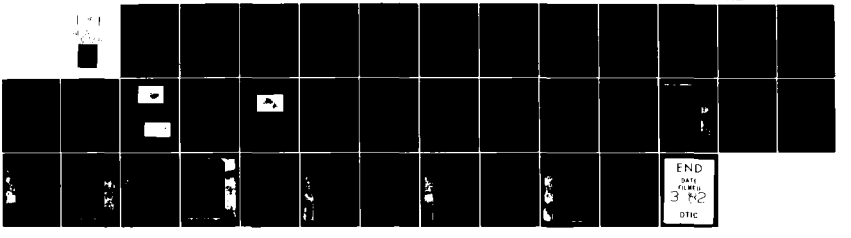
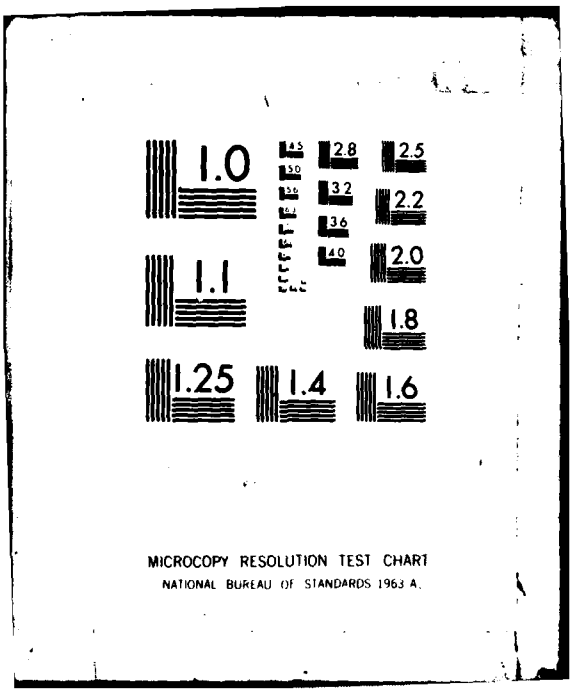
AD-A110 735 MISSOURI UNIV-COLUMBIA F/G 6/16
THE DEVELOPMENT OF CHRONIC INSERTABLE OXYGEN ELECTRODES.(U)
JUL 79 R E BARR, A W HAHN DADA17-71-C-1104
UNCLASSIFIED NL




1.0
1.1
1.25
1.4
1.6
1.8
2.0
2.2
2.5
2.8
3.2
3.6
4.0
MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS 1963 A.

LEVEL II

AD_____

THE DEVELOPMENT OF CHRONIC INSERTABLE OXYGEN ELECTRODES

Annual and Final Report

Ronald E. Barr
Allen W. Hahn

July 1979

Supported by

US Army Medical Research and Development Command
Fort Detrick, Frederick, MD 21701

Contract No. DADA17-71-C-1104

University of Missouri

Columbia and Rolla, Missouri

82

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER	2. GOVT ACCESSION NO. AD-A110	3. RECIPIENT'S CATALOG NUMBER 735
4. TITLE (and Subtitle) THE DEVELOPMENT OF CHRONIC INSERTABLE OXYGEN ELECTRODES		5. TYPE OF REPORT & PERIOD COVERED Annual and Final Report 1 Jun 1971 - 31 Jan 1978
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Ronald E. Barr Allen W. Hahn		8. CONTRACT OR GRANT NUMBER(s) DADA17-71-C-1104
9. PERFORMING ORGANIZATION NAME AND ADDRESS University of Missouri Columbia, MO 65211		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 62772A.3S162772A814.00.034
11. CONTROLLING OFFICE NAME AND ADDRESS US Army Medical Research and Development Command Fort Detrick Frederick, MD 21701		12. REPORT DATE July 1979
		13. NUMBER OF PAGES 36
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

electrode, blood oxygen, disc-shaped electrodes, telemetry system

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

See reverse side.

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

Summary

During the past contract year, progress was made in defining the aging process that occurs at the working electrode of a blood oxygen electrochemical sensor. A specific pre-treatment protocol was developed which led to consistent and predictable long term cathodic responses. The predictability of these responses is predicated on a model that was derived to explain the current responses of disc-shaped electrodes.

In addition, over the entire contract period an in vitro fluid flow-oxygenation system was developed to test and calibrate catheter electrodes in a simulated vascular environment. Preliminary in vivo experiments were performed to test the catheter electrode design and observe the effect of blood clotting on the electrode. A telemetry system was developed to transmit oxygen electrode current data continuously from an unrestrained subject. Portions of this research are summarized in the following publications: Adv. Exp. Med. and Biol. 94: 9-15 (1978) and Adv. Exp. Med. and Biol. 94: 17-23 (1978).

Summary

During the past contract year, progress was made in defining the aging process that occurs at the working electrode of a blood oxygen electrochemical sensor. A specific pre-treatment protocol was developed which led to consistent and predictable long term cathodic responses. The predictability of these responses is predicated on a model that was derived to explain the current responses of disc-shaped electrodes.

In addition, over the entire contract period an *in vitro* fluid flow-oxygenation system was developed to test and calibrate catheter electrodes in a simulated vascular environment. Preliminary *in vivo* experiments were performed to test the catheter electrode design and observe the effect of blood clotting on the electrode. A telemetry system was developed to transmit oxygen electrode current data continuously from an unrestrained subject. Portions of this research are summarized in the following publications: Adv. Exp. Med. and Biol. 94: 9-15 (1978) and Ad. Exp. Med. and Biol. 94: 17-23 (1978).

FOREWARD

In conducting the research described in this report, the investigator(s) adhered to the "Guide for Laboratory Animal Facilities and Care," as promulgated by the Committee on the Guide for Laboratory Animal Resources, National Academy of Sciences - National Research Council.

Contract Period: The period covered by this report is from 1 June, 1971 through 30 September, 1978.

Adherence to National Guidelines

In conducting the research described in this report, the investigator(s) adhered to the "Guide for Laboratory Animal Facilities and Care," as promulgated by the Committee on the Guide for Laboratory Animal Resources, National Academy of Sciences - National Research Council.

Contract Objectives:

The long range goal of the project was to develop a blood oxygen sensing electrode unit for in vivo long term continuous monitoring. The unit was to be designed for potential human applications in a catheter configuration. Progressing to this long term goal, four short term goals were pursued: (1) Continued work on long term electrode stability, (2) development of an in vitro flow system, (3) development of a multichannel telemeter and (4) design and development of a blood catheter system.

(1) Significant progress has been made in further defining the aging phenomenon. A specific pretreatment protocol was developed which led to consistent and predictable long term cathodic responses. The predictability of these responses is predicated on a model that was derived to explain the current responses of disc shaped electrodes. A description of the pretreatment protocol, the model and some of the responses predicted through its use are given in the two attached papers, T. E. Tang, et al (1) (Attachment 1) and R. E. Barr, et al (2) (Attachment 2). A brief summary follows:

Following the catalytic reduction process for oxygen at Pt surface described by Forbes and Lynn (3), a model for the electrode current was derived as detailed in (4). The working equation of this models is:

$$i = 8 F D_{O_2} R C^b_{O_2} \quad 1 + \frac{1}{4 R D_{H_2O_2}} \Big/ 1 + \frac{}{A k_2} \qquad (1)$$

where F = Faraday's constant, R = electrode radius, A = electrode area, D_{O_2} and $D_{H_2O_2}$ = diffusion constants for O_2 and H_2O_2 respectively, $C^b_{O_2}$ = oxygen concentration in the bulk media and k_2 = reaction rate for H_2O_2 to H_2O. The only variable in this equation is k_2. Based on responses obtained after electrodes had been pretreated according to the protocol described in (22), k_2 was given the form:

$$k_2 = C_1 \exp(-C_2 t) \qquad (2)$$

Using experimental data, values for C_1 = 15 cm/sec and C_2 = 0.75 H^{-1} were obtained. Applying these values in eq. (2) and substituting in eq. (1), comparison of experiment responses with the theoretical response for four 15 μm diameter electrodes is shown in Fig. 1.

