A Chemical Diode by Combination of Ferrocene and Cobalticinium Electrode Films

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Current *vs.* voltage curves of a device comprising ITO/Poly-$Cc^+BF_4^-$/Poly-Fc/ITO {where ITO, Poly-$Cc^+BF_4^-$, and Poly-Fc are In–Sn oxide, a polymer formed by electrochemical reduction of $[Co(C_5H_4CCl{=}CHCHO)_2]PF_6$, and that formed from $Fe(C_5H_4CHClMe)_2$ in air, respectively} showed diode characteristics under a nitrogen atmosphere.

It is of considerable current interest to develop novel electrical devices by utilizing electroactive polymer films.[1] Electrochemical diodes with polymer–polymer bilayer assemblies in an electrolyte solution have been by Murray and his coworkers.[2] We describe here a new chemical diode consisting of ferrocene and cobalticinium polymer electrode films which can function in the gas phase.

The device is a combination of ITO-A/poly(cobalticinium salt)/polyferrocene/ITO-B as shown in Figure 1 (ITO = indium–tin oxide). Electric current can flow through it only when the difference of potential between ITO-A and ITO-B is large enough to generate cobaltocene and ferricinium sites in the left- and right-hand films, respectively, because the conductivity is high in the mixed-valence state when electron self-exchange reactions can occur between neighbouring oxidized and reduced redox sites.[3,4] An advantage of this polymer combination is that the conducting state can be realized only by the movement of counter anion from the left-hand to the right-hand film, without the need for other substrates. This property enables the diode to function in the gas phase, as has been demonstrated by Jernigan *et al.* for an osmium bipyridine complex polymer film.[5]

In constructing the device it is necessary to produce uniform polymer films on the two ITO plates and to make an adhesive film contact between them. We overcame these difficulties by using a polymer film formed by electro-reduction of $[Co(C_5H_4CCl{=}CHCHO)_2]PF_6$ (**1**)[6] and that from $Fe(C_5H_4CHClMe)_2$ (**2**) which can polymerize in air even at room temperature and acts as a bonding agent. The ferrocene derivative (**2**) was prepared by the reaction of $Fe[C_5H_4CH(OH)Me]_2$ with PCl_3 and stored in a frozen benzene solution under nitrogen. In a typical procedure, the cobalticinium electrode film Poly-$Cc^+BF_4^-$ was prepared at an ITO electrode (ITO-A) in a solution of (**1**) in 0.1 M Bu_4NBF_4–MeCN, instead of the Bu_4NI–MeCN used previously,[6] by consecutive potential sweeps between −0.4 and −2.0 V *vs.* Ag/Ag^+. The film thus formed showed a reversible voltammetric wave with a formal potential $E_{Cc}{}^{0'} = -1.50$ V *vs.* Ag/Ag^+ in 0.1 M Bu_4NBF_4–MeCN as shown in Figure 2(a). A benzene solution of (**2**) was applied to the other plate (ITO-B) and the benzene allowed to evaporate in air. With a small amount of benzene still remaining on the plate, the ITO-A plate coated with Poly-$Cc^+BF_4^-$ was applied to it and clamped for a day under ambient conditions so as to polymerize (**2**) and stick the plates together. Figure 2(b) shows a cyclic voltammogram for an ITO electrode coated only with the polymer of (**2**), Poly-Fc, by the method above, in 0.1 M Bu_4NBF_4–MeCN. The formal potential for the redox reaction of ferrocene sites in the film, $E_{Fc}{}^{0'}$ was 0.01 V *vs.* Ag/Ag^+, more positive than $E_{Cc}{}^{0'}$ by 1.51 V.

