

Electrochemical Characterization of Microelectrodes for use in Cortical Tissue

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Abstract- Microelectrodes implanted in cortical tissue have been shown to effectively send and record electrical brain signals. The limitation encountered in the past is the robustness of these electrodes. New flexible electrodes are being developed to solve this problem, but electrochemical (EC) measurements are a required step in the characterization of these microelectrodes before they can be implanted in human cortical tissue. Initial cyclic voltammetry (CV) and electronic impedance spectroscopy (EIS) was run in rat tissue in order to understand the charge transfer and impedance characteristics of a model of the flexible microelectrode. Electrodeposited iridium oxide films were deposited on gold electrodes and compared to both gold and polyimide coated stainless steel electrodes. The stainless steel electrodes were found to have a chromium oxide layer that was depleted with each cycle of voltage (-600 mV – 800 mV). This caused a trend towards lower charge transfer abilities, but impedance remained unaffected. Iridium oxide coated gold electrodes resulted in larger charge transfer and lower impedance than pure gold and stainless steel electrodes in saline solution, but loss of the iridium oxide layer made comparison in formalin and rat brain tissue impossible. Both the pure gold and stainless steel electrodes were able to be modeled by an equivalent circuit with mixed kinetic and diffusion controls. The iridium oxide electrode could be modeled by a failed coating model which takes into account the porosity of the surface.

I. 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. This technology is independent of nerve and muscle pathways, which would allow patients who are deaf, blind, or paralyzed due to incomplete neuronal pathways to effectively communicate with the outside world. While the scope of this research is to be applied to the advancement of an implant for use in the auditory cortex, it is possible this technology could eventually be applied to patients suffering from many other brain-based disorders.

Advancement of BMI technology is contingent on the development of stable, high performance electrodes which can be used in long-term implant systems. Microelectrodes have previously been fabricated for implantation but have had short life spans in which they could effectively transmit and receive electrical signals due to several factors within the electrode-tissue interface [1, 2]. During insertion of the electrode, tissues and neurons are unavoidably damaged. The resulting cellular insult signals astrocytes to proliferate in the area in turn forming a capsule around the electrode, increasing the impedance of the electrode tissue interface thereby reducing charge transfer capability [3]. In addition, the infiltration of cellular elements, immune fluids and epithelial cells due to disruption of the local blood vessels further diminish the efficacy of the electrode [1]. 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].

Since the flow of electricity from the electrode (where electrons carry charge) into the tissue (where ions carry charge) is necessary to stimulate neurons, the electrochemical characteristics of the electrode

must be quantified. This is also true for recording electrode where the electric flow is reversed. Smaller surface area electrodes require higher current and charge density to effectively activate surrounding tissue, but the large amount of current that would be needed could cause unexpected electrochemical reactions [5]. It has been shown by McCreery *et al.* [6] that these reactions can cause damage to the tissue surrounding the electrode and diminish the electrical characteristics of the electrode. Thin iridium oxide films on metallic electrodes have been shown to mediate the reduction and oxidation processes that occur at the tissue interface to supply the charge necessary for neuronal stimulation. This mediation increases the charge transfer capabilities while reducing damage to the surrounding tissue [7].

Cyclic voltammetry (CV) traces the transfer of electrons during oxidation-reduction reactions that occur as the electrode potential changes. The potential of an electrode is linearly cycled by applying a slow triangle waveform over a determined potential range and the elicited current is measured to produce a current-voltage curve. The area under the current-voltage curve, as seen in Fig. 1, quantifies the capacitive charging capacity of the electrode in both the anodic and cathodic phases of current. In addition to this, it is possible to determine the reversibility of the electrode through the degree of symmetry of the anodic and cathodic current traces. If the reactions which occur at the tissue interface are not reversible, the build up and loss of electrode material will not only reduce the ability of the electrode to transfer charge, but could also damage surrounding tissues resulting in a dangerous immune response.

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. The electrode system can be considered pseudo-linear so the potential response to a sinusoidal current is a sinusoid at the same frequency but shifted in phase and magnitude. From EIS, it is possible to classify the electrode as resistive or capacitive by the magnitude and phase of impedance as well as ensuring maximum current is being delivered by the electrode to the electrolyte interface.

