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The biofuel cell: development of new materials for composing electron mediator-free and electrochemical active bacteria-free biofuel cell

*Park, Doohyun, [1]Park, Yongkeun, Kim, Sikyun, Lee, Daesik, Shin, Inho

Department of Biological Engineering, Seokyeong University, 16-1 Jungneung-dong, Sungbuk-ku, Seoul 136-704, Korea; 1Graduate School of Korea University, 5Ga-1 Anam-dong, Sungbuk-ku, Seoul 136-701, Korea

*e-mail address: baakdoo@seokyeong.ac.kr

Abstract

In this study biofuel cell is classified into 5 generation fuel cell system based on structural and structural difference. I optionally named the biofuel cell with electron mediators prototype, that with electrochemical active bacterium 2nd generation, that with modified electrode with NR 3rd generation, that with catalytic active electrode 4th generation, and that using air as a catholyte instead of ion selective membrane and cathode, respectively. The electricity production was compared among 5 types biofuel cell and was confirmed to be 50-100% higher in 4th and 5th generation than in 1st to 3rd generation.

Introduction

For about twenty years, researchers just have tried to repeatedly test and compare different electron mediators and bacterial catalysts without efforts for development of new biofuel cell system since Roller *et al.*(1984) tested a prototype of biofuel cell with electron mediator. Sibel *et al.* (1984) compare electron transfer rates of 14 electron mediators and dye reduction activity of 7 bacterial species in biofuel cell for electricity production, and Bennetto *et al.* (1985) tested efficiency of thionine on electricity production in biofuel cell with *Proteus vulgaris*, and Thurstone *et al.* (1985) measured electricity production metabolically coupled to bacterial glucose consumption in biofuel cell with thionine as an electron mediator. On the other hand, Habermann and Palmmer (1991) tried to make new system using sulfide as an electron donor which is produced coupled to bacterial metabolism, but this system is very similar to chemical fuel cell and excessively dependant on sulfate-reducing bacteria. In any biofuel cell system, electron mediators are big problem for composing of real system because those have to be continuously added to fuel cell system and waste of them are toxic for environment. Park and Kim (1996) reported that a mediator-less biofuel cell can be composed using a specific bacterium with electrochemical activity but the electron donor is very limited to lactate or H_2. Park and Zeikus (1999 and 2000) confirmed that neutral red is an electronophore (electron carrier across bacterial membrane) and better as an electron mediator for biofuel cell than other dyes such as thionine and 2-hydroxy-1,4-naphthoquinone. At the present time, the biofuel cell system using any electron mediator or any bacterial catalyst is not only same to prototype in their basic structure but also difficult for apply to real electricity production system or application system such as biosensor. Therefore, the biofuel cell system dependant on electron mediator or a specific bacterium has to be changed over to other system independant on the prototype biofuel cell, for which Park *et al.* (1997) tried to modify bacterial cell membrane with electron mediator and Park *et al.* (2000) composed a biofuel cell with modified carbon electrode with neutral red which was covalently bound to carbon electrode, in which the electricity production was 40% higher than that with non-modified carbon electrode. In biofuel cell with the covalently modified electrode with NR, addition of electron mediator is not required, but it is possible that neutral red bound to electrode may be biodegradable. To overcome this problem, I developed new electrode modified with inorganic materials and tested the function for electricity production, and then developed new biofuel cell system without cathode compartment and catholyte, in which cathode has two function as an electrode for electron movement and as a membrane with catalytic activity to promote reduction of protons and electrons to H_2O. In this paper, I will present the results obtained from biofuel cell with modified electrode with NR and inorganic materials, and classify the biofuel cell to 5 different generation according to the structural and functional differences.

Materials and Methods

Organism and Cultivation

Anaerobic bacterial consortium isolated from anaerobic digestive sludge of wastewater treatment system, and *E.coli* were used as an biocatalyst

Medium

Wastewater from dye industry (Daegu dye industry complex) and sewage form Jungrang wastewater treatment system was used as a medium for bacterial cultivation, and lactate or acetate was added to the wastewater.

Eletrode modification

Neutral red was bound to electrode using covalent bonding method, and transition element was bound to electrode surface using chelating method between carboxy of electrode (Ligand) and ion of transition elements. The function of electode was tested with cyclic voltammetry.

