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The application of the measurement of impedance to the corrosion of dental amalgams

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A preliminary experimental investigation of the electrochemical characteristics of a high and a low copper dental amalgam in contact with saline solution has been carried out. The impedance and the corrosion current (in the absence of dissolved oxygen) have been measured at each potential in the near steady state for fresh amalgam surfaces. Analysis of the electrochemical data produces charge transfer resistance, double layer capacity, ohmic resistance and Warburg coefficient curves, which are briefly discussed. The aim of the work is, ultimately, to determine the *in vivo* corrosion rates and heavy metal ion release from amalgams.

Nomenclature

a	anodic Tafel slope
C_{dl}	differential capacity
D_A	diffusion coefficient of A
E	potential with respect to SCE electrode
E_0	standard potential with respect to SCE
i	current density
j	square root of -1
R_ω	ohmic loss resistance
R_{ct}	charge transfer resistance
$Z(\omega)$	impedance
ω	frequency of a.c. potential
δ	diffusion layer thickness
σ	Warburg impedance parameter

1. Introduction

Dental amalgams and their chemical and physical properties have a long history which has been reviewed by Greener [1]. They consist primarily of silver, tin and mercury, often with additions of copper and small quantities of other metals. The popularity of particular dental amalgams is much determined by their convenience in use, e.g. ease of application, rate at which their mechanical strength develops and their subsequent resistance to creep. It is generally assumed that these properties are connected with the chemical constitution and phases of the amalgams, which develop when the powdered alloy of silver and tin, with additives, is amalgamated with the mercury to initiate the setting reaction. This reaction results when the powdered alloy containing a gamma phase, Ag_3Sn, reacts with mercury to produce a gamma-1 phase, Ag_2Hg_3 or $Ag_{22}SnHg_{27}$ [2], and sometimes a gamma-2 phase, $Sn_{7-8}Hg$. The formation of the gamma-2 phase is considered undesirable and can be avoided by the inclusion of copper in the alloy powder which reacts with tin in competition with the mercury reaction. Copper is also thought to improve the mechanical properties by forming a hard dispersed intermetallic eta-1 phase, Cu_6Sn_5. The gamma-2 phase is considered to be the most corrodable phase so that a 'non-gamma-2 amalgam' should give superior results by reducing corrosion cracks originating in surface reactions. These surface reactions occur because the amalgam fillings are in contact with the oral and interdentinal fluids which are electrolyte solutions. They are of considerable importance since they determine the electrical potential and the corrosion rate at which the

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constituents of the amalgam filling enter the body. Interfaces, in general, are not easy to investigate because of their small volume. Fortunately, in this case, however, the interface is the region between a conducting material and an electrolyte, and electrochemical methods offer a means of identifying and investigating the rates of surface processes which occur. Some investigations have already been attempted. The linear potential sweep method [3, 4] shows a number of current peaks which have been used to identify the potentials at which tin, mercury, silver and copper in dental amalgams dissolve or form films on the surface. Also, the solid corrosion products have been investigated under a number of conditions [1, 5–8]. For conventional amalgams it has been suggested that in the region of the corrosion potential the Sn_7Hg phase influences the behaviour, and a corrosion film containing tin is formed. The nature of the film will depend on potential and the chemical environment in which the amalgam is situated. From an electrochemical point of view these are the factors which determine the behaviour. The steady state current–potential curves for the dissolution of various amalgams have also been measured in the presence of oxygen around the corrosion potentials [9, 10]. The extrapolated corrosion current has been estimated using the Stern–Geary equation. The dependence of the corrosion current on chloride ion concentration has also been measured [11].

Although the overall pattern of the corrosion reactions is now known from linear potential sweep, chemical analysis of the solution and identification of the chemical nature of the phases formed, the details are unknown. For example the electrochemical steady state behaviour and the amounts of tin, silver and mercury ions instantaneously dissolving from the amalgam surface are unknown. The electrical state of the metal surface under particular conditions of potential and chemical environment has also not been investigated.