In this report, initial cyclic voltammetry (CV) and electronic impedance spectroscopy (EIS) was run on a single shaft, polyimide-based stainless steel microelectrode, a single shaft gold microelectrode and a single shaft iridium oxide-based gold microelectrode in order to be applied to the characterization of the impedance and charge transfer characteristics of the flexible polyimide based intracortical electrode being fabricated in the Rousche lab [4].

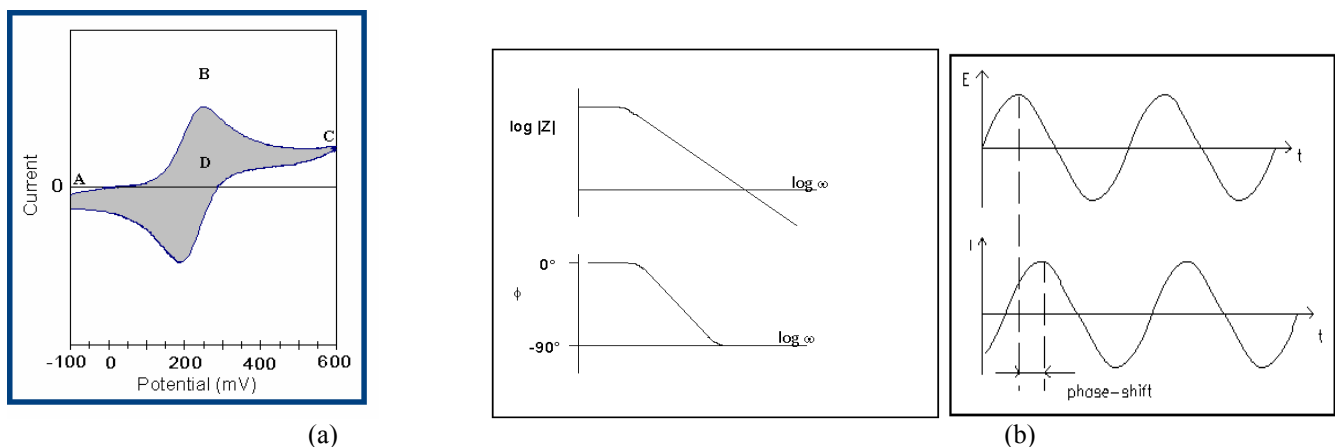


Fig. 1(a) A cyclic voltammogram of a typical but nonspecific metal. The total charge transfer of an electrode is defined by the area under the curve (D). Point B relates to the peak anodic current elicited by the potential sweep. The total anodic current charge transfer (TACT) and total cathodic charge transfer (TCCT) are found by summing the current elicited by the anodic cycle and cathodic cycle respectively. Point A defines the start and point C defines the end of the anodic cycle. Point C defines the start and point A defines the end of the cathodic cycle. (b) The typical output format for EIS is a bode plot where both magnitude (Z) and phase (Φ) 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. These figures represent a standard electrode model that can be represented as a parallel RC circuit. Figure (b) was modified from <http://www.gamry.com>.

II. METHODS

A. Electrode Fabrication

Metal electrodes were fabricated from stainless steel with a diameter of $125\ \mu\text{m}$ and gold with a diameter of $76.2\ \mu\text{m}$. The stainless steel wires were coated with a thin film ($0.5\ \mu\text{m}$) of polyimide to simulate as closely as possible the electrodes for which the testing will ultimately be applied to. The electrodes were then sealed in approximately 1 mm of methyl methacrylate and epoxy. A planer cut was made through the wire resulting in circular electrode with surface areas of $12,300\ \mu\text{m}^2$ and $4560\ \mu\text{m}^2$ respectively. The cross sectional geometry of the electrode can be seen in Fig. 1. The electrodes were cleaned in deionized water before each use.

