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Preparation and characterization of new electrocardiogram electrodes

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A new generation of electrocardiogram (ECG) electrodes have been fabricated and superficially modified by a special controlled precorrosion process. The electrodes have been characterized by scanning electron microscopy (SEM), resistance–capacitance measurements (RCM) and simulated defibrillation recovery (SDR). The resulting surface of the Sn alloys was rough, and, consequently, a large active surface area was available. As a result, a higher electrocardiogram electrode performance, including low alternating current (a.c.) impedance, excellent time stability and improved SDR, was achieved. Such new design can surely find important future applications in clinical diagnosis. © *1999 Kluwer Academic Publishers*

1. Introduction

In clinical applications, electrodes are widely used as biological sensors. The planar electrocardiogram (ECG) electrode targets on-line monitoring of the human body surface potential and the status of the electrocardiograph. From the clinical point of view, two properties, namely simulated defibrillation recovery (SDR) and low alternating current (a.c.) impedance, are the most important characteristics for such medical devices [1, 2].

During fibrillation, the cardiac muscle stops pumping blood almost completely and, frequently, severe cardiac damage, or even death, can result. In cardiac clinical emergency treatment, short time electrical pulses are applied, using the ECG electrodes, to rehabilitate the cardiac muscle. For continuous monitoring of the electrocardiograph, after defibrillation, the ECG electrodes must recover to the specified tolerance in 5–10 s. Meanwhile, defibrillation status will be analysed to determine if a further pulse is necessary. Within the 30 s after defibrillation, the potential shift rate of electrodes cannot be larger than $1\ \mathrm{mV\,s^{-1}}$. Therefore, SDR is one of the most important characteristics required to assure good clinical performance [1–3]. In addition, during on-line electrocardiograph monitoring, a low a.c. impedance value is a desired characteristic. High a.c. impedance values can cause imbalance between the two coupling electrodes and reduce the common mode reject ratio (CMRR) of the signal amplifier [4, 5]. The high a.c. impedance may further lead to an excessive generation of heat at the electrode–skin interface, causing electrode failure. In severe cases, the patient's skin in contact with the surface of the electrode can even be burned.

A number of studies on the ECG electrodes and electrode gels have been reported. In particular, in clinical diagnosis, the Ag–AgCl electrode is one of the most used systems. However, although the Ag–AgCl electrode shows good electrical properties, the complicated manufacturing process, electrical instability and excessive environmental sensitivity make it inadequate as an ideal replacement. Recently, the company 3M introduced new ECG electrodes made of Sn substrates. Due to their low resistance, low cost and easy fabrication process, pure Sn and Sn alloys are really adequate materials for such an application.

In this paper, a method to improve the performance of such Sn-based ECG electrodes using particular Sn alloys superficially modified by a controlled precorrosion treatment is described. In particular, the effect of the precorrosion treatment on the surface of the electrode has been investigated by scanning electron microscopy (SEM), resistance–capacitance measurements (RCM) and (SDR).

2. Experimental procedure

High purity (>99.9 wt %) Sn, Ag and Zn metallic powders (Aldrich) were used to form two different alloys: Sn–Ag (20 wt % Ag) and Sn–Zn (8 wt % Zn), referred to as Sn(I) and Sn(II), respectively. The precorrosion chemicals were mainly made by hydrochloric acid solution and ethanol (Aldrich).

The hydrochloric acid solution–ethanol (4 : 1 v/v) mixture was prepared by mixing corresponding amounts of acid solution and ethanol; then the system was diluted with distilled water up to a HCl concentration of 2 wt %. The Sn, Sn(I) and Sn(II) substrates were precorroded in such a solution for 5 min at 35 °C. Then, the substrates were rinsed twice with distilled water, and once with 200-proof ethanol. Finally, they were dried at 100 °C, and transferred to a desiccator for storage. The ECG gel used in this study was a poly(acrylic ester) based product (Beijing Chemical Reagent Factory). ECG gel was placed on the pretreated substrates at room temperature using a special brush.

A SEM (Cambridge S-240), with a working voltage of 20 kV, was used for surface characterization. Precorroded specimens were polished before microscopical observation. Faraday's resistance and capacitance were obtained, respectively, at SI-1287 and SI-1250 unities. The equipment was supplied by Solartron, and its schematic circuit is shown in Fig. 1. The working frequency used was 10 Hz. SDR tests were performed using an electric instrument projected by us, the equivalent circuit is shown in Fig. 2.

