

Molecular diodes fabricated by a junction between mixed- and nonmixed-valent polymer films

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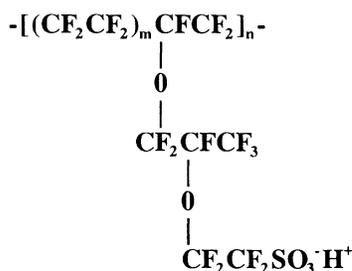
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A molecular junction between thin polymer films of occupied-state $[\text{Fe}^{\text{II}}(\text{phen})_3][\text{Naf-SO}_3]_2$ and half-occupied-state (mixed-valent) $[\text{Fe}^{\text{II,III}}(\text{phen})_3][\text{Naf-SO}_3]_{2.5}$ (where “phen” stands for 1,10-phenanthroline and “Nafion” is a perfluorosulfonate polymer) has been prepared. The junction exhibits current rectification and space-charge-limited current transients consistent with good hole injection into the occupied-state film from the mixed-valent film contact.

Electron current-rectifying interfaces between molecular materials containing localized sites between which electrons can hop are interesting both as possible devices and for the fundamental insights they yield about how charges cross molecular interfaces. We understand¹ the principles of such interfaces for cases where electron flow is accompanied by redistribution of ionic species within the two contracting molecular materials. Analogous examples have since been cited.² The present work describes a molecular junction at which electron flow is controlled by an electrostatic accumulation layer, which can only form when ionic motions are restricted or eliminated. For molecular materials containing localized electronic states, such control has not been previously demonstrated although related phenomena are known³ with delocalized state molecular materials fashioned into field-effect transistors.

The molecular junction presented is based on the 1100 equivalent weight perfluorosulfonate polymer, Nafion,



in which the proton has been ion exchanged with the electron transfer active metal complex $[\text{Fe}(\text{phen})_3]^{2+}$ (phen) is 1,10-phenanthroline). This fully reduced, occupied state form of the polymer, labeled $[\text{Fe}^{\text{II}}(\text{phen})_3][\text{Naf-SO}_3]_2$ is, when dried, a resistive material of resistivity ca. $10^7\text{--}10^9 \Omega \text{cm}$; both electronic and ionic conductivities are very low. Study of electron transport in $[\text{Fe}^{\text{II}}(\text{phen})_3][\text{Naf-SO}_3]_2$ by current injection from an electrode requires a facile injecting contact. Metal contacts of Pt, Au, and Ag yield only displacement

currents; the lack of good injection is apparently due to the large energy difference between the Fermi levels of the polymer and metal. On the other hand, metals do form good injecting contacts to dry polymers containing equal concentrations of reduced and oxidized (i.e., mixed valent) metal complex, $[\text{Fe}^{\text{II,III}}(\text{phen})_3][\text{Naf-SO}_3]_{2.5}$. The mixed-valent films have an electron (hopping) resistivity of ca. $10^5 \Omega \text{cm}$, and significantly, prove to make good injecting contacts to films of the nonmixed-valent polymer, $[\text{Fe}^{\text{II}}(\text{phen})_3][\text{Naf-SO}_3]_2$.

The junction between $[\text{Fe}^{\text{II,III}}(\text{phen})_3][\text{Naf-SO}_3]_{2.5}$ and $[\text{Fe}^{\text{II}}(\text{phen})_3][\text{Naf-SO}_3]_2$ was made by coating⁴ $1 \mu\text{m}$ Nafion films onto Pt electrodes, loading $[\text{Fe}(\text{phen})_3]^{2+}$ into one film, a ca. 1:1 $[\text{Fe}(\text{phen})_3]^{2+}/[\text{Fe}(\text{phen})_3]^{3+}$ mixture into the other, and pressing the films together in a mechanical press at 150°C for ca. 30 min to make a Pt/ $[\text{Fe}^{\text{II,III}}(\text{phen})_3][\text{Naf-SO}_3]_{2.5}/[\text{Fe}^{\text{II}}(\text{phen})_3][\text{Naf-SO}_3]_2/\text{Pt}$ structure

The apparatus for the space-charge-limit transient current measurements is shown in Fig. 1. The $10\text{-}\Omega$ load

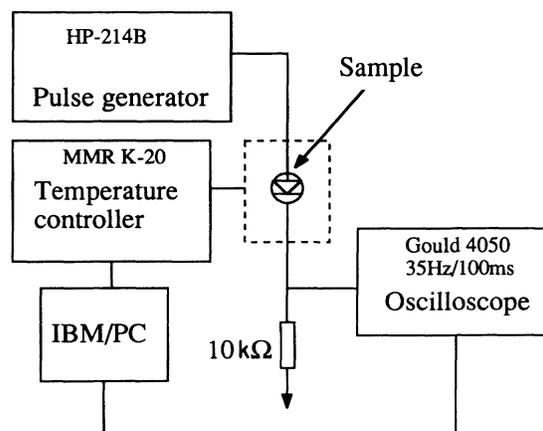


FIG. 1. Schematic diagram of the setup for transient space-charge-limited current measurements.

