Corrosion Behavior of Co28Cr6Mo Implant in the Presence of Bovine Serum Albumin and Hyaluronic Acid

by

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Abstract

CoCrMo is one of the most widely used materials for prostheses. CoCrMo has high wear resistance, excellent corrosion resistance, and good biocompatibility. High corrosion resistance is ascribed to the formation of an oxide layer. However, the oxide layer does not remain intact in the corrosive body environment that contains oxygen, chloride, proteins, and carbohydrates. The presence of organic and inorganic species changes the oxide layer of CoCrMo to facilitate corrosion. Corrosion is one of the main issues that lead to revision surgery.

CoCrMo has been used extensively in synovial joints replacements such as hip, knee, and shoulder. They are in contact with synovial fluid (SF) which mainly contains albumin and hyaluronic acid (HA). The concentrations of HA changes with age, sex, and diseases.

The objective of this study is to investigate the effect of the main constituents of SF which are bovine serum albumin (BSA) and HA, on the corrosion performance of CoCrMo. In addition, this study also investigates the effect of changing HA concentrations on the corrosion behavior of CoCrMo. Increasing HA concentrations has reduced the pain for people with osteoarthritis. It may also have an effect on reducing the corrosion rate.

To study the corrosion behavior of CoCrMo, different electrochemical techniques has been used to understand the formation and breakdown of the oxide
layer, and calculate the corrosion rate by measuring the corrosion resistances and corrosion current densities.

The results of electrochemical impedance spectroscopy (EIS) show that 4 gL⁻¹ of hyaluronic acid (HA) with bovine serum albumin (BSA) exhibited the highest corrosion resistance and the lowest corrosion rate of CoCrMo compared to only phosphate buffer saline (PBS), BSA, and PBS with different HA concentration.
Preface

This research has been done in the corrosion laboratory at the University of British Columbia. The work represented in this thesis is sponsored by The Ministry of Higher Education in Saudi Arabia. This thesis is under supervision of Professor Alfantazi, who helped me extensively during my studies. My research findings were presented as a conference poster in a NACE conference held in Texas.

Conference Poster:

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<thead>
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<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Atomic weight (g mol(^{-1}))</td>
</tr>
<tr>
<td>B</td>
<td>Tafel constant (0.026 V)</td>
</tr>
<tr>
<td>(\beta_{ox})</td>
<td>Anodic Tafel constant (mV)</td>
</tr>
<tr>
<td>(\beta_{red})</td>
<td>Cathodic Tafel constant (mV)</td>
</tr>
<tr>
<td>(C_{out})</td>
<td>Capacitor of the outer layer</td>
</tr>
<tr>
<td>(C_{in})</td>
<td>Capacitor of the oxide layer</td>
</tr>
<tr>
<td>CoCrMo</td>
<td>Cobalt Chromium Molybdenum</td>
</tr>
<tr>
<td>(E_b)</td>
<td>Breakdown potential</td>
</tr>
<tr>
<td>(E_{corr})</td>
<td>Corrosion potential (V vs. SCE)</td>
</tr>
<tr>
<td>Eq</td>
<td>Molar equivalent is a unit of electrical charge used in chemistry and biology science where 1eq = C</td>
</tr>
<tr>
<td>(\eta)</td>
<td>Overpotential (V)</td>
</tr>
<tr>
<td>F</td>
<td>Faraday constant (96500 C mol(^{-1}))</td>
</tr>
<tr>
<td>(i_{corr})</td>
<td>Corrosion current density ((\mu)A cm(^{-2}))</td>
</tr>
<tr>
<td>(I_p)</td>
<td>Passivation current ((\mu)A cm(^{-2}))</td>
</tr>
<tr>
<td>K</td>
<td>Constant in corrosion rate calculation (8.76 (\times) 10(^{-4}))</td>
</tr>
<tr>
<td>KCl</td>
<td>Potassium Chloride</td>
</tr>
<tr>
<td>KH(_2)PO(_4)</td>
<td>Potassium Phosphate</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>-------------</td>
</tr>
<tr>
<td>min</td>
<td>Minute</td>
</tr>
<tr>
<td>N</td>
<td>Equivalent exchange electrons</td>
</tr>
<tr>
<td>n</td>
<td>Deviation coefficient between real and pure capacitance (0 &lt; n &lt; 1)</td>
</tr>
<tr>
<td>NaCl</td>
<td>Sodium Chloride</td>
</tr>
<tr>
<td>Na$_2$HPO$_4$</td>
<td>Sodium Phosphate</td>
</tr>
<tr>
<td>$\omega$</td>
<td>Angular frequency (rad s$^{-1}$)</td>
</tr>
<tr>
<td>P</td>
<td>Density (g cm$^{-3}$)</td>
</tr>
<tr>
<td>R$_{in}$</td>
<td>Oxide layer resistor ($\Omega$)</td>
</tr>
<tr>
<td>R$_{out}$</td>
<td>Outer layer resistor ($\Omega$)</td>
</tr>
<tr>
<td>R$_p$</td>
<td>Polarization resistance (k$\Omega$ cm$^2$)</td>
</tr>
<tr>
<td>R$_{P-EIS}$</td>
<td>Polarization resistance obtained from the electrical circuit ($\Omega$)</td>
</tr>
<tr>
<td>R$_{P-LPR}$</td>
<td>Polarization resistance obtained from LPR curves-the slope of the linear polarization curves (k$\Omega$ cm$^2$)</td>
</tr>
<tr>
<td>R$_s$</td>
<td>Solution resistance ($\Omega$ cm$^2$)</td>
</tr>
<tr>
<td>Y$_0$</td>
<td>General admittance function ($\mu\Omega^{-1}$ (s$)^n_c$ cm$^{-2}$)</td>
</tr>
<tr>
<td>Z$_{CPE}$</td>
<td>Impedance of the constant phase element ($\mu\Omega^{-1}$ (rad)$^n_c$ cm$^{-2}$)</td>
</tr>
</tbody>
</table>
List of Acronyms

AFM                  Atomic force microscopy
ARC                  Agency of research on cancer
Arg-Gly-Asp          Arginine-Glycine-Aspartate
ASTM                 American Society for Testing and Materials
BSA                  Bovine serum albumin
CPE                  Constant phase element
EIS                  Electrochemical impedance spectroscopy
FCC                  Face centred cubic
GAG                  Glycosaminoglycan
HA                   Hyaluronic acid
HC                   High carbon wrought
HCP                  Hexagonal close packed
ICP-OES              Inductively-coupled plasma emission spectroscopy
LC                   Low carbon wrought
LPR                  Linear polarization resistance
OCP                  Open circuit potential
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAR</td>
<td>Princeton Applied Research</td>
</tr>
<tr>
<td>PBS</td>
<td>Phosphate buffer saline</td>
</tr>
<tr>
<td>PDP</td>
<td>Potentiodynamic polarization</td>
</tr>
<tr>
<td>QCM</td>
<td>Quartz crystal microbalance</td>
</tr>
<tr>
<td>SCE</td>
<td>Saturated calomel electrode</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>SF</td>
<td>Synovial fluid</td>
</tr>
<tr>
<td>SHE</td>
<td>Saturated hydrogen electrode</td>
</tr>
<tr>
<td>UHMWPE</td>
<td>Ultrahigh molecular weight polyethylene</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
</tr>
</tbody>
</table>
Acknowledgment

The author would like to show appreciation and thanks for the great questions, comments, and patience from Professor Akram Alfantazi, who helps me expanding my vision of Engineering.

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I would like to give sincere thanks to my parents for their support and encouragement to pursue my studies.

A deep thanks for the Ministry of Higher Education in Saudi Arabia and Saudi Arabian Culture Bureau for financially supporting me and my studies including this work.
Dedication

To:

My beloved Parents

(Rasim & Sahar)

My close sisters and brothers

(Ahmad, Leena, Rasha, Sawsan, and Muhammad)

& My adorable nieces and nephews

(Raed, Layan, Sara, Abdulhadi, Abdulrahman, and Besan)

“To all of you, thank you for the great love, moments, and support,

thank you for being you.”
1 Introduction

Prostheses have been used widely since they were introduced after the Second World War. Surgeons, along with scientists and engineers, started using materials that have been used in automobiles, airplanes, and radios to manufacture implants (Ratner, 2004). The main applications of metallic implants are prostheses and fixation devices. Hip and knee implants are some examples of prostheses for hard tissue replacement while screws, nails, and wires are fixation devices for stabilizing broken bones.

Replacing damaged tissue reduces patients’ pain and increases the efficiency of their lives. However, implantation is very costly (Ratner, 2004). The worldwide sale for orthopedics was about $14 billion in 2002 and the expenses are expected to increase by 7 to 9% per year (Hallab et al., 2004). This substantial amount of money is a serious issue that need to be tackled.

The most commonly-used alloys for orthopedics implants are titanium alloys (e.g. Ti6Al4V), cobalt alloys (e.g. CoCrMo), and stainless steel (e.g. 304, 316, and 316L). They have been used due to their biocompatibility, corrosion and wear resistance, hardness, elastic modulus, and ductility (Niinomi, 2002). However, complex body movements and reactions with human fluids could lead to implant failure and revision surgery. Fracture, loosing, ions release, and corrosion are some of the main issues related to implant failure (Ratner, 2004).
Corrosion is one of the serious causes of implant failure. Corrosion of stainless steel orthopedics was determined as one of the main causes of implants failure after fracture (Manivasagam et al., 2010). Another study ranked stress-corrosion fatigue as a first cause of failure in Ti6Al4V and 316L by collecting evidence from retrieved implants of patients from 1993 to 2002 using scanning electron microscopy (SEM). Corrosion also changes the surrounding pH environment to be more acidic which increases the corrosion rate (Aksakal et al., 2004).

Implant failure has serious consequences on a patients’ health due to ion release. The behavior of ions in the body depends mainly on the type of molecule that will bind with the metal ions. Metal ions can become toxic if they bind to biomolecules. However, if ions bind to oxide, hydroxide, or salts, they are non-toxic (Hanawa, 2004; Lundin et al., 2012). Ions can also accumulate in organs such as kidney, livers, lungs, and spleen (Rubio et al., 2008). Certainly, ion accumulation can change the pH of the surrounding environment and the partial pressure of oxygen (Cahoon & Paxton, 1968). Ions such as Co, Cr, and Ni show some toxicity and there is some debate whether they are carcinogenic or not (Rubio et al., 2008). Ion release decreases the predicted lifetime of implants. Knee prostheses can last for 10 years while hip can last for 15 years (Hallab et al., 2004). Increasing the lifetime of the prostheses will be a great success in the medical industry because it will decrease the number of revision surgeries, replacing failed implants. Revision surgeries are
expensive, painful, and the success percentage is small (Geetha et al., 2013; Rand et al. 2003)

Understanding the effect of the interaction between body constituents (e.g. proteins and carbohydrates) with implants on corrosion will help in the selecting and developing of new materials with better corrosion resistance and biocompatibility. This achievement will increase the lifetime of implants and decrease the number of revision surgeries.
2 Literature review

2.1 Metallic Prosthesis

Prostheses are being used in different parts of the body to restore functionality or replace damaged body organs. Some examples of implants used to replace organs, tissue, or functionality are arteries, stents, heart valve, knee, hip, ankle, shoulder, dentals, sensors, cardiovascular, and bone plates (Chrzanowski et al., 2012; Manivasagam et al., 2010). These prostheses are made of biomedical materials. Biomedical material is defined as “a material intended to interface with biological systems to evaluate, treat, augment or replace any tissue, organ or function of the body” (Williams, 2009). Figure 2-1 shows some of the implants applications in the human body (Manivasagam et al., 2010).

Prostheses are made of metals, ceramics, polymers, or composites depending on the functionality that is required from the implants. Ceramics are strong and chemically stable. They have been used in coatings due to their ability to interact with bone. Moreover, ceramic have good wear resistance therefore they have been used in implants such as knee, hip, and teeth. Polymers are repeating monomer units that have high molecular weight. Polymers are used in the human body due to the similar composition with the human body. Therefore, they can be used to replace skin, tendon, vessel walls, and articulating surfaces. Metals are usually used in applications that requiring load bearing due to its strength and ductility. Metallic implants are used mainly to replace damaged joints or to stabilize the fractured bone (Balamurugan et al., 2008; Singh & Dahotre, 2007).
Figure 2-1: Implant applications in the human body (Manivasagam et al., 2010)
The highest demand for implants is for the joints replacement. It has been estimated that the number of people who required a metallic implantable joints is about 307 million per year (Chrzanowski et al., 2012). Implants are required for young people who are active in sports and suffer fractures and strains. Diseases such as arthritis, osteoporosis, trauma, and Rheumatoid arthritis are the main causes of implant among the elderly. It is expected that 90% of the people over 40 will suffer from osteoarthritises. This will increase the worldwide demand by 174%, (572,000 procedures) for total hip replacement and 673% (3,48 million procedures) for knee replacement by the end of 2030. The revision surgeries are also expected to rise by 137% for total hip replacement and 607% for knee between 2005 and 2030. These revision surgeries are expensive, painful, and the success percentage is not high (Geetha et al., 2009; Kimura, 2013; Manivasagam et al., 2010).

The increasing the demand in aging population requires new implants with longer lifetime. It has been proven that total hip replacement lasts for 15 years. That was acceptable in the past, but not now due to the development of medicine and a longer lifespan of people. Therefore, the demand becomes higher to develop longer-life materials (Geetha et al., 2009). Knee prostheses can last up to 10 years. Increasing the lifetime of the prosthesis will decrease the number of revision surgeries (Rand et al., 2003).

Despite the fact that the implants need to be developed and the lifetime needs to be increased, not any materials can enter the human body. There are
specific requirements for materials to be used as implants such as biocompatibility, mechanical strength, and corrosion resistance (Manivasagam et al., 2010).

The definition of biocompatibility has evolved based on the development of biocompatibility. In 1986, the consensus of a U.K. conference defined biomaterials as “the ability of a material to perform with an appropriate host response in a specific application.” However, Ranter believes that this definition is not valid, because based on this definition, scientists cannot develop a test to measure, enhance, or increase the biocompatibility. Ranter believes that there is biotolerability. Biotolerability according to Ranter is “the ability of material to reside in the body for long periods of time with only low degrees of inflammatory reaction,” while biocompatibility is “ability of materials to locally trigger and guide normal wound healing, reconstruction, and tissue engineering” (Mertz, 2013; Ratner, 2004). Williams agrees with Ranter and defines biomaterials as “a substance that has been engineered to take a form which, alone or as a part of a complex system, is used to direct, by control of interactions with components of living systems, the course of any therapeutic or diagnostic procedure, in human or veterinary medicine (Williams, 2009). From the previous definitions, we can see that the definition has changed according to more knowledge that has been gained regarding new materials and new functions involved.

