

Surface Modification of Neural Stimulating/Recording Electrodes with High Surface Area Platinum-Iridium Alloy Coatings

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Abstract— High-surface area platinum–iridium alloys were electrodeposited by on Pt and Au microelectrodes using a potential sweep technique. Detailed investigations of the structure and morphology and the electrochemical properties of the electrodeposited Pt–Ir alloy coatings were performed. Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) were used for the determination of the surface morphology and the chemical composition of the Pt–Ir coatings, respectively. The elemental analysis by EDS showed a nearly 60–40% Pt–Ir composition of the coatings. The electrochemical properties of the Pt–Ir coatings were evaluated using cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). CV and EIS measurements revealed that the Pt–Ir coated electrodes exhibit significantly increased charge storage capacity and real surface area compared to uncoated Pt electrodes. Charge injection experiments of the Pt–Ir coated microelectrodes revealed low potential excursions, indicating high charge injection capabilities within safe potential limits.

I. INTRODUCTION

Requirements for neural electrodes include low impedance, high charge injection capability, corrosion resistance and biocompatibility [1]. The implanted electrode arrays, which are in direct contact with the living tissue, form an interface between the electronic device and the surrounding cells. By reducing the impedance of the electrode/tissue interface, the generated electrode voltage will decrease and as a result, the power consumption of the implanted devices could be minimized. Electrode stability is required since implanted neural electrodes should last the life time of the patient and significant drift in electrode properties will degrade implant performance. Smaller electrodes in an array improve the spatial resolution and selectivity. However, electrode impedance and charge storage capacity will increase with decreasing geometric size of the electrode, which may result tissue damage due to high charge density stimulation [2]. In order to improve the

charge transfer properties at the electrode/tissue interface, surface modification has to be done on the electrode surfaces. Different types of materials have been used for neural recording electrodes, such as platinum, platinum-iridium alloys, iridium oxide, stainless steel, titanium nitride, tungsten and poly (ethylenedioxythiophene) (PEDOT) [3]. A strong and mechanically robust connection between the electrode surface and the neurons may prevent the formation of a nonconductive, organic boundary layer that presumably, in the long term, is involved in diminished functional activity [4].

Electrodeposition of high-surface area Pt–Ir coating has many advantages over other methods in the surface modification of bioelectronic devices. The method can be used on many different electrically conductive surfaces and are valuable alternative to more conventional techniques for thin film deposition and metal plating. Electroplated Pt–Ir alloy modified electrodes exhibit higher charge storage capacity and lower electrochemical impedance relative to platinum electrodes in biomedical applications [5,6].

In our previous study, comprehensive investigations on the development of an efficient and reproducible electroplating method for producing Pt–Ir alloy thin coatings with improved mechanical properties and approximately 60% platinum–40% iridium were conducted [7]. The electrodeposited high-surface area Pt–Ir alloy coatings in this study showed significantly lowered impedance and excellent adhesion onto the substrates, capable of transferring large amounts of safe electrical charge to the biological tissues.

II. EXPERIMENTAL APPROACH

Electrodeposition

Pt–Ir coatings were electrodeposited on parylene-C microelectrode array (MEA) provided at the Caltech Micromachining Laboratory (Pasadena, CA) from a freshly prepared Pt–Ir solution as described by Petrossians et al. [7]. To achieve high surface area Pt–Ir alloy coating, the electrodeposition solution was constituted by adding 40 g/l of K_2SO_4 . An ultrasonic homogenizer (Misonix, Inc. Newtown, CT, USA) was used to increase the mass transfer and to control the electroplating bath temperature during the electrodeposition process at a frequency of 20 kHz with a power of 8 W. Electrodeposition was performed in a 50 ml beaker on microelectrodes using a three-electrode electrochemical cell. In this cell, microelectrodes with geometric size of 200 μm in diameter were applied as working electrodes and a platinum wire with diameter of 1 mm as counter electrode with respect to Ag/AgCl as a

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reference electrode. All electrochemical experiments were carried out using a Gamry potentiostat (FAS1, Gamry Instruments, Warminster, PA, USA). Electroplating was performed using a potential sweep technique at a scan rate of 0.2 mV/s for two or three potential sweeps. The potential range of $E = +0.1V$ to $-0.1V$ vs. Ag/AgCl was selected for deposition experiments since this range included potentials at which both Pt and Ir would be deposited.

