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Short Communication

Electron Tunneling through Monolayers of α,ω-thioalkanoic acids in Hg-Hg Electrochemical Tunnel Junctions in Water

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The efficiency of electron tunneling across monolayers of α,ω-thiocarboxylic acids and n-alkanethiols trapped between two liquid Hg contacts (Hg-Hg tunnel junction) was measured as a function of the interfacial structure of the monolayer/Hg non-covalent contact. A monolayer of a long-chain α,ω-thiocarboxylic acid or n-alkanethiol was formed in-situ, in EtOH/water solution, on one of the Hg drops via oxidative adsorption at the controlled electrochemical potential. The second Hg drop was kept at the electrochemical potential preventing the monolayer formation. Subsequently, the Hg drops were brought into contact and the steady-state tunneling current between the two electrodes was measured as a function of monolayer thickness. A plot of the logarithm of the tunneling current versus the number of carbon atoms in each junction yields identical tunneling coefficients for monolayers of n-alkanethiols and α,ω-thiocarboxylic acids (β=1.1 per methylene group). Careful examination of the tunneling current across the carboxy-terminated monolayer / Hg interface as a function of pH indicates that the structure of the non-covalent monolayer/electrode contact is critically important in the mechanism of electron transfer. While pH variation from 2 to 10 has no influence on the tunneling currents flowing across the methyl-terminated monolayer/Hg interface, it affects the values of tunneling current across the carboxy-terminated monolayer/Hg by as much as 300-fold. The nature of the non-covalent Hg/-COOH and Hg/-CH_3 interface is discussed in view of the reported data.

Keywords: Electron tunneling, self-assembled monolayers, electrochemically controlled tunnel junction

1. INTRODUCTION

The development of reliable and reproducible methods to incorporate discrete molecules and 2-D molecular assemblies into optical, magnetic, and electrical devices is at the forefront of molecular electronics[1-3]. Of particular importance is the effect of the interface between the bulk metallic and semiconductor electrode and the individual molecules or molecular assemblies on the electrical properties of the device.[4-6] Over the last decade multiple methods were developed to study the electrical properties of single molecules and 2-D monolayer systems.[7-10] Whitesides and others introduced a concept in which Hg drop or GaIn eutectic drop is used as an electrical contact in a tunnel junction consisting of monolayer or bilayer of thio-terminated molecules.[10-17]

In our previous reports we described an analogous tunnel junction assembled in the electrochemical cell with both metallic contacts being independently polarized to desired electrochemical potentials.[16, 17] Here we report data describing electron tunneling through SAMs consisting of n-alkanethiols or α,ω-thiocarboxylic acid trapped between 2 mercury drops (Hg // HCOO-C_n-S-Hg) measured in-situ in aqueous solution as a function of solution pH.

2. EXPERIMENTAL

The following chemicals were obtained from Aldrich and used as received: LiClO4 (99.99%), LiOH (99.0%), Hg (electronic grade), 11-Mercaptoundecanoic acid (95%), 16-Mercaptoundecanoic acid (99%). Millipore distilled water was used in all experiments. Tunnel junction was build in-house as described earlier [16].

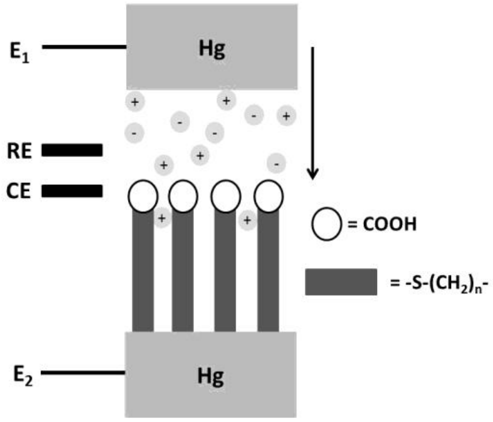

Figure 1. The scheme of the experimental setup. The 2 mercury drops are extruded at the tips of HMDE's (hanging mercury drop electrodes) and aligned coaxially in the enclosed electrochemical cell containing deoxygenated 80/20 (vol/vol) EtOH/water, 0.2M $LiClO_4$, and 2mM solution of appropriate n-alkanethiol or α,ω-thiocarboxylic acid. The Hg drops are polarized independently and simultaneously to electrochemical potentials E_1 and E_2. The circuit is completed with reference electrode (saturated silver-silver chloride electrode by CH Instruments) and counter electrode ($1cm^2$ Pt foil). The top Hg drop is brought into contact with the bottom, monolayer-covered, Hg drop using micromanipulator. The details of experimental setup are described in reference 16.