Another important feature of this model, is that by assuming a complete four electron reaction, eq. (1) can be used to calculate the theoretical maximum current I_{max} for a given electrode. These calculations were done and compared to experimental maximum currents, Fig. 2. The agreement was excellent, thus any currents higher than I_{max} would indicate a non-oxygen reduction component and any currents smaller than

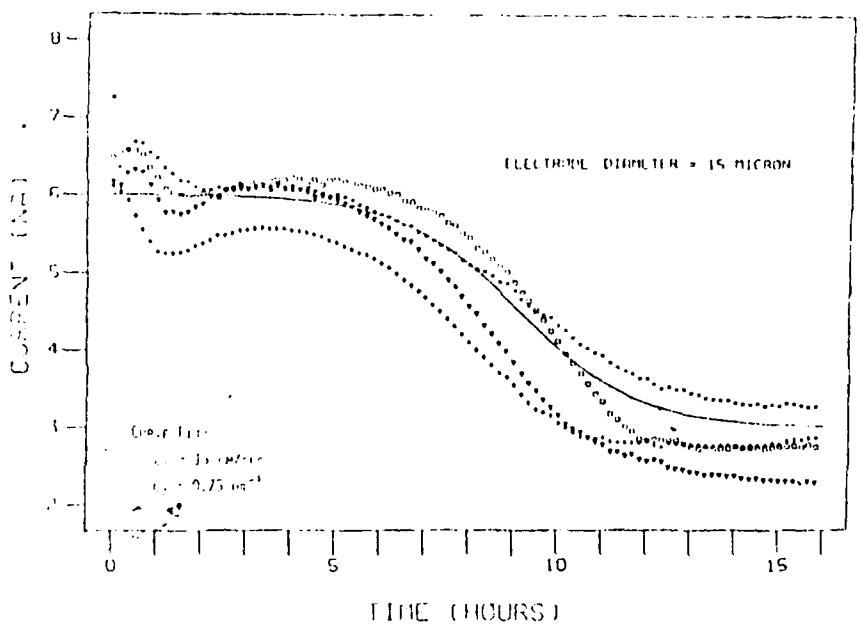


Fig. 1. Comparison of experimental responses to theoretical curve fit obtained with averaged C_1 and C_2 values.

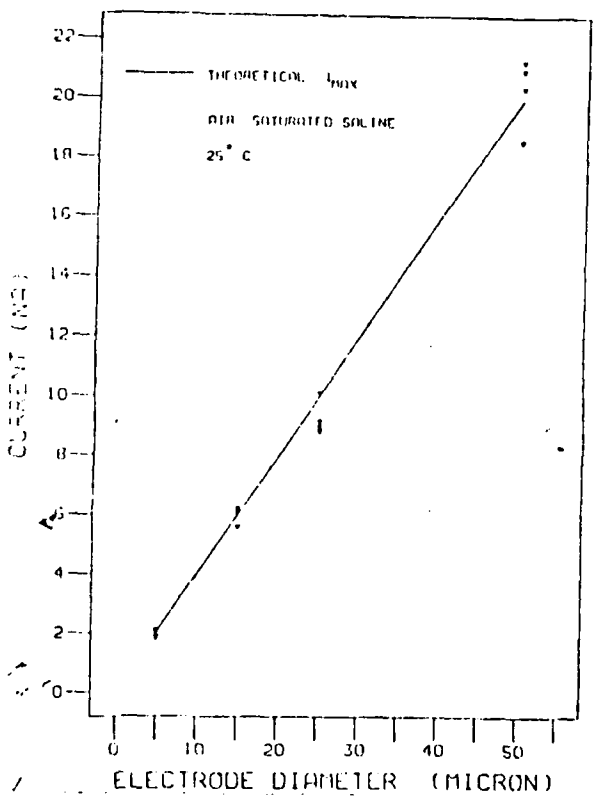


Fig. 2. Theoretical plot of Imax vs. electrode diameter compared to experimental data.

I_{max} would indicate reduced electrode sensitivity.

A significant finding was obtained when a membrane was placed on electrodes that had been pretreated. The type of responses obtained are shown in Fig. 3. The first few hours were influenced by what was thought to be membrane changes, chiefly hydration. After an initial decay period, the current stabilized at a value of about 3 nA for a period of about 30 hours. This was about one half the I_{max} value for 15 μm diameter electrodes (see Fig. 2), yet it was I_{max} for the system. This was demonstrated by the fact that after removing the membranes while the electrodes were still polarized, the bare tipped currents were at about 6 nA, i.e., I_{max}.

For the goal of this contract, the most important aspects of these findings are twofold. One, they give us a solid foundation on which to base further studies. Two, there are practical aspects of benefit to the program. For example, the pretreatment protocol has a shelf life of at least five days. That is, pretreated electrodes can be left unused for at least this period of time and still give the response predicted. Another example is that the pretreated electrodes appear to give encouraging responses when covered by a membrane, as shown in Fig. 3. Note that the current levels are the highest they can be for the system. This means these electrodes are operating at maximum possible sensitivity. We are confident that this is not true of most electrodes in use today.

(2) During the past year an in vitro fluid flow-oxygenation system has been constructed to test catheter electrodes in a simulated vascular environment. A block diagram of this system in shown in Fig. 4.

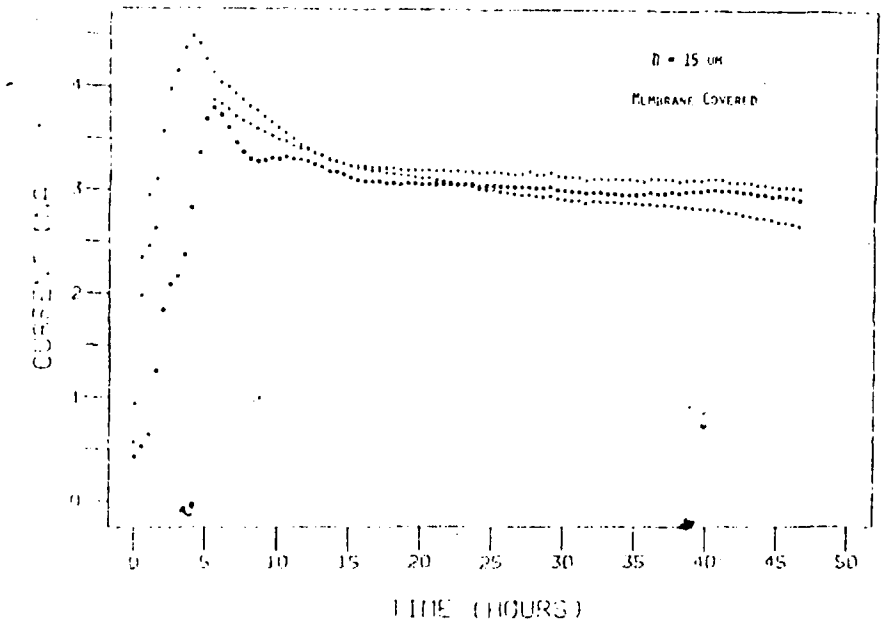


Fig. 3. Current responses for three pretreated electrodes covered by a dialysis membrane.

