Penetrating microelectrode arrays with low-impedance sputtered iridium oxide electrode coatings

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Abstract— **Sputtered iridium oxide (SIROF) is a candidate low-impedance coating for neural stimulation and recording electrodes. SIROF on planar substrates has exhibited a high charge-injection capacity and impedance suitable for indwelling cortical microelectrode applications. In the present work, the properties of SIROF electrode coatings deposited onto multi-shank penetrating arrays intended for intracortical and intraneural applications were examined. The charge-injection properties under constant current pulsing were evaluated for a range of pulsewidths and current densities using voltage transients to determine maximum potential excursions in an inorganic model of interstitial fluid at 37°C. The charge-injection capacity of the SIROFs was significantly improved by the use of positive potential biasing in the interpulse period, but even without bias, the SIROFs reversibly inject higher charge than other iridium oxides or platinum. Typical deliverable charge levels of 25 to 160 nC/phase were obtained with 2000 μm^2 electrodes depending on pulsewidth and interpulse bias. Similar sized platinum electrodes could inject 3 to 8 nC/phase.**

I. INTRODUCTION

NEURAL stimulation and recording electrodes intended for intracortical applications involving highly localized and selective neural excitation or recording of single-unit activity, require coatings that provide higher charge-injection capacities and lower impedance than is typically possible with noble metal electrodes [1], [2]. Penetrating multielectrode arrays suitable for intracortical or intraneural stimulation and recording, originally developed at the University of Utah and commonly known as the Utah Array [3], [4], have been coated with sputtered iridium oxide (SIROF) as a low impedance, high charge capacity electrode coating. The SIROF electrodes have been characterized electrochemically by cyclic voltammetry and impedance measurements to assess the quality and variability of the SIROF. Current pulsing studies, using voltage transient analysis, have been conducted for a range of pulsing conditions to assess the maximum charge-injection capacity of the electrodes. The same measurements were also made on platinum-coated, but otherwise identical electrodes. As expected, the SIROF greatly increases the charge-injection capacity and reduces impedance compared with platinum electrodes. While the SIROF charge-injection capacity benefits from a positive bias between current pulses, unlike activated iridium oxide (AIROF), the SIROF retains a comparatively high charge capacity without bias. The SIROF electrodes on the penetrating arrays had similar charge-injection properties to those observed previously on planar electrode arrays on polyimide substrates [5], [6], although aspects of the penetrating array fabrication process lead to more electrode variability.

II. EXPERIMENTAL

A. Multielectrode Arrays

Multielectrode arrays were fabricated at Blackrock Microsystems using methods that have been described previously [3], [4]. Each array was fabricated with 16 electrode shafts in a 4 x 4 arrangement and tip-to-tip separation of 400 μm, as shown in Fig. 1. Prior to encapsulating the arrays in Parylene-C, sputtered iridium oxide (SIROF) was deposited onto the electrode tips at EIC Laboratories using reactive dc sputtered in an oxidizing plasma. A 40 nm to 50 nm thick sputtered titanium film was used as an adhesion layer between the SIROF and the silicon substrate. The SIROF deposition process was the same as that described by Cogan *et al* for coating planar polyimide multielectrode arrays [5]. On accompanying planar glass substrates, the SIROF was 200-300 nm thick. The silicon
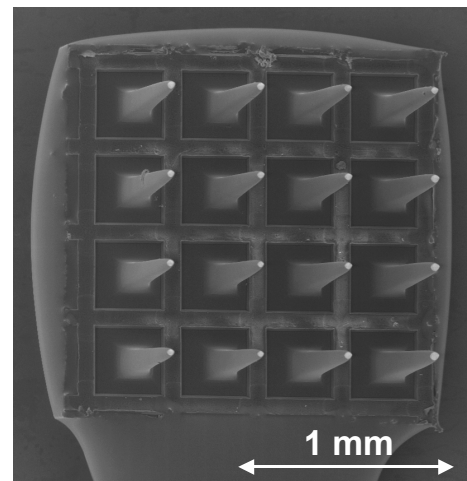

