

The Influence of Cathodic Polarization and Simulated Inflammation on Titanium Alloy Electrochemistry

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Statement of Purpose: Titanium - 6Aluminum - 4Vanadium (Ti64) is a common alloy used for orthopedic implants due to its corrosion resistance. Invasive orthopedic procedures can provoke a local inflammatory response that produces hydrogen peroxide (H₂O₂). In addition, fretting corrosion of titanium implants can cathodically shift the open circuit potential (OCP) of the implant^{1,2}. Previous work has shown that H₂O₂ and cathodic changes in OCP can individually affect the electrochemical properties of the titanium oxide layer^{3,4}. This study assessed the combined influence of cathodic polarization and inflammation on Ti64 electrochemistry.

Methods: Ti64 (Titanium Industries) samples (3.8 cm²) were sequentially wet sanded to a 600 grit finish, ultrasonically cleaned in deionized water, sterilized under UV light for 30 minutes, and mounted in a custom corrosion chamber. The Ti64 sample was the working electrode, a graphite rod served as the counter electrode, and a chlorided silver wire (Ag/AgCl) was the reference electrode. The electrochemical chamber was filled with either phosphate buffered saline (PBS, Mediatech) at pH 7.0 or 150mM H₂O₂ (J. T. Baker) in PBS that was titrated with hydrochloric acid (HCl, J. T. Baker) to pH 5.0. The latter solution was previously used to simulate inflammatory conditions⁵. The chambers were then placed into a humidified, 37°C, 5% CO₂ incubator and electrode connections were made to a potentiostat (Ref 600, Gamry Instruments). The cell was either held at static potential of -1V vs. Ag/AgCl or allowed to sit at the open circuit potential (OCP) for 24hrs. The experimental conditions were defined as normal (OCP in PBS at pH 7), inflammatory (OCP in H₂O₂ at pH 5) and inflammatory +fretting (-1V, H₂O₂ at pH 5). After 24hrs of incubation, electrochemical impedance spectroscopy (EIS) was performed (+/- 10mV from 100KHz-5mHz) to evaluate the electrochemical properties of the Ti-oxide-solution interface. A complex-non-linear-least-squares method was used to fit the impedance results to a modified Randles circuit using Gamry Instruments software (EIS 300). H₂O₂ concentration was measured at 0hrs, and at test completion (24hrs) using visual colorimetric analysis (CHEMetrics). The solution pH for each condition was also measured at 0hrs and 24hrs (Oakton Instruments). Polarization curves (+.3V to -1.5V vs. E_{oc}) were obtained for Ti64 in both the PBS and H₂O₂ solutions after equilibrating at OCP for 24hrs. Four Ti64 samples were assessed at each condition. The Welch test for equality of means followed by a Games-Howell post hoc was used to compare differences in outcomes (p < .05 was significant). Log transform data of polarization resistance (Rp) and the magnitude of the constant phase element (Y_o) was used for statistics due to a wide range of magnitudes.

Results: An examination of the 24hr impedance results in Table 1 reveals that the addition of inflammatory conditions produces statistically different values for

impedance parameters, while the addition of cathodic polarization again leads to significant changes. Rp decreases across the conditions, corresponding to an increase in the faradaic charge transfer processes. The non-faradaic process, characterized by Y_o, is significantly increased across all three conditions. The alpha parameter (α) also shows a statistically significant decrease across each of the conditions. Warburg admittance (ω), an indication of diffusion limited processes, was only observed in combined fretting+inflammatory conditions. OCP under inflammatory conditions is statistically more anodic compared to OCP under normal conditions. The concentration of H₂O₂ remained the same over 24hrs at OCP; however, was almost completely consumed after 24hrs under cathodic polarization. Analysis of the polarization data revealed that the addition of H₂O₂ caused a shift to larger I_{corr} values, and more anodic E_{corr} values. Inductively coupled plasma mass spectrometry (ICPMS) and surface morphology results are pending.

	Normal	Inflammatory	Fretting and Inflammatory
Rp ($\Omega \cdot \text{cm}^2$) ^a	6.5e6±4.4e6	2.3e5±8.9e4	1.2e4±3.5e3
Y _o (S*s ³ /cm ²) ^a	3.0e-5±4.2e-6	5.6e-5±1.2e-5	2.5e-4±9.1e-5
α ^a	.920±.004	.880±.014	.838±.018
ω (S*s ^{1/2} /cm ²)			.007±.005
OCP (mV vs Ag-AgCl) ^a	-218.0±120.5	128.2±18.6	
Current Density ($\mu\text{Amps}/\text{cm}^2$)			-12.11±2.04
Final pH	6.35±0.01	5.09±0.09	6.11±0.11
Initial H ₂ O ₂ (ppm)		5400±0.00	5400±0.00
Final H ₂ O ₂ (ppm) ^a		5400±0.00	66.67±57.74

Table 1: 24hr Results, ^a Significant differences across all conditions

Conclusions: The more positive OCP for Ti64 under inflammatory conditions is likely due to increased cathodic half-cell reactions. The porosity of the film formed in the presence of H₂O₂ gives rise to lower alpha values, lower resistance to charge transport (low Rp), and higher capacitive-like characteristics (Y_o). These changes are enhanced by the addition of cathodic potential to inflammatory conditions, which continues to change the oxide structure through reductive dissolution. The increase in pH (from 5 to ~6) and consumption of H₂O₂ observed under fretting+inflammatory conditions are due to an increase of cathodic reduction reactions. At this large cathodic potential the rate of the cathodic half-cell reaction became diffusion limited as was indicated by the presence of the Warburg parameter in the EIS data. The cathodic polarization associated with fretting corrosion while in the presence of H₂O₂ causes changes in the electrochemical properties of Ti64's protective oxide layer. This leaves the sample more susceptible to corrosion and at risk for failure.

References: 1.Goldberg, JR JBMR, 2003; 64B:78-93. 2.Contu, F Electroch Acta, 2004; 50:33-41. 3.Pan, J. Electroch Acta 1996; 41:1143-1153. 4.Ehrensberger, M. JBMR-B 2009; 40:233-243. 5.Fronseca, C. Corr Sci 2001; 43:547-559.