

Improved Chronic Neural Stimulation using High Surface Area Platinum Electrodes

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Abstract— We report a novel nano-cluster platinum (NCPt) film that exhibits enhanced performance as an electrode material for neural stimulation applications. Nano-cluster films were deposited using a custom physical vapor deposition process and patterned on a flexible polyimide microelectrode array using semiconductor processing technology. Electrode performance was characterized *in vitro* using electrochemical impedance spectroscopy and compared with sputtered thin-film platinum (TFPt) electrodes. We characterized electrode impedance, charge storage capacity, voltage transient properties, and relative surface area enhancement *in vitro*. Preliminary lifetime testing of the electrode reveals that the NCPT electrodes degrade more slowly than TFPt electrodes. The combination of material biocompatibility, electrochemical performance, and preliminary lifetime results point to a promising new electrode material for neural interface devices.

I. INTRODUCTION

The ability to chronically interact with neural tissue through electrical stimulation and/or recording enables us to identify the underlying mechanisms of the nervous system [1]. Ultimately, this understanding will aid in developing clinical treatments for Parkinson's disease, epilepsy, deafness, blindness, depression, and spinal cord injuries [2]. There are currently a few clinical neural stimulation treatments, but further technological advancement is necessary to effectively treat many more conditions. Most clinical devices use bulk electrodes, which limit their density and size. In certain treatments such as deep brain stimulation (DBS), cochlear implants, and spinal cord stimulation, performance and success rate may be enhanced by using multiple closely-spaced electrodes that can safely deliver large amounts of charge in a more targeted manner [3].

Microelectrode array technology promises to miniaturize neural prostheses, while enabling more complex interaction with the neural system with a higher density and number of electrode sites [4]. However, there are several hurdles before these devices can be widely adopted in clinical practice. In particular, implantable microelectrodes are needed that 1) elicit minimal cytotoxic response in the body, 2) do not corrode or degrade over time, and 3) can chronically record and/or stimulate over the device and patient lifetime.

High-density polyimide microelectrode arrays fabricated at Lawrence Livermore National Laboratory have demonstrated chronic biocompatibility under the Department of Energy Artificial Retina Program and through independent

testing of ISO 10993 standards for chronic biocompatibility [5]. Accelerated soak testing of the arrays was used to demonstrate lifetimes on the order of 20 years *in vitro*.

An unmet challenge for microelectrode-based neural prosthetics is the ability to maintain electrode performance over multi-year lifetimes. Many thin-film electrodes degrade after limited electrical pulsing [6,7]. This failure is further accelerated in applications like cochlear implants, where miniaturization of electrodes is desired, but greater charge is required in order to travel through bone to stimulate the neurons [8].

This work addresses the challenge of chronic electrode materials for neural stimulation using a biocompatible, high surface area, and electrochemically stable electrode material. We present the results of comprehensive characterization of nano-cluster platinum (NCPT) electrodes as they relate to the performance required for chronically stimulating electrodes.

II. FABRICATION

Fig. 1 shows the fabrication process for the nano-cluster platinum (NCPT) arrays using semiconductor processing technology [9]. A silicon wafer was used as the substrate (Fig. 1A) on which 5 μm of polyimide was spin-coated and cured (Fig. 1B). Thin-film Ti/Pt was sputter-deposited and patterned using contact lithography and plasma etching (Fig. 1C). This layer serves as both the electrical traces and the "seed" layer for the NCPT deposition. 1.3 μm thick NCPT was deposited using a custom physical vapor deposition method that results in high surface area. Electrodes were patterned on top of the patterned metal using lift-off (Fig. 1D). Next, a top layer of polyimide was spin-coated and cured (Fig. 1E). The polyimide was patterned with photoresist and etched with oxygen plasma to expose the Pt electrodes (Fig. 1F). Finally, the polyimide device was released from the silicon substrate (Fig. 1G). Fabrication of the thin-film platinum (TFPt) arrays followed the same process without the NCPT deposition or lift-off (Fig. 1D).

