Research Article

Corrosion Behavior of Metals in Ringer Solution-A Studied By Electrochemical Impedance Spectroscopy

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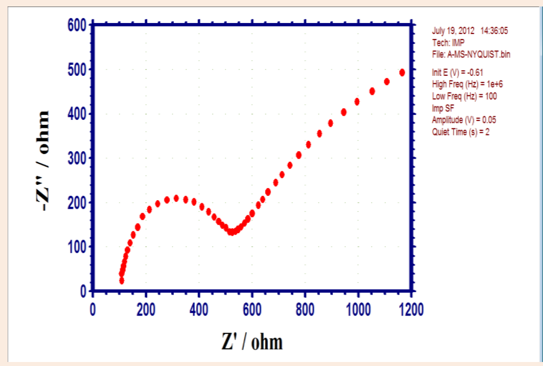
Abstract

This work aims at studying the electrochemical behavior of metals like Gold 22, Gold 18 and Mild Steel in the presence of Ringer Solution-A (RSA).Ringer Solution is used to simulate the body fluids. The behavior of the metal was monitored by electrochemical impedance spectroscopy (EIS). All the experiments were carried out at a constant temperature of 37°C. From the EIS spectra, it was concluded that the decreasing order of corrosion resistance of metals in RSA is as follows,

gold 22 > gold 18 > mild steel



Keywords: Gold 22, Gold 18, Mild Steel, EIS Corrosion

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Introduction

Surface properties and anti-corrosion characteristics are the most important material characteristics determining the bio functionality of all implant biomaterials. Gold18, Gold22 and mild steel has been a valuable biomaterial for manufacturing implants due to its unique properties such as shape memory effect, super elasticity and good mechanical property [1]-[4]. Many devices such as stent, orthodontic wires and root canal files have been used clinically [2]-[5].

Ringer's analysis of the influence of blood constituents on contraction of the frog heart (1882-1885) pioneered general development of artificial extracellular media for maintenance of living material during in vitro physiological studies. "Ringer's solutions" are thus defined here as those designed to substitute for the blood plasma, hemolymph, or other extracellular fluids of any species with respect to variables such as ionic concentrations, pH, and osmotic pressure. Media described in the literature as "physiological salines" and "balanced salt solutions" are included here under the general Ringer's heading. Mimicry of native conditions is achieved in varying degrees by the many different Ringer's formulations.

Ringer's solutions are typically intended for relatively short-term maintenance of living material, not for its growth or extended culture. In this respect they differ from cell, tissue, and organ culture media, which are more complex and beyond the scope of this Compendium.

Since Na^+ is normally the principal extracellular ion, sodium chloride is the major component of most Ringer's solutions. Some formulations have relatively few additional ingredients but are nevertheless more complex than most "buffered salines", consisting principally of sodium chloride and a pH buffer, presented Ions such as Na^+, K^+, Ca^{++}, and Mg^{++} are critical for many functions. Researchers initiating work are urged to select physiological solutions carefully for the particular species to be studied, and to consider developing new ones based on analysis of the natural extracellular medium. Many Ringer's solutions [6}],[7],[8], are the product of empirical testing for retention of the activity being studied. Thus, in addition to being used directly, recipes provided here can serve as a starting point for improved formulations.

Corrosion resistance of metals and alloys in various body fluids such as artificial saliva [9],[10],[11] ,artificial sweat [12],[13],[14] , blood plasma [15],[16],[17] ,artificial urine [18],[19],[20] has been investigated. The present work is undertaken to investigate the corrosion resistance of three metals namely, mild steel,22 carat gold,18 carat gold in Ringer solution-A by AC impedance measurements.

Electrochemical impedance spectroscopy:

The Electrochemical impedance spectroscopy (EIS) is a relatively modern technique widely extended in several scientific fields. The EIS consists on a non-destructive technique when working under equilibrium conditions (free corrosion potential or open circuit potential), particularly sensible to small changes in the system that allows characterizing material properties and electrochemical systems even in low conductive media.

The impedance method consists in measuring the response of an electrode to a sinusoidal potential modulation of small amplitude (typically 5-10 mV) at different frequencies. The alternative current (AC) modulation is superimposed either onto an applied anodic potential or cathodic potential or onto the corrosion potential [21], [22].

Temperature: Experiments were carried out at 37 ± 1^0C

Experimental:

Materials and Methods:

Corrosion resistance of three metals namely Mild Steel, 18 Carat Gold and 22 Carat Gold in Ringer Solution-A has been investigated by AC impedance measurements. Usually corrosion behavior of metals and alloys have been studied in Ringer solution-A (RSA) composition [6}],[7],[8], is given in Table 1.

