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Influence of the biological fluid on the corrosion of dental amalgam

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Abstract

An electrochemical study of corrosion of Tytin® dental amalgam was carried out in electrolytes similar to body fluids: artificial saliva with or without lactic acid, a polymer-containing product of the same composition as Glandosane® and in Krebs–Ringer solution. The electrochemical techniques of open circuit potential, polarisation curves, cyclic voltammetry and electrochemical impedance were employed as a function of immersion time to characterise the surface processes occurring and bring out the differences between the different solutions. The influence of pH was tested in solutions of artificial saliva with or without lactic acid. The results demonstrated the importance of the organic component on the rate of corrosion and of adsorption phenomena on the amalgam surface.

Keywords: Dental amalgam corrosion; Artificial body fluids; Artificial saliva

1. Introduction

In recent years many studies have been done in order to investigate the corrosion resistance of dental amalgam under different conditions (acidity, temperature and abrasion) due to concerns with its toxicity.

Dental amalgam is a metallic alloy formed by the reaction of mercury with a powder alloy containing silver (40–70%), tin (15–30%) and copper (10–30%) and sometimes also a small percentage of zinc [1]. The detailed composition and form of

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the powder alloy influence the microphase structure of the amalgam [2]. Depending on the technique of production and shape of the powder alloy particles, the amalgam can be classified as "lathe cut" (irregular particles), spherical (particles produced by spraying) or blend (mixed spherical and irregular alloy particles). The smaller the particles the shorter the setting time and the less the corrosion: for example, it was shown that the corrosion current is less from amalgams fabricated from particles $\leqslant 5$ μm than from those fabricated using particles $\leqslant 40$ μm diameter [3]. Similar, but less significant effects were observed with Pd-containing amalgams [4], and addition of small quantities of Pd was found to improve the corrosion resistance [5]. A number of electrochemical studies have been carried out on different phases of dental amalgam, particularly the Ag–Hg matrix phase, e.g. [1,6,7] as well as on different amalgams [8,9].

Another important aspect concerns the release of mercury from the amalgam surface, either in ionic form, which dissolves in the saliva, or in the zero oxidation state. Thus, the dissolution of mercury into solution from amalgams at different pH values and at applied electrode potentials has been studied [10–16], as well as the solubility of elemental mercury in solution and its influence on mercury vapour release [17,18].

Tytin® FC amalgam, which was used in this study, is made with a spherical, high-copper powder alloy that consists of 59% silver, 28% tin, and 13% copper by weight [1]. After mixing with mercury, it has a mercury-to-alloy ratio of approximately 43% by weight. The reaction between mercury and alloy should proceed within a few seconds: mercury diffuses into the alloy particles and begins to react with silver, tin and copper, forming various compounds. The exact compounds formed depend not only on the chemical composition of the powder but also on the particle shape. They are principally phases of the systems Sn–Hg, Ag–Hg, with Ag–Cu and Ag–Sn phases remaining from the reactants.

The influence of two types of bathing solution on the electrochemical corrosion of dental amalgams was studied, the solution being similar to saliva [19,20] or blood serum in terms of ionic strength and, as far as possible, ionic species. A previous systematic comparison of different electrolytes, but of similar compositions, used potentiodynamic polarisation [21] and demonstrated, as would be expected by analogy with other corrosion situations, that the most aggressive species towards metals in these solutions is the chloride ion.

2. Experimental

2.1. Electrodes and electrochemical instrumentation

Tytin® FC dental amalgam (KerrDental, USA) was provided in two-part plastic capsules separated by a membrane that must be broken by squeezing before they were intimately mixed with liquid mercury in a mechanical vibrator to wet efficiently the surface of the particles. The powder alloy composition of Tytin® is silver 61%, tin 26% and copper 13%, the mercury-to-alloy ratio being approximately 43%. After triturating it was cast into cylinder-shaped pieces of diameter ~0.6 cm and length ~3 mm.

One of the faces of the amalgam sample was covered with a flash-dry silver paint (SPI) and a copper wire was fixed to it. After drying in air for 12 h this face, together with the edges, was covered with a layer of Araldite® (Ciba-Geigy, Switzerland) epoxy-resin adhesive and dried again for at least 24 h, leaving just one face exposed. This was then polished with dry SiC paper down to 1200 grit and also with alumina foil of 25, 3, and 0.3 μm particle size until a smooth mirror-like finish was obtained. Between experiments, the metallic surface was polished with alumina foil as necessary. The exposed electrode area was 0.28 cm^2.

The three electrode system used for the electrochemical experiments included a saturated calomel electrode (SCE) as reference and a Pt foil auxiliary electrode.

