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Charge Injection Capacity of TiN Electrodes for an Extended Voltage Range

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Abstract—**Many applications of neural stimulation demand a high current density from the electrodes used for stimulus delivery. New materials have been searched that can provide such large current and charge densities where the traditional noble metal and capacitor electrodes are inadequate. Titanium nitride, which has been used in cardiac pacemaker leads for many years, is one of these materials recently considered for neural stimulation. In this short report, we investigated the charge injection capacity of TiN electrodes for an extended range of cathodic voltages. The injected charge increased first slowly as a function of the electrode voltage, and then at a faster rate beyond -1.6V. The maximum charge was 4.45mC/cm^2 (n=6) for a cathodic voltage peak of -3.0V and a bias voltage of -0.8V. There was no evidence of bubble generation under microscopic observation. The unrecoverable charges remained under 7% of the total injected charge for the largest cathodic voltage tested. These large values of charge injection capacity and relatively small unrecoverable charges warrant further investigation of the charge injection mechanism in TiN interfaces at this extended range of electrode voltages.**

Keywords--- **neural stimulation, microelectrodes, current density.**

I. INTRODUCTION

NEURAL stimulation as an application imposes special requirements on the electrodes to be used for the delivery of the stimulus current. Electrodes of micro scale are needed to localize the volume of activation in many applications, particularly in the central nervous system. Small electrode sizes demand materials that are capable of handling larger current and charge densities than traditional noble metal and capacitor electrodes, such as platinum and tantalum oxide electrodes.

Titanium nitride (TiN) has been used as an electrode material in cardiac pacemakers and recently considered for neural stimulation applications[1-4]. The surface roughness seems to play a major role in determining the interface capacitance[4]. However, the large interface capacitance measured with slow cyclic voltammetry is not available at fast rates of current injection[1,4]. Thus, the maximum injectable charge is compromised by this reduced interface capacitance for pulsing applications, such as neural stimulation. Several groups reported on maximum injectable charge of TiN electrodes within the voltage window of water electrolysis. In slow cyclic voltammetry (CV) experiments (5mV/s), the cathodic limit of the water window was determined as -1.2V conservatively[2]. Recently, another group studied rough surface TiN electrodes using voltammetry and found that at fast sweeping rates (>10V/s) neither oxidation/reduction nor hydrogen adsorption/desorption peaks could be observed in the CV plots within the voltage range of -3.0V to 1.0V. This group claimed that the charge-transfer process was "almost completely reversible" for this voltage range and no evidence of bubble generation was seen with the rough TiN electrodes.

Some chemical reactions will undoubtedly occur beyond the water window releasing byproducts into the medium. However, the rate of generation for these byproducts may be kept at a level such that they can be removed by blood circulation before their concentration become harmful to the local cells. Thus, it is worthwhile studying the charge injection capacity of TiN for an extended voltage range into the cathodic cycle. In this short report, we investigated the maximum injectable and the recoverable charges with TiN electrodes for extended cathodic voltages using current and voltage pulsing.

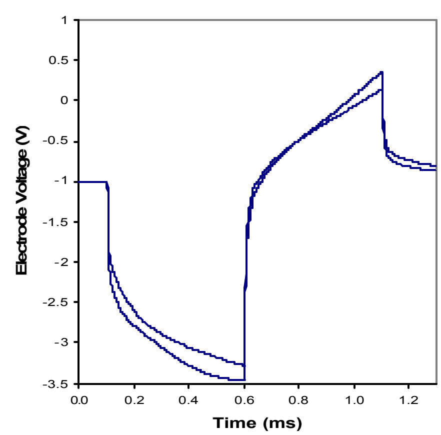

Fig. 1. Back voltage of a TiN electrode as a response to current pulses of 18µA (thick line) and 16.5µA (thin line) amplitude and a pulse duration of 0.5ms. The plateau at the end of the cathodic phase around -3.5V suggests faradaic reactions in the first plot. The second plot at a lower current seems free from any distortion. The bias voltage is -1.0V for both plots. The initial jump due to the access resistance was measured as -0.2V within the first 2µs.

II. METHODS

The electrodes of this study were provided by the Center of Neural Communication Technology at University of Michigan. The details of electrode fabrication were reported earlier by this group[1]. The electrodes were placed in a phosphate buffered normal saline (ph=7.4) at room temperature and the bias voltage was controlled with a custom-built circuit with respect to a large Ag/AgCl reference electrode. For measurements of charge injection capacity, a charge balanced, cathodic first, biphasic current stimulus pulse train was applied at 50Hz. Both cathodic and anodic phases were 0.5ms long and of the same amplitude. The current stimulator was custom designed to ensure a fast rise time (<0.5μs) and thereby allowing an accurate measurement of the access voltage at the onset of the current pulse. The back voltage from the electrode was first buffered with a unity gain FET amplifier before sampled into a computer using data acquisition board (PCI 6071) and LabVIEW software (both from National Inst.) at a sampling rate of 1MHz. Spike triggered averaging method was employed to reduce the noise signal. The bias voltage was set to -0.8, -1.0, and -1.2V and the current amplitudes were determined that generated a back voltage down to -3.0V in steps of -0.2V. The initial voltage jump due to the access resistance was subtracted in calculation of the back voltage. Six TiN contacts with an area of 177μm^2 were studied.

