

# Properties of the Enzyme Electrode Fabricated with a Film of Polythiophene Derivative and its Application to a Glucose Fuel Cell

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**ABSTRACT:** A polymer electrode in the form of a thin film was prepared by electrochemical copolymerization of 3-methylthiophene and thiophene-3-acetic acid. Glucose oxidase (GOx) was immobilized by covalent binding to the carboxyl groups on the electrode, and the GOx-immobilized electrode (GOx-electrode) was used as an anode in a glucose fuel cell. It was demonstrated by cyclic voltametry that in the presence of *p*-benzoquinone (BQ), which was adopted as an electron mediator, the GOx-electrode generated a significant glucose-oxidation current depending on the concentrations of both glucose and BQ. A large surface area of the

GOx-electrode was considered to afford effective environment for the enzyme reaction and electron transfer. The fuel cell using the GOx-electrode as an anode gave a power output of 42  $\mu\text{W}/\text{cm}^2$ -anode at 30°C, when its anodic compartment contained 100 mM glucose and 10 mM BQ. The performance of the cell was influenced by the concentrations of glucose and BQ in the anodic compartment. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 2947–2953, 2007

**Key words:** conducting polymers; electrochemical oxidation; energy transfer; enzyme electrode; glucose oxidase

## INTRODUCTION

In recent years, great attention has been paid to biofuel cells which generate electrical power using biomass as fuel.<sup>1–8</sup> Special interests are focused on glucose because of its important role in the substance metabolism of living bodies. Glucose is metabolized into carbon dioxide and water through gradual oxidation reactions by the catalysis of enzyme in living bodies. The free energy change in this process is  $-2823$  kJ/mol.<sup>9</sup> If it is possible to obtain the energy from glucose *ex vivo* effectively, glucose can be used as a safe and rich energy source in compact electric power supplies for portable and implantable devices.

The extraction of energy from glucose in the biofuel cell involves the electrical oxidation of glucose on an anode. The direct electrochemical oxidation of glucose may be carried out with some of metal or alloy catalysts. However, in general, energy extraction by the direct oxidation is difficult because of its relatively high potential.<sup>10,11</sup> It is a convenient approach to use biocatalysts in such a process.<sup>12–15</sup> For this reason, the enzyme electrode bearing glucose oxidase (GOx) on its

surface will be used as an effective glucose-oxidizing anode. GOx catalyzes the oxidation of glucose to D-glucono- $\delta$ -lactone<sup>16–18</sup> and, accompanying this process, electrons can be released from the reduced form of GOx and transferred to the anode at a proper potential. A considerable power output will be obtained by incorporating an appropriate electron mediator.

Enzyme electrodes have been fabricated by the modification of metal surfaces with self-assembled monolayers,<sup>19–21</sup> redox polymers,<sup>22–25</sup> and conducting polymers.<sup>26–29</sup> The immobilization of enzymes has been carried out by covalent attachment, electrostatic interaction, and entrapment.<sup>30–32</sup> Conducting polymers are promising candidates for the component of the enzyme electrodes because they are synthesized readily in the form of thin films by electrochemical polymerization of heterocyclic compounds such as thiophenes and pyrroles.<sup>33–35</sup> In addition, it is possible to introduce the functional groups as enzyme-binding sites to polymer chains by a choice of appropriate monomers.

In our previous works, polythiophenes and polypyrroles were used as conducting components of enzyme electrodes, such as the GOx-immobilized electrode (GOx-electrode) for glucose sensing.<sup>35,36</sup> The conducting polymers were synthesized in the form of thin films by electrochemical polymerization, and enzymes were immobilized by covalent-binding reaction with the functional groups on the polymer films. Especially, the copolymer of thiophene deriva-

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tives had a high conductivity and, therefore, was favorable as a component of the enzyme electrode. In the present study, the GOx-electrode was fabricated with the copolymer of 3-methylthiophene (3MT) and thiophene-3-acetic acid (T3A), and used as an anode in a glucose fuel cell employing *p*-benzoquinone (BQ) as an electron mediator (Scheme 1). With respect to the enzyme reaction and the electron transfer to the GOx-electrode, various factors were taken into consideration, and the influence of them on the performance of the glucose fuel cell was investigated.