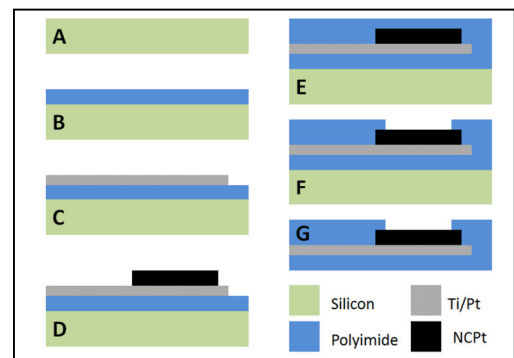


Figure 1: Process for microfabricating polymer microelectrode arrays with NCPT electrodes. (Note: Images not drawn to scale)

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III. *IN-VITRO* ELECTROCHEMICAL CHARACTERIZATION

Electrochemical impedance spectroscopy (EIS) data was collected to determine the effect of chronic stimulation pulses on the stability of the electrode material. EIS measurements were made at frequencies from 300 kHz to 1 Hz with a 10 mV amplitude sinusoidal signal. The stimulation waveform used was a biphasic, cathodic-first, charge-balanced pulse with a current density of 0.7 A/cm² at a frequency of 900 Hz. An impedance spectrum was recorded after every 1 million pulses.

All electrochemical data was acquired at room temperature in phosphate-buffered saline (PBS) using a 3-electrode system in a commercial electrochemical test system (PAR VersaSTAT 4 potentiostat, Oak Ridge, TN). A silver-silver chloride (Ag/AgCl) electrode was used as a reference electrode and a large surface area platinum wire was used as the counter electrode. All potentials were measured with respect to the Ag/AgCl reference electrode. Cyclic Voltammograms (CVs) were collected at a 100 mV/s scan rate over the potential range of -600 mV to +800 mV. All TFpT and NCpT electrodes had a geometric surface area of 125,000 μm².

Cyclic voltammetry (CV) was performed to determine the charge storage capacity (CSC) and relative effective surface area. CSC, a metric important for characterizing stimulating electrodes, is a measure of the ability of an electrode to store charge. It is calculated by the time integral of the cathodic current.

To compare the effective surface areas of the NCpT and TFpT electrodes, peak current measured from CVs were applied to the Cottrell equation. The Cottrell equation relates current peak amplitude to effective surface area:

$$i = \frac{nFAc_j^0 \sqrt{D_j}}{\sqrt{\pi t}}$$

where i is current, F is the Faraday constant, A is the effective surface area of electrode, c_j is the initial concentration of the electroactive analyte, D_j is the diffusion coefficient for species j , and t is time. This estimation is being used to compare relative surface areas of TFpT and NCpT films, and not as a method to calculate an absolute effective surface area. Measuring absolute effective surface areas are difficult and unreliable for porous materials, where the conditions of measurement can cause large fluctuations [10].

Another method to investigate the effects of current stimulation pulses on the stability of the electrode material is to measure the voltage transients of the electrode during a stimulation pulse. The electrochemical potential transients of the NCpT and TFpT films were determined using a biphasic, cathodic-first, current-controlled pulse. A 50 μs interpulse delay was included between the cathodic and anodic phases to more easily determine the access voltage which is associated with the ohmic voltage drop. The cathodic potential excursion was calculated by subtracting the access voltage from the cathodic voltage transient [1]. Electrodes that polarize beyond the safe water window of -600 mV and +800 mV generally undergo irreversible

reactions or dissolution, therefore electrodes that are capable of injecting maximum quantities of charge with minimal potential excursions are desired for chronic stimulation applications.

IV. RESULTS AND ANALYSIS

A. SEM and optical imaging

Fig. 2 shows a visual enhancement of the surface of the NCpT electrodes in comparison to traditional TFpT electrodes.