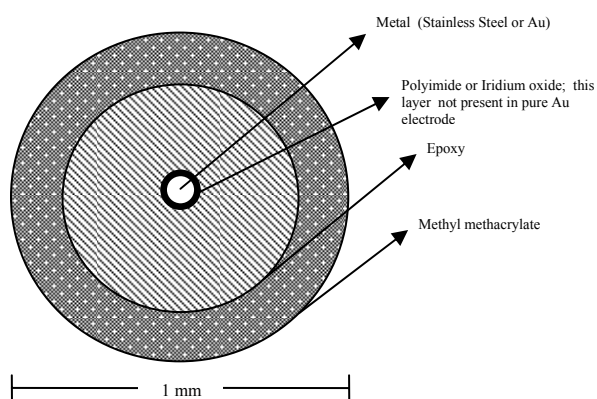


Fig. 3. Cross sectional diagram of the electrode viewed perpendicular to the electrode surface. The diameter of the coated or uncoated metal wire is exaggerated in this representation for better illustration.

B. Electrodeposition of Iridium Oxide

Iridium oxide was deposited onto a gold electrode from an aqueous solution of 0.014 g of 4 mM iridium chloride hydrate (IrCl_4) dissolved in an electrolyte of 0.04 g of 40 mM oxalic acid ($\text{C}_2\text{H}_2\text{O}_4$) and 0.5 g of 340 mM potassium carbonate (K_2CO_3), which was prepared in the same manner which is described by Yamanaka [8] and Marzouk *et al.* [9]. Hydrochloric acid (HCl) and potassium hydroxide (KOH) were used to adjust the solution's pH to 10.4. After 24 hours, the gold electrode, a large area platinum counter electrode and a Ag|AgCl reference electrode were placed into the equilibrium solution of $\text{Ir}^{3+}/\text{Ir}^{4+}$, which now had a purple tint. The depositions were carried out using a combination of potential cycling with a triangular waveform followed by rectangular potential pulses. The triangular waveform was cycled 50 times at 50 mV/s between the limits of 0 V and 0.55 V then immediately followed by 1600 pulses at the same potential limits for 0.5 s at each limits [8].

C. Electrochemical Measurements

Electrochemical measurements were made using Autolab with a potentiostat/galvanostat PGSTAT 30 differential electrometer/amplifier instrument. General Purpose Electrochemical System (GPES) and Frequency Response Analysis (FRA) software was used for measurement of CV and EIS data respectively. Data was analyzed using software custom-written in Matlab. A Pt rod ($30\ \text{mm}^2$ surface area) and a Ag|AgCl electrode were used as counter and reference electrodes of an EC cell. Working,

counter and reference electrodes were set at equidistant positions (1 mm) within phosphate buffer saline solution (PBS) at pH 7.4 ± 0.1 as shown in Fig. 4. The cell was located in a Faraday cage to minimize noise in the cell.

EIS measurements were taken by running a galvanostatic sinusoidal waveform ($A=1\mu\text{A rms}$, $f = 0.01\text{-}100000\text{Hz}$) through the electrode. CV measurements were made by cycling the working electrode within the ‘water window’ limits (-0.6 to 0.8 V) at a sweep rate of 50 mV/s and observing the elicited currents. The total anodic charge transfer (TACT) and total cathodic charge transfer (TCCT) possible for the electrode was determined by taking the time integral of the elicited currents of each respective phase (anodic and cathodic) per the electrode area (see Fig. 1).