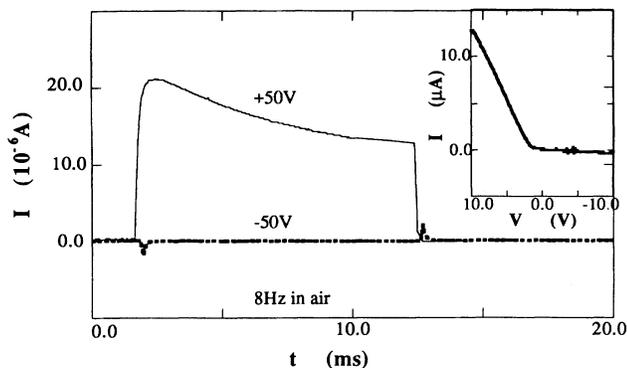


FIG. 2. The transient current response for 50-V forward (—) and reverse (---) bias pulses at room temperature. The inset is a I - V curve measured by a 10-Hz, ± 10 -V triangular wave.

resistor contributes to the short time RC time constant but has no influence on the longer time transient current response.

The rectification observed by applying a 10-Hz, ± 50 -V square wave signal to the polymer sample is shown in Fig. 2. The forward-bias current reached 2.2×10^{-5} A and the reverse bias showed a stable value of 2×10^{-8} A. The inset to Fig. 2 shows the analogous rectifying response to a ± 10 -V, 10-Hz triangular wave. In these experiments, the electrode contacting the mixed-valent film is positive on the forward bias cycle so that holes are being injected into the nonmixed valent, $[\text{Fe}^{\text{II}}(\text{phen})_3][\text{Naf-SO}_3]_2$ film; i.e., $[\text{Fe}(\text{phen})_3]^{3+}$ sites are being generated there. Figure 3 shows the dependency of the forward-bias transient currents on the applied voltage, which (inset) is close to a squared dependence on voltage. Polymer specimens containing only nonmixed valent $[\text{Fe}^{\text{II}}(\text{phen})_3][\text{Naf-SO}_3]_2$ exhibit no rectification and only small currents comparable to the reverse-bias levels in Fig. 2.

Figure 4 shows the transient current response for the mixed-valent–nonmixed-valent film junction over an extended range of times. After an initial decay of current due to displacement, there is a slow rise with the shape

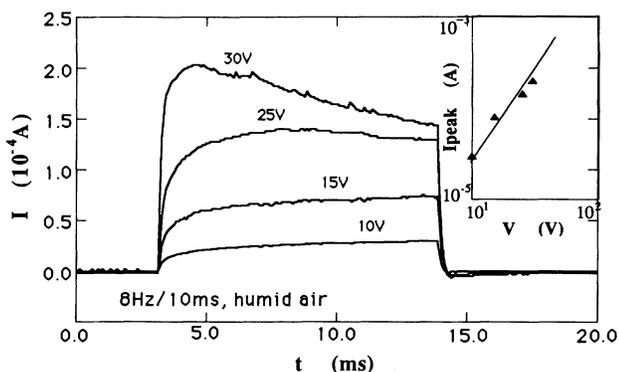


FIG. 3. Applied forward-bias voltage dependence of transient space-charge-limited current measured on the time scale of 1 ms / division. Inset is I_{max} - V curve.

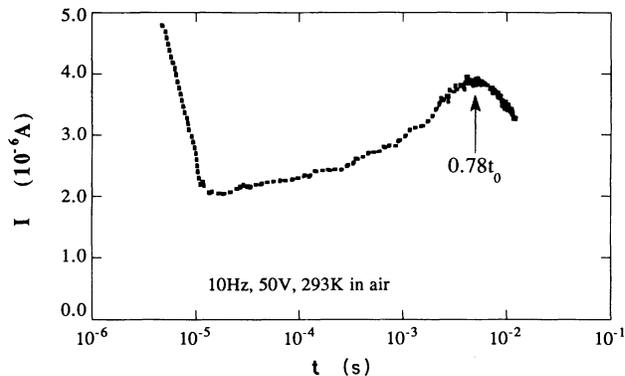


FIG. 4. A forward-bias typical transient space-charge-limited current curve which shows a peak indicating $0.78t_0$ where t_0 is the charge transit time.

characteristic of a transient space-charge-limit current.^{5,6} Taking the time at which the current maximum occurs as $0.78L^2/\mu V$ where L is the film thickness (1 μm), μ the charge mobility, and V the applied voltage (50 V) gives^{5,6} an electronic mobility of 4×10^{-8} $\text{cm}^2/\text{V sec}$ for the transport of holes in the $[\text{Fe}^{\text{II}}(\text{phen})_3][\text{Naf-SO}_3]_2$ material. Similar results were obtained for several samples. This mobility is consistent with independent measurements of the effective electron hopping or self-exchange rate constant $k_{\text{ex}} = 10^5 \text{ M}^{-1} \text{ s}^{-1}$ in these mixed-valent films⁷ by methods we have described.^{8,9}

