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Efficient bioelectrocatalytic CO_2 reduction on gas-diffusion-type biocathode with tungsten-containing formate dehydrogenase

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ABSTRACT

A new gas-diffusion-type biocathode was constructed for carbon dioxide (CO_2) reduction. In this work, tungsten-containing formate dehydrogenase (FoDH1), which is a promising enzyme for interconversion of formate and CO_2, was used as a catalyst and was absorbed on a Ketjen Black (KB)-modified electrode. We used 1,1′-trimethylene-2,2′-bipyridinium dibromide as a mediator, and the hydrophobicity of the FoDH1-absorbed electrode was optimized according to the weight ratio of the polytetrafluoroethylene binder to KB. We achieved cathodic current densities of about 20 mA cm^{-2} under mild and quiescent conditions (neutral pH, atmospheric pressure, and room temperature).

1. Introduction

The reduction of carbon dioxide (CO_2) to generate reduced carbon compounds as fuels and chemical feedstocks is an essential requirement for a carbon-based sustainable energy economy [1–8]. An interconversion system of formate ($HCOO^-$)/CO_2 is one of the strategies for this purpose. $HCOO^-$ is the first stable intermediate during the reduction of CO_2 to methanol or methane and is increasingly recognized as a new energy source [9–12]. However, when CO_2 is reduced to $HCOO^-$ directly on conventional electrodes, several byproducts are generated, and quite a high overpotential is required [8].

One of the most promising strategies for solving these issues is the utilization of enzymes as catalysts. Formate dehydrogenase (FoDH) generally catalyzes the oxidation of formate to CO_2. On the other hand, certain FoDHs have been reported to act as CO_2 reductases, and there are several reports of bioelectrocatalytic CO_2 reduction with such FoDHs [13–20]. The enzymes allow the system to function for a specific biological reaction under mild and safe conditions, such as neutral pH, room temperature, and atmospheric pressure [13–20]. The electro-enzymatic devices can be used as energy conversion systems, such as efficient bioelectrochemical systems for CO_2 reduction. However, several problems still exist, such as low current densities and low stability. We have electrochemically studied tungsten (W)-containing formate dehydrogenase (FoDH1) from *Methylobacterium extorquens* AM1 [21]. It has been shown that FoDH1 produces mediated electron transfer (MET)-type bioelectrocatalytic currents for both of the $HCOO^-$ oxidation and the CO_2 reduction. In the MET-type reaction system, artificial redox partners (mediators) enable enzymatic reactions to couple with electrode reactions by shuttling electrons between enzymes and electrodes. In addition, FoDH1 exhibits no specificity to the second substrate, and the electron transfer rate constants between the enzyme and mediators increases exponentially with an increase in the driving force. We have achieved a MET-type bioelectrochemical CO_2 reduction at high current densities and low overpotentials using FoDH1 [22].

A gas-diffusion-type electrode has been developed and employed for bioelectrocatalytic systems, such as efficient H_2 oxidation and O_2 reduction for biofuel cells [23–29]. On the other hand, electrochemical CO_2 reductions on various metals and metal compounds loaded in a gas-diffusion-type electrode were reported by several workers [30–34]. They achieved large current densities for CO_2 reduction, compared to electrolysis in aqueous electrolyte using metal electrodes.

In this study, we attempted to construct a new bioelectrocatalytic CO_2 reduction system under mild conditions. We focused on the introduction of a gas-diffusion-type electrode into an FoDH1-based bioelectrocatalytic system. From the viewpoints of the kinetics and the thermodynamics between FoDH1 and mediators [21], we used 1,1′-trimethylene-2,2′-bipyridinium dibromide (TQ; Fig. 1, inset) as a mediator. In addition, we focused on Ketjen Black (KB) as an electrode material to effectively immobilize FoDH1. This is the first report of a MET-type bioelectrocatalytic CO_2 reduction on gas-diffusion-type electrodes.