3. Results and discussion

3.1. Surface morphology of Sn substrates

The SEM micrographs reported in Fig. 3a, b show the microstructure of the Sn(I) alloy substrate. From Fig. 3a, it can be seen that two distinct phases are present. The composition of the alloy used in this study is not eutectic. During alloy cooling, Phase I (dark in Fig. 3a) precipitated first, and Phase II (white in Fig. 3a) precipitated later. Because of the difference in chemical composition, the two phases form a typical cell structure. A similar microstructure characterized the Sn(II) alloy substrate. This particular sample microstructure allows the precorrosion treatment used in this study. As can be seen in Fig. 3b, when the samples are immersed in the precorrosion solution, Phase I is first etched and Phase II lives almost totally unchanged.

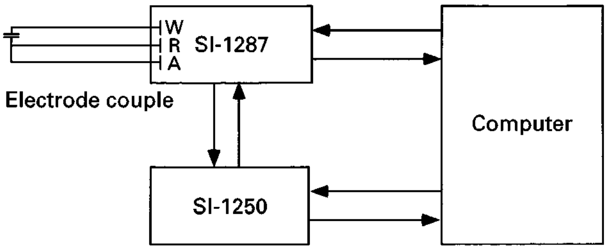

Figure 1 Schematic test circuit for a.c. impedance determination: w, R and A represent the working, reference and auxiliary electrodes, respectively.

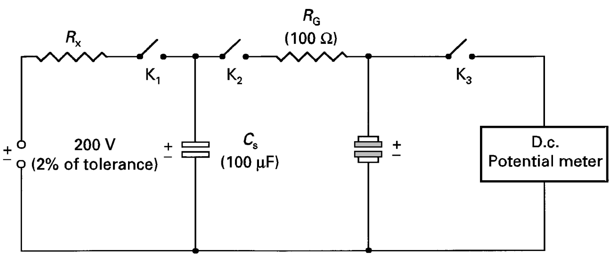

Figure 2 Equivalent test circuit for SDR evaluation: C_s, capacitor; K_1, K_2, K_3 are switches; R_x and R_G are resistors.

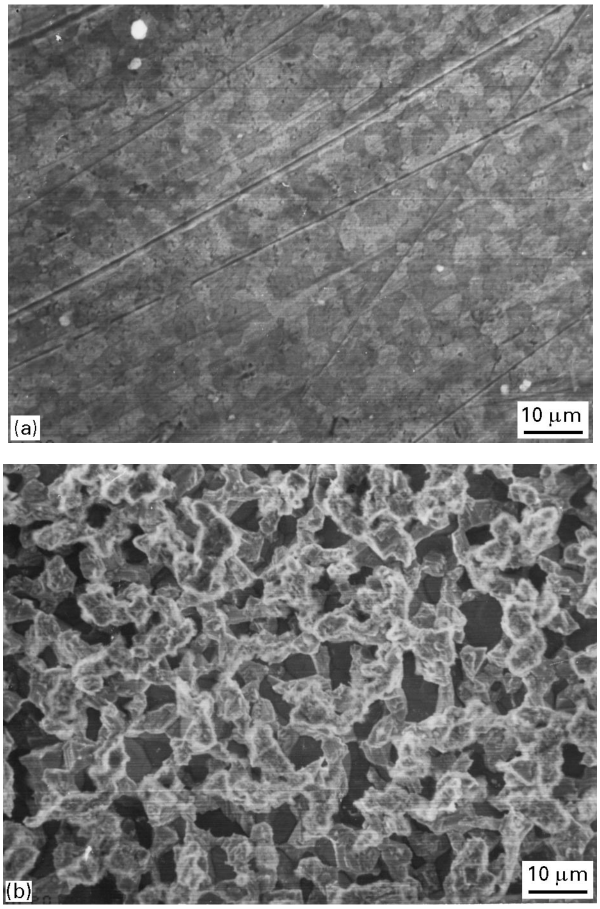

Figure 3 SEM micrographs of the surface of the Sn(I) alloy substrate before (a) and after (b) precorrosion treatment.

3.2. Precorrosion effect on a.c. impedance

Recently, most commercial ECG electrodes are made using Sn substrates manufactured, principally, by the company 3M. Clinical application requires stable and low a.c. impedance values. However, at present, very few reports have treated these problems. Here, the a.c. impedance values of ECG electrodes of the Sn substrate have been compared with those of two new substrate electrodes, i.e. Sn(I) and Sn(II). In particular, three groups of ECG electrode substrate samples of Sn, Sn(I) and Sn(II) were precorroded using the above-described method. Each group contained ten substrates. After one week of stabilization, the a.c. impedances were evaluated and compared with those of uncorroded or reference samples. The test results are given in Table I. A drastic reduction of a.c. impedance characterized the material obtained using the precorrosion process.