Composition of biofuel cell

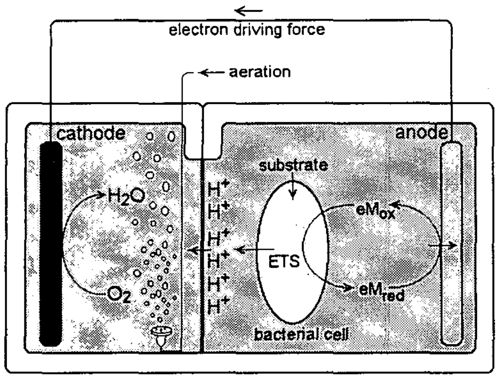
The basic structure of biofuel cell was functionally classified as shown in Fig 1. The prototype of biofuel cell is classified as 1st generation others are classified from 2nd to 5th generation according to the spicificity of biocatalyst, stuructural differences, electrode functions and membrane function.

Measurement of electricity production

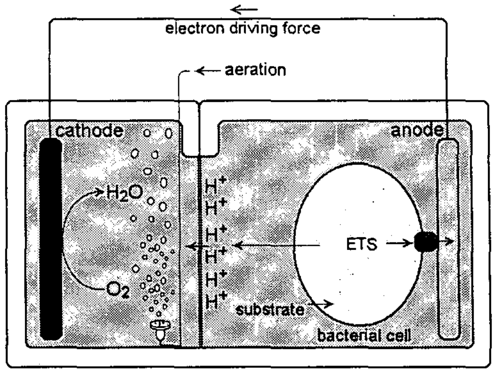
Electricity production was measure using precision volt and ampere meter (Fluke model 8842A multimeter) and was continuously recorded using pen recorder (Pharmacia model RED 102).

Results and Discussion

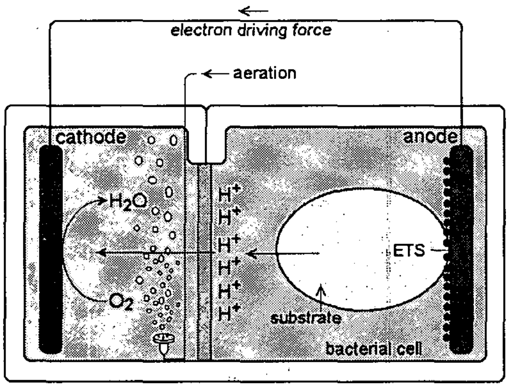
The biofuel cell is an apparatus for conversion of reducing power or free energy produced in bacterial energy metabolism to electricity, but the electrons can't be transferred across bacterial membrane. In 1st generation of biofuel cell, many electron mediators were tested to promote electron transfer from bacterial metabolism to anode and different electron mediators were functionally compared each other. Theoretically, electron mediators were reported to can be pass across bacterial membrane but the efficiency was not verified, and neutral red was confirmed to be bound to bacterial membrane but not pass across the membrane (Park and Zeikus, 1999, 2000). The neutral red bound to bacterial memebrane is better for electricity production than free electron mediators because the contact efficiency between bacterial electron carriers such as NAD and electron mediator can be increased, and the



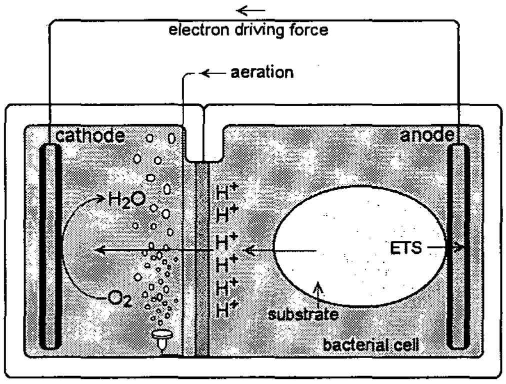
(A) Prototype (Roller *et al.*, 1984)



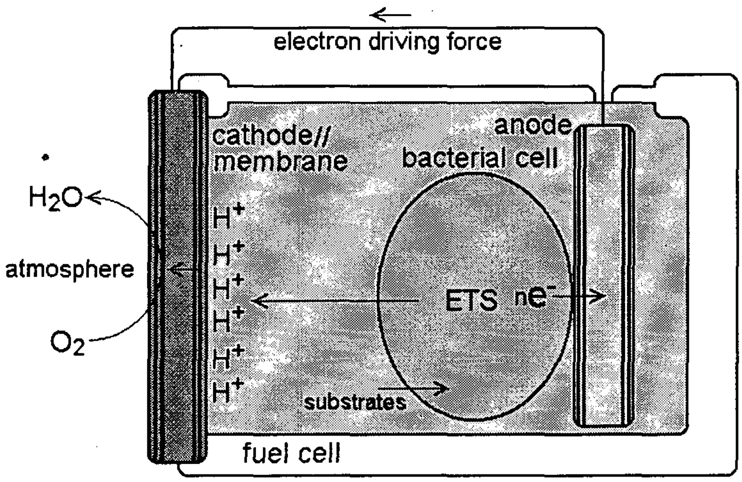
(B) 2nd generation (Park and Kim, 1986)



