

Research Paper

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Soil Microbial Fuel Cell with Hydrophilic Treated Buckypaper Anodes

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Abstract

Fossil fuels, the primary source of energy supply in modern society, are both unsustainable and damaging to the environment. The most cost-effective way to reduce the use of fossil fuels is to switch to renewable energy sources. Soil microbial fuel cells (SMFC) are a green energy production method because they use electron-generating bacteria in the soil to obtain electrical energy from organic matter. One way to improve the output of SMFCs is to increase the specific surface area of the anodes. The larger specific surface area allows more electrons to be received from the bacteria. In this study, bucky paper (BP) was utilized as the anode of SMFC. BP is a freestanding film fabricated from multi-walled carbon nanotubes (CNT) by vacuum filtration method. CNT has a high specific surface area and electrical conductivity. BP is also considered to be mechanically stable in soil due to its CNT network structure. However, the surface of the BP is hydrophobic. In SMFCs, the hydrophobic surface of the anode is a fatal disadvantage in terms of the affinity of microorganisms. Thus, heat treatment and ultraviolet (UV) ozone treatment were employed to make the surface of BP hydrophilic, and their output in SMFCs was investigated. As a result, SMFCs using UV-ozone-treated BPs as anodes produced the highest power density of 28.8 $\mu\text{W}/\text{cm}^2$. Also, unlike thermal treatment, UV ozone treatment did not damage the CNT structure. Hence, in this experiment, the output power of the SMFC was stable for at least 140 h. Among the BP hydrophilic treatments examined in this study, UV ozone treatment was confirmed to be the most effective in improving MFC performance.

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Keywords

Buckypaper; Soil microbial fuel cell; CNT; UV ozone treatment

1. Introduction

As the demand for energy increases due to rapid population growth and the growth of civilization, fossil fuels, the main source of energy supply, are unsustainable and damaging to the environment. Conversion to renewable energy sources is the most cost-effective way to eliminate fossil fuels (Olabi & Abdelkareem, 2022). There are various renewable energy sources, including solar, wind, hydro, biomass, and geothermal, but they all have their issues, so it is necessary to examine and select as many different types of renewable energy sources as possible (Rahman et al., 2022).

Soil microbial fuel cells (SMFCs) generate electricity using electron-generating bacteria found in soil and are one of the green energy-producing methods (Li et al., 2021). SMFCs can generate power at night and in areas with no wind blowing in, where solar and wind power generation cannot operate. Therefore, the use of SMFCs as a source of power supply for sensing devices in various areas is being considered. For example, temperature and moisture sensors are driven, and long-distance wireless data transmission is performed by charging capacitors (Yamashita et al., 2019). However, the problem that SMFCs face is their low output (Simeon et al., 2022). Increasing the specific surface area of the anode increases the power output of SMFCs because more bacteria can come in contact with the anodes, and more electrons can be received from the bacteria (Yu et al., 2021). Therefore, many researchers have investigated methods and materials to increase the specific surface area of the anode (Sahari et al., 2022).

Carbon nanotubes (CNTs) are carbon-based materials with a cylindrical structure, which is expected to improve specific surface area (Guo et al., 2022). In this study, buckypaper (BP) was fabricated from multi-walled CNTs by a vacuum filtration method and used as an anode of SMFC.

BP is a freestanding CNT film with a large surface area and high electrical conductivity (Mirabootalebi, 2020). The multilayer BPs are also expected to be stable when placed in soil due to the high mechanical stability of the CNT network. However, the surface of BP is hydrophobic. Hydrophobicity causes a reduction in microbial affinity. Thus, in SMFCs, the hydrophobic surface of the anode is a fatal drawback. Two methods were investigated to make it hydrophilic: thermal treatment and ultraviolet (UV) ozone treatment. SMFCs with hydrophilized BPs as anodes were evaluated by measuring the voltage transition over time and power density.

2. Method and Experiment

2.1. BP preparation

Two ml of surfactant Triton X-100 (Alfa Aesar, UK) was dispersed in 200 ml of purified water for 20 minutes using an ultrasonic homogenizer. Next, 40 ml of multilayer CNTs solution (N7006L, KJ SPECIALTY PAPER Co., Japan) was added to the Triton X dispersion and dispersed by ultrasonic homogenizer for 30 minutes. Multilayer CNT solution of 50 ml was deposited on a paper filter (pore size: 25 μm) by vacuum filtration [10]. After deposition, the BP was dried at 60 $^{\circ}\text{C}$ for 12 h, and the BP was peeled off the paper filter (Her & Hsu, 2020).

2.2. Hydrophilic treatment of BP

Triton X-100 was used in the BP to disperse the CNTs. Therefore, the BP was heated to remove impurities from the BP. In fact, an electric furnace (ROP-001, AS ONE Corporation, Japan) was used to heat the BP at 200 $^{\circ}\text{C}$ for 2 h in the air to make it hydrophilic.