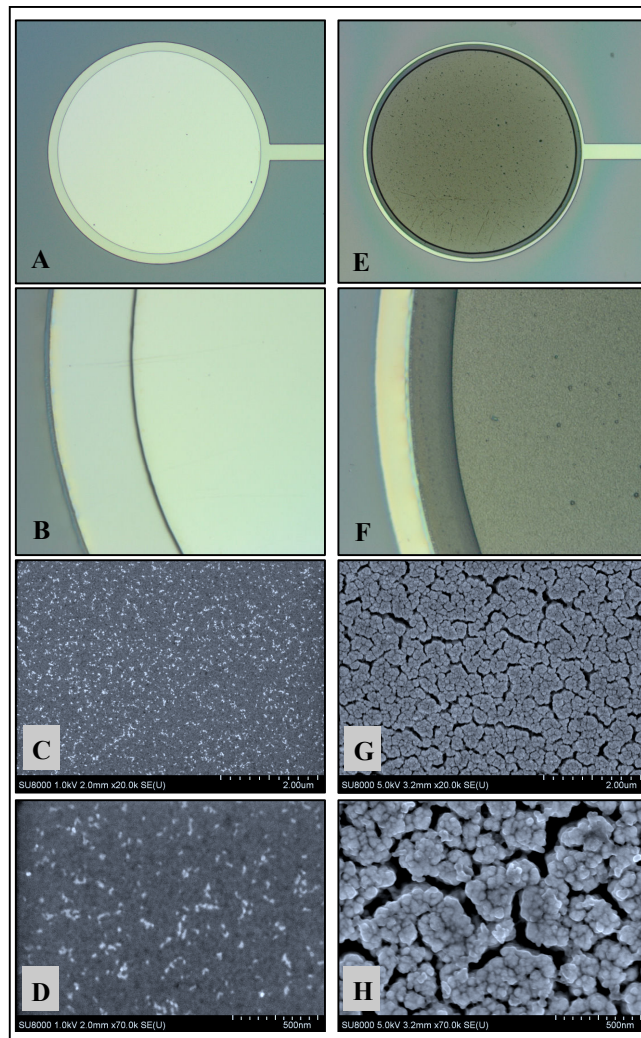


Figure 2: A) and B) optical microscope images of TFpT electrodes, C) and D) high-resolution SEM images of TFpT surface, E) and F) optical microscope images of NCpT, G) and H) high-resolution SEM images of NCpT electrode showing surface area enhancement due to Pt nanostructure. Note: the circular electrodes in A), B), E) and F) are 400μm in diameter

B. Electrochemical Testing

Electrochemical impedance spectroscopy was performed on the electrodes *in vitro* to record their impedances prior to long-term pulsing experiments. Lower impedance is desired for prosthetic devices to allow for a reduced supply voltage and lengthened battery lifetime. Fig. 3 shows the magnitude of the impedance spectra over a range of frequencies. Impedances of NCpT were found to be lower and more consistent at 0.87 +/- 0.07 kOhm (n = 20, f = 1 kHz) than TFpT measured at 2.94 +/- 0.2 kOhm (n = 30, f = 1 kHz).

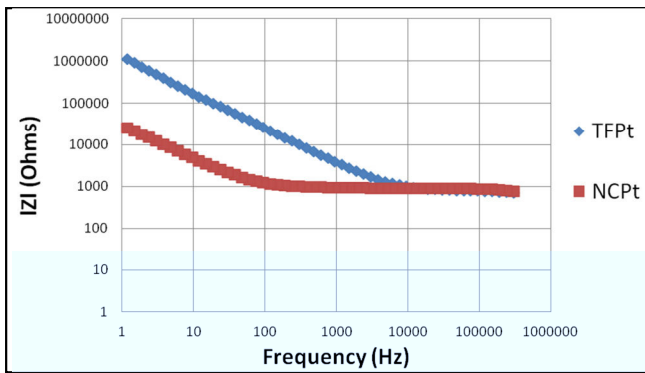


Figure 3: Representative impedances for TFPt and NCpt electrodes. The NCpt electrode impedance is more stable over a wider range of frequencies than the TFPt electrode impedance.

