



Photo-effect on the electromotive force in two-compartment hydrogen peroxide-photofuel cell

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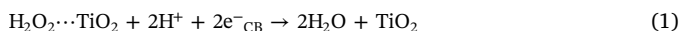
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ABSTRACT

Mesoporous TiO₂ nanocrystalline film was coated on fluorine-doped tin oxide electrode (mp-TiO₂/FTO) by the doctor blade method, and Prussian blue film was electrodeposited on FTO (PB/FTO). A two-compartment H₂O₂-PFC with the structure of mp-TiO₂/FTO (photoanode)|0.1 M KClO₄ (pH 3)|Nafion (separator)|0.1 M KClO₄ with 0.1 M H₂O₂ (pH 3)|PB/FTO (cathode) was constructed. Under UV-light irradiation, the two-compartment PFC provides short-circuit current (J_{sc}) = 1.14 mA cm⁻² and open-circuit potential (V_{oc}) = 952 mV much greater than the values of J_{sc} = 0.197 mA cm⁻² and V_{oc} = 607 mV for the one-compartment cell. Importantly, the electromotive force for the two-compartment H₂O₂-PFC exceeds the thermodynamic value of 534 mV calculated from the electrode potentials for the half-reactions.

1. Introduction

Photofuel cell (PFC) using TiO₂ as the photoanode has recently emerged as a new type of fuel cells [1–6]. Besides the usability of biomass and bio-related compounds as the fuel and the excellent stability, the PFC can be expected to provide high electromotive force (EMF) due to the input light energy. In practice, the EMF reported for the PFCs (EMF_{PFC}) using various fuels is significantly smaller than the thermodynamic value (EMF_{th}), e.g., the EMF_{PFC} for the ethanol-PFC is 43% of the EMF_{th} [2]. More recently, we have developed a one-compartment H₂O₂-PFC, but the EMF_{PFC} still remains ~70% of the EMF_{th} [7]. There are two possible reasons for the low EMF_{PFC}. One is the loss of the excited electrons in the CB of TiO₂ (e_{CB}⁻) due to the trapping by the H₂O₂-surface complex [8] during the transport to the electron-collecting electrode (Eq. 1) [9], while the surface complex gives visible-light responsibility to the cell [7].



The other is the large overpotential for H₂O₂ reduction at the cathode [10]. Previously, Itaya et al. showed that Prussian blue film deposited on fluorine-doped tin oxide (PB/FTO) possesses electrocatalytic activity for the reduction of O₂ and H₂O₂ [11]. Further, The research group of Shaegh and Nguyen has recently reported a H₂O₂-FC using PB as the cathode material [12].

To solve these two problems simultaneously, we constructed a two-compartment H₂O₂-PFC with the structure of mesoporous TiO₂ nanocrystalline film coated on fluorine-doped tin oxide electrode (mp-TiO₂/

FTO, photoanode)|0.1 M KClO₄|Nafion|0.1 M KClO₄ with 0.1 M H₂O₂ (pH 3)|PB film-deposited FTO electrode (PB/FTO, cathode). Here we show for the first time that the EMF_{PFC} far exceeds the EMF_{th}.

2. Experimental methods

A paste containing anatase TiO₂ particles with mean size of 20 nm (PST-18NR, Nikki Syokubai Kasei) was coated on FTO electrode (sheet resistance = 10 Ω/square) by the doctor blade technique. The as-coated film was heated at 773 K for 1 h to form mp-TiO₂/FTO. The specific surface area and pore volume of mp-TiO₂ were determined by nitrogen adsorption-desorption isotherms at 77 K with a micromeritics automatic surface area and porosimetry analyzer (TriStar 3000, Shimadzu). PB films were electrodeposited on FTO (PB/FTO) from an aqueous solution of ferric-ferricyanide [13]. A three-electrode photoelectrochemical cell with the structure of FTO working electrode|a mixed aqueous solution of 0.02 M FeCl₃ and 0.02 M K₃[Fe(CN)₆] (200 mL)|Ag/AgCl reference electrode (TOA-DKK)|GC counter electrode was fabricated. PB films were electrodeposited on FTO under a constant current of -40 μA cm⁻². The film thickness (l_{PB}) was controlled by the electrodeposition time (t_{ed}). Scanning electron microscopic (SEM) observation was carried out by Hitachi S-4800 Type II at an applied voltage of 20 kV.

