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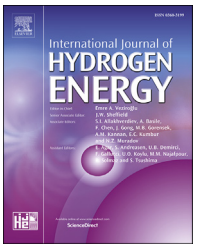

Improvement in methanogenesis by incorporating transition metal nanoparticles and granular activated carbon composites in microbial electrolysis cells

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ABSTRACT

Electromethanogenesis is a form of electrobiofuel production through a microbial electrolysis cell (MEC) where methane (CH_4) is directly produced from an electrical current and carbon dioxide (CO_2) using a cathode. With the aim of maximizing methanogenesis in an MEC, this study utilized granular activated carbon (GAC) and a transition metal catalyst to fabricate nickel (Ni) nanoparticle (NP)-loaded GAC (Ni–NP/GAC) composites and incorporated these into MECs. In this set-up, GAC acted as the main electrical conduit for direct interspecies electron transfer (DIET) between exoelectrogens and methanogenic electrotrophs, and the Ni NPs served as a catalyst to further improve microbe-to-GAC electron transfer. The Ni–NP/GAC-composites were prepared using two different methods (microwave irradiation and solution plasma ionization). The Ni NPs were determined to be well doped on the GAC surface according to a field emission scanning electron microscope (FE-SEM) and energy-dispersive X-ray (EDX) spectroscopy analysis. Adding GAC into MECs improved CH_4 production. The Ni–NP/GAC composites prepared by solution plasma ionization showed the highest CH_4 production (20.7 ml), followed by the Ni–NP/GAC composite prepared by microwave irradiation (19.6 ml), bare GAC (15.6 ml), and GAC-free control (9.6 ml). In the methanogenic MECs, 40.6% of CH_4 was produced from an electrode reaction (i.e., reduction of CO_2 to CH_4), and the remaining 59.4% was generated by nonelectrode reactions.

Introduction

A microbial electrolysis cell (MEC) is an attractive platform for the conversion of various organic compounds into a wide range of value-added chemicals, such as hydrogen (most typically), methane (CH_4), acetate, butanol, hydrogen peroxide, and acetate [1–9]. The conversion of these compounds takes place via a biocatalytic reaction involving electrochemically active microorganisms. The use of MECs is a

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new and promising approach for hydrogen or CH_4 production from diverse organic matter, including wastewater. It requires only a small amount of electric energy and has great potential for wastewater treatment and energy and resource recovery. In this process, electrochemically active bacteria growing on anode in MECs decompose a substrate into protons (H^+), electrons (e^-), and CO_2 as a byproduct. The resulting protons and electrons that are produced are delivered to a cathode and recombine to produce hydrogen or other value-added chemicals, with the assistance of an external power supply [2,10–13].

Electromethanogenesis is a form of electrobiofuel production through an MEC where CH_4 is directly produced at a cathode via the conversion of an electric current and carbon dioxide (CO_2) [5,14,15]. Typical half reactions in an electrode are shown in Eqs. (1) and (2), using acetate as an example substrate:

$$\text{Anode: } CH_3COOH + 2H_2O \rightarrow 2CO_2 + 8H^+ + 8e^- \quad (1)$$

$$\text{Cathode: } CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O. \quad (2)$$

Under standard conditions, an electromethanogenic reaction requires a theoretical potential of −0.224 V (vs. NHE) at pH 7. However, according to a report by Cheng et al., who was the first to show the direct production of CH_4 from CO_2 reduction using an electrode as the sole electron donor, CH_4 was generated at a cathode when the potential was more negative than −0.5 V (vs. NHE) due to diverse overpotentials [16].

