Micro-Reaction Chamber Electrodes for Neural Stimulation and Recording

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Abstract— **Biocompatible electrodes with smaller geometric area are preferred to improve the selectivity of the neural recording and stimulation applications. We introduce the concept of a micro-reaction chamber (μRC) in which a volume within the electrode back plane is used to confine and sequester the electrochemical reactions used for charge passage. The μRC electrode design helps decrease impedance and improves the charge storage capacity without altering the geometry of the active site. Here we demonstrate that μRC electrodes fabricated from 50 μm diameter microwire have significantly improved charge storage capacity and lowered impedance at physiologically relevant frequencies in phosphate buffered saline solution compared with other designs.**

I. INTRODUCTION

A successful neural prosthesis requires efficient communication to and from central and/or peripheral nervous systems. Neural recording and stimulation electrodes act as transducers that mediate signal transport between the ionic tissue environment and the solid-state electronic environment of prosthetic device.

Electrodes with smaller geometries are generally preferred to improve the spatial locality and to decrease the tissue damage resulting from insertion trauma. This however, leads to increase in interfacial impedance and increase in the required charge transfer density for a given stimulation pulse. Charge transfer takes place at the electrode-electrolyte interface by either Faradaic or capacitive mechanisms [1]. The two-dimensional interfacial area, also called the electrochemical surface area (ESA), determines the electrochemical activity of the electrodes. For an electrode with a given geometric surface area (GSA), improving the surface roughness either by etching the surface or by depositing porous coatings on the surface such as Pt black, iridium oxide or conductive polymer helps increase ESA and hence electrochemical activity of the electrodes [2], [3].

Modifying the surface morphology of the surface coatings using micro and nano scale templates to introduce pores have resulted in significant increase in ESA [4], [5]. However, the useful thickness of these coatings is limited by the chemical transport inside the pores and the possibility of the fragile surface coatings to cracking or delamination under mechanical stress *in situ*.

We introduce the concept of micro-reaction chambers (μRC) in which a volume within the electrode back plane is used to confine and sequester the electrochemical reactions that involve in charge passage. The connection from the μRC to the tissue is an opening that replaces the geometric surface of a classical electrode. In μRC electrodes, the 3D region replaces the two-dimensional ESA of the solid-planar (SPl) electrode for charge exchange, offering much higher electroactivity for the given GSA. Hence, μRC electrodes improve sensitivity without impairing selectivity. Also, the sequestering of the electrochemical reaction products within the micro-chamber helps enhance the reversibility of the charge transfer reactions. Further when implanted in the neural tissue, the reactive coatings are protected from the insertion related damages and tissue inflammatory reactions as they are encapsulated by the tube electrodes.

In order to test the concept of micro-reaction chambers we fabricated an implantable microwire based prototype. In this paper we describe an electrochemical fabrication route to produce microwire based μRC electrode. We previously reported a significant improvement in charge passing capacity of a three layer stack coatings on large area microwire electrodes [6]. We used a modification of this technology to further enhance the performance of the μRC electrodes. The *in vitro* electrochemical performances of the μRC electrodes were assessed in phosphate buffered saline solutions and are compared with their solid-planar electrode counterparts.

II. MATERIALS AND METHODS

A. Electrode Fabrication

Solid-planar (SPl) electrodes were prepared from polyimide insulated 50 μm diameter 316L stainless steel wire (Supplier: California Fine Wire Company, Grover beach, CA, USA). The tip of the electrode is cut flat using a razor blade and used as such.

Micro-reaction chamber (μRC) electrodes were prepared from a 1 μm thick gold plated 50 μm diameter 316L stainless steel microwires insulated with polyimide (Supplier: California Fine Wire Company, Grover beach,

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CA, USA). The schematic of the steps involved in the fabrication of the microwire based µRC electrode is shown in Fig. 1. Selective electrochemical dissolution of 316L leaves behind a hollow tubular region that is insulated from the outside. This hollow region is further filled with multi-layered coatings that contain stacks of electrodeposited iridium oxide (EIROF) and electropolymerized poly(3,4-ethylenedioxythiophene) (PEDOT) conductive polymer. These multilayer stacks were adopted to overcome some of the short fallings of single-element PEDOT and EIROF coatings, such as limited useful thicknesses, delamination of thicker coatings, and limited performance in low-buffering solutions.

