Effect of hydrogen peroxide and pH on corrosion behavior of CoCrMo alloy in phosphate buffered saline
Yangping Liu; Jeremy L. Gilbert

Biomedical and Chemical Engineering Department, Syracuse Biomaterials Institute, Syracuse University, Syracuse, NY

Statement of Purpose: Cobalt-chromium-molybdenum (CoCrMo) alloy has been widely used in a wide variety of implant devices. The effects of ions and particles released from Co-Cr-Mo based alloy caused by mechanically assisted corrosion have been recognized as major concerns. [1] Corrosion products are known to stimulate immune and inflammatory responses which cause cells to release acid and reactive chemical species such as hydrogen peroxide (H$_2$O$_2$). How inflammatory cell-generated H$_2$O$_2$ and acid (HCl) affects Co-Cr-Mo corrosion is not clear. Therefore, the goal of this study is to assess the effects of H$_2$O$_2$ and pH on the corrosion behavior of Co-Cr-Mo alloy in physiologically-representative solution.

Methods: Disks made of CoCrMo (ASTM F-1537) were prepared through sequential wet sanding to a 600 grit finish and cleaned with deionized water. A potentiostat (Solartron 1280C, Solartron Analytical) was used for electrochemical measurements. All electrochemical tests were made through a three electrode system with a reference electrode (Ag/AgCl), a counter electrode (Carbon rod) and a working electrode (CoCrMo disk). Open Circuit Potential (OCP) was monitored for 40 min for 4 different solutions, namely, phosphate buffered saline (PBS) solution (pH 7.4); PBS with 30 mM H$_2$O$_2$; PBS with HCl (pH 3) solutions and 30 mM H$_2$O$_2$ and PBS with HCl(pH 3). These solutions were used for polarization and Electrochemical Impedance Spectroscopy (EIS) tests. Samples were brought in contact with the electrolyte solution for 15 min before polarization testing with a starting and final potential of -1V (vs.Ag/AgCl), a vertex potential of +1V (vs.Ag/AgCl) and a scan rate of 1mV/s. EIS measurements were carried out at OCP immediately after solution was added. A 10 mV voltage was applied to the interface while varying the frequency of input voltage from 20 kHz to 10 mHz.

Results: OCP, polarization tests and EIS results show that the corrosion behavior of CoCrMo alloy is affected by small additions of H$_2$O$_2$ to PBS. OCP shifts positively from -0.35 V to 0.35V and 0.6V (vs Ag/AgCl) with 30 mM addition of H$_2$O$_2$ into PBS or PBS with HCl(pH 3) solutions, respectively (Fig.1). In the 0.6 V (vs Ag/AgCl) range, chromium oxide can be further oxidized according to the Pourbaix diagram to become Cr$^{6+}$. The polarization plots show that with 30 mM addition of H$_2$O$_2$ into PBS solution, the corrosion current density rises more than 40 times (Fig. 2). With HCl (pH 3) present, the corrosion current increases 10 times from the PBS alone, but only 5 times when H$_2$O$_2$ is added to pH3 HCl. Both of these are less than the PBS with 30mM H$_2$O$_2$ only solution which shows the highest corrosion currents. The impedance results indicate that the oxide impedance (low frequency) decreases the most with 30mM H$_2$O$_2$ in PBS, the next most with PBS and HCl (pH 3, Fig. 3). At low frequency (0.01Hz), the presence of 30mM H$_2$O$_2$ decreases the impedance value around 100 times from the PBS only case and 30 times for the PBS with HCl solution.

Conclusion: Corrosion susceptibility of CoCrMo alloy is significantly altered when PBS or PBS with HCl are modified with hydrogen peroxide. Increase of OCP to 0.6V range raises the oxidizing potential of the solution bringing Cr ion near to the +6 state. With H$_2$O$_2$ present, corrosion current density rises and oxide impedance decreases in PBS or PBS with HCl(pH=3).


Acknowledgements: Supported by Depuy Synthes