Power Generation by Harvesting Dissolved Oxygen in Water and Deoxidation Using Fuel Cells

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Fuel cells harvest dissolved oxygen (DO) in water, and can be utilized by same performances to the cell in air within the rated power output. It is also found that fuel cells remove O_2 from air and water in closed containers. In deoxidation, several methods, such as direct water supply, bubbling and artificial gill in DO water are studied. The ability of harvesting DO is discussed with relationships between electrical current and O_2 flow rate.

Key words: biofuel cell, water, dissolved oxygen, output

1. INTRODUCTION

Animals are breathing air, which contains O_2 by 20.9%. On the other hand, fishes live in water in spite of only 8ppm of O_2 . Living creatures started from sea and produced O_2 by photosynthesis from CO_2 in air since thousand million years ago. We have interested in, whether fuel cell works taking dissolved oxygen (DO) in water. Few reports on this topic have been found except for microbial fuel cells [1,2]. Research studies on biofuel cells [3,4] have been mainly devoted to improve performances of anode catalysts and ion exchange membrane from bio energy to electrical power. In this report, characteristics of biofuel cells (non-microbe) which harvest DO, are described.

It should be noted that the O_2 contents are equilibrated at the interface between air and water by the ambient condition. The fact indicates that the same number of O_2 molecules exchanged at the air/water interface. The difference is diffusion rates of O_2 in air and water, which determines performances of fuel cells. The small content of DO in water originates from the poor solubility, indicating favorable in release of O_2 in water.

Oxygen is crucial substance for all living creatures, and also cultivates putrefaction and accelerates corrosion. Removal of O_2 (deoxidation) is the key issue to preserve foods and medicines for long term, in combination of wrapping them by barrier films. Possibility and ability of deoxidation of DO water by fuel cell are also described.

2. FABRICATION OF BIOFUEL CELL

Schematics of a system to evaluate performances of fuel cells [5-7] are shown in Fig.1. The system was composed of four parts, (a) fuel cell, (b) fuel tank, (c) external circuit to evaluate cell performance, (d) water from open container and (e) DO gas from closed container. L-ascorbic acid (0.5M AsA) was used for the fuel, which was circulated by a pump to anode with the rate of 2mL/min. The electrical output from the fuel cell was measured by the external circuit for the cell voltage (E_{cell}) and current (i) by changing the load resistance (R_L).

DO was supplied to the cathode by methods of direct

DO water and gas harvesting DO by an artificial gill. Gills were fabricated by silicon tube, because it is known for the large oxygen permeability and commonly available (from AS ONE). The tube with the inner and outer diameters of 2.5mm $\times$ 3.5mm with the lengths of 1.0 and 2.5m was used. In the long tube, a steel wire with diameter of 1.6mm was inserted to keep the shape in coil. The diameter of coils was 5cm with lengths of 3 and 6cm. The gas from the gill was circulated to cathode by the rate of 100~150mL/min. Flow rates of DO water were 2~5 mL/min.

Fig.1 Schematic drawing for harvesting DO in water using fuel cell

The structure of biofuel cell is shown in Fig.2. The core laminate was composed of anode, cathode catalysts and a cation exchange membrane (CEM). A composite film of poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT*PSS) and single walled-carbon nanotube (SWCNT) was used for the anode catalyst [7]. This anode catalyst demonstrated the best performance for AsA fuel cell. Pt-black (PT-B) pasted on carbon sheet by the amount of 3mgcm⁻² was employed for the cathode catalyst. Nafion (N117) was used for the CEM. The surface area

of catalysts were $1 \times 1 \text{ cm}^2$. The typical performance of the cells, namely, open circuit voltage (E_0) was 0.55V, maximum output power ($P_{\max}$) and maximum current ($I_{\max}$) were $1.2 \sim 2.0 \text{ mW}$ and $10 \sim 15 \text{ mA}$, respectively. The experiment was carried out at air conditioned room temperature of $\text{ca. } 22^\circ \text{C}$. The water temperature was assumed to be equilibrated to the room temperature. The cell performances somehow depended on assembly of the core laminates. The detail structure and materials are described in our previous papers [5-8].

Fig.2 Structure of the biofuel cell

3. POWER GENERATION USING DO IN WATER

3.1 Harvesting DO directly from water

The cell performance was evaluated from polarization curves[5-8], that is, i (A) dependence of E_{cell} (V) and power $P = i \times E_{\text{cell}}$ (W). It is noted that i and P were values per unit area (cm^2) in this experiment. The typical results of polarization curve are shown in Fig.3, which were obtained by the cell operated using air, DO water and DO sea water using Fig.1 (d) open container. The definition of cell parameters E_0 , $P_{\max}$, $E_{\max}$ and $I_{\max}$ are also shown. E_0 was obtained at the switch S off in Fig.1 (c). $P_{\max}$, $E_{\max}$ and $I_{\max}$ are the values of P , E_{cell} and i obtained at the maximum P .

Fig.3 Typical polarization curves of the cells using air, DO water and DO sea water, and definition of cell parameters.