All experiments were carried out using an Autolab PGSTAT 10 (Ecochemie, Netherlands) controlled by GPES 4.7 software for open circuit potential and polarisation curve measurements and FRA software for impedance measurements. GPES and FRA software was used also for data analysis. Impedance spectra were recorded at the open circuit potential from 65 kHz down to 0.1 Hz, five steps per frequency decade with a sinusoidal perturbation of 5 mV rms.

Corrosion potential measurements were carried out during 2 h after immersion for each solution tested and for different pHs in the range 3–7. Polarisation curves and impedance spectra were recorded after 10 min, 1 and 2 h immersion. Cyclic voltammograms were recorded after 1 h of immersion.

2.2. Bathing solutions

The electrochemical behaviour was studied in three types of bathing solution: an artificial saliva as used previously [22], with and without lactic acid (in order to investigate the importance of the organic compound (lactic acid) in artificial saliva) a polymer containing solution of the same chemical composition as Glandosane® (Fresenius Kabi, Germany), and Krebs–Ringer solution.

Preparation of 1 l of each of the solutions in which the electrodes were immersed was as follows:

1. Artificial saliva (AS) with lactic acid (pH 6.5): 1.5 g KCl, 1.5 g $NaHCO_3$, 0.5 g NaH_2PO_4, 0.5 g KSCN and 0.9 g lactic acid.
2. AS without lactic acid (pH 7.5) had the same composition as above but without lactic acid.
3. A solution of the same chemical composition of Glandosane®, used in dental treatment to temporarily protect the amalgam surface, was made following the published formulation. It is composed of 0.84 g NaCl, 1.2 g KCl, 0.14 g $CaCl_2 \cdot 2H_2O$, 0.06 g $MgCl_2 \cdot 6H_2O$, 0.34 g K_2HPO_4, 30 g sorbitol and 10 g Na-carboxymethylcellulose. After mixing for 5 min in an ultrasonic bath, a further 72 h were necessary to dissolve the polymer. The pH of the solution was 6.8.
4. Krebs–Ringer solution was prepared by dissolving 6.98 g NaCl, 0.36 g KCl, 0.28 g $CaCl_2$ and 0.15 g $MgSO_4$ in 790 cm^3 water and mixing it with 210 cm^3 of pH 7.4

0.20 M phosphate buffer. The solution obtained formed a white $Ca_3(PO_4)$ precipitate, and the filtrate was used.

All solutions were prepared using Milli-Q ultrapure water of resistivity >18 MΩ cm and analytical grade reagents. The laboratory temperature was 25 ± 1 °C in all experiments.

3. Results and discussion

3.1. Open circuit potential measurements

Open circuit potential measurements were used to demonstrate the differences in corrosion behaviour under aerated conditions, the influence of the pH after the immersion of the electrode in artificial saliva with or without lactic acid and the differences in the phase structure of the dental amalgams.

Fig. 1 presents the variation of open circuit potential with time of the dental amalgam electrode in the various solutions tested. Fig. 1a refers to immersion in Glandosane® and in Krebs–Ringer solution, for both of which sharp variations toward more negative values of potential were recorded during the first minutes of immersion. After this period small variations in the positive direction are superimposed on the general trend toward more negative values, and the electrode surface seems to suffer slight passivation. The reasons for this behaviour are different in both cases. In Glandosane® the Na carboxymethylcellulose polymer seems to protect the surface against corrosion, whereas Krebs–Ringer solution contains sulphate ions that can react with silver and form sparingly soluble silver sulphate.

The variations of open circuit potential (OCP) in artificial saliva with and without lactic acid are shown in Fig. 1b. Both solutions, at the natural pH of 7.5 without lactic acid and 6.5 with lactic acid, lead to similar behaviour, but completely different to Glandosane® and Krebs–Ringer (Fig. 1a). In these two cases, the change of OCP with time is accompanied by the formation of a film of corrosion products seen by visual inspection and in agreement with other studies [1]. It is likely that the main constituents of the film are tin oxide [1]. The open circuit potential in artificial saliva without lactic acid is more positive than with lactic acid over the timescale of the experiment; the principal reason for this difference can be ascribed to the different pH of the bathing solutions.

For artificial saliva with and without lactic acid, the pH of the solution was varied from the natural pH down to pH 3.0, in order to investigate the influence of solution pH on oxide layer formation and any adsorption of lactate ion or of lactic acid, given that the pK_a of lactic acid is 3.86 [23], and in the pH range tested there is a transition between lactate ions and lactic acid in solution. Artificial saliva with lactic acid added has a lower natural pH (6.5 rather than 7.5).