The other important factor for materials to be used as implants is to have good mechanical properties such as elastic modulus, tensile strength, and yield strength to be able to tolerate the applied force without fracture (Narayan, 2012).
mechanical properties of the most commonly used implants are given in Table 2-1.

The chemical compositions of these alloys are given in Table 2-2.

Table 2-1: Comparison of mechanical properties of commonly-used orthopedics-redrawn (Narayan, 2012)

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Modulus</th>
<th>Yield strength</th>
<th>Ultimate tensile strength</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>GPa</td>
<td>MPa</td>
<td>ksi</td>
</tr>
<tr>
<td></td>
<td>10^6 psi</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stainless steel</td>
<td>200</td>
<td>170-750</td>
<td>25-110</td>
</tr>
<tr>
<td>CoCrMo</td>
<td>200-230</td>
<td>275-1585</td>
<td>600-1795</td>
</tr>
<tr>
<td>pure Ti</td>
<td>105</td>
<td>692</td>
<td>785</td>
</tr>
<tr>
<td>Ti-6Al-4V</td>
<td>110</td>
<td>850-900</td>
<td>960-970</td>
</tr>
</tbody>
</table>

Table 2-2: Chemical composition % of most used metallic biomaterials (Hallab et al., 2004)

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Ni</th>
<th>Co</th>
<th>Cr</th>
<th>Ti</th>
<th>Mo</th>
<th>Al</th>
<th>Fe</th>
<th>Mn</th>
<th>W</th>
<th>C</th>
<th>Si</th>
<th>V</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stainless steel</td>
<td>10-15.5</td>
<td>17-19</td>
<td>61-68</td>
<td>&lt;2</td>
<td>&lt;.06</td>
<td>&lt;1.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CoCrMo ASTM F75</td>
<td>&lt;2</td>
<td>61-66</td>
<td>27-30</td>
<td>4.5-7</td>
<td>&lt;1.5</td>
<td>&lt;1</td>
<td>&lt;.35</td>
<td>&lt;1.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CoCrMo ASTM F90</td>
<td>9-11</td>
<td>46-51</td>
<td>19-20</td>
<td>&lt;.3</td>
<td>&lt;2.5</td>
<td>14-16</td>
<td>&lt;.15</td>
<td>&lt;1.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CoCrMo ASTM F562</td>
<td>33-37</td>
<td>35</td>
<td>19-21</td>
<td>&lt;1</td>
<td>9-11</td>
<td>&lt;1</td>
<td>&lt;.15</td>
<td>&lt;.15</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CP Ti</td>
<td>99</td>
<td>.2-.5</td>
<td>&lt;.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ti-6 AL-4V</td>
<td>89-91</td>
<td>5.5-6.5</td>
<td>&lt;.08</td>
<td>3.5-4.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The third requirement is to have good corrosion resistance. The body is a corrosive environment due to the presence of chloride ions. The chloride ions concentrations in serum and interstitial fluid vary between 113 and 117 mEq/L respectively (Eliaz, 2012). Corrosion is considered to be one of the major issues that faces metallic implants after fracture because corrosion leads to implant failure and revision surgery becomes required.

2.1.1 CoCrMo alloy

CoCrMo has been used extensively in implants due to its mechanical strength, hardness, biocompatibility, and high corrosion and wear resistance. The relatively high corrosion resistance of this alloy is due to the formation of the Cr$_2$O$_3$ passive layer that prevents the extensive flow of ions from and to the implants. The formation of the Cr oxide layer rather than Co, which is the main element in the alloy, is due to a higher reactivity of Cr, which has a lower standard reduction potential of -0.74V vs SHE (Cr$^{3+}$ + 3e$^- = $ Cr) compared to Co 0.28V vs SHE (Co$^{2+}$ + 2e$^- = $ Co that makes the formation of a Cr oxide layer more favorable (Ahmad, Ebrary, 2006; Lewis et al., 2005). However, the passive layer does not remain intact in the corrosive body environment with time. CoCrMo tends to corrode and ions are released (Vidal et al., 2010).

There are cast and wrought CoCrMo used as biomedical alloys. CoCrMo changes its structure from face centred cubic (FCC) to hexagonal close packed (HCP) when the processing temperature is above 450°C while at room temperature FCC is present (Davis et al., 2003). Cobalt alloys have different microstructures that make
them suitable for specific functions. For example, cast alloys have been used in the stem of the hip because it cannot be machined while wrought alloys have been used for the femoral head because it is stronger and has better corrosion and wear resistance (Lewis et al., 2005).

The chemical compositions of all registered CoCrMo biomedical alloys in the American Society for Testing and Materials (ASTM) are shown in Table 2-3 (Niinomi, 2002). The one that has been used in this study is F1537.

Regarding the wrought cobalt-based alloys, there are two types: high and low carbon wrought (HC, LC). The composition of each one of them is illustrated in Table 2-4 (A. Lewis et al., 2005; Lippard & Kennedy, 1999). In a study has done by Yan and co-workers, the corrosion and wear of HC and LC CoCrMo were evaluated. They found that HC has lowest materials loss due to its higher corrosion resistance compared to LC CoCrMo (Yan et al., 2007).
Table 2-3: Chemical compositions (% by weight) of the ASTM Co alloy used in biomedical devices-redrawn (Niinomi, 2002)

<table>
<thead>
<tr>
<th>ASTM designation</th>
<th>Cr</th>
<th>Mo</th>
<th>Ni</th>
<th>W</th>
<th>Fe</th>
<th>Ti</th>
<th>C</th>
<th>Si</th>
<th>P</th>
<th>S</th>
<th>Mn</th>
<th>Co</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoCrMo(F75-92)Cast alloy</td>
<td>27.0-30.0</td>
<td>5.0-7.0</td>
<td>1</td>
<td></td>
<td>0.75</td>
<td>—</td>
<td>0.35</td>
<td>1</td>
<td>—</td>
<td>—</td>
<td>1</td>
<td>Bal</td>
</tr>
<tr>
<td>Co-20Cr-15W-10Ni(F9096) Wrought</td>
<td>19.0-21.0</td>
<td></td>
<td></td>
<td>9.00-11.0</td>
<td>14.00-16.0</td>
<td>3</td>
<td>0.05-0.15</td>
<td>0.4</td>
<td>0.03</td>
<td>0.03</td>
<td>1.00-2.00</td>
<td>Bal</td>
</tr>
<tr>
<td>alloy</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co-35Ni-20Cr-10Mo(F562-95)Wrought</td>
<td>19.0-21.0</td>
<td>9.0-10.5</td>
<td>33.0-37.0</td>
<td>1</td>
<td>1</td>
<td>0.025</td>
<td>0.15</td>
<td>0.015</td>
<td>0.01</td>
<td>0.15</td>
<td>Bal</td>
<td></td>
</tr>
<tr>
<td>alloy</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(F688-95)Wrought alloy</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co-Ni-Cr-Mo-W-Fe (F563-95) Wrought</td>
<td>18.00-22.0</td>
<td>3.00-4.00</td>
<td>15.00-25.00</td>
<td>3.00-4.00</td>
<td>4.00-6.00</td>
<td>0.50-3.50</td>
<td>0.05</td>
<td>0.5</td>
<td>—</td>
<td>0.01</td>
<td>1</td>
<td>Bal</td>
</tr>
<tr>
<td>alloy</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co-28Cr-6Mo(F799-96)Forgings</td>
<td>26.0-30.0</td>
<td></td>
<td></td>
<td>1 (N &lt; 0.25)</td>
<td></td>
<td>0.75</td>
<td>—</td>
<td>-0.35</td>
<td>1</td>
<td>—</td>
<td>—</td>
<td>1</td>
</tr>
<tr>
<td>Grade 1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Grade 2</td>
<td>19.0-21.0</td>
<td>6.0-8.0</td>
<td>14.0-16.0 (Be &lt; 0.10)</td>
<td></td>
<td></td>
<td></td>
<td>0.15</td>
<td>1.2</td>
<td>0.015</td>
<td>0.015</td>
<td>1.5-2.5</td>
<td>39.0-41.0</td>
</tr>
<tr>
<td>Co-28Cr-6Mo (F1537-94)Wrought alloy</td>
<td>26.0-30.0</td>
<td>5.0-7.0</td>
<td>1 (N &lt; 0.25)</td>
<td></td>
<td>0.75</td>
<td>0.35</td>
<td>1</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>1</td>
<td>Bal</td>
</tr>
</tbody>
</table>
One of the main features of cobalt-based alloys is their excellent wear resistance compared to titanium and stainless steel alloys. Therefore, they have been used mainly as a head for hip implants (Lippard & Kennedy, 1999; Niinomi, 2002). The wear rate in LC and HC alloy under a normal load is shown in Table 2-5.

Table 2-4: The composition of LC and HC CoCrMo alloy-redrawn (Lippard & Kennedy, 1999)

<table>
<thead>
<tr>
<th>Element, wt%</th>
<th>Low Carbon</th>
<th>High Carbon</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cobalt</td>
<td>Bal.</td>
<td>Bal.</td>
</tr>
<tr>
<td>Chromium</td>
<td>27.7</td>
<td>27.7</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>5.7</td>
<td>5.7</td>
</tr>
<tr>
<td>Manganese</td>
<td>0.7</td>
<td>0.7</td>
</tr>
<tr>
<td>Iron</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Nickel</td>
<td>0.7</td>
<td>0.7</td>
</tr>
<tr>
<td>Silicon</td>
<td>0.7</td>
<td>0.7</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>0.18</td>
<td>0.18</td>
</tr>
<tr>
<td>Carbon</td>
<td>0.05</td>
<td>0.25</td>
</tr>
</tbody>
</table>

Table 2-5: The wear rate of LC & HC CoCrMo under a normal load in an in vitro corrosive environment-redrawn (Niinomi, 2002)

<table>
<thead>
<tr>
<th>Normal load N</th>
<th>Wear rate (μg/m)</th>
<th>Wear rate (μg/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Low carbon</td>
<td>High carbon</td>
</tr>
<tr>
<td>10.50</td>
<td>0.07</td>
<td>0.10</td>
</tr>
<tr>
<td>61.70</td>
<td>0.31</td>
<td>0.28</td>
</tr>
<tr>
<td>89.80</td>
<td>0.55</td>
<td>0.94</td>
</tr>
</tbody>
</table>
A study done by Lewis and co-workers shows that the amount of released ions depends mainly on the chemical compositions of the solutions more than the carbon content. It shows that the amount of ion released in PBS was almost two times higher than the amount of ion released in synovial fluid (SF) (Lewis et al., 2005). Co is classified to group B2 which means that it could be carcinogenic according to the Agency of research on Cancer (ARC) while Cr is required for the body (60µg/day) (Konttinen et al., ). However, Cr(III) can get oxidize to Cr(VI) which is a toxic and carcinogenic species (Virtanen et al., 2008). Ni content in wrought CoCrMo is also a concern due to sensitivity toward Ni (Williams, 1971). Cast CoCrMo is susceptible to crevice corrosion because they are porous (Williams, 1971).

2.2 Synovial joints environment

Synovial joints are the most abundant joints in the human body that show the highest degree of mobility. Synovial joints consist of cartilage, synovial fluid (SF), and capsule. Cartilage covers bone-articulating surfaces and does not have vascular. SF is the fluid that fills the articular cavity. It provides the cartilage with nutrients and clears the metabolic waste. In addition, it works as a lubricant and adhesive for the joints. Normal SF is the ultrafiltration of plasma except for large proteins. The SF contains small proteins such as albumin while the large proteins like fibrinogen do not exist due to the double-barrier membrane where proteins diffuse at a rate that is inversely proportional to its size. The capsule encompasses the joint and consists of
ligaments that help in a normal movement. The general structure of synovial joints is illustrated in Figure 2-2 (Hui et al., 2012; Kingston, 2000). In addition to the plasma ultrafiltration, there are also molecules that have been secreted by the lining of the synovial membrane cells (e.g., chondrocytes and synoviocytes) which secretes hyaluronan and proteoglycan 4. These molecules are responsible for lubrication (Manivasagam et al., 2010).

In damaged joints due to disease or trauma, the joints look different, as shown in Figure 2-2. One of the main diseases that lead to implantation is osteoarthritis. Osteoarthritis is a chronic disease that leads to joints degeneration (Moore et al., 2013; Anderson & Loeser, 2010).

Figure 2-2: Synovial joints anatomy a) normal and b) diseased (Moore et al., 2013)
Osteoarthritis leads to intolerable pain and immobility. Eventually, people with osteoarthritis need implant (Manivasagam et al., 2010). The pH in the SF is 7.8 (Lewis et al., 2005). There is a similarity in the inorganic species between PBS and SF (Lewis et al., 2005). The inorganic component of the SF, interstitial fluid, and serum is shown in **Table 2-6**.

**Table 2-6: Inorganic component of interstitial fluid, synovial fluid, and serum (Kuhn et al., 1986)**

<table>
<thead>
<tr>
<th>Component</th>
<th>Interstitial Fluid (mg L⁻¹)</th>
<th>Synovial Fluid (mg L⁻¹)</th>
<th>Serum (mg L⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium</td>
<td>3280</td>
<td>3127</td>
<td>3265</td>
</tr>
<tr>
<td>Potassium</td>
<td>156</td>
<td>156</td>
<td>156</td>
</tr>
<tr>
<td>Calcium</td>
<td>100</td>
<td>60</td>
<td>100</td>
</tr>
<tr>
<td>Magnesium</td>
<td>24</td>
<td>-</td>
<td>24</td>
</tr>
<tr>
<td>Chloride</td>
<td>4042</td>
<td>3811</td>
<td>3581</td>
</tr>
<tr>
<td>Bicarbonate</td>
<td>1892</td>
<td>1880</td>
<td>1648</td>
</tr>
<tr>
<td>Phosphate</td>
<td>96</td>
<td>96</td>
<td>96</td>
</tr>
<tr>
<td>Sulfate</td>
<td>48</td>
<td>48</td>
<td>48</td>
</tr>
<tr>
<td>Organic Acids</td>
<td>245</td>
<td>-</td>
<td>210</td>
</tr>
<tr>
<td>Proteins</td>
<td>4144</td>
<td>15000</td>
<td>66300</td>
</tr>
</tbody>
</table>
2.3 Body response to metallic implants and body-implant interface

The biocompatibility of the implants can be determined by the body’s response characterized by inflammatory and wound healing (Anderson & McNally, 2011). The body’s response to the implants is summarized in Table 2-7.