It was confirmed that UV ozone treatment on the surface of BP improves its hydrophilicity (Wang et al., 2010). To improve the hydrophilicity, the surface of the BP was cleaned by applying UV irradiation to the surface (12.5 h) using a UV ozone cleaner (UV253E, Filgen, Inc., Japan). The distance between the UV lamp (3.7 mW/cm², 184.9nm) and the BP was 9 cm.

2.3. BP surface hydrophilicity test

The improvement of hydrophilicity by heat treatment and UV ozone treatment in BP was evaluated. The contact angle is commonly used to evaluate hydrophilicity (Azimi & Asselin, 2022). 15 μl of water was dropped on the surface of the BP, and its contact angle was measured.

2.4. BP Anode Preparation

Three types of BPs were used for the anodes of the SMFC, two each with only heat treatment, only UV ozone treatment, and both heat treatment and UV ozone treatment. A 3 mm wide stainless steel mesh (304, 400 mesh) was placed between two 1 $\times$ 1 cm BPs and glued with 30 μl of CNTs. Then, they were dried at 60 $^{\circ}\text{C}$ for 1 hour. BP anodes with only heat treatment and only UV ozone treatment, and both heat treatment and UV treatment are called BP-H, BP-U, and BP-HU, respectively.

2.5. SMFC with BP anodes

The SMFC configuration, shown in Fig. 1, was used to evaluate the performance of the BP as an anode. The SMFC case was made by a 3D printer using PLA filament. The soil was collected from Japanese rice fields (34°59'42.7986" N, 135°57'16.1892" E (34.9995222, 135.954497), Shiga, Japan), and a 5 mm deep layer of tap water was placed on top of the soil to prevent it from drying out. Soil was the only source of organic matter and bacteria. Tap water was replenished periodically to prevent the thickness of the water layer from changing due to evaporation.

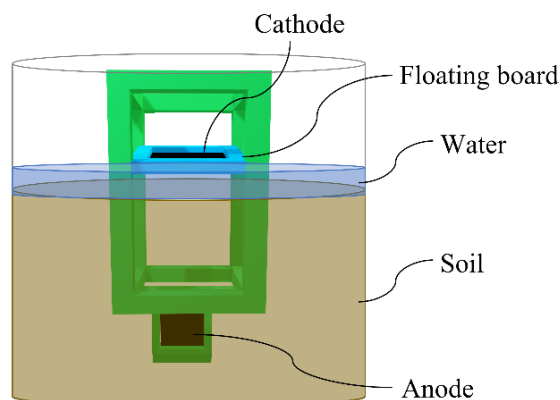


Figure 1. Schematic of SMFC setup.

An activated carbon sheet was used for the cathode, but a floating board (polyethylene foam) was attached around the activated carbon sheet to keep the air cathode function constant by fixing the positional relationship of the cathode in contact with the water surface, even if the water level fluctuates due to evaporation. The SMFC was placed in an incubator at 27 °C. This SMFC reactor was compact and made of low-cost materials.

2.6. SMFC operational tests

Discharge characteristics and power density curves were used to evaluate the use of SMFCs in BP. Discharge characteristics were obtained by measuring the load voltage every 15 minutes using a data acquisition system (National Instruments NI, USB-6210) when a 10 k Ω external resistor was connected. The power density curve was calculated by varying the external resistance in the range of [10-1 k Ω] and measuring the output voltage. The measurements were taken after waiting for the voltage to reach a steady state when the resistance value was switched.

3. Experimental Results and Discussion

3.1. Surface observation of BP

Fig. 2 shows a BP created by the vacuum filtration method. The surface of BP was observed using a Scanning electron microscope (SEM) (S-4300, Hitachi, Ltd., Japan). The SEM image shows that the CNTs are randomly entangled. The entanglement of CNTs is expected to increase surface area and improve physical strength.

3.2. Evaluation of hydrophilicity

BP-HU had the lowest contact angle, 39.7° . The next smallest was 49.1° for BP-U. Furthermore, BP-H had the largest at 56.3° (Fig. 3). These results confirm that all BPs treated with each of the three treatments are hydrophilic ($< 90^\circ$). UV ozone treatment improved hydrophilicity more than heat treatment, but both UV ozone and heat treatments were more effective in improving hydrophilicity.