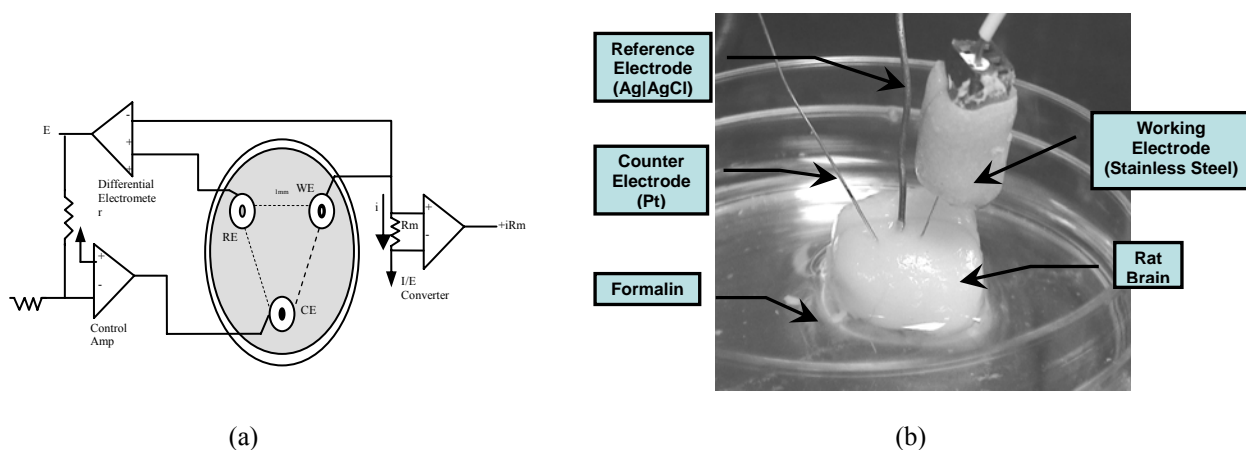


Fig. 4 (a) Schematic of the electrochemical cell. During fluid testing, the microelectrode array lies in a 100 mL beaker which is filled with 75 mL of solution. (b) Tissue testing follows the same setup but the beaker is replaced by a 100 mm culture dish which the tissue rests upon.

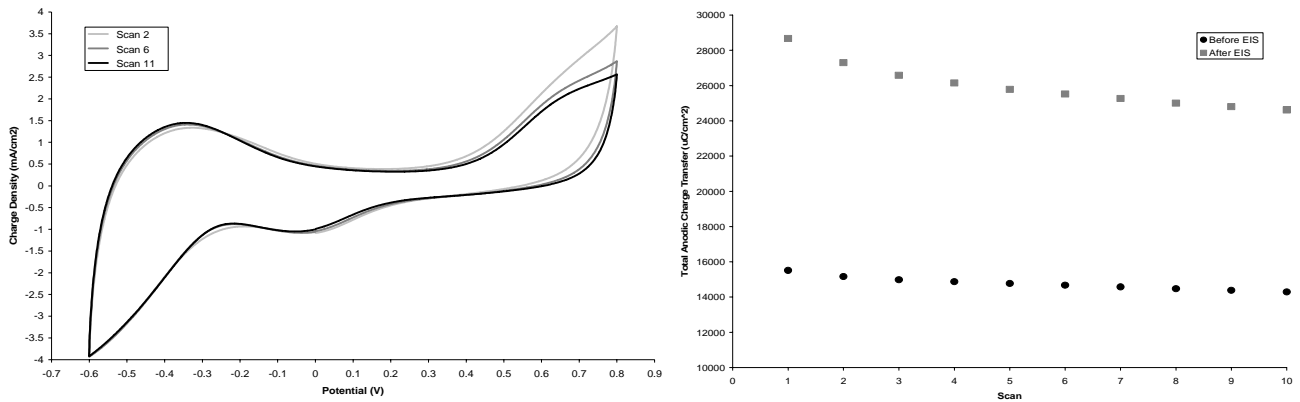
III. RESULTS

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 as is revealed in Fig. 5. The exponential decay seen in both peak current and TACT led to the possibility that the material properties of the electrode were coming into effect and the could be caused by the reduction of the chromium oxide layer that is known to exist on stainless steel.

However, to first rule out depletion of available current carrying ions in the solution as a cause for the decay, tests were run by replenishing the PBS solution after each set of 20 CV cycles. The time the electrode spent in the air during this change was minimized to reduce the amount of the chromium oxide reforming. Results from these tests resulted in little difference from the previous tests suggesting the problem is not due to ion depletion.

In the next set of experiments, the electrodes were allowed to sit in the air for 30 minutes between CV testing while the solution was held constant. This exposure to air would allow the stainless steel electrode to reoxidize in air. The results of this protocol were positive in that the CV trace of the electrode before and after exposure to air were nearly identical.