Table 2-7: Tissue response to implant material redrawn (Park, et al., 2007)

<table>
<thead>
<tr>
<th>Response</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toxic</td>
<td>If the materials are toxic, the tissue that surrounds the implant will die</td>
</tr>
<tr>
<td>Nearly Inert</td>
<td>This will trigger minimum tissue response which is a fibrous tissue capsule formation around the implant</td>
</tr>
<tr>
<td>Bioactive</td>
<td>Tissue will chemically bond to the surface of the implant which will enhance the integration between bone and tissue</td>
</tr>
<tr>
<td>Bioresorbable</td>
<td>If the material dissolves, the surrounding tissue will replace it</td>
</tr>
</tbody>
</table>

The surface properties of the implant are considered to be one of the important factors that affect the body response. This is ascribed to the interaction between the implant’s surface and the body fluid. The interaction results in the formation of the interface. The interface is not stable, it is dynamic and many changes could take place such as the detachment or denaturation of proteins. Moreover, the body cells sometimes do not attach to protein. These changes will change the oxide layer and lead to implants’ failure. The change on the interface could lead to implant loosing, corrosion, and wear. Therefore, not just the material sustainability is important, but the integrity of interface plays an important role in
determining the functionality and the biocompatibility of the prosthesis in the body environment (Fleck & Eifler, 2010).

After implantation, there is a series of reactions that take place in the body. These interactions are summarized in Figure 2-3 (Kang et al., 2010).

From Figure 2-3, we can see that device implantation and injury trigger the wound healing and inflammatory responses; the first molecules that come into contact with the device are water molecules. They will bind to the surface in nanoseconds resulting in the formation of a water monolayer (Kang et al., 2010). Then, ions such as $\text{PO}_4^{3-}$, $\text{Cl}^-$, $\text{Na}^+$, and $\text{Ca}^{+2}$ bind to the water monolayer and eventually proteins adsorption, which is part of wound healing. One theory proposed that $\text{PO}_4^{3-}$ adsorbed to water monolayer followed by $\text{Ca}^{+2}$, positive $\text{Ca}^{+2}$ will attract negative charges protein such as albumin to adsorb on the surface. After that cell might adsorp as well (Ellingsen, 1991).
Adsorption of proteins on solid surfaces and their interaction are a major concern in a number of fields such as biology, medicine, and biotechnology. Protein adsorption plays an important role in the system's performance and body environment. Therefore, it is important to look closely to protein adsorption (Geetha et al., 2009; Kang et al., 2010).
Proteins adsorption is not a single simple step. It consists of the initial stage, conformational changes, and maybe replacement of the protein depending on their affinity to the surface, size, and concentration (Kang et al., 2010). Proteins bind, rearrange, possibly denature, and detach. Protein adsorption guides the cell attachment which plays an important role in determining the biocompatibility and longevity of the implants. Adsorption at times should be prevented, especially in heart valves.

The main proteins in human serum are albumin, globulins, lipoproteins, plasminogen, and fibrinogen (Gettens et al., 2005). The adsorbed amount of proteins can be affected by the proteins properties (Nakanishi, et al., 2001). Surfaces physical characterizations such as roughness and morphology can also affect protein adsorption (Anand, 2010).

Proteins properties such as stability of the structure, charge, size, amino acid composition, and change in the proteins conformation upon adsorption can affect the adsorbed amount of proteins. In looking into proteins stability, there are two types of proteins depending on the stability which are highly stable (hard), and low stability (soft). Hard proteins such as α chymotrypsin, lysosome, and ribonuclease could adsorb on the surfaces that have opposite charge. They can adsorb on the surface of the same charge only when there is hydrophobic interaction. The structurally-unstable soft proteins, such as bovine serum albumin (BSA) and human serum albumin (HSA), tended to adsorb on all surfaces regardless of electrostatic
interactions owing to conformational entropy. However, they deforms on hydrophobic surfaces (Nakanishi et al., 2001; Noinville & Revault, 2006).

In looking at the size of the proteins, according to Vroman theory, smaller proteins that have the highest concentration will adsorb first to the surface. Depending on that theory, the sequence of adsorption starts with albumin, followed by immunoglobulin, then to fibrinogen and fibrenoectin, and finishing with a high-molecular-weight kininogen (Gettens et al., 2005; Noinville & Revault, 2006). However, albumin after the layer is formed, albumin might be replaced by immunoglobulin which has a greater affinity toward the implant surface (Hallab et al., 2003). The rate of protein adsorption is very important since the structure change of the proteins is kinetically controlled. The thickness of the adsorbed layer depends on the amino acid on proteins, and the type of the surface (Nakanishi et al., 2001). It has been found that the peptide with a high affinity to surface contains serine, threonine, asparagine, and glutamate residue. This suggests a large contribution to the acid residues on adsorption (Nakanishi et al., 2001). The thickness and the structure of adsorbed proteins on these materials were measured using atomic force microscopy (AFM) (Hedberg et al., 2012; Selvakumaran et al., 2008). Albumin dominates the interaction with the implants due to its high concentration and mobility (Narayan, 2012). Proteins concentration also plays a critical role on the adsorption. If the concentration of the albumin is low (e.g. < 0.04mg/ml), the adsorption will occur in one step, but if the concentration of albumin is high (> 0.2mg/ml) then, the adsorption will take place in two different
steps. The first one does not take time and the attached proteins do not change their conformation while the second step is slow and the thickness of the adsorbed layer increases (Nakanishi et al., 2001).

Proteins play a significant role on corrosion. They can enhance corrosion rate which will reduce the implants’ lifetime. This is due to proteins forming complexes that leave the implants and activate the surface. On the other hand, proteins adsorption can reduce corrosion rate by adsorbing on the implants surface and reducing ions transfer from and to the implants which will enhance the implants’ lifetime (Roach et al., 2005) Moreover, the adsorbed layer also serves as a lubricant that reduces the metal loss and friction (Yan et al., 2007).

The final stage is the cell attachment to the proteins via cell membranes. This stage depends on how the protein layer is composed and organized. Proteins layer formation and organization depends on water and ions binding to the implant’s surface (Kasemo & Gold, 1999). Protein layer is not static, and it is undergo a slow dynamic change in composition and conformation. It has been found that the main amino acid sequence that triggers the cell attachment is Arginine-Glycine-and Aspartate (Arg-Gly-Asp) (Puleo et al., 2002). What happens after cell attachment is summarized in Figure 2-4.
2.4 Metallic implant failures

There are many factors that can lead to an implants’ failure. As a consequence, revision surgery is required. The main causes of implant failure are stress shielding, corrosion, wear particle, and ion release (Geetha et al., 2009).

2.4.1 Stress shielding

Stress shielding happens because of the wide difference in elastic modulus between metals and the bone. This cause unequal transfer of the load consequently, the implant bears a larger load compared to the bone. This will lead to bone
reabsorption and prosthesis loosing. Bone reabsorption can also happen due to wear particles being released from an articulating surface. Scientists try to solve this dilemma by finding new alloys that have elastic modulus close to the bone modulus (40 Gpa). One of the proposed alloys is TiNi that has an elastic modulus of 48Gpa. However, this alloy has not had enough studies in vivo test studies (Oron et al., 2012; Perla & Webster, 2005). Scientists have also tried to solve this issue by coating implants with polymers such as hydroxyapatite. However, they noticed that the coating binding with bones increases but the binding with the implant decreases due to the difference in the thermal expansion coefficient which leads to the detachment of the coating from the implants (Tsui et al., 1998).

### 2.4.2 Corrosion

Corrosion is one of the main reasons for implant failure. Corrosion is defined as” *destructive results of chemical reaction between a metal or metal alloy and its environment*” (Jones, 1996). Corrosion impairs the implants integrity and may lead to implant fracture or corrosion products can invoke body response. Moreover, it can affect nearby cells because of the electrical current, or change the pH around the implant, or alter the metabolism of the cell due to the metal ions. Some of the most common types of corrosion in biomedical alloys are galvanic corrosion, fretting corrosion, crevice corrosion, and pitting corrosion (Balamurugan et al., 2008)

One important feature in metallic prostheses is the ability to form an oxide layer. The oxide layer consists mainly of metal oxides. This layer prevents ions and
electrons from migrating across the film which reduces oxidation reduction reactions. However, the layer must be fully covered and remain intact on the surface to reduce corrosion (Jacobs et al., 1998).

The environment in the body is a hostile environment due to the presence of different compositions like water, blood, proteins, plasma, dissolved oxygen and saliva. Body solutions have anions such as Cl\(^-\), PO\(_4\)^{3-}, and HCO\(_3\)^- and cations such as Na\(^+\), Ca\(^{2+}\), K\(^+\), and Mg\(^{2+}\). The presence of these constituents disturbs the oxide layer on metallic implants and accelerates corrosion. Most of the alloys that have been used in manufacturing prostheses can regenerate the passive layer which takes time. Hanawa (Hanawa, 2003) found that Ti6Al4V takes less time to re-passivate compared with Co28Cr6Mo and 316L, respectively. This means that the numbers of ions released from 316L are higher than CoCrMo and Ti6Al4V. Table 2-8 shows the effect of some ions in the body. Akaskal (Aksakal et al., 2004) investigated retrieved implants made of Ti6Al4V and 316L SS under SEM. The results showed that failures were due to fatigue and fretting corrosion which impair the implants and lead to intergranular cracking. Thus, it eventually leads to the loss of integrity of the implants and failure.
Table 2-8: Ions release damage to the human body (Manivasagam et al., 2010)

<table>
<thead>
<tr>
<th>Ions release from implants</th>
<th>Effect on the body</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nickel</td>
<td>Affect skin</td>
</tr>
<tr>
<td>Cobalt</td>
<td>Inhibit iron from binding to red blood cell which leads to anemia</td>
</tr>
<tr>
<td>Chromium</td>
<td>May disturb the nerve system</td>
</tr>
<tr>
<td>Aluminum</td>
<td>Can cause Alzheimer disease</td>
</tr>
<tr>
<td>Vanadium</td>
<td>May cause toxicity</td>
</tr>
</tbody>
</table>

In a study by Sivakumare on the causes of 316L failure, (Sivakumar et al., 1995) they found that ≈42% of 316L SS implant failures was due to fracture while corrosion ranked second with 24% followed by adverse tissue reaction, bending of the implants, severe wear, and cracking without fracture. A similar result was found in a recent study as well by Manivasagam (Manivasagam et al., 2010; Sivakumar et al., 1995).

Different techniques have been developed to study the formation and destruction of the oxide layer. One electrochemical test method to detect the formation of the oxide layer of different materials is open circuit potential (OCP). An increase of the potential toward more positive values is an indication of the passive layer formation, and a stable potential (5 mV change in 10 minutes) (Stansbury & Buchanan, 2000) indicates that the layer has reached to a steady state condition whereas the drop
of the potential in the negative direction means that there is a breakdown in the film (Karimi et al., 2011). Figure 2-5 shows that all the metals that have been used as prostheses are forming oxide layer due to the increase in the OCP values which indicates the formation and stabilization of the passive layer (Fleck & Eifler, 2010).

However, the passive layer does not remain completely inert in the body. The oxide layer breakdown leads to corrosion enhancement and ions release (Balamurugan et al., 2008).

![Figure 2-5: OCP as a function of time for different materials in deaerated Hank's solution at 37°C (Fleck & Eifler, 2010)](image)

### 2.5 Proteins effect on the corrosion behavior of CoCrMo

Proteins are the most abundant macromolecule that is present in the body with a multifunction. The building block of proteins is amino acids. There are 20
essential amino acids that form proteins. All amino acids consist of a carboxyl group, an amino group, a hydrogen atom, and a functional group (R) bonded to the same \( \alpha \) carbon. Depending on the chemical composition, size, and electrical charge of the R group, the function of the proteins can be determined (Nelson et al., 2013).

Amino acids connect through peptide bonds and form polypeptide. Proteins can be made from thousands of polypeptides depending on their size. Proteins can be found in the body as a small molecule or as a large macromolecule such as hormone, and enzyme (Nelson et al., 2013).

The proteins in human serum are classified into six different systems, depending on their functions which are: the clotting system, complement system, protein inhibitors, immunoglobins, lipoproteins, and carrier proteins such as hemoglobin, myoglobin, collagen, myosin, fibrinogen, fibronectin, and albumin (Nelson et al., 2013).

Albumin is one of the most abundant proteins in the body with concentrations ranging from 35 to 50 \( gL^{-1} \). Albumin is synthesized in the liver with 21 days as the average life span. It has a negative charge in the body pH (Anderson et al., 2004; Martel et al., 2011). Albumin is a multifunctional protein in the body which is capable of binding with metal ions through its binding sites, which is one of the reasons why it is highly studied (Roche et al., 2008). It is also considered to be protein inhibitor which is responsible for the inactivation of certain enzymes to maintain the equilibrium in the body. Moreover, albumin acts as a transporter protein. Albumin has a globular shape, and it is one of the rarest of proteins that
does not attach to carbohydrates (Padilla et al., 2005; Runaw et al., 2011). Since albumin is the most-abundant protein, it is one of the first adsorbed proteins due to its high concentration (Gettens et al., 2005; Padilla & Bronson, 2007; Roach et al., 2005). According to mass transport law, albumin arrives first to the implant because of its high concentrations. The role of albumin adsorption and conformation determines the longevity of the implants (Serro et al., 2010; Vidal et al., 2010).

Proteins play a significant role in the corrosion behavior of metallic implants due to its ability to bind with metal and form a biofilm that accelerates corrosion. This can be explained by the formation of a complex between the metal and proteins. The complex is transported from the metal surface. Therefore, the system is driving toward equilibrium by increasing the dissolution rate which will result in obstructing the passive layer formation. In a Ti based alloy, albumin was found to increase corrosion resistance by adsorbing on the surface of the metal which limits the metal dissolution by decreasing the oxygen evolution reaction (Virtanen et al., 2008). The corrosion behavior of Co28Cr6Mo has been studied widely in the presence of BSA at different concentrations. This is because albumin adsorption is one of the most important steps that determine the implant’s lubrication (Serro et al., 2010).