There have been significant improvements in the methods of electrode kinetics in recent years and it is the purpose of this paper to report the use of more powerful electrochemical methods to measure the surface properties and the steady state corrosion reactions for two dental amalgams, namely Amalcap and Dispersalloy in Ringer's solution. In order to cover a wide range of potential the measurements were made in the absence of oxygen. This is a usual device for simplifying the experimental conditions. It will be assumed that the metal dissolution reactions are a function of potential and the solution composition only and are independent of the particular reduction reaction which determines the corrosion potential.

2. Experimental details

A low copper amalgam, Amalcap, and a high copper amalgam, Dispersalloy (11.9% wt/wt copper in the powdered alloy) have been used in the present investigation. The amalgam specimens were made using premeasured capsules of alloy powder and mercury and mixed according to the manufacturers recommendations with a Silamat vibrator. The amalgam was then packed into an acrylic mould of 10 mm internal diameter and 1.6 mm depth. The mercury-rich surface layer was then removed. After ageing for one week in distilled water at 37° C, about 0.2 mm of the surface of the amalgam discs was removed by wet grinding on 800 grit silicon carbide paper. The discs were then mounted by potting in acrylic holders and the surface cloth-polished with wet gamma alumina.

The sample was used in the usual three-electrode configuration with the dental amalgam held in a p.t.f.e. holder. The area (0.79 or 0.13 cm^2) to be investigated was isolated with a suitable o-ring. The reference electrode was a commercial saturated calomel electrode (SCE) to which all the potentials refer. A glass frit separated the platinum subsidiary electrode compartment from the working electrode compartment. All the solutions were made up with distilled water and Analar reagents. A two-thirds concentration of the usual Ringer's solution was made up from Oxoid BR52 tablets. Oxygen was usually removed from the solution by bubbling nitrogen. It is assumed at this stage that the oxygen or other reduction reaction, which may be associated with amalgam electrochemical corrosion, only serves to fix the potential. In this investigation that function is carried out by the imposed potential, E, with respect to the SCE. Some preliminary investigations were carried out to determine at what potential amalgams sit when in service in the mouth and when isolated in a NaCl solution in the presence of oxygen.

The amalgams were investigated in contact with aqueous Ringer's solution using equipment which applies all the most powerful methods of electrode kinetics to the sample under test. Ringer's solution (containing NaCl 6.00, KCl 0.28, $CaCl_2$ 0.32 and $NaHCO_3$ 0.13 g l^{-1} respectively, and having a pH of 7) was used at two-thirds strength. This is isotonic with saliva and has roughly two-thirds the sodium, potassium and chloride concentration of the interdental fluid [12], thus representing a convenient compromise between the two electrolytes.

The equipment used for the electrochemical measurements was computer controlled and has been described in the literature [13]. Linear potential sweep, potential pulse and steady state potentiostatic methods are available with equal facility and can also be applied automatically. For the qualitative investigation of dental amalgams non-steady methods such as the well-known linear potential sweep methods are appropriate, but for investigating electrochemical corrosion under realistic conditions it is essential to go to the steady state. At the present time, the only satisfactory method of probing the steady state, determined by the potential of the sample with respect to a fixed reference electrode, is by the measurement of impedance [17, 18]. This method is used here as a quantitative tool for investigating the characteristics of the corrosion reaction of a sample of dental amalgam. As the steady state of a piece of dental amalgam in service can encompass a range of conditions it is essential to be able to measure the impedance as a function of frequency and potential over a wide range. This philosophy of experimentation has proved valuable for other similar problems such as electrocatalysis, corrosion reactions and electrosynthesis, all of which have been investigated by one of the present authors (JAH).