For comparison purposes, similar coatings were reproduced under the same electrodeposition conditions on SPl electrodes as well.

B. Electrodissolution

Selective electrochemical dissolution of 316L stainless steel from the gold plated microwire was carried out using a protocol suggested in ASTM B912 standard [7]. We used a 1:1 mixture (v/v) of concentrated sulphuric acid-phosphoric acid electrolyte heated to 75°C. Using a custom-built galvanostatic circuit we applied a current density of 11 mA/mm^2 between a Pt cathode and the gold plated 316L microwire anode for 300 seconds. After electrodissolution, the electrodes are dipped in a 20% (v/v) nitric acid at room temperature and rinsed thoroughly with deionized water.

C. Electrodeposition of Stack Coatings

We adopted a methodology that was modified from Meyer et al. [3] for the electrodeposition of iridium oxide. The iridium oxide electrodeposition solution (Solution A) was prepared by dissolving 4 mM IrCl$_4$ hydrate in 40 mM oxalic acid solution. The pH of this solution is adjusted to 10.4 by slowly adding 3 M K$_2$CO$_3$ buffer solution. This changes the color of the solution from dark purple to pale green. The solution is allowed to sit quiescently in the dark for a minimum of one week at room temperature before electrodeposition. The oxidation state of Ir in the oxalate complex attains equilibrium during this period. Electrodeposition of iridium oxide layer was carried out using a two-electrode cell potentiostat using a large surface area AgCl pellet as counter electrode.

PEDOT:PSS electropolymerization solution (Solution B) was prepared by dissolving 0.01 M of EDOT monomer in a 0.1 M poly(sodium 4-styrene sulfonate) solution [8]. Mixing the solution overnight ensures complete dissolution of EDOT monomer. PEDOT: PSS electropolymerization was performed using a three-electrode cell potentiostat.

Stack coatings on SPl electrode and µRC electrode substrates were applied in three stages. In stage I, using solution A, iridium oxide is electrodeposited by applying a combination of potential cycling with 50 triangular waveforms between limits of 0.0 V and 0.55 V at 50 mV/s sweep rate followed by 1000 rectangular potential pulses between the same voltage limits with 0.5 s width in each limits between the substrate and a large area AgCl pellet at room temperature. In stage II, the PEDOT:PSS conductive polymer is potentiostatically electropolymerized from solution B, at 0.9 V vs SCE reference in a three-electrode cell for 60 seconds. A large area Pt pellet served as the counter electrode in this case. The top layer of iridium oxide is electrodeposited from solution A in stage III, by applying 1800 rectangular potential pulses between 0.0 V and 0.55 V limits with 0.5 s width in each limit against a large area AgCl pellet.

D. Characterization

Morphology of the electrodes was imaged in a LEO 1530 field emission scanning electron microscope (FESEM).

All the *in vitro* electrochemical characterizations were performed in a phosphate buffered saline solution. Electrochemical Impedance spectroscopy (EIS) was recorded using an Autolab PGSTAT-12. An AC sinusoidal signal of 10 mV rms was used to record the impedance over a frequency range of 0.1–100000 Hz. The test electrodes are connected as working electrodes and a large area Pt foil served as a counter electrode. The saturated calomel electrodes were used as reference electrodes.

