On the Stability of PEDOT as Coating Material for Active Neural Implants

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Abstract

This paper is about the stability of PEDOT coatings under high loads of current pulses. Test parameters were chosen to match many peripheral nervous system (PNS) applications in regard of charge injection, pulse width and repetition frequency. PEDOT coatings were characterized with electrochemical impedance spectroscopes (EIS) and pulse tests. No decrease in charge injection capacities could be detected after ten million pulses, suggesting a stable coating for at least this time frame with superior properties in regard of conventional platinum electrodes.

***Keywords**: PEDOT, electrode, stability, pulse test, characterization*

Introduction

One of the most challenging aspects in functional electrical stimulation (FES) is the transfer of charge over the phase boundary of metallic conductor (electrode) and tissue. Since metallic conduction is based on electron flow and tissue conduction on ion flow, a transition has to occur which is mediated by the electrode in use. These reactions can basically be capacitive, i.e. charging and discharging of the electrode-electrolyte double layer, or faradic, which involves oxidation and reduction of surface confined species. Prominent examples for these mechanisms are titanium nitride (TiN) or tantalum/Ta_2O_5 for capacitive transition and iridium oxide or PEDOT (poly-ethylenedioxythiopene) as faradic material. Pt and PtIr alloys are special cases since faradic reactions are restricted to a surface monolayer and, hence, are called pseudocapacitive [1]. In general, capacitive charge-injection is preferable to faradic injection since no chemical species are created/consumed during a stimulation pulse. Furthermore, changes of electrolyte composition and finite rates of faradic reactions can lead to irreversible processes which may cause electrode or tissue damage (i.e. corrosion and alteration of pH-value). However, charging the double-layer of an electrode-electrolyte interface by capacitive means yields in only small charge injection capacities (Q_{inj}), since the charge per unit area at an interface is also small, and is often not sufficient to stimulate targeted structures like peripheral nerve fascicles [2]. Hence, it is of upmost importance to consider carefully which electrode material or coating is to be used and what restrictions, e.g. water window or stability under stimulating conditions, are implied.

This paper reports on the stability of PEDOT as coating material for stimulating electrodes under high loads of current pulses which was reported earlier to turn the polymer into an insulator and, thus, limits the actual use of this coating [3]. The goal of this research is to determine the count of current pulses which can be safely injected into the electrolyte without loosing the conductive properties or passing the water window, respectively.

Material and Methods

Preparation of samples:

Test electrodes were manufactured using micromachining techniques in a class 1000 cleanroom. Samples consist of a polyimide-platinum-polyimide stack (5µm-300nm-5µm in thickness), whereas active sites and interconnection pads are opened by reactive ion etching (RIE). Connection was done with zero insertion force adapters (ZIF), whereas the samples incorporate different electrode diameters ranging from 40 to 120 µm. In this study, however, 80 µm diameter electrodes were solely used.

The electrolyte for deposition of PEDOT was made up with following recipe: 0.1 M EDOT (Cat # 483028 Sigma–Aldrich) was doped with 0.05 M pTS (Cat # 152536 Sigma–Aldrich) in a 1 part acetonitrile : 1 part deionised (DI) water solution and used within two months after synthesis [4]. The polymer coating was electrodeposited using galvanostatic mode of a gain-phase analyzer with a

potentiostat (Solartron 1260 & 1287, Solartron Analytical, Farnborough, Hampshire, UK) in combination with the software CorrWare (version 3.1 by Scribner Associates Inc., Southern Pines, NC, USA) at 1 mA/cm^2 for 10 min in a three electrode setup, consisting of a Pt counter electrode and an Ag/AgCl (3M) reference electrode.

Characterization

Test samples were characterized by electrical impedance spectroscopy (EIS) and pulse testing. EIS measurements were done with the three electrode setup described above. Impedance spectroscopy was conducted with excitation amplitudes of 10 mV from 1 Hz to 100 kHz on a regular basis (e.g. immediately after deposition and after 3 million cycles) in phosphate buffered saline solution (PBS; 7.4 pH). To inject current pulses a custom made 12-channel pulse tester was developed, incorporating improved Howland current pumps and circuits to subtract the voltage drop over the access resistance [5]. Applied pulses were rectangular, biphasic and charge balanced in nature with a pulse width of 200 µs and a frequency of 25 Hz. Pulsing was done in non-agitated PBS solution (0.5l, regularly refilled with DI water) against a large area stainless steal counter electrode; temperature and pH value of the electrolyte were measured once per day. For PEDOT an injected charge of 20 nC (100µA x 200µs) was chosen and the voltage across the phase boundary (V_{PB}) was continuously monitored. Since, loss of conductive properties within the coating yields in increased charging of the phase boundary, while the injected charge is held constant, V_{PB} is expected to rise towards the limits of the water window. Hence, the criterion for exclusion is passing the limits of PEDOTs water window (-0.9-0.6V vs. Ag/AgCl). As reference material, a non-coated platinum electrode was tested in the same way, but pulsed to the safe limits of platinum's water window (-0.6–0.8V vs. Ag/AgCl) and the required current was measured. Additionally, the access resistance R_A of PEDOT and Pt was measured once per day.

Results

After electrodeposition of PEDOT, samples were optically inspected using a light microscope. The coating appeared black in colour and was confined to the actual electrode site, i.e. it didn't creep over the boundary of platinum and polyimide which suggests a coating thickness below 5 µm.

EIS measurements showed a significant decrease in mean impedance, cut-off frequency (f_g) and phase angle theta after PEDOT deposition (see Fig. 1, n=10). At 1 kHz, impedance decreased from 113 kΩ to only 4.7 kΩ and the phase angle was increased from -76.5 ° to -8.4 ° for Pt and PEDOT, respectively. Cut-off frequency was decreased from 20 kHz for platinum to 25 Hz for PEDOT. After 3 million load cycles no difference was found neither in impedance nor phase angle measurements.

