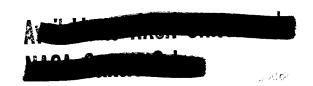
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### I. Introduction

Bicelectrochemical energy conversion (i.e., converting chemical free energy of biologically catalyzed reactions to electrical energy) is not a newly discovered phenomenon. As long ago as 1786 Galvani observed that a frog muscle twitched when touched with copper-zinc couples in this early insight into the electrical characteristics of biological systems.

Over 50 years ago (1912) Potter demonstrated that a "bacterial culture during the process of energy conversion is in a sense, therefore, a primary electrical half cell and as such should conceivably be able to perform work."

Cohen, in 1930, obtained 1.25 milliamps from six yeast cells biochemically converting glucose in solution. Through this process he later built a battery able to furnish 2 milliamps at about 35 volts.

During the past 10 years interest in biochemical energy has increased fantastically, reaching exponential proportions within the last five. Particular attention in the past two years has been directed to applying the results of research and development to this type of energy

conversion. This paper will consider these applications in a state-of-the-art review and will present a synopsis of suggested applications ranging from the use of bioelectric currents to identify toxic materials and power human implanted cardiac pace makers to the generation of electric power in remote areas of the world.

Research in biochemical energy conversion -- limited to the laboratory -- is in its infancy. Available data are inadequate to form a sound basis for defining specific engineering and economic criteria that might point the way toward selecting particular technology for development and later applications. Since criteria for bioelectrochemical systems cannot now be defined, it is strongly suggested that present and extrapolated characteristics of such systems should not be compared with those of other energy converters in use or being developed. Such a practice could be discouraged and might result in failure to realize the full potential of bioelectrochemical conversion.

### II. Fundamental Principles

The fundamental principles of bioelectrochemistry should be considered in order to fully realize the potentialities of this field. Some insight into the electrical potentials associated with bioelectrical-chemical systems may be derived from the Second Law of Thermodynamics. This law determines the relation between free energy changes and the standard oxidation potential of reactions occurring in biological systems.

### A. Change in Free Energy and Electrical Potentials

As is well known, the free energy F, of the reactants and products in the biochemical system

aA+bB \_\_\_\_\_ cC+dD+ --- may be expressed in terms of the chemical potentials as

$$F_{reat} = a/A + b/B + ----- (1)$$

$$F_{prod} = c \mu C + d \mu D + ----- (2)$$

At constant temperature and pressure, the free energy change of the reaction is given by

$$\Delta F_{TP} = c / C + d / D + ---$$

$$- a / A - b / B - ---$$
(3)

The chemical potential His given in the standard state Ho

$$W = M_0 + RT \ln \bar{a} \tag{4}$$

where  $\overline{a}$  is the activity of the species in question under defined conditions. Substitution of (4) and (3), and collecting terms,

$$\Delta F_{TP} = \Delta F_{T}^{c} + RT \ln \frac{c}{a} \cdot \frac{d}{a}$$

$$\frac{c}{a} \cdot \frac{d}{a}$$

When the reactants are incorporated in an electrochemical conversion system.

$$- \triangle F = nFE$$
 (6)

where F is the Faraday constant, E the electrode potential and n is the number of electrons associated with the reaction. Equation (6) is of great importance since it permits the calculation of standard electrode potentials  $E_O$  (standard conditions and unit activity) from free energy data. Substituting -nFE for  $\Delta$ F and nFE $_O$  for  $\Delta$ F° and substituting concentration (C) for activities (although an approximation).

Equation 5 becomes

$$E = E_{O} - \frac{RT}{nF} - \ln \frac{C_{C} \cdot C_{C}}{C_{A}^{a} \cdot C_{B}^{b}}$$

$$(7)$$

from the standard oxidation - reduction reaction

$$E = E_{O} - \frac{RT}{nF} \ln \frac{XOX}{Xred}$$
 (9)

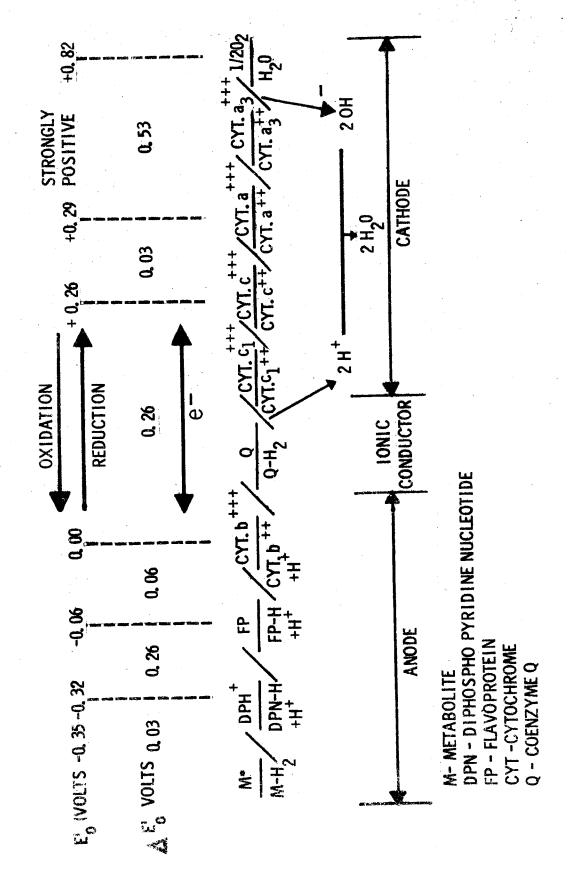
### B. Generation of Electrical Potentials in Biological Oxidation--Reduction Reactions

Energy transfer reactions in biological systems are of the oxidation-reduction type. Equation (9) permits the calculation of the electrical potential of these systems for various degrees of oxidation.