The P obtained by feeding DO water directly showed collapsed curves at large i as shown in Fig.3. This is resulted from oxygen deficiency due to small O_2 diffusion in water. However, it should be noted that the fuel cell by DO water can be practically utilized within the rated power output $< 2 \text{ mA}$, because the drop of E_{cell} were same between air and DO water. The performance of cell fed by

quasi-sea water (3.4% NaCl added to DO water) was unfavorable to use. The decrease of E_0 is supposed to originate from polarization at the interface of catalyst. The poor performance and enhanced oxygen deficiency feature probably resulted from lower deoxidation and diffusion in salt water due to strong interaction of ions and oxygen.

3.2 Harvesting DO using silicon coil gill

In this experiment, silicon coil gill was placed in DO water in open container, and in air for comparison. Before measurements, inside of the gill was purged with N_2 gas to remove air. Upon circulation of the inner gas and discharge cell at $R_L = 11 \Omega$, O_2 contents in the silicon tube leveled off in a few minutes. The O_2 contents were 14% in air and 5.3% in DO water, which was equilibrated between consumption by cathode reaction and permeation of O_2 from outer circumstance. The output characteristics of cells supplied O_2 through the gill placed in air and DO water are shown in Fig.4, to compare efficiencies of harvesting oxygen in air and water.

Fig.4 Cells performances harvesting O_2 by silicon tube gill placed in air and DO water, figures in (%) are O_2 contents in gill.

It is noted that the performance using the silicon coil in DO water was improved in comparison with the direct supply of DO water shown in Fig.3. The improvement is supposed to originate from the large diffusion coefficient of gas phase O_2 and storage effect in the silicon tube. The result indicates that the harvesting of DO in water could be improved by optimizing the materials and structure of gill.

4 DEOXIDATION FROM CLOSED CONTAINERS

4.1 Air container

Three type containers are fabricated as shown in Fig.5 to remove O_2 from (f) air, (g) bubbling DO and (h) direct supply of DO water, in addition to Fig.1 (e).

Fig.5 Closed containers for deoxidation from (f) air, (g) bubbling DO water and (h) direct supply of DO water

Fig.6 shows time responses of E_{cell} , i and P after the

circulation of gas using the air container Fig.5 (f) with the volume of $V_0 = 2.5\text{mL}$. The cell was discharged at $R_L = 11\ \Omega$. It is noted that the output current was limited by the supply rate of O_2 to cathode, not limited by fuel supply and external load resistance. The E_{cell} and i decreased and leveled off in 13min. The level off to finite values was due to leakage of air into circulation system. The decay of i reflects the O_2 content in the system. The content of O_2 in the container can be estimated from electric charges, which is obtained by integrating i with time during discharge, namely, $q = \int i dt$. The O_2 content at 35min was 1.7% and equilibrated with the leakage of air, indicating most O_2 gas was evacuated.

Fig.6 Time responses of cell parameters after gas circulation from air container.

As shown in Fig.1 (a) at the cathode, an O_2 molecule is reduced by four electrons, the number of O_2 (j) consumed at cathode per second is given [8] by Eq.(1) using (i), where e is electron charge ($= 1.6 \times 10^{-19}\text{C}$),

$$j = \frac{i}{4e}. \quad (1)$$

From (1), the flow rate of O_2 (v ; volume of O_2 flow per second) is given by Eq.(2), using the molar volume of gas ($V_m = 22.4\text{ L/mol}$, 0°C , 1 atm),

$$v = \frac{V_m}{N_A} j = \frac{V_m}{4F} i. \quad (2)$$

Where, N_A ($= 6.02 \times 10^{23}\text{ mol}^{-1}$) is the Avogadro Constant and F ($eN_A = 9.65 \times 10^4\text{ C/mol}$) is the Faraday constant. Then the volume of O_2 (V ; L) consumed during the discharge time is simply given by Eq.(3) in ,

$$V = \frac{V_m}{4F} \int i dt = \frac{V_m}{4F} q \quad (3)$$

It is convenient to note, $\frac{V_m}{4F} = 0.058\text{ mL/C}$.

From Fig.6, q is obtained to be 10C, which corresponds to $V = 0.58\text{mL}$. This O_2 content estimated from charges was a little larger than 0.53mL estimated from the volume of container, which is due to leakage of air.

4.2 Bubbling of DO water

DO in water was removed by bubbling in the container shown in Fig.5 (g). The volume of container was 55mL including air portion of 25mL and water of 30mL. The time response of i by discharge at $R_L = 11\Omega$ is shown in Fig.7(a). It took about 4 hours to complete harvesting O_2 .

The released charge was 92C, which corresponds to the 5.3mL of O_2 . The volume of O_2 obtained from the charge coincides to those estimated from the sum of air portion (5mL) and DO in water (0.19mL) of the container. The result indicated that the air portion should be minimized to remove O_2 by bubbling of DO in closed container.