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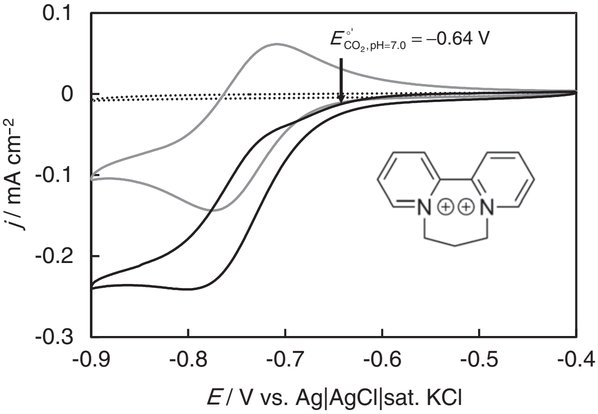

Fig. 1. CVs on a bare glassy carbon electrode under Ar atmosphere in 0.1 M potassium phosphate buffer (pH 7.0) containing 3.2 mM TQ and 50 mM K_2CO_3 in the absence (solid gray line) and presence (solid black line) of 1.2 μM FoDH1. The dotted line is a background CV (before addition of TQ, K_2CO_3, and FoDH1). $v = 20$ mV s^{-1}. The inset shows the structure of the TQ ion.

2. Experimental

2.1. Chemicals

Waterproof carbon cloth (WPCC, EC-CC1-060 T) was purchased from Toyo Corp. (Japan), and KB (EC300J) was kindly donated by Lion Corp. (Japan). Poly(1,1,2,2-tetrafluoroethylene) (PTFE, 6-J) fine powder was purchased from DuPont-Mitsui Fluorochemicals Co. Ltd. (Japan). The PTFE membrane filter T050A025A (pore size: 0.5 μm, thickness: 75 μm) was obtained from Advantec (Japan). Other chemicals were obtained from Wako Pure Chemical (Japan) and all solutions were prepared with distilled water. FoDH1 was purified according to a literature procedure [21].

2.2. Electrode preparation

Gas-diffusion-type electrodes were prepared as follows: KB powder (40 mg) was mixed with PTFE and homogenized in 3.5 mL of 2-propanol for 3 min at 0 °C to prepare a KB slurry ($L = dm^3$). Next, about 1.0 mL of the KB slurry was applied to one side of a 2.25 cm^2 piece of WPCC and dried. This electrode is called KB/PTFE/WPCC. The PTFE membrane filter was attached to the opposite side (without KB) of the KB/PTFE/WPCC electrode by pressure bonding to completely hold the electrolysis solutions. A 60 μL FoDH1 solution (20 μM of FoDH1 solution in 100 mM potassium phosphate buffer of pH 6.0) containing 0.5% (v/v) glutaraldehyde was applied to the KB/PTFE/WPCC electrode ($M = mol\ dm^{-3}$). The electrode was dried for 4 h under reduced pressure at 4 °C.

2.3. Preparation of TQ

TQ was synthesized according to a literature procedure [18]. Briefly, 2,2′-bipyridine (10 mmol) was dissolved in 300 mL of acetonitrile and then 1,3-dibromopropane (100 mmol) was added to this solution and the reaction mixture was refluxed for 48 h. The yellow precipitate was collected by filtration and washed with acetonitrile. The desired product was dried under vacuum overnight.

2.4. Electrochemical measurements

Cyclic voltammetry and chronoamperometry were carried out on an ALS 611B electrochemical analyzer. A handmade gas-diffusion-type electrolysis cell identical to that reported in a previous paper [35] was used for measurements with some modification. The projected surface area of the working electrode for gas-diffusion-type electrolysis was set to 0.27 cm^2. A Ti mesh served as a current collector. A Pt mesh and a homemade Ag|AgCl|sat.KCl electrode were used as counter and reference electrodes, respectively. All potentials in this study are given with respect to the reference electrode. The measurements were performed in 0.1 M (pH 7.0) or 1.0 M (pH 6.5) potassium phosphate buffer at 30 °C under quiescent conditions.

