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Design and Validation of an Electrochemical Cell for Surface Characterization of Biomedical Alloys

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Abstract

It is essential to develop a rigorous method for evaluating the biocompatibility of a given alloy. As such, an electrochemical cell has been designed in which biocompatibility can be evaluated through characterization of the surface oxide layer. Electrochemical impedance spectroscopy (EIS) and step polarization impedance spectroscopy (SPIS) will be utilized independently and also compared as never before to the knowledge of the authors.

Motivation

- Metal oxide layers naturally form on biomedical alloys [1]
- Oxide layer limits rate of electrochemical reactions
  - e.g. corrosion
- This directly impacts biocompatibility of the alloy

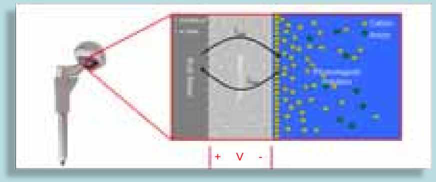
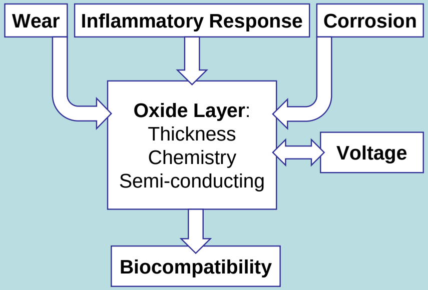


Fig 1 – Cross-section of oxide layer. Current is shown through the oxide layer, and is due to the voltage that naturally occurs when an implant is introduced to physiologic solution [2].

- Electrochemical potentials naturally occur across oxide layer



Wear **Inflammatory Response** **Corrosion**

Oxide Layer:
Thickness
Chemistry
Semi-conducting

Voltage

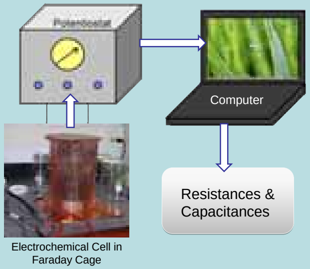
Biocompatibility

Fig 2 – Biocompatibility of a medical implant is regulated by the oxide layer

- Previous work has proven that wear, the inflammatory response, and the oxide layer are interrelated [2]
- Oxide layer affected by these factors in terms of thickness, chemistry, and semi-conducting properties
  - Directly affects the voltage across the oxide layer
- All of this impacts biocompatibility of alloy

Materials

- Electrochemical cell was custom built largely using non-conductive polycarbonate material [3]
- Faraday cage used to reduce electromagnetic noise
- Cell was attached to Gamry series G 300 potentiostat
  - Potentiostat is a voltage source
  - Can also make current measurements
- Voltage and current data sent to a PC
  - Utilizes customized programs to determine impedance information
- Impedance information used to determine resistance and capacitance of oxide layer
- Material tested was 316L SS, electropolished



Resistances & Capacitances

Electrochemical Cell in Faraday Cage

Fig 3 – Experimental setup

Methods

- Goal: Comparison of two impedance spectroscopy measurements: EIS & SPIS

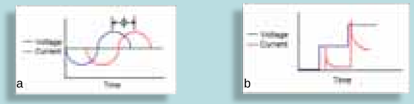


Fig 4 – Voltage input and current output for a) EIS and b) SPIS

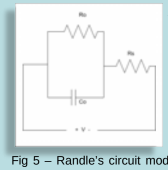
- EIS
  - application of a sinusoidal voltage
  - resulting current will be sinusoidal [2]
  - tested over a range of DC offset values

- SPIS
  - application of steps in voltage over a range of voltages
  - resulting current will be exponential decays
  - corresponding to voltage steps

- Significantly modified Gamry programs
  - LabVIEW v8.1 to control EIS and SPIS experiments
- Used Gamry framework to run EIS experiment
  - Used as validation of the LVEIS program