In general there are two main schemes for the biological oxidation of organic materials. The first (fig. 1) is based on an initial hydrogen removal from the reduced (or fuel) molecule, followed by a successive series of hydrogen atom and electron transfers along a chain of redox couples resulting in electron transfer to oxygen. The entire process is catalyzed by biological catalysts (enzymes).

The second involves the direct activation of molecular oxygen by the oxidase enzymes. Three types of oxidases are those which catalyze: (1) direct oxygen addition to a molecule, (2) recuction of one oxygen atom

## BOLOGICAL HECTRON TRANSPORT



(in  $O_2$ ) by electron transfer and direct addition of the other to a reacting molecule, and (3) reduction of oxygen to  $H_2O_2$  or  $H_2O_3$ .

In the work reported to date on application of the foregoing principles to bioelectrochemical cells the procedure has been to break the oxidation sequence so that the entire enzyme system is in one or the other of the electrode compartments. Systems such as those shown in figure 1 are divided into an oxygen electrode and an organic fuel-enzyme system separated by a suitable ionic conductor. Of particular significance is the step in the oxidation sequence at which electron transfer to an inert electrode can occur.

### 1. Bioanodes

electrochemical oxidation-reduction couples which are anodic to oxygen at the more normal biological pH of

7. The potentials in Table I indicate that with the appropriate enzyme catalysts, substances found in natural sources such as acetaldehyde, xanthine, glucose, and cysteine may be feasible as fuel electrodes with an

TABLE I

ELECTRODE POTENTIALS OF BIOCHEMICAL REACTIONS

Electrode Couple	Enzyme	E*m7		
Acetate/Acetaldehyde	Xanthine Oxidase	-0.58		
Latic Acid/Xanthine	Xanthine Oxidase	-0.39		
Gluconolactone/Glucose	Glucose oxidase	-0.36		
Cystine/Cysteine	None	-0.33		
Acetaldehyde/Ethanol	Alcohol dehydrogenase	-0.20		
Pyruvate/Lactate	Lactic dehydrogenase	-0.18		
Oxaloacetate/Malate	Malic dehydrogenase	-0.16		
Fumarate/Succinate	Succinic dehydrogenase	+0.02		
Dehydroascorbate Ascorbate	Ascorbic oxidase	+0.06		
Ferricytochrome c/Ferrocytochrome c				
Oxidized cyt. oxidase/Cytochrome oxidase				
$O_2 + 4H^+ + 4e = 2H_2O$		+0.82		

 $<sup>^*\!</sup>E_m 7$  is the potential at pH 7 in the presence of equal concentrations of oxidized and reduced forms of reactants.

oxygen (air) cathode. The energy density of these materials is on the order of 5 pounds per kilowatt-hour. Several enzymes catalyzed and whole organism-catalyzed redox couples have been studied under laboratory conditions. The results are discussed below:

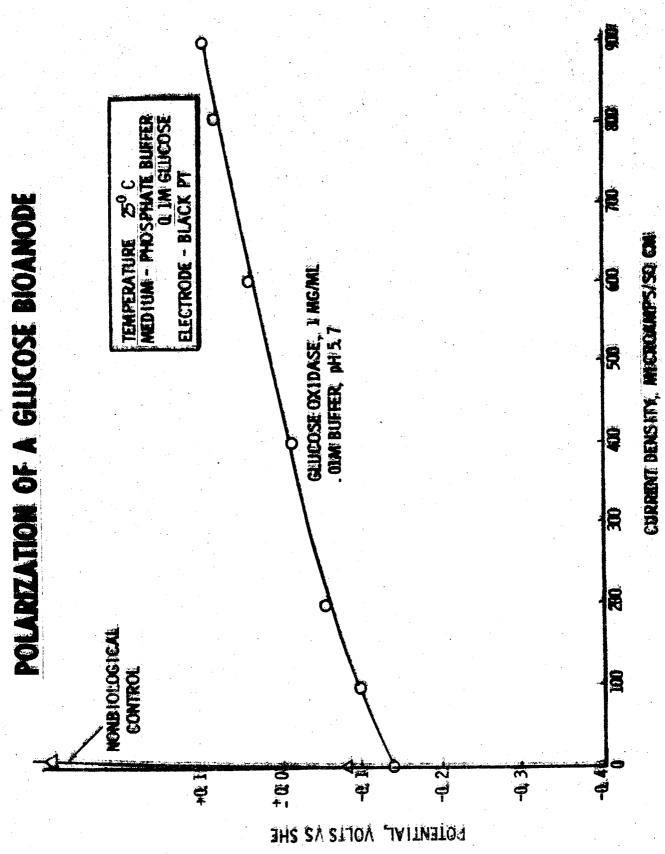
### (a) Glucose - Glucose Oxidase System