Fig. 1. Scanning electron micrograph of a 16-shaft penetrating microelectrode array with a 400 μm spacing between electrode tips

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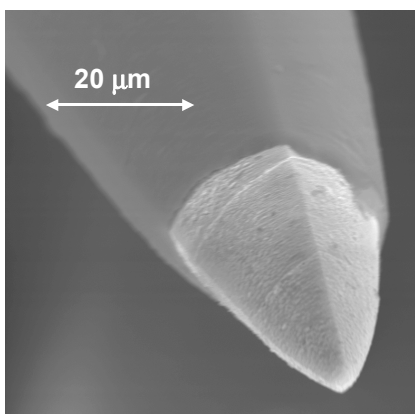
Fig. 2. Scanning electron micrograph of a SIROF-coated electrode tip. The insulation is Parylene-C.

substrate is heavily doped to provide electrical conductivity from the electrode tip to metallization at the base of the shaft. Following SIROF deposition, the entire array was overcoated with an encapsulating layer of Parylene-C. The exposed geometric surface area (GSA) of the SIROF electrodes was defined using an aluminum foil mask and reactive oxygen plasma etching to remove the Parylene-C from the electrode tips. The process exposes approximately a 50-60 µm length of each electrode shaft, creating electrode sites with an average surface area of ~2000 µm^2 (2 x 10^{-5} cm^2). The morphology of the SIROF at the electrode tips was slightly nodular, but the coatings were otherwise conformal as shown in Fig. 2. Similar arrays using sputtered platinum as a charge-injection coating were also fabricated at Blackrock and used for comparison with the SIROF-coated arrays.

B. Electrochemical Characterization

The SIROF was characterized by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) using an inorganic electrolyte model of interstitial fluid (model-ISF) having a composition of NaCl 110 mM, NaHCO$_3$ 28 mM, KHCO$_3$ 7.5 mM, Na$_2$HPO$_4$-7H$_2$O 2 mM, and 0.5 mM each of NaH$_2$PO$_4$-H$_2$O, MgSO$_4$, MgCl$_2$, and CaCl$_2$ [7]. The pH of model-ISF was maintained at 7.4 by bubbling 5%CO$_2$/6%O$_2$/89%N$_2$ gas through the electrolyte. All measurements in model-ISF were made at 37°C. Electrochemical measurements were made in a three-electrode cell using a large-area platinum counterelectrode and a Ag|AgCl reference electrode. All potentials are reported with respect to Ag|AgCl.

CV measurements were made at either 50 mV/s or 50,000 mV/s between potential limits of –0.6 V and 0.8 V, in PBS. The 50 mV/s CVs were used to calculate the cathodal charge storage capacity (CSC$_c$), which estimates the amount of available SIROF at the electrode tip and is determined from the time integral of the negative current during a full CV cycle [7]. The EIS measurements were made in model-ISF over a 0.1 – 10^5 Hz frequency range using a 10 mV rms sinusoidal excitation voltage about a fixed potential of 0.1 V. The CV and EIS measurements were made with Gamry PC4 or PC3 potentiostats and vendor supplied software. Prior to

electrochemical measurements all SIROF films were subjected to CV cycling in a phosphate buffered saline to rehydrate the films following the final fabrication steps.

Charge-injection limits were determined from potential transients measured during current pulsing. A Sigenics stimulator that delivers monophasic cathodal current pulses from a potentiostatically controlled interpulse bias was used for the pulsing studies. This strategy maintains charge-balance by reestablishing the bias potential in the interpulse period using an anodic recharge current that is sufficient to establish the bias within a few milliseconds of the cathodal pulse [1], [8]. The stimulator is designed to limit the recharge current so that the microelectrode cannot be polarized more positively than the 0.8 V water oxidation limit observed with iridium oxide or platinum electrodes. An interphase period of 1.1 ms between the end of the cathodal pulse and the onset of the anodic recharge current was employed to facilitate analysis of the voltage transients. The maximum negative potential excursion was determined from the transient waveform as the electrode potential immediately after the end of the cathodal current pulse [1], [9]. In the present study, cathodal pulse widths of 0.2–1.0 ms and interpulse bias levels of 0.08 V to 0.6 V vs. Ag|AgCl were investigated. For all conditions, pulses were delivered at a frequency of 50 Hz.