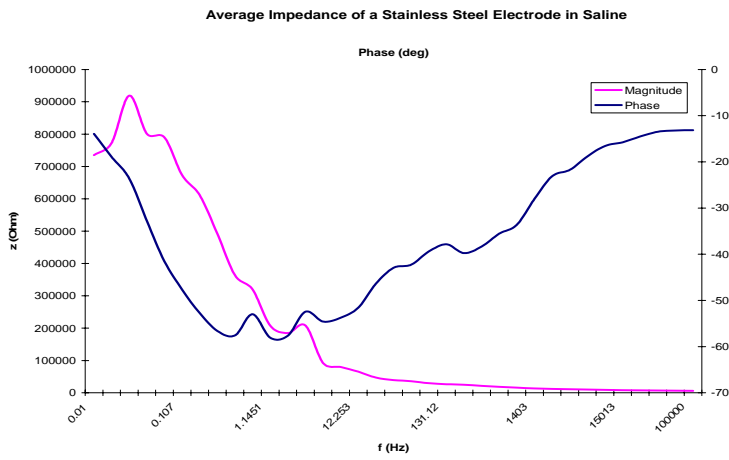
(b)

Fig. 5 (a) CV of stainless steel in PBS showing the decrease in peak current values for each successive scan. (b) TACT is decreasing with each successive run, but a large increase is noted after an EIS cycle is run.

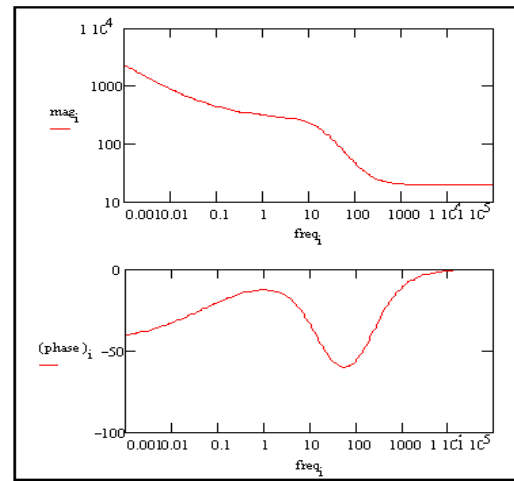
From this testing, it was determined that the correct sequence to use in order to get consistent data for the stainless steel electrode tests is to run a CV immediately followed by EIS and then let the electrode sit in air for 30 minutes before the cycle is repeated. This is the protocol used in all subsequent stainless steel tests. Since EIS was unaffected by the chromium oxide depletion, it is not necessary to reoxidize the electrode before EIS testing can begin. This is expected because the range of voltage at which the EIS operates displayed little variation in the CV testing.

The stainless steel electrode had the largest overall charge transfer in saline with $30667.96 \mu\text{C}/\text{cm}^2$. In formalin and brain tissue the overall charge transfer was 17199.64 and $17628.81 \mu\text{C}/\text{cm}^2$ respectively. There is large variance in the charge transfer necessary for neural stimulation, so it will be necessary to test whether an electrode is effective in the future. The reduction in charge transfer in the formalin and brain tissue can most likely be attributed to a reduced amount of available ions as compared to the saline solution. It was expected that formalin and rat tissue would be similar because the rat tissue was fixed in formalin for a long period of time before use. Overall, all mediums allowed for an acceptable level of reversibility of the reactions which occur at the tissue interface. It has been shown, however, that the material which is lost to the electrolyte is chromium which even in small amounts can be toxic.

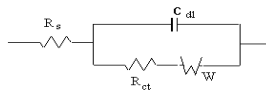
In saline, the impedance magnitude at higher frequencies (10 Hz – 100 kHz) was larger, but as the frequency decreased, the magnitude decreased. This is an expected result in reference to an equivalent circuit with mixed kinetic and charge transfer control as shown in Fig. 6. This circuit models a cell where polarization is due to a combination of kinetic and diffusion processes [10]. 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. The Warburg impedance is dependent on the frequency of the potential and at high frequencies the value is small since the diffusing ions do not have far to move. However, at lower frequencies, the ions have to diffuse further and therefore the Warburg impedance is increased [10]. This circuit also takes into account the resistance of the solution itself, R_s .