As a large amount of data is accumulated by this method a system of data handling and graphical output is necessary. The impedance data were fitted to Equation 1,

$$\frac{1}{Z(\omega) - R_\omega} = \frac{1}{R_{ct} + (1 - j)\sigma\omega^{-1/2}\tanh[\delta(j\omega/D)^{1/2}]} + j\omega C_{dl} \qquad (1)$$

and curves of the frequency-independent parameters $R_{ct} - E$, $R_\omega - E$, $C_{dl} - E$ and $\sigma - E$ produced as output. The set of curves constitute an electrochemical spectrum of the electrochemical processes occurring. In particular, the double layer capacity–potential curves are a sensitive measure of the electrical state of the interface, and the charge transfer and Warburg coefficient curves are governed by the nature and rate of the corrosion reactions.

An indication of which electrochemical processes might occur is provided by the tables of standard potentials of known processes. Electrochemical measurements on the pure metal constituents of the amalgams are also valuable. In the present investigation measurements have been made on silver and tin, in addition to those of Amalcap and Dispersalloy.

3. Results and discussion

3.1. *Non-steady state measurements*

An investigation of the electrochemical effects and rates of the processes which occur when the dental amalgams are in contact with Ringer's solution was carried out by linear potential sweep experiments. Typical results for the Amalcap and Dispersalloy amalgams are shown in Fig. 1a and b. To observe a response for Dispersalloy it was necessary to go to higher sweep rates indicating that some faster inhibition processes occur. The notable feature of Fig. 1a and b is the similarity in shape, in spite of the fact that Dispersalloy contains an appreciable amount of copper. However, the exact shape of the curves depends on the history of the electrode, but the various curves for different physical states of one particular amalgam were qualitatively similar. There seems to be a first current peak starting at about $E = -1000$ mV, then a series of current peaks from about $E = -550$ mV to more positive potentials. The

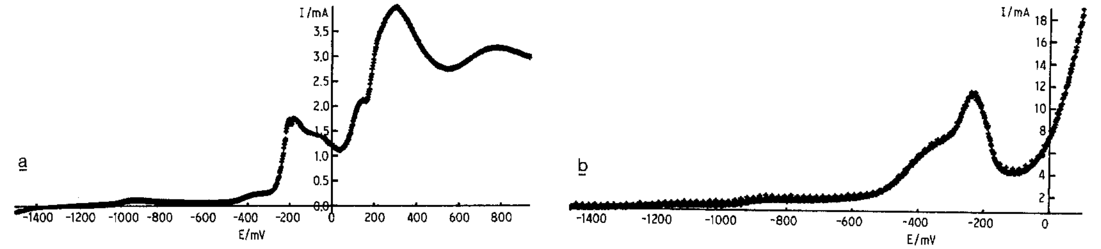

Fig. 1. Examples of linear potential sweep curves for Amalcap and Dispersalloy stationary electrodes (electrode area $0.79\,cm^2$) in two-thirds Ringer's solution. Start potential, $-1500\,mV$. (a) Linear potential sweep curve at $10\,mV\,s^{-1}$ (sweep size, 2500 mV), sweeping in the positive potential direction for an Amalcap electrode. (b) Linear potential sweep curve at $1000\,mV\,s^{-1}$ (sweep size, 1600 mV), sweeping in the positive potential direction for a Dispersalloy electrode.

peaks starting at about $E = -1000\,mV$ and at $E = -550\,mV$ are probably linked and are associated with the dissolution and then passivation of tin. Similar curves were seen when a pure tin electrode was investigated in 1 M NaCl solution. Investigations by other workers on the mechanism of electrochemical tin dissolution in phosphate buffer solutions [14, 15] indicate that the first peak is probably associated with the dissolution and the passivation of tin in the valancy two state, and the second peak with the dissolution and passivation in the valency four state; the precise reactions are not known. The sharp current peak starting at about $E = 100\,mV$ is probably due to the dissolution and then passivation of silver. According to the standard electrode potentials the passivating film is most likely to be AgCl, although an Ag_2O film is possible under some conditions of potential and pH. Similar statements can be made about the mercury oxidation reactions to form Hg_2Cl_2 and Hg_2O which are expected from the standard potentials at somewhat more positive potentials.

