Electrochemical characterization of microelectrodes for use in cortical tissue

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Introduction

Brain activity produces electrical activity which can be detected from within the cortical tissue of the brain. Brain Machine Interfaces (BMI's) have the potential to record and send these electrical signals through electrodes to facilitate communication between computer systems and the human brain.

Fig. 1. Basic design of a generic BMI System. Signals from the brain are acquired from electrodes and are then processed through a series of steps to extract specific features which reflect the motor intent. These signals are then translated into a signal that is read by and command device (Schalk et al. 2004).

Advancement of BMI technology is contingent on the development of stable, high performance electrodes which can be used in long-term implant systems. During insertion of the electrode, tissues and neurons are unavoidably damaged. However, it is believed that the damage zone could be minimized by using a smaller, more flexible electrode which could move freely within the dynamic environment of the brain, reducing the strain forces between the electrode surface and surrounding tissues which [4].

Cyclic voltammetry (CV) traces the transfer of electrons during oxidation-reduction reactions that occur as the electrode potential changes. Electronic impedance spectroscopy (EIS) utilizes a sinusoidal current signal applied to the electrochemical cell and then measures the elicited current from the electrode of interest to determine the impedance of the system.

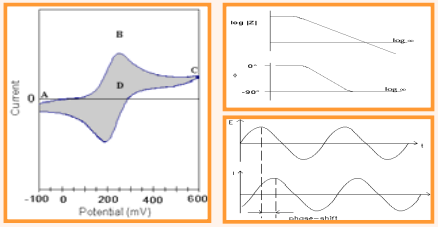


Fig. 2 (a) A cyclic voltammagram of a typical but nonspecific metal. The total charge transfer of an electrode is defined by the area under the curve (D). (b) The typical output format for EIS is a bode plot where both magnitude (Z) and phase (Θ) of the impedance is reported. Pseudo-linearity of the system is illustrated by the resulting sinusoid shift only in phase and magnitude, but equal in frequency. Figure (b) was modified from http://www.gamry.com.

Materials and methods

A. *Electrode Fabrication*

- Metal Wires
  - Stainless Steel (diameter = 125 µm)
  - Gold (diameter = 76.2 µm)
- Coatings
  - Stainless Steel = 0.5 µm of Polyimide (prefabricated)
  - Gold = ≤ 0.5 µm Iridium Oxide (Electrodeposited)
- Stability and Sealant
  - ≈ 1 mm of methyl methacrylate and epoxy

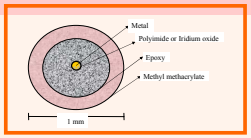


Fig. 3. Cross sectional diagram of the electrode viewed perpendicular to the electrode surface. The diameter of the coated or uncoated metal wire is exaggerated in this representation for better illustration.

B. *Electrodeposition of Iridium Oxide*

- Aqueous Solution of an equilibrium solution of Ir^{3+}/Ir^{4+} as prepared by Yamanaka [8] and Marzouk *et al*. [9]
  - -HCl and KOH were used to adjust the solution's pH to 10.4
- Deposition
  - Triangular Waveform
    - Cycled 50 time at 50 mV/s from 0V – 0.55 V
  - Rectangular Potential Pulses
    - 1600 0.5 s pulses (0V, 0.55 V)

C. *Electrochemical Measurements*

- Electrochemical Cell Setup
  - Counter electrode = Platinum rod (surface area = 30 mm^2)
  - Reference electrode = Ag|AgCl
  - Electrolytes
- Cyclic Voltammetry
  - -Working electrode cycled within the water window limits (-0.6 to 0.8 V)
- Electronic Impedance Spectroscopy (EIS)
  - Galvanostatic sinusoidal waveform (A = 1µA rms,f = 0.01-100kHz)
- Data was analyzed using software custom-written in Matlab

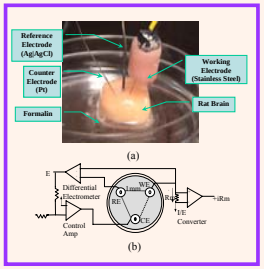


Fig. 4 (a) Schematic of the electrochemical cell. For testing, three different electrolytes are examined: phosphate buffer solution (PBS pH 7.4 ± 0.1), 10% formaldehyde fixing solution (formalin) and formalin fixed rat brain tissue. During fluid testing, the microelectrode array lies in a 100 mL beaker which is filled with 75 mL of solution. (b) Tissue testing follows the same setup but the beaker is replaced by a 100 mm culture dish which the tissue rests upon.

Results

A. *Stainless Steel*

CV of the stainless steel electrode revealed that each voltage scan resulted in a lower peak value of current and TACT than the previous curve (TCCT remained relatively stable). However, after the electrode is subjected to EIS testing, the peak value of current, TACT and TCCT resulting from the CV is much larger. The cause of this phenomena was determined to be the chromium oxide layer which forms on stainless steel depleting causing the properties to change, so for testing, special considerations needed to be made.