The electrode mechanism has not been critically described for this system. Several mechanisms are suggested. In a direct mechanism glucose and the enzyme glucose oxidase react to form a complex intermediate. The intermediate is oxidized at the anode to gluconolactone and the enzyme is liberated. (Equations 10 and 11).

$$C_6H_{12}O_6$$
 Glucose Oxidase (Glucose . Enzyme) (10)

(Glucose-Enzyme) Anode 
$$C_6H_{10}O_6 + 2H^+ + 2e^-$$
 (11)

Anodic polarization data for the glucoseglucose oxidase bio-anodes is shown as figure 2. In these
studies, the enzyme glucose oxidase is incorporated in the
pt-black electrode surface and glucose (reduced form is
added to the cell). As shown in figure 2, the electrochemical



oxidation of glucose on platinum is markedly enhanced by the incorporation of the glucose oxidase as a catalyst.

### (b) Amino Acid - D - Amino Acid Oxidase System

The normal aerobic reaction products of the amino acid D - amino acid oxidase (DAO) system in-clude the pyruvic acid derivative of the amino acid, hydrogen peroxide and ammonia.

Experiments have been conducted on the bioelectrochemical behavior of the three amino acids
Tryptophane, tyrosine and phenylalanine and their respective
D-amino acid oxidase reaction products indole-3-pyruvic acid,
para-hydroxy phenyl pyruvic acid, and phenyl pyruvic acid.
Results to date on platinum electrodes show that observed
currents are derived from the electrochemical oxidation of
the aromatic pyruvic reaction products. Ammonia not peroxide
contributed appreciably to the electrical currents. Currents
of the order of 350  $\mu$  A/cm<sup>2</sup> at 200 mv have been derived
with indole-3-pyruvic acid.

Currents on the order of 45  $\mu$  A/cm<sup>2</sup> at 200 mv have been derived from cells in which indole pyruvic acid is generated enzymatically from Tryptophane.

These studies indicate that: (1) the current limitation is enzymatic, (2) the reactive species is the enol form of the keto acid derivative of the naturally occurring amino acids (absorption spectra data), and (3) further studies are needed to determine optimal condition for enzyme and electrochemical activity in order that the potential of utilitizing complex natural occurring materials as electrode reactants may be exploited.

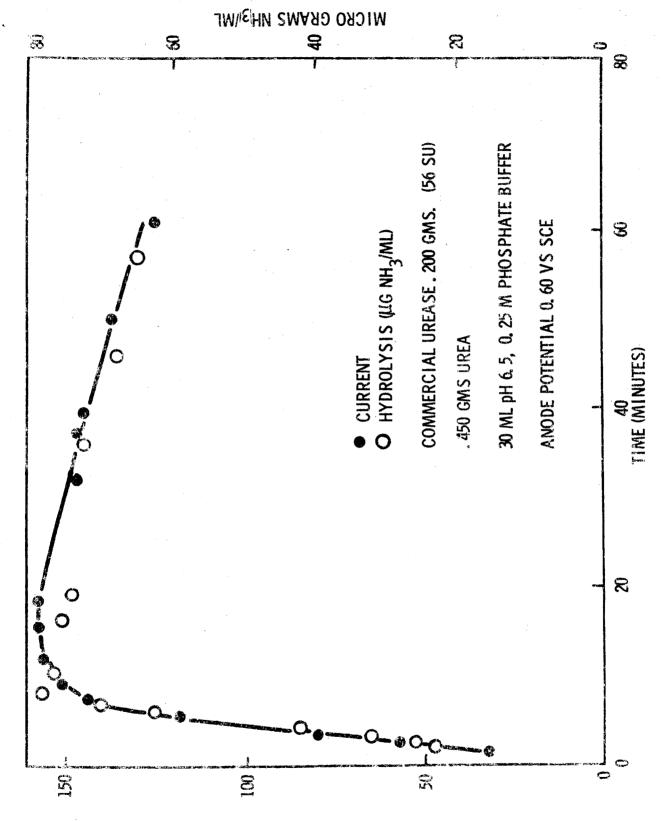
### (c) The Urea-Urease System

Theoretically it would be expected that in this cell the enzyme urease would generate ammonia from urea and the ammonia electrochemically oxidized:

$$CO (NH_2)_2 + H_2O \underline{Urease}_{>} 2 NH_3 + CO_2$$
 (12)

$$2 \text{ NH}_3 + 6 \text{ OH}^- \longrightarrow \text{N}_2 + 6 \text{ H}_2 \text{O} + 6\overline{\text{e}}$$
 (13)

In studies to date the Urea-Urease System has presented a rather consistant dilemma. In cells wich bright platinum electrodes in 0.25 m ammonium nitrate in tris buffer (tris-hydroxymethyl amino methand) at pH of 6.5 - 9.0 ammonia was reportedly not oxidized. In the same cell, nevertheless, the action of urease resulted in the augmentation of the cell current and the enzymatic hydrolysis of urea parellels the cell current, (fig. 3). Other studies have shown that



CHEBERT MICEO AMPS :CM 2

at pH 6 in a K Cl - citrate buffer using platinum impregnated carbon electrodes incorporating the urease enzyme, short circuit currents of 1-3 ma/cm<sup>2</sup> were derived on addition of urea. Further studies on this system are being conducted.