TABLE I A.c. impedance values (Ω) of ECG electrodes with and without precorrosion treatment

Conditions	Sn	Sn–Ag	Sn–Zn
With precorrosion treatment	111	102	120
Without precorrosion treatment	165	303	335

In order to further investigate the behaviour of the ECG electrodes, the electrically equivalent circuit shown in Fig. 4 was constructed and a theoretical model was established. Thus the theoretical value of the Z_{AD} impedance can be expressed as

$$Z_{AD} = Z_{AB} + R_e + Z_{CD} \tag{1}$$

where Z_{AB}, Z_{CD}, Z_{AD} are the impedances of the lines AB, CD and AD (Fig. 4); and R_e is the electrode gel resistance.

Structurally, the ECG electrodes are made using identical electrodes (i.e., $Z_{AB} = Z_{CD}$), and the electrode gel resistance R_e is negligible because it is very small. Therefore, Equation 1 can be simplified as

$$Z_{AD} \approx Z_{AB} + Z_{CD} = 2Z_{AB} \tag{2}$$

Theoretically, Z_{AB} can be expressed as

$$Z_{AB} = \frac{1}{R_f + 2\pi \times \phi \times C_d} \tag{3}$$

where ϕ is the frequency of the current. R_f is Faraday's resistance and C_d is the capacitor between electrode and gel. From Equations 2 and 3, Z_{AD} will decrease when the R_f and C_d values increase. Again, $C_d = \varepsilon S/d$, where S is the total active surface area of electrodes, ε the dielectric constant, and d the theoretical thickness of the double layer on the surface of the electrode. The C_d value is directly proportional to the total active surface area. As follows from the microscopic investigation (see Fig. 3b), the surface of the precorroded electrode substrate is very rough, and, consequently, the total active surface area is significantly increased. In addition, the surface oxide coating is removed and electrode reactivity is enhanced. As a result, the exchange current density of electrode reaction between ECG electrodes is increased. Once again, because of the promoted electrode reaction, the capacitance and the Faraday's resistance are reduced. More test results are tabulated in Table II.

3.3. Precorrosion effect on SDR properties

The SDR property refers to the recovery ability for normal electrocardiogram monitoring of ECG electrodes after defibrillation. The test equivalent circuit of the apparatus used is schematically shown in Fig. 2.

First, the capacitor C_s (10 μF), is charged by 200 V circuit (K_1 closed and K_2 open), and then it discharges to the ECG electrode couple and a 100 Ω resistor (K_2 closed and K_1 open). The requirements are: first, the voltage drop of the electrode couple must be less than 100 mV in 5 s after discharging; and second, the average 10 s shift rate of voltage drop, V_{drop}, must be less than 1 mV s^{-1} within 30 sec. The V_{drop} after 5 s, here indicated as $V(5)$, is selected as an index to evaluate SDR performance. The smaller the $V(5)$ value, the better the SDR performance.

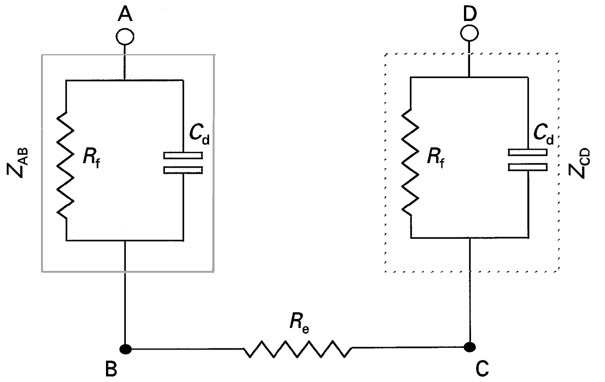

Figure 4 Equivalent circuit for AD impedance evaluation: Z_{AB}, Z_{CD}, Z_{AD} are the impedances of lines AB, CD and AD; R_e is the electrode gel resistance; R_f, Faraday's resistance; and C_d, the capacitor between electrode and gel.

Experimental values of $V(5)$ are reported in Table III. The $V(5)$ values of precorroded ECG electrodes were reduced by 50–60% on average in comparison with the $V(5)$ value of the same electrodes without precorrosion. It further means that SDR performance has been significantly improved. Among the three groups of metal substrates, Sn(II) again demonstrated the best performance.

