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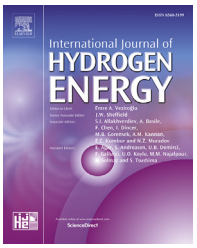

Electricity production from macroalgae by a microbial fuel cell using nickel nanoparticles as cathode catalysts

Mebrahtom Gebresemati [a,c], *Gautam Das* [a], *Bang Ju Park* [b], *Hyon Hee Yoon* [a,*]

[a] *Dept. of Chemical and Biological Engineering, Gachon University, Seongnam, Gyeonggi-do, 461-701, South Korea*
[b] *Dept. of Electronic Engineering, Gachon University, Seongnam, Gyeonggi-do, 461-701, South Korea*
[c] *Dept. of Chemical Engineering, EiT-M, Mekelle University, Mekelle, Tigray, 231, Ethiopia*

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ABSTRACT

Electricity production from macroalgae (*Saccharina japonica*) by microbial fuel cells (MFCs) was studied. The macroalgae were pretreated in alkaline solution and used as substrates in the MFC, or anaerobically fermented and then the fermentation broth was used as the MFC substrate. When pretreated *S. japonica*, fermentation broth, and acetate were used as substrates for a MFC with a Pt-based cathode, the maximum power densities achieved were 99, 584, and 721 mW/m^2, respectively. Ni particles with 3D nanostructure were also synthesized for use as cathode catalysts. The MFC with a Ni-based cathode delivered maximum power densities of 560 and 540 mW/m^2 using acetate and fermentation broth of *S. japonica*, respectively, which were close to those for the MFC with a Pt-based cathode. The results indicated that pretreatment of macroalgae by anaerobic fermentation can be used to realize high MFC performance and nanostructured Ni is a promising alternative catalyst in MFC application.

Introduction

Microbial fuel cells (MFCs) have recently attracted considerable attention because they can produce sustainable energy from various biomass feedstocks [1]. In an MFC, organic substrates are oxidized by microorganisms producing electrons in the anode chamber. The electrons are transferred to the cathode chamber through an electric circuit and consumed in the oxygen reduction reaction (ORR). Various organic substrates, such as acetate, glucose, ethanol, and volatile fatty acids (VFAs), can be used as substrates for MFCs [2,3]. Currently, acetate-fed MFCs show the highest Coulombic efficiency, followed by those fed with butyrate, propionate, and glucose [4], suggesting that effluents from anaerobic fermentation, which are composed of mainly VFAs, are suitable substrates for MFCs [5,6]. Furthermore, the energy conversion has been enhanced by combining anaerobic-fermentative hydrogen production and MFC [7,8].

Recently, macroalgae have been utilized as an alternative resource to lignocellulosic biomass for biological conversions such as anaerobic digestion [9], and ethanol fermentation [10]. Thermo-chemical conversions of macroalgae have been also investigated [11]. Fermentation of macroalgae into ethanol

* *Corresponding author.*
E-mail address: hhyoon@gachon.ac.kr (H.H. Yoon).
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exhibited a typical low yield of 8–12% [12], due to the high content of non-fermentable sugars such as alginate. Thermal conversion methods are not also attractive because of the high ash contents, low heating values, and high water content of macroalgae. In contrast, anaerobic fermentation platform with mixed culture is relatively inexpensive process because of the non-sterile fermentation conditions. Recently, macroalgae have been studied in hydrogen production by anaerobic fermentation (AF) [13]. During fermentative hydrogen production, VFAs are also produced via acetic acid and butyric acid pathways [14,15]. VFAs can be used as precursors in the production of mixed alcohols [16] and biochemicals [17]. However, VFAs are strongly hydrophilic, and thus the technical difficulty associated with the recovery of VFAs from fermentation broths is a considerable drawback that limits their practical implementation. In this context, use of VFAs as a substrate in MFCs can be an efficient method to utilize VFAs in AF broths because the broths can be used directly without purification. Meanwhile, marine macroalgae have been used directly as electron donors after pretreatment; however, the generated power density was relatively low (250 mW/m^2) [18].

Although the substrate conversion rate, overpotentials at the anode and cathode, and the membrane performance are the major factors determining the performance of MFCs [19,20], the cathode is important to realize high-performance MFCs because of the poor kinetics of the ORR in a neutral medium [21]. Platinum is by far the most efficient ORR catalyst; however, its high cost and sensitivity to poisoning limit its practical application [22]. Recently, nickel and nickel oxide, which are relatively inexpensive and display good electrochemical activity, have been used as alternative ORR catalysts in fuel cells and chemical batteries [22]. Despite extensive studies on Ni-based catalysts, they have seldom been used as the cathode materials of MFCs [23]. Only a few Ni-based catalysts for MFCs have been reported [21,24–26]. Most previous efforts focused on the synthesis of Ni nanostructures to ensure large catalytic surface area.