For the measurements of the recoverable/unrecoverable charge, six TiN contacts with larger surface areas (4000μm^2) were used to minimize the measurement errors of electrode current. A single cathodic voltage pulse (0.5ms) with a varying amplitude (0 to -3.0V) was applied. The voltage was clamped at zero following the pulse. The electrode current was integrated during the cathodic phase to find the injected charge and during the following 50ms as the charge recovered from the electrode. The difference of the two was taken as the unrecoverable charge.

III. RESULTS

Fig. 1 shows the electrode voltage with one of the contacts for a bias potential of -1.0V where the current amplitude was increased to 18μA until the H_2 evolution was evident with a plateau at the end of the cathodic cycle. The voltage step due to the access resistance was about -0.2V (measured within the first 2μs) and the plateau occurred around -3.5V. The second plot in Fig. 1 (thin line) shows the electrode voltage for a lower current amplitude (16.5μA) where neither the anodic nor the cathodic cycle exhibited any distortion. The total injected charge in this case was 4.66mC/cm^2.

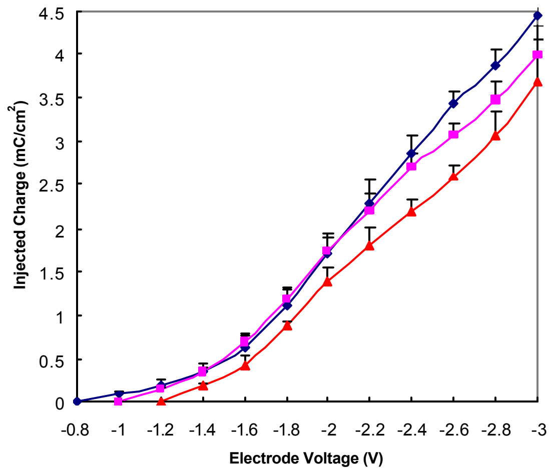

Fig. 2. Injected charge as a function of electrode voltage during a cathodic current pulse with a 0.5ms duration for three different bias voltages; -0.8(♦), -1.0(¦), and -1.2V(?). The mean charge for six TiN contacts and the standard deviations are shown (vertical bars).

The injected charge is shown in Fig. 2 as a function of the electrode peak voltage in the cathodic phase. The charge increases first slowly and then at a higher rate beyond the electrode voltage of -1.6V. The maximum injectable charge is 4.45mC/cm^2 at the peak electrode voltage of -3.0V.

The unrecoverable charge is plotted as a percentage of total injected charge in Fig. 3 against the voltage pulse amplitude. The unrecoverable part of the total charge, which is an indication that faradaic reactions are taking place, is a little over 1% within the water window. It increases to 7% for a voltage pulse of -3.0V.

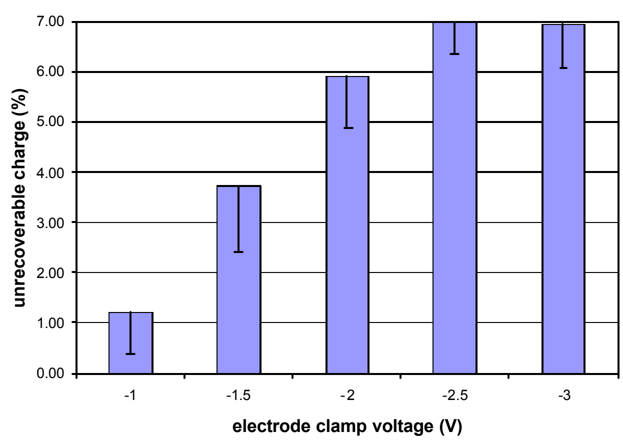

Fig. 3. Unrecoverable charge as a percentage of the total injected charge for voltage pulse amplitudes varying from -1V to -3V. The pulse width is 0.5ms and the electrode surface area is 4000μm^2. Standard deviations are vertical bars (n=6).

IV. DISCUSSION

The charge injection capacity of the TiN electrodes measured here for an extended voltage range is higher than the values of 0.9mC/cm^2[1] and 2.2-3.5mC/cm^2[2] reported earlier for the same pulse width. For most of our electrodes, the voltage waveform was distorted in the anodic phase when the holding potential was made more positive than -0.9V. The distortion was usually in the form of an exponential peak toward the end of the pulse. In these cases, the current level was severely limited if it was desired that the normal waveform was restored. The best voltage waveforms with minimal distortion were generated for the bias voltages more negative then -1.0. However, the total injectable charge decreased as the bias voltage was further moved in the negative direction (Fig. 2).

Under microscopic observation with high magnification (x130), gas bubbles were observed to form in this study for bias voltages below -1.4V. However, the peak electrode voltage during pulsing reached much more negative values without any evidence of gassing. The unrecoverable charge for these extended voltage limits did not exceed 7% of the total injected charge. The charge injection capacity increases several fold when the electrode voltage is allowed to exceed -1.6V compared to the value measured within the water window. The small increase in the unrecoverable charges cannot account for such a large change in the charge injection capacity. Therefore, most of this increase must be provided by fast recoverable faradaic reactions. The fact that such a high charge injection capacity is achievable warrants further investigation on the feasibility of safe neural stimulation with TiN interfaces in the extended voltage range.

ACKNOWLEDGMENT

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