In particular, in the steady state, the voltage drop of ECG electrode couples can be expressed as

$$V_{drop} = I \times (2R_f + R_e) \tag{4}$$

where I is the exchange current of the electrodes. Finally, I can be expressed as

$$I = \frac{RT}{n\mathrm{F}} \times \frac{1}{R_f} \tag{5}$$

where R is the universal gas constant; I is temperature, 288 K (in this study); F is Faraday's constant; and n is the number of exchanged electrons in the electrode reaction.

3.4. Time stability of ECG electrodes

Time stability is a further important characteristic for ECG electrodes. More specifically, the a.c. impedance and $V(5)$ values should remain relatively stable over the electrode service life-span. As in the above experiments, three groups of ECG electrodes were used. The electrodes were stored for 90 days at 15 °C, and their electrical properties were tested after periods of 15 days. The results obtained are shown in Figs 5 and 6.

Both a.c. impedance and $V(5)$ values decrease with time, which indicates electrical stabilization over time. In particular, the most significant decrease in a.c. impedance and $V(5)$ functions is observed in the first month. After three months, the electrical properties studied start to become stable. Such time stability behaviour is probably due to the establishment of an

TABLE II Calculated R_f (Faraday's resistance) and C_d values based on the equivalent circuit

Conditions	Sn $R_f(\Omega)$	$C_d(10^{-5}F)$	Sn–Ag $R_f(\Omega)$	$C_d(10^{-5}F)$	Sn–Zn $R_f(\Omega)$	$C_d(10^{-5}F)$
With precorrosion treatment	41.9	1.15	82.1	1.50	35.2	1.63
Without precorrosion treatment	688.7	0.94	548.7	0.84	630.8	0.68

TABLE III $V(5)$ (mV) performances of ECG electrodes with and without precorrosion treatment

Conditions	Sn	Sn–Ag	Sn–Zn
With precorrosion treatment	20.7	18.2	15.0
Without precorrosion treatment	53.7	35.6	45.8

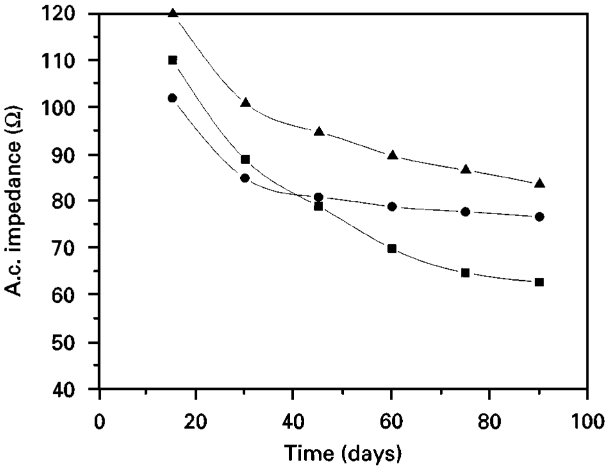

Figure 5 Time stability of a.c. impedance value for: (■) Sn by 3M, (●) Sn(I) alloy, and (▲) Sn(II) alloy substrates.

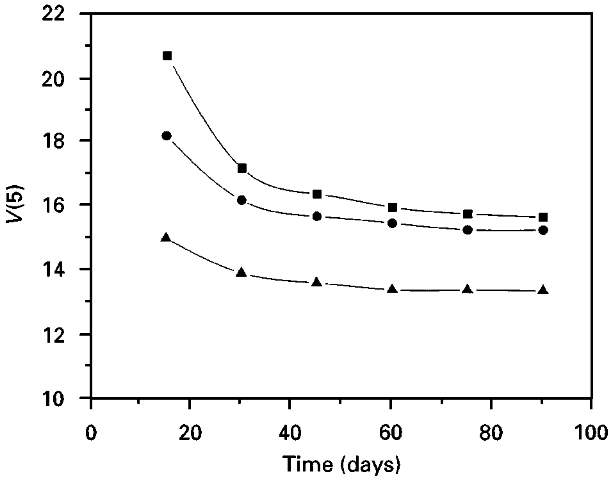

Figure 6 Time stability of $V(5)$ performance for: (■) Sn by 3M, (●) Sn(I) alloy, and (▲) Sn(II) alloy substrates.

electrode reaction equilibrium. After three months, the reaction is almost at a steady state or very close to an equilibrium state, and, therefore, a minimum shift of electrical properties is possible.

Again, the Sn(II) electrode showed the best behaviour among the tested group, and the validity of the proposed design further demonstrated.

4. Conclusions

This study describes the preparation and characterization of a new generation of ECG electrodes based on precorroded Sn alloys. The precorrosion process produces a significant improvement in electrode performance, because it modifies the surface microstructure, increasing its active surface area. In addition to this increased stability, a.c. impedance and SDR performance are also improved.

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