An Approach to Corrosion Control during Electrical Stimulation

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A form of cathodic protection has been developed for controlling the corrosion of stainless steel electrodes during electrical stimulation. The protection is achieved by using biphasic stimulation pulses with a slight ($\leqslant 1\%$) charge imbalance in favor of the cathodic phase. Tests *in vitro* indicate that the "safe" charge limit (the charge density per phase at which corrosion first becomes serious) can be at least tripled by the use of imbalanced pulses. If confirmed by tests *in vivo*, this result may find application in the field of intramuscular stimulation where the present "safe" charge limit for stainless steel electrodes ($\mp 40~\mu C~cm^{-2}$) does not permit an adequate range of stimulation intensities.

INTRODUCTION

Electrical stimulation of the nervous system has many potential applications in the treatment of neurological disorders, but most applications will entail the chronic implantation of electrodes in living tissue (Hambrecht and Frank, 1975). Compatibility of the metal electrode with the biological medium during current pulses will then be crucial. This compatibility requires that electric charge be transferred without generating toxic reaction products or degrading the electrodes. The major factors governing the type of electrode reactions that occur during a stimulation pulse are the electrode material, the fluid environment, the charge density, and the pulsing regime. For example, platinized Pt electrodes can safely inject charge densities of up to $\mp 300~\mu C^{1}~cm^{-2}$ (geometric as opposed to real surface area) per pulse provided that balanced, biphasic pulses are used and that the cathodic phase is applied first (Brummer *et al.*, 1977). Platinum lacks the mechanical strength required for many applications, however, and although nonnoble metals better satisfy the mechanical requirements for stimulation electrodes, their use is restricted by corrosion problems. For example, fine wire coils of stainless steel are used for muscle stimulation, but charge densities in balanced biphasic pulses must be kept below $\mp 40~\mu C~cm^{-2}$ (i.e., $\mp 6~\mu C$ per pulse on an electrode of geometric surface area about $0.15~cm^2$) to avoid severe corrosion damage (Mortimer, 1975). This charge limit does not provide an adequate range of stimulation intensities and an increase in the maximum charge density by 2 or 3 times would greatly

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[1] The symbol $\mp$ is used to denote cathodic-first pulses.

enhance the utility of the electrodes. In the present note, we describe a pulsing regime that permits such an increase in charge density *in vitro*, with no increase in the corrosion rate.

EXPERIMENTAL

Tests were performed *in vitro* and at room temperature, using an inorganic saline solution containing 7.30 g liter^{-1} NaCl, 0.23 g liter^{-1} Na$_2$SO$_4$; and 0.20 g liter^{-1} NaH$_2$PO$_4 \cdot$7H$_2$O. Test electrodes were made from 0.125 in. diameter rods of stainless steel (AISI Type 316, cold rolled) by sheathing them in heat-shrink FEP Teflon tubing and metallographically polishing one exposed end (geometric area 0.08 cm^2). Counter electrodes were made from a carbon black and Teflon mixture, pasted onto Ta screen (Brummer *et al.*, 1977). The experimental arrangement is shown in Fig. 1. The steel electrode was mounted face upwards in a test cell and 2 cm^3 of saline solution were pipetted into it.
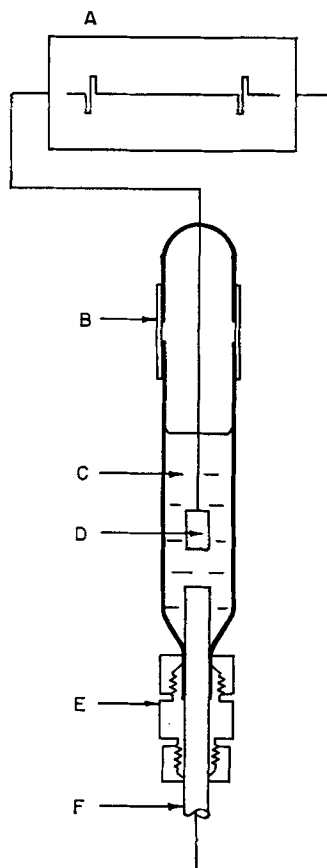

FIG. 1. Test cell: (A) pulse generator; (B) shrink Teflon; (C) electrolyte; (D) counter electrode; (E) Teflon union reducer (Beckman No. 501); (F) test electrode sheathed in shrinkable Teflon tubing.

The current waveform, comprising 1 mS biphasic pulses (0.5 mS per phase) was generated with circuitry of our own design and passed through duplicate cells in series. In most cases, the pulse repetition rate (p.r.r.) was 50 Hz but a few tests were performed at lower frequencies. The polarity was such that the steel electrodes received each biphasic pulse with the cathodic phase first. The cathodic current in each pulse was adjusted to yield a charge density of 80 or 120 μC cm^{-2} (geom.). In general, a small imbalance was maintained between cathodic and anodic charges in each biphasic pulse. The net dc resulting from the charge imbalance was measured by placing a 3 μF capacitor in the circuit and recording the buildup of dc voltage across it. The charge imbalance per pulse was then calculated from the measured value of the net dc. Pulsing was continued for 1 to 3 days and the solution analyzed for dissolved Fe. The analysis was performed spectrophotometrically using the Fe complex with 1,10-phenanthroline (I.U.P.A.C., 1963). Finally, the electrode surface was examined by light microscopy for signs of corrosion.