(C) 3rd generation (Park *et al.*, 2000)



(D) 4th generation (Park et al., in Press)



(E) 5th generation (Park et al., in Press)

Fig 1. Structural and functional classification of biofuel cell

electrons may be effectively transferred from bacterial cell to electrode by bacterial contacting to electrode (Table 1).

Table 1. Production of electricity from glucose in microbial fuel cells when different electron mediators were used

Authors	Microorganism	Electron mediator	Current (mA)[a]	Potential (V)	Electrical charge (C)[b]	Energy (J)	Energy rate(J/h)
Thurston et al[c]	*P. vulgaris*	Thionine	1.25	0.3[d]	18	5.4	1.35
Allen and Bennetto[c]	*P. vulgaris*	HNQ	0.5	0.5	7.2	3.6	0.9
Park and Zeikus[e]	*E. coli*	NR	4.5	0.68	64.8	44.1	11

[a]Mean values; [b]Values for 4h; [c]Resistance and potintial were measured, and current was calculated; [d]Maximum value; [e]Resistance, potential, and current were measured.

In 2nd generation of biofuel cell, an electrochemical active bacterium was firstly utilized for excluding electron mediator but electricity production is maximum 0.2 mA which is too low to apply to bioelectrochemical system such as biofuel cell or biosensor and substrate is limited to lactate and H_2 (Park and Kim, 1996). In third generation of biofuel cell, modified electrode with neutral red was utilized for excluding continuous addition of electron mediator, and electricity production was 40% higher in this system than that in biofuel cell with normal electrode (Park et al., 2000). In 4th generation of biofuel cell, catalytic active electrodes were used for excluding both electron mediators and bioelectrochemical bacterium, and electricity production was about 500% higher in this system than that in biofuel cell with normal electrode as shown in Fig 2 and 3. In 5th generation of biofuel cell, cathode has both catalytic activity for oxidation of electron and proton to H_2O and membrane for separation between anode compartment and cathode compartment. As shown in Fig 1(E), cathode compartment of 5th generation is atmosphere contacting with outside of cathode. From 1st to 4th generation, the biofuel cell operation has to accompany by the aeration of cathode compartment and separation between anode and cathode compartment with cation-selective septum such as nylon or plastic membrane which is very expensive and breakable during autoclave. Because the energy for aeration is very higher than that produced in biofuel cell, the development of biofuel cell system using wastewater or wastes is not valuable. Accordingly, the development of biofuel cell system without cathode compartment and aeration is urgent. In 3rd and 4th generation, septum was altered into ceramic material which is very strong by pressing and heating and ion transfer efficiency is higher than nylon membrane. In 5the generation, I developed the system for which separation between anode and cathode compartment and aeration of catholyte is not required. The electricity production in 5th generation was very similar to that in 4th generation as shown in Fig 4 and Table 2. Generally, the efficiency of fuel cell is tend to be dependant on bacterial catalyst (cell) or electron mediator, but in the system dependant on specific bacteria substrate has to be limited to the bacterial utilizing-materials and in that dependant on specific electron mediator recycle system of electron mediator has to be attached. The 5th generation is nearly reach to an ideal system without aeration, electron mediator, catholyte and ion-selective membrane but is a strong system which can be operated by any bacteria as a biocatalyst and with any biodegradable compounds as an electron donor. The electrode function can be measured

Table 2. Comparison of electricity production among each generation of biofuel cell

Generation of fuel cell (References)	Microorganism	Electron mediator	Current (mA)[a]	Potential (V)	Electrical charge (C)[b]	Energy (J)	Energy rate(J/h)
1st (Thurston *et al.*, 1984)[c]	*P. vulgaris*	Thionine	1.25	0.3[d]	18	5.4	1.35
2nd (Park and Kim, 1986)[e]	*P. vulgaris*	none	0.5	0.5	7.2	3.6	0.9
3rd (Park *et al.*, 2000)[e]	*E. coli*	none	1.5	0.15	21.6	3.24	0.81
4th (Park *et al.*, in press)[e]	*E. coli*	none	2.1	0.25	30.24	7.56	1.89
5th (Park *et al.*, in press)[e]	*E. coli*	none	1.9	0.21	27.36	5.75	1.44

[a]Mean values; [b]Values for 4h; [c]Resistance and potintial were measured, and current was calculated; [d]Maximum value; [e]Resistance, potential, and current were measured.

