



Dual gas-diffusion membrane- and mediatorless dihydrogen/air-breathing biofuel cell operating at room temperature



Hong-qi Xia^a, Keisei So^a, Yuki Kitazumi^a, Osamu Shirai^a, Koji Nishikawa^b, Yoshiki Higuchi^b, Kenji Kano^{a,*}

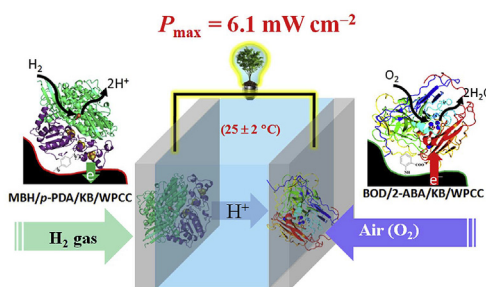
^a Division of Applied Life Sciences, Graduate School of Agriculture, Kyoto University, Kyoto 606-8502, Japan

^b Department of Life Science, Graduate School of Life Science, University of Hyogo, 3-2-1 Koto, Kamigori-cho, Ako-gun, Hyogo 678-1297, Japan

HIGHLIGHTS

- Improvement of DET-type bioelectrocatalysis of BOD at negatively charged electrode.
- Improvement of DET-type bioelectrocatalysis of MBH at positively charged electrode.
- Gas-diffusion system to improve fuel supply and suppress oxidative inactivation of MBH.
- H₂/air-breathing biofuel cell at room temperature with a high power density.

GRAPHICAL ABSTRACT



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ABSTRACT

A membraneless direct electron transfer (DET)-type dihydrogen (H₂)/air-breathing biofuel cell without any mediator was constructed wherein bilirubin oxidase from *Myrothecium verrucaria* (BOD) and membrane-bound [NiFe] hydrogenase from *Desulfovibrio vulgaris* Miyazaki F (MBH) were used as biocatalysts for the cathode and the anode, respectively, and Ketjen black-modified water proof carbon paper (KB/WPCC) was used as an electrode material. The KB/WPCC surface was modified with 2-aminobenzoic acid and *p*-phenylenediamine, respectively, to face the positively charged electron-accepting site of BOD and the negatively charged electron-donating site of MBH to the electrode surface. A gas-diffusion system was employed for the electrodes to realize high-speed substrate supply. As result, great improvement in the current density of O₂ reduction with BOD and H₂ reduction with MBH were realized at negatively and positively charged surfaces, respectively. Gas diffusion system also suppressed the oxidative inactivation of MBH at high electrode potentials. Finally, based on the improved bioanode and biocathode, a dual gas-diffusion membrane- and mediatorless H₂/air-breathing biofuel cell was constructed. The maximum power density reached 6.1 mW cm⁻² (at 0.72 V), and the open circuit voltage was 1.12 V using 1 atm of H₂ gas as a fuel at room temperature and under passive and quiescent conditions.

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1. Introduction

Enzymatic biofuel cells (EBFCs) are devices for converting chemical energy into electrical energy that utilize enzymes as

* Corresponding author.

E-mail address: kano.kenji.5z@kyoto-u.ac.jp (K. Kano).

electrocatalysts for the oxidation of fuels at the anode and the reduction of dioxygen (O_2) or hydrogen peroxide at the cathode [1–4]. In principle, a variety of compounds, such as sugar [5–13], alcohol [14–17], formate [18,19] and dihydrogen (H_2) [20–31], can be utilized as fuels of EBFCs. Thanks to substrate specificity and high catalytic efficiency under mild conditions (e.g., room temperature, around neutral pH), EBFCs are expected to be one of the next-generation energy conversion systems, comparable to conventional fuel cells, such as polymer electrolyte fuel cell [32]; however, the low power densities of EBFCs hinder technological applications [1–4]. The main factor limiting the performance of EBFCs has been reported to be relatively slow interfacial electron transfer between the enzyme and electrode [1–4].

The first step to construct an EBFC is the immobilization of a redox enzyme onto a solid electrode for bioelectrocatalysis that couples the enzymatic and electrode processes [1–4]; however, for mediatorless direct electron transfer (DET)-type bioelectrocatalysis, the electrochemical communication between the enzyme and electrode is mainly limited due to the long-distance electron transfer from the active center of the enzyme to the electrode surface, and when enzymes are adsorbed in random orientation on electrode surface, the apparent interfacial electron-transfer kinetics decrease [1–4,33]. In addition, details of the interaction between the enzyme and electrode remain to be elucidated, unlike the well understood interaction between the enzyme and its natural substrate [1–4]. Although some suitable redox mediators may assist electron transfer [34,35], several drawbacks arise [1–4,10,34,35]: (a) the toxicity of the mediator, (b) leakage of the mediator, and (c) cell voltage loss to set up the driving force in the electron transfer between the enzyme and mediator. Therefore, multiple studies, such as creating novel electrode materials [36–42], functionalizing electrode surface [9,43–51], and protein engineering [52–54], to improve DET-type bioelectrocatalysis have been reported.

H_2/O_2 biofuel cells wherein H_2 is oxidized by hydrogenase at the bioanode and O_2 is typically reduced by multi-copper oxidases (MCOs) at the biocathode are known as clean and highly efficient energy conversion devices that have attracted increasing attention for establishing a “hydrogen economy” [20–31].