To test material stability, the electrodes were subjected to a long-term stimulus protocol. Electrochemical impedance spectrums were recorded before stimulation and after every one million pulses of a 900 Hz biphasic charge-balanced stimulation waveform. After 10 million pulses, impedance measured at $f = 1$ kHz of a NCpt electrode changed by only 2.6%. In contrast, the impedance change after 10 million pulses for a TFPt electrode was 22%, nearly a factor of 10 higher. These results suggest that NCpt is a more stable electrode material with fewer irreversible reactions occurring at the NCpt electrode surface during current pulsing than at the TFPt electrodes surface. Data from voltage transient measurements support these results.

Electrode potential transients were estimated from voltage waveforms. Fig. 4 shows the difference in electrochemical potential transients between the NCpt and TFPt, given a current stimulation with amplitude of 200 μ A and a pulse width of 200 μ s. The TFPt electrode has a cathodic excursion 240 mV greater than that of the NCpt electrode, suggesting NCpt films are capable of greater charge injection without irreversible damage of the film.

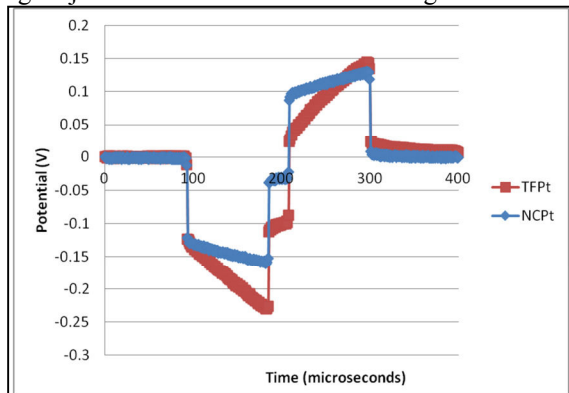


Figure 4: Voltage transients of TFPt and NCpt electrodes resulting from a stimulation pulse with 200 μ A current amplitude and 200 μ s pulse width.

As can be seen, the NCpt electrodes have significantly less cathodic and anodic voltage excursions than the TFPt electrodes, indicating that the NCpt is more electrically stable.

The CSC calculated for NCpt electrodes was more than thirty times larger than for TFPt electrodes (Table 1). This indicates that the NCpt electrodes have a significantly higher effective surface area than the TFPt electrodes. Fig. 5 illustrates the larger CSC and effective surface area.

Based on peak currents, NCpt electrodes were estimated to have more than 10 times the effective surface area of TFPt electrodes, consistent with CSC data.

TABLE I. CHARGE STORAGE CAPACITY COMPARISON

Electrode material	Average CSC (mC/cm ²) +/- std. dev.	n
TFPt	0.81 +/- 0.127	18
NCpt	27.05 +/- 1.20	20

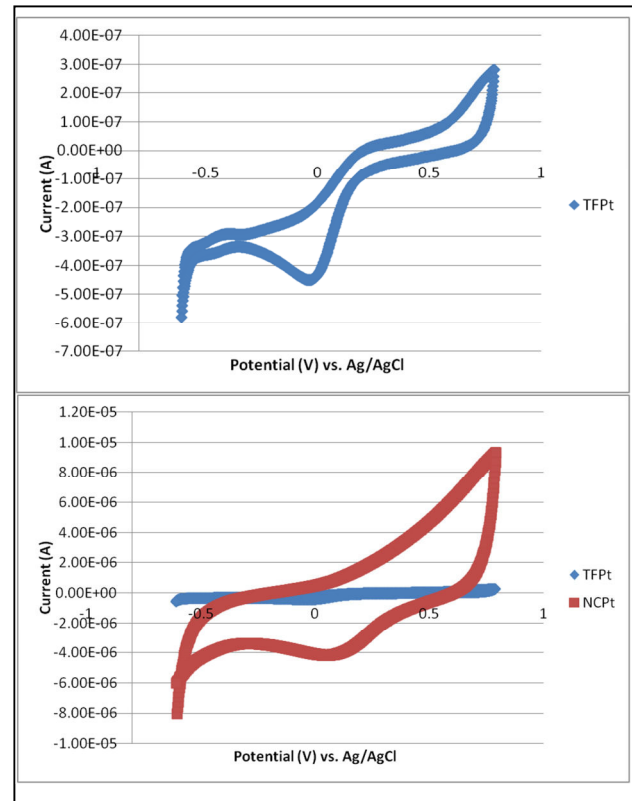


Figure 5: Representative CV curves for both NCpt and TFPt electrodes. The top graph shows only the TFPt electrode and the bottom graph shows the overlay of both the NCpt and TFPt electrodes. The NCpt CV shows both a larger CSC and a significantly higher peak current, indicative of a higher surface area.