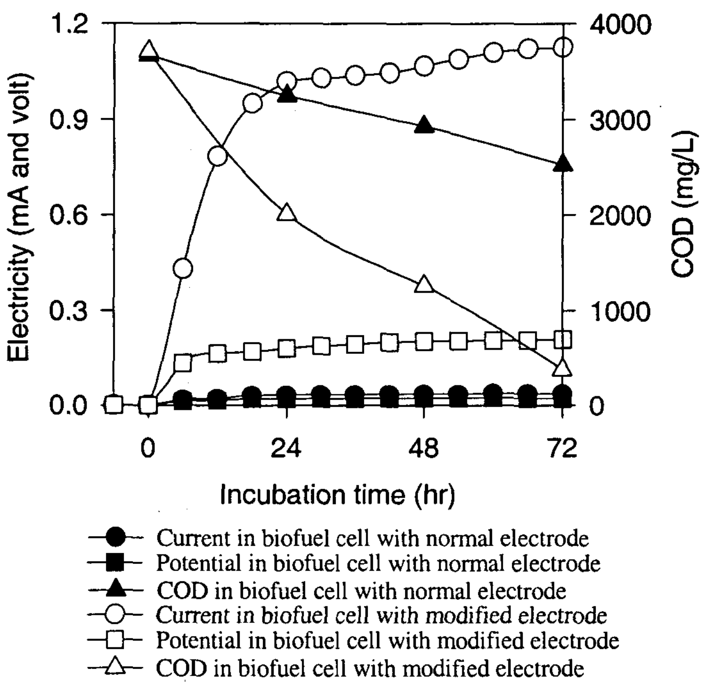


Fig 2. Relationship between electricity production and COD variation in biofuel cell with carbon electrode (solid symbols) and modified carbon electrode (open symbols). 10% anaerobic digestive sludge was inoculated into the system. The biofuel cell was poised for 6hr before inoculation.