In this study, the feasibility of electricity production from macroalgae is investigated by two methods (i) macroalgae pretreated in alkaline solution are directly used as an MFC substrate and (ii) macroalgae are fermented anaerobically to form VFAs, which are then used as substrates for MFCs. *Saccharina japonica*, which is a brown macroalgae and widely grown in Asia, is used as a model macroalgae. A novel nanostructured Ni catalyst is also synthesized for use as the cathode of the MFC and compared with a Pt catalyst.

Materials and methods

Substrate preparation

Air-dried brown macroalgae (*S. japonica* species) supplied by Wando Fisheries Cooperative, Wando (Korea) were used as the organic matter source. The samples were milled to a size of approximately 1 mm size. The *S. japonica* contained 62.7% (w/w) volatile solid consisting 82% carbohydrates, 15.6% proteins, and 2.4% lipids (Table S1).

For the AF of the *S. japonica* sample, anaerobically digested sludge collected from a local municipal wastewater treatment plant was used as inoculum. The inoculum was heat treated at 100 °C for 15 min to suppress methanogenesis. Each liter of the fermentation medium contained 4.0 g of NH_4HCO_3, 2.0 g of KH_2PO_4, 0.2 g of $MgSO_4 \cdot 7H_2O$, 0.02 g of NaCl, 0.021 g of Na_2MoO_4, 0.02 g of $CaCl_2$, 0.029 g of $MnSO_4 \cdot H_2O$, and 0.011 g of $FeCl_2 \cdot 4H_2O$. The *S. japonica* samples were pretreated by soaking in 0.5 M NaOH at room temperature for 6 h. The concentrations of the substrate and inoculum were 30.0 g/L (dry basis) and 10% v/v, respectively. The AF was carried out in a 250-mL bottle with 200-mL working volume in a shaking incubator at 35 °C and 150 rpm.

After five days of AF, the fermentation broth was centrifuged at 4000 rpm for 15 min, diluted, and then used as a substrate for MFC experiments. An *S. japonica* sample was also fed directly into an MFC after soaking in 0.5 M NaOH for 12 h at room temperature and being neutralized.

Cathode catalyst preparation

A nickel nanoparticle (Ni-NP) cathode catalyst was synthesized by chemical reduction of a nickel chloride aqueous solution [27]. Typically, the Ni precursor solution was prepared by dissolving $NiCl_2 \cdot 6H_2O$ (2.0 g) in deionized (DI) water (240 mL). The reducing solution was prepared by dissolving NaOH (4.0 g) in DI water (80 mL) and $N_2H_4 \cdot H_2O$ (80 mL). The reducing solution was added to the stirred Ni precursor solution and then sonicated for 15 min at 60 °C and for 25 min at 65 °C. The resulting suspension was centrifuged, washed with DI water and ethanol, and then the residue was dried in a vacuum oven overnight. The obtained Ni-NPs were blended with carbon black (Cabot, Korea) with Ni-NP/C weight ratio of 30:70 by ball milling for 48 h. The Ni-NP/C was mixed with 5% Nafion solution in isopropanol (Sigma-Aldrich, Korea) by stirring for 24 h and then sonication for 10 min. The resulting cathode-catalyst ink was painted on polytetrafluoroethylene-treated carbon cloth (2 × 4 cm, E-TEK, USA) and air-dried. The Ni loading was 1.8 mg/cm^2. A standard Pt/C (2 mg/cm^2, E-TEK, USA) based cathode was also prepared.

MFC configuration and operation

A 250-mL H-type MFC (Adams & Chittenden, Berkeley CA, USA) with a working volume of 200 mL in each chamber was used with a Nafion 117 proton exchange membrane (23.76 cm^2, FuelCells Etc., USA) held between the two chambers. The anode was made of carbon cloth (2 × 4 cm, E-TEK). The anode chamber was filled with a nutrient medium containing 4.33 g of Na_2HPO_4, 2.69 g of $NaH_2PO_4 \cdot H_2O$, 0.31 g of NH_4Cl, 0.13 g of KCl, and 25 mL of mineral and vitamin solutions per liter of 50 mM phosphate buffer solution (PBS, pH 7.0), as described elsewhere [28]. The medium was inoculated using anaerobically digested sludge at 25% v/v. The cathode chamber was filled with PBS (50 mM, pH 7.0) that was continuously aerated. Initially, the MFC with a standard Pt/C cathode was operated with sodium acetate as the substrate (1.64 g/L, 1279 mg/L COD) to immobilize electrochemically active microbes on the carbon cloth anode. When the cell voltage dropped to 50 mV across 100 Ω of an external resistance, a new MFC run was carried out. After five consecutive cycles of MFC operation to enrich the biofilm, sodium acetate

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