### 2. <u>Sulfate Biocathode</u>

Potentials associated with biologically catalyzed reductions have also been investigated. The reduction of sulfate to hydrogen sulfide by the organism <a href="Desulfovibrio desulfuricans">Desulfovibrio desulfuricans</a>, attached to porous iron electrodes, has been extensively studied. However, the mechanism for this electrode has not been completely established. It is thought that the reactions for the bioelectrochemical reduction of sulfate may be as follows:

$$2H_2O + 2e^- Cathode H_2 + 2OH^-$$
 (14)

$$SO4 + 4H_2 D. Desulfuricans S + 4H_2O$$
 (15)

$$SO_4^+ + 4H_2O + 8e^- D. Desulfuricans S^+ + 80H^- (16)$$

### C. <u>Biological Generation of Fuels for Electrical</u> Energy

Biological energy sources may also indirectly generate electricity. Biochemical agents may generate chemical species specifically tailored to a biological energy

conversion system optimized to the requirements and consistent with available fuel. Examples include the generation of hydrogen, ammonia, or methanol from higher molecular weight materials (such as sugars, proteins, fats, starches, urea) by means of whole living cells or cell free extracts or crystalized enzymes.

Samples of biochemical systems for the generation of primary fuels from complex materials are presented as Table II. The literature has been reviewed and over 200 references are included in the bibliography under "Generation of Bioelectrochemical Fuels."

Applications of bioelectrochemical conversion are discussed in the following paragraphs.

					-	Т	- 	
	LB/KWH		8.	1.2-3		1.8		1.0
E S	PRIMARY FUEL		NH <sub>3</sub>	NH <sub>3</sub>		Н2		CH A
BIOCHEMICAL GENERATION OF FUELS	CATALYST		UREASE (CRYSTALLINE ENZYME)	AMINO ACID OXIDASE (ENZYME)		FORMIC DEHYDROGENASE (ENZYME)		METHANOBACTERIUM PROPRIONICUM (LIVING BACTERIA)
BIOCHEMICAL	NATURAL SOURCE		URINE	PROTEIN DIGESTS				FATS, OILS
	NATURAL FUEL	AMMONIA	UREA	AMINO	HYDROGEN GENERATORS	FORMIC	METHANE GENERATORS	PROPRIONIC ACID

### III. Applications of Bioelectrochemical Conversion

### A. General

Research and development looking toward the applications of bioelectrochemical conversion is in its early phases. However, at present four general areas for potential future applications appear to be emerging.

### These include:

- Power sources for supplying relatively
   small amounts of electrical energy in
   specialized applications and locations.
- Detectors for specific contaminants in low concentrations.
- · Sensors for generation of control signals.
- · Catalysts for the generation of electrochemical reactants from complex naturally occurring materials and from waste materials.

Available information indicates that bioelectrochemical power generation will most likely be limited to specialized applications. Competition with major power generation methods is unlikely. Bioelectrochemical power generation will probably supply limited emergency power, serve remote and unattended power supplies, and supplement existing natural fuels (such as vegetation) when transportation costs for additional fuels are excessive.

### B. Sources of Energy or Power

As power sources bioelectrochemical converters may be arbitrarily classified in terms of power levels for suggested applications.

### 1. Requirement for 1-10 milliwatts

stimulators, and other electronic devices are needed to regulate physiological and biological functions.

For example, the present day peacemaker used in the regulation of the electrical profile of the human heart requires electrical energy at about 2.4 volts with current pulses 2 milliseconds in duration at a frequency of one to two/second. The average current and power are about 25 // amperes and 100 // watts, respectively. This energy is normally supplied by five primary cells, calculated to last for two to three years, which are made part of the implantable package. Surgery is required to replace the

dead batteries. The operating life of batteries for other implantable devices may be much less.

The development of implantable energy convertors which derive their energy on a continuous or periodic basis from physiological fluids may be quite advantageous. Consequently, the development of an implantable fuel cell with output of 200 µ watts at a voltage level in the vicinity of 1 volt may be a very worthwhile objective.