The effect of BSA can be seen in OCP graphs in Figure 2-6. Karimi noticed that the OCP values for CoCrMo drop upon increasing the concentration then increase until it stabilizes. This is ascribed to the competition between cobalt
dissolution and BSA adsorption. Moreover, Karimi noticed that at a higher concentration of BSA, the adsorption became predominant over the dissolution (Karimi et al., 2011). While Wang has found that upon immersing a Ni alloy, the OCP values increase directly until it reaches a plateau that is due to the formation and stabilization of the passive layer. This means that each metal reacts differently in the presence of phosphate ions and BSA (Karimi et al., 2011; Wang et al., 2012). This might be explained by Ni forms a passive layer upon immersion while CoCrMo OCP values drops due to Cobalt dissolution and increase due to passive layer formation.

![OCP plots showing the effect of different BSA concentrations on the E_{oCP} of CoCrMo (Karimi et al., 2011)](image)

**Figure 2-6: OCP plots showing the effect of different BSA concentrations on the E_{oCP} of CoCrMo (Karimi et al., 2011)**

Another study investigated the effect of BSA on NaCl and PBS solutions. They found a decrease in the corrosion potential upon adding $0.5gL^{-1}$ BSA to the NaCl
solution, however, the drop was greater in PBS solution as it is illustrated in Figure 2-7. This is due to the presence of phosphate and albumin in the solution. It was found that the phosphate shifts the corrosion potential to more anodic values while albumin shifted to more cathodic values. However, albumin dominates the electrochemical reactions over phosphate ions. Albumin increases the passive current while phosphate has the opposite effect. The trans-passive behavior was similar in the presence and absence of phosphate and albumin (Muñoz & Mischler, 2007; Vidal & Muñoz, 2010). Phosphate works as an anodic inhibitor while albumin acts as a cathodic inhibitor for the CoCrMo alloy (Vidal & Igual Muñoz, 2008). However, BSA is known for having double effects on the metallic implants. It can accelerate corrosion by forming complexes with metal product or decrease the corrosion by adsorbing on the surface and block charge transfer (Wang et al., 2012).
Figure 2-7: Potentiodynamic polarization curve showing the effect of BSA on the corrosion potential for a) NaCl b) and PBS (Vidal & Muñoz, 2010)

Vidal and co-workers analyzed the effect of temperature and the albumin concentration on CoCrMo. They concluded that temperature affects the corrosion potential and the breakdown potential, however, the corrosion current density and the passive current density were found to be affected by albumin concentrations. In low concentrations below 20 mgL\(^{-1}\) there is no change while in high concentrations above 200 mgL\(^{-1}\) there is a decrease in the corrosion current density. Moreover, they noticed that increasing the BSA concentration increases the semicircle diameter.
which means increasing the charge transfer resistance of CoCrMo despite the temperature as shown in Figure 2-8 (Vidal et al., 2010).

Vidal and colleagues studied the effect of pH on the corrosion behavior of CoCrMo as shown in Figure 2-9. They found that in acidic, alkaline, and neutral solutions, the presence of BSA reduces the corrosion potential. The effect was more obvious in the aerated solutions compared to deaerated solutions (Vidal & Muñoz, 2011).
Figure 2-9: Potentiodynamic polarization curves showing the effect of different pH a) 3 b) 7.4, and c) 10 at 37°C in the presence and absence of BSA in aerated and deaerated solutions (Vidal & Muñoz, 2011)
2.6 Hyaluronic acid and its effect on the corrosion behavior of CoCrMo

Hyaluronic acid (HA) is one of the main components of SF that could affect the corrosion behavior of biomaterials in human bodies. The effect of HA on the corrosion performance of CoCrMo can be investigated by testing CoCrMo using advanced electrochemical corrosion techniques. To our knowledge, there are few corrosion studies that investigated the corrosion behavior in the presence of HA.

One study by Milosev and co-workers investigated the effect of HA on the corrosion behavior of CoCrMo using Hank’s solution and NaCl solutions as background solutions (Milosev et al., 2013). The investigation addressed the effect of HA as a function of time on the variation of corrosion potentials ($E_{corr}$) and polarization resistance ($R_p$) as shown in Figure 2-10. They noticed that the $E_{corr}$ shifted to more negative values in the presence of HA compared to plain NaCl. However, longer immersion time shifted the corrosion potential of NaCl+HA to more positive values. The $R_p$ values show a similar trend in NaCl and Hank’s solution where they reached a plateau after 10 hours then it decreased sharply after 25 hours of immersion. In the presence of HA in both solutions the final $R_p$ values after 25 hours were higher compared to plain solutions. This shows that the layer becomes more protective upon adding HA.
The effect of the immersion time can also be seen in the potential dynamic curve (Milošev et al., 2013). In both solutions increasing the immersion time, shifted the corrosion potential toward more positive values in the presence and absence of HA. Figure 2-11 (Milošev et al., 2013)
Figure 2-11: The effect of HA and time on the potential dynamic curves a) NaCl and b) Hank’s solution (Milošev et al., 2013)
From the previous figure, adding HA to Hank’s solution in Figure 2-11(b) increased the potential after one hour. The same effect was found after 10 hours for the same solution while this effect was not obvious in NaCl solution in Figure 2-11(a).

A study was done by Serro and colleague (Serro et al., 2010) to examine the adsorption of BSA and HA on ultra-high molecular weight polyethylene (UHMWPE). They used 0.05-20 mg ml\(^{-1}\) of BSA and 0.5 mg ml\(^{-1}\) HA. These concentrations are similar to osteoarthritis patients. They found that BSA and HA competitively adsorbed on UHMWPE. However, BSA adsorbed strongly on UHMWPE while HA adsorbed weakly. When BSA and HA presents in the same solutions, there is a change in the adsorbed amount of BSA which could be related to low quantity of HA adsorb (Serro et al., 2010).

From the previous part, it is obvious that the effect of a high concentration of BSA on the corrosion behavior of CoCrMo, the effect of HA concentration and the synergetic effect of both BSA and HA on the corrosion behavior of CoCrMo is not fully studied.
3 Objective

Mimicking the SF environment which is the fluid that fills the cavity of the synovial joints can be done in the lab by adding similar inorganic components such as phosphate (PO$_4^{3-}$), sodium (Na$^+$), and chloride (Cl$^-$). Moreover, SF contains organic compounds such as proteins, and glycosaminoglycan (GAG). The dominant protein that exists in SF is albumin while the main GAG is hyaluronic acid. Based on literature review, there are a few studies which evaluate the corrosion performance of Co$_{28}$Cr$_6$Mo in the presence of HA but not in the presence of both BSA and HA. The objectives of this study can be summarized in the following points:

1- Study the effect of 10.5 gL$^{-1}$ BSA on the corrosion behaviour of CoCrMo.

2- Investigate a variety of HA concentrations (1.3, 2.3, 3, and 4 gL$^{-1}$) to evaluate the effect of HA concentration on corrosion performance of CoCrMo.

3- Identify the synergetic effect of HA and BSA on the corrosion performance of CoCrMo in PBS solutions.

To fulfill the objectives, electrochemical tests have been used. These techniques help in evaluating the oxidation layer growth and breakdown, cathodic and anodic behavior, and calculate the corrosion rate.
4 Approach and methodology

The aim of this work is to study corrosion behavior of Co28Cr6Mo in the presence of the main constituents of SF which are albumin with different concentrations of hyaluronic acid. Corrosion behavior was evaluated using advanced electrochemical corrosion experiments including open circuit potential (OCP), potentiodynamic polarization (PDP), electrochemical impedance spectroscopy (EIS), and linear polarization resistance (LPR). Details about the procedures and the electrolytes are given below:

4.1 Materials

4.1.1 CoCrMo metallography and chemical composition

A 2.5 cm rod of Co28Cr6Mo (ATI Allvac Limited) as cut into 2.5 mm long discs. The samples were polished using silicon carbide grinding paper starting from 120, 300, 600, and 1200 then to 6 µ, and 1µ using alumina powder. After that, samples were cleaned ultrasonically in soap for 5 minutes, distilled water for 5 minutes, rinsed with ethanol, and finally dried with hot air. The sample was then etched using 20 mL of 37 vol% hydrochloric acid (HCl) and 1mL of 30 vol % hydrogen peroxide (H2O2). After that the samples were examined under the optical microscope. The microstructure of Co28Co6Mo is illustrated in Figure 4-1.
Figure 4-1: The microstructure of Co28Cr6Mo etched with 20 mL 37 vol% hydrochloric acid (HCl) and 1 mL 30 vol% hydrogen peroxide (H2O2)

From the optically observed microstructure, interdendritic primary (M33C6) can be observed which is rich in chromium with a FCC matrix. The grain boundaries can also be seen. The formation of FCC phase depends mainly on the carbon content, and the other alloy elements.

Table 4-1: Chemical compositions of Co28Cr6Mo according to ASTM F1537

<table>
<thead>
<tr>
<th>Composition wt%</th>
<th>C</th>
<th>Fe</th>
<th>Cr</th>
<th>Ni</th>
<th>Mo</th>
<th>Co</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alloy Co28Cr6Mo</td>
<td>0.05-0.35</td>
<td>0.75 Max</td>
<td>26-30</td>
<td>1 Max</td>
<td>5-7</td>
<td>Bulk</td>
</tr>
</tbody>
</table>
4.1.2 CoCrMo preparation for corrosion tests

Co28Cr6Mo was connected to a wire using conductive silver epoxy to ensure the electrical conductivity. Then, the sample (1.256 cm$^2$) was buried in a cold-curing epoxy resin (LECO). After that, Co28Cr6Mo was mechanically polished starting from 120, 300, 600, and 1200 grit silicon carbide paper, then the polishing process was continued using 6 µ and 1 µ alumina powder. The sample was cleaned ultrasonically in soap for 5 minutes, deionized water for 5 minutes, rinsed with ethanol, and dried with hot air before each electrochemical test.

4.2 Electrolytes

The corrosion performance of Co28Cr6Mo was evaluated in the phosphate buffer saline solution (PBS) as a background solution. Bovine serum albumin (10.5 g L$^{-1}$) was added to PBS to investigate the effect of a high concentration of BSA in the corrosion behavior of the alloy. Different concentrations of Hyaluronic acid were added to PBS only and to PBS with BSA to study the effect of increasing HA concentrations in the presence and absence of BSA. The experiments were conducted in an aerated environment at 37°C.

4.2.1 Phosphate buffer saline

PBS was prepared according to ASTM-2129. The chemical composition of PBS is illustrated in Table 4-2. The PBS solution was prepared by carefully weighing the chemicals into a weight boat, putting them in 1 L flask, and diluted with distilled water until the water reached the meniscus of the flask. The solution was then
stirred until all the chemicals completely dissolve in distil water. PBS was chosen due to similarity to the inorganic components of SF (Lewis et al., 2005).

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Concentrations (gL⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>8.00</td>
</tr>
<tr>
<td>Na₂HPO₄</td>
<td>1.15</td>
</tr>
<tr>
<td>KCl</td>
<td>0.20</td>
</tr>
<tr>
<td>KH₂PO₄</td>
<td>0.20</td>
</tr>
</tbody>
</table>

### 4.2.2 Bovine serum albumin

Bovine serum albumin is a polypeptide chain composed of 585 amino acid (Hirayama et al., 1990; Roche et al., 2008). The molecular weight is 66430 Dalton (Dalton is a unit that has been used to describe mass on molecular scale and it is equivalent to g/mol)(Markelz et al., 2008) Albumin is present in all mammals. Bovine serum albumin (BSA) is used to simulate human serum albumin (HSA). 75.8% of BSA is identical to HSA (Bujac, 2012). This is the main reason for using BSA extensively in the laboratory as a substitute for HSA. One of the main differences between BSA and HSA is the number of tryptophan amino acids. Tryptophan is one of the essential amino acids. It is an aromatic amino acid that is involved in hydrophobic interactions. The structure of Tryptophan is illustrated in Figure 4-2. BSA has two tryptophans while HSA has only one (Moriyama et al., 1996). The BSA has a secondary structure that consists of 67% helix, 10% turn, and 23% extended chain (Bujac, 2012).
Figure 4-2: Chemical structure of tryptophan (Nelson et al., 2013)

The crystal structure of BSA has been taken from the protein data bank (PDB) which is shown in Figure 4-3. From the graph we can see that there are sex domains each color represents one domain. A domain in protein is a specific functional or structural unit which is responsible for specific interaction or function. The graph also shows a ligand, binding site, which is Triethylene glycol (C₆H₁₄O₄)

The BSA was received as a powder from Sigma Aldrich Inc. The concentration that has been used in this study is 10.5 gL⁻¹. This selection was based on the concentration of albumin in the synovial fluid in which the albumin concentration varied from 8 to 13 gL⁻¹. 10.5 gL⁻¹ of BSA was added to 1 L of PBS solution and stirred until BSA completely dissolved.
4.2.3 Hyaluronic acid

Hyaluronic acid is a long unbranched GAG that has a linear structure (Meyer, 1947). HA consists of repeating disaccharide units that are N-acetylglucosamine and glucuronic acid [(1→3)-β-D-GlcNAc-(1→4) β-D-GlcNAc]. The chemical structure of HA is illustrated in Figure 4-4.
In the body, HA has been found in salt form (Necas et al., 2008). HA is an extremely hydrophilic molecule (Necas et al., 2008). HA, as a part of the synovial fluid, has an important function. It acts as a lubricant, gives viscosity to synovial fluid, binds with water, absorbs shocks, helps in wound healing, and interacts with cell receptors which will affect a series of actions of the cell (Necas et al., 2008). Moreover, HA has been used as a treatment for people with osteoarthritis to reduce pain (Milošev et al., 2013). HA presents in normal people with a concentration range from 3.2 to 4.1 mg mL\(^{-1}\) and the molecular weights are 6-7MDa. These concentrations decrease sharply in people with osteoarthritis. Osteoarthritis damages the cartilage in the synovial joints which reduces HA concentration to 1.2-2.2 mg mL\(^{-1}\) (Cooper et al., 2013; Hui et al., 2012).

HA was provide from Stanford Chemicals as a powder. HA concentrations of 1.3, 2.3, 3, and 4 gL\(^{-1}\) were employed. These concentrations represent the concentrations in normal people and people with osteoarthritis. HA was added to 1 L of PBS and stirred for overnight due to its high molecular weight. HA also was added to PBS solutions containing BSA to simulate the synovial fluid environment.
The reason for studying PBS with BSA, PBS with HA, and PBS with both BSA and HA is to be able to determine what the effect of each one of them is separately. This will help in understanding corrosion performance of Co28Cr6Mo when both BSA and HA are present.