Bilirubin oxidase from *Myrothecium verrucaria* (BOD, EC 1.3.3.5) is a member of the MCOs, which catalyzes a four-electron reduction of O_2 to water under mild conditions with low overpotentials. The active site of BOD contains four copper atoms, which can be divided into three classes according to their spectroscopic and magnetic properties [55–57]: type I (T1), type II (T2), and type III (T3) coppers. T2/T3 is responsible for O_2 reduction, and T1 is the electron-accepting site from a donor or electrode [58,59]. In our previous study, enhanced DET-type bioelectrocatalysis using BOD was accomplished at a negatively charged surface, constructed by modifying 4-aminobenzoic acid on a carbon electrode [49]. The electrostatic and π - π interactions between BOD and the modified electrode surface are responsible for the improvement in DET-type bioelectrocatalysis [49].

Hydrogenase catalyzes the reversible reaction of H_2 oxidation and proton (H^+) reduction and can be classified according to the metal ion composition of their active sites into [NiFe], [FeFe], and [Fe] hydrogenases [60–65]. Among them, [NiFe] hydrogenases are the most widely investigated [62,66–71]. Membrane-bound [NiFe] hydrogenase from *Desulfovibrio Vulgaris* Miyazaki F (MBH) comprises a heterodimer with a total molecular mass of 91 kDa (α : 62.5 kDa and β : 28.8 kDa) [67]. The larger subunit hosts the [NiFe] center while the smaller subunit contains three iron-sulfur (FeS) clusters called the proximal, medial, and distal clusters, relative to the [NiFe] center [67]. The distal FeS cluster has been reported to be responsible for the electronic communication between the enzyme

and electrode [67,71]. From this viewpoint, it appears to be important for MBH to face the distal FeS toward the electrode surface to improve the performance of DET-type bioelectrocatalysis [67]. There are multiple reports focusing on the improvements of the DET-type bioelectrocatalytic performance of several [NiFe] hydrogenases with modified electrodes [72–75], but not for MBH to the best of our knowledge.

Other important issues for H_2/O_2 biofuel cells are the low-saturated concentrations of the gases in solution, the gas supply system, and risk of explosion [29,31,76]. Rotating disk electrodes (RDE) or stir bars are usually utilized to minimize the concentration depression near the electrode surface. These methods require external power to drive the RDEs or stir bars. More importantly, it may result in a biofuel cell that is too “fat” to improve the power density (power at a unit of surface area or volume). Recent findings have reported that MCOs [9,29,31,77–79] and several MBHs [76] could efficiently operate in a gas-diffusion system. In addition, a gas-diffusion system is useful for suppressing the oxidative inactivation that occurs at positive electrode potentials and competitively with the catalytic cycle, and is another important issue in hydrogenase applications [76]. On the other hand, to avoid the risk of explosion, the compartmentalization of fuel cells [20,21,23,25,27,31] and operation at low concentrations of H_2 and/or O_2 [22,24,26,28–30] are frequently explored. The former requires sophisticated cell construction and the latter results in low power density.

In this study, we attempt to construct a safe H_2 /air-breathing biofuel cell operating at room temperature with a high power density using BOD and MBH on the functionalized mesoporous carbon electrodes. This is the first attempt to fabricate a membrane- and mediatorless H_2 /air-breathing biofuel at room temperature.

2. Experimental

2.1. Biocatalysts, materials, and reagents

BOD (EC 1.3.3.5) from *Myrothecium verrucaria* was donated by Amano Enzyme Inc. (Japan) ($3.04 \text{ unit mg}^{-1}$) and used without further purification. O_2 -sensitive MBH from *Desulfovibrio vulgaris* Miyazaki F was purified according to the literature [80]. Ketjen black EC300J (KB) was kindly donated by Lion Co. (Japan). Waterproof carbon cloth (WPCC; EC-CC1-060T) was purchased from Toyo Co. (Japan), and polytetrafluoroethylene fine powder (PTFE, 6-J) was obtained from DuPont Mitsui Fluorochemicals (Japan). 4-Aminobenzoic acid (4-ABA), 4-aminobenzenesulfonic acid (4-ABS), methyl-4-aminobenzoate (MABA), 2-aminobenzoic acid (2-ABA), and *p*-phenylenediamine chloride (*p*-PDA) were purchased from Tokyo Chemical Industry Co. (Japan). All other chemicals used in this study were of analytical grade unless otherwise specified, and all solutions were prepared with distilled water.

2.2. Electrochemical measurement

Cyclic voltammetry and chronoamperometry were performed using an electrochemical analyzer ALS 701 E with a glassy carbon (GC) electrode as a working electrode, Pt wire as a counter electrode, and an Ag|AgCl|KCl (sat.) electrode as a reference electrode. For a gas-diffusion-type bioelectrode, WPCC and Pt mesh were used as a working electrode and a counter electrode, respectively. All potentials were referenced against the reference electrode.

2.3. Preparation of functionalized biocathodes

The gas-diffusion-type biocathode was prepared according to a previously reported method [31]. In brief, 40 mg of KB powder was

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