III. RESULTS

A comparison of the CV response of platinum and SIROF-coated electrodes is provided in Fig. 3. Based on a nominal geometric surface area of 2,000 µm^2, the CSC$_c$ is increased from 18 mC/cm^2 to 49 mC/cm^2 by the SIROF coating. The majority of the CSC$_c$ of the platinum arises from reduction of oxygen present in the model-ISF. This is seen in Fig. 3 by comparison of the Pt electrode in model-ISF with the response in an argon-purged phosphate buffered saline. Without oxygen present, the CSC$_c$ of the platinum electrode is reduced to 3.4 mC/cm^2. Oxygen reduction has also been reported on ~2 µm thick SIROF electrodes [9], although it was not observed in the present
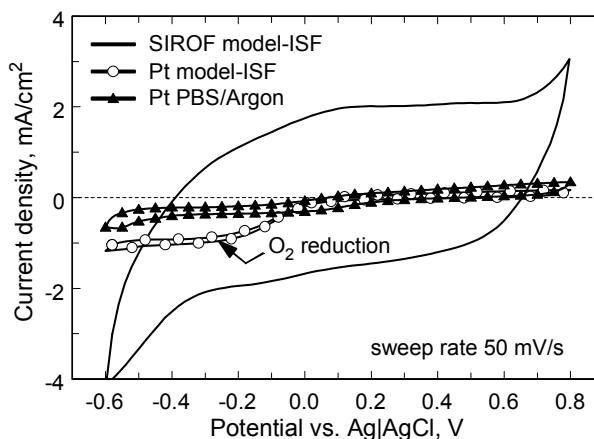

Fig. 3. Representative cyclic voltammograms of a SIROF-coated microelectrode in model-ISF with platinum microelectrodes in model-ISF and an oxygen-free PBS/Argon electrolyte.

study with 200 nm to 300 nm SIROF. Both the platinum and SIROF CVs are similar in appearance to those observed in previous studies [1], [5]. The foil masking to define the exposed geometric area of the SIROF electrodes does introduce variability and the average CSC_c based on a GSA of 2000 μm^2 was 35±12 mC/cm^2 (±s.d., n=16) for a 16-electrode array. The variability in CSC_c reflects the variability in area rather than differences in SIROF thickness and a similar variability was observed with platinum arrays.

The variability in CSC_c of the SIROF arrays when the CV data were acquired at a sweep rate of 50,000 mV/s was also significant, 10±4 mC/cm^2. The coefficients of variability of the 50 mV/s and 50,000 mV/s CSC_c distributions are similar, 0.34 and 0.4, respectively, which supports the assertion that the CSC_c variability is due to differences in geometric area and not from electrolyte leakage between the SIROF-coated shaft and the Parylene-C insulation [1].

Impedance spectra for SIROF and platinum-coated arrays measured in model-ISF are compared in Fig. 4. At frequencies below 10^4 Hz the SIROF reduces the electrode impedance, although more substantial reductions have been observed with SIROF coatings on planar substrates.

The charge-injection capacity of iridium oxide is significantly increased by the use of a positive potential bias in the interpulse region [10], [11]. Previous studies of activated iridium oxide suggest an optimum bias of 0.6 V for

