Electrodes for bio-application: recording and stimulation

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Abstract. Recording and stimulation electrodes applied on excitable tissue are the basis of electrophysiological research, such as brain, muscles, peripheral nerves or sensory systems. Electrode-electrolyte impedance is one of the important characteristics due to its influence on the signal/noise ratio, signal distortion and built-up voltage. Strategies to lowering and tuning the impedance are achieved by biasing iridium oxide modified platinum microelectrodes. Surface and impedance analysis after pulse stimulation are also addressed.

1. Introduction
The bioelectric potentials carried in electrolytic media in form of ionic currents are transduced by the electrodes into electronic signals. This takes place by means of capacitive coupling (without net charge transfer), as it happens during recording, and by charges transfer reactions in which the electrodes and ions in the physiologic environment exchange electrons through redox reactions. This process occurs mainly during stimulation. Those reactions can be reversible or irreversible, usually generating gases at the electrode site (H₂, O₂, Cl₂) and leading to damaging/poisoning of the tissue and electrode corrosion due to its oxidation [1-2].

Strategies to lower the impedance are of key importance in applications such as neural signal recordings. Iridium Oxide (IrO₂), a biocompatible metallic oxide, is an excellent candidate to accomplish this impedance reduction given its texture. Iridium Oxide is of particular importance in cases where electrical stimulation is required [3,4] because it is an electroactive material, i.e., it forms a fast-kinetics redox system on the electrode surface, therefore allowing Faradaic charge transfer. It is also known to exhibit electrochromic behavior, i.e. a reversible change of its color in response to the application of an electrical charge. Electrochromism is also followed by a change in impedance, whose value is decreased for anodic potentials [5]. Once the impedance is set, it will stay at that value until a new potential is applied. The process is fully reversible within a time scale of milliseconds.

2. Electrode Impedance
In the recording/stimulation of bioelectric events, the electrode performs the function of transduction from the ionic currents in the electrolyte to an electric current in the measurement system. The electric contact between an electrode and living tissue has an electric impedance whose high values reduce signal to noise ratio and increase signal distortion. This is particularly relevant for microelectrodes due to their reduced dimensions and also because their impedance has the tendency to increase even more due to adsorption of biological material [6,7].

Simulations based on simple Randles model show, Fig. 1, that for microscale electrodes, the
capacitive coupling is the major component for most physiological signals (mHz-kHz) and the electrode impedance and thermal noise (Johnson-Nyquist) increase as the electrode area decreases [8-10].

Figure 1. Platinum electrode (Φ=20µm) impedance simulation (left) and thermal noise at 1 KHz (right), based on Randles model.

3. Electrode Modification

IrO₂ coatings have been obtained by directly electroplating over platinum electrodes. The electroplating solution is water based containing iridium chloride (IrCl₄.H₂O), hydrogen peroxide (H₂O₂), oxalic acid (COOH)₂.₂H₂O and potassium carbonate (K₂CO₃) to adjust the pH to 10.5 [11]. Sample pre-treatment is performed through surface degreasing with acetone followed by isopropanol and rinsing in deionized water. A preliminary treatment to improve adhesion can be done by slightly etching the platinum surface in aqua regia solution (3 HCl : 1 HNO₃ : 2 H₂O) at 50°C, or by using the standard RCA organic silicon cleaning (1 NH₄OH: 1 H₂O₂ : 5 H₂O) at 70°C.

The use of electroplated IrO₂ has the advantage of attaining deposition on various electrode geometries and morphologies (cavities), easy control of process (hence material properties) and intrinsically low cost, especially if compared with sputtering. Furthermore, preliminary experiments show enhanced impedance tuneability in comparison with sputtered iridium oxide. On the other hand electroplating needs a base conductive layer, usually platinum (Pt), although this can be overcome by using electroless or autocatalytic deposition processes.