In vitro charge storage capacities (CSC) of the electrodes were measured by performing cyclic voltammetry at 50 mV/s sweep rate in between the voltage limits of -0.6 V and 0.8 V vs SCE reference in a three electrode potentiostat. Test electrode was connected as working electrode and a large area Pt pellet was used as counter electrode. The CV of the first cycle is discarded and the second cycle is reported. The currents are normalized with respect to the GSA, which is the same for both solid-planar and µRC electrodes. CSC of the electrodes was calculated as the time integral of the current during the second cycle of the voltage sweep and are
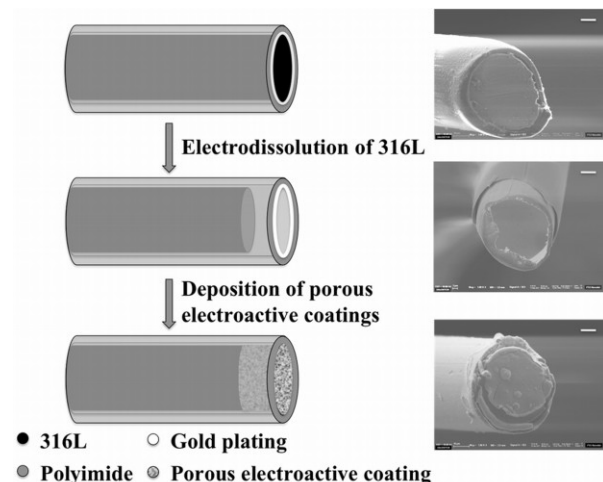

Fig. 1. Microwire µRC fabrication. LEFT: Schematic of fabrication steps. We start with an insulated, gold coated stainless steel wire. The core is dissolved, and the resulting chamber is plated for charge-passing. RIGHT: SEM images at the corresponding stages of fabrication are also shown. The micron marker in each figure corresponds to 10 µm length.
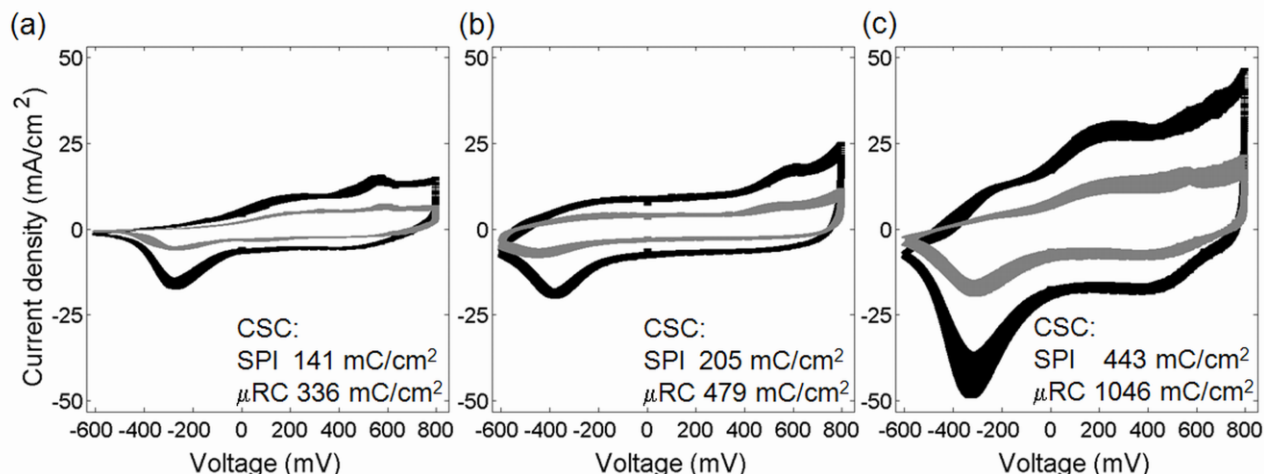
Fig. 2. CV (averaged over 5 electrodes) of the SPl (grey) and μRC (black) electrodes after (a) stage I, (b) stage II, and (c) stage III of the deposition of 3 layer stack coatings. μRC electrodes as substrates had ~2.3 times higher CSC than SPl substrates after each stage of deposition.

normalized with respect to GSA.

Because our aim is to compare overall performance of electrodes crafted from the same diameter base wires, and therefore with the same physical cross section, we use the same GSA for both SPl and μRC electrodes.