(a)



(b)



(c)

Fig. 6 (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 ($Ww = 150 \text{ W sec}^{-1/2}$), $R_s = 20 \text{ } \Omega$, $R_{ct} = 250 \text{ } \Omega$, and $C_{dl} = 40 \text{ } \mu\text{F}$. Areas of similarity to the stainless steel electrode can be found in the 0.01 Hz – 100000 Hz range.

As is seen in Fig. 7, EIS testing in formalin and rat brain tissue resulted in overall similar results as in saline with the exception of phase at frequencies larger than 1 kHz. Reasons for this have not yet been investigated. Formalin and rat brain tissue are nearly identical and have larger impedance than in saline solution. Once again, it was expected that formalin and rat tissue would be identical because the rat tissue was fixed in formalin for a long period of time before use. Future tests are planned to be done in live rat tissue which will be used as a model to extrapolate information of the electrodes performance in human brain tissue.

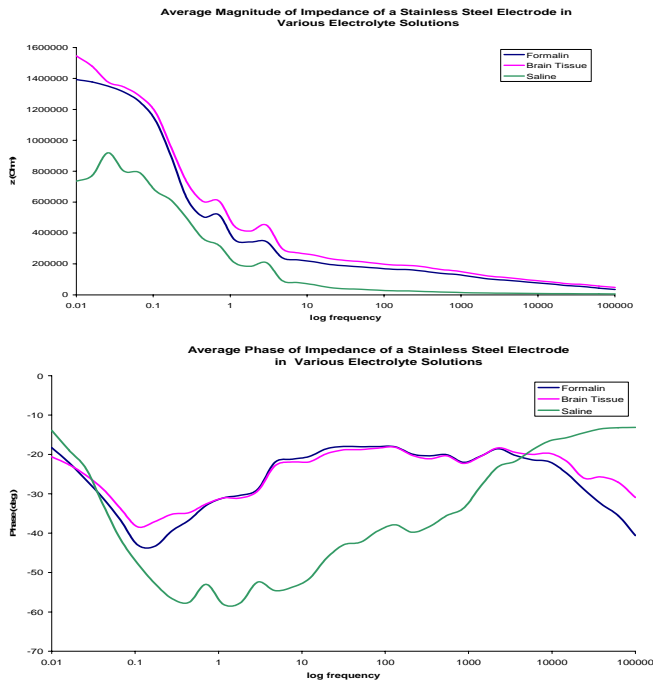


Fig. 7 Average EIS bode plot of a stainless steel electrode in saline, formalin solution and brain tissue (n=8). In saline, the impedance is reduced and the electrode is more capacitive. This is known because the phase in saline is more negative than in formalin and brain tissue and an purely capacitive electrode has a phase of -90 degrees.

B. Gold

It was determined from testing that gold is not readily oxidized in air, 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 $\mu\text{C}/\text{cm}^2$ and formalin and brain tissue were similarly less with 825.21 and 715.46 $\mu\text{C}/\text{cm}^2$ respectively. In the gold electrode model, the bulk of the charge transfer takes place during the cathodic current phase of the cycle. However, the overall charge transfer of the system is greatly reduced from that of the stainless steel electrode introducing the possibility of not being able to stimulate surrounding neurons.

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. The gold electrode is also largely capacitive in nature through most of the common operating frequencies (1-1000 Hz). At this point there is no definitive conclusion as to whether a capacitive electrode is preferred to a more resistive electrode. 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 $\mu\text{C}/\text{cm}^2$ respectively. It was noticed however, that with time the iridium oxide coat was reducing. This observation was based on the difference between the anodic and cathodic phase charge transfer. This parameter referred to as the degree of reversibility would be zero for a perfectly reversible reaction, but the large magnitudes which resulted from the iridium oxide reactions means there is ions being lost to the electrolyte with each cycle. 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. In the future, tests using this protocol and work to reduce the loss of iridium oxide will need to be done.

