

# Center for Neural Communication Technology

## Iridium Activation

Iridium grows a hydrous oxide layer on its surface when it is electrochemically activated in an electrolyte. The oxide is porous and can assume several oxidation states [6,14,8,10], which gives it a very high charge capacity as well as the ability to deliver large amounts of charge to aqueous solution. This material is also exceptionally resistant to dissolution and corrosion during *in vitro* and *in vivo* stimulation [13,1]. Activation can also be used to reduce the impedance of iridium sites for use in recording applications.

The process by which iridium is electrochemically oxidized is known as *activation*. Because of reliability and ease of use, the activation method used with our probes and discussed here is cyclic voltammetry [16]. A standard three electrode scheme is used to perform cyclic voltammetry (Figure 1). The voltage waveform is applied to a counter electrode (usually a large platinum electrode) in the electrolyte. The iridium site is the working electrode and provides a return current path. A saturated calomel electrode (SCE) provides a reference (Fisher Scientific, 800-766-7000, catalog # 13-620-52). The voltage on the counter electrode is cycled between anodic and cathodic potentials while the site is exposed to an electrolyte.

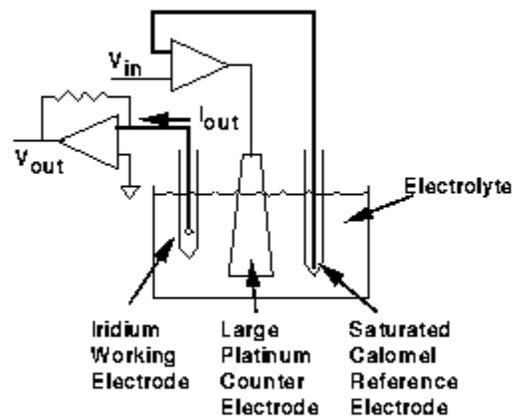


Figure 1: Three electrode configuration for cyclic voltammetry

Figure 2 describes the build up of the multilayer iridium oxide film formed by cyclic voltammetry. During the anodic sweep, an inner oxide ( $\text{IrO}_2$ ) is formed from pure iridium. As the potential increases, the inner oxide changes to a hydrous outer layer ( $\text{Ir}(\text{OH})_3$ ). The fact that this layer is hydrated (water molecules are attached) limits formation to a monolayer [11]. The cathodic sweep causes the reduction of the inner oxide back to iridium, but does not go low enough to reduce the outer layer. The outer layer remains. Since the oxide is porous, the metal maintains contact with the electrolyte. Therefore, on the next potential sweep the process will repeat. In this way, the hydrous, porous layer of iridium oxide is created. The potential limits depend on the electrolyte but should not exceed the water window (i.e. potential that results in oxygen or hydrogen evolution) [15].

