J. Basic. Appl. Chem., 9(1)1-7, 2019

ISSN 2090-424X
Journal of Basic and Applied Chemistry
www.textroad.com

Electrochemical Behavior of Nb and Mo Electrodes Compared with CoCr-alloy and Au Electrodes in Fluoride Solutions for Dental Application

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ABSTRACT

This work aimed to study the effect of both meat soup and 0.5M NaF solutions on the corrosion behavior of Nb, Mo electrodes compared with CoCr-alloy and Au electrodes at temperatures range from 20 to 50°C. The investigation was carried out using potentiodynamic polarization and open circuit potential tests. The corrosion rate values were always lower in meat soup than in 0.5M NaF solutions. The order of passivity according to rest potential and corrosion rates were illustrated. The calculated ΔH° values were 175, 163, 151 and 110 kJ/mol in meat soup, and were 169, 155, 193 and 143 in 0.5M NaF solution for Au, CoCr- alloy, Nb and Mo electrodes respectively. The recorded values of ΔS° were -197 J/mol K for all electrodes at all conditions.
KEYWORDS: CoCr-alloy, Mo, Nb, Au, meat soup, NaF solution, Open circuit, Potentiodynamic.

1. INTRODUCTION

Wires, crowns and bridges of dental materials placed in mouth cavity, may stay for months, years or all lifetime. Studying the corrosion behavior of these materials is very essential due to the corrosive action of saliva and other food stuff solutions that inter into the mouth. Gold is one of the ancient metals that used in dental application. It does not react with water, aqueous bases or halogens very easily [1, 2]. This produce low tendency to release in solutions, which make the metal had lower incidence of allergy. Nb and Mo metals are non-corrosive, non-sensitizer and non-permeator for skin. For both metals, carcinogenic, mutagenic and teratogenic effects are not available. Also developmental toxicity is not available. Accordingly Nb and Mo metals are not listed by NTP, IARC or regulated as carcinogen by OSHA [3]. Thus Nb and Mo metals had the primer ability to be used in dental applications.

The human body consists of many significant elements. One of the most important of them is the fluorides. They present as CaF_2 in the bones and teeth [4]. God provide us many natural sources to satisfy our bodies its need from fluorides. This was offered in most of our daily foods. Examples of vegetables that contain fluorides in high levels are white rice, spinach, beans, peas, tomatoes, potatoes, cucumber, carrots and dill herb. Examples of fruits with high fluoride levels are orange, grapefruit, apple and seedless raisins [4]. It is also present in tea, oats, coffee, cheese, meat and fish.

This study aimed to investigate the electrochemical behaviors of Nb and Mo electrodes compared with CoCr-alloy and Au electrodes at temperature range 20 - 50°C, so as to be used as alternatives of gold alloys in dental applications. Thus food containing fluorides was simulated by meat soup and 0.5M NaF solution in this study. The study was not aimed to compare between the two tested solutions, but focus on the behavior of the four electrodes in each solution.

2. Experimental

2.1. Electrode preparation

Massive cylindrical niobium of surface area 0.33 cm² supplied by Johnson Matthey- England, and molybdenum rod (0.196 cm²) supplied by Aldrich – Chemie were used as working electrodes. A commercial sample of CoCr-alloy (WIRONITR, BEGO, Germany) with 1.038 cm² surface area had the following composition: 64% Co, 28% Cr, 6% Mo, 2% (C + Si + Mn) was also used as a working electrode. Gold electrode of chemical composition: 98.2% Au, 1.7% Ti and 0.1% Ir, and surface area of 0.0184 cm² was used as a blank electrode.

The surfaces of electrodes were first polished with emery papers then rinsed with bi-distilled water and degreased in ethanol. Finally the electrodes surfaces were wrapped against a soft cloth and then immersed quickly in the test solution.

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2.2. Solution:

The solution of 0.5M NaF was prepared from analytical reagent grade. Meat soup was prepared by putting about 500g of refrigerated buffalo meat in 1L boiled water until pH become 6.4 according to *Egyptian standard specifications* Nos. 3602/2008 [5].

