

Influence of Fluoride and/or Bovine Albumin on Electrochemical Properties of Bare and ionic liquid- Coated Ni₄₇Ti₄₉Co₄ Orthodontic archwires in artificial saliva solution

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Drawn biodegradable metallic wires are expected to degrade or to be resorbed within the body. Subjected to inorganic ions as fluoride corrosive ions and organic compound as proteins can affect corrosion and induce health complications. Accordingly, surface modification materials are presently used as dental, orthopedic and cardiovascular applications. In this perspective, Ni₄₇Ti₄₉Co₄ orthodontic brackets and archwires were firstly coated with ionic liquid (IL) and then immersed in fluoride and/or bovine albumin containing simulated saliva solution; the corrosion behavior was examined and compared with bare Ni₄₇Ti₄₉Co₄ orthodontic archwires. The surface morphology before and after the immersion tests were analyzed while using scanning electron microscopy (SEM). The observations showed significant morphological changes with ionic liquid coat of the archwires surface. In addition, conventional electrochemical measurement methods, including cyclic voltammetry, corrosion potential and potentiodynamic measurements were also used to elucidate the effects of ions concentration, immersion time and coat stability on Ni₄₇Ti₄₉Co₄. The results showed that either the NaF(0–0.1%) and/or the presence of albumin (0–0.05%) in simulated saliva solution had a considerable impact on the corrosion potential (E_{corr}), corrosion rate (I_{corr}), and polarization resistance (R_p). The I_{corr} values increased with increasing the NaF concentration, but decreased with albumin addition in NaF-containing saliva solution. Furthermore, the presence of ionic liquid coat, irrespective of the testing media, greatly enhances the corrosion resistance of the Ni₄₇Ti₄₉Co₄ archwires.

Keywords: Ni₄₇Ti₄₉Co₄; Electrochemical impedance; coating; corrosion; fluoride.

1. INTRODUCTION

Metal alloys, such as Cr-Co-Ni alloy, nickel–titanium (NiTi) alloy, and stainless steel (SS) have a wide variety of medical applications, including dentistry, especially for orthodontic treatment. They are attractive due to their super elasticity behavior and martensitic phase transformation. Alloy elements influence the formation of oxide layers and play vital roles in their corrosion behavior. The

newly ternary alloy Ni₄₇Ti₄₉Co₄ SMAs which has similar nitinol alloy compositions except for Co is an example of the superior corrosion resistance owing to their stabilized oxide layer. Ni₄₇Ti₄₉Co₄ SMAs has been studied in physiological body fluid to confirm its excellent biocompatibility, while also retaining adequate mechanical properties [1-3]. During orthodontic treatment, brackets and archwires are maintained in the oral cavity for a long period of time, and so they are subjected to constant mechanical stress of chewing and wearing. Moreover, immersion in saliva and ingested fluids, variation of temperature and pH caused by diet, decomposition of foods, topical fluoride modalities (toothpaste, mouthwashes and varnish), oral microflora, and their byproducts, enzyme activity, and proteins [3-5], also affect the surface of the archwires. Thus, it is necessary to improve the surface as a research challenge and for safe use of archwires in the future.

Inside the mouth, Corrosion defects on the surface of the orthodontic appliance increases the friction between archwires and slot interface, and release metal or alloy ions such as titanium, chromium, manganese, nickel, and cobalt into the oral cavity [6-9]. Locally, the released ions consequently can result in discoloration of enamel and soft the oral tissues by inhibiting enzymes. Moreover, nickel ions may induce hypersensitivity and allergic reactions in predisposed patient [10]. On the other hand, the highly reactive titanium reacts with oxygen to form a protective oxide layer on the surface of the alloy, creating a physical barrier for the oxidation of nickel, leaving it deeper in the archwire [11]. Unfortunately, the passive titanium layer could be removed or destroyed by many different factors in the mouth. Consequently, the corrosion resistance of dental alloys in an acidic oral environment is surely a crucial subject when biocompatibility is of concern.

Consequently, Surface coatings techniques have been used heavily in biomedical applications to enhance the corrosion resistance performance of metals towards hostile environment through passive film formation [12, 13]. Among the various surface coating materials, ionic liquids (IL) are considered as the effective greenness materials in diverse applications. From simple barrier coatings to elaborate nanotechnology-based composites, ionic liquids offer good thermal and electrochemical stability, high ionic conductivity, negligible vapor pressure, low flammability and toxicity. In regard to biomedical devices and implants, such characteristics include corrosion protection, enhanced biocompatibility, electrical conductivity and tailored surface chemistry.

Although, Fluoride products is almost universally recommended for dental caries control, Unfortunately, the fluorides (e.g. in terms of NaF and/or Na₂FPO₄) from fluoride-containing products and prophylactic gels are aggressive ions that reacts with hydrogen ions from bacterial products, resulting in the formation of hydrofluoric acid (HF) [14]. This acid dissolves the protective oxide layer on the surface of metal orthodontic components, resulting in bracket and archwires corrosion [15]. Besides, oral environment contains dissolved foods remains and beverages, including various proteins and albumin, would also affect the corrosion resistance of metallic biomaterials; Furthermore, several reports have reported different behavior for protein adsorption on the corrosion behavior of metallic alloy [16-21].

Extending to our previous works on coated metal alloys and from the point of academic interest and clinical importance, the further sequential investigation on the electrochemical behavior of metal alloy bracket and archwires subjected to hostile oral environment is inevitable.

For an attempt to decrease metal ion release, enhance biocompatibility and corrosion resistance, Ni₄₇Ti₄₉Co₄ orthodontic brackets and archwires were coated with ionic liquid. Additionally, the effect of fluoride ions and/or bovine albumin concentration in simulated saliva solution and the effect of immersion time were elucidated via surface analysis and electrochemical impedance spectroscopy measurements.

2. EXPERIMENTAL

2.1. Materials and methods

2.1.1. Materials

Ni₄₇Ti₄₉Co₄ orthodontic archwires (melting technique under vacuum has been used for fabrication) with exposed cross-sectional area of 0.2 cm² were used as tested material in this study. 1-Butyl-3-methylimidazolium chloride ([Bmim]Cl) ionic liquid (IL) was purchased from Sigma Aldrich company. Artificial saliva with pH = 6.2 was prepared from the analytic grade agents and deionized water, and consisted of: 0.4 g/L NaCl, 0.4 g/L KCl, 0.795 g/L CaCl₂·2H₂O, 0.78 g/L NaH₂PO₄·2H₂O, 0.005 g/L Na₂S₉H₂O, 1.0 g/L Urea. A stock solution of 1-Butyl-3-methylimidazolium chloride as ionic liquid ([Bmim]Cl) (≥ 95%) with (0.1%) was prepared with isopropanol before usage.

Ni₄₇Ti₄₉Co₄ brackets and archwires samples were tested in artificial saliva solution containing different NaF (Sigma Co, USA) concentrations, including 0.005%, 0.02%, 0.04%, 0.06%, 0.09%, and 0.10%, to simulate the effect of fluoride based hygiene products. In order to evaluate the effect of albumin on the corrosion resistance of bare and coated Ni₄₇Ti₄₉Co₄ SMAs in absence and presence of 0.1% NaF, different bovine albumin (Sigma Co., USA) concentrations, including 0.015%, 0.025%, 0.035%, 0.045%, and 0.05% were added to the artificial saliva solution.

2.1.2. Coat Deposition

The ionic liquid coat was formed by ultra-sonicated Ni₄₇Ti₄₉Co₄ SMAs archwires in 0.1% [Bmim]Cl solution using (UC-06D Digital Ultrasonic Cleaner) for 1 h, and then exposed for heat treatment under 200°C for 10 min.

