

High-porous Platinum Electrodes for Functional Electrical Stimulation

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Abstract—This paper is about the preparation and characterization of highly porous platinum electrodes for functional electrical stimulation. Thin-film platinum electrodes were roughened by electrochemical deposition of platinum-copper alloys and subsequent removal of copper using cyclic voltammetry (CV). Prepared samples were characterized by electrochemical impedance spectroscopies (EIS), CVs and long-term pulse testing. The electrodes exhibited an increased porosity by a factor of ~238 when compared to sputtered platinum electrodes. EIS measurements showed a decreased impedance of about 85% and pulse tests suggested a stable coating over at least 250M pulses.

I. INTRODUCTION

PLATINUM is one of the most commonly used materials within the field of electrical stimulation and neuroprosthetics, because of its well known properties such as biostability, corrosion resistance, charge injection capacities and inertness in physiological environments [1;2]. Nevertheless, when platinum is used in microelectrodes, the safe limit of charge injection ($75 \mu\text{C}/\text{cm}^2$) is soon met and a further increase of current density will result in corrosion and, finally, in electrode failure. This can be improved by increasing the geometrical area of the active site or, if space is limited, by enhancing the electrochemical active area.

Various approaches have arisen in the past few decades to improve the active area, such as galvanization of Pt-black or -gray [3;4]. Although platinum black yields a highly porous layer and improves the electrodes' characteristics manifold, its deposition requires a lead-containing electrolyte that restricts the actual usage because of concerns in cytotoxicity. Other means to improve the active area include electrochemical deposition of third-party

components like metal oxides and nitrides (IrO_x , Ta_2O_5 , TiN) or conductive polymer coatings (PEDOT) [5;6]. Even though these coatings have superior properties in regard to conventional platinum electrodes, their use might sometimes be restricted due to the increased composition of materials, i.e. from an engineering point of view, it is always preferable to use as few different materials as possible to avoid parasitic effects like corrosion or delamination [7].

Therefore, a new method of producing highly porous thin-film platinum electrodes is presented, with which conventional platinum electrodes can be roughened similar to platinum-black coatings but without the need of lead-containing electrolytes. This is achieved by a co-deposition of platinum-copper alloy and the subsequent dissolution of copper during one CV cycle [8;9]. The number of repetitions of this cycle adjusts the porosity and layer thickness and, thus, enables one to control the properties of the resulting layer.

II. MATERIALS AND METHODS

A. Sample Preparation

Test samples consisted of a polyimide-platinum-polyimide stack ($5\mu\text{m}$ - 300nm - $5\mu\text{m}$ in thickness), whereas perimeter and electrode sites were opened via dry etching (RIE). Electrode diameters ranging from $40 \mu\text{m}$ to $120 \mu\text{m}$ were realized on the substrate, although only $80 \mu\text{m}$ sites were solely used in this study. Electrical contact was established through zero-insertion force (ZIF) adapters mounted on a PCB.

Electrode sites were prepared using cyclic voltammetry (50mV s^{-1} , between -0.6 and 1.4 V vs. a saturated calomel electrode (SCE)) in an acidic solution of H_2PtCl_6 (0.02mol l^{-1} , Pt-%: 40.02, Chempur, Germany) and CuSO_4 (0.02mol l^{-1} , $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, Merck, Germany). In one CV cycle, platinum-copper alloy is deposited within the cathodic phase and copper is subsequently removed during the anodic phase (Fig. 1). Overall 15 cycles were applied to form the designated porosity and layer thickness, whereas the samples were subjected to 1 min. of ultrasound (20W, Emmi-6, Schalltec, Germany) every 5 cycles to remove excess material.

After deposition, electrode sites were cleaned via CV in H_2SO_4 (0.5M) for 5 cycles between -0.4 and 1.2 V vs. SCE (50mV s^{-1}).