2.3. Experimental techniques

2.3.1. Open circuit potential measurements

Open circuit potential (OCP) measurements were carried out in 25 mL glass cell filled with the test solution. The potentials *vs.* time were performed with digital multimeter (KEITHLEY, Model 175, USA) using saturated calomel electrode (SCE) as a reference electrode.

2.3.2. Potentiodynamic polarization measurements

Potentiodynamic polarization measurements were generated using an Electronic Potentioscan Wenking (Model POS 73). A saturated calomel electrode and a platinum sheet (4 cm²) were used as the reference and the auxiliary electrodes, respectively. The working electrodes were polarized by submission to a potentiodynamic scan from -5 to +5 V/SCE at scan rate of 3.33 mV/s and the corresponding currents were recorded. Before polarization, the electrodes were immersed in the test solution for 90 min in order to reach a steady-state OCP value. Values of corrosion current (I_{corr}) and corrosion potential (E_{corr}) were evaluated from intersection of the linear anodic and cathodic branches of Tafel plots. The corrosion rate (C_R) in mpy, was calculated using Eq.1 [6]:

$$C_R = 0.13 \times I_{corr} \times e/d \qquad (1)$$

where 0.13 is the metric and time conversion factor, I_{corr}, is the corrosion current density in µA/cm², e and d are the equivalent weight and density of metal in geq/mol and g/cm³ respectively.

3. RESULTS AND DISCUSSION

3.1. Open circuit potential measurements

The variation of open circuit potentials with exposure time of the four electrodes in meat soup and in 0.5M NaF solutions at 20°C were illustrated in Figure 1. In 0.5M NaF solution, the potential of the four electrodes shifted toward the positive direction, and with increasing time, they reached the rest potential values. This indicates a spontaneous passivation due to development of an oxide film [7]. This continues as a result of the predominance of the cathodic processes over the anodic ones until the film acquires a stable thickness. The necessary electrons of the cathodic reaction are provided by the ionization of metal atoms entering the oxide phase [8].

The same behavior was observed in meat soup for Nb, Mo and CoCr-alloy. On the contrary, the potential of Au electrode shifted to negative values, which stabilized with further increase in immersion time. The same behavior was observed at 30, 40 and 50°C for all studied electrodes. The plots illustrated that CoCr-alloy had higher potential values than Au electrode after the first 20 and 50 minutes of immersion in meat soup and 0.5M NaF solution respectively.

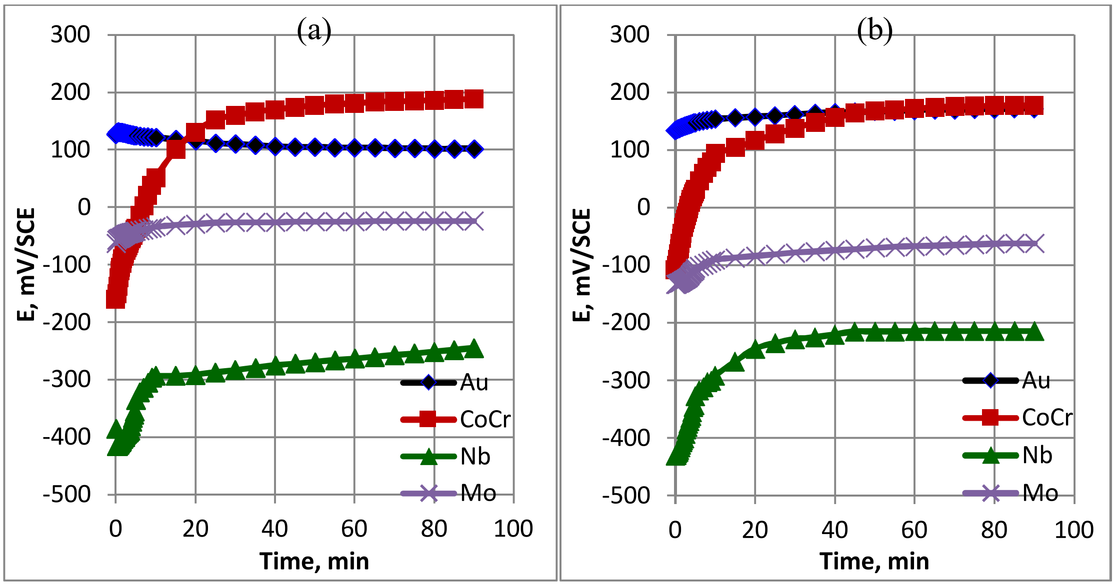

Figure1: Potential – time plots of the four studied electrodes in meat soup (a) and in 0.5M NaF solution (b) at 20°C.