3.2. *Corrosion potential measurements in the presence of oxygen*

In order to have some idea of the potential region of most interest, corrosion potential measurements (versus SCE) were made for samples of Amalcap and Dispersalloy in either two-thirds Ringer's solution containing oxygen, or in the mouth. For comparison, the potentials in the mouth of fillings (of unknown origin) were measured. The measurements were not precise as they depended on the history of the amalgams. However, freshly polished Amalcap in Ringer's solution seemed to have a corrosion potential of about $E = -500\,mV$ and Dispersalloy a corrosion potential of about $E = -296\,mV$. Similar values were measured for isolated amalgam samples in the mouth. Old fillings in teeth seemed to have corrosion potentials at more positive potentials, around $E = -130\,mV$ to $E = -200\,mV$. The potential-determining mechanism of amalgams in the mouth is unknown. It is probably determined by the oxygen reduction reaction as would be the case for an isolated amalgam sample sitting in Ringer's solution.

3.3. *Steady state current–potential and impedance–potential measurements on Dispersalloy*

Fig. 2a–c gives the results of the 'steady state' measurements on a specimen of freshly polished Dispersalloy. Fig. 2a gives the current–potential, Fig. 2b the charge–transfer resistance and Fig. 2c the double layer capacity–potential results. The electrode remained for about 60 s at each potential. Results taken in the potential range from $E = -1500\,mV$ to $E = -100\,mV$ were recorded in a single run in which the potential was transversed from the most negative potential in a positive direction. In the frequency range used (0.77–1000 Hz), the impedance data fitted Equation 1 at each potential with an ohmic resistance, a charge transfer resistance and a double layer capacity parameter, but the Warburg coefficient, σ, was negligible for Dispersalloy.