Circuit Models

- Electrical circuits used to model the device-solution interface
- Randle's Circuit used in this research



$$Ztot = Rs + \frac{Ro}{1+(wRoC)^2} + j\frac{wCRo^2}{1+(wRoC)^2}$$

$$i(t) = \left[\frac{V_S}{R_S} - \frac{V_S}{R_o + R_S}\right]e^{-\lambda t} + \frac{V_S}{R_o + R_S}$$

$$\lambda = -\frac{R_S + R_o}{CR_S R_o}$$

Fig 5 – Randle's circuit model and circuit equations describing impedance in terms of frequency and current in terms of time

- Goal of EIS and SPIS is to determine the values of Rs, Ro, and Co as shown in this circuit
- Both EIS and SPIS can be used to accomplish this
- The authors sought to determine which method was more desirable based on time constraints, accuracy, and precision

Validation

- An initial data collection from a 316L SS sample was taken in order to determine an appropriate range of DC offset values over which to test the 316L SS samples
- Data was collected using Gamry Framework from the sample at DC offsets from -1 V to +1 V in steps of 250 mV.
- Randle's Circuits were built using elements as determined by the Gamry Framework testing
- Gamry Framework was then used to test the circuits in order to validate the potentiostat

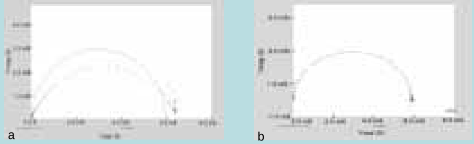


Fig 6 – Gamry Framework collections for a) 316L SS sample and b) Randle's Circuit based on 316L SS data collection

- All data collected is shown in the table below:

Table 1 – Circuit data for a) Solution impedance b) Oxide impedance, C) Oxide capacitance

a Voltage, V	Actual Element Value, Ω	EIS Result, Ω	% Error
-1.0	170	171	0.58
-0.5	168	169	0.65
0	167	170	1.79
+0.5	169	170	0.83
b Voltage, V	**Actual Element Value, Ω**	**EIS Result, Ω**	**% Error**
-1.0	5 k	5 k	5.96
-0.5	61 k	58 k	5.24
0	4 M	4 M	3.94
+0.5	2 M	2 M	5.60
c Voltage, V	**Actual Element Value, F**	**EIS Result, F**	**% Error**
-1.0	12.7 µ	12.65 µ	0.37
-0.5	17.10 µ	16.98 µ	0.72
0	5.30 µ	5.34 µ	0.82
+0.5	4.94 µ	5.06 µ	2.35

Results

- Data collected using Gamry Framework shows:
  - Rs remains constant, as predicted by the Randle's model
  - Impedance and capacitance of the oxide vary with changes in DC offset voltage
    - Indicates that voltage affects composition, structure, semi-conductive properties

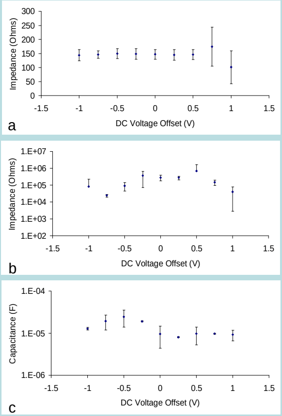


Fig 7 – Testing using Gamry Framework, sample area = 0.5858 cm^2. a) solution impedance c) oxide impedance c) oxide capacitance. Error bars indicate one standard deviation, n=3.

Conclusions

The electrochemical cell was validated using the Randle's Circuit model and Gamry Framework. An LVEIS method of testing 316L SS samples was designed. An SPIS program is currently being developed. Future work includes the comparison of the LVEIS and Framework programs, as well as the finalization of the SPIS program for comparison of EIS and SPIS.

References

[1] J.L. Gilbert, "Step-polarization impedance spectroscopy of implant alloys in physiologic solutions," *J Bio Mat Res*, vol 40, pp. 233-243, 1998.
[2] D.A. Jones, *Principles and Prevention of Corrosion.* Upper Saddle River, NJ: Prentice-Hall, 1996.
[3] R.C. Turner, K.E. Joyce, Western New England College senior project report, 2008.

Acknowledgements

The authors extend their gratitude to the Biomedical Engineering department, Pete Bennett and Mike McCarthy for machining and ordering parts, and Rob Sides for his technical assistance. This research supported by American Society for Quality (ASQ) Biomedical Division.