Examination of Fig. 2a, without lactic acid, and Fig. 2b, with lactic acid, shows immediately that the general variation of open circuit potential with time is the same in all cases but there are important differences. In particular, there are trends in the

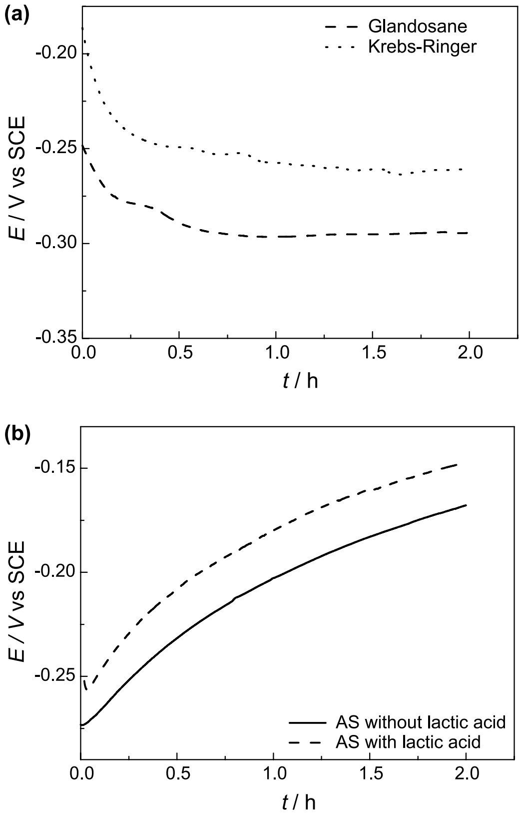

Fig. 1. Variation of open circuit potential with time of dental amalgams immersed in: (a) Glandosane® and Krebs–Ringer solutions and (b) artificial saliva without (pH 7.5) and with lactic acid (pH 6.5).

values of the potential with changing pH. Fig. 3 shows these values for an immersion time of 2 h. This plot immediately shows that there is a pH effect at values of pH above 5, but the two curves, with and without lactic acid, are almost coincident. At pH less than 5, differences begin to appear which is exactly when lactic acid begins to exist in large concentrations. The values are more negative with lactic acid than without it. This suggests that lactic acid is impeding the formation of the oxide layer, possibly by adsorption at the surface. More information is necessary from other techniques to reach a conclusion concerning this point.

3.2. Polarisation curves and cyclic voltammetry

Plots of E vs. lg I were recorded within the range −0.25 to +0.25 V vs. OCP in order to determine the corrosion current, I_{cor} and the corrosion potential, E_{cor}.

Fig. 4 shows results obtained in Glandosane and Krebs–Ringer solutions for two dental amalgam samples fabricated by the same experimental procedure. Some

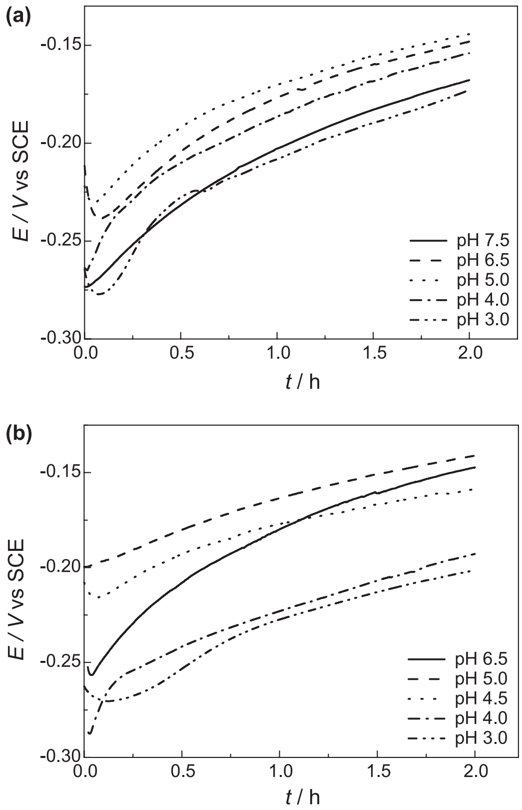

Fig. 2. Variation of open circuit potential with time of dental amalgam immersed in artificial saliva at different pHs: (a) without lactic acid and (b) with lactic acid.

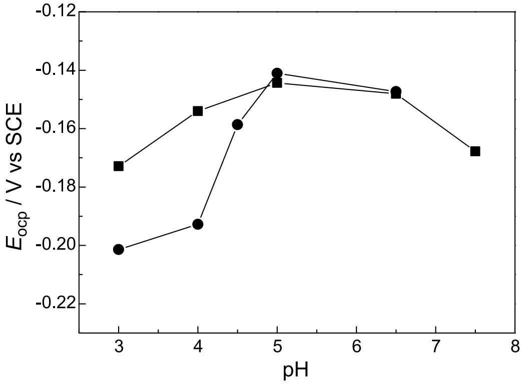

Fig. 3. Plots of the open circuit potential, E_{ocp} vs. pH after 2 h immersion of the dental amalgam in artificial saliva without (■) and with (●) lactic acid.