Several electroplating protocols applying potential control (potentiostatic) or current control (galvanostatic) were used [12]. We have utilized a CompactStat Electrochemical Analyzer (Ivium Technologies) to realize such depositions and to perform Electrochemical Impedance Spectroscopy (EIS) characterization of the obtained electrodes. We have used the standard three-electrode method in both procedures: Pt/IrO₂ (i.e. the electrode to be modified) as the working electrode, an Ag-AgCl reference electrode and a stainless steel cup as the auxiliary electrode. All EIS characterization was performed in physiological solution (0.9% NaCl, pH=7.4) except for the in situ monitoring where the deposition solution was used instead.

We monitored the impedance evolution during the deposition, scanning at a very slow rate the voltage (1mV/s for potentiostatic deposition) or the current (10µA/s in galvanostatic deposition), Fig. 2. We observed a drop in the impedance at 10 Hz when the voltage reaches 0.6V. The same behavior can be obtained at a current density of 2.5 A/m². The impedance does not change within the layer thickness. This is because the surface roughness stays approximately the same for as long as the deposition conditions are not changed.
Figure 2. In situ potentiostatic (left) and galvanostatic (right) deposition with impedance measurements over platinum sample A=2cm²

A series of galvanostatic depositions at a constant current (1 A/cm²) and at different times lead to the conclusion that indeed the impedance drops right away when the first layer covers the platinum underneath, Fig. 3.

SEM analysis showed that depositions beyond a thickness of 200 nm leads to film cracks and further impedance decreasing due, probably, to exposition of the underneath platinum layer. Below that thickness, very good uniformity was achieved. AFM analysis indicated a surface roughness around 8 times greater than that for the base platinum electrode.

Figure 3. Galvanostatic deposition at constant current showing changes in the impedance spectrum (left) and the time evolution (right) of iridium oxide plating on platinum samples with 2 cm² area.

Using the known voltage and current range, several depositions schemes were performed, including constant current and constant voltage, over platinum microelectrodes (Φ=100µm). Constant current deposition leads to a similar decreases on the impedance, evaluated at 1 KHz – about 14 times -but has better performance over a large frequency range, Fig. 4.

Simulation of the modified electrode was achieved by modifying the previously reported Randles model for a platinum electrode, with a large capacitor in parallel, resembling the additional active area (200x) provided from the IrO₂ film, also in Fig. 4.
4. Impedance Tuning

Electrochemical Impedance Spectroscopy (EIS) measurements are usually performed at equilibrium potential (E0) or at zero volts, but this value can be adjusted as a biasing to the superimposed AC signal [8].

In order to analyze how the electrode area influences the impedance tuning effect, an array of platinum microelectrodes with diameters ranging from 10 μm to 100 μm were electroplated with IrO2. No effect is observed for platinum electrodes when EIS is performed with a bias voltage ranging from 0 to 1 V in 100 mV steps, Fig. 5. On the other hand, platinum electrodes plated with IrO2 show bias dependent impedances for voltages above 500 mV, where impedance reduction up to two orders of magnitude could be achieved for 20 μm diameter electrode -@ 1 kHz , 1V -Fig. 6. at 1KHz, 1V-Fig. 6.

![Figure 4](image1.png)

**Figure 4.** Impedance change after galvanostatic deposition of IrO2 (left) and simulations and experimental data with and without IrOx covering a platinum microelectrode (right) with Φ=100μm and 50μm, respectively.

![Figure 5](image2.png)

**Figure 5.** Effect of biasing on the EIS measurements for a platinum electrode (Φ=100μm).

![Figure 6](image3.png)

**Figure 6.** Effect of biasing on the EIS measurements of IrO2 coated platinum electrodes: EIS scans at various bias voltages on a 100 μm diameter (left) and impedance versus bias voltage plots for various sample diameters (right).
Analyzing the biasing dynamic behaviour, we applied a 1V pulse train (width=5 s) to the platinum electrodes where no changes in impedance were observed, as expected, Fig. 7 (left). On the other hand, applying the same pulse train to IrO$_2$ coated electrodes, a reproducible and reversible impedance decrease was observed within a time response of less than 200 ms, Fig. 7 (right).