Surface and compositional analysis

Pt-Ir coatings' surface structures were imaged using a field emission scanning electron microscope (Zeiss LEO 1550VP, Carl Zeiss Inc., Germany). The chemical composition of the electrodeposited Pt-Ir coating was characterized using energy dispersive spectroscopy (Oxford INCA Energy 300 X-ray EDS system, Bucks, UK). All samples were analyzed at three separate locations.

Electrochemical measurements

Prior to the electrochemical measurements, the electrodeposited coatings were electrochemically cleaned in 0.05 M H_2SO_4 by cycling the working electrode potential in the range of $E = -0.3 V$ to $+1.2 V$ vs. Ag/AgCl at a scan rate of 250 mV/s until stable voltammograms were achieved [6]. The properties of the electrodeposited Pt-Ir thin coating and the uncoated Pt control electrode were determined using cyclic voltammetry (CV) in 0.05 M H_2SO_4 at a scan rate of 50 mV/s in the potential range of $-0.3 V$ to $1.2 V$ vs. Ag/AgCl. Electrochemical impedance spectroscopy (EIS) measurements were performed in 0.05 M H_2SO_4 at the open-circuit potential (OCP) with a ± 10 mV amplitude ac signal in a frequency range of 100 kHz to 10 mHz. The values of the solution resistance (R_s), polarization resistance (R_p) and capacitance (C) were obtained by fitting the experimental data to a one-time constant equivalent circuit (EC) using the ANALEIS software [8 -10].

Charge injection measurements

Charge injection measurements were performed on the microelectrodes, using a biphasic and symmetric current pulse in a two electrode configuration, using a pulse generator (Multi-Channel Systems, STG 2008, MCS GmbH, Germany) with a duration of 1 ms. [11]. The experiments were performed in phosphate buffered saline (PBS) (Sigma-Aldrich Corp., St. Louis, MO, USA) at pH of 7.4 at room temperature with a platinum wire as counter electrode.

III. RESULTS AND DISCUSSION

Very high surface area Pt-Ir alloy coatings were formed on Pt microelectrodes by the electrodeposition method that was previously described [8] except that a potential sweep technique was used, the scan rate was reduced to 0.2 mV/s and K_2SO_4 was added to the electrodeposition bath. The

potential sweep technique was used for co-deposition of Pt and Ir in potential ranges below the equilibrium potentials of both Pt and Ir. Rough Pt-Ir coatings with excellent adhesion were obtained on Pt substrates by applying potential limits of 0.1 to $-0.1 V$ vs. Ag AgCl.

Fig. 1 shows the SEM images of the electrodeposited Pt-Ir coatings on Parylene based Pt microelectrode arrays after electrodeposition using potential sweep technique. The electrodeposited coatings are granular consisting of numerous nodules resulting in an extremely high surface area Pt-Ir alloys coating. Comparison of the uncoated Pt microelectrode surface morphology (Fig. 1a) with that of Pt-Ir coated (Fig.1 b) suggested that the electrodeposited coatings roughness has drastically increased the real surface area compared to the uncoated platinum microelectrode that exhibits a smooth topography.