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. Every coating/metal combination is different so it is difficult to pinpoint to exact reactions that may be taking place, but a simple model of failed coatings can be used to approximate the electrodes behavior in the range of 1 Hz – 1 kHz. Beyond that range, the model fails and more interpretation will be needed. There is a lot of debate as to the processes that cause a failed coating so subsequently there are several models that have been proposed. The model used in this report is only one of those models and by no means is claimed to be the best model. For this model, the capacitance of the intact coating is represented by C_c . Pore resistance (R_{po}) is the resistance of ion conducting paths that develop in the coating. On the metal side of the pore, it is assumed that a small area of the coating has been completely lost and a sack filled with an electrolyte solution is present. It is probable, but uncertain at this location, the electrolyte solution is somewhat different from the solution outside of the coating due to reaction with the metal that was modeled with the previous electrodes.

The extreme differences in magnitude of impedance between formalin and brain tissue illustrates the loss of coating. It would be unreasonable to make any conclusions comparing the electrolyte mediums knowing that there was such wide variability in the testing conditions. It is only possible to compare the charge transfer characteristics of the iridium oxide electrode in saline to the other electrodes because it was tested earliest.

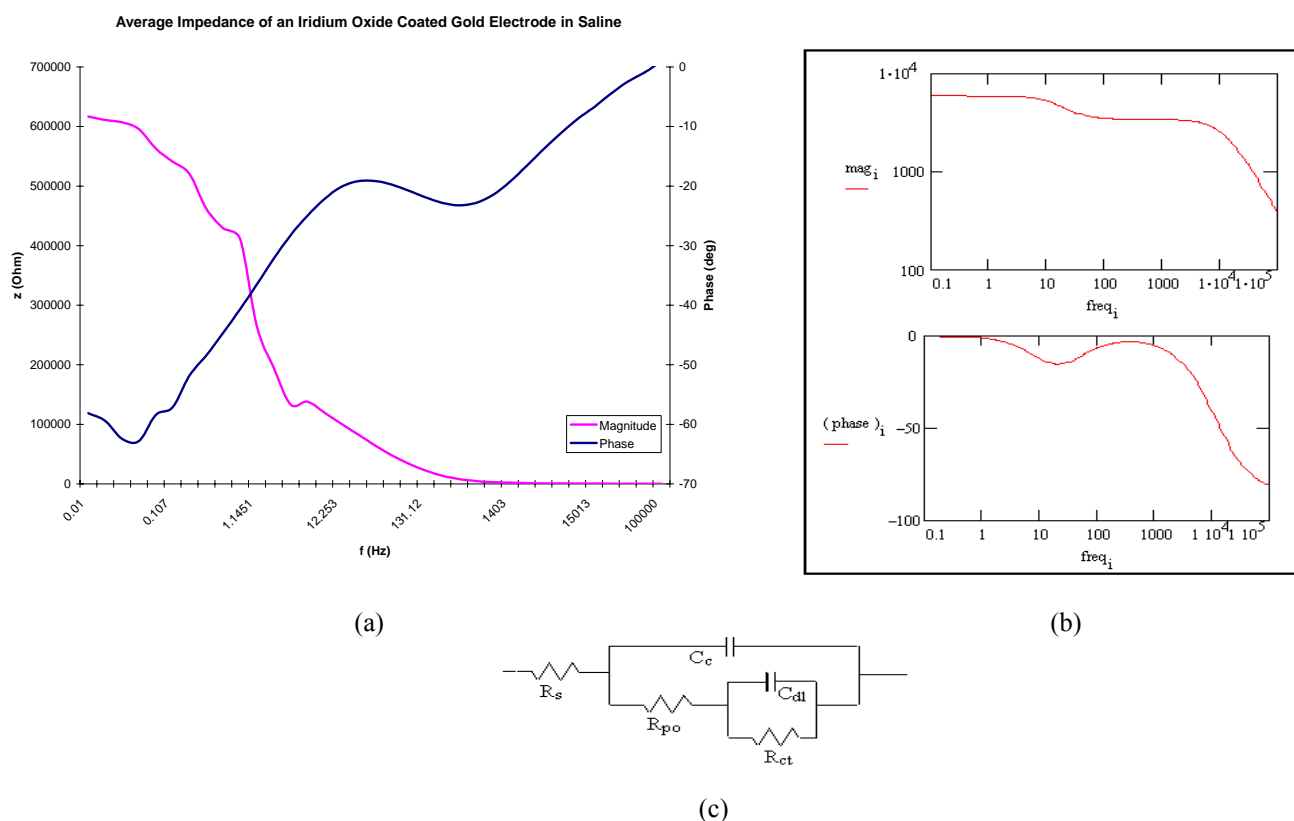


Fig. 8 (a) EIS bode plot of an iridium oxide coated gold electrode in saline when cycled from 0.01 Hz – 100000 Hz. (b) EIS bode plot of the equivalent circuit (c) using $C_c = 4$ nF calculated for a 10 cm^2 area, $\epsilon_r = 6$ and $12 \text{ }\mu\text{m}$ thickness, $R_{po} = 3400 \text{ }\Omega$ calculated assuming $k = 0.01 \text{ S/cm}$, $R_s = 20 \text{ }\Omega$ (assumed), $C_{dl} = 4 \text{ mF}$ calculated for 1% of 10 cm^2 area and assuming $40 \text{ }\mu\text{F/cm}^2$, $R_{ct} = 2500 \text{ }\Omega$ calculated for 1% of 10 cm^2 area.

TABLE 1
COMPARISON OF CHARGE TRANSFER CHARACTERISTICS FOR POLYIMIDE COATED STAINLESS