DISCUSSION

The results show that a rectifying junction is formed by contacting a fully reduced metal complex-Nafion phase with a mixed-valent one and that the latter can serve as a hole-injecting contact to the former whereas metals cannot. A schematic diagram of the injection and charge transport is shown in Fig. 5. The rate of electron hopping (which is proportional to electron conductivity) between the reduced and oxidized metal complex sites in the $[\text{Fe}^{\text{II,III}}(\text{phen})_3][\text{Naf-SO}_3]_{2.5}$ polymer is^{8,9} the product of their concentrations and the self-exchange rate constant k_{ex} . When either concentration is zero, the (nonmixed valent) material is insulating and the polymer equivalent of an intrinsic semiconducting material. At equal Fe^{II} and Fe^{III} concentrations, the hopping rate and electron conductivity are maximized and electron hopping occurs at the Fermi level.

We reasoned that a 1:1 $[\text{Fe}^{\text{II}}]:[\text{Fe}^{\text{III}}]$ ratio and an all Fe^{II} film would have sufficiently comparable values of their Fermi levels that a junction between them would result in an electrostatically limited accumulation of holes ($[\text{Fe}(\text{phen})_3]^{3+}$) on the $[\text{Fe}^{\text{II}}]$ side by electron transfers to the mixed-valent $[\text{Fe}^{\text{II}}][\text{Fe}^{\text{III}}]$ side. Provided the metal complex physical diffusivity in the dry Nafion is very low, for which we have other evidence,⁷ this junction should, and did, yield a hole-injecting contact. Figure 5 shows a schematic bandlike diagram for the junction based on the convention that the unoccupied $[\text{Fe}(\text{phen})_3]^{3+}$ level is depicted above the Fermi level and the occupied

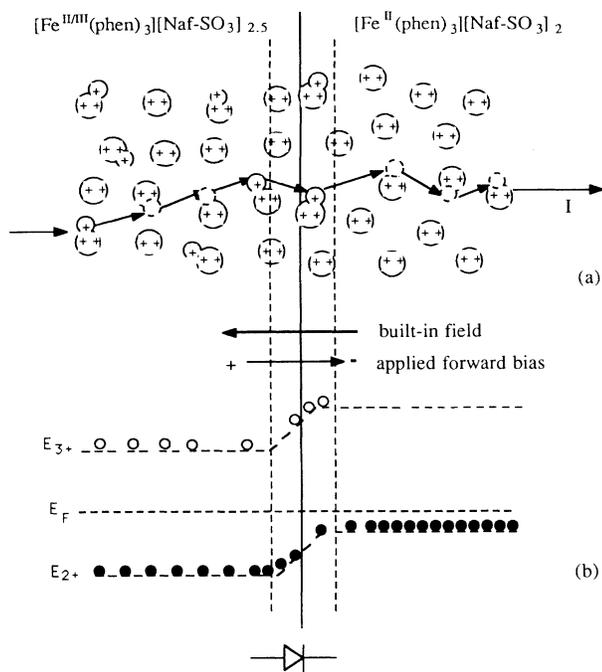


FIG. 5. (a) A schematic junction between $[\text{Fe}^{\text{II,III}}(\text{phen})_3][\text{Naf-SO}_3]_{2.5}$ and $[\text{Fe}^{\text{II}}(\text{phen})_3][\text{Naf-SO}_3]_2$; (b) an energy-band-like diagram for the junction.

$[\text{Fe}(\text{phen})_3]^{2+}$ below. The "band gap" corresponds to the reorganization energy for electron transfer between $[\text{Fe}(\text{phen})_3]^{2+}$ and $[\text{Fe}(\text{phen})_3]^{3+}$ states which is small, on the order of 0.3 eV.

Application of a forward-bias voltage to the junction, making the $[\text{Fe}^{\text{II}}(\text{phen})_3][\text{Naf-SO}_3]_2$ layer negative and the $[\text{Fe}^{\text{II,III}}(\text{phen})_3][\text{Naf-SO}_3]_{2.5}$ layer positive, drives holes from the positively charged accumulation layer across the latter layer. The charge passed during the resulting current transient is of order CV and was less than that required to generate a monomolecular layer of $[\text{Fe}(\text{phen})_3]^{3+}$ as expected. On the other hand, application of a voltage making the $[\text{Fe}^{\text{II}}(\text{phen})_3][\text{Naf-SO}_3]_2$ layer more positive places the junction into reverse bias, and little current flow is observed.

The results in Figs. 2–4 establish the existence of an injecting polymer-polymer contact, and a rectifying junction between polymer films where conduction takes place via hopping. Further experiments are needed to understand all aspects of these experiments, including resolving the uncertainty in the actual electrode contact areas and that the current levels are much smaller when the voltage pulse is applied to polymer samples exposed to vacuum or dry N_2 than those exposed to room air as illustrated by the difference in current scales in Figs. 3 and 4. The current responds with a few minutes upon switching from one bathing atmosphere to another. These features will need study, but Figs. 3 and 4 establish the essential, rectifying aspect of the experiment.

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