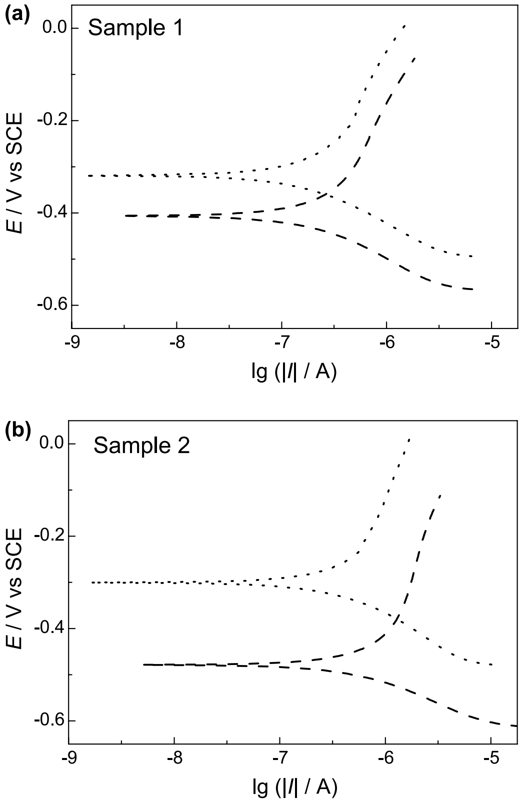

Fig. 4. Polarisation curves for two different dental amalgam samples after 2 h immersion in (- - -) Glandosane® and in (· · ·) Krebs–Ringer solutions.

difference is seen between the two samples, which reflects differences in surface microstructure, probably due to the γ_2-$Sn_{7–8}$ Hg phase that is the less resistant phase to the corrosion process [24] — it is possible that the mixture between the powder alloy and mercury is not well done and one of the samples contains more γ_2 phase. Table 1 summarises the analysis of the results obtained after different immersion times for the same sample used for the results obtained by the other techniques and in other solutions.

The corrosion potential values by themselves would indicate that there is less protective film formation in Glandosane® than in Krebs–Ringer, and this is corroborated by the corrosion currents. Although a steady-state has not been reached after 10 min immersion these values are useful to see how the corrosion current is varying and whether there is already any surface protection—at this point the rate of corrosion in Krebs–Ringer is notably faster. After 24 h the behaviour in Glandosane® is essentially similar to that after 2 h and in Krebs–Ringer, the corrosion current has increased.

Table 1
Tafel analyses of polarisation curves after 2 h immersion

Solution	Immersion time	I_{cor} (μA cm^{-2})	E_{cor} (V vs. SCE)
Glandosane®	10 min	1.15	−0.40
	1 h	1.25	−0.41
	2 h	1.51	−0.41
	24 h	1.58	−0.46
Krebs–Ringer	10 min	1.97	−0.27
	1 h	1.24	−0.34
	2 h	1.28	−0.32
	24 h	2.03	−0.31

Fig. 5a and b show polarisation curves obtained for artificial saliva without and with lactic acid, respectively. One can see from Table 2 an increase in the corrosion current in artificial saliva with lactic acid at lower pHs compared to without. Cor-

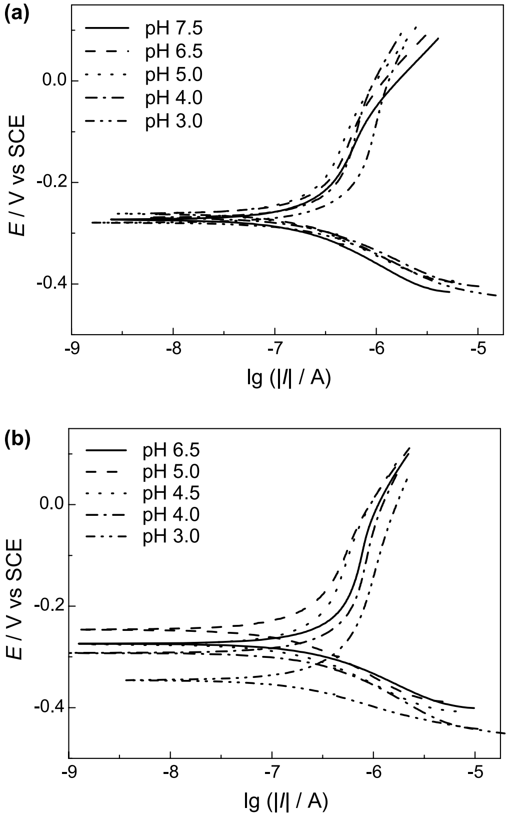

Fig. 5. Polarisation curves of dental amalgam after 2 h immersion in artificial saliva at different pHs: (a) without lactic acid (b) with lactic acid.

