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Generation behavior of elctricity in a microbial fuel cell

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Abstract–Electricity generation using a microbial fuel cell (MFC) was investigated with acetate as the fuel and *Geobacter sulfurreducens* as the biocatalyst on the anode electrode. The voltage and power density behaviors at various external resistances were observed, as were the coulombic efficiency and energy recovery behaviors at various acetate concentrations. A high voltage production was obtained when the pH in the cathode chamber was maintained in the range of 7-8, which is similar to that used in other MFC studies. After 72 hours of operation, the voltage production was decreased by 11.5% with 30 mM tris-HCl and by 33.7% with 10 mM tris-HCl.

Key words: Microbial Fuel Cell, *Geobacter sulfurreducens*, Electricity Generation

INTRODUCTION

The microbial fuel cell (MFC) has been studied as a new technology for electricity production from hydrogen carbon by using a biocatalyst [1-5]. Most of the previously reported cells were the mediator-MFC type where potassium ferricyanide [6], cobalt sepulchrate, anthraquinone [7], thionine [8], azure A [9] or neutral [10] are used as the mediator in an anode chamber. However, such mediators have limited practical applications due to their expense and toxicity to bacteria. Instead, electricity has usually been generated by using a variety of fuels such as glucose, lactate, pyruvate formate, benzoate, acetate, hydrogen, and wastewater in an MFC [1,11-16].

Many studies have examined potential improvement gains in electricity production achieved by using different techniques such as controlling the self growth of microbial cells [17], screening of more electrochemically active microbes [11], coupling with direct hydrogen oxidation [18], designing various new electrode materials [1,2,4,19,20], selecting suitable proton-conducting materials [2,21], and controlling the pH in the anode or cathode chamber [22,23] to achieve 1,540 mW/m^2 [3] with O_2/Pt as a cathode electrode.

In our previous study, the use of an MFC to generate electricity was investigated with acetate as the fuel and *Geobacter sulfurreducens* as the biocatalyst on the anode electrode [24]. A stable current production of 0.20-0.24 mA was obtained at 30-32 °C and a maximum power density of 418-470 mW/m^2, obtained at an external resistor of 1,000 Ω, was more than doubled (from 418 to 866 mW/m^2) as the Pt loading on the cathode electrode was increased from 0.5 to 3.0 mg Pt/cm^2. Furthermore, the MFC power density has been considerably improved by several orders of magnitude in some innovative studies without membrane. However, the coulombic efficiency and energy recovery decreased considerably due to the lack of membranes in the systems [3,5,16,25,26]. Therefore, the main issues for commercialization of an MFC are high coulombic efficiency and energy recovery, as well as power density.

In this study, the coulombic efficiency and energy recovery behaviors of an MFC with acetate as the fuel and *Geobacter sulfurreducens* as the biocatalyst on the anode electrode were investigated at various acetate concentrations and the external resistor.

EXPERIMENTAL

1. Culture and Growth Medium

Geobacter sulfurreducens, ATCC-51573, was grown in an anaerobic flask of 50 ml by following the reported procedure in our previous study.

NH_4Cl: 1.5 g/L, NaH_2PO_4: 0.6 g/L, KCl: 0.1 g/L, $NaHCO_3$: 2.5 g/L, Wolfe's mineral solution of 50 μl and Wolfe's vitamin solution of 50 μ, Sodium acetate: 0.82 g/L

The medium was continuously flushed under a mixture of 80% N_2 and 20% CO_2 to remove oxygen until a pH value of 6.8 was reached, and then autoclaved at 121 °C for 15 minutes. Finally, sodium fumarate was added to the medium to obtain a solution of 8.0 g/*l* using a sterilized-filter with a 0.45 μm diameter. Cultures were maintained by serial transfer of 10% inoculum into bottles containing 20% CO_2 and 80% N_2 at 30 °C in a shaking incubator at 54 rpm.