A two-compartment H₂O₂-PFC with the structure of mp-TiO₂/FTO (apparent area = 1.0 × 1.0 cm²)|0.1 M KClO₄|separator|0.1 M KClO₄ and 0.1 M H₂O₂|PB/FTO was constructed using Nafion (Aldrich) as the separator. PB is stable in acidic solution, while it easily dissolves into

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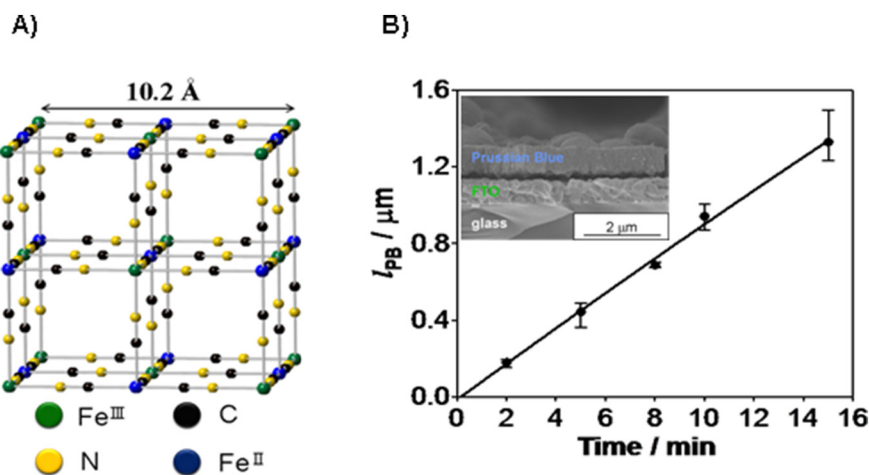


Fig. 1. (A) Crystal structure of PB. (B) Plots of the thickness of the PB film thickness versus electrodeposition time. The inset shows a SEM image for the cross-section of PB/FTO.

alkaline solution. Then, the pH of the catholyte was regulated at 3. For comparison, one-compartment H_2O_2 -PFC with the structure of mp-TiO₂/FTO (apparent area = $1.0 \times 1.0 \text{ cm}^2$)|0.1 M NaClO₄ and 0.1 M H₂O₂ (pH 3)|PB/FTO was fabricated. The current (J)-cell voltage (V_{cell}) curves for the cells were measured using a potentiogalvanostat (HZ-7000, Hokuto Denko) under irradiation of UV-light ($\lambda = 365 \pm 25 \text{ nm}$, $I_{365} = 31.2 \text{ mW cm}^{-2}$) by a UV-LED (HLV-24UV365-4WNRBTNJ, CCS) at 298 K.

3. Results and discussion

SEM observation confirmed that mp-TiO₂ film with thickness of $4.0 \mu\text{m}$ is formed on FTO. The specific surface area and pore volume of mp-TiO₂ were determined to be $17.28 \text{ m}^2 \text{ g}^{-1}$ and $0.72 \text{ cm}^3 \text{ g}^{-1}$, respectively. Pore size distribution analysis by the Barret-Joyner-Halenda (BJH) method afforded a peak pore size of $\sim 20 \text{ nm}$ [14]. As shown in Fig. 1A, PB possesses a cubic unit cell dimension of 10.2 \AA to form unique nanopores. The electrodeposition of PB on FTO induces a diffraction peak at $2\theta = 17.58^\circ$ assignable to the diffraction from its (200) plane (ICDD 00-052-1907). SEM image for a PB/FTO sample in the inset in Fig. 1B exhibits that a fairly uniform PB film is deposited on FTO. The thickness of PB film (l_{PB}) increases in proportion to t_{ed} according to the following equation of $l_{\text{PB}}(\mu\text{m}) = 0.0895t_{\text{ed}}/\text{min}$.