RESULTS AND DISCUSSION

The relationship between charge imbalance and Fe dissolution is illustrated in Fig. 2. Micrographs of representative electrodes are shown in Fig. 3. The
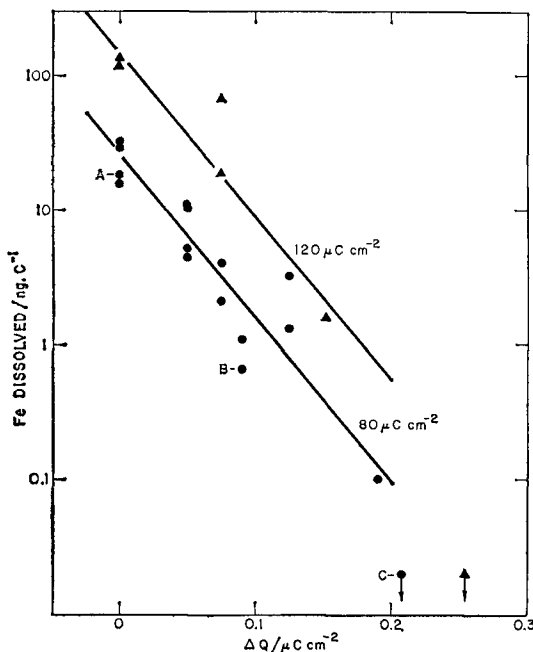

FIG. 2. Relationship between the nanograms of Fe dissolved per coulomb of cathodic charge injected and ΔQ, the excess cathodic charge in μC cm^{-2} per biphasic pulse. Electrodes pulsed $\mp$80 μC cm^{-2} ($\bullet$) or $\mp$120 μC cm^{-2} ($\blacktriangle$) at $\mp$160 mA cm^{-2}, 50 Hz in saline solution. The data points labeled A, B, and C correspond to the three electrodes shown in Fig. 3. Arrows ($\downarrow$) indicate that no Fe was detected in solution.
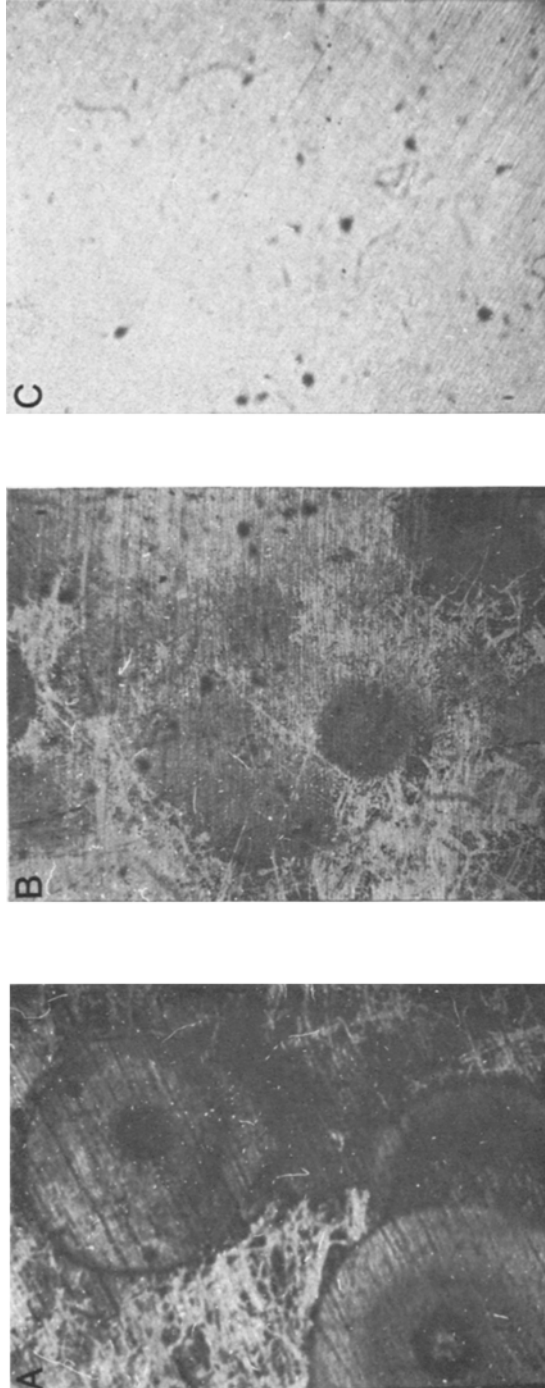
FIG. 3. Micrographs at 40× magnification of three electrodes after pulsing in saline solutions (cf. Fig. 2).
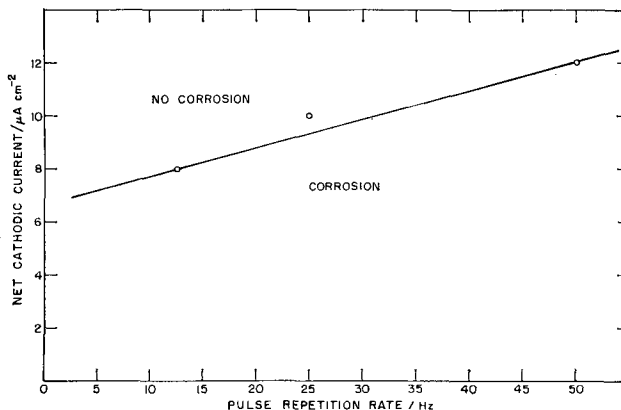
FIG. 4. Relationship between pulse repetition rate and the minimum net cathodic current density required to prevent corrosion. The net current is given by the products of the charge imbalance per pulse and the pulse repetition rate.