V. DISCUSSION

Microelectrode arrays were fabricated with NCpt electrodes, and directly compared with TFPt electrodes of the same size. As we have demonstrated, the custom NCpt deposition method is integrated with the standard fabrication approach for polymer-based neural interfaces [5].

The NCpt electrodes demonstrate a number of improvements over the standard thin-film electrodes primarily used for acute *in vivo* neural stimulation [11].

Increased surface area of the NCpt film is visibly apparent in the scanning electron microscope images in Figure 2. Though the real surface area of the porous NCpt film is difficult to measure, the surface area enhancement can be calculated using the Cottrell equation and the measured peak currents. The 10X surface area enhancement of the NCpt films over TFPt films is comparable to electrodeposited films reported in the literature [6]. Physical vapor deposition

of NCPT films has perceived advantages over electrodeposited films from the perspective of microfabrication process integration, scalability, reduced film lower stress, and the ability to deposit thicker films.

From electrochemical measurements *in vitro*, we established that NCPT electrodes exhibit a greater than 30X increase in charge storage capacity when compared with TFPT electrodes of the same size.

In practice, it is important to understand the implications of electrode material properties as they relate to safety of tissue during stimulation. There is a need to miniaturize electrodes in order to enable more complex interactions with neural tissue through a larger number and higher density of electrodes. If electrodes are geometrically miniaturized, then delivering the same charge per phase requires an increase in charge density. This, in turn, can lead to an increased risk of tissue damage, as quantified by McCreery and Shannon [12,13]. Thus, simply decreasing electrode size is not an acceptable strategy for neural stimulation. The demonstrated enhancement of the charge storage and charge injection capacity of NCPT electrodes is important for reducing the charge density. This reduction in charge density permits staying within safe limits of tissue stimulation while reducing electrode size.

An equally important practical consideration for chronically implanted electrode materials is to ensure that the stimulation parameters minimize the degradation of the electrode surface over the device lifetime. [7,14]. The voltage transient measurements of the NCPT show a significant improvement, with reduced potential excursions, compared to the TFPT films. In preliminary testing, we have demonstrated that the NCPT electrodes exhibit very little degradation (as measured by the change in impedance) over millions of cycles of electrical pulsing. Further *in vitro* pulsing of the electrode material is on-going.

A consequence of the enhanced surface area of the NCPT electrodes is an approximately 4X decrease in impedance. This is important in clinical treatment with implantable neural stimulators, as it reduces the power requirement, thus prolonging battery life of the implant.

It is difficult to make direct comparisons of electrochemical data with other electrode materials reported in the literature because the characterization results remain largely dependent on the specific application. As a result, there are a variety of stimulation parameters such as stimulation frequency, current amplitude and pulse width, electrode sizes and shapes, and test protocols that have been reported [1,7,8,10]. However, our results correlate with the trends seen in published work with electrodes of enhanced surface area [1,6,8,10,14].

In future experiments, the long-term degradation of NCPT films will be studied to quantify electrode lifetime. Based on the promising results thus far, we hope to extend polyimide microelectrode arrays with NCPT electrodes for clinical use.