Regarding the temperature effect on the rest potentials (E_r), Figure 2 illustrated that, for each electrode, E_r values decreased with increasing temperature. In meat soup, E_r decreased in the four electrodes at all temperatures according to the following order: CoCr-alloy > Au > Mo > Nb.

The same order was observed in 0.5M NaF solution at 20, and 50°C, while at 30 and 40°C this order changed to be: Au > CoCr-alloy > Mo > Nb.

It was noted that the values of rest potentials are higher in NaF solutions than in meat soup for Au and Nb electrodes, whereas E_r were higher in meat soup for CoCr-alloy and Mo electrodes.

Figure 2 also illustrated that the rest potentials of CoCr-alloy in 0.5M NaF solution about to coincide with that of Au electrode at all temperatures. On the other hand CoCr-alloy provides nobler E_r values than Au electrode in meat soup solutions. This meant that under open circuit conditions, Au electrode may be replaced by CoCr-alloy in meat soup and in 0.5M NaF solution.

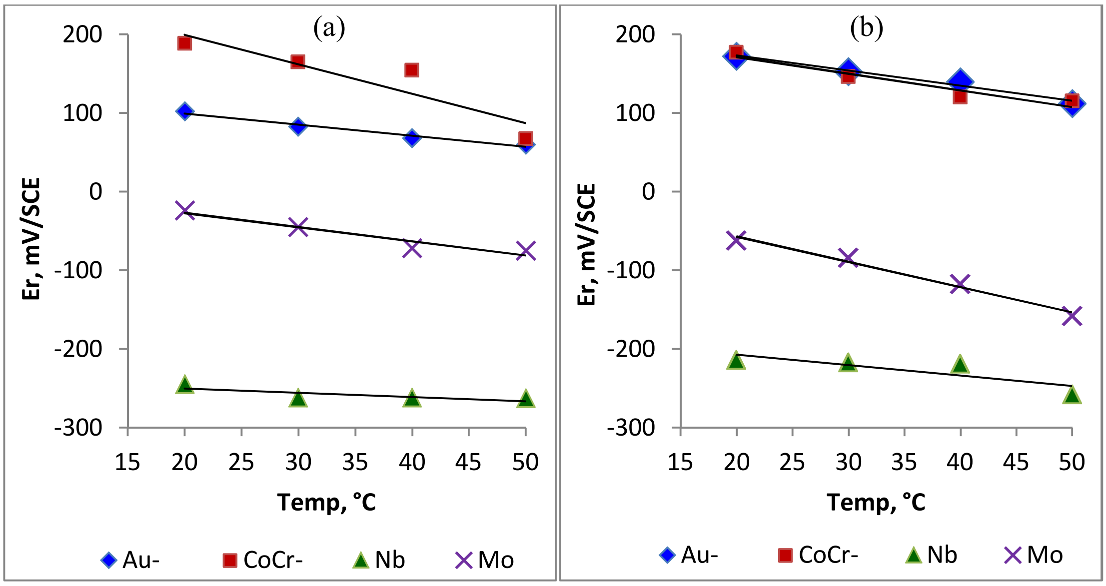

Figure 2: Effect of temperature on the rest potentials of the four electrodes in meat soup (a) and in 0.5M NaF solution (b).

Potentiodynamic measurements

Figure 3 represented the polarization plots for the four electrodes in meat soup and in 0.5M NaF solution at 20°C. For the two investigated solutions, two characteristic zones can be observed at the cathodic branches produced by all electrodes. One zone related to the reduction of the dissolved oxygen in the electrolyte, and the second related to the evolution of hydrogen.

