Electrical Energy From Biological Systems

J. J. KONIKOFF, L. W. REYNOLDS, and E. S. HARRIS

CHEMICAL REACTIONS which give rise to electrical energy in living and non-living systems have been studied extensively for many years.

Potter,[1] in 1911, measured the production of electrical energy by growing yeast cultures in one half cell of a typical oxidation-reduction system. At that time he reported that "the chemical action of their (the microorganisms) final processes was utilized to develop electrical energy in the manner parallel to the production of an emf by means of an ordinary galvanic battery."

Subsequent publications concerning the study of oxidation-reduction potentials derived from the metabolism of microorganisms have recently become extremely numerous. See for example, Reference 2.

Several systems called "Biological Fuel Cells" have been described by Sisler,[3] Rohrback,[4] Reynolds and Konikoff,[5] Davis and Yarbrough,[6] et al. However, although the name is the same, the mechanism by which the energy is produced may differ widely even though microorganisms are a contributing factor.

In general, there are three postulated mechanisms by which the microorganism contributes to the production of an emf.

1) The organism during its normal metabolism acts in such a manner as to depolarize the electrode.

2) The organism during its normal metabolism directly releases electrons which are collected on the electrode.

3) The organism during its normal metabolism produces fuel-cell-active material from a substrate which is in its normal state not active as a fuel.

This paper discusses these postulated mechanisms and indicates the validity of each.

DISCUSSION

Wilson[7] describes the first mechanism (depolarization) by considering the familiar magnesium sea water cell which produces electrical energy when the magnesium is oxidized upon contact with the sea water electrolyte, discharging electrons to the external circuit. This action may be represented by

$$Mg = Mg^{+} + 2e \qquad (1)$$

When shown in this manner the reaction connotes reversibility and the standard potential of 2.35 V. In sea water, however, a considerable departure from the above indicated condition of reversibility is observed so that the half cell potential is something less than 1.5 V. The reactions

$$Mg \longrightarrow Mg^{+} + e \qquad (2)$$

and then

$$Mg^{+} + H^{+} \longrightarrow Mg^{++} + \tfrac{1}{2}H_2 \qquad (3)$$

have been proposed as being more realistic than that shown in equation 1. These also account for the formation of hydrogen at the anode. At the cathode the reaction is as follows:

$$2\ H_2O + 2e = H_2 + 2OH^{-} \qquad (4)$$

and it can be seen that the production of hydrogen at this electrode essentially impedes the reaction. Now, if there were some means available to take up this hydrogen as it was liberated, then it would be possible to more nearly approach the theoretical standard potential. What is required is a hydrogenase enzyme system possessed by the bacterium Desulfovibrio desulfuricans, which in addition, has the ability to reduce

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From the Space Sciences Laboratory, Missile and Space Division, General Electric Company, P.O. Box 8555, Philadelphia, Pennsylvania.

sulfate to obtain its oxygen requirement. The action may be represented as follows:

$$4\ H_2 + H_2\ (SO_4^{--}) \xrightarrow[\text{bacteria}]{} H_2S + 4H_2O \qquad (5)$$

In this manner it has been demonstrated that the bacterial cell has a nearly 2:1 power advantage over the more conventional cell.

Of course, this system is a bio-galvanic cell requiring dissimilar electrode materials. As such, it probably should not be called a biological fuel cell. However, it demonstrates the validity of postulated mechanism No. 1.

Postulate No. 2 in which the organisms contribute directly to the equilibrium potential and/or participate in the transport of electrons directly, is of greater interest since it appears to be the approach to the pure biological fuel cell.

To date, this mechanism has not been demonstrated and, therefore, must remain in the realm of speculation. Moreover, it appears unlikely that electrons can be extracted from a microorganism and still have the organism remain viable.

The third postulate (fuel producer) is of great interest to the Space Sciences Laboratory because of a previous and continued association with the problems concerning closed ecologies, hence waste management. As a result, our experimental approach was predicated upon a proposition which states that a modified activated sludge system when coupled to an O_2 producer could be made to conform to the requirements of a biological fuel cell (i.e. evolve electricity).

Initial experimentation was conducted on a bioelectrogenic system consisting of one half cell containing the algae Chlorella pyrenoidosa, and the other half cell containing fecal bacteria plus glucose. The two halves were joined by a KCl agar bridge and the emf was measured by a test-meter connected to a pair of copper electrodes inserted into the cultures. The measured value was 0.3 V at 1.4 to 2.02 ma./ft.^{2}

A more convenient cell assembly was designed so that the agar bridge could be replaced by various membranes, thus lessening the internal resistance of the cell.