In Fig. 2a the steady state *i–E* curve indicates

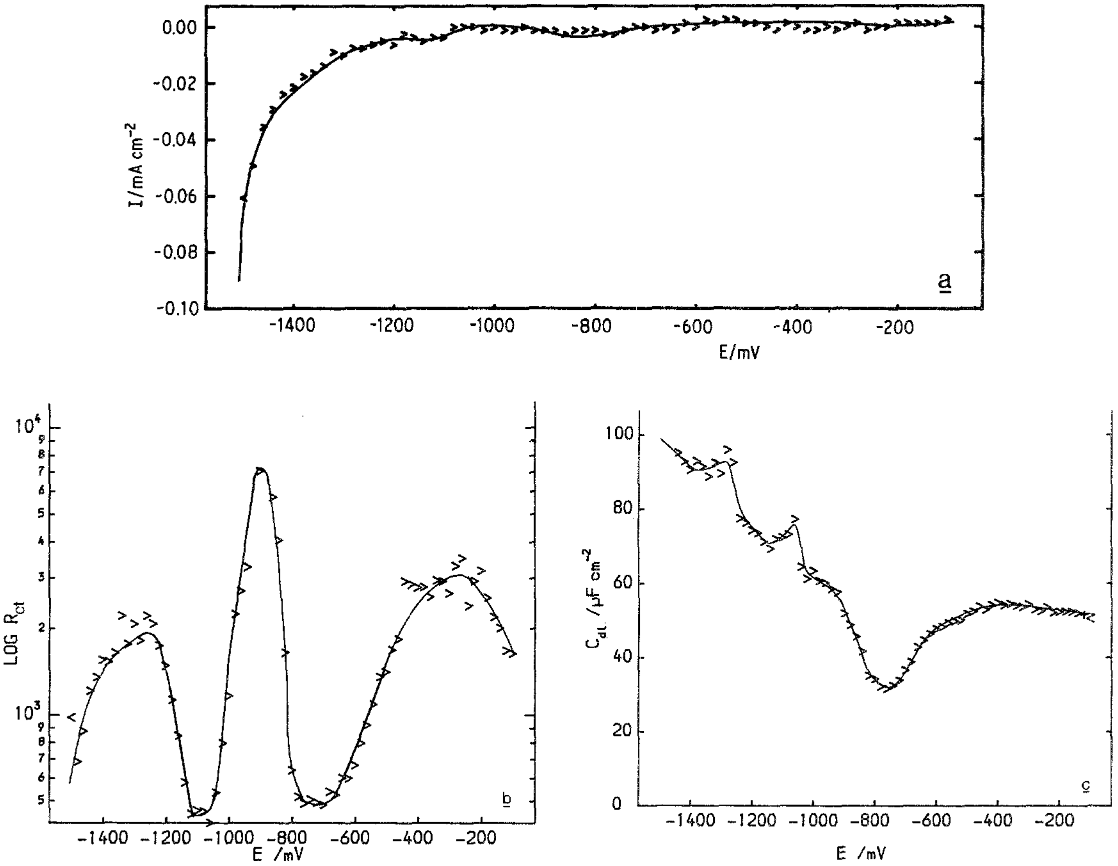

Fig. 2. Electrochemical characteristics for a stationary Dispersalloy electrode (0.79 cm^2) in two-thirds Ringer's solution. The analysis of the impedance at each potential was carried out according to Equation 1. (a) Measured 'steady state' *i–E* curve. (b) High frequency charge transfer resistance–potential curve. (c) High frequency double layer capacity–potential curve.

that at negative potentials the hydrogen evolution reaction occurs, and at potentials up to $E = -150$ mV a possible series of active–passive features are observed. However, these are at the limit of sensitivity of the equipment and, even through the current is averaged until the steady state value is reached, they are scarcely resolved from electrical noise.

The impedance can be measured more precisely than the steady state current in a situation where the currents are less than 1 μA cm^{-2}. The parameter curves $R_{ct} - E$ and $C_{dl} - E$ obtained from the use of Equation 1 show significant changes with potential. A further advantage of measuring the impedance is that the parameter curves have a physical interpretation.

Fig. 2b, in which the charge transfer resistance–potential curve is plotted, suggests two active passive dissolution reactions from $E = -1300$ mV to $E = -900$ mV and from $E = -900$ mV to -400 mV. A further dissolution reaction occurs at more positive potentials than $E = -300$ mV. If these steady state processes are identified with the effects in the linear potential sweep curves, then the first active–passive reaction would be identified with Sn to Sn(II), and the second with Sn to Sn(IV). The further dissolution may be primarily connected with silver and also mercury. The role of copper in the potential range $E = -1500$ mV to $E = -150$ mV seems to be an indirect one, as far as can be ascertained. Measurements on the active dissolution of copper in acid chloride-containing solutions show that the dissolution reaction occurs near to $E = 0$ mV SCE in 0.1 M chloride solution [19]. It seems likely that the charge transfer resistance is close to the steady state resistance of the interface. If that is the case then the charge transfer resistance curve in Fig. 2b is directly related to the corrosion current. In the absence of the oxygen reduction or another corrosion partner, as in the present investigation, the connection between current and charge transfer resistance is expected to be

$$\frac{1}{R_{\mathrm{ct}}} = \frac{2.303}{a} i \qquad (2)$$

for a simple metal dissolution reaction in which the metal forms a metal ion which then diffuses into solution. The low frequency resistance will be higher than the charge transfer resistance when diffusion becomes significant in the steady state current–potential curve. An order of magnitude calculation indicates, for $a = 40\,\mathrm{mV}$ (an expected value for active metal dissolution reactions), that at the corrosion potential $E = -296\,\mathrm{mV}$ where (from Fig. 2b) the charge transfer resistance is about $3000\,\Omega\,\mathrm{cm}^2$, the corrosion current should be about $5.8\,\mu\mathrm{A\,cm}^{-2}$. The interpretation of low frequency resistance in terms of corrosion current requires a model of the electrode process. This problem has been most investigated for the corrosion of iron (see Symposium proceedings [20]) and is not completely solved. A solution for amalgam corrosion might be to carry out a calibration experiment of weight loss to set against the electrochemical parameter curves.