## EXPERIMENTAL

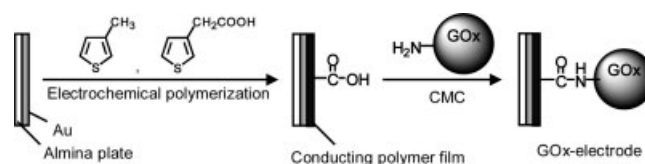
### Materials and instruments

All chemicals were of guaranteed-reagent grade and used without further purification: 3MT, BQ, and tetraethylammonium perchlorate from Nacalai Tesque (Kyoto, Japan); T3A from Tokyo Kasei Kogyo (Tokyo, Japan); GOx (EC 1.1.3.4., 154 U/mg,) from Toyobo; D-glucose from Wako Pure Chemical Industries (Osaka, Japan); 1-cyclohexyl-3-(2-morpholinoethyl)carbodiimide metho-*p*-toluenesulfonate (CMC) from Aldrich Chem. (St. Louis, MO) Nafion<sup>®</sup> 112 (perfluorinated membrane with a thickness of 0.002 inches.) was also purchased from Aldrich.

Electrochemical measurements (cyclic voltammetry and amperometry at a constant applied potential) were carried out by use of a potentiostat/galvanostat (Hokuto Denko Corp., Tokyo, Japan, HA-150G), a bipolar coulomb/ampere hour meter (Hokuto Denko Corp. HF-203D), and an arbitrary function generator (Hokuto Denko Corp. HB-105A).

### Preparation of conducting polymer and immobilization of GOx

Conducting polymer films were prepared electrochemically in a common three-electrode electrochemical cell consisting of Au working electrode, Pt coun-



Scheme 2 Preparation of GOx-electrode.

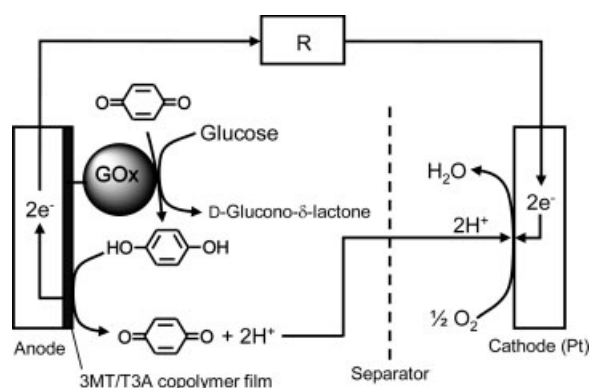
ter electrode, and saturated calomel electrode (SCE) which was used as a reference electrode. A solution of 3MT (0.45M), T3A (0.05M), and tetraethylammonium perchlorate (0.10M) in acetonitrile (20 mL) was placed in the electrochemical cell, and nitrogen gas was passed through the solution for more than 20 min. Then a potential of +2.2 V versus SCE was applied to the Au working electrode until the amount of passed charge was reached to 3.2 C/cm<sup>2</sup> at room temperature. The conducting polymer film was then rinsed with distilled water to remove the residual monomers and weakly adsorbed polymer.

Subsequently, the polymer deposited electrode was immersed in a solution containing GOx (5 mg/mL) and CMC (24 mg/mL) for 18 h at 4°C to immobilize GOx covalently on the surface of the conducting polymer film. The conducting polymer electrode bearing GOx (GOx-electrode) was rinsed with distilled water well and kept in a phosphate buffer (0.10M, pH 7.0) at 4°C.