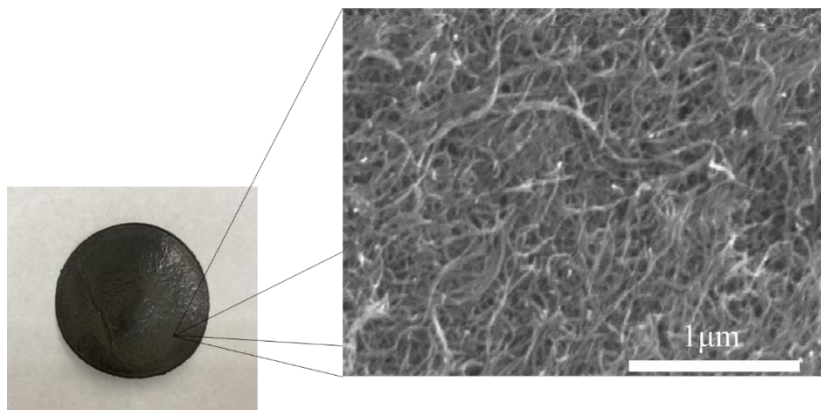


Figure 2. Photographs and SEM images of BP.

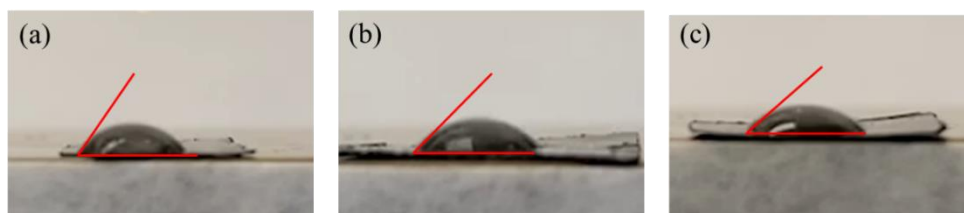


Figure 3. Contact angle with BP: (a) BP-H, (b) BP-U, (c) BP-HU.

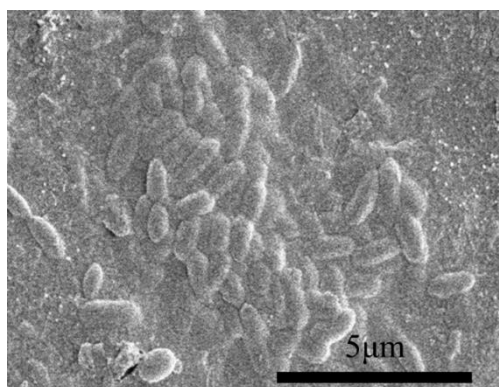


Figure 4. SEM image of the surface of BP after using SMFC.

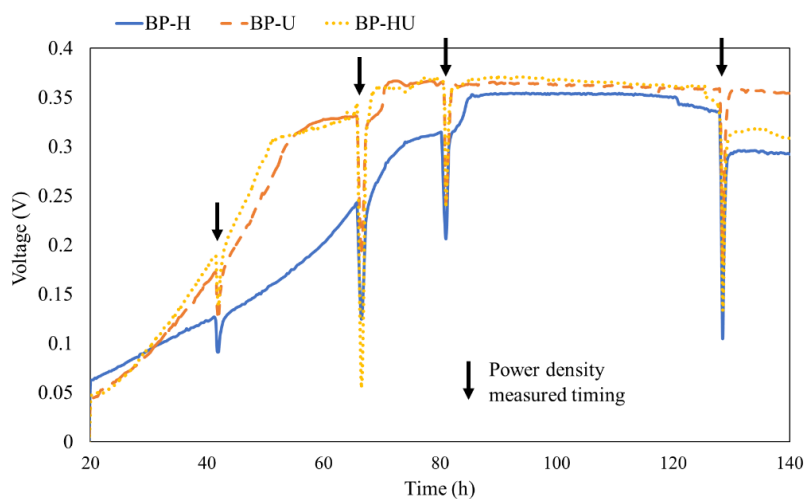


Figure 5. Comparison of temporal variation of voltage.

3.3. Affinity for bacteria on the surface of BP

After power generation, the BPs were removed from the SMFC, and the surface was observed. Before observation, the BP surface was fixed, dehydrated, and sputtered with gold. According to Fig. 4, biofilms are formed on the surface of BPs. These bacterial cells were soil bacteria such as *Geobacter* and *Shewanella*. This result confirms that BP has an affinity for bacteria that may potentially be used in the anodes of SMFCs.

3.4. Discharge characteristics of SMFC using BP

The time from SMFC activation to reaching at least 80% of maximum voltage was 53 and 50.5 h for BP-U and BP-HU, respectively. In contrast, BP-H took 70.75 h (Fig. 5). This suggests that UV ozone treatment of the BPs would reduce the start-up time of the SMFC. The voltage of BP-H and BP-U began to drop noticeably by the time they reached 130 h of operation. This suggests that if heat treatment is applied to BP, the long-term stability of the SMFC voltage is poor.