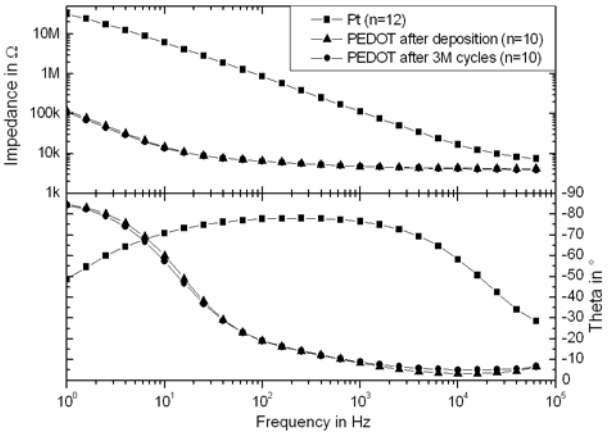

Fig. 1: Electrical impedance measurement of pure platinum and PEDOT coated electrodes.

Pulse tests were conducted for 10 million cycles on 10 electrodes coated with PEDOT. Figure 2 shows the voltage across the phase boundary after 100k and 10M cycles (upper graph) and the fixed current pulse with a charge of 20 nC (lower graph). Note that the voltage drop (iR) over the access resistance (R_A) is already subtracted. The access resistance was measured to 4.5 kΩ and 12 kΩ for PEDOT and Pt respectively, and stayed constant over the 10M pulses. These results are in accordance with the EIS measurements (5.3kΩ with PEDOT and 10.4kΩ for Pt).

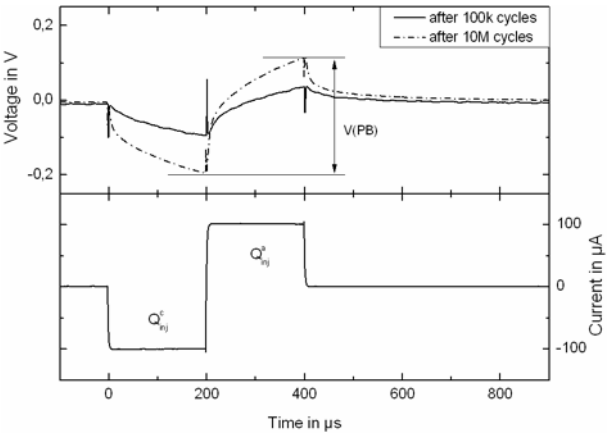

Fig. 2: Pulse test: upper graph depicts the voltage over the phase boundary after different load cycles. Lower graph shows one current pulse.

Peak-to-peak voltages over the phase boundary V_{PB} were measured and the mean values including standard deviations (rms) are depicted in Fig. 3 (upper graph; n=10). Since the water window for PEDOT is situated between -0.9 and 0.6V vs.

Ag/AgCl, the “water window line” would be situated at 1.5V and served as exclusion criterion, but was never met with any of the tested electrodes. Neither was any limit of safe charge injection, cathodic or anodic, met within these 10M pulses. The lower graph in Fig.3 shows the current needed to drive the platinum electrode, which served as reference material, to the safe limits of charge injection. The current stayed constant throughout the experiment which suggests that no faradic or irreversible processes occurred.

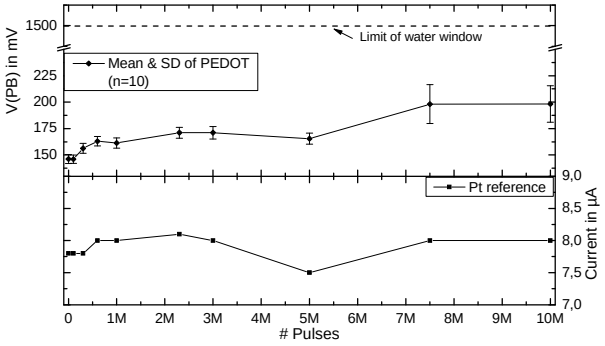

Fig. 3: Upper graph shows the mean peak-to-peak voltage across the phase boundary. Lower graph gives the current needed to drive platinum reference electrodes to safe limits of charge injection.

Discussion

PEDOT coatings were able to decrease the impedance about 95 % when compared to the original platinum electrodes and showed a much stronger resistive behaviour in EIS measurements suggesting properties comparable to iridium oxide coatings. A loss of conductivity could not be seen within the 10M pulses delivered to the electrodes which contradicts another report where PEDOT lost its conductive property after about 24k cycles in a cyclo voltammetric (CV) measurement [3]. This may be caused by another dopant which was used in the other study (PSS rather than pTS) or by an unconventional water window in which the CV was recorded (0-0.6V vs. Ag/AgCl).

Conclusions

The aim of this study was to investigate whether PEDOT is a useful material for stimulating electrodes or if the conductive property of this polymer decreases over time or pulse counts. Therefore, typical values for PNS applications were chosen, e.g. 20 nC of charge injection, 200 µs pulse width and 25 Hz repetition frequency, to model a “realistic” testing environment. Mortimer et al. reported on pulse counts for hand prosthesis and concluded that approximately 200k pulses per day were necessary to operate such a device [6]. In this context it could be shown that PEDOT is a feasible material for stimulating electrodes with superior properties compared to platinum for subchronic experiments. The durability lies in a range of at least 10M pulses or 50 days, but is expected to be much higher since the peak-to-peak voltage across the phase boundary reached merely 13 % of the available range of the water window.

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