

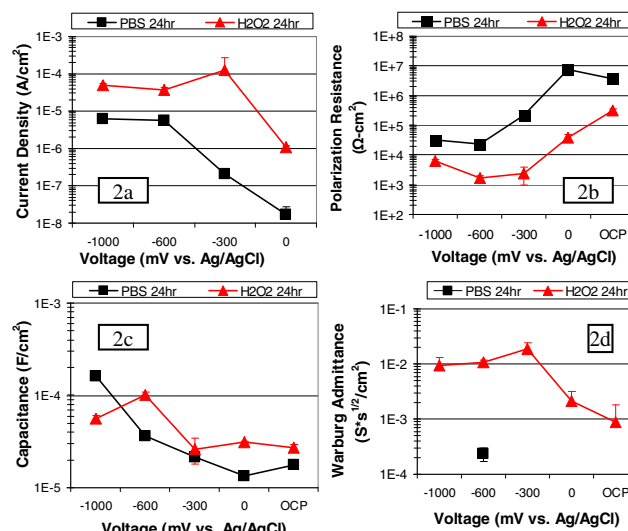
## Electrochemical Properties of Titanium Under Cathodic Polarization and Simulated Inflammatory Conditions

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**INTRODUCTION:** Invasive procedures are required to place Ti implants in the body and evoke an inflammatory response which includes the generation of hydrogen peroxide ( $H_2O_2$ ). Previous work has explored how  $H_2O_2$  alters the electrochemical properties of Ti by conducting electrochemical impedance spectroscopy (EIS) at Ti's open circuit potential[1-3]. However, abrasion of the Ti oxide film, such as that which occurs during fretting corrosion associated with modular Ti implants, can shift the voltage of Ti into the range of -300 to -1500 mV[4-5]. This study examined the combined effects of cathodic polarization and  $H_2O_2$  on Ti's electrochemical impedance.

**METHODS:** Grade 2 commercially pure titanium (Ti) samples ( $3.8\text{ cm}^2$ ) were wet sanded to a 600 grit finish, sonicated in DI- $H_2O$ , mounted in an electrochemical chamber that was filled with 15mL of phosphate buffered saline (PBS) at pH 7.4 or 150mM  $H_2O_2$  titrated to pH 5 with HCl to simulate inflammatory conditions[2]. The chamber was then placed into a humidified,  $37^\circ\text{C}$ , 5%  $CO_2$  incubator and the appropriate electrode (graphite counter electrode and a chlorided silver wire reference electrode) connections were to a potentiostat (Ref 600, Gamry Instruments). The Ti sample served as the working electrode and it was held at static potentials of -1000, -600, -300, 0 mV (v. Ag/AgCl), or at the open circuit potential (OCP) for 24 hrs. After 2hr, 12hrs, and 24 hrs of incubation EIS was performed ( $\pm 10\text{mV}$ , 100KHz to 5mHz) to evaluate the Ti-oxide-solution interface. The data were analyzed by a complex-non-linear-least-squares method used to fit the impedance results to electrically equivalent circuits using Gamry software (EIS 300). Reported outcomes included current density and polarization resistance ( $R_p$ ) as measures of the faradaic (charge transfer) processes, interfacial capacitance ( $C$ ) as a measure of the non-faradaic (surface charge) processes, and Warburg admittance ( $W_d$ ), where appropriate, to account for diffusion limited processes. Three Ti samples were assessed at each condition. Independent sample t-tests ( $\alpha=0.05$ ) compared the EIS outcomes between the electrolyte solutions at each polarized condition.

**RESULTS:** The 24 hr impedance outcomes for all experimental conditions are presented in Fig. 1a-d. An examination of Fig. 1a,b shows the faradaic processes are significantly larger (increased current and decreased  $R_p$ ) in  $H_2O_2$  as compared to PBS at all polarized conditions. All current densities are cathodic except for the anodic current at 0 mV in PBS. Fig. 2d indicates that a Warburg admittance ( $W_d$ ) component is present at all potentials in  $H_2O_2$  while only the -600 mV group displayed a  $W_d$  component in PBS. The  $W_d$  at -600 mV was significantly smaller in PBS as compared to  $H_2O_2$ . Fig. 2c shows that capacitance ( $C$ ) values at OCP, 0 mV, and -600 mV were significantly higher in  $H_2O_2$  as compared to PBS. The  $C$  values at -300 mV were not significantly different for the



**Fig. 2:** A panel of plots showing the current density (2a), polarization resistance (2b), capacitance (2c), and Warburg admittance (2d) at all potentials after 24hrs of incubation in 15 mL of phosphate buffered saline (PBS, pH 7.4) or 150mM hydrogen peroxide ( $H_2O_2$ , pH 5) at  $37^\circ\text{C}$ . The data points represent the mean value  $\pm$  standard error. Independent t-tests showed significant differences between  $H_2O_2$  and PBS at all potentials in all plots except for capacitance values at -300 mV.

$H_2O_2$  and PBS groups while the PBS group shows significantly higher  $C$  at -1000 mV as compared to  $H_2O_2$ .

**DISCUSSION:** The porous nature of the oxide film formed in the presence of  $H_2O_2$  is what gives rise to the mass transport diffusion control (Warburg component) of the electrochemical reactions at the Ti-oxide-solution interface. Furthermore, when coupled with cathodic polarization, where the oxide composition and structure can change through reductive dissolution and electric field effects, the interactions of Ti and  $H_2O_2$  produce an oxide film with very poor resistance to charge transport (low  $R_p$  and high current density) as compared to PBS. The capacitance ( $C$ ) results are more difficult to interpret. If the film is modeled as a parallel plate capacitor and since  $H_2O_2$  increases oxide film growth, the  $C$  in  $H_2O_2$  should be smaller. However, a smaller  $C$  in  $H_2O_2$  compared to PBS only occurs at -1000 mV. This finding may indicate that voltage dependent semiconducting properties (defect density and flat-band potential, both of which can influence the interfacial  $C$ ) may be altered by the  $H_2O_2$ . Differences in pH (as with the test solutions) are known to effect corrosion properties of Ti and this aspect also needs to be considered when examining these differences in electrochemical properties. The outcomes of this study show that across clinically relevant voltages the electrochemical properties of titanium are strongly altered by inflammatory conditions.

**REFERENCES:** 1.A1-Mobarak NA, Mat Chem and Phy 2006 2.Fonseca C, Cor Sci 2001 3.Pan J, Electrochimica Acta 1996 4.Contu F, Electrochimica Acta 2004 5.Goldberg JR, J Bio Mat Res 2003