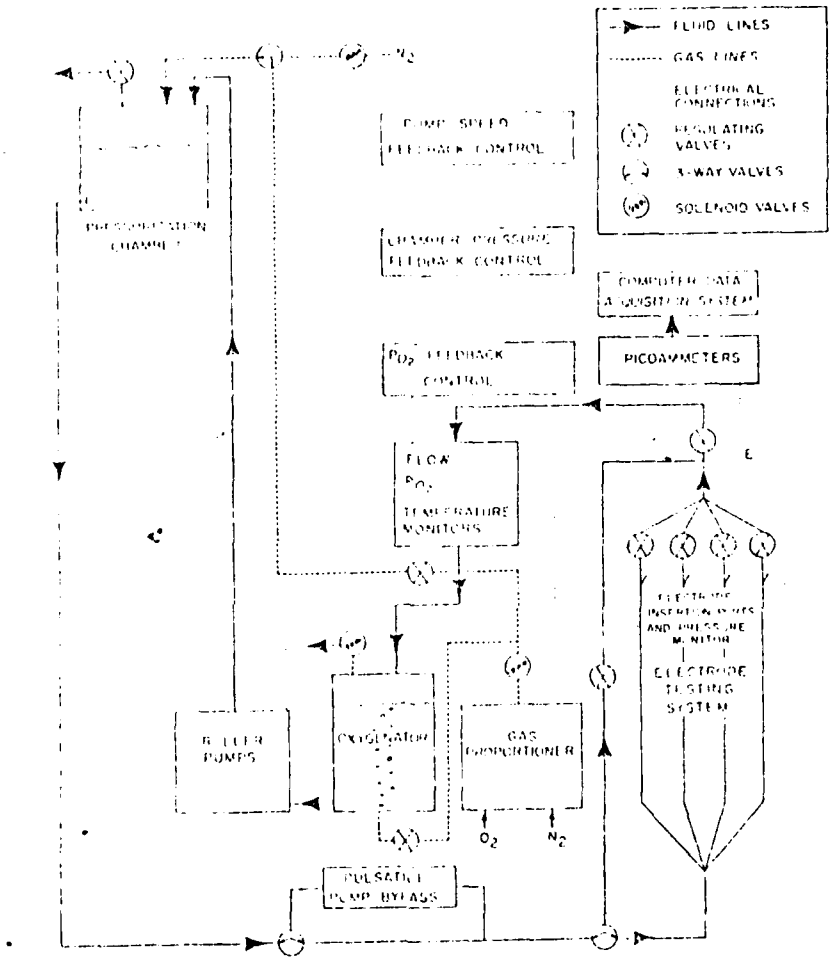


Fig. 4. Block diagram and flow pattern for the in vitro flow testing system. Note: The dashed line E is representative of four such lines, one each going from a test chamber to a corresponding amplifier.

As much of the system as possible was constructed of glass and copper tubing to minimize oxygen storage in the system. A mock system, using plastic tubing, was first constructed to work out some of the technical details of the system.

The flow system was designed with the following objectives in mind. 1) To produce conditions of constant flow rate, constant pressure, constant P_{O_2} and constant temperature, with the capacity to vary each condition independently of the others. 2) To vary these conditions within the ranges encountered in actual physiological conditions. 3) To automatically maintain these conditions at a constant level for an extended period of time. 4) To test electrode response to step changes in P_{O_2}. 5) To produce pulsatile flow analogous to actual physiological blood flow.

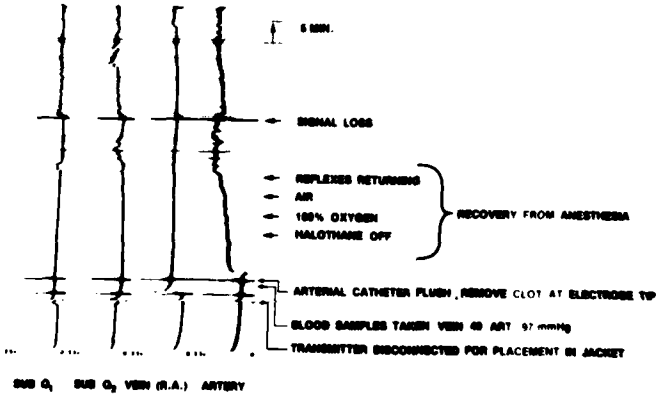
Prior to the purchase of a PDP11/03 microcomputer for dedicated use to our project, the in vitro static fluid cell test system utilized the Dalton Research Center's control computer for collecting and processing data. Since this is a shared system, our work was restricted to overnight runs of 10 to 15 hours and occasional longer weekend runs. Also this system had a limit of six data channels. Since then sufficient software was developed to permit bringing the system on line. Thus, the time of operation of a data run is limited only by the memory capacity of the computer. The PDP 11/03 computer also has 16 input channels, which permits much greater versatility and efficiency in planning and conducting experiments.

(3) One of the secondary goals was met. This was the development of a telemetry system to transmit oxygen electrode current data continuously from an unrestrained subject. The present design has four input (multiplexed) channels, which are readily adaptable to low level current input (oxygen electrode current), dc voltage input (pH and P_{CO_2} electrode signals, thermistor, pressure transducer) or ac voltage input (EKG, EEG). This telemetry package has been fabricated, bench tested and field tested (see below).

Two sets of in vivo experiments were performed; one on a dog and the other on horses. Both sets of experiments had multiple purposes: The primary purposes were to gain insight into some of the problems associated with catheter electrode design and to see what the effect of blood clotting was on electrode response. Another purpose was to field test the telemetry package.

In the dog experiment four oxygen electrodes were fabricated in a single package (Fig. 5A). Two were placed intravascularly, one in the right atrium through the jugular vein and on in the carotid artery and two were placed subcutaneously. The type of signals obtained are shown in Fig. 5B. Through a pulmonary gas forcing of 100% oxygen after surgical procedures were completed and technical (electronic) problems were solved, it was clear that the intravascularly placed electrodes had become insensitive to changes in oxygen tension. Presumably the cause of this was blood clotting. This hypothesis was supported by the observation of clotted blood around the electrode tips upon removal of the electrodes. Other technical aspects of this experiment fared better and the subject appeared able to carry the apparatus

A.



B.

Recording During Recovery From Anesthesia

C.

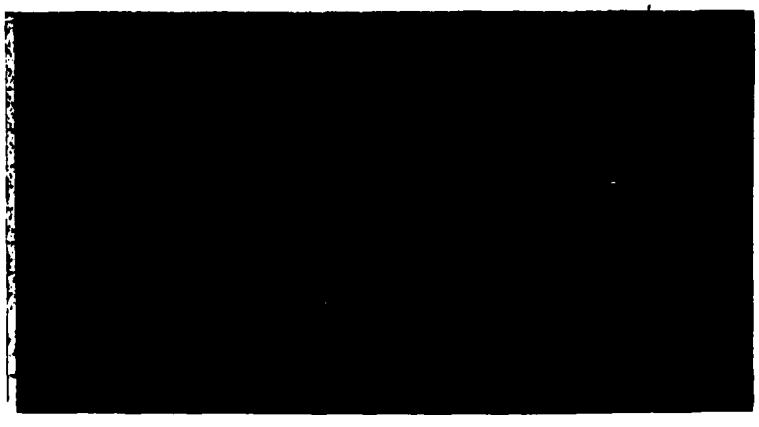


Fig. 5. In vivo testing of a four electrode package connected to a telemetry transmitter. A. The electrode package. B. Sample data, C. Unrestrained subject carrying the transducer - telemetry package.

adequately (Fig. 5C). The system was maintained in operation for almost 24 hours.