2. Construction of the Microbial Fuel Cell (MFC)

The MFC was composed of identical anode and cathode chambers with 30 ml of medium and 20 ml of headspace. Each chamber had two ports on the top to collect samples or supply gases. These ports were sealed using rubber stoppers. The cation exchange membrane (CEM; Nafion 117, Dupont Co., USA) separating the two chambers was physically clamped at the flattened ends of the two plastic tubes (diameter of 2.0 cm). Plane, circular carbon paper (without wet proofing, E-tek Co., USA) [5] with a diameter of 1.3 cm

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(surface area of 1.32 cm^2) was used as the anode electrode. The cathode was prepared by applying a mixture of Pt/C catalysts (10% Pt; E-tek Co., USA) and 5% Nafion solution (7 µl of Nafion solution/mg of Pt/C catalyst) onto one side of the carbon paper with dimensions of 2.0 cm×2.6 cm (5.2 cm^2), to produce a final Pt loading of 0.5 mg/cm^2. The coated cathode was dried for at least 1 day at room temperature before application.

3. Microbial Fuel Cell (MFC) Operation

The electrodes and chambers were sterilized and flushed with anaerobic gas (20% CO_2 and 80% N_2) in a glove box, and then the electrodes were assembled into the chambers. Cells collected from the culture medium were centrifuged at 3,000 rpm for 10 minutes under anaerobic condition at 5 °C to remove any remaining culture solution. After the cells were dispersed into the anode chamber, a gas mixture of 80% N_2 and 20% CO_2 was supplied into the 20 ml headspace of the anode chamber in order to eliminate any oxygen present [26]. The 30 ml of medium solution in the anode chamber was comprised as follows:

KCl: 0.1 g/L, NaH_2PO_4: 0.6 g/L, NaCl: 2.9 g/L, $NaHCO_3$: 2 g/L, Wolfe's mineral solution of 30 µl and Wolfe's vitamin solution of 30 µl, Acetate 1-30 mM

After the fumarate that was initially used as an electron acceptor was removed, NaCl was added to minimize differences in osmolarity between the fumarate (culture medium) and electrode (anode medium) media. In the cathode chamber, the cathode medium was filled with a similar anode medium in which $NaHCO_3$ was replaced with 30 mM Tris-HCl solution. In serial tests, tris-HCl solution at various concentrations was used to study the effect of pH on the MFC's performance. The cathode chamber was continuously provided with air through a 0.45 µm pore-size filter. The MFC was operated at 30 °C and 54 rpm in a shaking incubator for all experiments. In all other respects, the MFC operation procedure followed that in our previous report [24].

BACKGROUND

A conventional MFC consists of an anode chamber and a cathode chamber. In the former, fuel is oxidized by organisms to produce protons, electrons and simple carbonaceous matters. For example, acetate as a fuel is oxidized at the anode chamber, as described in Eq. (1):

$$CH_3COOH^- + 4H_2O \rightarrow 2HCO_3^- + 10H^+ + 8e^- + 2O_2 \quad (1)$$

Electrons are transferred to the anode electrode by either a mediator, such as ferric cyanide, thionine or neutral red, in the case of a mediator MFC (Fig. 1(a)), or directly from the organism immobilized onto the anode electrode, in the case of a mediator-less MFC (Fig. 1(b)). Electrons move from the anode electrode to the cathode electrode through a connected metal wire. Protons pass to the cathode chamber through a CEM which functions as a barrier to stop the diffusion of fuel and oxygen.

The reducing reaction of electrons, protons, and oxygen takes place at the cathode chamber to form water, as shown in Eq. (2):

$$2O_2 + 8H^+ + 8e^- \rightarrow 4H_2O \quad (2)$$

The definition of sustainable power is a constant power generation over time, and a constant cell potential after the external resistance is applied. However, the variation in external resistances