2.2. Surface analysis and electrochemical study

The surface morphologies of bare and IL/ coated Ni₄₇Ti₄₉Co₄ orthodontic wires before and after the corrosion tests were analyzed using a JEOL JXA-840A scanning electron microscope. Subsequently, the immersion solutions of both samples were analyzed with energy dispersive X-ray spectroscopy (EDS).

A potentiostat/galvanostat (Model 73022, Autolab Instruments, Metrohm) with a standard three electrode cell was used for electrochemical measurements. Ni₄₇Ti₄₉Co₄ archwires is the working

electrode (WE), Ag/AgCl/3M KCl (Satd.) as the reference electrode (RE), and platinum wire as the counter electrode (CE). The working electrode were mechanically polished with a series of abrasive papers of 400, 800, 1500 grades. Ni₄₇Ti₄₉Co₄ archwires were then cleaned with acetone and deionized water and dried with air stream. The cyclic voltammogram curves of bare and coated Ni₄₇Ti₄₉Co₄ archwires were measured from - 100 mV toward the anodic direction, with a scan rate 50 mV/s. After immersion in the tested solutions for 15 min, obtaining stable open circuit potential, Potentiodynamic polarization measurement were performed from range -0.5V (Ag/AgCl) with a scan rate of 1 mV/s. In addition, some other corrosion resistance parameters, including the corrosion potential (E_{corr} ; at this potential the sum of the anodic and cathodic reaction rates on the electrode surface is zero), corrosion current rate (I_{corr} ; the anodic current density at the potential of E_{corr} is the corrosion rate), and kinetic parameters such as anodic and cathodic tafel slopes (b_a and b_c), and corrosion potentials were obtained from tafel analyses based on the potentiodynamic polarization curves. The corrosion resistance parameters were statistically analyzed using linear analysis of tafel approximation using (ANOVA) software.

The impedance diagrams were recorded at the free immersion potential by applying a 10 mV sinusoidal potential through a frequency domain from 100 kHz down to 100 mHz. The real (Z) and imaginary (Z') parts of the impedance are calculated from the overall impedance (Z^*) as in equation (1) :

$$Z^*(\omega) = Z(\omega) + jZ'(\omega) \quad (1)$$

Where ω is the angular frequency that equals to $2\pi f$ (f/Hz is the frequency).The EIS were obtained in test solutions and plotted in the form of Nyquist diagram.

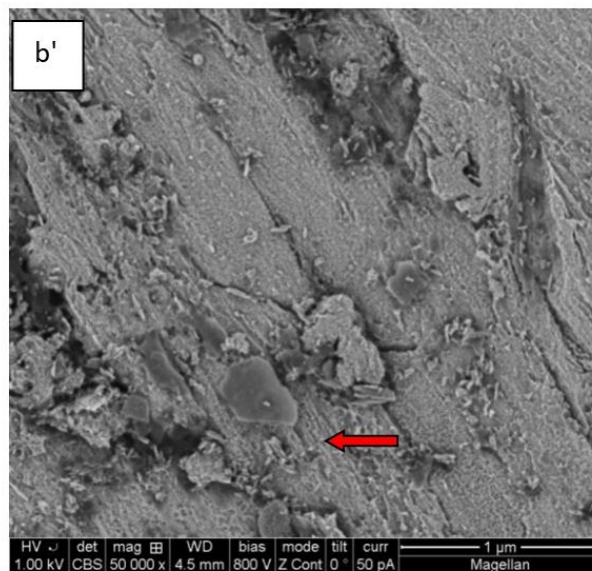
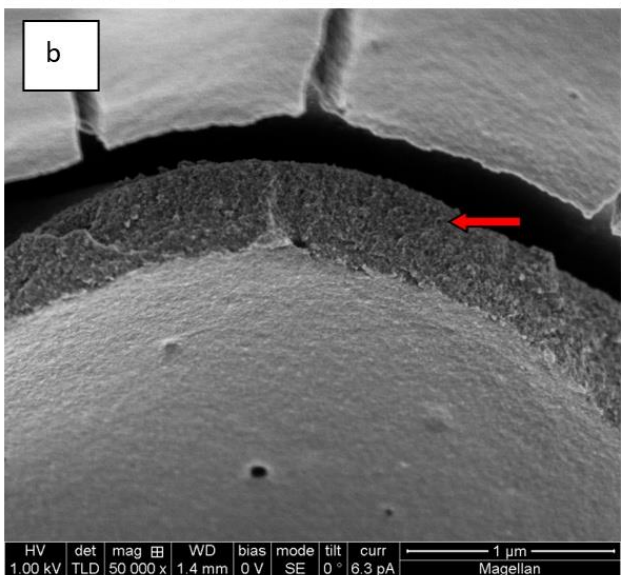
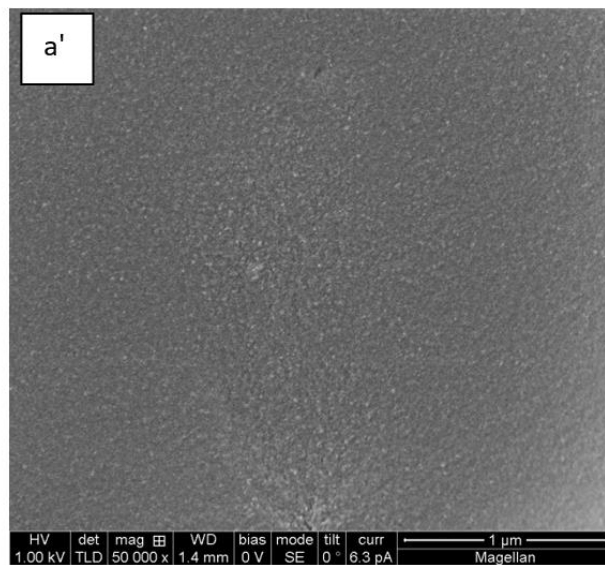
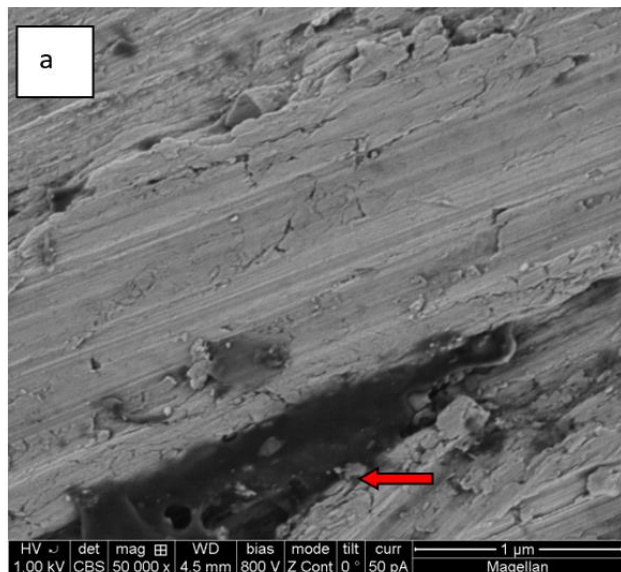
3. RESULT AND DISCUSSION

3.1. Surface characterization: Morphology and Elemental analysis

The morphological examination with SEM showed significant microstructure differences between bare and IL/coated archwires (Fig. 1a, a') in simulated saliva solution, respectively. Bare Ni₄₇Ti₄₉Co₄ archwire surface is rough, with local surface defects produced during manufacturing process, tending to fast release of elements from the surface into the medium, while the ionic liquid coated Ni₄₇Ti₄₉Co₄ archwire surface is smooth and without any other visible defects. This can be attributed to the uniform distributed coat over the metal surface Fig. 1 (a'). After immersion in 0.1% Sodium fluoride (NaF) containing simulated saliva solution for 4 hours, pitting corrosion with severe deep cracking were observed on bare Ni₄₇Ti₄₉Co₄archwire Fig. 1(b), fluoride ions lead to accelerate corrosion and increases metal ion release. Contrarily, less defects were noticed on coated Ni₄₇Ti₄₉Co₄ archwire due to the high density and low porosity of the deposit ionic liquid coat, Fig. 1 (b').