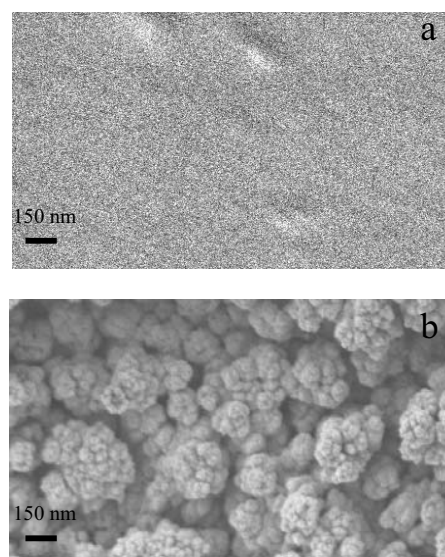


Fig.1 SEM micrographs of (a) Pt and (b) Pt-Ir electrodeposited MEAs.

Quantitative compositional analysis performed on the electrodeposited Pt-Ir coatings by an energy dispersive spectroscopy (EDS) system showed an average chemical composition of about 60-40% Pt-Ir contents in electroplated samples. Other studies showed that 60-40% Pt-Ir coatings have the largest electroactive surface area and consequently, the lowest charge transfer resistance [12].

Cyclic voltammograms of the Pt-Ir coatings were collected for characterization of their electrochemical properties and qualitative determination of their chemical composition and real surface area. Representative CVs for an uncoated Pt and a Pt-Ir electroplated electrode are shown in Fig. 2.

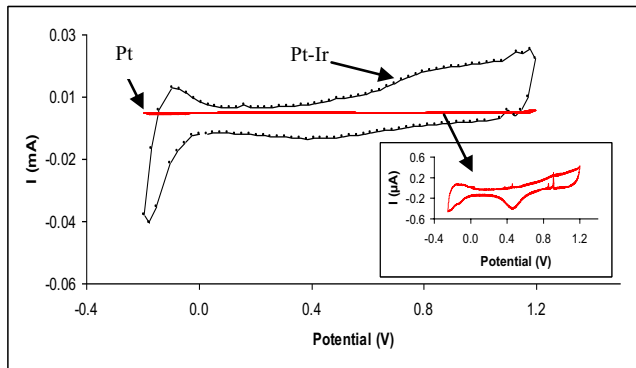


Fig.2. Cyclic voltammograms of uncoated Pt and Pt-Ir electroplated electrodes in 0.05 M H₂SO₄ at 50 mV/s.

The CV for Pt-Ir has shows much larger area under the curve than that for the uncoated Pt electrode. The area under the curve of the CV is representative of the charge storage capacity of the Pt-Ir coatings exhibiting a suitable material for neurostimulation applications [5].

In the neurostimulation process, low impedance electrodes consume less power thus improves systems efficiency. Electrochemical Impedance Spectroscopy (EIS) was used as a non-destructive method for materials characterization. EIS data for the uncoated and electrodeposited Pt-Ir microelectrodes with a geometric surface area of $3.14 \times 10^{-4} \text{ cm}^2$ in sulfuric acid solution are shown in the Bode-plot format in Fig. 3 in which the logarithm of the impedance modulus $|Z|$ and the phase angle Φ are plotted as a function of the logarithm of the applied signal frequency f . The impedance for the Pt-Ir electrodeposited microelectrode was reduced by more than two orders of magnitude compared to that of the uncoated Pt substrate. Other authors have performed similar studies of the impedance behavior for electroplating of platinum black [13] and poly (3,4-ethylenedioxythiophene) (PEDOT) [14] on Pt electrode surfaces. The impedance modulus $|Z|$ is inversely proportional to the electrode capacitance C ($|Z| = 1/2\pi fC$) and as a result, the decreased $|Z|$ value is due to an increase of capacitance of the coating, indicating the increased real surface area. The impedance spectra for uncoated and electrodeposited Pt-Ir coatings were fit to a one-time-constant model (OTCM) equivalent circuit (EC). The fit parameters' values of C for uncoated and Pt-Ir electrodeposited electrodes were evaluated to be $0.77 \mu\text{F}$ and $88.20 \mu\text{F}$, respectively. Comparison of the C values for uncoated Pt and electrodeposited Pt-Ir electrodes demonstrates that the real surface area of the Pt-Ir coating was significantly increased.

