

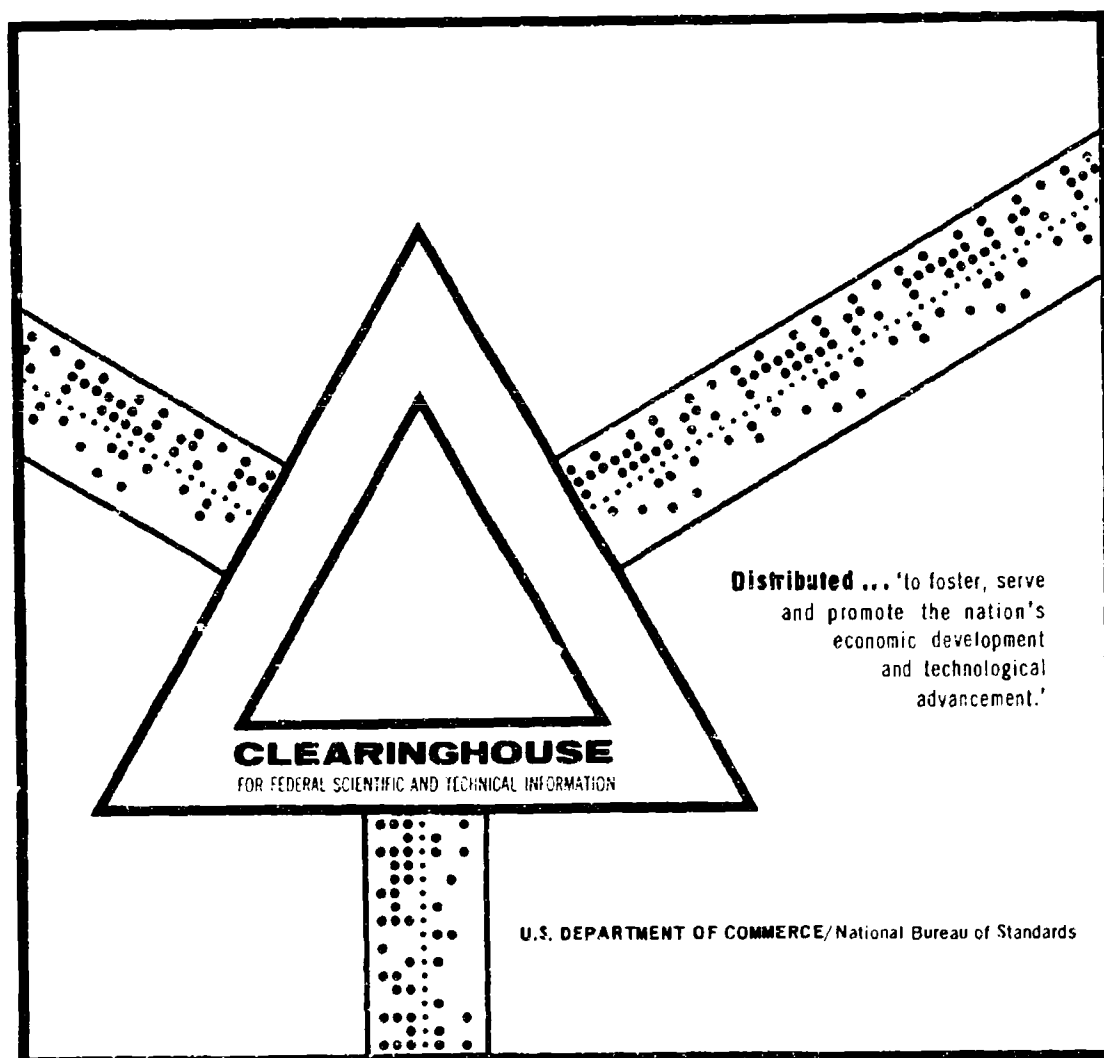
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THE USE OF A HYDROGENASE-METHYLENE BLUE SYSTEM
IN A BIOCHEMICAL FUEL CELL (AN ANODE REACTION)