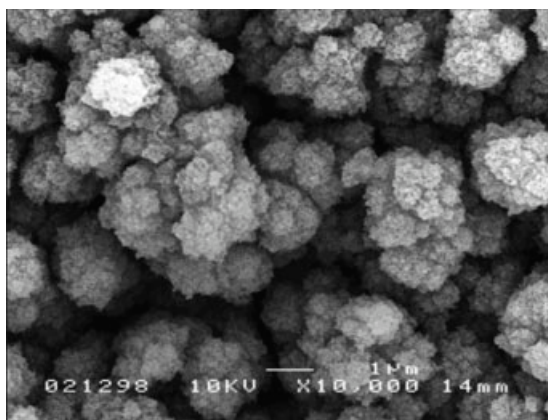
### Electrochemical measurements

Cyclic voltammetry of the GOx-electrode was carried out in phosphate buffers (0.10M, pH 7.0) containing various concentrations of BQ and glucose at 30°C under air. A Pt counter electrode and a SCE reference electrode were used and the scan rate was 5 mV/s in all measurements.

A two-compartment glass cell was used to investigate the performance of the fuel cell for power generation from glucose. The cell was constructed with anodic and cathodic compartments having the GOx-electrode and a Pt-mesh electrode, respectively. These compartments of the cell were isolated by a polyelectrolyte film, Nafion<sup>®</sup>. Phosphate buffer (0.10M, pH 7.0, 50 mL) was placed in each compartment of the cell, and BQ and glucose were added to the anodic compartment. Measurements of the cell performance for power generation were carried out by recording current values when arbitrary potentials were applied between the anode and the cathode at 30°C. Prior to the measurements, the Pt-mesh electrode was soaked in 50% H<sub>2</sub>SO<sub>4</sub> for 10 min and then rinsed thoroughly with distilled water. Both the anodic and cathodic compartments were kept under atmospheric pressure during experiments.



Scheme 1 Schematic illustration of glucose fuel cell using GOx-electrode as an anode.



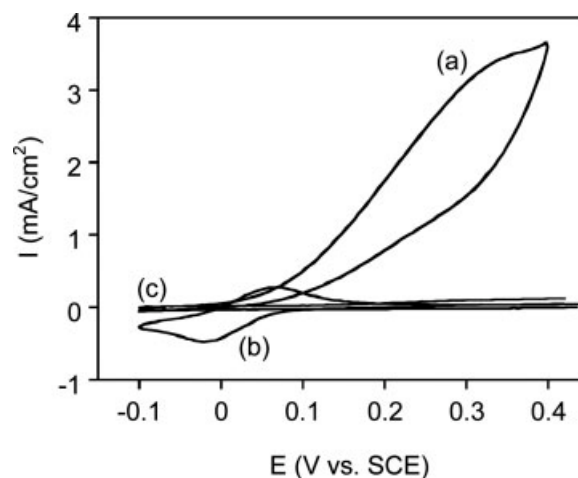
**Figure 1** SEM micrograph ( $\times 10000$ ) of 3MT/T3A copolymer surface.

## RESULTS AND DISCUSSION

### Preparation and characteristics of the GOx-electrode

The GOx-electrode was prepared by the two-step method as illustrated in Scheme 2. In advance, 3MT and T3A were copolymerized electrochemically on an Au working electrode ( $0.25 \text{ cm}^2$ ), and a black film (3MT/T3A copolymer) was obtained on the electrode. Succeedingly, GOx was immobilized on the film through amide linkages by condensation reaction between amino groups of GOx and carboxyl groups of T3A units in the copolymer. The content of T3A units in the copolymer was determined to be  $\sim 10\%$ . The composition was identical to that adopted in our previous studies for glucose sensing,<sup>33,36</sup> which was optimized on the basis of conductivity and GOx-immobilizing ability. The conductivity of the copolymer film may be related to its morphology.<sup>37</sup> Figure 1 shows the SEM micrograph of the GOx-electrode surface, in which granular structure is seen. With respect to the definition of conductivity, an allometric scaling law has been proposed for conducting polymers.<sup>38</sup>