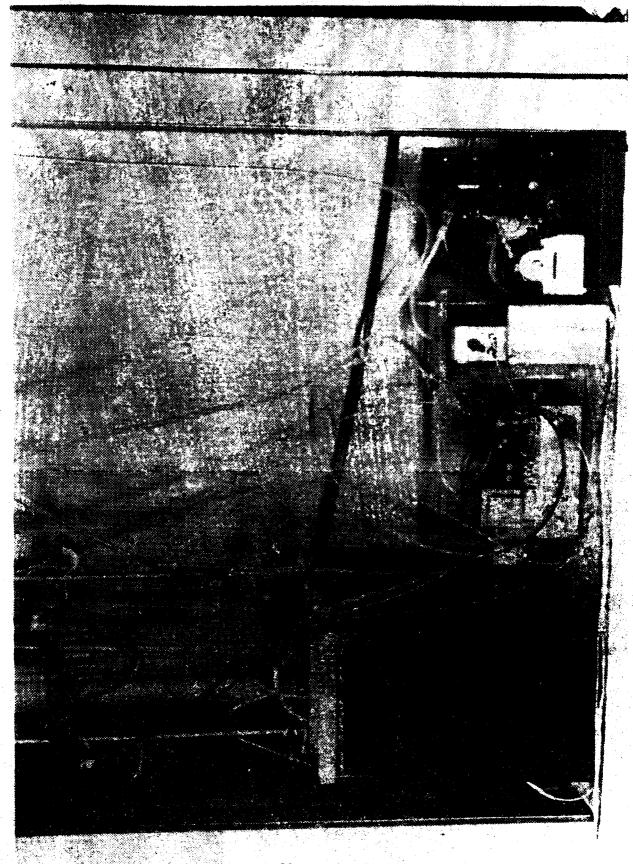
The literature available on the measurement of oxidation-reduction potentials of mammalian blood is extensive. Electrode potentials ranging from 0.5 to +0.3 are relatively common in mammalian body fluids. With a fuel cell of 0.5 volt at a current density of 10 // amperes per square centimeter, the power output would be 5 // watts per cm<sup>2</sup> of electrode surface area. Even at such low current densities the peacmaker power requirements could easily be satisfied with electrode surface areas of the order of 100 cm<sup>2</sup>.

In an experimental analog of the conditions found in the blood stream the open circuit voltage was

approximately 0.1 volt when platinum black electrodes were used. Current densities ranging from 10 to 50 µamps per square centimeter were found to be linear with the polarization voltages having a slope of nearly 2 1/2 millivolts per µampere per square centimeter.

### 2. Requirements for 2-5 watts

Attention has been given to the application of direct bioelectrochemical converters for long duration unattended power generation. Use of these converter systems to supply 2-5 watts of power in the ocean has been broadly explored. Sulfate, available in the ocean, has been studied extensively as the cathodic reactant of such a power source device. In this device bacteria (Desulfovibrio desulfuricans) are applied to the cathode where they consume hydrogen and reduce sulfate ion to sulfide ion. The anodic process is the oxidation of magnesium. Limiting current densities as high as 3 ma/cm<sup>2</sup> at -0.8V vs SCE have been reported under optimum conditions. Cell design has not been optimized but power densities in the range of 5-20 W/ft<sup>3</sup> and energy densities of approximately 30 KWH/ft<sup>3</sup> may be estimated for a cell to operate two years without attention. A laboratory fuel cell is shown in figure 4.



### 3. Requirements for 20 watts

The availability of used oxygen and the enzyme urease has suggested their use in an open-cycle power generator. Several investigations have been conducted of the electrochemical performance of a urease urea oxygen (air) battery. In the future this type of battery might be used to produce relatively low power (below 20 watts) for short periods of time (2 weeks, for example).

As anode materials platinum black electrodeposited platinum, platinum impregnated carbon, active impregnated carbon, activated carbon, Raney silver, and electrodeposited nickel have been investigated.

Crystalline enzyme catalysts would be incorporated in the electrodes; monel screens and porous carbon blocks used as current collectors. A 3 M KCl, citrate buffer at pH6, resulted in maximum limiting current densities. The air cathode is a porous platinized carbon electrode.

These fuel cells have achieved an open circuit voltage of about 0.8V and a short circuit density of 3.6 amp/ft<sup>2</sup> for short periods cf time.

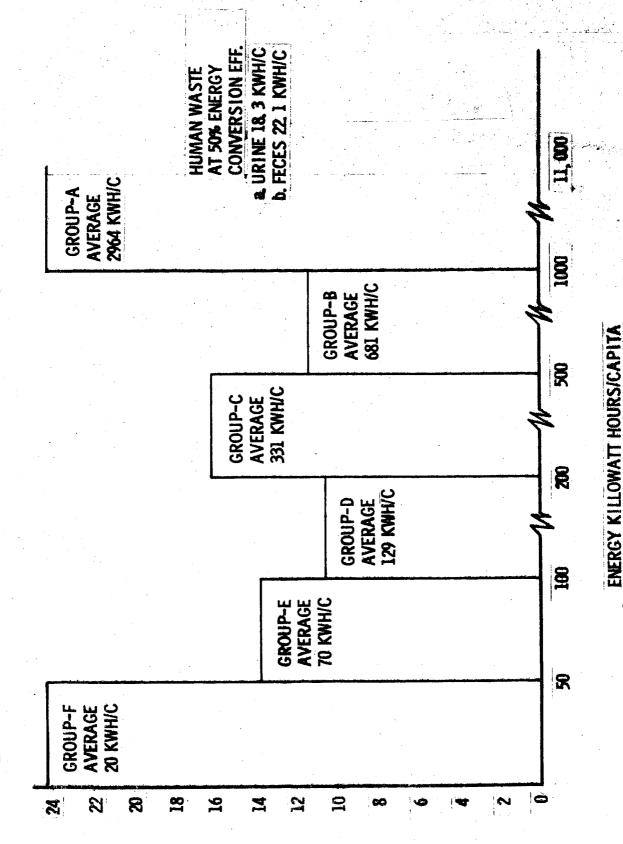
4. Power Requirements Greater than 20 watts Several factors need to be analyzed when considering bioelectrochemical convertors for power applications in excess of 20 watts. Worldwide energy demand and fuel logistics are two of these important considerations. A distribution of the world's yearly electrical energy consumption is shown as table III, distribution by country as figure 5, and distribution on the basis of world population as figure 6. These data show that about 24 percent of thw world's countries, with 37 percent of its population, have an average yearly electrical energy consumption of only 20 kilowatt hours per capita. It is evident from this fact that special remote locations throughout the world may well be provided with a minimal power source at minimal costs by using biological sources of energy.