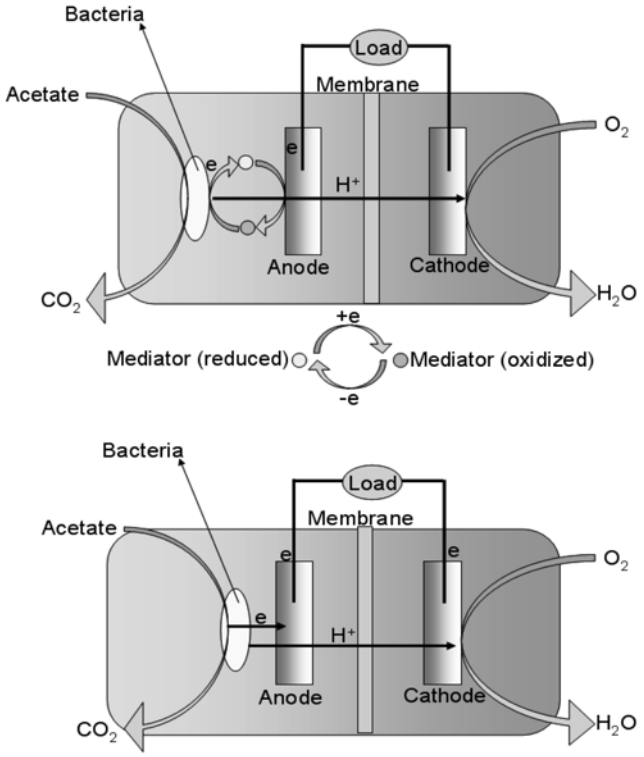

Fig. 1. Two microbial fuel cells (MFCs): (a) mediator and (b) mediator-less.

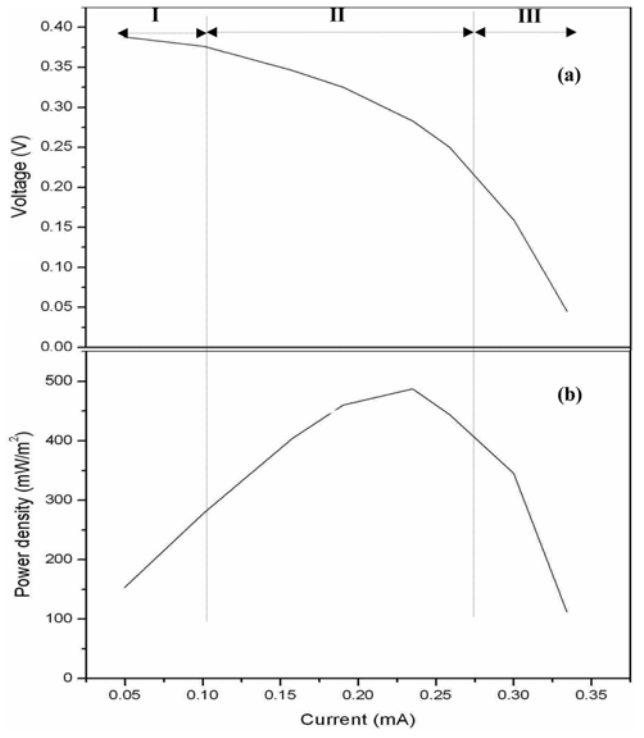

Fig. 2. MFC performance: (a) polarization and (b) power density curves.

affects the sustainable power and the MFC can generate maximum sustainable power for a special combination of external and internal resistors [27]. The power curve is obtained from the polarization curve, which is determined by applying variable resistors in an MFC, and the current is estimated from the measured voltage.

Polarization curves can be approximately divided into three zones, where the MFC properties can be characterized as follows [28] (Fig. 2).

I. When the current increases from zero, the voltage starts to decrease slightly. In this zone, the activation losses are dominant.

II. The voltage falls slowly at the initial step and then the voltage drop is fairly linear with increasing current. In this zone, the ohmic losses are dominant.

III. The voltage falls promptly at a high current, and thus the concentration losses are dominant in this zone.

Study of the polarization and power curve facilitates a good understanding of the MFC characterization. In many MFCs, the ohmic resistance plays a dominant role in defining the maximum sustainable power due to the low ionic conductivity of the substrate solution or the non-optimization design [20].

RESULTS AND DISCUSSION

Fig. 3 shows the voltage and power density of the MFC as a function of external resistance. The voltage decreased with decreasing external resistance, which can be explained simply by using Eq. (3). The power density increased sharply at the low external resistance to a maximum at an external resistance of 1 000 Ω (Fig. 3). Theoretically, the external resistance is equal to the internal resistance at the maximum power density (Eq. (4)). In this study, however, the internal resistance varied over the range from 1,460 to 1,757 Ω (average internal resistance of 1,538 Ω) as the external resistance increased from 125 to 3,000 Ω (Fig. 4). The small difference between the theoretical calculation and the experimental data was attributed to the unreasonable scan rate of the external resistance for determining the maximum power density [27], and to the uncertain fluctuation in voltage over time.