VI. ACKNOWLEDGMENTS

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REFERENCES

- [1] S. F. Cogan, "Neural stimulation and recording electrodes," *Annual review of biomedical engineering*, vol. 10, pp. 275–309, Jan. 2008.
- [2] D. R. Kipke, W. Shain, G. Buzsáki, E. Fetz, J. M. Henderson, J. F. Hetke, and G. Schalk, "Advanced neurotechnologies for chronic neural interfaces: new horizons and clinical opportunities," *The Journal of neuroscience: the official journal of the Society for Neuroscience*, vol. 28, no. 46, pp. 11830–8, Nov. 2008.
- [3] H. C. F. Martens, E. Toader, M. M. J. Decré, D. J. Anderson, R. Vetter, D. R. Kipke, K. B. Baker, M. D. Johnson, and J. L. Vitek, "Spatial steering of deep brain stimulation volumes using a novel lead design," *Clinical neurophysiology: official journal of the International Federation of Clinical Neurophysiology*, vol. 122, no. 3, pp. 558–66, Mar. 2011.
- [4] A. Tooker, K. G. Shah, V. Tolosa, H. Sheth, S. Felix, T. Delima, S. Pannu. "Chronically Implantable, 121-Channel, Polymer Microelectrode Array with Hermetically-Sealed Wireless Interface," *Solid-State Sensors, Actuators, and Microsystems Workshop*, Hilton Head, June 2012.
- [5] A. Tooker, V. Tolosa, K.G. Shah, H. Sheth, S. Felix, T. DeLima, and S. Pannu. "Polymer neural interface with dual-sided electrodes for neural stimulation and recording," *Engineering in Medicine and Biology Society (EMBC), 2012 Annual International Conference of the IEEE*. pp. 5999-6002. Aug. 2012.
- [6] D. Rodger, A. Fong, W. Li, H. Ameri, A. Ahuja, C. Gutierrez, I. Lavrov, H. Zhong, P. Menon, and E. Meng, "Flexible parylene-based multielectrode array technology for high-density neural stimulation and recording," *Sensors and Actuators B: Chemical*, vol. 132, no. 2, pp. 449–460, Jun. 2008.
- [7] S. Negi, R. Bhandari, L. Rieth, R. Van Wagenen, and F. Solzbacher, "Neural electrode degradation from continuous electrical stimulation: comparison of sputtered and activated iridium oxide," *Journal of neuroscience methods*, vol. 186, no. 1, pp. 8–17, Jan. 2010.
- [8] M. Tykocinski, Y. Duan, B. Tabor, and R. S. Cowan, "Chronic electrical stimulation of the auditory nerve using high surface area (HiQ) platinum electrodes," *Hearing research*, vol. 159, no. 1–2, pp. 53–68, Sep. 2001.
- [9] A. Tooker, V. Tolosa, K.G. Shah, H. Sheth, S. Felix, T. Delima, and S. Pannu. "Optimization of multi-layer metal neural probe design," *Engineering in Medicine and Biology Society (EMBC), 2012 Annual International Conference of the IEEE*. pp. 5995-5998. Aug. 2012.
- [10] A. Petrossians, J. J. Whalen, J. D. Weiland, and F. Mansfeld, "Surface modification of neural stimulating/recording electrodes with high surface area platinum-iridium alloy coatings," *Annual International Conference of the IEEE Engineering in Medicine and Biology Society. IEEE Engineering in Medicine and Biology Society. Conference*, vol. 2011, pp. 3001–4, Jan. 2011.
- [11] K. C. Cheung, "Implantable microscale neural interfaces," *Biomedical microdevices*, vol. 9, no. 6, pp. 923–38, Dec. 2007.
- [12] McCreery, Douglas B., William F. Agnew, Ted GH Yuen, and Leo Bullara. "Charge density and charge per phase as cofactors in neural injury induced by electrical stimulation," *IEEE transactions on Biomedical Engineering*. Vol. 37, no. 10 (1990): 996-1001.
- [13] R. V Shannon, "A model of safe levels for electrical stimulation," *IEEE transactions on biomedical engineering*, vol. 39, no. 4, pp. 424–6, Apr. 1992.
- [14] J. D. Weiland and D. J. Anderson, "Chronic neural stimulation with thin-film, iridium oxide electrodes," *IEEE transactions on biomedical engineering*, vol. 47, no. 7, pp. 911–8, Jul. 2000.