Biological sources of energy could be used for the generation of electrical power directly by bio-electrochemical energy conversion or indirectly by biocatalytic generation of simple fuels from complex

TABLE III

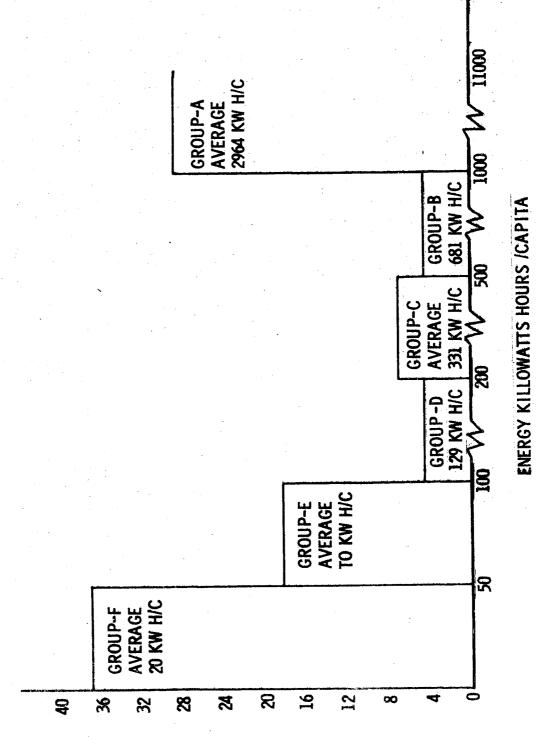
Group	Range KWH per capita	Average KWH per capita	Percent Countries	Percent Population
A	1,000-10,346	2,964	24.2	28.9
В	500-1,000	681	11.3	4.3
С	200-500	331	16.1	6.9
D	100-200	129	10.5	4.4
E	50-100	70	13.7	18.3
F	0-50	20	24.2	37.2

# YEARLY WORLD ENERGY-COUNTRY DISTRIBUTION



PERCENT OF COUNTRIES IN WORLD

### 



PERCENT OF POPULATION IN WORLD

naturally occurring materials. Of particular significance is the utilization of biological energy sources in their natural form.

(a) Urinary Waste as a Source of Energy

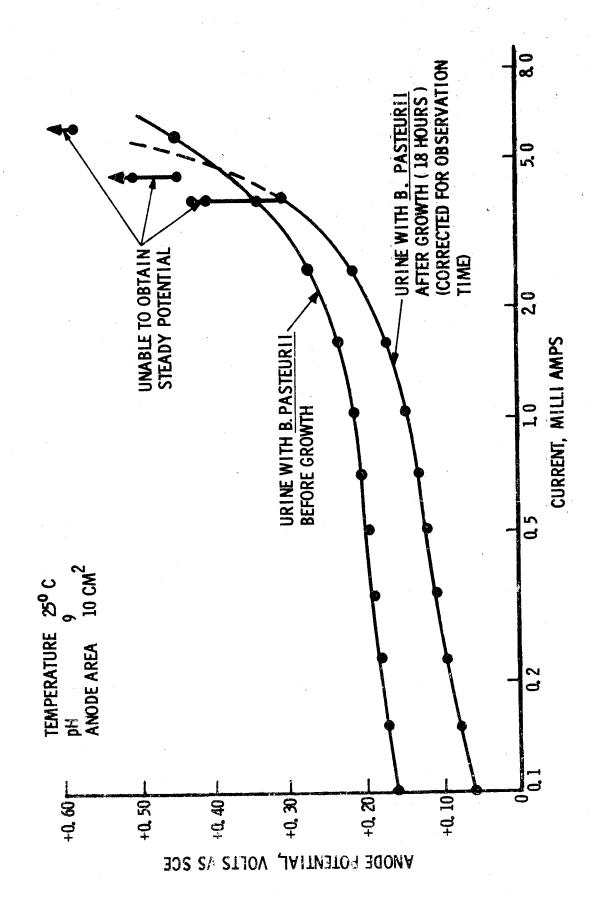
Theoretically, bioelectrochemical conversion of urea in human urinary wastes could supply on the order of 18 KWH per capita yearly based on a conversion efficiency of 50 percent.

