Effect of Deposition Characteristics on Electrochemically Prepared PEDOT Films

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Abstract:

Electrodes coated with poly(3,4-ethylenedioxytiophene), or PEDOT, are characterized by low impedance and high charge delivery capacity. However, papers in the literature present a broad spectrum of parameters for electrochemically depositing PEDOT. Presented here is a systematic evaluation of PEDOT deposition variables, with the goal of guiding the fabrication of a low-impedance, structurally stable electrode. The variables investigated were deposition charge, deposition time, PEDOT dopant, galvanostatic/potentiostatic deposition, pulsed deposition, temperature, substrate, and surface preparation.

Introduction:

The interface between neural tissue and implantable microelectrodes is of critical importance for neural stimulation and recording. The desire to record the activity of individual neurons *in vivo* has lead to the fabrication of microelectrodes, whose reduced geometrical area increases electrode impedance, decreases sensitivity, and decreases signal-to-noise ratio. A potential solution is to coat the electrodes with PEDOT, a conductive and biocompatible polymer film that has been shown to reduce electrode impedance [1]. However, no systematic survey of the polymer's deposition parameters has been reported in the literature, despite evidence that these variables significantly affect electrode performance and stability.

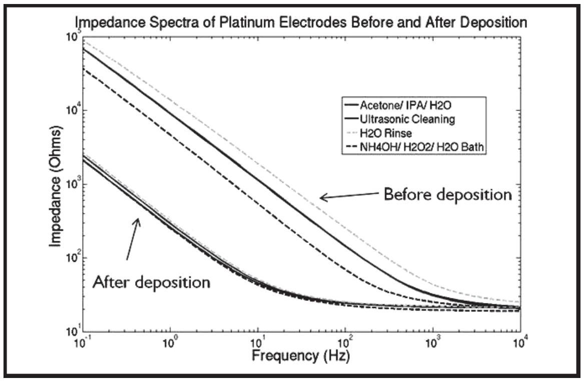

Figure 1: Electrochemical impedance spectra before and after cleaning procedures.

Methods:

All depositions were conducted in a three electrode cell. The working electrode was the substrate to be coated with PEDOT, the counter electrode was platinum or stainless steel, and the voltages were taken with respect to an silver/silver chloride reference electrode. The working electrode was taped to expose a 1 cm^2 surface area, and the deposition was controlled with an Ivium Technologies CompactStat [2].

Electrochemical impedance spectroscopy was performed in 0.9% sodium chloride to measure electrode impedance at 71 frequencies logarithmically spaced between 0.1 Hz and 1 MHz. Scanning electron microscopy (SEM) was used to observe surface roughness and estimate film thickness. A tape test was conducted to qualitatively measure film stability.

Results:

Four different methods of preparing the electrode surface were tested: a water wash, an acetone/isopropanol/water wash, ultrasonic cleaning in acetone, and a bath of ammonium hydroxide, hydrogen peroxide and water. Although the cleaning method was not observed to affect the electrodes' electrical properties (see Figure 1), it did affect their stability. Only the electrodes prepared with the ammonium hydroxide/hydrogen peroxide/water bath consistently passed the tape test, displaying superior adhesion.

Two PEDOT dopants were tested in the course of this experiment: chlorine and polystyrene sulfonate. PEDOT doped with polystyrene sulfonate was observed to yield films of lower impedance and superior stability compared to PEDOT doped with chlorine. The concentration of the

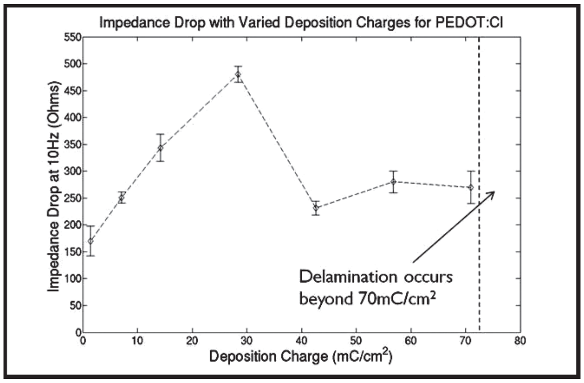

Figure 2: Impedance drop measured before and after PEDOT dep. Error bars represent standard error (n = 3).

dopant in the electrochemical cell also affected electrode performance; higher concentrations yielded superior films until saturation.