**Figure 7.** Effect of applying a pulsed bias on impedance measurements for platinum, $\Phi=100\mu$m, (left) and platinum modified IrO$_2$ (right) microelectrodes.

### 5. Electrode Stimulation

The aim of the stimulation is to provide enough charge to trigger an action potential at a given spot. For example, at the muscle, periferical nerve and cortical surface level requires charges up to 0.2 to 5 mC per stimulation pulse and intracortical region needs only 8 to 64 nC per stimulation pulse [3,4].

As the electrode area goes down, the amount of charge density increases leading to a failure of the electrode. Optimizing a parameter called Charge Store Capacity (CSC) provides more charge per electrode area, therefore prevent the electrode failure extending its usable life. This parameter can be extracted through the Cyclic Voltammetry (CV) wave, where the cathodic region (negative current) is related to the amount of electrons that the electrode can supply at a given range of voltage [1], Fig. 8 (left).

Stimulation protocols are usually carried out in form of pulses of voltage or current, where the last one is more common. Several combinations can be used but charge balanced biphasic protocols are usually standard due to the fact that the net charge is zero [2], Fig. 8 (right).

**Figure 8.** Cyclic voltammetry indicating the Charge Store Capacity (CSC) -filled area -for IrO$_2$ and Pt electrodes ($\Phi=40\mu$m) in saline solution (left) and balanced biphasic stimulation pulse protocol parameters (right).

Before and after stimulation, cyclic voltametry and impedance of the electrodes were performed. Results showed an improvement for platinum electrodes, most probably due to the
electrode cleaning. Iridium oxide coverage presents a decreasing of their CSC with decreasing impedance. Changes in the electrode surface, Fig. 9, were observed optically.

**Figure 9.** Cyclic voltametry and impedance measurements, before and after electrodes stimulation (Φ=40µm), for platinum (left) and iridium oxide (right).

One of the possible causes of the electrode surface modification or even its failure, during stimulation, is associated to the irreversible reactions described before, which happens outside of the water hydrolysis window (-1V to +1V against Ag/AgCl reference electrode) that generates oxygen and hydrogen, respectively. This building up voltage is minimized by low impedance values of the electrodes. All stimulated electrodes showed, at some extend, voltages on that region, indicating possible long-term degradation. This is particularly valid for the platinum electrode, where most of the time stays at the unsafe zone, compared with iridium oxide, Fig. 10.

**Figure 10.** Applied current and recorded voltage during the stimulation for all electrode materials (Φ=40µm), for platinum (left) and iridium oxide (right).

**Figure 11.** Large signal model of the stimulation for a platinum electrode (Φ=40µm).

Preliminary simulation for the pulses could be performed using the same Randles small signal model used for impedance, changing the transferance resistance to a diode model that resembles better the large current due to the faradic reactions, Fig. 11.
6. Conclusion
Modification of platinum microelectrodes using a biocompatible metallic oxide film -Iridium Oxide - successfully decreased their impedance by a factor of 14 at 1KHz. In situ Electrochemical Impedance Spectroscopy allowed determine the deposition window either for potentiostatic or galvanostatic processes. SEM images showed film cracks over 200nm thickness due to mechanical stress. A modified electrode-electrolyte model (Randles circuit), suggested an active area increasing over 200 times.

Impedance tuning of iridium oxide electrodes has been demonstrated. By applying a DC voltage between 0 and 1 V it is possible to vary electrode impedance by as much as two orders of magnitude, therefore enabling the electrode impedance to be electrically programmed. The process is fully reversible with a time response in the millisecond range. Iridium Oxide electrodes combines a low impedance and high charge storage capacity, therefore it is a superior candidate for recording and stimulation.

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