3.5. Power density of SMFC with BP

The maximum power density was higher for BP-U ($28.8 \mu\text{W}/\text{cm}^2$), BP-HU ($26.9 \mu\text{W}/\text{cm}^2$), and BP-H ($21.7 \mu\text{W}/\text{cm}^2$) in that order (Fig.6). The power density curve in Fig. 6 also shows that the order of lowest internal resistance is also BP-U, BP-HU, and BP-H.

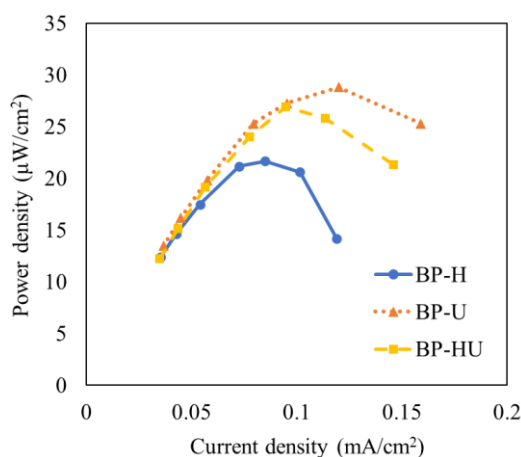


Figure 6. Comparison of power density curves at 80 h of operation.

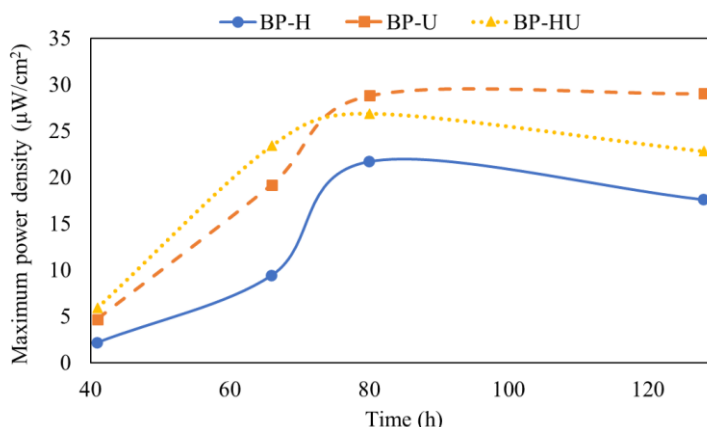


Figure 7. Comparison of temporal variation of maximum power density.

Fig. 7 is a graph of the maximum power density over time. According to Fig. 7, BP-HU, BP-U, and BP-H have shorter SMFC start-up times in that order, but BP-H and BP-HU lack long-term stability. This is the same as the result of the discharge characteristics (Fig. 5).

3.6. Overall evaluation

The results of the hydrophilicity test (Fig. 3) and the SMFC operation test (Fig. 5 and 7) show that the SMFC start-up time decreases in the order of hydrophilicity. This is probably due to the fact that as hydrophilicity increases, bacteria are more likely to come in contact with the surface of the BPs. However, Figs. 5, 6, and 7 show that the heat treatment causes a decrease in long-term stability and an increase in internal resistance. This is possible because heat treatment causes defects in the nanotubes (Park et al., 2009).

Table 1 compares the electrodes created with biochar (rice husk charcoal) and BPs by the performance of MFCs in similar systems (Hirose et al., 2023). Table 1 shows that both power density and current density are higher for BP than for rice husk charcoal. These results suggest that BP is expected to be effective for use as an anode in MFC.

Table 1. Comparison of MFC performance at different anodes.

Anode	Power density ($\mu\text{W}/\text{cm}^2$)	Current density ($\mu\text{A}/\text{cm}^2$)
BP-H	21.7	72.8
BP-U	28.8	120
BP-HU	26.9	94.6
Rice husk charcoal	9.52	34.5

4. Conclusion

In this study, BP with hydrophilic properties was examined for use in the anodes of SMFCs. Heat treatment and UV ozone treatment were investigated as methods to improve hydrophilicity. SMFCs using BPs with only UV ozone treatment as anodes obtained a maximum power density of $28.8 \mu\text{W}/\text{cm}^2$ and stable voltage for more than 140 h. This is thought to be due to the improved hydrophilicity and increased bacteria affinity of the BP surface by the UV ozone treatment. Although heat-treated BPs could also be used as anodes in SMFCs, the damage done to the nanotubes resulted in increased internal resistance and a lack of long-term stability. BP with both heat and UV treatments showed the highest hydrophilicity, but no long-term stability was observed due to heat treatment. Methods to improve the hydrophilicity of BP different from those considered in this paper may also be worth investigating in terms of anode utilization in SMFCs.

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Not applicable.

Conflict of interest:

The authors declare that there is no competing interest.

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