

THE GRADED BOUNDARY CARBON-SALINE ELECTRODE

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Summary.—A new type of electrode for measurement of dc potentials is described. Utilizing a porous graded boundary of carbon on fiber-glass wet with saline, this electrode makes possible highly drift free operation over long periods. With matched pairs of electrodes, base line drifts of less than 1 mv per hour are obtained. Examples of its use in measuring body potentials are given. The voltage-current characteristic shows a useful working region in which the electrode potential is independent of the current.

As interest in the relationship between biological direct current potentials and human and animal behavior has developed among behavioural scientists, the need for an electrode with minimal base line shift over long periods of time has become increasingly felt. The principal cause of base line instability is electrode polarization accompanying the dc operation. Most investigators have attempted to adapt the silver-silver chloride electrode to this type of application (Cole & Curtis, 1950; Burr, 1950; Feder, 1963; Shackel, Sloan, & Warr, 1958). In our investigations it was desirable to measure dc potentials on the surfaces of human beings with accuracies of the order of one millivolt and for periods of time of the order of one hour (Becker, *et al.*, 1962; Friedman, *et al.*, 1962). A new type of electrode characterized by a graded boundary of carbon in a fiberglass matt was developed and found to be superior to any other type in long term drift, convenience and ease of handling, and reproducibility of results.

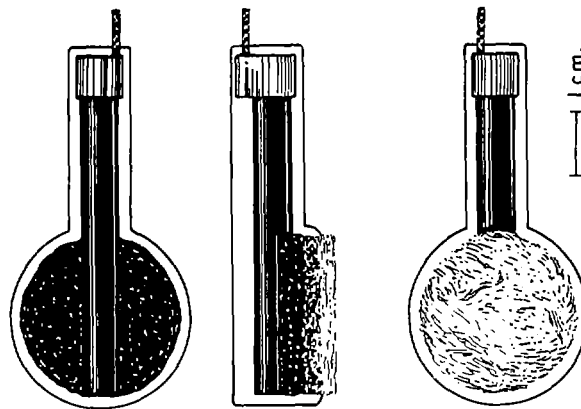


FIG. 1. Graded boundary electrode

In an unrelated investigation one of us had been concerned with the development of electrodes for a wick-fed steam generator. The relatively porous and open carbon-fiber-glass structure described here proved to have exceptional qualities in that application. On a hunch it was adapted for use as a bioelectrode where it also proved superior.

The general structure of the electrode is shown in Fig. 1. Using these electrodes the contour plot of the potentials on surface of the human body was

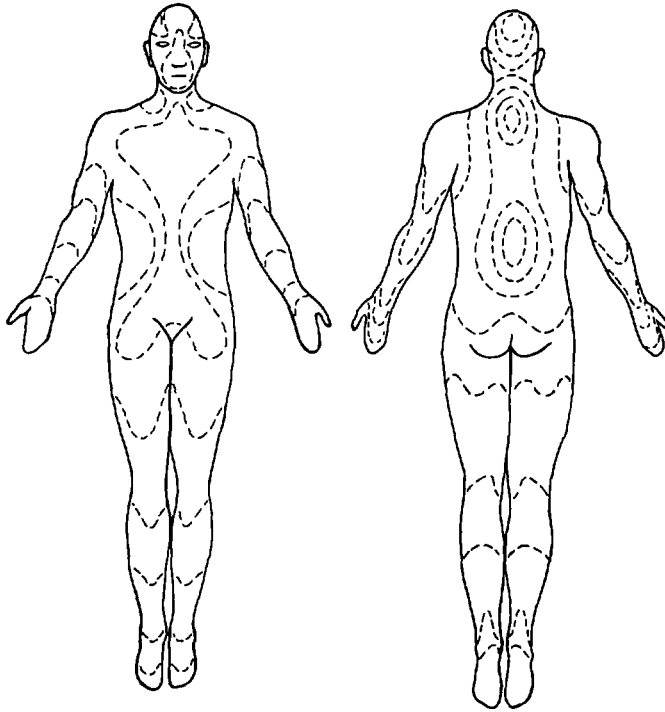


FIG. 2. Isopotential plot of human body

obtained (Fig. 2). Fig. 3 shows data from a clinical application where the electrodes were applied to the back of the head and the palm of the hand.

