

Gas Diffusion Biocathode Based on Direct Electron Transfer-type Bioelectrocatalysis

Ryota Kontani, Seiya Tsujimura, Katsumi Hamamoto and Kenji Kano

Division of Applied Life Science, Graduate School of Agriculture, Kyoto University, Sakyo-ku, Kyoto 606-8502, Japan

Introduction

Biofuel cells (BFCs) are kinds of fuel cells. BFCs utilize enzymes or micro-organisms as electrocatalysts instead of platinum and work under mild conditions [1]. In BFCs, sugars, amines, organic acids and hydrogen have been used as substrates at the anodes. On the other hand, dioxygen (O_2) has been used as substrate at the cathodes in most cases [2]. O_2 is the most abundant electron acceptor because of its availability in the environment and its high redox potential. The reaction at the cathodes is the four-electron reduction of O_2 to water. The previous BFCs have used O_2 dissolved in the electrolyte solution. However, the availability of the electron acceptor has been limited because of the low solubility and small diffusion coefficient of O_2 in water. In order to bring out the effectiveness of O_2 , we attempted to construct a gas diffusion biocathode using O_2 in the atmosphere (Scheme 1).

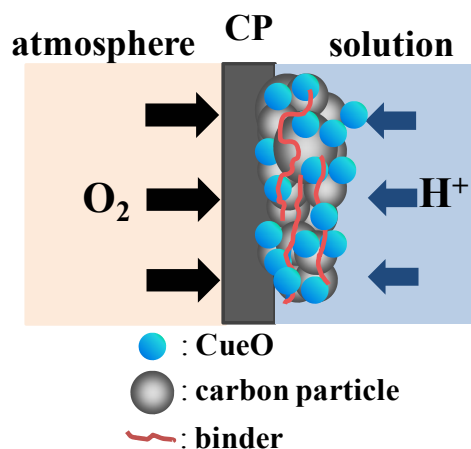
We utilized CueO from *Escherichia coli* as biocatalyst at the cathode. CueO is a member of multi-copper oxidases (MCOs) family including laccase, bilirubin oxidase (BOD), ascorbate oxidase, ceruloplasmin and CotA. Copper atoms in MCOs are classified into three types based on spectroscopic and magnetic properties. CueO was examined as a direct electron transfer (DET) type bioelectrocatalyst for the four-electron reduction of O_2 . The type I Cu site is the inlet of electrons from electrode and transfers the electrons to the trinuclear center composed of one type II Cu and two type III Cu atoms. The trinuclear center (type II-III Cu cluster) serves as the catalytic site to reduce O_2 into water. DET between enzymes and electrodes has attracted attention for construction of biofuel cells because of several advantages: reduction in thermodynamic loss and costs; increase in safety and environmental benefits. CueO was found to be superior to other MCOs from the viewpoint of the catalytic activity [3]. Nano-structured carbon materials which have very high porosity, large surface area, and electrical conductivity are worthwhile to increasing catalytic current density and to improving stability of enzyme modified electrode [4].

Experimental

Expression and purification of CueO were carried out as described previously [5]. Poly(vinylidene di-fluoride) (PVDF) was used as a binder and dissolved in *N*-methyl-2-pyrrolidone as a 10 % (w/w) solution. The carbon particles were ground with a homogenizer, and then mixed with the PVDF solution to prepare carbon particle slurry. The weight ratio of PVDF to carbon particles was adjusted to be 2 : 8. The carbon particle-modified carbon paper (CP) electrodes were made by applying the slurry to the surface of CP and drying in a drying oven at 60 °C for over 12 h. The slurry was made of two different kinds of carbon particle: Ketjen black (KB) and Vulcan. The carbon particle-modified CP electrodes were immersed in CueO solution to adsorb CueO on the carbon particle materials.

Result and Discussion

Figure 1 shows cyclic voltammograms of CueO-adsorbed on carbon particle-modified CP electrodes placed on the surface of quiescent air-saturated McIlvaine buffer solution of pH 5.0. Cyclic voltammograms were recorded using the handmade gas diffusion-type electrolysis cell. All potentials were referred to the Ag|AgCl(sat.) KCl reference electrode. The current density at 0 V was as high as 3 mA cm⁻² on KB-modified CP electrode using gas diffusion biocathode cell. In addition, the current was very stable. In contrast, the current density at 0 V decreased down to 0.9 mA cm⁻² on KB-modified CP electrode sunk in the buffer solution even in the beginning, and the current density gradually decreased with time during the electrolysis. Therefore, we can conclude that performance of biocathode was dramatically improved by using the gas diffusion system.



Scheme 1. Schematic representation of the CueO-adsorbed on carbon particle-modified CP electrode.

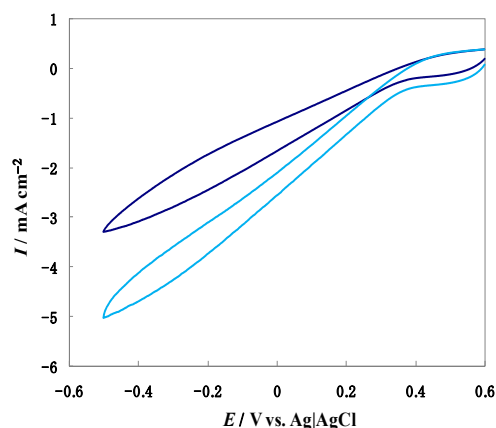


Fig. 1. Cyclic voltammograms of CueO-adsorbed on carbon particle-modified CP electrode recorded in quiet air-saturated McIlvaine buffer (pH 5.0), (a) vulcan-modified CP electrode, (b) KB-modified CP electrode. The data were taken at a scan rate of 20 mVs⁻¹.

References

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