(4) A different catheter design was employed in the horse experiments. Three experiments were attempted. All experiments utilized an elevated carotid artery prepared by previous surgery. Only local anesthesia was required for the catheterization procedures. The first two experiments produced no significant oxygen electrode current data. Numerous technical problems were encountered, solutions to which gave considerably insight into the requirements of successfully performing such experiments. The third experiment did produce meaningful data and, most importantly, pointed the way to an electrode design requirement for long term implantation.

In this experiment, after a successful insertion, Fig. 6, electrode current was recorded and compared with oxygen tension values obtained from blood samples run through a blood gas analyzer. Using the before experiment calibration line, the electrode gave oxygen tension values to within five percent of the blood gas analyzer values for a period of about 90 minutes. Following this, electrode current decreased significantly, while arterial P_{O_2} did not. Blood coagulation was suspected and a planned anticoagulation-electrode cleaning procedure was initiated.

The catheter system was designed so that the electrode could be pulled back into a sleeve, through which a heparinized saline solution could be injected. This was done, following which the electrode was reextended into the blood vessel. Electrode current was then at earlier high levels. However, a decreasing current began within about ten

Fig. 6. Photograph of an unanesthetized horse carrying an oxygen electrode in the carotid artery and a telemetry transmitter.

minutes and the above process was repeated with similar results. This happened a third time and it was decided to terminate the experiment. After removal of the catheter system, it was observed that a clot, adhering to the catheter sleeve, had formed a flap extending beyond the end of the sleeve. Apparently, this clot was only partially broken down during attempts to remove it.

The above series of experiments and all of the work leading up to them has taken the project significantly closer to the final goal of this project.

During the final six months of the project, progress was minimal. This was due to the investigators spending time seeking other sources of funds to carry on the project and to the loss of the post-doctoral research associate and one of the technicians associated with the project.

REFERENCES

1. T.E. Tang, R. E. Barr, V. G. Murphy and A. W. Hahn (1978), Adv. Exp. Med. and Biol. 94: 9-15.

2. R. E. Barr, T.E. Tang and A. W. Hahn (1978), Adv. Exp. Med. and Biol. 94: 17-23

3. M. Forbes and S. Lynn (1975), AICHE Jour. 21: 763-669.

4. T. E. Tang, R. E. Barr, V. G. Murphy and A. W. Hahn (1977), in Oxygen Transport to Tissue III, ed I. A. Silver. Plenum Press, New York, pp. 9-16.

BIBLIOGRAPHY
(of publications supported by contract DADA17-71-C-1104)

Tang, T. E., et al. "Modelling of Oxygen Reduction at Activated and Aged Oxygen Sensors," AICHE, J., Submitted (1978).

Tang. T. E., et al. "The Operation of Platinum Oxygen Sensing Microelectrodes." Journal of Bioengineering 2, 381-388 (1978).

Barr, R. E., et al. "Variations of the Response Characteristics of Oxygen Electrodes." In: Oxygen Transport to Tissues III, ed by I. A. Silver. Plenum Press, New York, pp. 17-23 (1977).

Tang, T., et al. "A Working Equation for Oxygen Sensing Disc Electrodes." In: Oxygen Transport to Tissues III, ed. by I. A. Silver. Plenum Press, New York, pp. 9-16 (1977).

Hartley, J. W., et al. "Short Rnage Telemetry of Tissue Oxygen Tension." In: Biotelemetry III; proceedings of the Third International Symposium on Biotelemetry. Academic Press, New York, pp. 259-262 (1976).

Murphy, V. G., R. E. Barr and A. W. Hahn. "Control of Electrode Aging by a Periodic Anodization Technique." In: Proceedings of Second International Symposium on Oxygen Transport to Tissue. Plenum Press, New York, pp. 69-76 (1976).

Murphy, V. G., R. E. Barr and A. W. Hahn. "Development of Chronically Implantable Electrodes for Monitoring Oxygen Tension in Skeletal Muscle. In: Proceedings of Twelfth Annual Rocky Mountain Bioengineering Symposium. Instrument Society of America, Pittsburgh, pp. 31-36 (1975).

ABSTRACTS AND PRESENTATIONS

Tang, T. E., R. E. Barr and A. W. Hahn. "Modelling of Oxygen Currents for Noble Metal Polarographic Electrodes." Annual Fall Meeting, American Physiological Society, Hollywood, Florida, October (1977).

Barr, R. E., T. E. Tang and A. W. Hahn. "Optimization Parameters for Stable Oxygen Probes." Third Symposium of International Society for Oxygen Transport to Tissue, Cambridge, England, p. 6 (1977).

Tang, T. E., et al. "A Working Equation for Oxygen Sensing Disc Electrodes." Third Symposium of International Society for Oxygen Transport to Tissue, Cambridge, England, p. 4 (1977).

Tang, T. E., et al. "The Stability of Oxygen Sensing Electrodes." Proc. 29th Annual Conference on Engineering in Medicine and Biology, p. 426 (abstract) (1976).

Bartel, R. W., et al. "Tissue Oxygen Tension by Multi-Channel Telemetry." Proc. 29th Annual Conference on Engineering in Medicine and Biology, p. 355 (abstract) (1976).

Abstracts and Presentations, Continued

Hartley, J., et al. "Short Range Telemetry of Tissue Oxygen Tensions." Third International Symposium on Biotelemetry. (1976).

Murphy, V. G., R. E. Barr and A. W. Hahn. "A Technique for Improving Long-Term Stability of O_2 Sensing Electrodes." Proc. 27th ACEMB, p. 398 (abstract) (1974).

PERSONNEL RECEIVING SUPPORT
FROM DADA17-71-C-1104

Ronald E. Barr, Ph.D.
Michael J. Devaney, Ph.D.
Allen W. Hahn, D.V.M., Ph.D.
Kenneth Mayhan, Ph.D.

Vincent G. Murphy, Ph.D. (Post Doctoral Research Associate)
Thomas Tang, Ph.D. (Post Doctoral Research Associate)

R. W. Bartel, Graduate Student - received Ph.D.
Jessie W. Hartley, Graduate Student - received Ph.D.
Marvin Havens, Graduate Student - received Ph.D.

Twilla Day (Technician)
Richard Lee, M.S. (Research Technician)
Bonnie McAlmon (Technician)
Michael Nichols, M.S. (Research Technician)

LAIR U

DISTRIBUTION LIST

4 copies	HQDA (SGRD-SI) Fort Detrick Frederick, MD. 21701
12 copies	Defense Technical Information Center (DTIC) ATTN: DTIC-DDA Cameron Station Alexandria, Virginia 22314
1 copy	Dean School of Medicine Uniformed Services University of the Health Sciences 4301 Jones Bridge Road Bethesda, Maryland 20014
1 copy	Superintendent Academy of Health Sciences, US Army ATTN: AHS-COM Fort Sam Houston, Texas 78234
4 copies	Commander Letterman Army Institute of Research (LAIR) Bldg. 1110 ATTN: Dr. J. Ryan Neville Presidio of San Francisco, CA 94129

A WORKING EQUATION FOR OXYGEN SENSING DISK ELECTRODES

T.E. Tang, R.E. Barr, V.G. Murphy and A.W. Hahn

John M. Dalton Research Center, University of Missouri-Columbia, Mo. 65201 USA

For more than 35 years, noble metal electrodes have been employed to measure oxygen partial pressure in biological fluids and other media. Anyone who has attempted to use these types of electrodes is well aware of the instability and drift attendant to them. While a great deal of material can be found in the electrochemical and analytical chemical literature regarding the catalytic interaction of noble metal surfaces with oxygen, this literature usually pertains to large surfaces, non isotonic media and/or rotating ring-disc systems. Comparatively little has been published concerning the interaction between oxygen and noble metal surfaces for electrode sizes employed in biological applications.

