

Characterization of Ruthenium Electrodes for Implantable Neurostimulation Applications

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Introduction:

Microelectrodes for use in neural recording and functional electrical stimulation (FES) have gained increasing interest over the last few years. These electrodes achieve stimulation by way of reversible charge injection which depolarizes specific cell membranes; this is obtained through capacitive or faradaic reactions [1]. Traditionally, platinum (Pt) or iridium oxide (IrO_2) electrodes have been used, due to exceptional biocompatibility and corrosion resistance. It is also known that charge can be stored or injected by way of valence changes in an electrode coating; oxidation and reduction (redox) reactions between different oxide states increase the ability of the electrode to quickly inject charge [1]. Namely, electrodes with multiple oxidation states have a higher injected charge rate.

Another metal that demonstrates promise as a stimulation electrode is ruthenium (Ru), which we have focused on in this study. Ruthenium has as many as seven oxidation states, though Ru^{2+} , Ru^{3+} and Ru^{4+} are the most common. With these three oxidation states, there is the potential for more charge delivery than with other electrode materials [2]. Additionally, Ru shares the biocompatibility and corrosion resistance associated with platinum-group metals [3]. In our study, we characterized Ru electrodes, focusing on generating low impedance values and high charge delivery capacity. Characterization was accomplished with cyclic voltammetry and electrochemical impedance spectroscopy.

Experimental Procedure:

Ru electrode films were electrochemically deposited onto gold wafers using varying current densities. In addition to electrochemically deposited (ED) films, samples made by atomic layer deposition (ALD) were also studied. We performed electrochemical tests on the samples in a suspended, clip-on cell; all tests used a three electrode system, with a $\text{Ag}|\text{AgCl}$ reference electrode, a Pt mesh and wire counter electrode, and the working electrode. Due to the cell set up, a piece of copper (Cu) foil over the Ru served as the working electrode; the foil was shielded by Teflon[®] tape to prevent unwanted Cu influence in the impedance or cyclic

voltammetry (CV) scans. A micropipette tip was placed in the cell to act as a Luggin capillary; the Pt mesh and wire combination were wrapped around the micropipette tip, and the reference electrode positioned in the top of the tip, to ensure identical electrode placement for every experiment.

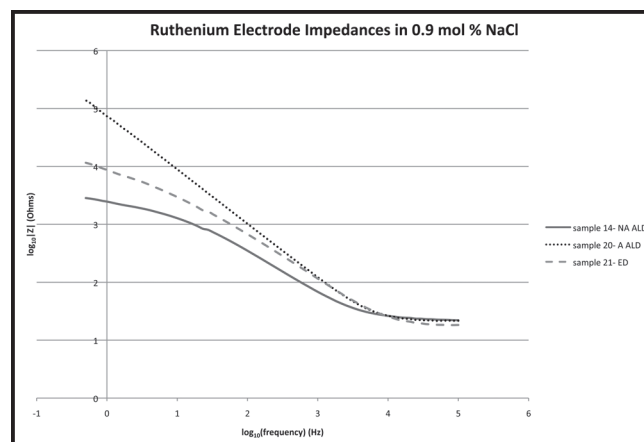


Figure 1: Impedance of ALD and ED samples in 0.9 mol% NaCl.

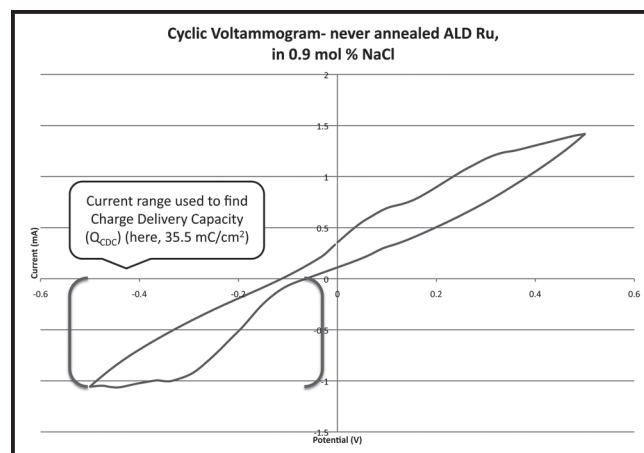


Figure 2: Never annealed ALD Ru data in 0.9 mol% NaCl.

Measurements were first conducted in 10% sulfuric acid by volume, due to concern that chlorine could etch the Ru samples. Further experiments were carried out in 0.9 mol% NaCl. All measurements were taken with a potentiostat (CompactStat, Ivium Technologies). Impedance data was gathered from 0.5 Hz to 100 kHz with 10 mV alternating current sinusoidal amplitude applied from the open circuit potential; cyclic voltammetry was run with 50 mV/s sweep rate and 10 mV step size through varying potential windows.

Results and Discussion:

Through analysis of our CV and impedance spectroscopy data, we have found that Ru fulfills the basic parameters needed for stimulation electrodes.

Interestingly, the ALD Ru samples that were never annealed demonstrate the best electrochemical properties, with the lowest overall impedance and a charge delivery capacity (CDC) of 35.5 mC/cm² for a potential window of -0.5 to +0.5 V (see Figures 1 and 2). Following these, the ED samples also performed relatively well, with CDCs of 13.4 mC/cm² for potentials of -0.25 to +0.3 V; the lowest charge delivery was found in ALD samples that had recently been annealed, which had CDCs of only 530 μ C/cm² for potentials of -0.25 to +0.25 V. We believe this is partially due to the removal of the oxide layer that takes place during annealing; while the oxide had time to re-form, a less developed oxide could mean less available oxidation states for reversible redox reactions, which are essential for good charge delivery capacity.

We encountered difficulties with Ru adhesion during testing in sulfuric acid: upon removal of the Ru sample from the cell, frequently it was found that part of the Ru had been removed. It is believed that this was occurring from water electrolysis effects at low potentials, and also the development of a soluble oxide at positive potentials which caused film damage. The importance of choosing an appropriate voltage window for CV scans is evident, as the amount of etching was significantly lowered by reducing the potential window during cyclic voltammetry scans. Additionally, we learned that choosing an appropriate current range during cyclic voltammetry scanning is important for obtaining smooth curves.

Conclusion and Future Work:

While the results are promising, the amount of data collected is inconclusive to explicitly declare Ru to be a superior metal for functional electrical stimulation, though it is certainly suitable for use in stimulation applications. It is recommended that the study be focused on fabricating Ru films of different thicknesses and varying surface roughness and porosity to determine the best fabrication parameters for FES usage. It would be beneficial to test the affects of electrochemical loading on the charge delivery capacity and impedance of Ru immediately after loading; also important is the testing of Ru in phosphate-buffered saline solutions, for more accurate comparison to current FES electrodes.

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