The anodic branches of Au and Mo electrodes represented the ideal behavior of Tafel plots. Broad current density plateaus were observed in the anodic branches of Nb electrode in the two tested solutions at all studied temperatures. Attia *et al.* illustrated similar behavior in saliva solution in a previous study [9]. In such cases, the corrosion rates and the corrosion current densities were obtained by extrapolation of the cathodic polarization curves alone to E_{corr}. CoCr-alloy illustrated a characteristic behavior at the anodic polarization curves. After the first anodic dissolution domain, it can be observed a first passivity range corresponding to the formation of an intermediate less stable passive film, consisting of nonstoichiometric cobalt oxides and oxides of alloying elements [10]. The first passivity ranges observed in meat soup were recorded in the range from 0.3 to 1.6 V/SCE at 20°C, from -0.1 to 1.5 V/SCE at 30°C, from 0.1 to 1.0 V/SCE at 40°C and from -0.3 to 0.6 V/SCE at 50°C. For 0.5M NaF solution, the first passivity ranges were recorded at 20°C (from -0.3 to 1.4 V/SCE), and 40°C (from 0.4 to 1.0V/SCE). The first passivity ranges in some cases were followed by a transpassive region and a second passivity range corresponds to a passive oxide stable film formation [10]. The second passivity range starts at ~ 2.6 and 3.7 V/SCE for meat soup and 0.5M NaF respectively at 20°C, and starts at 3.5 V/SCE for meat soup at 30°C, whereas starts at 2.5 V/SCE for 0.5M NaF at 40°C.

The respective potentiodynamic parameters including corrosion potential (E_{corr}), corrosion current density (I_{corr}), corrosion rate (C_R), anodic (β_a) and cathodic (β_c) Tafel slopes for the different four electrodes are tabulated in Tables 1and 2.

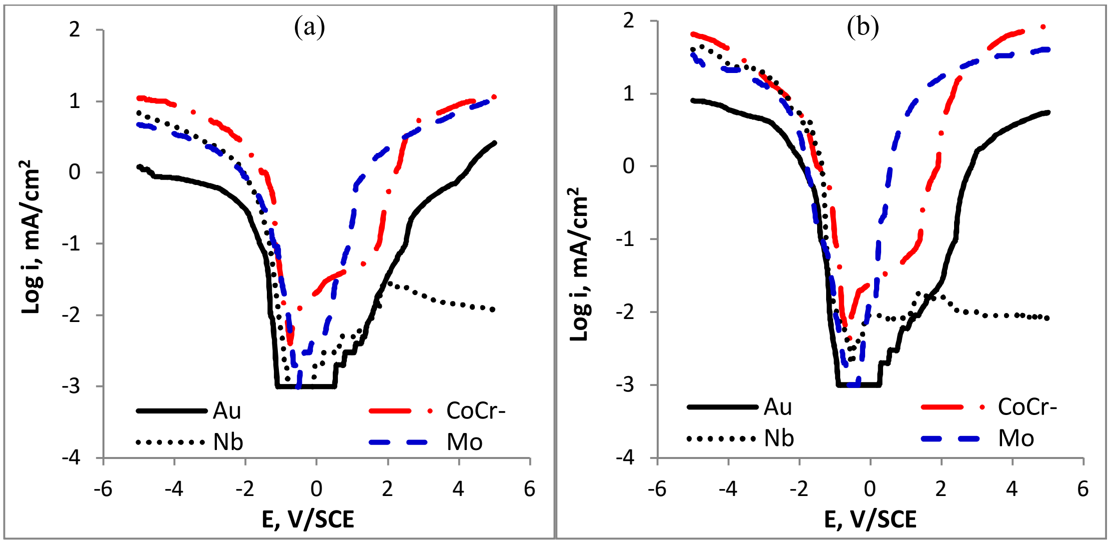

Figure 3: Potentiodynamic plots of CoCr-alloy, Nb, Mo and Au electrodes in meat soup (a) and in 0.5M NaF solution (b) at 20°C.