As shown in Fig. 1(c) and (c'), for bare and coated Ni₄₇Ti₄₉Co₄ archwire after immersion in 0.05 g/L albumin and 0.1% fluoride containing media for 4 hours, dramatic decrease in the pitting corrosion compared to that without albumin. This account on the adsorption of albumin on the alloy, forming a thick biofilm which intern protect alloy surface against corrosive fluoride ions attack [15-

16]. This behavior was also noticed for coated Ni₄₇Ti₄₉Co₄archwire Fig.(C'). This image shows thicker and smoother coverage [4, 8, 12].



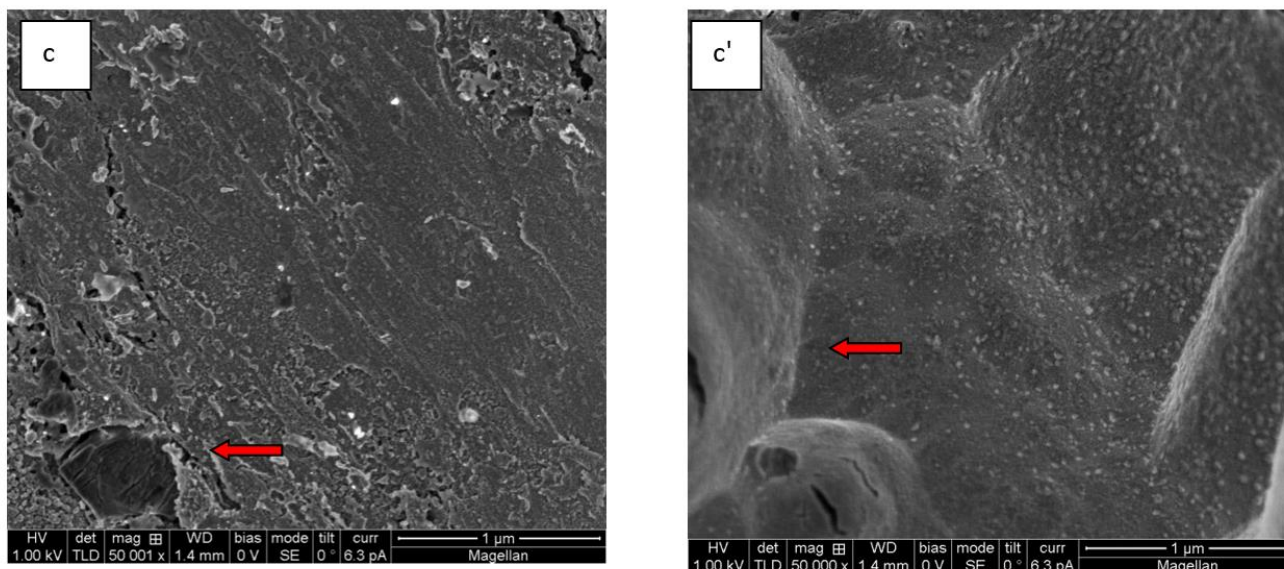


Figure 1. SEM micrographs showing the surface morphologies for (a) bare and (a') coated $\text{Ni}_{47}\text{Ti}_{49}\text{Co}_4$ SMAs in simulated saliva, (b) bare and (b') coated $\text{Ni}_{47}\text{Ti}_{49}\text{Co}_4$ SMAs in simulated saliva containing 0.1% NaF, (b) bare and (b') coated $\text{Ni}_{47}\text{Ti}_{49}\text{Co}_4$ SMAs in simulated saliva containing 0.1% NaF and 0.05 g/L (Alb).

In accordance with these SEM observations, no detectable metal ion release could be measured from the coated $\text{Ni}_{47}\text{Ti}_{49}\text{Co}_4$ archwire by means of EDX. Furthermore, a complete picture of chemical composition of the coating were also obtained by EDX revealing that the compositional distribution of the coating was found to be Carbon (70.36 at%), Nitrogen (10.94 at%) and Chloride (5.68 at%) elements, which are the main component of ionic liquid. Moreover, no presence of oxygen or carbon was observed, indicating the absence of oxide layer on the coated $\text{Ni}_{47}\text{Ti}_{49}\text{Co}_4$ archwire [2]. These observations point out that IL coat was successfully formed over $\text{Ni}_{47}\text{Ti}_{49}\text{Co}_4$ archwire surface with no evidence for oxides formation.

3.2. Electrochemical investigation

3.2.1. Effect of Solution nature on the Electrochemical Behavior of bare and coated $\text{Ni}_{47}\text{Ti}_{49}\text{Co}_4$ archwire

Cyclic voltammetry 'CV' is the one of the most useful techniques that provides information about surface properties in different solution media. The redox reactions at the surface of bare and coated $\text{Ni}_{47}\text{Ti}_{49}\text{Co}_4$ archwires were conducted with scanning rate of 50 mV/s and range of -1 to 1.5 V. In Fig. 2 (a), for bare $\text{Ni}_{47}\text{Ti}_{49}\text{Co}_4$ archwire in simulated saliva solution, in the first glance, charging current was noticed implies specifically electron transfer and oxide layer formation. By adding 0.1% NaF to simulated saliva solution, a swift increase in the anodic peak current was observed Fig. 2 (b). This increase corresponds to oxide layer dissolution via fluoride ions attack [4, 13]. Fig. 2 (c) illustrates the cyclic voltammogram for bare $\text{Ni}_{47}\text{Ti}_{49}\text{Co}_4$ archwire recorded in simulated saliva solution containing 0.05 g/L albumin. It is obvious from the cyclic voltammogram that the charging current

decreases owing to the protein layer deposition and biofilm formation. By addition of both 0.1% NaF and 0.05 g/L albumin to simulated saliva solution presented in Fig. 2 (d), the charging current begin to increases again. In contrast, the cyclic voltammogram for coated $\text{Ni}_{47}\text{Ti}_{49}\text{Co}_4$ archwire immersed in simulated saliva solution containing both 0.1% NaF and 0.05 g/L albumin was investigated and shown in Fig. 2 (e). As it can be seen, the current density decreases and the anodic peak current shifted to more positive value compared to the obtained peak for bare $\text{Ni}_{47}\text{Ti}_{49}\text{Co}_4$ archwire. It is clearly attributed to the passive ionic liquid coat which protects the surface from fluoride attack. The conclusion to be drawn is that, the corrosion current trend in various tested solutions could be represented as followed, higher corrosion for bare alloy in simulated saliva solution containing NaF > simulated saliva solution > simulated saliva solution containing NaF and Albumin > simulated saliva solution containing Albumin > coated alloy in simulated saliva solution containing NaF and Albumin which has better corrosion resistance.