The double layer capacity–potential curves are interesting and provide more information. In the potential region of the first active passive transition from $E = -1300\,\mathrm{mV}$ to $E = -900\,\mathrm{mV}$ the capacity rises in the active dissolution region and falls in the passive region. It is possible that the metal surface roughens during active dissolution, leading to the rise in capacity, then becomes covered with a thickening film as evidenced by the increasing charge transfer resistance and a decrease in the double layer capacity. In the potential region from $E = -900\,\mathrm{mV}$ to $E = -400\,\mathrm{mV}$ the capacity initially falls, suggesting dissolution in the presence of a film, and then rises with potential, possibly indicating a dissolution which involves roughening. At potentials positive to $E = -300\,\mathrm{mV}$ the capacity becomes approximately constant at a reasonably high value of $62\,\mu\mathrm{F\,cm}^{-2}$.

3.4. *Steady state current–potential and impedance–potential measurements on Amalcap*

The current–potential, charge transfer resistance and double layer capacity–potential curves reproduced in Fig. 3a–d are for a specimen of Amalcap in contact with the Ringer's solution. Over a potential range from $E = -1400\,\mathrm{mV}$ to $E = -150\,\mathrm{mV}$ the curve is similar in general to that for Dispersalloy, but has some significant differences.

Fig. 3a shows a pseudo steady state i–E curve. The currents were, in the early stages of an experiment, much higher than in the case of Dispersalloy. The potential was increased stepwise at about 60 s per potential point. Before a measurement was commenced the current was virtually steady with time; however, the corrosion inhibition processes are slow. This is shown by the currents at $E = -150$ and $E = -50\,\mathrm{mV}$ which show a downward trend with time on a long time scale of the order of minutes. The other parameters show a corresponding trend (see Fig. 3b–d).

The analysis of the impedance diagrams at each potential leads to the $R_{\mathrm{ct}} - E$, $C_{\mathrm{dl}} - E$, $\sigma - E$ parameter curves. A similar a.c. frequency range to those used for the Dispersalloy measurements was used. Over most of the potential range a high frequency semicircle, corresponding to the dominance of the R_{ct}, C_{dl}, R_{ω} terms in Equation 1, was obtained. However,a Warburg impedance type response, associated with the σ parameter, seems to appear in the potential range $E = -600\,\mathrm{mV}$ to $E = -500\,\mathrm{mV}$ and $E = -150\,\mathrm{mV}$ to $E = -50\,\mathrm{mV}$. In the potential interval $E = -500\,\mathrm{mV}$ to $E = -150\,\mathrm{mV}$ an impedance with a low frequency resistance characteristic of a passivating electrochemical reaction is observed. These effects have not been investigated further in this investigation as the emphasis has been on surveying the dependence of the parameter curves on potential. However, a more detailed investigation will be reported in a later publication.