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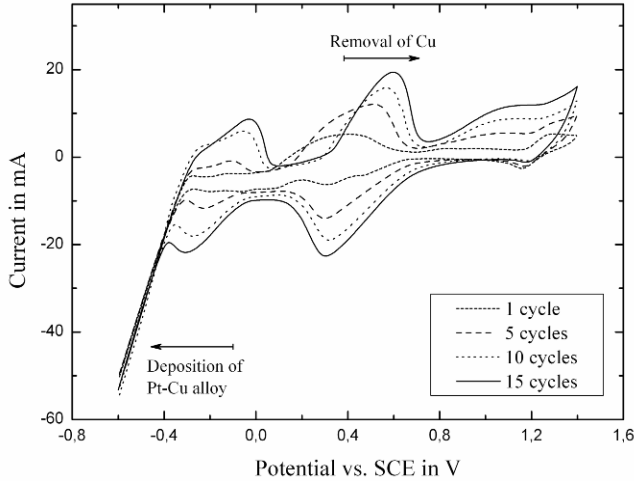


Fig. 1: Cyclic voltammogram during deposition of Pt-Cu alloy and subsequent removal of copper.

B. Electrochemical Characterization

The electrochemical active surface was determined by CV (last of 3 cycles from -0.25 to 1.2V vs. SCE; 25mV s⁻¹) in H₂SO₄ (0.5M) by measuring the charge of hydrogen desorption at the platinum interface [10]. Surface roughness was calculated according to

$$RF = \frac{Q_{HDes}}{Q_{ideal} \cdot A_g}$$

where RF is the roughness factor per cm², Q_{HDes} is the measured charge of hydrogen desorption, and A_g is the geometric area of the electrode site. Q_{ideal}, which is the value of ideally polished polycrystalline platinum, was assumed to be 210 μC cm⁻² [11].

Electrochemical impedance spectroscopy (EIS) was done within a three electrode configuration that consists of the working electrode, a large area platinum counter and a Ag/AgCl (3M) reference electrode using a potentiostat and frequency analyzer (Solartron 1260&1287 by Solartron Analytical, Farnborough, Hampshire, UK) in combination with the software Zplot (v3.1 by Scribner Associates Inc., Southern Pines, NC, USA). Impedance spectra were recorded from 1 Hz to 100 kHz with an excitation amplitude of 10 mV in phosphate-buffered saline solution (PBS; pH7.4). From these measurements, the double layer capacitance C_{dl} was fitted, using the Debye model with an R-R||C circuit. Fitting errors were always held below 5 % and standard deviation was calculated for n=10 measurements.

C. Pulse Test

Pulse testing was done using a custom 12-channel pulse tester, incorporating improved Howland current pumps and circuits to subtract the voltage drop over the access resistance [12]. Applied pulses were rectangular, biphasic, and charge balanced in nature with a pulse width of 200 μs/phase and a frequency of 200 Hz. Pulsing was

performed in non-agitated PBS solution (0.5L; regularly refilled with deionized water). A large area stainless steel electrode served as counter electrode. Injected charge was held constant at 20 nC/phase (200μs x 100μA) and charging of the phase boundary was monitored over the timeframe of 250M pulses. Additionally, impedance spectra were measured on a daily basis to further quantify possible alterations within the coating. From those pulse tests, the double layer capacitance was again calculated by

$$C_{dl} = \frac{Q_{inj}^c}{V_c}$$

where Q_{inj}^c is the cathodic charge of one phase, i.e. 20 nC, and V_c is the cathodic voltage excursion measured at the phase boundary.

Furthermore, test samples were optically characterized before and after pulse testing via scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) to quantify the amount of copper residues within the coating.

III. RESULTS

A. Sample Preparation

Test samples were successfully manufactured through state of the art micromachining processes. Preparation of electrode sites yielded reproducible coatings and optical inspections via microscope showed that the electrochemically deposited layer was confined to the electrode site and did not creep over the recess-boundary of platinum and polyimide, suggesting a coating thickness below 5 μm. These deposition parameters were found via trial and error, at which the application of ultrasound after every five CV cycles proved mandatory, in order to prevent excess material creeping over the Pt-PI boundary. Also, the maximal repetition of deposition cycles could be appointed to ~15, since more repetitions resulted in coating thicknesses above 5 μm, which spilled over the electrode site's brim.

B. Electrochemical Characterization

The roughness factor was calculated for as-deposited platinum, which served as reference, and for treated platinum sites. Pure platinum had a roughness factor of 1.5, indicating that the assumed value for ideally polished polycrystalline platinum is also applicable to sputtered thin-film platinum layers. Treated electrode sites showed an increased RF value of 238±31 (average value of n=10 and std. dev.), which corresponds to a two-hundred-fold increase of the electrochemically active area.