In our experimental approach, shown schematically in Figure 1, two hanging mercury drop electrodes (HMDEs) are positioned coaxially in an electrochemical cell containing EtOH/water (80/20) solution with appropriate n-alkanethiol or α,ω-thiocarboxylic acid (2mM solution) and supporting electrolyte (0.2M $LiClO_4$). The electrodes are polarized simultaneously and independently to desired electrochemical potentials and the mercury drops (ca. 0.02cm^2) are extruded at the tips of both capillaries. As reported earlier[16], the formation of a monolayer occurs via oxidative adsorption according to the reaction:

$Hg + n\,RSH \rightarrow Hg(RS)_n + n\,H^+ + n\,e$ ($E^{0`}$) (reaction1)

Following formation of a monolayer on one (or both) Hg contacts, the drops are brought together using micromanipulators.

3. RESULTS AND DISCUSSION

The formation of a junction is followed by steady-state current corresponding to a long-range electron tunneling across the monolayer in response to a constant bias voltage $\Delta E=E_1-E_2$.[15] The typical current-time responses for both channels of the bipotentiostat recorded in the course of junction are shown in Figure 2. The steady-state current indicate the junction is stable (i.e. does not undergo compression) for at least 20-50 seconds following its formation. As demonstrated earlier for n-alkanethiols and α,ω-alkaneditiols, one can vary the thickness of the junction by varying the chain-length of the used molecules. The described approach allows us to study both monolayer and bilayer junctions.[16] Thus for each particular n-alkanehiol or α,ω-thiocarboxilic acid, two distinct regimes of current values can be obtained for a particular bias voltage (E_1-E_2). For example, while E_1/E_2 combination reported in Figure 1 results in current in the order of 0.6 mA/cm^2, the E1, E2>-0.4V vs. SSCE results in currents that are roughly 4 orders of magnitude lower, signifying formation of a bilayer. We have explored this phenomenon thoroughly in our previous reports.[16, 17]

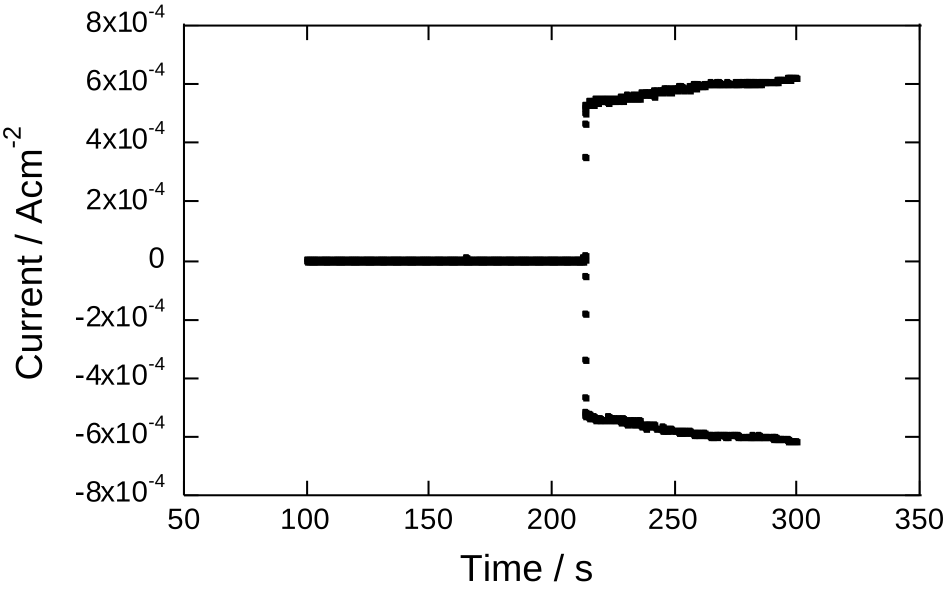

Figure 2. Current-time response recorded for Hg-Hg monolayer junction, experimental conditions are described in figure 1. Solution contains 2mM n-dodecanethiol, E_1=-1.0V; E_2=-0.6V, pH=12.01.