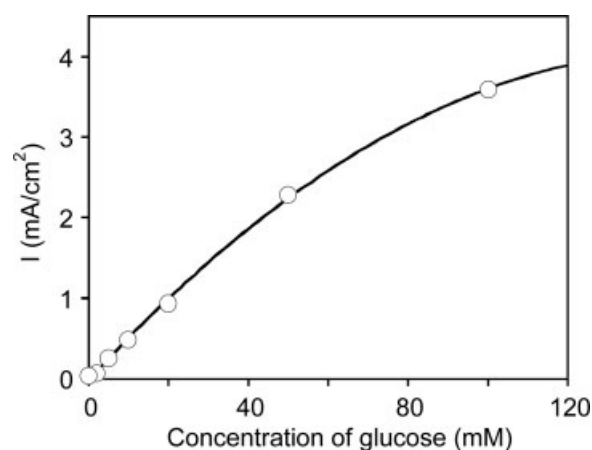
In the presence of glucose and/or BQ, the electrochemical properties of the GOx-electrode were investigated by cyclic voltammetry (Fig. 2). As shown in Figure 2(a), the GOx-electrode generated a large glucose oxidation current in the presence of both glucose and BQ. When glucose was absent in analyte solution, only redox peaks of BQ were observed as shown in Figure 2(b). Thus, the GOx-electrode fabricated with the conducting polymer film functioned effectively in both glucose oxidation and electron transfer. In addition, in the absence of BQ, no response to the glucose was seen as shown in Figure 2(c) but, after addition of BQ, a great increase in glucose oxidation current was observed as shown in Figure 2(a). It is generally accepted that the redox site of GOx is buried in the interior of its protein



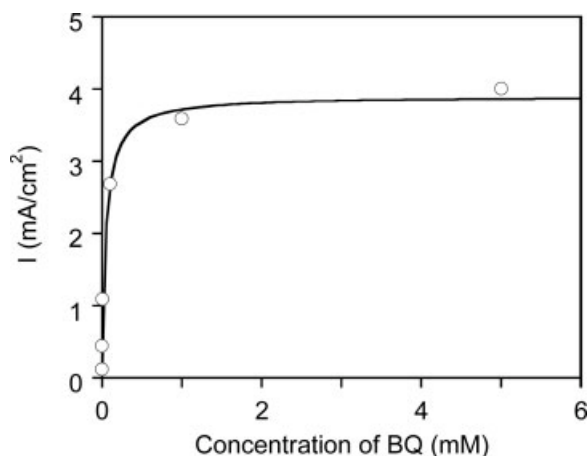
**Figure 2** Cyclic voltammograms measured with GOx-electrode in the presence of 1 mM of BQ and 100 mM of glucose (a), 1 mM of BQ (b), and 100 mM of glucose (c).

shell and the direct electron transfer from GOx to the electrode surface is very difficult. Therefore, the large current shown in Figure 2(a) was considered to demonstrate the important role of BQ in electron transfer from GOx to the electrode surface.

The influence of glucose and BQ concentrations on the oxidation current of the GOx-electrode was investigated by cyclic voltammetry. The values of glucose oxidation current extracted from cyclic voltammograms are plotted against glucose concentration in Figure 3. It was found that the oxidation current increased linearly with increasing concentration of glucose up to 50 mM. This result evidently means that the current generation was due to glucose oxidation on the GOx-electrode. Figure 4 shows the influence of BQ concentration on the glucose oxidation current. When the concentration of BQ was lower



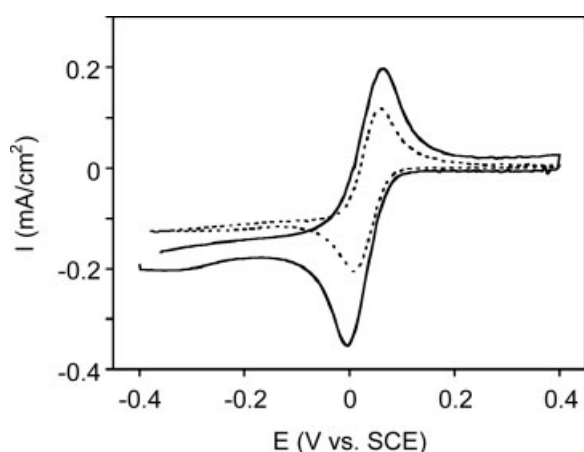
**Figure 3** Plots of value of glucose oxidation current against glucose concentration.