Table 1: Potentiodynamic parameters of the four electrodes in meat soup

electrode	Temp. °C	E_{corr} mV/SCE	I_{corr} $\mu A/cm^2$	β_c mV/dec	β_a mV/dec	C_R mpy
Au	20	200	25.1	-2000	2333	2.57E-06
	30	200	31.6	-2333	2000	3.24E-06
	40	100	39.8	-2000	2000	4.08E-06
	50	100	50.1	-1750	2000	5.14E-06
CoCr-alloy	20	-200	199	-1666	2000	6.14E-02
	30	-200	398	-2000	2333	1.23E-01
	40	-200	794	-2000	2500	2.45E-01
	50	-200	1259	-2000	2500	2.66E-01
Nb	20	-500	631	-3666	-	8.90E-02
	30	-500	1259	-3500	-	1.78E-01
	40	-500	1585	-3333	-	2.24E-01
	50	-500	1995	-5000	-	2.81E-01
Mo	20	-100	25	-1125	800	5.06E-03
	30	-200	63	-1000	1166	1.27E-02
	40	-300	79	-1000	1166	1.60E-02
	50	-400	100	-1125	1333	2.02E-02

Table 2: Potentiodynamic parameters of the four electrodes in 0.5M NaF solution

electrode	Temp. °C	E_{corr} mV/SCE	I_{corr} $\mu A/cm^2$	β_c mV/dec	β_a mV/dec	C_R mpy
Au	20	300	63.1	-1600	1666	6.47E-06
	30	100	79.4	-1400	1600	8.14E-06
	40	100	100	-1500	2000	1.03E-05
	50	-100	126	-1200	2333	1.29E-05
CoCr-alloy	20	-200	398	-1400	1500	1.23E-01
	30	-400	794	-1000	2000	2.45E-01
	40	-400	1585	-1600	2000	4.88E-01
	50	-400	2512	-1666	1666	7.74E-01
Nb	20	-500	2512	-3500	-	3.54E-01
	30	-500	3981	-3500	-	5.62E-01
	40	-500	7943	-4000	-	1.12E+00
	50	-500	12589	-4000	-	1.78E+00
Mo	20	-500	63	-1000	750	1.28E-02
	30	-500	100	-750	666	2.02E-02
	40	-500	251	-1000	600	5.08E-02
	50	-500	398	-1000	666	8.05E-02

From Tables 1and 2 it was observed that Au electrode in the two solutions provided the most noble corrosion potential (E_{corr}) values for all electrodes. On the contrary, niobium electrode provided the most negative corrosion potentials of all electrodes, with the same E_{corr} values (-500 mV/SCE) at all temperatures for the two solutions. Molybdenum electrode behaved similar to Nb electrode in 0.5M NaF solution, but in meat soup, the corrosion potential had less negative E_{corr} values and the negativity increased with increasing temperature. CoCr-alloy provided the same E_{corr} values (-200 mV/SCE) at all temperatures in meat soup, which equalized with that in 0.5M NaF solution at 20°C. With increasing temperature of the fluoride solution, the corrosion potential decreased to the same value (-400 mV/SCE) at 30, 40 and 50°C. This indicates more passivity of CoCr-alloy in meat soup. From Tables 1 and 2, it can be said that $E_{corr\,(meat\,soup)} \geq E_{corr\,(0.5\,M\,NaF)}$.

The corrosion rates (C_R) for all electrodes, increased with increasing temperature for the two studied solutions. The C_R values were always higher in 0.5M NaF solutions than in meat soup solutions.

The high values of β_a in comparison with the values of β_c for Au and CoCr- alloy electrodes in the two tested solutions indicated an anodic control in the corrosion process. The control implied the existence of a passive layer on the electrode surface [11].

The lower corrosive action of meat soup compared with that of 0.5M NaF solution on all electrodes; illustrated by the values of C_R in Tables 1and 2 may be illustrated according to the fact that the most abundant compounds extracted in meat soup are nitrogenous compounds (proteins, nucleotides, peptides, creatine, and creatinine), lipids, vitamins, carbohydrates and ash [12]. Based on the components of the meat soup, hetero atoms such as nitrogen, oxygen or even double bonds involved in the structure of food stuff in meat soup may enable adsorption on the electrodes surfaces. This process produces adsorbed film acts as a barrier separating the surface from the corrosive medium more than that produced from fluoride solution. The order of passivity according to corrosion rate values in the two solutions is: Au > Mo > CoCr-alloy > Nb