Table 2
Tafel analyses of polarisation curves in artificial saliva (AS) without and with lactic acid after 2 h immersion

Solution	pH	I_{cor} ($\mu A\,cm^{-2}$)	E_{cor} (V vs. SCE)
AS without lactic acid	6.5	3.62	−0.273
	5.0	3.78	−0.261
	4.5	2.20	−0.259
	4.0	3.31	−0.271
	3.0	3.22	−0.280
AS with lactic acid	7.5	3.73	−0.274
	6.5	2.81	−0.246
	5.0	3.27	−0.275
	4.0	3.37	−0.292
	3.0	3.69	−0.346

relation with the more negative corrosion potential values and in agreement with the variation of open circuit potential with pH, which means that the corrosion rate increases with lactic acid in solution and that the anodic process is rate determining, i.e. the presence of lactic acid molecules is preventing oxide formation.

Further information concerning the processes in artificial saliva with and without lactic acid can be obtained from cyclic voltammetry experiments (see Fig. 6) for results obtained after one hour of immersion. Fig. 6a, without lactic acid in solution, shows oxidation above zero volts, mainly of copper [24], and two reduction peaks on the inverse scan which can be attributed to copper and tin. The copper peaks increase in size on lowering the pH.

In artificial saliva with lactic acid (Fig. 6b) the peaks are originally smaller but this reflects the lower pH of the solution, as discussed above. With the decreasing of the pH, there is a greater change and differences in the voltammetric profile can be distinguished. In fact, at pH 3.0, the copper reduction peak is bigger for artificial saliva with than without lactic acid which is indicative of easier oxidation and then reduction of the surface during the experiment, i.e. there is less previous formation of oxide film.

In the light of these results, the conclusion is that after 2 h immersion Glandosane® is the least corrosive solution, Krebs–Ringer is slightly more corrosive and artificial saliva is significantly more, influenced by the presence of lactic acid.

3.3. Impedance measurements

Impedance spectra were recorded after 10 min, 1 and 2 h immersion of dental amalgam in the different bathing solutions.

Fig. 7 shows spectra of dental amalgam immersed for 2 h in Glandosane® (Fig. 7a) and Krebs–Ringer solution (Fig. 7b). The spectra in the two solutions have the same form; it is seen that Glandosane® presents the lower values of the magnitude of the impedance.

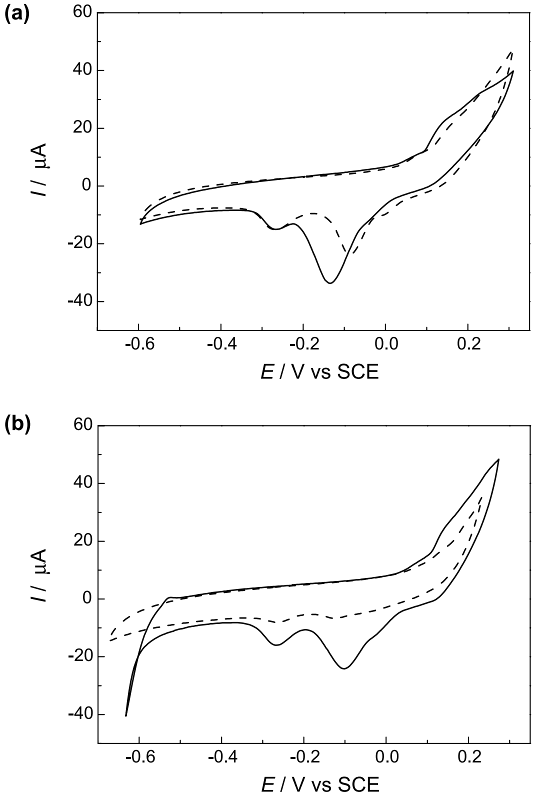

Fig. 6. Cyclic voltammograms for dental amalgam immersed in artificial saliva: (a) without lactic acid, at the natural pH 7.5 (- - -) and pH 4.5 (—) and (b) with lactic acid at the natural pH 6.5 (- - -) and pH 4.0 (—).