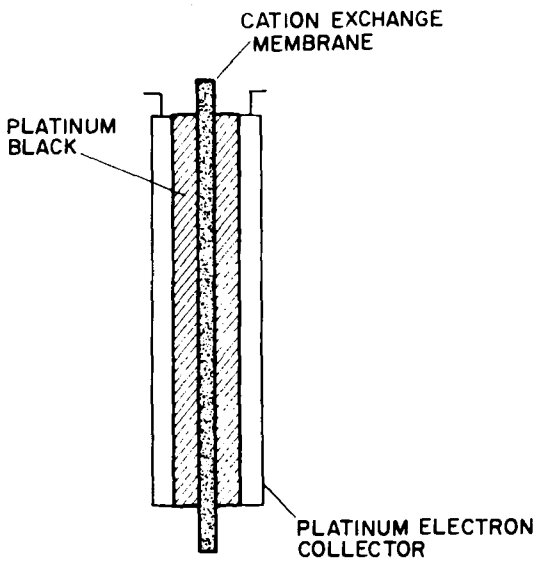

Fig. 1

The two half cells were formed by simply placing a membrane between a pair of quad rings and joining the two plastic plates with clamps. The test materials were allowed to flow into the cells via inlet tubes located at the bottom of the assembly. The outlet, located at the top of the cell, served as a gas vent. Several types of membrane materials, such as cellophane, anion and cation exchange materials were tested in this device. These membranes were evaluated by the shape of the polarization curve which was obtained by adding a series of resistances to the circuit. The change in voltage was plotted against the calculated values of current.

The best membrane was composed of a cation exchange material which had been covered with platinum black (Fig. 1). Two pieces of platinum screen, 12½ cm.,^{2} were used as electron collectors (this type of membrane electrode has been routinely used successfully by the General Electric Company's Direct Energy Conversion Operation, Lynn, Massachusetts in conventional hydrogen-oxygen fuel cells).

From a purely empirical point of view, the results just described indicated that a measurable emf can be obtained by the proper assembly of components and reactants into a biochemical fuel cell. Thus, it may be stated that feasibility had been demonstrated. However, from the scientific point of view, a considerable gap in our understanding of the mechanism from which the energy is produced existed. Considering the complexity of the biological component of the system just described, it became obvious that the elucidation of the role played by each of the several microorganisms present in the two half cells was too complicated to predict. Therefore, it was imperative that a simpler system be evolved. For this reason it was decided that yeast would be used in one half cell and air, oxygen, or aerated H_2O used in the other half cell.

This particular organism was selected because it will ferment, for a time, a non-electrolytic substrate, glucose. Therefore, the production of an emf could not be ascribed to a high concentration of electrolytes in the culture medium since one half cell contained a sugar solution while the other contained tap water or air. A more important reason for choosing yeast lies in the fact that the metabolism of glucose by yeast has been studied extensively for many years.

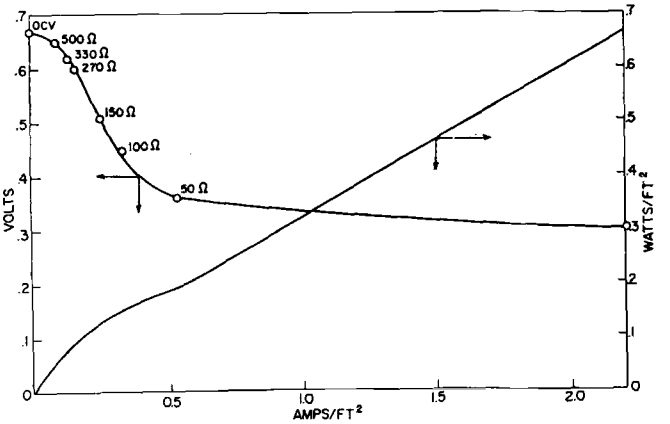

Fig. 2. Polarization curve of yeast/H_2O system.

The culture was prepared by adding one packet of Fleischmann's dry yeast to 500 ml. of a 5 per cent aqueous glucose solution. Ordinarily, the maximum open circuit voltage occurred two hours after inoculation; hence, the experiments were all conducted on two-hour cultures. At the end of the two-hour incubation period, about 20-30 ml. of the yeast solution was admitted to one side of the membrane and the air saturated water or air alone was allowed to flow into the other side. Using this technique, open circuit voltages ranging from 0.64 to 0.75 V were obtained.

The polarization curve on Figure 2 shows that a maximum power output of 0.66 w/ft.^{2} was obtained at a current density of 2.2 amps/ft^2. These values were increased to 1.4 w/ft.^{2} and 4.2 amps/ft.^{2} when the yeast was incubated in an O_2 free glucose solution. This increase in output is attributed to the fact that the oxygen in the solution partially inhibited the metabolism of the yeast.

This same emf was measured when the whole culture was replaced by the cell free of supernatant fluid.