The sequence of electrodes in this order can be explained according to the standard redox potential of elements. Gold had the highest standard electrode potential and is therefore the noblest material with the highest corrosion resistance [13].

$$Au^{+} + e^{-} \rightleftharpoons Au \qquad E^{o} = +1.69\ V \qquad (2)$$

$$Au^{3+} + 3e^{-} \rightleftharpoons Au \qquad E^{o} = +1.40\ V \qquad (3)$$

According to the standard reduction potential of Mo, Nb and major elements constituting the CoCr-alloy, illustrated in equations (4-7) [14], molybdenum take its place after Au electrode and Nb is the most corrosive electrode.

$$Mo^{3+} + 3e^{-} \rightleftharpoons Mo \qquad E^{o} = -0.200\ V \qquad (4)$$

$$Co^{2+} + 2e^{-} \rightleftharpoons Co \qquad E^{o} = -0.277\ V \qquad (5)$$

$$Cr^{3+} + 3e^{-} \rightleftharpoons Cr \qquad E^{o} = -0.740\ V \qquad (6)$$

$$Nb^{3+} + 3e^{-} \rightleftharpoons Nb \qquad E^{o} = -1.100\ V \qquad (7)$$

The values of dynamic potentials, scan rate, type of solution and temperature have many effects in the corrosion rate. Also the presence of different alloying elements, having different affinities to oxygen, affects the corrosion rate.

Thermodynamic considerations

The dependence of corrosion rate (C_R) on temperature can be expressed by the familiar Arrhenius equation:

$$\frac{d \log C_R}{d(1/T)} = -\frac{E_a}{R}$$

This form can be simplified to the following linear equation [15]:

$$\log C_R = A - (E_a/2.303\,RT) \qquad (8)$$

where A is a constant representing the frequency factor, E_a is the apparent activation energy of the dissolution reaction, R is the universal gas constant and T is the absolute temperature.

A plot of logarithmic variation of corrosion rates with reciprocal of absolute temperatures gave straight lines with slopes of $-(E_a/2.303\,R)$ (Figure 4). The obtained values were recorded in Table 3.

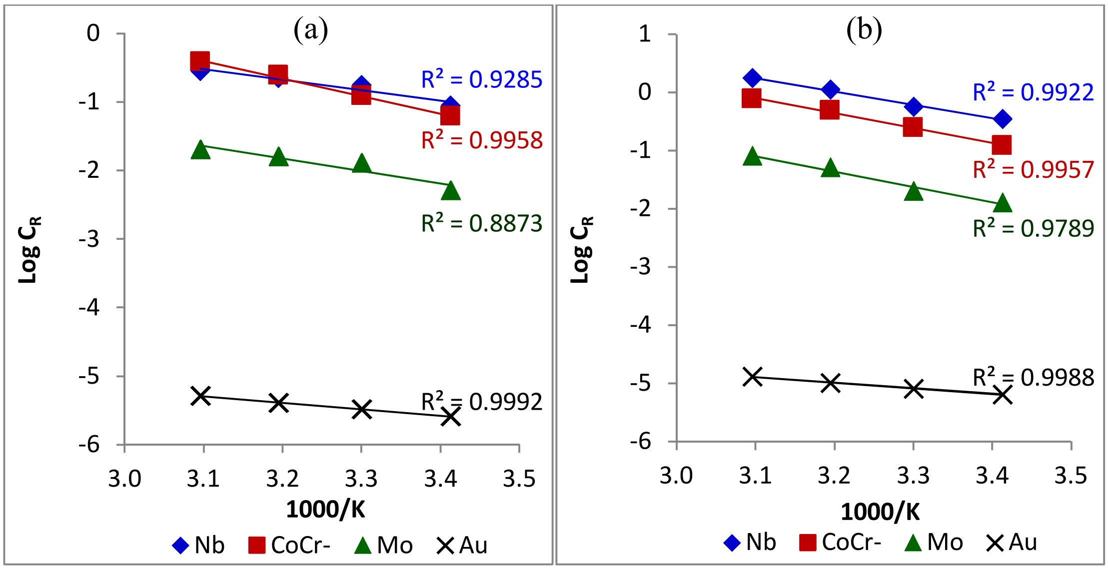

Figure 4: Arrhenius plots of the corrosion behavior of CoCr-alloy, Au, Nb and Mo electrodes in meat soup (a) and in 0.5M NaF solution (b).