**4.3 Electrochemical tests**

Electrochemical experiments were conducted using a three-electrode electrochemical cell (volume 1200 mL). The cell has a water jacket which was connected to water bath to maintain a temperature of 37°C. The solution pH was 7-7.4. A Saturated Calomel Electrode (SCE) was used as a reference electrode while a graphite counter electrode was used. The working electrode was embedded in an ultra-high molecular weight polyethylene (UHMWPE) holder with 1.256 cm² area of the sample exposed to the electrolyte. Corrosion tests were carried out using a Princeton Applied Research (PAR) Versastat 4 galvanostat. The setup is illustrated in Figure 4-5 and Figure 4-6.

Each test was repeated three times to ensure the reproducibility of the results. One representative graph was chosen in Figure 4-7 to show the reproducibility.
Figure 4-5: The electrochemical corrosion test setup

Figure 4-6: Potentialstat (Princeton Applied Research VersaSTAT 4)
The electrochemical corrosion tests were commenced by a potentiostatic corrosion experiment in which the voltage was set at -1 V vs. SCE for 10 minutes. The main purpose of this was to clean the surface and to remove the oxide layer formed in the air before immersing the samples into the solution.
The details about each experiment are given below:

1- Open circuit potential (OCP): The OCP were carried out for different times until a stable potential was reached. The purpose of this technique is to monitor the potential change with time, and to reach a steady state.

2- Potentiodynamic polarization (PDP): was conducted in the potential range of -0.50 to 1 V vs SCE. A scan rate of 0.167 mV vs SCE after OCP was used. PDP is a useful technique to evaluate the anodic, cathodic, passivity, and trans-passivity behavior of the electrode. The interpretations of the results were used to calculate the corrosion rate.

3- Electrochemical impedance spectroscopy (EIS): tests were performed in a frequency range of $10^{-2}$ to $10^4$ Hz with 10 points per decade and 10 mV amplitude. The experiment was conducted to investigate the growth and resistivity of barrier layers. Moreover, the corrosion rate can be calculated.

4- Linear polarization resistance (LPR): tests were conducted at ±20 mV vs SCE after OCP. The potential sweep is 0.167 mV s$^{-1}$. The corrosion rate was also calculated by obtaining the polarization resistance ($R_{P-LPR}$) from LPR.
5 Results and discussion

5.1 Corrosion behavior of CoCrMo in PBS+BSA solutions

5.1.1 Open circuit potential (OCP)

Examining the corrosion behavior of CoCrMo in PBS and BSA by electrochemical corrosion tests such as EIS, required a steady potential. This can be done by immersing a working electrode in the selected solutions and measuring the potential changes as a function of time until the potential variation is less than 5 mV in 10 min (Stansbury & Buchanan, 2000). CoCrMo immersed in PBS required 4 hours to reach a steady potential while CoCrMo needed 6 hours before it reached the steady potential in the presence of 10.5 gL⁻¹ BSA. The OCP graph for CoCrMo in PBS with 0 and 10.5 gL⁻¹ BSA is shown in Figure 5-1.

There was an increase in the potential when the sample was immersed in PBS solution with and without BSA. This can be explained by the formation and growth of the oxide layer on CoCrMo. This behavior was also observed in other studies (Karimi & Alfantazi, 2013; Vidal & Igual Muñoz, 2011). CoCrMo is well known for spontaneous passivation behavior when it contacts with body fluid (Vidal & Muñoz, 2008). Hodgeson et al investigated the chemical composition of CoCrMo passive layer and they found that it mainly contains Cr (III) with a small contribution of Cr(OH)₃. The relatively high corrosion resistance of CoCrMo was due to the presence of these chemical substances (Hodgson et al., 2004).
Phosphate ions are known to work as an anodic inhibitor which increases the potential for CoCrMo (Vidal & Muñoz, 2008) while albumin is known to work as a cathodic inhibitor for CoCrMo. BSA adsorbs onto CoCrMo and decreases the transport of O\(_2\) and therefore inhibits the cathodic reaction and shifts the potential toward more negative values. Meanwhile, albumin can work as an anodic accelerator by forming complexes with metal ions. This behavior is also seen in 316L stainless steel (Karimi et al., 2011; Vidal & Muñoz, 2010; Wang et al., 2012). The decrease in the OCP values upon adding BSA is not obvious. This can be explained by longer immersion time of CoCrMo in PBS of approximately 6 hours. Vidal has noticed that the change in the OCP values in the presence of BSA is not significant after 75 minutes. The change on the beginning of OCP is due to the combined effect of passivation and BSA adsorption. Therefore, Vidal concludes that the effect of BSA decreases with the increase in the passivation time which agrees with our findings (Vidal & Muñoz, 2010). The values for final OCP are illustrated in Table 5-1.

Overall, the BSA effect as a cathodic inhibitor in CoCrMo is not very obvious with a longer immersion time according to our results.
Table 5-1: OCP measurements after 4 and 6 hours immersion

<table>
<thead>
<tr>
<th>BSA (gL⁻¹)</th>
<th>OCP (V vs. SCE) at 14000 sec</th>
<th>Final OCP (V vs. SCE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>-0.0620 ± 0.004</td>
<td>-0.061 ± 0.003</td>
</tr>
<tr>
<td>10.5</td>
<td>-0.080 ± 0.023</td>
<td>-0.054 ± 0.020</td>
</tr>
</tbody>
</table>

5.1.2 Potentiodynamic polarization (PDP)

Potentiodynamic polarization is a good tool to investigate the general corrosion behavior of an alloy. To understand the polarization curve interpretation, Figure 5-2 shows the important areas in PDP curves and how to extract $E_{corr}$ and $i_{corr}$ form the graph.
From the graph, the lower part represents the cathodic branch where species in the solution are reduced. The part where the current increases is where the corrosion is taking place. The passive area is where the current decreased due to passive layer formation. The transpassive area is where the oxide layer is attacked and there is corrosion happening. The $E_{corr}$ and $i_{corr}$ can be obtained from the curve as shown in Figure 5-3.
Figure 5-3: Extrapolation of $i_{corr}$ and $E_{corr}$ from PDP curves

Figure 5-4 shows the potentiodynamic polarization curve for CoCrMo in a plain PBA and in PBS containing BSA. The cathodic branch includes potentials below -0.4 V vs SCE. The cathodic branch shifted to lower values upon adding BSA. This can be explained as decreasing oxygen reduction reaction due to BSA adsorption which blocks the active site of oxygen in the metal (Tang et al., 2006). Moreover, according to a study done by Stankovish and Bard, BSA reduces at -0.455 to -0.655 V vs. Ag/AgCl and a current range between 3.7-7.5µA cm² (Tang et al., 2006). Therefore, the cathodic branch in the presence of BSA could be the sum of BSA and $O_2$ reduction (Karimi et al., 2011). The cathodic current in PBS solution is mainly due to water and somewhat the oxygen reduction (Vidal et al., 2010). By water reduction, I think Vidal means by reduction is the reaction that takes place on the cathode which is hydrogen reaction. Therefore, the shift of the cathodic branch to lower values in
the presence of BSA could be due to BSA and hydrogen reduction. The second domain represents the current conversion from cathode to anode (-0.40 to -0.20 V vs. SCE).

The third domain represents the passive plateau which is from 0 to 0.5 V vs. SCE. The $E_{OCP}$ is different from the $E_{corr}$ due to the change in the oxide layer after cathodic scanning (Wang et al., 2012). In the presence of BSA, $E_{corr}$ shifted to lower values due to the effect of BSA which works as a cathodic inhibitor of CoCrMo. Phosphate and BSA compete in adsorption; however, BSA has more affinity to adsorb (Wang et al., 2012). Karimi and colleagues (Karimi et al., 2011) have investigated the passive layer composition of CoCrMo in a plain PBS solution and in the presence of 4 $gL^{-1}$ BSA at 0.007 V vs. Ag/AgCl. Karimi has found that in the presence of BSA in PBS solution, the amount of anions such as phosphate decreases. Moreover, Co was detected in PBS solution containing BSA while in a plain PBS solution, the Co was not observed. This can be interpreted by the high affinity of BSA to react with Co and form a protective layer that prevents anions from reaching the oxide layer (Karimi et al., 2011; Milošev et al., 2000).

There are two shoulders at around 0.50V vs. SCE. The first one is due to phosphate-chromium formation, chromium dissolution (Muñoz & Mischler, 2007; Vidal & Muñoz, 2008). The second one is due to water oxidation and chromium oxidation which cause transpassive behavior and activate the surface (Karimi et al., 2011; Vidal & Muñoz, 2008).
The results shown in this thesis showed that adding BSA did not cause a great change in the corrosion current density. However, there was a slight shift in the cathodic branch in a solution containing BSA which might be explained by a blockage of the CoCrMo surface by BSA adsorption. This leads to reducing the number of the active site in the cathodic branch. The obtained values of $E_{corr}$, $E_b$, $i_{corr}$, and $I_p$ are reported in Table 5-2.

![Potentiodynamic polarization curves of CoCrMo in the presence and absence of BSA in PBS solutions](image)

**Table 5-2: Electrochemical parameters of CoCrMo in PBS 0 and 10.5 gL⁻¹ BSA**

<table>
<thead>
<tr>
<th>BSA (gL⁻¹)</th>
<th>$E_{corr}$ (V vs. SCE)</th>
<th>$i_{corr} \times 10^{-7}$ (A.cm⁻²)</th>
<th>$I_p \times 10^{-5}$ (A.cm⁻²)</th>
<th>$E_b$ (V vs. SCE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>-0.204 ± 0.028</td>
<td>1.54 ± 0.050</td>
<td>1.00 ± 0.099</td>
<td>0.468 ± 0.024</td>
</tr>
<tr>
<td>10.5</td>
<td>-0.300 ± 0.045</td>
<td>1.61 ± 0.162</td>
<td>1.00 ± 0.084</td>
<td>0.444 ± 0.020</td>
</tr>
</tbody>
</table>
5.1.3 Electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy is a useful technique to investigate the resistance of the oxide film that form upon interaction between metallic implant and BSA. Moreover, it is useful in calculating the corrosion rate, and understanding the reactions that take place on the implant’s surface. In Figure 5-5, Bode plots of CoCrMo in PBS with and without BSA at 37 °C are shown.

![Bode plot of CoCrMo in the presence and absence of BSA](image)

Figure 5-5: Bode plot of CoCrMo in the presence and absence of BSA
At high frequency the absolute impedance was independent from frequency from $10^4$ to $10^3$ Hz. These frequency ranges represent the solution resistance between the working and reference electrodes. The phase reached the maximum degree of 70° in plain PBS solution and 75° in the presence of BSA at frequency range between $10^2$ and $10^{-1}$ Hz. This region represents the capacitive behavior of CoCrMo. Moreover, the passive behavior can be seen at these frequency ranges due to the increase in the absolute impedance and the independence of phase from frequency. In the frequency range of $10^{-1}$ to $10^{-2}$ Hz the phase shifted to lower values while the absolute impedance increased. In the presence of BSA, the absolute impedance of CoCrMo was slightly higher than PBS. This result indicates that the resistance increased in the presence of BSA compared to a solution without BSA. Moreover, from the Bode plots, two overlapped time constants can be observed. The presence of two overlapped time constants for CoCrMo is also observed in other studies (Vidal & Muñoz, 2008; Vidal & Muñoz, 2010). One layer is a compact inner oxide layer, while the other is an outer barrier layer representing a combination of adsorbents and passive layers.

A Nyquist diagram with a depressed semicircle arc is shown in Figure 5-6. Based on the existence of two overlapping time constants, an equivalent circuit with two RC circuits may be defined. This circuit is illustrated in Figure 5-7. The inner oxide layer has a resistor ($R_{in}$) along with a capacitor ($C_{in}$). Similar to the inner oxide layer, the outer barrier layer can be characterized by an RC circuit in series to the RC circuit of the inner oxide layer. The components of the outer oxide layer are a
resistor ($R_{out}$) and a capacitor ($C_{out}$) characterizing the combination of passive dissolution and passive layer growth. ($C_{out}$) is also known as the double-layer capacitance (Vidal et al., 2010).

![Nyquist diagram of CoCrMo in the presence and absence of BSA](image1)

**Figure 5-6:** Nyquist diagram of CoCrMo in the presence and absence of BSA

![Simulated circuit for CoCrMo in the presence and absence of BSA](image2)

**Figure 5-7:** The simulated circuit for CoCrMo in the presence and absence of BSA
A constant phase element (CPE) has been used to substitute the ideal capacitor due to non-uniform distribution of the current on the surface. This can be ascribed to surface roughness, dislocations, grain boundaries and impurities (Vidal et al., 2010). The impedance of a constant phase element ($Z_{CPE}$) can be defined according to equation 1.

$$Z_{CPE} = \frac{1}{(j\omega)^n Y_0}$$

(1)

where $n$ is the coefficient due to deviation between real and pure capacitance. $Y_0$ is the general admittance function, and $\omega$ is the angular frequency. The values of the electrical circuit component were determined using the ZimpWin package. All the values of parameters extracted from the software are summarized in Table 5-3. The obtained magnitudes of the simulated electrical circuit component showed a good fit to the Nyquist data $10^4$ Chi square. The good agreement is also shown in Figure 5-8.

Table 5-3: Equivalent circuit parameters of CoCrMo in the presence and absence of BSA

<table>
<thead>
<tr>
<th>BSA (gL⁻¹)</th>
<th>$R_c$ ($\Omega cm^2$)</th>
<th>$CPE_{out}$ ($S^{sec^n}$)</th>
<th>$n_{out}$</th>
<th>$R_{out}$ ($\Omega cm^2$)</th>
<th>$CPE_{in}$ ($S^{sec^n}$)</th>
<th>$n_{in}$</th>
<th>$R_{in}$ ($\Omega cm^2$)</th>
<th>$R_{in}+R_{out}$ ($\Omega cm^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>5.42</td>
<td>7.10e-15</td>
<td>0.428</td>
<td>6.00</td>
<td>7.15e-5</td>
<td>0.881</td>
<td>8.38e+4</td>
<td>(8.38±2.29)e+4</td>
</tr>
<tr>
<td>10.5</td>
<td>10.2</td>
<td>3.46e-4</td>
<td>0.800</td>
<td>231</td>
<td>6.81e-5</td>
<td>0.800</td>
<td>2.29e+5</td>
<td>(2.29±0.013)e+5</td>
</tr>
</tbody>
</table>
The polarization resistance can be calculated as a sum of $R_{in}$ and $R_{out}$ (Vidal et al., 2010). This resistance can then be used to calculate the corrosion rate.