When a pair of these electrodes is immersed in saline and sufficient current is caused to pass through them by an external source, a voltage drop builds up between them as shown in Fig. 4B. Such a drop will be reflected in any measurement made with the electrodes in which the corresponding current is drawn. It can be seen that currents up to about 10^{-10} amp. may be passed before this error exceeds 1 mv. The use of measuring instruments having high input re-

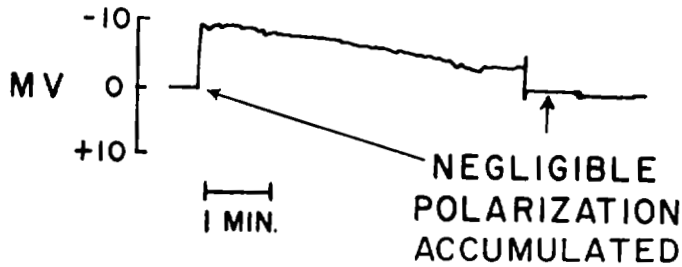


FIG. 3. DC potential between cervical area and palm of hand

sistance is necessary to avoid drawing such currents from the biological system. In the work described here a Keithley No. 600 Electrometer was used. This instrument makes possible measurements with input resistances up to 10^{11} ohms.

An instrument input resistance of about 10^8 ohms seems indicated if one is to keep such error low. Values about 10% low result if the input resistance is 10^6 ohms.

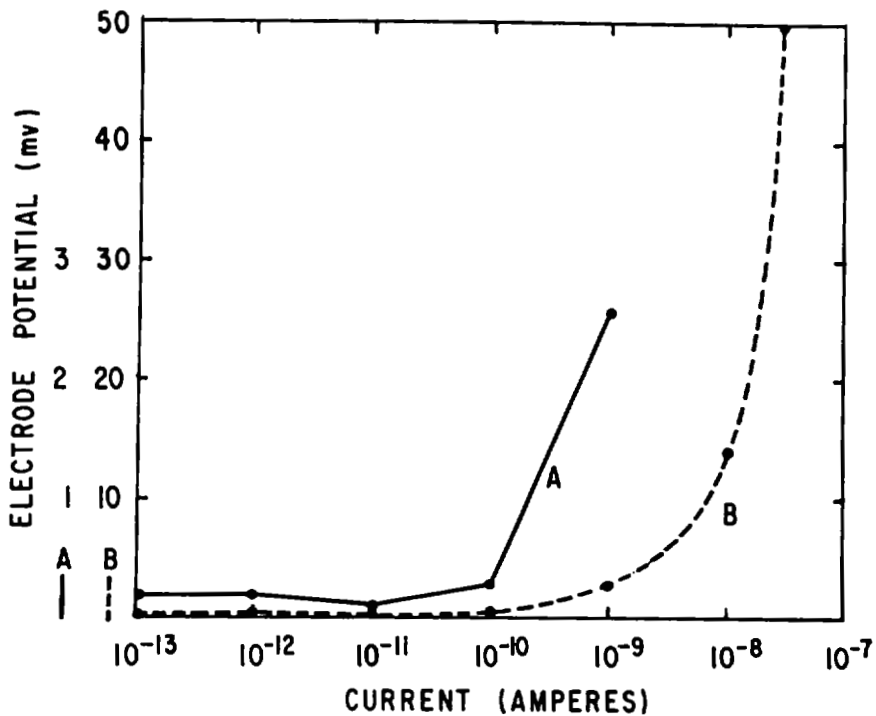


FIG. 4. Voltage-current curve for electrodes in saline

The electrodes are made as follows: A "grading" mix made up of colloidal graphite suspended in commercial phenolic resin dissolved in alcohol is applied to one side of the disc of needled glass-fiber matt. The consistency of the mix is such that it soaks into the fibers about $\frac{1}{4}$ in. While still moist the $\frac{1}{4}$ -in. rod of battery carbon is attached to the disc with a phenolic "holding" paste carrying coarse particles (greater than 200 mesh) of petroleum coke.