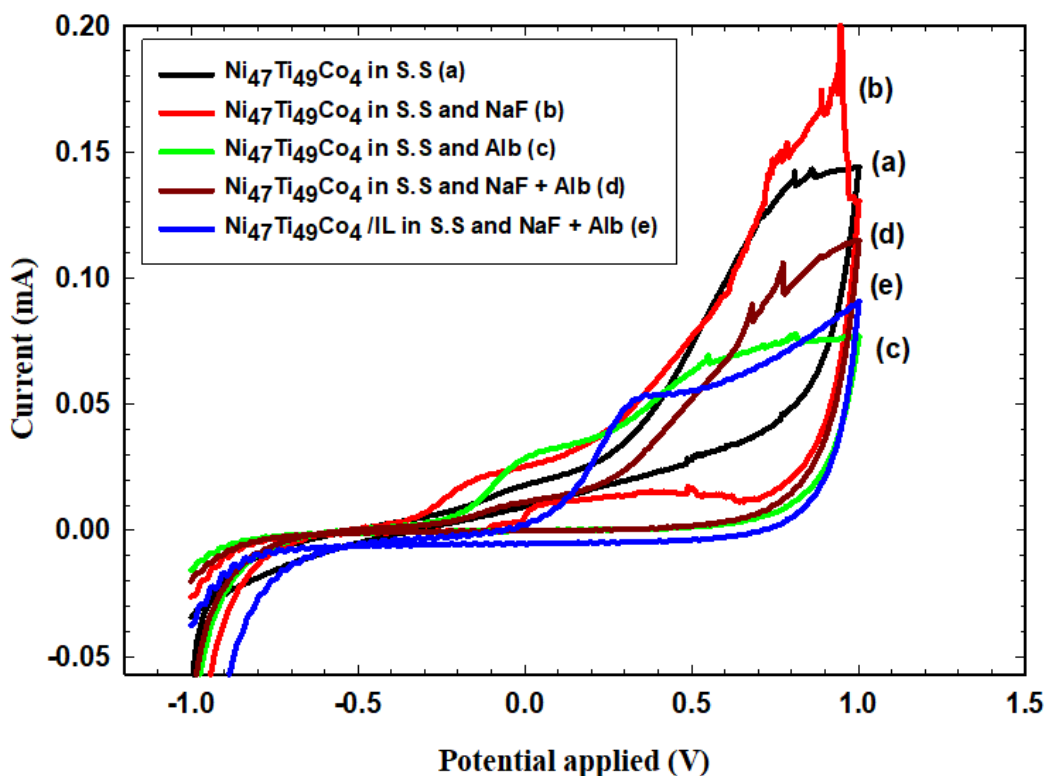
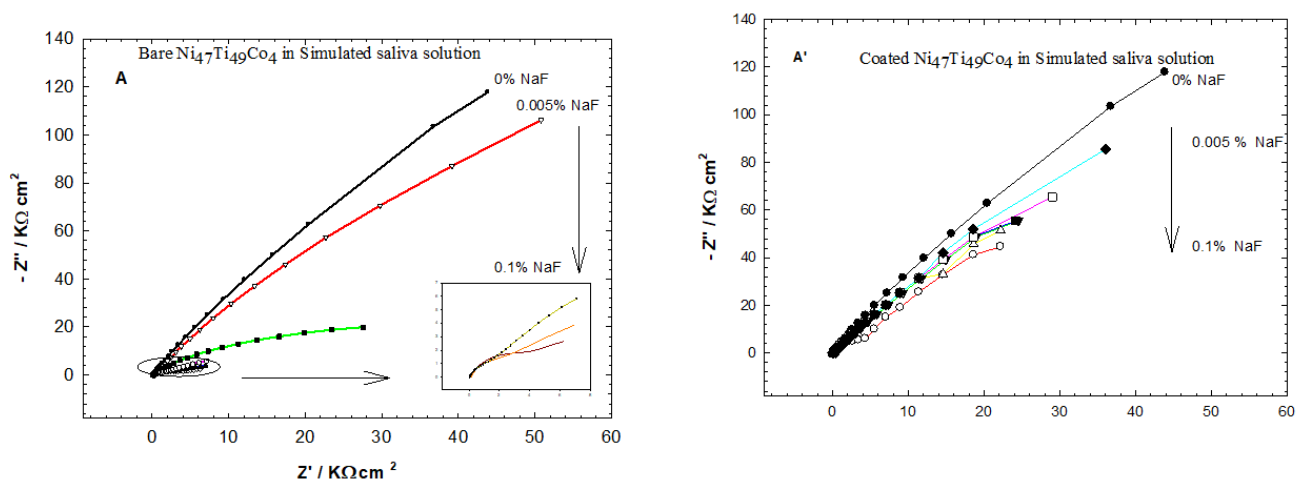


Figure 2. Cyclic voltammograms of bare $\text{Ni}_{47}\text{Ti}_{49}\text{Co}_4$ SMAs in (a) simulated saliva solution (S.S) (b) S.S containing 0.1% NaF (c) S.S containing 0.05 g/L Albumin (Alb) (d) S.S containing 0.1% NaF and 0.05 g/L Albumin. (e) Coated $\text{Ni}_{47}\text{Ti}_{49}\text{Co}_4$ SMAs in same solution used in (d).

3.2.2. Effect of NaF and/or Albumin concentration on bare and coated $\text{Ni}_{47}\text{Ti}_{49}\text{Co}_4$ archwire

The Nyquist plot for bare and coated $\text{Ni}_{47}\text{Ti}_{49}\text{Co}_4$ archwire in simulated saliva solution with different NaF concentrations (0.005%, 0.02%, 0.04%, 0.06%, 0.09%, and 0.10%) is shown in Fig. 3 (A). At (0%) fluoride concentrations, the impedance was approximately characterized by one large semicircle, namely one capacitive loop, corresponds to the capacitive effect of surface passive film.

After, addition of 0.005 % NaF to simulated saliva solution, the capacitive loop decreases. With increasing NaF concentration, the surface oxide film destroyed by the attack of corrosive fluoride ions via the formation of soluble fluoride compound [22-23]. Consequently, the corrosion resistance continuously decreases. In contrast, Fig. 3 (B) shows the Nyquist plot for bare $\text{Ni}_{47}\text{Ti}_{49}\text{Co}_4$ archwire in simulated saliva solution with different albumin concentrations (0.015, 0.025, 0.035, 0.045, 0.05 g/L). By the first small addition of 0.015 g/L albumin concentration to simulated saliva solution, the capacitive loop firstly decreases sharply indicating the instability of the surface oxide film in presence of albumin. But, the gradual increases in albumin concentration to 0.05 g/L, the corrosion resistance of bare $\text{Ni}_{47}\text{Ti}_{49}\text{Co}_4$ archwire increases, implying high resistivity owing to biofilm deposition on alloy surface. This behavior simulates the process occurring in oral environment. Altogether, The Nyquist plots of bare $\text{Ni}_{47}\text{Ti}_{49}\text{Co}_4$ archwire in 0.1% NaF containing artificial saliva with different albumin concentrations (0.015–0.05%) are shown in Fig. 3 (C). At (0%) albumin concentrations, the Nyquist plot was approximately characterized by one small semicircle (capacitive loop) which illustrates a marked decrease in corrosion resistance value owing to the fluoride ions attack. By gradual addition of albumin, the corrosion resistance began to increase, indicating the high ability of albumin to adhere to metal surface by electrostatic interaction forming metal-protein conjugate which enhances corrosion resistance [24]. One can conclude that, the addition of 0.015–0.05 g/L albumin in the 0.1% NaF-containing simulated saliva solution protected $\text{Ni}_{47}\text{Ti}_{49}\text{Co}_4$ archwire surface against the fluoride ions attack [3]. Same behavior was noticed for coated $\text{Ni}_{47}\text{Ti}_{49}\text{Co}_4$ archwire but with higher corrosion resistance, for all immersed solutions represented in Fig 3 (A', B', C') compared to the obtained values for bare $\text{Ni}_{47}\text{Ti}_{49}\text{Co}_4$ archwire. This attributed to the action of both the good coverage and low porosity of the ionic liquid coat beside the thick biofilm of the deposited protein.