The general behavior can be seen as increasing the semicircle diameter upon adding BSA. This behavior was seen in other studies for CoCrMo (Karimi et al., 2011; Vidal et al., 2010) and other alloys such as niobium (Wang et al., 2012).

The solution with BSA showed a higher resistance compared to plain PBS due to increasing the semicircle diameter in the presence of BSA. This result is in agreement with other studies (Karimi et al., 2011; Vidal et al., 2010).
5.1.4 Linear polarization resistance

The linear polarization (LPR) diagram in the presence and absence of BSA is shown in Figure 5-9. The technique is well known for calculating the corrosion rate by determining the polarization resistance and corrosion current density. The $E_{corr}$ is extracted from the linear polarization curves when the current is zero (Ijsseling, 1986). The over-potential is calculated by subtracting the potentials from $E_{corr}$.

The slope of the graph represents the polarization resistance ($R_{p-LPR}$). The calculated values of $R_{p-LPR}$ and corrosion current densities in the presence and absence of serum are shown in Table 5-4.

The resistance in the presence and absence of serum was similar. Corrosion current density was calculated using equation 2 while the B value was estimated according to equation 3.

$$i_{corr} = \frac{B}{R_p} \quad (2)$$

$$B = \frac{1}{2.3(\frac{1}{\beta_{ox}} + \frac{1}{\beta_{red}})} \quad (3)$$

A good estimation for B is 0.026 V. The assumption was taken from a book (Stansbury & Buchanan, 2000).
Table 5-4: The polarization resistance and the corrosion current density of CoCrMo in the presence and absence of BSA concentrations

<table>
<thead>
<tr>
<th>BSA (gL⁻¹)</th>
<th>$R_p$ (kΩ)</th>
<th>$i_{corr} \times 10^{-7}$ (A.cm⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>195 ± 4.644</td>
<td>1.32 ± 0.003</td>
</tr>
<tr>
<td>10.5</td>
<td>194 ± 17.4</td>
<td>1.33 ± 0.012</td>
</tr>
</tbody>
</table>

5.1.5 Corrosion rate calculations

The corrosion rate of CoCrMo can be calculated using $R_{P-LPR}$ and $R_{P-EIS}$ which were computed from LPR and EIS techniques. The $\beta_{oxi}$ and $\beta_{red}$ can usually be extracted from PDP to calculate B. However, due to the lack of linearity on the
anodic side, the $\beta_{\text{oxi}}$ cannot be calculated. Therefore, a good estimation of $\beta_{\text{oxi}}$ and $\beta_{\text{red}}$ is 60 mV to 120 mV and from 60 mV to infinity respectively and B is .026 V (Stansbury & Buchanan, 2000). The corrosion rate can be calculated using equation 4.

$$\text{corrosion rate (\mu m per year)} = 3.1536 \times 10^5 \frac{a \times i_{\text{corr}}}{n \times F \times \rho} \quad (4)$$

In equation 4, $a$ is the atomic weight in g mol$^{-1}$, $i_{\text{corr}}$ is corrosion current density in $\mu A$ cm$^{-2}$, N is the number of exchanged electrons, F is Faraday's constant (96500 Coulombs mol$^{-1}$), and $\rho$ is the density in g cm$^{-3}$. The equivalent density and atomic weight of the CoCrMo alloy is 8.30 g cm$^{-3}$ and 23.96 g mol$^{-1}$ used to calculate the corrosion rate of CoCrMo. Table 5-5 shows the values of all corrosion rates of CoCrMo in PBS solution with and without the albumin.

<table>
<thead>
<tr>
<th>BSA (gL$^{-1}$)</th>
<th>$N$</th>
<th>$R_P$ (LPR) (k$\Omega$)</th>
<th>$i_{\text{corr-LPR}} \times 10^{-7}$ (A.cm$^{-2}$)</th>
<th>Corrosion rate (LPR) (LPR) ($\mu A$/year)</th>
<th>$R_P$ (EIS) ($\Omega$)</th>
<th>$i_{\text{corr-EIS}} \times 10^{-7}$ (A.cm$^{-2}$)</th>
<th>Corrosion rate (EIS) ($\mu A$/year)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>3</td>
<td>195</td>
<td>1.32</td>
<td>0.420 ± 0.010</td>
<td>83.8</td>
<td>3.10</td>
<td>0.976 ± 0.265</td>
</tr>
<tr>
<td>10.5</td>
<td>194</td>
<td>1.33</td>
<td>0.420 ± 0.032</td>
<td>256</td>
<td>1.01</td>
<td>0.319 ± 0.016</td>
<td></td>
</tr>
</tbody>
</table>

To sum up, the presence of BSA in the solution decreased the corrosion potential due to the cathodic inhibition effect of BSA. The resistance of CoCrMo became stronger in a solution with serum. However, the corrosion rate did not show a noticeable change upon adding 10.5 gL$^{-1}$ of BSA.
5.2 Corrosion performance of CoCrMo in presence of PBS with different HA concentrations

5.2.1 Open circuit potential

OCP was carried out in PBS solutions with different HA concentrations (1.3, 2.3, 3, and 4 gL⁻¹) to study the effect of HA concentrations on the corrosion performance of CoCrMo. Different times were needed to reach a steady state potential for different concentrations. The required immersion time for the CoCrMo alloy immersed in 1.3 and 2.3 gL⁻¹ HA was 4 hours while the samples immersed in solutions with 3 gL⁻¹ needed 7 hours. 4 gL⁻¹ HA required a longer immersion period to reach to a steady potential (12 hours). This showed that increasing the concentrations of HA increased the required time to form and stabilize the oxide layer. Milosev et al. stated that CoCrMo alloy needs a longer time in NaCl and Hank’s solution in the presence of HA to reach to a steady potential compared to plain NaCl (Milošev et al., 2013). This could be due to the high molecular weight of HA which may need more time to arrange a steady accommodation on the surface of CoCrMo.

The result of OCP measurements are shown in Figure 5-10.

From the graph, we can see that there was a similar trend of an initial rapid increase in the corrosion potential upon immersion until reaching a plateau for OCP of CoCrMo for various HA concentrations. The increase of OCP can be explained by the formation and stabilization of the oxide layer. This behavior is noticed in the Hank’s solution for the CoCrMo alloy in another study (Milošev et al., 2013). Unlike
OCP increases in Hank’s and PBS solutions, the OCP decreases in the absence of phosphate ions and only in NaCl solutions (Milošev et al., 2013). Therefore, the precipitation of phosphate ions on CoCrMo could be the reason for increasing OCP values.

Increasing the concentration of HA decreased the OCP potential ($E_{OCP}$) measured after 14000 seconds. The HA concentration played a role in the OCP drops. For example, the addition of 1.3 and 2.3, and 3 gL$^{-1}$ of HA did not show a significant decrease in the OCP potential, however, adding 4 gL$^{-1}$ of HA decreased the OCP potential dramatically. Similar behavior of the OCP potential of CoCrMo was found in the presence of HA in Hank’s solution for final OCP (Milošev et al., 2013). Milošev explained that HA could work either as anodic or cathodic inhibitor. Therefore, it decreased the $E_{OCP}$ according to the mixed potential theory. The final values of $E_{OCP}$ are shown in Table 5-6.
Figure 5-10: The effect of increasing the concentration of HA in the open circuit potential

<table>
<thead>
<tr>
<th>HA ($gL^{-1}$)</th>
<th>OCP potential ($V$ vs SCE) at 14000 sec</th>
<th>Final OCP values ($V$ vs. SCE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>-0.062± 0.004</td>
<td>-0.061± 0.003</td>
</tr>
<tr>
<td>1.30</td>
<td>-0.142± 0.081</td>
<td>-0.142± 0.081</td>
</tr>
<tr>
<td>2.30</td>
<td>-0.154± 0.062</td>
<td>-0.154± 0.063</td>
</tr>
<tr>
<td>3.00</td>
<td>-0.263± 0.053</td>
<td>-0.229± 0.067</td>
</tr>
<tr>
<td>4.00</td>
<td>-0.441± 0.041</td>
<td>-0.370± 0.072</td>
</tr>
</tbody>
</table>

Therefore, the general trend was decreasing the $E_{OCP}$ values by increasing HA concentration.
5.2.2 Potentiodynamic polarization

In order to study the effect of HA on the corrosion potential, passivity, and the cathodic and anodic behavior of CoCrMo, PDP experiments were performed after OCP for different concentrations of HA (1.3, 2.3, 3, and $4 \text{ g L}^{-1}$). The results are illustrated in Figure 5-11. It showed that adding HA decreased $E_{\text{corr}}$ to lower values in PBS solutions.

Adding HA shifted the corrosion potential toward slightly lower values. The potential drop was up to 100 $\text{mV}$ vs SCE when HA was added. However, increasing the concentration up to $4 \text{ g L}^{-1}$ showed a great decrease in the corrosion potential ($\approx 200 \text{ mV}$ vs. SCE). This might be due to longer immersion time for CoCrMo in PBS with $4 \text{ g L}^{-1}$ HA according to Milošev who concluded that the immersion time has a significant effect on $E_{\text{corr}}$ (Milošev et al., 2013). This can be confirmed by referring to $E_{\text{corr}}$ of the CoCrMo alloy polarized in a solution of $4 \text{ g L}^{-1}$ HA with those having lower HA concentrations and immersion period prior to PDP measurements.

According to a study by Balogh and colleagues, they found that Co$^{2+}$ has a high affinity to react with HA due to the presence of the carboxyl group (COO$^-$) in the D-Glucuronic acid (Balogh et al., 2003). This may lead to covering the surface with Cobalt-HA and decreasing the transport of O$_2$ ions and decrease the cathodic reaction.

The highest $i_{\text{corr}}$ was determined for CoCrMo alloys immersed in the PBS solution and in which the HA concentration was the lowest. In another words, 1.3,
2.3 and 3 gL⁻¹ HA showed a similar \( i_{corr} \) while 4 gL⁻¹ HA showed the lowest \( i_{corr} \). The difference in the behavior between low and high concentration might be ascribed to the HA surface coverage at higher concentrations. When HA concentration is high, a more compact barrier layer formed on the CoCrMo alloy to inhibit oxygen diffusion.

**Figure 5-11:** The effect of different HA concentrations on the PDPs graph of CoCrMo

In the passive region, the overall trend between current and potential at various HA concentrations was similar. However, the measured passivation current \( (I_p) \) was shifted to new values when HA concentration was changed. The addition of HA shifted the \( I_p \) to lower values. The shift of \( I_p \) indicated that the passive layer
became more protective in the presence of HA. Cobalt and chromium from the CoCrMo alloy can bind to HA on the surface (Balogh et al., 2003). The binding can form a complex on the surface and form a barrier layer. Therefore, HA could form a better and more effective coat to protect the CoCrMo alloy from a corrosive environment. The transpassive behavior was not affected by the presence or absence of HA. The electrochemical parameters of the graph are shown in Table 5-7.

<table>
<thead>
<tr>
<th>HA (g/L)</th>
<th>$E_{corr}$ (V vs SCE)</th>
<th>$I_{corr} \times 10^{-7}$ (A/cm$^2$)</th>
<th>$E_b$ (V vs SCE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>-0.204 ± 0.028</td>
<td>1.54 ± 0.050</td>
<td>0.468 ± 0.024</td>
</tr>
<tr>
<td>1.30</td>
<td>-0.030 ± 0.080</td>
<td>1.20 ± 0.88</td>
<td>0.499 ± 0.029</td>
</tr>
<tr>
<td>2.30</td>
<td>-0.300 ± 0.094</td>
<td>1.50 ± 0.34</td>
<td>0.435 ± 0.047</td>
</tr>
<tr>
<td>3.00</td>
<td>-0.312 ± 0.07</td>
<td>1.58 ± 0.14</td>
<td>0.440 ± 0.018</td>
</tr>
<tr>
<td>4.00</td>
<td>-0.469 ± 0.172</td>
<td>1.70 ± 0.060</td>
<td>0.460 ± 0.021</td>
</tr>
</tbody>
</table>

To sum up, HA has a decisive effect on the corrosion potential of CoCrMo and the corrosion current density. HA worked as a cathodic inhibitor for CoCrMo. HA could form complexes with Co and Cr. These complexes might coat the surface of the alloy and enhance the passive behavior.

5.2.3 Electrochemical impedance spectroscopy

Studying the effect of different concentrations of HA on the interface of CoCrMo is important since the interface is one of the critical factors that determine
the longevity of the implants. Moreover, the effect of the resistivity of the implants can be determined from the simulated circuit parameters. The Bode plots diagram is presented in **Figure 5-12**.

![Bode plots diagram](image)

**Figure 5-12: Bode plots for PBS solution containing 1.3, 2.3, 3, and 4 g L⁻¹**

The solution resistance was in the frequency range of $10^4$ and $10^3$ Hz. In this high frequency range, the absolute impedance was independent from frequency for all concentrations. All concentrations showed almost the same solution resistance. The phases reached maximum values in the frequency range of $10^2$ to $10^{-1}$ Hz which represent the capacitive behavior for all solutions. The maximum phase was for 2.3
and 4 gL⁻¹ which reach ≈80° while the lowest was for 1.3 gL⁻¹ around ≈70°. Overall, a similar trend was found for all the HA concentrations.

At the lowest frequencies (10⁻¹ to 10⁻² Hz), the phase magnitude decreased. The absolute impedance continued to increase by decreasing frequency. This represents the passive behavior of the alloy.

Two overlapping time constants were observed for PBS solutions containing different HA concentrations. This result was also obtained for the Bode plots of the CoCrMo alloy in solutions of PBS and BSA. They were presented in section 5.1.3.

A Nyquist diagram is shown in Figure 5-13. The graph shows a typical semicircles. Two time constants mean that two passive layers formed on the samples’ surface. The inner layer represents the oxide layer while the outer layer is assumed to be the adsorbents ions from the solutions. A similar circuit with two resistors and capacitors was used. The simulated circuit parameters are represented in Table 5-8. The simulated circuit shows a good matching with measured impedance in which the Chi square is greater than 10⁻³.

The values of the total impedance were presented in the last column of the Table 5-8, the larger the values the higher the resistance. Thus, we can conclude that adding high concentration of HA (3, 4 gL⁻¹) enhanced the resistance of CoCrMo compared to plain PBS that showed the lowest resistance. Milošev studied the morphology of CoCrMo in NaCl and Hank’s solution using SEM and found that the
passive layer that forms in the presence of HA is denser and more homogenous compared to plain solutions (Milošev et al., 2013). Similar to Milošev results, our results determined that HA could improve the resistance of the alloy.