Fig. 3b shows the charge transfer resistance–

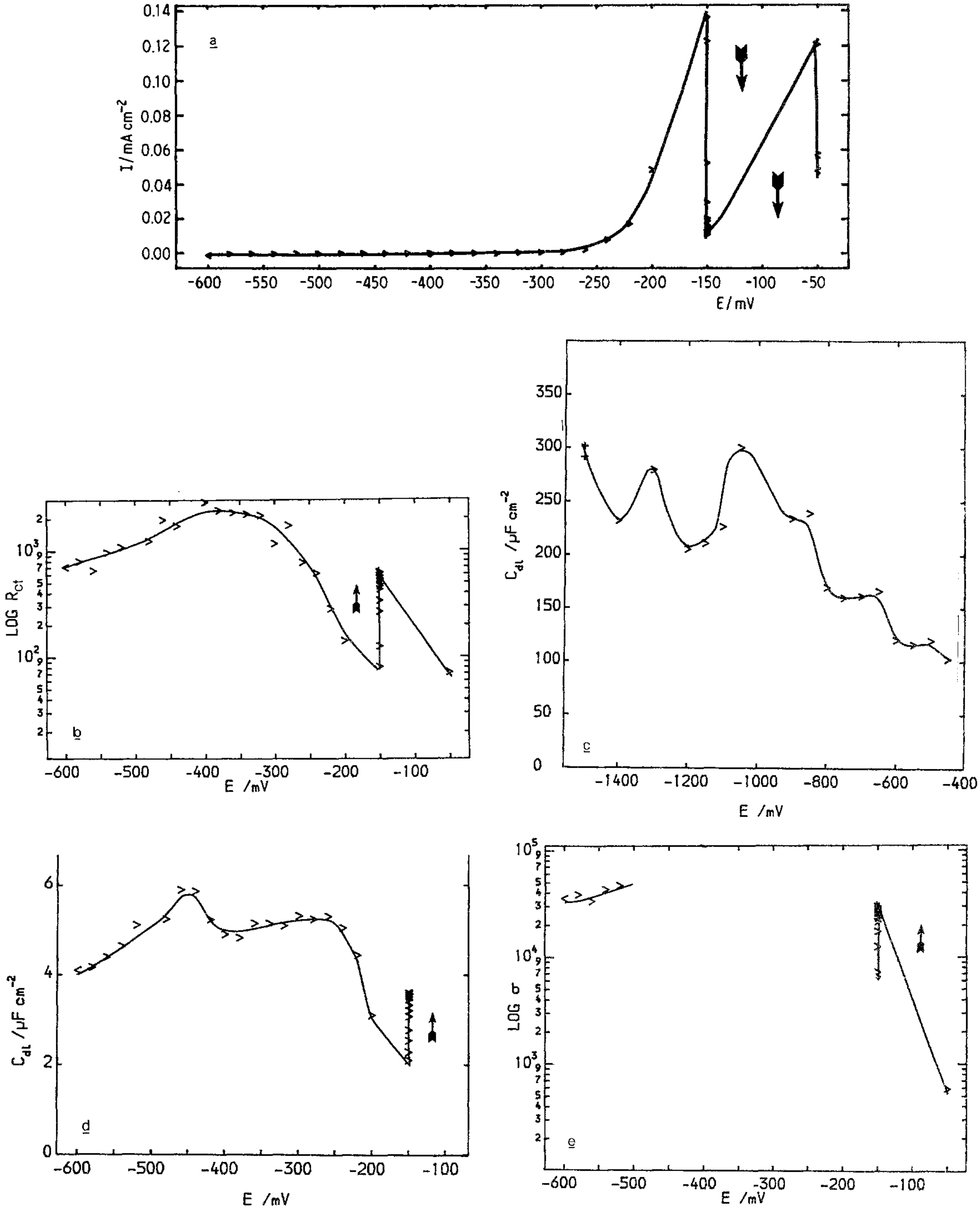

Fig. 3. Electrochemical characteristics for a stationary Amalcap electrode (0.79 cm^2) in two-thirds Ringer's solution. The analysis of the impedance at each potential was carried out according to Equation 1. (a) Measured 'steady state' i–E curve. The potential was held at $E = -150$ mV and $E = -50$ mV. (b) High frequency charge transfer resistance–potential curve. (c) High frequency double layer capacity–potential curve. (d) High frequency double layer capacity–potential curve. (e) Warburg coefficient–potential curve. The parameter $\delta(D)^{1/2}$ was 0.1. In the frequency range applied in the experiments, a Warburg impedance was only observed in the potential range shown.

potential curve. Equation 2 suggests that at the corrosion potential on a fresh Amalcap surface $E = -500$ m V, the corrosion current should be 0.017 mA cm^{-2}. However, a Warburg impedance is observed at this potential and in the limit the low frequency resistance related to the slope of the steady state current–potential curve, is an order of magnitude larger than the charge transfer resistance. The actual corrosion current must be of the order of 7 μA cm^{-2}.