Jun Mizuguchi, et al

Emmanuel College
Boston, Massachusetts

October 1969



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The Use of a Hydrogenase-Methylene Blue System in a Biochemical Fuel Cell (an Anode Reaction)

ヒドロゲナーゼ-メチレンブルー系の電池アノード反応への導入

JUN MIZUGUCHI 水口 純
SHUICHI SUZUKI 鈴木 周一
KENTARO KASHIWAYA 柏谷堅太郎
MASATOSHI TOKURA 戸倉正利

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Tokyo, Japan 67 (2): 410, 1964 (Emm-69-223)

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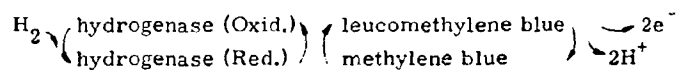
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AFCRL-69-0425: Translations, No. 56	<u>Fuel Cells Using Organic Redox Compounds</u> by Jun Mizuguchi Shuichi Suzuki Fujio Takahashi Kentaro Kashiwaya
AFCRL-69-0427: Translations, No. 57	<u>A Fuel Cell Using a Ferricyanide-Ferrocyanide System</u> by Fujio Takahashi Jun Mizuguchi Shuichi Suzuki
AFCRL-69-0428: Translations, No. 58	<u>Biochemical Fuel Cells</u> by Shuichi Suzuki
AFCRL-69-0430: Translations, No. 59	<u>The Use of an Electron Carrier System of $\text{NH}_4\text{Cl-CuSO}_4$ as a Biochemical Reaction Cell</u> by Jun Mizuguchi Shuichi Suzuki Kentaro Kashiwaya
AFCRL-69-0431: Translations, No. 60	<u>The Use of a Hydrogenase-Methylene Blue System in a Biochemical Fuel Cell (an Anode Reaction)</u> by Jun Mizuguchi Shuichi Suzuki Kentaro Kashiwaya Masatoshi Tokura

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Abstract

An electron carrier system similar to one found in living cells has been studied in vitro at the anode of a biochemical fuel cell. The reaction is

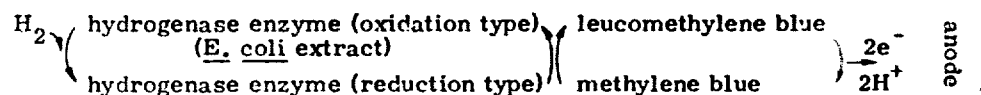


The action of an electron carrier system, composed of methylene blue as an organic redox compound and hydrogenase as an enzyme with hydrogen gas, has been analyzed at the anode of a biochemical fuel cell. A current of 0.16 mA/cm^2 has been shown using a hydrogenase solution obtained from E. coli. It gave evidence for general application of similar systems in biochemical fuel cells.

Further experimentation will be directed to obtain higher current-voltage by other enzyme-like substances.

The Use of a Hydrogenase-Methylene Blue System in a Biochemical Fuel Cell (an Anode Reaction)

The purpose of this study is to apply certain reactions seen in living systems to biochemical models. The authors previously studied cell-derived electron carrier systems at the cathode of fuel cells and obtained positive results (Mizuguchi *et al.*, 1962). In this paper an anode system is described. Using hydrogen gas as the energy source, a cell was constructed with an electron carrier system which combines an enzyme that catalyzes the transfer reaction of molecular hydrogen to the hydrogen carrier and organic compounds that perform reversible oxidation reduction. By the use of a cycle in which the oxidation type of hydrogen carrier formed as a result of the electrode reaction is converted to the reduction type by an enzyme, it was assumed that utilization of hydrogen at the anode would result in a high reaction rate and efficiency. The following is an example of electron carrier systems as applied to the reaction at the anode.



Methylene blue was used as the hydrogen carrier, and by adding a solution containing hydrogenase, an electron carrier system modeled after the standard biochemical reaction was formed and its significance as an anode-like reaction was examined.

