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## On the Mechanism of Negative Differential Resistance in Ferrocenylundecanethiol Self-Assembled Monolayers

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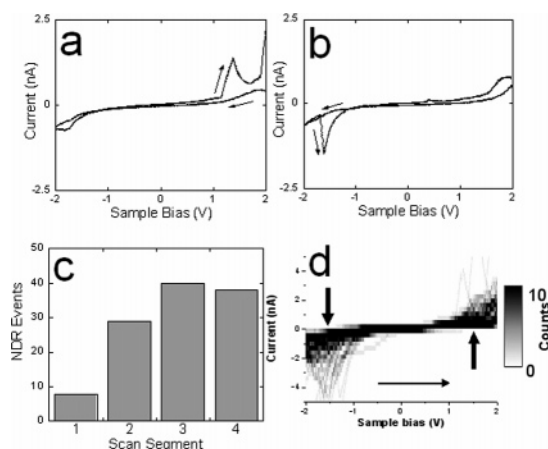
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Negative differential resistance (NDR) has been reported in a number of molecular films,<sup>1–5</sup> but the underlying mechanisms remain uncertain, although it appears to require the presence of an electroactive molecule.<sup>3,6,7</sup> By studying the conductance of oligo-(phenylene ethynylene)s under potential control, Xiao et al.<sup>8</sup> showed that the NDR (in aqueous medium) was caused by an irreversible reduction process. That is to say, the current falls with increasing bias because an irreversible chemical reaction removes the molecules from the current carrying path. This communication addresses the question of whether such irreversible chemistry underlies the NDR observed in ambient conditions in the two-electrode experiments on ferrocenylundecanethiol monolayers for which NDR was first reported by Gorman and co-workers.<sup>3</sup>

Tivanski and Walker<sup>9</sup> showed that positive charges were injected into ferrocenylundecanethiol SAMs at the onset of the NDR current peak, disappearing at higher bias where the current drops (i.e., where the current–voltage gradient becomes negative). If the charges reflect the usual reversible  $\text{Fe}^{\text{II}} \leftrightarrow \text{Fe}^{\text{III}}$  process, one must ask what causes the charges to disappear as the bias is raised. Two control experiments that address this point are (a) measurement of the reversibility of the process as the bias is swept up and down over the same group of molecules and (b) testing for the effect of ubiquitous reactive species, such as molecular oxygen. Such experiments do not appear to have been carried out to date. Here, we show that the process is not reversible, and that NDR is observed much less frequently as oxygen is removed from the system. This rules out a strictly electronic origin<sup>2</sup> for the NDR and shows that the decrease in current at higher bias is a consequence of reactions between the charged species and ambient oxygen.

We prepared ferrocenylundecanethiol self-assembled monolayers on Au(111) as described in the Supporting Information, submerging the samples in mesitylene and obtaining current–voltage ( $i$ – $v$ ) curves using custom LabView software to control a scanning tunneling microscope with a gold probe (PicoSTM from Molecular Imaging, Tempe, AZ). This allowed us to program the voltage applied to the sample and to collect data continuously while sweeping the bias both up and down. The probe must stay over the same location to within a small fraction of a nanometer during data acquisition; to avoid artifacts associated with instrumental drift, we scanned quickly (2.7 ms scanning from +2 to –2 V bias), resulting in a significant capacitive charging current. This same limitation prevented us from investigating the effects of sweep rates or the effects of multiple sweeps, beyond what is reported here. We subtracted the charging current (see Supporting Information), producing data like those shown in Figure 1a and b. NDR peaks occur near  $\pm 1.5$  V, but they are not reversible.

The time development of the NDR is quite complicated. NDR was observed in 33% of the scans as either a positive peak (cf.



**Figure 1.** Typical  $i$ – $v$  curves taken from ferrocenylundecanethiol SAMs under mesitylene in ambient conditions showing (a) a positive peak and (b) a negative peak. The arrows indicate the scan directions. The voltage scan was +2 to 0 V (segment 1), 0 to –2 V (segment 2), –2 to 0 V (segment 3), and 0 to 2 V (segment 4), and (c) shows the number of NDR events observed in each segment. A 2D histogram display of ca. 100 curves is shown in (d), where darker colors represent more frequent data (see scale bar). Thick arrows indicate the location of NDR peaks at ca.  $\pm 1.5$  V. The tunneling set point prior to scanning was 10 pA at 1 V bias.