The assembly is held for 24 hr. in a drying oven at 100°C and then oven fired at 850°C for $2\frac{1}{2}$ min. in air. The removal of all volatiles is indicated by the disappearance of the blue flame.

In this firing the electrodes are supported so that the entire active end of the electrode is open to its surroundings. After cooling in air the connector is crimped on to the carbon rod, and the electrode is encapsulated in plastic so that only the glass matt face is exposed. The result of this processing is a porous structure which has an unusually large carbon electrode area.

As received from the processing, the porous areas of the electrode consist of carbon contaminated in various degrees with the residue from the carbonization of the organic adhesive used to produce the diffuse boundary. This inorganic material, galvanic in nature together with the residual pH, influences the electrode potential so that the electrodes initially exhibit emfs scattered over an inconveniently wide range. Subsequent aging in saline stabilizes them, after which matched groups can be chosen. Matched electrodes are customarily chosen by selecting pairs which show inter-electrode potentials of less than one millivolt when placed in face to face contact. When electrodes so stabilized are used relative to each other there is very little inter-electrode drift.

As with other electrodes, any inter-electrode potential can be reduced essentially to zero by externally short circuiting the electrodes for a time in a common electrolyte. Two saturated electrodes can be held together face to face or they can be immersed in a common saline bath while shorted. Such electrodes, "depolarized" with respect to each other, immediately start to drift to their open circuit values when the external short is removed or is replaced by a sufficiently high resistance, for example, the high resistance input of an amplifier. The rate of this inter-electrode drift depends upon the current passed through the electrode, upon the electrode area, and upon the original open circuit inter-electrode emf.

In most applications the original low inter-electrode emf of the new electrodes may be biased out or subtracted from the data. Superior performance may then be obtained by omitting the shorting out procedure thus eliminating the slow drift back to the open circuit condition.

In Fig. 4A the ordinate scale is changed to make more clear the behavior of the electrodes in the useful range of currents. Although one might expect a steady and gradual increase in potential from even the smallest currents, note

that this does not occur. Repeated observations show that the interelectrode voltage holds constant with current until a break point is reached after which it climbs steeply. There is no apparent variation in this characteristic with concentration of electrolyte from normal to saturated saline.

A comparison was made of this characteristic and that of electrodes made of $\frac{1}{4}$ -in. rods of spectrographic carbon. The only difference found was in the time to establish equilibrium after a change in current. The rods required many minutes whereas the carbon-glass matt electrodes stabilized in seconds. The rather tight porous structure of the rod compared to the relatively open structure of the carbon-glass matt electrode seems to explain this difference.

To fit the observations the following mechanism is postulated. First, the effective electrode area is extremely great. The heat treatment used in the electrode preparation is similar to that used in preparing activated carbon. Dushman (1949) estimates that 1 cm^3 of activated carbon has an effective area of up to 1000 meters².

When completely unpolarized the resistance of the electrode is only a few ohms. When current flows ions are brought up and "plastered" on the cathode surface. These plastered areas present a very high electrical resistance. However, so long as any unplastered area remains the electrode voltage drop is determined by the parallel low resistance.

Assume that current flowing to the cathode maintains a constant current density so that increasing current is accommodated by the use of more and more cathode area until the cathode is completely covered. This regime is characterized by a constant low voltage drop across the electrodes. When the cathode area is finally covered with the occluded ion layer, much higher voltage is required to overcome the high resistance of this layer and provide further current increase—the curve turns up sharply.