Work in our laboratories has been aimed at developing oxygen microelectrodes with long term stability. There are two characteristics that must be addressed in such an effort: poisoning and aging (1). For the purposes of this paper, poisoning will refer to those interactions with the electrode surface that cause rapid changes in response characteristics. Aging will refer to the comparatively slow change in response characteristics, which seem to occur even in the "cleanest" media. In any systematic study, an attempt must be made to separately address these two phenomena. It is clear that if one does not understand the aging phenomenon, little can be done to achieve long term stability. The progress we have made in this regard is the subject of this paper.

According to Forbes and Lynn (2), there are two principal pathways involved in the catalytic reduction of oxygen at a noble metal surface. These are shown in Fig. 1. In this and following figures and text, superscripts b, s and a will refer to

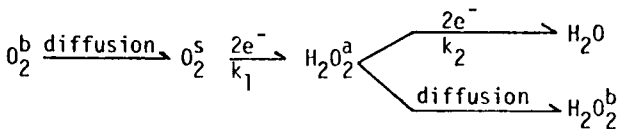


Fig. 1. The oxygen reduction process at a cathodically polarized electrode.

bulk, surface and adsorbed respectively. k_1 and k_2 are the reaction rate coefficients for the respective reduction processes. The current generated by this process is the sum of the number of electrons used in the reduction of O_2 to H_2O_2 and the reduction of H_2O_2 to H_2O, as given by the equation,

$$i = 2 F A k_1 C^s_{O_2} + 2 F A k_2 C^s_{H_2O_2} \quad (1)$$

where i = electrode current, F = Faraday's constant, A = electrode surface area, $C^s_{O_2}$ and $C^s_{H_2O_2}$ are the surface concentrations of O_2 and H_2O_2 respectively.

To generate a working model from this equation one must consider the reaction balance in the steady state for these two molecular species. The O_2 balance is between the rate of diffusion from the bulk media to the electrode surface and the rate of reduction to H_2O_2:

$$O_2 \text{ Balance:} \quad 4D_{O_2} R (C^b_{O_2} - C^s_{O_2}) = A k_1 C^s_{O_2} \quad (2)$$

The H_2O_2 balance is between the rate of production of H_2O_2 and its rate of reduction to H_2O plus its rate of diffusion into the bulk media.

$$H_2O_2 \text{ Balance:} \quad A k_1 C^s_{O_2} = A k_2 C^s_{H_2O_2} + 4 D_{H_2O_2} R C^s_{H_2O_2} \quad (3)$$

D_{O_2} and $D_{H_2O_2}$ are the diffusivities of O_2 and H_2O_2 respectively. Solving for the surface concentrations of O_2 and H_2O_2, $C^s_{O_2}$ and $C^s_{H_2O_2}$, and substituting into the current equation yields the current expressed by the following equation:

$$i = 8 F D_{O_2} R \left[\frac{C^b_{O_2}}{1 + \frac{4 R D_{O_2}}{A k_1}} + \frac{C^b_{O_2} - C^s_{O_2}}{1 + \frac{4 R D_{H_2O_2}}{A k_2}} \right] \quad (4)$$

For O_2 diffusion limited conditions, $4 R D_{O_2}/A k_1 \ll 1$ by definition

and $C^{s}_{O_2} = 0$, thus simplifying the current description to:

$$i = 8\,F\,D_{O_2}\,R\,C^{b}_{O_2}\left[1 + \frac{1}{4\,R\,D_{H_2O_2}/A\,k_2}\right] \qquad (5)$$

This is the working equation to which the remainder of this paper is directed. Note that i is proportional to the bulk concentration of oxygen which is the basis for this method, and that the factor $4\,R\,D_{H_2O_2}/Ak_2$ is a ratio corresponding to the H_2O_2 diffusion pathway divided by the H_2O_2 reduction pathway.

There are three aspects of equation (5) of particular interest. First, if the quantity $4RD_{H_2O_2}/Ak_2 \ll 1$, that is, if the dominant pathway for H_2O_2 is reduction to H_2O, the bracketed factor

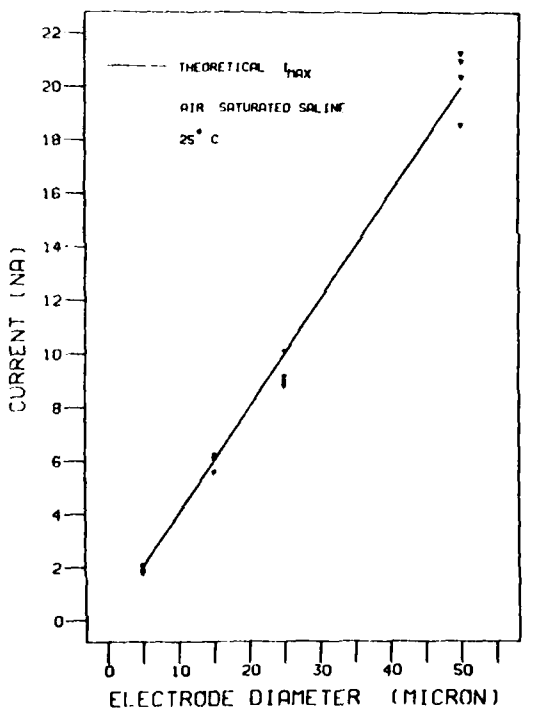


Fig. 2. Theoretical plot of Imax vs. electrode diameter compared to experimental data.

becomes 2 and i becomes

$$i = Imax = 16\ F\ D_{O_2}\ R\ C^{b}_{O_2} \qquad (6)$$

For bare disc platinum electrodes in air saturated saline at 25°C, values for Imax vs electrode diameter are shown in Fig. 2. Any current above the value shown for a given electrode diameter must be due to some reaction other than O_2 reduction. Most of the data to follow will relate to 15μm diameter electrodes which have an Imax = 6 na.

The second point of interest in equation (5) is that when $4RD_{H_2O_2}/Ak_2 >> 1$, that is, the dominant pathway for H_2O_2 is diffusion into the bulk media, the bracketed factor reduces to 1, and i becomes ½ Imax. The third aspect of interest is that in a constant environment, the only possible variable with time in equation (5) is k_2.

Under conditions of air saturated sterile saline at constant temperature of 25°C and for a prescribed set of electrode pretreatment conditions (3), a typical current vs. time response is shown in Fig. 3. There are 4 segments to this curve: (1) An initial unstable period, (2) a plateau region at Imax, (3) a region of current decay and (4) a second plateau at about ½ Imax. Since

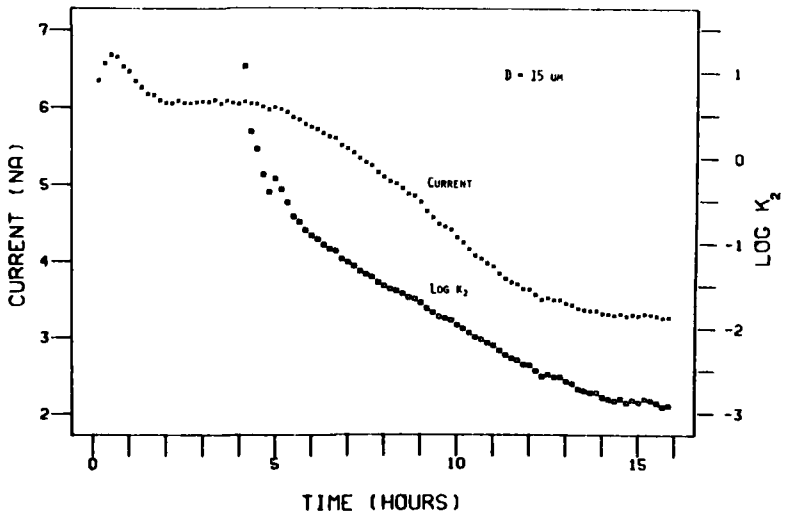


Fig. 3. Typical CURRENT response for a pretreated 15μm diameter electrode and a plot of LOG k_2 associated with the decay region of the CURRENT curve.

the two plateaus were at these levels, it was considered a good possibility that there was a degradation in the H_2O_2 reduction step. If this is true, one can obtain knowledge of k_2 from the decay region.