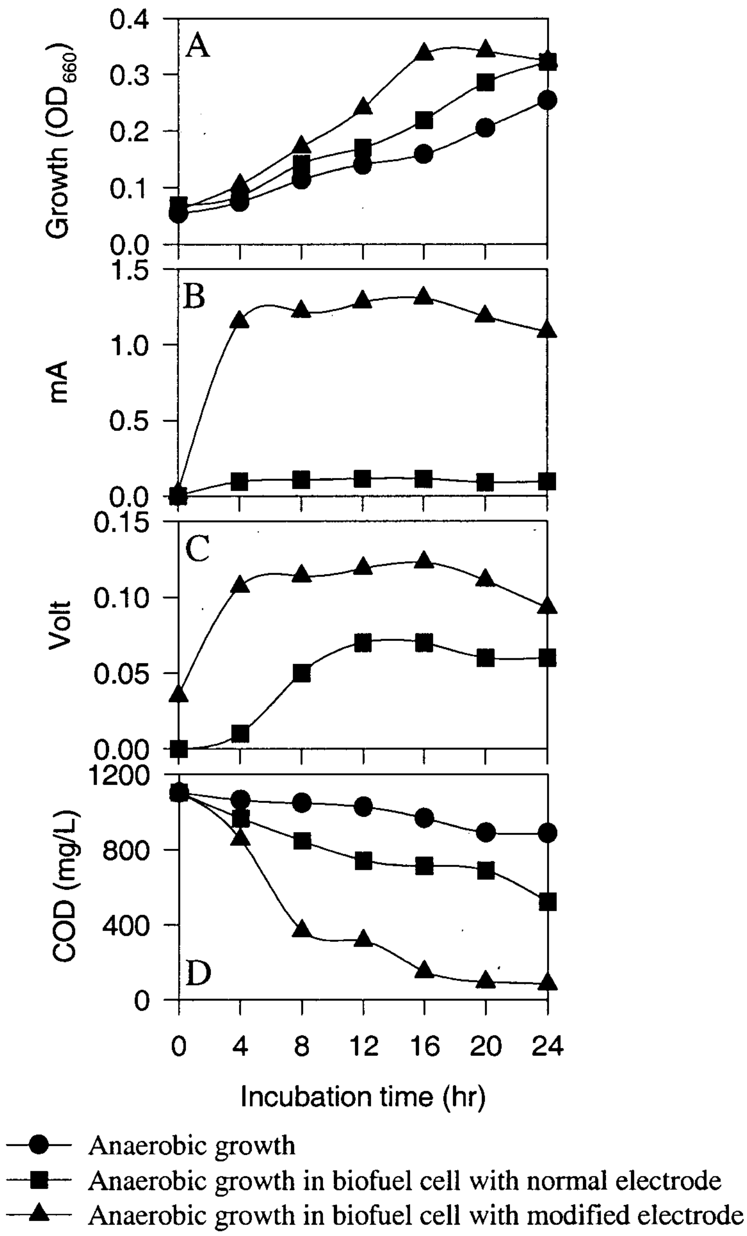


Fig 3. Bacterial growth (A), current production (B), potential between anode and cathode (C) and COD variation (D) in biofuel cell with *E.coli* as a biocatalyst in 4th generation of biofuel cell

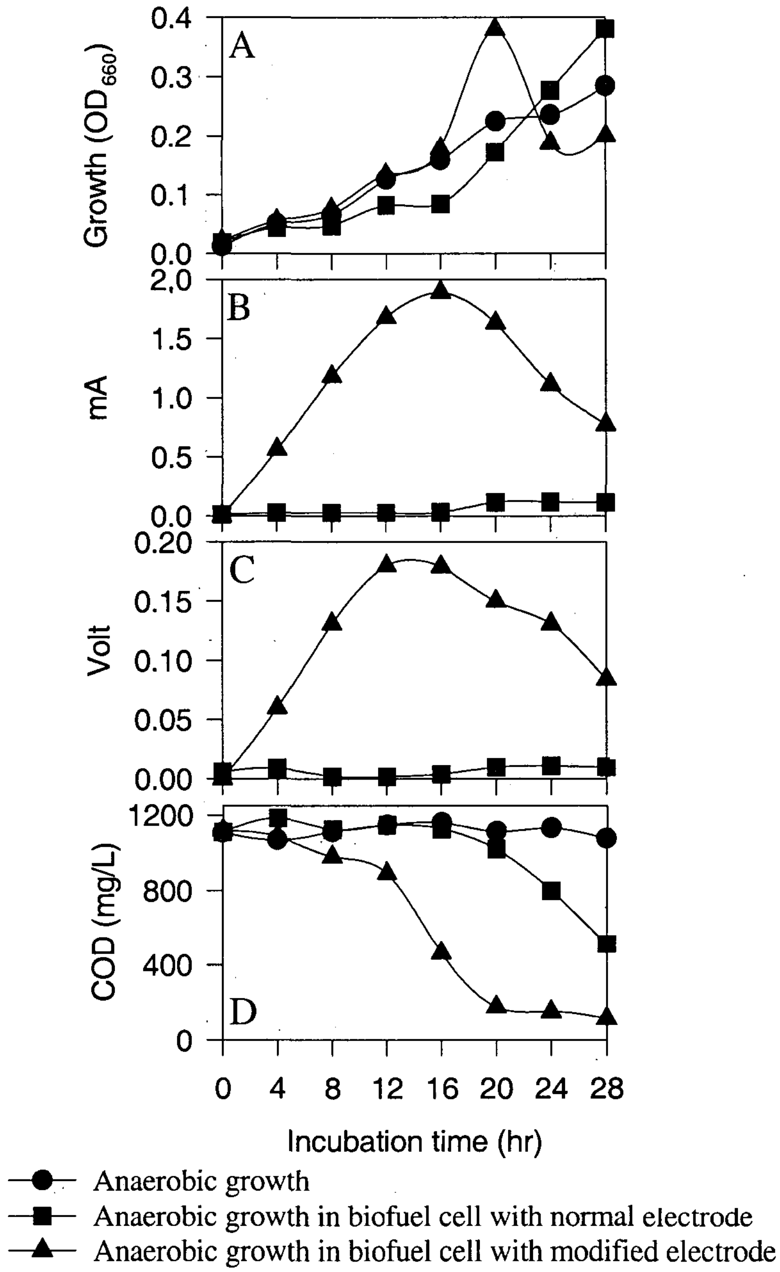


Fig 4. Bacterial growth (A), current production (B), potential between anode and cathode (C) and COD variation (D) in biofuel cell with *E.coli* as a biocatalyst in 5th generation of biofuel cell.

Acknowledgement

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