In meat soup, CoCr-alloy provided the most negative E_a value, while Au electrode provided the least negative value, indicating the ease of dissolution of the CoCr-alloy passive film in meat soup and the relative difficulty of dissolution process of Au electrode. In 0.5M NaF solution, Mo electrode provided the most negative E_a value, while Au provided the least negative value.

It was observed that Au electrode provide the same E_a value in meat soup and fluoride solutions. Also, CoCr-alloy provides the same E_a value in the two solutions. On the other hand, each of Nb and Mo electrodes provide less negative E_a values in meat soup. The less negative values of E_a in a certain medium implied that this media increased the height of the energy barrier of the corrosion reaction.

The thermodynamic functions for the dissolution process were obtained by applying the Eyring transition-state equation (Eq. 9) [6, 15]:

$$\log \mathrm{C_R}/T = \log\ (R/Nh) + (\Delta S^{\circ}/2.303R) - (\Delta H^{\circ}/2.303RT) \quad (9)$$

where N is Avogadro's number, h is Planck's constant, ΔS° and ΔH° are the entropy and enthalpy of activation, respectively. A plot of $\log \mathrm{C_R}/T$ *vs.* $1/T$ gave straight line with slope of $[-\Delta H^{\circ}/2.303R]$ and an intercept of $[\log(R/Nh) + (\Delta S^{\circ}/2.303R)]$ as illustrated in Figure 5. The obtained values were tabulated in Table 3.

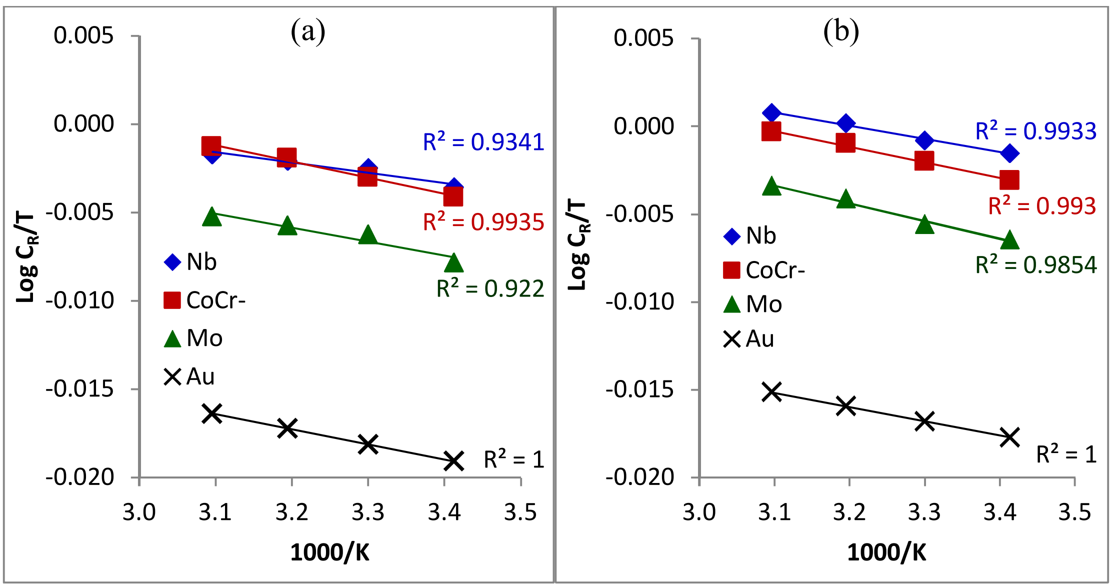

Figure 5: Transition state plots of the corrosion behavior of CoCr-alloy, Au, Nb and Mo electrodes in meat soup (a) and in 0.5M NaF solution (b).