**Figure 4** Relation between glucose oxidation current and concentration of BQ. Measurement was carried out with 100 mM of glucose.

than 0.1 mM, electron mediation could not occur sufficiently and, therefore, the glucose oxidation current became extremely small. Thus, backed up by the electron mediation with BQ, the glucose oxidation brought a large current. In view of the fact that the value of the glucose oxidation current was almost constant in the BQ concentration range above only 1 mM (Fig. 4), the dependence of the oxidation current on the glucose concentration up to 100 mM (Fig. 3) suggests that the rate determining step can be the reaction between glucose and the immobilized GOx. In addition, with respect to the nature of BQ as an electron mediator, it should be remarked that the oxidation current was observed even in the presence of only 1  $\mu$ M of BQ.

On the other hand, the redox behavior of BQ on the 3MT/T3A copolymer film was compared with



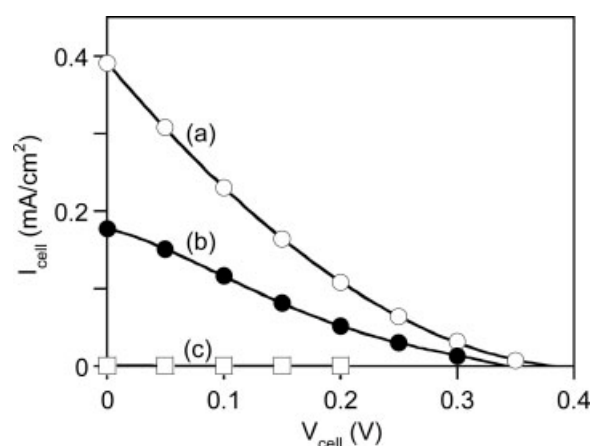
**Figure 5** Cyclic voltammograms measured with Au (dotted line) and 3MT/T3A copolymer (solid line) electrodes in the presence of 1 mM of BQ.

that on the Au electrode. As shown in Figure 5, the copolymer film gave larger redox peaks than the Au electrode. Taking it into account that the copolymer film has a lower conductivity than Au, the copolymer film can be considered to have a larger surface area, probably because of its granular surface structure, than the Au electrode. Therefore, the 3MT/T3A copolymer film is preferable to fabrication of enzyme electrodes in both aspects of electron transfer and enzyme immobilization. This is the reason why the conducting copolymer film was adopted as a component of the GOx-electrode.

#### Generation of electricity with the fuel cell using the GOx-electrode as an anode

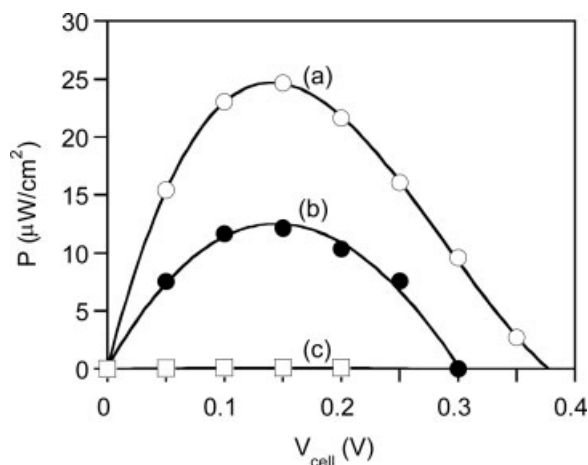
Figure 6 shows the current–voltage ( $I$ - $V$ ) behavior of the fuel cell using the GOx-electrode as an anode at different concentrations of glucose, in which it is seen that the value of cell current ( $I_{\text{cell}}$ ) increased with increasing concentration of glucose in the anodic compartment. The  $I_{\text{cell}}$  was not observed when glucose was absent in the analyte solution. These results were consistent with the data in Figure 3. Although the fuel cell gave an almost linear  $I$ - $V$  line at each glucose concentration, the short-circuit current ( $I_{\text{cell}}$  at 0 V of  $V_{\text{cell}}$ ) decreased with decreasing concentration of glucose. The open-circuit voltage ( $V_{\text{cell}}$  at 0 A of  $I_{\text{cell}}$ ) seemed independent of the glucose concentration. As to the  $I$ - $V$  behavior of the fuel cell at various concentration of glucose, the allometric scaling law may be derived as attempted for the electrospinning process used in the preparation of polymer fibers,<sup>39,40</sup> though a mathematical model describing the  $I$ - $V$  curves is still under consideration.