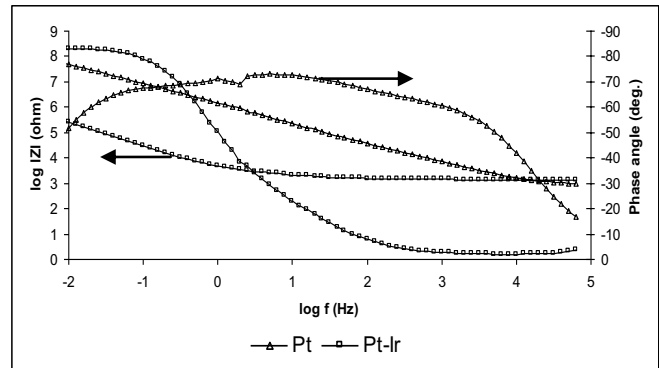


Fig.3 Bode plots for uncoated Pt and electroplated Pt-Ir electrodes measured in 0.05 M H₂SO₄.

Figure 4 represents the potential responses of Pt and Pt-Ir electrodeposited MEAs to the applied currents, measured between the working and counter electrodes with 1 ms duration in each phase and 0.1 ms of delay between two phases. For comparison purposes, low current amplitude of $60 \mu\text{A}$ was applied to the electrodes. As shown in figure 4, high-surface area Pt-Ir electrodeposited microelectrode show significantly small potential excursions compared with uncoated Pt electrode. Minimizing the potential excursion will benefit two very important results: First, preventing from hydrolysis of body fluid by decreasing the voltage drop to the safe regimen of the water window which in turn will prevent the cell/tissue damage. Second, the power required for current pulsing stimulation will be decreased which in turn will save the life time of the implanted device battery and hence will cause longer gaps between surgeries for battery replacements.

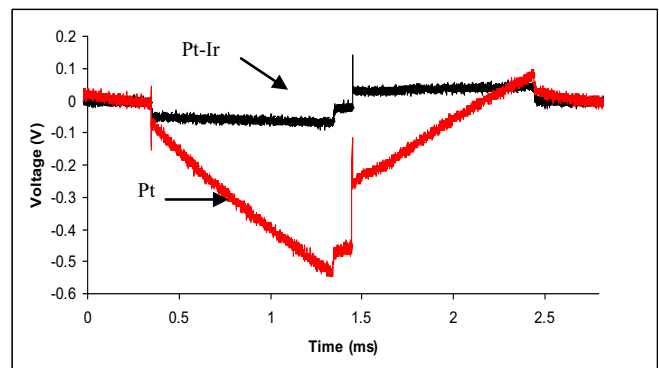


Fig.4. Voltage transient for Pt and Pt-Ir coated electrodes in response to a biphasic current pulse, with $60 \mu\text{A}$ amplitude and 1 ms current pulse.

IV. CONCLUSIONS

In this study, high-surface area Pt-Ir coatings with the optimum chemical composition of 60-40% exhibiting the highest Pt-Ir electro-active surface area were produced using a potential sweep technique [12]. Electroplating conditions such as potential scan rate, bath temperature and the ultrasonic homogenizer amplitude were found to play an important role in determining the properties and the structure of the electroplated Pt-Ir coatings with improved mechanical properties [7]. The high-surface area electrodeposited Pt-Ir coatings showed remarkable electrochemical properties compared to thin-film platinum that is used as a conventional interface material in neurostimulation applications. The increase of the capacitance of the electroplated Pt-Ir coatings compared to that of the uncoated control samples indicates that the real surface area of these coatings was significantly increased. The higher charge injection limits, charge storage capacity and drastically lower impedance of the electrodeposited Pt-Ir binary alloy show great promise as rough electrode coatings with greatly improved mechanical properties for neural stimulating/recording electrodes.

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