The stainless steel electrode had the largest overall charge transfer in saline with 30667.96 µC/cm^2. In formalin and brain tissue the overall charge transfer was 17199.64 and 17628.81 µC/cm^2 respectively. In saline, the impedance magnitude at higher frequencies (10 Hz – 100 kHz) was larger, but as the frequency decreased, the magnitude decreased. This is an expected result in reference to an equivalent circuit with mixed kinetic and charge transfer control as shown in Fig. 5.

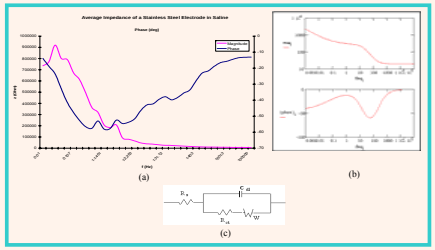


Fig. 5 (a) EIS bode plot of a stainless steel electrode in saline when cycled from 0.01 Hz – 100000 Hz. (b) EIS bode plot of the equivalent circuit (c) using Warburg coefficient (Ww) = 150 W sec-1/2, Rs = 20Ω , Rct = 250 Ω , and Cdl = 40 µF. For diffusion processes, which adds a new form of resistance, a new element is added to the circuit and is referred to as the Warburg impedance. Areas of similarity to the stainless steel electrode can be found in the 0.01 Hz – 100000 Hz range.

B. *Gold*

It was determined from testing that gold is not readily oxidized in air, so no reoxidation period was necessary and each test was run in succession.

Once again, saline resulted in the largest overall charge transfer with 4438.37 µC/cm^2 and formalin and brain tissue were similarly less with 825.21 and 715.46 µC/cm^2 respectively. When compared to the stainless steel electrode, the magnitude of impedance for the gold electrode is significantly larger which could be the cause of the reduction in charge transfer capabilities. It was found that the gold system still follows the same mixed control circuit model which was used to describe the stainless steel electrode

C. *Iridium Oxide*

As expected, the iridium oxide coating applied to the gold electrode greatly increased its charge transfer capabilities. After coating, the total charge transfer of the electrode in saline, formalin and brain tissue increased to 467809.12, 108593.53 and 60784.31 µC/cm^2 respectively. It was noticed however, that with time the iridium oxide coat was reducing. Knowing this, it is possible that the charge transfer in both formalin and brain tissue, which was tested after saline testing, would be higher if tested with a fresh iridium coating. The impedance for the iridium oxide resulted in more complex behavior than the stainless steel or pure gold due to the degradation of the coating. As the coating degraded, it became porous and the entering caused a new liquid-metal interface that added a factor to the electrode model.

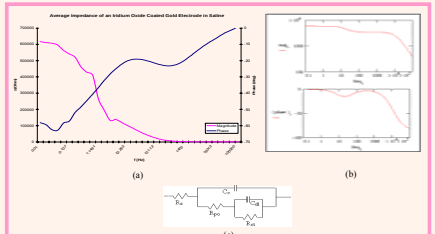
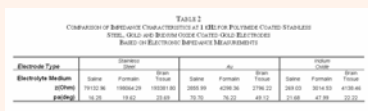


Fig. 6 (a) EIS bode plot of an iridium oxide coated gold electrode in saline when cycled from 0.01 Hz – 100000 Hz. (b) EIS bode plot of the equivalent circuit (c) using Cc = 4 nF calculated for a 10 cm2 area, er = 6 and 12 µm thickness, Rpo = 3400 Ω(assumed), Cdl = 4 mF calculated for 1% of 10 cm2 area and assuming 40 µF/cm2, Rct = 2500 Ω assuming k = 0.01 S/cm, Rs = 20 Ω calculated for 1% of 10 cm2 area. For this model, the capacitance of the intact coating is represented by Cc. Pore resistance (Rpo) is the resistance of ion conducting paths that develop in the coating.



Conclusions

Based on testing, gold coated with iridium oxide would be most effective as a neural stimulation electrode if there were a method of application which would ensure long term stability of the coating. The iridium oxide coating offers low impedance and high charge transfer capabilities to a gold electrode. It is known from previous work that when appropriately applied, iridium oxide is biocompatible [11] and using gold as a base ensures that should the coating be lost, metal will not be readily lost to the biological environment as would be the case of stainless steel electrodes. In the future, more work needs to be done on methods of coating electrodes as well as better models of the electrode need to be made for effective comparison. It is also proposed to add a new component to the system models in order to emulated the oscillations that would be seen when a an electrode is implanted into a living being. It is possible this resistance would be so high as to limit the effectiveness of the electrode as a stimulator or recorder.

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