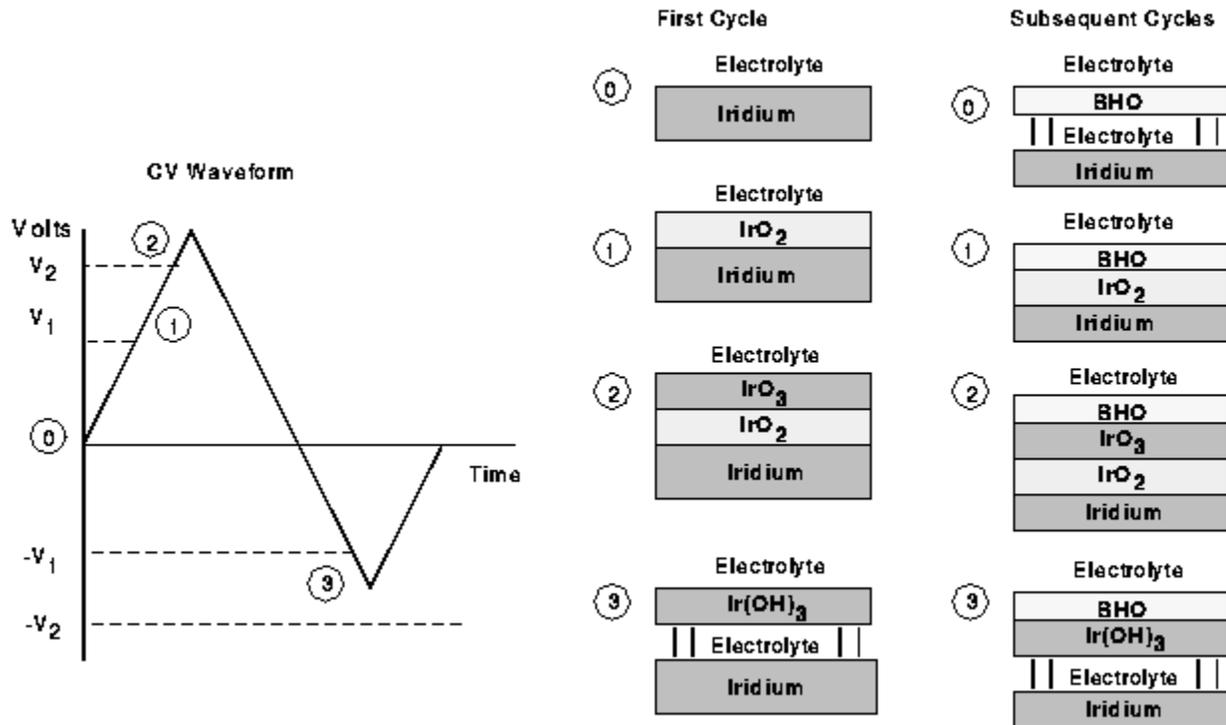


Figure 2: Formation of the multilayer iridium oxide film by cyclic voltammetry

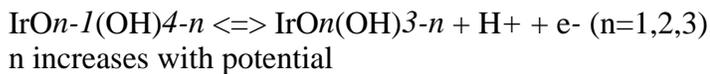
The process of activation has several variables that can be changed to achieve an optimum oxide in terms of maintaining consistent electrical characteristics. Studies are being conducted at EIC Laboratories, Inc. in Norwood, Massachusetts to determine such optimal activation parameters [15]. In summary, a high quality oxide is formed when the following activation procedure is used:

1. Use an electrolyte of 0.3 M Na<sub>2</sub>HPO<sub>4</sub>.
2. (Optional) Initially hold sites at potentials of -3.0 V and 2.5 V for approximately three minutes each to remove any oxide that has formed, essentially cleaning the metal.
3. Cycle the activation potential between -0.85 and 0.75 Volts. These limits are usually wide enough to grow an oxide but narrow enough to remain within the water window. As a rule, the voltage limits should be set approximately 100 mV inside of the water window (as determined by the high current peaks on the CV).
4. Use a square wave (0.5 - 1 Hz) to activate. This allows the metal to remain at the critical levels for hydrous oxide formation (0.75 V) and inner oxide reduction (-0.85 V) for a longer time than a ramp wave would. Holding the potential at these levels will allow a more complete oxide formation and reduction and also reduce the number of potential cycles needed to grow the oxide.
5. Activate to a limit of 30 mC/cm<sup>2</sup>. Previous studies have shown 100 mC/cm<sup>2</sup> to be the maximum usable storage capacity activated iridium [16]. However, it has also been shown that the lower level of 30 mC/cm<sup>2</sup> will allow the oxide to better maintain electrical characteristics. Also, given the current level needed for cortical stimulation [1], charge storage of 30 mC/cm<sup>2</sup> should be sufficient.

Tests completed by our group show that using the above activation protocol will grow an oxide of high quality

in fewer CV cycles. Ongoing *in vitro* pulse tests of the oxide grown with this method are showing that the activated sites maintain their electrical characteristics over at least 100 million pulses. The activation process is controlled by a PC/LabVIEW (National Instruments) based system that performs cyclic voltammetry tests to determine the  $Q_{cap}$ .  $Q_{cap}$  is calculated by integrating the area under the CV curve. This measurement and calculation should be made every 50-100 activation cycles in order to determine when the specified  $Q_{cap}$  is reached. Roughly 500-700 cycles will be required to reach the 30 mC/cm<sup>2</sup>. A ramp wave is still used to calculate  $Q_{cap}$ , even though a square wave is used for activation.

Activated iridium has characteristics that make it an attractive material for electrical stimulation of neural tissue. Iridium can store charge by going through valence changes which cause reversible redox reactions. The fact that these reactions are reversible is important for biocompatibility. Reversibility means that no new substance is formed and hence no reactants are released into tissue [14]. The state of the iridium will depend on the potential applied across the metal-electrolyte junction. However, neural stimulation is usually accomplished with a constant current source, so the voltage applied is dependent on the charge storage of the oxide. As the oxide absorbs more charge (positive current), the potential across the interface will increase, which will result in the oxide reacting with the electrolyte. Initially, with no applied voltage, the iridium oxide is in the Ir(OH)<sub>3</sub> state. As potential is increased, the iridium oxide will increase valence by ejecting protons into the solution [7]. The following reaction summarizes the sequential change in the oxide as potential increases:



The IrO<sub>3</sub> state (n=3) is unstable and its degradation will result in oxygen evolution. This reaction defines the water window on the positive voltage side. As charge is subsequently removed from the oxide (negative current), the reactions reverse.

