

The Electrochemical Impedance of Polarized 316L Stainless Steel: Structure-Property-Adsorption Correlation

Robert T. T. Gettens, Pritesh Patel, Jeremy L. Gilbert.

Syracuse University, Syracuse, NY 13244.

Statement of Purpose: The purpose of this study was to characterize the electrochemical impedance behavior of electrically polarized 316L stainless steel (SS) in electrolyte and protein solutions and to relate the impedance behavior of the surface to in-situ AFM observations of the metal oxide. Previously, we reported differences in fibrinogen (Fb) adsorption kinetics and morphology when adsorbed to polarized 316L SS surfaces.¹ We saw a reduction in Fb adsorption kinetics, height and surface area coverage when the 316L surface was held at cathodic potentials.¹ We wish to relate these adsorption observations to alloy surface properties including electrochemical impedance and structural oxide changes as driven by the process of electrochemical polarization.

Materials and Methods: The substrate material used was 316L SS (Medtronic, Inc.). The SS was mechanically followed by electrochemically polished, passivated and plasma etched. Tests were carried out both in phosphate buffered saline (PBS) and bovine Fb (Sigma), at 100 µg/ml in PBS. A standard electrochemical set-up was used with a Ag/AgCl reference. A Multi-Mode AFM-2 with Nanoscope IIIa controller (Veeco) was used with standard probes for imaging in tapping mode in fluid under potential control. The method to obtain the electrochemical properties was a modified version of step polarization impedance spectroscopy (SPIS).² The sample was held at -1V for a period of 5 min. then stepped in 50 mV increments (30 sec. between steps) to 1V while recording the current response. Rather than perform an analysis in the frequency domain², the data was fit to a time domain current response of a modified Randall's circuit (eqn. 1).

$$I(t) = \frac{dV}{R_e} e^{-\left(\frac{t}{\tau}\right)^n} + \frac{dV}{R_e + R_p} \left[1 - e^{-\left(\frac{t}{\tau}\right)^n} \right] + I_0 \quad 1$$

Where I is current, I_0 baseline I before the step, t time, dV voltage step, R_e early resistance, R_p polarization resistance, τ time constant and n an exponent used to represent the constant phase behavior of the interface.

Capacitance (C) was then determined using equation 2.

$$C = \frac{\tau(R_p + R_e)}{R_p * R_e} \quad 2$$

Results and Discussion: The electrochemical impedance closely correlated with surface oxide morphology imaged using in-situ AFM. Each of the impedance parameters (R_e , R_p , C , n) was seen to systematically vary with potential from -1 to 1 V. In particular, C (see Fig. 1) and R_p (not shown) varied in ways that correlated with changes in surface structure of the oxide (Fig. 3) and with regions of stability of the oxide. Furthermore, R_p and C varied inversely to each other (where C increased, R_p decreased etc.). The exponent n also varied with potential (Fig. 2) and the addition of protein in solution indicating changes in dispersion of the capacitive character of the film. The capacitance behavior may be attributed to changes in the oxide, electrical double layer, metal-oxide interface and/or adsorbed species. As we did not see major statistical differences in C in the presence of

Fb (Fig. 1), changes in C are most likely due to physical, chemical and electrical changes in the oxide. An exception is at voltages lower than -0.75 V. Looking at the surface structurally (Fig. 3) moving from -1V positively we initially see a rough surface with apparent reaction products forming, by -0.5 V (where we see a C peak) the surface stabilized and was less rough, at 0.5 V (just after the minimum in C) the surface appeared to break up. By 0.6 V the underlying surface became extremely smooth, leaving behind only some residual particles. It appears that several distinct oxide structures and/or chemistries are present on this surface, one below around -0.5 V, one between -0.5 V and 0.5 V and a third above 0.5 V. This may be attributed to the oxide formed by the electrochemical polishing procedure.

Fig 1: C of 316L SS vs. V in PBS and Fb. 3 samples for each condition.

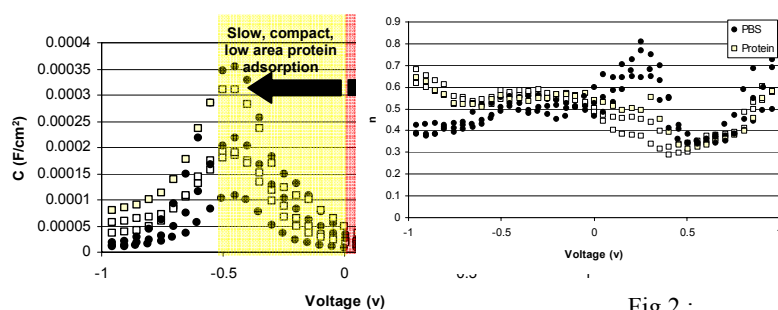


Fig 2 : Power (n)

representing constant phase behavior of 316L SS vs. V in PBS and Fb solutions.

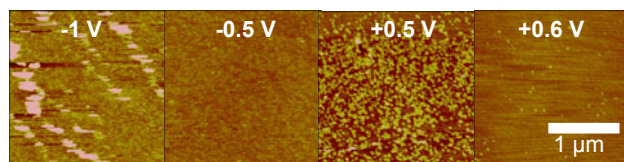


Fig 3: AFM height images of 316L SS polarized in PBS. The scale bar applies to all images. The height contrast is 10 nm.

Conclusions: The electrochemical impedance behavior of polarized 316L SS, particularly capacitance, closely matched structural characteristics on the alloy surface imaged by AFM and appears to correlate with different regions of protein-surface interaction.

References:

1. Gettens, R., Gilbert J.L. 2006 SFB Annual Meeting, Pittsburg, PA
2. Gilbert, J.L.: JBMR. 1998; 40(2): 233-243