The spectra obtained for different immersion times were fitted with the electrical equivalent circuit shown in Fig. 8. As would be expected at this type of interface there is some roughness and so a constant phase element (CPE) is necessary instead of a pure capacitance, according to CPE $= \{(Ci\omega)^{\alpha}\}^{-1}$, with α the roughness factor being equal to 1 for a smooth surface. The results of fitting are given in Table 3. Although from examination of the spectra in Fig. 7 it appears that the equivalent circuit requires only one *R*CPE, the quality of the fit is improved, and associated errors are reduced, if the second *R*CPE is introduced. In fact, it has been found that the circuit in Fig. 8 is the best circuit for fitting the spectra of amalgam individual phases [25], as well as of Tytin® dental amalgam in artificial salivas of varying compositions [26], and alternative models give a less good fit. The two *R*CPE elements can be attributed to charge transfer and separation processes at the metal–oxide film interface and to the oxide layer formed on the surface. This enables the determination of two capacitive contributions involved in the measured impedance, the capacitance associated with the charge transfer, C_1 and the oxide film capaci-

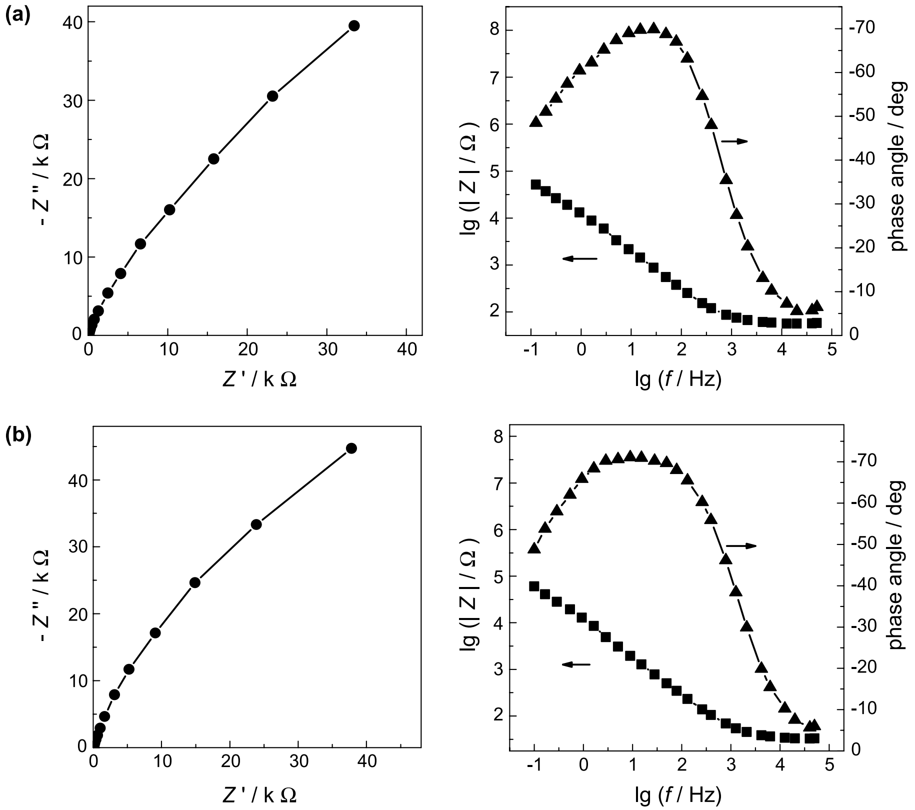

Fig. 7. Impedance spectra of dental amalgam recorded at the open circuit potential after immersion for 2 h in Glandosane® and Krebs–Ringer solutions.

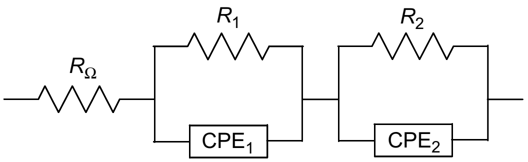

Fig. 8. The electrical equivalent circuit used for fitting the impedance data. R_Ω represents the cell resistance, and CPE constant phase elements.

tance, C_2 used to characterise the semiconducting and dielectric properties of the potentiodynamically formed oxide layer.