III. RESULTS AND DISCUSSIONS

SEM micrographs of the electrodes after each stage of the fabrication step are shown in Fig. 1. Electrodissolution in hot sulphuric-phosphoric acid mixture resulted in selective dissolution of the active 316L stainless steel leaving behind a hollow noble metal (gold) tube that is insulated with polyimide from the outside. By adjusting the duration of electrodissolution step we can control the depth of this micro reaction chamber. Selection of proper insulation material is crucial, as it needs to survive both the neural tissue environment and the electrodissolution solutions. Polyimide insulation does survive the electrodissolution treatment. Teflon and formvar insulations were severely degraded after electrodissolution.

We show in Fig. 2 the average CVs with error bars (n=5) of the SPl and μRC electrodes after different stages of deposition of the 3 layer stack coatings. CSC values presented next to each curve are the average of the 5 electrodes each. Similar shapes of the curves represent similar charge transfer reactions on both SPl and μRC electrodes. But the areas enclosed by the μRC electrode CV curves are significantly larger than those of the SPl electrodes. A corresponding factor of ~2.3 times improvement in CSC is observed for μRC electrodes over SPl electrodes after each stage of stack coating deposition.

Impedance plots of the different electrodes tested in PBS are presented in Fig. 3. The bare μRC electrodes (without coatings) demonstrated one order of magnitude lower impedance as compared to that of bare SPl electrodes for frequencies below 10 kHz. The addition of three-layered

stack coatings significantly reduced the impedance of both SPl and μRC electrodes.

Note that the μRC impedance flattens out by about 10 Hz, indicative that the measurement is dominated by the solution impedance and not the interface impedance. This interpretation is supported by the measured phase dependence, which crosses over from nearly 90° at low frequencies to nearly 0° by about 20 Hz. The phase behavior for the coated SPl is far less clear in interpretation.

IV. SUMMARY AND FUTURE WORK
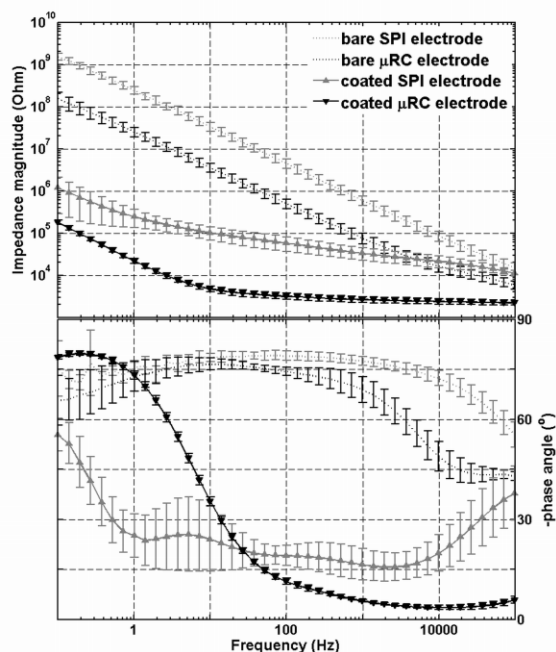
Micro-reaction chamber (μRC) electrodes with improved

Fig. 3. Electrochemical impedance spectroscopy of the electrodes tested in PBS.

in vitro electrochemical characteristics were prepared from microwire electrodes. Coated μRC electrodes showed about three orders of magnitude higher charge storage capacity than a bare solid-planar (SPl) electrode. Thus for a given GSA of the electrode, the μRC electrodes can pass significantly higher amount of charge. In other words, μRC electrodes with smaller GSA can replace its SPl counterpart with higher GSA. Thus μRC electrodes can help reduce the tissue trauma and increase the selectivity.

Both high frequency (~1 kHz) action potential recordings and lower frequency content (<300 Hz) local field potential (LFP) recordings provide useful information on the state and activity of the brain. Hence, lower impedance magnitude at 1 kHz and lower frequencies of μRC electrodes are expected to increase the signal-noise ratio of both action potential and LFP recordings.

The developed methodology for fabricating microwire based μRCs can directly be extended to batch production in multi-electrode bundles.

We are currently evaluating the performance of the μRC electrodes for both neural recording and micro stimulation under acute and chronic implantation conditions.

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