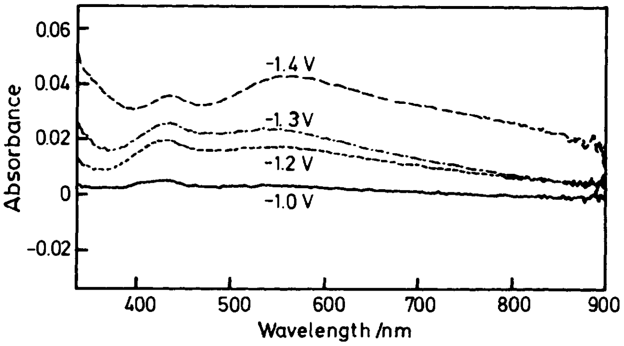

Figure 1. Difference of visible spectra for PBCFVC/ITO in 0.1 M Bu_4NBF_4/MeCN at given potentials from the spectrum at −0.4 V *vs.* Ag/Ag^+.

attributed to formation of the cobaltocene state. Electrochemical oxidation of ferrocene sites in PBCEF causes a spectral change of the peak at 665 nm due to formation of the ferrocenium state[2] as shown in Figure 2.

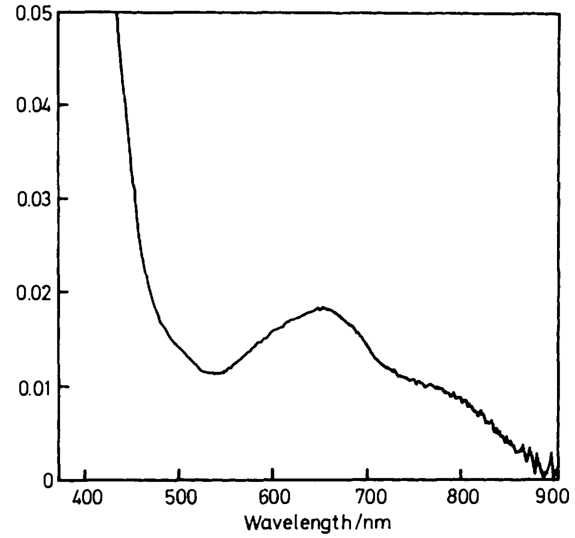

Figure 2. Spectral change for PBCEF/ITO in 0.1 M Bu_4NBF_4/MeCN from −0.5 V to +0.8 V *vs.* Ag/Ag^+.

Figure 3(a) displays spectral changes for the chemical diode when a voltage is applied to the two ITO's of the device under a nitrogen atmosphere. An absorption peak appears at *ca.* 500 nm when the applied voltage is more than 1.0 V and the external current can flow as shown in Figure 3(b). Our previous assumption[1] was that the electron hopping in the two films dominated by the mixed-valent state formation might play an important role in this process.[3] However, the peak at 500 nm is not assignable to either ferrocenium or cobaltocene, and thus the mixed-valent state formation in the films should be negligible in the electron transport process. The resistance of PBCFVC in the cobaltocenium state and that of PBCEF in the ferrocene state used for the diode were as low as 60 Ω cm^{-1} and 80 Ω cm^{-1}, respectively. These values imply that most of the voltage should be applied to the film/film interface when the diode is highly resistive. Thus, the peak at 500 nm should be caused by a change at the interface, which can be assumed to be the charge-transfer (CT) complexation between ferrocene and cobaltocenium sites because both sites may cause a π-orbital interaction. According to the study of Torrance and his co-workers[4] on the relation of the charge-transfer transition energy to the difference between the oxidation potential of the donor and acceptor, the value 500 nm is reasonable for the CT complexation between ferrocene sites in PBCEF and cobaltocenium sites in PBCFVC whose formal potential difference is 1.51 V. We suppose that the electric field decreases the energy barrier for the CT complexation. This study demonstrates a new method of CT complexation

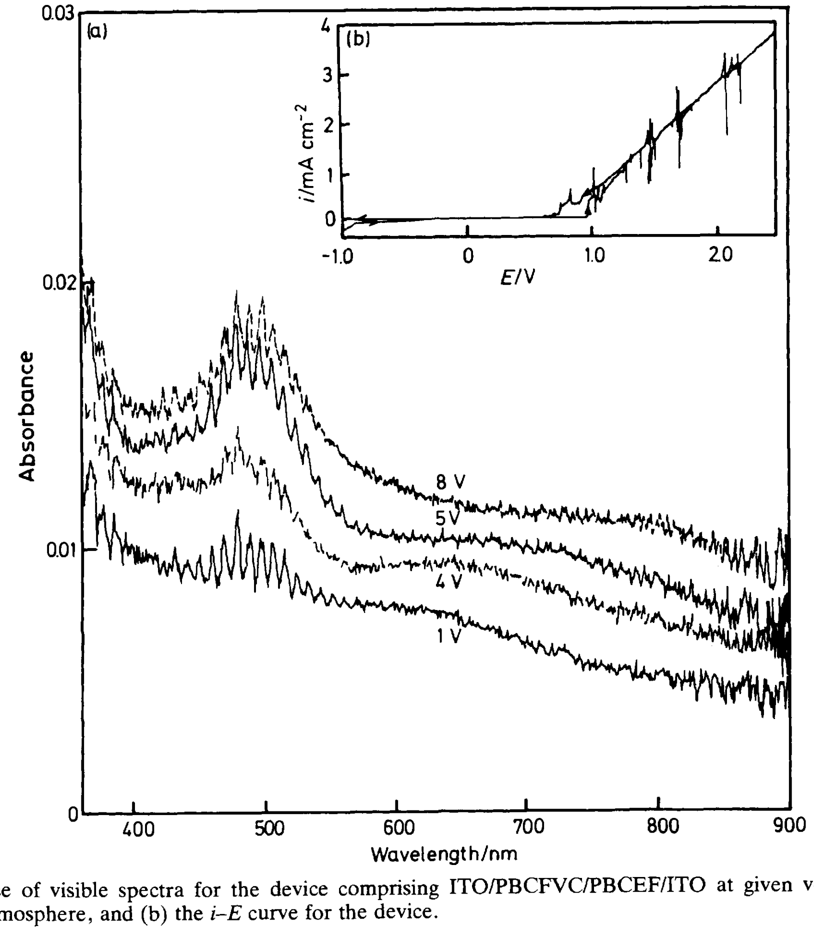

Figure 3. (a) Difference of visible spectra for the device comprising ITO/PBCFVC/PBCEF/ITO at given voltages from the spectrum at 0 V under a nitrogen atmosphere, and (b) the i–E curve for the device.

utilizing immobile hetero-molecular bilayers and an electric field.

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