



Photo-assisted flavin mediated electro-oxidation of NADH model compound using photogalvanic cell



Jun Yano^{a,*}, Akira Kitani^b

^a Department of Fundamental Science, Niihama National College of Technology, Yagumocho 7-1, Niihama, Ehime 792-8580, Japan

^b Faculty of Engineering, Hiroshima University, Kagamiyama 1-4-1, Higashihiroshima, Hiroshima 739-0046, Japan

ARTICLE INFO

Keywords:

Photogalvanic cell
NADH
Flavin
Biofuel cell

ABSTRACT

The electrochemical conversion of NADH to NAD⁺ is a key process for enzymatic biofuel cells in order to obtain a high performance. However, the direct electrochemical oxidation of NADH requires an extremely high overpotential (about 1.2 V). To promote this electrochemical conversion, an indirect electrochemical oxidation was performed by utilizing a photogalvanic cell. 1-Benzyl-1,4-dihydropyridinamide (BNAH) was used as a model compound of NADH, and riboflavin (RF) was selected as the current mediator. The anodic cell reaction is the oxidation of reduced riboflavin (RFH⁻) produced by the photocatalyzed redox reaction with BNAH, and the cathodic cell reaction is the reduction of the hydronium ion. The highly-efficient electrochemical conversion of BNAH to BNA⁺ provides both electricity and dihydrogen as by-products.

1. Introduction

Our ultimate objective is to develop photo-assisted enzymatic biofuel cells evolving H₂ gas as a by-product at the cathode. These cells will become promising candidates as alternative energy sources because both sunlight and biofuel can be used as well as fuel gas (H₂ gas) that can be obtained during the discharge. To achieve this objective, it is necessary to effectively allow the electrochemical conversion of NADH to NAD⁺, whose redox potential (E°) is -0.32 V. As is well known, however, the direct electrochemical oxidation of NADH requires the extremely high overpotential of about 1.2 V [1], thus the electrochemical conversion of NADH to NAD⁺ is difficult. In this paper, we show that photo-excited flavin acts as the current mediator, and effectively allows the NADH oxidation using 1-benzyl-1,4-dihydropyridinamide (BNAH) as an NADH model compound. As a result, we can construct a flavin-catalyzed photogalvanic cell with NADH oxidation as the anode and a hydrogen half-cell as the cathode.

Although it is reported that photogalvanic cells are available for energy conversion devices which carry out direct conversion of light energy to electric energy [2,3], our photogalvanic cell is not such an energy conversion device. Our purpose in this study is not to build the energy conversion devices, but to promote the oxidative conversion of NADH to NAD⁺ using the redox mediators and to fabricate a photogalvanic cell which is applicable for the enzymatic biofuel cell. In our photogalvanic cell, the light is employed only for promote the conversion. Gust and his co-workers reported that they have designed

hybrids of solar cells, and enzymatic biofuel cells have been designed [4,5]. They succeeded in converting NADH to NAD⁺ by employing dye-sensitized semiconductors as photoanodes. When the photoanodes are irradiated by sunlight, they oxidize NADH to produce NAD⁺. Using this NAD⁺, the corresponding enzymes oxidize the biofuels and NADH is reproduced from NAD⁺ during the oxidation process. Unfortunately, however, the availability of solar energy to these cells is not very high because sunlight is only available at the photoanodes. In other words, the surface areas of the photoanodes limit the amount of the generated NAD⁺ and the available biofuels.

If the oxidation of NADH took place in the entire electrolytic solution, the biofuels could be more efficiently oxidized than in the hybrid cells, and besides, no photoanodes would be necessary. Previously, in order to reduce the overpotential for the NADH oxidation, several organic compounds, such as catechols, diaminobenzenes or phenazines, were employed as the current mediator [6–13]. The redox potentials of these mediators, however, are still far apart from the formal redox potential of the NADH/NAD⁺ couple. Recently, although several better current mediators were found [14–19], they were still not sufficient to effectively cause the NADH oxidation.

Flavins, whose redox potential is fairly close to that of NADH ($E^\circ = \text{ca. } -0.22$ V), play an important role in the electron transport chain NADH dependent enzymatic processes. Because the reaction rates between NADH and oxidized flavins are not very fast, flavins are unsuitable as a current mediator for the electro-oxidation of NADH [20,21]. As we have shown in a previous communication, however, the

* Corresponding author.

E-mail address: yano@sci.niihama-nct.ac.jp (J. Yano).

redox reaction between the NADH model compound (BNAH) and riboflavin (RF) was significantly accelerated by light irradiation [22]. The apparent rate constant was determined to be $(3.7 \pm 0.2) \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ [20] and the visible light irradiation caused this value to increase by 5.3 times. Therefore, the electrochemical oxidation of NADH is possible at an extremely low overpotential (the oxidation potential of the reduced flavin) if the flavin (FL) acts as a light-activated catalyst. The mediated reaction can be written as follows:



where FLH^- denotes the reduced form of flavin.

In the present study, we tried to utilize a cell reaction instead of using an external power source. The cathodic reaction is the hydrogen evolution reaction in acidic media (Eq. (3)) overall cell reaction can be expressed by Eq. (4).



If the photo-assisted galvanic cell proposed here works well, both electric power and molecular dihydrogen are obtained during the oxidation process of NADH to NAD^+ . In addition, the reaction mechanism about the photo-assisted flavin-mediated electro-oxidation of BNAH was investigated and it was revealed that the photoexcited RF triggers the chain reactions between NADH and RF.

