

Electrochemical and Adhesion Properties of PEDOT:PSS as a Coating for Gold Electrodes for Applications in Metal-Molecule-Metal Junctions

Vivian Feig

Chemical Engineering, Columbia University

NNIN iREU Site: Institut Für Bio- Und Nanosysteme (IBN), Forschungszentrum, Jülich, Germany

NNIN iREU Principal Investigator(s): Dr. Dirk Mayer, Institute for Bio and Nanoelectronics (IBN-2), Forschungszentrum Jülich

NNIN iREU Mentor(s): Nils Sanetra, Institute for Bio and Nanoelectronics (IBN-2)

Contact: vivianfeig@gmail.com, dirk.mayer@fz-juelich.de, n.sanetra@fz-juelich.de

NNIN iREU Program

Introduction:

Crossbar junctions with gold top and bottom electrodes are a promising type of metal-molecule-metal junction for the purpose of electrically addressing defined small biomolecules. However, the surface roughness of gold poses a number of challenges for working at the single molecular scale, such as piercing the molecule and causing shorts in the device. To solve this problem, we investigated the application of a conducting polymer, poly(3,4-ethylenedioxythiophene)/poly(4-styrenesulfonic acid) (PEDOT:PSS), as a way to coat and smoothen the electrode surface.

For our application, it is further important to examine the adhesion of PEDOT:PSS to molecules that we hope to incorporate into our molecular electronics devices. This paper examines the electrochemical properties of PEDOT:PSS and its interaction with cytochrome *c* as well as certain self-assembled monolayers (SAMs).

Experimental Procedure:

Three different solutions of PEDOT:PSS were tested, each differing by amount of dopant: Clevius P and Clevius FE solutions provided by Sony, and a Clevius P solution made at the Forschungszentrum Jülich (Clevius P (FZJ)). PEDOT:PSS solutions were applied to silicon and gold substrates by spin coating. Substrates were prepared by cleaning in O₂ plasma at 140 W and 0.7 mbar for three minutes. The plasma additionally served to hydrophilize the substrate surface, which was important for PEDOT:PSS adhesion. Samples were spin-coated first at 1000 rpm for eight seconds, then for one minute at a variable rate. Afterwards, they were baked for two minutes at 150°C. Film thicknesses, at various spin rates, were measured using scanning electron microscopy, and were found to generally decrease with increasing spin rate until converging at around 4000-5000 rpm, with Clevius P (FZJ) and Clevius FE reaching a minimum thickness of about 50 nm, and Clevius P reaching a thickness of about 30 nm.

To examine electrochemical properties of PEDOT:PSS, 50 nm layers of each solution were spin-coated onto gold (Au) substrates and cyclic voltammetry (CV) measurements were

performed with an Autolab potentiostat. A three electrode setup was used with phosphate buffer solution (PBS, pH = 7) as the electrolyte. To test the interaction of PEDOT:PSS with octadecanethiol and 11-MUA SAMs, monolayers were assembled by immersing the substrate in solution for 20 minutes and 24 hours, respectively, then rinsing with ethanol and drying in a nitrogen stream. To test cytochrome *c* adhesion, 20 μM of cytochrome *c* in PBS was used as the electrolytic solution. CV analysis was performed directly using the GPES software.

Results and Analysis:

The CV of plain Au was dominated by capacitive current with a capacitance of 20 μF. By comparison, CVs of 50 nm PEDOT:PSS on Au also showed predominantly capacitive current, but of a larger magnitude. Clevius FE had a capacitance of 22.6 μF, Clevius P 22 μF, and Clevius P (FZJ) 30.2 μF, suggesting that the PEDOT:PSS layers are conductive. Further, the capacitive current also increased with PEDOT:PSS thickness: for a 140 nm layer of Clevius P (FZJ), the capacitance was 95.4 μF, significantly higher than for the 50 nm layer.

Next, the interaction of PEDOT:PSS with an octadecanethiol SAM was tested. On plain Au, octadecanethiol self-assembles effectively and forms a dielectric layer that decreases the capacitive current. We found that octadecanethiol is similarly capable of self-assembling to form a monolayer on top of PEDOT:PSS layers and has a similar effect on capacitance. For instance, the capacitance of SAM on Clevius P was 14 μF, as opposed to 22 μF for pure Clevius P.

Additionally, cyclic voltammograms of PEDOT:PSS coated on top of an SAM were measured. Since PEDOT:PSS requires a hydrophilic surface for successful coating, 11-mercaptoundecanoic acid (11-MUA), which has carboxylic acid end groups, was used to form the SAM. The capacitive current for Au/11-MUA/PEDOT:PSS actually increased compared to Au/PEDOT:PSS. This is surprising, as 11-MUA should form an insulating layer.

One explanation may be that PEDOT:PSS adheres better to the SAM than to gold, resulting in a thicker layer when spin coated at the same speed. This can be checked in the future by comparing PEDOT:PSS film thicknesses when spun at the same speed on 11-MUA and on gold.