The currently reported data pertains exclusively to experimental conditions resulting in formation of monolayer junctions. Figure 3 shows the plot of the natural logarithm of tunneling current density as a function of the chain-length of the CH_3-$(CH_2)_n$-SH and HOOC-$(CH_2)_n$-SH on a mercury electrode with the second electrode polarized to an electrochemical potential negative of E^0. For these junctions, for both n-alkanethiols and α,ω-thiocarboxylic acids, the tunneling current depends exponentially on monolayer thickness with tunneling coefficient $\beta \cong 1/CH_2$ in agreement with our previous work and the work by others.[3-17]

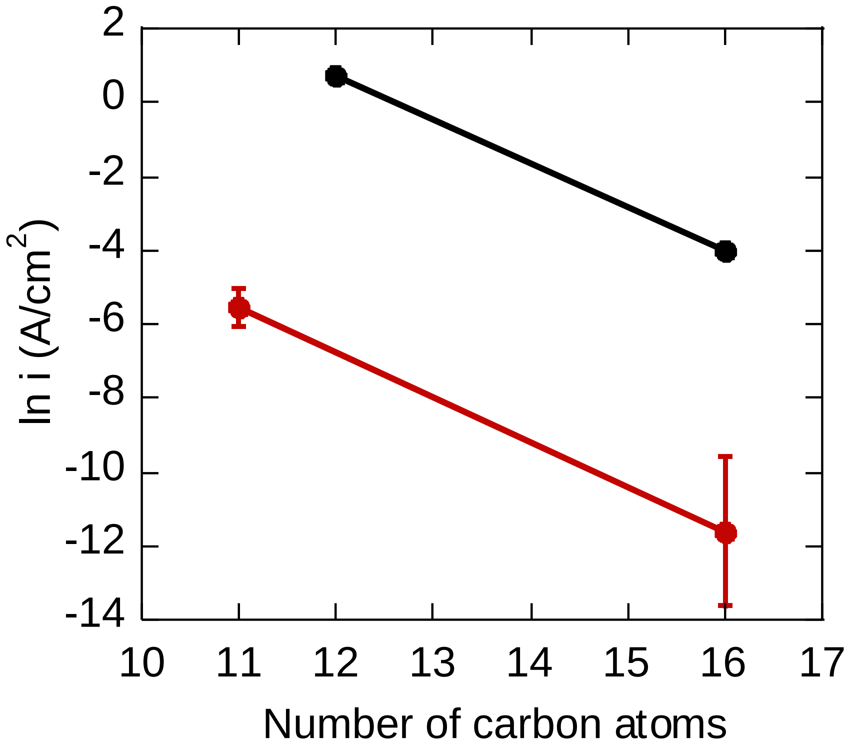

Figure 3. The plot of the natural logarithm of current density vs. the number of carbon atoms for n-alkanethiol and α,ω-thiocarboxylic acid monolayer junctions recorded for pH=2

In our previous reports we have studied extensively the reaction (1) in Hg/Hg and Hg/Ag electrochemically controlled tunnel junctions for methyl-terminated n-alkanethiols and α,ω-alkaneditiols. We have demonstrated that for hydrophobic methyl-terminated monolayers the ions and solvent molecules are squeezed out from the junction area in the process of its formation. The “squeezing” effect is also observed for surfactants that specifically adsorbed on Hg or the methyl-terminated monolayers.[16] For example, long-chain alcohols (n-hexanol) that specifically physisorb on both Hg and methyl-terminated SAMs are squeezed out from the junction in the course of its formation. In the current report we describe junctions containing –COOH terminated monolayer possessing two important features: (1) the SAM’s covered Hg electrodes are hydrophilic[18], (2) variation of pH of the solution used to form a junction results in varying degree of de-protonation of the monolayer thus introducing permanent charge within the junction area.[19]

To investigate the effect of the layer of ions/water that might be trapped within the junction containing hydrophilic monolayer or a monolayer possessing permanent charge[19], we compared electron tunneling across methyl-terminated and carboxy-terminated monolayers possessing the same number of carbon atoms within the molecule.

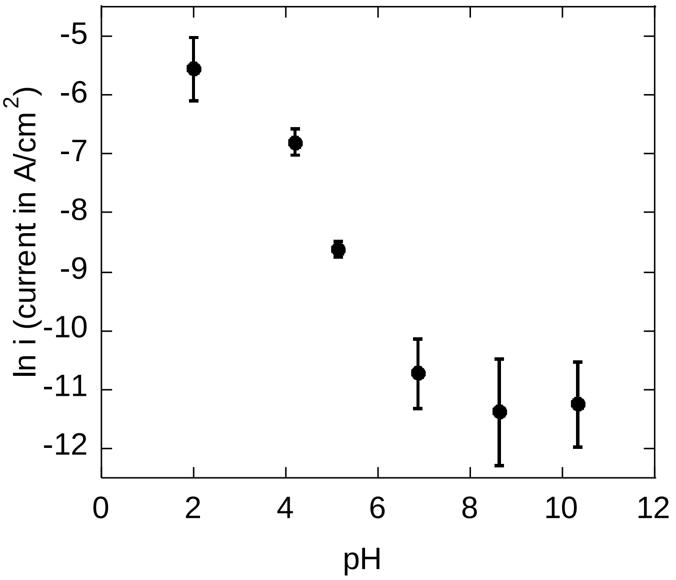

Figure 4. The natural logarithm of current density across the monolayer of HOOC-(CH$_2$)$_{15}$-SH trapped in a Hg-Hg junction as a function of solution pH. The potentials are adjusted to ensure monolayer junctions.