Further study of this particular experimental system indicated that the membrane system containing the electrolytic material resulted in unreliable data. It was found that reproducibility was relatively low.

Consequently, a liquid electrolyte fuel cell was obtained from General Electric Company's Direct Energy Conversion Operation. These cells utilized two platinum black catalytic membranes separated by 6 N H_2SO_4 (Fig. 3). Individually, the cells appear to provide reproducible results. By utilizing proper recording

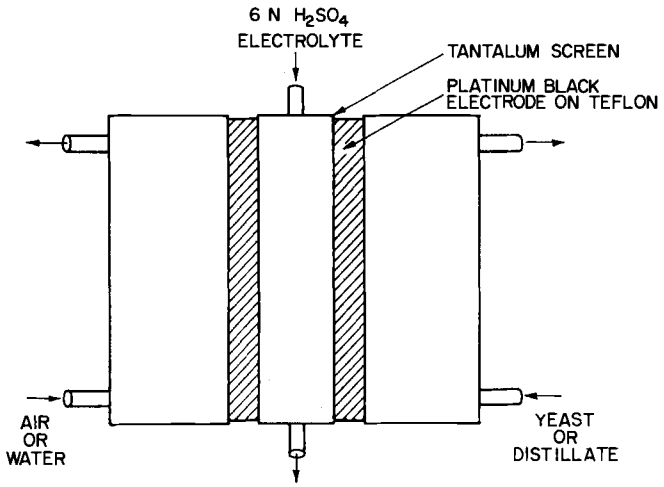

Fig. 3. Liquid electrolyte cell schematic.

equipment, it was determined that following initial equilibration, studies could be conducted with a high degree of assurance relating to the validity of the results.

Speculating on the possible mechanism for the contribution of yeast to a biological fuel cell results in the following three theorems:

1) Metabolites are produced during glycosis and electron transfer is enhanced by the catalytic action of platinum black.

2) Yeast, while metabolizing glucose, transfers electrons to the electrode.

3) Yeast produces a metabolite which is released into the medium and is further catalytically oxidized on the platinum black membrane.

In the third case, this system is essentially an organic fuel cell in which the microorganism is providing fuel for the cell by way of its metabolism. No. 1 and 2 can be separated from No. 3 by centrifugation of the yeast cells from the incubation system, and comparing the supernatant with the yeast containing mixture. By comparing polarization curves with and without yeast, it was determined that the presence of the yeast was not necessary, Figure 4. Thus, theorems No. 1 and 2

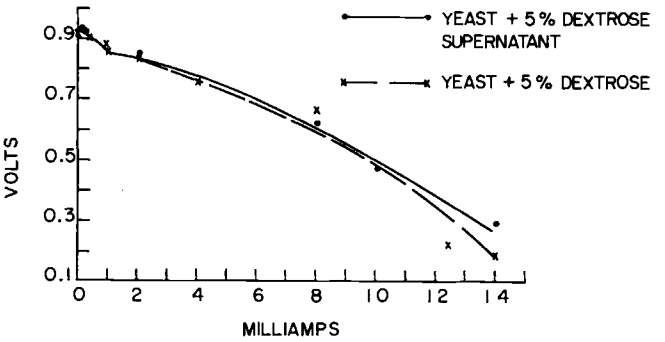

Fig. 4. Polarization curve–yeast/supernatant.

were eliminated, and we were left with theorem No. 3, an organic fuel cell. The nature of the fuel, however, was still to be determined.

Examination and quantitation of the material in the supernatant would appear to be the next obvious step. However, it was observed that glucose solutions gave values which, at times, equalled that of the supernatant. Several methods were tried to reduce the glucose or dextrose contribution and results were ambiguous. Lyophilization of yeast supernatant and collection of the lyophilizate on a liquid nitrogen cold finger produced a liquid sample free of dextrose which was fuel cell active. Similarly, distillation produced a fuel-cell-active material in the distillate.

The nature of the fuel-cell-active material could not be established until a quantitative relationship could be obtained between the output of the fuel cell and the

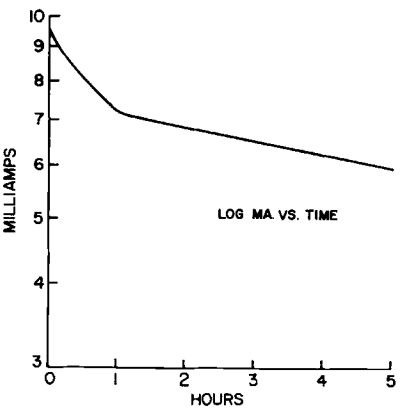

Fig. 5. Dilute yeast incubation distillate. Liquid electrolyte fuel cell.

metabolite which might be present in the distillate. Using the previously described liquid electrolyte fuel cell, such a relationship was obtained. By utilizing proper recording equipment, it was determined that following an initial equilibration, the current output by distillate appeared to follow simple first order kinetics for several hours and, therefore, is concentration dependent (Fig. 5).