$$V = \frac{V_{OCV}}{R_{in} + R_{ex}} R_{ex} \quad (3)$$

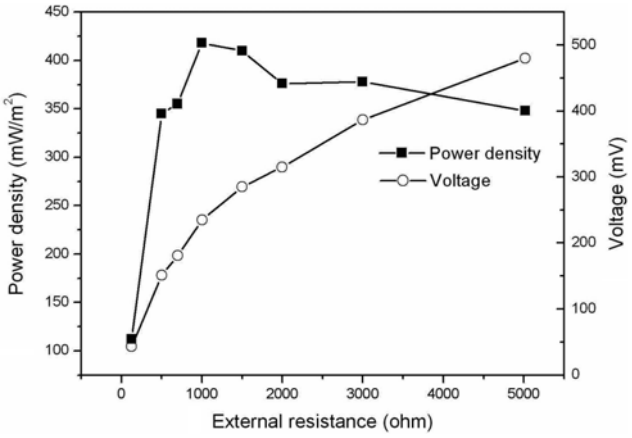

Fig. 3. Voltage and power density curves as a function of external resistance (T=30 ºC and 0.5 mg Pt/cm²-cathode).

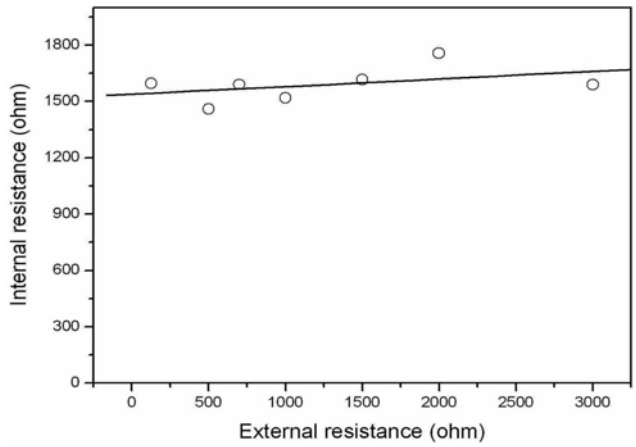

Fig. 4. Internal resistance as a function of external resistance (T= 30 ºC and 0.5 mg Pt/cm²-cathode).

$$P = \frac{(V_{OCV})^2}{(R_{in} + R_{ex})^2} R_{ex} \quad (4)$$

Where R_{in} and R_{ex} are internal and external resistances and V_{OCV} is the open circuit voltage.

Each MFC configuration has a different value in the internal resistance, which mainly depends on the electrolytes [20], membrane property [2], and electrode space [3]. Hence, the power density can be improved when the internal resistance is optimized in the MFC configuration [2].

Each experiment with different resistance values was run with the MFC operating for 6 hours. Fig. 5 shows the coulombic efficiency and energy recovery as a function of external resistance. The coulombic yield increased with decreasing resistance, as in other works [5], suggesting that at a high value of external resistance, only a limited number of electrons were transferred through the circuit. In this study, we obtained a coulombic yield of 27% (R_{ex}=1,000 Ω) at the maximum power density. The coulombic yield was lower than that reported in other works conducted with similar MFC systems, with coulombic efficiency yields of 80-95% (R_{ex}=5-100 Ω) [29], 89% (R_{ex}=100 Ω) [30], and 95% (R_{ex}=500 Ω) [4]. Therefore, it is

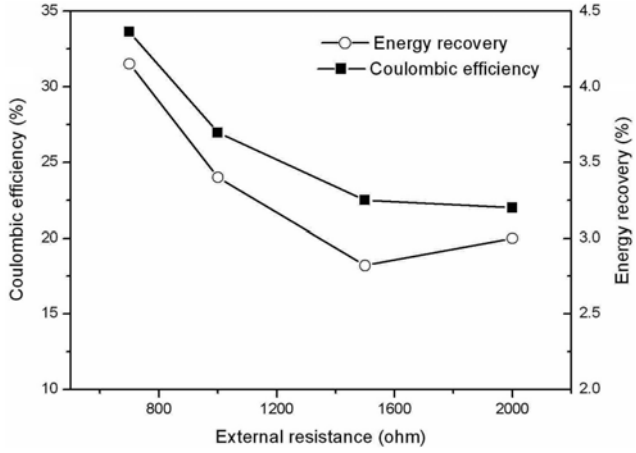

Fig. 5. Coulombic efficiency and energy recovery as a function of external resistance (T=30 ºC and 0.5 mg Pt/cm²-cathode).