As reported earlier for a given SAM, the monolayer or bilayer junction can be formed by varying the E_1 and E_2 potentials with respect to E^0 (see equation 1) while keeping the bias voltage (E_2-E_1) constant. We note that the E^0 potential depends on pH thus the E_1 and E_2 were adjusted experimentally to ensure that the monolayer forms on only one Hg drop. The experiments employing E_1/E_2 combinations corresponding to bilayer junctions show no measurable currents. Figures 3 and 4 show that junctions assembled in acidic solutions containing COOH-terminated SAMs exhibit ca. 3 orders of magnitude lower currents than the corresponding junctions containing methyl-terminated n-alkanethiols for acidic solutions while junctions assembled in alkaline solutions show ca. 6 orders of magnitude lower currents. Moreover, while bilayers junctions containing COOH-terminated alkanthiols can be easily assembled, the tunneling currents for these junctions are lower than the current sensitivity of the bipotentiostat used in the studies (below 10^{-11}A). Clearly, the non-covalent Hg/monolayer interface plays critical role in the overall electrical conductivity of the system. In order to further investigate the influence of the degree of protonation of COOH-terminated SAMs on the values of tunneling current we performed analogous tunneling measurements for solutions of varying pH. While pH has no influence on the value of current recorded for methyl-terminated monolayer junctions, it has a significant effect on the values of current for COOH-terminated monolayer junctions. Figure 4 shows tunneling currents measured for identical monolayer junctions at different solution pH and constant ionic strength (0.2M LiClO4) and for constant bias voltage (E_1-E_2).[20] The relationship shown in figure 4 is analogous to the titration curve with pKa of the monolayer of ca. 5, in reasonable agreement with pKa of carboxy-terminated SAMs on gold as reported previously in the literature.[19] Several conclusions concerning the nature of the non-covalent carboxy-terminated monolayer / Hg interface can be drawn based on the reported set of data. First, for acidic solutions (pH=2) the value of the current is about 1000 times lower than the corresponding tunneling current through methyl-terminated monolayer of alknethiols. For example the tunneling current measured through a monolayer of n-hexadecanethiol was ca. $3.5x10^{-2}A/cm^2$ while current measured through a monolayer of 16-thiohexadecanoic acid was $4.5x10^{-5}A/cm^2$. The tunneling current depends exponentially on distance. Assuming tunneling coefficient β=1/Å, this tunneling current difference corresponds to a distance of ca. ln $(3.5x10^{-2}/4.5x10^{-5})$ = 6.6Å corresponding roughly to two layers of water that are permanently bounded (i.e. cannot be physically removed in the course of junction formation) to the hydrophilic surface of the caboxy-terminated SAM. Second, the increase of pH results in deprotonating of the COOH/Hg interface and thus introduction of permanent change to the interface. This further lowers the values of observed tunneling current by additional ca. 300 fold which would correspond to additional 2 water layers permanently trapped within the tunnel junction. Thus, for pH=10 the tunnel junctions containing $HOOC\text{-}(CH_2)_{15}\text{-}SH$ show tunneling current that are 5-6 orders of magnitude lower than the corresponding tunneling currents for n-hexadecanethiol monolayers. We note that it appears that purely electrostatic effects play a minor role in the observed variation of tunnel currents, as the variation of supporting electrolyte concentration and chemical identity (Li vs Na, Cl^- vs ClO_4^-) does not influence the measured current within the experimental error. Thus it appears that the observed differences in tunneling currents are caused by additional layers of water and ions permanently trapped within the junction. In conclusion, the hydrophilic/hydrophobic character and permanent surface charge plays a critical role in efficiency of electron transfer across non-covalent metal/monolayer interface in macroscopic Hg/Hg tunnel junctions and should be taken into consideration while employing Hg/Hg junction as a test-bed for molecular electronics applications.

4. CONCLUSION

In summary, our data indicate that protonation/deprotonation of the non-covalent

Hg // $^-OOC\text{-}CH_2\text{-}S$ Hg interface within the tunnel junction results in significant changes in electrical conductivity of the system.

ACKNOWLEDGEMENT
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