An exponential decay with time was assumed for k_2, as shown in equation 7:

$$k_2 = C_1 \text{ EXP } (- C_2 t) \qquad (7)$$

C_1 and C_2 are constants of the system and t is time. When k_2 was evaluated in the decay region and plotted on a semi-Log scale (see Fig. 3), a linear relationship was obtained, verifying the hypothesis. The constants C_1 and C_2 can be evaluated from the Log k_2 vs t plot. C_1 is the intercept with the ordinate and C_2 is the slope of the line. From a number of plots of Log k_2 vs t, using the responses of 15 μm diameter electrodes, C_1 and C_2 values were obtained. These values were C_1 = 15 cm/sec and C_2 = 0.75 hr^{-1} (Fig. 4). Using these values of C_1 and C_2, theoretical curves were generated and compared to experimental data for 5 μm and 50 μm diameter electrodes. These comparisons are shown in Figs. 5A and B respectively. While the theoretical fit for the 50 μm diameter electrode data is reasonably good, the data of Fig. 5A are quite scattered, probably due to variations in electrode diameter, and

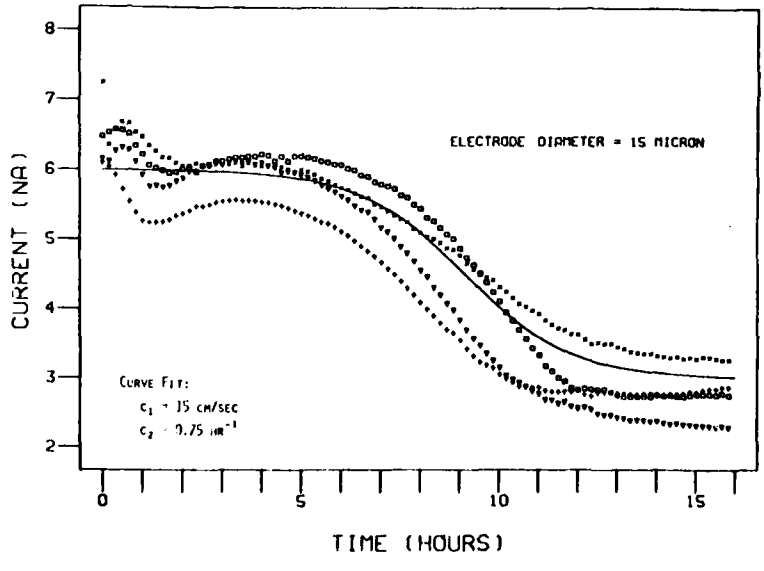


Fig. 4. Comparison of experimental responses to theoretical curve fit obtained with averaged C_1 and C_2 values.

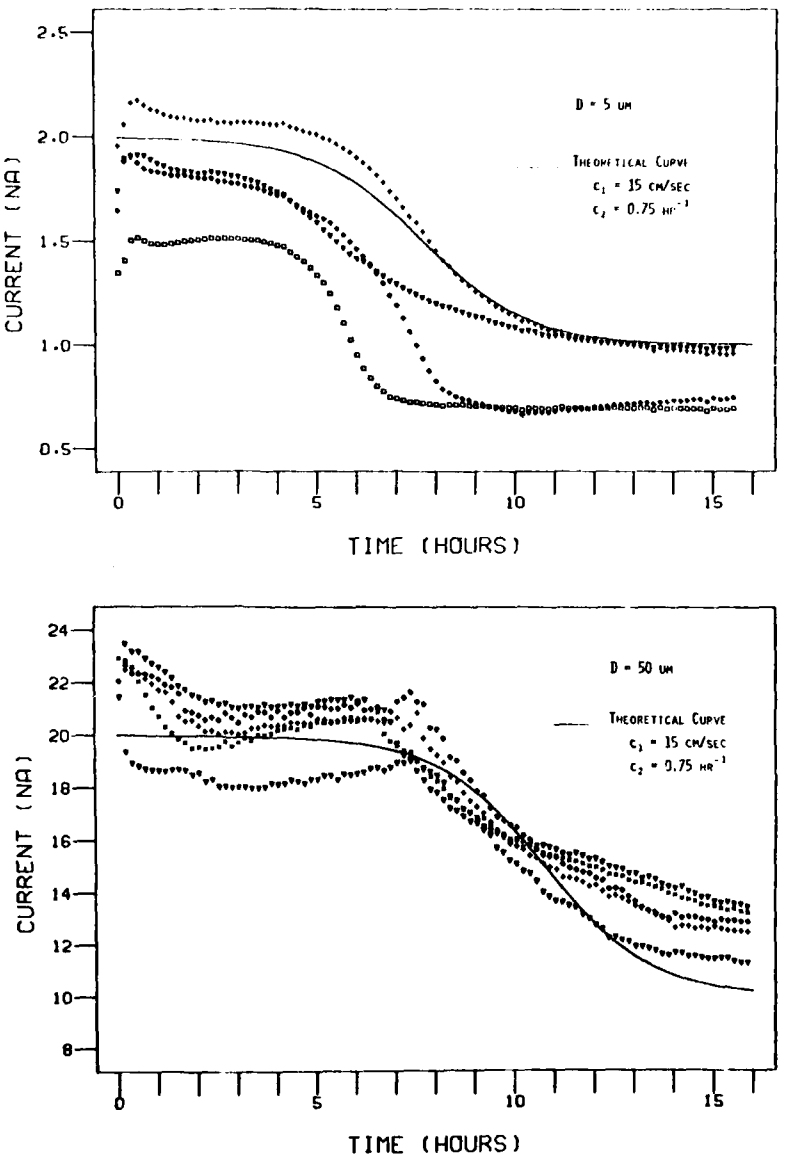


Fig. 5. Comparison of calculated response curves to experimental curves for A. 5μm and B. 50μm diameter electrodes.

hence a good model fit was not obtainable.

It is concluded that the model presented is a good working model from which further understanding of the operating of oxygen reduction at noble metal microelectrode surfaces should be forthcoming. The most salient feature of the model is that it assesses the importance of the H_2O_2 reduction step and the importance of the competing H_2O_2 diffusion into the bulk media.

REFERENCES

1. Silver, I.A. (1967) Polarography and Its Biological Applications. Phys. Med. Biol. 12:285-299.

2. Forbes, M. and Lynn, S. (1975) Oxygen Reduction at an Anodically Activated Platinum Rotating Disk Electrode. AICHE Jour. 21:763-769.

3. Barr, R.E., Tang, R.E. and Hahn, A.W. (1977) Variations on the Response Characteristics of Oxygen Electrodes. *In* 'Oxygen Transport to Tissue III' ed. by I.A. Silver, Plenum Publ. Corp., New York.

VARIATIONS ON THE RESPONSE CHARACTERISTICS OF OXYGEN ELECTRODES

R. E. Barr, T. E. Tang and A. W. Hahn

John M. Dalton Research Center, University of Missouri
Research Park, Columbia, Missouri. 65201

A multiple pathway process for the reduction of oxygen at a platinum electrode was described by Forbes and Lynn (1). Using their descriptive process, Tang, et al. (2) developed a mathematical model, eq. 1, which appeared to satisfactorily explain the electrode current vs. time response obtained.

$$i = 8 F D_{O_2} R C^{b}_{O_2} \left[1 + \frac{1}{1 + \frac{4 R D_{H_2O_2}}{A k_2}} \right] \qquad (1)$$

However, only after a prescribed electrode pretreatment protocol had been followed, could the equation be applied to the electrode response for an extended period of many hours. It is the purpose of this paper to describe this protocol and responses one obtains when varying pretreatment protocol and experimental conditions.