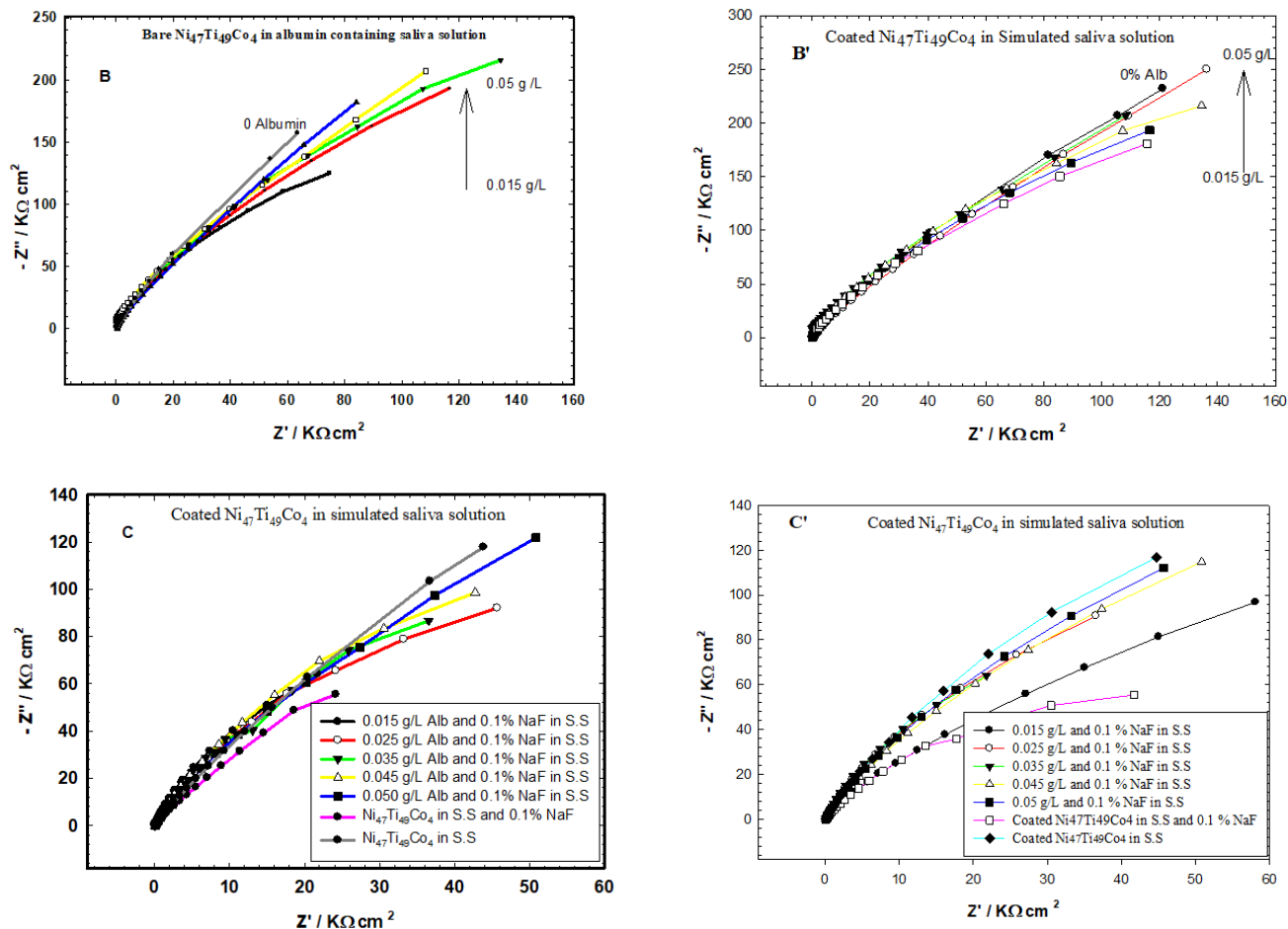


Figure 3. Nyquist plots of bare and Coated $Ni_{47}Ti_{49}Co_4$ archwire in (A) and (A') simulated saliva solution containing different concentrations of NaF (0.005 -0.1 %), (B) and (B') Fluoride free medium with different concentrations of Albumin (0.015 -0.05 g/L), (C) and (C') 0.1% NaF containing simulated saliva solution with different concentrations of Albumin (0.015 -0.05 g/L), respectively.

3.2.3. Effect of immersion time on corrosion behavior and coat stability for bare and coated $Ni_{47}Ti_{49}Co_4$ archwire

Fig. 4, shows the Nyquist plots for (a) bare and (b) coated $Ni_{47}Ti_{49}Co_4$ archwire immersed in simulated saliva solution containing 0.05 g/L albumin and 0.1% NaF, starting from 10 min immersion till 268 h. Inspection of Nyquist plot in Fig. 4 (A), for early immersion, it can be noticed a depression in the capacitive loop with a decrease in the diameter of the semicircle received for bare $Ni_{47}Ti_{49}Co_4$ archwire, when compared with the coated one. It can be noticed, with increasing immersion time the corrosion resistance began to increase for both bare and coated $Ni_{47}Ti_{49}Co_4$ archwire. By increasing immersion time shown in Fig. 4 (B), coated $Ni_{47}Ti_{49}Co_4$ archwire exhibited the same behavior till 74 h, indicating the high stability of the ionic liquid coat, in contrast to corrosion resistance of bare $Ni_{47}Ti_{49}Co_4$ archwire which decreases dramatically. With continuous increasing of immersion time, in Fig. 4 (C), the corrosion resistance began to decrease slightly but still coated $Ni_{47}Ti_{49}Co_4$ archwire has

more resistive values. Continues immersion for 11 days, the corrosion resistance for coated Ni₄₇Ti₄₉Co₄ archwire reaches stability as shown in Fig. 4 (D). Accordingly, the high corrosion resistance for coated Ni₄₇Ti₄₉Co₄ archwire implies an effective inhibition and therefore the best stability of the ionic liquid coat for all immersion times in simulated saliva solution containing 0.05 g/L albumin and 0.1 % NaF solution.