Finally, the interaction of PEDOT:PSS with cytochrome *c*, a heme protein involved in the electron transport chain within mitochondria and in cell apoptosis, was investigated. CVs of PEDOT:PSS films taken in 20 μ M cytochrome *c* and PBS solution showed clear redox peaks attributable to the protein. Integrating the current under the peaks and then dividing it by the potential sweep rate yields the total number of charges, which was roughly constant for different sweep rates.

Since the total number of charges per area stays about constant, it can be concluded that the cytochrome *c* was able to adsorb onto the PEDOT:PSS surface and form a relatively homogeneous surface, and that the redox behavior in the CVs was indicative of a surface-bound reaction and not diffusion from the bulk solution. Fluctuations in the total charge calculations were minimal and due perhaps to surface roughness. Additionally, the charge density at the surface was reasonable given the surface area of our samples, 8×10^{13} nm². For Clevis P (FZJ), considering that cytochrome *c* undergoes one electron transfer per oxidation/reduction [1], for an average total charge of 1.25×10^{-5} C, our results indicated a transfer rate of one electron per nm² area. Cytochrome *c* has a diameter of roughly 3-3.4 nm, so we would expect a transfer rate of one electron per at least 9.4-10.7 nm² area. Our large result may be due to some molecules being absorbed by the PEDOT:PSS film [2].

Conclusion and Future Work:

Our results show that PEDOT:PSS is a promising coating for gold electrodes in fabricating molecular crossbar junctions, since it can be spin-coated onto electrodes at small thicknesses and is capable of adhesion to SAMs and cytochrome *c*. To continue this research, future work may involve electrical tests once a top electrode has been placed on top of gold/PEDOT:PSS bottom electrode. Overall, PEDOT:PSS appears to be an effective coating for creating functional metal-molecule-metal junctions.

Acknowledgements:

Thank you to the National Nanotechnology Infrastructure Network International Research Experience for Undergraduates (NNIN iREU) Program and the National Science Foundation for this wonderful opportunity. Also thank you to Dr. Dirk Mayer and Nils Sanetra for their gracious help and supervision. Finally, thanks to everyone at IBN-2 for creating an intellectually stimulating and supportive work environment.

References:

- [1] Bernard, S., N. Leygue, H. Korri-Yousoufi, and S. Lecomte. "Kinetics of the electron-transfer reaction of Cytochrome *c* (552) adsorbed on biomimetic electrode studied by time-resolved surface-enhanced Raman spectroscopy and electrochemistry". *Eur. Biophys. J.* 36(8): 1039-48 (2007).
- [2] Guo, L., D. Pietkiewicz, E. V. Pavlov, S. M. Grigoriev, J. J. Kasianowicz, L. M. Dejean, S. J. Kormsmeier, B. Antonsson, and K. W. Kinnall. "Effects of cytochrome *c* on the mitochondrial apoptosis-induced channel MAC". *Am. J. Physiol. Cell Physiol.* 286:C1109-C1117 (2004).

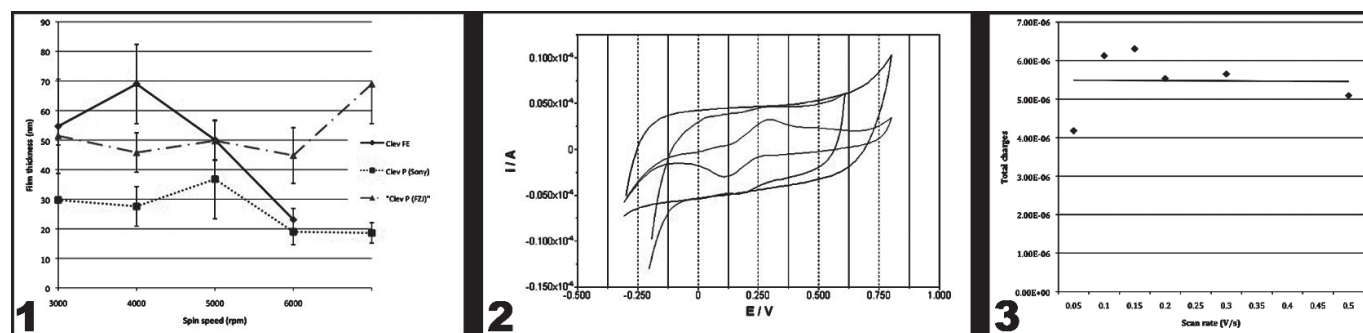


Figure 1: Thicknesses of Clevis solutions spin-coated at different rates.

Figure 2: CVs of plain gold chip; Clevis P (FZJ) on gold; and octadecanethiol SAM on Clevis P (FZJ) on gold.

Figure 3: Total charges under cathodic peaks for Clevis P (Sony) films in cytochrome *c* at different spin rates.