Deposition charge was observed to significantly affect electrode impedance. Figure 2 shows the reduction in electrode impedance as a function of deposition charge, with a clear optimum appearing at 30 mC/cm^2.

Longer deposition times were found to be superior to shorter deposition times when depositing at a fixed deposition charge, as seen in Figure 3. Very long depositions, however, necessitated an insufficiently low current density to drive the PEDOT polymerization reaction.

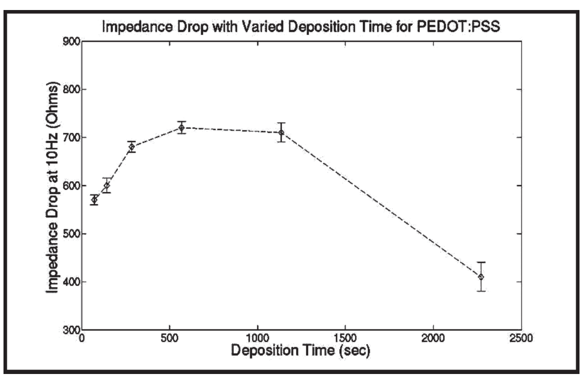

Figure 3: For a fixed deposition charge, the deposition time can be optimized for a low-impedance film.

There was no statistically significant difference observed between galvanostatic, potentiostatic, and pulsed deposition methods. For pulsed depositions, a range of pulse times and duty cycles were tested.

All three methods exhibited similar optimization windows. On one side of the window, low current densities or low potentials were insufficient to drive PEDOT's polymerization reaction. At high current densities or high potentials, oxidation occurred on the electrode surface and formed an insulating oxide layer. It was between these two extremes that ideal deposition parameters were located.

The temperature at which the deposition was performed was found to have little effect on electrode performance. At temperatures above 60°C, however, the adhesion of the polymerized film was poor and films consistently failed the tape test.

The substrate on which the PEDOT film was deposited was observed to affect the qualities of the final electrode. Of the four substrates tested (platinum, gold, indium tin oxide, and silver), indium tin oxide displayed the greatest reduction in impedance. Films deposited on silver consistently failed the tape test.

Discussion:

Of the results presented, one stands in contrast with the literature. It has been reported that potentiostatic depositions yield non-uniform films and inferior electrical characteristics on microelectrode arrays [3]. We report no morphological difference between galvanostatic and potentiostatic depositions, but because our electrodes are significantly larger than microelectrode arrays, further investigation is necessary.

Additional tests remain to be conducted to evaluate electrode performance. Cyclic voltammetry will measure electrical stability and charge delivery capacity, and a scratch test will yield a quantitative measure of film stability.

Conclusions:

Presented is a systematic evaluation of PEDOT deposition parameters. The parameters that were observed to significantly affect electrodes' electrical characteristics or stability were deposition charge, deposition time, polymer dopant, substrate, and the method for preparing the electrode surface. The parameters that would not be suitable for optimization were observed to be deposition type (galvanostatic/potentiostatic/pulsed) and temperature.

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References:

[1] Cogan, S; "Neural Stimulation and Recording Electrodes;" Annual Reviews Biomedical Engineering, 10, 275-309 (2008).

[2] Ivium Technologies. Retrieved from http://www.ivium.nl/.

[3] Martin, D; "Electrochemical Deposition and Characterization of Poly(3,4-Ethylenedioxythiophene) on Neural Microelectrode Arrays;" Sensors and Actuators B, 89, 92-102 (2003).