As shown in Figure 7, where the values of power output ( $P$ ) of the cell calculated from  $I_{\text{cell}}$  and  $V_{\text{cell}}$



**Figure 6** Current-voltage behavior of the fuel cell in the presence of 1 mM of BQ together with 100 mM (a), 5 mM (b), and none (c) of glucose.



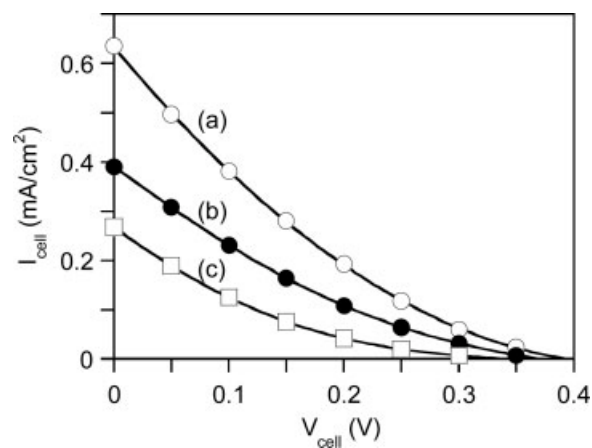


**Figure 7** Power output of the fuel cell in the presence of 1 mM of BQ together with 100 mM (a), 5 mM (b), and none (c) of glucose.

were plotted against  $V_{\text{cell}}$ , it was confirmed that a considerable value of  $P$  was obtained from glucose by using the GOx-electrode as an anode. It is commonly known as cell behavior that maximum power output ( $P_{\text{max}}$ ) is observed at a  $V_{\text{cell}}$  between 0 V and the open-circuit voltage. In the presence of 100 mM glucose and 1 mM BQ, a  $P_{\text{max}}$  was 25  $\mu\text{W}/\text{cm}^2$ -anode at 0.15 V of  $V_{\text{cell}}$  as seen in Figure 7(a). On the contrary, as seen in Figure 7(c),  $P$  was not observed at all when no glucose was present in the anodic compartment. As for Figure 7(a,b), it is interesting to note that  $P_{\text{max}}$  was observed at the same value of  $V_{\text{cell}}$  independently of the glucose concentration. However, as shown Table I, the value of  $P_{\text{max}}$  depended on the glucose concentration especially in the range lower than 10 mM. It was already shown in Figure 3 that the glucose oxidation current was influenced markedly by the glucose concentration. The value of  $P$  is given by the product of  $V_{\text{cell}}$  and  $I_{\text{cell}}$  and, therefore, it is apparent that the perform-

**TABLE I**  
Influence of Concentration of Glucose and BQ on Maximum Power Output of the Cell

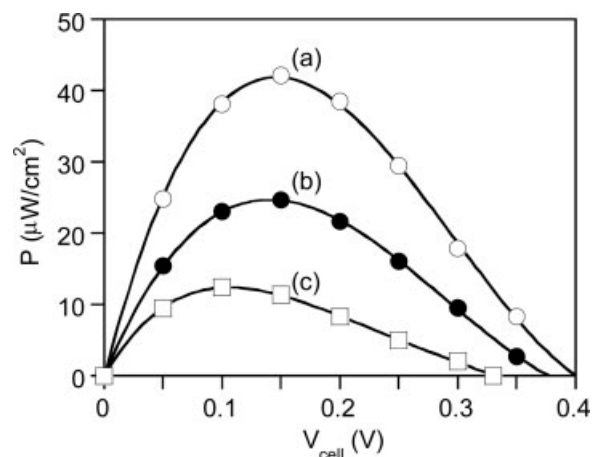
Concentration		$P_{\text{max}}$ ( $\mu\text{W}/\text{cm}^2$ )
Glucose	BQ	
0	1	0
1	1	1
5	1	12
10	1	23
50	1	22
100	0.01	6
100	0.1	12
100	1	25
100	5	38
100	10	42



**Figure 8** Current-voltage behavior of the fuel cell in the presence of 100 mM glucose together with 10 mM (a), 1 mM (b), and 0.1 mM (c) of BQ.

ance of the cell reflected the magnitude of glucose oxidation current.