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A cell was constructed by using platinum as the anode, MnO_2 -graphite mixture as the cathode, and an agar-agar bridge or unglazed cylindrical ceramic membrane. The hydrogenase extract was prepared by grinding a mixture of alumina and *E. coli* D according to Gest's method (Akabori, 1961). The brew was centrifuged and the precipitate discarded. With the circuit open, methylene blue chloride and hydrogenase extract were added to phosphoric acid buffer (pH 7) to form the anolyte through which hydrogen gas was passed continuously. As the catholyte, phosphoric acid buffer was used. The circuit was then closed. Methylene blue was reduced to the leuco form by the passage of hydrogen gas through the closed circuit.

As a result it was confirmed that this electron carrier system can validly simulate the reaction at the anode of a cell. This is shown in Figure 1. In contrast to the small current produced when phosphoric acid buffer (Curve 1) or methylene blue (Curve 2) was used alone, a greater discharge curve resulted when the hydrogenase solution was added to methylene blue (Curve 4). After an initial increase, there was a gradual decrease in the current when the hydrogenase extract was used alone (Curve 3). This is thought to be due to the reversible action of hydrogenase.

In summary, the authors have described a new electron carrier system combining an organic redox compound and an enzyme which simulates the reaction at the anode of the cell.

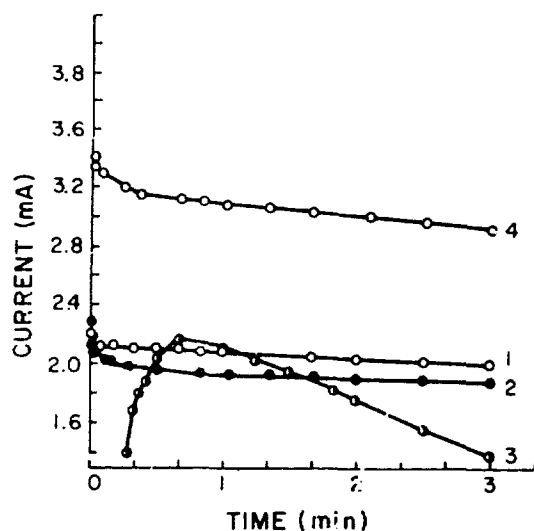


Figure 1. Discharge Curve of a Cell with the Hydrogenase-Methylene Blue System. Discharge started 3 hr after passing H_2 , H_2 introduced at $24-29^\circ\text{C}$. Anode: Smooth platinum (4 cm x 6 cm). Cathode: Electrode of MnO_2 -C mixture. Anolyte: 1/15 mol/l phosphoric acid buffer solution - 100 ml; methylene blue - 10 mg; enzyme-containing solution (equivalent to 9 g of hygric bacteria) - 50 ml. Catholyte: 1/15 mol/l phosphoric acid buffer solution - 60 ml. 1. Phosphoric acid buffer solution. 2. Phosphoric acid buffer solution + methylene blue. 3. Phosphoric acid buffer solution + enzyme-containing solution. 4. Phosphoric acid buffer solution + methylene blue + enzyme-containing solution.

Future investigations will involve a search for practical compounds which may be used to substitute for the hydrogenase enzyme action in the electron carrier system.

References

- Akabori (Ed.) (1961) Methods of Study of Enzymes, Asakura Publishers, Japan, p. 510.
- Mizuguchi, J., Suzuki, S., Takahashi, F. and Kashiwaya, K. (1962) Fuel cells using organic redox compounds, J. Chem. Soc. Japan, Ind. Chem. Sect. 65(10):1606-1608.

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Kentaro Kashiwaya

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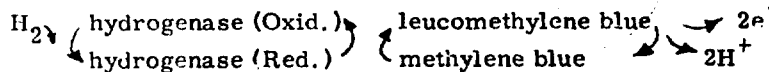
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13. ABSTRACT

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