In general, a methanogenic MEC has a high CH_4 content and yield, even at low temperatures, but this technology still needs to be improved further to enable its practical uses. Exoelectrogens attached to an electrode play an important role in the production of CH_4, but many suspended microbes, including methanogens or unknown bacteria symbiotically related to exoelectrogens, can also promote direct or indirect interspecies electron transfer (DIET) in methanogenic MECs. DIET is a strategic way for syntrophic growth in which electrons are exchanged between electron-donating bacteria (i.e., exoelectrogens) and electron-accepting bacteria (i.e., exoelectrotrophs) via biological electrical connections [17–22] or mediated by abiotic conductive materials [23–27]. According to recent studies, conductive carbon materials (e.g., granular activated carbon [GAC] and biochar) and magnetite can stimulate DIET in co-culture and the anaerobic digestion process by accelerating rates of anaerobic metabolism [25–27]. These studies demonstrated that DIET was an important mechanism in the methanogenesis of bioelectrochemical systems and that DIET via conductive materials, such as GAC, enhanced both the rate and stability of anaerobic CH_4 production [25,27]. Liu et al. demonstrated that the addition of GAC promoted DIET in methanogenesis in a co-culture of *Geobacter metallireducens* (exoelectrogen) and *Methanosarcina barkeri* (exoelectrotroph) by acting as a cell-to-cell conduit for electron exchange between both species [23]. Similarly, Lee et al. reported that GAC supplementation in an anaerobic reactor facilitated DIET between exoelectrogenic bacteria (*Geobacter* sp.) and hydrogenotrophic methanogens (*Methanospirillum* and *Methanolinea* spp.) [25]. In their study, CH4 production was increased 1.8-fold with the addition of 1% GAC in volume ratio [25].

Most previous studies of electromethanogenesis mainly focused on the role of DIET in enhancing electron exchange by different anaerobes, using bare electroconductive materials, such as biochar and GAC. Although the conductivity of GAC (3000 ± 327 μS/cm) is significantly greater than that of biochar, it is still less conductive than metals. We postulated that DIET-mediated methanogenesis might be further improved by adding transition metals or noble catalysts, such as nickel (Ni), platinum (Pt), palladium (Pd), and iridium (Ir), to GAC, because the loaded metal particles can serve not only as highly efficient conduits based on their intrinsic electric properties but also as catalysts for electromethanogenic reactions. In particular, Ni exhibits a higher electro-catalytic ability, as well as being more stable under alkaline conditions, than other noble metal catalysts, such as Pt [28]. GAC has a large surface area, thereby enhancing the amount of microbes that can attach to its surface. However, it is not a superior material for MECs due to its relatively low electrical conductivity. Therefore, to resolve the problem of the low conductivity of GAC and increase the overall performance of the methanogenic MEC, we used a Ni nanoparticle (NP)-loaded (Ni–NP/GAC) composite as the growth-supporting media, where electrons were conducted between different microbes growing on the GAC. At the same time, the Ni NPs, loaded onto the surface of the GAC to serve as a catalyst, improve the electric conductivity while simultaneously reducing the activation energy threshold of electron transfer at the GAC surface. The GAC composite is strongly biocompatible and free floating, allowing it to make frequent contact with the electrode.

As the major research aims, the present study investigated the effect of the Ni–NP/GAC composite (nanocatalyst-loaded GAC) on the performance of a CH_4-producing-MEC and compared the effectiveness of two different loading methods (electron sputtering with low-temperature solution plasma ionization and microwave irradiation method) for metal nanocatalysts.

Materials and methods

Synthesis of the Ni–NP/GAC composite

Deposition of Ni NPs via microwave irradiation

The Ni–NPs/GAC-composites were prepared by two different methods (microwave irradiation and solution plasma), as shown in Fig. 1. As a conductive material, coal-based GAC (Samchun Granular, South Korea) was used after washing completely using deionized water. The particle diameter, specific surface area, and electric conductivity of the GAC were 1.8–2.4 mm, 1020 m^2/g, and 1800 μS/cm, respectively. To deposit the Ni NPs on the GAC, they were irradiated in a microwave (with an output power of 700 W) for 3 h in a beaker containing 4 g of GAC and 1 g of nickel chloride ($NiCl_2 \cdot 6H_2O$), 100 ml of distilled water, and 300 ml of ethanol. Nickel chloride (Junsei; Extra Pure, Japan) was used as a Ni source, and ethanol was used as a reducing agent.

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