Two-compartment H_2O_2 -PFC with the structure of mp-TiO₂/FTO|0.1 M KClO₄ (pH 3)|Nafion|0.1 M KClO₄ with 0.1 M H₂O₂ (pH 3)|PB/FTO ($l_{\text{PB}} = 0.90 \mu\text{m}$), and the cell performance was compared with that for one-compartment cell with the structure of mp-TiO₂/FTO|0.1 M KClO₄ with 0.1 M H₂O₂ (pH 3)|PB/FTO ($l_{\text{PB}} = 0.90 \mu\text{m}$). In each cell, no current flowed in the dark. Fig. 2A shows photocurrent (J)-cell voltage (V_{cell}) curves for the H_2O_2 -PFCs were measured under UV-light irradiation at 298 K. The one-compartment cell provides a short-circuit current (J_{sc}) of 0.197 mA cm^{-2} and an open-circuit voltage (V_{oc}) of 607 mV. Strikingly, in the two-compartment cell, the J_{sc} and V_{oc} values increase to 1.14 mA cm^{-2} and 952 mV, respectively. Fig. 2B shows power density as a function of J for the cells. Both the curves exhibit volcano-shaped ones with a peak of $0.0493 \text{ mW cm}^{-2}$ at $J = 0.140 \text{ mA cm}^{-2}$ for the one-compartment cell and a peak of 0.247 mW cm^{-2} at $J = 0.635 \text{ mA cm}^{-2}$ for the two-compartment cell. Fig. 2C shows plots of J_{sc} and V_{oc} for the two-compartment H_2O_2 -PFC as a function of l_{PB} . The J_{sc} increases with increasing l_{PB} to reach a constant value of $\sim 1.1 \text{ mA cm}^{-2}$ at $l_{\text{PB}} > 0.1 \mu\text{m}$, while the V_{oc} is almost independent of l_{PB} . Clearly, the division of the H_2O_2 -PFC cell in two compartment dramatically enhances the cell performances, and PB contributes to the increase in J_{sc} . Fig. 2D shows the effect of light intensity at $\lambda = 365 \text{ nm}$ (I_{365}) on the J_{sc}

and V_{oc} for the two-compartment H_2O_2 -PFC with $l_{\text{PB}} = 0.90 \mu\text{m}$. The V_{oc} gradually increases with an increase in I_{365} to approach a saturated value of $940 \pm 12 \text{ mV}$. On the other hand, the J_{sc} increases almost in proportion to I_{365} at $I_{365} < 31.2 \text{ mW cm}^{-2}$.

The electrons in the valence band (VB) of TiO₂ are excited to the CB by UV-light irradiation. At the mp-TiO₂/FTO photoanode, the VB-holes with strong oxidation ability oxidize H₂O in the two-compartment PFC, while they preferentially oxidize H₂O₂ in the one-compartment PFC [7]. On the other hand, the excited electrons are accumulated in the CB of TiO₂ under open-circuit conditions, which causes the negative shift in the electrode potential (E_{ph}) with respect to the equilibrium value in the dark (E_{dark}). Thus, the potential change becomes negative ($V_{\text{oc}} = E_{\text{ph}} - E_{\text{dark}}$), and on stopping the irradiation, the V_{oc} gradually approaches to zero. The mean lifetime of the excited electrons in the CB of TiO₂ (τ_{n}) can be estimated by analyzing the decay curve by Eq. 2 [15].

$$\tau_{\text{n}} = -(k_{\text{B}}T/q)(dV_{\text{oc}}/dt)^{-1} \quad (2)$$

where k_{B} is the Boltzmann constant, and q is the elementary charge of electron.

Fig. 3A compares the $\log \tau_{\text{n}}-V_{\text{oc}}$ curves for the one-compartment and two-compartment PFCs. At the same V_{oc} , the τ_{n} for the two-compartment cell is much longer than that for the one-compartment cell. Evidently, the division of the H_2O_2 -PFC in two compartments leads to a significant extension of the lifetime of the electrons in the CB of TiO₂ or the enhancement of the electron transport to the FTO electrode without trapping by the surface complexes. Fig. 3B shows cyclic voltammetry (CV) curves for PB/FTO in 0.1 M KClO₄ without and with 0.1 M H₂O₂. In the absence of H₂O₂, a pair of current peaks corresponding to the redox reaction between PB and Evaritt's salt (ES, Fe₄[Fe^{II}(CN)₆]₃) is observed at the formal potential $E^{\circ} = +0.38 \text{ V}$ (Eq. 3). The cathodic current sharply weakens at $E < +0.2 \text{ V}$ as a result of the decrease in the number of Fe^{III} ions in the PB film. In the presence of H₂O₂, a large current continues to flow at $E < +0.2 \text{ V}$, and the anodic current peak disappears. Thus, the current at $E < -0.1 \text{ V}$ mainly results from the PB-mediated reduction of H₂O₂. PB/FTO exhibits electrochromism in aqueous electrolyte solution of KClO₄ [16]. As a result of the cyclic potential scan between $+0.8 \text{ V}$ and -0.2 V , the color reversibly changes between blue and colorless in the absence of H₂O₂, but it remains blue in the presence of H₂O₂. These results as well as the data in Fig. 2C strongly suggest that the electrons accumulated in PB are smoothly consumed by the H₂O₂ reduction, i.e., PB acts as an electrocatalyst for the H₂O₂ reduction (Eq. 4) [11]. In this case, the reduction of H₂O₂ is suggested to occur at not only the external surface but also the internal surface in the PB nanopores.

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