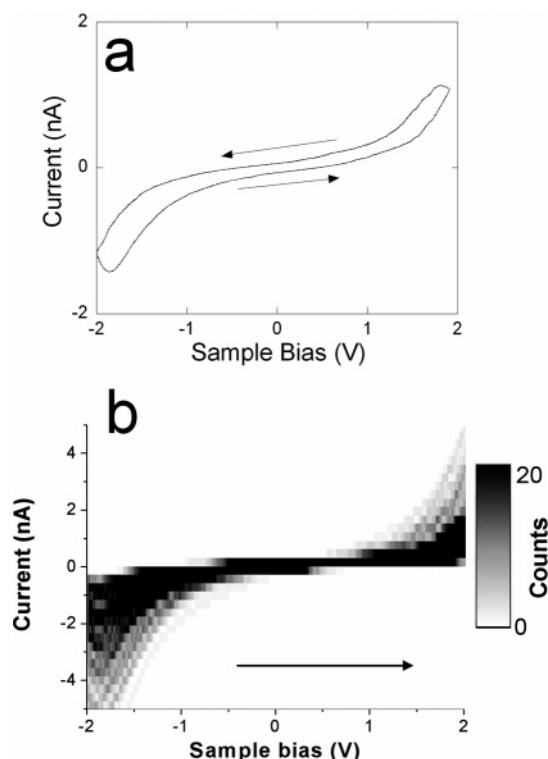
Figure 1a) occurring at  $1.5 \pm 0.3$  V ( $N = 104$ ) or a negative peak (cf. Figure 1b) occurring at  $-1.5 \pm 0.24$  V ( $N = 114$ ). The peak was never retraced (i.e., occurring on both up and down sweeps on a given side of the scan), and only a few (5%) of the scans contained both positive and negative peaks. Furthermore, peaks were rarely observed on the first sweep, as shown in Figure 1c. This displays the frequency with which peaks occurred in each sequential scan segment as the sample bias was swept from +2 to –2 V and then back to +2 V. Thus, generation of the charged species appears to require prior sweeping of the bias. The positions and intensities of the peaks fluctuated significantly, and these fluctuations were greater at the start of a scan than at its end. To summarize all of the data (as opposed to showing a small number of typical scans), we compiled a two-dimensional histogram of the data (Figure 1d), where the  $x$  axis is bias, the  $y$  axis is current, and the color density reflects the number of points in a given area.

This time-dependent behavior rules out a strictly electronic origin-like resonant tunneling<sup>2</sup> and is more consistent with an electrochemical generation of charged species. The applied bias can be related to the formal potential for oxidation in simple geometries,<sup>10</sup> but this is not possible here because the potential distribution in this geometry is unknown as is the distribution of screening ions (if indeed any are present). Regardless of the details of the generation of the charged species, their generation in the tunnel-gap should lead to a step, not a peak, in the  $i$ – $v$  characteristic, as demonstrated first by Snyder and White.<sup>11</sup> Though neutral ferrocene is quite stable in normal electrolyte, the one-electron oxidized

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**Figure 2.** (a) Typical  $i$ - $v$  curve taken for the same samples used for Figure 1, with oxygen largely removed as described in the Supporting Information. (b) A 2D histogram of ca. 250 curves made in the same manner as Figure 1d. The currents at high bias fluctuate considerably, but there is no evidence of NDR (cf. Figure 1d). (Rounding near the turning points is an artifact of the charging current correction.)

ferrocenium ion may undergo degradation by oxidizing agents.<sup>12</sup> To test for the possibility of an oxygen-reactive species, we took  $i$ - $v$  curves from the same samples after the concentration of oxygen was reduced substantially (see the Supporting Information). The frequency of NDR peaks fell to less than 6% (compared to 33% in ambient conditions). A typical curve is shown in Figure 2a, and a 2D histogram of ca. 250 curves that did not show NDR is displayed in Figure 2b (data for the opposite sweep direction are shown in Supporting Information Figure S2b). The absence of NDR peaks (compare Figures 1d and 2b) shows that the current-enhancing species are no longer destroyed at high bias. Thus, the current continues to rise as bias is increased, as expected for current mediated by the electrochemical generation of charged species.<sup>11</sup> A few curves (28 out of 500 up or down scans) displayed NDR in these low-oxygen conditions. These curves were similar to those obtained in the presence of oxygen and probably reflect the presence of residual oxygen.

What is the nature of the charging in this system? The slow time response (Figure 1c) indicates that the charge species is not formed immediately. It is possible that polarizable material must first be accumulated in the gap to stabilize the charged species. The

reproducibility of the phenomenon would require some universally available polarizable dielectric (like water molecules associated with the ferrocenes). Capping the ferrocene with  $\beta$ -cyclodextrin reduces the magnitude of the observed NDR.<sup>13</sup> This suppresses the formation of the ferrocenium salt and, presumably, also suppresses the formation of the complex (with water?) responsible for stabilizing this charged state.

In summary, we have shown that reactions of the ferrocene-based charged species with ambient oxygen at high bias is responsible for eliminating the species that enhances the tunnel current, causing the current to drop as bias is increased. Presumably, the reaction follows a similar pathway to that reported for ferrocenium.<sup>13</sup> The NDR, therefore, arises as a consequence of chemical changes in the material, and it is not reversible. We have not addressed the issue of NDR in the oligo(phenylene ethynylene)s, and further experiments will be needed to determine if the mechanism reported by Xiao et al. for oligo(phenylene ethynylene)s under potential control<sup>8</sup> applies to the types of films used in molecular electronic devices. However, studies made with the molecules under potential control have the advantage of allowing electrochemical events to be related to molecular electronic events directly.<sup>8,14</sup> Furthermore, a new type of low bias, reversible NDR is observed as a consequence of the modification of the double layer field by the probe bias.<sup>14</sup>

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**Supporting Information Available:** Sample preparation, additional  $i$ - $v$  curves. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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