Since OCV is an equilibrium function, an attempt was made to establish a relationship between the time to reach maximum OCV and the concentration of active material in a distillate, using successive dilution. A general relationship was found but it is too complex for use. Further experiments showed that this relationship was dependent upon the condition of the platinum-black membrane.

Finally, samples were introduced into the liquid electrolyte fuel cell, which was allowed to run under load until no measurable current was produced. The area under the resultant amp-time curve was integrated and the quantity of the fuel-cell-active material estimated.

If a two-step oxidation is assumed, then the amount of current produced is in agreement with the amount of ethanol present in the distillate as determined enzymatically and by gas chromatography.

Virtually identical results were obtained with ethanol as shown in Table I.

TABLE I

	Per Cent Et OH (v/v)			
	Gas Chromatography	Enzymatic	Fuel Cell	Theoretical
Diluted distillate	1.8	1.8	1.6	—
Ethyl alcohol	1.8	—	1.9	1.8
Ethyl alcohol	0.8	—	0.9	—

Biochemically, it would be anticipated that under the conditions of growth, the major product of metabolism would be ethyl alcohol. This has been verified by gas chromatography and enzymatic determinations. Although minor components of acetaldehyde, methanol and propanol, are found in distillates of yeast grown in blackstrap molasses and commercial M-yeast broth, Table II, all conditions are satisfied by ethanol. (Table I, Figs. 4 and 6). There are no indications of improved or further catalyzed yields as a result of trace components.

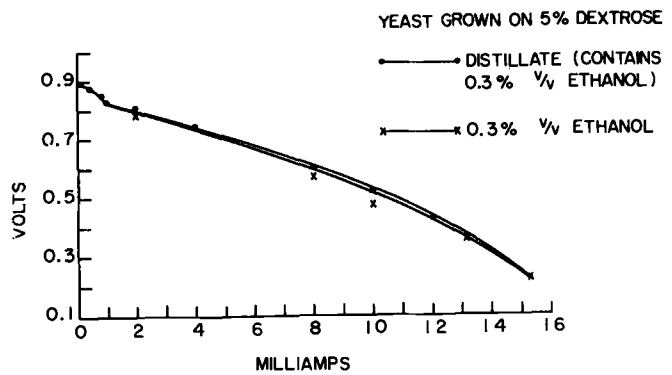

Fig. 6. Polarization curve. Distillate/ethanol.

In this manner, it was demonstrated that mechanism No. 3, which states that the yeast produces a metabolite which is released into the medium and is further catalytically oxidized on the platinum black membrane, is an accurate representation of a mechanism for the production of an emf by a microorganism.

RECOMMENDATIONS AND CONCLUSIONS

That microorganisms contribute to the production of an emf has been amply demonstrated.

However, since the mechanism by which the action occurs differs, care must be taken in defining a biological fuel cell. It would appear that a biological fuel cell is a device which is capable of producing a measurable emf as the result of microorganism metabolism only. In other words, if the organism is not present, then the potential is zero.

TABLE II. GAS CHROMATOGRAPHIC DETERMINATION OF COMPONENTS IN DISTILLATES

	Blackstrap Molasses #1 (Per Cent)	Blackstrap Molasses #2 (Per Cent)	M-Yeast Broth * (Per Cent)
Ethanol	79.2	80.0	27.4
Methanol	0.1	0.1	0
Acetaldehyde	0.03	0.06	0.03
Propanol	1.3	0	0
Water	19.7	19.9	72.6
Unidentified	ca. 0.1	ca. 0.1	0

* Distilled at a higher temperature than the blackstrap molasses samples.

Under this definition, the mechanism in which the microorganism depolarizes the electrode is not, strictly speaking, a biological fuel cell as much as a biogalvanic cell.

Mechanism No. 3 (fuel producer) does fit this definition. Moreover, since our primary interest lies in the field of closed ecologies for manned space flight, it would appear that this mechanism has more direct application in space. Since man and the processes which will feed and oxygenate him while in space will produce various forms of waste products, care must be taken to properly treat this material. Much of this material will be in a particular state that will not support fuel cell activity, (production of an emf). Through the judicious inoculation of specific microorganisms whose metabolism depends upon the uptake of these wastes, a fuel-cell-active material (metabolite) may be produced which, when introduced to a properly designed electrochemical fuel cell, will result in the evolution of an emf.

Consequently, it is upon this premise that the recommendation is made to study and evaluate a waste management system, incorporating a biological fuel cell system so that the energy reduction, type of organisms, size, weights, complexity, and product yield may be derived.

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