EIS measurements were conducted for non-treated platinum and for unpulsed platinum, according to a daily routine during pulse testing. Fig. 2 shows the results of these impedance spectra for sputtered, unpulsed, and pulsed

platinum sites after 175M and 250M pulses (average values of $n=10$). After deposition, the impedance decreased about 84 % from 32 ± 2.3 k Ω , for sputtered Pt, to merely 5 ± 0.8 k Ω while the phase angle increased from $-75 \pm 0.6^\circ$ to $-7 \pm 1.3^\circ$ at 1 kHz, respectively. Throughout the timeframe of pulse testing, the impedance and phase angle values stayed almost constant and showed only a slight difference within the capacitive regime from 1 Hz to 200 Hz. Cut-off frequencies were calculated to ~ 5.3 kHz for sputtered platinum and to ~ 58 Hz for treated platinum. The double layer capacitance was fitted to 53 ± 1 nF and 692 ± 24 nF for sputtered and treated platinum, respectively (see Table 1).

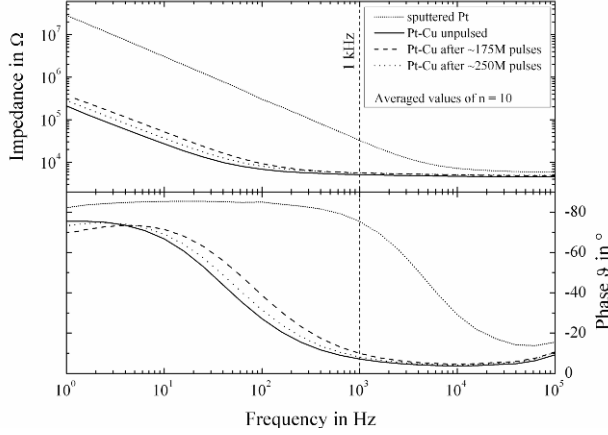


Fig. 2: EIS measurements after 0, 175M, and 250M pulses. As reference, an untreated sputtered platinum electrode is also shown.

C. Pulse Test

Pulse tests stayed constant, within their respective deviations, during the complete 250M injected pulses (see Fig. 3). The voltage drop over the phase boundary V_{PB} was measured to 360 ± 18 mV, 370 ± 28 mV, and 376 ± 27 mV for unpulsed, after 135M, and after 250M pulses, respectively. The safe limits of charge injection, which are given by the water window of platinum (-0.6 and 0.8 V vs. Ag/AgCl), were never exceeded during this experiment. Double layer capacitance was calculated to 129 ± 12 nF after 0 pulses, 97 ± 8 nF after 135M, and 92 ± 8 nF after 250M pulses (see Table 1).

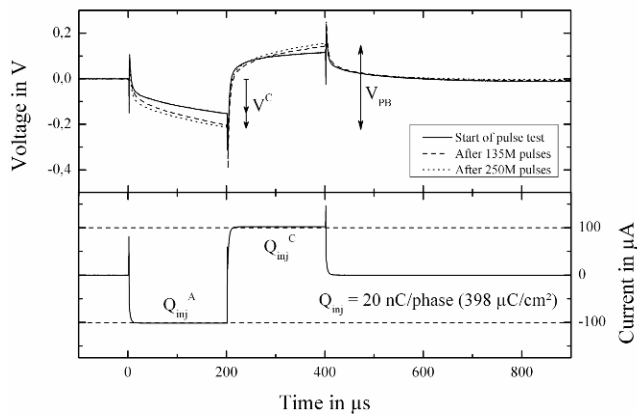


Fig. 3: Course of phase boundary charging after 0, 135M, and 250M pulses (upper graph). Note that the voltage drop over the access resistance is already subtracted. Fixed injected current of 20nC/phase (lower graph).