Figure 3 displays current *vs.* voltage curves when the voltage was applied between the two ITO plates of the device under

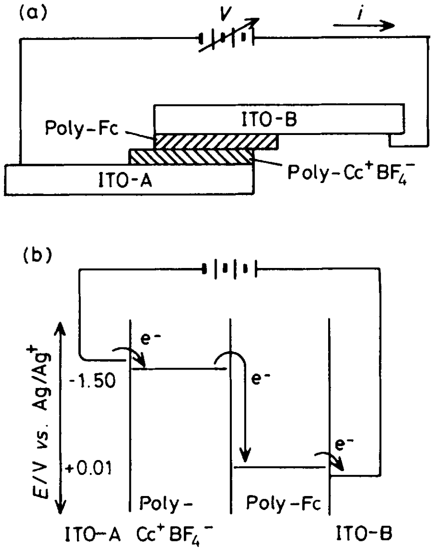

Figure 1. (a) A chemical diode composed of cobalticinium salt and ferrocene polymer films, and (b) the energetics of the device.

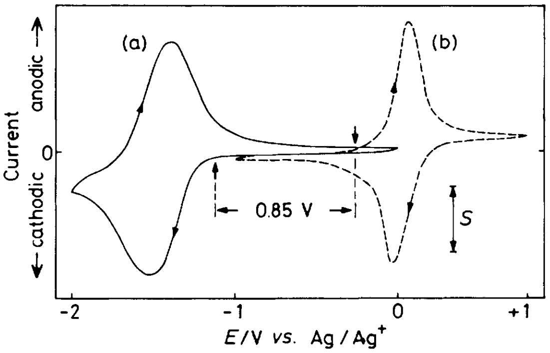

Figure 2. Cyclic voltammograms of (a) Poly-$Cc^+BF_4^-$ (Γ 7.3×10^{-9} mol cm^{-2}) and (b) Poly-Fc (Γ 1.3×10^{-8} mol cm^{-2}) on ITO electrodes in 0.1 M Bu_4NBF_4–MeCN at 0.1 V s^{-1}. $S = 89$ μA cm^{-2} for (a) 250 μA cm^{-2} for (b).

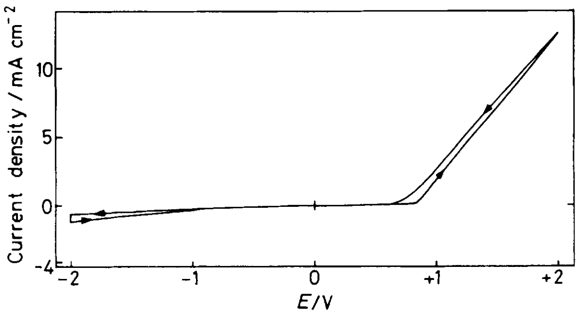

Figure 3. Current *vs.* voltage curves for the device ITO/Poly-$Cc^+BF_4^-$/Poly-Fc/ITO at a potential sweep rate of 20 mV s^{-1}. $\Gamma = 1.3 \times 10^{-8}$ mol cm^{-2} for both polymers.

dry nitrogen. Current flows when the potential of ITO-A is more negative than that of ITO-B by more than 0.85 V. This value is simply the potential difference between the negative edge of the Poly-Fc oxidation wave [Figure 2(b)] and the positive edge of the Poly-$Cc^+BF_4^-$ reduction wave [Figure 2(a)]. Consequently, it is certain that the current began to flow following the generation of mixed-valence states for both films. The current increased linearly with the voltage above 0.85 V, as shown in Figure 3, and the increase continued until at least $E = 6$ V. This fact suggests that the conductivities of the films are high over a wide range of high $Cc:Cc^+$ and $Fc^+:Fc$ ratios.[4] The resistance of the device was *ca.* 130 Ω cm^{-2}, which includes the resistances of two ITOs and those of the film–film and ITO–film interfaces besides those within the films.

The diode described above consists of redox polymers and does not fall into the categories of former diodes such as vacuum-tubes and semiconductors.[7] It is noteworthy that the voltage at which current rise occurs should be easy to regulate in the redox-polymer diode by combining two films with appropriate redox potentials.

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