believed that a high coulombic efficiency can be achieved when the MFC system is operated at low resistance [4,16]. This explains the low coulombic efficiency at R_{ex} of 1,000 Ω in this work. In addition, the coulombic efficiency may decrease because electrons are reduced by oxygen diffusion in the anode chamber [2,3,5]. Min et al. examined the effect of oxygen in the anode chamber, and found that the columbic yield increases from 19% (R_{ex}=1,286 Ω) to 47% or 55%, by removing any remaining oxygen by using sparging nitrogen or L-cysteine (a chemical oxygen scavenger) in the anode chamber. Although the coulombic yield increased noticeably, the power density was nearly the same as that reported in another study [2].

On the other hand, Logan et al. [3,5] used an air-cathode MFC without membranes to significantly improve the power density, even while decreasing the MFC cost. However, the coulombic efficiency also decreased drastically. Therefore, the optimal adjustment of both power density and coulombic efficiency represents a new challenge for MFC's improvement.

The overall coulombic efficiency was a function not only of the external resistor but also of acetate concentration. Fig. 6 shows that the coulombic efficiency decreased slightly from 25.9 to 24.7% as the acetate concentration increased from 2.5 to 10 mM. The phenomenon is similar to that reported in other works that investigated a two-chamber MFC comprising a membrane operated under a continuous mode [31], or a membrane-free, single-chamber MFC operated under batch mode [5,16].

The energy recovery, calculated from the acetate removal and power generation, ranged from 2.3 to 4.1% in this study (Fig. 5). A recently reported range for the energy recovery was between 2% and 23% [29], which mainly depended on the fuel, bacteria, and MFC configuration. The MFC energy recovery is too low in comparison with other effective technologies such as ethanol production (47% efficiency), or anaerobic digestion in combination with combustion (25-35% efficiency) [16]. However, current studies have suggested that MFC can be combined with both wastewater treatment and high efficient BOD removal, to give high energy recovery [15,16].

Protons and electrons are consumed at the cathode chamber, according to Eq. (2). We therefore assumed that the diffusion rate of protons through the membrane is the main key to control the cathode reaction rate. When using Nafion as MFC membrane, the number of protons diffusing through the membrane is typically 10^5 times lower than that of other cations such as Na^+, K^+, NH_4^+, Ca^{2+}, and Mg^{2+}. Therefore, the pH of the cathode chamber will be increased by the leakage of protons, if there is no pH control by using cathode buffer solution [23]. To confirm this hypothesis, 30 mM of acetate was used as the fuel to study the effect of pH in the cathode chamber on the MFC performance. A high and stable current was achieved for over 150 hours (data are not shown here). Due to the higher buffer capacity of the catholyte with 30 mM Tris-HCl buffer, the pH increase was slower than that of the 10 mM Tris-HCl buffer catholyte. Consequently, after 72 hours of operation, the voltage production was decreased by 11.5% with 30 mM tris-HCl and by 33.7% with 10 mM tris-HCl (Figs. 7 and 8). According to these experiments, a

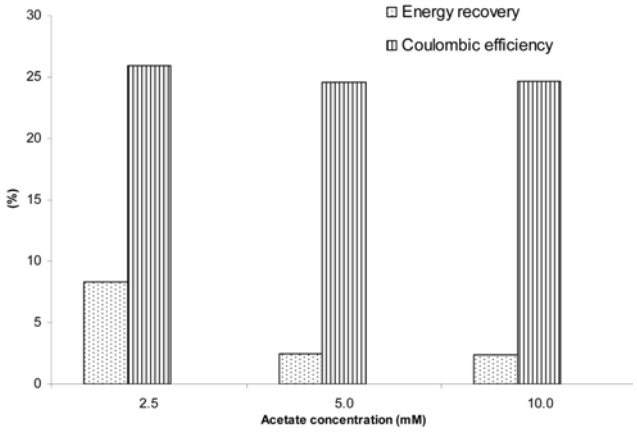

Fig. 6. Coulombic efficiency and energy recovery as a function of acetate concentration (T=30 °C, 0.5 mg Pt/cm²-cathode and R_{ex}=1,000 Ω).

