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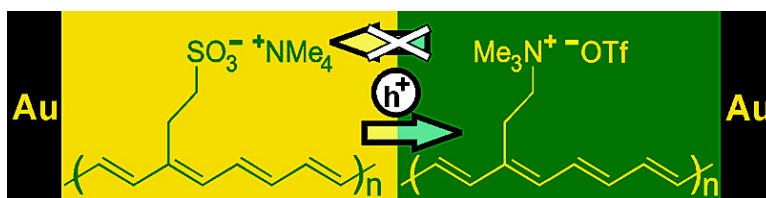
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# Unidirectional Current in a Polyacetylene Hetero-ionic Junction

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There is significant interest in constructing molecule-based junctions that mimic the technologically important behavior of traditional solid-state interfaces such as the asymmetric current—voltage behavior (unidirectional current) of the *pn* junction diode. In one class of interfaces, including bipolar membranes[1] and hydrogel reactors,[2] the underlying mechanism for unidirectional transport bears analogy to *pn* junctions,[1] but the current is ionic rather than electronic. In another class of interfaces, including membrane-separated liquid redox couples[3] and redox polymer interfaces,[4] the current is electronic, but the underlying mechanism bears stronger analogy to the charging of a dead battery than to a *pn* juction.[3] Two-dimensional device structures exploiting redox switching of conductive pathways have also provided examples of unidirectional transport.[5]

We report unidirectional electronic transport in a device based on a previously unexplored type of polymer—polymer interface, that between two conjugated ionomers with nominally the same redox-active backbone but with oppositely charged functional groups. Unidirectional current in this mixed ionic/electronic system is electronic, but its origin relies on asymmetry in ionic processes with respect to the sign of applied bias. The specific structure studied consists of the interface between two ionically functionalized, undoped polyacetylenes,[6] poly[(2-cyclooctatetraenylethyl)-trimethylammonium trifluoromethanesulfonate] ($P_C$) and poly-(tetramethylammonium 2-cyclooctatetraenylethanesulfonate) ($P_A$), sandwiched between gold electrodes (Figure 1, inset).

Figure 1 shows a 10 mV s$^{-1}$ current density–voltage ($J$–$V_{APP}$) sweep of the Au|$P_C$|$P_A$|Au device, and it clearly shows unidirectional current transport through the device. The scan rate of Figure 1 is sufficiently slow that the current is near steady-state, but with some hysteresis remaining. The current must be electronic because the Au electrodes are ion-blocking and hence cannot support steady-state ionic currents. For the device geometry studied, unidirectional current is observed at sweep rates up to 100 mV s$^{-1}$. At 10 mV s$^{-1}$, the rectification ratio at 3 V [($J$(3 V)/$J$(−3 V))] reaches a value of 200. At scan rates above 1 V s$^{-1}$, the observed $J$–$V_{APP}$ behavior is linear, with much less current observed and an apparent conductivity of 5 × 10$^{-12}$ S cm$^{-1}$.

An increase in electronic current with ion polarization, such as that observed in the Au|$P_C$|$P_A$|Au structure under positive bias, is common in mixed ionic/electronic conducting systems based on undoped conjugated polymers and ion-blocking electrodes.[7] The large fields created at the electrodes from ion polarization can facilitate carrier injection, which in turn can also enhance current by increasing the carrier density. The key question is why the current is only enhanced for one sign of the applied bias in the Au|$P_C$|$P_A$|Au structure.

One possible explanation for the unidirectional behavior is based on the idea that electron transport requires oxidative (p-type) doping
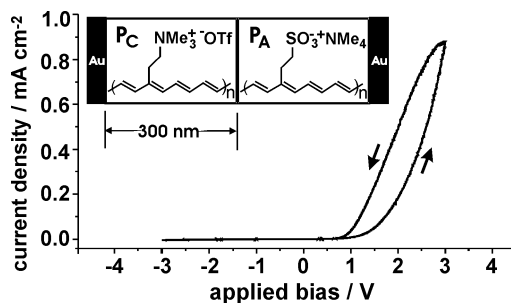
**Figure 1.** Slow scan rate (10 mV/s) $J$–$V_{APP}$ behavior for the Au|$P_C$|$P_A$|Au sandwich structure. The bias is applied to $P_A$ with respect to $P_C$. The inset shows a cross-sectional schematic of the structure studied.