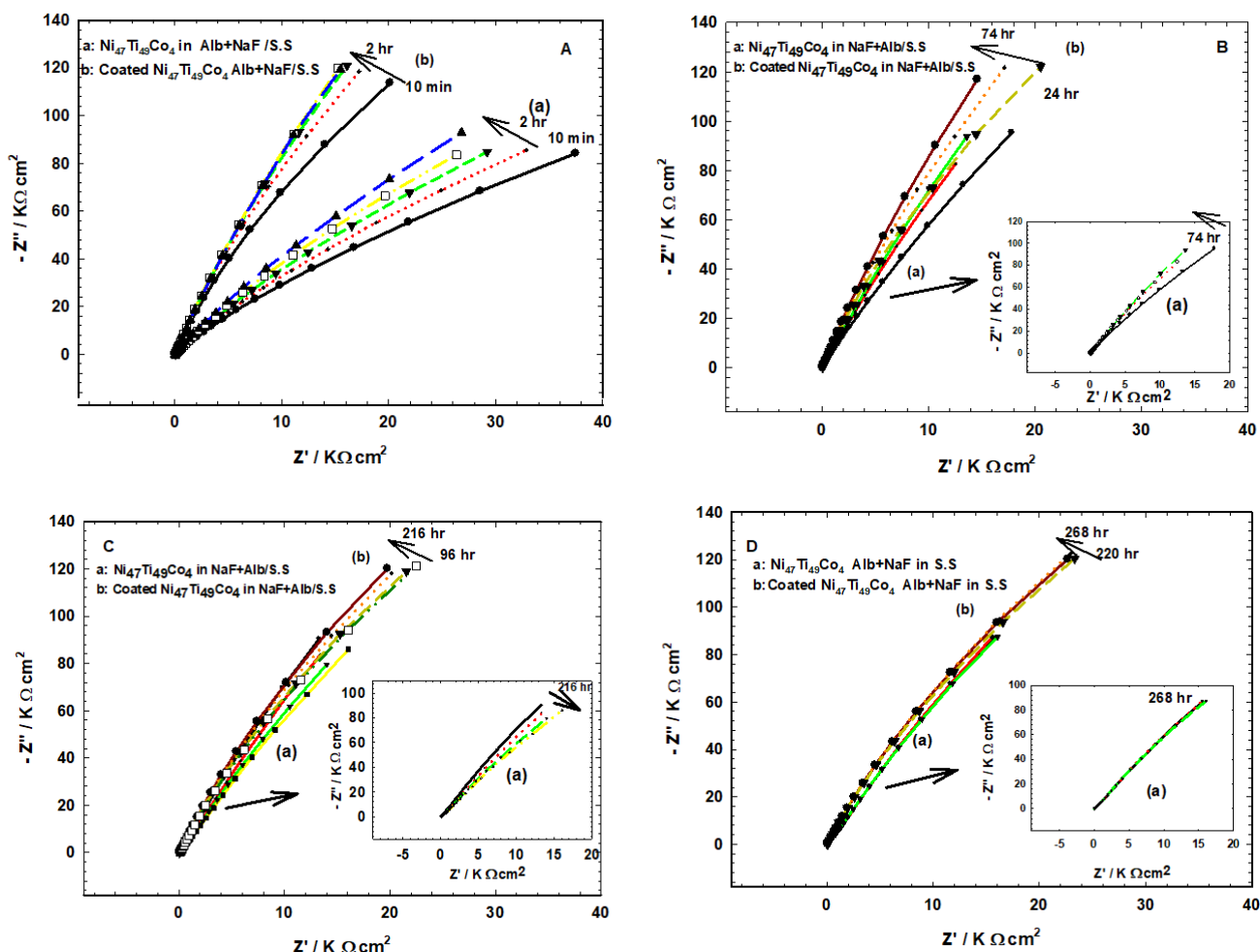


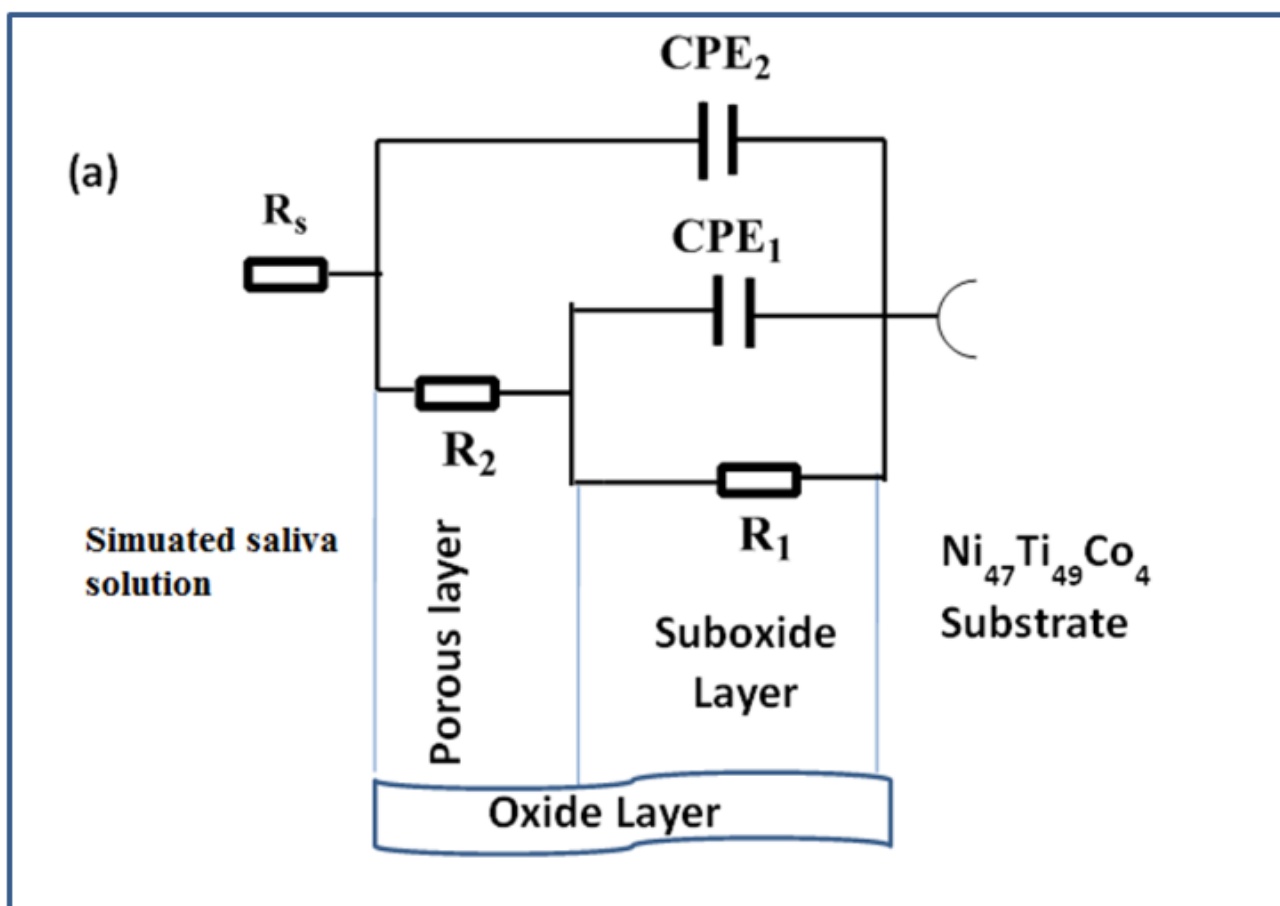
Figure 4. Nyquist plots for bare and coated Ni₄₇Ti₄₉Co₄ archwire (A) one day (B) 2-3 days (C) 4-9 days (D) 9-11 days in 0.1% NaF and 0.05 g/L Albumin in simulated saliva solution.

3.2.4. The Circuits Fitting of Impedance

A circuit model drawn in Fig. 5 used for fits experimental results for (a) bare and (b) coated Ni₄₇Ti₄₉Co₄ archwire immersed in 0.05 g/L albumin and 0.1 % NaF containing simulated saliva solution. EIS data was analyzed to equivalent circuit model with a two-time constant Fig. 5(a). This model includes resistance of solution (R_s) while (R₁) and (R₂) refer to the resistances of the two formed oxide layers, where R₁ is the inner most layer. The two parallel constant phase elements (CPE₁ suboxide layer and CPE₂ porous oxide layer) represent capacitance of naturally formed oxide layer. EIS show presence of two layers on metal surface having resistance as well as capacitance [25-26].