Only a small portion of the total charge storage capacity of the Iridium oxide is used in current pulsing. Currently, electrode activation protocol states that the electrodes should be activated to 30 mC/cm<sup>2</sup>. This is the charge storage in response to a slowly varying waveform, however, and represents the maximum charge storage capacity ( $Q_{cap}$ ). Studies have shown that, when using current pulses to deliver charge, only a small portion of  $Q_{cap}$  can be used during before the water window is violated [3]. The reason for this is that the charge builds up faster than reaction above can inject it into solution (i.e. the kinetics of the reaction limits the rate at which charge can be dispersed). Charge accumulation leads to a high potential across the double layer, which can eventually lead to gassing. This lower charge value is called the injectable charge ( $Q_{inj}$ ) and has been shown to be around 1.5 mC/cm<sup>2</sup> for a  $Q_{cap}$  of 30 mC/cm<sup>2</sup>. This lower level of charge capacity corresponds to a 150 uA, 100 usec pulse from a 1000 um<sup>2</sup> site, which corresponds well to the 100 uA of current required for CNS stimulation [9]. Higher values of  $Q_{inj}$  have been attained using an anodically biased electrode [3].

James Weiland performed the above mentioned studies on iridium sites here at the University of Michigan as part of his Ph.D. thesis. Dr. Weiland is now with the Dept of Ophthalmology at the University of Southern California. Any questions and/or comments can be addressed to him at JWeiland@DEI.HSC.USC.EDU.

## References

- [1] Agnew, W.F., Yuen, T.G.H., McCreery, D.B. and Bullara, L.A. "Histopathologic Evaluation of Prolonged Intracortical Electrical Stimulation", *Experimental Neurology*, vol. 92, pp. 162-185, 1986.
- [2] Anderson, D.J., Najafi, K., Tanghe, S.J., Evans, D.A., Levy, K.L., Hetke, J.F., Xue, X., Zappia, J.J. and Wise, K.D., "Batch-Fabricated Thin-Film Electrodes for Stimulation of the Central Auditory System", *IEEE Trans. on Biomed. Eng.*, vol. 36, pp. 693-704, 1989.
- [3] Beebe, X. and T.L. Rose, "Charge Injection Limits of Activated Iridium Oxide Electrodes with 0.2 ms Pulses in Bicarbonate Buffered Saline", *IEEE Trans. on Biomed. Eng.*, vol. 35, pp. 494-496, 1988.

- [4] Bockris, J. O'M., *Comprehensive Treatise of Electrochemistry, Volume 1: The Double Layer*, New York: Plenum Press, 1980.
- [5] Elzanowska, H., Birss, V.I., "Reversible ageing of Iridium Oxide Electrodes in Acidic Solutions", *Journal of Applied Electrochemistry*, vol. 23, 646-654, 1993.
- [6] Gottesfeld, S. and McIntyre, J., "Electrochromism in Anodic Iridium Oxide Films", *J. Electrochem. Soc.*, vol. 126, pp. 742-750, 1979.
- [7] Huppaff, M., Lengeler, B., "Valency and Structure of Iridium in Anodic Iridium Oxide Films", *J. Electrochem. Soc.*, vol. 140, 598-602, 1993.
- [8] Kotz, R., Neff, H. and Stucki, S., "Anodic Iridium Oxide Films: XPS-studies of Oxidation State Changes and O<sub>2</sub>-evolution", *J. Electrochem. Soc.*, vol. 131, pp. 72-77, 1984.
- [9] McCreery, D.B., Bullara L.A. and Agnew W.F. "Neuronal Activity Evoked by Chronically Implanted Intracortical Microelectrodes", *Exp. Neurol.*, vol. 92, pp. 147-161, 1986.
- [10] Ohtsuka, T. and Kunimatsu, K., "*In situ* Infrared Spectroscopy of Iridium Oxide", *J. Electrochem. Soc.*, vol. 134, p. 3090, 1987.
- [11] Pickup, P.G. and Birss, V.I., "A Model for Anodic hydrous Oxide Growth at Iridium", *J. Electroanal. Chem.*, vol. 220, pp. 83-100, 1987.
- [12] Plonsey, R. and Barr, R.C., *Bioelectricity: A Quantitative Approach* New York: Plenum Press, 1991.
- [13] Robblee, L.S., Kelliher, E.M., Langmuir, M.E., Vartanian, H., and McHardy, J., "Preparation of etched Ta semimicro capacitor stimulation electrodes," *J. Biomed. Mat. Res.*, vol. 17, pp. 327-343, 1983.
- [14] Robblee, L.S., Lefko, J.L. and Brummer, S.B., "Activated Ir: An Electrode Suitable for Reversible Charge Injection in Saline Solution," *J. Electrochem. Soc.*, vol. 130, pp. 731-733, 1983.
- [15] Robblee, L.S., Aurien-Blajeni, B., Cogan, S.F., Rose, T.L., Twardoch, U.M., Hills, D.V., Jones, R.B. and Kimball, A.G., *Studies of the Electrochemistry of Stimulating Electrodes, Final Report*, NIH NINDS Contract No. N01-NS-8-2313, 1991.
- [16] Tanghe, S.J., *Micromachined Silicon Stimulating Probes with CMOS Circuitry for use in the Central Nervous System*, Ph. D. Thesis, 1992.
-