Work has already been conducted on the electrochemical behavior of systems fueled by raw urine and catalyzed by growing bacteria. The bacteria <u>Bacillus</u> <u>pasteurii</u> has been studied in a system because of its established ureolytic activity. Preliminary data (fig. 7) indicate that a preliminary 18-hour incubation of raw uring with this bacteria provides increased current. At 170 mV, for example, the current carrying capacity of the electrode fueled by preincubated material was greater by a factor of 15 than the unincubated material.

(b) Vegetative Sources of Energy

Several other systems using natural materials as fuels have been studied. Laboratory studies have shown

### ANODIC POLARIZATION OF PLATINIUM IN URINE EFFECT OF B. PASTEURII GROWTH



that some power gains may be realized by the biological catalyzation of electrochemical systems using natural materials such as fresh mushrooms, toadstools, sucrose, and algae as fuels and oxygen (air) cathodes.

Chemical digestion of natural materials with sulfuric acid and potassium hydroxide results in the generation of electrochemically active organic and inorganic material and an over-all net reaction may be written:

$$1/2 \text{ CH}_2\text{O} + 1/2 \text{ O}_2 \longrightarrow 1/2 \text{ CO}_2 + 1/2 \text{ H}_2\text{O}$$
 (17) (Biological fuel)

Some laboratory results for the nonbiologically catalyzed systems are presented as figure 8.

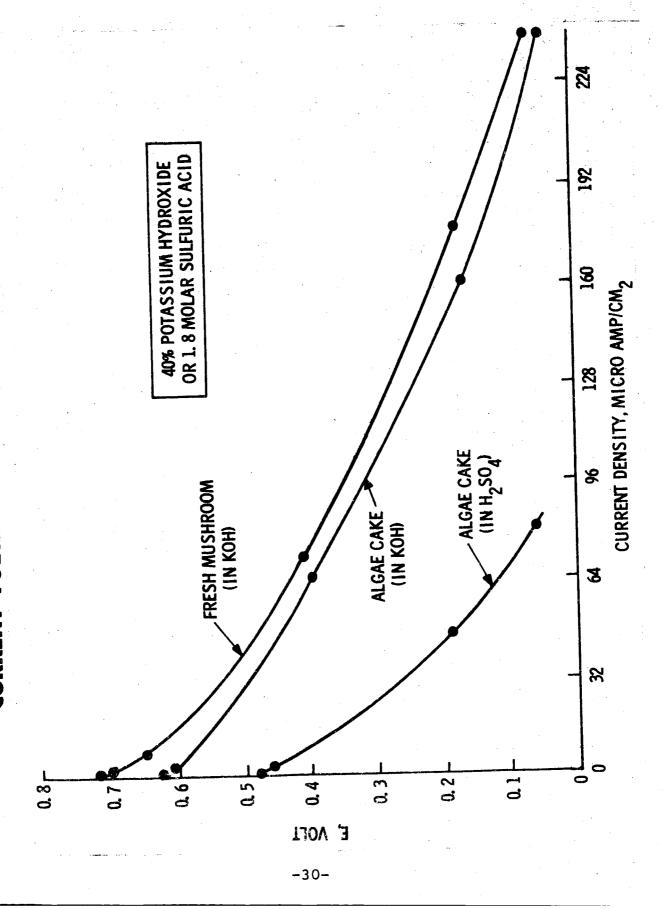
The biological catalyzed oxidation of natural fuels with sulfuric acid using the bacteria

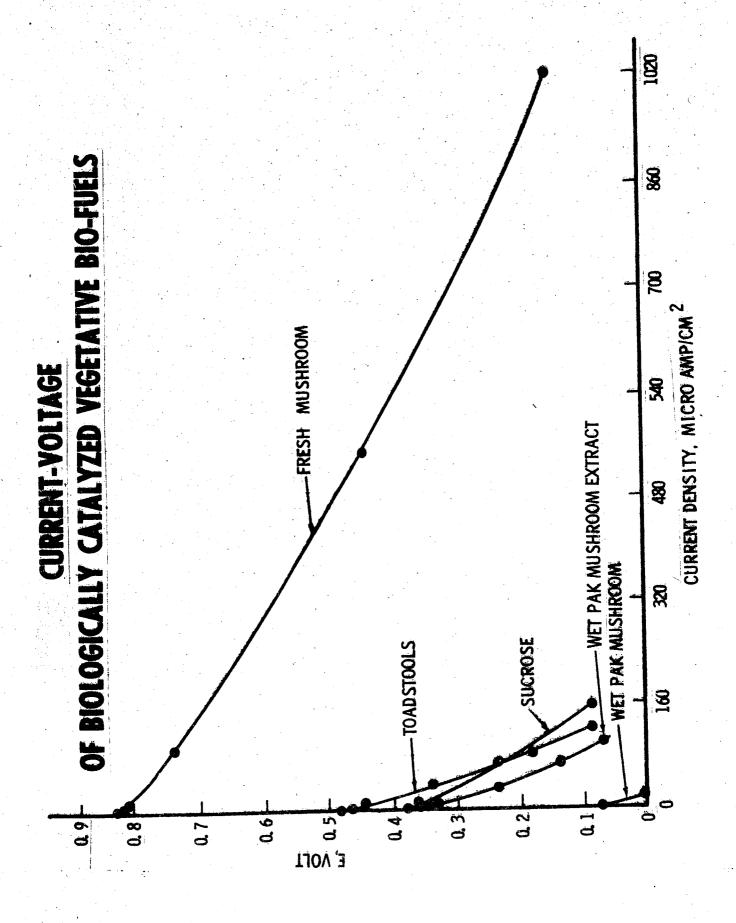
Desulflovibrio may be used as anodic reactants in a system with an oxygen (air) cathode. The over-all net reaction may be given as follows:

$$2 CH_2O + H_2SO_4 + 1/2 O_2 \longrightarrow CO_2 + 3H_2O+S$$
 (18)

Lakoratory results for several systems studied are presented as figure 9. A comparison of

## CURRENT-VOLTAGE OF VEGETATIVE BIO-FUELS





figures 8 and 9 indicates a greater than 4 fuel increase in current densities may be realized by biological catalysts in systems using complex natural fuels. These studies have been conducted under laboratory conditions in order to elucidate the parameters effecting bioelectrochemical activity. Much work remains to be done before the feasibility is established of utilizing such phenomena as practical applicants where complex natural materials are readily available.

### C. <u>Detection and Generation of Control Signals</u>

Another area of applications for bioelectrochemical conversion is in (1) the detection of simple and complex chemical species in extremely low concentrations, and (2) in the use of electric signals associated with biochemical systems for control. Illustrative work to date includes the toxic gas detector and myoelectric serve boost system.

The influence of various chemicals on the activity of naturally occurring microorganisms has been utilized in the detection of toxic agents.

The activity of the microorganism has been found to be proportional to the concentration of various agenct.

Specific biological agents have been preselected which will provide detection of trace materials at concentrations of parts per billion.

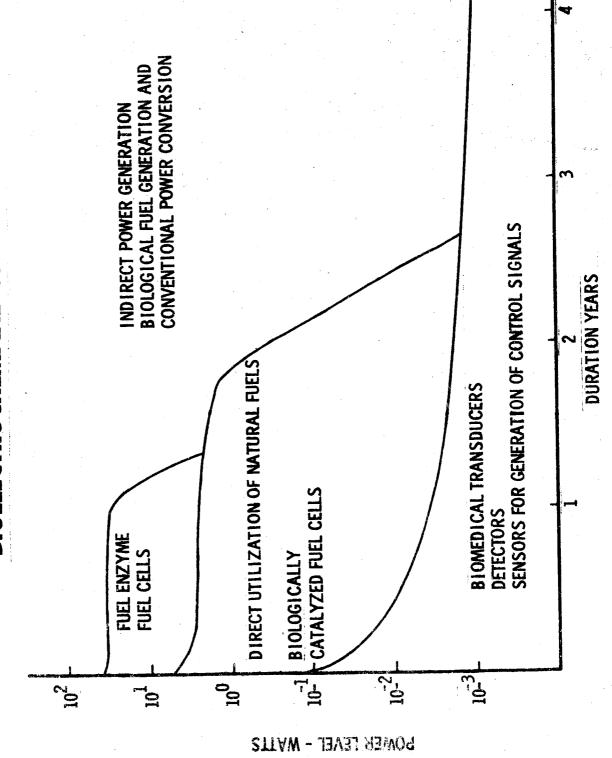
The feasibility has been demonstrated of using electrical signals associated with contraction of muscles to control a servo boost system which would enable an individual to remotely handle adverse tasks.

In this application silver foil electrodes are attached externally to a subject and a potential of 1-3 millivolts peak to peak at 3-1000 cycles/second are picked off and used to direct an external control logic.

Finally, in the broadest sense, bioelectrochemical energy conversion may show numerous and varied
applications. Such applications are arbitrarily organized
according to the level of associated power as figure 10.
The applications illustrated do not represent a complete
survey, since the entire area is relatively new and a
complete picture has not been developed.

However, it is hoped that the above discussion will serve to stimulate thinking in this area.

# APPLICABLE POWER LEVELS FOR BIOELECTROCHEMICAL CONVERSION



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## **BIBLIOGRAPHY**

The following bibliography on bioelectrochemical energy conversion and related subjects has been compiled from referenced works in the area of bioelectrochemistry. The listing is not complete. It is intended to establish a representative compilation of references needed by an investigator to embark upon research in this area. The following abbreviations were used in the bibliography to assist in the location of reports and documents.

- N numbers refer to Scientific and Technical Aerospace Reports (STAR)
- A numbers refer to International Aerospace Abstracts
- AD numbers refer to Armed Services Technical Information Agency (ASTIA) now called Defense Documentation Center (DDC)

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