TABLE 1:
COMPARISON OF CALCULATED AND FITTED DOUBLE LAYER CAPACITANCES
FOR A $80\mu\text{m}$ IN DIAMETER ELECTRODE SITE ($N=10$)

# of pulses	C_{dl} fitted from EIS in nF \pm std. dev.	C_{dl} calculated from pulse test in nF \pm std. dev.
Pt untreated	53 ± 1	n.a.
0	692 ± 24	129 ± 12
135M	n.a.	97 ± 8
175M	367 ± 12	102 ± 12
250M	509 ± 18	92 ± 8

Optical inspection (SEM) of treated platinum sites revealed a cauliflower-like pattern of the coating (see Fig. 4). Images taken before and after pulsing did not show any significant changes within the pattern. Note that differences in brightness within Figure 4 are only attributed to different voltages used to acquire the pictures and not due to alterations within the coating.

Energy dispersive X-ray spectroscopy (EDX) showed an amount of 9.1 ± 0.9 wt.-% of copper and 90.9 ± 0.9 wt.-% of platinum within one electrode site (average of 8 measurements on one single site). No other elements were found during all EDX measurements, suggesting a clean electrochemical deposition and removal process.

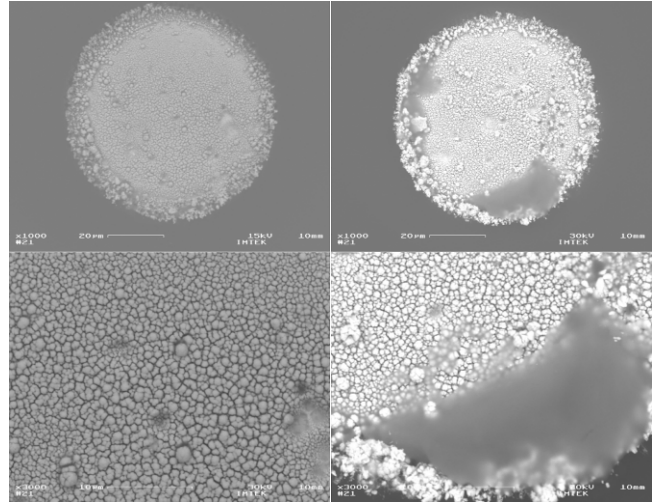


Fig. 4: SEM picture of Pt-Cu electrode site. Left column, before pulse testing and right column, after pulse testing. The grey area within the right column relates to residues of electrolyte.

IV. DISCUSSION

It was shown that electrochemical roughening of thin-film platinum is feasible via electro deposition of Pt-Cu alloy and subsequent removal of copper. The electrochemically active area was increased by a factor of 238 and, likewise, impedance values decreased by 84 % when compared to sputtered platinum sites and showed a much stronger resistive behavior, comparable to platinum-black or iridium oxide coatings. Pulse testing, which models the active site under load cycles, was done for 250

million cycles with a fixed injected charge of 20nC/phase, whereas the coating remained stable and showed only a minor increase of the phase boundary voltage (about 4 %). Similarly, the calculated double layer capacitance decreased by approximately 28 %. Electron microscopy revealed a cauliflower-like pattern of the surface, validating the increased active surface area when compared to mirror-like sputtered platinum. No alterations could be found in SEM pictures before and after load-cycles were applied, suggesting that the coating was stable. EDX spectra were measured to control the purity of the deposited layer and about 9 wt.-% of copper residues could be identified within the coating. However, the remaining 91 wt.-% were solely platinum, which indicates a clean deposition process.

V. CONCLUSION

The objective of this study was to determine whether the electrodeposition of high porous platinum, originally developed for biofuel-cell application [8] is also feasible on polyimide based thin-film electrodes for electrical stimulation. Samples could be manufactured successfully and were tested by various means, e.g. pulse testing that models an actual use as stimulating electrode. Parameters for pulsing were chosen to match many peripheral nervous system (PNS) applications with regard to injected charge and pulse width. Mortimer previously reported on probable pulse counts necessary to operate a hand prosthesis and concluded that approximately 200k pulses per day were necessary to operate such a device [13]. In this context it could be shown that the proposed high porous platinum sites are suitable for at least 250M pulses or 1250 days of use with superior properties when compared to traditional sputtered platinum sites. Since charging of the phase boundary remained stable within a small voltage regime, i.e. about 360 mV, and the safe limits of charge injection are situated far beyond this value ($\sim 1.4V$), it can be assumed that the present coating will last even longer. Cytotoxicity studies are currently in progress to estimate whether the copper residues are within physiological parameters or if cell vitality or proliferation might suffer.

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