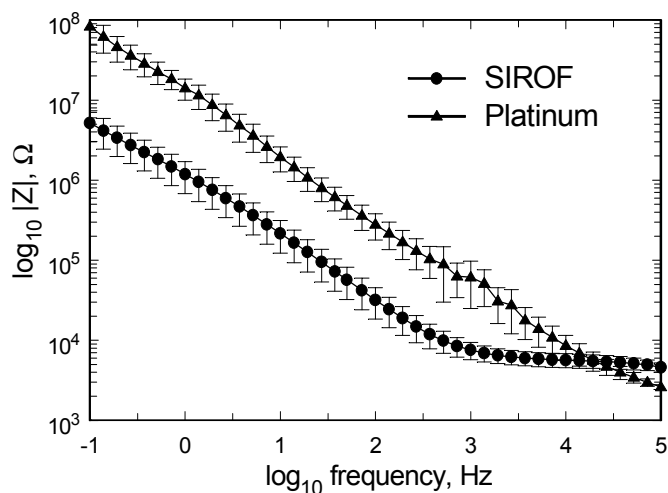Fig. 4. Comparison of the impedance modulus for SIROF and platinum-coated arrays (mean±s.d., n=16 SIROF, n=10 platinum), showing reduced impedance of the SIROF electrodes at neural recording frequencies.

cathodal-first current pulsing when using an asymmetric current waveform to avoid water oxidation during the anodal recharge phase [11]. In Fig. 5, the maximum deliverable charge/phase obtained in model-ISF is plotted as a function of interpulse bias from 0.08 V to 0.6 V for three SIROF electrodes with a CSC_c range of 15-20 mC/cm^2. The SIROF and platinum electrode data in Fig. 5 were acquired with 0.4 ms pulses at a frequency of 50 Hz. The deliverable charge is defined as the charge in a cathodal current pulse required to polarize the electrode to an average potential that just avoids
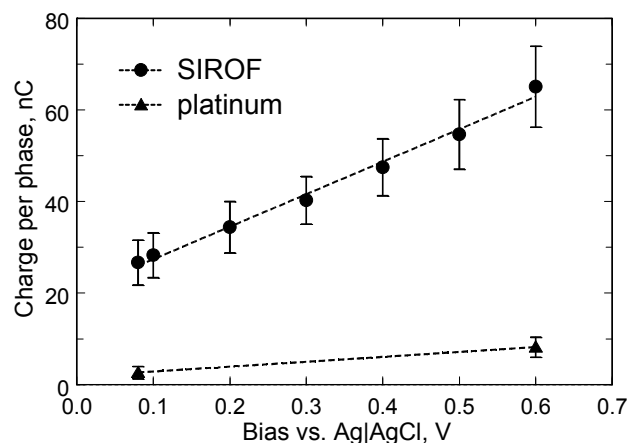

Fig. 5. The deliverable charge per phase of 2000 μm^2 SIROF microelectrodes is shown as a function of potential bias in the interpulse region (mean±s.d., n=3). Similar data are shown for platinum electrodes at 0.08 V and 0.6 V (mean±s.d., n=4). The dashed lines are for visualization.

water reduction (-0.6 V vs. Ag|AgCl). For these SIROF electrodes, the charge per phase increased from 27±5 nC/ph at 0.08 V to 65±9 nC/ph at 0.6 V. The deliverable charge/phase for 2000 μm^2 platinum-coated electrodes was considerably less, 2.6±1.4 nC/ph and 8.2±2.2 nC/ph at 0.08 V and 0.6 V, respectively. While the use of a positive bias significantly increases the deliverable charge with platinum electrodes, the corrosion resistance of biased platinum during long-term pulsing has not been evaluated.

As expected, the SIROF charge-injection capacity increases with increasing pulsewidth, as shown in Fig. 6 for a SIROF with CSC_c of 26 mC/cm^2. At a pulsewidth of 1 ms, the electrode had a deliverable charge of 160 nC/ph at a 0.6 V bias, corresponding to a charge density of 8 mC/cm^2.