2. Experimental

All the inorganic chemicals were of reagent grade and used without further purification. Riboflavin (RF; Katayama Chemical Co.) or flavinmononucleotide (FMN; Sigma Chemical Co.) was used as the current mediator. Dimethylsulfoxide (DMSO) was used as the solvent due to the limited solubility of RF in an aqueous solution. 1-Benzyl-1,4-dihydronicotinamide (BNAH) and its oxidized form (BNA^+) were synthesized and purified according to the literature [23]. β -Nicotinamide Adenine Dinucleotide (NADH; Nacalai Tesque Co.) was of reagent grade and used without further purification.

The cell is schematically depicted in Fig. 1. The anodic compartment was a quartz tube filled with a DMSO solution containing BNAH, RF, and 0.1 M (1 M = $1 \text{ mol} \cdot \text{dm}^{-3}$) tetraethylammonium perchlorate (TEAP) as the supporting electrolyte. The catholyte was a 2 M sulfuric acid aqueous solution and both the anolyte and catholyte were connected by an agar salt bridge filled with KCl. The anode was a platinum

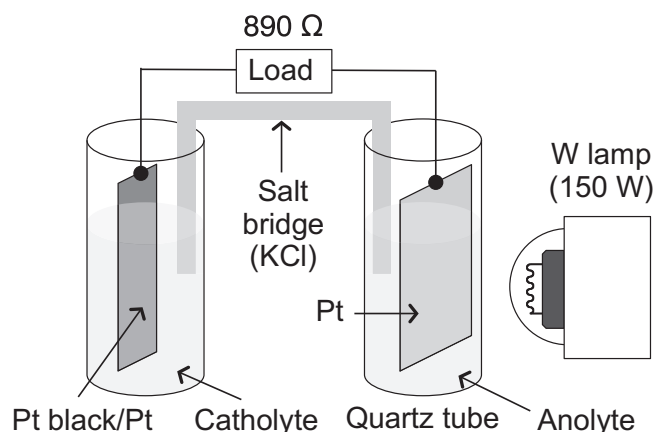


Fig. 1. Schematic depiction of the photogalvanic cell.

plate ($30 \text{ mm} \times 20 \text{ mm}$). To prevent the cathodic reaction (Eq. (3)) from determining the overall cell current, a platinized platinum plate was employed as the cathode. Although the geometric area of the platinum plate was $5 \text{ mm} \times 20 \text{ mm}$, the effective electrode surface area was much greater than the platinum plate substrate because the whole substrate was covered with a platinum black layer. A 150 W tungsten lamp was employed as the light source and only the anode compartment was irradiated. The emission energy of the tungsten lamp ranged in wavelength from 300 nm to near an infrared wavelength and indicated a broad peak at 850 nm. In addition, the experiment was carried out in a dark room. The transient current of the galvanic cell was measured under the constant load of 890Ω , but this value had little importance. The electrochemical measurements were carried out using a commercial potentiostat/galvanostat (Hokuto Denko Co., HAB-151B) under a nitrogen atmosphere at room temperature. Linear sweep voltammograms were measured to determine the RF ([RF]) concentration. Because the diffusion current in the voltammogram is proportional to the concentration of the dissolved species [24], the calibration curve, i.e., the relationship between the diffusion current and [RF], was made. Using the calibration curve, each [RF] value was determined by the measured diffusion current.

3. Results and discussion

3.1. Transient photocurrent of the BNAH/RF cell

The characteristics of the galvanic cell were studied using the NADH/flavin model system initially containing RF and BNAH. Fig. 2 shows the change in the cell current with time under light irradiation. The cell current significantly increases by the irradiation, then gradually decreases to a steady value. The steady value depends on the RF ([RF]) concentration when [RF] is less than 1 mM. The current-time curves were almost the same when [RF] = 1.5, 2.0, and 2.5 mM.

The steady value is $116 \mu\text{A}$ for [RF] = 1 mM and $87 \mu\text{A}$ for [RF] = 0.5 mM. The decrease in the cell current after turning off the light was not very rapid. A similar slow response of the cell current by the irradiation was also reported in other types of photogalvanic cells [25,26]. As can be readily seen in Fig. 2, the current increases with the RF amount. In addition, a considerable amount of residual current flow appears even in the absence of RF, mainly due to the pH difference between the anodic and cathodic compartments [25]. The output current-voltage relationships were measured by changing the external load (Fig. 3).

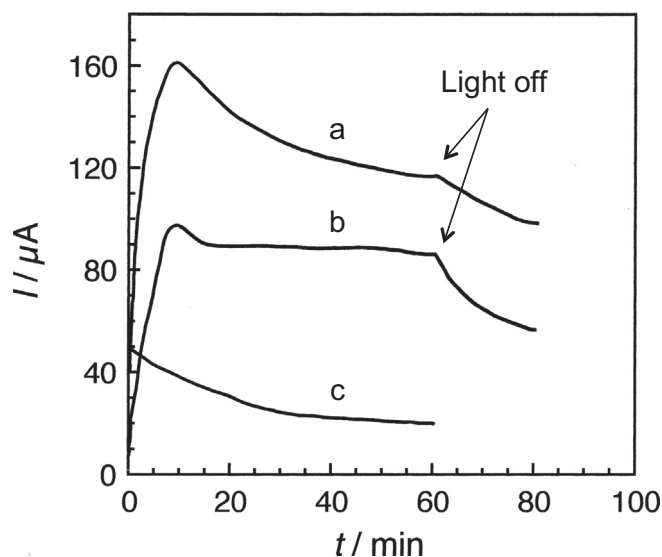


Fig. 2. Change in the cell current versus the irradiation time. The anode compartment contains RF and BNAH (10 mM) in a DMSO solution containing 0.1 M TEAP. Concentration of RF: 1 (a), 0.5 (b), and 0 mM (c).

Download English Version:

<https://daneshyari.com/en/article/4907772>

Download Persian Version:

<https://daneshyari.com/article/4907772>

[Daneshyari.com](https://daneshyari.com)