Table 1 Composition of Ringer Solution-A

NaCl	6g/lit
KCl	0.075g/lit
$CaCl_2$	0.1g/lit
$NaHCO_3$	0.1g/lit

The metal specimens namely mild Steel, 22 carat gold and 18 carat gold have composition as follows,

Table 2 The composition of mild steel is: [23]

Carbon	0.1%
Manganese	0.4 %
Phosphorous	0.06 %
Sulphur	0.026 %
Iron	Balance

Table 3 The composition of 22 Carat Gold is: [24]

Gold	91.67%
Silver	5%
Copper	2%
Zinc	1.33%

Table4 The composition of 18 Carat Gold is: [25]

Gold	75%
Copper	25%

Composition of Ringer Solution –A is given in Table-1 [6}], [7],[8],

AC impedance measurements:

H and CH electrochemical work station impedance analyzer model CHI 660 was used to record AC impedance measurements. A three-electrode cell assembly was used. The working electrode was one of the three metals. A saturated calomel electrode (SCE) was the reference electrode and platinum was the counter electrode [26], [27]. The real part (Z') of the cell impedance was measured in ohms for various frequencies. The change transfer resistance (R_t) and double layer capacitance (C_{dl}) values were calculated

$$R_t = (R_s + R_t) - R_s$$

Where R_s = solution resistance, and

$$C_{dl} = \frac{1}{2}\ \Pi\ R_t\ f\text{max}$$

Where $f$max = maximum frequency.

Result and Discussion

Corrosion resistance of three metals namely mild steel,22 carat gold, 18 carat gold in Ringer Solution-A has been investigated by AC impedance measurements. AC impedance measurements have been used to investigate the formation of protective film formed on the metal surface during corrosion process [26], [29], [30]. It is well known to everyone that mild steel should not be implanted in inside the body, because it will undergo corrosion due to the electrolytes present in body fluids. However in the present study, mild steel is used just for comparison.

AC impedance parameters such as charge transfer resistance (R_t), double layer Capacitance (C_{dl}) (derived from Nyquist plots) and impedance value log (Z/ohm) (derived from Bode plots) of various metals immersed in Simulated Ringer Solution-A are given in Table-5 Nyquist plots are shown in Figures (1,3,5) Bode plots are shown in Figures (2,4,6)

Table 5 Corrosion parameters of metals immersed in Ringer Solution-A obtained from AC impedance spectra study

System	**Charge transfer Resistance (R_t) Ohm.cm^2**	**Double layer Capacitance (C_{dl}) F/cm^2**	**Impedance log z/ohm**	**Phase angle degree**
Mild steel	1062.7	1.8067×10^{-8}	3.104	22.98
Gold 18	52150	3.6816×10^{-10}	5.027	61.60
Gold 22	286500	6.7015×10^{-11}	5.697	55.52

Mild Steel

It is observed from Table 5, that, when mild steel is immersed in Simulated Ringer solution-A (SRSA), the R_t value was 1062.7 ohm cm^2 and the C_{dl} value was 1.8067x10^{-8} F/cm^2. the impedance value log z/ohm is 3.104. (Figures 1 and 2). The phase angle value 22.98 degree (**Figures 1** and **2**).

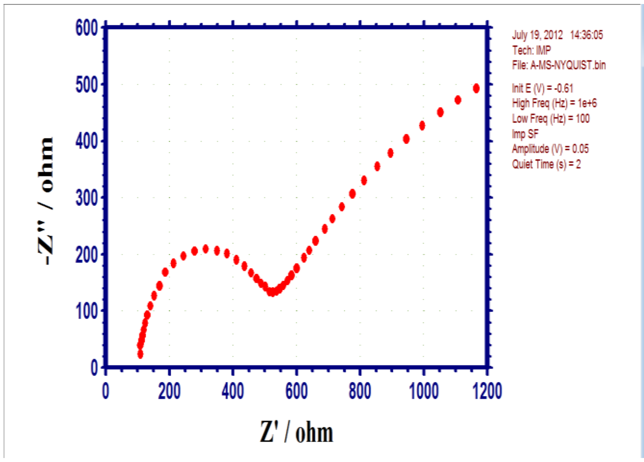


Figure 1 AC Impedance spectrum of mild steel immersed in SRSA (Nyquist plot)