STEEL, GOLD AND IRIIDIUM OXIDE COATED GOLD ELECTRODES
BASED ON CYCLIC VOLTAMMETRY MEASUREMENTS

Electrode Type	Electrolyte Medium	TACT	TCCT	APCT	CPCT	DOR	TCT
Stainless Steel	Saline	15144.97	-15522.99	16956.84 -1680.95	989.45 -16373.98	378.02	30667.96
	Formalin	8682.06	-8517.58	7363.72 -1234.84	549.32 -6730.99	164.48	17199.64
	Brain Tissue	9036.47	-8592.34	8371.14 -1564.17	903.77 -7034.92	444.12	17628.81
Gold	Saline	-1846.43	-2591.94	291.40	42.17	745.50	4438.37

				-2137.83	-2634.10		
	Formalin	256.89	-568.31	653.97 -397.08	143.36 -711.68	311.42	825.21
	Brain Tissue	87.80	-627.67	379.99 -292.19	52.42 -680.09	539.87	715.46
<i>Iridium Oxide</i>	Saline	236980	-230829	262509 -25529.2	3229.037 -234058	6151.00	467809.12
	Formalin	79023	-29570.6	84687.6 -5664.62	23070.06 -52640.6	49452.39	108593.53
	Brain Tissue	38919.4	-21864.9	43067.7 -4148.37	11702.14 -33567.1	17054.44	60784.31

*All units in $\mu\text{C}/\text{cm}^2$
** n = 8

TACT: Area under CV curve during anodic phase voltage ramp

TCCT: Area under CV curve during cathodic phase voltage ramp

APCT: Amount of each type of charge (positive and negative current) transferred during anodic phase

CPCT: Amount of each type of charge (positive and negative current) transferred during cathodic phase

DOR: Degree of reversibility representing charge not reabsorbed in the voltage cycle

TCT: Total charge transferred (both anodic and cathodic) during voltage cycle

TABLE 2
COMPARISON OF IMPEDANCE CHARACTERISTICS AT 1 KHZ FOR POLYIMIDE COATED STAINLESS
STEEL, GOLD AND IRIIDIUM OXIDE COATED GOLD ELECTRODES
BASED ON ELECTRONIC IMPEDANCE MEASUREMENTS

<i>Electrode Type</i>	<i>Stainless Steel</i>			<i>Au</i>			<i>Iridium Oxide</i>		
	Saline	Formalin	Brain Tissue	Saline	Formalin	Brain Tissue	Saline	Formalin	Brain Tissue
Electrolyte Medium									
z(Ohm)	79132.96	198064.29	193381.80	2855.99	4298.36	2796.22	269.03	3014.53	4138.46
pa(deg)	16.25	19.62	23.69	70.70	76.22	49.12	21.68	47.99	22.22

IV. CONCLUSION

Based on testing, gold coated with iridium oxide would be 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 models to emulated oscillations that would be seen when a the 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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