![Nyquist graph](image)

**Figure 5-13: Nyquist graph for different HA concentrations**

<table>
<thead>
<tr>
<th>HA (gL⁻¹)</th>
<th>Rᵢ (Ωcm²)</th>
<th>CPE&lt;sub&gt;out&lt;/sub&gt; (S&lt;sup&gt;sec&lt;/sup&gt;ⁿ)</th>
<th>n&lt;sub&gt;out&lt;/sub&gt;</th>
<th>R&lt;sub&gt;out&lt;/sub&gt; (Ωcm²)</th>
<th>CPE&lt;sub&gt;in&lt;/sub&gt; (S&lt;sup&gt;sec&lt;/sup&gt;ⁿ)</th>
<th>n&lt;sub&gt;in&lt;/sub&gt;</th>
<th>R&lt;sub&gt;in&lt;/sub&gt; (Ωcm²)</th>
<th>Total impedance (Ωcm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>5.42</td>
<td>7.11e-5</td>
<td>0.428</td>
<td>6.00</td>
<td>7.15e-5</td>
<td>0.881</td>
<td>8.38e+4</td>
<td>(8.38±2.29)e+4</td>
</tr>
<tr>
<td>1.30</td>
<td>11.2</td>
<td>9.29e-5</td>
<td>0.836</td>
<td>149</td>
<td>4.90e-4</td>
<td>0.744</td>
<td>7.82e+4</td>
<td>(7.97±1.04)e+4</td>
</tr>
<tr>
<td>2.30</td>
<td>12.4</td>
<td>1.45e-4</td>
<td>0.865</td>
<td>747</td>
<td>6.33e-5</td>
<td>0.877</td>
<td>1.84e+4</td>
<td>(9.02±0.470)e+4</td>
</tr>
<tr>
<td>3.00</td>
<td>13.0</td>
<td>1.46e-4</td>
<td>0.833</td>
<td>436</td>
<td>1.18e-5</td>
<td>0.837</td>
<td>9.98e+4</td>
<td>(1.00±0.560)e+5</td>
</tr>
<tr>
<td>4.00</td>
<td>11.06</td>
<td>1.60e-5</td>
<td>0.808</td>
<td>2840</td>
<td>1.50e-5</td>
<td>0.897</td>
<td>3.36e+5</td>
<td>(3.39±1.03)e+5</td>
</tr>
</tbody>
</table>
5.2.4 Linear polarization resistance

Different electrochemical tests have been used to calculate the corrosion rate. One well-known method is LPR. $i_{corr}$ is needed in order to calculate the corrosion rate. $i_{corr}$ can be calculated using equations 2 and 3. The B was estimated at 0.026 V since the linear section of anodic branch was not a decade long. The $R_{P\text{-LPR}}$ can be calculated from the slope of the over-potential and current. The graph that shows the LPR is represented in Figure 5-14.

![Graph showing linear polarization resistance](image)

**Figure 5-14**: Linear polarization of CoCrMo in different HA concentrations in PBS solutions
The calculated values of $R_{P-LPR}$ and $i_{corr}$ can be found in Table 5-9.

**Table 5-9: The polarization resistance and the corrosion current density of CoCrMo in different HA concentrations**

<table>
<thead>
<tr>
<th>HA (gL⁻¹)</th>
<th>$R_{P-LPR}$ (KΩ)</th>
<th>$i_{corr} \times 10^{-7}$ (A.cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>195 ± 4.64</td>
<td>1.33 ± 0.034</td>
</tr>
<tr>
<td>1.30</td>
<td>176 ± 8.21</td>
<td>1.47 ± 0.062</td>
</tr>
<tr>
<td>2.30</td>
<td>140 ± 34.7</td>
<td>1.85 ± 0.035</td>
</tr>
<tr>
<td>3.00</td>
<td>311 ± 47.2</td>
<td>0.835 ± 0.024</td>
</tr>
<tr>
<td>4.00</td>
<td>346 ± 3.66</td>
<td>0.750 ± 0.081</td>
</tr>
</tbody>
</table>

According to the results, we can say that adding HA to PBS increased the CoCrMo resistance. The highest resistance was in the presence of high concentrations of HA. These results matched with our findings from EIS. Milošev stated that the passive layer becomes denser and more homogenous in the presence of HA (Milošev et al., 2013). To study the effect of concentration, Milošev immersed CoCrMo in 1, 2, and 4 gL⁻¹ for 1.5 hours and found that increasing the concentration of HA increases the resistance of CoCrMo slightly (Milošev et al., 2013). Milošev also found that after 24 hours, the resistance of CoCrMo in the presence of 4 gL⁻¹ of HA is higher compared to plain NaCl and Hank’s solution. Therefore, increasing immersion time in the presence of HA in NaCl and Hank’s solution, increased the polarization resistance of the alloy (Milošev et al., 2013). This supports our finding that the highest resistance of CoCrMo alloys was achieved in 3 and 4 gL⁻¹ HA.
5.2.5 Corrosion rate calculations

The corrosion rate of CoCrMo was calculated after adding different concentrations of HA using two different techniques (EIS and LPR). The corrosion rate can be calculated using equation 3. The data are shown in Table 5-10.

<table>
<thead>
<tr>
<th>HA (gL⁻¹)</th>
<th>( R_{P,LPR} ) (kΩ)</th>
<th>( \frac{i_{corr-LPR}}{10^{-7}} ) (A.cm⁻²)</th>
<th>Corrosion rate (LPR) (μm/year)</th>
<th>( R_{P,EIS} ) (Ω)</th>
<th>( \frac{i_{corr-EIS}X}{10^{-7}} ) (A.cm⁻²)</th>
<th>Corrosion rate(EIS) (μm/year)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>195</td>
<td>1.33</td>
<td>0.419 ± 0.010</td>
<td>8.38e+4</td>
<td>3.10</td>
<td>0.976 ± 0.265</td>
</tr>
<tr>
<td>1.30</td>
<td>176</td>
<td>1.47</td>
<td>0.465 ± 0.021</td>
<td>7.79e+4</td>
<td>3.26</td>
<td>1.02 ± 0.081</td>
</tr>
<tr>
<td>2.30</td>
<td>140</td>
<td>1.85</td>
<td>0.585 ± 1.08</td>
<td>9.02e+4</td>
<td>2.88</td>
<td>0.906 ± 0.297</td>
</tr>
<tr>
<td>3.00</td>
<td>311</td>
<td>0.835</td>
<td>0.263 ± 0.075</td>
<td>1.00e+5</td>
<td>2.60</td>
<td>0.817 ± 0.104</td>
</tr>
<tr>
<td>4.00</td>
<td>346</td>
<td>0.750</td>
<td>0.236 ± 0.003</td>
<td>3.39e+5</td>
<td>0.767</td>
<td>0.241 ± 0.091</td>
</tr>
</tbody>
</table>

The calculated corrosion rate had very close values and the difference was less than an order of magnitude upon adding HA. The corrosion rate calculated using the two electrochemical techniques shows similar rates. Finally, adding different concentrations of HA did not have a strong effect on the corrosion rate of CoCrMo in the PBS solution.

5.3 Corrosion behavior of CoCrMo in the presence of PBS+BSA+HA

5.3.1 Open circuit potential

OCP has been used to study the effect of adding 10.5 gL⁻¹ BSA and different concentrations of HA (1.3, 2.3, 3, and 4 gL⁻¹) on the growth of the passive layer of CoCrMo in the PBS solution.
CoCrMo. The $E_{OCP}$ were measured to compare with the previous results where PBS had only either BSA or HA in different concentrations. Figure 5-15 showed the effect of BSA with different concentrations of HA compared to PBS and BSA.

Depending on HA concentrations, different times were needed to reach stable potentials. The required time for the CoCrMo alloy immersed in PBS and 10.5 $gL^{-1}$ BSA with various HA concentrations were: 6 hours for PBS and BSA, 7 hours for 1.3 $gL^{-1}$ HA, 11 hours for 2.3 $gL^{-1}$, 12 hours for 3 $gL^{-1}$HA and 4 $gL^{-1}$HA. Increasing HA concentrations increased the time needed for growing and stabilizing the oxide layer. The time with the potentials after 4 hours and final $E_{OCP}$ are shown in Table 5-11.

Looking to the graph, increasing the concentration of HA decreased the $E_{OCP}$. The same effect was seen in the presence of HA only in PBS solutions. Moreover, a similar effect was seen by adding BSA to PBS (about 100 $mV$ vs. SCE). To make it clear, one can compare the $E_{OCP}$ of BSA alone (-80.4 $mV$ vs. SCE) with BSA and 1.3 $gL^{-1}$ HA (-237 $mV$ vs. SCE) after 4 hours. It is clear that the presence of 1.3 $gL^{-1}$HA shifted the corrosion potential to significantly lower values. This can be explained by both HA and BSA working as cathodic inhibitors of CoCrMo.
Table 5-11: The corrosion potential of BSA and different concentrations after 4 hours and the final potentials

<table>
<thead>
<tr>
<th>Solution (gL⁻¹)</th>
<th>(E_{OCP}) at 14000 sec (V vs. SCE)</th>
<th>Final (E_{OCP}) (V vs SCE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.5 BSA</td>
<td>-0.080± 0.094</td>
<td>-0.054± 0.098</td>
</tr>
<tr>
<td>1.30 HA+BSA</td>
<td>-0.237± 0.98</td>
<td>-0.187± 0.067</td>
</tr>
<tr>
<td>2.30 HA+BSA</td>
<td>-0.284± 0.015</td>
<td>-0.197± 0.046</td>
</tr>
<tr>
<td>3.00 HA+BSA</td>
<td>-0.501± 0.094</td>
<td>-0.458± 0.077</td>
</tr>
<tr>
<td>4.00 HA+BSA</td>
<td>-0.655± 0.078</td>
<td>-0.509± 0.062</td>
</tr>
</tbody>
</table>

Figure 5-15: The OCP graph for CoCrMo in the presence of BSA with different concentrations of HA
To sum up, the corrosion potential shifted to lower values upon adding BSA to different concentrations of HA. The shift was more obvious in the presence of high concentrations of HA such as 3 and 4 gL⁻¹.

5.3.2 Potentiodynamic polarization

To study the effect of having both HA and BSA on the general behavior of corrosion of CoCrMo, PDP was conducted after OCP at 37°C in aerated solution. The results are shown in Figure 5-16.

The polarization graphs determined that the \( E_{corr} \) values of BSA, BSA+1.3, and BSA+2.3 gL⁻¹ HA had very close values. However, when HA concentrations increased up to 3 and 4 gL⁻¹, a dramatic decrease in the \( E_{corr} \) was obvious.

The \( I_P \) was different for plain BSA and BSA with different concentration of HA. Adding 1.3 and 2.3 gL⁻¹ of HA to BSA decreased \( I_P \) values compared to BSA whereas adding 3 and 4 gL⁻¹ of HA to BSA solutions showed one order of magnitude higher than \( I_P \). However, the active-passive behavior was more obvious in the presence of 3 and 4 gL⁻¹ of HA with BSA. However, the transpassive behavior of the CoCrMo alloy followed the same trend in the presence and absence of BSA and HA concentrations.

Comparing having both HA and BSA with a PBS solution that has only BSA, we can see that adding up to 2.3 gL⁻¹ of HA did not change the PDP curve for CoCrMo with BSA only except for reducing the \( I_P \). This might be explained by BSA controlling the electrochemical behavior over HA in the presence of only small concentrations of HA. However, increasing the concentration to 3, and 4 gL⁻¹ showed a different PDP
curve with lower $E_{corr}$, and a more stable passive layer. Data from PDP curves are shown in Table 5-12.

![PDP graph for CoCrMo in the presence of BSA and different concentrations of HA](image)

**Figure 5-16: PDP graph for CoCrMo in the presence of BSA and different concentrations of HA**

**Table 5-12: Electrochemical parameters of CoCrMo in PBS with BSA and different concentrations of HA**

<table>
<thead>
<tr>
<th>Solution ($g$L$^{-1}$)</th>
<th>$E_{corr}$ (V)</th>
<th>$i_{corr}$ (A.cm$^{-2}$) X 10$^{-7}$</th>
<th>$I_p$ (A.cm$^{-2}$) X 10$^{-6}$</th>
<th>$E_b$ (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBS</td>
<td>-0.204 ± 0.028</td>
<td>1.54 ± 0.050</td>
<td>1.00 ±0.19</td>
<td>0.468 ± 0.028</td>
</tr>
<tr>
<td>1.30HA+10.5BSA</td>
<td>-0.305 ±0.100</td>
<td>1.80 ± 0.23</td>
<td>1.70 ± 0.29</td>
<td>0.490 ± 0.005</td>
</tr>
<tr>
<td>2.30HA+10.5BSA</td>
<td>-0.300 ± 0.12</td>
<td>0.19 ± 0.005</td>
<td>1.50 ± 0.30</td>
<td>0.460 ± 0.011</td>
</tr>
<tr>
<td>3.00HA+10.5BSA</td>
<td>-0.400 ± 0.130</td>
<td>—</td>
<td>0.10 ± 0.77</td>
<td>0.500 ± 0.039</td>
</tr>
<tr>
<td>4.00HA+10BSA</td>
<td>-0.800± 0.030</td>
<td>—</td>
<td>0.15 ± 0.38</td>
<td>0.500 ± 0.019</td>
</tr>
</tbody>
</table>
Due to the lacking of the linearity in the cathodic side for both 3 and 4 \(gL^{-1}\), it was difficult to determine the \(i_{corr}\).

To sum up, HA concentration has a significant effect on \(E_{corr}\) and \(I_P\) of CoCrMo. In high concentration, the passive layer was more stable and the corrosion potential was significantly lower compared to low HA concentrations.

### 5.3.3 Electrochemical impedance spectroscopy

EIS is a well-known technique that has been used for understanding and investigating the interface between CoCrMo and solutions that have both BSA and different concentrations of HA. **Figure 5-17**

Figure 5-17 shows the Bode plots results for 10.5 \(gL^{-1}\) BSA and (1.3, 2.3, 3, and 4 \(gL^{-1}\)) HA.

We can see that the solution resistances were exhibited at high frequency \(10^4\) to \(10^3\) Hz. A frequency range between \(10^3\) and \(10^{-1}\) Hz showed a capacitive behavior for all solutions. The oxide layer growth can be observed due to the increase in the impedance magnitude with shifting the frequency to lower values. The maximum values of the phase were around \(90^\circ\) for almost all solutions and \(\approx 80^\circ\) for 4 \(gL^{-1}\) HA+BSA. Comparing the presence of different concentrations of HA with BSA on the capacitive behavior with only BSA, we can see that BSA shows more stable capacitor behavior. Adding HA decreased the capacitive behavior slightly.
Figure 5-17: Bode and bode diagram for CoCrMo in the presence of different concentrations of HA

Two time constants were observed and used to compare to the previous results where CoCrMo was studied in PBS and BSA, and BSA with different HA concentrations.