Regarding metal surface in homogeneities, Good fitting data were achieved by replacing pure capacitance with constant-phase element (CPE).

In Fig. 5 (b) for coated $Ni_{47}Ti_{49}Co_4$ archwire can be modeled as the model used in Fig. 5 (a) however, it includes Warburg impedance in series with R_2 which can be linked to ion diffusion through the passive coat, CPE_1 represent capacitance of naturally formed oxide layer [27], and CPE_2 represent capacitance of ionic liquid coat at metal – electrolyte interface. Data analysis circuit output are listed in Table 1. Results show significant smaller resistances of bare $Ni_{47}Ti_{49}Co_4$ archwire than coated $Ni_{47}Ti_{49}Co_4$ archwire, whose resistances increase with immersion time increase indicating the high performance of the passive layer. Whereas, the value of CPE_2 is slightly large for the passive oxide film, propose surface smoothing occurrence. Based on the obtained result values, it can be concluded, achieving high corrosion resistance against corrosive ions aroused from reducing the specific surface area by forming a dense uniform IL coat over $Ni_{47}Ti_{49}Co_4$ archwire surface, [28].



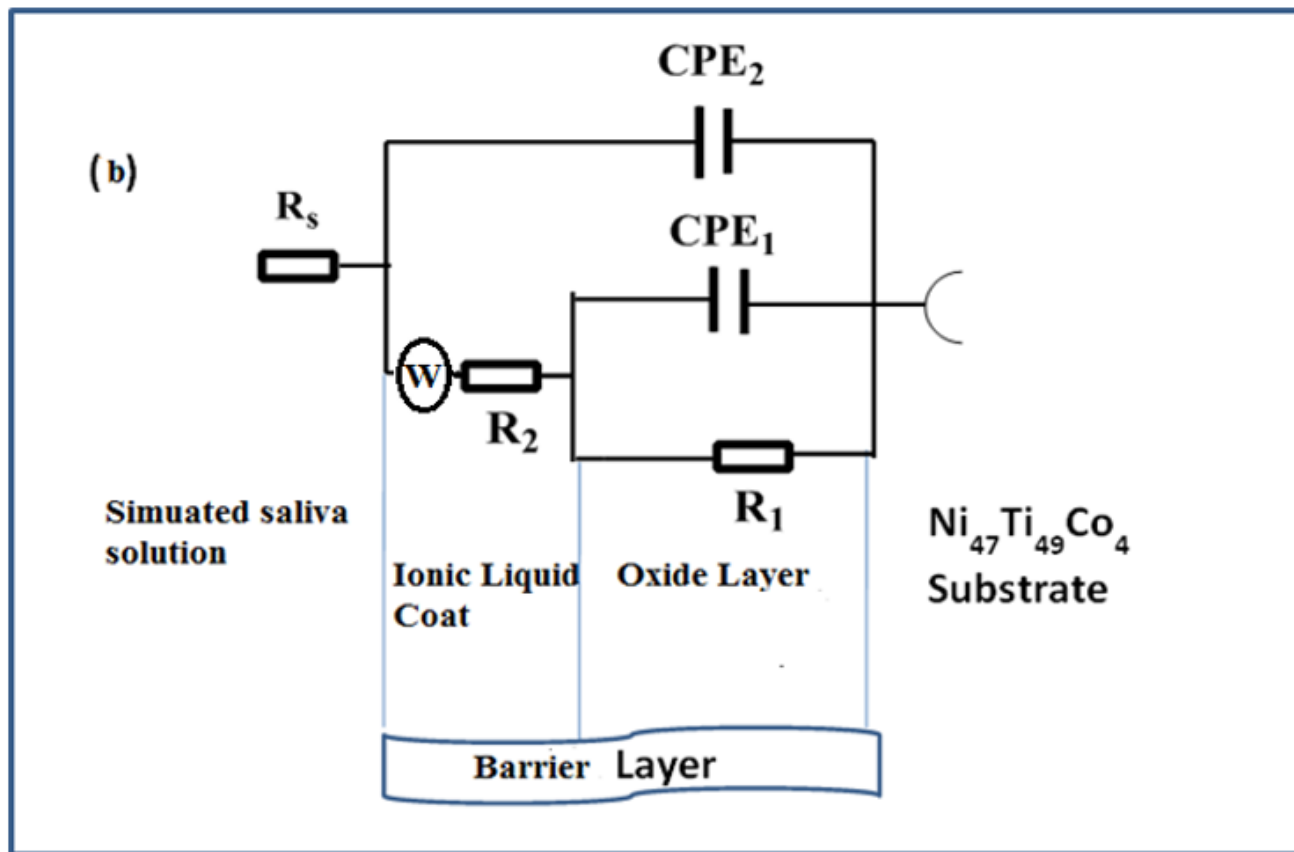


Figure 5. Proposed equivalent circuit for (a) bare $Ni_{47}Ti_{49}Co_4$ archwire and (b) Coated $Ni_{47}Ti_{49}Co_4$ archwire used to obtain impedance parameters.

Table 1. Impedance parameters of bare and coated $Ni_{47}Ti_{49}Co_4$ SMAs in 0.1 % NaF and 0.05 g/L Alb containing simulated saliva solution with immersion time.

Sample	Time (h)	R_1 ($K\Omega cm^2$)	CPE_1 ($\mu F cm^{-2}$)	R_2 ($K\Omega cm^2$)	CPE_2 ($\mu F cm^{-2}$)	W ($\mu \Omega cm^2 S^{-1/2}$)	R_s (Ωcm^2)
$Ni_{47}Ti_{49}Co_4$ in 0.1% NaF+ 0.05 g/L Alb containing S.S	0	177	4.95	566	8.20	-	22.4
	0.5	188	5.38	577	7.32	-	32.3
	1	198	5.86	579	6.83	-	34.5
	2	219	6.09	579	6.40	-	31.0
	24	280	5.91	579	5.79	-	31.4
	48	287	6.34	587	5.40	-	38.7
	74	288	6.45	588	5.20	-	39.9
	168	289	8.49	589	4.86	-	43.3
	196	290	10.5	590	4.72	-	43.0

	216	298	12.5	598	4.95	-	44.7
	220	299	13.4	599	5.84	-	42.5
	244	300	12.4	599	6.00	-	46.4
Coated Ni ₄₇ Ti ₄₉ Co ₄ C ₁ in 0.1% NaF+ 0.05 g/L Alb containing S.S	0	284	11.1	494	4.44	31.1	68.9
	0.5	446	10.5	626	3.90	31.3	64.6
	1	446	10.4	626	3.86	34.5	69.3
	2	447	10.4	627	3.87	41.2	66.7
	24	448	10.9	628	3.81	50.2	81.7
	48	449	10.6	2630	2.72	54.5	84.6
	74	447	10.2	629	3.90	57.1	88.0
	168	449	11.4	629	4.97	52.3	89.8
	196	456	11.1	636	4.67	57.1	88.9
	216	457	11.4	637	5.17	60.3	83.0
	220	458	9.92	638	4.48	61.4	87.3
	244	477	10.2	639	4.83	61.6	87.7