3. Results and discussion

3.1. MET-type bioelectrocatalysis of CO_2 reduction with TQ in solution

TQ gave a pair of redox waves in cyclic voltammetry at a scan rate (v) of 20 mV s^{-1} (Fig. 1). The formal potential of TQ was evaluated as $E^{\circ\prime}_{TQ} = -0.74$ V (-0.54 V vs. SHE) as a mid-point potential in the cyclic voltammogram (CV) of TQ. In the presence of FoDH1, a large catalytic reduction wave with sigmoidal and steady-state characteristics was observed in 0.1 M potassium phosphate buffer (pH 7.0) containing 50 mM K_2CO_3 on a glassy carbon electrode (Fig. 1). The sigmoidal wave is due to typical mediated bioelectrocatalysis of the CO_2 reduction. The half-wave potential of the catalytic wave was close to $E^{\circ\prime}_{TQ}$ and only 0.1 V more negative than the formal potential of the $CO_2/HCOO^-$ couple ($E^{\circ\prime}_{CO_2,pH\ 7.0} = -0.64$V, -0.44 V vs. SHE [8]). This means that the system achieves efficient CO_2 reduction with a very small overpotential.

In solution, the acid-base equilibrium and low diffusion coefficient of CO_2 become limiting factors when we aim to achieve a high current density with bioelectrocatalytic CO_2 reduction. A gas-diffusion-type electrode, which can supply a gaseous substrate from the gas phase, could be utilized to solve this problem. Given this hypothesis, we attempted to develop a new bioelectrocatalytic CO_2 reduction on a gas-diffusion-type electrode with FoDH1 and TQ.

3.2. Bioelectrocatalytic CO2 reduction on a gas-diffusion-type electrode

Fig. 2A shows CVs of the FoDH1-adsorbed KB/PTFE/WPCC electrode in 1.0 M phosphate buffer (pH 6.5) containing 10 mM TQ in a CO_2 or Ar atmosphere under quiescent conditions. The PTFE content was 20% (PTFE/PTFE + KB, w/w). The FoDH-adsorbed electrode did not give a significant cathodic wave in the absence of TQ under CO_2 atmosphere (inset of Fig. 2A). However, the faradic wave is ascribed to CO_2 reduction to $HCOO^-$, due to MET-type bioelectrocatalysis with FoDH1 and TQ. A stable steady-state catalytic current density of -18 mA cm^{-2} was obtained after at least 60 s from chronoamperograms (CAs) at -0.8 V on the electrode. The current density corresponds to an $HCOO^-$ production rate of 0.1 μmol cm^{-2} s^{-1}. This is the first report of a gas-diffusion-type biocathode that is used for MET-type bioelectrocatalysis, and an enzyme-based bioelectrocatalytic CO_2 reduction system at such a high current density and low overpotential under quiescent and mild conditions. Unfortunately, the non-catalytic broadened wave of TQ (in the absence of FoDH1) indicates relatively poor interfacial electron transfer kinetics at the electrode.

The catalytic CV in Fig. 2A was recorded at the second scan. The steady-state anodic wave in a potential region more positive than -0.6 V is assigned to the bioelectrocatalytic oxidation of $HCOO^-$ generated near the electrode surface during the cathodic reaction in the first and second scans. This indicates that FoDH1 can work as a MET-type bioelectrocatalyst for the interconversion of $HCOO^-$ and CO_2. Since the oxidation is uphill due to a situation, in which $E^{\circ\prime}_{TQ}$ (-0.74 V) < $E^{\circ\prime}_{CO_2,pH\ 6.5}$ (-0.61 V), the reaction rate constant is small under the reaction conditions used, and a steady-state current with relatively small current density was observed without concentration depletion of $HCOO^-$ during the anodic scan.

In order to optimize the performance of the gas-diffusion electrodes, we need to consider several factors, such as the CO_2 permeability and the hydrophilicity/hydrophobicity of the electrode. In this work, we optimized the PTFE content. The catalytic reduction current densities at