at one electrode and reductive (n-type) doping at the other. Herein, such a process is termed Faradaic because both reduction and oxidation occur along with the diffusion of ions; both local and overall charge neutrality are preserved. With our sign convention, positive bias would drive the reaction (i) $P_A + P_C \rightarrow$ p-$P_A$ + n-$P_C$, and negative bias would drive (ii) $P_A + P_C \rightarrow$ n-$P_A$ + p-$P_C$. Any difference in the values of $\Delta G°$ for these two reactions would then result in the magnitude of the bias required to drive transport being sign dependent. This mechanism of unidirectional transport has been observed in bilayers based on more widely studied redox polymers and has been compared to the charging of a dead battery.[3] Faradaic charging of the battery is required for transport, and most batteries only charge for one sign of the applied bias.

Analysis of cyclic voltammetry data[6] for $P_A$ and $P_C$ may at first appear to support the asymmetric Faradaic charging model above. Both $P_A$ and $P_C$ have similar apparent formal reduction potentials ($E°′$) for p-doping, 0.3 and 0.4 V vs SCE, respectively. Only $P_C$, however, can be reduced to n-type in a standard three-electrode cell, with $E°′ = -1.04$ V vs SCE. Despite having a UV/vis absorption spectrum nearly identical to that of $P_C$, $P_A$ does not exhibit an n-doping wave to potentials as reducing as $-1.5$ V vs SCE. The inability to reduce $P_A$ implies that reaction (ii) above cannot be driven, thereby providing an apparent explanation for the observed asymmetry in $J$–$V_{APP}$ behavior. This explanation, however, is at odds with a number of additional observations.

Data on single-layer films do not support the idea that Faradaic charging is required for transport, as is central to the model above. The absence of an n-doping wave for $P_A$ would then suggest that current enhancement would not be possible for single-layer films of $P_A$ because the disproportionation reaction $2P_A \rightarrow$ n-$P_A$ + p-$P_A$ could not be driven. Contrary to this prediction, films of $P_A$ exhibit current enhanced by ion polarization just as films of $P_C$ do. The steady-state $J$–$V_{APP}$ curves in both cases are nonlinear but symmetric. In the case of single-layer $P_A$ films, transport is presumably dominated by hole injection from whichever electrode is biased positive. Such unipolar behavior is common in thin-film conjugated polymer devices, and although the density of charges that can be injected is limited by space-charge effects, substantial current can
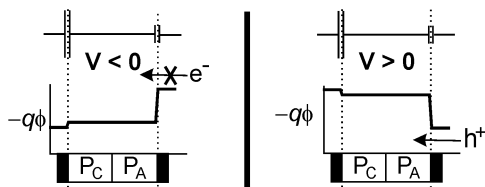
**Figure 2.** Schematic of the potential ($\phi$) drops for negative and positive biases in the Au|$P_C$|$P_A$|Au structure.

still be supported through thin films.[8] Herein, the injection of a single type of charge is not termed Faradaic, as it does not preserve overall charge neutrality, and therefore substantial redox chemistry is prohibited.

The voltammetry data do not preclude reaction (i) and, hence, Faradaic charging for positive bias. Discharge measurements and spectroscopic studies, however, show no evidence for such charging, let alone asymmetry. The charge recovered upon short-circuiting the device after application of ±2 V to steady state corresponds to less than 1 e$^-$ per 200 000 double bonds. Note that in this discharge experiment some fraction of any doped state will discharge internally and hence not be measurable. Electronic absorption spectra collected during potential step experiments show no measurable change, indicating doping of less than 1 e$^-$ per 1000 double bonds over the range interrogated (±3 V).