From Table 3 it is seen that as the corrosion process progresses the charge transfer at the solution–oxide interface becomes more difficult (R_1 increases with time), although the change in R_1 is faster in Glandosane® solution. The significant decrease of R_2 in Krebs–Ringer solution can be explained by a break of the protective film. In the case of Glandosane, R_2 also decreases with time but the value is larger which

Table 3
Results of the fitting for the impedance measurements in Glandosane® and Krebs–Ringer solutions

Solution	Immersion time	R_1 (kΩ cm^2)	C_1 (μF cm^{-2})	α_1	R_2 (kΩ cm^2)	C_2 (μF cm^{-2})	α_2
Glandosane®	10 min	31.1	6.1	0.85	400	9.00	0.81
	1 h	40.0	2.5	0.88	380	3.90	0.80
	2 h	70.0	2.3	0.80	300	5.00	0.90
Krebs–Ringer	10 min	50.0	8.4	0.91	125	1.90	0.70
	1 h	55.0	5.5	0.88	100	2.00	0.70
	2 h	57.7	3.7	0.82	56	3.80	0.82

must be associated with the formation of the protective film on the surface of the electrode by Na-carboxymethylcellulose. Indeed, this film is difficult to remove by polishing. Interpretation of the values of C_2 is difficult since the nature of the oxide film may change over time, as will the role played by adsorption of the organic component on the amalgam surface; this represents a limitation in the use of impedance spectra.

Examples of impedance spectra obtained for artificial saliva without and with lactic acid are shown in Fig. 9. The shape of the spectra is rather different from in Glandosane® and Krebs–Ringer solution. Results from the analysis of the spectra are more complex, but can be modelled by the same equivalent circuit, and are the subject of further work [26]. However, they agree with the results obtained by the polarisation curves, which is particularly evident from the magnitude of the imaginary components of the impedance that are largest at pH 5.

3.4. Comparison of results

Comparing the results obtained by different electrochemical techniques, the data obtained after short immersion times suggests that artificial saliva without lactic acid is more corrosive than artificial saliva with lactic acid and also that Glandosane® is more corrosive than Krebs–Ringer solution. Thus, the organic component present in artificial saliva (lactic acid) and in Glandosane® (Na-carboxymethylcellulose) it is very important since it seems to participate in the passivation process.

Trends in open circuit potential show that the solutions can be divided into two groups Glandosane® and Krebs–Ringer on the one hand, and artificial saliva without and with lactic acid on the other. Comparing the rate of corrosion of the dental amalgam in all the solutions at their natural pH after 2 h of immersion, one can see the following order:

$$\text{Glandosane}^{\circledR} < \text{Krebs–Ringer} < \text{AS without lactic acid} \sim \text{AS with lactic acid}$$

Glandosane® and Krebs–Ringer also show some differences, which can be attributed mainly to the existence of polymer in the former case. Interestingly, its influence in Glandosane® is not to immediately reduce the corrosion rate on a fresh surface, since the adsorption process of the polymer is relatively slow.

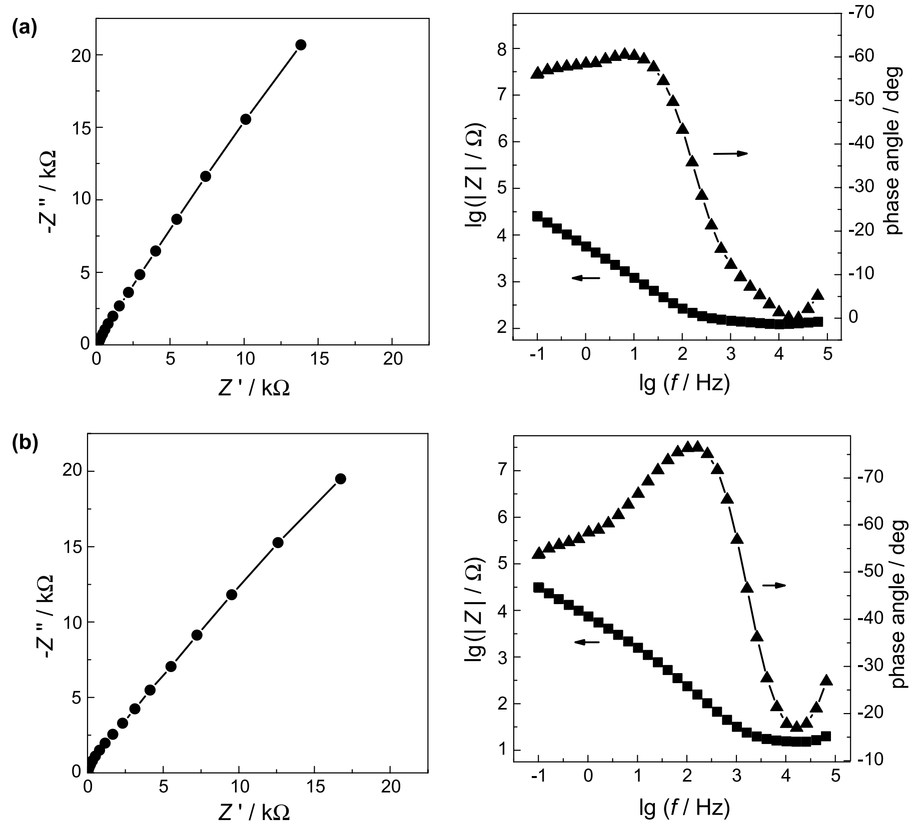

Fig. 9. Impedance spectra of dental amalgam recorded at the open circuit potential after immersion for 2 h at the natural pH in artificial saliva: (a) without lactic acid (b) with lactic acid (complex plane and Bode format).