A comparison of representative maximum voltage transients for SIROF and platinum electrodes is provided in Fig. 7. The point on the voltage transients at which the maximum negative potential (E_{mc}) reaches –0.6 V is

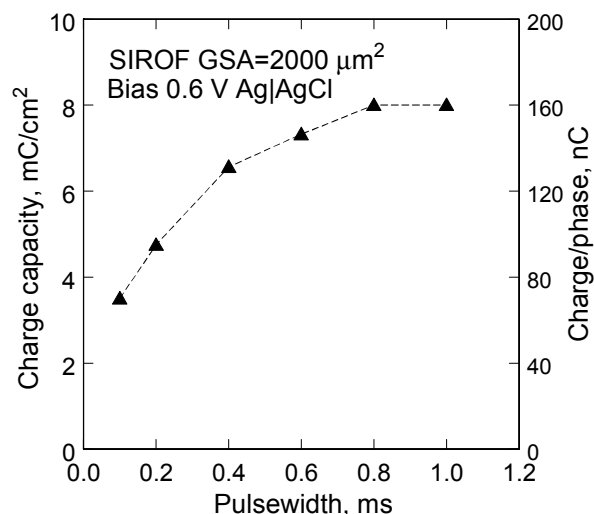

Fig. 6. The dependence of charge-injection capacity and deliverable charge per phase of a CSC_c=26 mC/cm^2 SIROF electrode as a function of pulsewidth.

indicated by an arrow and asterisk. Since the current is zero, no correction for ohmic (iR) voltage drops in the electrolyte is necessary [1]. Both the SIROF and platinum were pulsed from a bias of 0.6 V with a 0.4 ms pulsewidth, resulting in a maximum deliverable charge of 74 nC/ph and 8 nC/ph, respectively.

The deliverable charge with the SIROF-coated electrodes greatly exceeds reported neural excitation thresholds for penetrating microelectrodes in cortex, which are typically 1-3 nC/ph [12], [13]. Although the charge-injection capacity of
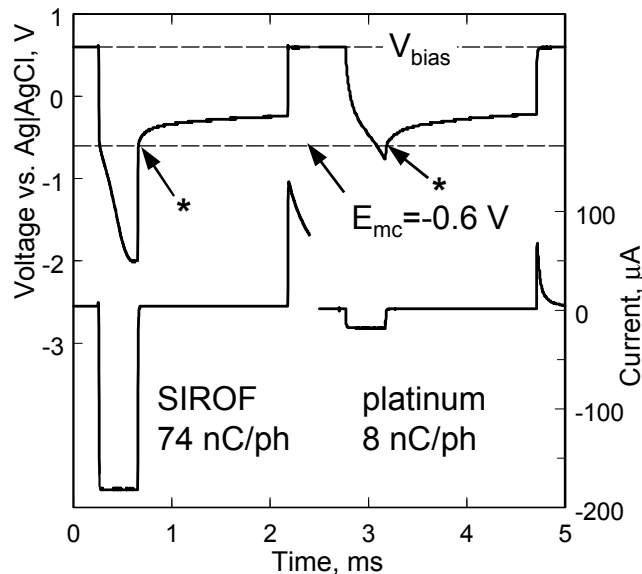

Fig. 7. Comparison of maximum voltage transients (upper curves) and current waveforms for SIROF and platinum microelectrodes (2000 μm^2). The point on the voltage transients at which the maximum negative potential equals –0.6 V (water reduction limit) is indicated by an arrow with asterisk.

SIROF decreases significantly as the interpulse bias is made less negative (Fig. 5), a deliverable charge of 25 nC/phase was obtained at a bias of 0.08 V. Since 0.08 V is close to the *in vivo* equilibrium potential observed with both SIROF and AIROF [1], it is not necessary to use a positive bias with SIROF to readily achieve neural excitation thresholds with 2000 μm^2 electrodes. This is not the case for AIROF electrodes, which exhibit a more pronounced decrease in charge injection capacity at *in vivo* equilibrium potentials and typically require biasing for high levels of charge-injection.

IV. CONCLUSION

SIROF coatings have been deposited onto penetrating multielectrode arrays suitable for intracortical and intraneural stimulation and recording applications. The SIROF coatings reduce the impedance of the microelectrodes at neural recording frequencies and provide deliverable charge-injection at levels well above observed neural excitation thresholds for intracortical stimulation. Although the short-term *in vitro* performance of the SIROF is promising, the chronic stability of the SIROF-coated

arrays has not been demonstrated. Ongoing *in vitro* and *in vivo* studies are underway to evaluate the electrode stability for chronic use.

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