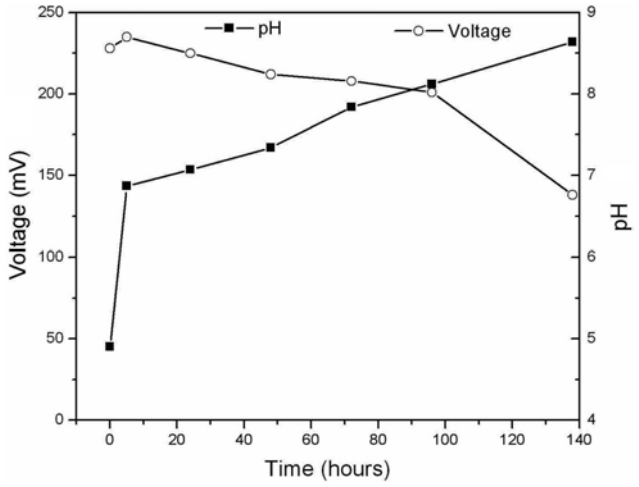

Fig. 7. Temporal variations of voltage in the MFC and pH in the cathode chamber during MFC operation with 30 mM tris-HCl as the catholyte (T=30 °C, 0.5 mg Pt/cm²-cathode, and R_{ex}=1,000 Ω).

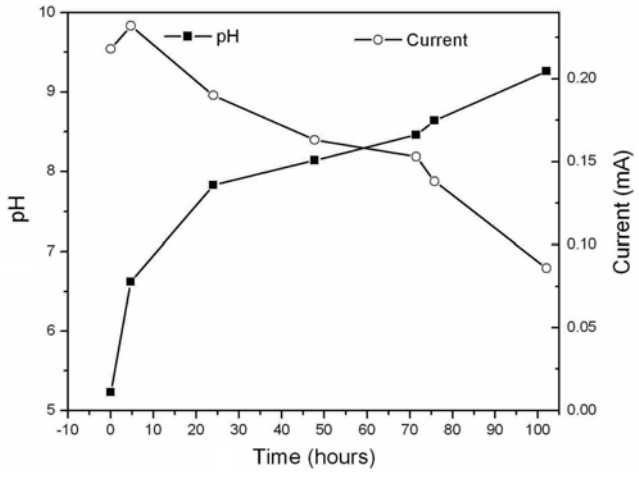

Fig. 8. Temporal variations of current in the MFC and pH in the cathode chamber during MFC operation with 10 mM tris-HCl as the catholyte (T=30 °C, 0.5 mg Pt/cm²-cathode, and R_{ex}=1,000 Ω).

high voltage production was generated when the pH in the cathode chamber was maintained in the range of 7-8, which is similar to that used in other MFC studies [22,23]. Rozendal et al. showed that the potential at the anode was largely unaffected but was significantly decreased at the cathode during the MFC's performance. Thus, the decreasing MFC potential was mainly affected by the insufficient protons supplied at the cathode chamber [23]. In the initial stage, the pH increased suddenly, while the voltage generation decreased slowly at the cathode chamber. We assumed that sufficient protons were consumed at the cathode chamber, suggesting that proton diffusion through membrane was the more limiting step, and that the low pH value at the anode chamber caused the loss of the active biofilm of the bacteria. Gil et al. reported an optimum pH of 7-8 at the anode chamber using activated sludge, with lower current generation being achieved at pH below 6 and over 9 [22]. Cathode potential is inversely proportional to pH, and thus decreases with increasing pH at the cathode chamber, which consequently decreases the MFC potential.

CONCLUSIONS

An MFC was operated with stable current production by using *Geobacter sulfurreducens* as the biocatalyst and acetate as the fuel. The power density was maximized at an external resistance of 1,000 Ω, while the coulombic efficiency decreased with increasing external resistance. The decrease of the power density was attributed to the leakage of protons in the cathode solution during the operation of the two MFC chambers. The overall coulombic efficiency was dependent not only on the external resistor but also on the acetate concentration.

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