This picture is analogous to a similar situation in the conduction of electricity in gas. The regime of the incompletely filled cathode is called the normal discharge. When operated in this manner such discharges are used as voltage regulators, maintaining fairly constant voltage over a range of currents. With higher currents the voltage drop climbs rapidly.

The relatively drift free performance of our electrodes is related to this region in which the voltage is independent of current variations. Normally, slow changes in factors, such as temperature, pressure, strain, and slowly diffusing impurities, can result in slow current variations. With a sloping voltage-current curve such current variations would result in corresponding drift in electrode voltage. When operated on the flat portion of the curve, the carbon-saline electrodes tolerate large current variations without a change in voltage drop.

This mechanism thus makes possible the long periods of measurement

with insignificant inter-electrode drift. It must be remembered that this ideal picture presupposes that the electrodes have in common the normal saline solution. Any differential in quality or concentration of solution will produce inter-electrode potentials. Such conditions might arise, for example, if excessive perspiration took place under one electrode, thus changing the concentration.

Since the porous graded boundary electrode holds about 3 cc of electrolyte and because of the very large effective surface area, a given amount of contamination is diluted and produces far less change in electrode potential than in the "hard surface" type of electrode. To minimize inter-electrode drift which might occur as a result of differential contamination during long time measurements, it has been found desirable to make sure that the skin at the point of electrode application is free of contaminants such as soap or medication.

When not in use the electrodes are stored in a common saline bath so that their electrolytes will tend to equalize. The leads are kept apart in such storage, of course, to maintain the open circuit potentials.

Since the inter-electrode potential is dependent upon saline concentration it might be thought that evaporation during a long experiment might produce some drift. However, the only exposed part of the electrode is the working face. In operation this is covered by skin surface so that evaporation is insignificant.

Although irritation from the glass fibers has not been encountered, padding (as with cotton) introduces no significant electrical effect if such skin sensitivity should be manifest. In applying the electrodes rubbing or grinding them across the skin should be avoided. The saline ensures that simple application will result in good electrical contact. The elastic bandage has been found to be a convenient method of support for application to the human body.

Because of the very large carbon area constituting the basic electrode surface, the electrode resistance is determined for the most part by the saline saturated glass matt. This material with normal saline solution has been found to have a resistivity of 57 ohm inches (145 ohm cm). Electrode resistance is typically less than 10 ohms.

Smith and Cullen (1962) have pointed to the problem of polarization of electrodes by direct current in applications to electronarcosis. We have used the electrodes described here in the electronarcosis of dogs and find that they pass adequate currents for long times without polarization and with no contact burnings.

REFERENCES

- BECKER, R. O., BACHMAN, C. H., & FRIEDMAN, H. The direct current control system. *N. Y. State J. Med.*, 1962, 63, 1169-1176.
- BURR, H. S. Bioelectricity: potential gradients. In O. Glasser (Ed.), *Medical physics*. Chicago: Yearbook Publ., 1950. Vol. 2. Pp. 90-94.

- COLE, K. S., & CURTIS, H. J. Bioelectricity: electrical physiology. In O. Glasser (Ed.), *Medical physics*. Chicago: Yearbook Publ., 1950. Vol. 2. Pp. 82-90.
- DUSHMAN, S. *Vacuum technique*. New York: Wiley, 1949.
- FEDER, W. Silver-silver chloride electrode as nonpolarizable bioelectrode. *J. appl. Physiol.*, 1963, 18, 397-401.
- FRIEDMAN, H., BECKER, R. O., & BACHMAN, C. H. Direct current potentials in hypnoanalgesia. *AMA Arch. gen. Psychiat.*, 1962, 7, 193-197.
- SHACKEL, B., SLOAN, R. C., & WARR, H. J. Detector plots eye movement. *Electronics* (Engng ed.), 1958, 31, 36-39.
- SMITH, R. H., & CULLEN, S. C. Electronarcosis by combination of direct and alternating current. *Anesthesiol.*, 1962, 23, 682-687.

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