Fig.7 Time responses of i obtained by various deoxidation methods of DO in water, (a) bubbling, (b) direct flow of water and (c) using silicon coil gill

4.3 Deoxidation of DO by direct flow of water

In this experiment the container was filled with DO water of 55mL. DO water was directly supplied to cathode by circulating water shown in Fig.5 (h). The time response of i is shown by the curve (b) in Fig.7. The i was approximately 3mA at the beginning, and then decreased gradually to nearly level off current of 0.35mA in 2 hours. The released charge was 5.6C, corresponding to 0.32mL O_2 . The amount of O_2 was nearly equal to that estimated from the volume of DO in water being 0.35mL. It is noted that the i of Fig.7(b) was noisy and smaller than the others, which originated from oxygen deficiency as shown by curve of DO water in Fig.3.

4.4 Deoxidation of DO by silicon coil gill

It has been found that the silicon coil gill is efficient to harvest DO in water because of large oxygen permeability coefficient being approximately $4 \times 10^{-8}\text{ cm}^2\text{s}^{-1}$ [8,9]. The silicon coil gill with the tube length of 2.5m was used to remove DO by the setup shown in Fig.1(e). DO water of 85mL was poured in a 100mL beaker, and purged with N_2 gas at the top. The gas from the gill was circulated by the rate of 100mL/min. Curve Fig.7(c) shows the time response of i , being similar decay to Fig.7(b). The plots of i vs t is depicted in Fig.8 to show that the i nearly leveled off after 2 hours. The released charge was 38C, corresponding to 2.2mL of O_2 volume. It is noted that the volume of inner silicon coil and connecting tubes was approximately 10mL (O_2 contents: 2.1mL) and the volume of DO water was 85mL (O_2 : 0.54mL). The total amount of O_2 in the system was estimated to be 2.6mL, which indicates at most 0.4mL O_2 remained in water.

The O_2 content in the container was monitored simultaneously by circulating DO water between DO meter and container. To keep the homogeneity in the container, water was stirred at 300 rpm. Curves in Fig.8 are time responses of i and content of DO after starting circulation of gas.

Fig.8 Time responses of DO and i during deoxidation of DO water by silicon coil gill

It is interesting to note that i decreased sharply at the beginning, and then slowly leveled off to 2.8mA at approximately 2hs. Contrary to this, the DO dropped linearly all the way. The fact could be explained by a hypothesis that the sharp decrease of i is due to deoxidation of the air part of inner tube, and the level off i is from DO in water. This hypothesis accounts for the linear decrease of DO in water. Furthermore, the residual DO content of 3.5mgL^{-1} at 3hs was not harvested yet. The residual DO of 3.5mgL^{-1} corresponds to 0.21mL in volume of O_2 in the container, which is estimated from simple calculation using the molar volume V_m . The volume of O_2 reasonably agrees with the value of 0.4mL mentioned previously. It is noted that the level off current of 2.8mA indicates the rate of permeated O_2 through the gill being $0.16\mu\text{Ls}^{-1}$ given by Eq.(2).

5. POWER PERFORMANCE vs. O_2 CONTENTS.

O_2 content dependences of cell performances were also studied to explore the limitation of cathodic reaction. As shown in Fig.9, the E_0 at lower O_2 contents increased slightly with increasing O_2 contents and leveled off around 0.55V, which is determined by redox potentials of AsA and O_2 . The $P_{\max}$ depended linearly on O_2 contents, showing no sign of saturation. The fact indicates that the fuel cell system was limited by the O_2 contents.

Fig.9 Cell performances at various contents of O_2 in silicon coil gill

If the cell performance was controlled by the other factors or variables, for example, fuel concentrations [7] and catalytic reactions, the $P_{\max}$ should saturate in this region. In other words, the $P_{\max}$ can be increased as the function of O_2 contents until the saturation by the other factors. In fact, the fuel concentration dependence of $P_{\max}$

showed saturation [7]. We found that this saturation is possibly due to the limitation by O_2 contents at this stage of experiment.

SUMMARY

It was found that fuel cells can be operated by harvesting DO in water by either way of direct water supply, bubbling and artificial gill in water. The cell harvesting DO demonstrated the same performances to that in air within the rated power output. We discussed the relationship between electric charges and contents of oxygen in detail to assure the accuracy of present methods.

The disadvantage of using DO originates to the small diffusion coefficient of O_2 in water [10]. That is, the diffusion coefficient in water is $2.0 \sim 2.4 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, which is approximately 4 orders of magnitude smaller than that in air. This resulted in oxygen deficiency at the cathode in use for heavy loads or high powers. For deoxidation from DO in water using closed containers, the air portion in the system should be exhausted by purging with inert gas before use.

Initial packing of fresh foods, medicines and drinks were perfectly sealed at factories using barrier films. Consumers have to break the seals in use; however, it is hard to repack the stuffs again in inert conditions. The technique mentioned here could be used to deoxidize containers after repacking of stuffs in home. Biofuel cells for this purpose could be manufactured in small size and low cost. Fuels could be sugars or alcohols available in home. The devices may be equipped in home refrigerators.

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