results demonstrate that corrosion is diminished when there is an excess cathodic charge in the biphasic pulses. At a p.r.r. of 50 Hz, an excess charge of about 0.2 μC cm^{-2} per pulse (i.e., 0.2–0.3%) appeared sufficient to reduce Fe dissolution below detectable limits (<0.5 μg) and to eliminate visible evidence of pitting. At 50 Hz, this charge imbalance gives rise to a net cathodic current density of 10–15 μA cm^{-2} and to a first approximation, a similar net current density was also required at lower p.r.r. The minimum net current density needed to prevent visible corrosion by pulses of $\mp$80 μC cm^{-2} in a 3 day test is plotted against p.r.r. in Fig. 4. The data in Fig. 4 indicate that the net cathodic current required to prevent corrosion actually tended to diminish slightly as the p.r.r. was lowered. In terms of charge imbalance, the minimum current density corresponded to an excess cathodic charge density per pulse of 0.64 μC cm^{-2} (0.8%) at 12.5 Hz, 0.40 μC cm^{-2} (0.5%) at 25 Hz and 0.24 μC cm^{-2} (0.3%) at 50 Hz. These values, and the data in Fig. 2 contain a degree of uncertainty because of drift in the control circuit. We estimate that the uncertainty in a given net current or charge density was no more than ±20% over 3 days and somewhat less in shorter tests.

In order to understand the relationship between charge imbalance and electrode corrosion, it is necessary to consider the various electrode reactions that can occur in this system. The most probable cathodic reaction is H$_2$ deposition:

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^-, \tag{1}$$
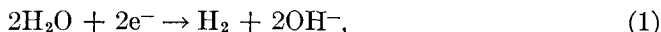
and the most probable anodic reactions are H$_2$ oxidation (the reverse of (1)) and Fe dissolution:

$$Fe \rightarrow Fe^{2+} + 2e^-. \tag{2}$$

In a balanced biphasic pulse, the net charge transfer is zero. However, when the products of charge transfer in the cathodic phase are soluble, they will tend to diffuse away and be only partially available for reoxidation in the sub-

sequent anodic phase. Consequently, some other anodic reaction must take place to make up for the "lost" charge. In the present system, the cathodic charge that goes into H_2 deposition must be balanced by the sum of anodic charges going into H_2 oxidation and Fe dissolution. The proportion of the anodic charge going into Fe dissolution will depend not only on the amount of H_2 available, but also on the kinetics of the H_2 oxidation reaction. In a biphasic pulse with cathodic imbalance, the excess cathodic charge will produce extra H_2 in solution and offset losses due to diffusion. So long as the kinetics of the hydrogen oxidation reaction are relatively rapid, the electrode potential will remain below that for Fe dissolution and no corrosion will occur. The present results demonstrate that H_2 oxidation on stainless steel in saline solution is sufficiently rapid that at least 120 μC cm^{-2} per phase can be injected during imbalanced biphasic pulses without causing appreciable Fe dissolution.

Suppressing corrosion by the use of cathodically imbalanced pulses may be viewed as a form of cathodic protection. This process involves the passage of current from a "sacrificial anode" to a structure that requires protection. In effect, the corrosion is transferred from the protected structure to the sacrificial anode. The corresponding effect in the present context is to produce an anodic charge imbalance at the counter electrode. Fortunately, the counter electrode employed by Mortimer (1975) is a large one, placed external to the body, and a small increase in its corrosion rate should present no threat.

The overall effects of applying cathodically imbalanced biphasic pulses to a stainless steel electrode are to replace Fe in solution with H_2 and to raise the pH around the electrode (cf. Eq. (1)). The extent to which these effects can be physiologically tolerated will only be known after *in vivo* tests but there is reason for optimism. The net cathodic current density required to prevent corrosion in the present tests was only 6–12 μA cm^{-2}, depending on p.r.r. In contrast, healthy muscle has been found to tolerate net cathodic current densities of at least 1000 μA cm^{-2} without damage (Mortimer, 1975). Further testing is clearly justified.

ACKNOWLEDGMENT

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