Figures 8 and 9 show the influence of BQ concentration on the  $I$ - $V$  line and the  $P$  value of the fuel cell, respectively. It can be seen that the concentration of BQ in the anodic compartment, as well as that of glucose, is an important factor in the performance of the fuel cell. The values of  $P_{\text{max}}$  at various concentration of BQ are listed in Table I. The value of  $P_{\text{max}}$  reached 42  $\mu\text{W}/\text{cm}^2$ -anode when the concentrations of glucose and BQ were 100 and 10 mM, respectively. The influence of the concentration of BQ appeared markedly at a lower concentration than 1 mM. This result is consistent with the results of cyclic voltammetry in Figure 4. Although  $P_{\text{max}}$  of the cell was dependent on the concentration of BQ,  $\sim 14\%$  of the output at 10 mM BQ was kept even at



**Figure 9** Power output of the fuel cell in the presence of 100 mM of glucose together with 10 mM (a), 1 mM (b), and 0.1 mM (c) of BQ.

0.01 mM of BQ. As shown in Scheme 1, being different from glucose, BQ is not consumed in the anodic reaction and, therefore, a considerable value of  $P_{\max}$  can be obtained at such low concentration of BQ.

Enzyme reactions are influenced by various factors, among which the products of enzyme reaction are of importance. The influence of D-glucono- $\delta$ -lactone, which is the product of glucose oxidation by GOx, on the glucose oxidation current, was investigated. It was found that, in the presence of 100 mM glucose, the glucose oxidation current was decreased by 25% when the equivalent amount of D-glucono- $\delta$ -lactone was added to the cell. In addition, when its concentration was increased to 500 mM (5 times of the glucose concentration), the oxidation current was lowered by  $\sim$  50%. As for the cell performance, the value of  $P_{\max}$  fell down to 50% when the same concentrations (100 mM) of D-glucono- $\delta$ -lactone and glucose were present in the anodic compartment. The cell operation using 100 mM of glucose gave the result that it took the period of 3.5 days to generate 5 mM of D-glucono- $\delta$ -lactone which lowered  $P_{\max}$  to 80% of the initial value. Thus, the influence of enzyme reaction products seemed not significant in the present experimental conditions though it should be taken into account when long-term operation is carried out.

## CONCLUSIONS

The GOx-electrode was prepared by immobilizing GOx on a 3MT/T3A copolymer film, and a glucose fuel cell was constructed with the GOx-electrode and Pt as an anode and a cathode, respectively. In the presence of both glucose (fuel) and BQ (an electron mediator), the GOx-electrode generated a significant current because of glucose oxidation depending on the concentrations of them. The merit of the GOx-electrode was confirmed with regard to glucose oxidation and electron transfer, which was attributed to a large surface area of the 3MT/T3A copolymer. The fuel cell gave 42  $\mu\text{W}/\text{cm}^2$ -anode of  $P_{\max}$  at 0.15 V of  $V_{\text{cell}}$  at 30°C when its anodic compartment contained 100 mM of glucose and 10 mM of BQ. The cell performance was found to be affected by the concentrations of glucose and BQ. These effects of the concentrations on the performance of the fuel cell showed a similar tendency to those on the glucose oxidation current generated by the GOx-electrode. Thus, it was demonstrated that the GOx-electrode functioned well as an anode in the glucose fuel cell system.

In the present study, the GOx-electrode was evaluated as an anode of a glucose fuel cell by use of BQ as an electron mediator. Therefore, the potential of the GOx-electrode was comparable to the redox potential of BQ. It is needless to say that the performance of the fuel cell can be

improved by an adequate choice of the mediator having a lower redox potential and higher electron-transferring ability. In addition, the fuel cell may be constructed with no separator by immobilization of mediators on the GOx-electrode. The choice of an optimal mediator and its immobilization on the GOx-electrode are under investigation as the important subjects relevant to the development of the glucose fuel cell.

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