3.2.5. Potentiodynamic Polarization measurements

In order to evaluate the passivation ability of bare Ni₄₇Ti₄₉Co₄ SMAs orthodontic wires in (a) simulated saliva solution (b) containing 0.1% NaF (c) 0.05 g/L Albumin (d) 0.1% NaF and 0.05 g/L Albumin and (e) coated Ni₄₇Ti₄₉Co₄ SMAs in same solution used in (d), Potentiodynamic polarization measurements were carried out after 1 hour immersion. The representative result is shown in Fig. 6. Two distinct stages for the cathodic section could be seen. The nearly vertical stage at lower potential and the sloped region are evidence for the hydrogen generation process and the oxygen consumption process, respectively. For the anodic polarization curves, Ni₄₇Ti₄₉Co₄ SMAs exhibited a typical passive region up to the pitting potential. The corresponding corrosion potentials (E_{corr}) were 690, 613, 510, 452 and 408 mV/SCE for bare Ni₄₇Ti₄₉Co₄ archwire in simulated saliva solution containing NaF> neutral simulated saliva solution> simulated saliva solution containing NaF and Alb> simulated saliva solution containing Alb> coated Ni₄₇Ti₄₉Co₄ archwire in simulated saliva solution containing NaF and Alb, respectively. The explanation of this behavior is based on the synergistic effect of protein adsorption and precipitation of insoluble salts on alloy surface which act as corrosion inhibitor. The anodic branch for of coated Ni₄₇Ti₄₉Co₄ archwire maintains the widest passive region, suggesting the highest corrosion resistance in saliva containing NaF and Alb. This behavior stands to the double protective action of protein and ionic liquid coat. Moreover, from results shown in Table 2, one can conclude that addition of NaF led to a significant increase in the I_{corr} and further decrease in R_p value. After, albumin addition to 0.1% NaF containing simulated saliva solution a dramatic decrease in I_{corr}

and a considerable increase in R_p compared to that without albumin. This implied that albumin addition to 0.1% NaF-containing acid media protected the $Ni_{47}Ti_{49}Co_4$ archwire passive film against fluoride ions attack. The highest R_p value for coated $Ni_{47}Ti_{49}Co_4$ implies the higher corrosion resistance of the archwire by formation of a stable passive oxide film. Therefore, the corrosion resistance of an ionic liquid coated $Ni_{47}Ti_{49}Co_4$ archwire showed higher protection performance compared with that of the oxide layer on bare $Ni_{47}Ti_{49}Co_4$ in fluoride containing simulated saliva solution [16].

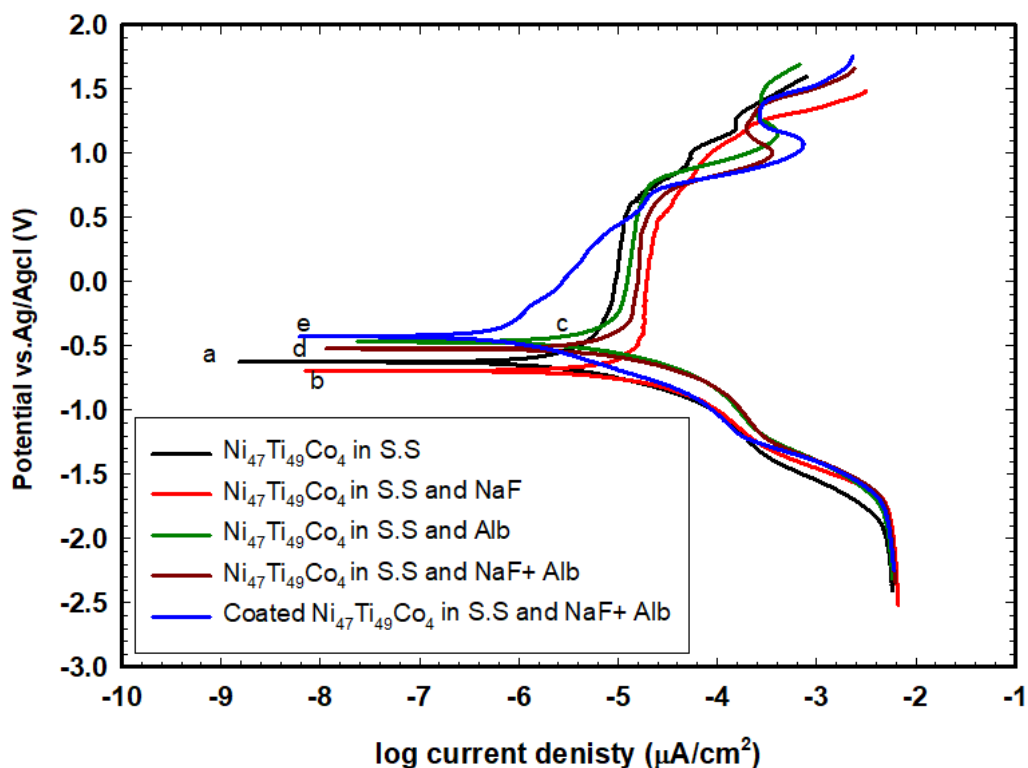


Figure 6. Potentiodynamic polarization curves of $Ni_{47}Ti_{49}Co_4$ archwire in (a) Simulated saliva solution containing (b) 0.1% NaF (c) 0.05g/L Albumin (d) 0.1% NaF and 0.05g/L Albumin and (e) Coated $Ni_{47}Ti_{49}Co_4$ archwire in same solution used in (d).

Table 2. Corrosion parameters of $Ni_{47}Ti_{49}Co_4$ SMA in different medium solutions obtained from the potentiodynamic polarization test

Solutions	E_{corr} mV	I_{corr} $\mu A cm^{-2}$	Ba $V dec^{-1}$	β_c $V dec^{-1}$	Corr. Rate mm/year	R_p Ω/cm_2	$\eta_{PE\%}$ efficiency
$Ni_{47}Ti_{49}Co_4$ in S.S	-613	0.68	0.261	0.460	0.18	25949	-
$Ni_{47}Ti_{49}Co_4$ in S.S ing NaF	-690	0.75	0.431	6.483	.89	10734	-
$Ni_{47}Ti_{49}Co_4$ in S.S containing Alb	-452	0.71	0.311	2.181	0.12	32620	-

Ni ₄₇ Ti ₄₉ Co ₄ in S.S containing NaF + Alb	-510	0.47	0.386	3.920	0.28	26488	-
Coated Ni ₄₇ Ti ₄₉ CO ₄ in S.S containing NaF + Alb	-408	0.10	0.184	0.866	0.04	38820	98.7

E_{corr} = corrosion potential; i_{corr} = corrosion current; β_a = rate of anodic half reaction; β_c = rate of cathodic half reaction, R_p = polarization resistance.

4. CONCLUSION

Orthodontic surface treatment is an important area as a research challenge for safe use of nitinol archwires in the future. The fluoride-containing products present in mouthwashes and dentifrices at different concentrations, simultaneously with the proteins from food remains contribute to corrosion of dental alloys in the oral environments.

Under the experimental conditions of this study for Ni₄₇Ti₄₉CO₄ orthodontic archwires coated with ionic liquid, the following conclusions were drawn:

1. SEM investigations for the coated Ni₄₇Ti₄₉CO₄ archwires surface revealed evident modification in the roughness, and the surface became smoother.
2. Bare Ni₄₇Ti₄₉CO₄ archwires was more affected by fluoride than coated one.
3. Electrochemical and immersion experiments proved that the formed ionic liquid coat on archwire surface had excellent corrosion resistance. However, the addition of albumin (0.015–0.05%), regardless of the concentration, to the fluoride-containing media considerably improved the corrosion resistance onto coated and bare surface via protein deposition.
4. The protective ionic liquid coat showed high stability with increasing immersion time.

DECLARATION OF COMPETING INTEREST

None.

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