Electrochemical characterization of boron-doped nanocrystalline diamond electrodes for neural stimulation

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THE use of diamond for neural stimulation has been of interest, as the mechanical, chemical and biological stability of the material are advantageous [1, 2]. Electrochemically, it is advantageous that diamond electrodes have a wide potential window in which safe stimulation can be applied. However, as diamond naturally is an insulating material, a dopant must be employed in order to improve its electrical properties [1]. In this paper, the electrochemical properties of B-NCD electrodes are compared to those of smooth and porous TiN electrodes. The electrodes are compared using the electrode impedance magnitude ($|Z|$), its charge injection capacity (Q_{inj}), its cathodic charge storage capacity (CSC_c) and its capacitance.

All coatings were applied to a semi-spherical monopolar Ti6Al4V substrate (surface area: 0.06 cm^2). The TiN coatings were deposited using magnetron sputtering and had a thickness of ~4 µm. B-NCD was grown using a pulsed microwave plasma enhanced chemical vapor deposition apparatus with linear antenna delivery system [3] operating at low pressures with a CH_4-H_2-CO_2 chemistry with trimethylboron (TMB) as a boron dopant.

Electrochemical measurements on three B-NCD electrodes were compared to measurements on a smooth and a porous TiN electrode. Measurements were performed in phosphate buffered saline (PBS) at room temperature. EIS was performed using Solartron, Model 1294 in conjunction with 1260 Impedance/gain-phase Analyzer (Solartron Analytical, UK). The impedance spectrum was measured from 0.1 Hz – 100 kHz using a current of 5.0 µA. The electrolyte resistance was subtracted from the measured impedance. Voltage transient measurements (VTM) and cyclic voltammetry (CV) were performed using a VersaSTAT 3 potentio- galvanostat (Princeton applied research, USA). The water window potentials were established for the B-NCD electrodes, after which CV measurements were made at sweep rates of 0.05, 0.1, 0.5 and 1.0 V/s. For TiN -0.6 and 0.9 V vs. Ag|AgCl were used as water window potentials. The CSC_c was computed at 0.05 V/s [4]. VTM was performed using a biphasic cathodic-first current pulse (phase width: 0.2 ms) with a 40 µs interphase. Q_{inj} was reached when the electrode potential exceeded the water window potential. The electrode capacitance is computed using the CV and the VTM data [1].

Table 1 shows that the porous TiN electrode outperforms the smooth TiN and the B-NCD electrodes at all aspects. The B-NCD and smooth TiN electrodes show comparable values, especially when it comes to $|Z|$, Q_{inj} and capacitance. Q_{inj} could not be determined for the porous TiN electrodes, due to machine limitations. The typical wide water window was found for B-NCD electrodes, from -1.7 to 1.4 V vs. Ag|AgCl [1].

The properties of the B-NCD electrodes are comparable to those described in literature [1] and in the same range as the properties of the smooth TiN electrode. However, the porous TiN electrode clearly outperforms both. So is there any future for B-NCD neural stimulation electrodes? We believe so. Nano-structures may be a means to increase the electrochemical surface area and thus further improve the electrochemical properties of the B-NCD electrodes. A diamond coating has been grown on a nanostructured polymer substrate before [5], but challenges remain depositing diamond on a porous metal substrate [6].

TABLE I. $|Z|$, CSC_C, Q_{INJ} AND CAPACITANCE OF B-NCD, SMOOTH AND POROUS TIN ELECTRODES (MEAN±STANDARD ERROR).

	EIS		**CV**		**VTM**	
Electrode	*$|Z|$ at 1 kHz (Ω)*	*$|Z|$ at 1 Hz (Ω)*	*CSC_c (mC/cm^2)*	*Capacitance ($\mu F/cm^2$)*	*Q_{inj} ($\mu C/cm^2$)*	*Capacitance ($\mu F/cm^2$)*
B-NCD	212 ± 12	$(195 \pm 22) \cdot 10^3$	5.1 ± 0.64	40 ± 6	26 ± 1	8.2 ± 0.1
Smooth TiN	138	$92 \cdot 10^3$	0.14	51	27	15.2 ± 0.7
Porous TiN	0	35	86	$23 \cdot 10^3$	-	$(1.9 \pm 0.09) \cdot 10^3$

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