Table 3: Activation and thermodynamic parameters for the four electrodes in meat soup and in 0.5M NaF solutions

	meat soup			0.5M NaF		
Type of Electrode	E_a kJ/mol	ΔH° kJ/mol	ΔS° J/mol K	E_a kJ/mol	ΔH° kJ/mol	ΔS° J/mol K
Au	-18	175	-197	-18	169	-197
CoCr-alloy	-49	163	-197	-49	155	-197
Nb	-23	151	-197	-38	193	-197
Mo	-35	110	-197	-50	143	-197

The positive signs of ΔH° provided by all electrodes reflected the endothermic nature of the dissolution process which suggested the difficult and slow dissolution of electrodes in presence of meat soup or 0.5M NaF solutions [15]. The high values for ΔH° indicated high protection efficiency. This might be attributed to the presence of an energy barrier for the reaction, that is, a process of adsorption of solutions on the surface of electrodes led to a high enthalpy of the corrosion process [16].

The enthalpy provided by Au and CoCr-alloy electrodes was higher in meat soup, while that provided by Nb and Mo electrodes was higher in NaF solution. In fluoride solution, Nb electrode provided the highest value, while in meat soup; Au electrode provided the highest value.

In addition, the entropy values ΔS° for all electrodes had the same magnitude in the two solutions. The large and negative entropy value reflects the formation of an ordered stable layer on the electrode surface and the increase in the system ordering accompanied the dissolution process [16].

CONCLUSION

1. The C_R values were always higher in 0.5M NaF solutions than in meat soup solutions.
2. The order of passivity according to corrosion rate values in the two solutions is:
   Au > Mo > CoCr-alloy > Nb
3. The calculated ΔH° values indicated that the protection provided by CoCr-alloy is better than that provided by Au electrode in both of meat soup and 0.5M NaF solution. However the protection provided by Mo electrode is better than that provided by Au and CoCr-alloy in 0.5M NaF solution.

REFERENCES

1. https://www.webelements.com/gold/chemistry.html
2. http://www.chemistryexplained.com/elements/C-K/Gold.html
3. http://www.rembar.com/MSDS.html
4. https://www.dovemed.com/healthy-living/wellness-center/which-foods-contain-most-fluoride/
5. https://law.resource.org/pub/eg/manifest.eg.html
6. E. M. Attia, N. S. Hassan and A. M. Hyba; Corrosion Protection of Tin in 1M HCl by Expired Primperan and E-mox Drugs-Part I. *J. Basic. Appl. Chem.*, 7(1) (2017) 9-25.
7. A.M. Shams El-Din and N.J. Paul, Thin Solid Films 189 (1990) 205.
8. F. El-Taib Heakal, A.A. Ghoneim and A.M. Fekry; Stability of spontaneous passive films on high strength Mo-containing stainless steels in aqueous solutions. *J. Appl. Electrochem.* 37 (2007) 405–413.
9. E. M. Attia, R.M. Abou Shahba and F.M. Abou Koffa; Open circuit potential and potentiodynamic view on the behavior of different four electrodes in artificial saliva solution for usage in dental application. *J. Basic. Appl. Chem.*, 8(3)(2018) 9-18.
10. I. V. Branzoi, M. Iordoc, M. M. Codescu; corrosion behaviour of CoCrMo and CoCrTi alloys in simulated body fluids. U.P.B. Sci. Bull., Series B, 69, (4) 2007
11. D. Mareci, D. Sutiman, A. Cailean and Bolat; Bull. Mater. Sci., 33(4) (2010) 491–500.
12. Á. Cobos and O. Díaz; Chemical Composition of Meat and Meat Products. Handbook of Food Chemistry
13. R.C. Weast, *CRC* Handbook of Chemistry and Physics; CRC Press: Cleveland, OH, USA, 1978; pp. 141–146.
14. P. Atkins and J.D. Paula; (2014): Atkins' Physical Chemistry. 10th Ed., Oxford: Oxford Press. pp 937.
15. E. M. Attia; Dipron: an eco-friendly corrosion inhibitor for iron in HCl media in both micro and nano scale particle size - Comparative study. IJAR 4 (3) (2016), 986-1003.
16. E. M. Attia, N. S. Hassan and A. M. Hyba; Corrosion Protection of Tin in 1M HCl by Expired Novacid Drug-Part I. IJAR 4 (2) (2016), 872-886.