Concerning the artificial saliva solutions, the role of the pH of the AS solutions containing acid becomes clear in this study and all electrochemical parameters have some dependence on it. For instance, there are maxima in open circuit potential values for artificial saliva with and without lactic acid at pH 5.0, attributed to oxide stability. Once again this demonstrates the importance of adsorption phenomena on the electrode surface, particularly of organic components, such as lactic acid.

Comparing these artificial body fluids with solutions containing only chloride ion [1], the lower rate of corrosion is significant. Even though in these solutions the chloride ion is one of the most aggressive ions, the other constituents of the solutions are also determinant in the corrosion behaviour.

4. Conclusions

This work has shown that the solutions similar to saliva as well as those similar to physiological serum lead to different corrosion behaviour in Tytin® dental amalgam.

Also, the surface of amalgam reveals rough material with non-uniform phase distributions, and differences between amalgam samples made in exactly the same way have been illustrated. All these factors demonstrate the importance of amalgam preparation and of choice of the artificial body fluids for in vitro studies in the detailed investigation of corrosion process occurring in the oral cavity.

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References

[1] H.A. Acciari, A.C. Guastaldi, C.M.A. Brett, Electrochim. Acta 46 (2001) 3887.
[2] I.H. Brown, D.R. Miller, Am. J. Dent. 6 (1993) 248.
[3] B. Westerhoff, M. Darwish, R. Holze, J. Oral Rehabil. 22 (1995) 121.
[4] J.H. Chern Lin, K.I. Chen, C.P. Ju, Biomaterials 23 (2002) 597.
[5] P. Colon, N. Pradelle-Plasse, J. Galland, Dent. Mater. 19 (2003) 232.
[6] M. Marek, Dent. Mater. 13 (1997) 353.
[7] C.M.A. Brett, H.A. Acciari, A.C. Guastaldi, Key Eng. Mat. 230–232 (2002) 463.
[8] B. Westerhoff, M. Darwish, R. Holze, J. Appl. Electrochem. 22 (1992) 1142.
[9] H.A. Acciari, E.N. Codaro, A.C. Guastaldi, Mater. Lett. 36 (1998) 148.
[10] M. Marek, J. Dent. Res. 69 (1990) 1167.
[11] M. Marek, J. Dent. Res. 76 (1997) 1308.
[12] M. Marek, J. Dent. Res. 72 (1993) 1315.
[13] G. Sanna, M.I. Pilo, P.C. Piu, N. Spano, A. Tapparo, G.G. Campus, R. Seeber, Talanta 58 (2002) 979.
[14] M. Pizzichini, M. Fonzi, L. Sugherini, F. Fonzi, A. Gasparoni, M. Comporti, A. Pompella, Sci. Total Environ. 284 (2002) 19.
[15] M. Sweeney, S.L. Creanor, R.A. Smith, R.H. Foye, J. Dent. 30 (2002) 243.
[16] T. Okabe, B. Elvebak, L. Carrasco, J.L. Ferracane, R.G. Keanini, H. Nakajima, Dent. Mater. 19 (2002) 38.
[17] M. Marek, Dent. Mater. 13 (1997) 312.
[18] D.B. Mahler, J.D. Adey, L.E. Simms, M. Marek, Dent. Mater. 18 (2002) 407.
[19] V.W.H. Leung, B.W. Darvell, J. Dent. 25 (1997) 475.
[20] J.Y. Gal, Y. Fovet, M. Adib-Yadzi, Talanta 53 (2001) 1103.
[21] R.I. Holland, Dent. Mater. 8 (1992) 241.
[22] C.M.A. Brett, I. Muresan, Key Eng. Mat. 230–232 (2002) 459.
[23] P.W. Atkins, Physical Chemistry, sixth ed., Oxford University Press, Oxford, 1998, p. 933.
[24] N. Horasawa, H. Nakajima, J.L. Ferracane, S. Takahashi, T. Okabe, Dent. Mater. 12 (1996) 154.
[25] H.A. Acciari, A.C. Guastaldi, C.M.A. Brett, Corros. Sci., in press.
[26] C.M.A. Brett, F. Trandafir, J. Electroanal. Chem., in press.