Electrode Pretreatment Protocol. The principle conditions of pretreatment that yielded electrode current responses described in the previous paper (2) were as follows. Disc shaped electrodes were first polished and then were cathodically polarized at 700 mv with respect to a SCE in sterile saline at 25°C for periods exceeding 15 hours. They were then ultrasonically cleaned in distilled H_2O and anodized at two volts with respect to a SCE for five minutes in 1.0 N H_2SO_4. Following this they were ultrasonically cleaned in distilled H_2O, alcohol and again in distilled H_2O, five minutes each. The test cathodic runs were then conducted.

Table 1 is a list of factors that are known to influence electrode current characteristics. Some of these factors are obvious

TABLE 1. PARAMETERS CONTROLLING ELECTRODE RESPONSE CHARACTERISTICS.

Cathodization Voltage	Anodization Solution
Electrode Diameter	Saline
Preconditioning	H_2SO_4
Anodization	Other
Cathodization	Membrane Coating
Electrode History	Operating Time(s)
Fresh Surface	Electrode Shape
Used Surface	Periodic Anodization

and well known; a few are not well recognized. Some of these factors will be addressed in this paper.

Cathodization Voltage. The quantity k_2 is a positive exponential function of the applied cathodic voltage (3). For a larger cathodic potential difference between the reference electrode (Standard Calomel Half Cell (SCE)) and the recording electrode, the effect of the k_2 dependency on voltage is seen as a delay in current decay from Imax (2) and a slower current decay to the ½ Imax plateau. An example is shown in Figure 1. A response curve for an applied potential of 700 mv is compared to the current responses for three 15μm diameter electrodes polarized at 850 mv.

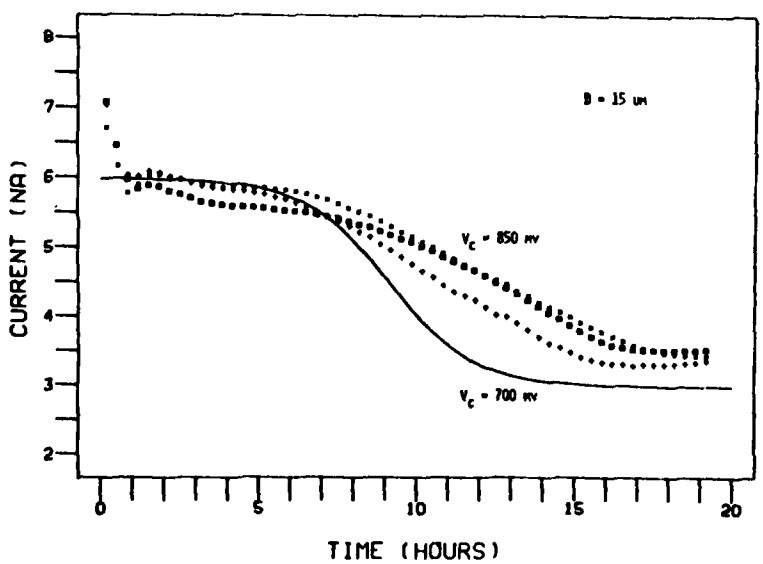


Fig. 1. Comparison between electrode responses for V_c = 700 mv and V_c = 850 mv. The 700 mv curve is an averaged composite of 4 electrode responses.

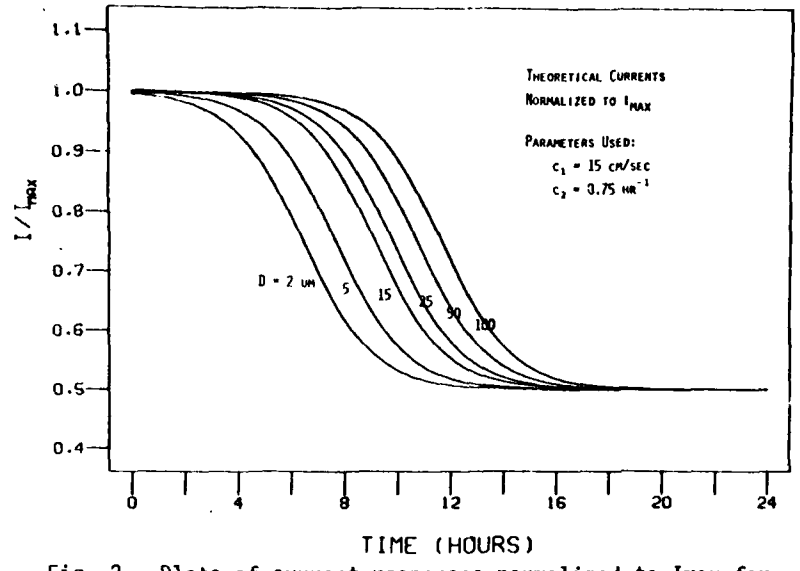


Fig. 2. Plots of current responses normalized to Imax for electrodes with diameters of 2,5,15,25,50 and 100μm.

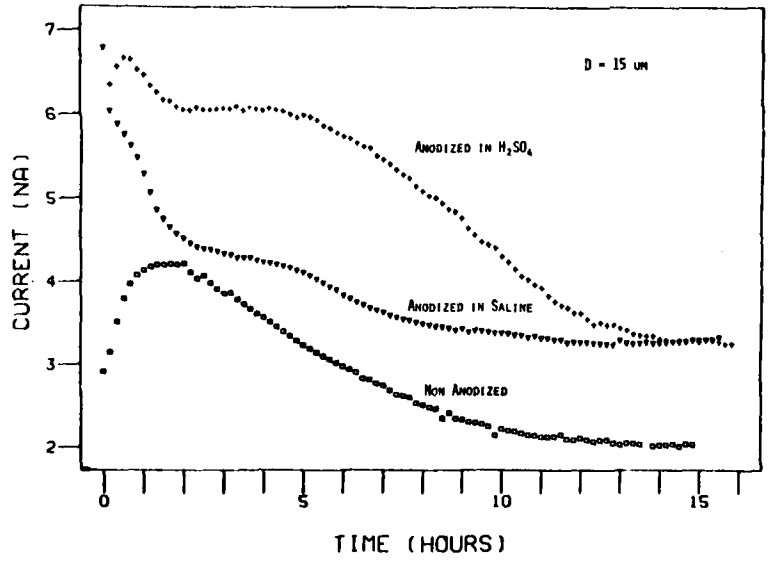


Fig. 3. Current responses for three electrodes pretreated in three different ways as described in the text.

Electrode Diameter. On an absolute scale, a larger electrode diameter current response shows a longer Imax plateau and a smaller slope in the decay region (2). If one normalizes such data to Imax, a family of curves is obtained as shown in Figure 2. In this type of presentation, the longer Imax plateau is obvious, but the smaller decay slope is hidden by the normalization process.

Preconditioning. The treatment given to an electrode surface prior to a test cathodization has a marked effect on the response obtained. For example, in Figure 3, three electrodes preconditioned in three different ways yielded the three totally different responses shown. Anodization in media other than those indicated and at potentials different from the 2 volts used would likely yield somewhat different curves from these.