Swelling of the Au|$P_C$|$P_A$|Au structure also argues against an asymmetric Faradaic charging model. Any asymmetry in the thermodynamics for (i) and (ii) should not be substantially altered by exposure to either a nonaqueous solvent or electrolyte, and consequently, the retention of asymmetric $J-V_{APP}$ behavior would be predicted. Contrary to this, exposure to either $CH_3CN$ or 0.1 M $Bu_4NBF_4$/$CH_3CN$ removes the unidirectional behavior, with electronic current enhanced by ion polarization observed for both signs of the applied bias. This result, along with all of the data above, argues that, although the energetics of the doping processes are important in governing electron vs hole injection, they are not the primary cause of the unidirectional behavior.

One hypothesis is that the observed behavior is from an asymmetry in ion polarization processes at the Au|$P_C$ vs Au|$P_A$ electrodes. Discharge measurements on single-layer films of $P_A$ or $P_C$ sandwiched between Au electrodes demonstrate that the capacitance of the Au|$P_A$ interface (<0.1 $\mu$F cm$^{-2}$) is much smaller than that of the Au|$P_C$ interface (~10 $\mu$F cm$^{-2}$). The smaller capacitance of the former is consistent with a lower free ion density in $P_A$, as supported by its lower ionic conductivity and stronger basicity of $-CH_2-SO_3^-$ vs $CF_3SO_3^-$. The lower capacitance of the Au|$P_A$ interface implies that a greater fraction of the applied potential will drop at this interface relative to the Au|$P_C$ interface. Figure 2 shows a schematic of this situation under positive and negative bias, neglecting for the moment any potential drop across the $P_C$|$P_A$ interface. Due to the asymmetry in capacitances, bias drives charge injection primarily at the Au|$P_A$ interface. Positive bias drives hole injection, and substantial current is observed. Negative bias would drive electron injection, but because $P_A$ is blocking to electrons, little current is observed.

The model of Figure 2 predicts that even for positive bias, the current will be dominated by hole injection into $P_A$, with little electron injection into $P_C$. This is consistent with the lack of Faradaic charging for either sign of the applied bias. A differential in the non-Faradaic charging of the Au|$P_C$ vs Au|$P_A$ interfaces is also consistent with the swelling results. Swelling the structure with a relatively high dielectric solvent, such as $CH_3CN$, is expected to substantially reduce ion pairing in both polymer layers. The ion activities in the two swollen polymers are expected to become

comparable, resulting in similar capacitances at their interfaces with Au and, consequently, a potential drop balanced between the two interfaces. The potential drop at the Au|$P_C$ interface in the swollen structure will drive hole injection into $P_C$ at negative bias, resulting in enhanced current, as observed. A potential drop more balanced between the Au|$P_A$ and Au|$P_C$ interfaces would also be expected to drive reaction (i) in positive bias, with electron injection into $P_C$ and hole injection into $P_A$. Indeed, bleaching of the $\pi-\pi^*$ absorption, characteristic of polymer doping,[9] occurs when a swollen bilayer structure is driven to positive bias. No such bleaching is observed at negative bias because electron injection into $P_A$ remains prohibited.

The model above relies on electrochemical concepts of double-layer charging at ion-blocking electrodes. Charge separation at the $P_C$|$P_A$ interface was considered secondary, and at the least, this leads to Figure 2 being an oversimplified picture. It is also possible that the $P_C$|$P_A$ interface plays the dominant role, with the observed behavior originating from traditional semiconductor device concepts focusing on potential barrier formation at the $P_C$|$P_A$ interface. Such a barrier can arise from charge separation driven by ion exchange or precipitation of $Me_4NOTf$. Indeed, the sign of forward bias is consistent with analogy to a traditional *pn* junction. The relation, however, is complicated because the potential profile at the $P_C$|$P_A$ interface will be governed by the distribution of both ions and injected charge, and will be influenced by ion polarization at the blocking electrodes

In summary, we have described a conjugated ionomer-based device exhibiting unidirectional electronic transport. As its relies on ion motion, the response time of the device is slow compared to traditional devices, but faster response times could be achieved with improved ionic conductance. Further studies are underway to better understand the interplay between traditional semiconductor junction and solid-state electrochemical concepts in manifesting the observed behavior.

**Supporting Information Available:** Experimental procedures and supporting spectroscopic, $J-V_{APP}$, and discharge data. This material is available free of charge via the Internet at http://pubs.acs.org.

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