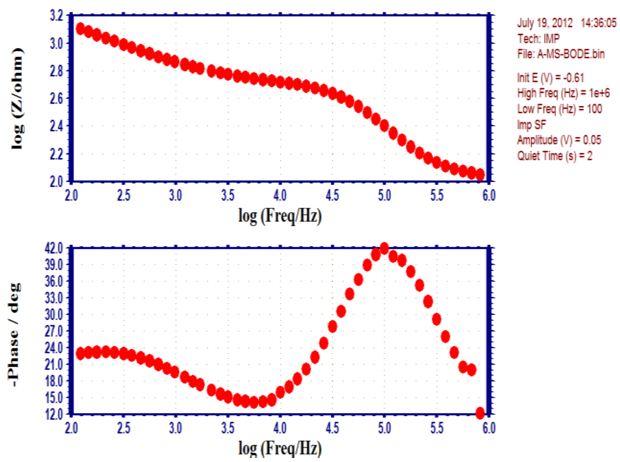


Figure 2 AC Impedance spectrum of mild steel immersed in SRSA (Bode Plot)

18 Carat Gold

When 18 Carat Gold is immersed in Simulated Ringer solution-A (SRSA), the R_t value is 52150 ohm cm^2,C_{dl} Value is 3.6816 x10^{-10} F/cm^2;the impedance value logz/ohm is 5.027.It is observed that the Rt value increased,cdl value decreased. There is an increase in the value of impedance [log(z/ohm)] (Figure 3 &4).These observations indicate in the presence of Ringer solution-A, the corrosion rate of 18 Carat Gold is reduced, due to the formation of a protective film formed on the metal surface. Because of the presence of protective film on the metal surface, electron transfer from the metal surface to the bulk of the solution was restricted. This results in an increase of charge transfer resistance and a decrease in double layer capacitance, since they are related to each other inversely. It is inferred that

Gold 18 is more corrosion resistant than mild steel. This indicates the 18 carat Gold is nobler than mild steel, due to the formation of passive film on the metal surface.

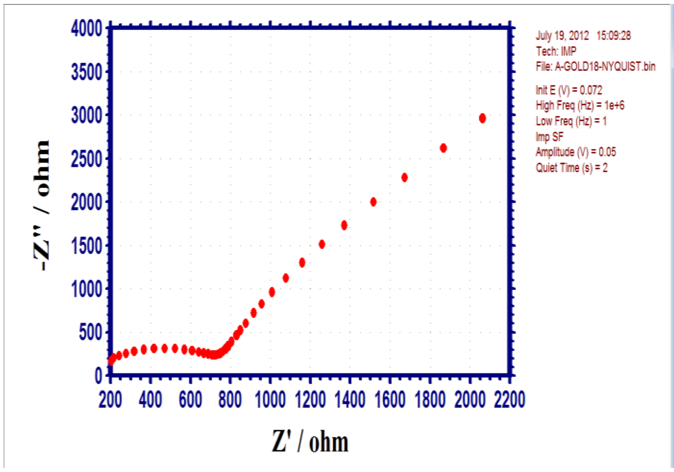


Figure 3 AC Impedance spectrum of 18 carat gold immersed in SRSA (Nyquist plot)

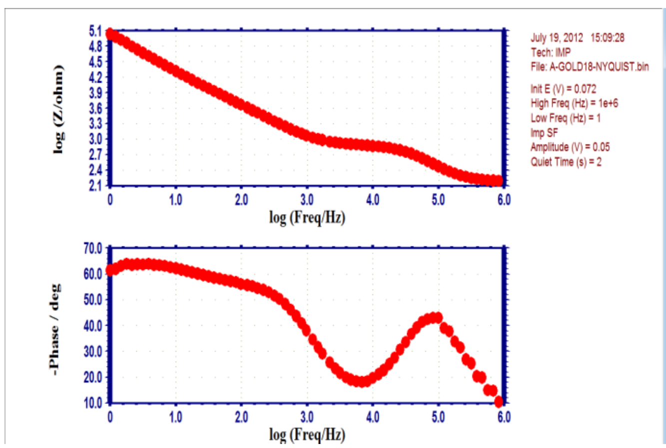
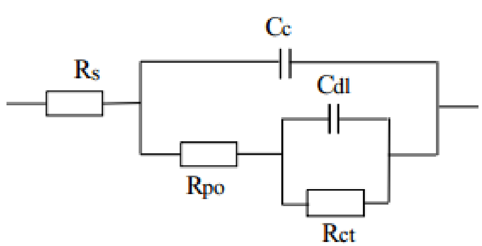


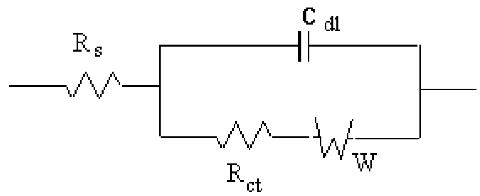
Figure 4 AC Impedance spectrum of 18 Carat gold immersed in SRSA (Bode Plot)

The equivalent circuit diagram for such system is shown in Scheme 1.