Electrode History. This is also an important parameter. A common response of a fresh polished disc electrode, with (Fig. 4) or without (Non Anodized curve of Fig. 3) anodic pretreatment procedures is shown by the indicated curves. These are consistent and reproducible responses. The problem with these preparations is that often the current may take a very long time to become stable, if at all, and then it is almost always well below the Imax level. A used surface may give an entirely different response, as shown in Figure 5. These data were obtained using the same elec-

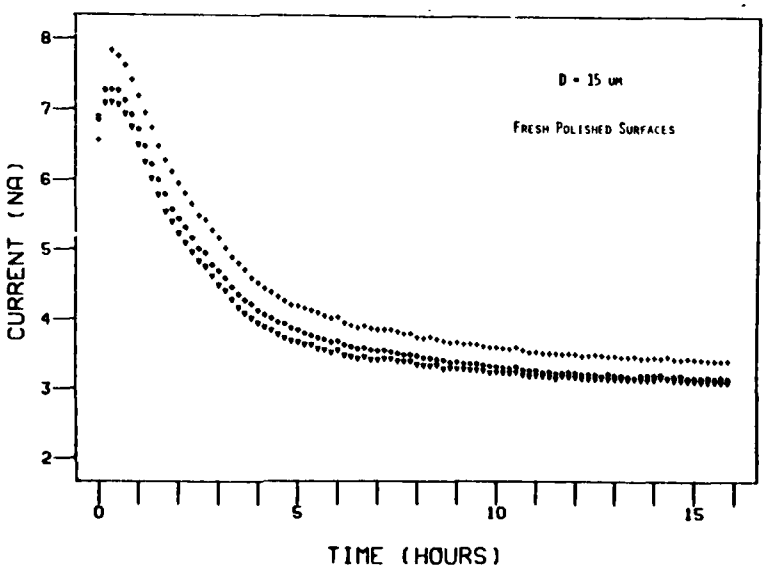


Fig. 4. Current responses of three freshly polished, anodized electrodes.

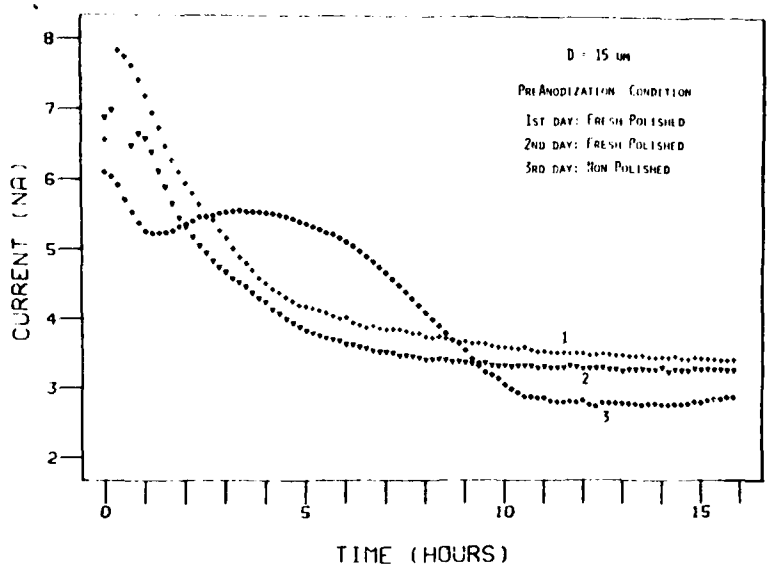


Fig. 5. Current responses for one electrode for three consecutive runs before which the electrode was 1) fresh polished, 2) fresh polished and 3) not fresh polished, respectively, and then anodized in H_2SO_4.

trode which was freshly polished before the first two runs and was not polished for the third run. Before each cathodic current response shown, the anodization and cleaning process described above was followed. It is clear that freshly polished surfaces and used surfaces yield totally different responses.

Anodization Solution. It is apparent from Fig. 3 that a significant difference in current response is obtained when different types of solutions are used for electrode anodization. Although we have only used 0.15 M NaCl (Saline) and 1.0 N H_2SO_4, it is our suspicion that the presence of chloride ions may be the most significant factor associated with the differences observed.

Membrane Coating. A membrane coating that has a smaller O_2 and H_2O_2 diffusivity will increase the length of time an electrode operates at its Imax plateau. The reduced O_2 diffusivity will decrease the Imax value, while the reduced H_2O_2 diffusivity reduces the competing H_2O_2 diffusion into the bulk media. Also the surface is protected against molecules that may slowly change surface conditions. An example is shown in Figure 6. All three of these electrodes operated at Imax for almost two days. That the

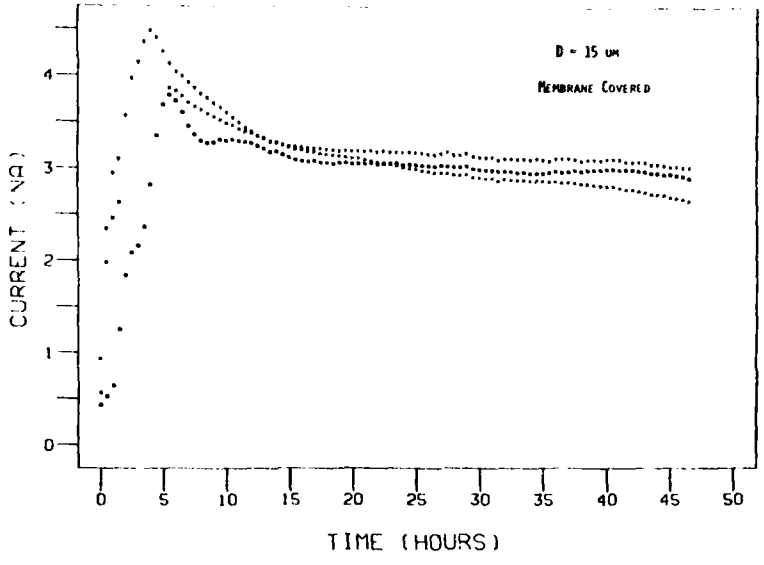


Fig. 6. Current responses for three pretreated electrodes covered by a dialysis membrane.

current levels shown were indeed Imax values for the membrane covered electrodes was demonstrated by the fact that, after removing the membranes while the electrodes were polarized, the resulting bare tipped electrode currents were at theoretical Imax levels.

To summarize: The works presented in this and the previous paper (2) have produced an operational model for describing the oxygen reduction process in common medical grade sterile saline media at a platinum disc shaped electrode with a fairly specific surface conditioning. This paper has illustrated some of the variations possible in electrode current responses. An important feature of these data is that they are highly consistent and repeatable and can be discussed in terms of the model.

However, the question still remains: What is the aging process? Is it due to a decrease of active sites for the electrochemical reduction process, brought about by the reduction process itself, or is it a process caused by other species in the media? To answer these questions, it may be necessary to employ some of the sophisticated techniques such as angle-resolved photoelectron spectroscopy (4) and extended x-ray absorption fine structure (5), available today for the study of atomic and molecular arrangements on solid surfaces.

REFERENCES

1. Forbes, M. and Lynn, S. (1975) Oxygen Reduction at an Anodically Activated Platinum Rotating Disk Electrode. AICHE Jour. 21:763-769.

2. Tang, T.E., Barr, R.E., Murphy, V.G. and Hahn, A.W. (1977) A Working Equation for Oxygen Sensing Disk Electrodes. In "Oxygen Transport to Tissue III. Ed. by I.A. Silver, Plenum Publ. Corp., New York.

3. Delahay, P. (1954) New Instrumental Methods in Electrochemistry. Interscience Publ., New York, p. 34.

4. Robinson, A.L. (1977) Surface Science (I): A Way to Tell Where the Atoms Are. Science 196:1306-1308.

5. Robinson, A.L. (1977) Surface Science (II): An X-Ray Probe for Adsorbed Molecules. Science 197:34-36.

END

DATE
FILMED

3-82

DTIC