Fig. 3d shows a double layer capacity–potential curve for a freshly polished electrode in which the potential was taken from negative values in a positive direction, stopping short of the main dissolution potential region. The meaning of this complex curve has not yet been elucidated completely. It is probably characteristic of the particular chemical composition of this amalgam and its surface structure. At negative potentials ($E = -1500$ to $E = -1100$ mV) the values of the double layer capacity are typical of those for a metal in contact with an electrolyte. In fact the curves are close to those observed for solid silver in contact with an electrolyte [16], but larger, thus indicating that the surface is fairly rough. From $E = -1100$ to $E = -1000$ mV the rise in capacity may be associated with active dissolution of the amalgam and a roughening of the surface. The downward trend from $E = -1000$ mV is associated with the films formed on the electrode surface which are responsible for the corrosion inhibition. The double layer capacity curve at more positive potentials (Fig. 3d) which was measured in a separate run, confirms the downward trend and the low value of the capacity compared to the value observed at negative potentials. An inference would be that in this potential region the electrode is always covered by a film. As the curve has a peak this may indicate a dissolution process, at $E = -600$ mV to $E = -450$ mV, with further passivation and film thickening with potential and time at more positive potentials. The chemical nature of the film is unknown. However, at these potentials it may contain four-valent tin as hydroxide and possibly chloride. At the potential of interest, $E = -150$ mV, the capacity increases with time on holding the potential constant. In spite of the presence of a substantial passivating film the electrode surface seems to roughen with time as the amalgam dissolves.

In a particular potential range a Warburg impedance response as contained in Equation 1 and described by the parameter σ is observed. The result is shown in Fig. 3e. The fact that a Warburg response is observed in the impedance is consistent with the lower charge transfer resistance for Amalcap compared with Dispersalloy and hence the higher rate of the metal dissolution reaction.

The only work that seems to be comparable with the present work is that of Grajower and Greener [9]. They were limited to making d.c. i–E measurements about the corrosion potential for a number of amalgams in the presence of oxygen. They found, for example for an NTDA amalgam, a corrosion potential of $E = -546$ mV and a corrosion current of 1.4 μA cm^{-2}.

4. Conclusions

A comprehensive investigation of the electrochemical corrosion characteristics of a range of amalgams of different compositions would be desirable. Problems of this type also have wider interest in corrosion research. The present limited investigation of Amalcap and Dispersalloy suggests:

1. Measurement of steady current–potential and impedance–potential data are powerful electrochemical methods and would be very suitable for the routine characterization of dental amalgams. Even when the currents are small, the parameter curves derived from the impedance measurements show a characteristic pattern. It should be possible to carry out accelerated testing by following the parameters as a function of time.

2. The parameter curves $R_{ct} - E$, $C_{dl} - E$, $R_{\omega} - E$, $\sigma - E$ have been derived from a simple model of an electrochemical corrosion reaction. More detailed investigation over a wider frequency and potential range and at smaller potential intervals would be desirable in order to develop a better electrochemical model for the interpretation of the data.

3. Even at the level of investigation presented in this paper it seems evident that Dispersalloy is

more protected against corrosion in the steady state compared to Amalcap.

4. In view of the high impedance of the interface as films build up on the metal surface under some conditions of potential, ionic environment and time, and the expected very low currents for the direct measurement of the corrosion rate, there is further work in progress. This is attempting to optimize the measurement of current and impedance for the routine testing of dental amalgams.

5. In this investigation Ringer's solution alone has been used. It would be desirable to vary the ionic environment.

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