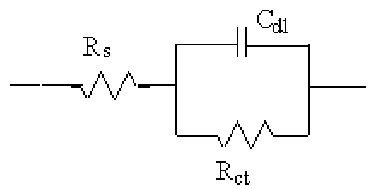


Scheme 1 Equivalent circuit for a failed coating

C_c - The capacitance of the intact coating, R_{po} - pore resistance, R_{ct} - charge transfer resistance, R_s - solution resistance, C_{dl} - double layer capacitance



Scheme 2
Rs - Solution resistance, Rct - Charge transfer resistance, W - Warburg diffusion resistance, Cdl - Double layer capacitance



Scheme 3
Cdl - Double layer capacitance. Rs - Solution resistance, Rct - Charge transfer resistance

22 Carat Gold

When 22 Carat Gold is immersed in Simulated Ringer solution-A (SRSA), the R_t value is 286500 Ohm cm^2, C_{dl} Value is 6.7015 $x10^{-11}$ F/Cm^2, the impedance value logZ/Ohm is 5.697.It is observed that the R_t value increased and the C_{dl} value decreased. There is an increase in the value of impedance [log(z/ohm)](Figure 5&6). These observations indicate in the presence of Ringer solution-A, the corrosion rate of 22 carat gold is reduced, due to the formation of a protective film formed on the metal surface. Because of the presence of protective film on the metal surface, electron transfer from the metal surface to the bulk of the solution is restricted.

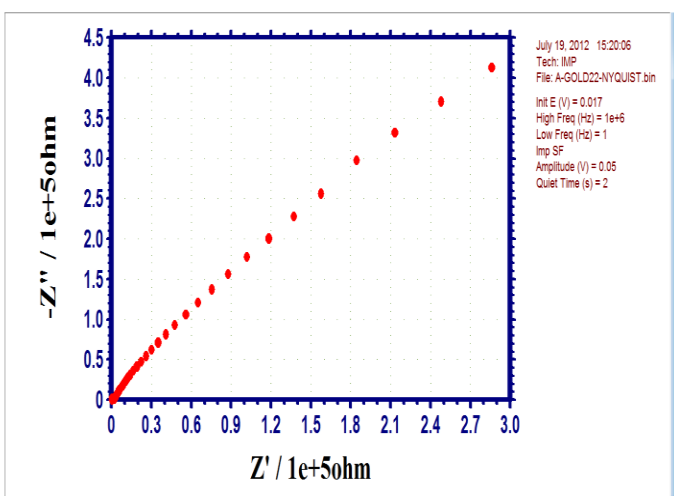


Figure 5 AC Impedance spectrum of 22 Carat gold immersed in SRSA (Nyquist plot)

This results in an increase of charge transfer resistance and a decrease in double layer capacitance, since they are related to each other inversely. It is inferred that Gold 22 is more corrosion resistant than Gold 18.This indicates the 22 carat Gold is nobler than Gold 18,due to the formation of passive film on the metal surface [26],[28] to [46].

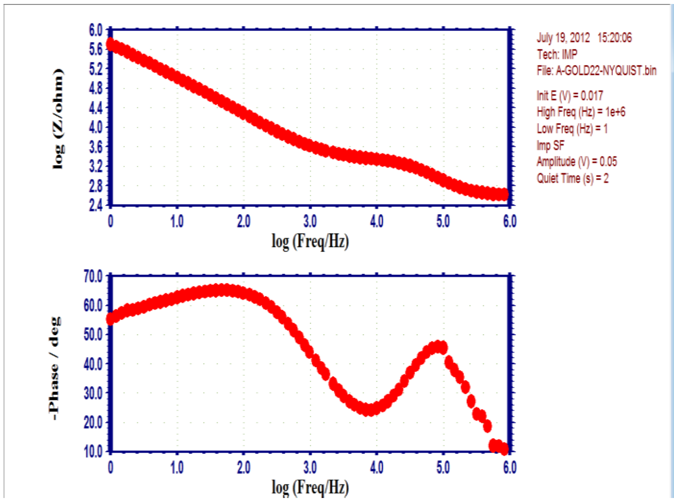


Figure 6 AC Impedance spectrum of 22 Carat gold immersed in SRSA (Bode Plot)

Conclusion

Thus, AC impedance spectra leads to the conclusion that the decreasing order of Corrosion resistance of metals under investigation, in simulated Ringer solution-A is:

22 Carat Gold > 18 Carat Gold > Mild Steel

The above order may be explained by the fact that, there is variation the composition of various types of Gold.

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