The data from the Nyquist diagram is shown in Figure 5-18. Behavior similar to the previous sections was observed with a depressed semicircle. A similar equivalent circuit with two overlapped time constant was selected (Figure 5-7). As explained previously, the passive layer has two layers in which the inner layer represents the oxide layer and the outer layer represents the adsorbent. The simulated circuit parameters are given in Table 5-13. These data can also be used to
calculate the corrosion current density and corrosion rate for CoCrMo in the presence of BSA with different concentrations of HA.

![Nyquist diagram for CoCrMo in the presence of different concentrations of HA](image)

**Figure 5-18: Nyquist diagram for CoCrMo in the presence of different concentrations of HA**

Adding BSA and HA to PBS showed an increase in the impedance of CoCrMo which means enhancing the corrosion resistance of the alloy in the presence of HA and BSA. Similar results were obtained when having only BSA, and only HA as it is shown in Table 5-3 and Table 5-8 respectively. The results of having only high concentrations of HA (3, 4 gL⁻¹) showed an increase in the resistance of the alloy. However, when BSA was added to 4 gL⁻¹ HA, the resistance of CoCrMo became stronger. This might be explained by the BSA interaction with HA which could coat the surface and enhance the resistance of the alloy (Bhusari, 2007).
Table 5-13: The circuit parameters of a solution with different concentrations of HA and BSA

<table>
<thead>
<tr>
<th>Solution (gL⁻¹)</th>
<th>Rx (Ωcm²)</th>
<th>CPE out Sⁿsec⁻ⁿ</th>
<th>n_out</th>
<th>Rout (Ωcm²)</th>
<th>CPE_in Sⁿsec⁻ⁿ</th>
<th>n_in</th>
<th>Rin (Ωcm²)</th>
<th>Total impedance (Ωcm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBS</td>
<td>5.42</td>
<td>7.10e-15</td>
<td>0.428</td>
<td>6.00</td>
<td>7.15e-5</td>
<td>0.881</td>
<td>8.38e+4</td>
<td>(8.38±2.29)e+4</td>
</tr>
<tr>
<td>10.5 BSA</td>
<td>10.2</td>
<td>3.46e-4</td>
<td>0.800</td>
<td>231</td>
<td>6.81e-5</td>
<td>0.800</td>
<td>2.29e+5</td>
<td>(2.56±0.002)e+5</td>
</tr>
<tr>
<td>1.30 HA+10.5 BSA</td>
<td>12.7</td>
<td>1.10e-4</td>
<td>0.864</td>
<td>980</td>
<td>9.96e-5</td>
<td>0.875</td>
<td>1.18e+5</td>
<td>(1.91±0.780)e+5</td>
</tr>
<tr>
<td>2.30 HA+10.5 BSA</td>
<td>12.8</td>
<td>2.40e-3</td>
<td>0.815</td>
<td>567</td>
<td>1.20e-4</td>
<td>0.835</td>
<td>1.57e+5</td>
<td>(1.58±0.516)e+5</td>
</tr>
<tr>
<td>3.00 HA+10.5 BSA</td>
<td>6.48</td>
<td>1.20e-4</td>
<td>0.840</td>
<td>1.99e+5</td>
<td>1.70e-4</td>
<td>0.820</td>
<td>1.58e+4</td>
<td>(2.15±0.416)e+5</td>
</tr>
<tr>
<td>4.00 HA+10.5 BSA</td>
<td>9.69</td>
<td>1.60e-4</td>
<td>0.929</td>
<td>3.30e+6</td>
<td>1.40e-4</td>
<td>0.837</td>
<td>3.61e+4</td>
<td>(3.34±0.201)e+6</td>
</tr>
</tbody>
</table>

Comparing the resistance of CoCrMo in the presence of only BSA to presence of only different concentrations of HA, we found that both components increased the resistance of the alloy. However, the increase was more profound in the presence of 4 gL⁻¹ HA+BSA.

5.3.4 Linear polarization resistance

To study the effect of having both chemicals in the corrosion behavior of CoCrMo, i_corr and R_P-LPR values were calculated in the presence of 10.5 gL⁻¹ BSA and a range of HA concentrations (1.3, 2.3, 3, and 4 gL⁻¹). An LPR figure is shown in Figure 5-19. The R_P-LPR values and i_corr are illustrated in Table 5-14.
Figure 5-19: Linear polarization resistance of CoCrMo in the presence of BSA and different concentrations of HA

Table 5-14: Corrosion resistance and corrosion current densities for CoCrMo with BSA and different concentrations of HA

<table>
<thead>
<tr>
<th>Solution (gL⁻¹)</th>
<th>(R_{P-LPR}(k\Omega))</th>
<th>(i_{corr}(A.cm^{-2}) \times 10^{-7})</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.5 BSA</td>
<td>194 ± 17.4</td>
<td>1.33 ± 0.012</td>
</tr>
<tr>
<td>1.30HA+10.5BSA</td>
<td>213 ± 9.64</td>
<td>1.22 ±0.062</td>
</tr>
<tr>
<td>2.30HA+10.5BSA</td>
<td>188 ± 6.88</td>
<td>1.38 ± 0.041</td>
</tr>
<tr>
<td>3.00HA+10.5BSA</td>
<td>466 ±20.2</td>
<td>0.558 ±0.029</td>
</tr>
<tr>
<td>4.00HA+10.5BSA</td>
<td>740 ± 29.9</td>
<td>0.351 ±0.013</td>
</tr>
</tbody>
</table>
From the previous table, it was obvious that CoCrMo had the highest resistance in the presence of 3 and 4 gL⁻¹ HA and BSA. This resistance is higher than a solution with only BSA which has only small corrosion current density 1.34e⁻⁷A.cm⁻².

5.3.5 Corrosion rate calculations

In order to judge the effect of the presence of BSA and different concentrations of HA, the corrosion rate need to be calculated according to equation 3. The same a, F, N, and P were used as Table 5-5.

Table 5-15 shows the calculated corrosion rates from EIS and LPR upon adding BSA and four different concentrations of HA.

<table>
<thead>
<tr>
<th>Solution (gL⁻¹)</th>
<th>Rₚ-LPR (KΩ)</th>
<th>icorr-LPR X 10⁻⁷ (A.cm⁻²)</th>
<th>Corrosion rate (LPR) (μm/year)</th>
<th>Rₚ-EIS (Ω)</th>
<th>icorr-EIS X 10⁻⁷ (A.cm⁻²)</th>
<th>Corrosion rate (EIS) (μm/year)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBS</td>
<td>196</td>
<td>1.33</td>
<td>0.419± 0.010</td>
<td>8.38e+4</td>
<td>3.10</td>
<td>0.976 ± 0.267</td>
</tr>
<tr>
<td>1.30HA+BSA</td>
<td>214</td>
<td>1.22</td>
<td>0.383±0.018</td>
<td>1.91e+5</td>
<td>1.36</td>
<td>0.639 ± 0.201</td>
</tr>
<tr>
<td>2.30HA+BSA</td>
<td>189</td>
<td>1.38</td>
<td>0.433 ± 0.015</td>
<td>1.58e+5</td>
<td>1.65</td>
<td>0.518 ± 0.0081</td>
</tr>
<tr>
<td>3.00HA+BSA</td>
<td>465</td>
<td>0.526</td>
<td>0.165 ± 0.007</td>
<td>2.15e+5</td>
<td>1.21</td>
<td>0.380 ± 0.192</td>
</tr>
<tr>
<td>4.00HA+BSA</td>
<td>740</td>
<td>0.351</td>
<td>0.111 ± 0.004</td>
<td>3.34e+6</td>
<td>0.078</td>
<td>0.024 ± 0.095</td>
</tr>
</tbody>
</table>

From the previous table, there was a difference in the corrosion rate calculated from the EIS and LPR measurements when HA concentration was 4 gL⁻¹. This might be due to the assumption of B value (0.026V) and the difficulty to get a
linear area in the anodic side of the PDPs curves. Therefore, the corrosion rate calculated from LPR data might be overestimated.

To conclude the electrochemical parts, having BSA with a high concentration of HA (4 gL⁻¹) showed enhancement in the corrosion resistance and a corrosion rate of CoCrMo according to EIS results. While according to LPR, the resistance of the alloy enhanced in the presence of BSA with 3, and 4 gL⁻¹.

5.4 The effect of having BSA, different concentration of HA, and both BSA and HA

Comparing the effect of having BSA, different concentration of HA, and both BSA and HA on the corrosion performance of CoCrMo was one of the objectives of this study. Therefore, the control sample (PBS), then BSA was added to PBS, 1.3 gL⁻¹ and 4 gL⁻¹ were selected, after that having both 1.3 and 4 gL⁻¹ of HA added to BSA to simulate SF on people with OA and normal people. 1.3 and 4 gL⁻¹ were selected to represent normal and osteoarthritis people. This will enable us to understand the effect of increasing HA concentration on the corrosion performance of CoCrMo.

The $R_p$ of CoCrMo in the presence of the previous mentioned chemicals are investigated from EIS is shown in Figure 5-20 while $R_p$ from LPR is shown in Figure 5-21.
Figure 5-20: The polarization resistance of CoCrMo obtained from EIS in the presence of BSA, different concentrations of HA, and both BSA and HA.

From Figure 5-20, we can see that the lowest resistance was in PBS solution and PBS with 1.3 gL⁻¹ of HA. Adding BSA, 1.3 gL⁻¹ did not show a change on the resistance of the alloy. However, adding 4 gL⁻¹ increases the resistance slightly. The highest resistance of the alloy was in the presence of BSA and high concentration of HA which represents normal people. The resistance in the presence of BSA and 4 gL⁻¹ was about three times higher compared to PBS with only BSA or 4 gL⁻¹ of HA.

The $R_p$ was also calculated from LPR as shown in Figure 5-21.
The polarization resistance of CoCrMo obtained from LPR in the presence of BSA, HA, and both BSA and HA.

![Bar chart showing polarization resistance in different solutions.](image)

**Figure 5-21:** The polarization resistance of CoCrMo obtained from LPR in the presence of BSA, HA, and both BSA and HA.

From **Figure 5-21**, similar trend was observed compared to $R_p$ calculated EIS. The $R_p$ increased slightly upon adding 4 gL$^{-1}$ of HA. However, the highest resistance of CoCrMo was in the presence of 4 gL$^{-1}$ HA and BSA. This showed that increasing HA concentration increased the resistance of the alloy. The results showed that increasing HA value in the presence of BSA enhanced the resistance of the alloy. However, these results did not simulate the body environment because it was under normal load while in the body, there is a complex movement in the body which was not considered in this study.
The B value was estimated 0.26 V. This might be due to overestimating the B value.

The corrosion rate was calculated using equation 4. The calculated values for PBS, BSA, 1.3 gL⁻¹ HA, 4 gL⁻¹ HA, 1.3 gL⁻¹ HA+BSA, 4 gL⁻¹ HA+BSA is shown in Figure 5-22.

![Corrosion rate graph](image)

**Solution**

**Figure 5-22**: Corrosion rate calculated from EIS, and LPR for CoCrMo in the presence of different constituents of SF.

From the graph, we can see that the lowest corrosion rate was in the presence of BSA with 4 gL⁻¹ HA which represents normal people. Form both techniques, the
corrosion rate was lower in the presence of $4 \, gL^{-1}$ HA with BSA, normal people, compared to BSA with $1.3 \, gL^{-1}$ of HA, osteoarthritis people. This showed the increasing HA concentration decreased the corrosion rate of CoCrMo. More studies are needed before giving HA as a medication for people with implants to reduce the corrosion rate of CoCrMo.
6 Conclusion

Corrosion behavior of CoCrMo in PBS with BSA

- BSA worked as a cathodic inhibitor for CoCrMo. However, this effect was not obvious upon adding BSA to PBS solution. This could be related to longer immersion time.

- The EIS results showed that the resistance of CoCrMo increased in the presence of BSA. However, the corrosion rate did not show a significant effect on the corrosion resistance.

Corrosion performance of CoCrMo PBS with different HA concentrations

- Increasing concentrations of HA shifted the $E_{OCP}$ to lower values which could be due to HA working as a cathodic or anodic inhibitor of CoCrMo.

- According to LPR, and EIS results, adding (3 and 4 $gL^{-1}$) increased the polarization resistance of CoCrMo.

- The PDPs curve showed that HA may work as a cathodic inhibitor for CoCrMo due to the shift of the cathodic branch.

Corrosion behavior of CoCrMo in PBS with BSA and different concentrations of HA

- The presence of both BSA and range concentrations of HA showed a more profound decrease of $E_{OCP}$. This could be due to both HA and BSA working as cathodic inhibitors for CoCrMo.
• The passive layer of CoCrMo became more stable in the presence of BSA with 3 gL⁻¹ and BSA+4 gL⁻¹ HA with BSA as well.

• The corrosion rate was one order of magnitude lower in the presence of 4 gL⁻¹ HA with BSA according to EIS compared to PBS with BSA and lower concentrations of HA with HA.

• LPR results showed that the highest resistance of CoCrMo was in the presence of 4 gL⁻¹ HA with BSA.

To sum up, increasing the concentration of HA from 1.3 gL⁻¹ to 4 gL⁻¹ with BSA showed an enhancement of the polarization resistance of the alloy. Moreover, it decreased the corrosion rate. Therefore, HA may be given to people with implants to increase the resistance of the alloy. This could enhance the lifetime of the implants.
7 Future work

- A long immersion test for CoCrMo with BSA, HA, and BSA with different concentrations of HA.
- Studying the effect of HA and BSA in 316L stainless steel, and Ti6Al4V.
- Studying the same system in deaerated solutions and in an acidic environment.
- Detecting the ion release in the surface using X-ray photoelectron spectroscopy (XPS) and in the solution using inductively coupled plasma atomic emission spectroscopy (ICP-OES)
- Studying the adsorption of BSA and HA using Quartz crystal microbalance (QCM).
- Study the effect of HA on the corrosion behavior of CoCrMo, Ti6Al4V, and 316l SS under a fretting motion.
References


doi:10.1107/S0907444912027047


polarization resistance measurement as an example of a simple method that can be performed with commercially available instruments. *British Corrosion Journal, 21*(2), 95-101.


